Acyl Fluorides as Direct Precursors to Fluoride Ketyl Radicals: Reductive Deuteration using SmI_2 and D_2O

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Supplementary Information

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2. General Information

Glassware was dried in an oven overnight before use. Thin layer chromatography was carried out on SIL G/UV254 silica-glass plates and plates were visualized using ultra-violet light (254 nm) and $KMnO_4$ solution. For flash column chromatography, silica gel 60, 35-70 μm was used. NMR data was collected at 300 MHz, 400 MHz or 500 MHz. Data was manipulated directly from the spectrometer or via a networked PC with appropriate software. All samples were analyzed in $CDCl_3$ unless otherwise stated. Reference values for residual solvent were taken as $\delta = 7.27$ ($CDCl_3$) for ^1H NMR; $\delta = 77.1$ ($CDCl_3$) for $^{13}C\{^1H\}$ NMR. Multiplicities for coupled signals were designated using the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, br = broad signal, and are given in Hz.

All solvents and reagents were used as supplied. Samarium (II) iodide (0.100 M in THF) was prepared by standard methods.[1] The deuterium incorporations of D_2O used in this study was 99.9%. Acyl fluorides were prepared by known methods.[2]

Determination of deuterium incorporation by ^{1}HNMR according to the equation below:

$$\text{Deuterium Incorporation} = 100\% - \left(\frac{\text{area}_{\text{R-CH}_2\text{-OH}}}{2} \right)$$

$\text{area}_{\text{R-CH}_2\text{-OH}}$ means the integration of the R-CH_2-OH peak.

3. Experimental Procedures and Characterization Data

3.1 Optimization Studies (Table 1)

To a solution of samarium (II) iodide (0.100 M in THF; 9.00 - 15.0 mL, 0.900 - 1.50 mmol, 3.00 - 5.00 equiv), was added deuterium oxide (3.00 - 15.0 mmol, 10.0 - 50.0 equiv). A solution of acyl fluoride (0.300 mmol, 1.00 equiv) in THF (1.00 mL) was then added under Ar at room temperature and stirred vigorously. After 0.500 - 30.0 min, excess SmI_2 was oxidized by bubbling air through the reaction mixture. The reaction mixture was diluted with EtOAc (10.0 mL) and HCl (5.00 mL, 1.00 M, aq). The aqueous layer was extracted with EtOAc (3 × 10.0 mL), organic layers were combined, washed with $Na_2S_2O_3$ (2 × 5.00 mL, sat., aq), dried over Na_2SO_4, filtered and concentrated. Then the sample was analyzed by ^{1}H NMR ($CDCl_3$, 500 MHz) to obtain the deuterium incorporation and yield using internal standard (1,1,2,2 - tetrachlorethan) and comparison with corresponding samples.

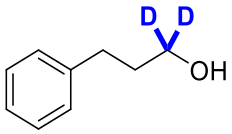
3.2 General Procedure for the Reductive Deuteration of Acyl fluorides by SmI_2–D_2O

To a solution of samarium (II) iodide (0.100 M in THF; 15.0 mL, 1.50 mmol, 5.00 equiv), was added deuterium oxide (180 mg, 9.00 mmol, 30.0 equiv). A characteristic burgundy red color of SmI_2-D_2O complex was observed. A solution of acyl fluoride (0.300 mmol, 1.00 equiv) in THF (1.00 mL) was then added under Ar at room temperature and stirred vigorously. After 30.0

min, excess SmI_2 was oxidized by bubbling air through the reaction mixture. The reaction mixture was diluted with EtOAc (10.0 mL) and HCl (5.00 mL, 1.00 M, aq). The aqueous layer was extracted with EtOAc (3 × 10.0 mL), organic layers were combined, washed with $Na_2S_2O_3$ (2 × 5.00 mL, sat., aq), dried over Na_2SO_4, filtered and concentrated. The crude product was purified by flash chromatography (silica, 0 - 25% EtOAc/Hexane). The sample was analyzed by ^1H NMR ($CDCl_3$, 500 MHz) to obtain the deuterium incorporation.

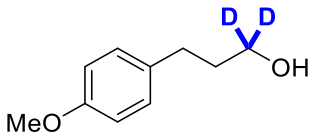
3.3 Reductive Deuteration of Acyl fluorides by SmI_2–D_2O (Scheme 1)

3-Phenylpropan-1,1-*d*$_2$-1-ol[3] (2a, Scheme 1)



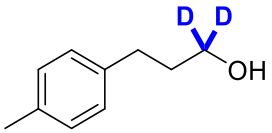
To a solution of samarium (II) iodide (0.100 M in THF; 50.0 mL, 5.00 mmol, 5.00 equiv), was added deuterium oxide (601 mg, 30.0 mmol, 30.0 equiv). A characteristic burgundy red color of SmI_2-D_2O complex was observed. A solution of 3-phenylpropanoyl fluoride (152 mg, 1.00 mmol, 1.00 equiv), in THF (3.00 mL) was then added under Ar at room temperature and stirred vigorously. After 60.0 min, excess SmI_2 was oxidized by bubbling air through the reaction mixture. The reaction mixture was diluted with EtOAc (30.0 mL) and HCl (15.0 mL, 1.00 M, aq). The aqueous layer was extracted with EtOAc (3 × 30.0 mL), organic layers were combined, washed with $Na_2S_2O_3$ (2 × 15.0 mL, sat., aq), dried over Na_2SO_4, filtered and concentrated. The crude product was purified by flash chromatography (silica, 9 - 20% EtOAc/Hexane), afforded 131 mg of **2a** in 95% yield as a colorless oil. D_2 incorporation > 98%. ^1H NMR (500 MHz, $CDCl_3$) δ 7.33 – 7.24 (m, 2H), 7.21 – 7.16 (m, 3H), 2.71 (t, J = 7.7 Hz, 2H), 1.88 (t, J = 7.7 Hz, 2H), 1.43 (br, 1H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 141.9, 128.5 (×2), 125.9, 61.6 (m), 34.1, 32.1.

3-(4-Methoxyphenyl)propan-1,1-*d*$_2$-1-ol[3] (2b, Scheme 1)



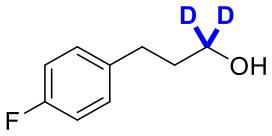
According to the general procedure, the reaction of 3-(4-methoxyphenyl)propanoyl fluoride (54.7 mg, 0.300 mmol), samarium (II) iodide (15.0 mL, 1.50 mmol), and deuterium oxide (180 mg, 9.00 mmol), after chromatography (9 - 20% EtOAc/ Hexane), afforded 49.5 mg of **2b** in 98% yield as a colorless oil. D_2 incorporation > 98%. ^1H NMR (500 MHz, $CDCl_3$) δ 7.11 (m, 2H), 6.83 (m, 2H), 3.78 (s, 3H), 2.64 (t, J = 7.7 Hz, 2H), 1.84 (t, J = 7.7 Hz, 2H), 1.70 (br, 1H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 157.8, 133.9, 129.4, 113.9, 61.5 (m), 55.3, 34.3, 31.1.

3-(*p*-Tolyl)propan-1,1-d_2-1-ol[3] (2c, Scheme 1)



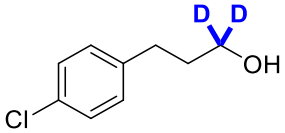
According to the general procedure, the reaction of 3-(*p*-tolyl)propanoyl fluoride (49.9 mg, 0.300 mmol), samarium (II) iodide (15.0 mL, 1.50 mmol), and deuterium oxide (180 mg, 9.00 mmol), after chromatography (9 - 20% EtOAc/ Hexane), afforded 44.8 mg of **2c** in 98% yield as a colorless oil. D_2 incorporation = 98%. ^{1}H NMR (500MHz, $CDCl_3$) δ 7.11 – 7.07 (m, 4H), 2.66 (t, J = 7.8 Hz, 2H), 2.31 (s, 3H), 1.85 (t, J = 7.8 Hz, 2H), 1.65 (br, 1H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 138.8, 135.4, 129.1, 128.4, 61.6 (m), 34.2, 31.6, 21.0.

3-(4-Fluorophenyl)propan-1,1-d_2-1-ol[3] (2d, Scheme 1)



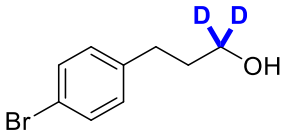
According to the general procedure, the reaction of 3-(4-fluorophenyl)propanoyl fluoride (51.1 mg, 0.300 mmol), samarium (II) iodide (15.0 mL, 1.50 mmol), and deuterium oxide (180 mg, 9.00 mmol), after chromatography (9 - 20% EtOAc/ Hexane), afforded 45.9 mg of **2d** in 98% yield as a colorless oil. D_2 incorporation = 98%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.14 (m, 2H), 6.96 (m, 2H), 2.68 (t, J = 7.8 Hz, 2H), 1.85 (t, J = 7.8 Hz, 2H), 1.51 (br, 1H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 161.3 (d, $J_{C\text{-}F}$ = 243.5 Hz), 137.5 (d, $J_{C\text{-}F}$ = 2.9 Hz), 129.8 (d, $J_{C\text{-}F}$ = 7.5 Hz), 115.2 (d, $J_{C\text{-}F}$ = 21.1 Hz), 61.4 (m), 34.2, 31.2.

3-(4-Chlorophenyl)propan-1,1-d_2-1-ol[3] (2e, Scheme 1)



According to the general procedure, the reaction of 3-(4-chlorophenyl)propanoyl fluoride (56.0 mg, 0.300 mmol), samarium (II) iodide (15.0 mL, 1.50 mmol), and deuterium oxide (180 mg, 9.00 mmol), after chromatography (9 - 20% EtOAc/ Hexane), afforded 50.2 mg of **2e** in 97% yield as a colorless oil. D_2 incorporation = 98%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24 (m, 2H), 7.12 (m, 2H), 2.67 (t, J = 7.7 Hz, 2H), 1.84 (t, J = 7.7 Hz, 2H), 1.62 (br, 1H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 140.3, 131.6, 129.8, 128.5, 61.3 (m), 33.9, 31.4.

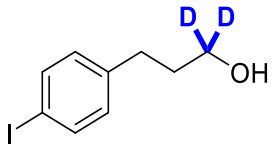
3-(4-Bromophenyl)propan-1,1-d_2-1-ol[3] (2f, Scheme 1)



According to the general procedure, the reaction of 3-(4-bromophenyl)propanoyl fluoride (69.3 mg, 0.300 mmol), samarium (II) iodide (15.0 mL, 1.50 mmol), and deuterium oxide (180 mg,

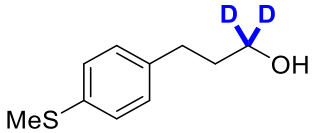
9.00 mmol), after chromatography (9 - 20% EtOAc/ Hexane), afforded 62.5 mg of **2f** in 96% yield as a colorless oil. D_2 incorporation = 98%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 (m, 2H), 7.07 (m, 2H), 2.65 (t, *J* = 7.7 Hz, 2H), 1.84 (t, *J* = 7.7 Hz, 2H), 1.67 (br, 1H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 140.8, 131.5, 130.3, 119.6, 61.3 (m), 33.8, 31.4.

3-(4-Iodophenyl)propan-1,1-*d*$_2$-1-ol[4] (2g, Scheme 1)



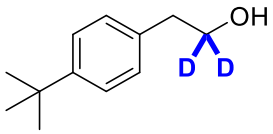
According to the general procedure, the reaction of 3-(4-iodophenyl)propanoyl fluoride (83.4mg, 0.300 mmol), samarium (II) iodide (15.0 mL, 1.50 mmol), and deuterium oxide (180 mg, 9.00 mmol), after chromatography (9 - 25% EtOAc/ Hexane), afforded 80.1 mg of **2g** in 96% yield as a colorless oil. D_2 incorporation = 98%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (m, 2H), 6.95 (m, 2H), 2.65 (t, *J* = 7.7 Hz, 2H), 1.84 (t, *J* = 7.7 Hz, 2H), 1.62 (br, 1H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 141.5, 137.5, 130.6, 90.9, 61.5 (m), 33.8, 31.6.

3-(4-(Methylthio)phenyl)propan-1,1-*d*$_2$-1-ol[3] (2h, Scheme 1)



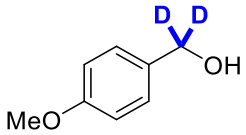
According to the general procedure, the reaction of 3-(4-(methylthio)phenyl)propanoyl fluoride (59.5 mg, 0.300 mmol), samarium (II) iodide (15.0 mL, 1.50 mmol), and deuterium oxide (180 mg, 9.00 mmol), after chromatography (9 - 20% EtOAc/ Hexane), afforded 54.2 mg of **2h** in 98% yield as a colorless oil. D_2 incorporation = 98%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.20 (m, 2H), 7.12 (m, 2H), 2.66 (t, *J* = 7.7 Hz, 2H), 2.46 (s, 3H), 1.84 (t, *J* = 7.7 Hz, 2H), 1.67 (br, 1H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 139.0, 135.4, 129.0, 127.2, 61.4 (m), 34.0, 31.5, 16.4.

2-(4-(*Tert*-butyl)phenyl)ethan-1,1-*d*$_2$-1-ol[5] (2i, Scheme 1)



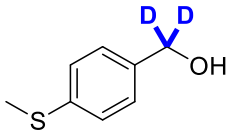
According to the general procedure, the reaction of 2-(4-(*tert*-butyl)phenyl)acetyl fluoride (58.3 mg, 0.300 mmol), samarium (II) iodide (15.0 mL, 1.50 mmol), and deuterium oxide (180 mg, 9.00 mmol), after chromatography (9 - 20% EtOAc/ Hexane), afforded 37.9 mg of **2i** in 70% yield as a colorless oil. D_2 incorporation > 98%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (m, 2H), 7.15 (m, 2H), 2.80 (s, 2H), 1.86 (br, 1H), 1.30 (s, 9H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 149.3, 135.4, 128.7, 125.5, 62.9 (m), 38.5, 34.4, 31.4.

(4-Methoxyphenyl)methan-d_2-ol[3] (2j, Scheme 1)



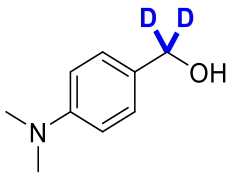
According to the general procedure, the reaction of 4-methoxybenzoyl fluoride (46.2 mg, 0.300 mmol), samarium (II) iodide (15.0 mL, 1.50 mmol), and deuterium oxide (180 mg, 9.00 mmol), after chromatography (9 - 17% EtOAc/ Hexane), afforded 41.2 mg of **2j** in 98% yield as a colorless oil. D_2 incorporation > 98%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27 (m, 2H), 6.89 (m, 2H), 3.80 (s, 3H), 1.84 (br, 1H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 159.3, 133.1, 128.7, 114.0, 64.4 (m), 55.4.

(4-(Methylthio)phenyl)methan-d_2-ol[6] (2k, Scheme 1)



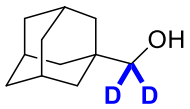
According to the general procedure, the reaction of 4-(methylthio)benzoyl fluoride (51.1 mg, 0.300 mmol), samarium (II) iodide (15.0 mL, 1.50 mmol), and deuterium oxide (180 mg, 9.00 mmol), after chromatography (9 - 25% EtOAc/ Hexane), afforded 42.2 mg of **2k** in 90% yield as a pale yellow solid. D_2 incorporation > 98%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 – 7.08 (m, 4H), 2.48 (s, 3H), 1.76 (br, 1H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 137.9, 137.7, 127.7, 126.9, 64.3 (m), 16.0.

(4-(Dimethylamino)phenyl)methan-d_2-ol[6] (2l, Scheme 1)



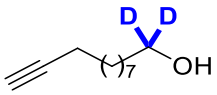
To a solution of samarium (II) iodide (0.100 M in THF; 15.0 mL, 1.50 mmol, 5.00 equiv), was added deuterium oxide (180 mg, 9.00 mmol, 30.0 equiv). A characteristic burgundy red color of SmI_2-D_2O complex was observed. A solution of 4-(dimethylamino)benzoyl fluoride (50.2 mg, 0.300 mmol, 1.00 equiv) in THF (1.00 mL) was then added under Ar at room temperature and stirred vigorously. After 30.0 min, excess samarium (II) iodide was oxidized by bubbling air through the reaction mixture. The reaction mixture was diluted with EtOAc (10.0 mL) and NaOH (5.00 mL, 1.00 M, aq). The aqueous layer was extracted with EtOAc (3 × 10.0 mL), organic layers were combined, washed with $Na_2S_2O_3$ (2 × 5.00 mL, sat., aq), dried over Na_2SO_4, filtered and concentrated. The crude product was purified by flash chromatography (silica, 9 - 25% EtOAc/Hexane) , afforded 41.4 mg of **2l** in 90% yield as a yellow oil. D_2 incorporation > 98%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24 (m, 2H), 6.72 (m, 2H), 2.94 (s, 6H), 1.61 (br, 1H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 150.4, 128.9, 128.7, 112.7, 64.7 (m), 40.7.

((3*r*,5*r*,7*r*)-Adamantan-1-yl)methan-*d*$_2$-ol[3] (2m, Scheme 1)



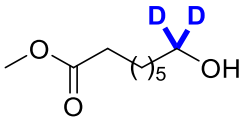
According to the general procedure, the reaction of (3*r*,5*r*,7*r*)-adamantane-1-carbonyl fluoride (54.7 mg, 0.300 mmol), samarium (II) iodide (15.0 mL, 1.50 mmol), and deuterium oxide (180 mg, 9.00 mmol), after chromatography (9 - 15% EtOAc/ Hexane), afforded 49.5 mg of **2m** in 98% yield as a white solid. D_2 incorporation = 98%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.99 (m, 3H), 1.75 – 1.72 (m, 3H), 1.67 – 1.63 (m, 3H), 1.51 (m, 6H), 1.41 (br, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 73.1(m), 39.1, 37.3, 34.4, 28.2.

Undec-10-yn-1,1-*d*$_2$-1-ol[3] (2n, Scheme 1)



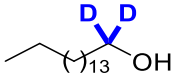
According to the general procedure, the reaction of undec-10-ynoyl fluoride (55.3 mg, 0.300 mmol), samarium (II) iodide (15.0 mL, 1.50 mmol), and deuterium oxide (180 mg, 9.00 mmol), after chromatography (9 - 17% EtOAc/ Hexane), afforded 50.1 mg of **2n** in 98% yield as a colorless oil. D_2 incorporation > 98%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.18 (td, J = 7.1, 2.6 Hz, 2H), 1.94 (t, J = 2.6 Hz, 1H), 1.63 (br, 1H), 1.58 – 1.48 (m, 4H), 1.41 – 1.27 (m, 10H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 84.8, 68.1, 62.3 (m), 32.6, 29.5, 29.4, 29.1, 28.8, 28.5, 25.7, 18.4.

Methyl 8-hydroxyoctanoate-8,8-*d*$_2$[3] (2o, Scheme 1)



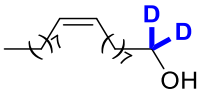
According to the general procedure, the reaction of methyl 8-fluoro-8-oxooctanoate (57.1 mg, 0.300 mmol), samarium (II) iodide (15.0 mL, 1.50 mmol), and deuterium oxide (180 mg, 9.00 mmol), after chromatography (9 - 20% EtOAc/ Hexane), afforded 42.3 mg of **2o** in 80% yield as a colorless oil. D_2 incorporation = 98%.^{1}H NMR (500 MHz, $CDCl_3$) δ 3.67 (s, 3H), 2.31 (t, J = 7.5 Hz, 2H), 1.63 (m, 2H), 1.54 (m, 2H), 1.37 – 1.32 (m, 6H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 174.4, 62.2 (m), 51.5, 34.1, 32.5, 29.1 (×2), 25.5, 24.9.

Hexadecan-1,1-*d*$_2$-1-ol[3] (2p, Scheme 1)



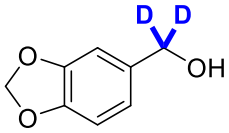
According to the general procedure, the reaction of palmitoyl fluoride (77.5 mg, 0.300 mmol), samarium (II) iodide (15.0 mL, 1.50 mmol), and deuterium oxide (180 mg, 9.00 mmol), after chromatography (9 - 20% EtOAc/ Hexane), afforded 68.2 mg of **2p** in 93% yield as a colorless oil. D_2 incorporation = 98%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.55 (t, J = 7.2 Hz, 2H), 1.36 – 1.23 (m, 26H), 0.88 (t, J = 6.9 Hz, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 62.4 (m), 32.7, 32.0, 29.8(×4), 29.7(×4), 29.5(×2), 25.8, 22.8, 14.2.

(*Z*)-Octadec-9-en-1,1-d_2-1-ol[3] (2q, Scheme 1)



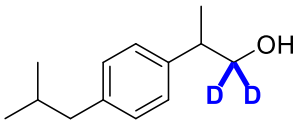
According to the general procedure, the reaction of oleoyl fluoride (85.3 mg, 0.300 mmol), samarium (II) iodide (15.0 mL, 1.50 mmol), and deuterium oxide (180 mg, 9.00 mmol), after chromatography (9-15% EtOAc/ Hexane), afforded 77.1 mg of **2q** in 95% yield as a colorless oil. D_2 incorporation = 98%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.38 – 5.30 (m, 2H), 2.05 – 1.96 (m, 4H), 1.55 (m, 2H), 1.45 – 1.13 (m, 22H), 0.88 (t, *J* = 6.9 Hz, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 130.0, 129.9, 62.3 (m), 32.7, 32.0, 29.8 (×2), 29.6 (×2), 29.5, 29.4 (×2), 29.3, 27.3 (×2), 25.8, 22.8, 14.2.

Benzo[*d*][1,3]dioxol-5-ylmethan-d_2-ol[6] (2r, Scheme 1)



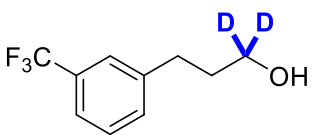
According to the general procedure, the reaction of benzo[*d*][1,3]dioxole-5-carbonyl fluoride (50.4 mg, 0.300 mmol), samarium (II) iodide (15.0 mL, 1.50 mmol), and deuterium oxide (180 mg, 9.00 mmol), after chromatography (9 - 25% EtOAc/ Hexane), afforded 41.6 mg of **2r** in 90% yield as a pale yellow oil. D_2 incorporation > 98%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.87 (d, *J* = 1.6 Hz, 1H), 6.81 (dd, *J* = 8.0, 1.6 Hz, 1H), 6.78 (d, *J* = 8.0 Hz, 1H), 5.95 (s, 2H), 1.71 (br, 1H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 147.9, 147.2, 134.8, 120.6, 108.3, 108.0, 101.1, 64.7 (m).

2-(4-Isobutylphenyl)propan-1,1-d_2-1-ol[7] (2s, Scheme 1)



According to the general procedure, the reaction of 2-(4-isobutylphenyl)propanoyl fluoride (62.5 mg, 0.300 mmol), samarium (II) iodide (15.0 mL, 1.50 mmol), and deuterium oxide (180 mg, 9.00 mmol), after chromatography (9 - 20% EtOAc/ Hexane), afforded 52.5 mg of **2s** in 90% yield as a colorless oil. D_2 incorporation > 98%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.15 – 7.10 (m, 4H), 2.92 (q, *J* = 7.0 Hz, 1H), 2.45 (d, *J* = 7.2 Hz, 2H), 1.85 (m, 1H), 1.61 (br, 1H), 1.26 (d, *J* = 7.1 Hz, 3H), 0.90 (d, *J* = 6.6 Hz, 6H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 140.8, 140.2, 129.5, 127.2, 68.1 (m), 45.1, 41.9, 30.3, 22.5, 17.7.

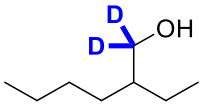
3-(3-(Trifluoromethyl)phenyl)propan-1,1-d_2-1-ol[8] (2t, Scheme 1)



To a solution of samarium (II) iodide (0.100 M in THF; 50.0 mL, 5.00 mmol, 5.00 equiv), was added deuterium oxide (601 mg, 30.0 mmol, 30.0 equiv). A characteristic burgundy red color

of SmI_2-D_2O complex was observed. A solution of 3-(3-(trifluoromethyl)phenyl)propanoyl fluoride (220 mg, 1.00 mmol, 1.00 equiv), in THF (3.00 mL) was then added under Ar at room temperature and stirred vigorously. After 60.0 min, excess SmI_2 was oxidized by bubbling air through the reaction mixture. The reaction mixture was diluted with EtOAc (30.0 mL) and HCl (15.0 mL, 1.00 M, aq). The aqueous layer was extracted with EtOAc (3 × 30.0 mL), organic layers were combined, washed with $Na_2S_2O_3$ (2 × 15.0 mL, sat., aq), dried over Na_2SO_4, filtered and concentrated. The crude product was purified by flash chromatography (silica, 9 - 20% EtOAc/Hexane), afforded 202 mg of **2t** in 98% yield as a colorless oil. D_2 incorporation = 98%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 – 7.42 (m, 2H), 7.41 – 7.38 (m, 2H), 2.77 (t, J = 7.8 Hz, 2H), 1.89 (t, J = 7.8 Hz, 2H), 1.75 (br, 1H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 142.8, 131.9, 130.8 (q, $J_{C\text{-}F}$ = 32.1 Hz), 128.9, 125.2 (q, $J_{C\text{-}F}$ = 4.1 Hz), 124.3 (q, $J_{C\text{-}F}$ = 272.1 Hz), 122.8 (q, $J_{C\text{-}F}$ = 3.9 Hz), 61.2 (m), 33.8, 31.9.

2-Ethylhexan-1,1-*d*$_2$-1-ol[8] (2u, Scheme 1)

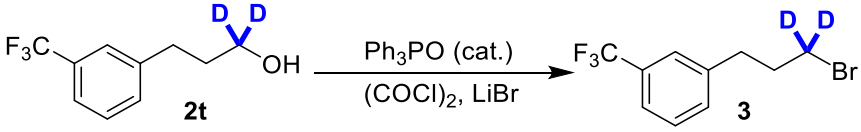


To a solution of samarium (II) iodide (0.100 M in THF; 50.0 mL, 5.00 mmol, 5.00 equiv), was added deuterium oxide (601 mg, 30.0 mmol, 30.0 equiv). A characteristic burgundy red color of SmI_2-D_2O complex was observed. A solution of 2-ethylhexanoyl fluoride (146 mg, 1.00 mmol, 1.00 equiv), in THF (3.00 mL) was then added under Ar at room temperature and stirred vigorously. After 60.0 min, excess SmI_2 was oxidized by bubbling air through the reaction mixture. The reaction mixture was diluted with EtOAc (10.0 mL) and HCl (5.00 mL, 1.00 M, aq). The aqueous layer was extracted with EtOAc (3 × 10.0 mL), organic layers were combined, washed with $Na_2S_2O_3$ (2 × 5.00 mL, sat., aq), dried over Na_2SO_4, filtered and concentrated. The crude product was purified by flash chromatography (silica, 9 - 20% EtOAc/Hexane), afforded 119 mg of **2u** in 90% yield as a colorless oil. D_2 incorporation = 98%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.42 – 1.25 (m, 9H), 0.90 (t, J = 6.8 Hz, 6H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 64.7 (m), 41.9, 30.2, 29.2, 23.4, 23.2, 14.2, 11.2.

3.4 Synthesis of (±) Cinacalcet-*d*$_2$ and 2,4-D 2-Ethylhexyl ester-*d*$_2$

Synthesis of (±) Cinacalcet-*d*$_2$

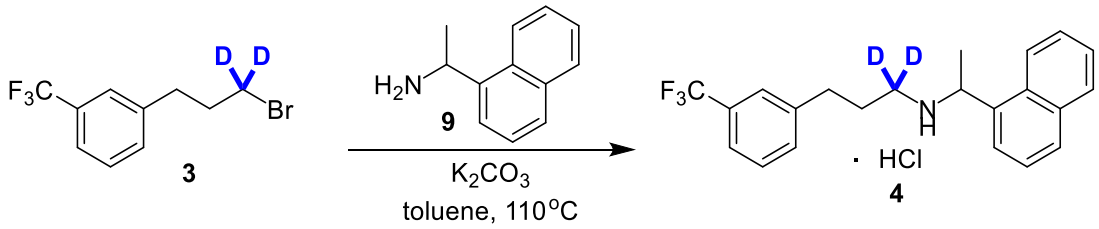
1-(3-Bromopropyl-3,3-*d*$_2$)-3-(trifluoromethyl)benzene[9] (3, Scheme 1)



To a solution of triphenylphosphine oxide (28.0 mg, 0.100 mmol) in 1.50 mL $CHCl_3$, were added oxalyl chloride (8.50 µL, 0.100 mmol) and LiBr (130 mg, 1.50 mmol), and the reaction mixture stirred for 5.00 min. The **2t** (103 mg, 0.500 mmol, 1.00 equiv) and oxalyl chloride (46.5 µL, 0.550 mmol) as solutions in $CHCl_3$ (1.00 mL) were then added simultaneously over

5.00 h via syringe pump at room temperature. The reaction mixture was filtered. The solvent was removed in vacuo. The crude product was purified by flash chromatography (silica, 9 - 20% EtOAc/Hexane) to afford 132 mg of **3** in 98% yield as a pale-yellow liquid. D_2 incorporation = 98%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 – 7.44 (m, 2H), 7.43 – 7.39 (m, 2H), 2.85 (t, J = 7.5 Hz, 2H), 2.18 (t, J = 7.5 Hz, 2H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 141.6, 132.1, 130.1 (q, $J_{C\text{-}F}$ = 32.0 Hz), 129.0, 125.3 (q, $J_{C\text{-}F}$ = 4.0 Hz), 124.2 (q, $J_{C\text{-}F}$ =272.2Hz), 123.2 (q, $J_{C\text{-}F}$ = 3.7 Hz), 33.8, 33.7, 32.3 (m).

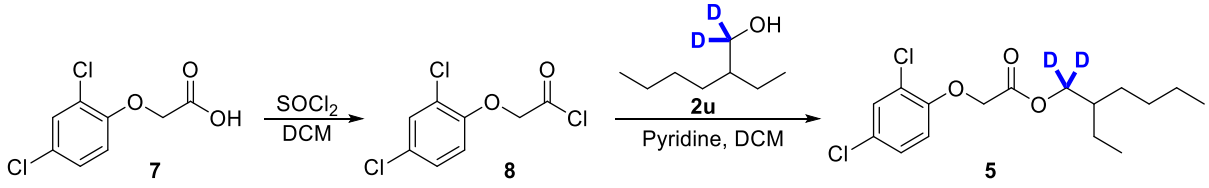
(±)Cinacalcet-d_2[9] (4, Scheme 1)



To a solution of **3** (80.7 mg, 0.300 mmol, 1.00 equiv) in toluene (1.00 mL), were added 1-(naphthalen-1-yl)ethan-1-amine **9** (62.7 mg, 0.360 mmol, 1.20 equiv) and K_2CO_3 (82.9 mg, 0.600 mmol, 2.00 equiv) at room temperature. Then the reaction mixture was warmed to 110°C and stirred vigorously for 56 hours. The mixture was cooled to room temperature and additional K_2CO_3 (82.9 mg, 0.600 mmol, 2.00 equiv) was added. Then, the reaction mixture was again stirred vigorously at 110°C for 16.0 hours. After cooling to room temperature, water (2.60 mL) was added and the phases separated. The aqueous phase was extracted with toluene (3 × 0.500 mL). The combined organic phases were extracted at 50°C with HCl (1.00 M, aq.; 3 × 1.00 mL) and then dried over Na_2SO_4, filtered, and concentrated in vacuo. Addition of n-hexane and concentration led to solid formation. The solid was washed with n-hexane (3 × 1.00 mL), then recrystallized from toluene/ n-hexane (1:3) affording 101 mg of **4** in 85% yield as a white solid. D_2 incorporation = 98%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.50 (br, 1H), 9.97 (br, 1H), 8.22 (d, J = 7.2 Hz, 1H), 8.00 – 7.87 (m, 3H), 7.65 – 7.53 (m, 3H), 7.31 (m, 1H), 7.24 (m, 1H), 7.21 – 7.17 (m, 2H), 5.21 (m, 1H),2.54 (m, 2H), 2.25 (m, 2H), 1.97 (d, J = 6.7 Hz, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 140.9, 133.9, 132.2, 131.6, 130.8, 130.7 (q, $J_{C\text{-}F}$ = 32.0 Hz), 129.6, 129.5, 128.9, 127.4, 126.3, 126.2, 125.0, 125.0 (q, $J_{C\text{-}F}$ = 3.7 Hz), 124.0 (q, $J_{C\text{-}F}$ = 272.3 Hz), 123.1 (q, $J_{C\text{-}F}$ = 4.0 Hz), 121.3, 53.5, 44.9 (m), 32.5, 27.1, 21.4.

Synthesis of 2,4-D 2-Ethylhexyl ester-d_2

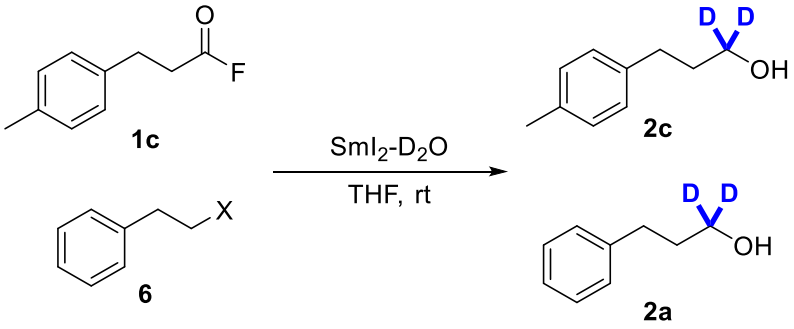
2,4-D 2-Ethylhexyl ester-d_2[10] (5, Scheme 1)



Carboxylic acid **7** (66.3 mg, 0.300 mmol, 1.00 equiv) and two drops of DMF was dissolved in

dichloromethane (5.00 mL). The solution was cooled to 0℃ and oxalyl chloride (0.0305 mL, 0.360 mmol, 1.20 equiv) was added dropwise. After the reaction mixture was stirred for 3.00 hours, a solution of **2u** (39.6 mg, 0.300 mmol, 1.00 equiv) and pyridine (23.7 mg, 0.300 mmol, 1.00 equiv) in dichloromethane (15.0 mL) was added dropwise and the mixture was stirred overnight. Then the reaction mixture was diluted with EtOAc (10.0 mL) and NaOH (5.00 mL, 1.00 M, aq). The aqueous layer was extracted with EtOAc (3 × 10.0 mL). Organic layers were combined, dried over Na_2SO_4, filtered and concentrated. The crude product was purified by flash chromatography (silica, 6 - 11% EtOAc/Petroleum ether), afforded 77.1 mg of **5** in 80% yield as a colorless oil. D_2 incorporation = 98%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (d, J = 2.6 Hz, 1H), 7.16 (dd, J = 8.8, 2.6 Hz, 1H), 6.77 (d, J = 8.8 Hz, 1H), 4.70 (s, 2H), 1.56 (m, 1H), 1.27 – 1.21 (m, 8H), 0.89 – 0.84 (m,6H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 168.4, 152.5, 130.4, 127.6, 127.1, 124.3, 114.5, 67.3(m), 66.4, 38.6, 30.3, 29.8, 29.0, 23.7, 14.1, 11.0.

3.5 Competition Experiments between 1a and representative carbonyl compounds



Entry	X	**2c**	**2a**
1	COOH	95%	5%
2	COOEt	95%	5%
3	COOpfp	95%	5%

According to the general procedure, the reaction of **6** (0.200 mmol, 1.00 equiv) and **1c**(0.200 mmol, 1.00 equiv), samarium(II) iodide (0.100 M in THF; 8.00 mL, 0.800 mmol, 4.00 equiv) and deuterium oxide (96.0 mg, 4.80 mmol, 24.0 equiv) for 30.0 min at rt, afforded **2a** and **2c**. The relative quantity of each product was determined by ^{1}H NMR (500 MHz, $CDCl_3$).

3.6 General Procedure for the Synthesis of Acyl fluorides

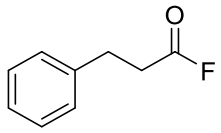
Acyl fluoride was synthesized using reported method without modification[2]: To a solution of the carboxylic acid (5.00 mmol, 1.00 equiv) in CH_2Cl_2 (5.00 mL) was added Bis(2-methoxyethyl)aminosulfur trifluoride (BAST) (1.33 g, 6.00 mmol, 1.20 equiv) under Ar and

stirred for 3.00 hours at room temperature. After this time, the vial was opened, and the reaction mixture was diluted with hexanes (20.0 mL), and the mixture was added to silica gel in hexanes and stirred for 10.0 min. The combined organic layers were filtered and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to give acid fluoride.

Note: 2-bromo-5-iodobenzoic acid cannot be converted into the corresponding acyl fluoride under the typical reaction conditions.

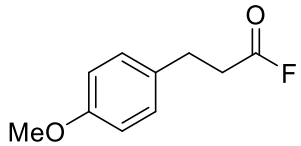
4. The Synthesis of Acyl fluorides

3-Phenylpropanoyl fluoride[11] (1a, Scheme 1)



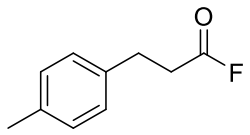
According to the general procedure, the reaction of 3-phenylpropanoic acid (751 mg, 5.00 mmol), CH_2Cl_2 (5.00 mL), BAST (1.33 g, 6.00 mmol), after chromatography (5 - 9% EtOAc/ petroleum ether), afforded **1a** as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 – 7.27 (m, 2H), 7.27 – 7.17 (m, 3H), 2.99 (t, J = 7.6 Hz, 2H), 2.81 (t, J = 7.6 Hz, 2H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 162.9 (d, $J_{C\text{-}F}$ = 360.4 Hz), 139.0, 128.8, 128.3, 126.9, 33.9 (d, $J_{C\text{-}F}$ = 50.5 Hz), 30.0 (d, $J_{C\text{-}F}$ = 2.6 Hz).

3-(4-Methoxyphenyl)propanoyl fluoride (1b, Scheme 1)



According to the general procedure, the reaction of 3-(4-methoxyphenyl)propanoic acid (901 mg, 5.00 mmol), CH_2Cl_2 (5.00 mL), BAST (1.33 g, 6.00 mmol), after chromatography (5 - 9% EtOAc/ petroleum ether), afforded **1b** as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 (m, 2H), 6.84 (m, 2H), 3.78 (s, 3H), 2.92 (t, J = 7.5 Hz, 2H), 2.78 (t, J = 7.5 Hz, 2H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 162.9 (d, $J_{C\text{-}F}$ = 361.0 Hz), 158.5, 131.0, 129.3, 114.2, 55.3, 34.2 (d, $J_{C\text{-}F}$ = 49.9 Hz), 29.2 (d, $J_{C\text{-}F}$ = 2.2 Hz); HRMS (FTMS-ESI) m/z: $[M - H]^-$ (of the carboxylic acid derived from acyl fluoride) calc for $C_{10}H_{11}O_3^-$ 179.0714, found 179.0722.

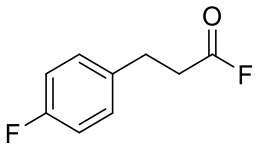
3-(*p*-Tolyl)propanoyl fluoride[12] (1c, Scheme 1)



According to the general procedure, the reaction of 3-(*p*-tolyl)propanoic acid (821 mg, 5.00 mmol), CH_2Cl_2 (5.00 mL), BAST (1.33 g, 6.00 mmol), after chromatography (5 - 9%EtOAc/ petroleum ether), afforded **1c** as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 – 7.05 (m,

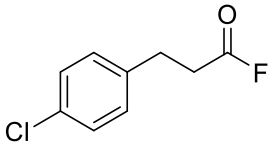
4H), 2.94 (t, J = 7.6 Hz, 2H), 2.78 (t, J = 7.6 Hz, 2H), 2.32 (s, 3H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 162.9 (d, $J_{C\text{-}F}$ = 360.4 Hz), 136.5, 135.9, 129.5, 128.2, 34.1 (d, $J_{C\text{-}F}$ = 50.0 Hz), 29.6 (d, $J_{C\text{-}F}$ = 2.2 Hz), 21.1.

3-(4-Fluorophenyl)propanoyl fluoride[12] (1d, Scheme 1)



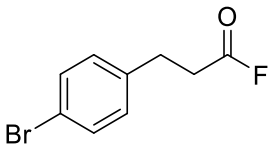
According to the general procedure, the reaction of 3-(4-fluorophenyl)propanoic acid (841 mg, 5.00 mmol), CH_2Cl_2 (5.00 mL), BAST (1.33 g, 6.00 mmol), after chromatography (5 - 9% EtOAc/ petroleum ether), afforded **1d** as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 (m, 2H), 7.00 (m, 2H), 2.97 (t, J = 7.5 Hz, 2H), 2.81 (t, J = 7.5 Hz, 2H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 163.8 (d, $J_{C\text{-}F}$ = 360.5 Hz), 160.8 (d, $J_{C\text{-}F}$ = 245.1 Hz), 134.6 (d, $J_{C\text{-}F}$ = 3.3 Hz), 129.9 (d, $J_{C\text{-}F}$ = 8.0 Hz), 115.7 (d, $J_{C\text{-}F}$ = 21.3 Hz), 34.1 (d, $J_{C\text{-}F}$ = 50.5 Hz), 29.3 (d, $J_{C\text{-}F}$ = 2.4 Hz).

3-(4-Chlorophenyl)propanoyl fluoride[12] (1e, Scheme 1)



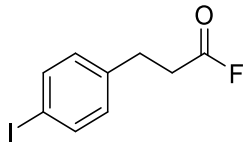
According to the general procedure, the reaction of 3-(4-chlorophenyl)propanoic acid (923 mg, 5.00 mmol), CH_2Cl_2 (5.00 mL), BAST (1.33 g, 6.00 mmol), after chromatography (5 - 9% EtOAc/ petroleum ether), afforded **1e** as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (m, 2H), 7.14 (m, 2H), 2.95 (t, J = 7.5 Hz, 2H), 2.80 (t, J = 7.5 Hz, 2H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 162.6 (d, $J_{C\text{-}F}$ = 360.7 Hz), 137.4, 132.7, 129.7, 128.9, 33.7 (d, $J_{C\text{-}F}$ = 51.2 Hz), 29.4 (d, $J_{C\text{-}F}$ = 2.3 Hz).

3-(4-Bromophenyl)propanoyl fluoride[12] (1f, Scheme 1)



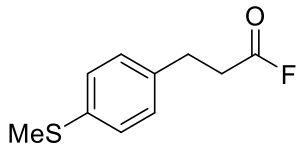
According to the general procedure, the reaction of 3-(4-bromophenyl)propanoic acid (1.15 g, 3.00 mmol), CH_2Cl_2 (5.00 mL), BAST (1.33 g, 6.00 mmol), after chromatography (5 - 9% EtOAc/ petroleum ether), afforded **1f** as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (m, 2H), 7.09 (m, 2H), 2.94 (t, J = 7.4 Hz, 2H), 2.80 (t, J = 7.4 Hz, 2H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 162.6 (d, $J_{C\text{-}F}$ = 360.7 Hz), 137.9, 131.9, 130.1, 120.8, 33.7 (d, $J_{C\text{-}F}$ = 50.8 Hz), 29.4 (d, $J_{C\text{-}F}$ = 2.8 Hz).

3-(4-Iodophenyl)propanoyl fluoride[12] (1g, Scheme 1)



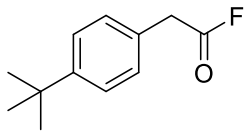
According to the general procedure, the reaction of 3-(4-iodophenyl)propanoic acid (1.38 g, 5.00 mmol), CH_2Cl_2 (5.00 mL), BAST (1.33 g, 6.00 mmol), after chromatography (5 - 9% EtOAc/ petroleum ether), afforded **1g** as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (m, 2H), 6.97 (m, 2H), 2.94 (t, J = 7.3 Hz, 2H), 2.81 (t, J = 7.3 Hz, 2H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 162.6 (d, $J_{C\text{-}F}$ = 360.4 Hz), 138.6, 137.9, 130.4, 92.2, 33.7 (d, $J_{C\text{-}F}$ = 50.7 Hz), 29.6 (d, $J_{C\text{-}F}$ = 2.1 Hz).

3-(4-(Methylthio)phenyl)propanoyl fluoride (1h, Scheme 1)



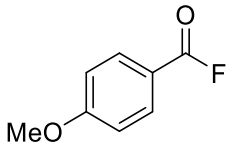
According to the general procedure, the reaction of 3-(4-(methylthio)phenyl)propanoic acid (981 mg, 5.00 mmol), CH_2Cl_2 (5.00 mL), BAST (1.33 g, 6.00 mmol), after chromatography (5 - 9% EtOAc/ petroleum ether), afforded **1h** as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (m, 2H), 7.13 (m, 2H), 2.94 (t, J = 7.5 Hz, 2H), 2.80 (t, J = 7.5 Hz, 2H), 2.46 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 162.8 (d, $J_{C\text{-}F}$ = 360.3 Hz), 136.9, 135.8, 128.8, 127.2, 33.9 (d, $J_{C\text{-}F}$ = 50.5 Hz), 29.5 (d, $J_{C\text{-}F}$ = 2.3 Hz), 16.0; HRMS (FTMS-ESI) m/z: $[M - H]^-$ (of the carboxylic acid derived from acyl fluoride) calc for $C_{10}H_{11}O_2S^-$ 195.0485, found 195.0491.

