Highly efficient desymmetrisation of a chromiumtricarbonyl dibromonaphthalene complex by asymmetric Suzuki-Miyaura coupling

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CONTENTS:

1. General remarks

All reactions and manipulations were carried out under an inert atmosphere of argon or nitrogen. Solvents were purified on Al_2O_3 drying columns using a Solvtek system (unless otherwise noted) and further degassed by three successive "freeze-pump-thaw" cycles. ^{1}H- and ^{13}C-NMR spectra were recorded on a AMX-500 Bruker Avance spectrometer in the solvent indicated. ^{1}H- and ^{13}C-NMR chemical shifts (δ) are quoted in parts per million (ppm) relative to the TMS scale (C_6D_6: $\delta_C \equiv 128.0$ ppm; residual C_6D_5H: $\delta_H \equiv 7.15$ ppm; $CDCl_3$: $\delta_C \equiv 77.05$ ppm; residual $CHCl_3$: $\delta_H \equiv 7.26$ ppm; CD_2Cl_2: $\delta_C \equiv 53.9$ ppm; residual $CHDCl_2$: $\delta_H \equiv 5.32$ ppm). Coupling constants J are quoted in Hz. Infrared spectra were recorded on a Perkin–Elmer Spectrum One spectrophotometer using a diamond ATR Golden Gate sampler. Electron impact (EI) HRMS mass spectra were obtained using a *Finningan MAT 95* operating at 70eV. Electrospray ionization (ESI) HRMS analyses were measured on a VG analytical 7070E instrument. Optical rotations were measured on a Perkin Elmer 241 polarimeter using a quartz cell (l = 10 cm) with a Na high-pressure lamp (λ = 589 nm). Analytical HPLC was performed using an Alligent 1100 series with a JASCO PU–980 pump and Aligent 1100 Series detection system.

Commercially available chemicals were used as received unless otherwise stated: toluene purum (VWR), $PhB(OH)_2$ (Acros), *p*-$MePhB(OH)_2$ (Acros), *p*-$MeOPhB(OH)_2$ (Acros), *p*–$CF_3PhB(OH)_2$ (Aldrich), (*cis*-propenyl)$B(OH)_2$ (Aldrich), (*trans*-cyclohexylvinyl)$B(OH)_2$ (Aldrich), *n*-$BuB(OH)_2$ (Acros), KF (Aldrich, dried under vacuum), (*t*-Bu)$_3$P (Acros, stored in glove-box), $NaBH_3CN$ (Acros), $LiBH_4$ (Acros, stored in glove-box), DABCO (Fluka, sublimed under vacuum and stored in glove-box). $Pd(dba)_2$ [1] and $[(t\text{-}Bu)_3PH][BF_4]$ [2] were prepared according to reported procedures. $[Cr(CO)_3$(5,8-dibromonaphthalene)] (**1**), [3] [Cr(5-bromonaphthalene)$(CO)_3$] ((*S*)-**3**), [4] [Cr((5-phenyl)naphthalene)$(CO)_3$] ((*S*)-**8a**) [5] and phosphoramidite ligand L* [6] were synthesised using our protocols. $LiBH_4$ solution in DME was prepared according to a literature procedure[7] and titrated before use by injecting an aliquot into a hydrolyzing mixture of glycerine and water and measuring the hydrogen gas evolved.

2. Representative procedure for the asymmetric Suzuki-Miyaura coupling

A Schlenk containing $Pd(dba)_2$ (3.0 mg, 0.005 mmol, 5 mol%) and phosphoramidite ligand L* (4.4 mg, 0.006 mmol, 6 mol%) was purged by three successive vacuum/Ar sequences and refilled with Ar. Degassed toluene (3 mL) was added and the solution was stirred for 45 min at room temperature. Then, the solution was cooled to 10 ^{o}C and stirred for an additional 20 min before adding complex **1** (42.8 mg, 0.101 mmol, 1 eq.), boronic acid **6** (0.502 mmol, 5 eq.) and KF (21.7 mg, 0.369 mmol, 3.5 eq.). The reaction mixture was stirred at 10 °C for the amount of time indicated. The solution was filtered through silica gel under N_2 atmosphere, washed with toluene until no color remained and concentrated under vacuum The conversion was assessed by ^{1}H NMR spectroscopy and the enantioselectivity by HPLC.

Pure samples of compounds **4a-g** and **5a-g** were obtained after flash chromatography on silica gel (cyclohexane/toluene 3:1) or alternatively by preparative HPLC (Chiralcel OD, hexane:*i*PrOH 99:1; 3 mL.min^{-1}; λ = 355 nm).

Coupling with $PhB(OH)_2$ 6a:

4a: ^{1}H NMR (500 MHz, C_6D_6): δ 7.25-7.18 (m, 5H), 7.01 (d, J = 7.5 Hz, 1H), 6.43 (d, J = 7.5 Hz, 1H), 6.06 (d, J = 6.9 Hz, 1H), 5.48 (d, J = 6.9 Hz, 1H), 4.53 (t, J = 6.4 Hz, 1H), 4.48 (t, J = 6.4 Hz, 1H). ^{13}C NMR (125 MHz, C_6D_6): δ 231.4, 140.5, 138.1, 130.9, 129.8, 128.6, 128.4, 122.9, 106.6, 103.4, 91.9, 91.7, 89.4, 87.8. IR (ν_{max}/cm^{-1}): 1946, 1850, 1358, 1159, 849, 621. HRMS: *m/z* (EI) calcd. for $C_{19}H_{11}BrCrO_3$ $[M]^+$: 417.9297, found: 417.9294. HPLC (Chiralcel OD-H; hexane:*i*PrOH 95:5; 1 mL.min^{-1}; λ = 355 nm): t_{R1} = 10.8 min, t_{R2} = 11.6 min.

5a: ^{1}H NMR (500 MHz, C_6D_6): δ 7.32-7.19 (m, 10H), 6.88 (s, 2H), 5.76 (dd, J = 5.2, 2.8 Hz, 2H), 4.55 (dd, J = 5.2, 2.8 Hz, 2H). ^{13}C NMR (125 MHz, C_6D_6): δ 232.2, 140.6, 138.8, 130.6, 130.2, 130.0, 128.5, 105.3, 92.2, 89.2. IR (ν_{max}/cm^{-1}): 1963, 1889, 1267, 751, 728. HRMS: *m/z* (EI) calcd. for $C_{25}H_{16}CrO_3$ $[M]^+$: 416.0505, found: 416.0497. HPLC (Chiralcel OD-H; hexane:*i*PrOH 95:5; 1 mL.min^{-1}; λ = 355 nm): t_R = 9.5 min.

Coupling with *p*-MePhB(OH)$_2$ 6b:

4b: ^{1}H NMR (500 MHz, C_6D_6): δ 7.20-7.15 (m, 2H), 7.04 (br d, J = 7.5 Hz, 1H + 2H), 6.49 (d, J = 7.5 Hz, 1H), 6.08 (dd, J = 6.8, 1.2 Hz, 1H), 5.58 (dd, J = 6.8, 1.2 Hz, 1H), 4.55 (ddd, J = 6.8, 6.0, 1.2 Hz, 1H), 4.50 (ddd, J = 6.8, 6.0, 1.2 Hz, 1H), 2.16 (s, 3H). ^{13}C NMR (125 MHz, C_6D_6): δ 231.5, 140.7, 138.2, 135.2, 131.0, 129.7, 129.6, 128.6, 122.7, 106.7, 104.0, 92.1, 92.1, 89.8, 88.3, 21.1. IR (ν_{max}/cm^{-1}): 3108, 3023, 2921, 1944, 1885, 1844, 1468, 1360, 816, 662, 623, 511. HRMS: *m/z* (EI) calcd. for $C_{20}H_{13}BrCrO_3$ $[M]^+$: 431.9453, found: 431.9450. HPLC (Chiralcel OD-H; hexane:*i*PrOH 95:5; 1 mL. min^{-1}; λ = 355 nm): t_{R1} = 8.5 min, t_{R2} = 9.4 min.

5b: ^{1}H NMR (500 MHz, C_6D_6): δ 7.40-7.10 (m, 4H), 7.09 (d, J = 8.0 Hz, 4H), 6.96 (s, 2H), 5.88 (dd, J = 5.2, 2.9 Hz, 2H), 4.61 (dd, J = 5.2, 2.9 Hz, 2H), 2.19 (s, 6H). ^{13}C NMR (125 MHz, C_6D_6): δ 232.4, 140.6, 137.9, 136.0, 130.0, 128.4, 128.3, 105.6, 92.2, 89.4, 21.1. IR (ν_{max}/cm^{-1}): 1962, 1887, 1265, 751, 705. HRMS: *m/z* (EI) calcd. for $C_{27}H_{20}CrO_3$ $[M]^+$: 444.0818, found: 444.0812. HPLC (Chiralcel OD-H; hexane:*i*PrOH 95:5; 1 mL.min^{-1}; λ = 355 nm): t_R = 7.0 min.

Coupling with *p*-MeOPhB(OH)$_2$ 6c:

4c: ^{1}H NMR (500 MHz, C_6D_6): δ 7.21-7.17 (m, 2H), 7.05 (d, J = 7.5 Hz, 1H), 6.83 (d, J = 8.6 Hz, 2H), 6.50 (d, J = 7.5 Hz, 1H), 6.10 (d, J = 6.6 Hz, 1H), 5.60 (d, J = 6.6 Hz, 1H), 4.57 (t, J = 6.1 Hz, 1H), 4.53 (t, J = 6.1 Hz, 1H), 3.34 (s, 3H). ^{13}C NMR (125 MHz, C_6D_6): δ 231.5, 160.2, 140.5, 131.0, 130.9, 128.6, 122.5, 114.5, 106.8, 104.0, 92.2, 92.1, 89.8, 88.3, 54.9. IR (ν_{max}/cm^{-1}): 1953, 1856, 1607, 1508, 1246, 1028, 828, 622. HRMS: *m/z* (EI) calcd. for $C_{20}H_{13}BrCrO_4$ $[M]^+$: 447.9402, found: 447.9393. HPLC (Pirkle Covalent; hexane:*i*PrOH 95:5; 1 mL.min^{-1}; λ = 355 nm): t_{R1} = 8.9 min, t_{R2} = 9.9 min.

5c: ^{1}H NMR (500 MHz, C_6D_6): δ 7.40-7.27 (m, 4H), 6.99 (s, 2H), 6.88 (d, J = 8.7 Hz, 4H), 5.91 (dd, J = 5.2, 2.9 Hz, 2H), 4.95 (dd, J = 5.2, 2.9 Hz, 2H), 3.37 (s, 6H). ^{13}C NMR (125 MHz, C_6D_6): δ 232.5, 160.1, 140.3, 131.2, 131.0, 128.4, 114.5, 105.8, 92.3, 89.5, 54.9. IR (ν_{max}/cm^{-1}): 1962, 1882, 1273, 1251, 759, 720. HRMS: *m/z* (EI) calcd. for

$C_{27}H_{20}CrO_5$ $[M]^+$: 476.0716, found: 476.0712. HPLC (Pirkle Covalent; hexane:*i*PrOH 95:5; 1 mL.min^{-1}; λ = 355 nm): t_R = 13.1 min.

Coupling with *p*-CF_3PhB(OH)$_2$ 6d:

4d: ^{1}H NMR (500 MHz, C_6D_6): δ 7.37 (d, J = 8.1 Hz, 2H), 7.32-7-17 (m, 2H), 7.00 (d, J = 7.5 Hz, 1H), 6.25 (d, J = 7.5 Hz, 1H), 6.05 (dd, J = 6.6, 1.0 Hz, 1H), 5.14 (dd, J = 6.6, 1.0 Hz, 1H), 4.53 (2td, J = 5.9, 1.3 Hz, 2H). ^{13}C NMR (125 MHz, C_6D_6): δ 231.1, 141.6, 138.6, 130.6, 130.5 (q, $^2J_{C\text{-}F}$ = 32.4 Hz), 130.1, 128.7, 123.8, 125.9, 125.7 (q, $^1J_{C\text{-}F}$ = 271.7 Hz), 106.0, 103.4, 92.3, 92.0, 89.7, 87.2. HRMS: *m/z* (EI) calcd. for $C_{20}H_{10}F_3BrCrO_3$ $[M]^+$: 485.9170, found: 485.9165. HPLC (Chiralpak AD; hexane:*i*PrOH 99:1; 1 mL.min^{-1}; λ = 355 nm): t_{R1} = 12.3 min, t_{R2} = 14.1 min.

5d: ^{1}H NMR (500 MHz, C_6D_6): δ 7.43 (d, J = 8.1 Hz, 4H), 7.32-7.17 (m, 4H), 6.69 (s, 2H), 5.41 (dd, J = 5.2, 2.9 Hz, 2H), 4.59 (dd, J = 5.2, 2.9 Hz, 2H). ^{13}C NMR (125 MHz, C_6D_6): δ 231.7, 142.0, 139.7, 130.6 (q, $^2J_{C\text{-}F}$ = 32.4 Hz), 130.3, 128.1, 125.9 (br), 124.8 (q, $^1J_{C\text{-}F}$ = 271.7 Hz), 104.5, 92.3, 88.3. IR (ν_{max}/cm^{-1}): 1966, 1893, 1324, 1220, 752, 710. HRMS: *m/z* (EI) calcd. for $C_{27}H_{14}F_6CrO_3$ $[M]^+$: 552.0252, found: 552.0245. HPLC (Chiralpak AD; hexane:*i*PrOH 99:1; 1 mL.min^{-1}; λ = 355 nm): t_R = 10.3 min.

Coupling with (*cis*-propenyl)B(OH)$_2$ 6e:

4e: ^{1}H NMR (500 MHz, C_6D_6): δ 7.01 (d, J = 7.5 Hz, 1H), 6.42 (d, J = 7.5 Hz, 1H), 6.22 (d, J = 11.4 Hz, 1H), 6.02 (d, J = 6.7 Hz, 1H), 5.75 (dq, J = 11.4, 7.0 Hz, 1H), 5.42 (d, J = 6.5 Hz, 1H), 4.57 (2t, J = 6.5 Hz, 2H), 1.48 (dd, J = 7.0, 1.5 Hz, 3H). ^{13}C NMR (125 MHz, C_6D_6): δ 231.4, 135.3, 131.2, 130.9, 128.0, 125.2, 121.8, 106.0, 104.4, 92.1, 91.8, 89.6, 87.1, 14.5. IR (ν_{max}/cm^{-1}): 1945, 1850, 1345, 1238, 854, 660, 621, 508. HRMS: *m/z* (EI) calcd. for $C_{16}H_{11}BrCrO_3$ $[M]^+$: 381.9297, found: 381.9294. HPLC (Chiralpak AS-H; gradient hexane:*i*PrOH from 99:1 to 90:10; 1 mL.min^{-1}; λ = 355 nm): t_{R1} = 14.4 min, t_{R2} = 15.8 min.

