Supporting Information

Unusual Biaryl Torsional Strain Promoted Reactivity in Cu-Catalyzed Sommelet-Hauser Rearrangement

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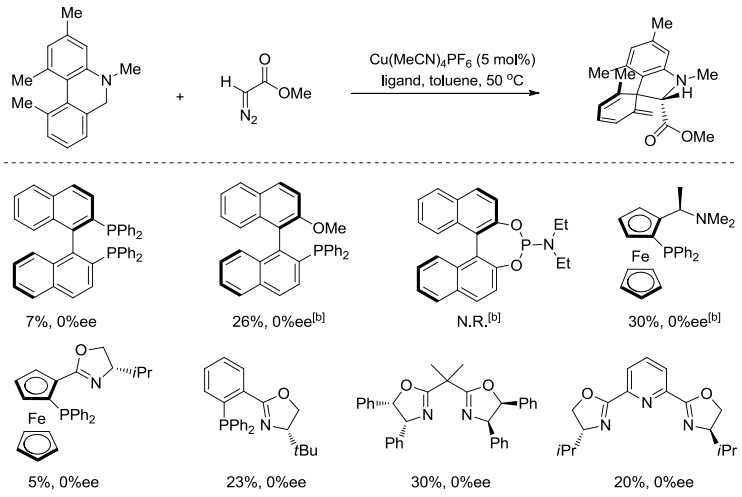
Contents:

General Information

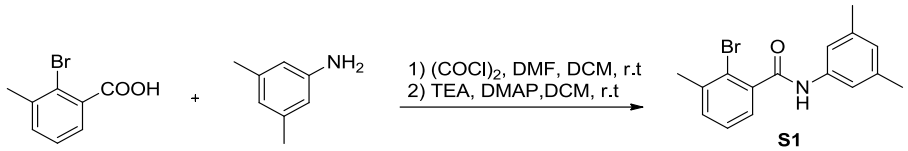
Nuclear magnetic resonances were recorded on Bruker-400 MHz instruments. Reference values for residual solvents were taken as δ = 7.26 ppm ($CDCl_3$), 2.50 ppm (DMSO-d_6) for ^{1}H NMR; δ = 77.00 ppm ($CDCl_3$), δ = 40.00 ppm (DMSO-d_6) for ^{13}C NMR. High resolution mass spectral analysis (HRMS) was performed on Waters XEVO G2 Q-TOF (Waters Corporation). All reactions were performed under an inert atmosphere of dry nitrogen in flame-dried glassware, unless otherwise stated. Tetrahydrofuran and *t*-butylmethyl ether were distilled over sodium in the presence of benzophenone under an atmosphere of nitrogen. Toluene, dichloromethane, 1,2-dichloroethane, *N*,*N*-dimethylformamide and triethylamine was distilled over calcium hydride under an atmosphere of nitrogen.

Ligand screened for catalytically asymmetric transformation for this rearrangement
However, no any enantioselectivity has been observed yet.



The reaction was conducted with **1a** (0.10 mmol), diazo compound (0.20 mmol), and $Cu(MeCN)_4PF_6$ (0.005 mmol, 5 mol%), ligand (0.005 mmol, 5 mol%), toluene at 50 °C. [b] 10 mol% of ligand was used.

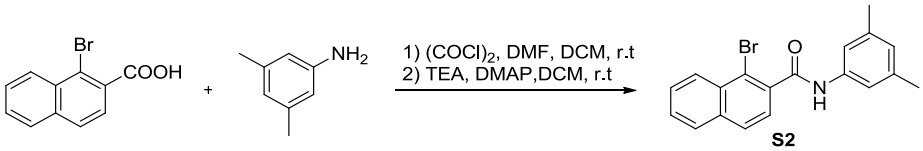
Typical Procedure for S1 (Typical Procedure A)



To a solution of 2-bromo-3-methylbenzoic acid (2.15 g, 10.0 mmol, 1.0 equiv) and DMF (2 drops) in DCM (50 mL) was added oxalyl chloride (1.30 mL, 15.0 mmol, 1.50 equiv) dropwise. It was stirred at room temperature for 1 h and concentrated under reduced pressure.

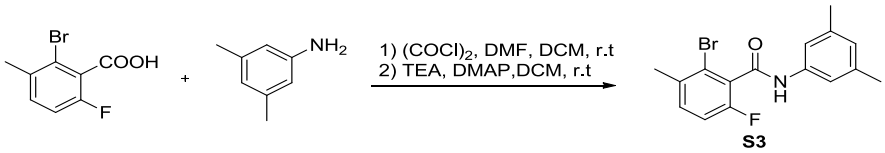
To a solution of the above acid chloride in DCM (20 mL) was added DMAP (61.1 mg, 0.50 mmol, 5 mol%), TEA (4.2 mL, 30.0 mmol, 3.0 equiv) and 3,5-dimethylaniline (1.50 mL, 12.0 mmol, 1.2 equiv) at 0 °C. The reaction mixture was stirred at rt for 10 h. Water was added, and the mixture was extracted with DCM (30 mL x 2). The combined organic phase was washed with aqueous hydrochloric acid (1 M, 50 mL x 2), saturated aqueous $NaHCO_3$ (30 mL) and brine (30 mL) and dried over Na_2SO_4. After filtration the solvent was removed by evaporation, and the resulting mixture was purified by column chromatography on silica gel (hexanes/ethyl acetate = 10 :1) to afford the desired product **S1** (3.07 g, 96%) as a white solid. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 10.29 (s, 1 H), 7.45 (d, *J* = 6.4 Hz, 1 H), 7.37 (t, *J* = 7.4 Hz, 1 H), 7.33 (s, 2 H), 7.29 (dd, *J* = 7.2, 1.2 Hz, 1 H), 6.74 (s, 1 H), 2.41 (s, 3 H), 2.25 (s, 6 H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 166.7, 140.7, 139.4, 138.7, 138.2, 131.9, 128.0, 126.5, 125.7, 121.7, 117.8, 23.4, 21.6. HRMS (ESI) calcd for $C_{16}H_{17}BrNO$ $[M+H]^+$ 318.0494, found 318.0493.

Compound **S2** was prepared following the **Typical Procedure A**



The reaction of 1-bromo-2-naphthoic acid (2.51 g, 10 mmol), oxalyl chloride (1.30 mL, 15.0 mmol, 1.5 equiv), DMAP (61.1 mg, 0.50 mmol, 5 mol%), TEA (4..2 mL, 30.0 mmol, 3.0 equiv) and 3,5-dimethylaniline (1.5 mL, 12.0 mmol, 1.2 equiv) afforded **S2** (3.30 g, 93%) as a white solid. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 10.43 (s, 1 H), 8.29 (d, *J* = 8.4 Hz, 1 H), 8.09 (d, *J* = 8.4 Hz, 1 H), 8.08 (d, *J* = 8.0 Hz, 1 H), 7.78 (t, *J* = 7.4 Hz, 1 H), 7.70 (t, *J* = 7.4 Hz, 1 H), 7.59 (d, *J* = 8.4 Hz, 1 H), 7.38 (s, 2 H), 6.77 (s, 1 H), 2.27 (s, 6 H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 166.8, 139.4, 138.3, 134.4, 131.6, 129.1, 129.0, 128.8, 128.1, 127.3, 125.9, 125.6, 119.4, 117.9, 21.6. HRMS (ESI) calcd for $C_{19}H_{17}BrNO$ $[M+H]^+$ 354.0494, found 354.0492.

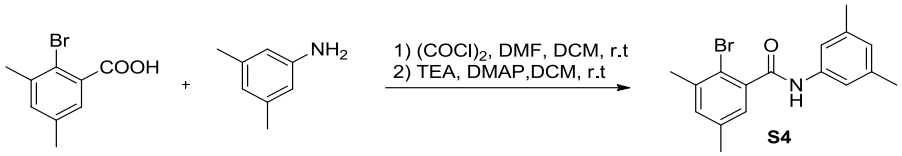
Compound **S3** was prepared following the **Typical Procedure A**



The reaction of 2-bromo-6-fluoro-3-methylbenzoic acid[1] (2.73 g, 11.7 mmol), oxalyl chloride (1.50 mL, 17.5 mmol, 1.5 equiv), DMAP (72.1 mg, 0.59 mmol, 5 mol%), TEA (4.9 ml, 35.1 mmol, 3.0 equiv) and 3,5-dimethylaniline (1.7 ml, 14.0 mmol, 1.2 equiv) afforded **S3** (3.49 g, 88%) as a

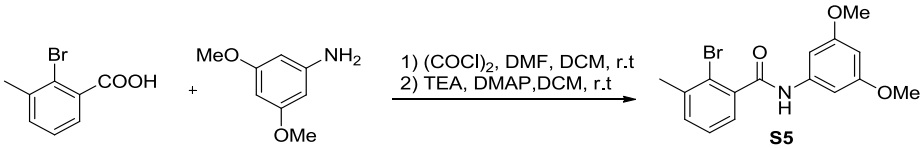
white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29 (s, 1 H), 7.28 – 7.23 (m, 3 H), 7.03 (t, *J* = 8.4 Hz, 1 H), 6.83 (s, 1 H), 2.41 (s, 3 H), 2.33 (s, 6 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 161.8, 157.3 (d, J_{C-F} = 248.2 Hz), 138.9, 137.1, 134.8 (d, J_{C-F} = 3.7 Hz), 132.0 (d, J_{C-F} = 8.0 Hz), 127.6 (d, J_{C-F} = 21.4 Hz), 126.8, 122.4 (d, J_{C-F} = 4.5 Hz), 117.9, 114.7 (d, J_{C-F} = 21.1 Hz), 22.6, 21.3. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -116.3. HRMS (ESI) calcd for $C_{16}H_{16}BrFNO$ $[M+H]^+$ 336.0399, found 336.0398.

Compound **S4** was prepared following the **Typical Procedure A**



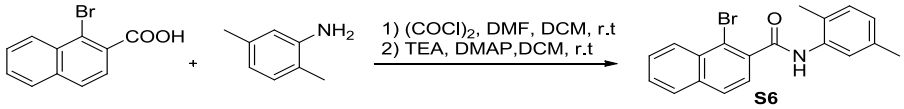
The reaction of 2-bromo-3,5-dimethylbenzoic acid[2] (2.30 g, 10.0 mmol), oxalyl chloride (1.30 mL, 15.0 mmol, 1.5 equiv), DMAP (61.1 mg, 0.50 mmol, 5 mol%), TEA (4.2 mL, 30.0 mmol, 3.0 equiv) and 3,5-dimethylaniline (1.50 mL, 12.0 mmol, 1.2 equiv) afforded **S4** (2.87 g, 86%) as a white solid. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 10.24 (s, 1 H), 7.33 (s, 2 H), 7.11 (s, 1 H), 6.73 (s, 1 H), 2.36 (s, 3 H), 2.28 (s, 3 H), 2.24 (s, 6 H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 166.7, 140.4, 139.4, 138.3, 138.1, 137.5, 132.5, 127.0, 125.7, 118.4, 117.8, 23.2, 21.6, 20.6. HRMS (ESI) calcd for $C_{17}H_{18}BrNO$ $[M+H]^+$ 332.0650, found 332.0654.

Compound **S5** was prepared following the **Typical Procedure A**



The reaction of 2-bromo-3-methylbenzoic acid (2.15 g, 10.0 mmol), oxalyl chloride (1.30 mL, 15.0 mmol, 1.5 equiv), DMAP (61.1 mg, 0.50 mmol, 5 mol%), TEA (4.2 mL, 30.0 mmol, 3.0 equiv) and 3,5-dimethoxyaniline (1.84 g, 12.0 mmol, 1.2 equiv) afforded **S5** (2.97 g, 85%) as a white solid. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 10.39 (s, 1 H), 7.45 (d, *J* = 7.2 Hz, 1 H), 7.38 (t, *J* = 7.4 Hz, 1 H), 7.31 (d, *J* = 7.2 Hz, 1 H), 6.982 (s, 1 H), 6.977 (s, 1 H), 6.27 (s, 1 H), 3.72 (s, 6 H), 2.42 (s, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.5, 160.8, 139.4, 139.1, 138.7, 131.9, 127.1, 126.1, 121.4, 98.0, 96.9, 55.2, 23.4. HRMS (ESI) calcd for $C_{16}H_{17}BrNO_3$ $[M+H]^+$ 350.0392, found 350.0385.

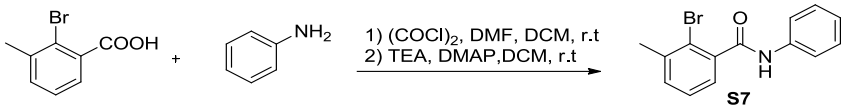
Compound **S6** was prepared following the **Typical Procedure A**



The reaction of 1-bromo-2-naphthoic acid (2.51 g, 10.0 mmol), oxalyl chloride (1.30 mL, 15.0 mmol, 1.5 equiv), DMAP (61.1 mg, 0.50 mmol, 5 mol%), TEA (4.2 mL, 30.0 mmol, 3.0 equiv) and 2,5-dimethylaniline (1.5 mL, 12.0 mmol, 1.2 equiv) afforded **S6** (2.79 g, 79%) as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.38 (d, *J* = 8.4 Hz, 1 H), 8.00 – 7.81 (m, 3 H), 7.68 (t, *J* = 7.4 Hz, 1 H), 7.65 – 7.50 (m, 2 H), 7.49 (s, 1 H), 7.12 (d, *J* = 8.0 Hz, 1 H), 6.96 (d, *J* = 7.6 Hz, 1 H), 2.38 (s, 3 H), 2.31 (s, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.6, 136.7, 136.5, 135.1, 134.7, 131.9,

130.4, 128.5, 128.3, 127.9, 127.8, 126.4, 126.1, 125.2, 123.5, 119.8, 21.2, 17.6. HRMS (ESI) calcd for $C_{19}H_{17}BrNO$ $[M+H]^+$ 354.0494, found 354.0485.

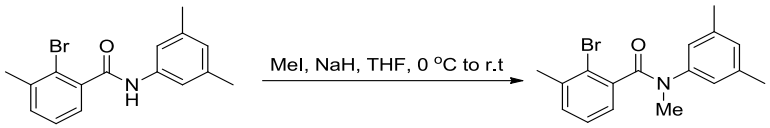
Compound **S**7 was prepared following the **Typical Procedure A**



S7

The reaction of 2-bromo-3-methylbenzoic acid (2.15 g, 10.0 mmol), oxalyl chloride (1.30 mL, 15.0 mmol, 1.5 equiv), DMAP (61.1 mg, 0.50 mmol, 5 mol%), TEA (4.2 mL, 30.0 mmol, 3.0 equiv) and 3,5-dimethylaniline (1.10 mL, 12.0 mmol, 1.2 equiv) afforded **S7** (2.40 g, 83%) as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.83 (s, 1 H), 7.61 (d, *J* = 8.0 Hz, 2 H), 7.35 (t, *J* = 7.8 Hz, 2 H), 7.29 (d, *J* = 7.6 Hz, 2 H), 7.23 (t, *J* = 7.4 Hz, 1 H), 7.15 (t, *J* = 7.4 Hz, 1 H), 2.44 (s, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.5, 139.2, 138.9, 137.6, 132.1, 129.0, 127.3, 126.3, 124.6, 121.6, 112.0, 23.5. HRMS (ESI) calcd for $C_{14}H_{13}BrNO$ $[M+H]^+$ 290.0181, found 290.0185.

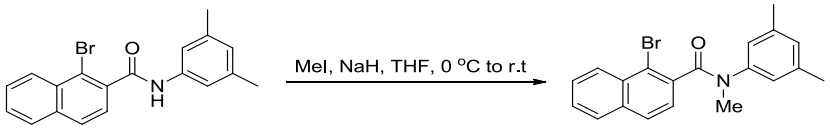
Typical Procedure for S8 (Typical Procedure B)



S1 **S8**

To a suspension of NaH (60% in mineral oil, 0.40 g, 10.0 mmol, 2.0 equiv) in dry THF (5.0 mL) was added **S1** (1.59 g, 5.0 mmol, 1.0 equiv) in dry THF (15.0 mL) dropwise at 0 °C. After stirring for 30 min at 0 °C, MeI (0.75 mL, 12.0 mmol, 2.4 equiv) added dropwise and the reaction mixture was allowed to warm to room temperature and stirred for additional 2 h. Water (1.0 mL) was added at 0 °C, and the mixture was extracted with EtOAc (30 mL x 2). The combined organic phase was washed with brine (30 mL) and dried over Na_2SO_4. After filtration the solvent was removed by evaporation, and the resulting mixture was purified by column chromatography on silica gel (hexanes/ethyl acetate = 10 :1) to afford the desired product **S8** (1.58 g, 95%) as a white solid. A mixture of rotamers were observed and the followings are selected peaks: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.02 – 6.99 (m, 1 H), 6.96 (t, *J* = 7.4 Hz, 1 H), 6.90 (d, *J* = 7.2 Hz, 1 H), 6.78 (s, 2 H), 6.72 (s, 1 H), 3.46 (s, 3 H), 2.31 (s, 3 H), 2.16 (s, 6 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.3, 143.1, 139.2, 138.9, 138.4, 130.3, 128.7, 127.7, 126.3, 126.1, 124.4, 123.6, 122.0, 37.1, 23.2, 20.9. HRMS (ESI) calcd for $C_{17}H_{19}BrNO$ $[M+H]^+$ 332.0650, found 332.0656.

Compound **S9** was prepared following the **Typical Procedure B**

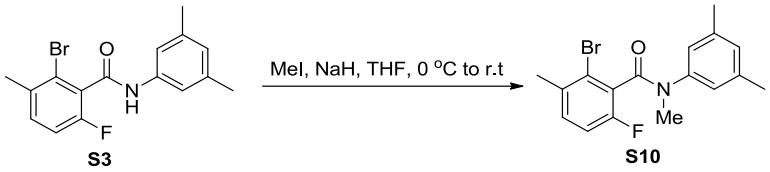


S2 **S9**

The reaction of **S2** (2.48 g, 7.0 mmol), NaH (60% in mineral oil, 0.467 g, 11.9 mmol, 1.7 equiv) and CH_3I (0.90 mL, 11.9 mmol, 2.0 equiv) afforded **S9** (2.50 g, 97%) as a white solid. A mixture of rotamers were observed and the followings are selected peaks: **^{1}H NMR** (400 MHz, DMSO-d_6) δ 8.14 (d, *J* = 8.4 Hz, 1 H), 7.90 (d, *J* = 8.0 Hz, 1 H), 7.83 (d, *J* = 8.4 Hz, 1 H), 7.64 (t, *J* = 7.6 Hz, 1 H), 7.58 (t, *J* = 7.4 Hz, 1 H), 7.45 (d, *J* = 8.4 Hz, 1 H), 6.94 (s, 2 H), 6.68 (s, 1 H), 3.39 (s, 3 H),

2.04 (s, 6 H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 168.3, 143.1, 138.4, 137.8, 133.7, 131.2, 129.2, 128.9, 128.8, 127.9, 127.86, 126.9, 126.1, 125.1, 124.6, 119.2, 37.2, 21.0. HRMS (ESI) calcd for $C_{20}H_{19}BrNO$ $[M+H]^+$ 368.0650, found 368.0647.

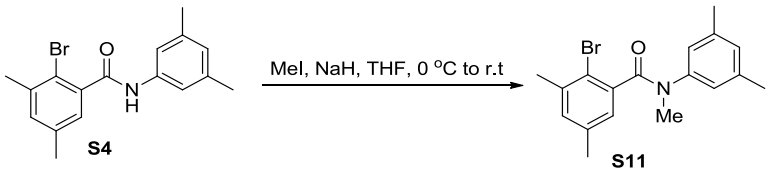
Compound **S10** was prepared following the **Typical Procedure B**



S3 **S10**

The reaction of **S3** (3.32 g, 9.88 mmol), NaH (60% in mineral oil, 0.672 g, 16.8 mmol, 1.7 equiv) and CH_3I (1.23 mL, 16.8 mmol, 2.0 equiv) afforded **S10** (3.11 g, 90%) as a white solid. A mixture of rotamers were observed and the followings are selected peaks: **^{1}H NMR** (400 MHz, $CDCl_3$) 7.00 (t, *J* = 7.4 Hz, 1 H), 6.89 (s, 2 H), 6.78 (s, 1 H), 6.74 (t, *J* = 8.4 Hz, 1 H), 3.45 (s, 3 H), 2.25 (s, 3 H), 2.18 (s, 6 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.6, 156.3 (d, J_{C-F} = 245.8 Hz), 142.4, 138.5, 134.0 (d, J_{C-F} = 3.5 Hz), 131.0 (d, J_{C-F} = 8.1 Hz), 129.5, 127.8 (d, J_{C-F} = 21.8 Hz), 123.7, 122.1 (d, J_{C-F} = 5.2 Hz), 113.7 (d, J_{C-F} = 21.3 Hz), 37.0, 22.4, 21.0. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -114.6. HRMS (ESI) calcd for $C_{17}H_{18}BrFNO$ $[M+H]^+$ 350.0556, found 350.0555.

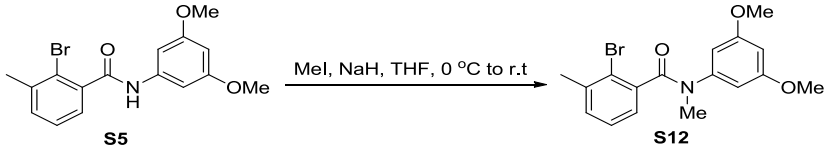
Compound **S11** was prepared following the **Typical Procedure B**



S4 **S11**

The reaction of **S4** (1.92 g, 5.78 mmol), NaH (60% in mineral oil, 0.393 g, 9.826 mmol, 1.7 equiv) and CH_3I (0.72 mL, 11.56 mmol, 2.0 equiv) afforded **S11** (1.65 g, 83%) as a white solid. A mixture of rotamers were observed and the followings are selected peaks: **^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.04 (s, 1 H), 6.97 (s, 1 H), 6.91 (s, 1 H), 6.87 (s, 1 H), 6.76 (s, 1 H), 2.30 (s, 3 H), 2.19 (s, 3 H), 2.11 (s, 9 H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 168.4, 143.4, 143.0, 139.6, 138.6, 138.3, 137.6, 136.6, 131.6, 129.0, 127.6, 125.0, 124.0, 118.4, 37.1, 23.0, 21.1, 20.5. HRMS (ESI) calcd for $C_{18}H_{21}BrNO$ $[M+H]^+$ 346.0807, found 346.0808.

Compound **S12** was prepared following the **Typical Procedure B**

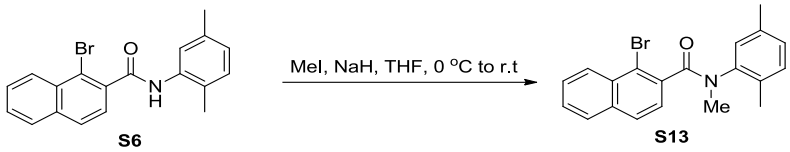


S5 **S12**

The reaction of **S5** (2.10 g, 6.0 mmol), NaH (60% in mineral oil, 0.408 g, 10.2 mmol, 1.7 equiv) and CH_3I (0.75 mL, 12.0 mmol, 2.0 equiv) afforded **S12** (2.16 g, 99%) as a white solid. A mixture of rotamers were observed and the followings are selected peaks: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.05 (d, *J* = 6.8 Hz, 1 H), 7.00 (t, *J* = 7.6 Hz, 1H), 6.90 (d, *J* = 7.6 Hz, 1 H), 6.34 (s, 1 H), 6.337 (s, 1 H), 6.20 (t, *J* = 2.2 Hz, 1 H), 3.65 (s, 6 H), 3.48 (s, 3 H), 2.33 (s, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.1, 160.6, 145.0, 139.2, 138.5, 130.6, 126.6, 126.0, 122.2, 104.9, 99.4, 55.3, 37.0,

23.2. HRMS (ESI) calcd for $C_{17}H_{19}BrNO_3$ $[M+H]^+$ 364.0548, found 364.0548.

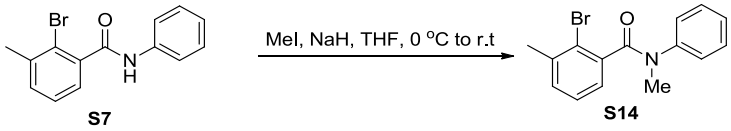
Compound **S13** was prepared following the **Typical Procedure B**



S6 **S13**

The reaction of **S6** (2.30 g, 6.5 mmol), NaH (60% in mineral oil, 0.442 g, 11.05 mmol, 1.7 equiv), CH_3I (0.81 mL, 13.0 mmol, 2.0 equiv) afforded **S13** (2.21 g, 92%) as a white solid. A mixture of rotamers were observed and the followings are selected peaks: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.25 (d, *J* = 8.4 Hz, 1 H), 7.67 (d, *J* = 5.2 Hz, 1 H), 7.59 – 7.54 (m, 2 H), 7.43 (td, *J* = 6.8, 0.8 Hz, 1 H), 7.23 (d, *J* = 7.6 Hz, 1 H), 7.10 (d, *J* = 7.6 Hz, 1 H), 6.95 (d, *J* = 7.6 Hz, 1 H), 6.79 (d, *J* = 7.2 Hz, 1 H), 3.46 (s, 3 H), 2.36 (s, 3 H), 2.06 (s, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.4, 141.3, 136.3, 133.9, 133.5, 131.7, 130.7, 128.9, 128.8, 128.2, 128.1, 127.9, 127.6, 127.3, 126.9, 123.7, 120.3, 36.4, 20.4, 17.5. HRMS (ESI) calcd for $C_{20}H_{19}BrNO$ $[M+H]^+$ 368.0650, found 368.0649.

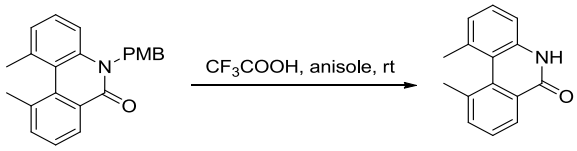
Compound **S14** was prepared following the **Typical Procedure B**



S7 **S14**

The reaction of **S7** (2.03 g, 7.0 mmol), NaH (60% in mineral oil, 0.476 g, 11.9 mmol, 1.7 equiv), CH_3I (0.90 mL, 14.0 mmol, 2.0 equiv) afforded **S14** (2.11 g, 99%) as a white solid. A mixture of rotamers were observed and the followings are selected peaks: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.21 – 7.14 (m, 4 H), 7.14 – 7.08 (m, 1 H), 7.02 (dd, *J* = 7.6, 1.2 Hz, 1 H), 6.98 (t, *J* = 7.6 Hz, 1 H), 6.90 (dd, *J* = 7.6, 1.6 Hz, 1 H), 3.51 (s, 3 H), 2.30 (s, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.2, 143.2, 139.0, 138.5, 130.5, 128.9, 127.1, 126.7, 126.5, 126.2, 125.8, 124.8, 122.0, 37.1, 23.2. HRMS (ESI) calcd for $C_{15}H_{15}BrNO$ $[M+H]^+$ 304.0337, found 304.0336.

Synthesis of Compound **S15**

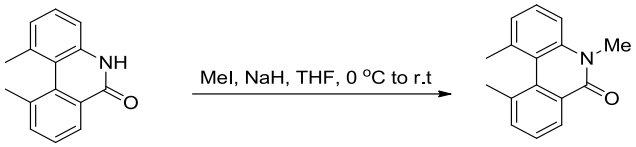


S15

The solution of 5-(4-methoxybenzyl)-1,10-dimethylphenanthridin-6(5H)-one[3] (0.96 g, 2.8 mmol) in trifluoroacetic acid (20.0 mL) and anisole (2.0 mL) was stirred at rt for 3 h. The reaction mixture was quenched slowly with the addition of saturated aqueous $NaHCO_3$, followed by extraction with EtOAc (20 mL x 3). The combined organic phase was washed with brine (30 mL × 2) and dried over Na_2SO_4. After filtration the solvent was removed by evaporation, and the resulting mixture was purified by column chromatography on silica gel (hexanes/ethyl acetate = 20 :1) to afford the desired product **S15** (0.60 g, 96%) as a white solid. **^{1}H NMR** (400 MHz,

$CDCl_3$) δ 8.90 (s, 1 H), 8.32 (d, *J* = 7.6 Hz, 1 H), 7.61 (d, *J* = 7.6 Hz, 1 H), 7.52 (t, *J* = 7.6 Hz, 1 H), 7.34 (t, *J* = 7.6 Hz, 1 H), 7.12 (d, *J* = 7.2 Hz, 1 H), 6.98 (d, *J* = 8.0 Hz, 1 H), 2.49 (s, 3 H), 2.45 (s, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.4, 136.7, 136.4, 135.5, 134.84, 134.77, 128.2, 128.1, 126.9, 125.2, 125.0, 119.0, 112.9, 22.2, 22.1. HRMS (ESI) calcd for $C_{15}H_{14}NO$ $[M+H]^+$ 224.1075, found 224.1079.

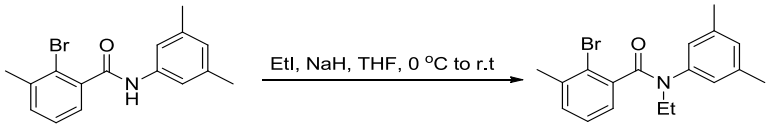
Compound **S16** was prepared following the **Typical Procedure B**



S15 **S16**

The reaction of **S15** (0.60 g, 2.69 mmol), NaH (60% in mineral oil, 0.183 g, 4.57 mmol, 1.7 equiv), CH_3I (0.34 mL, 5.38 mmol, 2.0 equiv) afforded **S16** (0.635 g, 99%) as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (dd, *J* = 7.6, 0.8 Hz, 1 H), 7.56 (d, *J* = 6.4 Hz, 1 H), 7.49 (t, *J* = 7.6 Hz, 1 H), 7.41 (t, *J* = 7.8 Hz, 1 H), 7.18 (d, *J* = 8.0 Hz, 1 H), 7.15 (d, *J* = 7.6 Hz, 1 H), 3.67 (s, 3 H), 2.453 (s, 3 H), 2.447 (s, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.3, 138.3, 136.4, 135.1, 134.0, 133.5, 128.5, 127.9, 126.9, 125.2, 124.8, 119.6, 110.8, 30.3, 22.0, 21.6. HRMS (ESI) calcd for $C_{16}H_{16}NO$ $[M+H]^+$ 238.1232, found 238.1234.

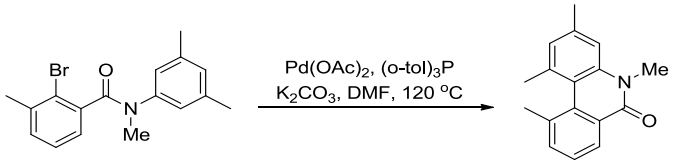
Compound **S17** was prepared following the **Typical Procedure B**



S1 **S17**

The reaction of **S1** (0.64 g, 2.0 mmol), NaH (60% in mineral oil, 0.134 g, 3.34 mmol, 1.7 equiv), EtI (0.32 mL, 4.0 mmol, 2.0 equiv) at 50 °C afforded **S17** (0.690 g, 99%) as a white solid. A mixture of rotamers were observed and the followings are selected peaks: **^{1}H NMR** (400 MHz, $CDCl_3$) 7.01 – 6.96 (m, 2 H), 6.87 (d, *J* = 7.2 Hz, 1 H), 6.79 (s, 2 H), 6.73 (s, 1 H), 4.20 – 3.67 (m, 2 H), 2.31 (s, 3 H), 2.17 (s, 6 H), 1.25 (t, *J* = 7.2 Hz, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.7, 141.4, 140.1, 139.4, 139.0, 138.4, 130.2, 129.0, 127.5, 126.3, 126.0, 125.5, 125.3, 122.1, 44.1, 23.2, 21.0, 12.9. HRMS (ESI) calcd for $C_{18}H_{21}BrNO$ $[M+H]^+$ 346.0807, found 346.0807.

Typical Procedure for S18 (Typical Procedure C)

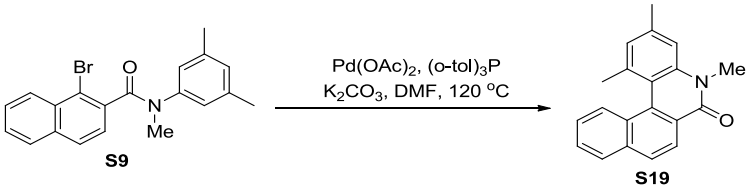


S8 **S18**

Under nitrogen atmosphere, a mixture of **S8** (1.58 g, 4.74 mmol, 1.0 equiv), $Pd(OAc)_2$ (53.3 mg, 0.237 mmol, 5 mol%), (*o*-tol)$_3$P (144 mg, 0.474 mmol, 10 mol%), K_2CO_3 (1.95 g, 14.2 mmol, 3.0 equiv) in anhydrous DMF (15 mL) was heated at 120 °C for 24 h. After being cooled to room temperature, the solution was diluted with water (50 mL) and extracted with EtOAc (30 mL x 2). The combined organic layer was washed with brine (20 mL × 3) and dried over Na_2SO_4. After

filtration the solvent was removed by evaporation, and the resulting mixture was purified by column chromatography on silica gel (hexanes/ethyl acetate = 10 :1) to afford the desired product **S18** (1.19 g, 99%) as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.30 (d, *J* = 7.6 Hz, 1 H), 7.54 (d, *J* = 7.2 Hz, 1 H), 7.46 (t, *J* = 7.6 Hz, 1 H), 6.99 (s, 3 H), 6.97 (s, 3 H), 3.66 (s, 3 H), 2.47 (s, 3 H), 2.44 (s, 3 H), 2.41 (s, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.4, 138.4, 138.0, 136.2, 134.8, 134.0, 133.7, 128.3, 126.6, 125.9, 125.2, 117.4, 111.5, 30.3, 21.9, 21.7, 21.6. HRMS (ESI) calcd for $C_{17}H_{18}NO$ $[M+H]^+$ 252.1388, found 252.1392.

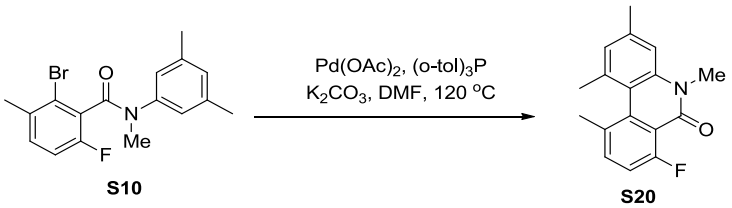
Compound **S19** was prepared following the **Typical Procedure C**



S9 **S19**

The reaction of **S9** (2.21 g, 6.0 mmol), $Pd(OAc)_2$ (67.4 mg, 0.3 mmol, 5 mol%), (*o*-tol)$_3$P (183 mg, 0.60 mmol, 10 mol%) and K_2CO_3 (2.48 g, 18.0 mmol, 3.0 equiv) afforded **S19** (1.60 g, 93%) as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.45 (d, *J* = 8.4 Hz, 1 H), δ 7.95 (d, *J* = 8.4 Hz, 1 H), 7.94 (d, *J* = 6.8 Hz, 2 H), 7.61 (t, *J* = 7.6 Hz, 1 H), 7.53 (t, *J* = 7.4 Hz, 1 H), 7.14 (s, 1 H), 7.07 (s, 1 H), 3.79 (s, 3 H), 2.54 (s, 3 H), 2.24 (s, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.0, 139.0, 138.8, 136.7, 135.0, 133.2, 129.2, 128.9, 127.8, 127.7, 127.5, 126.9, 125.5, 125.3, 123.4, 116.7, 112.0, 30.5, 24.4, 21.8. HRMS (ESI) calcd for $C_{20}H_{18}NO$ $[M+H]^+$ 288.1388, found 288.1391.

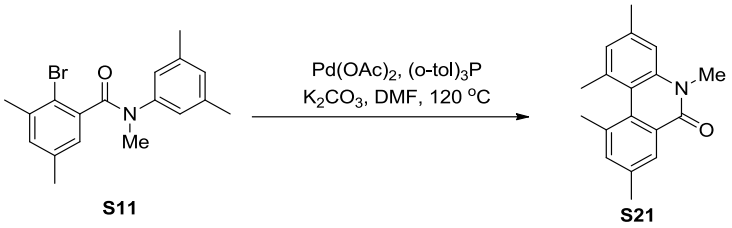
Compound **S20** was prepared following the **Typical Procedure C**



S10 **S20**

The reaction of **S10** (2.80 g, 8.0 mmol), $Pd(OAc)_2$ (89.8 mg, 0.4 mmol, 5 mol%), (*o*-tol)$_3$P (244 mg, 0.80 mmol, 10 mol%) and K_2CO_3 (3.31 g, 24.0 mmol, 3.0 equiv) afforded **S20** (2.08 g, 97%) as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.48 (dd, *J* = 8.0, 5.6 Hz, 1 H), δ 7.14 (dd, *J* = 10.4, 8.8 Hz, 1 H), 6.94 (s, 1 H), 6.93 (s, 1 H), 3.59 (s, 3 H), 2.46 (s, 3 H), 2.38 (s, 3 H), 2.36 (s, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 160.1 (d, $J_{C\text{-}F}$ = 260.2 Hz), 160.0 (d, $J_{C\text{-}F}$ = 4.7 Hz), 138.7, 138.5, 136.5, 135.9, 135.1 (d, $J_{C\text{-}F}$ = 9.5 Hz), 130.5 (d, $J_{C\text{-}F}$ = 4.2 Hz), 125.8, 116.8 (d, $J_{C\text{-}F}$ = 2.3 Hz), 116.4 (d, $J_{C\text{-}F}$ = 3.8 Hz), 114.6 (d, $J_{C\text{-}F}$ = 22.1 Hz), 111.1, 30.1, 21.64, 21.56, 21.2. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -116.9. HRMS (ESI) calcd for $C_{17}H_{17}FNO$ M+H]$^+$ 270.1294, found 270.1296.

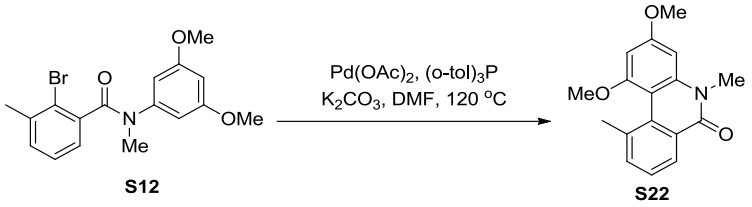
Compound **S21** was prepared following the **Typical Procedure C**



S11 **S21**

The reaction of **S11** (1.56 g, 4.5 mmol), $Pd(OAc)_2$ (50.5 mg, 0.225 mmol, 5 mol%), $(o\text{-tol})_3P$ (137 mg, 0.45 mmol, 10 mol%) and K_2CO_3 (3.11 g, 22.5 mmol, 5.0 equiv) afforded **S21** (1.10 g, 92%) as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.11 (s, 1 H), 7.36 (s, 1 H), 6.98 (s, 1 H), 6.96 (s, 1 H), 3.65 (s, 3 H), 2.48 (s, 3 H), 2.46 (s, 3 H), 2.404 (s, 3 H), 2.397 (s, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.5, 138.2, 137.6, 136.6, 136.0, 135.2, 134.7, 131.4, 128.2, 125.9, 125.4, 117.5, 111.5, 30.4, 22.0, 21.6, 21.5, 21.0. HRMS (ESI) calcd for $C_{18}H_{20}NO$ $[M+H]^+$ 266.1545, found 266.1546.

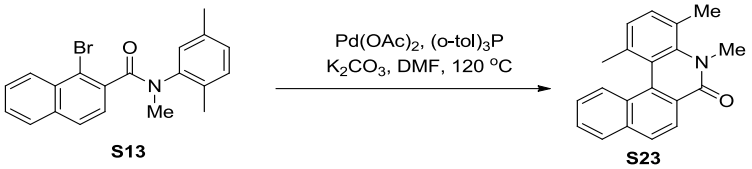
Compound **S22** was prepared following the **Typical Procedure C**



S12 **S22**

The reaction of **S12** (2.0 g, 5.5 mmol), $Pd(OAc)_2$ (61.8 mg, 0.275 mmol, 5 mol%), $(o\text{-tol})_3P$ (167 mg, 0.55 mmol, 10 mol%) and K_2CO_3 (2.28 g, 16.5 mmol, 3.0 equiv) afforded **S22** (1.42 g, 91%) as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.27 (dd, *J* = 7.8, 1.0 Hz, 1 H), 7.53 (dd, *J* = 7.4, 0.8 Hz, 1 H), 7.39 (t, *J* = 7.6 Hz, 1 H), 6.50 (d, *J* = 2.4 Hz, 1 H), 6.42 (d, *J* = 2.4 Hz, 1 H), 3.94 (s, 3 H), 3.91 (s, 3 H), 3.66 (s, 3 H), 2.40 (s, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.9, 161.0, 158.0, 140.4, 135.8, 134.6, 132.0, 126.7, 125.9, 125.0, 103.6, 92.5, 91.6, 55.5, 55.1, 30.7, 23.1. HRMS (ESI) calcd for $C_{17}H_{18}NO_3$ $[M+H]^+$ 284.1287, found 284.1290.

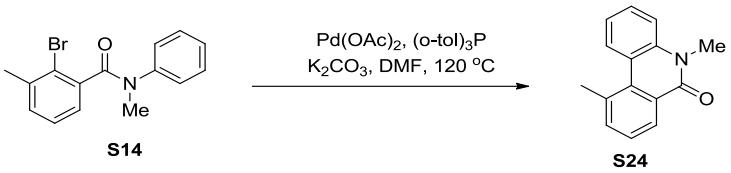
Compound **S23** was prepared following the **Typical Procedure C**



S13 **S23**

The reaction of **S13** (1.84 g, 5.0 mmol), $Pd(OAc)_2$ (56.2 mg, 0.25 mmol, 5 mol%), $(o\text{-tol})_3P$ (152 mg, 0.50 mmol, 10 mol%) and K_2CO_3 (3.45 g, 25.0 mmol, 5.0 equiv) afforded **S23** (1.34 g, 93%) as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.40 (d, *J* = 8.4 Hz, 1 H), 7.96 (d, *J* = 8.4 Hz, 2 H), 7.92 (d, *J* = 8.4 Hz, 1 H), 7.61 (td, *J* = 7.4, 0.8 Hz, 1 H), 7.53 (td, *J* = 7.6, 1.2 Hz, 1 H), 7.29 (d, *J* = 7.6 Hz, 1 H), 7.11 (d, *J* = 8.0 Hz, 1 H), 3.86 (s, 3 H), 2.74 (s, 3 H), 2.16 (s, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.2, 139.6, 134.8, 134.3, 133.5, 133.1, 129.0, 128.9, 128.0, 127.8, 127.4, 126.2, 126.0, 125.5, 123.0, 122.2, 120.8, 37.8, 24.4, 23.6. HRMS (ESI) calcd for $C_{20}H_{18}NO$ $[M+H]^+$ 288.1388, found 288.1390.

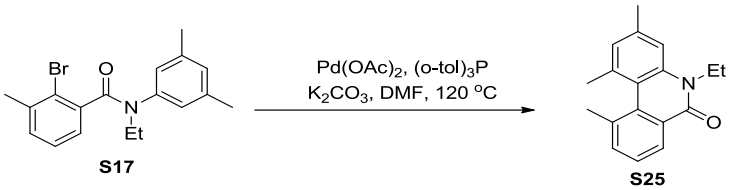
Compound **S24** was prepared following the **Typical Procedure C**



S14 **S24**

The reaction of **S14** (2.04 g, 6.7 mmol), $Pd(OAc)_2$ (75.2 mg, 0.335 mmol, 5 mol%), (*o*-tol)$_3$P (204 mg, 0.67 mmol, 10 mol%) and K_2CO_3 (4.62 g, 33.5 mmol, 5.0 equiv) afforded **S24** (1.20 g, 95%) as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.53 (d, *J* = 6.8 Hz, 1 H), 8.46 (d, *J* = 7.2 Hz, 1 H), 7.61 (d, *J* = 6.8 Hz, 1 H), 7.55 (ddd, *J* = 8.4, 7.2, 1.6 Hz, 1 H), 7.49 (t, *J* = 7.6 Hz, 1 H), 7.46 (dd, *J* = 8.4, 1.2 Hz, 1 H), 7.32 (ddd, *J* = 8.4, 7.2, 1.2 Hz, 1 H), 3.81 (s, 3 H), 2.97 (s, 3 H). Spectral datas were in agreement with those reported in the literature.[12]

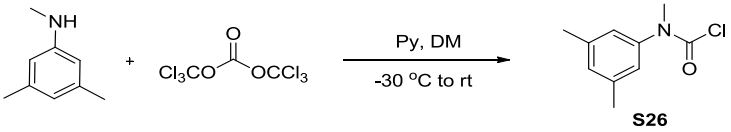
Compound **S25** was prepared following the **Typical Procedure C**



S17 **S25**

The reaction of **S17** (0.52 g, 1.5 mmol), $Pd(OAc)_2$ (16.8 mg, 0.075 mmol, 5 mol%), (*o*-tol)$_3$P (45.7 mg, 0.15 mmol, 10 mol%) and K_2CO_3 (1.04 g, 7.5 mmol, 5.0 equiv) afforded **S25** (0.374 g, 94%) as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.30 (d, *J* = 7.6 Hz, 1 H), 7.53 (d, *J* = 7.2 Hz, 1 H), 7.46 (t, *J* = 7.6 Hz, 1 H), 7.02 (s, 1 H), 6.96 (s, 1 H), 4.47 – 4.14 (m, 2 H), 2.47 (s, 3 H), 2.44 (s, 3 H), 2.41 (s, 3 H), 1.41 (t, *J* = 7.0 Hz, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 161.8, 137.9, 137.3, 136.5, 134.7, 134.0, 133.7, 128.2, 126.6, 125.6, 125.2, 117.6, 111.5, 37.9, 22.0, 21.7, 21.6, 12.7. HRMS (ESI) calcd for $C_{18}H_{20}NO$ $[M+H]^+$ 266.1545, found 266.1549.

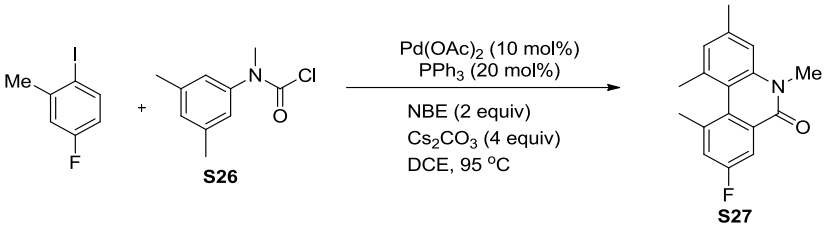
Synthesis of compound **S26**[4]



S26

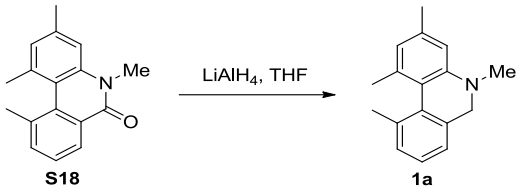
To a solution of triphosgene (1.25 g, 4.22 mmol, 0.5 equiv) in dry DCM (25 mL) was added pyridine (2.6 mL) dropwise under nitrogen atmosphere at - 30 °C. After stirring for 15 min at –30 ℃, *N*-Methyl-3,5-dimethylaniline[5] (1.20 g, 8.432 mmol, 1.0 equiv) was slowly added to the mixture. The mixture was warmed to room temperature and stirred for 6 h at room temperature. The reaction mixture was carefully quenched by the addition of aqueous hydrochloric acid (1 M, 10 mL) and was extracted with CH_2Cl_2 (20 mL x 3). The combined organic layer was dried with Na_2SO_4, filtrated and evaporated. The residue was purified by chromatography on silica gel (PE/EtOAc 20:1) to afford **S26** (1.21 g, 73%) as a white solid. A mixture of rotamers were observed and the followings are selected peaks: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.01 (s, 1 H), 6.86 (s, 2 H), 3.34 (s, 3 H), 2.34 (s, 6 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 142.9, 139.1, 129.9, 124.7, 40.1, 20.9. HRMS (ESI) calcd for $C_{10}H_{13}ClNO$ $[M+H]^+$ 198.0686, found 198.0684.

