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Supplementary Materials for

Bioinspired design of a robust d_3-methylating agent

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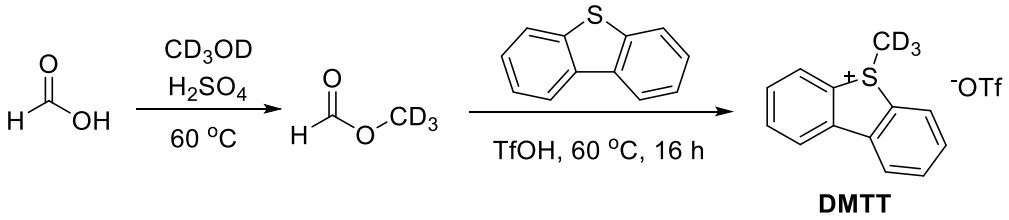
This PDF file includes:

Section S1. The synthesis of trideuteromethyl reagent DMTT

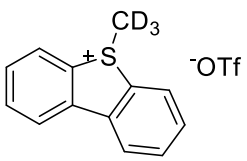


DMTT

According to our patent, to a 50 mL round flask was added formic acid (7.8 mL, 150 mmol, 3 equiv, 88 wt.% aqueous solution), CD_3OD (20.2 mL, 500 mmol, 10 equiv, d = 0.89 g/mL, 99% D). Then sulphuric acid (8.8 mL, 165 mmol, 11 equiv, 98%) was added dropwise to the above solution with stirring. The reaction was heated at 60 °C and stirring for 4 h. The methyl-d_3 formate containing a small amount of deuterated methanol was directly distilled at atmospheric pressure (33-38 °C). The methyl-d_3 formate was used without further purification.

A 50 mL round flask was charged with dibenzothiophene (9.2 g, 50 mmol, 1 equiv) and above distilled methyl-d_3 formate. The mixture was stirred at 0 °C and Tf_2O (20 mL) was dropwise with stirring. Then the reaction was heated up to 60 °C. When the mixture became a clear solution, the reaction was poured into water (100 mL), extracted with CH_2Cl_2 (50 mL × 3), dried with $MgSO_4$, and concentrated in vacuo. The obtained crude product was washed with Et_2O (50 mL × 3) and dried under vacuum to afford the trideuteromethyl reagent **DMTT** (16.0 g, 91%, 99% D).

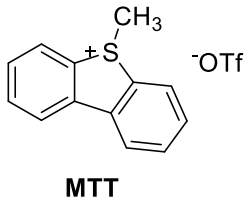
5-(Methyl-d_3)-5*H*-dibenzo[*b,d*]thiophen-5-ium trifluoromethanesulfonate **DMTT**:



DMTT

^{1}H NMR (500 MHz, CD_3CN) δ 8.30 - 8.22 (m, 4 H), 7.93 -7.85 (m, 2 H), 7.78 - 7.70 (m, 2 H). ^{13}C NMR (126 MHz, CD_3CN) δ 140.2, 134.9, 132.0, 131.5, 128.6, 125.1. ATR-FTIR (cm^{-1}): 3097, 3049, 2944, 1420, 1257, 1160, 1033, 755, 641. HRMS (ESI^+) Calcd for $C_{13}H_8D_3S$ $[M\text{-}OTf]^+$: 202.0764, found: 202.0767.

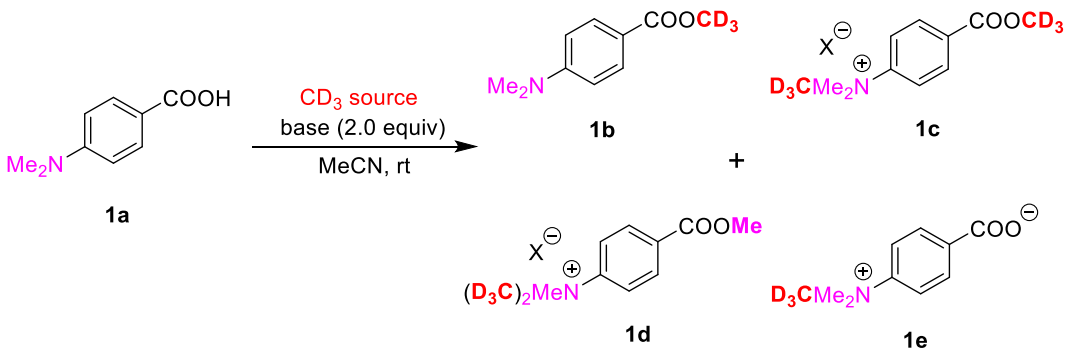
The corresponding non-deuterated product **MTT**:



MTT

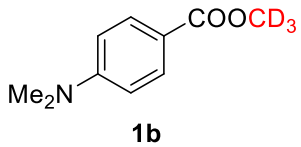
^{1}H NMR (500 MHz, CD_3CN) δ 8.30 - 8.20 (m, 4 H), 7.93 - 7.84 (m, 2 H), 7.78 - 7.68 (m, 2 H), 3.33 (s, 3 H). ^{13}C NMR (126 MHz, CD_3CN) δ 140.1, 134.8, 131.9, 131.6, 128.6, 125.1, 35.0.

Section S2. Reaction development



To a Schlenk tube was added carboxylic acid **1a** (0.2 mmol, 1.0 equiv), CD_3 source, base (0.4 mmol, 2.0 equiv), and MeCN (2 mL). The reaction was stirring at room temperature for 12 h. Then the resulting mixture was concentrated in vacuo and the residue was purified by column chromatography to afford the corresponding product **1b** and side products **1c**, **1d**, and **1e**.

Methyl-*d*$_3$ 4-(dimethylamino)benzoate (**1b**)

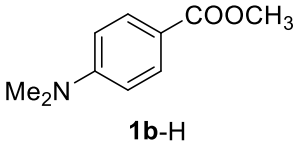


1b

The reaction of 4-(dimethylamino)benzoic acid **1a** (27.4 mg, 0.2 mmol, 1.0 equiv), **DMTT** (70.2 mg, 0.2 mmol, 1.0 equiv), K_2CO_3 (55.2 mg, 0.4 mmol, 2.0 equiv), and MeCN (2 mL) at room temperature for 12 h afford **1b** (32.7 mg, 90%, 99% D) as a white solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 - 7.86 (m, 2 H), 6.68 - 6.59 (m, 2 H), 3.03 (s, 6 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.4, 153.2, 131.2, 116.9, 110.6, 40.0.

ATR-FTIR (cm^{-1}): 2948, 2903, 2824, 1702, 1620, 1436, 1284, 1190, 1133, 914, 828, 770, 743. HRMS (ESI^+) Calcd for $C_{10}H_{11}D_3NO_2$ $[M+H]^+$: 183.1207, found: 183.1207.

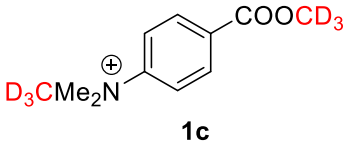
The corresponding non-deuterated product:



1b-H

Methyl 4-(dimethylamino)benzoate **1b**-H (CAS: 1202-25-1): ^1H NMR (400 MHz, $CDCl_3$) δ 7.97 - 7.85 (m, 2 H), 6.70 - 6.58 (m, 2 H), 3.85 (s, 3 H), 3.03 (s, 6 H). ^{13}C NMR (101 MHz, CD_3OD) δ 167.4, 153.2, 131.2, 116.9, 110.6, 51.4, 40.0.

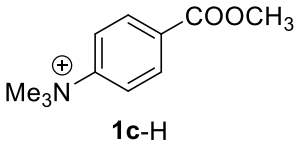
4-((Methoxy-*d*$_3$)carbonyl)-*N*,*N*-dimethyl-*N*-(methyl-*d*$_3$)benzenaminium (**1c**)



1c

The reaction of 4-(dimethylamino)benzoic acid **1a** (27.4 mg, 0.2 mmol, 1.0 equiv), **DMTT** (70.2 mg, 0.2 mmol, 1.0 equiv), DBU (60 μL, d = 1.019 g/mL, 0.4 mmol, 2.0 equiv), and MeCN (2 mL) at room temperature for 12 h afford **1c** as a white solid: ^1H NMR (400 MHz, DMSO-*d*$_6$) δ 8.20 - 8.15 (m, 2 H), 8.15 - 8.10 (m, 2 H), 3.63 (s, 6 H). ^{13}C NMR (101 MHz, DMSO-*d*$_6$) δ 130.7, 121.3, 56.3. ATR-FTIR (cm^{-1}): 2952, 1718, 1653, 1293, 1055, 1008, 823, 761. HRMS (ESI^+) Calcd for $C_{11}H_{10}D_6NO_2$ $[M]^+$: 200.1552, found: 200.1554.

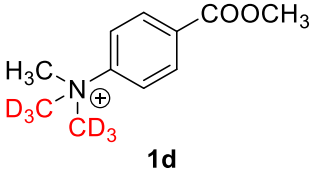
The corresponding non-deuterated product:



1c-H

4-(Methoxycarbonyl)-*N*,*N*,*N*-trimethylbenzenaminium **1c**-H[4]: ^1H NMR (400 MHz, $CDCl_3$) δ 8.24 - 8.14 (m, 2 H), 8.16 - 8.05 (m, 2 H), 3.86 (s, 3 H), 3.68 (s, 9 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.9, 150.4, 131.0, 130.7, 121.6, 56.5, 52.8.

4-(methoxycarbonyl)-*N*-methyl-*N*,*N*-bis(methyl-*d*$_3$)benzenaminium (**1d**)

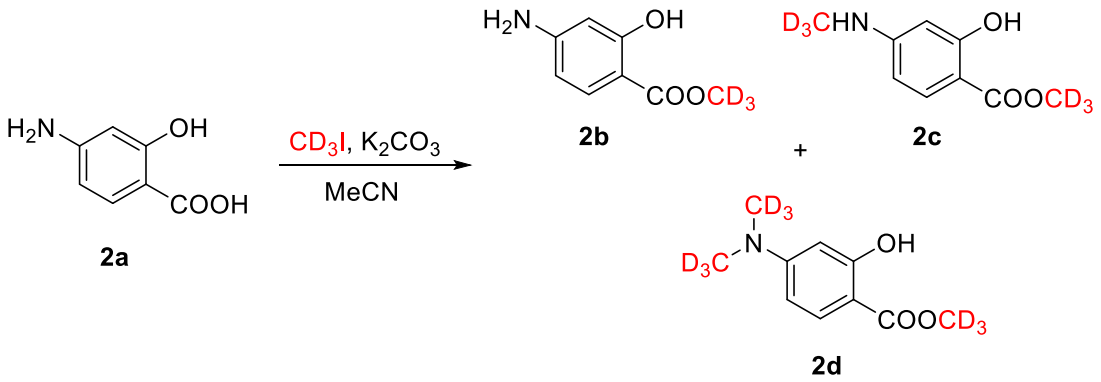


1d

The reaction of 4-(dimethylamino)benzoic acid **1a** (27.4 mg, 0.2 mmol, 1.0 equiv), CD_3I (62 μL, d = 2.33 g/mL, 1.0 mmol, 5.0 equiv), K_2CO_3 (55.2 mg, 0.4 mmol, 2.0 equiv), and MeCN (2 mL) at room temperature for 12 h afford **1d** as a white solid: ^1H NMR (400 MHz, DMSO-*d*$_6$) δ 8.22 - 8.14 (m, 2 H), 8.14 - 8.05

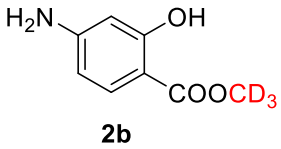
(m, 2 H), 3.86 (s, 3 H), 3.68 (s, 3 H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 164.9, 150.4, 130.9, 130.7, 121.6, 56.4, 52.8. ATR-FTIR (cm^{-1}): 2948, 2933, 1719, 1658, 1295, 1010, 823, 761. HRMS (ESI$^+$) Calcd for $C_{11}H_{10}D_6NO_2$ [M]$^+$: 200.1552, found: 200.1555.

Section S3. Further investigations of compound 2a with DMTT reagent.



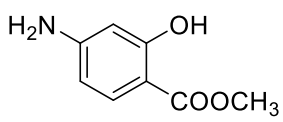
To a Schlenk tube was added carboxylic acid **2a** (30.6 mg, 0.2 mmol, 1.0 equiv), CD_3I (62.2 μL, d = 2.33 g/mL, 1.0 mmol, 5.0 equiv), K_2CO_3 (55.2 mg, 0.4 mmol, 2.0 equiv), and MeCN (2 mL). The reaction was stirring at room temperature for 12 h. Then the resulting mixture was concentrated in vacuo and the residue was purified by column chromatography to afford the byproduct **2b** (white solid, 8.9 mg, 26%, 99% D), **2c** (white solid, 6.7 mg, 18%, 99% D), and **2d** (white solid, 5.0 mg, 20%, 99% D).

Methyl-d_3 4-amino-2-hydroxybenzoate (**2b**)



^{1}H NMR (400 MHz, $CDCl_3$) δ 10.93 (s, 1 H), 7.74 - 7.40 (m, 1 H), 6.30 - 5.87 (m, 2 H), 4.09 (s, 2 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.5, 163.6, 153.3, 131.6, 106.8, 103.0, 100.7. ATR-FTIR (cm^{-1}): 3474, 3380, 3247, 2928, 1653, 1623, 1517, 1436, 1355, 1285, 1190, 1153, 1080, 914, 780, 749. HRMS (ESI$^+$) Calcd for $C_8H_7D_3NO_3$ [M+H]$^+$: 171.0843, found: 171.0843.

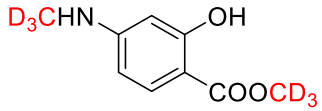
The corresponding non-deuterated product:



2b-H

Methyl 4-amino-2-hydroxybenzoate **2b**-H (CAS: 4136-97-4): ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.93 (s, 1 H), 7.71 - 7.51 (m, 1 H), 6.23 - 6.01 (m, 2 H), 4.09 (s, 2 H), 3.87 (s, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.4, 163.6, 153.3, 131.6, 106.8, 103.0, 100.7, 51.7.

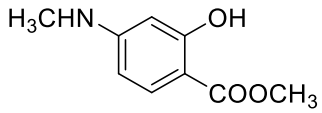
Methyl-*d*$_3$ 2-hydroxy-4-((methyl-*d*$_3$)amino)benzoate (**2c**)



2c

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.01 (s, 1 H), 7.59 (d, *J* = 8.6 Hz, 1 H), 6.23 - 5.90 (m, 2 H), 4.19 (s, 1 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.6, 163.8, 155.3, 131.1, 105.4, 101.6, 97.2. ATR-FTIR (cm^{-1}): 3415, 2993, 2948, 1680, 1635, 1528, 1349, 1282, 1149, 914, 749. HRMS (ESI^{+}) Calcd for $C_9H_6D_6NO_3$ $[M+H]^{+}$: 188.1188, found: 188.1185.

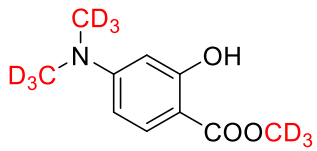
The corresponding non-deuterated product:



2c-H

Methyl 2-hydroxy-4-(methylamino)benzoate **2c**-H (CAS: 1175090-85-3): ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.00 (s, 1 H), 7.59 (d, *J* = 8.5 Hz, 1 H), 6.20 - 5.97 (m, 2 H), 4.21 (s, 1 H), 3.87 (s, 3 H), 2.86 (d, *J* = 5.0 Hz, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 131.1, 105.4, 97.2, 51.6, 30.0.

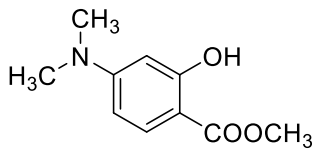
Methyl-*d*$_3$ 4-(bis(methyl-*d*$_3$)amino)-2-hydroxybenzoate (**2d**)



2d

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.92 (s, 1 H), 7.64 (d, *J* = 9.0 Hz, 1 H), 6.20 (dd, *J* = 9.0, 2.5 Hz, 1 H), 6.13 (d, *J* = 2.5 Hz, 1 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.2, 131.0, 104.0, 97.7. ATR-FTIR (cm^{-1}): 3392, 2994, 2951, 1706, 1653, 1541, 1340, 1296, 914, 744. HRMS (ESI^{+}) Calcd for $C_{10}H_5D_9NO_3$ $[M+H]^{+}$: 205.1533, found: 205.1534.

The corresponding non-deuterated product:

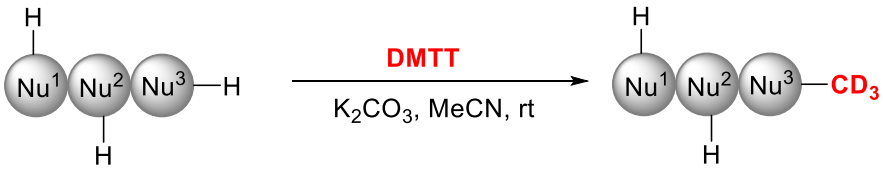


2d-H

Methyl 4-(dimethylamino)-2-hydroxybenzoate **2d**-H (CAS: 27559-59-7): ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.91 (s, 1 H), 7.64 (d, *J* = 9.0 Hz, 1 H), 6.21 (dd, *J* = 9.0, 2.6 Hz, 1 H), 6.14 (d, *J* = 2.6 Hz, 1 H), 3.88 (s, 3 H), 3.02 (s, 6 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 130.9, 104.0, 97.8, 51.5, 40.0.

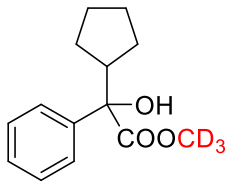
Section S4. The synthesis of products b

General Procedure A:



To a Schlenk tube was added carboxylic acid **a** (0.2 mmol, 1.0 equiv), **DMTT**, K_2CO_3, and MeCN (2 mL). The reaction was stirring at room temperature for 12 h. Then the resulting mixture was concentrated in vacuo and the residue was purified by column chromatography to afford the corresponding product **b**.

Methyl-*d*$_3$ 2-cyclopentyl-2-hydroxy-2-phenylacetate (**3b**)

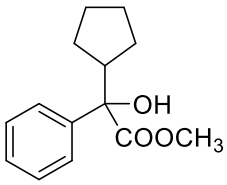


3b

Following the general procedure A, the reaction of **3a** (44.0 mg, 0.2 mmol, 1.0 equiv), **DMTT** (70.2 mg, 0.2 mmol, 1.0 equiv), K_2CO_3 (55.2 mg, 0.4 mmol, 2.0 equiv), and MeCN (2 mL) at room temperature for 12 h afford **3b** (46.9 mg, 99%, 99% D) as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 - 7.60 (m, 2 H), 7.38 - 7.29 (m, 2 H), 7.29 - 7.22 (m, 1 H), 3.74 (s, 1 H), 2.95 - 2.85 (m, 1 H), 1.73 - 1.40 (m, 6 H), 1.39 - 1.29 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.1, 141.7, 128.0, 127.4, 125.9, 79.2, 47.2, 26.9, 26.31, 26.25, 25.9. ATR-FTIR (cm^{-1}): 3512, 2954, 2868, 1725, 1445, 1253,

1173, 740, 698. HRMS (ESI$^+$) Calcd for $C_{14}H_{15}D_3O_3Na$ [M+Na]$^+$: 260.1336, found: 260.1333.

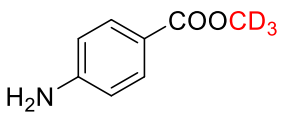
The corresponding non-deuterated product:



3b-H

Methyl 2-cyclopentyl-2-hydroxy-2-phenylacetate **3b**-H (CAS: 19833-96-6): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 - 7.61 (m, 2 H), 7.37 - 7.30 (m, 2 H), 7.29 - 7.23 (m, 1 H), 3.76 (s, 3 H), 3.73 (d, *J* = 0.7 Hz, 1 H), 2.95 - 2.85 (m, 1 H), 1.73 - 1.40 (m, 6 H), 1.38 - 1.29 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.1, 141.7, 128.0, 127.4, 125.9, 79.2, 53.2, 47.2, 26.9, 26.33, 26.26, 25.9.

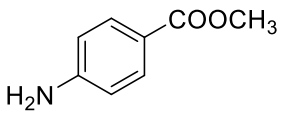
Methyl-*d*$_3$ 4-aminobenzoate (**4b**)



4b

Following the general procedure A, the reaction of **4a** (27.4 mg, 0.2 mmol, 1.0 equiv), **DMTT** (70.2 mg, 0.2 mmol, 1.0 equiv), K_2CO_3 (55.2 mg, 0.4 mmol, 2.0 equiv), and MeCN (2 mL) at room temperature for 12 h afford **4b** (21.6 mg, 70%, 99% D) as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.7 Hz, 2 H), 6.63 (d, *J* = 8.7 Hz, 2 H), 4.09 (bs, 2 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.2, 150.8, 131.5, 119.6, 113.7. ATR-FTIR (cm^{-1}): 3676, 3080, 1685, 1508, 1457, 1288, 773, 669. HRMS (ESI$^+$) Calcd for $C_8H_7D_3NO_2$ [M+H]$^+$: 155.0894, found: 155.0890.

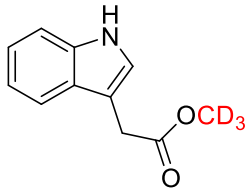
The corresponding non-deuterated product:



4b-H

Methyl 4-aminobenzoate **4b**-H (CAS: 619-45-4): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.7 Hz, 2 H), 6.63 (d, *J* = 8.7 Hz, 2 H), 4.07 (bs, 2 H), 3.85 (s, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.2, 150.8, 131.6, 119.7, 113.8, 51.6.

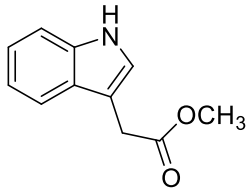
Methyl-*d*$_3$ 2-(1*H*-indol-3-yl)acetate (**5b**)



5b

Following the general procedure A, the reaction of **5a** (35.0 mg, 0.2 mmol, 1.0 equiv), **DMTT** (70.2 mg, 0.2 mmol, 1.0 equiv), K_2CO_3 (55.2 mg, 0.4 mmol, 2.0 equiv), and MeCN (2 mL) at room temperature for 12 h afford **5b** (32.3 mg, 84%, 99% D) as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (s, 1 H), 7.66 - 7.61 (m, 1 H), 7.35 - 7.31 (m, 1 H), 7.25 - 7.13 (m, 2 H), 7.12 - 7.08 (m, 1 H), 3.81 (d, *J* = 0.9 Hz, 2 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.6, 136.1, 127.2, 123.1, 122.2, 119.7, 118.8, 111.2, 108.3, 31.1. ATR-FTIR (cm^{-1}): 3408, 2950, 1720, 1456, 1431, 1163, 1094, 1007, 743, 587. HRMS (ESI$^+$) Calcd for $C_{11}H_8D_3NO_2Na$ [M+Na]$^+$: 215.0870, found: 215.0872.

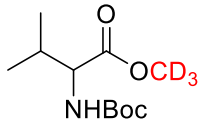
The corresponding non-deuterated product:



5b-H

Methyl 2-(1*H*-indol-3-yl)acetate **5b**-H (CAS: 1912-33-0): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (s, 1 H), 7.67 - 7.58 (m, 1 H), 7.37 - 7.31 (m, 1 H), 7.24 - 7.15 (m, 2 H), 7.14-7.11 (m, 1 H), 3.80 (d, *J* = 0.9 Hz, 2 H), 3.72 (s, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.6, 136.1, 127.2, 123.1, 122.2, 119.6, 118.8, 111.2, 108.3, 52.0, 31.1.

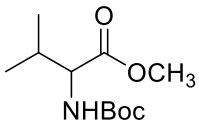
Methyl-*d*$_3$ (tert-butoxycarbonyl)valinate (**6b**)



6b

Following the general procedure A, the reaction of **6a** (43.4 mg, 0.2 mmol, 1.0 equiv), **DMTT** (70.2 mg, 0.2 mmol, 1.0 equiv), K_2CO_3 (55.2 mg, 0.4 mmol, 2.0 equiv), and MeCN (2 mL) at room temperature for 12 h afford **6b** (41.5 mg, 89%, 99% D) as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.02 (d, *J* = 9.2 Hz, 1 H), 4.20 (dd, *J* = 9.2, 4.9 Hz, 1 H), 2.17 - 2.02 (m, 1 H), 1.42 (s, 9 H), 0.93 (d, *J* = 6.8 Hz, 3 H), 0.87 (d, *J* = 6.9 Hz, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.9, 155.6, 79.7, 58.5, 31.3, 28.3, 18.9, 17.6. ATR-FTIR (cm^{-1}): 3369, 2970, 2880, 1715, 1504, 1366, 1163, 1014. HRMS (ESI$^+$) Calcd for $C_{11}H_{18}D_3NO_4Na$ [M+Na]$^+$: 257.1551, found: 257.1552.

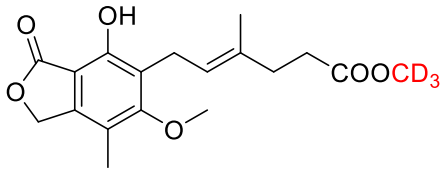
The corresponding non-deuterated product:



6b-H

Methyl (tert-butoxycarbonyl)valinate **6b**-H (CAS: 145618-65-1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.02 (d, *J* = 9.2 Hz, 1 H), 4.20 (dd, *J* = 9.2, 4.9 Hz, 1 H), 3.72 (s, 3 H), 2.16 - 2.04 (m, 1 H), 1.43 (s, 9 H), 0.94 (d, *J* = 6.9 Hz, 3 H), 0.87 (d, *J* = 6.9 Hz, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.9, 155.6, 79.7, 58.5, 52.0, 31.3, 28.3, 18.9, 17.6.

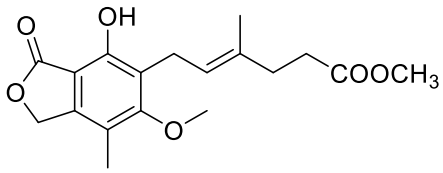
Methyl-d_3 (*E*)-6-(4-hydroxy-6-methoxy-7-methyl-3-oxo-1,3-dihydroisobenzofuran-5-yl)-4-methylhex-4-enoate (**7b**)



7b

Following the general procedure A, the reaction of **7a** (64.0 mg, 0.2 mmol, 1.0 equiv), **DMTT** (70.2 mg, 0.2 mmol, 1.0 equiv), K_2CO_3 (55.2 mg, 0.4 mmol, 2.0 equiv), and MeCN (2 mL) at room temperature for 12 h afford **7b** (58.3 mg, 86%, 99% D) as a white solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (s, 1 H), 5.27 - 5.19 (m, 1 H), 5.18 (s, 2 H), 3.74 (s, 3 H), 3.36 (d, *J* = 7.0 Hz, 2 H), 2.42 - 2.34 (m, 2 H), 2.32 - 2.24 (m, 2 H), 2.13 (s, 3 H), 1.78 (s, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.8, 172.8, 163.6, 153.5, 143.9, 134.1, 122.7, 122.0, 116.7, 106.3, 70.0, 60.9, 34.5, 32.8, 22.5, 16.0, 11.5. ATR-FTIR (cm^{-1}): 3428, 2947, 2852, 1707, 1625, 1454, 1367, 1136, 1076, 1030, 970. HRMS (ESI^+) Calcd for $C_{18}H_{20}D_3O_6$ $[M+H]^+$: 338.1677, found: 338.1677.

The corresponding non-deuterated product:

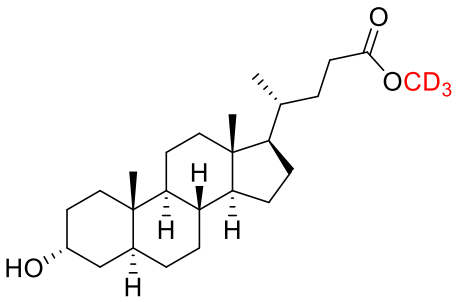


7b-H

Methyl (*E*)-6-(4-hydroxy-6-methoxy-7-methyl-3-oxo-1,3-dihydroisobenzofuran-5-yl)-4-methylhex-4-enoate **7b**-H (CAS: 31858-66-9): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (s, 1 H), 5.26 - 5.19 (m, 1 H), 5.17 (s, 2 H), 3.74 (s, 3 H), 3.59 (s, 3 H), 3.36 (d, *J* = 7.0 Hz, 2 H), 2.42 - 2.34 (m, 2 H), 2.31 - 2.24 (m, 2 H), 2.13 (s, 3 H), 1.78

(s, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.8, 172.9, 163.6, 153.6, 144.0, 134.1, 122.7, 122.1, 116.7, 106.3, 70.0, 61.0, 51.4, 34.6, 32.8, 22.6, 16.1, 11.5.

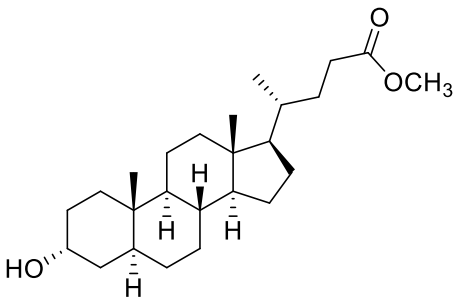
Methyl-d_3 (*R*)-4-((3*R*,5*S*,8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-3-hydroxy-10,13-dimethylhexadecahydro-1*H*-cyclopenta[*a*]phenanthren-17-yl)pentanoate (**8b**)



8b

Following the general procedure A, the reaction of **8a** (75.2 mg, 0.2 mmol, 1.0 equiv), **DMTT** (70.2 mg, 0.2 mmol, 1.0 equiv), K_2CO_3 (55.2 mg, 0.4 mmol, 2.0 equiv), and MeCN (2 mL) at room temperature for 12 h afford **8b** (63.8 mg, 81%, 99% D) as a white solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.68 - 3.48 (m, 1 H), 2.38 - 2.27 (m, 1 H), 2.25 - 2.14 (m, 1 H), 1.97 - 1.90 (m, 1 H), 1.90 - 1.70 (m, 6 H), 1.69 - 1.59 (m, 1 H), 1.59 - 1.44 (m, 2 H), 1.44 - 1.17 (m, 11 H), 1.17 - 0.93 (m, 6 H), 0.92 - 0.86 (m, 6 H), 0.62 (s, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.8, 71.7, 56.4, 55.9, 42.7, 42.0, 40.4, 40.1, 36.4, 35.8, 35.3, 34.5, 31.0, 30.9, 30.5, 28.1, 27.1, 26.4, 24.1, 23.3, 20.8, 18.2, 12.0. ATR-FTIR (cm^{-1}): 3344, 2900, 2863, 1740, 1448, 1373, 1167, 1038. HRMS (ESI^+) Calcd for $C_{25}H_{39}D_3O_3Na$ $[M+Na]^+$: 416.3214, found: 416.3216.

The corresponding non-deuterated product:

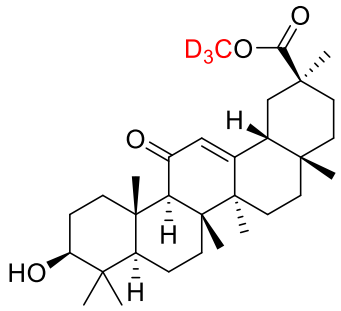


8b-H

Methyl (*R*)-4-((3*R*,5*S*,8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-3-hydroxy-10,13-dimethylhexadecahydro-1*H*-cyclopenta[*a*]phenanthren-17-yl)pentanoate **8b**-H (CAS: 1249-75-8): ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.64 (s, 3 H), 3.63 - 3.54 (m, 1 H), 2.40 - 2.27 (m, 1 H), 2.27 - 2.13 (m, 1 H), 1.99 - 1.89 (m, 1 H), 1.90 - 1.68 (m, 6 H), 1.69 - 1.58 (m, 1 H), 1.59 - 1.45 (m, 2 H), 1.44 - 1.16 (m, 11 H), 1.17 - 0.93 (m, 6 H), 0.93 - 0.85 (m, 6

H), 0.62 (s, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.7, 71.7, 56.4, 55.9, 51.4, 42.7, 42.0, 40.4, 40.1, 36.4, 35.8, 35.3, 34.5, 31.0, 30.9, 30.5, 28.1, 27.1, 26.4, 24.2, 23.3, 20.8, 18.2, 12.0.

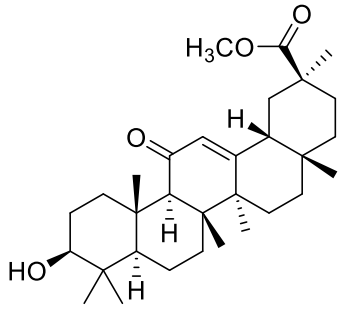
Methyl-d_3 (2*S*,4a*S*,6a*S*,6b*R*,8a*R*,10*S*,12a*S*,12b*R*,14b*R*)-10-hydroxy-2,4a,6a,6b,9,9,12a-heptamethyl-13-oxo-1,2,3,4,4a,5,6,6a,6b,7,8,8a,9,10,11,12,12a,12b,13,14b-icosahydropicene-2-carboxylate (**9b**)



9b

Following the general procedure A, the reaction of **9a** (94.0 mg, 0.2 mmol, 1.0 equiv), **DMTT** (70.2 mg, 0.2 mmol, 1.0 equiv), K_2CO_3 (55.2 mg, 0.4 mmol, 2.0 equiv), and MeCN (2 mL) at room temperature for 12 h afford **9b** (93.9 mg, 96%, 99% D) as a white solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.62 (s, 1 H), 3.24 - 3.12 (m, 1 H), 2.81 - 2.68 (m, 1 H), 2.30 (s, 1 H), 2.08 - 1.72 (m, 6 H), 1.65 - 1.54 (m, 5 H), 1.40 - 1.24 (m, 8 H), 1.18 - 1.06 (m, 11 H), 1.02 - 0.90 (m, 4 H), 0.77 (s, 6 H), 0.66 (d, *J* = 11.5 Hz, 1 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.2, 176.9, 169.1, 128.4, 78.6, 61.7, 54.8, 48.3, 45.3, 43.9, 43.1, 41.0, 39.0, 37.7, 37.0, 32.7, 31.7, 31.0, 28.4, 28.2, 28.0, 27.2, 26.4, 26.3, 23.3, 18.6, 17.4, 16.3, 15.5. ATR-FTIR (cm^{-1}): 3343, 2942, 2870, 1723, 1657, 1461, 1386, 1215, 1160, 1042, 913, 741. HRMS (ESI^+) Calcd for $C_{31}H_{45}D_3O_4Na$ $[M+Na]^+$: 510.3633, found: 510.3628.

The corresponding non-deuterated product:

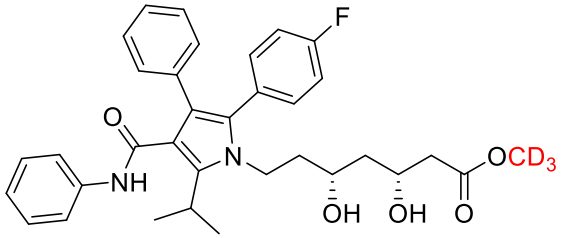


9b-H

Methyl (2*S*,4a*S*,6a*S*,6b*R*,8a*R*,10*S*,12a*S*,12b*R*,14b*R*)-10-hydroxy-2,4a,6a,6b,9,9,12a-heptamethyl-13-oxo-1,2,3,4,4a,5,6,6a,6b,7,8,8a,9,10,11,12,12a,12b,13,14b-icosahydropicene-2-carboxylate **9b**-H (CAS: 1477-44-7): ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.63 (s, 1 H), 3.66 (s, 3 H), 3.27 - 3.13

(m, 1 H), 2.84 - 2.70 (m, 1 H), 2.31 (s, 1 H), 2.11 - 1.72 (m, 6 H), 1.69 - 1.52 (m, 5 H), 1.45 - 1.26 (m, 8 H), 1.20 - 1.06 (m, 10 H), 1.03 - 0.90 (m, 5 H), 0.78 (s, 6 H), 0.67 (d, *J* = 11.9 Hz, 1 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.2, 176.9, 169.1, 128.5, 78.7, 61.7, 54.9, 51.7, 48.3, 45.3, 44.0, 43.1, 41.0, 39.1, 37.7, 37.0, 32.7, 31.8, 31.1, 28.5, 28.3, 28.0, 27.2, 26.4, 26.4, 23.3, 18.6, 17.4, 16.3, 15.5.

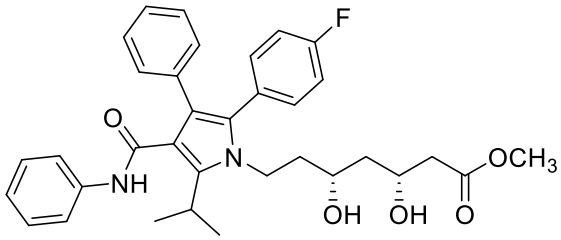
Methyl-d_3 (3*R*,5*R*)-7-(2-(4-fluorophenyl)-5-isopropyl-3-phenyl-4-(phenylcarbamoyl)-1*H*-pyrrol-1-yl)-3,5-dihydroxyheptanoate (**10b**)



10b

Following the general procedure A, the reaction of **10a** (111.7 mg, 0.2 mmol, 1.0 equiv), **DMTT** (70.2 mg, 0.2 mmol, 1.0 equiv), K_2CO_3 (55.2 mg, 0.4 mmol, 2.0 equiv), and MeCN (2 mL) at room temperature for 12 h afford **10b** (50.9 mg, 44%, 99% D) as a white solid: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.22 - 7.13 (m, 9 H), 7.06 (d, *J* = 8.0 Hz, 2 H), 7.03 - 6.96 (m, 3 H), 6.86 (s, 1 H), 4.24 - 4.04 (m, 2 H), 4.04 - 3.88 (m, 1 H), 3.82 - 3.71 (m, 1 H), 3.70 - 3.48 (m, 3 H), 2.41 (d, *J* = 6.1 Hz, 2 H), 1.74 - 1.58 (m, 3 H), 1.54 (d, *J* = 7.1 Hz, 6 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.0, 164.8, 162.2 (d, *J* = 247.5 Hz), 141.5, 138.3, 134.6, 133.2 (d, *J* = 8.1 Hz), 130.5, 128.69, 128.65, 128.3, 126.5, 123.5, 121.8, 119.6, 115.4 (d, *J* = 21.4 Hz), 69.6, 68.9, 41.7, 41.2, 41.1, 39.1, 26.1, 21.8, 21.7. ^{19}F NMR (471 MHz, $CDCl_3$) δ -113.5. ATR-FTIR (cm^{-1}): 3416, 2958, 2924, 2854, 1727, 1657, 1509, 1313, 1156, 909, 733. HRMS (ESI^+) Calcd for $C_{34}H_{34}D_3FN_2O_5Na$ $[M+Na]^+$: 598.2767, found: 598.2764.

The corresponding non-deuterated product:

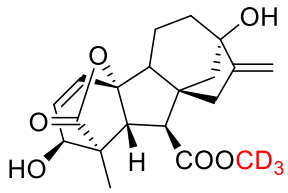


10b-H

Methyl (3*R*,5*R*)-7-(2-(4-fluorophenyl)-5-isopropyl-3-phenyl-4-(phenylcarbamoyl)-1*H*-

pyrrol-1-yl)-3,5-dihydroxyheptanoate **10b**-H[5]: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 - 7.12 (m, 9 H), 7.06 (d, *J* = 8.0 Hz, 2 H), 7.03 - 6.94 (m, 3 H), 6.87 (s, 1 H), 4.24 - 4.04 (m, 2 H), 4.03 - 3.86 (m, 1 H), 3.80 - 3.65 (m, 5 H), 3.62 - 3.51 (m, 2 H), 2.41 (d, *J* = 6.1 Hz, 2 H), 1.72 - 1.61 (m, 3 H), 1.54 (d, *J* = 7.1 Hz, 6 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.0, 164.8, 162.2 (d, *J* = 247.6 Hz), 141.5, 138.3, 134.6, 133.2 (d, *J* = 8.1 Hz), 130.4, 128.7, 128.6, 128.3, 126.5, 123.5, 121.8, 119.6, 115.4 (d, *J* = 21.4 Hz), 69.6, 68.9, 51.9, 41.7, 41.2, 41.1, 39.0, 26.1, 21.8, 21.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.5.

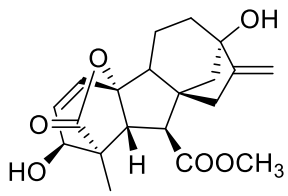
Methyl-d_3 (1*S*,2*S*,4a*R*,7*S*,9a*S*,10*S*,10a*R*)-2,7-dihydroxy-1-methyl-8-methylene-13-oxo-1,2,4b,5,6,7,8,9,10,10a-decahydro-4a,1-(epoxymethano)-7,9a-methanobenzo[*a*]azulene-10-carboxylate (**11b**)



11b

Following the general procedure A, the reaction of **11a** (69.2 mg, 0.2 mmol, 1.0 equiv), **DMTT** (70.2 mg, 0.2 mmol, 1.0 equiv), K_2CO_3 (55.2 mg, 0.4 mmol, 2.0 equiv), and MeCN (2 mL) at room temperature for 12 h afford **11b** (64.3 mg, 89%, 99% D) as a white solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.32 (dd, *J* = 9.3, 0.9 Hz, 1 H), 5.91 (dd, *J* = 9.3, 3.7 Hz, 1 H), 5.28 (dd, *J* = 3.1, 1.9 Hz, 1 H), 4.97 (d, *J* = 2.2 Hz, 1 H), 4.16 (dd, *J* = 7.3, 3.7 Hz, 1 H), 3.21 (d, *J* = 10.7 Hz, 1 H), 2.79 (d, *J* = 10.7 Hz, 1 H), 2.26 - 2.12 (m, 2 H), 2.12 - 2.01 (m, 2 H), 2.00 - 1.88 (m, 3 H), 1.88 - 1.79 (m, 1 H), 1.79 - 1.70 (m, 1 H), 1.72 - 1.63 (m, 2 H), 1.25 (s, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.9, 133.0, 132.3, 107.6, 78.2, 69.8, 53.4, 52.8, 51.1, 50.6, 50.5, 44.8, 43.1, 38.2, 17.0, 14.4. ATR-FTIR (cm^{-1}): 3375, 2941, 1764, 1748, 1267, 753. EI-MS (*m/z*, relative intensity): 301 (M^+-$COOCD_3$, 16), 239 (34), 238 (100), 223 (24), 209 (27), 195 (27), 193 (23), 181 (20), 180 (22), 165 (37), 155 (42), 152 (26), 141 (24), 128 (22), 115 (21). HRMS (ESI^+) Calcd for $C_{20}H_{21}D_3O_6Na$ $[M+Na]^+$: 386.1653, found: 386.1651.

The corresponding non-deuterated product:

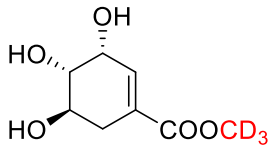


11b-H

Methyl (1*S*,2*S*,4a*R*,7*S*,9a*S*,10*S*,10a*R*)-2,7-dihydroxy-1-methyl-8-methylene-13-oxo-1,2,4b,5,6,7,8,9,10,10a-decahydro-4a,1-(epoxymethano)-7,9a-methanobenzo[*a*]azulene-10-carboxylate

11b-H (CAS: 510-50-9): ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.32 (dd, *J* = 9.3, 0.9 Hz, 1 H), 5.91 (dd, *J* = 9.3, 3.7 Hz, 1 H), 5.28 (dd, *J* = 3.0, 1.9 Hz, 1 H), 4.97 (d, *J* = 2.1 Hz, 1 H), 4.16 (dd, *J* = 7.1, 3.7 Hz, 1 H), 3.74 (s, 3 H), 3.21 (d, *J* = 10.7 Hz, 1 H), 2.79 (d, *J* = 10.7 Hz, 1 H), 2.26 - 2.12 (m, 2 H), 2.12 - 2.01 (m, 2 H), 2.00 - 1.87 (m, 3 H), 1.86 - 1.78 (m, 1 H), 1.80 - 1.70 (m, 1 H), 1.72 - 1.62 (m, 2 H), 1.25 (s, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.3, 172.5, 156.9, 133.0, 132.3, 107.6, 90.4, 78.2, 69.8, 53.4, 52.8, 52.2, 51.1, 50.6, 50.5, 44.8, 43.1, 38.2, 17.0, 14.4.

Methyl-*d*$_3$ (3*R*,4*S*,5*R*)-3,4,5-trihydroxycyclohex-1-ene-1-carboxylate (**12b**)



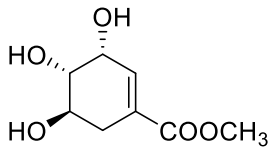
12b

Following the general procedure A, the reaction of **12a** (34.8 mg, 0.2 mmol, 1.0 equiv), **DMTT** (70.2 mg, 0.2 mmol, 1.0 equiv), K_2CO_3 (55.2 mg, 0.4 mmol, 2.0 equiv), and MeCN (2 mL) at room temperature for 12 h afford **12b** (35.2 mg, 92%, 99% D) as a white solid: ^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 6.64 - 6.59 (m, 1 H), 4.97 - 4.80 (m, 2 H), 4.67 (d, *J* = 4.2 Hz, 1 H), 4.28 - 4.16 (m, 1 H), 3.92 - 3.79 (m, 1 H), 3.62 - 3.51 (m, 1 H), 2.47 - 2.36 (m, 1 H), 2.11 - 1.99 (m, 1 H). ^{13}C NMR (101 MHz, DMSO-*d*$_6$) δ 166.8, 139.9, 127.4, 70.0, 66.9, 65.5, 29.6. ATR-FTIR (cm^{-1}): 3430, 1653, 1255, 1027, 825, 764, 626. HRMS (ESI$^+$) Calcd for $C_8H_9D_3O_5Na$ $[M+Na]^+$: 214.0765, found: 214.0763.

The gram scale reaction of **12b**:

The reaction of **12a** (0.8700 g, 5.0 mmol, 1.0 equiv), **DMTT** (1.7400 g, 5.0 mmol, 1.0 equiv), K_2CO_3 (1.3800 g, 10.0 mmol, 2.0 equiv), and MeCN (50 mL) at room temperature for 12 h afford **12b** (0.8734 g, 91%, 99% D) as a white solid.

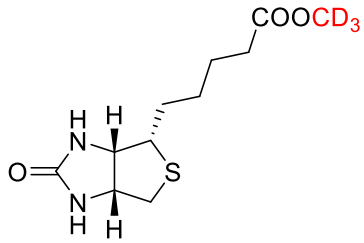
The corresponding non-deuterated product:



12b-H

Methyl (3*R*,4*S*,5*R*)-3,4,5-trihydroxycyclohex-1-ene-1-carboxylate **12b**-H (CAS: 40983-58-2): ^{1}H NMR (400 MHz, DMSO-d_6) δ 6.64 - 6.58 (m, 1 H), 4.94 - 4.81 (m, 2 H), 4.67 (s, 1 H), 4.21 (s, 1 H), 3.92 – 3.78 (m, 1 H), 3.66 (s, 3 H), 3.63 - 3.52 (m, 1 H), 2.48 - 2.36 (m, 1 H), 2.11 - 1.99 (m, 1 H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 166.8, 139.9, 127.4, 70.0, 66.9, 65.5, 51.7, 29.7.

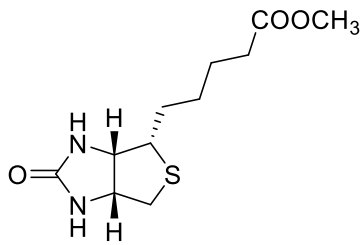
Methyl-d_3 5-((3a*S*,4*S*,6a*R*)-2-oxohexahydro-1*H*-thieno[3,4-*d*]imidazol-4-yl)pentanoate (**13b**)



13b

Following the general procedure A, the reaction of **13a** (48.9 mg, 0.2 mmol, 1.0 equiv), **DMTT** (70.2 mg, 0.2 mmol, 1.0 equiv), K_2CO_3 (55.2 mg, 0.4 mmol, 2.0 equiv), and MeCN (2 mL) at room temperature for 12 h afford **13b** (33.8 mg, 65%, 99% D) as a white solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.01 (s, 1 H), 5.81 (s, 1 H), 4.60 - 4.44 (m, 1 H), 4.41 - 4.28 (m, 1 H), 3.24 - 3.06 (m, 1 H), 2.89 (dd, *J* = 12.9, 4.9 Hz, 1 H), 2.75 (d, *J* = 13.1 Hz, 1 H), 2.32 (t, *J* = 7.4 Hz, 2 H), 1.82 - 1.54 (m, 4 H), 1.52 - 1.33 (m, 2 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.2, 164.2, 62.1, 60.3, 55.6, 40.5, 33.6, 28.4, 28.2, 24.7. ATR-FTIR (cm^{-1}): 3440, 1676, 1515, 1465, 997, 750. HRMS (ESI$^+$) Calcd for $C_{11}H_{15}D_3N_2O_3SNa$ $[M+Na]^+$: 284.1119, found: 284.1120.

The corresponding non-deuterated product:

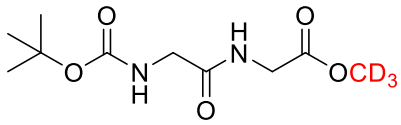


13b-H

Methyl 5-((3a*S*,4*S*,6a*R*)-2-oxohexahydro-1*H*-thieno[3,4-*d*]imidazol-4-yl)pentanoate **13b**-H (CAS: 608-16-2): ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.99 (s, 1 H), 5.70 (s, 1 H), 4.62 - 4.42 (m, 1 H), 4.41 - 4.24 (m, 1 H), 3.65 (s, 3 H), 3.25 -

3.06 (m, 1 H), 2.89 (dd, *J* = 12.9, 4.9 Hz, 1 H), 2.74 (d, *J* = 12.8 Hz, 1 H), 2.32 (t, *J* = 7.5 Hz, 2 H), 1.83 - 1.53 (m, 4 H), 1.54 - 1.33 (m, 2 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.1, 164.0, 62.0, 60.2, 55.5, 51.5, 40.5, 33.6, 28.4, 28.2, 24.7.

Methyl-d_3 (tert-butoxycarbonyl)glycylglycinate (**14b**)



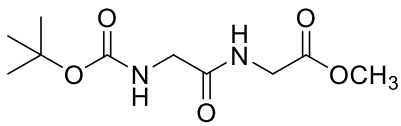
14b

Following the general procedure A, the reaction of **14a** (46.5 mg, 0.2 mmol, 1.0 equiv), **DMTT** (70.2 mg, 0.2 mmol, 1.0 equiv), K_2CO_3 (55.2 mg, 0.4 mmol, 2.0 equiv), and MeCN (2 mL) at room temperature for 12 h afford **14b** (41.2 mg, 83%, 99% D) as a colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.97 (t, *J* = 5.5 Hz, 1 H), 5.45 (s, 1 H), 4.02 (d, *J* = 5.4 Hz, 2 H), 3.83 (d, *J* = 5.9 Hz, 2 H), 1.42 (s, 9 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.2, 170.0, 156.1, 80.2, 44.0, 41.0, 28.2. ATR-FTIR (cm^{-1}): 3326, 2979, 2935, 1749, 1663, 1522, 1368, 1171, 1032, 945, 743. HRMS (ESI^+) Calcd for $C_{10}H_{15}D_3N_2O_5Na$ $[M+Na]^+$: 272.1296, found: 272.1296.

The gram scale reaction of **14b**:

The reaction of **14a** (1.230 g, 5.3 mmol, 1.0 equiv), **DMTT** (1.844 g, 5.3 mmol, 1.0 equiv), K_2CO_3 (1.463 g, 10.6 mmol, 2.0 equiv), and MeCN (53 mL) at room temperature for 12 h afford **14b** (1.2141 g, 92%, 99% D) as a white solid.

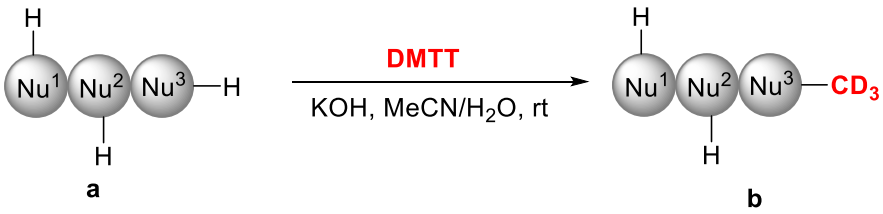
The corresponding non-deuterated product:



14b-H

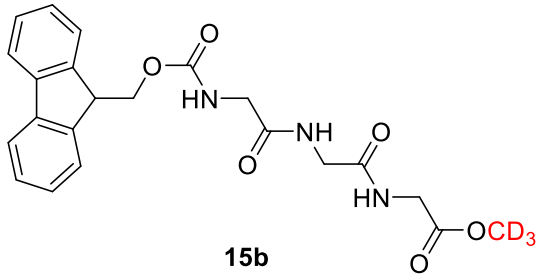
Methyl (tert-butoxycarbonyl)glycylglycinate **14b**-H (CAS: 53487-98-2): ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.95 (t, *J* = 6.9 Hz, 1 H), 5.43 (s, 1 H), 4.03 (d, *J* = 5.3 Hz, 2 H), 3.83 (d, *J* = 5.9 Hz, 2 H), 3.72 (d, *J* = 1.1 Hz, 3 H), 1.42 (d, *J* = 1.0 Hz, 9 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.2, 170.0, 156.1, 80.3, 52.3, 44.0, 41.0, 28.2.

General Procedure B:



To a Schlenk tube was added carboxylic acid **a** (0.2 mmol, 1.0 equiv), **DMTT** (0.2 mmol, 2.0 equiv), KOH (22.4 mg, 0.4 mmol, 2.0 equiv), H_2O (1 mL), and MeCN (1 mL). The reaction was stirring at room temperature for 12 h. The resulting mixture was concentrated in vacuo and the residue was purified by column chromatography to afford the corresponding product **b**.

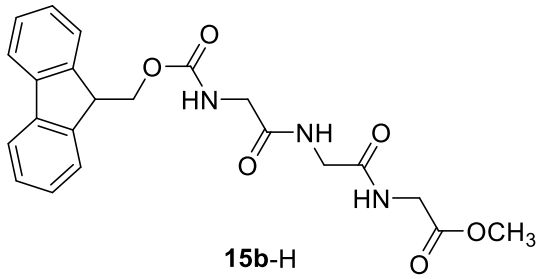
Methyl-*d*$_3$ (((9*H*-fluoren-9-yl)methoxy)carbonyl)glycylglycylglycinate (**15b**)



15b

Following the general procedure B, the reaction of **15a** (82.2 mg, 0.2 mmol, 1.0 equiv), **DMTT** (70.2 mg, 0.2 mmol, 1.0 equiv), KOH (22.4 mg, 0.4 mmol, 2.0 equiv), H_2O (1 mL), and MeCN (1 mL) at room temperature for 12 h afford **15b** (39.8 mg, 46%, 99% D) as a white solid: ^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 8.30 (t, *J* = 5.9 Hz, 1 H), 8.17 (t, *J* = 5.9 Hz, 1 H), 7.89 (d, *J* = 7.5 Hz, 2 H), 7.73 (s, 1 H), 7.58 (t, *J* = 6.1 Hz, 1 H), 7.42 (t, *J* = 7.4 Hz, 2 H), 7.36 - 7.31 (m, 2 H), 4.29 (d, *J* = 7.5 Hz, 1 H), 4.25 - 4.20 (m, 1 H), 3.85 (d, *J* = 5.8 Hz, 2 H), 3.76 (d, *J* = 5.8 Hz, 2 H), 3.67 (d, *J* = 6.0 Hz, 2 H). ^{13}C NMR (101 MHz, DMSO-*d*$_6$) δ 170.2, 169.5, 169.4, 156.5, 143.9, 140.7, 127.7, 127.1, 125.3, 120.1, 65.8, 46.7, 43.5, 41.7, 40.5. ATR-FTIR (cm^{-1}): 3429, 1655, 1002, 825, 764, 627. EI-MS (*m/z*, relative intensity): 207 (93), 206 (90), 205 (59), 194 (28), 193 (45), 192 (45), 191 (40), 190 (25), 179 (22), 178 (70), 177 (100), 176 (60), 175 (30), 133 (20), 89 (22), 57 (28). HRMS (ESI$^+$) Calcd for $C_{22}H_{20}D_3N_3O_6Na$ $[M+Na]^+$: 451.1667, found: 451.1676.

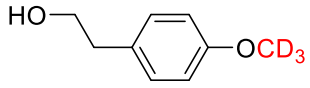
The corresponding non-deuterated product:



15b-H

Methyl (((9H-fluoren-9-yl)methoxy)carbonyl)glycylglycylglycinate **15b**-H[6]: ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.30 (t, *J* = 6.0 Hz, 1 H), 8.16 (t, *J* = 5.9 Hz, 1 H), 7.89 (d, *J* = 7.5 Hz, 2 H), 7.72 (d, *J* = 7.4 Hz, 1 H), 7.57 (t, *J* = 6.1 Hz, 1 H), 7.42 (td, *J* = 7.4, 1.1 Hz, 2 H), 7.33 (td, *J* = 7.4, 1.2 Hz, 2 H), 4.29 (d, *J* = 7.4 Hz, 1 H), 4.27 - 4.18 (m, 1 H), 3.85 (d, *J* = 5.9 Hz, 2 H), 3.75 (d, *J* = 5.8 Hz, 2 H), 3.66 (d, *J* = 6.0 Hz, 2 H), 3.62 (s, 3 H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 170.2, 169.5, 169.4, 156.5, 143.9, 140.7, 127.7, 127.1, 125.3, 120.1, 65.8, 51.7, 46.6, 43.5, 41.7, 40.5.

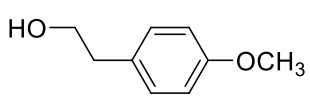
2-(4-(Methoxy-d_3)phenyl)ethan-1-ol (**16b**)



16b

Following the general procedure A, the reaction of **16a** (27.6 mg, 0.2 mmol, 1.0 equiv), **DMTT** (70.2 mg, 0.2 mmol, 1.0 equiv), K_2CO_3 (55.2 mg, 0.4 mmol, 2.0 equiv), and MeCN (2 mL) at room temperature for 12 h afford **16b** (26.6 mg, 86%, 99% D) as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 (d, *J* = 8.5 Hz, 2 H), 6.86 (d, *J* = 8.5 Hz, 2 H), 3.90 - 3.64 (m, 2 H), 2.80 (t, *J* = 6.6 Hz, 2 H), 1.64 (bs, 1 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.2, 130.4, 129.9, 114.0, 63.8, 38.2. ATR-FTIR (cm^{-1}): 3401, 1711, 1615, 1516, 1448, 1370, 1219, 1088, 828. HRMS (ESI^{+}) Calcd for $C_9H_9D_3O_2Na$ $[M+Na]^{+}$: 178.0918, found: 178.0916.

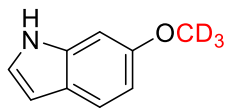
The corresponding non-deuterated product:



16b-H

2-(4-Methoxyphenyl)ethan-1-ol **16b**-H (CAS: 702-23-8): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.15 (d, *J* = 8.6 Hz, 2 H), 6.86 (d, *J* = 8.6 Hz, 2 H), 3.85 - 3.80 (m, 2 H), 3.79 (s, 3 H), 2.81 (t, *J* = 6.5 Hz, 2 H), 1.43 (bs, 1 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.2, 130.4, 130.0, 114.0, 63.8, 55.3, 38.2.

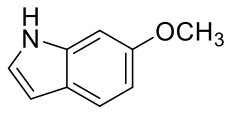
6-(Methoxy-d_3)-1*H*-indole (**17b**)



17b

Following the general procedure A, the reaction of **17a** (26.6 mg, 0.2 mmol, 1.0 equiv), **DMTT** (70.2 mg, 0.2 mmol, 1.0 equiv), K_2CO_3 (55.2 mg, 0.4 mmol, 2.0 equiv), and MeCN (2 mL) at room temperature for 12 h afford **17b** (27.6 mg, 92%, 99% D) as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (s, 1 H), 7.54 (d, *J* = 8.5 Hz, 1 H), 7.15 - 7.05 (m, 1 H), 6.89 - 6.80 (m, 2 H), 6.52 - 6.49 (m, 1 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.3, 136.5, 123.0, 122.1, 121.2, 109.8, 102.4, 94.5. ATR-FTIR (cm^{-1}): 3395, 2955, 2909, 2835, 1627, 1502, 1458, 1161, 1025, 811, 717. HRMS (ESI^+) Calcd for $C_9H_7D_3NO$ $[M+H]^+$: 151.0945, found: 151.0945.

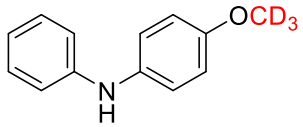
The corresponding non-deuterated product:



17b-H

6-(Methoxy-*d*$_3$)-1*H*-indole **17b**-H (CAS: 3189-13-7): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (s, 1 H), 7.55 (d, *J* = 8.5 Hz, 1 H), 7.12 - 7.04 (m, 1 H), 6.92 - 6.79 (m, 2 H), 6.57 - 6.42 (m, 1 H), 3.86 (s, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.3, 136.5, 123.0, 122.1, 121.2, 109.8, 102.3, 94.5, 55.6.

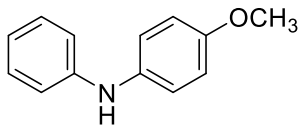
4-(Methoxy-*d*$_3$)-*N*-phenylaniline (**18b**)



18b

Following the general procedure A, the reaction of **18a** (37.0 mg, 0.2 mmol, 1.0 equiv), **DMTT** (70.2 mg, 0.2 mmol, 1.0 equiv), K_2CO_3 (55.2 mg, 0.4 mmol, 2.0 equiv), and MeCN (2 mL) at room temperature for 12 h afford **18b** (24.2 mg, 60%, 99% D) as a white solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 - 7.18 (m, 2 H), 7.14 - 7.04 (m, 2 H), 6.99 - 6.77 (m, 5 H), 5.50 (s, 1 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.2, 145.1, 135.7, 129.3, 122.2, 119.5, 115.6, 114.6. ATR-FTIR (cm^{-1}): 3395, 3057, 3032, 2962, 2928, 2834, 1598, 1515, 1247, 1031, 829, 744. HRMS (ESI^+) Calcd for $C_{13}H_{10}D_3NONa$ $[M+Na]^+$: 225.1078, found: 225.1080.

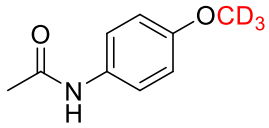
The corresponding non-deuterated product:



18b-H

4-(Methoxy-d_3)-*N*-phenylaniline **18b**-H (CAS: 1208-86-2): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 - 7.20 (m, 2 H), 7.12 - 7.07 (m, 2 H), 6.96 - 6.81 (m, 5 H), 5.51 (s, 1 H), 3.82 (s, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.2, 145.1, 135.7, 129.3, 122.2, 119.5, 115.6, 114.6, 55.5.

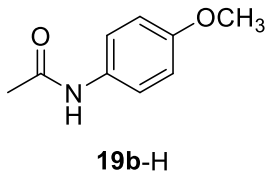
N-(4-(Methoxy-d_3)phenyl)acetamide (**19b**)



19b

Following the general procedure A, the reaction of **19a** (30.2 mg, 0.2 mmol, 1.0 equiv), **DMTT** (70.2 mg, 0.2 mmol, 1.0 equiv), K_2CO_3 (55.2 mg, 0.4 mmol, 2.0 equiv), and MeCN (2 mL) at room temperature for 12 h afford **19b** (32.9 mg, 98%, 99% D) as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (s, 1 H), 7.37 (d, *J* = 9.0 Hz, 2 H), 6.80 (d, *J* = 8.9 Hz, 2 H), 2.09 (s, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.7, 156.3, 131.0, 122.0, 114.0, 24.1. ATR-FTIR (cm^{-1}): 3244, 3070, 2961, 1651, 1603, 1515, 1318, 1113, 1029, 818, 773. HRMS (ESI^+) Calcd for $C_9H_8D_3NO_2Na$ $[M+Na]^+$: 191.0871, found: 191.0868.

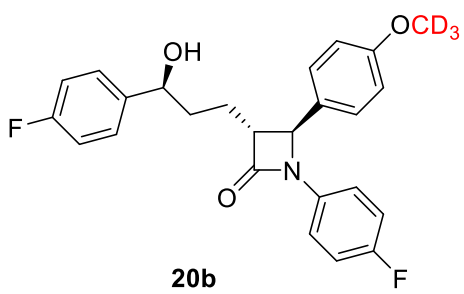
The corresponding non-deuterated product:



19b-H

N-(4-(Methoxy-d_3)phenyl)acetamide **19b**-H (CAS: 51-66-1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (s, 1 H), 7.37 (d, *J* = 9.0 Hz, 2 H), 6.81 (d, *J* = 9.0 Hz, 2 H), 3.75 (s, 3 H), 2.10 (s, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.7, 156.3, 131.0, 122.0, 114.0, 55.4, 24.1.

(3*R*,4*S*)-1-(4-Fluorophenyl)-3-((*S*)-3-(4-fluorophenyl)-3-hydroxypropyl)-4-(4-(methoxy-d_3)phenyl)azetidin-2-one (**20b**)



20b

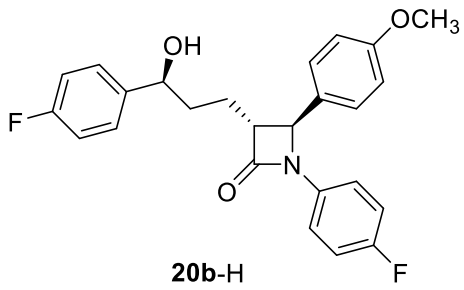
Following the general procedure A, the reaction of **20a** (81.9 mg, 0.2 mmol, 1.0 equiv), **DMTT** (70.2 mg, 0.2 mmol, 1.0 equiv), K_2CO_3 (55.2 mg, 0.4 mmol, 2.0 equiv), and MeCN (2 mL) at

room temperature for 12 h afford **20b** (83.9 mg, 98%, 99% D) as a white solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 - 7.20 (m, 6 H), 7.06 - 6.99 (m, 2 H), 6.98 - 6.87 (m, 4 H), 4.72 (t, *J* = 5.9 Hz, 1 H), 4.61 (d, *J* = 2.3 Hz, 1 H), 3.17 - 2.95 (m, 2 H), 2.06 - 1.85 (m, 4 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.7, 162.0 (d, *J* = 245.3 Hz), 159.7, 158.9 (d, *J* = 243.4 Hz), 140.1 (d, *J* = 3.1 Hz), 133.7 (d, *J* = 2.7 Hz), 129.2, 127.3 (d, *J* = 8.0 Hz), 127.1, 118.4, 118.3 (d, *J* = 7.7 Hz), 115.7 (d, *J* = 22.7 Hz), 115.2 (d, *J* = 21.3 Hz), 114.5, 72.9, 61.0, 60.1, 36.5, 24.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.0, -118.0. ATR-FTIR (cm^{-1}): 3650, 3623, 3504, 2917, 2847, 1741, 1511, 1251, 1223, 750. HRMS (ESI^+) Calcd for $C_{25}H_{20}D_3F_2NO_3Na$ $[M+Na]^+$: 449.1727, found: 449.1723.

The gram scale reaction of **20b**:

The reaction of **20a** (1.085 g, 2.65 mmol, 1.0 equiv), **DMTT** (0.922 g, 2.65 mmol, 1.0 equiv), K_2CO_3 (0.731 g, 5.3 mmol, 2.0 equiv), and MeCN (2 mL) at room temperature for 12 h afford **20b** (1.0737 g, 95%, 99% D) as a white solid.

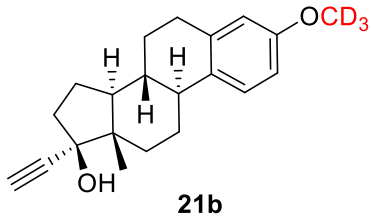
The corresponding non-deuterated product:



20b-H

(3*R*,4*S*)-1-(4-Fluorophenyl)-3-((*S*)-3-(4-fluorophenyl)-3-hydroxypropyl)-4-(4-methoxyphenyl)azetidin-2-one **20b**-H: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 - 7.20 (m, 6 H), 7.09 - 6.98 (m, 2 H), 6.99 - 6.86 (m, 4 H), 4.72 (t, *J* = 5.9 Hz, 1 H), 4.61 (d, *J* = 2.4 Hz, 1 H), 3.83 (s, 3 H), 3.14 - 3.05 (m, 1 H), 2.85 (s, 1 H), 2.07 - 1.84 (m, 4 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.7, 162.0 (d, *J* = 245.5 Hz), 159.7, 158.9 (d, *J* = 243.2 Hz), 140.1 (d, *J* = 3.1 Hz), 133.7 (d, *J* = 2.7 Hz), 129.2, 127.3 (d, *J* = 7.9 Hz), 127.1, 118.4, 118.3 (d, *J* = 7.8 Hz), 115.7 (d, *J* = 22.7 Hz), 115.2 (d, *J* = 21.3 Hz), 114.6, 72.9, 61.0, 60.2, 55.2, 36.5, 24.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.0, -118.1.

(8*R*,9*S*,13*S*,14*S*,17*R*)-17-Ethynyl-3-(methoxy-d_3)-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-17-ol (**21b**)



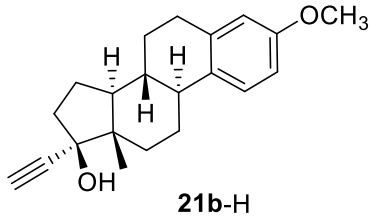
21b

Following the general procedure A, the reaction of **21a** (59.3 mg, 0.2 mmol, 1.0 equiv), **DMTT** (70.2 mg, 0.2 mmol, 1.0 equiv), K_2CO_3 (55.2 mg, 0.4 mmol, 2.0 equiv), and MeCN (2 mL) at room temperature for 12 h afford **21b** (61.6 mg, 98%, 99% D) as a white solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (d, *J* = 8.6 Hz, 1 H), 6.73 (dd, *J* = 8.6, 2.8 Hz, 1 H), 6.65 (d, *J* = 2.7 Hz, 1 H), 2.91 - 2.83 (m, 2 H), 2.62 (s, 1 H), 2.44 - 2.31 (m, 2 H), 2.28 - 2.20 (m, 1 H), 2.12 (s, 1 H), 2.10 - 2.00 (m, 1 H), 1.99 - 1.86 (m, 2 H), 1.84 - 1.67 (m, 3 H), 1.59 - 1.32 (m, 4 H), 0.90 (s, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.3, 137.9, 132.5, 126.3, 113.7, 111.4, 87.5, 79.8, 74.0, 49.4, 47.1, 43.5, 39.4, 38.9, 32.7, 29.8, 27.2, 26.3, 22.8, 12.7. ATR-FTIR (cm^{-1}): 3284, 2904, 2868, 1611, 1501, 1448, 1287, 1251, 1139, 1060, 906, 735. HRMS (ESI^+) Calcd for $C_{21}H_{24}D_3O_2$ $[M+H]^+$: 314.2194, found: 314.2193.

The gram scale reaction of **21b**:

The reaction of **21a** (1.097 g, 3.7 mmol, 1.0 equiv), **DMTT** (1.288 g, 3.7 mmol, 1.0 equiv), K_2CO_3 (1.021 g, 7.4 mmol, 2.0 equiv), and MeCN (2 mL) at room temperature for 12 h afford **21b** (1.1133 g, 96%, 99% D) as a white solid.

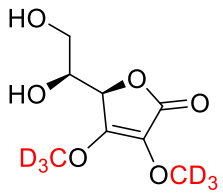
The corresponding non-deuterated product:



21b-H

(8*R*,9*S*,13*S*,14*S*,17*R*)-17-Ethynyl-3-methoxy-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-17-ol **21b**-H (CAS: 72-33-3): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (d, *J* = 8.7 Hz, 1 H), 6.73 (dd, *J* = 8.6, 2.8 Hz, 1 H), 6.64 (d, *J* = 2.7 Hz, 1 H), 3.79 (s, 3 H), 2.93 - 2.79 (m, 2 H), 2.62 (s, 1 H), 2.44 - 2.30 (m, 2 H), 2.28 - 2.17 (m, 1 H), 2.07 - 1.97 (m, 2 H), 1.98 - 1.86 (m, 2 H), 1.84 - 1.69 (m, 3 H), 1.60 - 1.30 (m, 4 H), 0.90 (s, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.4, 137.9, 132.5, 126.3, 113.8, 111.4, 87.5, 79.8, 74.0, 55.2, 49.4, 47.1, 43.5, 39.4, 38.9, 32.7, 29.8, 27.2, 26.4, 22.8, 12.7.

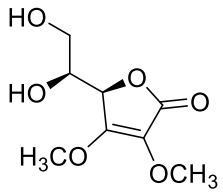
(*R*)-5-((*S*)-1,2-Dihydroxyethyl)-3,4-bis(methoxy-d_3)furan-2(5*H*)-one (**22b**)



22b

Following the general procedure A, the reaction of **22a** (35.2 mg, 0.2 mmol, 1.0 equiv), **DMTT** (140.4 mg, 0.4 mmol, 2.0 equiv), K_2CO_3 (110.4 mg, 0.8 mmol, 4.0 equiv), and MeCN (2 mL) at room temperature for 12 h afford **22b** (38.4 mg, 91%, 99% D) as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.67 (d, *J* = 2.9 Hz, 1 H), 3.97 - 3.88 (m, 1 H), 3.88 - 3.75 (m, 2 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 75.8, 69.9, 63.3. ATR-FTIR (cm^{-1}): 3743, 3476, 3417, 1752, 1677, 1515, 1068, 746. HRMS (ESI$^+$) Calcd for $C_8H_6D_6O_6Na$ [M+Na]$^+$: 233.0903, found: 233.0903.

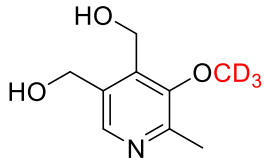
The corresponding non-deuterated product:



22b-H

(*R*)-5-((*S*)-1,2-Dihydroxyethyl)-3,4-bis(methoxy)furan-2(5*H*)-one **22b**-H[9]: ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.67 (d, *J* = 2.7 Hz, 1 H), 4.16 (s, 3 H), 3.97 - 3.89 (m, 1 H), 3.88 - 3.72 (m, 2 H), 3.83 (s, 3 H), 3.03 (s, 1 H), 2.67 (s, 1 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.6, 157.8, 122.9, 75.8, 69.9, 63.3, 60.5, 59.5.

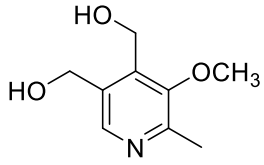
(5-(Methoxy-d_3)-6-methylpyridine-3,4-diyl)dimethanol (**23b**)



23b

Following the general procedure A, the reaction of **23a** (33.8 mg, 0.2 mmol, 1.0 equiv), **DMTT** (70.2 mg, 0.2 mmol, 1.0 equiv), K_2CO_3 (55.2 mg, 0.4 mmol, 2.0 equiv), and MeCN (2 mL) at room temperature for 12 h afford **23b** (30.8 mg, 83%, 99% D) as a colorless oil: ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.38 (s, 1 H), 4.58 (s, 2 H), 4.40 (s, 2 H), 3.16 (s, 2 H), 2.36 (s, 3 H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 166.1, 142.2, 137.0, 134.8, 121.6, 58.7, 58.1, 12.0. ATR-FTIR (cm^{-1}): 3425, 1653, 1026, 825, 764, 629. HRMS (ESI$^+$) Calcd for $C_9H_{11}D_3NO_3$ [M+H]$^+$: 187.1156, found: 187.1158.

The corresponding non-deuterated product:



23b-H

(5-Methoxy-6-methylpyridine-3,4-diyl)dimethanol **23b**-H[10]: ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.37 (s, 1 H), 4.59 (s, 2 H),

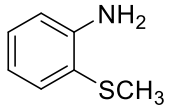
4.40 (s, 2 H), 3.97 (s, 3 H), 2.37 (s, 3 H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 166.2, 142.0, 136.8, 134.6, 121.3, 58.9, 58.0, 45.0, 11.9.

2-((Methyl-d_3)thio)aniline (**24b**)

24b

Following the general procedure A, the reaction of 2-aminobenzenethiol **24a** (25.0 mg, 0.2 mmol, 1.0 equiv), **DMTT** (70.2 mg, 0.2 mmol, 1.0 equiv), K_2CO_3 (55.2 mg, 0.4 mmol, 2.0 equiv), and MeCN (2 mL) at room temperature for 12 h afford **24b** (19.3 mg, 68%, 99% D) as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (dd, *J* = 7.9, 1.5 Hz, 1 H), 7.10 (td, *J* = 7.7, 1.5 Hz, 1 H), 6.80 - 6.65 (m, 2 H), 4.27 (bs, 2 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.0, 133.4, 128.8, 120.1, 118.7, 114.8. ATR-FTIR (cm^{-1}): 3421, 3346, 3057, 3016, 1653, 1607, 1465, 1437, 1300, 914, 744. HRMS (ESI$^+$) Calcd for $C_7H_7D_3NS$ [M+H]$^+$: 143.0717, found: 143.0715.

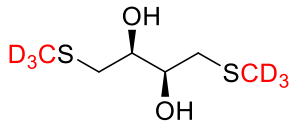
The corresponding non-deuterated product:



24b-H

2-(Methylthio)aniline **24b**-H (CAS: 2987-53-3): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (dd, *J* = 7.9, 1.5 Hz, 1 H), 7.15 - 7.04 (m, 1 H), 6.77 - 6.67 (m, 2 H), 4.27 (s, 2 H), 2.36 (s, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.0, 133.4, 128.9, 120.2, 118.7, 114.8, 17.7.

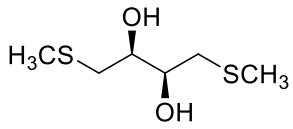
DL-1,4-bis((methyl-d_3)thio)butane-2,3-diol (**25b**)



25b

Following the general procedure A, the reaction of DL-1,4-dithiothreitol **25a** (30.8 mg, 0.2 mmol, 1.0 equiv), **DMTT** (140.4 mg, 0.4 mmol, 2.0 equiv), K_2CO_3 (110.4 mg, 0.8 mmol, 4.0 equiv), and MeCN (2 mL) at room temperature for 12 h afford **25b** (28.8, 76%, 99% D) as a white solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.77 - 3.69 (m, 2 H), 2.83 - 2.78 (m, 2 H), 2.77 - 2.64 (m, 4 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 70.0, 38.1. ATR-FTIR (cm^{-1}): 3235, 2915, 1695, 1429, 1320, 1034, 967, 876, 706. HRMS (ESI$^+$) Calcd for $C_6H_8D_6O_2S_2Na$ [M+Na]$^+$: 211.0704, found: 211.0702.

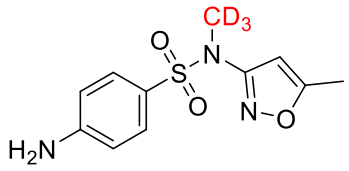
The corresponding non-deuterated product:



25b-H

DL-1,4-bis((methylthio)butane-2,3-diol **25b**-H: ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.79 - 3.68 (m, 2 H), 2.91 - 2.77 (m, 2 H), 2.76 - 2.67 (m, 4 H), 2.13 (s, 6 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 70.0, 38.2, 15.6.

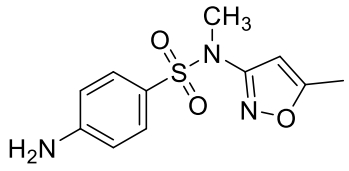
4-Amino-*N*-(methyl-d_3)-*N*-(5-methylisoxazol-3-yl)benzenesulfonamide (**26b**)



26b

Following the general procedure A, the reaction of sulfamethoxazole **26a** (50.7 mg, 0.2 mmol, 1.0 equiv), **DMTT** (70.2 mg, 0.2 mmol, 1.0 equiv), K_2CO_3 (55.2 mg, 0.4 mmol, 2.0 equiv), and MeCN (2 mL) at room temperature for 12 h afford **26b** (51.2 mg, 95%, 99% D) as a white solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 - 7.40 (m, 2 H), 6.61 - 6.56 (m, 2 H), 6.45 (d, *J* = 0.9 Hz, 1 H), 4.28 (s, 2 H), 2.34 (s, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.1, 160.9, 151.4, 129.2, 124.2, 113.9, 97.5, 12.6. ATR-FTIR (cm^{-1}): 3480, 3385, 3236, 2936, 1597, 1446, 1350, 1162, 1003, 917, 834, 692. HRMS (ESI^+) Calcd for $C_{11}H_{10}D_3N_3O_3S$ $[M]^+$: 270.0866, found: 270.0867.

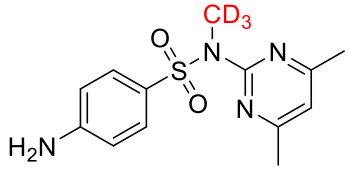
The corresponding non-deuterated product:



26b-H

4-Amino-*N*-methyl-*N*-(5-methylisoxazol-3-yl)benzenesulfonamide **26b**-H[12]: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 - 7.39 (m, 2 H), 6.65 - 6.54 (m, 2 H), 6.46 (d, *J* = 0.9 Hz, 1 H), 4.27 (s, 2 H), 3.20 (s, 3 H), 2.35 (d, *J* = 0.9 Hz, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.1, 161.0, 151.4, 129.3, 124.3, 113.9, 97.5, 34.8, 12.6.

4-Amino-*N*-(4,6-dimethylpyrimidin-2-yl)-*N*-(methyl-d_3)benzenesulfonamide (**27b**)

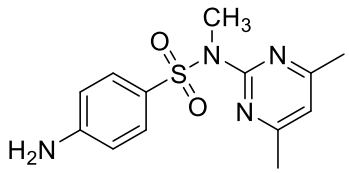


27b

Following the general procedure A, the reaction of sulfamethazine **27a** (55.7 mg, 0.2 mmol, 1.0 equiv),

DMTT (70.2 mg, 0.2 mmol, 1.0 equiv), K_2CO_3 (55.2 mg, 0.4 mmol, 2.0 equiv), and MeCN (2 mL) at room temperature for 12 h afford **27b** (36.6 mg, 62%, 99% D) as a white solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.8 Hz, 2 H), 7.32 (s, 1 H), 6.62 (d, *J* = 8.7 Hz, 2 H), 4.17 (s, 2 H), 2.53 (s, 3 H), 2.43 (s, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.8, 159.7, 151.2, 129.5, 126.3, 113.9, 107.3, 25.8, 24.3. ATR-FTIR (cm^{-1}): 3474, 3383, 3213, 1581, 1359, 1152, 930, 681. HRMS (ESI^+) Calcd for $C_{13}H_{13}D_3N_4O_2SNa$ $[M+Na]^+$: 318.1074, found: 318.1079.

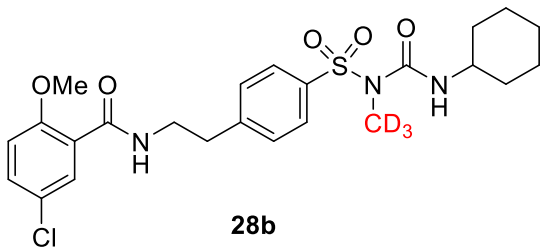
The corresponding non-deuterated product:



27b-H

4-Amino-*N*-(4,6-dimethylpyrimidin-2-yl)-*N*-methylbenzenesulfonamide **27b**-H[12b]: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.7 Hz, 2 H), 7.31 (s, 1 H), 6.61 (d, *J* = 8.7 Hz, 2 H), 4.21 (s, 2 H), 3.38 (s, 3 H), 2.52 (s, 3 H), 2.42 (s, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.8, 159.6, 151.1, 129.5, 126.1, 113.8, 107.3, 34.0, 25.8, 24.3.

5-Chloro-*N*-(4-(*N*-(cyclohexylcarbamoyl)-*N*-(methyl-*d*$_3$)sulfamoyl)phenethyl)-2-methoxybenzamide (**28b**)

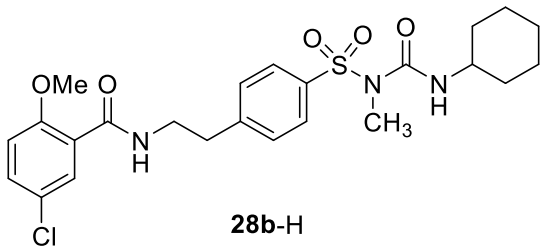


28b

Following the general procedure A, the reaction of glibenclamide **28a** (98.8 mg, 0.2 mmol, 1.0 equiv), **DMTT** (70.2 mg, 0.2 mmol, 1.0 equiv), K_2CO_3 (55.2 mg, 0.4 mmol, 2.0 equiv), and MeCN (2 mL) at room temperature for 12 h afford **28b** (62.2 mg, 61%, 99% D) as a white solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 2.8 Hz, 1 H), 7.81 (t, *J* = 5.8 Hz, 1 H), 7.75 (d, *J* = 8.3 Hz, 2 H), 7.41 (d, *J* = 8.3 Hz, 2 H), 7.36 (dd, *J* = 8.8, 2.8 Hz, 1 H), 7.19 (d, *J* = 7.8 Hz, 1 H), 6.86 (d, *J* = 8.8 Hz, 1 H), 3.77 (s, 3 H), 3.72 (q, *J* = 6.7 Hz, 2 H), 3.66 - 3.54 (m, 1 H), 3.01 (t, *J* = 6.9 Hz, 2 H), 1.91 - 1.81 (m, 3 H), 1.74 - 1.64 (m, 2 H), 1.63 - 1.53 (m, 1 H), 1.37 - 1.25 (m, 2 H), 1.25 - 1.18 (m, 2 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.0, 155.8, 151.8, 146.0, 136.1, 132.4, 131.8, 129.8, 127.1, 126.7, 122.5,

112.8, 56.2, 49.8, 40.5, 35.5, 32.9, 25.4, 24.5. ATR-FTIR (cm^{-1}): 3394, 2934, 2855, 1700, 1655, 1527, 1352, 1270, 1158, 93, 745. HRMS (ESI^+) Calcd for $C_{24}H_{27}D_3ClN_3O_5S$ $[M]^+$: 510.1783, found: 510.1788.

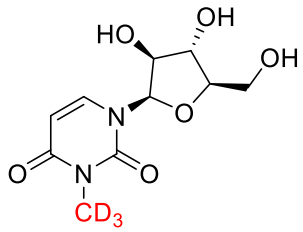
The corresponding non-deuterated product:



28b-H

5-Chloro-*N*-(4-(*N*-(cyclohexylcarbamoyl)-*N*-(methylsulfamoyl)phenethyl-2-methoxybenzamide **28b**-H: ^1H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 2.7 Hz, 1 H), 7.81 (t, *J* = 5.5 Hz, 1 H), 7.75 (d, *J* = 8.3 Hz, 2 H), 7.41 (d, *J* = 8.3 Hz, 2 H), 7.35 (dd, *J* = 8.8, 2.8 Hz, 1 H), 7.19 (d, *J* = 7.8 Hz, 1 H), 6.86 (d, *J* = 8.9 Hz, 1 H), 3.77 (s, 3 H), 3.72 (q, *J* = 6.7 Hz, 2 H), 3.67 - 3.53 (m, 1 H), 3.10 (s, 3 H), 3.00 (t, *J* = 7.0 Hz, 2 H), 1.94 - 1.79 (m, 3 H), 1.76 - 1.63 (m, 2 H), 1.63 - 1.51 (m, 1 H), 1.37 - 1.25 (m, 2 H), 1.25 - 1.15 (m, 2 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.0, 155.8, 151.8, 146.0, 136.0, 132.4, 131.8, 129.8, 127.1, 126.7, 122.5, 112.8, 56.2, 49.8, 40.4, 35.4, 32.9, 32.4, 25.3, 24.5.

1-((2*R*,3*S*,4*S*,5*R*)-3,4-dihydroxy-5-(hydroxymethyl)tetrahydrofuran-2-yl)-3-(methyl-*d*$_3$)pyrimidine-2,4(1*H*,3*H*)-dione (**29b**)

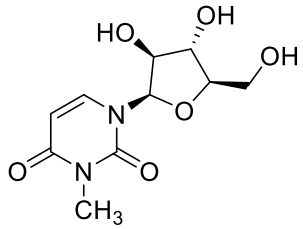


29b

Following the general procedure A, the reaction of spongouridine **29a** (48.8 mg, 0.2 mmol, 1.0 equiv), **DMTT** (70.2 mg, 0.2 mmol, 1.0 equiv), K_2CO_3 (55.2 mg, 0.4 mmol, 2.0 equiv), and MeCN (2 mL) at room temperature for 12 h afford **29b** (47.3 mg, 91%, 99% D) as a white solid: ^1H NMR (400 MHz, CD_3OD) δ 7.85 (d, *J* = 8.1 Hz, 1 H), 6.14 (d, *J* = 4.1 Hz, 1 H), 5.74 (d, *J* = 8.1 Hz, 1 H), 4.24 - 4.13 (m, 1 H), 4.10 - 4.05 (m, 1 H), 3.99 - 3.91 (m, 1 H), 3.87 - 3.74 (m, 2 H). ^{13}C NMR (101 MHz, CD_3OD) δ 165.6, 152.6, 142.2, 100.4, 88.7, 86.7, 77.8, 77.1, 62.7. ATR-FTIR (cm^{-1}): 2931, 2496, 2240, 2223, 2073, 1660, 1471, 1121, 989, 808. EI-MS (*m/z*, relative intensity): 131 (25), 130 (61), 129 (55), 128 (36),

127 (30), 71 (44), 70 (100), 69 (69). HRMS (ESI$^+$) Calcd for $C_{10}H_{11}D_3N_2O_6Na$ $[M+Na]^+$: 284.0932, found: 284.0935.

The corresponding non-deuterated product:



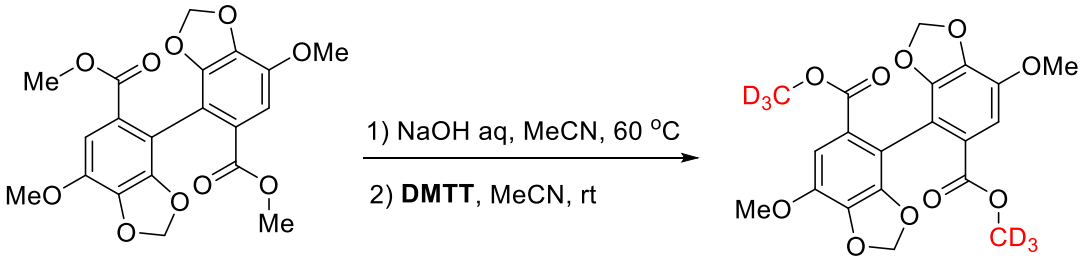
29b-H

1-((2*R*,3*S*,4*S*,5*R*)-3,4-dihydroxy-5-(hydroxymethyl)tetrahydrofuran-2-yl)-3-(methyl)pyrimidine-2,4(1*H*,3*H*)-dione

29b-H[13]: ^{1}H NMR (400 MHz, CD_3OD) δ 7.85 (d, *J* = 8.1 Hz, 1 H), 6.14 (d, *J* = 4.1 Hz, 1 H), 5.74 (d, *J* = 8.1 Hz, 1 H), 4.21 - 4.14 (m, 1 H), 4.07 (t, *J* = 3.1 Hz, 1 H), 3.98 - 3.89 (m, 1 H), 3.86 - 3.73 (m, 2 H), 3.29 (s, 3 H). ^{13}C NMR (101 MHz, CD_3OD) δ 165.6, 152.6, 142.2, 100.4, 88.7, 86.8, 77.8, 77.1, 62.7, 28.0.

Section S5. The application in synthesis of deuterated pharmaceuticals

Synthesis of *d*$_3$-bifendataum:



30a

Bifendatatum:
anti-hepatitis drug

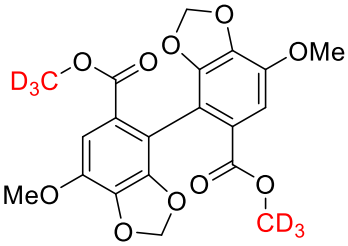
30b

64% for two steps, 99% D

To a 10 mL round flask was added ester **30a** (83.6 mg, 0.2 mmol, 1.0 equiv), NaOH aq. (1 M, 0.8 mmol, 4.0 equiv), and MeCN (2 mL). The mixture was stirring at 60 °C until the starting material was disappeared completely. **DMTT** (140.4 mg, 0.4 mmol, 2.0 equiv) was added and the reaction was stirring at room temperature for 12 h. The resulting mixture was concentrated in vacuo and the residue was purified by

column chromatography to afford the corresponding product **30b** (54.0 mg, 64%, 99% D) as a white solid.

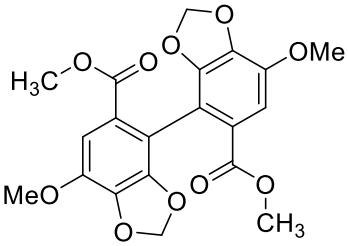
Bis(methyl-d_3) 7,7'-dimethoxy-[4,4'-bibenzo[*d*][1,3]dioxole]-5,5'-dicarboxylate (**30b)**



30b

^{1}H NMR (400 MHz, CD_3OD) δ 7.38 (s, 2 H), 5.99 (s, 4 H), 3.96 (s, 6 H). ^{13}C NMR (101 MHz, CD_3OD) δ 166.3, 147.1, 142.4, 138.1, 123.4, 112.2, 110.9, 102.3, 56.5. ATR-FTIR (cm^{-1}): 2951, 2902, 2844, 1723, 1638, 1592, 1432, 1531, 1319, 1173, 1044, 912, 742. HRMS (ESI^+) Calcd for $C_{20}H_{12}D_6O_{10}Na$ $[M+Na]^+$: 447.1169, found: 447.1165.

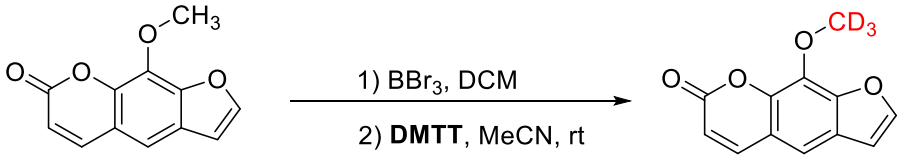
The corresponding non-deuterated product:



30a

Bismethyl 7,7'-dimethoxy-[4,4'-bibenzo[*d*][1,3]dioxole]-5,5'-dicarboxylate **30a (**CAS: 73536-69-3): ^{1}H NMR (400 MHz, CD_3OD) δ 7.37 (s, 2 H), 5.98 (s, 4 H), 3.95 (s, 6 H), 3.66 (s, 6 H). ^{13}C NMR (101 MHz, CD_3OD) δ 166.3, 147.0, 142.3, 138.0, 123.2, 112.1, 110.7, 102.3, 56.4, 51.8.

Synthesis of d_3-methoxsalen:



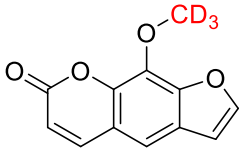
31a **31b**

To a 25 mL dried Schlenk tube was added **31a** (43.2 mg, 0.2 mmol, 1.0 equiv) and anhydrous CH_2Cl_2 (2 mL). Then BBr_3 in DCM (0.8 mL, 0.8 mmol, 1 M, 4.0

equiv) was dropwise at 0 ºC slowly under nitrogen atmosphere. The mixture was warmed to room temperature naturally and stirring for 6 h. After that, 2 mL H_2O was added to quench the reaction. The two liquid layers were separated, and the aqueous layer was extracted with DCM. The combined organic layers were washed with brine and dried with $MgSO_4$. After filtration and evaporation, the residue was purified by column chromatography to give the corresponding phenol derivatives.

To a Schlenk tube was added the corresponding phenol derivatives, **DMTT** (70.2 mg, 0.2 mmol, 1.0 equiv), K_2CO_3 (55.2 mg, 0.4 mmol, 2.0 equiv), and MeCN (2 mL). The mixture was stirring at room temperature for 12 h. The resulting mixture was concentrated in vacuo and the residue was purified by column chromatography to afford the corresponding product **31b** (36.1 mg, 82%, 99% D) as a white solid.

