

# CHEMISTRY

## A **European** Journal

### Supporting Information

#### **Rearrangement of a Transient Gold Vinylidene into Gold Carbenes**

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## SUPPORTING CRYSTALLOGRAPHIC INFORMATION

**X-ray Crystal Structure Analysis of Complex 20:**  $C_{42}H_{45}AuN_2O$ ,  $M_r = 790.76 \text{ g} \cdot \text{mol}^{-1}$ , colorless plate, crystal size 0.105 x 0.049 x 0.018 mm, monoclinic, space group  $C2/c$ ,  $a = 35.178(5) \text{ \AA}$ ,  $b = 14.896(2) \text{ \AA}$ ,  $c = 15.689(2) \text{ \AA}$ ,  $\beta = 103.551(2)^\circ$ ,  $V = 7992.6(18) \text{ \AA}^3$ ,  $T = 100 \text{ K}$ ,  $Z = 8$ ,  $D_{calc} = 1.314 \text{ g} \cdot \text{cm}^3$ ,  $\lambda = 0.71073 \text{ \AA}$ ,  $\mu(Mo-K\alpha) = 3.712 \text{ mm}^{-1}$ , Empirical absorption correction ( $T_{min} = 0.78$ ,  $T_{max} = 0.95$ ), Bruker-AXS Kappa Mach3 APEX-II diffractometer,  $2.657 < \theta < 30.997^\circ$ , 111843 measured reflections, 12733 independent reflections, 9279 reflections with  $I > 2\sigma(I)$ , Structure solved by direct methods and refined by full-matrix least-squares against  $F^2$  to  $R_1 = 0.041 [I > 2\sigma(I)]$ ,  $wR_2 = 0.116$ , 423 parameters, H atoms riding,  $S = 1.064$ , residual electron density 2.9 (1.19  $\text{\AA}$  from Au)/ -1.9  $e \text{ \AA}^{-3}$ . **CCDC-1528267**.

**X-ray Crystal Structure Analysis of Complex 22:**  $C_{43}H_{45}AuF_3N_2O_4S$ ,  $M_r = 939.83 \text{ g} \cdot \text{mol}^{-1}$ , yellow prism, crystal size 0.16 x 0.08 x 0.05 mm, monoclinic, space group  $P2_1/c$ ,  $a = 9.6453(14) \text{ \AA}$ ,  $b = 17.203(2) \text{ \AA}$ ,  $c = 24.454(2) \text{ \AA}$ ,  $\beta = 98.350(8)^\circ$ ,  $V = 4014.6(9) \text{ \AA}^3$ ,  $T = 100 \text{ K}$ ,  $Z = 4$ ,  $D_{calc} = 1.555 \text{ g} \cdot \text{cm}^3$ ,  $\lambda = 0.71073 \text{ \AA}$ ,  $\mu(Mo-K\alpha) = 3.774 \text{ mm}^{-1}$ , Empirical absorption correction ( $T_{min} = 0.65$ ,  $T_{max} = 0.84$ ), Bruker AXS Enraf-Nonius KappaCCD diffractometer,  $3.458 < \theta < 26.372^\circ$ , 50889 measured reflections, 8196 independent reflections, 6737 reflections with  $I > 2\sigma(I)$ , Structure solved by direct methods and refined by full-matrix least-squares against  $F^2$  to  $R_1 = 0.068 [I > 2\sigma(I)]$ ,  $wR_2 = 0.173$ , 495 parameters, H atoms riding,  $S = 1.104$ , residual electron density 2.6 (0.79  $\text{\AA}$  from Au)/ -3.1  $e \text{ \AA}^{-3}$ . **CCDC-1528266**.

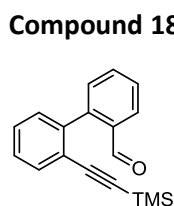
**X-ray Crystal Structure Analysis of Complex 24:**  $C_{46}H_{54}AuBCl_6F_4N_2O$ ,  $M_r = 1147.39 \text{ g} \cdot \text{mol}^{-1}$ , light-yellow prism, crystal size 0.115 x 0.071 x 0.056 mm, triclinic, space group  $P1$ ,  $a = 13.2236(18) \text{ \AA}$ ,  $b = 14.2167(19) \text{ \AA}$ ,  $c = 15.450(2) \text{ \AA}$ ,  $\alpha = 110.570(2)^\circ$ ,  $\beta = 110.818(2)^\circ$ ,  $\gamma = 95.093(2)^\circ$ ,  $V = 2464.9(6) \text{ \AA}^3$ ,  $T = 100 \text{ K}$ ,  $Z = 2$ ,  $D_{calc} = 1.546 \text{ g} \cdot \text{cm}^3$ ,  $\lambda = 0.71073 \text{ \AA}$ ,  $\mu(Mo-K\alpha) = 3.360 \text{ mm}^{-1}$ , Empirical absorption correction ( $T_{min} = 0.78$ ,  $T_{max} = 0.89$ ), Bruker-AXS Kappa Mach3 APEX-II diffractometer,  $3.399 < \theta < 37.490^\circ$ , 192124 measured reflections, 24384 independent reflections, 20927 reflections with  $I > 2\sigma(I)$ , Structure solved by direct methods and refined by full-matrix least-squares against  $F^2$  to  $R_1 = 0.027 [I > 2\sigma(I)]$ ,  $wR_2 = 0.062$ , 576 parameters, H atoms riding,  $S = 1.030$ , residual electron density 2.4 (0.76  $\text{\AA}$  from Au)/ -1.7  $e \text{ \AA}^{-3}$ . **CCDC-1528269**.

**X-ray Crystal Structure Analysis of Complex 27b:**  $C_{56.72}H_{46.15}F_6O_{1.28}P_3Ru$ ,  $M_r = 1056.27 \text{ g} \cdot \text{mol}^{-1}$ , orange prism, crystal size 0.145 x 0.120 x 0.056 mm, monoclinic, space group  $P2_1/c$ ,  $a = 10.9382(12) \text{ \AA}$ ,  $b = 23.960(3) \text{ \AA}$ ,  $c = 17.9441(19) \text{ \AA}$ ,  $\beta = 96.479(2)^\circ$ ,  $V = 4672.7(9) \text{ \AA}^3$ ,  $T = 100 \text{ K}$ ,  $Z = 4$ ,  $D_{calc} = 1.501 \text{ g} \cdot \text{cm}^3$ ,  $\lambda = 0.71073 \text{ \AA}$ ,  $\mu(Mo-K\alpha) = 0.505 \text{ mm}^{-1}$ , Empirical absorption correction ( $T_{min} = 0.87$ ,  $T_{max} = 0.95$ ), Bruker-AXS Kappa Mach3 APEX-II diffractometer,  $3.229 < \theta < 37.412^\circ$ , 182923 measured reflections, 23582 independent reflections, 18401 reflections with  $I > 2\sigma(I)$ , Structure solved by direct methods and refined by full-matrix least-squares against  $F^2$  to  $R_1 = 0.035 [I > 2\sigma(I)]$ ,  $wR_2 = 0.085$ , 624 parameters, H atoms riding,  $S = 1.046$ , residual electron density 0.8 (0.57  $\text{\AA}$  from Ru)/ -1.1  $e \text{ \AA}^{-3}$ . **CCDC-1528268**.

## PREPARATIVE DATA

**General.** Unless stated otherwise, all reactions were carried out under Ar in carefully dried glassware using Schlenk techniques. The solvents were purified by distillation over the drying agents indicated and were transferred under Ar: THF (Mg/anthracene), CH<sub>2</sub>Cl<sub>2</sub> (CaH<sub>2</sub>), toluene, pentane (Na/K), MeOH, EtOH (Mg). Flash chromatography: Merck silica gel 60 (40–63 μm). NMR: Spectra were recorded on a Bruker AV 400 or AV 500 spectrometer in the solvents indicated; 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. IR: Spectrum One (Perkin-Elmer) spectrometer, wavenumbers ( $\tilde{\nu}$ ) in cm<sup>-1</sup>. MS (EI): Finnigan MAT 8200 (70 eV), ESIMS: ESQ 3000 (Bruker), accurate mass determinations: Bruker APEX III FT-MS (7 T magnet) or MAT 95 (Finnigan).

Unless stated otherwise, all commercially available compounds (ABCR, Acros, Aldrich, Strem, Apollo Scientific, TCI, Fluorochem) were used as received. Compound **17** was prepared in 84% yield as a yellow oil according to a literature procedure;<sup>1</sup> its spectral and analytical data matched those reported in ref.<sup>2</sup>



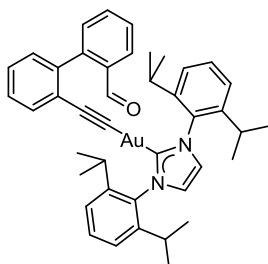
**Compound 18.** A flame-dried 25 mL Schlenk flask was charged with 2-formylphenylboronic acid (279 mg, 1.86 mmol, 1.5 equiv), K<sub>3</sub>PO<sub>4</sub> (527 mg, 2.48 mmol, 2 equiv), RuPhos (58 mg, 0.12 mmol, 0.1 equiv)<sup>3</sup> and Pd<sub>2</sub>dba<sub>3</sub> (57 mg, 0.062 mmol, 0.05 equiv). The Schlenk flask was evacuated and backfilled with Ar (3 x). Toluene (5 mL) and arylbromide **17** (314 mg, 1.24 mmol) were added and the resulting mixture was stirred at reflux temperature for 16 h. The mixture was allowed to reach ambient temperature before it was diluted with ethyl acetate and filtered through a short pad of silica. The combined filtrates were evaporated and the residue purified by flash chromatography (98/2, hexanes/EtOAc) to give the title compound as a yellow oil (283 mg, 82%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298K): δ = 9.84 (d, *J* = 0.8 Hz, 1H; CHO), 8.03 (dd, *J* = 7.8, 2.2 Hz, 1H; CH), 7.64 (ddd, *J* = 7.5, 7.5, 1.5 Hz, 1H; CH), 7.58–7.56 (m, 1H; CH), 7.53–7.49 (m, 1H; CH), 7.45–7.34 (m, 4H; 4xCH), 0.00 ppm (s, 9H, TMS); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 298K): δ = 191.8 (CHO), 144.3 (Cq), 141.0 (Cq), 134.2 (Cq), 133.5 (CH), 132.1 (CH), 131.2 (CH), 130.1 (CH), 128.9 (CH), 128.1 (2x CH), 126.8 (CH), 123.7 (Cq), 103.6 (CCTMS), 99.6 (CCTMS), –0.5 ppm (TMS); IR (ATR)  $\tilde{\nu}$  = 2158, 1694, 1597, 1248 cm<sup>-1</sup>; MS (EI): *m/z* (%): 278 (10) [*M*]<sup>+</sup>, 263 (100) [*M*-CH<sub>3</sub>]<sup>+</sup>; HRMS (APPI): *m/z* calcd. for [C<sub>18</sub>H<sub>18</sub>OSi]<sup>+</sup> 278.1121, found 278.1119; Anal. calcd. for C<sub>18</sub>H<sub>18</sub>OSi: C 77.65, H 6.52; found C 77.80, H 6.41.

<sup>1</sup> Á. Ilvarez-Pérez, C. González-Rodríguez, C. García-Yebra, J. A. Varela, E. Oñate, M. A. Esteruelas, C. Saá, *Angew. Chem. Int. Ed.* **2015**, *54*, 13357–13361; *Angew. Chem.* **2015**, *127*, 13555–13559.

<sup>2</sup> C. Körner, P. Starkov, T. D. Sheppard, *J. Am. Chem. Soc.* **2010**, *132*, 5968–5969.

<sup>3</sup> a) J. E. Milne, S. L. Buchwald, *J. Am. Chem. Soc.* **2004**, *126*, 13028–13032; b) T. E. Barder, S. D. Walker, J. R. Martinelli, S. L. Buchwald, *J. Am. Chem. Soc.* **2005**, *127*, 4685–4696.

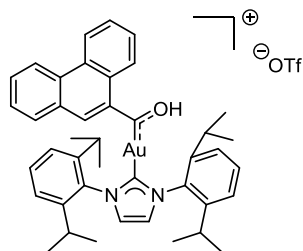
**Complex 20.** IPrAuOH (**19**) (50 mg, 0.083 mmol)<sup>4</sup> was added to a solution of compound **18** (23 mg, 0.083 mmol) in MeOH/EtOH (1/1, 3 mL) and the resulting mixture was



stirred for 16 h at 60°C in air, without any precautions to eliminate moisture. The solvent was evaporated in vacuo and the residue was washed with pentane, leaving the desired complex in analytically pure form as a white solid material (59 mg, 94%). Crystals suitable for X-ray diffraction were grown by diffusing pentane into a concentrated solution of this

complex in CH<sub>2</sub>Cl<sub>2</sub>. m.p. = 98-100°C; <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298K): δ = 9.67 (s, 1H; CHO), 7.76 (dd, *J* = 7.7, 1.5 Hz, 1H; CH), 7.56 (dd, *J* = 7.8, 7.8 Hz, 2H; 2xCH), 7.48 (ddd, *J* = 7.5, 7.5, 1.5 Hz, 1H; CH), 7.38-7.28 (m, 7H; 7xCH), 7.24-7.14 (m, 5H; 5xCH), 2.51 (sept, *J* = 6.9 Hz, 4H; 4xCH(CH<sub>3</sub>)<sub>2</sub>), 1.28 (d, *J* = 6.9 Hz, 12H; 2xCH(CH<sub>3</sub>)<sub>2</sub>), 1.22 ppm (d, *J* = 6.9 Hz, 12H; 2xCH(CH<sub>3</sub>)<sub>2</sub>); <sup>13</sup>C NMR (100 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298K): δ = 191.9 (CHO), 190.9 (AuCN<sub>2</sub>), 146.2 (4xCq), 145.4 (Cq), 140.5 (Cq), 136.6 (Cq), 134.6 (Cq), 134.5 (Cq), 133.1 (CH), 132.6 (CH), 131.5 (CH), 130.8 (2xCH), 130.3 (CH), 127.9 (CH), 127.6 (CH), 126.9 (Cq), 126.6 (CH), 126.1 (CH), 124.7 (Cq), 124.5 (4xCH), 123.7 (2xCH), 102.1 (CCAu), 29.1 (4xCH(CH<sub>3</sub>)<sub>2</sub>), 24.8 (2xCH(CH<sub>3</sub>)<sub>2</sub>), 24.1 ppm (2xCH(CH<sub>3</sub>)<sub>2</sub>); IR (ATR)  $\tilde{\nu}$  = 2960, 2115, 1690, 1597, 1467 cm<sup>-1</sup>; MS (EI): *m/z* (%): 790 (18) [M]<sup>+</sup>; HRMS (ESI): *m/z* calcd. for [C<sub>42</sub>H<sub>45</sub>N<sub>2</sub>OAuNa]<sup>+</sup> 813.3090, found 813.3084; Anal. calcd. for C<sub>42</sub>H<sub>45</sub>AuN<sub>2</sub>O: C 63.79, H 5.74, N 3.54; found C 63.54, H 5.56, N 3.68.