Synthesis of compound **S27**[6]



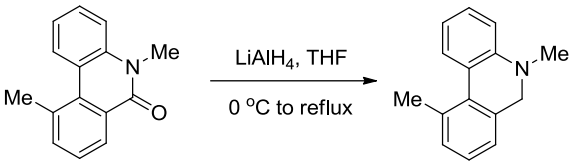
Under nitrogen atmosphere, in a thick wall flask capped with a screw cap, a mixture of 4-fluoro-1-iodo-2-methylbenzene (0.42 mL, 3.2 mmol, 1.0 equiv), **S26** (948.8 mg, 4.8 mmol, 1.5 equiv), $Pd(OAc)_2$ (71.8 mg, 0.32 mmol, 10 mol%), PPh_3 (167.9 mg, 0.64 mmol, 20 mol%), norbornene (0.603 g, 6.4 mmol, 2.0 equiv), Cs_2CO_3 (4.17 g, 12.8 mmol, 4.0 equiv) in dry DCE (20 mL) was heated at 95 °C for 10 h. After being cooled to room temperature, the reaction mixture was diluted with AcOEt (5.0 mL). The solvent was removed and the residue was purified by chromatography on silica gel (PE/EtOAc 20:1) to afford **S27** (0.814 g, 94%) as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.97 (dd, *J* = 8.4, 2.8 Hz, 1 H), 7.26 (dd, *J* = 9.0, 2.6 Hz, 1 H), 6.99 (s, 1 H), 6.98 (s, 1 H), 3.66 (s, 3 H), 2.46 (s, 3 H), 2.44 (s, 3 H), 2.39 (s, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 161.7 (d, $J_{C\text{-}F}$ = 3.2 Hz), 161.2 (d, $J_{C\text{-}F}$ = 246.6 Hz), 138.1, 137.8 (d, $J_{C\text{-}F}$ = 7.1 Hz), 135.9, 130.4 (d, $J_{C\text{-}F}$ = 2.7 Hz), 130.0 (d, $J_{C\text{-}F}$ = 7.9 Hz), 126.2, 121.3 (d, $J_{C\text{-}F}$ = 21.7 Hz), 116.9, 111.7, 111.3 (d, $J_{C\text{-}F}$ = 23.0 Hz), 30.5, 22.01, 21.97 (d, $J_{C\text{-}F}$ = 1.7 Hz), 21.6. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -114.8. HRMS (ESI) calcd for $C_{17}H_{17}FNO$ $[M+H]^+$ 270.1294, found 270.1296.

Typical Procedure for 1a (Typical Procedure D)



To a suspension of $LiAlH_4$ (0.270 g, 7.10 mmol, 1.5 equiv) in dry THF (5.0 mL) was added **S18** (1.19 g, 4.735 mmol, 1.0 equiv) in dry THF (15.0 mL) dropwise at 0 °C. After stirring at 0 ˚C for 1 h, the reaction mixture was gradually heated to reflux and stirred at reflux overnight. The reaction mixture was quenched slowly with the addition of H_2O (0.3 mL) at 0 °C, followed by NaOH solution (10% aq, 0.3 mL) and H_2O (0.9 mL). The solid was filtered off through a pad of celite and the filtrate was concentrated by evaporation, and the resulting mixture was purified by column chromatography on silica gel (hexanes/ethyl acetate = 50 :1) to afford the desired product **1a** (1.10 g, 98%) as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.21 (d, *J* = 7.2 Hz, 1 H), 7.17 (t, *J* = 7.2 Hz, 1 H), 7.07 (d, *J* = 7.2 Hz, 1 H), 6.68 (s, 1 H), 6.51 (s, 1 H), 3.78 (s, 2 H), 2.88 (s, 3 H), 2.37 (s, 3 H), 2.27 (s, 6 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 150.8, 138.7, 137.2, 135.3, 134.7, 131.8, 130.0, 125.7, 122.5, 122.4, 122.0, 110.1, 57.2, 39.0, 21.6, 21.0, 20.9. HRMS (ESI) calcd for $C_{17}H_{20}N$ $[M+H]^+$ 238.1596, found 238.1601.

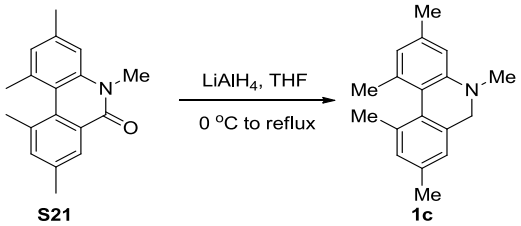
Compound **5** was prepared following the **Typical Procedure D**



S24 **5**

The reaction of **S24** (1.12 g, 5.0 mmol) and $LiAlH_4$ (0.285 g, 7.5 mmol, 1.5 equiv) afforded **5** (0.779 g, 74%) as white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.70 (dd, *J* = 7.8, 1.4 Hz, 1 H), 7.29 – 7.23 (m, 1 H), 7.20 (d, *J* = 6.8 Hz, 1 H), 7.15 (t, *J* = 7.4 Hz, 1 H), 7.05 (d, *J* = 7.2 Hz, 1 H), 6.93 (td, *J* = 7.6, 0.8 Hz, 1 H), 6.84 (d, *J* = 8.4 Hz, 1 H), 3.97 (s, 2 H), 2.91 (s, 3 H), 2.64 (s, 3 H). Spectral data were in agreement with those reported in the literature.[7]

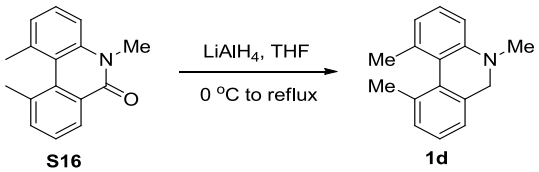
Compound **1c** was prepared following the **Typical Procedure D**



S21 **1c**

The reaction of **S21** (1.00 g, 3.77 mmol) and $LiAlH_4$ (0.215 g, 5.66 mmol, 1.5 equiv) afforded **1c** (0.678 g, 72%) as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.03 (s, 1 H), 6.89 (s, 1 H), 6.67 (s, 1 H), 6.50 (s, 1 H), 3.76 (d, *J* = 12.4 Hz, 1 H), 3.72 (d, *J* = 12.4 Hz, 1 H), 2.87 (s, 3 H), 2.37 (s, 3 H), 2.35 (s, 3 H), 2.27 (s, 3 H), 2.24 (s, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 150.7, 138.9, 137.0, 135.5, 135.3, 134.8, 130.8, 129.2, 123.0, 122.6, 122.5, 110.1, 57.4, 39.2, 21.6, 21.1, 20.93, 20.89. HRMS (ESI) calcd for $C_{18}H_{22}N$ $[M+H]^+$ 252.1752, found 252.1754.

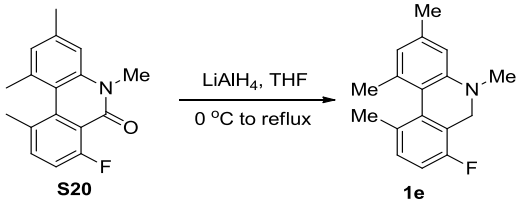
Compound **1d** was prepared following the **Typical Procedure D**



S16 **1d**

The reaction of **S16** (0.638 g, 2.69 mmol) and $LiAlH_4$ (0.153 g, 4.04 mmol, 1.5 equiv) afforded **1d** (0.575 g, 96%) as white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.25 – 7.20 (m, 2 H), 7.18 (d, *J* = 7.6 Hz, 1 H), 7.08 (d, *J* = 6.8 Hz, 1 H), 6.84 (d, *J* = 7.6 Hz, 1 H), 6.69 (d, *J* = 8.0 Hz, 1 H), 3.79 (s, 2 H), 2.89 (s, 3 H), 2.31 (s, 3 H), 2.28 (s, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 150.9, 139.2, 135.7, 135.1, 131.8, 130.1, 127.5, 126.2, 125.0, 122.1, 121.7, 109.2, 57.3, 39.1, 21.1, 20.9. HRMS (ESI) calcd for $C_{16}H_{18}N$ $[M+H]^+$ 224.1439, found 224.1444.

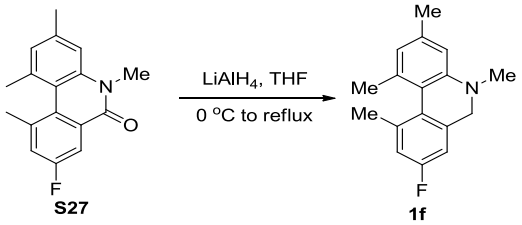
Compound **1e** was prepared following the **Typical Procedure D**



S20 **1e**

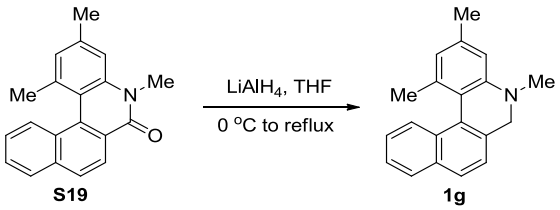
The reaction of **S20** (2.15 g, 8.0 mmol) and $LiAlH_4$ (0.455 g, 12.0 mmol, 1.5 equiv) afforded **1e** (1.88 g, 92%) as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) 7.16 (t, *J* = 7.2 Hz, 1 H), 6.94 (t, *J* = 8.6 Hz, 1 H), 6.69 (s, 1 H), 6.53 (s, 1 H), 4.21 (d, *J* = 12.8 Hz, 1 H), 3.51 (d, *J* = 12.8 Hz, 1 H), 2.90 (s, 3 H), 2.38 (s, 3 H), 2.27 (s, 3 H), 2.24 (s, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 155.6 (d, J_{C-F} = 239.6 Hz), 150.7, 137.9, 135.6, 133.9 (d, J_{C-F} = 4.0 Hz), 130.6 (d, J_{C-F} = 8.0 Hz), 130.3 (d, J_{C-F} = 3.0 Hz), 125.1 (d, J_{C-F} = 16.3 Hz), 122.8, 122.1 (d, J_{C-F} = 2.7 Hz), 112.8 (d, J_{C-F} = 21.3 Hz), 110.4, 49.4 (d, J_{C-F} = 4.2 Hz), 39.1, 21.6, 21.0, 20.5. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -126.5. HRMS (ESI) calcd for $C_{17}H_{19}FN$ $[M+H]^+$ 256.1502, found 256.1512.

Compound **1f** was prepared following the **Typical Procedure D**



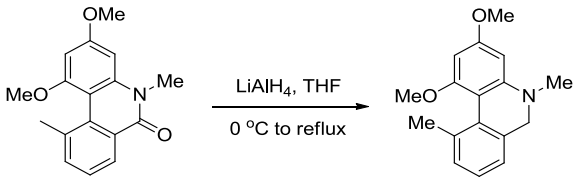
The reaction of **S27** (0.627 g, 2.33 mmol) and $LiAlH_4$ (0.133 g, 3.50 mmol, 1.5 equiv) afforded **1f** (0.411 g, 69%) as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.93 (dd, *J* = 10.0, 2.4 Hz, 1 H), 6.81 (dd, *J* = 8.0, 2.4 Hz, 1 H), 6.69 (s, 1 H), 6.52 (s, 1 H), 3.82 – 3.63 (m, 2 H), 2.88 (s, 3 H), 2.38 (s, 3 H), 2.27 (s, 3 H), 2.25 (s, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 161.0 (d, J_{C-F} = 244.3 Hz), 150.5, 140.8 (d, J_{C-F} = 7.7 Hz), 137.3, 137.2 (d, J_{C-F} = 7.8 Hz), 135.3, 128.2 (d, *J* = 2.9 Hz), 122.8, 121.9, 116.2 (d, J_{C-F} = 20.3 Hz), 110.3, 109.4 (d, J_{C-F} = 21.5 Hz), 57.3 (d, J_{C-F} = 2.1 Hz), 39.1, 21.6, 21.2 (d, J_{C-F} = 1.6 Hz), 21.0. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -118.0. HRMS (ESI) calcd for $C_{17}H_{19}FN$ $[M+H]^+$ 256.1502, found 256.1507.

Compound **1g** was prepared following the **Typical Procedure D**



The reaction of **S19** (1.15 g, 4.0 mmol) and $LiAlH_4$ (0.228 g, 6.0 mmol, 1.5 equiv) afforded **1g** (0.875 g, 80%) as a green foam. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.87 – 7.80 (m, 1 H), 7.75 (d, *J* = 8.0 Hz, 2 H), 7.45 – 7.39 (m, 2 H), 7.37 (d, *J* = 8.0 Hz, 1 H), 6.76 (s, 1 H), 6.60 (s, 1 H), 4.03 (d, *J* = 12.8 Hz, 1 H), 3.93 (d, *J* = 12.8 Hz, 1 H), 2.94 (s, 3 H), 2.43 (s, 3 H), 2.16 (s, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 150.9, 137.9, 136.1, 135.8, 133.5, 129.5, 129.1, 128.0, 127.2, 126.8, 125.2, 124.9, 123.4, 123.2, 121.8, 110.6, 56.9, 39.0, 22.9, 21.8. HRMS (ESI) calcd for $C_{20}H_{20}N$ $[M+H]^+$ 274.1596, found 274.1603.

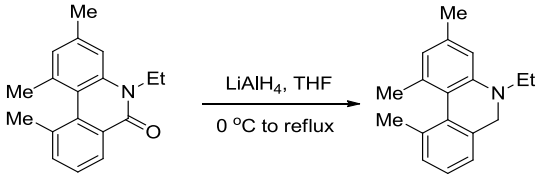
Compound **1h** was prepared following the **Typical Procedure D**



S22 1h

The reaction of **S30** (1.36 g, 4.80 mmol) and $LiAlH_4$ (0.273 g, 7.20 mmol, 1.5 equiv) afforded **1h** (1.265 g, 98%) as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.19 (d, *J* = 7.6 Hz, 1 H), 7.11 (t, *J* = 7.4 Hz, 1 H), 7.02 (d, *J* = 7.2 Hz, 1 H), 6.16 (d, *J* = 2.0 Hz, 1 H), 6.09 (d, *J* = 2.0 Hz, 1 H), 3.95 – 3.75 (m, 2 H), 3.88 (s, 3 H), 3.85 (s, 3 H) , 2.90 (s, 3 H), 2.25 (s, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 160.8, 157.4, 152.5, 136.9, 135.5, 130.2, 129.7, 125.4, 122.0, 107.2, 91.3, 89.3, 57.2, 55.2, 54.8, 39.0, 22.0. HRMS (ESI) calcd for $C_{17}H_{20}NO_2$ $[M+H]^+$ 270.1494, found 270.1498.

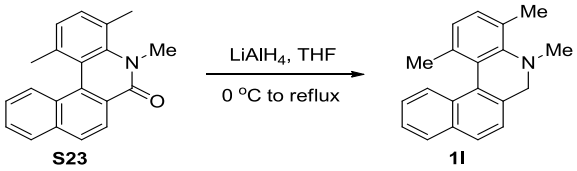
Compound **1j** was prepared following the **Typical Procedure D**



S25 1j

The reaction of **S25** (0.374 g, 1.41 mmol) and $LiAlH_4$ (80.5 mg, 2.12 mmol, 1.5 equiv) afforded **1j** (0.340 g, 96%) as colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29 (d, *J* = 6.8 Hz, 1 H), 7.25 (t, *J* = 7.4 Hz, 1 H), 7.15 (d, *J* = 6.8 Hz, 1 H), 6.73 (s, 1 H), 6.66 (s, 1 H), 3.94 (d, *J* = 12.4 Hz, 1 H), 3.90 (d, *J* = 12.4 Hz, 1 H), 3.43 (q, *J* = 7.2 Hz, 2 H), 2.46 (s, 3 H), 2.37 (s, 3 H), 2.36 (s, 3 H), 1.33 (t, *J* = 7.0 Hz, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 149.5, 139.0, 137.1, 135.7, 134.7, 132.0, 130.0, 125.7, 122.5, 121.9, 121.8, 110.5, 53.4, 44.9, 21.7, 21.1, 21.0, 11.0. HRMS (ESI) calcd for $C_{18}H_{22}N$ $[M+H]^+$ 252.1752, found 252.1756.

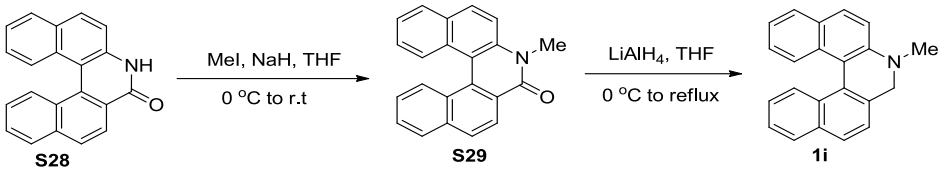
Compound **1l** was prepared following the **Typical Procedure D**



S23 1l

The reaction of **S23** (1.15 g, 4.0 mmol), $LiAlH_4$ (0.228 g, 6.0 mmol, 1.5 equiv) afforded **1l** (0.943 g, 86%) as white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89 (dd, *J* = 5.8, 3.4 Hz, 1 H), 7.86 – 7.76 (m, 2 H), 7.51 – 7.40 (m, 3 H), 7.15 (d, *J* = 8.0 Hz, 1 H), 7.07 (d, *J* = 7.6 Hz, 1 H), 4.19 (d, *J* = 15.2 Hz, 1 H), 4.03 (d, *J* = 15.2 Hz, 1 H), 2.43 (s, 3 H), 2.33 (s, 3 H), 2.17 (s, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 148.5, 135.0, 133.4, 133.3, 130.0, 129.7, 129.6, 129.5, 128.8, 128.3, 127.2, 126.9, 126.6, 125.4, 124.82, 124.77, 56.8, 38.5, 22.4, 17.4. HRMS (ESI) calcd for $C_{20}H_{20}N$ $[M+H]^+$ 274.1596, found 274.1600.

Synthesis of compound **1i**

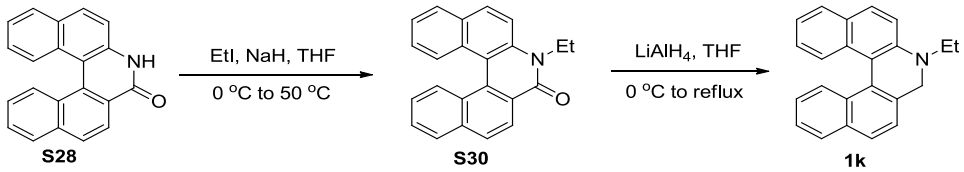


S28 S29 1i

To a suspension of NaH (60% in mineral oil, 0.340 g, 8.5 mmol, 1.7 equiv) in dry THF (5.0 mL) was added **S28**[8] (1.48 g, 5.0 mmol, 1.0 equiv) in dry THF (15.0 mL) dropwise at 0 °C. After stirring at 0 °C for 30 min, MeI (0.70 mL, 10.0 mmol, 2.0 equiv) added dropwise. The reaction mixture was allowed to warm to room temperature and stirred for another 2 h. Water (1 mL) was added at 0 °C carefully, and the mixture was filtered through a pad of celite. The residue was dried by infrared lamp to afford the crude **S29** (1.19 g, 77%) as a dark green solid.

To a suspension of $LiAlH_4$ (0.171 g, 4.5 mmol, 1.5 equiv) in dry THF (15.0 mL) was added crude **S29** (0.928 g, 3.0 mmol) at 0 °C. After stirring at 0 °C for 1 h, the reaction mixture was was gradually heated to reflux and stirred at reflux overnight. The reaction mixture was quenched slowly with the addition of H_2O (170 uL) at 0 °C, followed by NaOH solution (10% aq, 170 uL) and H_2O (510 uL). The solid was filtered off through a pad of celite and the filtrate was concentrated by evaporation, and the resulting mixture was purified by column chromatography on silica gel (hexanes/ethyl acetate = 50 :1) to afford the desired product **1i** (0.172 g, 19%) as a yellow foam. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.93 – 7.78 (m, 4 H), 7.63 (d, *J* = 8.4 Hz, 1 H), 7.57 (d, *J* = 8.4 Hz, 1 H), 7.44 (d, *J* = 14.0 Hz, 1 H), 7.42 (d, *J* = 13.2 Hz, 1 H), 7.36 – 7.28 (m, 2 H), 7.28 – 7.20 (m, 2 H), 4.17 (d, *J* = 12.8 Hz, 1 H), 4.07 (d, *J* = 12.8 Hz, 1 H), 3.09 (s, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 148.6, 135.6, 133.8, 131.0, 129.5, 129.3, 128.25, 128.20, 128.17, 128.0, 127.7, 127.4, 126.6, 125.2, 125.0, 124.9, 123.6, 122.5, 117.6, 114.7, 56.9, 38.7. HRMS (ESI) calcd for $C_{22}H_{18}N$ $[M+H]^+$ 296.1439, found 296.1448.

Synthesis of compound **1k**



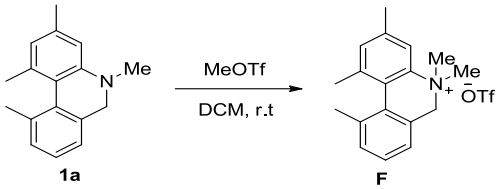
S28 S30 1k

To a suspension of NaH (60% in mineral oil, 0.340 g, 8.5 mmol, 1.7 equiv) in dry THF (5.0 mL) was added **S28** (1.48 g, 5.0 mmol, 1.0 equiv) in dry THF (15.0 mL) dropwise at 0 °C. After stirring for 30 min at 0 °C, EtI (0.80 mL, 10.0 mmol, 2.0 equiv) added dropwise. The resulting mixture was stirred at room temperature for 30 min and 50 °C overnight. Water (1 mL) was added at 0 °C carefully, and the mixture was filtered through a pad of celite. The residue was dried by infrared lamp to afford the crude **S30** (0.71 g, 44%) as a dark yellow solid.

To a suspension of $LiAlH_4$ (0.114 g, 3.0 mmol, 1.5 equiv) in dry THF (10.0 mL) was added crude **S30** (0.647 g, 2.0 mmol) at 0 °C. After stirring at 0 ˚C for 1 h, the reaction mixture was gradually heated to reflux and stirred at reflux overnight. The reaction mixture was quenched slowly with the addition of H_2O (115 uL) at 0 °C, followed by NaOH solution (10% aq, 115 uL) and H_2O (345 uL). The solid was filtered off through a pad of celite and the filtrate was concentrated by evaporation, and the resulting mixture was purified by column chromatography

on silica gel (hexanes/ethyl acetate = 50 :1) to afford the desired product **1k** (0.149 g, 24%) as a yellow foam. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.8 Hz, 1 H), 7.85 – 7.78 (m, 3 H), 7.60 (d, *J* = 8.4 Hz, 1 H), 7.55 (d, *J* = 8.4 Hz, 1 H), 7.44 (d, *J* = 8.4 Hz, 1 H), 7.40 (d, *J* = 8.0 Hz, 1 H), 7.34 (d, *J* = 8.8 Hz, 1 H), 7.30 – 7.18 (m, 3 H), 4.26 (d, *J* = 12.8 Hz, 1 H), 4.13 (d, *J* = 12.8 Hz, 1 H), 3.75 – 3.61 (m, 1 H), 3.58 – 3.42 (m, 1 H), 1.29 (t, *J* = 7.0 Hz, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 147.2, 135.3, 133.7, 131.5, 129.3, 129.1, 128.3, 128.2, 127.9, 127.8, 127.6, 127.2, 126.6, 125.1, 124.9, 124.8, 123.5, 122.3, 117.4, 115.4, 53.3, 45.1, 11.5. HRMS (ESI) calcd for $C_{23}H_{20}N$ $[M+H]^+$ 310.1596, found 310.1595.

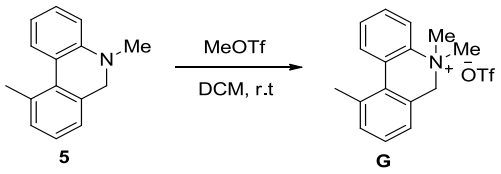
Synthesis of compound **F**[9]



1a **F**

To a solution of **1a** (0.475 g, 2.0 mmol, 1.0 equiv) in DCM (2 mL) was added methyl trifluoromethanesulfonate (0.40 mL, 3.0 mmol, 1.5 equiv) dropwise at room temperature. The reaction mixture was stirred at rt for 2 h. The reaction mixture was concentrated by evaporation and the residue was treated with MTBE (2 mL). The resultant solid was collected by filtration and the solid was washed with MTBE and hexanes, and dried under vacuum to give desired product **F** (0.70 g, 87%) as a white solid. The single crystal was obtained by slow volatilization of a saturation solution of **F** in mixed solvent DCM/PE. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.49 – 7.44 (m, 3 H), 7.42 (t, *J* = 7.2 Hz, 1 H), 7.31 (s, 1 H), 5.08 (d, *J* = 13.6 Hz, 1 H), 4.53 (d, *J* = 13.6 Hz, 1 H), 3.91 (s, 3 H), 3.05 (s, 3 H), 2.48 (s, 3 H), 2.33 (s, 3 H), 2.30 (s, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 143.3, 139.9, 138.0, 135.9, 133.4, 133.3, 128.90, 128.86, 127.8, 126.3, 120.4 (q, J_{C-F} = 318.2 Hz), 124.5, 116.4, 68.5, 53.2, 50.5, 21.1, 20.8, 20.6. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -78.4. HRMS (ESI) calcd for $C_{18}H_{22}N$ $[M-OTf]^+$ 252.1752, found 252.1751.

Synthesis of compound **G**



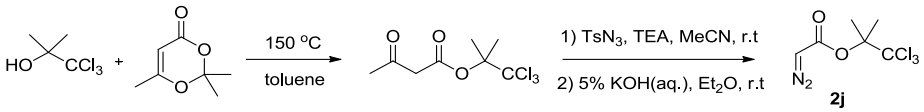
5 **G**

To a solution of **5** (0.105 g, 0.50 mmol, 1.0 equiv) in DCM (2 mL) was added methyl trifluoromethanesulfonate (62 ul, 0.55 mmol, 1.1 equiv) dropwise at room temperature. The reaction mixture was stirred at rt for 2 h. The reaction mixture was concentrated by evaporation and the residue was treated with MTBE (2 mL). The resultant solid was collected by filtration and the solid was washed with MTBE and hexanes, and dried under vacuum to give desired product **G** (93.5 mg, 50%) as a white solid. The single crystal was obtained by slow volatilization of a saturation solution of **G** in mixed solvent DCM/PE. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.92 (td, *J* = 9.2, 1.2 Hz, 2 H), 7.75 – 7.55 (m, 2 H), 7.47 (t, *J* = 7.6 Hz, 2 H), 7.41 (t, *J* = 7.8 Hz, 1 H), 4.93 (s, 2 H), 3.63 (s, 6 H), 2.69 (s, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 141.8, 135.2, 134.4, 130.1, 129.9, 129.8, 129.5 (q, J_{C-F} = 3.2 Hz), 128.1, 127.6 (q, J_{C-F} = 3.2 Hz), 127.1, 126.6 (q, J_{C-F} = 4.5 Hz),

120.6 (q, J_{C-F} = 318.2 Hz), 118.9, 67.0, 52.2, 22.5. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -78.4. HRMS (ESI) calcd for $C_{16}H_{18}N$ [M-OTf]$^+$ 224.1439, found 224.1442.

Synthesis of compound **2j**[10a]

The diazo compound **2c**, **2d**, **2e, 2f, 2g, 2h, 2i, 2n, 2o, 2p, 2q** and **2r** was prepared according to the previous literatures.[10]

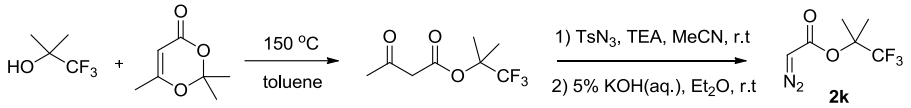


A mixture of 1,1,1-trichloro-2-methylpropan-2-ol (5.594 g, 30.0 mmol) and 2,2,6-trimethyl-4H-1,3-dioxin-4-one (4.0 mL, 30.0 mmol, 1.0 equiv) in 6 mL of toluene was heated at 150 °C for 6 h. After being cooled to room temperature, the toluene was removed by evaporation, and the product was distilled.

To a solution of 1,1,1-trichloro-2-methylpropan-2-yl-3-oxobutanoate (2.62 g, 10.0 mmol) and Et_3N (1.80 mL, 13.0 mmol, 1.3 equiv) in acetonitrile (20 mL) was added tosyl azide (75% in ethyl acetate, 2.50 g, 9.50 mmol, 0.95 equiv) was added slowly at rt. After stirring for 10 h, the solvent was removed under reduced pressure.

To a solution of the above residue in ethyl ether (20 mL) was added KOH (5% aq, 50 mL) and the reaction mixture was stirred rt for 1 h. The mixture was extracted with ethyl ether (30 mL x 2). The combined organic phase was washed with brine (30 mL) and dried over Na_2SO_4. After filtration the solvent was removed by evaporation, and the resulting mixture was purified by column chromatography on silica gel (hexanes/ethyl acetate = 20 :1) to afford the desired product **2j** (2.19 g, 89%) as a yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.72 (bs, 1 H), 1.95 (s, 6 H). **^{13}C** NMR (100 MHz, $CDCl_3$) δ 106.0, 89.2, 47.2, 21.6.

Synthesis of compound **2k**



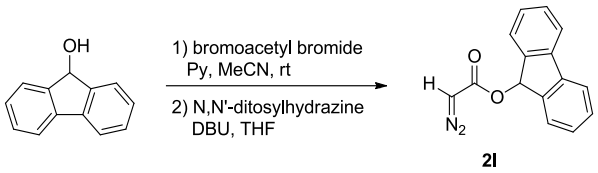
A mixture of 1,1,1-trifluoro-2-methylpropan-2-ol (3.3 mL, 30.0 mmol) and 2,2,6-trimethyl-4H-1,3-dioxin-4-one (4.0 mL, 30.0 mmol, 1.0 equiv) in 6 mL of toluene was heated at 150 °C for 6 h. After being cooled to room temperature, the toluene was removed by evaporation, and the product was distilled.

To a solution of 1,1,1-trifluoro-2-methylpropan-2-yl-3-oxobutanoate (1.76 g, 8.32 mmol) and Et_3N (1.5 mL, 10.82 mmol, 1.3 equiv) in acetonitrile (8 mL) was added tosyl azide (75% in ethyl acetate, 2.08 g, 7.91 mmol, 0.95 equiv) was added slowly at rt. After stirring for 10 h, the solvent was removed under reduced pressure.

To a solution of the above residue in ethyl ether (20 mL) was added KOH (5% aq, 40 mL) and the reaction mixture was stirred rt for 1 h. The mixture was extracted with ethyl ether (30 mL x 2). The combined organic phase was washed with brine (30 mL) and dried over Na_2SO_4. After filtration the solvent was removed by evaporation, and the resulting mixture was purified by distillation to afford the desired product **2k** (588.4 mg, 30%) as a yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.75 (bs, 1 H), 1.72 (q, J = 1.2 Hz, 6 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 124.8 (q, J_{C-F} =

280.9 Hz), 80.8 (q, J_{C-F} = 29.4 Hz), 47.1, 19.6. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -84.0.

Synthesis of compound **2l**[10e]

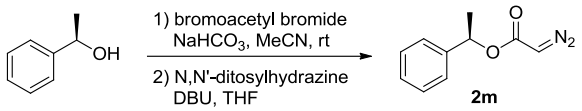


2l

To a solution of 9-hydroxyfluorene (0.5467 g, 3.0 mmol) and pyridine (0.50 mL, 6.0 mmol, 2.0 equiv) in acetonitrile (6.0 mL) was added bromoacetyl bromide (0.40 mL, 4.5 mmol, 1.5 equiv) dropwise at 0 ℃. After stirring 10 min at the temperarture, the reaction was quenched with H_2O. The solution was extracted with CH_2Cl_2 (30 mL x 2). The combined organic phase was washed with brine (30 mL) and dried over Na_2SO_4. After filtration, the solvent was removed by evaporation, and the residue was used in the next reaction without purification.

To a solution of the above bromoacetate and N,N'-ditosylhydrazine (2.04 g, 6.0 mmol, 2.0 equiv) in THF (15.0 mL) was added DBU (2.30 mL, 15.0 mmol, 5.0 equiv) dropwise at 0 ℃ and stirred at the same temperature for 10 minutes. After the quenching of the reaction by the addition of saturated $NaHCO_3$ solution, the mixture was extracted with Et_2O (30 mL x 2). The combined organic phase was washed with brine (30 mL) and dried over Na_2SO_4. After filtration the solvent was removed by evaporation, and the resulting mixture was purified by column chromatography on silica gel (hexanes/ethyl acetate = 20 :1) to afford the desired product **2l** (0.193 g, 26%) as a yellow foam. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.67 (d, J = 7.2 Hz, 2 H), 7.58 (d, J = 7.6 Hz, 2 H), 7.42 (t, J = 7.4 Hz, 2 H), 7.30 (t, J = 7.4 Hz, 2 H), 6.86 (s, 1 H), 4.87 (s, 1 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 141.8, 140.9, 129.5, 127.8, 125.9, 120.0, 75.4, 46.7. HRMS (ESI) calcd for $C_{15}H_{10}N_2O_2Na$ $[M+Na]^+$ 273.0640, found 273.0642

Synthesis of compound **2m**



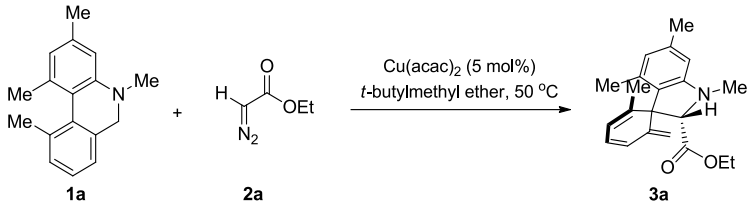
2m

To a solution of (R)-1-phenylethanol (0.367 g, 3.0 mmol) and $NaHCO_3$ (0.756 g, 9.0 mmol, 3.0 equiv) in acetonitrile (6.0 mL) was added bromoacetyl bromide (0.40 mL, 4.50 mmol, 1.5 equiv) dropwise at 0 ℃. After stirring 10 min at the temperarture, the reaction was quenched with H_2O. The solution was extracted with CH_2Cl_2 (30 mL x 2). The combined organic phase was washed with brine (30 mL) and dried over Na_2SO_4. After filtration, the solvent was removed by evaporation, and the residue was used in the next reaction without purification.

To a solution of the above bromoacetate and *N,N'*-ditosylhydrazine (2.04 g, 6.0 mmol, 2.0 equiv) in THF (15.0 mL) was added DBU (2.30 mL, 15.0 mmol, 5.0 equiv) dropwise at 0 ℃ and stirred at the same temperature for 10 minutes. After the quenching of the reaction by the addition of saturated $NaHCO_3$ solution, the mixture was extracted with Et_2O (30 mL x 2). The combined organic phase was washed with brine (30 mL) and dried over Na_2SO_4. After filtration the solvent was removed by evaporation, and the resulting mixture was purified by column chromatography on silica gel (hexanes/ethyl acetate = 20 :1) to afford the desired product **2m** (0.293 g, 51%) as a pale yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 – 7.345 (m, 4 H), 7.345 – 7.28 (m, 1 H), 5.99

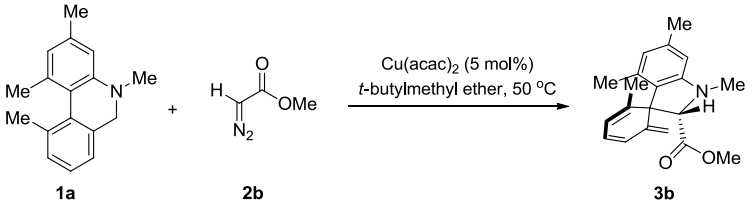
(q, *J* = 6.8 Hz, 1 H), 4.78 (s, 1 H), 1.58 (d, *J* = 6.8 Hz, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.1, 141.4, 128.4, 127.9, 125.9, 72.7, 46.4, 22.3. HRMS (ESI) calcd for $C_{10}H_{10}N_2O_2Na$ $[M+Na]^+$ 213.0640, found 213.0635.

Typical Procedure for 3a (Typical Procedure E)



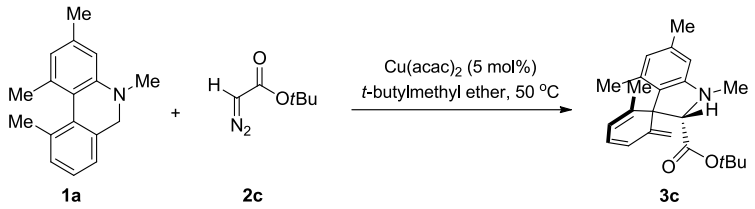
Under argon atmosphere, the amine **1a** (23.8 mg, 0.10 mmol, 1.0 equiv), ethyl diazoacetate **2a** (22.8 mg, 0.20 mmol, 2.0 equiv), $Cu(acac)_2$ (1.3 mg, 0.005 mmol, 5 mol%) and dry MTBE (2.0 mL) were added to a 25 mL Schlenk tube. The tube was capped with a screw cap and stirred at 50 °C for 18 h. After being cooled to room temperature, the solvent was removed and the residue was purified by flash chromatography on silica gel (hexanes/ethyl acetate = 20:1) to afford **3a** (25.6 mg, 79%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.35 (s, 1 H), 6.24 (s, 1 H), 6.04 (d, *J* = 9.2 Hz, 1 H), 5.92 (d, *J* = 6.0 Hz, 1 H), 5.77 (t, *J* = 7.4 Hz, 1 H), 5.10 (s, 1 H), 4.66 (s, 1 H), 4.23 – 3.94 (m, 2 H), 4.05 (s, 1 H), 2.78 (s, 3 H), 2.27 (s, 3 H), 1.99 (s, 3 H), 1.69 (s, 3 H), 1.22 (t, *J* = 7.2 Hz, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.5, 152.1, 144.8, 138.3, 137.7, 134.3, 131.7, 126.7, 122.3, 122.1, 121.9, 118.8, 106.3, 77.4, 60.9, 58.5, 35.1, 21.6, 20.2, 17.6, 14.0. HRMS (ESI) calcd for $C_{21}H_{26}NO_2$ $[M+H]^+$ 324.1964, found 324.1970.

Compound **3b** was prepared following the **Typical Procedure E**



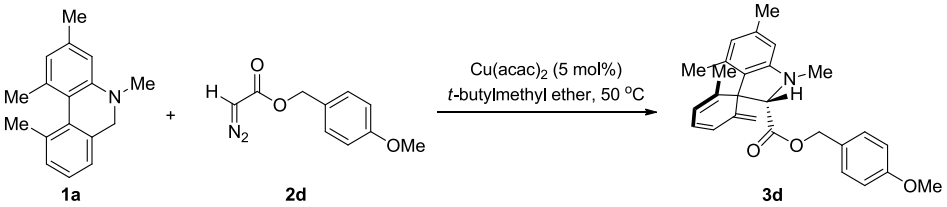
The reaction of **1a** (23.8 mg, 0.10 mmol) and **2b** (20.0 mg, 0.20 mmol, 2.0 equiv) in MTBE (2.0 mL) afforded **3b** (29.0 mg, 94%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.36 (s, 1 H), 6.25 (s, 1 H), 6.05 (d, *J* = 9.6 Hz, 1 H), 5.94 (d, *J* = 5.6 Hz, 1 H), 5.78 (dd, *J* = 8.4, 6.8 Hz, 1 H), 5.12 (s, 1 H), 4.63 (s, 1 H), 4.06 (s, 1 H), 3.64 (s, 3 H), 2.78 (s, 3 H), 2.27 (s, 3 H), 1.98 (s, 3 H), 1.68 (s, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.0, 152.1, 144.8, 138.4, 137.8, 134.3, 131.3, 126.4, 122.3, 122.2, 122.0, 118.8, 106.3, 77.6, 58.7, 51.9, 35.1, 21.6, 20.1, 17.7. HRMS (ESI) calcd for $C_{20}H_{24}NO_2$ $[M+H]^+$ 310.1807, found 310.1811.

Compound **3c** was prepared following the **Typical Procedure E**



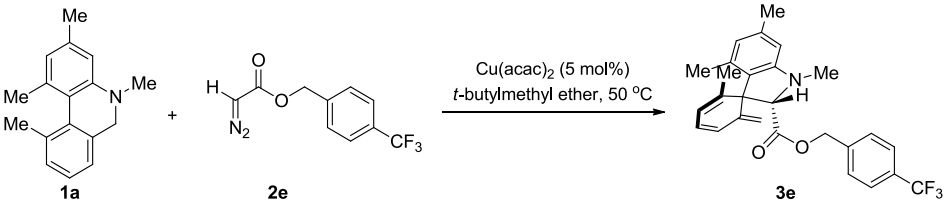
The reaction of **1a** (23.8 mg, 0.10 mmol) and **2c** (28.4 mg, 0.20 mmol, 2.0 equiv) in MTBE (2.0 mL) afforded **3c** (28.7 mg, 82%) at 50 °C for 18 h. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.31 (s, 1 H), 6.22 (s, 1 H), 6.06 (d, *J* = 9.2 Hz, 1 H), 5.89 (d, *J* = 6.4 Hz, 1 H), 5.77 (t, *J* = 7.8 Hz, 1 H), 5.07 (s, 1 H), 4.75 (s, 1 H), 4.00 (s, 1 H), 2.79 (s, 3 H), 2.26 (s, 3 H), 1.99 (s, 3 H), 1.67 (s, 3 H), 1.41 (s, 9 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.3, 152.0, 145.1, 138.1, 137.8, 134.1, 133.1, 127.4, 122.1, 121.8, 121.6, 118.6, 106.1, 81.0, 77.7, 58.1, 35.1, 27.6, 21.6, 20.2, 17.3. HRMS (ESI) calcd for $C_{23}H_{29}NO_2Na$ $[M+Na]^+$ 374.2096, found 374.2097.

Compound **3d** was prepared following the **Typical Procedure E**



The reaction of **1a** (23.8 mg, 0.10 mmol) and **2d** (41.2 mg, 0.20 mmol, 2.0 equiv) in MTBE (2.0 mL) afforded **3d** (37.2 mg, 90%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.32 – 7.23 (m, 2 H), 6.87 (d, *J* = 8.4 Hz, 2 H), 6.34 (s, 1 H), 6.24 (s, 1 H), 5.95 – 5.80 (m, 2 H), 5.67 (dd, *J* = 8.8, 6.4 Hz, 1 H), 5.11 (d, *J* = 12.0 Hz, 1 H), 5.04 (s, 1 H), 4.93 (d, *J* = 12.0 Hz, 1 H), 4.64 (s, 1 H), 4.08 (s, 1 H), 3.82 (s, 3 H), 2.77 (s, 3 H), 2.27 (s, 3 H), 1.97 (s, 3 H), 1.66 (s, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.4, 159.5, 152.1, 144.7, 138.3, 137.7, 134.3, 131.5, 130.4, 127.8, 126.5, 122.3, 122.1, 121.9, 118.9, 113.6, 106.2, 77.5, 66.6, 58.6, 55.3, 35.0, 21.6, 20.1, 17.6. HRMS (ESI) calcd for $C_{27}H_{30}NO_3$ $[M+H]^+$ 416.2226, found 416.2229.

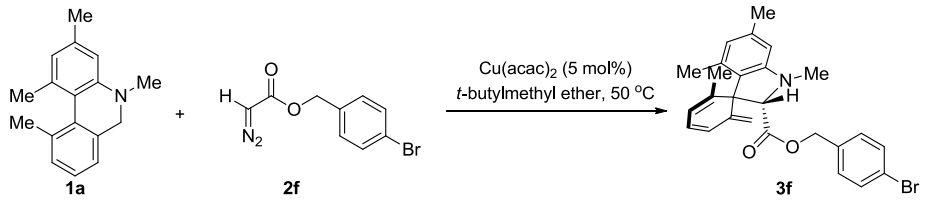
Compound **3e** was prepared following the **Typical Procedure E**



The reaction of **1a** (23.8 mg, 0.10 mmol) and **2e** (48.8 mg, 0.20 mmol, 2.0 equiv) in MTBE (2.0 mL) afforded **3e** (31.6 mg, 70%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.0 Hz, 2 H), 7.46 (d, *J* = 8.0 Hz, 2 H), 6.36 (s, 1 H), 6.26 (s, 1 H), 5.98 – 5.83 (m, 2 H), 5.64 (dd, *J* = 9.4, 6.2 Hz, 1 H), 5.23 (d, *J* = 12.8 Hz, 1 H), 5.05 (s, 1 H), 5.02 (d, *J* = 12.8 Hz, 1 H), 4.67 (s, 1 H), 4.14 (s, 1 H), 2.79 (s, 3 H), 2.28 (s, 3 H), 1.97 (s, 3 H), 1.69 (s, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.3, 151.9, 144.7, 139.5, 138.5, 137.8, 134.3, 131.5, 130.3 (q, J_{C-F} = 32.2 Hz), 128.4, 126.5, 125.5 (q, J_{C-F} = 3.8 Hz), 125.3 (q, J_{C-F} = 3.8 Hz), 122.33, 122.27, 121.9, 121.3 (q, J_{C-F} = 273.1 Hz), 119.0,

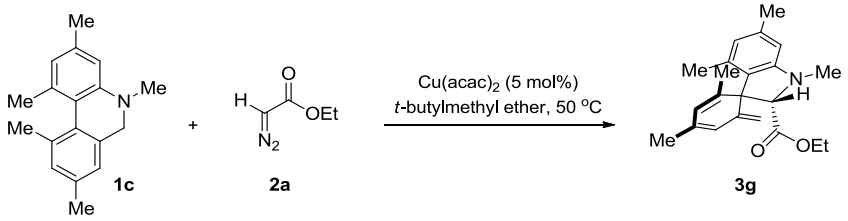
106.3, 77.6, 65.8, 58.7, 35.1, 21.6, 20.1, 17.6. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.6. HRMS (ESI) calcd for $C_{27}H_{27}F_3NO_2$ $[M+H]^+$ 454.1994, found 454.2000.

Compound **3f** was prepared following the **Typical Procedure E**



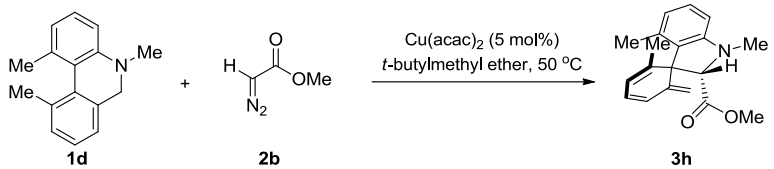
The reaction of **1a** (23.8 mg, 0.10 mmol) and **2f** (51.0 mg, 0.20 mmol, 2.0 equiv) in MTBE (2.0 mL) afforded **3f** (36.1 mg, 78%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.4 Hz, 2 H), 7.22 (d, *J* = 8.4 Hz, 2 H), 6.35 (s, 1 H), 6.25 (s, 1 H), 5.89 (d, *J* = 8.8 Hz, 2 H), 5.65 (dd, *J* = 8.4, 6.8 Hz, 1 H), 5.11 (d, *J* = 12.4 Hz, 1 H), 5.04 (s, 1 H), 4.93 (d, *J* = 12.4 Hz, 1 H), 4.66 (s, 1 H), 4.11 (s, 1 H), 2.78 (s, 3 H), 2.27 (s, 3 H), 1.97 (s, 3 H), 1.67 (s, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.3, 152.0, 144.7, 138.4, 137.8, 134.6, 134.3, 131.6, 131.5, 130.3, 126.5, 122.3, 122.21, 122.16, 121.9, 119.0, 106.3, 77.6, 66.0, 58.6, 35.0, 21.6, 20.1, 17.6. HRMS (ESI) calcd for $C_{26}H_{27}BrNO_2$ $[M+H]^+$ 464.1225, found 464.1227.

Compound **3g** was prepared following the **Typical Procedure E**



The reaction of **1c** (25.1 mg, 0.10 mmol) and **2a** (22.8 mg, 0.20 mmol, 2.0 equiv) in MTBE (2.0 mL) afforded **3g** (26.4 mg, 78%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.34 (s, 1 H), 6.24 (s, 1 H), 5.84 (s, 1 H), 5.81 (s, 1 H), 4.98 (s, 1 H), 4.51 (s, 1 H), 4.17 – 4.02 (m, 2 H), 4.00 (s, 1 H), 2.77 (s, 3 H), 2.27 (s, 3 H), 1.97 (s, 3 H), 1.81 (s, 3 H), 1.69 (s, 3 H), 1.19 (t, *J* = 7.0 Hz, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.5, 152.2, 144.9, 138.2, 137.7, 134.3, 131.3, 130.5, 125.8, 123.1, 122.1, 116.0, 106.3, 77.4, 60.8, 58.1, 35.1, 21.6, 21.4, 20.1, 17.7, 13.9. HRMS (ESI) calcd for $C_{22}H_{28}NO_2$ $[M+H]^+$ 338.2120, found 338.2123.

