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Supporting Information

Bis(cyclopropenium)phosphines: Synthesis, Reactivity, and Applications

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Table of Contents

Experimental Procedures	S1
Characterization of new compounds	S2
NMR spectra	S31
X-ray structure analyses	S80

Experimental procedures:

General: All reactions were carried out in flame-dried glassware under Ar. All solvents were purified by distillation over the appropriate drying agents and were transferred under Ar. IR: Spectrum One (Perkin-Elmer) spectrometer, wavenumbers ($\tilde{\nu}$) in cm^{-1} ; all measurements were carried out on solid samples. MS (EI): Finnigan MAT 8200 (70 eV), ESIMS: Finnigan MAT 95. Accurate mass determinations: Bruker APEX III FT-MS (7 T magnet). NMR: Spectra were recorded on a Bruker AV 400 or DPX 300; ^1H and ^{13}C chemical shifts (δ) are given in ppm relative to TMS, coupling constants (J) in Hz. The solvent signals were used as references and the chemical shifts converted to the TMS scale. Column chromatography separations were performed on Merck 60 silica gel (40-63 μm). Thin-layer chromatography (TLC) analysis was performed using Merck silica gel 60 F254 TLC plates, and visualized by UV. Optical rotations ($[\alpha]_{20}^D$) were measured with a Perkin-Elmer model 343 polarimeter.

All commercially available compounds (ABCR, Acros, Aldrich, Fischer) were used as received. Compounds **1a**,¹ **2**,² **3**,³ **5a**,¹ **16**,¹ **34**¹ and **38**⁴ were prepared according to literature procedures.

Elemental analysis measured at the microanalysis laboratories of H. Kolbe.

¹ Carreras, J.; Gopakumar, G.; Gimeno, A.; Linowski, P.; Petuškova, J.; Thiel, W.; Alcarazo, M.; *J. Am. Chem. Soc.* **2013**, *135*, 18815-18823.

² Weiss, R.; Wagner, K.-G.; Priesner, C.; Macheleid, J., *J. Am. Chem. Soc.* **1985**, *107*, 4491-4499.

³ Curnow, O. J.; MacFarlane, D. R.; Walst, K. J., *Chem. Commun.* **2011**, *47*, 10248-10250.

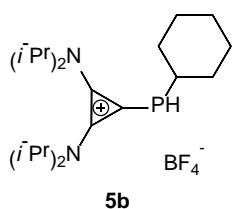
⁴ Hayashi, K.; Yamazoe, A.; Ishibashi, Y., Kusaka, N.; Oono, N.; Nozaki, H., *Bioorg. Med. Chem.*; **2008**, *73*, 5331.

Characterization of new compounds

General Procedure for the synthesis of **5a-h**:

A dry *Schlenk*-flask was charged with the desired primary phosphine (2.0-3.0 equiv.), chloro cyclopropenium salt **2** (1.0 equiv.) and THF (or diglyme) and the resulting mixture was heated overnight (in THF: 60 °C; in diglyme: 100 °C). After cooling the reaction mixture to room temperature, the solvent was removed *in vacuo*, the residue dissolved in DCM and the organic phase washed with a saturated aqueous solution of NaBF₄. Then the organic phase was dried over sodium sulfate, and the solvent evaporated *in vacuo* to afford a residue that was further purified by column chromatography on silica gel (DCM/Acetone, 9/1). The desired products **5a-g** were obtained as white solids.

Compound **5b**



Prepared according to the general procedure from cyclohexylphosphine (2.44 g, 21.0 mmol) and chloro cyclopropenium salt **2** (2.5 g, 7.0 mmol) in THF (30.0 mL). White solid (2.0 g, 65%).

¹H-NMR (400 MHz, CDCl₃): δ = 1.07-1.23 (m, 4H), 1.30 (d, *J* = 6.6 Hz, 6H), 1.33 (d, *J* = 6.6 Hz, 12H), 1.38 (d, *J* = 6.6 Hz, 6H), 1.65-1.90 (7H), 3.85 (sept., *J* = 6.4 Hz, 2H), 4.07 (dd, *J* = 220 Hz, *J* = 9.5 Hz, 1H), 4.09 ppm (sept., *J* = 6.4 Hz, 2H).

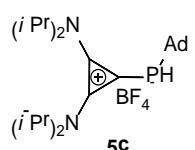
¹³C{¹H}-NMR (101 MHz, CD₂Cl₂): δ = 20.6 (d, *J*_{P-C} = 2.9 Hz), 21.0 (d, *J*_{P-C} = 1.7 Hz), 22.2 (d, *J*_{P-C} = 3.7 Hz), 25.2, 26.5, 26.6 (d, *J* = 1.7 Hz), 31.0 (d, *J*_{P-C} = 19.8 Hz), 32.3 (d, *J*_{P-C} = 10.8 Hz), 35.1, 49.2, 56.1, 103.0 (d, *J*_{P-C} = 62.2 Hz), 138.9 ppm (d, *J*_{P-C} = 3.4 Hz).

³¹P{¹H}-NMR (161 MHz, CDCl₃): δ = -59.4 ppm.

HRMS (ESI) *calcd.* for C₂₁H₄₀N₂P⁺: 351.292360 [M-BF₄]⁺; *found:* 351.292146.

IR: $\tilde{\nu}$ = 732, 891, 1033, 1142, 1348, 1542, 1859, 2933 cm⁻¹.

Compound **5c**



Prepared according to the general procedure from adamantylphosphine (2.44 g, 21.0 mmol) and chloro cyclopropenium salt **2** (2.56 g, 7.1 mmol) in THF (15.0 mL). White solid (3.0 g, 87%).

¹H-NMR (400 MHz, CDCl₃): δ = 1.35 (d, *J* = 6.8 Hz, 18H), 1.41 (d, *J* = 6.8 Hz, 6H), 1.67 (m, 6H), 1.81-1.82 (m, 6H), 1.97 (m, 3H), 3.96 (sept., *J* = 6.8 Hz, 2H), 3.99 (d, *J* = 221.3 Hz, 1H), 4.13 ppm (sept., *J* = 6.8 Hz, 2H).

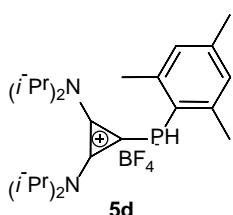
$^{13}\text{C}\{\text{H}\}$ -NMR (101 MHz, CDCl_3): δ = 20.6, 20.9, 21.0, 21.4, 28.4 (d, J = 8.6 Hz), 35.5, 36.7 (d, J = 11.2 Hz), 42.7 (d, J = 9.5 Hz), 51.4, 53.6, 101.9 (d, J = 67.7 Hz), 140.3 ppm.

$^{31}\text{P}\{\text{H}\}$ -NMR (162 MHz, CDCl_3): δ = -44.5 ppm.

HRMS (ESI) *calcd.* for $\text{C}_{25}\text{H}_{44}\text{N}_2\text{P}^+$: 403.323658 [$\text{M}-\text{BF}_4$]⁺; *found*: 403.323727.

IR: $\tilde{\nu}$ = 607, 1045, 1153, 1376, 1543, 1863, 2903 cm^{-1} .

Compound 5d



Compound **5d** was prepared according to the general procedure from mesitylphosphine (2.44 g, 17.7 mmol) and chloro cyclopropenium salt **2** (3.1g, 8.64 mmol) in diglyme (20.0 mL). White solid (2.9 g, 71%).

^1H -NMR (400 MHz, CDCl_3): δ = 1.08 (d, J = 6.9 Hz, 6H), 1.19 (d, J = 6.9 Hz, 6H), 1.35 (d, J = 6.9 Hz, 6H), 1.37 (d, J = 6.9 Hz, 6H), 2.30 (s, 3H), 2.48 (s, 6H), 3.58 (sept., J = 6.4 Hz, 2H), 4.08 (sept., J = 6.4 Hz, 2H), 5.44 (d, J = 240 Hz, 1H), 7.00 ppm (d, J = 2.6 Hz, 2H).

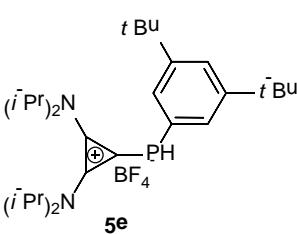
$^{13}\text{C}\{\text{H}\}$ -NMR (101 MHz, CD_2Cl_2): δ = 21.0, 21.1, 21.4 (d, $J_{\text{P-C}}$ = 5.6 Hz), 22.3, 23.4, 23.5, 49.9, 54.7, 105.4 (d, $J_{\text{P-C}}$ = 62.5 Hz), 120.5 (d, J = 9.6 Hz), 29.7 (d, $J_{\text{P-C}}$ = 5.0 Hz), 137.9, 142.2, 144.7 ppm (d, $J_{\text{P-C}}$ = 8.1 Hz).

$^{31}\text{P}\{\text{H}\}$ -NMR (161 MHz, CDCl_3): δ = -94.4 ppm.

HRMS (ESI) *calcd.* for $\text{C}_{24}\text{H}_{40}\text{N}_2\text{P}^+$: 387.292359 [$\text{M}-\text{BF}_4$]⁺; *found*: 387.292161.

IR: $\tilde{\nu}$ = 520, 562, 658, 803, 1050, 1093, 1155, 1345, 1538, 1868, 2982 cm^{-1} .

Compound 5e



Compound **5e** was prepared according to the general procedure from 3,5-(di-*t*-butylphenylphosphine (0.61 g, 2.76 mmol) and chloro cyclopropenium salt **2** (0.33 g, 0.92 mmol) in THF (5.0 mL). White solid (0.18 g, 36%).

^1H -NMR (500 MHz, CDCl_3): δ = 1.06 (d, J = 6.6 Hz, 6H), 1.28 (d, J = 7.2 Hz, 6H), 1.30 (s, 18H), 1.35 (d, J = 7.2 Hz, 6H), 1.38 (d, J = 7.2 Hz, 6H), 3.69 (sept., J = 6.7 Hz, 2H), 4.12 (sept., J = 6.4 Hz, 2H), 5.59 (d, J = 236 Hz, 1H), 7.38 (dd, J = 9.5 Hz, J = 1.7 Hz, 2H), 7.46 ppm (s, 1H).

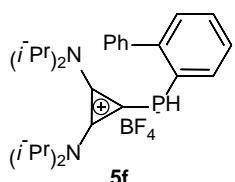
$^{13}\text{C}\{\text{H}\}$ -NMR (75 MHz, CDCl_3): δ = 20.2, 20.3, 21.3, 21.4, 30.5, 34.0, 48.3, 55.2, 103.3 (d, $J_{\text{P-C}}$ = 62.0 Hz), 124.5, 129.6 (d, $J_{\text{P-C}}$ = 5.0 Hz), 137.0, 144.7 (d, $J_{\text{P-C}}$ = 8.1 Hz), 151.3 ppm.

$^{31}\text{P}\{\text{H}\}$ -NMR (161 MHz, CDCl_3): $\delta = -67.3\text{ ppm}$.

HRMS (ESI) *calcd.* for $\text{C}_{29}\text{H}_{50}\text{N}_2\text{P}^+$: 457.370609 [$\text{M}-\text{BF}_4$] $^+$; *found:* 457.371021.

IR: $\tilde{\nu} = 708, 801, 891, 1047, 1139, 1349, 1457, 1545, 1876, 2964 \text{ cm}^{-1}$.

Compound 5f



Compound **5f** was prepared according to the general procedure from 1,1'-(Biphenyl-2-yl)-phosphine (2.24 g, 12.0 mmol) and chloro cyclopropenium salt **2** (2.15 g, 6.0 mmol) in diglyme (20.0 mL). White solid (1.86 g, 61%).

^1H -NMR (400 MHz, CDCl_3): $\delta = 1.08$ (d, $J = 6.8 \text{ Hz}$, 6H), 1.16 (d, $J = 6.8 \text{ Hz}$, 6H), 1.34 (d, $J = 6.8 \text{ Hz}$, 6H), 1.37 (d, $J = 6.8 \text{ Hz}$, 6H), 3.65 (sept. d, $J = 6.8, 1.8 \text{ Hz}$, 2H), 4.12 (sept., $J = 6.9 \text{ Hz}$, 2H), 5.39 (d, $J = 233.3 \text{ Hz}$, 1H), 7.22-7.23 (m, 1H), 7.26 (m, 1H, overlaps with solvent signal) 7.31-7.51 (m, 6H), 7.69-7.75 ppm (m, 1H).

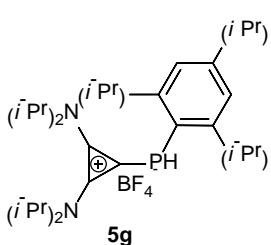
$^{13}\text{C}\{\text{H}\}$ -NMR (101 MHz, CDCl_3): $\delta = 21.0, 21.0, 21.5, 21.5, 22.1, 22.2, 49.4, 56.5, 103.4$ ($d, J_{P-C} = 58.4 \text{ Hz}$), 124.9 (d, $J_{P-C} = 8.1 \text{ Hz}$), 128.2, 128.7, 128.9 (d, $J_{P-C} = 4.4 \text{ Hz}$), 129.1 (d, $J_{P-C} = 3.0 \text{ Hz}$), 130.6 (d, $J_{P-C} = 4.0 \text{ Hz}$), 131.0, 136.8 (d, $J_{P-C} = 9.3 \text{ Hz}$), 138.9 (d, $J_{P-C} = 2.0 \text{ Hz}$), 141.0 (d, $J_{P-C} = 4.0 \text{ Hz}$), 147.9 ppm (d, $J_{P-C} = 20.2 \text{ Hz}$).

$^{31}\text{P}\{\text{H}\}$ -NMR (161 MHz, CDCl_3): $\delta = -78.0 \text{ ppm}$.

HRMS (ESI) *calcd.* for $\text{C}_{27}\text{H}_{38}\text{N}_2\text{P}^+$: 421.276711 [$\text{M}-\text{BF}_4$] $^+$; *found:* 421.276383.

IR: $\tilde{\nu} = 702, 762, 861, 884, 1029, 1152, 1340, 1458, 1562, 1874, 2297, 2984 \text{ cm}^{-1}$.

Compound 5g



Compound **5g** was prepared according to the general procedure from 2,4,6-triisopropylphenylphosphine (1.63 g, 6.90 mmol) and chloro cyclopropenium salt **2** (1.24 g, 3.45 mmol) in diglyme (20.0 mL). White solid (1.20 g, 62%).

^1H -NMR (500 MHz, CDCl_3): $\delta = 1.12$ (d, $J = 6.8 \text{ Hz}$, 6H), 1.16 (d, $J = 6.8 \text{ Hz}$, 6H), 1.21 (d, $J = 6.8 \text{ Hz}$, 6H), 1.24 (d, $J = 6.8 \text{ Hz}$, 6H), 1.25 (d, $J = 6.8 \text{ Hz}$, 6H), 1.36 (d, $J = 6.8 \text{ Hz}$, 6H), 1.37 (d, $J = 6.8 \text{ Hz}$, 6H), 2.91 (sept, $J = 6.8 \text{ Hz}$, 1H), 3.48 (m, 2H), 3.59 (m, 2H), 4.08 (sept, $J = 6.8 \text{ Hz}$, 2H), 5.51 (d, $J = 238 \text{ Hz}$, 1H), 7.11 ppm (d, $J = 2.6 \text{ Hz}$, 2H).

$^{13}\text{C}\{\text{H}\}$ -NMR (75 MHz, CDCl_3): $\delta = 21.1, 21.3$ (d, $J = 4.9 \text{ Hz}$), 22.0, 23.7 (d, $J = 3.8 \text{ Hz}$), 24.0, 24.2, 33.5 (d, $J_{P-C} = 14.5 \text{ Hz}$), 34.5, 51.2, 53.9, 106.9 (d, $J_{P-C} = 63.6 \text{ Hz}$), 119.3 (d, $J_{P-C} = 9.7 \text{ Hz}$), 122.4 (d, $J_{P-C} = 4.8 \text{ Hz}$), 136.9 (d, $J_{P-C} = 5.5 \text{ Hz}$), 153.6, 154.7 ppm (d, $J_{P-C} = 13.7 \text{ Hz}$).

$^{31}\text{P}\{\text{H}\}$ -NMR (202 MHz, CDCl_3): $\delta = -101.7 \text{ ppm}$.

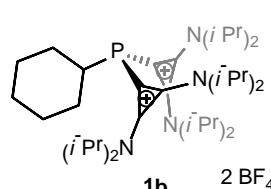
HRMS (EI) *calcd.* for C₃₀H₅₂N₂P⁺: 471.386263[M-BF₄]⁺; *found:* 471.386759.

IR: $\tilde{\nu}$ = 688, 806, 882, 1047, 1152, 1357, 1459, 1542, 1599, 1876, 2295, 2955 cm⁻¹.

General Procedure for the synthesis of **1a-g**, **7a** and **8a** from **5a-g**.

Dry THF was added to a cooled (-40°C) solid mixture of KHMDS (1.0 equiv.) and phosphines **5a-g** (1.0 equiv.) and the resulting suspension was stirred at this temperature for 2 hours. Then, the desired chloro cyclopropenium salt (1.0 equiv.) was added, and the reaction warmed to room temperature overnight. Removal of the solvent *in vacuo* afforded a residue that was dissolved in DCM and washed with a saturated solution of NaBF₄ (3x). Once dried over sodium sulfate, the organic phase was concentrated and the obtained residue washed with THF to afford the desired compounds.

Compound **1b**



Prepared according to the general procedure from KHMDS (49.9 mg, 0.25 mmol), phosphine **5b** (109.6 mg, 0.25 mmol) and chloro cyclopropenium salt **2** (89.7 mg, 0.25 mmol). Dry THF (6 mL) was used as solvent. White solid (80.0 mg, 42%)

¹H-NMR (400 MHz, CD₂Cl₂): δ = 1.26-1.37 (m, 4H), 1.28 (d, *J* = 6.9 Hz, 12H), 1.30 (d, *J* = 6.9 Hz, 12H), 1.35 (d, *J* = 6.9 Hz, 12H), 1.37 (d, *J* = 6.9 Hz, 12H), 1.71-1.84 (m, 6H), 2.59 (m, 1H), 3.90 (sept, *J* = 6.9 Hz, 4H), 4.13 (sept, *J* = 6.9 Hz, 4H) ppm.

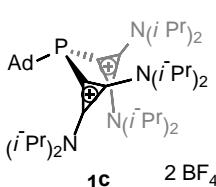
¹³C{¹H}-NMR (101 MHz, CD₂Cl₂): δ = 21.2, 21.4, 21.4, 21.6, 21.6, 21.8, 25.3, 26.6 (d, *J*_{P-C} = 13.0 Hz), 30.5 (d, *J*_{P-C} = 16.1 Hz), 36.6 (d, *J*_{P-C} = 10.5 Hz), 53.0, 54.1, 98.5 (d, *J*_{P-C} = 70.1 Hz), 140.4 ppm.

³¹P{¹H}-NMR (161 MHz, CD₂Cl₂): δ = -43.7 ppm.

HRMS (ESI) *calcd.* for C₃₆H₆₇BF₄N₄P⁺: 673.512703 [M-BF₄]⁺; *found:* 673.512360.

IR: $\tilde{\nu}$ = 519, 576, 684, 892, 1030, 1049, 1151, 1355, 1455, 1547, 1851, 2937 cm⁻¹.

Compound **1c**



Compound **1c** was prepared according to the general procedure from KHMDS (49.9 mg, 0.25 mmol), phosphine **5c** (122.6 mg, 0.25 mmol) and chloro cyclopropenium salt **2** (89.7 mg, 0.25 mmol). Dry THF (6.0 mL) was used as solvent. White solid (102.0 mg, 50%).

¹H-NMR (400 MHz, CD₂Cl₂): δ = 1.32 (d, *J* = 6.8 Hz, 12H), 1.30 (d, *J* = 6.9 Hz,

12H), 1.46 (dd, J = 6.8, 4.0 Hz, 24H), 1.76-1.85 (m, 6H), 2.04 (m, 6H), 2.17 (m, 3H), 4.15-4.28 ppm (m, 8H) .

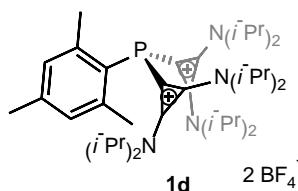
$^{13}\text{C}\{\text{H}\}$ -NMR (101 MHz, CD_2Cl_2): δ = 21.4, 21.7, 21.8, 28.6 (d, $J_{\text{P-C}}$ = 10.3 Hz), 35.8, 39.4 (d, $J_{\text{P-C}}$ = 16.5 Hz), 40.0 (d, $J_{\text{P-C}}$ = 11.2 Hz), 53.0- 55.0 ($\text{CH}_{\text{i-Pr}}$ signal covered by CD_2Cl_2), 98.2 (d, $J_{\text{P-C}}$ = 76.1 Hz), 140.5 ppm.

$^{31}\text{P}\{\text{H}\}$ -NMR (162 MHz, CD_2Cl_2): δ = -21.8 ppm.

HRMS (ESI) *calcd.* for $\text{C}_{40}\text{H}_{71}\text{BF}_4\text{N}_4\text{P}^+$: 725.544003 [M-BF_4]⁺; *found*: 725.544080.

IR: $\tilde{\nu}$ = 520, 575, 685, 893, 1033, 1051, 1151, 1358, 1458, 1555, 1845, 2910, 2978 cm^{-1} .

Compound 1d



Prepared according to general the general procedure from KHMDS (69.0 mg, 0.35 mmol), phosphine **5d** (164.0 mg, 0.35 mmol) and chloro cyclopropenium salt **2** (125.5 mg, 0.35 mmol). Dry THF (10 mL) was used as solvent. White solid (88.0 mg, 32%).

^1H -NMR (400 MHz, CD_2Cl_2): δ = 1.08 (d, J = 6.6 Hz, 12H), 1.26 (d, J = 6.8 Hz, 12H), 1.32 (d, J = 6.8 Hz, 12H), 1.33 (d, J = 6.8 Hz, 12H), 2.26 (s, 3H), 2.40 (s, 6H), 3.71 (sept., J = 6.6 Hz, 4H), 4.13 (sept., J = 6.6 Hz, 4H), 7.03 ppm (d, J = 3.9 Hz, 2H).

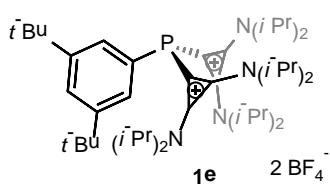
$^{13}\text{C}\{\text{H}\}$ -NMR (101 MHz, CDCl_3): δ = 21.2, 21.4, 21.4, 21.5, 21.5, 21.6, 21.6, 21.8, 53.7, 54.3, 99.1 (d, $J_{\text{P-C}}$ = 58.0 Hz), 118.9 (d, $J_{\text{P-C}}$ = 9.6 Hz), 131.1, 131.2, 139.2, 144.2 ppm.

$^{31}\text{P}\{\text{H}\}$ -NMR (161 MHz, CD_2Cl_2): δ = -64.7 ppm.

HRMS (ESI) *calcd.* for $\text{C}_{39}\text{H}_{67}\text{BF}_4\text{N}_4\text{P}^+$: 709.512703 [M-BF_4]⁺; *found*: 709.513703.

IR: $\tilde{\nu}$ = 520, 579, 645, 689, 893, 1034, 1051, 1151, 1362, 1455, 1551, 1852, 2974 cm^{-1} .

Compound 1e



Prepared according to the general procedure from KHMDS (75.4 mg, 0.38 mmol), phosphine **5e** (206.0 mg, 0.38 mmol) and chloro cyclopropenium salt **2** (135.6 mg, 0.38 mmol). Dry THF (10 mL) was used as solvent. White solid (76.0 mg, 23%).

^1H -NMR (400 MHz, CDCl_3): δ = 1.10 (d, J = 6.8 Hz, 12H), 1.22 (d, J = 6.8 Hz, 12H), 1.25 (s, 18H), 1.32 (d, J = 6.8 Hz, 12H), 1.37 (d, J = 6.8 Hz, 12H), 3.62 (sept, J = 6.6 Hz, 4H), 4.15 (sept, J = 6.6 Hz, 4H), 7.43 d, J = 9.6 Hz, 2H), 7.54 ppm (s, 1H).

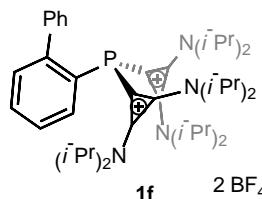
$^{13}\text{C}\{\text{H}\}$ -NMR (101 MHz, CDCl_3): δ = 20.8, 21.1, 21.2, 21.2, 21.4, 21.5, 21.6, 21.8, 31.3, 35.3, 52.4, 54.9, 99.6 (d, $J_{\text{P}-\text{C}} = 58.7$ Hz), 123.9 (d, $J_{\text{P}-\text{C}} = 7.1$ Hz), 126.7, 134.7, 139.8, 153.3 ppm.

$^{31}\text{P}\{\text{H}\}$ -NMR (161 MHz, CDCl_3): δ = -44.6 ppm.

HRMS (ESI) *calcd.* for $\text{C}_{44}\text{H}_{77}\text{B}_2\text{F}_8\text{N}_4\text{P}$: 779.592814 [$\text{M}-\text{BF}_4^-$] $^+$; *found*: 779.592742.

IR: $\tilde{\nu}$ = 691, 892, 1033, 1051, 1151, 1352, 1462, 1557, 1857, 2966 cm^{-1} .

Compound 1f



Prepared according to the general procedure employing KHMDS (325 mg, 1.63 mmol), phosphine **5f** (830 mg, 1.63 mmol) and chloro cyclopropenium salt **2** (580 mg, 1.63 mmol). Dry THF (20 mL) was used as solvent. White solid (660 mg, 49%).

^1H -NMR (400 MHz, CD_3CN): δ = 0.97 (d, J = 6.8 Hz, 12H), 1.16 (d, J = 6.8 Hz, 12H), 1.32 (d, J = 6.8 Hz, 12H), 1.35 (d, J = 6.8 Hz, 12H), 3.68-3.71 (m_{br} , 4H), 4.13 (sept, J = 6.8 Hz, 4H), 7.17-7.19 (m, 2H), 7.44-7.50 (m, 3H), 7.52-7.56 (m, 1H), 7.60-7.64 (m, 1H), 7.67-7.70 (m, 1H), 7.73 ppm (td, J = 7.5 Hz, 1.3 Hz, 1H).

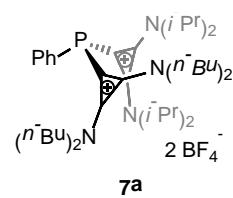
$^{13}\text{C}\{\text{H}\}$ -NMR (101 MHz, CD_3CN): δ = 21.1, 21.2, 21.5, 21.6, 21.6, 21.7, 53.2, 56.0, 98.7 (d, $J_{\text{P}-\text{C}} = 60.6$ Hz), 125.7, 129.7, 129.8, 129.9 (d, $J_{\text{P}-\text{C}} = 4.0$ Hz), 130.2, 132.4 (d, $J_{\text{P}-\text{C}} = 6.5$ Hz), 134.0, 136.2 (d, $J_{\text{P}-\text{C}} = 3.1$ Hz), 140.6 (d, $J_{\text{P}-\text{C}} = 2.0$ Hz), 140.7, 150.0 (d, $J_{\text{P}-\text{C}} = 36.1$ Hz) ppm.

$^{31}\text{P}\{\text{H}\}$ -NMR (162 MHz, CD_3CN): δ = -54.7 ppm.

HRMS (ESI) *calcd.* for $\text{C}_{42}\text{H}_{65}\text{BF}_4\text{N}_4\text{P}^+$: 743.497053 [$\text{M}-\text{BF}_4^-$] $^+$; *found*: 743.498110.

IR: $\tilde{\nu}$ = 440, 519, 549, 578, 616, 640, 666, 688, 705, 740, 761, 891, 1028, 1048, 1150, 1182, 1204, 1283, 1353, 1376, 1457, 1552, 1852, 2879, 2939, 2976 cm^{-1} .

Compound 7a



Prepared according to the general procedure from KHMDS (115.6 mg, 0.78 mmol), phosphine **5a** (338.0 mg, 0.78 mmol) and chloro cyclopropenium salt **3** (414.8 mg, 0.78 mmol). Dry THF (20 mL) was used as solvent. After the work-up, the crude product was washed with pentane (4x, instead of THF). Red oil (353.0 mg, 56%).

^1H -NMR (400 MHz, CDCl_3): δ = 0.82 (t, J = 7.4 Hz, 6H), 0.93 (t, J = 7.4 Hz, 6H), 0.99-1.09 (m, 4H), 1.20 (d, J = 6.8 Hz, 6H), 1.28-1.33 (m, 4H), 1.37 (d, J = 6.8 Hz, 6H), 1.40 (d, J = 6.8 Hz, 6H), 1.42 (d, J = 6.8 Hz, 6H), 1.46-1.54 (m, 4H), 1.56-1.65 (m, 4H), 3.16-3.20 (m, 4H), 3.46-3.50 (m, 4H), 3.84 (sept. d, J = 6.8 Hz, 1.5, 2H), 4.18 (sept., J = 6.8 Hz, 2H), 7.50-7.59 (m, 3H), 7.70-7.75 ppm (m, 2H).

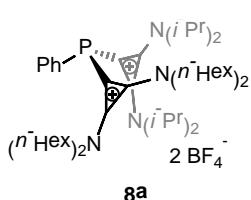
$^{13}\text{C}\{\text{H}\}$ -NMR (101 MHz, CDCl_3): δ = 13.8, 19.9, 20.1, 21.1, 21.2, 21.3, 21.3, 30.0, 30.7, 52.1, 53.9, 53.9, 55.6, 97.1 (d, $J_{\text{P}-\text{C}} = 60.8$ Hz), 98.4 (d, $J_{\text{P}-\text{C}} = 54.5$ Hz), 126.4 (d, $J_{\text{P}-\text{C}} = 4.2$ Hz), 130.5 (d, $J_{\text{P}-\text{C}} = 8.7$ Hz), 132.2, 133.9 (d, $J_{\text{P}-\text{C}} = 22.4$ Hz), 139.8 (d, $J_{\text{P}-\text{C}} = 3.7$ Hz), 141.6 ppm (d, $J_{\text{P}-\text{C}} = 1.8$ Hz).

$^{31}\text{P}\{\text{H}\}$ -NMR (162 MHz, CDCl_3): δ = -51.5 ppm.

HRMS (ESI) *calcd.* for $\text{C}_{40}\text{H}_{69}\text{BF}_4\text{N}_4\text{P}^+$: 723.528353 [$\text{M}-\text{BF}_4$]⁺; *found*: 723.528140.

IR: $\tilde{\nu}$ = 519, 696, 753, 892, 1031, 1046, 1152, 1377, 1437, 1460, 1563, 1862, 1897, 2874, 2936, 2961 cm^{-1} .

Compound 8a



Prepared according to the general procedure from KHMDS (502.4 mg, 2.56 mmol), phosphine **5a** (1.11 g, 2.56 mmol) and chloro cyclopropenium salt **4** (414.8 mg, 0.78 mmol). Dry THF was used as solvent (16 mL). After the work-up the crude product was purified by column chromatography on silica gel (DCM/Acetone, 2/1), affording the desired product as a dark red solid (1.53 g, 65%).

^1H -NMR (400 MHz, CDCl_3): δ = 0.84-0.91 (m, 12H), 0.99-1.06 (m, 4H), 1.23 (d, J = 6.8 Hz, 10H), 1.26-1.30 (m, 15H), 1.37-1.46 (m, 19H), 1.51-1.56 (m, 4H), 1.60-1.68 (m_{br}, 4H), 3.17-3.22 (m, 4H), 3.46-3.51 (m, 4H), 3.85 (sept., J = 6.8 Hz, 2H), 4.19 (sept., J = 6.8 Hz, 2H), 7.49-7.62 (m, 3H), 7.73-74 (m, 1H), 7.76-7.77 ppm (m, 1H).

$^{13}\text{C}\{\text{H}\}$ -NMR (101 MHz, CDCl_3): δ = 14.1, 14.1, 21.1, 21.1, 21.2, 21.3, 21.3, 22.6, 22.7, 26.3, 26.5, 27.9, 28.7, 31.4, 31.5, 51.9, 54.0, 54.2, 55.6, 96.8 (d, $J_{\text{P}-\text{C}} = 57.4$ Hz), 98.1 (d, $J_{\text{P}-\text{C}} = 54.9$ Hz), 126.5 (d, $J_{\text{P}-\text{C}} = 4.1$ Hz), 130.5 (d, $J_{\text{P}-\text{C}} = 8.2$ Hz), 132.1, 133.9 (d, $J_{\text{P}-\text{C}} = 22.2$ Hz), 139.7 (d, $J_{\text{P}-\text{C}} = 2.9$ Hz), 141.5 ppm (d, $J_{\text{P}-\text{C}} = 2.02$ Hz).

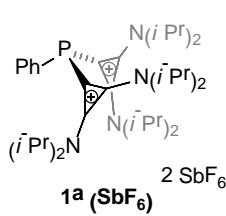
$^{31}\text{P}\{\text{H}\}$ -NMR (122 MHz, CDCl_3): δ = -52.6 ppm.

$^{19}\text{F}\{\text{H}\}$ -NMR (282 MHz, CDCl_3): δ = -152.4 ppm.

HRMS (ESI) *calcd.* for $\text{C}_{48}\text{H}_{85}\text{BF}_4\text{N}_4\text{P}^+$: 835.653553 [$\text{M}-\text{BF}_4$]⁺; *found*: 835.654050.

IR: $\tilde{\nu}$ = 411, 441, 583, 646, 695, 725, 751, 892, 1031, 1041, 1153, 1182, 1207, 1282, 1315, 1351, 1377, 1437, 1460, 1563, 1864, 1897, 2859, 2930, 2956 cm^{-1} .

Compound 1a (SbF_6)



Prepared from known dicationic phosphine **1a** (110 mg, 0.14 mmol), by anion exchange with sodium hexafluoroantimonate (264 mg, 1.0 mmol) in acetonitrile (1.4 mL). White solid (114 mg, 74%).

^1H -NMR (300 MHz, CD_3CN): δ = 1.14 (d, J = 6.8 Hz, 12H), 1.21 (d, J = 6.8 Hz, 12H), 1.38 (pt, J = 7.2 Hz, 24H), 3.67 (sept_{br}, J = 6.8 Hz, 4H), 4.18 (sept,

J = 6.9 Hz, 4H), 7.68-7.70 ppm (m, 5H).

$^{13}\text{C}\{\text{H}\}$ -NMR (101 MHz, CD₃CN): δ = 21.3, 21.4, 21.6, 21.7, 21.8, 21.9, 53.6(s_{br}), 55.6(s_{br}), 98.2 (d, J_{P-C} = 57.2 Hz), 126.1 (d, J_{P-C} = 4.0 Hz), 131.5 (d, J_{P-C} = 8.8 Hz), 133.8, 135.2 (d, J_{P-C} = 23.0 Hz), 140.6 ppm.

$^{31}\text{P}\{\text{H}\}$ -NMR (122 MHz, CD₃CN): δ = -48.7 ppm.

$^{19}\text{F}\{\text{H}\}$ -NMR (282 MHz, CD₃CN): δ = -124.0 ppm (sext, $J_{F-Sb(l=5/2)} = 1930.5$ Hz, $Sb(l=7/2) = 1054.7$ Hz).

ESI-MS (negative): m/z = 234.9 [SbF₆⁻].

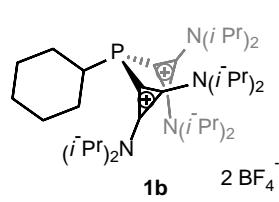
HRMS calcd. for C₃₆H₆₁F₆N₄PSb⁺: 815.357003 [M-SbF₆]⁺; found: 815.357470.

IR: $\tilde{\nu}$ = 499, 549, 579, 653, 752, 892, 1012, 1038, 1148, 1182, 1204, 1352, 1377, 1438, 1458, 1552, 1854, 2883, 2939 cm⁻¹.

Alternative general procedure for the synthesis of **1a-g**.

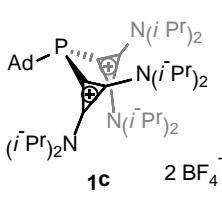
n-BuLi (2.1 equiv.) was added to a suspension of chloro cyclopropenium salt **2** (2.0 equiv.) in Et₂O at -78 °C. The reaction was stirred for 15 minutes and then warmed to room temperature. After removal of the volatiles *in vacuo* and washing the crude with hexane (40 mL), the carbene-lithium complex was obtained as a white powder. To a solution of this solid in THF (10 mL) at -78 °C, the desired dichlorophosphine RPCl₂ (1.0 equiv.) was added and the reaction mixture allowed to warm to room temperature overnight. A solid precipitated during this time. The solvent was then filtered and the remaining solid washed with THF, affording the desired compounds as a white solids.

Compound **1b**



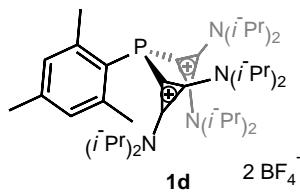
Prepared accordingly to the general procedure from chlorocyclopropenium salt **2** (1.69 g, 4.70 mmol), CyPCl₂ (0.36 mL, 2.35 mmol) and *n*-BuLi (3.10 mL, 1.6 M, 4.93 mmol) in Et₂O (40mL). White solid. (1.05 g, 63%).

Compound **1c**



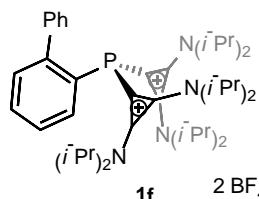
Prepared accordingly to the general procedure from chloro cyclopropenium salt **2** (1.66 g, 4.63 mmol), AdPCl₂ (0.58 g, 2.31 mmol) and *n*-BuLi (3.0 mL, 1.6 M, 4.86 mmol) in Et₂O (40 mL). White solid. (1.55 g, 41%).

Compound **1d**



Prepared accordingly to the general procedure from chlorocyclopropenium salt **2** (1.40 g, 3.90 mmol), MesPCl₂ (0.43 g, 1.95 mmol) and *n*-BuLi (2.6 mL, 1.6M, 4.10 mmol) in Et₂O (40 mL). White solid (1.14 g, 73%).

Compound 1f



Prepared accordingly to the general procedure from chloro cyclopropenium salt **2** (1.65 g, 4.60 mmol), biphenylPCl₂ (0.59 g, 2.30 mmol) and *n*-BuLi (3.0 mL, 1.6 M, 4.83 mmol) in Et₂O (40 mL). White solid (0.61 g, 32%).

Compound 4

Tetrachlorocyclopropene (5.0g, 28.1 mmol) was dissolved in DCM (100 mL) and cooled to -78 °C. Then, HN(*n*-Hex)₂ (20.85 g, 112.5 mmol) was slowly added over 1 hour and the resulting reaction mixture allowed to warm to room temperature during 18 hours. After that, the crude reaction was cooled to 0 °C, HBF₄ (100 mL, 25%) in water was added, and the mixture extracted with DCM (3x). The combined organic phases were then washed with HBF₄ (20 mL, 48%) and water until the pH was neutral. Finally, they were dried over sodium sulfate. Addition of *n*-pentane to this solution promoted the precipitation of 1,2,3-tris(di(hexylamino)cyclopropenium) tetrafluoroborate (13.4 g). Small impurities of dihexylammonium tetrafluoroborate could not be removed. Anyway, this mixture was used for the next step without further purification.

¹H-NMR (400 MHz, CDCl₃): δ = 0.82 (t, *J* = 6.7 Hz, 18H), 1.24 (*m*_{br}, 36H), 1.55 (*m*_{br}, 12H), 3.21 ppm (pt, *J* = 7.9 Hz, 12H).

HRMS *calcd.* for C₃₉H₇₈N₃⁺: 588.619021 [M-BF₄]⁺; *found*: 588.619280.

To an aqueous KOH solution (15.6 g, 277 mmol, 100 mL), 1,2,3-tris(di(hexylamino)cyclopropenium) tetrafluoroborate (18.75 g, 27.7 mmol) was added dissolved in MeOH (15.0 mL). The reaction mixture was heated to 60°C for 16 hours and then cooled to room temperature. Then the crude was extracted with DCM (4x) and the combined organic phases dried over sodium sulfate. Column chromatography purification of the crude (silica gel; DCM/Acetone, 15/1) afforded 1,2-bis(di(hexylamino)cyclopropanone as a transparent oil (11.1 g, 95.0%).

¹H-NMR (400 MHz, CDCl₃): δ = 0.81 (t, *J* = 6.88 Hz, 12H), 1.22 (*ps*_{br}, 24H), 1.52 (*m*_{br}, 8H), 3.06-3.09 ppm (*m*, 8H).

¹³C{¹H}-NMR (101 MHz, CDCl₃) : δ = 13.2, 21.8, 25.7, 27.9, 31.0, 51.1, 118.7, 132.8 ppm.

HRMS *calcd.* for C₂₇H₅₃N₂O⁺: 421.415237 [M+H]⁺; *found*: 421.415390.

IR: $\tilde{\nu}$ = 726, 1105, 1261, 1375, 1420, 1463, 1597, 1893, 2856, 2925, 2955 cm⁻¹.

Finally, oxalyl chloride (3.5 mL, 41.1 mmol) was added dropwise to bis(di(hexylamino)cyclopropanone (5.4 g, 12.8 mmol) at 0 °C. Strong gas evolution was observed. After the addition was finished, the reaction mixture was stirred at room temperature for an additional hour and then the excess of oxalyl chloride was removed *in vacuo*. The residue was dissolved in DCM and the solution washed with a saturated aqueous solution of NaBF₄ (3x). The organic phase was subsequently dried over sodium sulfate, the solvent removed *in vacuo* and the crude product purified by column chromatography on silica gel (DCM/acetone, 15/1) to afford **4** as a red liquid (4.57 g, 67.6%).

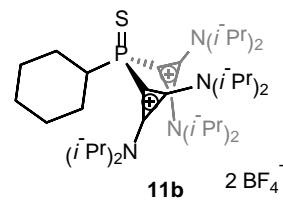
¹H-NMR (400 MHz, CDCl₃): δ = 0.86-0.88 (m, 6H), 0.88-0.89 (m, 6H), 1.28- 1.36 (m, 24H), 1.63 (m_{br}, 4H), 1.68-1.74 (m, 4H), 3.41-3.45 (m, 4H), 3.46-3.49 ppm (m, 4H).

¹³C{¹H}-NMR (101 MHz, CDCl₃): δ = 14.0, 14.1, 22.5, 22.7, 26.3, 26.5, 28.0, 28.7, 31.3, 31.6, 53.1, 54.4, 92.5, 133.9 ppm.

HRMS (ESI) *calcd.* for C₂₇H₅₂N₂Cl⁺: 439.381351[M-BF₄]⁺; *found:* 439.380970.

IR: $\tilde{\nu}$ = 520, 731, 1048, 1269, 1377, 1414, 1604, 1933, 2858, 2927, 2955 cm⁻¹.

Compound 11b



Sulfur (1.7 mg, 0.051 mmol), phosphine **1b** (39.0mg, 0.051 mmol) and TCE (2.0 ml) were stirred at 140°C for 20 hours. Removal of the volatiles in *vacuo* provided a solid which was washed with Et₂O (2 x 2.0 mL) and crystallized from DCM/Et₂O affording the desired product **11b** as a white solid. (19 mg, 46%).

¹H-NMR (400 MHz, CD₂Cl₂): δ = 1.38 (d, *J* = 6.7 Hz, 12H), 1.38-1.40 (m, 2H, overlaps with signals at 1.38 and 1.40 ppm), 1.40 (d, *J* = 6.7 Hz, 12H), 1.41 (d, *J* = 6.6 Hz, 12H), 1.42 (d, *J* = 6.6 Hz, 12H), 1.65-1.76 (m, 6H), 1.85-1.95 (m, 2H), 2.65 (m, 1H), 4.14-4.24 ppm (m, 8H).

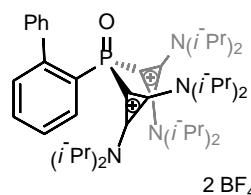
¹³C{¹H}-NMR (101 MHz, CD₂Cl₂): δ = 21.5, 21.8, 22.1, 22.3, 25.4, 25.5, 25.6, 25.8, 42.5, 43.1, 95.6(d, *J*_{P-C} = 69.8 Hz), 138.0 ppm.

³¹P{¹H}-NMR (161 MHz, CD₂Cl₂): δ = 18.6 ppm.

HRMS (ESI) *calcd.* for C₃₆H₆₇BF₄N₄PS⁺: 705.484776 [M-BF₄]⁺; *found:* 705.484500.

IR: $\tilde{\nu}$ = 519, 585, 680, 891, 1029, 1048, 1148, 1378, 1454, 1558, 1845, 2936 cm⁻¹.

Compound 11f



3-mCPBA (33.5 mg, 70%, 0.136 mmol), phosphine **1f** (113.0mg, 0.136 mmol) and DCM (2.0 ml) were stirred at room temperature for 3 hours. Removal of the volatiles *in vacuo* provided an off-white solid which was washed with Et₂O (2 x 2.0 mL) affording the desired product **11f** as a colorless powder. (75 mg, 65%).

¹H-NMR (400 MHz, d₆-Aceton): δ = 1.06 (d, J = 6.9 Hz, 12H), 1.24 (d, J = 6.7 Hz, 12H), 1.38 (d, J = 7.1 Hz, 12H), 1.40 (d, J = 7.1 Hz, 12H), 3.77-3.83 (m, 4H), 4.32- 4.39 (m, 4H), 7.20-7.23 (m, 2H), 7.30-7.34 (m, 3H), 7.43-7.56 (m, 1H), 7.72-7.87 (m, 2H), 8.30 ppm (dd, J = 19.3 Hz, J = 7.3 Hz, 1H).

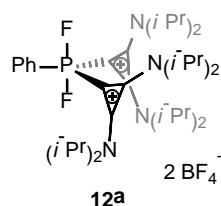
¹³C{¹H}-NMR (101 MHz, d₆-Aceton): δ = 19.6, 19.8, 20.1, 20.2, 53.8, 54.7, 96.5 (d, J = 115.0 Hz), 127.0, 127.4, 127.6, 128.1, 129.0, 132.8 (d, J_{P-C} = 4.3 Hz), 133.0, 133.1, 134.6 (d, J_{P-C} = 3.0 Hz), 136.8(d, J_{P-C} = 6.9 Hz), 147.0 ppm (d, J_{P-C} = 10.8 Hz).

³¹P{¹H}-NMR (162 MHz, CDCl₃): δ = -1.4 ppm.

HRMS (ESI) *calcd.* for C₄₂H₆₅BF₄N₄OP⁺: 759.491967 [M-BF₄]⁺; *found:* 759.492730.

IR: ν = 458, 519, 558, 590, 654, 687, 763, 893, 1028, 1050, 1147, 1182, 1204, 1283, 1358, 1378, 1462, 1568, 1852, 2881, 2942, 2982 cm⁻¹.

Compound 12a



In an argon filled glove box solid XeF₂ (11.6 mg, 0.069 mmol, 1.0 equiv.) was added to a stirred CH₂Cl₂ solution (2 mL) of phosphine **1a** (52.0 mg, 0.069 mmol, 1 equiv.). Some gas evolution was observed, and the solution was allowed to stir overnight at room temperature. Removal of the volatiles *in vacuo* provided a white solid which was washed with THF (3 x 0.5 mL) to give **12a** as a colorless powder. (36.5 mg, 68%).

¹H-NMR (400 MHz, CD₃CN, 25 °C): δ = 1.24 (d, J = 6.9 Hz, 24H), 1.36 (d, J = 6.9 Hz, 24H), 4.05 (sept., J = 6.9 Hz, 4H), 4.16 (sept., J = 6.9 Hz, 4H), 7.62-7.70 (m, 2H), 7.75-7.89 (m, 1H), 8.05-8.15 ppm (m, 2H).

¹³C{¹H}-NMR (101 MHz, CD₃CN): δ = 20.4, 21.0, 52.8, 57.5, 97.3 (dt, J_{P-C} = 243.4 Hz, J_{F-C} = 53.6 Hz), 128.9 (dt, J_{P-C} = 189.5 Hz, J_{F-C} = 22.5 Hz), 130.6 (d, 97.3, J_{P-C} = 18.5 Hz), 136.1 (d, J_{P-C} = 3.9 Hz), 136.7 (dt, J_{P-C} = 14.7 Hz, J_{F-C} = 9.3 Hz), 139.5 ppm (dt, J_{P-C} = 7.0 Hz, J_{F-C} = 6.0 Hz).

³¹P{¹H}-NMR (162 MHz, CD₃CN): δ = -75.6 (t, J = 684.0 Hz) ppm.

¹⁹F{¹H}-NMR (282 MHz, CD₃CN): δ = -22.3 (d, J = 684.0 Hz), -151.9 ppm.

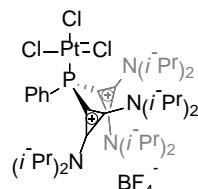
¹¹B{¹H}-NMR (96 MHz, CD₃CN): δ = -1.18 (s) ppm.

ESI-MS: $m/z = 309.3$ ($C_{36}H_{61}F_2N_4P^+$, $[M-2BF_4]^{2+}$), 637.5 ($C_{36}H_{61}F_3N_4P^+$, $[M + F-2BF_4]^+$).

General procedure for the synthesis of Pt complexes:

K_2PtCl_4 was added to a precooled (-20 °C) suspension of salt **1** in dry DCM. The reaction mixture was allowed to warm to room temperature and stirred overnight. The solvent was then removed *in vacuo* affording the desired products **13-15** as pale yellow solids.

Compound 13



Prepared following the general procedure from K_2PtCl_4 (48.4 mg, 0.117 mmol) and **1a** (88.0 mg, 0.117 mmol). Pale yellow solid (111 mg, 98%).

1H -NMR (400 MHz, CD_2Cl_2): $\delta = 1.10$ (d, $J = 6.4$ Hz, 12H), 1.14 (d, $J = 6.4$ Hz, 12H), 1.33 (d, $J = 7.0$ Hz, 12H), 1.36 (d, $J = 7.0$ Hz, 12H), 4.05-4.18 (m, 4H), 4.29-4.43 (m, 4H), 7.58-7.67 (m, 3H), 8.37-8.46 ppm (m, 2H).

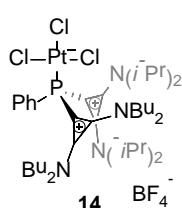
$^{13}C\{^1H\}$ -NMR (100 MHz, CD_2Cl_2): $\delta = 17.5, 18.1, 18.5, 53.4, 90.6$ (d, $J_{P-C} = 51.5$ Hz), 118.9 (d, $J_{P-C} = 70.8$ Hz), 126.8 (d, $J_{P-C} = 12.9$ Hz), 130.9 (d, $J_{P-C} = 2.3$ Hz), 133.5 (d, $J_{P-C} = 13.5$ Hz), 134.7 ppm (d, $J_{P-C} = 8.6$ Hz).

$^{31}P\{^1H\}$ -NMR (161 MHz, CD_2Cl_2): $\delta = -21.2$ ($^1J_{Pt-P} = 3989.6$ Hz) ppm .

HRMS (ESI) *calcd.* for $C_{36}H_{61}Cl_3N_4PPt^+$: 880.333066 $[M-BF_4]^+$; *found* 880.333903.

IR: $\tilde{\nu} = 679, 1050, 1148, 1376, 1557, 1850, 2977 \text{ cm}^{-1}$.

Compound 14



Prepared following the general procedure from K_2PtCl_4 (49.1 mg, 0.118 mmol) and **3** (96.0 mg, 0.118 mmol). Once obtained, **14** was washed with Et_2O (2x 2mL). Red-brown solid (109 mg, 90%).

1H NMR (400 MHz, $CDCl_3$): $\delta = 0.76$ (t, $J = 7.0$ Hz, 6H), 0.89 (t, $J = 7.4$ Hz, 6H), 1.01 (d, $J = 6.6$ Hz, 6H), 1.14 (m, 4H), 1.23 (d, $J = 7.0$ Hz, 6H), 1.29 (d, $J = 7.0$ Hz, 6H), 1.34 (m, 4H), 1.38 (d, $J = 7.0$ Hz, 6H), 1.51-1.63 (m, 8H), 3.31-3.44 (m, 4H), 3.64-3.76 (m, 4H), 3.85-3.92 (m, 2H), 4.01-4.13 (m, 2H), 7.58-7.61 (m, 3H), 8.53-8.59 ppm (m, 2H).

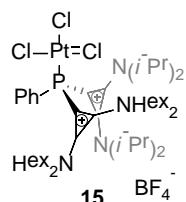
$^{13}C\{^1H\}$ -NMR (100 MHz, $CDCl_3$): $\delta = 13.7, 13.8, 19.6, 19.8, 20.9, 21.1, 21.5, 21.6, 29.3, 30.5, 53.1, 54.4, 92.0$ (d, $J_{P-C} = 57.0$ Hz), 94.5 (d, $J_{P-C} = 57.0$ Hz), 122.5 (d, $J_{P-C} = 73.3$ Hz), 130.0 (d, $J_{P-C} = 13.5$ Hz), 133.7 (d, $J_{P-C} = 2.8$ Hz), 136.6 (d, $J_{P-C} = 13.9$ Hz), 137.9 (d, $J_{P-C} = 9.0$ Hz), 140.1 ppm (d, $J = 7.5$ Hz).

$^{31}\text{P}\{\text{H}\}$ -NMR (161 MHz, CDCl_3): $\delta = -20.2$ ($^1J_{\text{Pt-P}} = 3980$ Hz) ppm.