**Complex 22.** The product has to be kept cold (≤ -20°C) at all time. TBSOTf (10 mg, 0.038 mmol) was



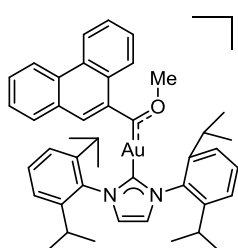
added at -78°C via microsyringe to a solution of compound **20** (30 mg, 0.038 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (0.7 mL), causing an instantaneous color change from almost colorless to orange-red and later bright yellow. After stirring for 20 min, the mixture was warmed to -20°C and the solvent was evaporated at this temperature in high vacuum. The residual oil was redissolved in the minimum amount of CH<sub>2</sub>Cl<sub>2</sub> and pentane was added

dropwise, causing the precipitation of an orange oil. The supernatant was removed via syringe and the residue was dried in high vacuum at -20°C. This manipulation was repeated 3 times to remove all non-ionic impurities. The residue was then dissolved in a minimal amount of CH<sub>2</sub>Cl<sub>2</sub> and pentane was slowly added until the mixture started to become turbid. Slow cooling of this mixture from -20°C to -78°C furnished the title complex in the form of yellow crystals, which were triturated with cold pentane and dried in vacuo (25 mg, 75%). <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 193K): δ = 8.60 (d, *J* = 8.4 Hz, 1H; CH), 8.45-8.41 (m, 2H; 2xCH), 8.15 (s, 1H; CH), 7.81 (d, *J* = 7.7 Hz, 1H; CH), 7.78-7.68 (m, 3H; 3xCH), 7.54-7.43 (m, 7H; 7xCH), 7.42 (s, 2H; 2xCH), 2.45 (sept, *J* = 7.2 Hz, 4H; 4xCH(CH<sub>3</sub>)<sub>2</sub>), 1.26 (d, *J* = 6.8 Hz, 12H; 2xCH(CH<sub>3</sub>)<sub>2</sub>), 1.22 ppm (d, *J* = 6.6 Hz, 12H; 2xCH(CH<sub>3</sub>)<sub>2</sub>), OH not visible, traces of CH<sub>2</sub>Cl<sub>2</sub> and *n*-pentane present; <sup>13</sup>C NMR (100 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 193K): δ = 283.5 (AuCOH), 184.8 (AuCN<sub>2</sub>), 154.1 (br; CH), 145.5 (4xCq), 138.0 (Cq), 133.0 (CH), 132.8 (2xCH), 132.1 (CH), 131.6 (CH), 130.9 (CH), 129.4 (Cq), 128.7 (CH), 128.3 (CH), 127.3 (Cq), 127.1 (CH), 126.1 (Cq), 125.8 (CH), 124.1 (4xCH), 124.0 (Cq), 122.5 (CH), 122.4 (CH), 121.2 (Cq), 118.1 (Cq), 28.4 (4xCH(CH<sub>3</sub>)<sub>2</sub>), 24.6 (2xCH(CH<sub>3</sub>)<sub>2</sub>), 23.0 ppm

<sup>4</sup> F. Nahra, S. R. Patrick, A. Collado, S. P. Nolan, *Polyhedron* **2014**, *33*, 59-62.

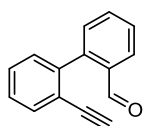
(2xCH(CH<sub>3</sub>)<sub>2</sub>), traces of CH<sub>2</sub>Cl<sub>2</sub> and *n*-pentane present, trifluoromethanesulfonate signals not visible; <sup>19</sup>F NMR (376 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 193K): δ = -79.2 ppm (s; OS(O)<sub>2</sub>CF<sub>3</sub>); IR (ATR)  $\tilde{\nu}$  = 3360, 2960, 1530, 1470, 1287, 1245, 1225, 1168, 1029 cm<sup>-1</sup>; MS (ESI): *m/z* (%): 791 (90) [M]<sup>+</sup>; HRMS (ESI): *m/z* calcd. for [C<sub>42</sub>H<sub>46</sub>N<sub>2</sub>OAu]<sup>+</sup> 791.3270, found 791.3266.

**Complex 24.** The product has to be kept cold ( $\leq -20^{\circ}\text{C}$ ) at all time. Prepared analogously at ambient



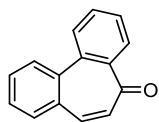
temperature with Me<sub>3</sub>OBF<sub>4</sub> instead of TBSOTf; yellow crystals (14 mg, 55%). <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 223K): δ = 8.69 (d, *J* = 8.5 Hz, 1H; CH), 8.64 (d, *J* = 8.5 Hz, 1H; CH), 8.61 (d, *J* = 8.5, 1.3 Hz, 1H; CH), 8.50 (s, 1H; CH), 7.97 (ddd, *J* = 8.5, 7.1, 1.4 Hz, 1H; CH), 7.83-7.63 (5H, m; 5xCH), 7.52-7.46 (7H, m; 7xCH), 4.17 (s, 3H; OCH<sub>3</sub>), 2.50 (sept, *J* = 6.8 Hz, 4H; 4xCH(CH<sub>3</sub>)<sub>2</sub>), 1.27 (d, *J* = 6.8 Hz, 12H; 2xCH(CH<sub>3</sub>)<sub>2</sub>), 1.25 ppm (d, *J* = 6.8 Hz, 12H; 2xCH(CH<sub>3</sub>)<sub>2</sub>); <sup>13</sup>C NMR (100 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 223K): δ = 283.4 (AuCOCH<sub>3</sub>), 185.2 (AuCN<sub>2</sub>), 157.8 (CH), 145.9 (4x Cq), 145.2 (Cq), 137.9 (Cq), 134.6 (Cq), 134.0 (CH), 133.1 (CH), 132.5 (Cq), 131.1 (CH), 130.2 (Cq), 129.22 (CH), 129.19 (Cq), 128.4 (CH), 127.9 (CH), 126.4 (CH), 126.0 (Cq), 124.7 (CH), 124.3 (4x CH), 124.01 (CH), 123.97 (CH), 123.5 (CH), 123.0 (CH), 68.8 (OCH<sub>3</sub>), 28.7 (4xCH(CH<sub>3</sub>)<sub>2</sub>), 24.9 (2xCH(CH<sub>3</sub>)<sub>2</sub>), 23.5 ppm (2xCH(CH<sub>3</sub>)<sub>2</sub>), traces of CH<sub>2</sub>Cl<sub>2</sub> and *n*-pentane present; <sup>19</sup>F NMR (376 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 223K): δ = -152.4 ppm; <sup>11</sup>B NMR (128 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298K): δ = -1.2 ppm; IR (ATR)  $\tilde{\nu}$  = 2961, 1693, 1467, 1328, 1051 cm<sup>-1</sup>; MS (ESI): *m/z* (%): 805 (100) [M]<sup>+</sup>; HRMS (ESI): *m/z* calcd. for [C<sub>43</sub>H<sub>48</sub>N<sub>2</sub>OAu]<sup>+</sup> 805.3427, found 805.3425.

**Compound 25.** TBAF (1 M in THF, 0.22 mL, 0.22 mmol) was added dropwise to a solution of



compound **18** (40 mg, 0.144 mmol) in THF/MeOH (10/1, 1.1 mL) at 0°C. The cooling bath was removed and the mixture stirred for 2 h at ambient temperature before it was diluted with brine (1 mL). The mixture was extracted with EtOAc (3 x 2 mL), the combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub> and filtered through a plug of silica, eluting with hexanes/EtOAc (9/1). Evaporation of the combined filtrates afforded product **27** as a pale yellow syrup (28 mg, 95%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298K): δ = 9.86 (d, *J* = 0.8 Hz, 1H; CHO), 8.04 (ddd, *J* = 7.8, 1.5, 0.6 Hz, 1H; CH), 7.68-7.62 (m, 2H; 2xCH), 7.53 (dddd, *J* = 7.5, 7.5, 1.0, 1.0 Hz, 1H; CH), 7.48-7.39 (m, 3H; 3xCH), 7.34 (ddd, *J* = 7.4, 1.6, 0.6 Hz, 1H; CH), 2.96 ppm (s, 1H; CCH); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 298K): δ = 191.9 (CHO), 144.0 (Cq), 141.9 (Cq), 134.1 (Cq), 133.6 (CH), 133.1 (CH), 131.2 (CH), 130.5 (CH), 129.0 (CH), 128.4 (CH), 128.2 (CH), 127.2 (CH), 122.5 (Cq), 82.1 (CCH), 81.7 ppm (CCH); IR (ATR)  $\tilde{\nu}$  = 3284, 2106, 1691, 1596, 1195 cm<sup>-1</sup>; MS (EI): *m/z* (%): 206 (9) [M]<sup>+</sup>, 178 (100) [M-CO]<sup>+</sup>; HRMS (ESI): *m/z* calcd. for [C<sub>15</sub>H<sub>10</sub>ONa]<sup>+</sup> 229.0624, found 229.0622; Anal. calcd. for C<sub>15</sub>H<sub>10</sub>O: C 87.36, H 4.89; found C 87.18, H 4.77.

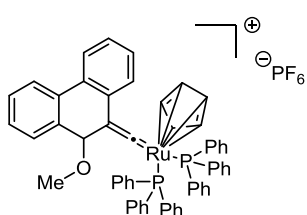
**Compound 28.** TBSOTf (13  $\mu$ L, 14.6 mg, 0.055 mmol) was added to a solution of alkyne **27** (11 mg,



0.055 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (1mL) at -78°C. The cooling bath was removed and the resulting solution allowed to reach ambient temperature. After stirring overnight, the reaction was quenched with water, the aqueous layer was extracted with EtOAc (3 x 2 mL), the combined organic phases were dried and evaporated, and the residue purified by flash

chromatography to give the title compound as a pale yellow solid (9 mg, 82%). The spectral data correspond to those reported in the literature.<sup>5</sup> m.p. = 81-83°C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298K): δ = 7.96 (ddd, *J* = 7.8, 1.7, 0.5 Hz, 1H; CH), 7.93-7.89 (m, 2H; 2xCH), 7.68 (ddd, *J* = 8.1, 7.2, 1.6 Hz, 1H; CH), 7.61-7.48 (m, 4H; 4xCH), 7.37 (d, *J* = 12.2 Hz, 1H; CH), 6.68 ppm (d, *J* = 12.2 Hz, 1H; CH); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 298K): δ = 192.8 (CO), 141.4 (Cq), 140.1 (CH), 138.4 (Cq), 137.2 (Cq), 133.8 (Cq), 133.3 (CH), 131.69 (CH), 131.66 (CH), 131.3 (CH), 130.4 (CH), 129.5 (CH), 129.2 (CH), 128.7 (CH), 128.4 ppm (CH); IR (ATR)  $\tilde{\nu}$  = 3063, 1645, 1592, 1295, 733 cm<sup>-1</sup>; MS (EI): *m/z* (%): 206 (16), [*M*]<sup>+</sup> 178 (100) [*M*-CO]<sup>+</sup>; HRMS (ESI): *m/z* calcd. for [C<sub>15</sub>H<sub>10</sub>O]<sup>+</sup> 206.0732, found 206.0734; Anal. calcd. for C<sub>15</sub>H<sub>10</sub>O: C 87.36, H 4.89; found C 87.30, H 4.69.

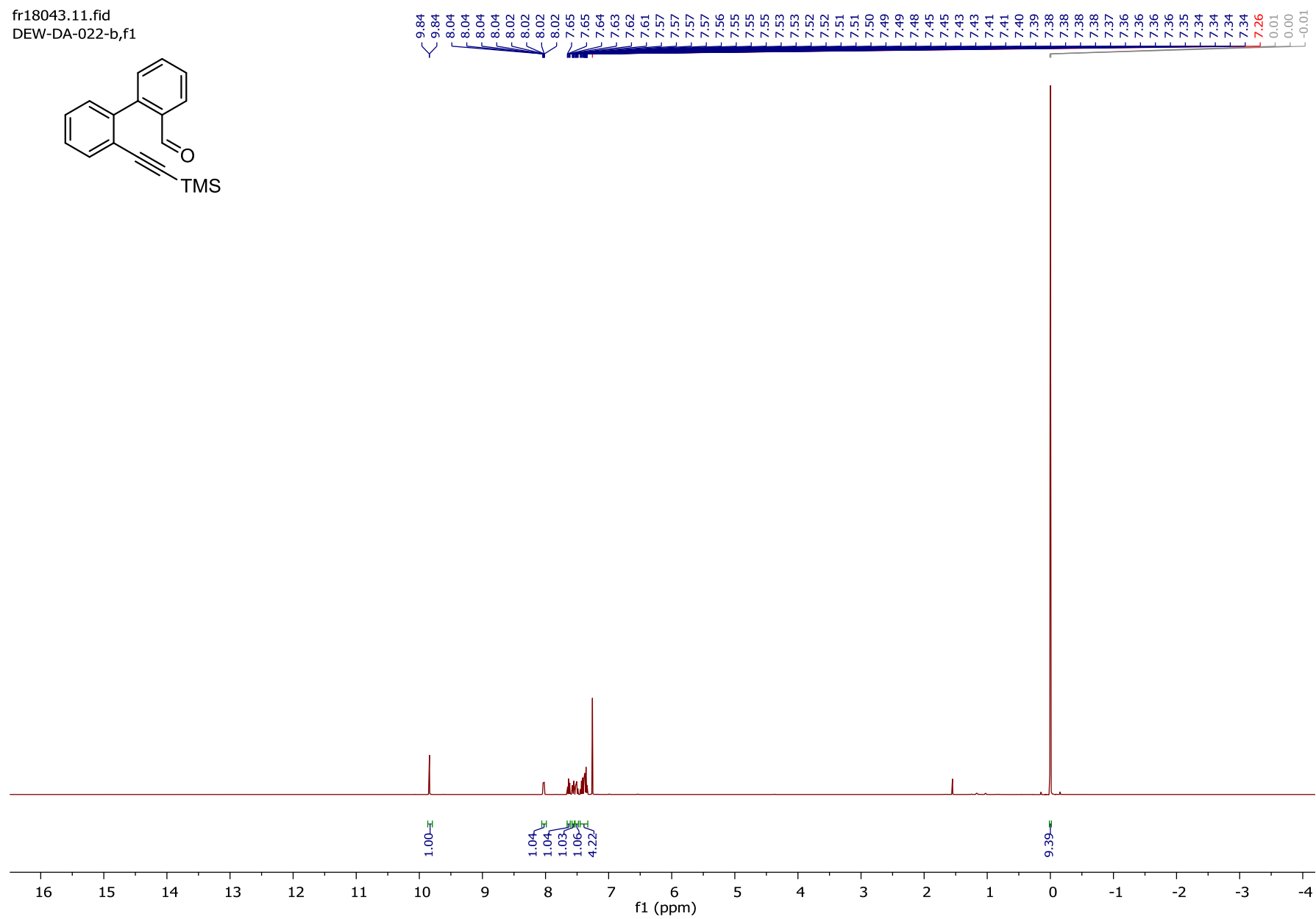
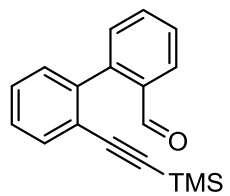
**Complex 29.** Alkyne **27** (17 mg, 0.082 mmol) was added to a solution of NH<sub>4</sub>PF<sub>6</sub> (18 mg, 0.11 mmol) and Cp(PPh<sub>3</sub>)<sub>2</sub>RuCl (40 mg, 0.055 mmol) in MeOH (4 mL) and the resulting red solution was stirred at reflux temperature for 1 h. After reaching ambient temperature, the precipitate was allowed to settle and the supernatant was removed via canula. The residue was triturated with MeOH and pentane (3 x 4 mL each) and the resulting orange powder was



