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Supporting Information

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Enantioselective Gold Catalysis: Opportunities Provided by Monodentate Phosphoramidite Ligands with an Acyclic TADDOL Backbone**

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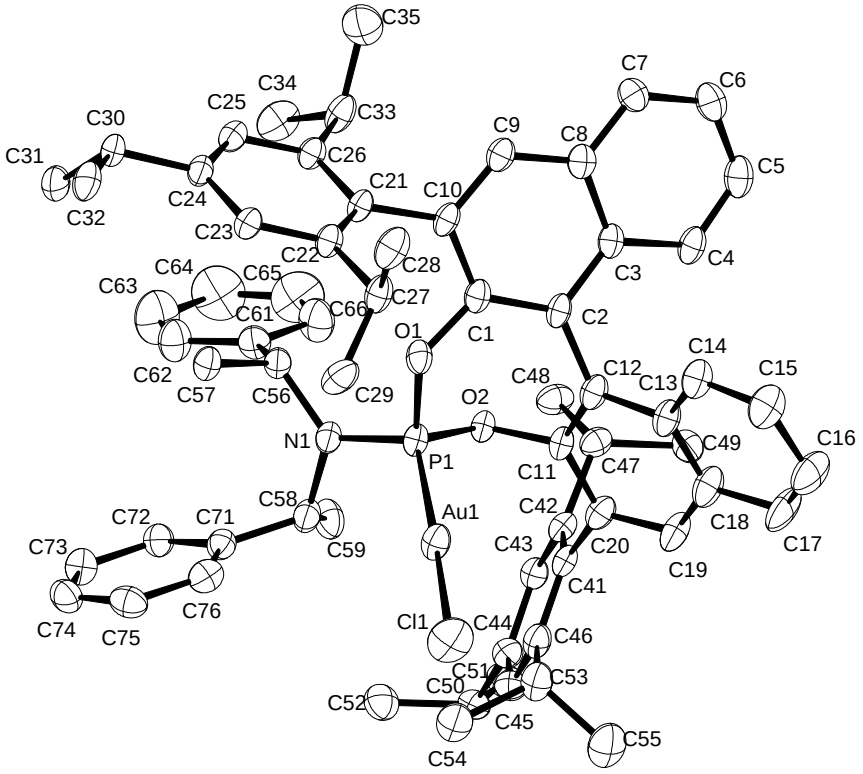
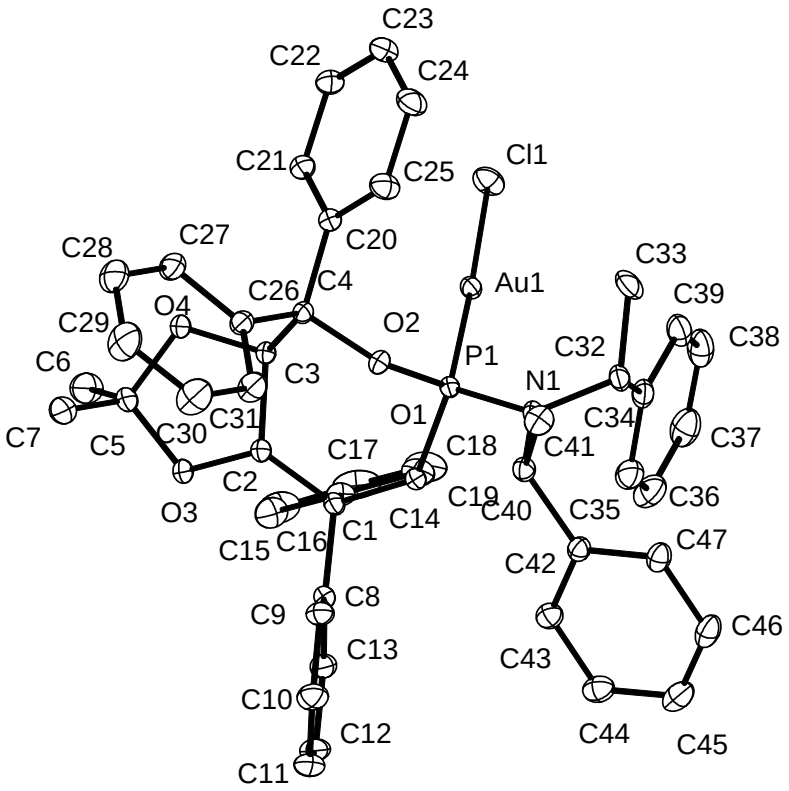
SUPPORTING INFORMATION



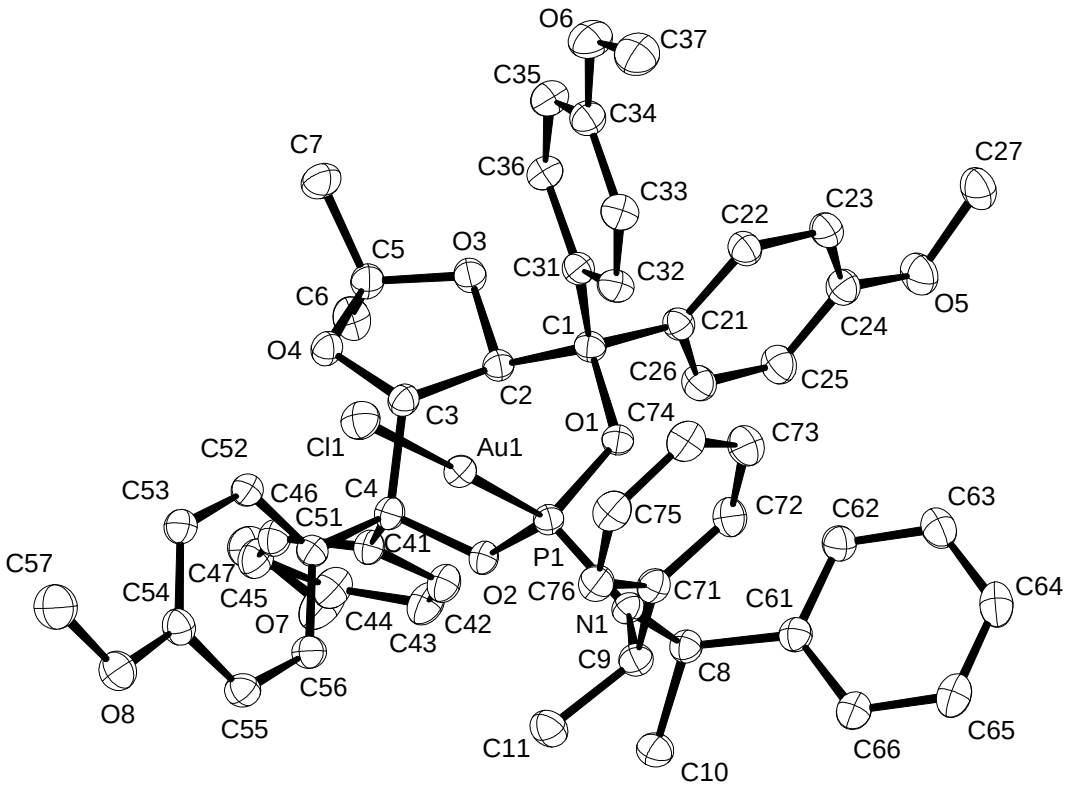
Scheme S-1. Structure of complex [**8**·AuCl] in the solid state. Anisotropic displacement parameters are drawn at the 50% probability level and hydrogen atoms are omitted for clarity.

X-ray Crystal Structure Analysis of [8·AuCl]: $C_{66}H_{74}AuClNO_2P$, M_r = 1176.65 g · mol^{-1}, colorless plate, crystal size 0.22 x 0.12 x 0.03 mm^3, orthorhombic, space group $P2_12_12_1$, a = 13.85030(10) Å, b = 15.9072(2) Å, c = 28.5459(3) Å, V = 6289.22(11) Å^3, T = 100 K, Z = 4, D_{calc} = 1.243 g·cm^3, λ = 0.71073 Å, μ(*Mo-K*$_\alpha$) = 2.447 mm^{-1}, empirical absorption correction (T_{min} = 0.52, T_{max} = 0.82), Nonius KappaCCD diffractometer, 2.93 < θ < 33.10°, 167605 measured reflections, 23758 independent reflections, 19726 reflections with $I > 2\sigma(I)$. Structure solved by direct methods and refined by full-matrix least-squares against F^2 to R_1 = 0.043 [$I > 2\sigma(I)$], wR_2 = 0.111, 663 parameters, absolute structure parameter = 0.057(4), H atoms riding, S = 1.035, residual electron density 2.2 / -1.2 e Å^{-3}. CCDC 754596.



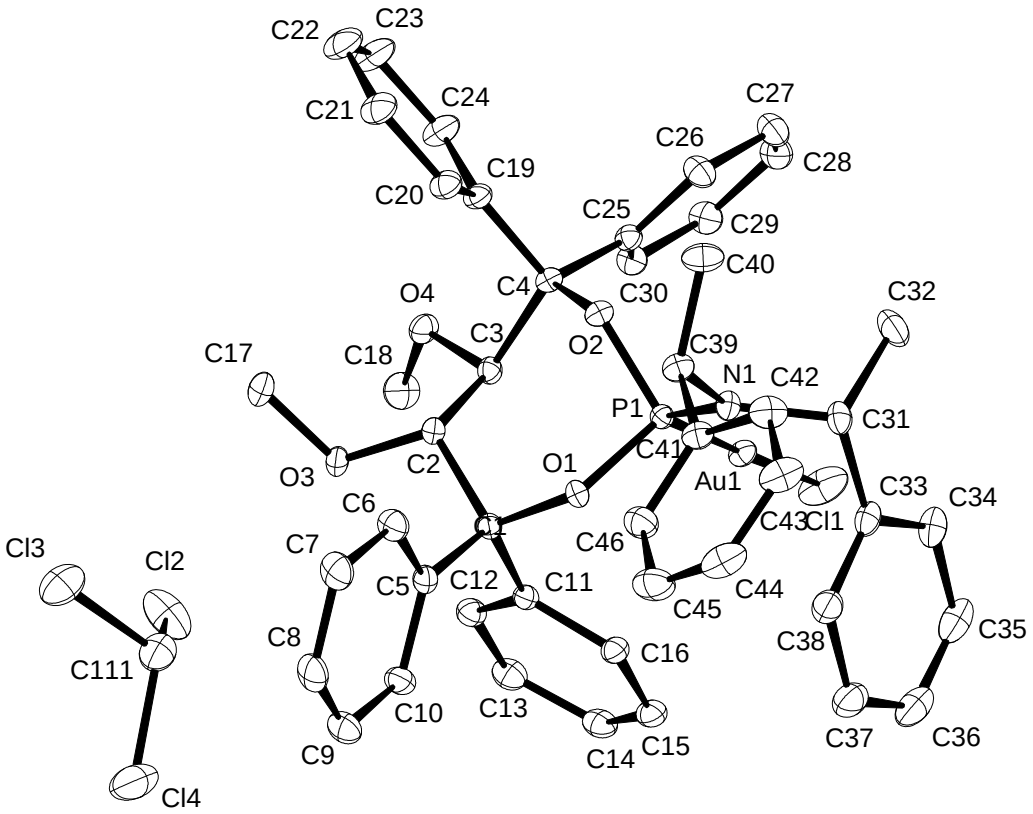
Scheme S-2. Structure of complex **12a** (Ar = Ph) in the solid state. Anisotropic displacement parameters are drawn at the 50% probability level and hydrogen atoms are omitted for clarity.

X-ray Crystal Structure Analysis of 12a (Ar = Ph): C_{47} H_{46} Au Cl N O_4 P, M_r = 952.23 g·mol^{-1}, colorless plate, crystal size 0.22 x 0.16 x 0.14 mm^3, orthorhombic, space group $P2_12_12_1$, a = 10.5607(1) Å, b = 17.5963(1) Å, c = 22.0553(1) Å, V = 4098.52(5) Å^3, T = 100 K, Z = 4, D_{calc} = 1.543 g·cm^3, λ = 0.71073 Å, μ(*Mo*-K_α) = 3.739 mm^{-1}, Semi-empirical absorption correction (T_{min} = 0.78, T_{max} = 1.00), Nonius KappaCCD diffractometer, 2.96 < θ < 36.35°, 137519 measured reflections, 19567 independent reflections, 18930 reflections with $I > 2\sigma(I)$, Structure solved by direct methods and refined by full-matrix least-squares against F^2 to R_1 = 0.023 [$I > 2\sigma(I)$], wR_2 = 0.054, 500 parameters, absolute structure parameter = 0.007(2), H atoms riding, S = 1.043, residual electron density 0.9 / -1.8 e Å^{-3}. CCDC 754597.



Scheme S-3. Structure of complex **12b** (Ar = $-C_6H_4OMe$) in the solid state. Anisotropic displacement parameters are drawn at the 50% probability level and hydrogen atoms are omitted for clarity.

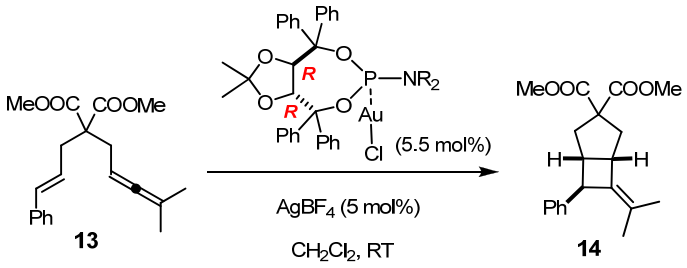
X-ray Crystal Structure Analysis of 12b (Ar = $-C_6H_4OMe$): C_{51} H_{54} Au Cl N O_8 P, M_r = 1072.34 g · mol^{-1}, colorless plate, crystal size 0.03 x 0.02 x 0.02 mm^3, orthorhombic, space group $P2_12_12_1$, a = 10.4646(10) Å, b = 17.6711(17) Å, c = 24.258(2) Å, V = 4485.8(7) $Å^3$, T = 100 K, Z = 4, D_{calc} = 1.588 g·cm^3, λ = 0.71073 Å, μ(*Mo*-K_α) = 3.432 mm^{-1}, empirical absorption correction (T_{min} = 0.02, T_{max} = 0.05), Nonius KappaCCD diffractometer, 1.43 < θ < 36.68°, 169929 measured reflections, 19567 independent reflections, 20489 reflections with $I > 2\sigma(I)$, 97.5% of the data collected to θ of 36.68° but 99% to θ of 27.0°. Structure solved by direct methods and refined by full-matrix least-squares against F^2 to R_1 = 0.027 [$I > 2\sigma(I)$], wR_2 = 0.071, 576 parameters, absolute structure parameter = -0.014(2), H atoms riding, S = 1.124, residual electron density 1.7 / -1.3 e $Å^{-3}$. CCDC 754598.

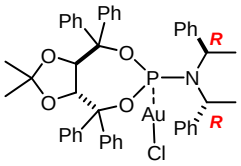
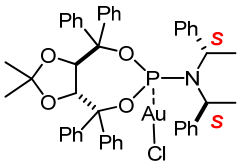
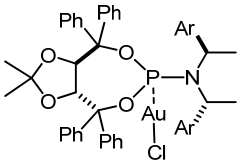
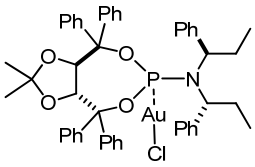
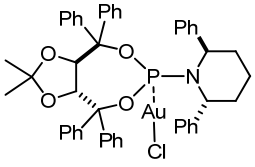
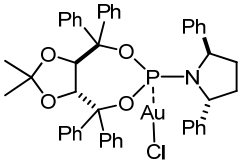


Scheme S-4. Structure of complex **20a** in the solid state. Anisotropic displacement parameters are drawn at the 50% probability level and hydrogen atoms are omitted for clarity.

X-ray Crystal Structure Analysis of 20a: $C_{47}\ H_{47}\ Au\ Cl_4\ N\ O_4\ P$, M_r = 1059.59 g · mol^{-1}, colorless plate, crystal size 0.04 x 0.02 x 0.02 mm^3, monoclinic, space group $P2_1$, a = 10.3792(10) Å, b = 19.1477(18) Å, c = 11.5800(11) Å, β = 106.941(2)°, V = 1.598 Å^3, T = 100 K, Z = 2, D_{calc} = 1.900 g·cm^3, λ = 0.71073 Å, μ(*Mo-K*$_\alpha$) = 3.665 mm^{-1}, Gaussian absorption correction (T_{min} = 0.87, T_{max} = 0.94), Nonius KappaCCD diffractometer, 3.65 < θ < 33.14°, 73413 measured reflections, 16746 independent reflections, 16457reflections with $I > 2\sigma(I)$. Structure solved by direct methods and refined by full-matrix least-squares against F^2 to R_1 = 0.014 [$I > 2\sigma(I)$], wR_2 = 0.035, 527 parameters, absolute structure parameter = -0.0082(14), H atoms riding, S = 1.044, residual electron density +1.5 / -0.7 e Å^{-3}.

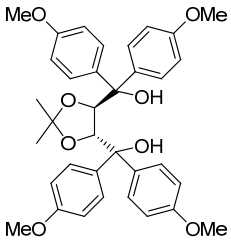
Screening: Variation of the Amine Part of the Phosphoramidite



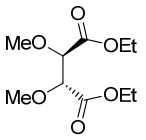
Entry	Complex	*ee*	δ_P (C_6H_6, ppm)
1		84%	113.5
2		0%	113.1
3	 Ar = 2-naphthyl	73%	118.6
4		37%	113.5
5		45%	110.9
6		8%	112.8

General. All reactions were carried out in flame-dried glassware under Ar. All the solvents were purified by distillation over the drying agents indicated and were transferred under Ar. THF, Et_2O (Mg-anthracene), CH_2Cl_2 (CaH_2), MeCN, Et_3N (CaH_2), MeOH (Mg), hexane, toluene (Na/K). Flash chromatography: Merck silica gel 60 (230-400 mesh). IR: Nicolet FT-7199 spectrometer, wavenumbers in cm^{-1}. MS (EI): Finnigan MAT 8200 (70 eV), ESI MS: Finnigan MAT 95; accurate mass determinations: Bruker APEX III FT-MS (7 T magnet). NMR: Spectra were recorded on a Bruker DPX 300, AV 400 and AV 600 spectrometer in the solvents indicated; ^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. Melting points: Büchi melting point apparatus B-540 (corrected). Elemental analyses: H. Kolbe, Mülheim/Ruhr. *ee*-Determinations were performed by HPLC or GC using the chiral stationary phases and conditions specified in the individual entries; they are considered to be ± 0.2% accurate. Unless stated otherwise, all commercially available compounds (Acros, Fluka, Lancaster, Aldrich) were used as received.

((4*R*,5*R*)-2,2-Dimethyl-1,3-dioxolane-4,5-diyl)bis(bis(4-methoxyphenyl)methanol). A

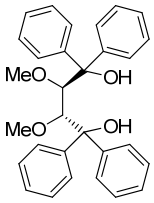


solution of *p*-bromoanisole (6.23 mL, 50.0 mmol) in THF (50 mL) was cooled to −78 °C before *n*-BuLi (1.6 M in *n*-hexane, 31.3 mL, 50.0 mmol) was slowly added. The resulting white suspension was stirred for 1h at that temperature before a solution of (4*R*,5*R*)-dimethyl 2,2-dimethyl-1,3-dioxolane-4,5-dicarboxylate (1.83 mL, 10.0 mmol) in THF (20 mL) was added dropwise. The resulting yellow solution was stirred for 1h at −78 °C and for another 2h at ambient temperature. The reaction was quenched with sat. aq. NH_4Cl (50 mL). 1 M HCl (5 mL) was added, the aqueous phase was extracted with ethyl acetate (3 x 50 mL), the combined organic layers were dried over $MgSO_4$, filtered and evaporated, and the residue was purified by flash chromatography (EtOAc/*n*-hexane, 1/4) to give the title compound as a yellow foam (2.99 g, 51%). $[\alpha]_D^{20} = -44.5$ ($CHCl_3$, $c = 1.0$); ^1H NMR (300 MHz, $CDCl_3$): δ = 7.73 (4 H, d, *J* = 8.7 Hz), 7.51 (4 H, d, *J* = 8.7 Hz), 6.88 (4 H, d, *J* = 8.7 Hz), 6.66 (4 H, d, *J* = 8.7 Hz), 4.92 (2 H, s), 4.82 (2 H, brs), 3.34 (6 H, s), 3.25 (6 H, s), 1.07 (6 H, s) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.3, 159.2, 139.4, 135.9, 130.5, 129.6, 128.5, 113.6, 112.9, 109.5, 82.1, 78.1, 54.7, 54.7, 27.4 ppm; IR (neat): $\tilde{\upsilon}$ = 3324, 2988, 2933, 2904, 2835, 1607, 1582, 1508, 1462, 1441, 1416, 1379, 1370, 1299, 1245, 1172, 1121, 1083, 1052, 1029, 908, 884, 827, 805, 785, 759, 732, 695 cm^{-1}; MS (70 eV): *m/z* (%): 586 [M^+] (<1), 268 (53), 243 (100), 135 (75), 77 (6); HRMS (ESI): *calcd.* for $C_{35}H_{38}Na_1O_8$ [M^+ + Na]: 609.2459, *found*: 609.2466.