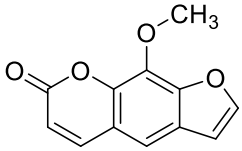
9-(Methoxy-*d*$_3$)-7*H*-furo[3,2-*g*]chromen-7-one (**31b**)



31b

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 9.6 Hz, 1 H), 7.65 (d, *J* = 2.2 Hz, 1 H), 7.30 (s, 1 H), 6.78 (d, *J* = 2.2 Hz, 1 H), 6.31 (d, *J* = 9.6 Hz, 1 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.4, 147.4, 146.5, 144.3, 142.7, 132.5, 126.0, 116.3, 114.4, 112.8, 106.6. ATR-FTIR (cm^{-1}): 3140, 3114, 3067, 1712, 1585, 1442, 1038, 1159, 1107, 872. HRMS (ESI^+) Calcd for $C_{12}H_5D_3O_4Na$ $[M+Na]^+$: 242.0503, found: 242.0507.

The corresponding non-deuterated product:

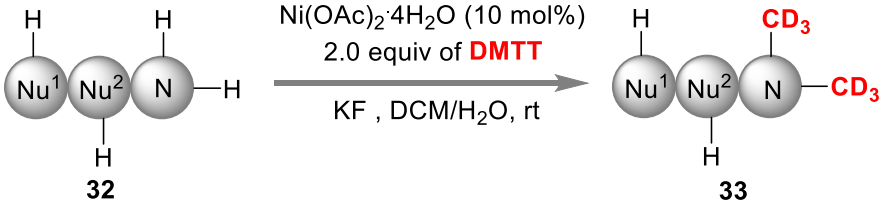


31a

9-Methoxy-7*H*-furo[3,2-*g*]chromen-7-one **31a** (CAS: 298-81-7): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 9.6 Hz, 1 H), 7.66 (d, *J* = 2.2 Hz, 1 H), 7.32 (s, 1 H), 6.79 (d, *J* = 2.2 Hz, 1 H), 6.33 (d, *J* = 9.6 Hz, 1 H), 4.25 (s, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.4, 147.5, 146.5, 144.3, 142.8, 132.6, 126.0, 116.3, 114.5, 112.9, 106.6, 61.2.

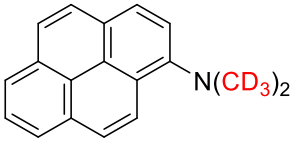
Section S6. The Synthesis of N,N-dimethylamines 33

General Procedure C:



To a Schlenk tube was added amines **32** (0.2 mmol, 1.0 equiv), **DMTT** (0.4 mmol, 2.0 equiv), $Ni(OAc)_2 \cdot 4H_2O$ (5.0 mg, 0.02 mmol, 0.1 equiv), KF (23.2 mg, 0.4 mmol, 2.0 equiv), and DCM/H_2O (2 mL, v:v = 20/1). The mixture was stirring at room temperature for 12 hours. Then the resulting mixture was concentrated in vacuo and the residue was purified by column chromatography to afford the corresponding product **33**.

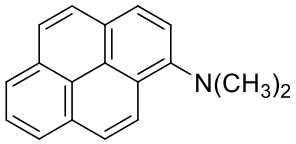
N,*N*-bis(methyl-d_3)pyren-1-amine (**33a**)



33a

Following the general procedure C, the reaction of pyren-1-amine **32a** (43.5 mg, 0.2 mmol, 1.0 equiv), **DMTT** (140.4 mg, 0.4 mmol, 2.0 equiv), $Ni(OAc)_2 \cdot 4H_2O$ (5.0 mg, 0.02 mmol, 0.1 equiv), KF (23.2 mg, 0.4 mmol, 2.0 equiv), and DCM/H_2O (2 mL, v:v = 20/1) at room temperature for 12 h afford **33a** (42.7 mg, 85%, 99% D) as a yellow solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (d, *J* = 9.2 Hz, 1 H), 8.19 - 8.07 (m, 4 H), 8.04 - 7.92 (m, 3 H), 7.75 (d, *J* = 8.2 Hz, 1 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.9, 131.6, 131.3, 127.3, 126.9, 126.3, 125.97, 125.87, 125.4, 125.2, 124.3, 124.3, 123.4, 116.3. ATR-FTIR (cm^{-1}): 3038, 1598, 1487, 1433, 1278, 1179, 913, 839, 747. HRMS (ESI^+) Calcd for $C_{18}H_{10}D_6N$ $[M+H]^+$: 252.1654, found: 252.1653.

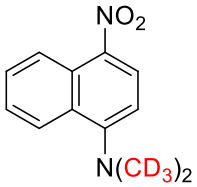
The corresponding non-deuterated product:



33a-H

N,*N*-dimethylpyren-1-amine **33a**-H: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (d, *J* = 9.2 Hz, 1 H), 8.20 - 8.06 (m, 4 H), 8.04 - 7.90 (m, 3 H), 7.76 (d, *J* = 8.2 Hz, 1 H), 3.08 (s, 6 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.9, 131.6, 131.3, 127.3, 127.0, 126.3, 125.97, 125.88, 125.5, 125.2, 124.3, 124.3, 123.4, 116.4, 45.6.

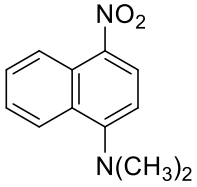
N,*N*-bis(methyl-*d*$_3$)-4-nitronaphthalen-1-amine (**33b**)



33b

Following the general procedure C, the reaction of 4-nitronaphthalen-1-amine **32b** (37.6 mg, 0.2 mmol, 1.0 equiv), **DMTT** (140.4 mg, 0.4 mmol, 2.0 equiv), $Ni(OAc)_2{\cdot}4H_2O$ (5.0 mg, 0.02 mmol, 0.1 equiv), KF (23.2 mg, 0.4 mmol, 2.0 equiv), and DCM/H_2O (2 mL, v:v = 20/1) at room temperature for 12 h afford **33b** (30.2 mg, 68%, 99% D) as a yellow solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.78 (d, *J* = 8.8 Hz, 1 H), 8.30 (d, *J* = 8.6 Hz, 1 H), 8.19 (d, *J* = 8.6 Hz, 1 H), 7.73 - 7.62 (m, 1 H), 7.58 - 7.48 (m, 1 H), 6.89 (d, *J* = 8.6 Hz, 1 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.4, 139.4, 129.3, 127.6, 127.4, 126.6, 125.7, 125.5, 124.0, 110.4. ATR-FTIR (cm^{-1}): 3080, 2924, 1505, 1427, 1291, 826, 763, 652. HRMS (ESI^+) Calcd for $C_{12}H_7D_6N_2O_2$ $[M+H]^+$: 223.1348, found: 223.1347.

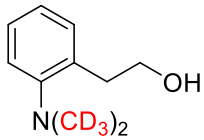
The corresponding non-deuterated product:



33b-H

N,*N*-dimethyl-4-nitronaphthalen-1-amine **33b**-H: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.78 (d, *J* = 8.7 Hz, 1 H), 8.31 (d, *J* = 8.6 Hz, 1 H), 8.20 (d, *J* = 8.6 Hz, 1 H), 7.72 - 7.61 (m, 1 H), 7.59 - 7.49 (m, 1 H), 6.91 (d, *J* = 8.6 Hz, 1 H), 3.04 (s, 6 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.3, 139.5, 129.3, 127.6, 127.5, 126.6, 125.7, 125.5, 124.0, 110.5, 44.7.

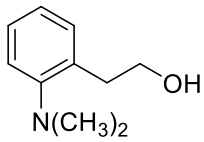
2-(2-(bis(methyl-*d*$_3$)amino)phenyl)ethan-1-ol (**33c**)



33c

Following the general procedure C, the reaction of 2-(2-aminophenyl)ethan-1-ol **32c** (27.4 mg, 0.2 mmol, 1.0 equiv), **DMTT** (140.4 mg, 0.4 mmol, 2.0 equiv), $Ni(OAc)_2 \cdot 4H_2O$ (5.0 mg, 0.02 mmol, 0.1 equiv), KF (23.2 mg, 0.4 mmol, 2.0 equiv), and DCM/H_2O (2 mL, v:v = 20/1) at room temperature for 12 h afford **33c** (24.3 mg, 71%, 99% D) as oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27 - 7.20 (m, 1 H), 7.22 - 7.16 (m, 1 H), 7.17 - 7.11 (m, 1 H), 7.11 - 7.04 (m, 1 H), 5.60 (bs, 1 H), 3.93 - 3.74 (m, 2 H), 3.07 - 2.90 (m, 2 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.0, 136.5, 131.2, 127.7, 125.1, 120.0, 64.6, 36.4. ATR-FTIR (cm^{-1}): 3295, 2924, 2854, 1490, 1262, 1045, 936, 760. HRMS (ESI^+) Calcd for $C_{10}H_{10}D_6NO$ $[M+H]^+$: 172.1603, found: 172.1605.

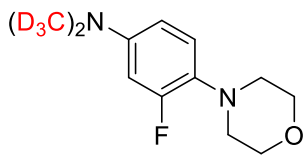
The corresponding non-deuterated product:



33c-H

2-(2-(dimethylamino)phenyl)ethan-1-ol **33c**-H: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27 – 7.20 (m, 1 H), 7.23 - 7.17 (m, 2 H), 7.17 - 7.11 (m, 1 H), 7.11 - 7.04 (m, 1 H), 5.51 (bs, 1 H), 3.91 - 3.76 (m, 2 H), 3.06 - 2.92 (m, 2 H), 2.70 (s, 6 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.0, 136.5, 131.2, 127.7, 125.2, 120.1, 64.6, 44.9, 36.4.

3-Fluoro-*N*,*N*-bis(methyl-d_3)-4-morpholinoaniline (**33d**)

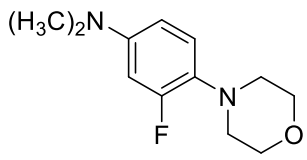


33d

Following the general procedure C, the reaction of 3-fluoro-4-morpholinoaniline **32d** (39.2 mg, 0.2 mmol, 1.0 equiv), **DMTT** (140.4 mg, 0.4 mmol, 2.0 equiv), $Ni(OAc)_2 \cdot 4H_2O$ (5.0 mg, 0.02 mmol, 0.1 equiv), KF (23.2 mg, 0.4 mmol, 2.0 equiv), and DCM/H_2O (2 mL, v:v = 20/1) at room temperature for 12 h afford **33d** (28.1 mg, 61%, 99% D) as a white solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.89 (dd, *J* = 9.8, 8.7 Hz, 1H), 6.54 - 6.37 (m, 2 H), 3.94 - 3.78 (m, 4 H), 3.06 - 2.89 (m, 4 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.9 (d, *J* = 243.7 Hz), 147.8 (d, *J* = 9.9 Hz), 129.9 (d, *J* = 9.7 Hz), 120.0 (d, *J* = 4.8 Hz), 108.1 (d, *J* = 2.7 Hz), 101.4 (d, *J* =

24.8 Hz), 67.2, 51.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ -122.6. ATR-FTIR (cm^{-1}): 2963, 2852, 1629, 1562, 1520, 1234, 1116, 936, 745. HRMS (ESI^+) Calcd for $C_{12}H_{12}D_6FN_2O$ $[M+H]^+$: 231.1774, found: 231.1771.

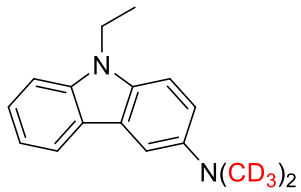
The corresponding non-deuterated product:



33d-H

3-fluoro-N,N-dimethyl-4-morpholinoaniline **33d**-H: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.89 (dd, *J* = 9.8, 8.7 Hz, 1 H), 6.55 - 6.36 (m, 2 H), 3.93 - 3.79 (m, 4 H), 3.05 - 2.94 (m, 4 H), 2.89 (s, 6 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.9 (d, *J* = 243.9 Hz), 147.7 (d, *J* = 10.0 Hz), 129.9 (d, *J* = 9.9 Hz), 120.0 (d, *J* = 4.9 Hz), 108.1 (d, *J* = 2.7 Hz), 101.5 (d, *J* = 24.9 Hz), 67.2, 51.8 (d, *J* = 2.3 Hz), 40.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ -122.6.

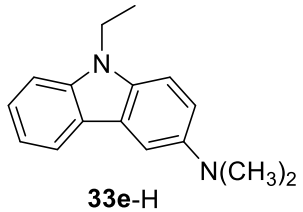
9-Ethyl-*N*,*N*-bis(methyl-d_3)-9*H*-carbazol-3-amine (**33e**)



33e

Following the general procedure C, the reaction of 9-ethyl-9*H*-carbazol-3-amine **32e** (42.0 mg, 0.2 mmol, 1.0 equiv), **DMTT** (140.4 mg, 0.4 mmol, 2.0 equiv), $Ni(OAc)_2{\cdot}4H_2O$ (5.0 mg, 0.02 mmol, 0.1 equiv), KF (23.2 mg, 0.4 mmol, 2.0 equiv), and DCM/H_2O (2 mL, v:v = 20/1) at room temperature for 12 h afford **33e** (36.3 mg, 74%, 99% D) as a yellow solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 - 8.02 (m, 1 H), 7.54 - 7.47 (m, 1 H), 7.44 - 7.38 (m, 1 H), 7.34 - 7.27 (m, 2 H), 7.18 - 7.07 (m, 2 H), 4.29 (q, *J* = 7.2 Hz, 2 H), 1.38 (t, *J* = 7.2 Hz, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.3, 140.3, 134.0, 125.3, 123.4, 122.8, 120.3, 117.9, 115.2, 108.8, 108.3, 105.2, 37.5, 13.8. ATR-FTIR (cm^{-1}): 3049, 2974, 1490, 1472, 1314, 1231, 851, 723. HRMS (ESI^+) Calcd for $C_{16}H_{13}D_6N_2$ $[M+H]^+$: 245.1919, found: 245.1918.

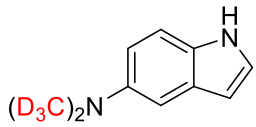
The corresponding non-deuterated product:



33e-H

9-Ethyl-*N*,*N*-dimethyl-9*H*-carbazol-3-amine **33e**-H: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11-8.06 (m, 1 H), 7.56 (d, *J* = 2.4 Hz, 1 H), 7.49 - 7.40 (m, 1 H), 7.41 - 7.29 (m, 2 H), 7.24 - 7.11 (m, 2 H), 4.33 (q, *J* = 7.2 Hz, 2 H), 3.02 (s, 4 H), 1.42 (t, *J* = 7.2 Hz, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.1, 140.3, 134.2, 125.3, 123.4, 122.8, 120.3, 118.0, 115.4, 108.8, 108.3, 105.5, 43.0, 37.5, 13.9.

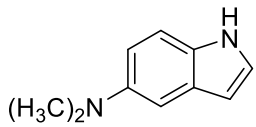
N,*N*-bis(methyl-*d*$_3$)-1*H*-indol-5-amine (**33f**)



33f

Following the general procedure C, the reaction of 1*H*-indol-5-amine **32f** (26.4 mg, 0.2 mmol, 1.0 equiv), **DMTT** (140.4 mg, 0.4 mmol, 2.0 equiv), $Ni(OAc)_2{\cdot}4H_2O$ (5.0 mg, 0.02 mmol, 0.1 equiv), KF (23.2 mg, 0.4 mmol, 2.0 equiv), and DCM/H_2O (2 mL, v:v = 20/1) at room temperature for 12 h afford **33f** (15.2 mg, 46%, 99% D) as oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (s, 1 H), 7.28 (d, *J* = 8.8 Hz, 1 H), 7.13 (t, *J* = 2.8 Hz, 1 H), 7.07 (d, *J* = 2.0 Hz, 1 H), 6.92 (dd, *J* = 8.8, 2.4 Hz, 1 H), 6.49 - 6.42 (m, 1 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.0, 130.3, 128.5, 124.5, 113.1, 111.3, 104.9, 102.0. ATR-FTIR (cm^{-1}): 3404, 1578, 1474, 1322, 1255, 1185, 752, 723. HRMS (ESI^+) Calcd for $C_{10}H_7D_6N_2$ $[M+H]^+$: 167.1450, found: 167.1449.

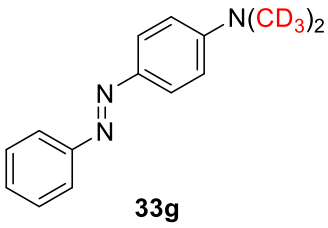
The corresponding non-deuterated product:



33f-H

N,*N*-dimethyl-1*H*-indol-5-amine **33f**-H: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (s, 1 H), 7.28 (d, *J* = 8.8 Hz, 1 H), 7.14 (t, *J* = 2.8 Hz, 1 H), 7.07 (d, *J* = 2.3 Hz, 1 H), 6.93 (dd, *J* = 8.8, 2.4 Hz, 1 H), 6.50 - 6.42 (m, 1 H), 2.94 (s, 6 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.1, 130.3, 128.5, 124.5, 113.2, 111.3, 104.9, 102.0, 43.0.

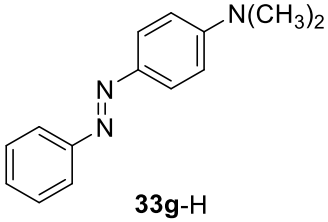
(*E*)-*N*,*N*-bis(methyl-*d*$_3$)-4-(phenyldiazenyl)aniline (**33g**)



33g

Following the general procedure C, the reaction of (*E*)-4-(phenyldiazenyl)aniline **32g** (39.4 mg, 0.2 mmol, 1.0 equiv), **DMTT** (140.4 mg, 0.4 mmol, 2.0 equiv), $Ni(OAc)_2 \cdot 4H_2O$ (5.0 mg, 0.02 mmol, 0.1 equiv), KF (23.2 mg, 0.4 mmol, 2.0 equiv), and DCM/H_2O (2 mL, v:v = 20/1) at room temperature for 12 h afford **33g** (34.5 mg, 75%, 99% D) as a yellow solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 - 7.80 (m, 4 H), 7.54 - 7.44 (m, 2 H), 7.44 - 7.35 (m, 1 H), 6.81 - 6.70 (m, 2 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.2, 152.4, 143.6, 129.3, 128.9, 124.9, 122.2, 111.4. ATR-FTIR (cm^{-1}): 3064, 3022, 1599, 1512, 1373, 1149, 913, 818, 747. HRMS (ESI^+) Calcd for $C_{14}H_{10}D_6N_3$ $[M+H]^+$: 232.1715, found: 232.1715.

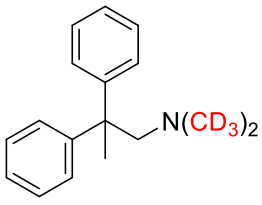
The corresponding non-deuterated product:



33g-H

(E)-N,N-dimethyl-4-(phenyldiazenyl)aniline **33g**-H: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 - 7.82 (m, 4 H), 7.54 - 7.44 (m, 2 H), 7.43 - 7.35 (m, 1 H), 6.81 - 6.72 (m, 2 H), 3.08 (s, 6 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.2, 152.4, 143.6, 129.3, 128.9, 124.9, 122.2, 111.5, 40.3.

N,N-bis(methyl-*d*$_3$)-2,2-diphenylpropan-1-amine (**33h**)

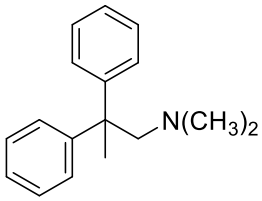


33h

Following the general procedure C, the reaction of 2,2-diphenylpropan-1-amine hydrochloride **32h** (49.4 mg, 0.2 mmol, 1.0 equiv), **DMTT** (140.4 mg, 0.4 mmol, 2.0 equiv), $Ni(OAc)_2 \cdot 4H_2O$ (5.0 mg, 0.02 mmol, 0.1 equiv), KF (23.2 mg, 0.4 mmol, 2.0 equiv), and DCM/H_2O (2 mL, v:v = 20/1) at room temperature for 12 h afford **33h** (30.1 mg, 61%, 99% D) as a white solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 - 7.20 (m, 4 H), 7.19 - 7.13 (m, 1 H), 3.01 (s, 1 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.9, 127.8, 127.6, 125.6, 70.1, 26.7. ATR-FTIR

(cm^{-1}): 3025, 2967, 2935, 1494, 1444, 1200, 913, 746, 698. HRMS (ESI^+) Calcd for $C_{17}H_{16}D_6N$ $[M+H]^+$: 246.2123, found: 246.2123.

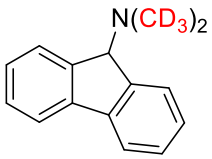
The corresponding non-deuterated product:



33h-H

N,*N*-dimethyl-2,2-diphenylpropan-1-amine **33h**-H: ^1H NMR (400 MHz, $CDCl_3$) δ 7.29 - 7.20 (m, 4 H), 7.20 - 7.13 (m, 1 H), 3.02 (s, 1 H), 2.02 (s, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.9, 127.8, 127.6, 125.6, 70.2, 48.4, 26.7.

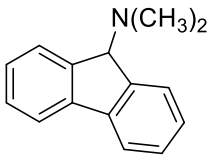
N,*N*-bis(methyl-*d*$_3$)-9*H*-fluoren-9-amine (**33i**)



33i

Following the general procedure C, the reaction of 9*H*-fluoren-9-amine **32i** (36.2 mg, 0.2 mmol, 1.0 equiv), **DMTT** (140.4 mg, 0.4 mmol, 2.0 equiv), $Ni(OAc)_2{\cdot}4H_2O$ (5.0 mg, 0.02 mmol, 0.1 equiv), KF (23.2 mg, 0.4 mmol, 2.0 equiv), and DCM/H_2O (2 mL, v:v = 20/1) at room temperature for 12 h afford **33i** (22.0 mg, 51%, 99% D) as a oil: ^1H NMR (400 MHz, $CDCl_3$) δ 7.70 (dt, *J* = 7.5, 0.9 Hz, 2 H), 7.64 (dd, *J* = 7.4, 1.0 Hz, 2 H), 7.42 - 7.34 (m, 1 H), 7.30 (td, *J* = 7.4, 1.2 Hz, 2 H), 4.85 (s, 1 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.0, 141.0, 128.0, 127.0, 125.9, 119.7, 70.1. ATR-FTIR (cm^{-1}): 2957, 2931, 1498, 1456, 1361, 1174, 882, 705. HRMS (ESI^+) Calcd for $C_{15}H_{10}D_6N$ $[M+H]^+$: 216.1654, found: 216.1653.

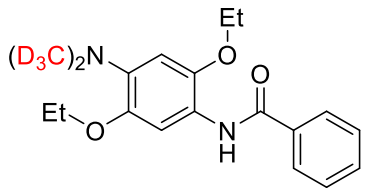
The corresponding non-deuterated product:



33i-H

N,*N*-dimethyl-9H-fluoren-9-amine **33i**-H: ^1H NMR (400 MHz, $CDCl_3$) δ 7.70 (dt, *J* = 7.5, 0.9 Hz, 2 H), 7.64 (dd, *J* = 7.4, 1.0 Hz, 2 H), 7.42 - 7.35 (m, 2 H), 7.30 (td, *J* = 7.5, 1.2 Hz, 2 H), 4.86 (s, 1 H), 2.35 (s, 6 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.9, 141.0, 128.0, 127.0, 125.9, 119.7, 70.2, 41.2.

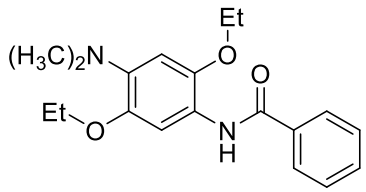
N-(4-(bis(methyl-d_3)amino)-2,5-diethoxyphenyl)benzamide (**33j**)



33j

Following the general procedure C, the reaction of *N*-(4-amino-2,5-diethoxyphenyl)benzamide **32j** (60.0 mg, 0.2 mmol, 1.0 equiv), **DMTT** (140.4 mg, 0.4 mmol, 2.0 equiv), $Ni(OAc)_2 \cdot 4H_2O$ (5.0 mg, 0.02 mmol, 0.1 equiv), KF (23.2 mg, 0.4 mmol, 2.0 equiv), and DCM/H_2O (2 mL, v:v = 20/1) at room temperature for 12 h afford **33j** (51.5 mg, 77%, 99% D) as a white solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (s, 1 H), 8.25 (s, 1 H), 7.93 - 7.82 (m, 2 H), 7.57 - 7.44 (m, 3 H), 6.56 (s, 1 H), 4.20 - 4.05 (m, 4 H), 1.52 - 1.40 (m, 6 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.6, 145.3, 141.3, 138.2, 131.5, 128.7, 126.8, 122.1, 105.4, 103.3, 65.2, 64.0, 15.1, 14.9. ATR-FTIR (cm^{-1}): 3430, 2978, 2930, 1669, 1522, 1419, 1243, 1202, 1046, 913, 708. HRMS (ESI^+) Calcd for $C_{19}H_{19}D_6N_2O_3$ $[M+H]^+$: 335.2236, found: 335.2237.

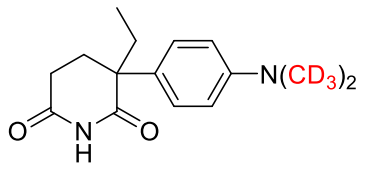
The corresponding non-deuterated product:



33j-H

N-(4-(dimethylamino)-2,5-diethoxyphenyl)benzamide **33j**-H: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (s, 1 H), 8.25 (s, 1 H), 7.91 - 7.83 (m, 2 H), 7.54 - 7.45 (m, 3 H), 6.57 (s, 1 H), 4.18 - 4.09 (m, 4 H), 2.80 (s, 6 H), 1.52 - 1.40 (m, 6 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.6, 145.4, 141.3, 138.2, 135.3, 131.5, 128.7, 126.8, 122.2, 105.4, 103.4, 65.2, 64.0, 43.3, 15.1, 14.9.

3-(4-(Bis(methyl-d_3)amino)phenyl)-3-ethylpiperidine-2,6-dione (**33k**)

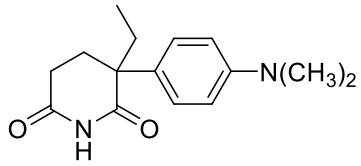


33k

Following the general procedure C, the reaction of aminoglutethimide **32k** (46.4 mg, 0.2 mmol, 1.0 equiv), **DMTT** (140.4 mg, 0.4 mmol, 2.0 equiv), $Ni(OAc)_2 \cdot 4H_2O$ (5.0 mg, 0.02 mmol, 0.1 equiv), KF

(23.2 mg, 0.4 mmol, 2.0 equiv), and DCM/H_2O (2 mL, v:v = 20/1) at room temperature for 12 h afford **33k** (36.1 mg, 68%, 99% D) as a white solid: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (s, 1 H), 7.12 (d, *J* = 8.9 Hz, 2 H), 6.68 (d, *J* = 8.9 Hz, 2 H), 2.62 - 2.53 (m, 1 H), 2.52 - 2.41 (m, 1 H), 2.37 - 2.29 (m, 1 H), 2.22 - 2.12 (m, 1 H), 2.06 - 1.95 (m, 1 H), 1.94 - 1.83 (m, 1 H), 0.85 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.7, 172.6 149.7, 126.9, 125.6, 112.5, 50.1, 32.9, 29.4, 26.9, 9.0. ATR-FTIR (cm^{-1}): 3291, 3190, 3028, 1659, 1529, 1451, 1275, 1016, 765, 749. HRMS (ESI^+) Calcd for $C_{15}H_{15}D_6N_2O_2$ $[M+H]^+$: 267.1974, found: 267.1974.

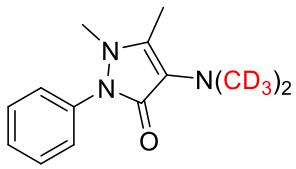
The corresponding non-deuterated product:



33k-H

3-(4-(dimethylamino)phenyl)-3-ethylpiperidine-2,6-dione **33k**-H: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (s, 1 H), 7.12 (d, *J* = 8.9 Hz, 2 H), 6.69 (d, *J* = 8.9 Hz, 2 H), 2.94 (s, 6 H), 2.64 - 2.52 (m, 1 H), 2.53 - 2.39 (m, 1 H), 2.39 - 2.28 (m, 1 H), 2.24 - 2.11 (m, 1 H), 2.08 - 1.94 (m, 1 H), 1.96 - 1.81 (m, 1 H), 0.85 (t, *J* = 7.4 Hz, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.6, 172.6, 149.7, 126.9, 125.7, 112.6, 50.1, 40.4, 32.9, 29.4, 26.9, 9.0.

4-(bis(methyl-*d*$_3$)amino)-1,5-dimethyl-2-phenyl-1,2-dihydro-3*H*-pyrazol-3-one (**33l**)

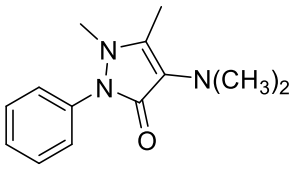


33l

Following the general procedure C, the reaction of 4-aminoantipyrine **32l** (40.6 mg, 0.2 mmol, 1.0 equiv), **DMTT** (140.4 mg, 0.4 mmol, 2.0 equiv), $Ni(OAc)_2{\cdot}4H_2O$ (5.0 mg, 0.02 mmol, 0.1 equiv), KF (23.2 mg, 0.4 mmol, 2.0 equiv), and DCM/H_2O (2 mL, v:v = 20/1) at room temperature for 12 h afford **33l** (19.4 mg, 41%, 99% D) as a yellow solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 - 7.36 (m, 4 H), 7.25 - 7.19 (m, 1 H), 2.94 (s, 3 H), 2.19 (s, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.6, 150.1, 135.3, 128.9, 125.8, 123.1, 36.7, 10.3. ATR-FTIR (cm^{-1}):

3025, 2911, 1657, 1593, 1458, 1504, 758, 698. HRMS (ESI$^+$) Calcd for $C_{13}H_{12}D_6N_3O$ $[M+H]^+$: 238.1821, found: 238.1821.

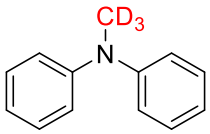
The corresponding non-deuterated product:



33l-H

4-(Dimethylamino)-1,5-dimethyl-2-phenyl-1,2-dihydro-3*H*-pyrazol-3-one **33l**-H: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 - 7.37 (m, 4 H), 7.25 - 7.19 (m, 1 H), 2.94 (s, 3 H), 2.78 (s, 6 H), 2.19 (s, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.6, 135.3, 128.9, 125.8, 123.1, 43.9, 36.7, 10.3.

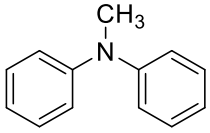
N-(methyl-d_3)-*N*-phenylaniline (**33m**)



33m

Following the general procedure C, the reaction of diphenylamine **32m** (33.8 mg, 0.2 mmol, 1.0 equiv), **DMTT** (70.2 mg, 0.2 mmol, 1.0 equiv), $Ni(OAc)_2{\cdot}4H_2O$ (5.0 mg, 0.02 mmol, 0.1 equiv), KF (23.2 mg, 0.4 mmol, 2.0 equiv), and DCM/H_2O (2 mL, v:v = 20/1) at room temperature for 12 h afford **33m** (27.6 mg, 74%, 99% D) as a light grey solid: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 – 7.27 (m, 4H), 7.09 – 7.03 (m, 4H), 6.98 (tt, *J* = 7.2, 1.1 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.0, 129.2, 121.2, 120.4. ATR-FTIR (cm^{-1}): 3034, 2995, 1589, 1491, 1332, 1254, 1185, 1155, 792, 743, 691. HRMS (ESI$^+$) Calcd for $C_{13}H_{11}D_3N$ $[M+H]^+$: 187.1309, found: 187.1305.

The corresponding non-deuterated product:

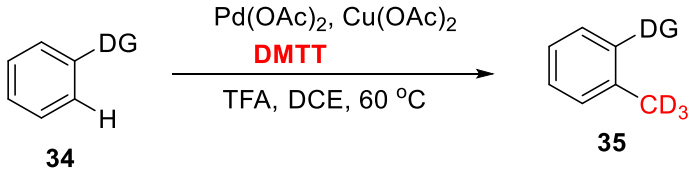


33m-H

N-methyl-*N*-phenylaniline **33m**-H: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 – 7.26 (m, 4H), 7.05 – 7.00 (m, 4H), 6.98 – 6.93 (m, 2H), 3.32 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.0, 129.2, 121.2, 120.4, 40.2.

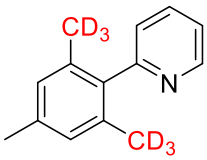
Section S7. Pd-catalyzed C–H bond methylation-d3

General Procedure D:



The 25 mL Schlenk tube was purged with argon for three times. Then the tube was added substrates **34** (0.2 mmol, 1.0 equiv), **DMTT** (0.24-0.6 mmol, 1.2-3.0 equiv), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol, 0.1 equiv), $Cu(OAc)_2$ (43.6 mg, 0.24 mmol, 1.2 equiv), TFA (74.3 μL, d = 1.535 g/mL, 1.0 mmol, 5.0 equiv), and DCE (2 mL). The mixture was stirring at 60 ºC for 12 hours. Then the resulting mixture was cooled down and concentrated in vacuo. The residue was purified by column chromatography to afford the corresponding product **35**.

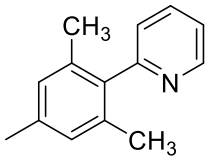
2-(4-Methyl-2,6-bis(methyl-d_3)phenyl)pyridine (**35a**)



35a

Following the general procedure D, the reaction of 2-(*p*-tolyl)pyridine **34a** (33.8 mg, 0.2 mmol, 1.0 equiv), **DMTT** (210.6 mg, 0.6 mmol, 3.0 equiv), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol, 0.1 equiv), $Cu(OAc)_2$ (43.6 mg, 0.24 mmol, 1.2 equiv), TFA (74.3 μL, d = 1.535 g/mL, 1.0 mmol, 5.0 equiv), and DCE (2 mL) at 60 ºC for 12 hours afford **35a** (25.1 mg, 62%, 99% D) as oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 (s, 1 H), 7.74 (td, *J* = 7.6, 1.8 Hz, 1 H), 7.26 - 7.17 (m, 2 H), 6.93 (s, 2 H), 2.32 (s, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.0, 149.5, 137.7, 137.3, 136.1, 135.5, 128.2, 124.7, 121.5, 21.1. ATR-FTIR (cm^{-1}): 3004, 2921, 1608, 1586, 1563, 1451, 1424, 913, 712. HRMS (ESI^+) Calcd for $C_{14}H_{10}D_6N$ $[M+H]^+$: 204.1654, found: 204.1654.

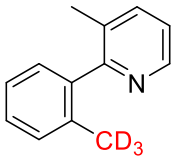
The corresponding non-deuterated product:



35a-H

2-Mesitylpyridine **35a**-H: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 (s, 1 H), 7.75 (td, *J* = 7.7, 1.8 Hz, 1 H), 7.28 - 7.16 (m, 3 H), 6.93 (s, 2 H), 2.32 (s, 3 H), 2.01 (s, 6 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.0, 149.5, 137.4, 136.3, 135.6, 128.2, 124.7, 121.5, 21.1 , 20.1.

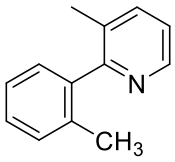
3-Methyl-2-(2-(methyl-*d*$_3$)phenyl)pyridine (**35b**)



35b

Following the general procedure D, the reaction of 3-methyl-2-phenylpyridine **34b** (33.8 mg, 0.2 mmol, 1.0 equiv), **DMTT** (105.3 mg, 0.3 mmol, 1.5 equiv), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol, 0.1 equiv), $Cu(OAc)_2$ (43.6 mg, 0.24 mmol, 1.2 equiv), TFA (74.3 μL, d = 1.535 g/mL, 1.0 mmol, 5.0 equiv), and DCE (2 mL) at 60 °C for 12 hours afford **35b** (24.2 mg, 65%, 99% D) as oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (dd, *J* = 5.0, 1.6 Hz, 1 H), 7.63 - 7.54 (m, 1 H), 7.31 - 7.22 (m, 3 H), 7.23 - 7.12 (m, 2 H), 2.11 (s, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.7, 137.7, 130.1, 128.4, 127.9, 125.7, 122.1, 19.0. ATR-FTIR (cm^{-1}): 2599, 2853, 1566, 1447, 1276, 1261, 913, 790, 748. HRMS (ESI^+) Calcd for $C_{13}H_{11}D_3N$ $[M+H]^+$: 187.1309, found: 187.1309.

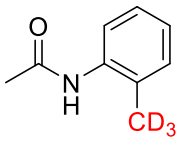
The corresponding non-deuterated product:



35b-H

3-Methyl-2-(*o*-tolyl)pyridine **35b**-H: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (dd, *J* = 4.9, 1.6 Hz, 1 H), 7.64 - 7.54 (m, 1 H), 7.31 - 7.23 (m, 3 H), 7.21 - 7.13 (m, 2 H), 2.10 (s, 3 H), 2.08 (s, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.6, 146.7, 140.2, 137.7, 135.5, 131.5, 130.1, 128.4, 127.9, 125.7, 122.1, 29.7, 19.3, 19.0.

N-(2-(Methyl-*d*$_3$)phenyl)acetamide (**35c**)

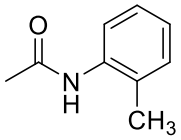


35c

Following the general procedure D, the reaction of *N*-phenylacetamide **34a** (27.0 mg, 0.2 mmol, 1.0 equiv), **DMTT** (84.2 mg, 0.24 mmol, 1.2 equiv), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol, 0.1 equiv), $Cu(OAc)_2$ (43.6 mg, 0.24 mmol, 1.2 equiv), TFA (74.3 μL, d = 1.535 g/mL, 1.0 mmol, 5.0 equiv), and DCE (2 mL) at 60 °C for 12 hours afford **35c** (20.7

mg, 68%, 99% D) as oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 7.9 Hz, 1 H), 7.24 - 7.13 (m, 3 H), 7.12 - 7.02 (m, 1 H), 2.17 (s, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.5, 135.6, 130.4, 129.6, 126.6, 125.4, 123.6, 24.1. ATR-FTIR (cm^{-1}): 3178, 3083, 1687, 1364, 1271, 1198, 913, 748. HRMS (ESI^+) Calcd for $C_9H_9D_3NO$ $[M+H]^+$: 153.1102, found: 153.1100.

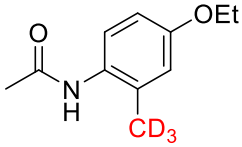
The corresponding non-deuterated product:



35c-H

N-(*o*-tolyl)acetamide **35c**-H: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.0 Hz, 1 H), 7.24 - 7.11 (m, 3 H), 7.12 - 7.02 (m, 1 H), 2.24 (s, 3 H), 2.18 (s, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.4, 135.6, 130.4, 129.6, 126.6, 125.3, 123.6, 24.2, 17.7.

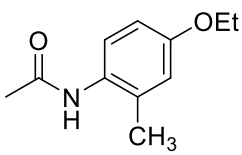
N-(4-Ethoxy-2-(methyl-*d*$_3$)phenyl)acetamide (**35d**)



35d

Following the general procedure D, the reaction of *N*-(4-ethoxyphenyl)acetamide **34d** (35.8 mg, 0.2 mmol, 1.0 equiv), **DMTT** (84.2 mg, 0.24 mmol, 1.2 equiv), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol, 0.1 equiv), $Cu(OAc)_2$ (43.6 mg, 0.24 mmol, 1.2 equiv), TFA (74.3 μL, d = 1.535 g/mL, 1.0 mmol, 5.0 equiv), and DCE (2 mL) at 60 ^{o}C for 12 hours afford **35d** (29.5 mg, 75%, 99% D) as oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, *J* = 8.3 Hz, 1 H), 7.24 - 6.96 (m, 1 H), 6.78 - 6.55 (m, 2 H), 3.97 (q, *J* = 7.1 Hz, 2 H), 2.13 (s, 3 H), 1.38 (t, *J* = 7.0 Hz, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.1, 156.8, 133.0, 128.3, 126.2, 116.4, 112.0, 63.5, 14.8. ATR-FTIR (cm^{-1}): 3271, 2980, 2928, 1657, 1531, 1479, 1287, 1180, 1049, 913, 746. HRMS (ESI^+) Calcd for $C_{11}H_{13}D_3NO_2$ $[M+H]^+$: 197.1364, found: 197.1364.

The corresponding non-deuterated product:



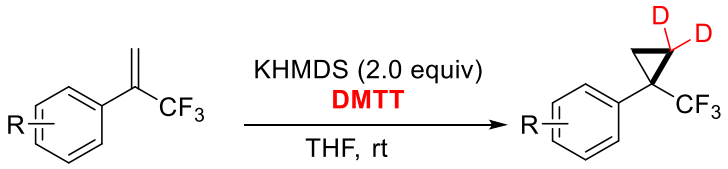
35d-H

N-(4-Ethoxy-2-methylphenyl)acetamide **35d**-H: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.3 Hz, 1 H), 7.20 - 7.90 (m, 1 H), 6.80 - 6.53 (m, 2 H), 3.98 (q, *J* = 6.9 Hz, 2 H), 2.19 (s, 3 H), 2.15 (s, 3 H), 1.38 (t, *J* = 7.0 Hz, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ

169.1, 156.8, 133.0, 128.3, 126.2, 116.5, 112.1, 63.5, 18.1, 14.8.

Section S8. Methyleneation of trifluoromethyl substituted alkenes

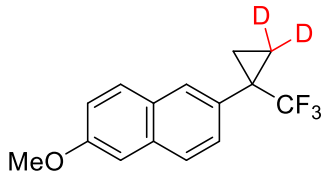
General Procedure E:



36 **37**

The 25 mL Schlenk tube was purged with argon for three times. Then the tube was added substrates **36** (0.2 mmol, 1.0 equiv), **DMTT** (0.4 mmol, 2.0 equiv), KHMDS (0.4 mmol, 2.0 equiv), and THF (2 mL). The reaction was stirring at room temperature for 12 hours. Then the resulting mixture was concentrated in vacuo and the residue was purified by column chromatography to afford the corresponding product **37**.

2-Methoxy-6-(1-(trifluoromethyl)cyclopropyl-2,2-d_2)naphthalene (**37a**)

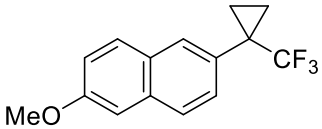


37a

Following the general procedure *E*, the reaction of 2-methoxy-6-(3,3,3-trifluoroprop-1-en-2-yl)naphthalene **36a** (50.4 mg, 0.2 mmol, 1.0 equiv), **DMTT** (140.4 mg, 0.4 mmol, 2.0 equiv), KHMDS (0.4 mL, 1.0 M in THF, 0.4 mmol, 2.0 equiv), and THF (2 mL) at room temperature for 12 hours afford **37a** (38.4 mg, 72%, 99% D) as oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 - 7.77 (m, 1 H), 7.75 - 7.68 (m, 2 H), 7.56 - 7.44 (m, 1 H), 7.18 - 7.12 (m, 2 H), 3.92 (s, 3 H), 1.42 - 1.36 (m, 1 H), 1.19 - 1.01 (m, 1 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.1, 134.3, 131.4, 130.4, 129.9, 129.4, 129.2, 126.8, 126.6 (q, J = 273.3 Hz), 119.2, 105.5, 55.3,

9.6 (q, J = 2.5 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -69.9. ATR-FTIR (cm^{-1}): 3008, 2940, 1608, 1487, 1353, 1263, 1198, 913, 747. HRMS (ESI^+) Calcd for $C_{15}H_{12}D_2F_3O$ $[M+H]^+$: 269.1117, found: 269.1110.

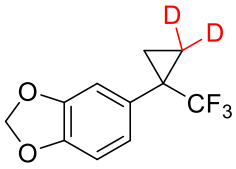
The corresponding non-deuterated product:



37a-H

2-Methoxy-6-(1-(trifluoromethyl)cyclopropyl)naphthalene **37a**-H: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 - 7.77 (m, 1 H), 7.74 - 7.68 (m, 2 H), 7.54 - 7.45 (m, 1 H), 7.18 - 7.12 (m, 2 H), 3.92 (s, 3 H), 1.43 - 1.37 (m, 2 H), 1.18 - 1.05 (m, 2 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.1, 134.3, 131.2, 130.4, 129.9, 129.4, 129.2, 126.8, 126.5 (q, J = 273.4 Hz), 119.2, 105.5, 55.3, 9.8 (q, J = 2.6 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -70.0.

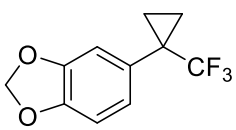
5-(1-(Trifluoromethyl)cyclopropyl-2,2-d_2)benzo[d][1,3]dioxole (**37b**)



37b

Following the general procedure *E*, the reaction of 5-(3,3,3-trifluoroprop-1-en-2-yl)benzo[d][1,3]dioxole **36b** (43.2 mg, 0.2 mmol, 1.0 equiv), **DMTT** (140.4 mg, 0.4 mmol, 2.0 equiv), KHMDS (0.4 mL, 1.0 M in THF, 0.4 mmol, 2.0 equiv), and THF (2 mL) at room temperature for 12 hours afford **37b** (23.1 mg, 50%, 99% D) as oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.97 - 6.83 (m, 2 H), 6.80 - 6.71 (m, 1 H), 5.96 (s, 2 H), 1.33 - 1.26 (m, 1 H), 1.04 - 0.91 (m, 1 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.6, 147.4, 124.9, 111.6, 108.0, 101.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ -70.42. ATR-FTIR (cm^{-1}): 2989, 2924, 1508, 1275, 1261, 1136, 1041, 913, 748. HRMS (ESI^+) Calcd for $C_{11}H_8D_2F_3O_2$ $[M+H]^+$: 233.0753, found: 233.0750.

The corresponding non-deuterated product:

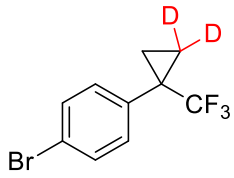


37b-H

5-(1-(Trifluoromethyl)cyclopropyl)benzo[d][1,3]dioxole **37b**-H: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.95 - 6.87 (m, 2 H), 6.78 - 6.72 (m, 1 H), 5.96 (s, 2 H), 1.34 - 1.26 (m, 2 H), 1.09 - 0.91 (m, 2 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 124.9, 111.6, 108.0, 101.2, 10.0

(q, J = 2.4 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -70.43.

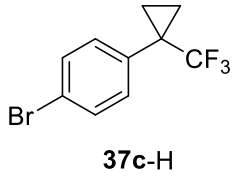
1-Bromo-4-(1-(trifluoromethyl)cyclopropyl-2,2-d_2)benzene (**37c**)



37c

Following the general procedure *E*, the reaction of 1-bromo-4-(3,3,3-trifluoroprop-1-en-2-yl)benzene **36c** (50.0 mg, 0.2 mmol, 1.0 equiv), **DMTT** (140.4 mg, 0.4 mmol, 2.0 equiv), KHMDS (0.4 mL, 1.0 M in THF, 0.4 mmol, 2.0 equiv), and THF (2 mL) at room temperature for 12 hours afford **37c** (34.0 mg, 64%, 99% D) as oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 - 7.43 (m, 2 H), 7.37 - 7.25 (m, 2 H), 1.39 - 1.31 (m, 1 H), 1.01 - 0.96 (m, 1 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.1, 132.9, 131.5, 126.0 (q, J = 273.4 Hz), 122.5, 9.6 (q, J = 2.2 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -70.2. ATR-FTIR (cm^{-1}): 2990, 1491, 1348, 1157, 1012, 913, 825, 747. HRMS (ESI^+) Calcd for $C_{10}H_7D_2BrF_3$ $[M+H]^+$: 266.9950, found: 266.9956.

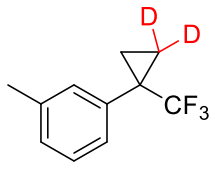
The corresponding non-deuterated product:



37c-H

1-Bromo-4-(1-(trifluoromethyl)cyclopropyl)benzene **37c**-H: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 - 7.43 (m, 2 H), 7.35 - 7.26 (m, 2 H), 1.39 - 1.31 (m, 2 H), 1.11 - 0.93 (m, 2 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.1, 132.9, 131.5, 126.0 (q, J = 273.4 Hz), 122.5, 9.75 (q, J = 1.6 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -70.2.

1-Methyl-3-(1-(trifluoromethyl)cyclopropyl-2,2-d_2)benzene (**37d**)

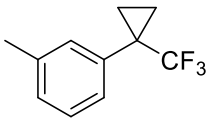


37d

Following the general procedure *E*, the reaction of 1-methyl-3-(3,3,3-trifluoroprop-1-en-2-yl)benzene **36d** (37.2 mg, 0.2 mmol, 1.0 equiv), **DMTT** (140.4 mg, 0.4 mmol, 2.0 equiv), KHMDS (0.4 mL, 1.0 M in THF, 0.4 mmol, 2.0 equiv), and THF (2 mL) at room temperature for 12 hours afford **37d** (27.5 mg, 68%, 99% D) as oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 - 7.20 (m, 3 H), 7.16 - 7.11 (m, 1 H), 2.36 (s, 3 H), 1.35 - 1.28 (m, 2 H), 1.06 - 0.97 (m, 1 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.0, 132.7, 132.0, 129.0, 128.3, 128.2, 126.4 (q, J = 273.3 Hz), 21.3, 9.5 (q, J = 2.6 Hz).

ATR-FTIR (cm^{-1}): 3027, 2925, 1610, 1491, 1352, 1218, 913, 785, 746. HRMS (ESI^+) Calcd for $C_{11}H_{10}D_2F_3$ $[M+H]^+$: 203.1011, found: 203.1005.

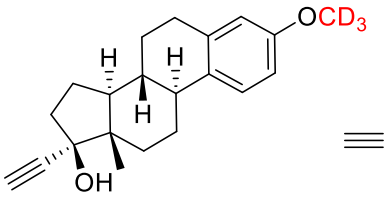
The corresponding non-deuterated product:



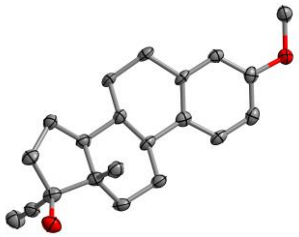
37d-H

1-Methyl-3-(1-(trifluoromethyl)cyclopropyl)benzene **37d**-H: ^1H NMR (400 MHz, $CDCl_3$) δ 7.31 - 7.18 (m, 3 H), 7.16 - 7.10 (m, 1 H), 2.36 (s, 3 H), 1.36 - 1.31 (m, 2 H), 1.10 - 0.95 (m, 2 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.0 132.7, 132.0, 129.0, 128.3, 128.2, 126.4 (q, *J* = 273.4 Hz), 21.3, 9.6 (q, d = 1.7 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -70.1.

Section S9. Crystallographic Data



21b



CCDC: 1892897

Crystal data and structure refinement:

Empirical formula	C21 H26 O2
Formula weight	310.42
Temperature	173(2) K
Wavelength	1.54178 Å
Crystal system	Monoclinic
Space group	$P2_1$
Unit cell dimensions	a = 6.8051(6) Å α= 90°.
	b = 39.706(4) Å β= 117.644(4)°.
	c = 6.9518(6) Å γ = 90°.
Volume	1664.0(3) $Å^3$

Z	4
Density (calculated)	1.239 Mg/m^3
Absorption coefficient	0.604 mm^{-1}
F(000)	672
Crystal size	0.190 x 0.180 x 0.150 mm^3
Theta range for data collection	4.454 to 68.548°.
Index ranges	-7<=h<=8, -45<=k<=47, -8<=l<=7
Reflections collected	9682
Independent reflections	5231 [R(int) = 0.0468]
Completeness to theta = 67.679°	98.2 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5231 / 1 / 421
Goodness-of-fit on F^2	1.166
Final R indices [I>2sigma(I)]	R1 = 0.0739, wR2 = 0.1984
R indices (all data)	R1 = 0.0743, wR2 = 0.1986
Absolute structure parameter	0.13(13)
Extinction coefficient	n/a
Largest diff. peak and hole	0.370 and -0.344 $e.Å^{-3}$

Bond lengths [Å] and angles [°]:

C(1)-O(1)	1.438(8)	C(3)-H(3A)	0.9500
C(1)-H(1A)	0.9800	C(4)-C(5)	1.393(9)
C(1)-H(1B)	0.9800	C(4)-H(4)	0.9500
C(1)-H(1C)	0.9800	C(5)-C(6)	1.405(8)
C(2)-O(1)	1.367(8)	C(5)-C(11)	1.521(9)
C(2)-C(3)	1.389(9)	C(6)-C(7)	1.399(9)
C(2)-C(7)	1.390(9)	C(6)-C(8)	1.520(8)
C(3)-C(4)	1.387(9)	C(7)-H(7)	0.9500

C(8)-C(9)	1.512(9)	C(17)-H(17B)	0.9900
C(8)-H(8A)	0.9900	C(18)-O(2)	1.412(8)
C(8)-H(8B)	0.9900	C(18)-C(20)	1.477(10)
C(9)-C(10)	1.522(8)	C(19)-H(19A)	0.9800
C(9)-H(9A)	0.9900	C(19)-H(19B)	0.9800
C(9)-H(9B)	0.9900	C(19)-H(19C)	0.9800
C(10)-C(15)	1.519(8)	C(20)-C(21)	1.185(11)
C(10)-C(11)	1.560(8)	C(21)-H(21)	0.9500
C(10)-H(10)	1.0000	C(22)-O(4)	1.421(8)
C(11)-C(12)	1.532(8)	C(22)-H(22A)	0.9800
C(11)-H(11)	1.0000	C(22)-H(22B)	0.9800
C(12)-C(13)	1.543(9)	C(22)-H(22C)	0.9800
C(12)-H(12A)	0.9900	C(23)-O(4)	1.360(8)
C(12)-H(12B)	0.9900	C(23)-C(24)	1.391(9)
C(13)-C(14)	1.517(9)	C(23)-C(28)	1.391(8)
C(13)-H(13A)	0.9900	C(24)-C(25)	1.388(9)
C(13)-H(13B)	0.9900	C(24)-H(24)	0.9500
C(14)-C(19)	1.537(9)	C(25)-C(26)	1.394(8)
C(14)-C(15)	1.540(8)	C(25)-H(25)	0.9500
C(14)-C(18)	1.580(9)	C(26)-C(27)	1.414(8)
C(15)-C(16)	1.541(9)	C(26)-C(29)	1.531(8)
C(15)-H(15)	1.0000	C(27)-C(28)	1.398(9)
C(16)-C(17)	1.550(9)	C(27)-C(32)	1.504(8)
C(16)-H(16A)	0.9900	C(28)-H(28)	0.9500
C(16)-H(16B)	0.9900	C(29)-C(33)	1.535(8)
C(17)-C(18)	1.546(9)	C(29)-C(30)	1.539(8)
C(17)-H(17A)	0.9900	C(29)-H(29)	1.0000

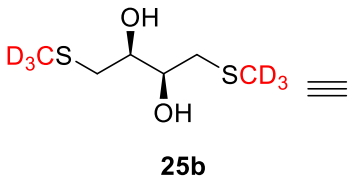
C(30)-C(31)	1.518(9)	C(40)-H(40A)	0.9800
C(30)-C(36)	1.524(8)	C(40)-H(40B)	0.9800
C(30)-H(30)	1.0000	C(40)-H(40C)	0.9800
C(31)-C(32)	1.529(9)	C(41)-C(42)	1.179(10)
C(31)-H(31A)	0.9900	C(42)-H(42)	0.9500
C(31)-H(31B)	0.9900	O(2)-H(2)	0.8400
C(32)-H(32A)	0.9900	O(3)-H(3)	0.8400
C(32)-H(32B)	0.9900	O(1)-C(1)-H(1A)	109.5
C(33)-C(34)	1.541(9)	O(1)-C(1)-H(1B)	109.5
C(33)-H(33A)	0.9900	H(1A)-C(1)-H(1B)	109.5
C(33)-H(33B)	0.9900	O(1)-C(1)-H(1C)	109.5
C(34)-C(35)	1.542(8)	H(1A)-C(1)-H(1C)	109.5
C(34)-H(34A)	0.9900	H(1B)-C(1)-H(1C)	109.5
C(34)-H(34B)	0.9900	O(1)-C(2)-C(3)	115.8(5)
C(35)-C(36)	1.540(9)	O(1)-C(2)-C(7)	125.0(6)
C(35)-C(40)	1.543(9)	C(3)-C(2)-C(7)	119.1(6)
C(35)-C(39)	1.556(9)	C(4)-C(3)-C(2)	119.7(6)
C(36)-C(37)	1.535(9)	C(4)-C(3)-H(3A)	120.2
C(36)-H(36)	1.0000	C(2)-C(3)-H(3A)	120.2
C(37)-C(38)	1.543(10)	C(3)-C(4)-C(5)	122.5(6)
C(37)-H(37A)	0.9900	C(3)-C(4)-H(4)	118.7
C(37)-H(37B)	0.9900	C(5)-C(4)-H(4)	118.7
C(38)-C(39)	1.559(9)	C(4)-C(5)-C(6)	117.3(6)
C(38)-H(38A)	0.9900	C(4)-C(5)-C(11)	121.6(5)
C(38)-H(38B)	0.9900	C(6)-C(5)-C(11)	121.2(5)
C(39)-O(3)	1.451(8)	C(7)-C(6)-C(5)	120.5(5)
C(39)-C(41)	1.474(9)	C(7)-C(6)-C(8)	117.3(5)

C(5)-C(6)-C(8)	122.3(6)	C(10)-C(11)-H(11)	107.1
C(2)-C(7)-C(6)	120.9(6)	C(11)-C(12)-C(13)	112.5(5)
C(2)-C(7)-H(7)	119.6	C(11)-C(12)-H(12A)	109.1
C(6)-C(7)-H(7)	119.6	C(13)-C(12)-H(12A)	109.1
C(9)-C(8)-C(6)	113.2(5)	C(11)-C(12)-H(12B)	109.1
C(9)-C(8)-H(8A)	108.9	C(13)-C(12)-H(12B)	109.1
C(6)-C(8)-H(8A)	108.9	H(12A)-C(12)-H(12B)	107.8
C(9)-C(8)-H(8B)	108.9	C(14)-C(13)-C(12)	110.1(5)
C(6)-C(8)-H(8B)	108.9	C(14)-C(13)-H(13A)	109.6
H(8A)-C(8)-H(8B)	107.8	C(12)-C(13)-H(13A)	109.6
C(8)-C(9)-C(10)	110.6(5)	C(14)-C(13)-H(13B)	109.6
C(8)-C(9)-H(9A)	109.5	C(12)-C(13)-H(13B)	109.6
C(10)-C(9)-H(9A)	109.5	H(13A)-C(13)-H(13B)	108.2
C(8)-C(9)-H(9B)	109.5	C(13)-C(14)-C(19)	110.9(5)
C(10)-C(9)-H(9B)	109.5	C(13)-C(14)-C(15)	109.2(5)
H(9A)-C(9)-H(9B)	108.1	C(19)-C(14)-C(15)	113.5(5)
C(15)-C(10)-C(9)	113.2(5)	C(13)-C(14)-C(18)	116.4(5)
C(15)-C(10)-C(11)	108.5(5)	C(19)-C(14)-C(18)	107.2(5)
C(9)-C(10)-C(11)	108.3(5)	C(15)-C(14)-C(18)	99.3(5)
C(15)-C(10)-H(10)	109.0	C(10)-C(15)-C(14)	112.1(5)
C(9)-C(10)-H(10)	109.0	C(10)-C(15)-C(16)	119.4(5)
C(11)-C(10)-H(10)	109.0	C(14)-C(15)-C(16)	104.2(5)
C(5)-C(11)-C(12)	114.0(5)	C(10)-C(15)-H(15)	106.9
C(5)-C(11)-C(10)	110.4(5)	C(14)-C(15)-H(15)	106.9
C(12)-C(11)-C(10)	110.7(5)	C(16)-C(15)-H(15)	106.9
C(5)-C(11)-H(11)	107.1	C(15)-C(16)-C(17)	104.7(5)
C(12)-C(11)-H(11)	107.1	C(15)-C(16)-H(16A)	110.8

C(17)-C(16)-H(16A)	110.8	O(4)-C(22)-H(22C)	109.5
C(15)-C(16)-H(16B)	110.8	H(22A)-C(22)-H(22C)	109.5
C(17)-C(16)-H(16B)	110.8	H(22B)-C(22)-H(22C)	109.5
H(16A)-C(16)-H(16B)	108.9	O(4)-C(23)-C(24)	117.4(5)
C(18)-C(17)-C(16)	106.4(5)	O(4)-C(23)-C(28)	124.2(6)
C(18)-C(17)-H(17A)	110.4	C(24)-C(23)-C(28)	118.5(6)
C(16)-C(17)-H(17A)	110.4	C(25)-C(24)-C(23)	120.3(5)
C(18)-C(17)-H(17B)	110.4	C(25)-C(24)-H(24)	119.9
C(16)-C(17)-H(17B)	110.4	C(23)-C(24)-H(24)	119.9
H(17A)-C(17)-H(17B)	108.6	C(24)-C(25)-C(26)	121.8(5)
O(2)-C(18)-C(20)	110.4(6)	C(24)-C(25)-H(25)	119.1
O(2)-C(18)-C(17)	110.6(5)	C(26)-C(25)-H(25)	119.1
C(20)-C(18)-C(17)	108.6(5)	C(25)-C(26)-C(27)	118.2(5)
O(2)-C(18)-C(14)	114.0(5)	C(25)-C(26)-C(29)	122.2(5)
C(20)-C(18)-C(14)	111.1(5)	C(27)-C(26)-C(29)	119.6(5)
C(17)-C(18)-C(14)	101.7(5)	C(28)-C(27)-C(26)	119.1(5)
C(14)-C(19)-H(19A)	109.5	C(28)-C(27)-C(32)	117.7(5)
C(14)-C(19)-H(19B)	109.5	C(26)-C(27)-C(32)	123.1(5)
H(19A)-C(19)-H(19B)	109.5	C(23)-C(28)-C(27)	122.0(6)
C(14)-C(19)-H(19C)	109.5	C(23)-C(28)-H(28)	119.0
H(19A)-C(19)-H(19C)	109.5	C(27)-C(28)-H(28)	119.0
H(19B)-C(19)-H(19C)	109.5	C(26)-C(29)-C(33)	112.8(5)
C(21)-C(20)-C(18)	176.3(7)	C(26)-C(29)-C(30)	111.3(5)
C(20)-C(21)-H(21)	180.0	C(33)-C(29)-C(30)	111.7(5)
O(4)-C(22)-H(22A)	109.5	C(26)-C(29)-H(29)	106.9
O(4)-C(22)-H(22B)	109.5	C(33)-C(29)-H(29)	106.9
H(22A)-C(22)-H(22B)	109.5	C(30)-C(29)-H(29)	106.9

C(31)-C(30)-C(36)	113.0(5)	C(33)-C(34)-H(34B)	109.6
C(31)-C(30)-C(29)	109.5(5)	C(35)-C(34)-H(34B)	109.6
C(36)-C(30)-C(29)	108.1(5)	H(34A)-C(34)-H(34B)	108.1
C(31)-C(30)-H(30)	108.7	C(36)-C(35)-C(34)	108.9(5)
C(36)-C(30)-H(30)	108.7	C(36)-C(35)-C(40)	114.2(5)
C(29)-C(30)-H(30)	108.7	C(34)-C(35)-C(40)	109.2(6)
C(30)-C(31)-C(32)	109.8(5)	C(36)-C(35)-C(39)	99.1(5)
C(30)-C(31)-H(31A)	109.7	C(34)-C(35)-C(39)	116.6(5)
C(32)-C(31)-H(31A)	109.7	C(40)-C(35)-C(39)	108.7(5)
C(30)-C(31)-H(31B)	109.7	C(30)-C(36)-C(37)	119.0(5)
C(32)-C(31)-H(31B)	109.7	C(30)-C(36)-C(35)	113.4(5)
H(31A)-C(31)-H(31B)	108.2	C(37)-C(36)-C(35)	103.7(5)
C(27)-C(32)-C(31)	113.7(5)	C(30)-C(36)-H(36)	106.7
C(27)-C(32)-H(32A)	108.8	C(37)-C(36)-H(36)	106.7
C(31)-C(32)-H(32A)	108.8	C(35)-C(36)-H(36)	106.7
C(27)-C(32)-H(32B)	108.8	C(36)-C(37)-C(38)	104.9(5)
C(31)-C(32)-H(32B)	108.8	C(36)-C(37)-H(37A)	110.8
H(32A)-C(32)-H(32B)	107.7	C(38)-C(37)-H(37A)	110.8
C(29)-C(33)-C(34)	112.8(5)	C(36)-C(37)-H(37B)	110.8
C(29)-C(33)-H(33A)	109.0	C(38)-C(37)-H(37B)	110.8
C(34)-C(33)-H(33A)	109.0	H(37A)-C(37)-H(37B)	108.8
C(29)-C(33)-H(33B)	109.0	C(37)-C(38)-C(39)	105.5(5)
C(34)-C(33)-H(33B)	109.0	C(37)-C(38)-H(38A)	110.6
H(33A)-C(33)-H(33B)	107.8	C(39)-C(38)-H(38A)	110.6
C(33)-C(34)-C(35)	110.3(5)	C(37)-C(38)-H(38B)	110.6
C(33)-C(34)-H(34A)	109.6	C(39)-C(38)-H(38B)	110.6
C(35)-C(34)-H(34A)	109.6	H(38A)-C(38)-H(38B)	108.8

O(3)-C(39)-C(41)	109.0(5)	C(35)-C(40)-H(40C)	109.5
O(3)-C(39)-C(35)	115.4(6)	H(40A)-C(40)-H(40C)	109.5
C(41)-C(39)-C(35)	112.5(5)	H(40B)-C(40)-H(40C)	109.5
O(3)-C(39)-C(38)	108.4(5)	C(42)-C(41)-C(39)	178.4(8)
C(41)-C(39)-C(38)	109.1(6)	C(41)-C(42)-H(42)	180.0
C(35)-C(39)-C(38)	102.1(5)	C(2)-O(1)-C(1)	116.4(5)
C(35)-C(40)-H(40A)	109.5	C(18)-O(2)-H(2)	109.5
C(35)-C(40)-H(40B)	109.5	C(39)-O(3)-H(3)	109.5
H(40A)-C(40)-H(40B)	109.5	C(23)-O(4)-C(22)	117.8(5)



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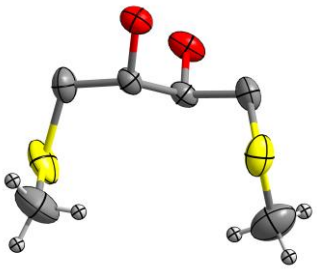


CCDC: 1892896

Crystal data and structure refinement:

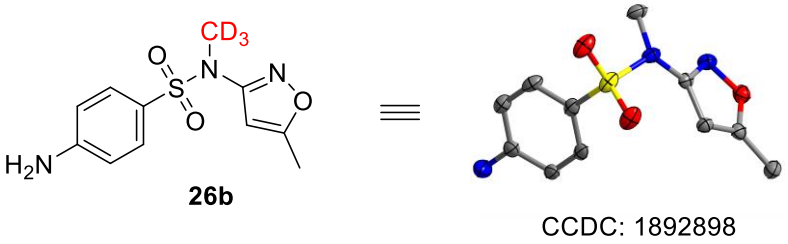
Empirical formula	C6 H14 N0 O2 S2	
Formula weight	182.29	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 11.659(3) Å	α= 90°.
	b = 4.9631(11) Å	β= 103.359(3)°.
	c = 16.709(4) Å	γ = 90°.
Volume	940.7(4) $Å^3$	
Z	4	

Density (calculated)	1.287 Mg/m^3
Absorption coefficient	0.513 mm^{-1}
F(000)	392
Crystal size	0.220 x 0.180 x 0.170 mm^3
Theta range for data collection	2.506 to 25.010°.
Index ranges	-13<=h<=13, -5<=k<=3, -19<=l<=19
Reflections collected	5663
Independent reflections	1641 [R(int) = 0.0622]
Completeness to theta = 25.010°	99.3 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1641 / 0 / 95
Goodness-of-fit on F^2	1.033
Final R indices [I>2sigma(I)]	R1 = 0.0503, wR2 = 0.1375
R indices (all data)	R1 = 0.0550, wR2 = 0.1436
Extinction coefficient	n/a
Largest diff. peak and hole	0.345 and -0.479 $e.Å^{-3}$

Bond lengths [Å] and angles [°]:

S(1)-C(1)	1.784(3)	C(4)-H(4)	0.9800
S(1)-C(2)	1.799(3)	C(3)-C(2)	1.520(3)
S(2)-C(6)	1.781(4)	C(3)-H(3)	0.9800
S(2)-C(5)	1.799(3)	C(2)-H(2A)	0.9700
O(1)-C(4)	1.430(3)	C(2)-H(2B)	0.9700
O(1)-H(003)	0.8200	C(5)-H(5A)	0.9700
O(2)-C(3)	1.425(2)	C(5)-H(5B)	0.9700
O(2)-H(004)	0.8200	C(1)-H(1A)	0.9600
C(4)-C(5)	1.518(3)	C(1)-H(1B)	0.9600
C(4)-C(3)	1.520(3)	C(1)-H(1C)	0.9600

C(6)-H(6A)	0.9600	C(3)-C(2)-H(2B)	108.6
C(6)-H(6B)	0.9600	S(1)-C(2)-H(2B)	108.6
C(6)-H(6C)	0.9600	H(2A)-C(2)-H(2B)	107.6
C(1)-S(1)-C(2)	100.92(14)	C(4)-C(5)-S(2)	114.97(17)
C(6)-S(2)-C(5)	100.18(14)	C(4)-C(5)-H(5A)	108.5
C(4)-O(1)-H(003)	109.5	S(2)-C(5)-H(5A)	108.5
C(3)-O(2)-H(004)	109.5	C(4)-C(5)-H(5B)	108.5
O(1)-C(4)-C(5)	108.51(18)	S(2)-C(5)-H(5B)	108.5
O(1)-C(4)-C(3)	111.07(16)	H(5A)-C(5)-H(5B)	107.5
C(5)-C(4)-C(3)	113.77(19)	S(1)-C(1)-H(1A)	109.5
O(1)-C(4)-H(4)	107.8	S(1)-C(1)-H(1B)	109.5
C(5)-C(4)-H(4)	107.8	H(1A)-C(1)-H(1B)	109.5
C(3)-C(4)-H(4)	107.8	S(1)-C(1)-H(1C)	109.5
O(2)-C(3)-C(4)	110.14(17)	H(1A)-C(1)-H(1C)	109.5
O(2)-C(3)-C(2)	105.87(16)	H(1B)-C(1)-H(1C)	109.5
C(4)-C(3)-C(2)	112.77(19)	S(2)-C(6)-H(6A)	109.5
O(2)-C(3)-H(3)	109.3	S(2)-C(6)-H(6B)	109.5
C(4)-C(3)-H(3)	109.3	H(6A)-C(6)-H(6B)	109.5
C(2)-C(3)-H(3)	109.3	S(2)-C(6)-H(6C)	109.5
C(3)-C(2)-S(1)	114.64(14)	H(6A)-C(6)-H(6C)	109.5
C(3)-C(2)-H(2A)	108.6	H(6B)-C(6)-H(6C)	109.5
S(1)-C(2)-H(2A)	108.6		



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CCDC: 1892898

Crystal data and structure refinement:

Empirical formula	C11 H13 N3 O3 S
Formula weight	267.30
Temperature	173(2) K
Wavelength	1.54178 Å
Crystal system	Hexagonal
Space group	$P6_1$
Unit cell dimensions	a = 10.2409(9) Å α= 90°.
	b = 10.2409(9) Å β= 90°.
	c = 19.9884(18) Å γ = 120°.
Volume	1815.5(4) $Å^3$
Z	6
Density (calculated)	1.467 Mg/m^3
Absorption coefficient	2.445 mm^{-1}
F(000)	840
Crystal size	0.190 x 0.170 x 0.160 mm^3
Theta range for data collection	4.986 to 64.762°.
Index ranges	-11<=h<=12, -11<=k<=11, -21<=l<=23
Reflections collected	9406
Independent reflections	1864 [R(int) = 0.0297]
Completeness to theta = 64.762°	100.0 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1864 / 1 / 166
Goodness-of-fit on F^2	1.097
Final R indices [I>2sigma(I)]	R1 = 0.0264, wR2 = 0.0677
R indices (all data)	R1 = 0.0264, wR2 = 0.0677
Absolute structure parameter	0.052(6)
Extinction coefficient	0.0034(5)

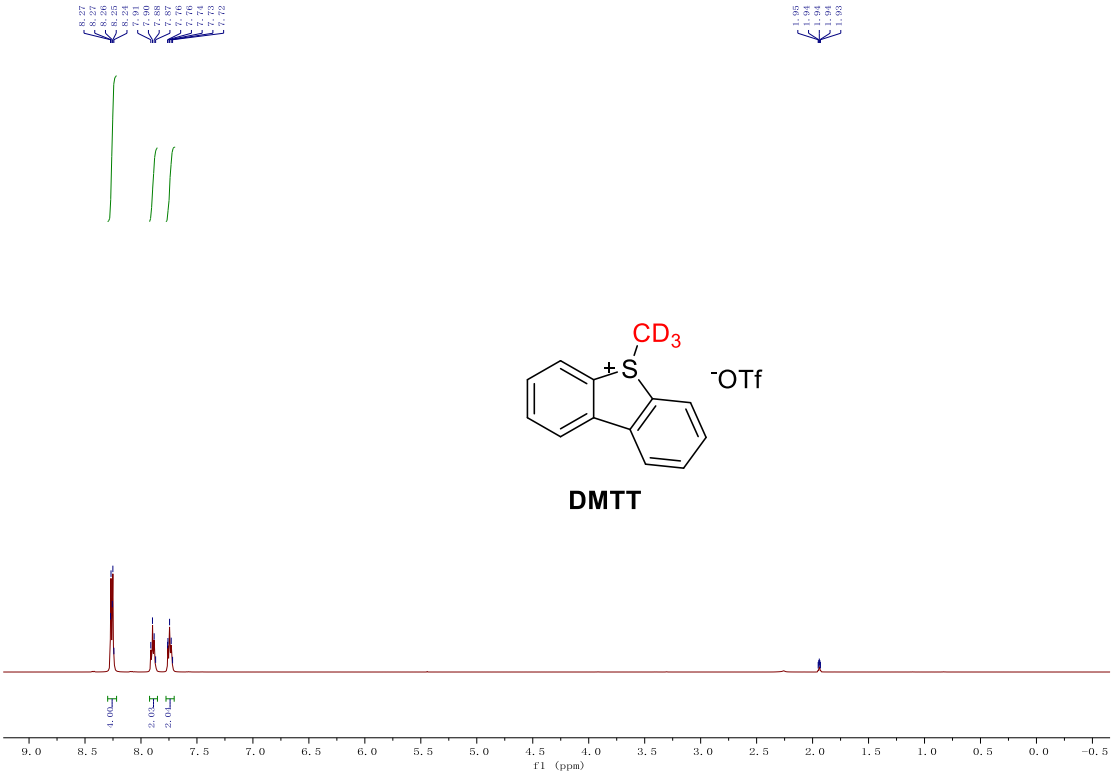
Largest diff. peak and hole 0.354 and -0.253 e.Å^{-3}

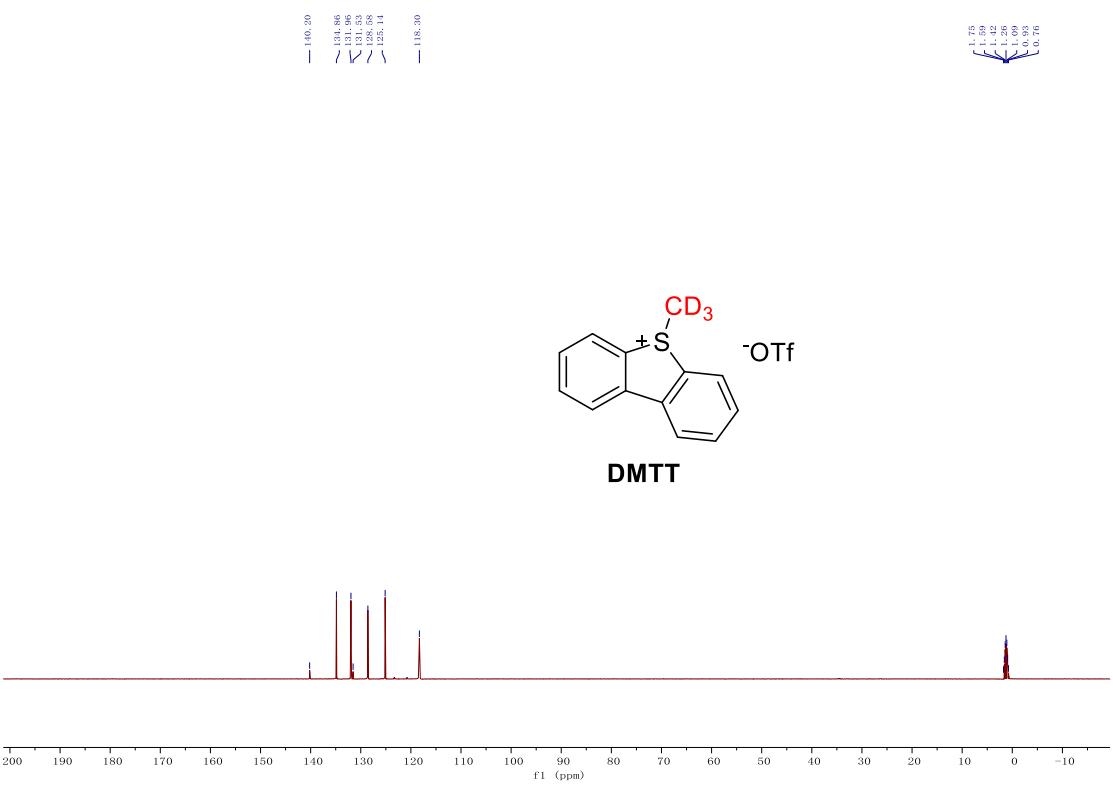
Bond lengths [Å] and angles [°]:

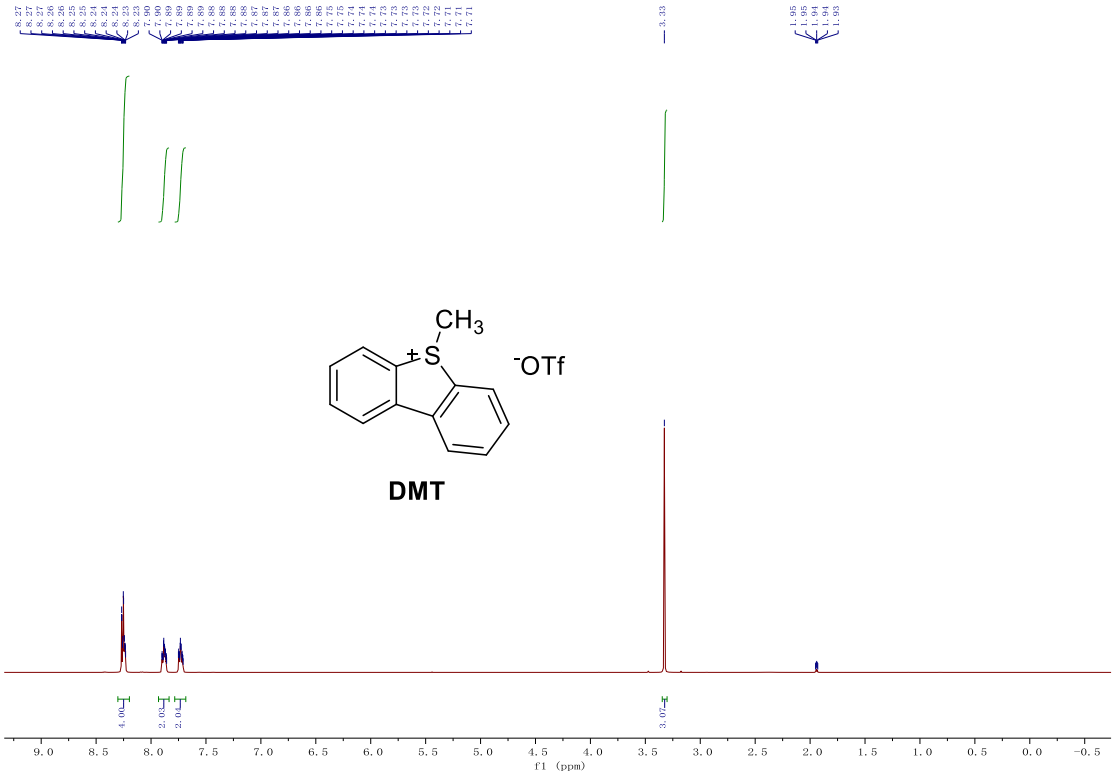
C(1)-C(2)	1.485(4)	C(11)-H(11)	0.9500
C(1)-H(1A)	0.9800	N(1)-O(1)	1.412(3)
C(1)-H(1B)	0.9800	N(2)-S(1)	1.668(2)
C(1)-H(1C)	0.9800	N(3)-H(3A)	0.8800
C(2)-C(3)	1.348(3)	N(3)-H(3B)	0.8800
C(2)-O(1)	1.351(3)	O(2)-S(1)	1.432(2)
C(3)-C(4)	1.424(3)	O(3)-S(1)	1.4274(18)
C(3)-H(3)	0.9500	C(2)-C(1)-H(1A)	109.5
C(4)-N(1)	1.313(3)	C(2)-C(1)-H(1B)	109.5
C(4)-N(2)	1.396(3)	H(1A)-C(1)-H(1B)	109.5
C(5)-C(11)	1.376(4)	C(2)-C(1)-H(1C)	109.5
C(5)-C(7)	1.395(4)	H(1A)-C(1)-H(1C)	109.5
C(5)-H(5)	0.9500	H(1B)-C(1)-H(1C)	109.5
C(6)-N(2)	1.477(3)	C(3)-C(2)-O(1)	110.1(2)
C(6)-H(6A)	0.9800	C(3)-C(2)-C(1)	133.9(2)
C(6)-H(6B)	0.9800	O(1)-C(2)-C(1)	116.0(2)
C(6)-H(6C)	0.9800	C(2)-C(3)-C(4)	104.17(19)
C(7)-C(8)	1.400(4)	C(2)-C(3)-H(3)	127.9
C(7)-S(1)	1.741(3)	C(4)-C(3)-H(3)	127.9
C(8)-C(9)	1.363(4)	N(1)-C(4)-N(2)	117.9(2)
C(8)-H(8)	0.9500	N(1)-C(4)-C(3)	111.9(2)
C(9)-C(10)	1.415(4)	N(2)-C(4)-C(3)	130.1(2)
C(9)-H(9)	0.9500	C(11)-C(5)-C(7)	120.3(2)
C(10)-N(3)	1.354(4)	C(11)-C(5)-H(5)	119.8
C(10)-C(11)	1.411(4)	C(7)-C(5)-H(5)	119.8

N(2)-C(6)-H(6A)	109.5	C(5)-C(11)-C(10)	120.9(2)
N(2)-C(6)-H(6B)	109.5	C(5)-C(11)-H(11)	119.5
H(6A)-C(6)-H(6B)	109.5	C(10)-C(11)-H(11)	119.5
N(2)-C(6)-H(6C)	109.5	C(4)-N(1)-O(1)	105.04(18)
H(6A)-C(6)-H(6C)	109.5	C(4)-N(2)-C(6)	115.7(2)
H(6B)-C(6)-H(6C)	109.5	C(4)-N(2)-S(1)	120.23(17)
C(5)-C(7)-C(8)	119.5(3)	C(6)-N(2)-S(1)	115.02(18)
C(5)-C(7)-S(1)	120.6(2)	C(10)-N(3)-H(3A)	120.0
C(8)-C(7)-S(1)	119.9(2)	C(10)-N(3)-H(3B)	120.0
C(9)-C(8)-C(7)	120.3(2)	H(3A)-N(3)-H(3B)	120.0
C(9)-C(8)-H(8)	119.8	C(2)-O(1)-N(1)	108.74(17)
C(7)-C(8)-H(8)	119.8	O(3)-S(1)-O(2)	119.37(11)
C(8)-C(9)-C(10)	121.3(2)	O(3)-S(1)-N(2)	106.66(11)
C(8)-C(9)-H(9)	119.3	O(2)-S(1)-N(2)	104.77(12)
C(10)-C(9)-H(9)	119.3	O(3)-S(1)-C(7)	109.23(12)
N(3)-C(10)-C(11)	121.2(2)	O(2)-S(1)-C(7)	108.48(12)
N(3)-C(10)-C(9)	121.2(2)	N(2)-S(1)-C(7)	107.72(11)
C(11)-C(10)-C(9)	117.6(2)		

Section S10. ^{1}H, ^{13}C, ^{19}F NMR spectra of the products






8.27
8.27
8.27
8.26
8.26
8.25
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8.24
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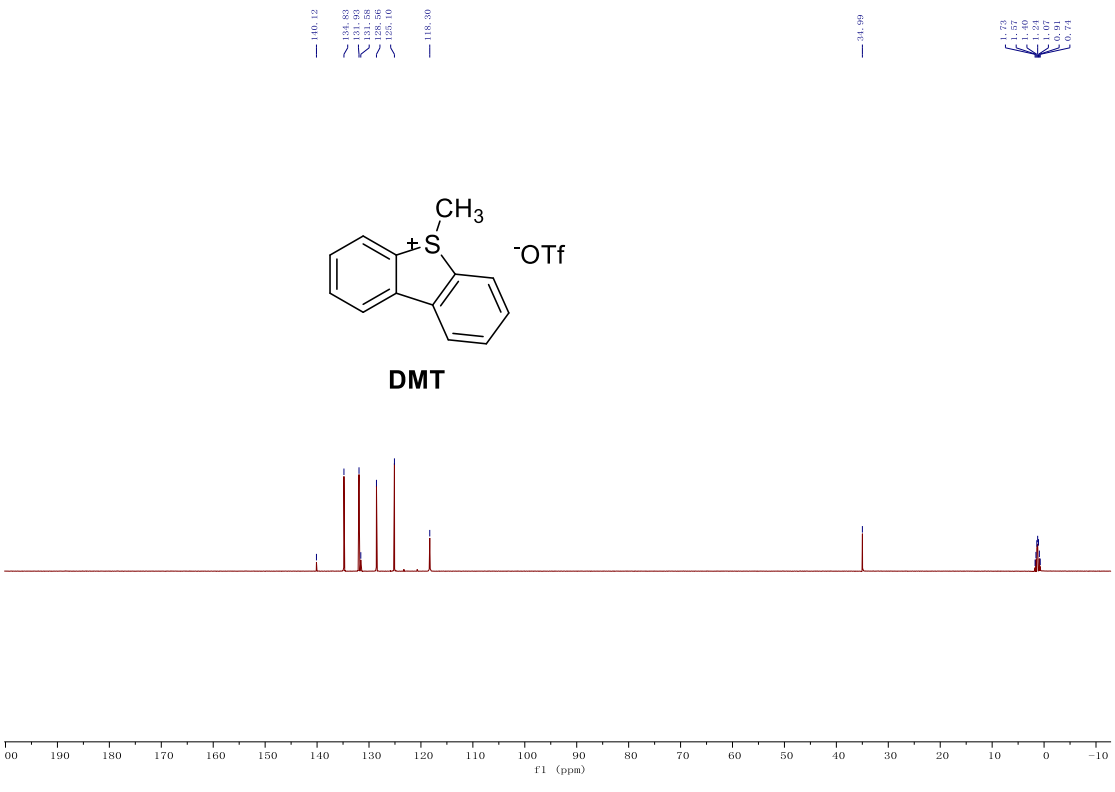
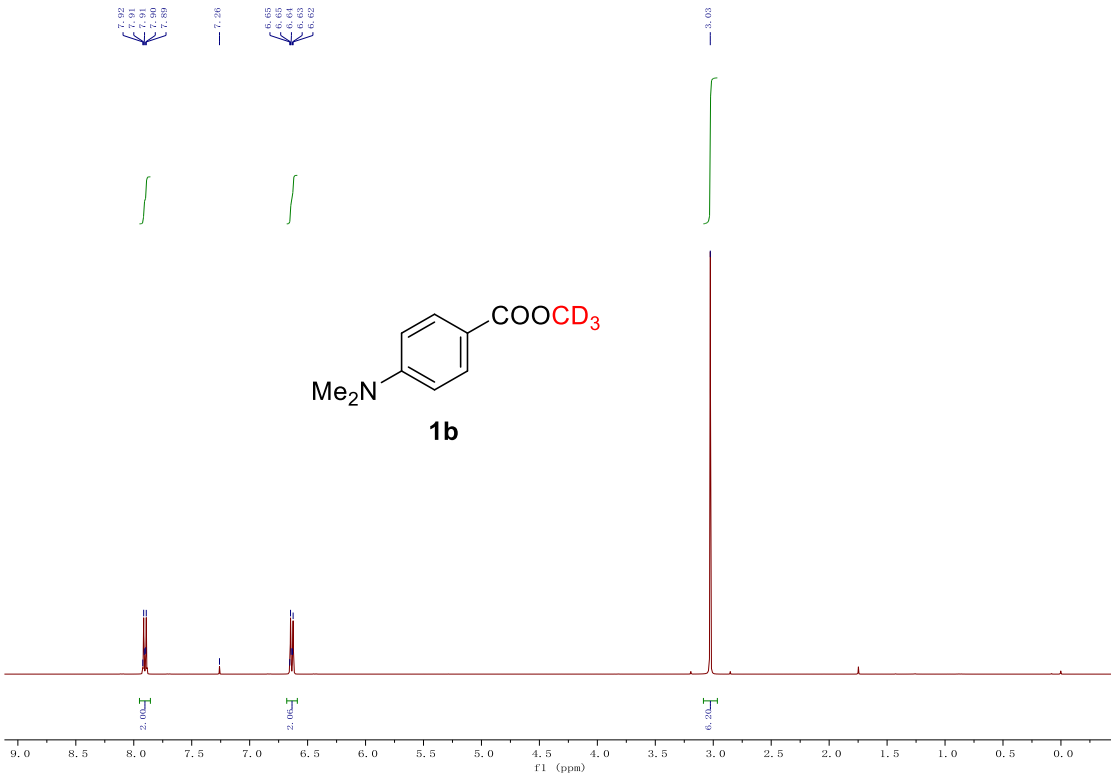
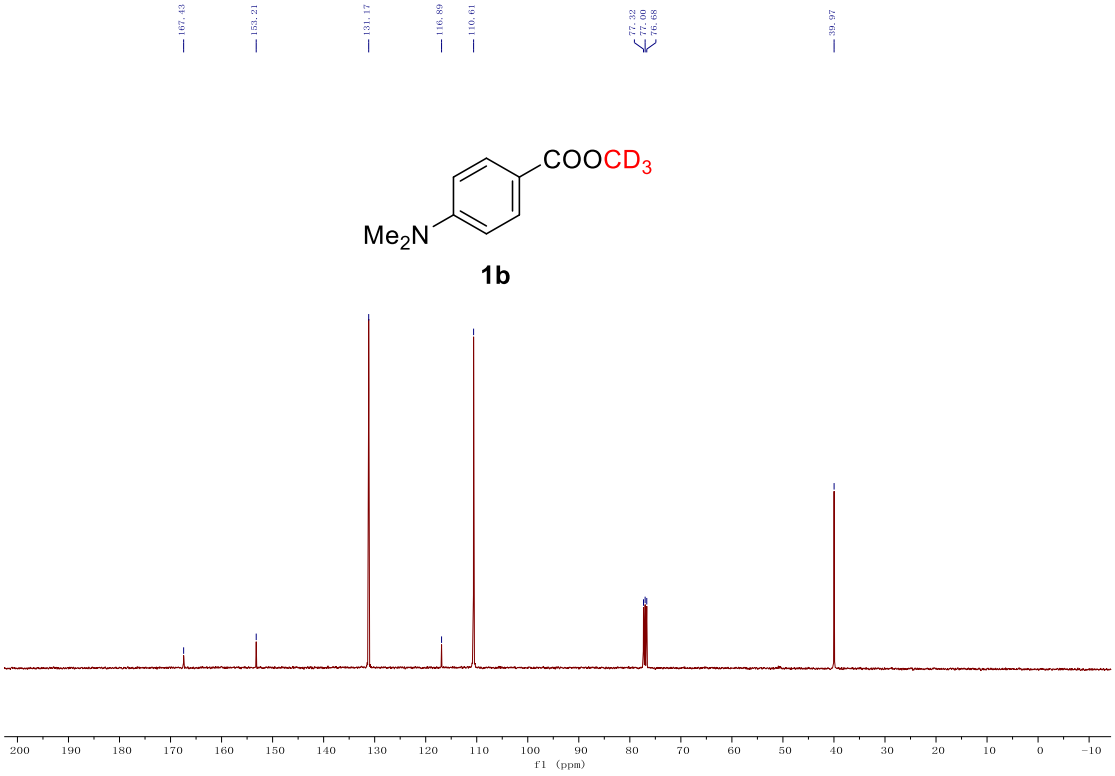
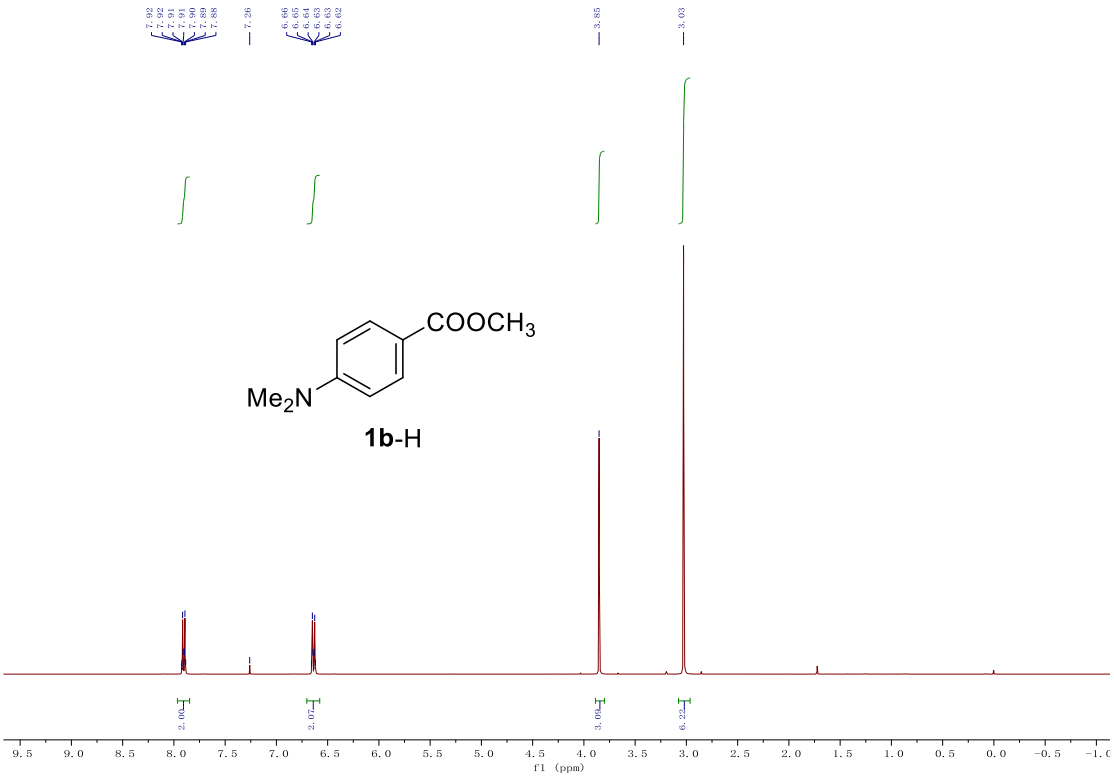
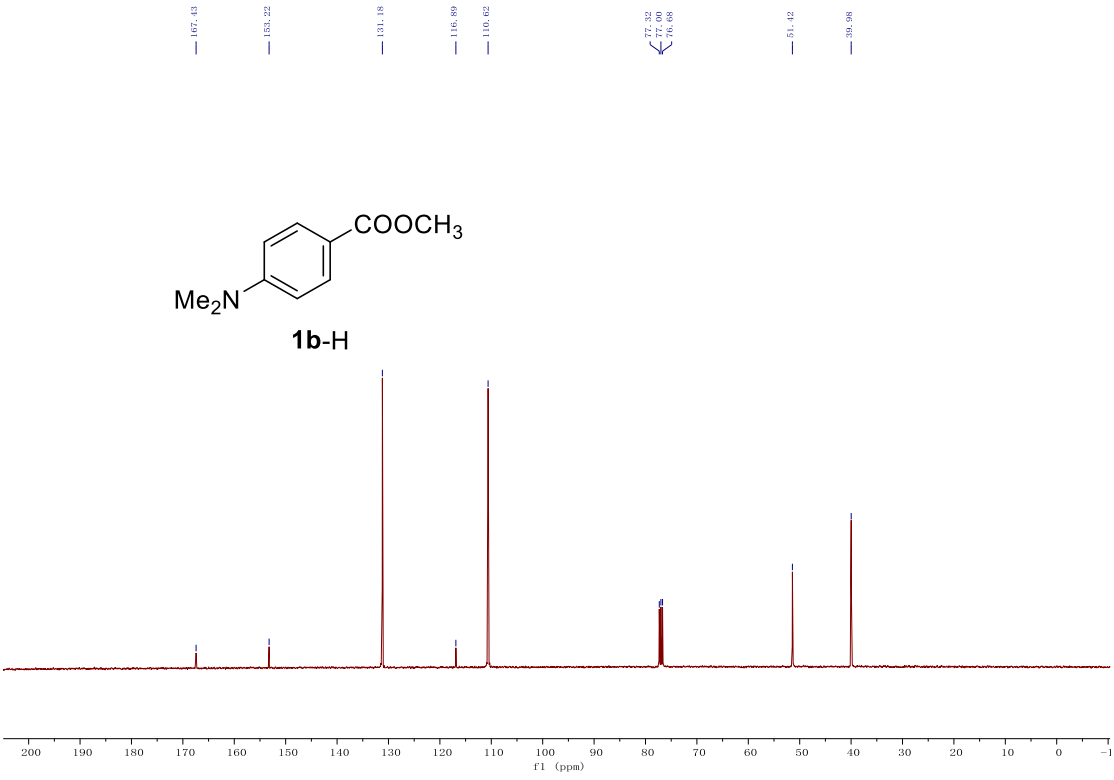
8.23
7.90
7.90
7.89
7.89
7.89
7.88
7.88
7.88
7.87
7.87
7.86
7.86
7.86
7.75
7.75
7.74
7.74
7.74
7.73
7.73
7.73
7.72
7.72
7.71
7.71
7.71
3.33
1.95
1.95
1.94
1.94
1.93
CH3
S
+
-OTf
DMT
4.00
2.05
2.04
3.07
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