HRMS (ESI) *calcd.* for $\text{C}_{40}\text{H}_{69}\text{Cl}_3\text{N}_4\text{PPt}^+$: 936.396806 [M-BF_4]⁺, *found*: 936.396960.

IR: $\tilde{\nu} = 520, 693, 1050, 1148, 1376, 1456, 1558, 1866, 2959 \text{ cm}^{-1}$.

Compound 15



Prepared following the general procedure from K_2PtCl_4 (68.8 mg, 0.166 mmol) and **4** (139.0 mg, 0.150 mmol). Once obtained **15** was washed with Et_2O (2x 2mL). Redbrown solid (164 mg, 95.7%).

^1H -NMR (400 MHz, CDCl_3): $\delta = 0.78$ (t, $J = 7.6$ Hz, 6H), 0.82 (t, $J = 7.6$ Hz, 6H), 1.00 (d, $J = 6.6$ Hz, 6H), 1.20-1.27 (m, 24H), 1.30 (d, $J = 6.6$ Hz, 6H), 1.33 (covered, 6H), 1.38 (d, $J = 6.9$ Hz, 6H), 1.46 (m, 4H), 1.55 (m, 4H), 3.33-3.43 (m, 4H), 3.60-3.67 (m, 4H), 3.77-3.92 (m, 2H), 4.02-4.12 (m, 2H), 7.54-7.63 (m, 3H), 8.52-8.57 ppm (m, 2H).

$^{13}\text{C}\{\text{H}\}$ -NMR (100 MHz, CDCl_3): $\delta = 13.2, 13.3, 20.1, 20.2, 20.4, 20.7, 21.7, 21.8, 25.2, 25.6, 26.5, 27.8, 30.6, 30.7, 52.5, 53.8, 91.1$ (d, $J_{\text{P-C}} = 55.0$ Hz), 93.8 (d, $J_{\text{P-C}} = 58.0$ Hz), 121.8 (d, $J_{\text{P-C}} = 70.6$ Hz), 129.3 (d, $J_{\text{P-C}} = 13.4$ Hz), 133.0, 135.9 (d, $J_{\text{P-C}} = 14.0$ Hz), 137.1 (d, $J_{\text{P-C}} = 7.8$ Hz), 139.3 ppm (d, $J_{\text{P-C}} = 7.3$ Hz).

$^{31}\text{P}\{\text{H}\}$ -NMR (161 MHz, CDCl_3): $\delta = -21.6$ ($^1J_{\text{Pt-P}} = 3966$ Hz) ppm.

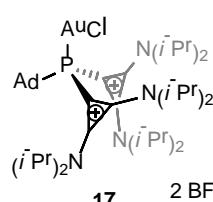
HRMS (ESI) *calcd.* for $\text{C}_{48}\text{H}_{85}\text{Cl}_3\text{N}_4\text{PPt}^+$: 1048.522006 [M-BF_4]⁺; *found*: 1048.521810.

IR: $\tilde{\nu} = 520, 693, 1049, 1148, 1376, 1456, 1559, 1868, 2930 \text{ cm}^{-1}$.

General procedure for the synthesis of Au complexes:

$[\text{AuCl}(\text{SMe}_2)]$ (1 equiv.) was added to a precooled (-20 °C) suspension of salts **5a-g** in dry DCM. Then the reaction mixture was allowed to warm to r.t. and stirred for 30 minutes. Removal of the solvents in *vacuo* afforded the desired product as a white solid.

Compound 17



Prepared according to the general procedure from $[\text{AuCl}(\text{SMe}_2)]$ (22.1 mg, 0.075 mmol) and **1c** (61.0 mg, 0.075 mmol) in DCM (2.0 mL). White solid (66.2 mg, 84%).

^1H -NMR (400 MHz, CD_3CN): $\delta = 1.37-1.41$ (m, 21H), 1.43 (d, $J = 7.0$ Hz, 12H), 1.48 (d, $J = 6.5$ Hz, 12H), 1.76-1.86 (m, 6H), 2.12-2.14 (m, 6H), 2.18 (s, 3H),

2.22 (s, 3H), 4.21 (sept, $J = 6.8$ Hz, 4H), 4.30 ppm (m_{br}, 4H).

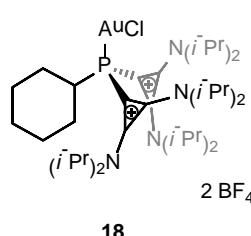
¹³C{¹H}-NMR (101 MHz, CD₃CN): δ = 21.3, 22.0, 22.3 (s_{br}, overlaps with former signal), 28.9 (d, $J_{P-C} = 12.5$ Hz), 35.7, 39.6 (d, $J_{P-C} = 3.4$ Hz), 56.4 (s_{br}), 139.9 ppm (C_q signals for C_{Ad-P} and C_{Cpr-P} are missing due to signal broadening).

³¹P{¹H}-NMR (162 MHz, CD₃CN): δ = 12.2 (br s) ppm.

HRMS (ESI) *calcd.* for C₄₀H₇₁AuBClF₄N₄P⁺: 957.479409 [M-BF₄]⁺; *found:* 905.479480.

IR: $\tilde{\nu}$ = 453, 520, 557, 586, 641, 684, 801, 893, 1029, 1051, 1149, 1182, 1357, 1377, 1454, 1556, 1846, 2858, 2915, 2972 cm⁻¹.

Compound 18



Prepared according to the general procedure from [AuCl(SMe₂) (31 mg, 0.105 mmol) and **1d** (80 mg, 0.105 mmol) in DCM (3.2 mL). White solid (82 mg, 79%).

¹H-NMR (400 MHz, CD₂Cl₂): δ = 1.34-1.39 (m, 2H), 1.47 (dd, $J = 7.0$ Hz, 2.0 Hz, 24H), 1.55 (pt, $J = 7.0$ Hz, 24H), 1.61-1-67 (m, 3H), 1.81-1.84 (m_{br}, 1H), 1.98-2.00 (m_{br}, 4H), 2.93 (m, 1H), 4.13-4.20 ppm (m, 8H).

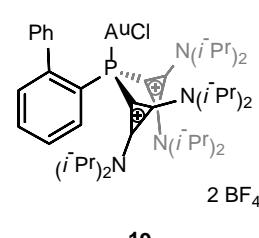
¹³C{¹H}-NMR (100 MHz, CD₂Cl₂): δ = 21.9, 22.0, 22.5, 25.2 (d, $J_{P-C} = 2.0$ Hz), 25.7 (d, $J_{P-C} = 18.2$ Hz), 30.6 (d, $J_{P-C} = 6.1$ Hz), 38.5 (d, $J_{P-C} = 37.0$ Hz), 57.8 (s_{br}), 89.9 (d, $J_{P-C} = 42.2$ Hz), 139.7 ppm (d, $J_{P-C} = 8.6$ Hz).

³¹P{¹H}-NMR (162 MHz, CD₂Cl₂): δ = -9.9 ppm.

HRMS (ESI) *calcd.* for C₃₆H₆₇AuBClF₄N₄P⁺: 905.448109 [M-BF₄]⁺; *found:* 905.449040.

IR: $\tilde{\nu}$ = 457, 519, 557, 581, 645, 664, 684, 892, 1026, 1047, 1148, 1180, 1358, 1377, 1453, 1561, 1848, 2858, 2936, 2978 cm⁻¹.

Compound 19



Prepared according to the general procedure from [AuCl(SMe₂) (17.7 mg, 0.06 mmol) and **1f** (50mg, 0.06 mmol) in DCM (1.8 mL). White solid (58 mg, 91%).

¹H-NMR (400 MHz, CD₃CN): δ = 1.12 (d, $J = 6.8$ Hz, 12H), 1.22 (d, $J = 7.4$ Hz, 12H), 1.41 (d, $J = 6.9$ Hz, 24H), 3.91 (sept, $J = 6.8$ Hz, 4H), 4.25 (sept, $J = 6.8$ Hz, 4H), 7.24-7.25 (m, 2H), 7.51-7.56 (m, 3H), 7.63 (t, $J = 7.4$ Hz, 1H), 7.78-7.81 (m, 1H), 7.89 (td, $J = 7.7$, 0.9 Hz, 1H), 7.94-8.00 ppm (m, 1H).

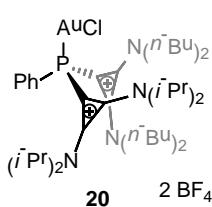
$^{13}\text{C}\{\text{H}\}$ -NMR (100 MHz, CD_3CN): δ = 21.5, 21.6, 22.2, 56.2(s_{br}), 92.0 (d, J_{P-C} = 54.1 Hz), 121.5 (d, J_{P-C} = 71.7 Hz), 130.2, 130.6, 130.7, 130.8, 134.4 (d, J_{P-C} = 9.4 Hz), 135.9, 136.1 (d, J_{P-C} = 2.0 Hz), 139.1, 140.3 (d, J_{P-C} = 10.1 Hz), 149.3 ppm (d, J_{P-C} = 21.2 Hz).

$^{31}\text{P}\{\text{H}\}$ -NMR (162 MHz, CD_3CN): δ = -17.9 ppm.

HRMS calcd. for $\text{C}_{42}\text{H}_{65}\text{AuBClF}_4\text{N}_4\text{P}^+$: 975.432459 [M-BF₄]⁺; found: 975.432440.

IR: $\tilde{\nu}$ = 447, 498, 519, 552, 582, 617, 644, 685, 704, 737, 760, 891, 1029, 1048, 1147, 1180, 1201, 1355, 1377, 1459, 1565, 1848, 2878, 2941, 2977 cm^{-1} .

Compound 20



Prepared according to the general procedure from $[\text{AuCl}:\text{SMe}_2]$ (39.2 mg, 0.133 mmol) and **7a** (107 mg, 0.133 mmol) in DCM (4.2 mL). White solid (121 mg, 88%).

^1H -NMR (400 MHz, CDCl_3): δ = 0.87 (t, J = 7.3 Hz, 6H), 0.93 (t, J = 7.3 Hz, 6H), 0.98-1.06 (m_{br}, 2H), 1.12-1.20 (m_{br}, 2H), 1.26-1.32 (m, 4H), 1.34-1.36 (m, 8H), 1.41 (d, J = 6.5 Hz, 6H), 1.46 (dd, J = 6.9 Hz, J = 1.7 Hz, 12H), 1.61-1.70 (m, 6H), 3.20-3.28 (m, 2H), 3.46-3.52 (m, 6H), 3.84 (sept, J = 6.6 Hz, 2H), 4.22 (m_{br}, 2H), 7.57-7.61 (m, 2H), 7.65-7.69 (m 1H), 7.86-7.88 (m, 1H), 7.92 ppm (m, 1H).

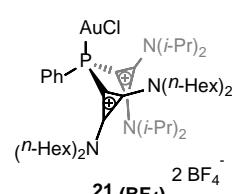
$^{13}\text{C}\{\text{H}\}$ -NMR (101 MHz, CDCl_3): δ = 13.7, 13.9, 19.8, 20.0, 21.2, 21.3, 21.4, 21.8, 29.6, 30.2, 53.7, 54.9, 55.0(s_{br}), 88.5 (d, J_{P-C} = 60.6 Hz), 88.5 (d, J_{P-C} = 59.6 Hz), 121.8 (d, J_{P-C} = 72.8 Hz), 130.9 (d, J_{P-C} = 13.8 Hz), 132.3 (d, J_{P-C} = 15.5 Hz), 134.7, 139.0 (d, J_{P-C} = 5.4 Hz), 140.5 ppm (d, J_{P-C} = 7.1 Hz).

$^{31}\text{P}\{\text{H}\}$ -NMR (162 MHz, CDCl_3): δ = -20.51 ppm.

HRMS (ESI) calcd. for $\text{C}_{40}\text{H}_{69}\text{AuBClF}_4\text{N}_4\text{P}^+$: 955.463759 [M-BF₄]⁺; found: 955.46400.

IR: $\tilde{\nu}$ = 454, 520, 554, 586, 652, 690, 727, 754, 798, 893, 1031, 1042, 1148, 1316, 1355, 1377, 1439, 1458, 1573, 1607, 1863, 1898, 2874, 2934, 2961 cm^{-1} .

Compound 21



Prepared according to the general procedure from $[\text{AuCl}:\text{SMe}_2]$ (58.4 mg, 0.2 mmol) and **8a** (183 mg, 0.20 mmol) in DCM (0.7 mL). Red solid (28 mg, 86%).

^1H -NMR (400 MHz, CDCl_3): δ = 0.81-0.85 (m, 12H), 0.96 (m_{br}, 2H), 1.10 (m_{br}, 2H), 1.21-1.26 (m, 19H), 1.32-1.35 (m, 7H), 1.39 (d, J = 6.7 Hz, 6H), 1.44 (dd,

$J = 6.8$ Hz, 2.0 Hz, 12H), 1.51-1.58 (m_{br}, 2H), 1.65-1.74 (m, 6H), 3.20-3.27 (m, 2H), 3.41-3.53 (m, 6H), 3.80-3.83 (m_{br}, 2H), 4.19 (m_{br}, 2H), 7.53-7.57 (m, 2H), 7.62-7.65 (m, 1H), 7.84 (d, $J = 7.6$ Hz, 1H), 7.88 ppm (d, $J = 7.6$ Hz, 1H).

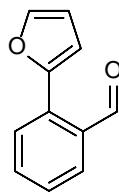
$^{13}\text{C}\{\text{H}\}$ -NMR (101 MHz, CDCl₃): $\delta = 14.1, 14.2, 21.3, 21.4, 21.6, 22.1, 22.7, 22.7, 26.3, 26.6, 27.7, 28.4, 31.4, 31.5, 54.0, 55.2, 55.3$ (s_{br}), 88.5 (d, $J_{P\text{-}C} = 58.0$ Hz), 88.7 (d, $J_{P\text{-}C} = 60.4$ Hz), 121.8 (d, $J_{P\text{-}C} = 71.8$ Hz), 131.0 (d, $J_{P\text{-}C} = 13.5$ Hz), 132.2 (d, $J_{P\text{-}C} = 15.5$ Hz), 134.8 (d, $J_{P\text{-}C} = 2.0$ Hz), 139.1 (d, $J_{P\text{-}C} = 6.3$ Hz), 140.5 ppm (d, $J_{P\text{-}C} = 7.1$ Hz).

$^{31}\text{P}\{\text{H}\}$ -NMR (162 MHz, CDCl₃): $\delta = -23.3$ ppm.

HRMS (ESI) *calcd.* for C₄₈H₈₅N₄AuBClF₄P⁺: 1067.588959 [M-BF₄]⁺, *found*: 1067.588230.

IR: $\tilde{\nu} = 448, 520, 586, 652, 690, 726, 752, 797, 863, 1049, 1149, 1377, 1463, 1573, 1607, 1863, 1898, 2859, 2930$ cm⁻¹.

Starting materials for the synthesis of naphthofurans:



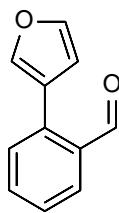
A microwave vial was charged with 2-bromobenzaldehyde (316 μL , 500.0 mg, 2.70 mmol), furan-2-boronic acid (393.1 mg, 3.51 mmol), sodium carbonate (429.6 mg, 4.15 mmol), bis(triphenylphosphine)palladium chloride (94.8 mg, 0.135 mmol) and acetonitrile/water mixture as solvent (1/1, 16.2 mL). The vessel was sealed and the suspension heated to 150 °C under microwave irradiation for 1.5 hours. Then brine was added and the aqueous phase extracted with ethyl acetate (3x). The combined organic phases were dried over sodium sulfate and the solvent was removed *in vacuo* to afford a crude material, which was purified by column chromatography on silica gel (pentane/MTBE, 30/1). Yellow oil (302.7 mg, 65%).

^1H -NMR (300 MHz, CDCl₃): $\delta = 6.56$ (dd, $J = 3.5, 1.9$ Hz, 1H), 6.63 (dd, $J = 3.3, 0.6$ Hz, 1H), 7.41-7.46 (m, 1H), 7.58-7.70 (m, 3H), 7.98 (dd, $J = 7.7, 1.3$ Hz, 1H), 10.38 ppm (d, $J = 0.8$ Hz, 1H).

$^{13}\text{C}\{\text{H}\}$ -NMR (75 MHz, CDCl₃): $\delta = 111.4, 112.1, 128.2, 128.7, 128.6, 133.4, 133.6, 133.7, 144.2, 151.4, 192.5$ ppm.

HRMS (EI) *calcd.* for C₁₁H₈O₂⁺: 172.052432 [M]⁺; *found*: 172.052257.

IR: $\tilde{\nu} = 671, 692, 740, 761, 823, 885, 905, 960, 1006, 1028, 1078, 1105, 1156, 1194, 1217, 1254, 1277, 1300, 1343, 1375, 1397, 1439, 1461, 1476, 1498, 1598, 1683, 1774, 2759, 2854, 3067, 3120, 3146$ cm⁻¹.



A microwave vial was charged with 2-bromobenzaldehyde (148 μl , 234.3 mg, 1.27 mmol), furan-3-boronic acid (170 mg, 1.52 mmol), triethylamine (529 μL , 385 mg, 3.80 mmol), tetrakis(triphenylphosphine)palladium (117.1 mg, 0.101 mmol) and DMF

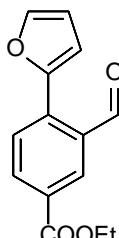
(9 mL). The vessel was sealed and the suspension was heated to 130 °C under microwave irradiation for 5 hours. Then the reaction was diluted with an equal amount of water, and extracted with MTBE (4x). The combined organic phases were washed with saturated NH₄Cl_(aq) (1x), and brine (3x), and dried over sodium sulfate. Finally, the solvent was removed *in vacuo* and the crude material purified by column chromatography on silica gel (pentane/MTBE, 30/1). Yellow oil (132.2 mg, 60%).

¹H-NMR (300 MHz, CDCl₃): δ = 6.59 (dd, *J* = 1.8, 1.0 Hz, 1H), 7.43-7.49 (m, 2H), 7.54-7.56 (m, 2H), 7.59-7.64 (m, 1H), 7.98-8.01 (m, 1H), 10.23 ppm (d, *J* = 0.7 Hz, 1H).

¹³C{¹H}-NMR (75 MHz, CDCl₃): δ = 112.4, 122.7, 128.0, 128.0, 130.8, 134.0, 134.2, 136.6, 141.4, 143.7, 192.8 ppm.

HRMS (EI) *calcd.* for C₁₁H₈O₂⁺: 172.052433 [M]⁺; *found:* 172.052273.

IR: $\tilde{\nu}$ = 659, 690, 762, 798, 824, 873, 923, 961, 1015, 1035, 1055, 1116, 1161, 1197, 1238, 1262, 1290, 1312, 1356, 1394, 1447, 1474, 1506, 1585, 1600, 1649, 1686, 1775, 2759, 2852, 3067, 3130, 3146 cm⁻¹.



A microwave vial was charged with ethyl 4-bromo-3-formylbenzoate (234.0 mg, 0.91 mmol), furan-2-boronic acid (122.1 mg, 0.109 mmol), triethylamine (381 μL, 276.2 mg, 2.73 mmol), tetrakis(triphenyl-phosphine)palladium (84.1 mg, 0.073 mmol) and DMF (6.5 mL) as solvent. The vessel was sealed and the suspension heated to 130 °C under microwave irradiation for 5 hours. After this time, the reaction mixture was diluted with an equal amount of water and extracted with MTBE (4x). The combined organic phases were washed with saturated NH₄Cl and brine (3x), and dried over sodium sulfate. Removal of the solvents *in vacuo* afforded a residue, which was purified by column chromatography on silica gel (pentane/MTBE, 20/1). Yellow solid (113 mg, 51%).

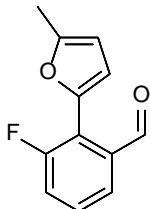
¹H-NMR (400 MHz, CDCl₃): δ = 1.42 (t, *J* = 7.2 Hz, 3H), 4.41 (q, *J* = 7.2 Hz, 2H), 6.60-6.61 (m, 1H), 6.78 (d, *J* = 3.6 Hz, 1H), 7.66 (d, *J* = 1.8 Hz, 1H), 7.78 (d, *J* = 8.0 Hz, 1H), 8.25 (dd, *J* = 8.2, 1.9 Hz, 1H), 8.61 (d, *J* = 1.8 Hz, 1H), 10.46 ppm (s, 1H).

¹³C{¹H}-NMR (101 MHz, CDCl₃): δ = 14.5, 61.7, 112.6, 113.1, 128.3, 129.9, 131.5, 133.0, 134.2, 136.5, 145.0, 150.7, 165.7, 191.8 ppm.

HRMS (EI) *calcd.* for C₁₄H₁₂O₄⁺: 244.075362 [M]⁺; *found:* 244.073364.

IR: $\tilde{\nu}$ = 679, 710, 746, 765, 820, 858, 869, 887, 905, 928, 951, 1017, 1043, 1074, 1097, 1116, 1128, 1159, 1183, 1229, 1244, 1279, 1302, 1367, 1398, 1448, 1458, 1476, 1499, 1550, 1577, 1602, 1677, 1707, 1772, 2910, 2974, 2996, 3119, 3147 cm⁻¹.

This compound was prepared according to literature known⁵ procedure in a two-step one pot reaction.^{[5], [6]}



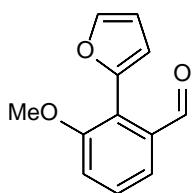
¹H-NMR (300 MHz, CDCl₃): δ = 2.40 (s, 3H), 6.19-6.20 (m, 1H), 6.74 (t, J = 3.3 Hz, 1H), 7.33-7.41 (m, 2H), 7.75-7.77 (m, 1H), 10.33 ppm (s, 1H).

¹³C{¹H}NMR (75 MHz, CDCl₃): δ = 13.9, 108.3, 115.4 (d, J_{F-C} = 8.1 Hz), 120.7, 120.9, 123.8 (d, J_{F-C} = 3.0 Hz), 128.7 (d, J_{F-C} = 9.1 Hz), 135.4, 143.1, 154.8, 159.4 (d, J_{F-C} = 251.6), 192.1 ppm (d, J_{F-C} = 3.5 Hz).

¹⁹F{¹H}-NMR (282 MHz, CDCl₃): δ = -113.1 ppm.

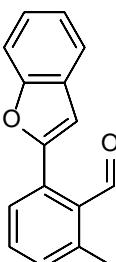
HRMS (EI) *calcd.* for C₁₂H₁₀O₂F⁺: 204.058657 [M+H]⁺; *found:* 204.058680.

IR: $\tilde{\nu}$ = 707, 734, 778, 852, 920, 939, 1025, 1047, 1088, 1135, 1160, 1201, 1235, 1249, 1352, 1394, 1446, 1462, 1480, 1543, 1569, 1602, 1689, 1784, 2753, 2876, 2923, 3079, 3416 cm⁻¹.



2-Chloro-3-methoxy-benzaldehyde (150 mg, 0.879 mmol), furane-2-boronic acid (147.6 mg, 1.319 mmol), tris(dibenzylideneacetone)dipalladium(0) (64.4 mg, 0.070 mmol), S-Phos (57.8 mg, 0.141 mmol) and cesium carbonate (487.0 mg, 1.490 mmol) were suspended in a degassed toluene/1,4-dioxane mixture (1.1/1, 2.1 mL). The vessel was sealed and the suspension heated to 115 °C under microwave irradiation for 7 hours. Then, the crude material was filtrated over a short pad of silica and the residue rinsed with a pentane/MTBE mixture (2/1, 50 mL). Removal of the solvents *in vacuo* afforded a crude product, which was purified by column chromatography on silica gel (pentane/MTBE, 50/1), 118.0 mg. Residues of dibenzylideneacetone were still present in this material, therefore it was used for the next step without further purification attempts.

HRMS (EI) *calcd.* for C₁₂H₁₀O₃⁺: 202.062997 [M]⁺; *found:* 202.063172.



A microwave vial was charged with 2-bromo-6-methylbenzaldehyde (215 mg, 1.08 mmol), benzofuran-2-ylboronic acid (227 mg, 1.40 mmol), sodium carbonate (172 mg, 1.62 mmol), bis(triphenylphosphine)-palladium chloride (38.9 mg, 0.054 mmol) and an acetonitrile/water mixture (1/1, 6.4 mL). Then the vessel was sealed and the mixture heated to 150 °C under microwave irradiation for 1.5 hours. Brine was added subsequently, and the aqueous phase extracted with ethyl acetate (3x). The combined organic phases were then dried over sodium sulfate and the solvent was removed *in vacuo*. The crude material thus obtained was purified by

^[5] Robbins, D; Hartwig, J. F., *Org. Lett.* **2012**, *14*, 16, 4266-4269.

^[6] Ishiyama, T.; Takagi, J.; Yanekawa, Y.; Hartwig, J. F.; Miyaura, N.; *Adv. Synth. Catal.* **2003**, *345*, 1103-1106.

column chromatography on silica gel (pentane/MTBE, 15/1) affording the desired product as a yellow solid (201 mg, 79%).

$^1\text{H-NMR}$ (400 MHz, CDCl_3): δ = 2.63 (s, 3H), 6.87 (d, J = 0.9 Hz, 1H), 7.29 (td, J = 7.5, 7.5, 1.0 Hz, 1H), 7.33-7.37 (m, 2H), 7.52 (d, J = 7.7 Hz, 1H), 7.54-7.56 (m, 1H), 7.63-7.65 (m, 1H), 7.69 (d, J = 7.7 Hz, 1H), 10.31 ppm (s, 1H).

$^{13}\text{C}\{\text{H}\}$ -NMR (101 MHz, CDCl_3): δ = 21.3, 108.4, 111.5, 121.4, 123.4, 125.2, 127.2, 128.7, 132.2, 132.4, 133.1, 133.9, 139.7, 153.1, 155.5, 194.1 ppm.

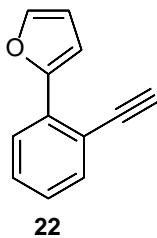
HRMS (EI) *calcd.* for $\text{C}_{16}\text{H}_{12}\text{NaO}_2^+$: 259.072950 [M+Na]⁺; *found*: 259.072988.

IR: $\tilde{\nu}$ = 688, 733, 747, 760, 783, 818, 836, 855, 873, 905, 939, 975, 1009, 1034, 1076, 1098, 1112, 1141, 1167, 1183, 1238, 1259, 1298, 1309, 1349, 1382, 1408, 1425, 1444, 1456, 1474, 1566, 1597, 1686, 2925, 2968, 3062, 3104 cm^{-1} .

General procedure for the preparation of 1-furyl-2-alkynylbenzenes:

Dimethyl (1-diazo-2-oxopropyl)phosphonate (*Ohira-Bestmann* reagent,^[7] 1.5 equiv.), potassium carbonate (2 equiv.) and the corresponding aldehyde (1.0 equiv.) were suspended in methanol (c(aldehyde) = 0.13) and stirred overnight at room temperature. Subsequently, the solvent was removed *in vacuo* and the residue obtained dissolved in ethyl acetate and washed with brine (3x). Then, the organic phase was dried over sodium sulfate, the solvent was removed *in vacuo* and the crude product purified by column chromatography on silica gel.

Compound 22



Prepared according to general procedure from the corresponding aldehyde. Pentane was used as solvent for the column chromatography. Yellow oil (115 mg, 66%).

$^1\text{H-NMR}$ (300 MHz, CDCl_3): δ = 3.41 (s, 1H), 6.52 (dd, J = 3.4, 1.8 Hz, 1H), 7.22 (td, J = 7.7, 1.3 Hz, 1H), 7.38-7.42 (m, 2H), 7.50 (d, J = 1.5 Hz, 1H), 7.58 (dd, J = 8.3, 0.6 Hz, 1H), 7.85 ppm (dd, J = 8.1, 1.0 Hz, 1H).

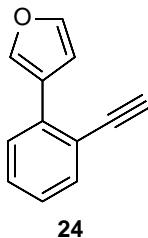
$^{13}\text{C}\{\text{H}\}$ -NMR (75 MHz, CDCl_3): δ = 82.2, 83.9, 109.9, 111.9, 117.3, 125.8, 127.0, 129.3, 132.6, 135.0, 142.4, 151.9 ppm.

HRMS *calcd.* for $\text{C}_{12}\text{H}_8\text{O}^+$: 168.057516 [M]⁺; *found*: 168.057600.

IR: $\tilde{\nu}$ = 660, 735, 756, 781, 814, 886, 901, 952, 1006, 1029, 1050, 1082, 1114, 1158, 1189, 1214, 1255, 1276, 1288, 1378, 1430, 1478, 1498, 1561, 1599, 1631, 1735, 3065, 3119, 3146, 3285 cm^{-1} .

^[7]Müller, S.; Liepold, B.; Roth, G. J.; Bestmann, H. J.; *Synlett* **1996**, 521-522.

Compound 24



Prepared according to general procedure from the corresponding aldehyde. Pentane was used as solvent for the column chromatography. Yellow oil (63 mg, 64%).

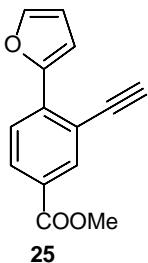
¹H-NMR (300 MHz, CDCl₃): δ = 3.27 (s, 1H), 6.84 (dd, *J* = 1.8, 0.9 Hz, 1H), 7.23 (td, *J* = 7.6, 7.6, 1.4 Hz, 1H), 7.37 (td, *J* = 7.5, 7.5, 1.5 Hz, 1H), 7.44 (ddd, *J* = 7.9, 1.4, 0.5 Hz, 1H), 7.48 (t, *J* = 1.7 Hz, 1H), 7.58 (dd, *J* = 7.9, 1.4 Hz, 1H), 8.06 ppm (dd, *J* = 1.5, 0.9 Hz, 1H).

¹³C{¹H}-NMR (75 MHz, CDCl₃): δ = 81.4, 83.9, 110.6, 119.8, 124.7, 126.8, 128.2, 129.3, 134.6, 134.9, 141.3, 142.8 ppm.

HRMS (EI) *calcd.* for C₁₂H₈O⁺: 168.057513 [M]⁺; *found*: 168.057368.

IR: $\tilde{\nu}$ = 561, 596, 617, 657, 728, 753, 793, 871, 923, 950, 1015, 1032, 1055, 1086, 1162, 1233, 1306, 1356, 1438, 1474, 1509, 1566, 1585, 1599, 2852, 2924, 3025, 3063, 3151, 3285 cm⁻¹.

Compound 25



Prepared according to general procedure from the corresponding aldehyde. A pentane/MTBE 20/1 mixture was used as solvent for the column chromatography. White solid (31.8 mg, 54%).

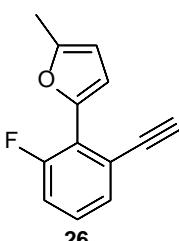
¹H-NMR (300 MHz, CDCl₃): δ = 3.46 (s, 1H), 3.92 (s, 3H), 6.54 (d, *J* = 3.5, 1.8 Hz, 1H), 7.53-7.54 (m, 1H), 7.56 (dd, *J* = 3.5, 0.6 Hz, 1H), 7.92 (d, *J* = 8.4 Hz, 1H), 8.02 (dd, *J* = 8.4, 1.9 Hz, 1H), 8.25 ppm (d, *J* = 1.8 Hz, 1H).

¹³C{¹H}-NMR (101 MHz, CDCl₃): δ = 52.3, 82.9, 83.1, 112.0, 112.2, 116.9, 125.4, 128.2, 130.1, 135.8, 136.2, 143.2, 151.0, 166.2 ppm.

HRMS (EI) *calcd.* for C₁₄H₁₀O₃⁺: 226.062994 [M]⁺; *found*: 226.063200.

IR: $\tilde{\nu}$ = 655, 671, 677, 691, 733, 746, 767, 817, 848, 886, 918, 970, 1007, 1032, 1106, 1128, 1159, 1220, 1254, 1267, 1296, 1373, 1389, 1434, 1476, 1500, 1555, 1600, 1711, 1834, 2960, 3087, 3247 cm⁻¹.

Compound 26



Prepared according to general procedure from the corresponding aldehyde. A pentane/MTBE 30/1 mixture was used as solvent for the column chromatography. White solid (12 mg, 84%).

¹H-NMR (300 MHz, CDCl₃): δ = 2.39 (s, 3H), 3.23 (s, 1H), 6.12-6.14 (m, 1H), 6.82 (dd, J = 2.9, 2.3 Hz 1H), 7.08-7.21 (m, 2H), 7.36-7.39 ppm (m, 1H).

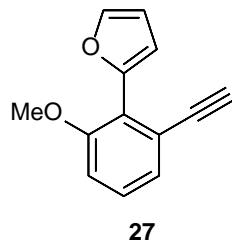
¹³C{¹H}-NMR (75 MHz, CDCl₃): δ = 14.1, 81.3, 82.5 (d, J_{C-F} = 4.9 Hz), 107.5 (d, J_{C-F} = 0.8 Hz), 113.6 (d, J_{C-F} = 5.6 Hz), 116.9 (d, J_{C-F} = 23.0 Hz), 121.3 (d, J_{C-F} = 4.5 Hz), 121.9 (d, J_{C-F} = 14.6 Hz), 128.0 (d, J_{C-F} = 9.4 Hz), 130.4 (d, J_{C-F} = 3.3 Hz), 144.8 (d, J_{C-F} = 1.8 Hz), 152.9 (d, J_{C-F} = 1.6 Hz), 159.4 ppm (d, J_{C-F} = 250.2 Hz).

¹⁹F-NMR (282 MHz, CDCl₃): δ = -112.74 ppm.

HRMS *calcd.* for C₁₃H₉FO⁺: 200.063743 [M]⁺; *found*: 200.063560.

IR: ̄ = 664, 735, 791, 857, 922, 946, 973, 1025, 1045, 1090, 1161, 1201, 1222, 1229, 1252, 1282, 1355, 1382, 1438, 1459, 1537, 1567, 1603, 1677, 1785, 2857, 2924, 2956, 2992, 3075, 3292 cm⁻¹.

Compound 27



Prepared according to general procedure from the corresponding aldehyde. A pentane/MTBE 20/1 mixture was used as solvent for the column chromatography. White solid (70 mg, 40% over two steps).

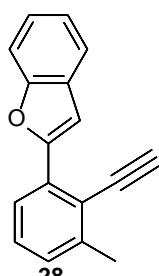
¹H-NMR (400 MHz, CDCl₃): δ = 3.12 (s, 1H), 3.86 (s, 3H), 6.52-6.53 (m, 1H), 6.72 (d, J = 3.6 Hz, 1H), 6.97 (d, J = 7.8 Hz, 1H), 7.20-7.28 (m, 2H, overlaps with solvent signal), 7.56 ppm (s, 1H).

¹³C{¹H}-NMR (75 MHz, CDCl₃): δ = 56.3, 80.3, 83.1, 110.9, 111.7, 112.2, 122.8, 123.1, 126.5, 129.0, 142.1, 148.6, 157.4 ppm.

HRMS (EI) *calcd.* for C₁₃H₁₀O₂⁺: 198.068079 [M]⁺; *found*: 198.068225.

IR: ̄ = 736, 789, 812, 885, 901, 1003, 1028, 1066, 1098, 1155, 1186, 1210, 1231, 1265, 1290, 1376, 1432, 1463, 1500, 1567, 1609, 2838, 2939, 2963, 3005, 3069, 3118, 3142, 3285 cm⁻¹.

Compound 28



Prepared according to general procedure from the corresponding aldehyde. A pentane/MTBE 60/1 mixture was used as solvent for the column chromatography. White solid (45 mg, 92%).

¹H-NMR (400 MHz, CDCl₃): δ = 2.55 (s, 3H), 3.74 (s, 1H), 7.22-7.27 (m, 2H, overlaps with solvent signal), 7.29-7.33 (m, 1H), 7.36 (t, J = 7.8 Hz, 1H), 7.52 (dd, J = 8.1, 0.8 Hz, 1H), 7.62-7.64 (d, 1H), 7.79 (d, J = 0.9 Hz 1H), 7.89 ppm (d, J = 8.6 Hz, 1H).

¹³C-NMR (101 MHz, CDCl₃): δ = 21.6, 81.8, 87.8, 106.2, 111.1, 118.5, 121.5, 122.9, 124.5, 124.8, 128.7, 129.3, 132.5, 142.8, 154.0, 154.4 ppm.

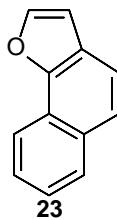
HRMS (EI) calcd. for C₁₆H₁₂O⁺: 232.088816 [M]⁺; found: 232.088602.

IR: $\tilde{\nu}$ = 738, 749, 784, 814, 854, 888, 936, 1009, 1036, 1074, 1088, 1110, 1146, 1172, 1220, 1242, 1259, 1307, 1347, 1379, 1443, 1455, 1565, 1571, 2916, 2952, 3035, 3063, 3289 cm⁻¹.

Synthesis of naphtha[1,2-b]furanes:

A solution of the desired alkyne (1.0 equiv.) in 1,2-DCE (c = 0.05 M) at 50 °C was transferred *via* cannula to a prewarmed Schlenk-flask, which was already charged with **19** (0.02 equiv) and silver hexafluoroantimonate (0.02 equiv.). The reaction mixture was stirred at 50 °C until the reaction was finished (no more than 30 minutes) and then filtered over a short pad of silica gel. The residue was then rinsed with DCM and purified by column chromatography on silica gel.

Compound 23



Prepared accordingly to general procedure. Pentane was used as solvent for the column chromatography. White solid (21 mg, 91%).

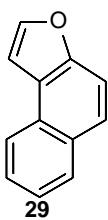
¹H-NMR (400 MHz, CDCl₃): δ = 6.92 (d, J = 1.8 Hz, 1H), 7.50 (t, J = 7.5 Hz, 1H), 7.60 (t, J = 7.6 Hz, 1H), 7.67 (s, 2H), 7.78 (d, J = 1.9 Hz, 1H), 7.95 (d, J = 9.9 Hz, 1H), 8.33 ppm (d, J = 8.20 Hz, 1H).

¹³C{¹H}-NMR (101 MHz, CDCl₃): δ = 107.8, 119.9, 120.2, 121.7, 123.1, 123.6, 125.3, 126.5, 128.5, 131.6, 144.3, 150.8 ppm.

HRMS (EI) calcd. for C₁₂H₈O⁺: 168.057518 [M]⁺; found: 168.057388.

IR: $\tilde{\nu}$ = 685, 736, 785, 806, 869, 881, 945, 955, 1002, 1021, 1039, 1068, 1127, 1169, 1208, 1268, 1321, 1391, 1438, 1454, 1468, 1511, 1592, 1700, 1748, 1807, 2857, 2932, 3019, 3055, 3146 cm⁻¹.

Compound 29



Prepared accordingly to general procedure. Pentane was used as eluent of the column chromatography. Yellow solid (31 mg, 94%).

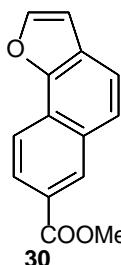
¹H-NMR (400 MHz, CDCl₃): δ = 7.28 (d, J = 1.1 Hz, 1H), 7.50 (t, J = 7.4 Hz, 1H), 7.60 (t, J = 7.3 Hz, 1H), 7.69 (d, J = 8.9 Hz, 1H), 7.75 (d, J = 9.0 Hz, 1H), 7.78 (d, J = 1.8 Hz, 1H), 7.96 (d, J = 8.1 Hz, 1H), 8.16 ppm (d, J = 8.2 Hz, 1H).

¹³C-NMR (101 MHz, CDCl₃): δ = 105.8, 112.7, 122.8, 123.6, 124.7, 125.4, 126.5, 128.0, 128.9, 130.5, 144.4, 152.7 ppm.

HRMS (EI) *calcd.* for C₁₂H₈O: 168.057515 [M]⁺; *found:* 168.057385.

IR: $\tilde{\nu}$ = 683, 727, 787, 803, 860, 905, 952, 972, 1022, 1047, 1071, 1133, 1165, 1206, 1245, 1269, 1320, 1347, 1385, 1448, 1515, 1584, 1628, 1734, 2849, 2926, 3059, 3115, 3146 cm⁻¹.

Compound 30



Prepared accordingly to general procedure. A Pentane/MTBE mixture (20:1) was used as eluent of the column chromatography. White solid (27 mg, 95%).

¹H-NMR (400 MHz, CDCl₃): δ = 4.00 (s, 3H), 6.94 (d, J = 2.1 Hz, 1H), 7.75 (q, J = 8.7 Hz, 2H), 7.84 (d, J = 2.0 Hz, 1H), 8.19 (dd, J = 8.6, 1.6 Hz, 1H), 8.35 (d, J = 8.6 Hz, 1H), 8.71 ppm (d, J = 1.3 Hz, 1H).

¹³C{¹H} (101 MHz, CDCl₃): δ = 52.4, 108.0, 120.4, 120.8, 123.6, 124.8, 125.3, 126.2, 126.7, 130.6, 131.5, 145.4, 150.4, 167.4 ppm.

HRMS (EI) *calcd.* for C₁₄H₁₀O₃⁺: 226.06299 [M]⁺; *found:* 226.062770.

IR: $\tilde{\nu}$ = 426, 442, 505, 546, 585, 605, 624, 684, 750, 791, 808, 843, 883, 917, 974, 1002, 1044, 1067, 1104, 1130, 1194, 1263, 1292, 1320, 1369, 1402, 1421, 1437, 1464, 1502, 1576, 1635, 1702, 1762, 1805, 2848, 2924, 2950, 2998, 3114, 3144 cm⁻¹.

Compound 31



Prepared accordingly to general procedure. A Pentane/MTBE mixture (20:1) was used as eluent of the column chromatography. White solid (12 mg, 84%).

¹H-NMR (300 MHz, CDCl₃): δ = 2.61 (s, 3H), 6.53-6.53 (m, 1H), 7.20-7.27 (m, 1H), 7.32-7.37 (m, 1H), 7.63-7.63 (m, 2H), 7.69 ppm (dd, J = 8.7, 0.5 Hz, 1H).

¹³C{¹H}-NMR (101 MHz, CDCl₃): δ = 14.5, 103.5, 110.9 (d, J_{F-C} = 19.1 Hz), 120.6 (d, J_{F-C} = 1.4 Hz), 122.8 (d, J_{F-C} = 2.9 Hz), 124.1 (d, J_{F-C} = 4.3 Hz), 124.3 (d, J_{F-C} = 7.6 Hz), 126.2 (d, J_{F-C} = 0.9 Hz), 126.8, 133.2 (d, J_{F-C} = 5.2 Hz), 147.4 (d, J_{F-C} = 1.8 Hz), 155.8 (d, J_{F-C} = 2.4 Hz), 157.1 ppm (d, J_{F-C} = 251.4 Hz).

¹⁹F{¹H}-NMR (282 MHz, CDCl₃): δ = -117.69 ppm.

HRMS (EI) *calcd.* for C₁₃H₉OF⁺: 200.063741 [M]⁺; *found:* 200.063635.

IR: $\tilde{\nu}$ = 688, 733, 747, 760, 783, 818, 836, 855, 873, 905, 939, 975, 1009, 1034, 1076, 1112, 1141, 1167, 1183, 1239, 1259, 1298, 1309, 1349, 1382, 1408, 1425, 1444, 1456, 1474, 1566, 1597, 1686, 2925, 2968, 3062, 3104 cm⁻¹.

Compound 32



Prepared accordingly to general procedure. A Pentane/MTBE mixture (20:1) was used as eluent of the column chromatography. White solid (40 mg, 95%).

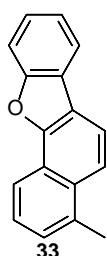
¹H-NMR (400 MHz, CDCl₃): δ = 4.13 (s, 3H), 6.91 (d, *J* = 2.1 Hz, 1H), 7.00 (d, *J* = 7.8 Hz, 1H), 7.41 (t, *J* = 8.0 Hz, 1H), 7.55 (d, *J* = 8.2 Hz, 1H), 7.65 (d, *J* = 8.5 Hz, 1H), 7.69 (d, *J* = 8.4 Hz, 1H), 7.85 ppm (d, *J* = 2.0 Hz, 1H).

¹³C-NMR (101 MHz, CDCl₃): δ = 56.3, 105.9, 107.1, 114.1, 120.7, 121.0, 123.6, 124.2, 125.3, 133.7, 144.5, 149.9, 154.9 ppm.

HRMS (EI) *calcd.* for C₁₃H₁₀O⁺: 198.068083 [M]⁺; *found*: 198.067909.

IR: $\tilde{\nu}$ = 434, 475, 504, 527, 589, 626, 660, 691, 733, 754, 799, 810, 867, 881, 950, 997, 1021, 1061, 1087, 1134, 1162, 1200, 1216, 1254, 1268, 1257, 1377, 1404, 1431, 1461, 1515, 1536, 1575, 1622, 1743, 1815, 1907, 2839, 2961, 3011, 3058, 3123, 3147 cm⁻¹.

Compound 33



Prepared accordingly to general procedure. A Pentane/MTBE mixture (50:1) was used as eluent of the column chromatography. White solid (28 mg, 90%).

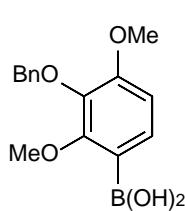
¹H-NMR (400 MHz, CDCl₃): δ = 2.79 (s, 3H), 7.39-7.43 (m, 2H), 7.46-7.50 (m, 1H), 7.53-7.57 (m, 1H), 7.72 (d, *J* = 8.3 Hz, 1H), 7.94 (dd, *J* = 8.7, 0.7 Hz, 1H), 8.01-8.04 (m, 1H), 8.04 (d, *J* = 8.7 Hz, 1H), 8.35 ppm (d, *J* = 8.3 Hz, 1H).

¹³C{¹H}-NMR(101 MHz, CDCl₃): δ = 20.3, 111.9, 118.3, 119.0, 119.3, 119.6, 120.4, 121.5, 123.0, 125.1, 126.3, 127.2, 132.2, 135.2, 152.7, 156.1 ppm.

HRMS (EI) *calcd.* for C₁₇H₁₂O⁺: 232.088815 [M]⁺; *found*: 232.088643.

IR: $\tilde{\nu}$ = 436, 489, 565, 607, 682, 747, 767, 813, 909, 1010, 1032, 1069, 1088, 1118, 1150, 1183, 1201, 1268, 1306, 1343, 1378, 1397, 1441, 1460, 1529, 1583, 2860, 2928, 2946, 2968, 3063 cm⁻¹.

Compound 37



37

To a suspension of 3-bromo-2,6-dimethoxyphenol (1.8 g, 7.72 mmol) and potassium carbonate (1.6 g 11.59 mmol) in acetone (40 mL), benzyl bromide (0.96 mL, 1.38 g, 8.07 mmol) was added and the reaction mixture stirred overnight at room temperature. Removal of the solvents *in vacuo* afforded a crude material, which was purified by column chromatography on silica gel (hexane/ethyl acetate, 9/1) affording 2-(Benzylxy)-4-bromo-1,3-dimethoxybenzene as a colorless oil (2.2 g, 88%).

¹H-NMR (400 MHz, CDCl₃): δ = 3.82 (s, 3H), 3.90 (s, 3H), 5.03 (s, 2H), 6.59 (d, *J* = 9.0 Hz, 1H), 7.22 (d, *J* = 8.9 Hz, 1H), 7.32-7.39 (m, 3H), 7.48-7.53 ppm (m, 2H).

¹³C{¹H}-NMR (101 MHz, CDCl₃): δ = 56.3, 61.3, 75.6, 108.6, 108.9, 127.1, 128.2, 128.5, 137.5, 142.7, 151.5, 153.8 ppm.

HRMS (ESI) *calcd.* for C₁₅H₁₅BrNaO₃⁺: 345.009358 [M+Na]⁺; *found:* 345.009358.

IR $\tilde{\nu}$ = 694, 734, 791, 876, 915, 980, 1008, 1088, 1179, 1214, 1226, 1271, 1293, 1371, 1413, 1438, 1460, 1473, 1574, 2837, 2937 cm⁻¹.

2-(Benzylxy)-4-bromo-1,3-dimethoxybenzene (1.6 g, 4.95 mmol) was dissolved in diethyl ether (40 mL) and cooled to -78 °C. *n*-Butyl lithium (1.98 mL, 4.95 mmol, c = 2.5 M in hexanes) was then added dropwise over 30 minutes and the resulting solution stirred for 1 hour at -78 °C. Then, trimethylborate (1.69 mL, 14.85 mmol) was added and the mixture allowed to warm to room temperature overnight. After quenching the reaction with HCl_(aq) (20 mL, c = 3 M), the aqueous phase was extracted with MTBE (3x) and dried over sodium sulfate. Removal of the solvent *in vacuo* afforded crude 37. Purification by column chromatography on silica gel (hexane/ethyl acetate, 6/4) gave a white solid (935 mg, 66%). The compound should be stored at -20 °C under argon as it decomposes slowly over time at room temperature.

¹H-NMR (300 MHz, CD₃CN): δ = 3.86 (s, 3H), 3.94 (s, 3H), 4.99 (s, 2H), 6.32 (s, 2H), 6.82 (d, *J* = 8.4 Hz, 1H), 7.33-7.42 (m, 3H), 7.46 (d, *J* = 8.4, 1H), 7.48-7.51 ppm (m, 2H).

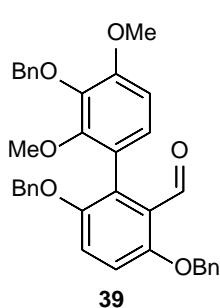
¹³C{¹H}-NMR (75 MHz, CD₃CN): δ = 56.7, 62.5, 75.7, 109.3, 129.0, 120.0, 129.3, 129.4, 132.1, 138.9, 141.0, 157.7, 160.2 ppm.

¹¹B{¹H}-NMR (96 MHz, CD₃CN): δ = 28.7 ppm.

HRMS (ESI) *calcd.* for C₁₅H₁₇BNaO₅⁺: 311.107456 [M+Na]⁺; *found:* 311.107270.

IR: $\tilde{\nu}$ = 693, 725, 751, 805, 896, 981, 1004, 1063, 1089, 1185, 1225, 1278, 1342, 1377, 1434, 1457, 1498, 1596, 2838, 2929, 3000, 3358 cm⁻¹.

Compound 39



3,6-Dibenzylxy-2-bromobenzaldehyde **38** (110 mg, 0.28 mmol), 3-(benzylxy)-2,4-dimethoxyphenylboronic acid **37** (120 mg, 0.42 mmol), tris(dibenzylideneacetone)-dipalladium(0) (12.7 mg, 0.014 mmol), tricyclohexylphosphine (8.5 mg, 0.031 mmol) and cesium carbonate (180 mg, 0.554 mmol) were suspended in a toluene/1,4-dioxane mixture (6/4, 3.5 mL) and heated to 85 °C for 24 hours. Then, the reaction mixture was filtered through a pad of Celite®. The solvent was then removed *in vacuo* and the crude product purified by column chromatography on silica gel (hexane/ethylacetate, 4/1) to afford the desired product **39** as a pale yellow solid (84%, 130 mg).

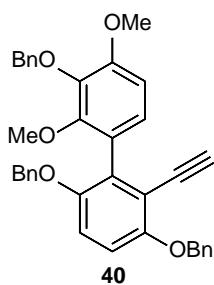
¹H-NMR (400 MHz, CDCl₃): δ = 3.61 (s, 3H), 3.81 (s, 3H), 4.86 (d, J = 12.2 Hz, 1H), 4.90 (d, J = 12.2 Hz, 1H), 4.99 (s, 2H), 5.11 (s, 2H), 6.67 (d, J = 8.5 Hz, 1H), 6.78 (d, J = 8.5 Hz, 1H), 6.93 (d, J = 9.1 Hz, 1H), 7.07- 7.11 (m, 3H), 7.16- 7.22 (m, 3H), 7.24- 7.36 (m, 6H), 7.43- 7.45 (m, 4H), 10.11 ppm (s, 1H).

¹³C{¹H}-NMR (101 MHz, CDCl₃): δ = 56.3, 61.1, 71.6, 71.9, 75.4, 107.4, 113.8, 120.0, 121.8, 126.0, 126.2, 127.1, 127.4, 127.8, 128.0, 128.2, 128.4, 128.5, 128.6, 128.8, 132.0, 136.9, 137.3, 138.0, 141.3, 151.0, 152.2, 154.1, 154.4, 191.4 ppm.

HRMS (ESI) *calcd.* for C₃₆H₃₂NaO₆⁺: 583.209108 [M+Na]⁺; *found:* 583.208933.

IR: ν = 692, 731, 744, 767, 800, 810, 841, 906, 965, 991, 1088, 1130, 1171, 1197, 1262, 1286, 1374, 1382, 1411, 1452, 1477, 1497, 1586, 1683, 2863, 2935, 3032, 3064 cm⁻¹.

Compound 40



Compound **40** was prepared according to the general procedure from carbaldehyde **39** (130 mg, 0.23 mmol). Purification of the crude material thus obtained was performed by column chromatography on silica gel (pentane/ethyl acetate, 10/1). Pale yellow solid (86 mg, 67%).

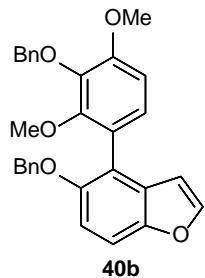
¹H-NMR (400 MHz, CDCl₃): δ = 3.20 (s, 1H), 3.74 (s, 3H), 3.89 (s, 3H), 4.92 (d, J = 12.1 Hz, 1H), 4.98 (d, J = 12.2 Hz, 1H), 5.08 (s, 2H), 5.19 (s, 2H), 6.76 (d, J = 8.6 Hz, 1H), 6.86 (d, J = 9.0 Hz, 1H), 6.93- 6.97 (m, 2H), 7.19- 7.28 (m, 5H), 7.31- 7.42 (m, 6H), 7.51- 7.54 ppm (m, 4H).