(2*R*,3*R*)-Diethyl 2,3-dimethoxysuccinate (17). Diethyl tartrate **16** (3.41 mL, 20.0 mmol) and dimethyl sulfate (3.89 mL, 41.0 mmol) were added in parallel to a cooled (0°C) suspension of NaH (960 mg, 40.0 mmol) in diethyl ether (200 mL) and the resulting mixture was stirred overnight at ambient temperature. The reaction was quenched with sat. $NaHCO_3$ (100 mL), the aqueous phase extracted with diethyl ether (3 x 50 mL), the combined organic layers were washed with NH_4OH (50 mL, 10% in H_2O), dried over $MgSO_4$, filtered and the solvent was removed under reduced pressure to provide the title compound in quantitative yield as a colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.33-4.19 (4 H, m), 4.21 (2 H, s), 3.45 (6 H, s), 1.30 (6 H, t, *J* = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.2, 81.2, 61.3, 59.6, 14.2; IR (neat): $\tilde{\upsilon}$ = 2985, 2933, 2833, 1754, 1730, 1465, 1447, 1390, 1369, 1348, 1267, 1218, 1185, 1149, 1108, 1026, 926, 858, 810, 701 cm^{-1}; MS (70 eV): *m/z* (%): 234 [M^+] (8), 161 (18), 133 (55), 117 (73), 105 (19), 89 (35), 73 (23), 61 (55), 45 (89), 29 (100). The physical and spectroscopic properties matched those described in the literature.[1]

(2*R*,3*R*)-2,3-Dimethoxy-1,1,4,4-tetraphenylbutane-1,4-diol (18a). Phenylmagnesium bromide (1 M in THF, 25 mL, 25 mmol) was added dropwise to a solution of compound **17** (1.17 g, 5.00 mmol) in THF (10 mL) at 0 °C and the resulting mixture allowed to reach ambient temperature. After stirring for 2h, the reaction was quenched with sat. aq. NH_4Cl (20 mL). 1 M HCl (2 mL) was added, the aqueous phase was extracted with diethyl ether (3 x 20 mL), the combined organic layers were dried over $MgSO_4$, filtered and evaporated. The crude material was purified by flash chromatography (Et_2O/*n*-hexane, 1/9) to give the title compound as a white foam (1.29 g, 57%). $[\alpha]_D^{20} = -157.6$ ($CHCl_3$, *c* = 1.05); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.62 (4 H, d, *J* = 8.2 Hz), 7.56 (4 H, d, *J* = 8.2 Hz), 7.43 (4 H, t, *J* = 7.5 Hz), 7.30 (2 H, t, *J* = 7.4 Hz), 7.23 (4 H, t, *J* = 7.4 Hz), 7.13 (2 H, t, *J* = 7.4 Hz), 4.86 (2 H, brs), 4.42 (2 H, s), 2.56 (6 H, s) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 145.6, 144.9, 128.4, 127.9, 127.2, 126.8, 126.0, 125.8, 85.2, 80.1, 77.4, 77.0, 76.6, 61.0 ppm; IR (neat): $\tilde{\upsilon}$ = 3453, 3064, 3029, 2965, 2933, 2842, 1598, 1490, 1449, 1387, 1353, 1320, 1183, 1171, 1139, 1122, 1071, 1028, 1014, 1001, 979, 931, 900, 856, 814, 797, 770, 759, 747, 728, 709, 697, 668 cm^{-1}; MS (70 eV): *m/z* (%): 208 (44), 183 (100), 167 (7), 105 (71), 88 (18), 77 (29); HRMS (ESI): *calcd.* for $C_{30}H_{30}O_4Na$ [M^+ + Na]: 477.2036, *found*: 477.2040. The physical and spectroscopic properties matched those described in the literature.[2]



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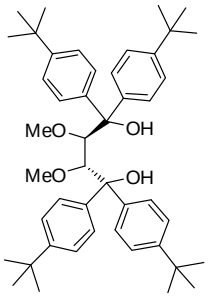
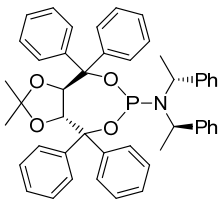
[1] K. Shishido, K. Takahashi, K. Fukamoto, T. Kametani, T. Honda, *J. Org. Chem.* **1987**, *52*, 5704-5714.
[2] F. Toda, K. Tanaka, Z. Stein, J. Goldberg, *J. Chem. Soc. Perkin Trans. 2* ***1993****, 2359-2361*.

(2*R*,3*R*)-1,1,4,4-Tetrakis(4-*tert*-butylphenyl)-2,3-dimethoxybutane-1,4-diol (18b). A



solution of *p*-(*tert*-butyl)-bromobenzene (14.2 mL, 82 mmol) in THF (62 mL) was added dropwise to a suspension of activated magnesium turnings (2.00 g, 82.0 mmol) in THF (20 mL) at such a rate as to maintain gentle reflux. Once the addition was complete, the mixture was stirred for 1h at 60 °C and subsequently cooled to 0 °C (ice bath) before (2*R*,3*R*)-diethyl 2,3-dimethoxysuccinate **17** (3.83 g, 16.3 mmol) was introduced. The mixture was allowed to reach ambient temperature and stirring continued for 2h before the reaction was quenched with sat. aq. NH_4Cl (50 mL). 1 M HCl (5 mL) was added, the aqueous phase was extracted with diethyl ether (3 x 50 mL), the combined organic layers were dried over $MgSO_4$, filtered and evaporated. The residue was purified by flash chromatography (Et_2O/*n*-hexane, 1/19) to give the title compound as a white foam (7.36 g, 67%). $[\alpha]_D^{20} = -101.5$ ($CHCl_3$, $c = 1.03$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.52 (4 H, d, $J = 8.5$ Hz), 7.49 (4 H, d, $J = 8.5$ Hz), 7.42 (4 H, d, $J = 8.5$ Hz), 7.25 (4 H, d, $J = 8.5$ Hz), 4.72 (2 H, s), 4.34 (2 H, s), 2.57 (6 H, s), 1.37 (18 H, s), 1.24 (18 H, s) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.8, 149.4, 142.6, 142.0, 125.8, 125.6, 125.1, 124.6, 85.2, 79.9, 60.8, 34.4, 34.2, 31.4, 31.3 ppm; IR (neat): $\tilde{\upsilon}$ = 3438, 3031, 2960, 2904, 2867, 1508, 1461, 1405, 1362, 1269, 1179, 1109, 1077, 1018, 974, 910, 826, 764, 732, 710, 679 cm^{-1}; MS (ESI): *m/z* = 717 [M^+ + K], 701 [M^+ + Na]; HRMS (ESI): *calcd.* for $C_{46}H_{62}O_4Na$ [M^+ + Na]: 701.4540, *found*: 701.4539.

Representative Procedures for the Preparation of TADDOL- derived Phosphoramidite Ligands. Method A: (3a*R*,8a*R*)-2,2-Dimethyl-4,4,8,8-tetraphenyl-*N*,*N*-bis((*R*)-1-phenylethyl)tetrahydro-[1,3]dioxolo[4,5-*e*][1,3,2]dioxaphosphepin-6-amine: *n*-BuLi (1.6

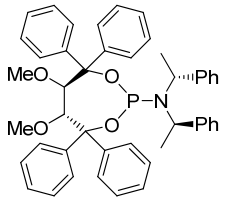


M in *n*-hexane, 1.25 mL, 2.00 mmol) was added to a solution of ((4*R*,5*R*)-2,2-dimethyl-1,3-dioxolane-4,5-diyl)bis(diphenylmethanol) (TADDOL, 467 mg, 1.00 mmol) in THF (5 mL) at −78 °C and the resulting pale yellow mixture stirred for 10 min at this temperature and for another 90 min at ambient temperature before it was cooled again to −78 °C. PCl_3 (87 µL, 1.0 mmol) was introduced and the resulting colorless chlorophosphite solution stirred for 90 min at ambient temperature.

In parallel, *n*-BuLi (1.6 M in *n*-hexane, 0.63 mL, 1.00 mmol) as added to a solution of (+)-bis-[(*R*)-1-phenylethyl]-amine **15** (230 µL, 1.00 mmol) in THF (2 mL) at −10 °C. The resulting orange mixture was stirred for 30 min at this temperature before it was added via cannula to the chlorophosphite solution at −78 °C. After stirring for 14 h at ambient temperature, the solvent was evaporated, the remaining orange foam redissolved in toluene (5 mL) and the

suspension stirred for 2 h. Filtration through a plug of Celite® (toluene), evaporation of the filtrate and purification of the residue by flash chromatography (hexanes:EtOAc:NEt_3, 95:5:1) gave the title compound as a white foam (510 mg, 71%). $[\alpha]_D^{20} = -1.9$ ($CHCl_3$, c = 0.51); ^{1}H NMR (400 MHz, C_6D_6): δ = 7.94-7.86 (4 H, m), 7.77-7.73 (4 H, m), 7.17-6.96 (22 H, m), 5.66 (1 H, dd, J = 3.8, 8.6 Hz), 5.29 (1 H, d, J = 8.6 Hz), 5.04 (2 H, br s), 1.64 (6 H, d, J = 6.9 Hz), 1.39 (3 H, s), 0.33 (3 H, s) ppm; ^{13}C NMR (100 MHz, C_6D_6): δ = 148.0, 147.1, 147.1, 143.8, 142.7, 142.6, 142.3, 129.6, 129.6, 129.5, 128.6, 128.5, 128.3, 128.0, 128.0, 128.0, 127.9, 127.9, 127.8, 127.6, 127.5, 127.5, 127.4, 126.7, 111.6, 83.4, 83.4, 83.1, 82.8, 82.3, 82.2, 82.2, 52.7, 52.5, 27.8, 25.4, 21.8 ppm; ^{31}P NMR (162 MHz, C_6D_6): δ = 141.1 ppm; IR (neat): $\tilde{\upsilon}$ = 3058, 3027, 2968, 2926, 1493, 1446, 1371, 1250, 1202, 1164, 1125, 1080, 1048, 1031, 1012, 996, 965, 877, 820, 784, 731, 695, 665 cm^{-1}; MS (70 eV): *m/z* (%): 719 [M^+] (<1), 524 (13), 288 (24), 238 (12), 237 (66), 207 (13), 184 (30), 180 (18), 179 (100), 178 (23), 105 (22); HRMS (ESI) *calcd.* for $C_{47}H_{46}NO_4PNa$ [M^+ + Na]: 742.3056, *found*: 742.3050. The physical and spectroscopic properties matched those described in the literature.[3]

Method B: (5*R*,6*R*)-5,6-Dimethoxy-4,4,7,7-tetraphenyl-*N*,*N*-bis((*R*)-1-phenylethyl)-1,3,2-dioxa-phosphepan-2-amine (19a). Triethylamine (416 µL, 3.00 mmol) and PCl_3 (92 µL, 1.05 mmol) were successively added to solution of (2*R*,3*R*)-2,3-dimethoxy-1,1,4,4-tetraphenylbutane-1,4-diol **18a** (455 mg, 1.00 mmol) and 4Å molecular sieves (100 mg) in toluene (50 mL) at 0°C. The cloudy mixture was then heated to 60 °C for 1 h. After cooling to ambient temperature, the mixture was filtered under argon atmosphere, the filtrate was evaporated and the resulting yellowish foam was dissolved in THF (5 mL).

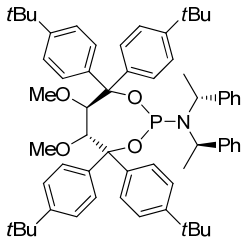


In parallel, *n*BuLi (1.6 M in *n*-hexane, 0.63 mL, 1.00 mmol) as added to a solution of (+)-bis-[(*R*)-1-phenylethyl]-amine (230 µL, 1.00 mmol) in THF (2 mL) at −10 °C and the resulting orange solution stirred at this temperature for 30 min before it was transferred via cannula to the chlorophosphite solution at −78 °C. The resulting orange mixture was stirred for 14 h at ambient temperature, the solvent was evaporated, the residue redissolved in toluene (5 mL) and the suspension stirred for 2 h at ambient temperature. Filtration through a plug of Celite® (toluene), evaporation of the filtrate and purification of the residue by flash chromatography (hexanes:EtOAc:NEt_3, 95:5:1) gave the title compound as a white foam (414 mg, 58%). $[\alpha]_D^{20} = +22.6$ ($CHCl_3$, c = 0.55); ^{1}H NMR (400 MHz, C_6D_6): δ = 7.93 (2 H, d, J = 7.1 Hz), 7.86 (2 H, d, J = 7.1 Hz), 7.61-7.59 (4 H, m), 7.26-7.05 (15 H, m), 7.00-6.97 (7 H, m), 5.02

[3] A. Alexakis, J. Burton, J. Vastra, C. Benhaim, X. Fournioux, A. van den Heuvel, J.-M. Levêque, F. Mazé, S. Rosset, *Eur. J. Org. Chem.* **2000**, *2*, 4011-4027.

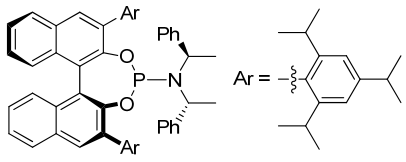
(2 H, brs), 4.88 (1 H, dd, *J* =5.6, 7.5 Hz), 4.52 (1 H, d, *J* = 7.3 Hz), 3.43 (3 H, s), 2.54 (3 H, s), 1.57 (6 H, d, *J* = 6.21 Hz) ppm; ^{13}C NMR (100 MHz, C_6D_6): δ = 147.5, 147.0, 147.0, 143.8, 143.0, 142.0, 129.8, 129.7, 129.5, 128.6, 128.3, 128.2, 128.1, 128.0, 127.9, 127.8, 127.7, 127.4, 127.3, 127.2, 127.2, 126.7, 86.2, 85.1, 83.4, 83.1, 81.8, 81.7, 60.2, 60.0, 54.4, 54.3, 21.6 ppm; ^{31}P NMR (162 MHz, C_6D_6): δ = 139.7 ppm; IR (neat): $\tilde{\upsilon}$ = 3058, 3029, 2968, 2926, 2829, 1600, 1493, 1445, 1374, 1315, 1278, 1182, 1126, 1090, 1041, 1031, 1018, 966, 927, 915, 872, 817, 800, 786, 768, 747, 721, 693, 655 cm^{-1}; MS (ESI): *m/z*: 730 [M^+ + Na]; HRMS (ESI): *calcd* for $C_{46}H_{46}NO_4PNa$ [M^+ + Na] 730.3057, *found*: 730.3055.

(5*R*,6*R*)-4,4,7,7-Tetrakis(4-*tert*-butylphenyl)-5,6-dimethoxy-*N*,*N*-bis((*R*)-1-phenylethyl)-1,3,2-dioxaphosphepan-2-amine (19b). Prepared according to Method B as a yellow foam



(1.26 g, 67%). $[\alpha]_D^{20°C}$ = +14.1 ($CHCl_3$, *c* = 0.66); ^{1}H NMR (600 MHz, C_6D_6): δ = 7.98 (2 H, d, *J* = 8.4 Hz), 7.92 (2 H, d, *J* = 8.4 Hz), 7.62 (2 H, d, *J* = 8.7 Hz), 7.59 (2 H, d, *J* = 8.7 Hz), 7.39 (2 H, d, *J* = 8.6 Hz), 7.35 (2 H, d, *J* = 8.6 Hz), 7.14-7.12 (7 H, m), 7.05-7.00 (7 H, m), 5.06 (2 H, brs), 4.96 (1 H, dd, *J* =6.0, 7.3 Hz), 4.77 (1 H, d, *J* = 7.3 Hz), 3.50 (3 H, s), 2.73 (3 H, s), 1.64 (6 H, brm), 1.28 (9 H, s), 1.21 (9 H, s), 1.20 (9 H, s), 1.15 (9 H, s) ppm; ^{13}C NMR (150 MHz, C_6D_6): δ = 150.1, 149.9, 149.7, 149.6, 144.5, 144.4, 144.4, 140.3, 140.3, 139.7, 129.7, 129.6, 129.3, 128.6, 128.3, 128.2, 128.1, 127.9, 127.8, 126.6, 124.9, 124.8, 124.6, 124.1, 85.4, 84.8, 83.1, 83.0, 81.6, 81.5, 59.9, 59.7, 52.2, 52.1, 34.5, 34.4, 34.4, 34.3, 31.5, 31.5, 31.4 ppm; ^{31}P NMR (162 MHz, C_6D_6): δ = 140.5 ppm; IR (neat): $\tilde{\upsilon}$ = 2961, 2903, 2867, 1602, 1510, 1494, 1460, 1393, 1362, 1269, 1187, 1126, 1107, 1043, 1019, 966, 926, 840, 830, 785, 765, 751, 697, 674 cm^{-1}; MS (ESI): m/z = 955 [M^+ + Na]; HRMS (ESI): *calcd*. for $C_{62}H_{78}N_1Na_1O_4P$ [M^+ + Na] 954.5561, *found*: 954.5561.

(11b*S*)-*N*,*N*-Bis((*R*)-1-phenylethyl)-2,6-bis(2,4,6-triisopropylphenyl)dinaphtho-[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-amine (8). Prepared according to Method B as a

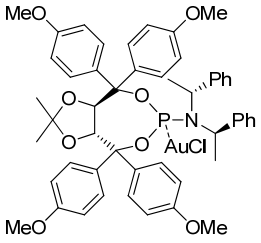


colorless foam (210 mg, 51%). $[\alpha]_D^{20}$ = +93.0 ($CHCl_3$, *c* = 0.42); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.98 (1 H, s), 7.92 (1 H, d, *J* = 8.1 Hz), 7.91 (1 H, d, *J* = 8.0 Hz), 7.88 (1 H, s), 7.46-7.40 (2 H, m), 7.28-7.14 (7 H, m), 7.09 (1 H, s), 7.02 (1 H, d, *J* = 8.6 Hz), 6.90-6.78 (6 H, m), 6.55 (3 H, d, *J* = 7.3 Hz), 3.36 (1 H, sept, *J* = 6.6 Hz), 3.09-2.81 (4 H, m), 2.74 (1 H, sept, *J* = 6.7 Hz), 1.53 (3 H, d, *J* = 6.5 Hz), 1.38 (6 H, d, *J* = 6.9 Hz), 1.35 (3 H, d, *J* = 6.7 Hz), 1.27 (3 H, d, *J* = 6.9 Hz), 1.26 (3 H, d, *J* = 7.0 Hz), 1.24 (3 H, d, *J* = 6.8 Hz), 1.16 (3 H, d, *J* = 6.7 Hz), 1.09 (3 H, d, *J* = 6.8 Hz), 1.06 (3 H, d, *J* = 6.9 Hz), 0.99 (3 H, d, *J* = 6.8 Hz), 0.83 (9 H, t, *J* = 7.0 Hz) ppm; ^{13}C NMR (100 MHz,

$CDCl_3$): δ = 149.2, 148.7, 148.0, 147.9, 147.7, 146.9, 146.5, 145.9, 133.3, 133.0, 132.6, 132.0, 131.7, 131.3, 131.2, 130.8, 130.4, 128.9, 127.7, 127.5, 126.8, 126.8, 126.8, 125.4, 125.1, 125.1, 124.4, 124.3, 123.7, 120.9, 120.7, 120.5, 119.8, 34.2, 34.0, 30.8, 30.6, 30.5, 29.9, 27.9, 26.2, 25.3, 24.9, 24.0, 24.0, 23.9, 23.7, 22.4, 21.9 ppm; ^{31}P NMR (121 MHz, $CDCl_3$): δ = 142.3 ppm; IR (neat): $\tilde{\upsilon}$ = 3058, 2959, 2926, 2868, 1606, 1494, 1447, 1402, 1381, 1361, 1315, 1240, 1202, 1147, 1115, 960, 927, 853, 823, 795, 747, 695 cm^{-1}; MS (70 eV): *m/z* (%): 943 [M^+] (1), 841 (4), 840 (20), 839 (63), 838 (100), 105 (18); HRMS (ESI): *calcd*. for $C_{66}H_{74}NO_2PNa$ [M + Na^+]: 966.5349, *found*: 966.5353; Elemental analysis: *calcd.* for $C_{66}H_{74}NO_2P$: C 83.95, H 7.90, N 1.48, *found*: C 84.02, H 8.06, N 1.42.