140.12
134.83
131.93
131.58
125.56
125.10
118.30
34.99
1.73
1.57
1.49
1.34
1.07
0.91
0.74
CH3
S
+
-OTf
DMT
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.92
7.91
7.91
7.90
7.89
7.26
6.65
6.65
6.64
6.63
6.62
3.03
COOCD3
Me2N
1b
2.00
2.06
6.20
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)


167.43
153.21
131.17
116.89
110.61
77.32
77.00
76.68
39.97
COOCD3
Me2N
1b
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.92
7.92
7.91
7.91
7.90
7.89
7.88
7.26
6.66
6.65
6.64
6.63
6.63
6.62
3.85
3.03
COOCH3
Me2N
1b-H
2.00
2.07
3.09
6.22
f1 (ppm)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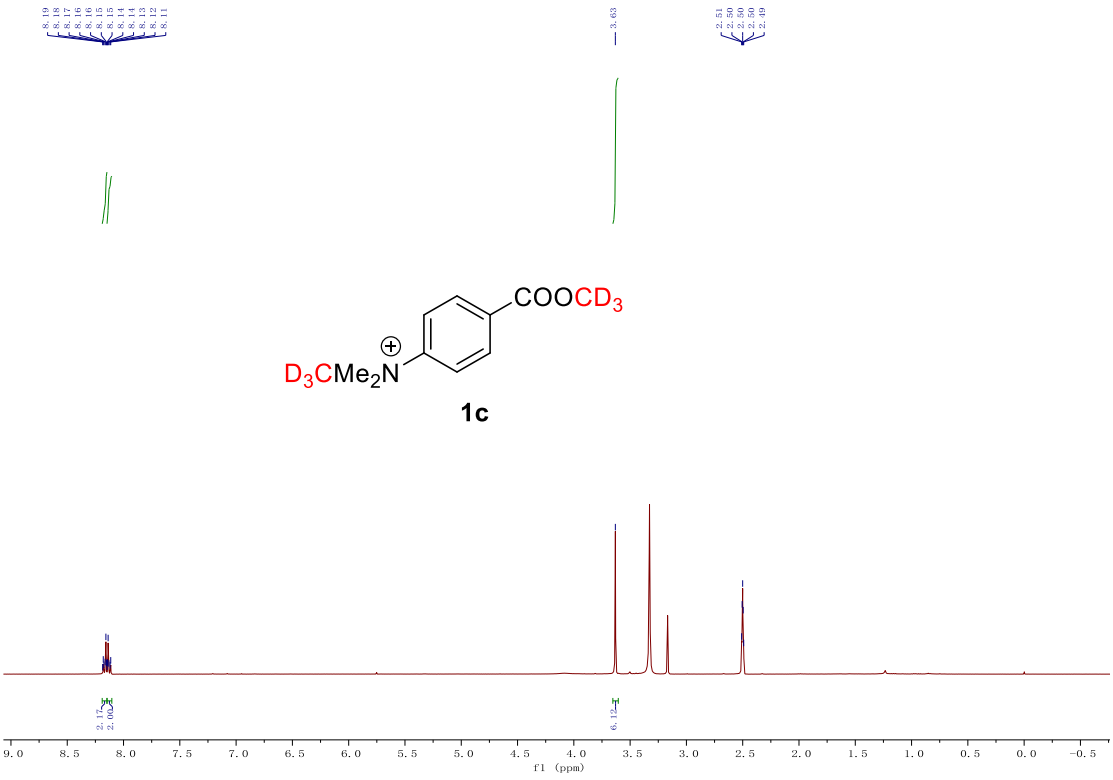
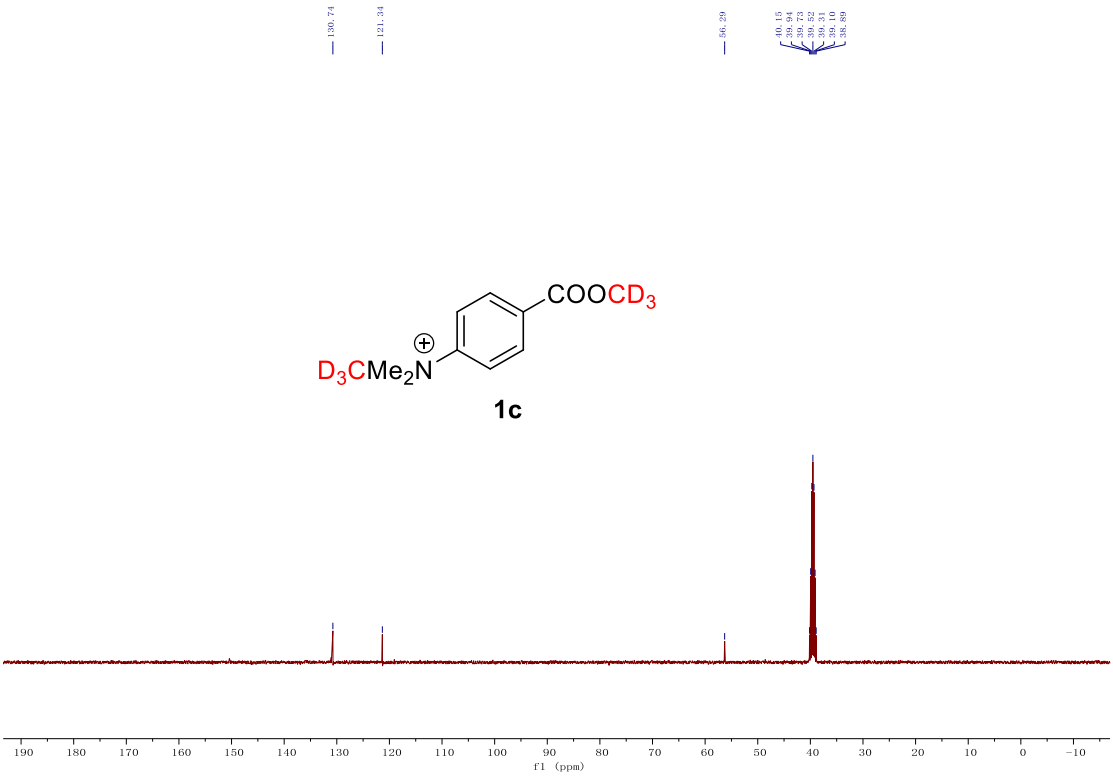
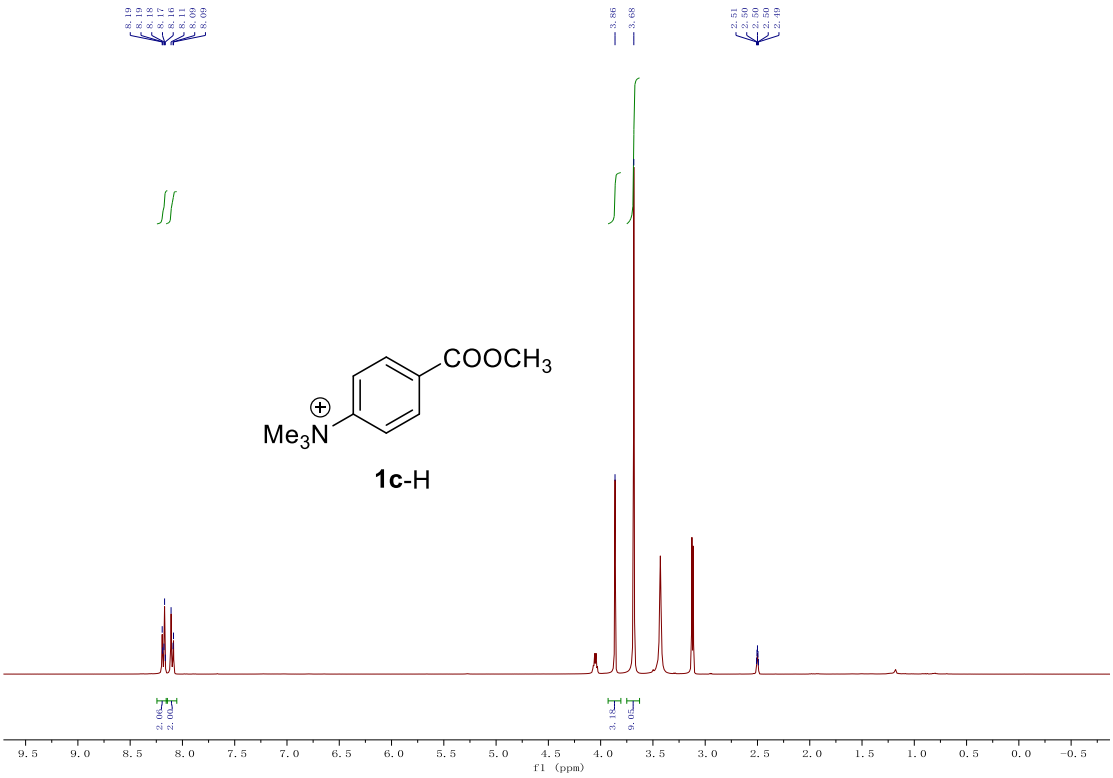
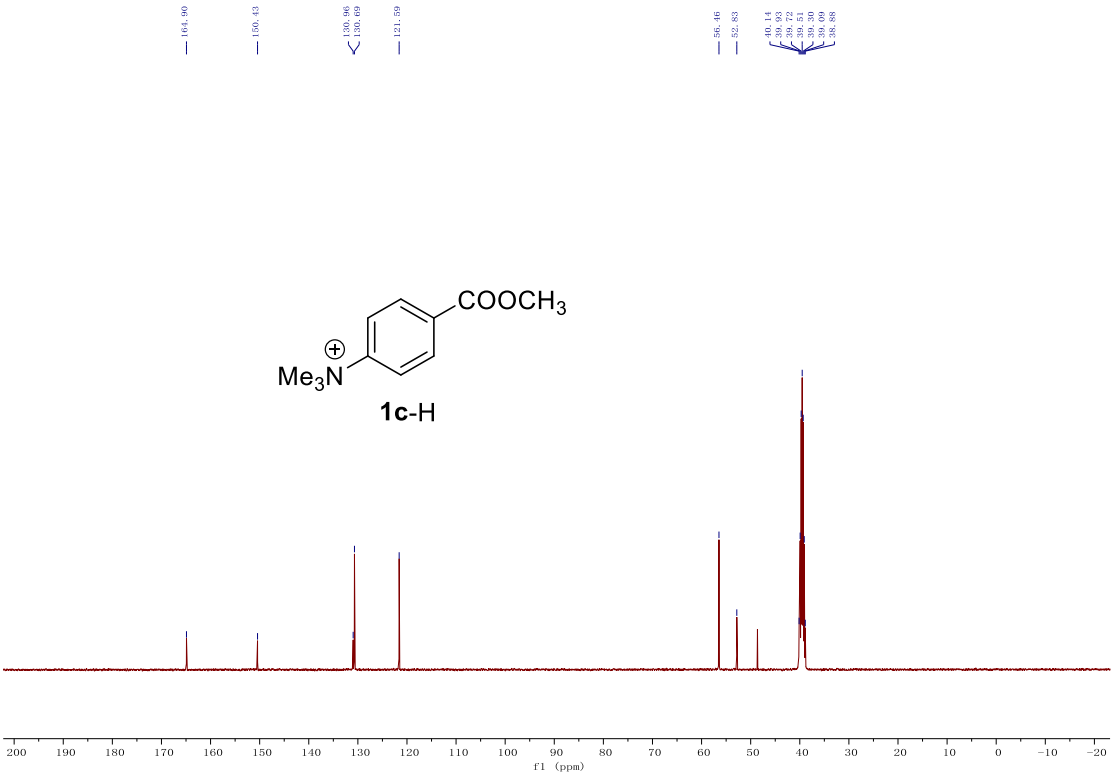
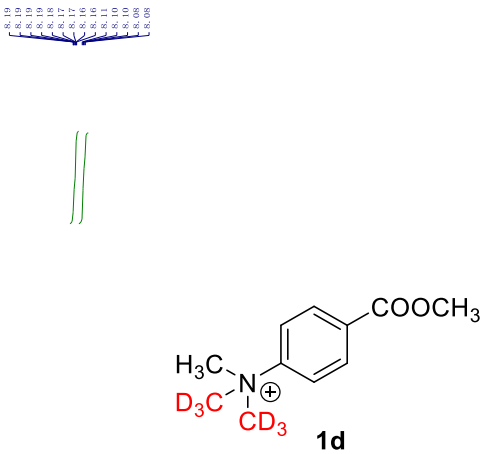
153.22
131.18
116.89
110.62
77.32
77.00
76.68
51.42
39.98
COOCH3
Me2N
1b-H
f1 (ppm)


8.19
8.18
8.17
8.16
8.16
8.15
8.15
8.14
8.13
8.12
8.11
3.63
2.51
2.50
2.50
2.50
2.49
COOCD3
D3CMe2N
1c
2.17
2.00
6.12
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
-0.5
f1 (ppm)


130.74
121.34
66.29
40.15
39.94
39.73
39.52
39.31
39.10
38.89
COOCD3
D3CMe2N
1c
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

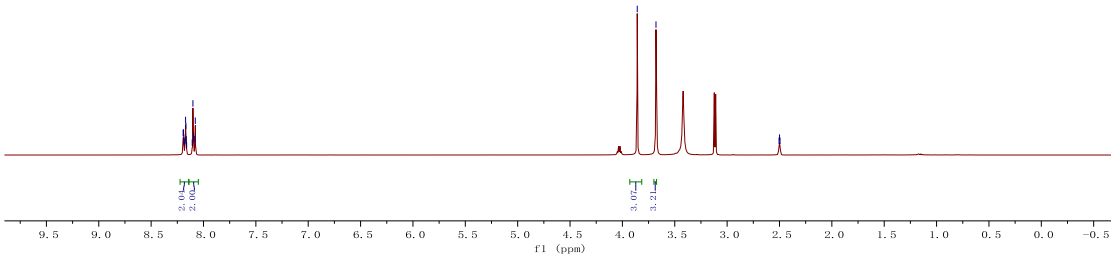

8.19
8.19
8.18
8.17
8.16
8.11
8.09
8.09
3.86
3.68
2.51
2.50
2.50
2.50
2.49
COOCH3
Me3N
1c-H
2.00
2.00
3.18
9.03
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


164.90
150.43
130.96
130.69
121.59
56.46
52.83
40.14
39.93
39.72
39.51
39.30
39.09
38.88
COOCH3
Me3N
1c-H
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

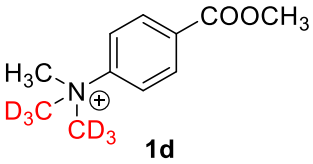

8.19
8.19
8.19
8.19
8.18
8.17
8.17
8.16
8.16
8.11
8.10
8.10
8.08
8.08
3.86
3.68
2.50
2.50
2.49

COOCH3
H3C
N
D3C
CD3

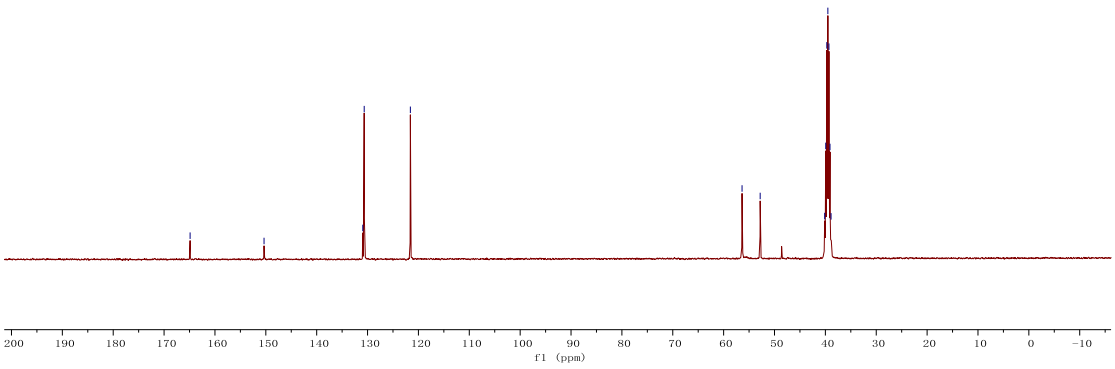
1d


2.04
2.06
3.07
3.21
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 -0.5
f1 (ppm)


164.89
150.35
130.94
130.66
121.59
56.38
52.82
40.14
39.93
39.72
39.51
39.30
39.09
38.88


COOCH3
H3C
N
D3C
CD3

1d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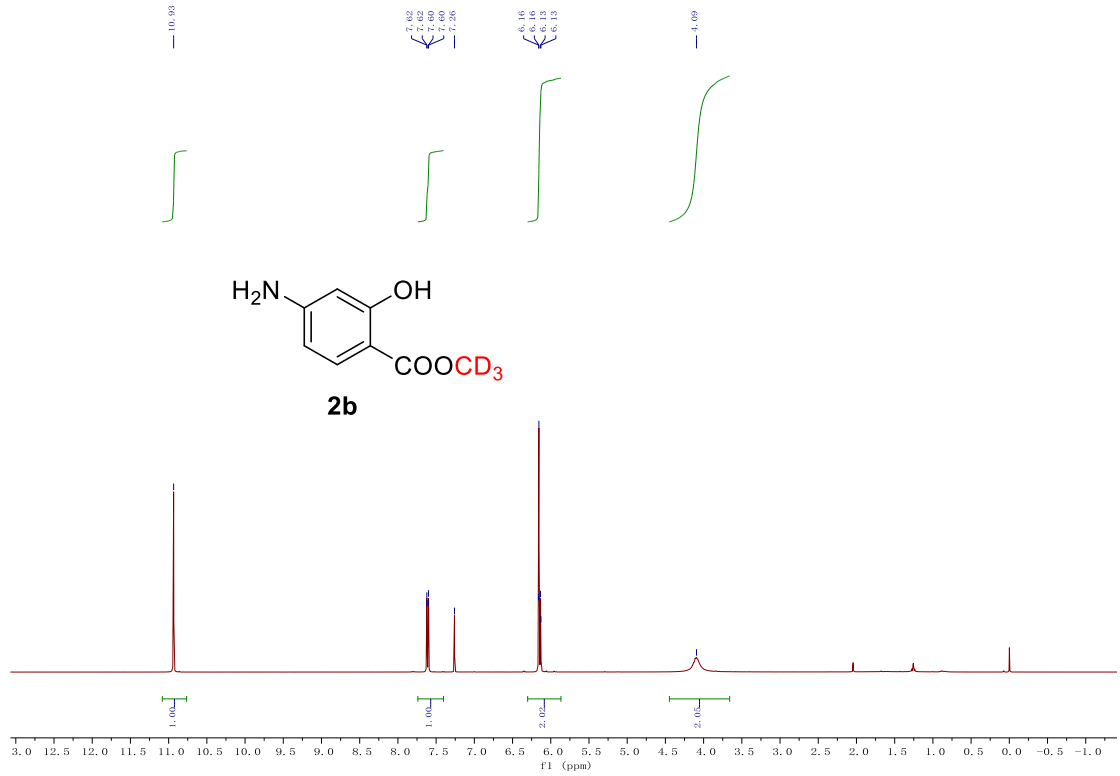
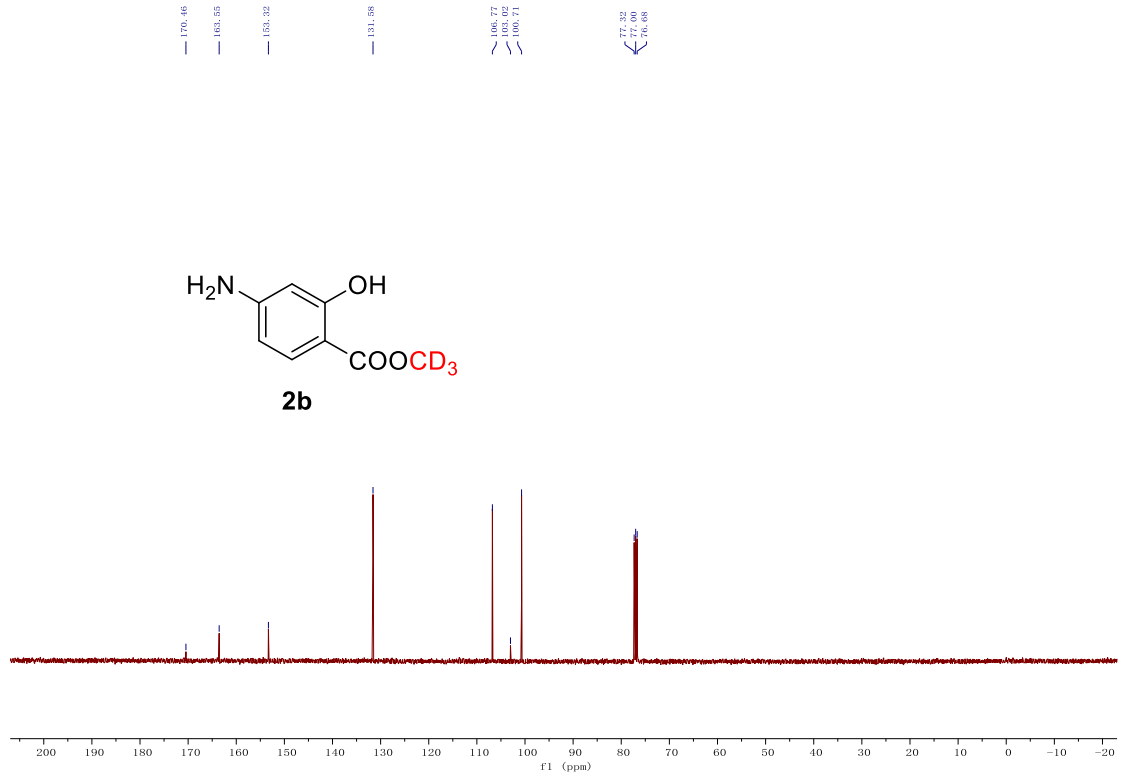
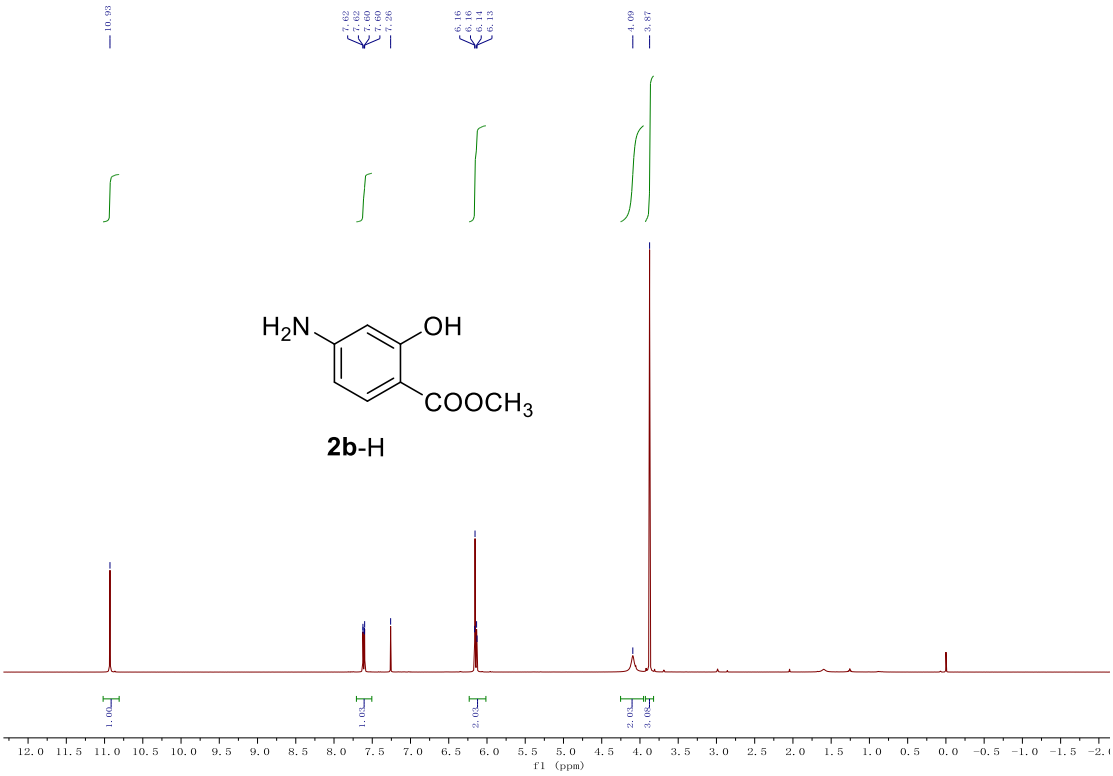
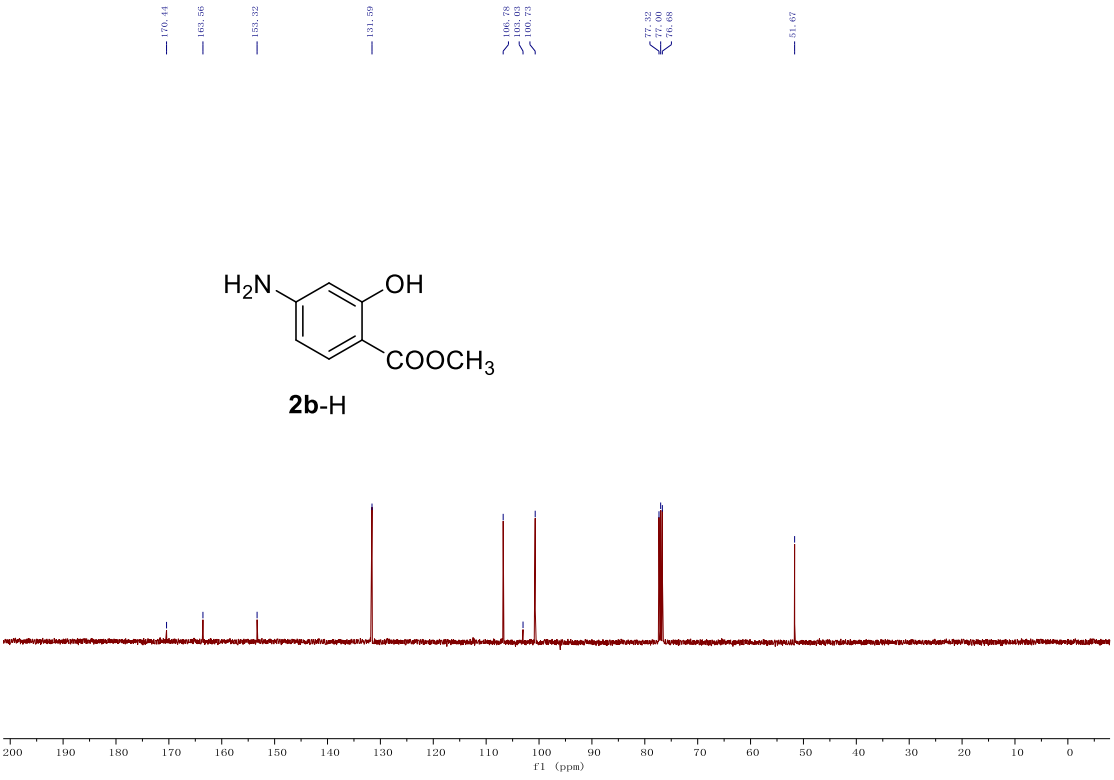
f1 (ppm)


10.93
7.62
7.62
7.60
7.60
7.26
6.16
6.16
6.13
6.13
4.09
H2N
OH
COOCD3
2b
1.00
1.00
2.02
2.08
3.0 12.5 12.0 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 -0.5 -1.0
f1 (ppm)


170.46
163.55
153.32
131.58
106.77
103.02
100.71
77.32
77.00
76.68
H2N
OH
COOCD3
2b
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

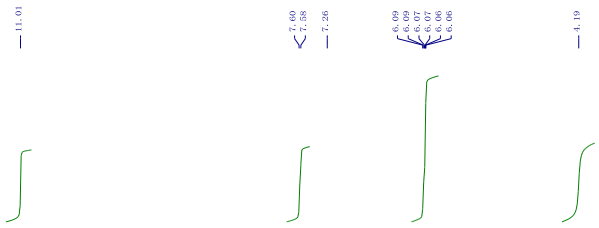


2b-H



H_2N
OH
$COOCH_3$

2b-H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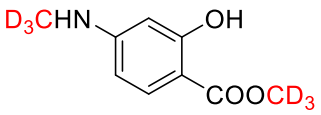
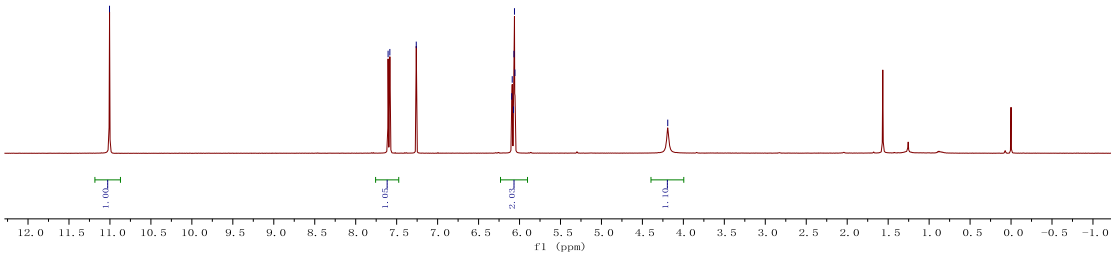
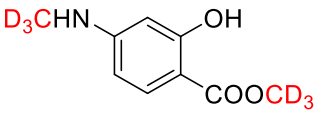
7.58
7.26
6.09
6.09
6.07
6.07
6.06
6.06
4.19


D3CHN
OH
COOCD3

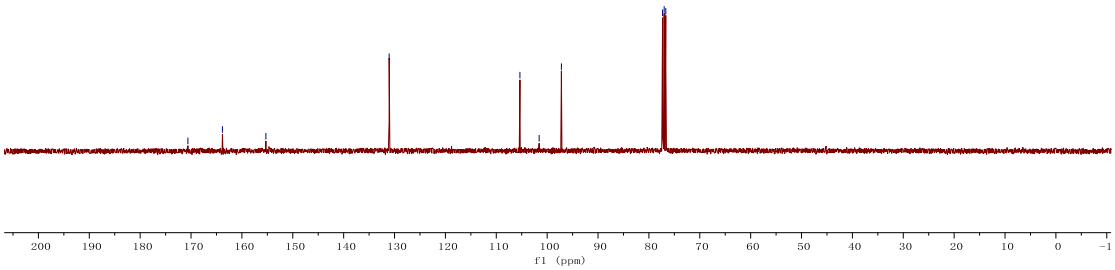
2c


1.00
1.05
2.03
1.10
12.0 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 -0.5 -1.0
f1 (ppm)


170.62
163.83
155.29
131.06
105.35
101.57
97.20
77.32
77.00
76.68


D3CHN
OH
COOCD3

2c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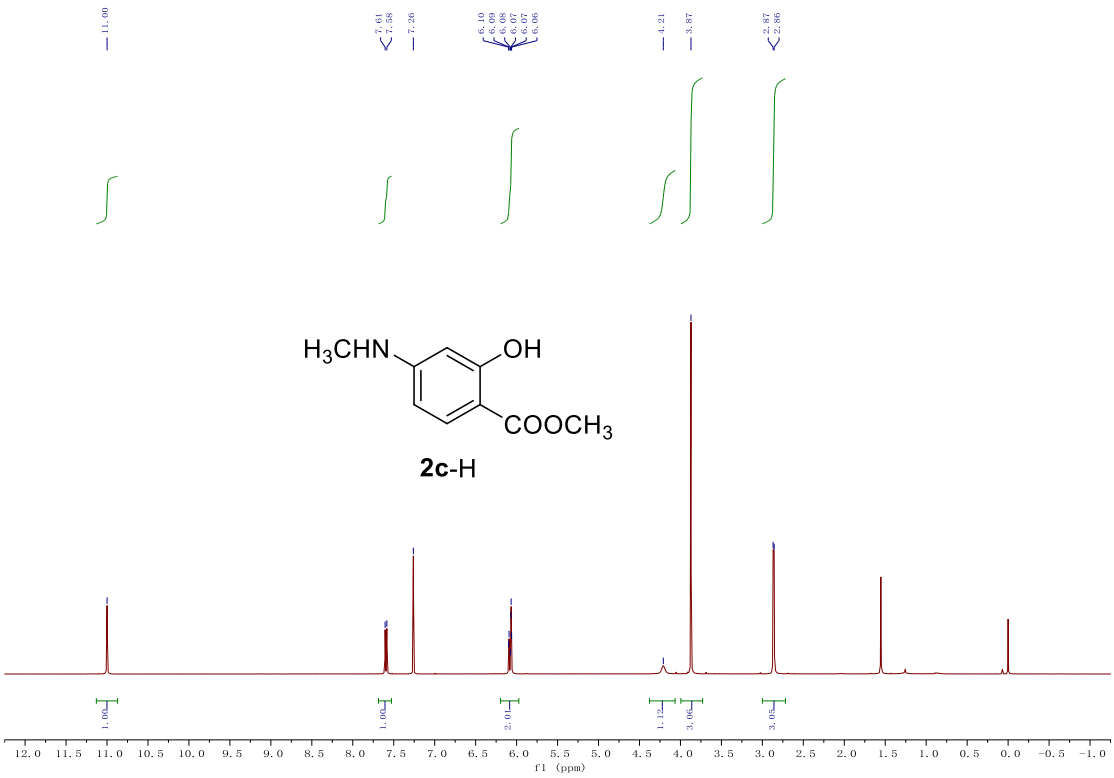
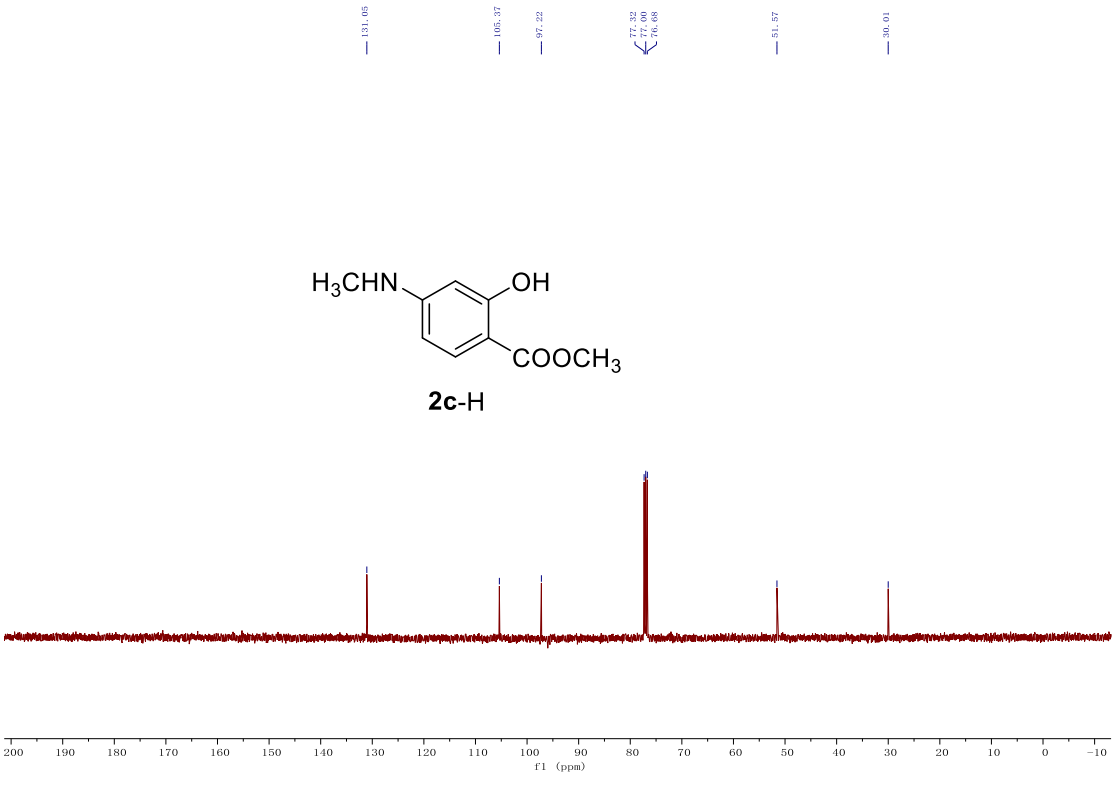
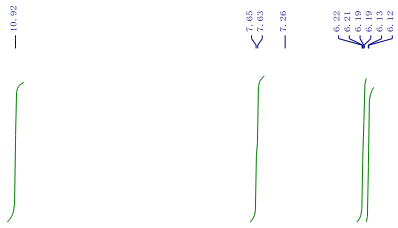
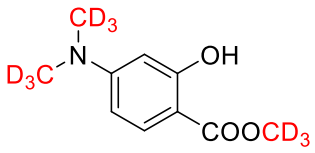
f1 (ppm)

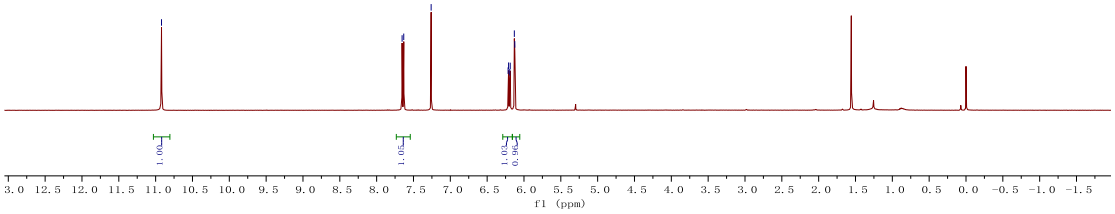

11.00
7.61
7.58
7.26
6.10
6.09
6.08
6.07
6.07
6.06
4.21
3.87
2.87
2.86
H3CHN
OH
COOCH3
2c-H
1.00
1.00
2.01
1.12
3.06
3.05
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


131.05
105.37
97.22
77.32
77.00
76.68
51.57
30.01
H3CHN
OH
COOCH3
2c-H
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

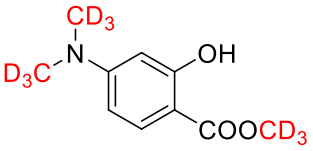

10.92
7.65
7.63
7.26
6.22
6.21
6.19
6.19
6.13
6.12


CD3
N
D3C
OH
COOCD3

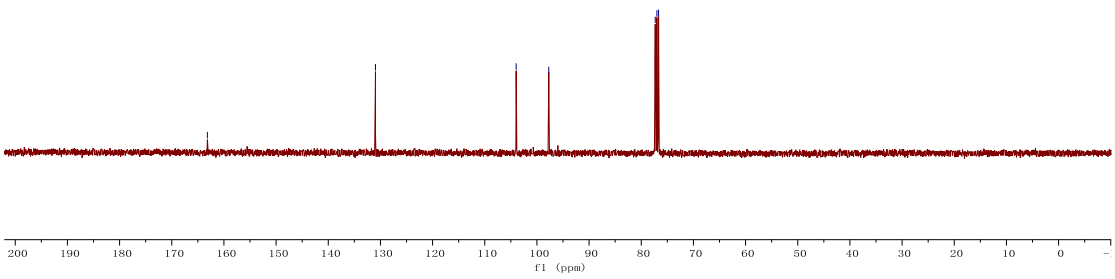
2d

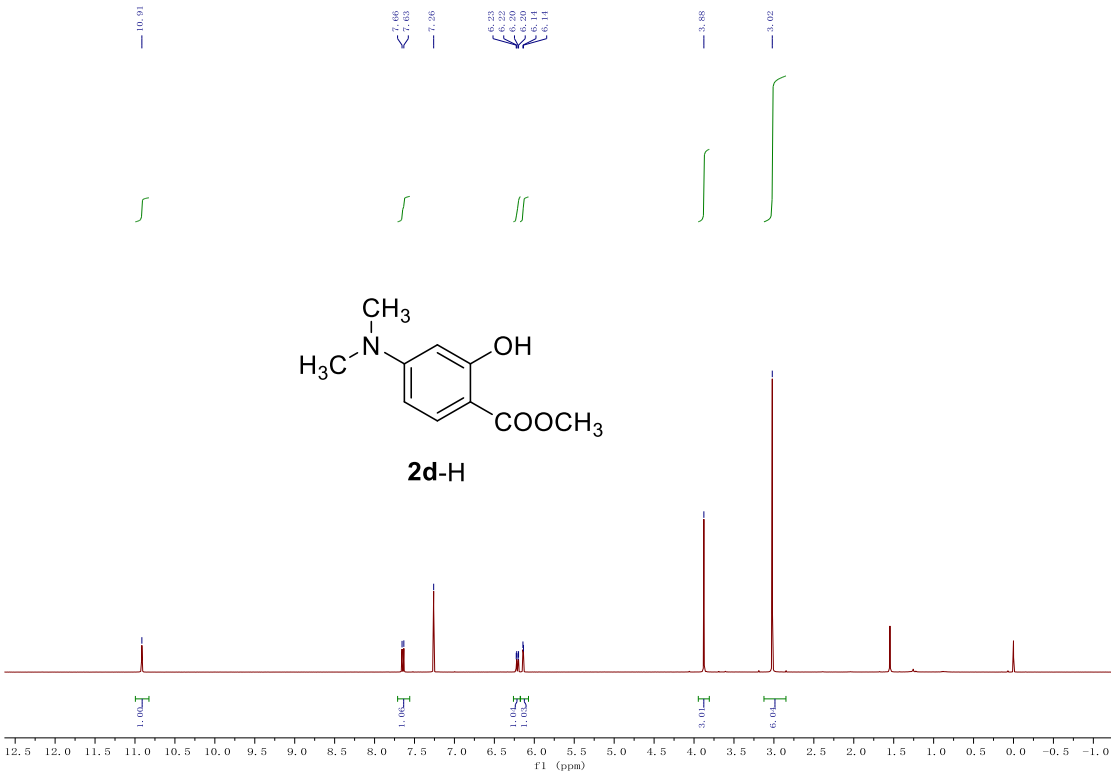

1.00
1.05
1.03
0.96
3.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5
f1 (ppm)


163.17
130.95
103.98
97.73
77.32
77.00
76.68

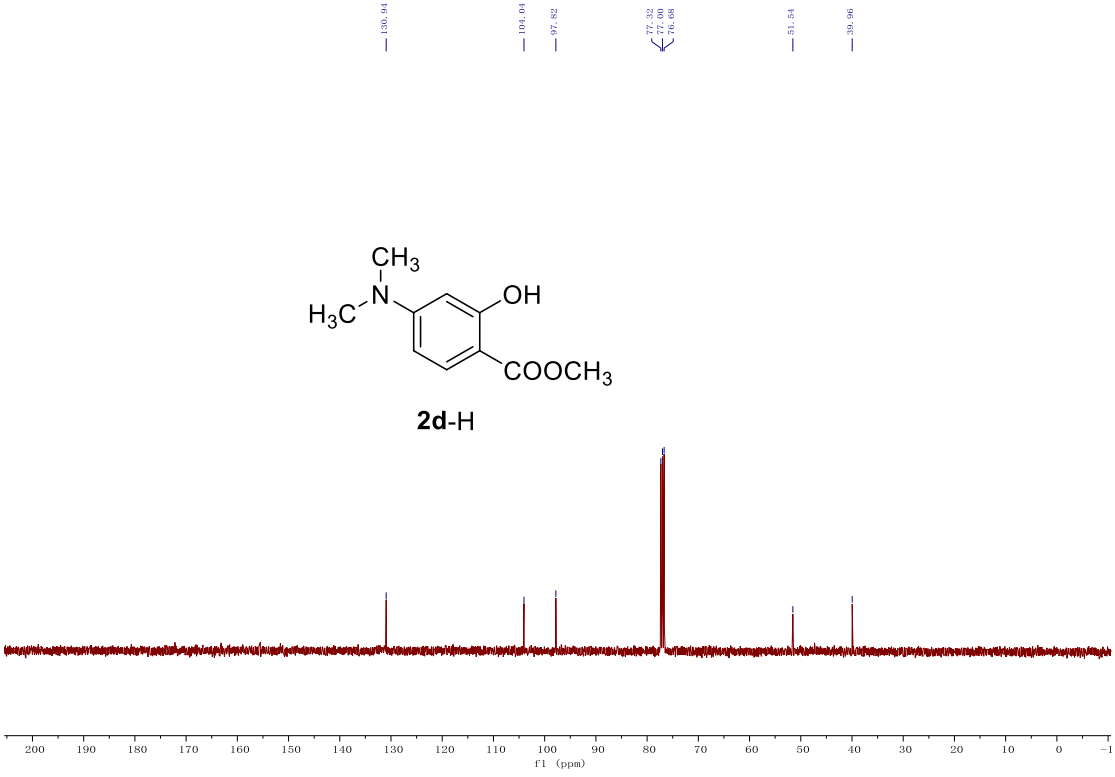

CD3
N
D3C
OH
COOCD3

2d

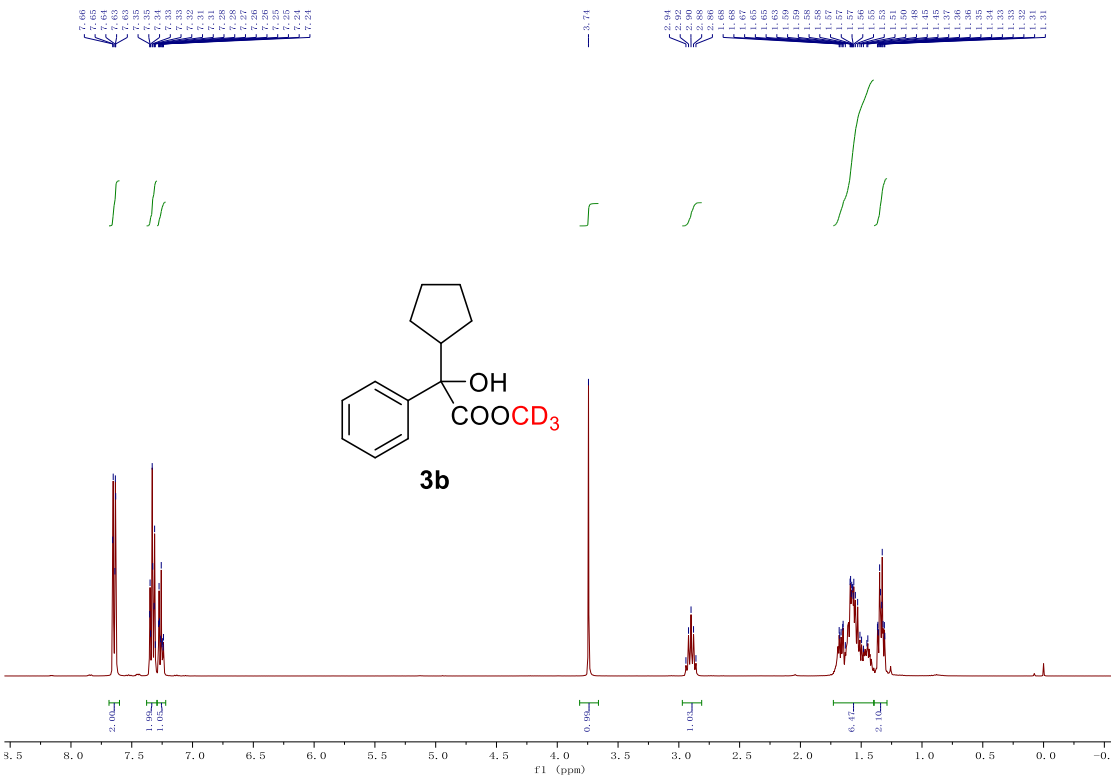

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

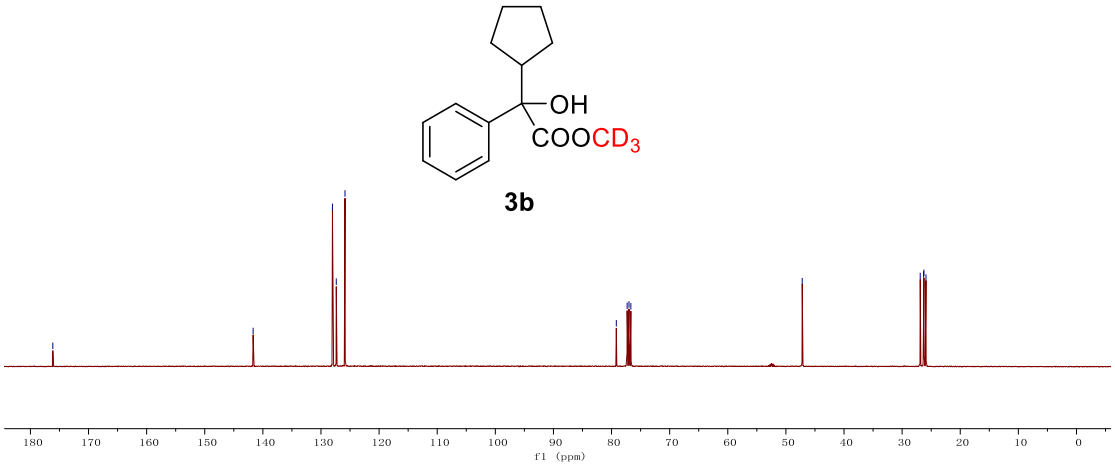

10.91
7.66
7.65
7.26
6.23
6.22
6.20
6.14
6.14
3.88
3.02
CH3
N
H3C
OH
COOCH3
1.00
1.06
1.04
1.05
3.01
6.04
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

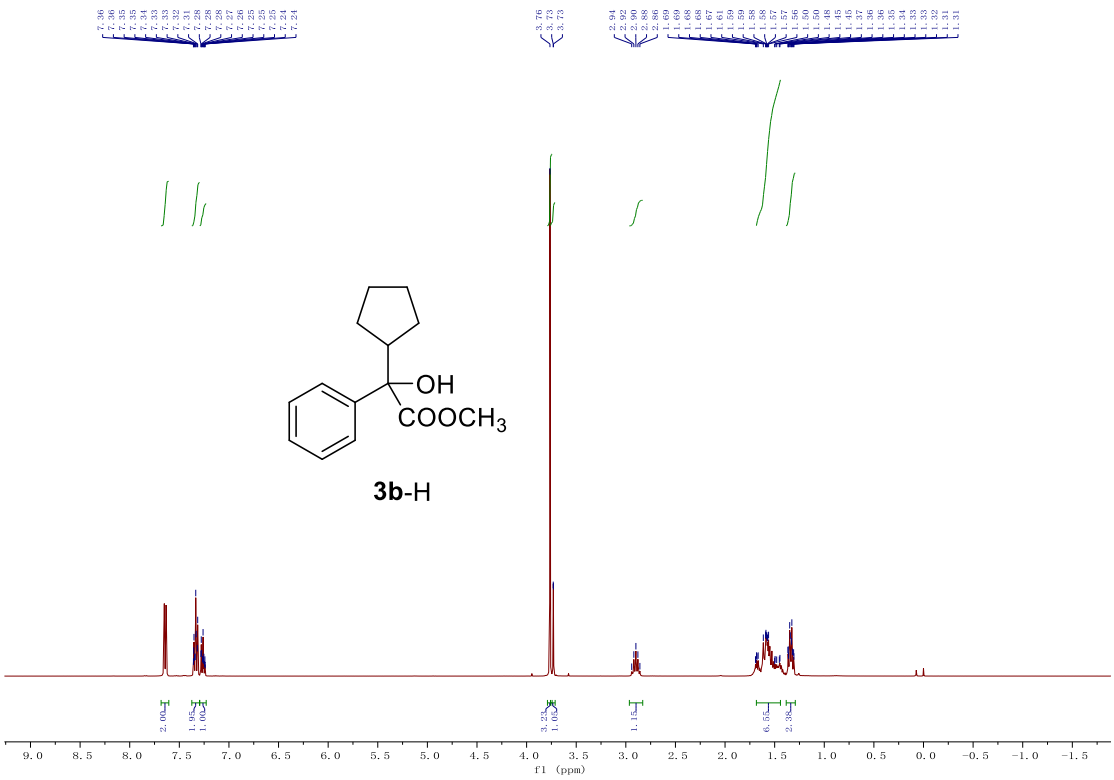
2d-H

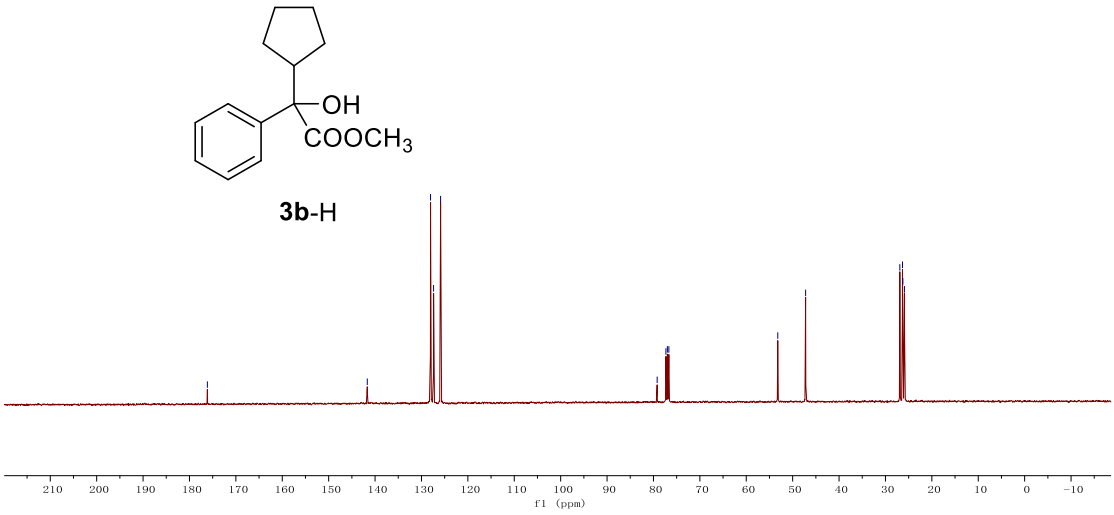

130.94
104.04
97.82
77.32
77.00
76.68
51.54
39.96
CH3
N
H3C
OH
COOCH3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

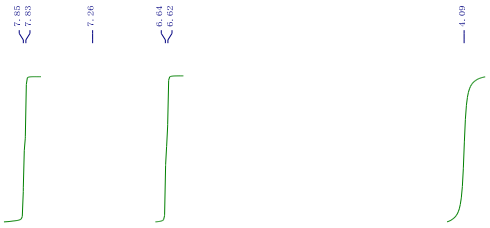
2d-H

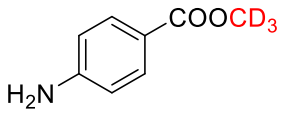

OH
COOCD3
3b
f1 (ppm)


OH
COOCD3
3b
f1 (ppm)

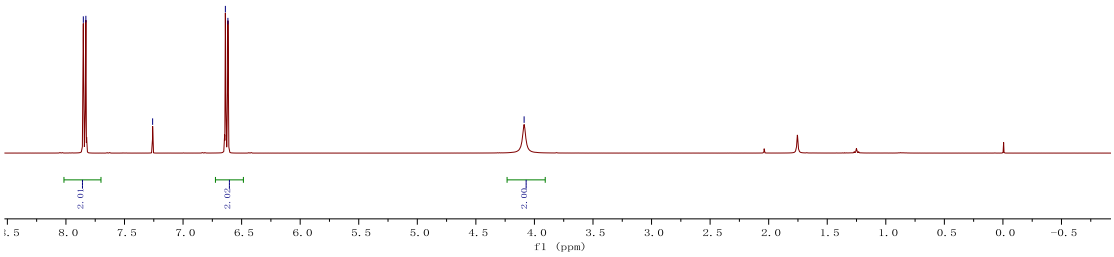

OH
COOCH3
3b-H
f1 (ppm)


OH
COOCH3
3b-H
f1 (ppm)

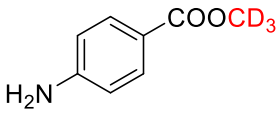

7.85
7.83
7.26
6.64
6.62
1.09


COOCD3
H2N

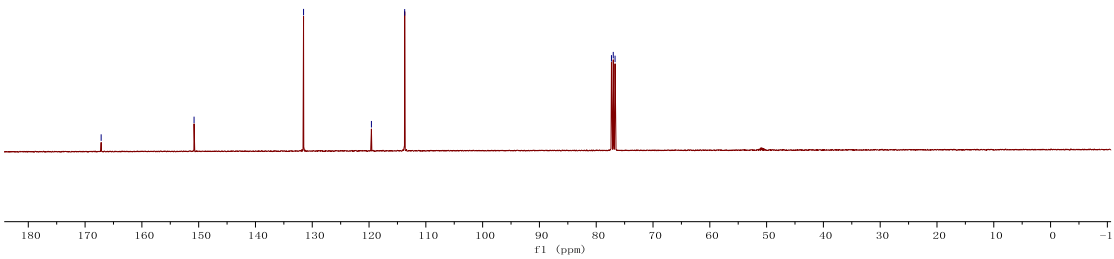
4b

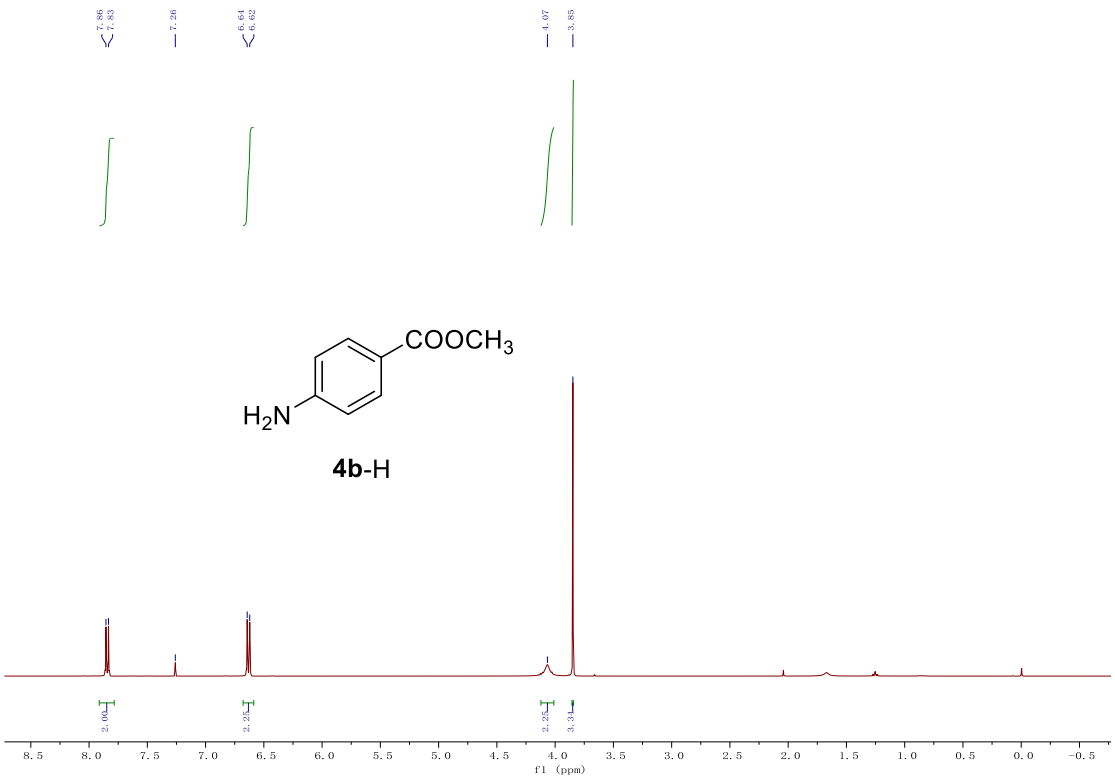

2.01
2.02
2.00
f1 (ppm)

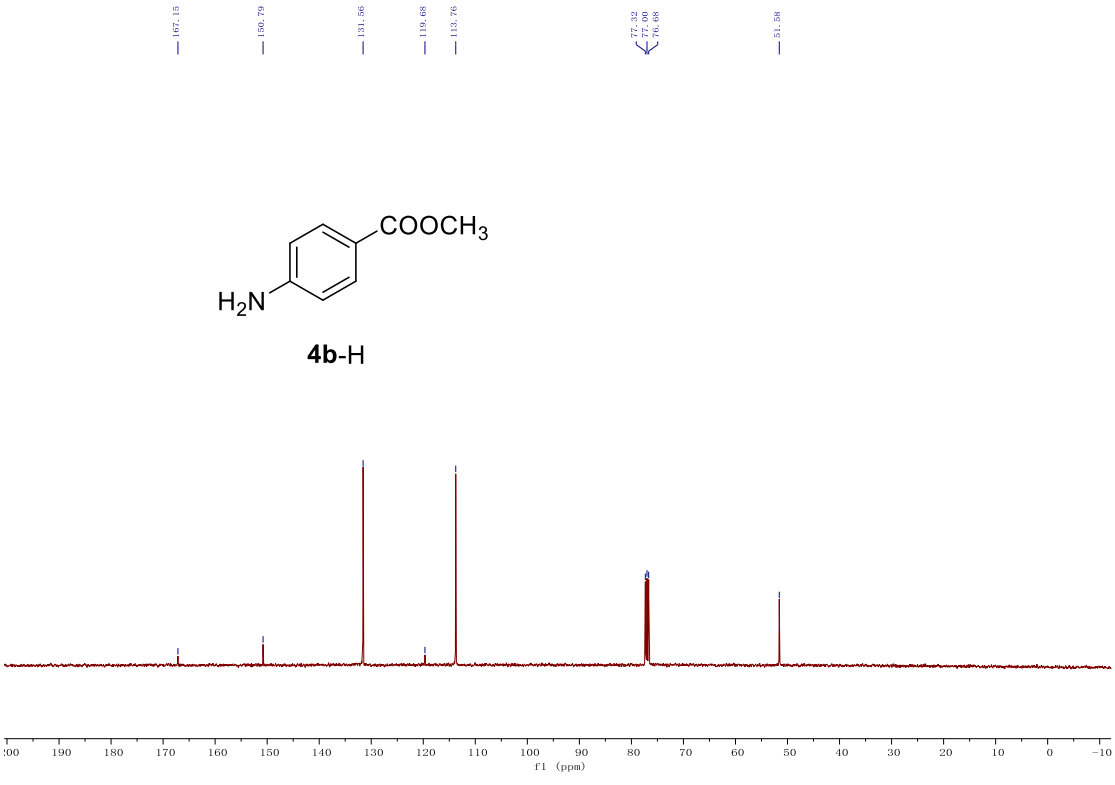

167.17
150.81
131.53
119.58
113.73
77.32
77.00
76.68

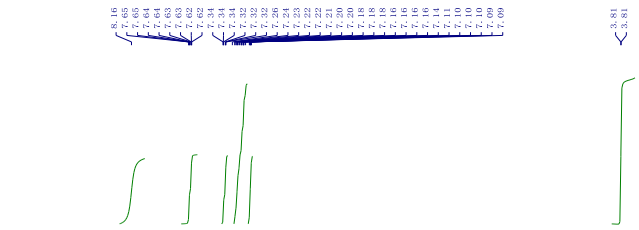

COOCD3
H2N

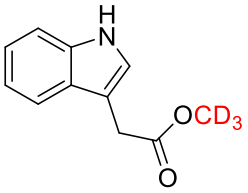
4b


f1 (ppm)

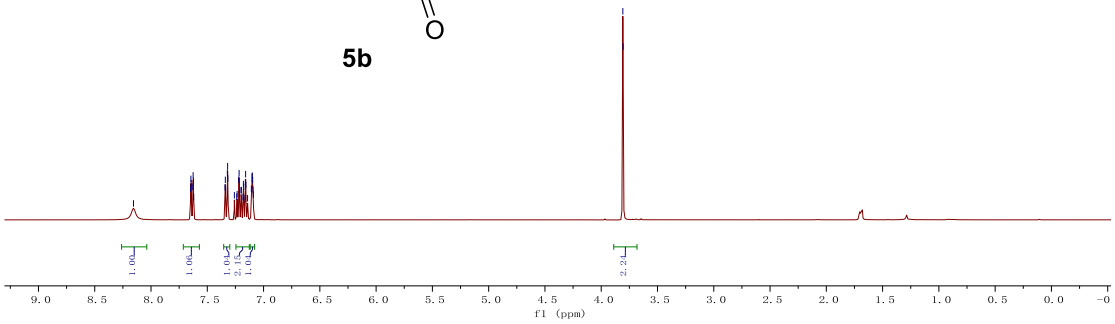

7.86
7.83
7.26
6.64
6.62
4.07
3.85
COOCH3
H2N
4b-H
2.00
2.24
2.25
3.34
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

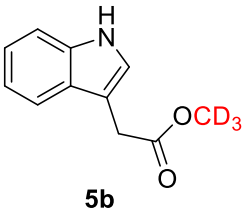

167.15
150.79
131.56
119.68
113.76
77.32
77.00
76.68
51.58
COOCH3
H2N
4b-H
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



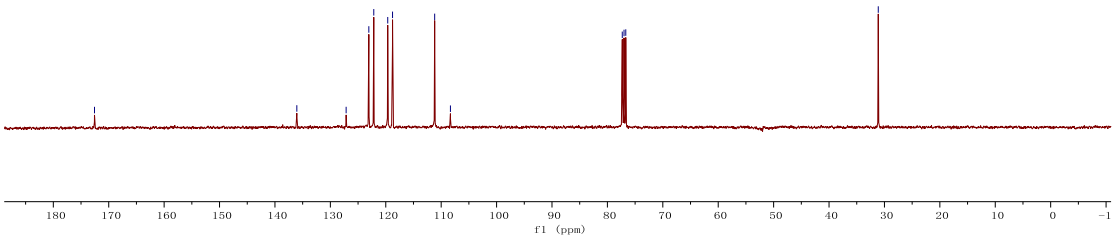


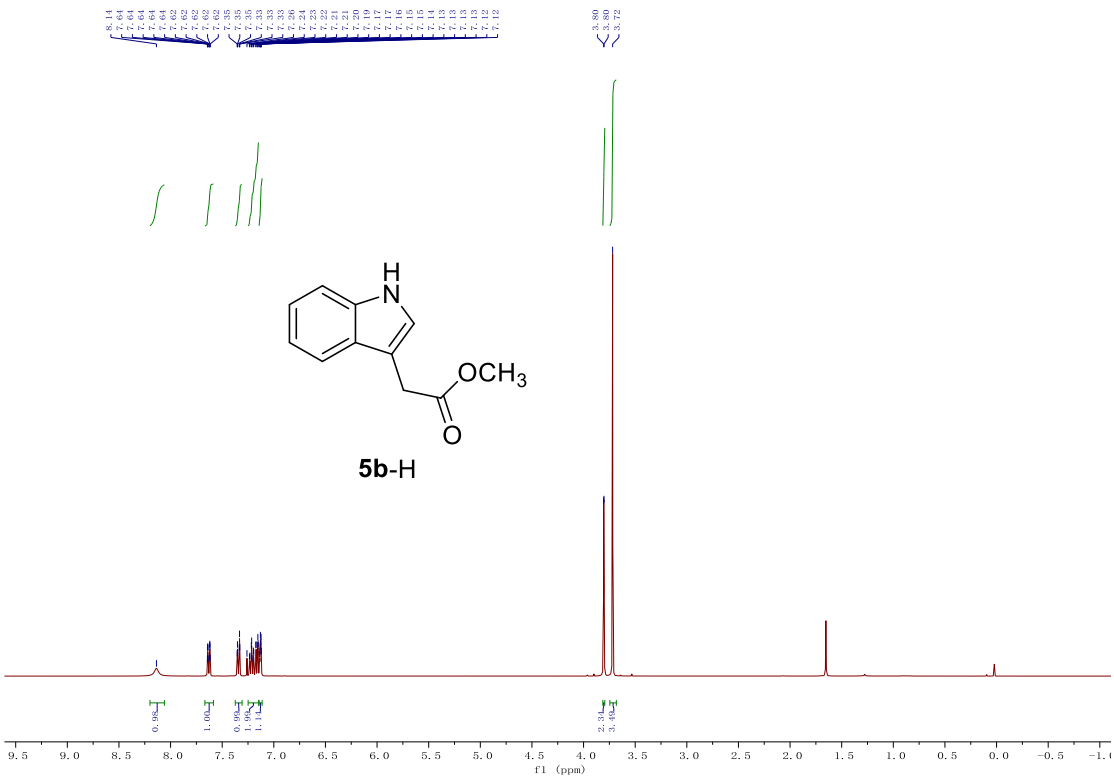
5b



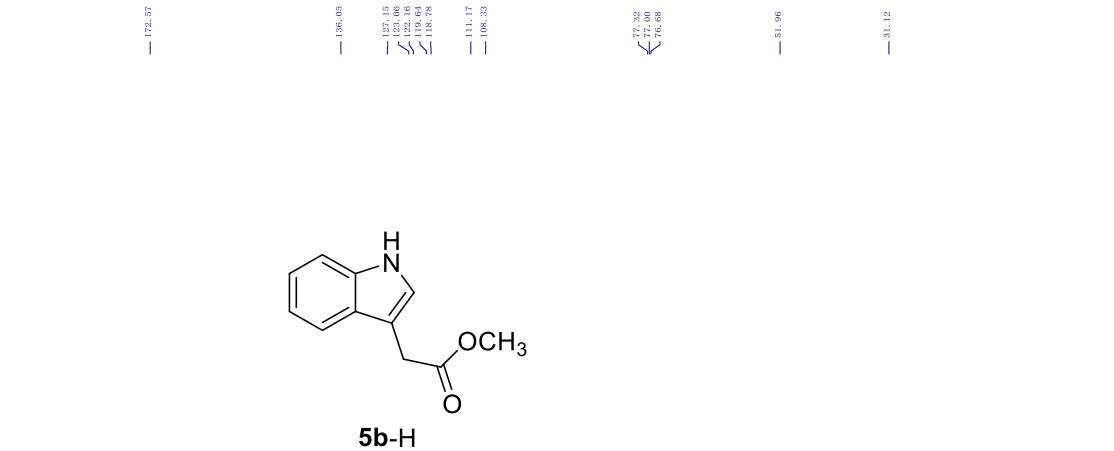


5b



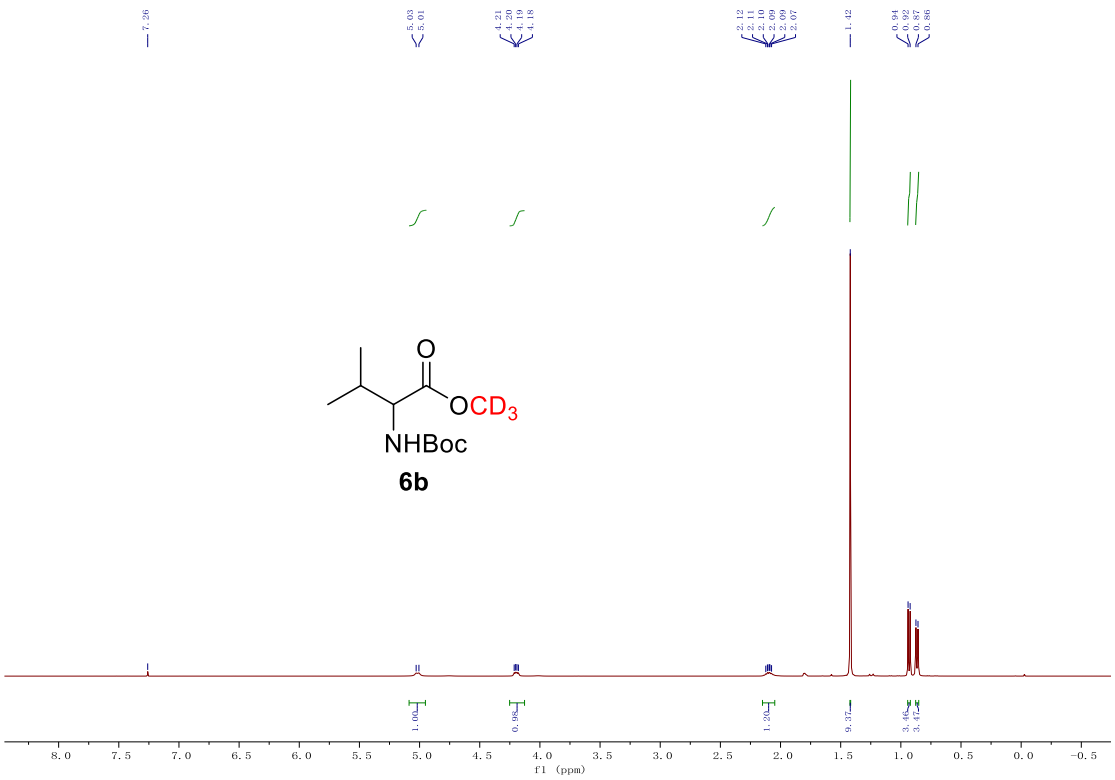

8.14
7.64
7.64
7.64
7.64
7.62
7.62
7.62
7.62
7.62
7.35
7.35
7.33
7.33
7.26
7.24
7.23
7.22
7.22
7.21
7.21
7.20
7.19
7.17
7.17
7.16
7.15
7.15
7.14
7.13
7.13
7.13
7.13
7.12
7.12
3.80
3.80
3.72
H
N
OCH3
O
0.98
1.00
0.99
1.99
1.14
2.34
3.49
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f1 (ppm)

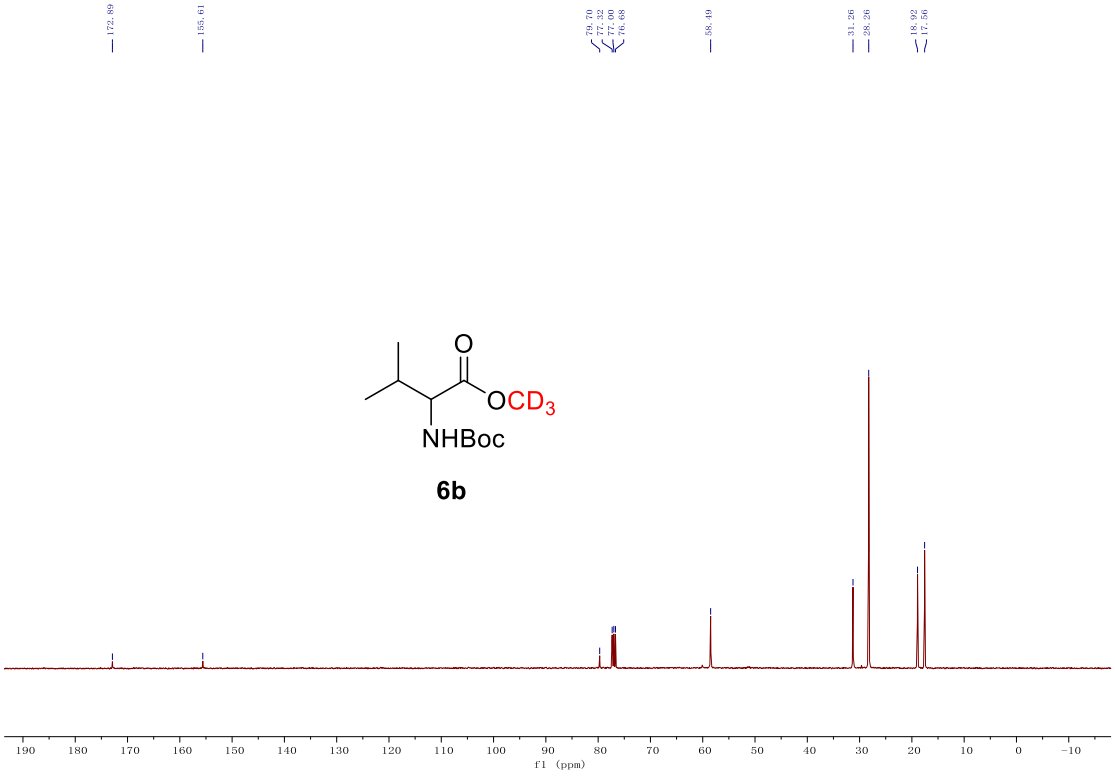
5b-H

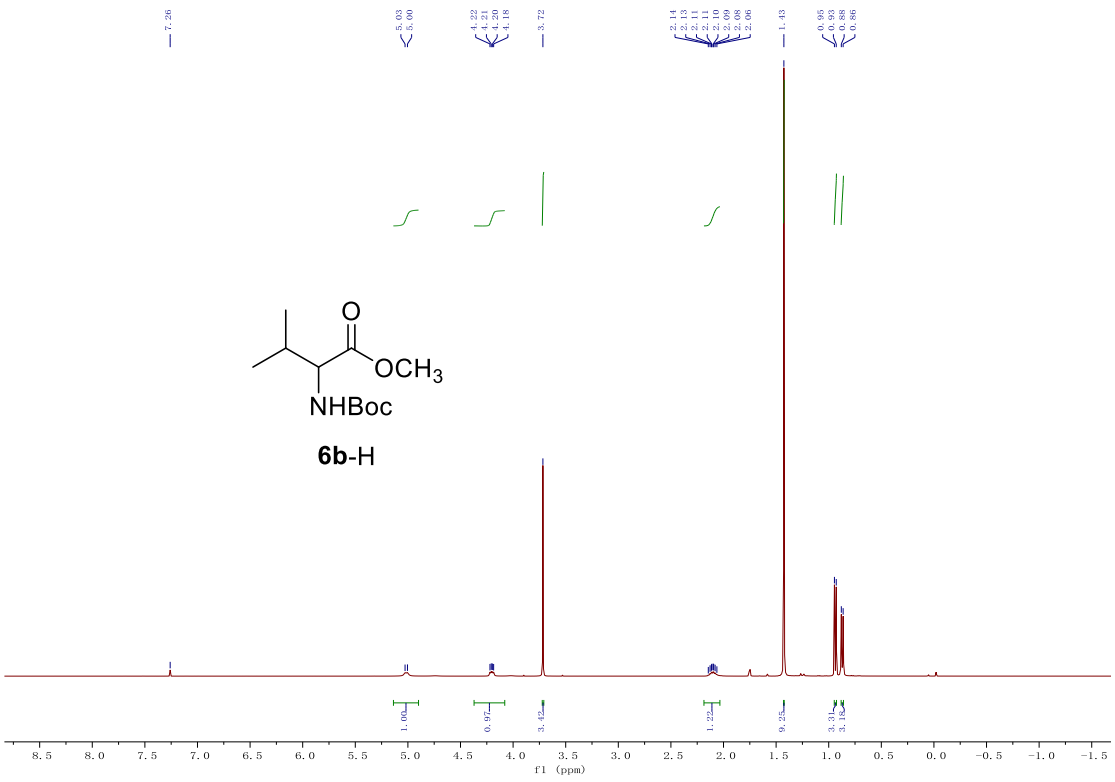

172.57
136.05
127.15
123.06
122.05
119.64
118.78
111.17
108.33
77.32
77.00
76.68
51.96
31.12

H
N
OCH3
O
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

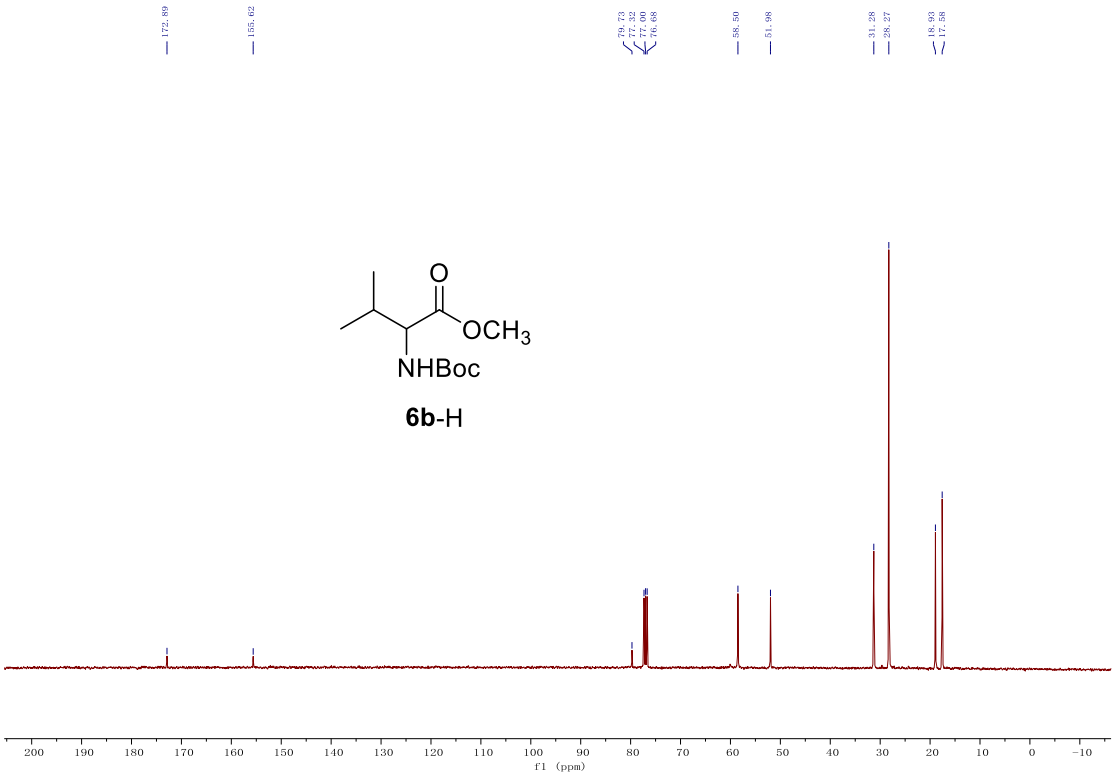
5b-H


7.26
5.03
5.01
4.21
4.20
4.19
4.18
2.12
2.11
2.10
2.09
2.08
2.07
1.42
0.94
0.92
0.87
0.86
O
OCD3
NHBoc
6b
1.00
0.98
1.20
9.37
3.46
3.47
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)

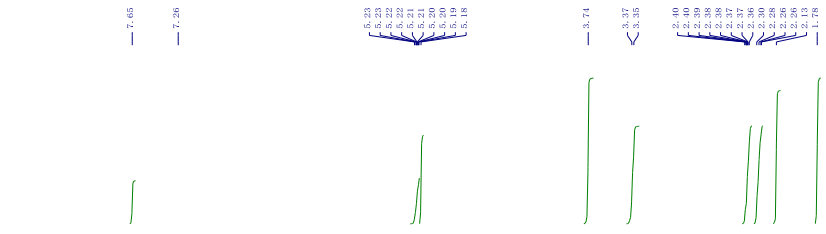

172.89
155.61
79.70
77.32
77.00
76.68
58.49
31.26
28.26
18.92
17.86
O
OCD3
NHBoc
6b
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

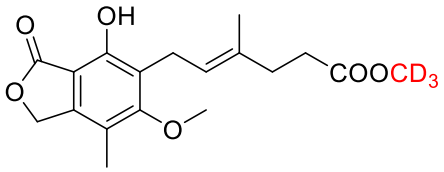

7.26
5.03
5.00
4.22
4.21
4.20
4.18
3.72
2.14
2.13
2.11
2.11
2.10
2.09
2.08
2.06
1.43
0.95
0.93
0.88
0.88
O
OCH3
NHBoc
1.00
0.97
3.42
1.23
9.25
3.31
3.18
f1 (ppm)

6b-H

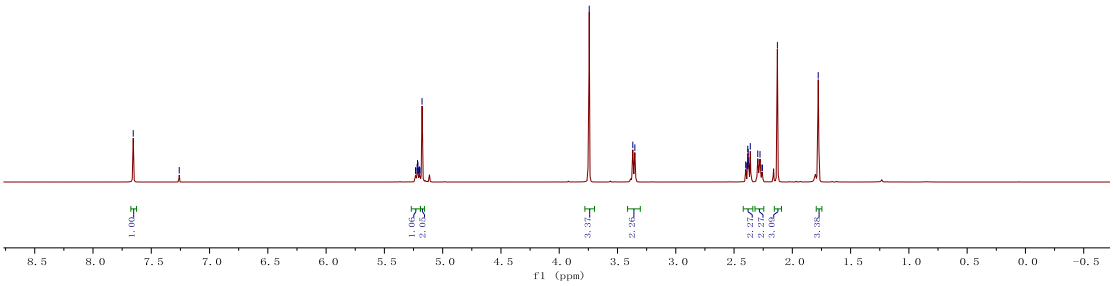

172.89
155.62
79.73
77.32
77.00
76.68
58.50
51.98
31.28
28.27
18.93
17.58
O
OCH3
NHBoc
f1 (ppm)

6b-H

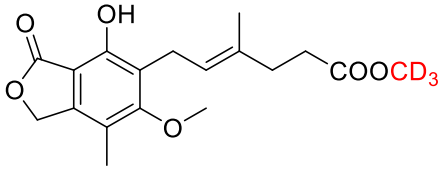

7.65
7.26
5.23
5.23
5.22
5.22
5.21
5.21
5.20
5.19
5.18
3.74
3.37
3.35
2.40
2.40
2.39
2.39
2.38
2.38
2.37
2.37
2.36
2.30
2.28
2.26
2.26
2.13
1.78


O
OH
O
O
COOCD3

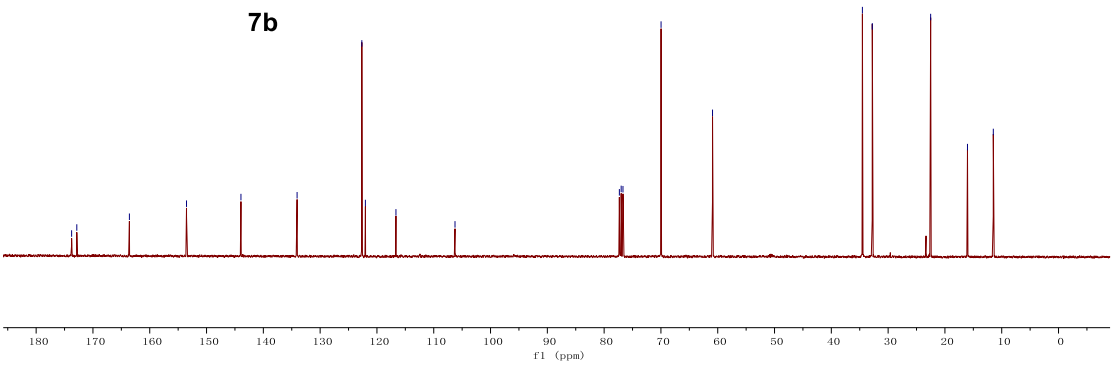
7b

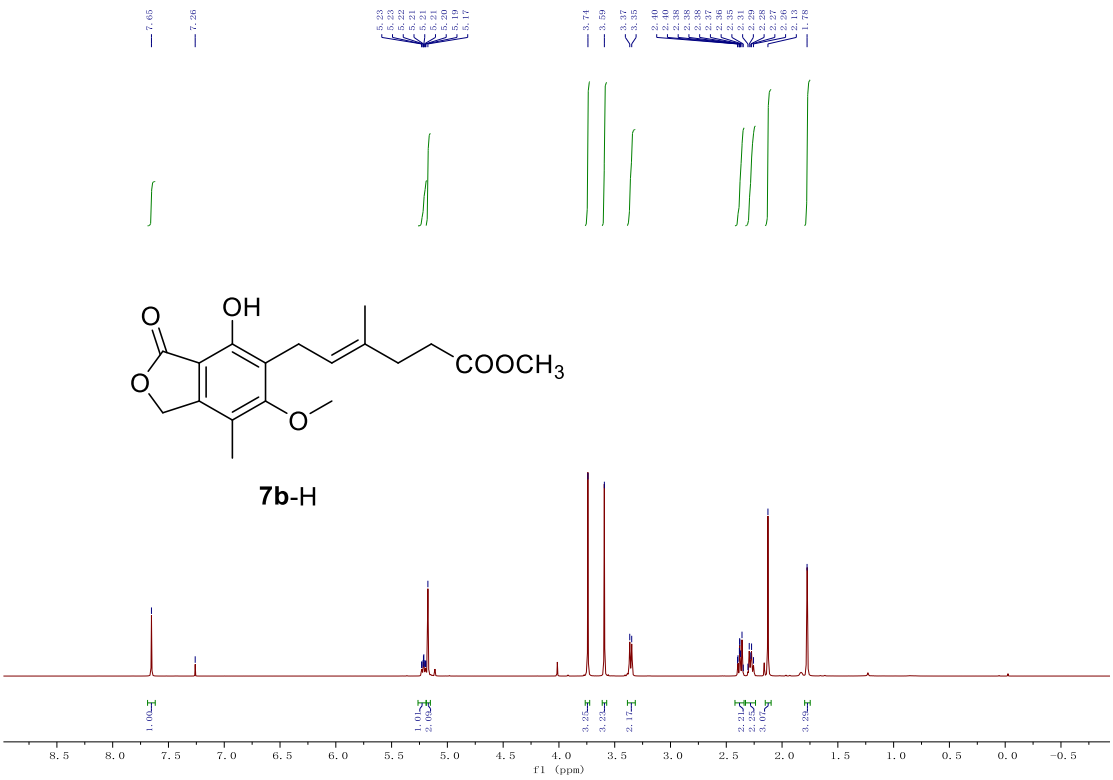

1.00
1.06
2.02
3.37
2.26
2.27
2.27
3.00
3.38
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)


173.75
172.84
163.58
153.53
143.94
134.06
122.66
122.03
116.65
106.25
77.32
77.00
76.68
69.98
60.92
34.53
32.79
22.51
16.03
11.48

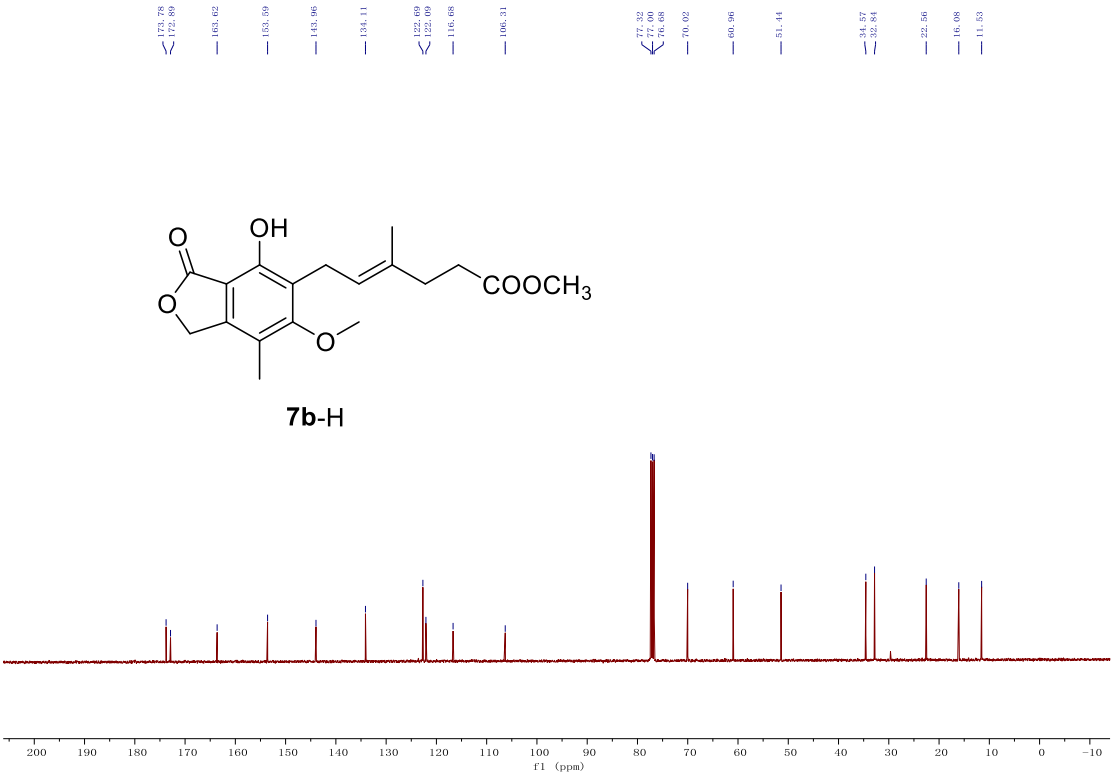

O
OH
O
O
COOCD3

7b


180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

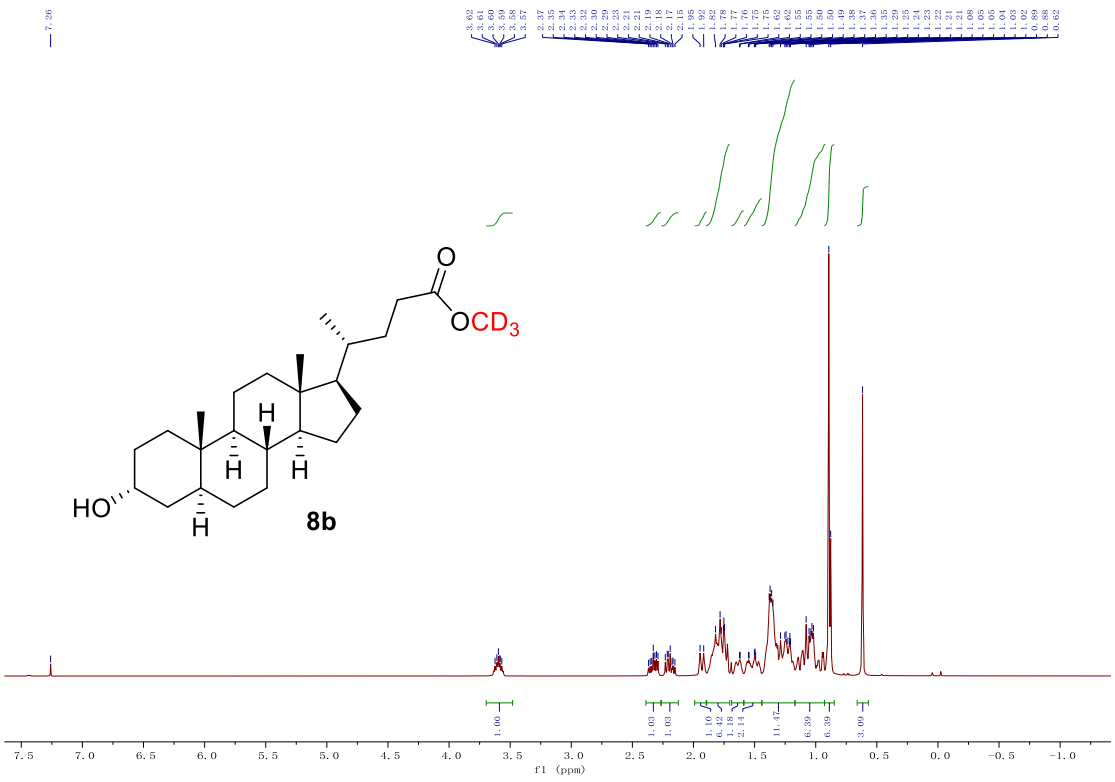

7.65
7.26
5.23
5.23
5.22
5.21
5.21
5.21
5.20
5.19
5.17
3.74
3.59
3.37
3.35
2.40
2.40
2.38
2.38
2.38
2.38
2.37
2.36
2.35
2.31
2.29
2.28
2.27
2.26
2.13
1.78
OH
O
O
O
COOCH3
1.00
1.01
2.00
3.24
3.24
2.17
2.21
2.24
3.07
3.29
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)