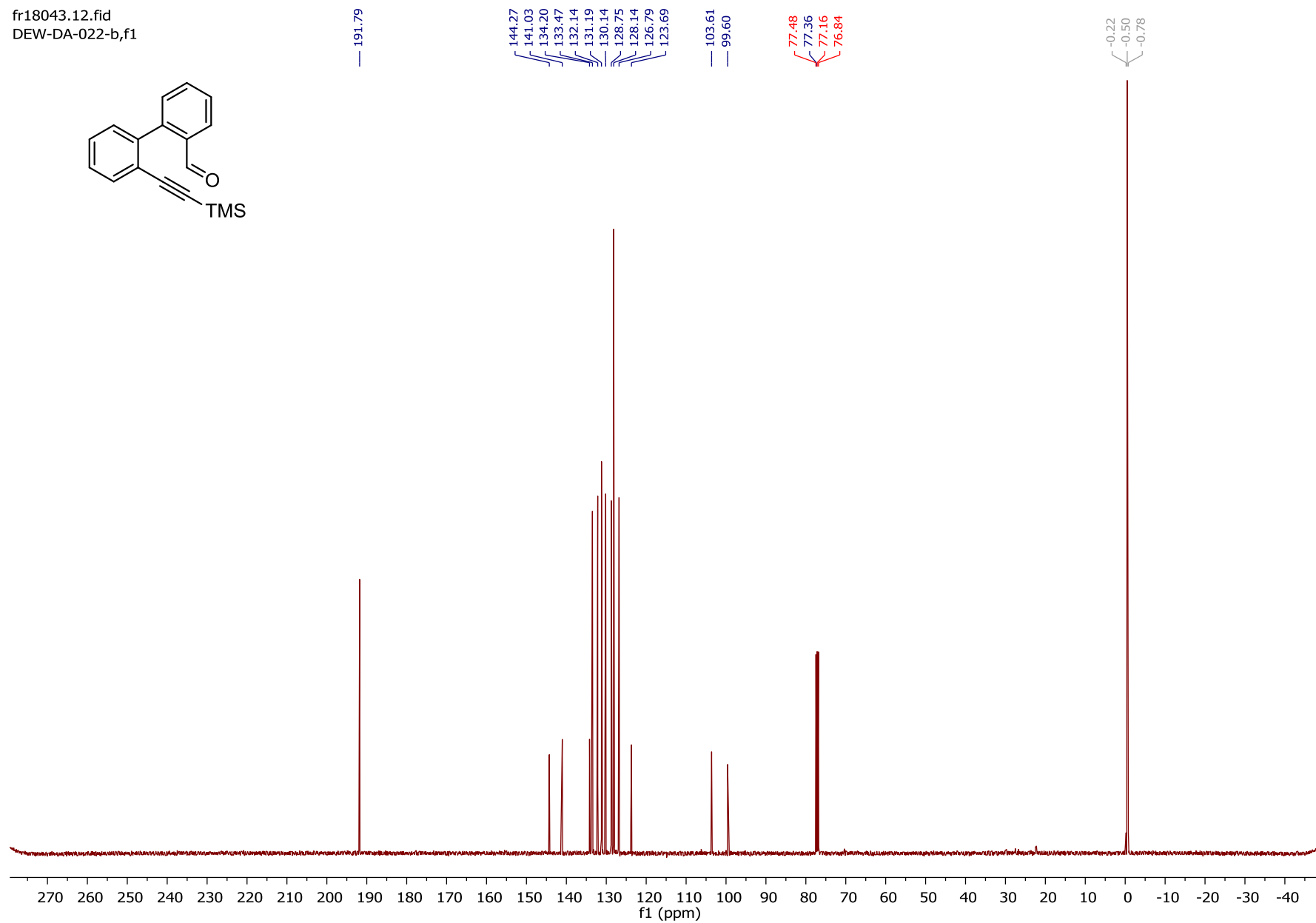
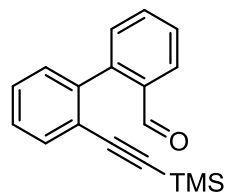
dried in vacuo to give complex **29** (51 mg, 88%; 3:7 mixture of **29a**:**29b**). Single crystals of analytically pure **29b** were obtained by recrystallization from MeOH. This compound showed the following analytical and spectroscopic properties: m.p. = 197-198°C; <sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 273K): δ = 8.04-7.97 (m, 2H; 2xCH), 7.71 (dd, *J* = 7.6, 1.7 Hz, 1H; CH), 7.58 (ddd, *J* = 7.6, 7.6, 1.4 Hz, 1H; CH), 7.46-7.38 (m, 5H; 5xCH), 7.34-7.26 (m, 4H; 4xCH), 7.23-7.09 (m, 6H; 6xCH), 7.08-6.99 (m, 12H; 12x CH), 6.92-6.56 (m, 7H; 7xCH), 5.45 (s, 5H; Cp), 4.15 (s, 1H; CHOCH<sub>3</sub>), 2.94 ppm (s, 3H; OCH<sub>3</sub>); <sup>13</sup>C NMR (125 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 273K): δ = 341.7 (dd, *J* = 14.8, 14.8 Hz, CRu), 135.0 (br, 2xCq), 134.6 (br, 2xCq), 133.6 (br, 6xCH), 132.9 (Cq), 132.8-132.7 (br, 7xCH), 132.5 (Cq), 131.8 (2xCH), 130.94 (CH), 130.92 (CH), 130.74 (Cq), 130.0 (CH), 129.8 (CH), 129.4 (CH), 129.0-128.8 (br, 13xCH), 128.78 (CH), 128.4 (CH), 127.8 (CH), 126.5 (Cq), 125.1 (2xCH), 125.0 (Cq), 95.2 (5xCH; Cp), 71.7 (CHOCH<sub>3</sub>), 55.4 ppm (OCH<sub>3</sub>), two quaternary carbons could not be unambiguously assigned due to overlap with other signals in the aromatic region; <sup>19</sup>F NMR (470 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 273K): δ = -73.2 ppm (d, *J* = 710.6 Hz, 6xF; PF<sub>6</sub><sup>-</sup>); <sup>31</sup>P NMR (202 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 273K): δ = 40.88 (d, *J* = 26.0 Hz, 1P; PPh<sub>3</sub>), 38.43 (d, *J* = 26.0 Hz, 1P; PPh<sub>3</sub>), -144.54 ppm (sept, *J* = 710.6 Hz, 1P; PF<sub>6</sub><sup>-</sup>); IR (ATR)  $\tilde{\nu}$  = 1629, 1435, 1093, 832 cm<sup>-1</sup>; MS (ESI): *m/z* (%): 911 (100) [*M*]<sup>+</sup>; HRMS (ESI): *m/z* calcd. for [C<sub>57</sub>H<sub>47</sub>OP<sub>2</sub>Ru]<sup>+</sup> 911.2140, found 911.2146; Anal. calcd. for C<sub>57</sub>H<sub>43</sub>F<sub>6</sub>P<sub>3</sub>ORu: C 65.08, H 4.12; found C 65.32, H 4.25.

<sup>5</sup> Y. L. Choi, C.-M. Yu, B. T. Kim, J.-N. Heo, *J. Org. Chem.* **2009**, *74*, 3948-3951.

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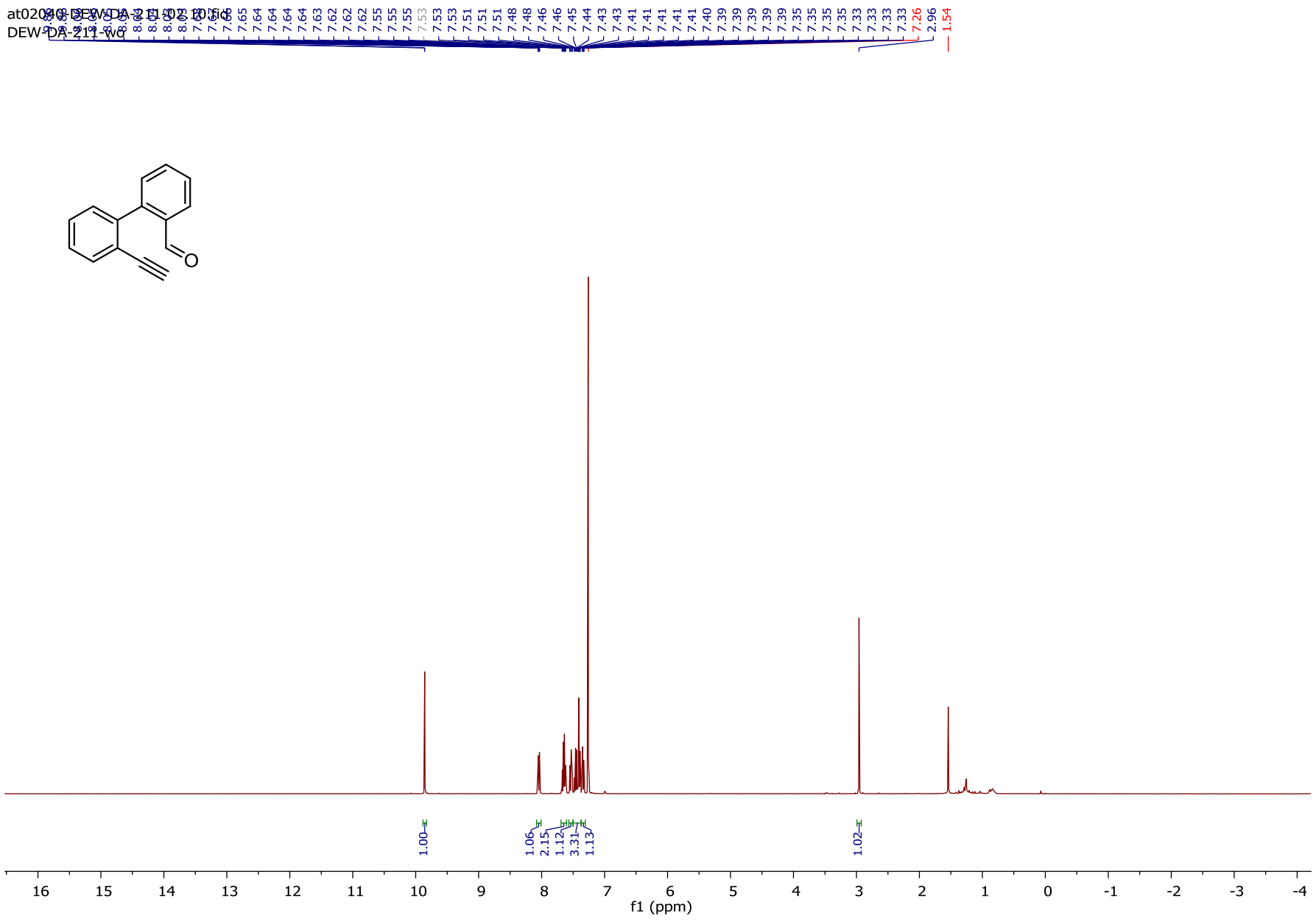
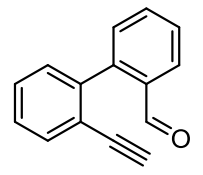


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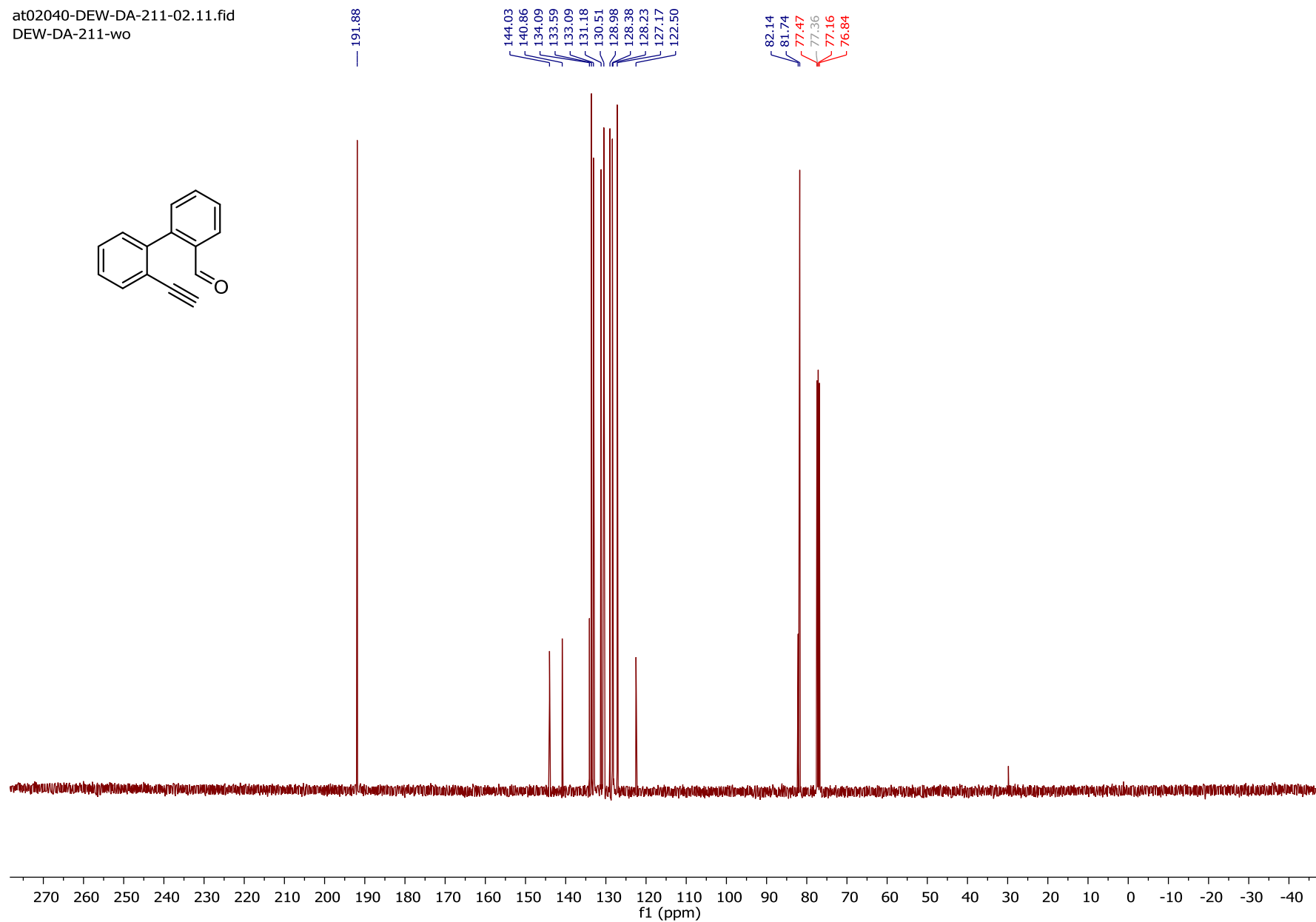
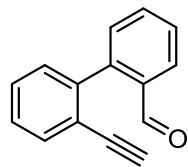