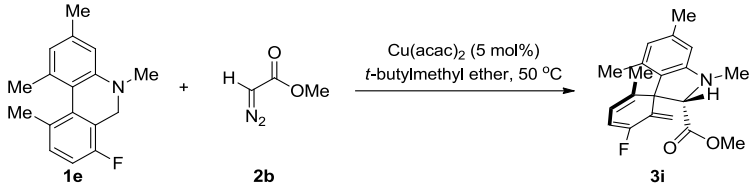
Compound **3h** was prepared following the **Typical Procedure E**



The reaction of **1d** (22.3 mg, 0.10 mmol) and **2b** (20.0 mg, 0.20 mmol, 2.0 equiv) in MTBE (2.0 mL) afforded **3h** (28.4 mg, 96%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.07 (t, *J* = 7.6 Hz, 1 H), 6.52 (d, *J* = 7.6 Hz, 1 H), 6.42 (d, *J* = 7.6 Hz, 1 H), 6.06 (d, *J* = 9.6 Hz, 1 H), 5.95 (d, *J* = 5.2 Hz, 1 H), 5.79 (dd, *J* = 8.0, 6.4 Hz, 1 H), 5.13 (s, 1 H), 4.62 (s, 1 H), 4.07 (s, 1 H), 3.65 (s, 3 H), 2.80 (s, 3 H), 2.03 (s, 3 H), 1.68 (s, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.9, 151.9, 144.6, 137.5, 134.7,

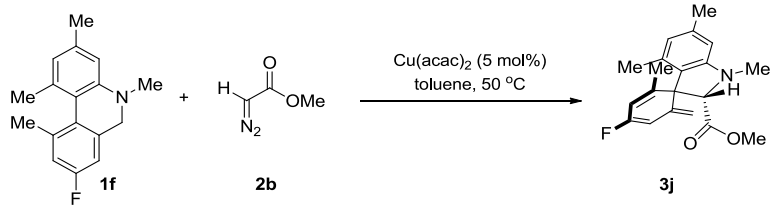
133.9, 128.5, 126.4, 122.3, 122.0, 121.4, 118.9, 105.4, 77.3, 58.9, 51.9, 35.0, 20.1, 17.8. HRMS (ESI) calcd for $C_{19}H_{22}NO_2$ $[M+H]^+$ 296.1651, found 296.1656.

Compound **3i** was prepared following the **Typical Procedure E**



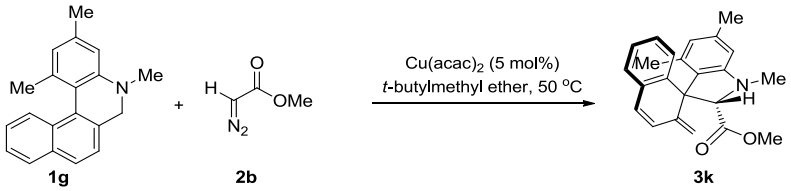
The reaction of **1e** (25.5 mg, 0.10 mmol) and **2b** (20.0 mg, 0.20 mmol, 2.0 equiv) in MTBE (2.0 mL) afforded **3i** (27.7 mg, 85%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.36 (s, 1 H), 6.26 (s, 1 H), 5.80 (t, *J* = 5.2 Hz, 1 H), 5.61 – 5.43 (m, 2 H), 4.77 (t, *J* = 2.2 Hz, 1 H), 4.08 (s, 1 H), 3.66 (s, 3 H), 2.80 (s, 3 H), 2.28 (s, 3 H), 1.97 (s, 3 H), 1.65 (s, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.5, 158.2 (d, J_{C-F} = 257.8 Hz), 152.1, 138.9, 138.3 (d, J_{C-F} = 17.4 Hz), 135.1 (d, J_{C-F} = 5.2 Hz), 134.3, 130.5, 122.2, 119.1 (d, J_{C-F} = 7.4 Hz), 115.1 (d, J_{C-F} = 3.1 Hz), 106.3, 101.8 (d, J_{C-F} = 21.3 Hz), 77.8, 60.8 (d, J_{C-F} = 3.7 Hz), 51.7, 34.9, 21.6, 19.8, 17.7. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -126.8. HRMS (ESI) calcd for $C_{20}H_{23}FNO_2$ $[M+H]^+$ 328.1713, found 328.1720.

Compound **3j** was prepared following the **Typical Procedure E**



The reaction oE **1f** (25.5 mg, 0.10 mmol) and **2b** (20.0 mg, 0.20 mmol, 2.0 equiv) in toluene (2.0 mL) afforded **3j** (27.2 mg, 83%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.37 (s, 1 H), 6.25 (s, 1 H), 5.93 (d, *J* = 8.4 Hz, 1 H), 5.69 (dd, *J* = 11.2, 0.8 Hz, 1 H), 5.05 (s, 1 H), 4.54 (s, 1 H), 4.01 (s, 1 H), 3.67 (s, 3 H), 2.78 (s, 3 H), 2.27 (s, 3 H), 1.98 (s, 3 H), 1.74 (s, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.5, 157.5 (d, J_{C-F} = 249.8 Hz), 152.1, 142.9 (d, J_{C-F} = 9.3 Hz), 142.6 (d, J_{C-F} = 8.2 Hz), 138.8, 134.3, 130.0, 122.3, 118.0 (d, J_{C-F} = 35.2 Hz), 117.4 (d, J_{C-F} = 11.9 Hz), 106.5, 104.1 (d, J_{C-F} = 19.9 Hz), 77.3, 58.8, 51.9, 35.0, 21.6, 20.1 (d, J_{C-F} = 2.3 Hz), 17.8. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -117.5. HRMS (ESI) calcd for $C_{20}H_{23}FNO_2$ $[M+H]^+$ 328.1713, found 328.1716.

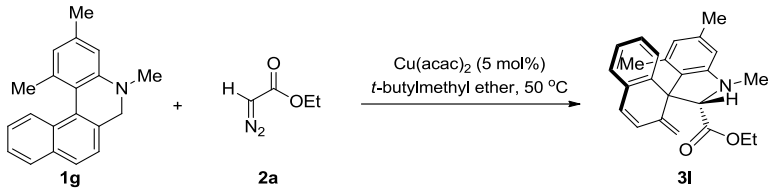
Compound **3k** was prepared following the **Typical Procedure E**



The reaction of **1g** (27.3 mg, 0.10 mmol) and **2b** (20.0 mg, 0.20 mmol, 2.0 equiv) in MTBE (2.0 mL) afforded **3k** (29.7 mg, 86%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.18 (t, *J* = 7.2 Hz, 1 H), 7.12 (d, *J* = 14.4 Hz, 1 H), 7.10 (d, *J* = 14.8 Hz, 1 H), 7.04 (d, *J* = 7.6 Hz, 1 H), 6.43 – 6.34 (m, 3 H), 6.31 (d, *J* = 9.6 Hz, 1 H), 5.20 (s, 1 H), 4.77 (s, 1 H), 4.10 (s, 1 H), 3.59 (s, 3 H), 2.80 (s, 3 H), 2.32 (s,

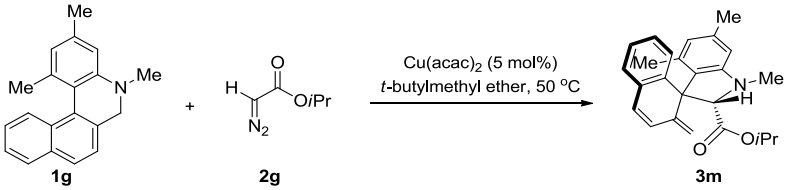
3 H), 1.60 (s, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.4, 152.5, 143.0, 141.3, 138.6, 134.4, 132.6, 132.1, 128.4, 128.1, 127.8, 126.9, 126.5, 126.2, 122.9, 119.0, 106.5, 85.3, 56.7, 51.7, 35.3, 21.6, 18.5. HRMS (ESI) calcd for $C_{23}H_{24}NO_2$ $[M+H]^+$ 346.1807, found 346.1803.

Compound **3l** was prepared following the **Typical Procedure E**



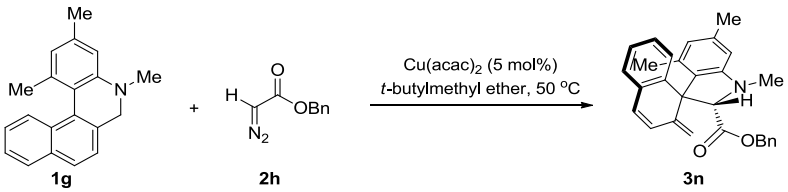
The reaction of **1g** (27.3 mg, 0.10 mmol) and **2a** (22.8 mg, 0.20 mmol, 2.0 equiv) in MTBE (2.0 mL) afforded **3l** (28.3 mg, 79%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.17 (t, *J* = 7.0 Hz, 1 H), 7.12 (t, *J* = 7.4 Hz, 1 H), 7.06 (t, *J* = 8.4 Hz, 2 H), 6.43 – 6.27 (m, 3 H), 6.30 (d, *J* = 9.6 Hz, 1 H), 5.19 (s, 1 H), 4.79 (s, 1 H), 4.09 (s, 1 H), 4.05 (q, *J* = 7.2 Hz, 2 H), 2.81 (s, 3 H), 2.32 (s, 3 H), 1.59 (s, 3 H), 1.13 (t, *J* = 7.2 Hz, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.0, 152.4, 143.0, 141.4, 138.6, 134.3, 132.6, 132.5, 128.7, 128.2, 127.7, 126.8, 126.4, 126.2, 122.8, 119.0, 106.6, 85.2, 60.8, 56.5, 35.4, 21.6, 18.4, 13.8. HRMS (ESI) calcd for $C_{24}H_{26}NO_2$ $[M+H]^+$ 360.1964, found 360.1963.

Compound **3m** was prepared following the **Typical Procedure E**



The reaction of **1g** (27.3 mg, 0.10 mmol) and **2g** (25.6 mg, 0.20 mmol, 2.0 equiv) in MTBE (2.0 mL) afforded **3m** (28.1 mg, 75%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.16 (td, *J* = 7.2, 1.2 Hz, 1 H), 7.10 (td, *J* = 7.2, 1.2 Hz, 1 H), 7.08 – 6.99 (m, 2 H), 6.41 – 6.33 (m, 3 H), 6.30 (d, *J* = 10.0 Hz, 1 H), 5.18 (s, 1 H), 4.92 (hept, *J* = 6.4 Hz, 1 H), 4.83 (s, 1 H), 4.07 (s, 1 H), 2.81 (s, 3 H), 2.31 (s, 3 H), 1.58 (s, 3 H), 1.15 (d, *J* = 6.4 Hz, 3 H), 1.11 (d, *J* = 6.2 Hz, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.4, 152.3, 143.1, 141.5, 138.5, 134.3, 133.1, 132.5, 129.0, 128.2, 127.7, 126.7, 126.4, 126.2, 122.7, 118.9, 106.5, 85.4, 68.4, 56.3, 35.4, 21.8, 21.6, 21.3, 18.3. HRMS (ESI) calcd for $C_{25}H_{28}NO_2$ $[M+H]^+$ 374.2120, found 374.2121.

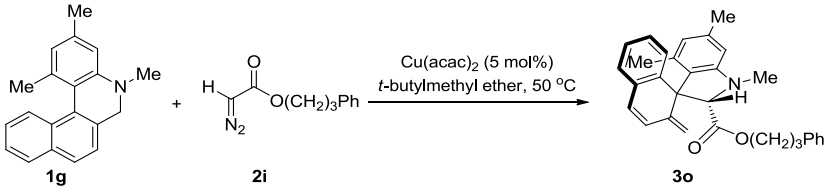
Compound **3n** was prepared following the **Typical Procedure E**



The reaction of **1g** (27.3 mg, 0.10 mmol) and **2h** (35.2 mg, 0.20 mmol, 2.0 equiv) in MTBE (2.0 mL) afforded **3n** (33.3 mg, 79%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33 – 7.27 (m, 3 H), 7.20 – 7.13 (m, 3 H), 7.10 (t, *J* = 7.4 Hz, 1 H), 7.04 (d, *J* = 7.6 Hz, 1 H), 7.00 (d, *J* = 7.6 Hz, 1 H), 6.39 (s, 1 H), 6.37 (s, 1 H), 6.19 (d, *J* = 9.6 Hz, 1 H), 6.14 (d, *J* = 9.6 Hz, 1 H), 5.13 (s, 1 H), 5.10 (d, *J* = 12.8 Hz, 1 H), 5.01 (d, *J* = 12.8 Hz, 1 H), 4.79 (s, 1 H), 4.16 (s, 1 H), 2.81 (s, 3 H), 2.32 (s, 3 H),

1.59 (s, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.8, 152.5, 142.8, 141.2, 138.6, 135.3, 134.4, 132.6, 132.2, 128.5, 128.24, 128.20, 128.16, 128.0, 127.8, 126.8, 126.6, 126.3, 122.8, 119.1, 106.5, 85.1, 66.5, 56.7, 35.3, 21.7, 18.5. HRMS (ESI) calcd for $C_{29}H_{28}NO_2$ $[M+H]^+$ 422.2120, found 422.2122.

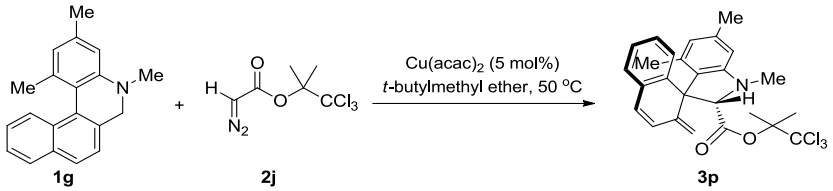
Compound **3o** was prepared following the **Typical Procedure E**



1g **2i** **3o**

The reaction of **1g** (27.3 mg, 0.10 mmol) and **2i** (40.8 mg, 0.20 mmol, 2.0 equiv) in MTBE (2.0 mL) afforded **3o** (35.3 mg, 78%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.27 (t, *J* = 7.2 Hz, 2 H), 7.22 – 7.16 (m, 2 H), 7.13 (td, *J* = 7.4, 1.6 Hz, 1 H), 7.10 – 7.04 (m, 4 H), 6.39 (s, 1 H), 6.36 (d, *J* = 9.6 Hz, 2 H), 6.30 (d, *J* = 9.6 Hz, 1 H), 5.19 (s, 1 H), 4.82 (s, 1 H), 4.12 (s, 1 H), 4.06 (dt, *J* = 10.8, 6.4 Hz, 1 H), 3.98 (dt, *J* = 10.8, 6.4 Hz, 1 H), 2.82 (s, 3 H), 2.49 (t, *J* = 7.8 Hz, 2 H), 2.32 (s, 3 H), 1.89 – 1.73 (m, 2 H), 1.60 (s, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.0, 152.4, 143.0, 141.4, 141.3, 138.6, 134.3, 132.7, 132.6, 128.7, 128.4, 128.32, 128.28, 127.8, 126.8, 126.5, 126.2, 125.9, 122.8, 119.1, 106.6, 85.3, 64.2, 56.5, 35.4, 32.2, 30.0, 21.6, 18.4. HRMS (ESI) calcd for $C_{31}H_{32}NO_2$ $[M+H]^+$ 450.2433, found 450.2441.

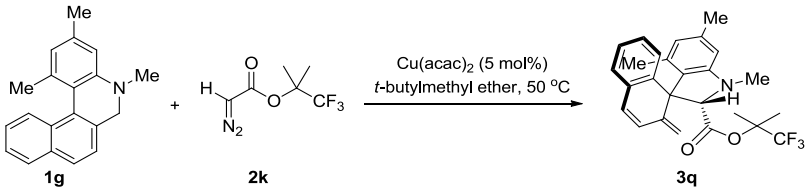
Compound **3p** was prepared following the **Typical Procedure E**



1g **2j** **3p**

The reaction of **1g** (27.3 mg, 0.10 mmol) and **2j** (49.1 mg, 0.20 mmol, 2.0 equiv) in MTBE (2.0 mL) afforded **3p** (30.6 mg, 62%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.14 (td, *J* = 7.2, 1.2 Hz, 1 H), 7.09 (td, *J* = 7.4, 1.2 Hz, 1 H), 7.04 (d, *J* = 7.2 Hz, 1 H), 7.00 (d, *J* = 7.6 Hz, 1 H), 6.39 (d, *J* = 9.6 Hz, 1 H), 6.36 (s, 1 H), 6.33 (s, 1 H), 6.32 (d, *J* = 9.6 Hz, 1 H), 5.22 (s, 1 H), 4.92 (s, 1 H), 4.14 (s, 1 H), 2.80 (s, 3 H), 2.32 (s, 3 H), 1.88 (s, 3 H), 1.84 (s, 3 H), 1.60 (s, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.1, 152.2, 142.4, 140.8, 138.6, 134.4, 132.50, 132.48, 128.7, 128.2, 127.8, 126.9, 126.72, 126.70, 122.6, 119.7, 106.1, 105.8, 89.6, 85.4, 56.8, 34.9, 21.6, 21.4, 21.2, 18.5. HRMS (ESI) calcd for $C_{26}H_{27}Cl_3NO_2$ $[M+H]^+$ 490.1107, found 490.1107.

Compound **3q** was prepared following the **Typical Procedure E**

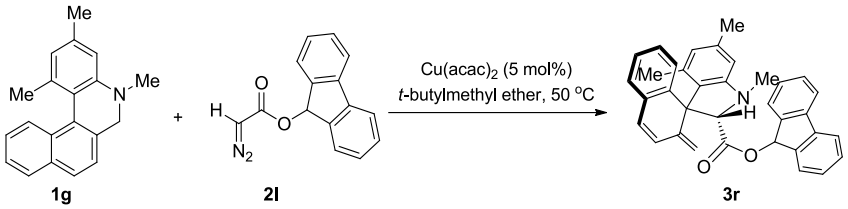


1g **2k** **3q**

The reaction of **1g** (27.3 mg, 0.10 mmol) and **2k** (39.2 mg, 0.20 mmol, 2.0 equiv) in MTBE (2.0 mL) afforded **3q** (35.5 mg, 80%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.15 (td, *J* = 7.2, 1.2 Hz, 1 H),

7.12 – 7.04 (m, 2 H), 7.02 – 6.96 (m, 1 H), 6.40 (d, *J* = 9.6 Hz, 1 H), 6.36 (s, 1 H), 6.34 (s, 1 H), 6.29 (d, *J* = 9.6 Hz, 1 H), 5.19 (s, 1 H), 4.88 (s, 1 H), 4.13 (s, 1 H), 2.80 (s, 3 H), 2.31 (s, 3 H), 1.62 (s, 6 H), 1.58 (s, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.9, 152.0, 142.8, 141.0, 138.6, 134.3, 133.1, 132.4, 128.4, 128.1, 127.7, 126.84, 126.80, 126.7, 124.6 (q, J_{C-F} = 281.2 Hz), 122.7, 119.1, 106.3, 85.4, 80.6 (q, J_{C-F} = 29.6 Hz), 56.4, 35.0, 21.6, 19.3, 18.8, 18.3. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -83.4. HRMS (ESI) calcd for $C_{26}H_{27}F_3NO_2Na$ $[M+H]^+$ 442.1994, found 442.1995.

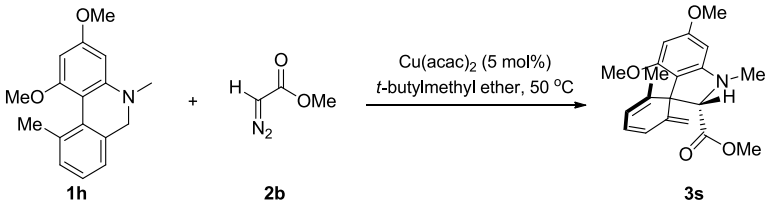
Compound **3r** was prepared following the **Typical Procedure E**



1g **2l** **3r**

The reaction of **1g** (27.3 mg, 0.10 mmol) and **2l** (50.1 mg, 0.20 mmol, 2.0 equiv) in MTBE (2.0 mL) afforded **3r** (36.0 mg, 73%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 7.6 Hz, 2 H), 7.57 (d, *J* = 7.6 Hz, 1 H), 7.46 (d, *J* = 7.6 Hz, 1 H), 7.40 (d, *J* = 7.6 Hz, 1 H), 7.36 (d, *J* = 7.6 Hz, 1 H), 7.29 -7.24 (m, 1 H), 7.22 (t, *J* = 7.4 Hz, 1 H), 7.04 (ddd, *J* = 14.1, 6.9, 1.5 Hz, 2 H), 6.99 (d, *J* = 7.2 Hz, 1 H), 6.91 (dd, *J* = 6.8, 1.2 Hz, 1 H), 6.67 (s, 1 H), 6.38 (s, 1 H), 6.36 (s, 1 H), 6.19 (d, *J* = 9.6 Hz, 1 H), 6.07 (d, *J* = 9.6 Hz, 1 H), 5.15 (s, 1 H), 4.89 (s, 1 H), 4.22 (s, 1 H), 2.85 (s, 3 H), 2.31 (s, 3 H), 1.57 (s, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.0, 152.3, 143.0, 141.9, 141.4, 141.2, 141.1, 141.0, 138.6, 134.3, 132.8, 132.4, 129.4, 129.3, 128.8, 128.1, 127.7, 127.6, 127.4, 126.72, 126.71, 126.5, 126.3, 126.2, 122.9, 119.7, 119.3, 106.5, 85.4, 75.9, 56.5, 35.5, 21.6, 18.4. HRMS (ESI) calcd for $C_{35}H_{30}NO_2$ $[M+H]^+$ 496.2277, found 496.2276.

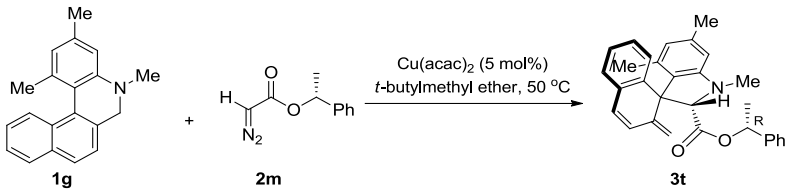
Compound **3s** was prepared following the **Typical Procedure E**



1h **2b** **3s**

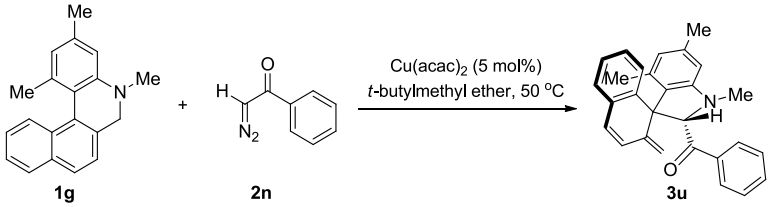
The reaction of **1h** (26.9 mg, 0.10 mmol) and **2b** (20.0 mg, 0.20 mmol, 2.0 equiv) in MTBE (2.0 mL) afforded **3s** (18.6 mg, 54%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.03 (d, *J* = 9.2 Hz, 1 H), 5.92 (s, 1 H), 5.90 (d, *J* = 5.6 Hz, 1 H), 5.84 (s, 1 H), 5.78 (dd, *J* = 8.8, 6.4 Hz, 1 H), 5.11 (s, 1 H), 4.63 (s, 1 H), 3.96 (s, 1 H), 3.80 (s, 3 H), 3.70 (s, 3 H), 3.64 (s, 3 H), 2.74 (s, 3 H), 1.73 (s, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.6, 162.3, 155.9, 154.1, 144.5, 138.9, 125.9, 123.1, 120.9, 117.9, 113.0, 90.0, 87.3, 77.4, 57.8, 55.5, 55.3, 52.0, 34.9, 20.2. HRMS (ESI) calcd for $C_{20}H_{24}NO_4$ $[M+H]^+$ 342.1705, found 342.1699.

Compound **3t** was prepared following the **Typical Procedure E**



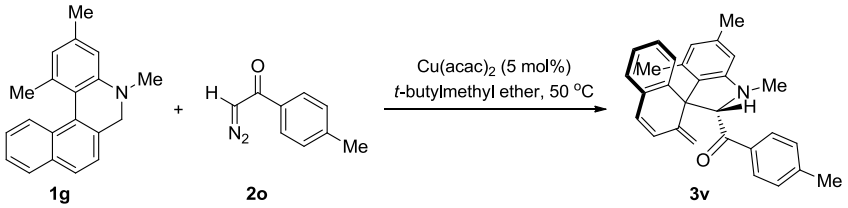
The reaction of **1g** (27.3 mg, 0.10 mmol) and **2m** (38.0 mg, 0.20 mmol, 2.0 equiv) in MTBE (2.0 mL) afforded **3t** (33.3 mg, 76%, dr 1:1). Analytic datas for diastereomers: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34 – 7.28 (m, 1.5 H), 7.25 – 7.21 (m, 1.5 H), 7.21 – 7.13 (m, 2 H), 7.13 – 7.04 (m, 3 H), 7.01 (d, *J* = 7.6 Hz, 0.5 H), 6.82 (d, *J* = 6.8 Hz, 0.5 H), 6.44 (d, *J* = 9.6 Hz, 0.5 H), 6.40 – 6.34 (m, 2 H), 6.31 (d, *J* = 10.0 Hz, 0.5 H), 5.93 (d, *J* = 9.6 Hz, 0.5 H), 5.85 (t, *J* = 6.4 Hz, 0.5 H), 5.80 (t, *J* = 6.2 Hz, 0.5 H), 5.75 (d, *J* = 9.6 Hz, 0.5 H), 5.18 (s, 0.5 H), 5.03 (s, 0.5 H), 4.92 (s, 0.5 H), 4.75 (s, 0.5 H), 4.20 (s, 0.5 H), 4.11 (s, 0.5 H), 2.81 (s, 1.5 H), 2.79 (s, 1.5 H), 2.31 (s, 3 H), 1.60 (s, 1.5 H), 1.55 (s, 1.5 H), 1.46 (d, *J* = 6.4 Hz, 1.5 H), 1.45 (d, *J* = 6.4 Hz, 1.5 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.2, 169.1, 152.4, 152.2, 143.3, 142.6, 141.7, 141.6, 141.1, 140.8, 138.5, 134.4, 134.2, 133.9, 132.7, 132.6, 132.3, 129.4, 128.5, 128.3, 128.2, 128.1, 128.0, 127.8, 127.7, 127.55, 127.50, 126.7, 126.5, 126.4, 126.3, 126.1, 125.8, 122.8, 122.7, 119.1, 118.7, 106.6, 106.4, 85.6, 85.2, 73.2, 73.0, 56.6, 56.1, 35.5, 35.2, 22.6, 22.5, 21.6, 18.5, 18.2. HRMS (ESI) calcd for $C_{30}H_{30}NO_2$ $[M+H]^+$ 436.2277, found 436.2281.

Compound **3u** was prepared following the **Typical Procedure E**



The reaction of **1g** (27.3 mg, 0.10 mmol) and **2n** (29.0 mg, 0.20 mmol, 2.0 equiv) in MTBE (2.0 mL) afforded **3u** (32.1 mg, 82%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38 (t, *J* = 7.4 Hz, 1 H), 7.34 – 7.27 (m, 3 H), 7.20 (t, *J* = 7.2 Hz, 1 H), 7.16 (t, *J* = 7.2 Hz, 1 H), 7.09 (t, *J* = 7.6 Hz, 2 H), 6.77 (d, *J* = 7.2 Hz, 1 H), 6.41 (s, 1 H), 6.39 (s, 1 H), 5.92 (d, *J* = 9.6 Hz, 1 H), 5.73 (d, *J* = 9.6 Hz, 1 H), 5.16 (s, 1 H), 5.03 (s, 1 H), 4.71 (s, 1 H), 2.79 (s, 3 H), 2.34 (s, 3 H), 1.57 (s, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 196.4, 152.8, 142.0, 141.1, 138.6, 137.2, 134.4, 133.3, 132.7, 132.0, 129.1, 128.5, 128.2, 128.0, 127.6, 127.0, 126.6, 125.7, 122.7, 119.8, 106.5, 87.5, 57.8, 35.2, 21.7, 18.5. HRMS (ESI) calcd for $C_{28}H_{26}NO$ $[M+H]^+$ 392.2014, found 392.2017.

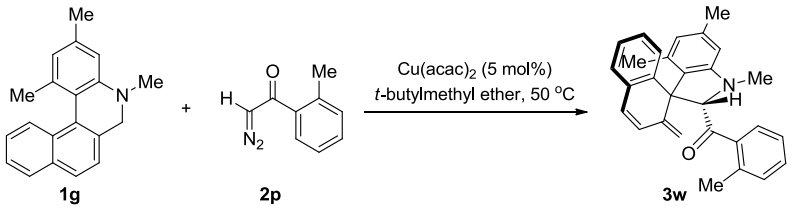
Compound **3v** was prepared following the **Typical Procedure E**



The reaction of **1g** (27.3mg, 0.10 mmol) and **2o** (32.0 mg, 0.20 mmol, 2.0 equiv) in MTBE (2.0 mL) afforded **3v** (33.6 mg, 83%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.27 (d, *J* = 9.2 Hz, 1 H), 7.24 –

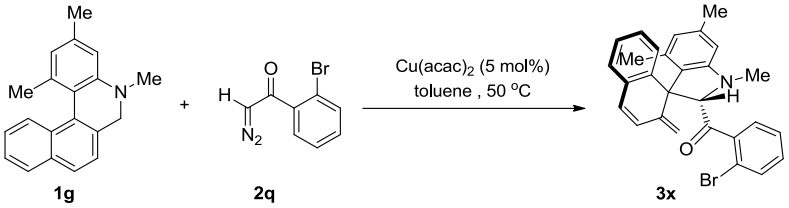
7.18 (m, 3 H), 7.18 – 7.13 (m, 1 H), 6.89 (d, *J* = 8.0 Hz, 2 H), 6.80 (d, *J* = 6.8 Hz, 1 H), 6.39 (s, 2 H), 5.94 (d, *J* = 9.6 Hz, 1 H), 5.77 (d, *J* = 9.6 Hz, 1 H), 5.16 (s, 1 H), 4.99 (s, 1 H), 4.70 (s, 1 H), 2.76 (s, 3 H), 2.33 (s, 3 H), 2.31 (s, 3 H), 1.58 (s, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 195.8, 152.9, 143.4, 142.0, 141.2, 138.5, 134.7, 134.4, 133.3, 131.9, 129.2, 128.6, 128.3, 128.2, 128.0, 127.0, 126.5, 125.7, 122.6, 119.8, 106.4, 87.3, 57.9, 35.1, 21.7, 21.6, 18.6. HRMS (ESI) calcd for $C_{29}H_{28}NO$ $[M+H]^+$ 406.2171, found 406.2174.

Compound **3w** was prepared following the **Typical Procedure E**



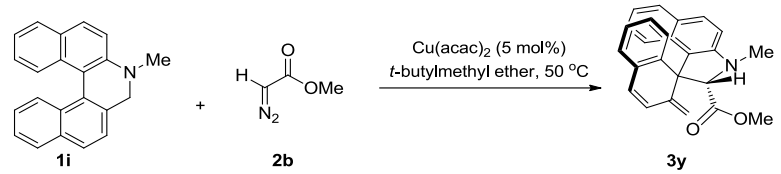
The reaction of **1g** (27.3 mg, 0.10 mmol) and **2p** (32.0 mg, 0.20 mmol, 2.0 equiv) in MTBE (2.0 mL) afforded **3w** (29.4 mg, 72%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.19 (td, *J* = 7.4, 1.2 Hz, 2 H), δ 7.19 (td, *J* = 7.2, 1.6 Hz, 1 H), 7.12 – 7.09 (m, 1 H), 7.09 – 7.05 (m, 1 H), 6.74 (d, *J* = 6.8 Hz, 1 H), 6.68 (dd, *J* = 7.6, 1.2 Hz, 1 H), 6.61 (t, *J* = 7.2 Hz, 1 H), 6.43 (s, 1 H), 6.35 (s, 1 H), 5.90 (d, *J* = 10.0 Hz, 1 H), 5.66 (d, *J* = 9.6 Hz, 1 H), 5.13 (d, *J* = 0.8 Hz, 1 H), 5.08 (s, 1 H), 4.82 (s, 1 H), 2.89 (s, 3 H), 2.43 (s, 3 H), 2.32 (s, 3 H), 1.50 (s, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 198.8, 152.5, 142.8, 141.5, 139.5, 138.4, 136.7, 134.2, 134.0, 133.0, 131.2, 128.8, 128.24, 128.16, 127.8, 126.7, 126.3, 125.2, 124.3, 122.7, 119.4, 106.6, 89.2, 56.0, 35.9, 21.7, 21.0, 18.0. HRMS (ESI) calcd for $C_{29}H_{28}NO$ $[M+H]^+$ 406.2171, found 406.2173.

Compound **3x** was prepared following the **Typical Procedure E**



The reaction of **1a** (273.4 mg, 0.10 mmol) and **2q** (329.8 mg, 1.50 mmol, 1.5 equiv) in toluene (2.0 mL) afforded **3x** (322.3 mg, 69%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.45 (dd, *J* = 8.0, 1.2 Hz, 1 H), 7.18 (d, *J* = 7.6 Hz, 1 H), 7.12 (m, 2 H), 7.06 (td, *J* = 7.2, 1.6 Hz, 1 H), 6.89 (dd, *J* = 7.8, 1.8 Hz, 1 H), 6.87 (td, *J* = 7.2, 1.2 Hz, 1 H), 6.67 (dd, *J* = 7.4, 1.4 Hz, 1 H), 6.43 (s, 1 H), 6.35 (s, 1 H), 6.07 (d, *J* = 10.0 Hz, 1 H), 5.73 (d, *J* = 10.0 Hz, 1 H), 5.231 (s, 1 H), 5.226 (s, 1 H), 4.92 (s, 1 H), 2.93 (s, 3 H), 2.32 (s, 3 H), 1.49 (s, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 197.2, 152.2, 142.4, 141.1, 138.5, 137.8, 134.6, 134.0, 133.9, 132.8, 131.9, 130.6, 129.0, 128.4, 127.8, 126.7, 126.2, 126.0, 124.9, 122.8, 121.6, 120.4, 106.7, 89.7, 55.8, 36.0, 21.7, 17.9. HRMS (ESI) calcd for $C_{28}H_{25}BrNO$ $[M+H]^+$ 470.1120, found 470.1115.

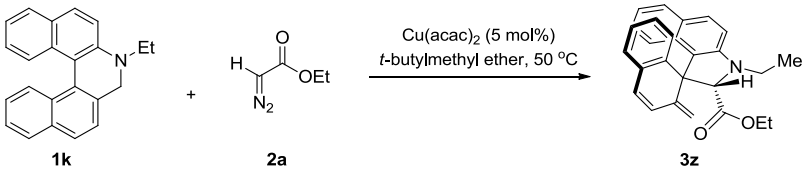
Compound **3y** was prepared following the **Typical Procedure E**



1i 2b 3y

The reaction of **1i** (29.5 mg, 0.10 mmol) and **2b** (20.0 mg, 0.20 mmol, 2.0 equiv) in MTBE (2.0 mL) afforded **3y** (29.6 mg, 81%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.8 Hz, 1 H), 7.73 (d, *J* = 8.0 Hz, 1 H), 7.22 – 7.15 (m, 2 H), 7.15 – 7.07 (m, 3 H), 7.07 – 6.98 (m, 2 H), 6.94 (d, *J* = 7.6 Hz, 1 H), 6.51 (d, *J* = 9.6 Hz, 1 H), 6.39 (d, *J* = 9.6 Hz, 1 H), 5.18 (s, 1 H), 4.64 (s, 1 H), 4.25 (s, 1 H), 3.64 (s, 3 H), 2.94 (s, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.2, 150.2, 142.5, 141.3, 132.4, 130.3, 129.8, 129.5, 128.8, 128.6, 128.4, 128.0, 127.1, 126.7, 126.43, 126.40, 125.7, 123.4, 122.0, 119.6, 110.9, 85.8, 57.6, 51.8, 35.8. HRMS (ESI) calcd for $C_{25}H_{22}NO_2$ $[M+H]^+$ 368.1651, found 368.1652.

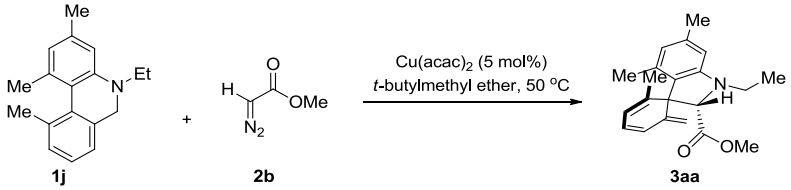
Compound **3z** was prepared following the **Typical Procedure E**



1k 2a 3z

The reaction of **1k** (30.9 mg, 0.10 mmol) and **2a** (22.8 mg, 0.20 mmol, 2.0 equiv) in MTBE (2.0 mL) afforded **3z** (27.7 mg, 70%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.8 Hz, 1 H), 7.74 – 7.67 (m, 1 H), 7.20 – 7.13 (m, 2 H), 7.12 – 7.04 (m, 3 H), 7.04 – 6.96 (m, 2 H), 6.95 – 6.89 (m, 1 H), 6.50 (d, *J* = 9.6 Hz, 1 H), 6.39 (d, *J* = 9.2 Hz, 1 H), 5.17 (s, 1 H), 4.68 (s, 1 H), 4.50 (s, 1 H), 4.09 (q, *J* = 7.2 Hz, 2 H), 3.67 (dq, *J* = 14.8, 7.2 Hz, 1 H), 3.26 (dq, *J* = 14.8, 7.2 Hz, 1 H), 1.22 – 1.11 (m, 6 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.2, 148.8, 143.1, 142.1, 132.2, 130.2, 129.7, 129.5, 128.8, 128.7, 128.5, 128.1, 127.0, 126.6, 126.4, 126.3, 123.1, 121.7, 119.8, 111.1, 81.8, 60.9, 57.4, 41.1, 13.9, 9.9. HRMS (ESI) calcd for $C_{27}H_{26}NO_2$ $[M+H]^+$ 396.1964, found 396.1959.

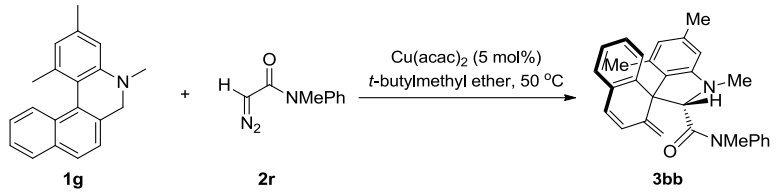
Compound **3aa** was prepared following the **Typical Procedure E**



1j 2b 3aa

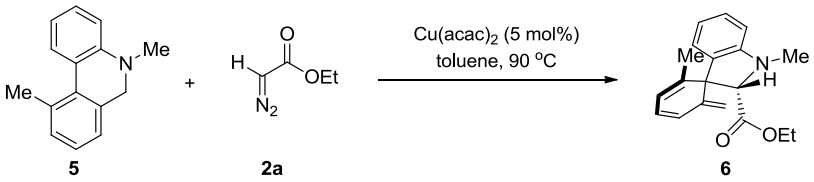
The reaction of **1j** (25.1 mg, 0.10 mmol) and **2b** (20.0 mg, 0.20 mmol, 2.0 equiv) in MTBE (2.0 mL) afforded **3aa** (22.6 mg, 70%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.31 (s, 1 H), 6.21 (s, 1 H), 6.05 (d, *J* = 9.6 Hz, 1 H), 5.91 (d, *J* = 6.0 Hz, 1 H), 5.78 (dd, *J* = 8.4, 7.2 Hz, 1 H), 5.12 (s, 1 H), 4.63 (s, 1 H), 4.37 (s, 1 H), 3.62 (s, 3 H), 3.46 (dq, *J* = 14.4, 7.2 Hz, 1 H), 3.14 (dq, *J* = 14.4, 7.2 Hz, 1 H), 2.26 (s, 3 H), 1.96 (s, 3 H), 1.67 (s, 3 H), 1.09 (t, *J* = 7.0 Hz, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.3, 150.6, 145.3, 138.33, 138.30, 134.4, 131.6, 126.3, 122.2, 121.5, 121.3, 118.8, 106.1, 74.2, 58.5, 51.8, 40.6, 21.6, 20.0, 17.8, 9.4. HRMS (ESI) calcd for $C_{21}H_{26}NO_2$ $[M+H]^+$ 324.1964, found 324.1967.

Compound **3bb** was prepared following the **Typical Procedure E**



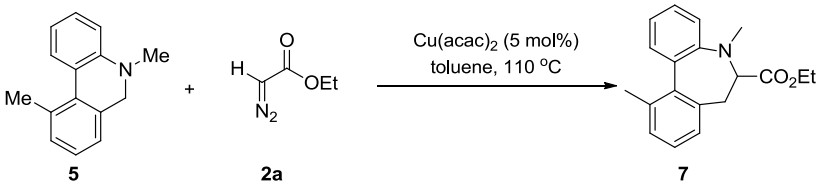
The reaction of **1g** (27.3 mg, 0.10 mmol) and **2r** (35.0 mg, 0.20 mmol, 2.0 equiv) in MTBE (2.0 mL) afforded **3bb** (38.6 mg, 92%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.14 – 7.05 (m, 2 H), 7.05 – 6.93 (m, 3 H), 6.78 (td, *J* = 7.4, 1.6 Hz, 1 H), 6.66 (d, *J* = 7.6 Hz, 1 H), 6.51 – 6.43 (m, 3 H), 6.38 (d, *J* = 9.6 Hz, 1 H), 6.35 (s, 1 H), 6.28 (s, 1 H), 5.32 (s, 1 H), 4.67 (s, 1 H), 4.13 (s, 1 H), 3.17 (s, 3 H), 2.72 (s, 3 H), 2.27 (s, 3 H), 1.54 (s, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.7, 153.0, 143.2, 141.3, 139.7, 138.2, 134.6, 133.3, 130.5, 130.1, 129.1, 128.2, 127.6, 127.0, 126.7, 126.6, 126.1, 125.0, 122.8, 119.9, 106.4, 79.3, 58.1, 38.4, 34.4, 21.6, 19.0. HRMS (ESI) calcd for $C_{29}H_{29}N_2O$ $[M+H]^+$ 421.2280, found 421.2276.

Compound **6** was prepared following the **Typical Procedure E**



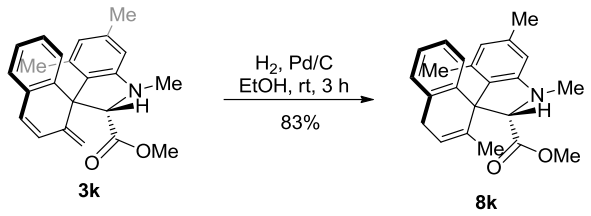
The reaction of **5** (20.9 mg, 0.10 mmol) and **2a** (22.8 mg, 0.20 mmol, 2.0 equiv) in toluene (2.0 mL) afforded **6** (7.3 mg, 25%) at 90 °C for 24 h. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.15 (td, *J* = 7.6, 1.2 Hz, 1 H), 6.86 (dd, *J* = 7.4, 0.8 Hz, 1 H), 6.74 (td, *J* = 7.2, 1.8 Hz, 1 H), 6.58 (d, *J* = 7.6 Hz, 1 H), 6.05- 5.94 (m, 2 H), 5.86 – 5.75 (m, 1 H), 5.13 (s, 1 H), 4.78 (s, 1 H), 4.20 – 4.03 (m, 2 H), 4.12 (s, 1 H), 2.82 (s, 3 H), 1.72 (s, 3 H), 1.22 (t, *J* = 7.2 Hz, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.2, 151.8, 146.0, 137.8, 136.1, 128.3, 126.1, 124.7, 122.3, 122.2, 119.4, 119.2, 107.9, 77.6, 60.9, 59.0, 35.0, 20.4, 14.0. HRMS (ESI) calcd for $C_{19}H_{22}NO_2$ $[M+H]^+$ 296.1651, found 296.1654.

Compound **7** was prepared following the **Typical Procedure E**



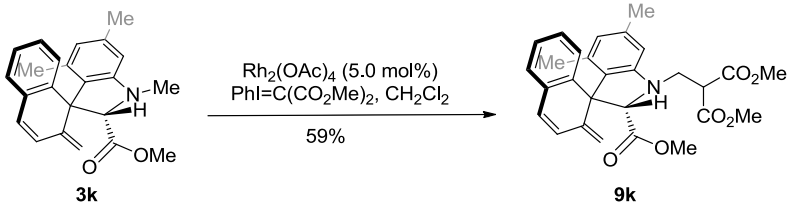
The reaction of **5** (20.9 mg, 0.10 mmol) and **2a** (22.8 mg, 0.20 mmol, 2.0 equiv) in toluene (2.0 mL) afforded **7** (9.9 mg, 33%, a pair of diastereomers) at 110 °C for 24 h. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33 (td, *J* = 7.6, 1.6 Hz, 1 H), 7.30 – 7.27 (m, 1 H), 7.25 – 7.16 (m, 3 H), 7.15 – 7.08 (m, 2 H), 4.27 – 4.18 (m, 1 H), 4.18 – 4.13 (m, 1 H), 4.13 – 4.07 (m, 1 H), 2.84 – 2.75 (m, 5 H), 2.33 (s, 3 H), 1.29 (t, *J* = 7.0 Hz, 3 H). HRMS (ESI) calcd for $C_{19}H_{22}NO_2$ $[M+H]^+$ 296.1651, found 296.1657.

Synthesis of compound **8k**



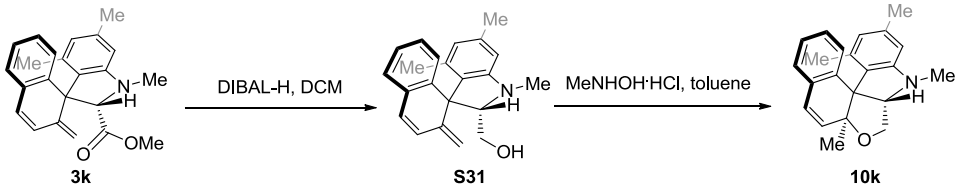
A 25 mL flask containing a mixture of **3k** (172.7 mg, 0.5 mmol, 1.0 equiv), K_2CO_3 (69 mg, 0.5 mmol, 1.0 equiv), 10% Pd/C (75 mg) in EtOH (10 mL) was purged with H_2 and stirred at rt for 15 min with a hydrogen balloon. The mixture was filtered through a pad of celite, washed with EtOAc and the filtrate was removed by evaporation, and the resulting mixture was purified by column chromatography on silica gel (hexanes/ethyl acetate = 20 :1) to afford the desired product **8k** (145 mg, 83%) as a white solid. The single crystal was obtained by slow volatilization of a saturation solution of **8k** in mixed solvent DCM/PE. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.21 – 7.09 (m, 3 H), 7.05 (d, *J* = 7.6 Hz, 1 H), 6.37 (s, 1 H), 6.34 (s, 1 H), 5.83 (s, 1 H), 4.20 (s, 1 H), 3.64 (s, 3 H), 3.39 (s, 2 H), 2.80 (s, 3 H), 2.31 (s, 3 H), 1.52 (s, 3 H), 1.51 (s, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.7, 152.6, 141.4, 138.4, 134.7, 134.1, 133.4, 128.4, 128.1, 127.4, 126.5, 125.9, 122.54, 122.53, 106.7, 84.4, 56.3, 51.8, 36.1, 30.5, 21.6, 20.6, 17.3. HRMS (ESI) calcd for $C_{23}H_{26}NO_2$ $[M+H]^+$ 348.1964, found 348.1963.

Synthesis of compound **9k**



Under argon atmosphere, **3k** (27.6 mg, 0.08 mmol, 1.0 equiv), bis(methoxycarbonyl)(phenyliodinio)methanide[11] (30.3 mg, 1.04 mmol, 1.3 equiv), $Rh_2(OAc)_4$ (1.8 mg, 0.004 mmol, 5 mol%) and DCM (1.0 mL) were added to a 25 mL Schlenk tube. The tube was capped with a screw cap and stirred at rt for 2 h. The mixture was directly purified by flash chromatography on silica gel (hexanes/ethyl acetate = 20:1) to afford **9k** (22.4 mg, 59%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.15 (t, *J* = 7.4 Hz, 1 H), 7.12 - 7.03 (m, 2 H), 6.80 (d, *J* = 7.6 Hz, 1 H), 6.41 (d, *J* = 9.6 Hz, 1 H), 6.38 – 6.28 (m, 3 H), 5.19 (s, 1 H), 4.75 (s, 1 H), 4.35 (s, 1 H), 3.97 – 3.85 (m, 2 H), 3.78 – 3.71 (m, 1 H), 3.69 (s, 3 H), 3.58 (s, 3 H), 3.57 (s, 3 H), 2.31 (s, 3 H), 1.60 (s, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.4, 168.9, 168.4, 150.4, 143.6, 140.8, 138.8, 134.9, 131.8, 130.9, 128.5, 127.9, 127.5, 126.9, 126.7, 126.2, 122.4, 118.9, 104.9, 82.9, 56.8, 52.7, 51.6, 49.5, 46.1, 21.7, 19.0. HRMS (ESI) calcd for $C_{28}H_{29}NO_6Na$ $[M+Na]^+$ 498.1893, found 498.1894.