¹³C{¹H}-NMR (101 MHz, CDCl₃): δ = 56.1, 61.3, 71.3, 71.6, 75.3, 79.0, 85.0, 107.1, 112.8, 114.3, 115.4, 123.8, 125.9, 127.0, 127.1, 127.6, 127.8, 127.9, 128.3, 128.4, 128.4, 128.6, 133.9, 137.3, 137.5, 138.1, 141.1, 151.0, 152.4, 153.8, 154.8 ppm.

HRMS (ESI) *calcd.* for C₃₇H₃₂NaO₅⁺: 579.214195[M+Na]⁺; *found:* 579.214523.

IR : $\tilde{\nu}$ = 691, 726, 808, 852, 913, 970, 1007, 1065, 1094, 1137, 1172, 1203, 1222, 1265, 1288, 1376, 1413, 1447, 1475, 1497, 1588, 1604, 2931, 3027, 3067, 3255 cm⁻¹.

Compound 40b



Compound **40b** was isolated as side product of the Seydel-Gilbert reaction for the synthesis of compound **30**. This side-product was isolated as a yellow oil (25 mg, 23%).

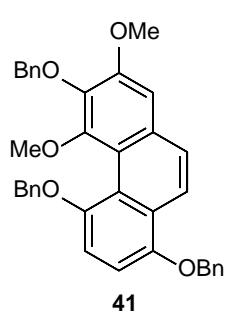
¹H-NMR (400 MHz, CDCl₃): δ = 3.59 (s, 3H), 3.92 (s, 3H), 5.01 (d, *J* = 11.9 Hz; 1H), 5.05 (d, *J* = 12.0 Hz; 1H), 5.10 (s, 2H), 6.47 (dd, *J* = 2.1, 0.8 Hz, 1H), 6.77 (d, *J* = 8.6 Hz, 1H), 7.04 (d, *J* = 8.5 Hz, 1H), 7.07 (d, *J* = 9.0 Hz, 1H), 7.23-7.27 (m, 3H), 7.30-7.38 (m, 5H), 7.41 (d, *J* = 8.9, 0.8 Hz, 1H), 7.52-7.54 (m, 2H), 7.58 ppm (d, *J* = 2.3 Hz, 1H).

¹³C{¹H}-NMR (101 MHz, CDCl₃): δ = 56.2, 61.3, 72.8, 75.4, 106.8, 107.3, 110.6, 112.9, 121.1, 123.0, 126.3, 127.4, 127.6, 128.0, 128.4, 128.4, 128.5, 129.1, 137.9, 138.0, 141.3, 145.8, 150.3, 152.1, 152.7, 153.7 ppm.

HRMS (ESI) *calcd.* for C₃₇H₃₂NaO₅⁺: 489.167248 [M+Na]; *found*: 489.167179.

IR: $\tilde{\nu}$ = 696, 733, 796, 843, 911, 994, 1028, 1044, 1081, 1112, 1150, 1194, 1216, 1262, 1346, 1370, 1439, 1464, 1497, 1510, 1602, 1659, 2848, 2931, 3032 cm⁻¹.

Compound 41



A solution of **40** (78.0 mg, 0.12 mmol) in toluene (0.48 mL) was heated to 50 °C and transferred *via* cannula to a Schlenk-flask charged with Au(I)-precatalyst **21 (SbF₆)** (0.9 mg, 0.61 µmol) and silver hexafluoroantimonate (0.22 mg, 0.61 µmol)^[8]. The reaction was stirred at 50 °C until full consumption of the starting material could be detected by TLC (4 hours). Then, the reaction mixture was filtered over a short pad of silica gel. Solvent removal *in vacuo* afforded a crude material, which was purified by column chromatography on silica gel (pentane/ethyl acetate, 9/1). White solid (69 mg, 89%).

¹H-NMR (400 MHz, CDCl₃): δ = 3.61 (s, 3H), 3.96 (s, 3H), 5.00 (s, 2H), 5.14 (s, 2H), 5.24 (s, 2H), 6.98 (d, *J* = 7.8 Hz, 1H), 6.99 (s, 1H), 7.08 (d, *J* = 8.6 Hz, 1H), 7.17-7.27 (m, overlaps with solvent, 3H), 7.29 - 7.38 (m, 4H), 7.41-7.56 (m, 9H), 8.11 ppm (d, *J* = 8.8 Hz, 1H).

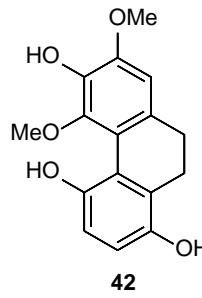
^[8] Small amounts of AgSbF₆ can be transferred into the vessel by making a stock solution of AgSbF₆ in 1,2-DCE first. DCM doesn't dissolve AgSbF₆ completely.

¹³C{¹H}-NMR (100 MHz, CDCl₃): δ = 56.1, 61.1, 71.2, 71.9, 75.9, 103.2, 107.6, 110.0, 117.3, 120.0, 121.2, 124.9, 126.2, 127.6, 127.7, 127.8, 127.9, 128.0, 128.3, 128.4, 128.7, 130.8, 137.7, 138.2, 138.3, 141.4, 148.8, 151.4, 153.2, 152.2 ppm.

HRMS (ESI) *calcd.* for C₃₇H₃₂NaO₅⁺: 579.214196 [M+Na]⁺; *found:* 579.214280.

IR: $\tilde{\nu}$ = 696, 733, 796, 843, 911, 994, 1028, 1044, 1081, 1112, 1150, 1194, 1216, 1262, 1346, 1370, 1439, 1464, 1497, 1510, 1602, 1659, 2848, 2931, 3032 cm⁻¹.

Compound 42 : Calanhydroquinone A



Compound **41** (140 mg, 0.25 mmol) and (10% m/w) Pd/C (26.5 mg, 0.025 mmol) were suspended in an ethanol/DCM mixture (3/1, 8 mL) in an autoclave, and stirred overnight at room temperature under a hydrogen atmosphere of 20 bar. Then, the suspension was filtered over a short pad of Celite®, the residue rinsed with acetone (80 mL) and the solvent removed *in vacuo*. The crude material obtained was purified by column chromatography on silica gel (pentane/ethyl acetate, 6/4) affording **42** as an orange solid (65 mg, 89%).

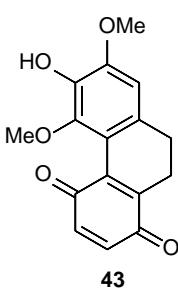
¹H-NMR (400MHz, CD₃CN): δ = 2.54-2.57 (m, 2H), 2.65 (m, 2H), 3.62 (s, 3H), 3.88 (s, 3H), 6.49 (s, 1H), 6.54 (s, 1H), 6.72 (d, *J* = 8.6 Hz, 1H), 6.76 (d, *J* = 8.8 Hz, 1H), 6.83 (s, 1H), 8.10 ppm (s, 1H).

¹³C{¹H}-NMR (125 MHz, CDCl₃): δ = 22.7, 30.2, 56.5, 62.1, 107.8, 116.2, 117.8, 119.2, 121.4, 125.8, 132.3, 137.3, 142.8, 145.2, 146.5, 147.9 ppm.

HRMS (ESI) *calcd.* for C₁₆H₁₆NaO₅⁺: 311.088993 [M+Na]⁺; *found:* 311.089100.

IR: $\tilde{\nu}$ = 731, 800, 834, 899, 929, 978, 1014, 1032, 1050, 1093, 1147, 1191, 1231, 1258, 1282, 1329, 1356, 1385, 1455, 1499, 1559, 1609, 1646, 2851, 2925, 3226, 3408 cm⁻¹.

Compound 43: Calanquinone C



Cerium ammonium nitrate (140 mg, 0.255 mmol) was dissolved in water (2 mL) and added to a solution of **42** (37 mg, 0.128 mmol) in THF (6 mL) over 30 minutes at room temperature. After extracting the reaction mixture with diethyl ether (20 mL), the organic phase was washed with saturated NaHCO_{3(aq)} (2x) and water (1x). Then, the organic phase was dried over sodium sulfate. Subsequent solvent removal afforded crude **43** which was purified by column chromatography on silica gel (pentane/ethyl acetate, 7/3). Deep red solid (25.3 mg, 69%).

¹H-NMR (300 MHz, CDCl₃): δ = 2.51-2.57 (m, 2H), 2.60-1.66 (m, 2H), 3.89 (s, 3H), 3.92 (s, 3H), 5.52 (s_{br}, 1H), 6.55 (s, 1H), 6.72 (d, *J* = 10.1 Hz, 1H), 6.83 ppm (d, *J* = 10.1 Hz, 1H).

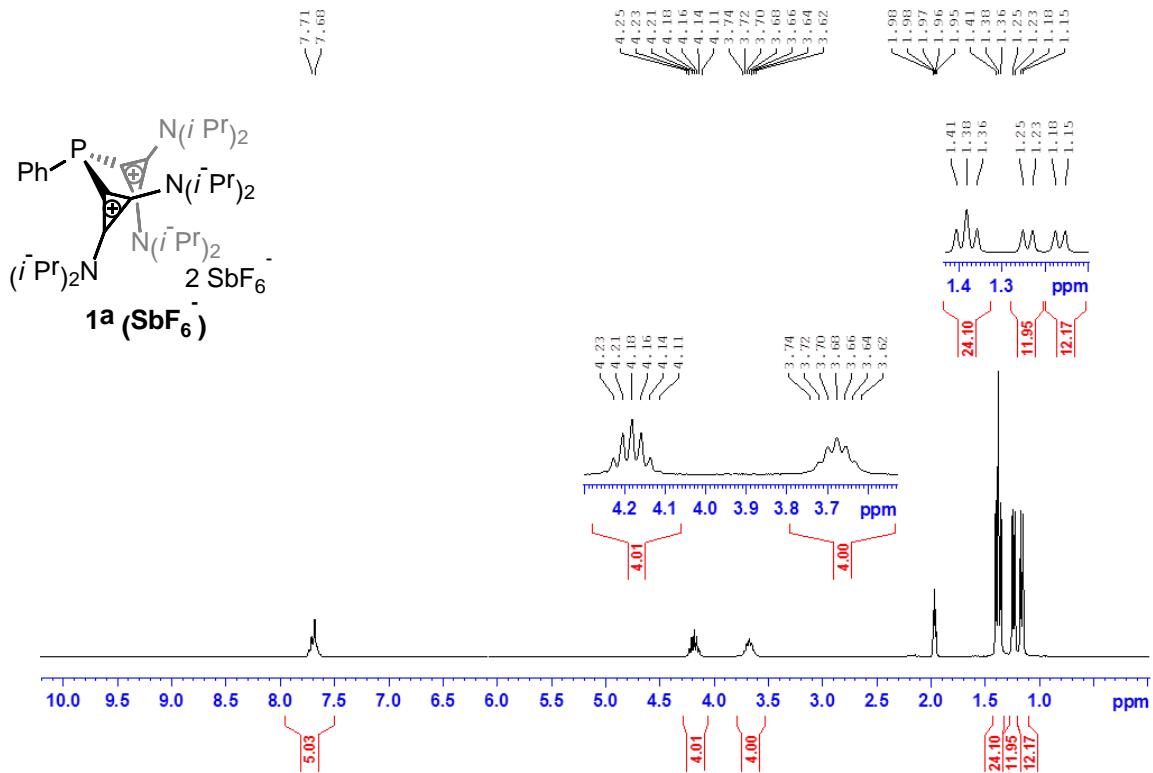
¹³C{¹H}-NMR (75 MHz, CDCl₃): δ = 20.5, 28.5, 56.5, 60.9, 105.6, 116.3, 131.9, 135.5, 137.4, 137.5, 140.5, 141.0, 145.5, 149.3, 185.6, 185.9 ppm.

HRMS (ESI) *calcd.* for C₁₆H₁₄NaO₅⁺: 309.073341 [M+Na]; *found*: 309.073410.

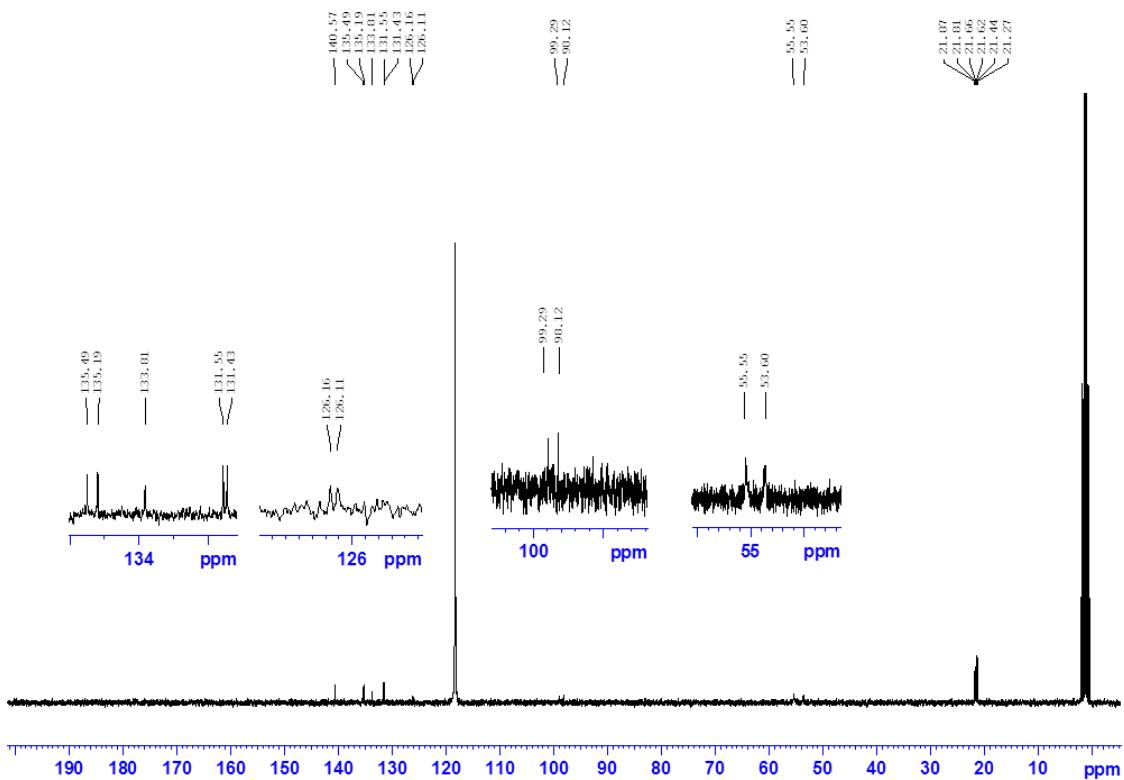
IR: $\tilde{\nu}$ = 834, 915, 1061, 1095, 1138, 1283, 1358, 1385, 1465, 1497, 1558, 1607, 1646, 1664, 2848, 2927, 3402 cm⁻¹.

Selected NMR spectra:

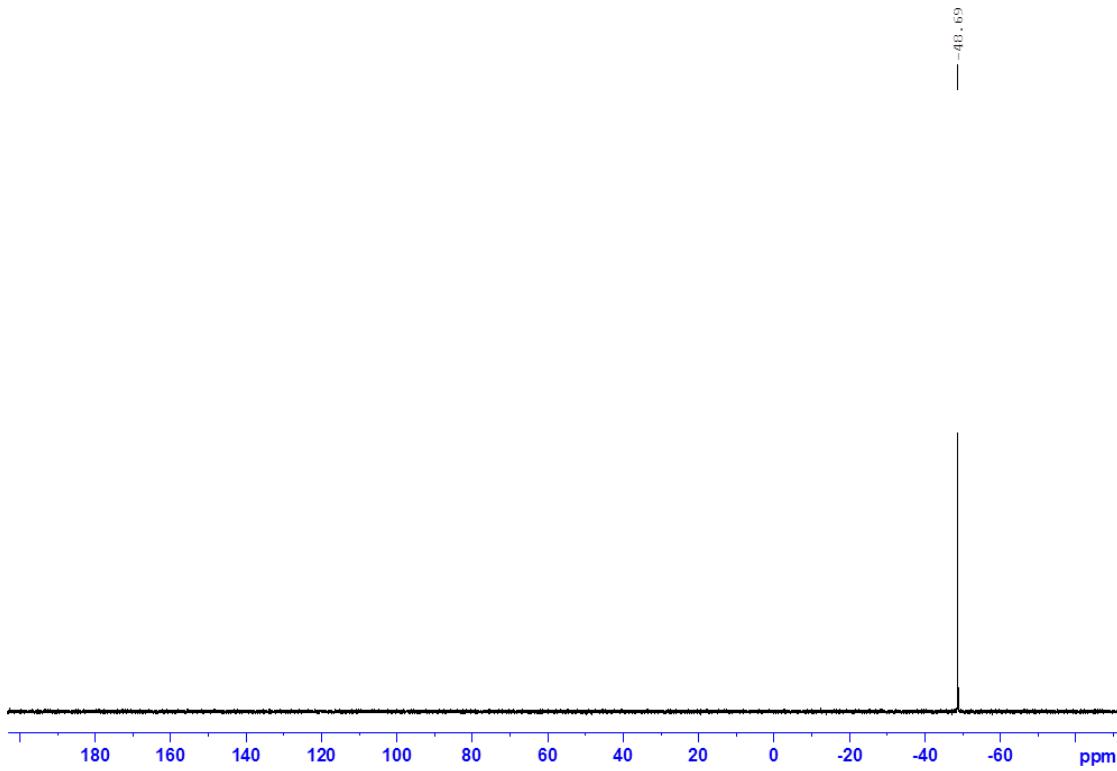
¹H-NMR (300 MHz, CD₃CN): compound 1a (SbF₆)



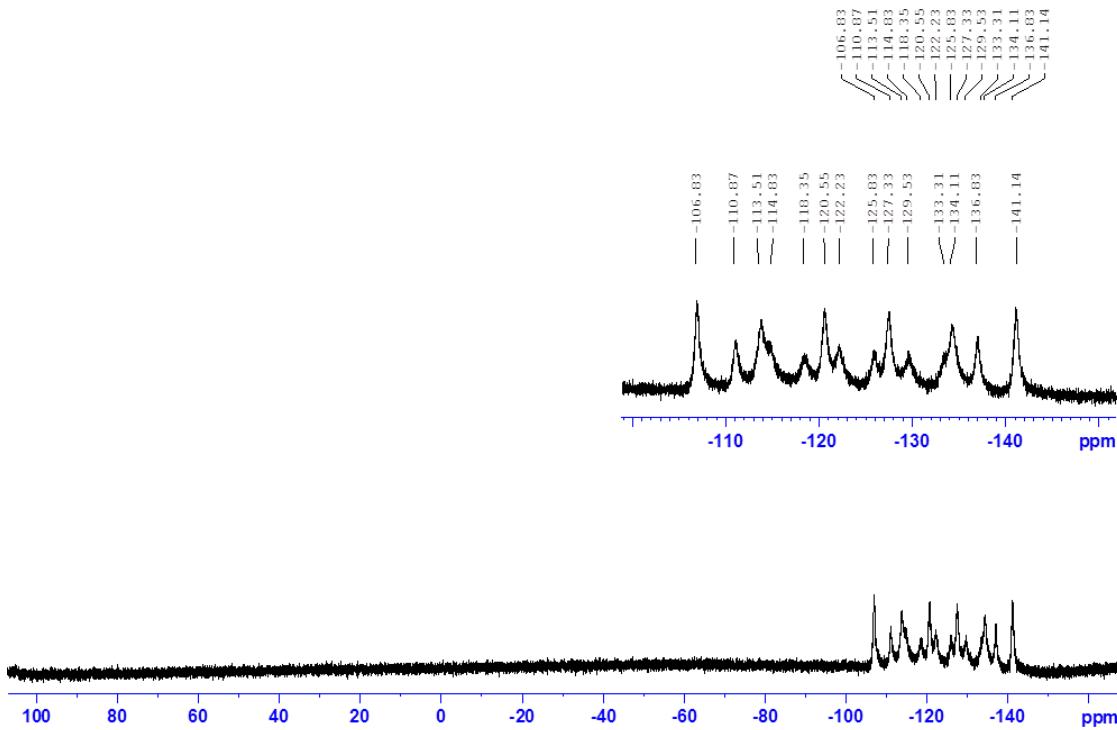
¹³C{¹H}-NMR (CD₃CN, 75 MHz): compound **1a** (SbF₆)



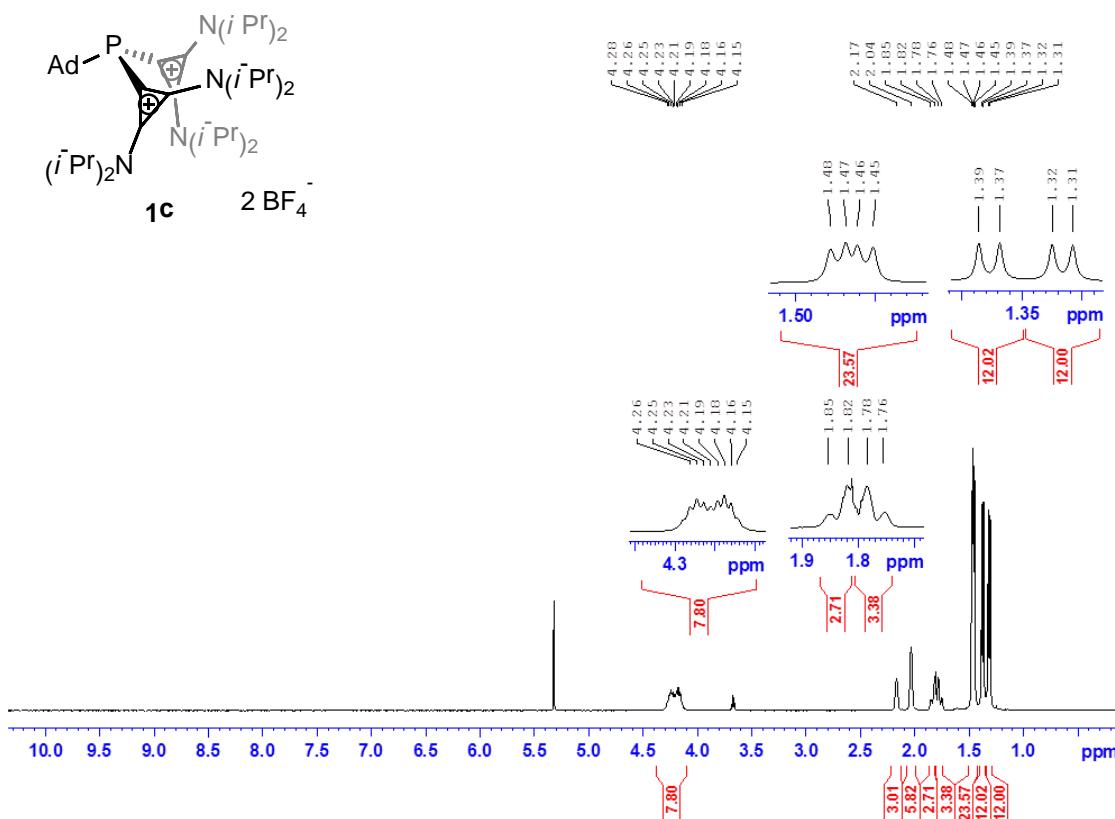
$^{31}\text{P}\{\text{H}\}$ -NMR (CD_3CN , 122 MHz): compound **1a** (SbF_6)



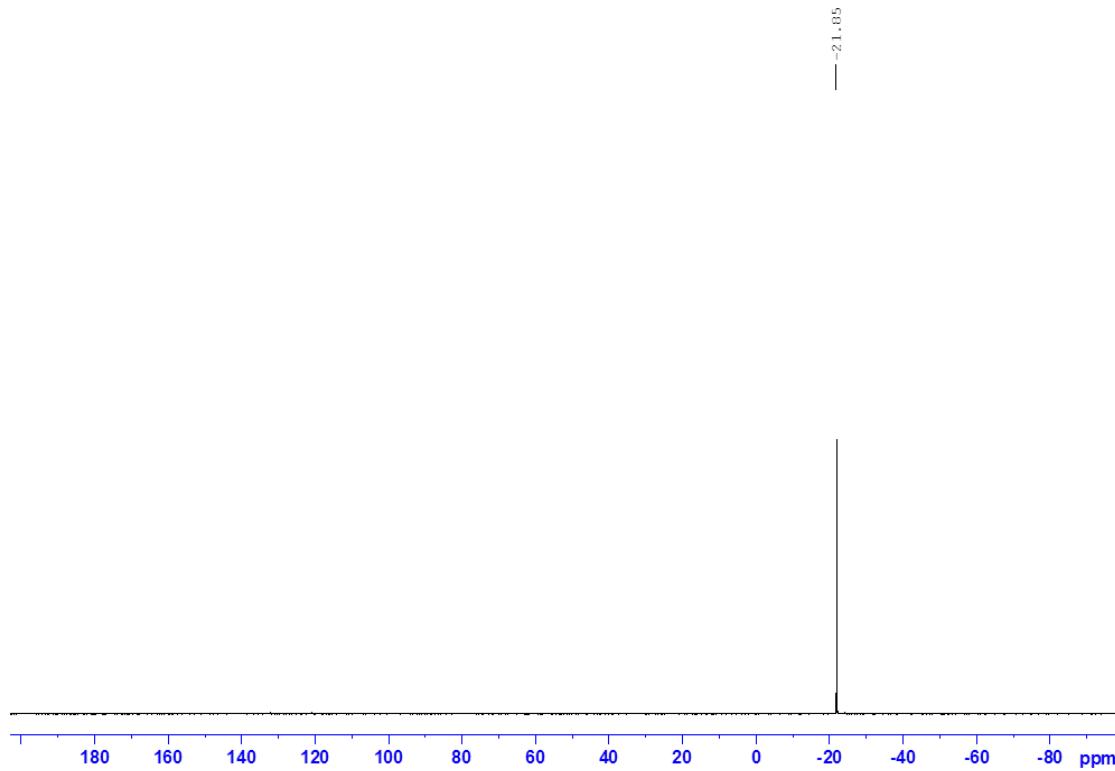
$^{19}\text{F}\{\text{H}\}$ -NMR (CD_3CN , 282 MHz): compound **1a** (SbF_6)



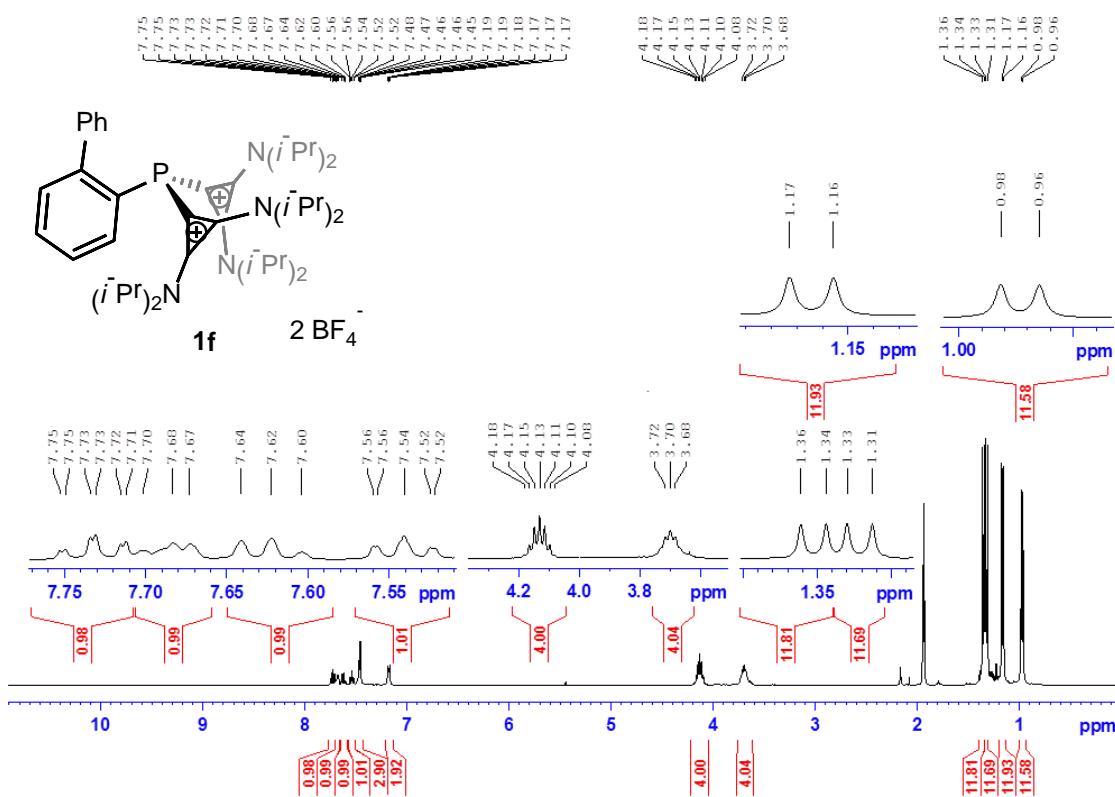
¹H-NMR (400 MHz, CD₂Cl₂): compound **1c**



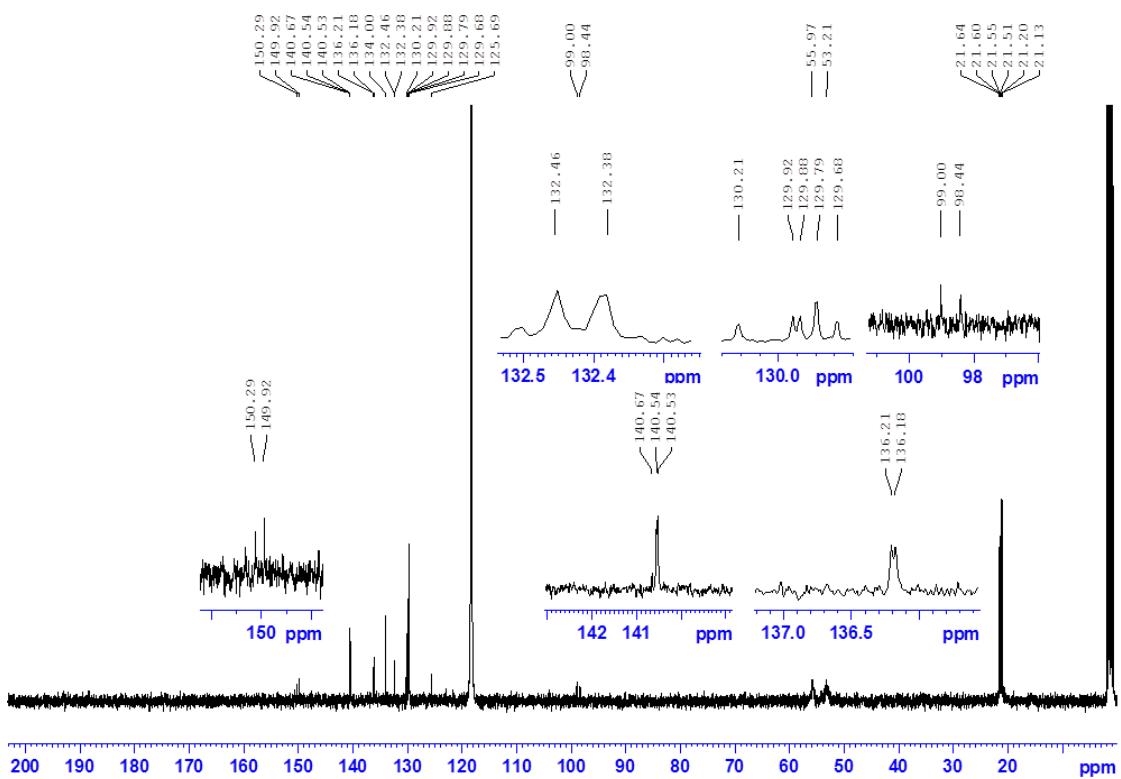
$^{31}\text{P}\{\text{H}\}$ -NMR (400 MHz, CD_2Cl_2): compound **1c**



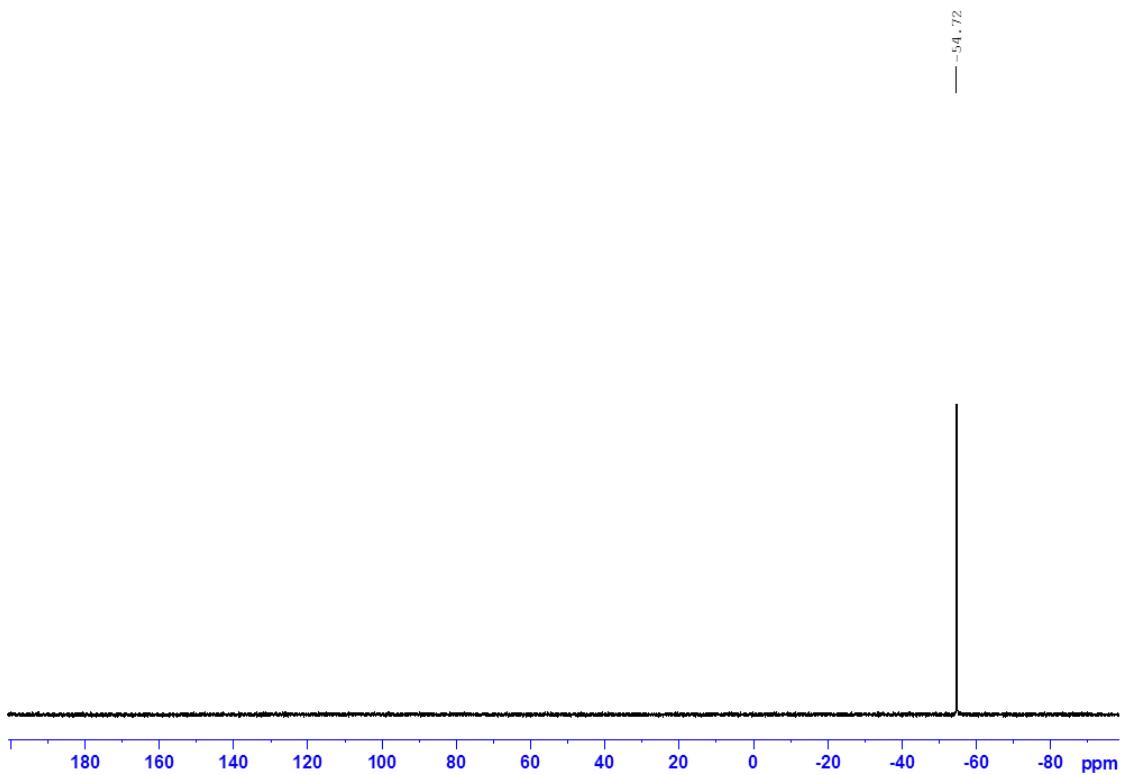
^1H -NMR (400 MHz, CD_3CN): compound **1f**



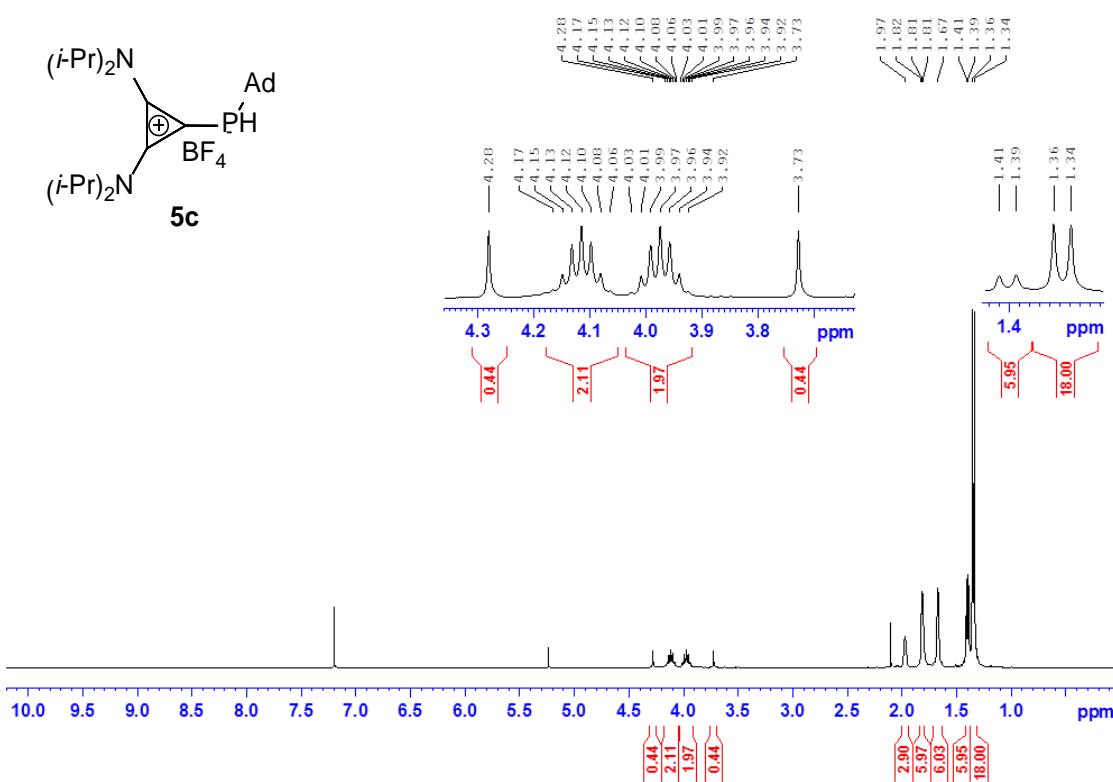
$^{13}\text{C}\{\text{H}\}$ -NMR (101 MHz, CD_3CN): compound 1f



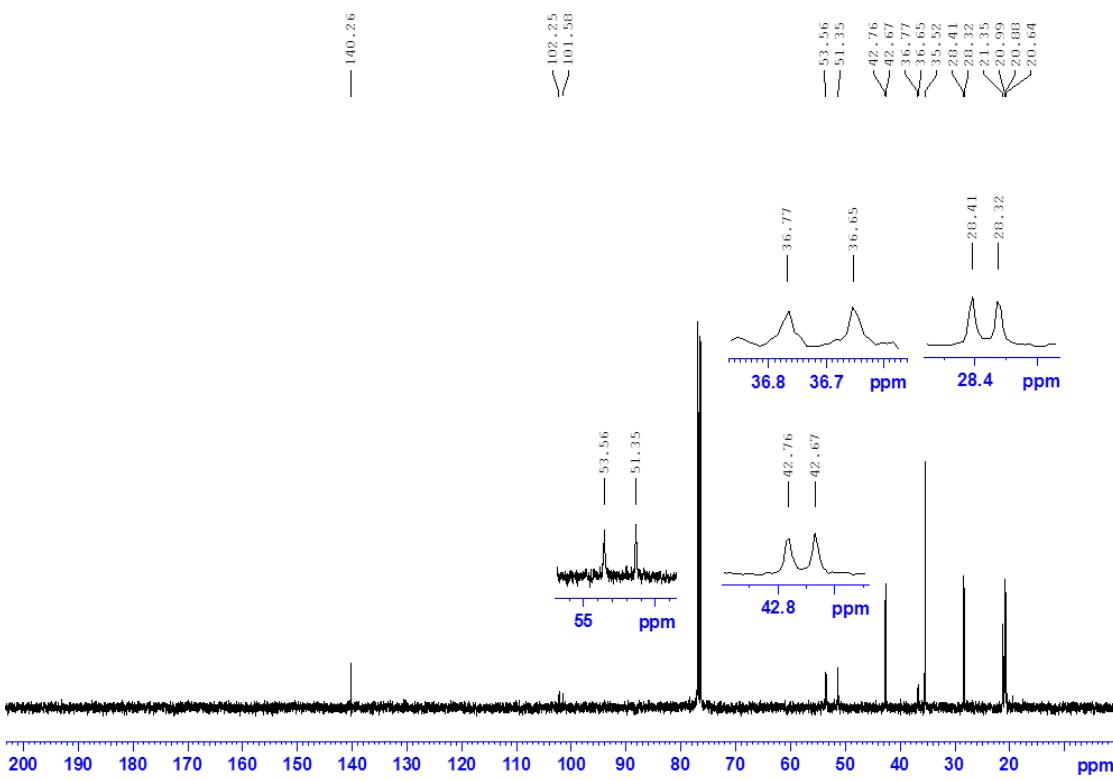
$^{31}\text{P}\{\text{H}\}$ -NMR (CD_3CN , 162 MHz): compound 1f



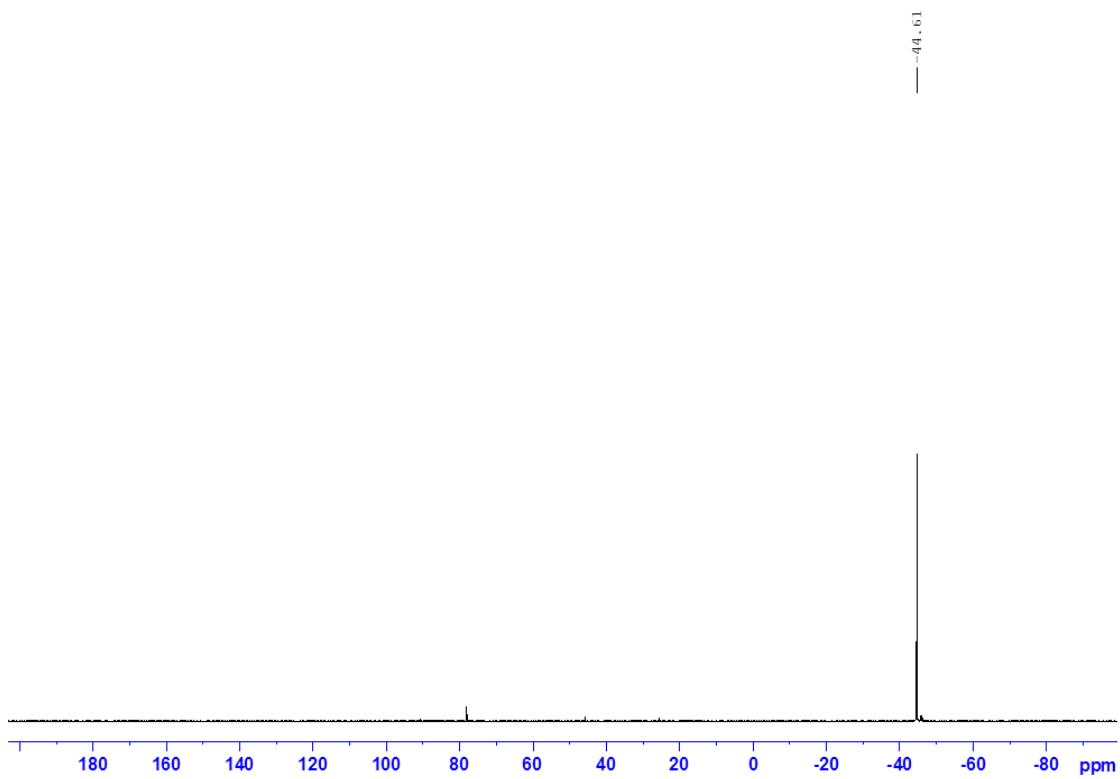
¹H-NMR (400, MHz, CDCl₃): compound 5c



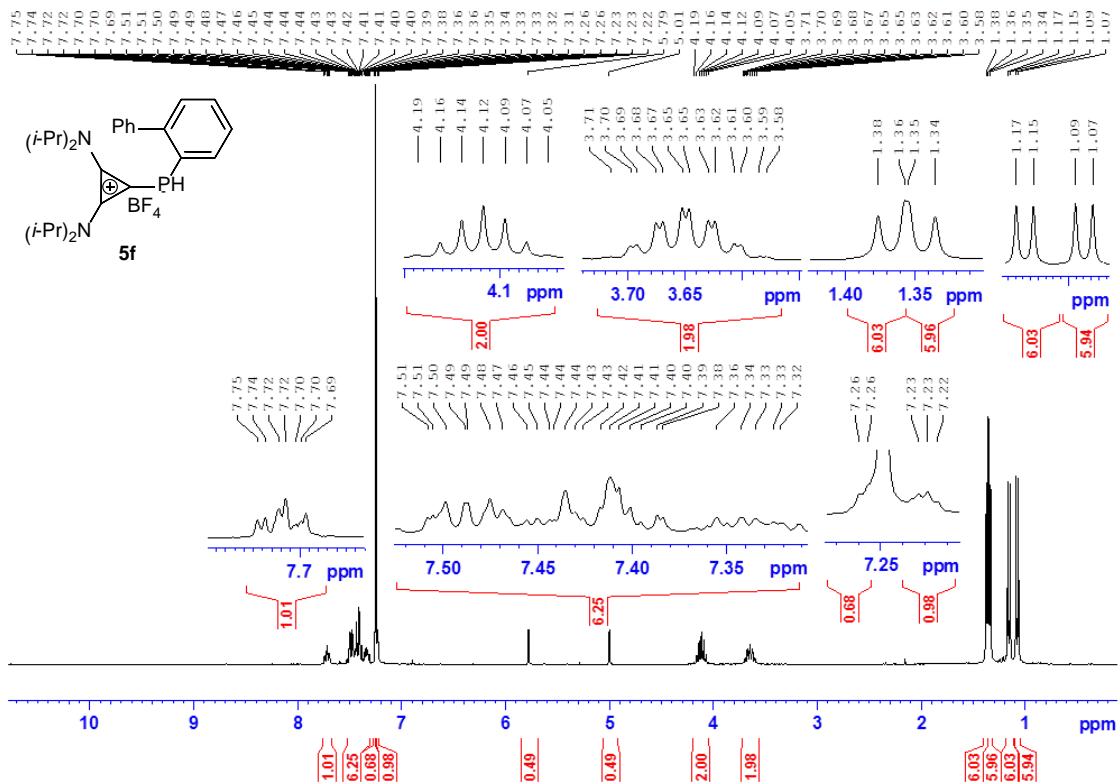
¹³C{¹H}-NMR (101, MHz, CDCl₃): compound 5c



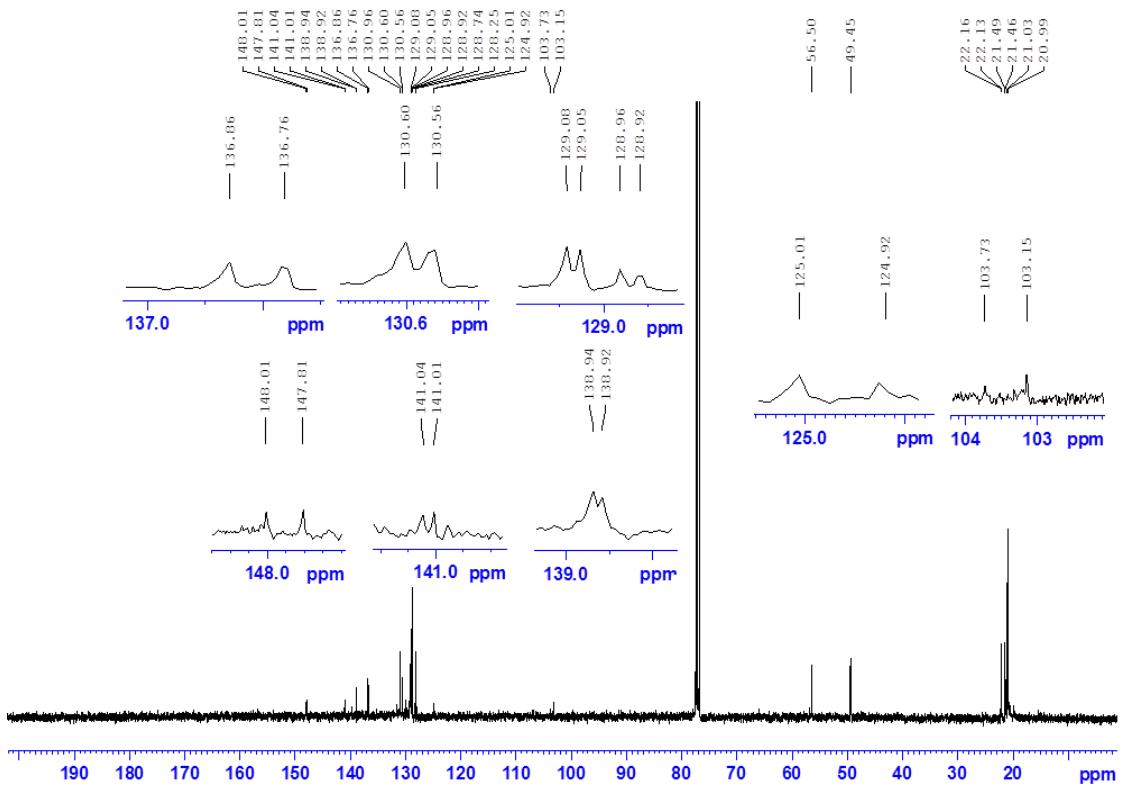
$^{31}\text{P}\{\text{H}\}$ -NMR (162, MHz, CDCl_3): compound 5c



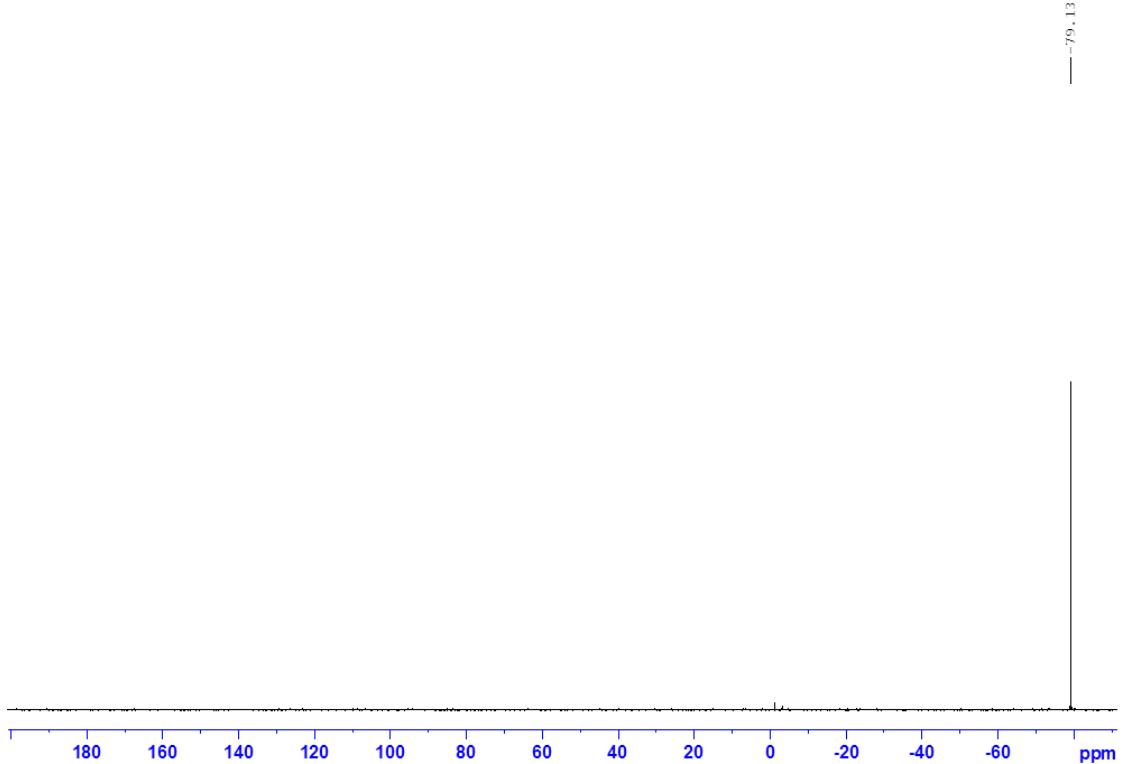
¹H-NMR (400 MHz, CDCl₃): compound 5f



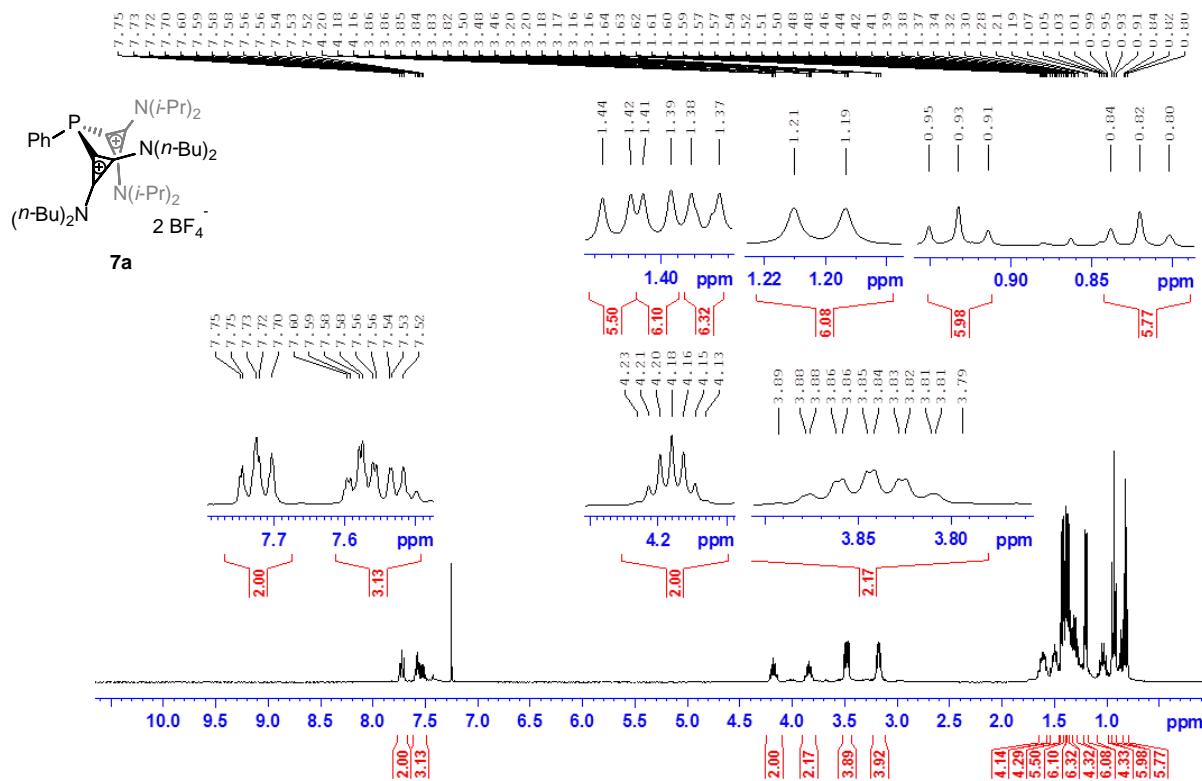
¹³C{¹H}-NMR (CDCl₃, 101 MHz): compound 5f