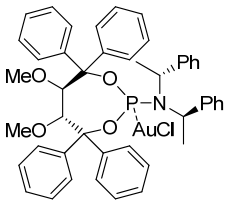
Representative Procedure for the Preparation of Gold(I)-Phosphoramidite Complexes. [(3a*R*,8a*R*)-2,2-Dimethyl-4,4,8,8-tetraphenyl-*N*,*N*-bis((*R*)-1-phenylethyl)tetrahydro-[1,3]dioxolo[4,5-*e*][1,3,2]dioxaphosphepin-6-amine] gold(I)chloride (12a). 2,2'-Thiodiethanol (90 μL, 0.90 mmol) was slowly added to a solution of sodium tetrachloroaurate dihydrate (119 mg, 0.30 mmol) in water (15 mL) at 0 °C. A solution of the phosphoramidite (216 mg, 0.30 mmol) in chloroform (3 mL) was added and the resulting heterogenous mixture stirred for 1 h at 0 °C and for 3 h at ambient temperature. For work up, the phases were separated and the aqueous layer extracted with CH_2Cl_2 (3 x 10 mL). The combined organic phases were washed with sat. aq. $NaHCO_3$, dried over $MgSO_4$, filtered and evaporated to give the title complex as a colorless foam. Recrystallization from CH_2Cl_2/pentane afforded complex **12a** in form of colorless crystals (286 mg, 98%). Mp.: 237-238 °C (decomp.); $[\alpha]_D^{20} = -13.3$ ($CHCl_3$, *c* = 0.51); ^{1}H NMR (400 MHz, C_6D_6): δ = 7.90 (2 H, d, *J* = 6.7 Hz), 7.75 (2 H, d, *J* = 7.5 Hz), 7.67 (2 H, d, *J* = 7.4 Hz), 7.56 (2 H, d, *J* = 7.4 Hz), 7.30-6.99 (22 H, m), 6.50 (1 H, dd, *J* = 1.3, 8.6 Hz), 5.28 (1 H, d, *J* = 8.6 Hz), 5.12-5.00 (2 H, m), 1.68 (6 H, d, *J* = 7.1 Hz), 1.39 (3 H, s), 0.16 (3 H, s) ppm; ^{13}C NMR (100 MHz, C_6D_6): δ = 145.4, 145.3, 144.7, 141.4, 141.4, 141.3, 141.2, 139.0, 139.0, 129.3, 129.2, 129.2, 129.1, 128.8, 128.7, 128.7, 128.5, 128.5, 128.4, 128.3, 128.2, 128.0, 128.0, 127.8, 127.8, 112.2, 86.5, 85.6, 83.3, 81.2, 81.1, 53.6, 53.5, 27.6, 24.8, 21.0 ppm; ^{31}P NMR (162 MHz, C_6D_6): δ = 113.5 ppm; IR (Film): $\tilde{\nu}$ = 3058, 3032, 2989, 1494, 1447, 1382, 1252, 1204, 1163, 1084, 1049, 1028, 997, 969, 917, 885, 861, 788, 767, 739, 695, 678 cm^{-1}; MS (EI): *m/z* (%) = 952 [M^+] (3), 951 (6), 524 (11), 288 (22), 238 (11), 237 (61), 208 (32), 207 (30), 184 (29), 179 (100), 178 (31); HRMS (ESI) *calcd* for $C_{47}H_{46}AuClNO_4P$+Na [M + Na^+]: 974.2410, *found*: 974.2406; elemental analysis *calcd* (%) for $C_{47}H_{46}AuClNO_4P$: C 59.28, H 4.87, N 1.47, *found*: C 58.98, H 5.12, N 1.39.

[(*3aR*,8a*R*)-4,4,8,8-Tetrakis(4-methoxyphenyl)-2,2-dimethyl-*N*,*N*-bis((*R*)-1-phenylethyl)-tetrahydro-[1,3]dioxolo[4,5-*e*][1,3,2]dioxaphosphepin-6-amine] gold(I)chloride (12b).



Prepared analogously as a white solid (302 mg, 94%). Mp.: 201-202 °C (decomp.); $[\alpha]_D^{20} = -10.3$ ($CHCl_3$, $c = 0.56$); ^{1}H NMR (600 MHz, C_6D_6): δ = 7.89 (2 H, d, *J* = 8.8 Hz), 7.73 (2 H, d, *J* = 8.8 Hz), 7.67 (2 H, d, *J* = 8.8 Hz), 7.55-7.53 (2 H, m), 7.28-7.25 (4 H, m), 7.10 (2 H, d, *J* = 7.4 Hz), 7.09 (2 H, d, *J* = 7.4 Hz), 7.04-7.01 (2 H, m), 6.97 (2 H, d, *J* = 8.8 Hz), 6.90 (2 H, d, *J* = 8.8 Hz), 6.80-6.77 (4 H, m), 6.55 (1 H, dd, *J* = 1.3, 8.6 Hz), 5.30 (1 H, d, *J* = 8.6 Hz), 5.08-4.98 (2 H, brm), 3.48 (3 H, s), 3.34 (3 H, s), 3.26 (3 H, s), 3.19 (3 H, s), 1.66 (6 H, d, *J* = 7.3 Hz), 1.46 (3 H, s), 0.35 (3 H, s) ppm; ^{13}C NMR (150 MHz, C_6D_6): δ = 160.9, 160.5, 160.0, 159.8, 141.6, 137.9, 137.9, 137.1, 133.9, 133.9, 131.1, 130.5, 129.7, 129.5, 128.7, 128.6, 128.6, 128.3, 127.8, 114.7, 114.2, 113.8, 113.2, 112.0, 86.4, 85.8, 85.7, 83.5, 81.2, 81.1, 55.3, 55.0, 54.8, 54.7, 53.4, 53.4, 27.8, 25.1, 20.9 ppm; ^{31}P NMR (162 MHz, C_6D_6): δ = 112.5 ppm; IR (neat): $\tilde{\upsilon}$ = 2984, 2934, 2870, 2836, 1606, 1582, 1507, 1479, 1462, 1452, 1441, 1414, 1377, 1344, 1298, 1247, 1216, 1171, 1146, 1122, 1092, 1046, 1027, 1013, 995, 972, 962, 936, 909, 892, 871, 846, 830, 812, 803, 788, 769, 753, 719, 700, 679, 660 cm^{-1}; MS (ESI): *m/z* = 1117 [M^+ + 2Na], 1094 [M^+ + Na]; HRMS (ESI): *calcd*. for $C_{51}H_{54}NO_8PAuCl$+Na [M^+ + Na]: 1094.2833, *found*: 1094.2837.

[(5*R*,6*R*)-5,6-Dimethoxy-4,4,7,7-tetraphenyl-*N*,*N*-bis((*R*)-1-phenylethyl)-1,3,2-dioxaphosphepan-2-amine] gold(I)chloride (20a). Prepared analogously as colorless crystals



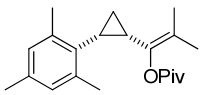
(279 mg, 99%). Mp.: 231-232 °C (decomp.); $[\alpha]_D^{20} = -9.1$ ($CHCl_3$, $c = 0.54$); ^{1}H NMR (400 MHz, C_6D_6): δ = 7.91 (2 H, d, *J* = 3.9 Hz), 7.67 (2 H, d, *J* = 7.4 Hz), 7.52 (4 H, dt, *J* = 1.0, 8.1 Hz), 7.37 (2 H, t, *J* = 7.6 Hz), 7.24-7.17 (6 H, m), 7.12-7.02 (14 H, m), 5.62 (1 H, dd, *J* = 2.0, 7.6 Hz), 4.99-4.93 (2 H, m), 4.61 (1 H, d, *J* = 7.6 Hz), 3.33 (3 H, s), 2.44 (3 H, s), 1.60 (6 H, d, *J* = 7.6 Hz) ppm; ^{13}C NMR (400 MHz, C_6D_6): δ = 145.5, 145.4, 144.3, 141.8, 141.7, 141.5, 141.4, 138.8, 129.6, 129.1, 129.1, 128.9, 128.8, 128.7, 128.6, 128.5, 128.2, 128.2, 127.8, 127.7, 127.2, 89.5, 89.5, 86.1, 84.6, 81.2, 81.0, 60.2, 60.0, 53.4, 53.3, 20.9 ppm; ^{31}P NMR (162 MHz, C_6D_6): δ = 113.7 ppm; IR (neat): $\tilde{\upsilon}$ = 3058, 3034, 2974, 2933, 2833, 1600, 1494, 1445, 1378, 1349, 1318, 1281, 1197, 1132, 1122, 1085, 1052, 1027, 1016, 1000, 961, 935, 912, 901, 859, 790, 767, 745, 725, 694, 679, 657 cm^{-1}; MS (70 eV): *m/z* (%): 939 (1) [M^+], 757 (10), 254 (14), 223 (37), 210 (100), 167 (22), 105 (14), 77 (2); HRMS (ESI): *calcd.* for $C_{46}H_{46}NO_4PAuCl$+Na [M^+ + Na]: 962.2411, *found*: 962.2415.

[(5*R*,6*R*)-4,4,7,7-Tetrakis(4-*tert*-butylphenyl)-5,6-dimethoxy-*N*,*N*-bis((*R*)-1-phenylethyl)-1,3,2-dioxaphosphepan-2-amine] gold(I)chloride (20b). Prepared analogously as a white solid (332 mg, 95%). Mp.: 183-185 °C (decomp.); $[\alpha]_D^{20}$ = +6.4 ($CHCl_3$, *c* = 0.56); ^{1}H NMR (600 MHz, C_6D_6): δ = 7.99 (2 H, d, *J* = 8.6 Hz), 7.76 (2 H, d, *J* = 8.6 Hz), 7.58 (2 H, d, *J* = 8.6 Hz), 7.55 (2 H, d, *J* = 8.6 Hz), 7.49 (2 H, d, *J* = 8.6 Hz), 7.43 (2 H, d, *J* = 8.6 Hz), 7.38 (2 H, d, *J* = 8.6 Hz), 7.16 (2 H, d, under the solvent peak), 7.11-7.03 (10 H, m), 5.53 (1 H, dd, *J* = 1.8, 7.4 Hz), 4.98 (2 H, dd, *J* = 6.6, 17.7 Hz), 4.92 (1 H, d, *J* = 7.4 Hz), 3.42 (3 H, s), 2.67 (3 H, s), 1.70 (6 H, d, *J* = 7.1 Hz), 1.38 (9 H, s), 1.32 (9 H, s), 1.20 (9 H, s), 1.14 (9 H, s) ppm. ^{13}C NMR (150 MHz, C_6D_6): δ = 151.9, 151.8, 151.1, 150.7, 142.6, 142.5, 141.6, 141.6, 139.1, 139.0, 136.4, 136.4, 129.8, 129.0, 128.6, 128.4, 128.4, 128.3, 127.7, 127.5, 125.8, 125.3, 124.2, 90.6, 90.5, 86.1, 82.7, 81.3, 81.2, 59.9, 59.7, 53.2, 53.2, 34.7, 34.6, 34.5, 34.4, 31.5, 31.4, 31.3, 30.2, 27.1, 21.1 ppm; ^{31}P NMR (162 MHz, C_6D_6): δ = 113.7 ppm; IR (neat): $\tilde{\upsilon}$ = 2961, 2868, 1611, 1509, 1451, 1393, 1363, 1270, 1200, 1124, 1107, 1054, 1019, 999, 970, 950, 934, 870, 839, 816, 787, 765, 749, 697, 677 cm^{-1}; MS (ESI): *m/z* = 1202 [M^+ + K], 1186 [M^+ + Na]. HRMS (ESI): *calcd.* for $C_{62}H_{78}NO_4PAuCl$+Na [M^+ + Na]: 1186.4915, *found*: 1186.4916.

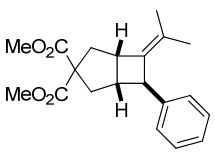
[(11b*S*)-*N*,*N*-Bis((*R*)-1-phenylethyl)-2,6-bis(2,4,6-triisopropylphenyl)dinaphtho-[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-amine] gold(I)chloride ([8·AuCl]). Prepared analogously as colorless crystals (220 mg, 98%). Mp.: > 195 °C (decomp.); $[\alpha]_D^{20}$ = –36.0 ($CHCl_3$, *c* = 0.35); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.97 (2 H, s), 7.93 (2 H, dd, *J* = 8.1, 12.4 Hz), 7.49 (2 H, dt, *J* = 7.2, 14.9 Hz), 7.30-7.25 (1 H, m), 7.24-7.16 (4 H, m), 7.15-7.02 (8 H, m), 6.93 (1 H, d, *J* = 8.6 Hz), 6.79 (4 H, d, *J* = 7.4 Hz), 4.80 (1 H, q, *J* = 7.2 Hz), 4.76 (1 H, q, *J* = 7.2 Hz), 3.39 (1 H, sept, *J* = 6.7 Hz), 3.03 (2 H, sept, *J* = 6.8 Hz), 2.94 (1 H, sept, *J* = 6.6 Hz), 2.93 (1 H, sept, *J* = 6.8 Hz), 2.84 (1 H, sept, *J* = 6.8 Hz), 1.52 (3 H, d, *J* = 6.8 Hz), 1.36 (3 H, d, *J* = 6.7 Hz), 1.34 (3 H, d, *J* = 6.9 Hz), 1.33 (3 H, d, *J* = 6.9 Hz), 1.31 (3 H, d, *J* = 6.6 Hz), 1.26 (6 H, d, *J* = 6.9 Hz), 1.18 (3 H, d, *J* = 6.8 Hz), 1.08 (3 H, d, *J* = 6.8 Hz), 0.97 (3 H, d, *J* = 6.7 Hz), 0.97 (3 H, d, *J* = 6.7 Hz), 0.93 (3 H, d, *J* = 6.7 Hz), 0.65 (6 H, d, *J* = 7.3 Hz) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.0, 148.7, 148.7, 147.9, 147.7, 147.0, 146.9, 146.3, 139.9, 139.9, 133.5, 133.4, 133.0, 132.8, 131.8, 131.3, 131.0, 130.9, 130.6, 130.0, 128.3, 128.1, 128.0, 127.9, 127.4, 127.2, 126.8, 126.1, 126.0, 125.3, 124.0, 121.6, 121.3, 120.5, 119.1, 53.6, 34.4, 34.4, 31.5, 31.4, 30.9, 30.3, 27.6, 26.7, 25.7, 25.2, 24.9, 24.3, 24.1, 24.0, 23.9, 23.6, 23.4, 22.6, 19.5

ppm; ^{31}P NMR (162 MHz, $CDCl_3$): δ = 118.7 ppm; IR (neat): $\tilde{\upsilon}$ = 2960, 2926, 2869, 1606, 1495, 1452, 1404, 1381, 1361, 1314, 1208, 1138, 1105, 1053, 1020, 992, 967, 933, 877, 776, 750, 697, 675 cm^{-1}; MS (70 eV) *m/z* (%): 1175 [M^+] (8), 1140 (11), 1139 (16), 840 (20), 839 (63), 838 (100), 105 (42); HRMS (ESI): *calcd.* for $C_{66}H_{74}AuClNO_2P$+Na [M + Na^+]: 1198.4703, *found*: 1198.4726.

Gold(I)-catalyzed Asymmetric Cyclopropanation: *cis*-1-(2-Mesitylcyclopropyl)-2-methylprop-1-enyl pivalate (11). A mixture containing $AgSbF_6$ (17.2 mg, 0.05 mmol, 5 mol%) and complex [**8**·AuCl] (58.8 mg, 0.05 mmol, 5 mol%) in CH_2Cl_2 (10 mL) was stirred for 10 min before the precipitated silver salts were allowed to settle during 10 min. The supernatant solution of the cationic gold catalyst was transferred under Ar to a Schlenk flask and cooled to –25°C before 1,3,5-trimethyl-2-vinylbenzene **10** (644 mg, 4.00 mmol) and 2-methylbut-3-yn-2-yl pivalate **9** (168 mg, 1.00 mmol) were successively added. The resulting mixture was stirred until TLC showed complete conversion of the substrate. The mixture was filtered through a plug of silica (EtOAc), the filtrate was evaporated, and the residue purified by flash chromatography (*n*-hexane/EtOAc, 80:1) to give the title compound as a colorless oil (204 mg, 65%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.74 (2 H, s), 2.33-2.27 (1 H, m), 2.32 (6 H, s), 2.21 (3 H, s), 2.04 (1 H, q, J = 8.3 Hz), 1.88 (3 H, s), 1.40 (3 H, s), 1.33 (1 H, dt, J = 5.1, 8.9 Hz), 0.85 (9 H, s), 0.78-0.70 (1 H, m) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 175.5, 140.3, 138.4, 135.2, 132.6, 128.3, 119.0, 38.6, 26.8, 20.7, 20.3, 19.1, 19.0, 18.4, 11.7 ppm; IR (neat): $\tilde{\upsilon}$ = 2960, 2918, 2865, 1743, 1682, 1612, 1479, 1455, 1395, 1368, 1285, 1260, 1192, 1121, 1062, 1030, 910, 849, 731 cm^{-1}; MS (70 eV): *m/z* (%): = 314 [M^+] (13), 230 (18), 212 (26), 197 (47), 187 (11), 159 (31), 144 (13), 129 (12), 57 (100), 41 (20); HRMS (ESI) *calcd.* for $C_{21}H_{30}O_2Na$ [M + Na^+]: 337.2137, *found*: 337.2135; Elemental analysis *calcd.* for $C_{21}H_{30}O_2$: C 80.21, H 9.62, *found*: C 80.06, H 9.58. The enantiomeric excess was determined by HPLC: 250 mm Chiralpak IA, *n*-heptane/*i*-propanol = 99/1, flow rate = 0.5 mL/min; major enantiomer t_R = 8.29 min; minor enantiomer t_R = 8.99 min.