Synthesis of compound **10k**



To a solution of **3k** (0.207 g, 0.60 mmol, 1.0 equiv) in anhydrous DCM (10.0 mL) was added DIBAL-H (1 M in toluene, 3.0 mL, 3.0 mmol, 5.0 equiv) dropwise at - 78 ^{o} C. After stirring for 3 h at -78 ^{o}C, MeOH (3.0 mL) was added dropwise and the reaction mixture was allowed to warm to room temperature. The reaction mixture was added saturated aqueous potassium sodium tartrate (30 mL) and stirred for additional 2 h, followed by extraction with DCM (30 mL x 3). The combined organic phase was washed with brine (30 mL) and dried over Na_2SO_4. After filtration, the solvent was removed by evaporation, and the resulting mixture was purified by column chromatography on silica gel (hexanes/ethyl acetate = 10 :1) to afford **S31** (0.143 g, 75%) as a light yellow foam. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.18 – 7.10 (m, 2 H), 7.08 (d, *J* = 7.6 Hz, 2 H), 6.48 (d, *J* = 10.8 Hz, 2 H), 6.43 (s, 1 H), 6.37 (s, 1 H), 5.19 (s, 1 H), 4.59 (s, 1 H), 3.89 (s, 2 H), 3.34 (t, *J* = 5.0 Hz, 1 H), 2.82 (s, 3 H), 2.34 (s, 3 H), 1.81 (bs, 1 H), 1.61 (s, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 154.2, 143.0, 142.3, 138.4, 134.5, 132.2, 131.8, 129.2, 128.7, 128.1, 126.9, 126.7, 126.6, 123.1, 118.5, 106.9, 83.7, 61.4, 55.7, 35.4, 21.7, 18.9. HRMS (ESI) calcd for $C_{22}H_{24}NO$ $[M+H]^+$ 318.1858, found 318.1861.

A mixture of **S31** (15.9 mg, 0.05 mmol) and MeNHOH·HCl (8.4 mg, 0.10 mmol, 2.0 equiv) in toluene (1 mL) was heated at 110 ^{o}C for 20 h. The mixture was cooled to room temperature and directly purified by column chromatography on silica gel (hexanes/ethyl acetate = 10 :1) to afford the desired product **10k** (9.0 mg, 57%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.17 – 7.09 (m, 2 H), 7.07 (dd, *J* = 7.2, 1.2 Hz, 1 H), 6.98 (d, *J* = 7.2 Hz, 1 H), 6.52 (d, *J* = 10.0 Hz, 1 H), 6.29 (s, 1 H), 6.23 (s, 1 H), 5.77 (d, *J* = 10.0 Hz, 1 H), 4.04 (d, *J* = 3.2 Hz, 1 H), 3.98 (d, *J* = 10.0 Hz, 1 H), 3.63 (dd, *J* = 9.6, 3.4 Hz, 1 H), 2.83 (s, 3 H), 2.29 (s, 3 H), 1.54 (s, 3 H), 1.15 (s, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 153.8, 139.4, 138.5, 134.6, 130.9, 130.6, 129.7, 128.3, 128.0, 126.9, 126.7, 126.4, 121.7, 105.7, 88.2, 83.9, 67.6, 61.6, 35.2, 25.9, 21.6, 18.9. HRMS (ESI) calcd for $C_{22}H_{24}NO$ $[M+H]^+$ 318.1858, found 318.1858.

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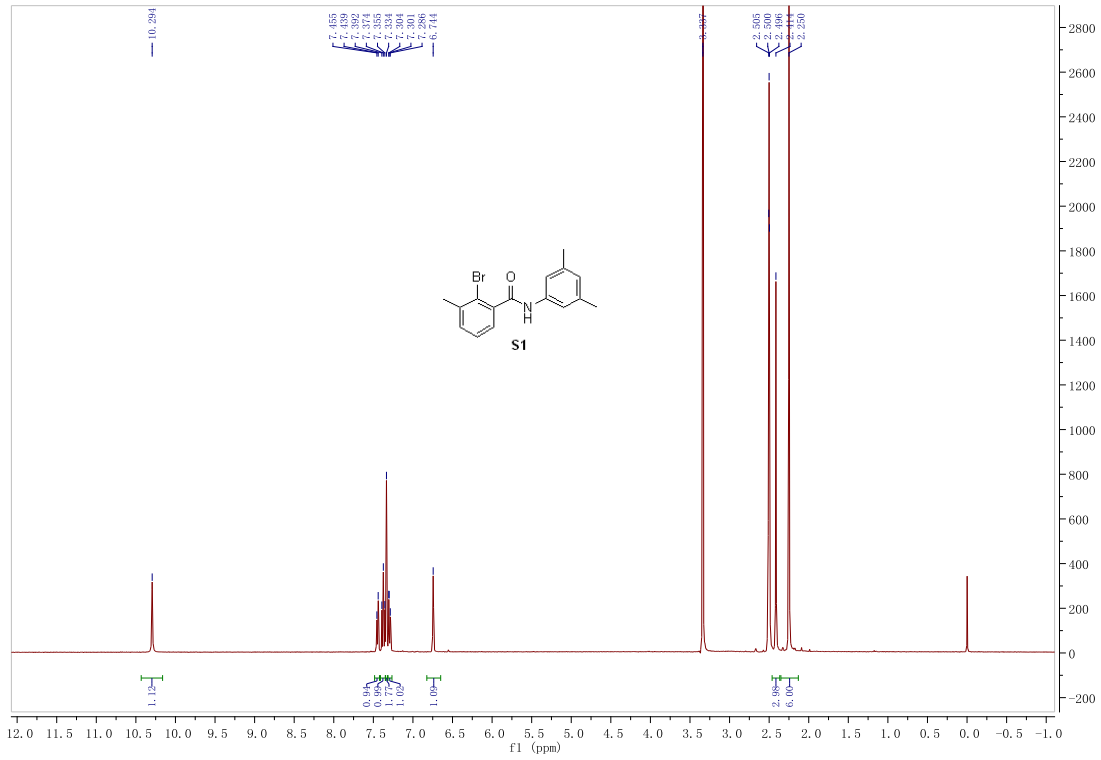
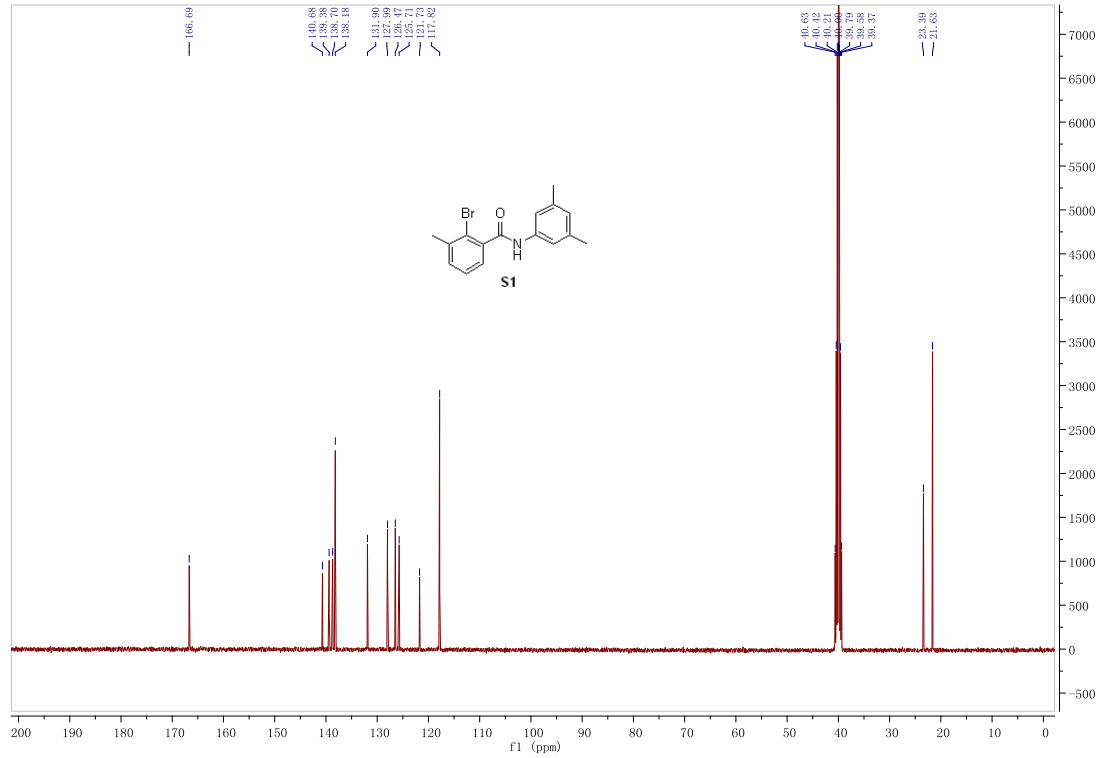
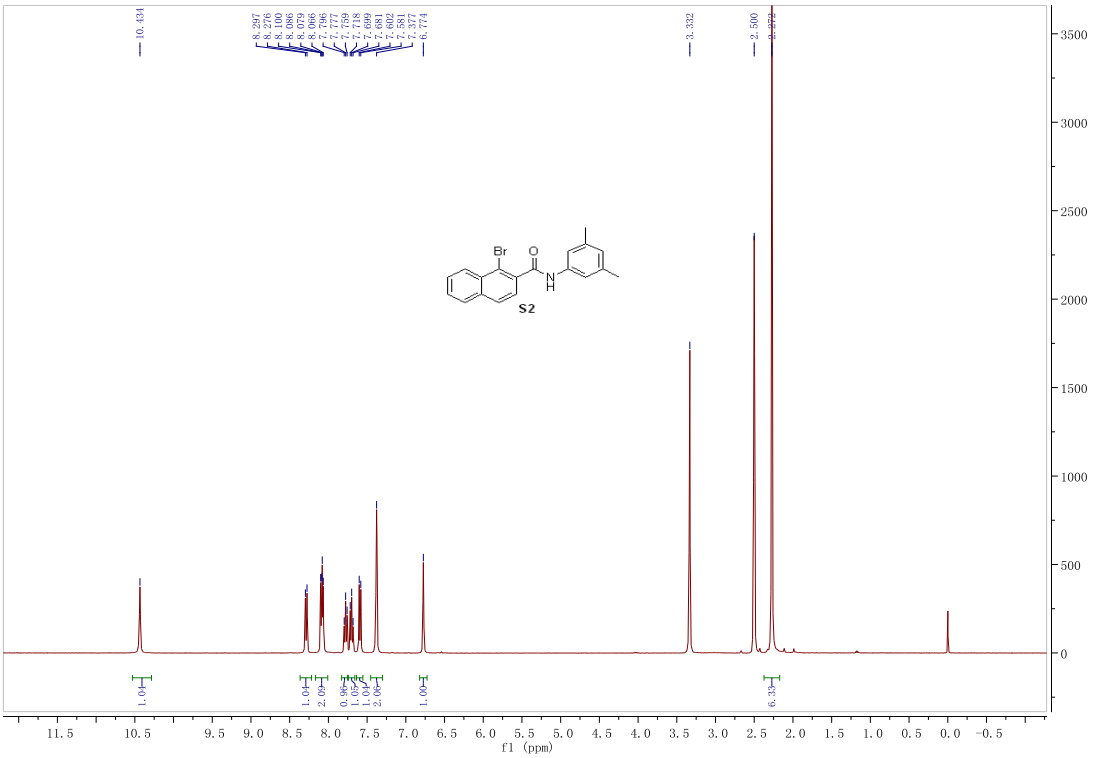
Copies of NMR Spectroscopies



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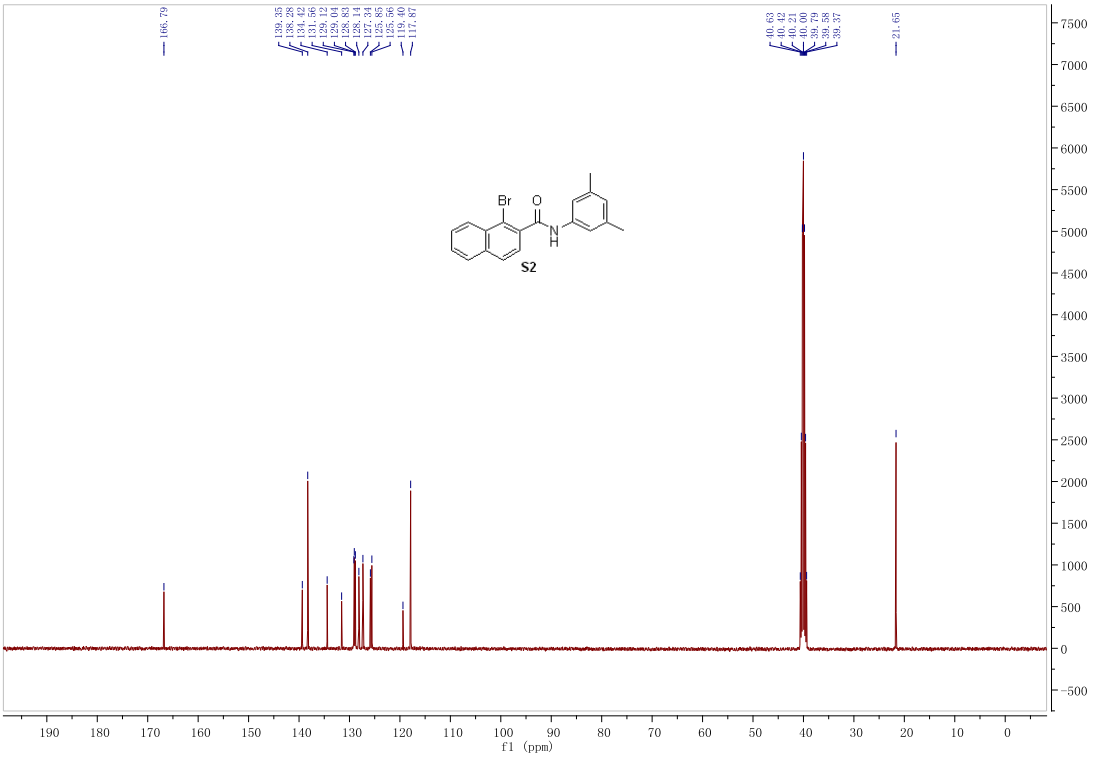
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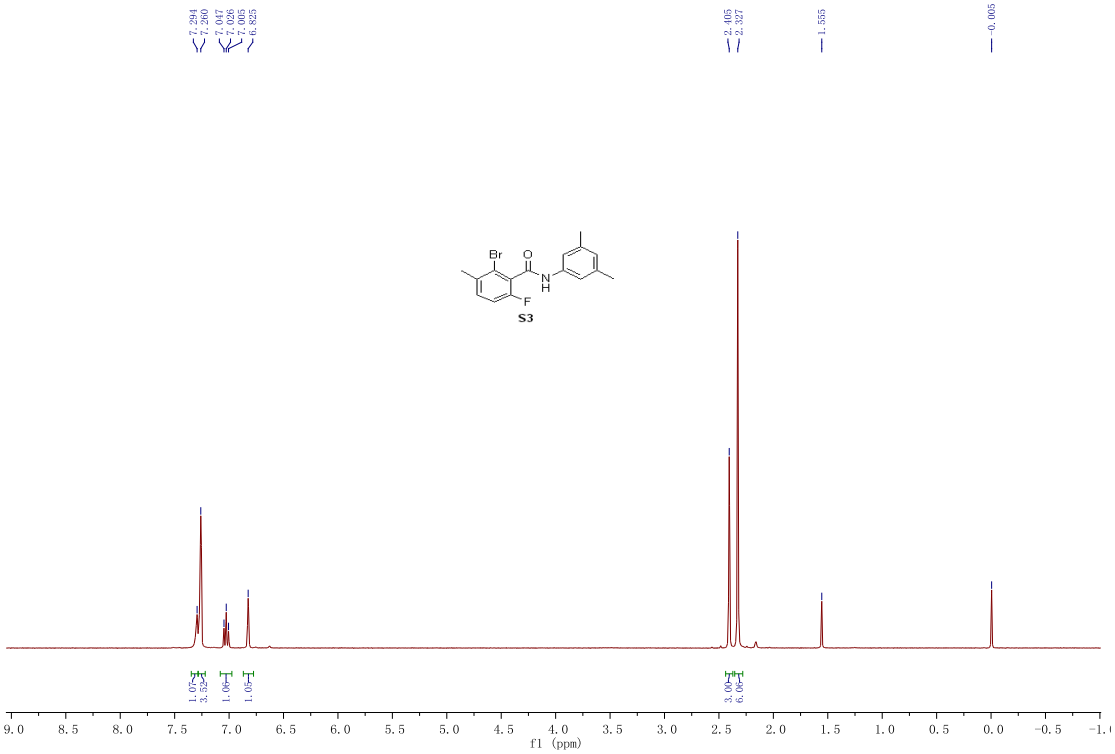
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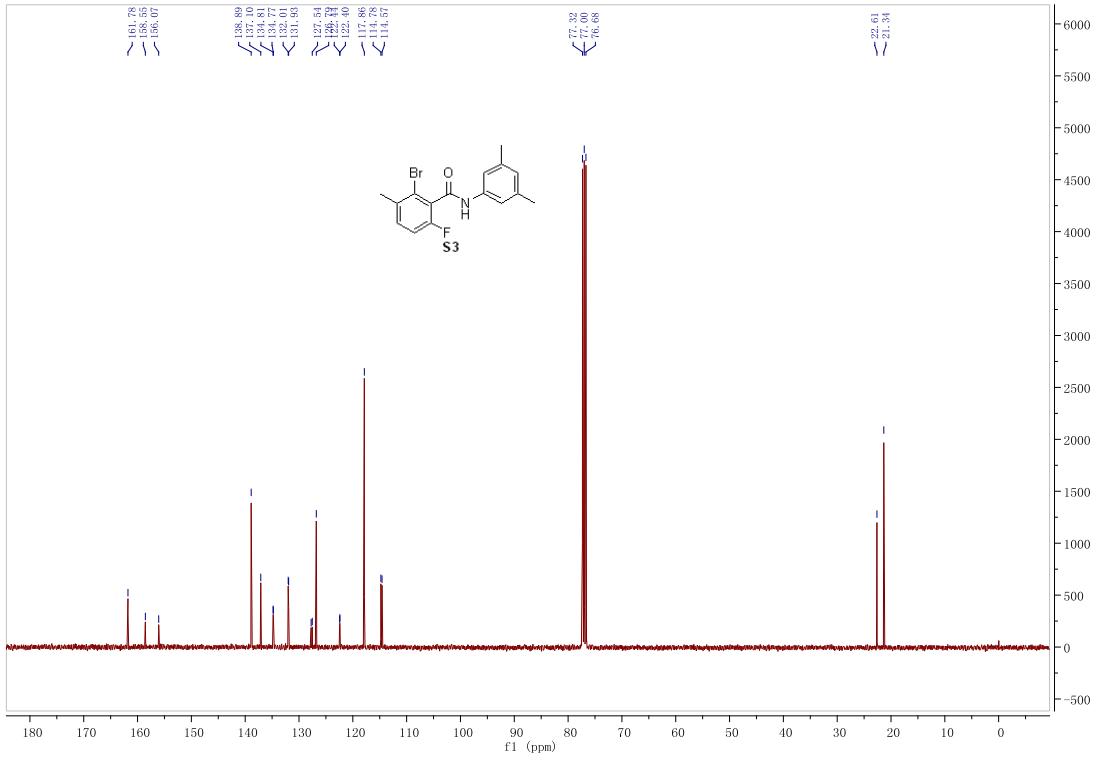
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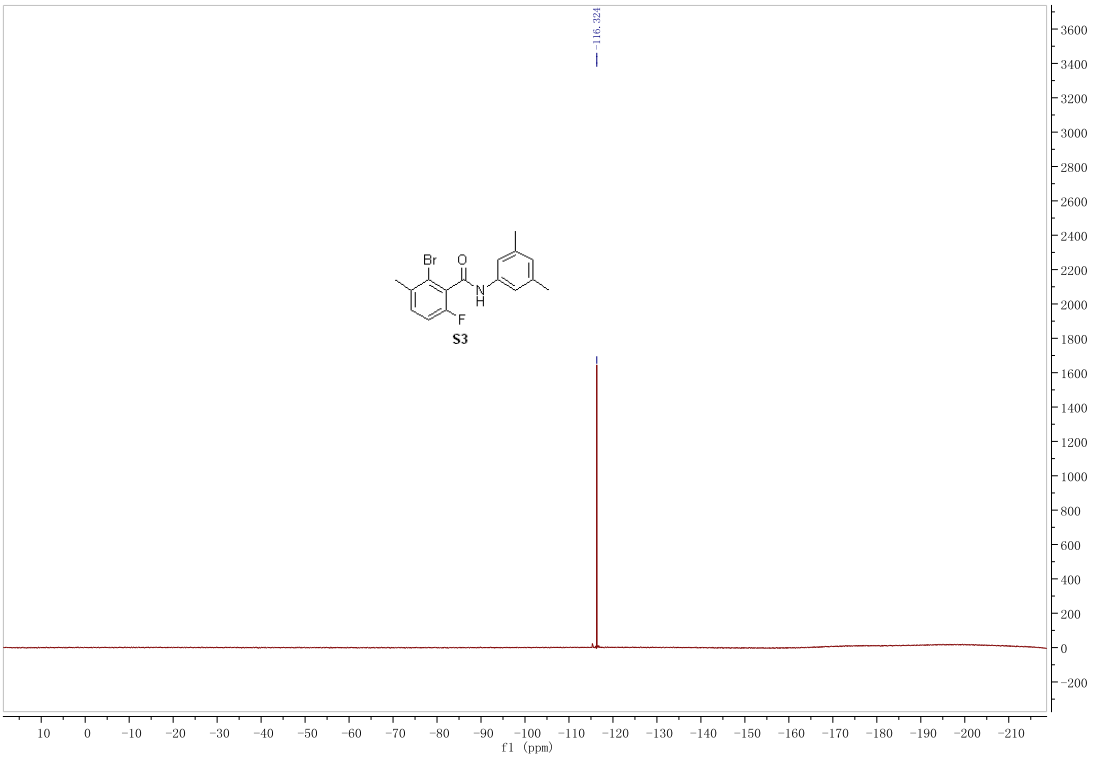
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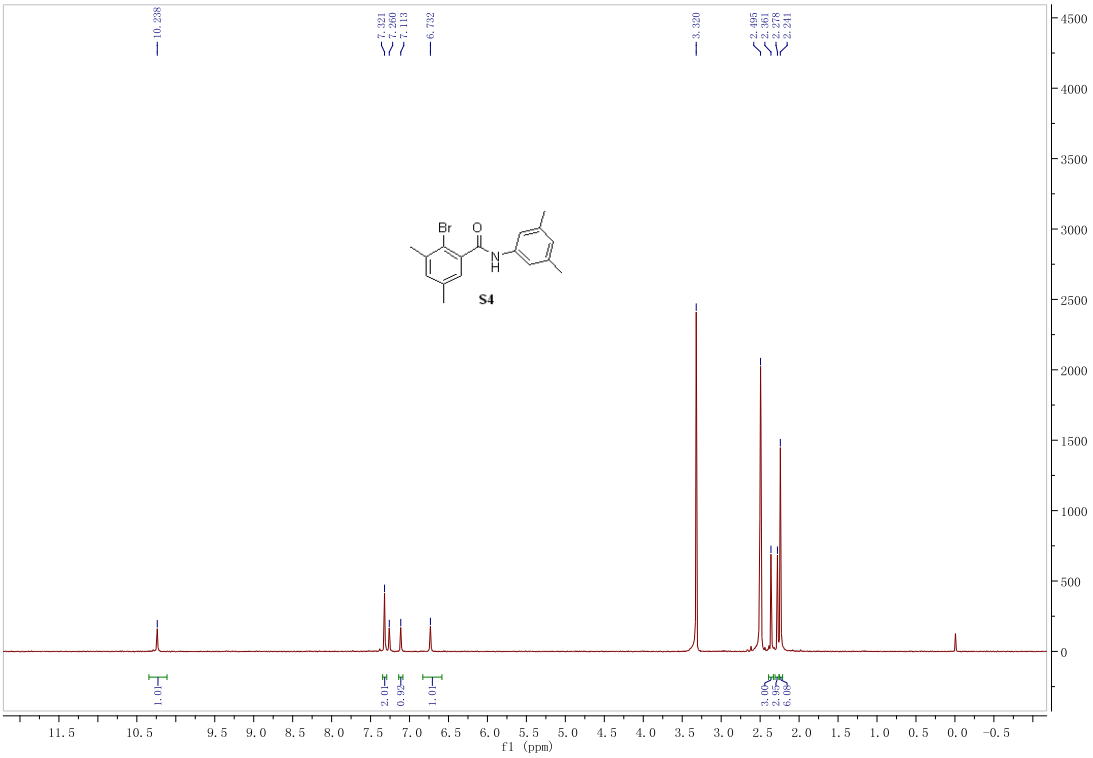
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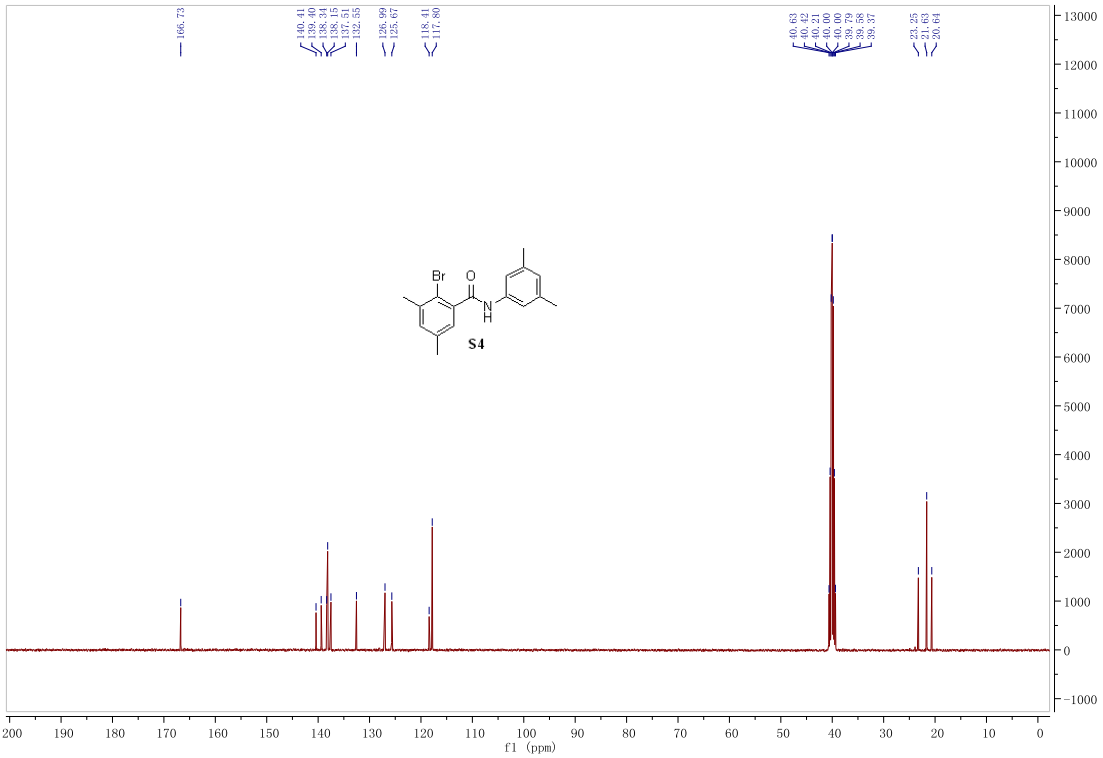
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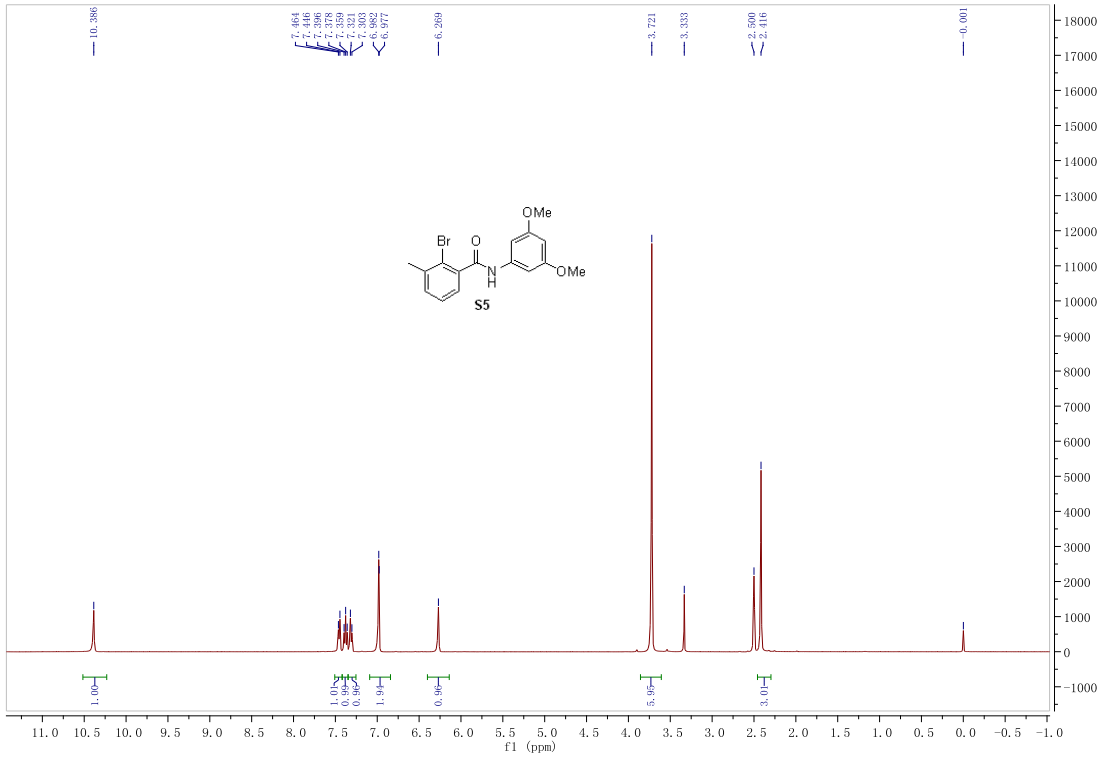
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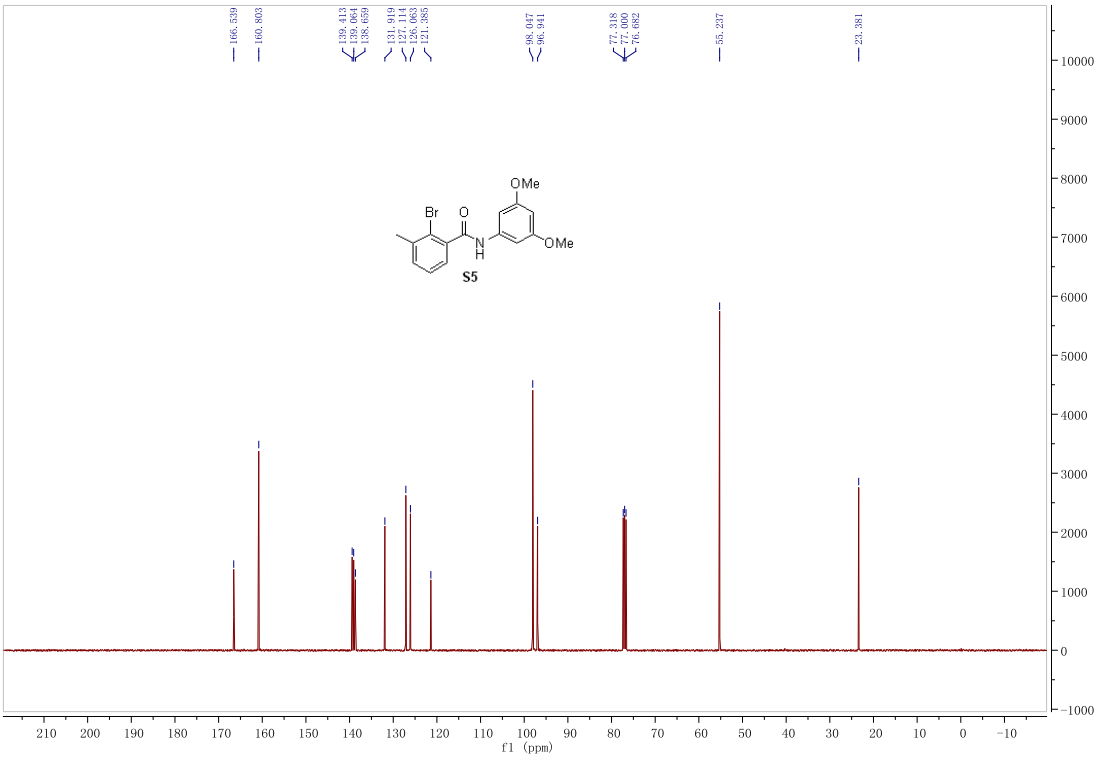
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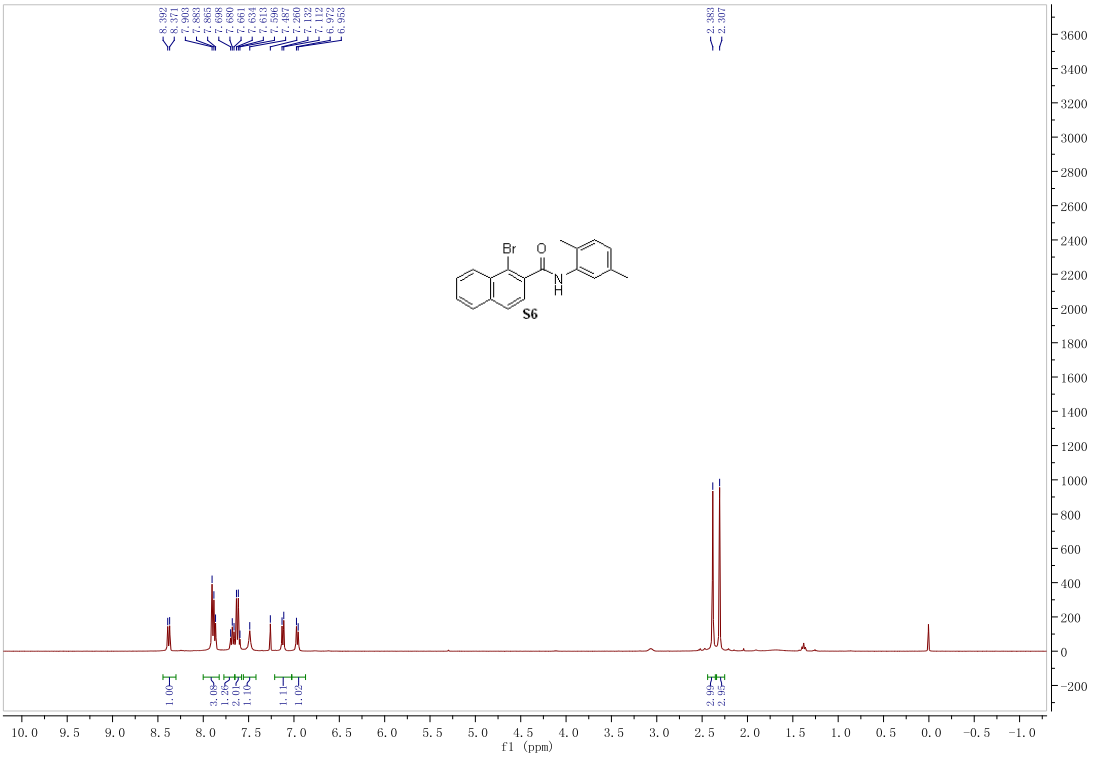
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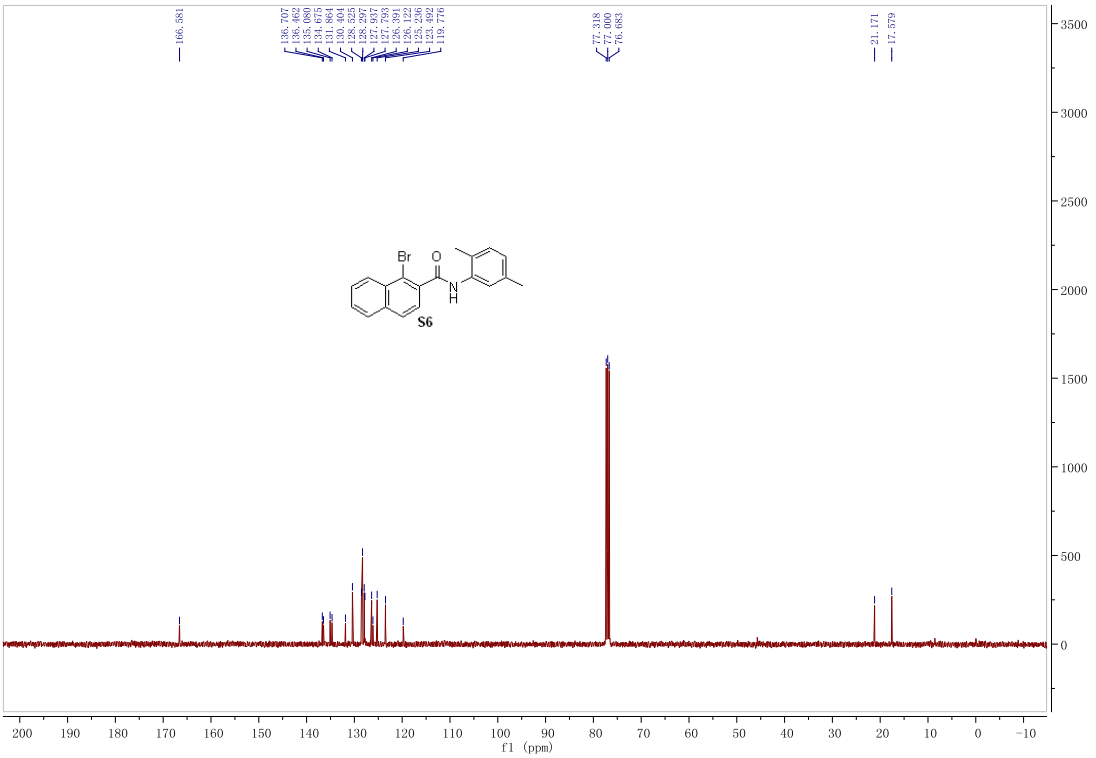
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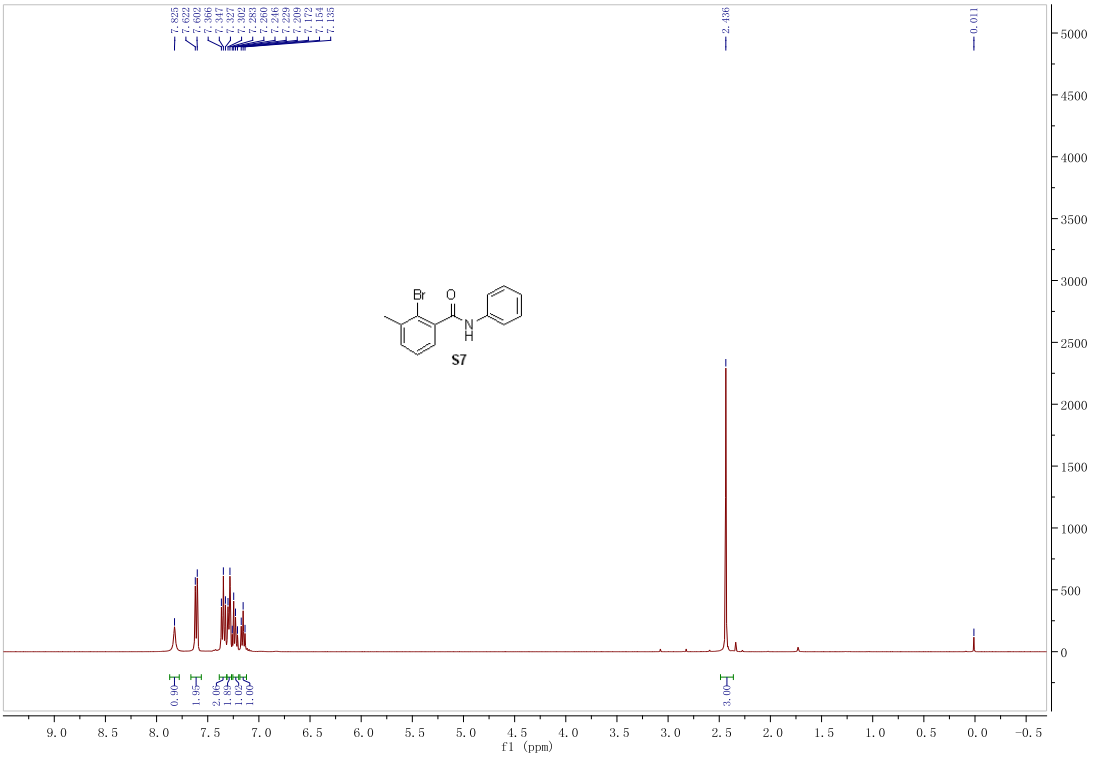
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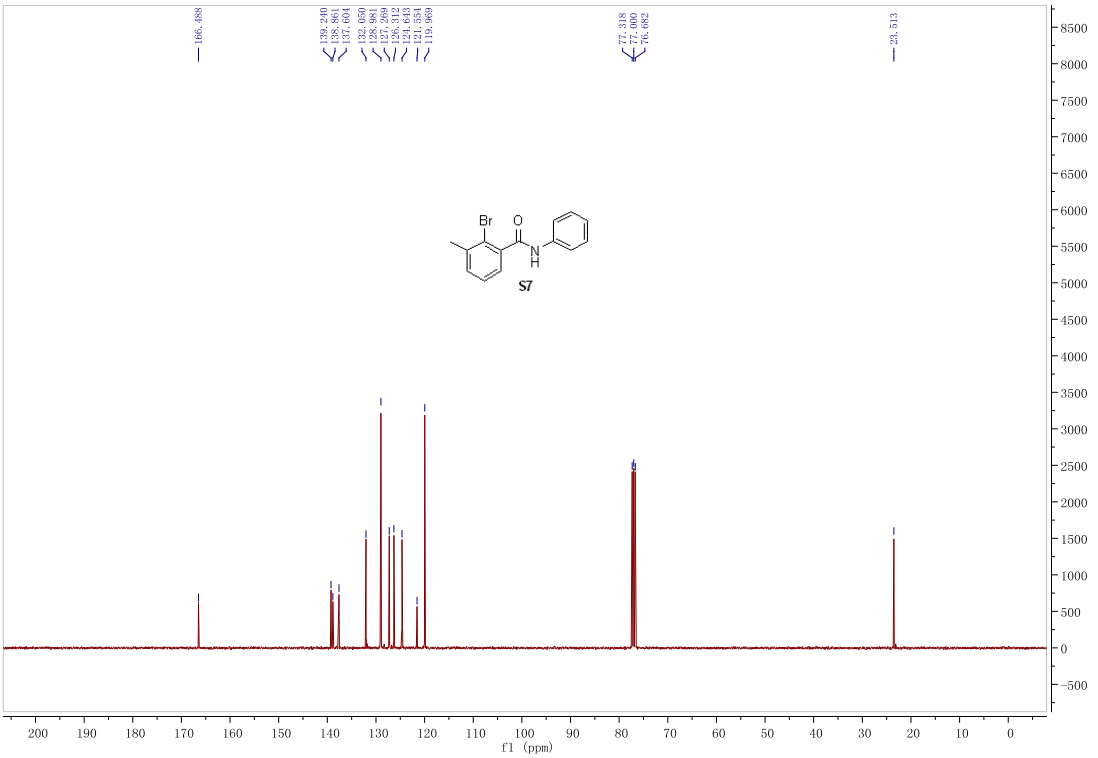
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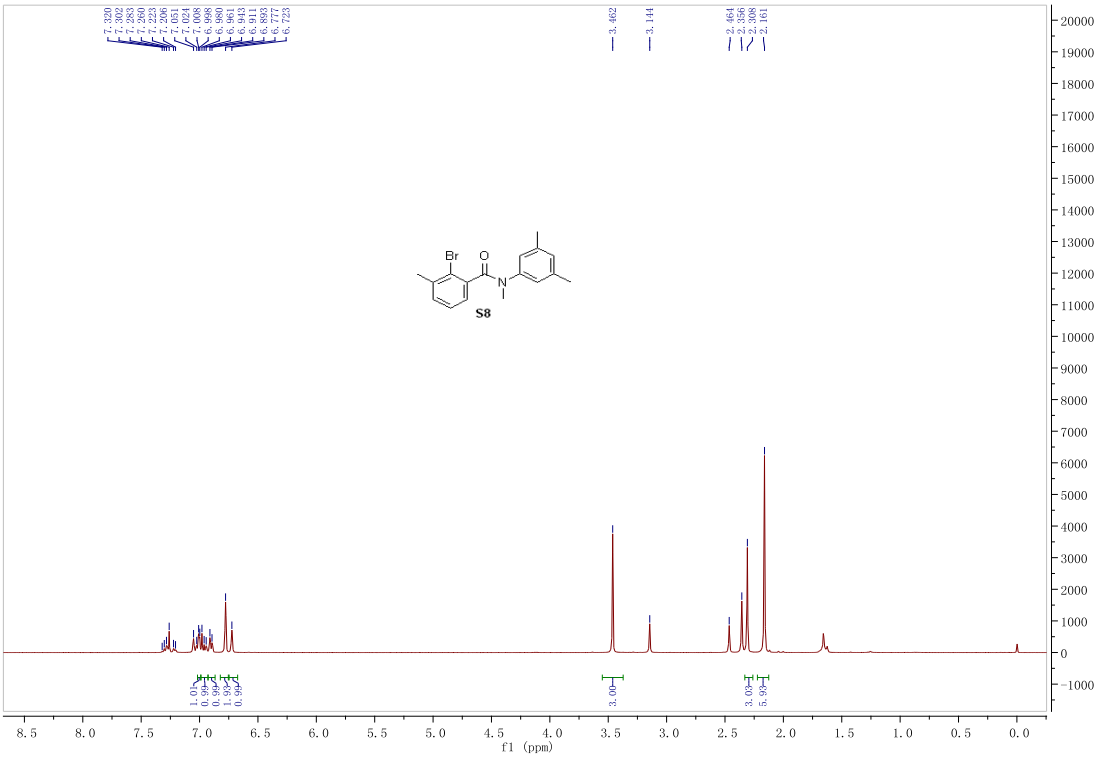
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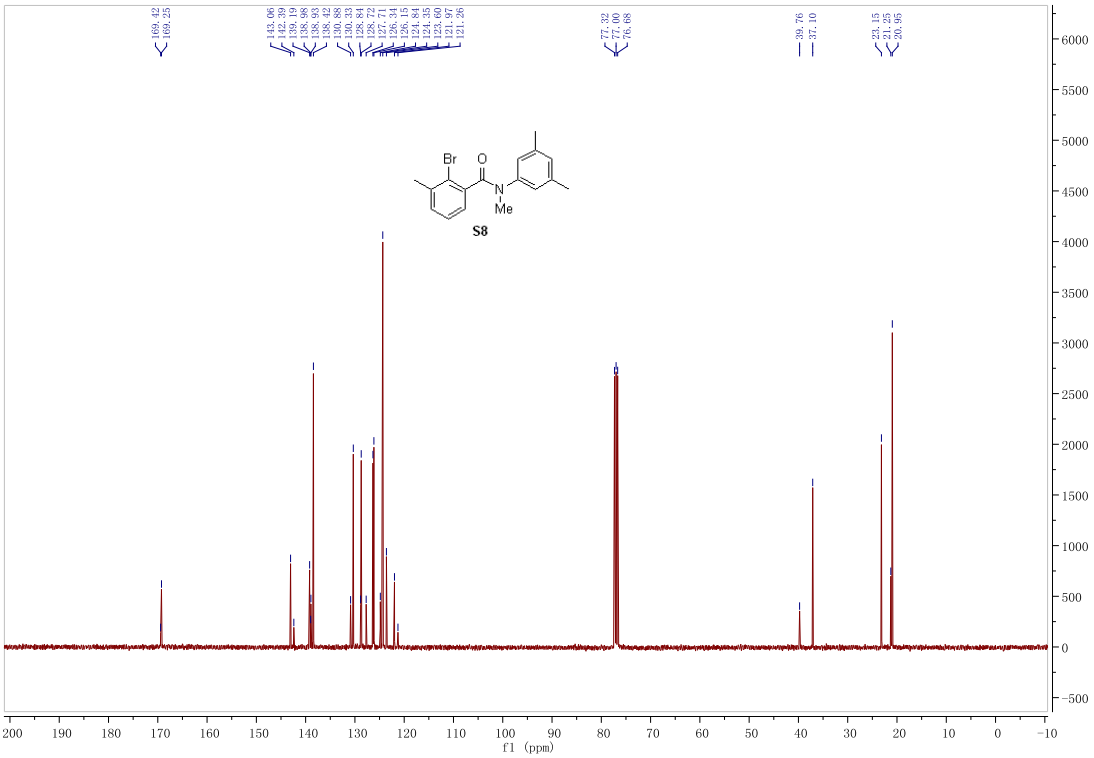
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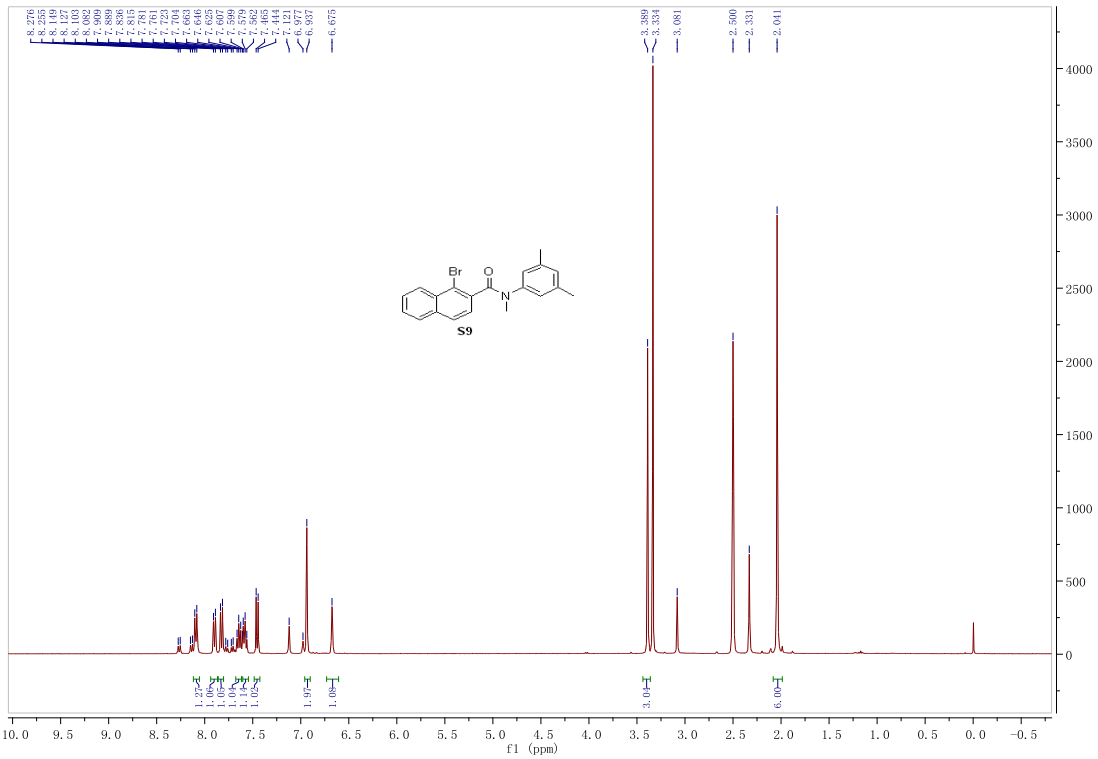
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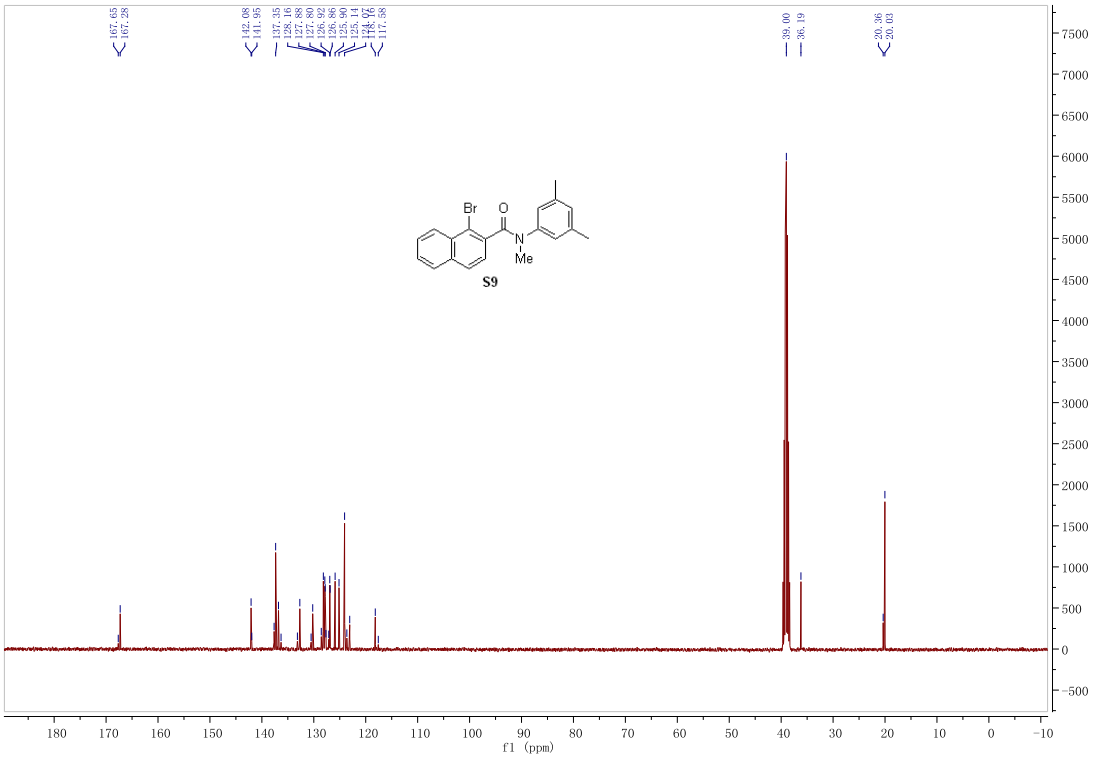
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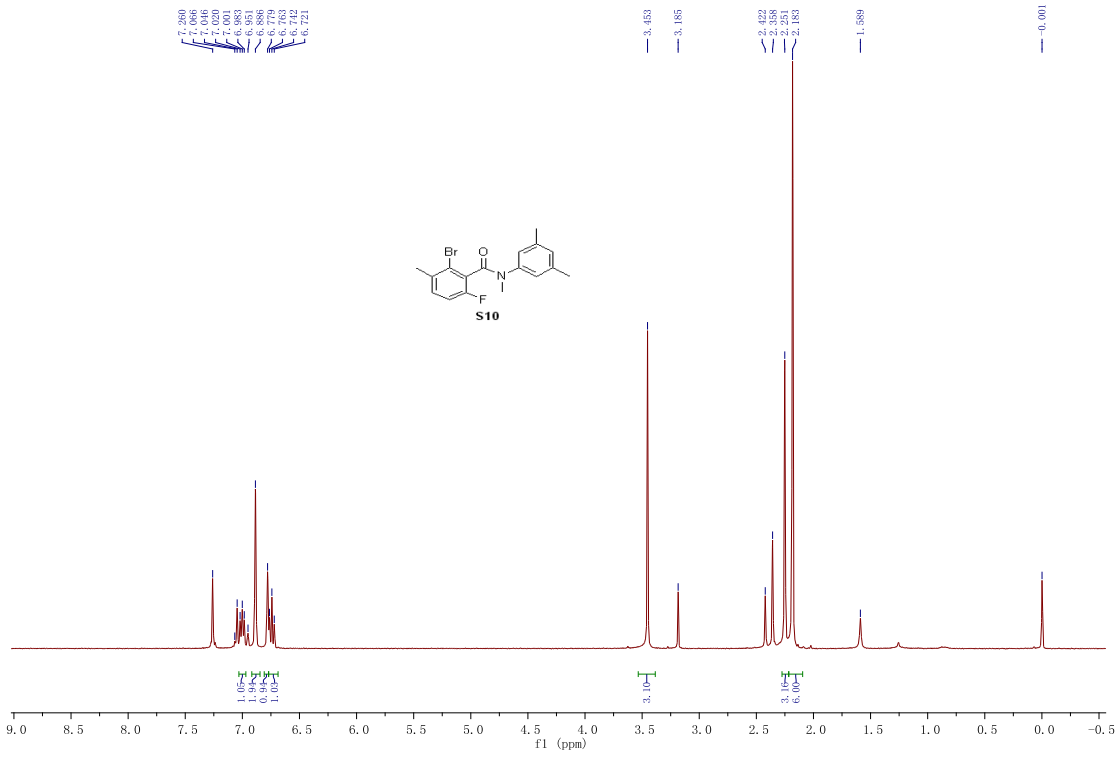
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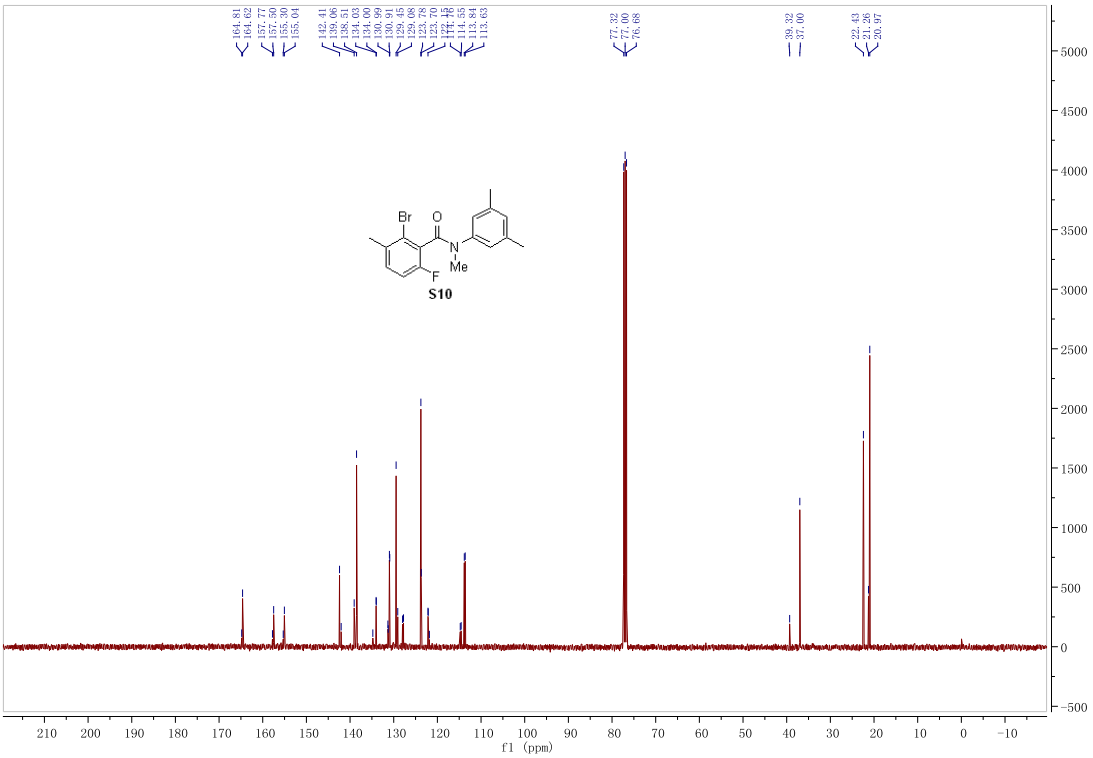
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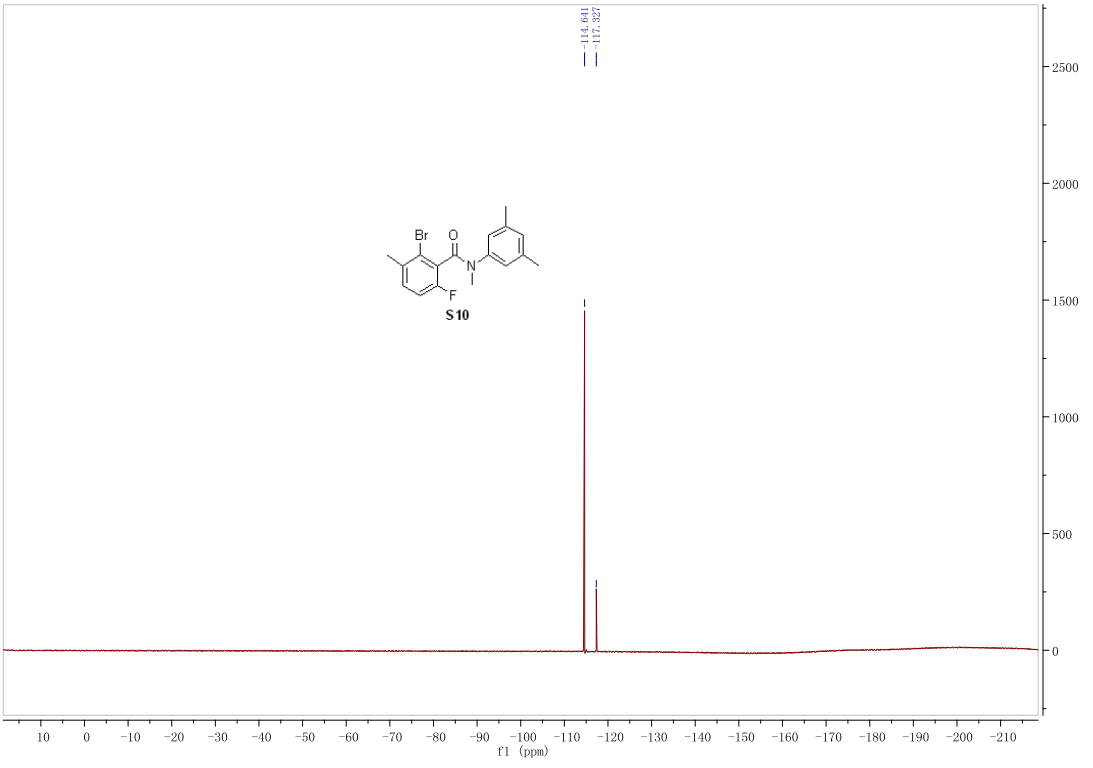
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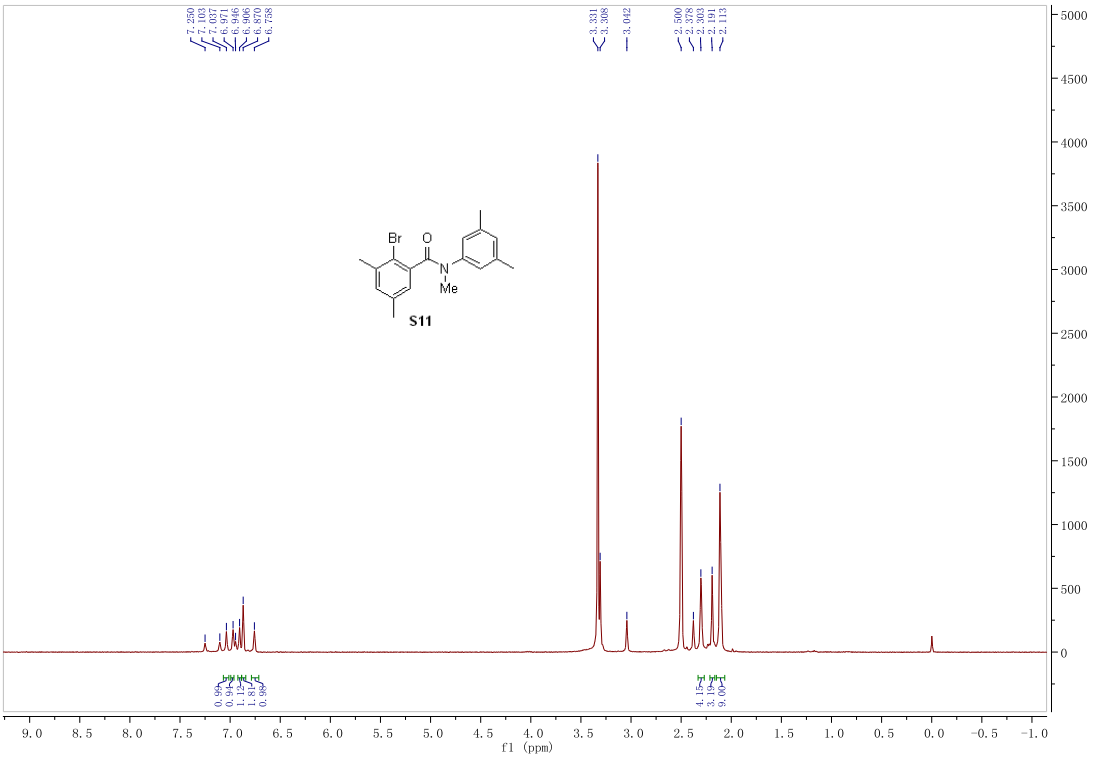
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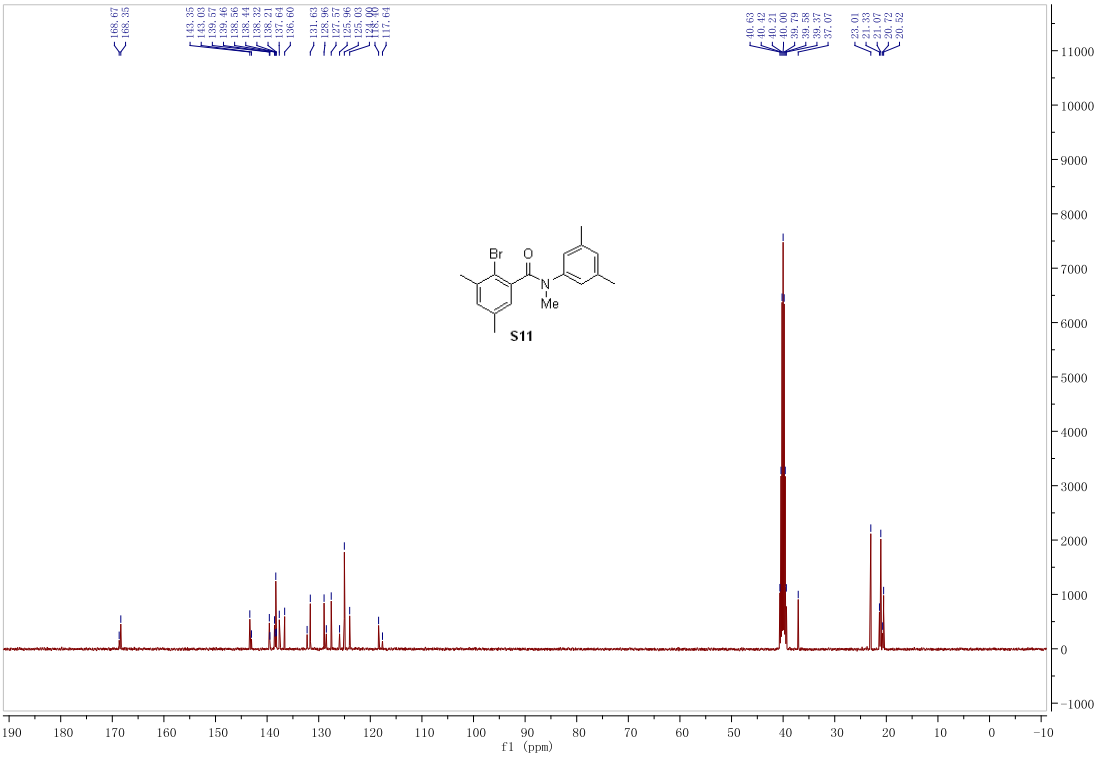
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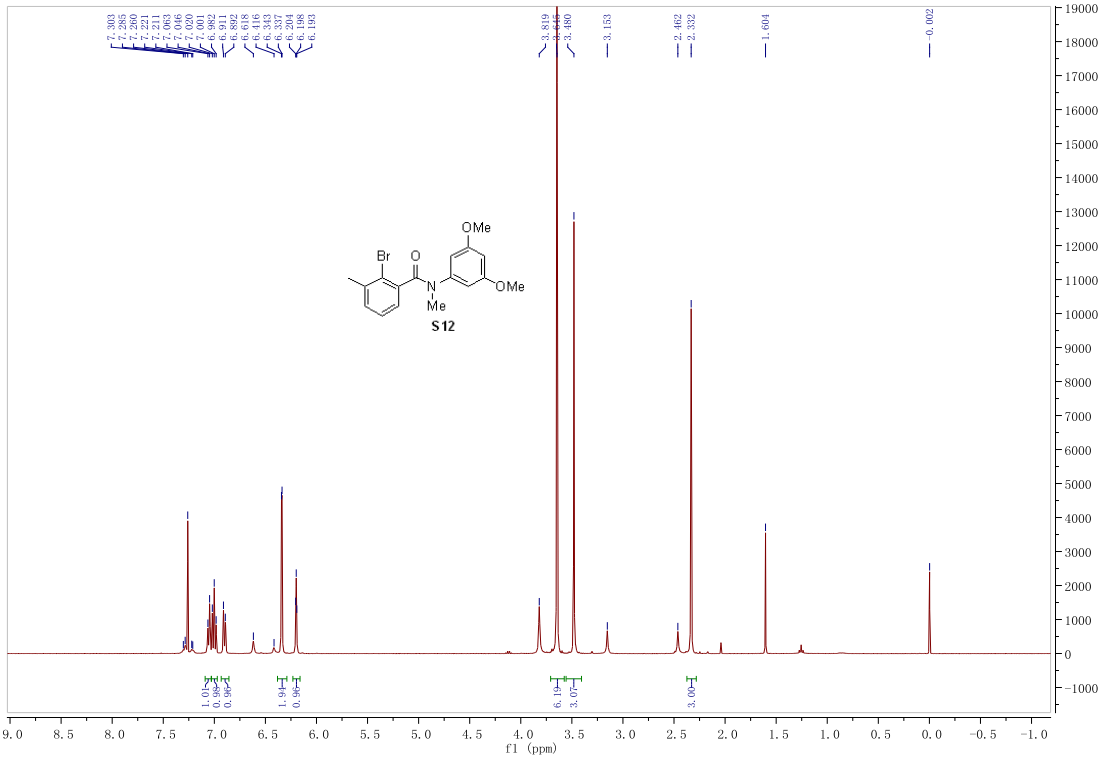
S11
f1 (ppm)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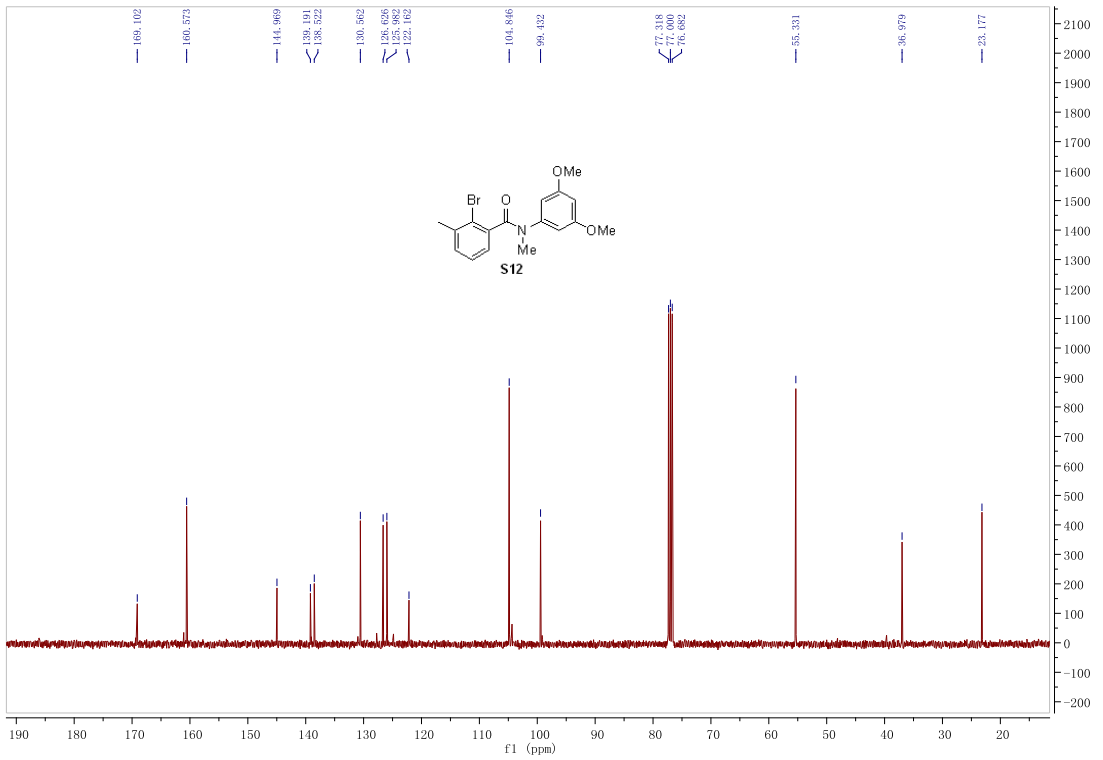
7.285
7.260
7.221
7.211
7.063
7.046
7.000
7.001
6.982
6.911
6.892
6.658
6.416
6.343
6.337
6.304
6.198
6.193
3.819
3.446
3.380
3.153
2.462
2.332
1.604
-0.002
OMe
Br
O
N
Me
OMe
S12
1.01
0.98
0.96
1.94
0.96
6.19
3.07
3.00
f1 (ppm)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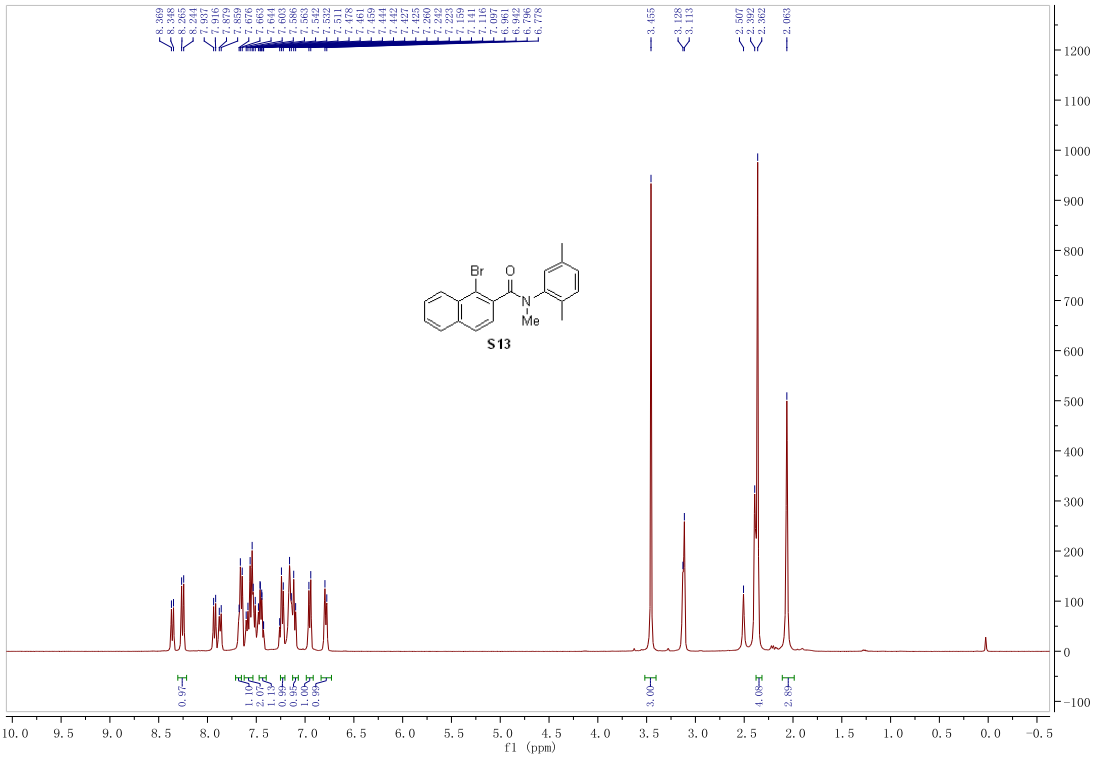
144.969
139.191
138.522
130.562
126.626
125.982
122.162
104.846
99.432
77.318
77.000
76.682
55.331
36.979
23.177
OMe
Br
O
N
Me
OMe
S12
f1 (ppm)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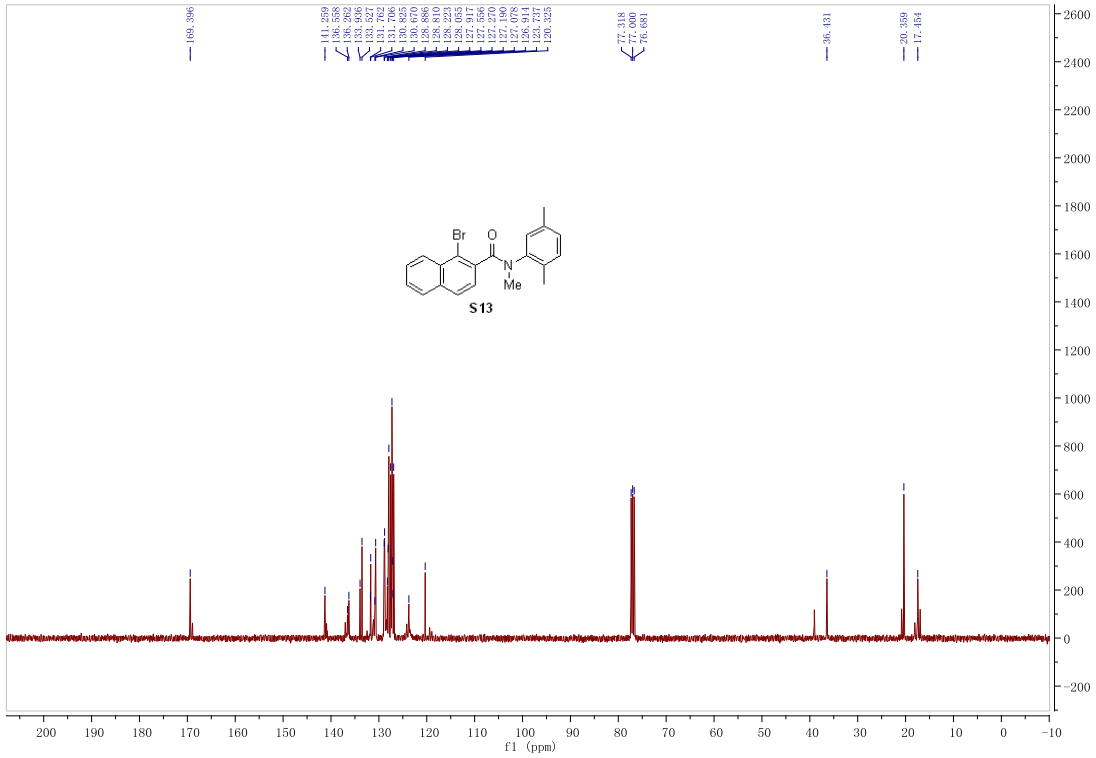
8.265
8.244
8.097
7.916
7.879
7.859
7.676
7.653
7.644
7.603
7.586
7.563
7.552
7.532
7.511
7.478
7.461
7.459
7.444
7.442
7.427
7.425
7.260
7.242
7.223
7.159
7.141
7.116
7.097
6.961
6.942
6.796
6.778
3.455
3.128
3.113
2.507
2.392
2.382
2.063
Br
O
N
Me
S13
0.97
1.10
2.07
2.13
0.99
0.95
1.06
0.98
3.00
4.08
2.89
f1 (ppm)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136.558
136.262
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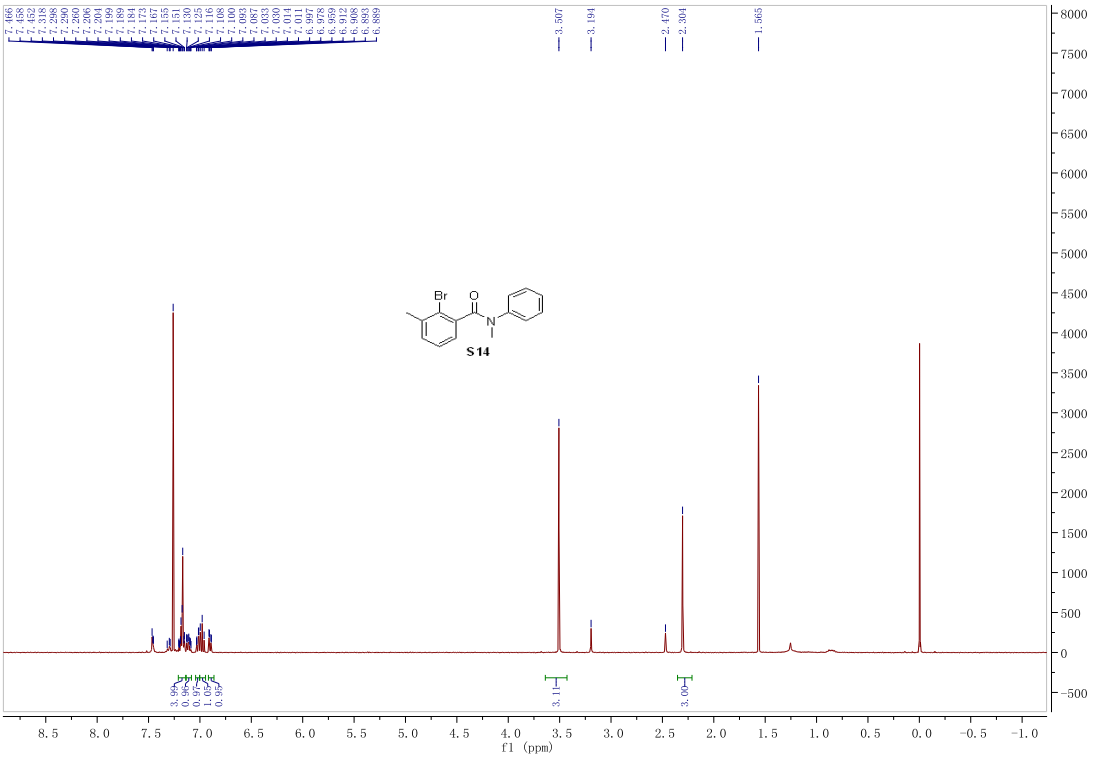
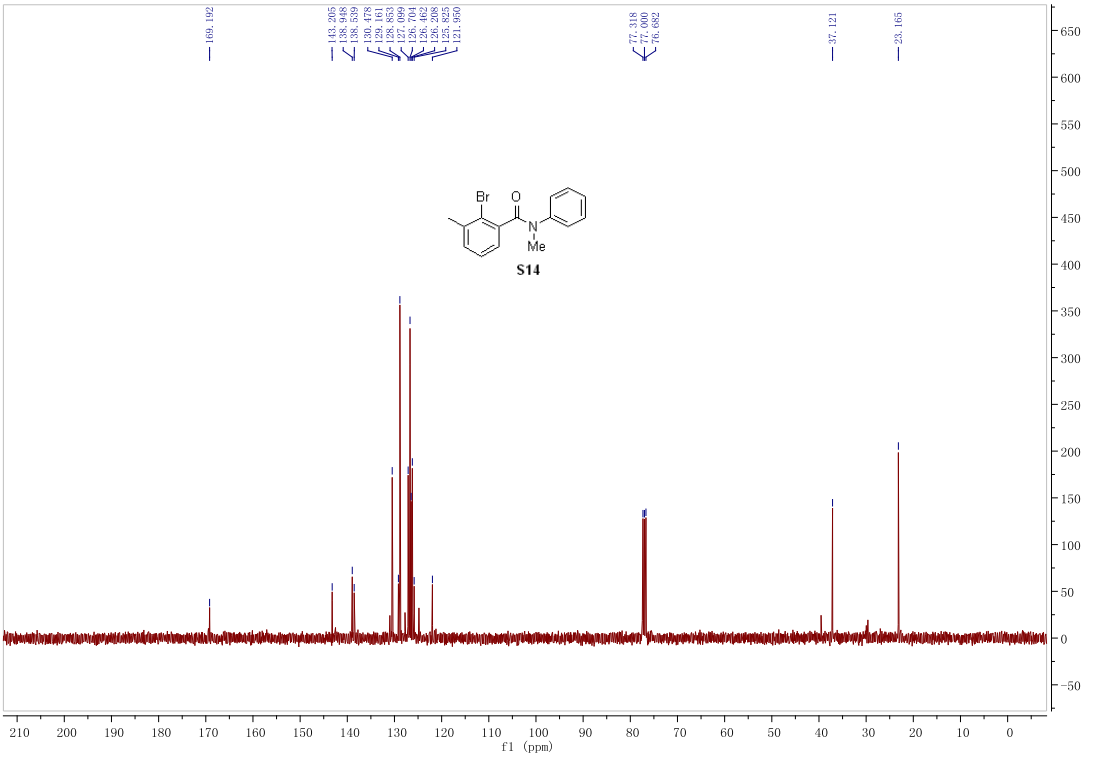
133.327
131.762
131.706
130.825
130.677
128.886
128.810
128.223
128.055
127.617
127.556
127.270
127.190
127.078
126.944
123.737
120.325
77.318
77.000
76.681
36.431
20.359
17.454
Br
O
N
Me
S13
f1 (ppm)