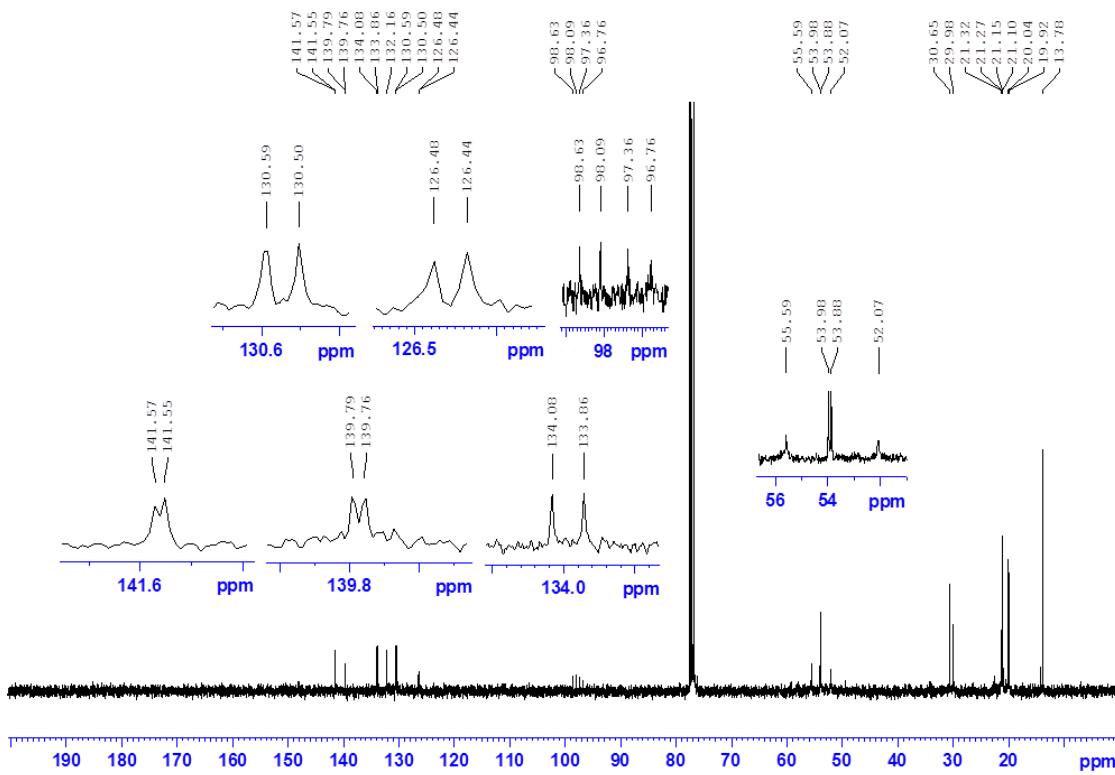
³¹P{¹H}-NMR (CDCl₃, 162 MHz): compound 5f



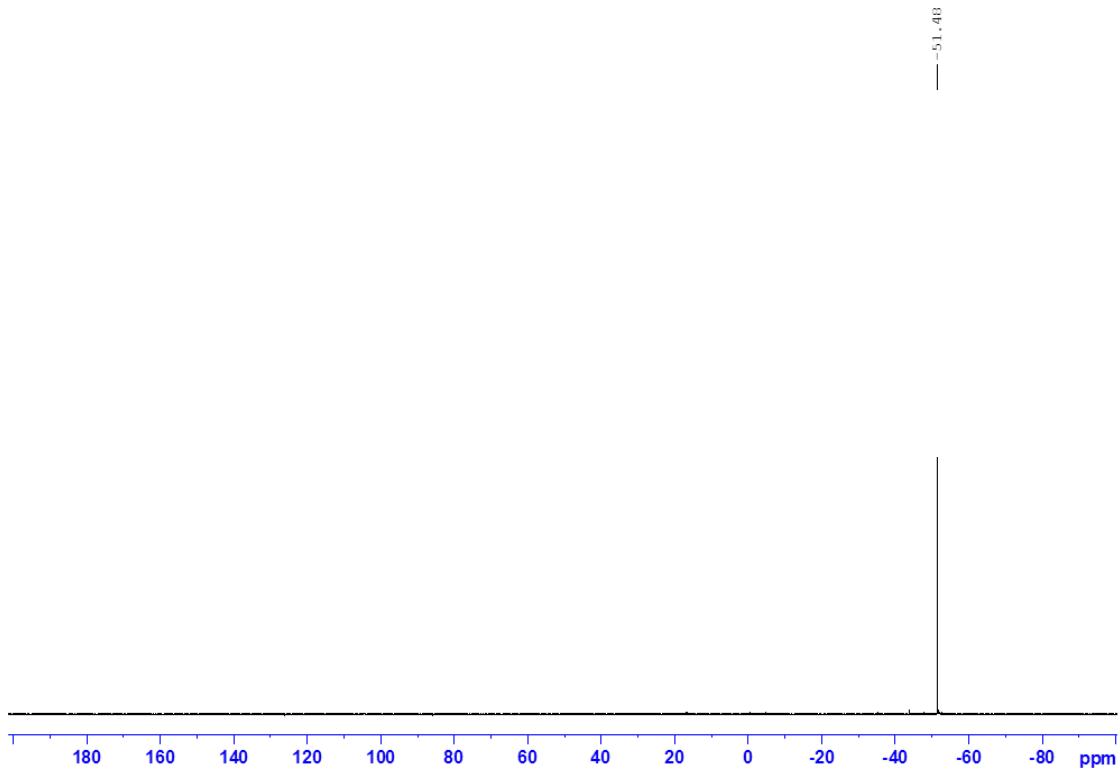
¹H-NMR (400 MHz, CDCl₃): Compound 7a



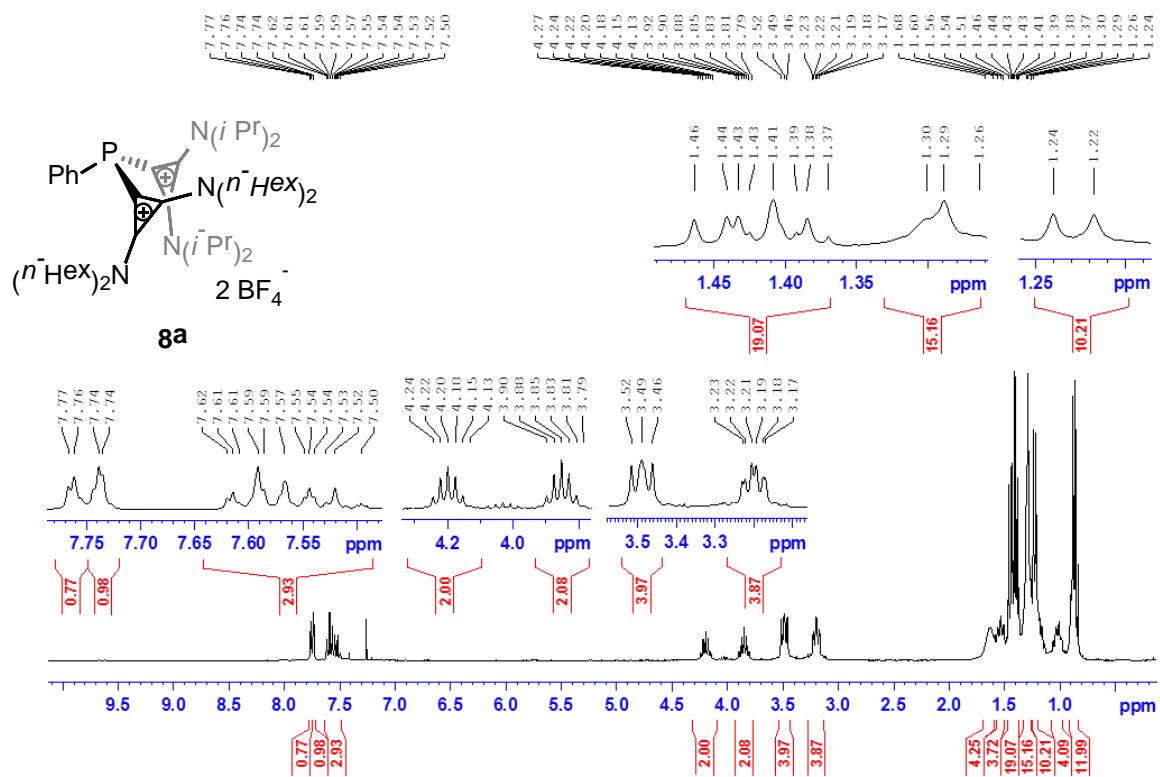
¹³C{¹H}-NMR (101 MHz, CDCl₃): Compound 7a



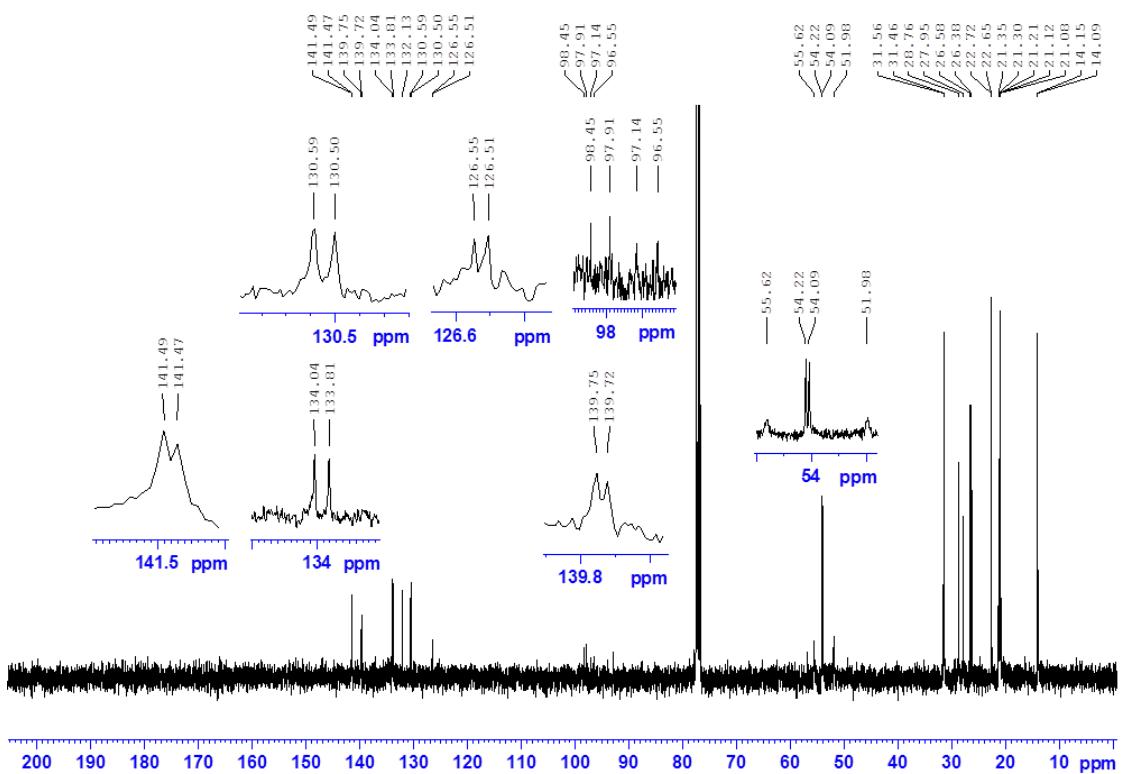
³¹P{¹H}-NMR (162 MHz, CDCl₃): Compound 7a



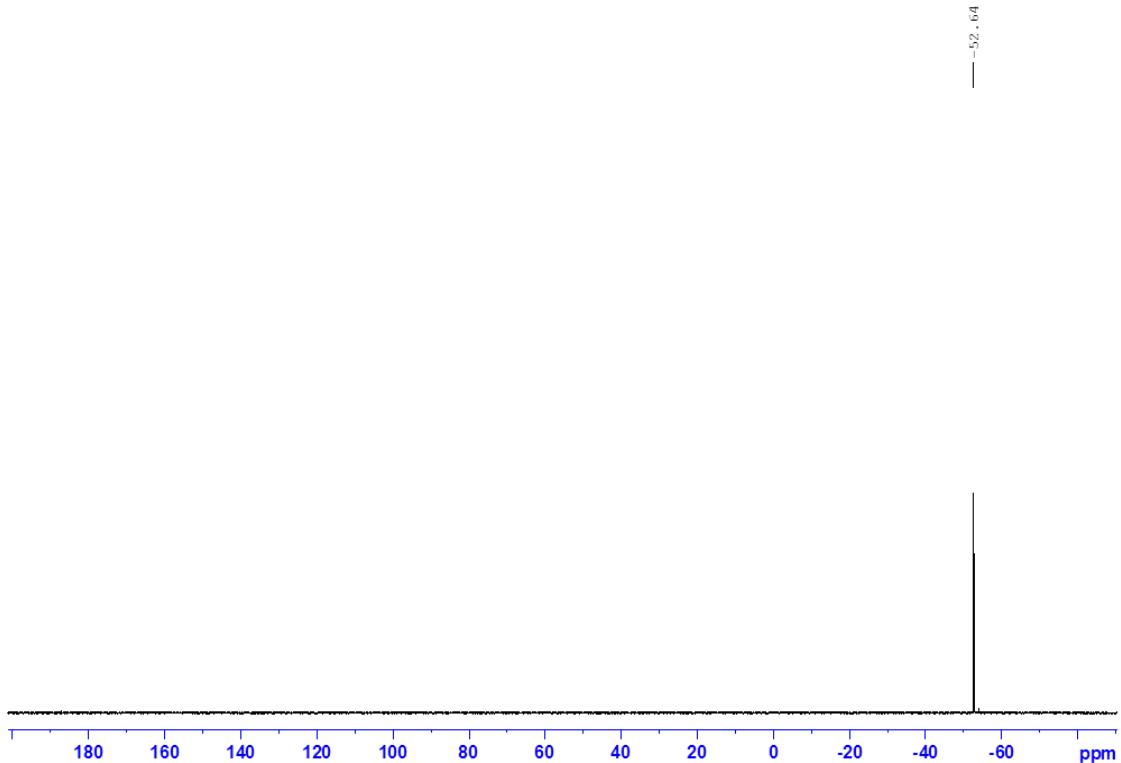
¹H-NMR (300 MHz, CDCl₃): Compound 8a



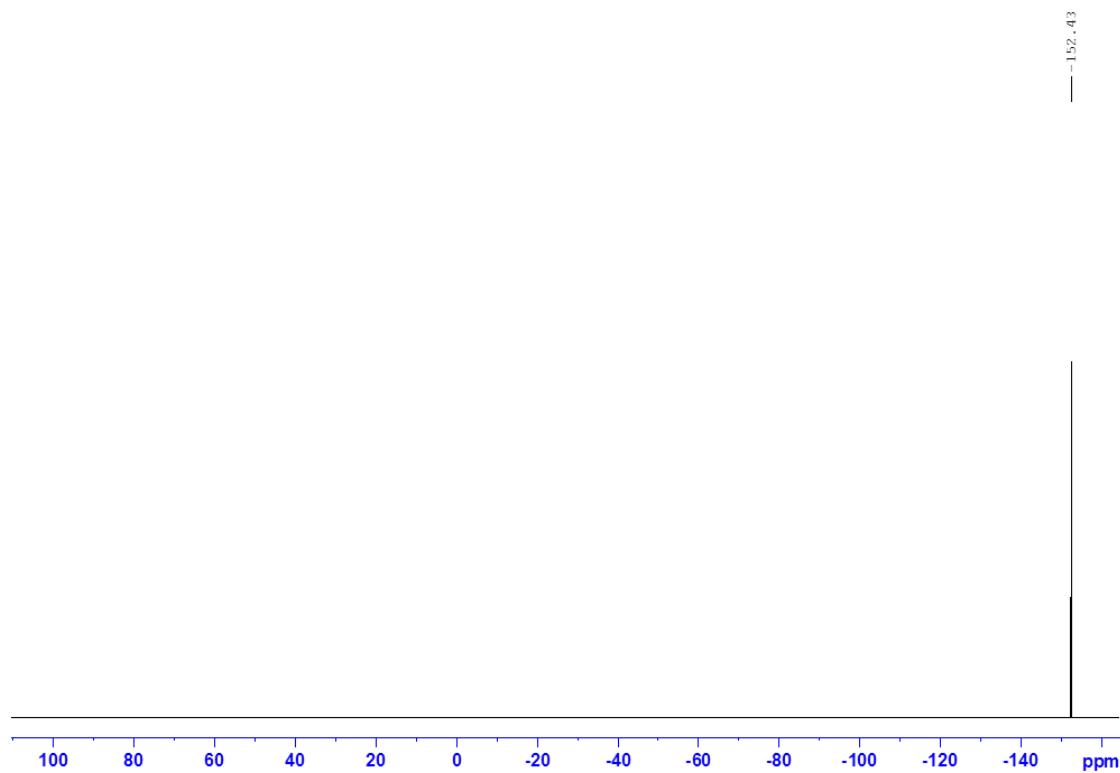
$^{13}\text{C}\{\text{H}\}$ -NMR (75 MHz, CDCl_3): Compound 8a



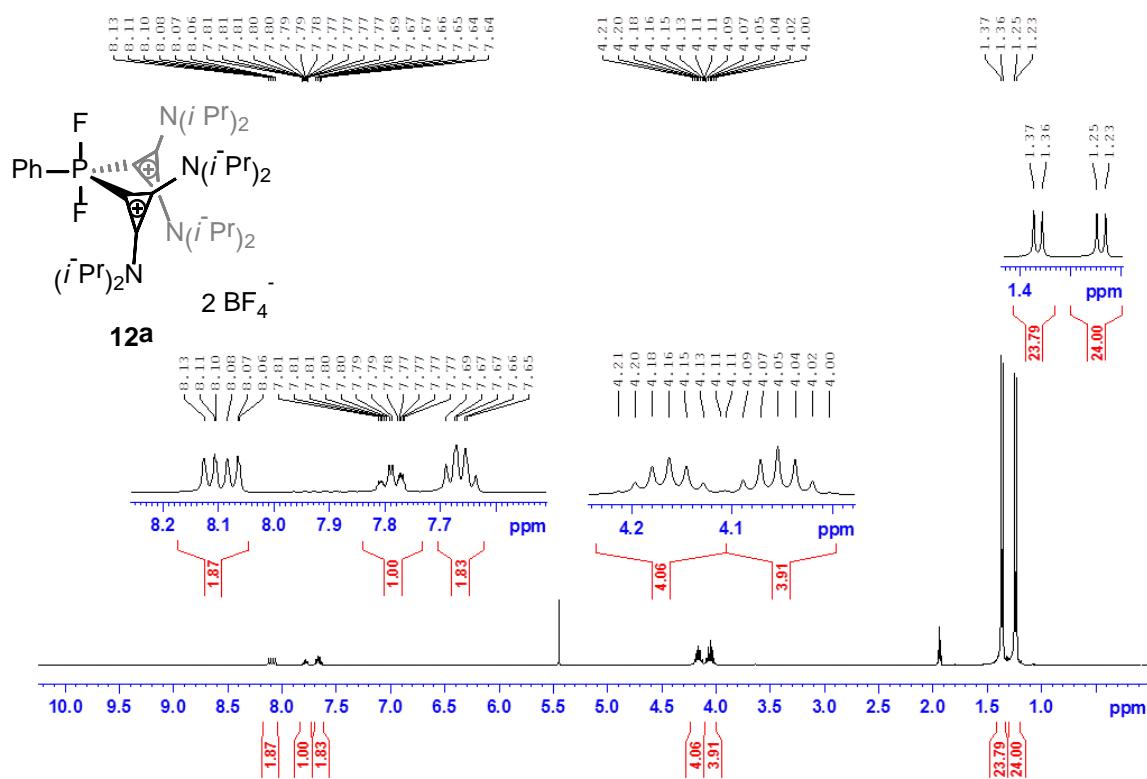
$^{31}\text{P}\{\text{H}\}$ -NMR (122 MHz, CDCl_3): Compound 8a



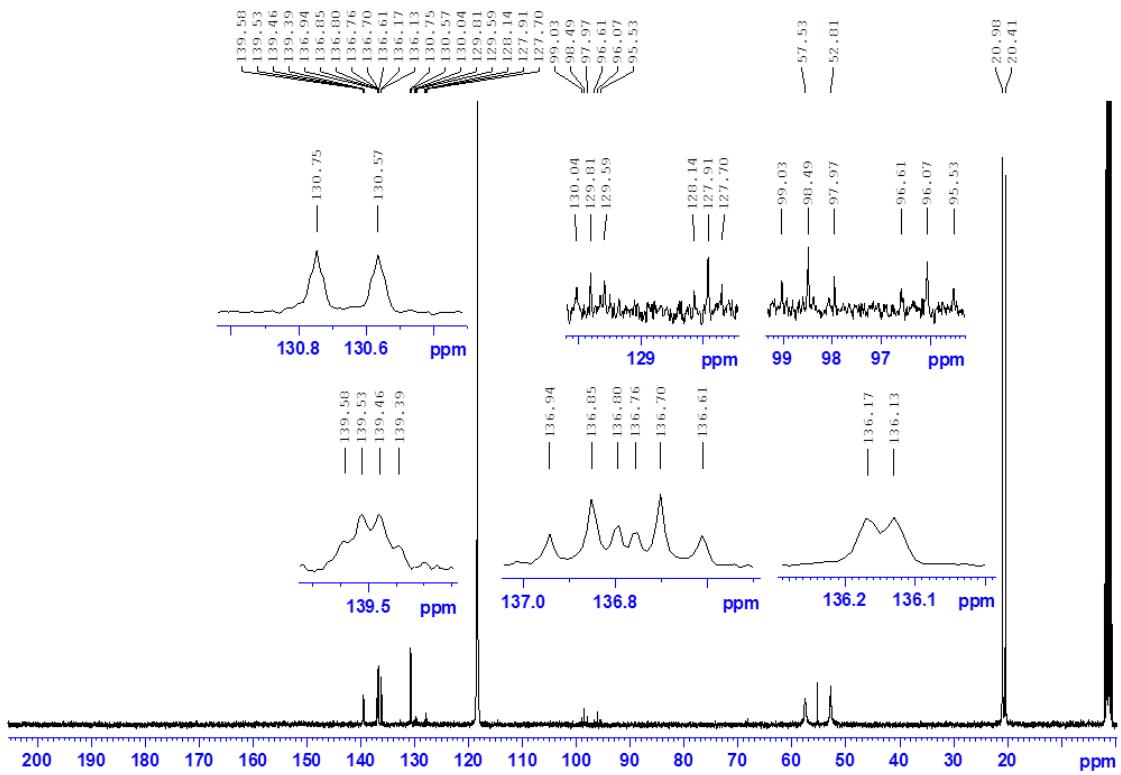
¹⁹F{¹H}-NMR (282 MHz, CDCl₃): Compound **8a**



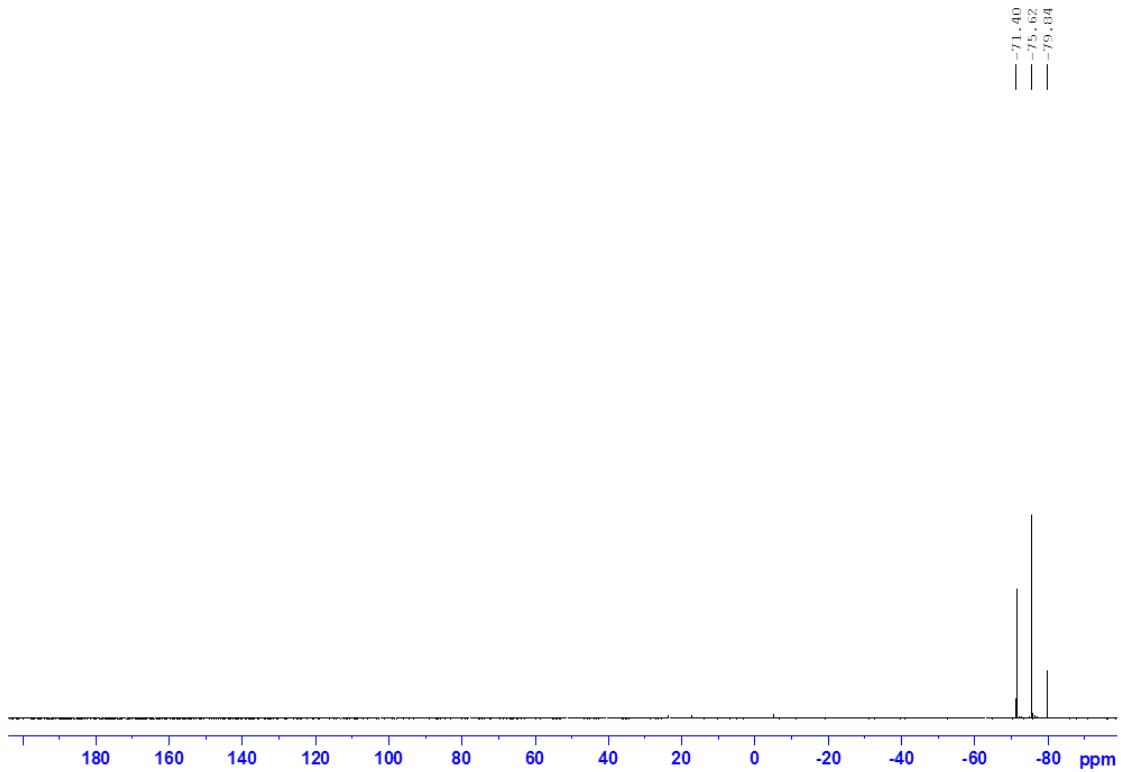
¹H-NMR (400, MHz, CD₃CN): compound **12a**



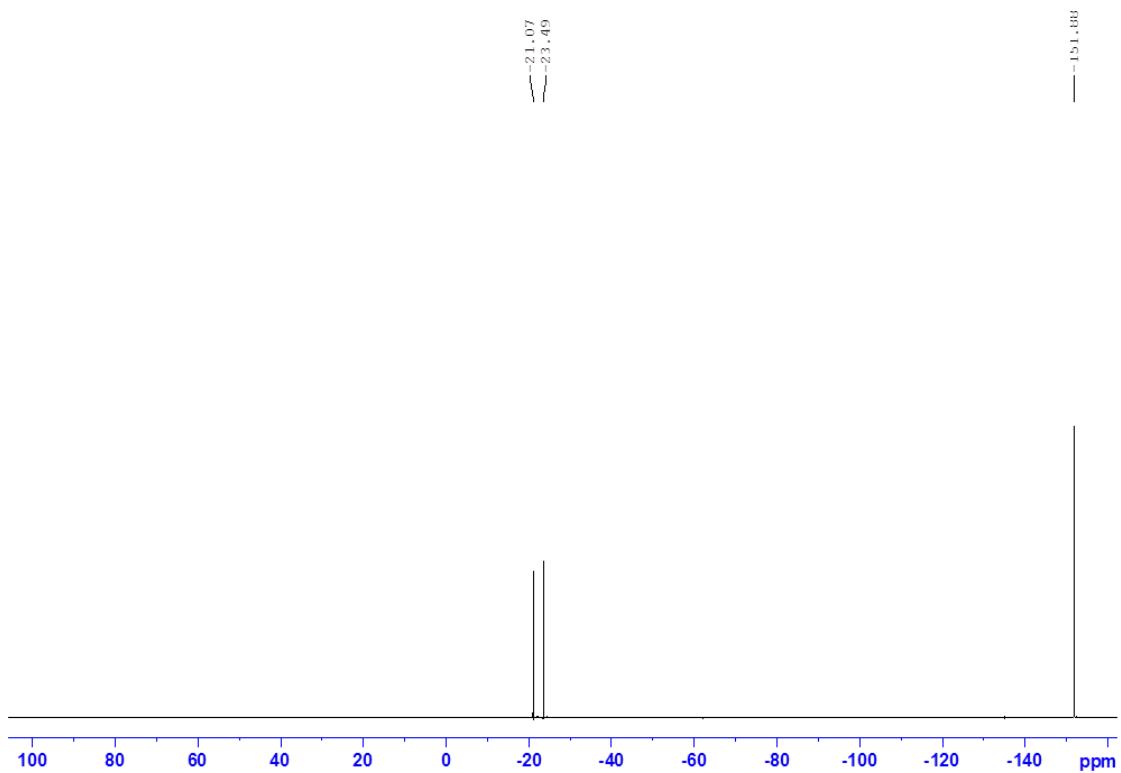
¹³C{¹H}-NMR (101, MHz, CD₃CN): compound 12a



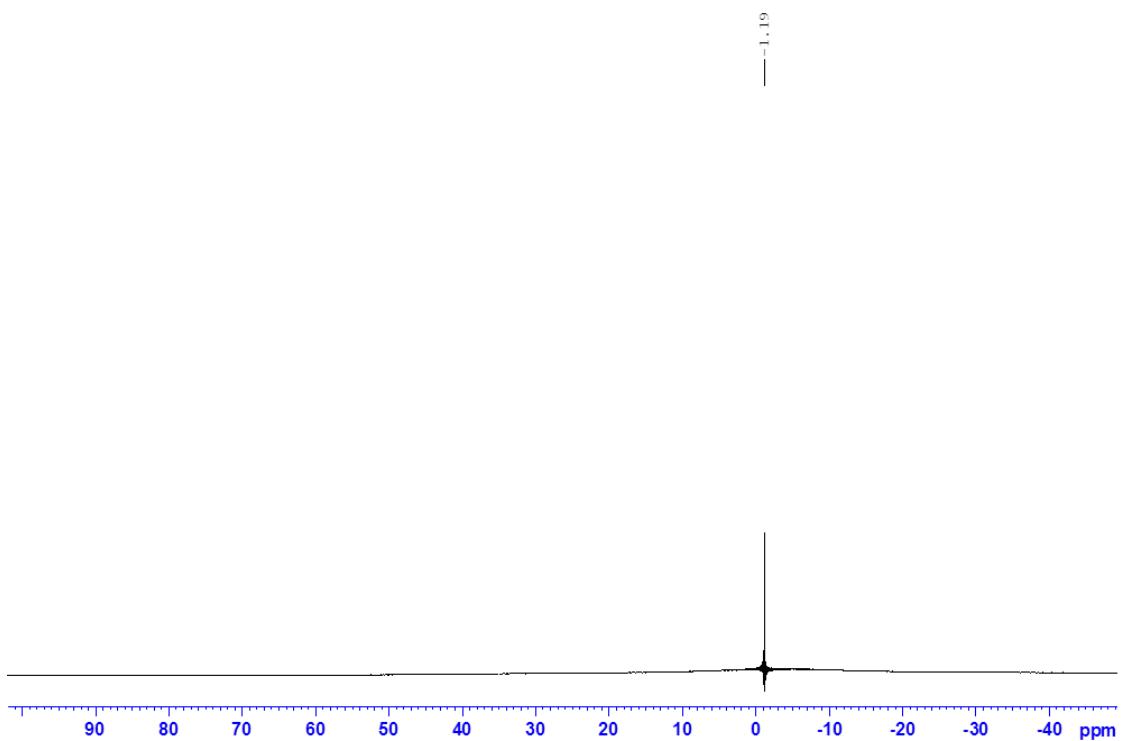
$^{31}\text{P}\{\text{H}\}$ -NMR (162, MHz, CD_3CN): compound **12a**



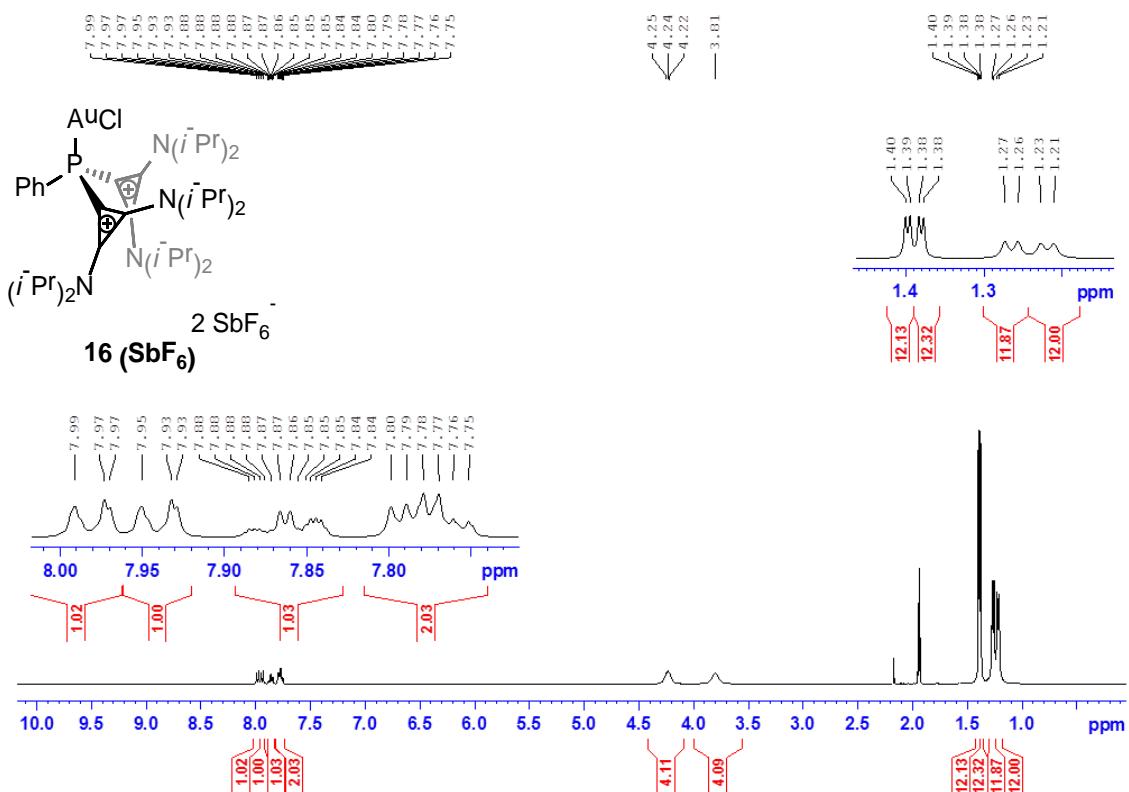
¹⁹F{¹H}-NMR (282, MHz, CD₃CN): compound **12a**



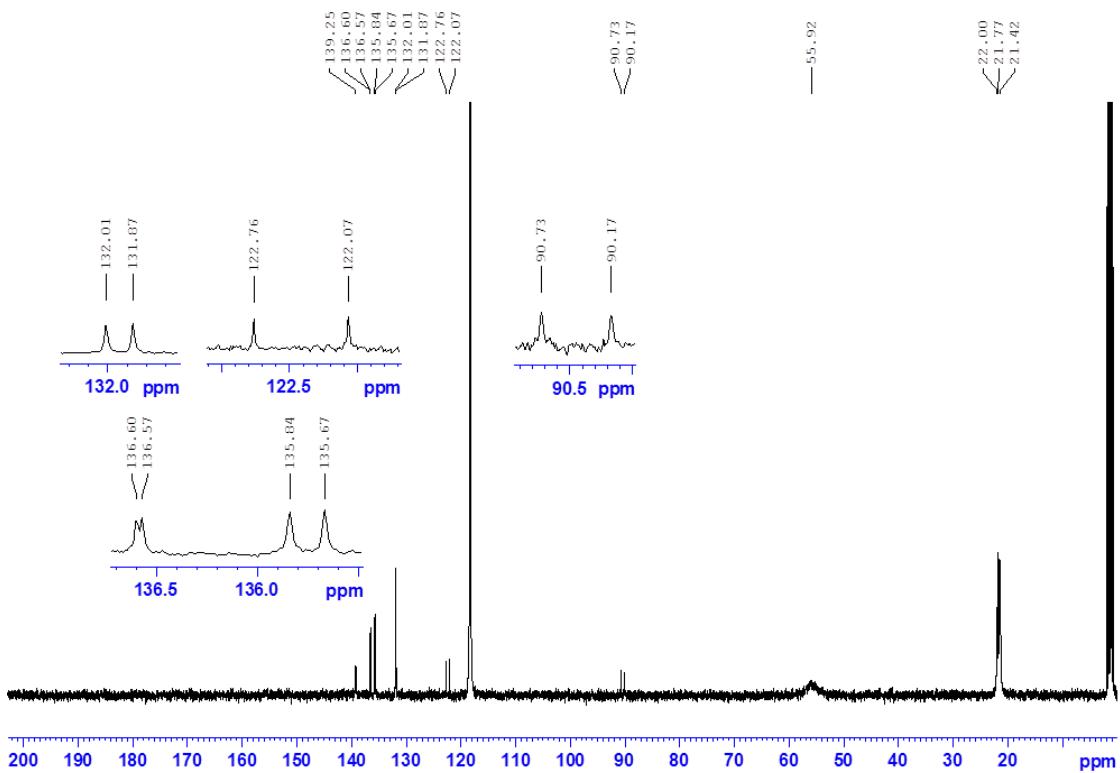
¹¹B{¹H}-NMR (96, MHz, CD₃CN): compound **12a**



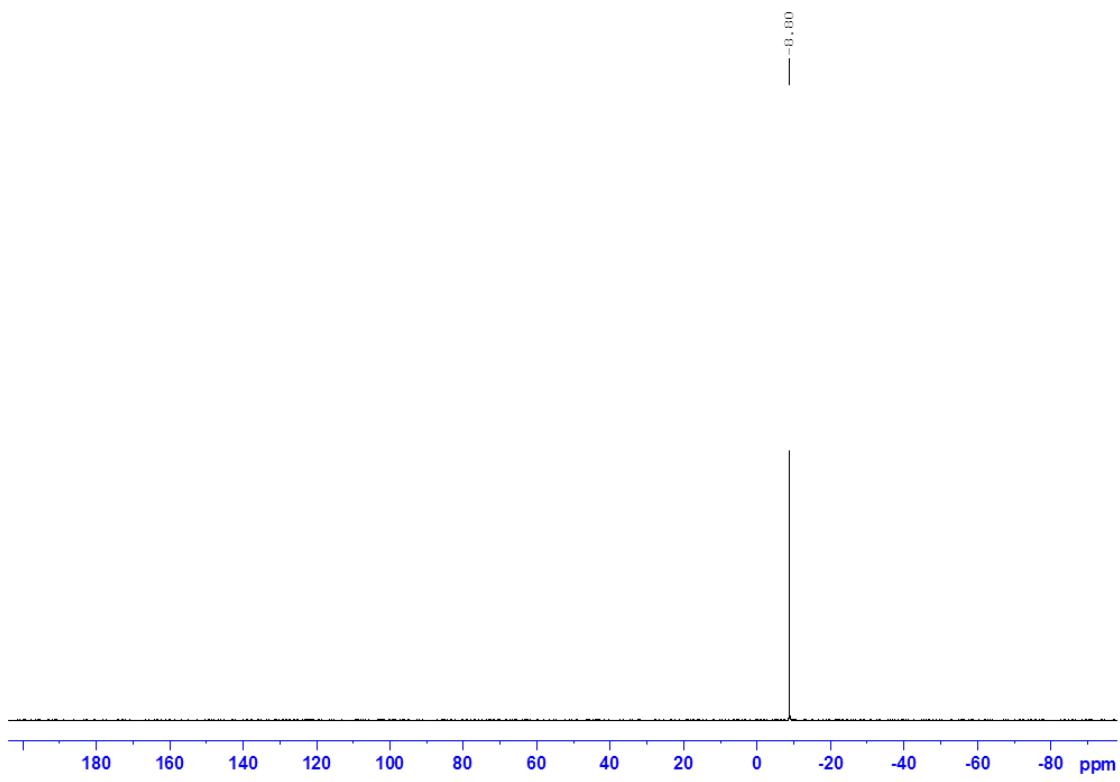
¹H-NMR (400 MHz, CD₃CN): Compound **16** (SbF₆)



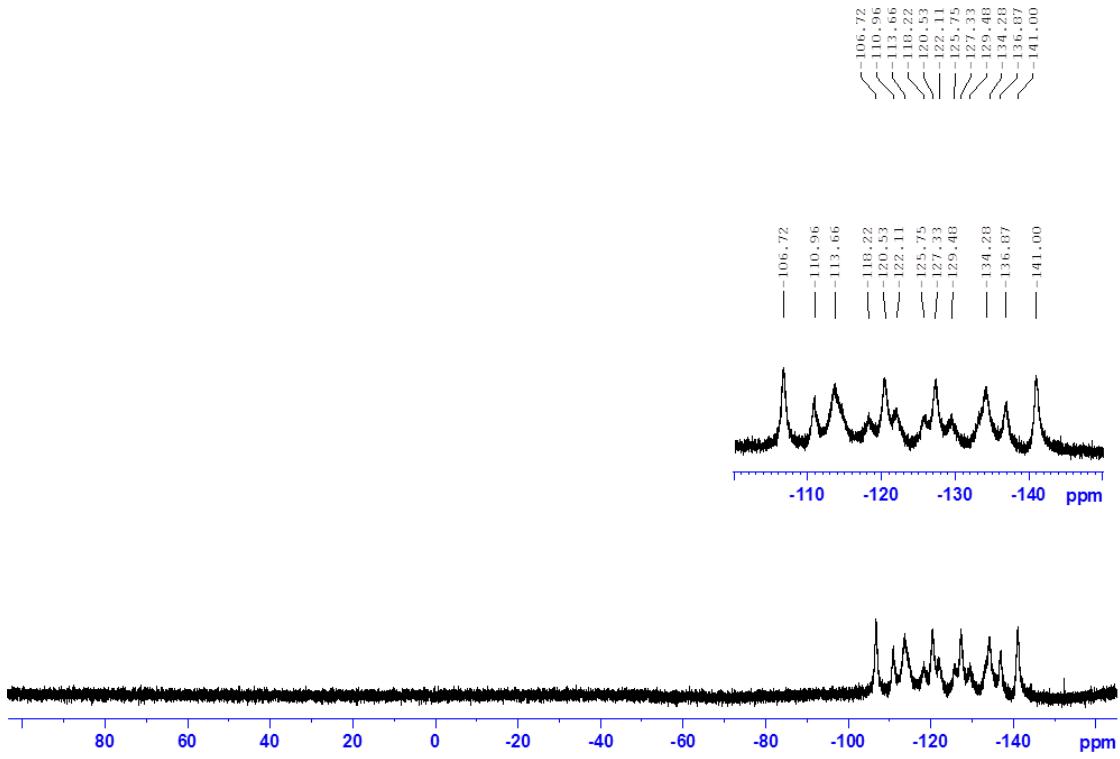
¹³C{¹H}-NMR (125 MHz, CD₃CN): Compound **16** (SbF₆)



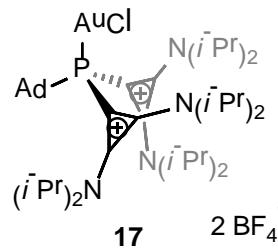
$^{31}\text{P}\{\text{H}\}$ -NMR (162 MHz, CD_3CN): Compound 16 (SbF_6)



$^{19}\text{F}\{\text{H}\}$ -NMR (282 MHz, CD_3CN): Compound 16 (SbF_6)

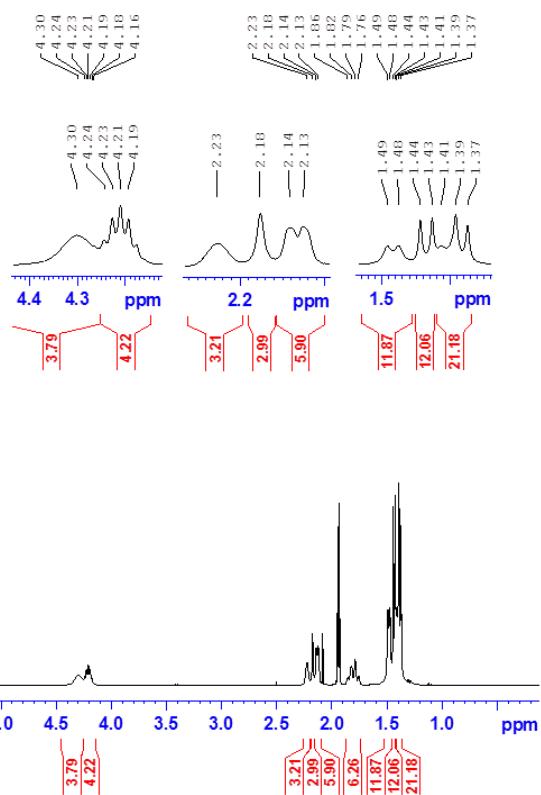


¹H-NMR (400 MHz, CD₃CN): compound 17

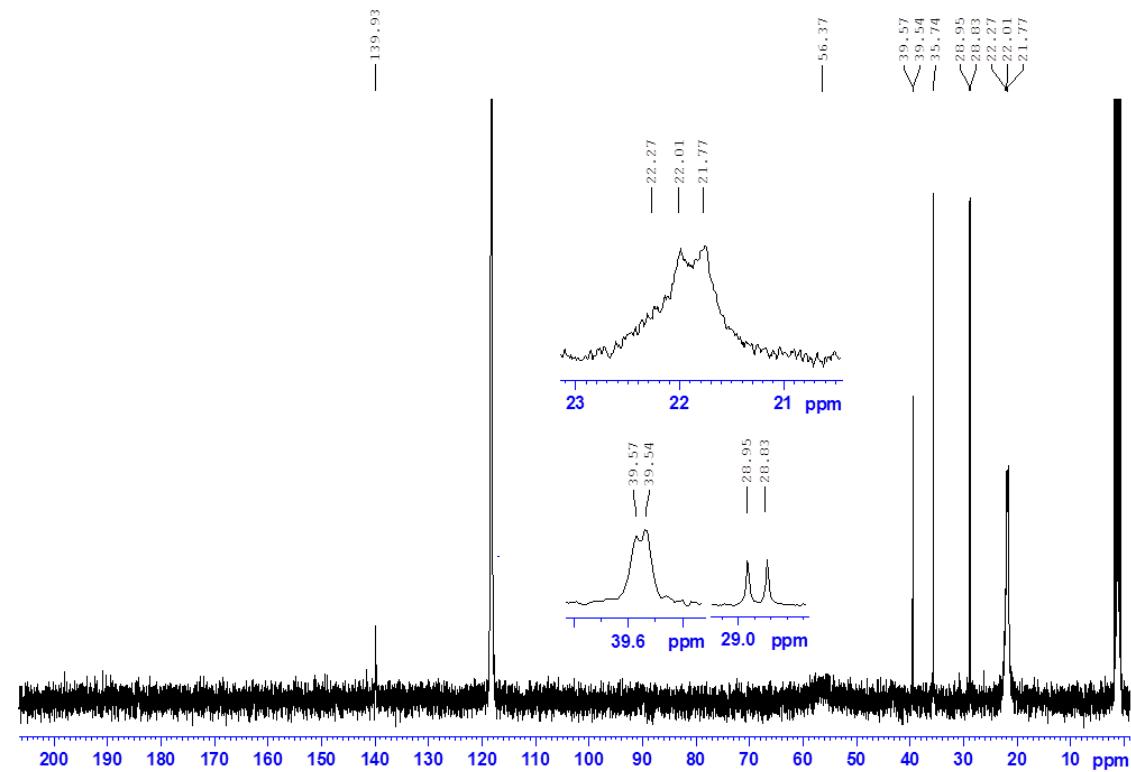


BF₄

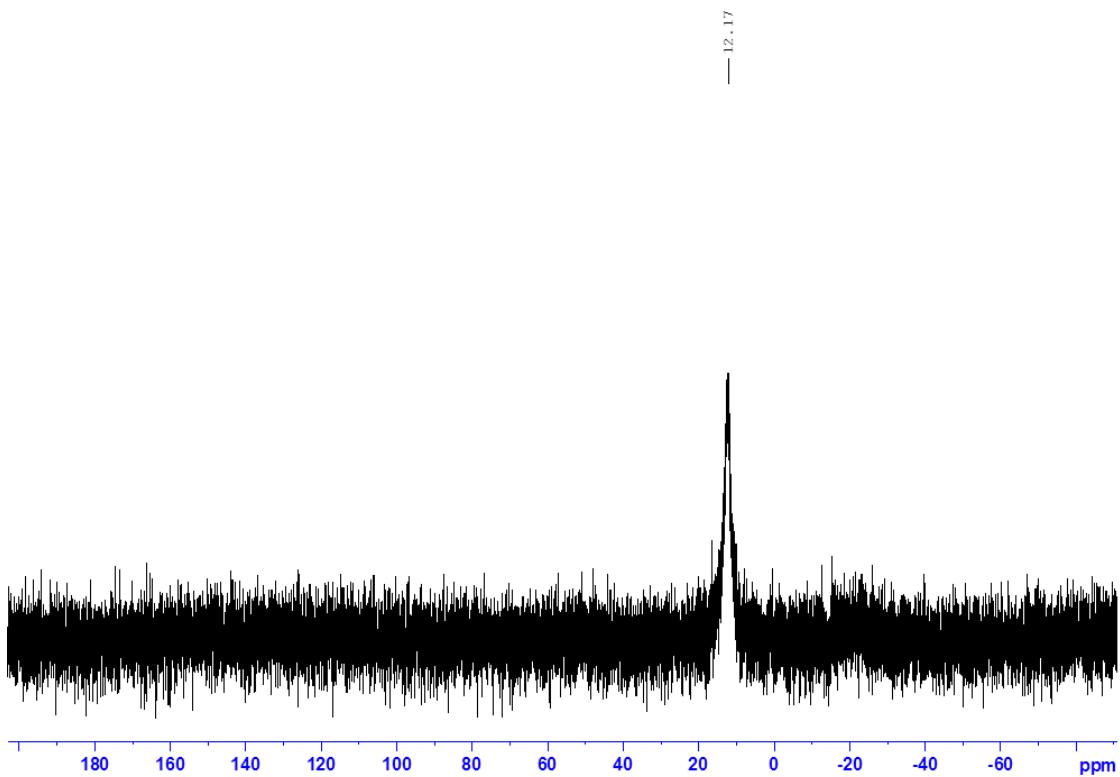
BF₄



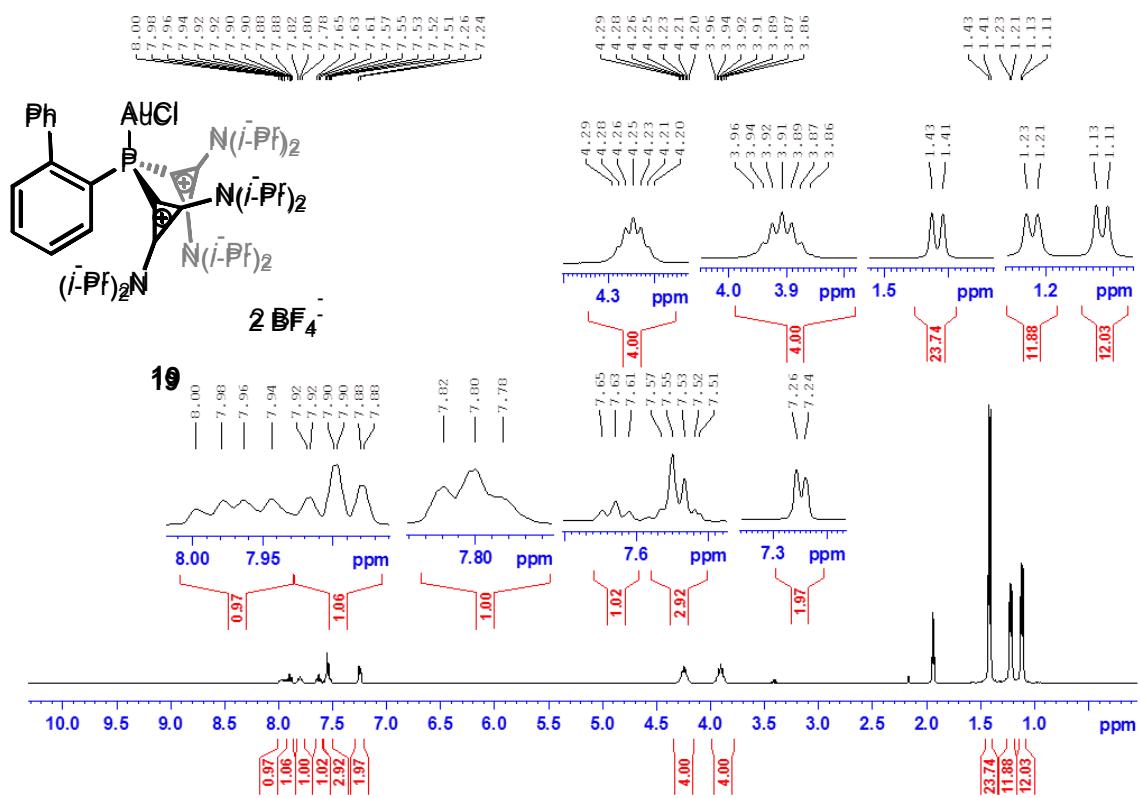
$^{13}\text{C}\{\text{H}\}$ -NMR (400 MHz, CD_3CN): compound 17