5e: ^{1}H NMR (500 MHz, C_6D_6): δ 6.86 (s, 2H), 6.44 (dd, J = 11.4, 1.1 Hz, 2H), 5.82 (dq, J = 11.4, 7.0 Hz, 2H), 5.67 (dd, J = 5.1, 2.9 Hz, 2H), 4.69 (dd, J = 5.2, 2.9 Hz, 2H), 1.59

(dd, *J* = 7.0, 1.4 Hz, 6H). ^{13}C NMR (125 MHz, C_6D_6): δ 232.3, 134.4, 130.5, 127.7, 125.9, 105.2, 91.9, 88.1, 14.6. IR (ν_{max}/cm^{-1}): 1963, 1889, 502, 465. HRMS: *m/z* (EI) calcd. for $C_{19}H_{16}CrO_3$ $[M]^+$: 344.0505, found: 344.0500. HPLC (Chiralpak AS-H; gradient hexane:*i*PrOH from 99:1 to 90:10; 1 mL.min^{-1}; λ = 355 nm): t_R = 10.8 min.

Coupling with (*trans*-cyclohexylvinyl)B(OH)$_2$ 6f:

4f: ^{1}H NMR (500 MHz, C_6D_6): δ 7.07 (d, *J* = 7.7 Hz, 1H), 6.59 (d, *J* = 7.7 Hz, 1H), 6.43 (d, *J* = 15.6 Hz, 1H), 6.06 (dd, *J* = 6.7, 1.0 Hz, 1H), 5.90 (dd, *J* = 15.6, 7.0 Hz, 1H), 5.55 (d, *J* = 6.5 Hz, 1H), 4.61 (2td, *J* = 6.3, 1.3 Hz, 2H), 2.08-1.98 (m, 1H), 1.80-1.65 (m, 4H), 1.27-1.22 (m, 2H), 1.17-1.08 (m, 4H). ^{13}C NMR (125 MHz, C_6D_6): δ 231.5, 143.4, 137.5, 131.5, 125.2, 122.5, 121.4, 104.7, 104.4, 92.1, 91.8, 89.7, 86.4, 41.8, 32.9, 32.9, 26.3, 26.2, 26.2. IR (ν_{max}/cm^{-1}): 2921, 2850, 1940, 1869, 1448, 960, 660, 624, 511. HRMS: *m/z* (EI) calcd. for $C_{21}H_{19}BrCrO_3$ $[M]^+$: 449.9923, found: 449.9919. HPLC (Chiralcel OD-H; hexane:*i*PrOH 95:5; 1 mL.min^{-1}; λ = 355 nm): t_{R1} = 7.4 min, t_{R2} = 8.7 min.

5f: ^{1}H NMR (500 MHz, C_6D_6): δ 7.10 (s, 2H), 6.64 (d, *J* = 15.6 Hz, 2H), 6.05 (dd, *J* = 15.6, 7.0 Hz, 2H), 5.83 (dd, *J* = 4.9, 2.8 Hz, 2H), 4.78 (dd, *J* = 4.9, 2.8 Hz, 2H), 2.06-2.14 (m, 2H), 1.85-1.60 (m, 10H), 1.30-1.13 (m, 10H). ^{13}C NMR (125 MHz, C_6D_6): δ 232.5, 142.4, 136.4, 125.5, 123.3, 104.1, 91.8, 87.5, 41.8, 33.1, 33.0, 26.4, 26.3, 26.3. IR (ν_{max}/cm^{-1}): 2920, 2849, 1952, 1868, 1446, 961, 621. HRMS: *m/z* (EI) calcd. for $C_{29}H_{32}CrO_3$ $[M]^+$: 480.1757, found: 480.1754. HPLC (Chiralcel OD-H; hexane:*i*PrOH 95:5; 1 mL.min^{-1}; λ = 355 nm): t_R = 5.7 min.

Coupling with *n*-BuB(OH)$_2$ 6g:

4g: ^{1}H NMR (500 MHz, C_6D_6): δ 7.04 (d, *J* = 7.6 Hz, 1H), 6.29 (d, *J* = 7.6 Hz, 1H), 6.08 (dd, *J* = 6.5, 1.6 Hz, 1H), 5.33 (dd, *J* = 6.5, 1.6 Hz, 1H), 4.61 (2td, *J* = 6.5, 1.6 Hz, 2H), 2.50-2.34 (m, 2H), 1.39-1.28 (m, 2H), 1.24-1.15 (m, 2H), 0.85 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (125 MHz, C_6D_6): δ 231.6, 139.8, 131.2, 127.0, 120.9, 106.0, 104.5, 92.0, 91.9, 90.1, 86.1, 32.1, 31.1, 22.8, 14.0. IR (ν_{max}/cm^{-1}): 2954, 2932, 2870, 1950, 1857, 1359, 1226, 835, 620, 501. HRMS: *m/z* (EI) calcd. for $C_{17}H_{15}BrCrO_3$ $[M]^+$: 397.9610, found:

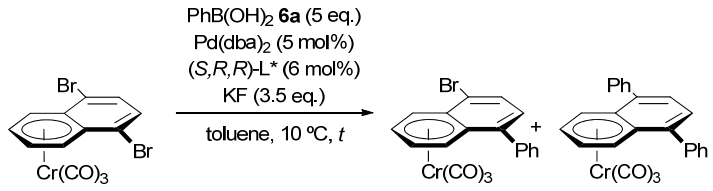
397.9610. HPLC (Chiralcel OD-H; gradient hexane:*i*PrOH from 99:1 to 90:10; 1 mL.min^{-1}; λ = 355 nm): t_{R1} = 13.6 min, t_{R2} = 15.5 min.

5g: ^{1}H NMR (500 MHz, C_6D_6): δ 6.75 (s, 2H), 5.64 (dd, J = 5.1, 2.9 Hz, 2H), 4.78 (dd, J = 5.1, 2.9 Hz, 2H), 2.70-2.62 (m, 2H), 2.59-2.51 (m, 2H), 1.55-1.41 (m, 4H), 1.33-1.22 (m, 4H), 0.88 (t, J = 7.3 Hz, 6H). ^{13}C NMR (125 MHz, C_6D_6): δ 232.8, 137.7, 127.1, 105.6, 91.9, 87.7, 32.3, 31.5, 22.9, 14.1. IR (ν_{max}/cm^{-1}): 2927, 2959, 2859, 1949, 1866, 1414, 1377, 844, 624, 511. HRMS: *m/z* (EI) calcd. for $C_{21}H_{24}CrO_3$ $[M]^+$: 376.1131, found: 376.1123. HPLC (Chiralcel OD-H; gradient hexane:*i*PrOH from 99:1 to 90:10; 1 mL.min^{-1}; λ = 355 nm): t_R = 9.0 min.

3. Monitoring experiment

The asymmetric Suzuki-Miyaura coupling of complex **1** with $PhB(OH)_2$ (**5a**) was monitored by means of ^1H NMR and chiral HPLC.

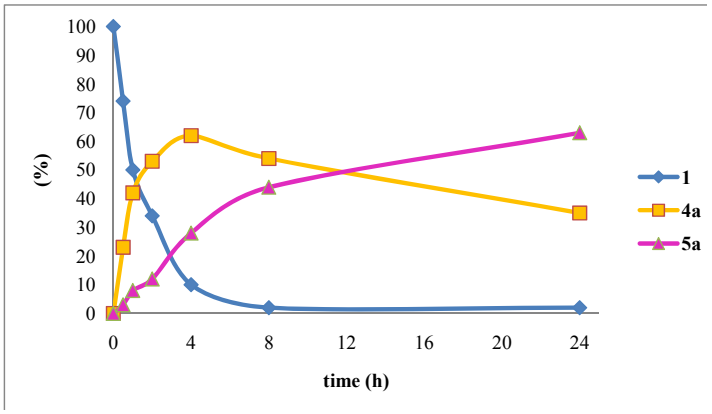
Table S1 Monitoring experiment at +10 ºC

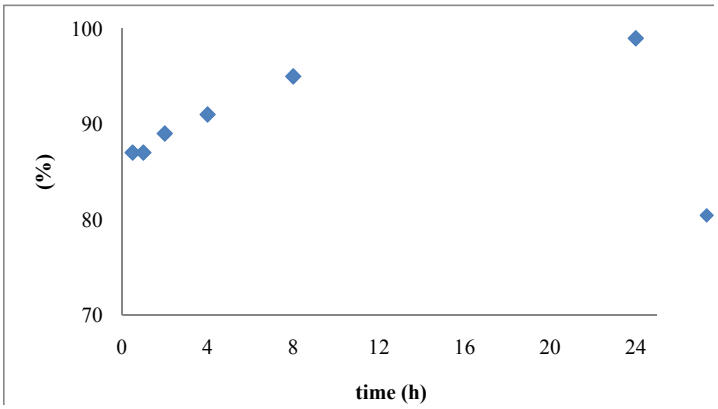


1 (*S*)-**4a** **5a**

Entry	*t*/h	**1** (%)[a]	**4a** (%)[a]	**5a** (%)[a]	*ee* **4a** (%)[b]	**4a/5a**[a]
1	0.5	74	23	3	87	88/12
2	1	50	42	8	87	83/17
3	2	34	53	12	89	81/19
4	4	10	62	28	91	69/31
5	8	2	54	44	95	55/45
6	24	2	35	63	99	36/64

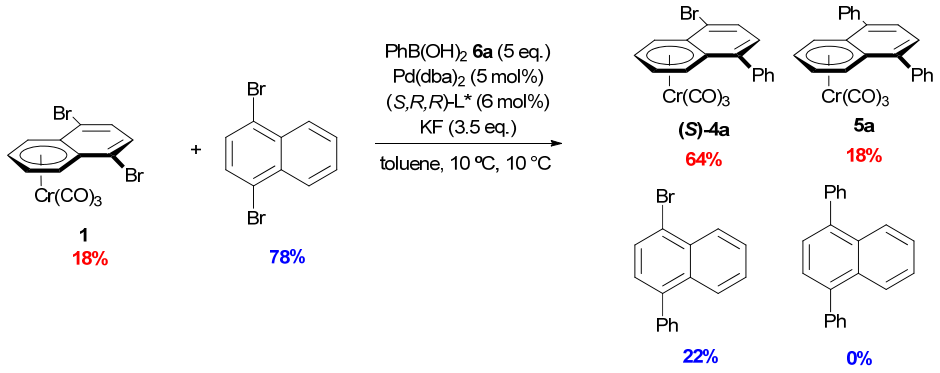
[a] Determined by ^1H NMR. [b] Determined by chiral HPLC.





4. Competition experiment

A competition experiment between [Cr(CO)$_3$(5,8-dibromonaphthalene)] (**1**) and free 1,4-dibromonaphthalene was carried out to assess the activation effect of the tricarbonylchromium fragment (Scheme S1). Under standard conditions, the major compound formed was **4a**. The rest of the mixture was composed of unreacted starting materials, bisphenylated complex **5a** and 1-bromo-4-phenylnaphthalene. This result showcases the strong influence of the tricarbonylchromium moiety. Whilst the latter is not directly bound to the dibrominated ring, the reactivity is greatly enhanced compared to the free ligand system.



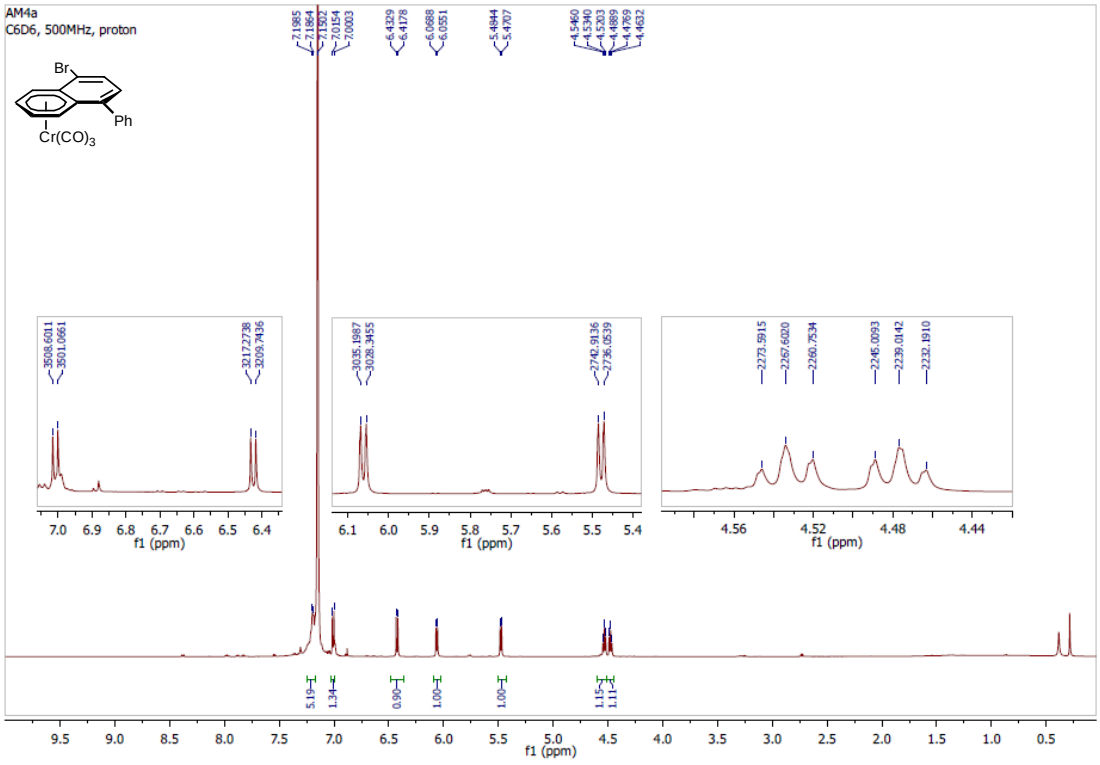
Scheme S1

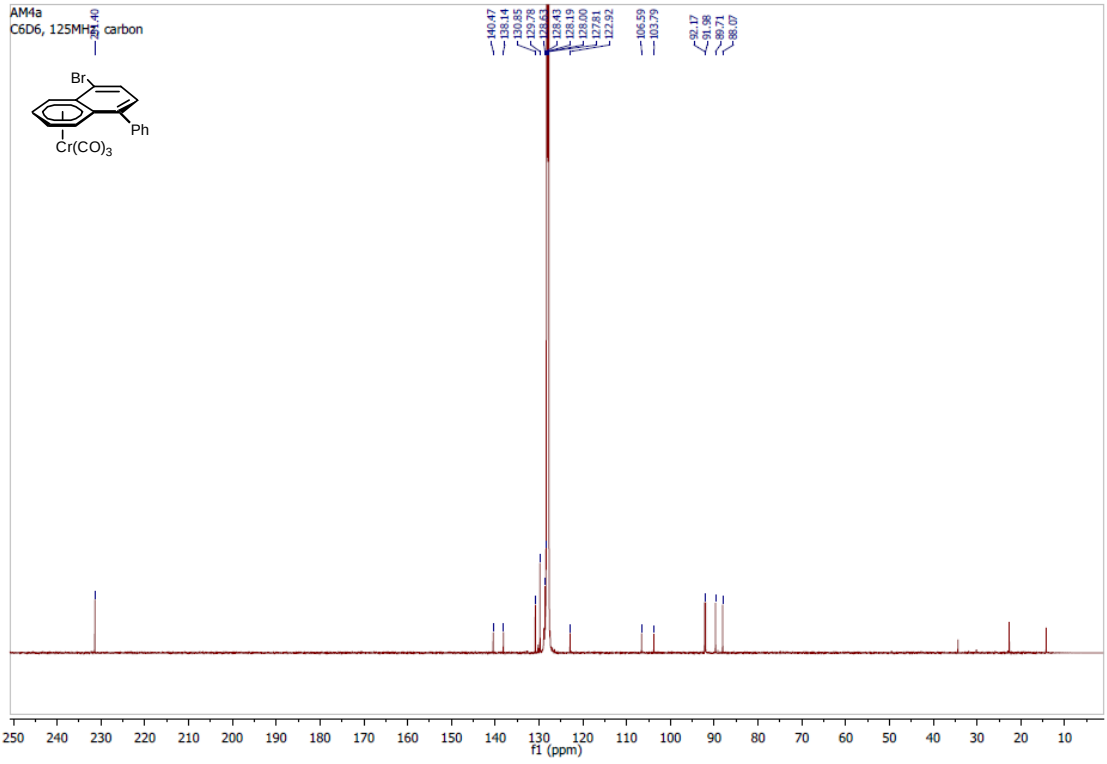
5. [Pd(η^3-allyl)(1,2-η-Ph-L*-κ*P*)][SbF$_6$] (7)[8]