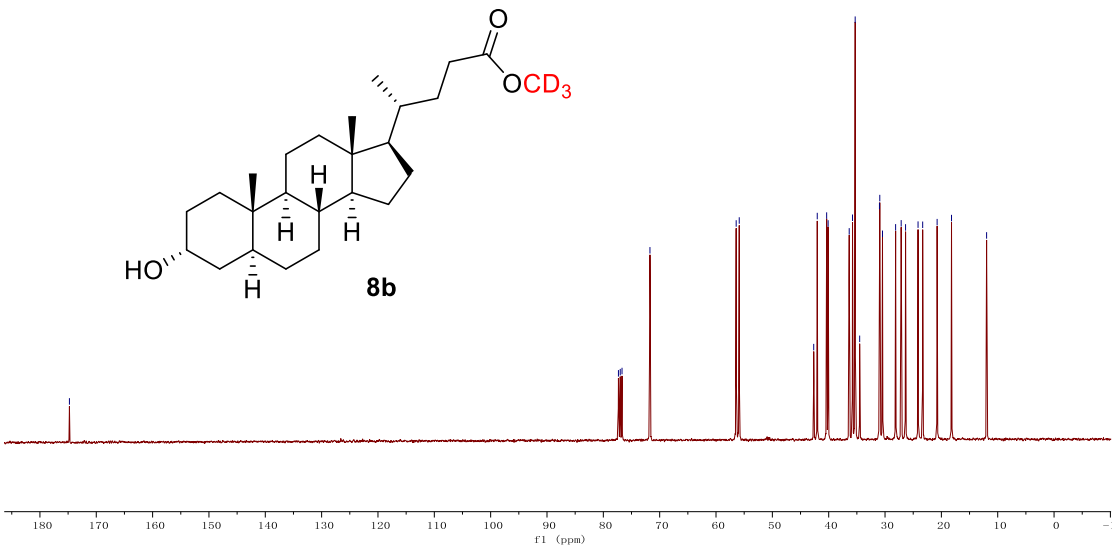
7b-H

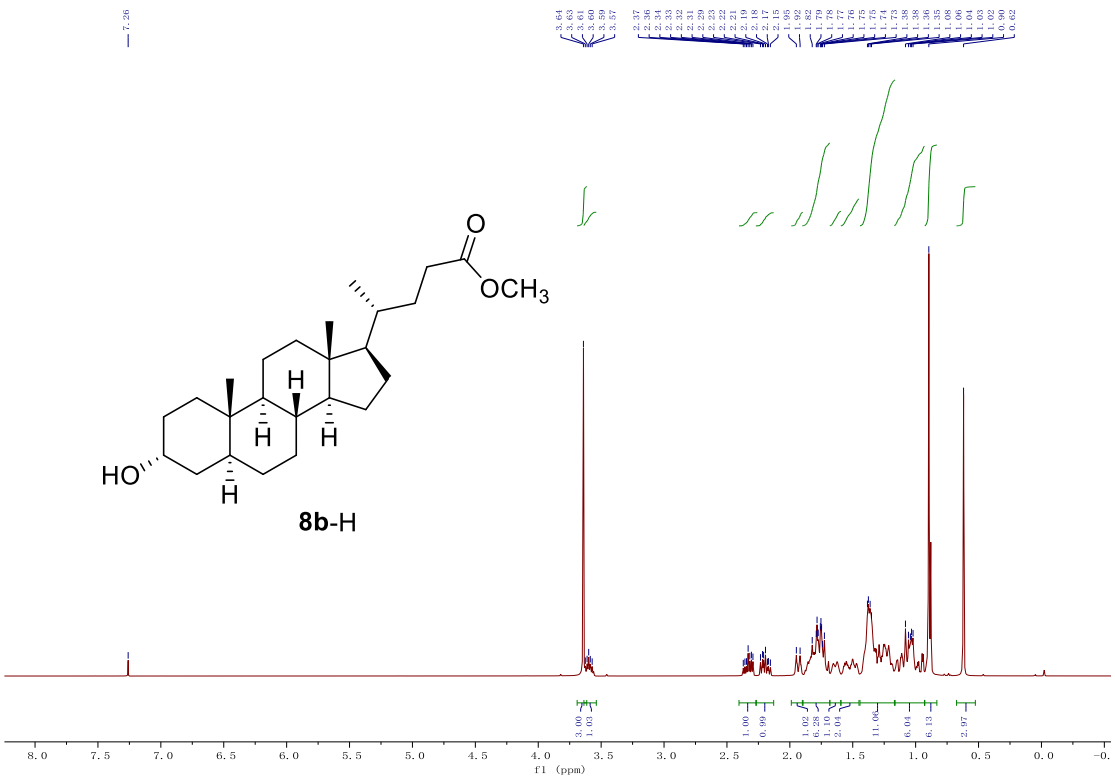

173.78
172.89
163.62
153.59
143.96
134.11
122.69
122.09
116.68
106.31
77.32
77.00
76.68
70.02
60.96
51.44
34.57
32.84
22.56
16.08
11.53
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

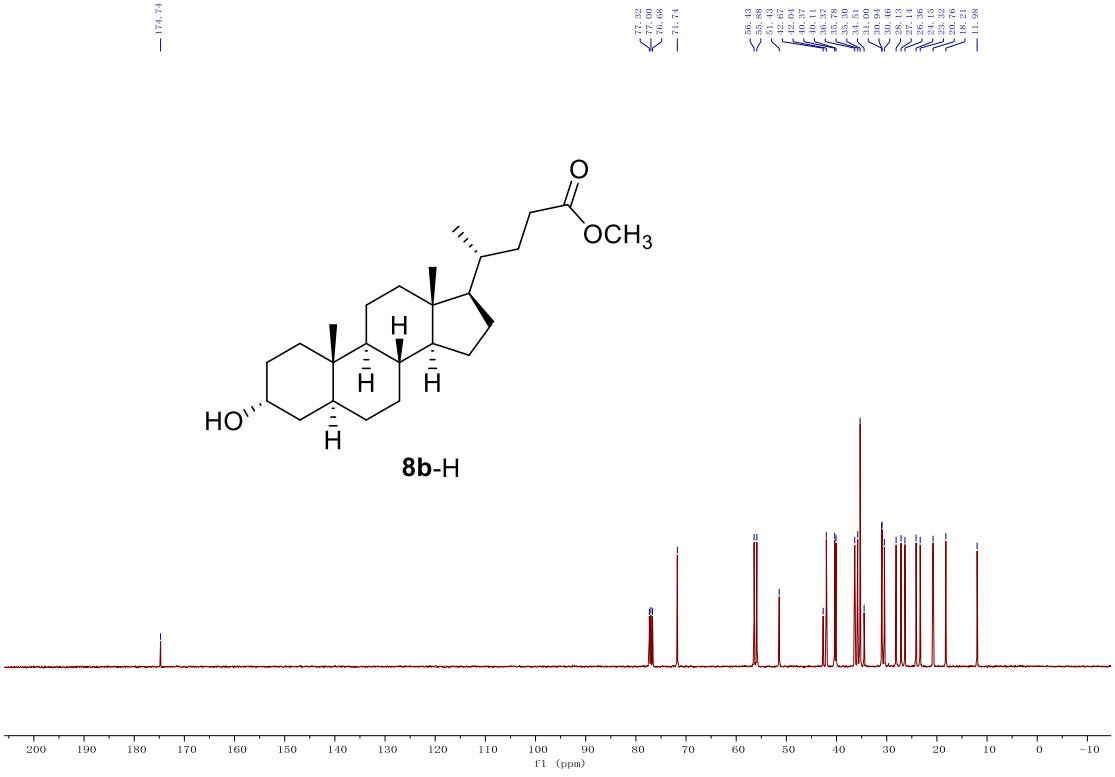
O
OH
O
O
COOCH3

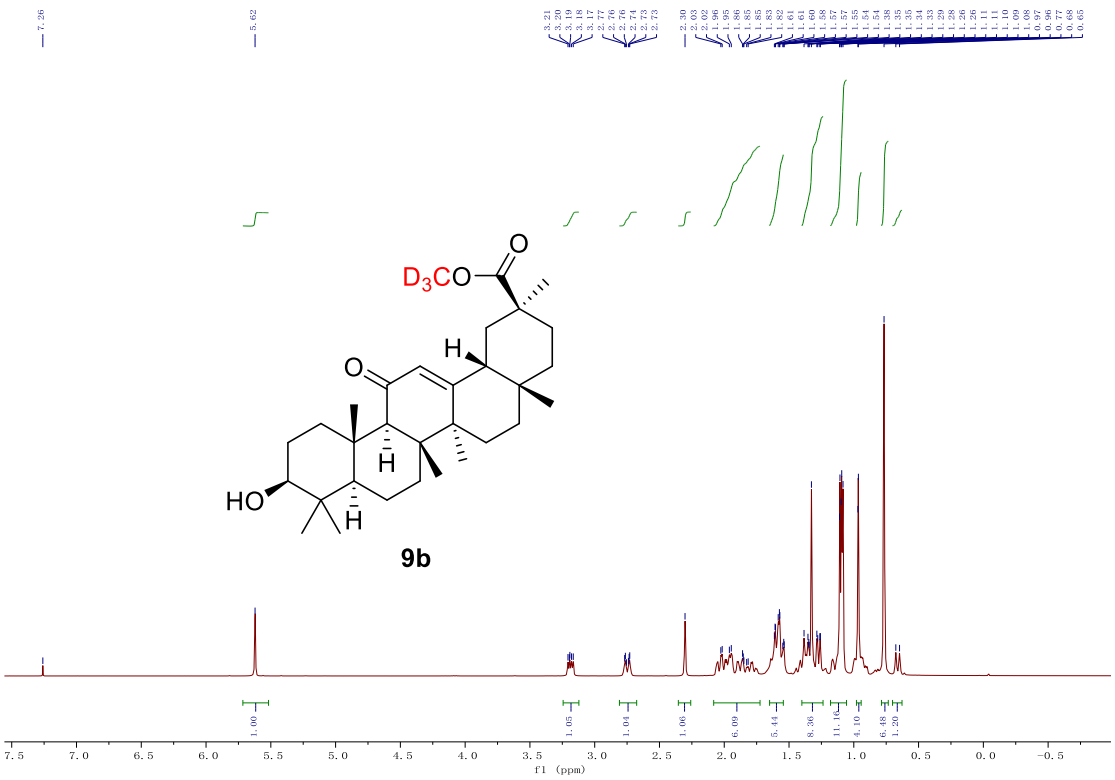
7b-H

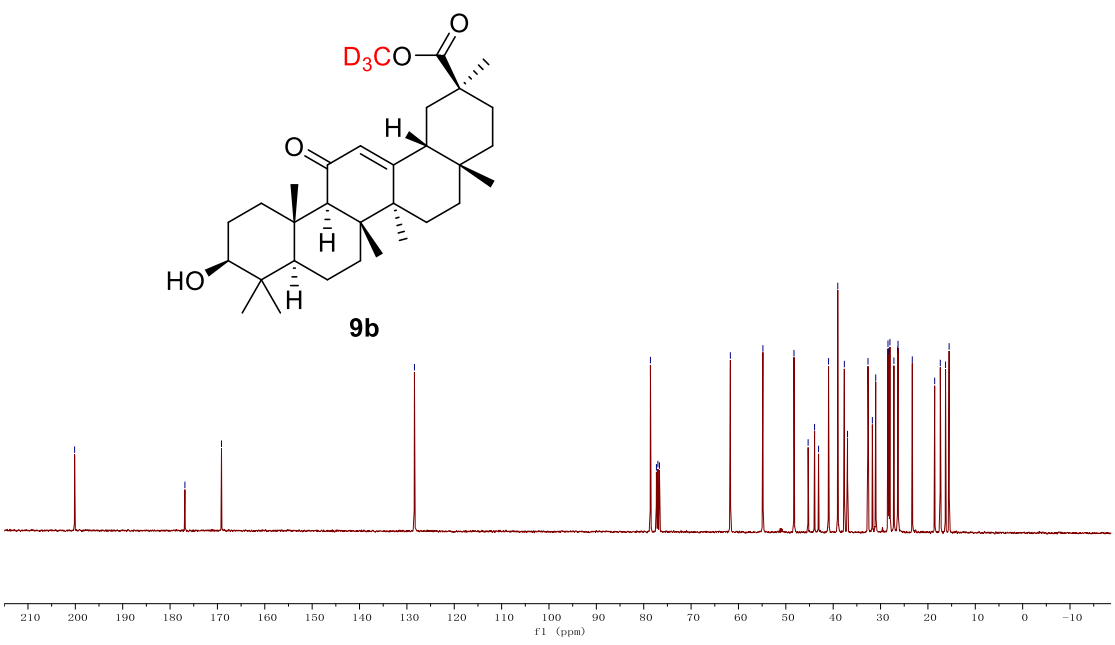

O
OCD3
H
H
H
HO
H
8b
7.26
3.62
3.61
3.60
3.59
3.58
3.57
2.37
2.35
2.34
2.33
2.32
2.30
2.29
2.25
2.21
2.19
2.18
2.17
2.15
1.95
1.92
1.82
1.78
1.77
1.76
1.75
1.62
1.60
1.55
1.50
1.49
1.48
1.38
1.37
1.36
1.35
1.29
1.25
1.24
1.23
1.22
1.21
1.21
1.08
1.07
1.05
1.04
1.03
1.02
0.89
0.88
0.62
1.00
1.03
1.03
1.10
6.42
1.18
2.14
11.47
6.39
6.39
3.09
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
−1.0
f1 (ppm)

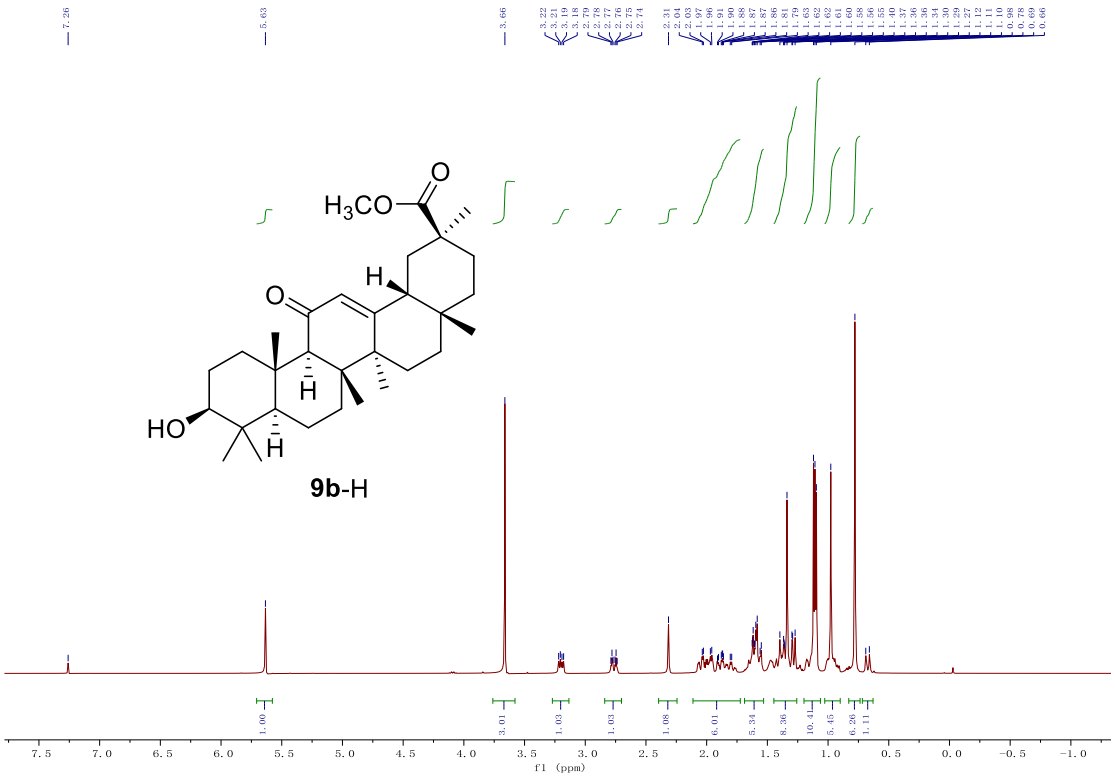

O
OCD3
H
H
H
HO
H
8b
174.76
77.32
77.00
76.68
71.72
56.42
55.88
42.68
42.03
41.36
40.10
36.36
35.77
35.50
34.50
30.99
30.93
30.45
28.12
27.14
26.36
24.14
23.32
20.76
18.20
11.97
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

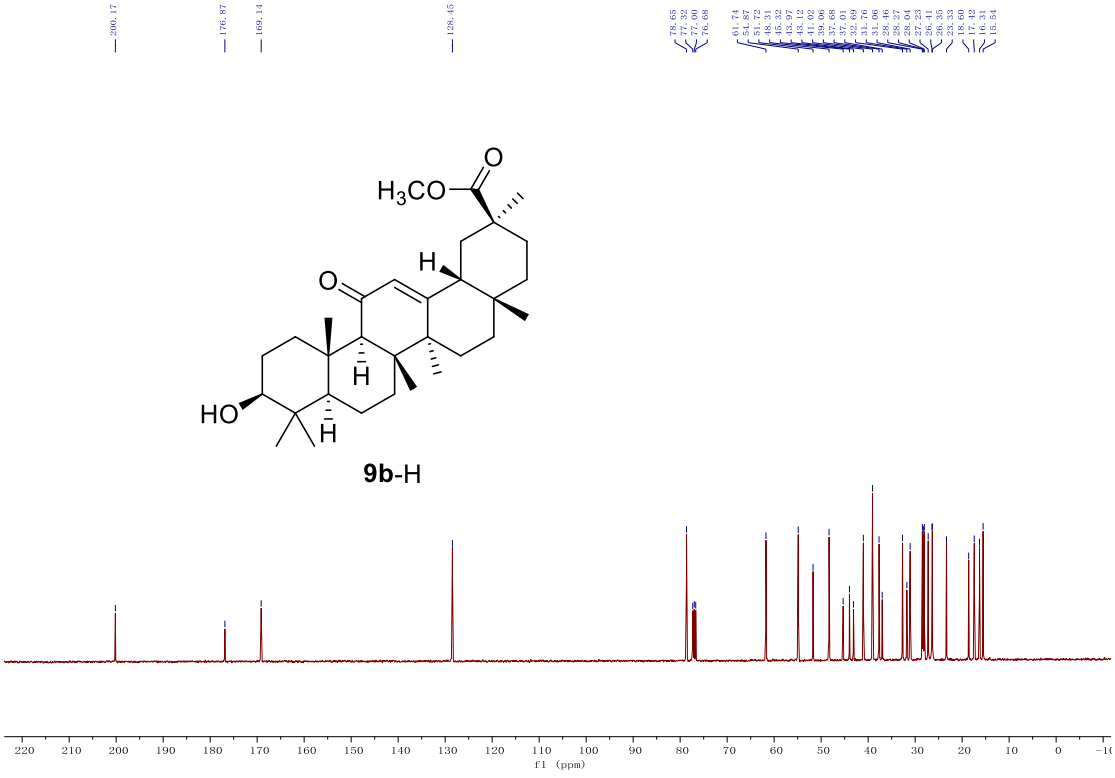

O
OCH3
H
H
H
HO
H
8b-H
f1 (ppm)

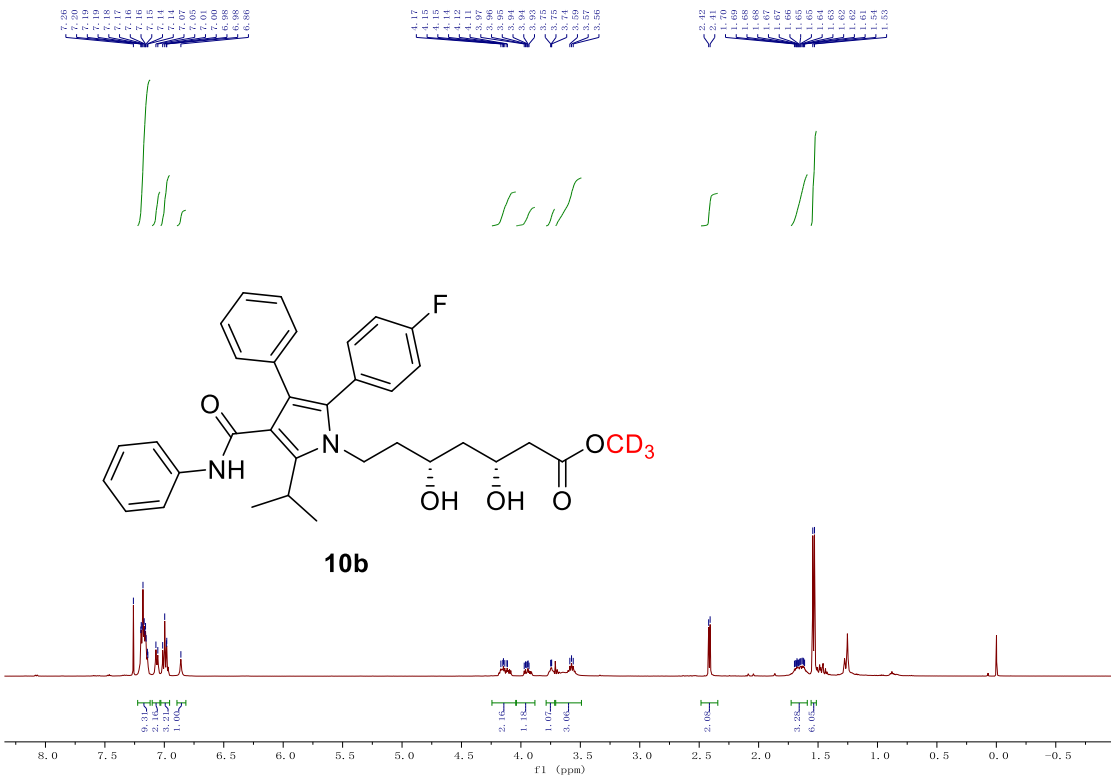

O
OCH3
H
H
H
HO
H
8b-H
f1 (ppm)

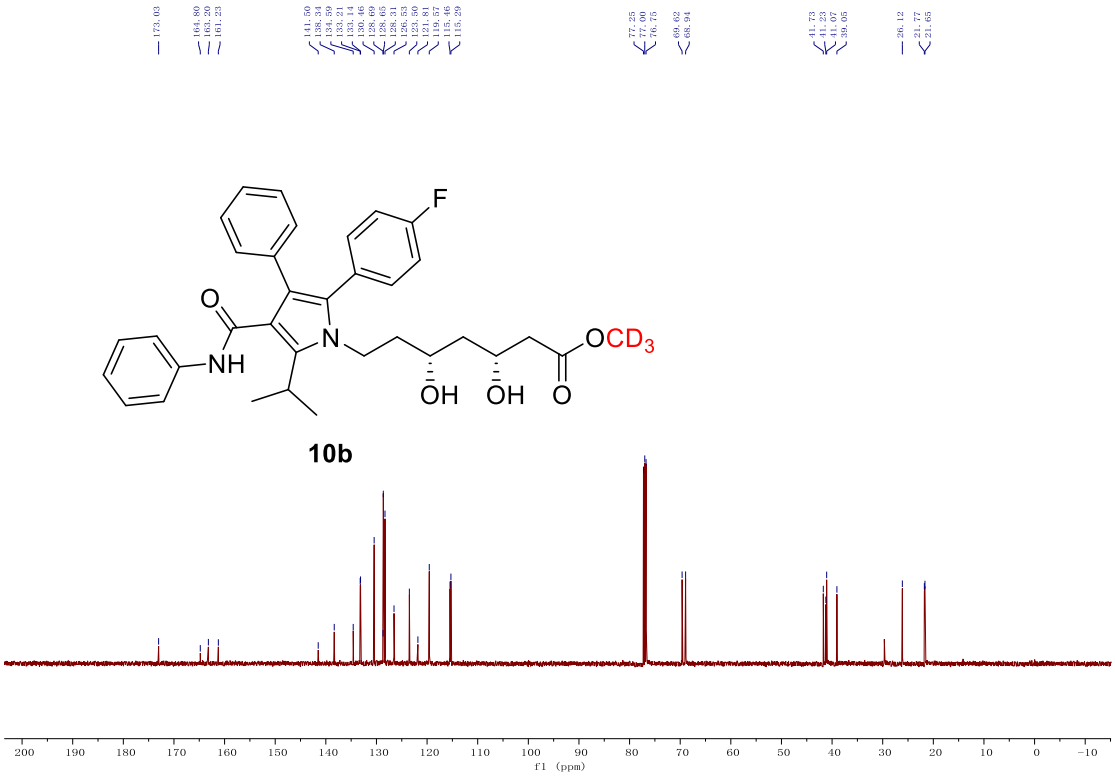

D3CO
O
H
O
H
HO
H
9b
f1 (ppm)

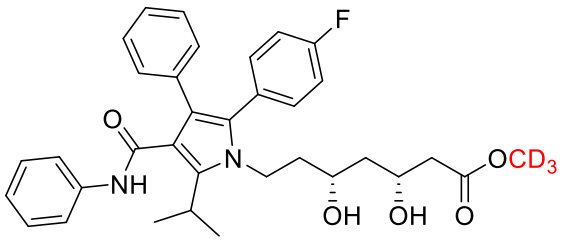

D3CO
O
H
O
H
HO
H
9b
f1 (ppm)


7.26
5.63
3.66
3.22
3.21
3.19
3.18
2.79
2.78
2.77
2.76
2.75
2.74
2.31
2.04
2.03
1.97
1.96
1.91
1.90
1.88
1.87
1.86
1.85
1.79
1.63
1.62
1.62
1.61
1.60
1.58
1.56
1.55
1.40
1.37
1.36
1.36
1.34
1.30
1.29
1.27
1.12
1.11
1.10
1.08
0.78
0.69
0.66
H3CO
O
H
O
H
HO
H
9b-H
1.00
3.01
1.03
1.03
1.08
6.01
5.34
8.36
10.44
5.45
6.26
1.11
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
−1.0
f1 (ppm)


200.17
176.87
169.14
128.45
78.65
77.32
77.00
76.68
61.74
54.87
53.72
48.31
45.32
43.97
43.12
41.02
39.06
37.68
37.01
32.60
31.76
31.06
28.46
28.37
28.04
27.23
26.41
26.35
23.33
18.60
17.42
16.71
15.54
H3CO
O
H
O
H
HO
H
9b-H
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

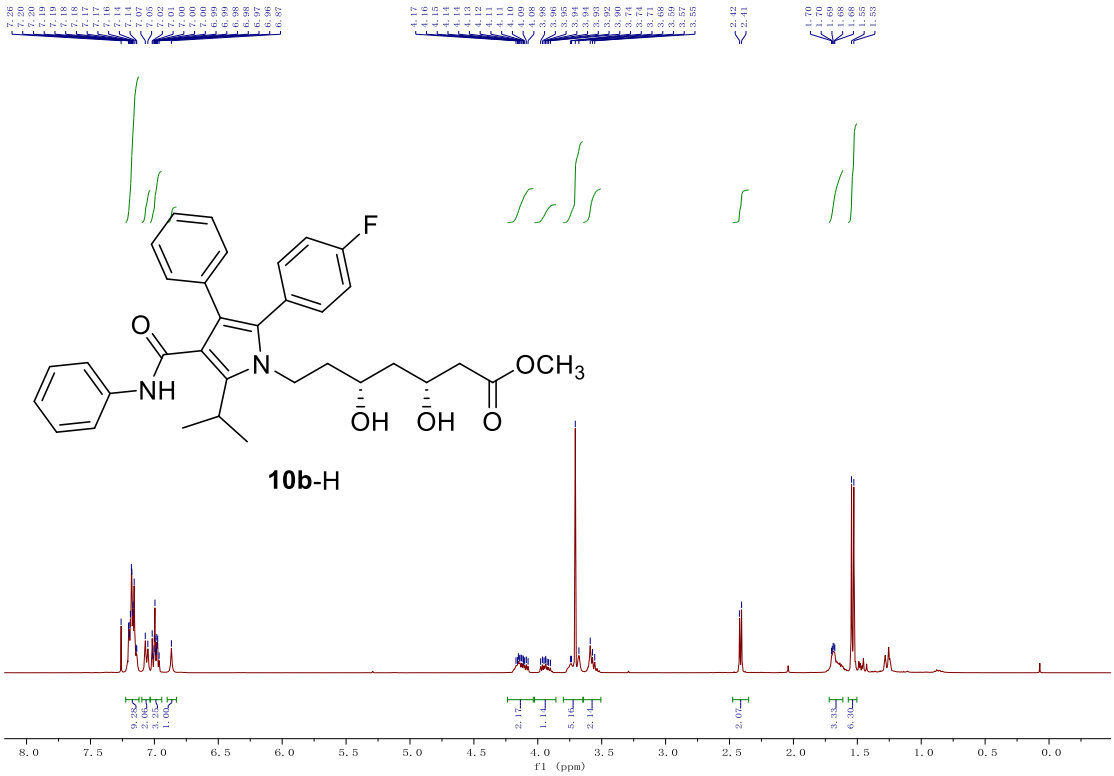

F
O
N
NH
OCD3
OH
OH
O
10b
f1 (ppm)


F
O
N
NH
OCD3
OH
OH
O
10b
f1 (ppm)


F
O
NH
N
OCD3
OH
OH
O

10b

-113.53
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
f1 (ppm)


7.26
7.20
7.20
7.19
7.18
7.18
7.17
7.17
7.16
7.14
7.14
7.07
7.05
7.02
7.01
7.00
7.00
6.99
6.98
6.98
6.97
6.96
6.87
4.17
4.16
4.15
4.14
4.14
4.13
4.12
4.11
4.11
4.10
4.09
4.08
3.98
3.96
3.95
3.94
3.94
3.93
3.92
3.90
3.74
3.71
3.68
3.59
3.57
3.55
2.42
2.41
1.70
1.70
1.69
1.68
1.68
1.55
1.53
9.28
2.06
2.05
1.00
2.17
1.14
5.16
2.14
2.07
3.33
6.30
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)

F
O
NH
N
OCH3
OH
OH
O

10b-H

172.97
164.82
163.43
160.97
141.47
138.31
134.57
133.20
133.12
130.43
128.69
128.64
128.30
126.52
123.51
121.90
119.57
115.47
115.26
77.32
77.00
76.68
69.60
68.90
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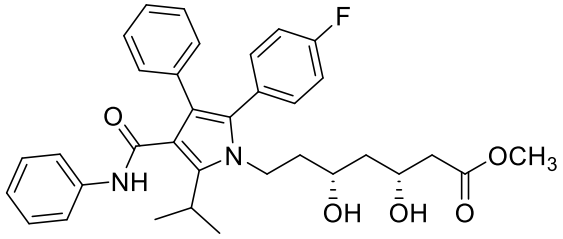
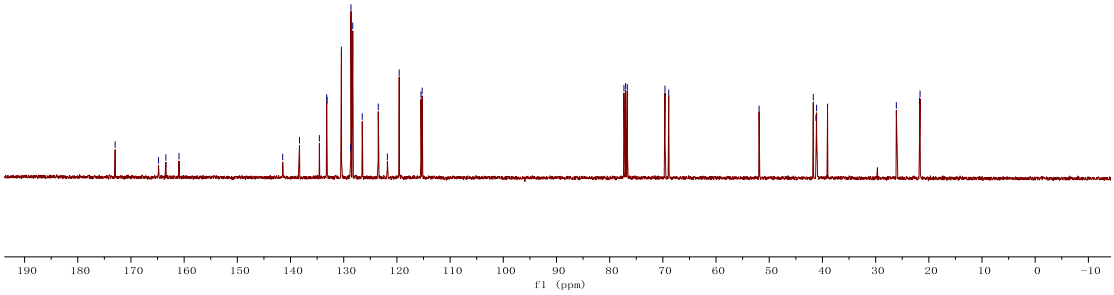
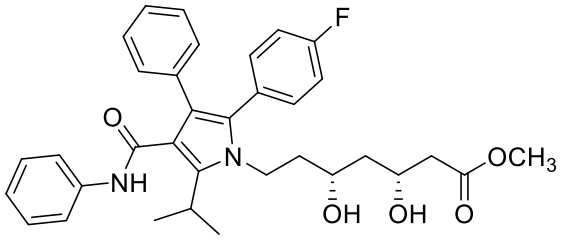
41.72
41.22
41.10
39.04
26.10
21.76
21.65



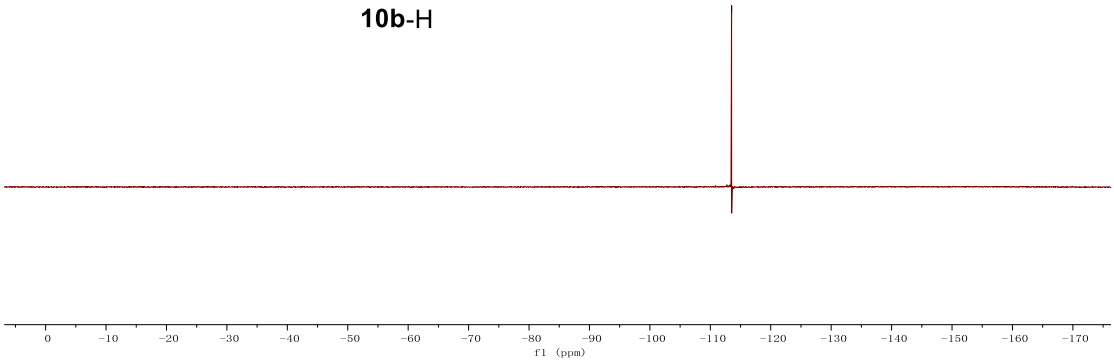
10b-H

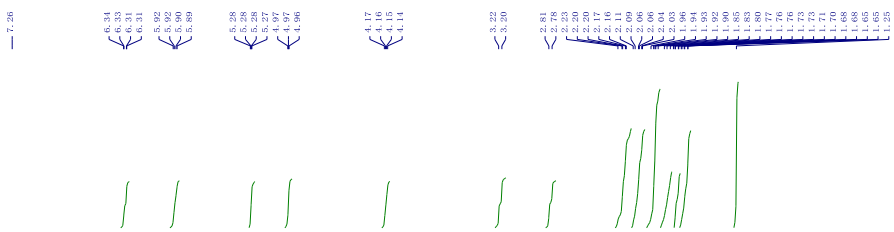


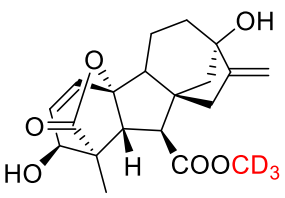
−113.62



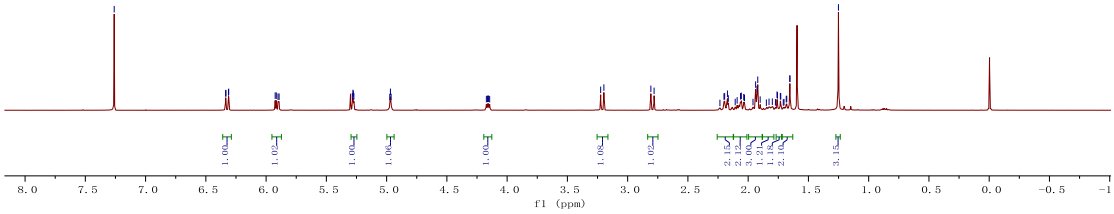
10b-H

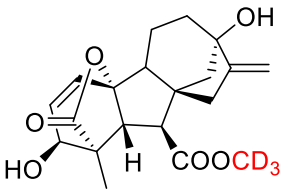




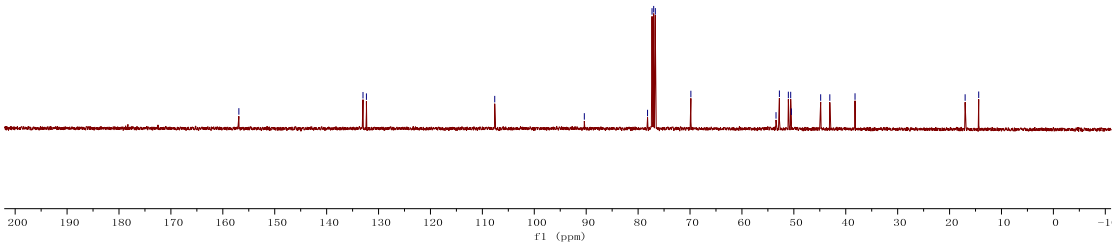


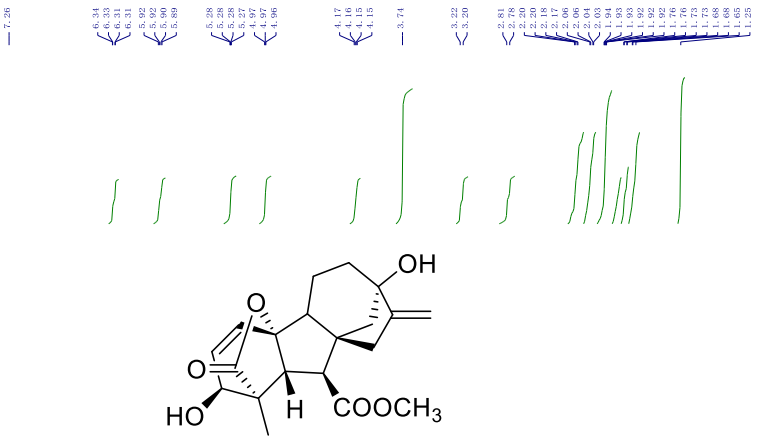
11b





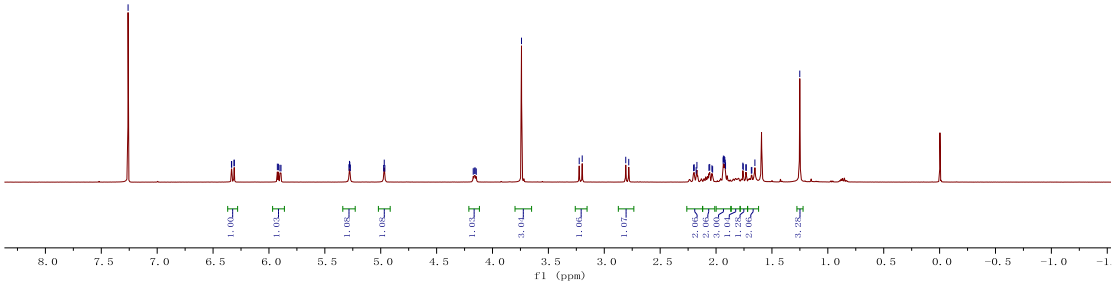
11b



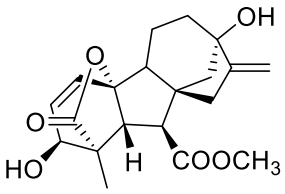

7.26
6.34
6.33
6.31
6.31
5.92
5.92
5.89
5.89
5.28
5.28
5.28
5.27
4.97
4.97
4.96
4.17
4.16
4.15
4.15
3.74
3.22
3.20
2.81
2.78
2.29
2.20
2.18
2.17
2.06
2.06
2.04
2.03
1.94
1.93
1.92
1.92
1.92
1.76
1.76
1.73
1.73
1.68
1.68
1.65
1.25

OH
O
O
HO
H
COOCH3

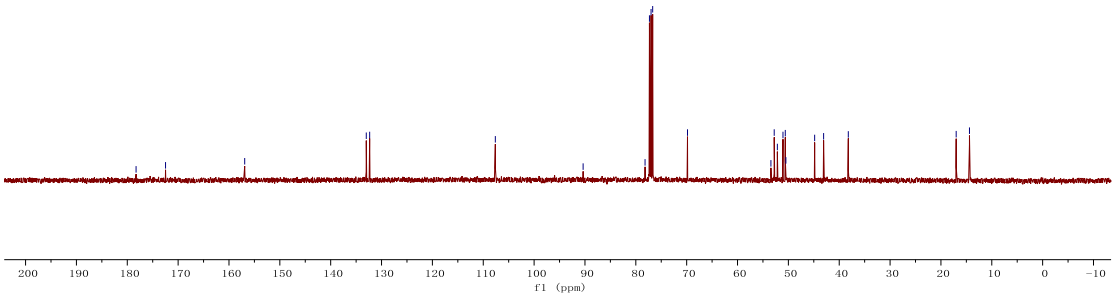
11b-H

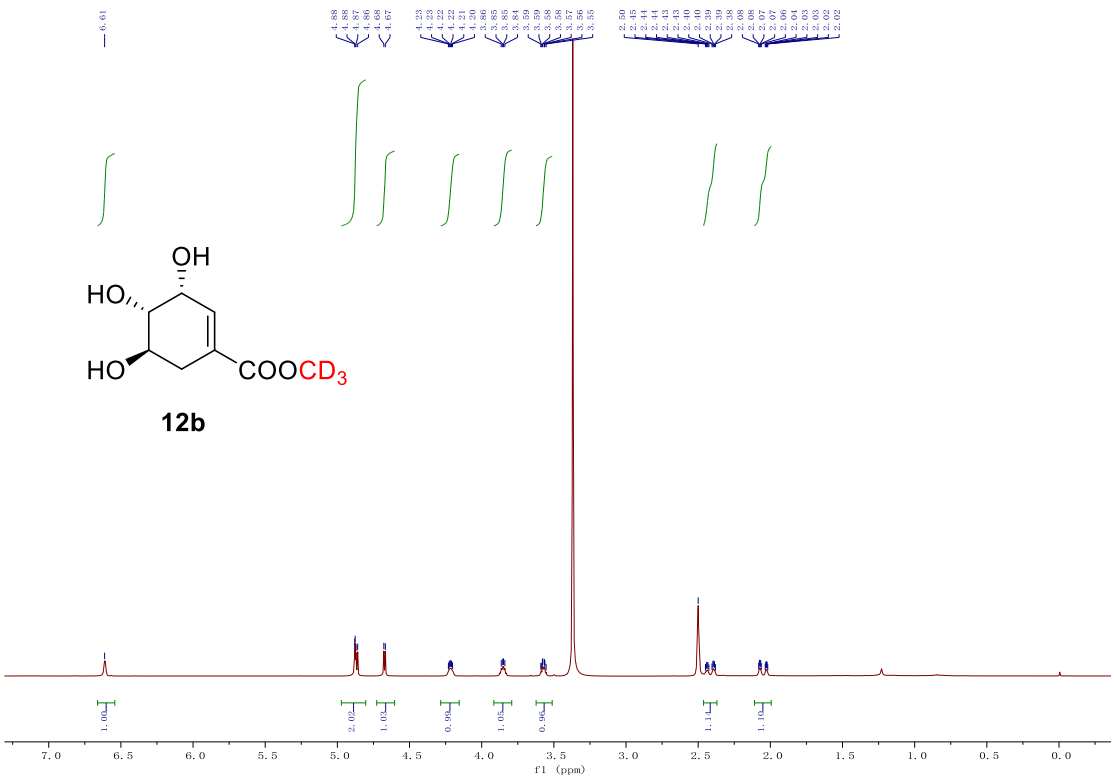

1.00
1.03
1.05
1.05
1.03
3.04
1.06
1.07
2.06
2.06
3.00
3.04
1.28
2.06
3.28
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

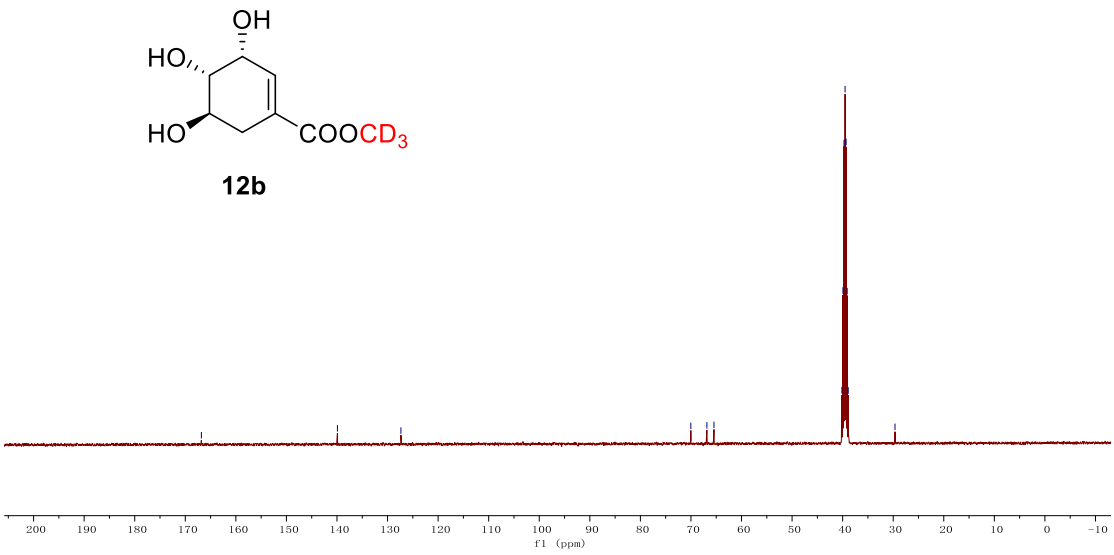

178.27
172.48
156.91
133.00
132.34
107.63
90.36
78.18
77.32
77.00
76.68
69.84
53.43
52.78
52.17
51.06
50.61
50.49
44.85
43.07
38.21
17.00
14.39

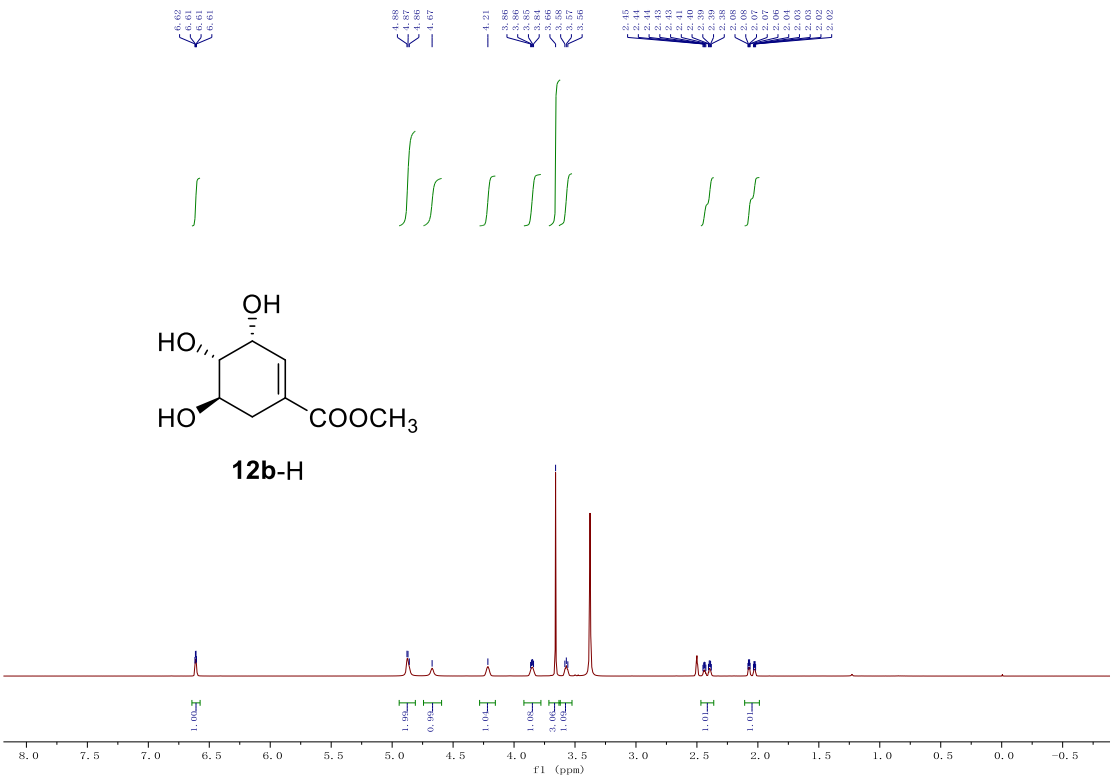

OH
O
O
HO
H
COOCH3

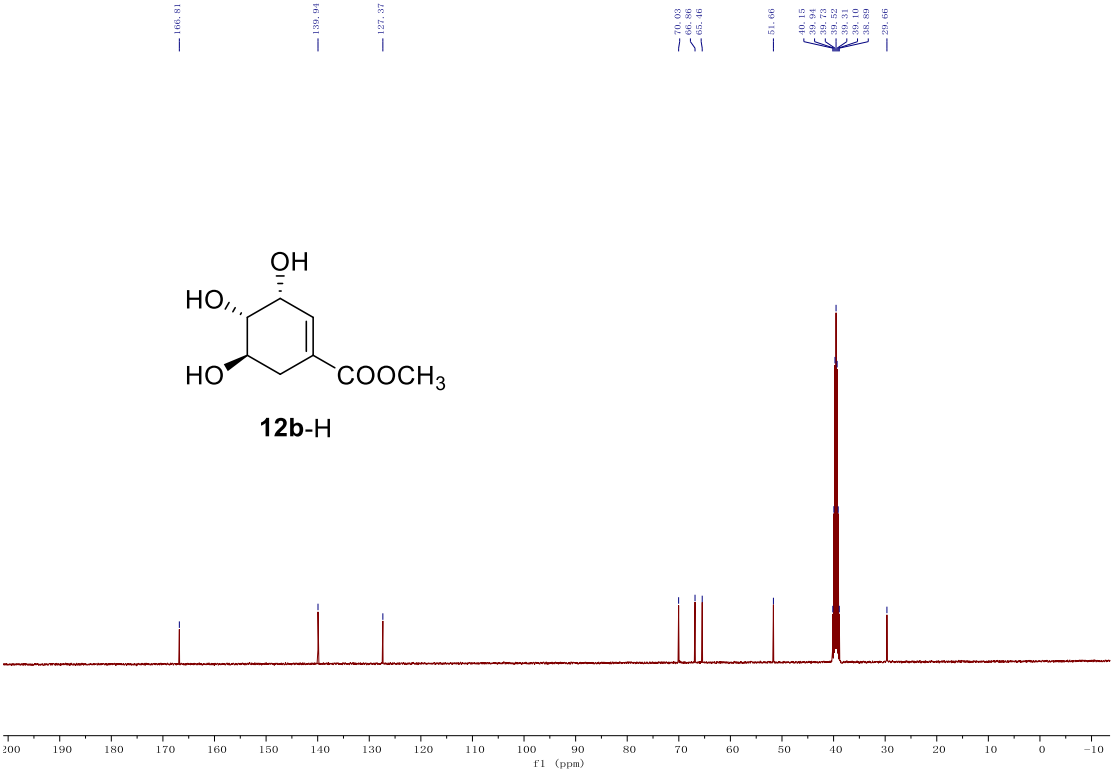
11b-H

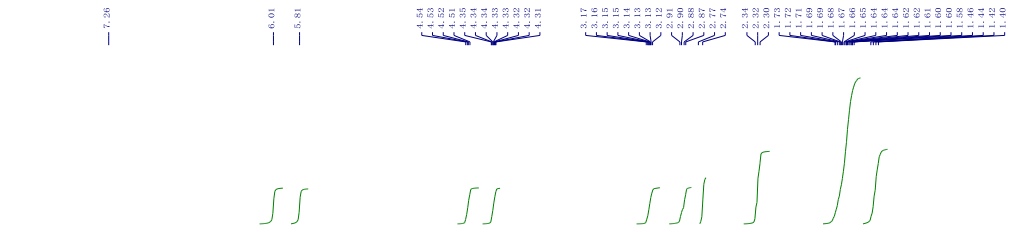

200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

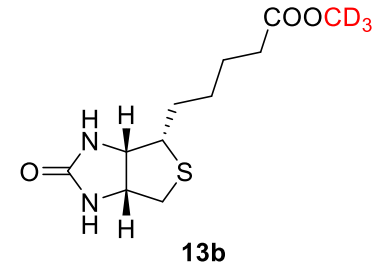

OH
HO
HO
COOCD3
12b
f1 (ppm)


OH
HO
HO
COOCD3
12b
f1 (ppm)

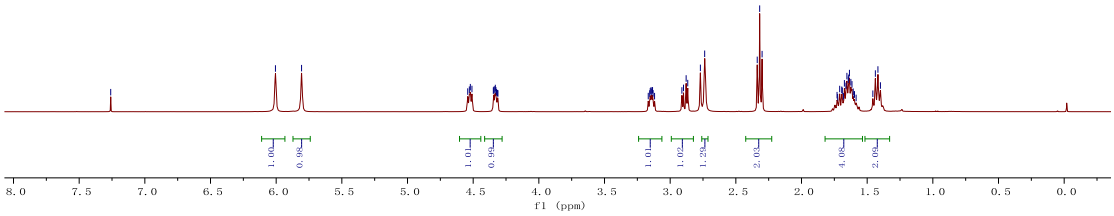

OH
HO
HO
COOCH3
12b-H
f1 (ppm)

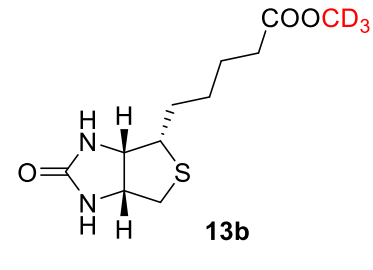

OH
HO
HO
COOCH3
12b-H
f1 (ppm)



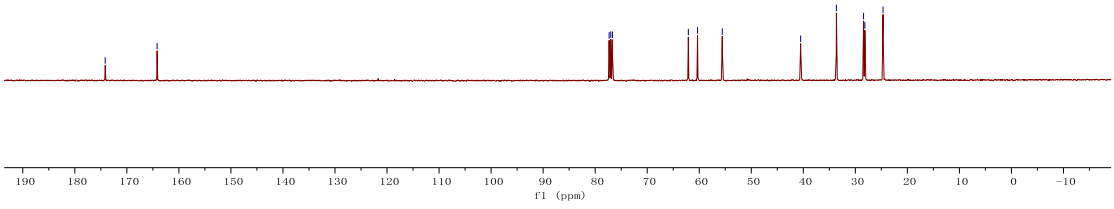

COOCD3
H
H
N
O
S
N
H
H

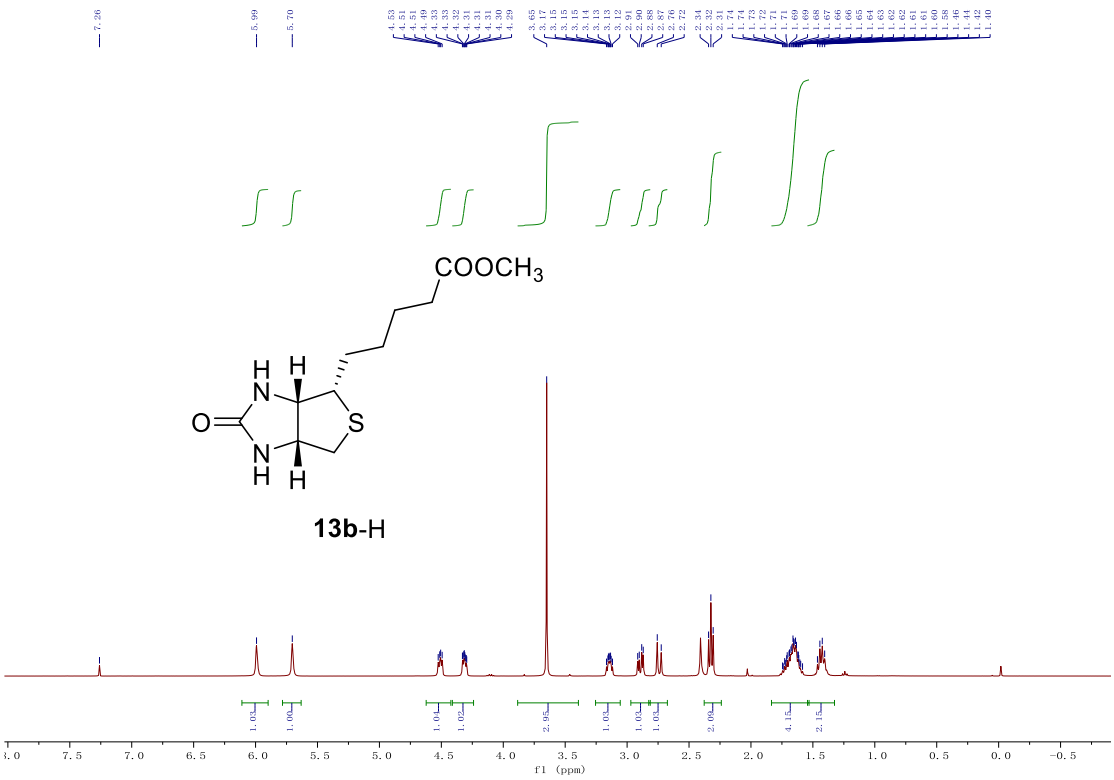
13b


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)

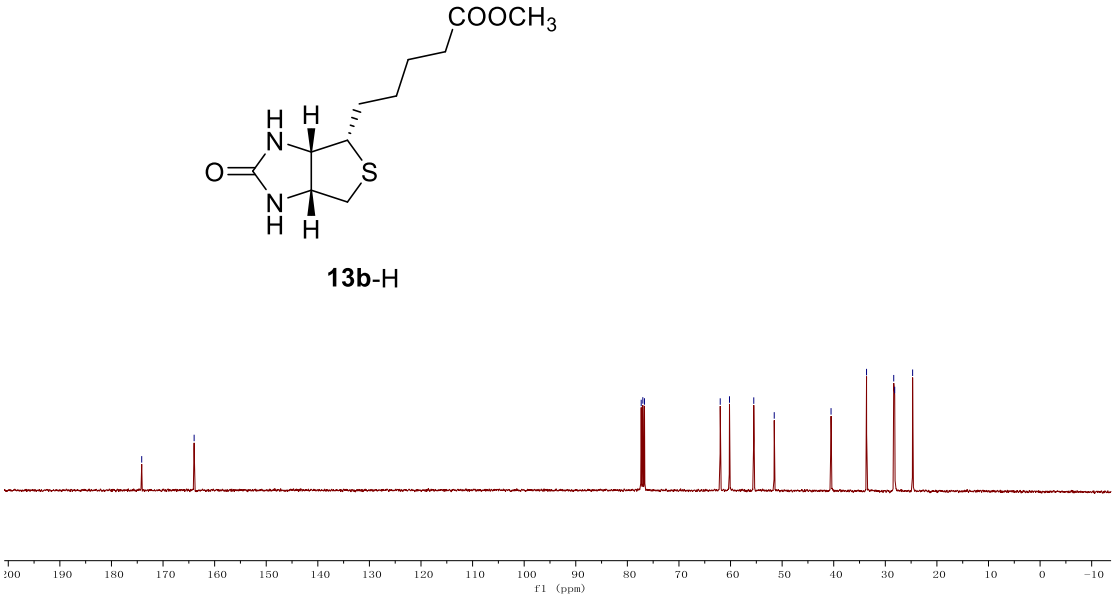

COOCD3
H
H
N
O
S
N
H
H

13b

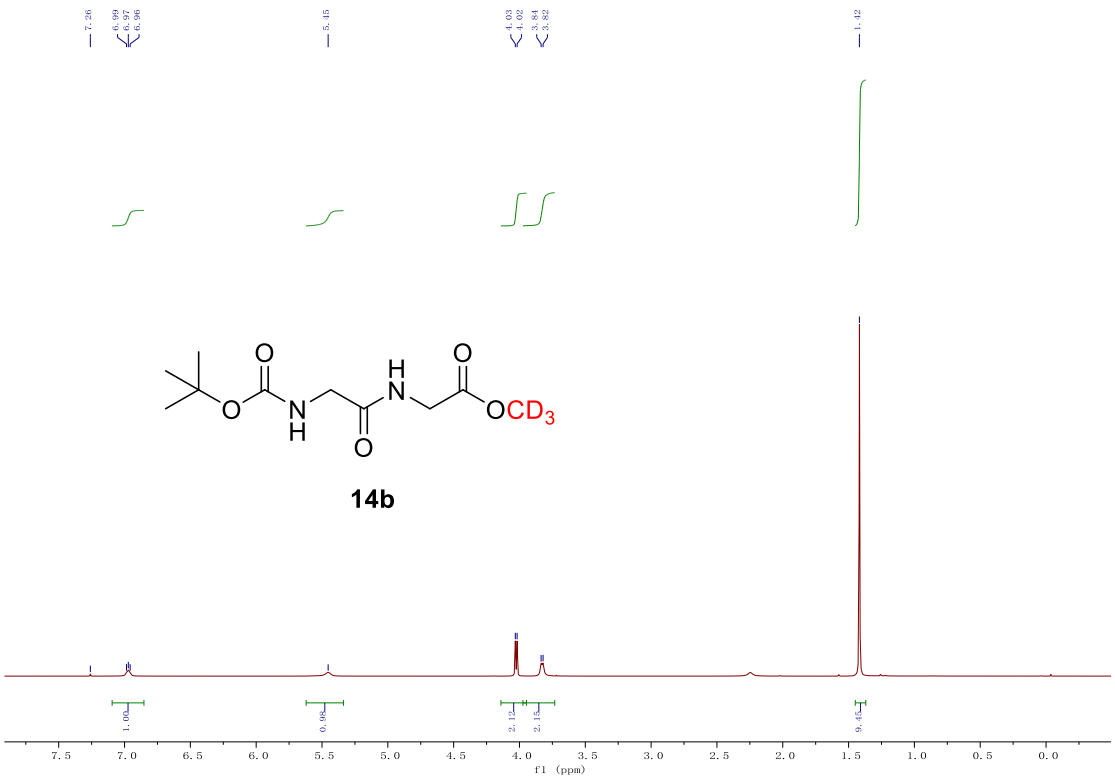

190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)



13b-H

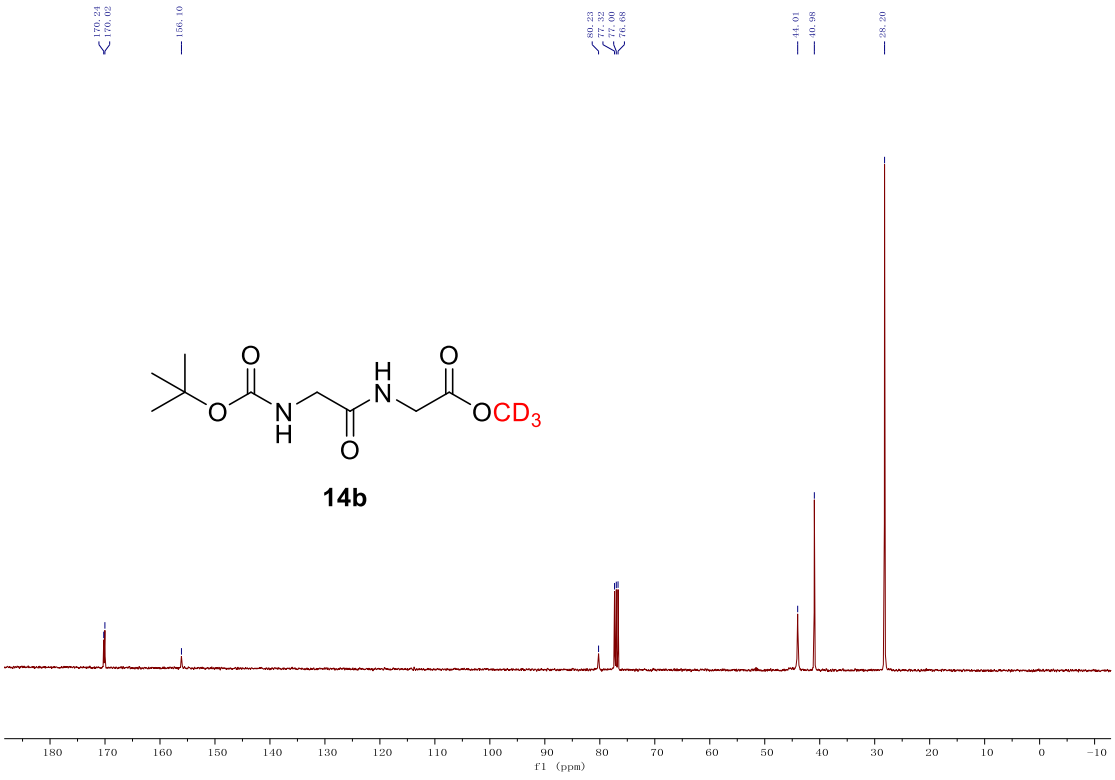


13b-H


7.26
6.99
6.97
6.96
5.45
4.03
4.02
3.84
3.82
1.42
1.00
0.98
2.12
2.18
9.48
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)

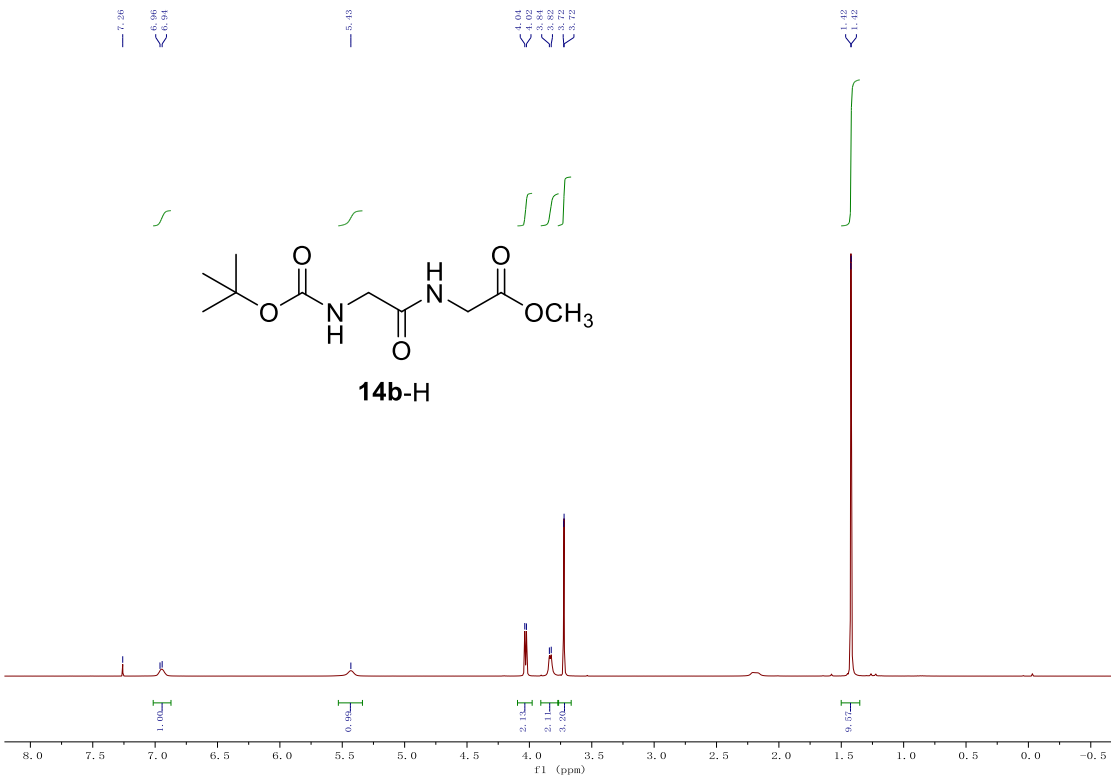
O
O
N
H
H
N
O
O
OCD3

14b

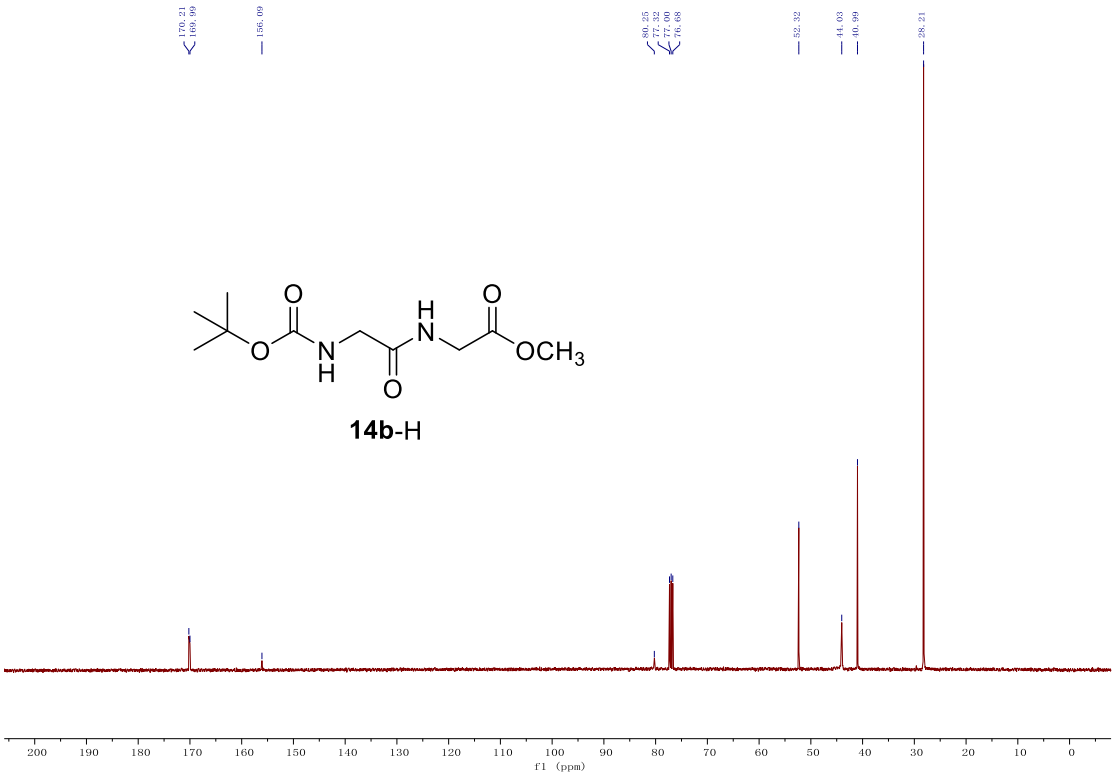

170.24
170.02
166.10
80.23
77.32
77.00
76.68
44.01
40.98
28.20
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

O
O
N
H
H
N
O
O
OCD3

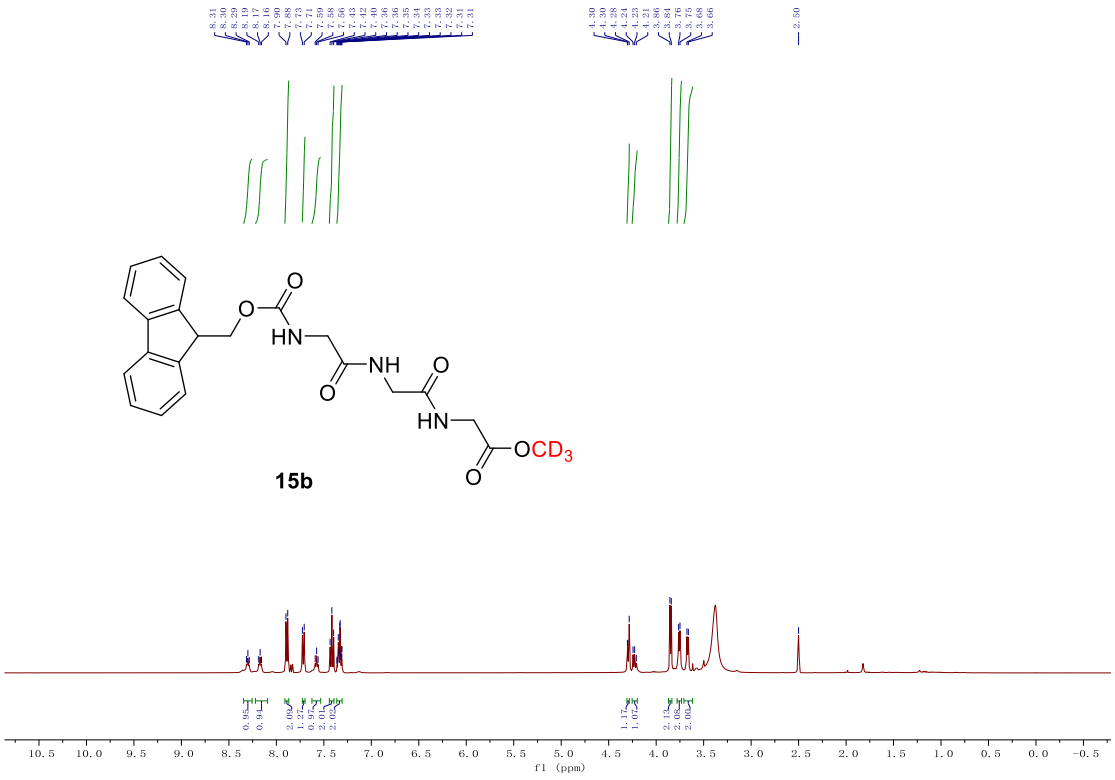
14b


7.26
6.96
6.94
5.43
4.04
4.02
3.84
3.82
3.72
3.72
1.42
1.42
1.00
0.96
2.17
2.11
3.26
9.57
f1 (ppm)

14b-H

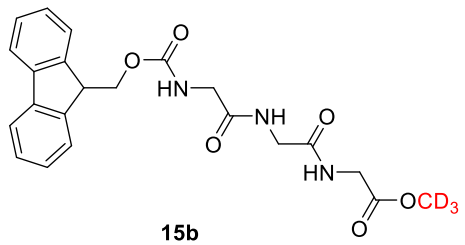

170.21
169.99
156.09
80.95
77.32
77.00
76.68
52.32
44.03
40.99
28.21
f1 (ppm)

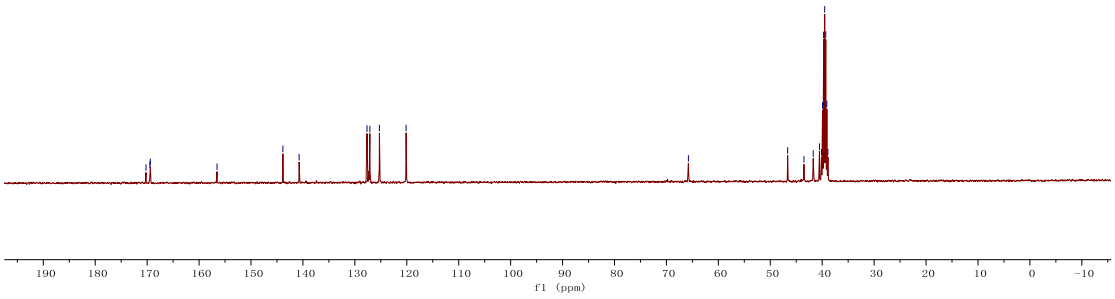
14b-H

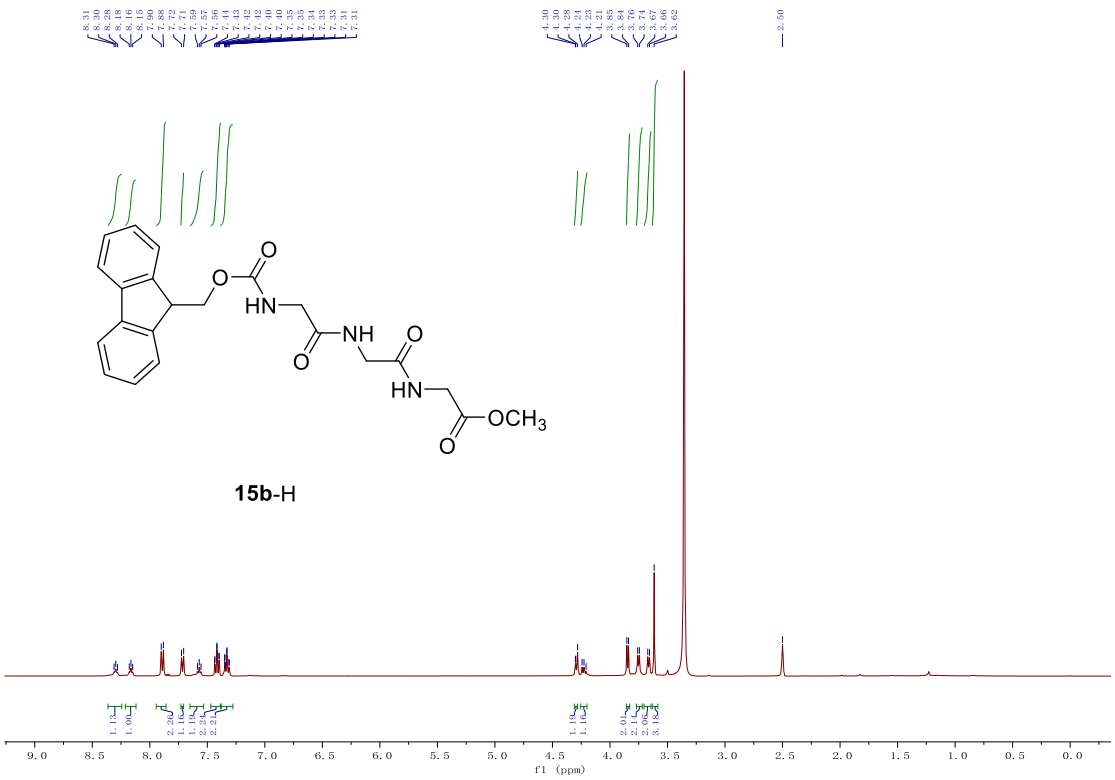

8.31
8.30
8.29
8.19
8.17
8.16
7.90
7.88
7.73
7.71
7.59
7.58
7.56
7.43
7.42
7.40
7.36
7.35
7.34
7.33
7.33
7.32
7.31
7.31
4.30
4.30
4.28
4.24
4.23
4.21
3.86
3.84
3.76
3.75
3.68
3.66
2.50
O
HN
O
NH
O
O
HN
OCD3
O
15b

0.99
0.94
2.09
1.27
0.97
2.04
2.02
1.17
1.07
2.13
2.08
2.00
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 -0.5
f1 (ppm)

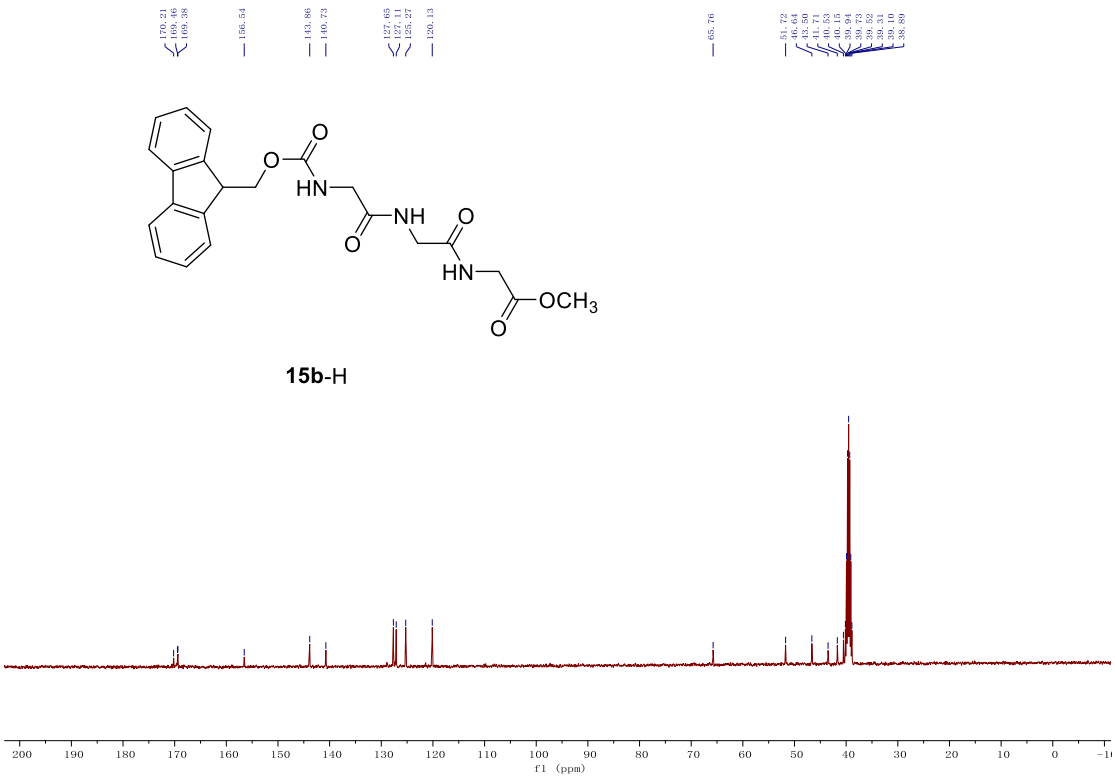

170.22
169.47
169.38
156.54
143.86
140.73
127.66
127.11
125.27
120.13
65.76
46.65
43.51
41.73
40.58
40.15
39.94
39.73
39.52
39.31
39.10
38.89


O
O
HN
NH
O
O
HN
OCD3
O
15b

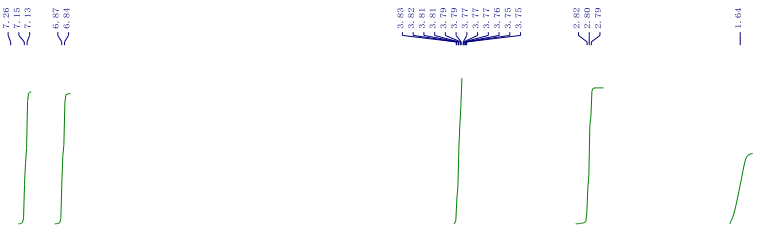

190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

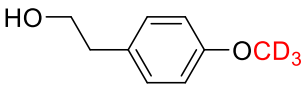

8.31
8.30
8.28
8.18
8.16
8.15
7.90
7.88
7.72
7.71
7.59
7.57
7.56
7.44
7.43
7.42
7.40
7.40
7.35
7.34
7.33
7.31
7.31
4.30
4.30
4.28
4.24
4.23
4.21
3.85
3.84
3.76
3.74
3.67
3.66
3.62
2.50
O
O
HN
NH
O
O
HN
OCH3
O
1.13
1.00
2.96
1.16
1.19
2.24
2.21
1.19
1.16
2.01
2.14
2.06
3.18
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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)

15b-H

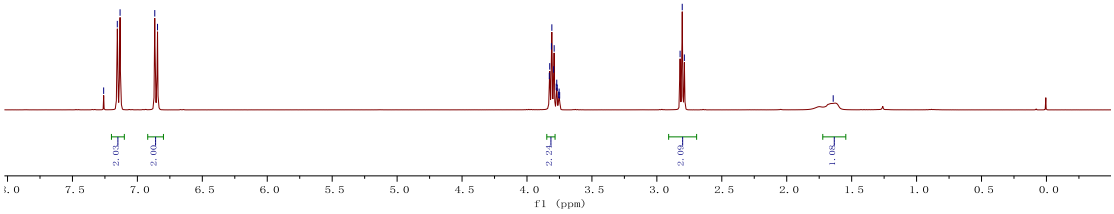

170.21
169.46
169.38
156.54
143.86
140.73
127.65
127.11
125.27
120.13
65.76
51.72
46.64
43.50
41.71
40.65
40.15
39.94
39.73
39.52
39.31
39.10
38.89
O
O
HN
NH
O
O
HN
OCH3
O
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

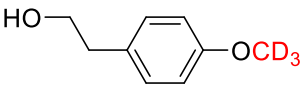
15b-H



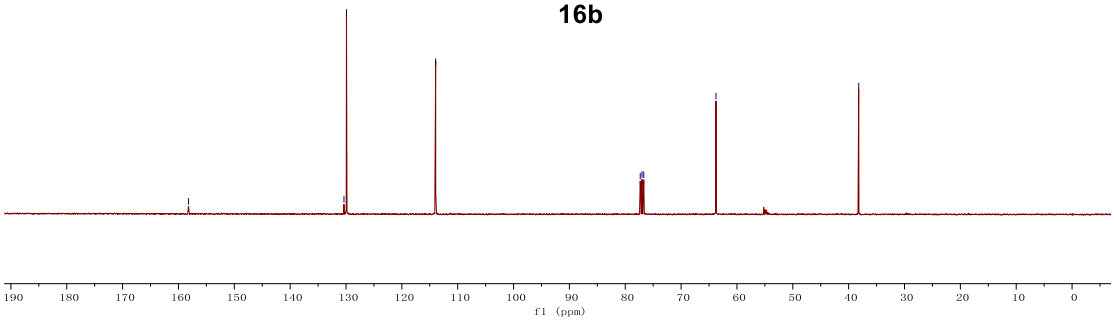


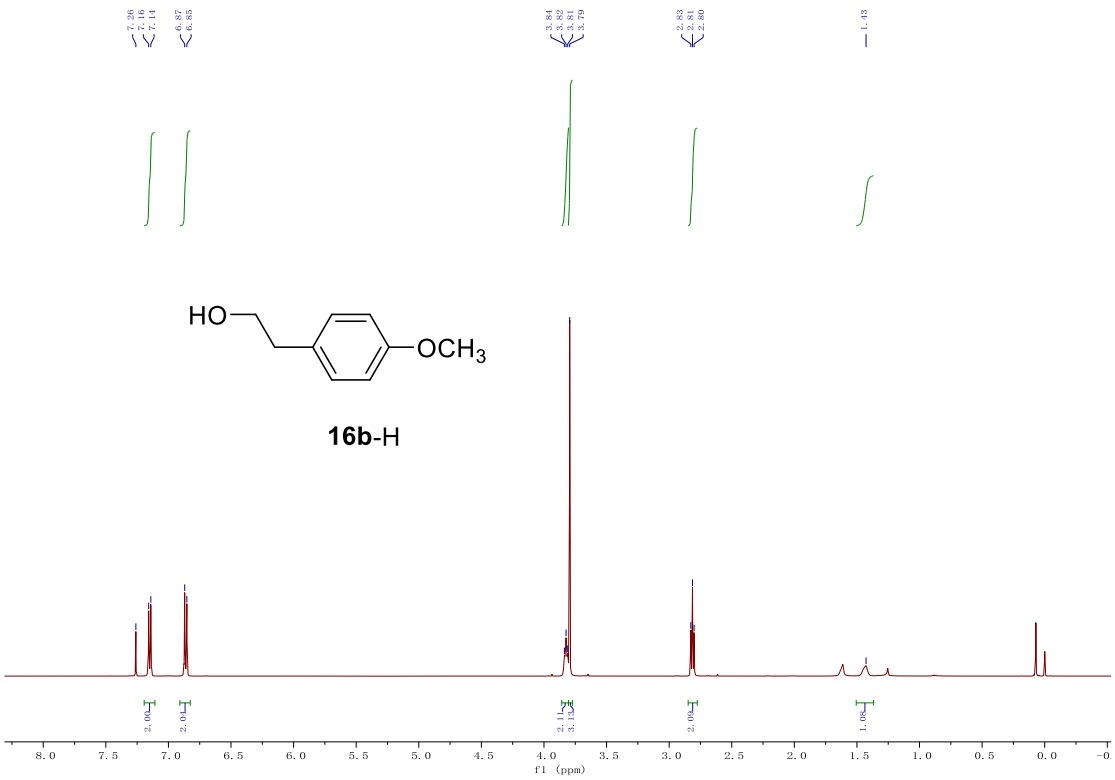
16b



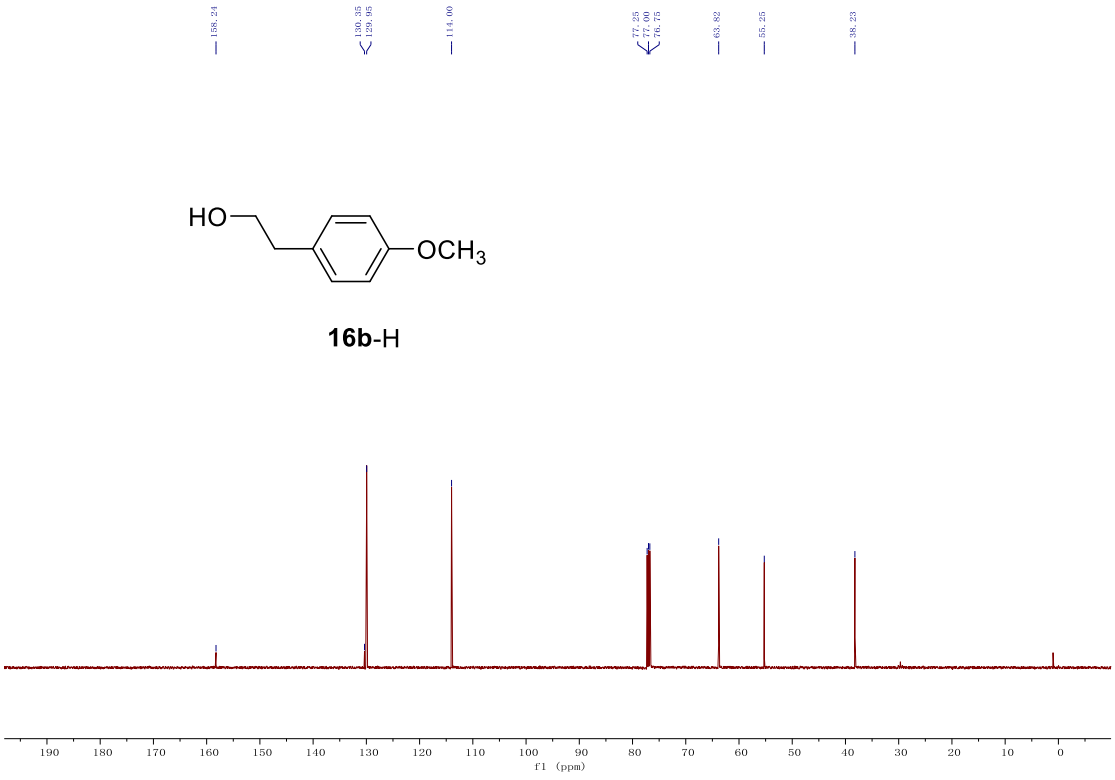


16b

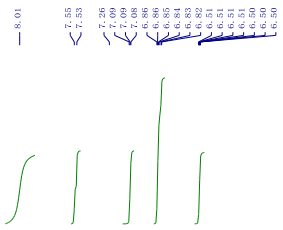


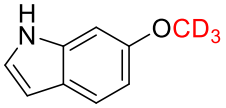

7.26
7.16
7.14
6.87
6.85
3.84
3.82
3.81
3.79
2.83
2.81
2.80
1.43
HO
OCH3
2.00
2.04
2.11
3.13
2.04
1.08
f1 (ppm)

16b-H

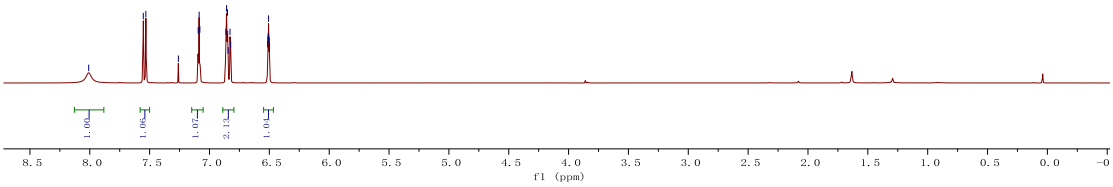

138.24
130.35
129.95
114.00
77.25
77.00
76.75
63.82
55.25
38.23
HO
OCH3
f1 (ppm)