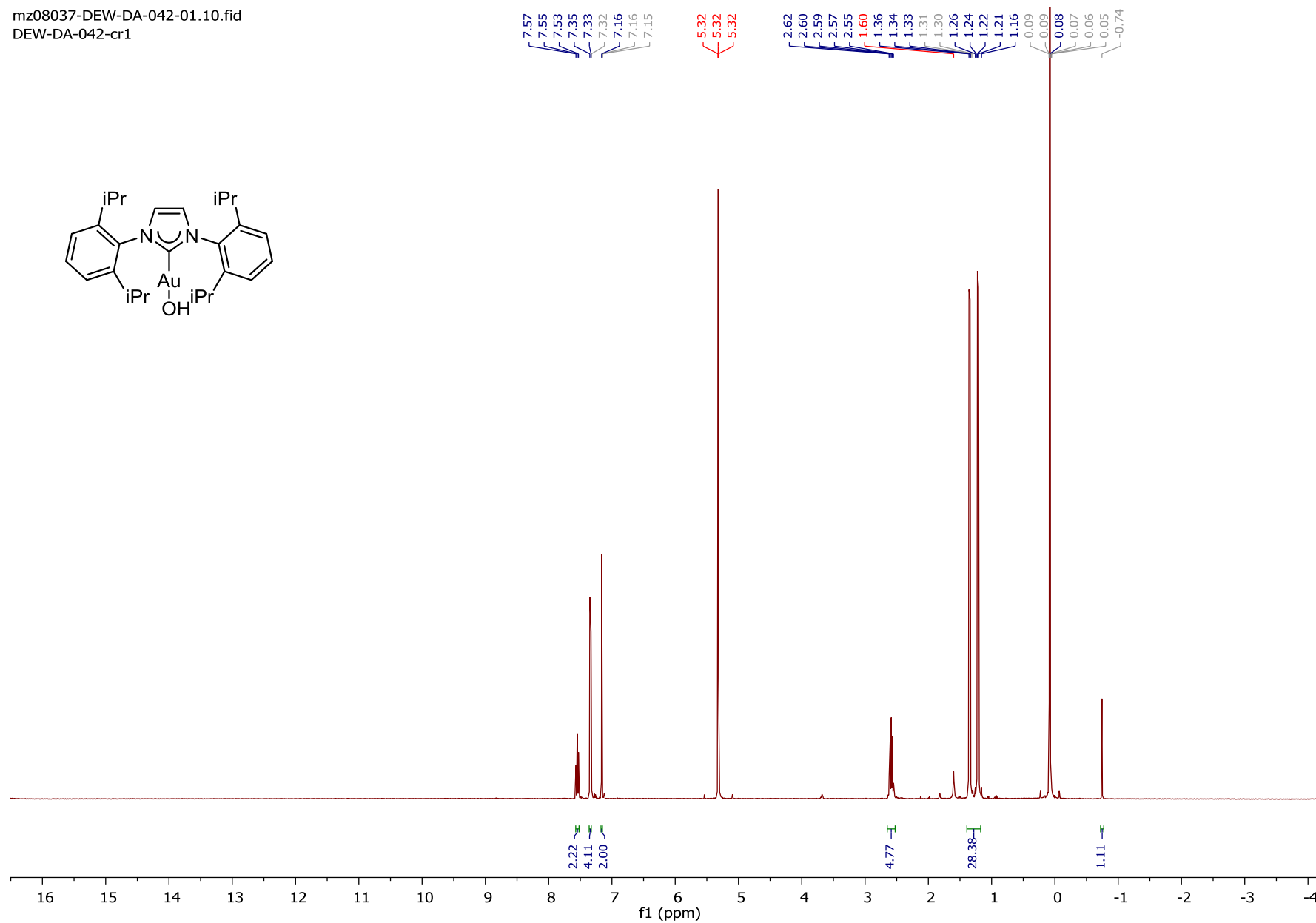
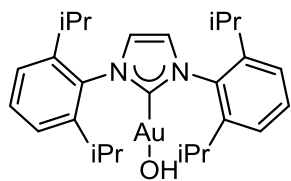
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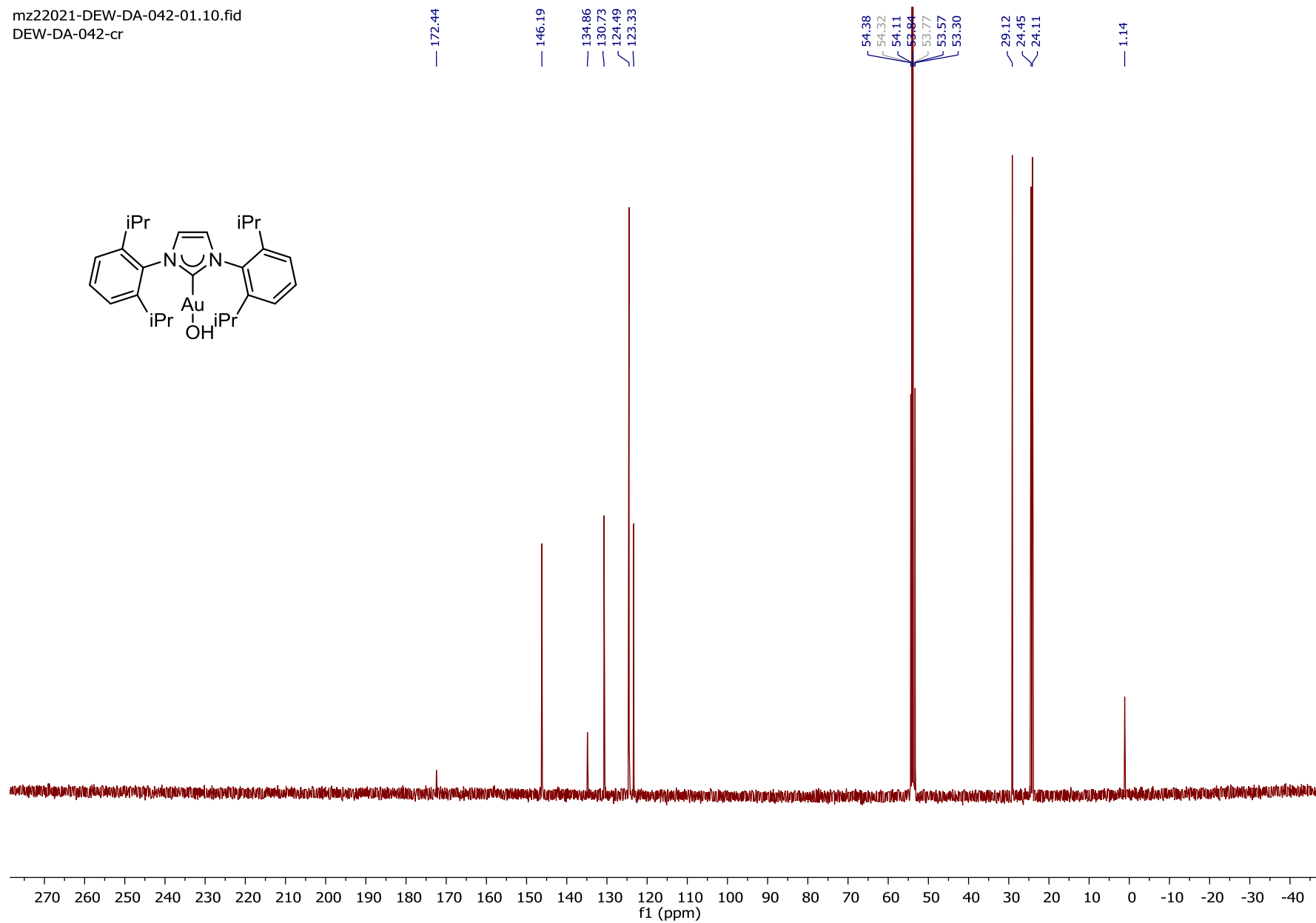
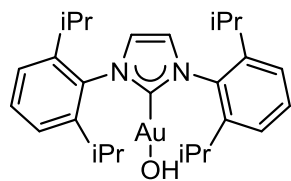
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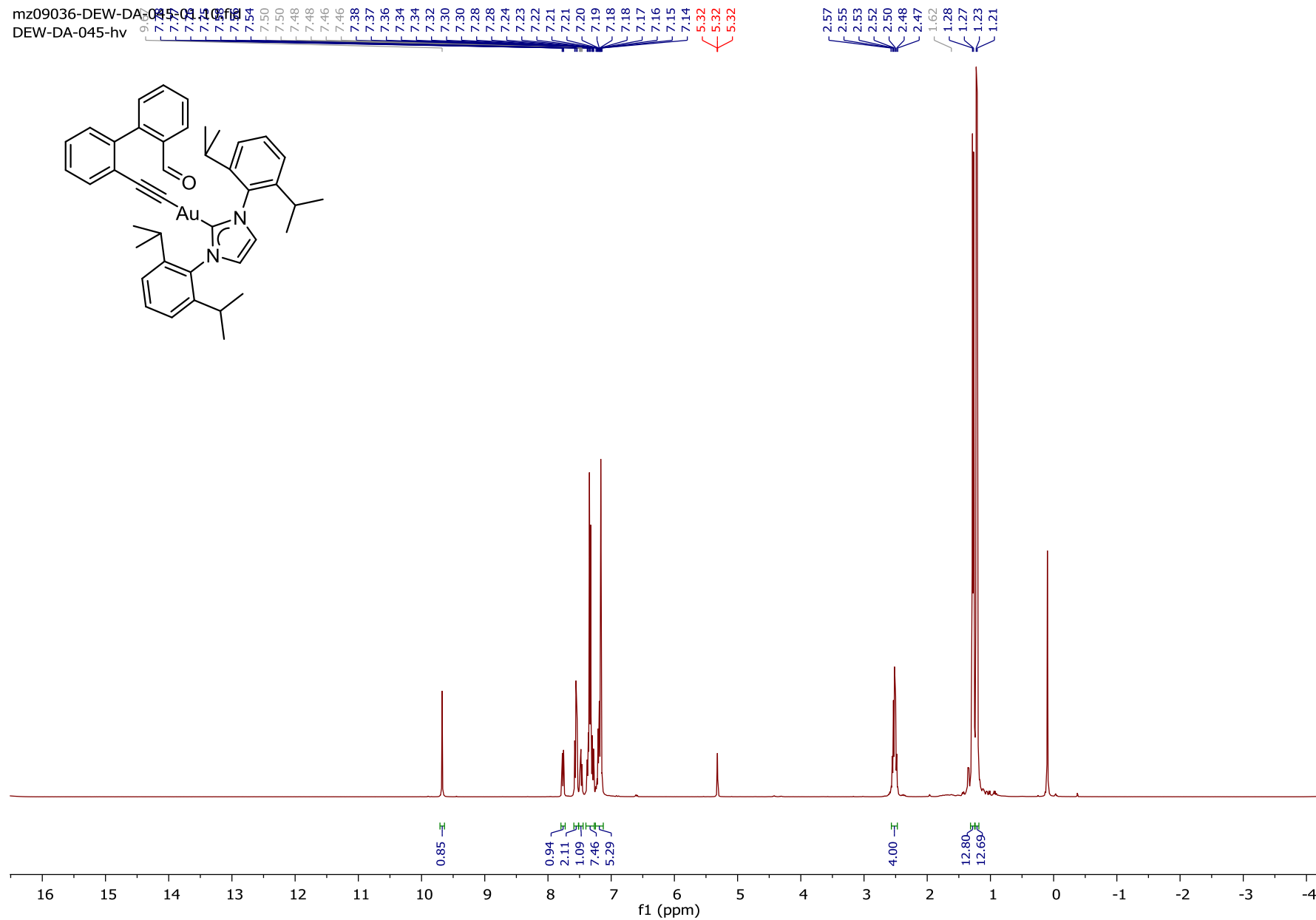
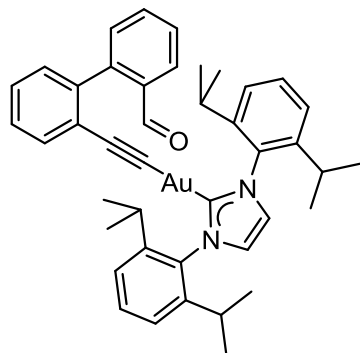
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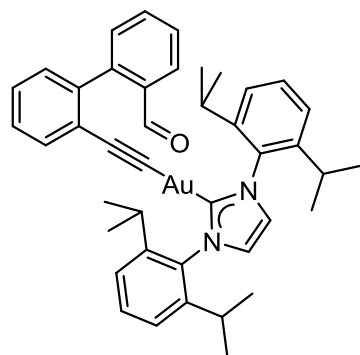
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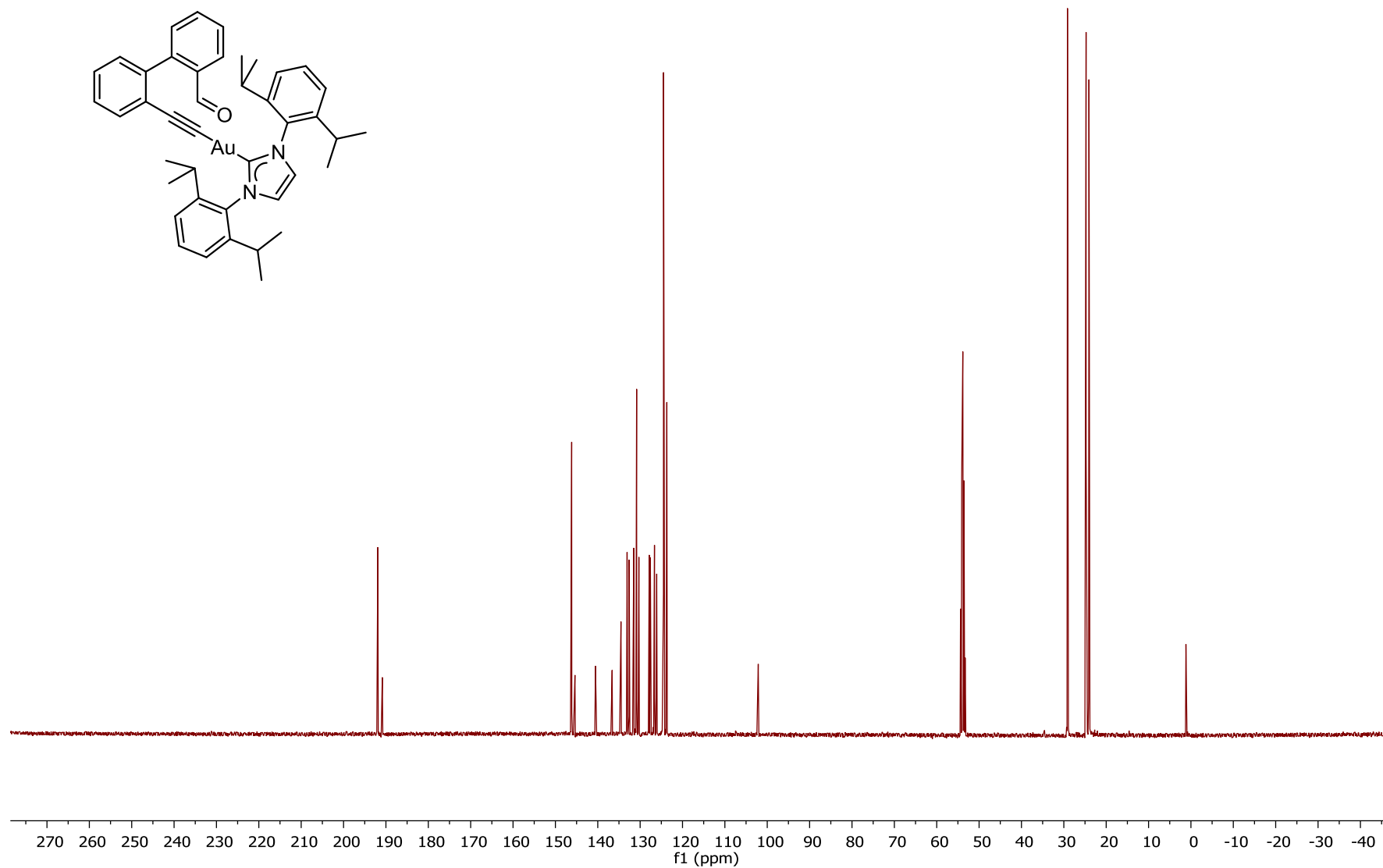


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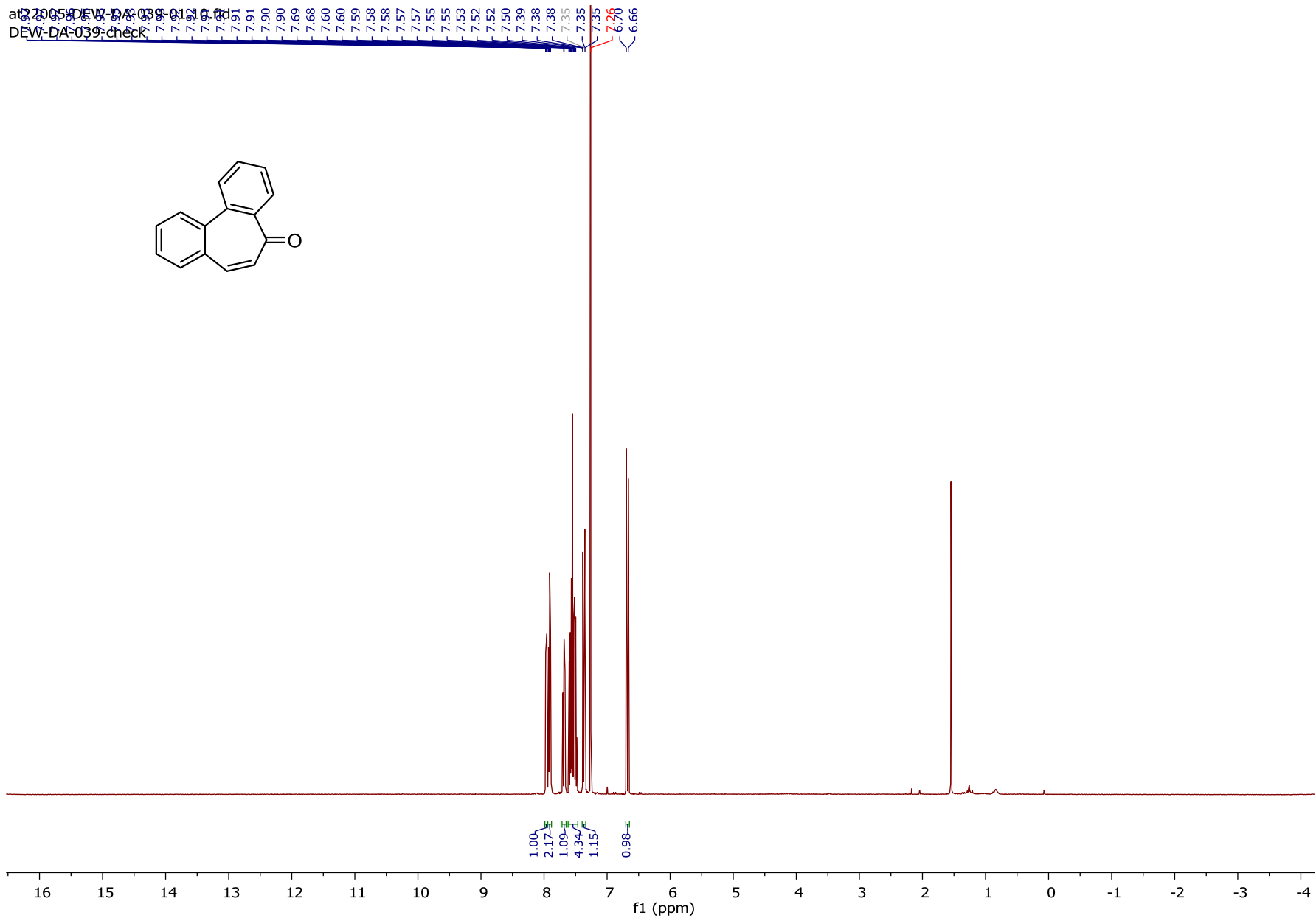
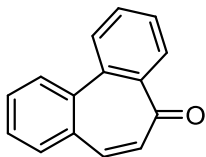
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126.62  
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102.12