2-(4-(*Tert*-butyl)phenyl)acetyl fluoride (1i, Scheme 1)



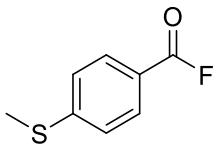
According to the general procedure, the reaction of 2-(4-(*tert*-butyl)phenyl)acetic acid (971 mg, 5.00 mmol), CH_2Cl_2 (5.00 mL), BAST (1.33 g, 6.00 mmol), after chromatography (5 - 9% EtOAc/ petroleum ether), afforded **1i** as colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 (m, 2H), 7.22 (m, 2H), 3.77 (s, 2H), 1.32 (s, 9H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 161.7 (d, $J_{C\text{-}F}$ = 362.1 Hz), 151.1, 129.0, 127.8 (d, $J_{C\text{-}F}$ = 2.4 Hz), 126.0, 38.5 (d, $J_{C\text{-}F}$ = 54.3 Hz), 34.6, 31.3; HRMS (FTMS-ESI) m/z: $[M - H]^-$ (of the carboxylic acid derived from acyl fluoride) calc for $C_{12}H_{15}O_2^-$ 191.1078, found 191.1081.

4-Methoxybenzoyl fluoride[12] (1j, Scheme 1)



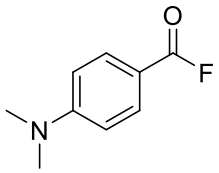
According to the general procedure, the reaction of 4-methoxybenzoic acid (761 mg, 5.00 mmol), CH_2Cl_2 (5.00 mL), BAST (1.33 g, 6.00 mmol), after chromatography (5 - 9% EtOAc/ petroleum ether), afforded **1j** as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (m, 2H), 6.98 (m, 2H), 3.90 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 165.3, 157.3 (d, $J_{C\text{-}F}$ = 340.0 Hz), 133.8 (d, $J_{C\text{-}F}$ = 3.8 Hz), 116.9 (d, $J_{C\text{-}F}$ = 61.8 Hz), 114.5, 55.7.

4-(Methylthio)benzoyl fluoride[13] (1k, Scheme 1)



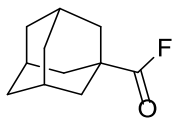
According to the general procedure, the reaction of 4-(methylthio)benzoic acid (841 mg, 5.00 mmol), CH_2Cl_2 (5.00 mL), BAST (1.33 g, 6.00 mmol), after chromatography (5 - 9% EtOAc/ petroleum ether), afforded **1k** as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (m, 2H), 7.29 (m, 2H), 2.53 (s, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 157.3 (d, $J_{C\text{-}F}$ = 341.2 Hz), 149.4, 131.5 (d, $J_{C\text{-}F}$ = 3.8 Hz), 125.1, 120.4 (d, $J_{C\text{-}F}$ = 62.1 Hz), 14.5.

4-(Dimethylamino)benzoyl fluoride[14] (1l, Scheme 1)



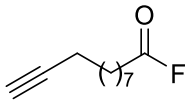
According to the general procedure, the reaction of 4-(dimethylamino)benzoic acid (826 mg, 5.00 mmol), CH_2Cl_2 (5.00 mL), BAST (1.33 g, 6.00 mmol), after chromatography (5 - 9% EtOAc/ petroleum ether), afforded **1l** as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (m, 2H), 6.64 (m, 2H), 3.08 (s, 6H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 158.2 (d, $J_{C\text{-}F}$ = 334.6 Hz), 154.6, 133.4 (d, $J_{C\text{-}F}$ = 4.0 Hz), 111.0, 110.2 (d, $J_{C\text{-}F}$ = 61.1 Hz), 40.0.

(3*r*,5*r*,7*r*)-Adamantane-1-carbonyl fluoride[12] (1m, Scheme 1)



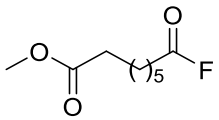
According to the general procedure, the reaction of (3*r*,5*r*,7*r*)-adamantane-1-carboxylic acid (901 mg, 5.00 mmol), CH_2Cl_2 (5.00 mL), BAST (1.33 g, 6.00 mmol), after chromatography (5 - 9% EtOAc/ petroleum ether), afforded **1m** as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.07 (m, 3H), 1.97 (m, 6H), 1.74 (m,6H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 167.1 (d, $J_{C\text{-}F}$ = 373.0 Hz), 40.5 (d, $J_{C\text{-}F}$ = 43.9 Hz), 37.9, 35.8, 27.4.

Undec-10-ynoyl fluoride (1n, Scheme 1)



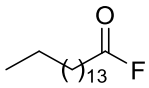
According to the general procedure, the reaction of undec-10-ynoic acid (911 mg, 5.00 mmol), CH_2Cl_2 (5.00 mL), BAST (1.33 g, 6.00 mmol), after chromatography (5 - 9% EtOAc/ petroleum ether), afforded **1n** as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.50 (m, 2H), 2.18 (m, 2H), 1.94 (m, 1H), 1.68 (m, 2H), 1.52 (m, 2H), 1.41 – 1.27 (m, 8H); $^{13}C\{^1H\}$NMR (126 MHz, $CDCl_3$) δ 163.6 (d, $J_{C\text{-}F}$ = 360.4 Hz), 84.6, 68.2, 32.1 (d, $J_{C\text{-}F}$ = 49.7 Hz), 28.9, 28.8, 28.6, 28.6, 28.4, 23.9 (d, $J_{C\text{-}F}$ = 1.26 Hz), 18.4; HRMS (FTMS-ESI) m/z: $[M - H]^-$ (of the carboxylic acid derived from acyl fluoride) calc for $C_{11}H_{17}O_2^-$ 181.1234, found 181.1234.

Methyl 8-fluoro-8-oxooctanoate (1o, Scheme 1)



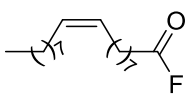
According to the general procedure, the reaction of 8-methoxy-8-oxooctanoic acid (941mg, 5.00 mmol), CH_2Cl_2 (5.00 mL), BAST (1.33 g, 6.00 mmol), after chromatography (5 - 9% EtOAc/ petroleum ether), afforded **1o** as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.67 (s, 3H), 2.51 (t, J = 7.3 Hz, 2H), 2.32 (t, J = 7.5 Hz, 2H), 1.73 – 1.60 (m, 4H), 1.45 – 1.31 (m, 4H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 174.1, 163.5 (d, $J_{C\text{-}F}$ = 360.5 Hz), 51.5, 33.9, 32.0 (d, $J_{C\text{-}F}$ = 50.0 Hz), 28.6, 28.3, 24.6, 23.7; HRMS (FTMS-ESI) m/z: $[M - H]^-$ (of the carboxylic acid derived from acyl fluoride) calc for $C_9H_{15}O_4^-$ 187.0976, found 187.0982.

Palmitoyl fluoride[12] (1p, Scheme 1)



According to the general procedure, the reaction of palmitic acid (1.28 g, 5.00 mmol), CH_2Cl_2 (5.00 mL), BAST (1.33 g, 6.00 mmol), after chromatography (5 - 9% EtOAc/ petroleum ether), afforded **1p** as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.49 (t, J = 7.4 Hz, 2H), 1.67 (m, 2H), 1.38 – 1.24 (m, 24H), 0.88 (t, J = 6.6 Hz, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 163.6 (d, $J_{C\text{-}F}$ = 360.4 Hz), 32.2 (d, $J_{C\text{-}F}$ = 40.7 Hz), 32.0, 29.8 (×6), 29.5 (×2), 29.2, 28.8, 24.0, 22.8, 14.2.

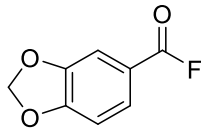
Oleoyl fluoride (1q, Scheme 1)



According to the general procedure, the reaction of oleic acid (1.41 g, 5.00 mmol), CH_2Cl_2 (5.00 mL), BAST (1.33 g, 6.00 mmol), after chromatography (5 - 9% EtOAc/ petroleum ether), afforded **1q** as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.39 – 5.30 (m, 2H), 2.50 (t, J =

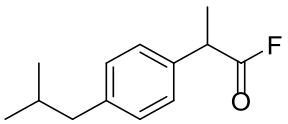
7.4 Hz, 2H), 2.09 – 1.91 (m, 4H), 1.68 (p, J = 7.3 Hz, 2H), 1.42 – 1.18 (m, 20H), 0.88 (t, J = 6.7 Hz, 3H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 163.7 (d, $J_{C\text{-}F}$ = 360.6 Hz), 130.2, 129.7, 32.2 (d, $J_{C\text{-}F}$ = 50.0 Hz), 32.0, 29.9, 29.7, 29.6, 29.4 (×2), 29.1 (×2), 28.8, 27.3, 27.2, 24.0 (d, $J_{C\text{-}F}$ = 1.3 Hz), 22.8, 14.2; HRMS (FTMS-ESI) m/z: $[M - H]^-$ (of the carboxylic acid derived from acyl fluoride) calc for $C_{18}H_{33}O_2^-$ 281.2486, found 281.2494.

Benzo[*d*][1,3]dioxole-5-carbonyl fluoride[15] (1r Scheme 1)



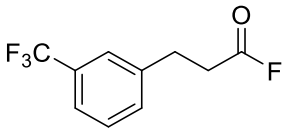
According to the general procedure, the reaction of benzo[*d*][1,3]dioxole-5-carboxylic acid (831 mg, 5.00 mmol), CH_2Cl_2 (5.00 mL), BAST (1.33 g, 6.00 mmol), after chromatography (5 - 9% EtOAc/ petroleum ether), afforded **1r** as a white solid. ^1H NMR (500 MHz, $CDCl_3$) δ 7.67 (m, 1H), 7.41 (m, 1H), 6.90 (m, 1H), 6.10 (s, 2H); $^{13}C\{^1H\}$ NMR (126MHz, $CDCl_3$) δ 156.9 (d, $J_{C\text{-}F}$ = 340.1 Hz), 153.8, 148.4, 128.3 (d, $J_{C\text{-}F}$ = 4.4 Hz), 118.4 (d, $J_{C\text{-}F}$ = 62.2 Hz), 110.7 (d, $J_{C\text{-}F}$ = 4.4 Hz), 108.7, 102.5.

2-(4-Isobutylphenyl)propanoyl fluoride[14] (1s, Scheme 1)



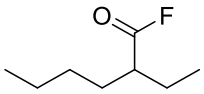
According to the general procedure, the reaction of 2-(4-isobutylphenyl)propanoic acid (1.03 g, 5.00 mmol), CH_2Cl_2 (5.00 mL), BAST (1.33 g, 6.00 mmol), after chromatography (5 - 9% EtOAc/ petroleum ether), afforded **1s** as a colorless oil. ^1H NMR (500 MHz, $CDCl_3$) δ 7.20 (m, 2H), 7.14 (m, 2H), 3.84 (m, 1H), 2.47 (m, 2H), 1.85 (m, 1H), 1.58 (m, 3H), 0.90 (m, 6H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 164.5 (d, $J_{C\text{-}F}$ = 367.0 Hz), 141.7, 134.7, 129.8, 127.3, 45.1, 44.0 (d, $J_{C\text{-}F}$ = 49.1 Hz), 30.2, 22.4, 18.1.

3-(3-(Trifluoromethyl)phenyl)propanoyl fluoride (1t, Scheme 1)



According to the general procedure, the reaction of 3-(3-(trifluoromethyl)phenyl)propanoic acid (1.09 g, 5.00 mmol), CH_2Cl_2 (5.00 mL), BAST (1.33 g, 6.00 mmol), after chromatography (5 - 9% EtOAc/ petroleum ether), afforded **1t** as a colorless oil. ^1H NMR (400 MHz, $CDCl_3$) δ 7.52 (m, 1H), 7.47 (m, 1H), 7.45 – 7.39 (m, 2H), 3.06 (t, J = 7.5 Hz, 2H), 2.86 (t, J = 7.5 Hz, 2H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 162.5 (d, $J_{C\text{-}F}$ = 360.2 Hz), 139.8, 131.8, 131.2 (q, $J_{C\text{-}F}$ = 32.4 Hz), 129.4, 125.1 (q, $J_{C\text{-}F}$ = 3.8 Hz), 124.1 (q, $J_{C\text{-}F}$ = 272.7 Hz), 123.9 (q, $J_{C\text{-}F}$ = 3.7 Hz), 33.6 (d, $J_{C\text{-}F}$ = 51.5 Hz), 29.8 (d, $J_{C\text{-}F}$ = 2.9 Hz); HRMS (FTMS-ESI) m/z: $[M - H]^-$ (of the carboxylic acid derived from acyl fluoride) calc for $C_{10}H_8F_3O_2^-$ 217.0482, found 217.0488.

2-Ethylhexanoyl fluoride[16] (1u, Scheme 1)



According to the general procedure, the reaction of 2-ethylhexanoic acid (721 mg, 5.00 mmol), CH_2Cl_2 (5.00 mL), BAST (1.33 g, 6.00 mmol), after chromatography (5 - 9% EtOAc/ petroleum ether), afforded **1u** as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.46 (m, 1H), 1.76 – 1.60 (m, 4H), 1.38 – 1.29 (m, 4H), 0.97 (m, 3H), 0.91 (m, 3H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 165.8 (d, $J_{C\text{-}F}$ = 369.5 Hz), 46.0 (d, $J_{C\text{-}F}$ = 44.7 Hz), 30.6, 29.3, 24.4, 22.5, 13.9, 11.5.

5. Computational Details

Computational Methods. All calculations of the solution phase electrochemical redox potentials were performed using Gaussian 09 suite of programs according to the procedure described by Nicewicz et al. (Roth, H. G.; Romero, N. A.; Nicewicz, D. A. *Synlett* **2016**, *27*, 714) at the B3LYP/6-311++G(d,p) and B3LYP/6-311++G(d,p)+QZVP level of theory. All of the optimized geometries were verified as minima (no imaginary frequencies). Previous studies have shown that this method gives an excellent agreement with the published data for available compounds (Shi, S.; Lalancette, R.; Szostak, R.; Szostak, M. *Chem. Eur. J.* **2016**, *22*, 11949; Shi, S.; Szostak, R.; Szostak, M. *Org. Biomol. Chem.* **2016**, *14*, 9151 and references cited therein). Studies on the determination of the redox potential of Sm(II) reductants have been published (Dahleń, A.; Nilsson, A.; Hilmersson, G. *J. Org. Chem.* **2006**, *71*, 1576; Szostak, M.; Spain, M.; Procter, D. J. *J. Org. Chem.* **2014**, *79*, 2522 and references cited therein). Note that the established accuracy in experimentally measured redox potentials due to solvent effects is ±0.1 V (Bard, A. J. *Encyclopedia of Electrochemistry of the Elements*, Marcel Dekker, 1978; Bard, A. J.; Faulkner, L. R. *Electrochemical Methods: Fundamentals and Applications*, Wiley, 2000). For selected monographs, see: Vanysek, P. *CRC Handbook of Chemistry and Physics*,

CRC Press, 2000; Bard, A. J. *Encyclopedia of Electrochemistry of the Elements*, Marcel Dekker, 1978.

Full Reference for Gaussian 09

Gaussian 09, Revision D.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, M. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2009.

Table SI-1. *Redox Potentials of Compounds **SI-1-SI-11** vs. SCE in CH_3CN Calculated at the B3LYP/6-311++G(d,p) Level.*[a]

Entry	Compound	Entry	G° (neutral)	G° (ketyl radical)	$DG°_{1/2}$ [kcal/mol]	$E°_{1/2}$ [V]
1	PhCHO	**SI-1**	-345.597605	-345.695655	-61.55	-1.75
2	PhCOF	**SI-2**	-444.900051	-445.001153	-63.46	-1.67
3	PhCOCl	**SI-3**	-805.246540	-805.357003	-69.34	-1.42
4	PhCOBr	**SI-4**	-2919.168282	-2919.282476	-71.68	-1.31
5	PhCHO	**SI-1**	-345.599397	-345.697456	-61.55	-3.83
6	PhCOF	**SI-2**	-345.592259	-345.614142	-13.74	-3.70
7	PhCOCl	**SI-3**	-444.910680	-444.937281	-16.70	-3.40
8	PhCOBr	**SI-4**	-805.257224	-805.294869	-23.63	-3.27
9	PhCOI	**SI-5**	-2919.252123	-2919.294529	-26.62	-3.16
10	MeCOF	**SI-6**	-253.164766	-253.242401	-48.73	-2.31
11	*t*-BuCOF	**SI-7**	-371.058462	-371.134777	-47.90	-2.34
12	CF_3COF	**SI-8**	-550.983489	-551.100578	-73.50	-1.23
13	PhCOMe	**SI-9**	-384.905288	-384.996967	-57.55	-1.93
14	MeCHO	**SI-10**	-153.858517	-153.925210	-41.86	-2.61
15	MeCOMe	**SI-11**	-193.169706	-193.229377	-37.46	-2.80

[a] $DG°_{1/2}$ = G°(ketyl radical) – G°(neutral). See Roth, H. G.; Romero, N. A.; Nicewicz, D. A. *Synlett* **2016**, *27*, 714 for details. The accuracy is approximately ± 0.1 V due to solvent effects. Entries 1-4, 10-15: B3LYP/6-311++G(d,p), CH_3CN; Entries 5-9: B3LYP/6-311++G(d,p)+QZVP, in vacuum. Redox potentials of compounds SI-9, SI-10 and SI-11 have been previously reported (Shi, S.; Szostak, R.; Szostak, M. *Org. Biomol. Chem.* **2016**, *14*, 9151 and references cited therein).

Additional Discussion. In addition to compounds shown in Figure 1 in the main manuscript, we have also determined redox potentials of the corresponding trifluoromethyl derivatives, CF_3COX (Table SI-2). Structures of all compounds **SI-1-SI-15** are shown in Chart SI-1 below.

While the reduction potential of the corresponding benzoyl chloride and benzoyl bromide was determined in CH_3CN (*Synlett* **2016**, *27*, 714), we found that under these conditions (CH_3CN) the corresponding iodide, PhCOI underwent dissociation of the ketyl radical to release iodide anion. Furthermore, in the case of less stabilized a-aliphatic derivatives (alkyl vs. benzyl) even the corresponding acyl bromides and acyl chlorides (e.g. MeCOBr, MeCOCl) underwent dissociation of bromide and chloride anions from their corresponding ketyl radicals, consistent with the high instability of the ketyl radicals.

Interestingly, we found that all a-trifluoromethyl CF_3COX derivatives (X = H, F, Cl, Br, I) are stable and characterized by a significantly lower redox potential than benzoyl halides (CF_3CHO, $E_{1/2}$ = -1.28 V vs. SCE in CH_3CN vs. PhCHO, $E_{1/2}$ = -1.75 V vs. SCE in CH_3CN; CF_3COF, $E_{1/2}$ = -1.29 V vs. SCE in CH_3CN vs. PhCOF, $E_{1/2}$ = -1.70 V vs. SCE in CH_3CN; CF_3COCl, $E_{1/2}$ = -0.95 V vs. SCE in CH_3CN vs. PhCOCl, $E_{1/2}$ = -1.46 V vs. SCE in CH_3CN; CF_3COBr, $E_{1/2}$ = -0.77 V vs. SCE in CH_3CN vs. PhCOBr, $E_{1/2}$ = -1.37 V vs. SCE in CH_3CN; CF_3COI, $E_{1/2}$ = -0.71 V vs. SCE in CH_3CN vs. PhCOI, $E_{1/2}$ = -1.30 V vs. SCE in CH_3CN, approximated value) (Chart SI-2). This finding allows to further support the observed correlation with respect to the reduction potentials in the series PhCOX (X = H, F, Cl, Br, I) (Chart SI-3 and Chart SI-4). Furthermore, these findings indicate the relative order of the stability of ketyl radicals with respect to the a-stabilizing group: CF_3 > Ph > alkyl. Thus, our study strongly suggests that acyl fluorides should behave as privileged acid halide precursors for the generation of ketyl type radicals (X = F vs. Cl, Br, I) for synthetic applications, including reductions, reductive cyclizations and tandem reductive couplings.

Further studies on the investigation of carboxylic acid derivatives to facilitate electron transfer to the carbonyl group are underway in our laboratories and will be reported in due course.

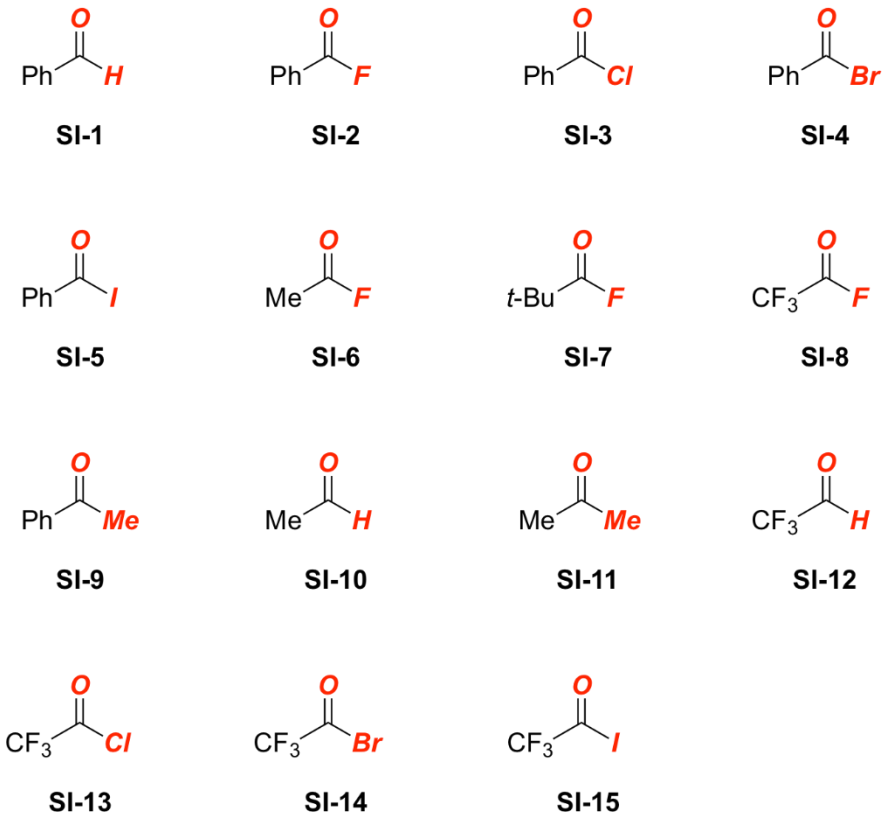


Chart SI-1. *Structures of Esters **SI-1-SI-15** used for Determination of Redox Potentials at the B3LYP/6-311++G(d,p) Level.*

Table SI-2. *Redox Potentials of Compounds* ***SI-8, SI-12-SI-15*** *vs. SCE in CH_3CN Calculated at the B3LYP/6-311++G(d,p)+QZVP Level.*[a]

Entry	Compound	Entry	G° (neutral)	G° (ketyl radical)	$DG°_{1/2}$ [kcal/mol]	$E°_{1/2}$ [V]
1	CF_3CHO	**SI-12**	-451.692407	-451.807932	-72.52	-1.28
2	CF_3COF	**SI-8**	-551.001763	-551.116751	-72.18	-1.29
3	CF_3COCl	**SI-13**	-911.351053	-911.478507	-80.00	-0.95
4	CF_3COBr	**SI-14**	-3025.345608	-3025.479897	-84.29	-0.77
5	CF_3COI	**SI-15**	-748.912177	-749.048379	-85.50	-0.71

[a]$DG°_{1/2}$ = G°(ketyl radical) – G°(neutral). See Roth, H. G.; Romero, N. A.; Nicewicz, D. A. *Synlett* **2016**, *27*, 714 for details. The accuracy is approximately ± 0.1 V due to solvent effects (Shi, S.; Szostak, R.; Szostak, M. *Org. Biomol. Chem.* **2016**, *14*, 9151 and references cited therein).

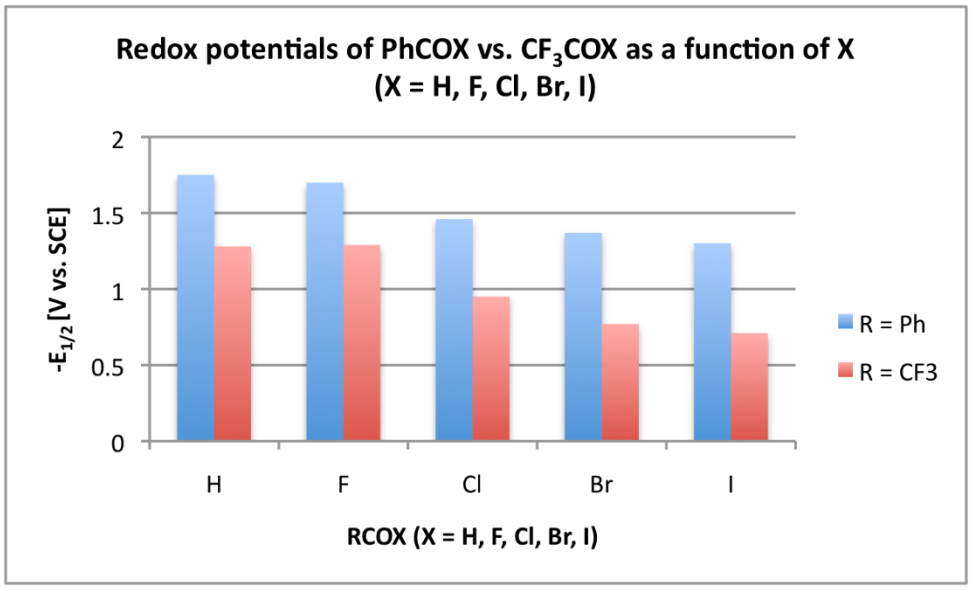


Chart SI-2. *Redox Potentials of PhCOX (X = H, F, Br, Cl) in CH_3CN vs. CF_3COX (X = H, F, Br, Cl) in CH_3CN at B3LYP/6-311++G(d,p)+QZVP.*

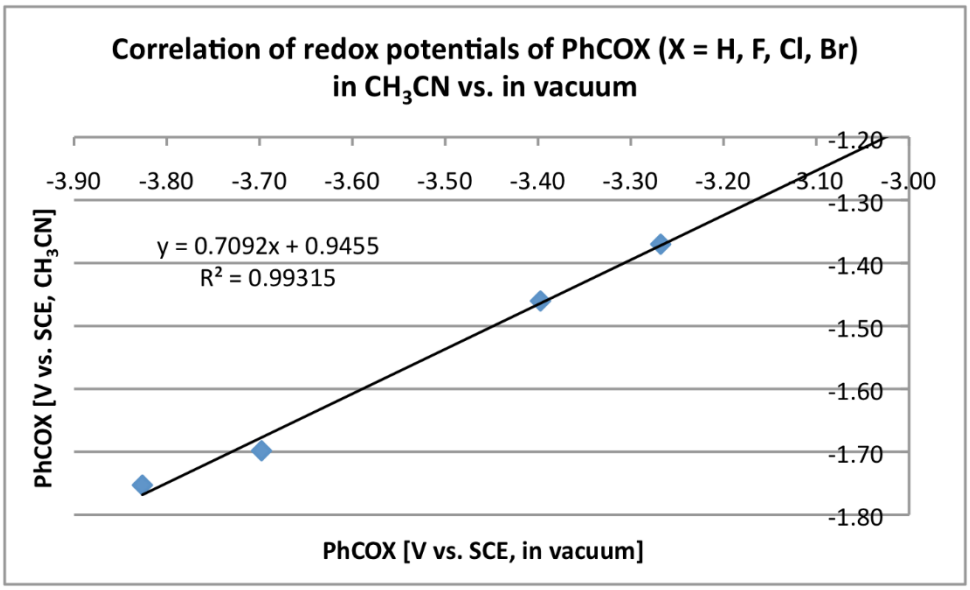


Chart SI-3. *Correlation of Redox Potentials of PhCOX (X = H, F, Br, Cl) in CH3CN vs. in Vacuum Calculated at B3LYP/6-311++G(d,p)+QZVP (Y = 0.71X + 0.95, R^2 = 0.993). PhCOI, $E_{1/2}$ = -1.2946 V vs. SCE.*

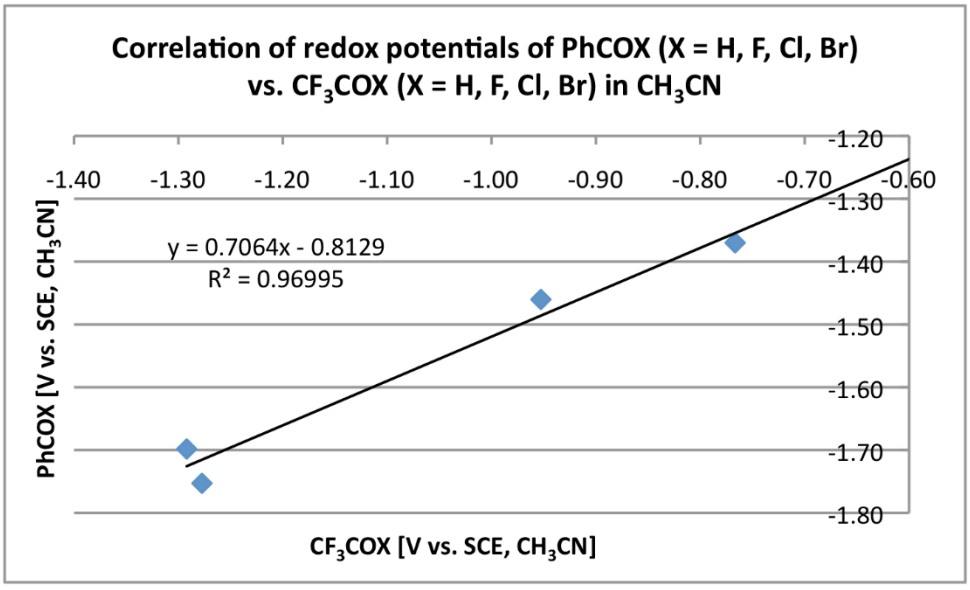


Chart SI-4. *Correlation of Redox Potentials of PhCOX (X = H, F, Br, Cl) in CH_3CN vs. CF_3COX (X = H, F, Br, Cl) in CH_3CN at B3LYP/6-311++G(d,p)+QZVP (Y = 0.71X - 0.81, R^2 = 0.970). PhCOI, $E_{1/2}$ = -1.3180 V vs. SCE.*

6. References

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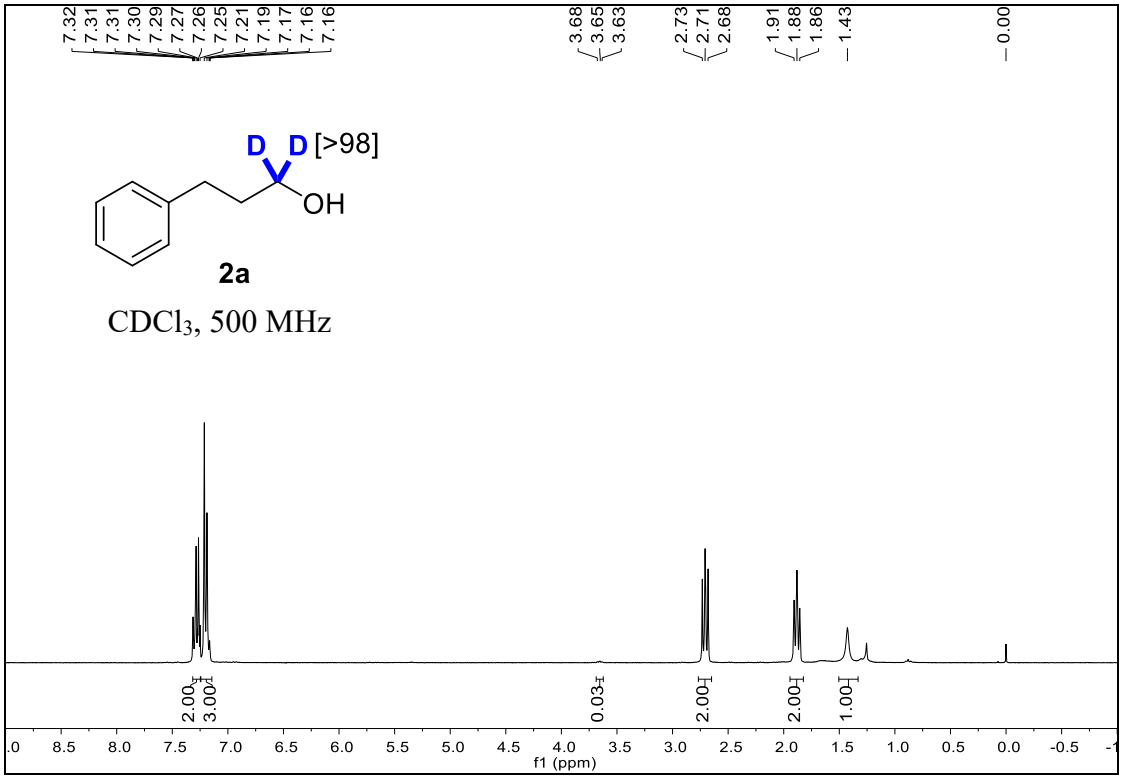
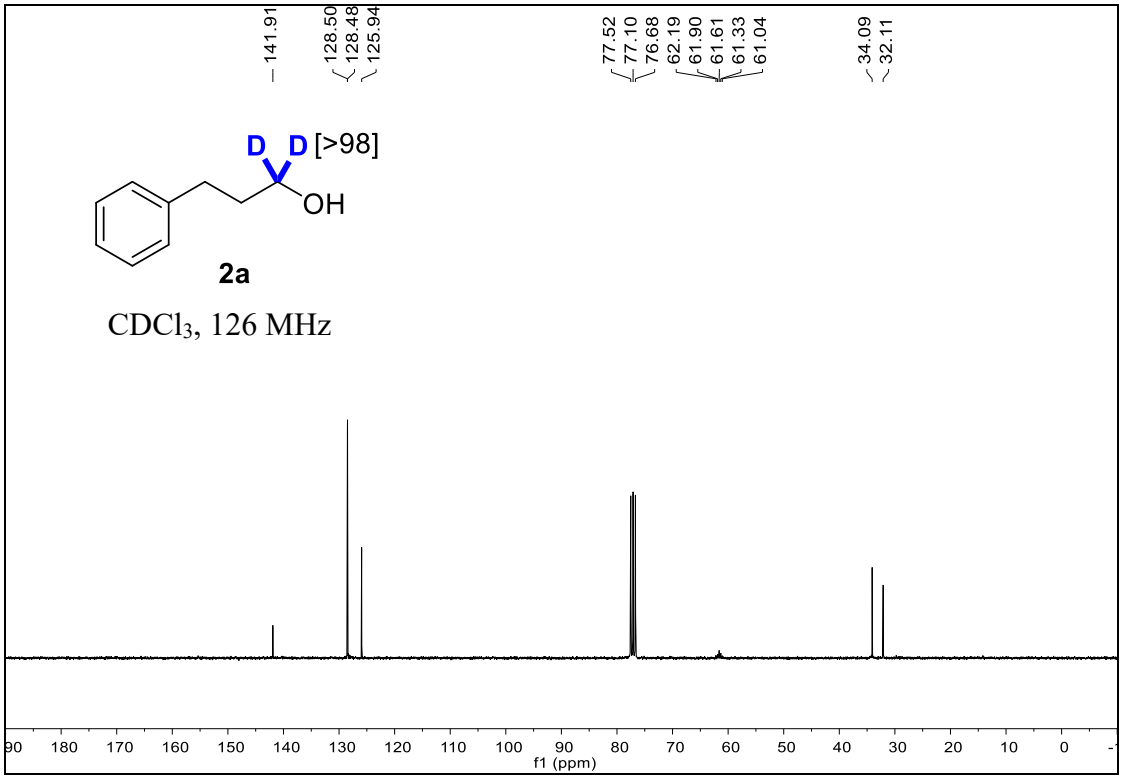
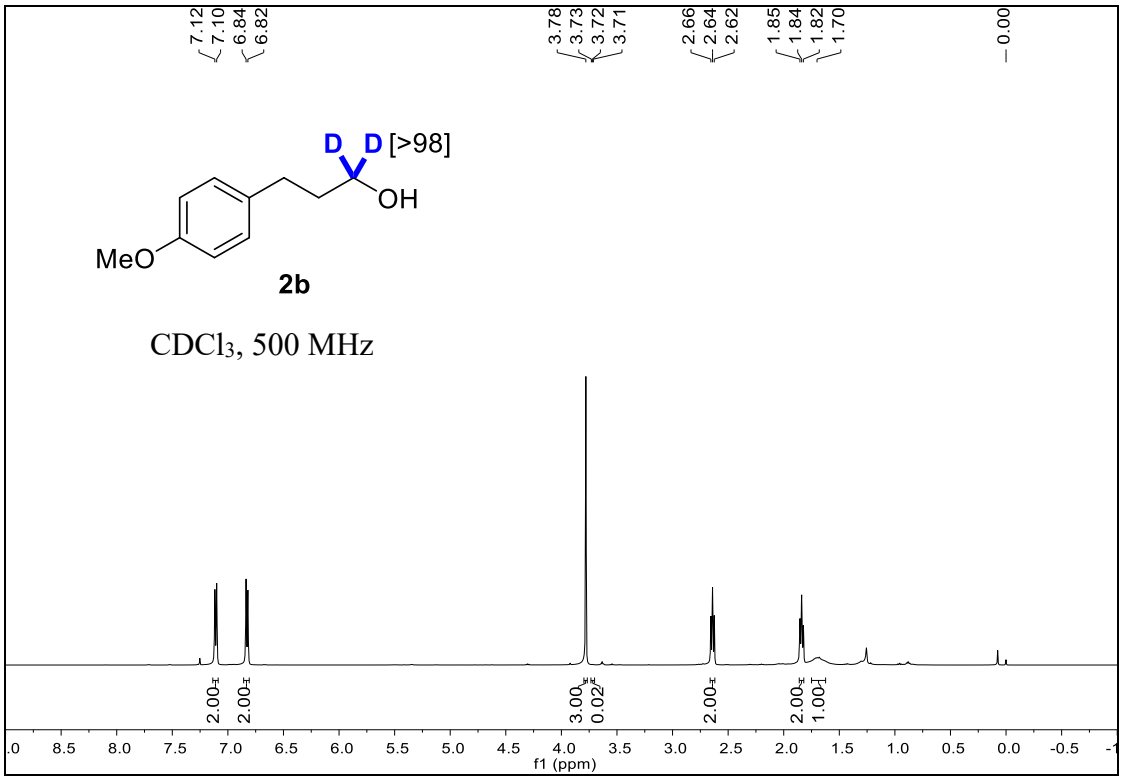
(16) Commercially available from Chemieliva Pharmaceutical.