16b-H

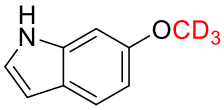

8.01
7.55
7.53
7.26
7.09
7.08
6.86
6.85
6.84
6.83
6.52
6.51
6.51
6.51
6.50
6.50


H
N
OCD3

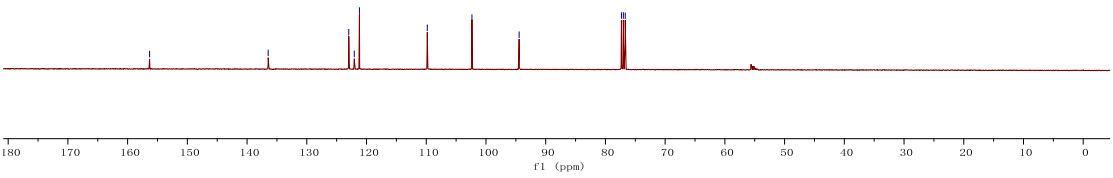
17b

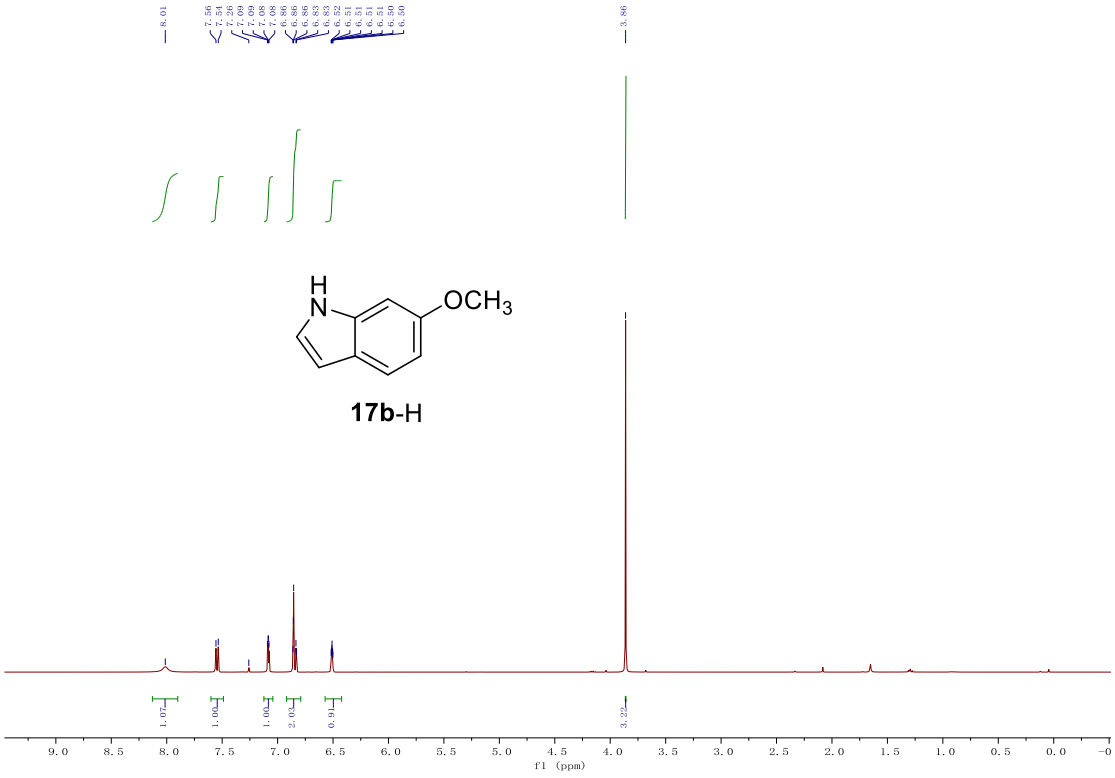

1.00
1.06
1.07
2.15
1.04
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


156.32
136.47
122.97
122.06
121.19
109.83
102.35
94.45
77.32
77.00
76.68


H
N
OCD3

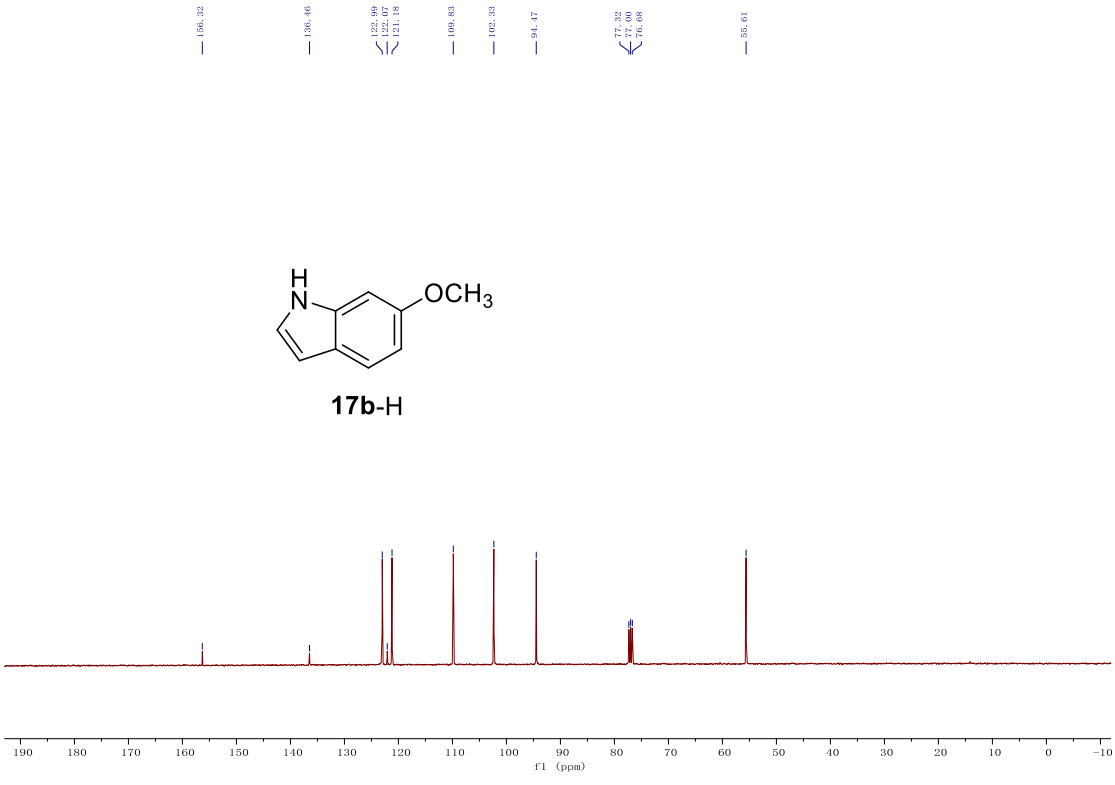
17b


180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.01
7.56
7.54
7.26
7.09
7.09
7.08
7.08
6.86
6.86
6.86
6.83
6.83
6.52
6.51
6.51
6.51
6.51
6.50
6.50
3.86
1.07
1.04
1.00
2.03
0.91
3.23
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 −0
f1 (ppm)

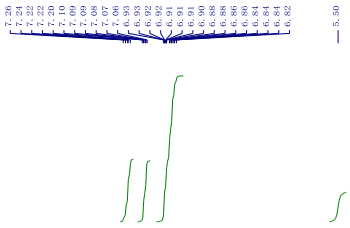
H
N
OCH3

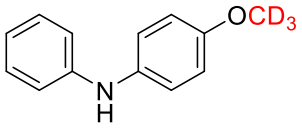
17b-H


156.32
136.46
122.99
122.07
121.18
109.83
102.33
94.47
77.32
77.00
76.68
55.61
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

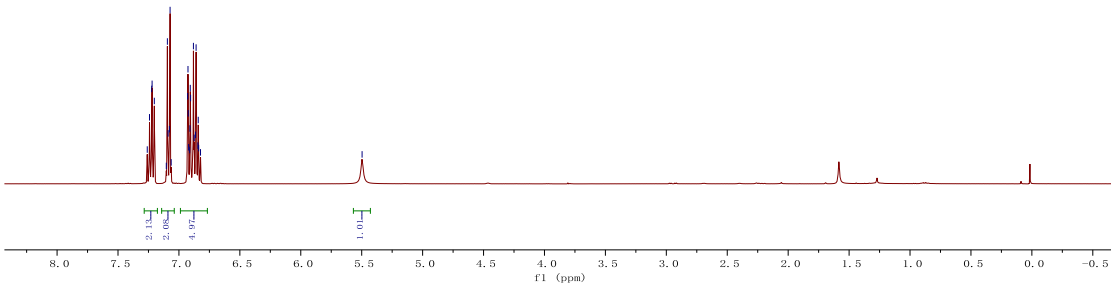
H
N
OCH3

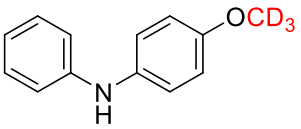
17b-H



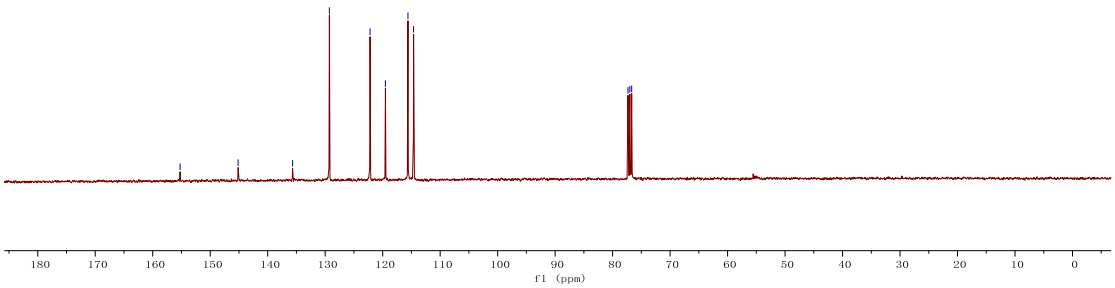

OCD3
N
H

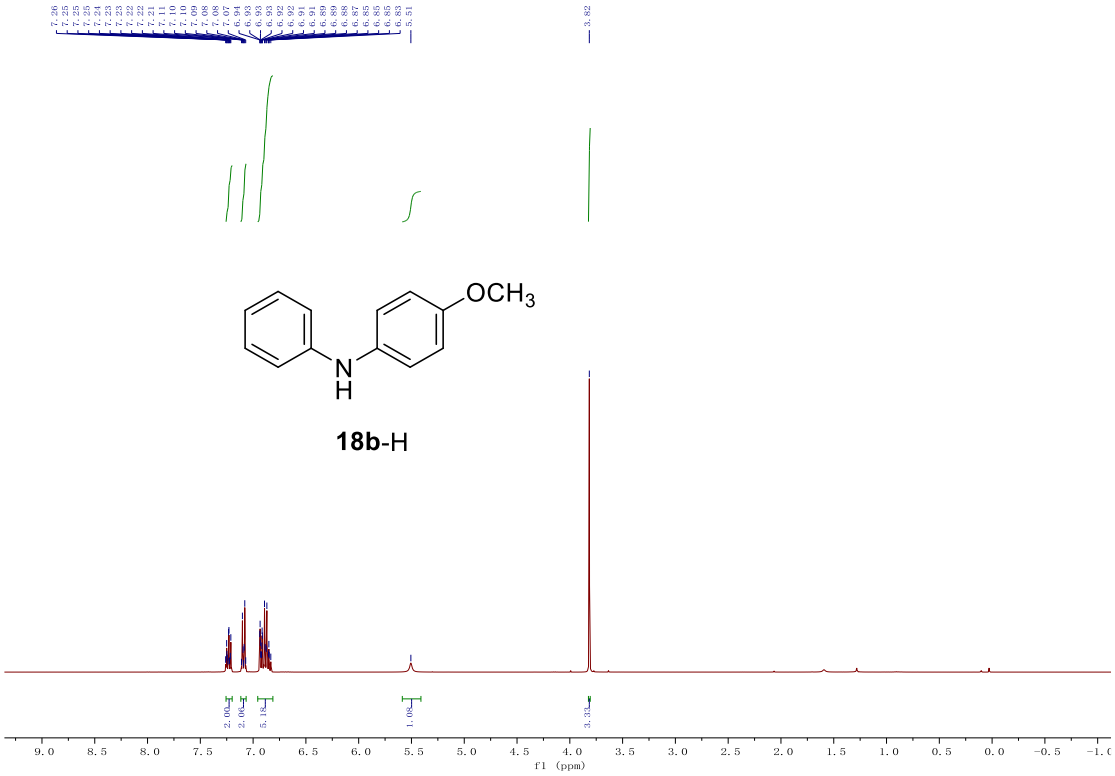
18b

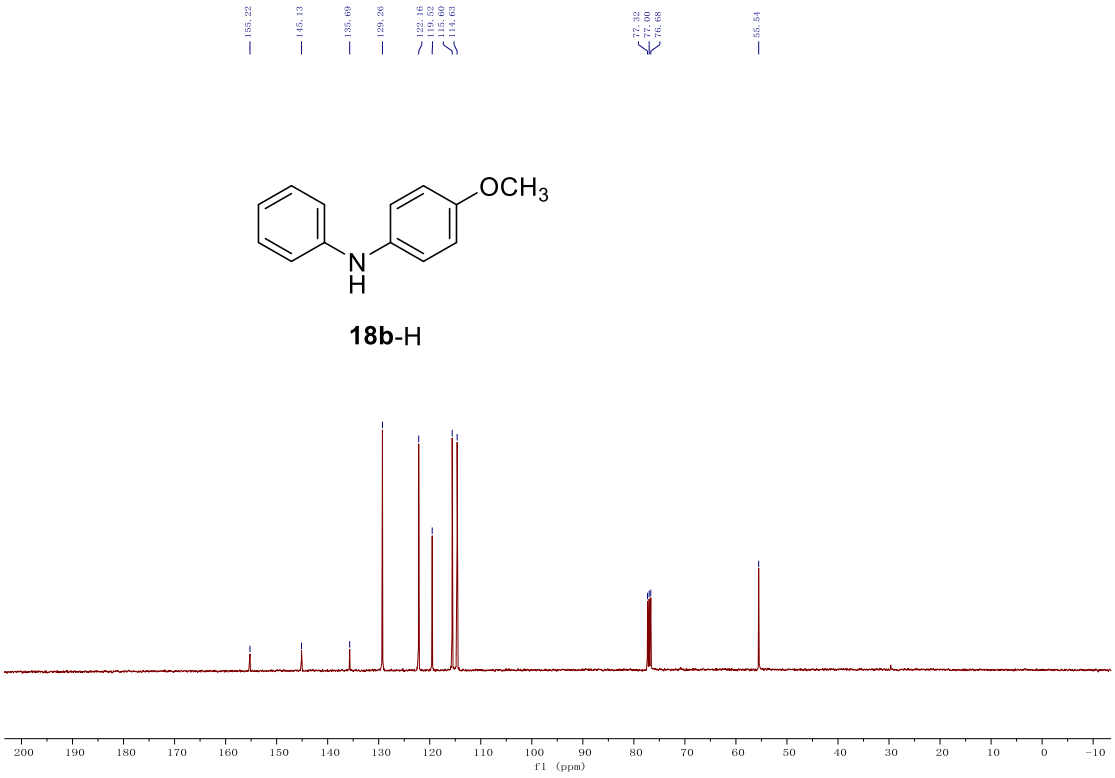

2.13
2.08
4.97
1.01
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


OCD3
N
H

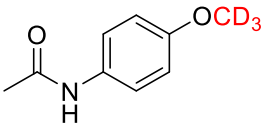
18b


180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

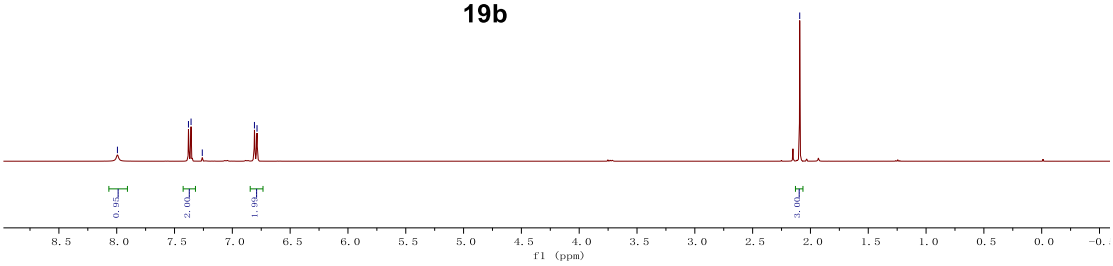

7.26
7.25
7.25
7.25
7.25
7.24
7.23
7.23
7.22
7.22
7.22
7.21
7.10
7.10
7.10
7.09
7.08
7.08
7.07
6.94
6.93
6.93
6.93
6.92
6.92
6.91
6.91
6.89
6.89
6.88
6.87
6.85
6.85
6.85
6.83
5.51
3.82
OCH3
N
H
18b-H
2.00
2.06
5.18
1.00
3.33
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


155.22
145.13
135.69
129.26
122.16
119.52
115.60
114.63
77.32
77.00
76.68
55.54
OCH3
N
H
18b-H
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

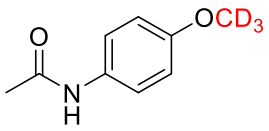

7.99
7.38
7.36
7.26
6.81
6.79
2.09


O
N
H
OCD3

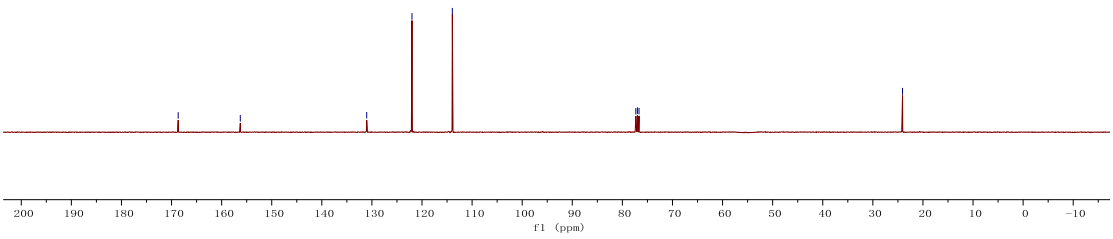
19b

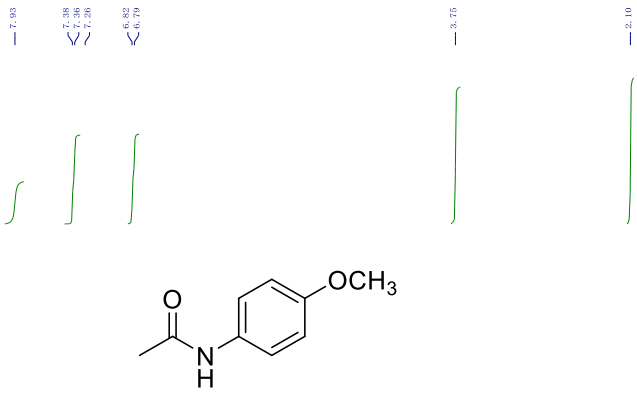

0.98
2.00
1.98
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


168.68
156.27
131.04
122.00
113.95
77.32
77.00
76.68
24.07

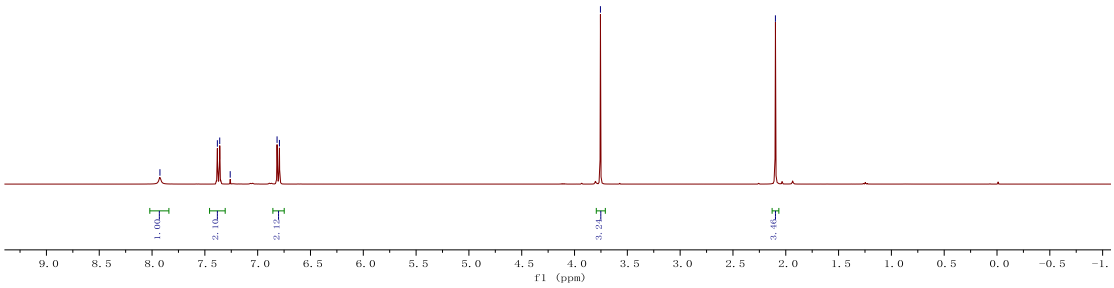

O
N
H
OCD3

19b

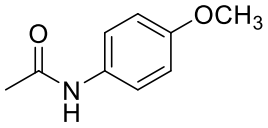

200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


7.93
7.38
7.36
7.26
6.82
6.79
3.75
2.10
O
N
H
OCH3

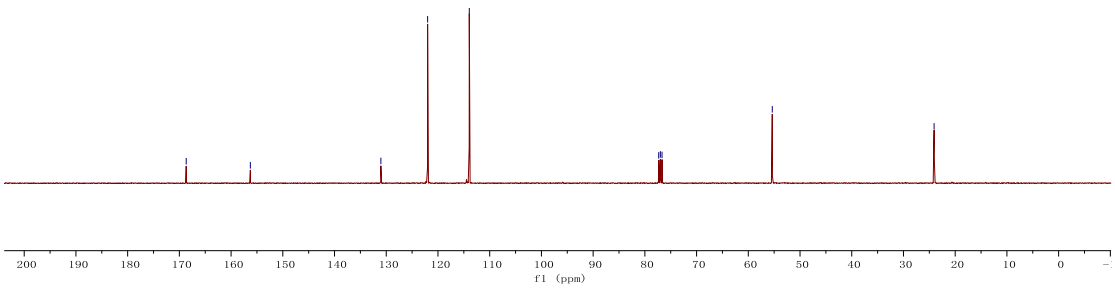
19b-H

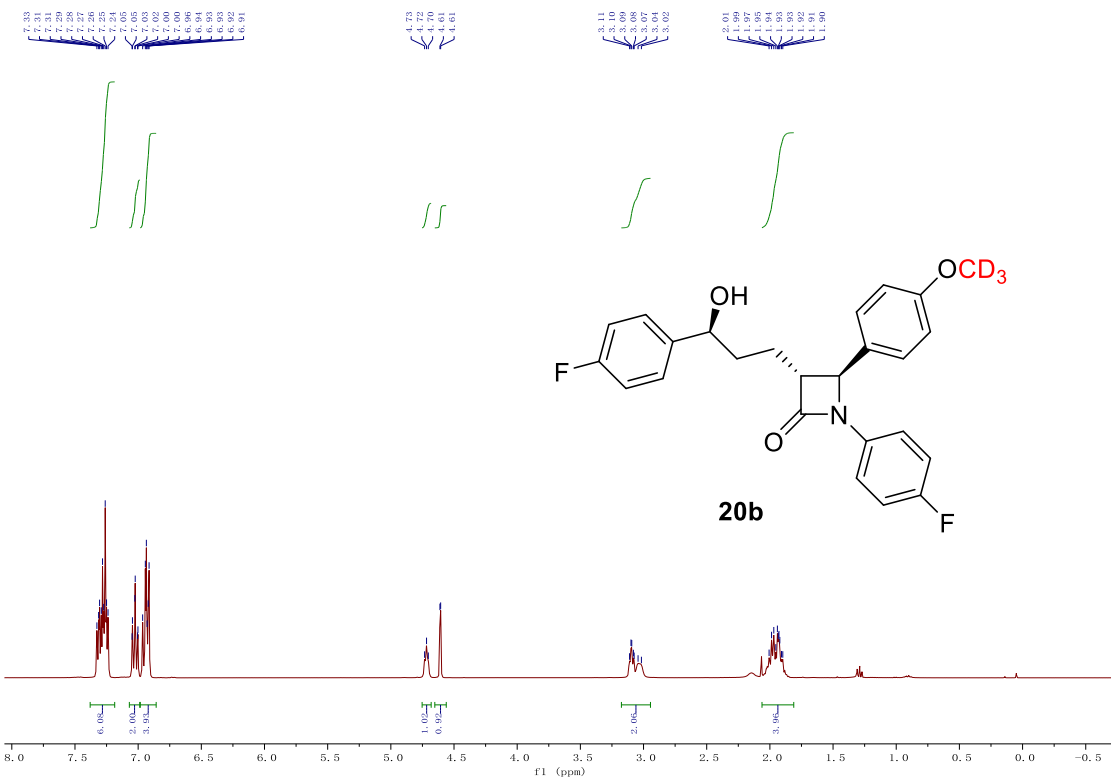

1.00
2.10
2.12
3.24
3.46
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)

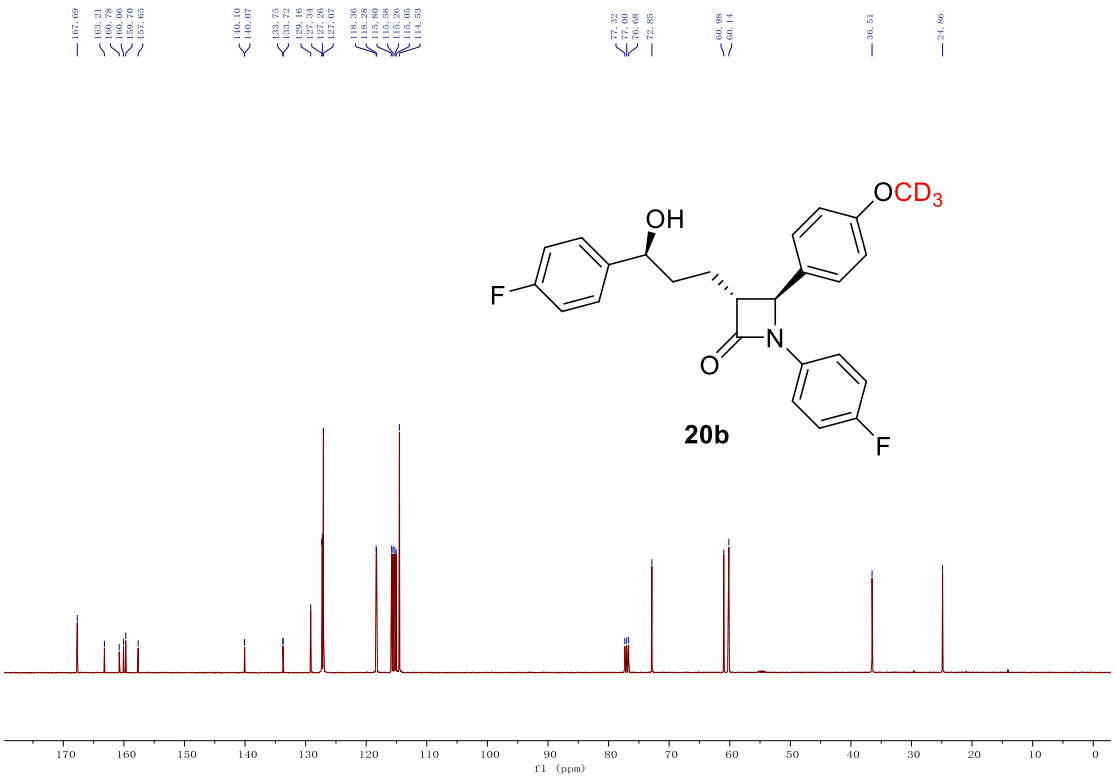

168.68
156.27
131.04
122.00
113.95
77.32
77.00
76.68
55.37
24.07

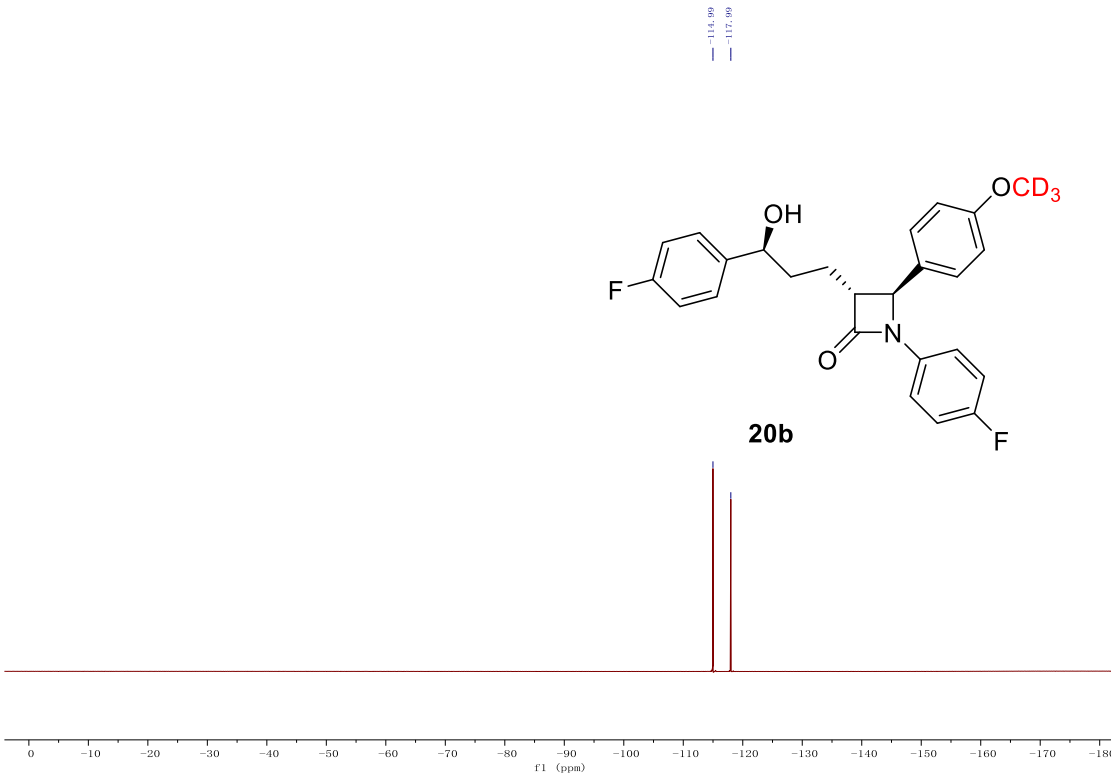

O
N
H
OCH3

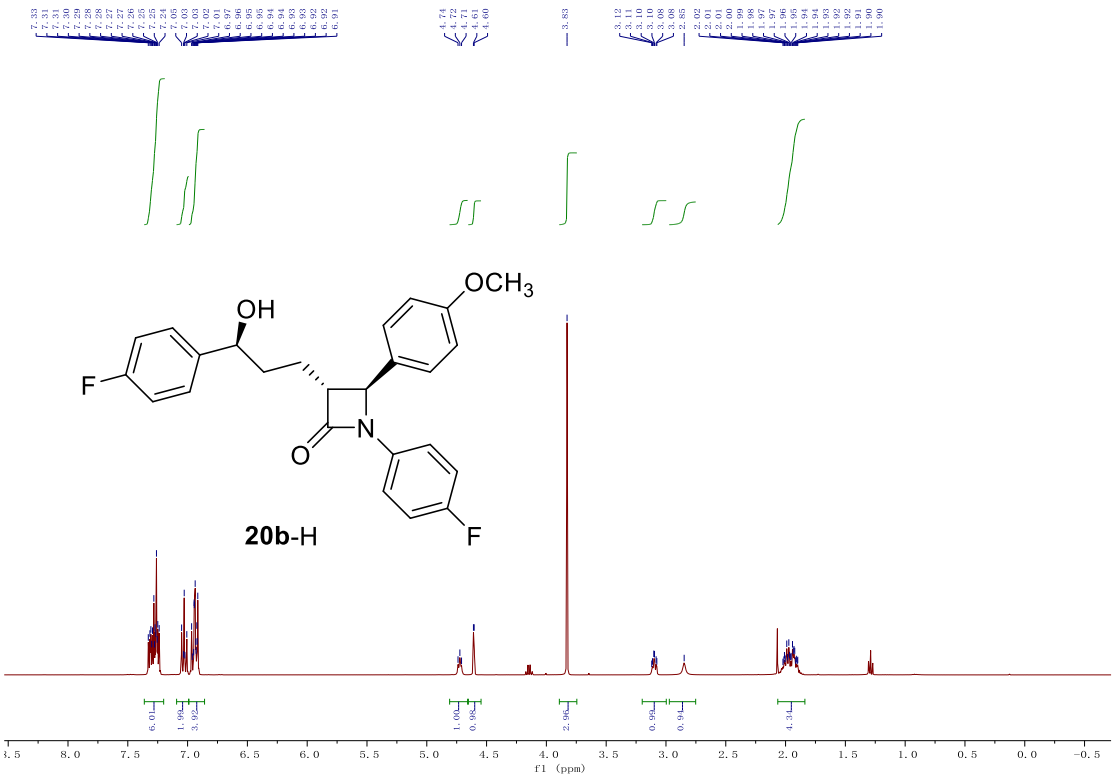
19b-H

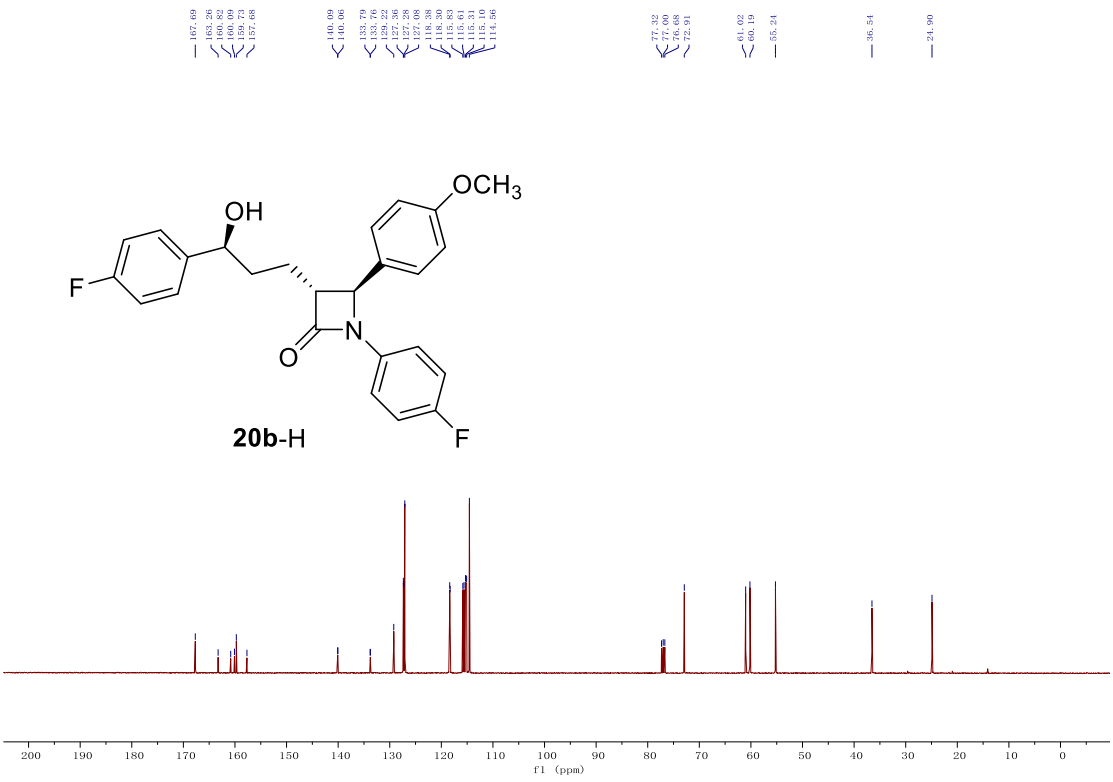

200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

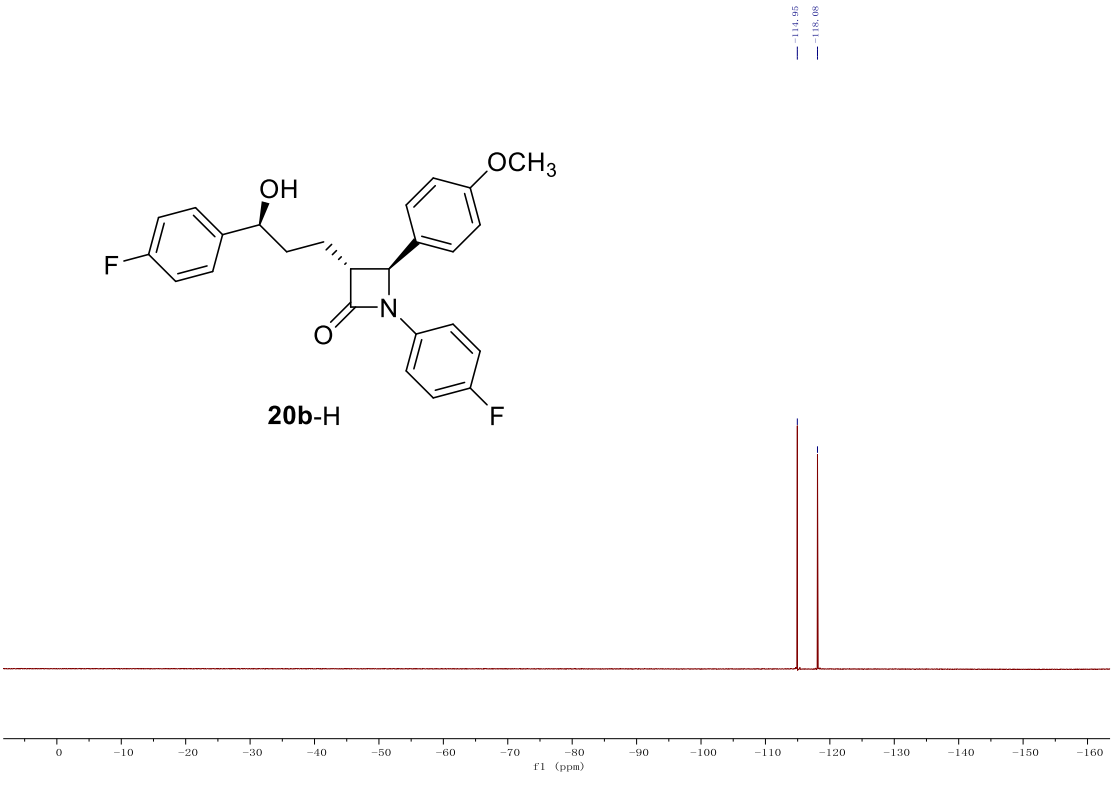

OCD3
OH
F
N
O
F
20b
f1 (ppm)

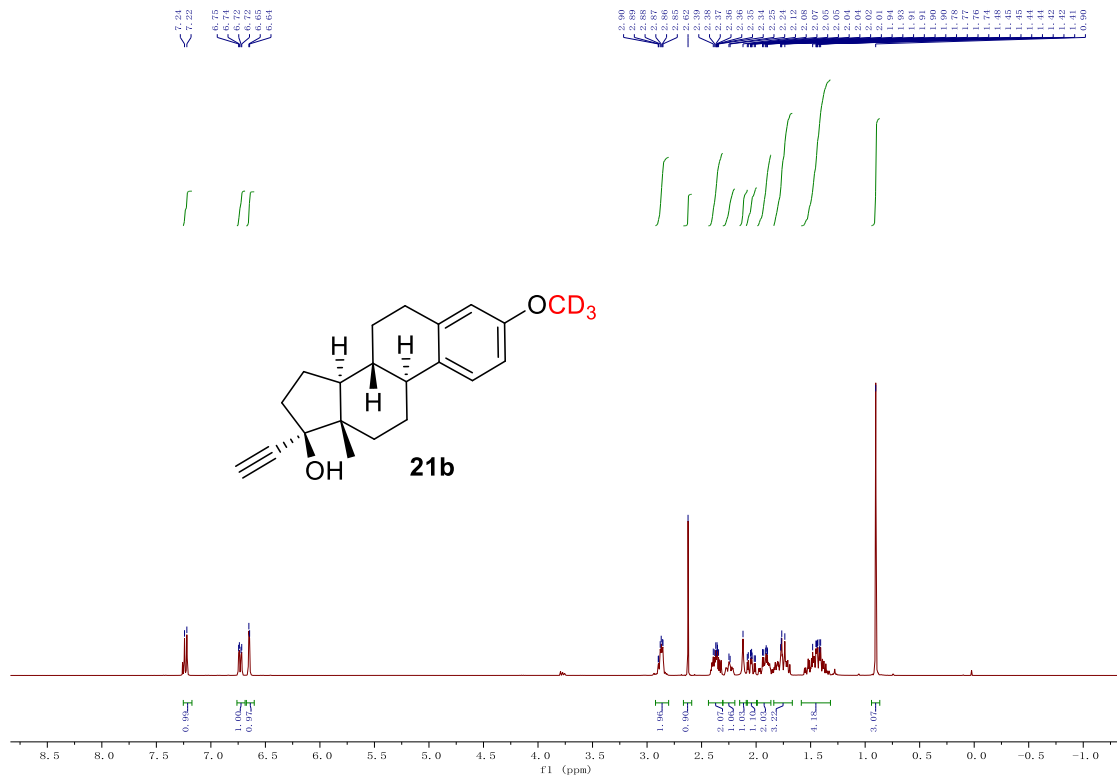

OCD3
OH
F
N
O
F
20b
f1 (ppm)

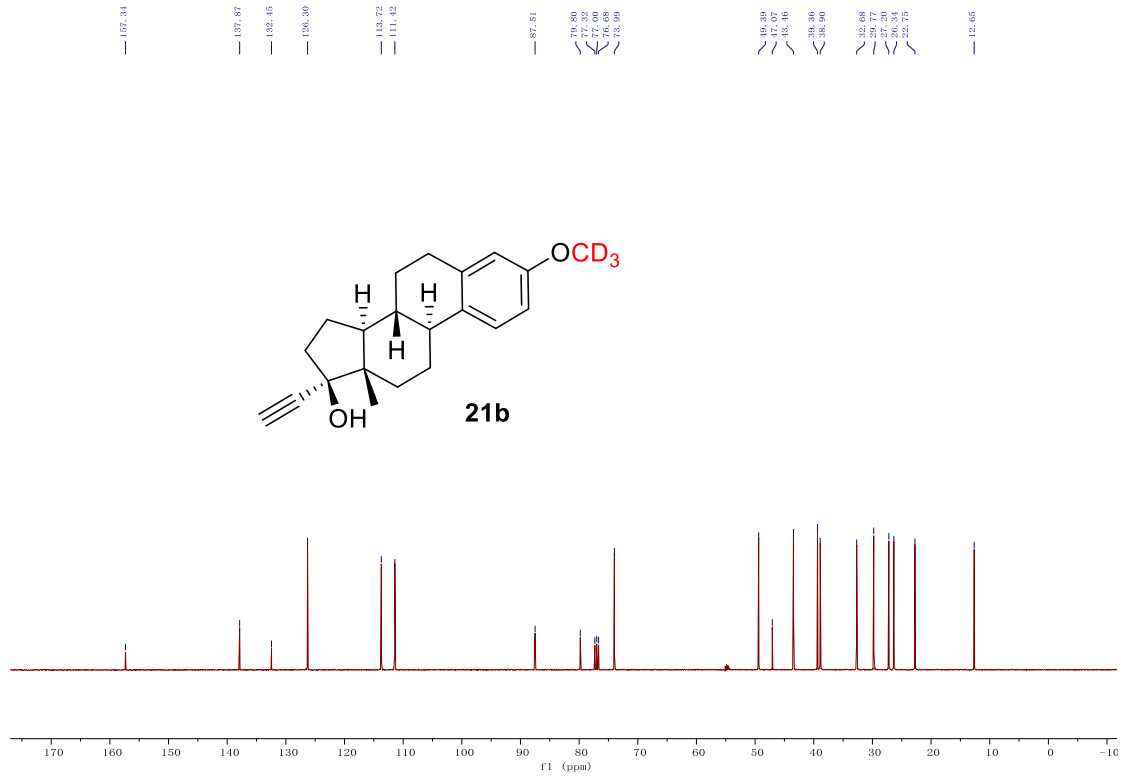

-114.99
-117.99
OCD3
OH
F
N
O
F
20b
f1 (ppm)

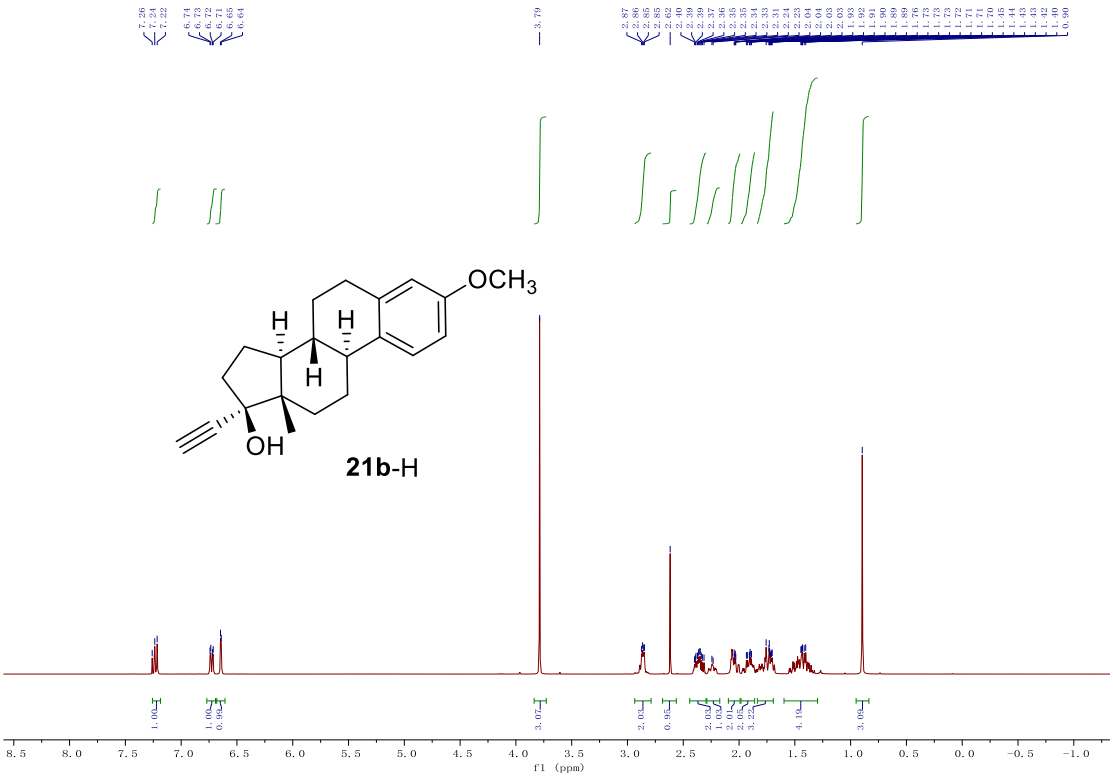

OCH3
OH
F
N
O
F
20b-H
f1 (ppm)

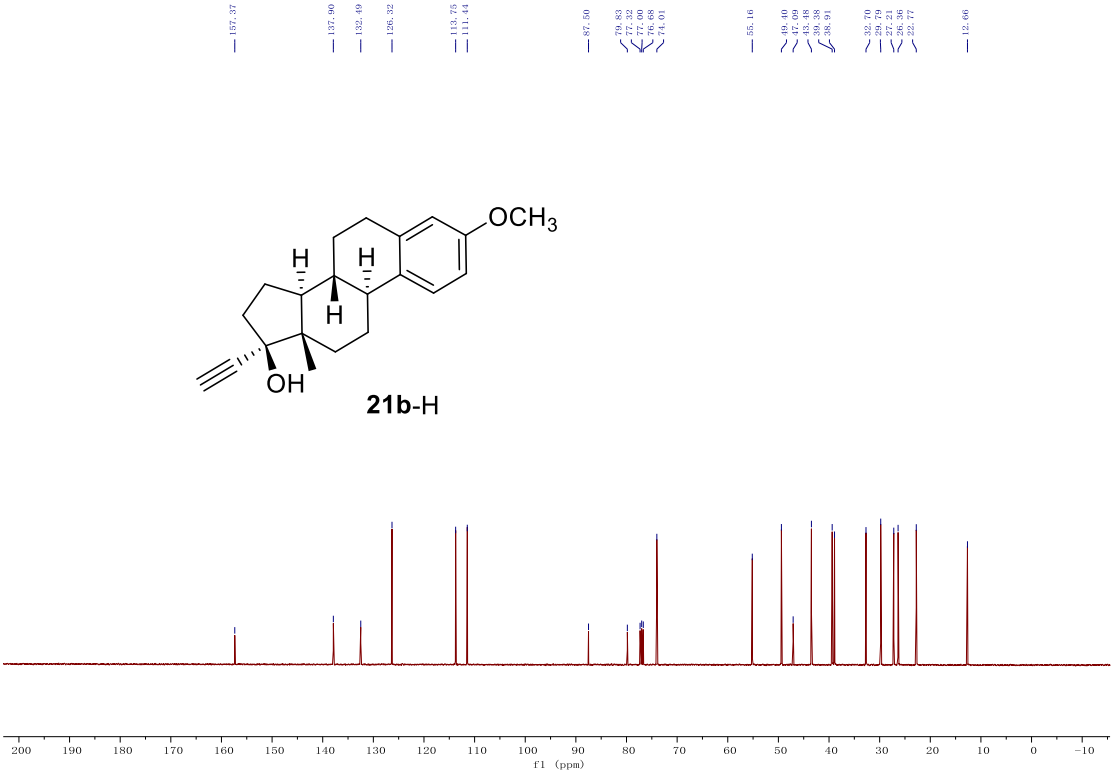

167.69
163.36
160.82
160.09
159.73
157.68
140.09
140.06
133.79
133.76
129.22
127.36
127.28
127.08
118.38
118.30
115.83
115.61
115.31
115.10
114.56
77.32
77.00
76.68
72.91
61.02
60.19
55.24
36.54
24.90
OCH3
OH
F
O
N
F
20b-H
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

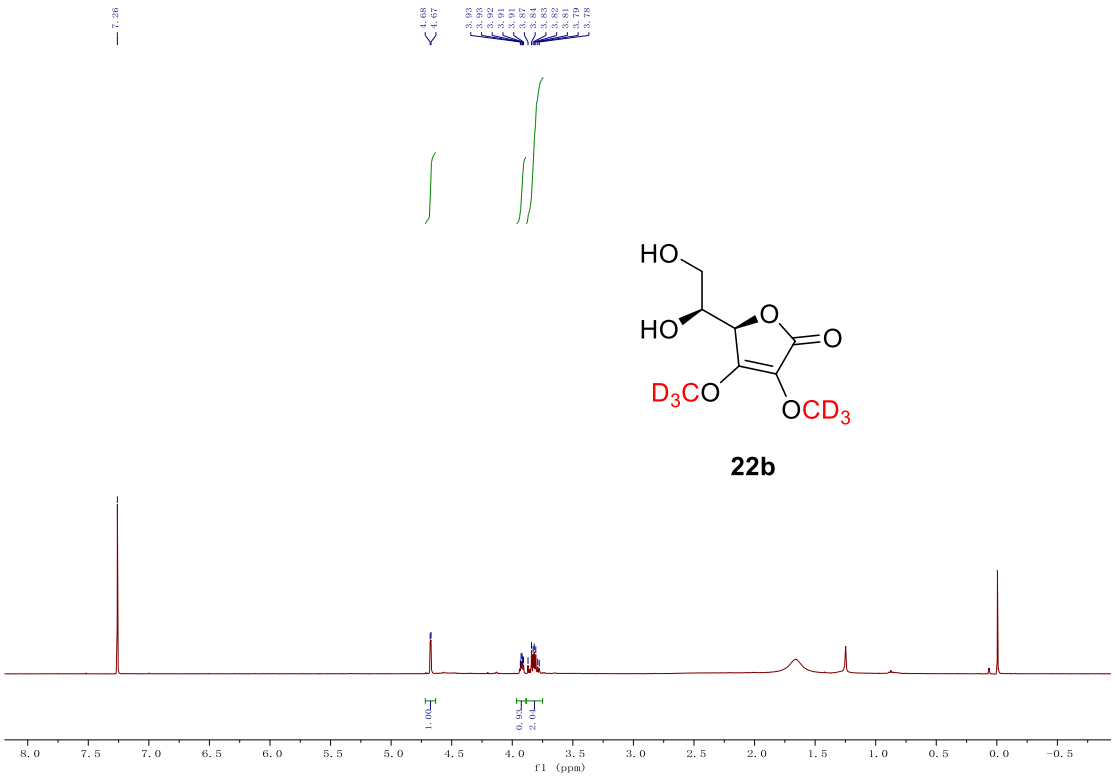

-114.95
-118.08
OCH3
OH
F
O
N
F
20b-H
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
f1 (ppm)


OCD3
H
H
H
OH
21b
f1 (ppm)

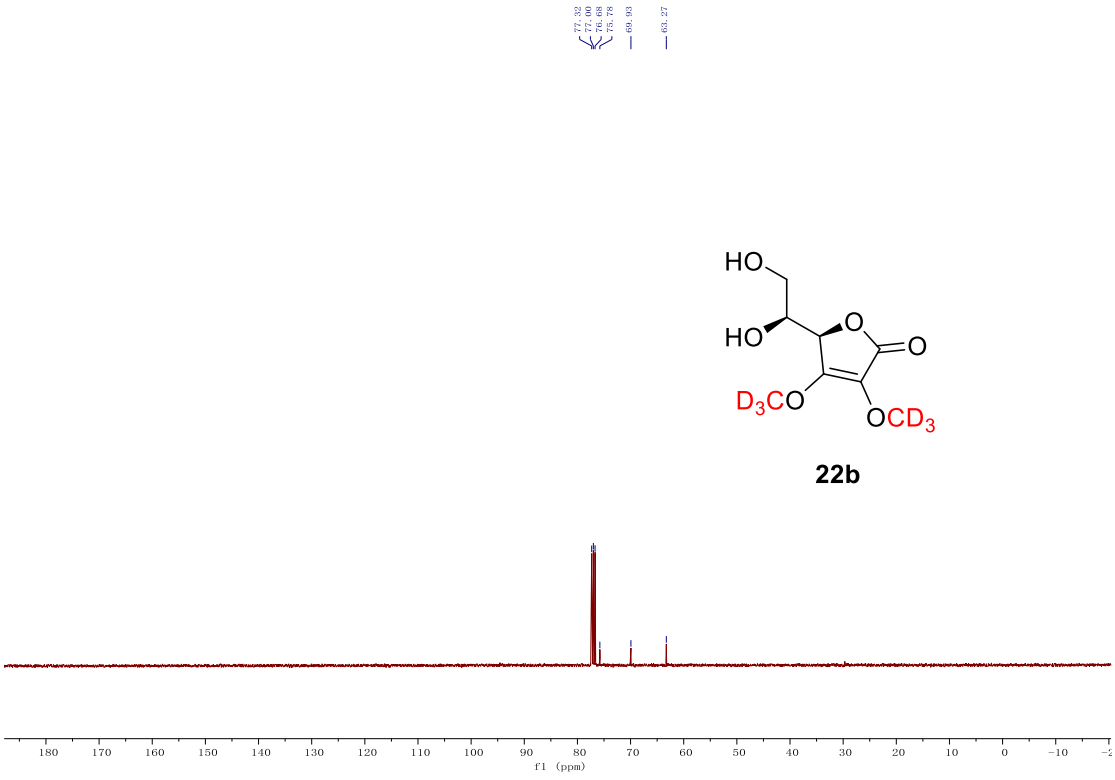

OCD3
H
H
H
OH
21b
f1 (ppm)


OCH3
H
H
H
OH
21b-H
f1 (ppm)

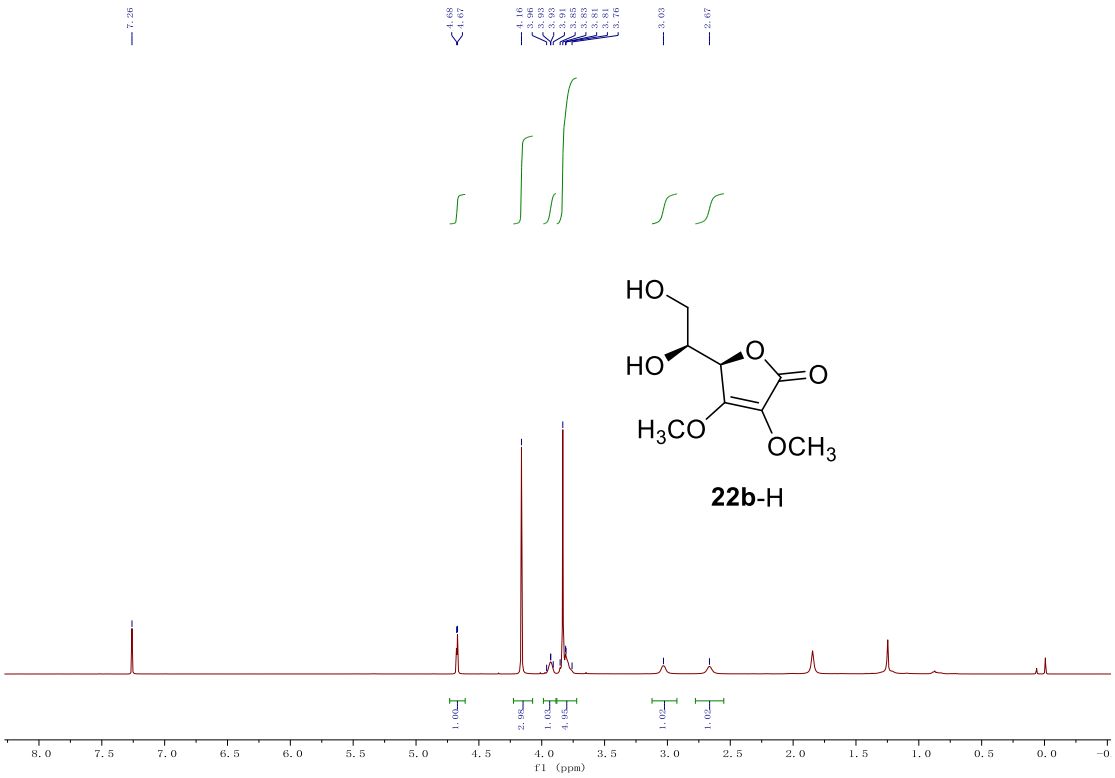

OCH3
H
H
H
OH
21b-H
f1 (ppm)


7.26
4.68
4.67
3.93
3.93
3.92
3.91
3.91
3.87
3.84
3.83
3.82
3.81
3.79
3.78
HO
HO
O
O
D3CO
OCD3
1.00
0.93
2.01
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)

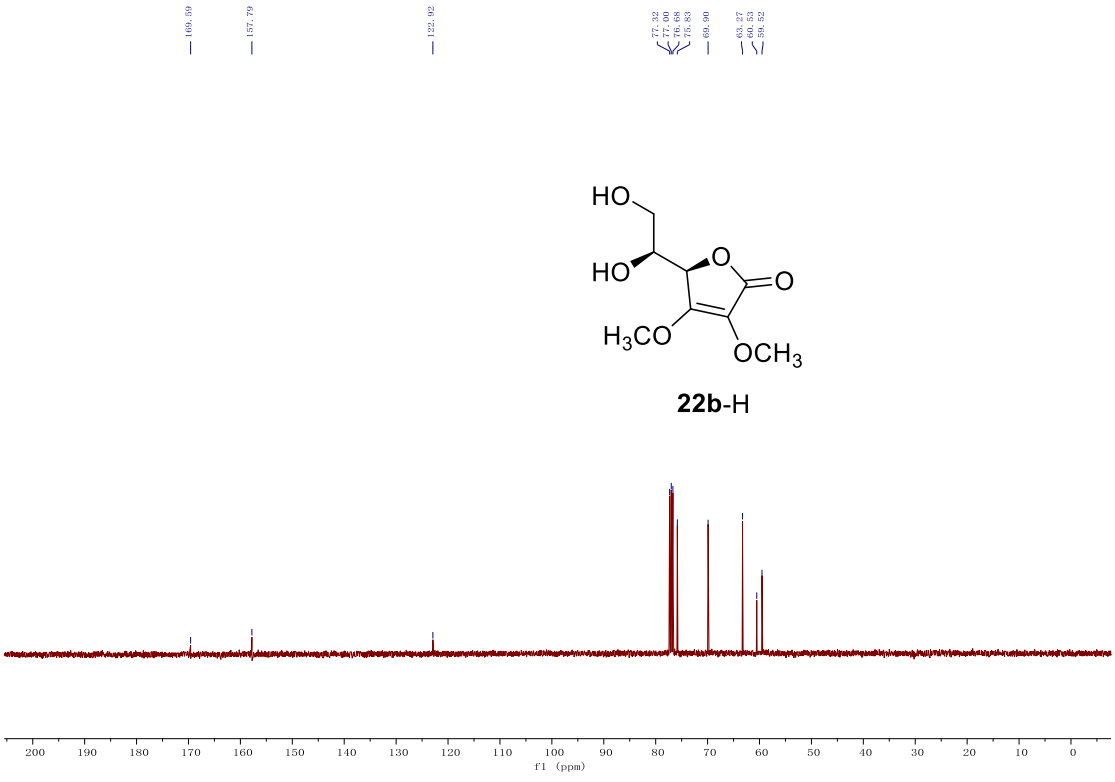
22b


77.32
77.00
76.68
75.78
69.93
63.27
HO
HO
O
O
D3CO
OCD3
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

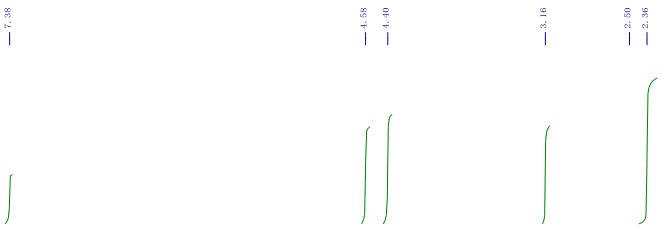
22b

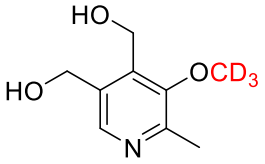

7.26
4.68
4.67
4.16
3.96
3.93
3.93
3.91
3.85
3.83
3.81
3.81
3.76
3.03
2.67
HO
HO
O
O
H3CO
OCH3
1.00
2.98
1.03
4.96
1.00
1.02
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

22b-H

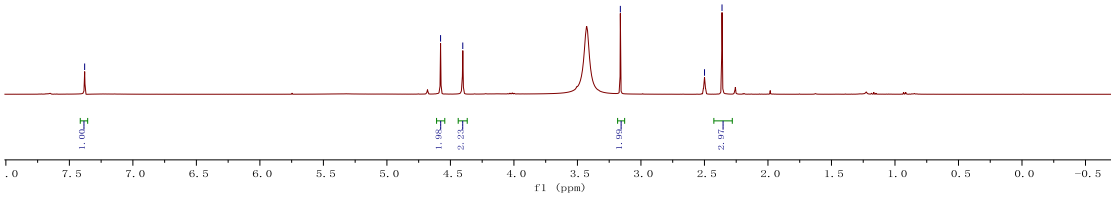

169.59
157.79
122.92
77.32
77.00
76.68
75.83
69.90
63.27
60.53
59.52
HO
HO
O
O
H3CO
OCH3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

22b-H

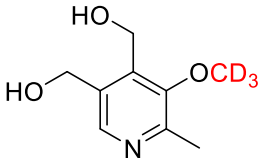

7.38
4.58
4.40
3.16
2.50
2.36


HO
HO
OCD3
N

23b

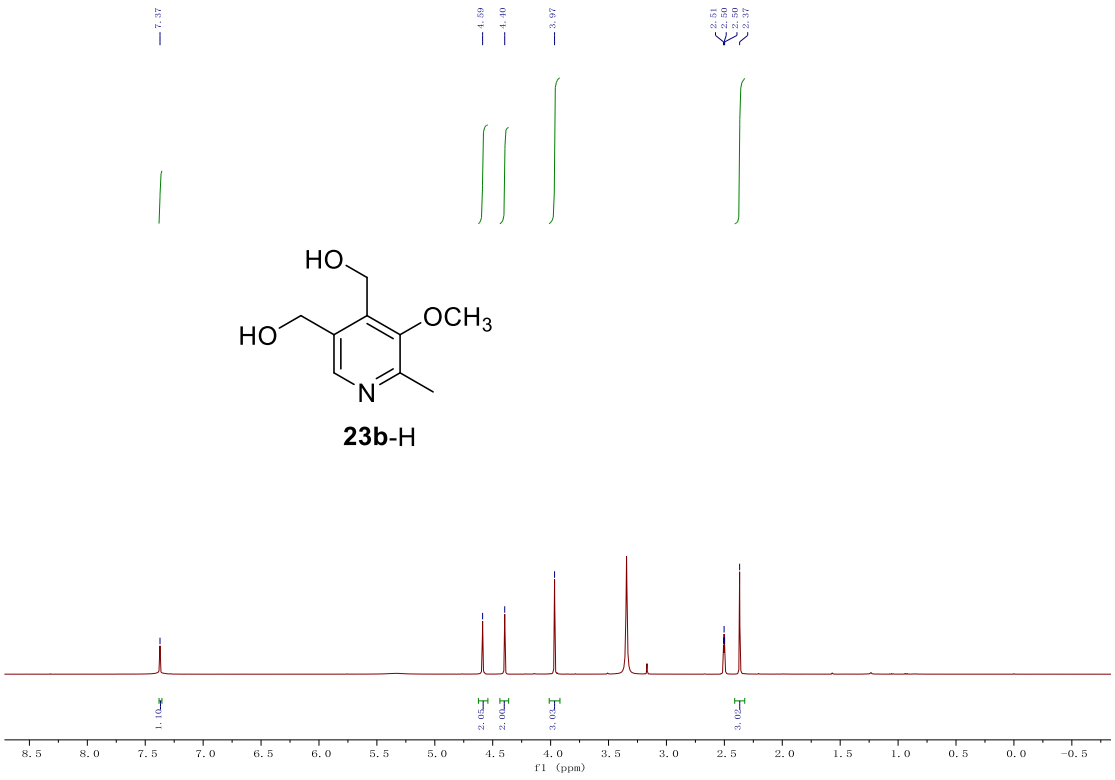

1.00
1.98
2.24
1.98
2.97
f1 (ppm)


166.07
142.22
136.98
134.76
121.63
58.72
58.13
40.15
39.94
39.73
39.52
39.31
39.10
38.90
12.04

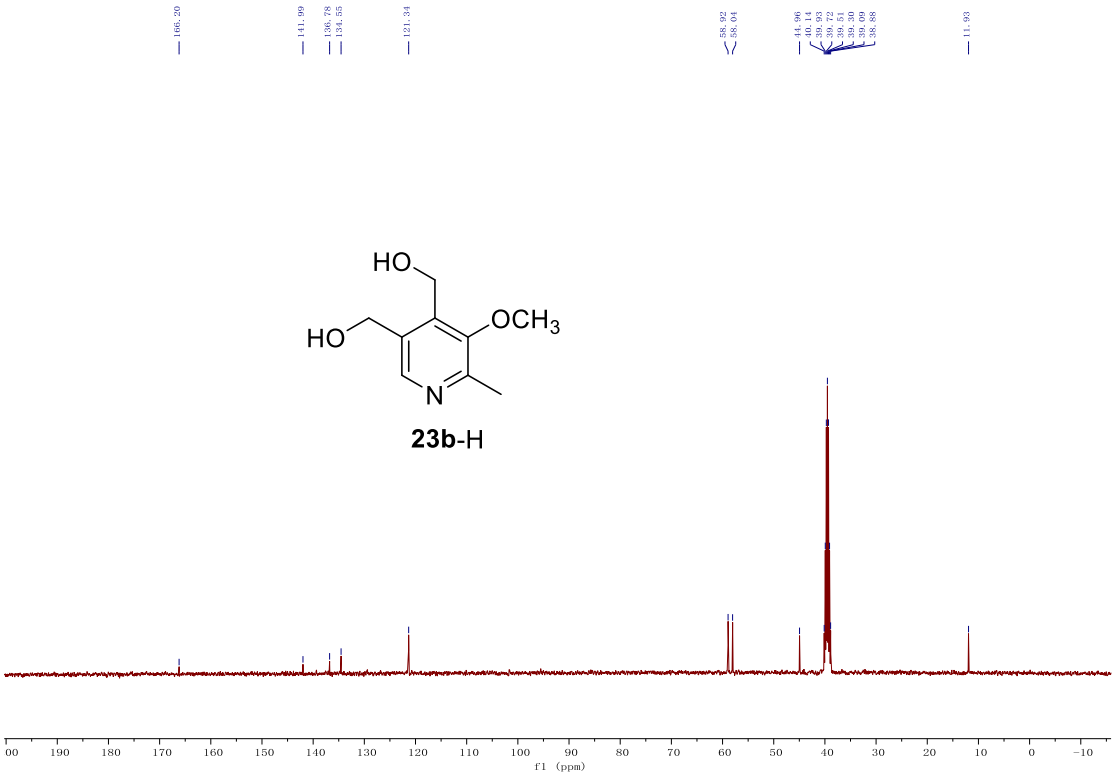

HO
HO
OCD3
N

23b

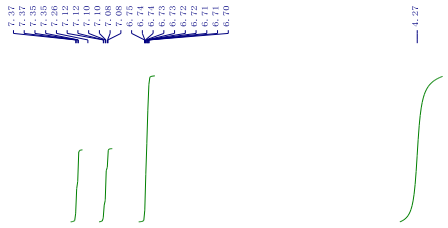
f1 (ppm)


7.37
4.59
4.40
3.97
2.51
2.50
2.50
2.37
HO
HO
OCH3
N
1.10
2.05
2.00
3.03
3.02
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)

23b-H

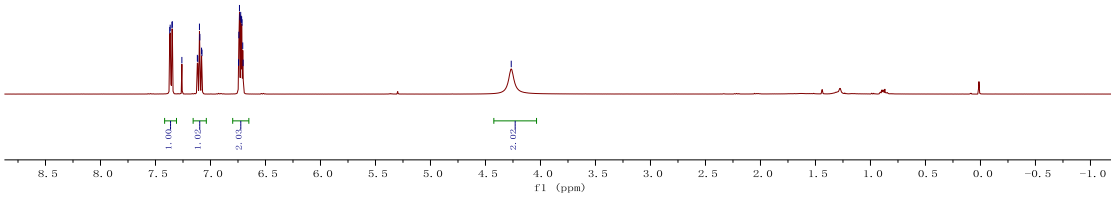

166.20
141.99
136.78
134.55
121.34
58.92
58.04
44.96
40.14
39.93
39.72
39.51
39.30
39.09
38.88
11.93
HO
HO
OCH3
N
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

23b-H


7.37
7.37
7.35
7.35
7.26
7.12
7.12
7.10
7.10
7.08
7.08
6.76
6.74
6.74
6.73
6.73
6.72
6.72
6.71
6.71
6.70
4.27


NH2
SCD3

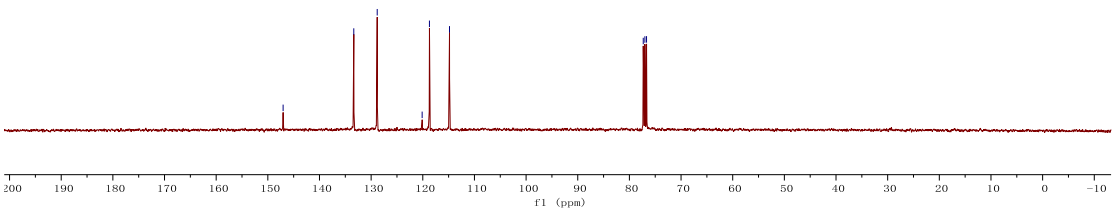
24b

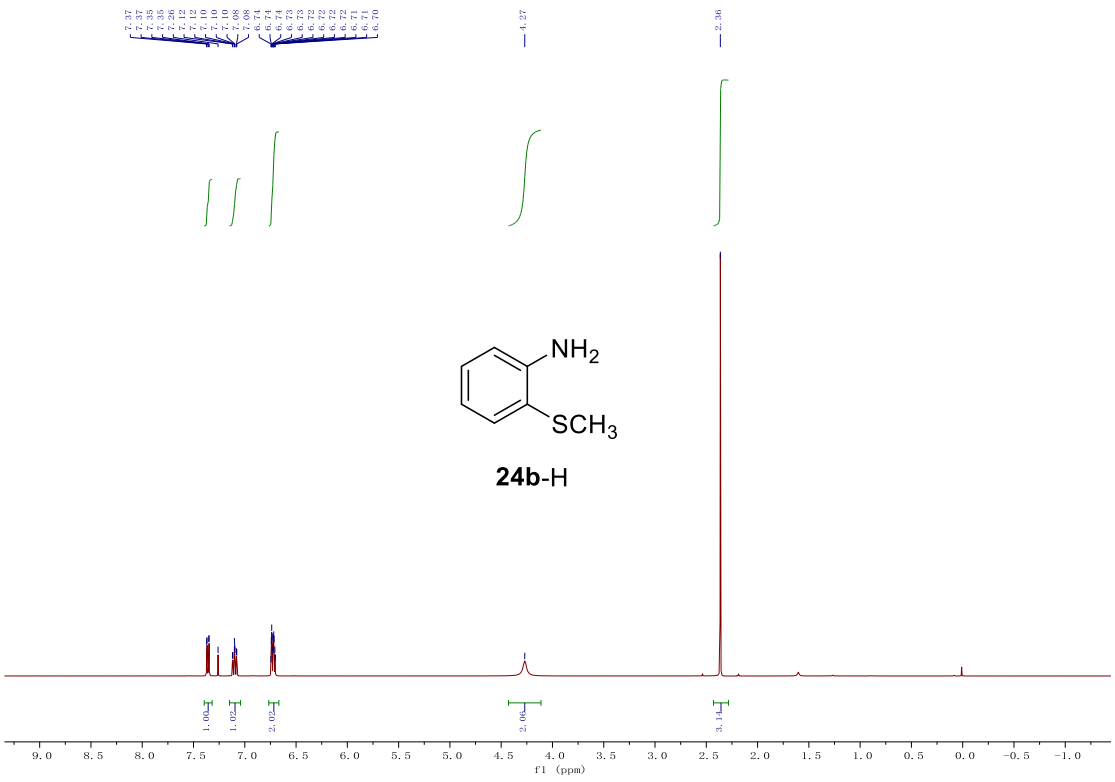

1.00
1.03
2.03
2.02
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)


147.04
133.36
128.82
120.12
118.71
114.83
77.32
77.00
76.68

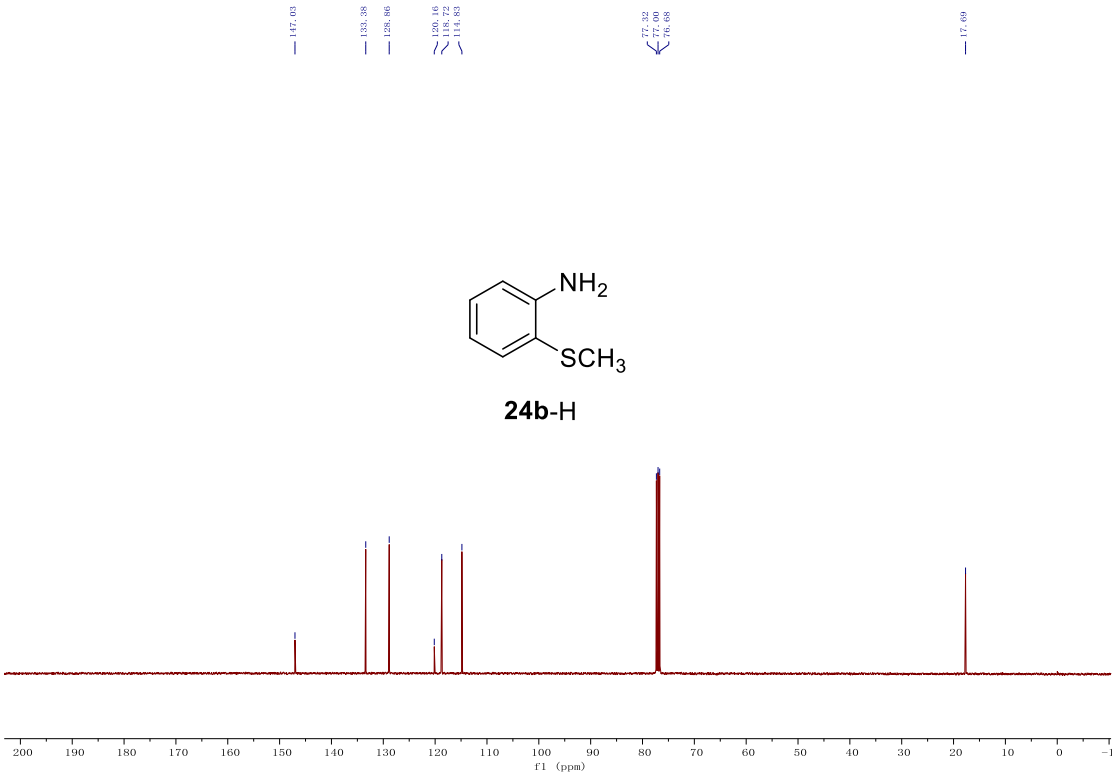

NH2
SCD3

24b

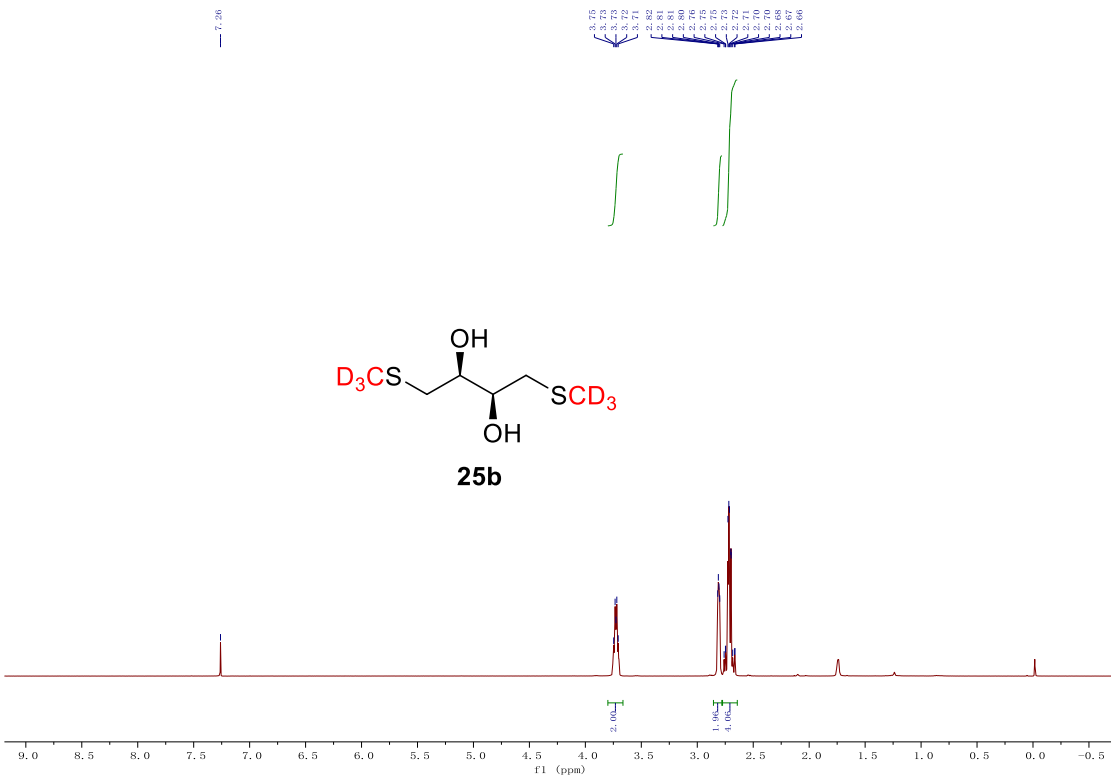

200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

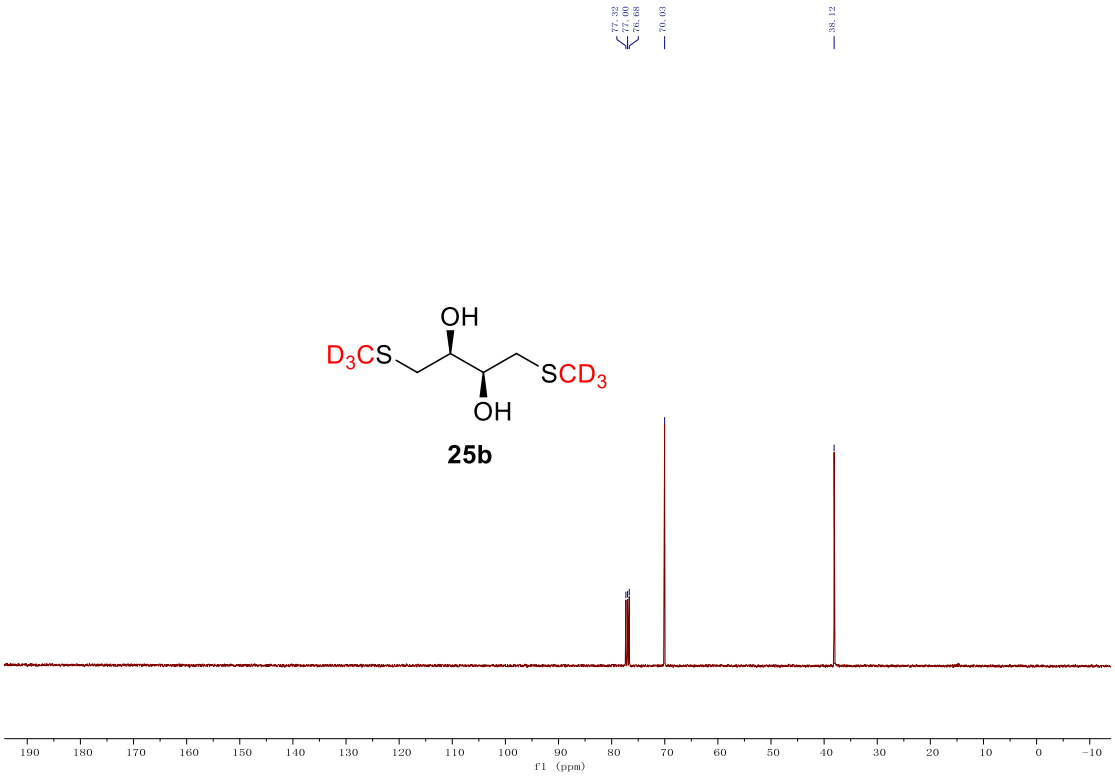

7.37
7.37
7.35
7.35
7.26
7.13
7.12
7.10
7.10
7.10
7.08
6.74
6.74
6.74
6.73
6.72
6.72
6.72
6.72
6.71
6.71
6.70
4.27
2.36
NH2
SCH3
1.00
1.02
2.02
2.00
3.14
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

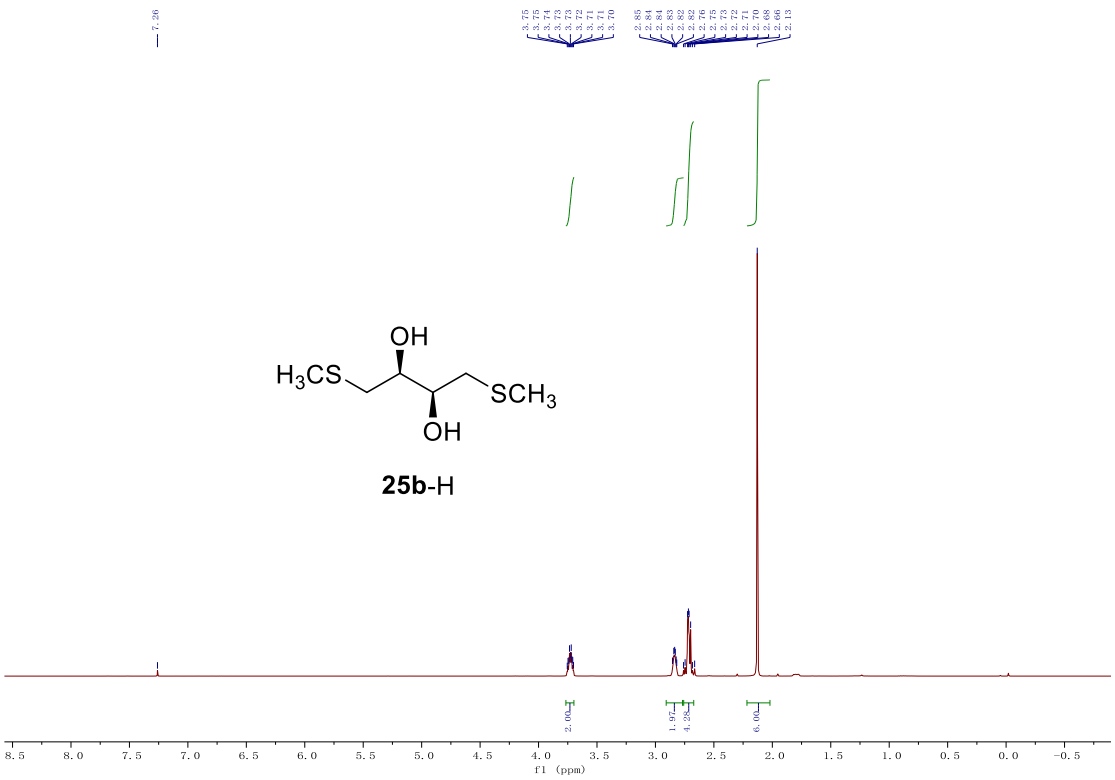
24b-H


147.03
133.38
128.86
120.16
118.72
114.83
77.32
77.00
76.68
17.69
NH2
SCH3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

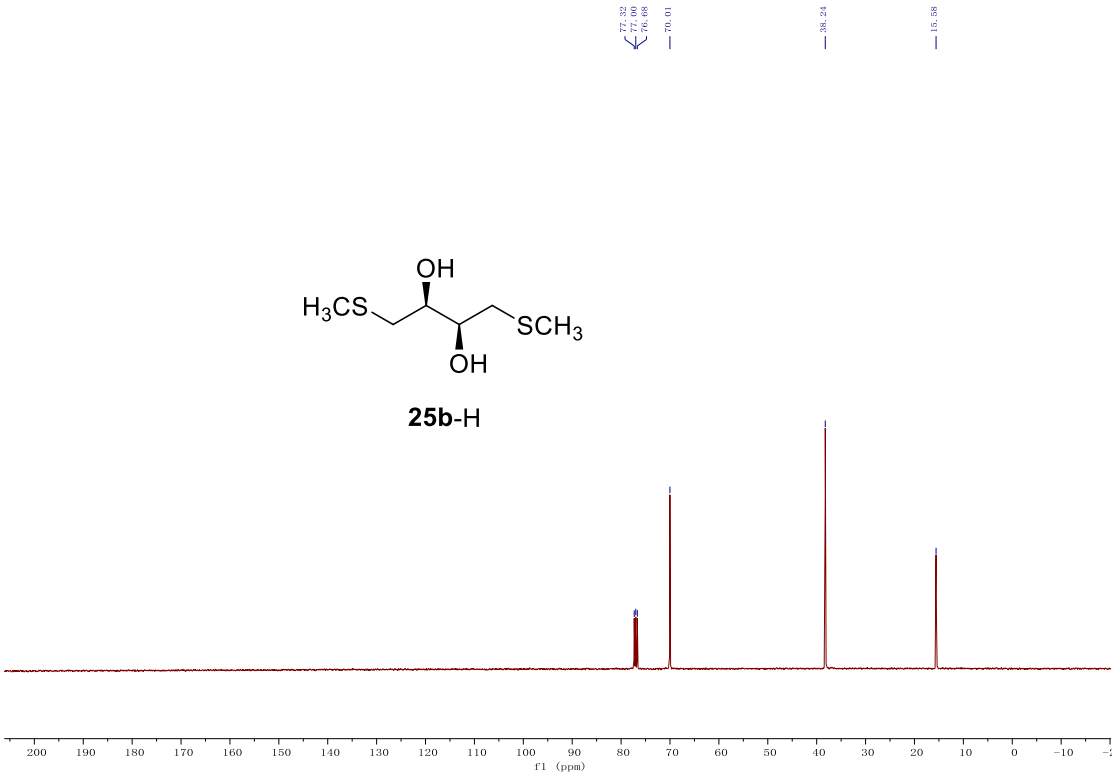
24b-H


7.26
3.75
3.73
3.73
3.72
3.71
2.82
2.81
2.81
2.80
2.76
2.75
2.75
2.73
2.72
2.71
2.70
2.70
2.68
2.67
2.66
OH
D3CS
SCD3
OH
25b
2.00
1.96
4.06
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
−0.5
f1 (ppm)

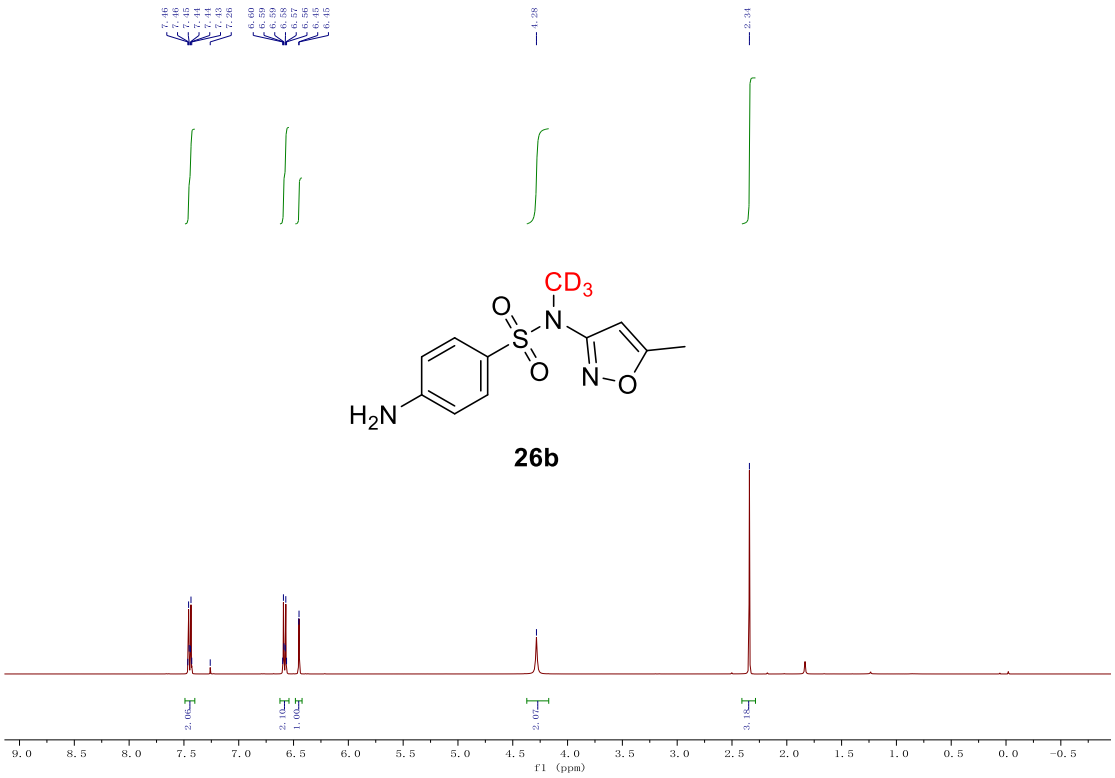

77.32
77.00
76.68
70.03
38.12
OH
D3CS
SCD3
OH
25b
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


7.26
3.75
3.75
3.74
3.73
3.73
3.72
3.71
3.71
3.70
2.85
2.84
2.84
2.83
2.82
2.82
2.76
2.75
2.73
2.72
2.71
2.71
2.68
2.66
2.13
OH
H3CS
SCH3
OH
2.00
1.97
4.28
6.00
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)

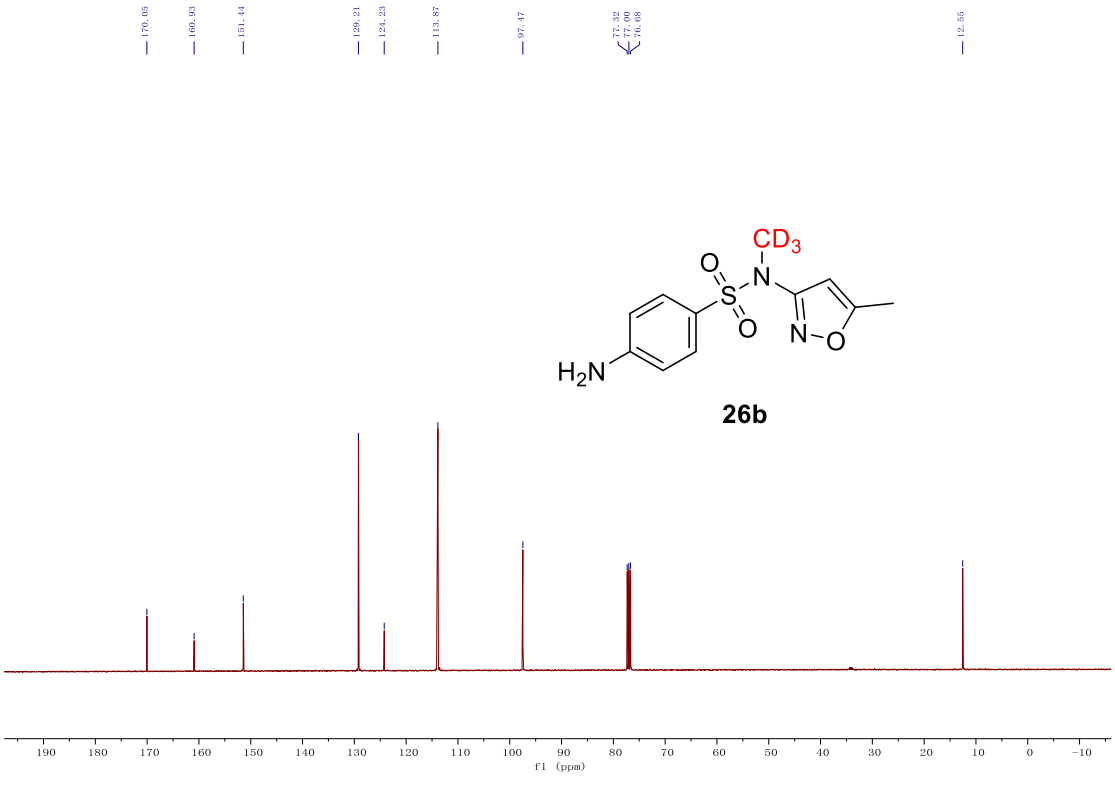
25b-H


77.32
77.00
76.68
70.01
38.24
15.58
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

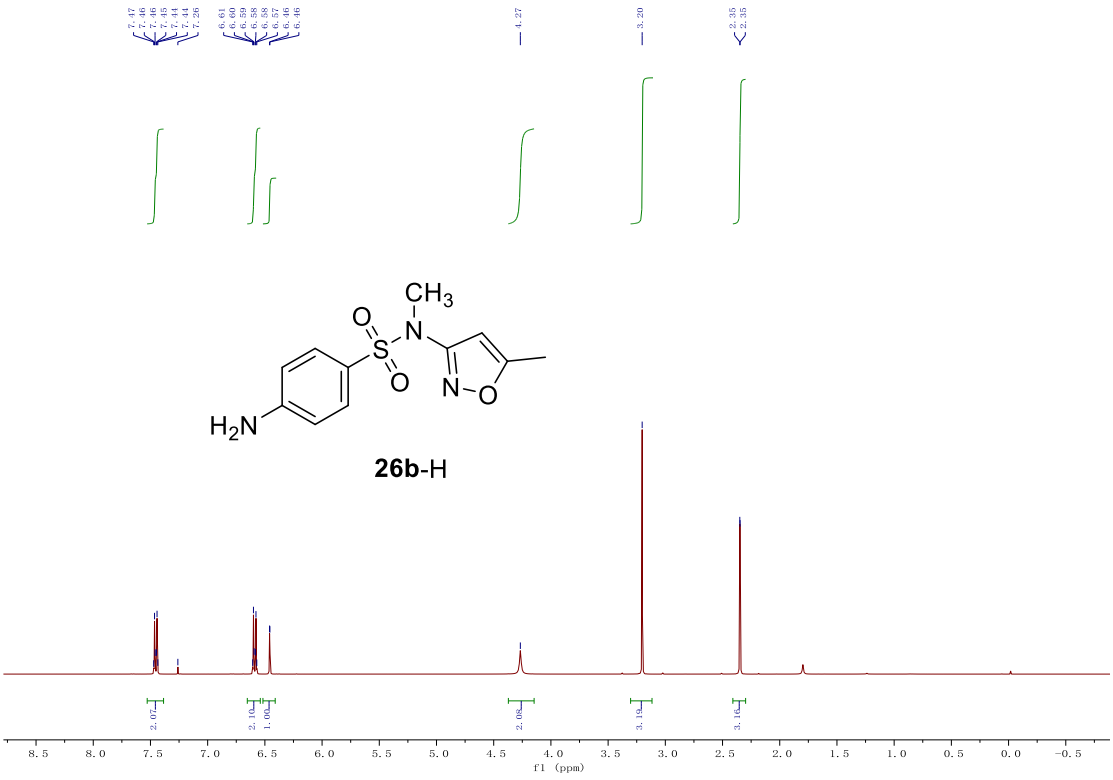
25b-H

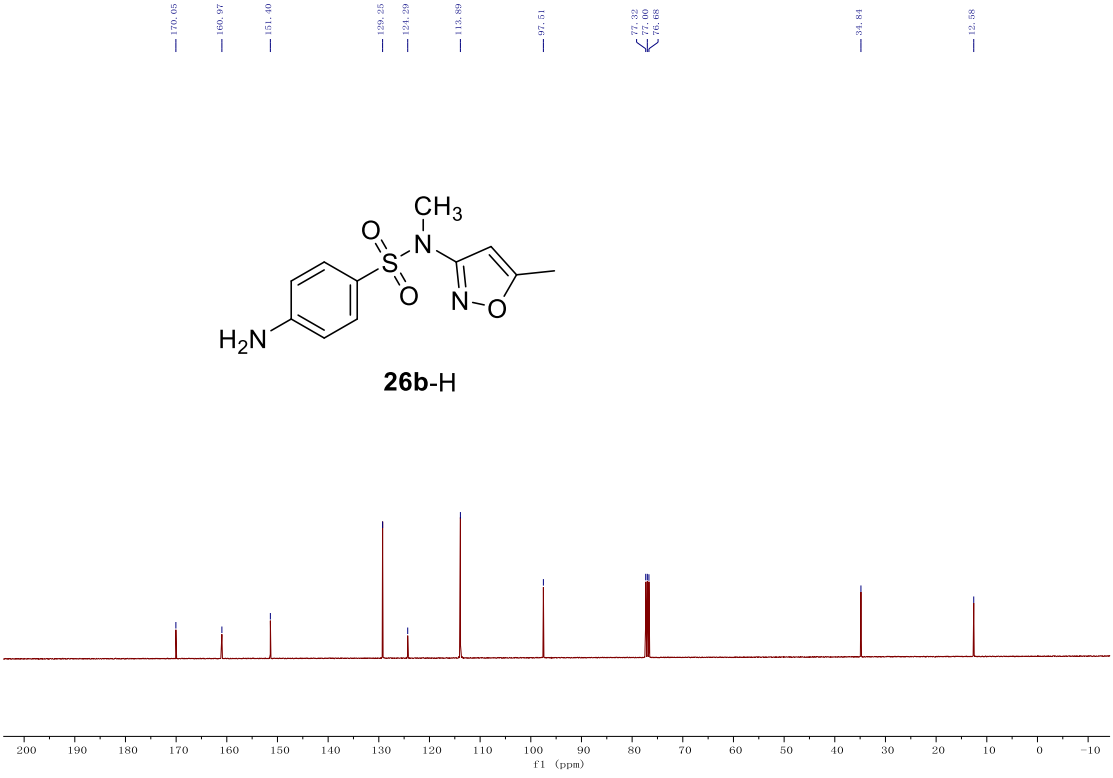

7.46
7.46
7.45
7.44
7.44
7.43
7.26
6.60
6.59
6.58
6.57
6.56
6.45
6.45
4.28
2.34
CD3
O
N
S
O
N
O
H2N
2.06
2.10
1.06
2.07
3.18
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