54.38  
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53.57  
53.30

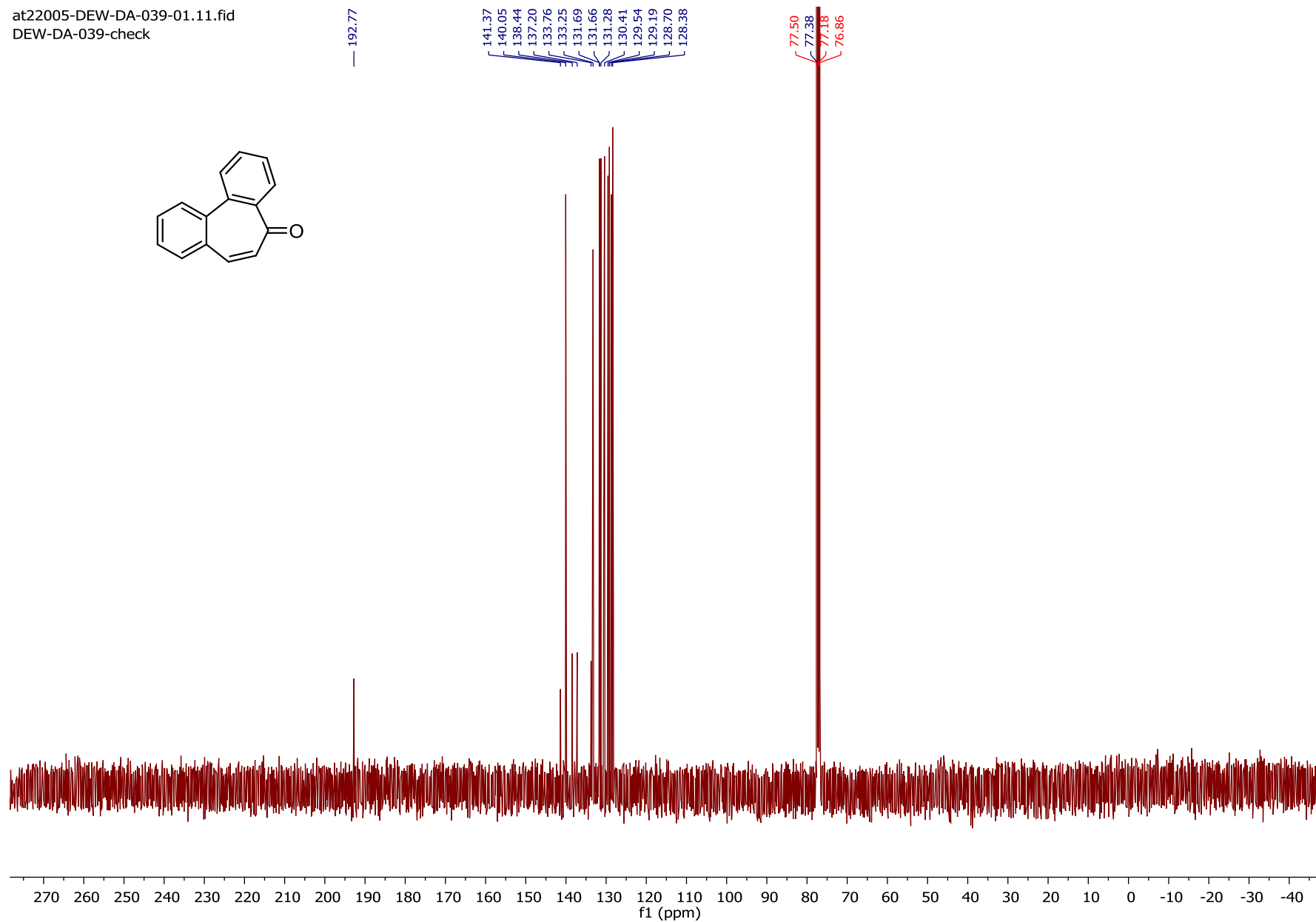
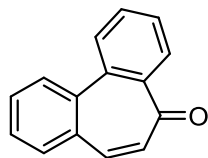
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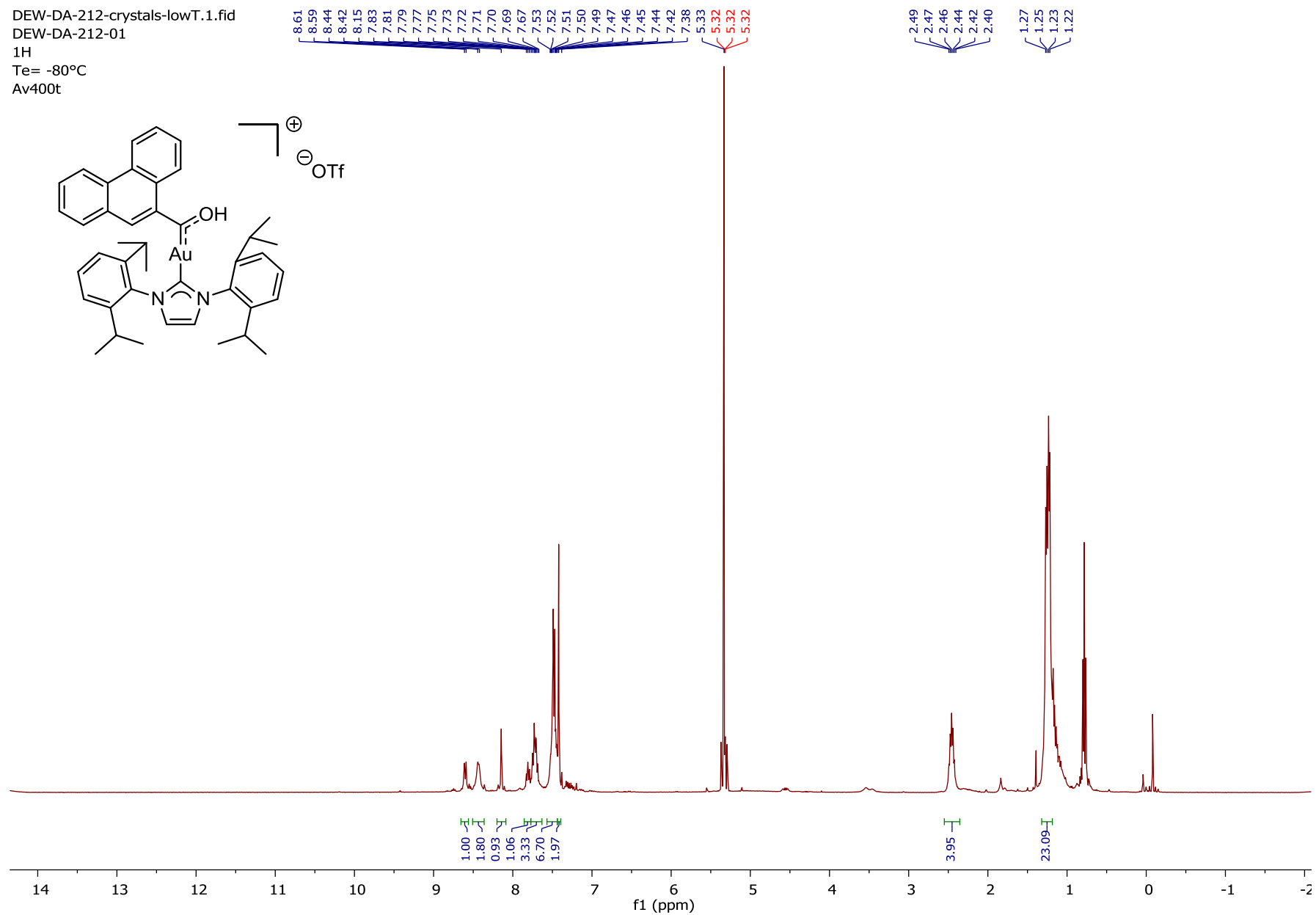
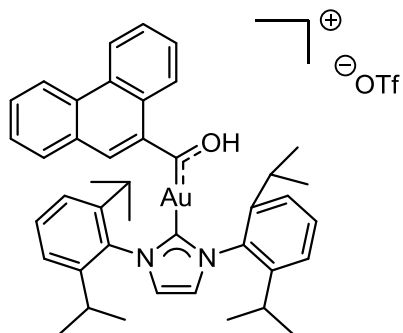


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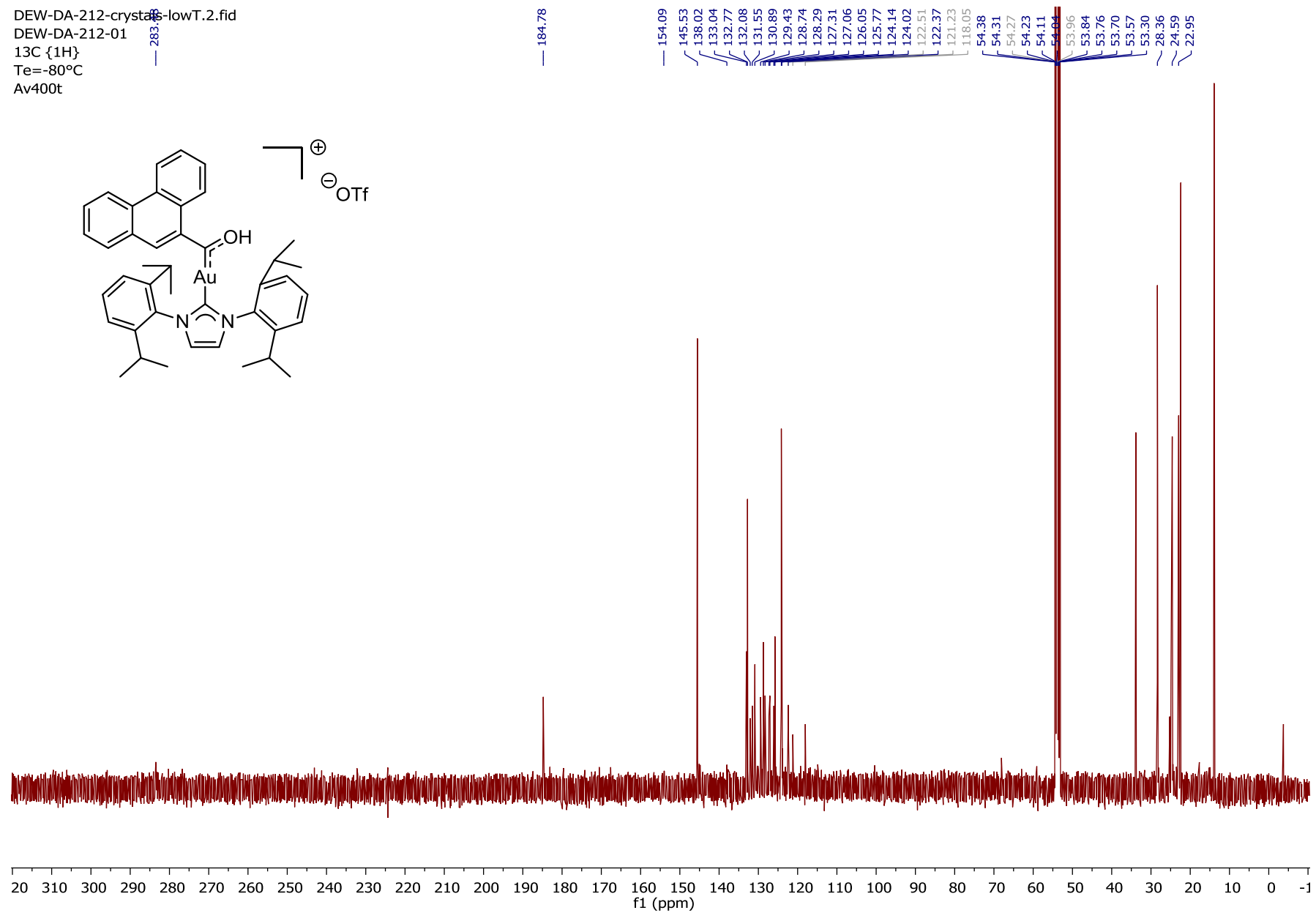
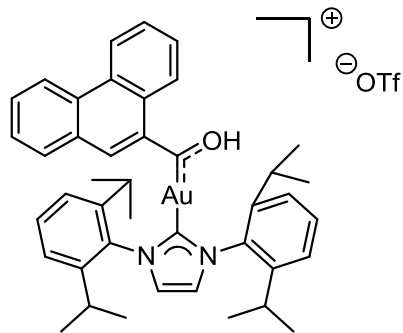