7. ^{1}H and ^{13}C NMR Spectra of Products



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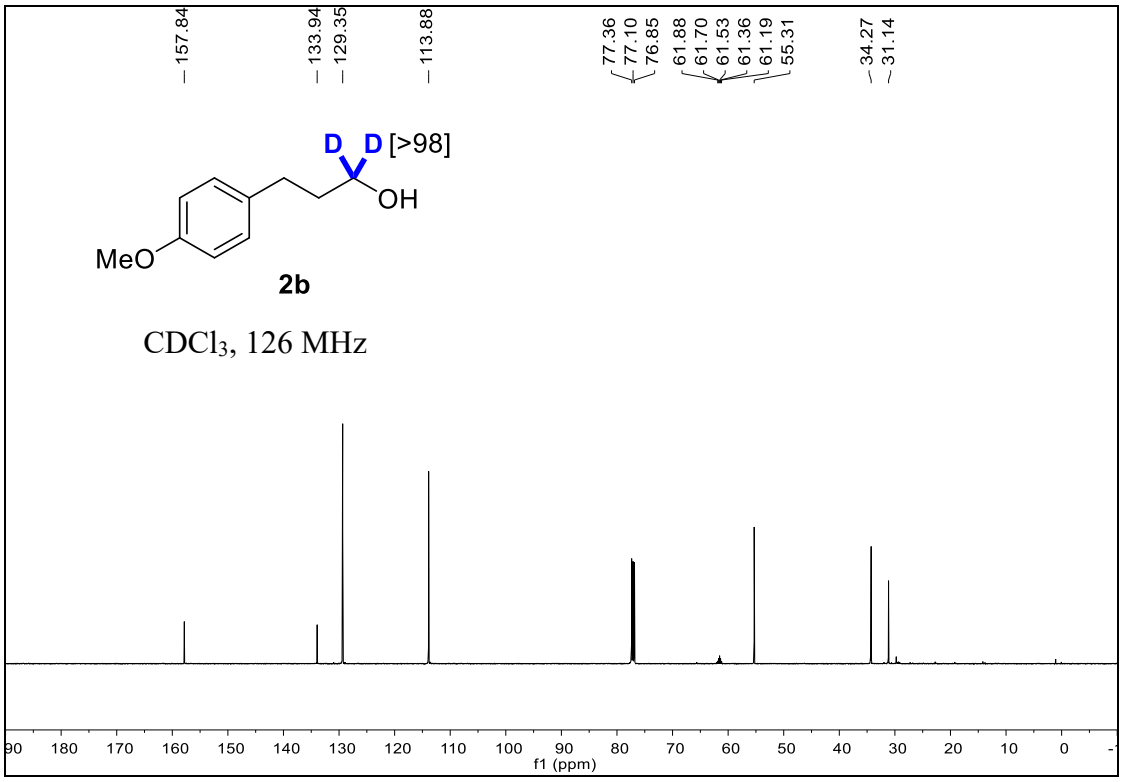
f1 (ppm)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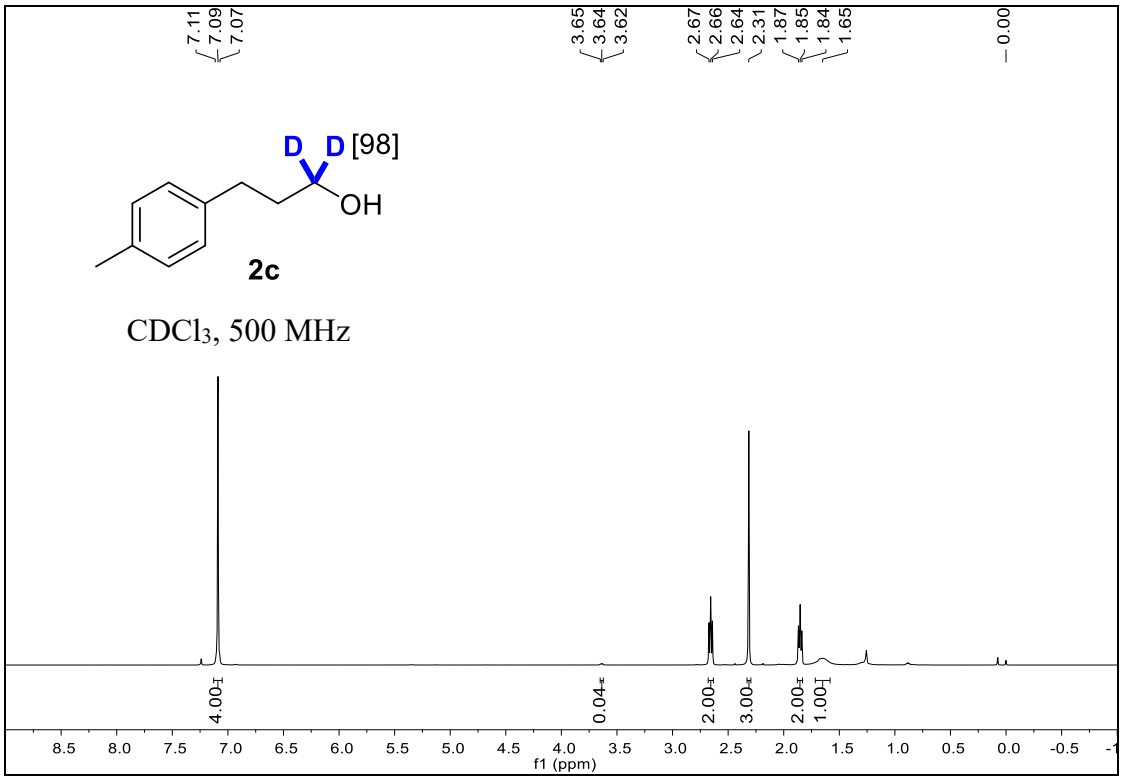
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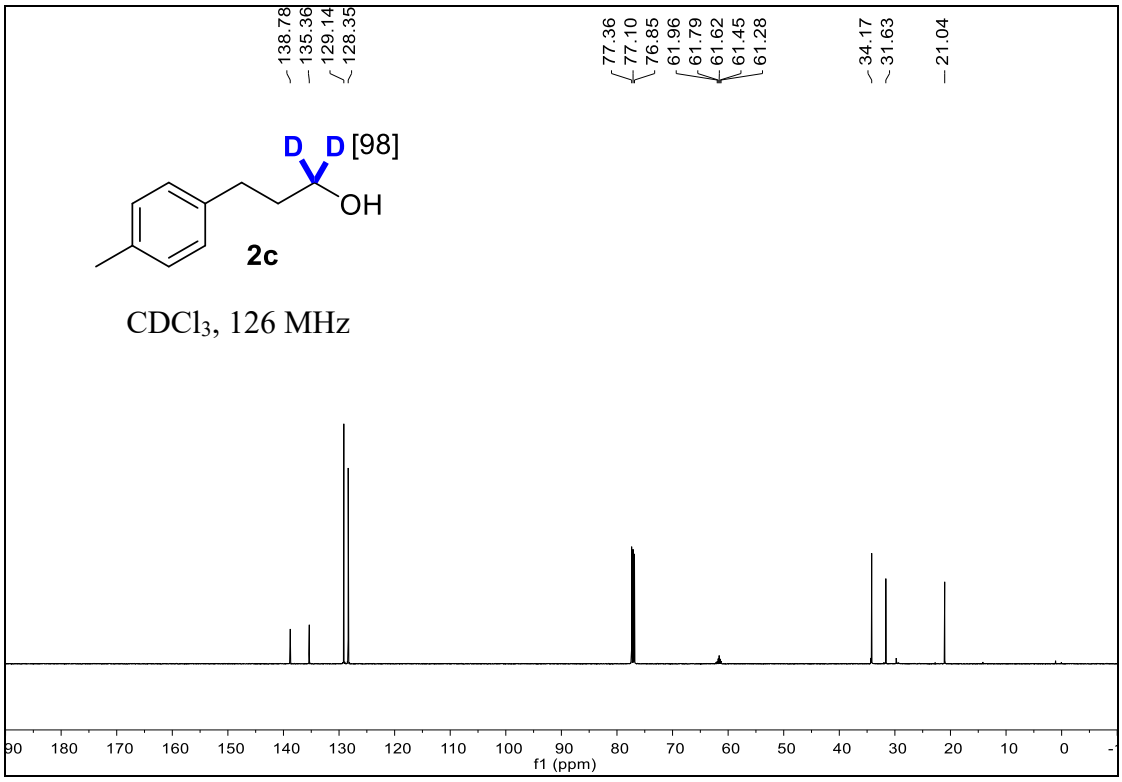
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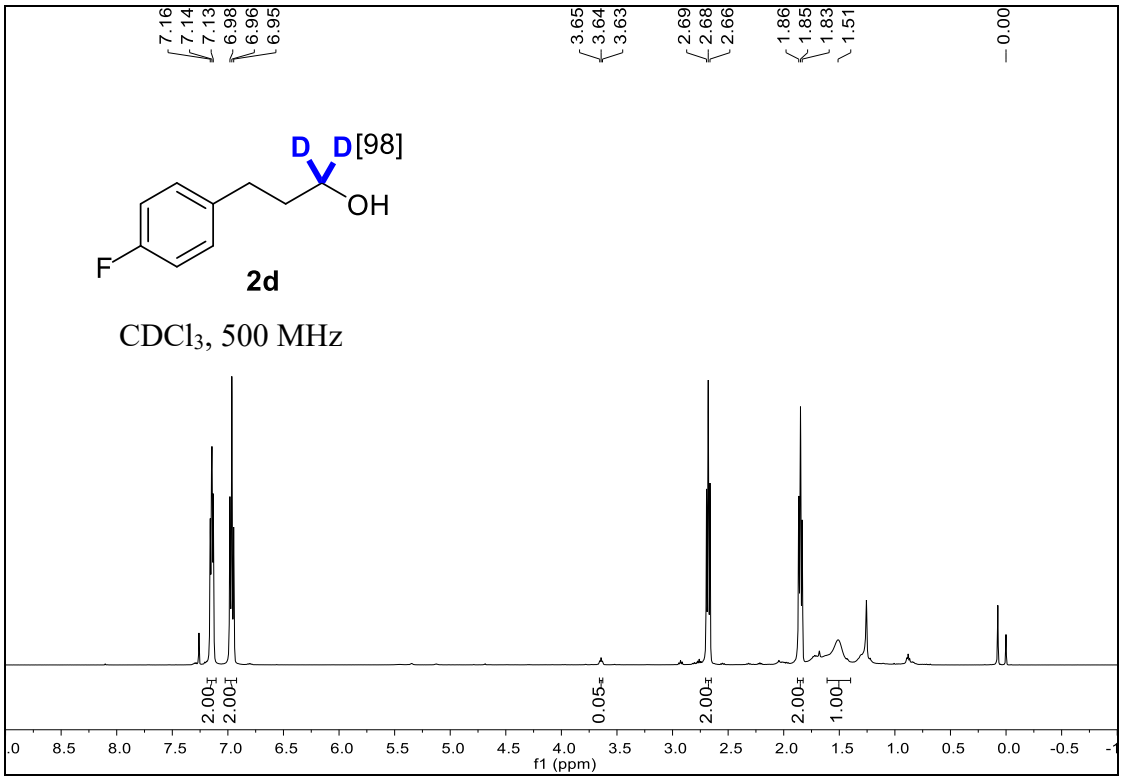
OH
2c
CDCl3, 126 MHz
f1 (ppm)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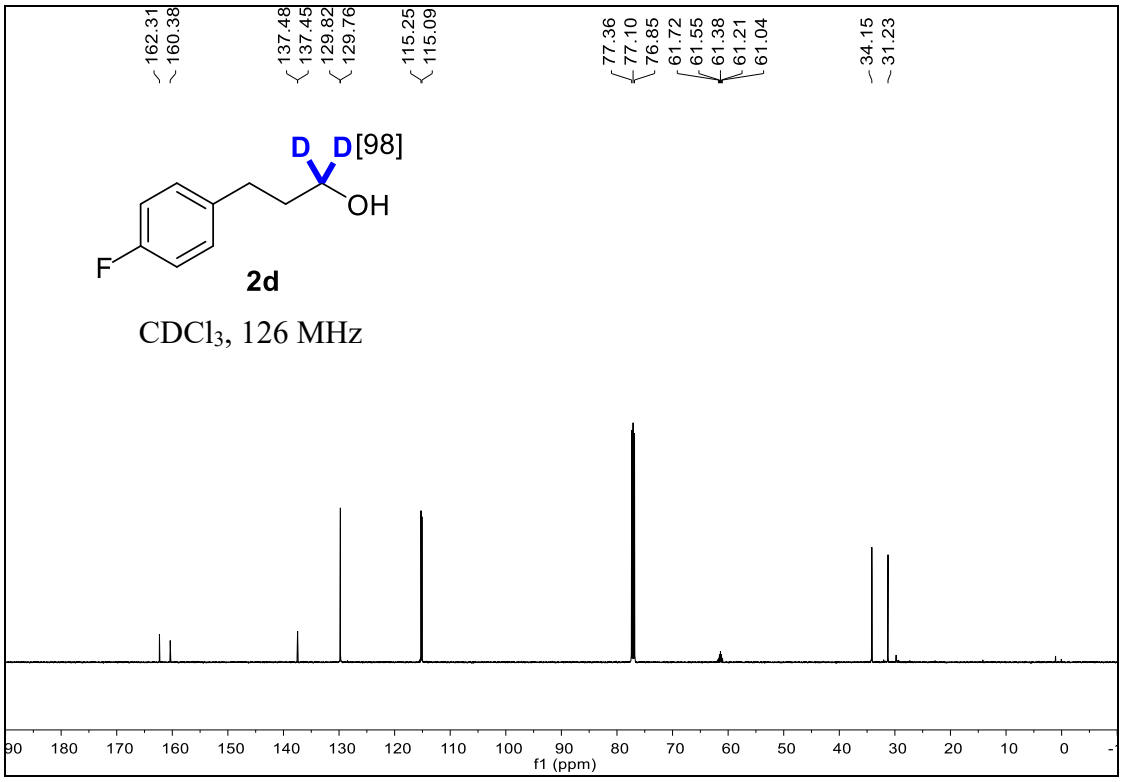
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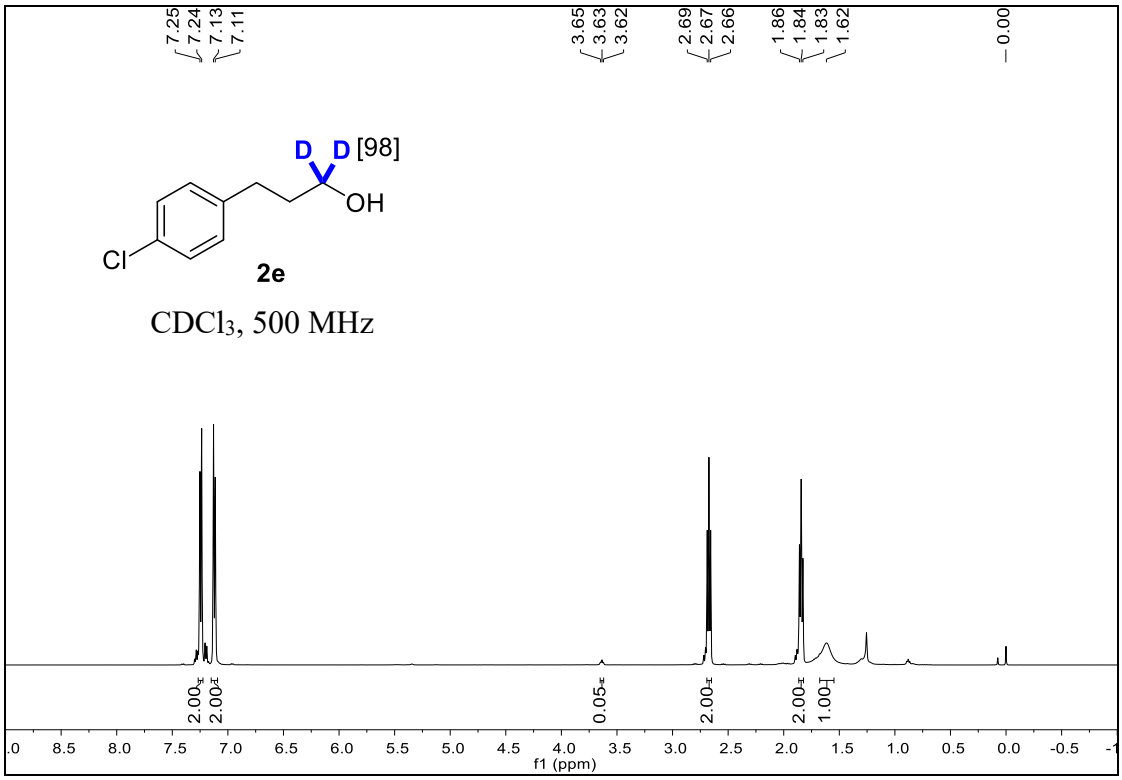
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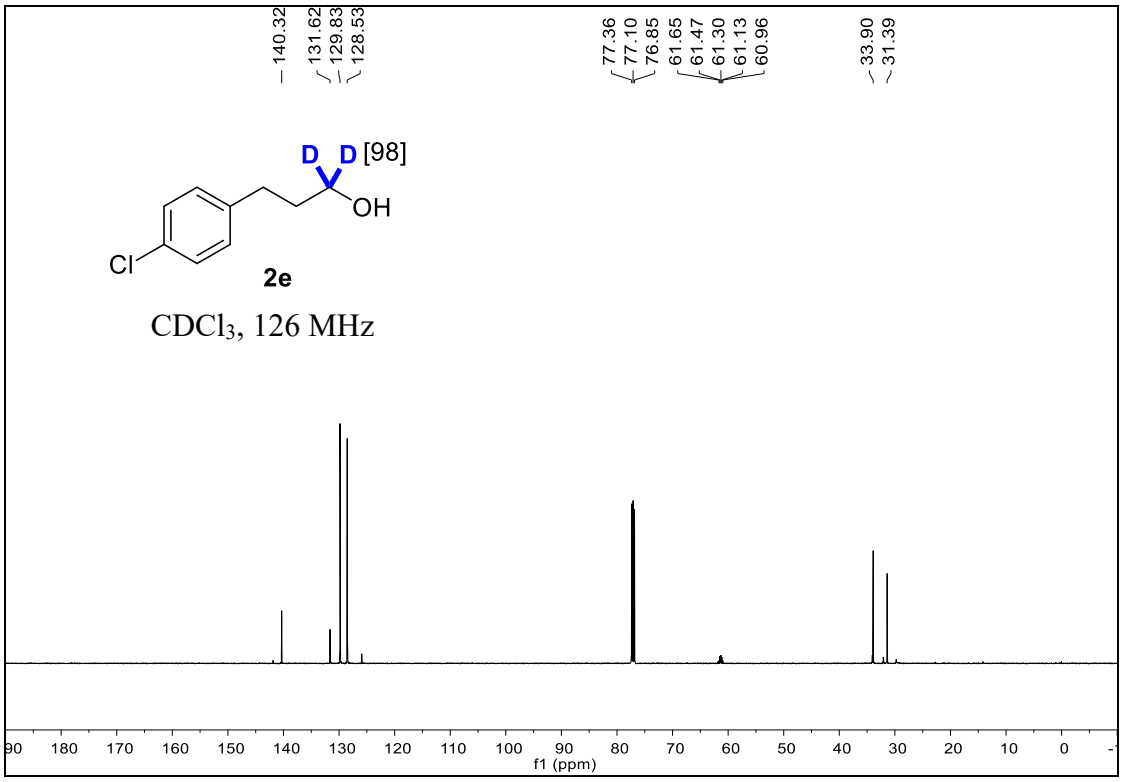
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CDCl3, 126 MHz
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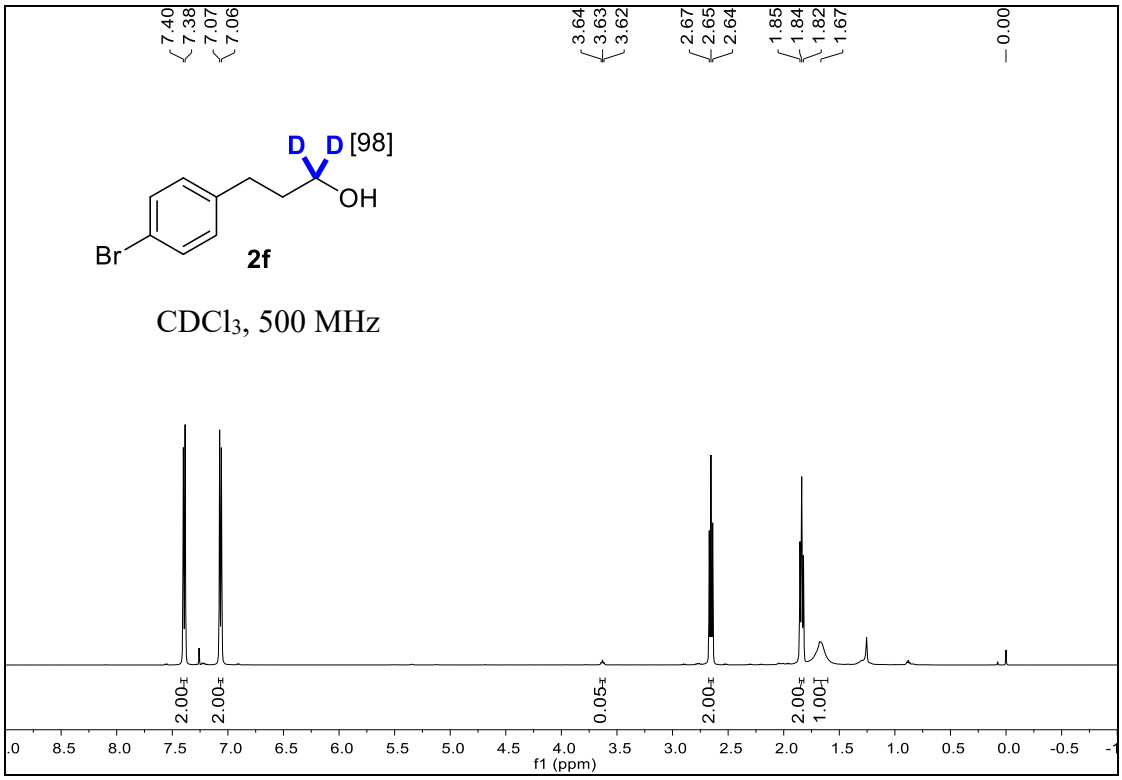
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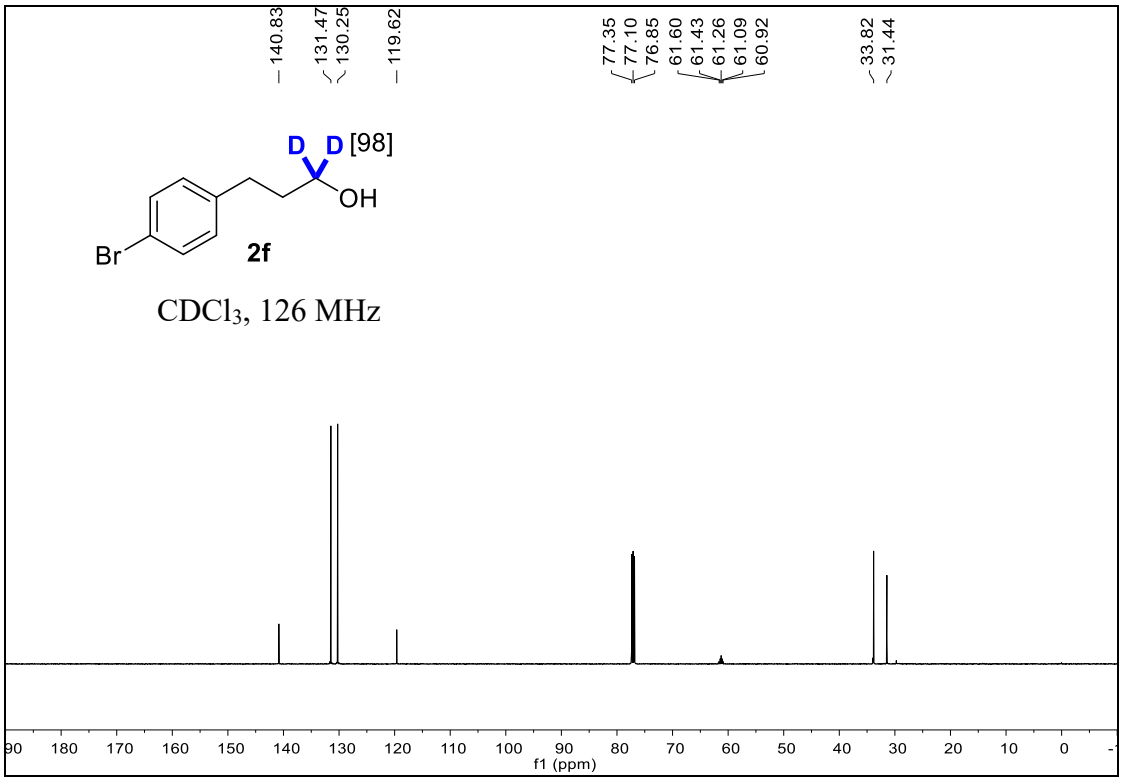
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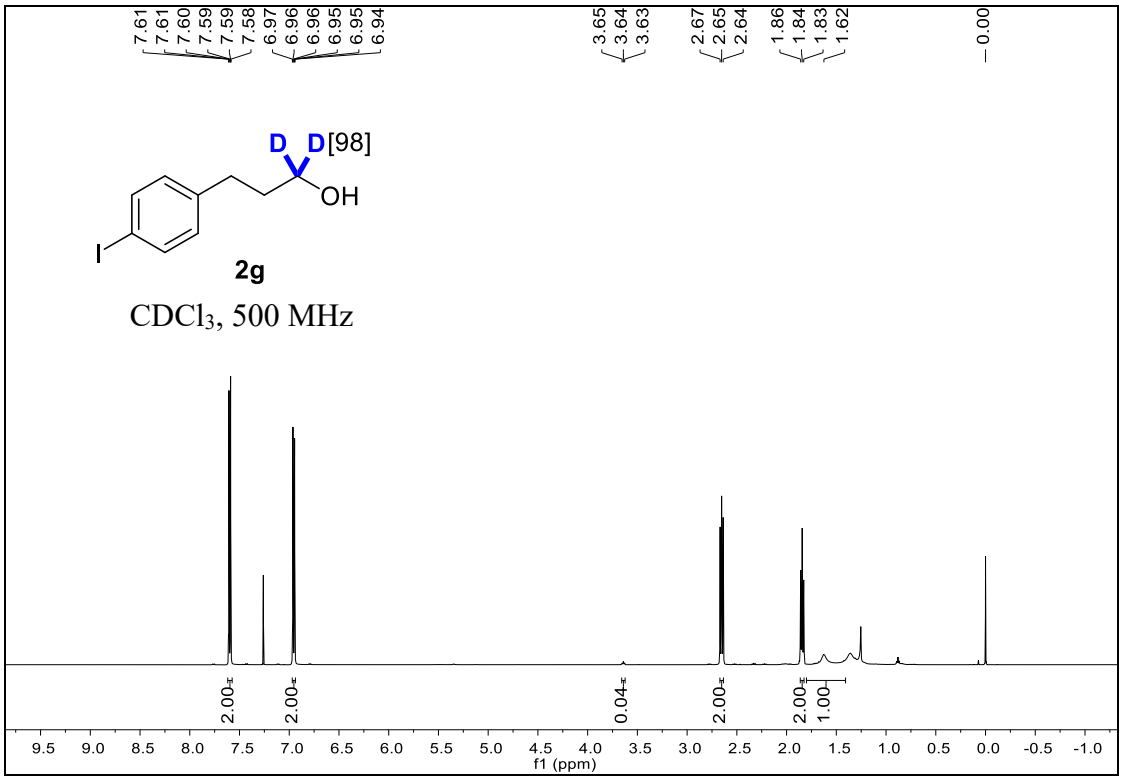
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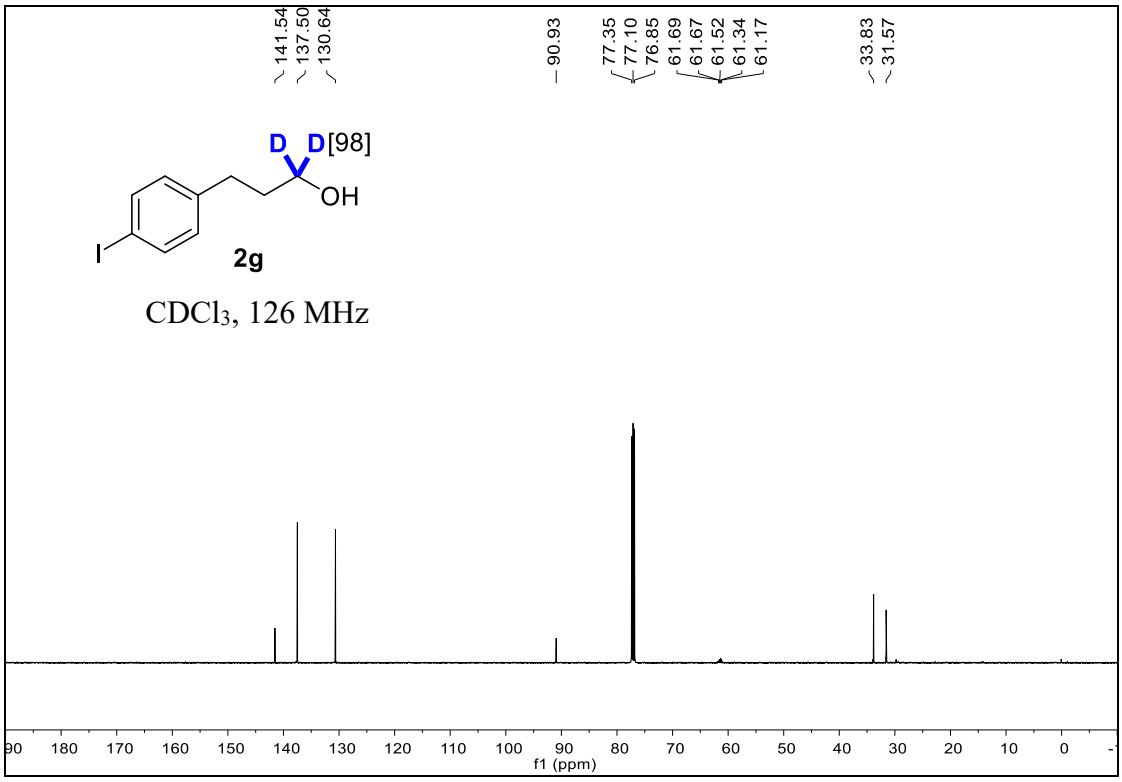
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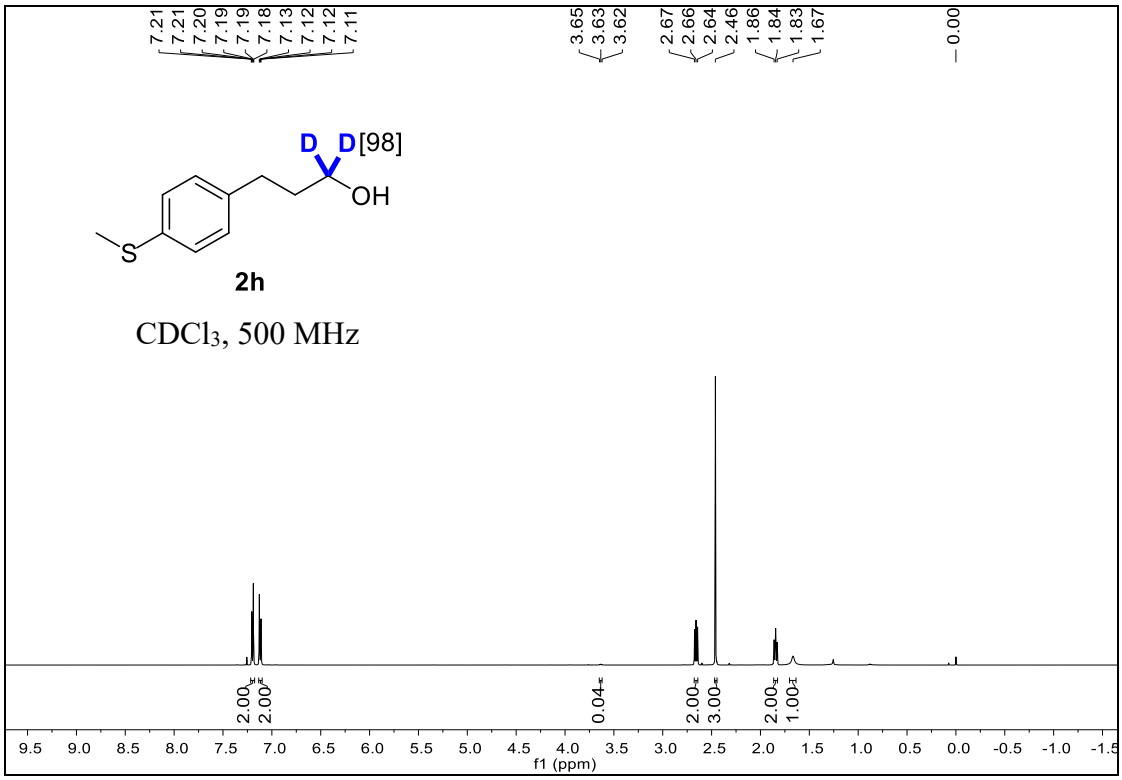
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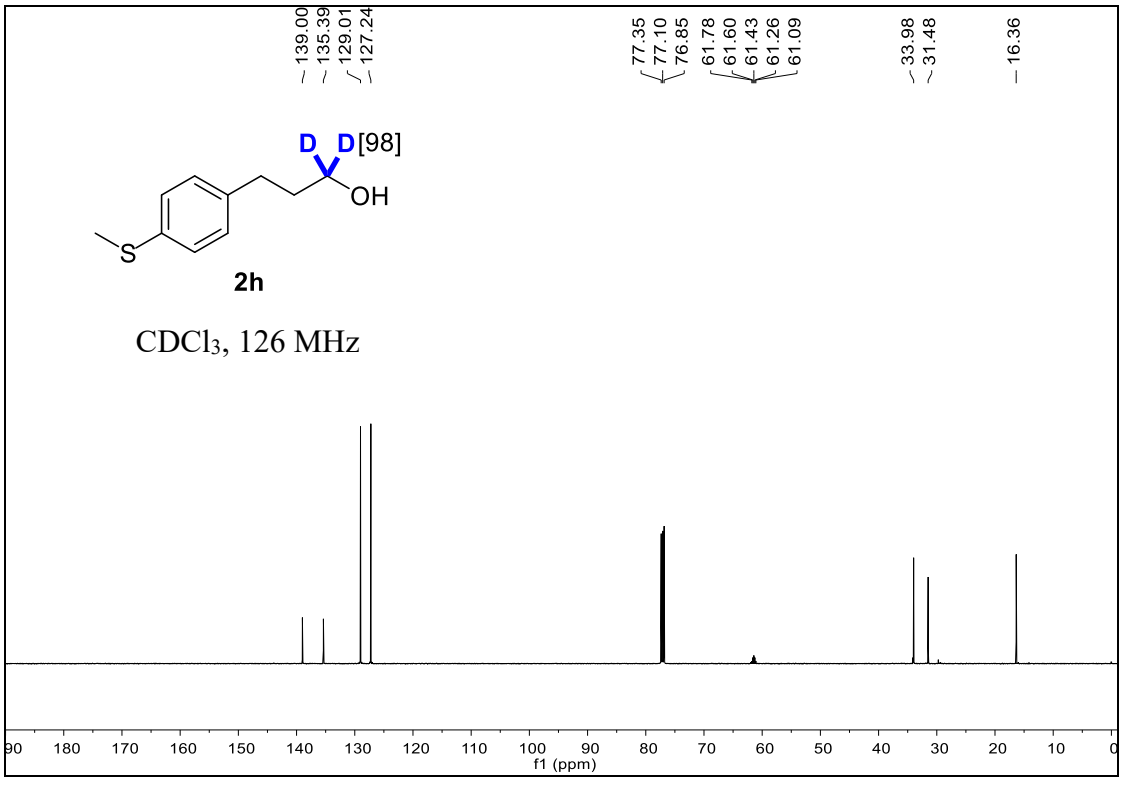
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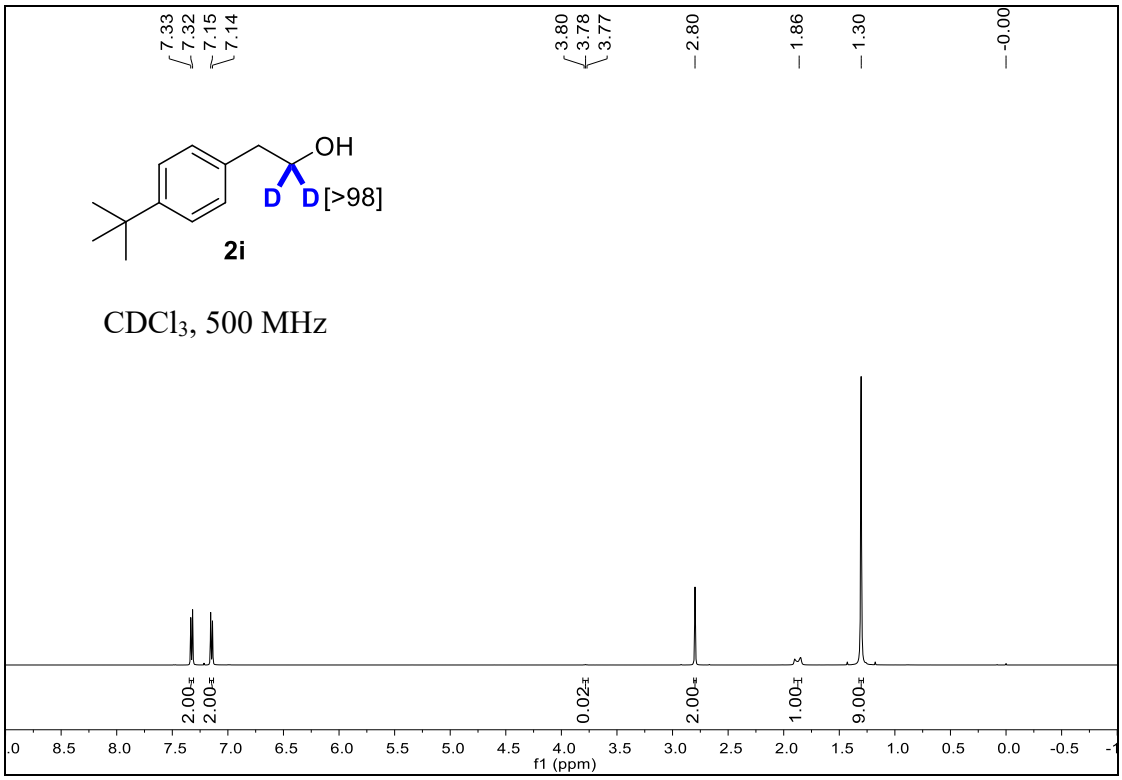
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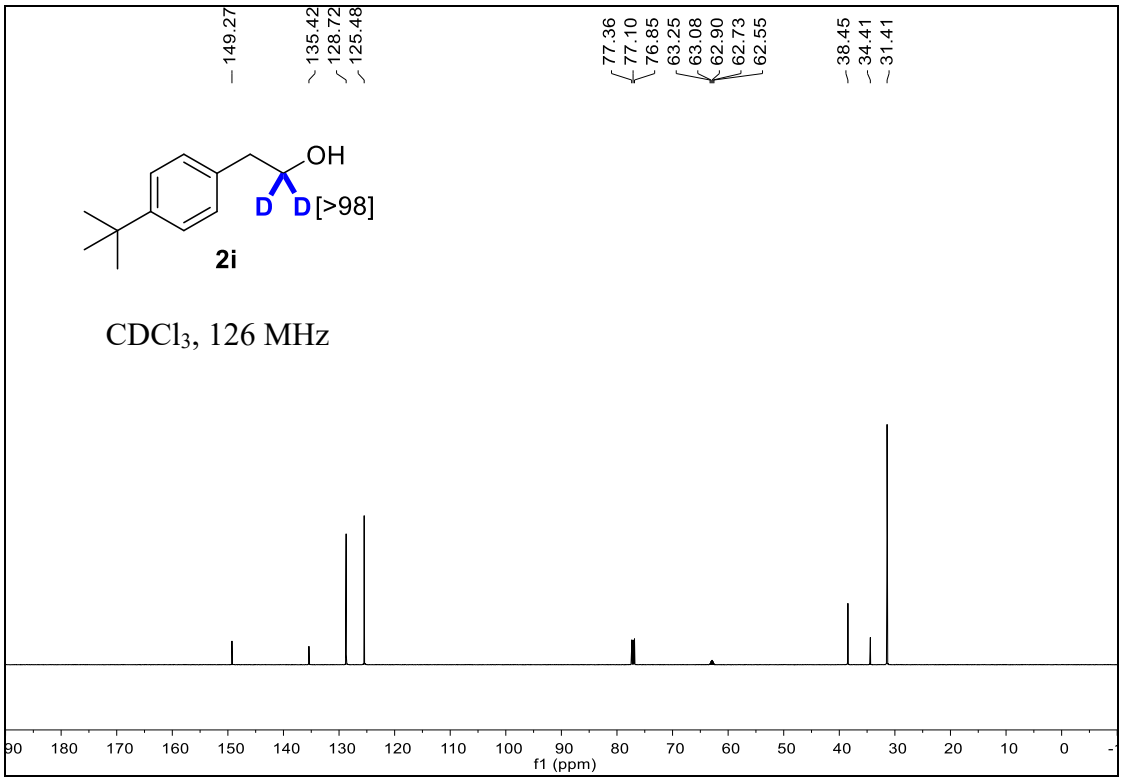
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2i
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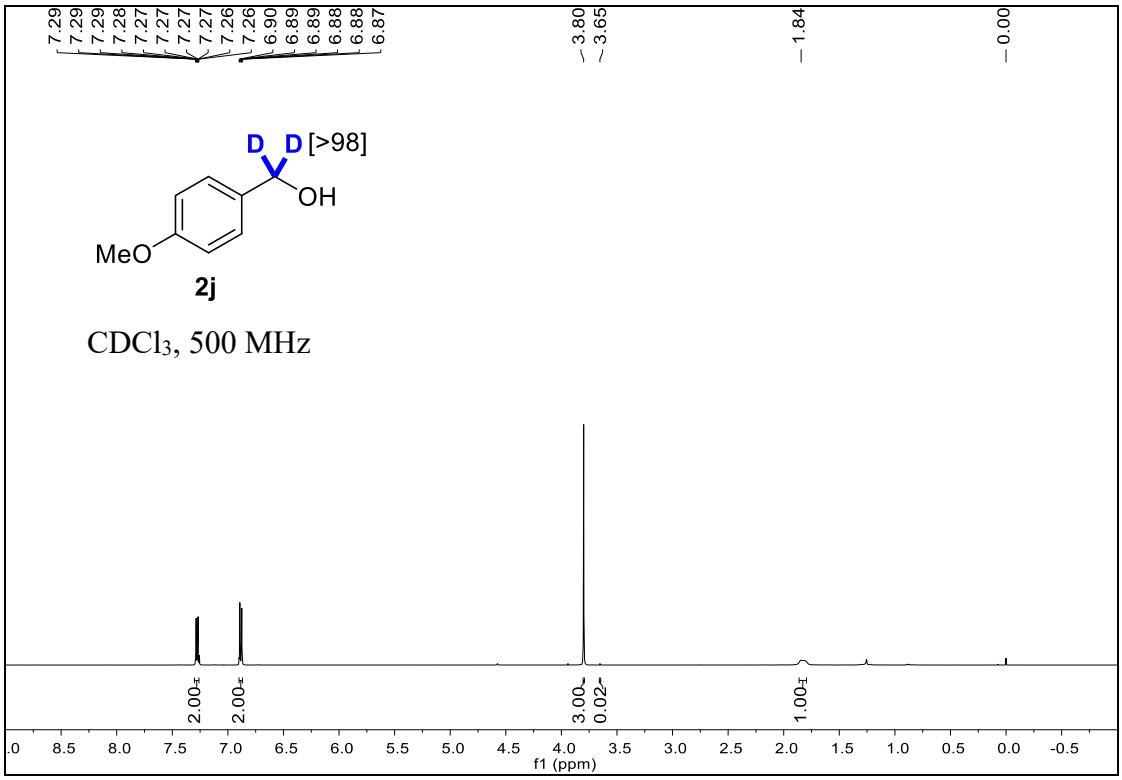
f1 (ppm)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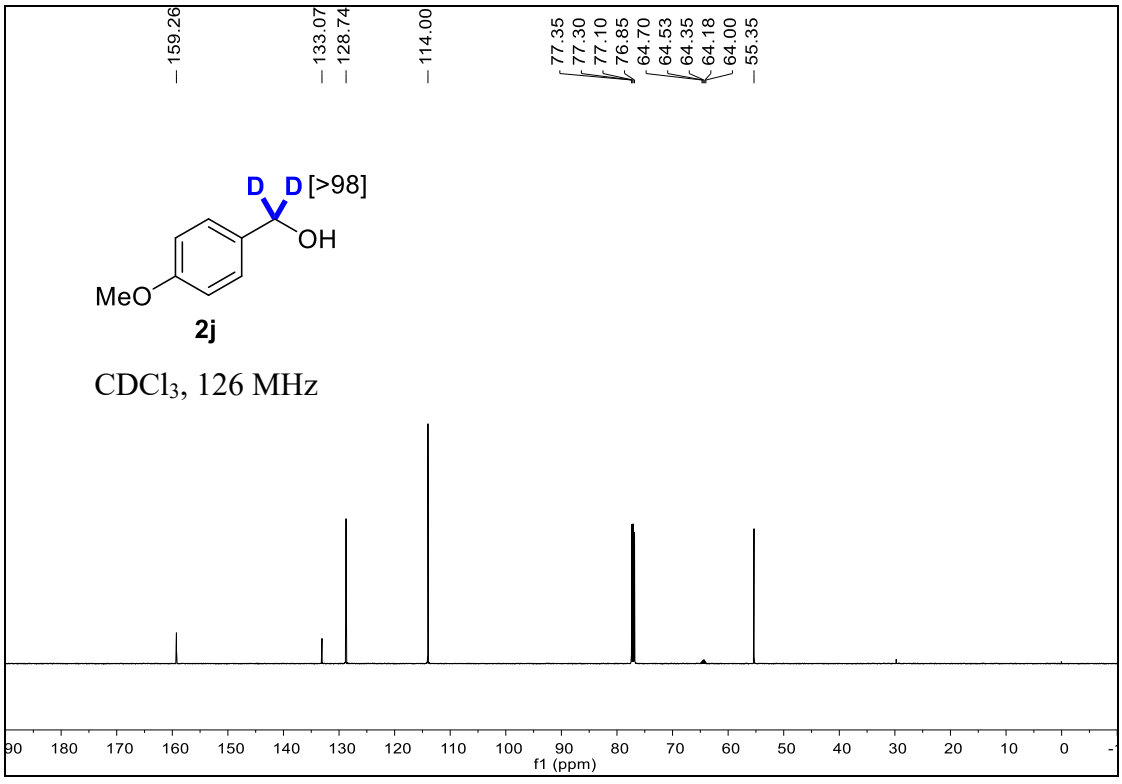
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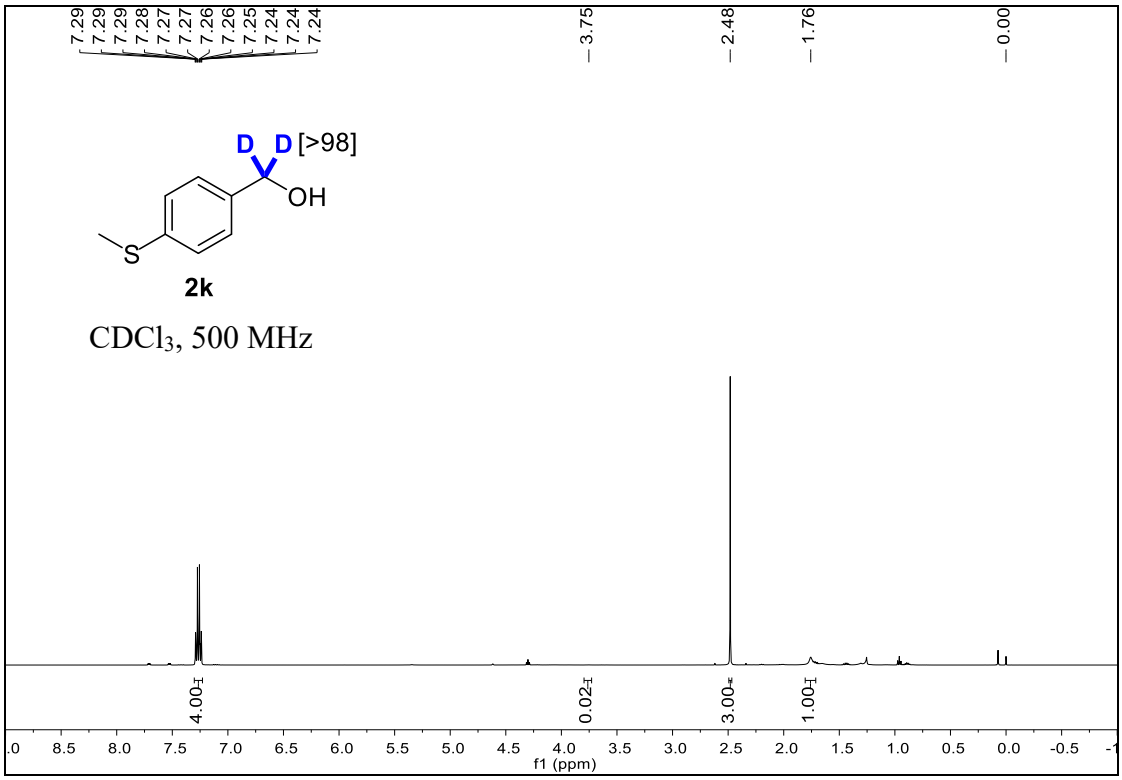
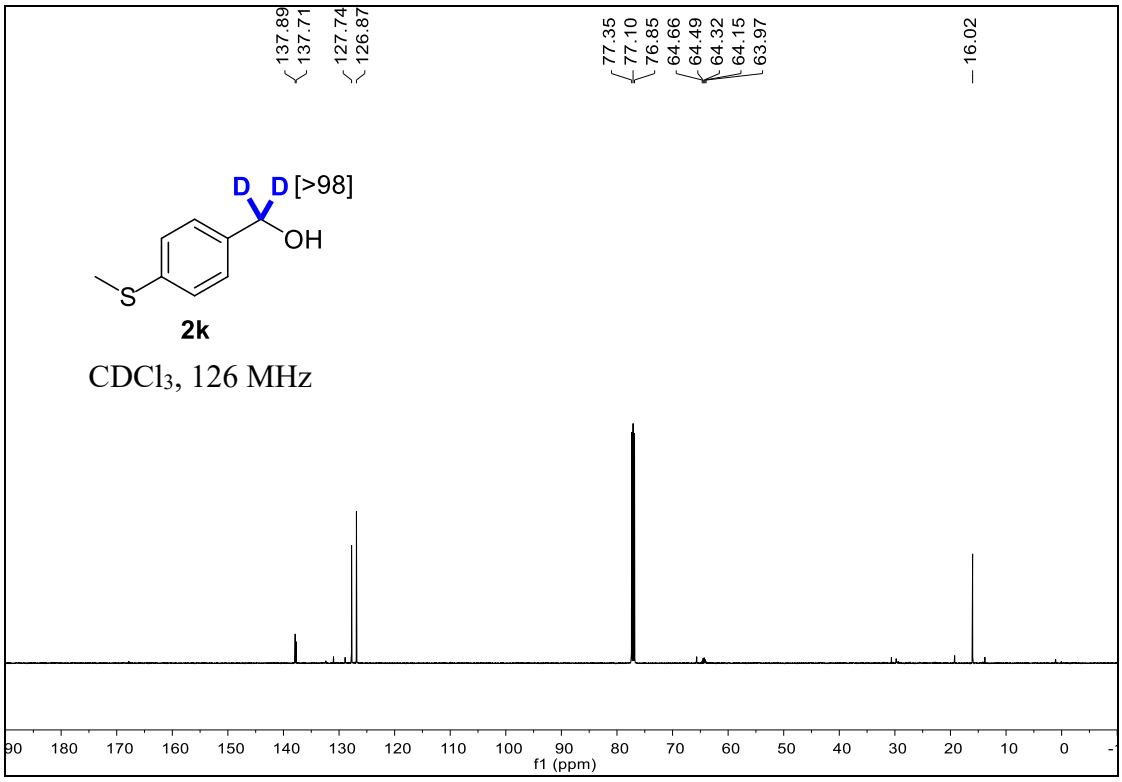
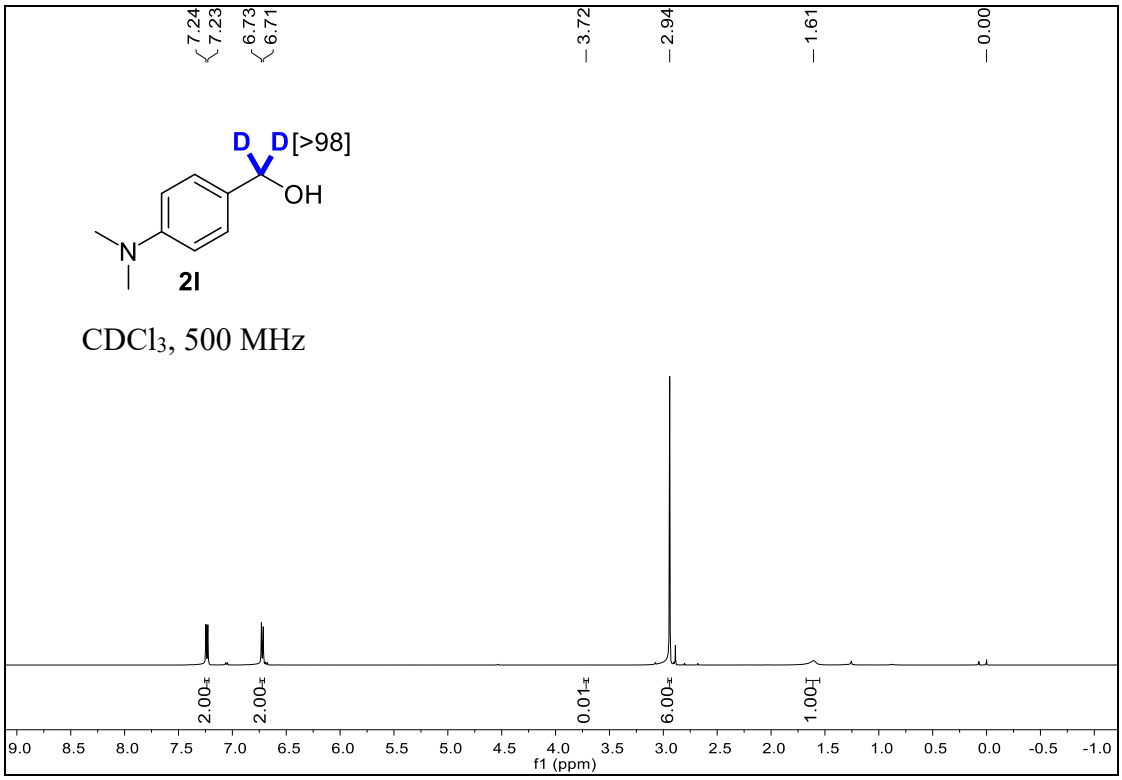
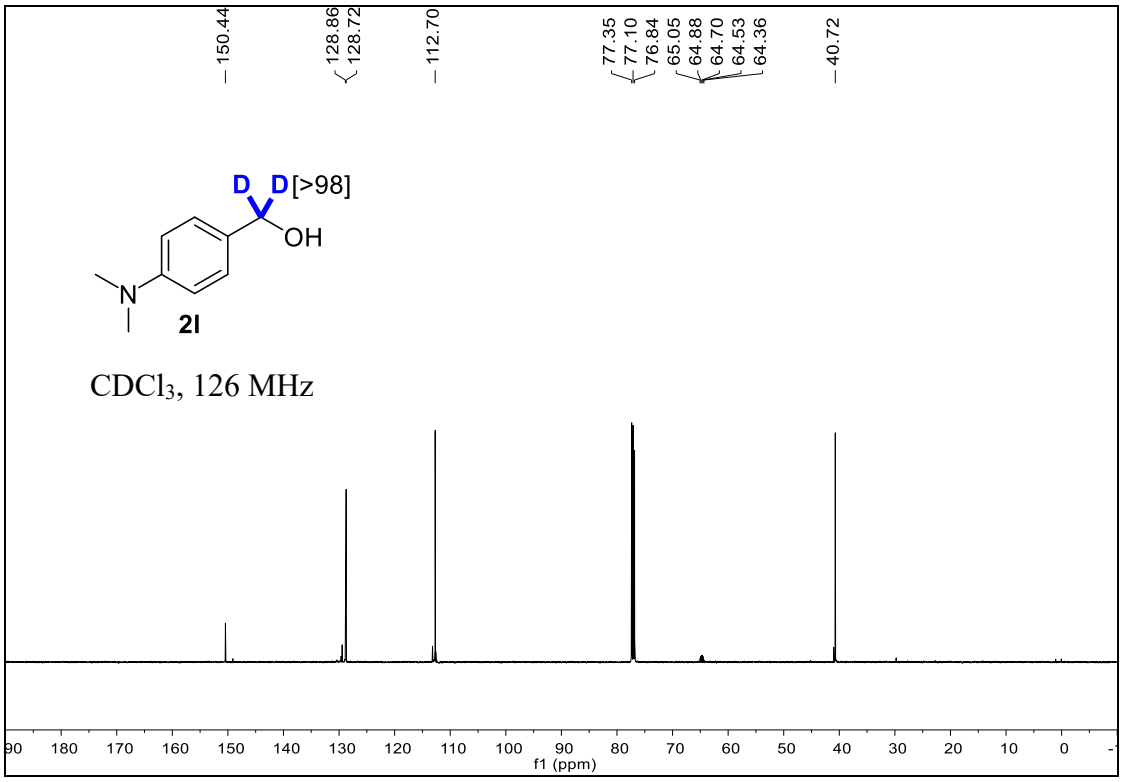
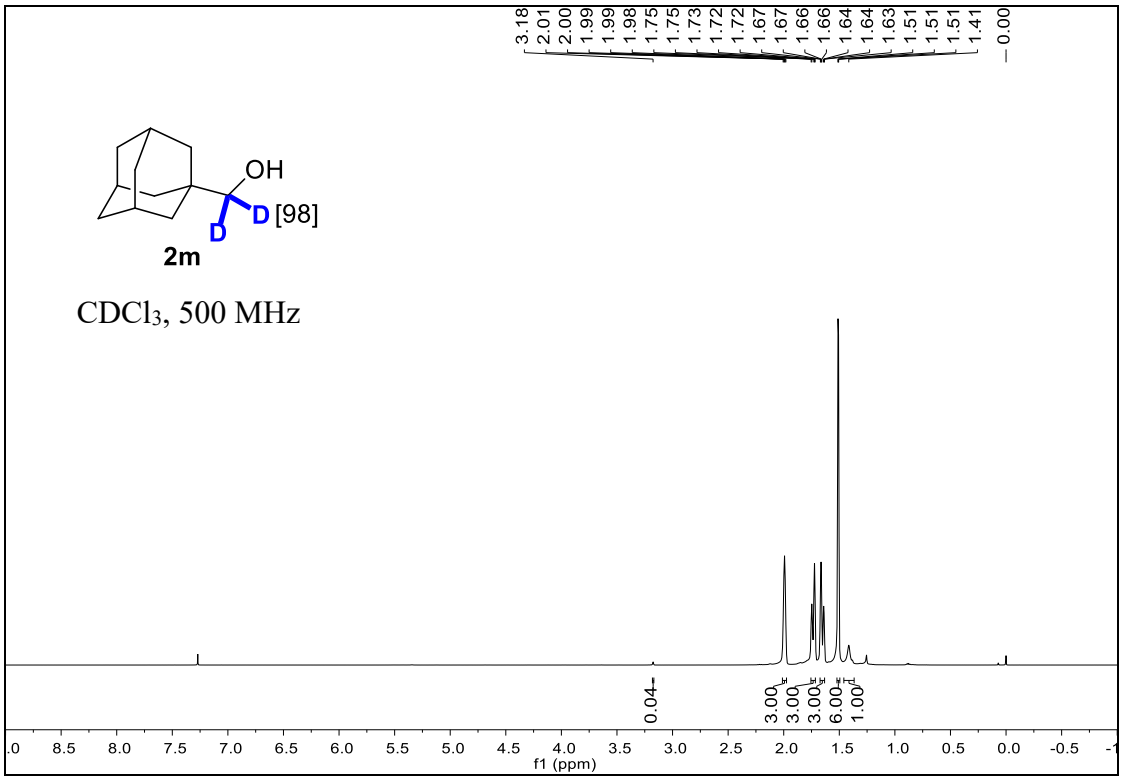
64.00
55.35
D D [>98]
OH
MeO
2j
CDCl3, 126 MHz
f1 (ppm)