7.466
7.458
7.452
7.318
7.298
7.290
7.209
7.206
7.204
7.199
7.189
7.184
7.173
7.167
7.155
7.151
7.139
7.135
7.116
7.108
7.100
7.093
7.087
7.033
7.030
7.014
7.011
6.997
6.978
6.959
6.912
6.908
6.893
6.889
3.507
3.194
2.470
2.304
1.565
Br
O
N
S14
3.99
0.96
0.97
1.09
0.99
3.11
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 -0.5 -1.0
f1 (ppm)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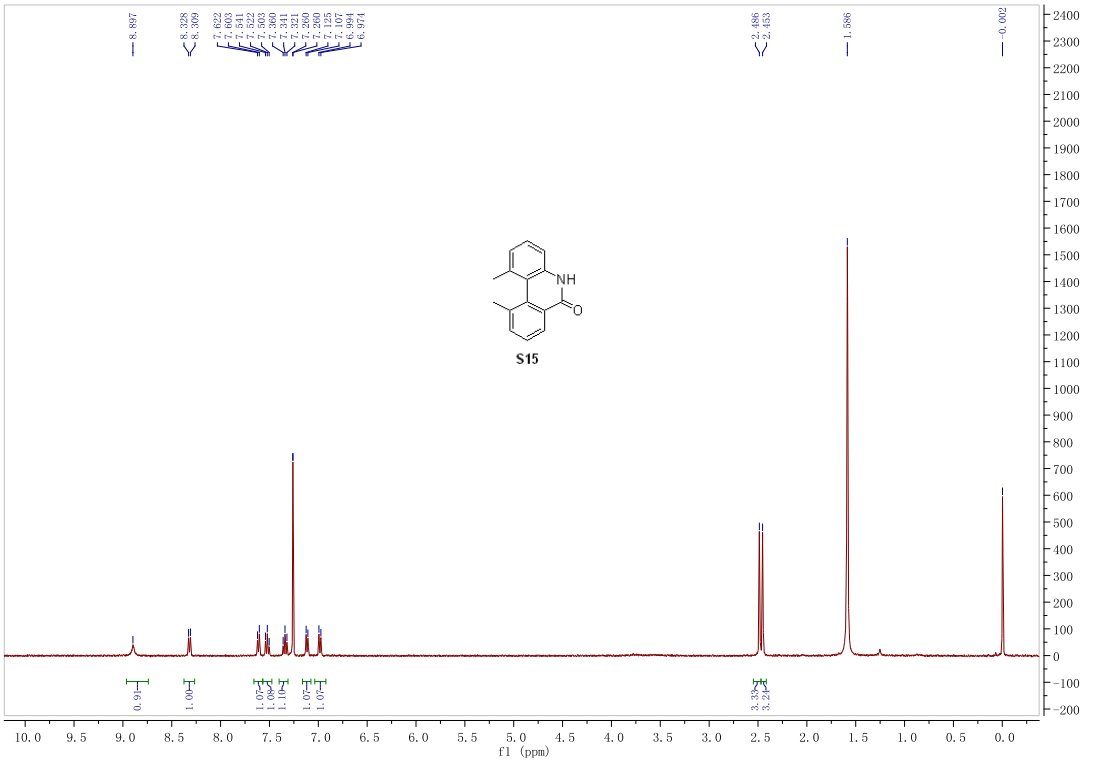
143.205
138.948
138.539
130.478
129.161
128.853
127.099
126.704
126.462
126.208
125.825
121.950
77.318
77.000
76.682
37.121
23.165
Br
O
N
Me
S14
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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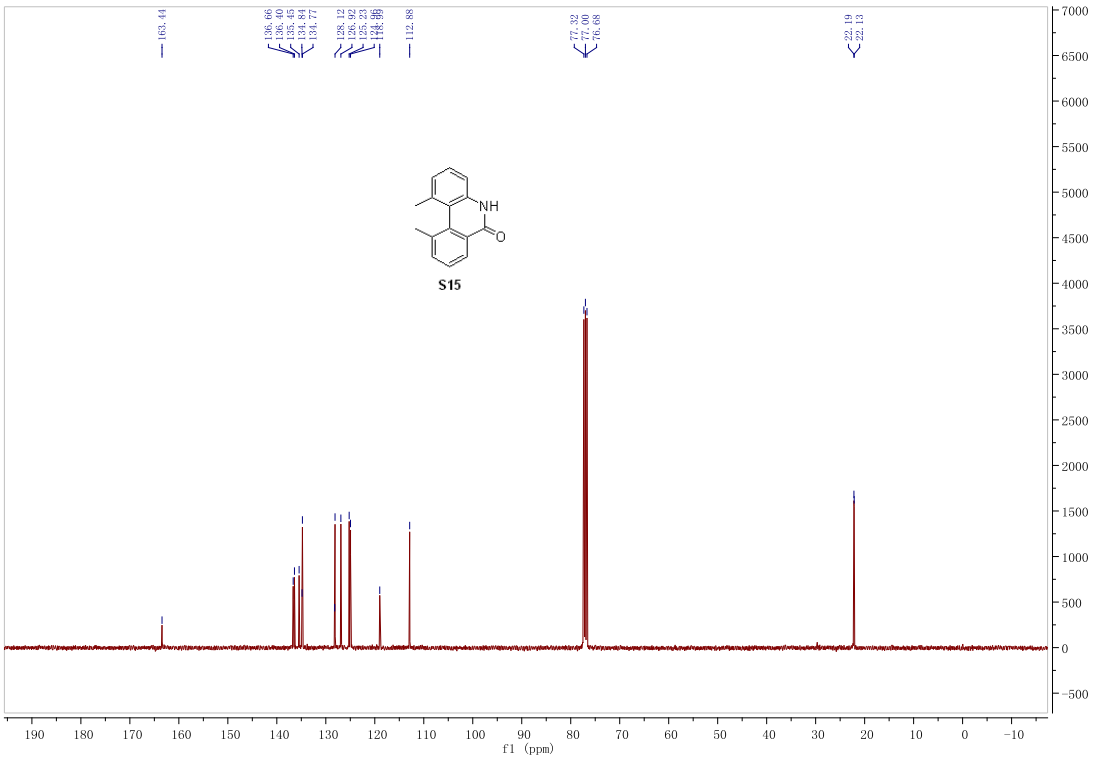
8.328
8.309
7.622
7.605
7.541
7.522
7.503
7.360
7.341
7.321
7.260
7.200
7.175
7.107
6.994
6.974
2.486
2.453
1.586
0.002
NH
O
S15
0.91
1.00
1.07
1.08
1.10
1.07
1.07
3.33
3.24
f1 (ppm)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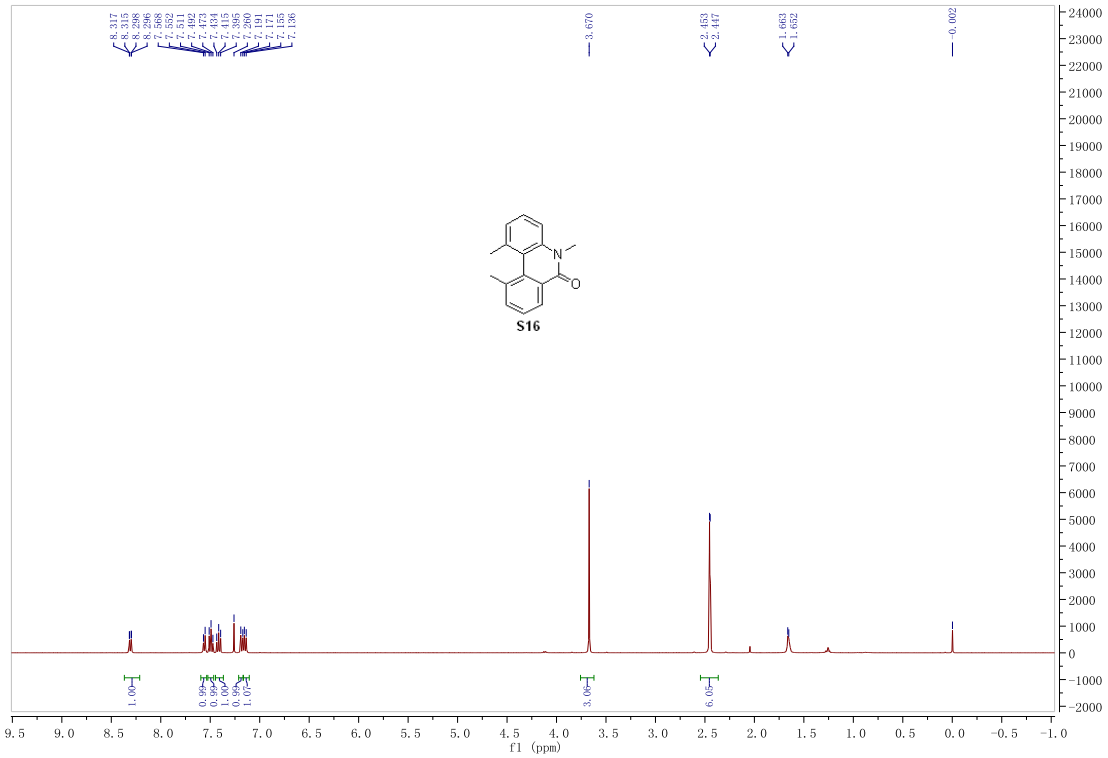
136.66
136.40
135.45
134.84
134.77
128.12
126.92
125.23
112.88
77.32
77.00
76.68
22.19
22.13
NH
O
S15
f1 (ppm)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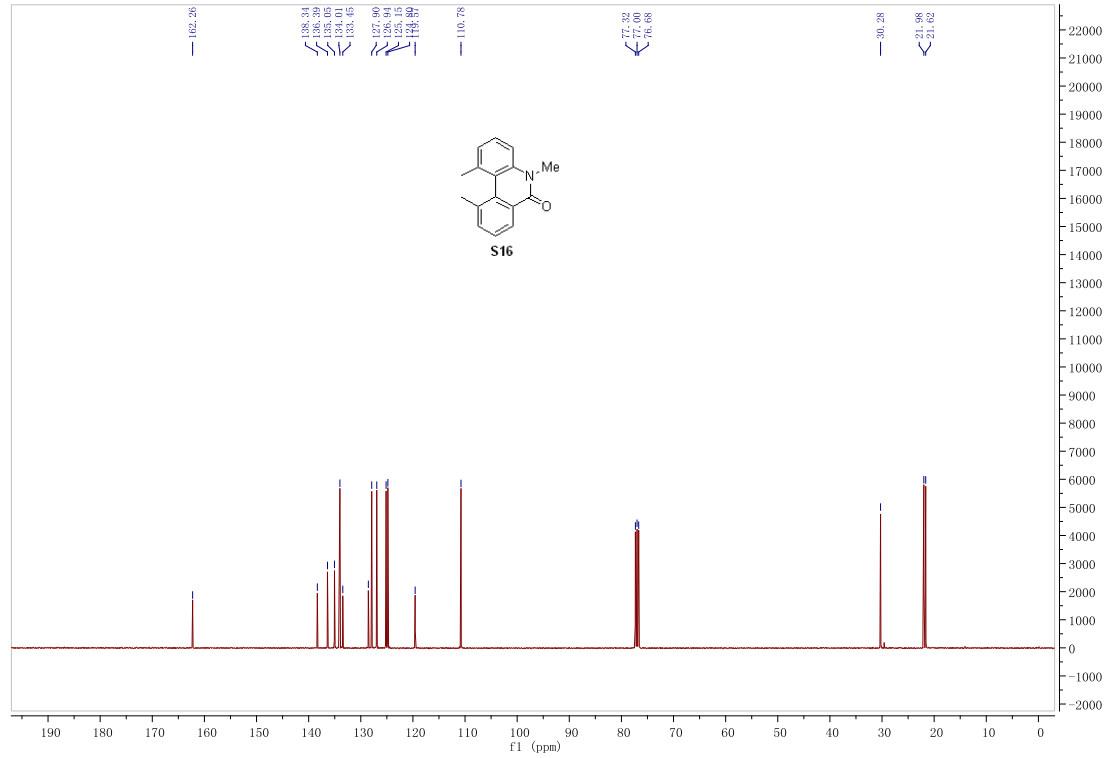
8.315
8.298
8.296
7.568
7.562
7.511
7.492
7.473
7.434
7.415
7.398
7.260
7.191
7.171
7.155
7.106
3.670
2.453
2.447
1.663
1.652
-0.002
N
O
S16
1.00
0.99
0.99
1.06
0.98
1.07
3.06
6.05
f1 (ppm)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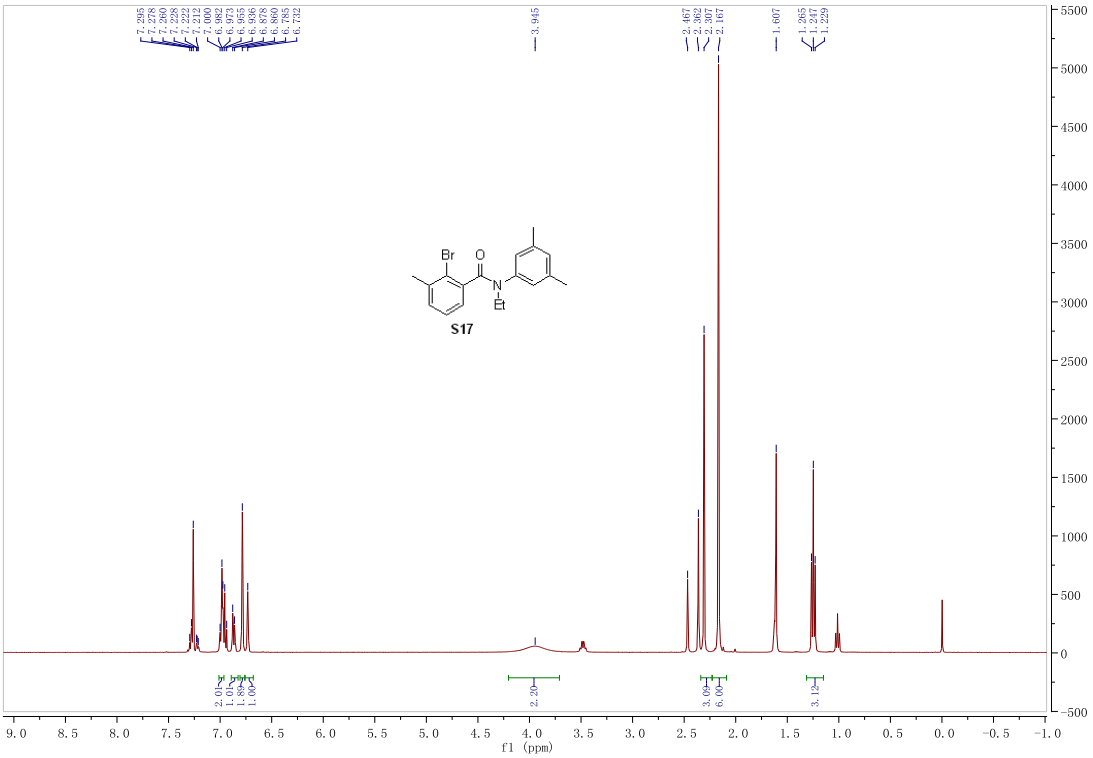
138.34
136.39
135.05
134.01
133.45
127.90
126.94
125.15
110.78
77.32
77.00
76.68
30.28
21.98
21.62
N
Me
O
S16
f1 (ppm)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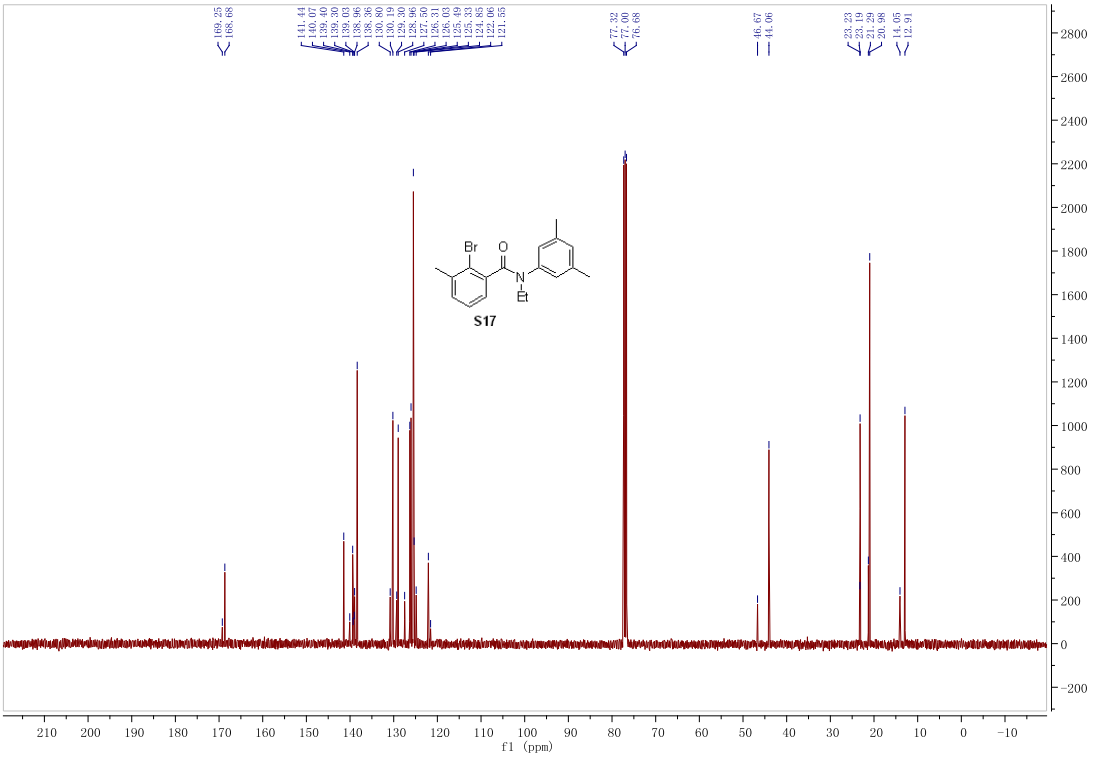
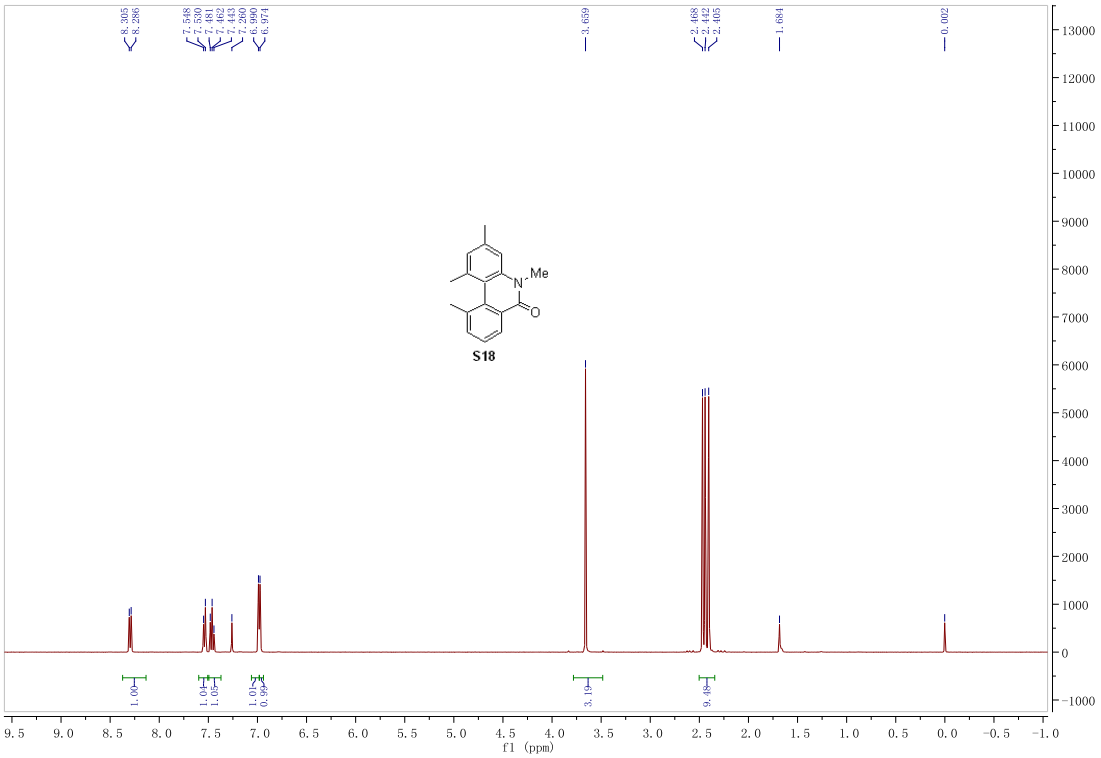
7.278
7.260
7.228
7.221
7.212
7.000
6.982
6.973
6.955
6.936
6.878
6.860
6.785
6.732
3.945
2.467
2.362
2.307
2.167
1.607
1.265
1.247
1.229
Br
O
N
Et
S17
2.01
1.65
1.89
1.00
2.20
3.09
6.00
3.12
f1 (ppm)