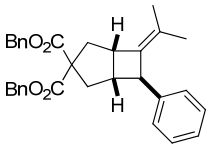
Representative Procedure for the Gold(I)-catalyzed Asymmetric Cycloadditions. Dimethyl 6-phenyl-7-(propan-2-ylidene)bicyclo[3.2.0]heptane-3,3-dicarboxylate (14). A mixture containing complex **20b** (3.3 mg, 2.8 μmol) and $AgBF_4$ (0.5 mg, 2.5 μmol) in CH_2Cl_2 (1 mL) was stirred for 10 min at ambient temperature and 5 min at 0 °C in a capped vial before it was transferred to a cold (0°C) solution of ene-allene **1a** (16.4 mg, 0,05 mmol)[4] in CH_2Cl_2 (0.5 mL) via canula equipped with a PTFE filter (Perfect-Flow®, 0.45 μm pore size, ∅ 13 mm) to retain all precipitates. The



resulting colorless solution was stirred until GC or HPLC showed complete conversion of the substrate. At this point, the solution was loaded on top of a silica gel column and the product purified by flash chromatography. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.30-7.25 (2 H, m), 7.20-7.13 (3 H, m), 3.71 (3 H, s), 3.71 (3 H, s), 3.70-3.67 (1 H, m), 3.62-3.55 (1 H, m), 2.77 (1 H, dd, *J* = 1.7, 13.8 Hz), 2.70 (1 H, d, *J* = 13.3 Hz), 2.63-2.57 (1 H, m), 2.35 (1 H, dd, *J* = 7.7, 13.3 Hz), 2.23 (1 H, dd, *J* = 8.8, 13.7 Hz), 1.60 (3 H, s), 1.29 (3 H, s) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.7, 171.9, 144.9, 134.0, 129.1, 128.3, 126.9, 125.7, 62.6, 52.7, 52.3, 51.8, 44.6, 44.4, 40.1, 38.9, 18.8, 18.8 ppm; IR (neat): $\tilde{\upsilon}$ = 2951, 2909, 1731, 1601, 1494, 1433, 1370, 1331, 1248, 1204, 1173, 1158, 1094, 1063, 1027, 1002, 967, 922, 869, 795, 756, 718, 699 cm^{-1}; MS (70 eV): *m/z* (%): 328 (94) [M^+], 313 (37), 296 (24), 268 (100), 253 (58), 236 (10), 225 (20), 209 (39), 193 (35), 177 (14), 169 (79), 145 (95), 129 (99), 117 (45), 91 (43), 77 (13), 65 (11), 59 (21), 41 (14); HRMS (ESI): *calcd.* for $C_{20}H_{24}O_4$+Na [M^+ + Na]: 351.1567, *found*: 351.1569. The enantiomeric excess was determined by HPLC: 250 mm Chiralpak IA, 5 μm, No.: IA00CE-LH028, *n*-heptane/*i*-propanol = 95/5, flow rate = 1.0 mL/min; major enantiomer t_R = 4.86 min; minor enantiomer t_R = 5.65 min. The physical and spectroscopic properties matched those described in the literature.[4]

All other compounds were prepared analogously. Their spectral and analytical data are compiled below.

Dibenzyl 6-phenyl-7-(propan-2-ylidene)bicyclo[3.2.0]heptane-3,3-dicarboxylate (21).

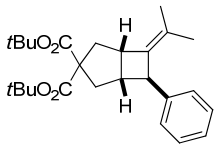


^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.28-7.20 (12 H, m), 7.12-7.09 (3 H, m), 5.13 (1 H, d, *J* = 12.5 Hz), 5.08 (2 H, d, *J* = 4.1 Hz), 4.94 (1 H, d, *J* = 12.5 Hz), 3.65 (1 H, brs), 3.53 (1 H, brs), 2.75 (1 H, d, *J* = 13.5 Hz), 2.68 (1 H, d, *J* = 13.4 Hz), 2.58-2.53 (1 H, m), 2.35 (1 H, dd, *J* = 7.8, 13.3 Hz), 2.22 (1 H, dd, *J* = 8.6, 13.7 Hz), 1.47 (3 H, s), 1.21 ppm (3 H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.0, 171.3, 144.9, 135.5, 134.1, 129.0, 128.5, 128.5, 128.3, 128.2, 127.8, 127.0, 125.7, 67.2, 67.1, 63.0, 51.8, 44.7, 44.4, 40.1, 39.0, 18.8, 18.8 ppm; IR (neat): $\tilde{\upsilon}$ = 3063, 3030, 2926, 2853, 1728, 1601, 1494, 1453, 1370, 1330, 1229, 1202, 1173, 1151, 1116, 1095, 1059, 1028, 1000, 972, 908, 883, 842, 790, 734, 695 cm^{-1}; MS (70 eV): *m/z* (%): 480 (3) [M^+], 389 (42), 343 (5), 253 (6), 167 (5), 129 (15), 91 (100); HRMS (ESI): *calcd*. for $C_{32}H_{32}O_4$+Na [M^+ + Na]: 503.2192, *found*: 503.2190; The enantiomeric excess was determined by HPLC: 250 mm Chiralpak IA, 5 μm, No.: IA00CE-LH028, *n*-heptane/*i*-propanol = 95/5, flow rate = 1.0 mL/min; major enantiomer t_R = 6.24 min; minor enantiomer

[4] M. R. Luzung, P. Mauleón, F. D. Toste, *J. Am. Chem. Soc*. **2007**, *129*, 12402-12403.

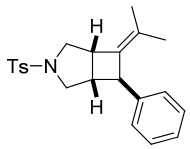
t_R = 6.86 min. The physical and spectroscopic properties matched those described in the literature.[4]

Di-*tert*-butyl 6-phenyl-7-(propan-2-ylidene)bicyclo[3.2.0]heptane-3,3-dicarboxylate (22).

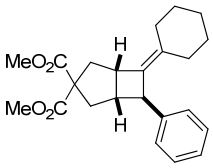


^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.29-7.25 (2 H, m), 7.19-7.13 (3 H, m), 3.77 (1 H, brs), 3.54 (1 H, brs), 2.62 (1 H, dd, *J* = 2.0, 13.5 Hz), 2.58-2.53 (1 H, m), 2.50 (1 H, dd, *J* = 2.0, 13.9 Hz), 2.35 (1 H, dd, *J* = 8.2, 13.3 Hz), 2.11 (1 H, dd, *J* = 8.7, 13.8 Hz), 1.61 (3 H, s), 1.46 (9 H, s), 1.44 (9 H, s), 1.23 ppm (3 H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.6, 170.8, 145.3, 135.2, 128.3, 127.8, 127.1, 125.6, 81.2, 80.7, 64.6, 51.8, 45.1, 44.2, 39.9, 38.6, 27.8, 18.8, 18.8 ppm; IR (neat): $\tilde{\upsilon}$ = 3058, 3027, 3004, 2954, 2979, 2954, 2934, 2906, 1741, 1721, 1601, 1493, 1477, 1452, 1392, 1364, 1330, 1296, 1284, 1270, 1257, 1218, 1167, 1142, 1115, 1098, 1074, 1064, 1051, 1036, 1022, 998, 971, 939, 911, 900, 883, 852, 807, 785, 761, 739, 721, 698 cm^{-1}; MS (70 eV): *m/z* (%): 412 [M^+] (4), 356 (29), 300 (100), 285 (28), 255 (35), 239 (11), 209 (16), 184 (28), 169 (17), 155 (10), 129 (27), 117 (28), 91 (16), 57 (51), 41 (17); HRMS (ESI): ***calcd.*** for $C_{26}H_{36}O_4$+Na [M^+ + Na]: 435.2506, *found*: 435.250; The enantiomeric excess was determined by HPLC: 150 mm Chiralpak AD-RH, acetonitrile/water = 55/45, flow rate = 1.0 mL/min; major enantiomer t_R = 19.26 min; minor enantiomer t_R = 21.56 min.

Phenyl-7-(propan-2-ylidene)-3-tosyl-3-azabicyclo[3.2.0]heptane (23). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.72 (2 H, d, *J* = 8.2 Hz), 7.34 (2 H, d, *J* = 8.2 Hz), 7.30-7.28 (2 H, m), 7.20-7.15 (3 H, m), 3.81 (1 H, brs), 3.67 (2 H, dd, *J* = 2.0, 10.0 Hz), 3.44 (1 H, brs), 2.70-2.63 (2 H, m), 2.59-2.54 (1 H, m), 2.44 (3 H, s), 1.60 (3 H, s), 1.27 ppm (3 H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.7, 143.5, 132.3, 131.8, 129.5, 128.5, 128.1, 127.1, 126.1, 53.8, 53.0, 51.8, 43.7, 42.8, 21.5, 18.9, 18.6 ppm; IR (neat): $\tilde{\upsilon}$ = 3058, 3025, 2977, 2964, 2917, 2886, 2865, 1729, 1596, 1494, 1469, 1450, 1398, 1368, 1335, 1320, 1303, 1291, 1247, 1216, 1185, 1157, 1120, 1087, 1051, 1021, 1003, 970, 915, 860, 839, 818, 807, 756, 717, 706, 698, 663 cm^{-1}; MS (70 eV): *m/z* (%): 367 (32) [M^+], 212 (100), 195 (7), 183 (22), 169 (26), 129 (16), 91 (45), 68 (14), 42 (24); HRMS (ESI): ***calcd.*** for $C_{22}H_{25}NO_2S$ [M^+]: 367.1606, *found*: 367.1606; The enantiomeric excess was determined by HPLC: 250 mm Chiralpak IA, 5 μm, No.: IA00CE-LH028, *n*-heptane/*i*-propanol = 95/5, flow rate = 1.0 mL/min; major enantiomer t_R = 11.94 min; minor enantiomer t_R = 15.84 min. The physical and spectroscopic properties matched those described in the literature.[4]

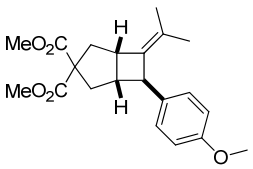


Dimethyl 6-cyclohexylidene-7-phenylbicyclo[3.2.0]heptane-3,3-dicarboxylate (24).



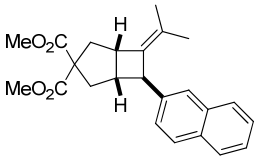
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.29-7.25 (2 H, m), 7.20-7.14 (3 H, m), 3.74 (3 H, s), 3.71 (3 H, s), 3.63-3.55 (1 H, m), 2.77 (1 H, dd, *J* = 2.0, 14.0 Hz), 2.63 (1 H, dd, *J* = 1.1, 13.6 Hz), 2.60-2.55 (1 H, m), 2.39 (1 H, dd, *J* = 8.2, 13.4 Hz), 2.22 (1 H, dd, *J* = 8.6, 13.6 Hz), 2.11-1.96 (2 H, m), 1.69-1.20 (9 H, m) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.9, 172.1, 145.3, 136.6, 130.9, 128.3, 126.9, 125.7, 62.7, 52.8, 52.5, 51.3, 45.1, 43.9, 40.2, 39.6, 29.4, 29.2, 27.3, 27.0, 26.3 ppm; IR (neat): $\tilde{\upsilon}$ = 3025, 2925, 2852, 1731, 1600, 1493, 1448, 1433, 1330, 1257, 1244, 1199, 1170, 1097, 1069, 1058, 1029, 1003, 961, 921, 894, 852, 819, 793, 739, 698 cm^{-1}; MS (70 eV): *m/z* (%): 368 [M^+] (88), 325 (14), 308 (100), 277 (31), 249 (36), 217 (90), 209 (65), 183 (40), 167 (35), 145 (54), 117 (23), 91 (31); HRMS (ESI): *calcd.* for $C_{23}H_{28}O_4$+Na [M^+ + Na]: 391.1878, *found*: 391.1880; The enantiomeric excess was determined by HPLC: 250 mm Chiralpak IA, 5 μm, No.: IA00CE-LH028, *n*-heptane/*i*-propanol = 95/5, flow rate = 1.0 mL/min; major enantiomer t_R = 5.56 min; minor enantiomer t_R = 6.28 min. The physical and spectroscopic properties matched those described in the literature.[4]

Dimethyl 6-(4-methoxyphenyl)-7-(propan-2-ylidene)bicyclo[3.2.0]heptane-3,3-dicarboxylate (25).



^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.10 (2 H, d, *J* = 8.6 Hz), 6.82 (2 H, d, *J* = 8.6 Hz), 3.78 (3 H, s), 3.71 (3 H, s), 3.70 (3 H, s), 3.63 (1 H, brs), 3.57 (1 H, brs), 2.74 (1 H, dd, *J* = 1.6, 13.8 Hz), 2.69 (1 H, dd, *J* = 1.4, 13.6 Hz), 2.58-2.52 (1 H, m), 2.33 (1 H, dd, *J* = 7.5, 13.4 Hz), 2.21 (1 H, dd, *J* = 8.8, 13.6 Hz), 1.59 (3 H, s), 1.29 ppm (3 H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.8, 172.0, 157.7, 137.2, 134.5, 128.9, 128.2, 127.9, 113.8, 62.6, 55.2, 52.8, 52.4, 51.0, 44.8, 44.3, 40.1, 39.0, 29.7, 18.9, 18.8 ppm; IR (neat): $\tilde{\upsilon}$ = 2951, 2910, 2851, 1730, 1609, 1582, 1509, 1433, 1370, 1332, 1299, 1242, 1204, 1174, 1158, 1108, 1092, 1064, 1035, 1002, 983, 917, 822, 807, 754, 686 cm^{-1}; MS (70 eV): *m/z* (%): 358 [M^+] (86), 343 (26), 327 (4), 298 (29), 283 (24), 267 (7), 255 (37), 239 (16), 223 (23), 199 (98), 174 (28), 159 (55), 145 (100), 121 (49), 113 (25), 91 (24), 77 (13), 59 (23), 41 (17); HRMS (ESI): *calcd.* for $C_{21}H_{26}O_5$+Na [M^+ + Na]: 381.1672, *found*: 381.1667; The enantiomeric excess was determined by HPLC: 150 mm Chiralpak AS-RH, acetonitrile/water = 50/50, flow rate = 1.0 mL/min; major enantiomer t_R = 25.93 min; minor enantiomer t_R = 24.12 min.

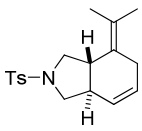
Dimethyl 6-(naphthalen-2-yl)-7-(propan-2-ylidene)bicyclo[3.2.0]heptane-3,3-dicarboxylate (26).



^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.80-7.76 (3 H, m), 7.58 (1 H, s), 7.46-7.38 (2 H, m), 7.34 (1 H, dd, *J* = 1.7, 8.5 Hz), 3.85 (1 H, brs), 3.73 (6 H, s), 3.66 (1 H, brs), 2.82 (1 H, d, *J* = 13.9 Hz), 2.74 (1 H, d,

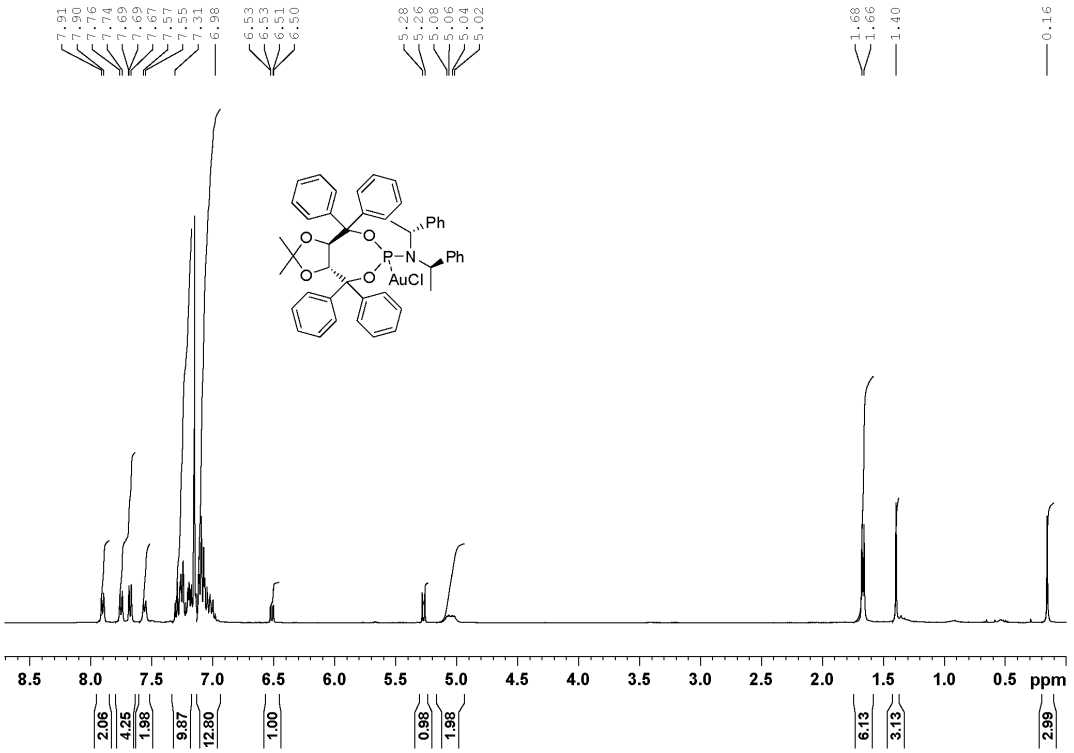
J = 13.3 Hz), 2.70-2.64 (1 H, m), 2.37 (1 H, dd, *J* = 7.6, 13.4 Hz), 2.25 (1 H, dd, *J* = 8.8, 13.7 Hz), 1.64 (3 H, s), 1.31 ppm (3 H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.8, 172.0, 142.3, 133.9, 133.6, 132.1, 129.5, 128.2, 127.6, 127.5, 126.0, 125.8, 125.1, 124.8, 62.6, 52.8, 52.4, 52.0, 44.5, 40.2, 39.0, 18.9, 18.9 ppm; IR (neat): $\tilde{\upsilon}$ = 3053, 3008, 2958, 2917, 2851, 1753, 1730, 1630, 1596, 1507, 1431, 1369, 1328, 1309, 1287, 1273, 1243, 1230, 1195, 1177, 1154, 1138, 1121, 1088, 1068, 1056, 1027, 1006, 951, 930, 893, 879, 862, 846, 818, 798, 777, 758, 741, 709, 685, 654 cm^{-1}; MS (70 eV): *m/z* (%): 378 [M^+] (100), 363 (29), 346 (8), 318 (37), 303 (37), 275 (27), 259 (24), 243 (26), 234 (12), 219 (68), 194 (31), 179 (60), 167 (22), 145 (32), 113 (5), 91 (2), 59 (7), HRMS (ESI): *calcd.* for $C_{24}H_{26}O_4$+Na [M^+ + Na]: 401.1723, *found*: 401.1727; The enantiomeric excess was determined by HPLC: 250 mm Chiralpak IA, 5 μm, No.: IA00CE-LH028, *n*-heptane/*i*-propanol = 95/5, flow rate = 1.0 mL/min; major enantiomer t_R = 5.24 min; minor enantiomer t_R = 5.88 min. The physical and spectroscopic properties matched those described in the literature.[4]

(3a*S*,7a*R*)-4-(propan-2-ylidene)-2-tosyl-2,3,3a,4,5,7a-hexahydro-1*H*-isoindole (28).