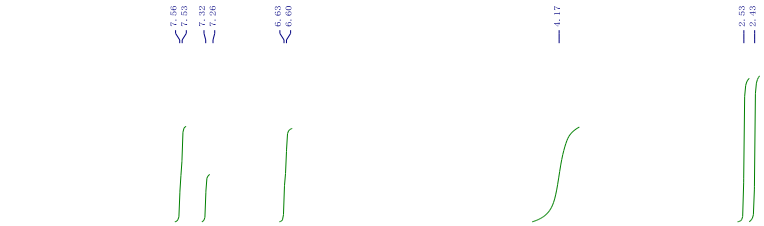
26b

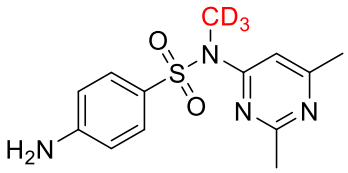

170.05
160.93
151.44
129.21
124.23
113.87
97.47
77.32
77.00
76.68
12.55
CD3
O
N
S
O
N
O
H2N
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

26b

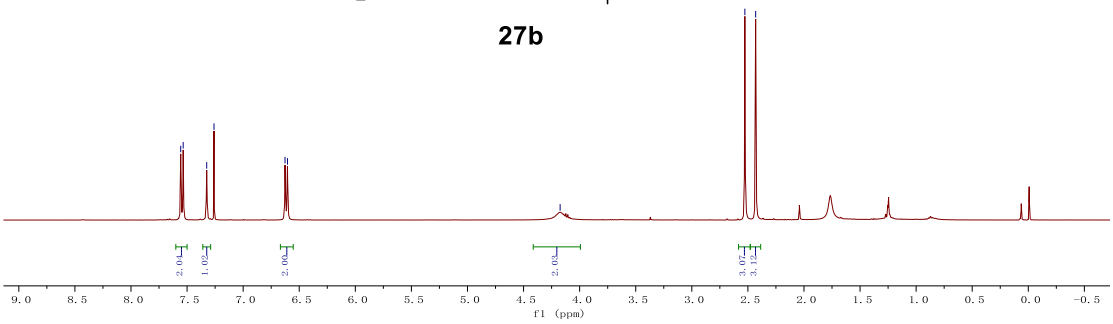

7.47
7.46
7.46
7.45
7.44
7.44
7.25
6.61
6.60
6.59
6.58
6.58
6.57
6.46
6.46
4.27
3.20
2.35
2.35
CH3
O
S
N
O
N
O
H2N
26b-H
2.07
2.10
1.00
2.08
3.19
3.16
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)


170.05
160.97
151.40
129.25
124.29
113.89
97.51
77.32
77.00
76.68
34.84
12.98
CH3
O
S
N
O
N
O
H2N
26b-H
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

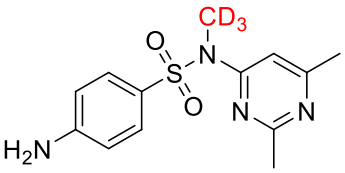

7.56
7.53
7.32
7.26
6.63
6.60
4.17
2.53
2.43


CD3
O
S
O
N
N
N
H2N

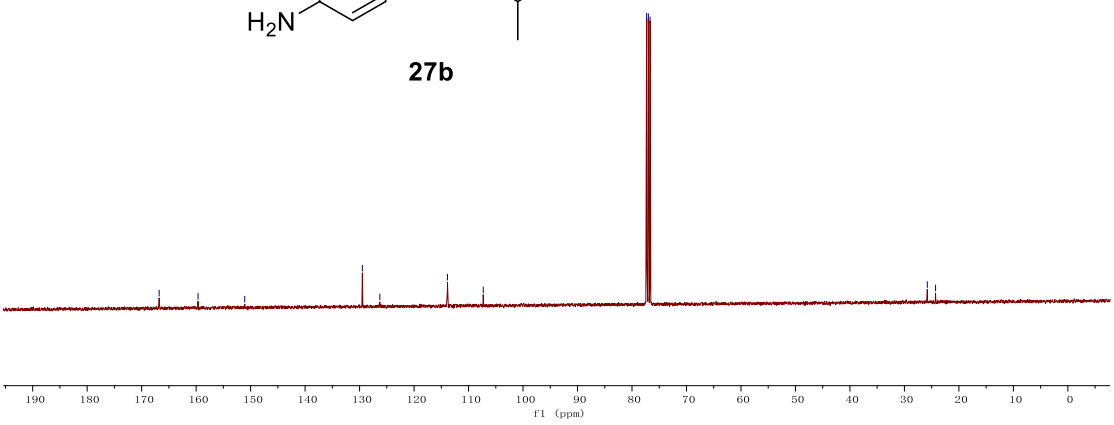
27b

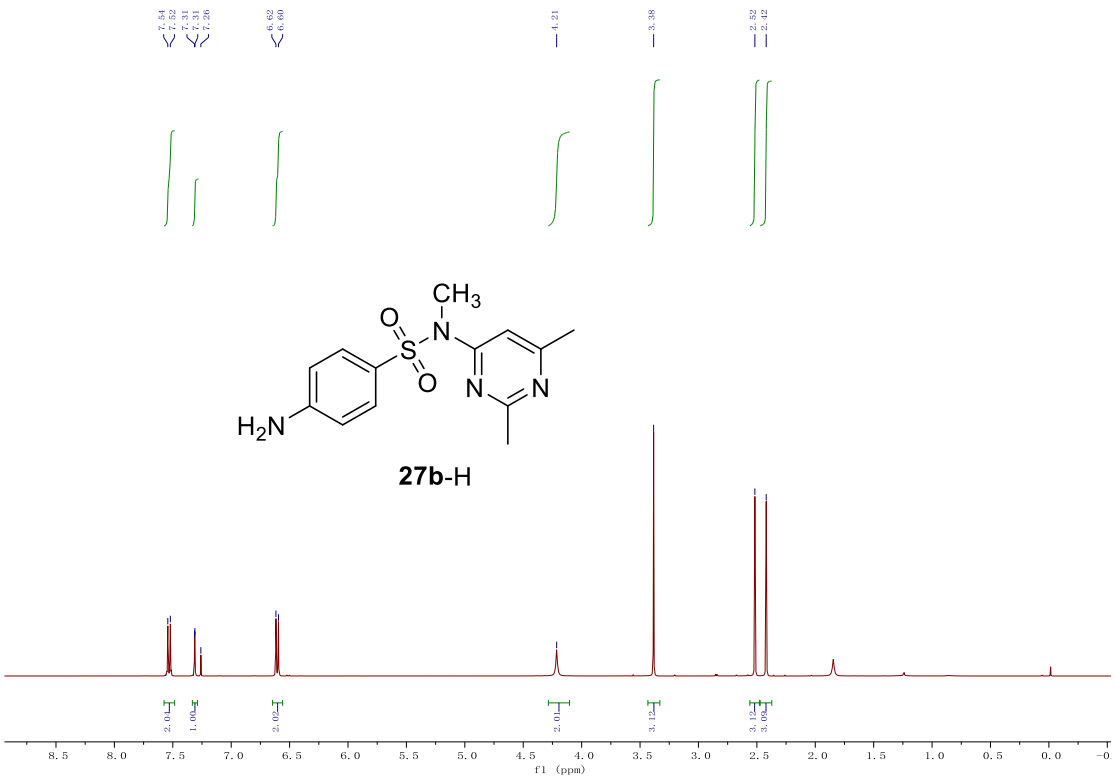

2.04
1.02
2.00
2.03
3.07
3.14
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)


166.79
159.65
151.08
129.49
126.28
113.87
107.31
77.32
77.00
76.68
25.80
24.28

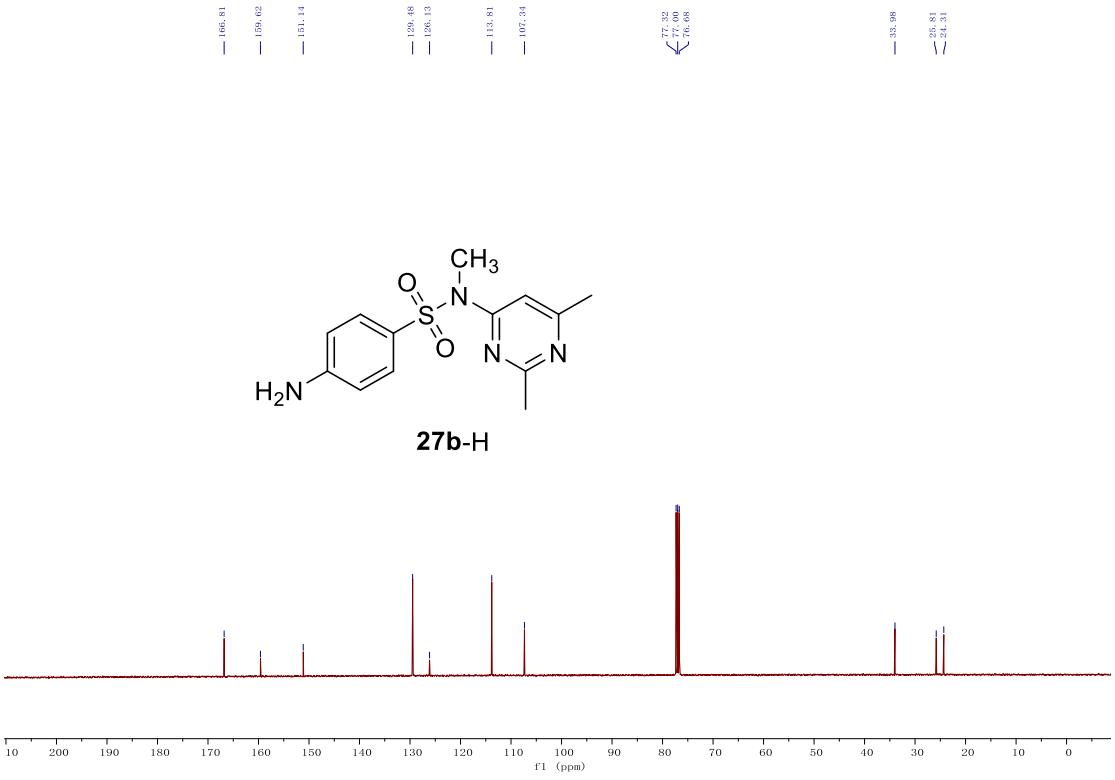

CD3
O
S
O
N
N
N
H2N

27b

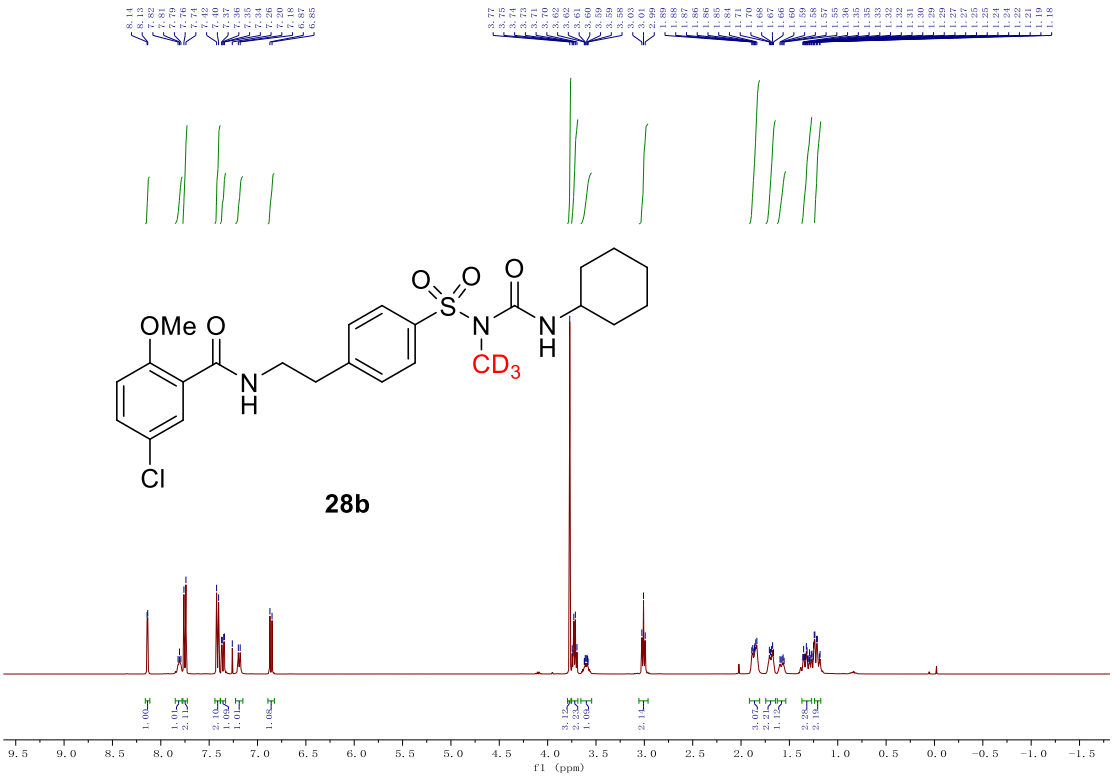

190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

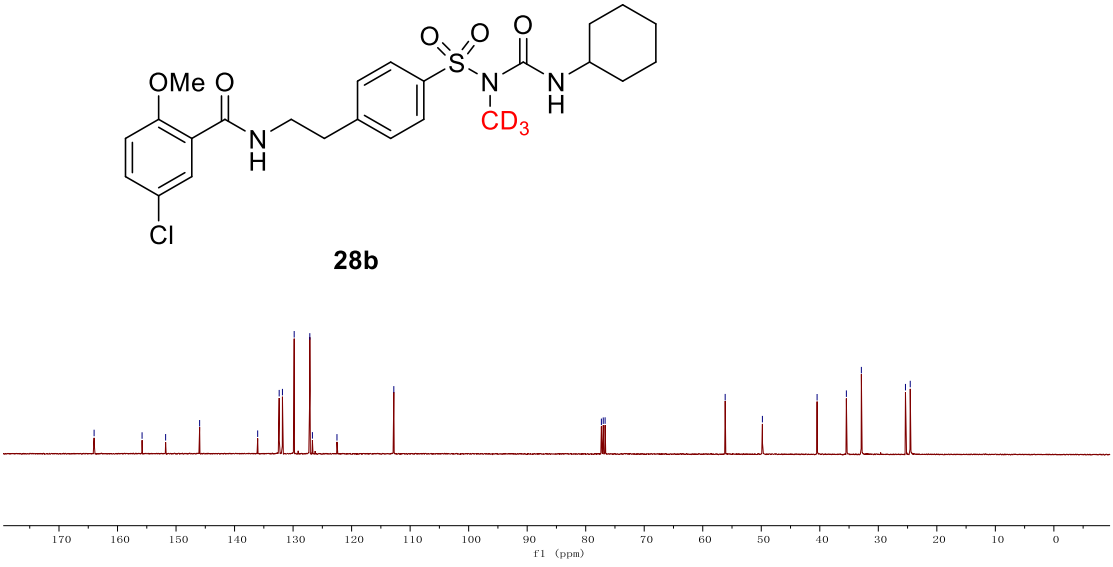

7.54
7.52
7.31
7.31
7.26
6.62
6.60
4.21
3.38
2.52
2.42
CH3
O
S
O
N
N
N
H2N
2.04
1.00
2.05
2.01
3.12
3.15
3.09
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

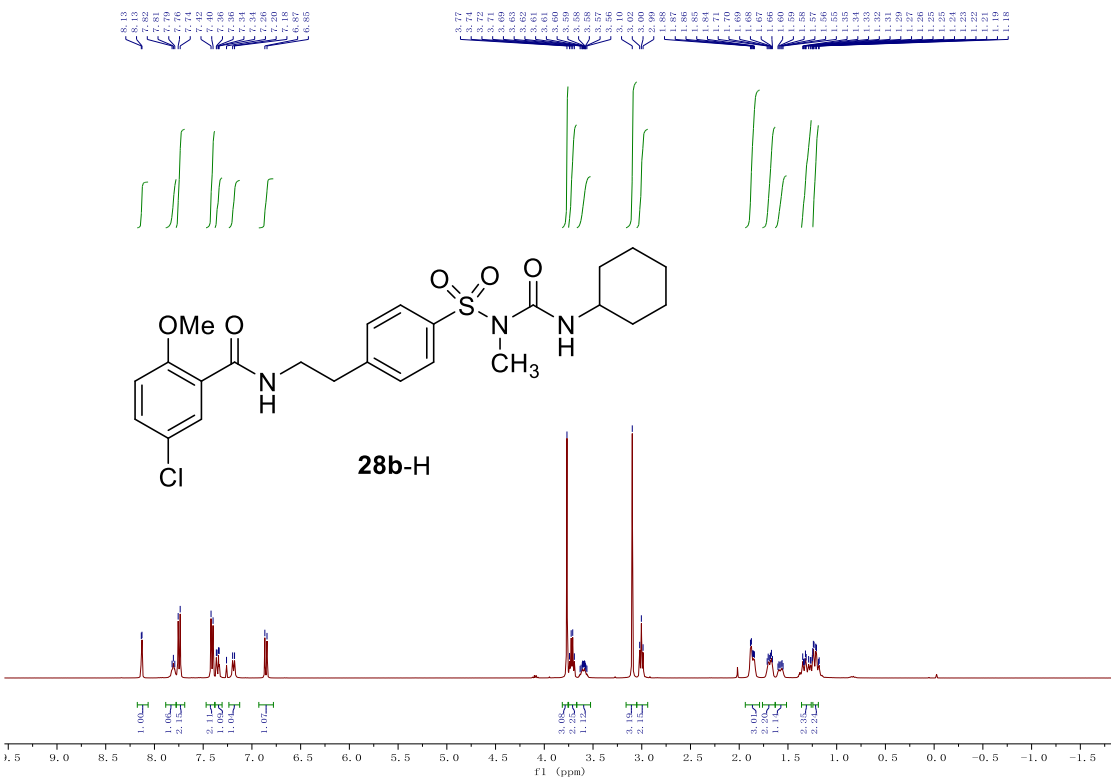
27b-H

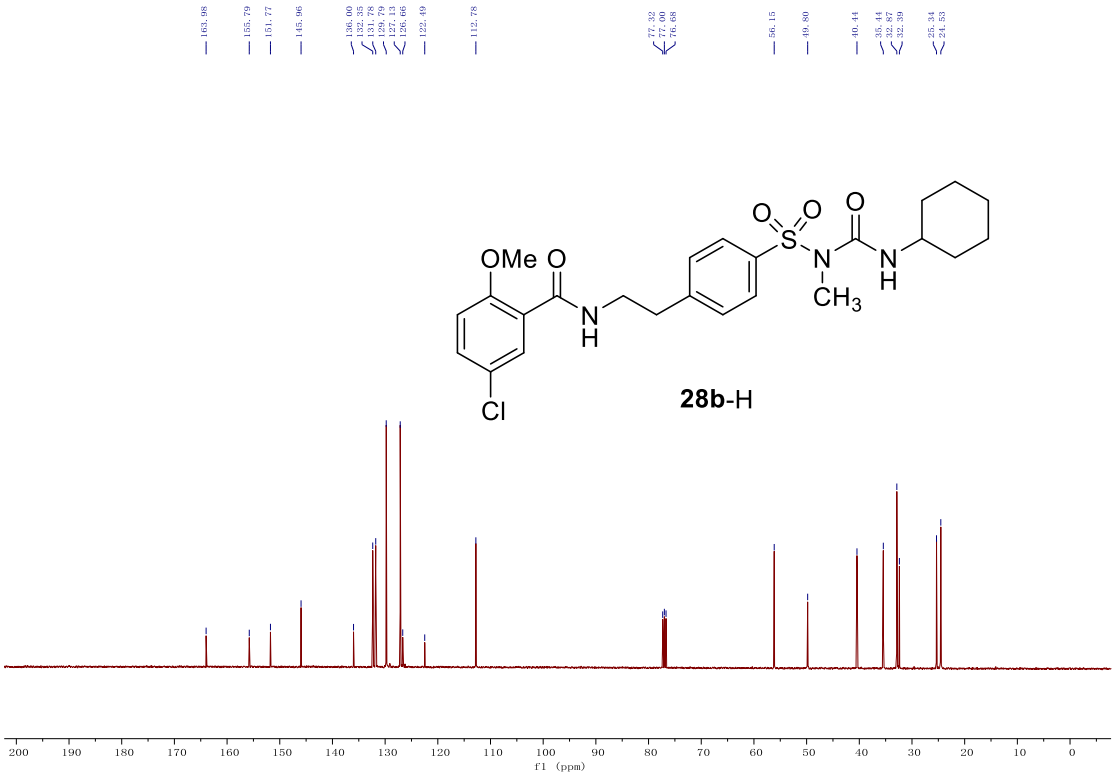

166.81
159.62
151.14
129.48
126.13
113.81
107.34
77.32
77.00
76.68
33.98
25.81
24.31
CH3
O
S
O
N
N
N
H2N
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

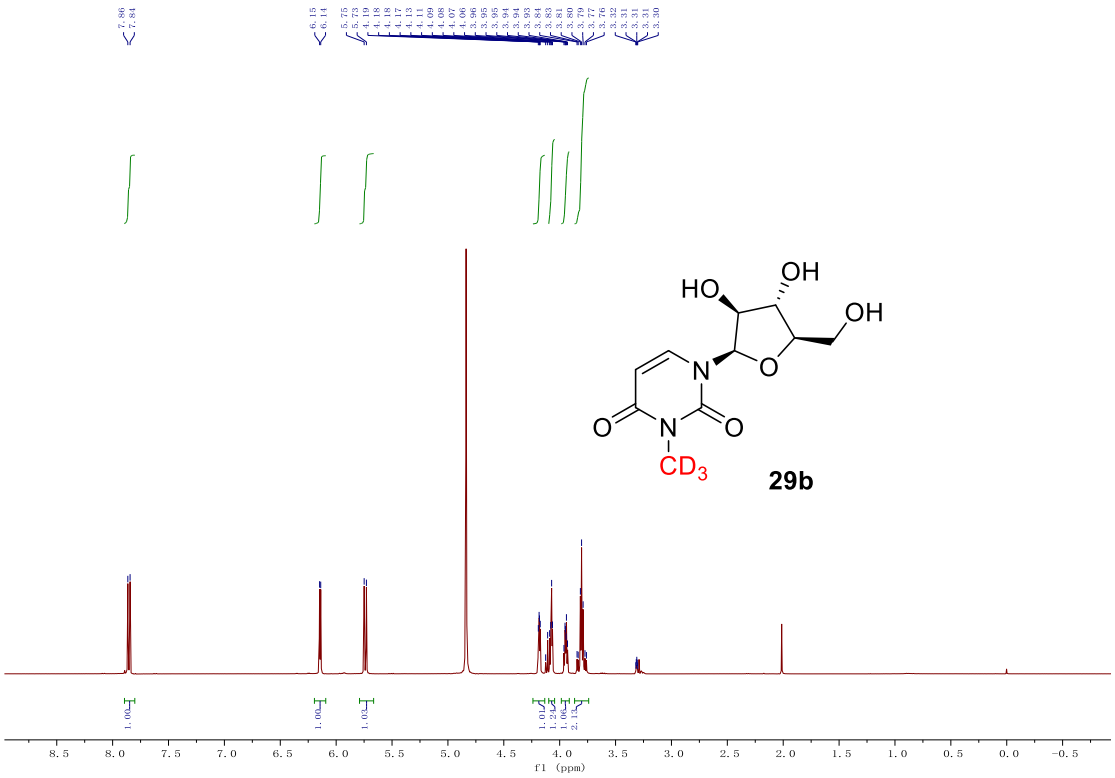
27b-H


OMe O
O
S
O
N
CD3
O
N
H
N
H
Cl
28b
f1 (ppm)

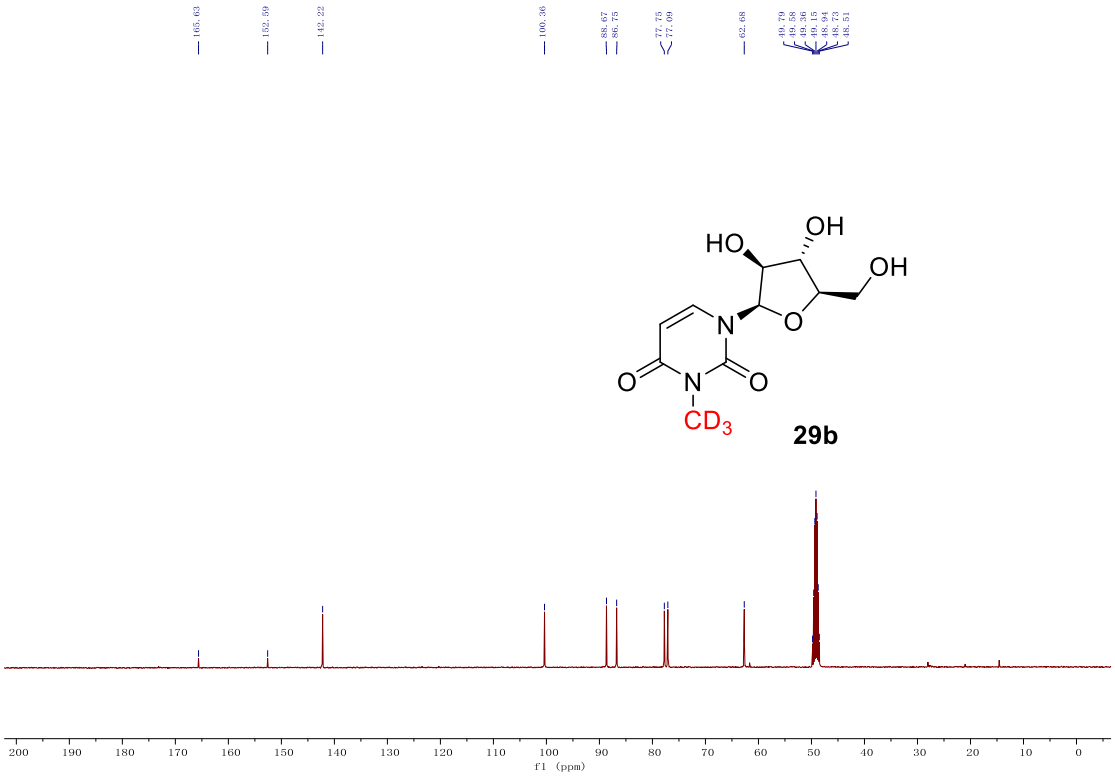

OMe O
O
S
O
N
CD3
O
N
H
N
H
Cl
28b
f1 (ppm)


OMe O
O
S
O
N
CH3
O
N
H
N
H
Cl
28b-H
f1 (ppm)

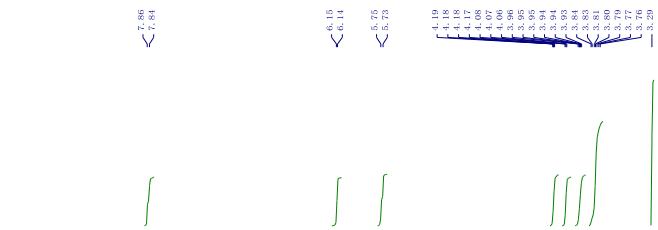

OMe O
O
S
O
N
CH3
O
N
H
N
H
Cl
28b-H
f1 (ppm)

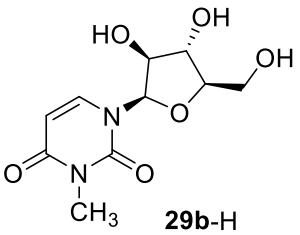


29b

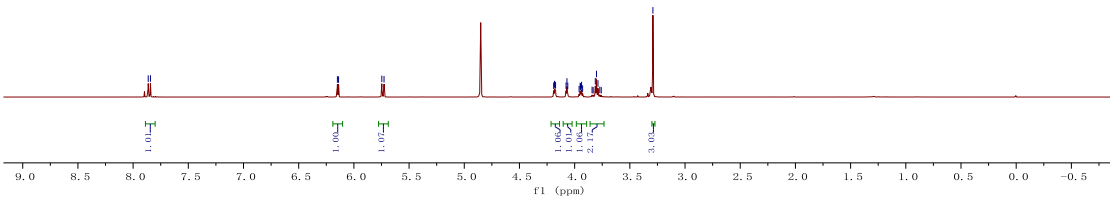


29b

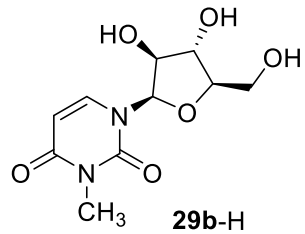

7.86
7.84
6.15
6.14
5.75
5.73
4.19
4.18
4.18
4.17
4.08
4.07
4.06
3.96
3.95
3.95
3.94
3.94
3.93
3.84
3.83
3.81
3.80
3.79
3.77
3.76
3.29


HO
OH
OH
N
O
O
N
O
CH3

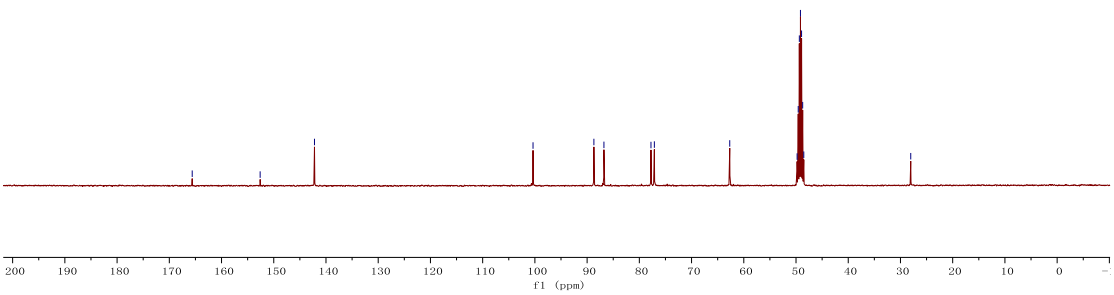
29b-H

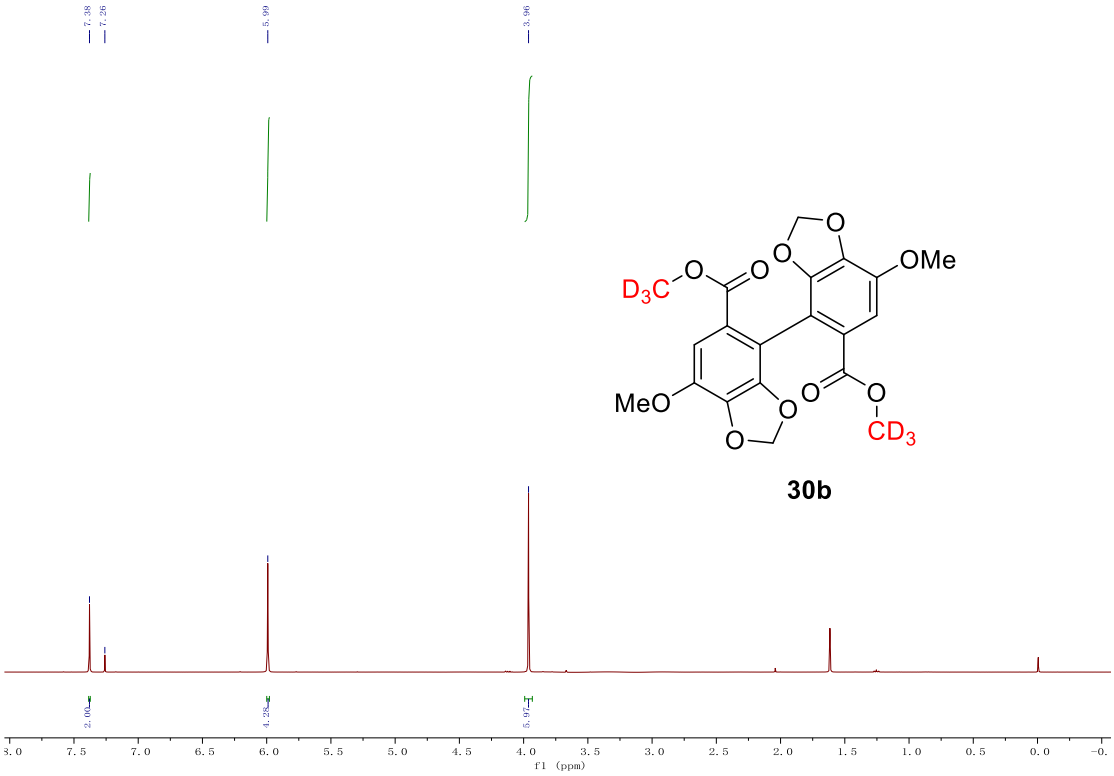

1.01
1.00
1.07
1.06
1.01
1.06
2.17
3.05
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)


165.62
152.61
142.20
100.35
88.70
86.78
77.77
77.12
62.69
49.79
49.58
49.36
49.15
48.94
48.72
48.51
28.03

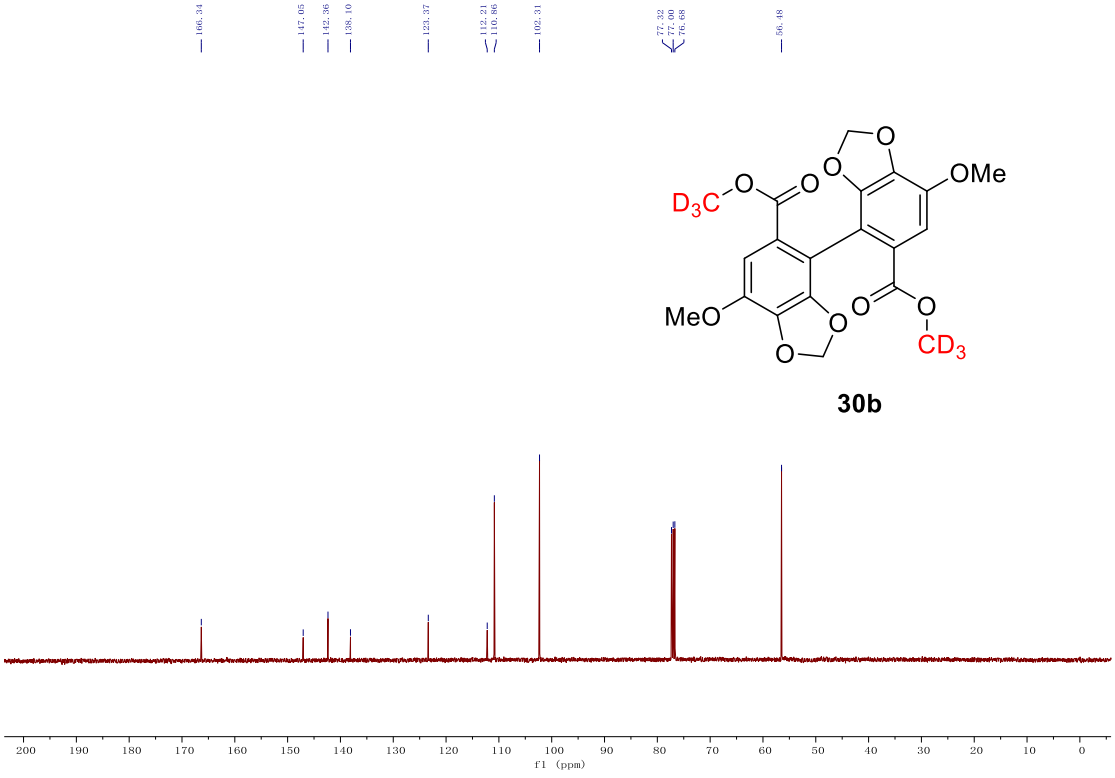

HO
OH
OH
N
O
O
N
O
CH3

29b-H

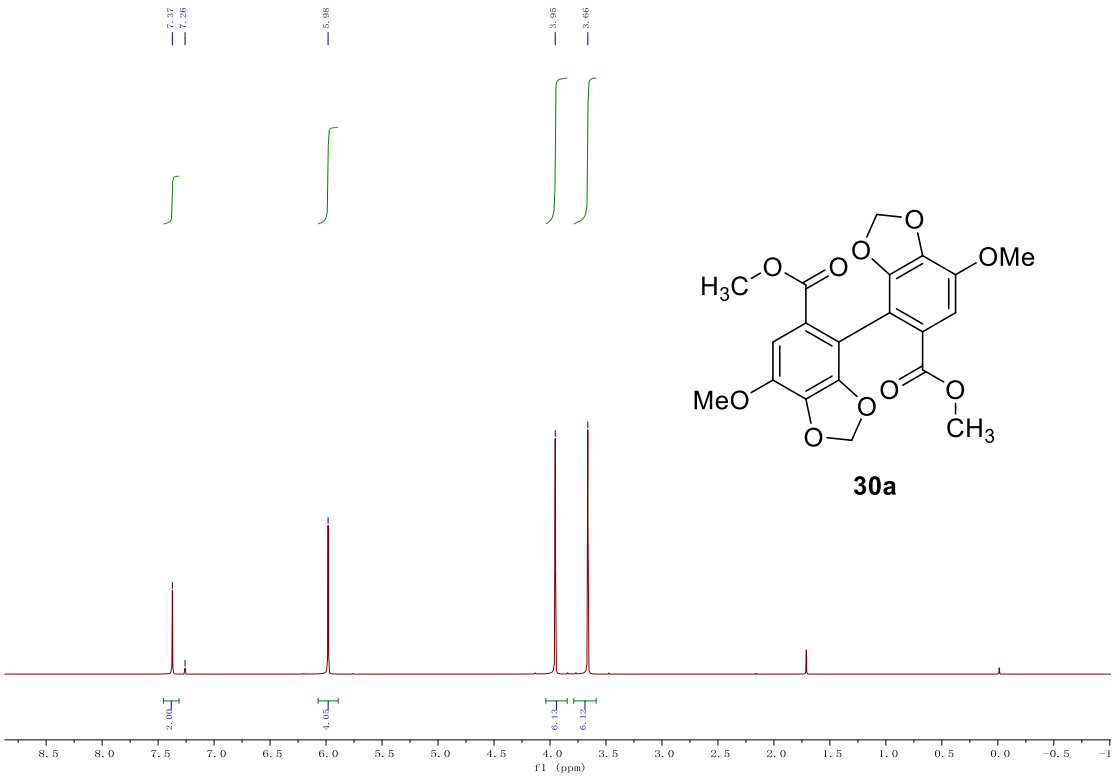

200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.38
7.26
5.99
5.96
OMe
D3C
O
MeO
CD3
2.00
4.28
5.97
3.0
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)

30b

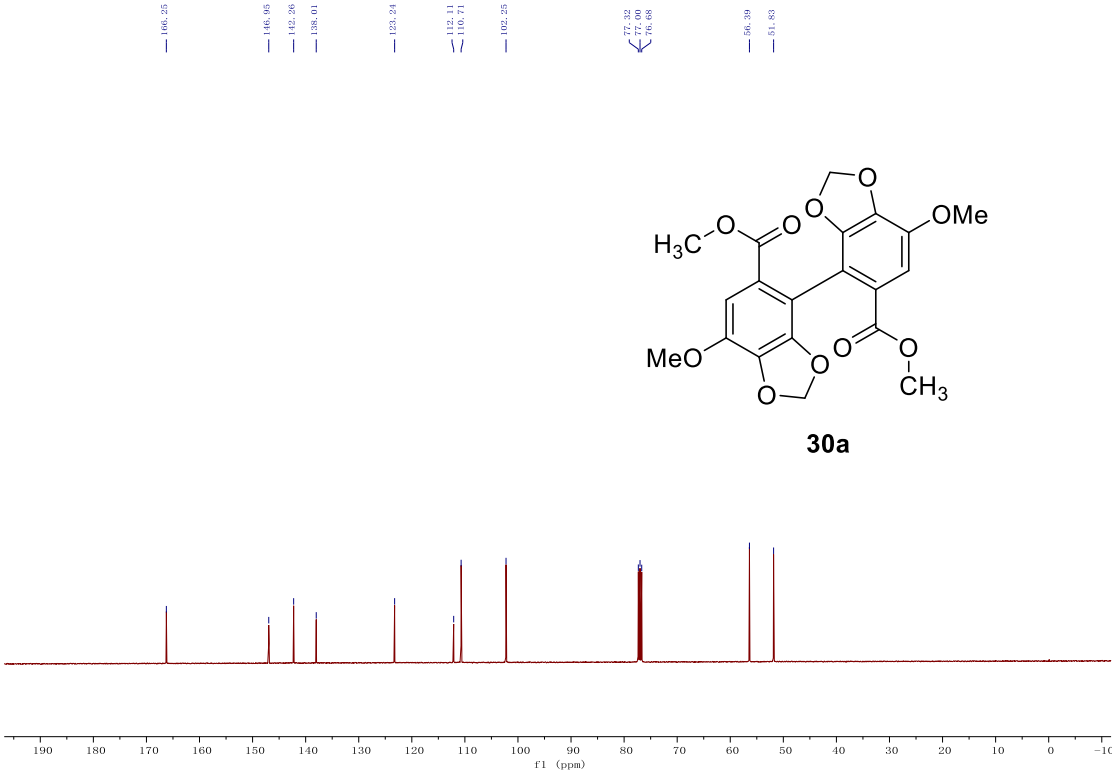

166.34
147.05
142.36
138.10
123.37
112.21
110.86
102.31
77.32
77.00
76.68
56.48
OMe
D3C
O
MeO
CD3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

30b


7.37
7.26
5.98
3.95
3.66
2.00
4.05
6.10
6.12
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)

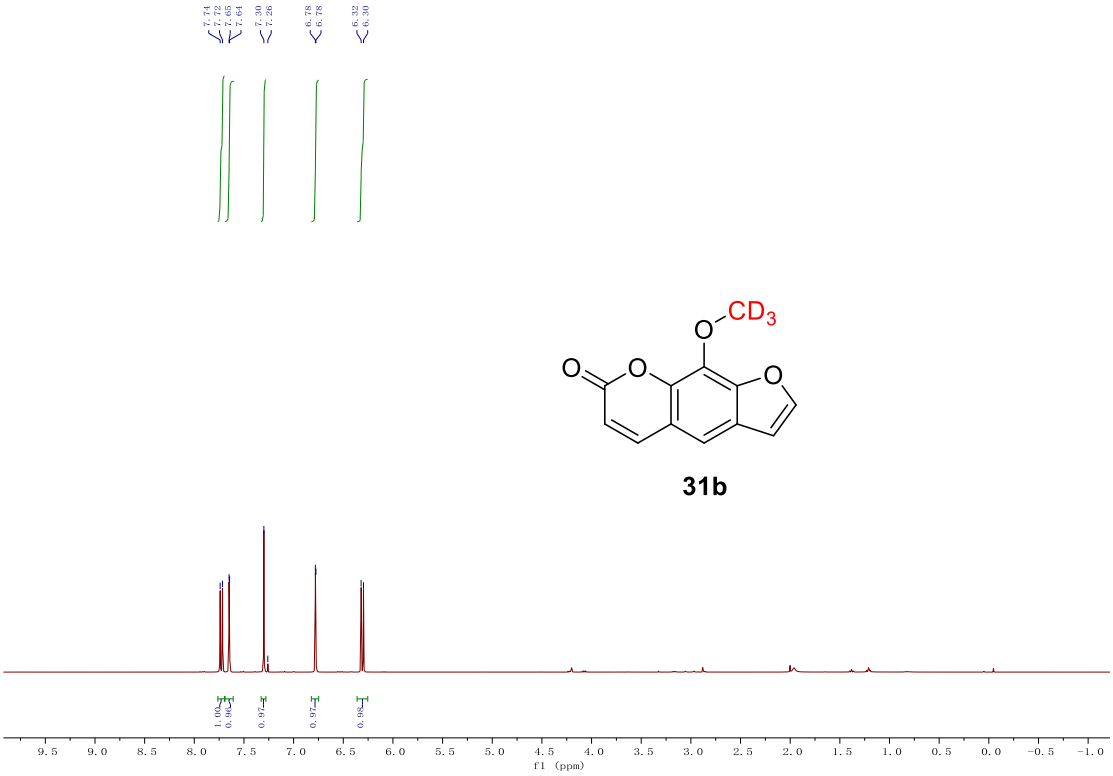
H3C
O
O
O
O
OMe
MeO
O
O
O
O
CH3

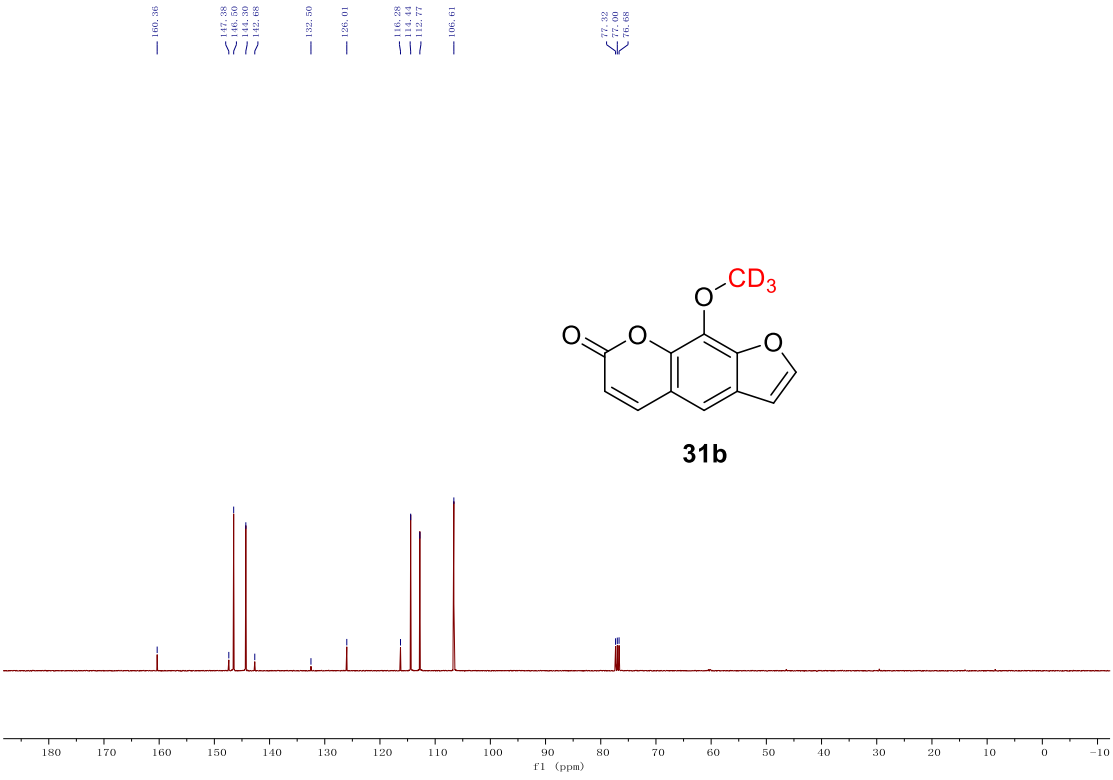
30a

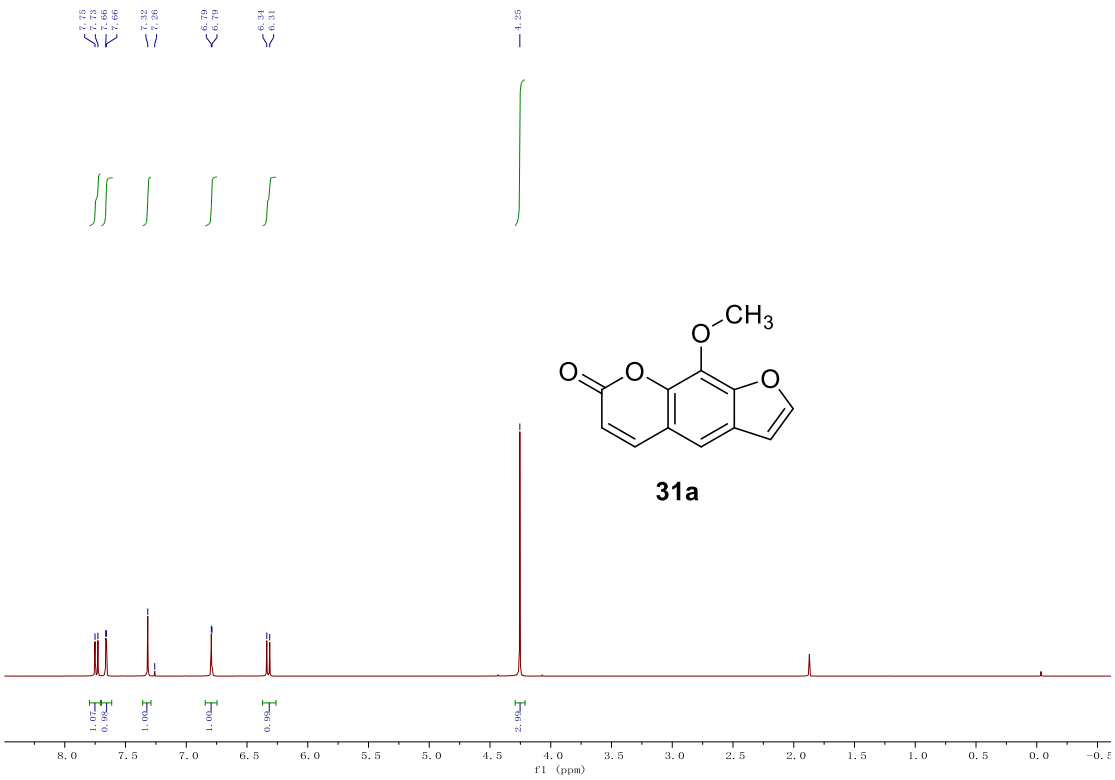

166.25
146.95
142.26
138.01
123.24
112.11
110.71
102.25
77.32
77.00
76.68
56.39
51.83
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

H3C
O
O
O
O
OMe
MeO
O
O
O
O
CH3

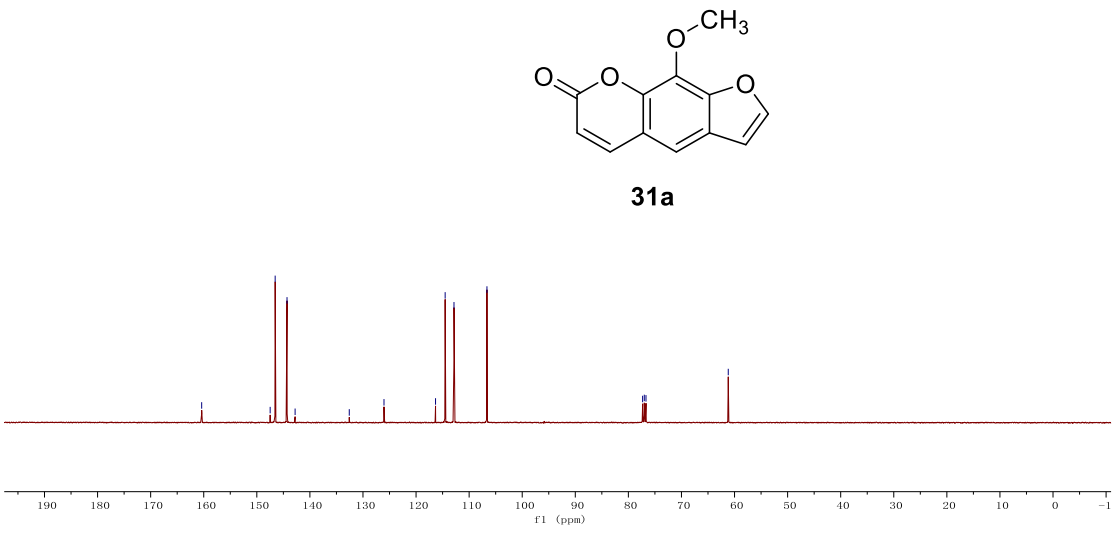
30a


7.74
7.72
7.65
7.64
7.30
7.26
6.78
6.78
6.32
6.30
CD3
O
O
O
O
31b
1.00
0.96
0.97
0.97
0.98
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 -0.5 -1.0
f1 (ppm)


160.36
147.38
146.50
144.30
142.68
132.50
126.01
116.28
114.44
112.77
106.61
77.32
77.00
76.68
CD3
O
O
O
O
31b
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

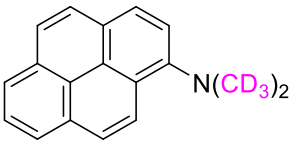

7.75
7.73
7.66
7.66
7.32
7.26
6.79
6.79
6.34
6.31
4.25
O
O
O
CH3
1.07
0.98
1.00
1.00
0.99
2.99
f1 (ppm)

31a

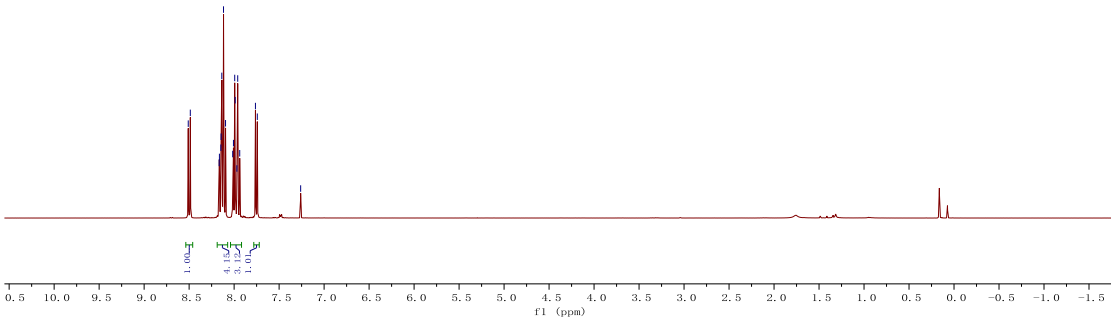

160.39
147.48
146.54
144.31
142.79
132.58
126.04
116.33
114.52
112.85
106.64
77.32
77.00
76.68
61.18
O
O
O
CH3
f1 (ppm)

31a

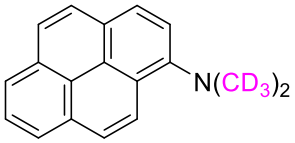

8.51
8.49
8.17
8.16
8.15
8.14
8.14
8.12
8.10
8.02
8.01
7.99
7.98
7.97
7.96
7.94
7.76
7.74
7.26


N(CD3)2

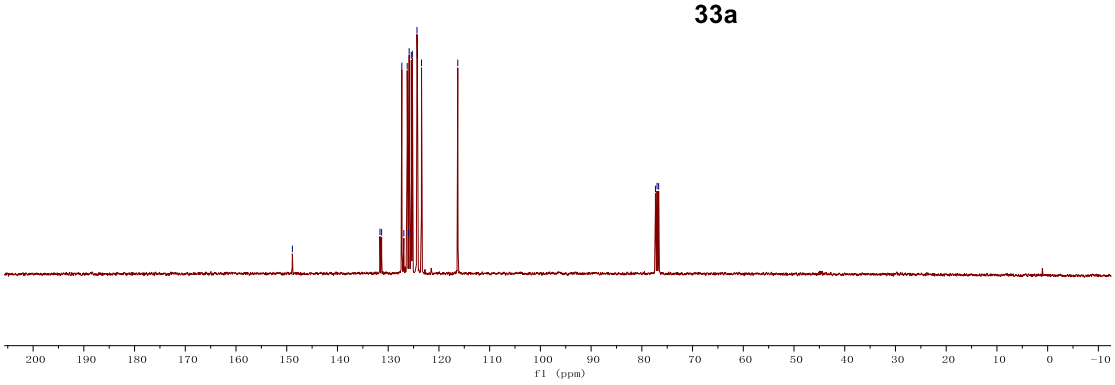
33a

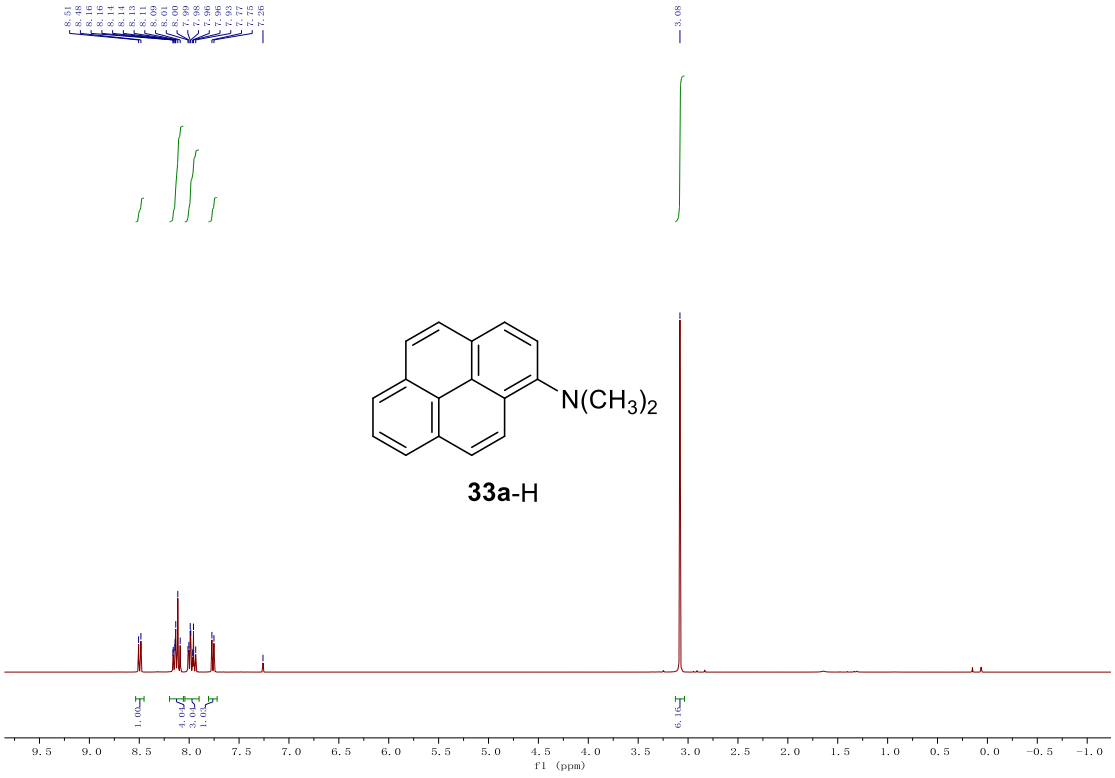

1.00
4.12
3.12
1.01
0.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5
f1 (ppm)


148.89
131.62
131.00
127.31
126.92
126.25
126.07
125.87
125.44
125.24
124.33
124.25
123.43
116.28
77.32
77.00
76.68

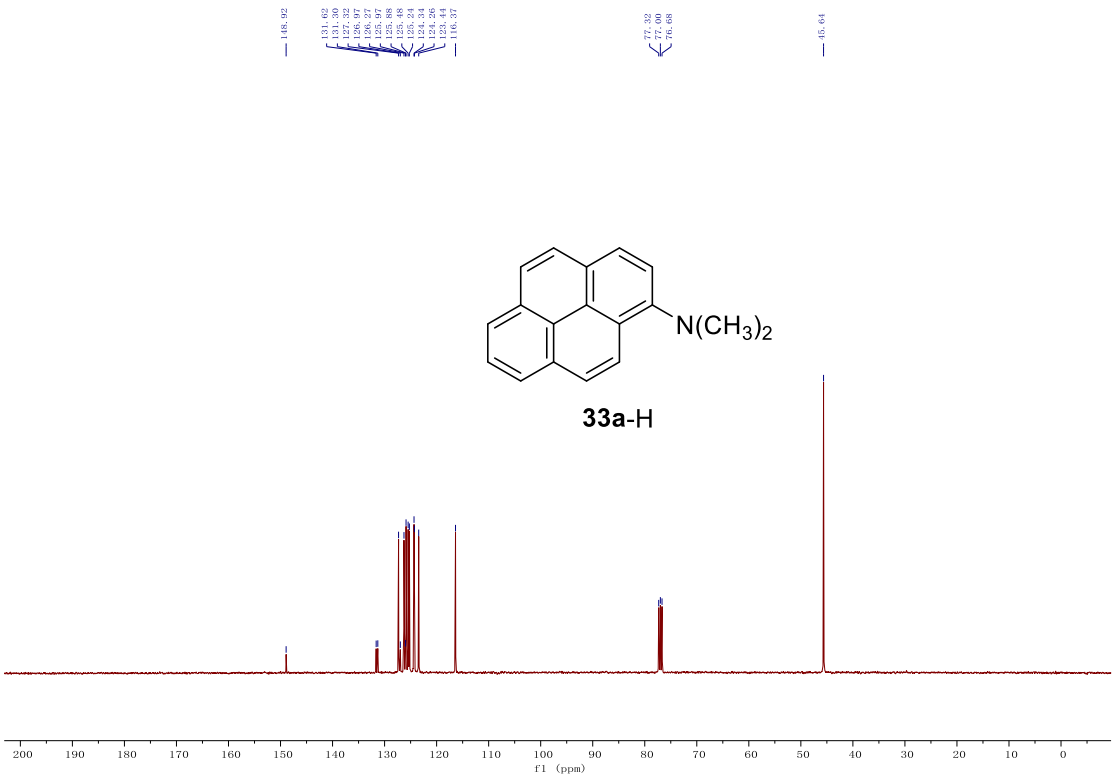

N(CD3)2

33a

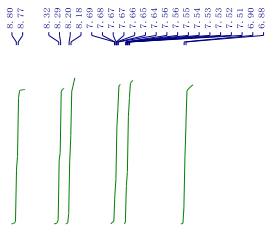

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

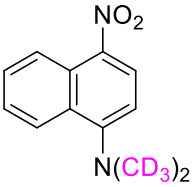

8.51
8.48
8.15
8.15
8.14
8.14
8.13
8.11
8.00
8.00
7.99
7.98
7.96
7.96
7.93
7.77
7.77
7.75
7.26
3.08
N(CH3)2
1.00
4.04
3.04
1.03
6.16
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

33a-H

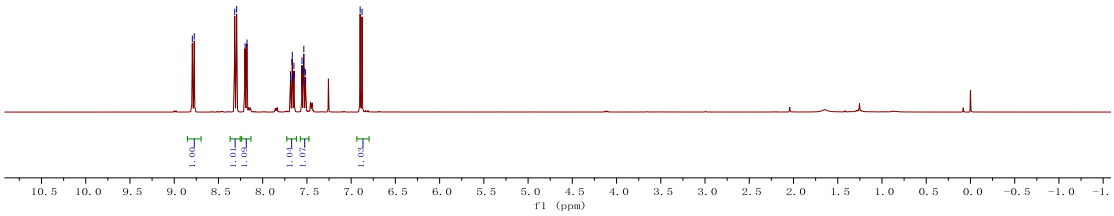

148.92
131.62
131.30
127.32
126.97
126.27
125.57
125.48
125.24
124.34
124.26
123.44
116.37
77.32
77.00
76.68
45.64
N(CH3)2
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

33a-H

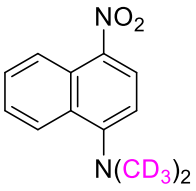

8.80
8.77
8.32
8.29
8.20
8.18
7.69
7.68
7.67
7.67
7.66
7.65
7.64
7.56
7.56
7.55
7.54
7.53
7.53
7.52
7.51
6.90
6.88


NO2
N(CD3)2

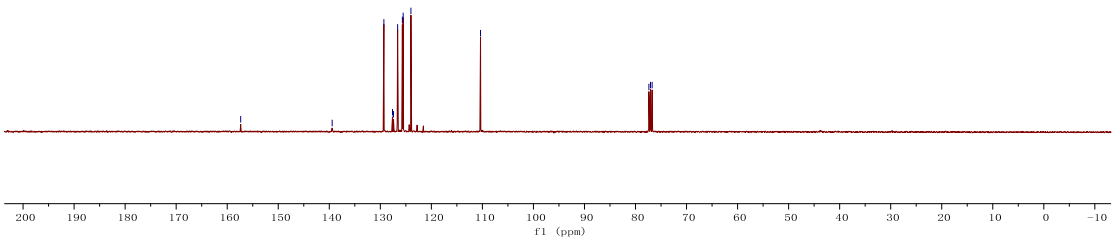
33b

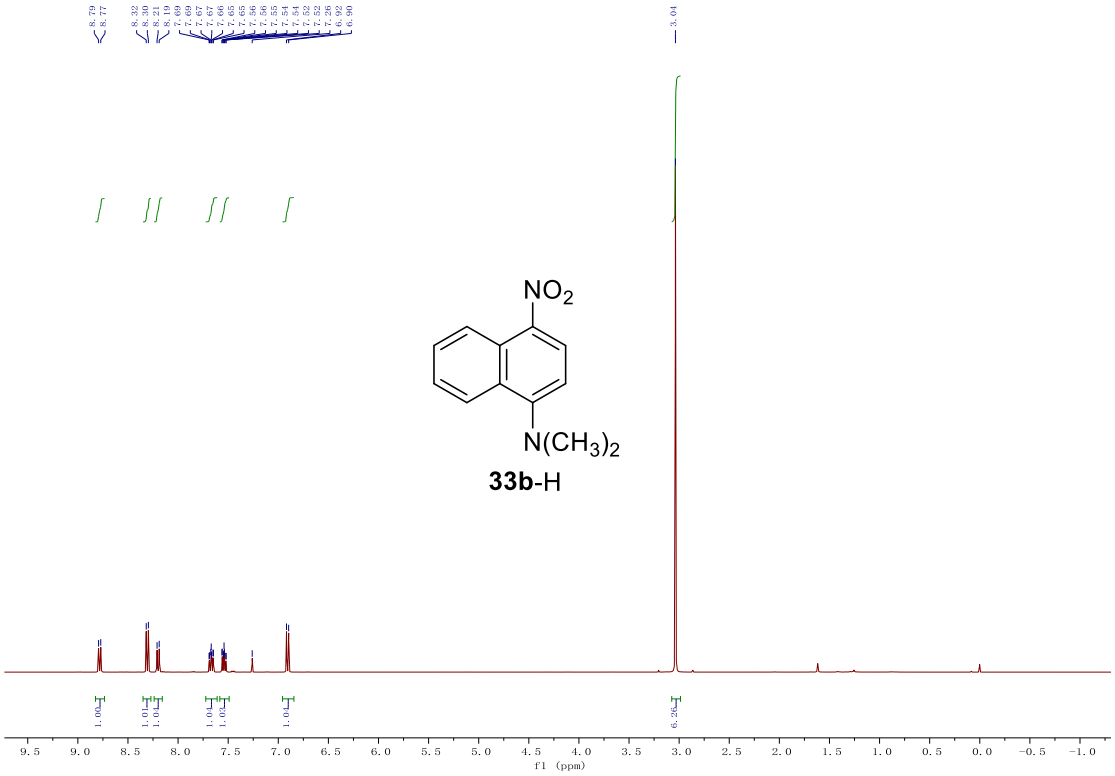

1.00
1.01
1.05
1.04
1.07
1.03
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.
f1 (ppm)

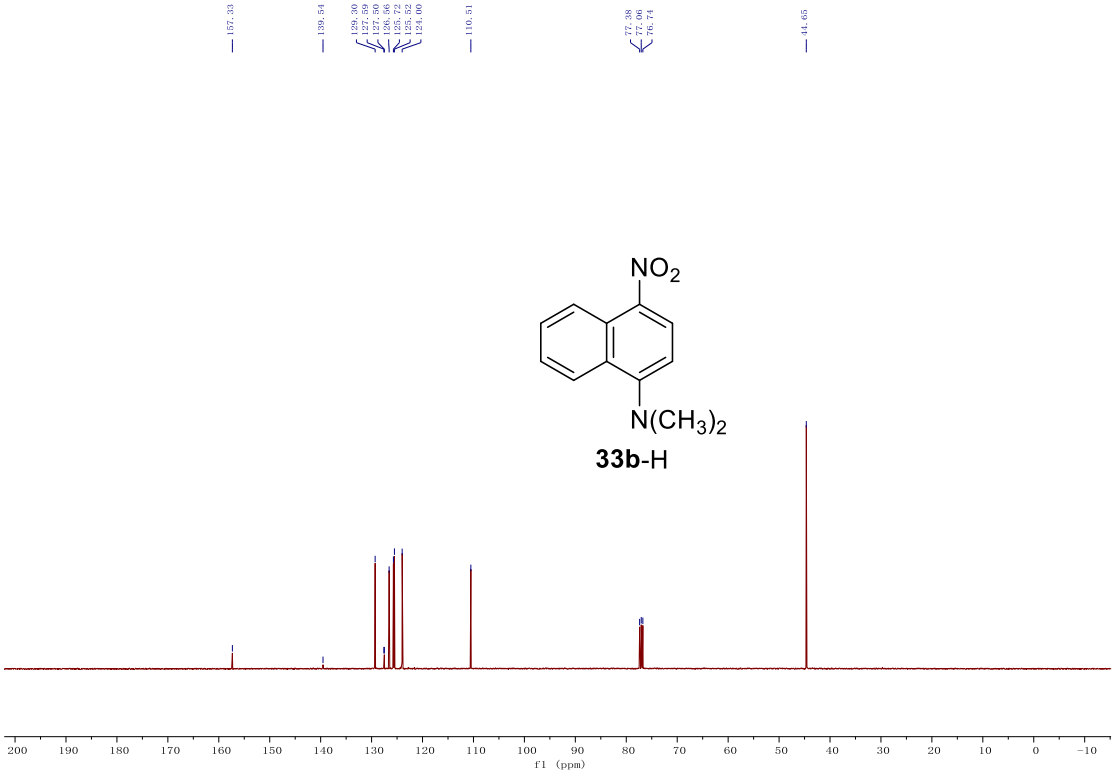

157.36
139.44
129.30
127.62
127.43
126.61
125.68
125.52
124.01
110.37
77.38
77.06
76.74

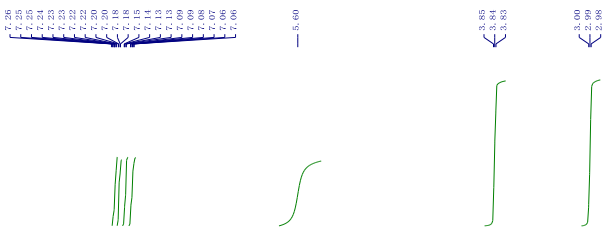

NO2
N(CD3)2

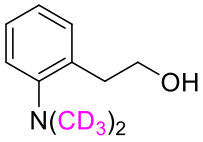
33b


200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

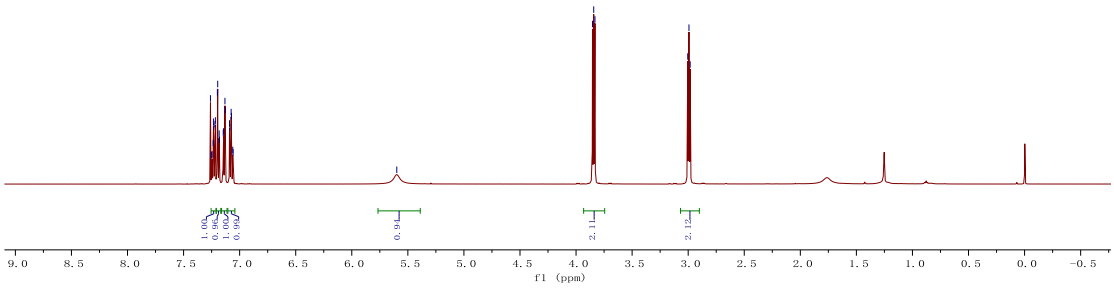

8.79
8.77
8.32
8.30
8.13
8.11
7.69
7.67
7.67
7.66
7.65
7.65
7.56
7.56
7.55
7.54
7.54
7.52
7.52
7.26
6.92
6.90
3.04
NO2
N(CH3)2
33b-H
1.00
1.01
1.04
1.04
1.02
1.04
6.26
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

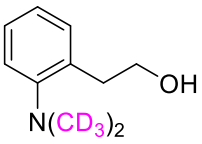

157.33
139.54
129.30
127.89
127.50
126.96
125.72
125.52
124.00
110.51
77.38
77.06
76.74
44.65
NO2
N(CH3)2
33b-H
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



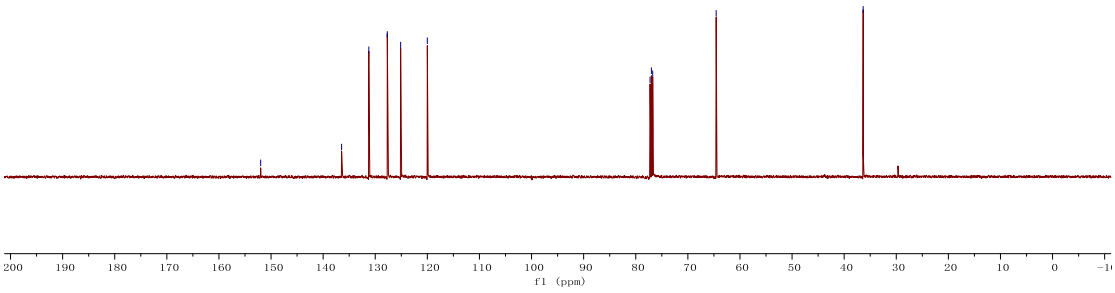


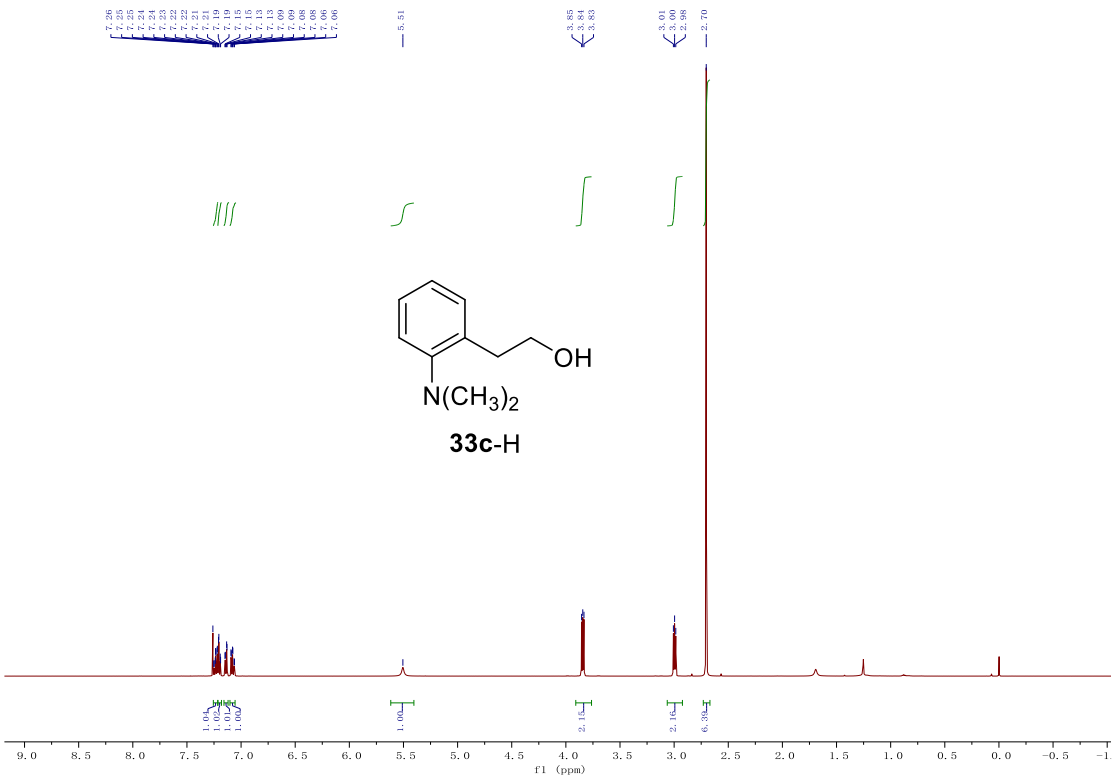
33c

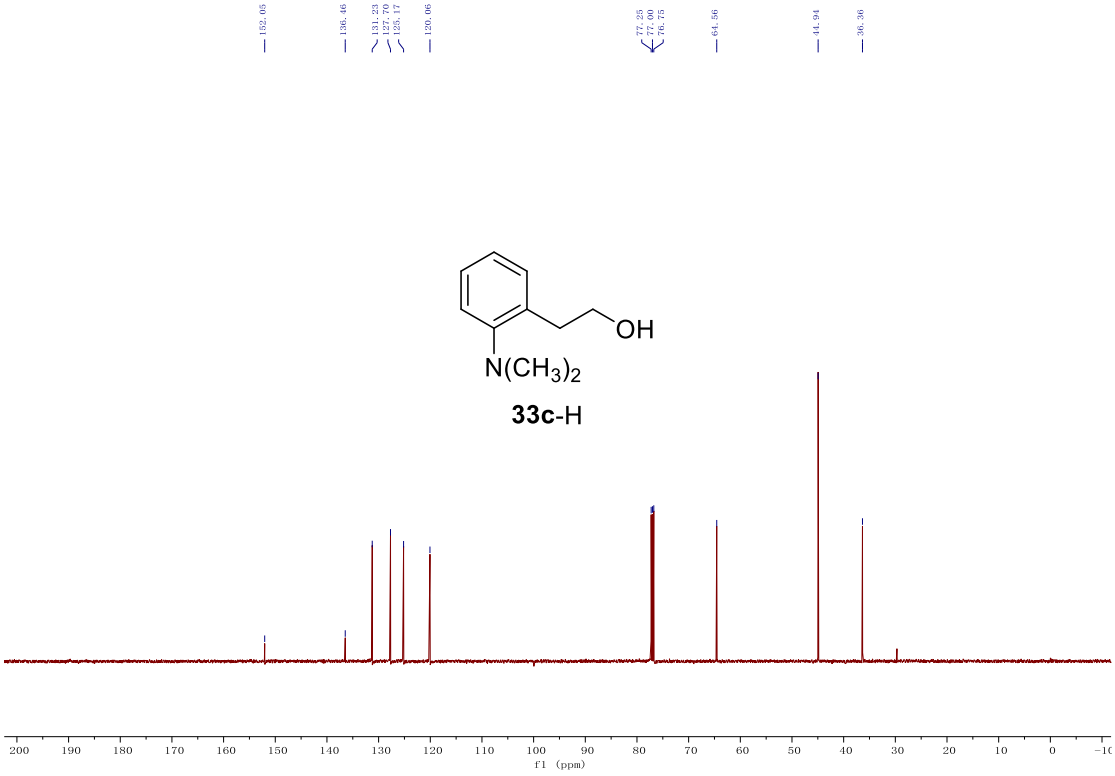


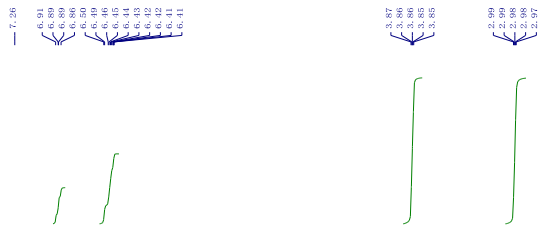


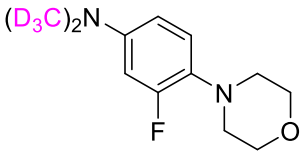
33c



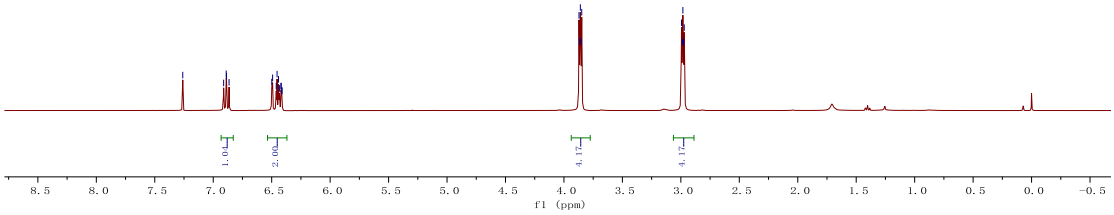

7.26
7.25
7.25
7.24
7.24
7.24
7.23
7.22
7.22
7.22
7.21
7.21
7.19
7.19
7.17
7.15
7.13
7.13
7.09
7.09
7.08
7.08
7.06
7.06
5.51
3.85
3.84
3.83
3.01
3.00
2.98
2.70
OH
N(CH3)2
33c-H
1.04
1.02
1.01
1.00
1.00
2.16
2.16
6.38
f1 (ppm)

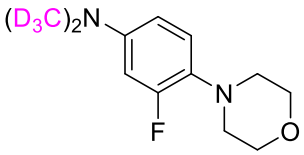

192.05
136.46
131.23
127.70
125.17
120.06
77.25
77.00
76.75
64.56
44.94
36.36
OH
N(CH3)2
33c-H
f1 (ppm)



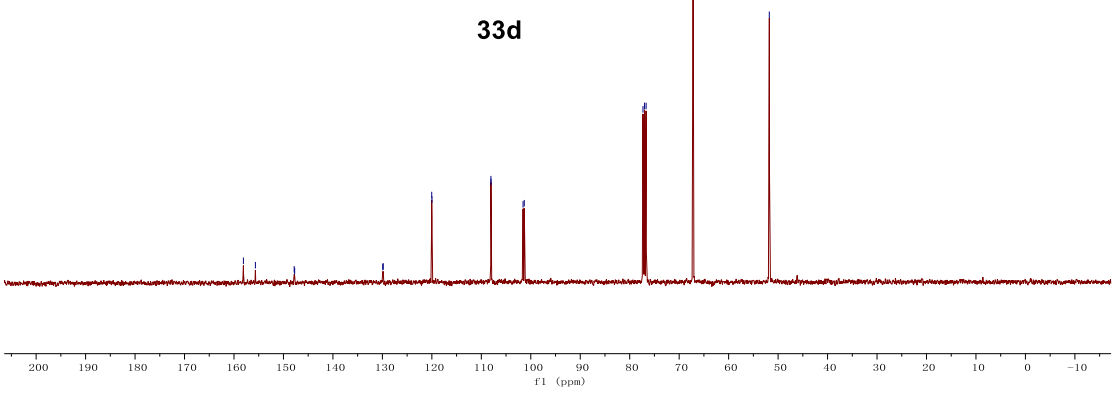


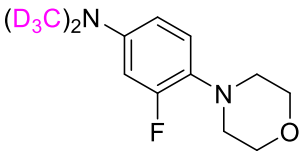
33d



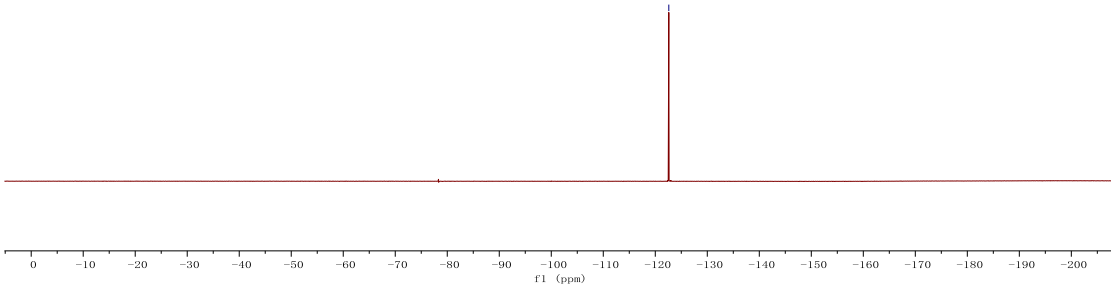


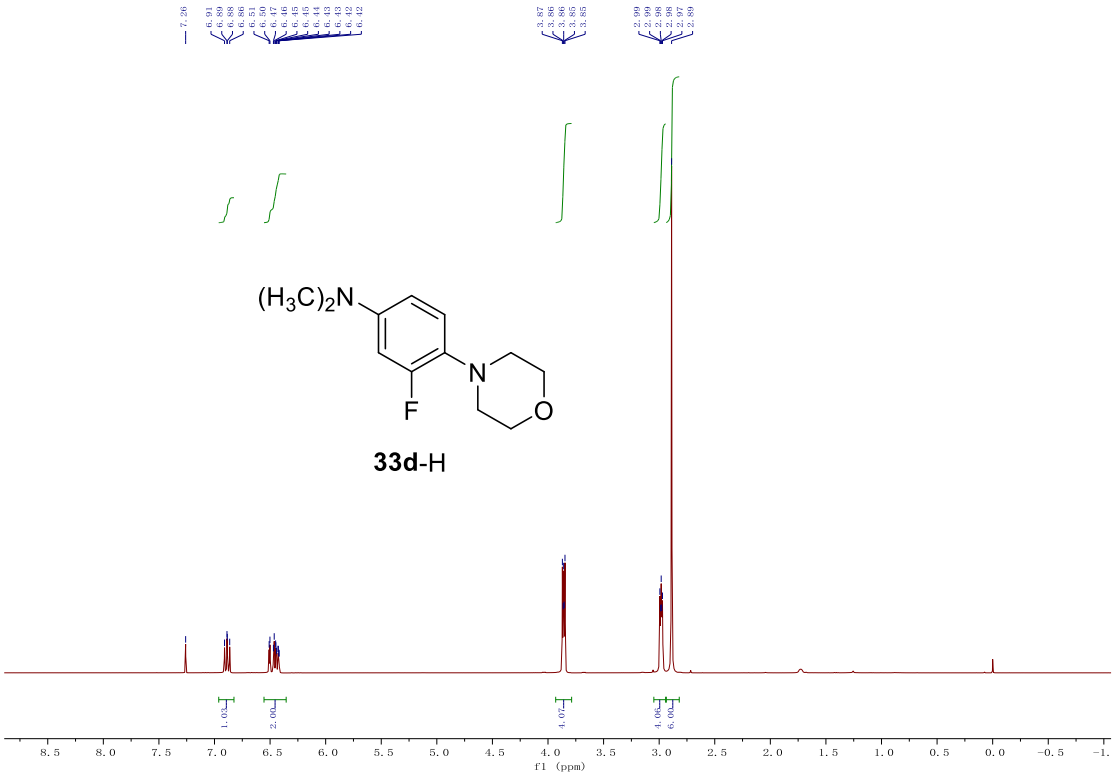
33d




(D3C)2N
F
N
O

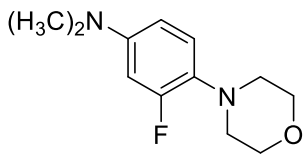
33d


-122.60
f1 (ppm)

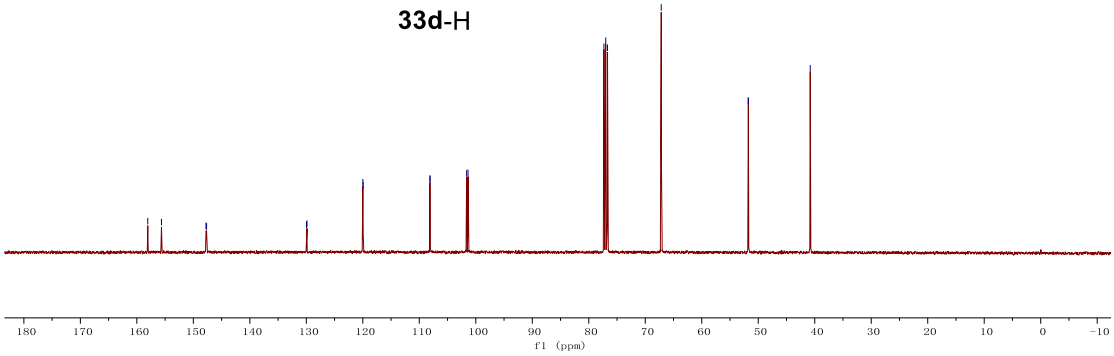

7.26
6.91
6.89
6.88
6.86
6.53
6.50
6.47
6.46
6.45
6.45
6.44
6.43
6.43
6.42
6.42
3.87
3.86
3.86
3.85
3.85
2.99
2.99
2.98
2.98
2.97
2.89
(H3C)2N
F
N
O
1.03
2.00
4.07
4.08
6.00
f1 (ppm)

33d-H

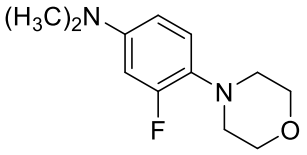
158.07
155.64
147.76
147.66
129.98
129.88
119.99
119.94
108.12
108.09
101.62
101.38
77.32
77.00
76.68
67.17
51.78
51.75
40.80