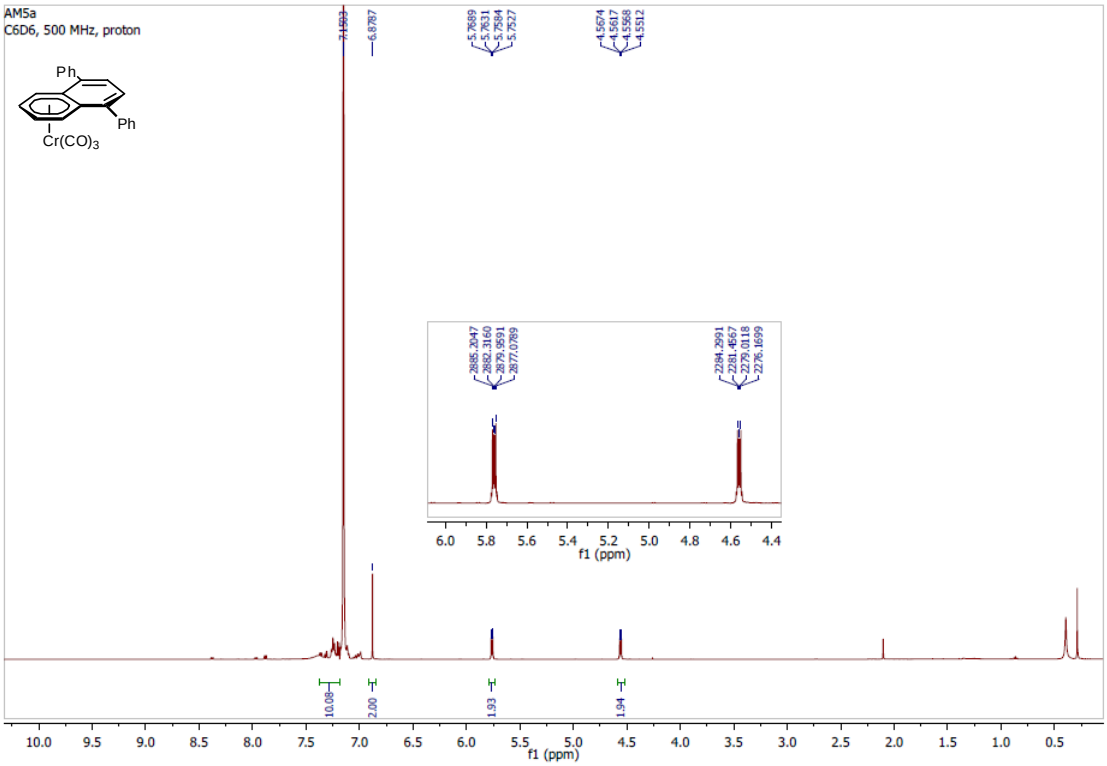
A CH_2Cl_2 solution (5 mL) of ligand (*R,S,S*)-L* (138.4 mg, 0.2 mmol) was added dropwise to CH_2Cl_2 solution (5 mL) of [Pd(allyl)Cl]$_2$ (36.1 mg, 0.1 mmol) over 10 min at room temperature upon stirring. The resulting solution was added to $AgSbF_6$ (68 mg, 0.2 mmol), and the resulting slurry was stirred for 2 h at room temperature. AgCl was filtered off, and the filter was rinsed with CH_2Cl_2. The resulting clear solution was evaporated, and the white solid was washed with a small amount of diethyl ether (2x10 mL) and pentane (2x10 mL). Evaporation of the solvent gave the product as a pale beige microcrystalline powder (192 mg, 89% yield). Crystals suitable for an X-ray analysis were grown by layering cyclohexane over a dichloromethane solution.

mp 208-210°C (decomp.). $[\alpha]_D$ = +249 (*c* = 0.34 in $CHCl_3$, 20 °C). ^{1}H NMR (CD_2Cl_2, 500 MHz, -85 °C): δ 8.30 (d, *J* = 5.5 Hz, 1H), 8.18 (d, *J* = 10.0 Hz, 2H), 8.13 (d, *J* = 8.3 Hz, 2H), 8.07 (t, *J* = 9.0 Hz, 2H), 7.85 (d, *J* = 7.6 Hz, 2H), 7.82 (d, *J* = 7.5 Hz, 2H), 7.73-7.70 (m, 4H), 7.66 (d, *J* = 7.4 Hz, 2H), 7.63 – 7.45 (m, 22H), 7.38 – 7.30 (m, 18H), 7.15 (t, *J* = 6.8 Hz, 1H), 7.06 (t, *J* = 7.3 Hz, 1H), 7.02 (t, *J* = 7.4 Hz, 1H), 6.85 (t, *J* = 7.4 Hz, 1H), 5.50 – 5.47 (m, 2H), 5.37 – 5.29 (m, 1H), 5.12 – 5.04 (m, 1H), 4.67 – 4.61 (m, 2H), 3.85 (dd, *J* = 14.7, 6.7 Hz, 1H), 3.77 (dd, *J* = 12.0, 6.2 Hz, 1H), 3.66 (t, *J* = 14.3 Hz, 1H), 3.41 (d, *J* = 6.7 Hz, 1H), 3.31 – 3.25 (m, 2H), 3.17 (dq, *J* = 7.0, 1.5 Hz, 1H), 2.81 (br s, 1H), 2.65 (t, *J* = 8.5 Hz, 1H), 2.39 (d, *J* = 12.0 Hz, 1H), 2.22 (t, *J* = 8.8 Hz, 1H), 2.08 (d, *J* = 11.8 Hz, 1H), 1.30 – 1.25 (m, 6H), 1.13 (s, 2H), 0.81 (br s, 3H), 0.73 (br s, 3H). ^{13}C NMR (CD_2Cl_2, 125 MHz, -85 °C): δ 144.52 (d, *J* = 15.6 Hz), 143.63 (d, *J* = 5.0 Hz), 143.54 (d, *J* = 5.2 Hz), 138.87 (d, *J* = 2.0 Hz), 138.75 (d, *J* = 2.3 Hz), 135.73 (d, *J* = 2.0 Hz), 135.69, 135.29, 134.48, 132.74 (d, *J* = 2.2 Hz), 132.46, 132.32 (d, *J* = 2.0 Hz), 132.12, 132.05 (d, *J* = 2.0 Hz), 131.95 (d, *J* = 6.0 Hz), 131.31 (d, *J* = 9.3 Hz), 131.11 (d, *J* = 7.0 Hz), 130.90, 129.99 (d, *J* = 20.8 Hz), 129.52, 128.68, 128.54, 128.34 (d, *J* = 9.7 Hz), 128.15 (d, *J* = 4.9 Hz), 127.98 (d, *J* = 7.2 Hz), 127.54, 127.34 (d, *J* = 10.4 Hz), 126.64, 126.57, 126.52, 126.46, 126.08 (d, *J* = 19.4 Hz), 124.45 (d, *J* = 2.8 Hz), 124.31 (d, *J* = 2.7 Hz), 122.84 (d, *J* = 2.7 Hz), 122.72 (d, *J* = 2.7 Hz), 121.94 (d, *J* = 9.8 Hz), 121.49 (d, *J* = 10.9 Hz), 111.42, 102.33, 99.14 (d, *J* = 41.2 Hz), 97.34 (d, *J* = 42.1 Hz), 55.31, 51.19 (d, *J* = 3.7 Hz), 50.99 (d, *J* = 5.7 Hz), 46.75, 22.45, 21.28 (d, *J* = 3.2 Hz), 20.99 (d, *J* = 4.3 Hz), 18.90 (d, *J* = 12.4 Hz), 8.52. ^{31}P NMR (CD_2Cl_2, 202 MHz, 25 °C): δ 145.0 (s, 49%), 143.2 (s, 51%). IR (ν_{max}/cm^{-1}): 3057, 2975, 1594, 1498, 1406, 1193, 1152, 1134, 1118, 1094, 1068, 1052, 1031, 960, 884, 858, 827, 766, 701, 653. HR-MS (ESI) for $C_{51}H_{43}NO_2PPd$ $[M\text{-}SbF_6]^+$: calcd 838.2066, found 838.2051. Elemental analysis (%) calcd for $C_{51}H_{43}NO_2F_6PPdSb$ (1075.04): C 56.98, H 4.03, N 1.30; found: C 56.24, H 3.91, N 1.23.

6. Spectroscopic and HPLC data



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5.7527
4.5674
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4.5568
4.5512
3885.2047
3882.3160
3875.9591
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2276.1699
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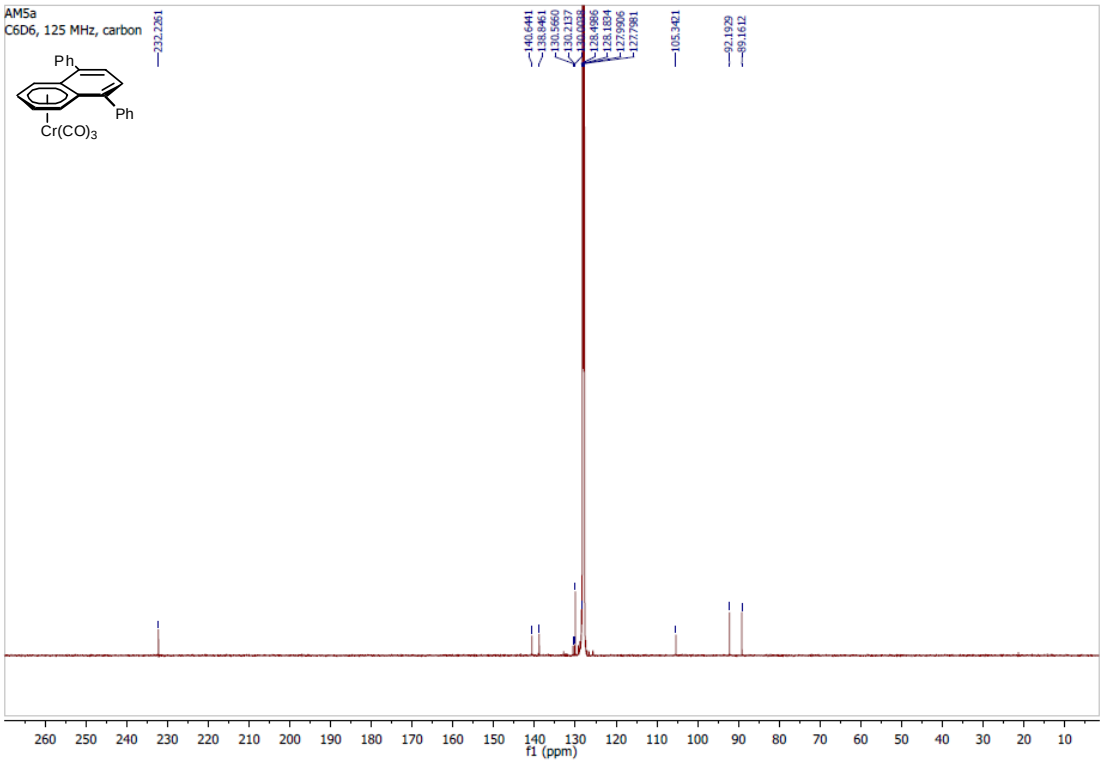
2.00
1.93
1.94
f1 (ppm)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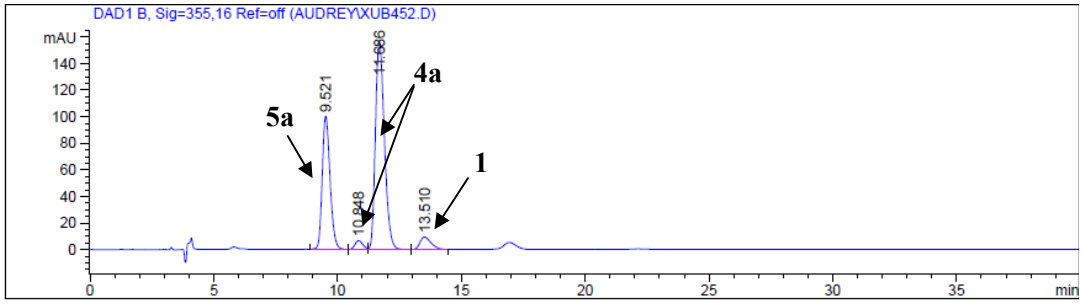
89.1612
f1 (ppm)

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Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=254,4 Ref=off