^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.73 (2 H, d, *J* = 8.5 Hz), 7.31 (2 H, d, *J* = 7.9 Hz), 5.75 (2 H, s), 3.96 (1 H, dd, *J* = 6.3, 9.5 Hz), 3.63 (1 H, dd, *J* = 7.3, 9.1 Hz), 3.34 (1 H, dd, *J* = 9.6, 11.1 Hz), 2.87 (1 H, dd, *J* = 9.3, 11.3 Hz), 2.86-2.67 (2 H, m), 2.42 (3 H, s), 2.28-2.10 (2 H, m), 1.65 (3 H, s), 1.61 ppm (3 H, s); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 143.2, 134.7, 129.7, 129.0, 127.3, 125.7, 125.1, 125.1, 52.1, 50.4, 46.8, 42.8, 31.1, 21.8, 21.5 ppm; IR (neat): $\tilde{\upsilon}$ = 3029, 2923, 2859, 1597, 1493, 1452, 1398, 1376, 1339, 1305, 1288, 1263, 1217, 1159, 1108, 1089, 1063, 1029, 1014, 911, 844, 814, 778, 728, 707, 673, 656 cm^{-1}; MS (70 eV): *m/z* (%): 317 [M^+] (5), 197 (4), 162 (31), 155 (14), 133 (17), 119 (13), 105 (19), 91 (65), 79 (7), 65 (10), 55 (5), 42 (100), 30 (31); HRMS (ESI): *calcd.* for $C_{18}H_{21}O_2S_1$+Na [M^+ + Na]: 340.1342, *found*: 340.1345; The enantiomeric excess was determined by HPLC: 150 mm Chiralpak IC-3, No.: IC30CD-NB011, methanol/water = 90/10, flow rate = 1.0 mL/min; major enantiomer t_R = 11.17 min; minor enantiomer t_R = 12.15 min. The physical and spectroscopic properties matched those described in the literature.[5]

[5] I. Alonso, B. Trillo, F. López, S. Montserrat, G. Ujaque, L. Castedo, A. Lledós, J. L. Mascareñas, *J. Am. Chem. Soc*. **2009**, *131*, 13020-13030.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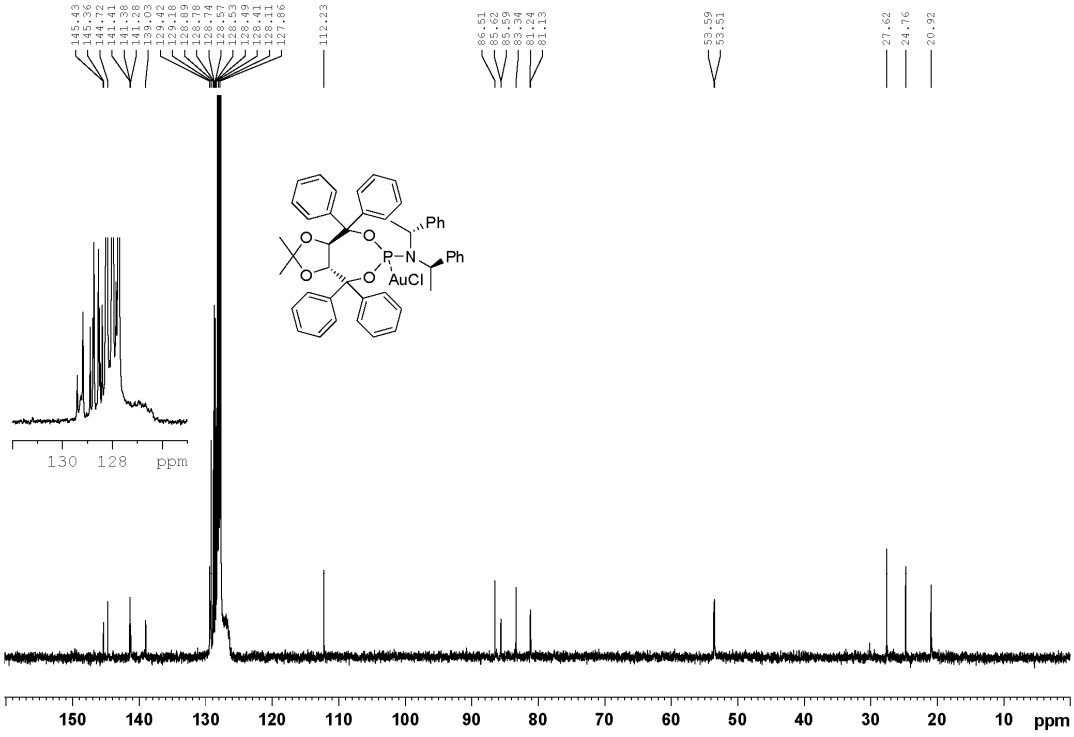
7.90
7.76
7.74
7.69
7.69
7.67
7.57
7.55
7.31
6.98
6.53
6.53
6.51
6.50
5.28
5.26
5.08
5.06
5.04
5.02
1.68
1.66
1.40
0.16
Ph
Ph
P
N
O
O
O
O
AuCl
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.06
4.25
1.98
9.87
12.80
1.00
0.98
1.98
6.13
3.13
2.99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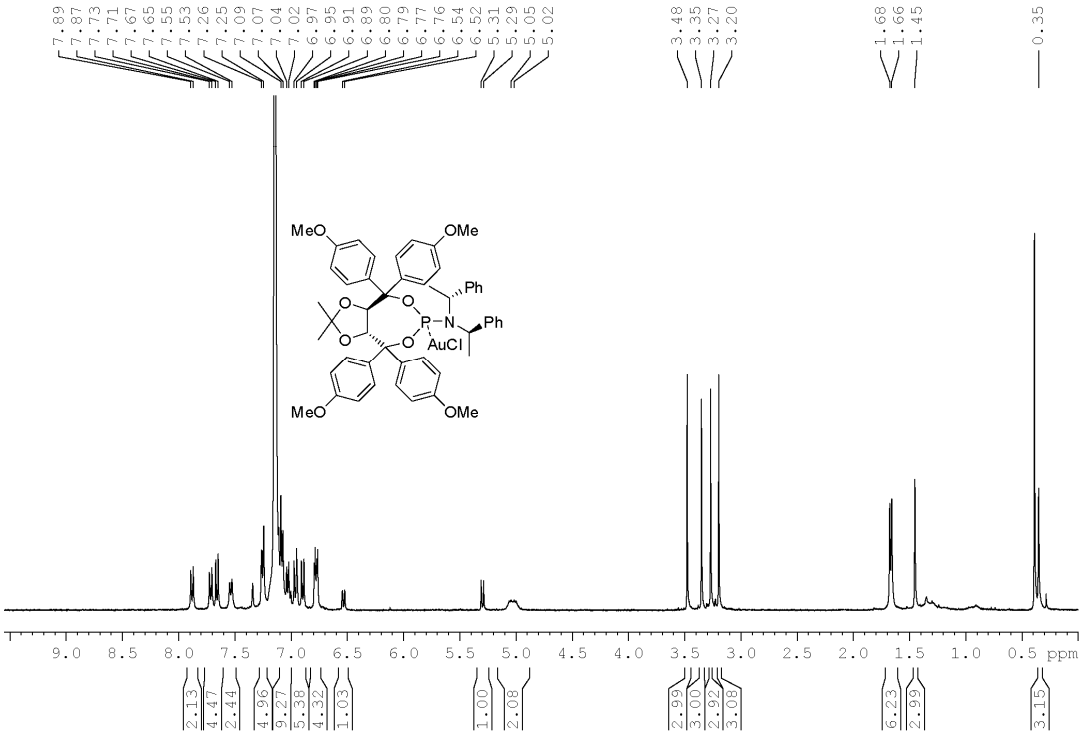
145.36
144.72
141.41
141.38
141.28
131.03
129.42
129.18
128.89
128.78
128.74
128.57
128.53
128.49
128.41
128.11
127.86
112.23
86.51
85.62
85.59
83.34
81.24
81.13
53.59
53.51
27.62
24.76
20.92
Ph
Ph
P
N
O
O
O
O
AuCl
130 128 ppm
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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7.87
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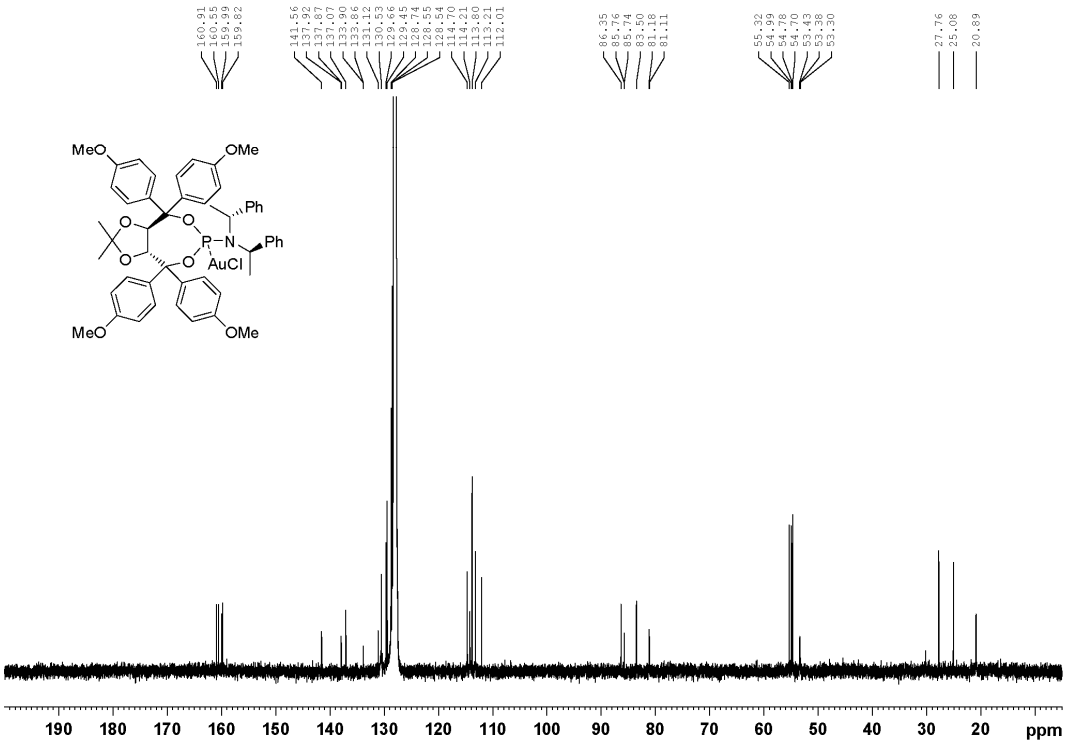
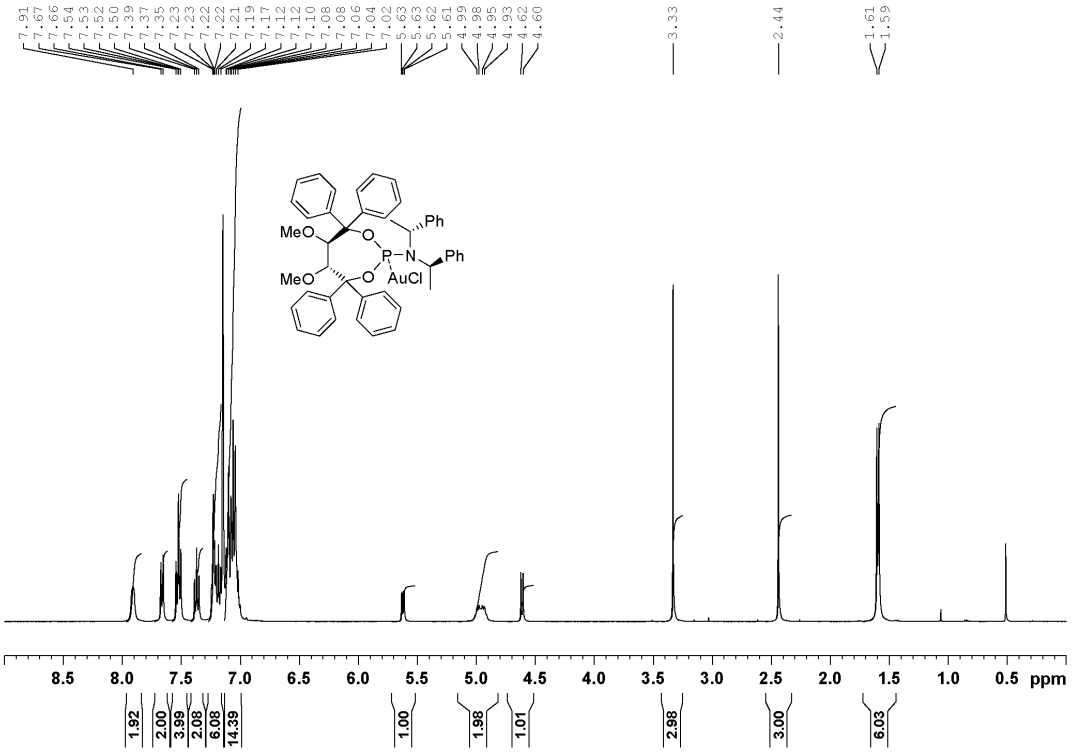
7.71
7.67
7.65
7.55
7.53
7.26
7.25
7.09
7.07
7.04
7.02
6.97
6.95
6.91
6.89
6.80
6.79
6.77
6.76
6.54
6.52
5.31
5.29
5.05
5.02
3.48
3.35
3.27
3.20
1.68
1.66
1.45
0.35
MeO
OMe
Ph
P
N
Ph
AuCl
MeO
OMe
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.13
4.47
2.44
4.96
9.27
5.38
4.32
1.03
1.00
2.08
2.99
3.00
2.92
3.08
6.23
2.99
3.15