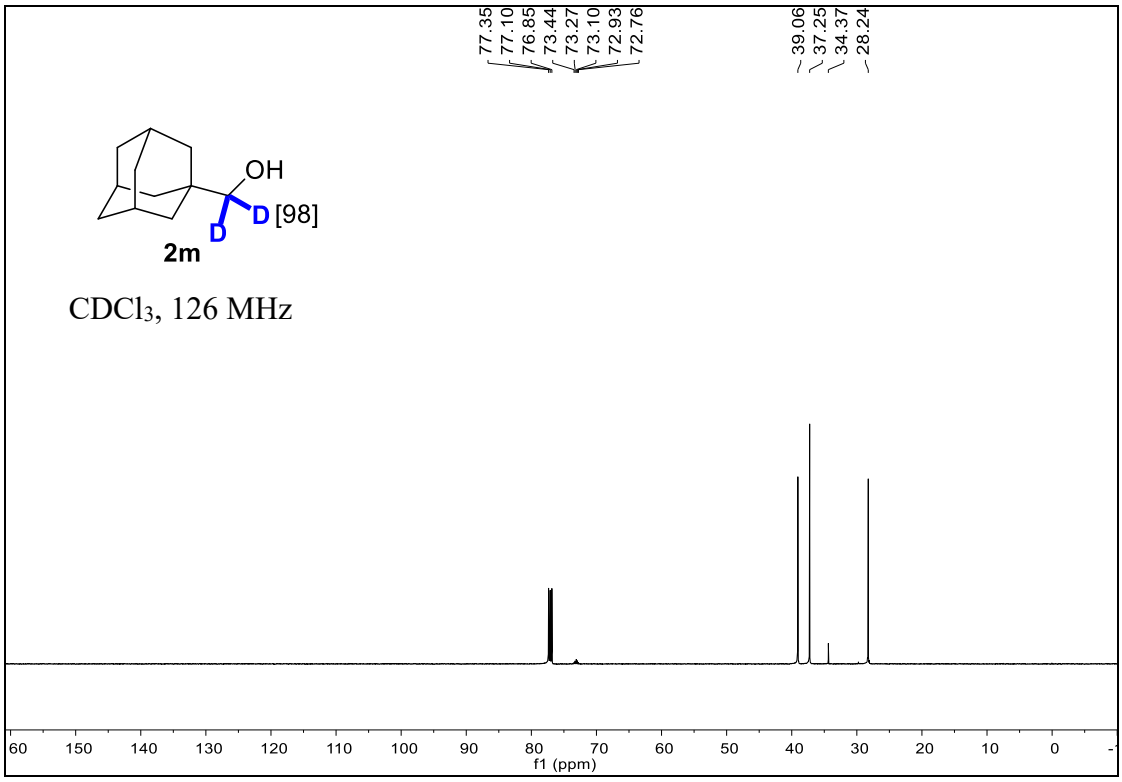

7.29
7.29
7.29
7.28
7.27
7.27
7.26
7.26
7.25
7.24
7.24
7.24
3.75
2.48
1.76
0.00
D D [>98]
OH
S
2k
CDCl3, 500 MHz
4.00
0.02
3.00
1.00
f1 (ppm)

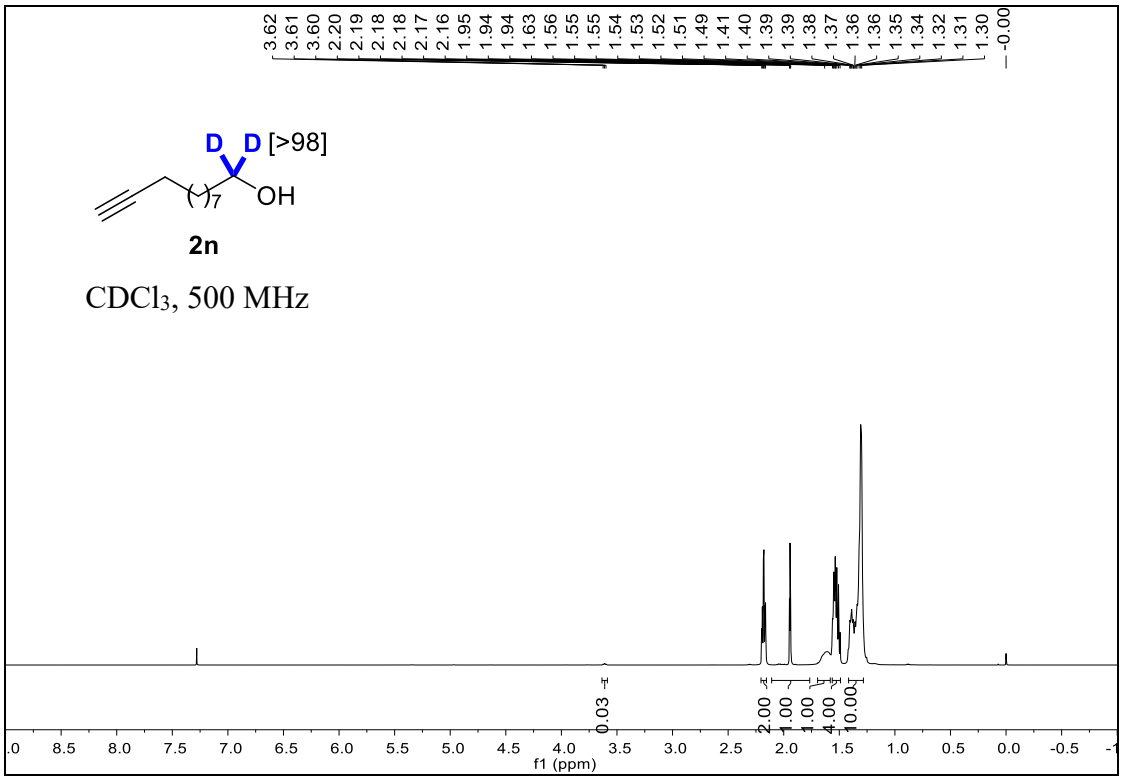

137.89
137.71
127.74
126.87
77.35
77.10
76.85
64.66
64.49
64.32
64.15
63.97
16.02
D D [>98]
OH
S
2k
CDCl3, 126 MHz
f1 (ppm)

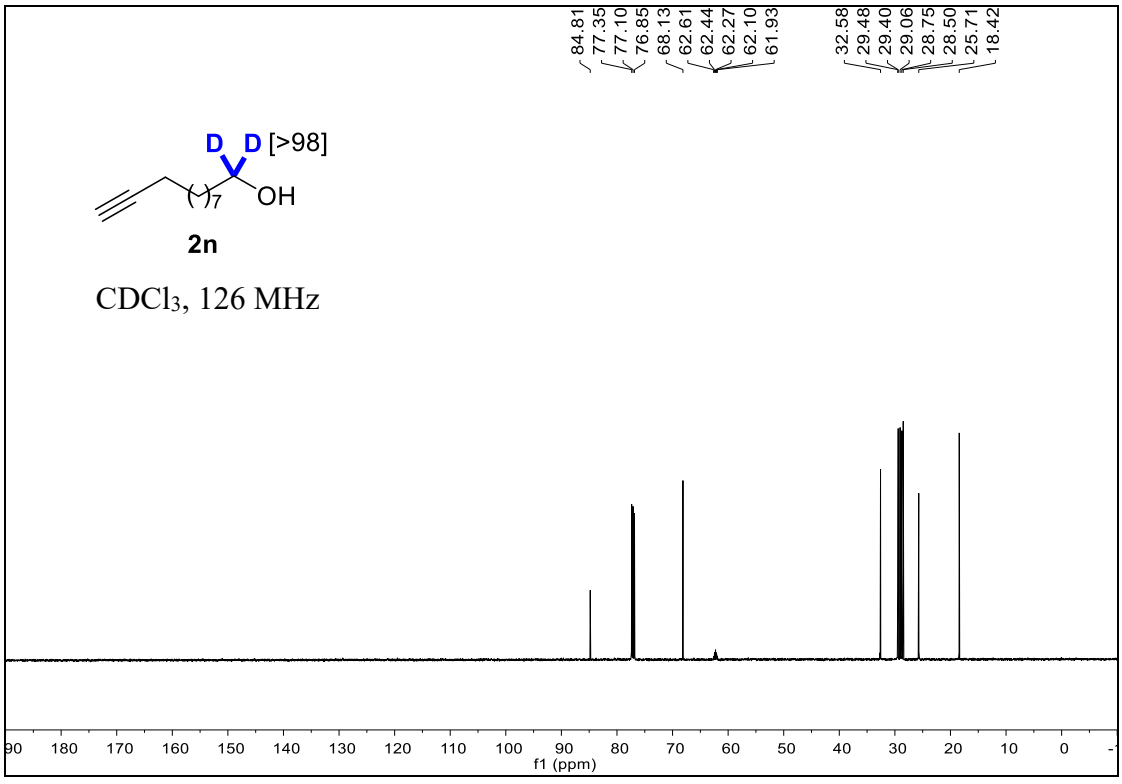

7.24
7.23
6.73
6.71
3.72
2.94
1.61
0.00
D D[>98]
OH
N
2l
CDCl3, 500 MHz
2.00
2.00
0.01
6.00
1.00
f1 (ppm)

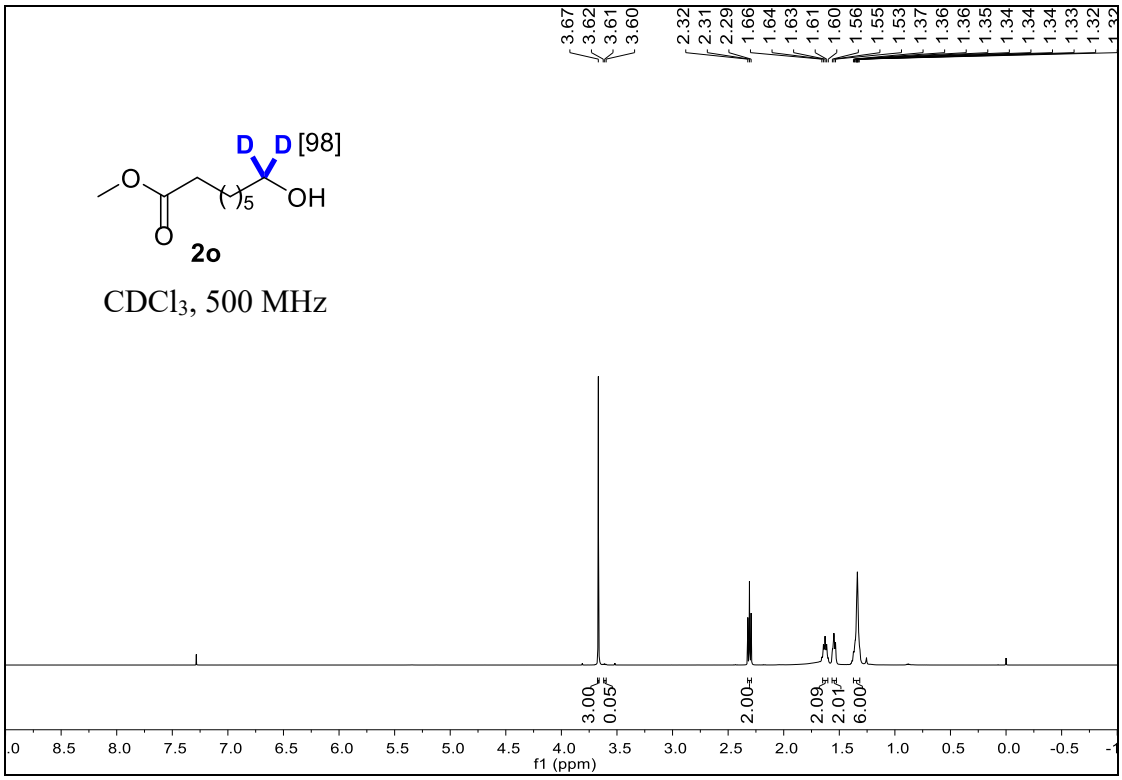

150.44
128.86
128.72
112.70
77.35
77.10
76.84
65.05
64.88
64.70
64.53
64.36
40.72
D D[>98]
OH
N
2l
CDCl3, 126 MHz
f1 (ppm)

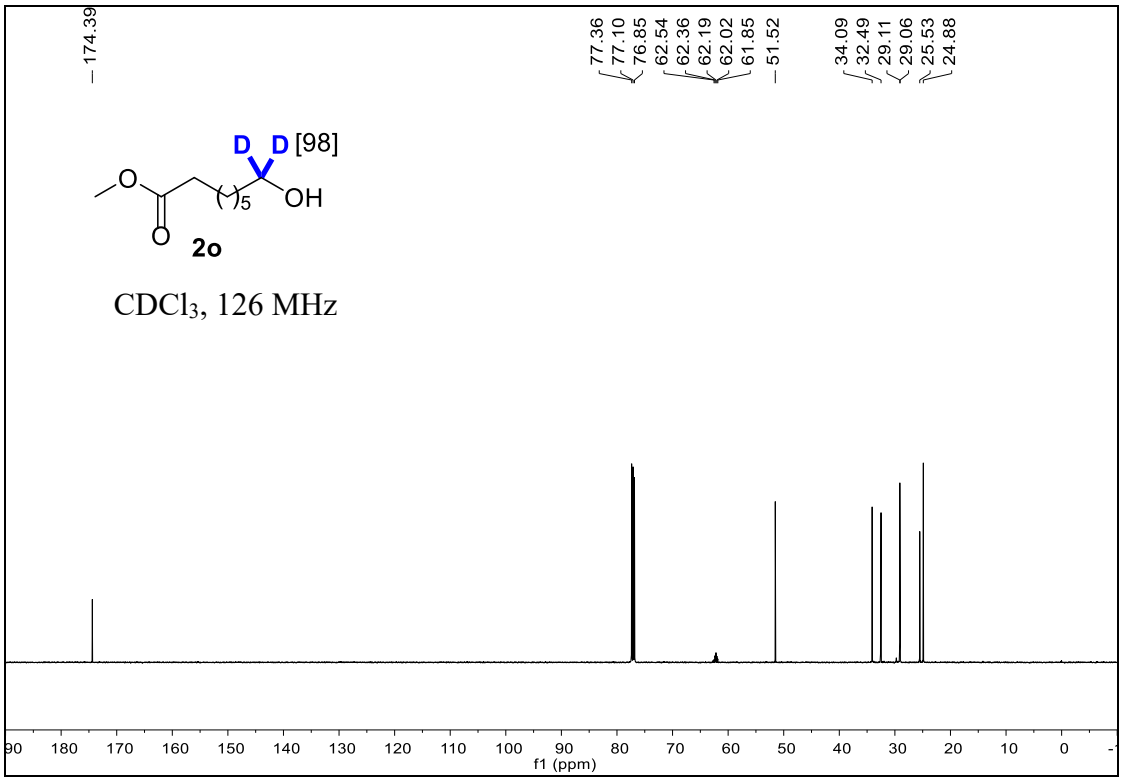

3.18
2.01
2.00
1.99
1.99
1.98
1.75
1.75
1.73
1.72
1.72
1.67
1.67
1.66
1.66
1.64
1.64
1.63
1.51
1.51
1.51
1.41
0.00
OH
D [98]
D
2m
CDCl3, 500 MHz
0.04
3.00
3.00
3.00
6.00
1.00
f1 (ppm)

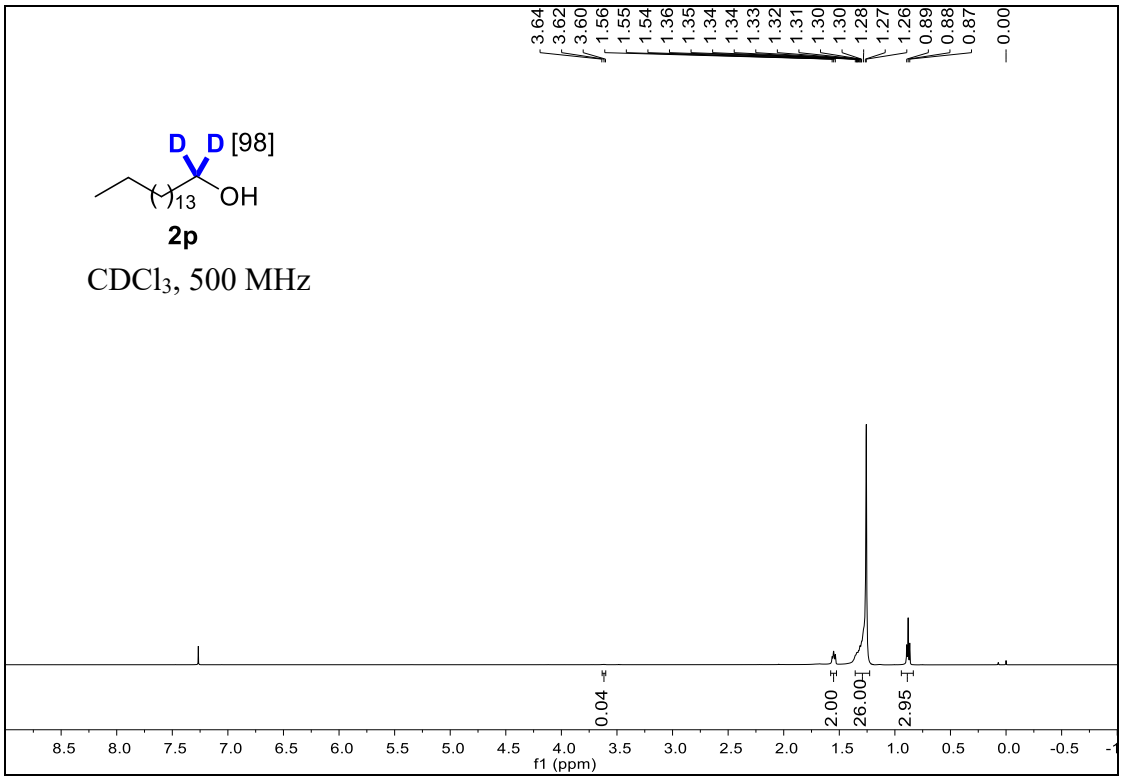

77.35
77.10
76.85
73.44
73.27
73.10
72.93
72.76
39.06
37.25
34.37
28.24
OH
D [98]
D
2m
CDCl3, 126 MHz
f1 (ppm)

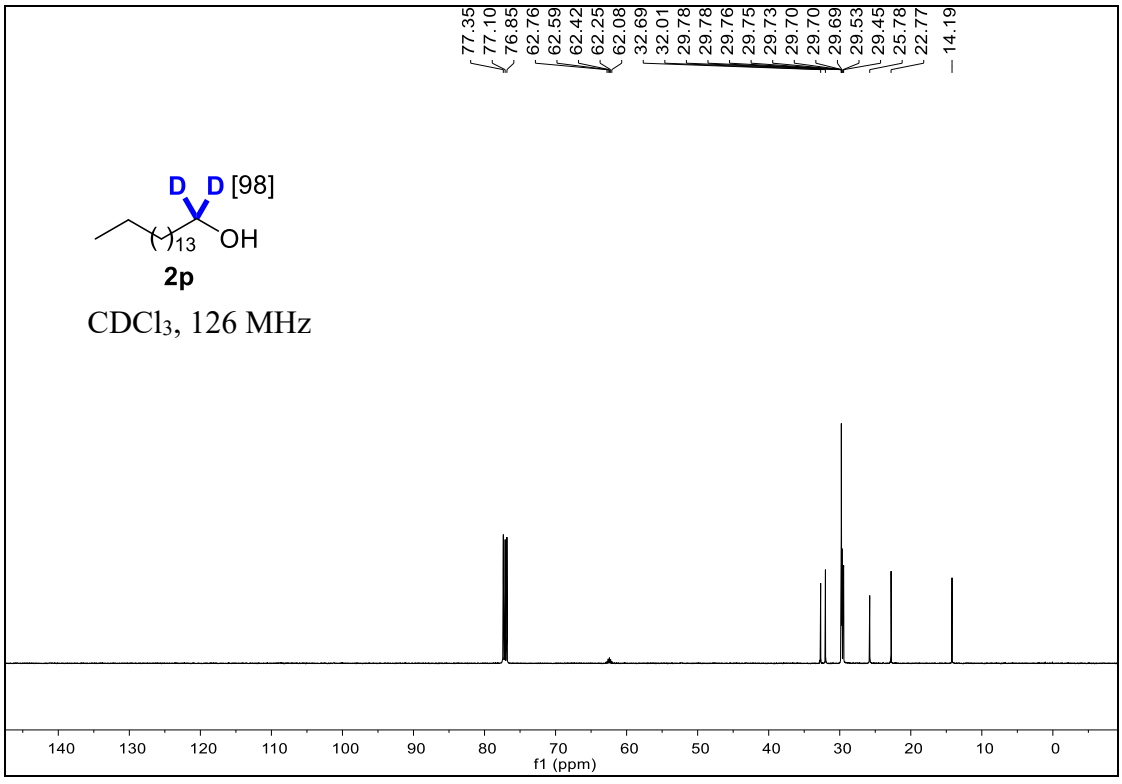

3.62
3.61
3.60
2.20
2.19
2.18
2.18
2.17
2.16
1.95
1.94
1.94
1.63
1.56
1.55
1.55
1.54
1.53
1.52
1.51
1.49
1.41
1.40
1.39
1.39
1.38
1.37
1.36
1.36
1.35
1.34
1.32
1.31
1.30
-0.00
D D [>98]
OH
7
2n
CDCl3, 500 MHz
0.03
2.00
1.00
1.00
4.00
10.00
f1 (ppm)

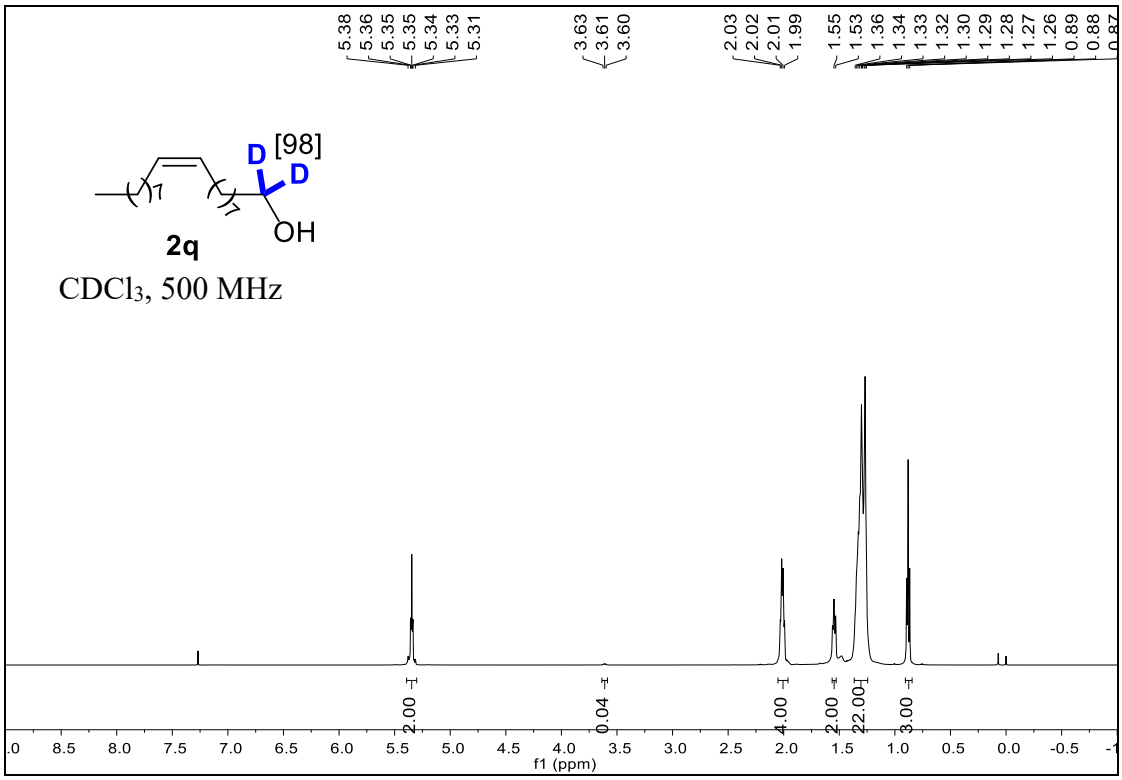

84.81
77.35
77.10
76.85
68.13
62.61
62.44
62.27
62.10
61.93
32.58
29.48
29.40
29.06
28.75
28.50
25.71
18.42
D D [>98]
OH
7
2n
CDCl3, 126 MHz
f1 (ppm)

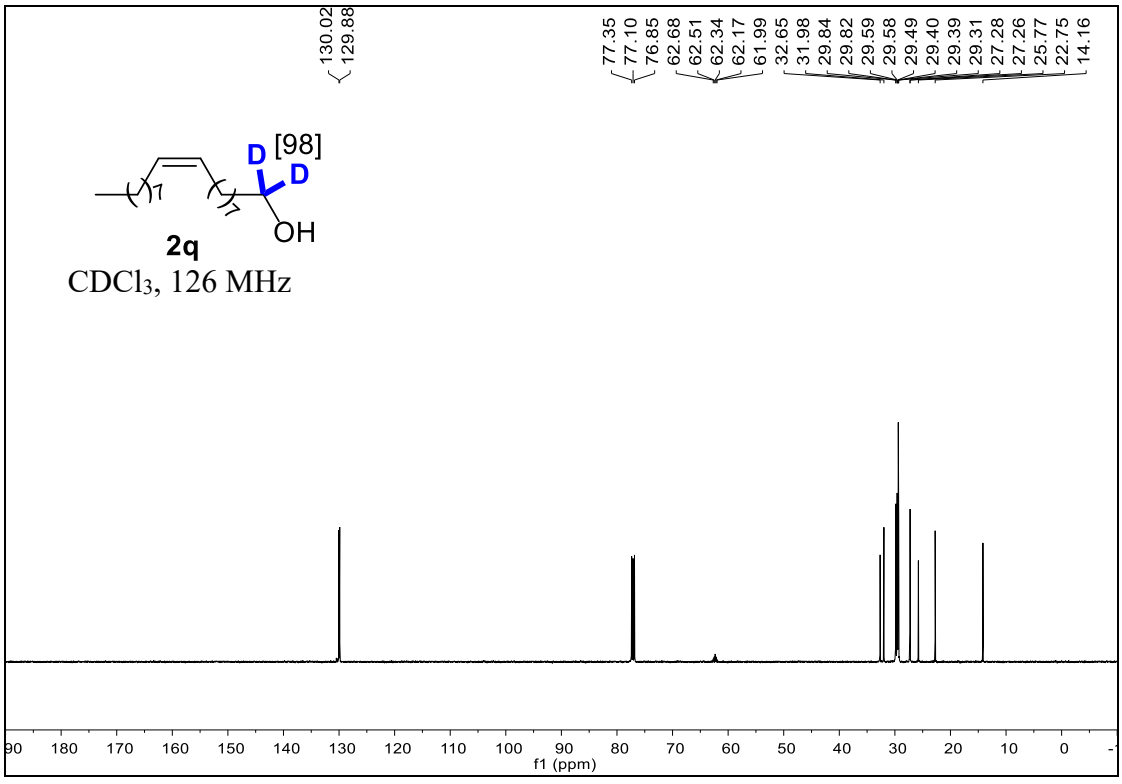

3.67
3.62
3.61
3.60
2.32
2.31
2.29
1.66
1.64
1.63
1.61
1.60
1.56
1.55
1.53
1.37
1.36
1.36
1.35
1.34
1.34
1.34
1.33
1.32
D D [98]
O
OH
5
O
2o
CDCl3, 500 MHz
3.00
0.05
2.00
2.09
2.01
6.00
f1 (ppm)

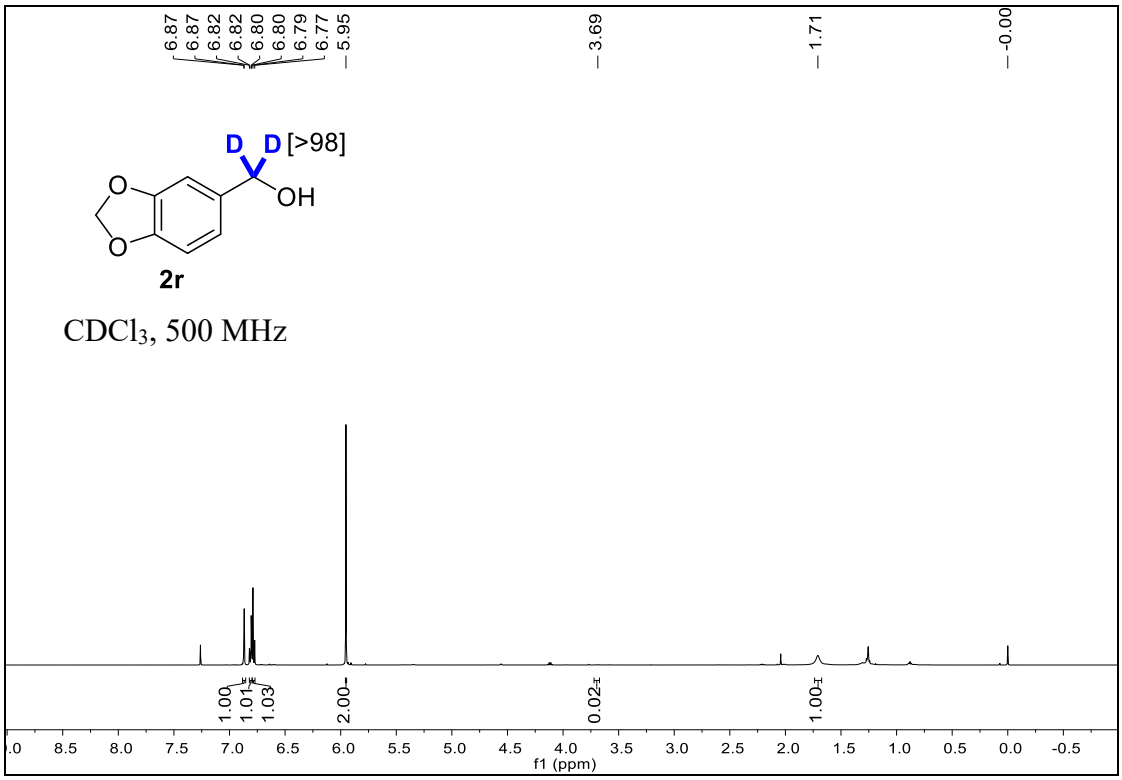

174.39
77.36
77.10
76.85
62.54
62.36
62.19
62.02
61.85
51.52
34.09
32.49
29.11
29.06
25.53
24.88
D D [98]
O
OH
5
O
2o
CDCl3, 126 MHz
f1 (ppm)

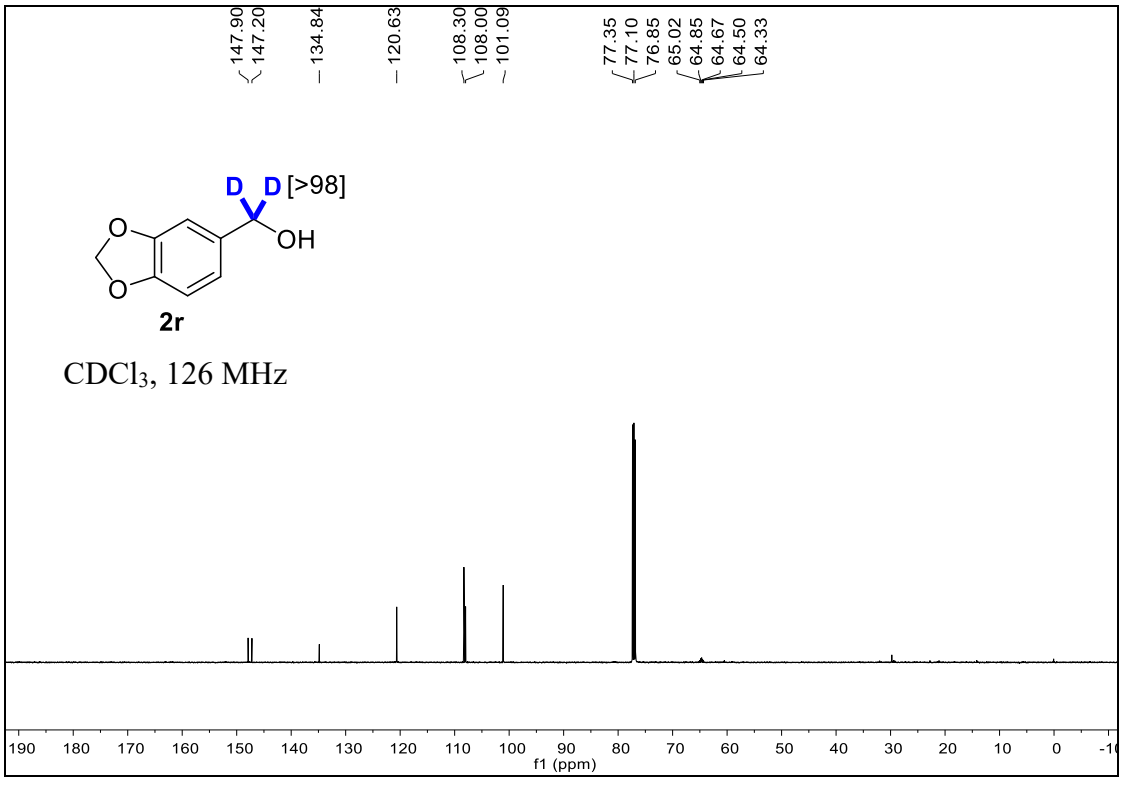

3.64
3.62
3.60
1.56
1.55
1.54
1.36
1.35
1.34
1.34
1.33
1.32
1.31
1.30
1.30
1.28
1.27
1.26
0.89
0.88
0.87
0.00
D D [98]
13
OH
2p
CDCl3, 500 MHz
0.04
2.00
26.00
2.95
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