Signal 2: DAD1 B, Sig=355,16 Ref=off

Peak RetTime Type  Width     Area      Height     Area
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   2  10.848 VV    0.3518  151.45158    6.69742   2.2870
   3  11.686 VV    0.3903 3961.29565  157.05586  59.8177
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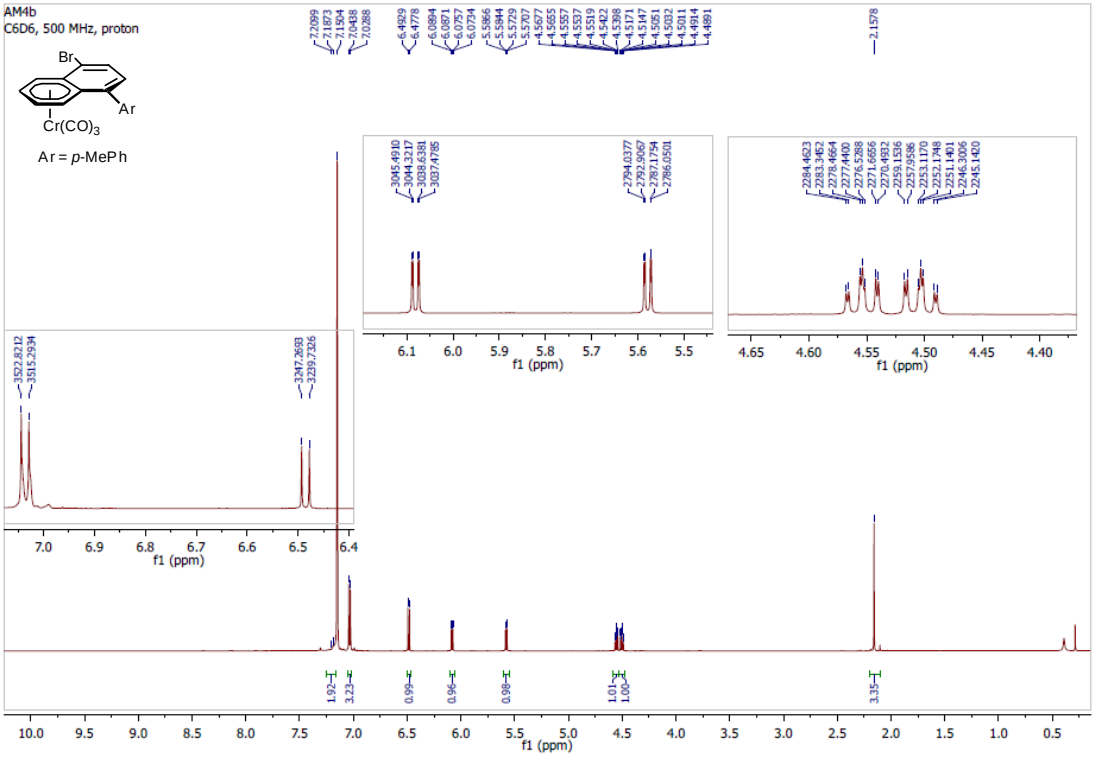
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Ar
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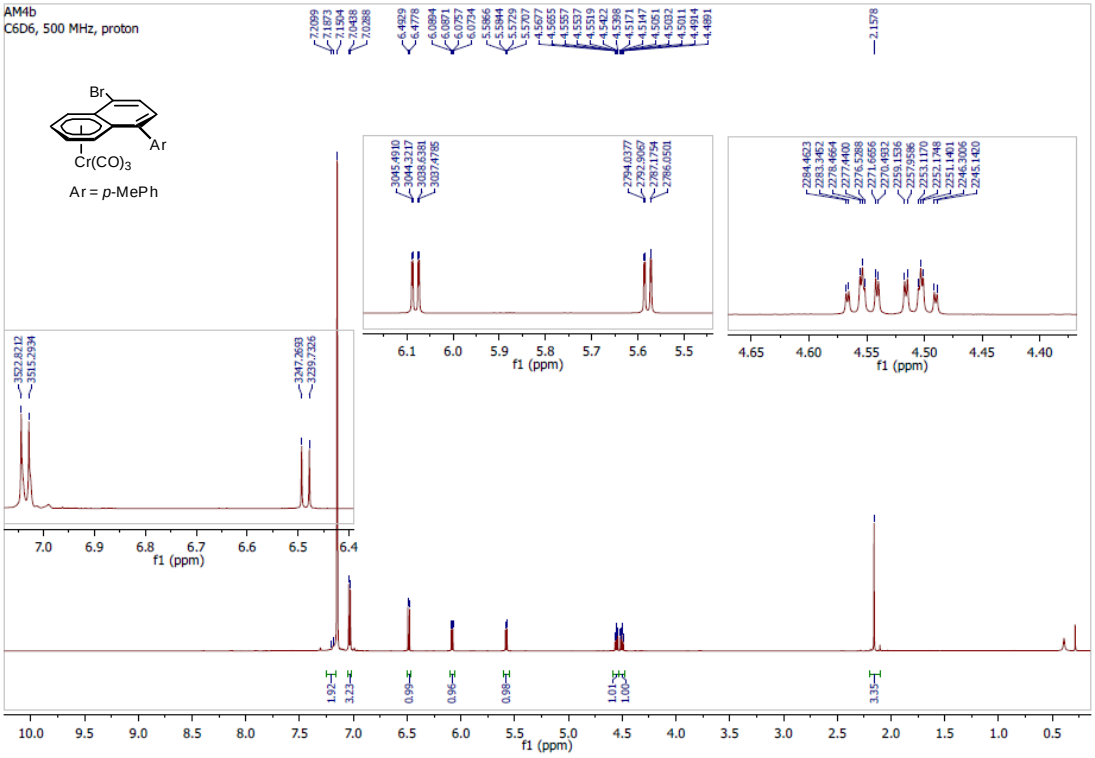
f1 (ppm)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C6D6, 500 MHz, proton
Br
Ar
Cr(CO)3
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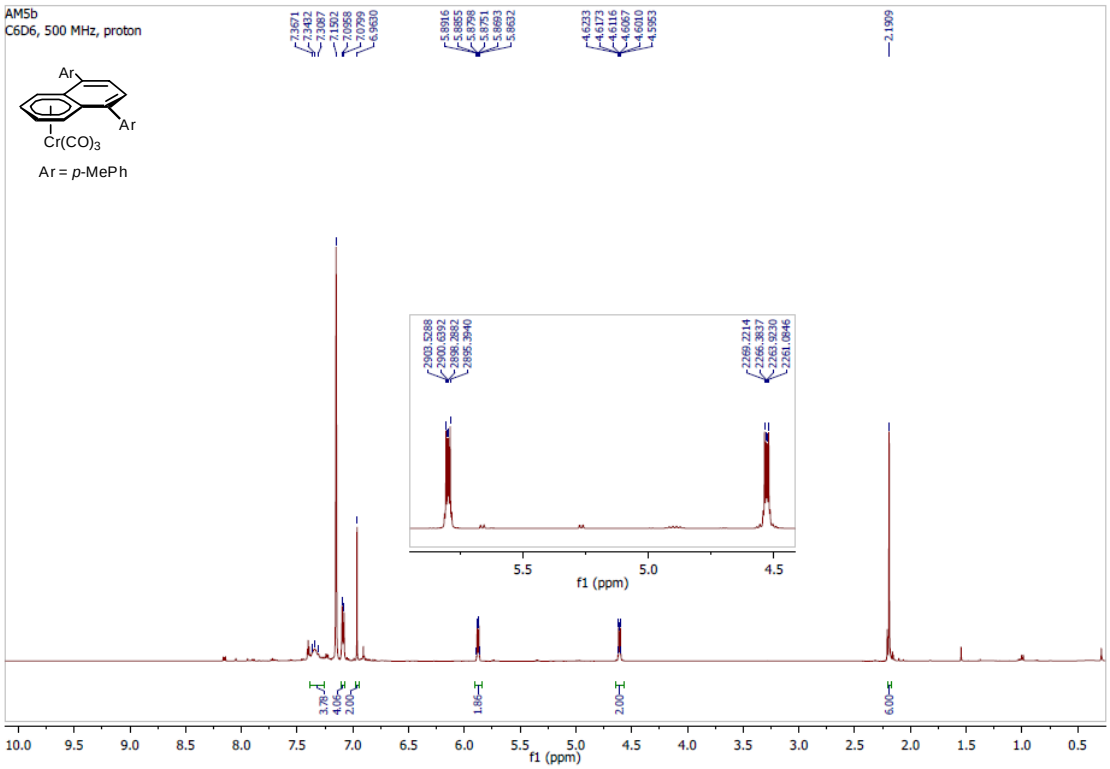
f1 (ppm)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Ar
Cr(CO)3
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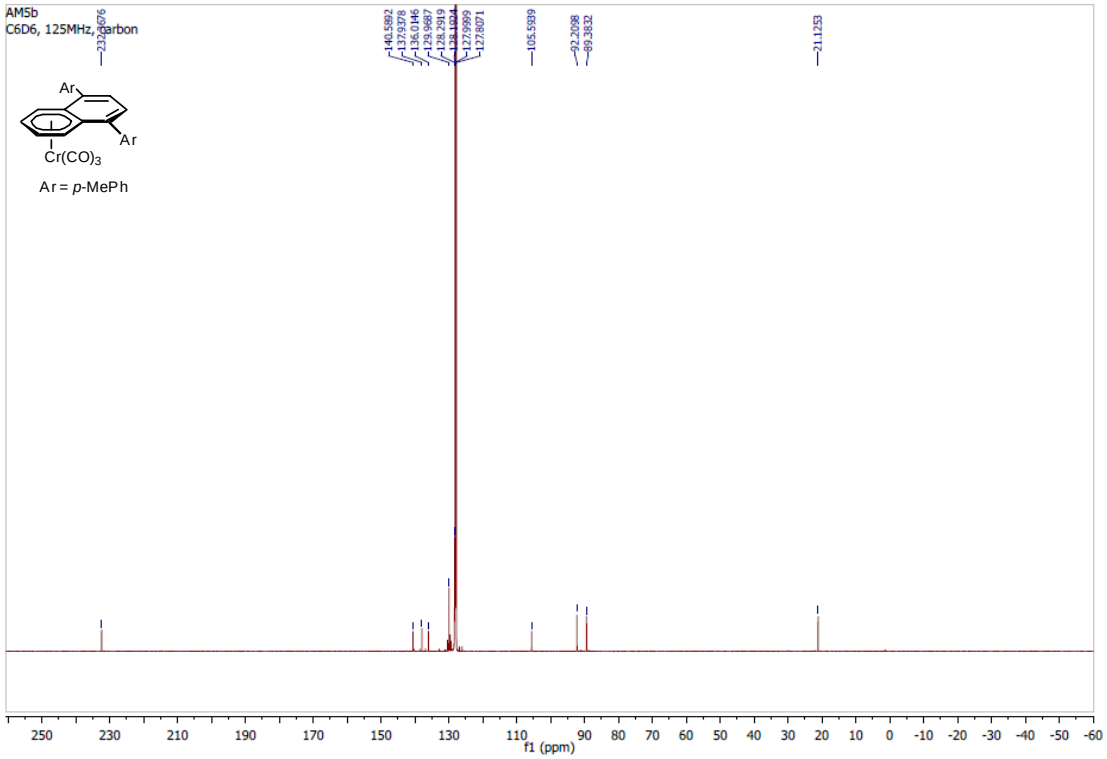
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Ar
Cr(CO)3
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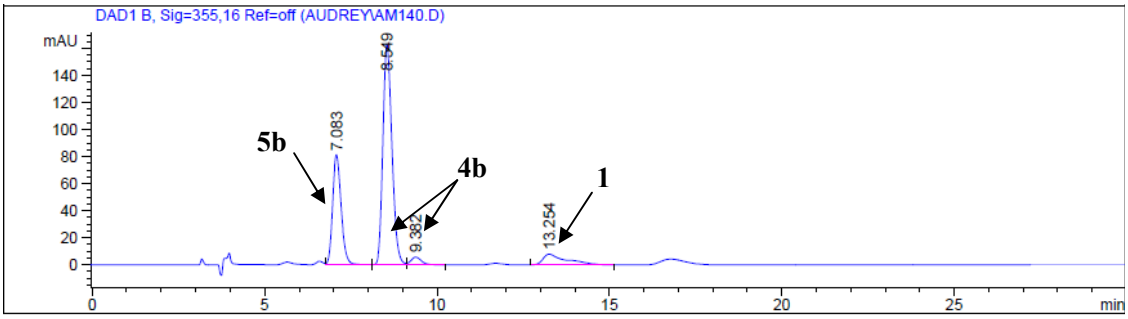
f1 (ppm)

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Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


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Signal 2: DAD1 B, Sig=355,16 Ref=off