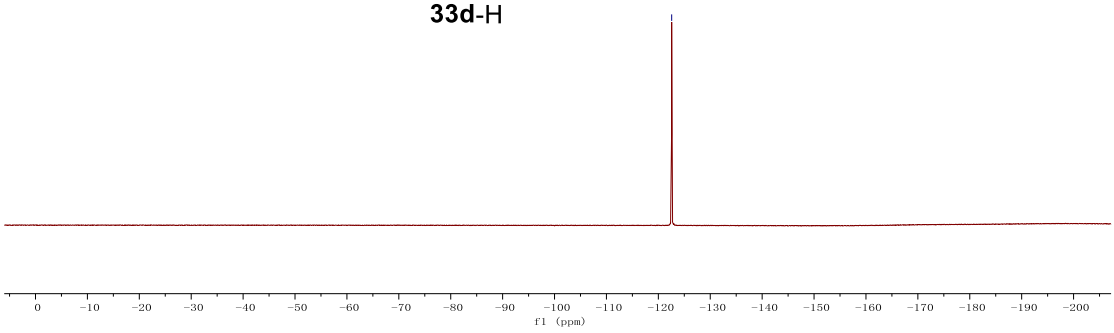
33d-H

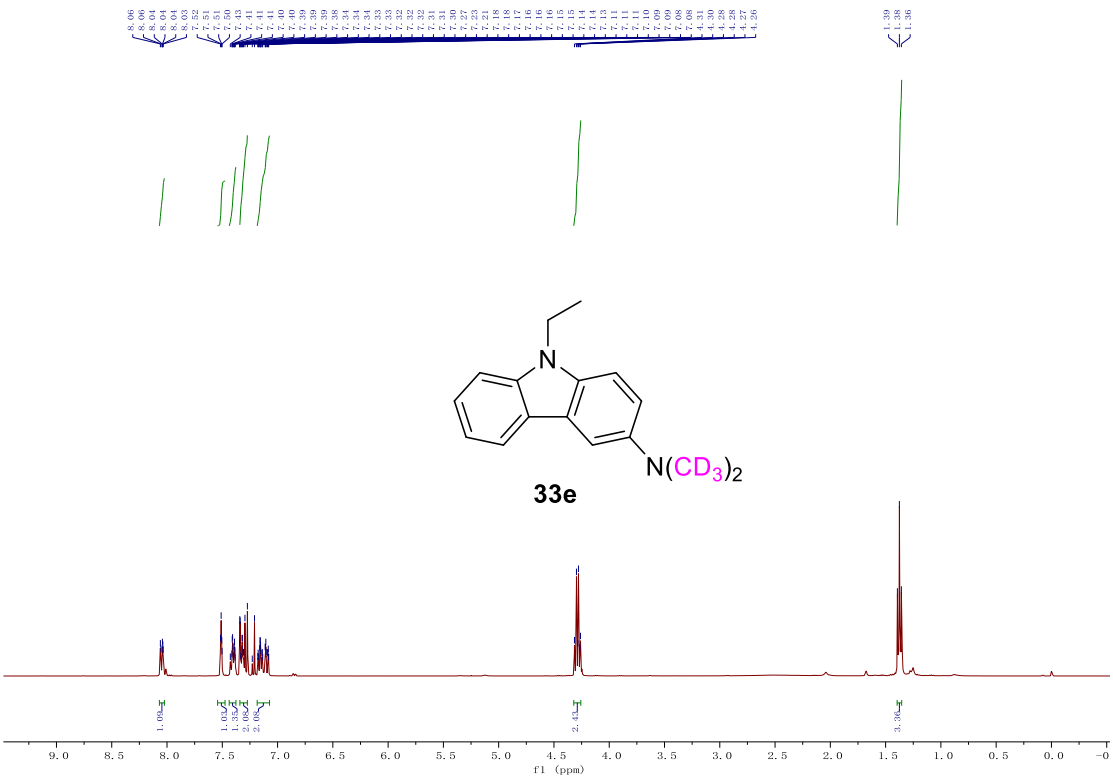


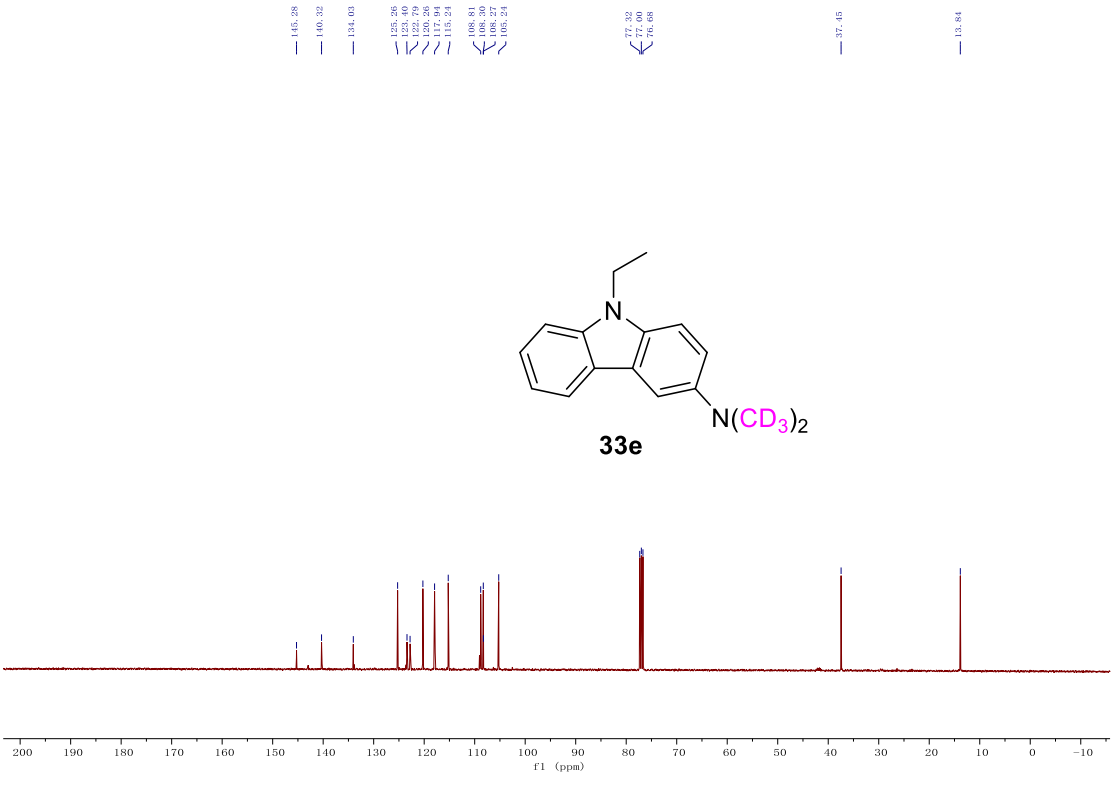
−122.57

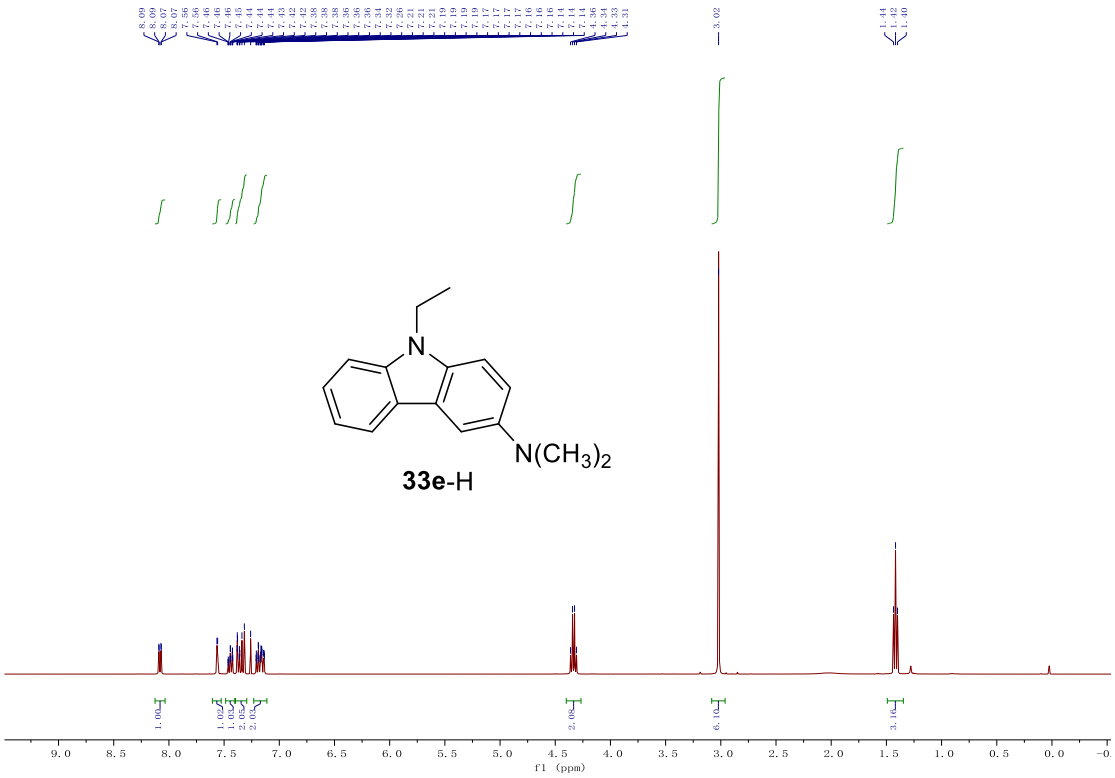


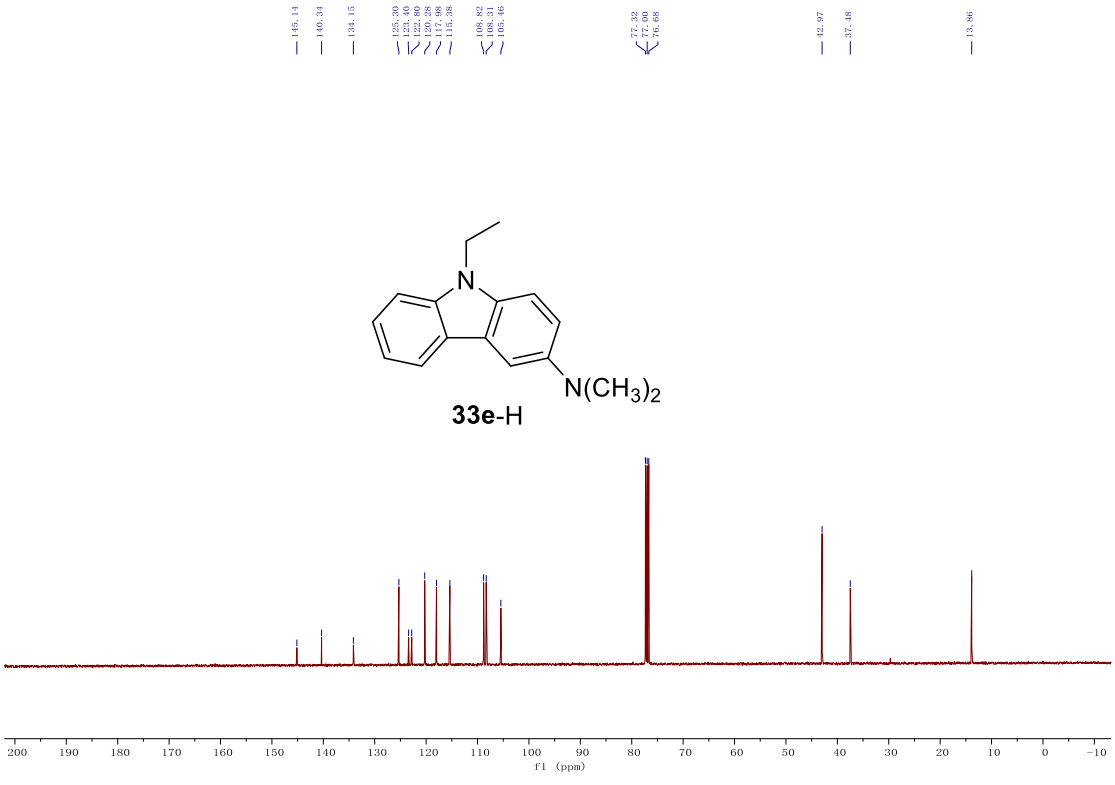
33d-H

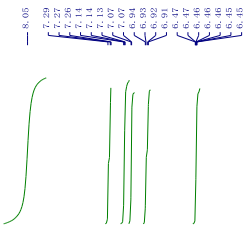


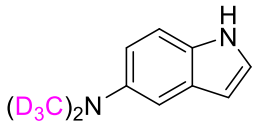

8.06
8.06
8.04
8.04
8.04
8.03
7.52
7.51
7.50
7.45
7.41
7.41
7.41
7.40
7.40
7.39
7.39
7.38
7.34
7.34
7.33
7.33
7.32
7.32
7.31
7.30
7.27
7.26
7.21
7.18
7.17
7.17
7.16
7.16
7.16
7.15
7.15
7.14
7.14
7.13
7.11
7.11
7.10
7.09
7.09
7.08
7.08
7.31
7.31
7.30
7.28
7.28
7.27
7.26
1.39
1.38
1.38
N(CD3)2
33e
1.00
1.03
1.33
2.08
2.00
2.44
3.38
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 −0
f1 (ppm)


145.28
140.32
134.03
125.26
123.40
122.79
120.26
117.94
115.24
108.81
108.30
108.27
105.24
77.32
77.00
76.68
37.45
13.84
N(CD3)2
33e
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

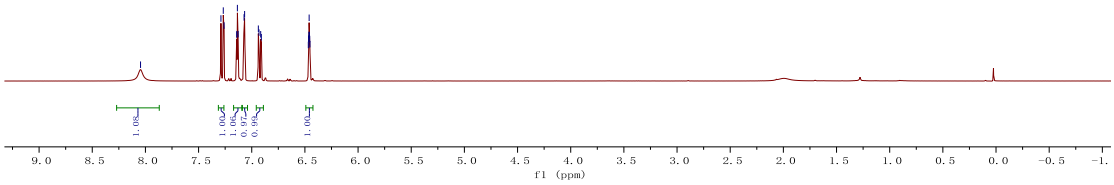

8.09
8.09
8.07
8.07
7.56
7.56
7.46
7.46
7.45
7.45
7.44
7.44
7.43
7.43
7.42
7.42
7.38
7.38
7.38
7.36
7.36
7.36
7.34
7.32
7.26
7.21
7.21
7.21
7.19
7.19
7.19
7.17
7.17
7.17
7.17
7.16
7.16
7.16
7.15
7.14
7.14
4.36
4.34
4.33
4.31
3.02
1.44
1.42
1.40
N
N(CH3)2
33e-H
1.00
1.02
1.03
2.02
2.00
2.08
6.10
3.10
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)

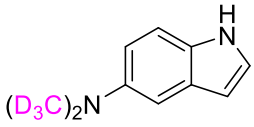

145.14
140.34
134.16
125.30
123.40
122.80
120.28
117.98
115.38
108.82
108.31
105.46
77.32
77.00
76.68
42.97
37.48
13.86
N
N(CH3)2
33e-H
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



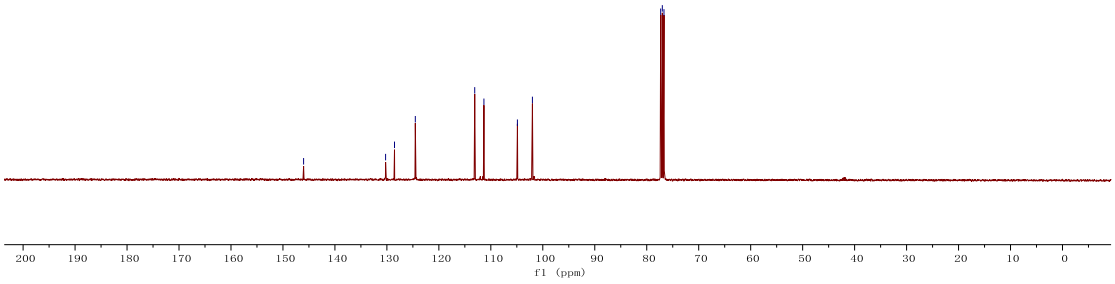


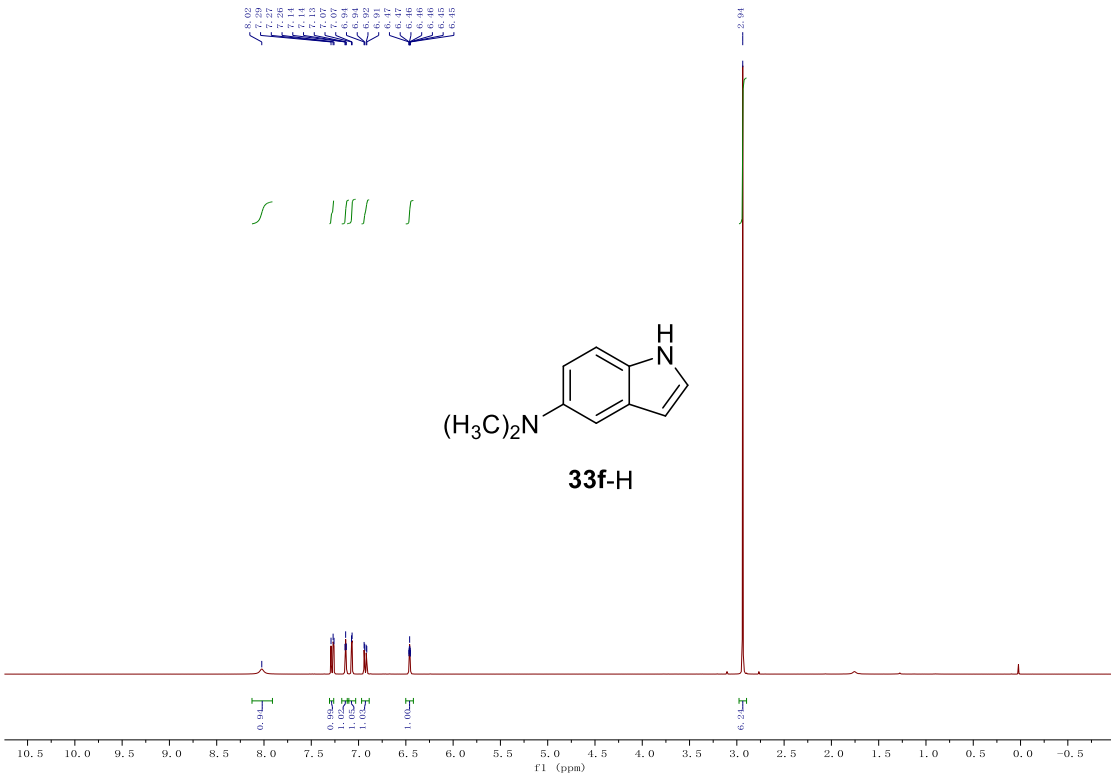
33f



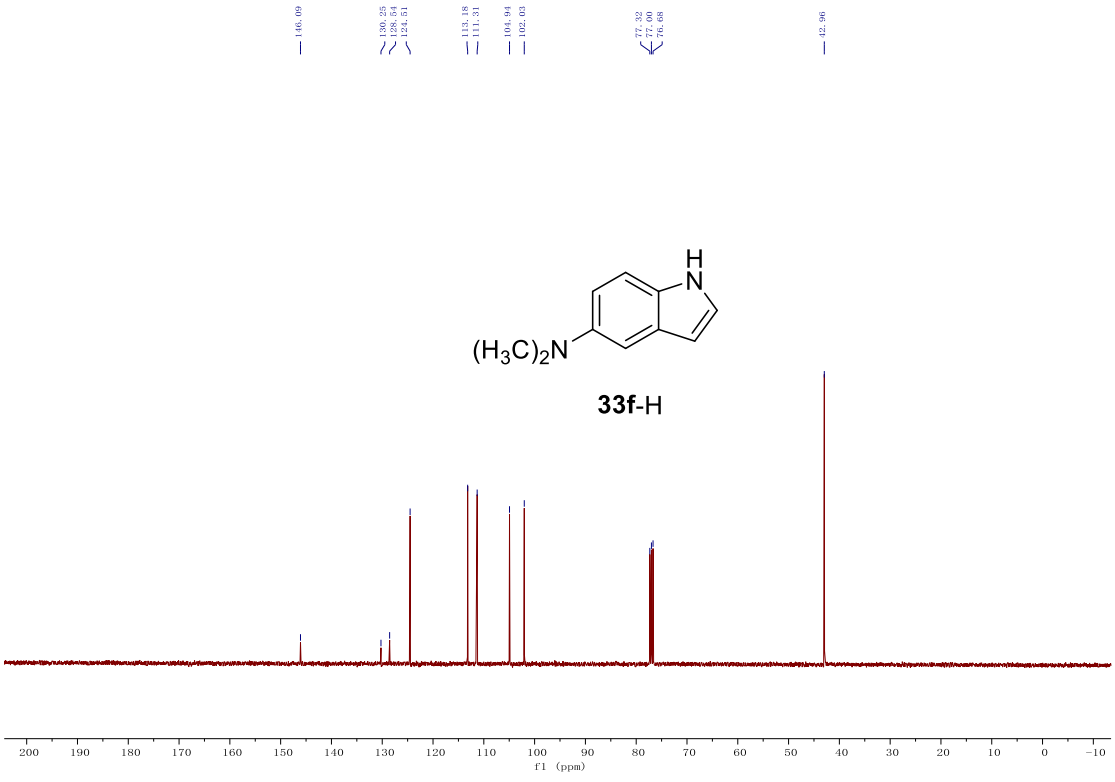


33f

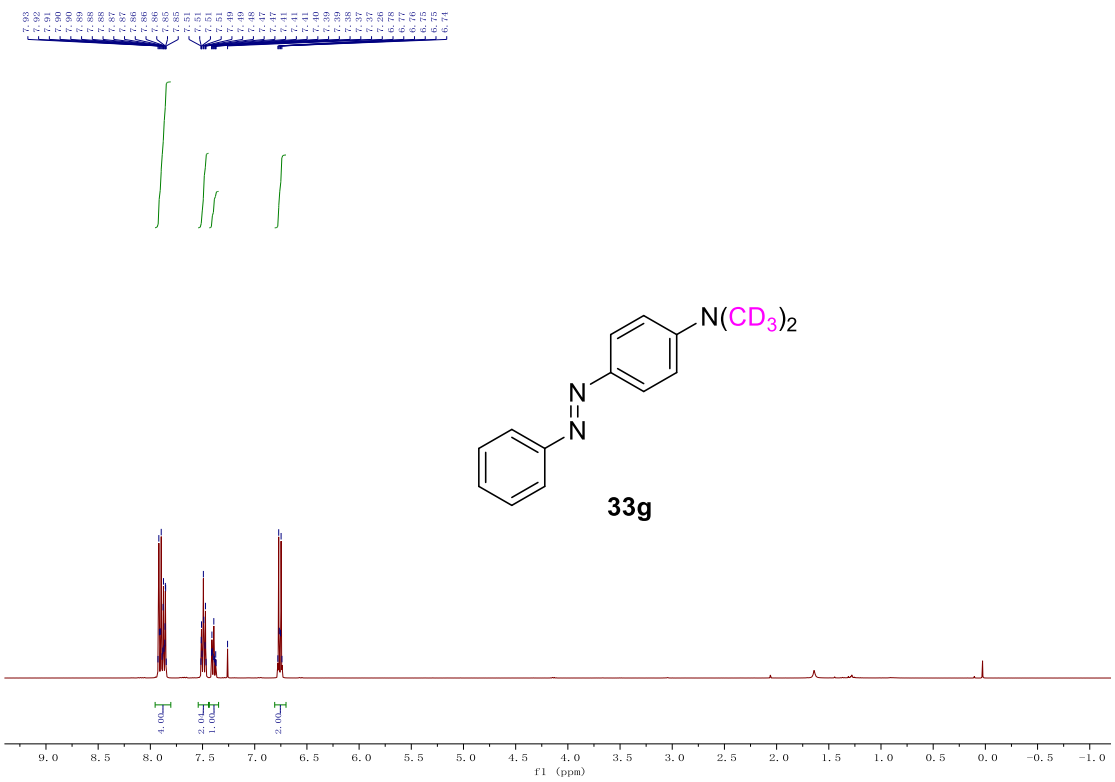


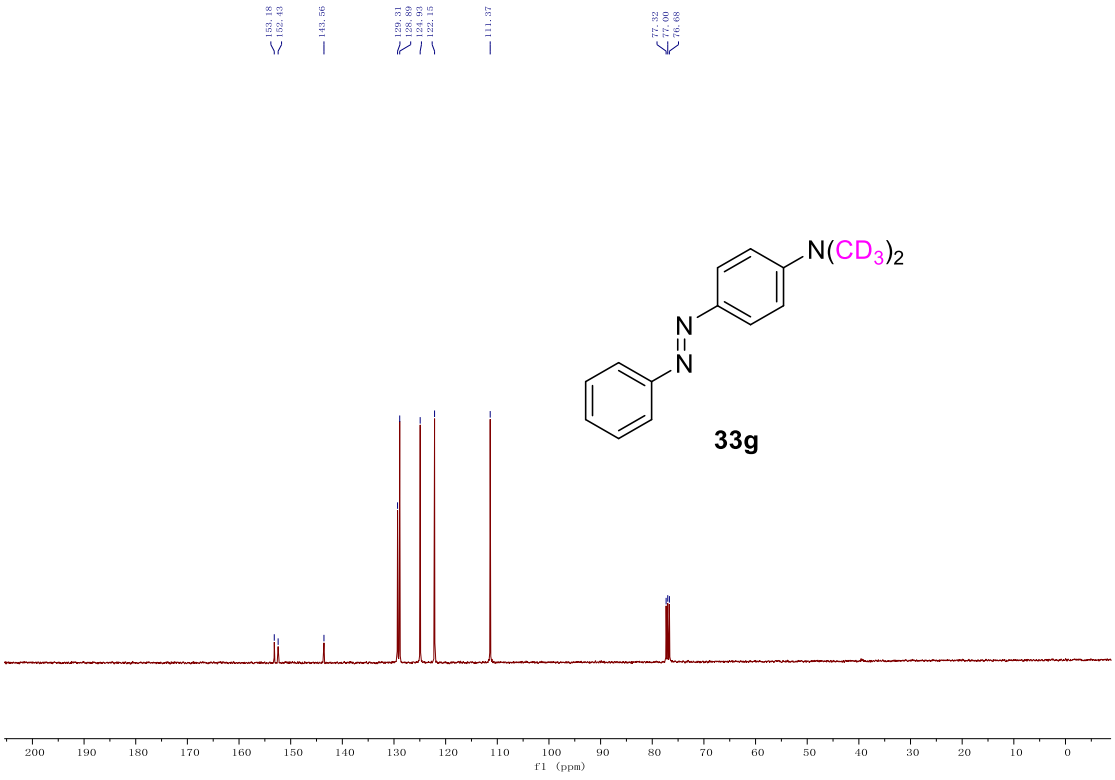

8.02
7.29
7.27
7.26
7.14
7.13
7.07
7.07
6.94
6.94
6.92
6.91
6.47
6.47
6.46
6.46
6.46
6.45
6.45
2.94
H
N
(H3C)2N
0.94
0.99
1.02
1.02
1.03
1.00
6.24
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

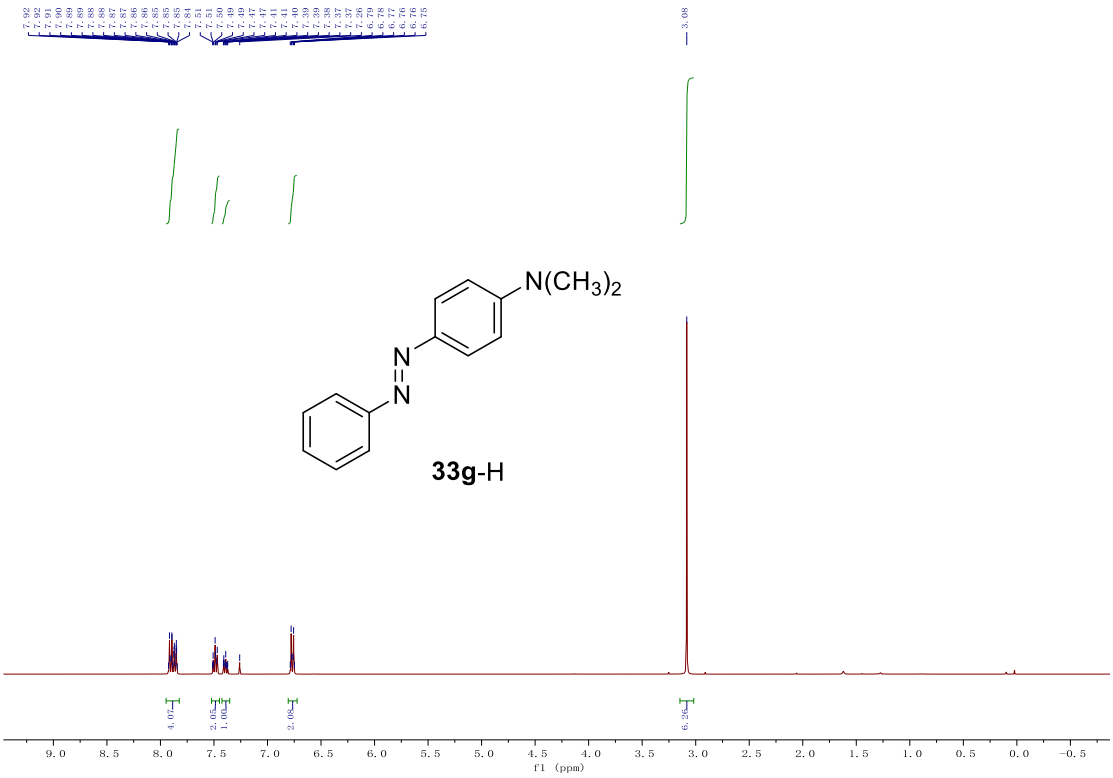
33f-H

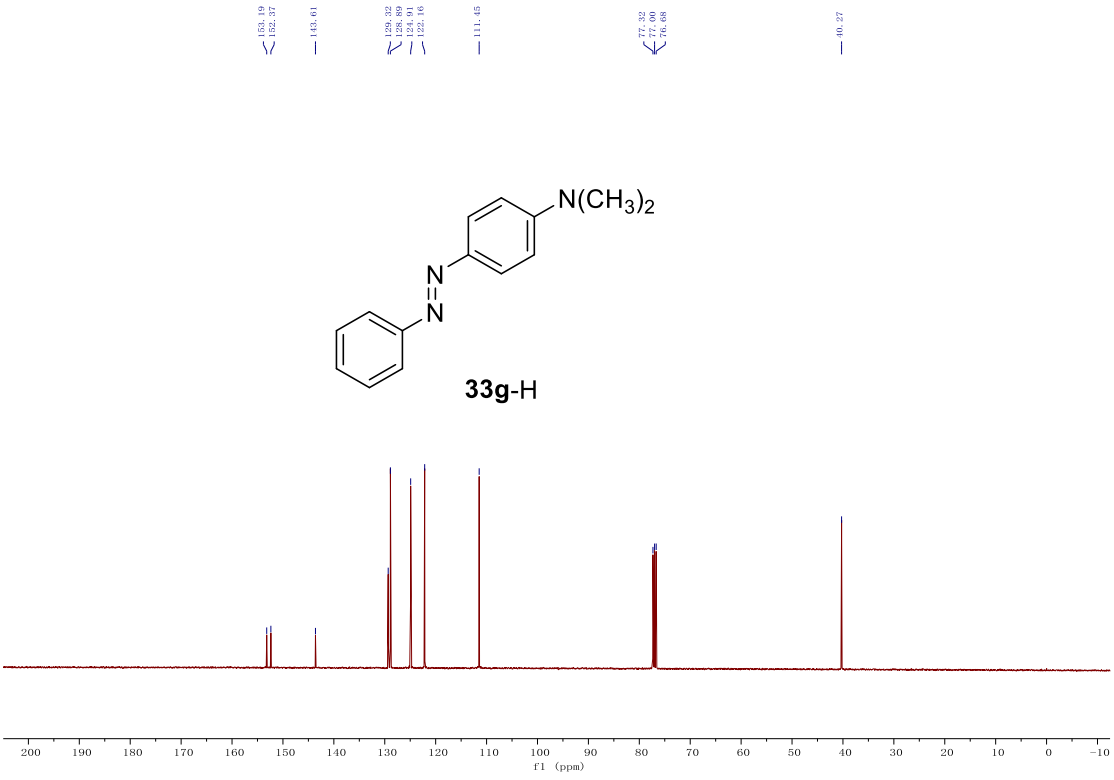

146.09
130.25
128.54
124.51
113.18
111.31
104.94
102.03
77.32
77.00
76.68
42.96
H
N
(H3C)2N
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

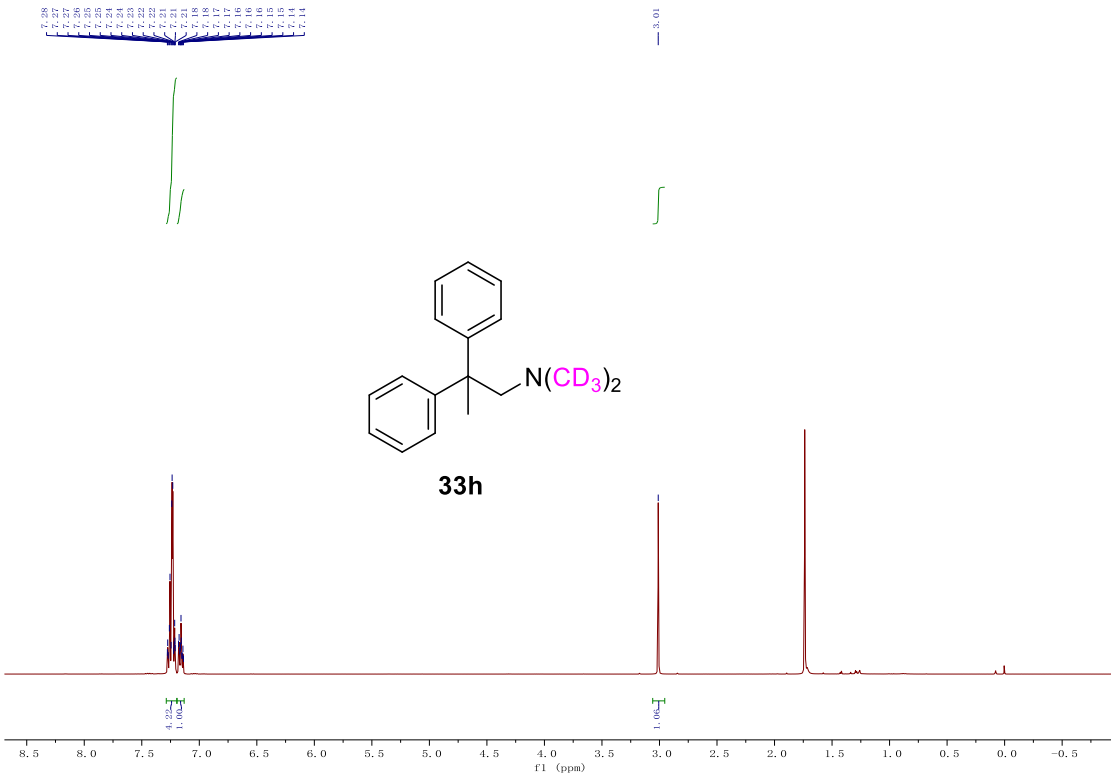
33f-H

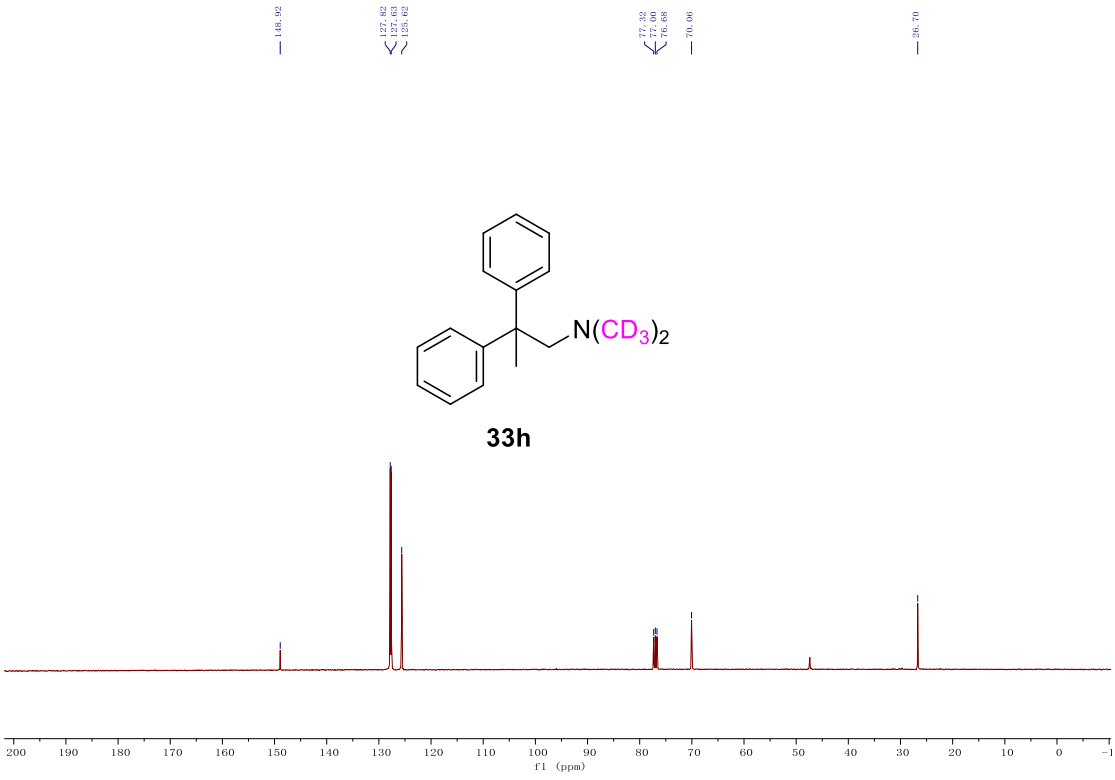

N(CD3)2
N
N
33g
4.00
2.01
1.00
2.04
f1 (ppm)

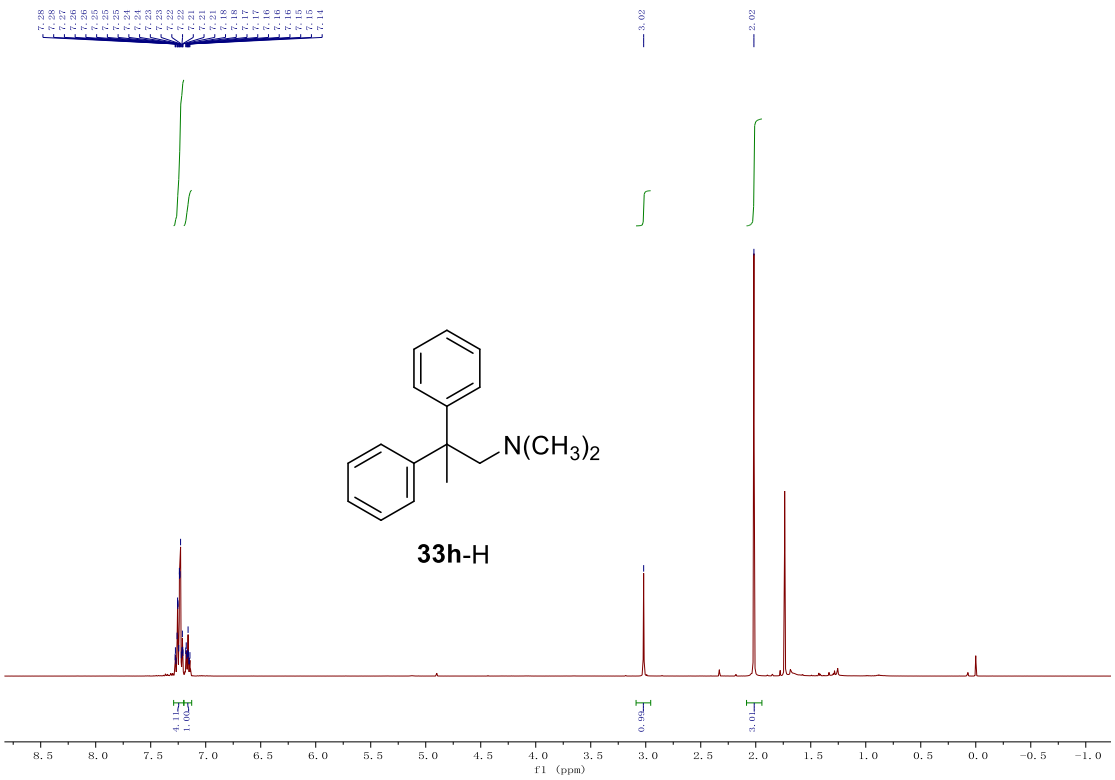

N(CD3)2
N
N
33g
f1 (ppm)


7.92
7.92
7.91
7.90
7.89
7.89
7.88
7.88
7.87
7.87
7.86
7.86
7.85
7.85
7.84
7.51
7.51
7.50
7.49
7.49
7.47
7.47
7.41
7.40
7.39
7.38
7.37
7.37
7.26
6.79
6.78
6.77
6.76
6.76
6.75
3.08
N(CH3)2
N
N
33g-H
4.07
2.05
1.00
2.08
6.26
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 -0.5
f1 (ppm)

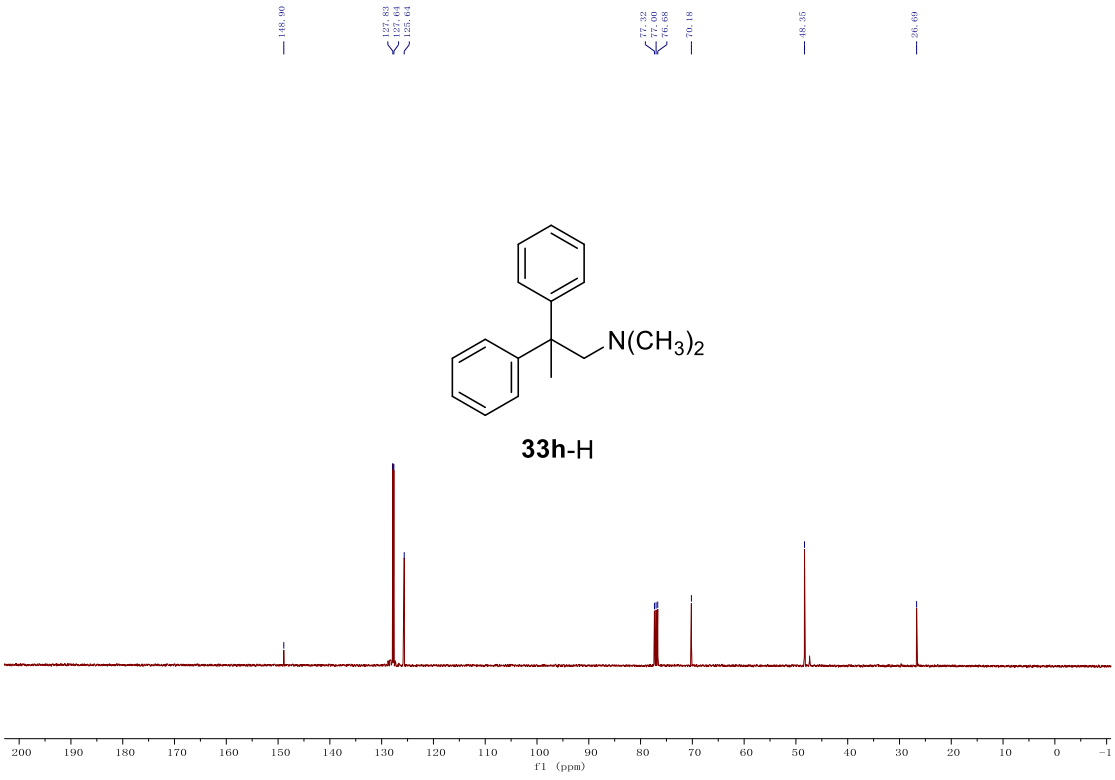

153.19
152.37
143.61
129.32
128.89
124.91
122.46
111.45
77.32
77.00
76.68
40.27
N(CH3)2
N
N
33g-H
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.28
7.27
7.27
7.27
7.26
7.25
7.25
7.25
7.24
7.24
7.23
7.23
7.22
7.22
7.21
7.21
7.21
7.18
7.18
7.17
7.17
7.17
7.16
7.16
7.16
7.15
7.15
7.15
7.14
7.14
3.01
N(CD3)2
33h
4.22
1.00
1.06
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)

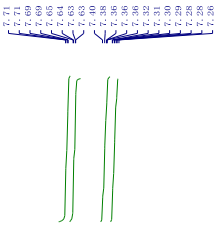

148.92
127.82
127.63
125.62
77.32
77.00
76.68
70.06
36.70
N(CD3)2
33h
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −1
f1 (ppm)

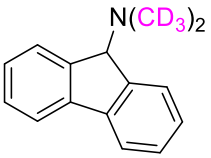

7.28
7.27
7.26
7.25
7.24
7.23
7.22
7.21
7.18
7.17
7.16
7.15
7.14
3.02
2.02
N(CH3)2
4.11
1.06
0.99
3.01
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
−1.0
f1 (ppm)

33h-H

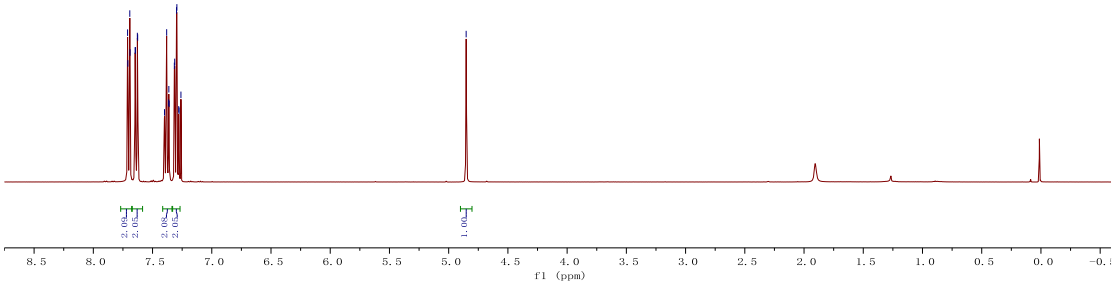

148.90
127.83
127.64
125.64
77.32
77.00
76.68
70.18
48.35
26.69
N(CH3)2
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−1
f1 (ppm)

33h-H

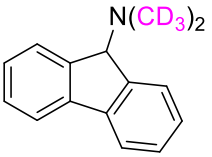

7.71
7.71
7.69
7.69
7.66
7.66
7.64
7.63
7.63
7.40
7.38
7.36
7.36
7.36
7.32
7.31
7.30
7.29
7.28
7.28
7.26
4.85


N(CD3)2

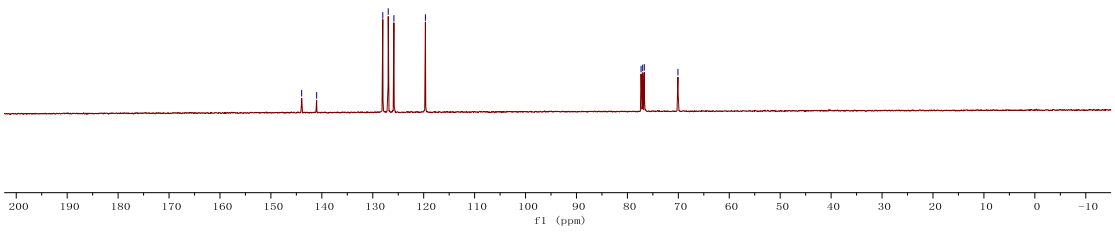
33i

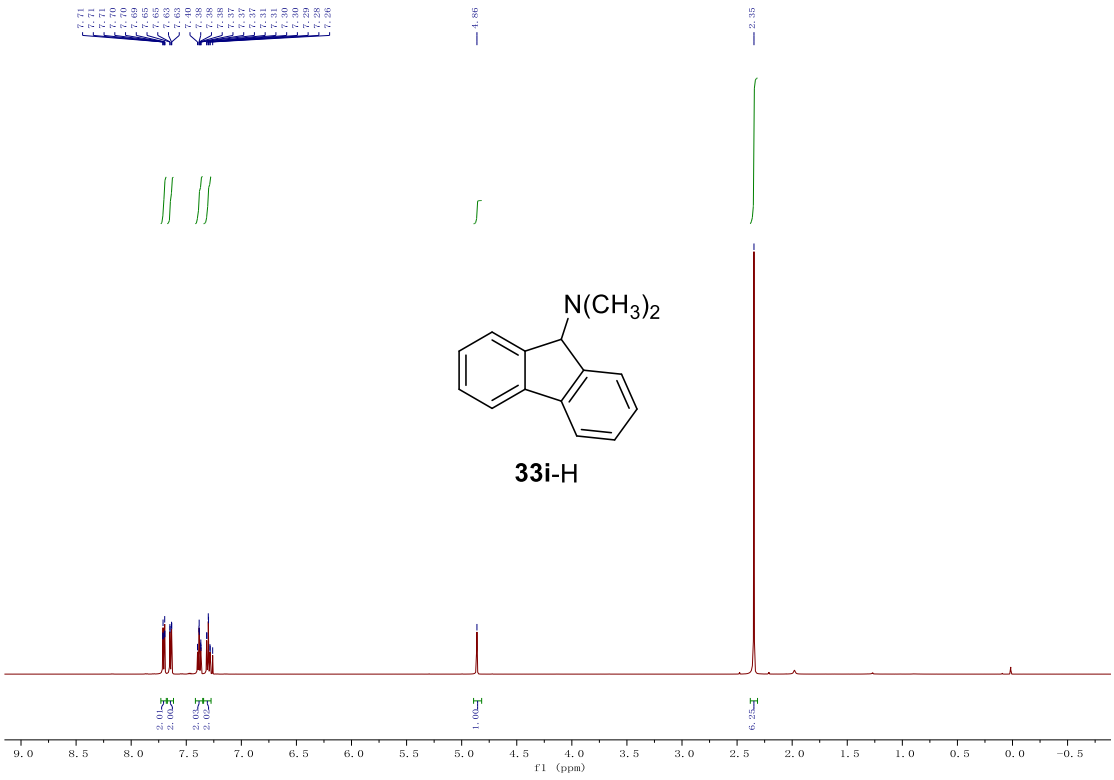

2.09
2.05
2.08
2.05
1.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


143.96
141.02
128.03
126.96
125.85
119.66
77.32
77.00
76.68
70.08

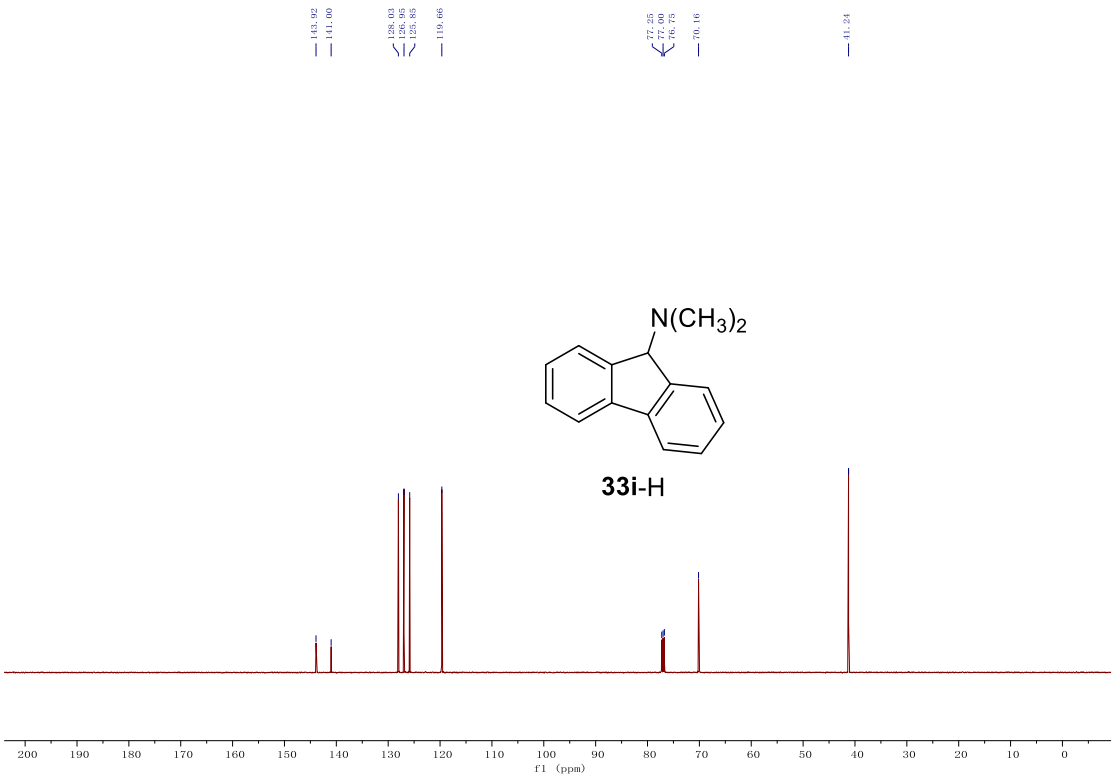

N(CD3)2

33i

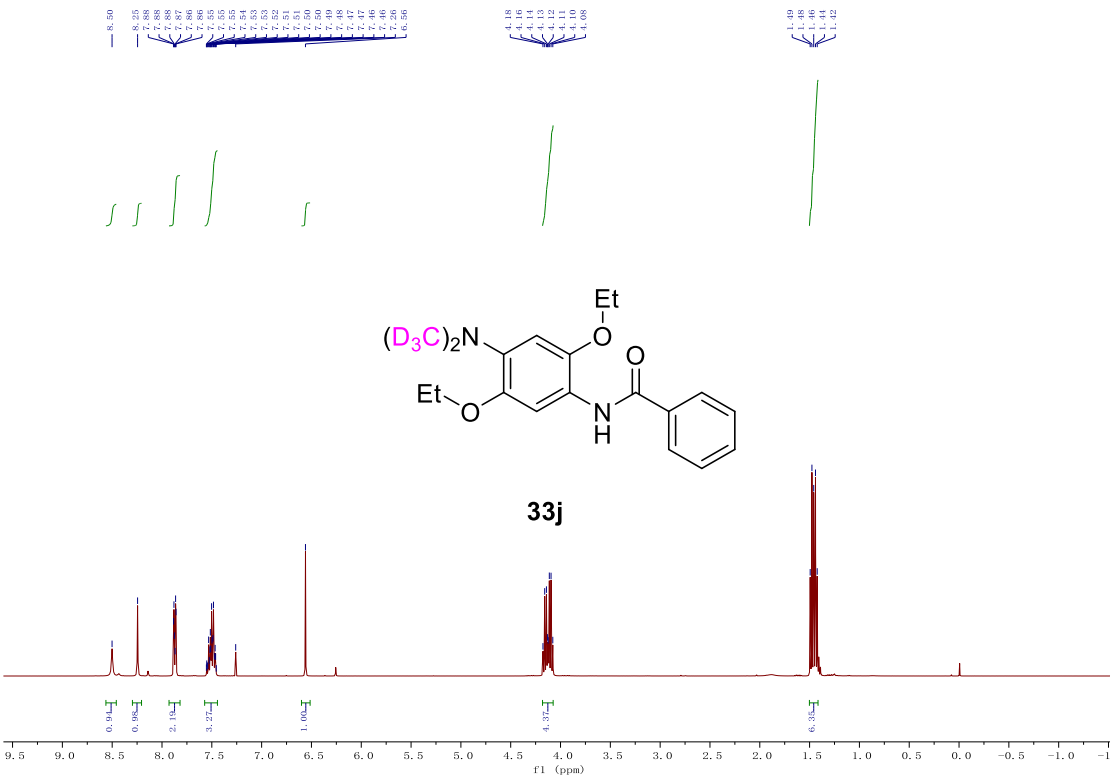

200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.71
7.71
7.71
7.70
7.70
7.69
7.65
7.65
7.63
7.63
7.40
7.38
7.38
7.37
7.37
7.37
7.31
7.30
7.30
7.29
7.28
7.26
4.86
2.35
N(CH3)2
2.01
2.00
2.02
2.01
1.00
6.25
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 -0.5
f1 (ppm)

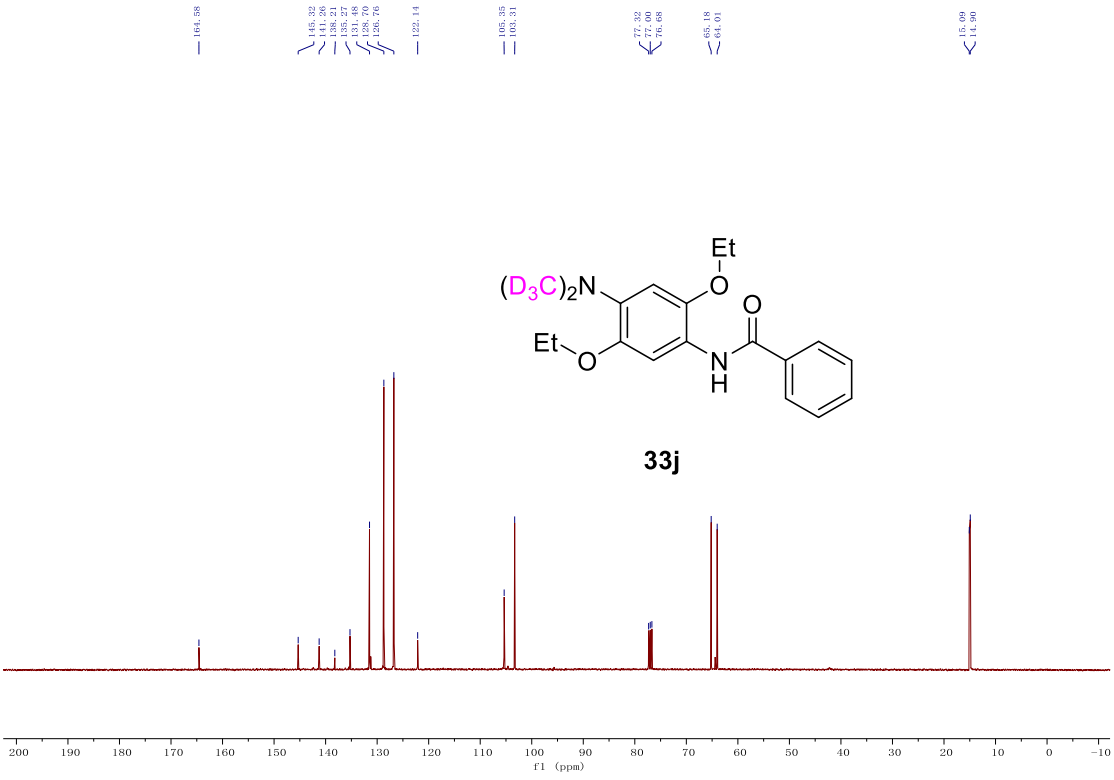
33i-H


143.92
141.00
128.03
126.95
125.85
119.66
77.25
77.00
76.75
70.16
41.24
N(CH3)2
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

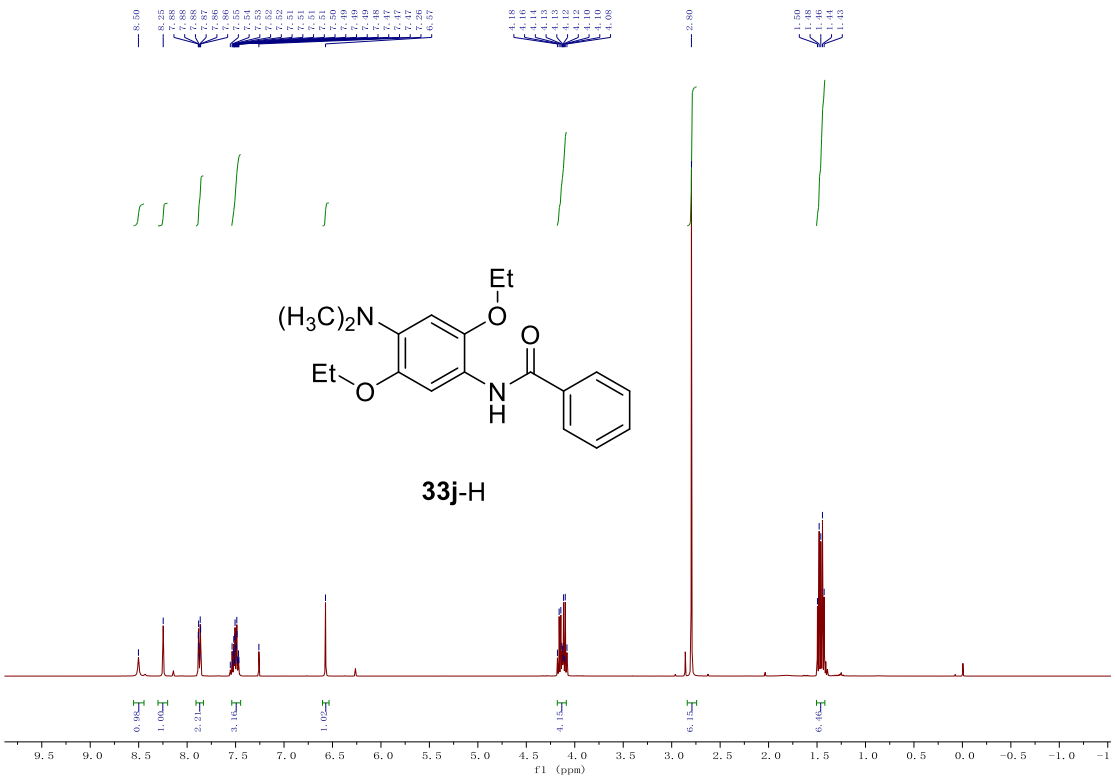
33i-H


8.50
8.25
7.88
7.88
7.87
7.86
7.86
7.55
7.55
7.55
7.54
7.53
7.53
7.52
7.51
7.51
7.50
7.50
7.49
7.48
7.47
7.47
7.46
7.46
7.36
6.59
4.18
4.15
4.14
4.13
4.12
4.11
4.10
4.08
1.49
1.48
1.46
1.44
1.42
Et
O
(D3C)2N
O
Et
O
N
H
0.94
0.98
2.18
3.27
1.00
4.37
6.37
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 -0.5 -1.0 -1
f1 (ppm)

33j

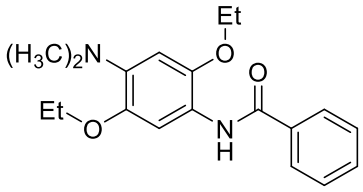

164.58
145.32
141.26
138.21
135.27
131.48
129.70
128.76
122.14
105.35
103.31
77.32
77.00
76.68
65.18
64.01
15.09
14.90
Et
O
(D3C)2N
O
Et
O
N
H
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

33j

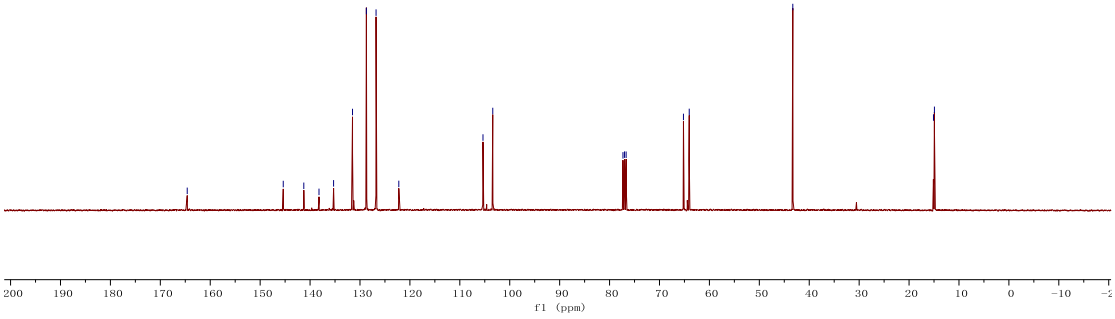

8.50
8.25
7.88
7.86
7.88
7.87
7.86
7.86
7.55
7.54
7.53
7.52
7.52
7.51
7.51
7.51
7.50
7.49
7.49
7.49
7.48
7.47
7.47
7.47
7.26
6.57
4.18
4.16
4.14
4.13
4.13
4.12
4.12
4.10
4.10
4.08
2.80
1.50
1.48
1.46
1.44
1.43
Et
(H3C)2N
O
O
Et
O
N
H
0.98
1.00
2.21
3.16
1.03
4.15
6.14
6.46
f1 (ppm)

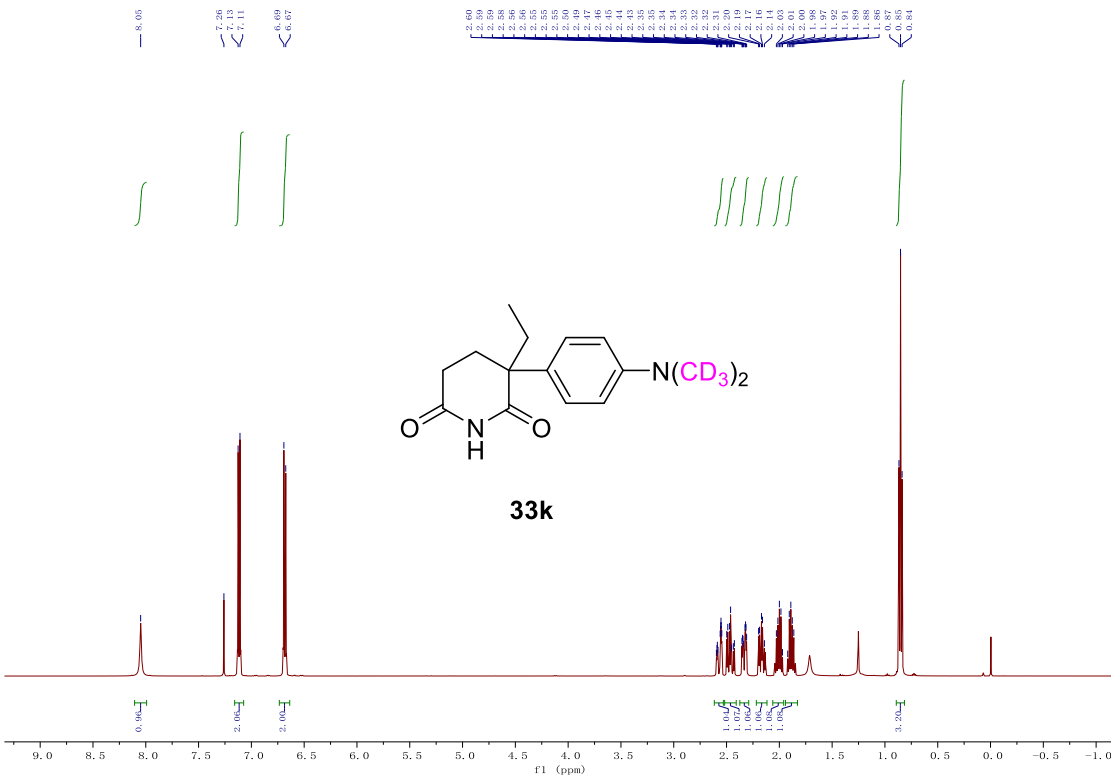
33j-H

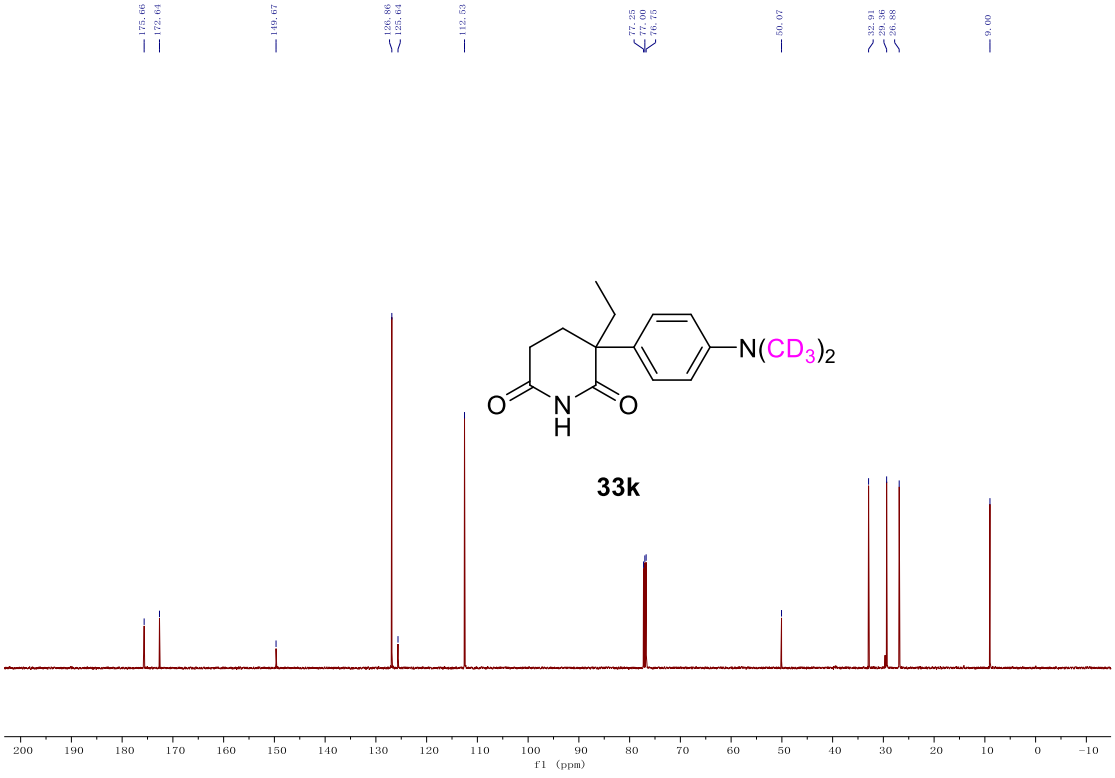

164.61
145.37
141.26
138.21
135.29
131.69
131.72
128.78
126.78
122.22
105.36
103.40
77.32
77.00
76.68
65.20
64.04
43.29
15.11
14.92

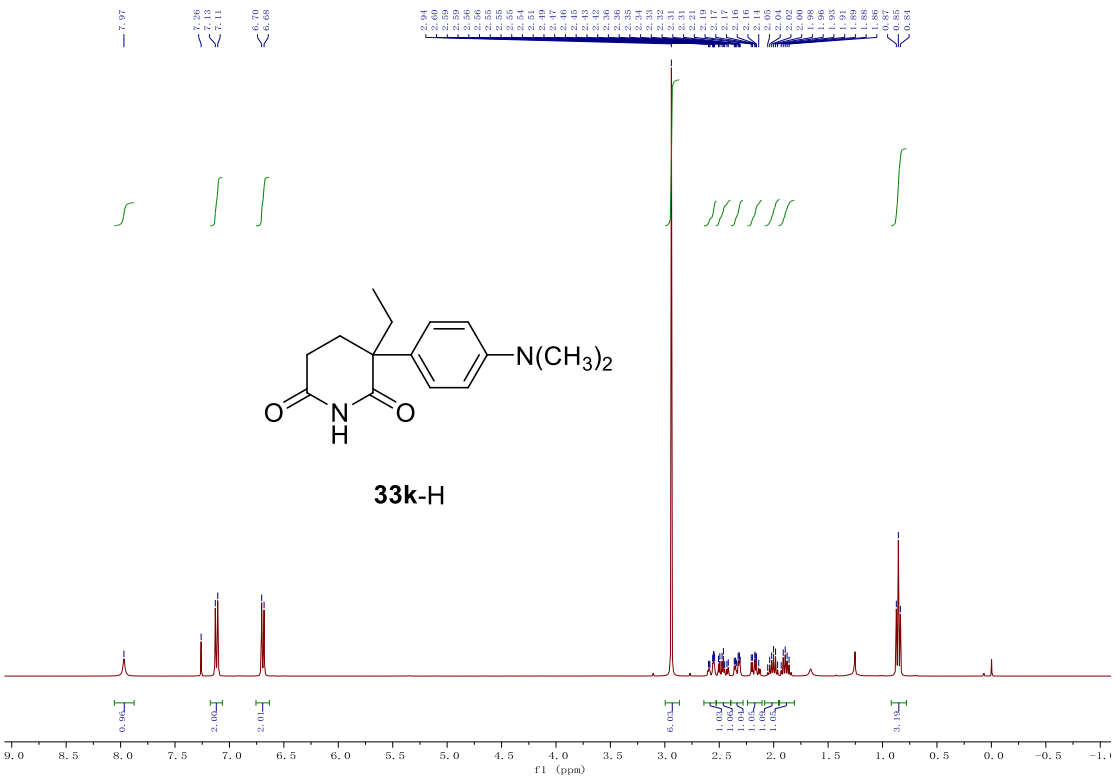

Et
(H3C)2N
O
O
Et
O
N
H

33j-H

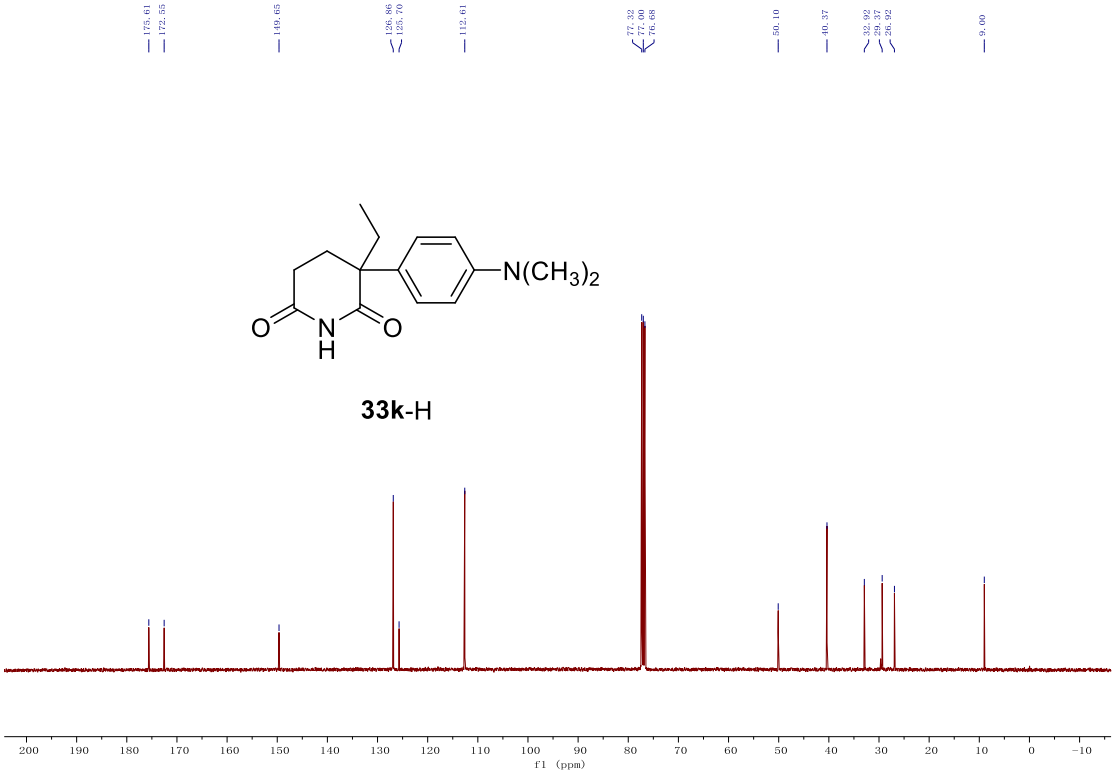

f1 (ppm)


8.05
7.26
7.13
7.11
6.69
6.67
2.60
2.59
2.58
2.58
2.56
2.56
2.55
2.55
2.50
2.49
2.47
2.46
2.45
2.44
2.43
2.35
2.34
2.34
2.33
2.32
2.31
2.20
2.19
2.17
2.16
2.14
2.03
2.01
2.00
1.98
1.97
1.92
1.91
1.89
1.88
1.86
0.87
0.85
0.84
N(CD3)2
O
N
H
O
33k
0.96
2.08
2.00
1.04
1.07
1.06
1.06
1.06
1.08
3.20
f1 (ppm)

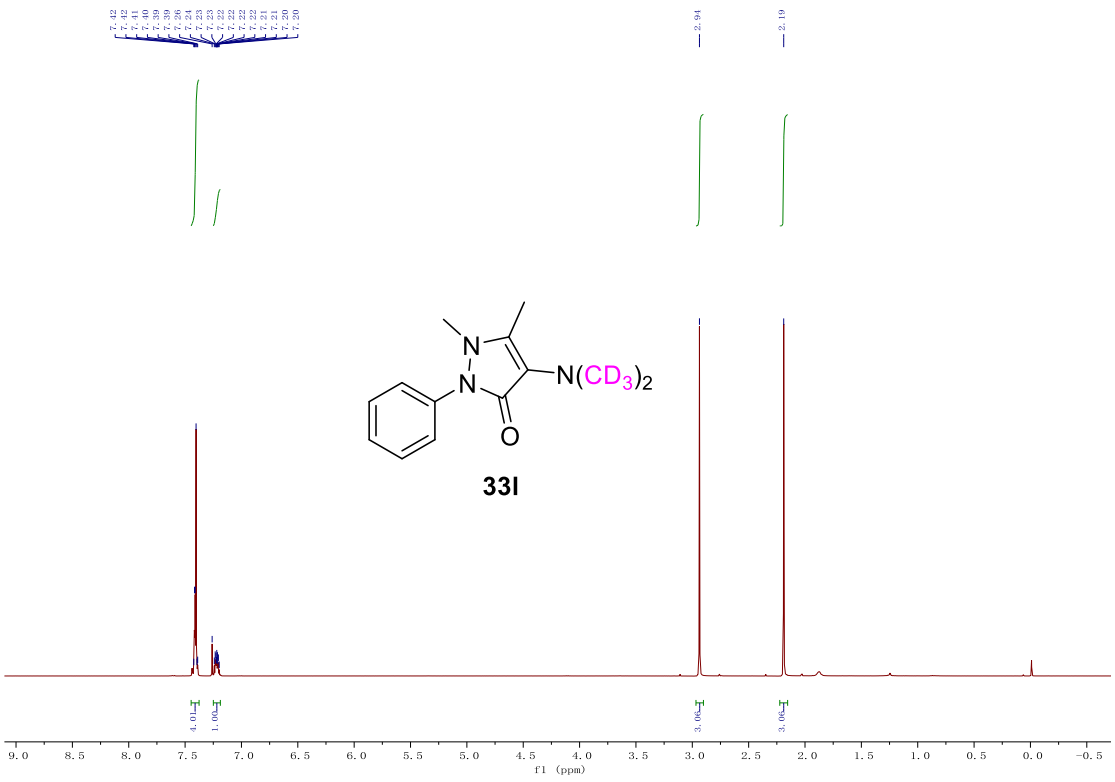

175.66
172.64
149.67
126.86
125.64
112.53
77.25
77.00
76.75
50.07
32.91
29.36
26.88
9.00
N(CD3)2
O
N
H
O
33k
f1 (ppm)


7.97
7.26
7.13
7.11
6.70
6.68
N(CH3)2
O
N
H
O
0.96
2.00
2.01
6.03
3.19
f1 (ppm)

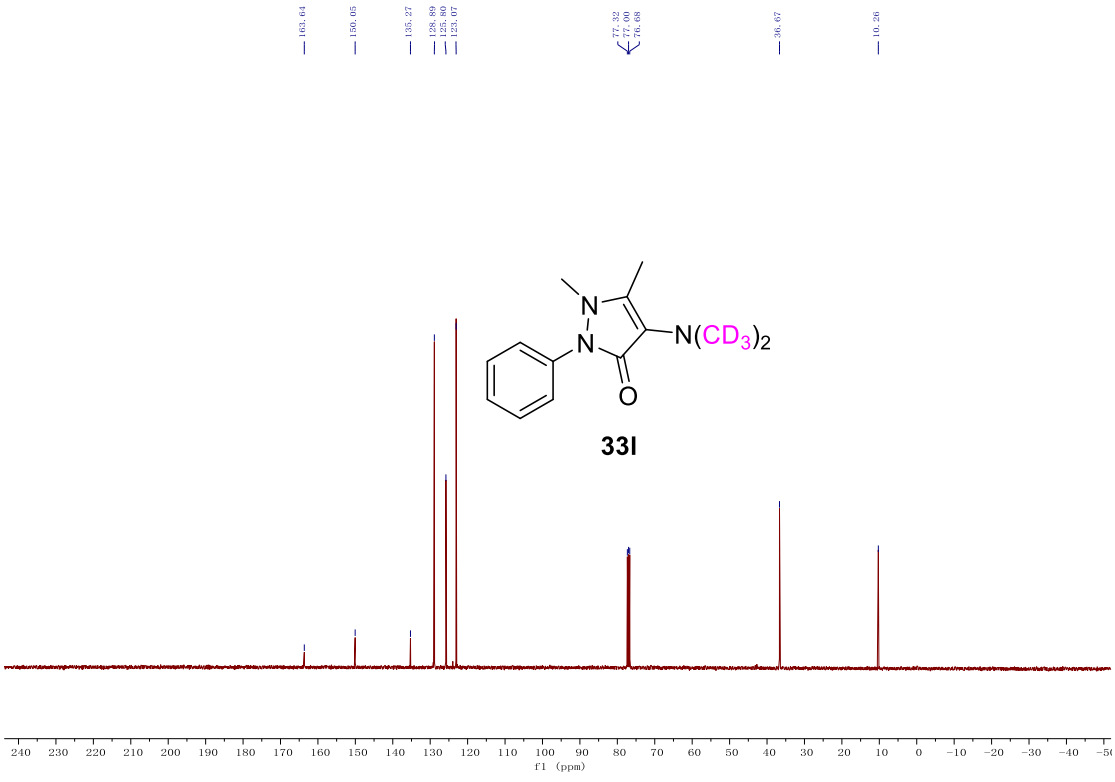
33k-H


175.61
172.55
149.65
126.86
125.70
112.61
77.32
77.00
76.68
50.10
40.37
32.92
29.37
26.92
9.00
N(CH3)2
O
N
H
O
f1 (ppm)

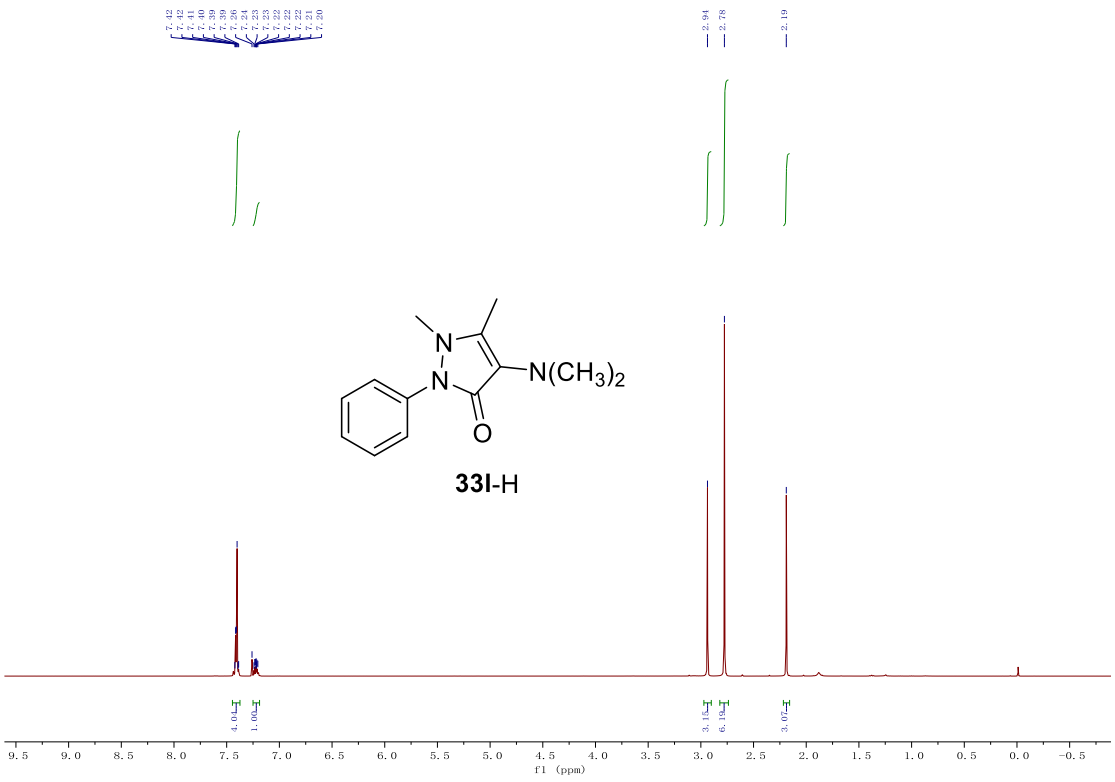
33k-H


7.42
7.42
7.41
7.40
7.39
7.39
7.26
7.24
7.23
7.23
7.22
7.22
7.22
7.22
7.21
7.21
7.20
7.20
2.94
2.19
N
N
N(CD3)2
O
4.01
1.06
3.06
3.06
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 -0.5
f1 (ppm)

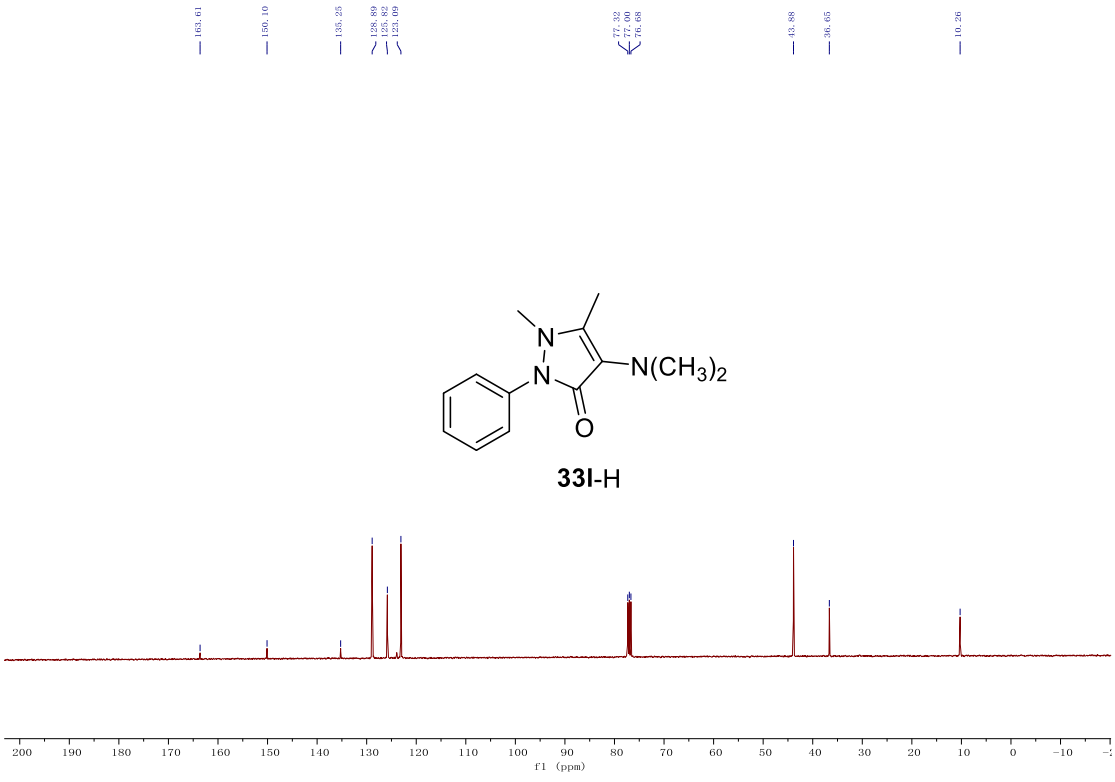
33l


163.64
150.05
135.27
128.89
125.80
123.07
77.32
77.00
76.68
36.67
10.26
N
N
N(CD3)2
O
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40
f1 (ppm)

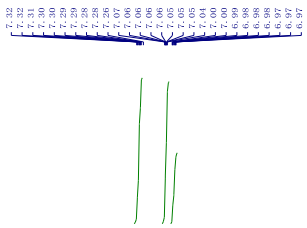
33l

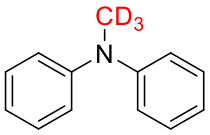

7.42
7.42
7.41
7.40
7.39
7.39
7.26
7.24
7.23
7.23
7.22
7.22
7.22
7.21
7.21
7.20
2.94
2.78
2.19
N
N
N(CH3)2
O
4.04
1.00
3.15
6.19
3.07
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f1 (ppm)

33l-H

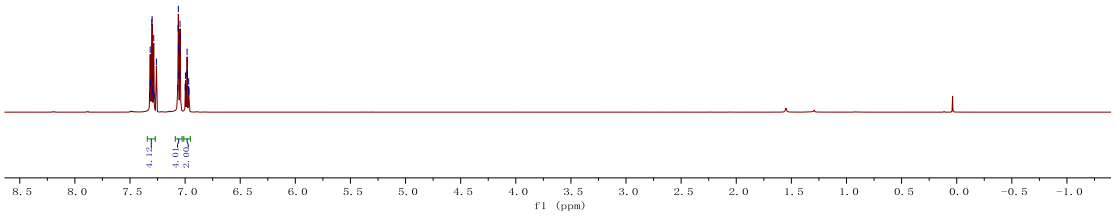

163.61
150.10
135.25
128.89
125.82
124.09
77.32
77.00
76.68
43.88
36.65
10.26
N
N
N(CH3)2
O
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

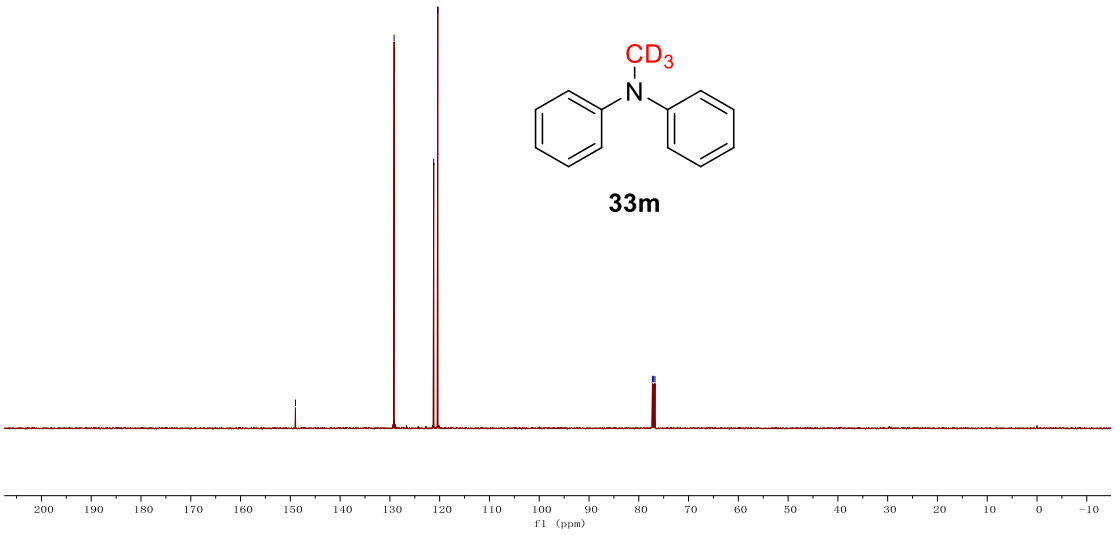
33l-H




CD3
N

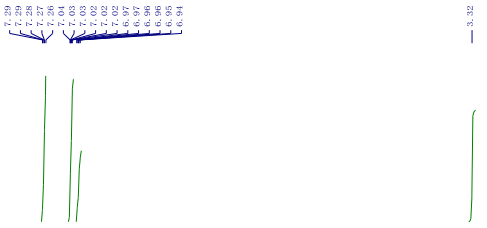
33m

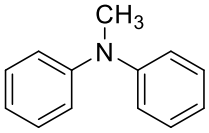

4.12
4.01
2.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


148.97
129.15
121.19
120.38
77.25
77.00
76.75
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

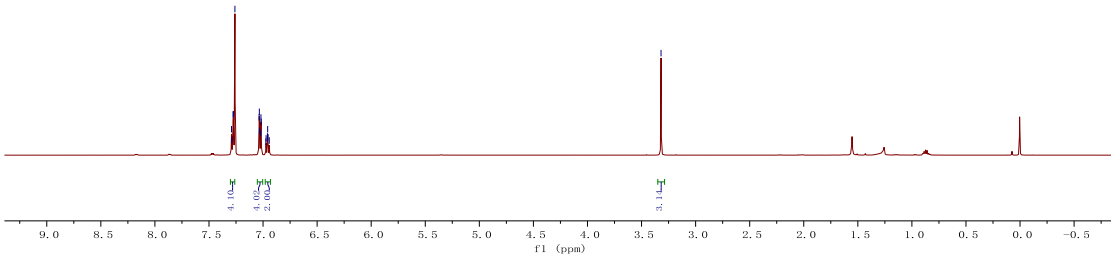
CD3
N

33m

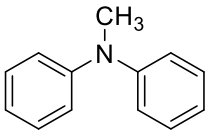

7.29
7.29
7.28
7.27
7.05
7.04
7.03
7.03
7.02
7.02
7.02
6.97
6.97
6.96
6.96
6.95
6.94
3.32


CH3
N

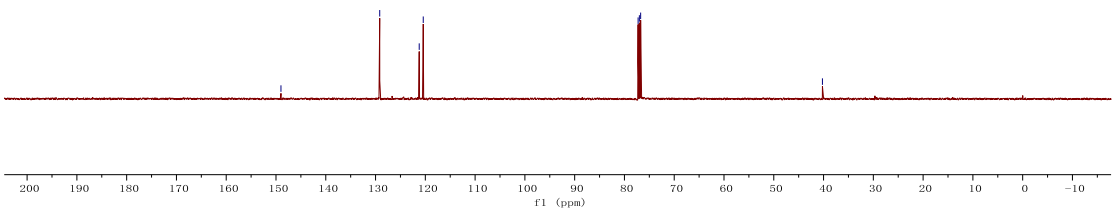
33m-H

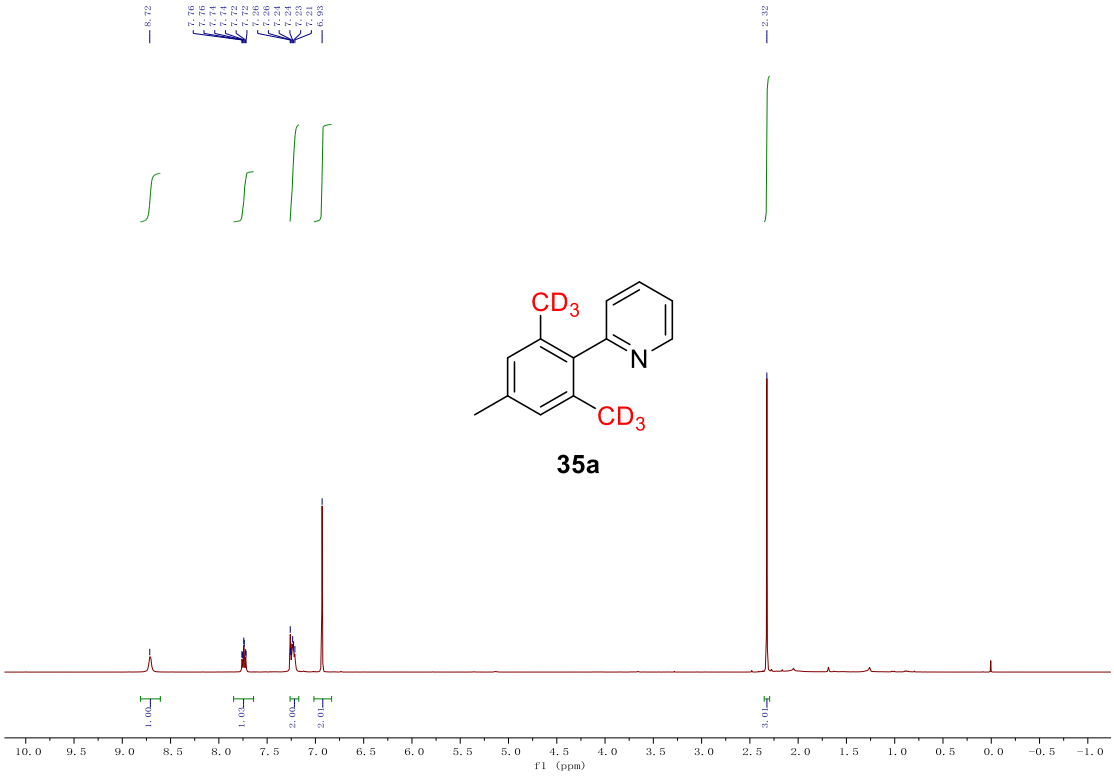

4.10
4.05
2.00
3.14
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)


149.00
129.16
121.23
120.42
77.25
77.00
76.75
40.22

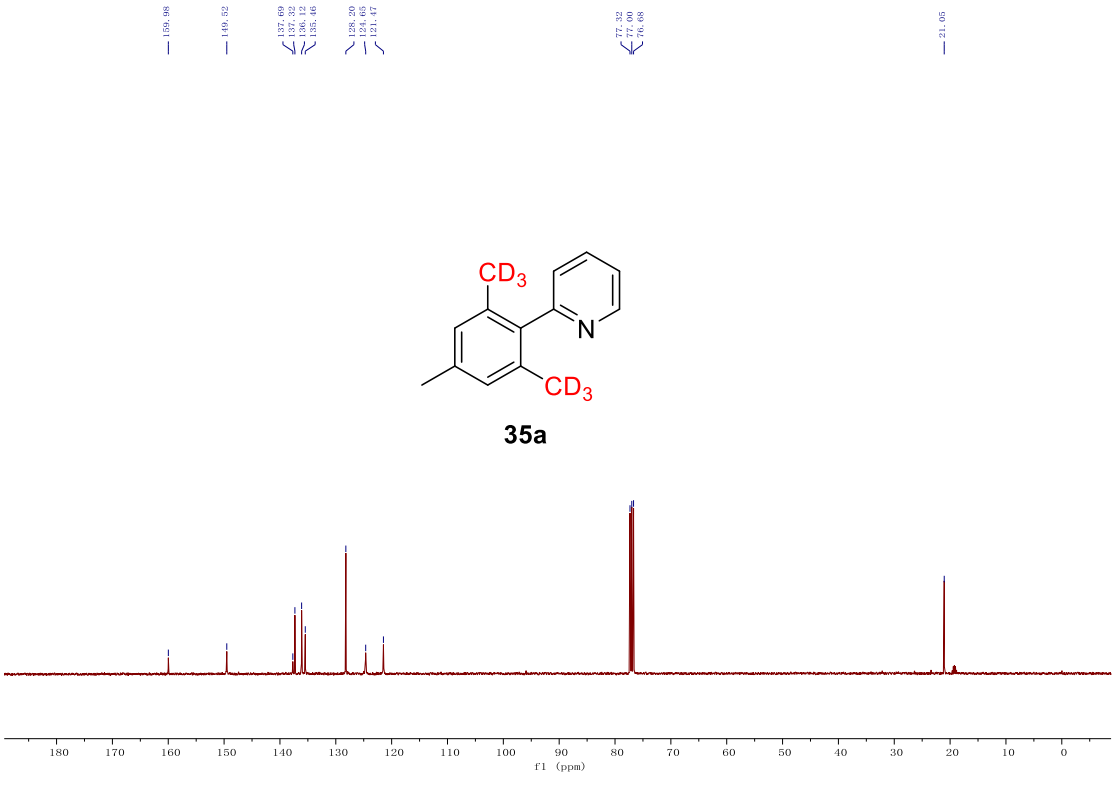

CH3
N

33m-H

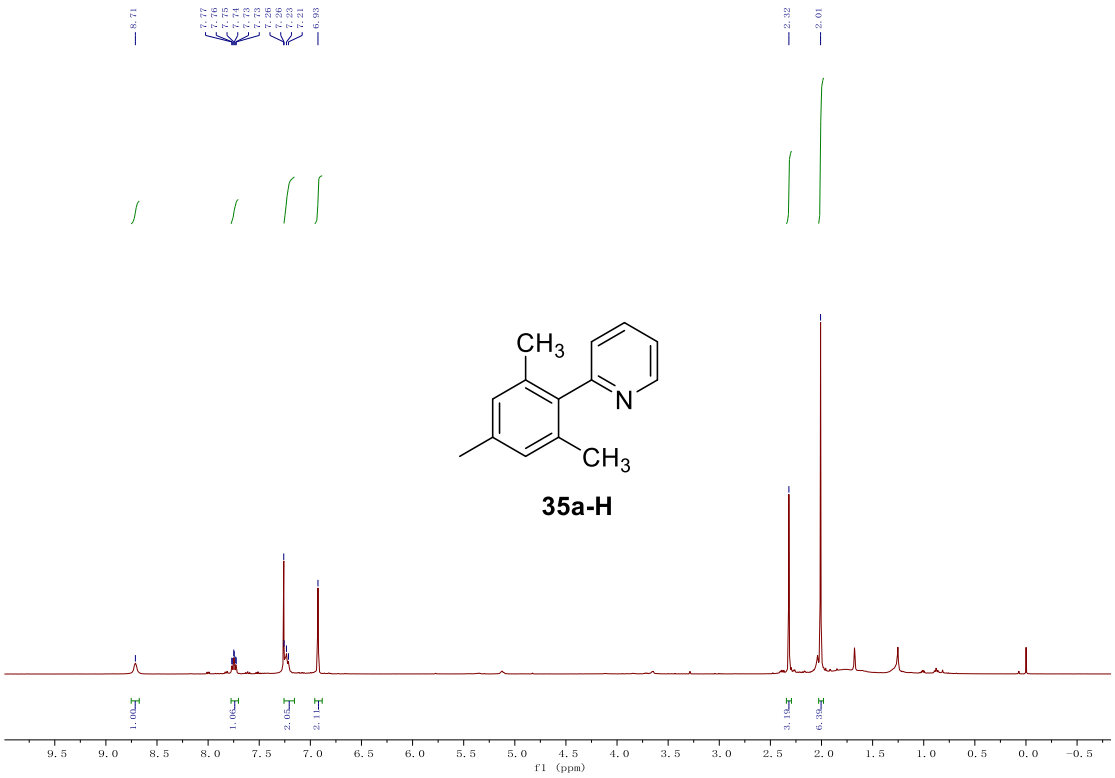

200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


8.72
7.76
7.76
7.74
7.74
7.72
7.72
7.26
7.26
7.24
7.24
7.23
7.21
6.93
2.32
CD3
N
CD3
1.00
1.00
2.00
2.01
3.01
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 -0.5 -1.0
f1 (ppm)