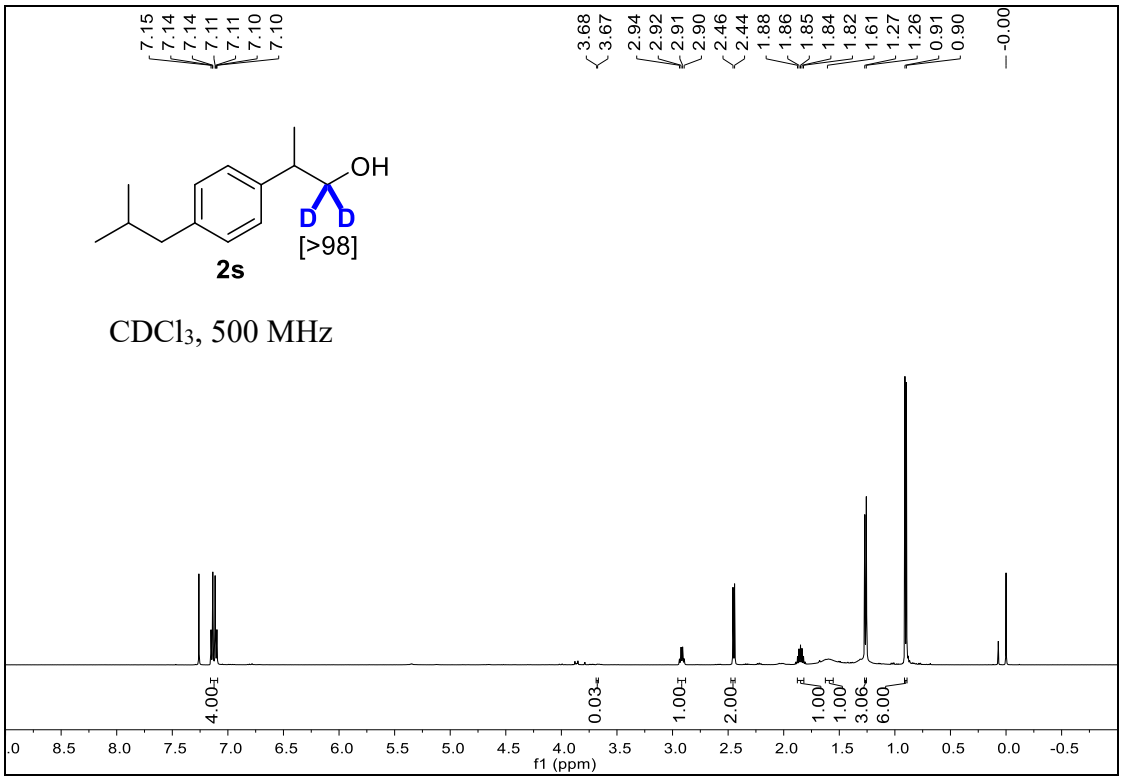

77.35
77.10
76.85
62.76
62.59
62.42
62.25
62.08
32.69
32.01
29.78
29.76
29.75
29.73
29.70
29.70
29.69
29.53
29.45
25.78
22.77
14.19
D D [98]
13
OH
2p
CDCl3, 126 MHz
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

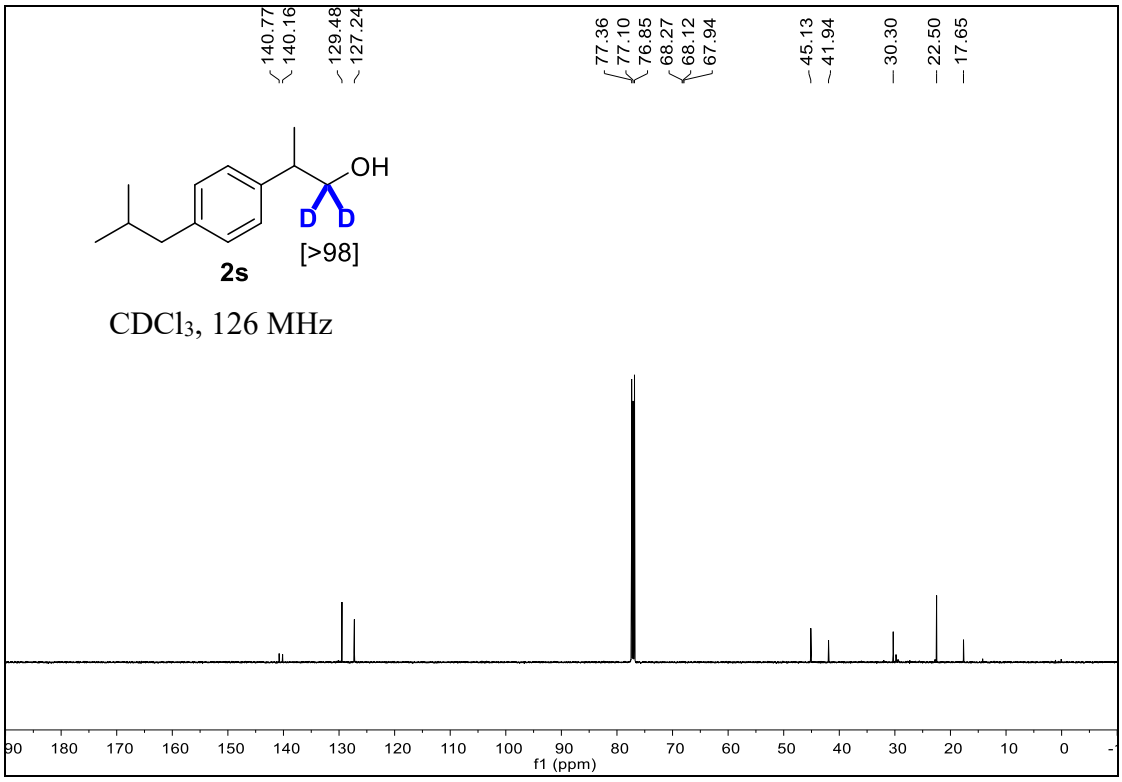

5.38
5.36
5.35
5.35
5.34
5.33
5.31
3.63
3.61
3.60
2.03
2.02
2.01
1.99
1.55
1.53
1.36
1.34
1.33
1.32
1.30
1.29
1.28
1.27
1.26
0.89
0.88
D
[98]
D
OH
2q
CDCl3, 500 MHz
2.00
0.04
4.00
2.00
22.00
3.00
f1 (ppm)

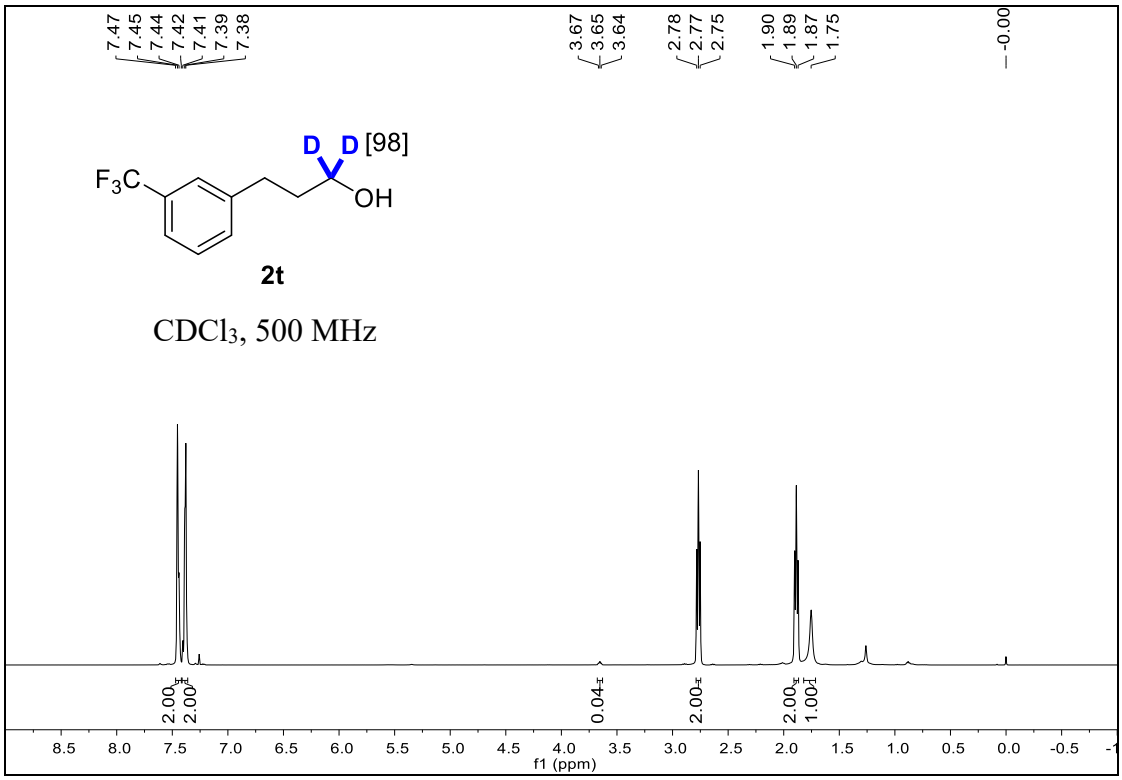

130.02
129.88
77.35
77.10
76.85
62.68
62.51
62.34
62.17
61.99
32.65
31.98
29.84
29.82
29.59
29.58
29.49
29.40
29.39
29.31
27.28
27.26
25.77
22.75
14.16
D
[98]
D
OH
2q
CDCl3, 126 MHz
f1 (ppm)

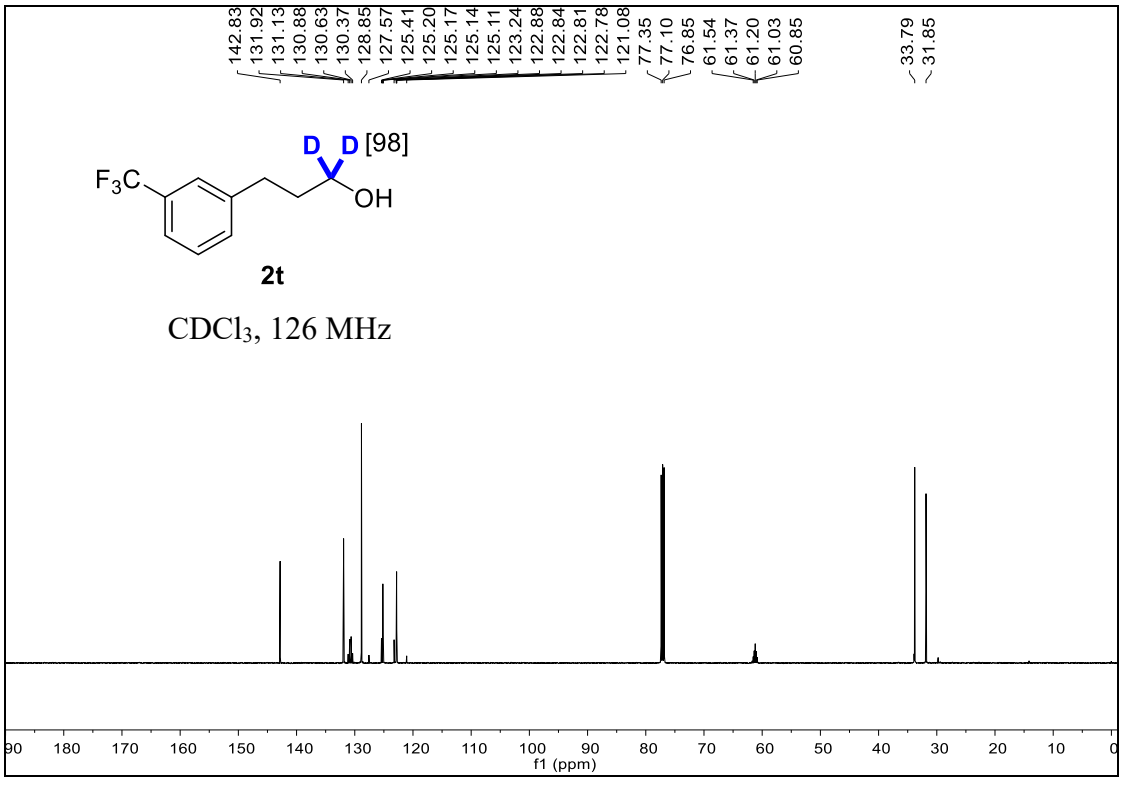

6.87
6.87
6.82
6.82
6.80
6.80
6.79
6.77
5.95
3.69
1.71
-0.00
D D [>98]
OH
O
O
2r
CDCl3, 500 MHz
1.00
1.01
1.03
2.00
0.02
1.00
f1 (ppm)

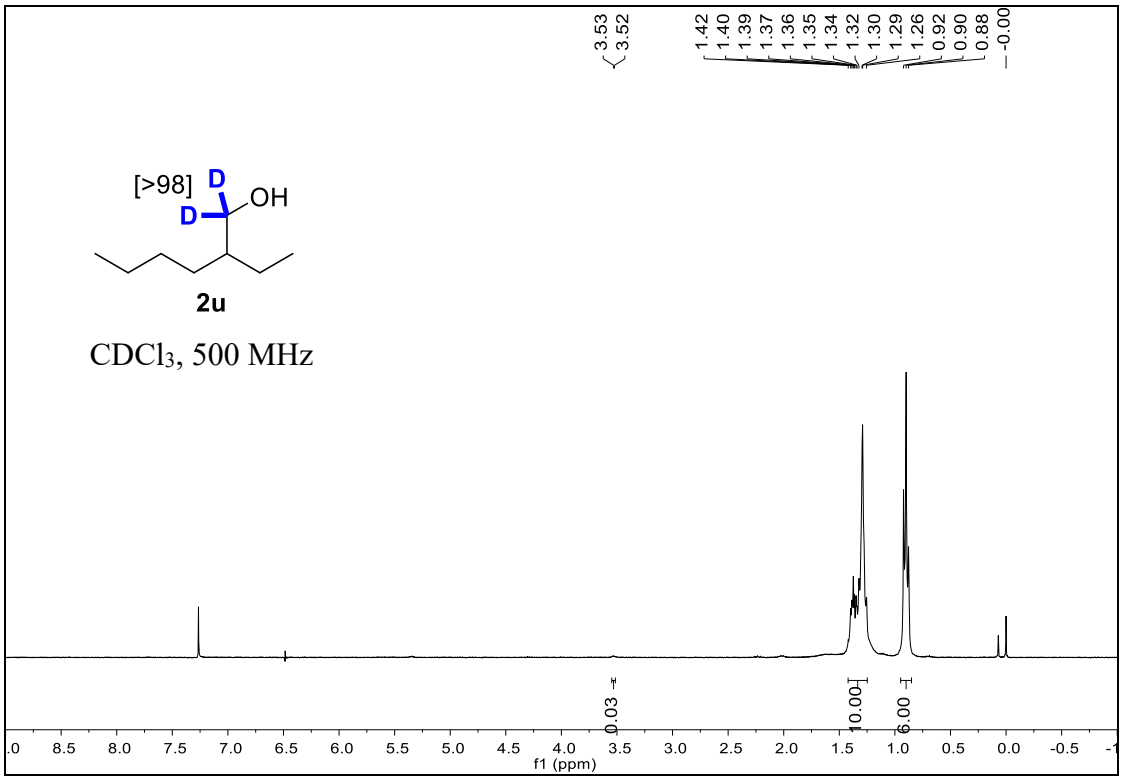

147.90
147.20
134.84
120.63
108.30
108.00
101.09
77.35
77.10
76.85
65.02
64.85
64.67
64.50
64.33
D D [>98]
OH
O
O
2r
CDCl3, 126 MHz
f1 (ppm)

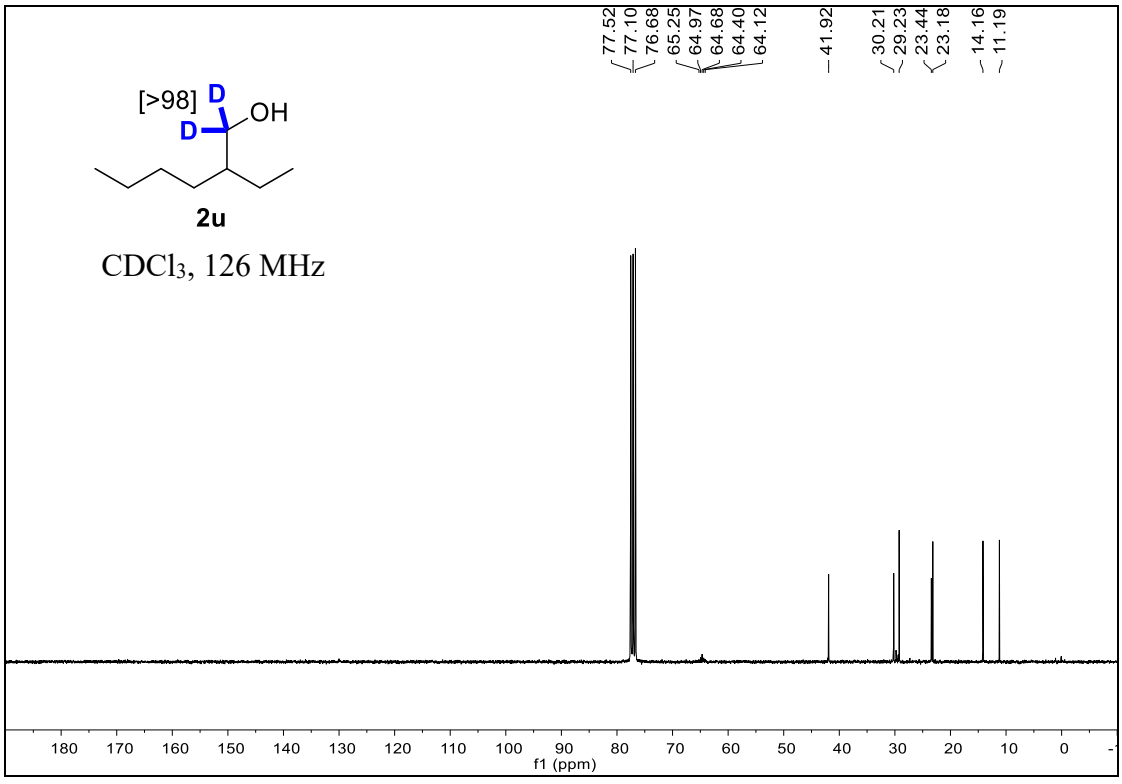

7.15
7.14
7.14
7.11
7.11
7.10
7.10
3.68
3.67
2.94
2.92
2.91
2.90
2.46
2.44
1.88
1.86
1.85
1.84
1.82
1.61
1.27
1.26
0.91
0.90
-0.00
OH
D
D
[>98]
2s
CDCl3, 500 MHz
4.00
0.03
1.00
2.00
1.00
1.00
3.06
6.00
f1 (ppm)

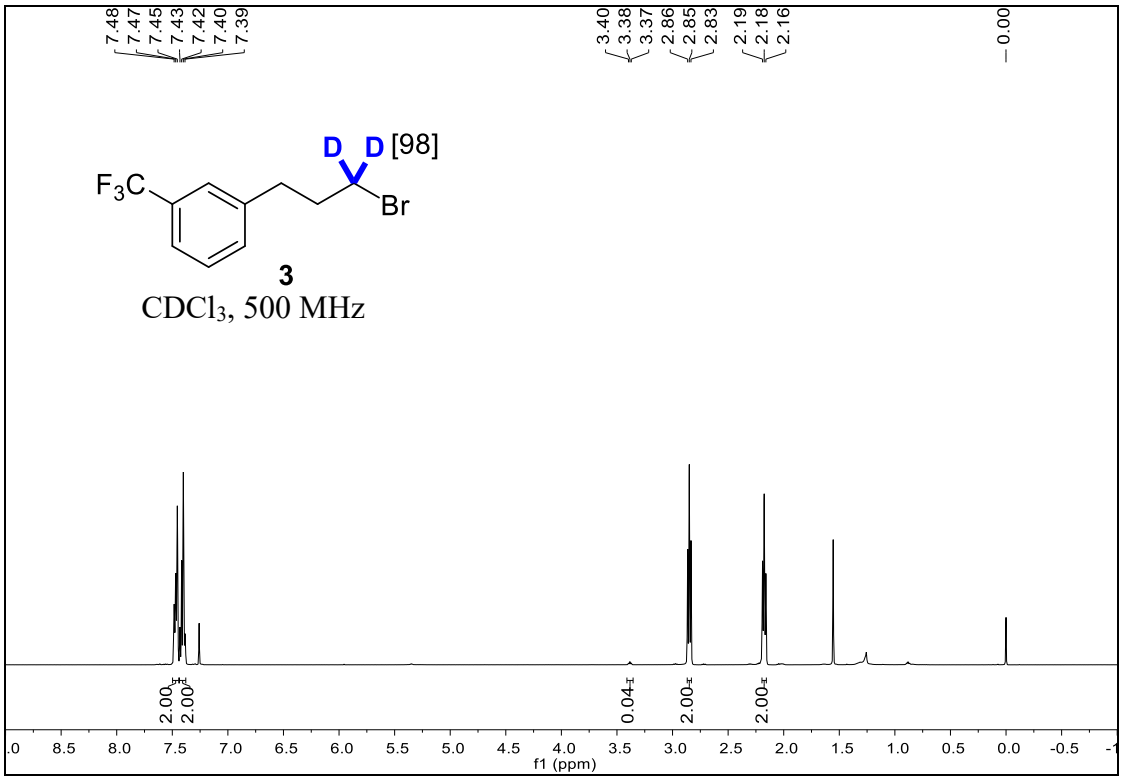

140.77
140.16
129.48
127.24
77.36
77.10
76.85
68.27
68.12
67.94
45.13
41.94
30.30
22.50
17.65
OH
D
D
[>98]
2s
CDCl3, 126 MHz
f1 (ppm)

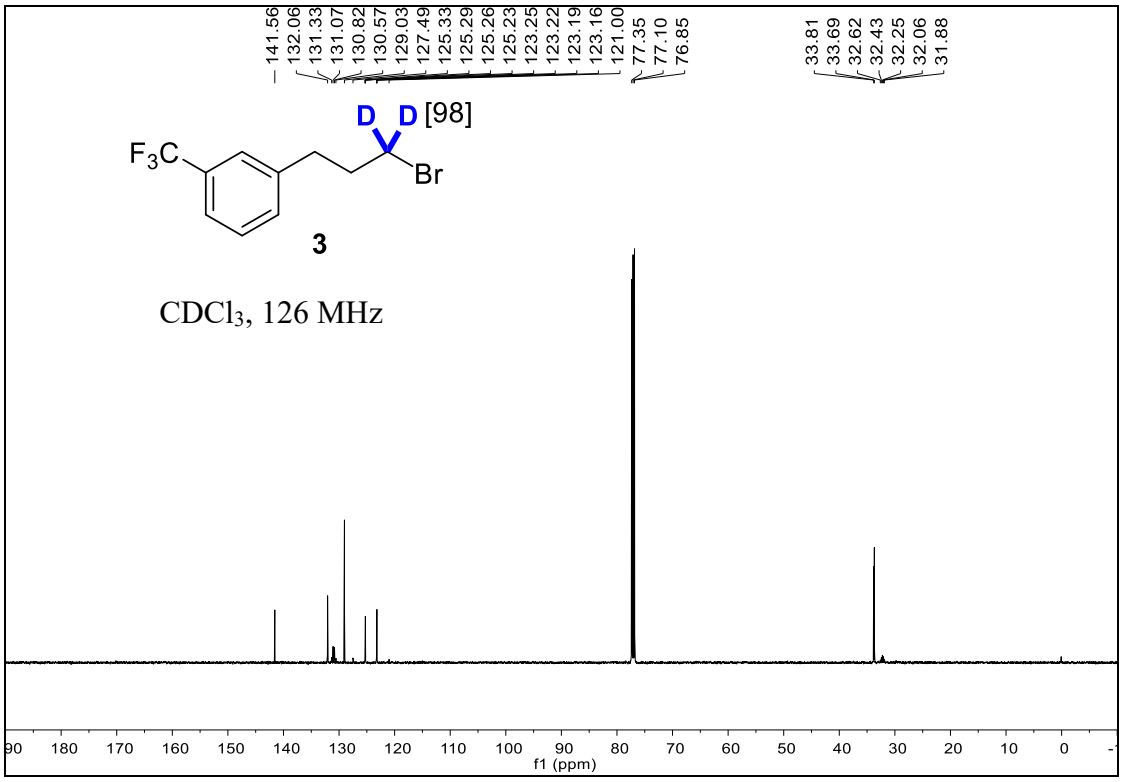

7.47
7.45
7.44
7.42
7.41
7.39
7.38
3.67
3.65
3.64
2.78
2.77
2.75
1.90
1.89
1.87
1.75
-0.00
D D [98]
F3C
OH
2t
CDCl3, 500 MHz
2.00
2.00
0.04
2.00
2.00
1.00
f1 (ppm)

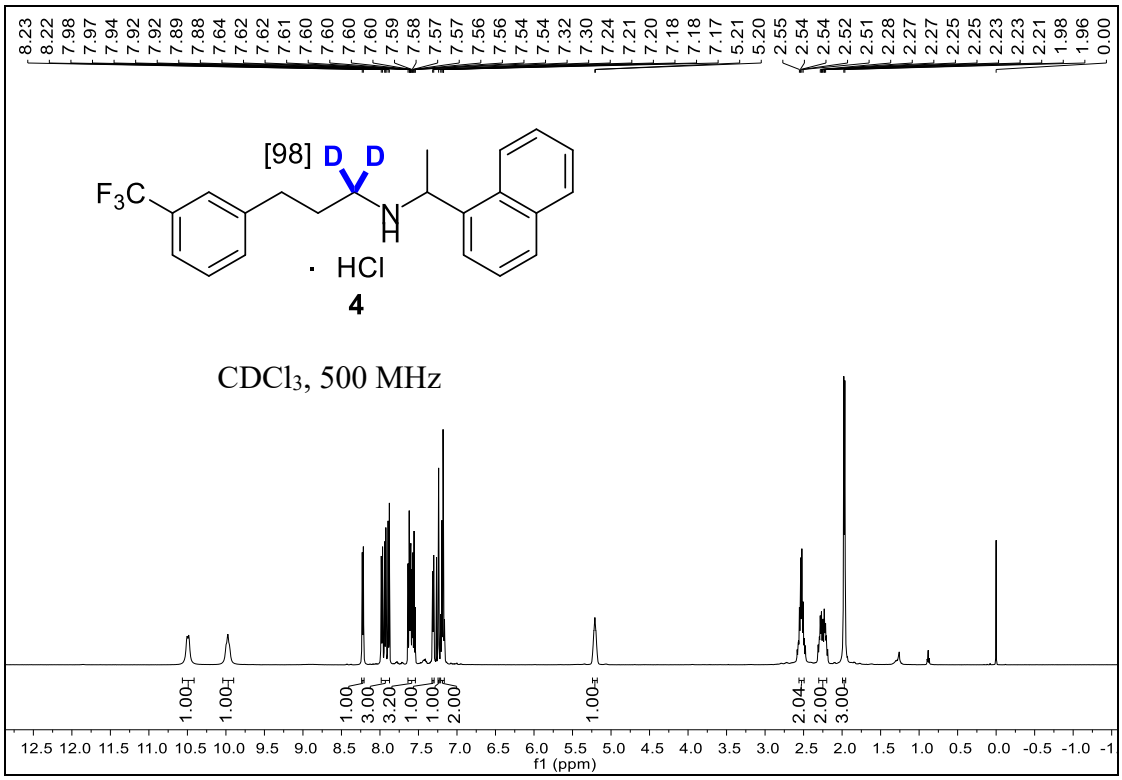

142.83
131.92
131.13
130.88
130.63
130.37
128.85
127.57
125.41
125.20
125.17
125.14
125.11
123.24
122.88
122.84
122.81
122.78
121.08
77.35
77.10
76.85
61.54
61.37
61.20
61.03
60.85
33.79
31.85
D D [98]
F3C
OH
2t
CDCl3, 126 MHz
f1 (ppm)

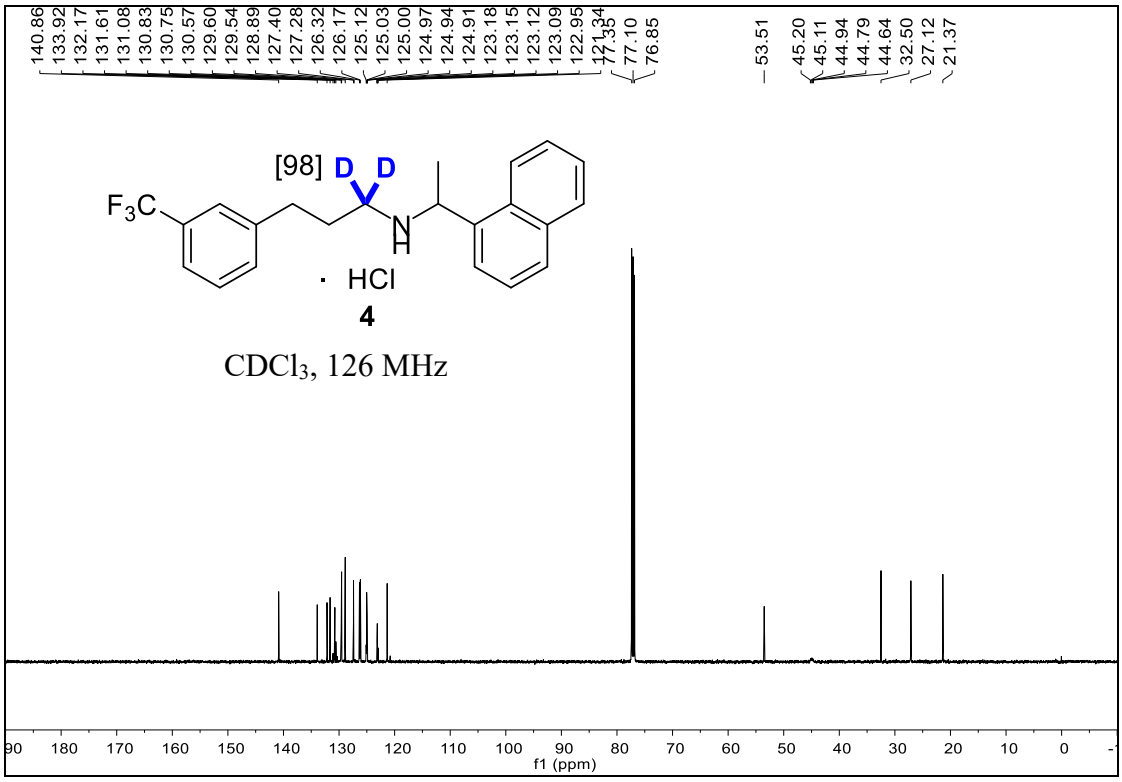

3.53
3.52
1.42
1.40
1.39
1.37
1.36
1.35
1.34
1.32
1.30
1.29
1.26
0.92
0.90
0.88
-0.00
[>98] D
D
OH
2u
CDCl3, 500 MHz
0.03
10.00
6.00
f1 (ppm)

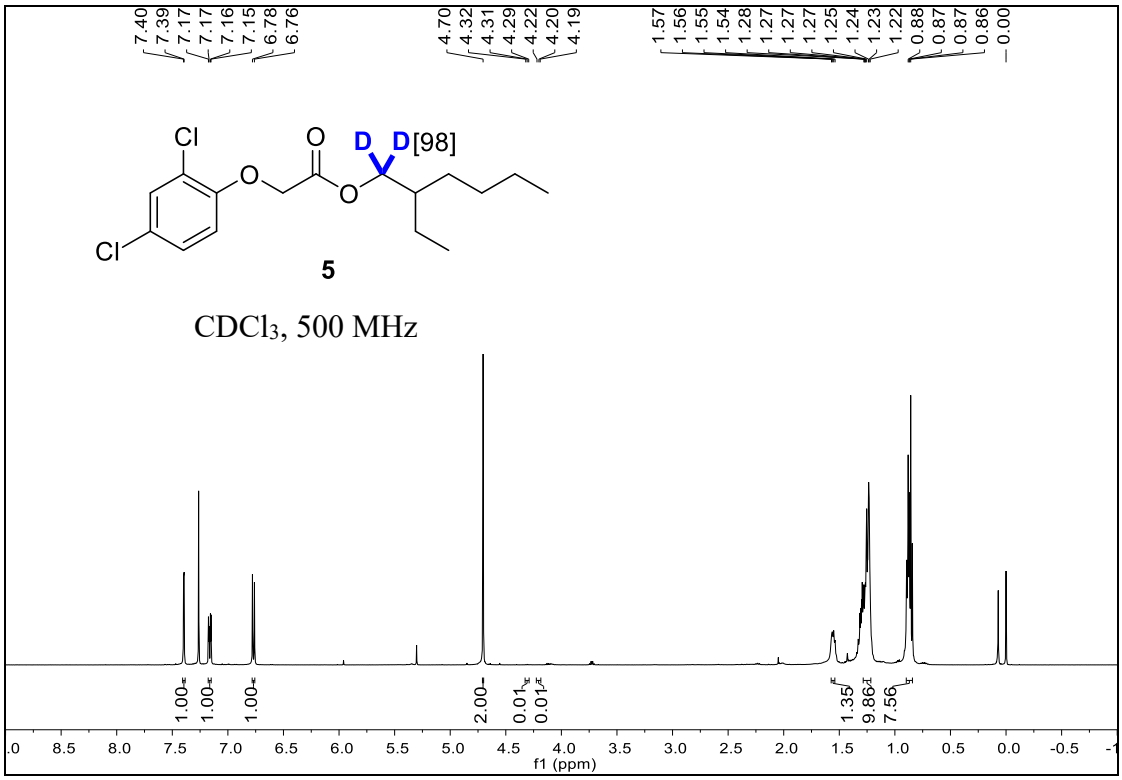

77.52
77.10
76.68
65.25
64.97
64.68
64.40
64.12
41.92
30.21
29.23
23.44
23.18
14.16
11.19
[>98] D
D
OH
2u
CDCl3, 126 MHz
f1 (ppm)

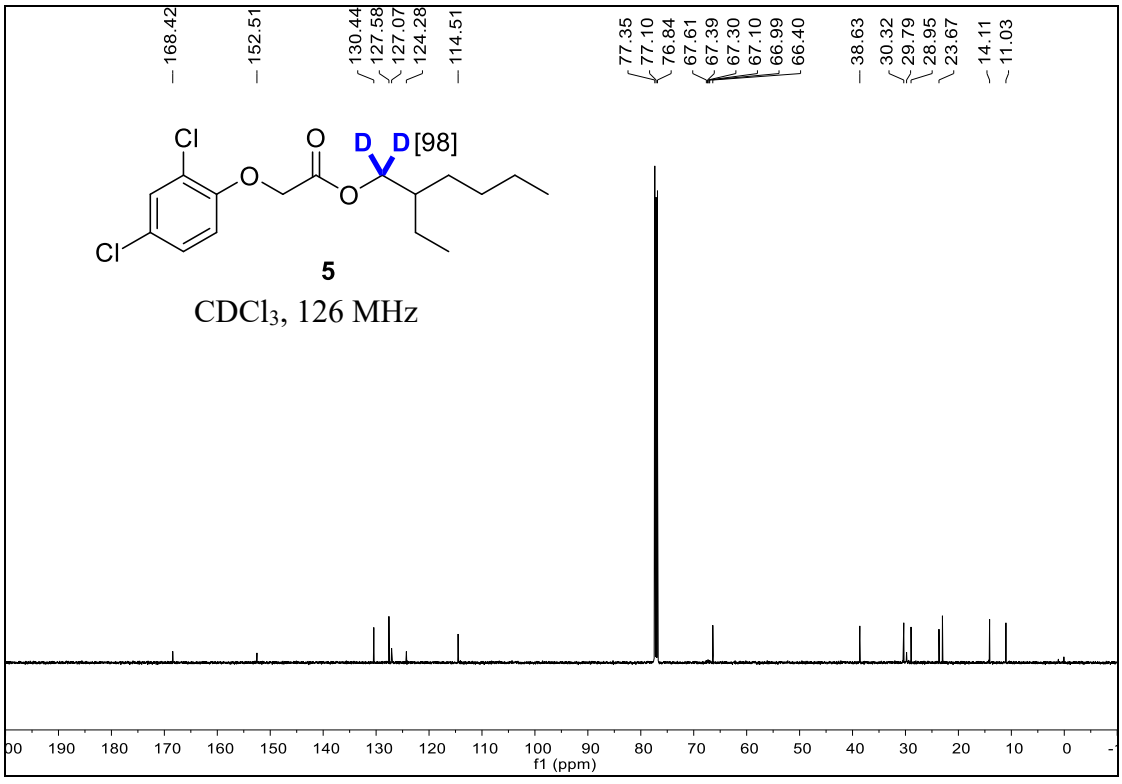

7.48
7.47
7.45
7.43
7.42
7.40
7.39
3.40
3.38
3.37
2.86
2.85
2.83
2.19
2.18
2.16
0.00
D D [98]
F3C
Br
3
CDCl3, 500 MHz
2.00
2.00
0.04
2.00
2.00
f1 (ppm)


141.56
132.06
131.33
131.07
130.82
130.57
129.03
127.49
125.33
125.29
125.26
125.23
123.25
123.22
123.19
123.16
121.00
77.35
77.10
76.85
33.81
33.69
32.62
32.43
32.25
32.06
31.88
D D [98]
F3C
Br
3
CDCl3, 126 MHz
f1 (ppm)

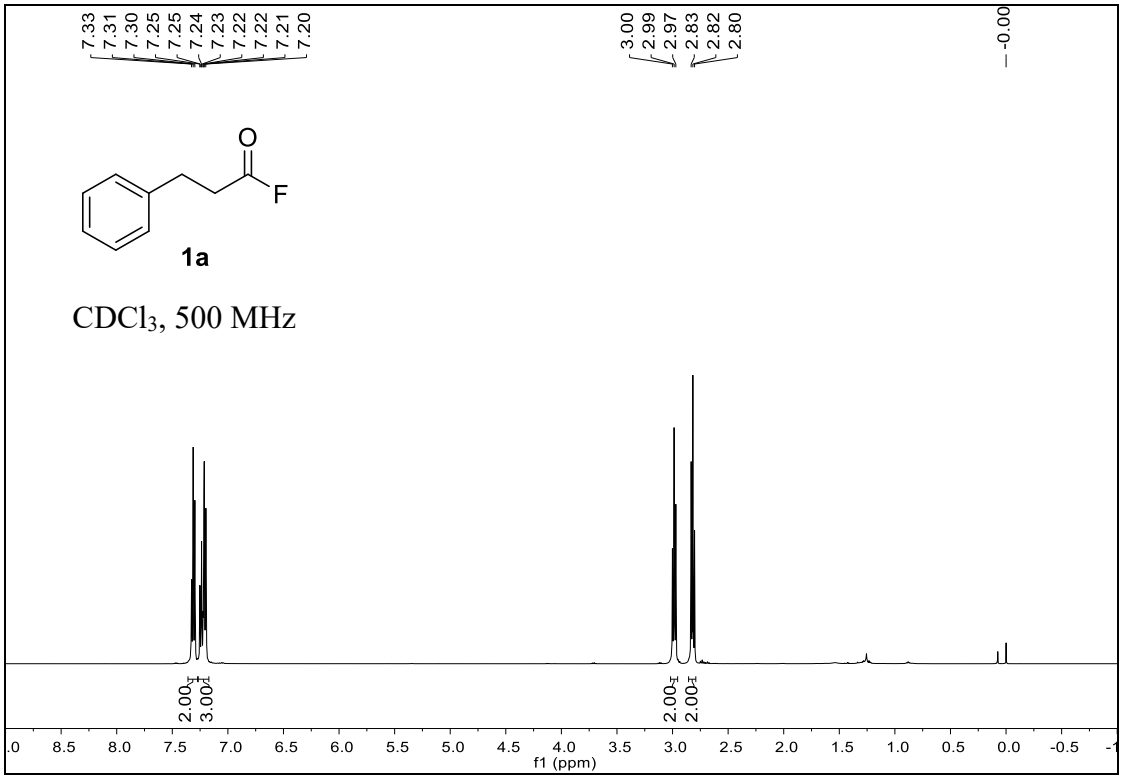

[98] D D
F3C
HCl
4
CDCl3, 500 MHz
f1 (ppm)

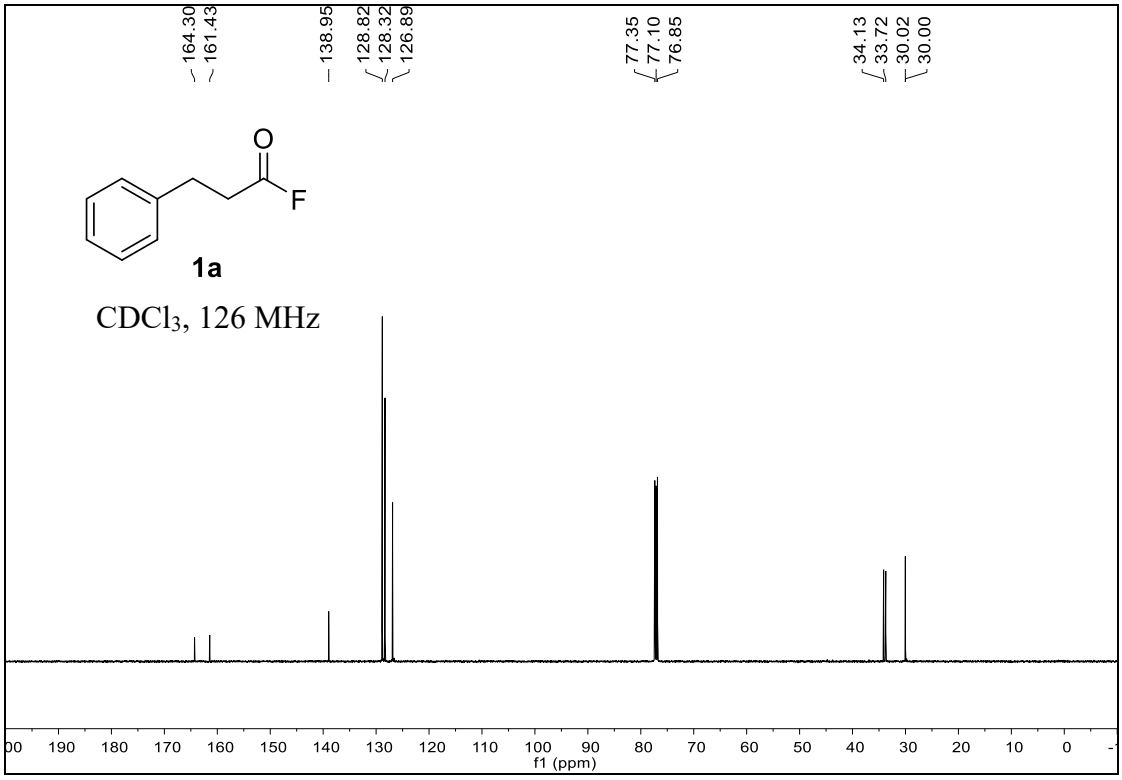

[98] D D
F3C
HCl
4
CDCl3, 126 MHz
f1 (ppm)

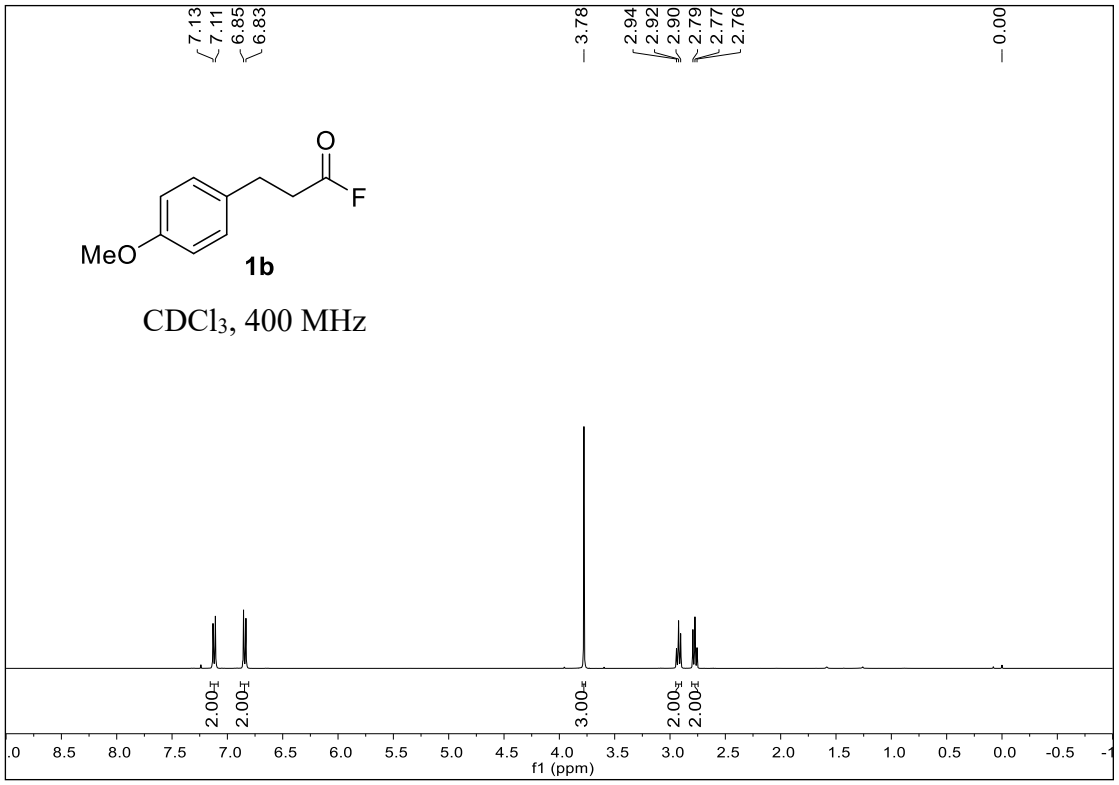

7.40
7.39
7.17
7.17
7.16
7.15
6.78
6.76
4.70
4.32
4.31
4.29
4.22
4.20
4.19
1.57
1.56
1.55
1.54
1.28
1.27
1.27
1.27
1.25
1.24
1.23
1.22
0.88
0.87
0.87
0.86
0.00
Cl
O
D D[98]
O
O
Cl
5
CDCl3, 500 MHz
1.00
1.00
1.00
2.00
0.01
0.01
1.35
9.86
7.56
f1 (ppm)