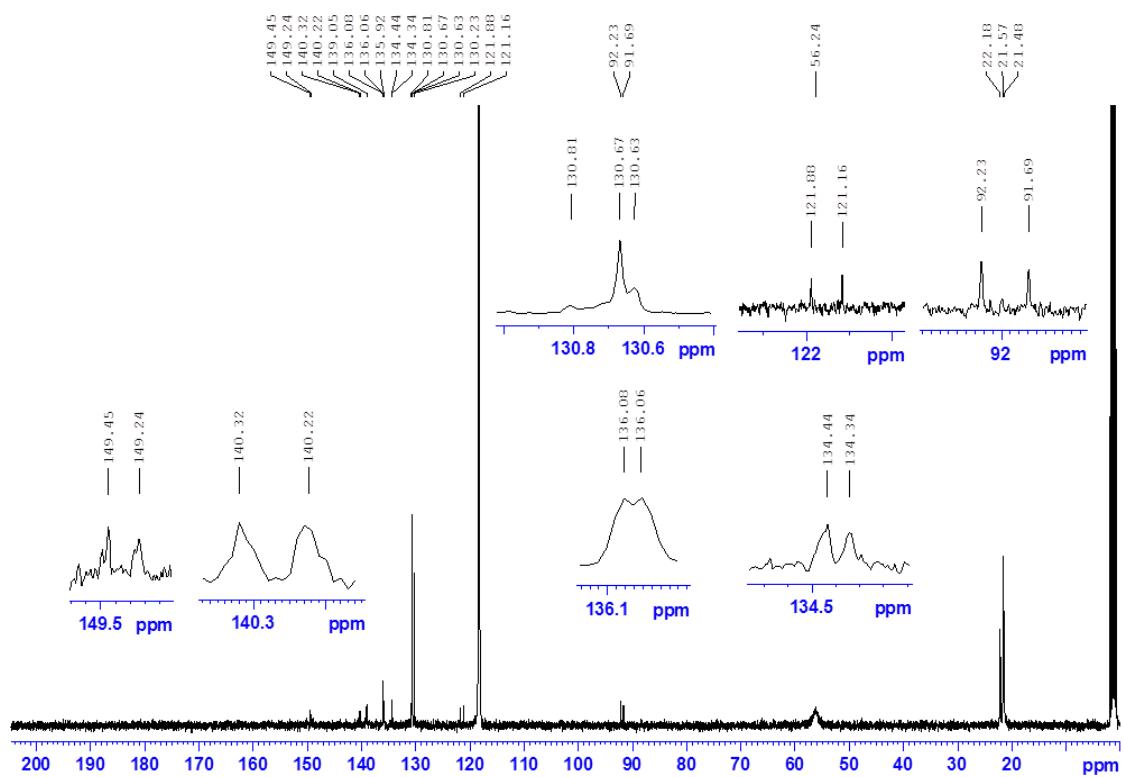
³¹P{¹H}-NMR (101 MHz, CD₃CN): compound 17



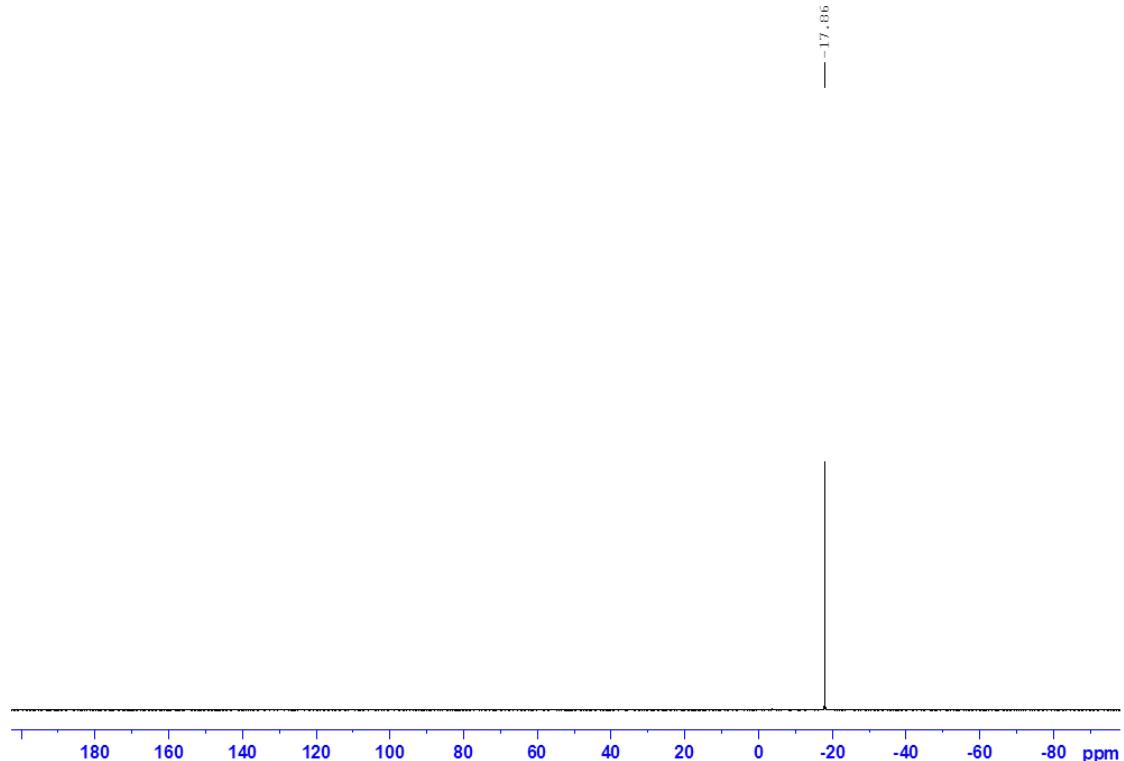
¹H-NMR (400 MHz, CD₃CN): Au(I)-complex **19**



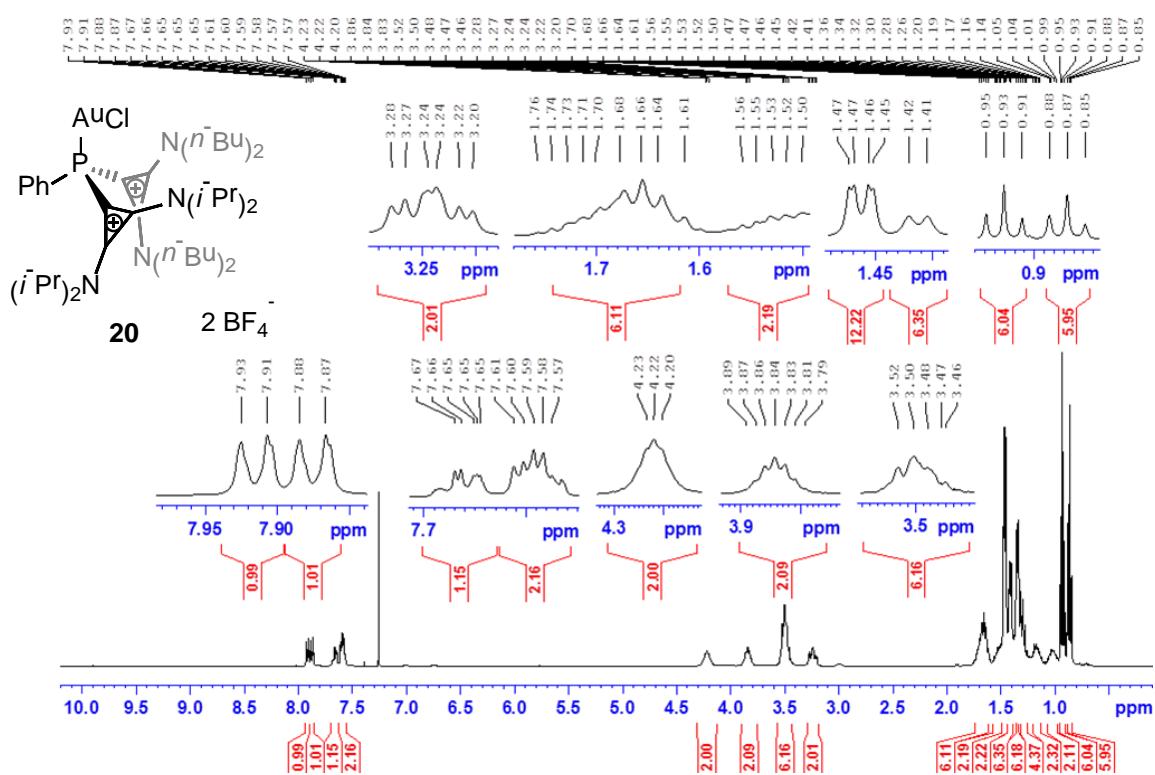
$^{13}\text{C}\{\text{H}\}$ -NMR (125 MHz, CD_3CN): Au(I)-complex 19



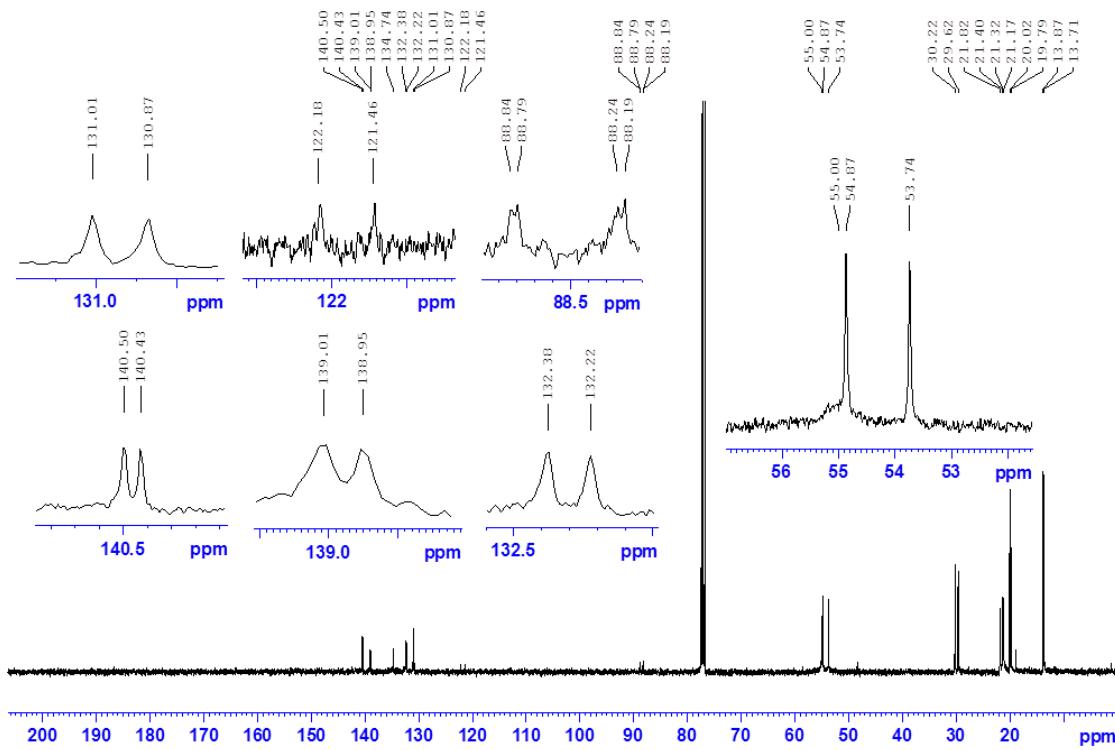
$^{31}\text{P}\{\text{H}\}$ -NMR (162 MHz, CD_3CN): Au(I)-complex 19



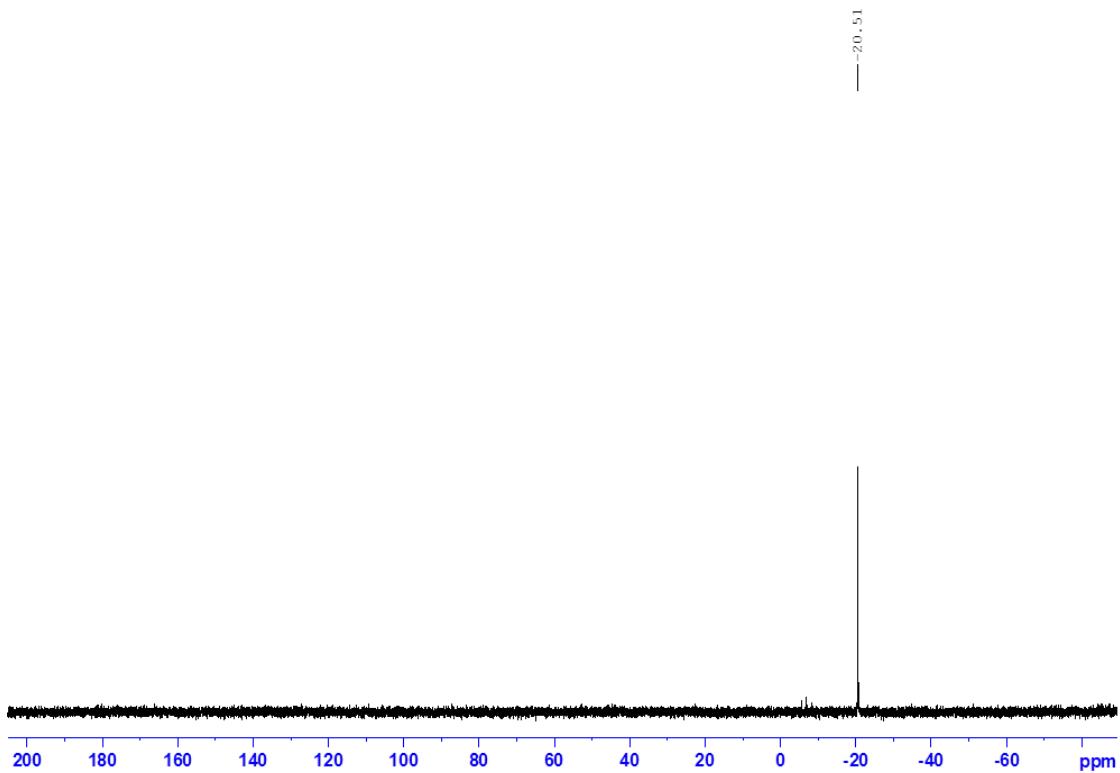
¹H-NMR (400 MHz, CDCl₃): compound 20



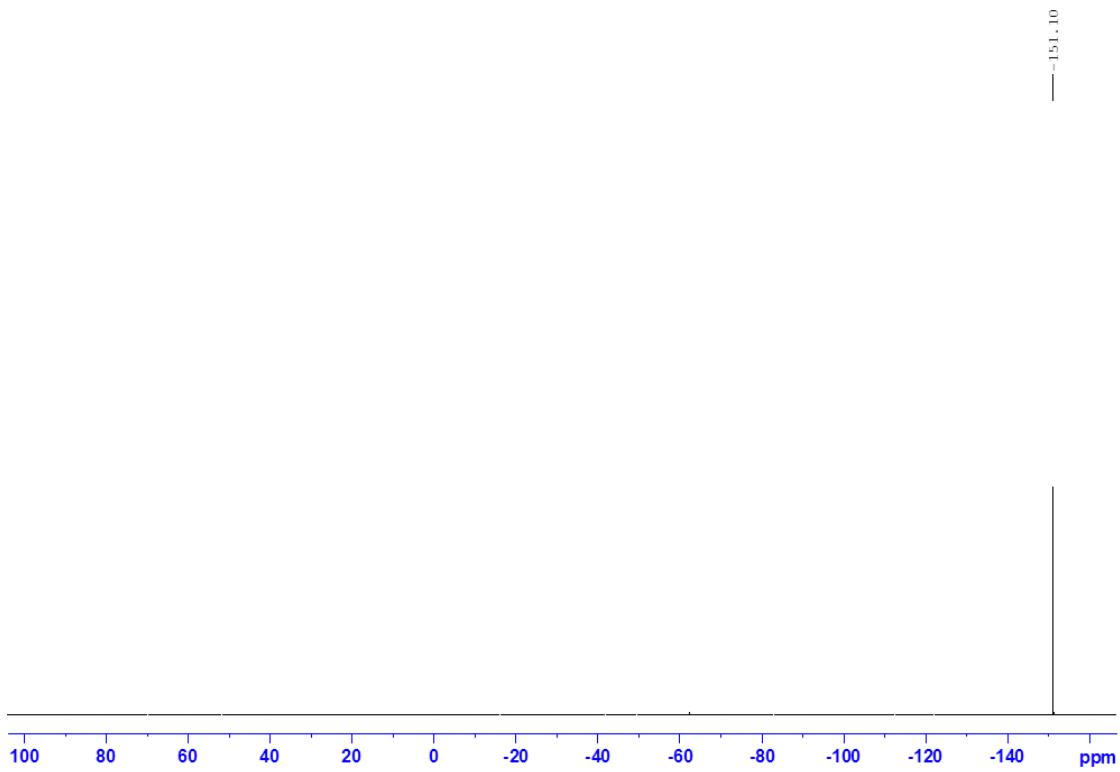
$^{13}\text{C}\{\text{H}\}$ -NMR (101 MHz, CDCl_3): compound **20**



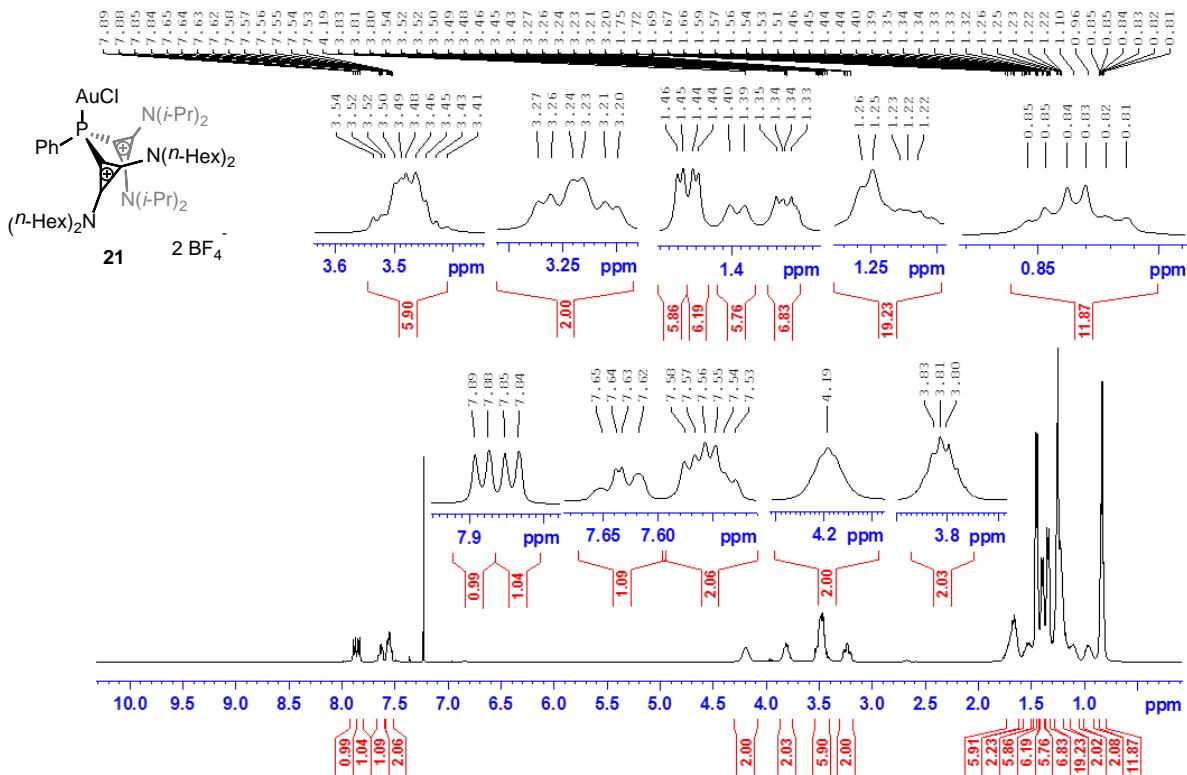
$^{31}\text{P}\{\text{H}\}$ -NMR (122 MHz, CDCl_3): compound **20**



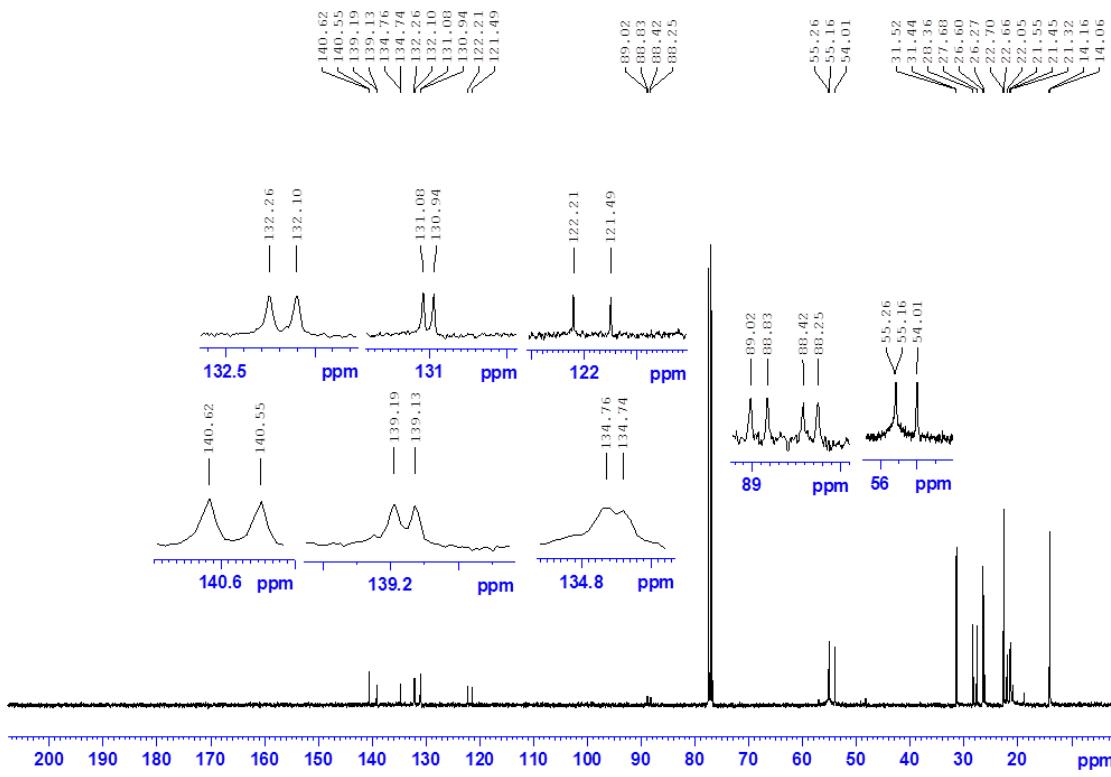
$^{19}\text{F}\{\text{H}\}$ -NMR (470 MHz, CDCl_3): compound **20**



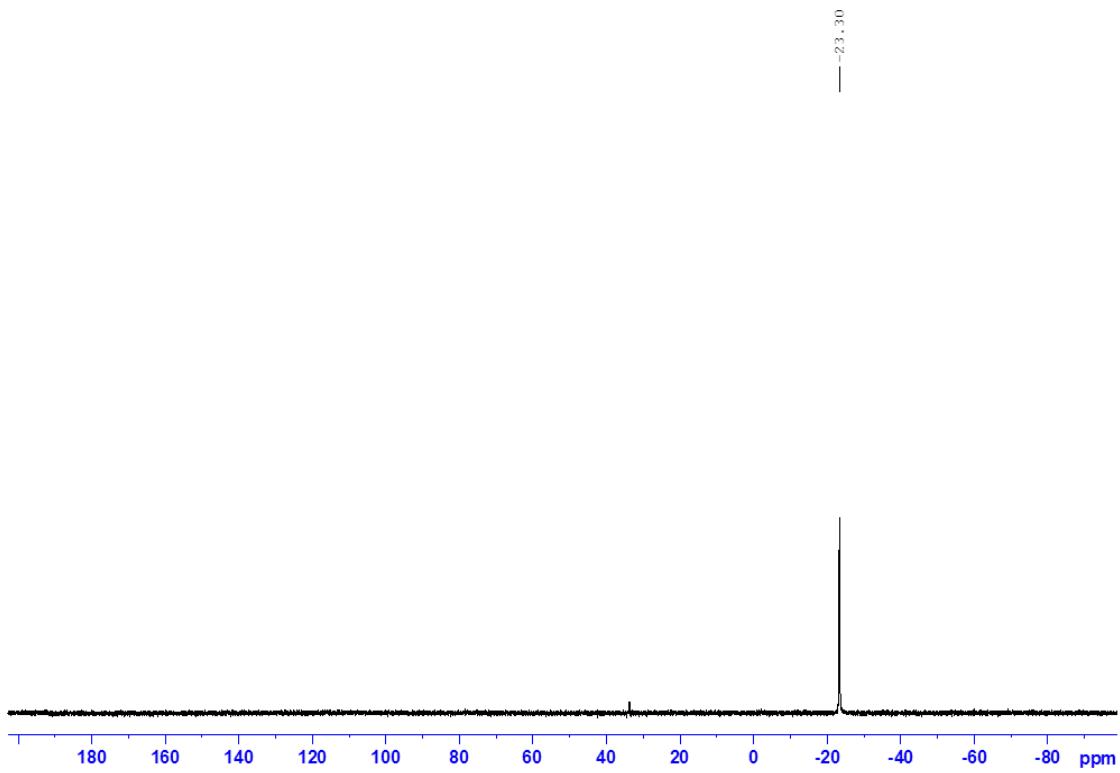
¹H-NMR (400 MHz, CDCl₃): compound 21



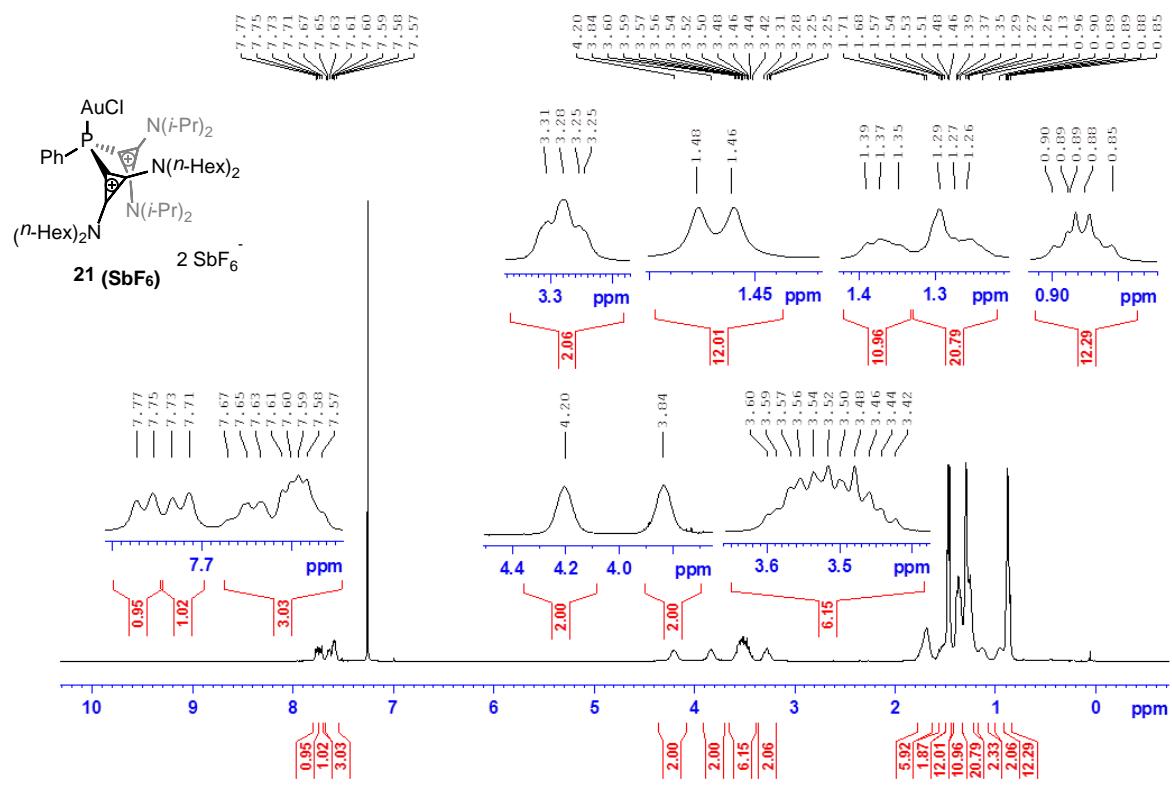
¹³C{¹H}-NMR (101 MHz, CDCl₃): compound 21



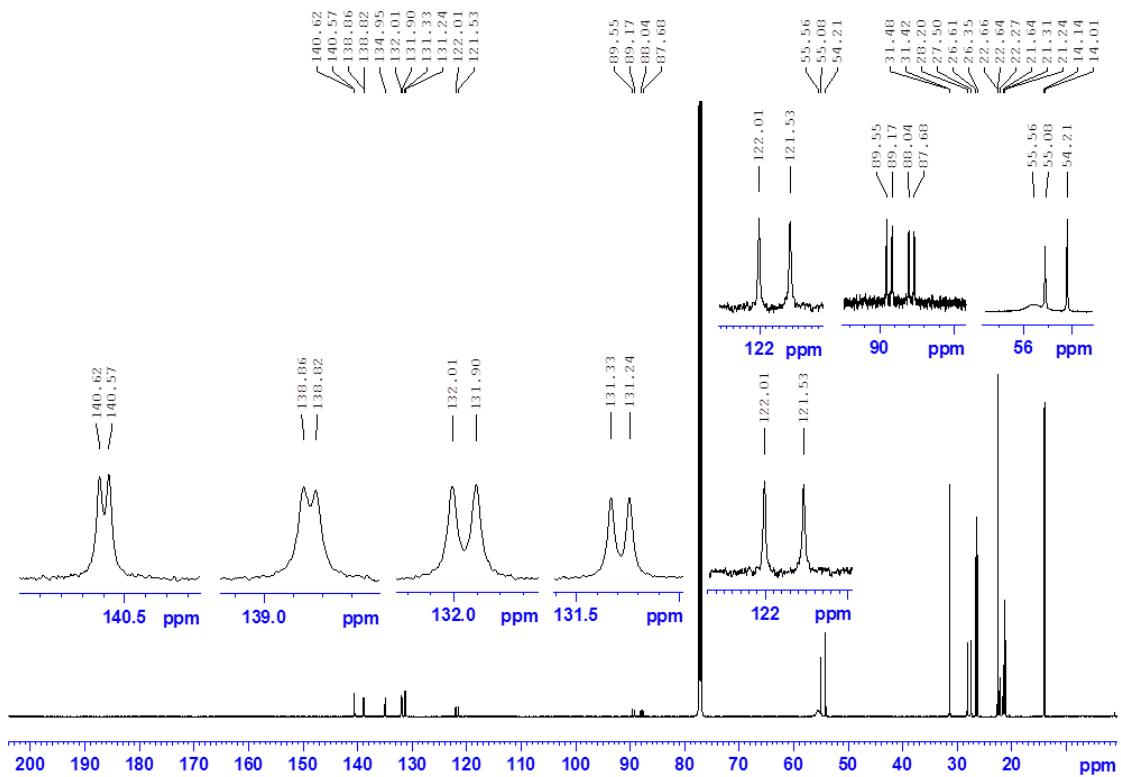
$^{31}\text{P}\{\text{H}\}$ -NMR (162 MHz, CDCl_3): compound 21



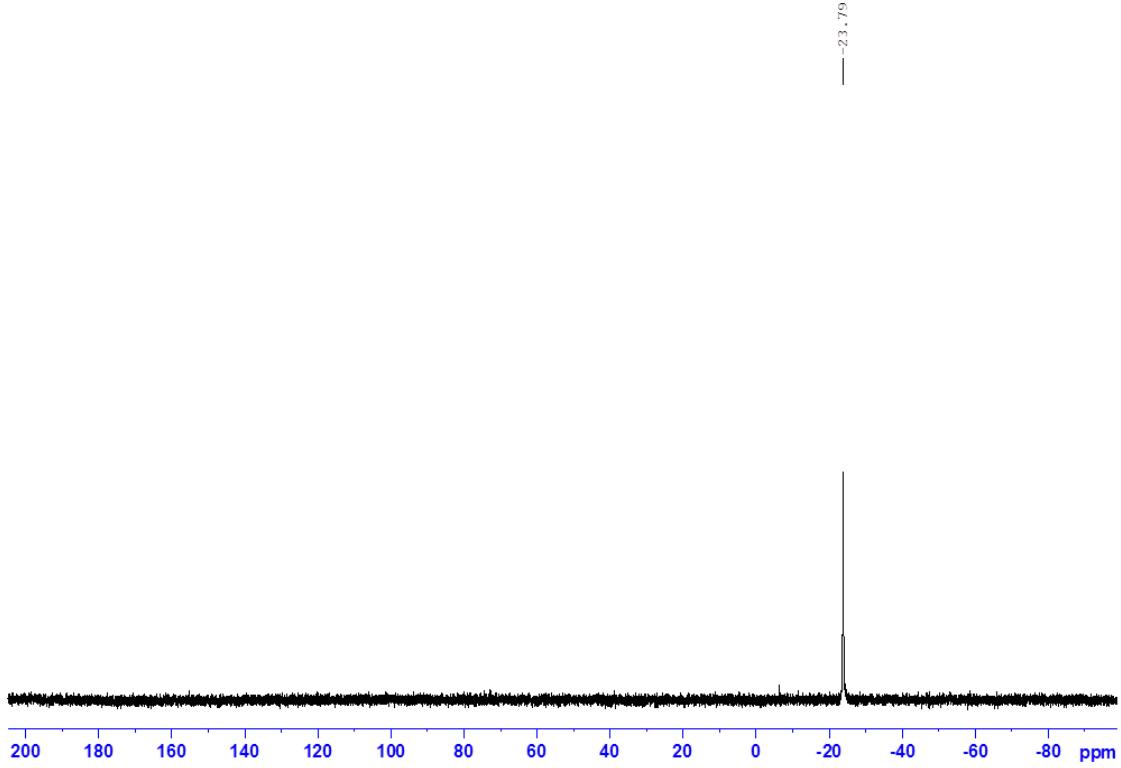
^1H -NMR (400 MHz, CDCl_3): compound 21



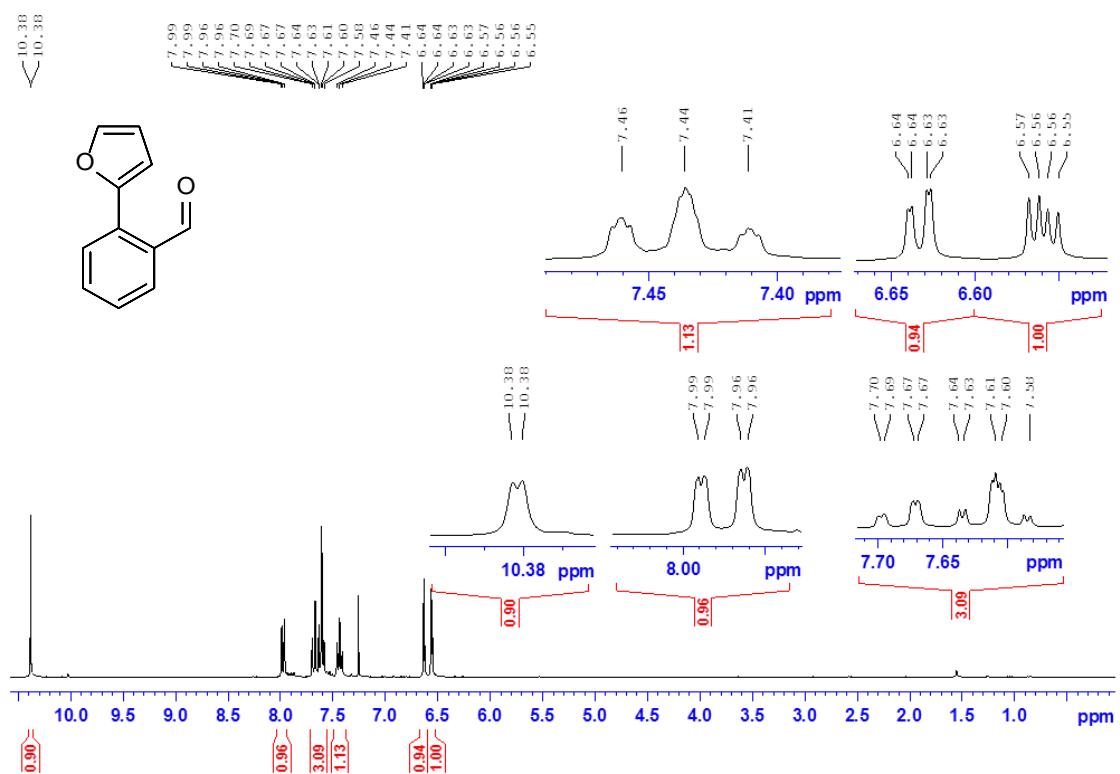
¹³C{¹H}-NMR (150 MHz, CDCl₃): compound 21 (SbF₆)



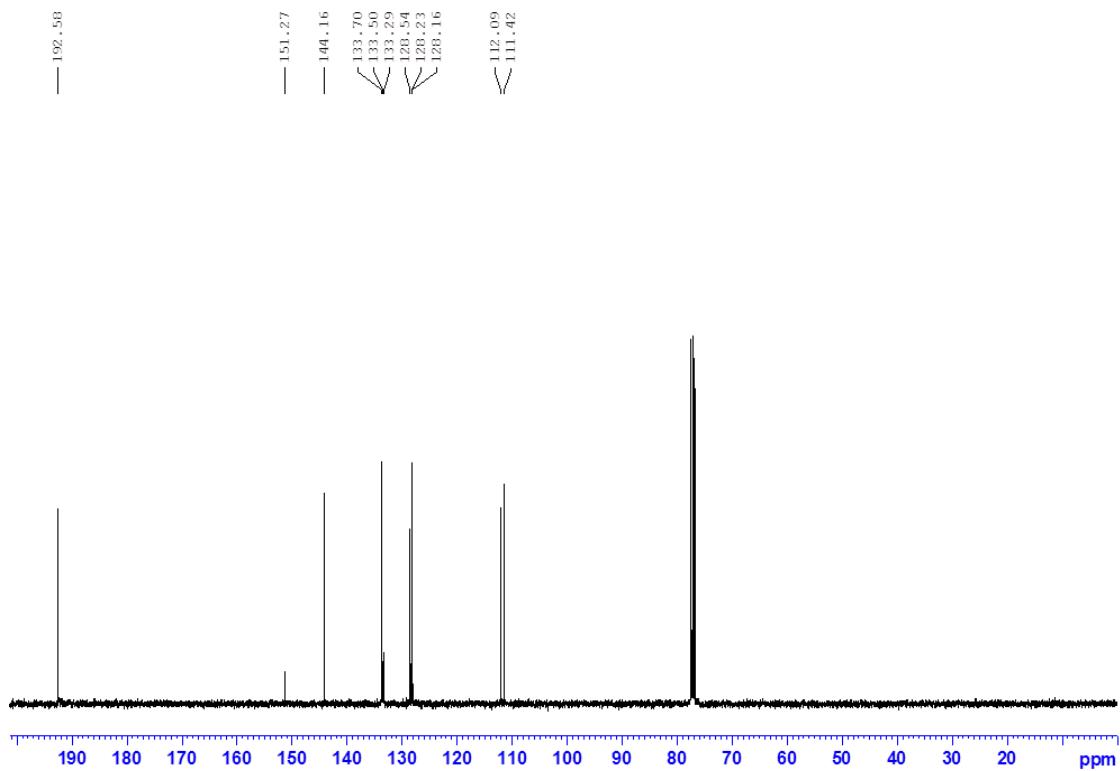
³¹P{¹H}-NMR (162 MHz, CDCl₃): compound 21 (SbF₆)



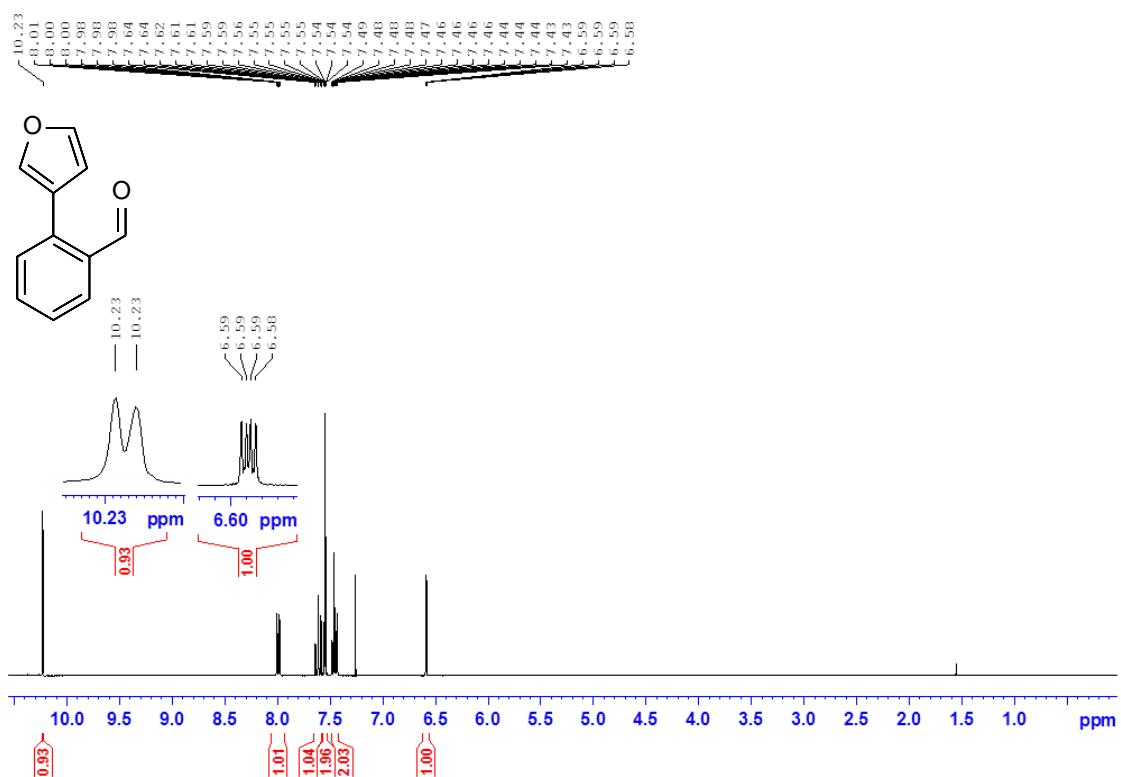
^1H -NMR (300 MHz, CDCl_3):



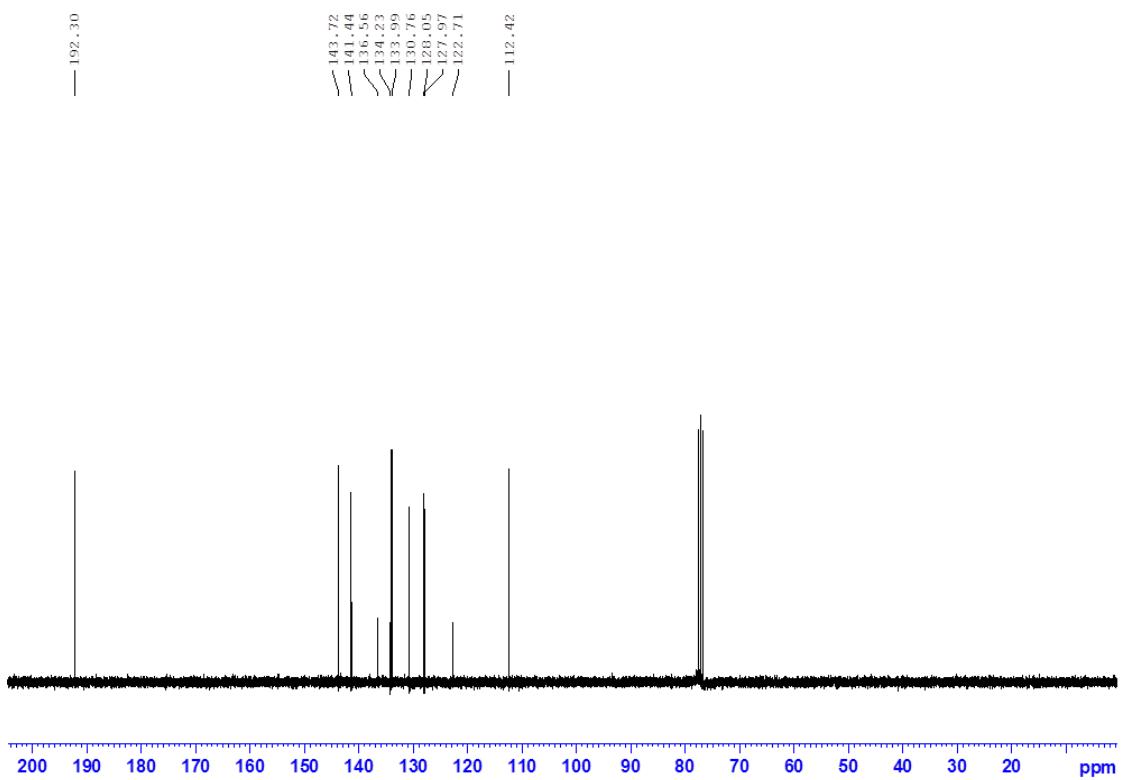
$^{13}\text{C}\{^1\text{H}\}$ -NMR (75 MHz, CDCl_3):



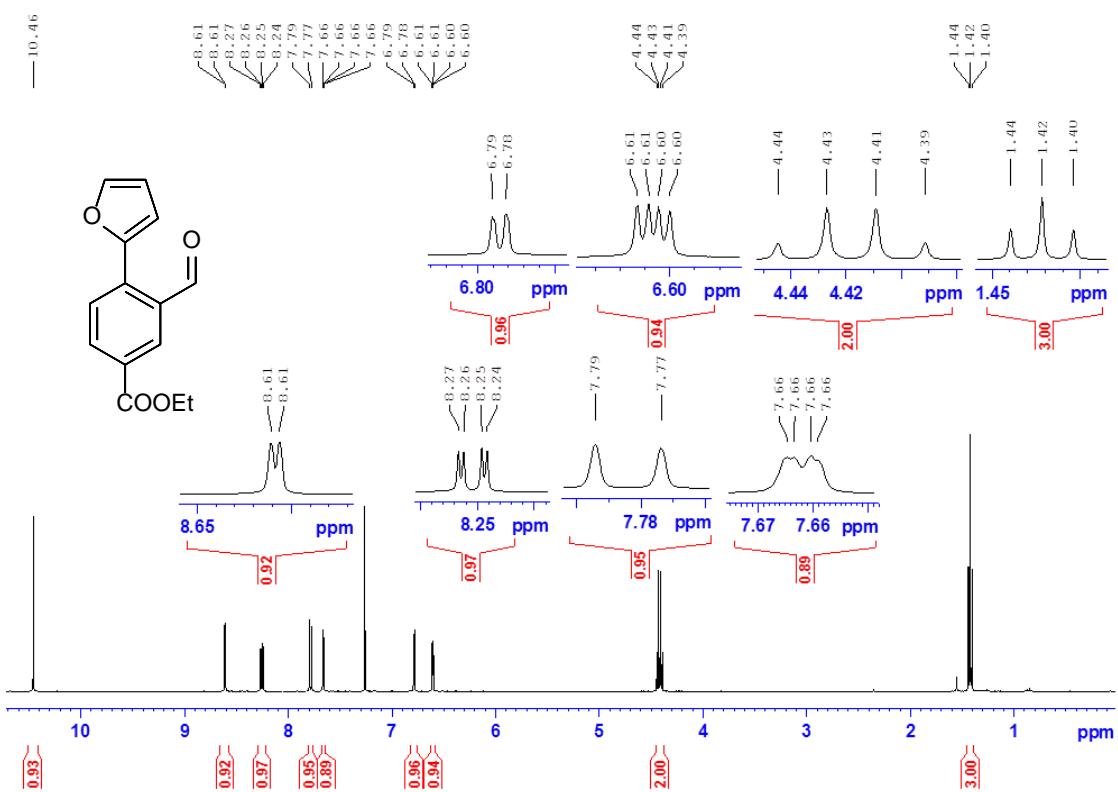
^1H -NMR (300 MHz, CDCl_3):



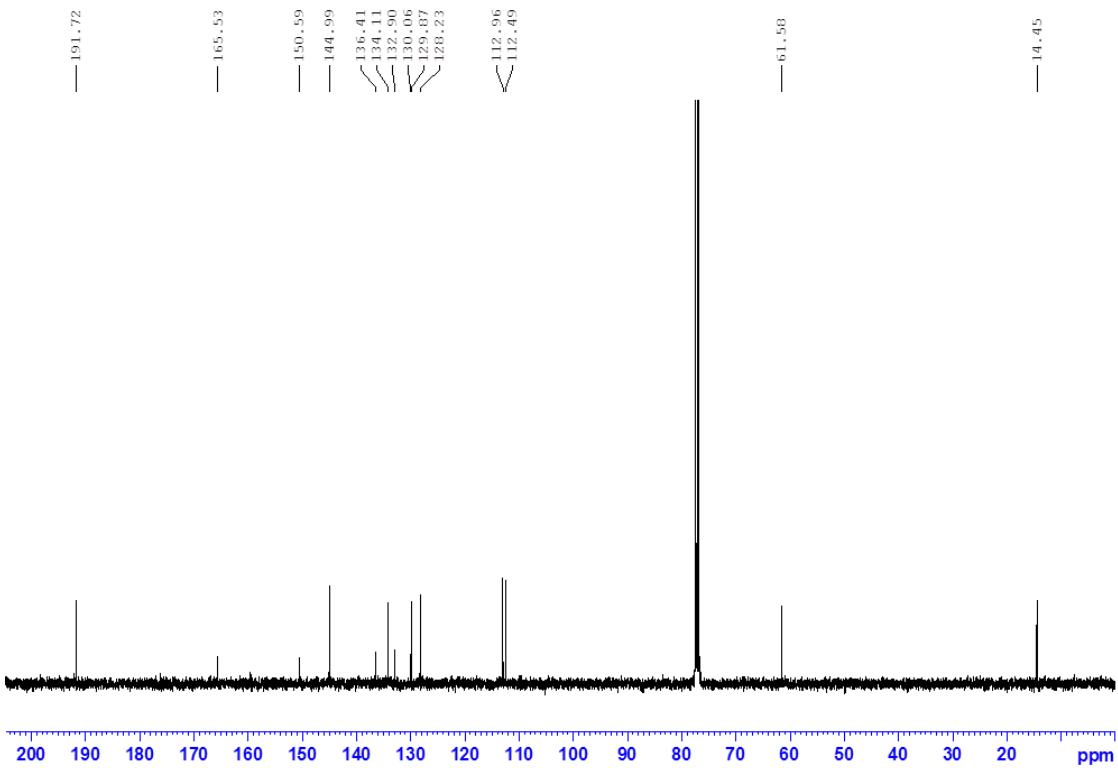
$^{13}\text{C}\{^1\text{H}\}$ -NMR (75 MHz, CDCl_3):