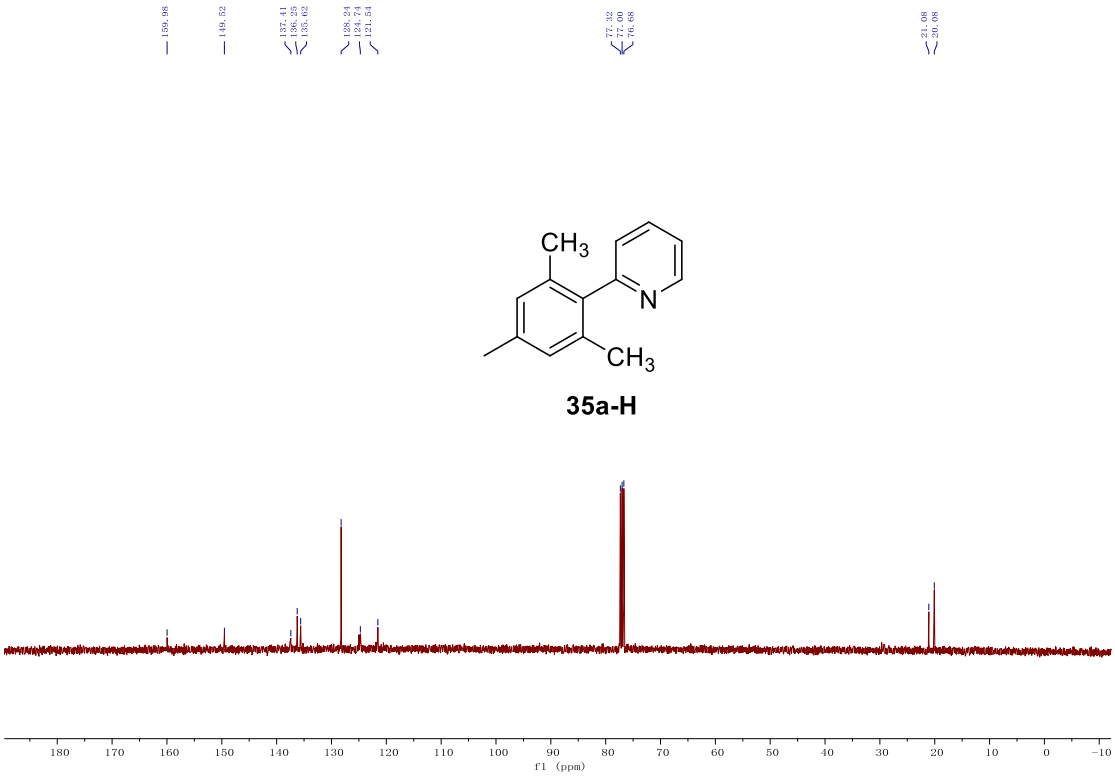
35a


159.98
149.52
137.69
137.32
136.12
135.46
128.20
124.65
121.47
77.32
77.00
76.68
21.65
CD3
N
CD3
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

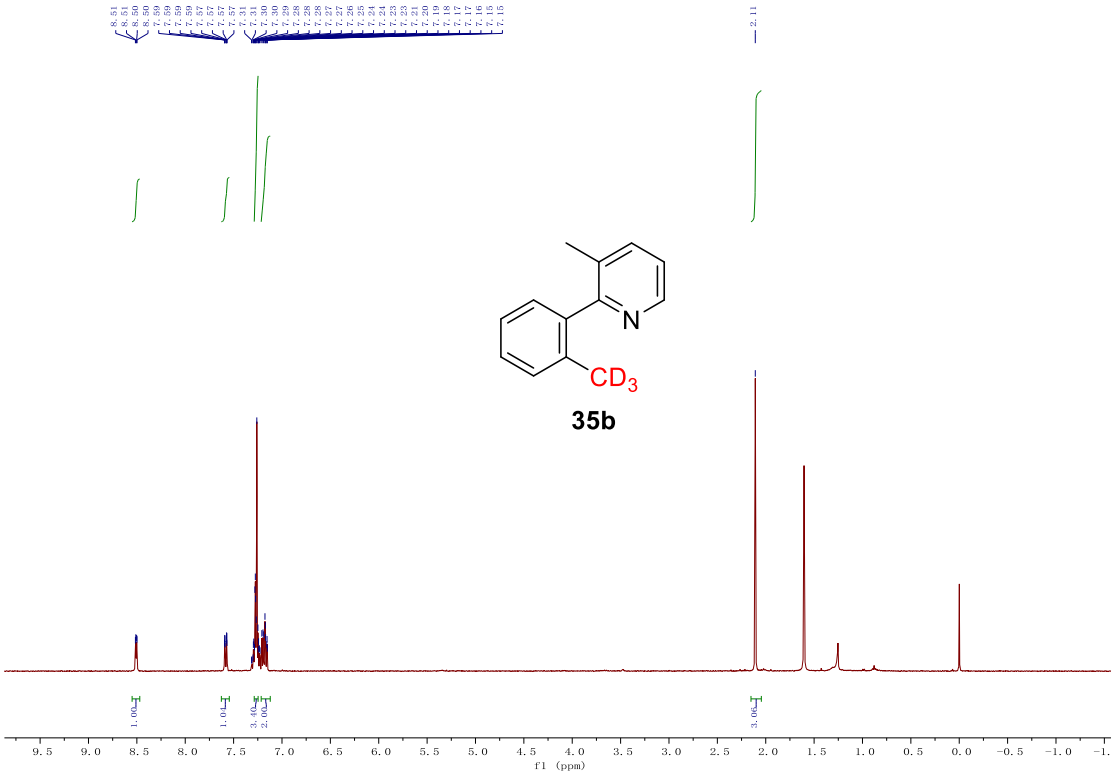
35a


8.71
7.77
7.76
7.75
7.74
7.73
7.73
7.26
7.23
7.21
6.93
2.32
2.01
CH3
N
CH3
1.00
1.06
2.05
2.11
3.18
6.35
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 -0.5
f1 (ppm)

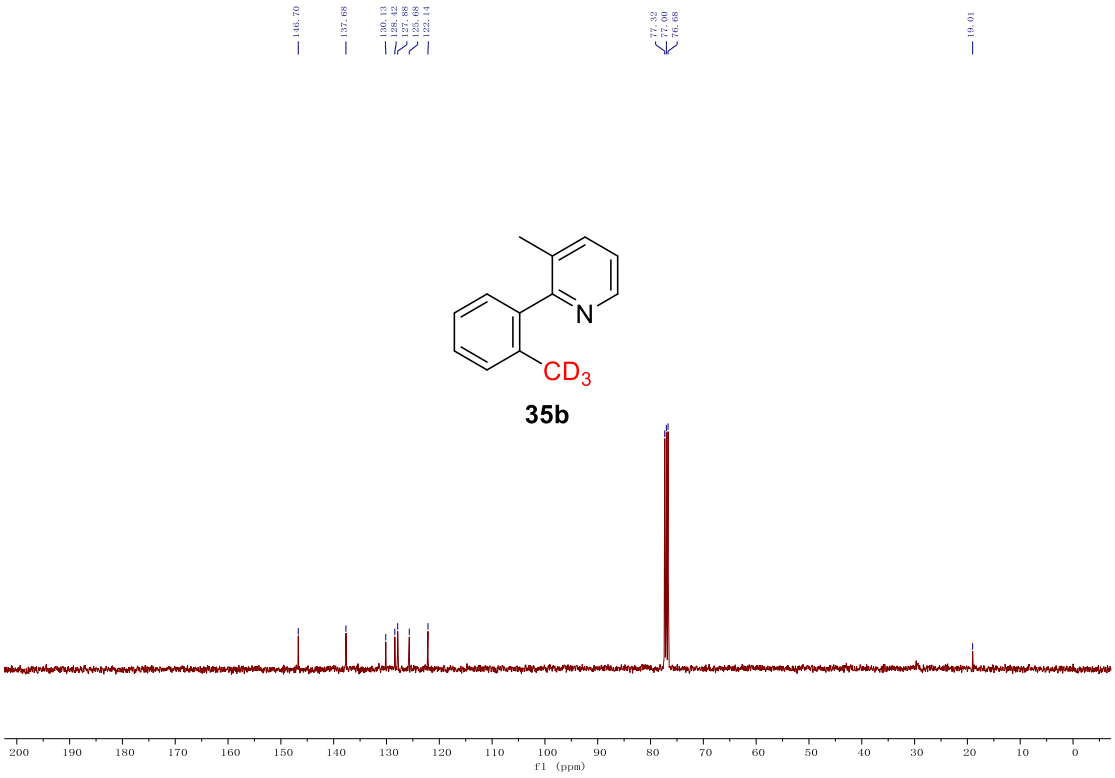
35a-H


159.98
149.52
137.41
136.25
135.62
128.24
124.74
121.54
77.32
77.00
76.68
21.08
20.08
CH3
N
CH3
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

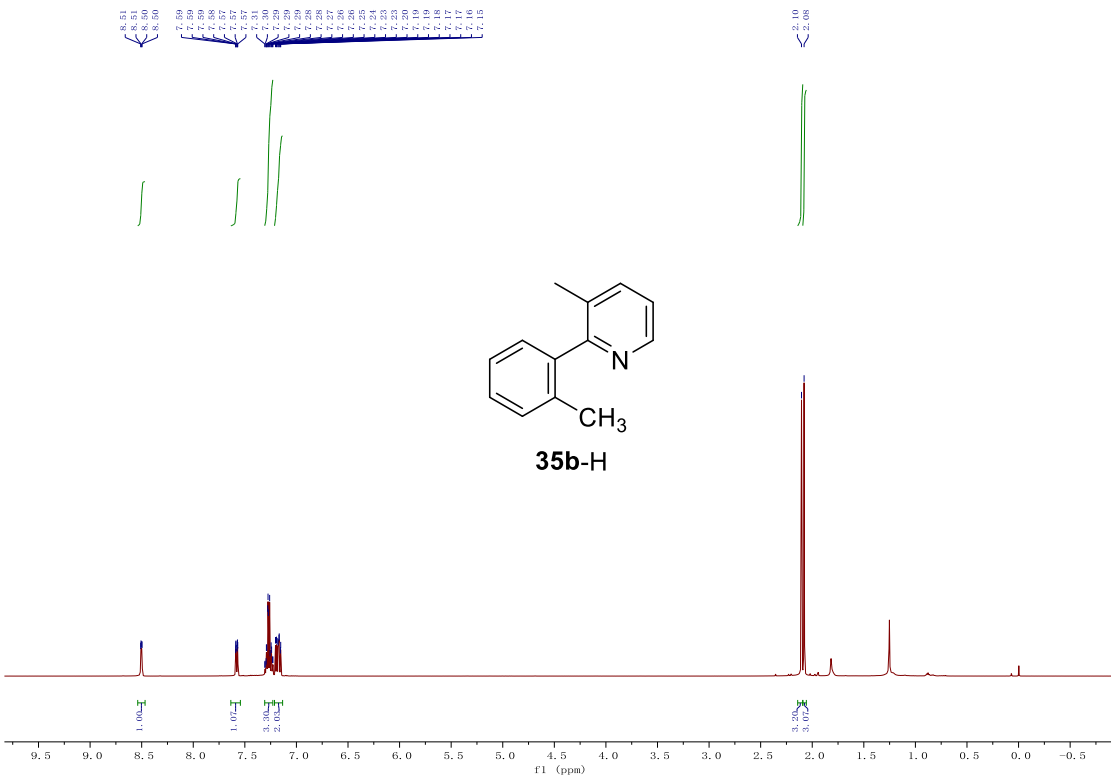
35a-H


8.51
8.51
8.50
8.50
7.59
7.59
7.59
7.59
7.57
7.57
7.57
7.57
7.31
7.31
7.30
7.30
7.29
7.29
7.28
7.28
7.28
7.27
7.27
7.26
7.25
7.24
7.24
7.23
7.23
7.23
7.21
7.20
7.19
7.18
7.17
7.17
7.16
7.15
7.15
2.11
N
CD3
1.00
1.01
3.40
2.00
3.06
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 -0.5 -1.0 -1.
f1 (ppm)

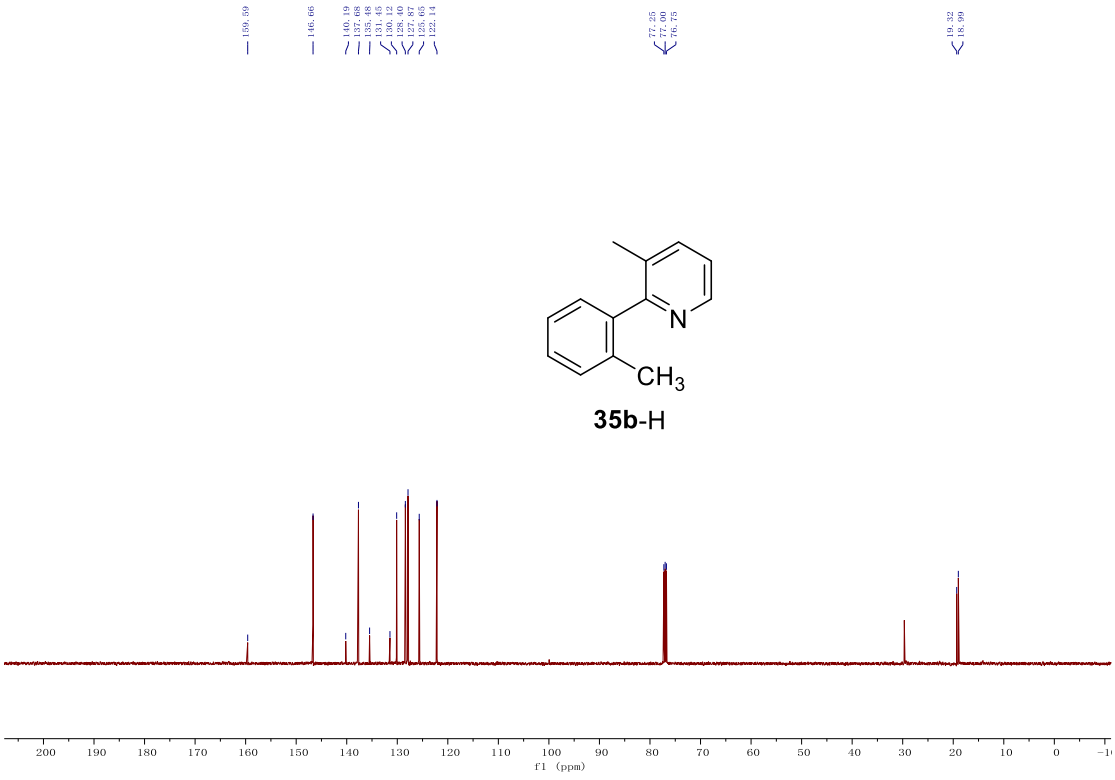
35b


146.70
137.68
130.13
128.42
127.85
125.68
122.14
77.32
77.00
76.68
19.01
N
CD3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

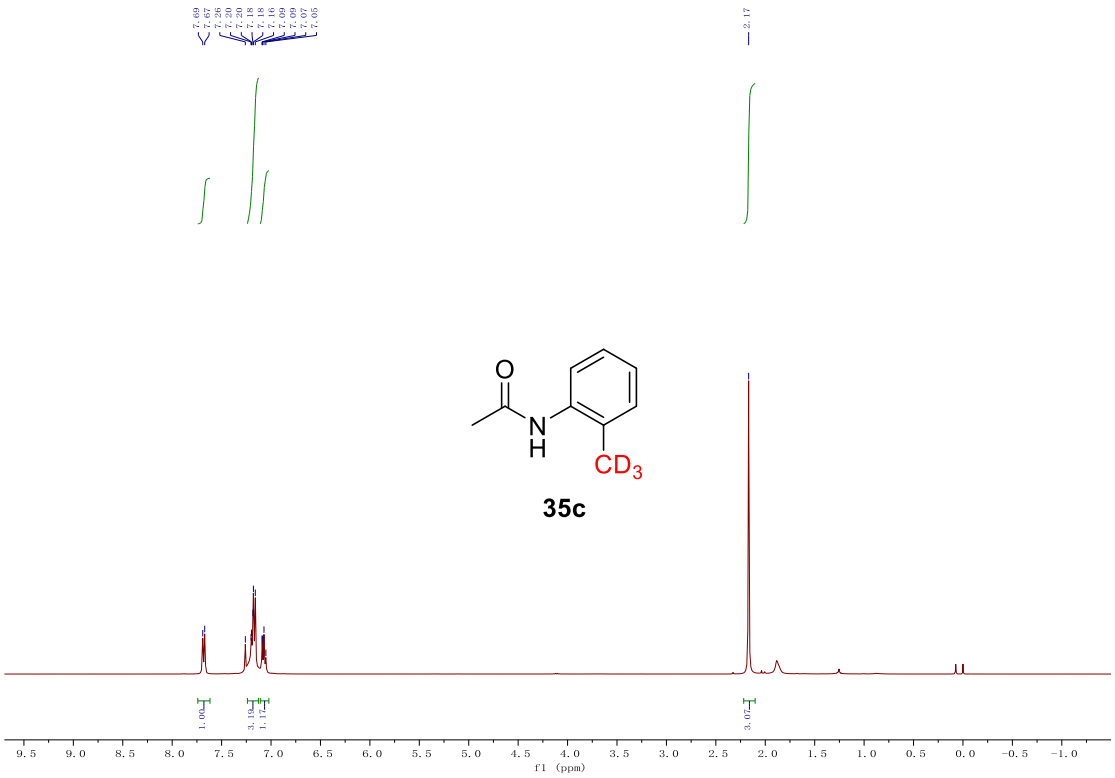
35b


8.51
8.51
8.50
8.50
7.59
7.59
7.59
7.58
7.57
7.57
7.57
7.31
7.30
7.29
7.29
7.29
7.28
7.28
7.27
7.26
7.26
7.25
7.24
7.23
7.23
7.20
7.19
7.18
7.17
7.17
7.16
7.15
2.10
2.08
N
CH3
1.00
1.07
3.30
2.03
3.20
3.07
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 −0.5
f1 (ppm)

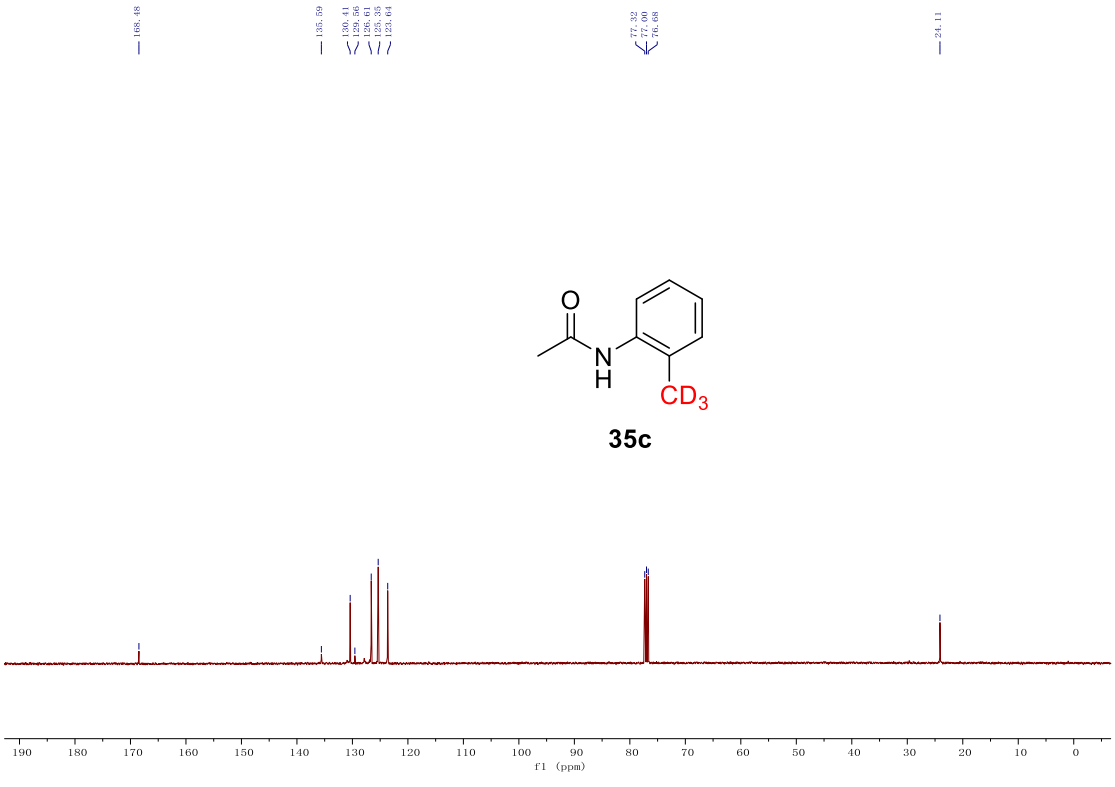
35b-H


159.59
146.66
140.19
137.68
135.48
131.65
130.12
128.40
127.87
125.66
122.14
77.25
77.00
76.75
19.32
18.99
N
CH3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

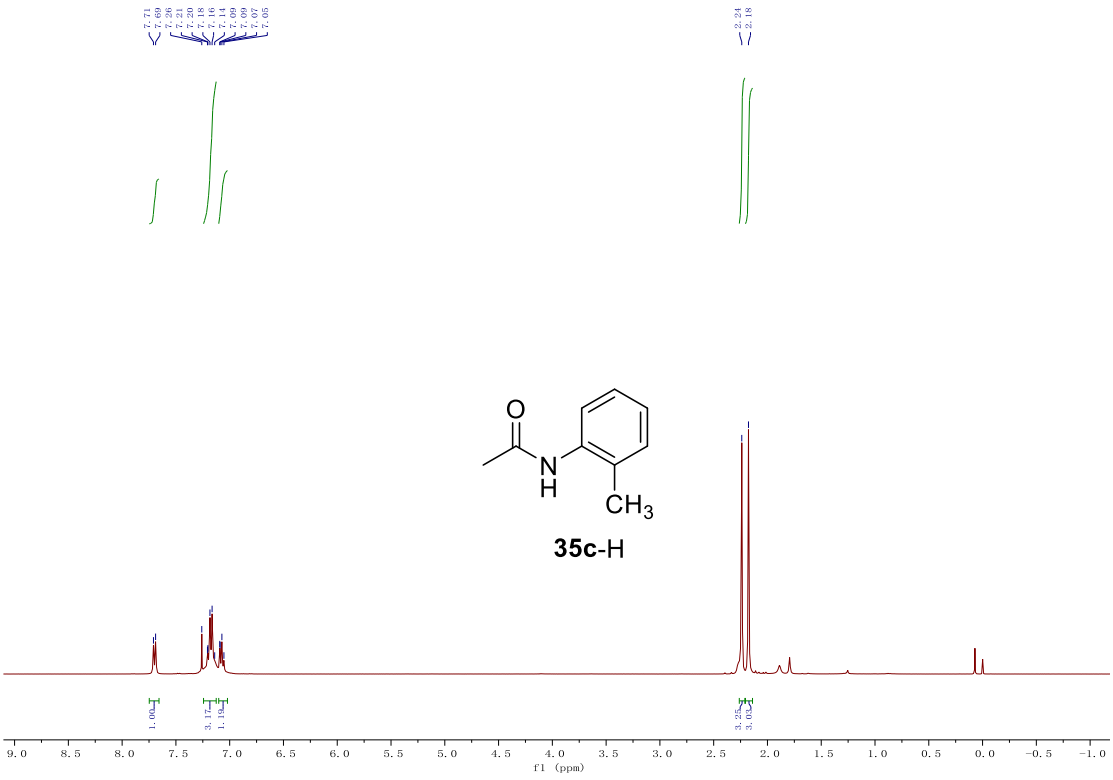
35b-H


7.69
7.67
7.26
7.20
7.20
7.18
7.18
7.16
7.09
7.09
7.07
7.05
2.17
O
N
H
CD3
1.00
3.19
1.17
3.07
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 -0.5 -1.0
f1 (ppm)

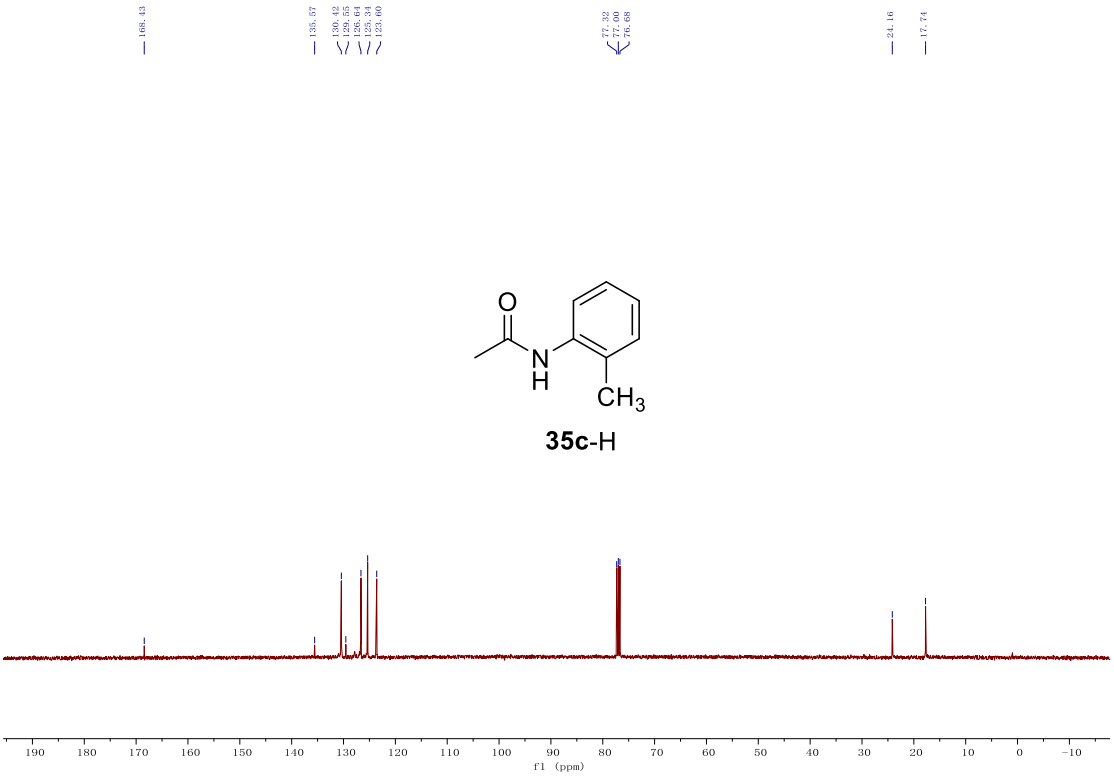
35c


168.48
135.59
130.41
129.56
126.61
125.58
123.64
77.32
77.00
76.68
24.11
O
N
H
CD3
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

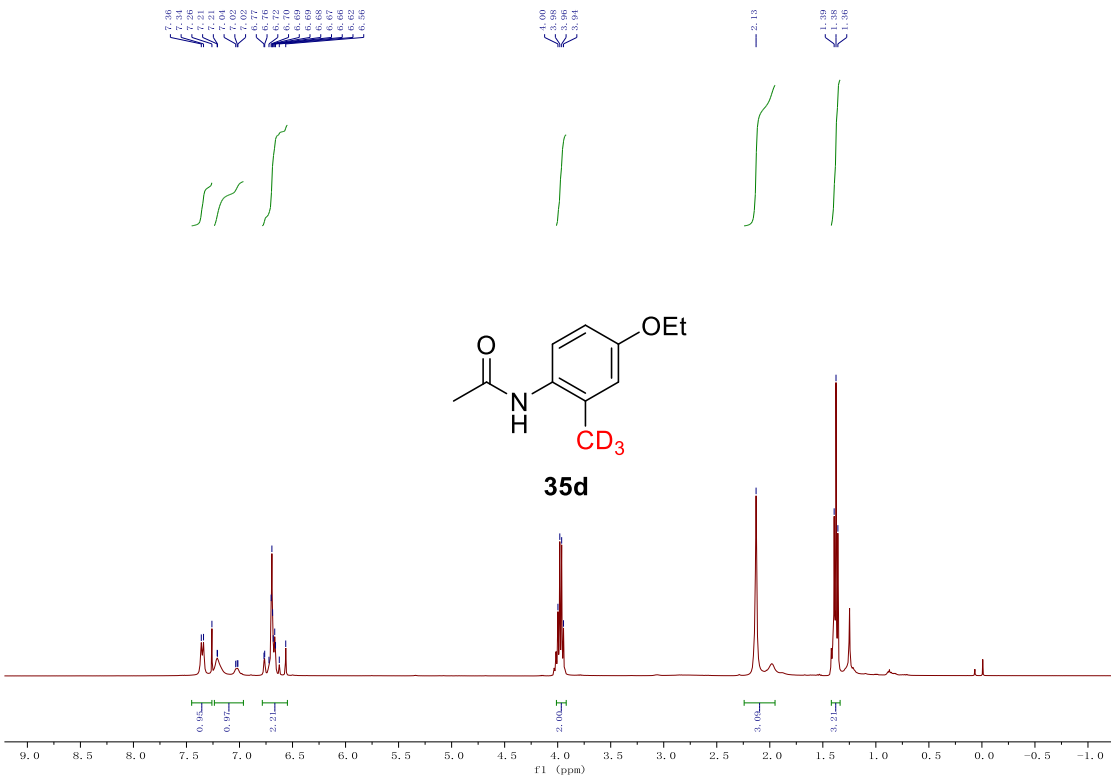
35c

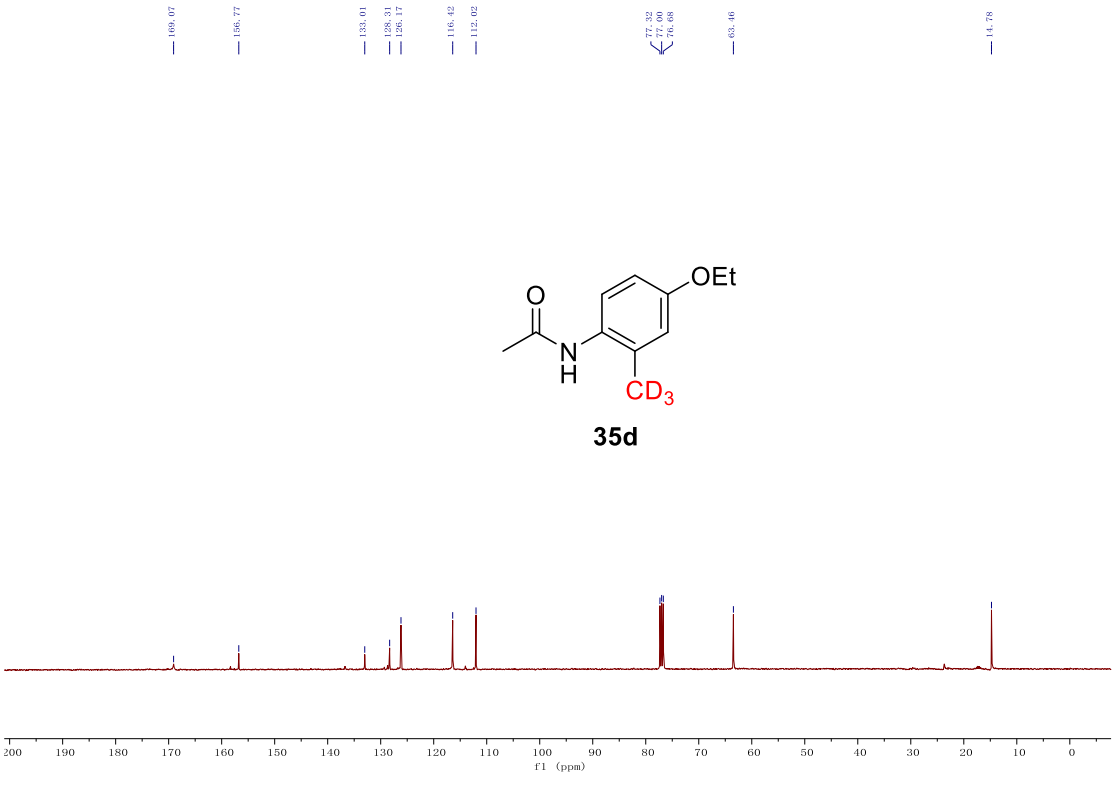

7.71
7.69
7.35
7.21
7.20
7.18
7.16
7.14
7.09
7.07
7.05
2.24
2.18
1.00
3.17
1.14
3.25
3.03
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

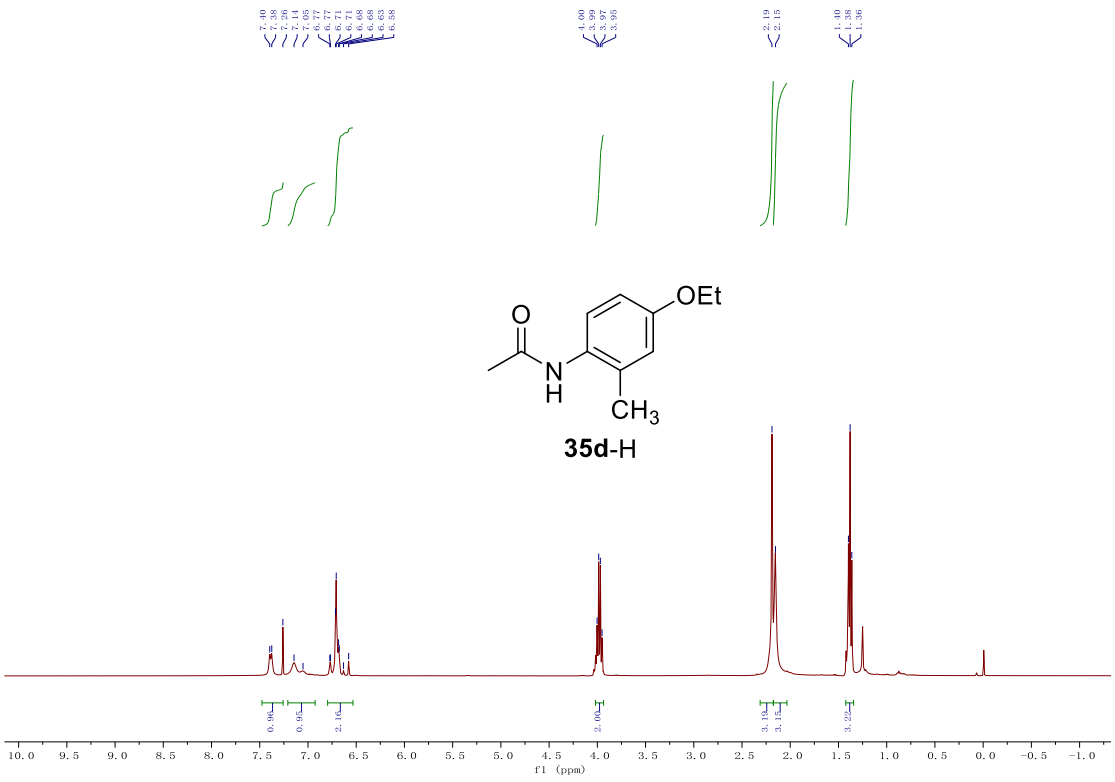
35c-H

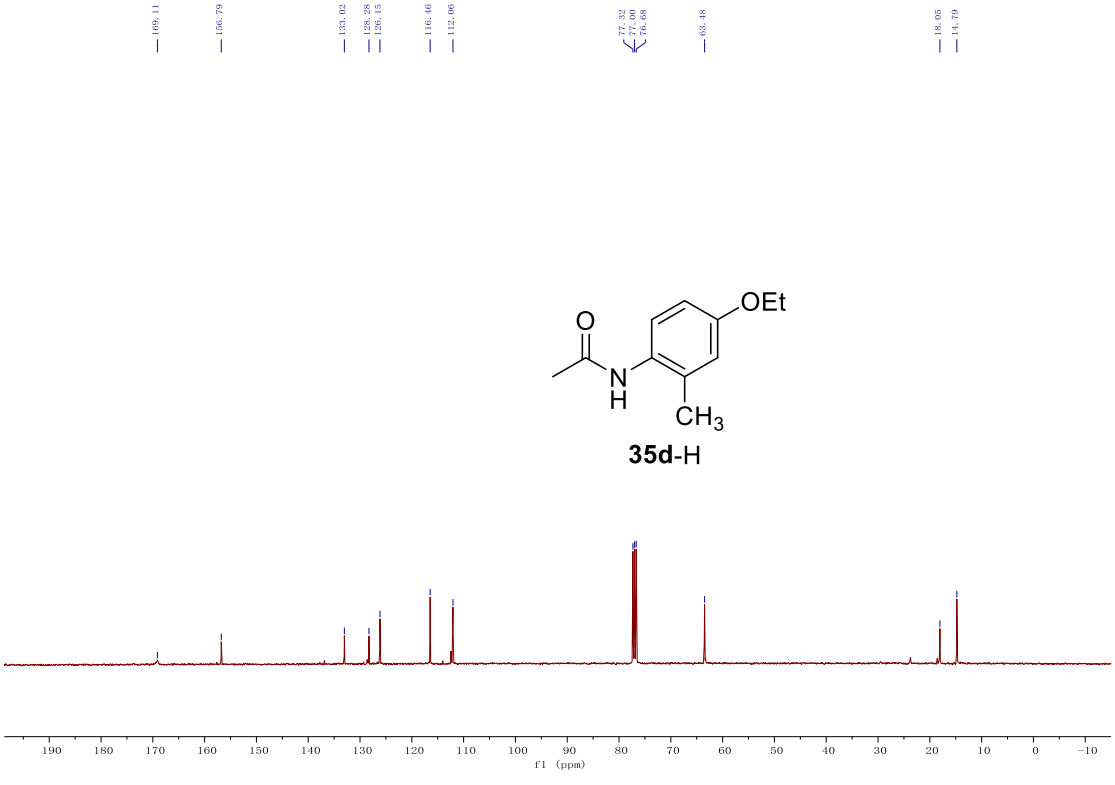

168.43
135.57
130.42
129.55
126.64
125.34
123.60
77.32
77.00
76.68
24.16
17.74
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

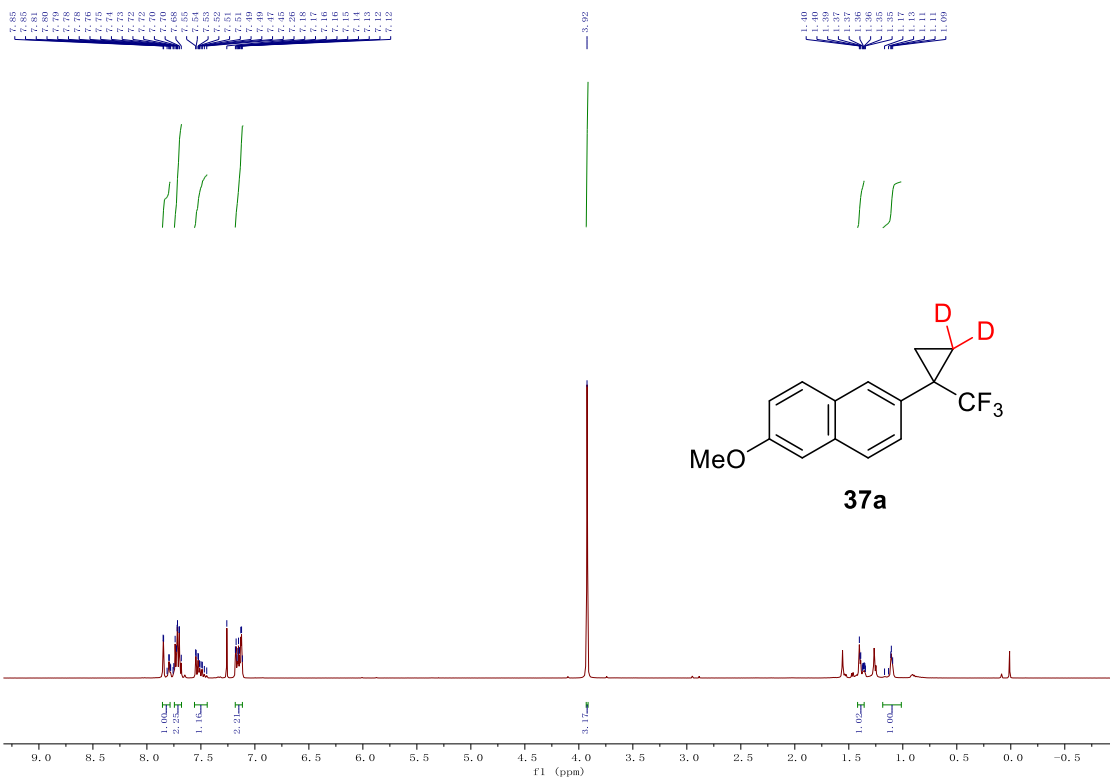
35c-H

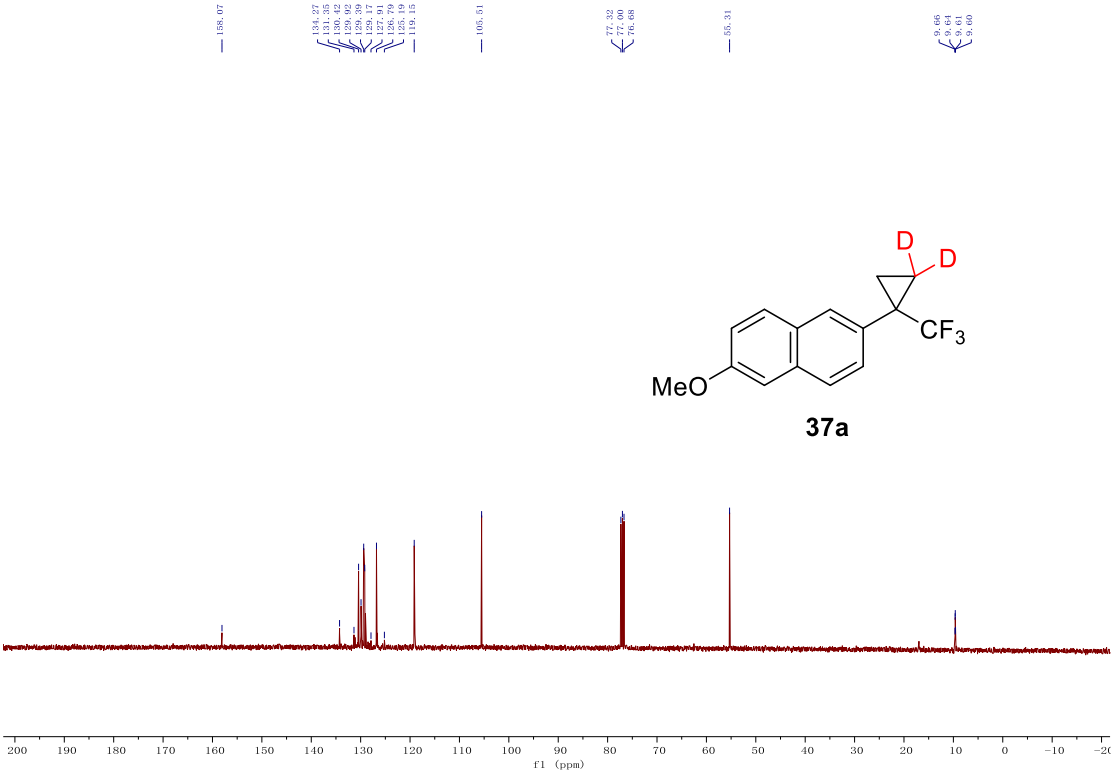

7.36
7.34
7.26
7.21
7.21
7.11
7.04
7.02
7.02
6.77
6.76
6.72
6.70
6.69
6.69
6.68
6.67
6.66
6.65
6.62
6.56
4.00
3.98
3.96
3.94
2.13
1.39
1.38
1.36
O
N
H
OEt
CD3
35d
0.98
0.97
2.21
2.00
3.00
3.24
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

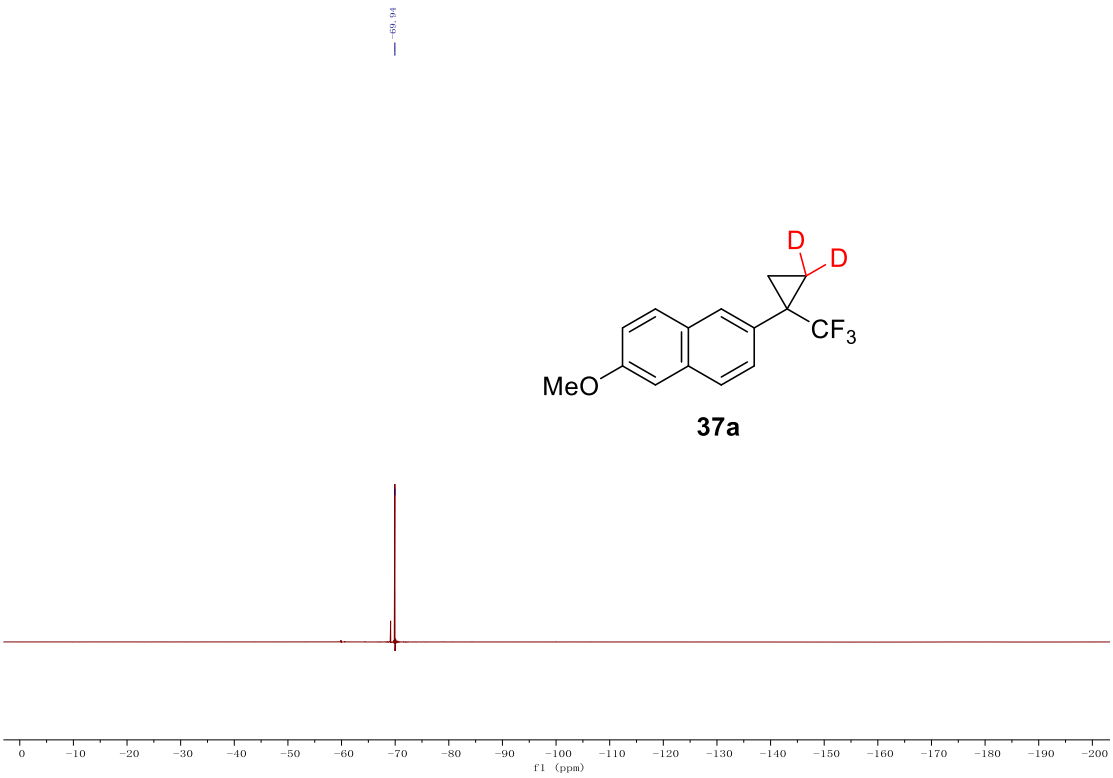

169.07
156.77
133.01
128.31
126.17
116.42
112.02
77.32
77.00
76.68
63.46
14.78
O
N
H
OEt
CD3
35d
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

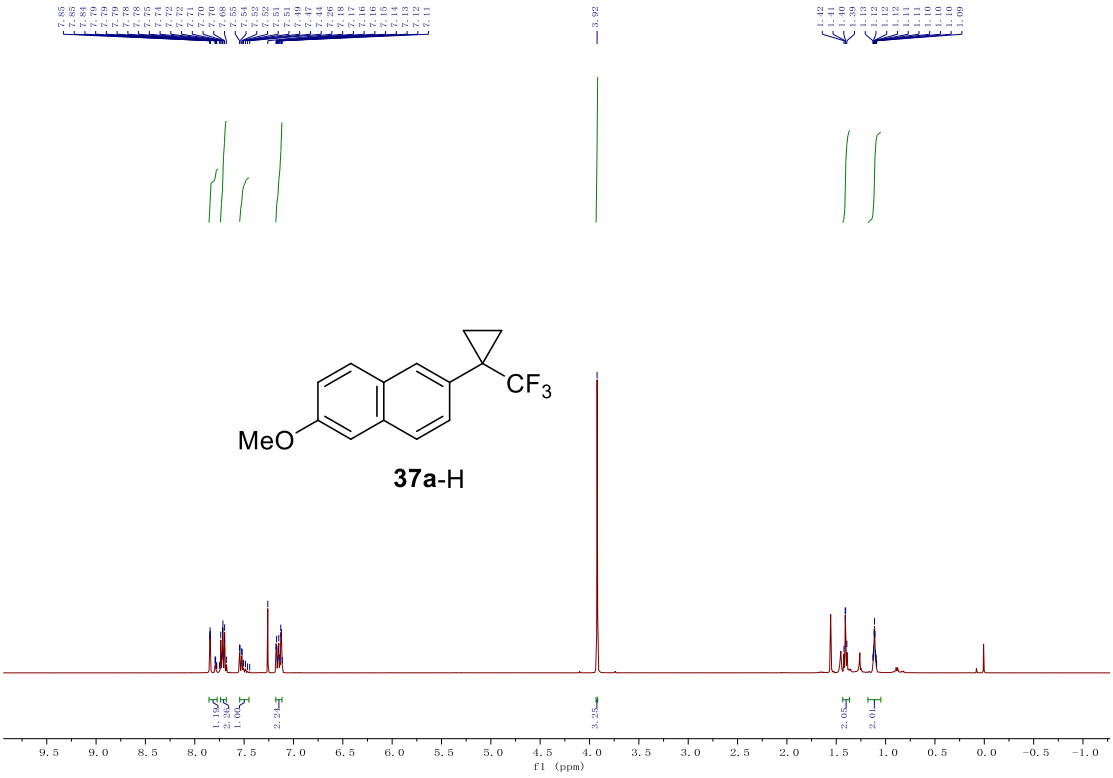

7.40
7.38
7.26
7.14
7.05
6.77
6.77
6.71
6.71
6.68
6.68
6.63
6.58
4.00
3.99
3.97
3.95
2.19
2.15
1.40
1.38
1.36
OEt
O
N
H
CH3
35d-H
0.96
0.96
2.14
2.00
3.19
3.15
3.22
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

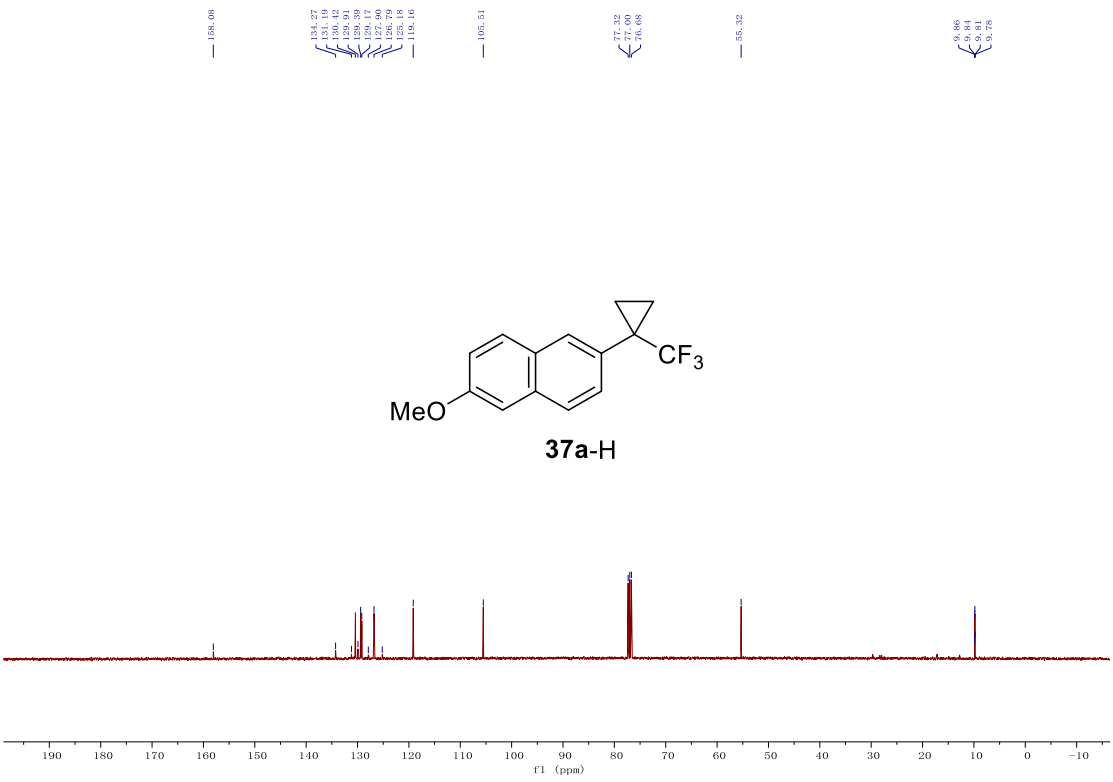

169.11
156.79
133.02
128.28
126.15
116.46
112.06
77.32
77.00
76.68
63.48
18.05
14.79
OEt
O
N
H
CH3
35d-H
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

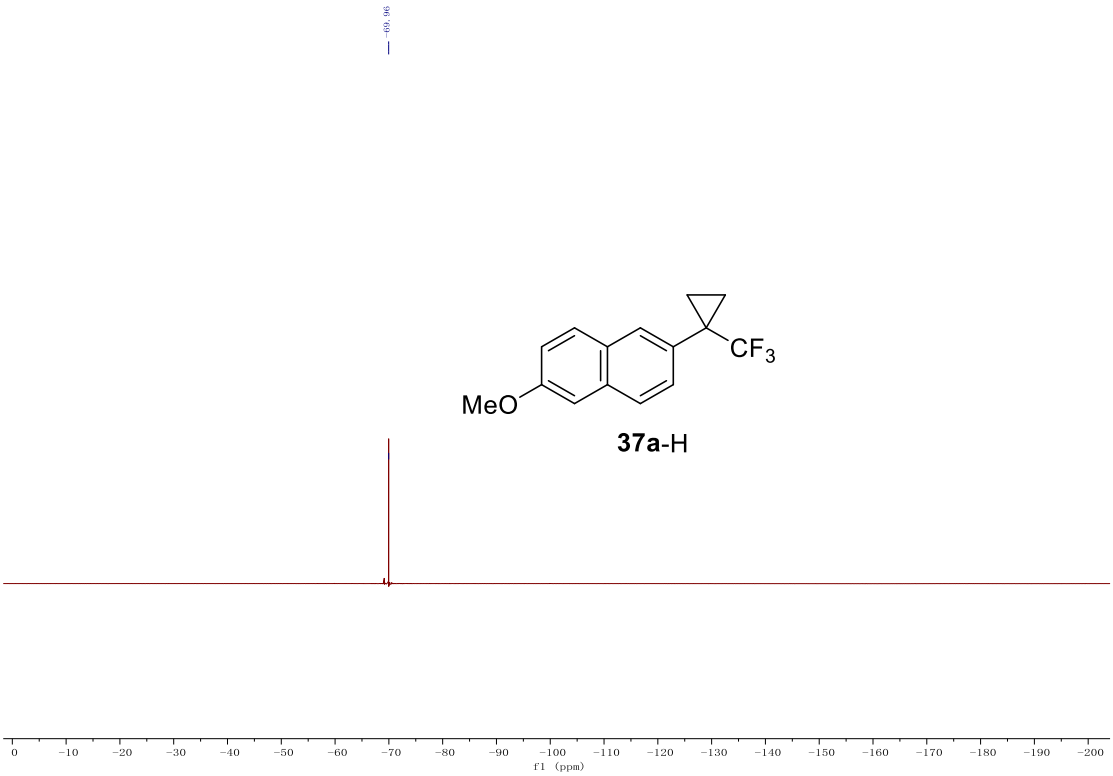

D
D
CF3
MeO
37a
f1 (ppm)

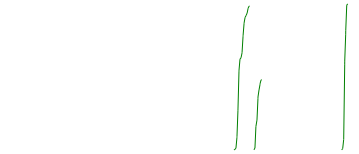

D
D
CF3
MeO
37a
f1 (ppm)

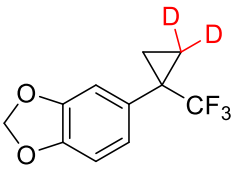

-69.94
D
D
CF3
MeO
37a
f1 (ppm)


7.85
7.85
7.84
7.84
7.79
7.79
7.79
7.78
7.78
7.75
7.74
7.72
7.72
7.71
7.70
7.70
7.68
7.55
7.54
7.52
7.52
7.51
7.49
7.47
7.47
7.44
7.26
7.18
7.17
7.16
7.16
7.15
7.14
7.13
7.12
7.11
3.92
1.42
1.41
1.40
1.39
1.13
1.12
1.12
1.12
1.11
1.11
1.10
1.10
1.10
1.10
1.09
CF3
MeO
37a-H
1.19
2.36
1.00
2.24
3.25
2.05
2.01
f1 (ppm)

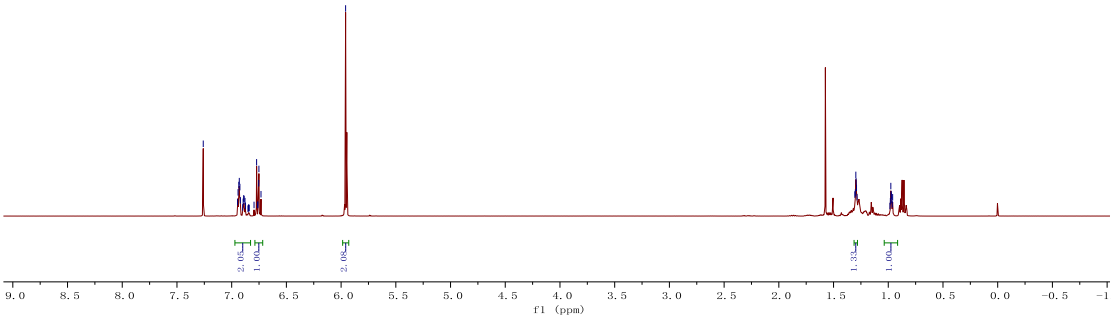

158.08
134.27
131.19
130.42
129.91
129.39
129.17
127.96
126.79
125.18
119.16
105.51
77.32
77.00
76.68
55.32
9.86
9.84
9.81
9.78
MeO
CF3
37a-H
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

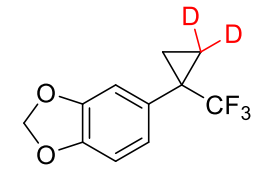

-69.96
MeO
CF3
37a-H
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−200
f1 (ppm)



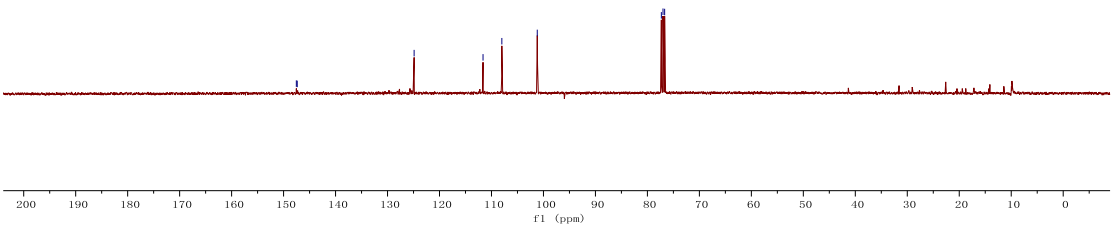

D
D
O
O
CF3

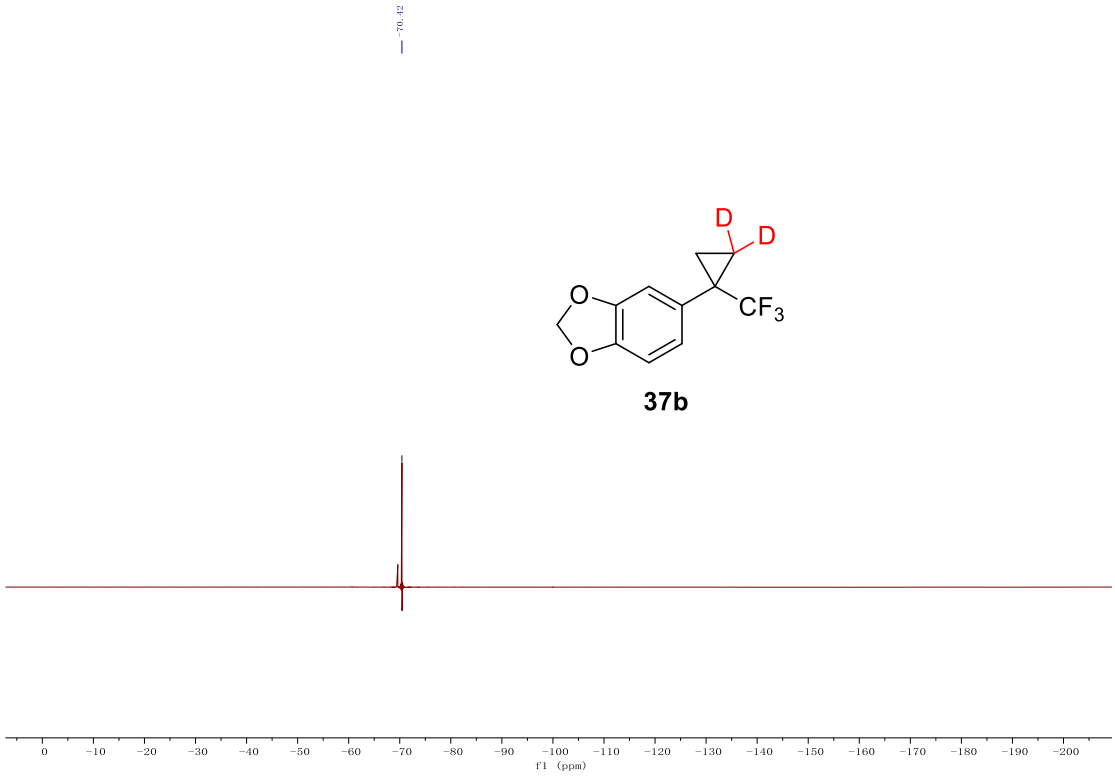
37b

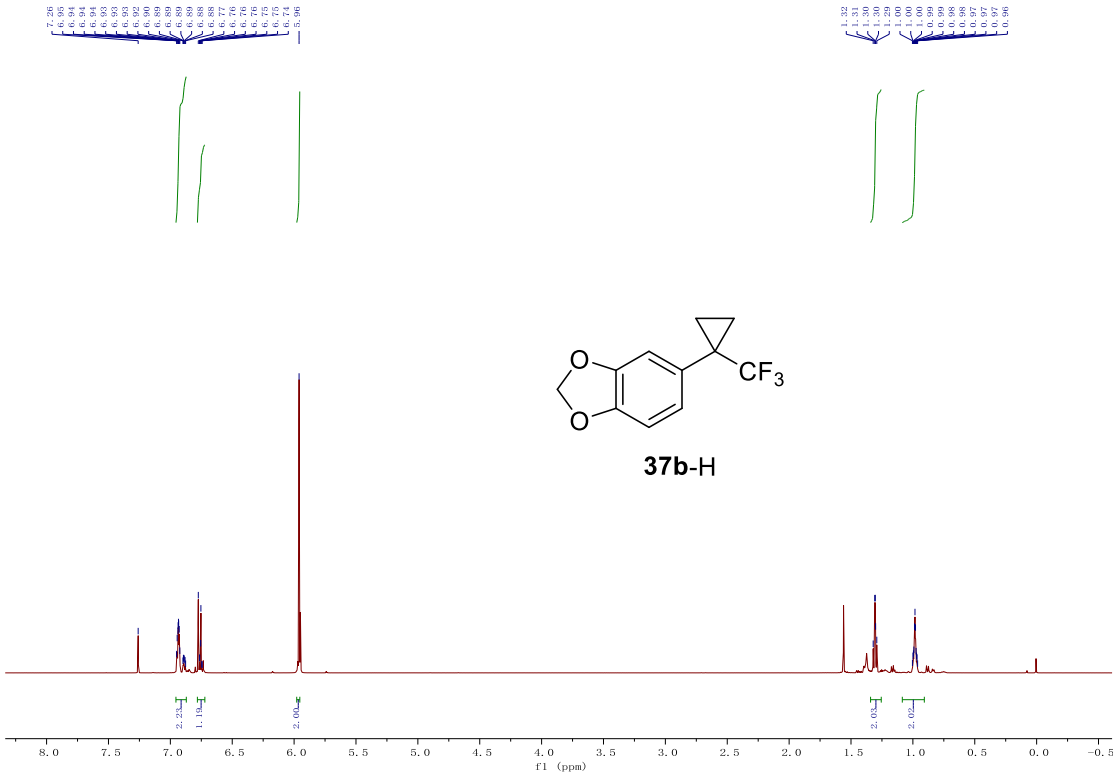

2.00
1.00
2.00
1.33
1.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1
f1 (ppm)

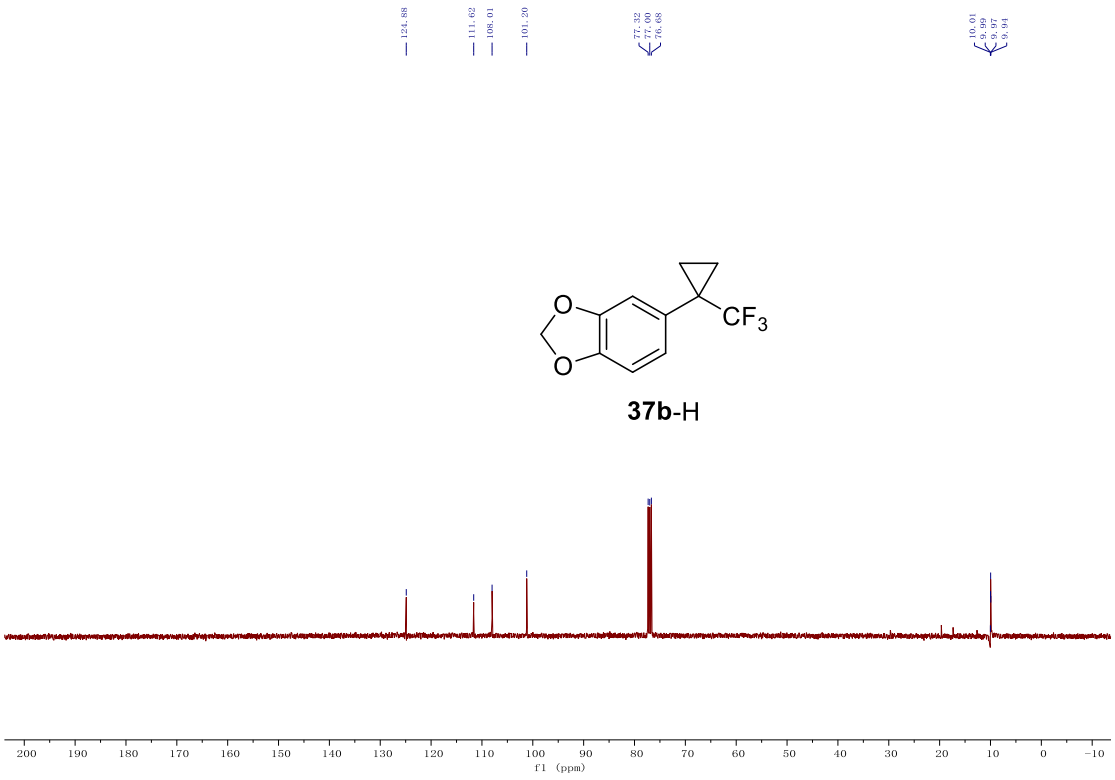

D
D
O
O
CF3

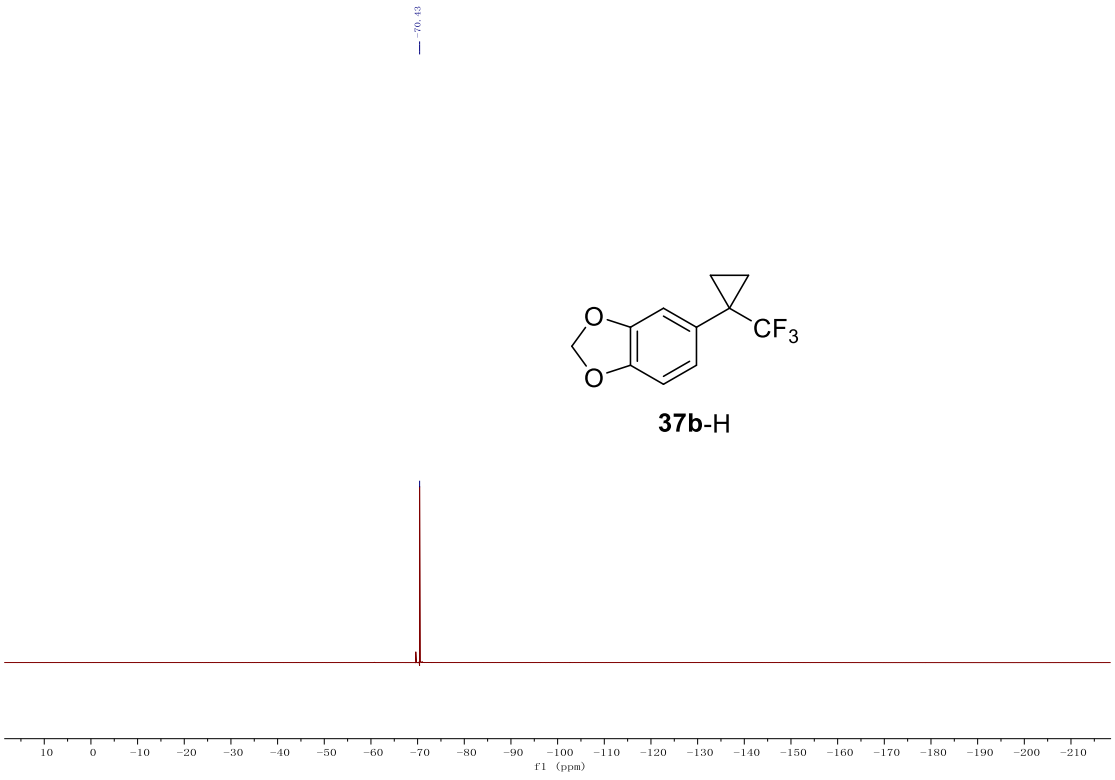
37b

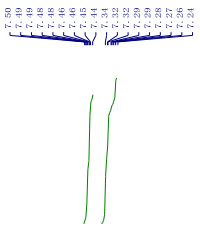

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

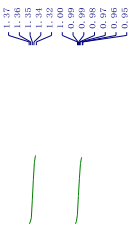

-70.42
D
D
O
O
CF3
37b
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−200
f1 (ppm)

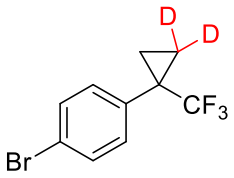

7.26
6.95
6.94
6.94
6.94
6.93
6.93
6.93
6.92
6.90
6.89
6.89
6.89
6.88
6.88
6.77
6.76
6.76
6.75
6.75
6.74
5.96
1.32
1.31
1.30
1.30
1.29
1.00
1.00
1.00
0.99
0.99
0.98
0.98
0.97
0.97
0.97
0.96
O
O
CF3
37b-H
2.23
1.19
2.00
2.03
2.02
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


124.88
111.62
108.01
101.20
77.32
77.00
76.68
10.01
9.99
9.97
9.94
O
O
CF3
37b-H
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

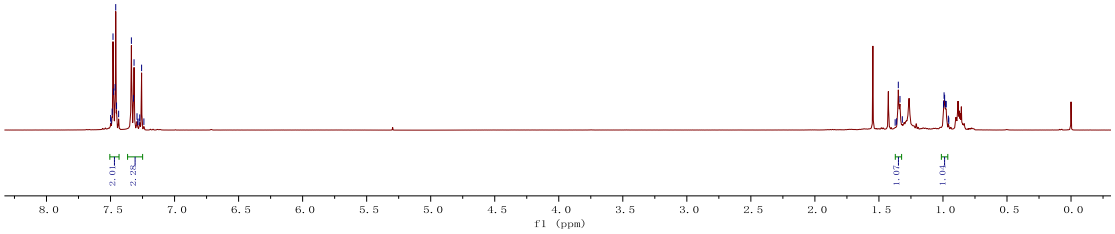

-70.43
O
O
CF3
37b-H
10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210
f1 (ppm)

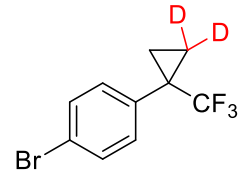




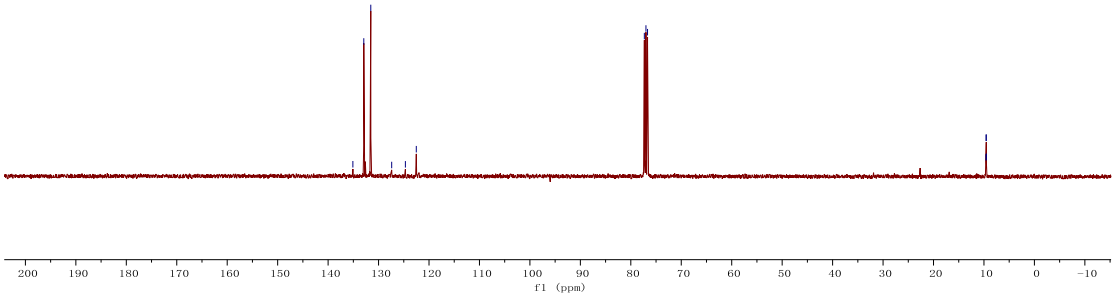

D
D
CF3
Br

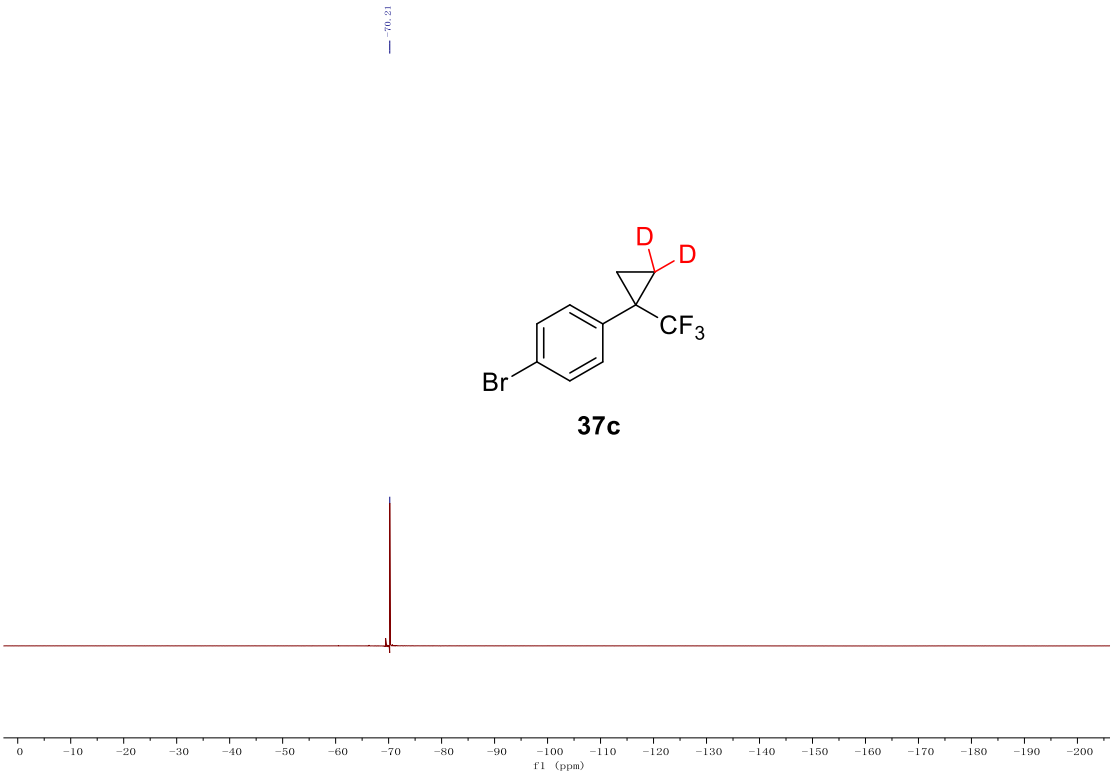
37c

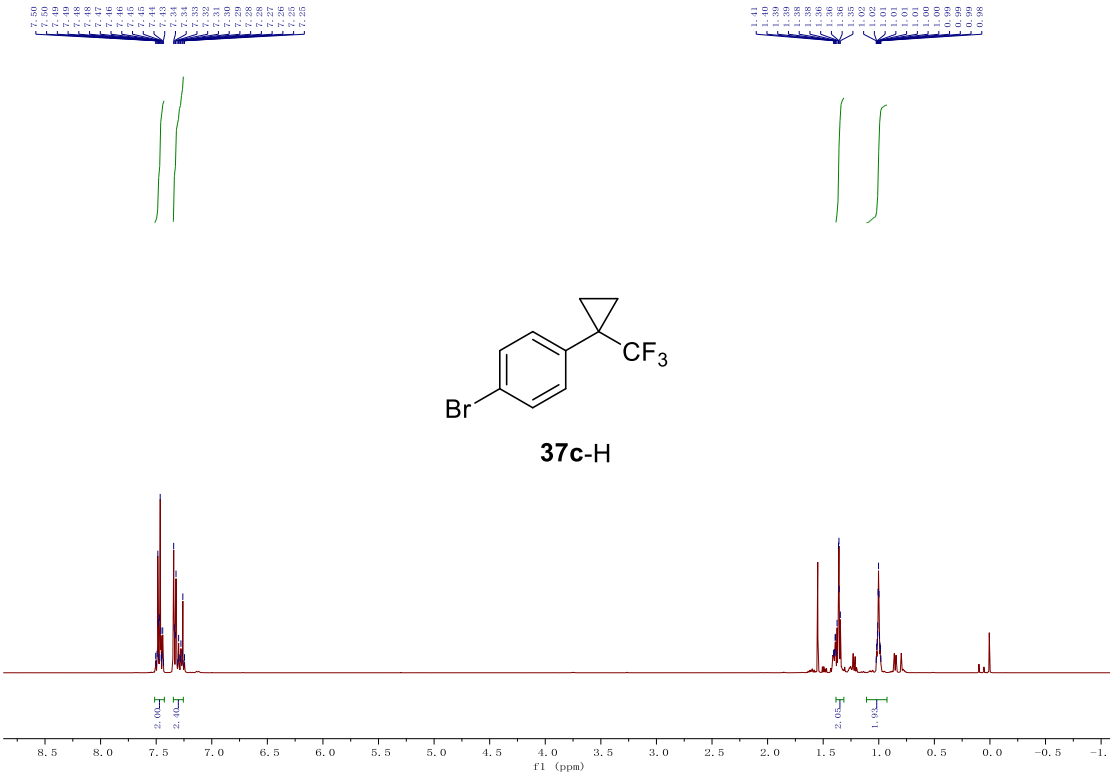

2.01
2.28
1.07
1.04
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


D
D
CF3
Br

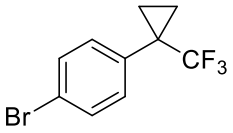
37c


200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

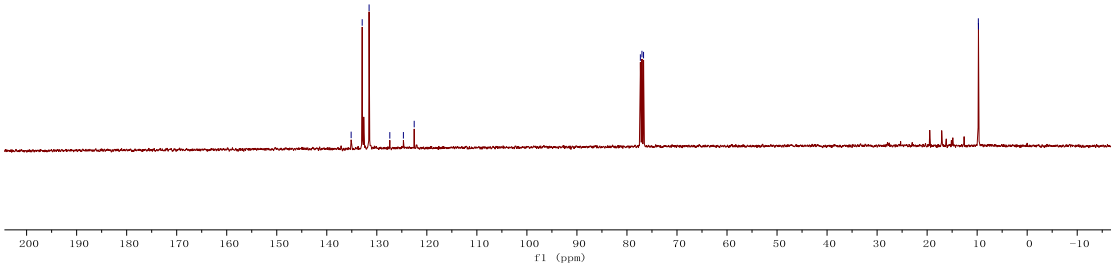

-70.21
D
D
CF3
Br
37c
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)


7.50
7.49
7.49
7.48
7.48
7.47
7.47
7.46
7.46
7.45
7.45
7.44
7.43
7.34
7.33
7.32
7.31
7.30
7.29
7.28
7.27
7.26
7.25
1.41
1.40
1.39
1.39
1.38
1.38
1.36
1.36
1.35
1.35
1.02
1.01
1.01
1.01
1.00
1.00
0.99
0.99
0.98
CF3
Br
37c-H
2.00
2.40
2.05
1.93
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)

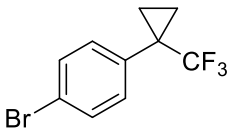

135.13
130.82
131.54
127.40
124.68
122.53
77.32
77.00
76.68
9.76
9.74


CF3
Br

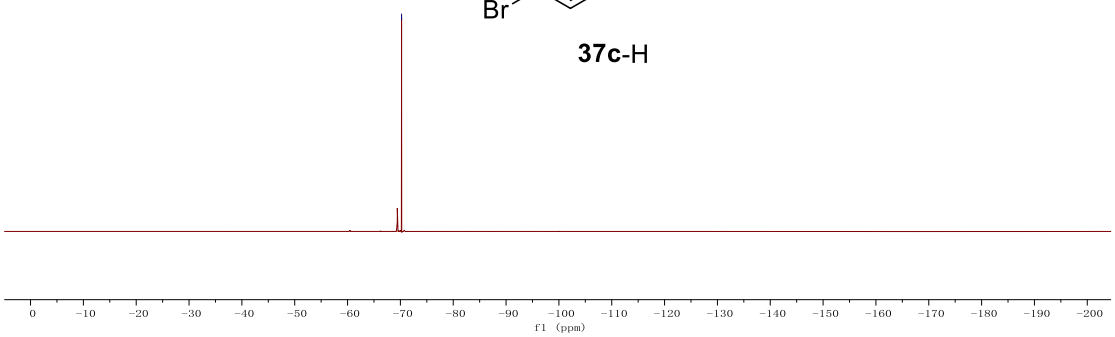
37c-H

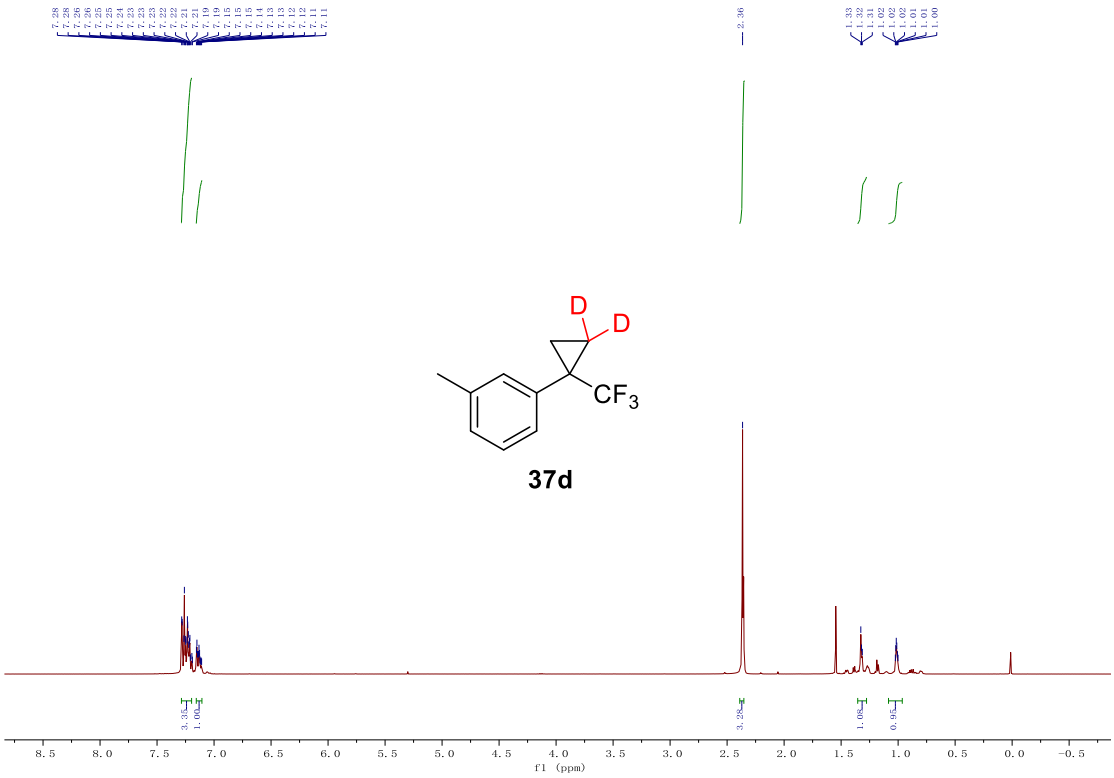

200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

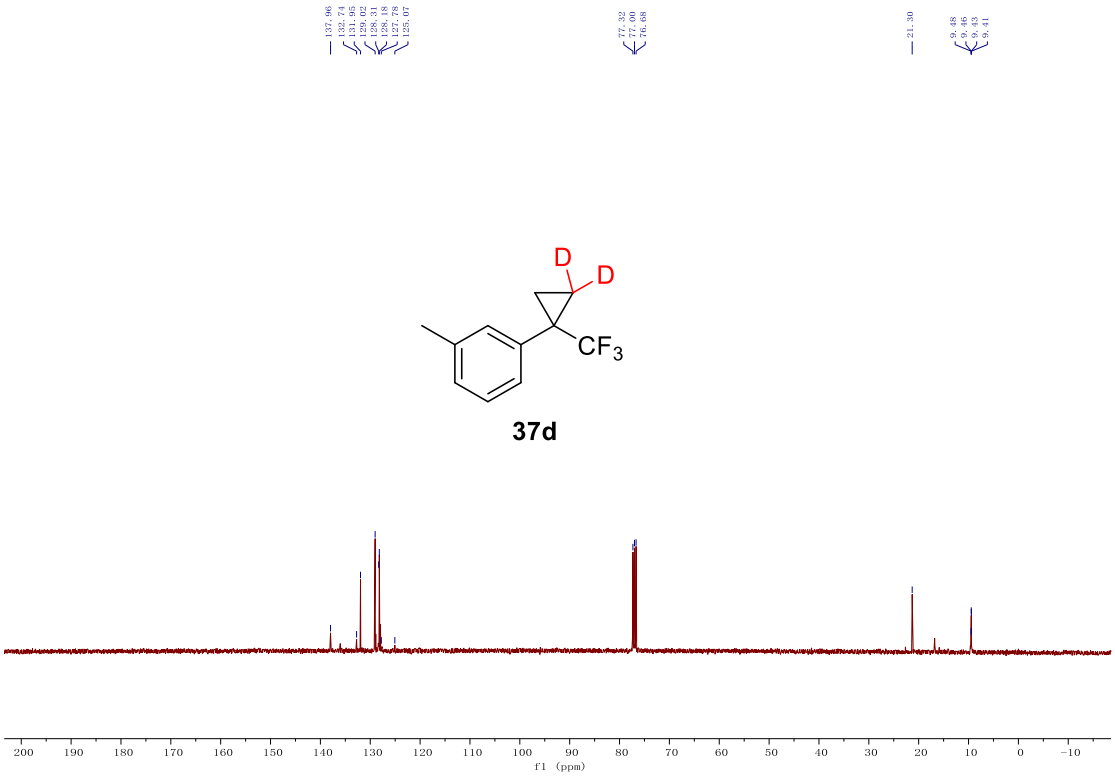
-70.22

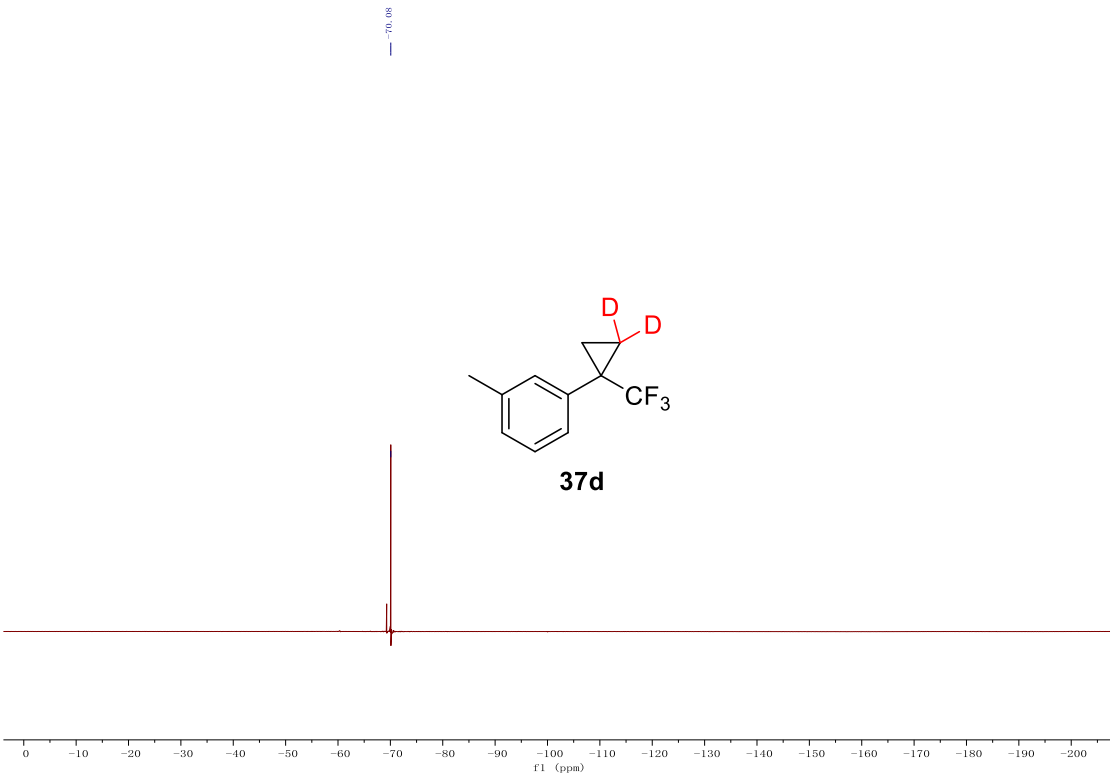

CF3
Br

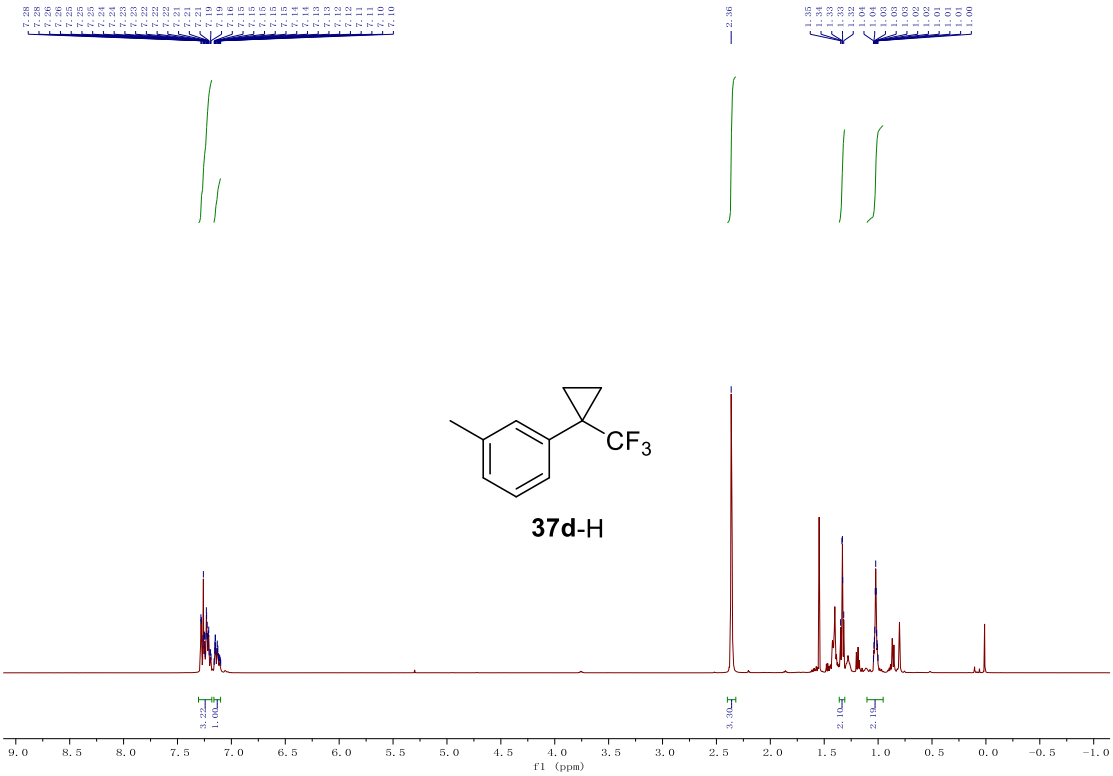
37c-H


0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−200
f1 (ppm)

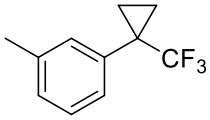

D
D
CF3
37d
f1 (ppm)


D
D
CF3
37d
f1 (ppm)

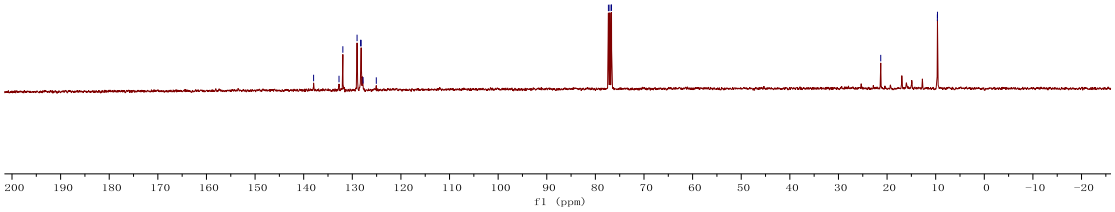

-70.08
D
D
CF3
37d
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)


7.28
7.26
7.25
7.24
7.23
7.22
7.21
7.19
7.16
7.15
7.14
7.13
7.12
7.11
7.10
2.36
1.35
1.34
1.33
1.32
1.04
1.03
1.02
1.01
1.00
CF3
37d-H
3.22
1.00
3.30
2.10
2.19
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
-0.5
-1.0
f1 (ppm)

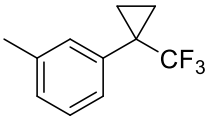

137.96
132.73
131.95
129.02
128.30
125.18
122.78
125.06
77.32
77.00
76.68
21.30
9.65
9.63


CF3

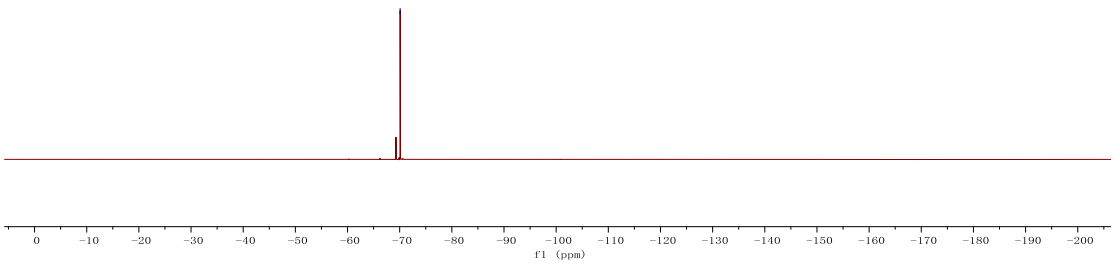
37d-H


200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
−20
f1 (ppm)

70.09


CF3

37d-H


0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−200
f1 (ppm)