168.42
152.51
130.44
127.58
127.07
124.28
114.51
77.35
77.10
76.84
67.61
67.39
67.30
67.10
66.99
66.40
38.63
30.32
29.79
28.95
23.67
14.11
11.03
Cl
O
D D[98]
O
O
Cl
5
CDCl3, 126 MHz
f1 (ppm)

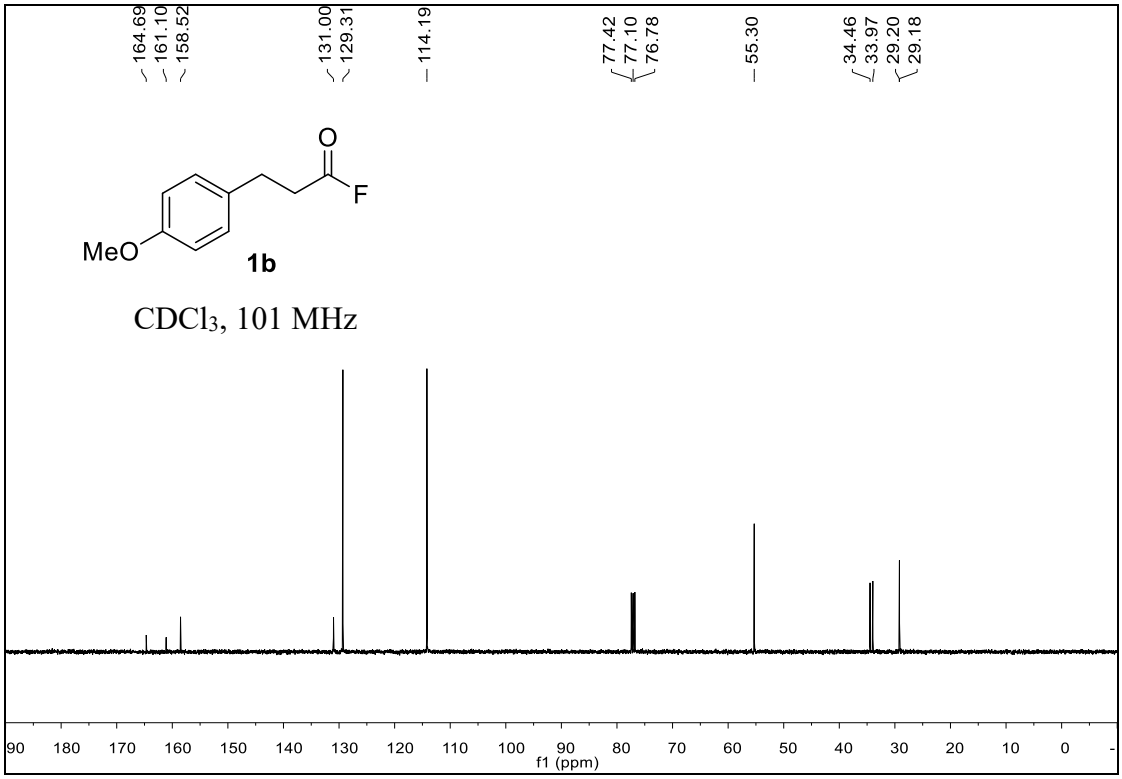
8. ^{1}H and ^{13}C NMR Spectra of Substrates



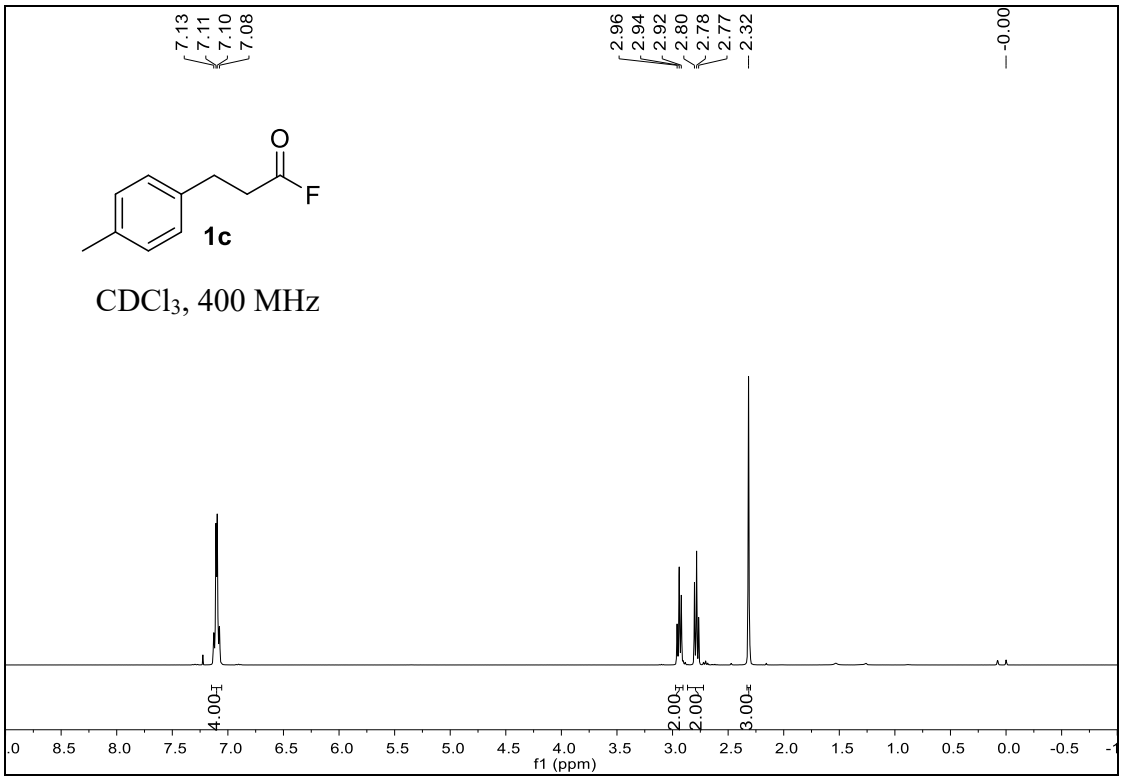


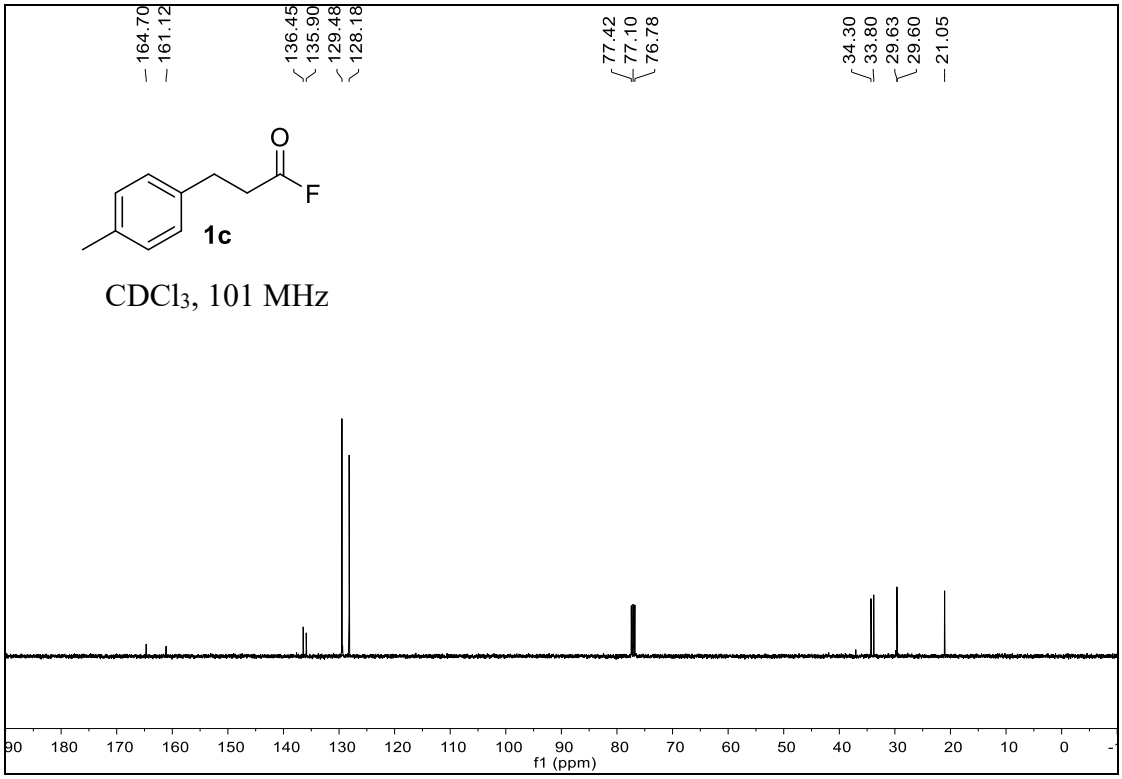


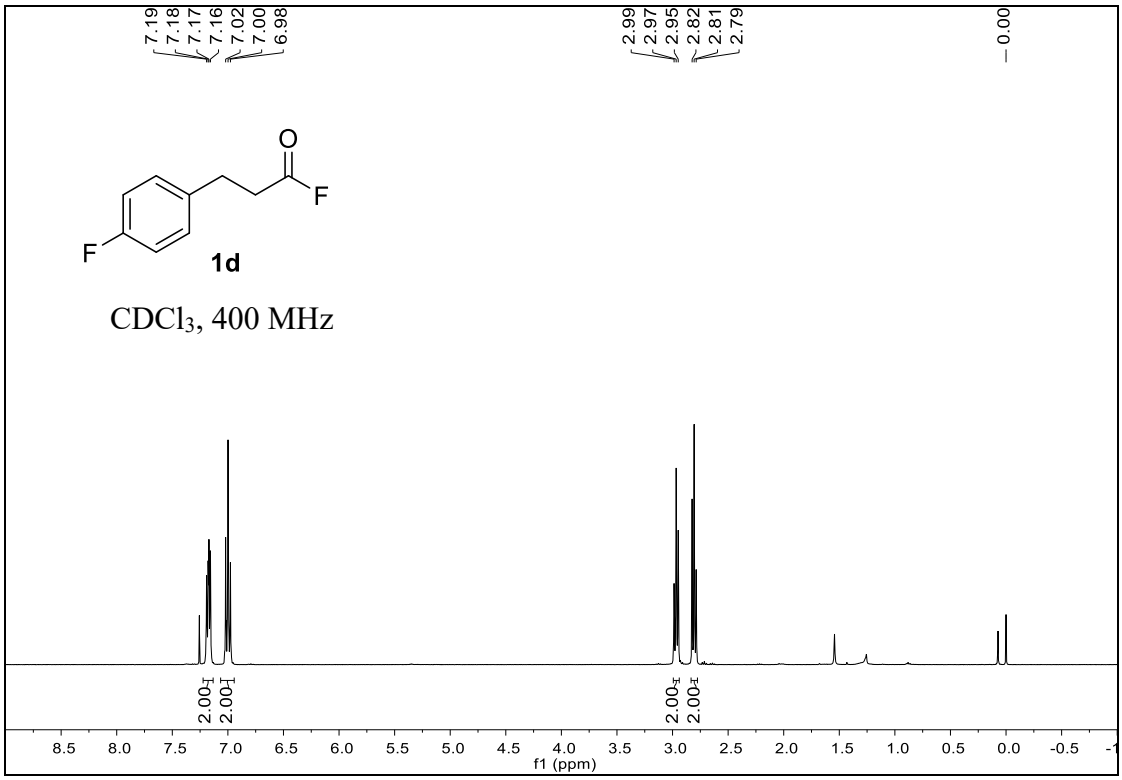
$CDCl_3$, 400 MHz

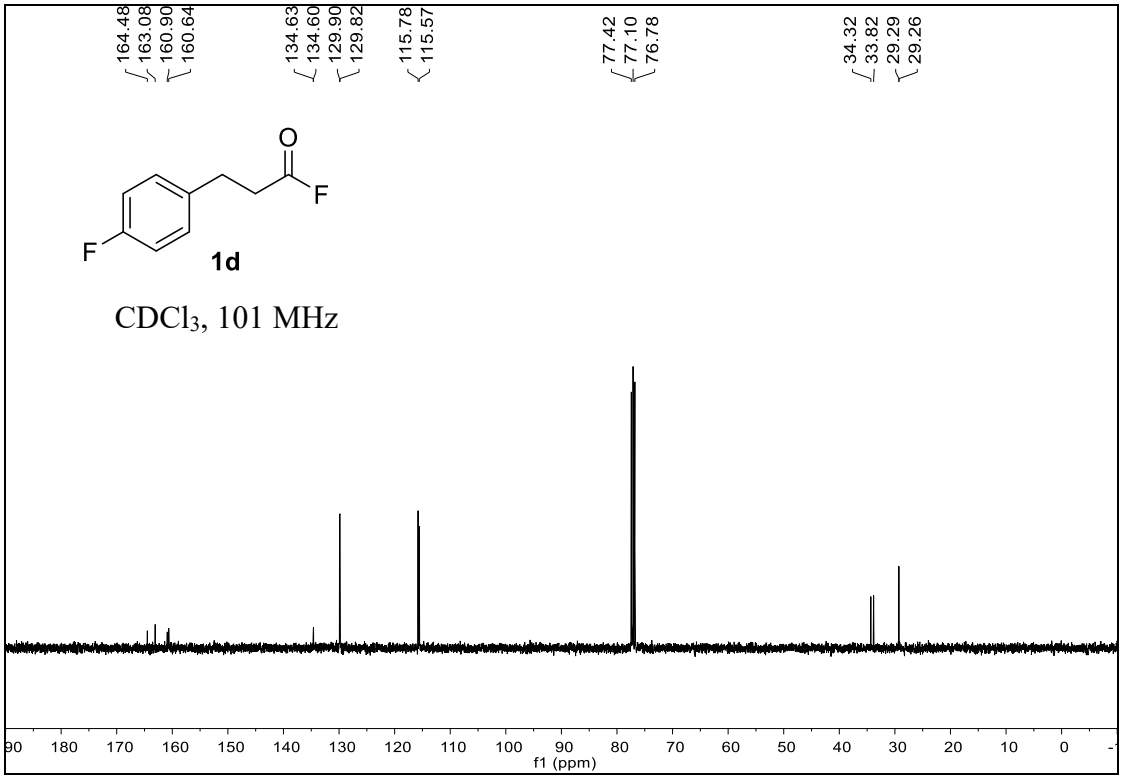


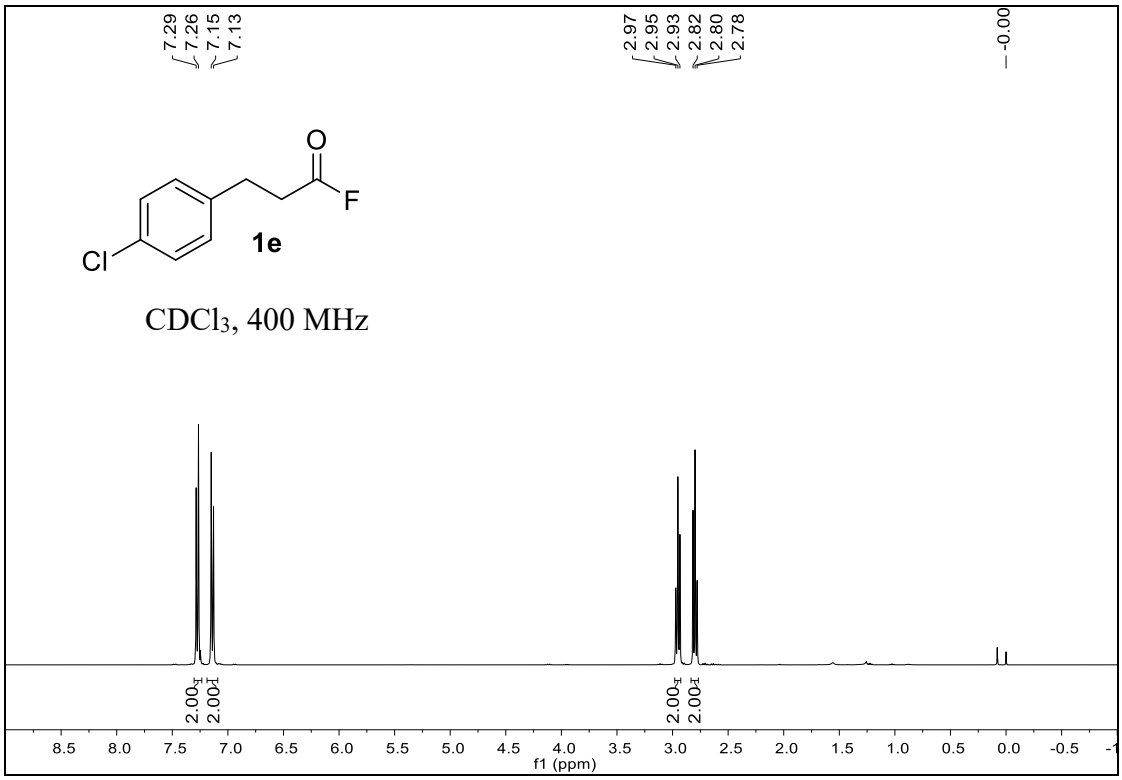
$CDCl_3$, 101 MHz


7.13
7.11
7.10
7.08
2.96
2.94
2.92
2.80
2.78
2.77
2.32
-0.00
O
F
1c
CDCl3, 400 MHz
4.00
2.00
2.00
3.00
f1 (ppm)

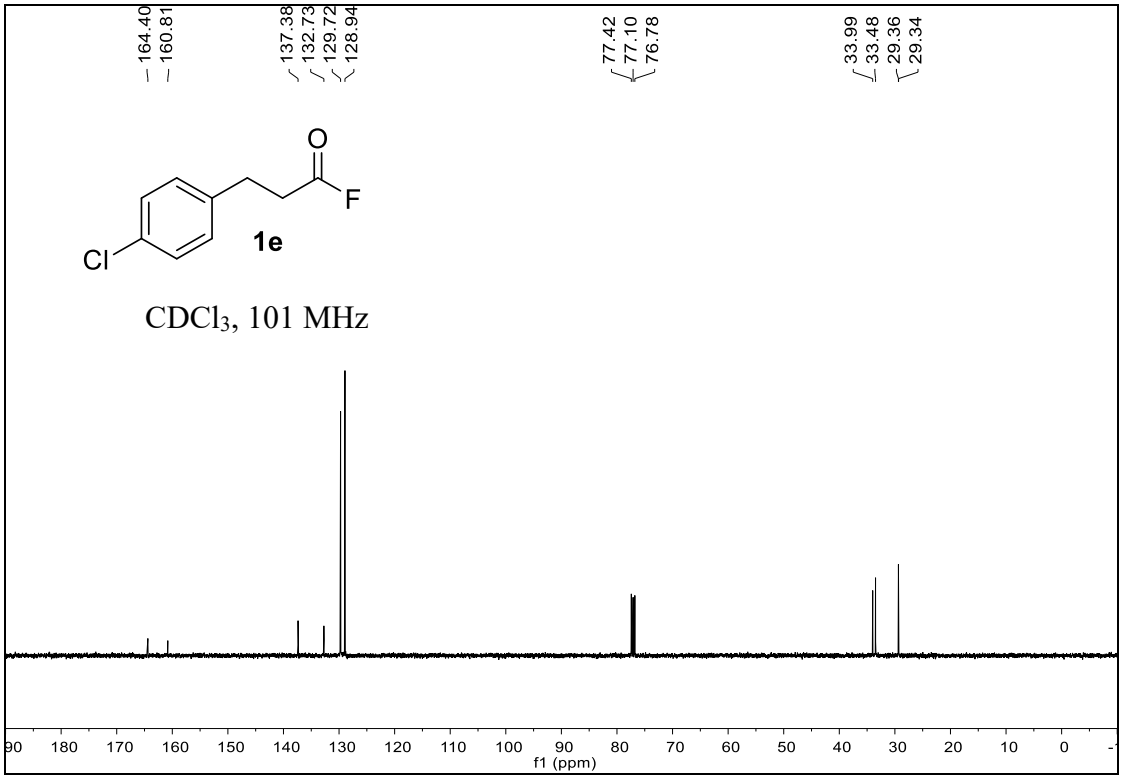

164.70
161.12
136.45
135.90
129.48
128.18
77.42
77.10
76.78
34.30
33.80
29.63
29.60
21.05
O
F
1c
CDCl3, 101 MHz
f1 (ppm)


7.19
7.18
7.17
7.16
7.02
7.00
6.98
2.99
2.97
2.95
2.82
2.81
2.79
0.00
O
F
F
1d
CDCl3, 400 MHz
2.00
2.00
2.00
2.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

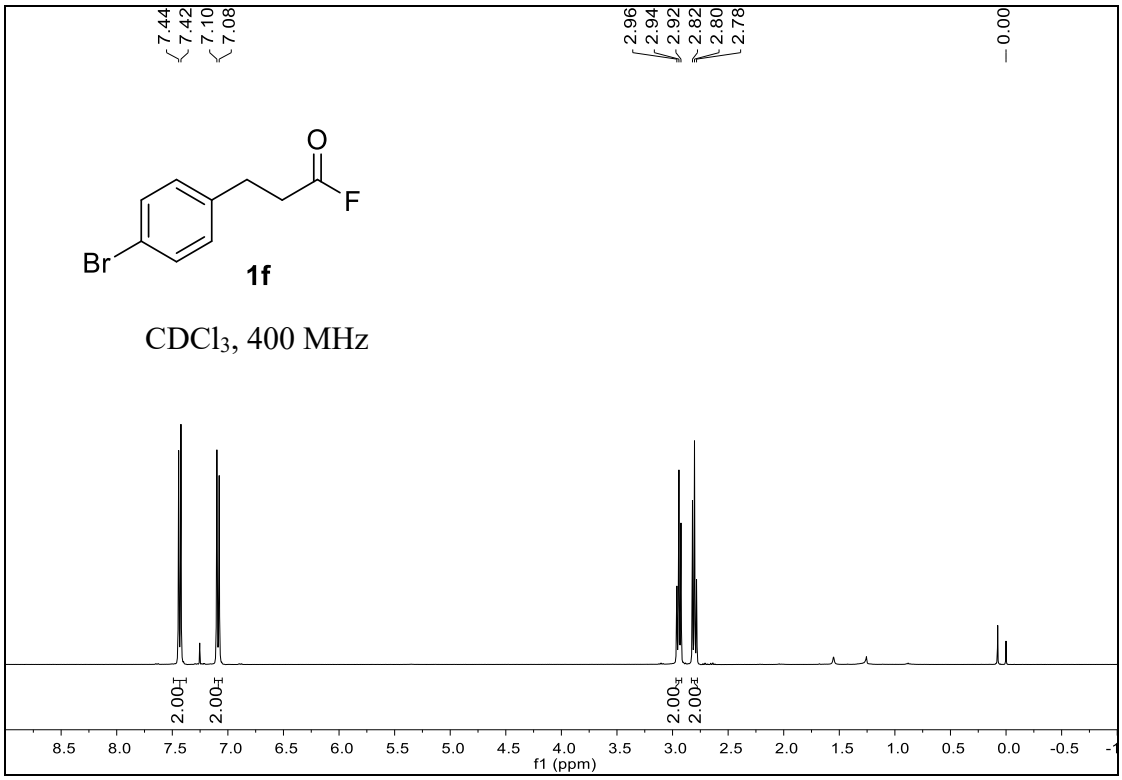

164.48
163.08
160.90
160.64
134.63
134.60
129.90
129.82
115.78
115.57
77.42
77.10
76.78
34.32
33.82
29.29
29.26
O
F
F
1d
CDCl3, 101 MHz
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

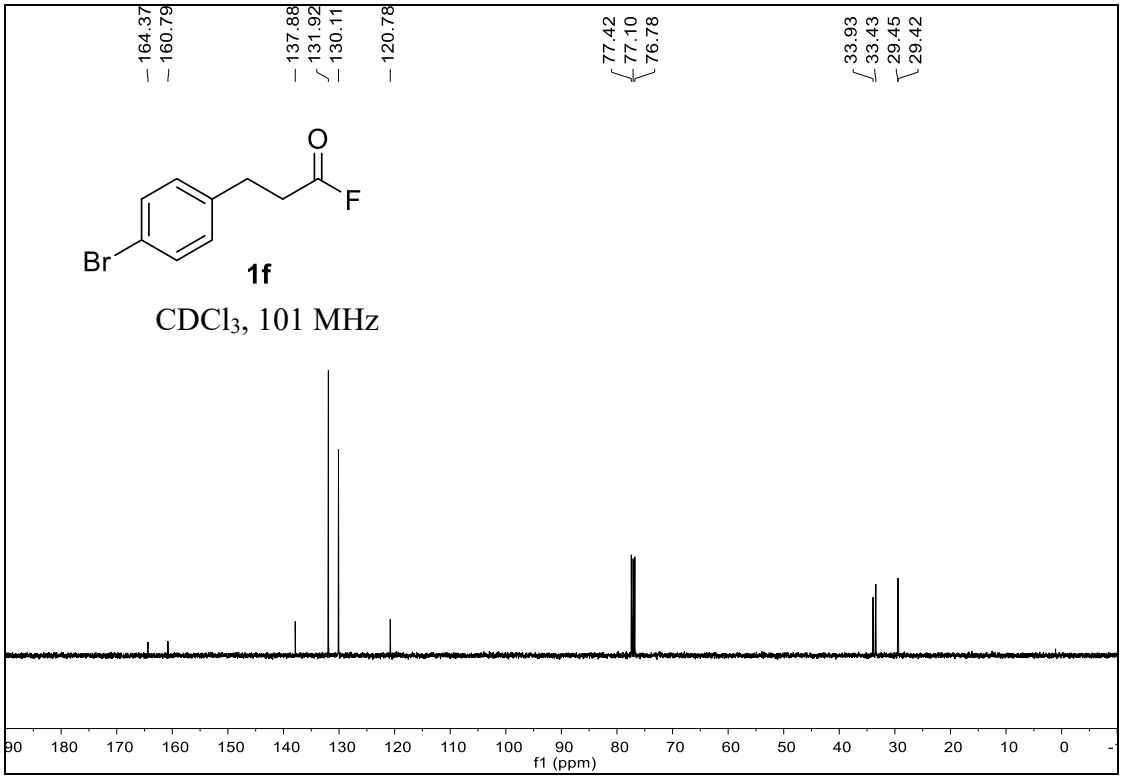


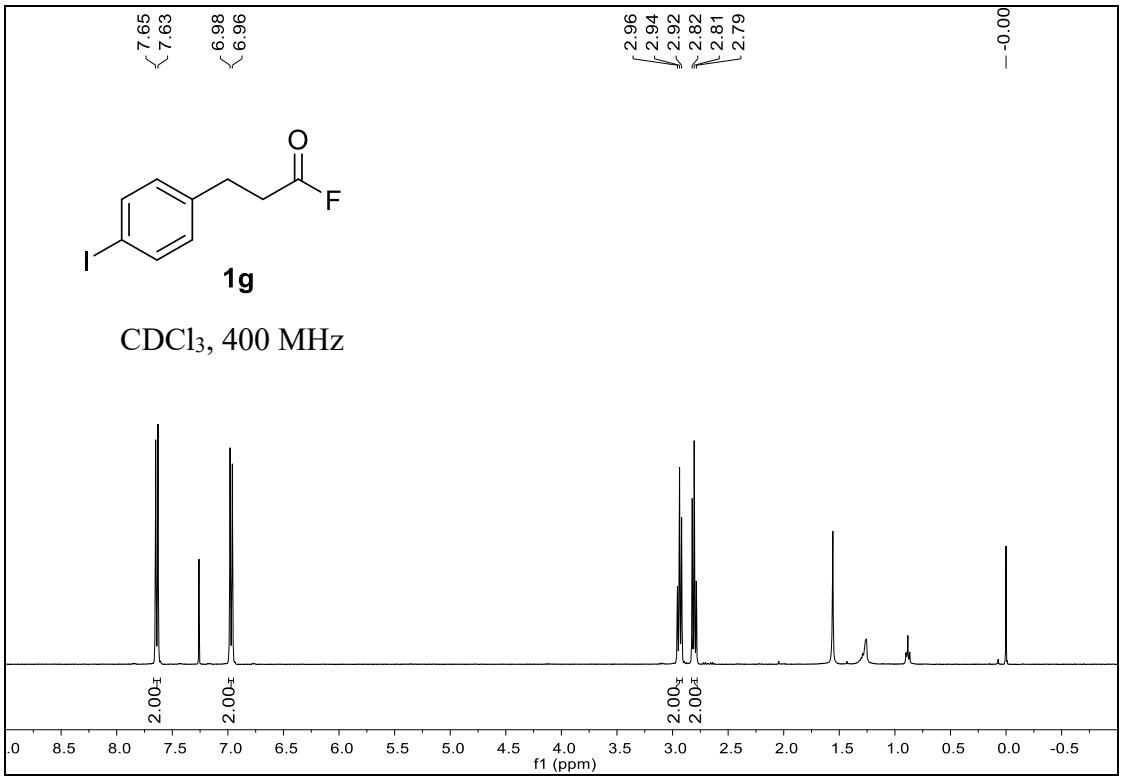
$CDCl_3$, 400 MHz

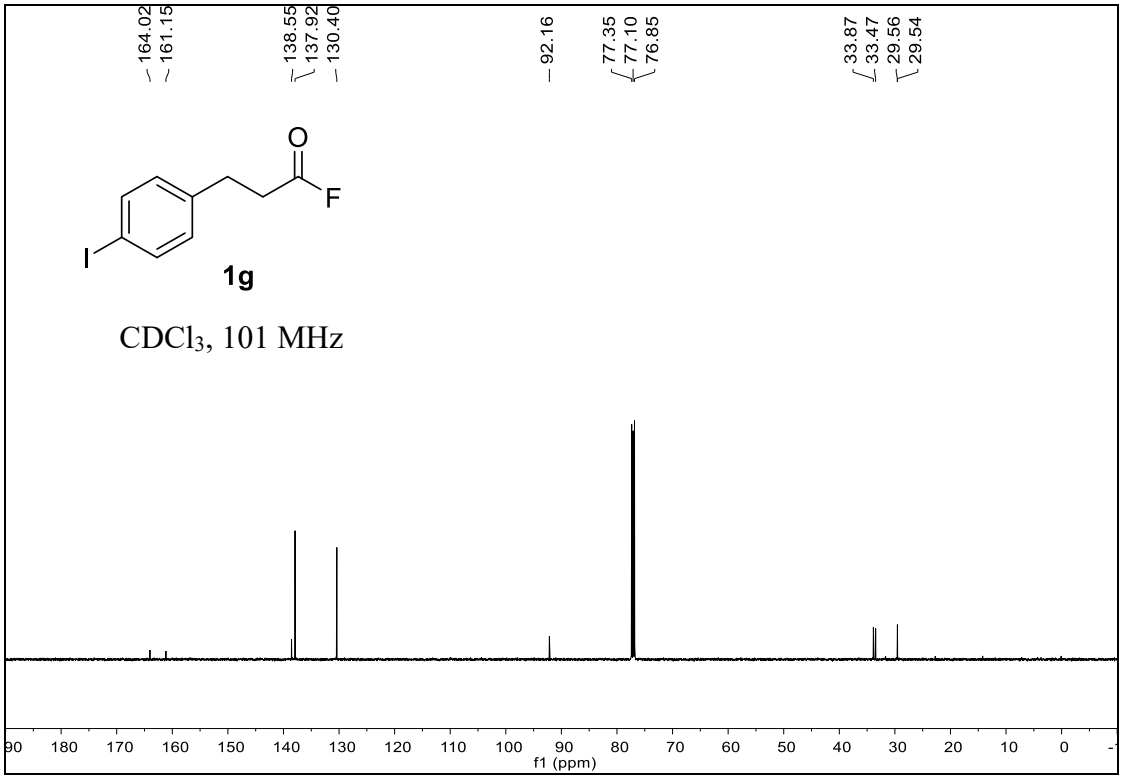


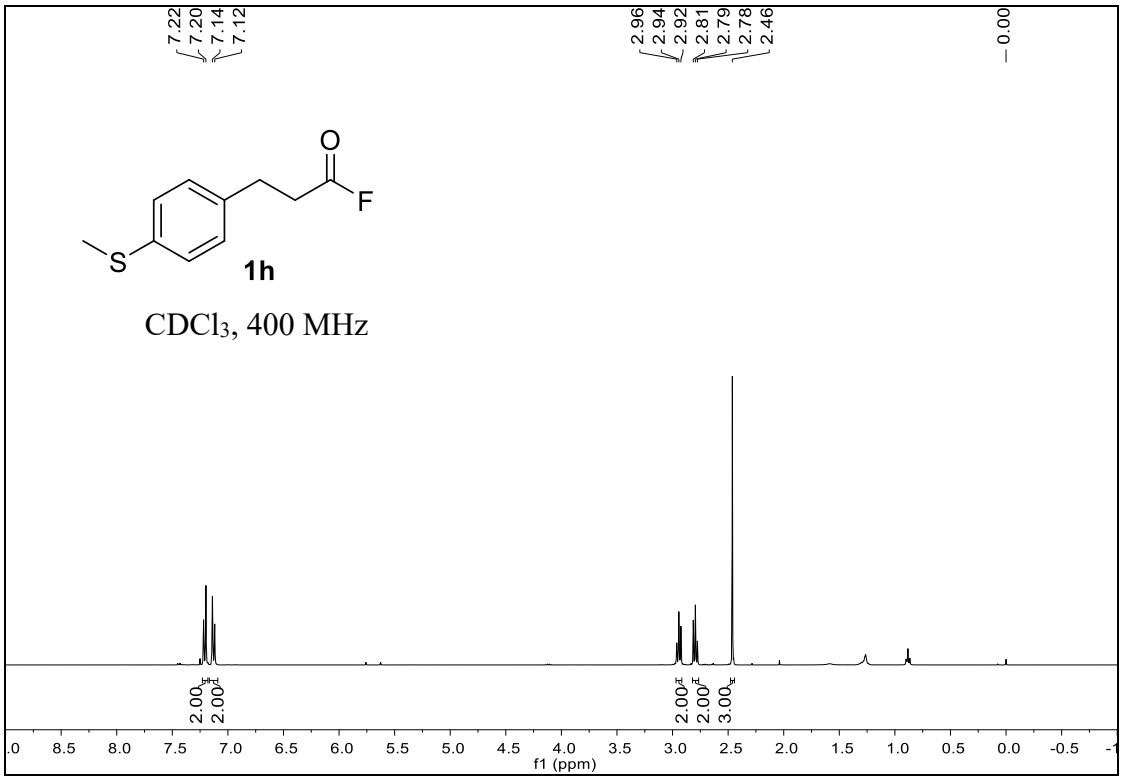
$CDCl_3$, 101 MHz


7.44
7.42
7.10
7.08
2.96
2.94
2.92
2.82
2.80
2.78
0.00
O
F
Br
1f
CDCl3, 400 MHz
2.00
2.00
2.00
2.00
f1 (ppm)

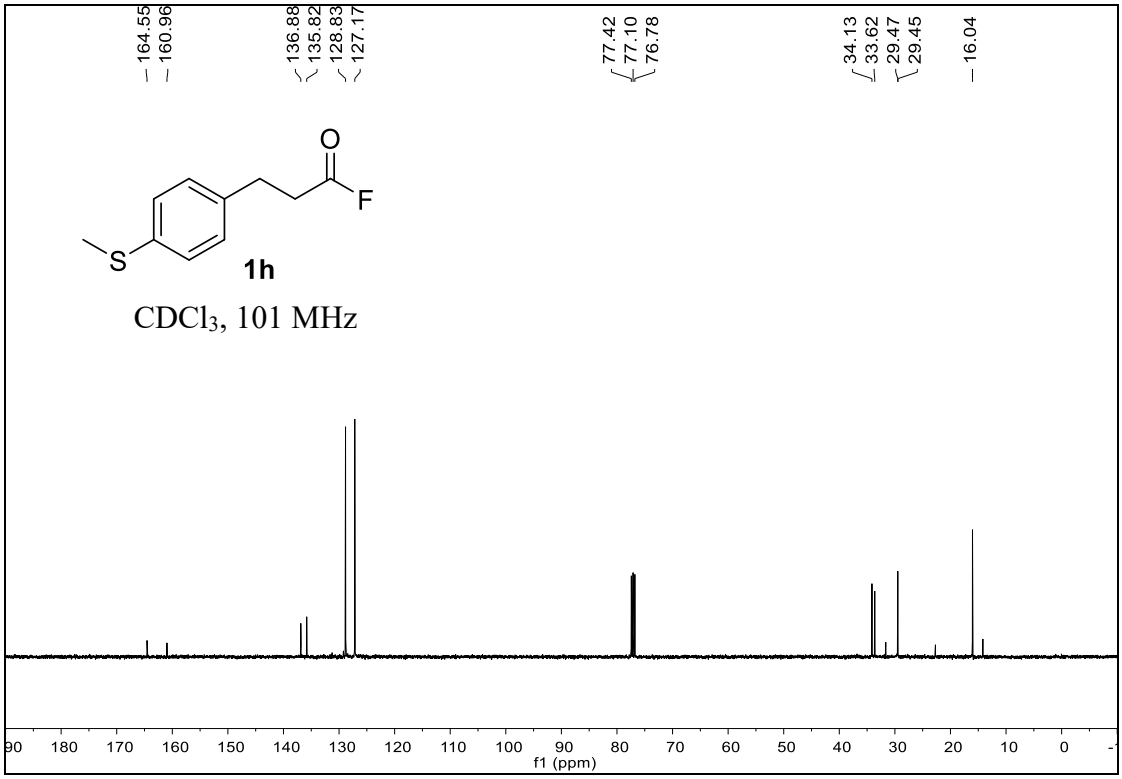

164.37
160.79
137.88
131.92
130.11
120.78
77.42
77.10
76.78
33.93
33.43
29.45
29.42
O
F
Br
1f
CDCl3, 101 MHz
f1 (ppm)


7.65
7.63
6.98
6.96
2.96
2.94
2.92
2.82
2.81
2.79
-0.00
O
F
I
1g
CDCl3, 400 MHz
2.00
2.00
2.00
2.00
f1 (ppm)

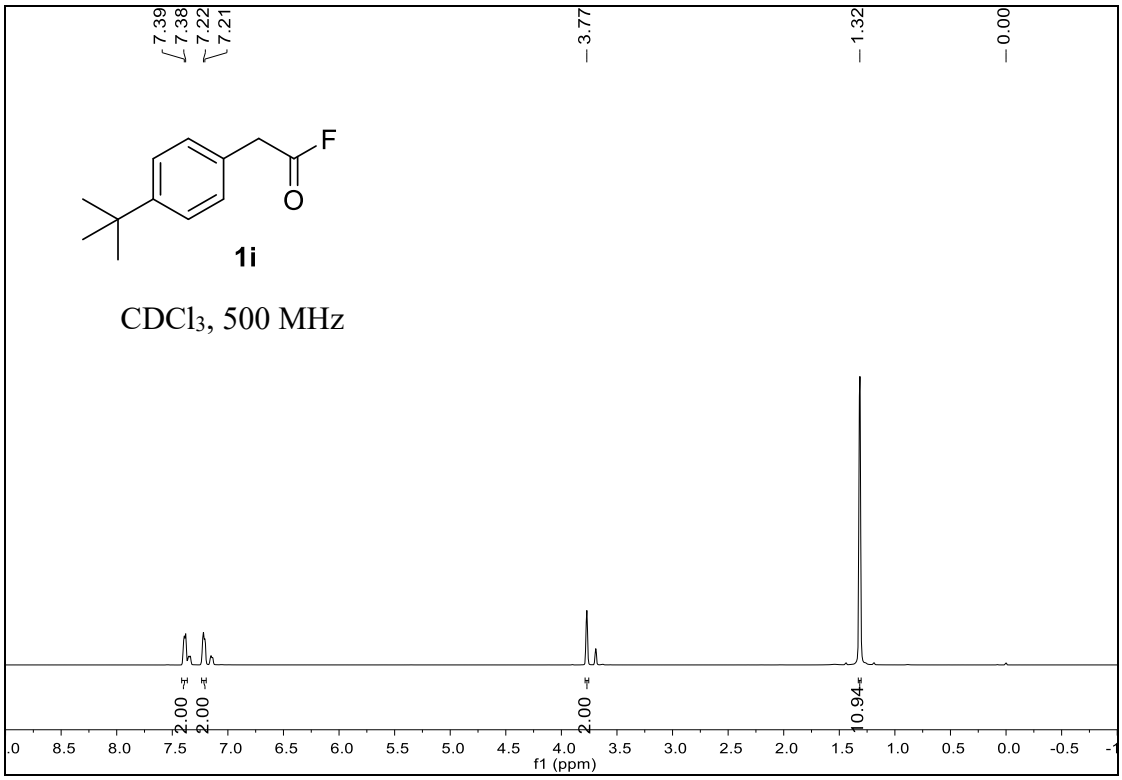

164.02
161.15
138.55
137.92
130.40
92.16
77.35
77.10
76.85
33.87
33.47
29.56
29.54
O
F
I
1g
CDCl3, 101 MHz
f1 (ppm)