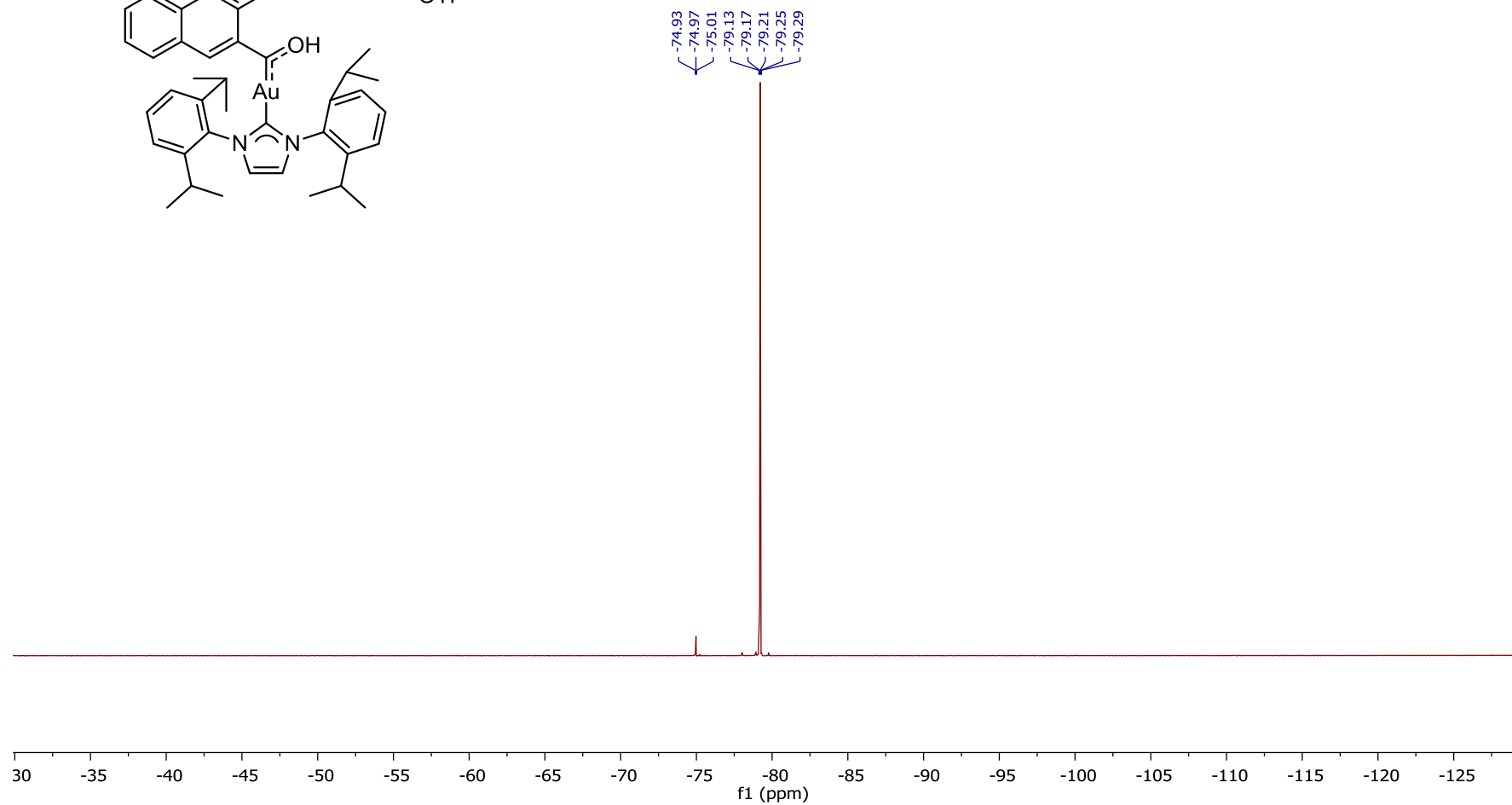
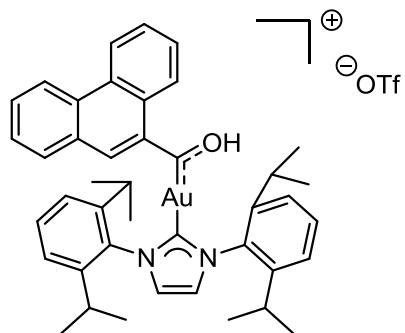
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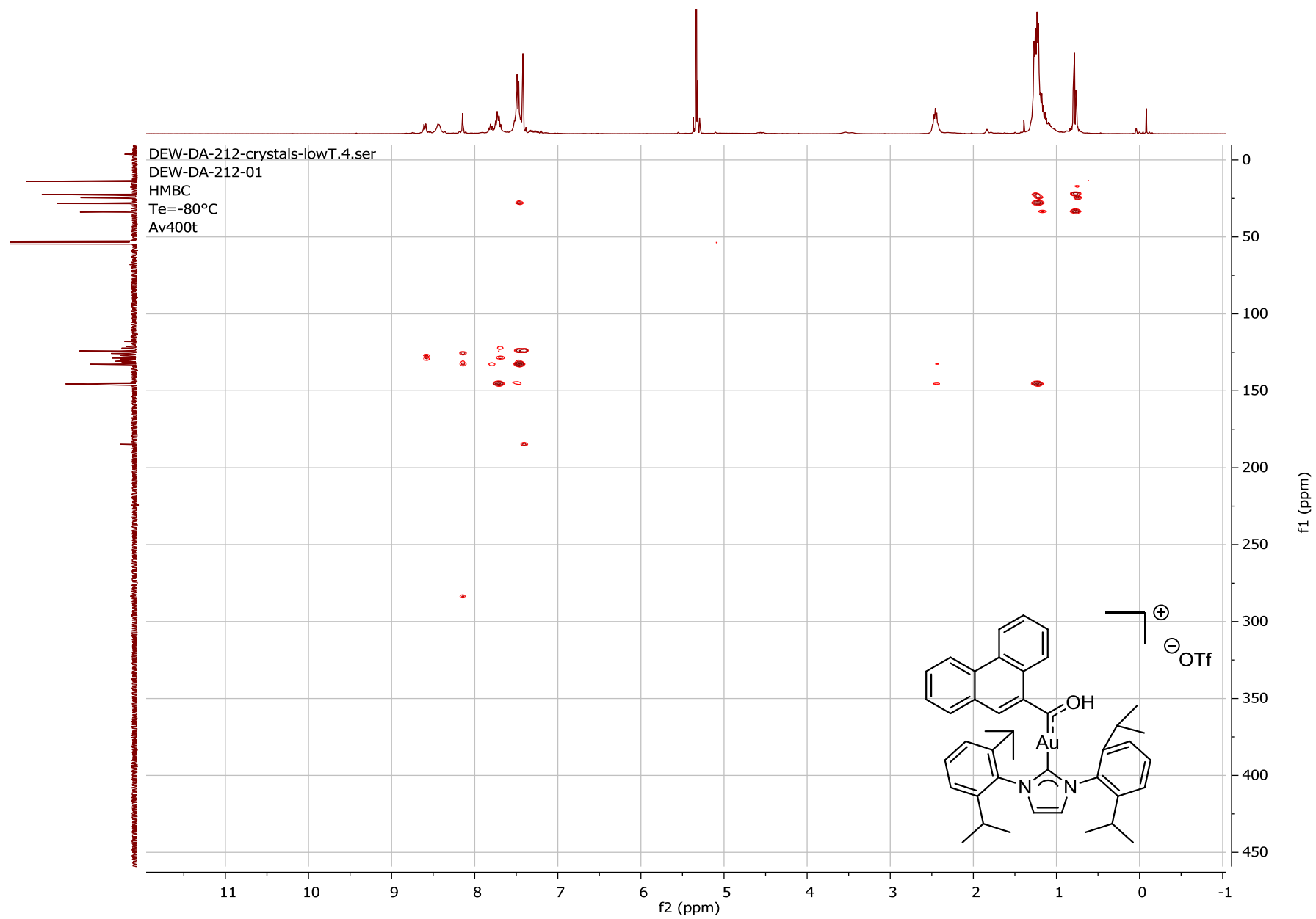


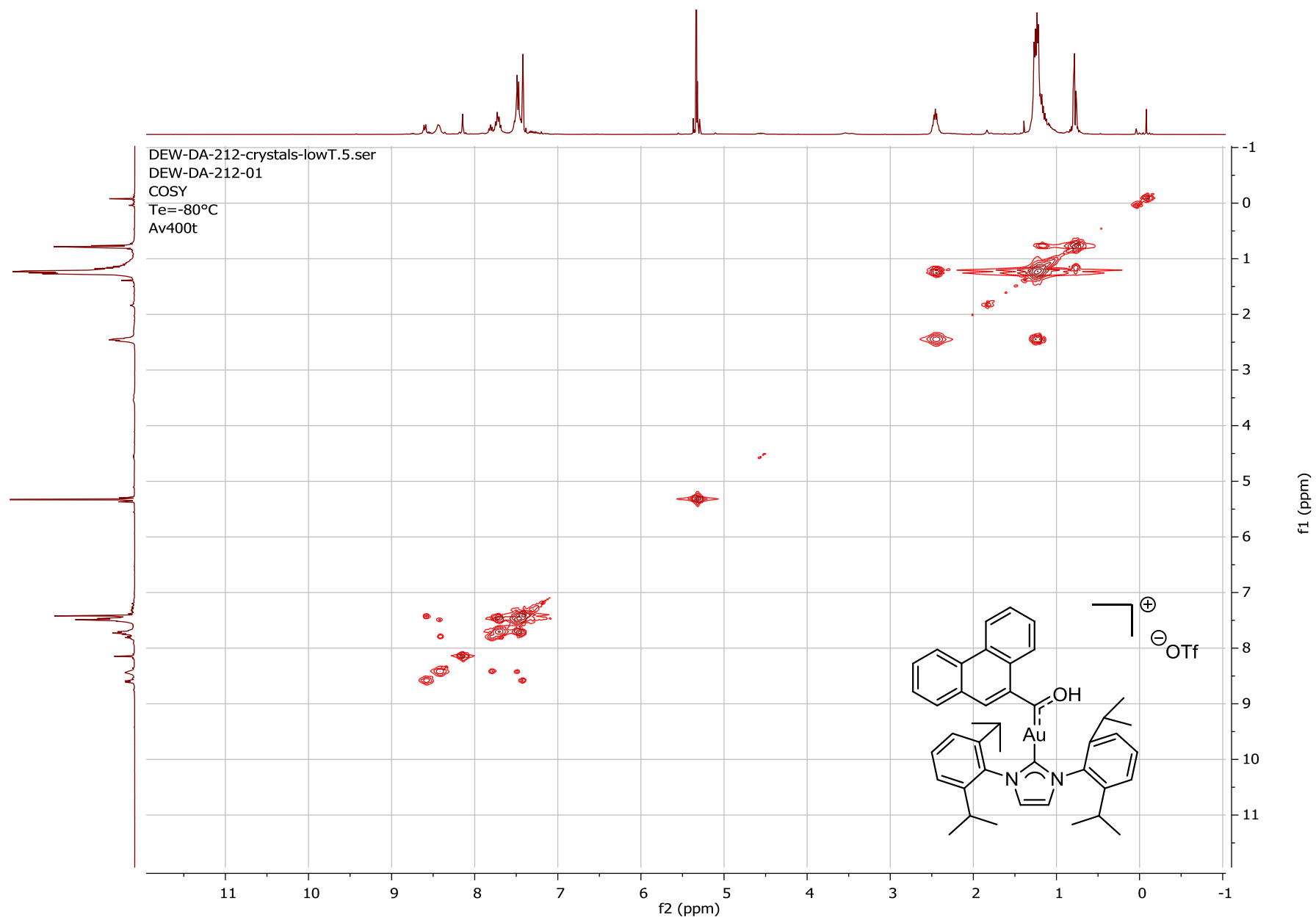
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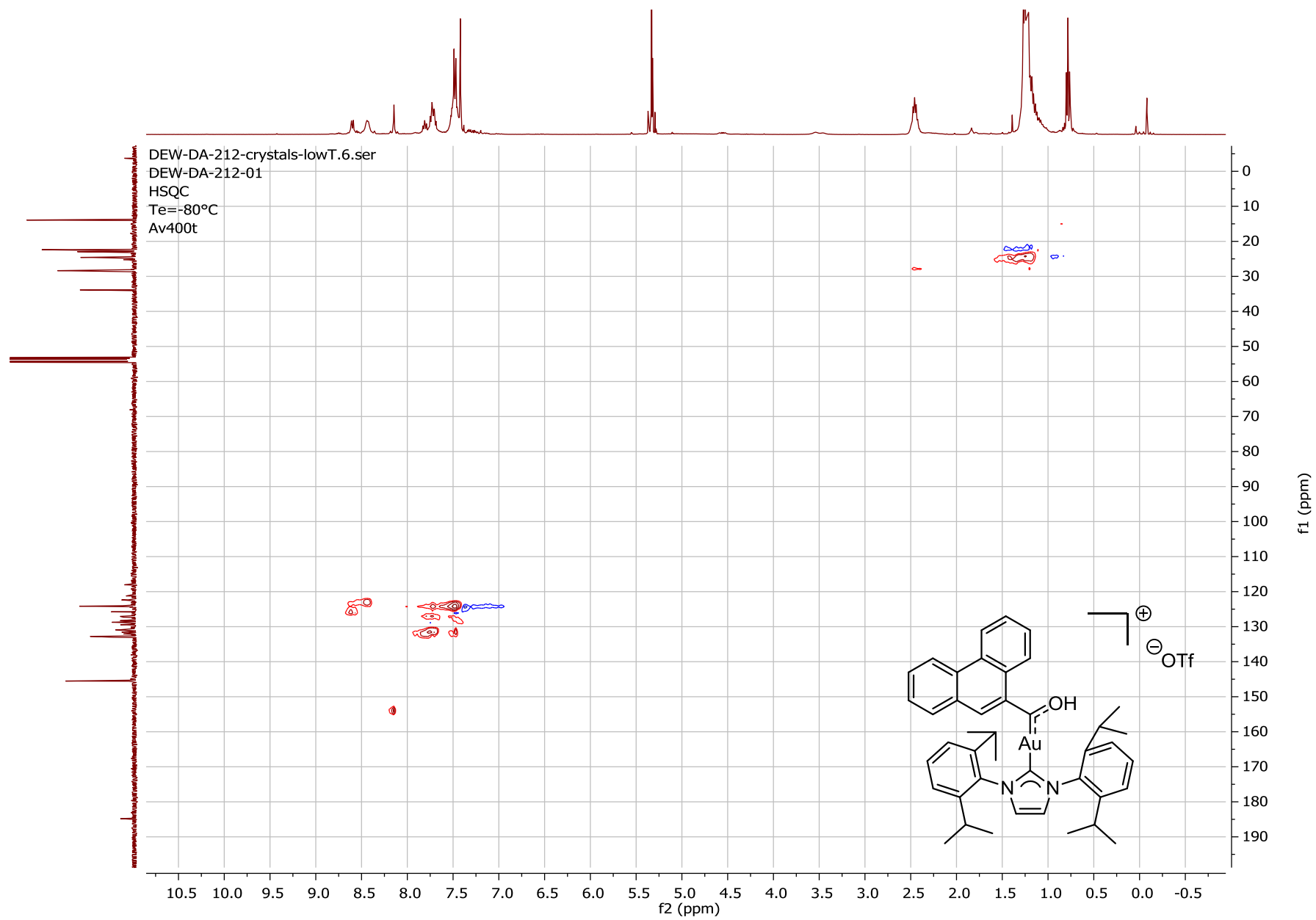


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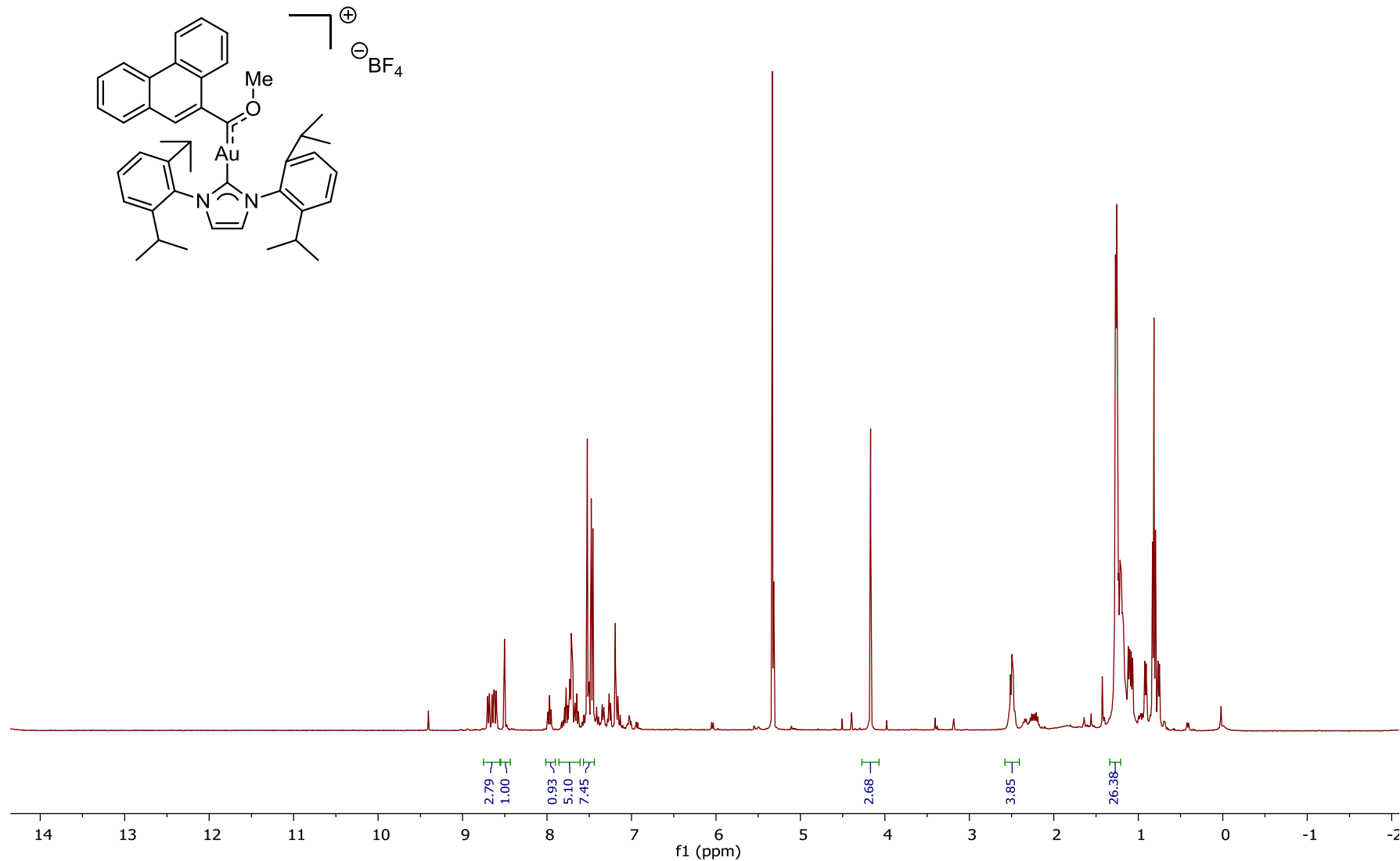
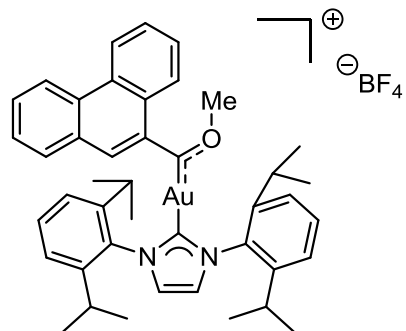