169.25
168.68
141.44
140.07
139.40
139.30
139.03
138.96
138.36
130.80
130.19
129.30
128.96
127.80
127.50
126.31
126.03
125.49
125.33
124.85
122.06
121.55
77.32
77.00
76.68
46.67
44.06
23.23
23.04
21.29
20.98
14.05
12.91
Br
O
N
Et
S17
f1 (ppm)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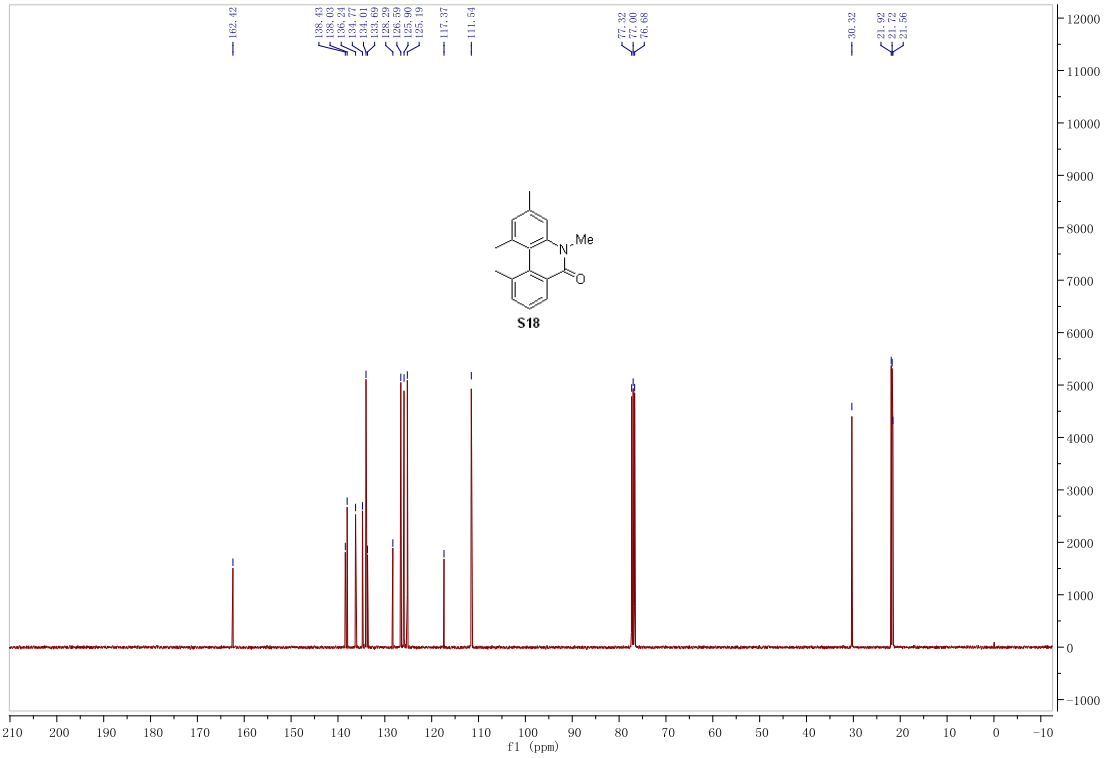
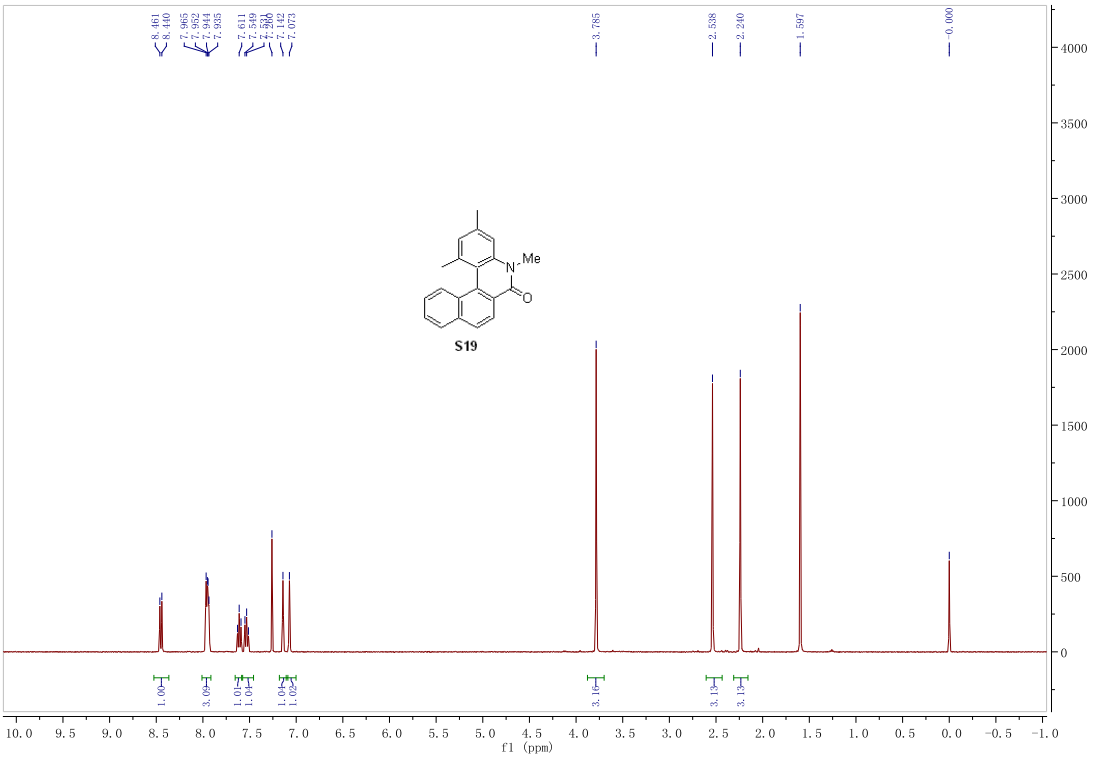
8.286
7.548
7.530
7.481
7.462
7.443
7.290
6.990
6.974
3.639
2.468
2.437
2.405
1.684
0.002
Me
N
O
S18
1.00
1.04
1.05
1.01
0.99
3.19
9.48
f1 (ppm)


162.42
138.43
138.03
136.24
134.77
134.01
133.69
128.29
126.59
125.90
125.19
117.37
111.54
77.32
77.00
76.68
30.32
21.92
21.72
21.56
Me
N
O
S18
f1 (ppm)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8.440
7.965
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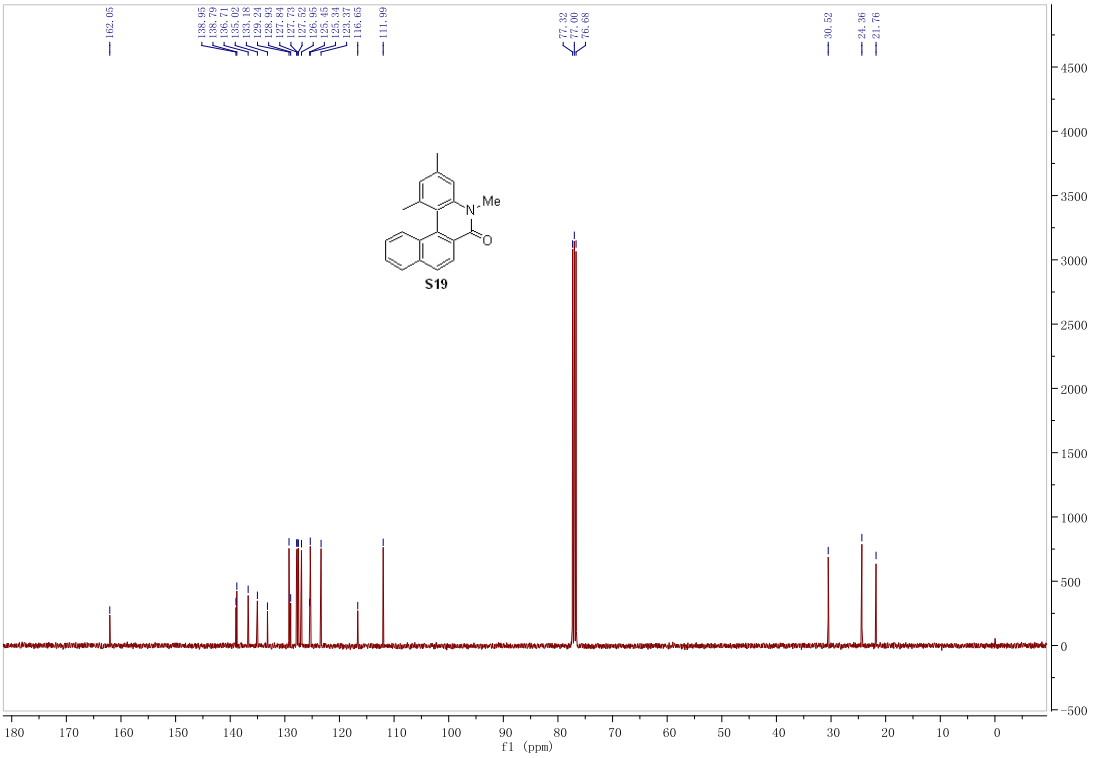
7.944
7.935
7.611
7.549
7.530
7.142
7.073
3.785
2.538
2.240
1.597
-0.000
Me
N
O
S19
1.00
3.09
1.01
1.04
1.04
1.02
3.16
3.13
3.13
f1 (ppm)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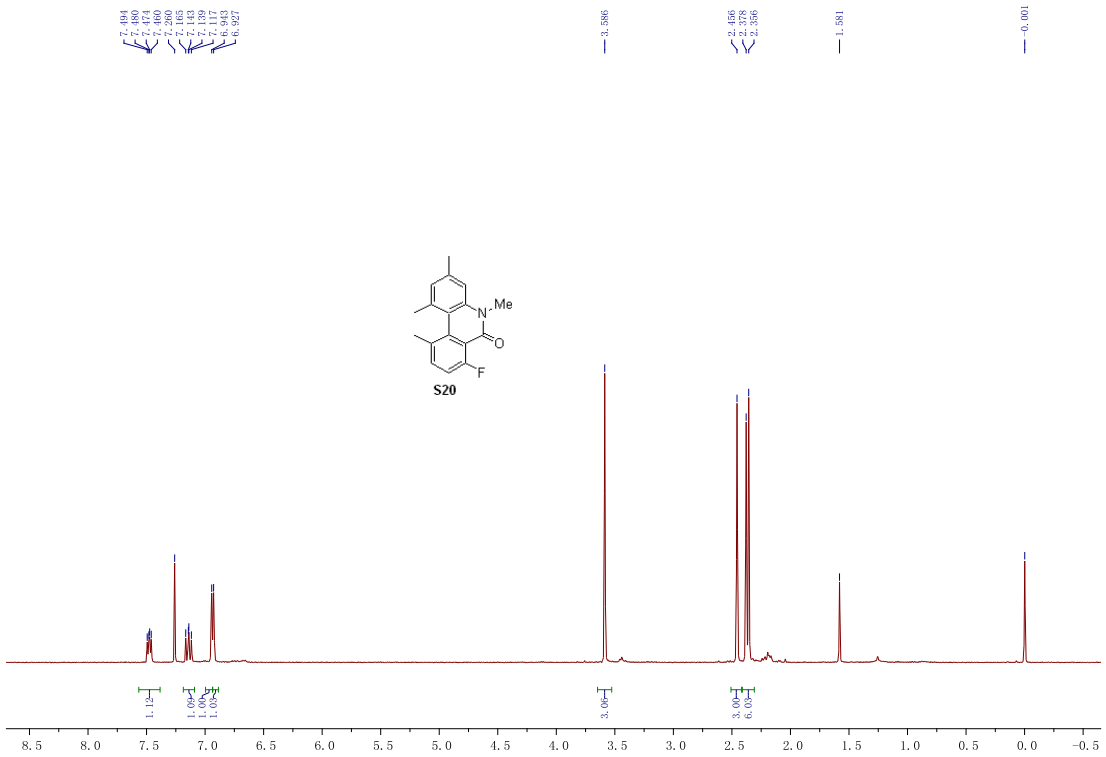
138.79
136.71
135.02
133.18
129.24
128.43
127.84
127.73
127.52
126.65
125.45
125.34
123.37
116.65
111.99
77.32
77.00
76.68
30.52
24.36
21.76
Me
N
O
S19
f1 (ppm)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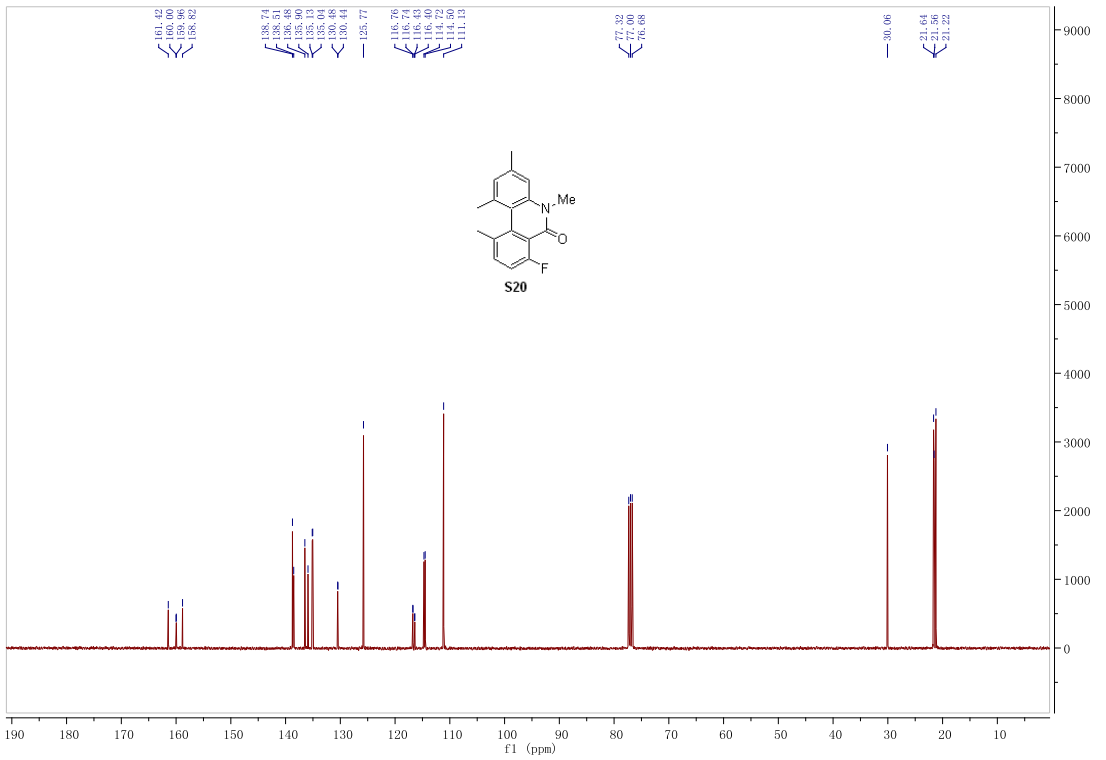
7.490
7.474
7.460
7.260
7.165
7.143
7.139
7.117
6.943
6.927
3.586
2.456
2.378
2.356
1.581
-0.001
Me
N
O
F
S20
1.12
1.09
1.06
1.03
3.06
3.00
6.03
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5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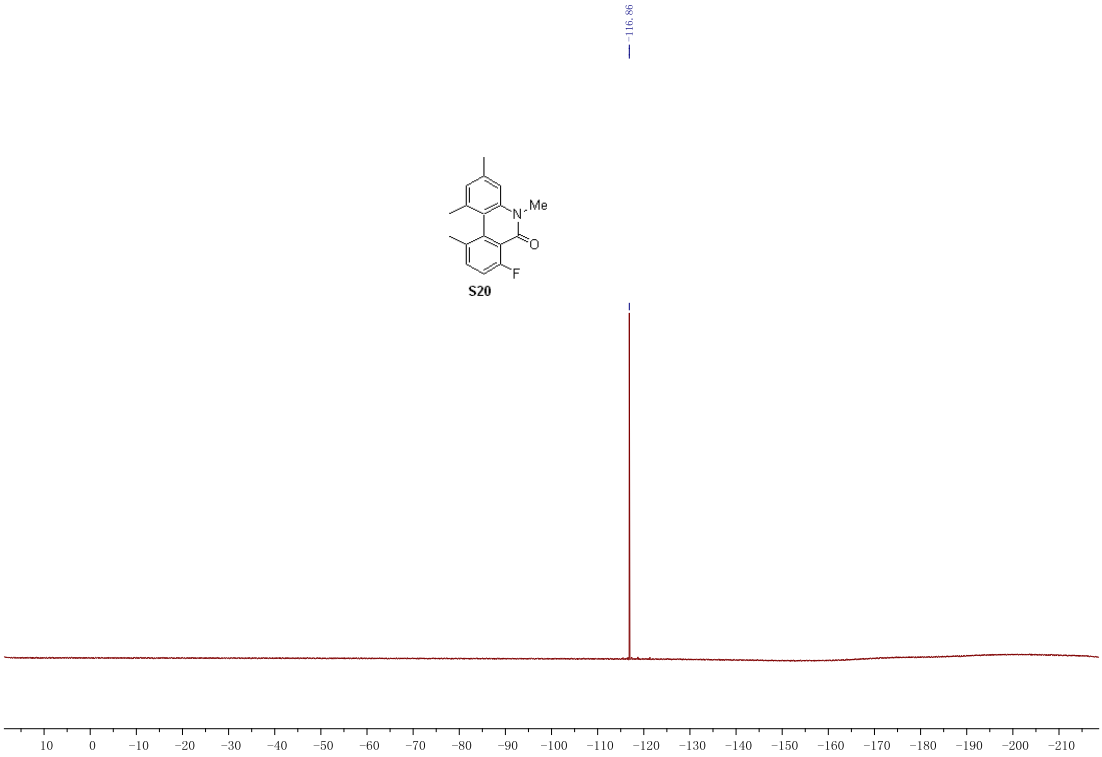
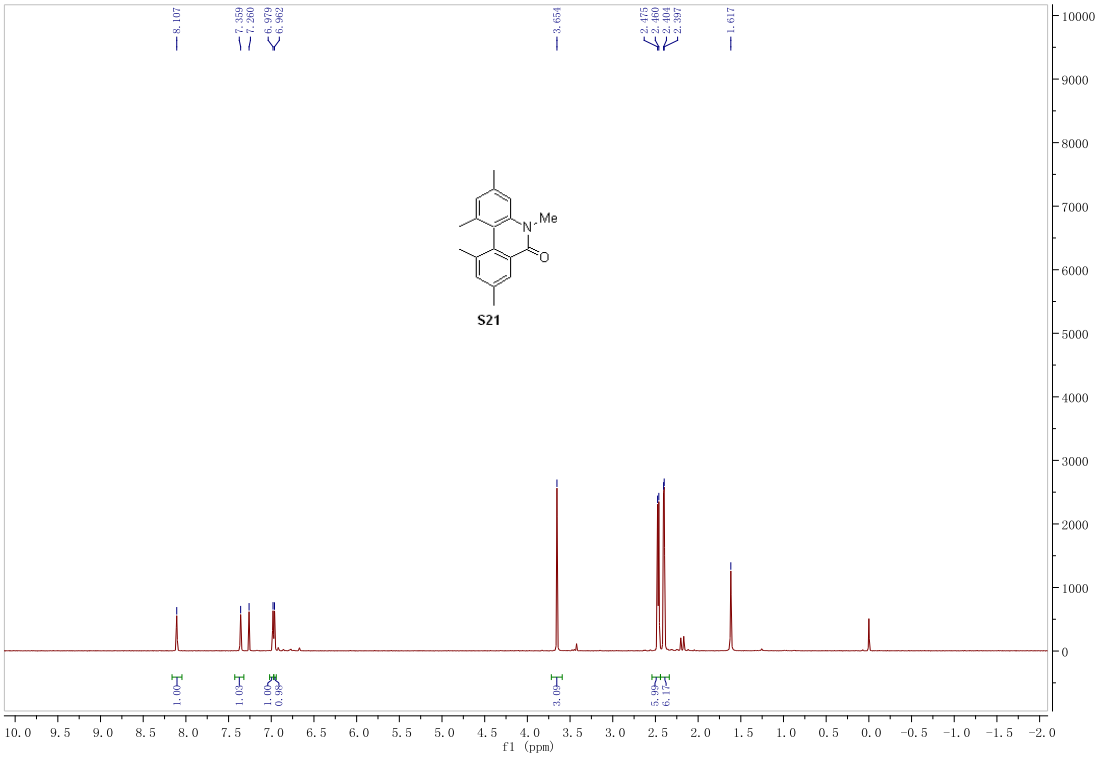
160.00
159.96
158.82
138.74
138.51
136.48
136.45
135.90
135.13
135.04
130.48
130.44
125.77
116.76
116.74
116.43
116.40
114.72
114.56
111.13
77.32
77.00
76.68
30.06
21.64
21.56
21.22
Me
N
O
F
S20
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


-116.86
Me
N
O
F
S20
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210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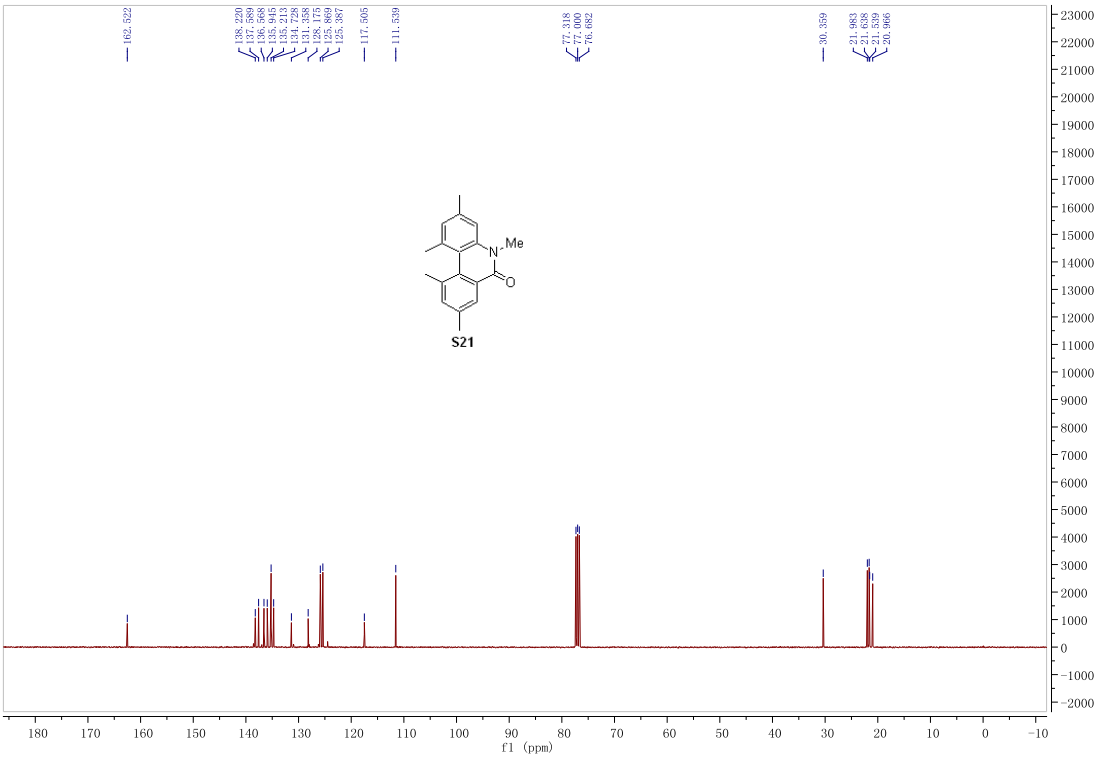
7.359
7.290
6.979
6.962
3.654
2.475
2.460
2.404
2.397
1.617
Me
N
O
S21
1.00
1.03
1.00
0.99
3.09
5.99
6.17
10000 9000 8000 7000 6000 5000 4000 3000 2000 1000 0
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5 -2.0
f1 (ppm)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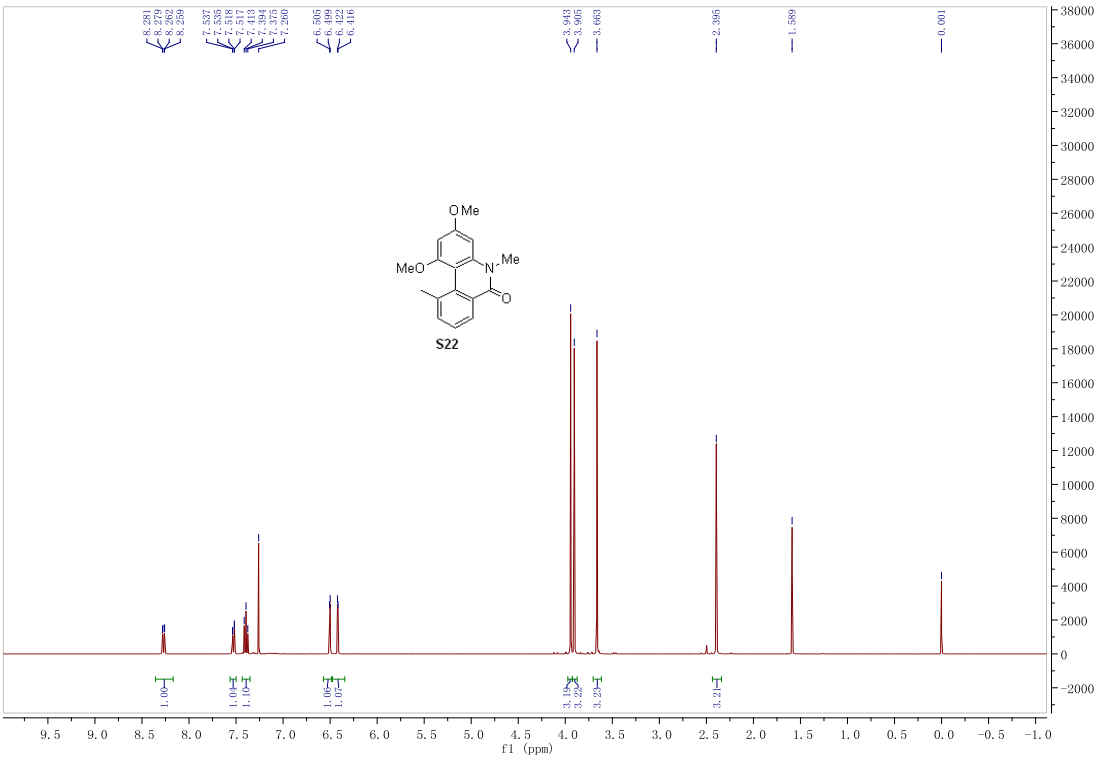
136.568
135.945
135.213
134.728
131.358
128.175
125.869
125.387
117.505
111.539
77.318
77.000
76.682
30.359
21.983
21.638
21.539
20.966
N
Me
O
S21
f1 (ppm)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7.535
7.518
7.517
7.413
7.394
7.375
7.290
6.505
6.499
6.422
6.416
3.943
3.906
3.663
2.395
1.589
0.001
O Me
MeO
N
Me
O
S22
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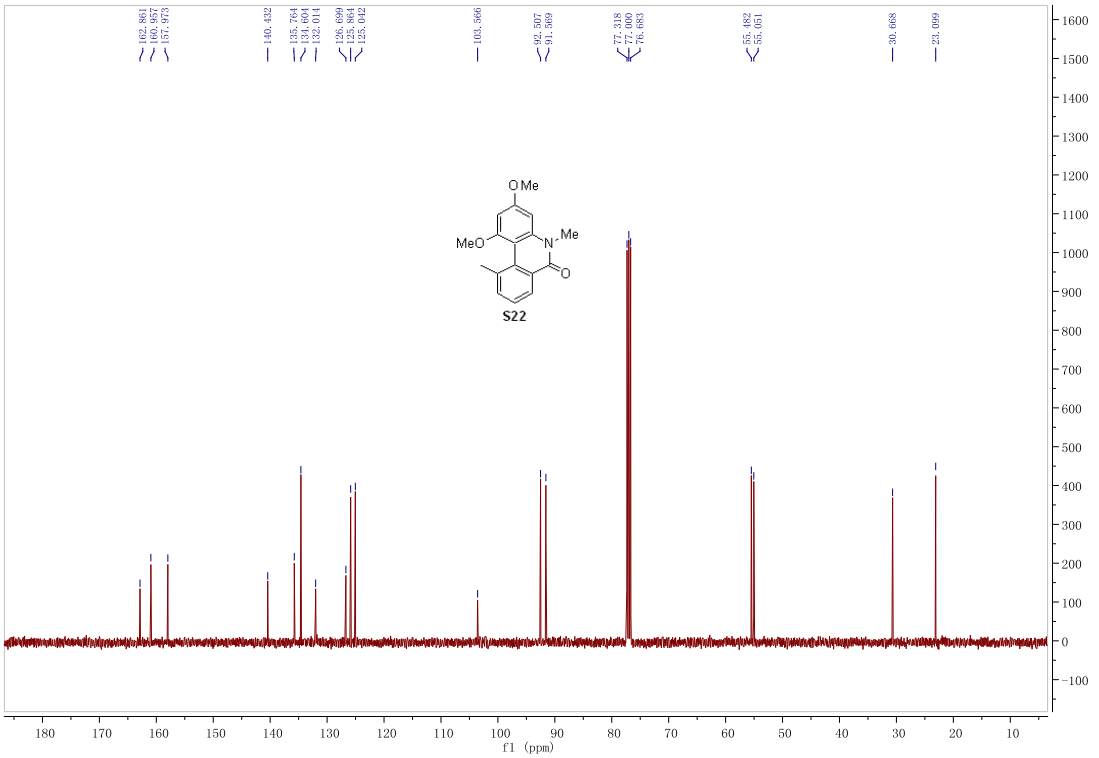
1.04
1.10
1.06
1.07
3.19
3.22
3.23
3.21
f1 (ppm)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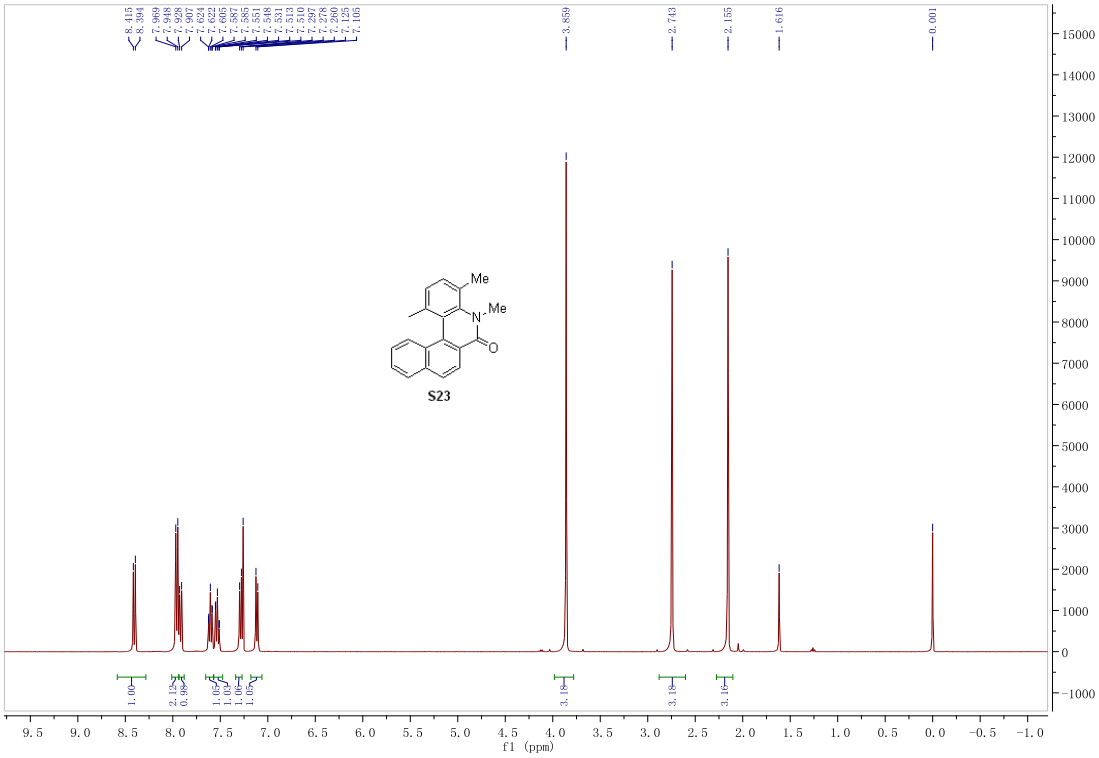
126.699
125.864
125.042
103.566
92.507
91.569
77.318
77.000
76.683
55.482
55.051
30.668
23.099
OMe
MeO
N
Me
O
S22
f1 (ppm)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7.969
7.948
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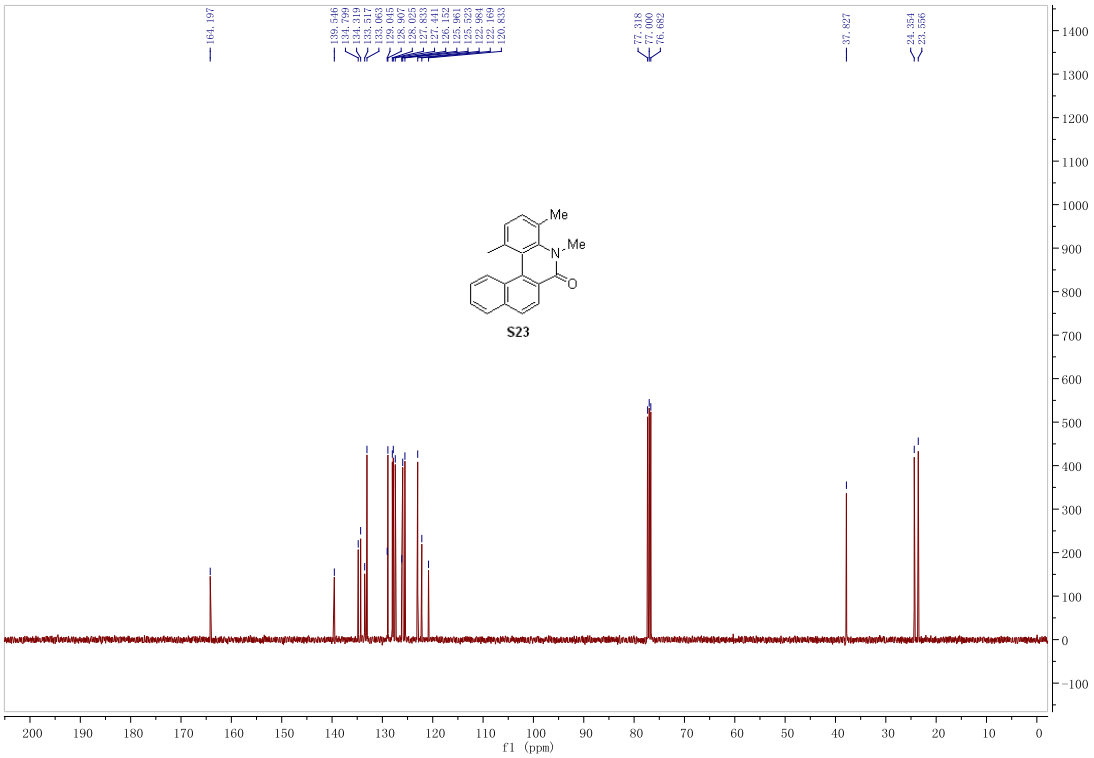
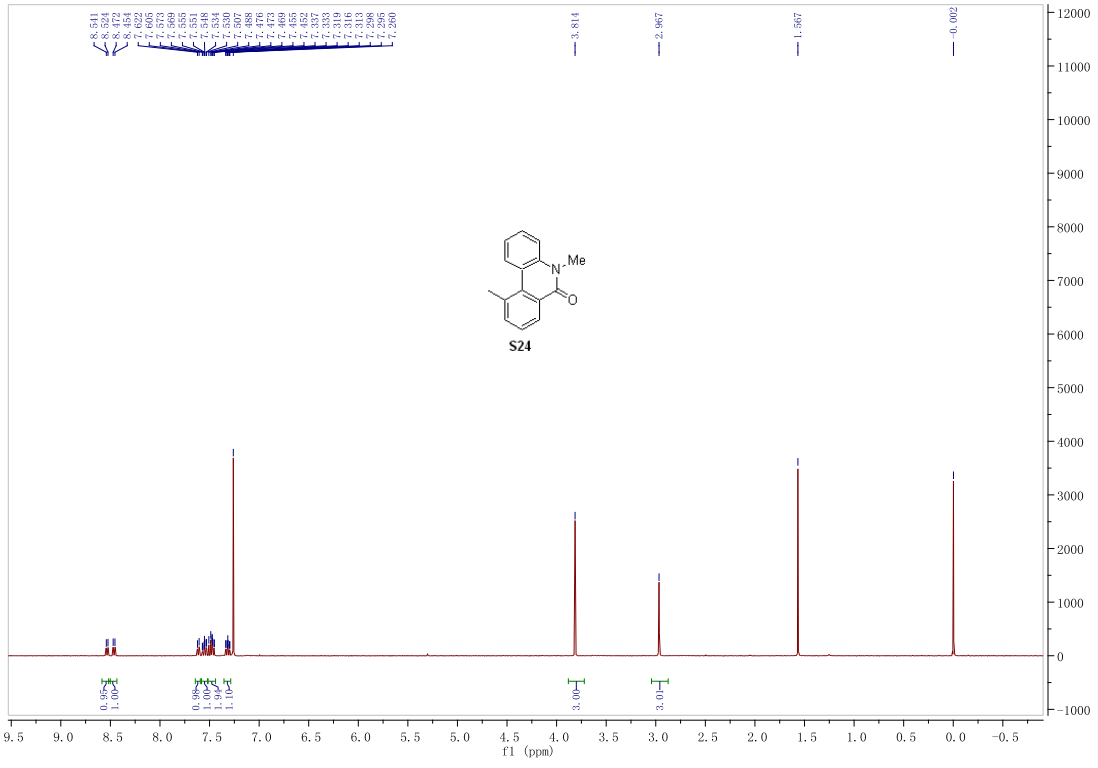
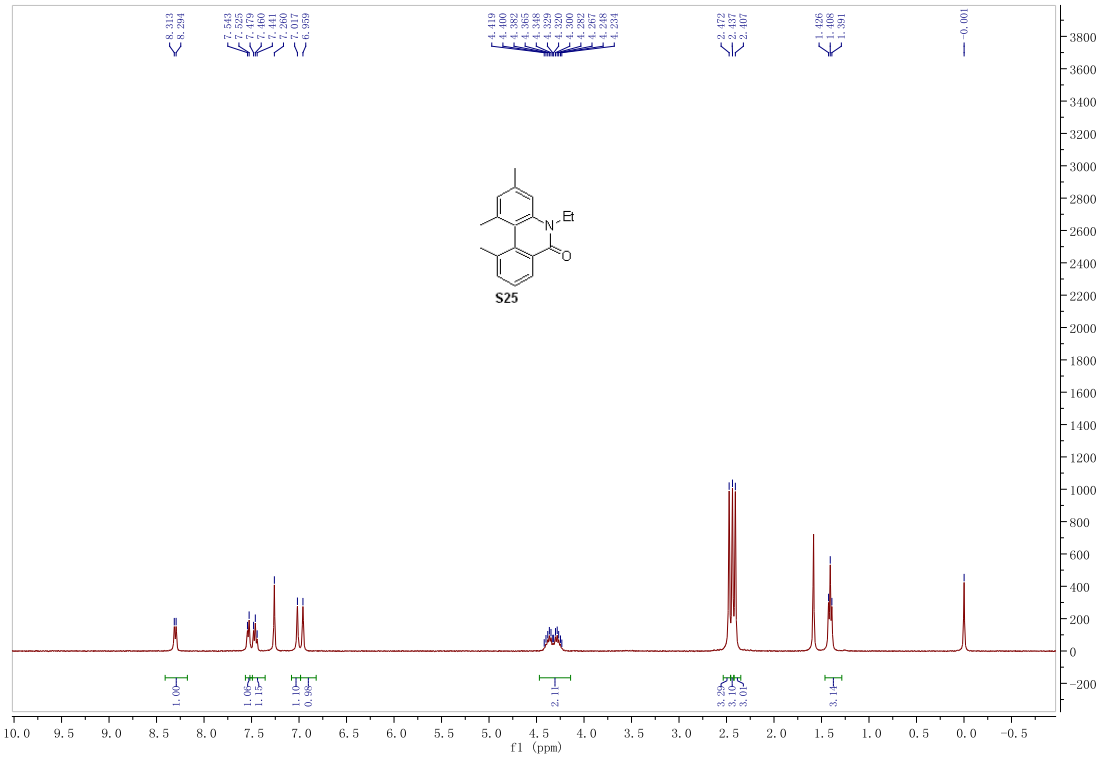
7.907
7.624
7.622
7.606
7.587
7.585
7.551
7.548
7.531
7.513
7.510
7.397
7.278
7.260
7.125
7.105
3.859
2.743
2.155
1.616
0.001
Me
N
Me
O
S23
1.00
2.12
0.98
1.05
1.02
1.10
1.05
3.18
3.18
3.16
f1 (ppm)