$CDCl_3$, 400 MHz

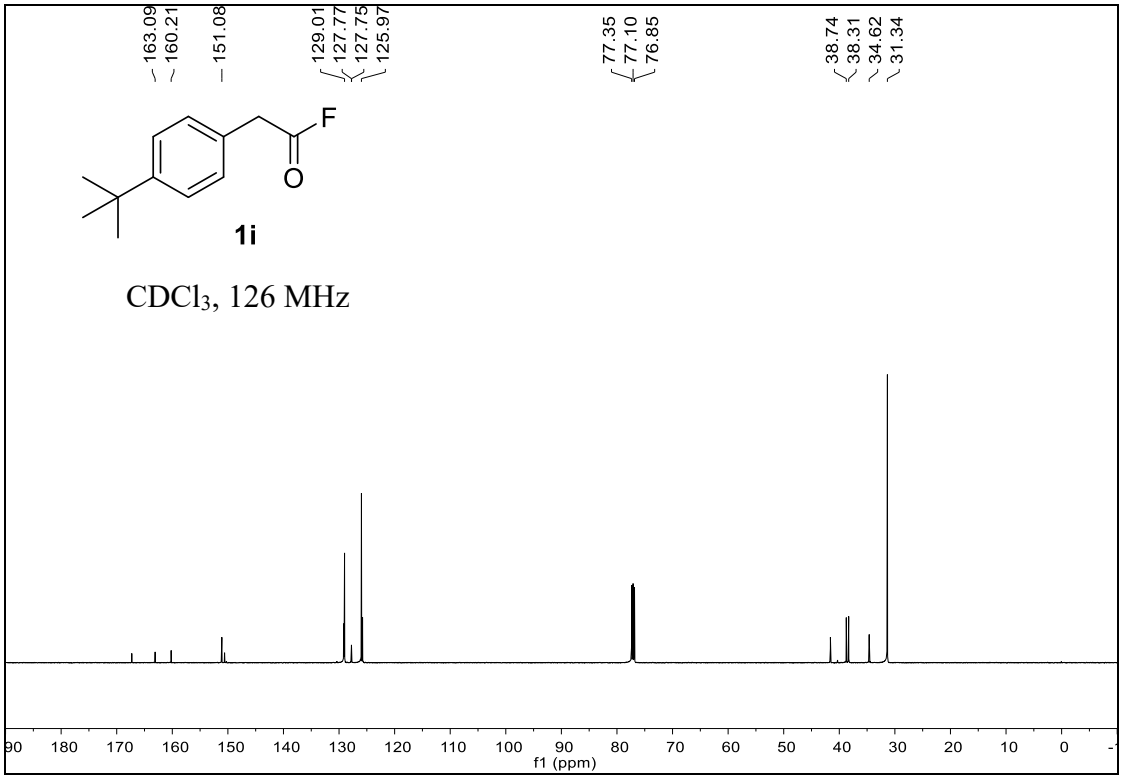


$CDCl_3$, 101 MHz



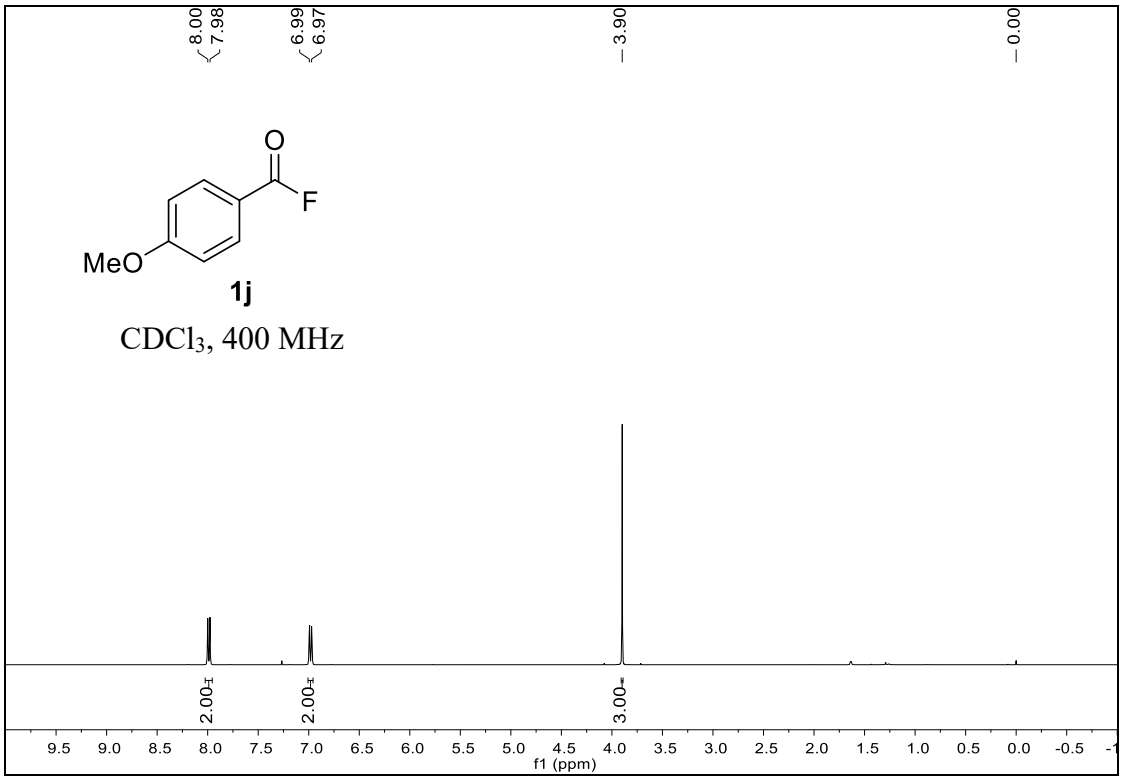
1i

$CDCl_3$, 500 MHz



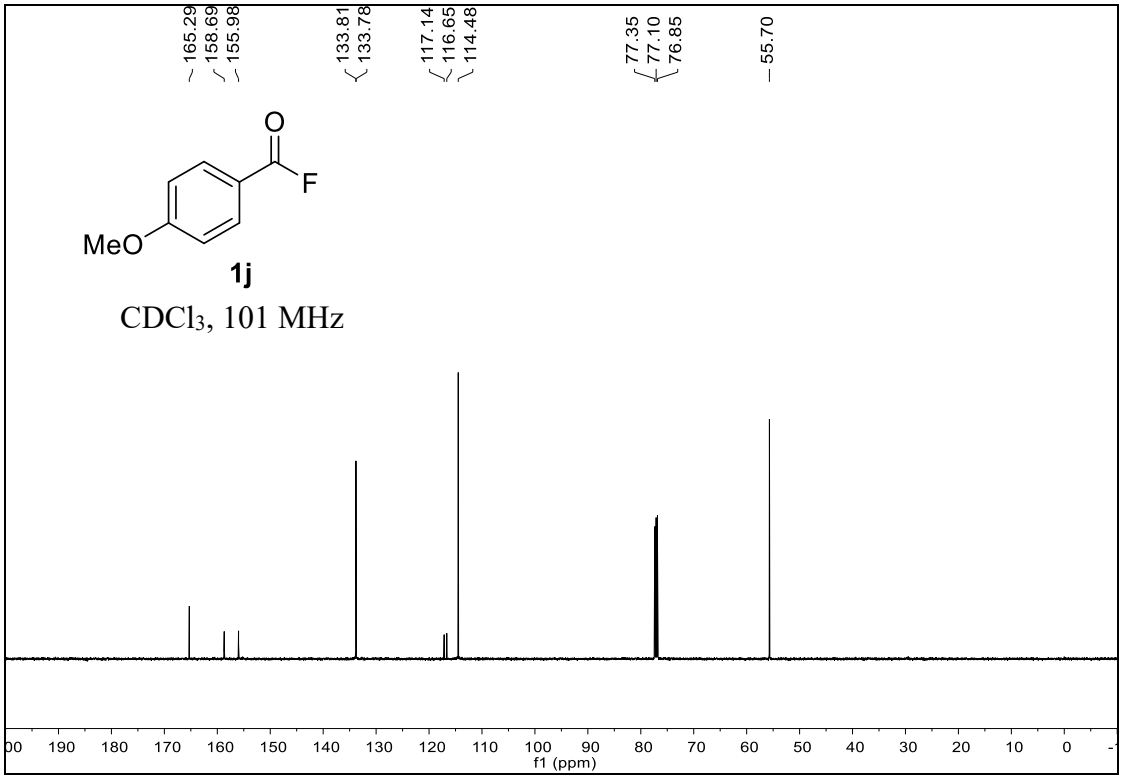
1i

$CDCl_3$, 126 MHz



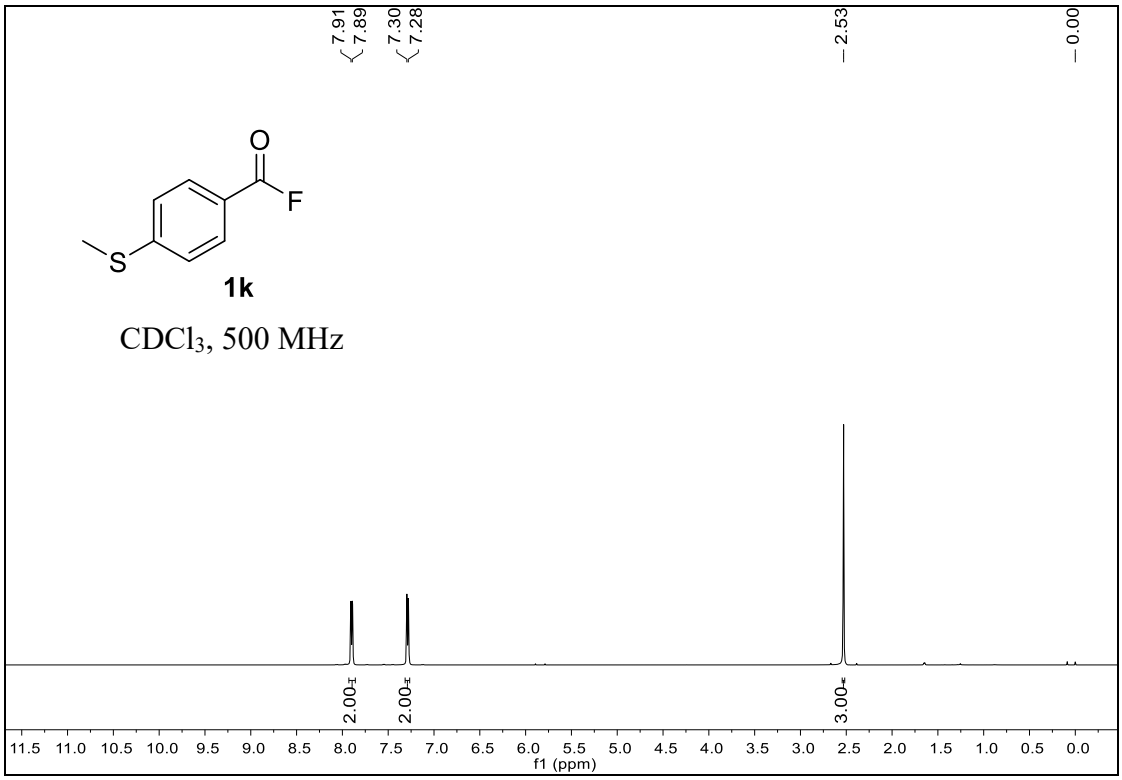
1j

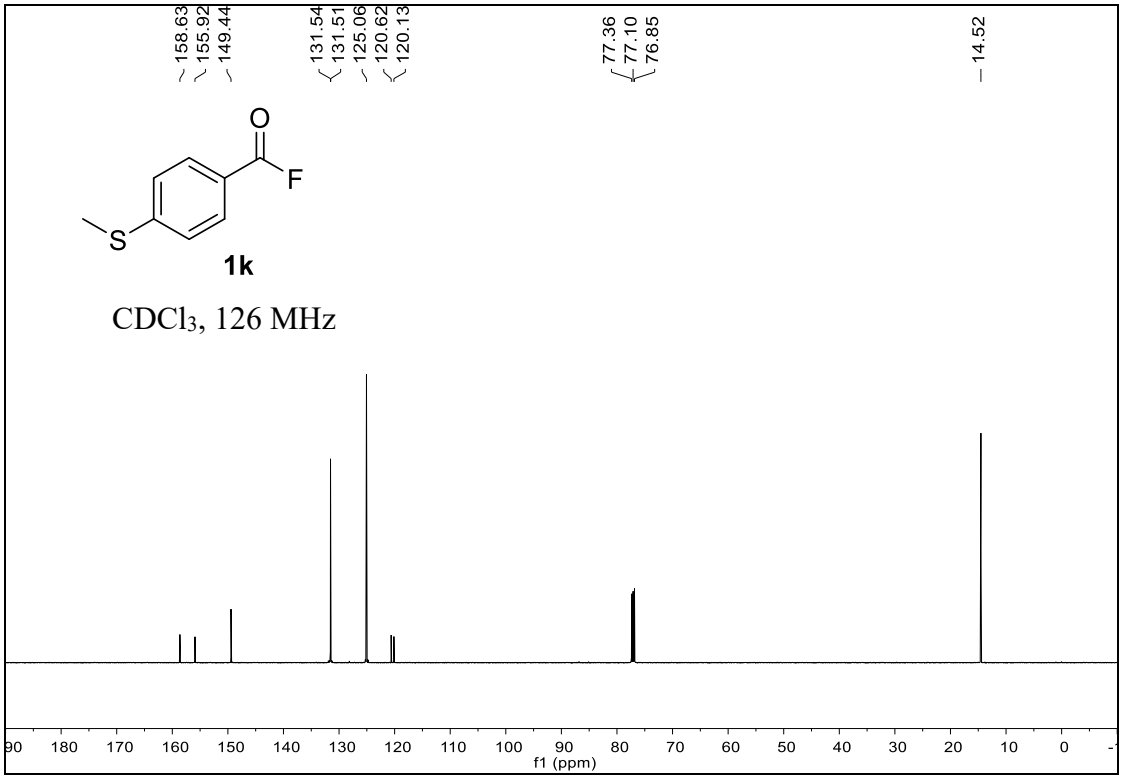
$CDCl_3$, 400 MHz

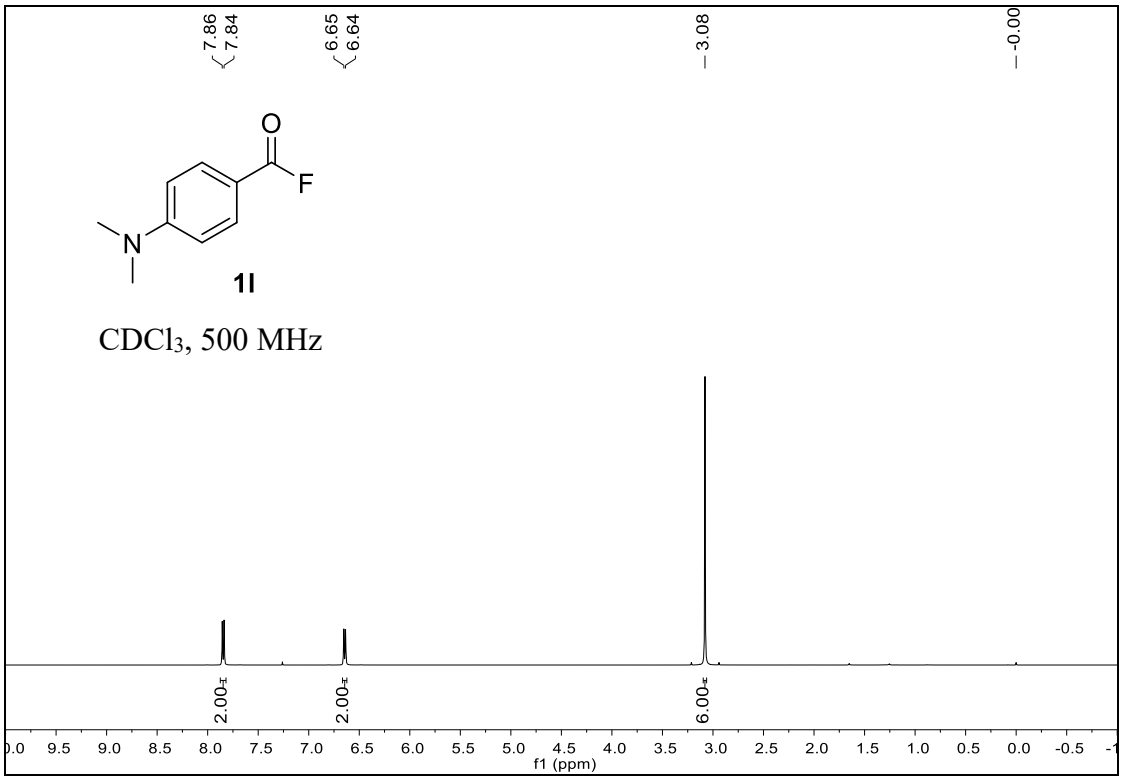


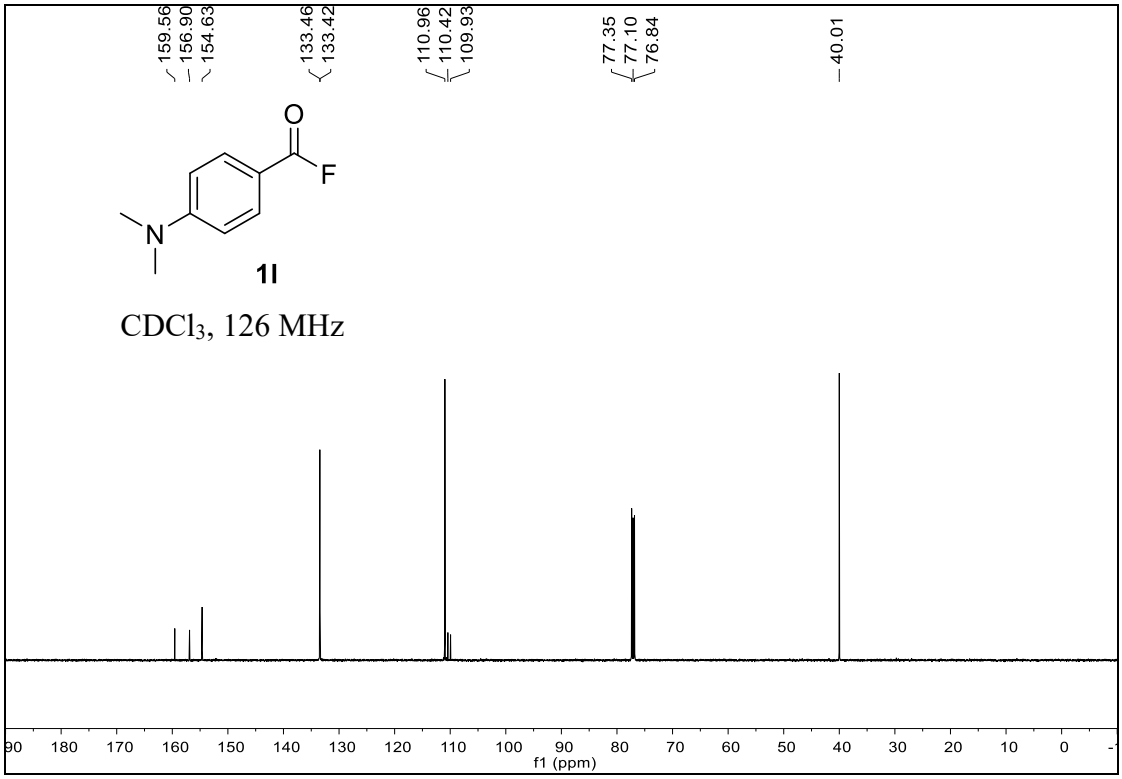
1j

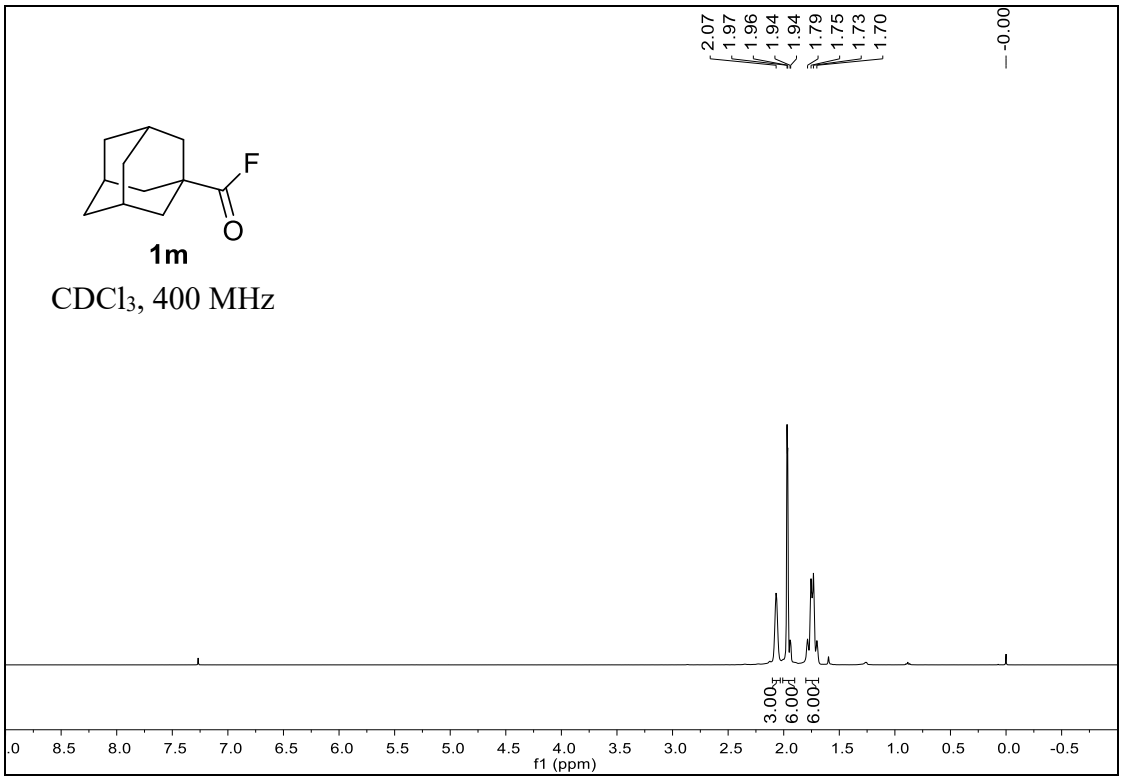
$CDCl_3$, 101 MHz

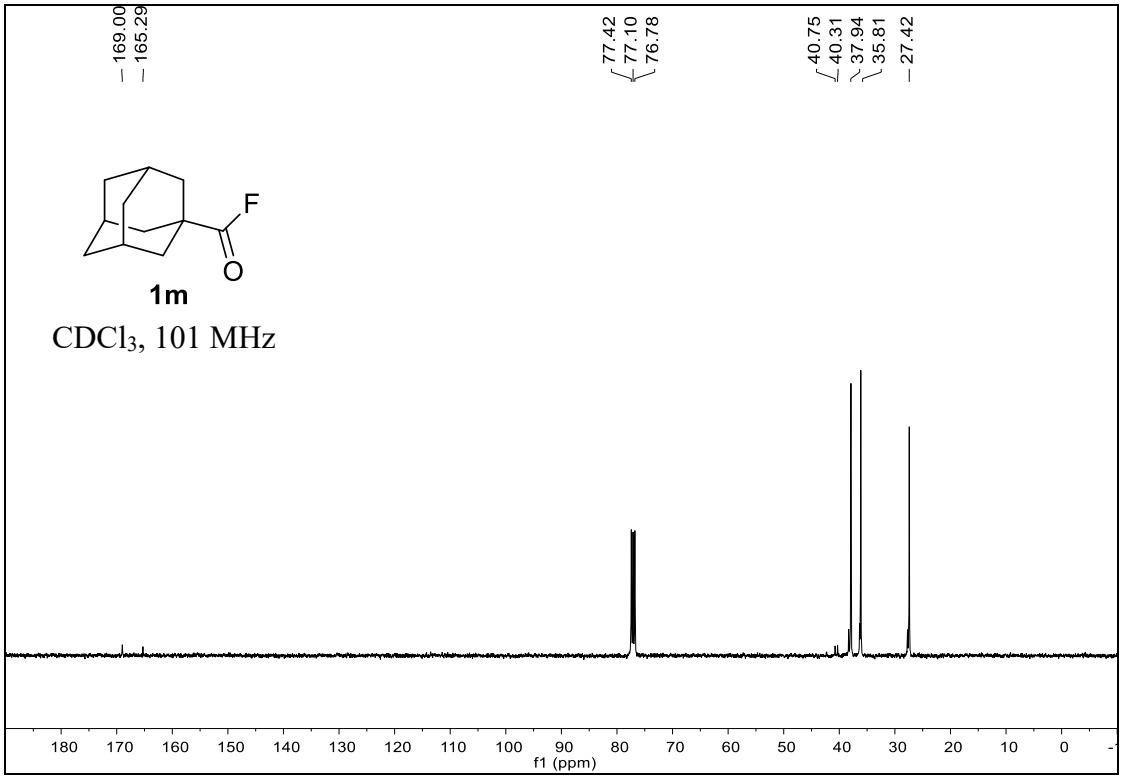

7.91
7.89
7.30
7.28
2.53
0.00
O
F
S
1k
CDCl3, 500 MHz
2.00
2.00
3.00
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

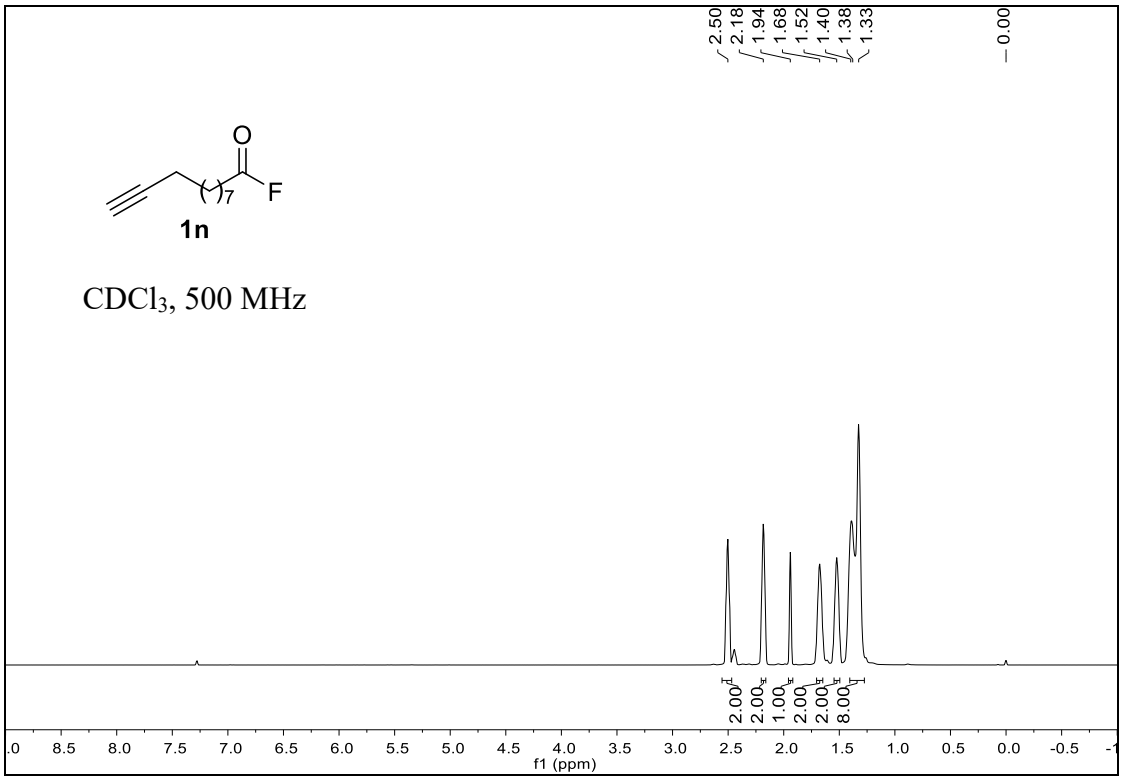

158.63
155.92
149.44
131.54
131.51
125.06
120.62
120.13
77.36
77.10
76.85
14.52
O
F
S
1k
CDCl3, 126 MHz
90 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

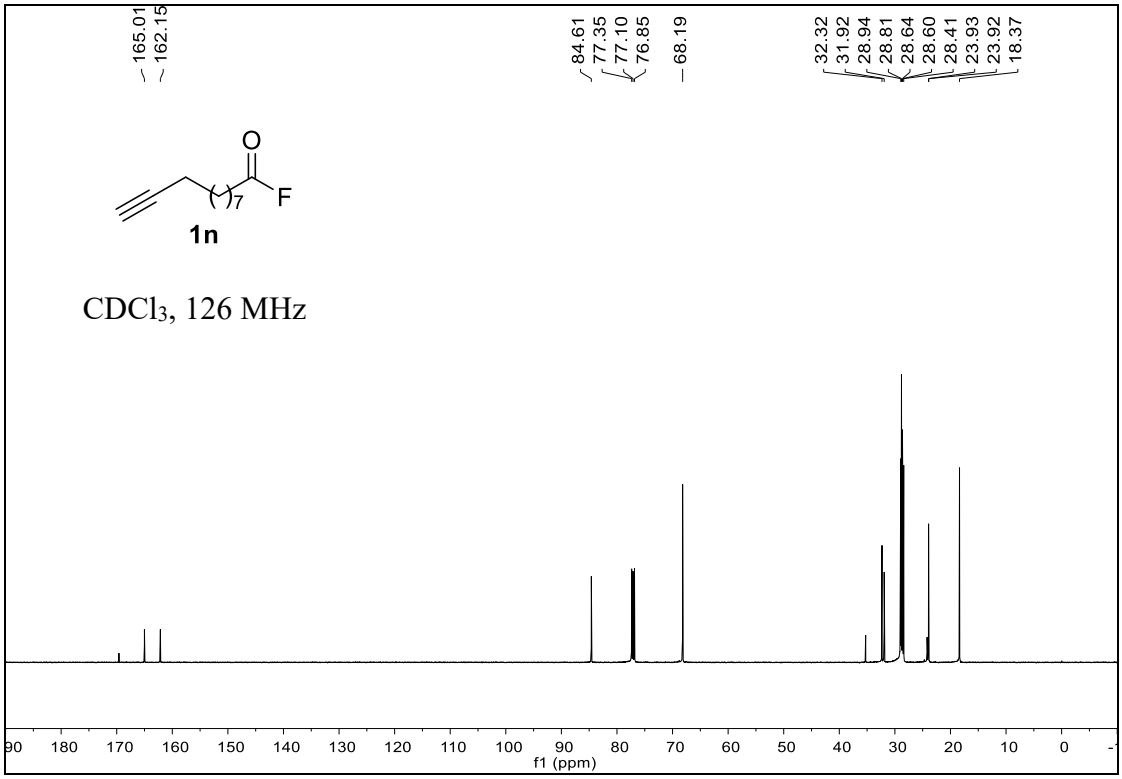

7.86
7.84
6.65
6.64
3.08
-0.00
O
F
N
1l
CDCl3, 500 MHz
2.00
2.00
6.00
f1 (ppm)

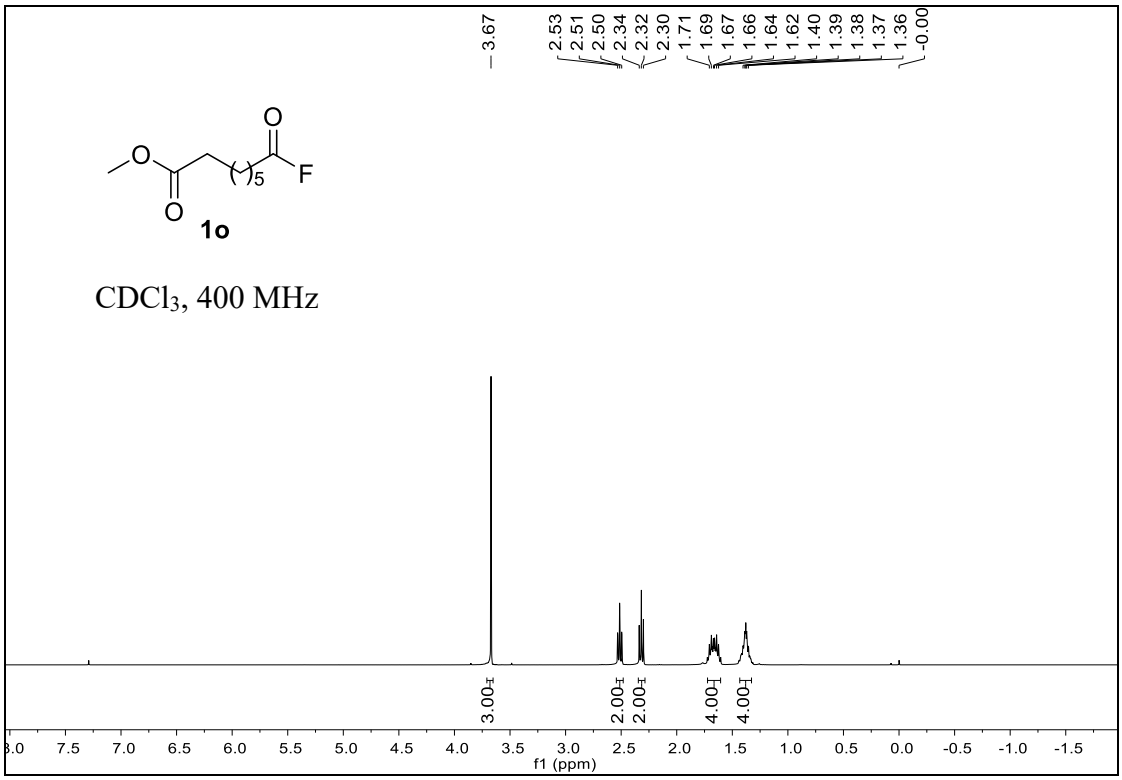

159.56
156.90
154.63
133.46
133.42
110.96
110.42
109.93
77.35
77.10
76.84
40.01
O
F
N
1l
CDCl3, 126 MHz
f1 (ppm)

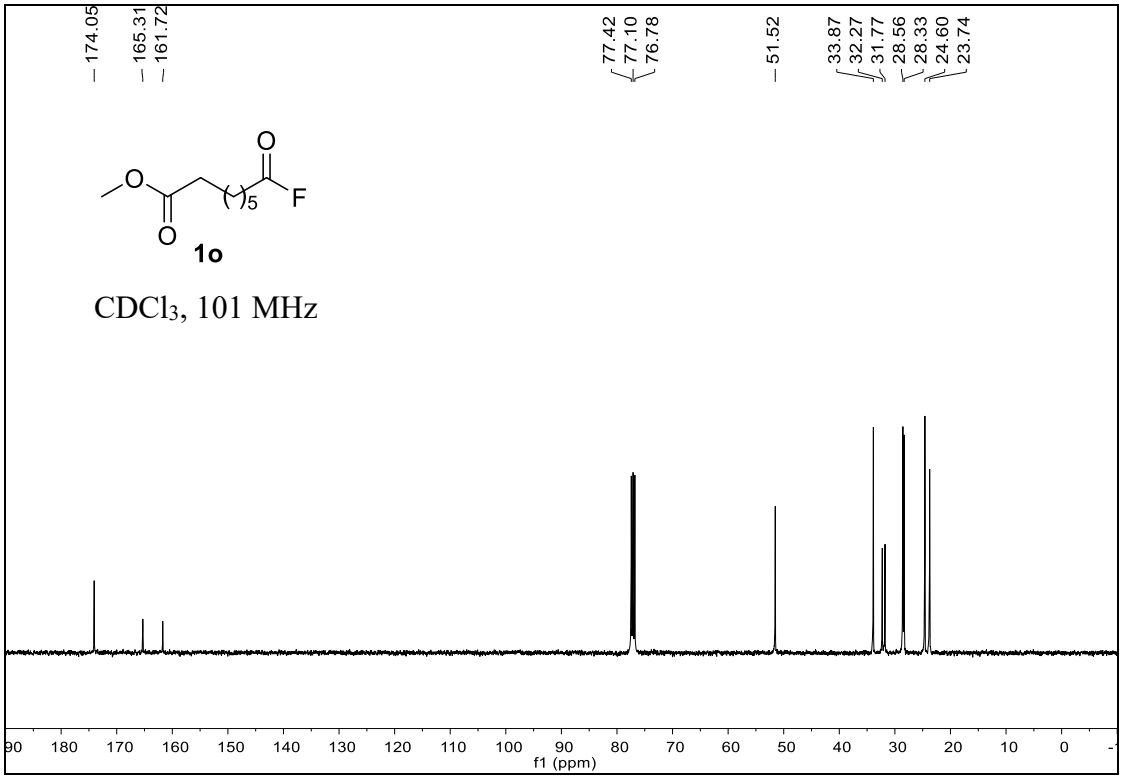

2.07
1.97
1.96
1.94
1.94
1.79
1.75
1.73
1.70
-0.00
F
O
1m
CDCl3, 400 MHz
3.00
6.00
6.00
f1 (ppm)

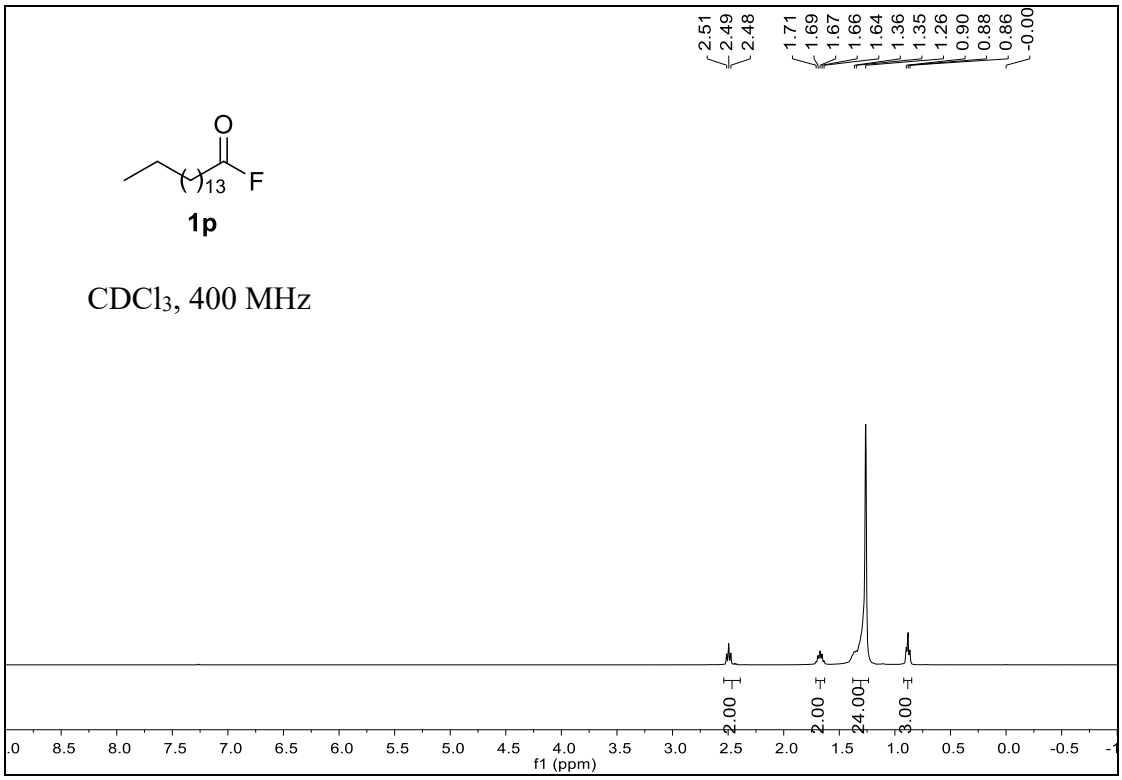

169.00
165.29
77.42
77.10
76.78
40.75
40.31
37.94
35.81
27.42
F
O
1m
CDCl3, 101 MHz
f1 (ppm)

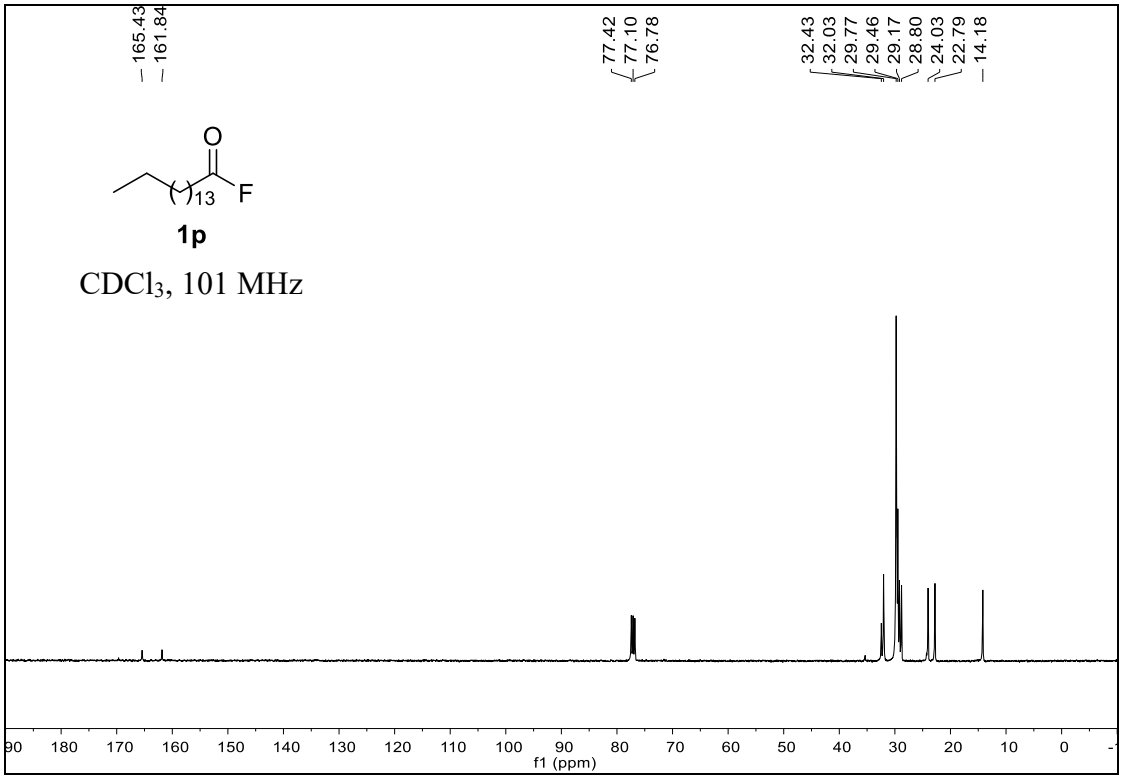

2.50
2.18
1.94
1.68
1.52
1.40
1.38
1.33
0.00
O
F
7
1n
CDCl3, 500 MHz
2.00
2.00
1.00
2.00
2.00
8.00
f1 (ppm)

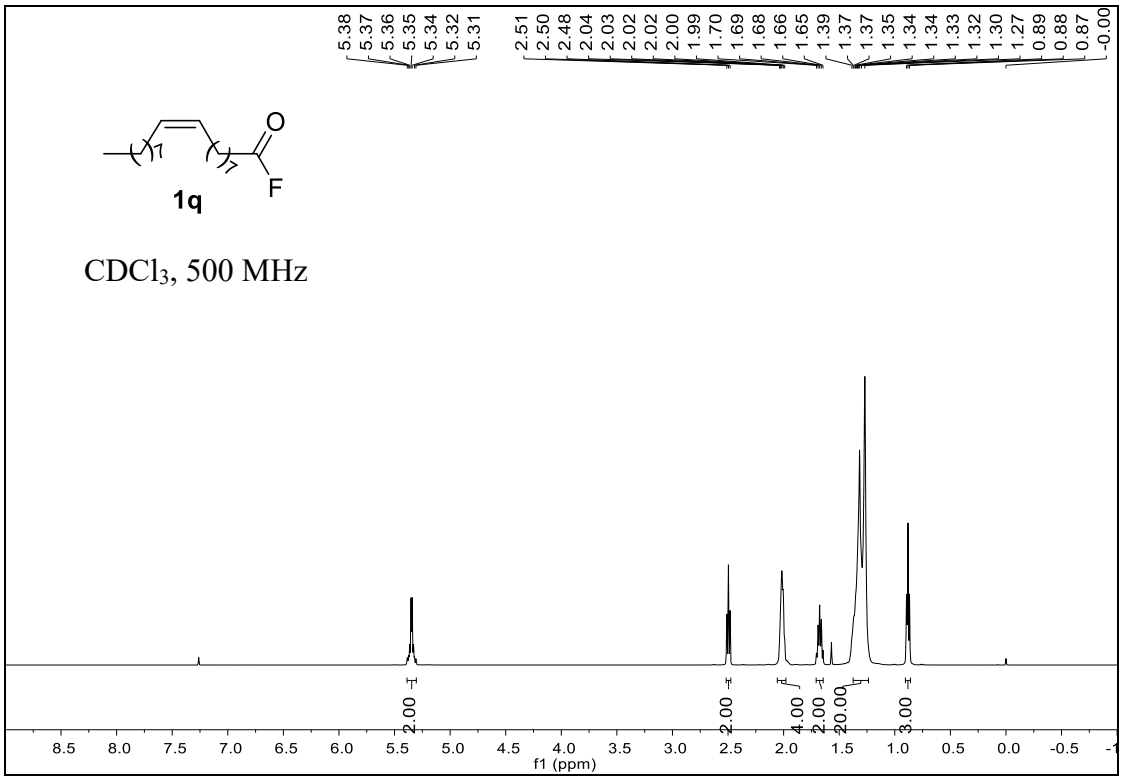

165.01
162.15
84.61
77.35
77.10
76.85
68.19
32.32
31.92
28.94
28.81
28.64
28.60
28.41
23.93
23.92
18.37
O
F
7
1n
CDCl3, 126 MHz
f1 (ppm)


3.67
2.53
2.51
2.50
2.34
2.32
2.30
1.71
1.69
1.67
1.66
1.64
1.62
1.40
1.39
1.38
1.37
1.36
-0.00
O
O
O
F
5
1o
CDCl3, 400 MHz
3.00
2.00
2.00
4.00
4.00
f1 (ppm)

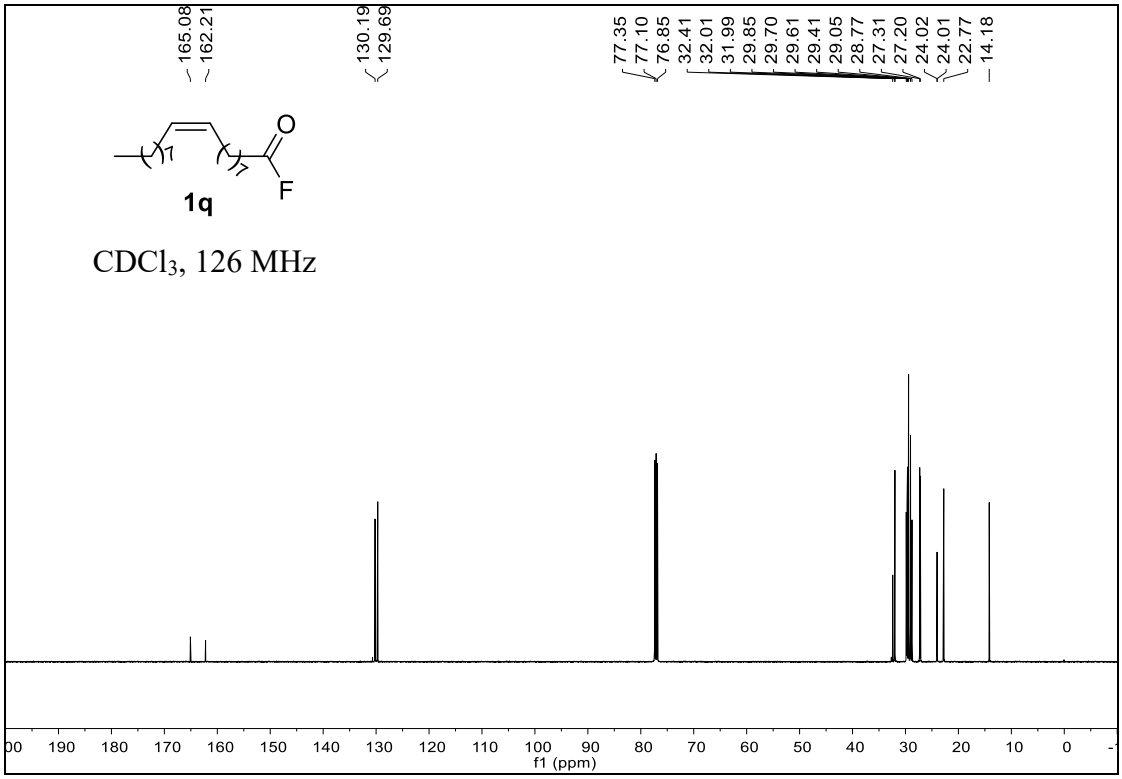

174.05
165.31
161.72
77.42
77.10
76.78
51.52
33.87
32.27
31.77
28.56
28.33
24.60
23.74
O
O
O
F
5
1o
CDCl3, 101 MHz
f1 (ppm)