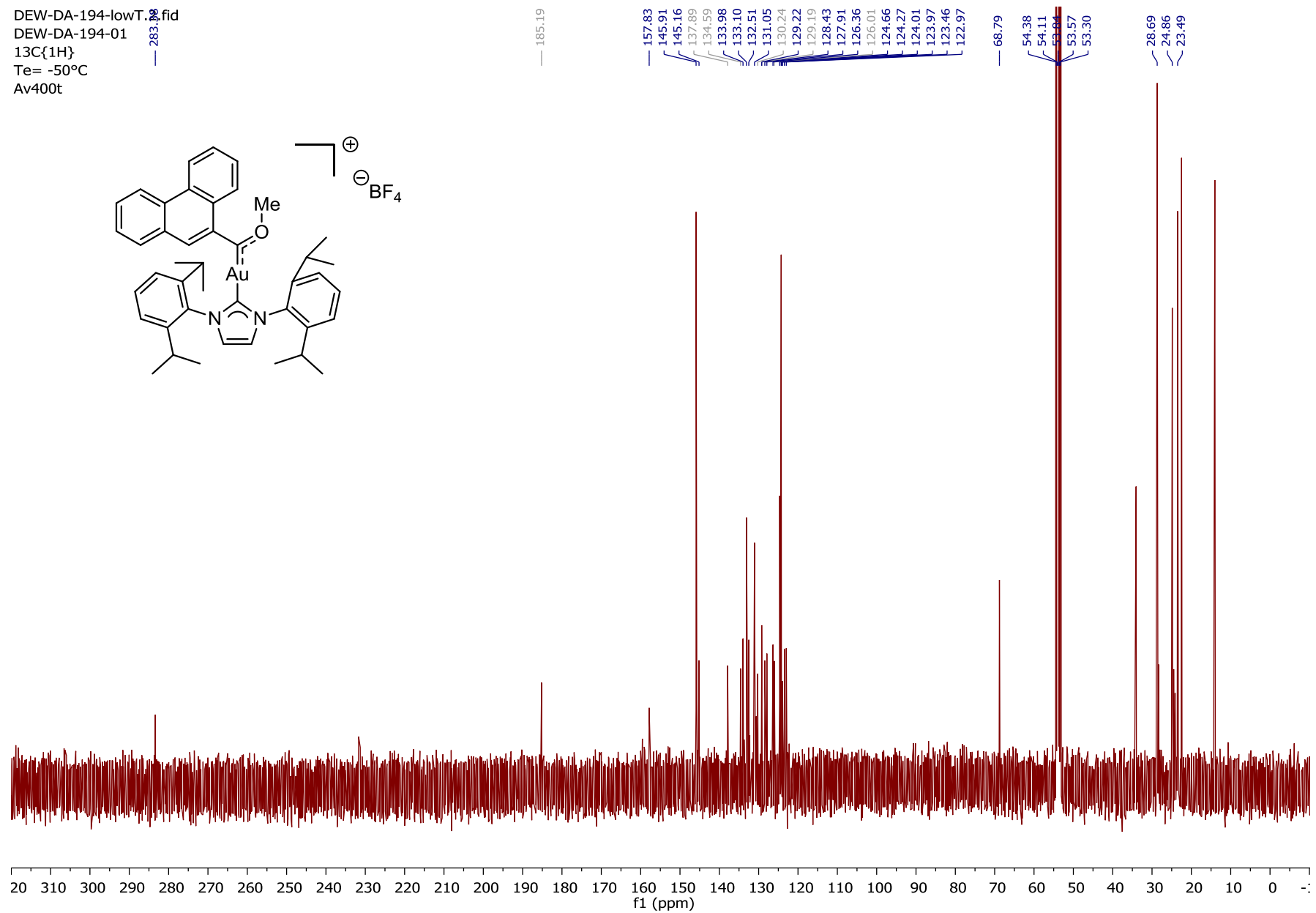
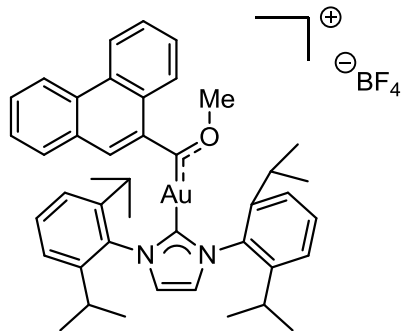
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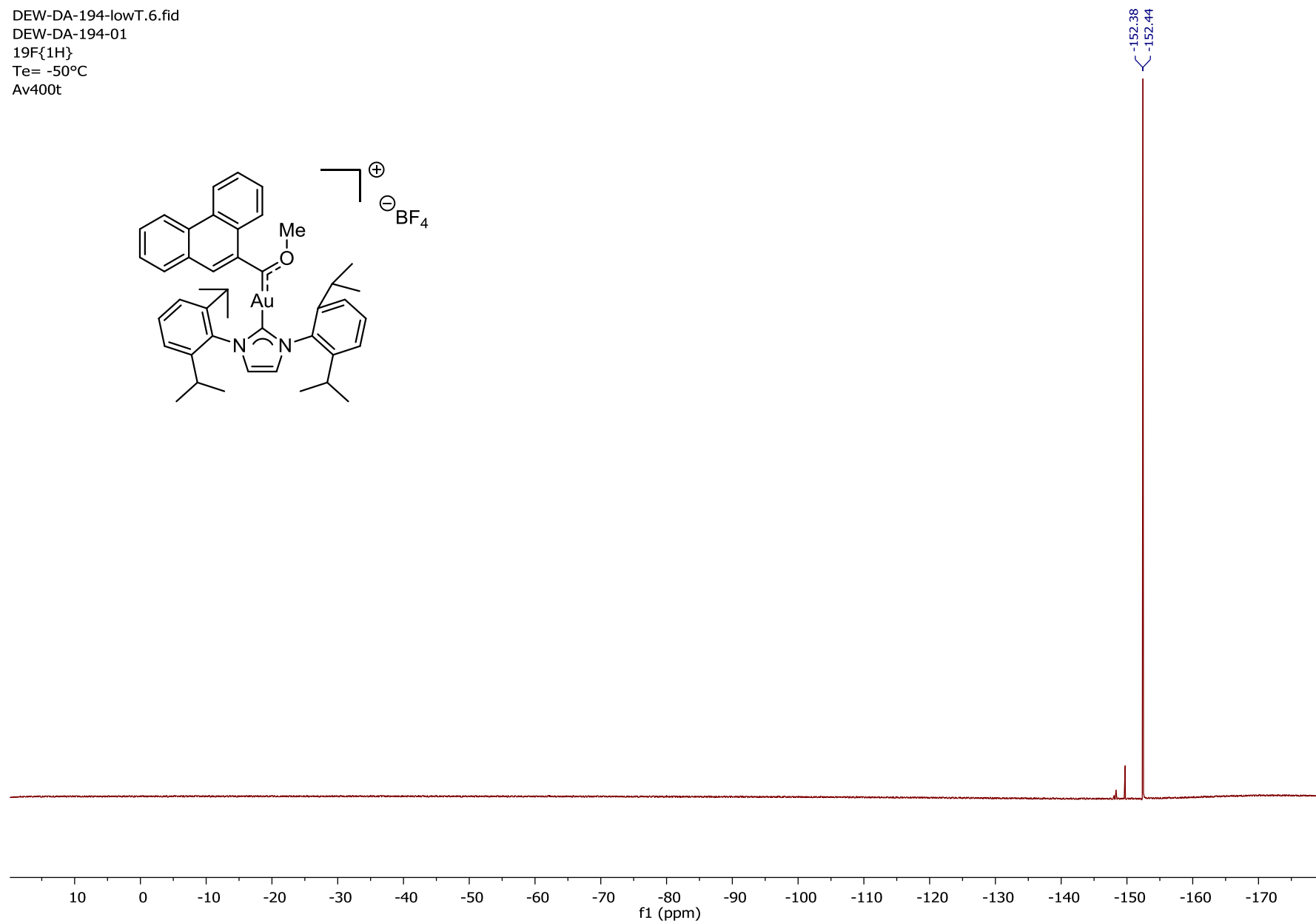
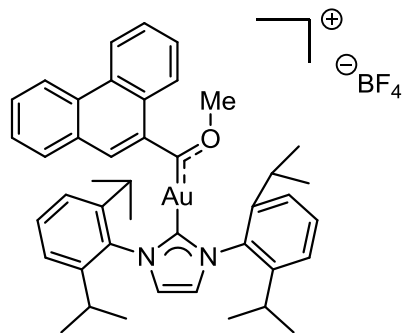


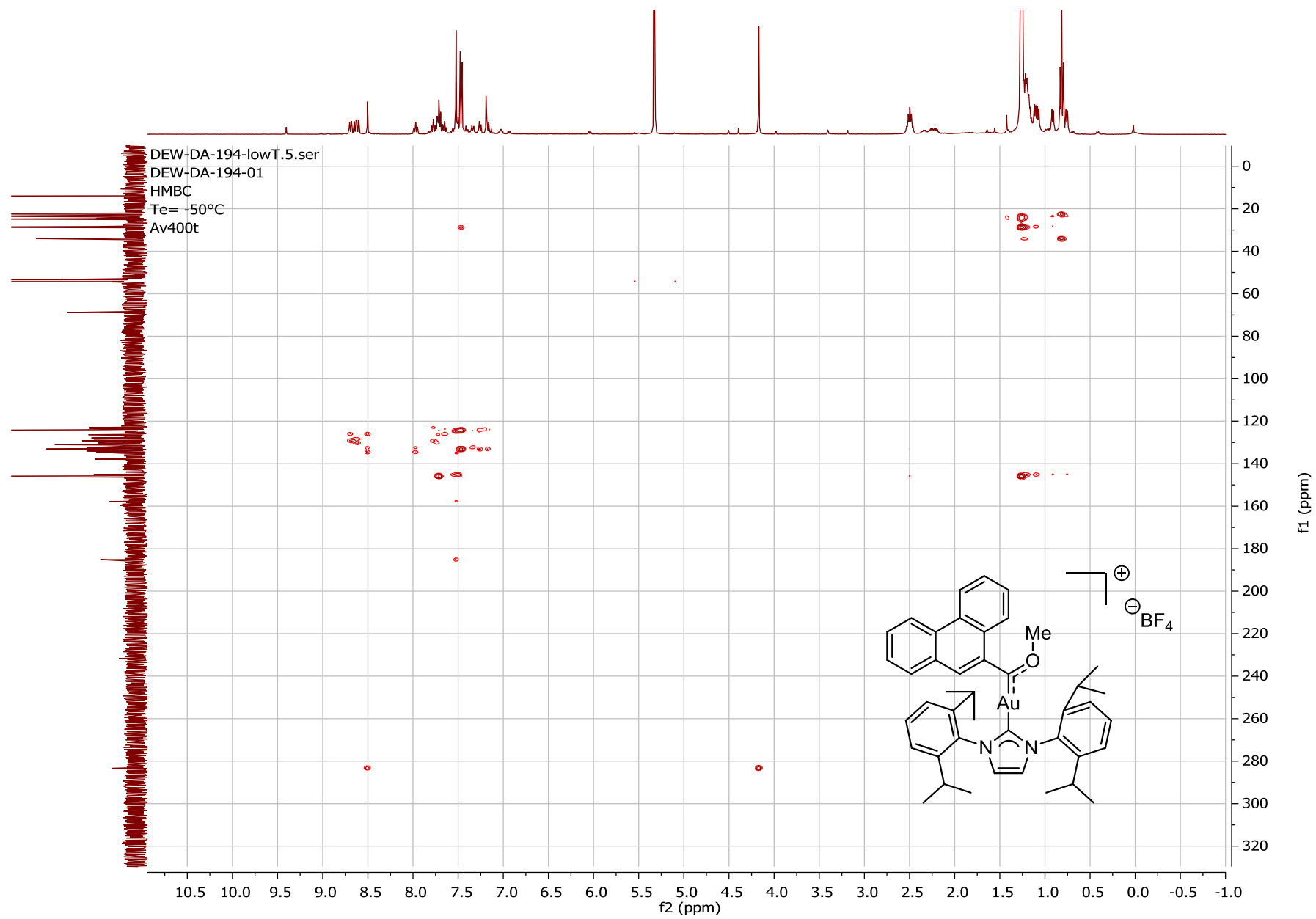
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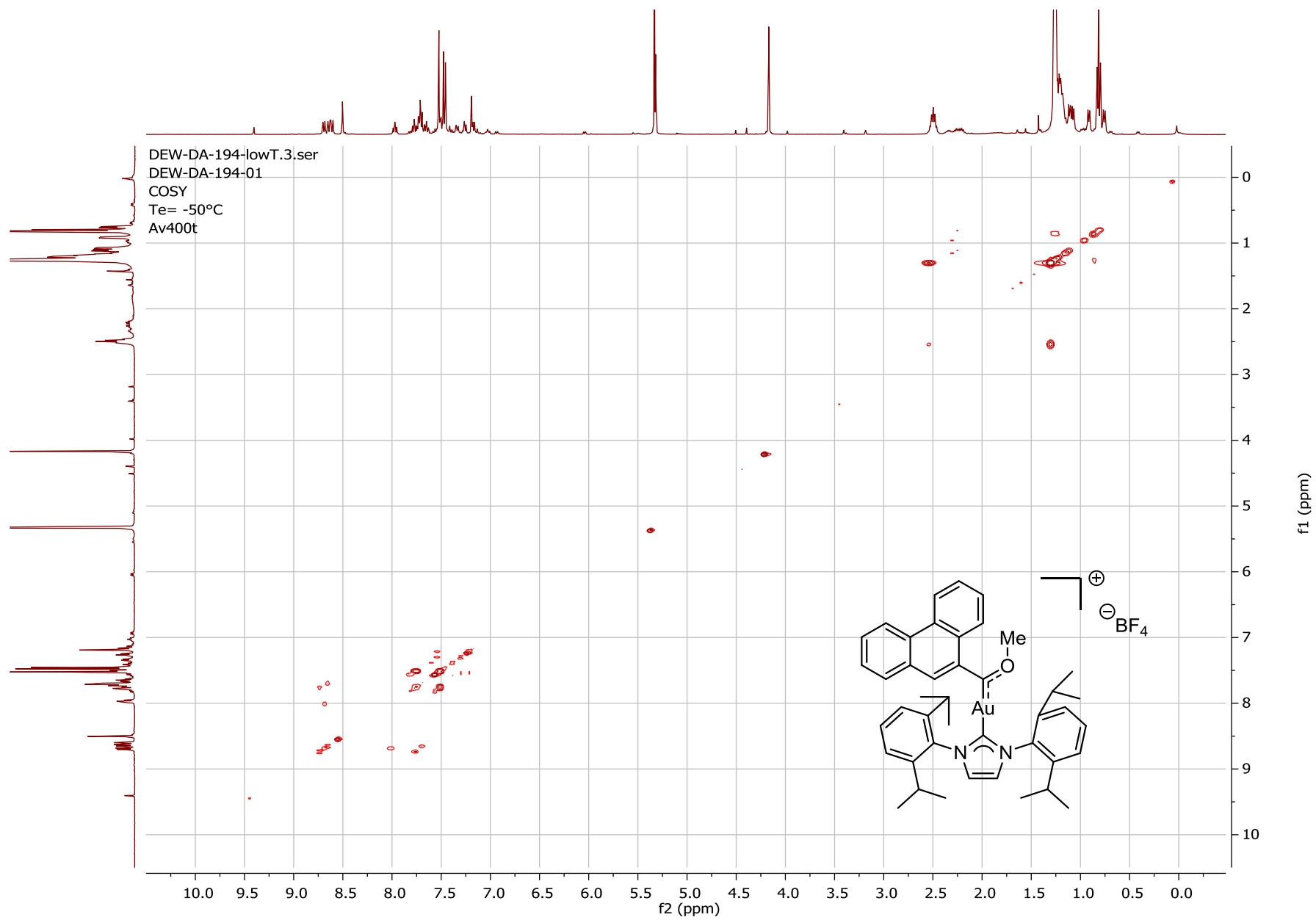