160.91
160.55
159.99
159.82
141.56
137.92
137.87
137.07
133.90
133.86
133.12
130.53
129.66
129.45
128.74
128.55
128.54
114.70
114.21
113.80
113.21
112.01
86.35
85.76
85.74
83.50
81.18
81.11
55.32
54.99
54.78
54.70
53.43
53.38
53.30
27.76
25.08
20.89
MeO
OMe
Ph
P
N
Ph
AuCl
MeO
OMe
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm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7.52
7.50
7.39
7.37
7.35
7.23
7.23
7.22
7.22
7.21
7.19
7.17
7.12
7.12
7.10
7.08
7.08
7.06
7.04
7.02
5.63
5.63
5.62
5.61
4.99
4.98
4.95
4.93
4.62
4.60
3.33
2.44
1.61
1.59
MeO
MeO
O
P
N
O
AuCl
Ph
Ph
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
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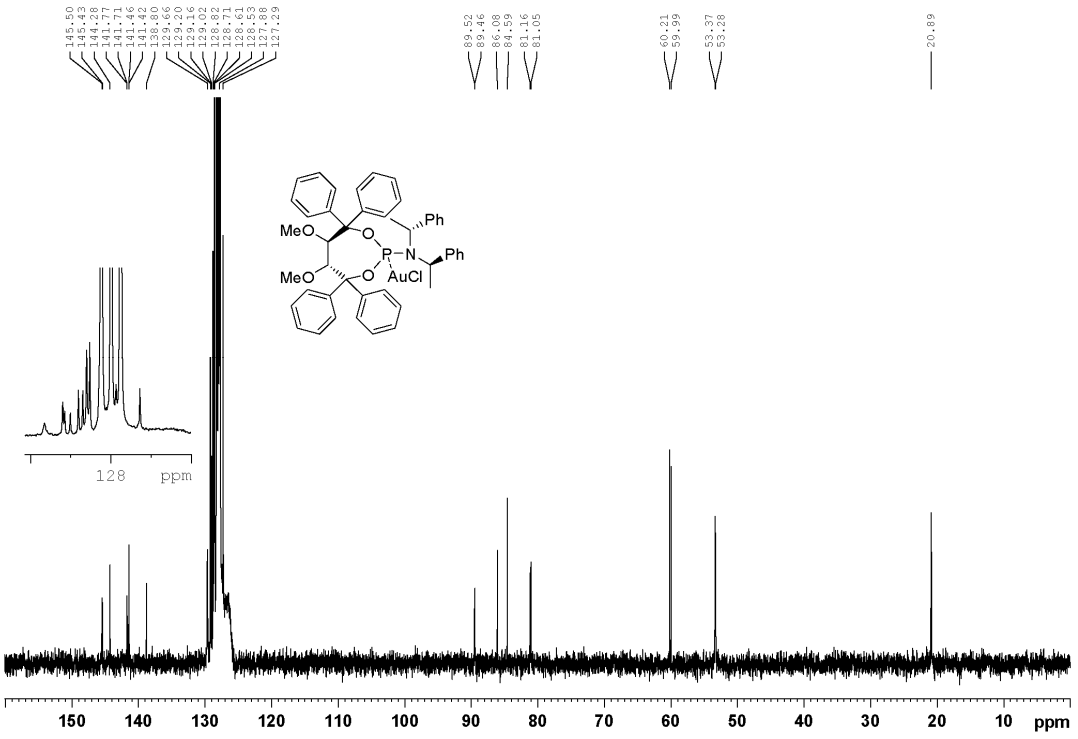
2.00
3.99
2.08
6.08
14.39
1.00
1.98
1.01
2.98
3.00
6.03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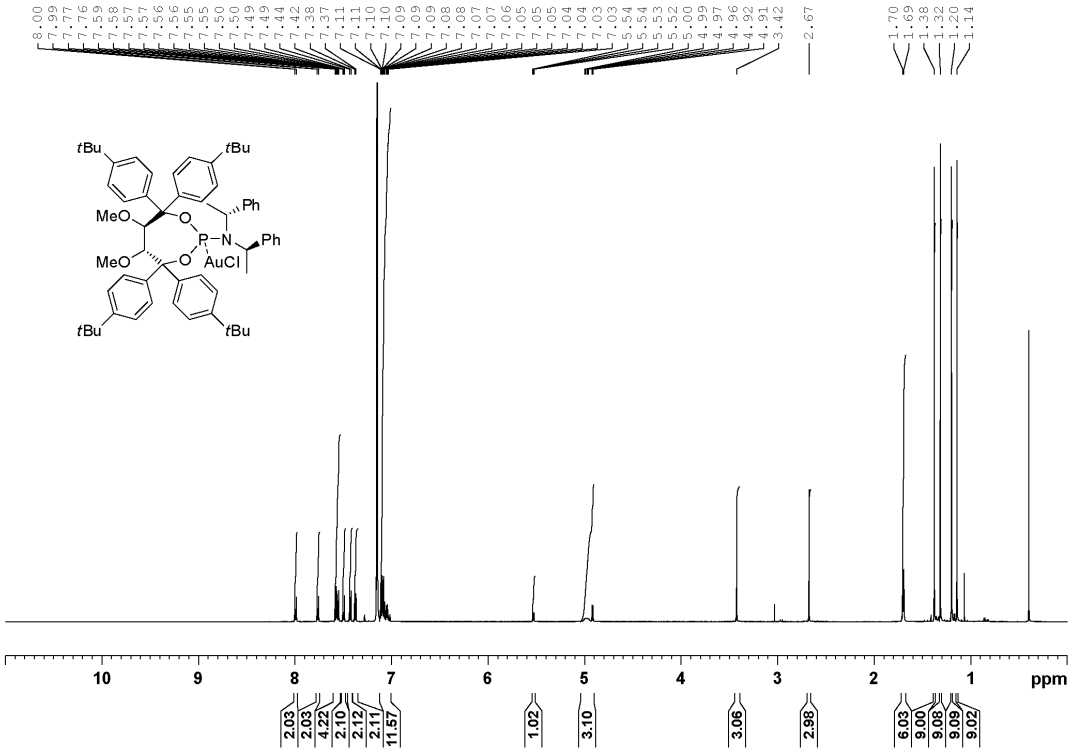
145.43
144.28
141.77
141.71
141.46
141.42
138.80
129.66
129.20
129.16
129.02
128.82
128.71
128.61
128.53
127.88
127.29
89.52
89.46
86.08
84.59
81.16
81.05
60.21
59.99
53.37
53.28
20.89
MeO
MeO
O
P
N
O
AuCl
Ph
Ph
128 ppm
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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7.76
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7.58
7.57
7.57
7.56
7.56
7.55
7.55
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7.50
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7.44
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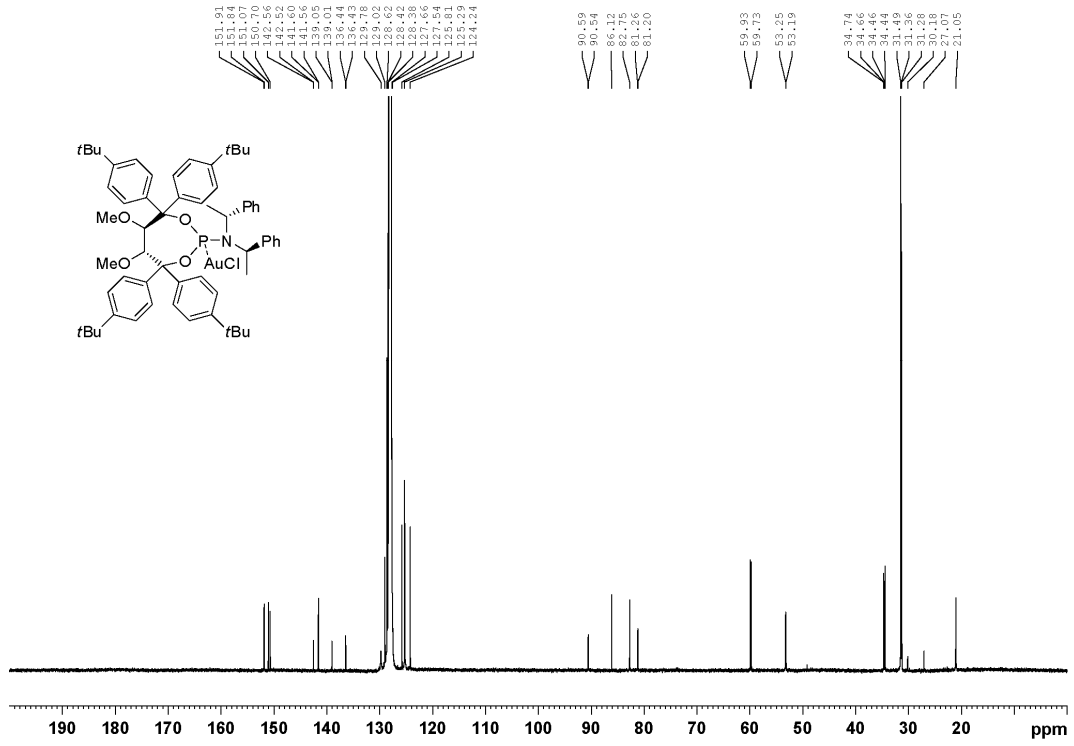
7.38
7.37
7.11
7.11
7.10
7.10
7.09
7.09
7.09
7.08
7.08
7.07
7.07
7.06
7.05
7.05
7.05
7.04
7.04
7.03
7.03
5.54
5.54
5.53
5.52
5.00
4.99
4.97
4.96
4.92
4.91
3.42
2.67
1.70
1.69
1.38
1.32
1.20
1.14
tBu
tBu
MeO
Ph
P
N
Ph
MeO
O
AuCl
tBu
tBu
10
9
8
7
6
5
4
3
2
1
ppm
2.03
2.03
4.22
2.10
2.12
2.11
11.57
1.02
3.10
3.06
2.98
6.03
9.00
9.08
9.09
9.02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141.56
141.05
139.01
136.44
136.43
129.78
129.02
128.62
128.42
128.38
127.66
127.54
125.81
125.29
124.24
90.59
90.54
86.12
82.75
81.26
81.20
59.93
59.73
53.25
53.19
34.74
34.66
34.46
34.44
31.49
31.36
31.28
30.18
27.07
21.05
tBu
tBu
MeO
Ph
P
N
Ph
MeO
O
AuCl
tBu
tBu
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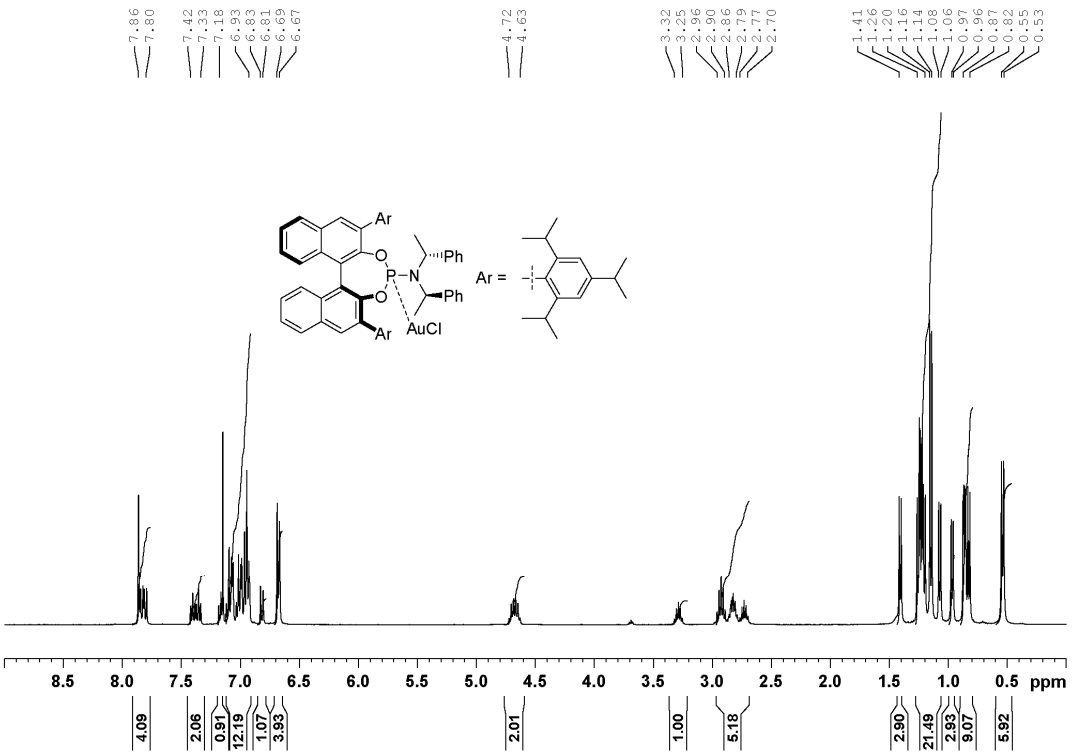
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm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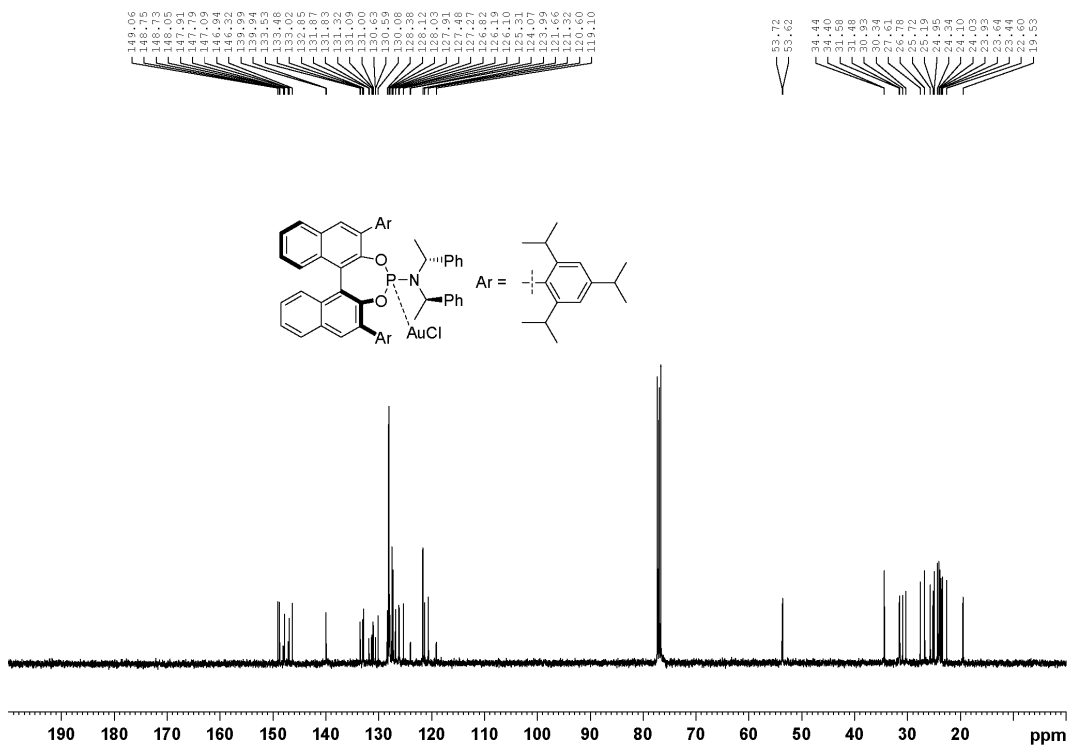
7.80
7.42
7.33
7.18
6.93
6.83
6.81
6.69
6.67
4.72
4.63
3.32
3.25
2.96
2.90
2.86
2.79
2.77
2.70
1.41
1.26
1.20
1.16
1.14
1.08
1.06
0.97
0.96
0.87
0.82
0.55
0.53
Ar
O
P
N
Ph
Ph
O
Ar
AuCl
Ar =
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
4.09
2.06
0.91
12.19
1.07
3.83
2.01
1.00
5.18
2.90
21.49
2.93
9.07
5.92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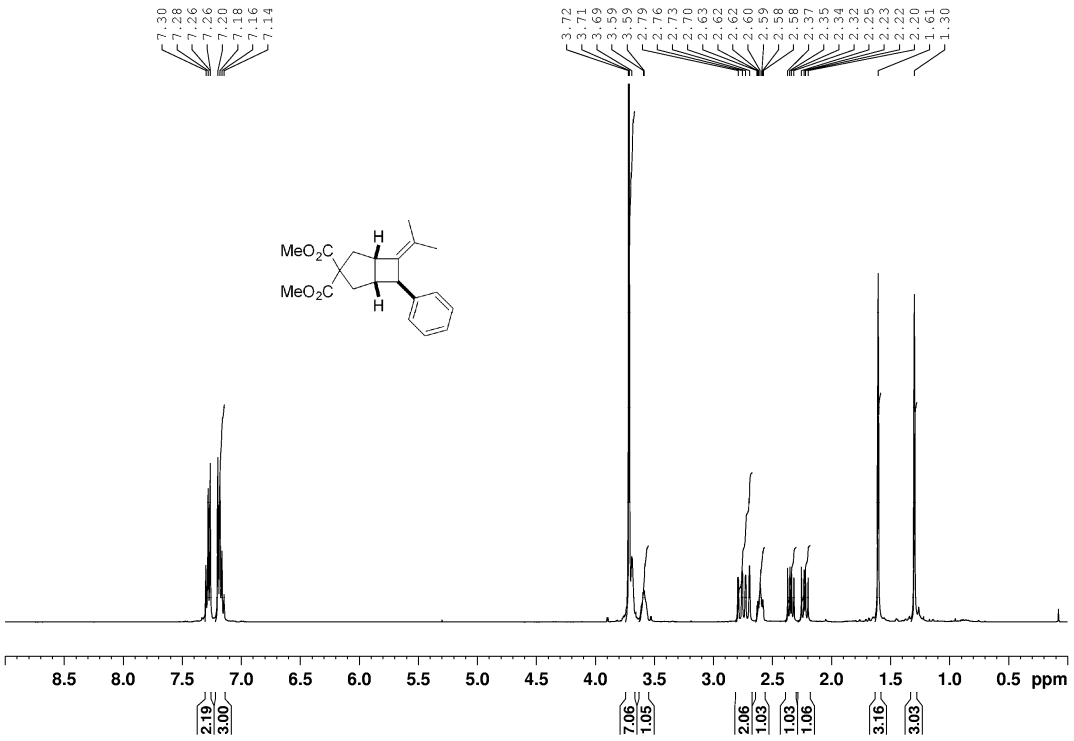
148.73
148.05
147.91
147.79
147.09
146.94
146.32
139.99
139.94
133.53
133.48
133.02
132.55
131.87
131.83
131.32
131.09
131.00
130.63
130.59
130.08
128.38
128.12
128.03
127.91
127.48
127.47
127.42
126.19
126.10
125.31
124.07
123.99
121.66
121.22
120.60
119.10
53.72
53.62
34.44
34.40
31.58
31.48
30.93
30.34
27.61
26.78
25.72
25.19
24.95
24.34
24.10
24.03
23.93
23.64
23.44
22.60
19.53
Ar
O
P
N
Ph
Ph
O
Ar
AuCl
Ar =
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm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7.26
7.26
7.20
7.18
7.16
7.14
3.72
3.71
3.69
3.59
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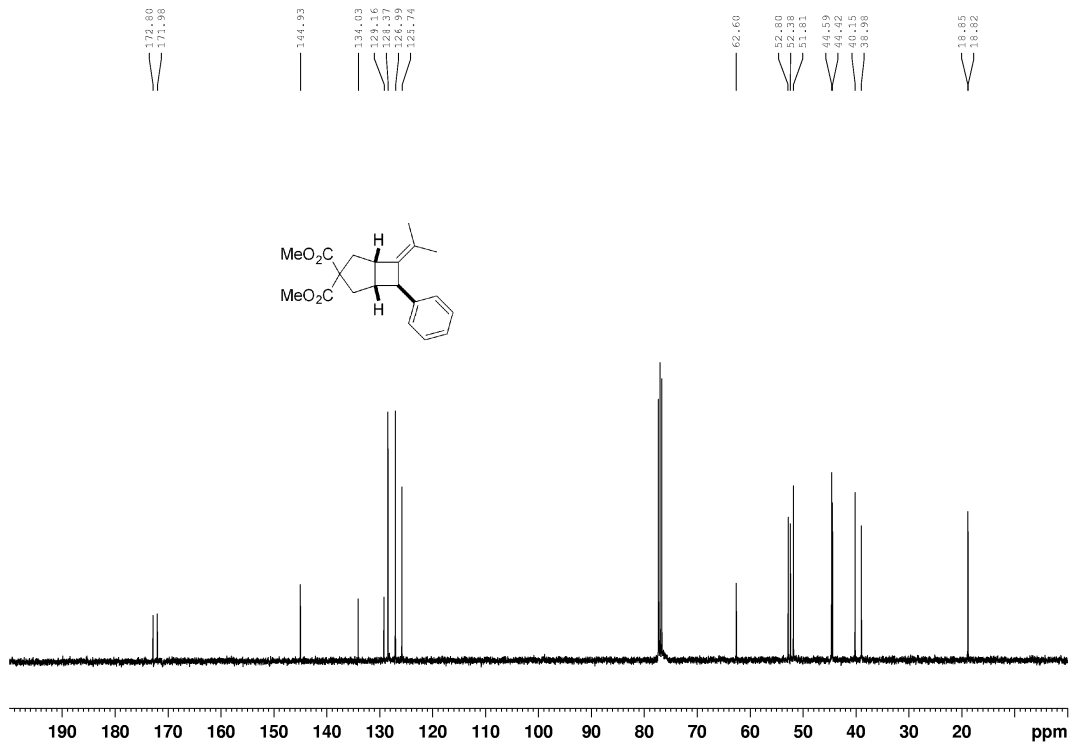
2.79
2.76
2.73
2.70
2.63
2.62
2.62
2.60
2.59
2.58
2.58
2.37
2.35
2.34
2.32
2.25
2.23
2.22
2.20
1.61
1.30
MeO2C
MeO2C
H
H
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.19
3.00
7.06
1.05
2.06
1.03
1.03
1.06
3.16
3.03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134.03
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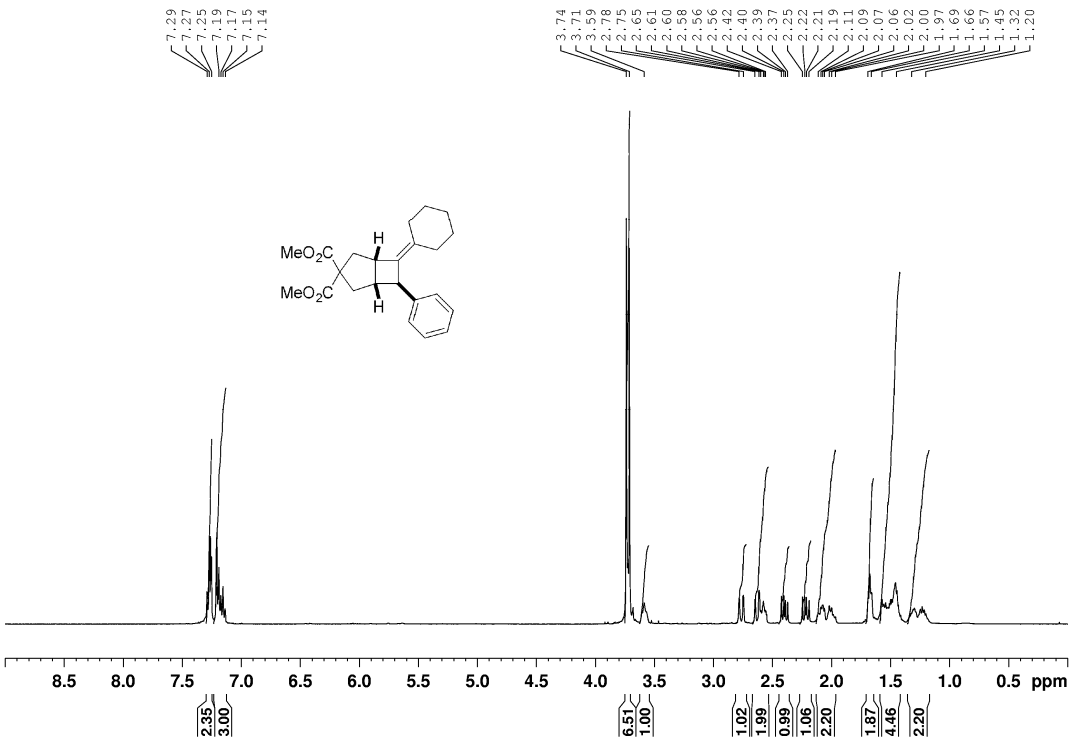
128.32
126.99
125.74
62.60
52.80
52.38
51.81
44.59
44.42
40.15
38.98
18.85
18.82
MeO2C
MeO2C
H
H
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm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2.75
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2.58
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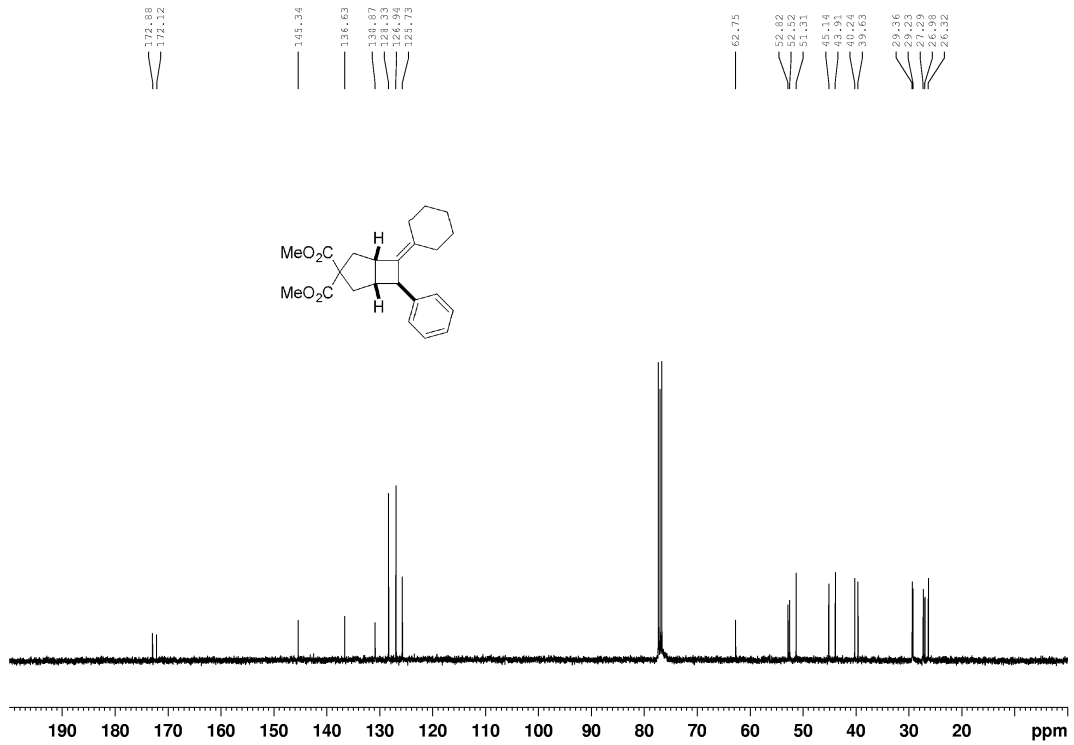
2.39
2.37
2.25
2.22
2.21
2.19
2.11
2.09
2.07
2.06
2.02
2.00
1.97
1.69
1.66
1.57
1.45
1.32
1.20
MeO2C
MeO2C
H
H
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.35
3.00
6.51
1.00
1.02
1.99
0.99
1.06
2.20
1.87
4.46
2.20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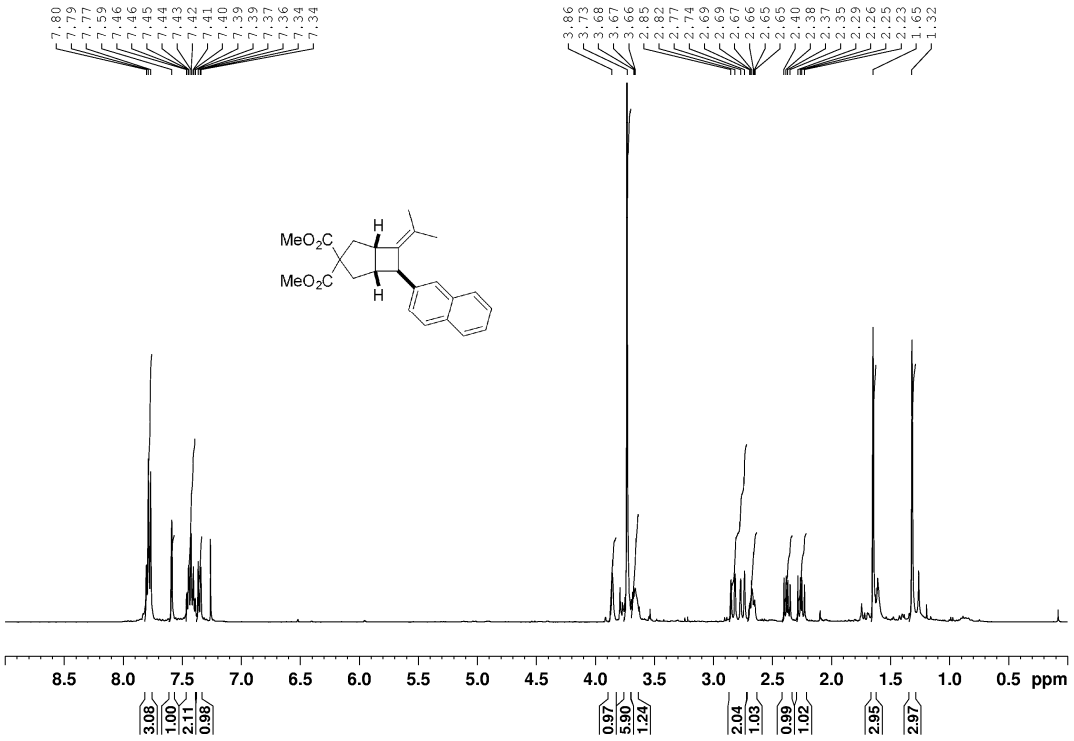
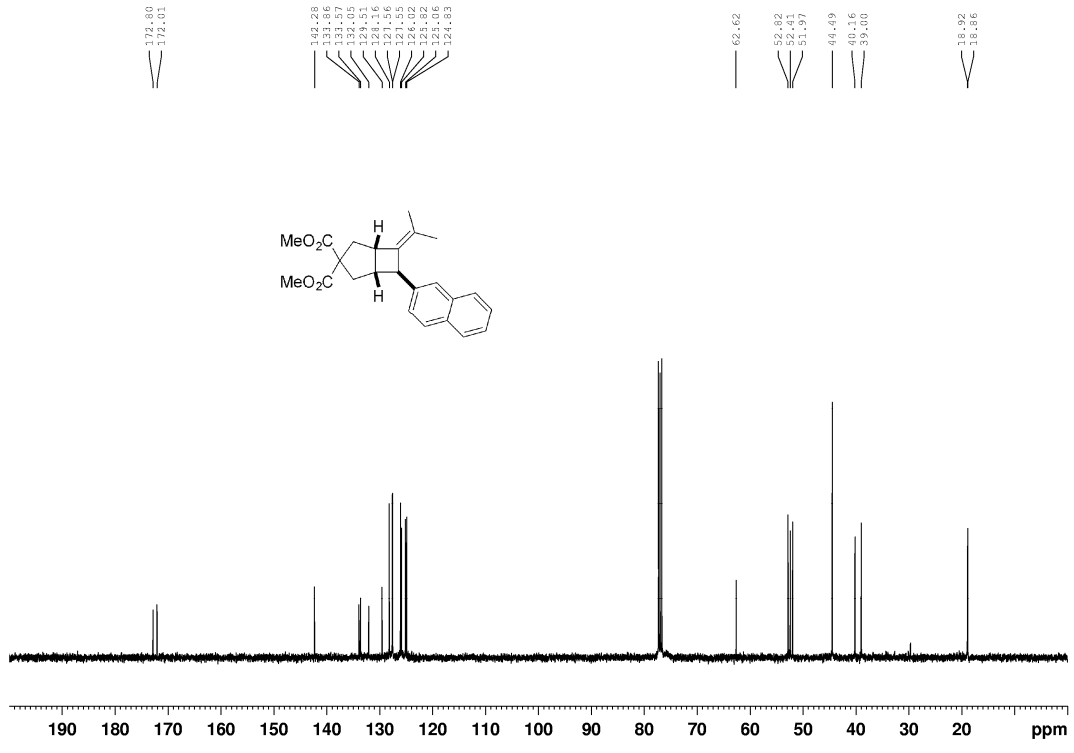
128.33
126.94
125.73
62.75
52.82
52.52
51.31
45.14
43.91
40.24
39.63
29.36
29.23
27.29
26.98
26.32
MeO2C
MeO2C
H
H
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm


7.80
7.79
7.77
7.59
7.46
7.46
7.45
7.44
7.43
7.42
7.41
7.40
7.39
7.39
7.37
7.36
7.34
7.34
3.86
3.73
3.68
3.67
3.66
2.85
2.82
2.77
2.74
2.69
2.69
2.67
2.66
2.65
2.65
2.40
2.38
2.37
2.35
2.29
2.26
2.25
2.23
1.65
1.32
MeO2C
MeO2C
H
H
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
3.08
1.00
2.11
0.98
0.97
5.90
1.24
2.04
1.03
0.99
1.02
2.95
2.97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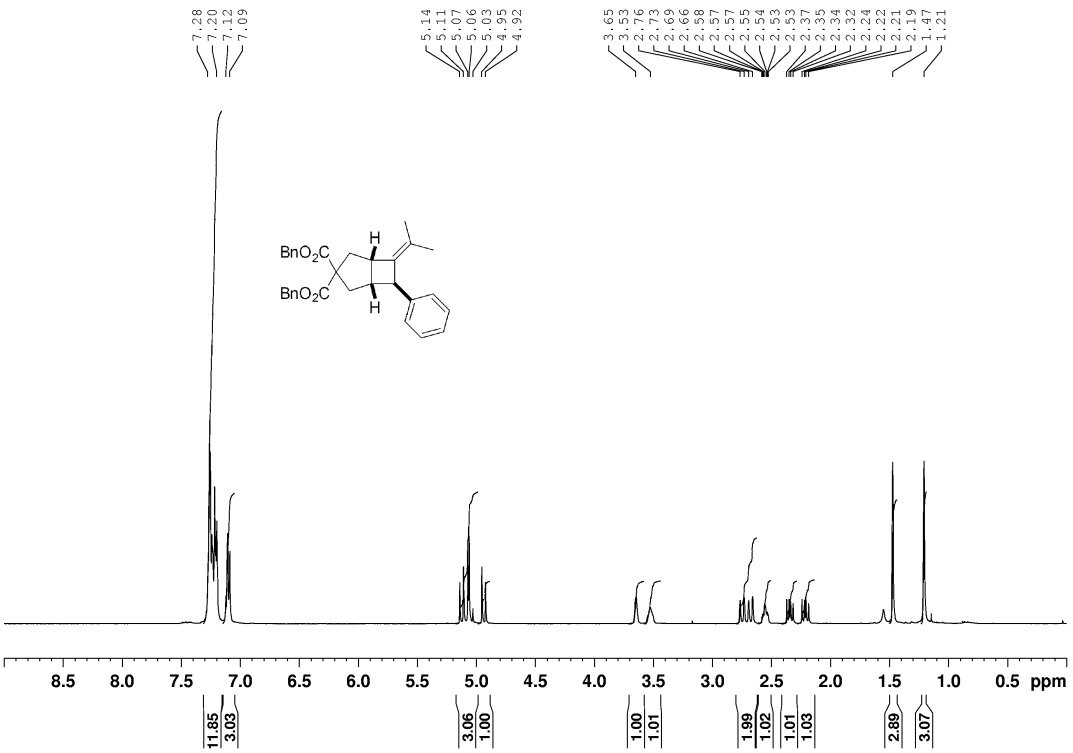
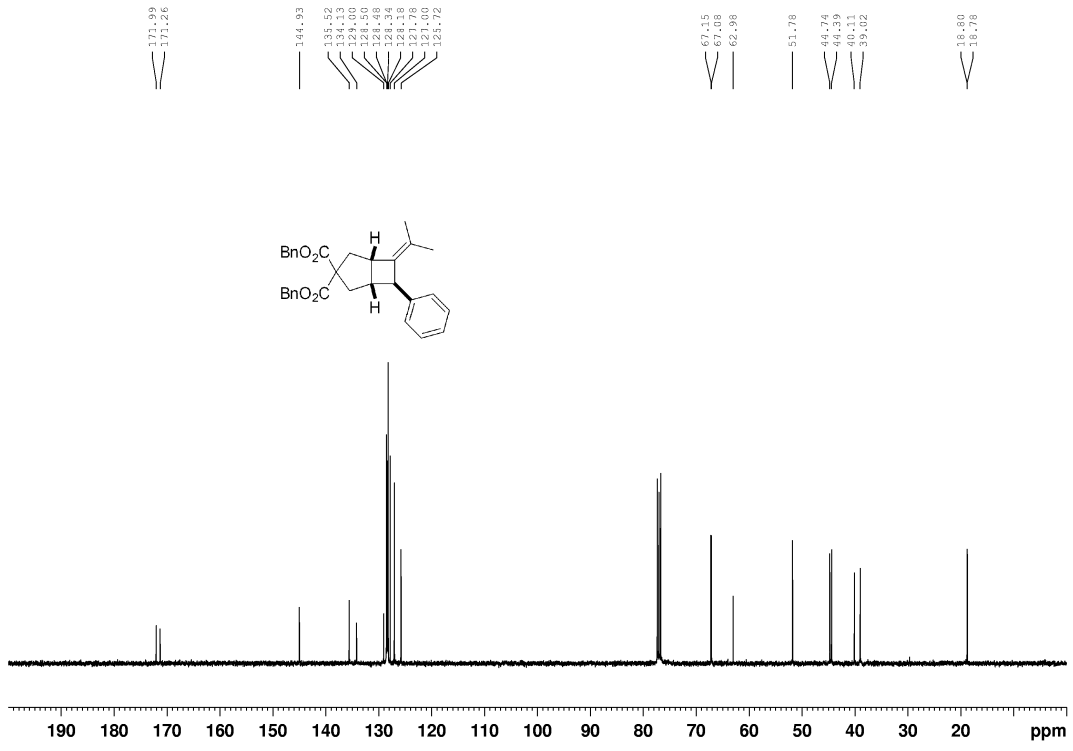
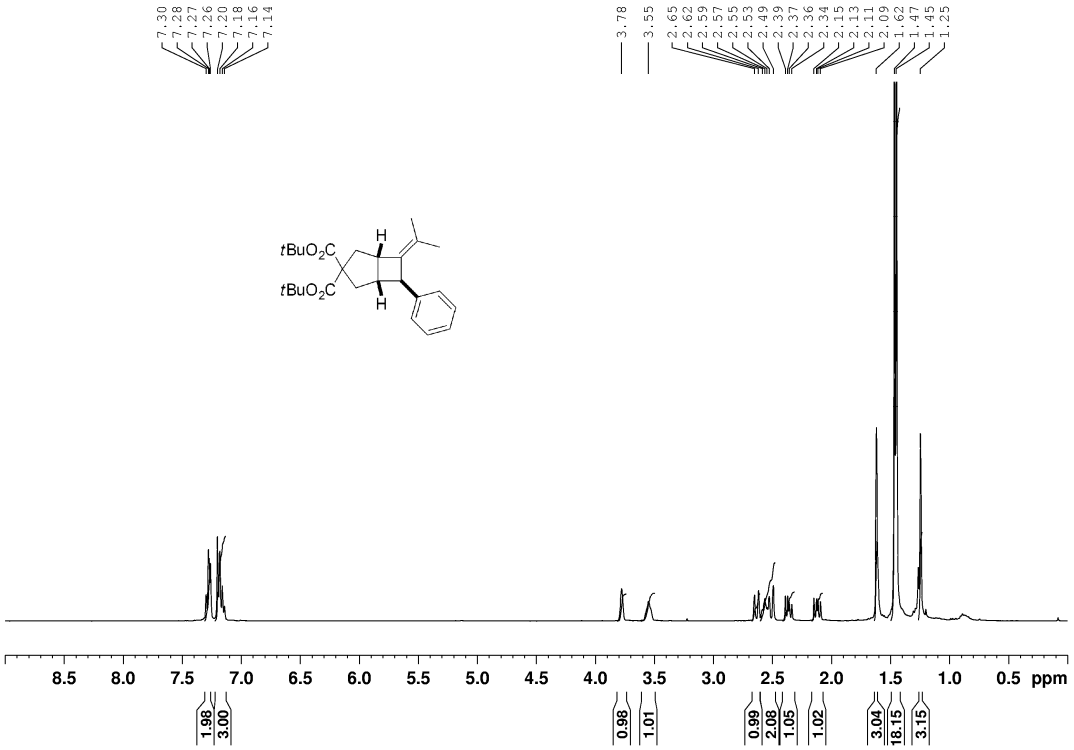
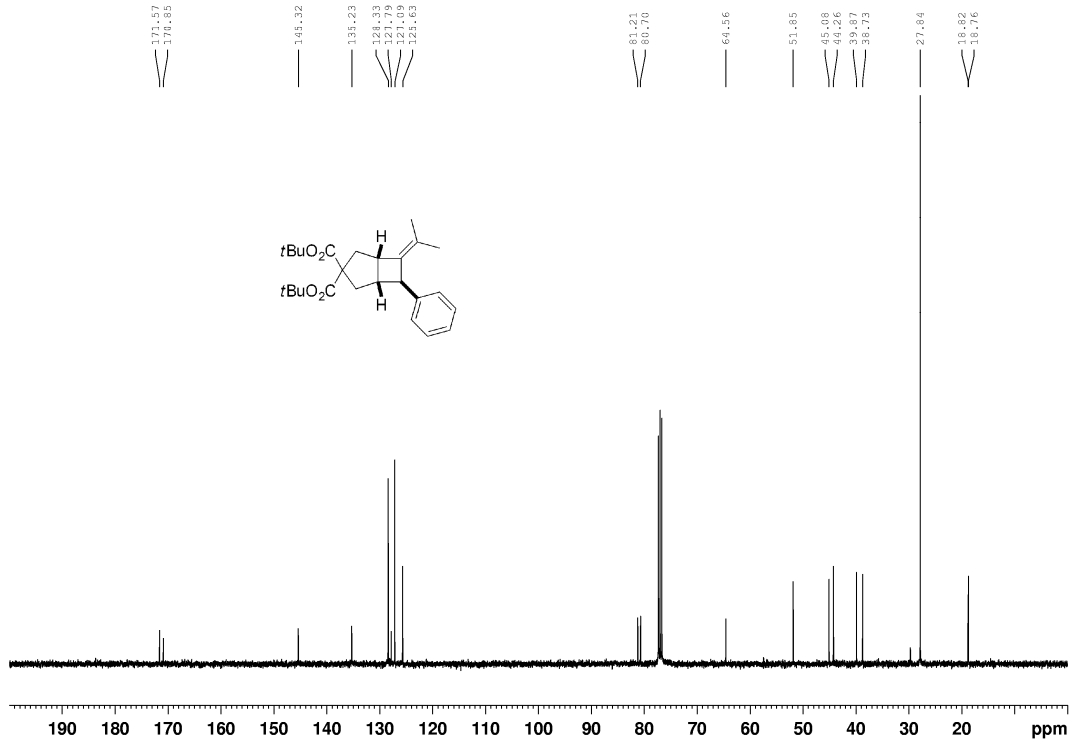
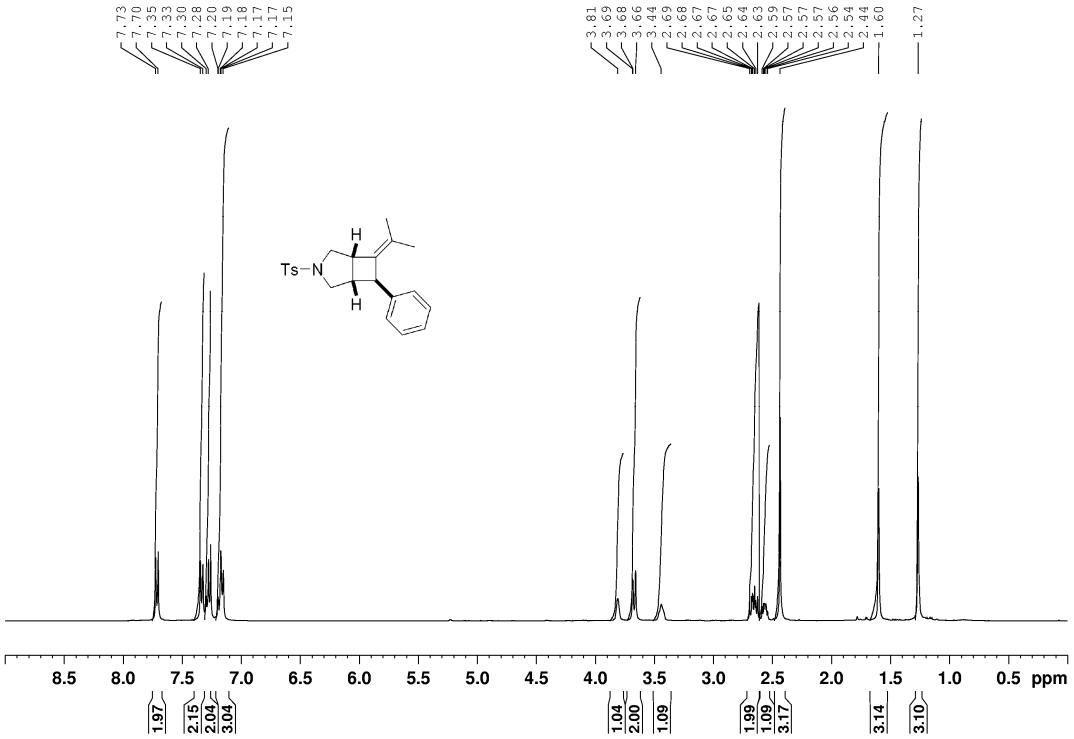
172.01
142.28
131.86
131.57
132.05
129.51
128.16
127.56
127.15
126.02
125.82
125.06
124.83
62.62
52.82
52.41
51.97
40.49
40.16
39.00
18.92
18.86
MeO2C
MeO2C
H
H
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

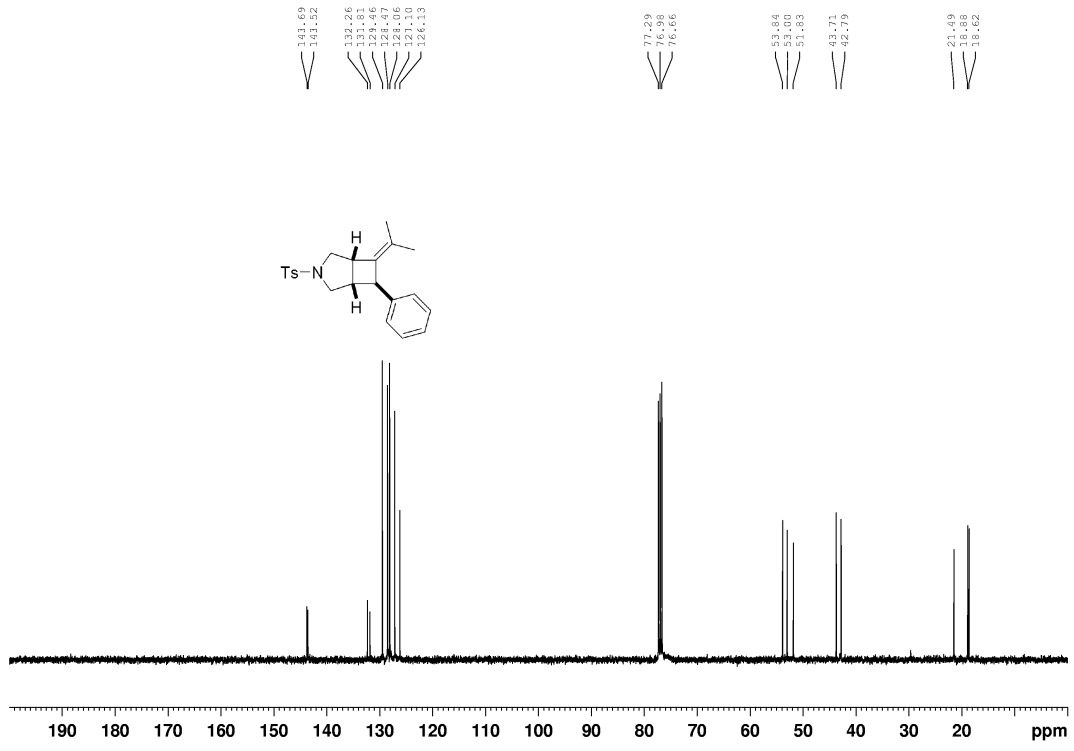

7.28
7.20
7.12
7.09
5.14
5.11
5.07
5.06
5.03
4.95
4.92
3.65
3.53
2.76
2.73
2.69
2.66
2.58
2.57
2.57
2.55
2.54
2.53
2.53
2.37
2.35
2.34
2.32
2.24
2.22
2.21
2.19
1.47
1.21
BnO2C
BnO2C
H
H
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
11.85
3.03
3.06
1.00
1.00
1.01
1.99
1.02
1.01
1.03
2.89
3.07