S23



S24


8.313
8.294
7.543
7.525
7.469
7.460
7.441
7.260
7.237
6.989
4.419
4.400
4.382
4.365
4.348
4.329
4.300
4.282
4.267
4.248
4.234
2.472
2.437
2.407
1.426
1.408
1.391
-0.001
Et
N
O
S25
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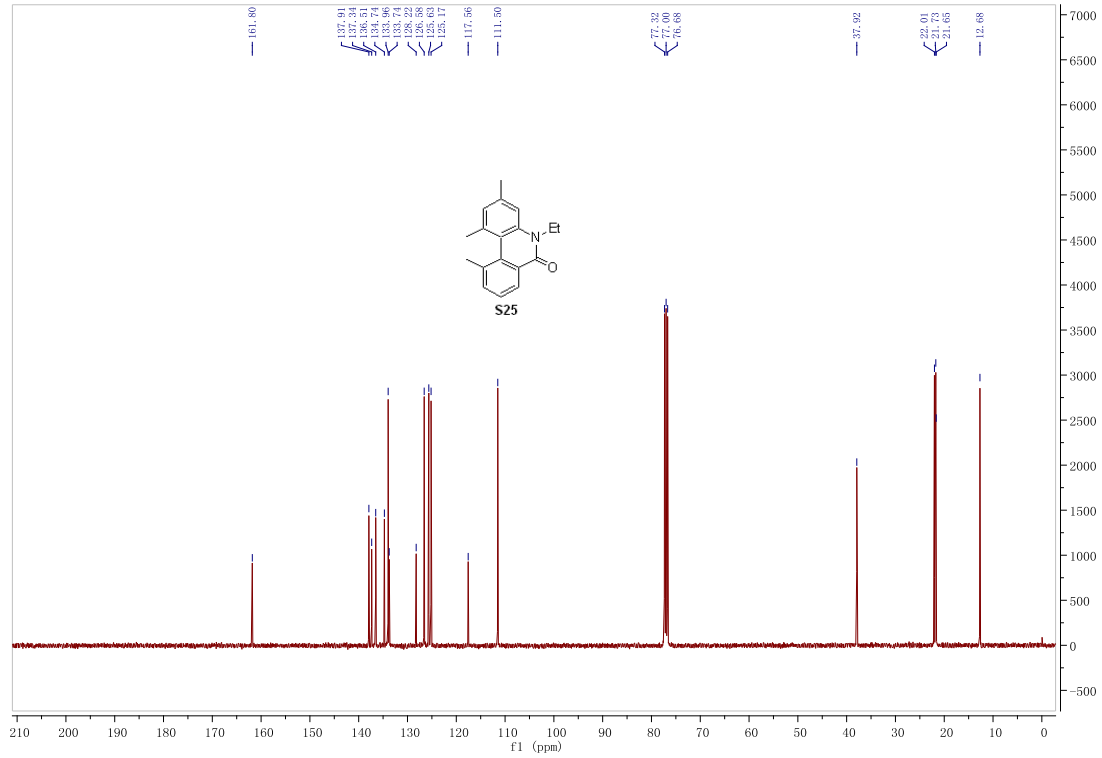
1.06
1.15
1.10
0.96
2.11
3.29
3.10
3.01
3.14
f1 (ppm)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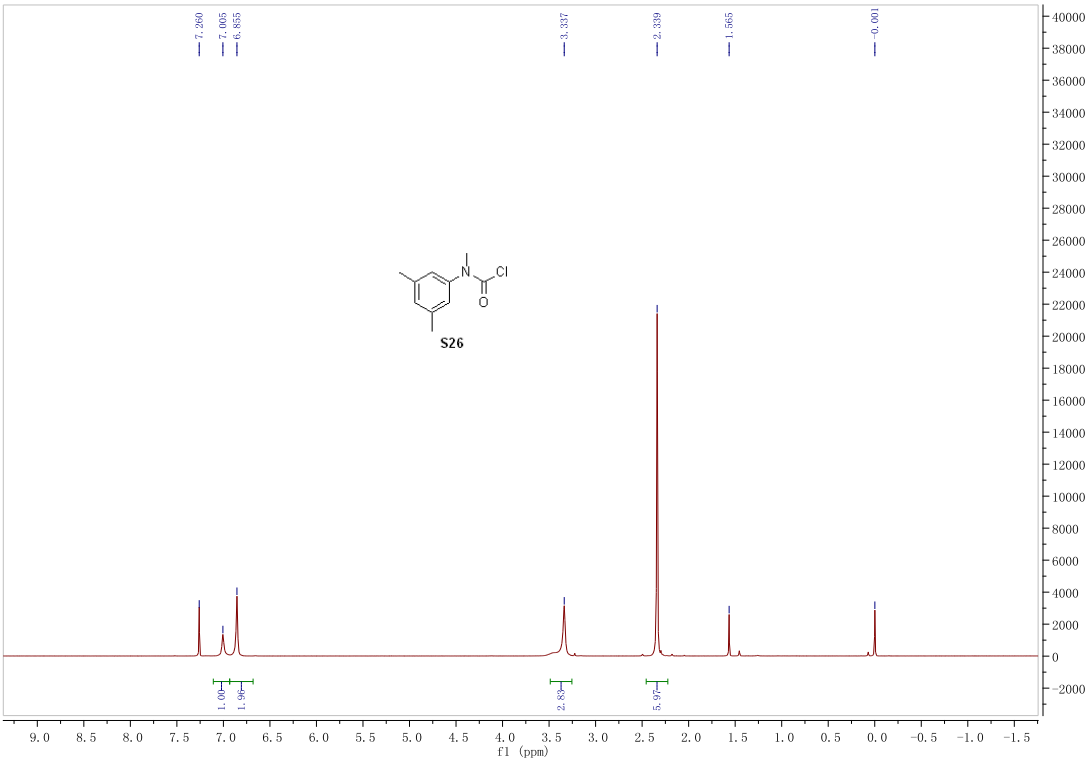
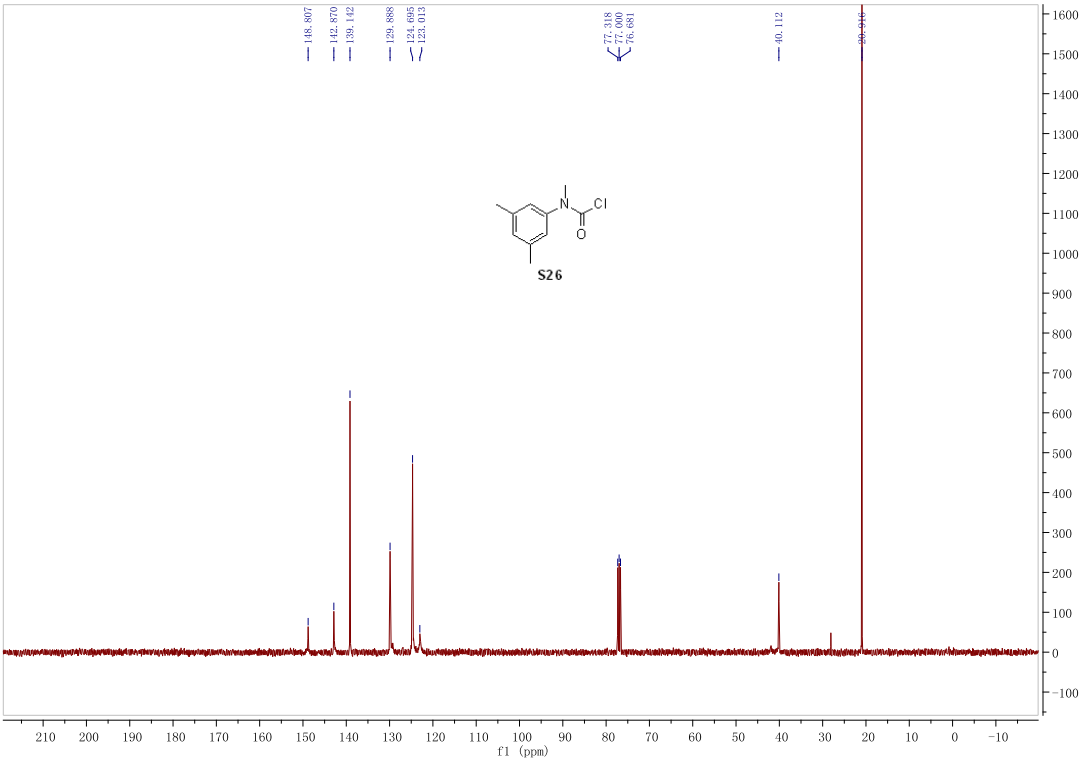
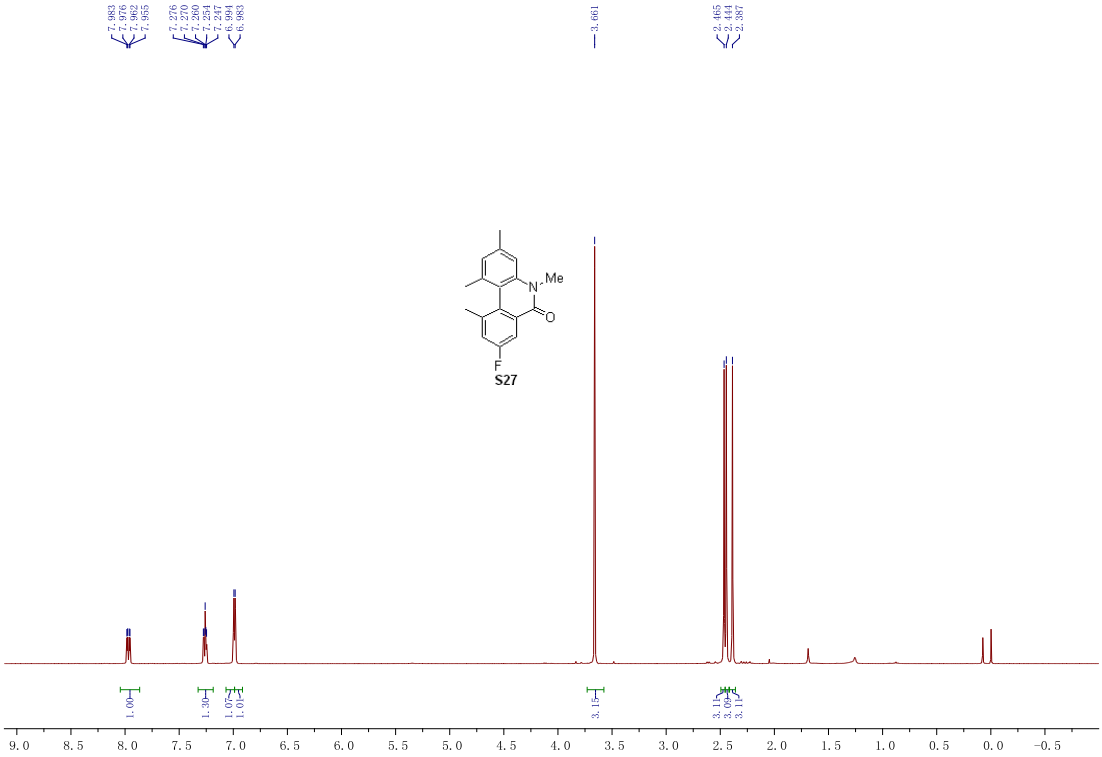
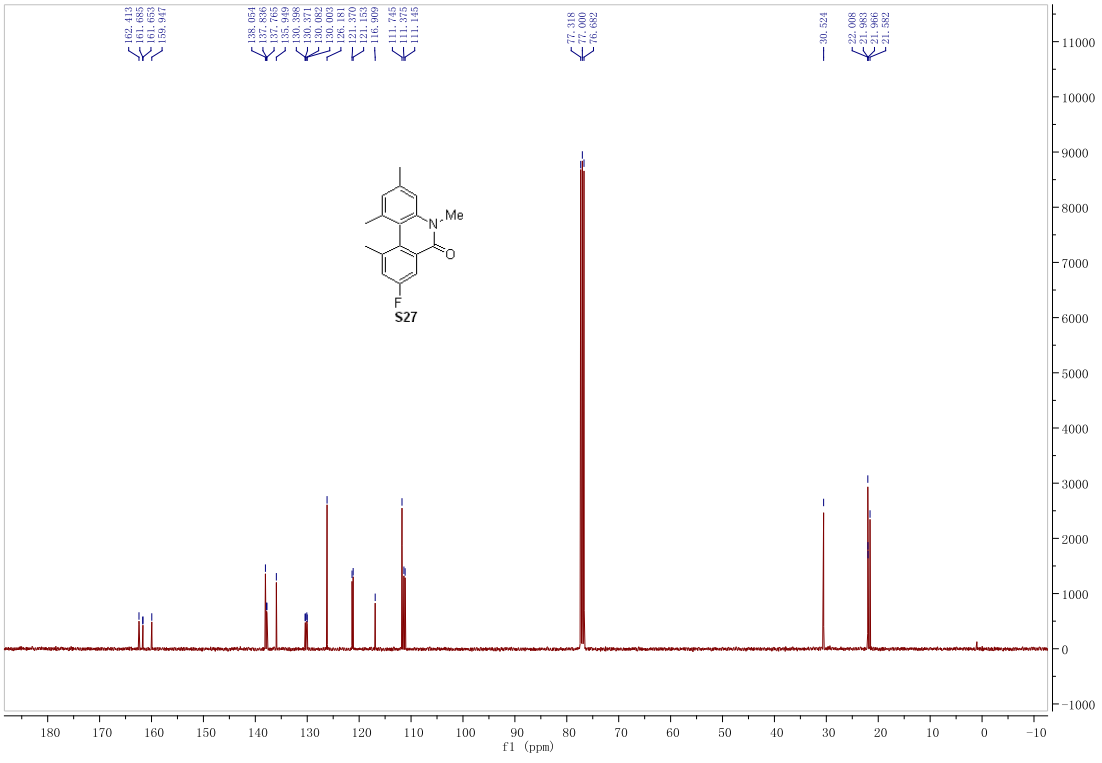
134.74
133.96
133.74
128.22
126.58
125.63
125.17
117.56
111.50
77.32
77.00
76.68
37.92
22.01
21.73
21.65
12.68
Et
N
O
S25
f1 (ppm)


7.260
7.005
6.855
3.337
2.339
1.565
-0.001
S26
1.00
1.96
2.83
5.97
f1 (ppm)


148.807
142.870
139.142
129.888
124.695
123.013
77.318
77.000
76.681
40.112
20.946
S26
f1 (ppm)


7.983
7.976
7.962
7.955
7.276
7.270
7.260
7.254
7.247
6.994
6.983
3.661
2.465
2.444
2.387
Me
N
O
F
S27
1.00
1.30
1.07
1.01
3.15
3.11
3.09
3.12
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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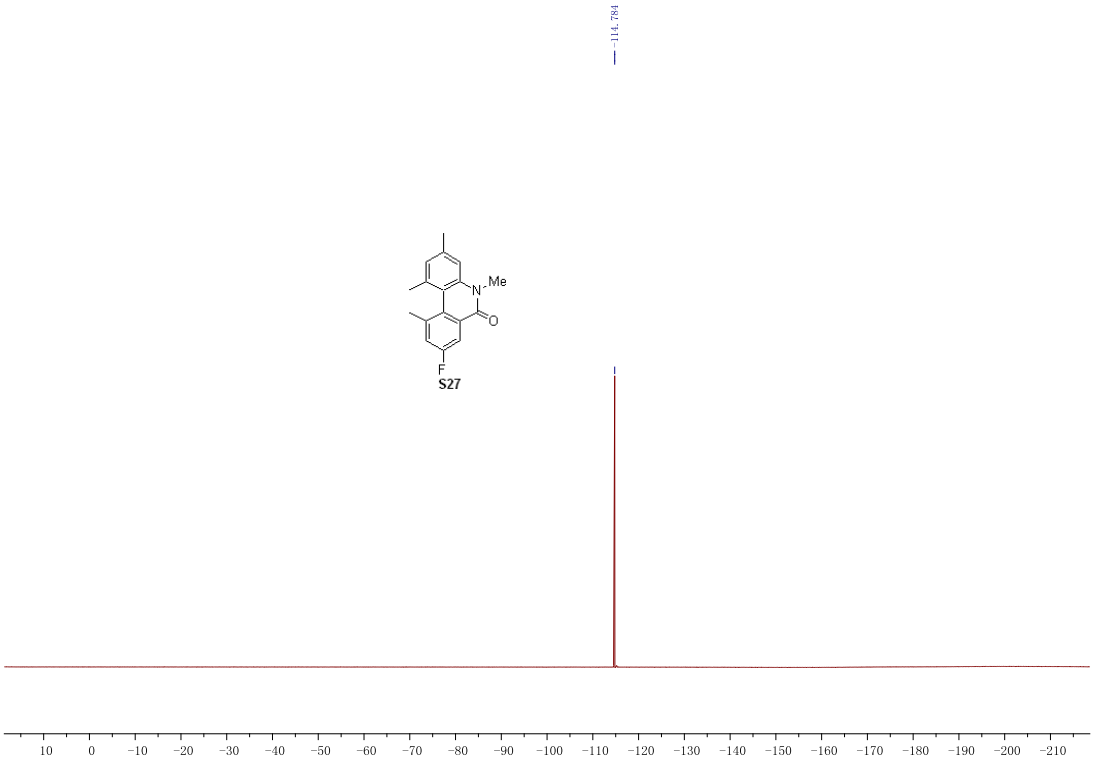
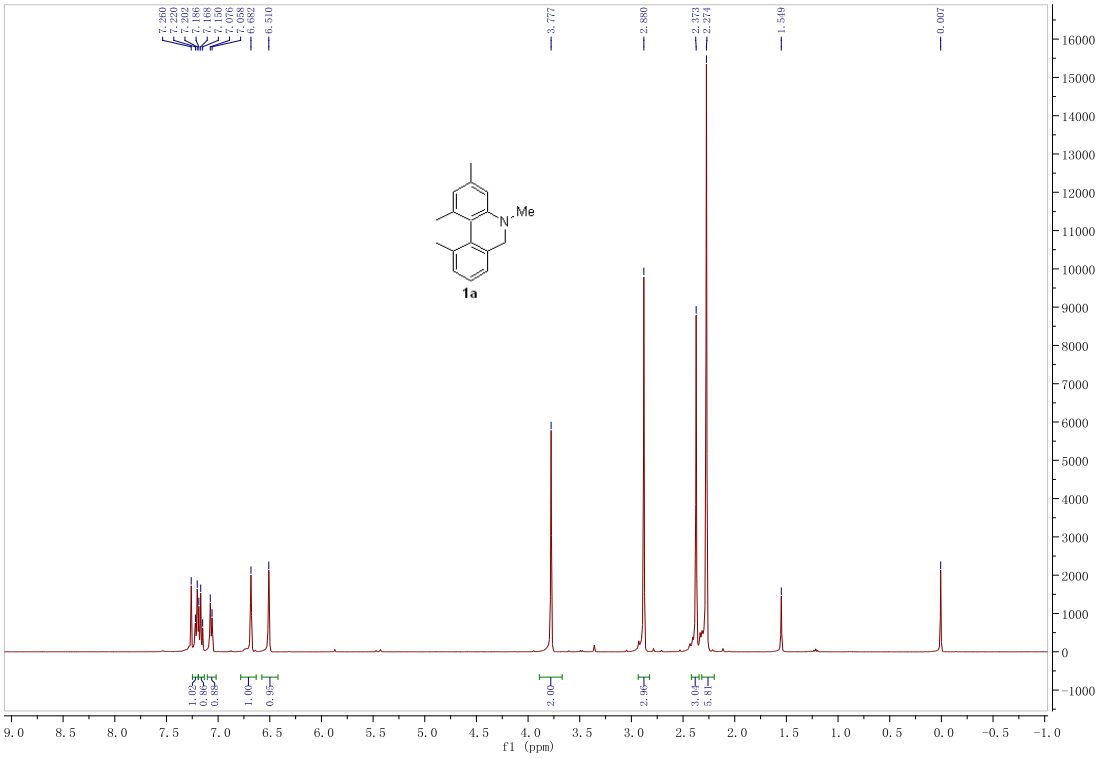
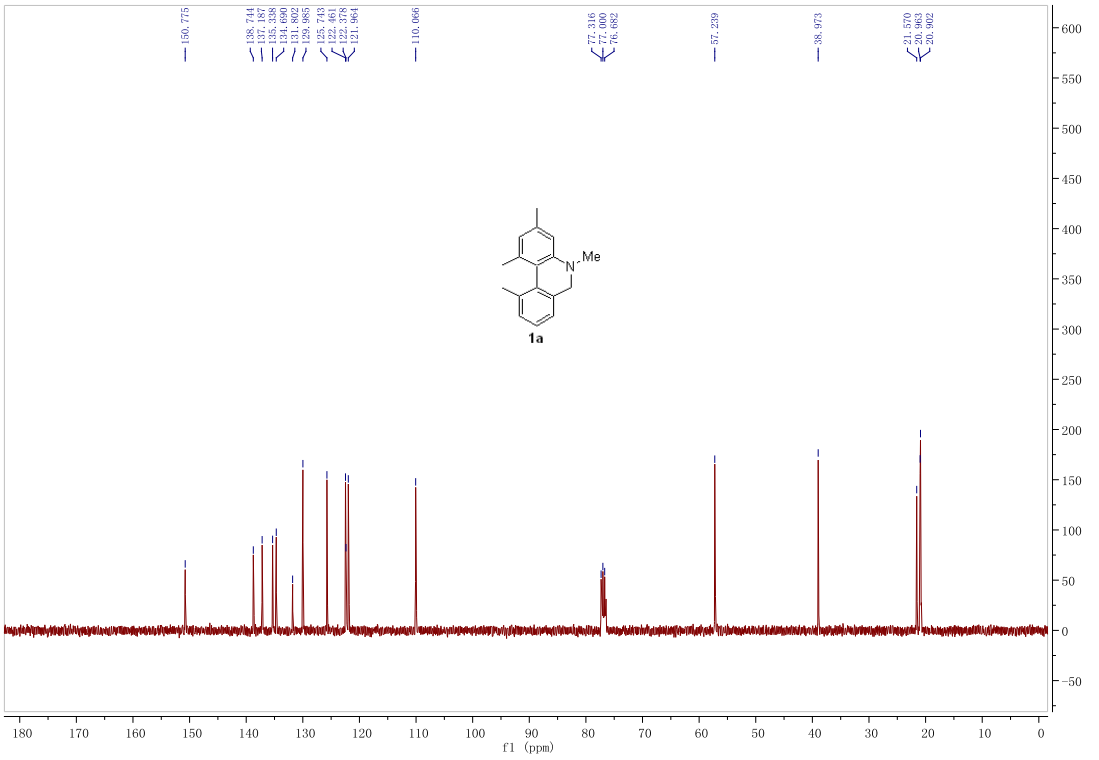
161.653
159.947
138.054
137.836
137.765
135.946
130.398
130.371
130.082
130.003
126.161
121.370
121.153
116.909
111.745
111.375
111.145
77.318
77.000
76.682
30.524
22.008
21.983
21.966
21.582
Me
N
O
F
S27
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


-114.784
Me
N
O
F
S27
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210


7.260
7.209
7.202
7.186
7.168
7.150
7.095
7.058
6.882
6.510
3.777
2.880
2.373
2.274
1.549
0.007
Me
N
1a
1.02
0.89
0.89
1.00
0.95
2.00
2.90
3.04
5.81
f1 (ppm)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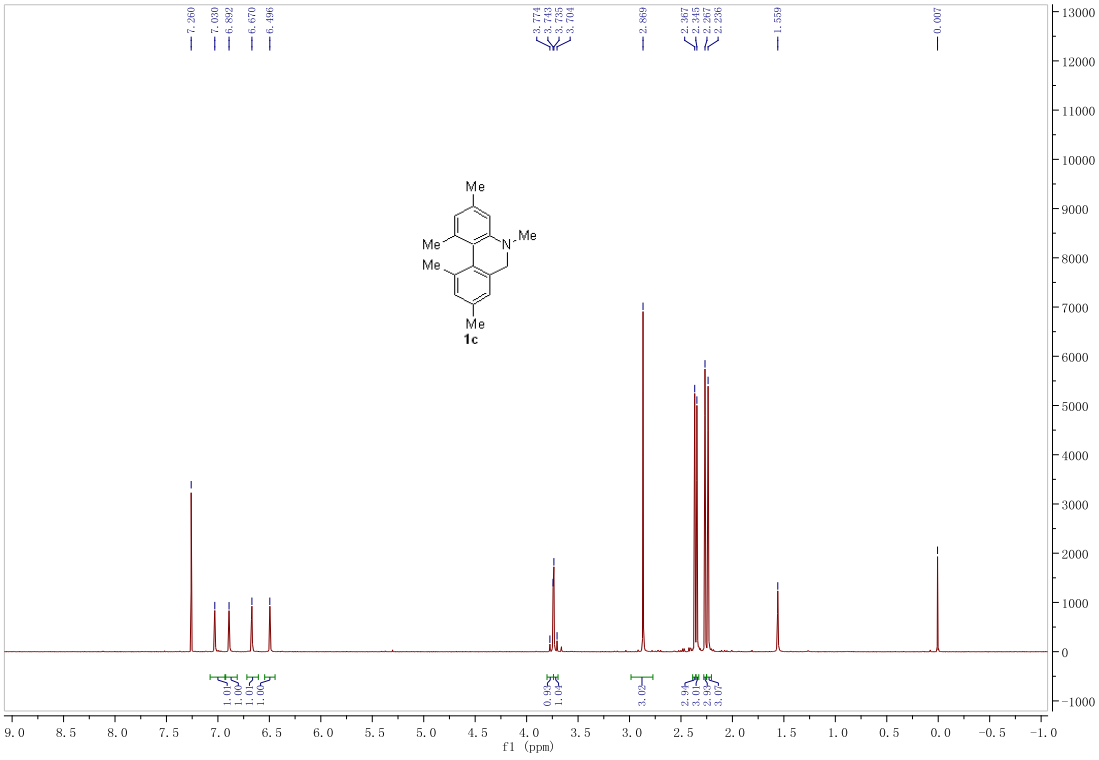
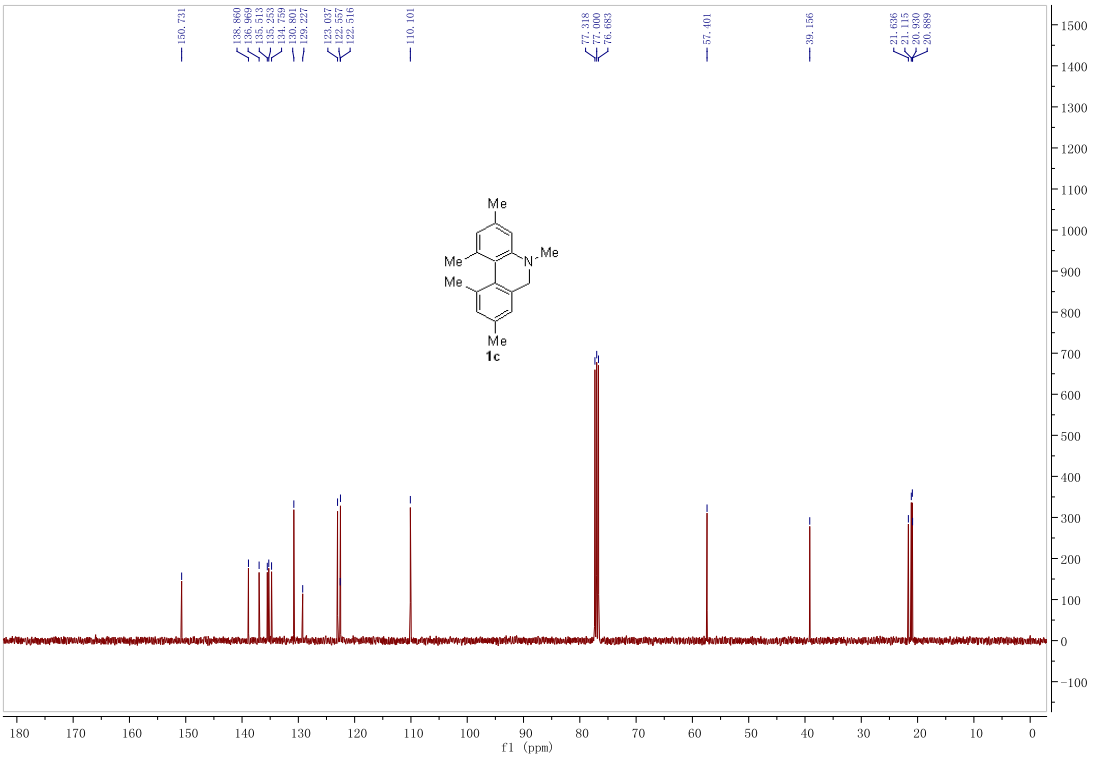
138.744
137.187
135.398
134.636
131.802
129.985
125.743
122.461
122.378
121.984
110.066
77.316
77.000
76.682
57.239
38.973
21.570
20.963
20.962
Me
N
1a
f1 (ppm)


7.260
7.030
6.892
6.670
6.496
3.774
3.743
3.735
3.704
2.869
2.367
2.345
2.297
2.286
1.559
0.007
Me
Me
Me
N
Me
1c
f1 (ppm)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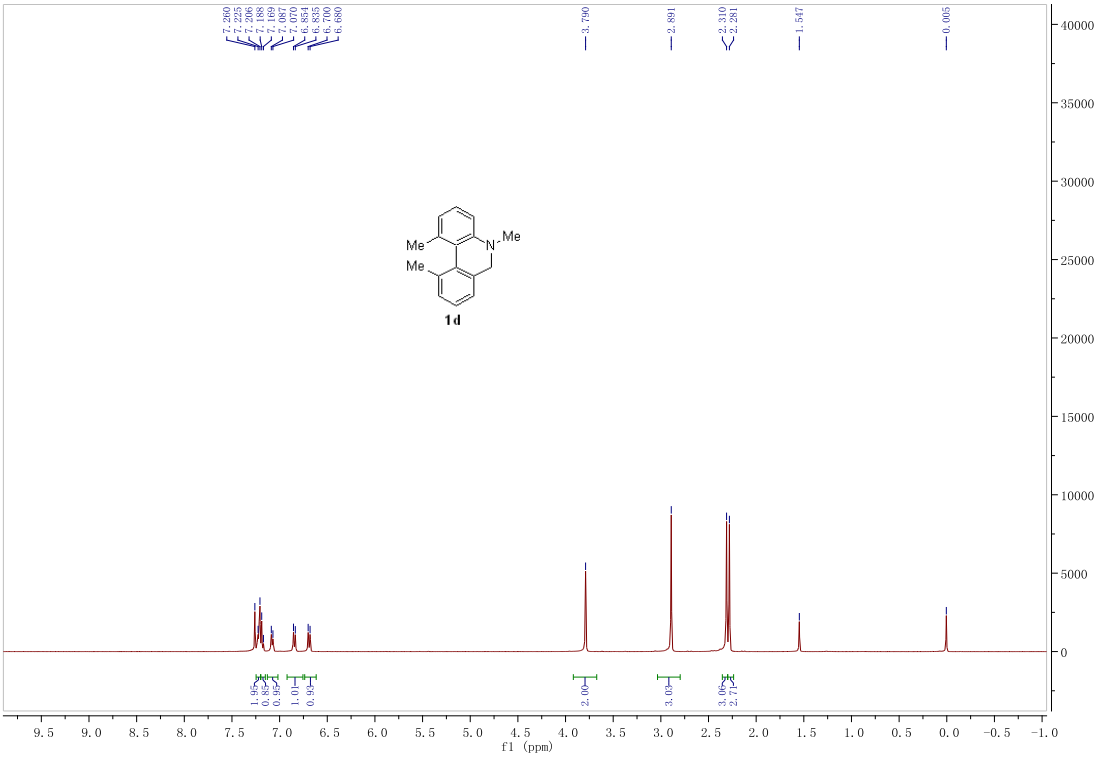
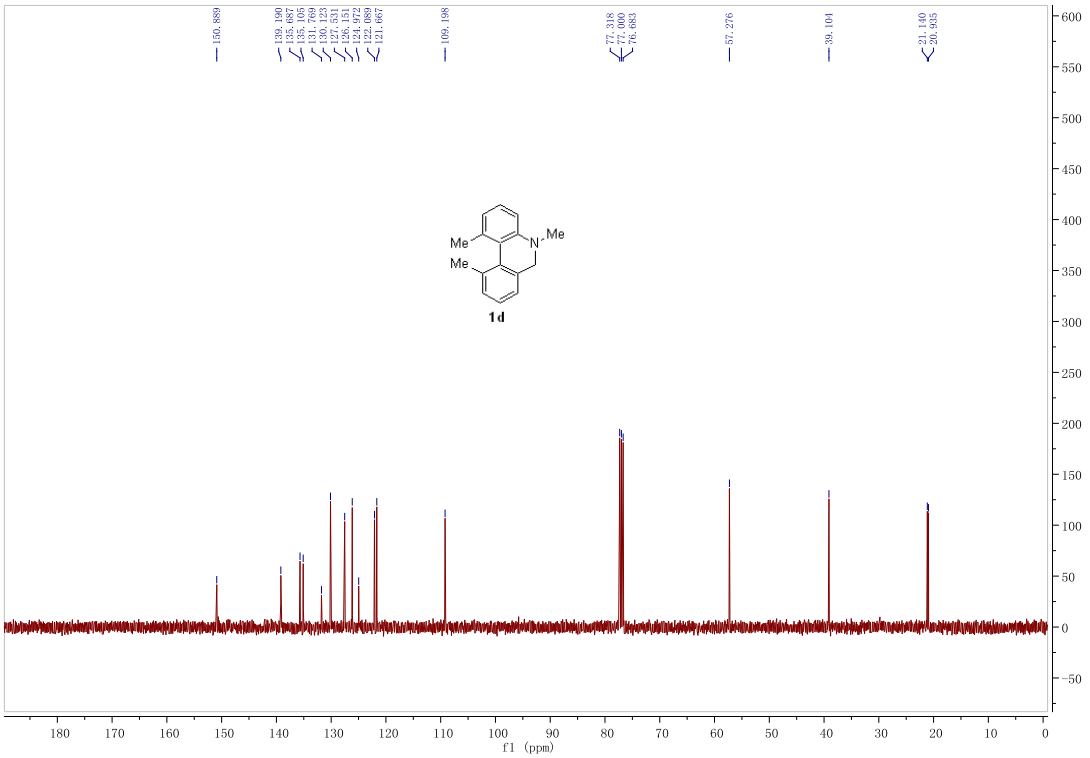
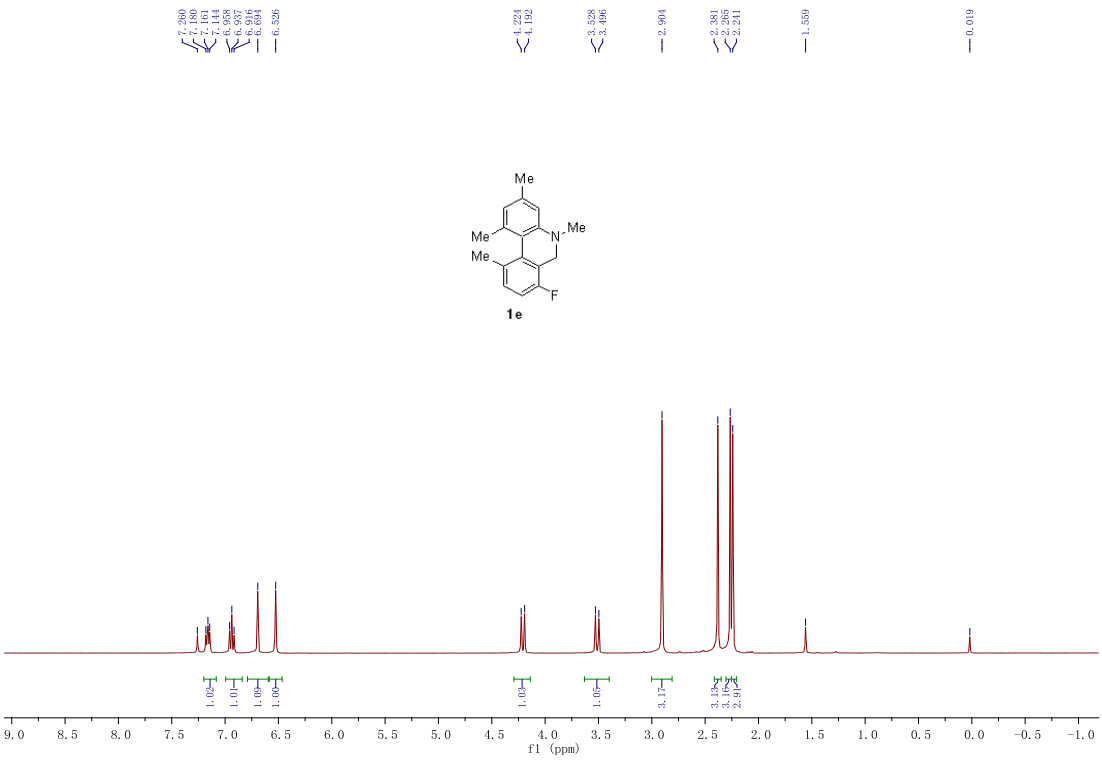
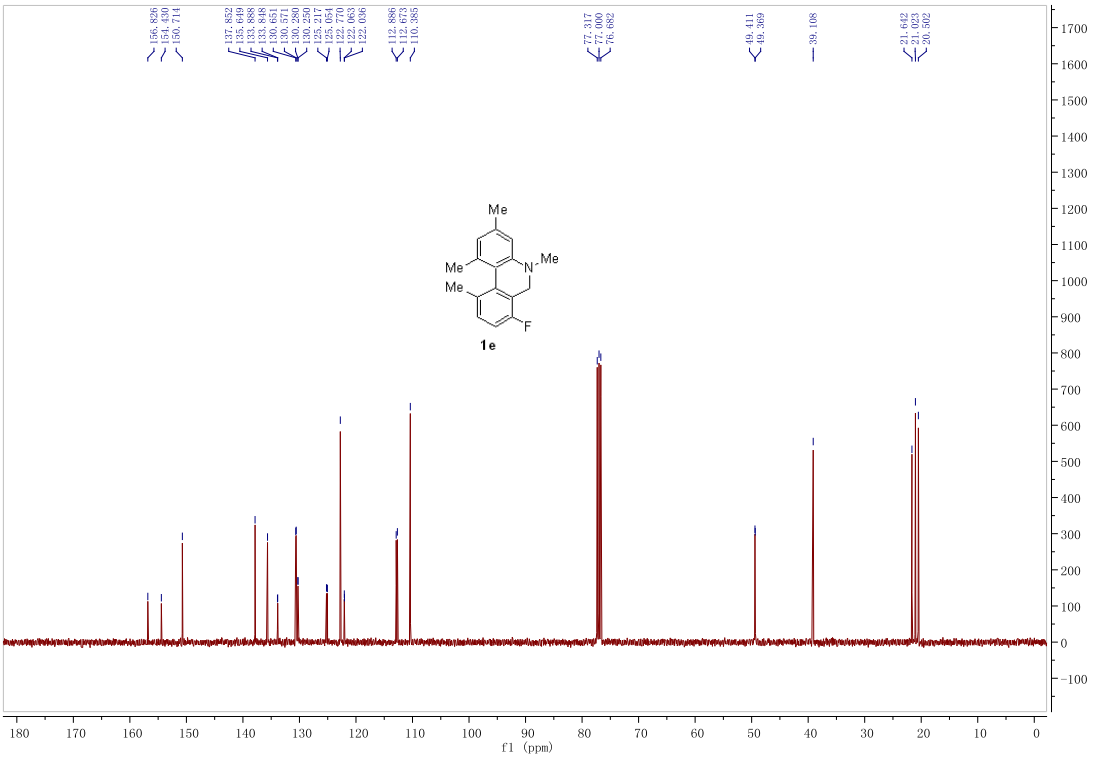
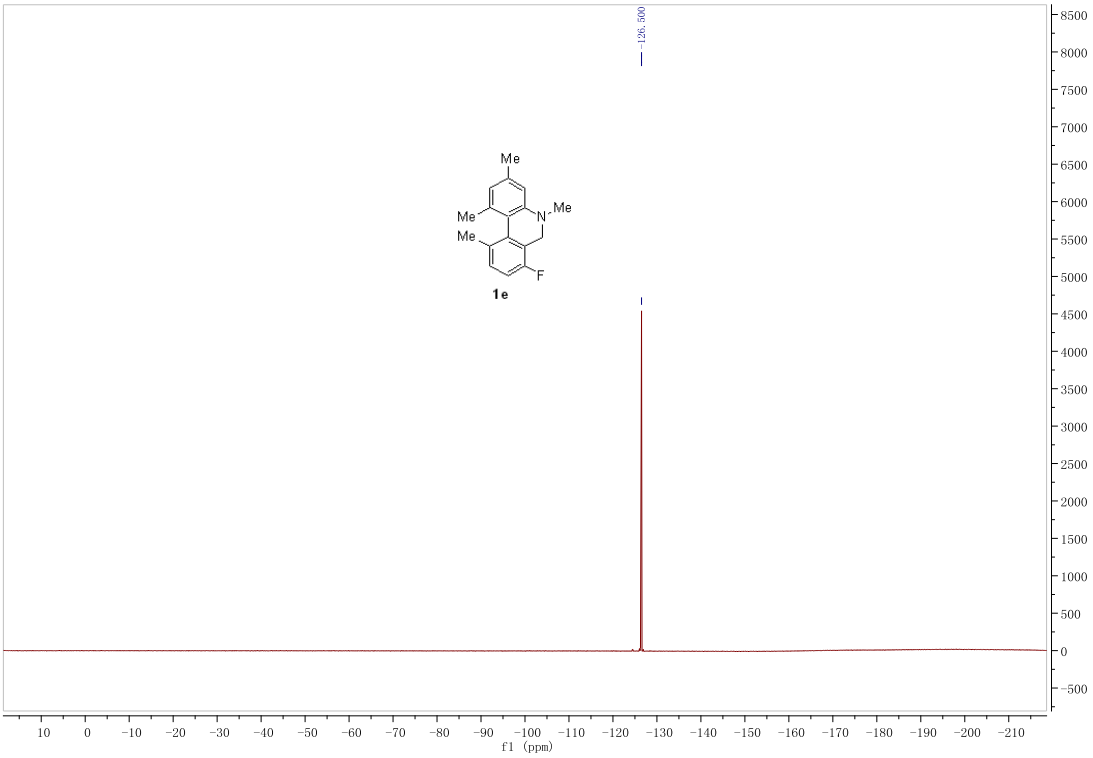
138.860
136.969
135.513
135.253
134.759
130.801
129.227
123.037
122.557
122.516
110.101
77.318
77.000
76.683
57.401
39.156
21.636
21.115
20.880
20.889
Me
Me
Me
N
Me
1c
f1 (ppm)

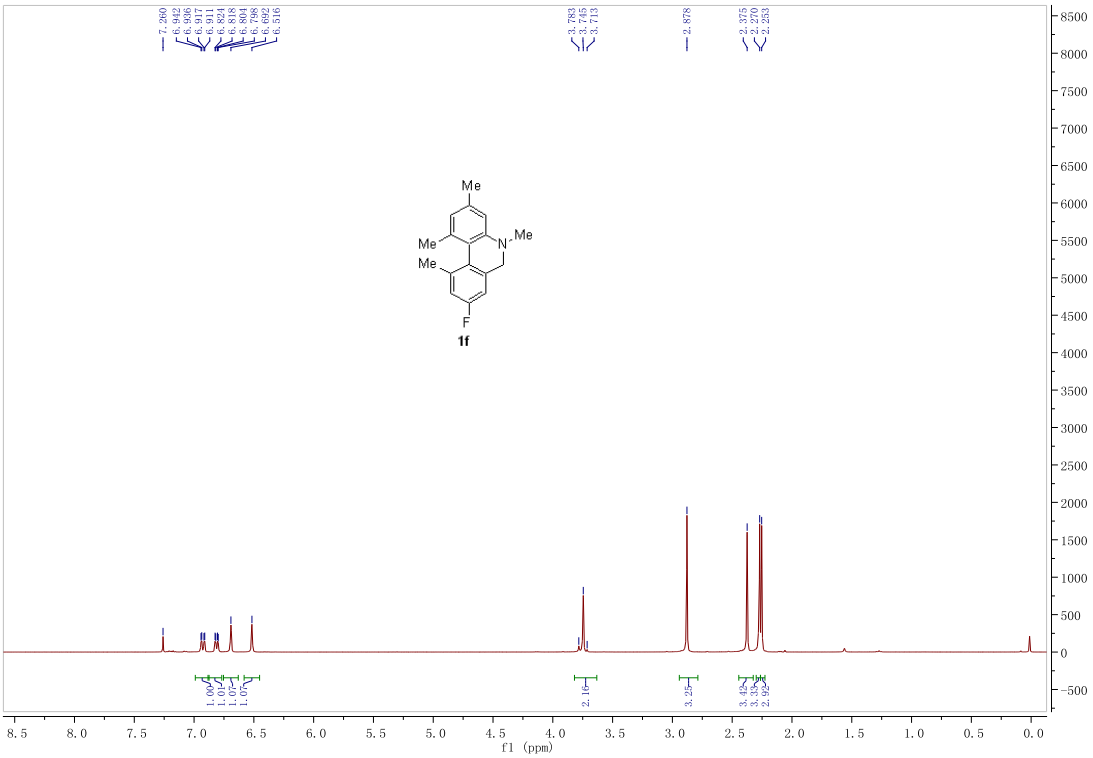

7.260
7.225
7.206
7.188
7.169
7.087
7.070
6.854
6.835
6.700
6.680
3.790
2.891
2.310
2.281
1.547
0.005
Me
Me
N
Me
1d
1.95
0.85
0.95
1.01
0.99
2.00
3.03
3.06
2.71
f1 (ppm)


150.889
139.190
135.687
135.105
131.764
130.123
127.531
126.151
124.872
122.698
121.667
109.198
77.318
77.000
76.683
57.276
39.104
21.140
20.935
Me
Me
N
Me
1d
f1 (ppm)


7.260
7.180
7.161
7.144
6.958
6.937
6.916
6.694
6.526
4.224
4.192
3.528
3.496
2.904
2.381
2.265
2.241
1.559
0.019
Me
Me
N
Me
F
1e
1.02
1.01
1.09
1.00
1.03
1.05
3.17
3.13
3.16
2.91
f1 (ppm)


156.826
154.430
150.714
137.852
135.649
133.888
133.848
130.651
130.571
130.290
130.250
125.217
125.054
122.770
122.063
122.036
112.886
112.673
110.385
77.317
77.000
76.682
49.411
49.369
39.108
21.642
21.073
20.502
Me
Me
Me
N
F
1e
f1 (ppm)