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   2   8.549 VV    0.2850 2982.16553  163.34175  61.2885
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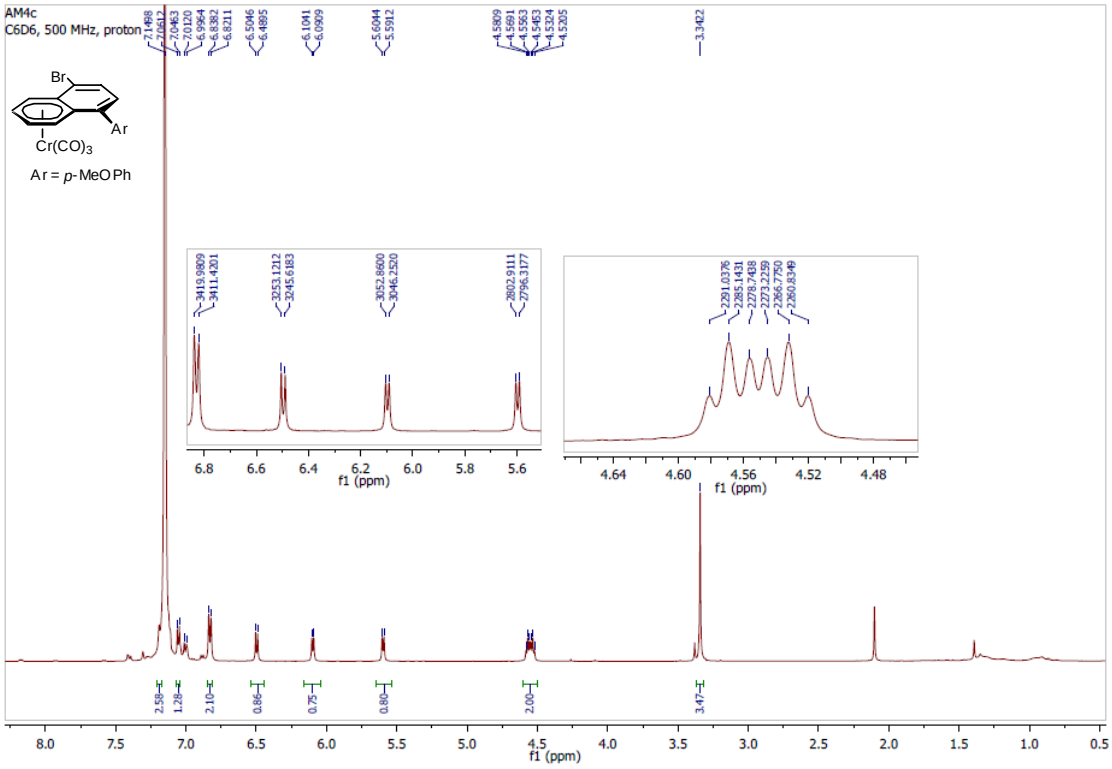
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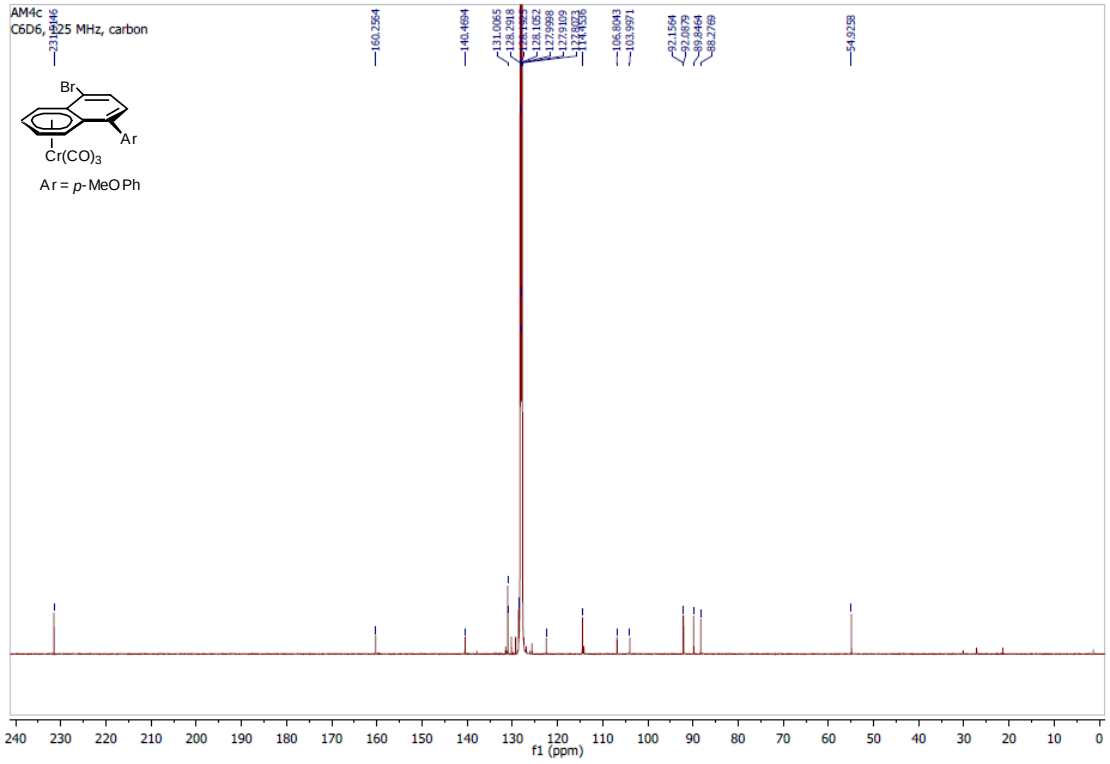
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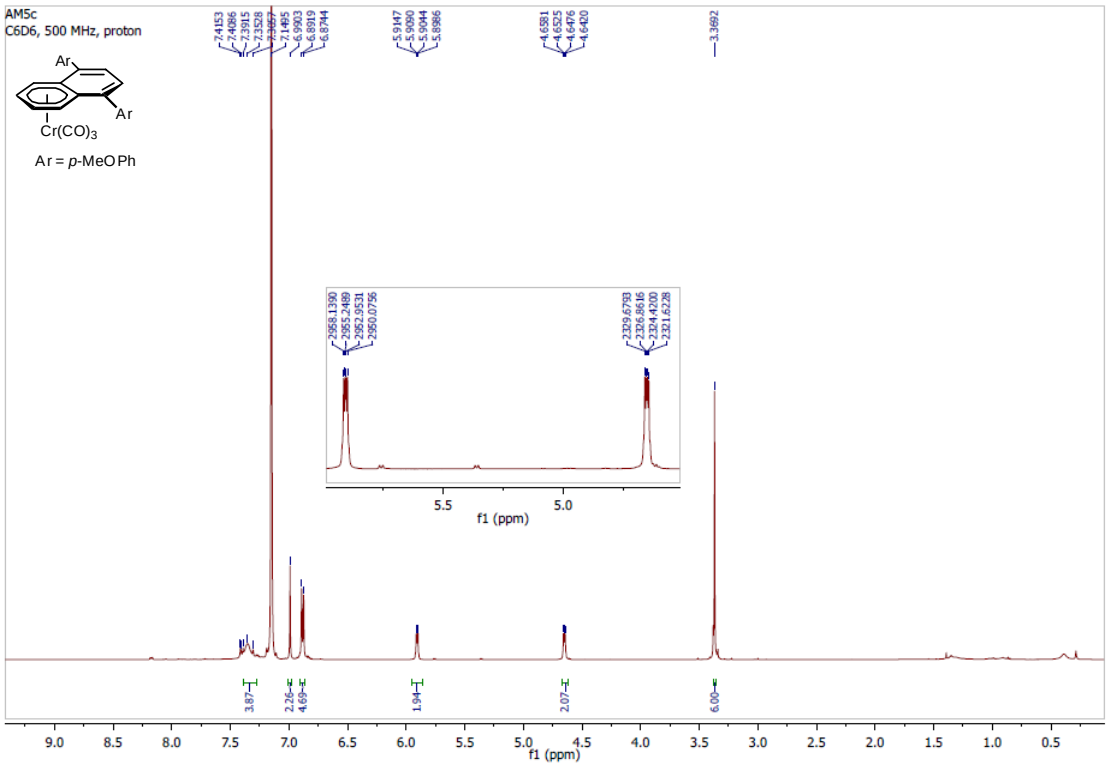
f1 (ppm)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Ar
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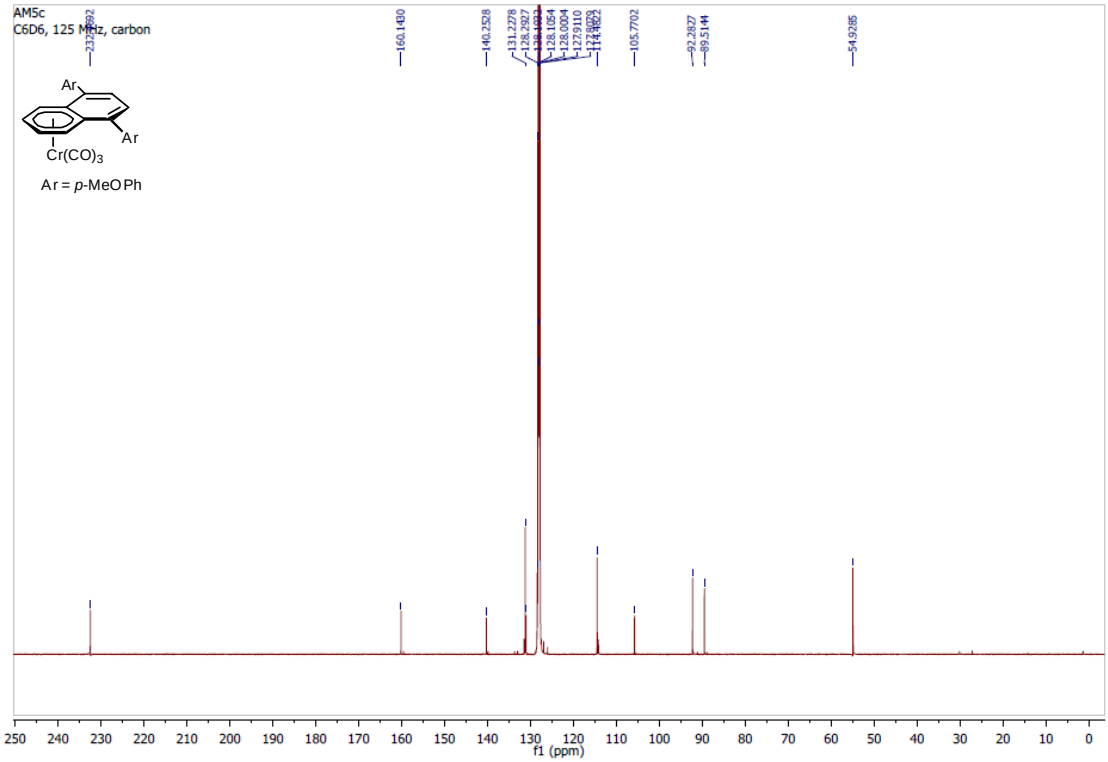
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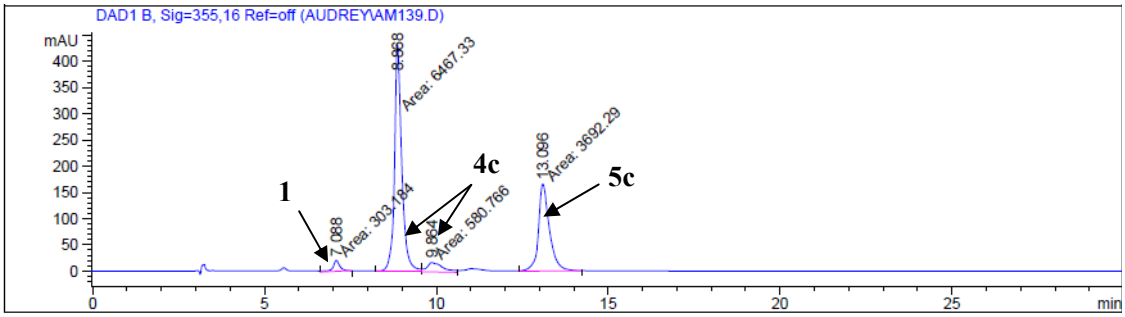
Ar
Cr(CO)3
Ar = p-MeOPh
f1 (ppm)

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Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


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Signal 2: DAD1 B, Sig=355,16 Ref=off

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   2   8.868 MM    0.2477 6467.32520  435.12698  58.5619
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   4  13.096 MM    0.3707 3692.29248  166.00282  33.4339
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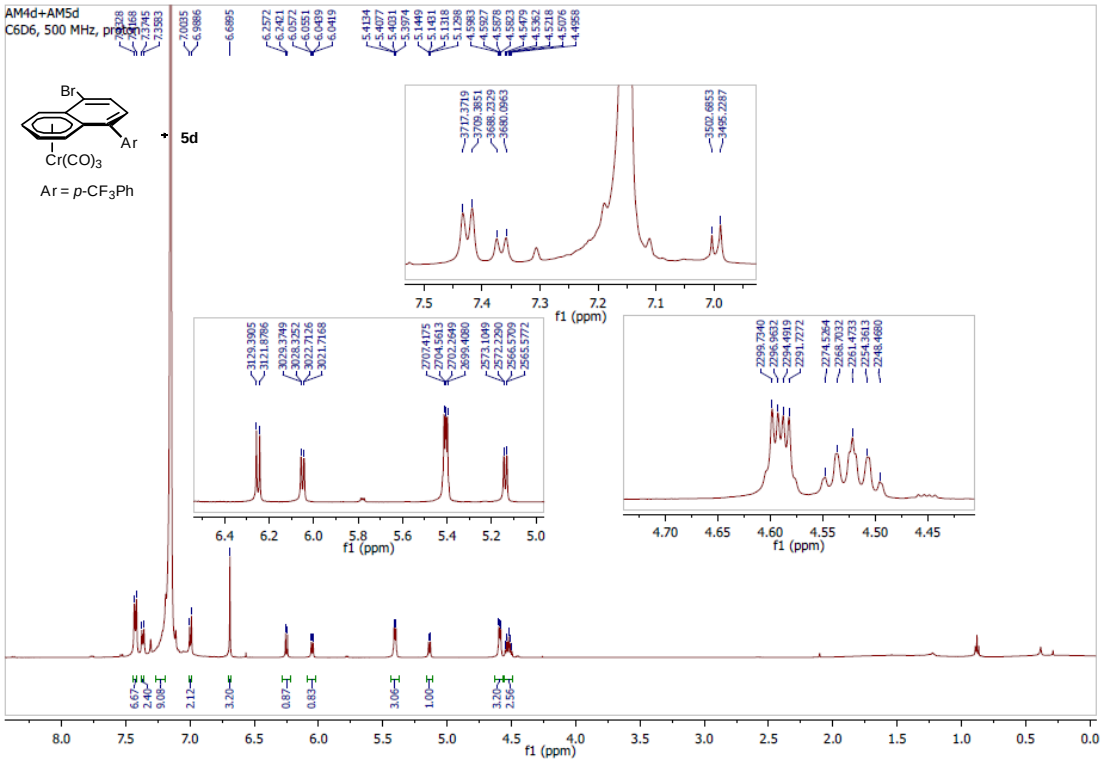
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Ar
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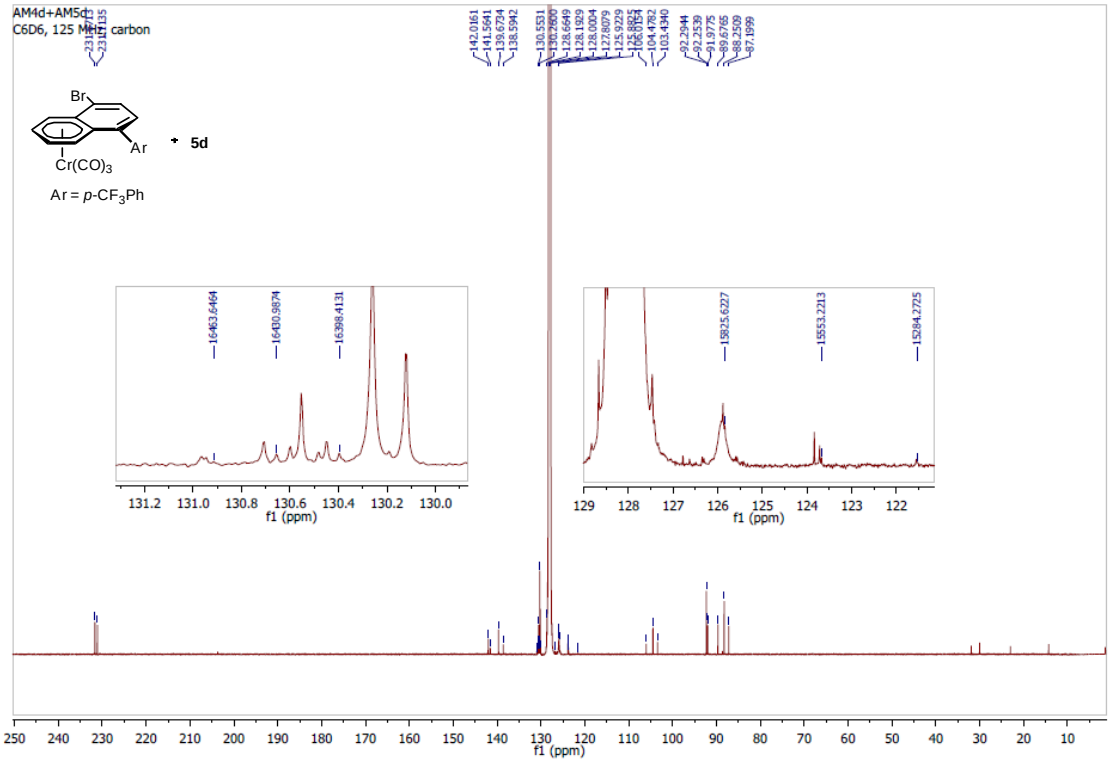
f1 (ppm)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Ar
Cr(CO)3
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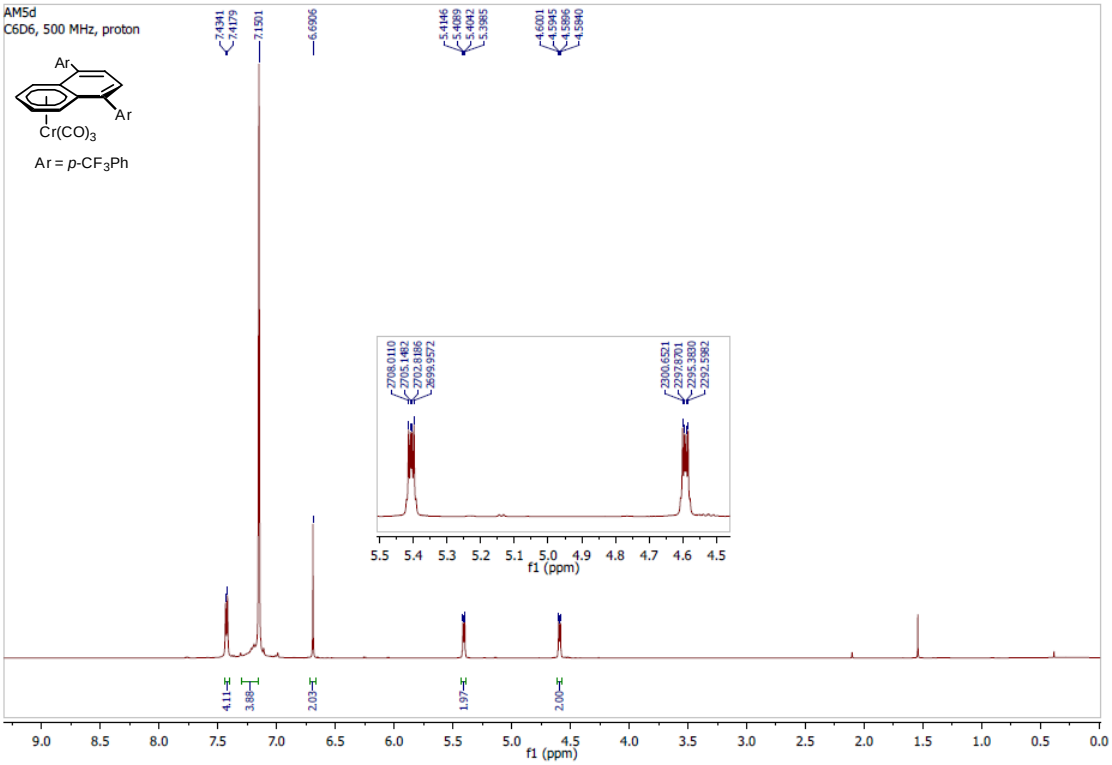
5d
f1 (ppm)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Ar
Ar
Cr(CO)3
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4.6001
4.5945
4.5896
4.5840
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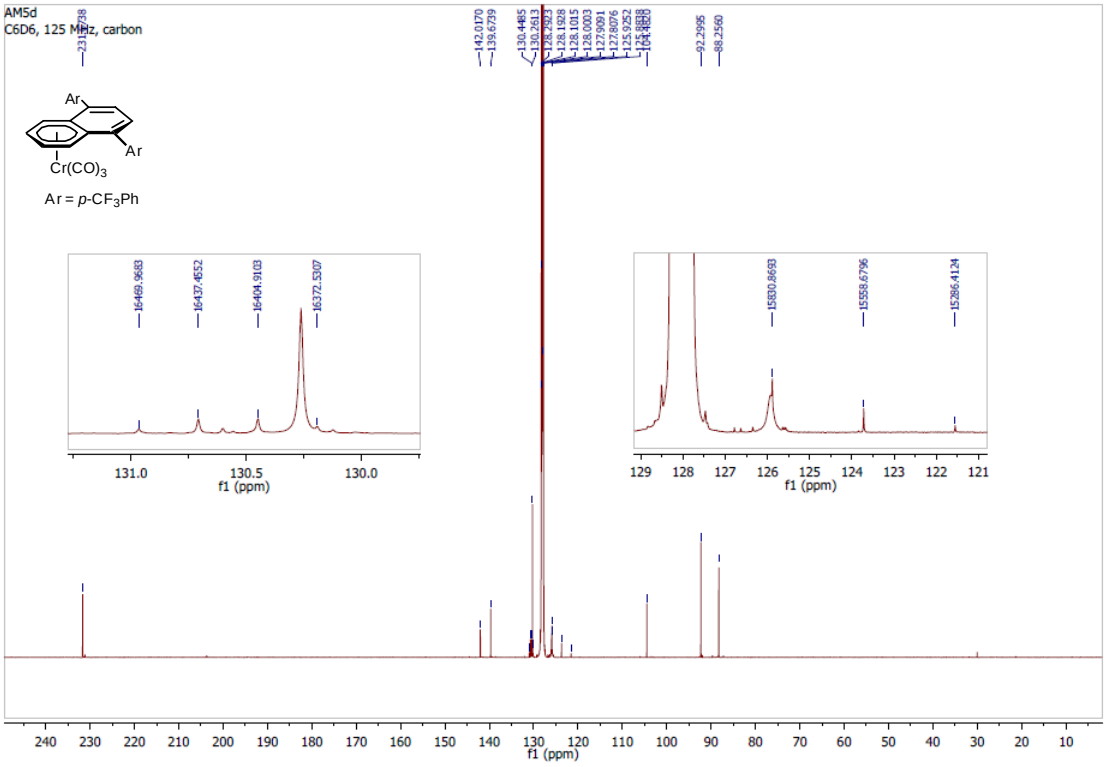
2.03
1.97
2.00
f1 (ppm)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Ar
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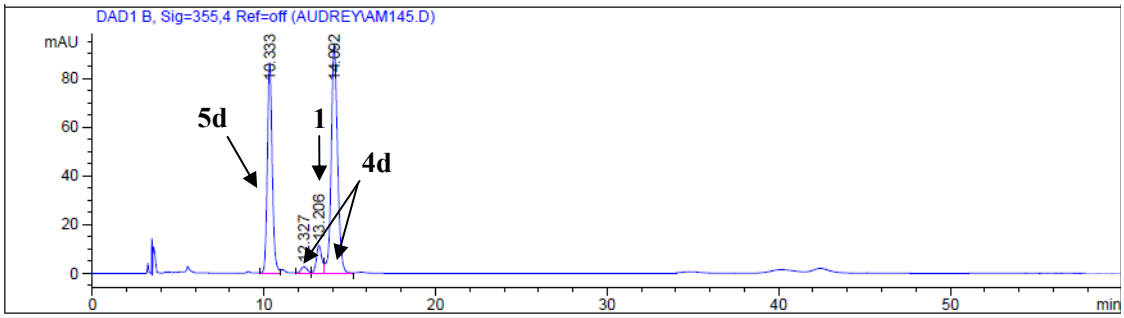


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Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


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Signal 2: DAD1 B, Sig=355,4 Ref=off

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   2  12.327 BV    0.3948   65.98025    2.64749   1.4938
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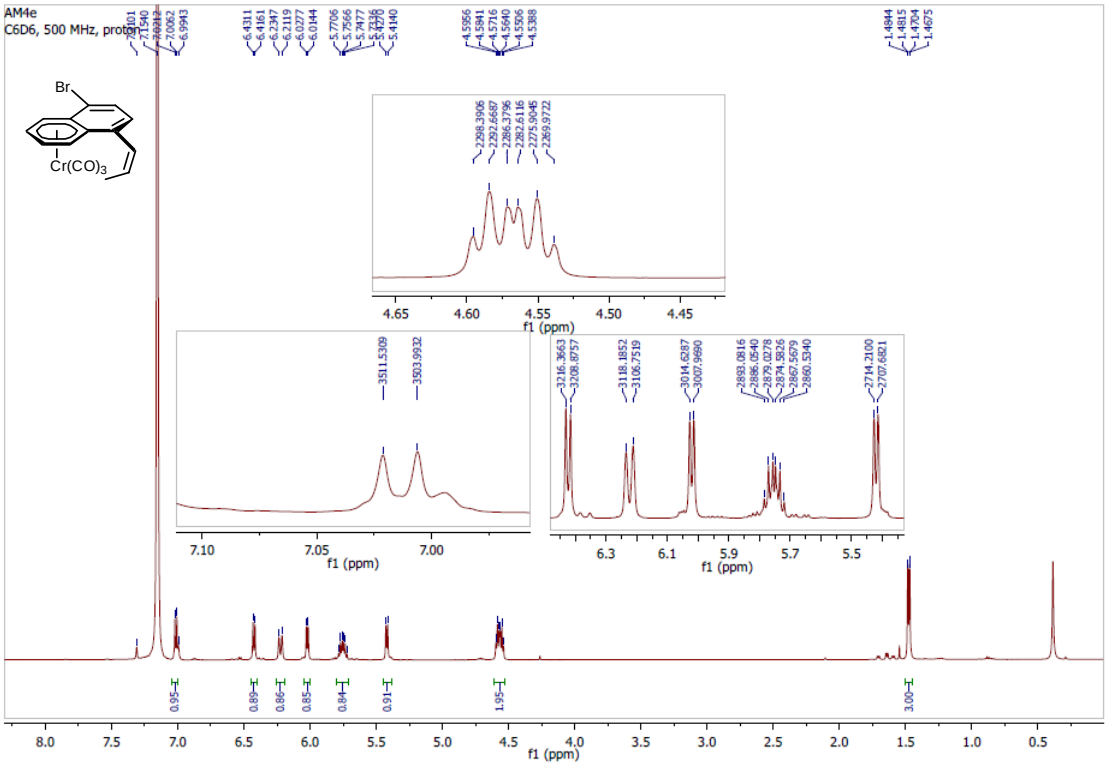
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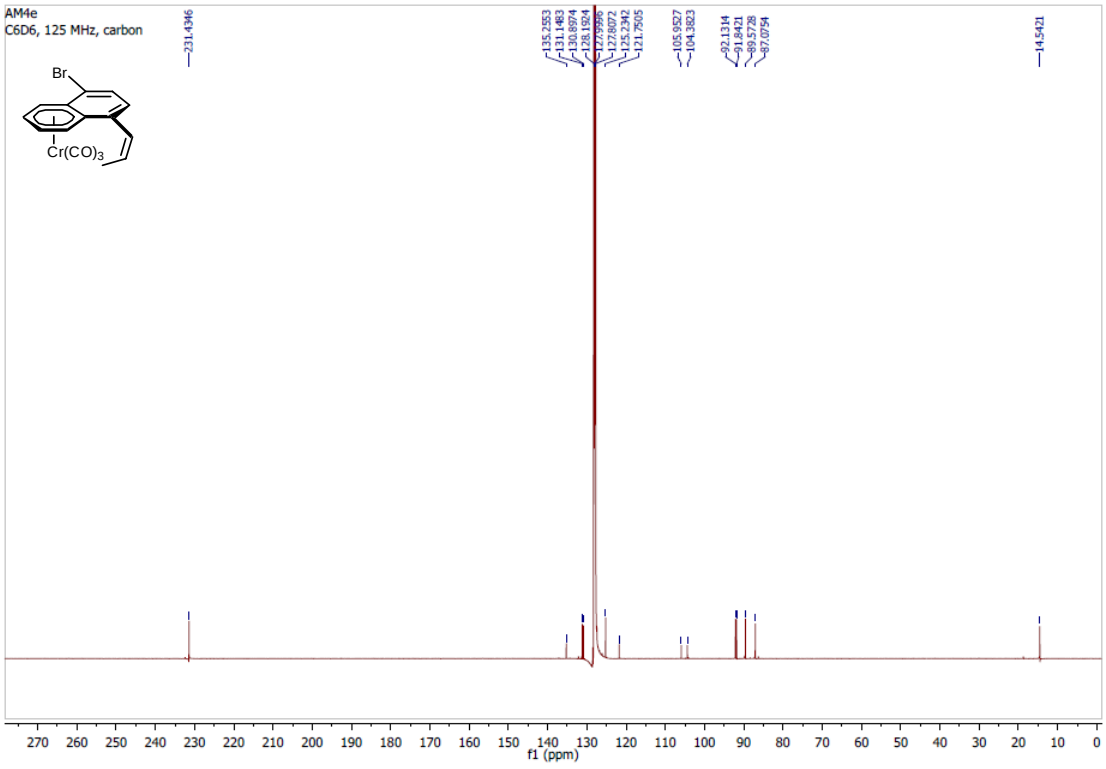
Br
Cr(CO)3
f1 (ppm)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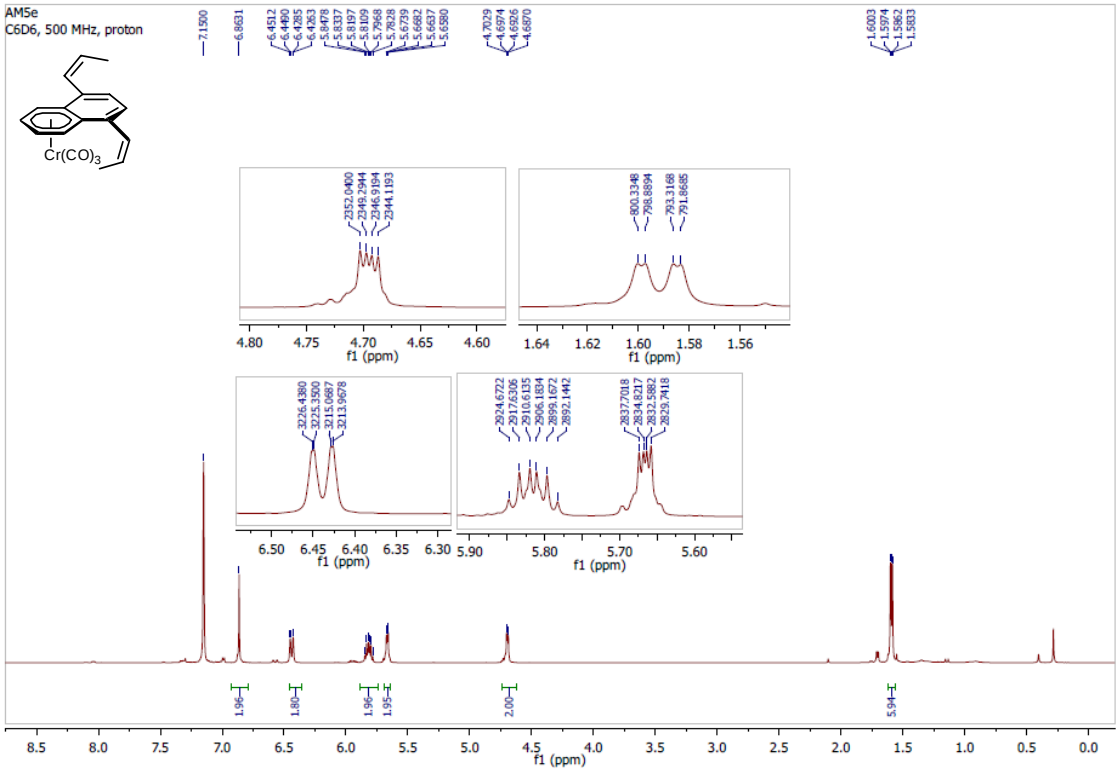
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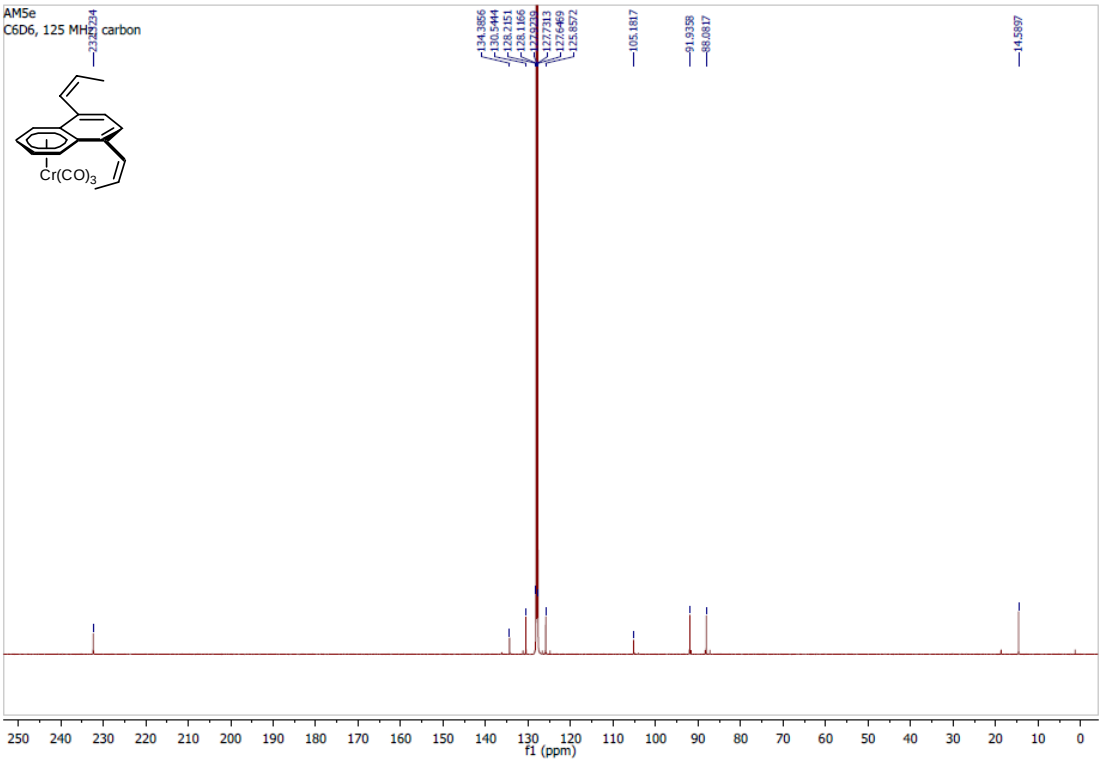
C6D6, 500 MHz, proton
Cr(CO)3
f1 (ppm)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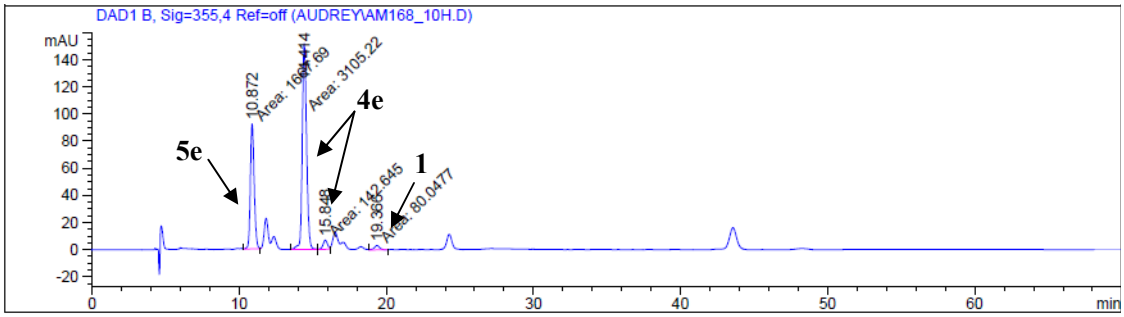
C6D6, 125 MHz, carbon
Cr(CO)3
f1 (ppm)

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Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=254,4 Ref=off


Signal 2: DAD1 B, Sig=355,4 Ref=off

Peak RetTime Type  Width     Area      Height     Area
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   2  14.414 MM    0.3409 3105.21851  151.82996  62.1591
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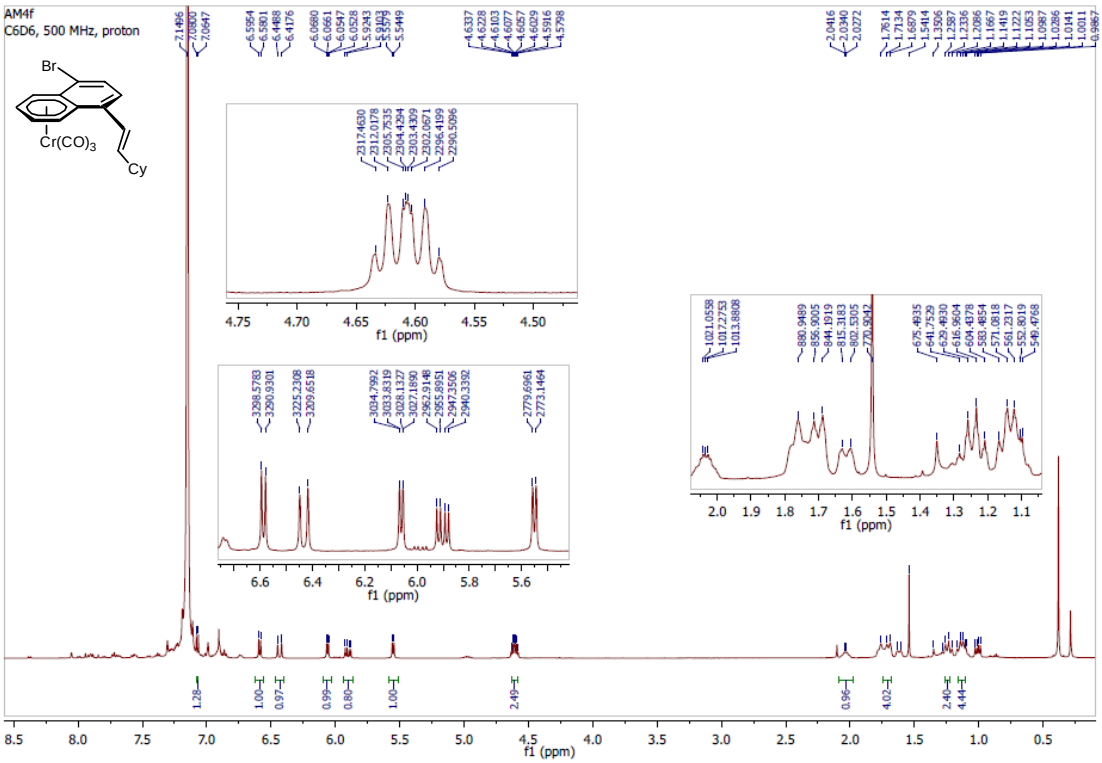
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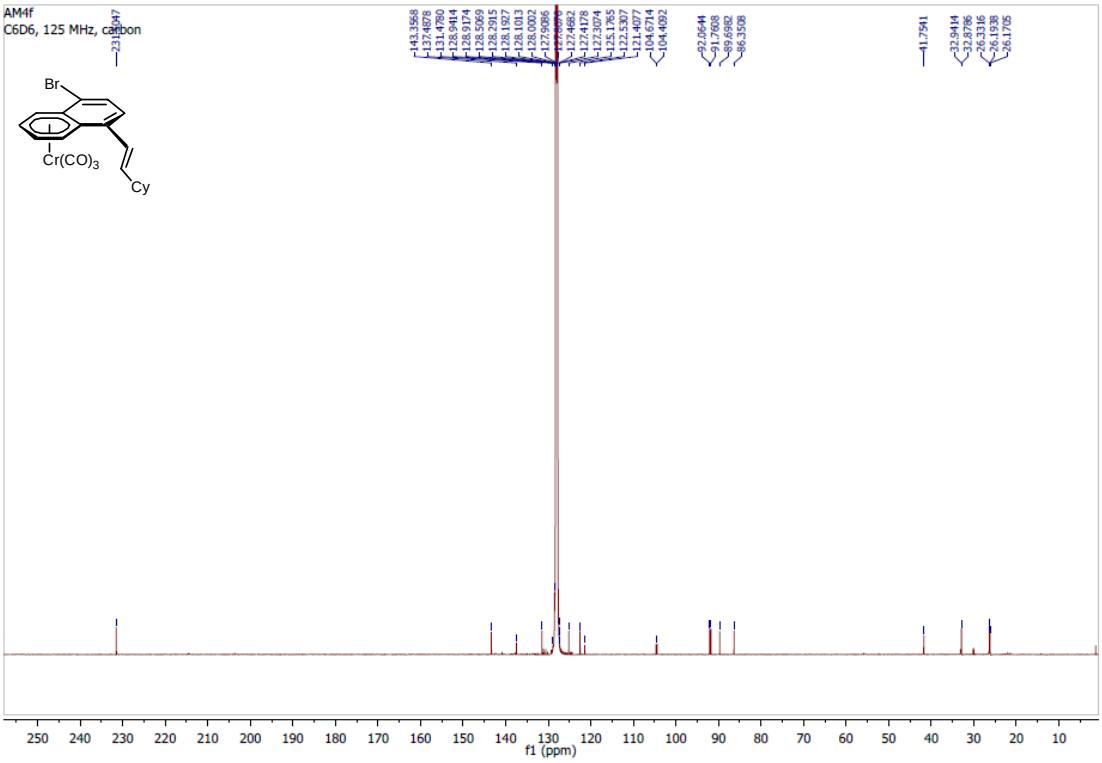
Br
Cr(CO)3
Cy
f1 (ppm)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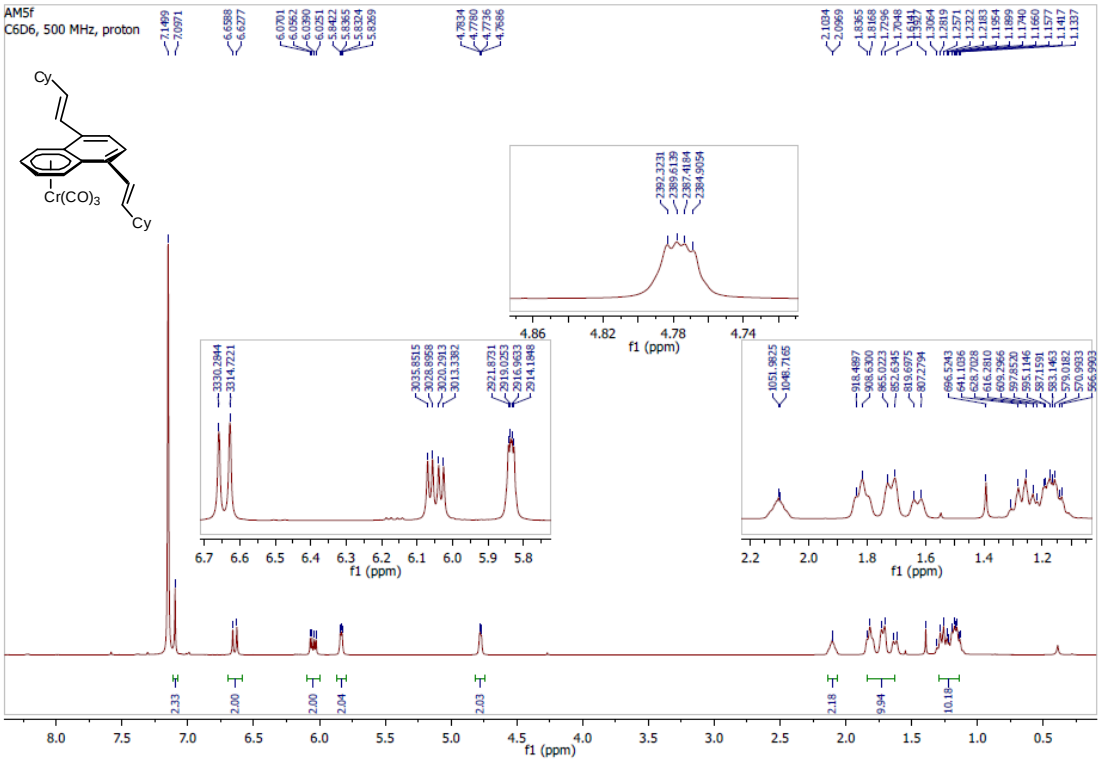
Cy
f1 (ppm)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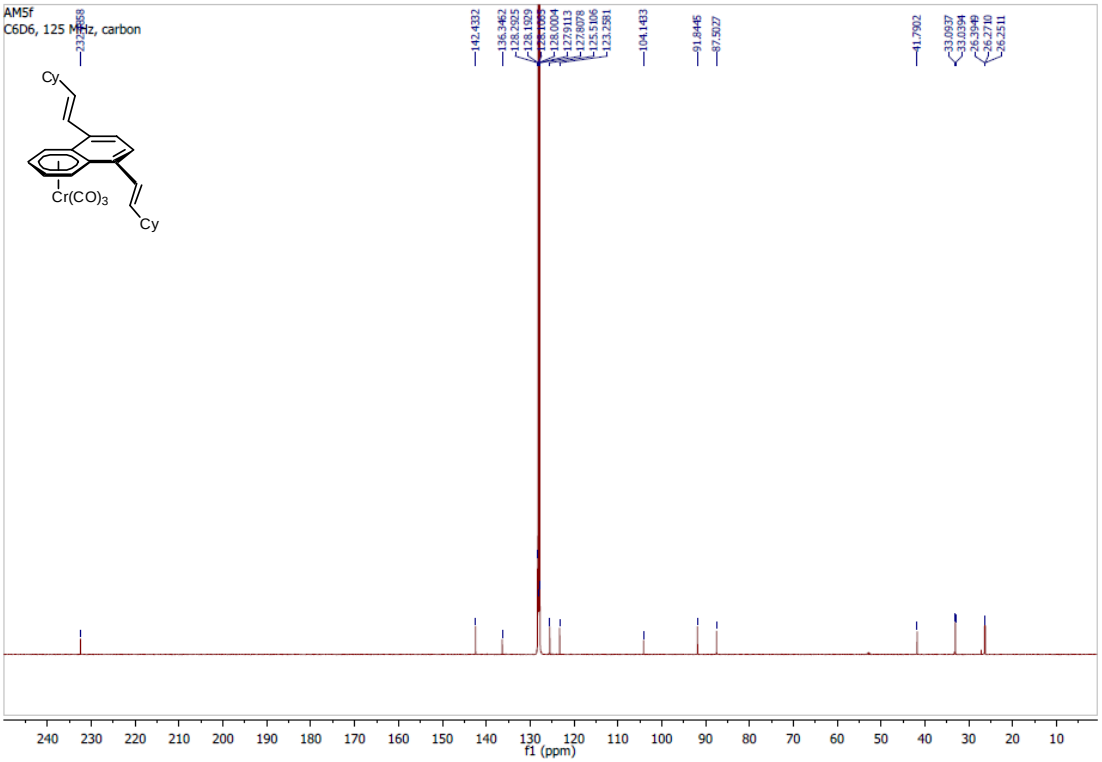
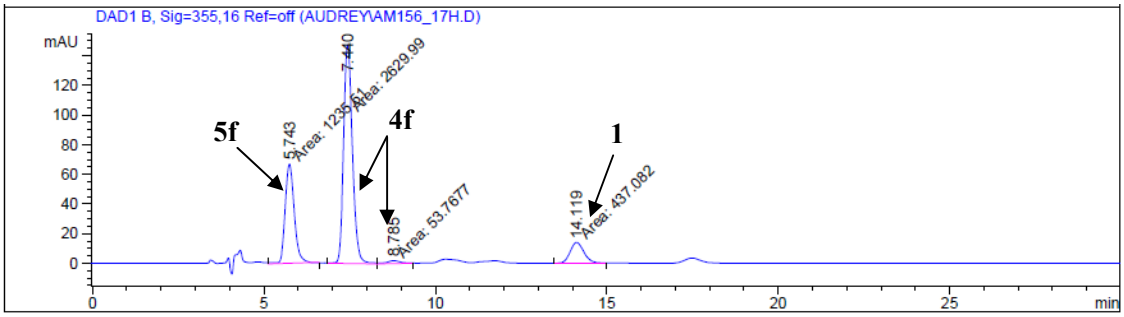
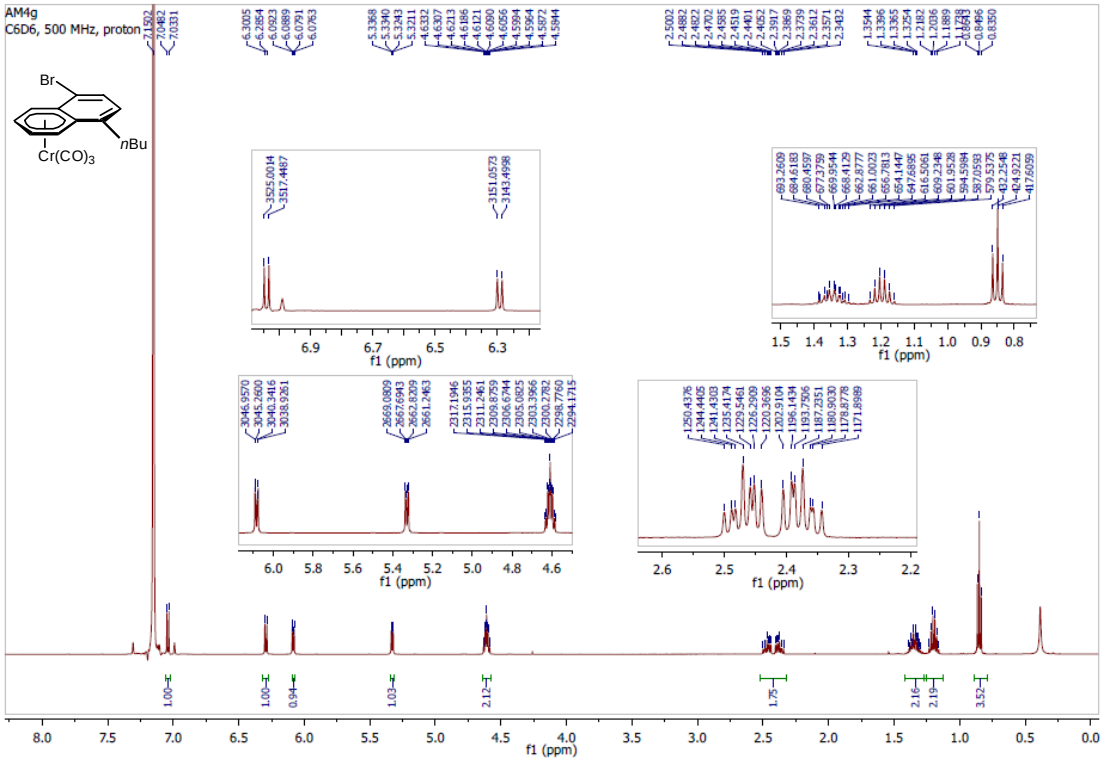
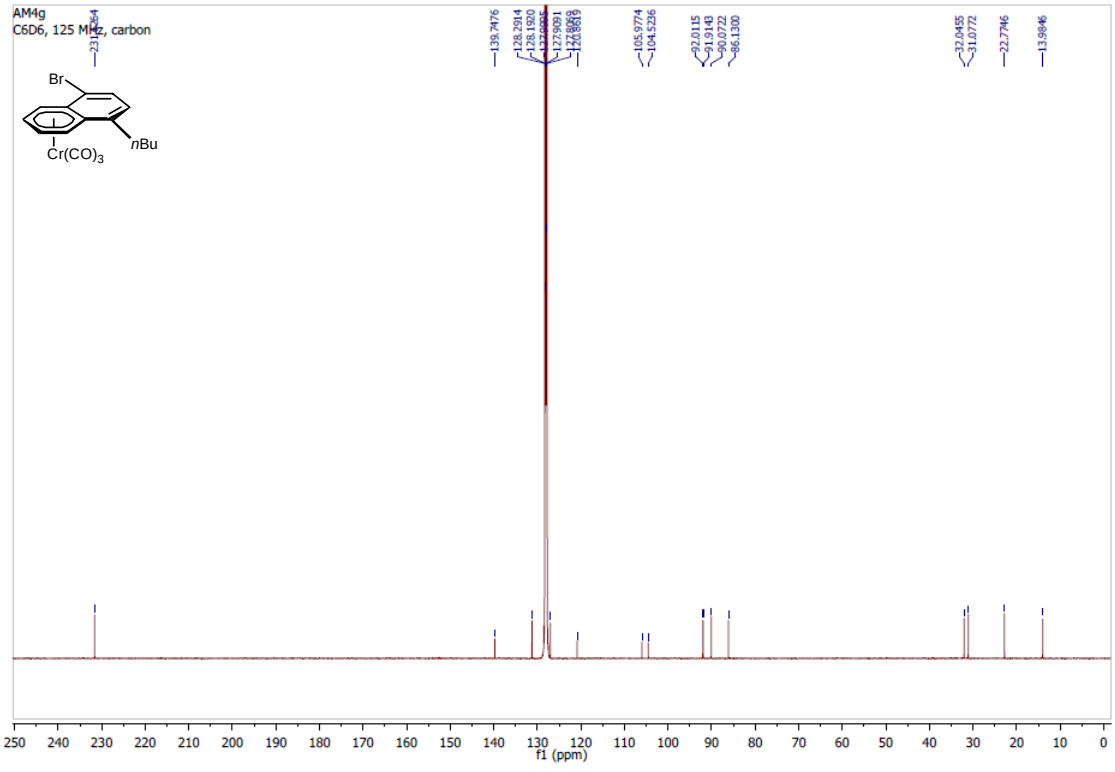
Cy
Cr(CO)3
Cy
f1 (ppm)

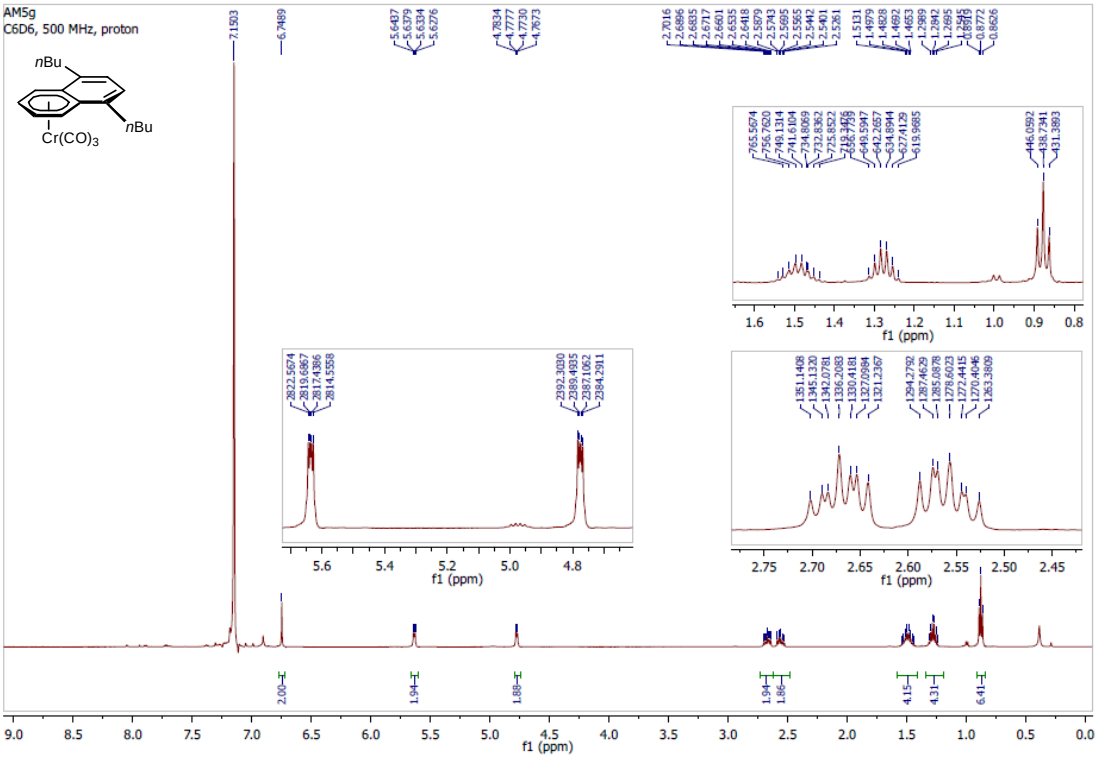

AM5f
C6D6, 125 MHz, carbon
Cy
Cr(CO)3
Cy
f1 (ppm)

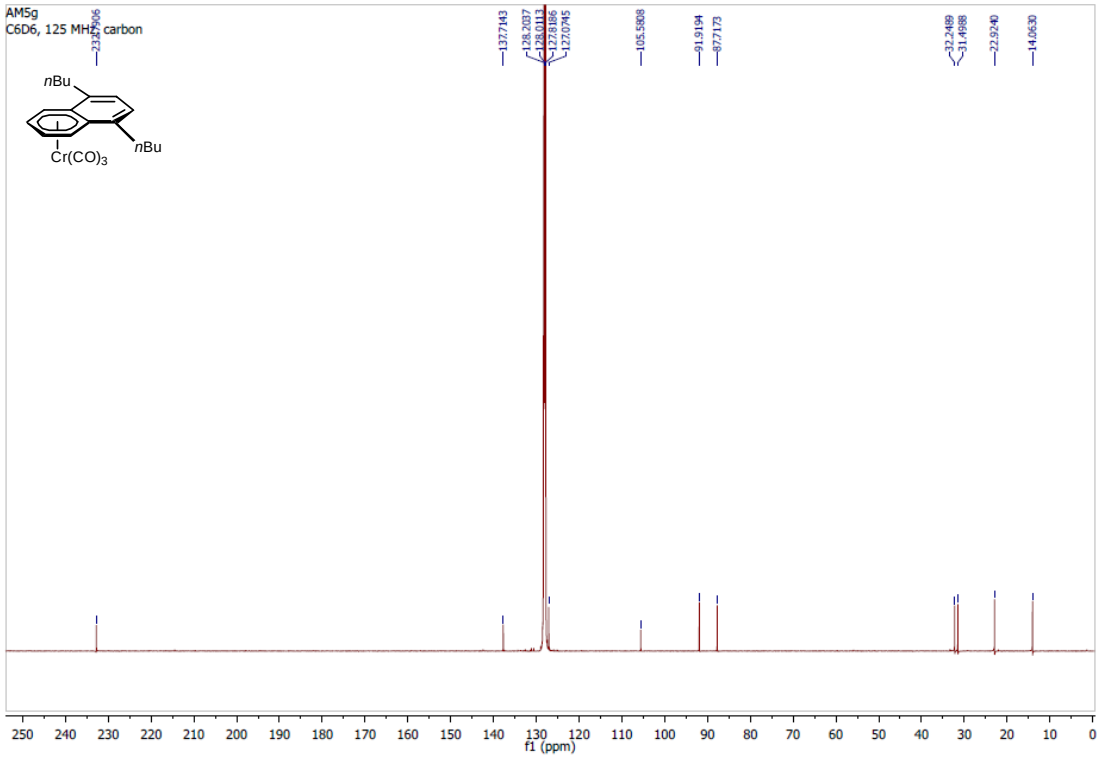


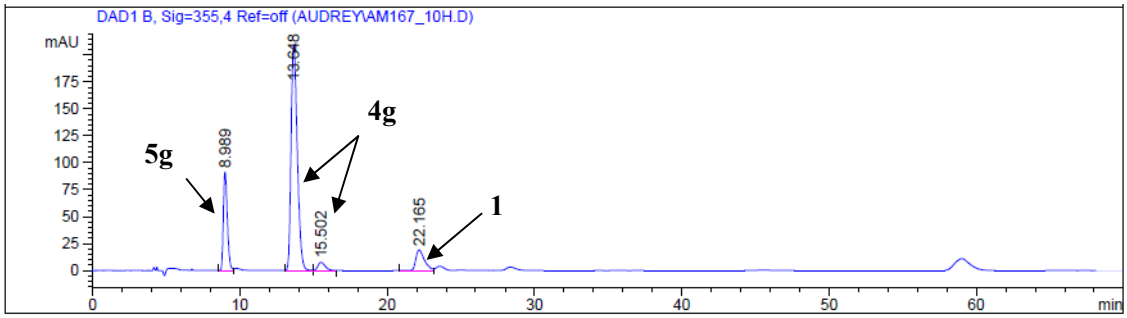

```
=====================================================================
                      Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=254,4 Ref=off


Signal 2: DAD1 B, Sig=355,16 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]    [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   5.743 MM    0.3076 1235.51282   66.93975  28.3612
   2   7.440 MM    0.2970 2629.98584  147.58998  60.3713
   3   8.785 MM    0.4576   53.76768    1.95822   1.2342
   4  14.119 MM    0.5000  437.08249   14.56855  10.0332
```


AM4g
C6D6, 500 MHz, proton
Br
nBu
Cr(CO)3
f1 (ppm)


AM4g
C6D6, 125 MHz, carbon
Br
nBu
Cr(CO)3
f1 (ppm)


AM5g
C6D6, 500 MHz, proton
nBu
nBu
Cr(CO)3
f1 (ppm)


AM5g
C6D6, 125 MHz, carbon
nBu
nBu
Cr(CO)3
f1 (ppm)




```
=====================================================================
                      Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=254,4 Ref=off


Signal 2: DAD1 B, Sig=355,4 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   8.989 BV    0.2923 1722.66150   91.20966  19.3654
   2  13.648 BV    0.4506 6144.23389  209.23358  69.0706
   3  15.502 VV    0.5394  258.80597    7.48424   2.9094
   4  22.165 BV    0.6044  769.88159   19.01349   8.6547
```

7. References

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