2.51
2.49
2.48
1.71
1.69
1.67
1.66
1.64
1.36
1.35
1.26
0.90
0.88
0.86
-0.00
O
13
F
1p
CDCl3, 400 MHz
2.00
2.00
24.00
3.00
f1 (ppm)

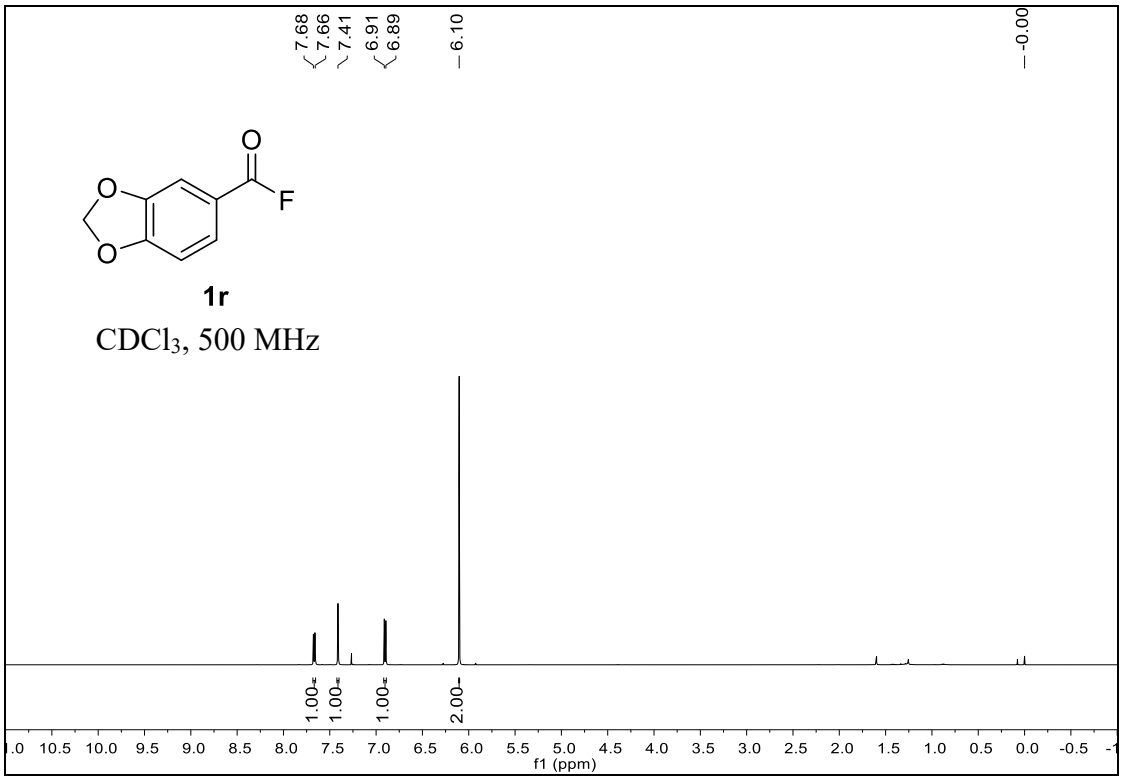

165.43
161.84
77.42
77.10
76.78
32.43
32.03
29.77
29.46
29.17
28.80
24.03
22.79
14.18
O
13
F
1p
CDCl3, 101 MHz
f1 (ppm)

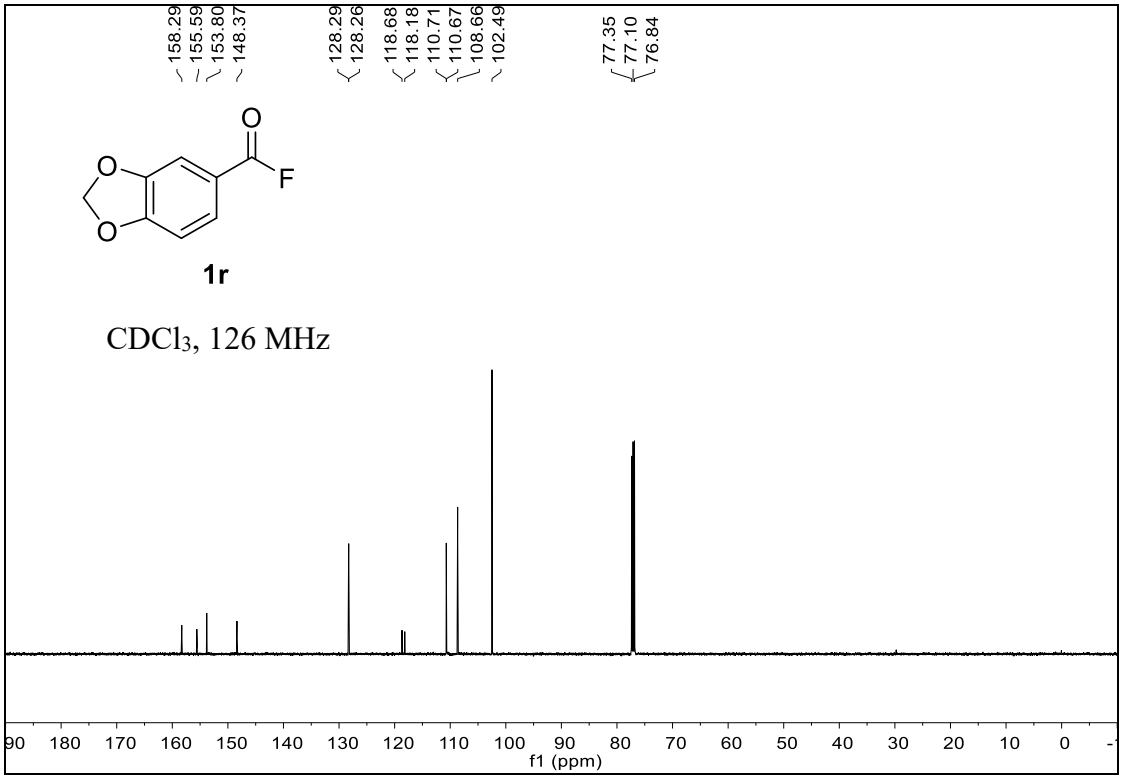


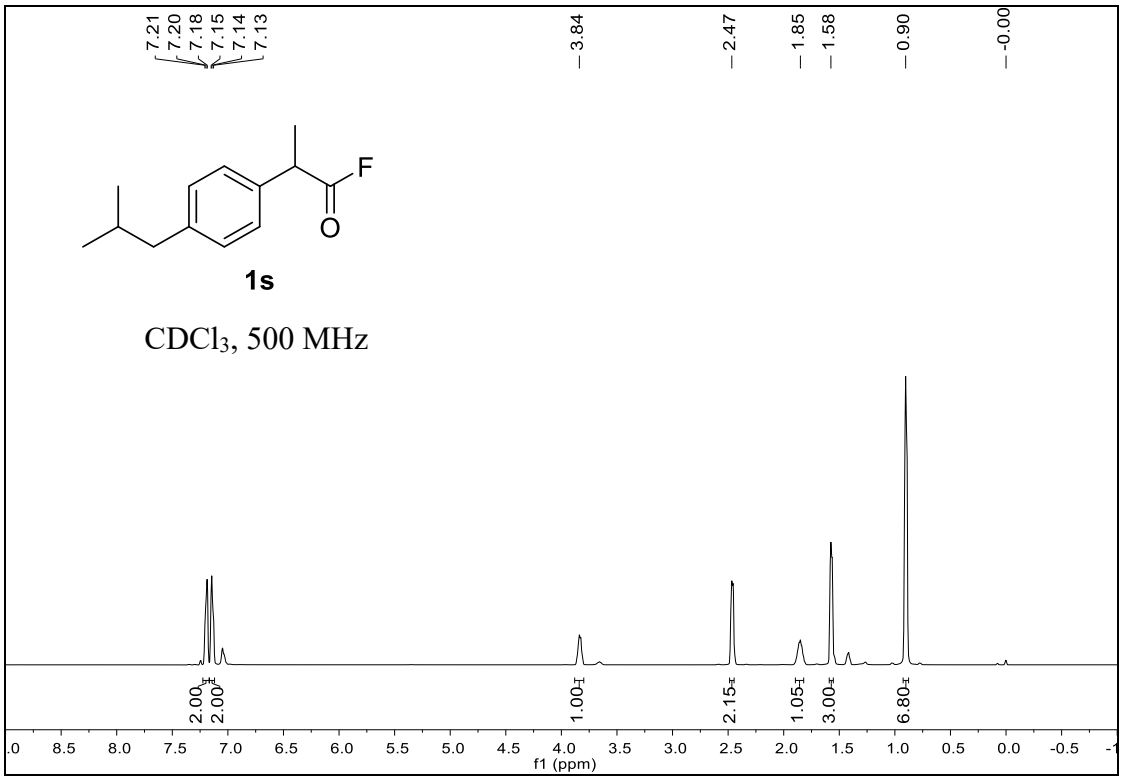
$CDCl_3$, 500 MHz



$CDCl_3$, 126 MHz

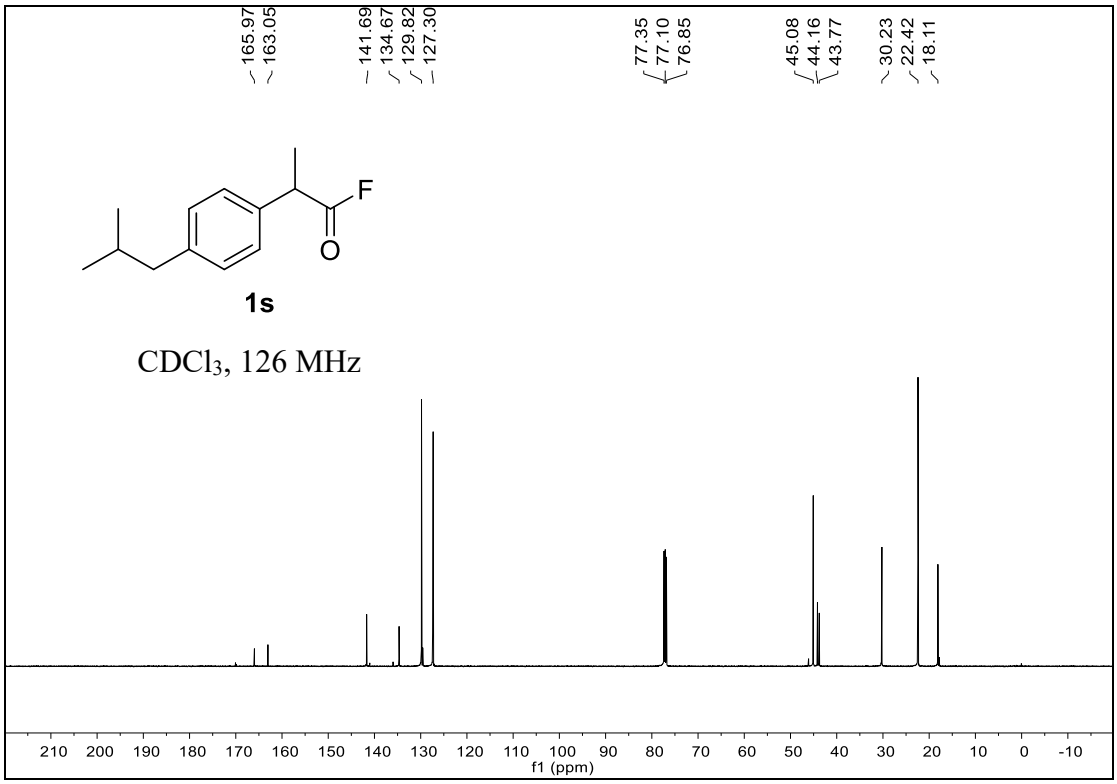

7.68
7.66
7.41
6.91
6.89
6.10
-0.00
O
O
O
F
1r
CDCl3, 500 MHz
1.00
1.00
1.00
2.00
f1 (ppm)


158.29
155.59
153.80
148.37
128.29
128.26
118.68
118.18
110.71
110.67
108.66
102.49
77.35
77.10
76.84
O
O
O
F
1r
CDCl3, 126 MHz
f1 (ppm)



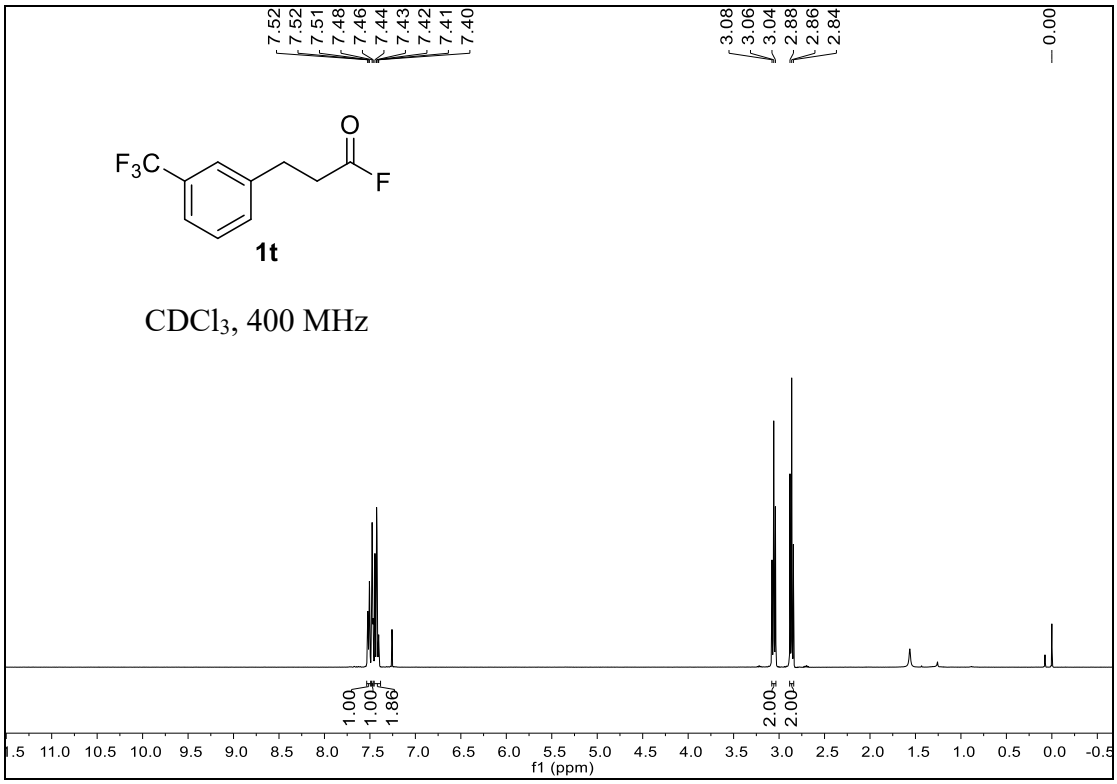
1s

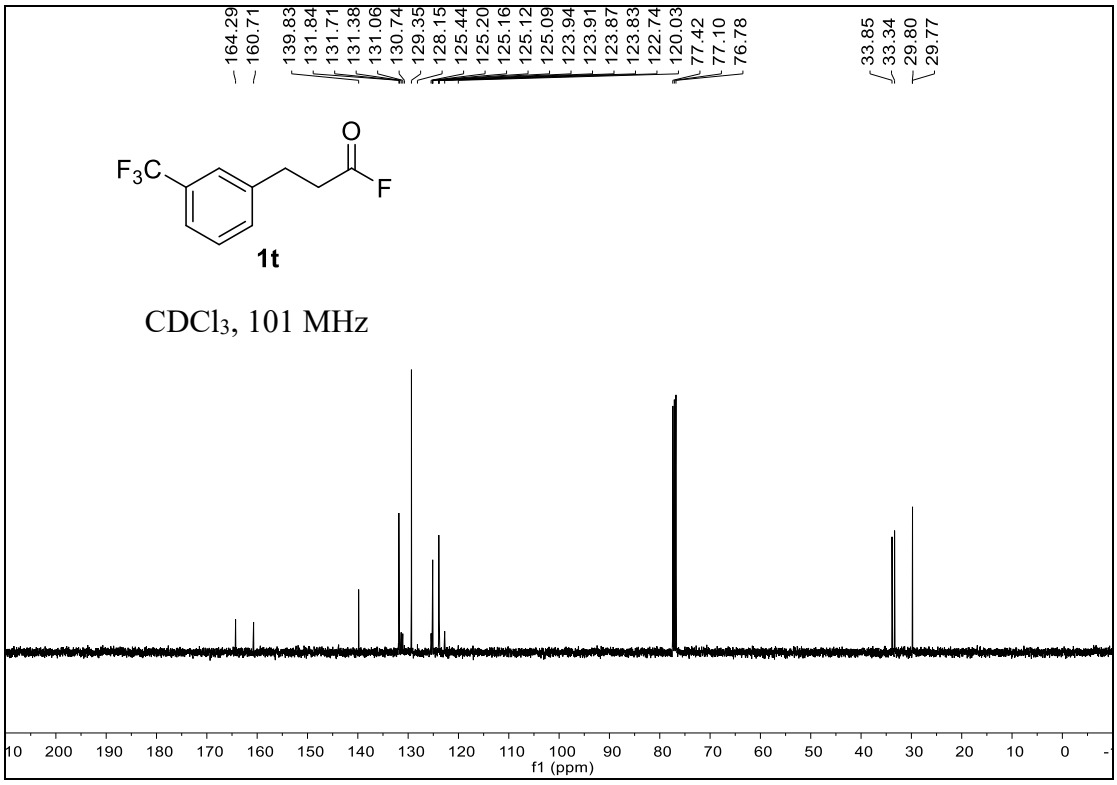
$CDCl_3$, 500 MHz

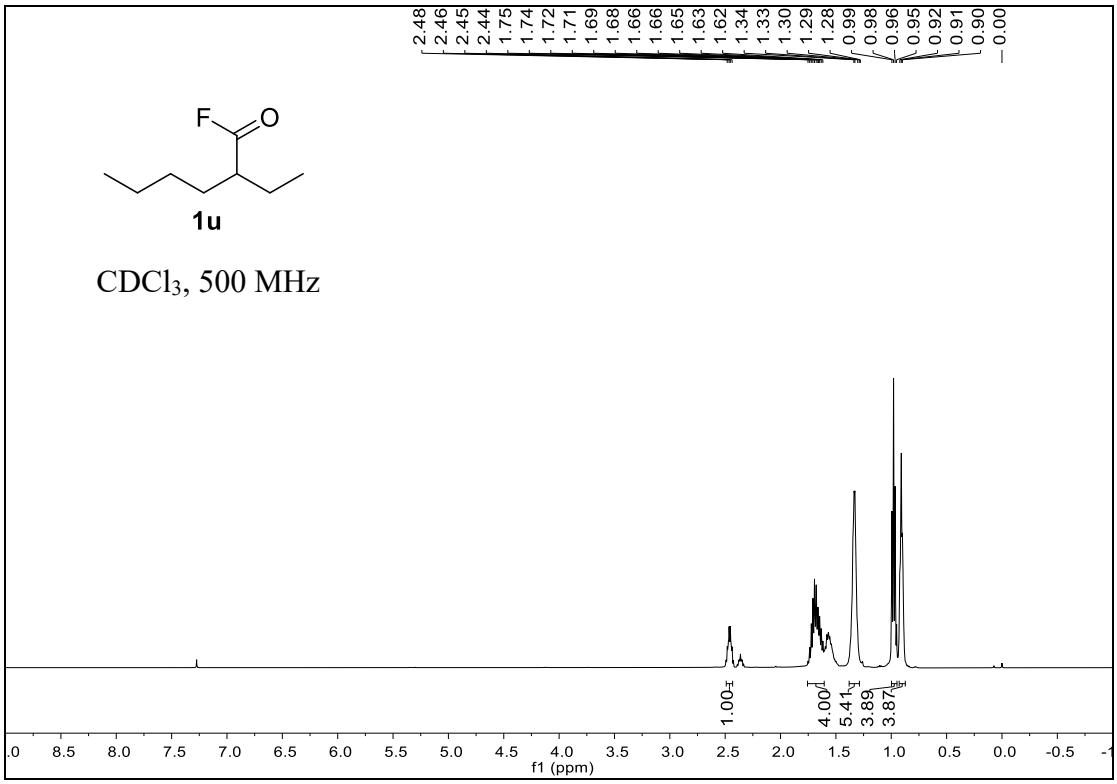


1s

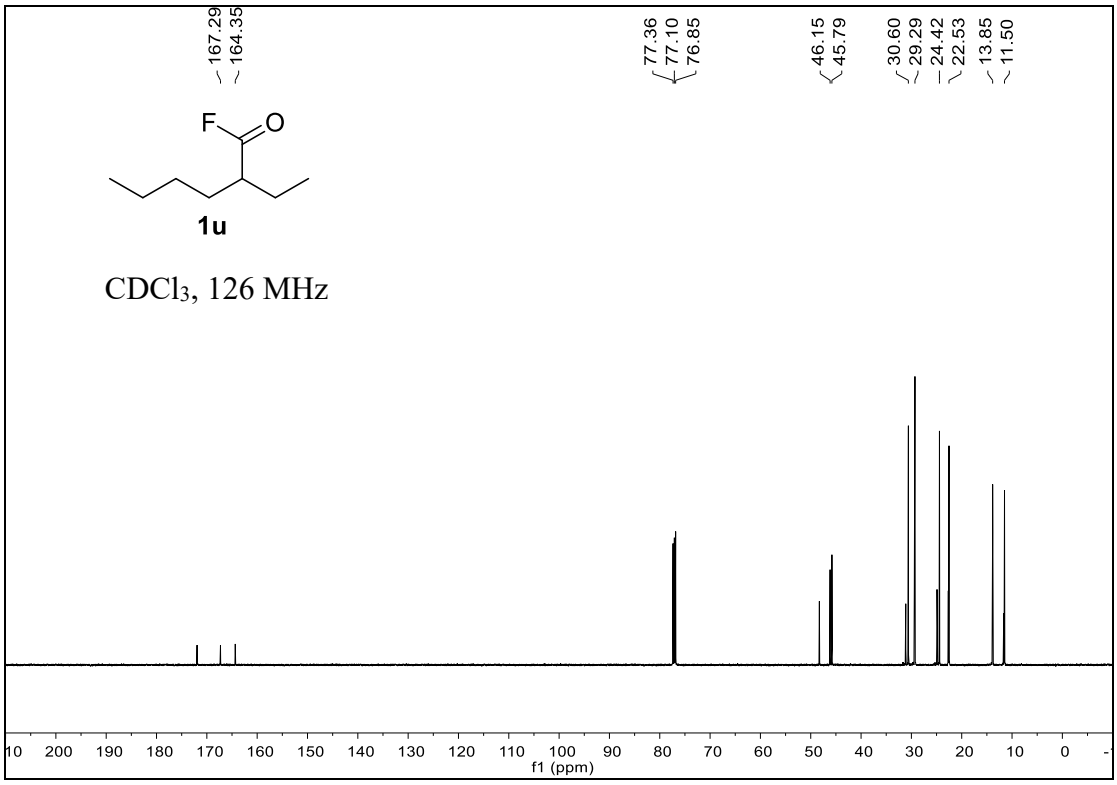
$CDCl_3$, 126 MHz


7.52
7.52
7.51
7.48
7.46
7.44
7.43
7.42
7.41
7.40
3.08
3.06
3.04
2.88
2.86
2.84
0.00
O
F3C
F
1t
CDCl3, 400 MHz
1.00
1.00
1.86
2.00
2.00
f1 (ppm)


164.29
160.71
139.83
131.84
131.71
131.38
131.06
130.74
129.35
128.15
125.44
125.20
125.16
125.12
125.09
123.94
123.91
123.87
123.83
122.74
120.03
77.42
77.10
76.78
33.85
33.34
29.80
29.77
O
F3C
F
1t
CDCl3, 101 MHz
f1 (ppm)



$CDCl_3$, 500 MHz



$CDCl_3$, 126 MHz

9. Cartesian Coordinates with Zero-Point Energies and Thermal Corrections

PhCHO_CH_3CN - b3lyp/6-311++g(d,p)

Energy: -345.676370 au

Sum of electronic and thermal Free Energies: -345.597605 au

Geometry:

O	-2.85430600	-0.39146600	-0.00000700
C	-1.98670400	0.46372700	0.00000000
C	-0.53559800	0.20083100	0.00000100
C	-0.03396000	-1.10991800	-0.00000200
H	-0.72801800	-1.94196800	-0.00000400
C	1.33777400	-1.32572400	-0.00000100
H	1.72885000	-2.33644400	-0.00000200
C	2.21723700	-0.23723300	0.00000200
H	3.28745300	-0.41011800	0.00000300
C	1.72514800	1.06799800	0.00000400
H	2.40970100	1.90789400	0.00000700
C	0.34978400	1.28670500	0.00000300
H	-0.04290400	2.29829900	0.00000500
H	-2.26272500	1.53574900	-0.00000300

PhCHO_CH_3CN anion radical - b3lyp/6-311++g(d,p)

Energy: -345.770542 au

Sum of electronic and thermal Free Energies: -345.695655 au

Geometry:

O	-2.90651700	-0.39907500	-0.00000500

C	-1.97222800	0.47870500	-0.00000300
C	-0.57200400	0.22013600	-0.00000100
C	-0.03162100	-1.10952700	-0.00000100
H	-0.71735100	-1.94944600	-0.00000300
C	1.33761200	-1.32698500	0.00000100
H	1.71273600	-2.34717700	0.00000100
C	2.24948400	-0.25685200	0.00000300
H	3.31831400	-0.43734300	0.00000500
C	1.73852200	1.06016200	0.00000400
H	2.42509800	1.90215300	0.00000500
C	0.37653700	1.29400500	0.00000200
H	0.00587900	2.31624500	0.00000200
H	-2.25035700	1.55030500	-0.00000300

PhCOF_CH_3CN - b3lyp/6-311++g(d,p)

Energy: -444.969983 au

Sum of electronic and thermal Free Energies: -444.900051 au

Geometry:

O	-2.38504500	-1.11807100	-0.00000800
C	-1.69792100	-0.14519800	0.00000300
C	-0.23240400	-0.04650300	0.00000300
C	0.50742500	-1.23889400	0.00000000
H	-0.01258300	-2.18860900	-0.00000100
C	1.89550100	-1.19005600	0.00000000
H	2.46838800	-2.10944900	-0.00000200

C	2.54980100	0.04415600	0.00000300
H	3.63310900	0.07984100	0.00000200
C	1.81619500	1.23124100	0.00000500
H	2.32730200	2.18635600	0.00000700
C	0.42580000	1.19153800	0.00000500
H	-0.14630900	2.10944100	0.00000700
F	-2.30843600	1.08769800	-0.00000700

PhCOF_CH_3CN anion radical - b3lyp/6-311++g(d,p)

Energy: -445.066652 au

Sum of electronic and thermal Free Energies: -445.001153 au

Geometry:

O	-2.43323600	-1.13794900	0.00000500
C	-1.67208800	-0.16540300	-0.00001100
C	-0.26975800	-0.05569800	-0.00001400
C	0.53119100	-1.25313800	-0.00001000
H	0.03153300	-2.21510300	-0.00001500
C	1.91113000	-1.18696800	0.00000000
H	2.48390000	-2.11012700	0.00000300
C	2.58712900	0.05059800	0.00000600
H	3.66995900	0.09203700	0.00001400
C	1.81819300	1.23330900	0.00000200
H	2.31957800	2.19705300	0.00000700
C	0.43664700	1.19729000	-0.00000800
H	-0.12747500	2.12140700	-0.00001100

F	-2.32958600	1.12204300	0.00001900

PhCOCl_CH_3CN - b3lyp/6-311++g(d,p)

Energy: -805.313587 au

Sum of electronic and thermal Free Energies: -805.246540 au

Geometry:

O	1.72102300	1.71269700	-0.00001300
C	1.28536200	0.60552300	-0.00000600
C	-0.13453600	0.20490600	-0.00000100
C	-1.07991000	1.24635500	0.00001000
H	-0.73937200	2.27373800	0.00001700
C	-2.43648500	0.95174200	0.00001700
H	-3.16232400	1.75595500	0.00002900
C	-2.86196000	-0.37862600	0.00000700
H	-3.92149500	-0.60686400	0.00001200
C	-1.92762500	-1.41436900	-0.00000800
H	-2.25847500	-2.44580300	-0.00001700
C	-0.56644000	-1.12830000	-0.00001200
H	0.15432400	-1.93374500	-0.00002500
Cl	2.49933700	-0.78048500	0.00000200

PhCOCl_CH_3CN anion radical - b3lyp/6-311++g(d,p)

Energy: -805.419631 au

Sum of electronic and thermal Free Energies: -805.357003 au

Geometry:

O	1.74928000	1.78454800	0.00003800
C	1.21965500	0.68300500	-0.00000400
C	-0.11582800	0.23940400	0.00000300
C	-1.13872200	1.25600500	-0.00003800
H	-0.83786500	2.29674000	-0.00008000
C	-2.47878800	0.91882800	-0.00002700
H	-3.22085400	1.71186200	-0.00006400
C	-2.89490500	-0.42532300	0.00002300
H	-3.94792800	-0.68051500	0.00004100
C	-1.90932100	-1.43000700	0.00006400
H	-2.20857600	-2.47387700	0.00010700
C	-0.56075200	-1.12303200	0.00005300
H	0.17257700	-1.91756100	0.00008300
Cl	2.54825700	-0.81919500	-0.00004900

PhCOBr_CH_3CN - b3lyp/6-311++g(d,p)

Energy: -2919.233403 au

Sum of electronic and thermal Free Energies: -2919.168282 au

Geometry:

O	0.89829300	2.05535600	-0.00009700
C	0.61266900	0.90376900	-0.00004500
C	-0.73795800	0.31151600	-0.00003200
C	-1.81410300	1.21881800	-0.00002200
H	-1.61408600	2.28244800	-0.00002000
C	-3.11886000	0.74566900	-0.00001300

H	-3.94533000	1.44604900	-0.00000100
C	-3.36301000	-0.62966400	-0.00001900
H	-4.38258700	-0.99723900	-0.00001300
C	-2.29895800	-1.53155500	-0.00003300
H	-2.48931700	-2.59782700	-0.00004100
C	-0.98814800	-1.06663500	-0.00003800
H	-0.16528600	-1.76755900	-0.00004900
Br	2.16172800	-0.41486400	0.00006000

PhCOBr_CH_3CN anion radical - b3lyp/6-311++g(d,p)

Energy: -2919.342267 au

Sum of electronic and thermal Free Energies: -2919.282476 au

Geometry:

O	-0.87945800	2.16593300	0.00000700
C	-0.47970500	1.02316800	0.00000300
C	0.75708500	0.36472500	0.00000100
C	1.92569100	1.21425800	0.00000300
H	1.78994300	2.28902100	0.00000600
C	3.19615900	0.67216400	0.00000100
H	4.05188800	1.34067300	0.00000300
C	3.39799300	-0.71998500	-0.00000200
H	4.39858500	-1.13533400	-0.00000400
C	2.26892000	-1.56005500	-0.00000400
H	2.40295700	-2.63745300	-0.00000700
C	0.98432300	-1.04932700	-0.00000300

H	0.13415000	-1.71686500	-0.00000400
Br	-2.22984700	-0.43249100	-0.00000100

PhCHO - b3lyp/6-311++g(d,p)/QZVP

Energy: -345.671060 au

Sum of electronic and thermal Free Energies: -345.592259 au

Geometry:

O	-2.84806600	-0.39234600	-0.00000500
C	-1.99211300	0.46436100	-0.00000200
C	-0.53420000	0.20610600	0.00000000
C	-0.03828300	-1.10482900	-0.00000200
H	-0.74258400	-1.92842800	-0.00000500
C	1.33253800	-1.32583800	0.00000000
H	1.71934800	-2.33853300	-0.00000200
C	2.21639400	-0.24225100	0.00000300
H	3.28624200	-0.41901600	0.00000400
C	1.72913300	1.06388600	0.00000500
H	2.41707700	1.90143600	0.00000700
C	0.35448900	1.28653600	0.00000300
H	-0.03573600	2.29977900	0.00000400
H	-2.26756500	1.53569600	0.00000000

PhCHO anion radical - b3lyp/6-311++g(d,p)/QZVP

Energy: -345.688050 au

Sum of electronic and thermal Free Energies: -345.614142 au

Geometry:

O	-2.89871100	-0.39509700	-0.00001900
C	-1.97822600	0.47165200	0.00000800
C	-0.57335700	0.22353300	0.00000600
C	-0.03315800	-1.10820300	0.00000200
H	-0.73290200	-1.93668900	0.00000100
C	1.33189300	-1.32715100	-0.00000100
H	1.70457500	-2.35016700	-0.00000400
C	2.25321500	-0.25922900	0.00000000
H	3.32264700	-0.44238100	-0.00000200
C	1.73951400	1.05963100	0.00000400
H	2.42684900	1.90334700	0.00000500
C	0.37867500	1.29348700	0.00000700
H	0.00691500	2.31657200	0.00001000
H	-2.24974800	1.54778000	-0.00001100

PhCOF - b3lyp/6-311++g(d,p)/QZVP

Energy: -444.980900 au

Sum of electronic and thermal Free Energies: -444.910680 au

Geometry:

O	-2.37690200	-1.12204200	-0.00000200
C	-1.70717000	-0.14100700	-0.00000800
C	-0.23322000	-0.04234300	-0.00000300
C	0.50330500	-1.23462400	-0.00000300
H	-0.02594400	-2.17946700	-0.00000600
C	1.89179500	-1.19059300	0.00000000

H	2.46173800	-2.11226700	0.00000000
C	2.55037200	0.04031700	0.00000400
H	3.63409700	0.07299400	0.00000600
C	1.81977900	1.22811300	0.00000300
H	2.33365200	2.18219000	0.00000600
C	0.42880000	1.19161000	0.00000100
H	-0.14390800	2.10941700	0.00000100
F	-2.30737600	1.08829300	0.00000400

PhCOF anion radical - b3lyp/6-311++g(d,p)/QZVP

Energy: -445.002540 au

Sum of electronic and thermal Free Energies: -444.937281 au

Geometry:

O	-2.42369100	-1.13702500	-0.00000500
C	-1.68122600	-0.16246500	-0.00000100
C	-0.27271800	-0.05220300	0.00000000
C	0.52743000	-1.25028400	-0.00000100
H	0.01573800	-2.20606400	-0.00000300
C	1.90519300	-1.18911500	0.00000000
H	2.47483700	-2.11615700	-0.00000100
C	2.59061800	0.04741200	0.00000300
H	3.67459000	0.08616600	0.00000400
C	1.81899000	1.23194100	0.00000400
H	2.32169500	2.19689100	0.00000600
C	0.43898500	1.19798400	0.00000300

H	-0.12769700	2.12095500	0.00000400
F	-2.32591900	1.11942100	-0.00000200

PhCOCl - b3lyp/6-311++g(d,p)/QZVP

Energy: -805.324575 au

Sum of electronic and thermal Free Energies: -805.257224 au

Geometry:

O	1.71876000	1.70808800	0.00000600
C	1.30090300	0.59473100	0.00000700
C	-0.12969100	0.19987900	0.00000700
C	-1.06927400	1.24375000	0.00001700
H	-0.71710100	2.26748700	0.00002300
C	-2.42787900	0.95693400	0.00001800
H	-3.14958000	1.76539600	0.00002500
C	-2.86117000	-0.37001400	0.00000900
H	-3.92221300	-0.59290900	0.00001000
C	-1.93195800	-1.40905100	0.00000000
H	-2.26803700	-2.43924200	-0.00000700
C	-0.56891300	-1.12895000	-0.00000200
H	0.15301100	-1.93373100	-0.00000900
Cl	2.48716100	-0.77972800	-0.00002500

PhCOCl anion radical - b3lyp/6-311++g(d,p)/QZVP

Energy: -805.357571 au

Sum of electronic and thermal Free Energies: -805.294869 au

Geometry:

O	1.74656500	1.77074800	-0.00005500
C	1.23986100	0.66331200	-0.00002300
C	-0.10549500	0.23246000	-0.00000900
C	-1.12316600	1.25463300	-0.00003800
H	-0.80656700	2.29088100	-0.00006900
C	-2.46453500	0.92926800	-0.00002600
H	-3.20056600	1.73019100	-0.00004800
C	-2.89630200	-0.41238100	0.00001600
H	-3.95227100	-0.65991500	0.00002500
C	-1.91246900	-1.42352200	0.00004400
H	-2.21811800	-2.46716600	0.00007600
C	-0.56380800	-1.12604500	0.00003300
H	0.16929500	-1.92110300	0.00005600
Cl	2.52889400	-0.81442500	0.00002400

PhCOBr - b3lyp/6-311++g(d,p)/QZVP

Energy: -2919.317650 au

Sum of electronic and thermal Free Energies: -2919.252123 au

Geometry:

O	0.89889100	2.04937600	-0.00000400
C	0.63245300	0.89359500	0.00000200
C	-0.73023300	0.30654500	0.00000300
C	-1.80049700	1.21744100	0.00000100
H	-1.58823300	2.27901000	-0.00000100

C	-3.10869500	0.75267500	0.00000200
H	-3.93117900	1.45836300	0.00000000
C	-3.36196400	-0.62011200	0.00000400
H	-4.38402900	-0.98184200	0.00000500
C	-2.30304800	-1.52650800	0.00000600
H	-2.49907900	-2.59220100	0.00000800
C	-0.98927100	-1.06817400	0.00000500
H	-0.16631600	-1.76945400	0.00000700
Br	2.15272100	-0.41490400	-0.00000400

PhCOBr anion radical - b3lyp/6-311++g(d,p)/QZVP

Energy: -2919.355324 au

Sum of electronic and thermal Free Energies: -2919.294529 au

Geometry:

O	-0.88847400	2.14191800	0.00000600
C	-0.52166200	0.98943800	0.00000200
C	0.73449000	0.35342600	0.00000000
C	1.89272400	1.21629400	0.00000300
H	1.73428500	2.28812900	0.00000600
C	3.17062200	0.69508300	0.00000100
H	4.01683700	1.37828100	0.00000300
C	3.39786100	-0.69495800	-0.00000300
H	4.40537200	-1.09617800	-0.00000400
C	2.27540600	-1.54941900	-0.00000500
H	2.42308700	-2.62652400	-0.00000800

C	0.98578400	-1.05703300	-0.00000400
H	0.14168800	-1.73280800	-0.00000600
Br	-2.20642400	-0.43037800	0.00000000

PhCOI - b3lyp/6-311++g(d,p)/QZVP

Energy: -642.881292 au

Sum of electronic and thermal Free Energies: -642.817161 au

Geometry:

O	0.28163300	2.19955800	0.00008000
C	0.10656600	1.02565600	0.00004000
C	-1.21498300	0.34520400	0.00003000
C	-2.34594100	1.18048200	0.00006000
H	-2.20728400	2.25414800	0.00008900
C	-3.61872900	0.62634900	0.00005500
H	-4.48798300	1.27365500	0.00007800
C	-3.77692600	-0.76078800	0.00001900
H	-4.77165500	-1.19204500	0.00001500
C	-2.65808100	-1.59186800	-0.00001100
H	-2.77966400	-2.66858000	-0.00003900
C	-1.37930600	-1.04304400	-0.00000600
H	-0.50978800	-1.68690300	-0.00003000
I	1.92127700	-0.26922100	-0.00003500

PhCOI anion radical - b3lyp/6-311++g(d,p)/QZVP

Energy: -642.922677 au

Sum of electronic and thermal Free Energies: -642.863575 au

Geometry:

O	0.24474000	2.30420600	0.00007100
C	-0.04612200	1.13336800	0.00004900
C	-1.24380900	0.39641900	0.00003900
C	-2.46504000	1.16943500	0.00006700
H	-2.38930500	2.25018200	0.00009700
C	-3.69875900	0.55095900	0.00005800
H	-4.59476000	1.16716400	0.00008100
C	-3.81776600	-0.85167000	0.00002000
H	-4.79134300	-1.32911100	0.00001300
C	-2.63362000	-1.61752400	-0.00000900
H	-2.69778700	-2.70252000	-0.00003800
C	-1.38583000	-1.02771000	0.00000000
H	-0.49262400	-1.63786900	-0.00002300
I	1.97648300	-0.27738000	-0.00003800

MeCOF_CH_3CN - b3lyp/6-311++g(d,p)

Energy: -253.186381 au

Sum of electronic and thermal Free Energies: -253.164766 au

Geometry:

O	-0.80979300	-1.10557900	-0.00000200
C	-0.11096600	-0.14793200	-0.00000300
C	1.37261600	-0.03235000	-0.00000100
H	1.82214000	-1.02230200	-0.00000300

H	1.69178000	0.52877000	0.88106100
H	1.69178200	0.52877500	-0.88105900
F	-0.69969600	1.09900900	0.00000400

MeCOF_CH_3CN anion radical - b3lyp/6-311++g(d,p)

Energy: -253.259622 au

Sum of electronic and thermal Free Energies: -253.242401 au

Geometry:

O	0.44445200	1.33146800	0.09951400
C	0.02288100	0.24418800	-0.32580700
C	-1.33055500	-0.32357000	0.04733400
H	-2.10704600	0.36557600	-0.29648200
H	-1.42310500	-0.42364000	1.14133100
H	-1.50216000	-1.29893500	-0.40872700
F	1.03586000	-0.97982800	0.04873400

*t*BuCOF_CH_3CN - b3lyp/6-311++g(d,p)

Energy: -371.158686 au

Sum of electronic and thermal Free Energies: -371.058462 au

Geometry:

C	-0.93866200	0.21699100	-0.00001000
O	-1.57037600	1.22102900	-0.00000100
C	0.55985200	0.00117600	0.00000000
C	0.94130700	-0.80061100	1.26669400
H	0.46608000	-1.78248700	1.27738500

H	2.02436700	-0.94267500	1.27901800
H	0.65882600	-0.26513400	2.17645700
C	0.94132600	-0.80060100	-1.26669400
H	0.65885900	-0.26511700	-2.17645700
H	2.02438700	-0.94266500	-1.27900200
H	0.46609900	-1.78247700	-1.27740000
C	1.25792600	1.36979000	0.00001100
H	2.34001500	1.22148500	0.00001900
H	0.99216100	1.95177200	-0.88494700
H	0.99214700	1.95176500	0.88496900
F	-1.62560300	-0.98146300	-0.00000500

*t*BuCOF_CH_3CN anion radical - b3lyp/6-311++g(d,p)

Energy: -371.230145 au

Sum of electronic and thermal Free Energies: -371.134777 au

Geometry:

C	-0.87302200	0.33442700	-0.44687700
O	-1.44955500	1.36673500	-0.07740000
C	0.56292300	-0.03470000	-0.00771200
C	0.63654700	-0.15756900	1.52874400
H	0.00251200	-0.97418500	1.88105400
H	1.66466200	-0.35652200	1.85159100
H	0.30317800	0.76721300	2.00820700
C	1.02150600	-1.34701500	-0.66067400
H	0.94817300	-1.28517400	-1.75120800

H	2.06509300	-1.55802100	-0.40264500
H	0.40614400	-2.18405600	-0.32727300
C	1.48034000	1.11275300	-0.47361100
H	2.52002400	0.89822500	-0.20587800
H	1.42947000	1.23939100	-1.55985200
H	1.19422700	2.05920900	-0.00876600
F	-1.76742400	-0.99859300	-0.05613900

$CF_3COF\_CH_3CN$ - b3lyp/6-311++g(d,p)

Energy: -550.977862 au

Sum of electronic and thermal Free Energies: -550.983489 au

Geometry:

C	0.59049400	0.01543300	-0.00000500
C	-0.95142300	0.15940400	0.00001400
O	-1.56049100	1.16519900	-0.00002900
F	1.16293600	1.21704800	-0.00007600
F	0.99109700	-0.65756800	1.08802700
F	0.99106000	-0.65767900	-1.08798300
F	-1.51737100	-1.05409100	0.00005200

$CF_3COF\_CH_3CN$ anion radical - b3lyp/6-311++g(d,p)

Energy: -551.091419 au

Sum of electronic and thermal Free Energies: -551.100578 au

Geometry:

C	-0.53833800	0.00959500	-0.03561600

C	0.92371900	0.20249100	-0.35478000
O	1.53297600	1.22255500	0.02592700
F	-1.26595000	1.06464200	-0.48112200
F	-1.06987900	-1.10376900	-0.60031900
F	-0.83331100	-0.09322100	1.31115800
F	1.54957400	-1.09575800	0.00750100