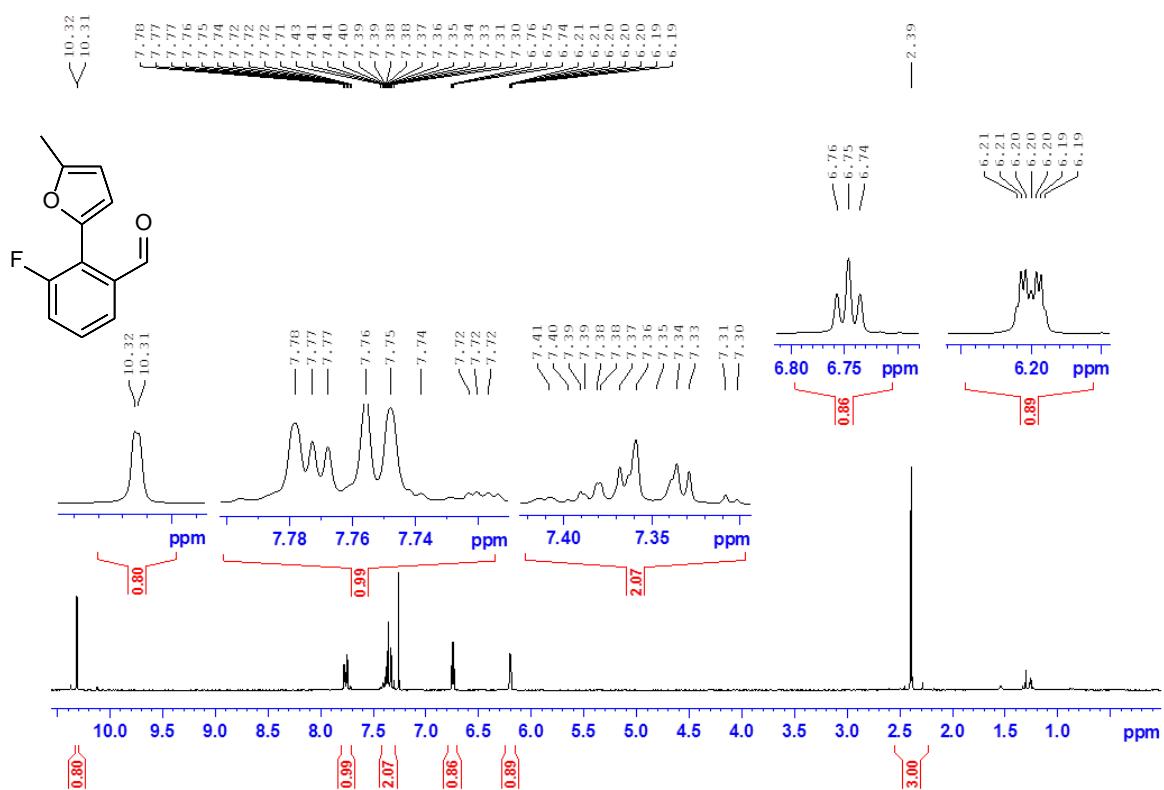
¹H-NMR (400 MHz, CDCl₃):



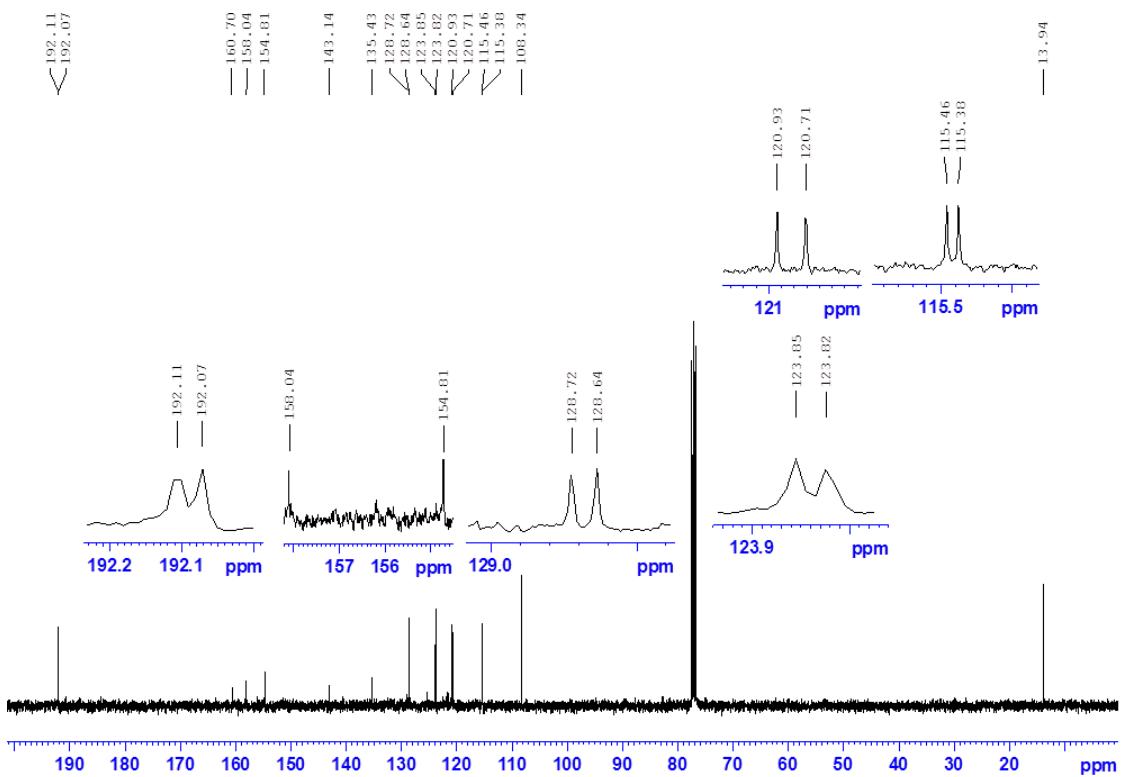
¹³C{¹H}-NMR (101 MHz, CDCl₃):



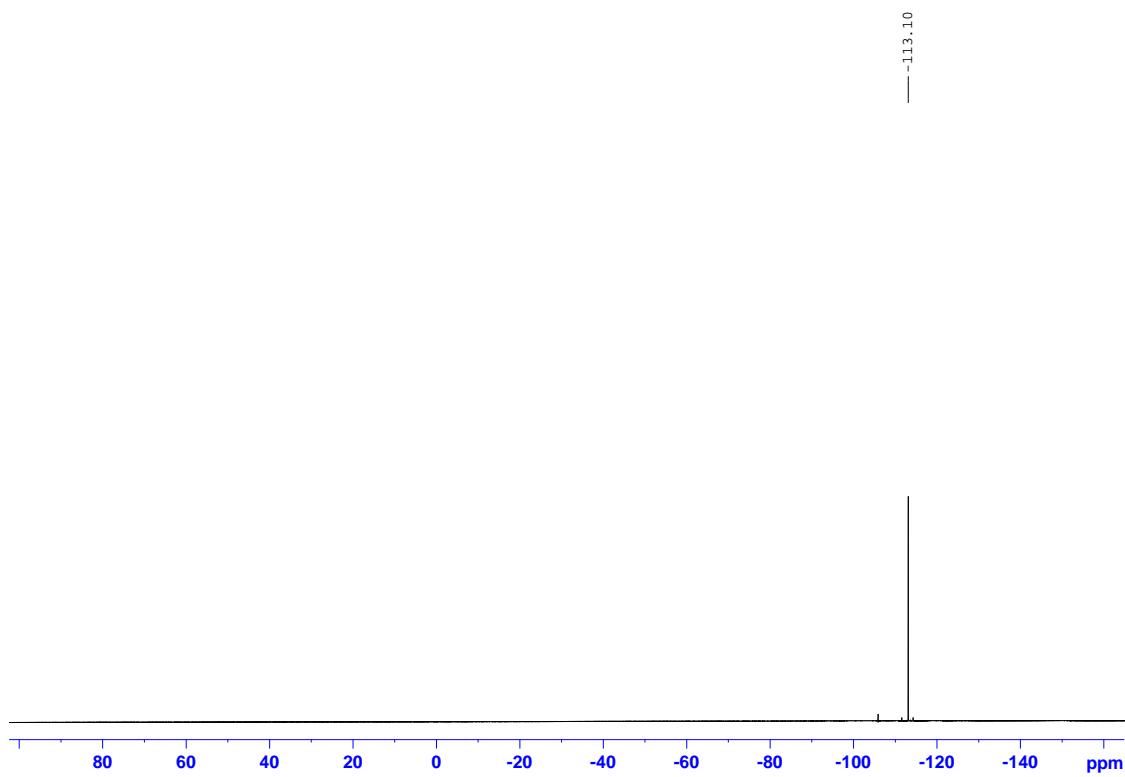
¹H-NMR (300 MHz, CDCl₃):



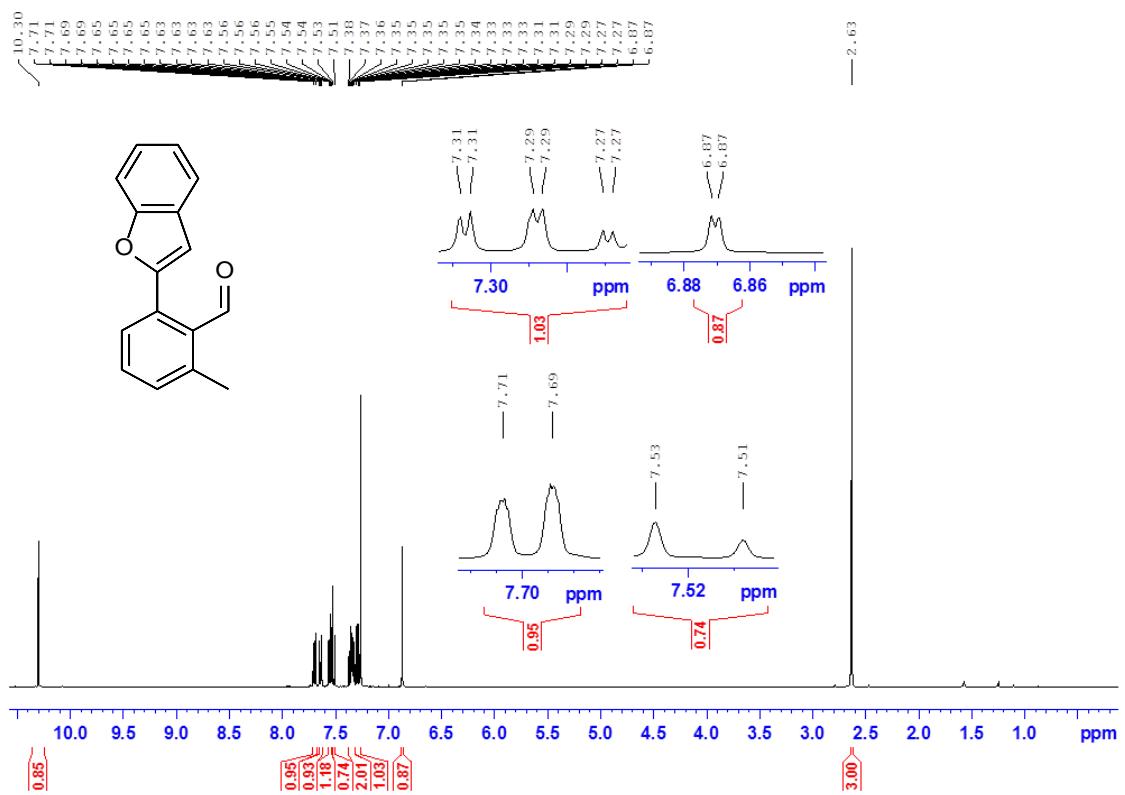
¹³C{¹H}-NMR (101 MHz, CDCl₃):



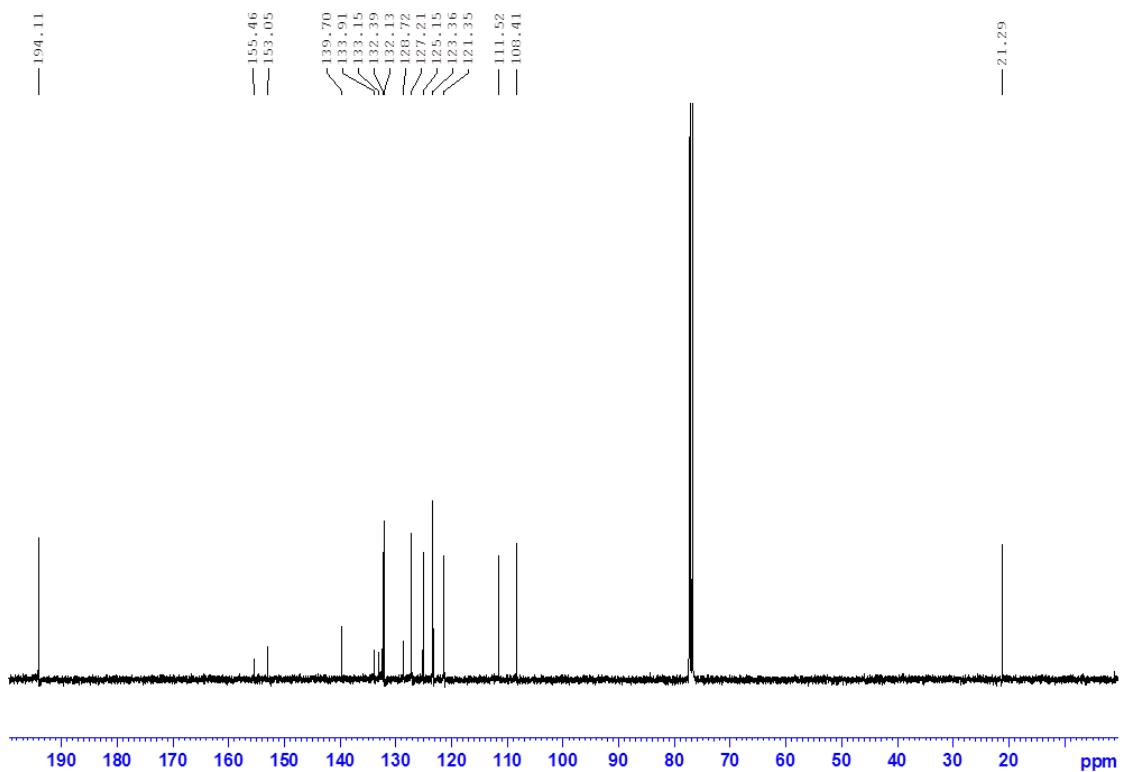
¹⁹F{¹H}-NMR (282 MHz, CDCl₃):



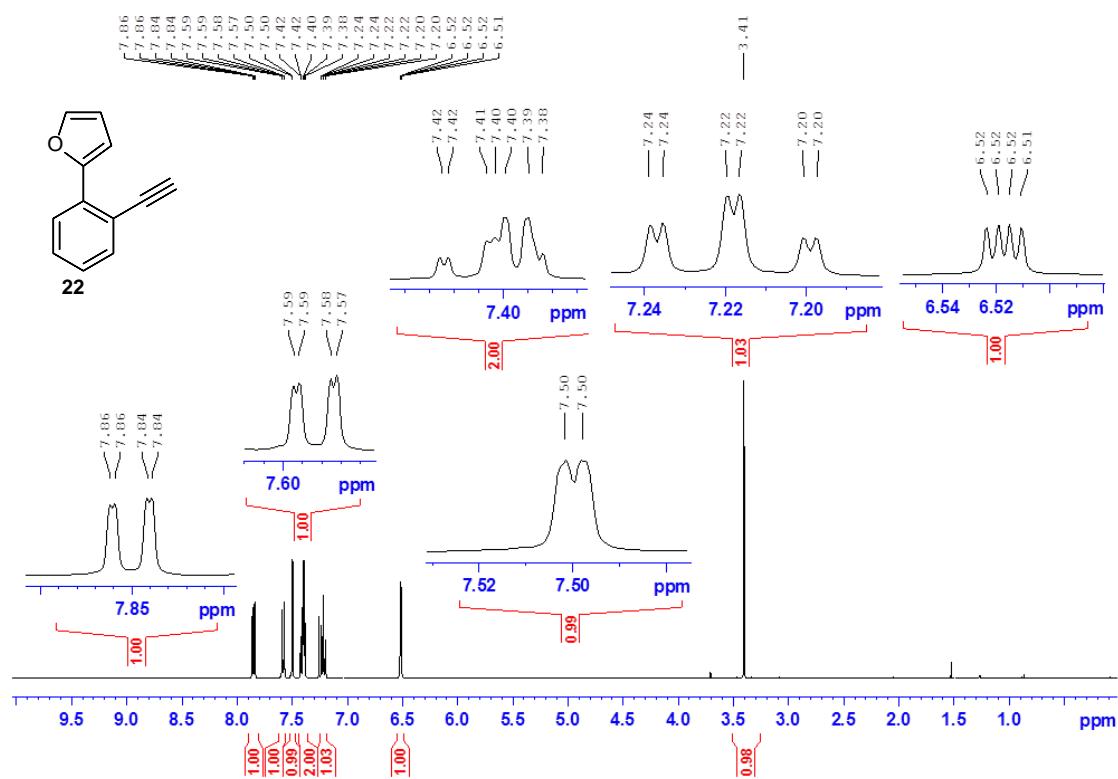
¹H-NMR (400 MHz, CDCl₃):



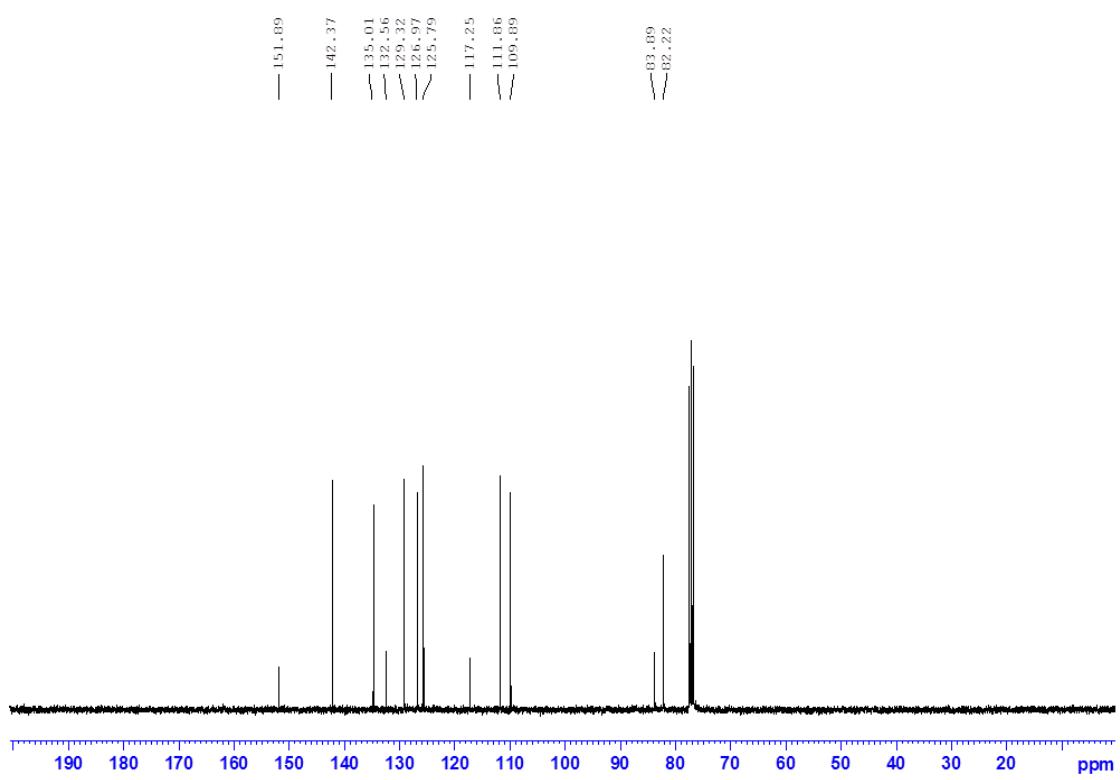
$^{13}\text{C}\{^1\text{H}\}$ -NMR (101MHz, CDCl_3):



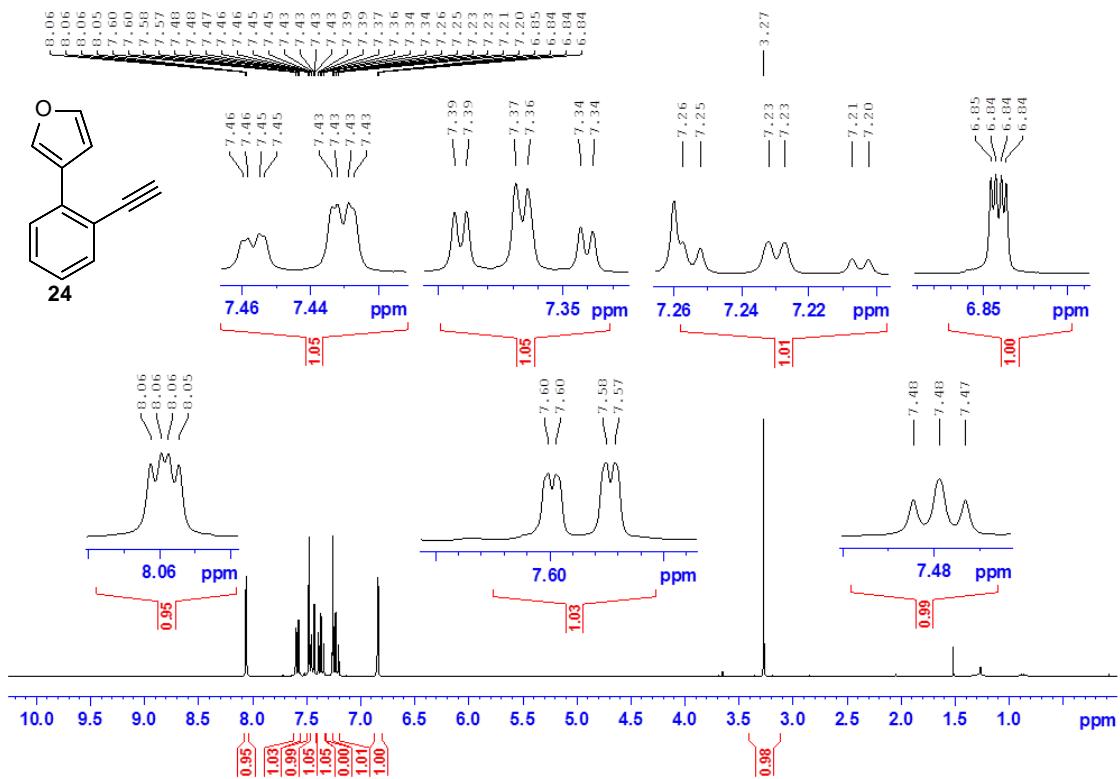
¹H-NMR (300 MHz, CDCl₃):



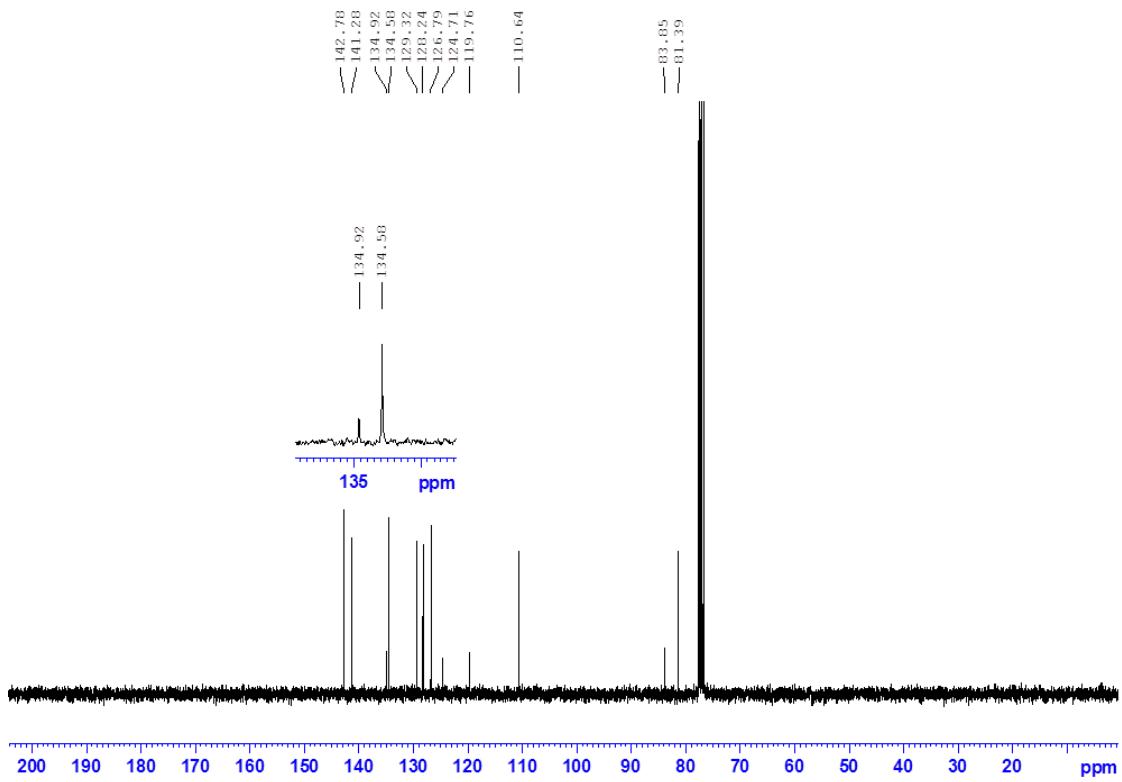
¹³C{¹H}-NMR (75 MHz, CDCl₃): Compound 22



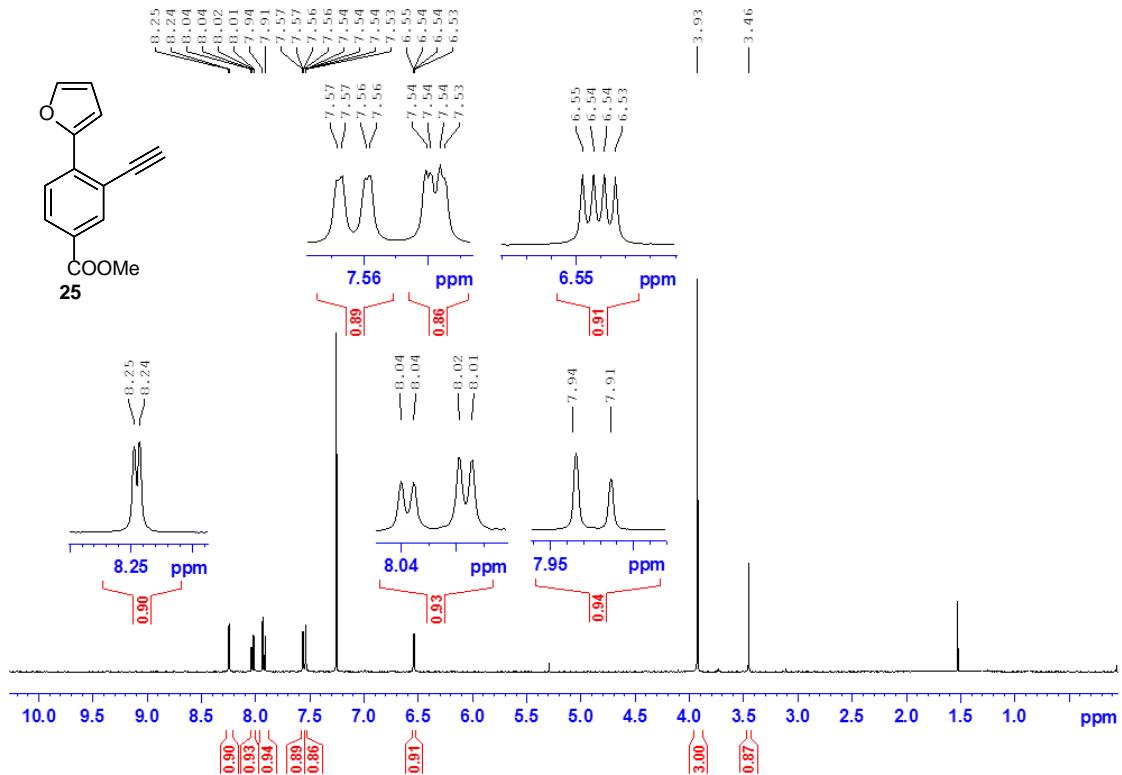
¹H-NMR (300 MHz, CDCl₃): Compound 24



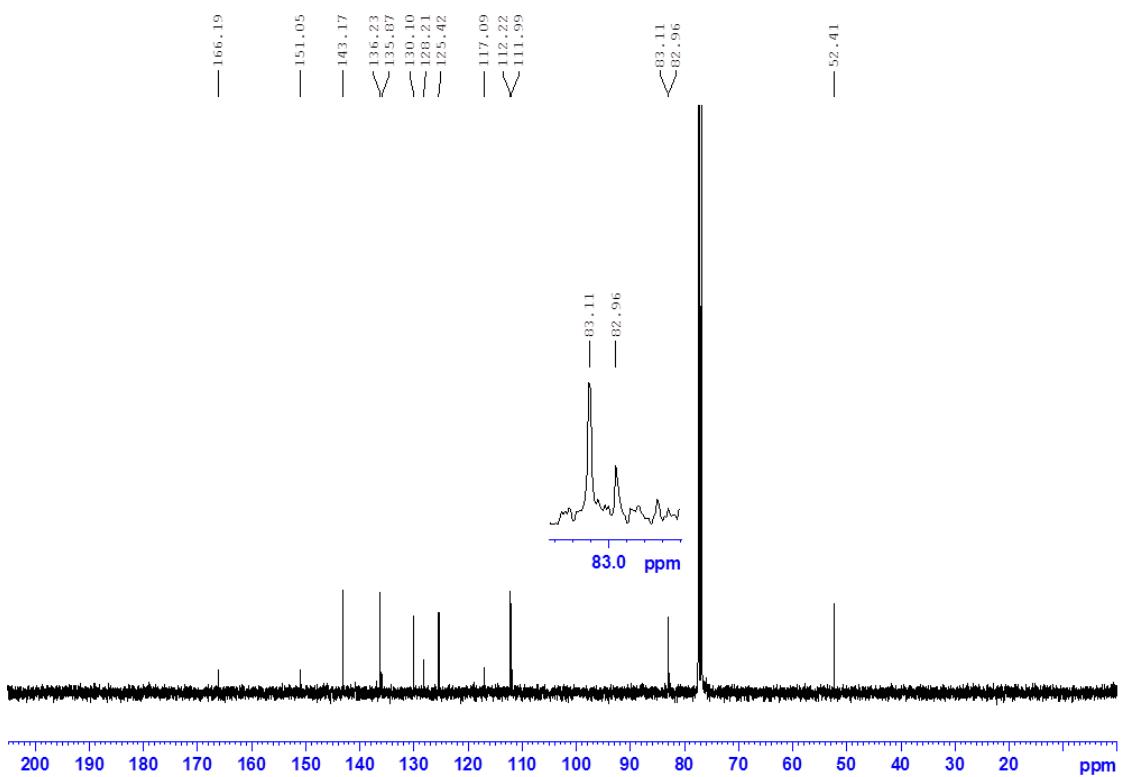
¹³C{¹H}-NMR (75 MHz, CDCl₃): Compound 24



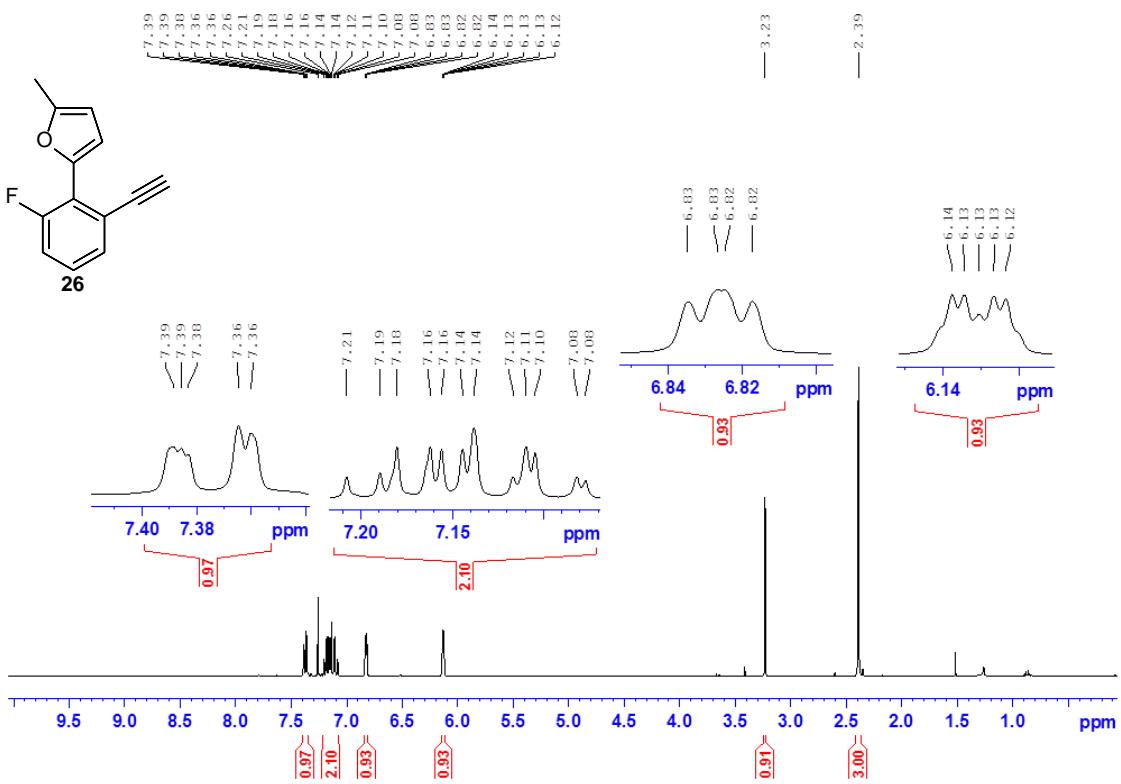
¹H-NMR (400 MHz, CDCl₃): Compound 25



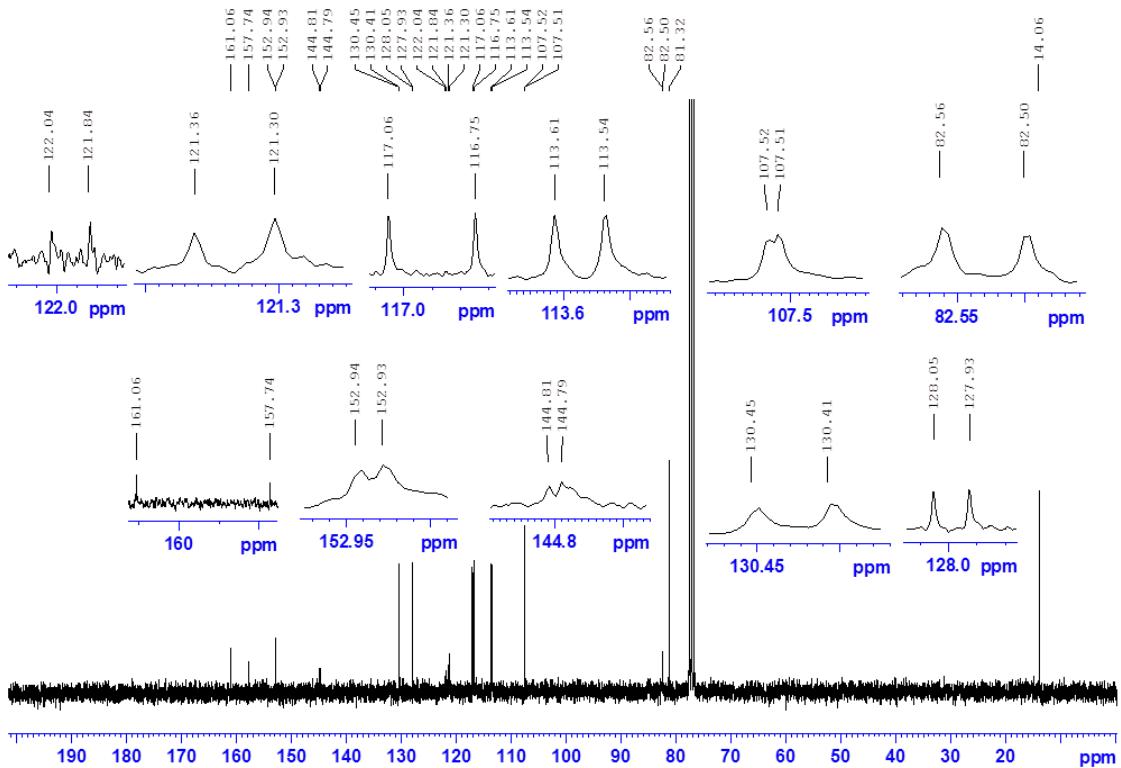
¹³C{¹H}-NMR (75 MHz, CDCl₃): Compound 25



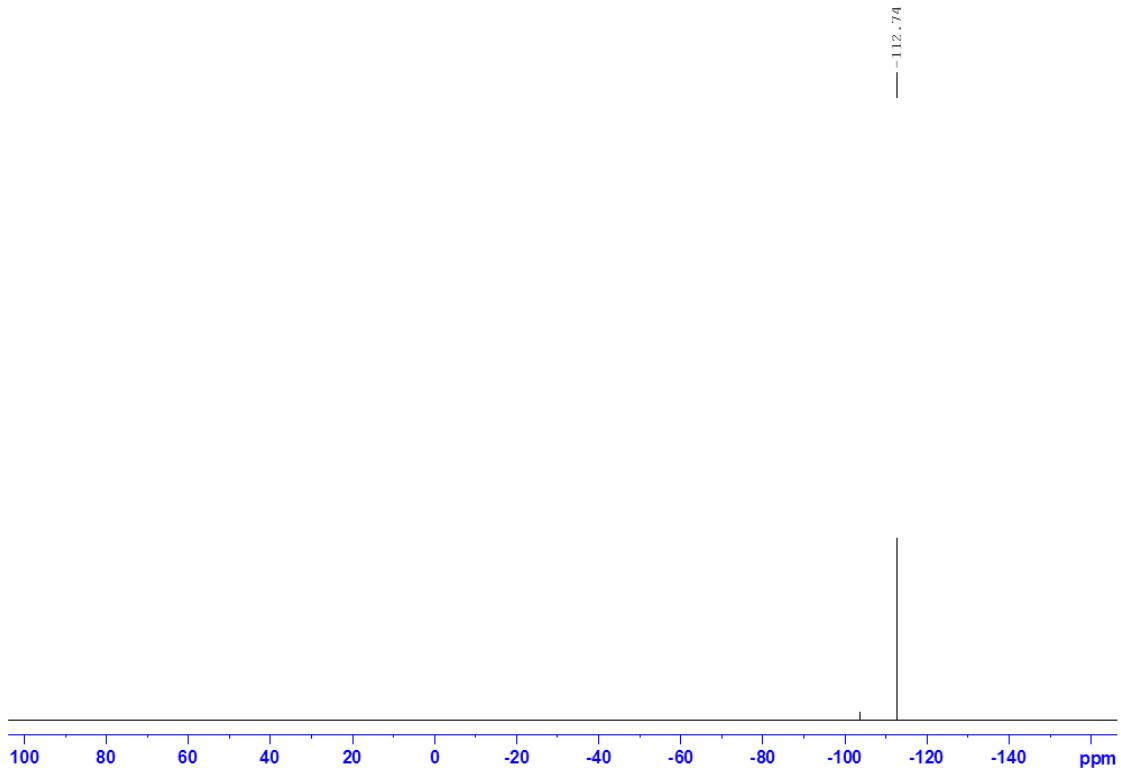
¹H-NMR (300 MHz, CDCl₃): Compound **26**



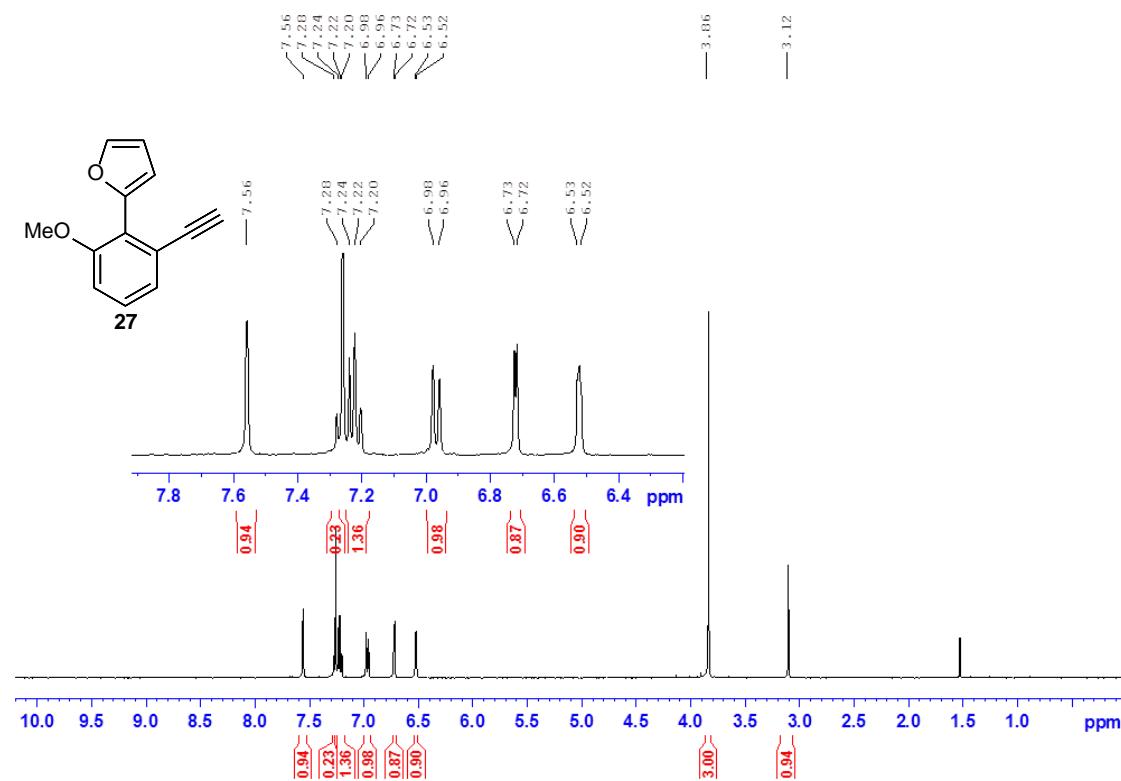
$^{13}\text{C}\{\text{H}\}$ -NMR (101 MHz, CDCl_3): Compound 26



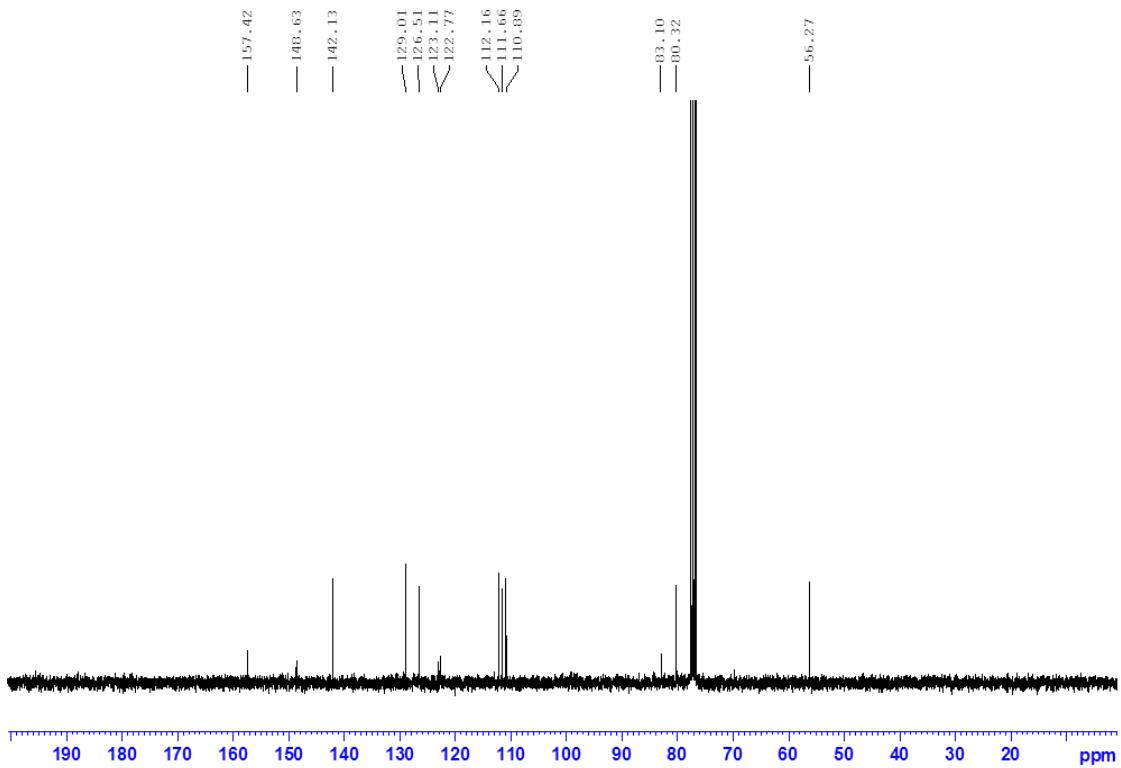
$^{19}\text{F}\{\text{H}\}$ -NMR (282 MHz, CDCl_3): Compound 26



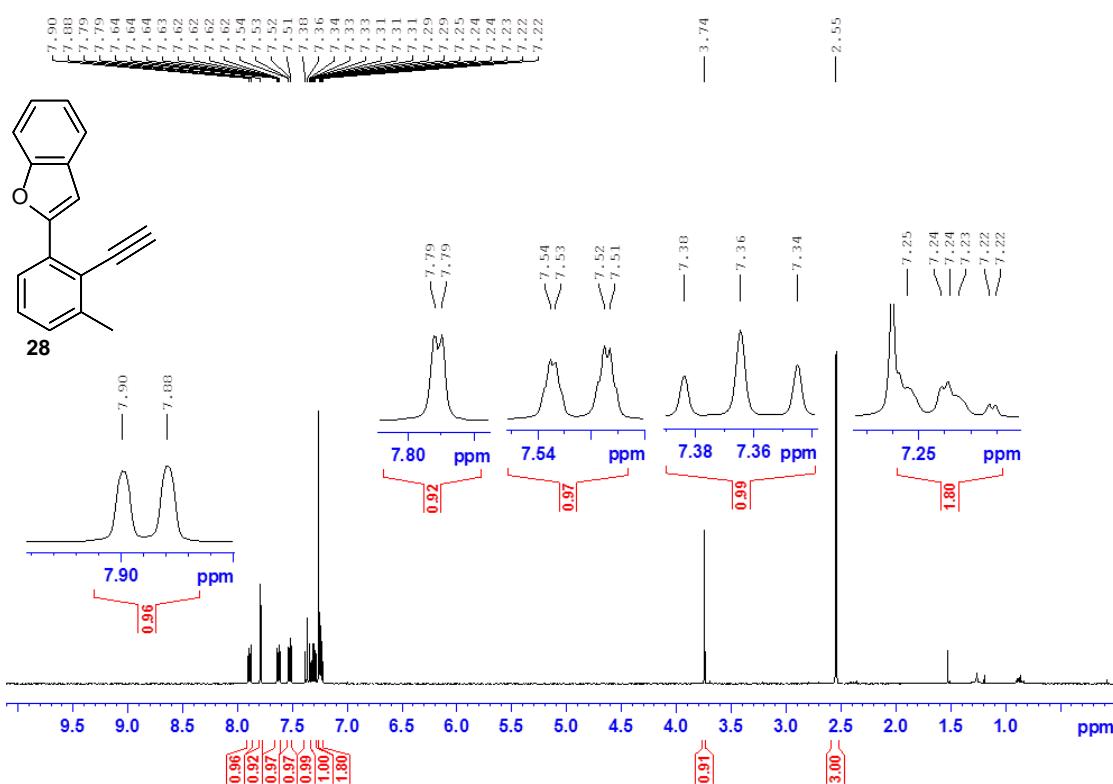
^1H -NMR (400 MHz, CDCl_3): Compound 27



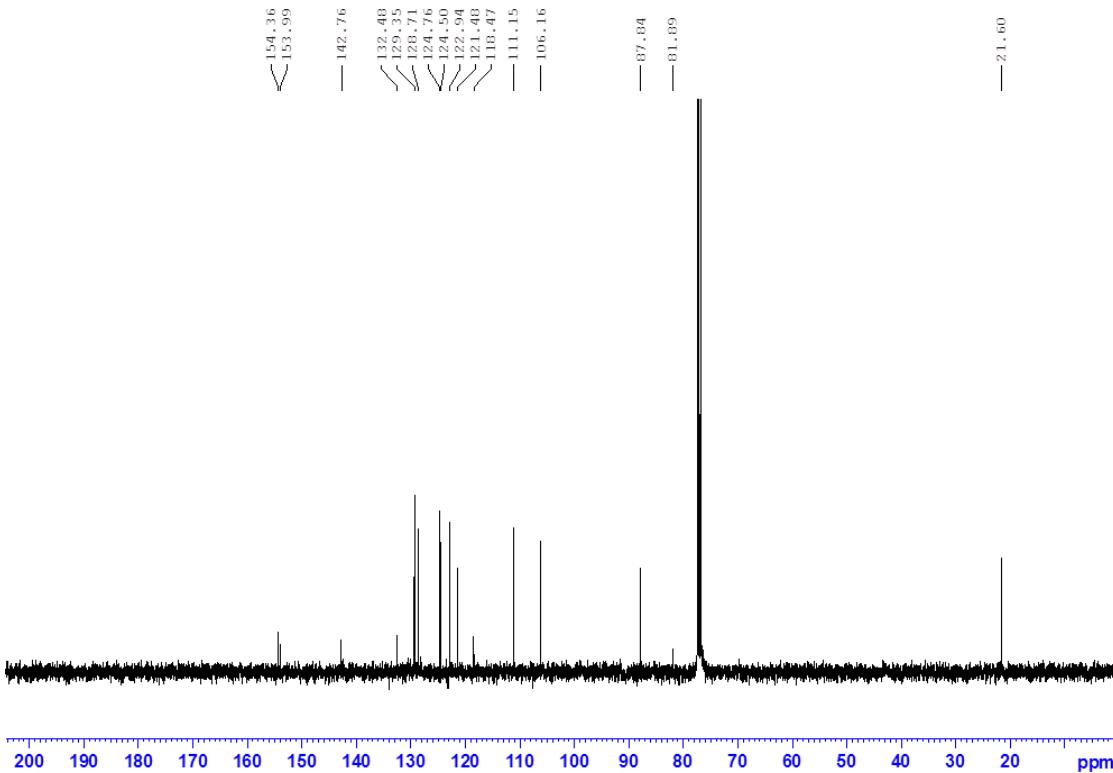
$^{13}\text{C}\{\text{H}\}$ -NMR (101 MHz, CDCl_3): Compound 27



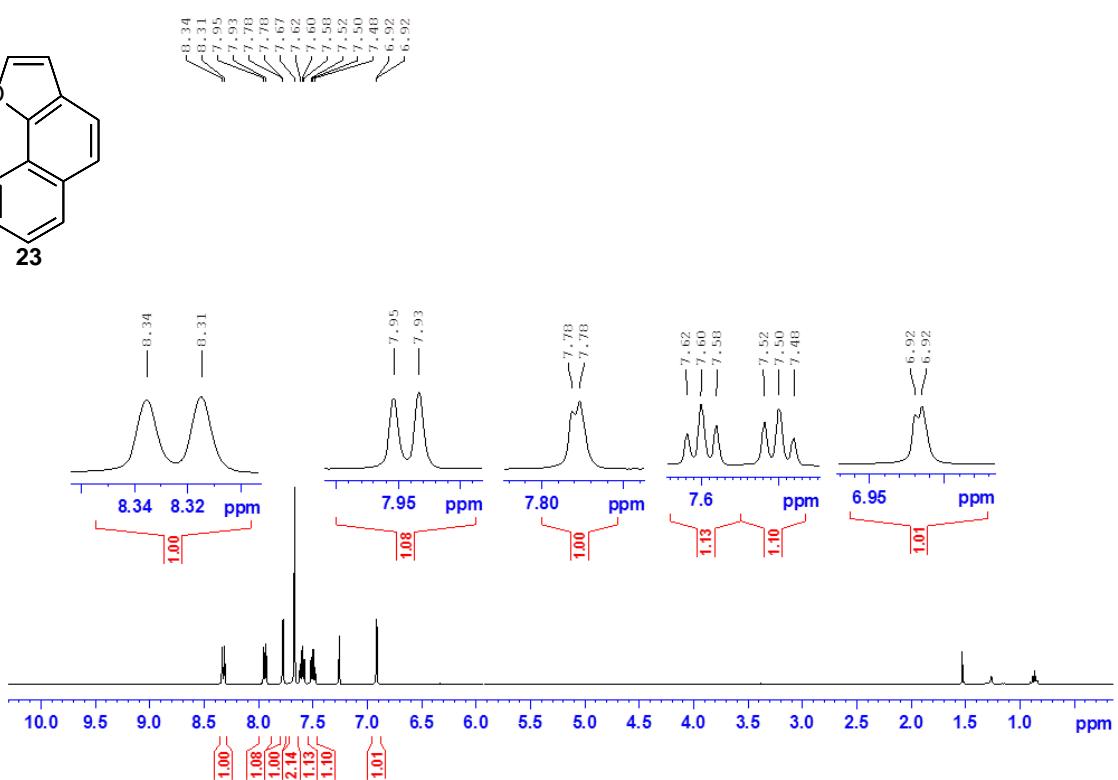
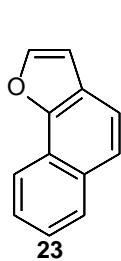
¹H-NMR (400 MHz, CDCl₃): Compound 28