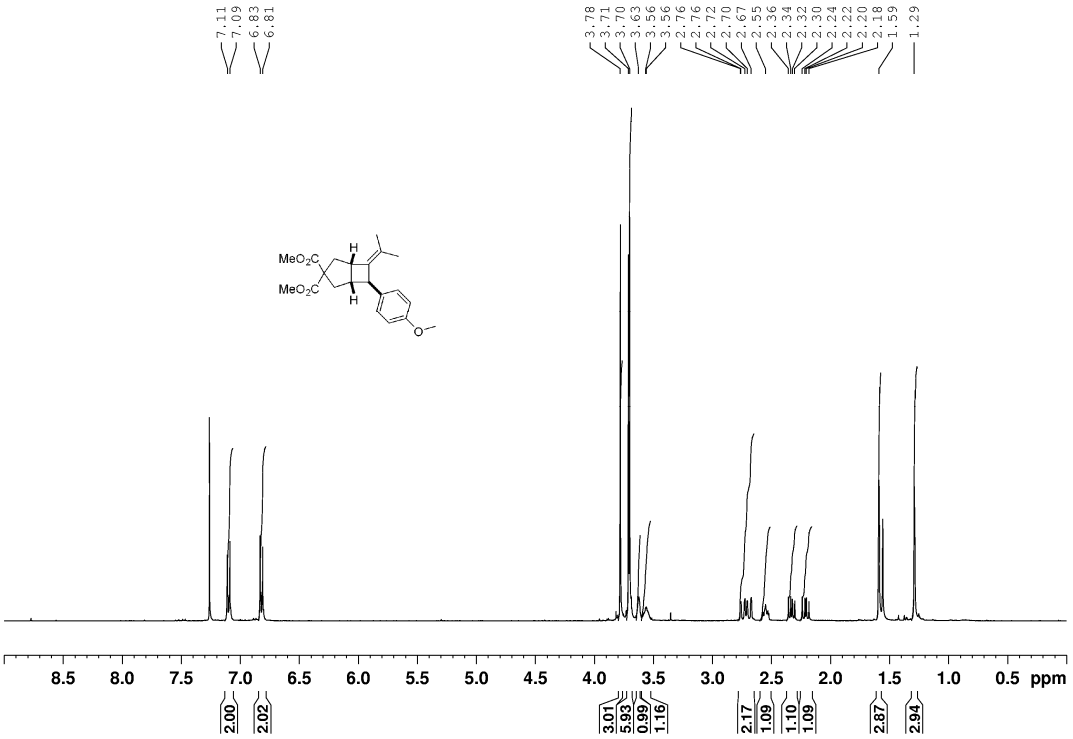

171.99
171.26
144.93
135.52
134.13
129.00
128.50
128.48
128.34
128.18
128.08
127.00
126.72
67.15
67.08
62.98
51.78
44.74
44.39
40.11
39.02
18.80
18.78
BnO2C
BnO2C
H
H
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

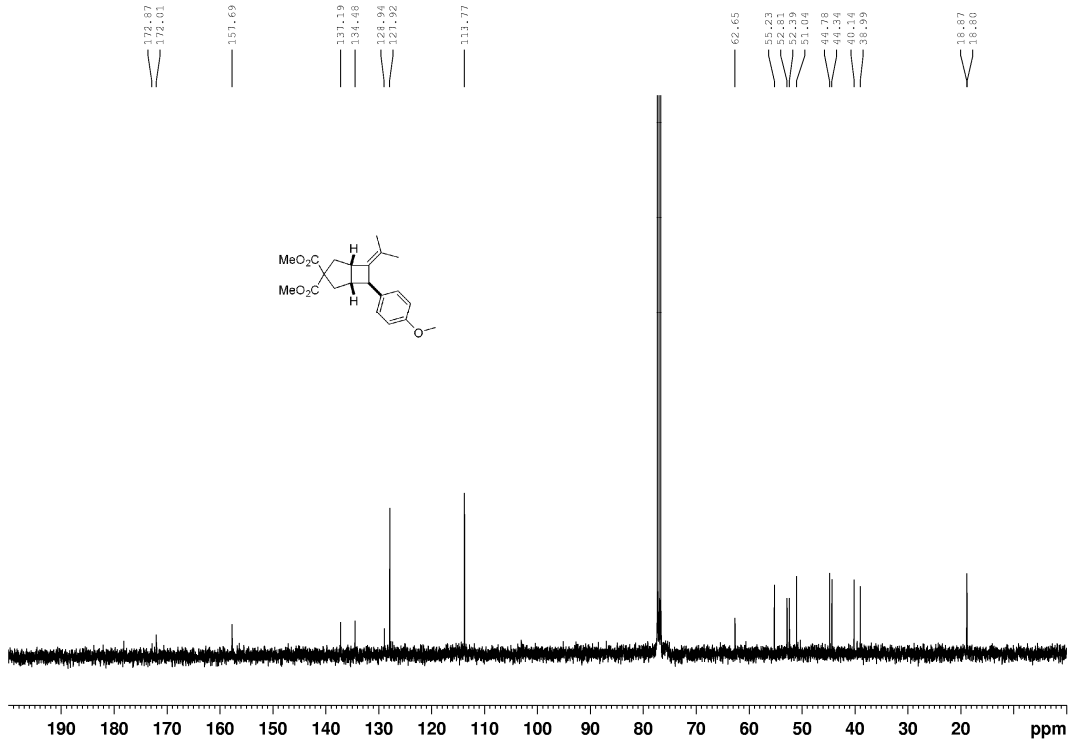

7.30
7.28
7.27
7.26
7.20
7.18
7.16
7.14
3.78
3.55
2.65
2.62
2.59
2.57
2.55
2.53
2.49
2.39
2.37
2.36
2.34
2.15
2.13
2.11
2.09
1.62
1.47
1.45
1.25
tBuO2C
tBuO2C
H
H
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.98
3.00
0.98
1.01
0.99
2.08
1.05
1.02
3.04
18.15
3.15

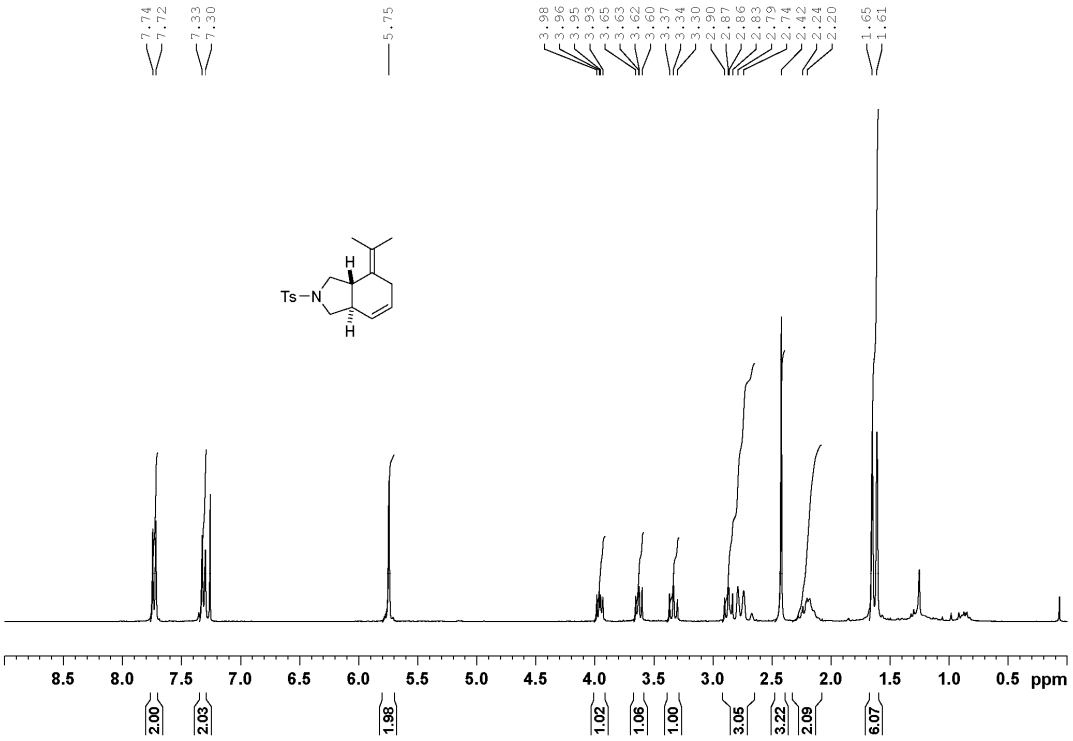

171.57
170.85
145.32
135.23
128.33
127.79
127.09
125.63
81.21
80.70
64.56
51.85
45.08
44.26
39.87
38.73
27.84
18.82
18.76
tBuO2C
tBuO2C
H
H
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

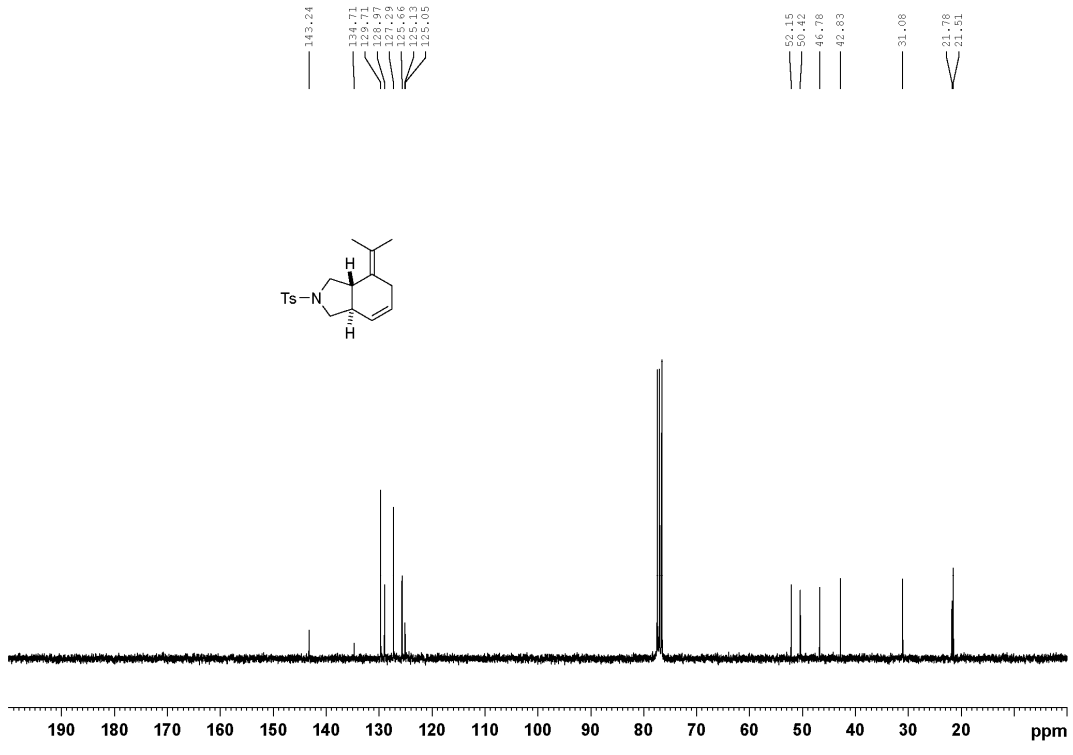

7.73
7.70
7.35
7.33
7.30
7.28
7.20
7.19
7.18
7.17
7.17
7.15
3.81
3.69
3.68
3.66
3.44
2.69
2.68
2.67
2.67
2.65
2.64
2.63
2.59
2.57
2.57
2.57
2.56
2.54
2.44
1.60
1.27
Ts
N
H
H
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.97
2.15
2.04
3.04
1.04
2.00
1.09
1.99
1.09
3.17
3.14
3.10

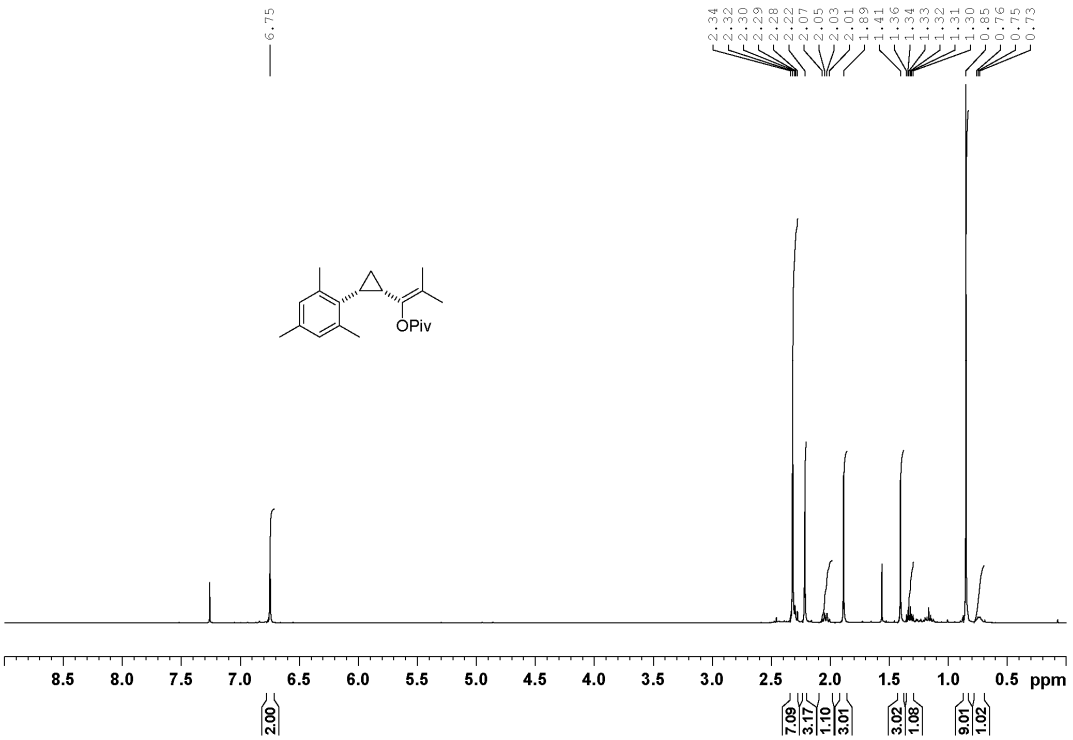

141.69
141.52
132.26
131.81
129.45
128.47
128.06
127.10
126.13
77.29
76.98
76.66
53.84
53.00
51.83
43.71
42.79
21.49
18.88
18.62
Ts
N
H
H
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

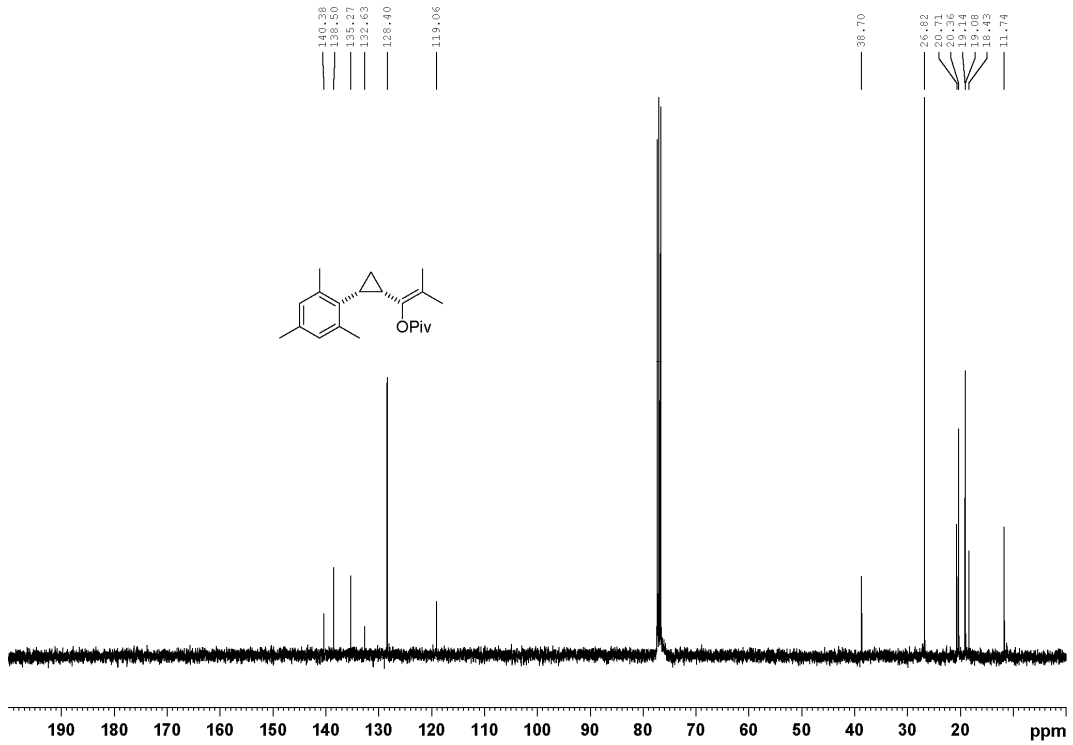

7.11
7.09
6.83
6.81
3.78
3.71
3.70
3.63
3.56
3.56
2.76
2.76
2.72
2.70
2.67
2.55
2.36
2.34
2.32
2.30
2.24
2.22
2.22
2.20
2.18
1.59
1.29
MeO2C
MeO2C
H
H
O
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.00
2.02
3.01
5.93
0.99
1.16
2.17
1.09
1.10
1.09
2.87
2.94


172.87
172.01
151.69
137.19
134.46
128.94
121.92
113.77
62.65
55.23
52.81
52.39
51.04
44.78
40.34
40.14
38.99
18.87
18.80
MeO2C
MeO2C
H
H
O
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm


7.74
7.72
7.33
7.30
5.75
3.98
3.96
3.95
3.93
3.65
3.63
3.62
3.60
3.37
3.34
3.30
2.90
2.87
2.86
2.83
2.79
2.74
2.42
2.24
2.20
1.65
1.61
Ts—N
H
H
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.00
2.03
1.98
1.02
1.06
1.00
3.05
3.22
2.09
6.07


143.24
134.71
129.71
128.97
127.29
125.46
125.13
125.05
52.15
50.42
46.78
42.83
31.08
21.78
21.51
Ts—N
H
H
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm


6.75
2.34
2.32
2.30
2.29
2.28
2.22
2.07
2.05
2.03
2.01
1.89
1.41
1.36
1.34
1.33
1.32
1.31
1.30
0.85
0.76
0.75
0.73
OPiv
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.00
7.08
3.17
1.10
3.01
3.02
1.08
9.01
1.02


140.38
138.50
135.27
132.63
128.40
119.06
38.70
26.82
20.71
20.36
19.14
19.08
18.43
11.74
OPiv
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm