

Supporting Information for

Nickel and nucleophilic cobalt-catalyzed trideuteriomethylation of aryl halides using trideuteriomethyl *p*-toluenesulfonate

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General Information.

All reactions were performed on oven-and flame-dried glassware under argon using standard Schlenk techniques. Flash column chromatography was performed with silica gel 60 (KANTO Chemical Co. Inc., 40-50 nm). TLC monitoring was carried out with silica gel aluminum sheets (Merck, type 60 F₂₅₄). Gas chromatography (GC) monitoring was carried out on Shimadzu GC-2014. Nuclear magnetic resonance (NMR) spectra were recorded with Varian-400 (¹H NMR: 400 MHz; ¹³C NMR: 101 MHz) spectrometer or Varian-500 (¹H NMR: 500 MHz; ¹³C NMR: 126 MHz) spectrometers, calibrated from residual chloroform and deuterated chloroform as internal standards at 7.26 ppm for ¹H NMR spectra and at 77.0 ppm for ¹³C NMR spectra, respectively. ²H NMR (77 MHz on Varian-500) was recorded in CHCl₃ solvent using CDCl₃ (7.26 ppm) as an external standard. Low-resolution mass spectrum (LRMS) was recorded on Shimadzu GCMS-QP2010SE (EI, 70 eV). High-resolution mass spectrum (HRMS) was performed by the Natural Science Center for Basic Research and Development (N-BARD) of Hiroshima University using LTQ Orbitrap XL from Thermo Fisher Scientific.

Materials.

Nickel complexes were synthesized by the literature method.¹ CoCl(dmgH)₂py,² Co(salen) derivatives,³ and Me–Co(salen)(H₂O)⁴ were prepared by the reported methods. N,N-dimethylformamide (DMF) were dried over activated MS 4Å, distilled and stored with activated MS 4Å under argon. Unless otherwise noted, commercially available reagents were used as received without further purification.

Representative procedure for the trideuteriomethylation of aryl halides (Table 1 by Co(salen)).

In an oven-dried Schlenk tube, Mn powder (110.0 mg, 2.0 mmol) was added and heated at 400 °C for 15 min under vacuum. After cooling, the Schlenk tube was charged with NiBr₂bpy (37.5 mg, 0.1 mmol) and Co(salen) (32.5 mg, 0.1 mmol), and then heated again at ca. 80 °C under vacuum. After cooling, DMF (4 mL) and TMSCl (6.4 µL) were poured and stirred for 10 min at room temperature. 4-Phenyl iodobenzene (**1a**, 280.1 mg, 1.0 mmol) and CD₃OTs (283.9 mg, 1.5 mmol) were successfully added. The reaction mixture was stirred for 24 h at 30 °C. The obtained mixture was diluted and quenched with ethyl acetate and brine. The aqueous phase was extracted with ethyl acetate. The combined organic phase was dried over MgSO₄. After filtration and removal of the solvent, the residue was purified by a silica-gel column chromatography to get **3a**⁵ as a white solid (Mp.: 255–255.5 °C) in 140.4 mg (82%). ¹H NMR (500 MHz, CDCl₃) δ 7.61 – 7.55 (m, 2H), 7.52 – 7.47 (m, 2H), 7.45 – 7.39 (m, 2H), 7.32 (ddt, *J* = 7.9, 6.8, 1.2 Hz, 1H), 7.28 – 7.22 (m, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 141.14, 138.34, 136.89, 129.46, 128.68, 126.97, 126.95, 126.94, 20.26 (hept, *J* = 19.3 Hz); ²H NMR (77 MHz, CHCl₃) δ 2.31; EI-MS m/z (relative intensity): 171(M⁺, 100), 154 (11).

3b: Isolated as a colorless oil in 62% yield (137.1 mg); ¹H NMR (400 MHz, CDCl₃) δ 7.72 (d, *J* = 8.1 Hz, 2H), 7.20 (d, *J* = 8.1 Hz, 2H), 1.35 (s, 12H); ¹³C NMR (101 MHz, CDCl₃) δ 141.26, 134.77, 128.49, 83.59, 20.88 (hept, *J* = 19.0 Hz); ²H NMR (77 MHz, CHCl₃) δ 2.33; EI-MS m/z (relative intensity): 221 (M⁺, 25), 206(29), 135(73), 122(100); HRMS calcd for C₁₃H₁₆D₃BO₂ [M⁺]: 221.1666, found: 221.1666.

3c: Isolated as a colorless oil in 40% yield (95.0 mg); ¹H NMR (500 MHz, CDCl₃) δ 7.08 (d, *J* = 8.7 Hz, 2H), 6.80 (d, *J* = 8.7 Hz, 2H), 3.93 (t, *J* = 6.6 Hz, 2H), 1.82 – 1.72 (m, 1H), 1.50 – 1.40 (m, 1H), 1.39 – 1.24 (m, 3H), 0.93 – 0.86 (m, 2H); ¹³C NMR (500 MHz, CDCl₃) δ 157.29, 130.53, 126.68, 120.00, 110.87, 67.86, 31.83, 29.36, 29.28, 26.16, 22.67, 15.44 (hept. *J* = 19.3 Hz), 14.11; ²H NMR (77 MHz, CHCl₃) δ 2.22; EI-MS m/z (relative intensity): 223 (M⁺, 10), 111 (100); HRMS calcd for C₁₅H₂₁D₃O [M⁺]: 223.2015, found: 223.2015.

3d: Isolated as a colorless oil in 55 yield (103.0 mg); ¹H NMR (400 MHz, CDCl₃) δ 7.36 –

7.27 (m, 2H), 7.18 – 7.10 (m, 2H), 7.07 (tt, J = 7.1, 1.1 Hz, 1H), 7.02 – 6.94 (m, 1H), 6.97 – 6.88 (m, 2H); ^{13}C NMR (101 MHz, CDCl_3) δ 157.79, 154.69, 132.78, 130.21, 129.62, 122.76, 119.10, 118.31, 19.87 (hept, J = 19.2 Hz); ^2H NMR (77 MHz, CHCl_3) δ 2.21; EI-MS m/z (relative intensity): 187 (M^+ , 100), 169 (5), 94 (64), 77 (18); HRMS calcd for $\text{C}_{13}\text{H}_9\text{D}_3\text{O} [\text{M}^+]$: 187.1076, found: 187.1076.

A gram-scale procedure for the trideuteriomethylation of **1e**.

In an oven-dried 50mL Schlenk tube, Mn powder (769.0 mg, 14.0 mmol) was added and heated at 400 °C for 15 min under vacuum. After cooling, the Schlenk tube was charged with NiBr_2bpy (259.5 mg, 0.7 mmol) and Co(salen) (227.7 mg, 0.7 mmol), and then heated again at ca. 80 °C under vacuum. After cooling, DMF (28 mL) and TMSCl (20.0 μL) were poured and stirred for 1 h at room temperature. **1e** (1.93 g, 7.0 mmol) and CD_3OTs (1.99 g, 10.5 mmol) were successfully added. The reaction mixture was stirred for 30 h at 30 °C. The obtained mixture was diluted and quenched with ethyl acetate and brine. The aqueous phase was extracted with ethyl acetate. The combined organic phase was dried over MgSO_4 . After filtration and removal of the solvent, the residue was purified by a silica-gel column chromatography to get **3e** as a white solid (Mp.: 81–81.5 °C) in 87% yield (1.01 g); ^1H NMR (400 MHz, CDCl_3) δ 7.20 (d, J = 8.3 Hz, 2H), 7.05 (d, J = 8.3 Hz, 2H), 3.23 (s, 3H), 1.85 (s, 3H); ^{13}C NMR (125.72 MHz, CDCl_3) δ 168.16, 135.33, 133.83, 129.46, 120.02, 24.49, 20.00 (hept, J = 19.3 Hz); ^2H NMR (77 MHz, CHCl_3) δ 2.34; EI-MS m/z (relative intensity): 166 (M^+ , 37), 124 (100); HRMS calcd for $\text{C}_{10}\text{H}_{10}\text{D}_3\text{NO}_2 [\text{M}+\text{H}]^+$: 167.1185, found: 167.1257.

3f: Isolated as a white solid (Mp.: 180–180.5 °C) in 65% yield (156.2 mg); ^1H NMR (500 MHz, CDCl_3) δ 7.91–7.88 (m, 4H), 7.75–7.72 (m, 4H); ^{13}C NMR (125.72 MHz, CDCl_3) δ 167.43, 138.08, 134.30, 131.83, 129.78, 128.97, 126.45, 123.68, 20.58 (hept, J = 19.3 Hz); ^2H NMR (77 MHz, CHCl_3) δ 2.37; EI-MS m/z (relative intensity): 240 (M^+ , 100), 196 (50); HRMS calcd for $\text{C}_{15}\text{H}_8\text{D}_3\text{NO}_2 [\text{M}^+]$: 240.09878, found: 240.09878.

3g: Isolated as a yellow oil in 62% yield (123.5 mg); ^1H NMR (400 MHz, CDCl_3) δ 7.88 (d, J = 8.4 Hz, 2H), 7.28 (d, J = 8.3 Hz, 2H), 2.60 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 197.86, 143.77, 134.74, 129.24, 128.43, 26.65 – 26.45 (m), 20.83 (hept, J = 19.5 Hz); ^2H NMR (77 MHz, CHCl_3) δ 2.49; EI-MS m/z (relative intensity): 137 (M^+ , 31), 122 (100);

HRMS calcd for C₉H₇D₃O [M⁺]: 137.0920, found: 137.0925.

3h: Isolated as a colorless oil in 58% yield (137.7 mg); ¹H NMR (500 MHz, CDCl₃) δ 7.15 (m, 2H), 6.84 (m, 2H), 3.96 (t, J = 6.5 Hz, 2H), 1.81 (q, J = 6.5 Hz, 2H), 1.55–1.30 (m, 10H), 0.90 (t, J = 6.4 Hz, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 157.28, 130.52, 126.71, 126.67, 119.99, 110.87, 67.86, 31.82, 29.37, 29.36, 29.26, 26.15, 22.66, 15.42 (hept, J = 19.3 Hz), 14.10; ²H NMR (77 MHz, CHCl₃) δ 2.20; EI-MS m/z (relative intensity): 223 (M⁺, 9), 111 (100); HRMS calcd for C₁₅H₂₁D₃O [M⁺]: 223.2015, found: 223.2015.

3i: Isolated as a colorless oil in 61% yield (163.2 mg); ¹H NMR (400 MHz, CDCl₃) δ 7.13 – 7.11 (m, 1H), 7.06 – 7.02 (m, 1H), 6.85 – 6.78 (m, 1H), 1.35 – 1.26 (m, 3H), 1.12 (d, J = 7.4 Hz, 18H); ¹³C NMR (101 MHz, CDCl₃) δ 154.32, 130.84, 128.43, 126.52, 120.57, 117.92, 18.04, 16.21 (hept, J = 19.8 Hz), 13.02; ²H NMR (77 MHz, CHCl₃) δ 2.20; EI-MS m/z (relative intensity): 267 (M⁺, 29), 224 (100), 196(56); HRMS calcd for C₁₆H₂₅D₃OSi [M⁺]: 267.2098, found: 267.2097.

3j: Isolated as a colorless oil in 65% yield (129.5 mg); ¹H NMR (400 MHz, CDCl₃) δ 7.82 – 7.79 (m, 2H), 7.61 – 7.56 (m, 1H), 7.48 – 7.44 (m, 2H), 7.42 – 7.38 (m, 1H), 7.33 – 7.28 (m, 2H), 7.27 – 7.23 (m, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 198.65, 138.60, 137.72, 133.11, 130.97, 130.12, 128.52, 128.44, 125.18, 19.18 (hept, J = 19.3 Hz); ²H NMR (77 MHz, CHCl₃) δ 2.28; EI-MS m/z (relative intensity): 199 (M⁺, 11), 197 (100), 121(70); HRMS calcd for C₁₄H₉D₃O [M⁺]: 199.1076, found: 199.1080.

3k: Isolated as a colorless oil in 58% yield (111.5 mg); ¹H NMR (500 MHz, CDCl₃) δ 7.28 – 7.24 (m, 1H), 7.22 – 7.19 (m, 3H), 3.67 (t, J = 6.2 Hz, 2H), 3.14 (t, J = 6.2 Hz, 2H); ¹³C NMR (125.72 MHz, CDCl₃) δ 137.92, 133.60, 130.35, 128.69, 125.84, 125.11, 48.33, 45.26, 25.99, 24.60, 10.14 (hept, J = 19.3); ²H NMR (77 MHz, CHCl₃) δ 2.29; EI-MS m/z (relative intensity): 192 (M⁺, 42), 122 (100); HRMS calcd for C₁₂H₁₂D₃NO [M⁺]: 192.1342, found: 192.1344.

3l: Isolated as a white solid (Mp.: 179 – 179.5 °C) in 45% yield (108.1 mg); ¹H NMR (400 MHz, CDCl₃) δ 7.96 – 7.80 (m, 4H), 7.37 – 7.21 (m, 4H), ¹³C NMR (101 MHz, CDCl₃) δ 167.34, 136.41, 134.30, 132.00, 131.13, 130.57, 129.43, 128.68, 126.87, 123.75, 17.23

(hept, $J = 19.0$ Hz); ^2H NMR (77 MHz, CHCl_3) δ 2.18; EI-MS m/z (relative intensity): 240 (M^+ , 89), 220 (100), 76 (64); HRMS calcd for $\text{C}_{15}\text{H}_8\text{D}_3\text{NO}_2$ [M^+]: 240.0978, found: 240.0978.

3m: Isolated as a colorless oil in 48% yield (115.4 mg); ^1H NMR (500 MHz, CDCl_3) δ 7.65 (d, $J = 7.7$ Hz, 1H), 7.28–7.08 (m, 6H), 7.00 (d, $J = 2.5$ Hz, 1H), 6.74 (d, $J = 7.4$ Hz, 1H), 6.54 (d, $J = 2.2$ Hz, 1H), 5.27 (s, 2H); ^{13}C NMR (125.72 MHz, CDCl_3) δ 136.34, 135.57, 135.18, 130.38, 128.60, 127.95, 127.69, 127.35, 126.35, 121.61, 120.95, 119.50, 109.53, 101.57, 48.08, 18.26 (hept, $J = 19.3$ Hz); ^2H NMR (77 MHz, CHCl_3) δ 2.27; EI-MS m/z (relative intensity): 224 (M^+ , 34), 108 (100); HRMS calcd for $\text{C}_{16}\text{H}_{12}\text{D}_3\text{N}$ [M^+]: 224.1393, found: 224.1393.

3n:⁵ Isolated as a white solid (Mp.: 105–105.5 °C) in 60% yield (173.0 mg); ^1H NMR (500 MHz, CDCl_3) δ 7.98 (dt, $J = 8.3, 0.9$ Hz, 1H), 7.74 (d, $J = 8.4$ Hz, 2H), 7.45 (dt, $J = 7.4, 1.1$ Hz, 1H), 7.35 – 7.27 (m, 2H), 7.24 (td, $J = 7.4, 0.9$ Hz, 1H), 7.19 (d, $J = 8.1$ Hz, 2H), 2.32 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 144.59, 135.38, 135.21, 131.76, 129.73, 126.70, 124.51, 123.04, 122.92, 119.34, 118.43, 113.63, 21.51, 8.92 (hept, $J = 19.9$ Hz); ^2H NMR (77 MHz, CHCl_3) δ 2.19; EI-MS m/z (relative intensity): 288 (M^+ , 28), 133 (100), 91 (23).

3o: Isolated as a yellow oil in 45% yield (65.8 mg); ^1H NMR (500 MHz, CDCl_3) δ 8.77 (d, $J = 2.2$ Hz, 1H), 8.07 (d, $J = 8.6$ Hz, 1H), 7.91 (d, $J = 2.4$ Hz, 1H), 7.74 (dd, $J = 8.1, 1.7$ Hz, 1H), 7.64 (ddt, $J = 8.4, 6.8, 1.3$ Hz, 1H), 7.51 (tt, $J = 6.7, 1.3$ Hz, 1H); ^{13}C NMR (126 MHz, CDCl_3) δ 152.40, 146.54, 134.69, 130.33, 129.14, 128.41, 128.11, 127.11, 126.52, 17.93 (hept, $J = 19.7$ Hz); ^2H NMR (77 MHz, CDCl_3) δ 2.60; EI-MS m/z (relative intensity): 146 (M^+ , 100), 118 (26), 91 (7); HRMS calcd for $\text{C}_{10}\text{H}_6\text{D}_3\text{N}$ [M^+]: 146.0923, found: 146.0922.

3p: Isolated as a red oil in 67% yield (133.5 mg); ^1H NMR (500 MHz, CDCl_3) δ 7.78 (d, $J = 6.2$ Hz, 2H), 7.73 (d, $J = 6.7$ Hz, 2H), 7.57 (s, 1H), 7.48 (s, 2H), 7.31 – 7.24 (m, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 196.51, 143.10, 137.91, 134.85, 132.13, 130.27, 129.90, 128.94, 128.17, 20.81 (hept, $J = 19.6$ Hz); ^2H NMR (77 MHz, CHCl_3) δ 2.41; EI-MS m/z (relative intensity): 199 (M^+ , 38), 181 ($\text{M}^+ - \text{CD}_3$, 8), 122 (100), 105 (27), 94 (33), 77 (25);

HRMS calcd for C₁₄H₉D₃O [M⁺]: 199.1076, found: 199.1076

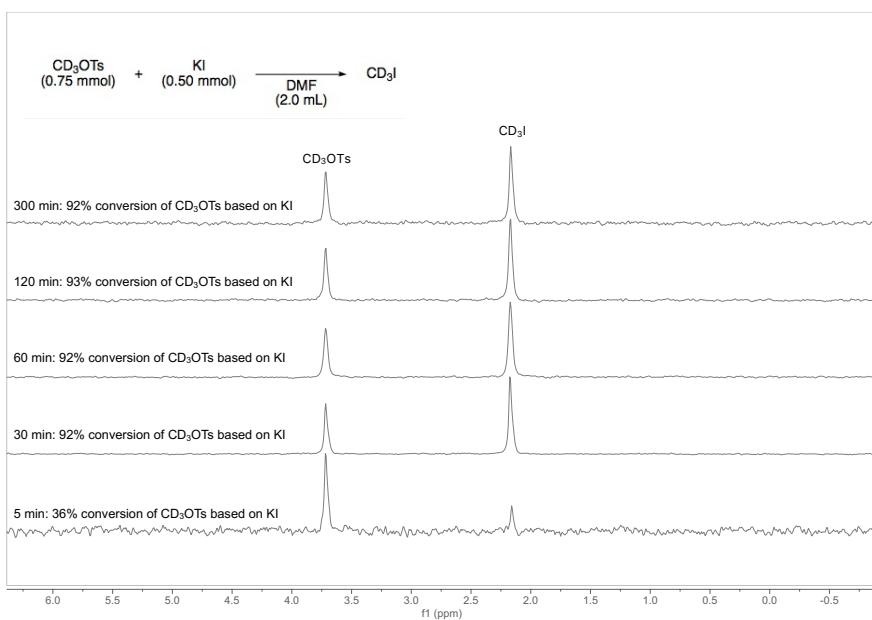
4:⁶ Isolated as a white solid (Mp.81–81.5 °C) in 75% yield (122.4 mg); ¹H NMR (500 MHz, CDCl₃) δ 7.21 (d, J = 7.9 Hz, 2H), 7.06 (d, J = 8.2 Hz, 2H), 3.24 (s, 3H), 2.38 (s, 3H), 1.86 (s, 3H); ¹³C NMR (125.72 MHz, CDCl₃) δ 170.71, 142.05, 137.60, 130.32, 126.80, 37.17, 21.04; EI-MS m/z (relative intensity): 163 (M⁺, 30), 120 (100), 91(22).

5:⁷ Isolated as a colorless oil in 54% yield (142.8 mg); ¹H NMR (400 MHz, CHCl₃) δ 7.13 – 7.11 (m, 1H), 7.04 – 7.02(m, 1H), 6.85 – 6.77(m, 1H), 2.25 (s, 3H), 1.33 – 1.29(m, 3H), 1.12 (d, J = 7.3 Hz, 18H); ¹³C NMR (101 MHz, CDCl₃) δ 154.31, 130.86, 128.54, 126.52, 120.58, 117.95, 18.04, 16.99, 13.05; EI-MS m/z (relative intensity): 264 (M⁺, 29), 221 (100).

6:⁸ Isolated as a colorless oil in 63% yield (161.5 mg); ¹H NMR (500 MHz, CDCl₃) δ 7.91 – 7.83 (m, 2H), 7.48 – 7.36 (m, 4H), 7.34 (t, J = 7.2 Hz, 1H), 6.90 (d, J = 9.3 Hz, 1H), 5.14 (s, 2H), 3.88 (s, 3H), 2.31 (s, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 166.98, 160.51, 136.56, 132.00, 129.16, 128.51, 127.90, 126.99, 126.90, 122.12, 110.44, 69.79, 51.74, 16.28; EI-MS m/z (relative intensity): 256 (M⁺, 5), 91 (100).

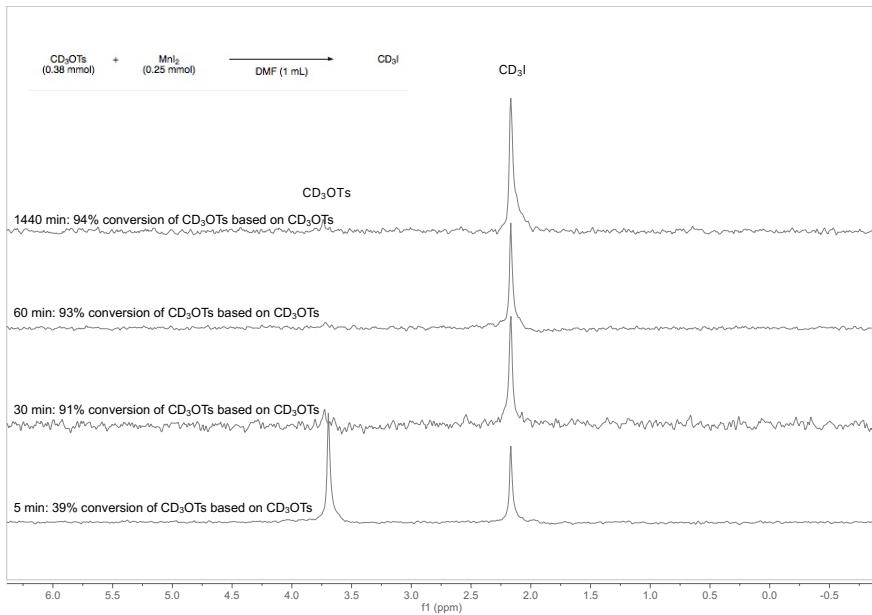
²H NMR monitoring of the reaction of CD₃OTs with KI

In an oven-dried Schlenk tube, KI (84.0 mg, 0.50 mmol), DMF (2 mL), and CD₃OTs (118 μL, 0.75 mmol) were successfully added and then followed by stirring. A part of the mixture (ca. 100 μL) was collected, diluted with chloroform to monitor by ²H NMR using CDCl₃ as an external standard.

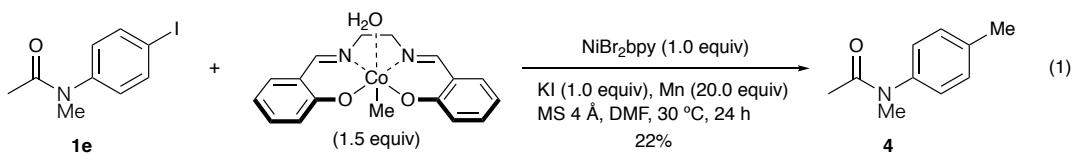


^2H NMR monitoring of the reaction of CD_3OTs with MnI_2

In an oven-dried Schlenk tube, MnI_2 (77.0 mg, 0.25 mmol), DMF (1 mL), and CD_3OTs (59 μL , 0.38 mmol) were successfully added and then followed by stirring. A part of the mixture (ca. 100 μL) was collected, passed through a short Celite-column, and diluted with chloroform to monitor by ^2H NMR using CDCl_3 as an external standard.



Stoichiometric reaction of 1e with Me–Co(salen) in the presence of NiBr_2bpy and Mn powder (eq 1).

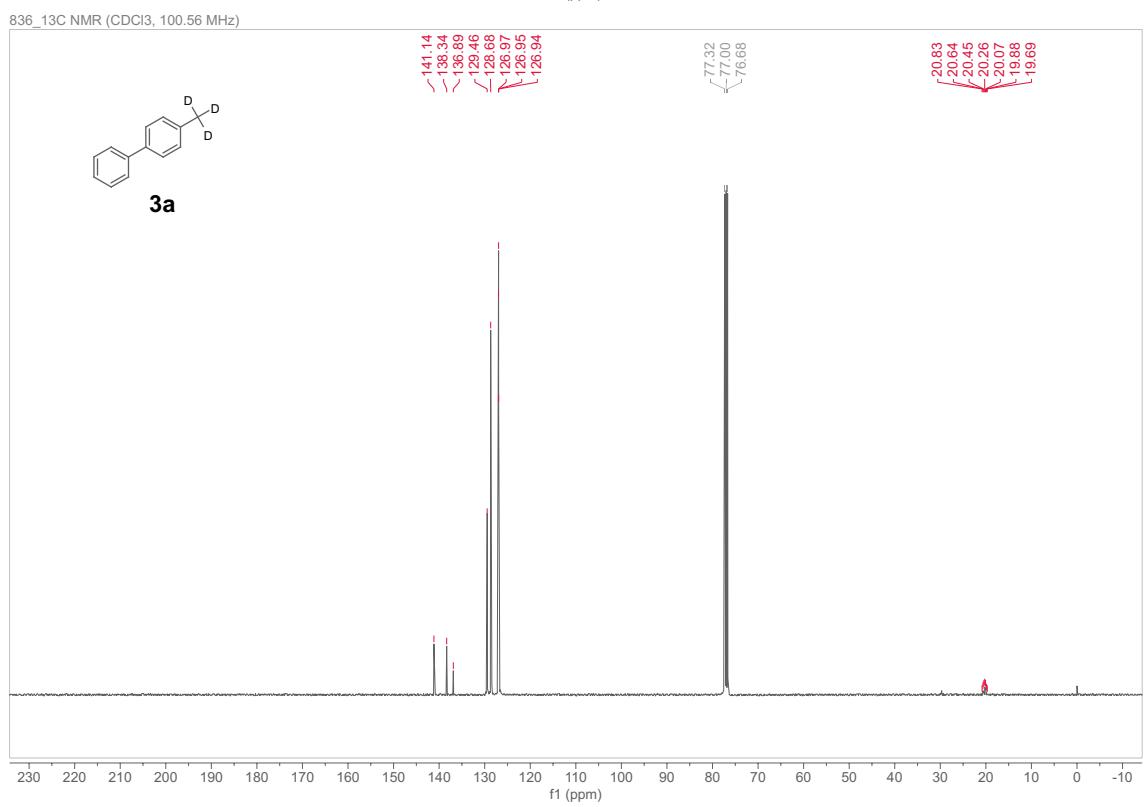
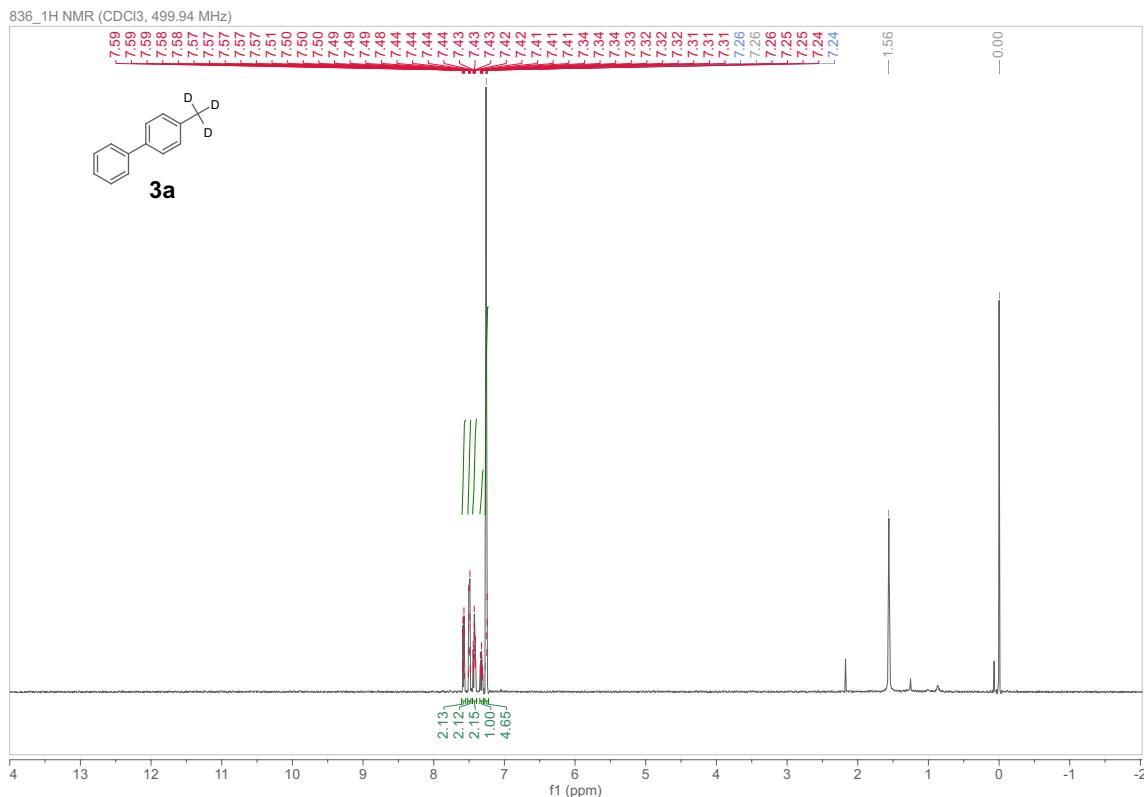


In an oven-dried Schlenk tube, Mn powder (274.0 mg, 5 mmol) and activated MS 4Å (80 mg) were added and heated at 400 °C for 15 min under vacuum. After cooling, the Schlenk tube was charged with NiBr₂bpy (93.5 mg, 0.25 mmol), KI (42.0 mg, 0.25 mmol), DMF (1.0 mL), and TMSCl (38 µL, 0.3 mmol) were successfully added and then followed by stirring for 10 min. 4-acetylmethylaminophenyl iodide (**1e**, 70.0 mg, 0.25 mmol) and Me-Co(salen)(H₂O) (134.0 mg, 0.38 mmol) were added into the solution. The reaction mixture was stirred for 24 h at 30 °C. The reaction mixture was quenched with water and poured EtOAc to dilute the mixture. The yield of the product **4** (22%) was estimated by gas chromatography using triisopropylbenzene as an internal standard.

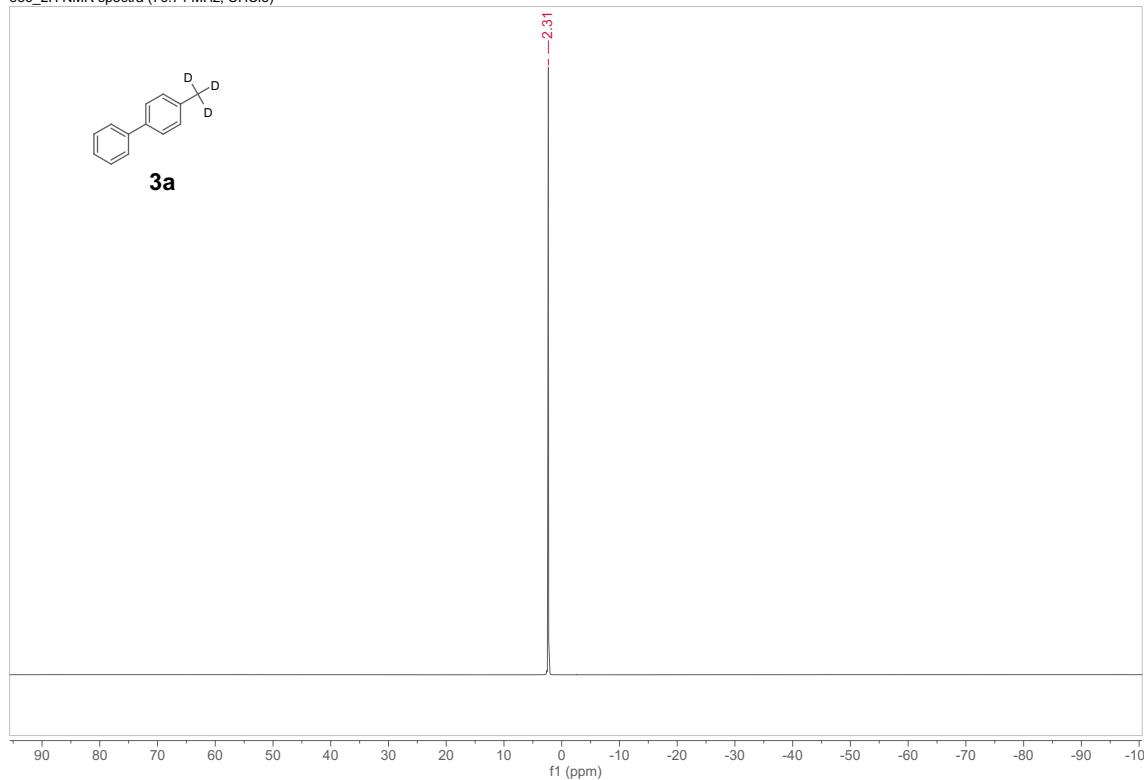
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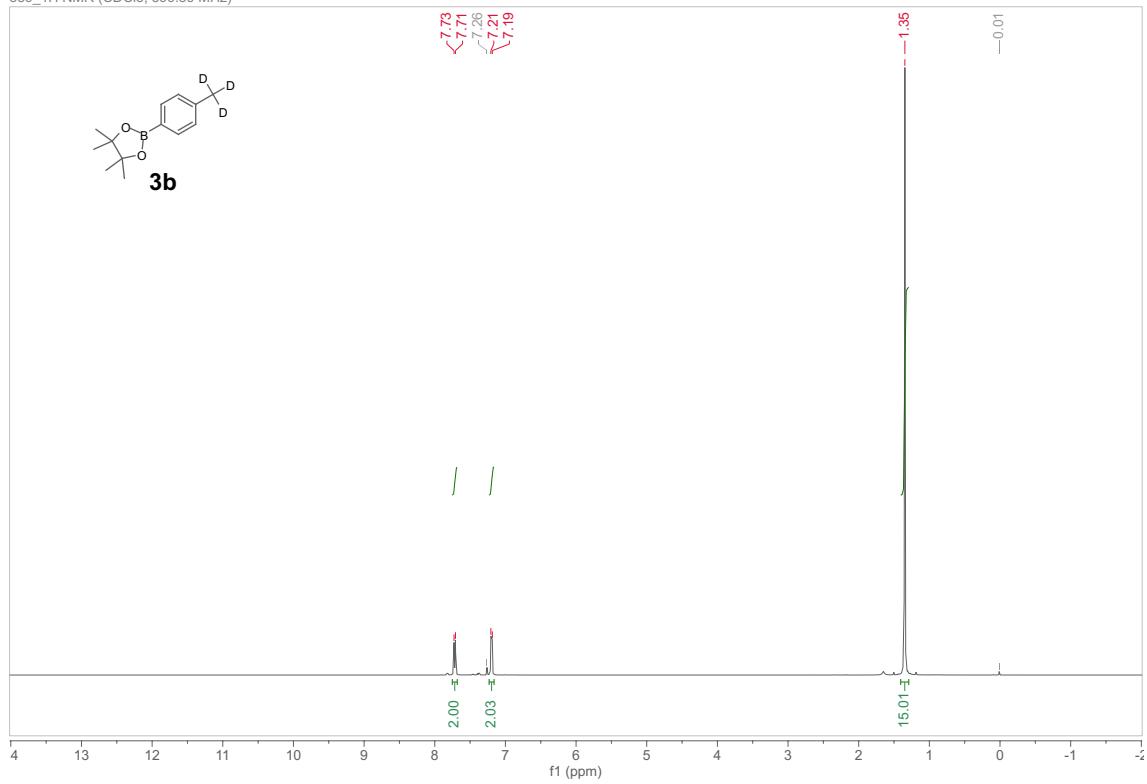
NMR chart for products



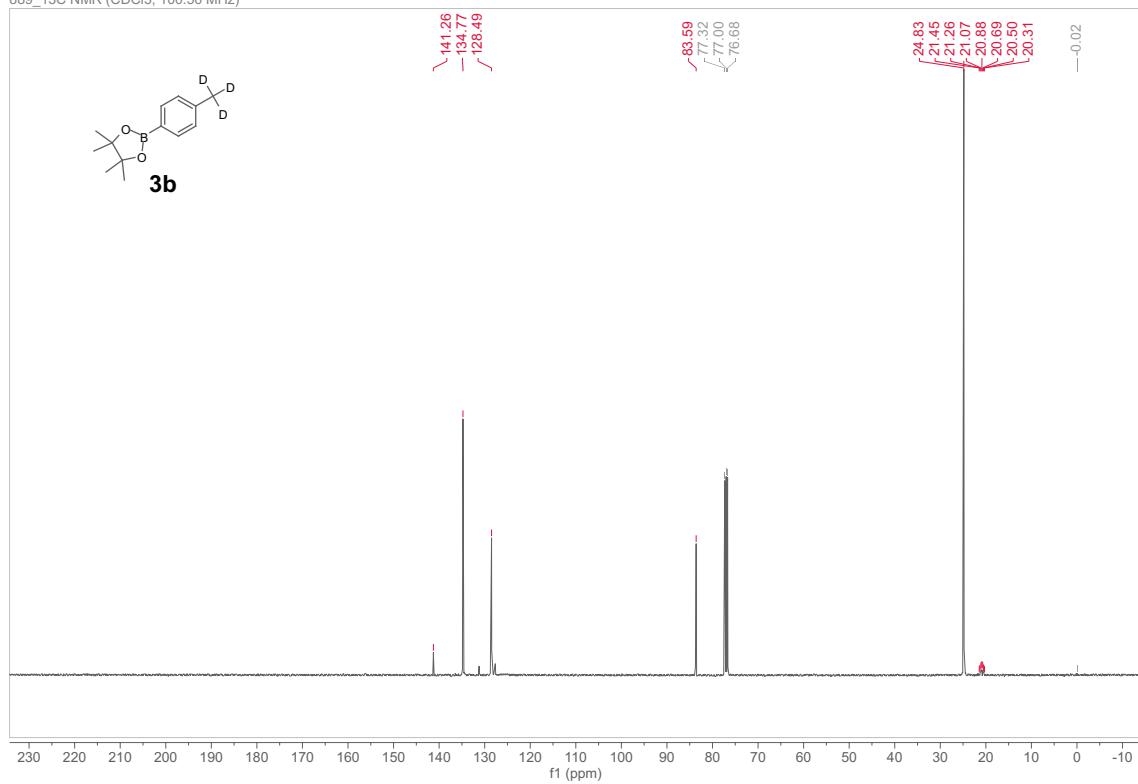
836_2H NMR spectra (76.74 MHz, CHCl₃)



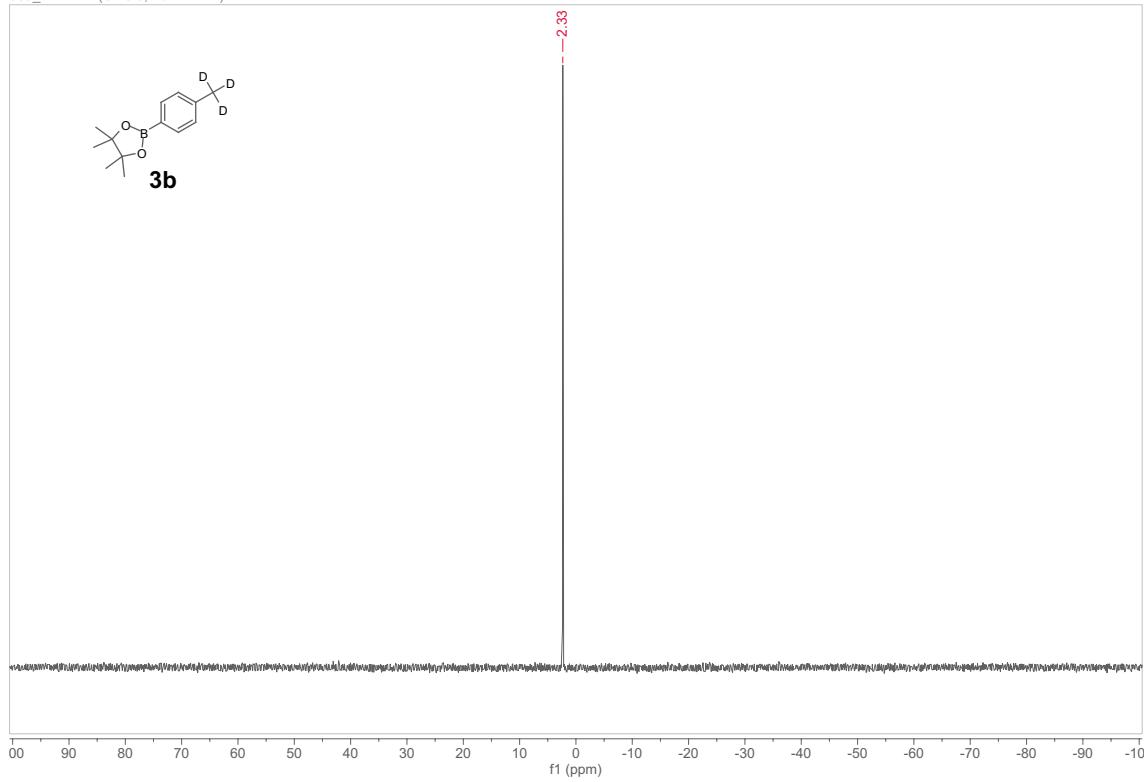
889_1H NMR (CDCl₃, 399.89 MHz)

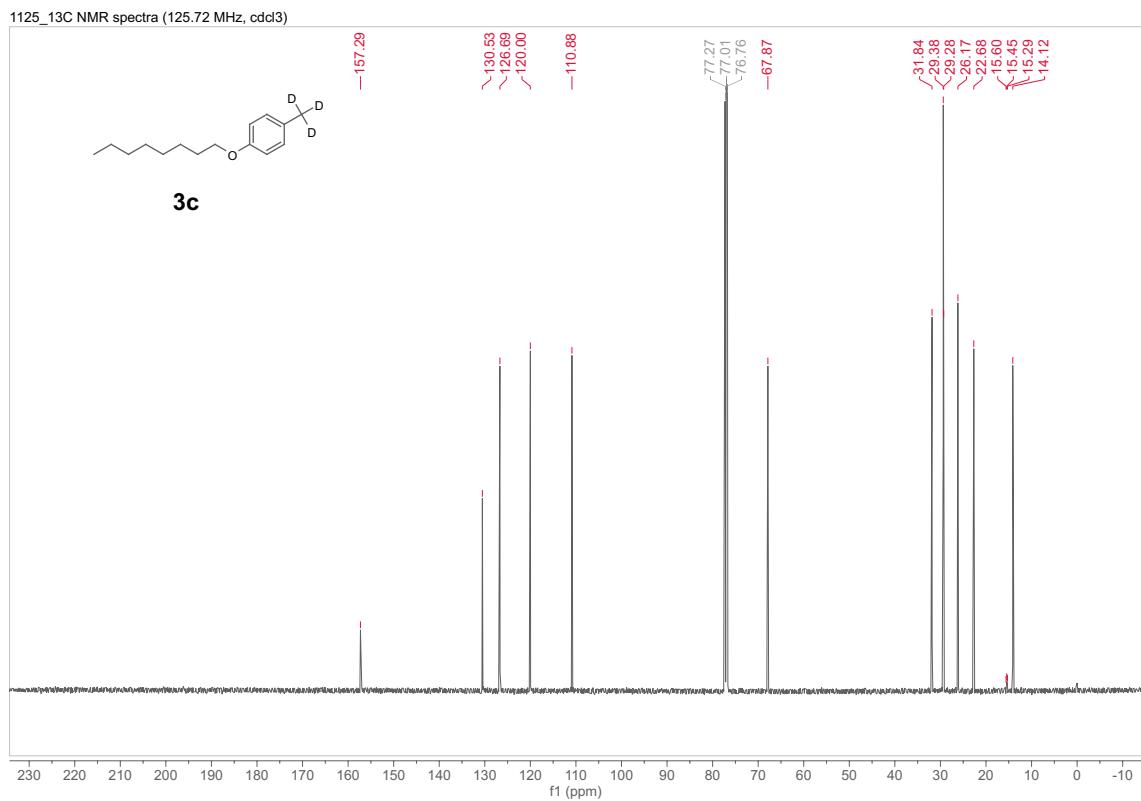
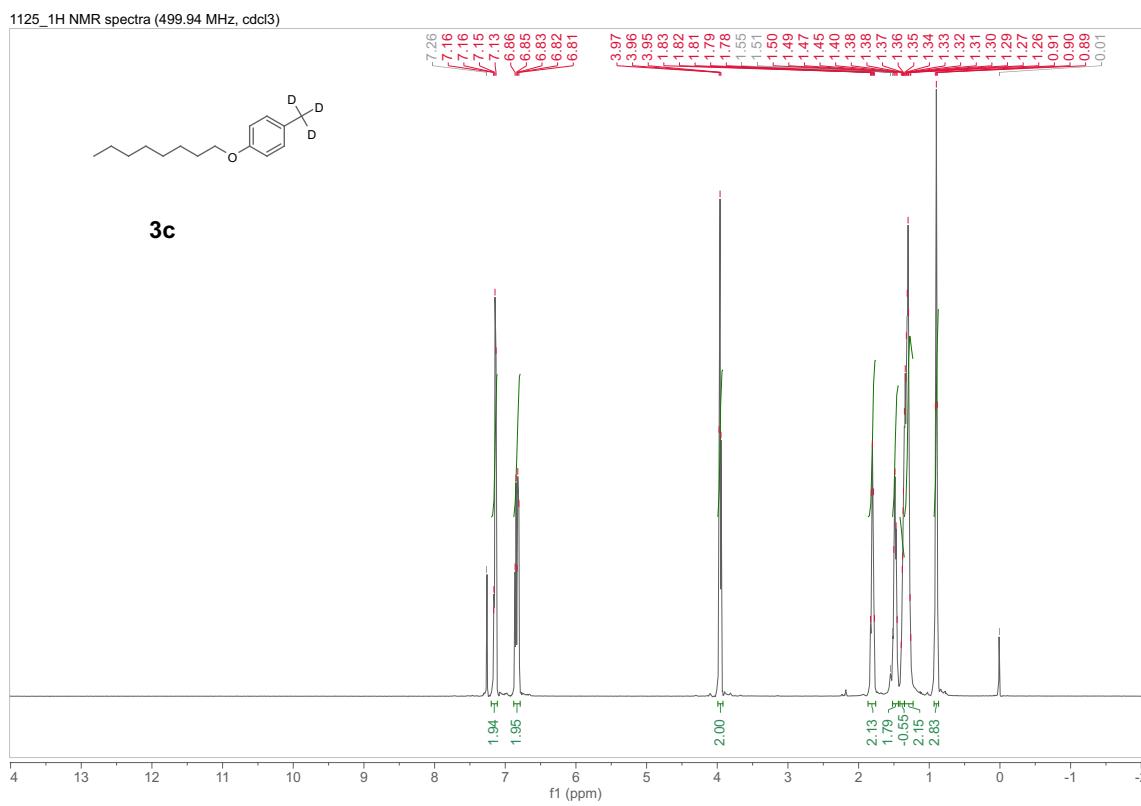


889_13C NMR (CDCl_3 , 100.56 MHz)

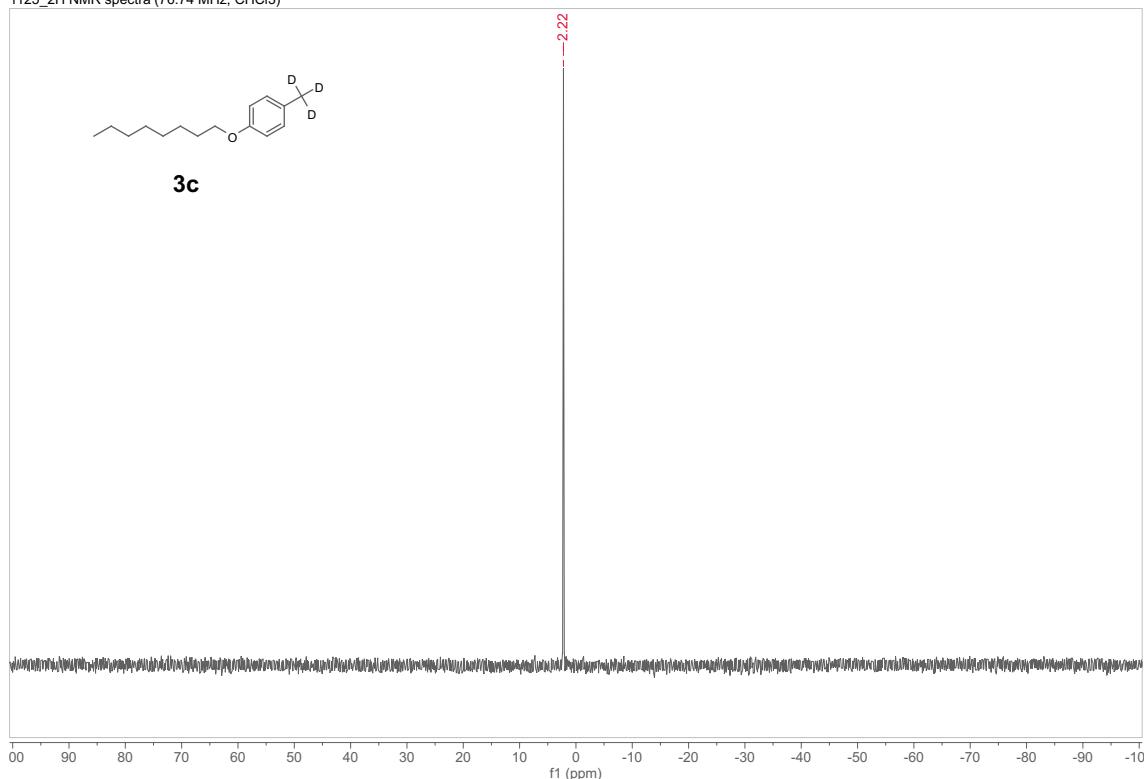


889_2H NMR (CHCl_3 , 76.74 MHz)

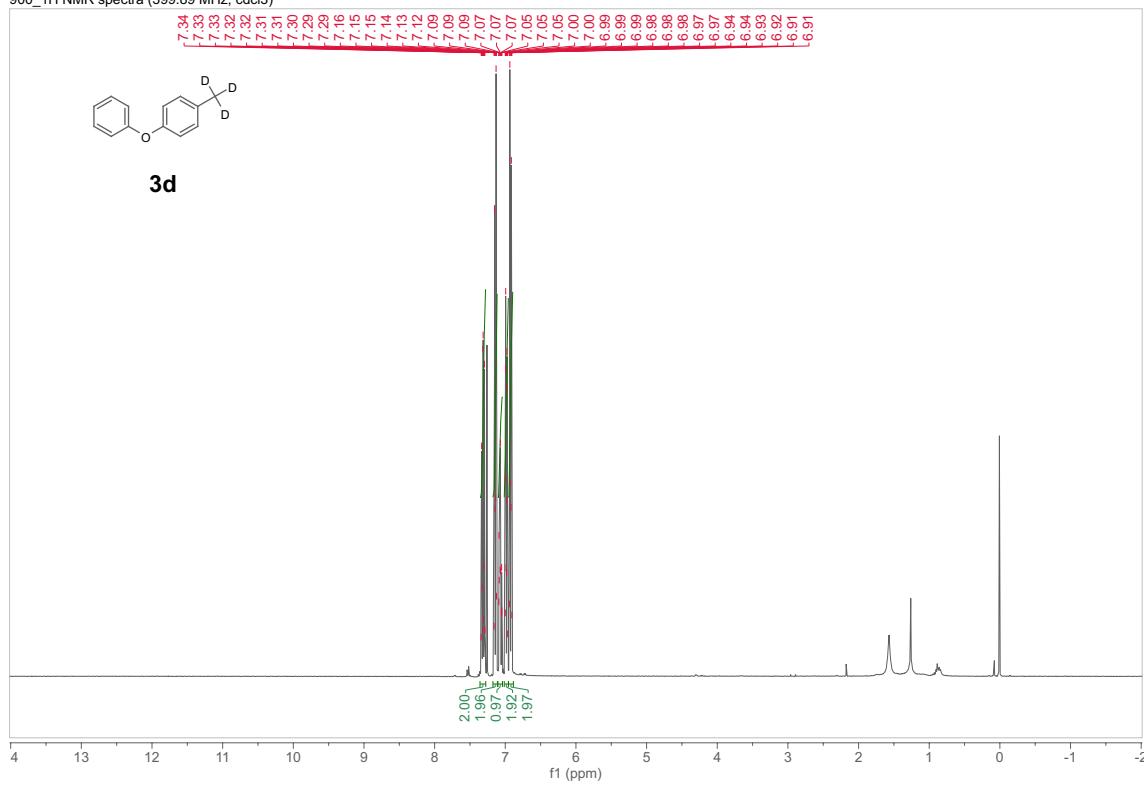


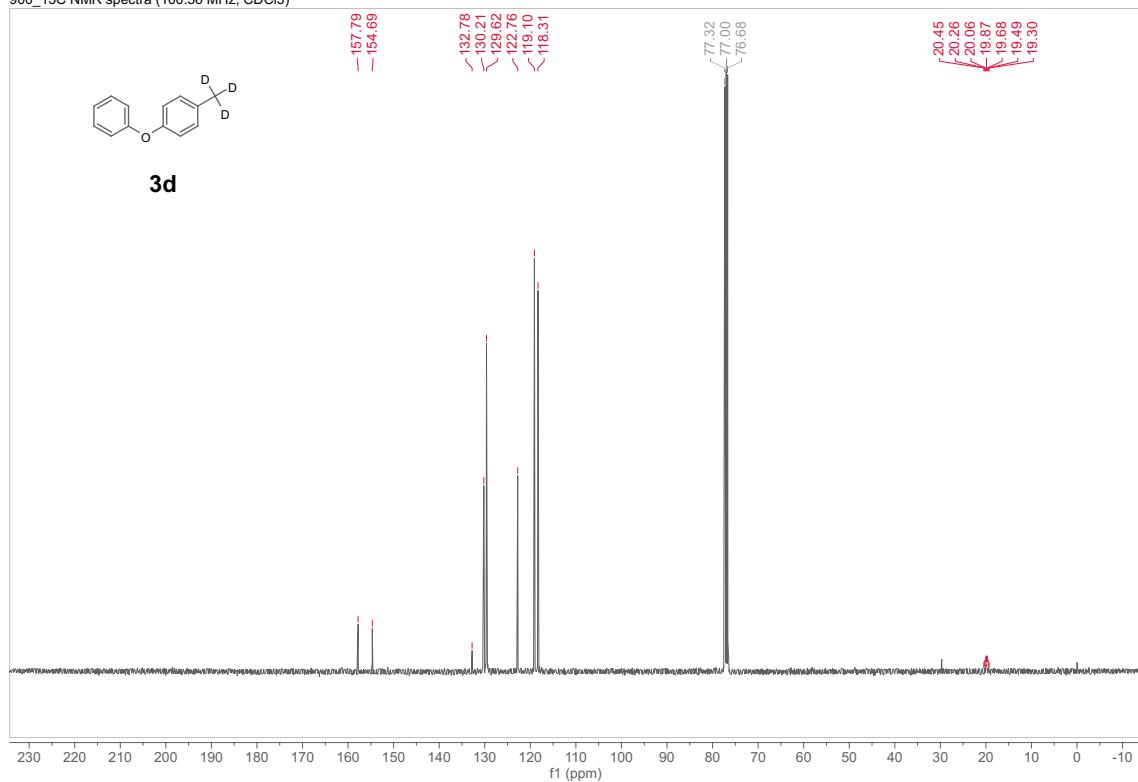
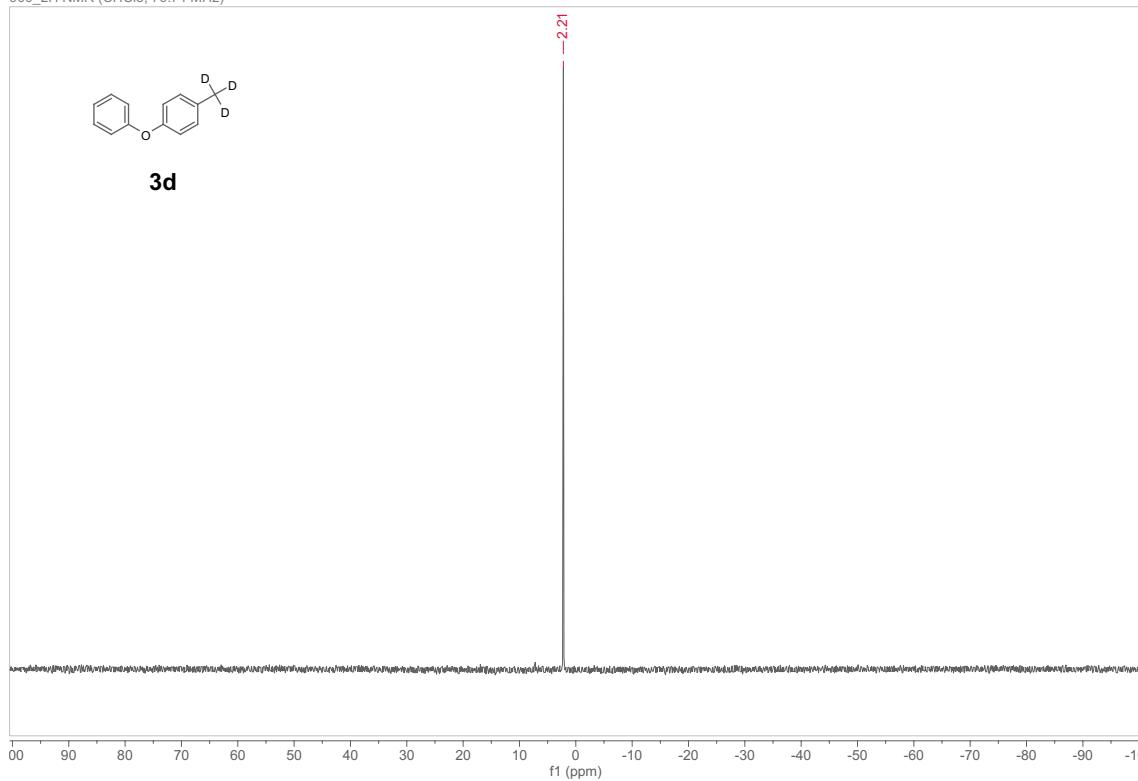


1125_2H NMR spectra (76.74 MHz, CHCl₃)

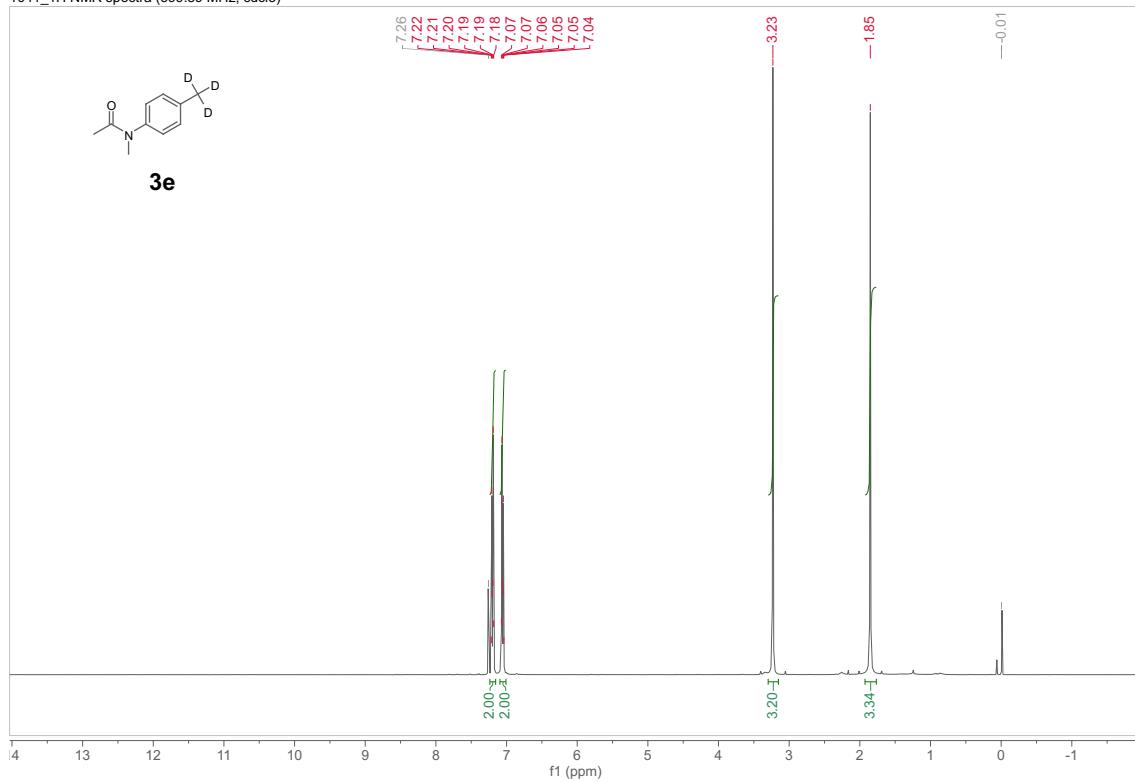


900_1H NMR spectra (399.89 MHz, cdcl₃)

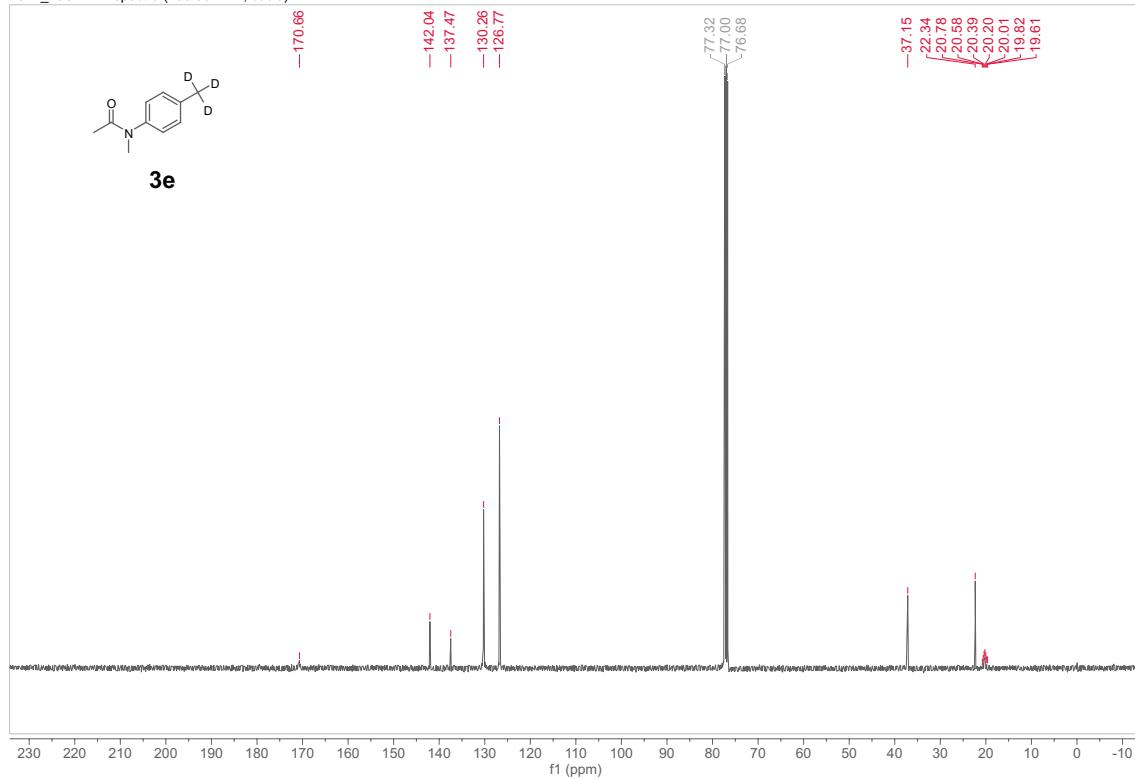


900_13C NMR spectra (100.56 MHz, CDCl₃)900_2H NMR (CHCl₃, 76.74 MHz)

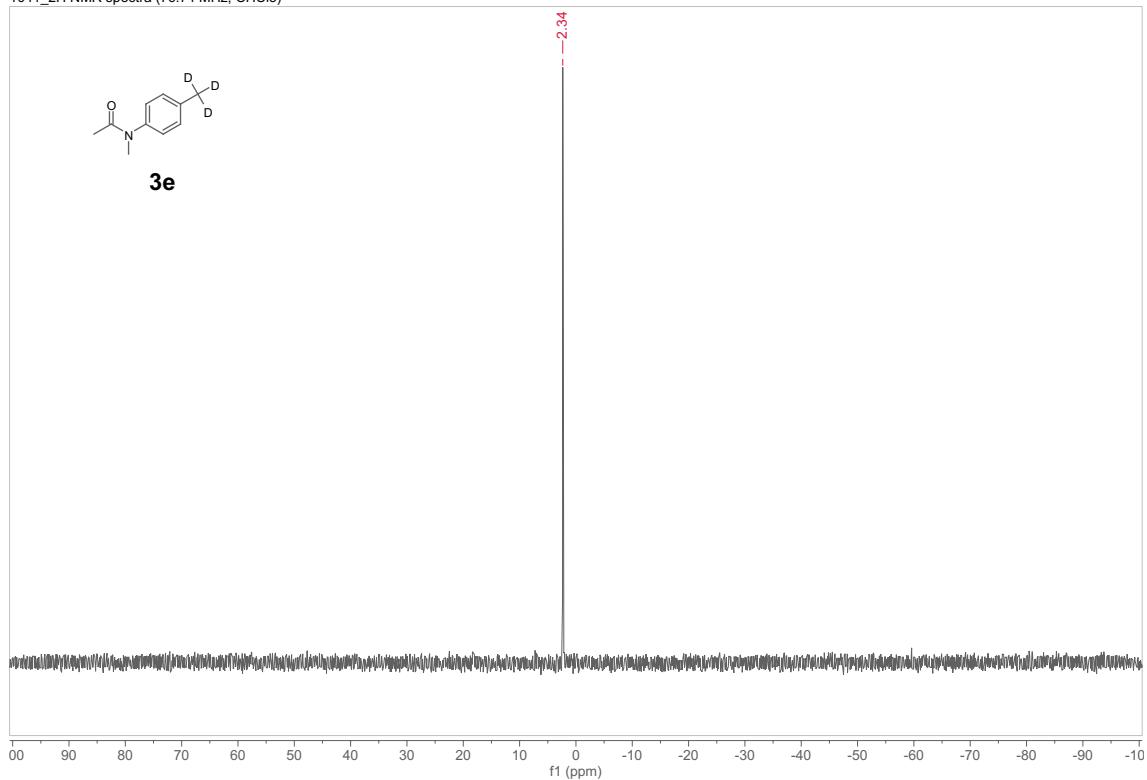
1041_1H NMR spectra (399.89 MHz, cdcl3)



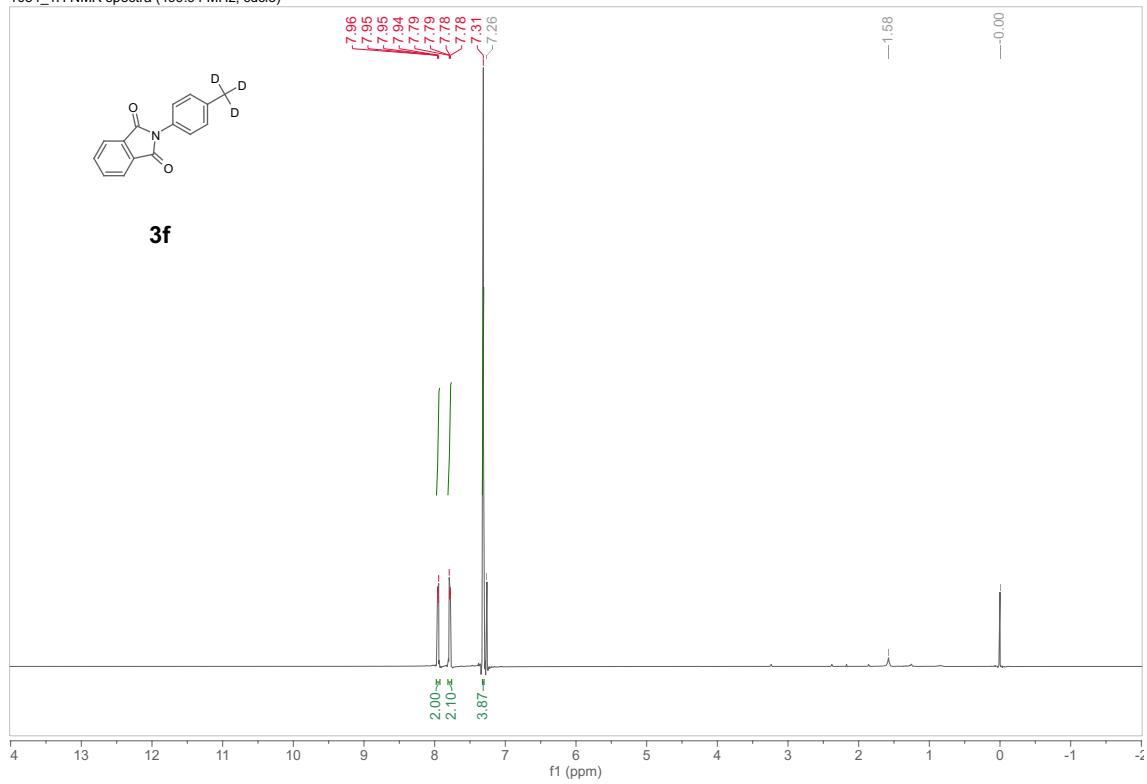
1041_13C NMR spectra (100.56 MHz, cdcl3)

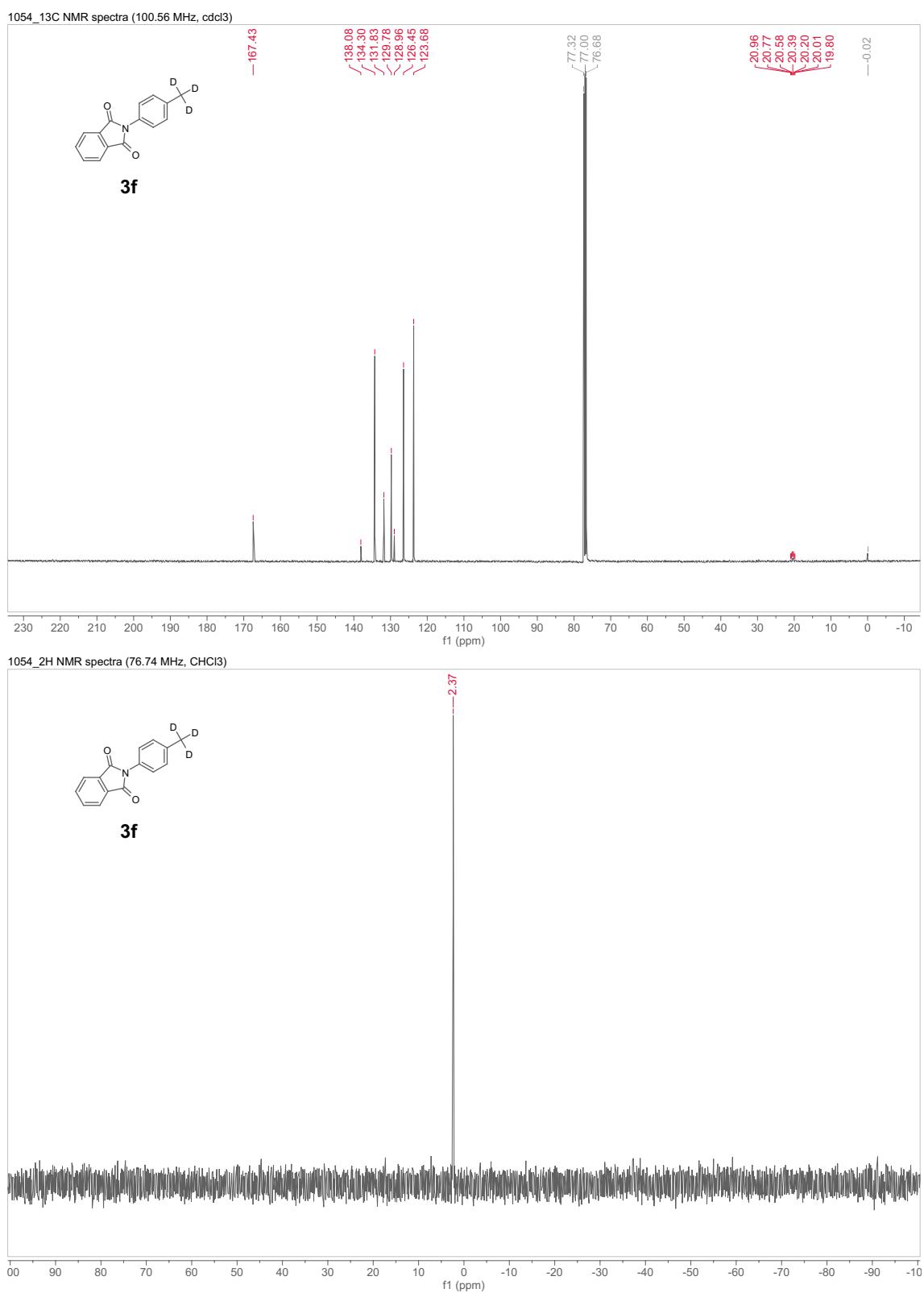


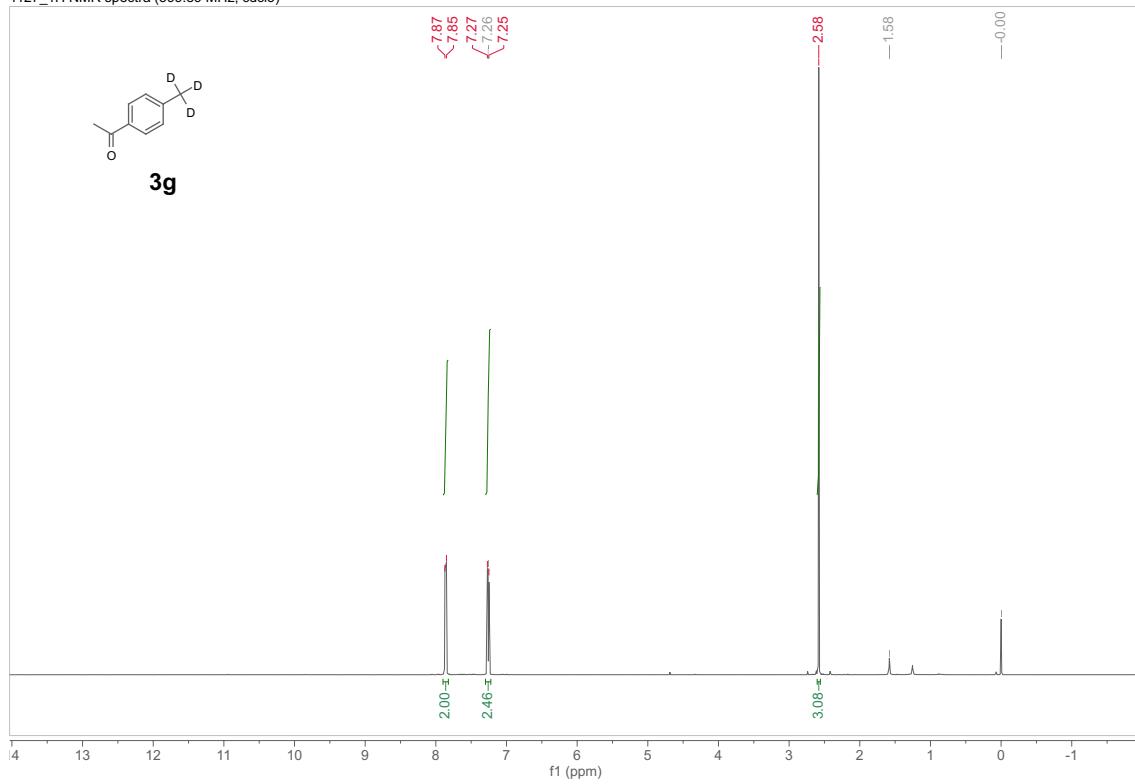
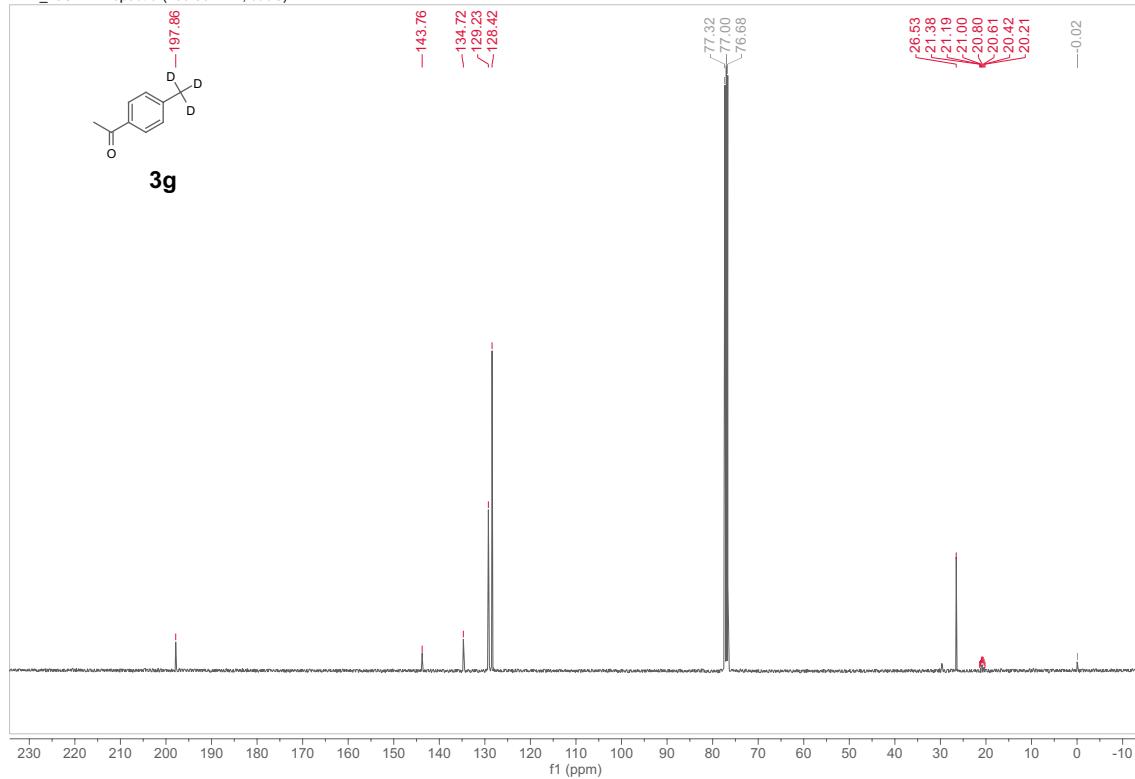
1041_2H NMR spectra (76.74 MHz, CHCl₃)



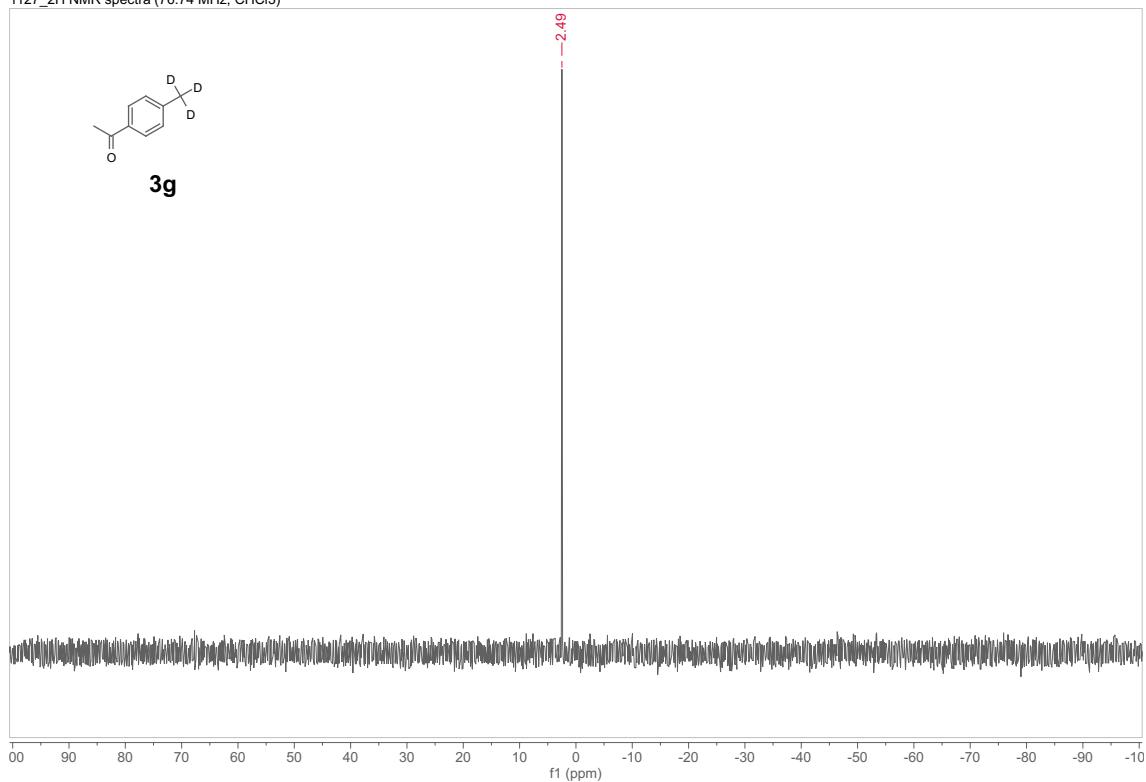
1054_1H NMR spectra (499.94 MHz, cdcl₃)



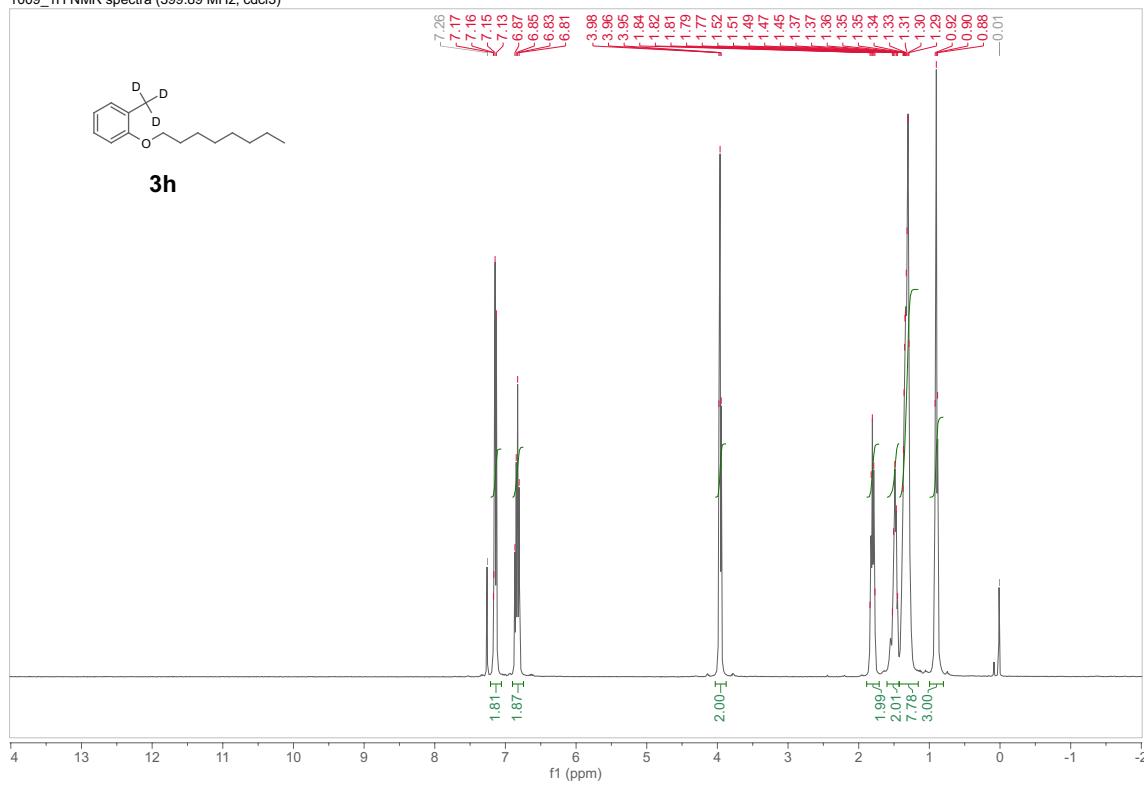


1127_1H NMR spectra (399.89 MHz, *cdcl*3)1127_13C NMR spectra (100.56 MHz, *cdcl*3)

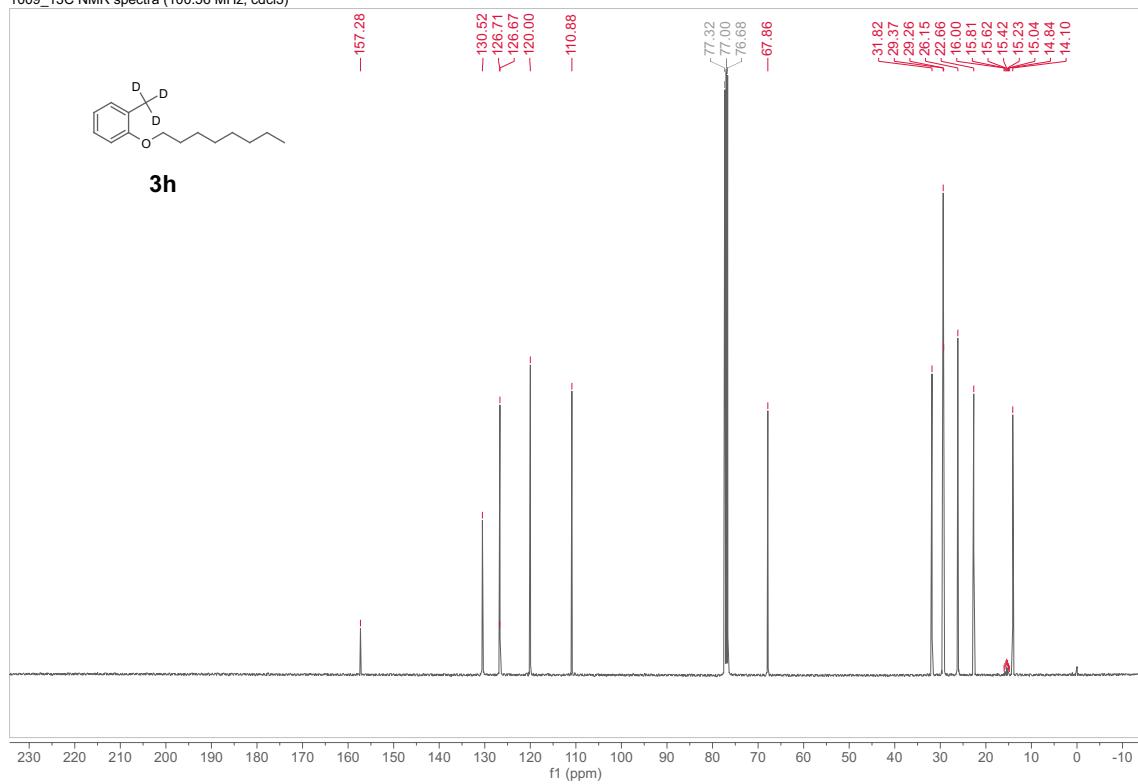
1127_2H NMR spectra (76.74 MHz, CHCl₃)



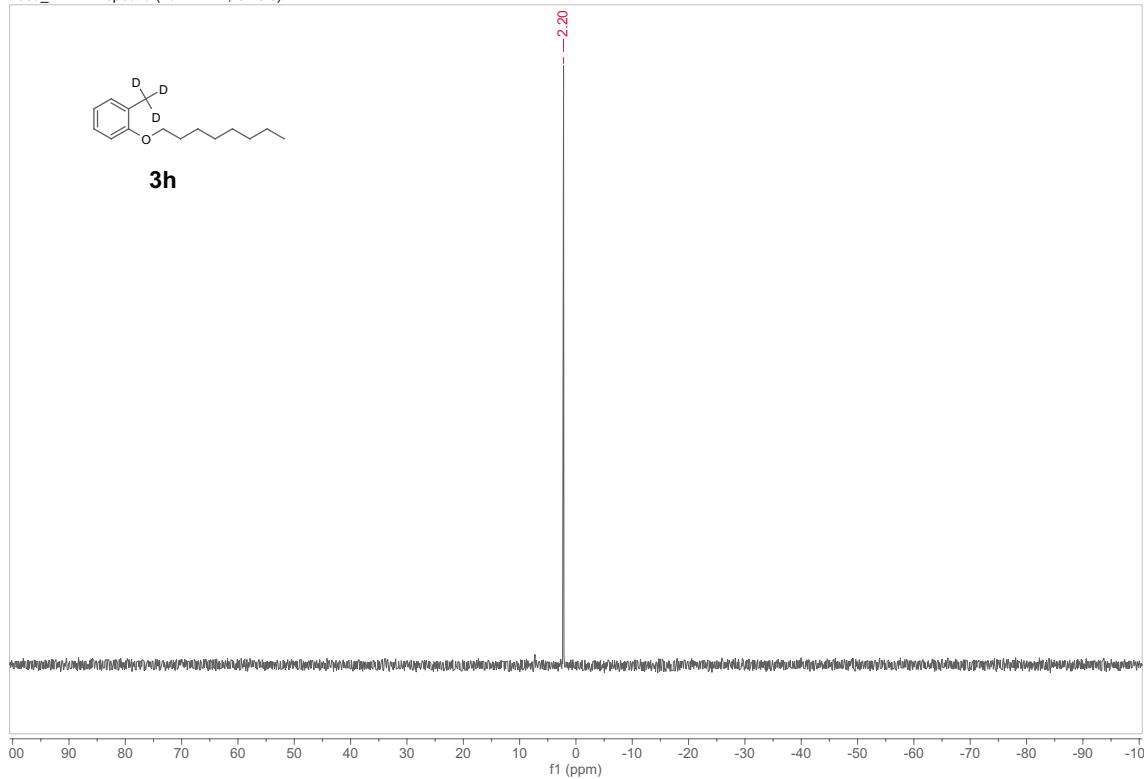
1009_1H NMR spectra (399.89 MHz, cdcl₃)

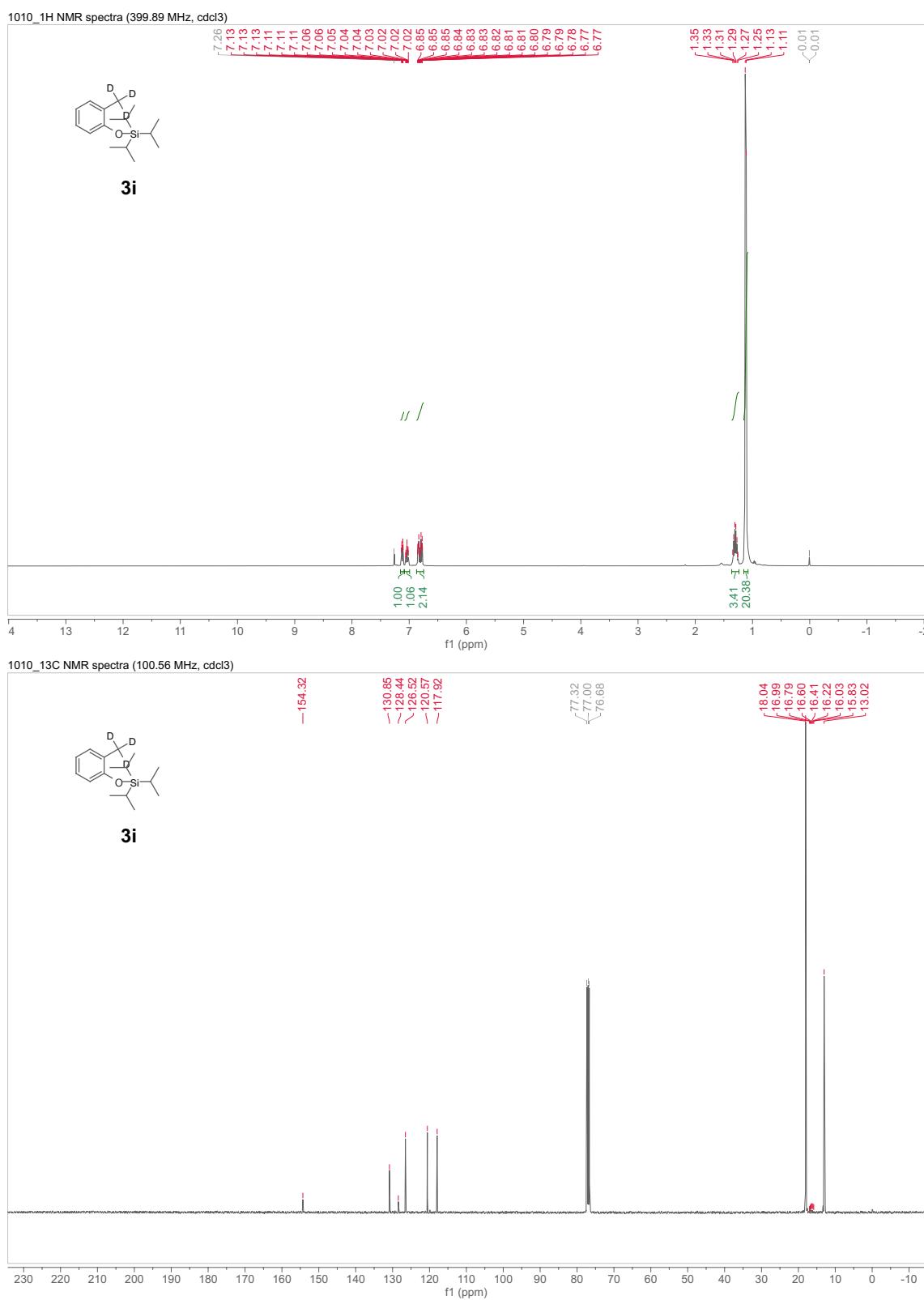


1009_13C NMR spectra (100.56 MHz, CDCl_3)

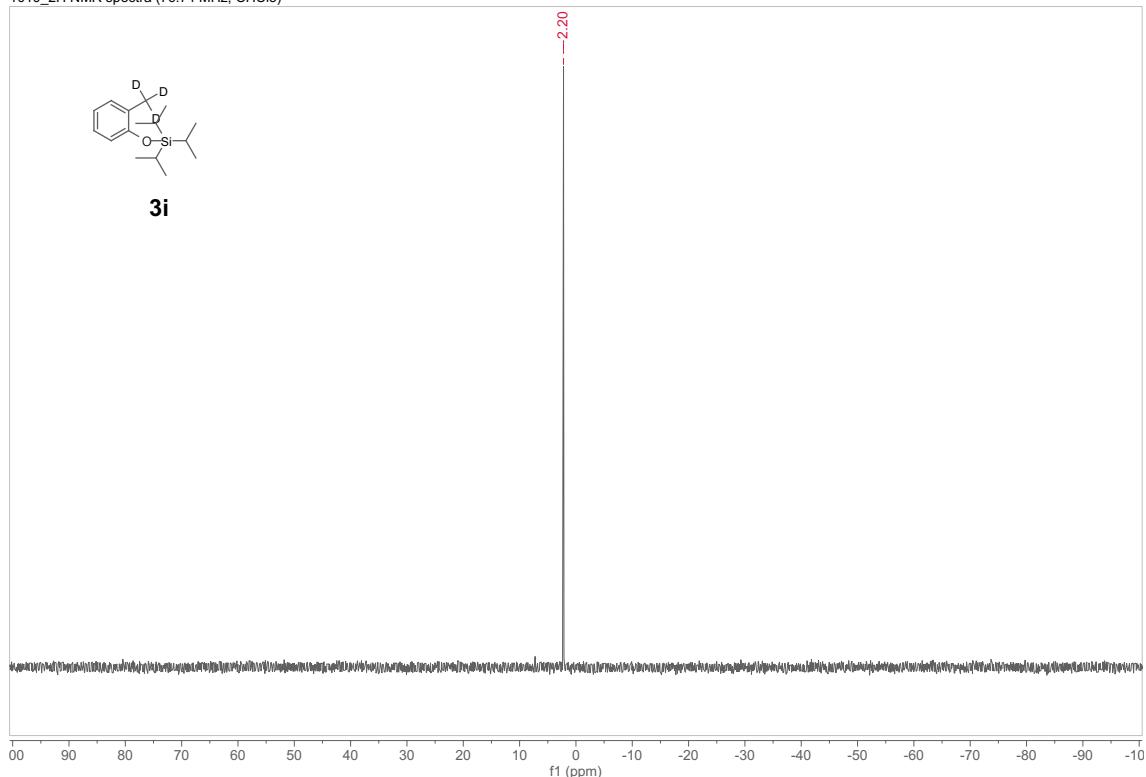


1009_2H NMR spectra (76.74 MHz, CHCl_3)

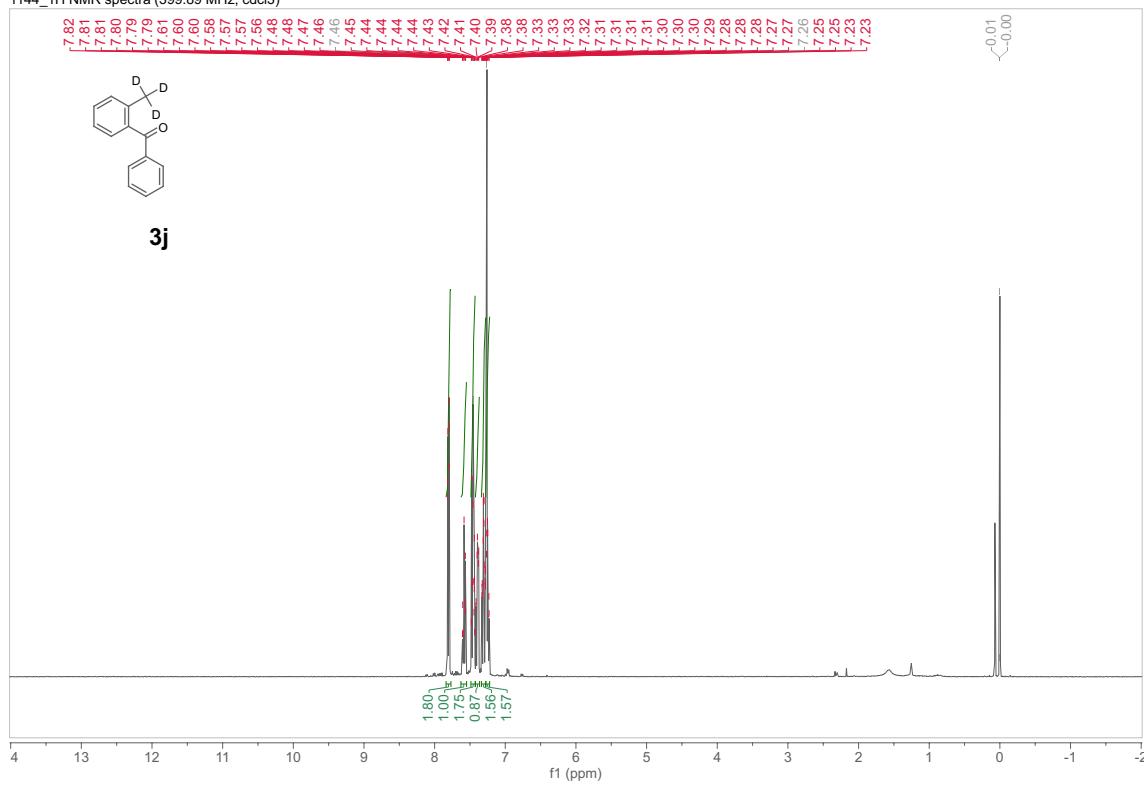




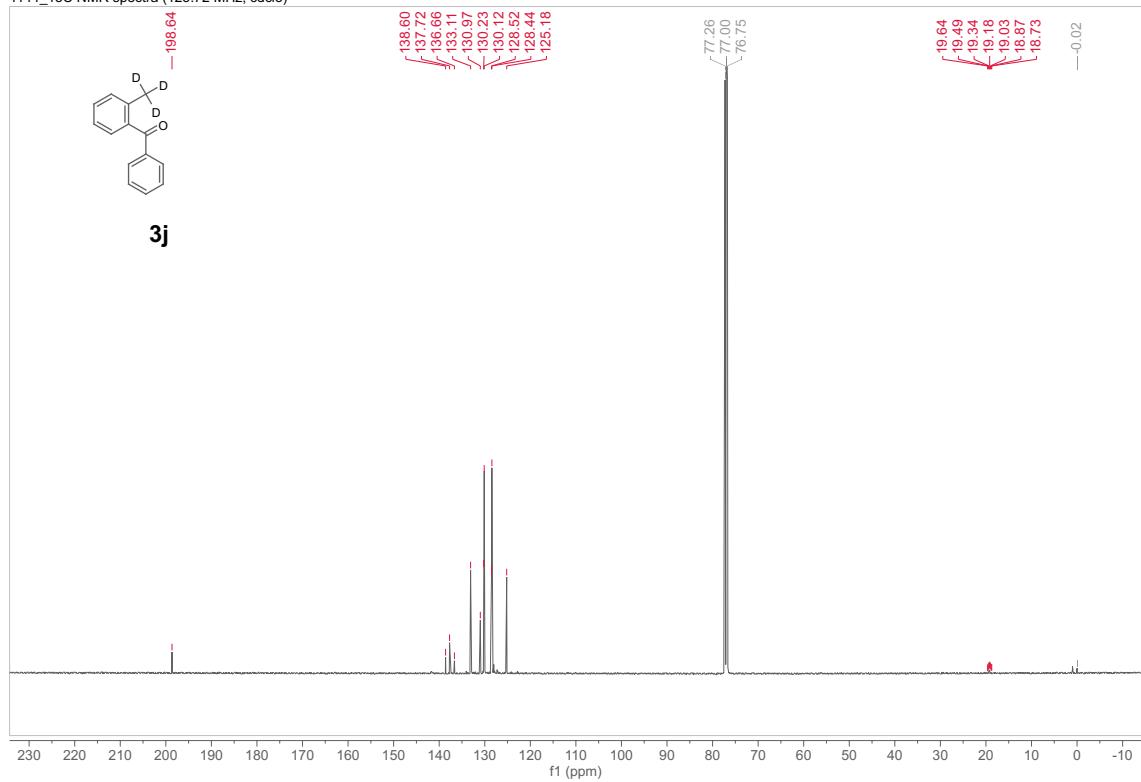
1010_2H NMR spectra (76.74 MHz, CHCl₃)



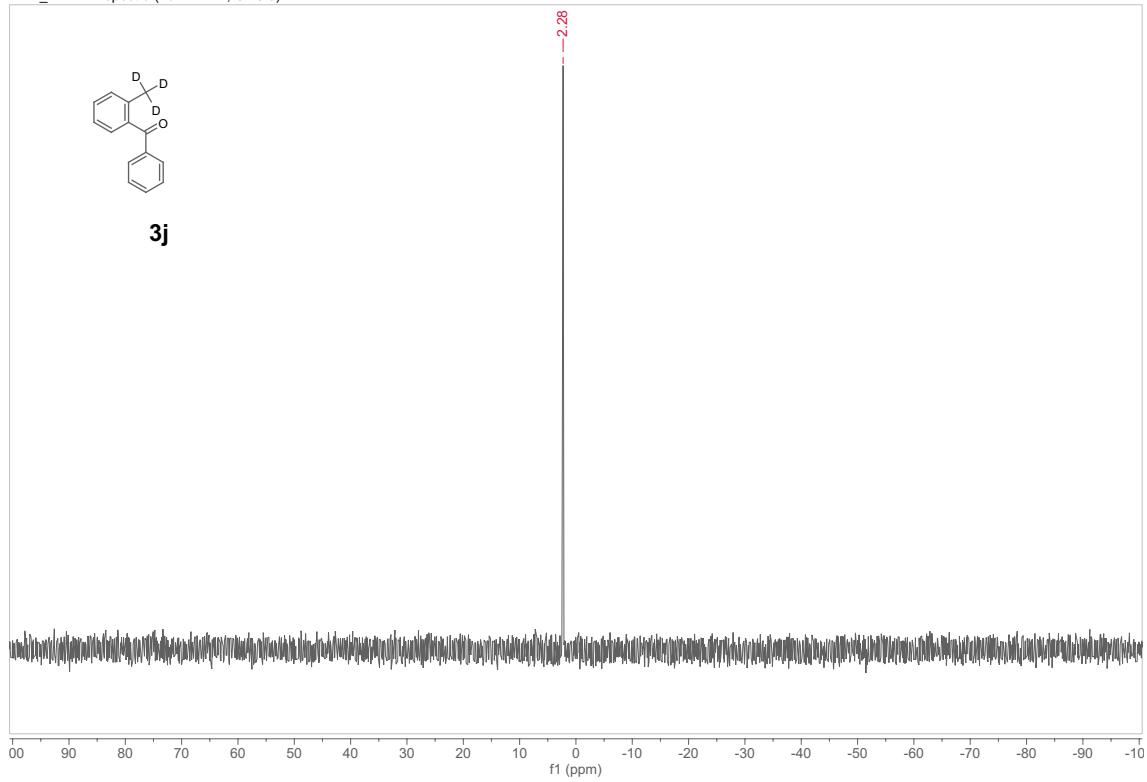
1144_1H NMR spectra (399.89 MHz, cdcl₃)

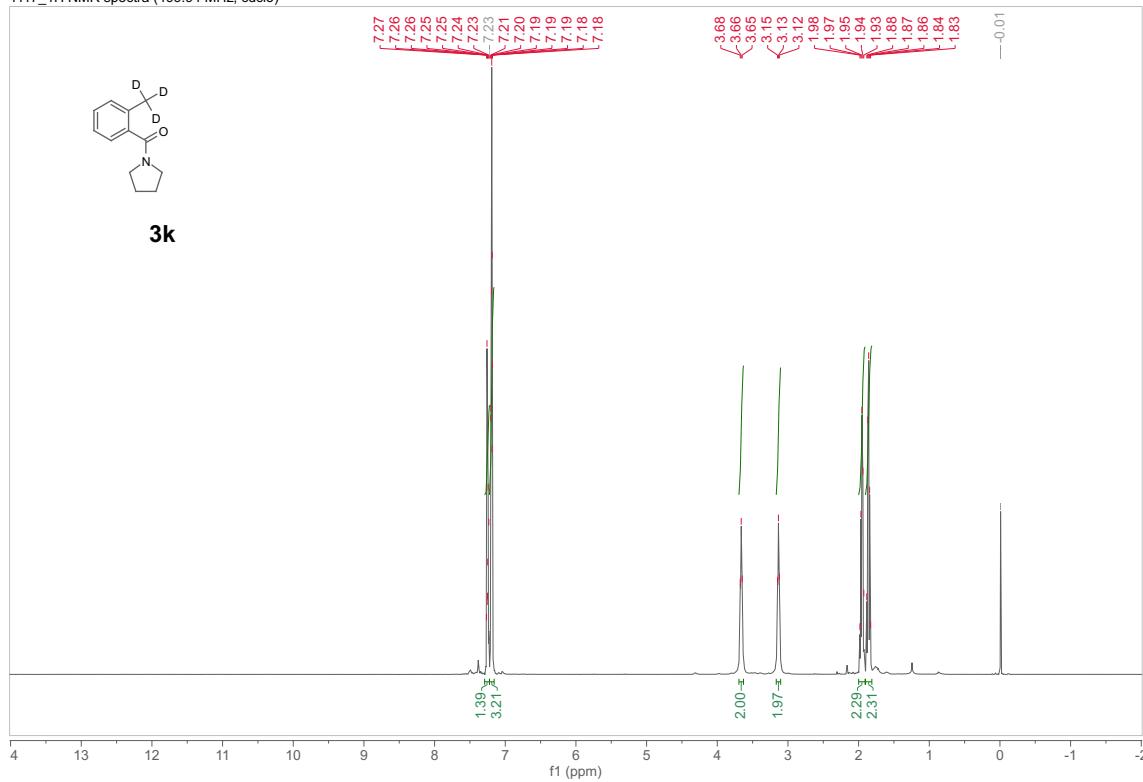
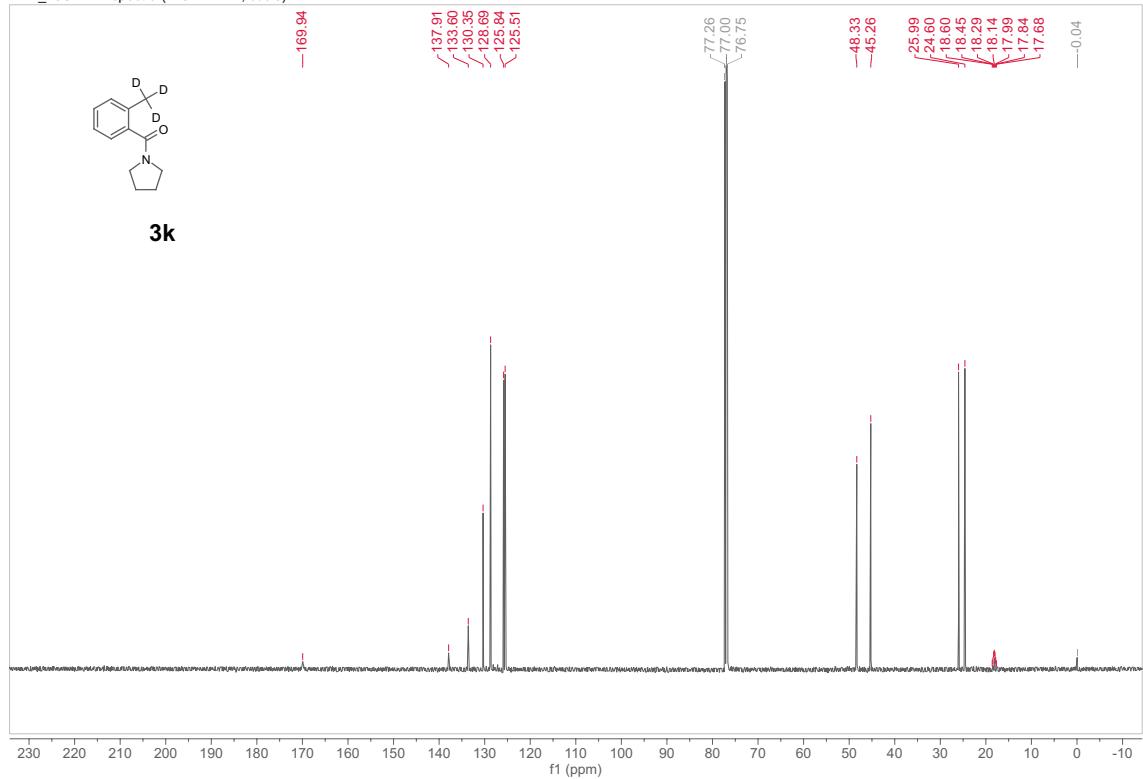


1144_13C NMR spectra (125.72 MHz, CDCl_3)

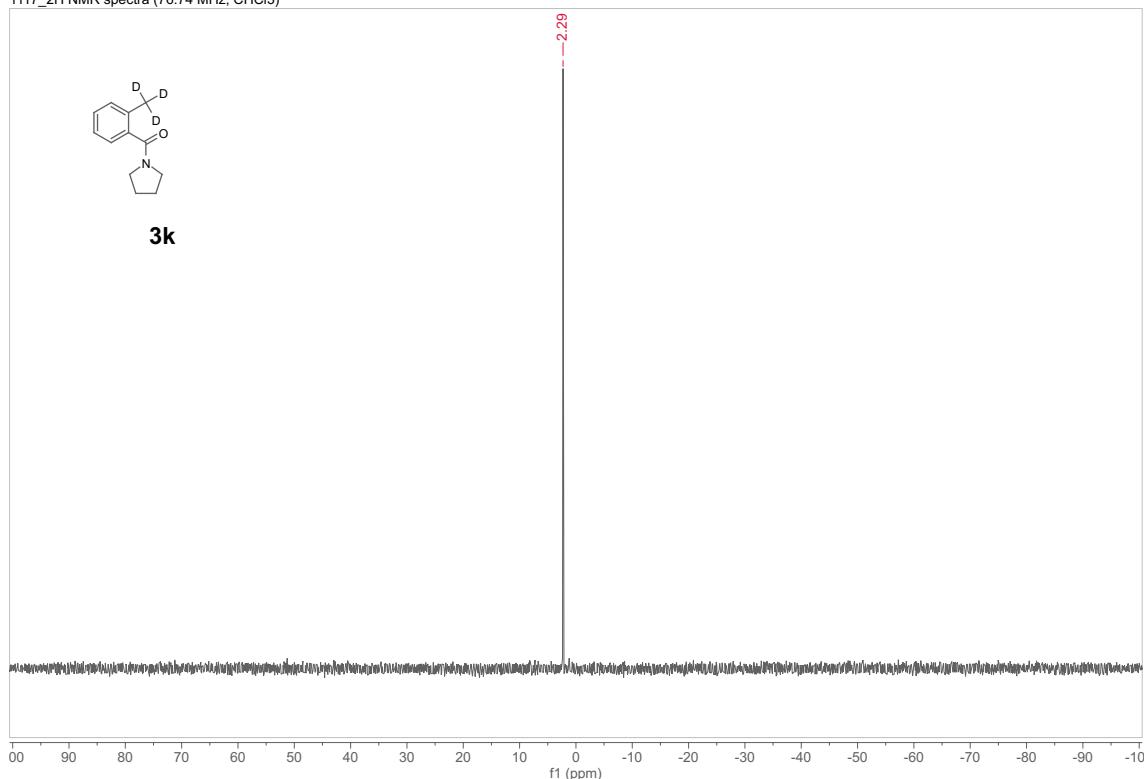


1144_2H NMR spectra (76.74 MHz, CHCl_3)

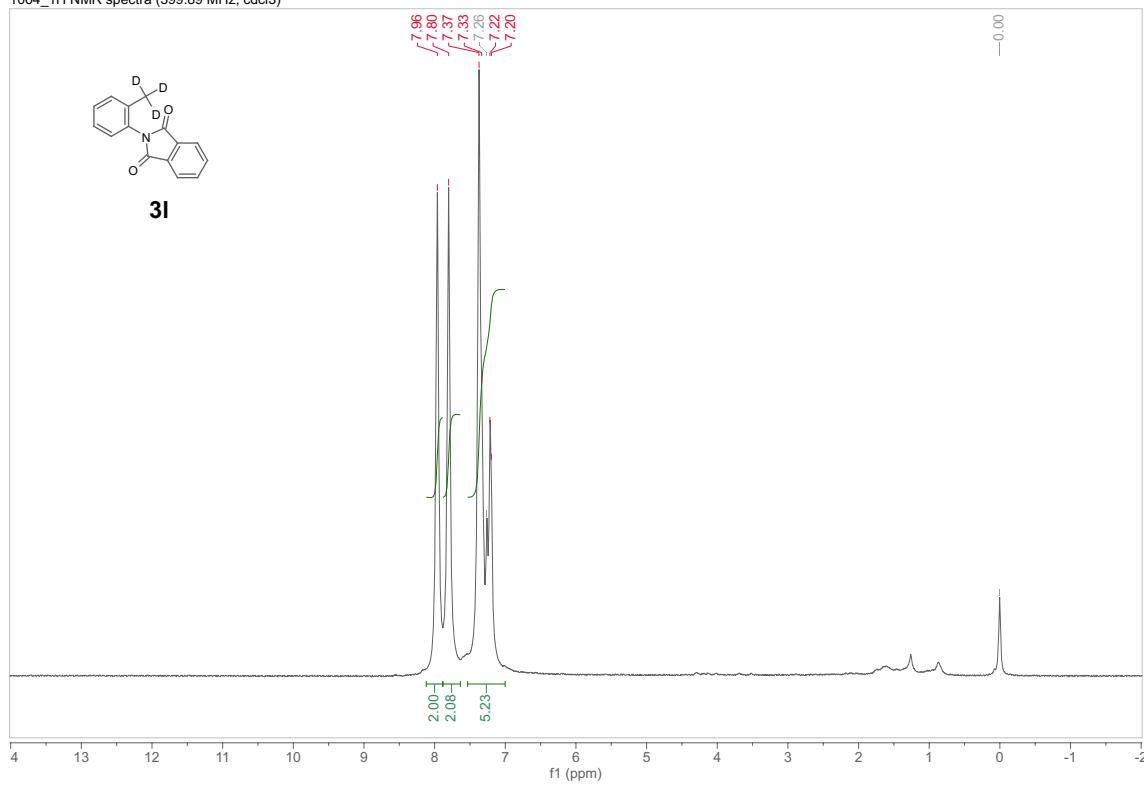


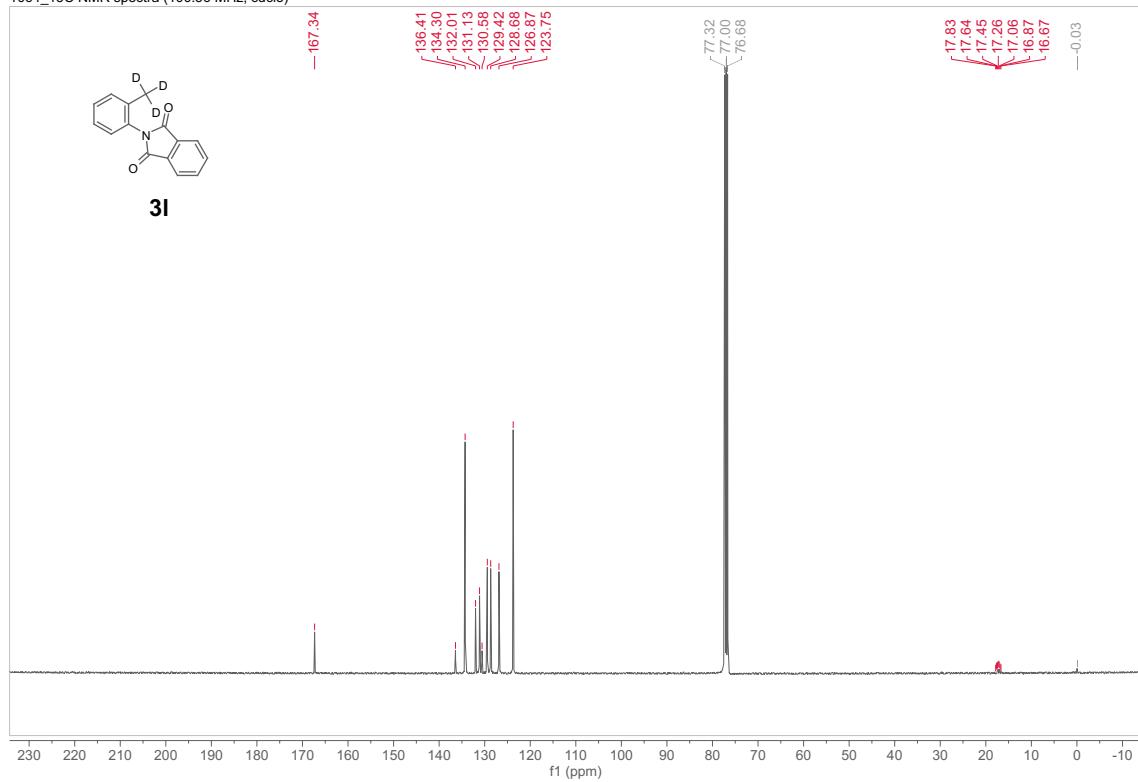
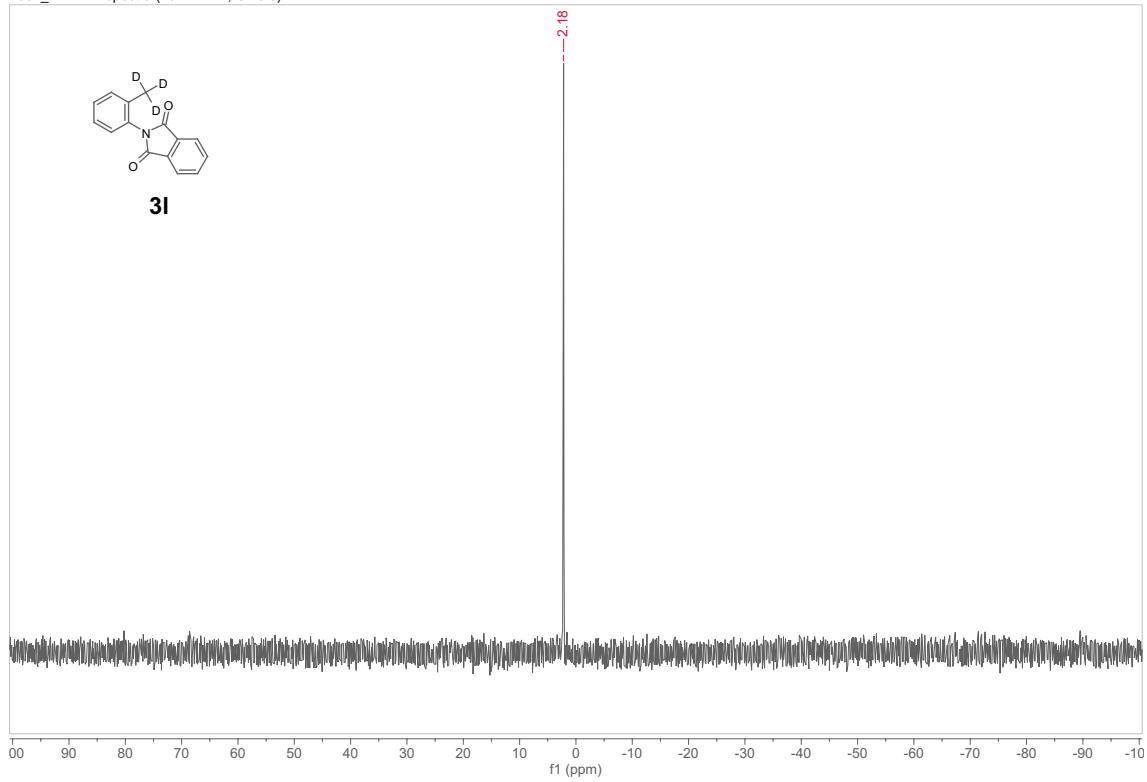
1117_1H NMR spectra (499.94 MHz, cdcl_3)1117_13C NMR spectra (125.72 MHz, cdcl_3)

1117_2H NMR spectra (76.74 MHz, CHCl₃)

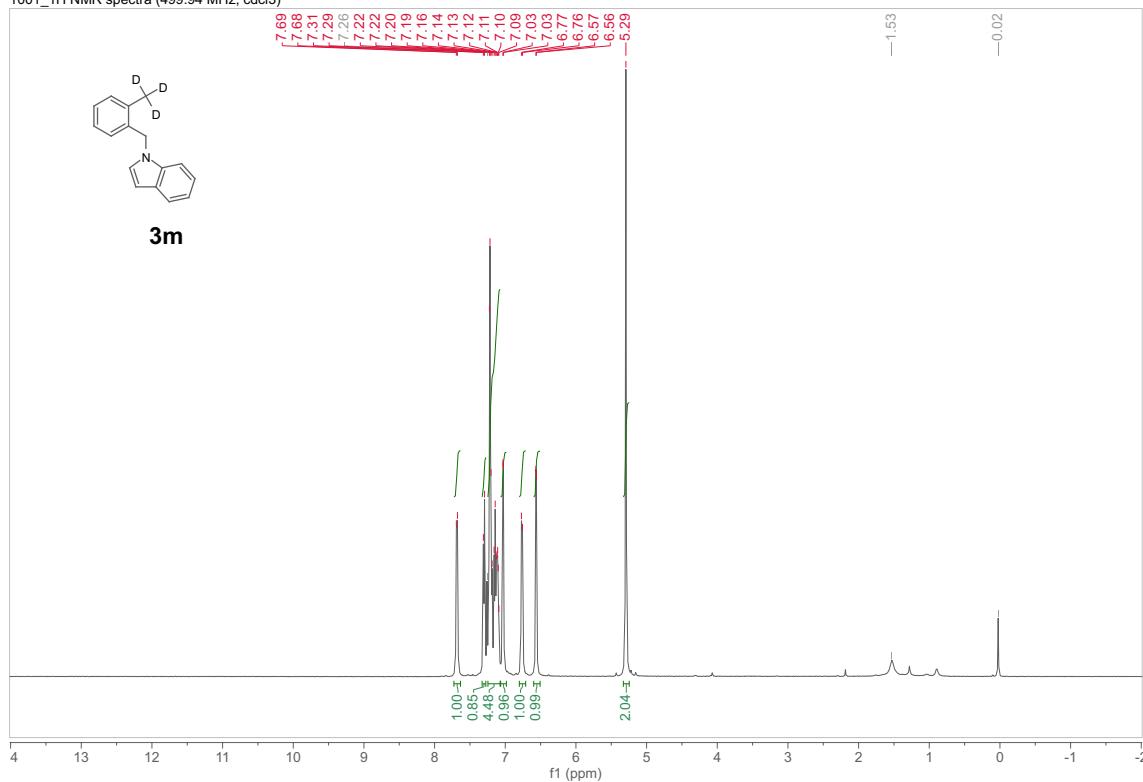


1064_1H NMR spectra (399.89 MHz, CDCl₃)

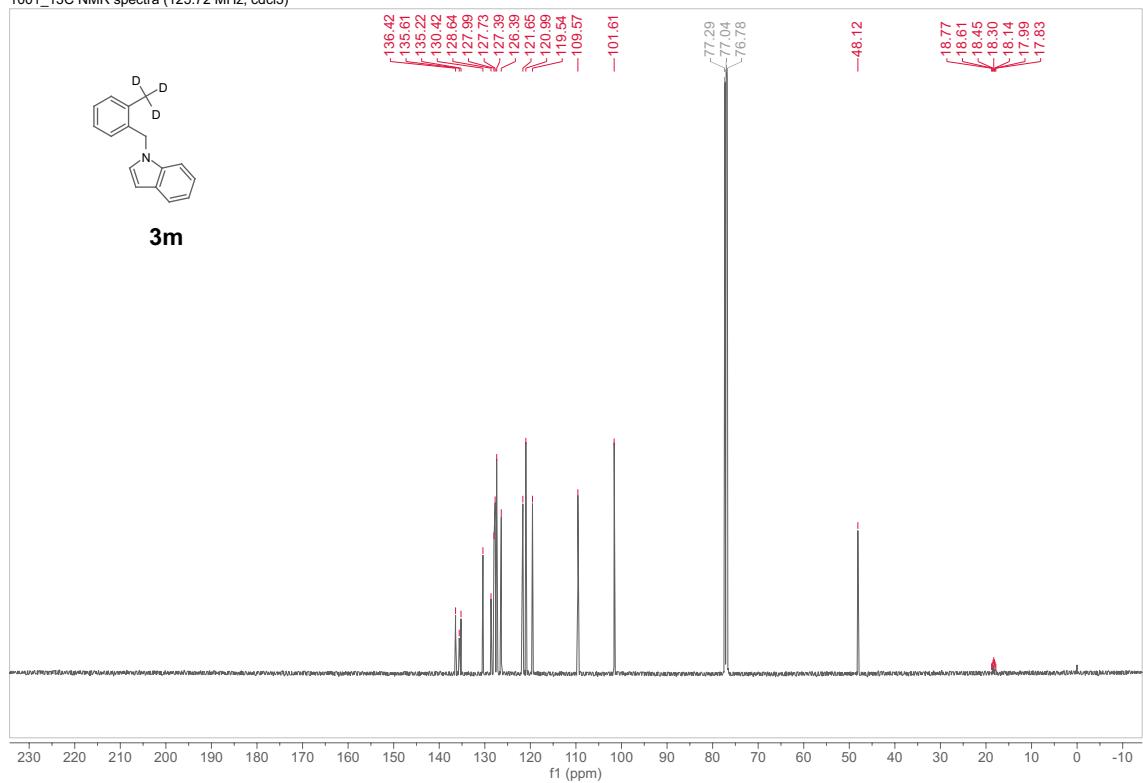


1064_13C NMR spectra (100.56 MHz, CDCl_3)1064_2H NMR spectra (76.74 MHz, CHCl_3)

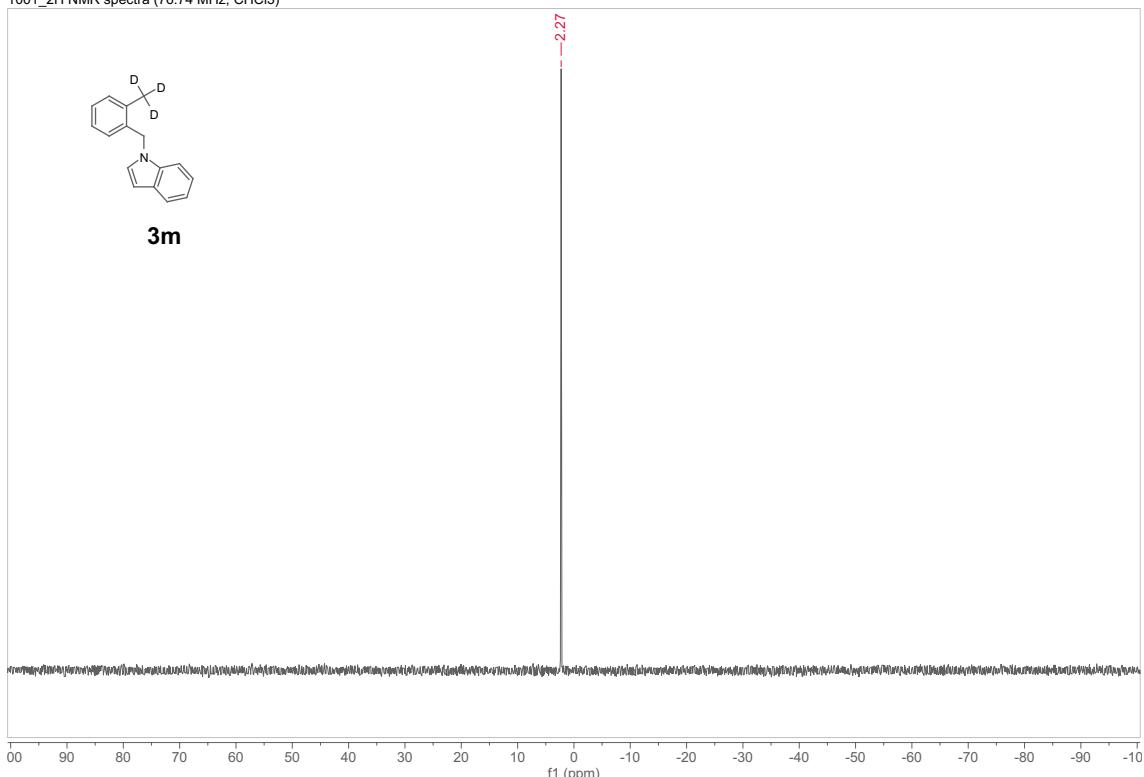
1001_1H NMR spectra (499.94 MHz, cdcl3)



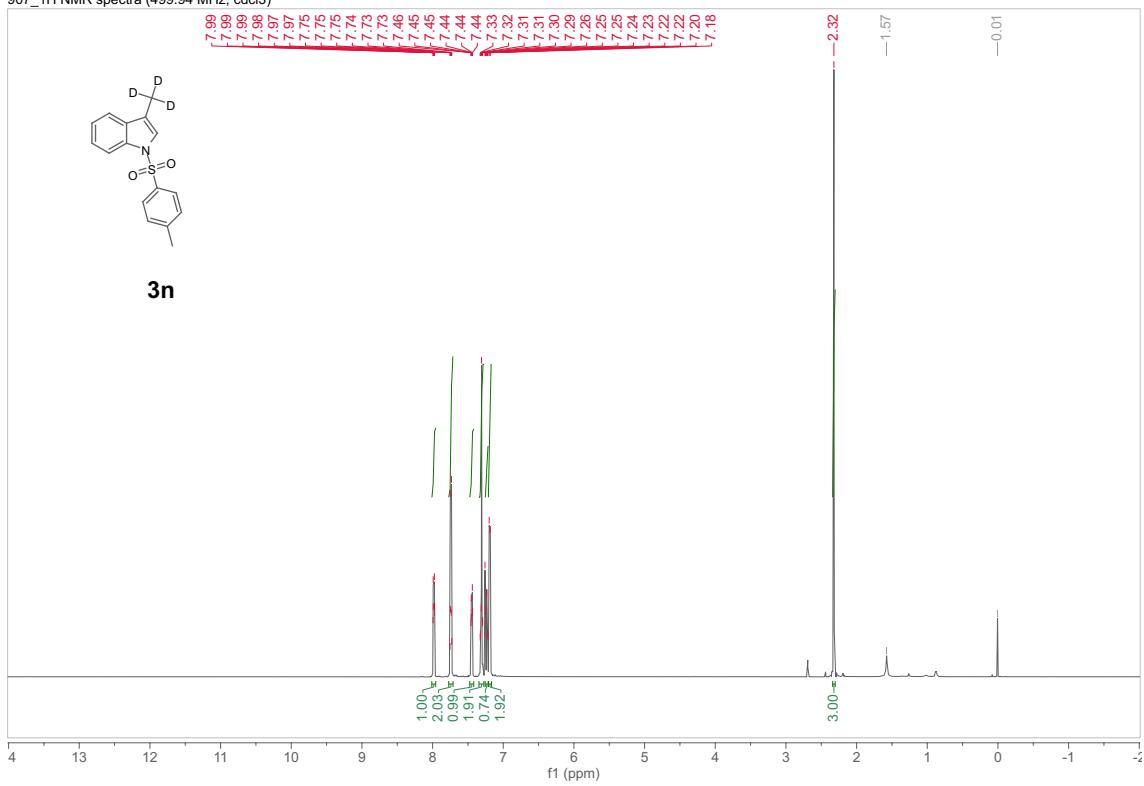
1001_13C NMR spectra (125.72 MHz, cdcl3)



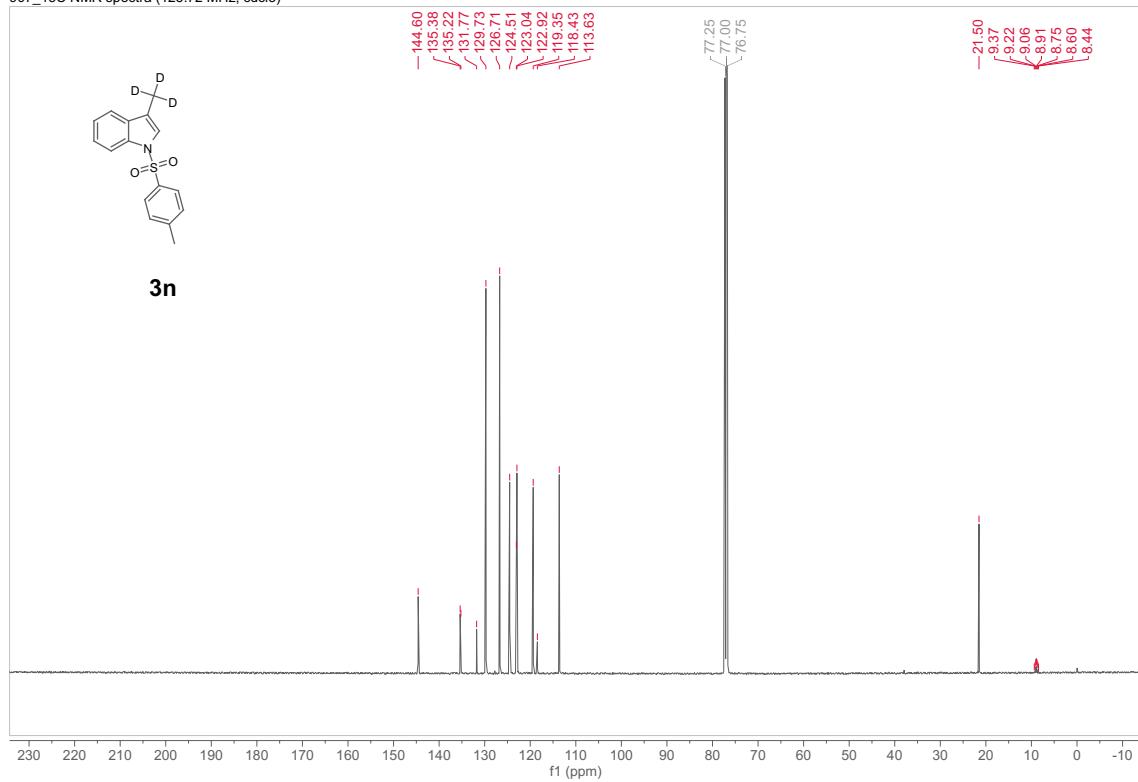
1001_2H NMR spectra (76.74 MHz, CHCl₃)



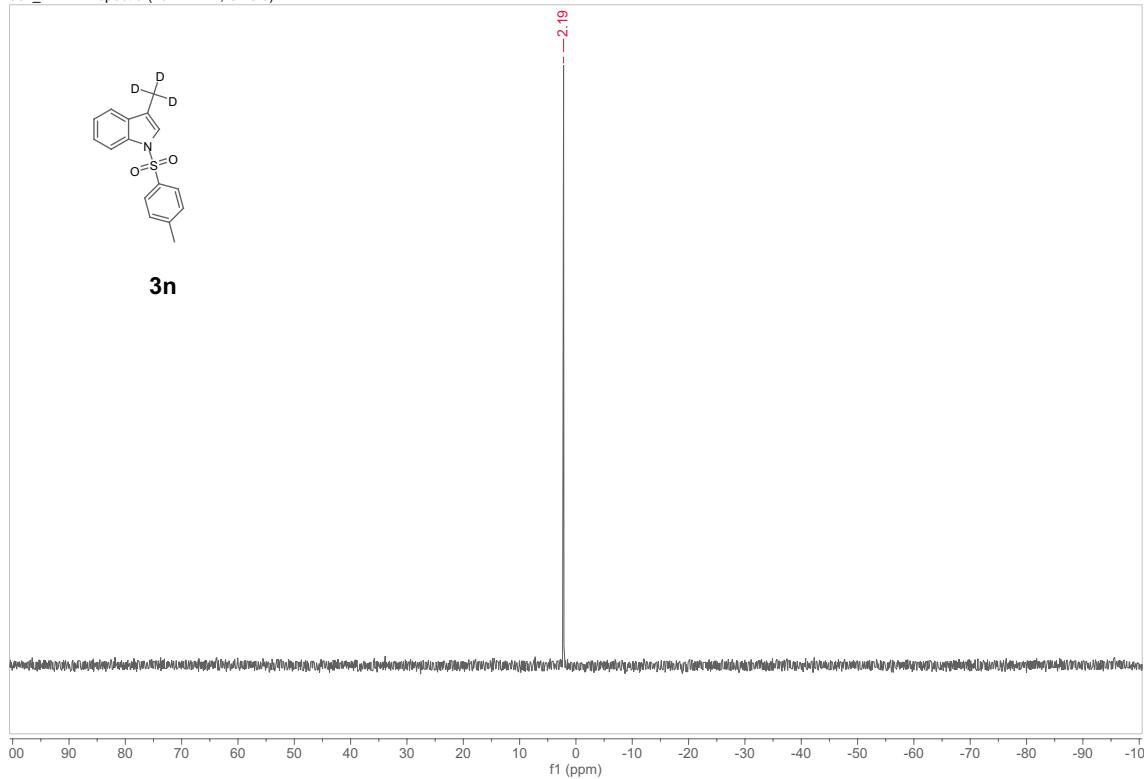
907_1H NMR spectra (499.94 MHz, cdcl₃)

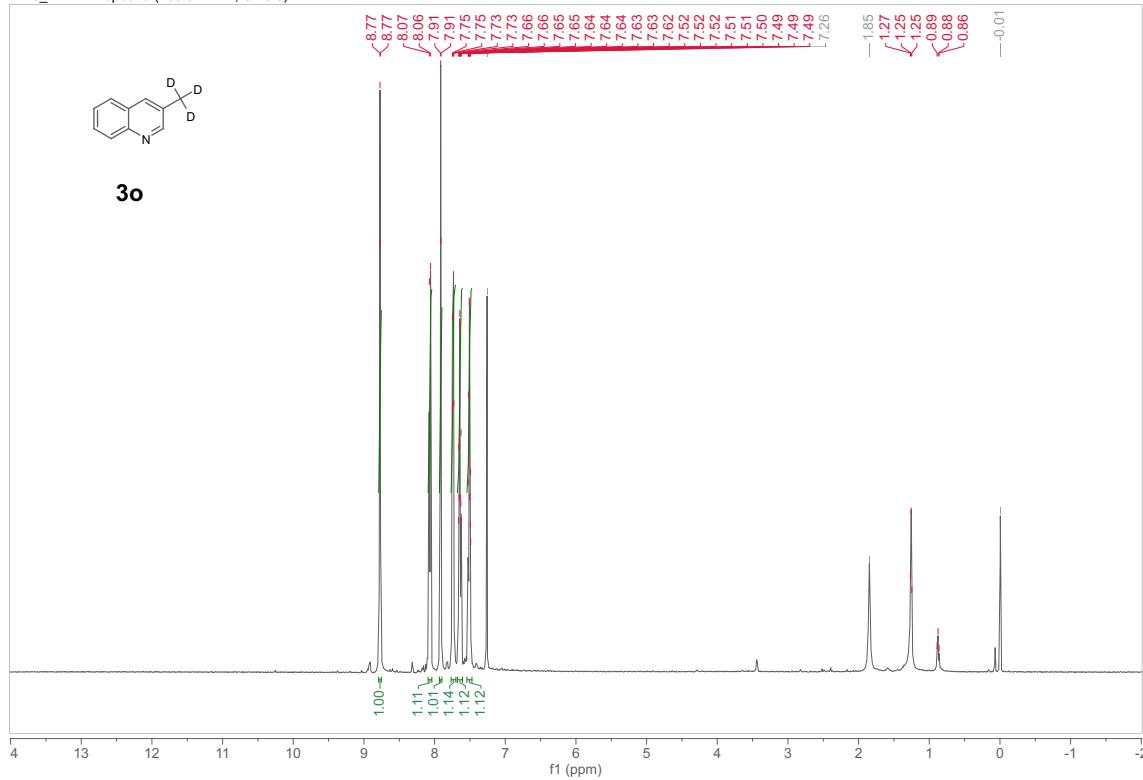


907_13C NMR spectra (125.72 MHz, CDCl_3)

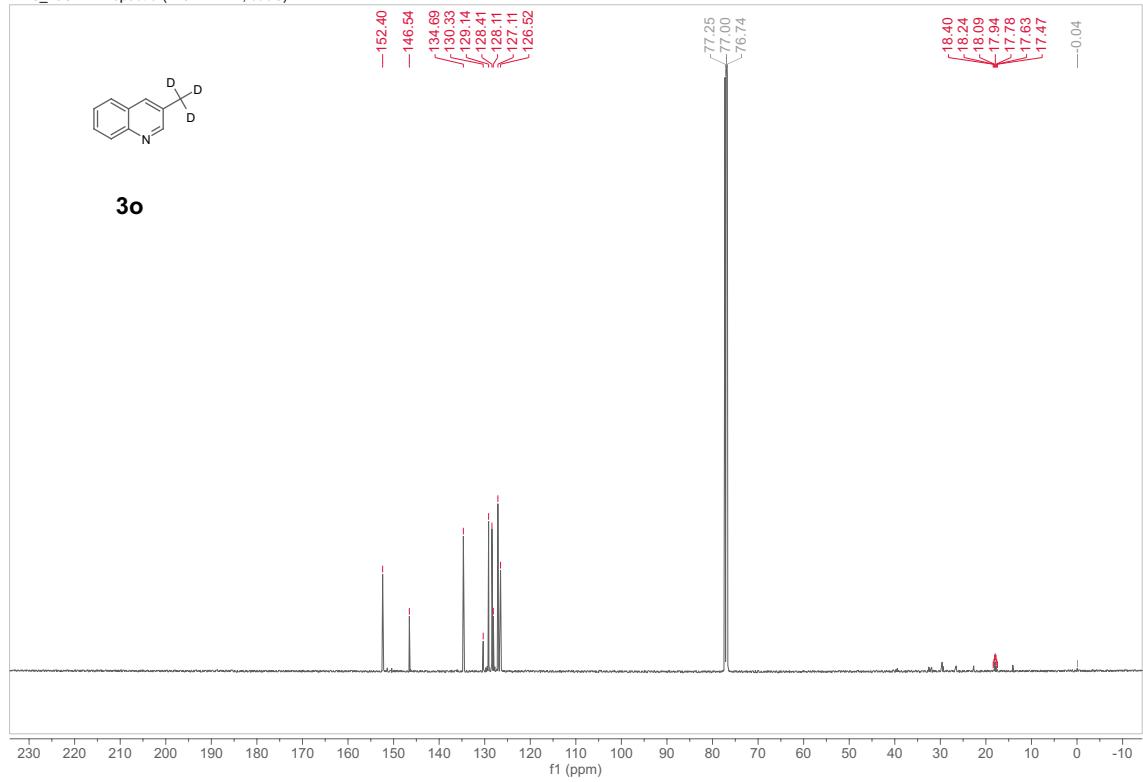


907_2H NMR spectra (76.74 MHz, CHCl_3)

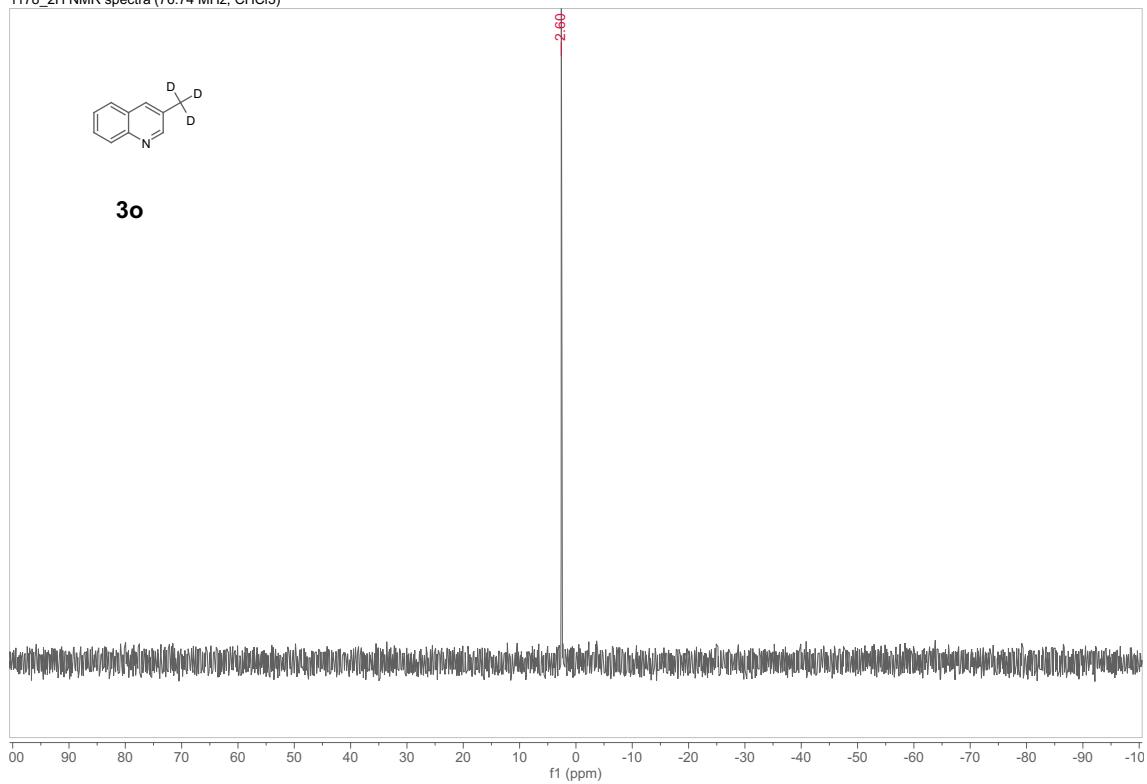


1178_1H NMR spectra (499.94 MHz, CDCl₃)

1178_13C NMR spectra (125.72 MHz, cdcl3)

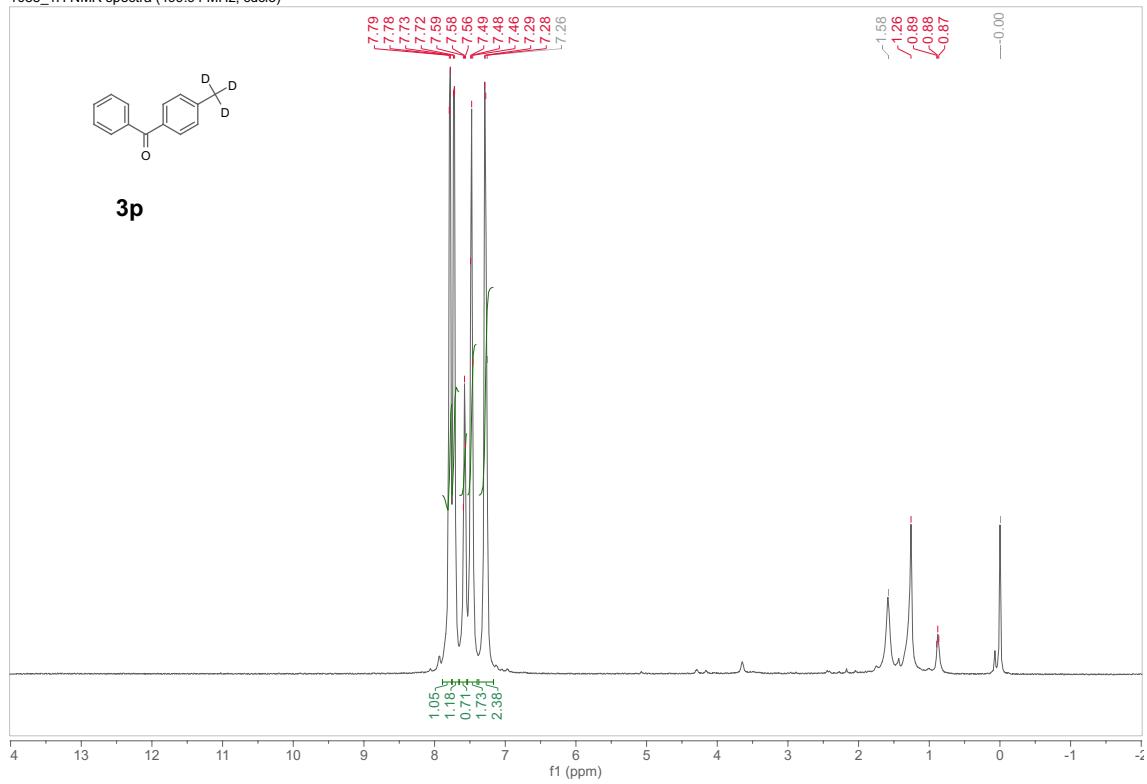


1178_2H NMR spectra (76.74 MHz, CHCl₃)



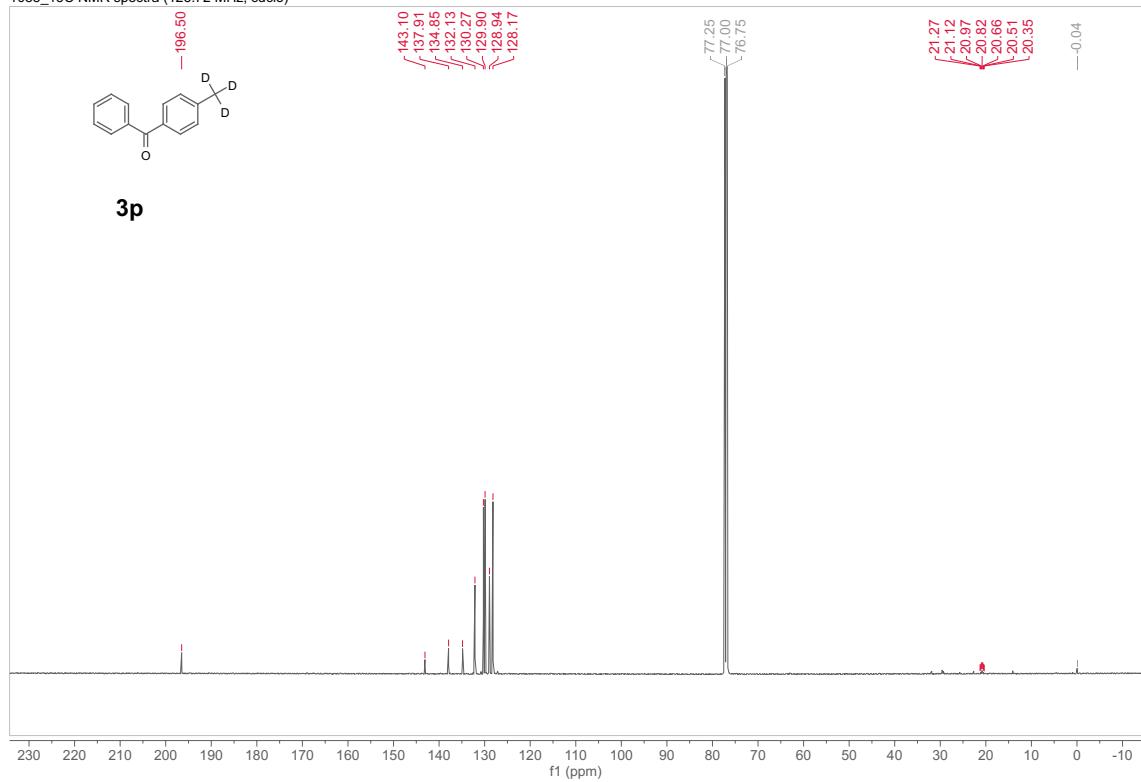
3o

1088_1H NMR spectra (499.94 MHz, cdcl₃)

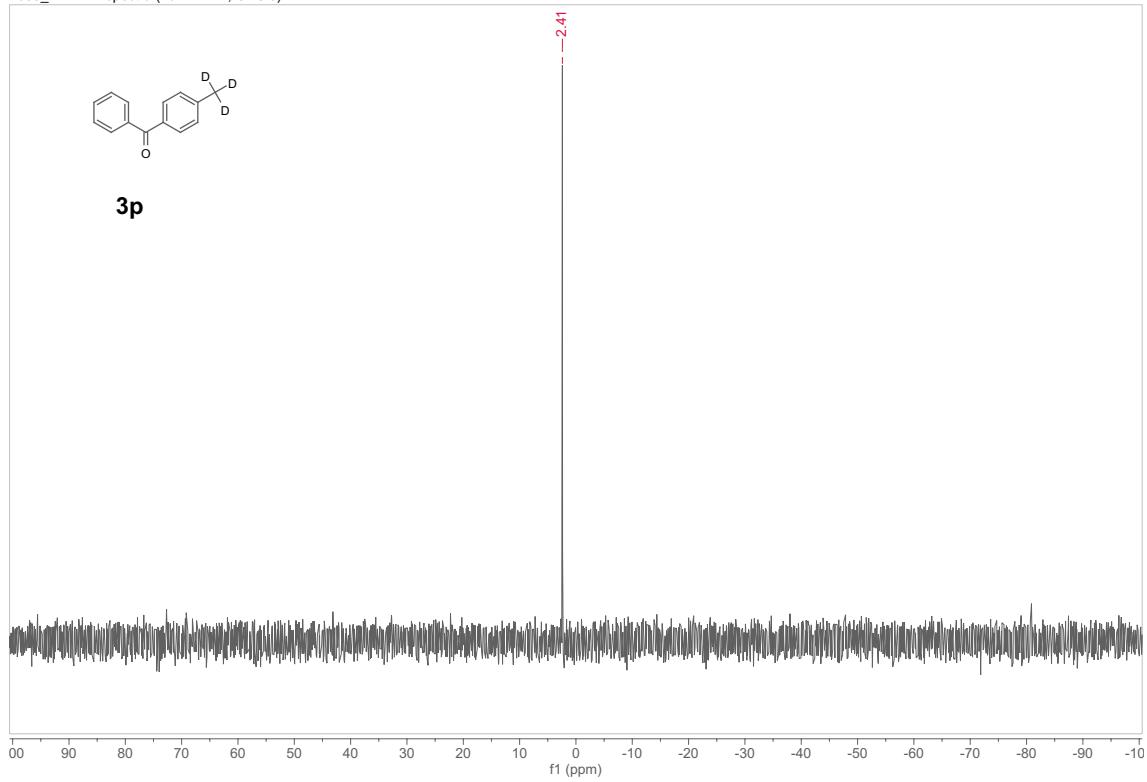


3p

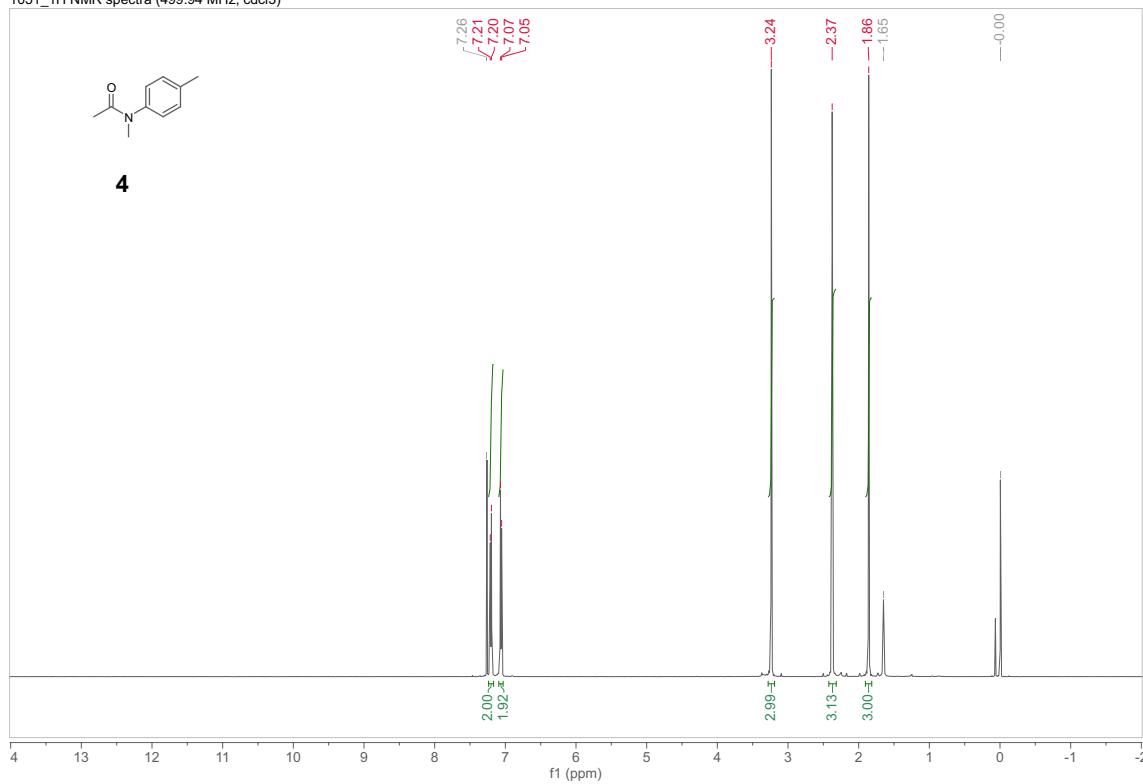
1088_13C NMR spectra (125.72 MHz, CDCl_3)



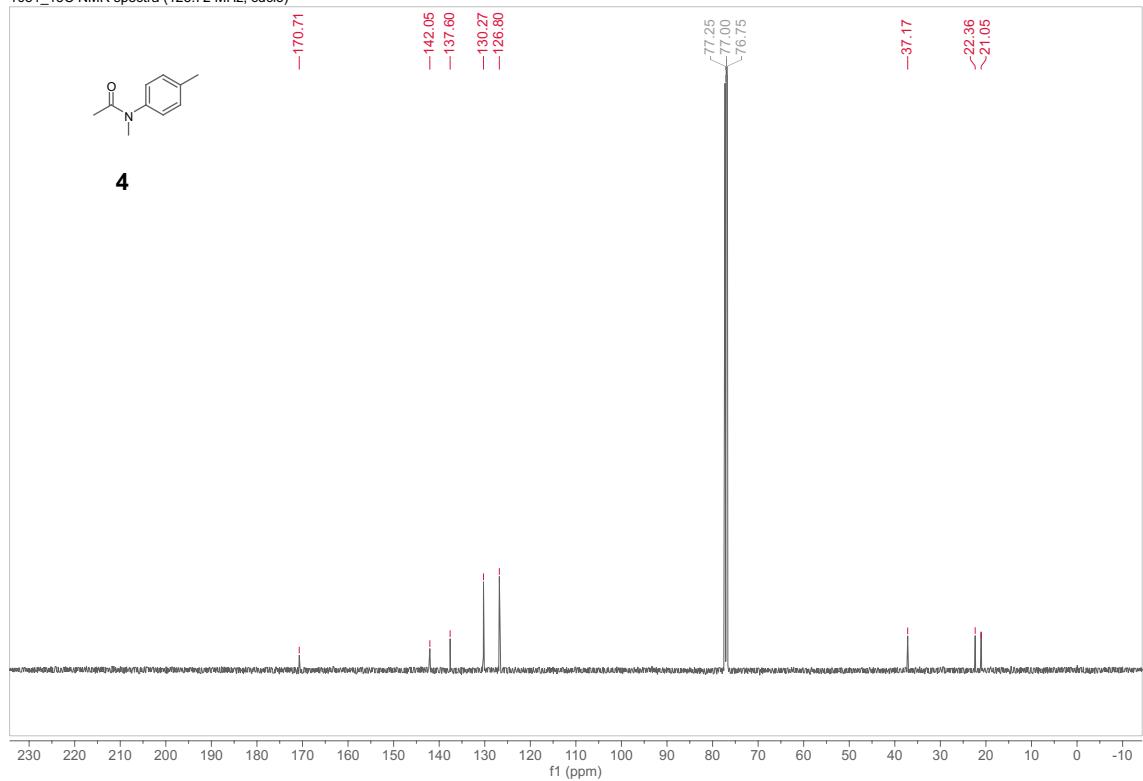
1088_2H NMR spectra (76.74 MHz, CHCl_3)



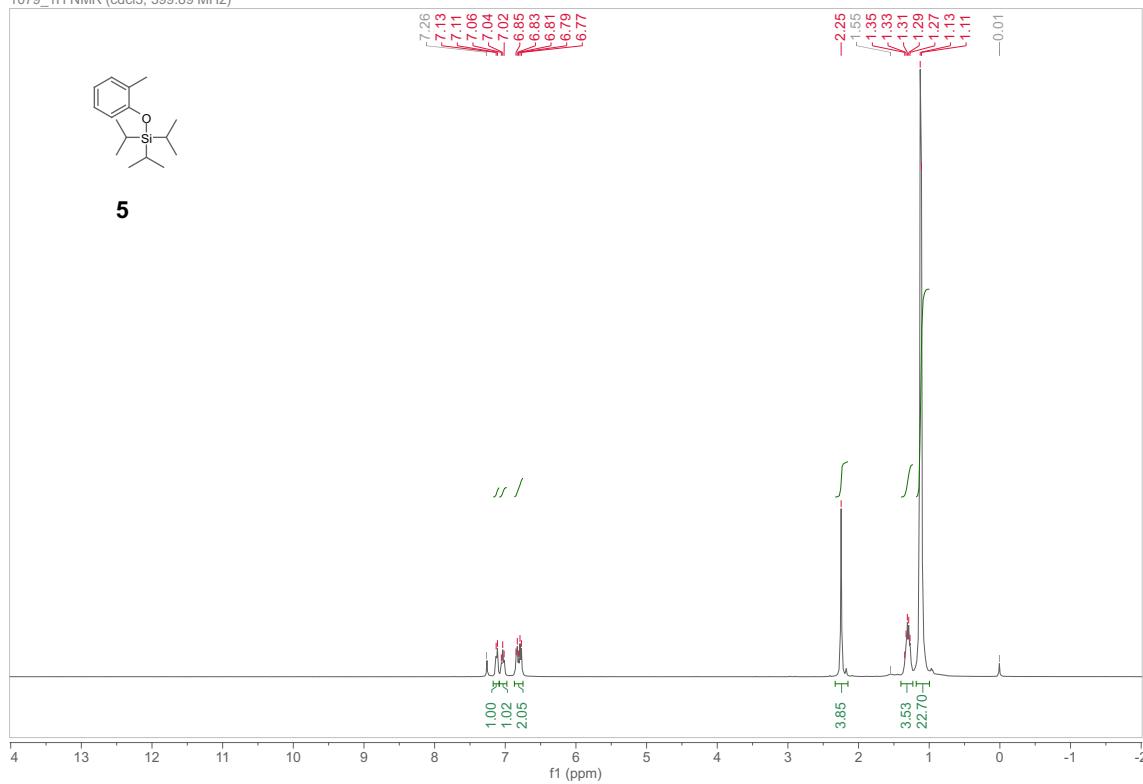
1051_1H NMR spectra (499.94 MHz, cdcl3)



1051_13C NMR spectra (125.72 MHz, cdcl3)



1079_1H NMR (cdcl₃, 399.89 MHz)



5

1079_13C NMR (cdcl₃, 100.56 MHz)