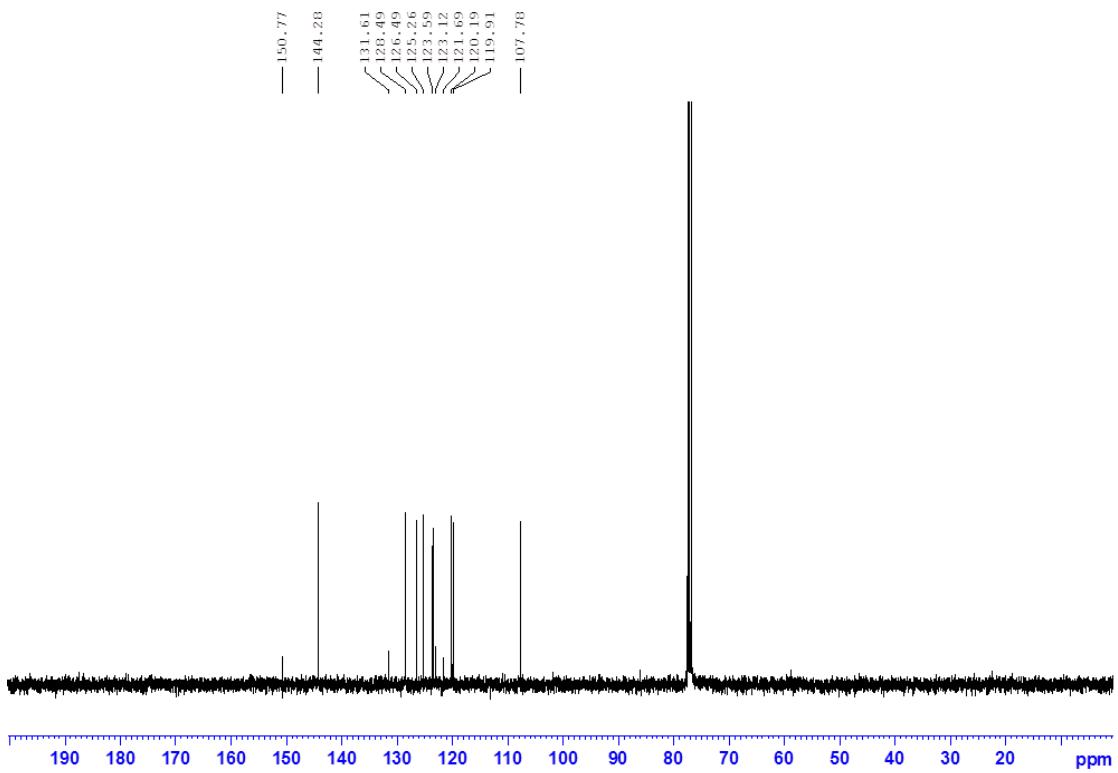
¹³C{¹H}-NMR (101 MHz, CDCl₃): Compound 28



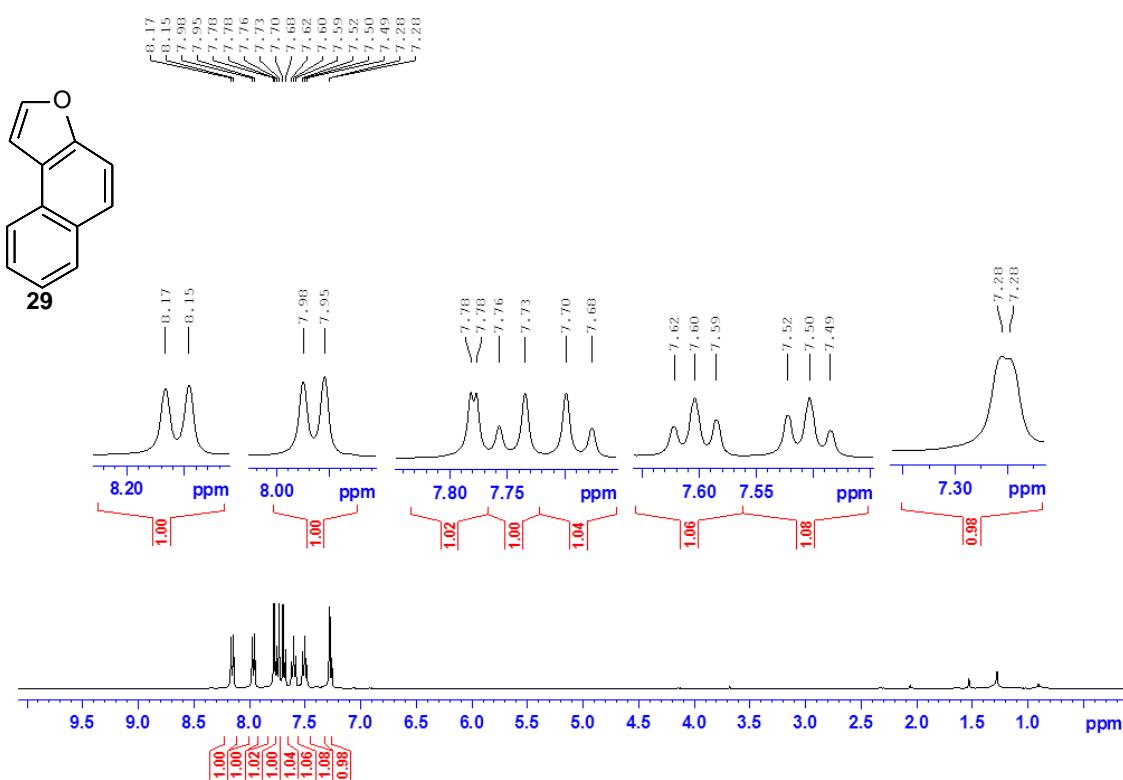
¹H-NMR (300 MHz, CDCl₃): Compound 23



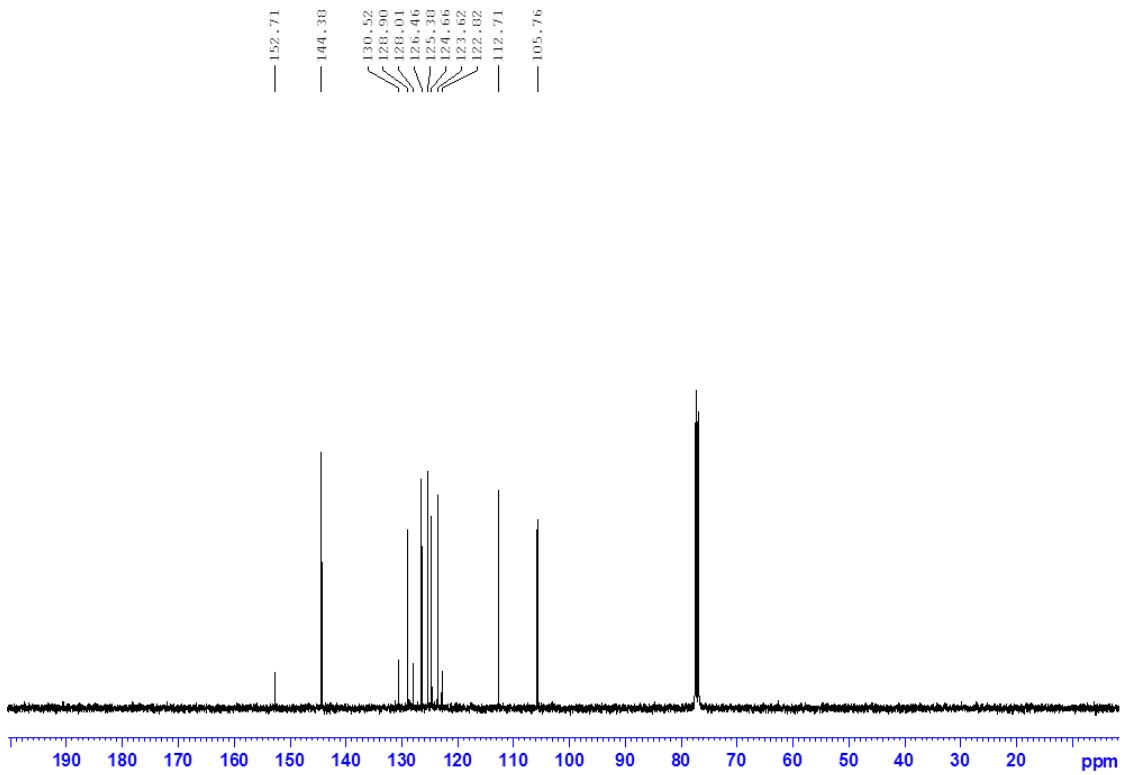
¹³C{¹H}-NMR (75MHz, CDCl₃): Compound 23



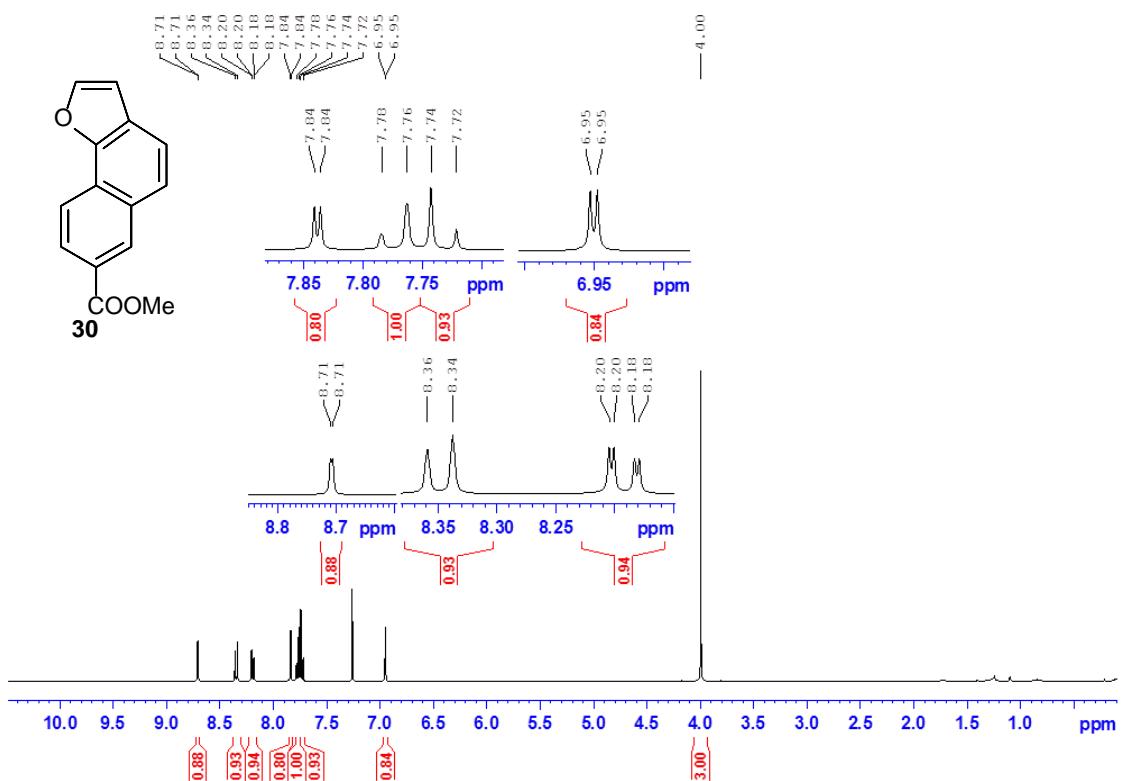
^1H -NMR (300 MHz, CDCl_3): Compound 29



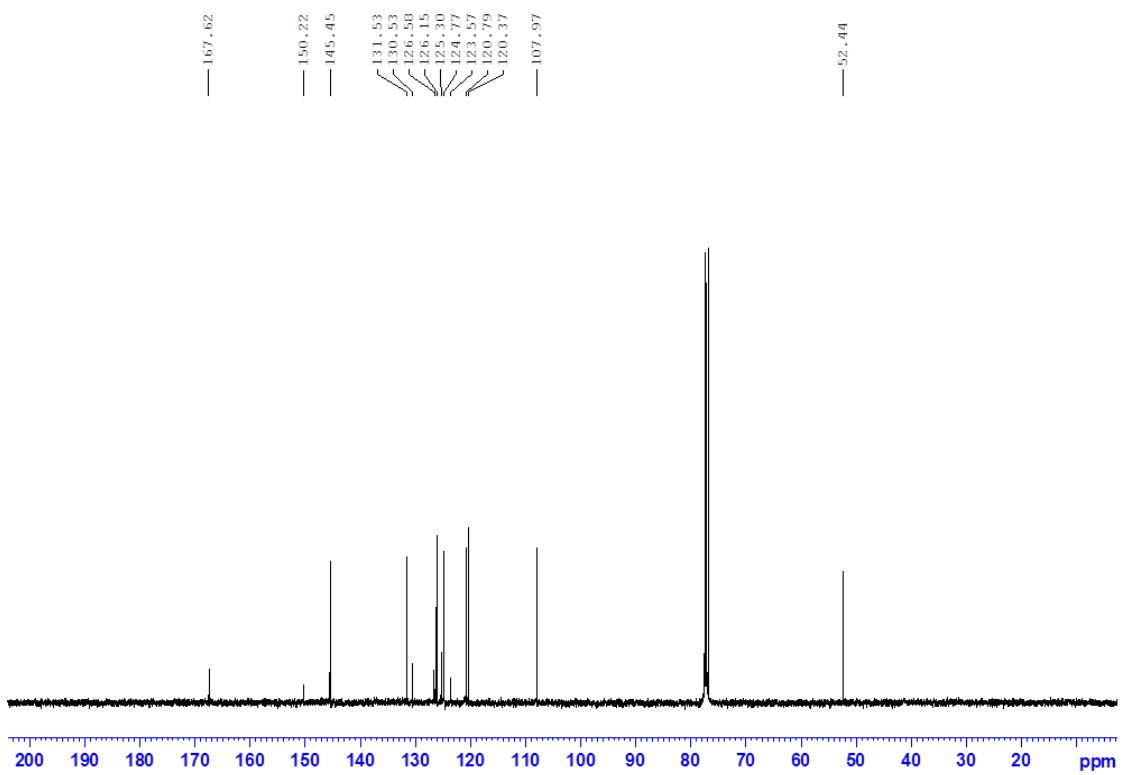
$^{13}\text{C}\{\text{H}\}$ -NMR (75MHz, CDCl_3): Compound 29



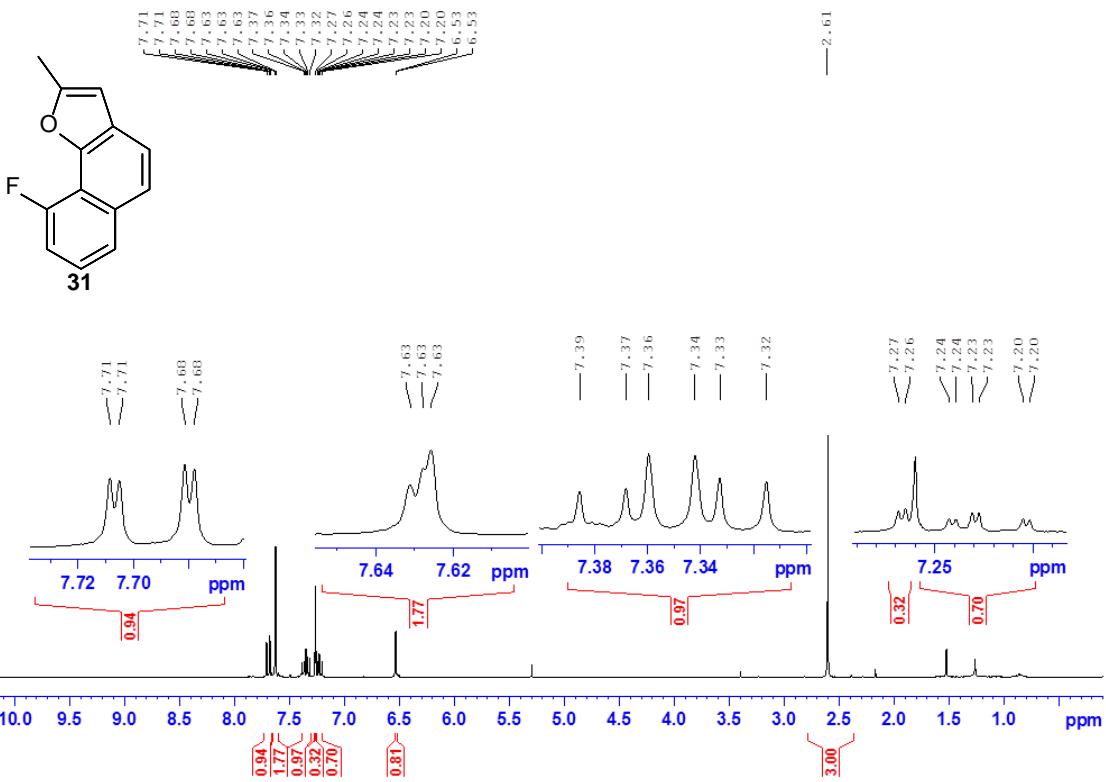
¹H-NMR (400 MHz, CDCl₃): Compound 30



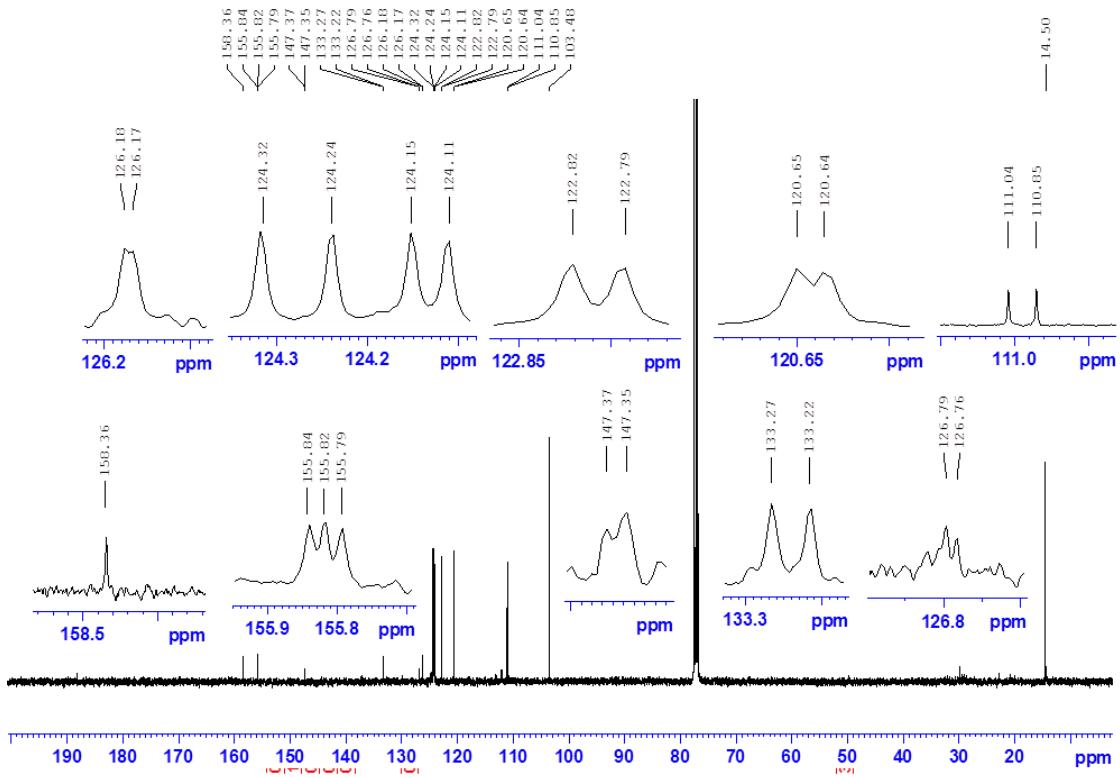
¹³C{¹H}-NMR (101MHz, CDCl₃): Compound 30



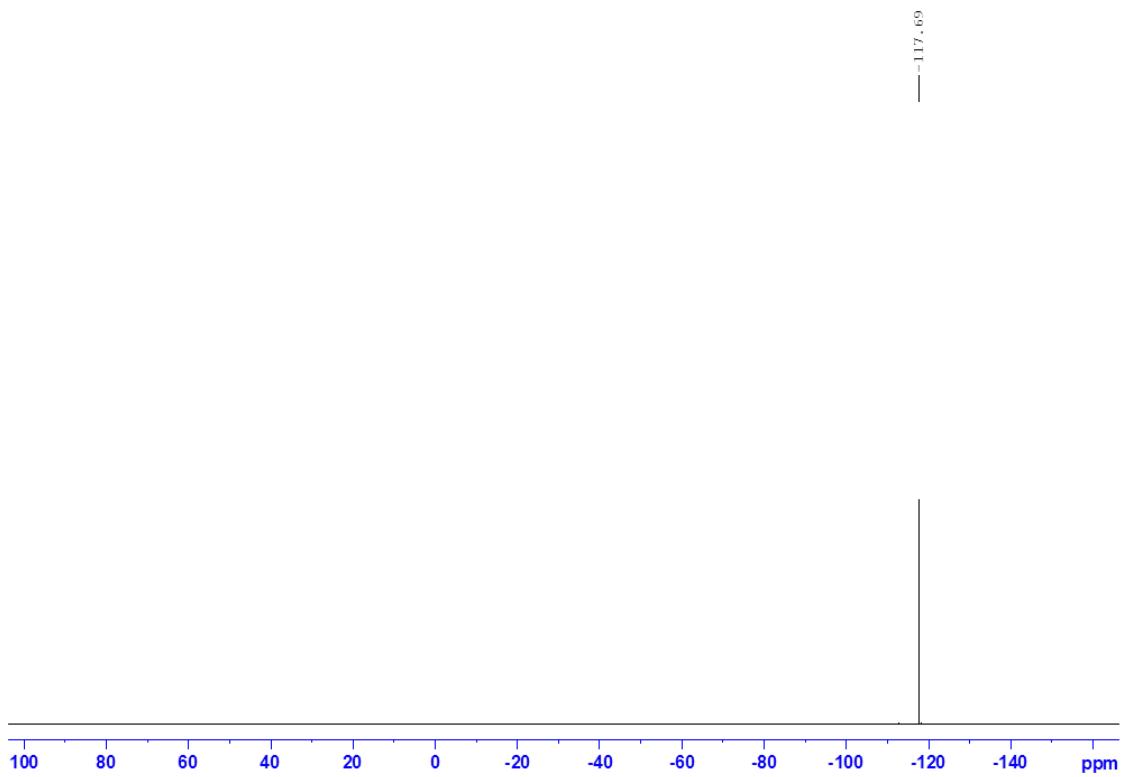
¹H-NMR (300 MHz, CDCl₃): Compound 31



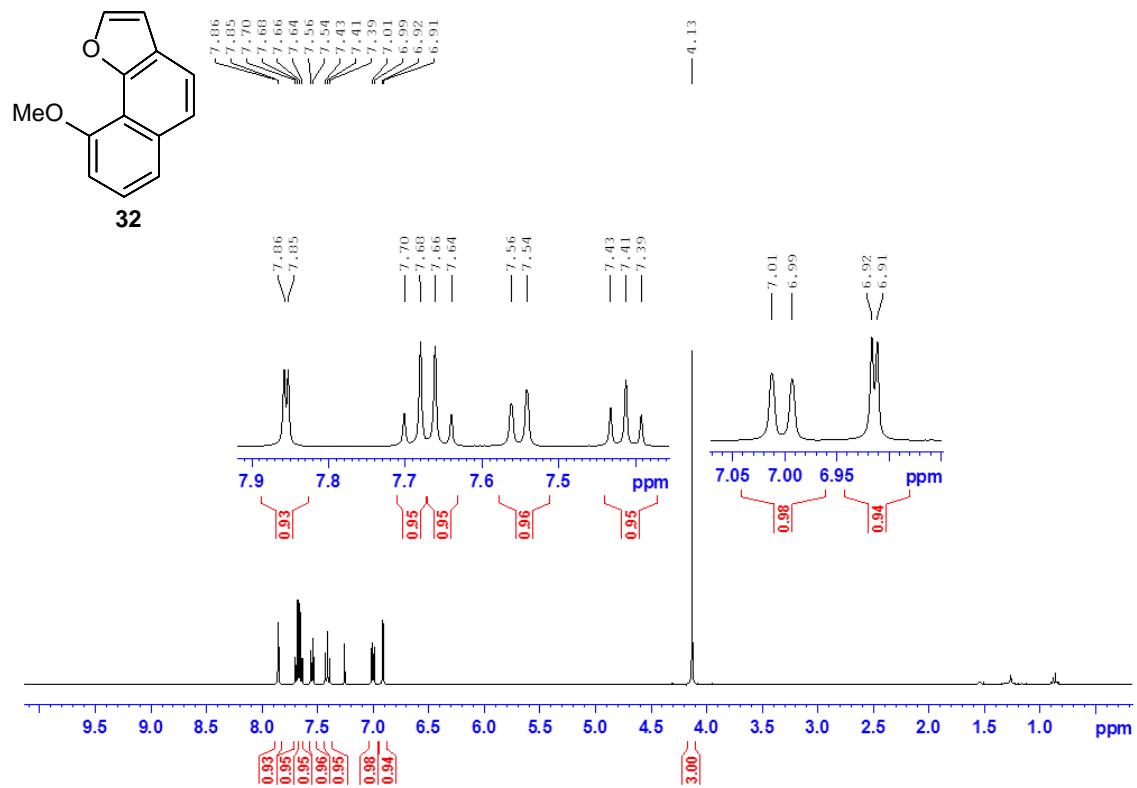
¹³C{¹H}-NMR (101MHz, CDCl₃): Compound 31



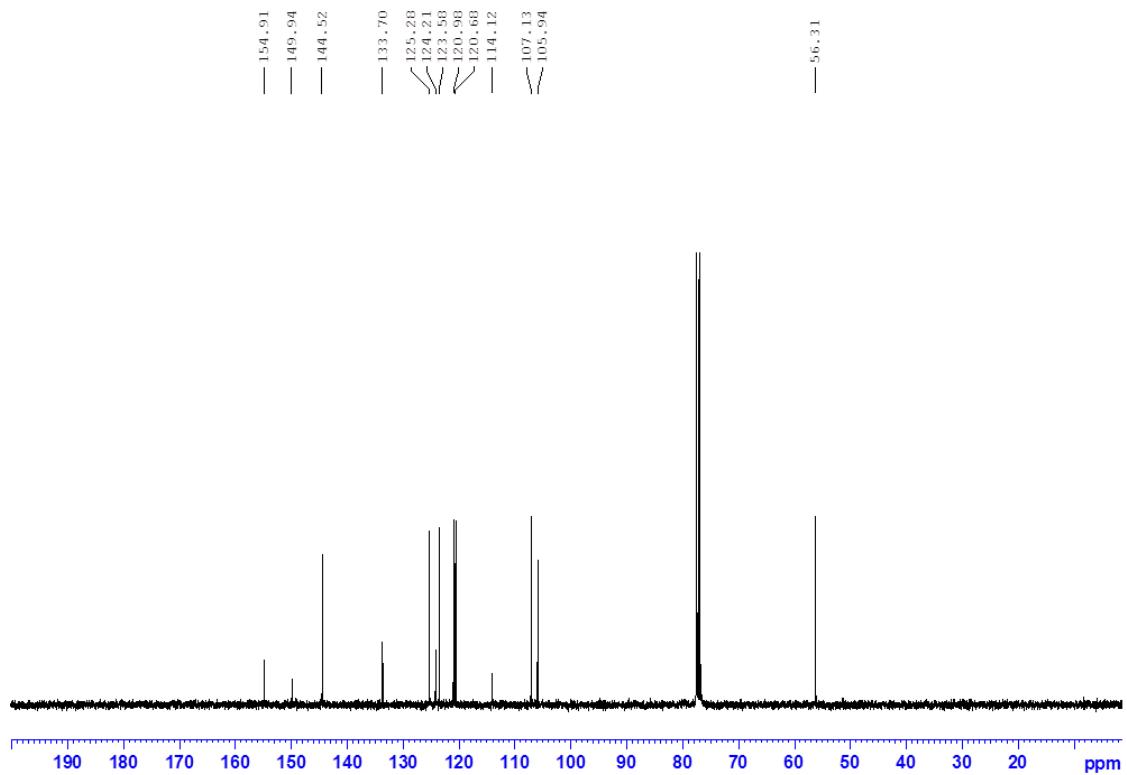
¹⁹F{¹H}-NMR (282 MHz, CDCl₃): Compound 31



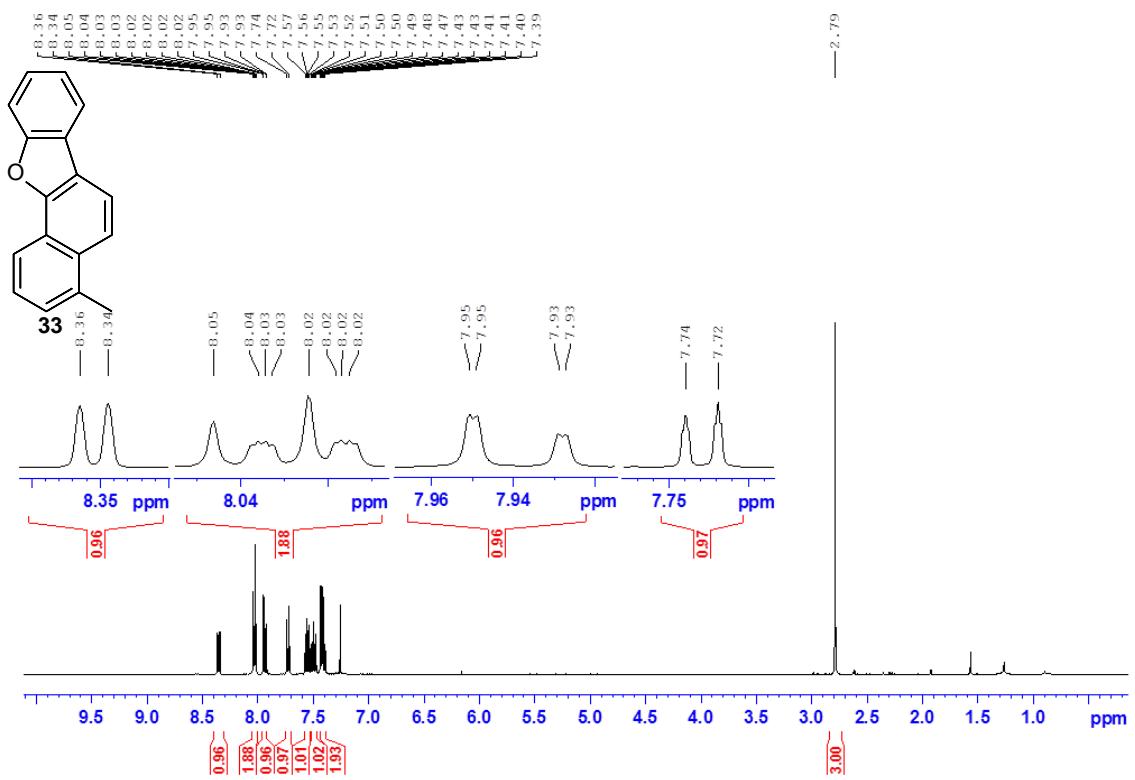
¹H-NMR (300 MHz, CDCl₃): Compound 32



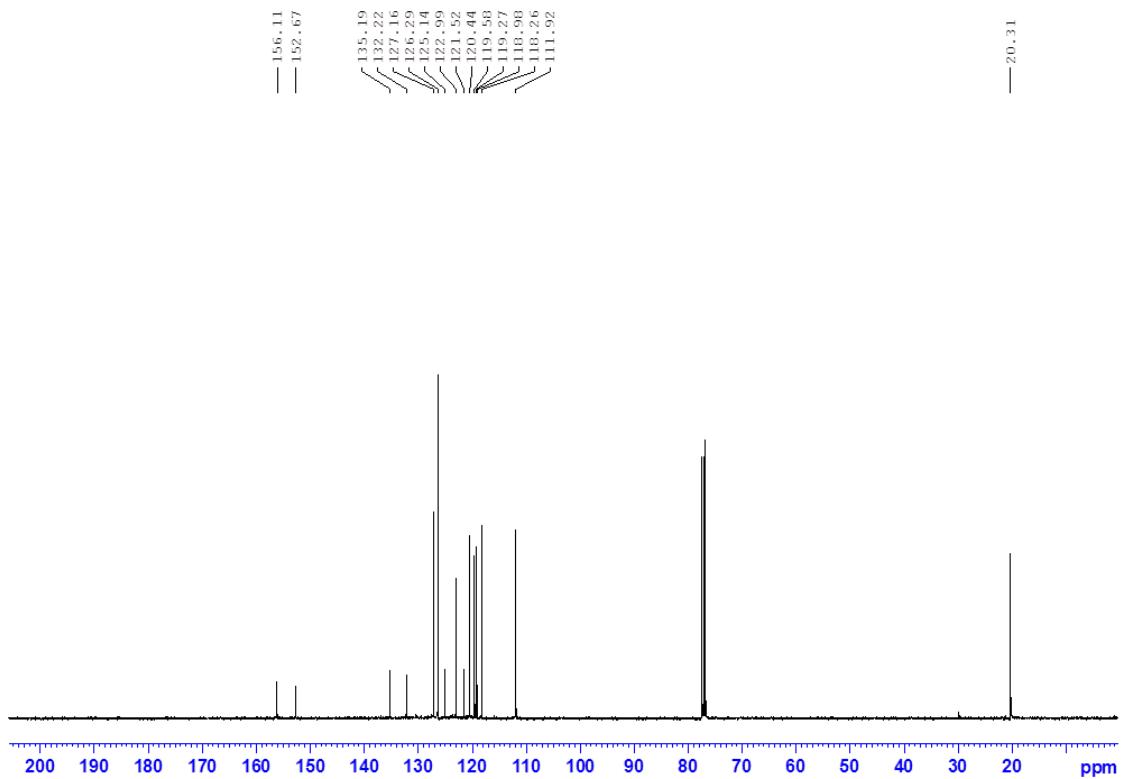
¹³C{¹H}-NMR (101MHz, CDCl₃): Compound 32



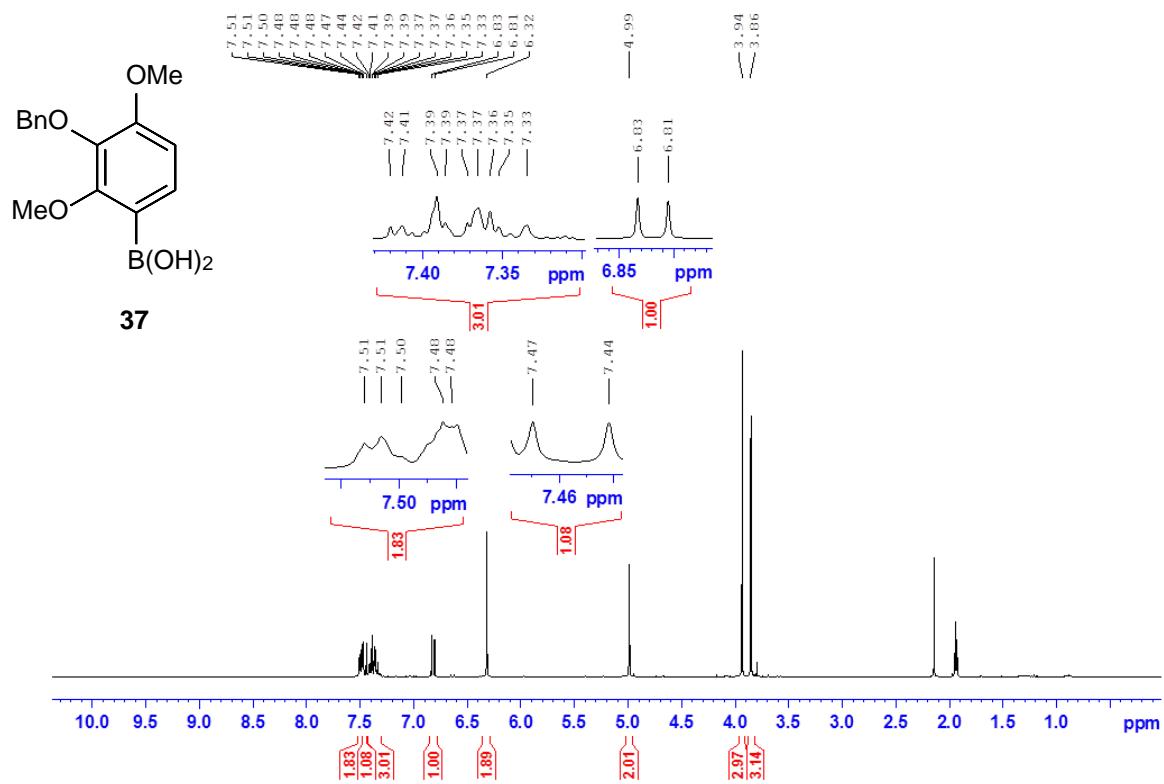
¹H-NMR (400 MHz, CDCl₃): Compound 33



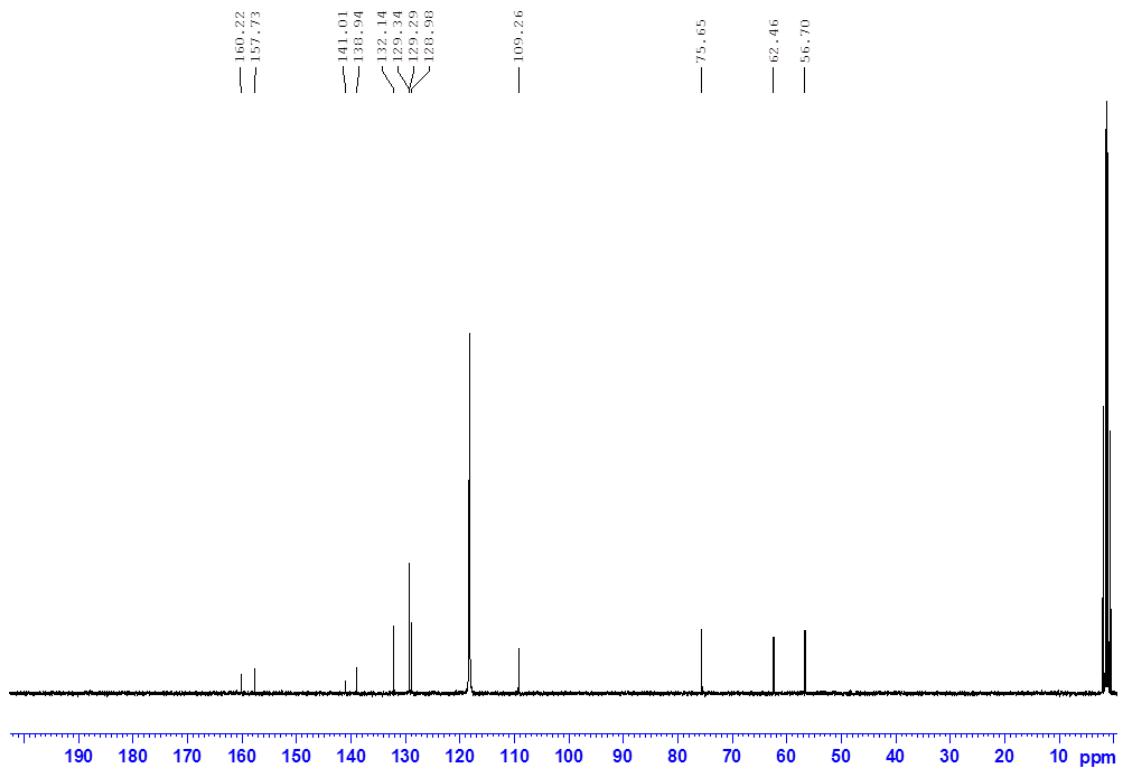
$^{13}\text{C}\{\text{H}\}$ -NMR (101MHz, CDCl_3): Compound 33



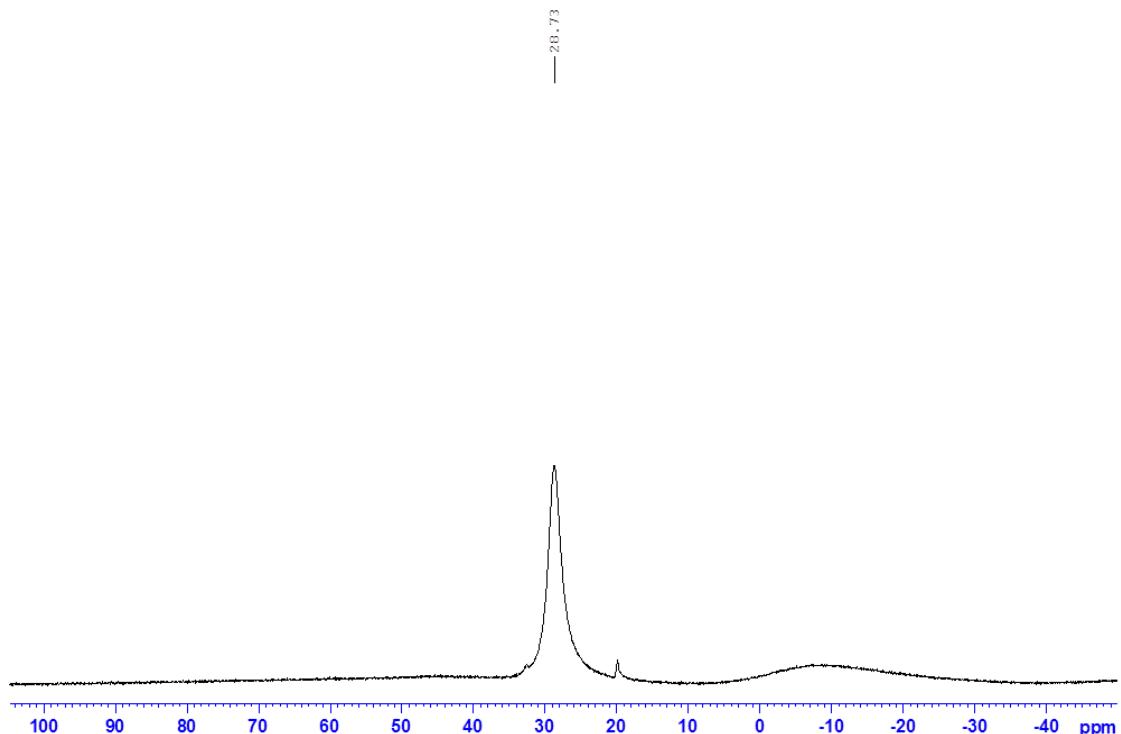
¹H-NMR (300 MHz, CD₃CN): compound 37



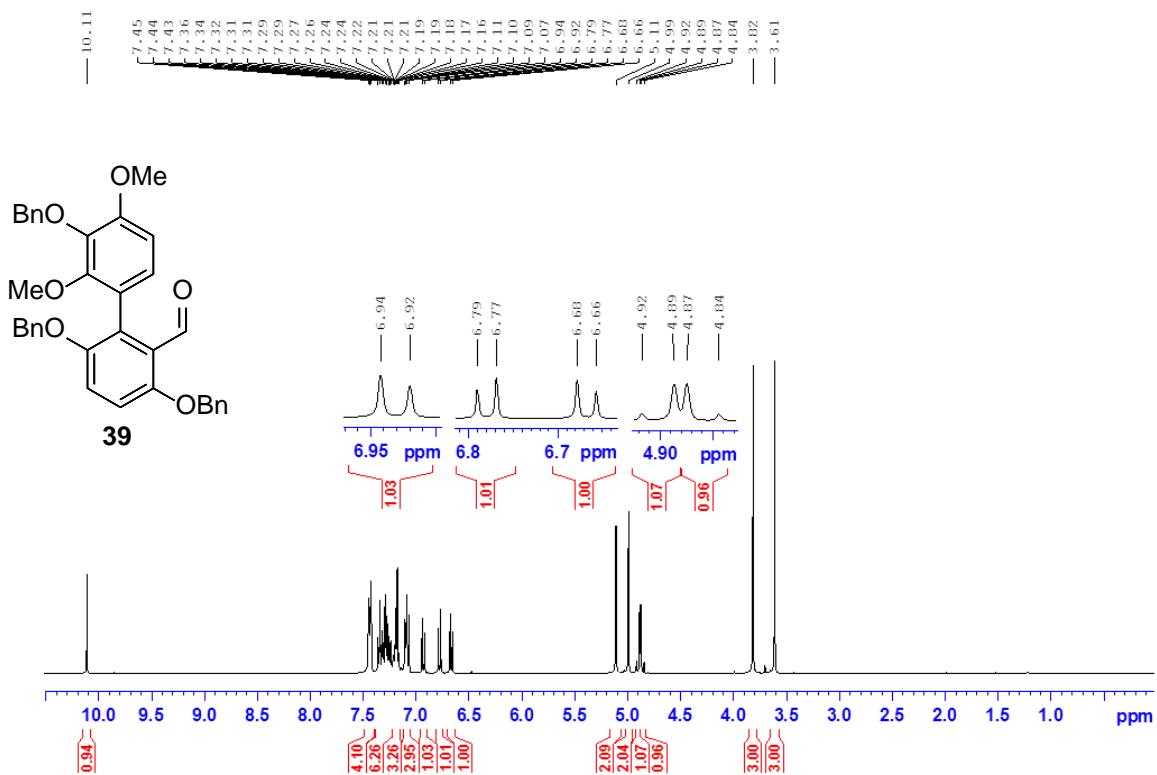
$^{13}\text{C}\{\text{H}\}$ -NMR (75 MHz, CD_3CN): compound 37



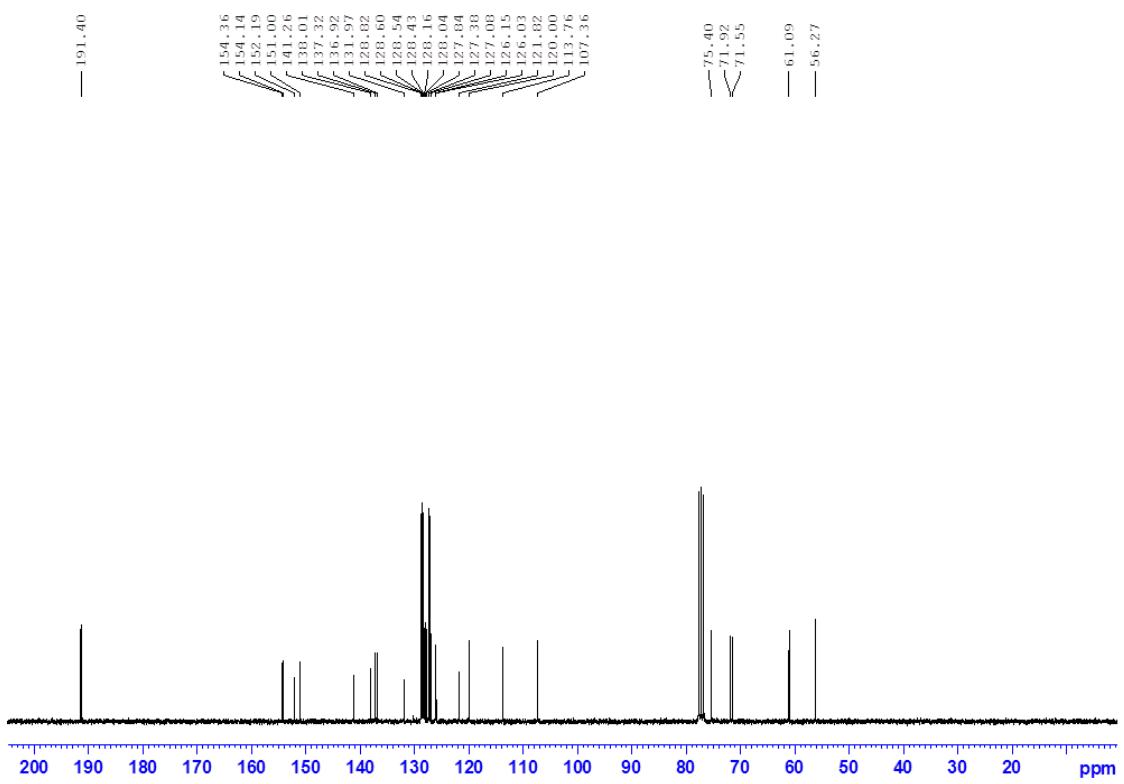
$^{11}\text{B}\{\text{H}\}$ -NMR (96 MHz, CD_3CN): compound 37



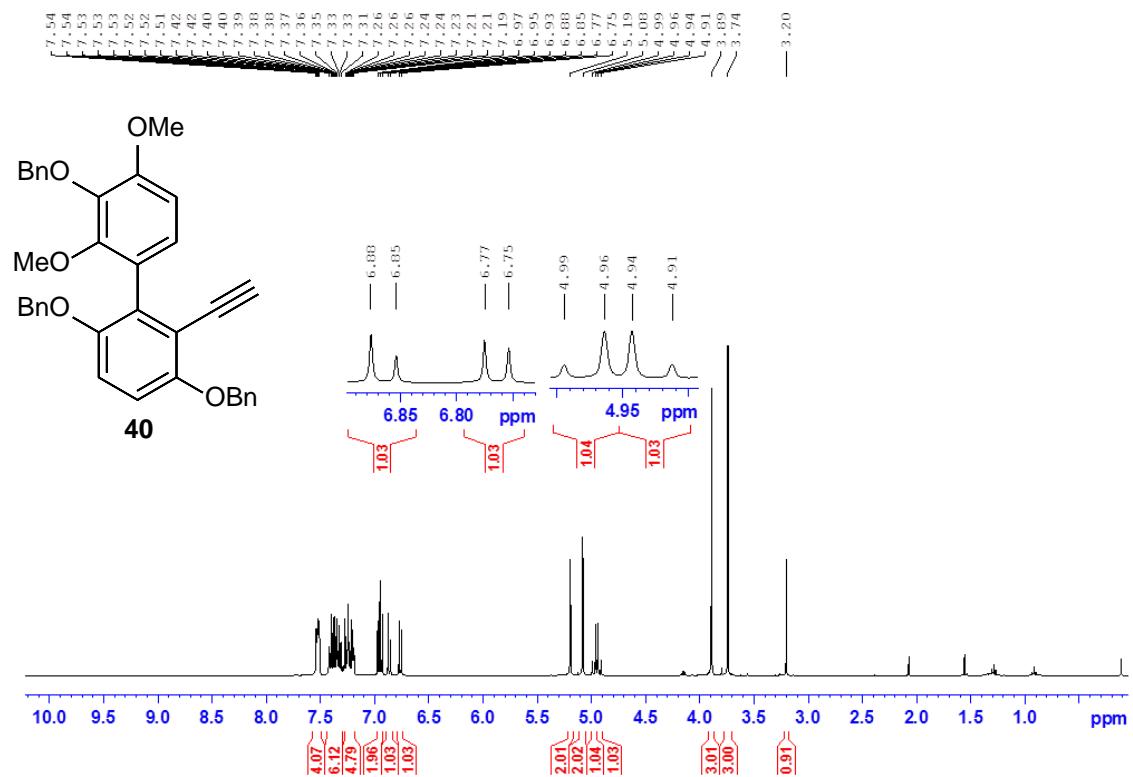
¹H-NMR (400 MHz, CDCl₃): compound 39



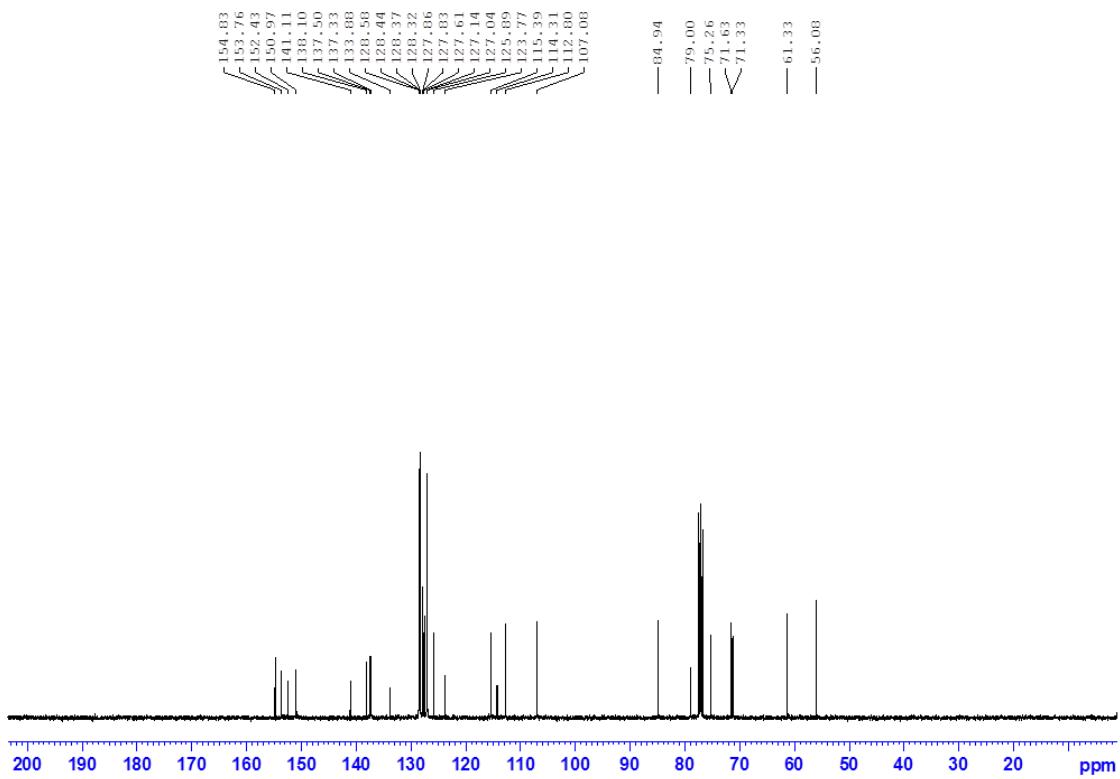
$^{13}\text{C}\{\text{H}\}$ -NMR (101 MHz, CDCl_3): compound 39