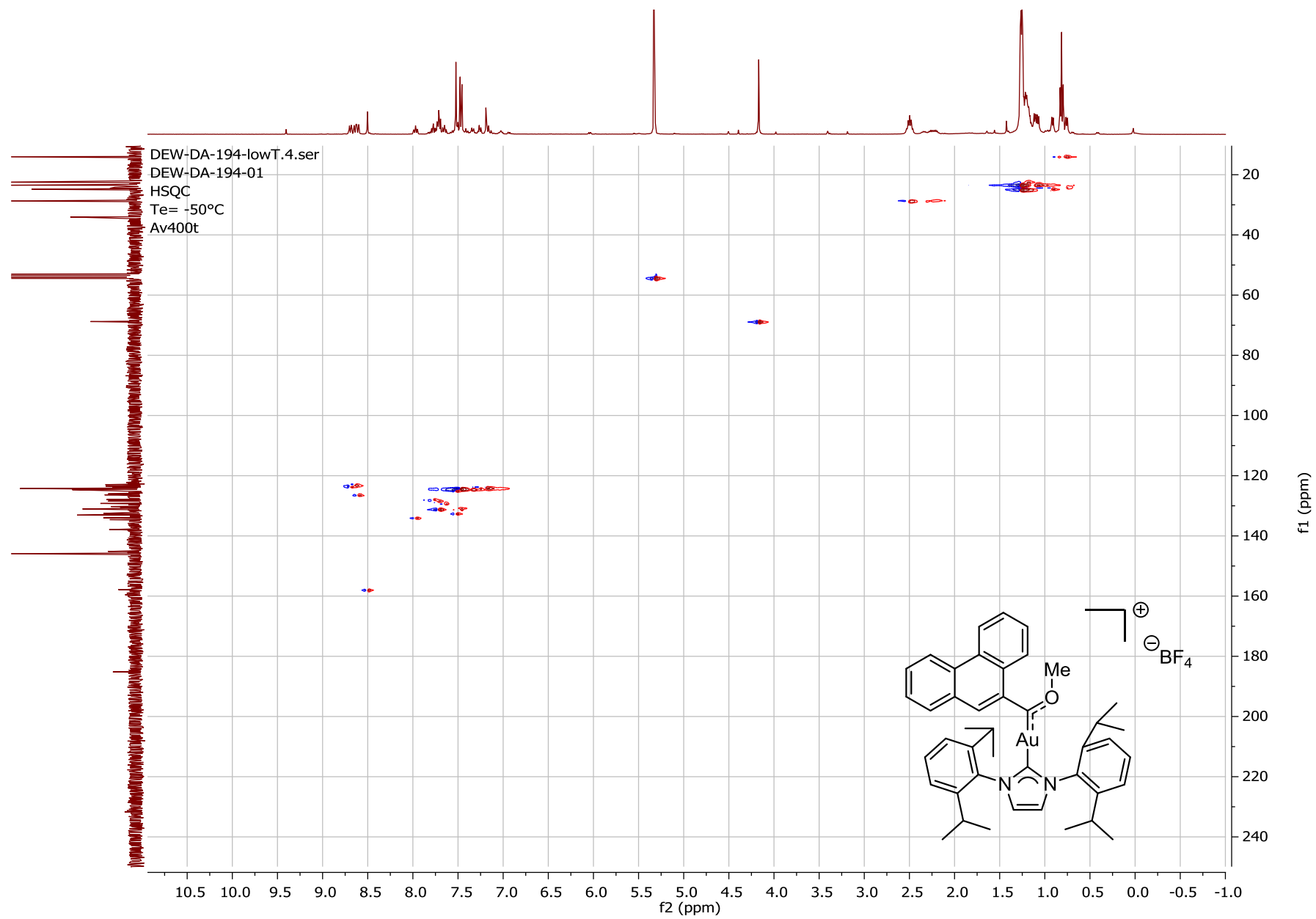


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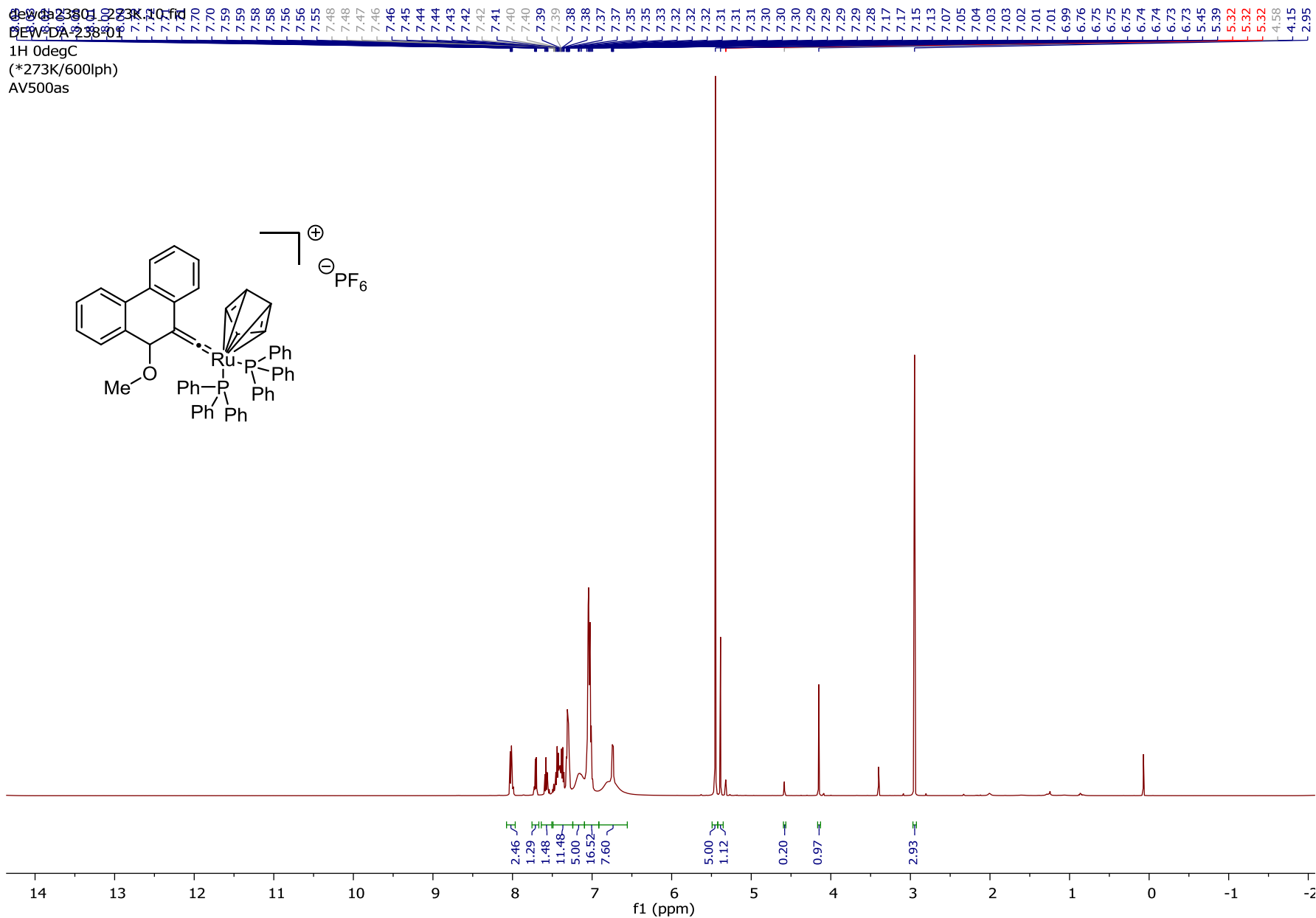
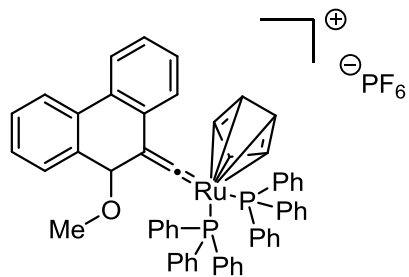








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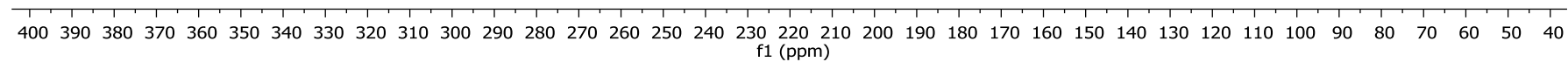
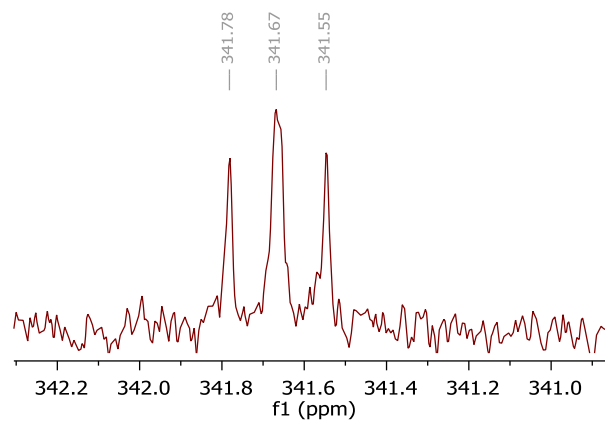
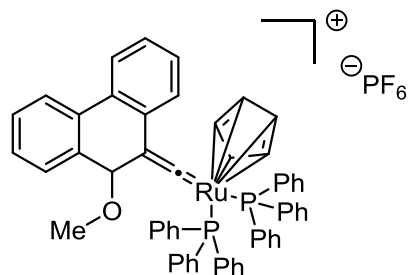


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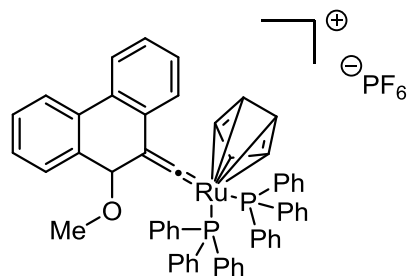
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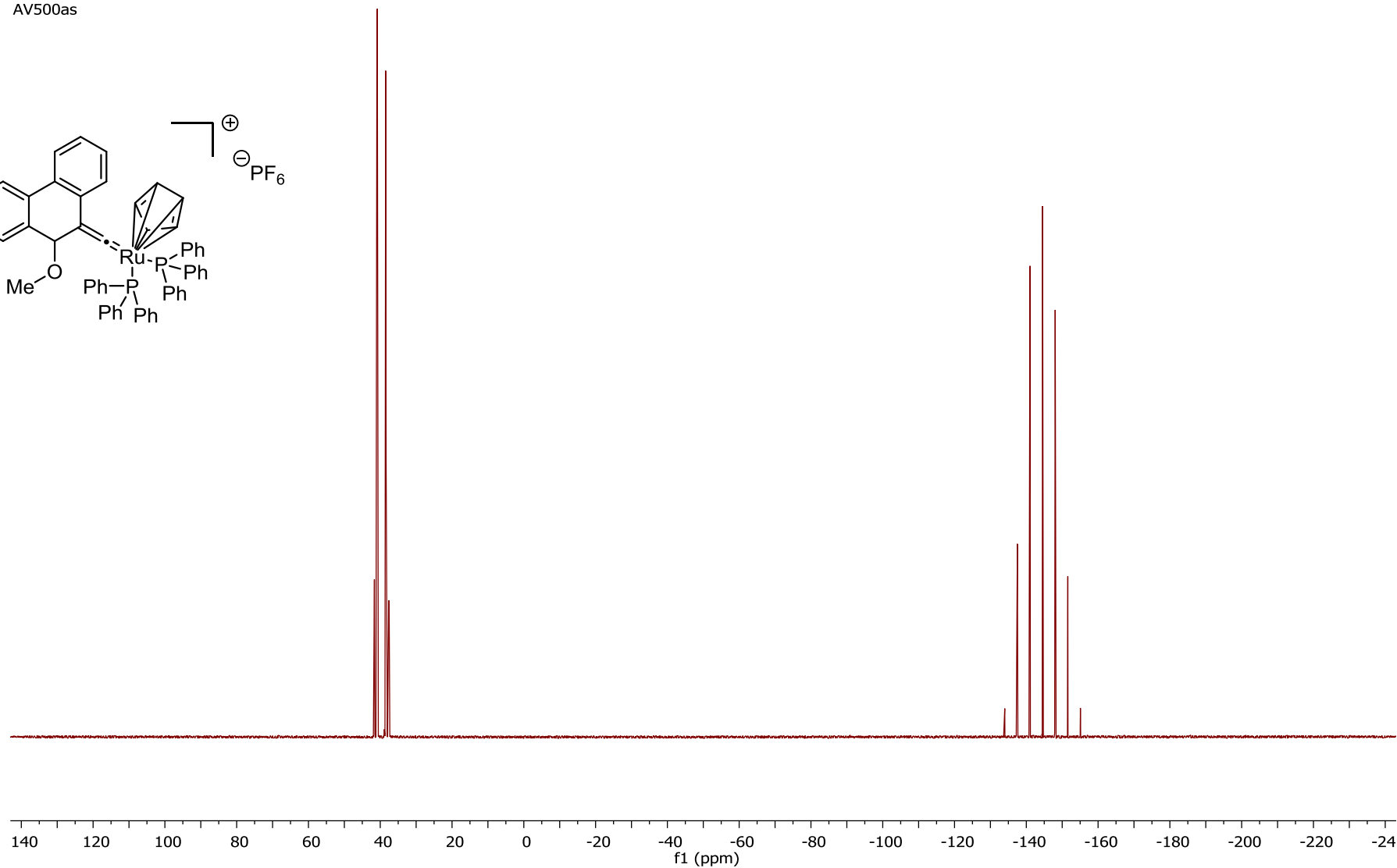
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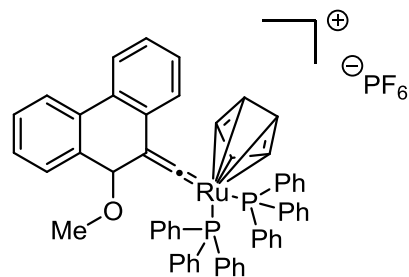
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AV500as



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AV500as



-72.43  
-73.94