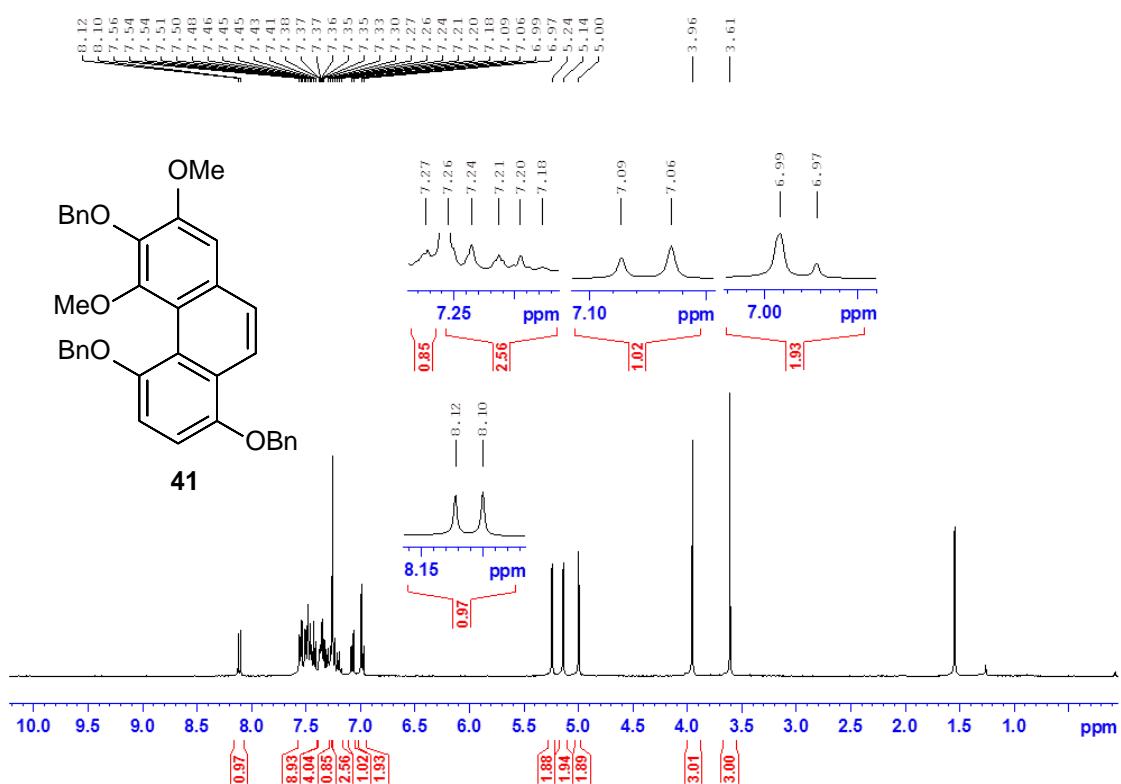
¹H-NMR (400 MHz, CDCl₃): compound 40



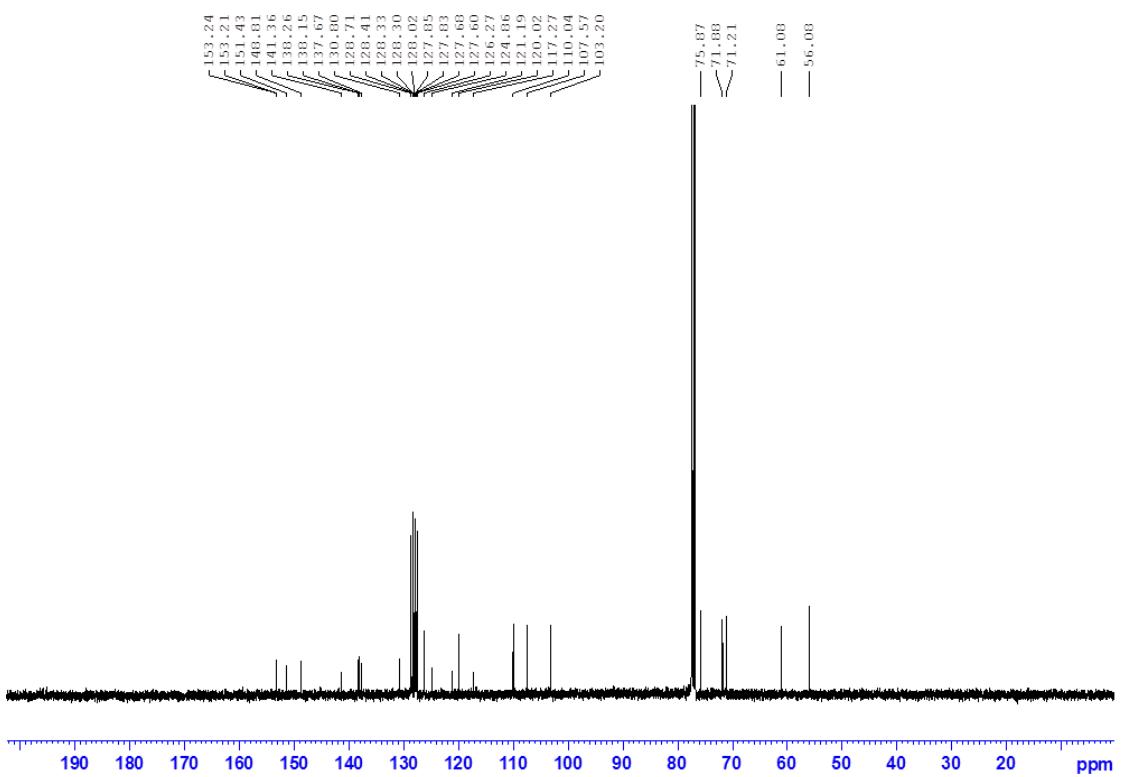
¹³C{¹H}-NMR (400 MHz, CDCl₃): compound 40



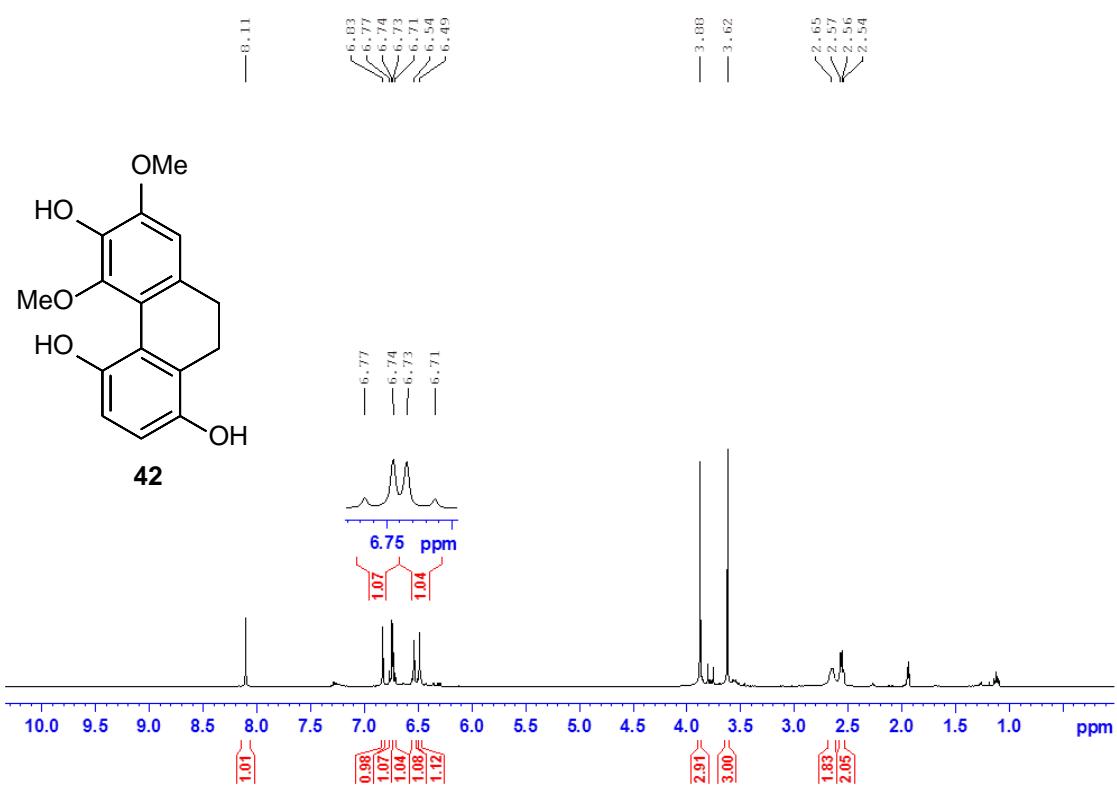
^1H -NMR (400 MHz, CDCl_3): compound 41



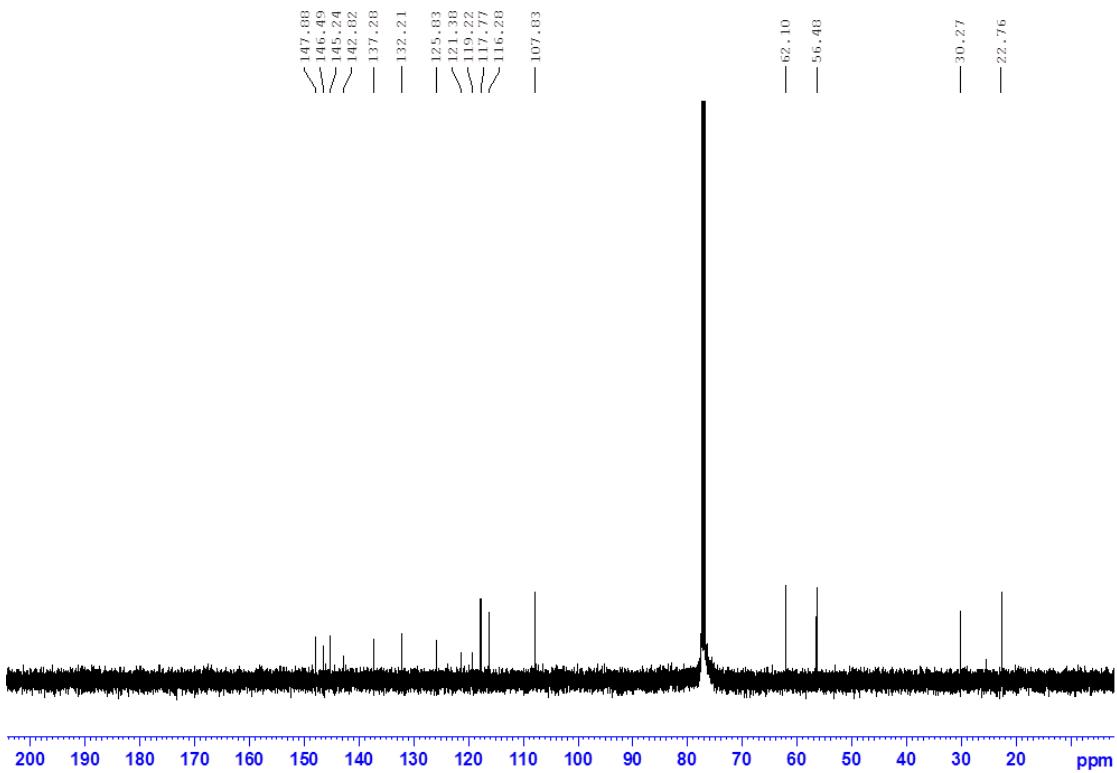
$^{13}\text{C}\{^1\text{H}\}$ -NMR (101 MHz, CDCl_3): compound 41



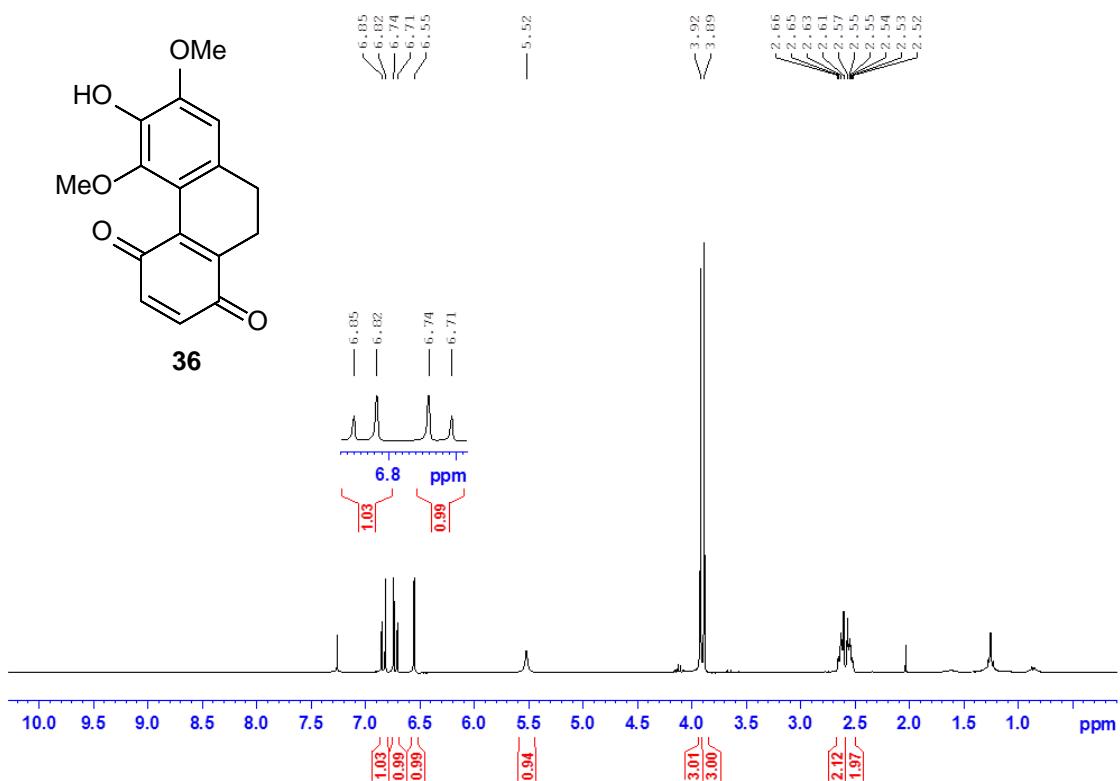
¹H-NMR (400 MHz, CD₃CN): *Calanhydroquinone A 42*



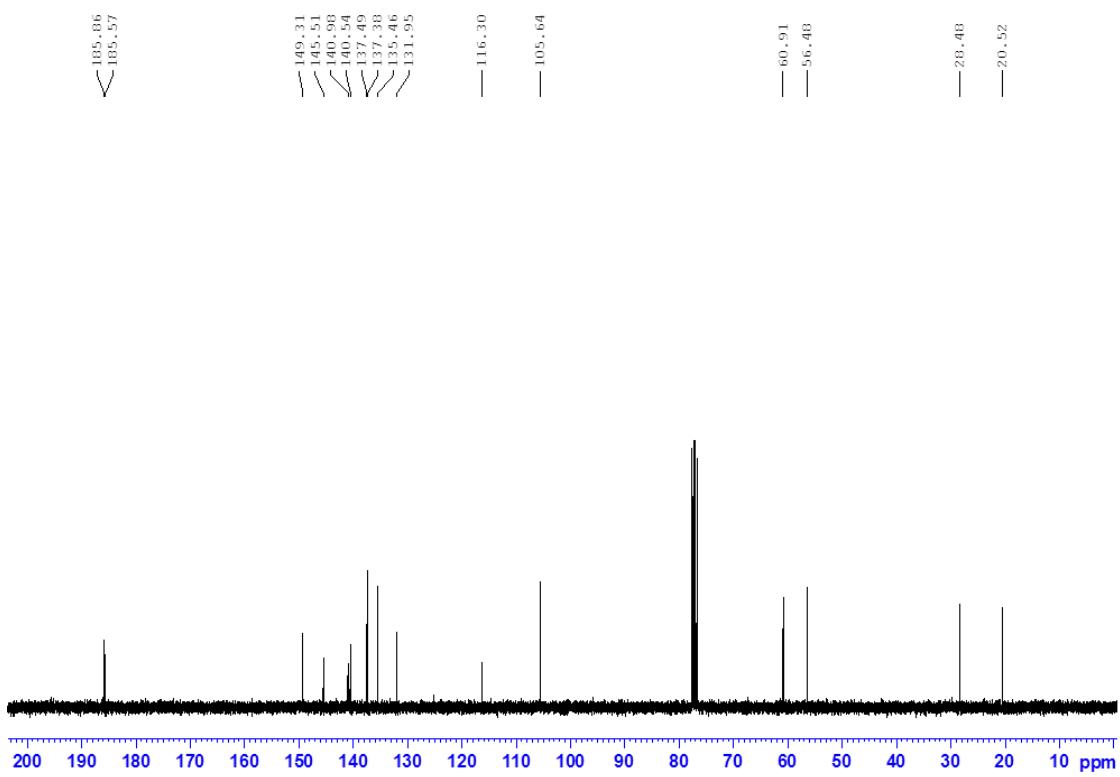
¹³C{¹H}-NMR (125 MHz, CDCl₃): Calanhydroquinone A 42



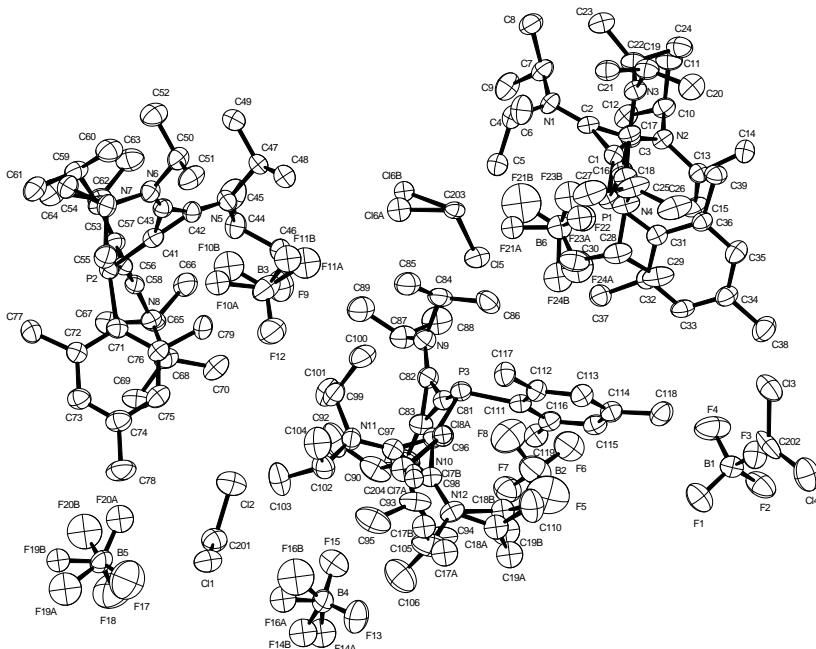
¹H-NMR (300 MHz, CD₃CN): *Calanquinone C* **36**



¹³C{¹H}-NMR (75 MHz, CDCl₃): *Calanquinone C* **36**

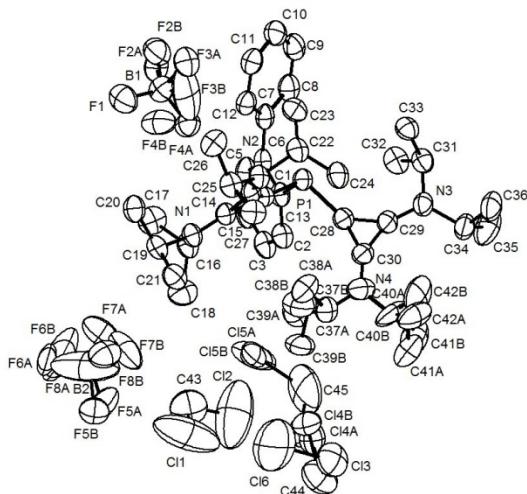


Compound 1d



Empirical formula	$C_{119.50} H_{204} Cl_5 F_{24} N_{12} P_3$
Color	yellow
Formula weight	2599.97 g · mol ⁻¹
Temperature	100 K
Wavelength	1.54178 Å
Crystal system	ORTHORHOMBIC
Space group	Pca2 ₁ , (no. 29)
Unit cell dimensions	$a = 15.5427(6)$ Å $\alpha = 90^\circ$. $b = 45.2303(17)$ Å $\beta = 90^\circ$. $c = 20.8064(7)$ Å $\gamma = 90^\circ$.
Volume	14626.9(9) Å ³
Z	4
Density (calculated)	1.181 Mg · m ⁻³
Absorption coefficient	1.859 mm ⁻¹
F(000)	5524 e
Crystal size	0.70 x 0.51 x 0.05 mm ³
□ range for data collection	1.95 to 67.58°
Index ranges	-16 ≤ h ≤ 18, -53 ≤ k ≤ 53, -24 ≤ l ≤ 24
Reflections collected	329335
Independent reflections	25642 [R _{int} = 0.0895]
Reflections with I > 2□(I)	23377
Completeness to □ = 67.58°	98.9 %
Absorption correction	Gaussian
Max. and min. transmission	0.94 and 0.46
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	25642 / 1 / 1601
Goodness-of-fit on F ²	1.045
Final R indices [I > 2□(I)]	R ₁ = 0.0917 wR ² = 0.2462
R indices (all data)	R ₁ = 0.0977 wR ² = 0.2555
Absolute structure parameter	0.038(15)
Extinction coefficient	0.00174(10)
Largest diff. peak and hole	1.806 and -0.528 e · Å ⁻³

Compound 1f

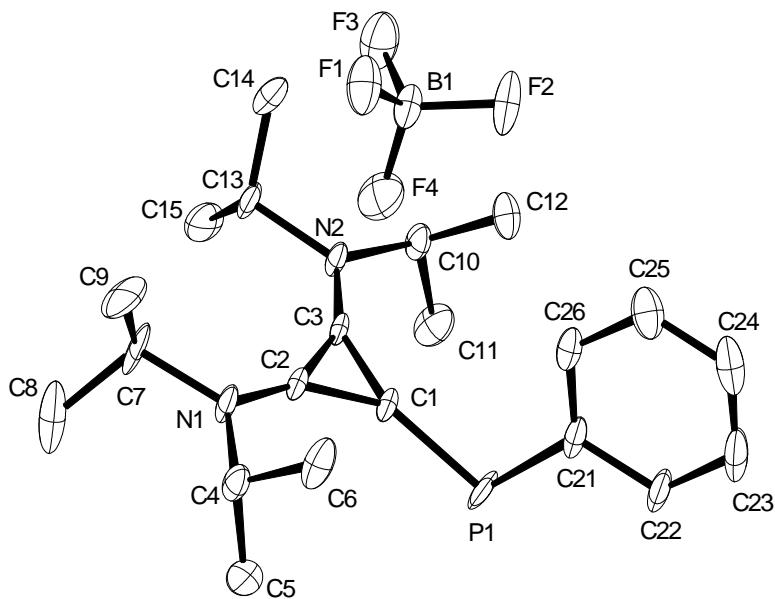


Comment: Two of the isopropyl groups and both tetrafluoroborate anions are disordered. In addition, the crystal contains badly disordered dichloromethane. The dichloromethane was modelled by C, H and Cl atoms. The refined occupancies summed up to C 2.28, H 4.55 and Cl 4.36. This approximates to 2.25 (CH_2Cl_2) per mole. Out of 6 attempts to obtain suitable crystals this was the best result, which could be obtained.

Crystal data and structure refinement.

Empirical formula	$\text{C}_{44.28}\text{H}_{69.55}\text{B}_2\text{Cl}_{4.36}\text{F}_8\text{N}_4\text{P}$
Color	colourless
Formula weight	1016.90 g·mol ⁻¹
Temperature	100 K
Wavelength	1.54178 Å
Crystal system	orthorhombic
Space group	P b c a, (no. 61)
Unit cell dimensions	$a = 15.3679(7)$ Å $\alpha = 90^\circ$. $b = 21.1957(10)$ Å $\beta = 90^\circ$. $c = 32.9485(16)$ Å $\gamma = 90^\circ$.
Volume	10732.4(9) Å ³
Z	8
Density (calculated)	1.259 Mg·m ⁻³
Absorption coefficient	2.970 mm ⁻¹
F(000)	4274 e
Crystal size	0.33 x 0.24 x 0.07 mm ³
Θ range for data collection	2.682 to 67.845°.
Index ranges	-17 ≤ h ≤ 16, -25 ≤ k ≤ 25, -39 ≤ l ≤ 39
Reflections collected	240324
Independent reflections	9610 [$R_{\text{int}} = 0.1195$]
Reflections with $I > 2\sigma(I)$	7562
Completeness to $\Theta = 67.679^\circ$	99.0 %
Absorption correction	Gaussian
Max. and min. transmission	0.90807 and 0.67634
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	9610 / 0 / 756
Goodness-of-fit on F^2	1.103
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0906$ $wR^2 = 0.2460$
R indices (all data)	$R_1 = 0.1077$ $wR^2 = 0.2598$
Extinction coefficient	0.00196(14)
Largest diff. peak and hole	0.443 and -0.768 e·Å ⁻³

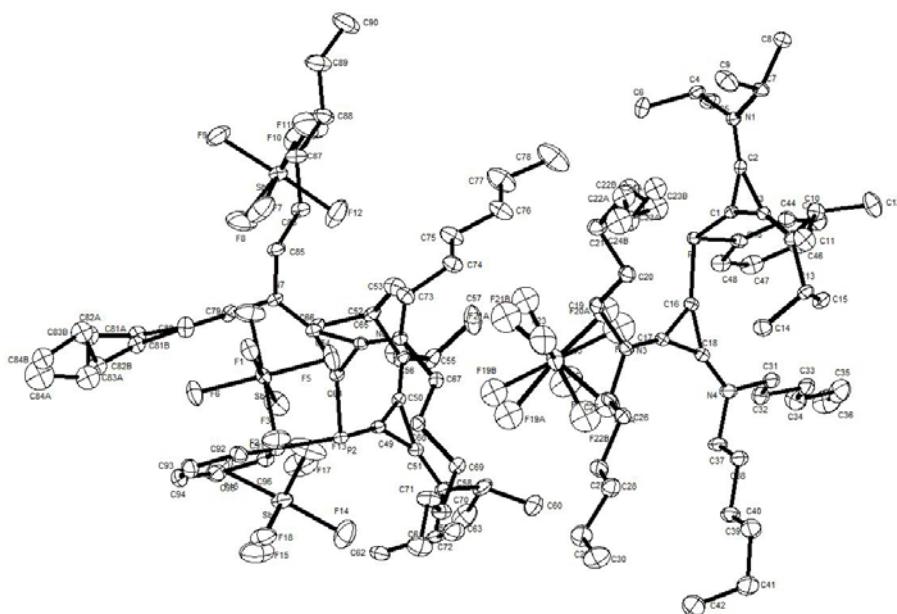
Compound 5a



Crystal data and structure refinement.

Empirical formula	$C_{21}H_{34}BF_4N_2P$
Color	colorless
Formula weight	432.28 g mol ⁻¹
Temperature	100 K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	Cc, (no. 9)
Unit cell dimensions	$a = 11.811(5)$ Å $\alpha = 90^\circ$. $b = 15.362(6)$ Å $\beta = 101.797(8)^\circ$. $c = 13.008(5)$ Å $\gamma = 90^\circ$.
Volume	2310.3(16) Å ³
Z	4
Density (calculated)	1.243 Mg m ⁻³
Absorption coefficient	0.160 mm ⁻¹
F(000)	920 e
Crystal size	0.10 x 0.04 x 0.02 mm ³
Θ range for data collection	2.20 to 31.15°
Index ranges	-17 ≤ h ≤ 17, -22 ≤ k ≤ 22, -18 ≤ l ≤ 17
Reflections collected	19071
Independent reflections	6768 [$R_{\text{int}} = 0.0889$]
Reflections with $I > 2\sigma(I)$	4970
Completeness to $\Theta = 31.15^\circ$	99.2 %
Absorption correction	Empirical
Max. and min. transmission	1.00 and 0.50
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6768 / 2 / 274
Goodness-of-fit on F^2	1.052
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0542$ $wR^2 = 0.1318$
R indices (all data)	$R_1 = 0.0837$ $wR^2 = 0.1632$
Absolute structure parameter	0.20(10)
Largest diff. peak and hole	0.461 and -0.675 e Å ⁻³

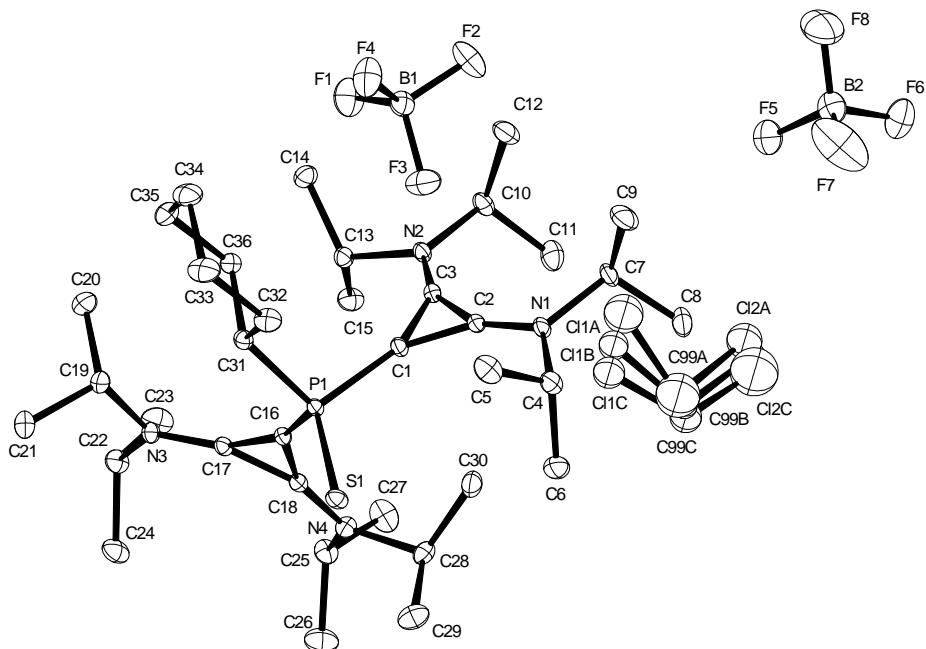
Compound 8a (SbF_6)



Crystal data and structure refinement.

Empirical formula	$\text{C}_{48}\text{H}_{85}\text{F}_{12}\text{N}_4\text{PSb}_2$
Color	colourless
Formula weight	1220.66 g·mol ⁻¹
Temperature	100 K
Wavelength	0.71073 Å
Crystal system	MONOCLINIC
Space group	p 21/n, (no. 14)
Unit cell dimensions	$a = 14.879(2)$ Å $\alpha = 90^\circ$. $b = 30.262(5)$ Å $\beta = 95.646(3)^\circ$. $c = 27.205(5)$ Å $\gamma = 90^\circ$.
Volume	12191(3) Å ³
Z	8
Density (calculated)	1.330 Mg·m ⁻³
Absorption coefficient F(000)	0.981 mm ⁻¹ 5008 e
Crystal size	0.29 x 0.08 x 0.07 mm ³
Θ range for data collection	1.346 to 31.024°.
Index ranges	-21 ≤ h ≤ 21, 0 ≤ k ≤ 43, 0 ≤ l ≤ 39
Reflections collected	38745
Independent reflections	38745 [R _{int} = 0.0451]
Reflections with I > 2σ(I)	31443
Completeness to Θ = 25.242°	100.0 %
Absorption correction	Gaussian
Max. and min. transmission	0.94595 and 0.77201
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	38745 / 0 / 1222
Goodness-of-fit on F ²	1.115
Final R indices [I > 2σ(I)]	R ₁ = 0.0435 wR ² = 0.1141
R indices (all data)	R ₁ = 0.0565 wR ² = 0.1197
Extinction coefficient	n/a
Largest diff. peak and hole	1.340 and -1.212 e·Å ⁻³

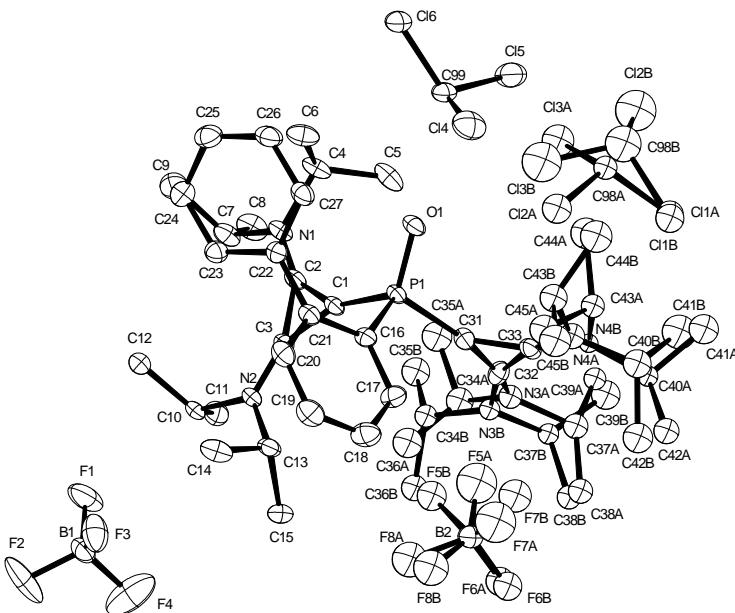
Compound 11b



Crystal data and structure refinement.

Empirical formula	C ₃₇ H ₆₉ B ₂ Cl ₂ F ₈ N ₄ P S
Color	colorless
Formula weight	877.51 g · mol ⁻¹
Temperature	100 K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P1, (no. 2)
Unit cell dimensions	a = 12.8504(15) Å b = 13.9976(16) Å c = 14.7610(17) Å α = 67.579(2) $^\circ$. β = 70.358(2) $^\circ$. γ = 73.257(2) $^\circ$.
Volume	2272.3(5) Å ³
Z	2
Density (calculated)	1.283 Mg · m ⁻³
Absorption coefficient	0.288 mm ⁻¹
F(000)	932 e
Crystal size	0.16 x 0.14 x 0.09 mm ³
□ range for data collection	1.544 to 33.400 $^\circ$.
Index ranges	-19 ≤ h ≤ 19, -21 ≤ k ≤ 21, -22 ≤ l ≤ 22
Reflections collected	77633
Independent reflections	17546 [R _{int} = 0.0373]
Reflections with I > 2σ(I)	13874
Completeness to □ = 25.242 $^\circ$	99.6 %
Absorption correction	Gaussian
Max. and min. transmission	0.99 and 0.97
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	17546 / 0 / 521
Goodness-of-fit on F ²	1.042
Final R indices [I > 2σ(I)]	R ₁ = 0.0505 wR ² = 0.1269
R indices (all data)	R ₁ = 0.0674 wR ² = 0.1378
Largest diff. peak and hole	1.4 and -2.0 e · Å ⁻³

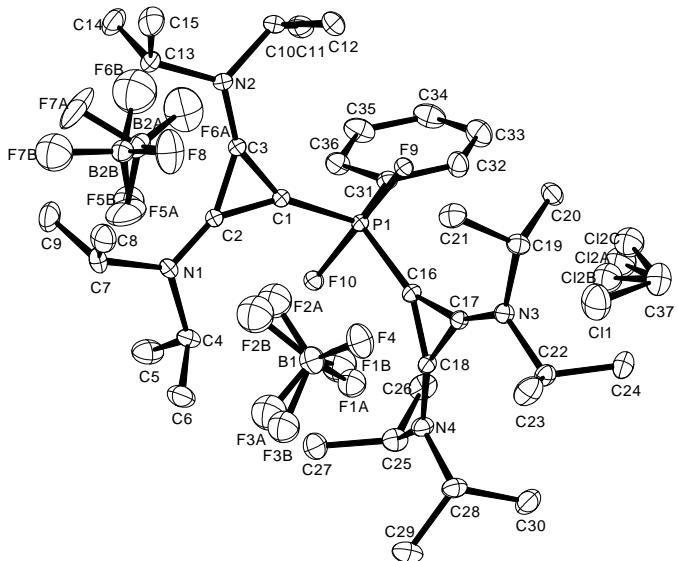
Compound 11f



Crystal data and structure refinement.

Empirical formula	$C_{44}H_{66}B_2Cl_6F_8N_4O_P$
Color	colorless
Formula weight	1084.29 g · mol ⁻¹
Temperature	100 K
Wavelength	0.71073 Å
Crystal system	MONOCLINIC
Space group	P2₁, (no. 4)
Unit cell dimensions	a = 11.907(3) Å b = 18.936(4) Å c = 13.438(3) Å
Volume	2722.0(10) Å ³
Z	2
Density (calculated)	1.323 Mg · m ⁻³
Absorption coefficient	0.409 mm ⁻¹
F(000)	1130 e
Crystal size	0.45 x 0.29 x 0.12 mm ³
☐ range for data collection	1.687 to 31.002°.
Index ranges	-17 ≤ h ≤ 17, -27 ≤ k ≤ 27, -19 ≤ l ≤ 19
Reflections collected	80496
Independent reflections	17348 [R _{int} = 0.0337]
Reflections with l>2☐ l	15450
Completeness to ☐ =	25.242°
Absorption correction	100.0 %
Max. and min. transmission	Gaussian 0.98 and 0.90
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	17348 / 1 / 597
Goodness-of-fit on F ²	1.024
Final R indices [l>2☐ l]	R ₁ = 0.0627
R indices (all data)	wR ² = 0.1598
Absolute structure parameter	R ₁ = 0.0719
Largest diff. peak and hole	0.026(10) 1.2 and -1.3 e · Å ⁻³

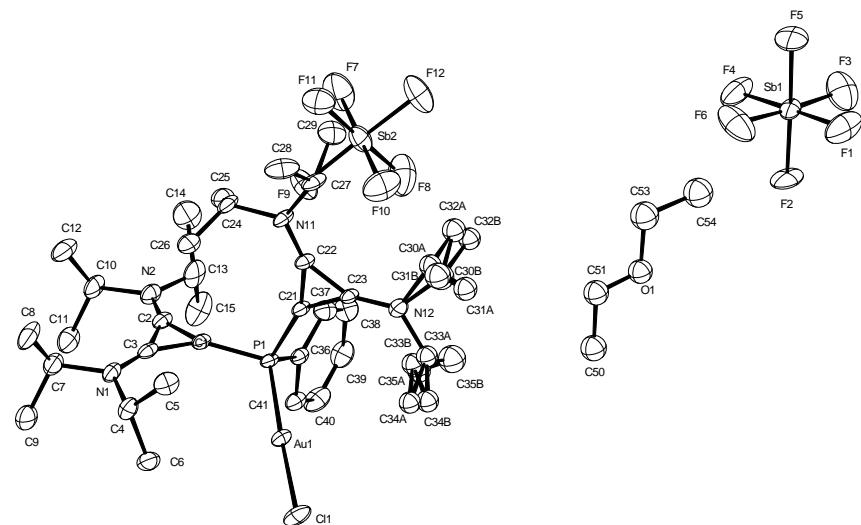
Compound 12a



Crystal data and structure refinement.

Empirical formula	$C_{37}H_{63}B_2Cl_2F_{10}N_4P$
Color	colourless
Formula weight	$877.40 \text{ g}\cdot\text{mol}^{-1}$
Temperature	100 K
Wavelength	0.71073 Å
Crystal system	TRICLINIC
Space group	p -1, (no. 2)
Unit cell dimensions	$a = 9.6706(9) \text{ Å}$ $b = 13.0637(12) \text{ Å}$ $c = 18.6347(17) \text{ Å}$ $\alpha = 81.557(2)^\circ$. $\beta = 80.425(2)^\circ$. $\gamma = 75.063(2)^\circ$.
Volume	2229.6(4) \AA^3
Z	2
Density (calculated)	1.307 $\text{Mg}\cdot\text{m}^{-3}$
Absorption coefficient	0.255 mm^{-1}
F(000)	924 e
Crystal size	0.48 x 0.43 x 0.36 mm ³
q range for data collection	1.115 to 36.859°
Index ranges	-16 ≤ h ≤ 16, -21 ≤ k ≤ 21, -31 ≤ l ≤ 31
Reflections collected	169310
Independent reflections	21991 [$R_{\text{int}} = 0.0304$]
Reflections with $ l > 2s(l)$	17796
Completeness to $q = 25.242^\circ$	100.0 %
Absorption correction	Gaussian
Max. and min. transmission	0.96258 and 0.94931
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	21991 / 0 / 537
Goodness-of-fit on F^2	1.040
Final R indices [$ l > 2s(l)$]	$R_1 = 0.0627$ $wR^2 = 0.1712$
R indices (all data)	$R_1 = 0.0776$ $wR^2 = 0.1872$
Extinction coefficient	n/a
Largest diff. peak and hole	1.592 and -1.297 $e\cdot\text{\AA}^{-3}$

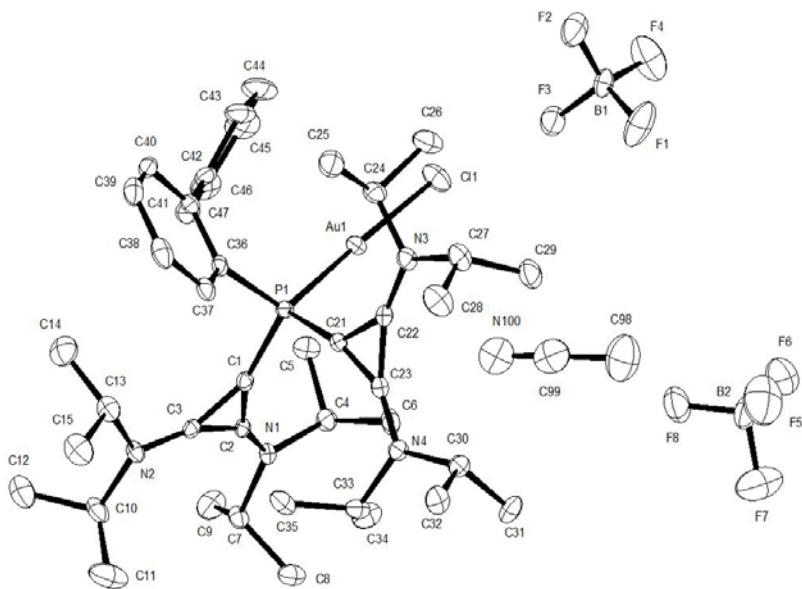
Compound 16 (SbF_6)



Crystal data and structure refinement.

Empirical formula	$\text{C}_{76}\text{H}_{132}\text{Au}_2\text{Cl}_2\text{F}_{24}\text{N}_8\text{O P}_2\text{Sb}_4$
Color	colorless
Formula weight	2643.66 g mol ⁻¹
Temperature	100 K
Wavelength	0.71073 Å
Crystal system	MONOCLINIC
Space group	P2₁/c, (no. 14)
Unit cell dimensions	$a = 18.222(3)$ Å $\alpha = 90^\circ$. $b = 10.6242(15)$ Å $\beta = 92.535(3)^\circ$. $c = 27.563(4)$ Å $\gamma = 90^\circ$.
Volume	5330.9(13) Å ³
Z	2
Density (calculated)	1.647 Mg m ⁻³
Absorption coefficient F(000)	3.903 mm ⁻¹ 2588 e
Crystal size	0.22 x 0.04 x 0.02 mm ³
Θ range for data collection	2.055 to 28.363°.
Index ranges	-24 ≤ h ≤ 24, -14 ≤ k ≤ 14, -36 ≤ l ≤ 36
Reflections collected	126469
Independent reflections	13286 [$R_{\text{int}} = 0.0855$]
Reflections with $I > 2\sigma(I)$	10302
Completeness to $\Theta = 25.242^\circ$	99.9 %
Absortion correction	Gaussian
Max. and min. transmission	0.93 and 0.61
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	13286 / 0 / 554
Goodness-of-fit on F^2	1.055
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0501$ $wR^2 = 0.1197$
R indices (all data)	$R_1 = 0.0724$ $wR^2 = 0.1307$
Largest diff. peak and hole	3.5 and -2.1 e Å ⁻³

Compound 19



Crystal data and structure refinement.

Empirical formula	$C_{44}H_{68}AuB_2ClF_8N_5P$
Color	colourless
Formula weight	1104.04 g·mol ⁻¹
Temperature	100 K
Wavelength	0.71073 Å
Crystal system	orthorhombic
Space group	P b c a, (no. 61)
Unit cell dimensions	$a = 14.720(2)$ Å $\alpha = 90^\circ$. $b = 17.611(3)$ Å $\beta = 90^\circ$. $c = 38.084(6)$ Å $\gamma = 90^\circ$.
Volume	9872(3) Å ³
Z	8
Density (calculated)	1.486 Mg·m ⁻³
Absorption coefficient	3.133 mm ⁻¹
F(000)	4480 e
Crystal size	0.11 x 0.09 x 0.07 mm ³
Θ range for data collection	1.069 to 26.439°.
Index ranges	-18 ≤ h ≤ 18, -22 ≤ k ≤ 22, -47 ≤ l ≤ 46
Reflections collected	204020
Independent reflections	10150 [$R_{\text{int}} = 0.0510$]
Reflections with $l > 2\sigma(l)$	8558
Completeness to $\Theta = 25.242^\circ$	100.0 %
Absorption correction	Gaussian
Max. and min. transmission	0.82715 and 0.70856
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	10150 / 0 / 576
Goodness-of-fit on F^2	1.065
Final R indices [$l > 2\sigma(l)$]	$R_1 = 0.0313$ $wR^2 = 0.0723$
R indices (all data)	$R_1 = 0.0406$ $wR^2 = 0.0774$
Extinction coefficient	0
Largest diff. peak and hole	3.207 and -1.089 e·Å ⁻³

Compound 30

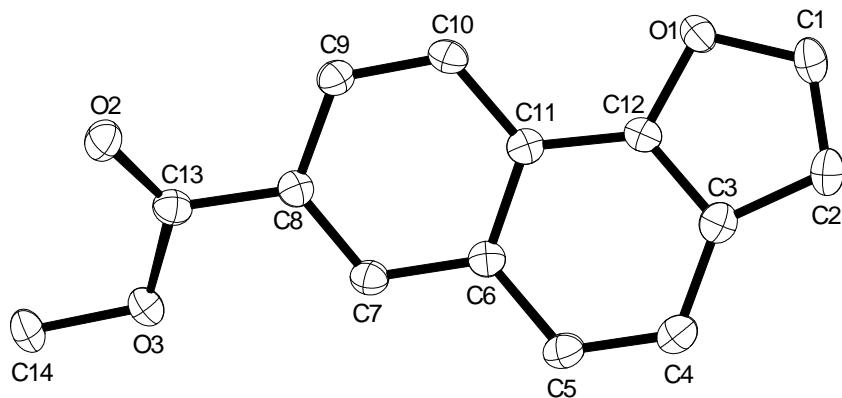
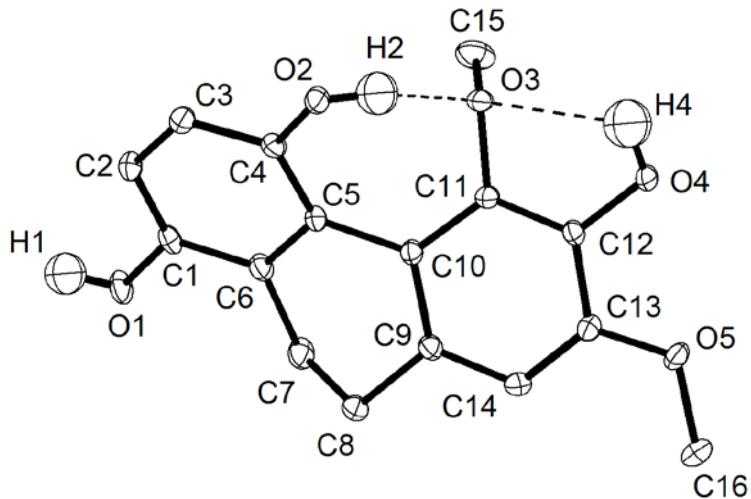


Table 1. Crystal data and structure refinement.

Identification code	9355sadabs	
Empirical formula	C ₁₄ H ₁₀ O ₃	
Color	colourless	
Formula weight	226.22 g·mol ⁻¹	
Temperature	100 K	
Wavelength	1.54178 Å	
Crystal system	MONOCLINIC	
Space group	p 21, (no. 4)	
Unit cell dimensions	a = 7.6215(3) Å b = 6.1218(2) Å c = 11.6856(4) Å	
Volume	528.75(3) Å ³	
Z	2	
Density (calculated)	1.421 Mg·m ⁻³	
Absorption coefficient	0.824 mm ⁻¹	
F(000)	236 e	
Crystal size	0.30 x 0.07 x 0.06 mm ³	
□ range for data collection	3.900 to 67.297°.	
Index ranges	-9 ≤ h ≤ 9, -7 ≤ k ≤ 6, -13 ≤ l ≤ 13	
Reflections collected	12502	
Independent reflections	1771 [R _{int} = 0.0379]	
Reflections with I > 2σ(I)	1684	
Completeness to □ = 67.297°	99.9 %	
Absorption correction	Gaussian	
Max. and min. transmission	0.95884 and 0.83568	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	1771 / 1 / 156	
Goodness-of-fit on F ²	1.049	
Final R indices [I > 2σ(I)]	R ₁ = 0.0422	wR ² = 0.1081
R indices (all data)	R ₁ = 0.0441	wR ² = 0.1099
Absolute structure parameter	-0.1(3)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.173 and -0.229 e·Å ⁻³	

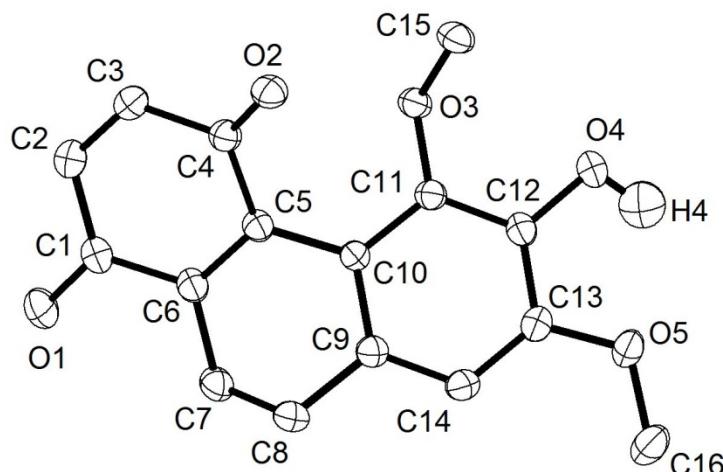
Compound 42



Crystal data and structure refinement.

Empirical formula	$C_{16}H_{16}O_5$
Color	colourless
Formula weight	288.29 g·mol ⁻¹
Temperature	100 K
Wavelength	0.71073 Å
Crystal system	monoclinic
Space group	p 2/n, (no. 14)
Unit cell dimensions	$a = 7.4040(11)$ Å $\alpha = 90^\circ$. $b = 9.3488(14)$ Å $\beta = 90.669(3)^\circ$. $c = 20.526(3)$ Å $\gamma = 90^\circ$.
Volume	1420.7(4) Å ³
Z	4
Density (calculated)	1.348 Mg·m ⁻³
Absorption coefficient	0.100 mm ⁻¹
F(000)	608 e
Crystal size	0.473 x 0.146 x 0.080 mm ³
Θ range for data collection	1.984 to 28.538°.
Index ranges	-9 ≤ h ≤ 9, -12 ≤ k ≤ 12, -27 ≤ l ≤ 27
Reflections collected	32312
Independent reflections	3606 [$R_{\text{int}} = 0.0389$]
Reflections with $I > 2\sigma(I)$	3017
Completeness to $\Theta = 25.242^\circ$	100.0 %
Absorption correction	Gaussian
Max. and min. transmission	0.99236 and 0.96919
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3606 / 0 / 204
Goodness-of-fit on F^2	1.037
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0378$ $wR^2 = 0.1026$
R indices (all data)	$R_1 = 0.0475$ $wR^2 = 0.1089$
Extinction coefficient	0
Largest diff. peak and hole	0.489 and -0.227 e·Å ⁻³

Compound 36



Crystal data and structure refinement.

Empirical formula	$C_{16}H_{14}O_5$
Color	orange
Formula weight	286.27 g·mol ⁻¹
Temperature	100 K
Wavelength	0.61992 Å
Crystal system	orthorhombic
Space group	P b c a, (no. 61)
Unit cell dimensions	$a = 16.566(3)$ Å $\alpha = 90^\circ$. $b = 7.5009(15)$ Å $\beta = 90^\circ$. $c = 21.041(4)$ Å $\gamma = 90^\circ$.
Volume	2614.5(9) Å ³
Z	8
Density (calculated)	1.455 Mg·m ⁻³
Absorption coefficient	0.109 mm ⁻¹
F(000)	1200 e
Crystal size	0.032 x 0.025 x 0.005 mm ³
Θ range for data collection	2.730 to 28.551°.
Index ranges	-22 ≤ h ≤ 25, -11 ≤ k ≤ 11, -32 ≤ l ≤ 32
Reflections collected	108289
Independent reflections	4979 [R _{int} = 0.0617]
Reflections with I > 2σ(I)	3900
Completeness to Θ = 21.836°	99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.0 and 0.3142
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	4979 / 0 / 195
Goodness-of-fit on F ²	1.069
Final R indices [I > 2σ(I)]	R ₁ = 0.0477 wR ² = 0.1316
R indices (all data)	R ₁ = 0.0641 wR ² = 0.1466
Extinction coefficient	0
Largest diff. peak and hole	0.369 and -0.317 e·Å ⁻³

Diffraction data were collected at the P11 beamline of the Petra III synchrotron facility Hamburg.