-126.500
Me
Me
Me
N
F
1e
f1 (ppm)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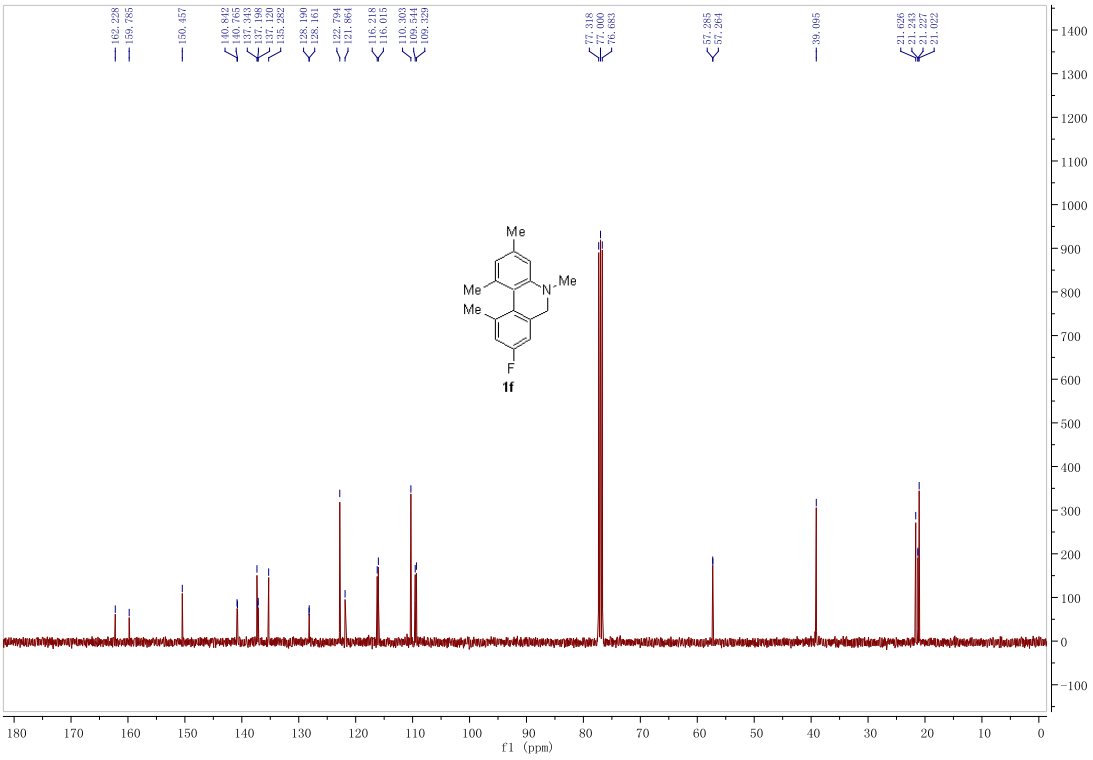
6.911
6.824
6.818
6.804
6.798
6.692
6.516
3.783
3.745
3.713
2.878
2.375
2.270
2.253
Me
Me
Me
N
F
1f
1.00
1.01
1.07
1.07
2.16
3.25
3.42
3.35
2.92
f1 (ppm)


162.228
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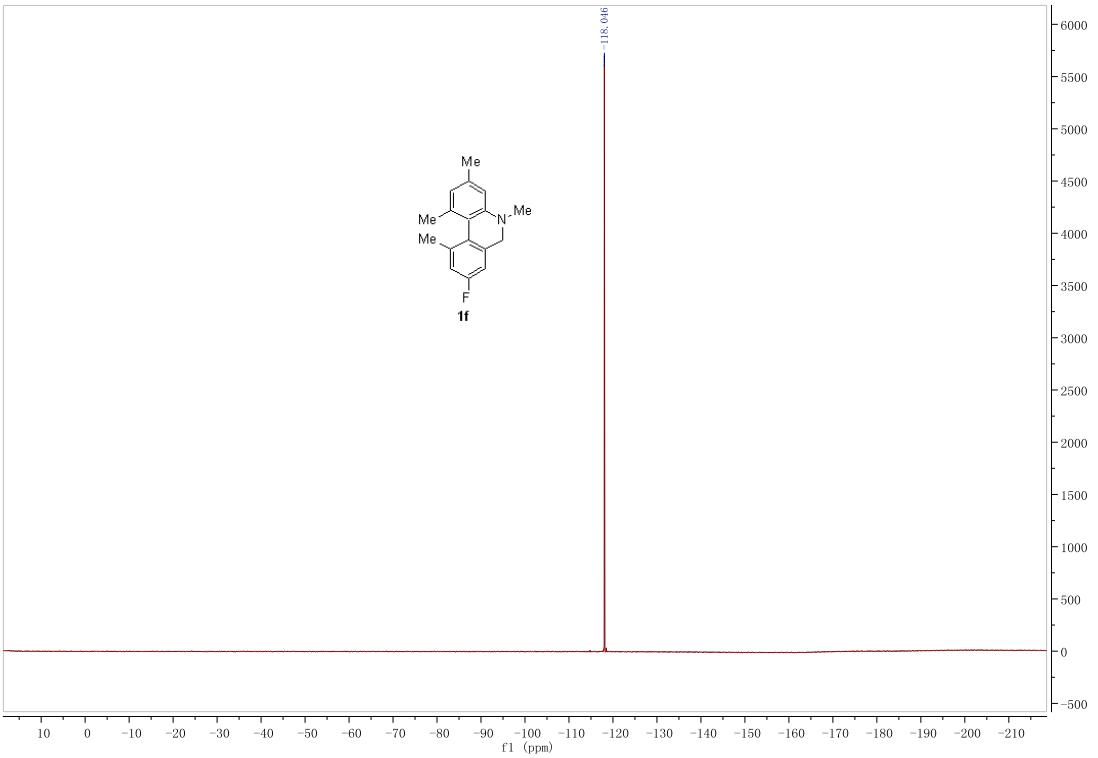
150.457
140.812
140.765
137.343
137.198
137.110
135.282
128.190
128.161
122.794
121.864
116.218
116.015
110.303
109.544
109.329
77.318
77.000
76.683
57.285
57.264
39.095
21.626
21.243
21.227
21.022
Me
Me
Me
N
F
1f
f1 (ppm)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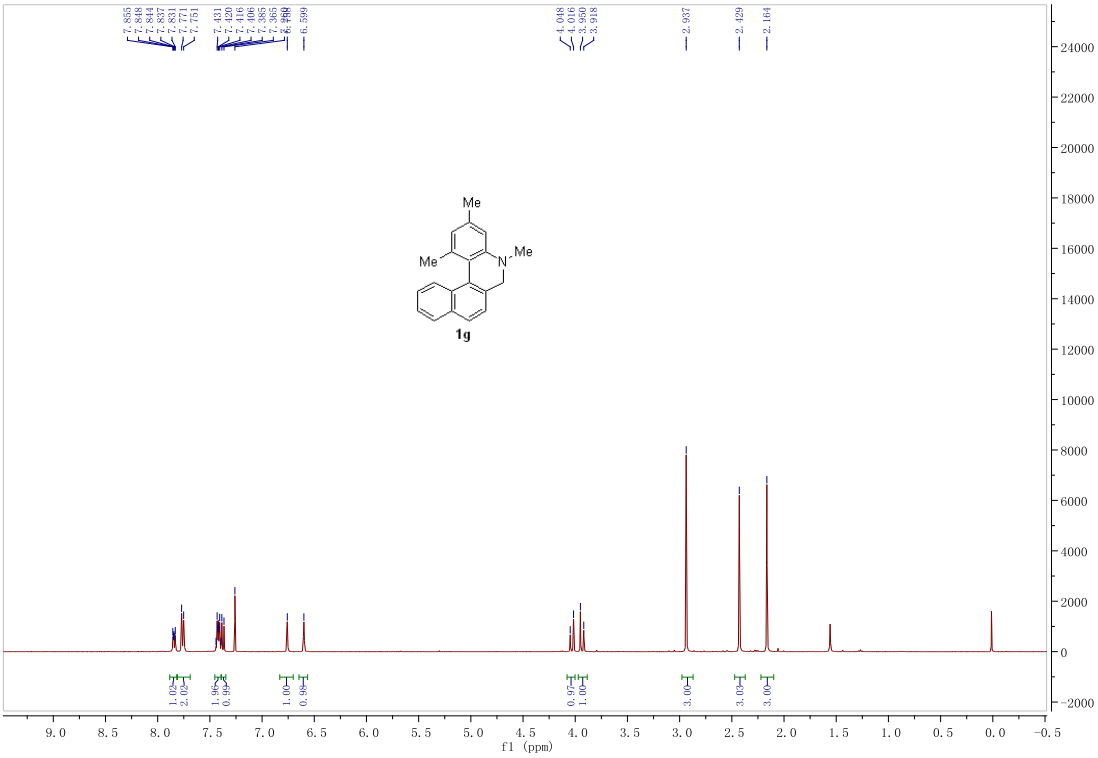
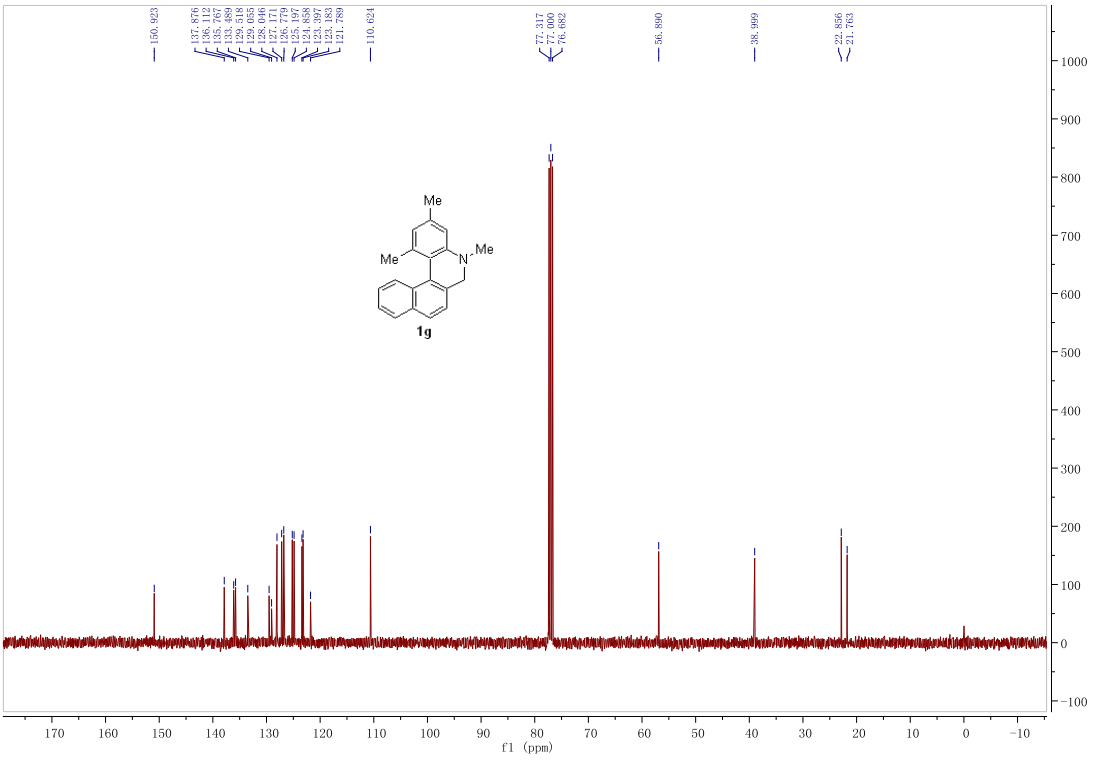
Me
Me
Me
N
Me
F
1f
f1 (ppm)


7.855
7.848
7.844
7.837
7.831
7.771
7.751
7.431
7.410
7.416
7.406
7.385
6.599
4.048
4.016
3.950
3.918
2.937
2.429
2.164
Me
Me
N
Me
1g
f1 (ppm)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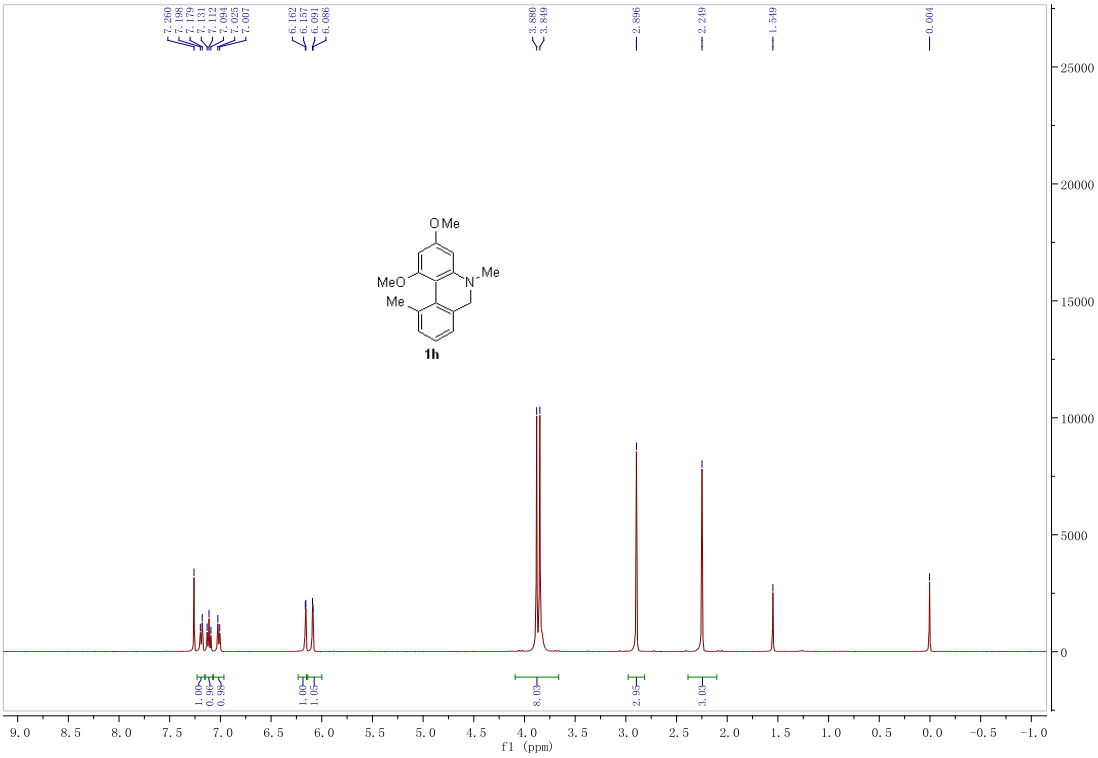
128.046
127.171
126.779
125.197
124.838
123.397
123.183
121.769
110.624
77.317
77.000
76.682
56.890
38.999
22.856
21.763
Me
Me
N
Me
1g
f1 (ppm)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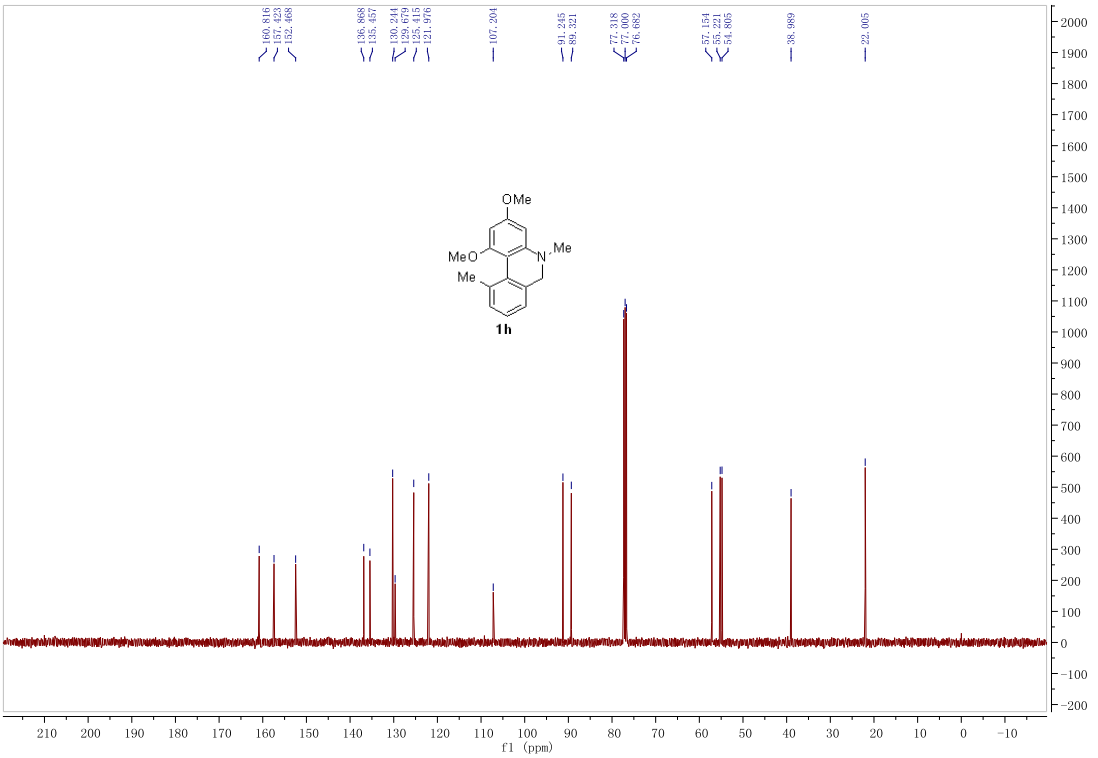
7.198
7.179
7.131
7.112
7.094
7.025
7.007
6.162
6.157
6.091
6.086
3.880
3.849
2.896
2.249
1.549
0.004
OMe
MeO
Me
N
Me
1h
1.00
0.98
0.98
1.00
1.05
8.03
2.95
3.03
f1 (ppm)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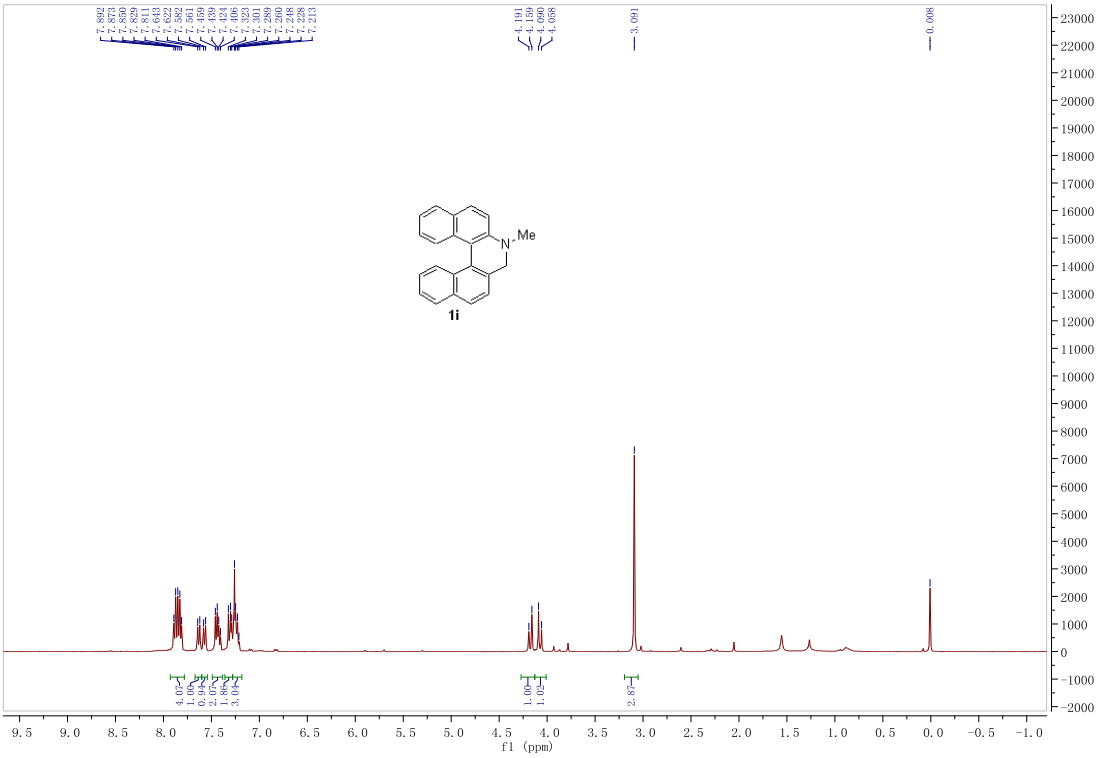
135.457
130.244
129.679
125.415
121.976
107.204
91.245
89.321
77.318
77.000
76.682
57.154
55.221
54.805
38.989
22.005
OMe
MeO
Me
N
Me
1h
f1 (ppm)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7.811
7.645
7.622
7.382
7.361
7.359
7.439
7.424
7.406
7.323
7.301
7.289
7.260
7.248
7.228
7.213
4.191
4.159
4.090
4.058
3.091
0.008
N
Me
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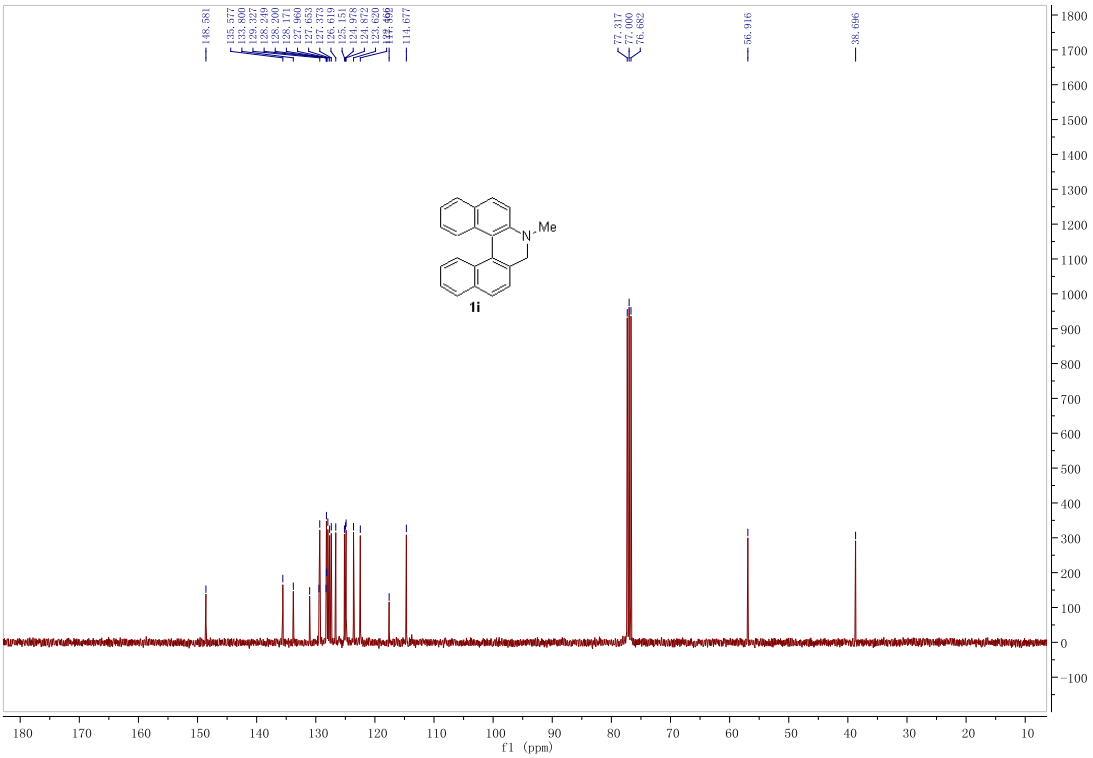
1.05
0.94
0.97
1.88
3.04
1.00
1.02
2.87
f1 (ppm)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127.960
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127.373
126.619
125.151
124.976
124.872
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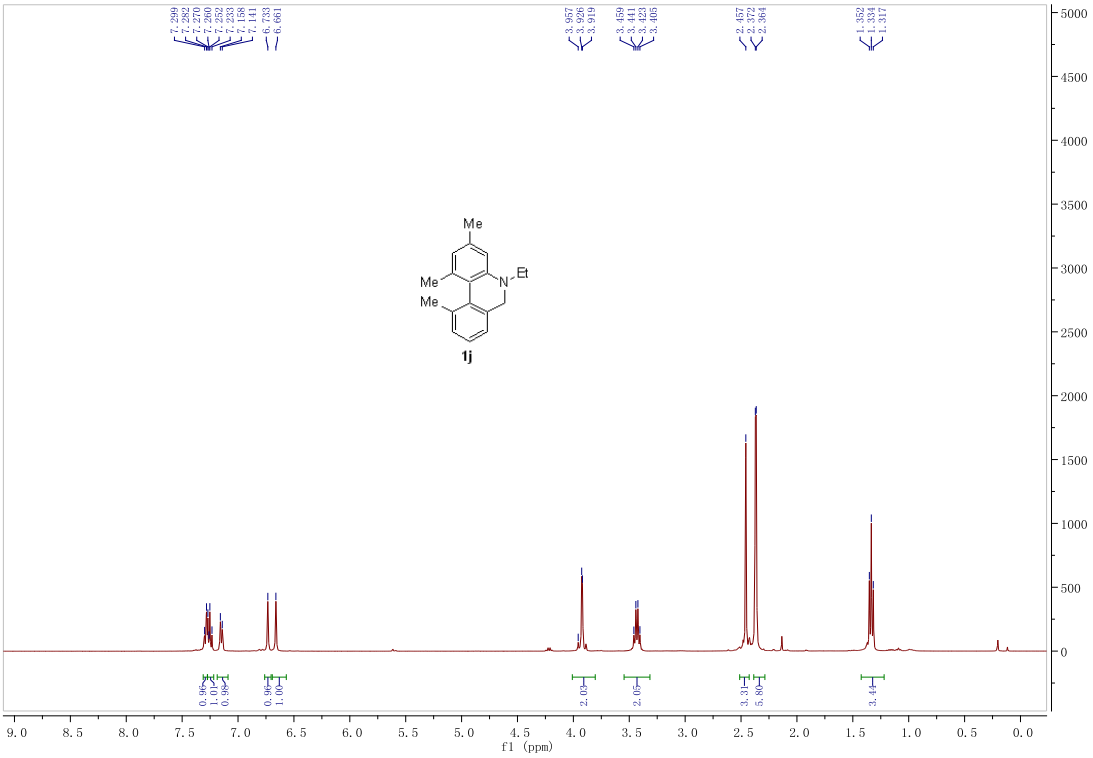
114.677
77.317
77.000
76.682
56.916
38.696
Me
N
1i
f1 (ppm)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7.198
7.141
6.733
6.661
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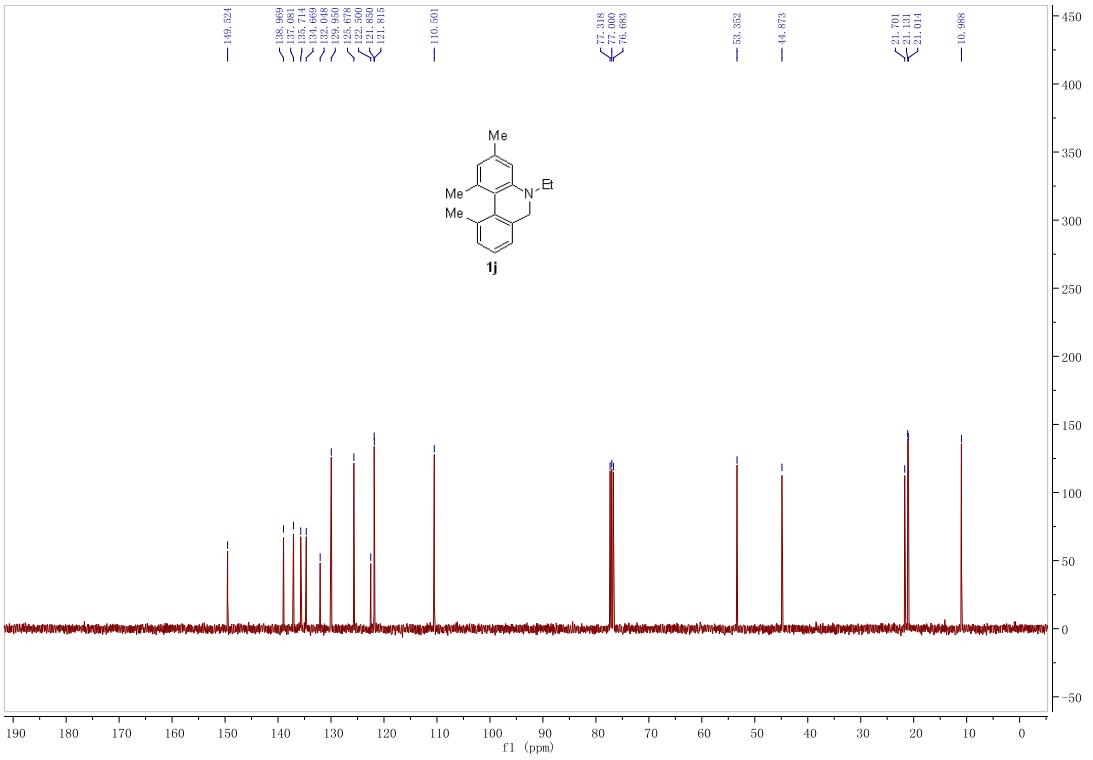
3.919
3.459
3.441
3.423
3.405
2.457
2.372
2.364
1.352
1.334
1.317
Me
Me
Me
N
Et
1j
f1 (ppm)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135.714
134.698
132.048
129.950
125.678
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121.950
121.815
110.501
77.318
77.000
76.683
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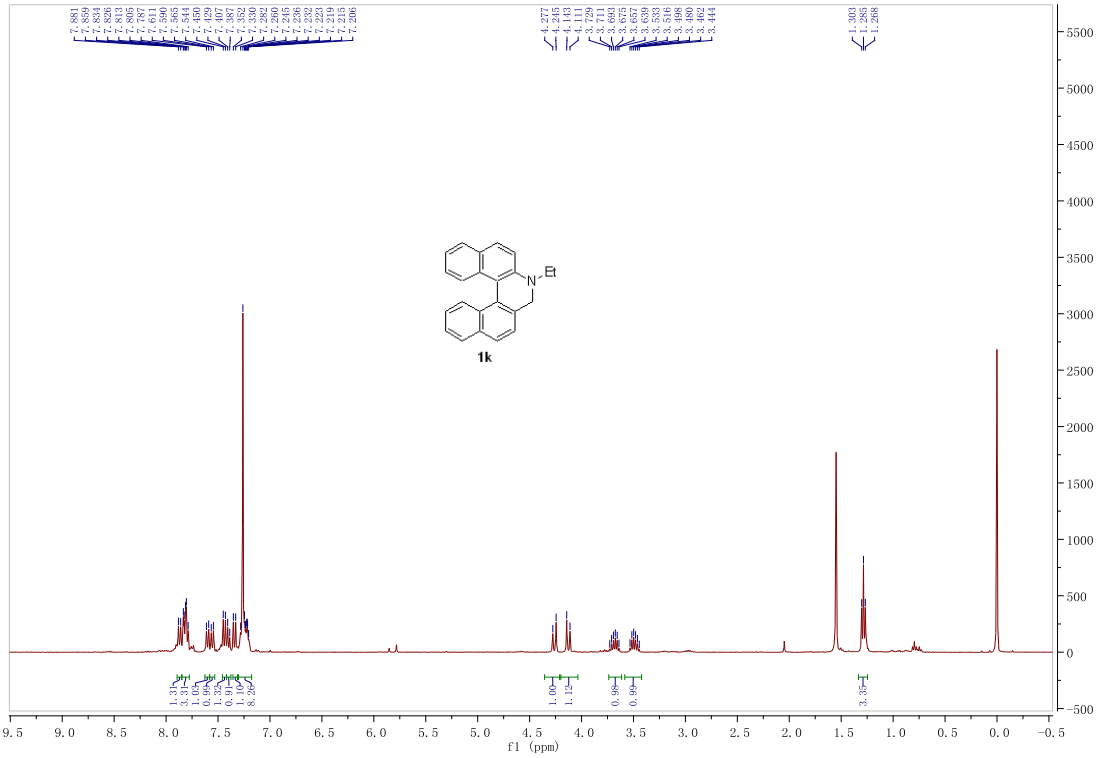
21.701
21.131
21.014
10.988
Me
Me
Me
N
Et
1j
f1 (ppm)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7.813
7.805
7.787
7.611
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7.544
7.450
7.429
7.407
7.387
7.352
7.330
7.292
7.260
7.245
7.236
7.232
7.223
7.219
7.215
7.206
4.277
4.245
4.143
4.111
3.729
3.711
3.695
3.675
3.657
3.639
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3.462
3.444
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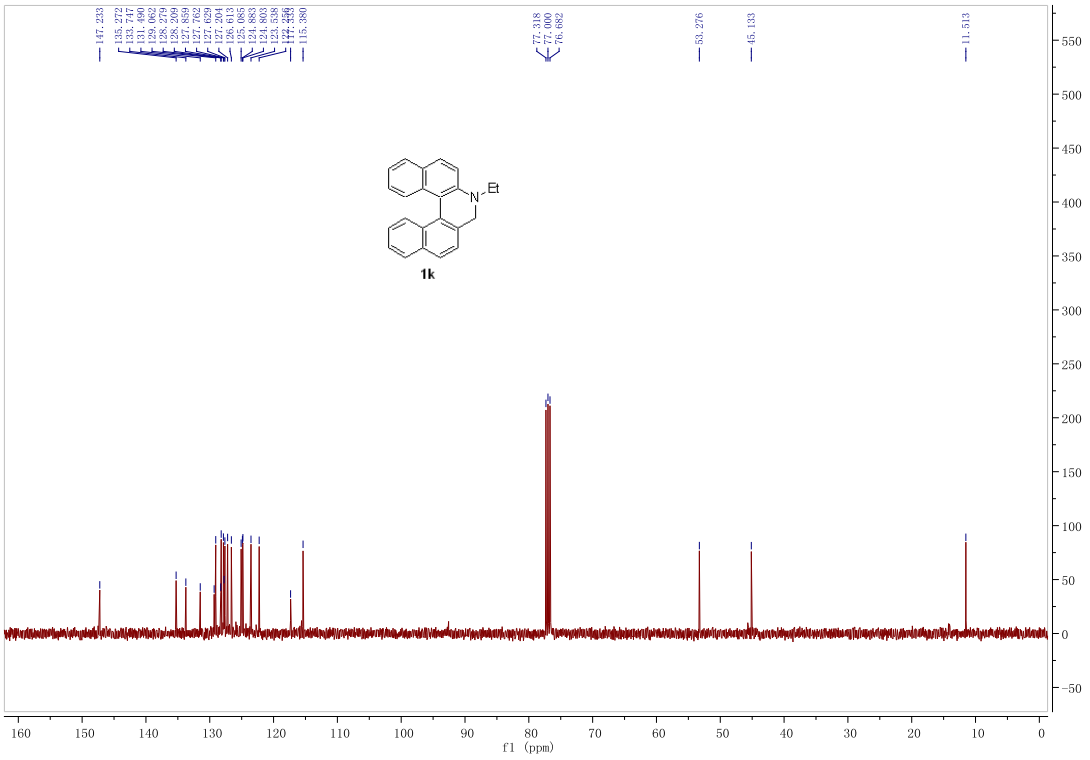
1.268
N
Et
1k
f1 (ppm)


147.233
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129.062
128.279
128.094
127.859
127.762
127.629
127.204
126.743
125.085
124.803
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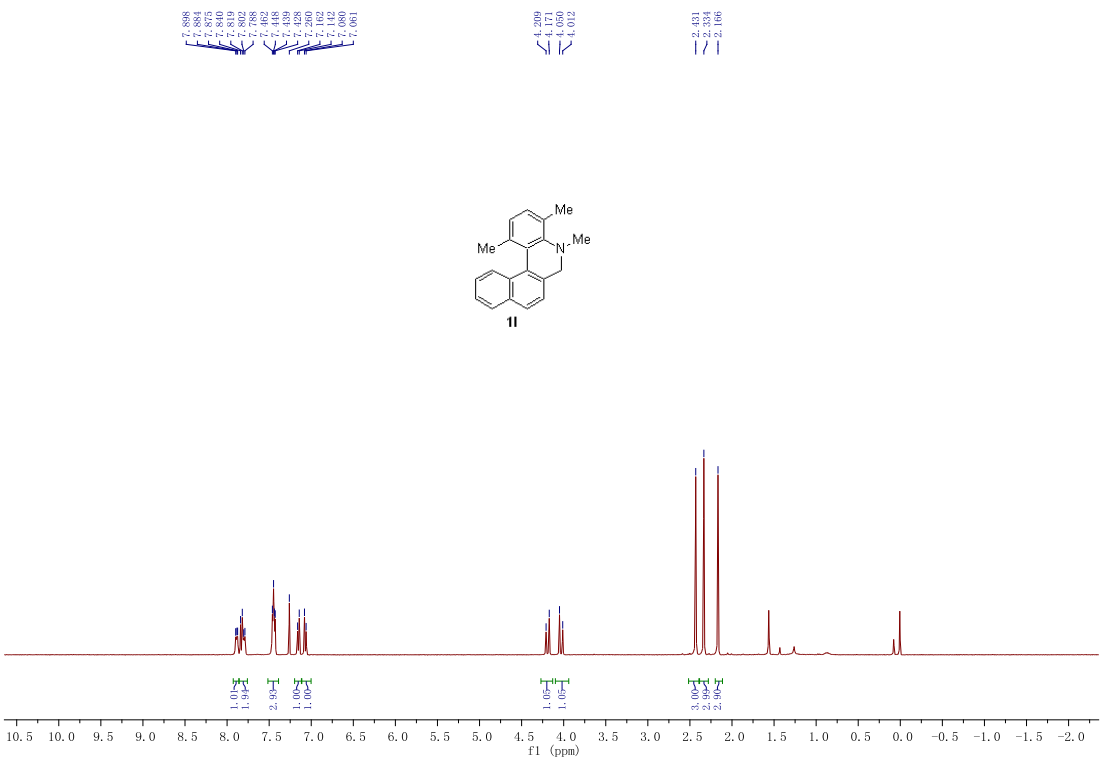
77.318
77.000
76.682
53.276
45.133
11.513
N
Et
1k
f1 (ppm)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7.812
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7.439
7.290
7.162
7.142
7.090
7.081
4.209
4.171
4.050
4.012
2.431
2.334
2.166
Me
Me
N
Me
1l
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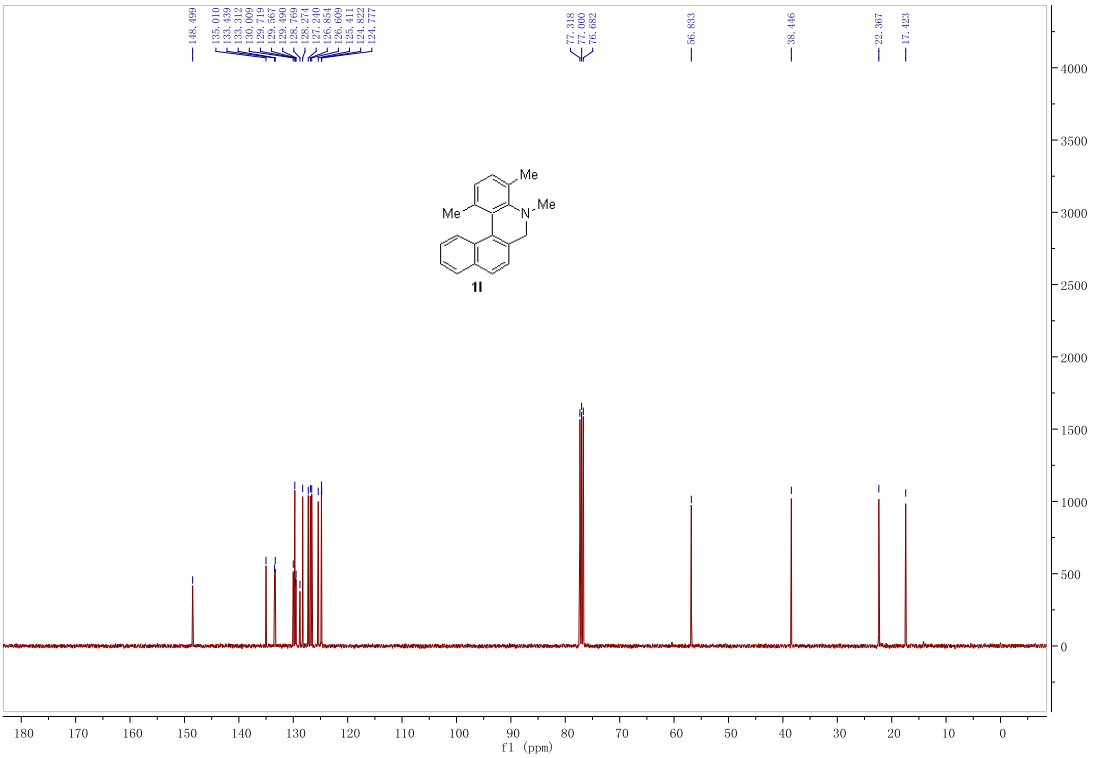
2.89
1.00
1.00
1.05
1.05
3.00
2.04
2.05
f1 (ppm)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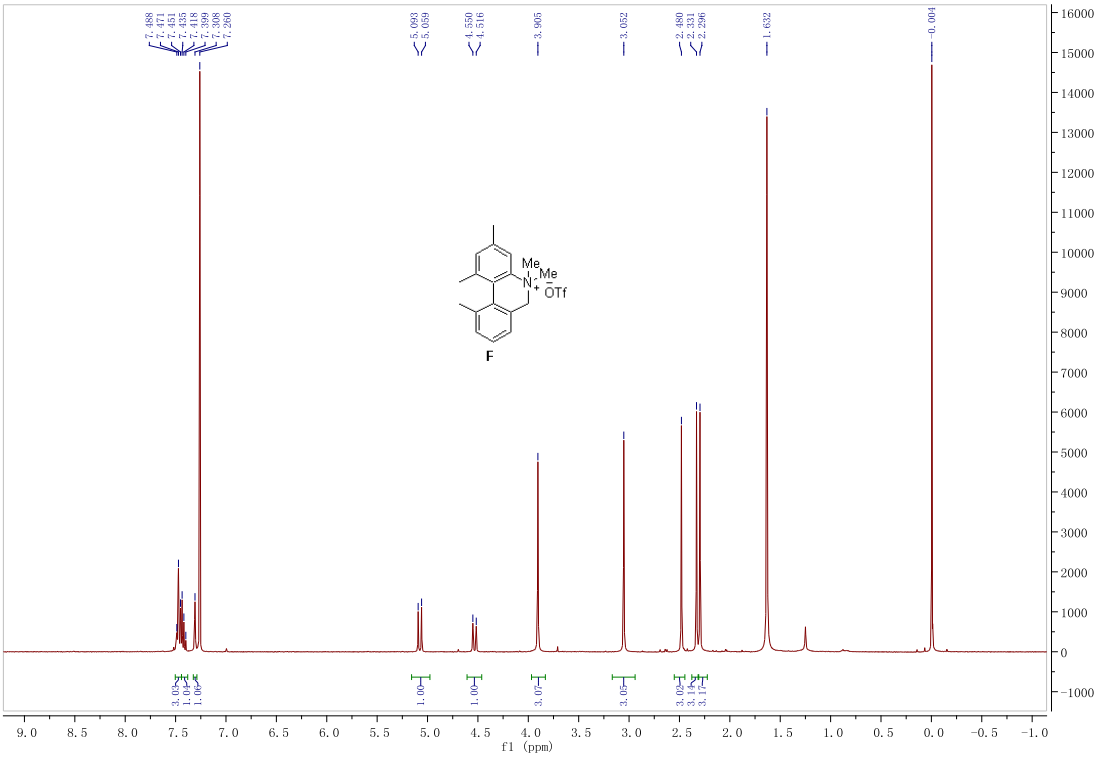
135.010
133.439
133.312
130.009
129.719
129.557
129.460
128.769
128.274
127.240
126.694
126.609
125.411
124.822
124.777
77.318
77.000
76.682
56.833
38.446
22.367
17.423
Me
Me
N
Me
1l
f1 (ppm)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7.288
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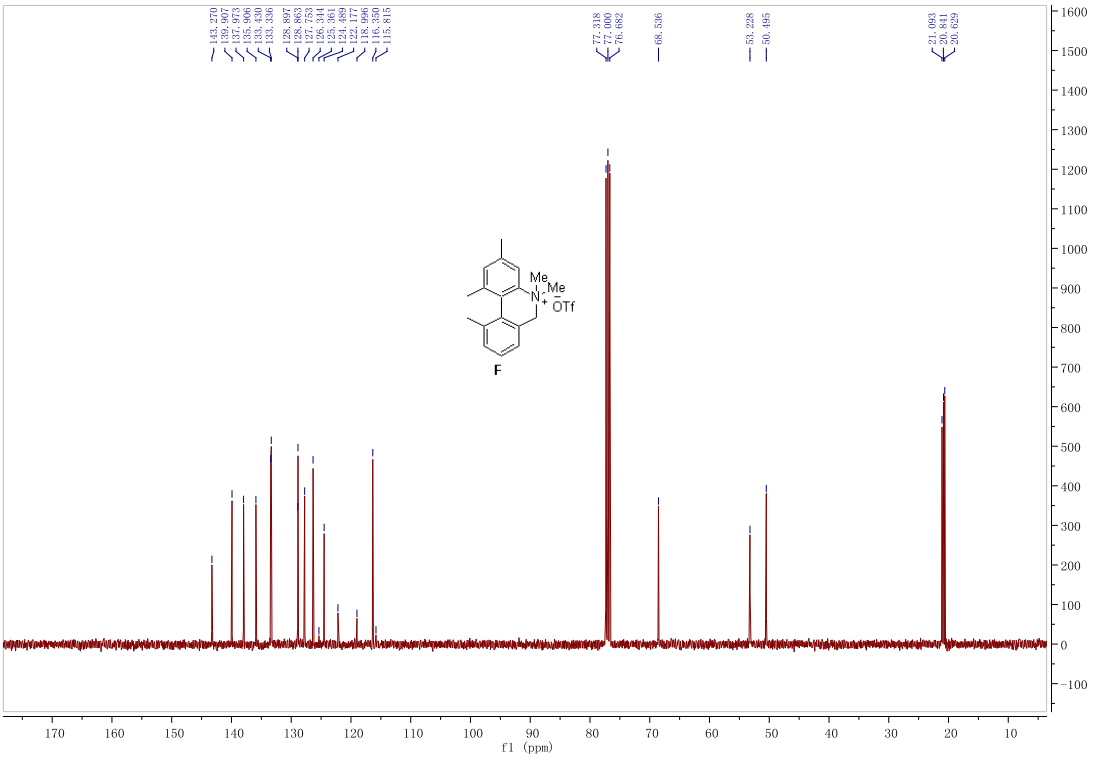
5.059
4.550
4.516
3.965
3.052
2.489
2.331
2.296
1.632
-0.004
Me
N
Me
OTf
F
3.03
1.04
1.00
1.00
1.00
3.07
3.05
3.02
3.14
3.17
f1 (ppm)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128.897
128.865
127.753
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122.177
118.996
116.350
115.815
77.318
77.000
76.682
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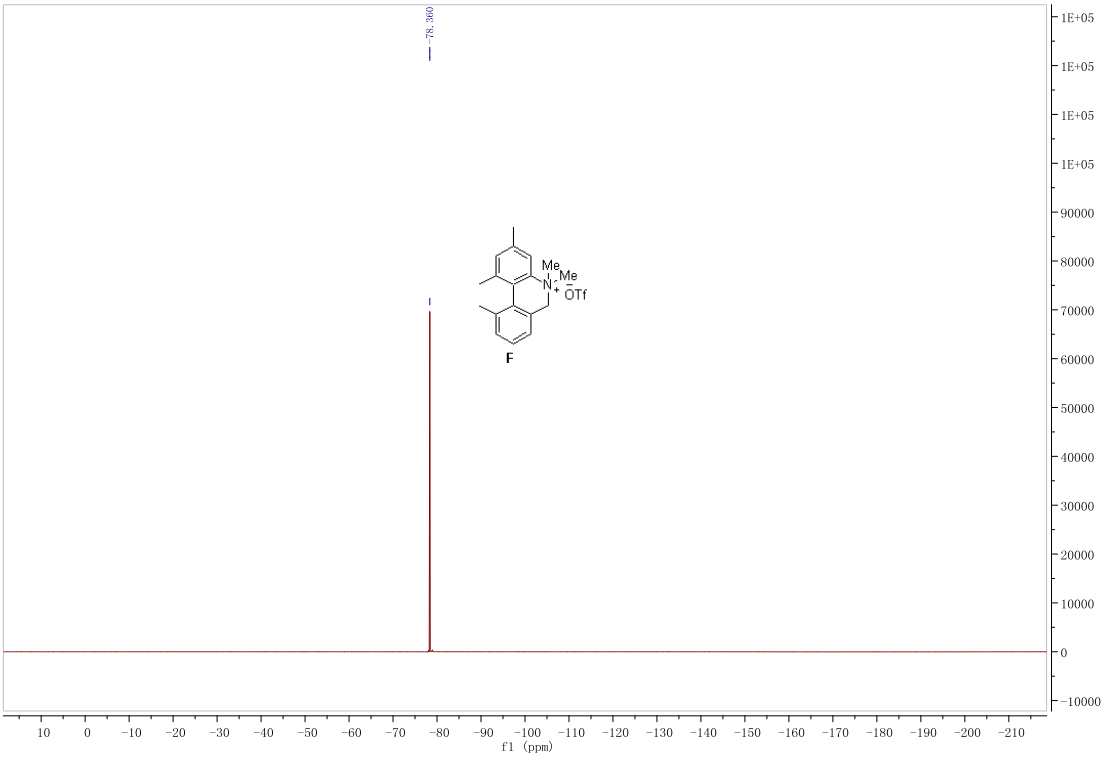
53.228
50.495
21.093
20.841
20.629
Me
Me
N
OTf
F
f1 (ppm)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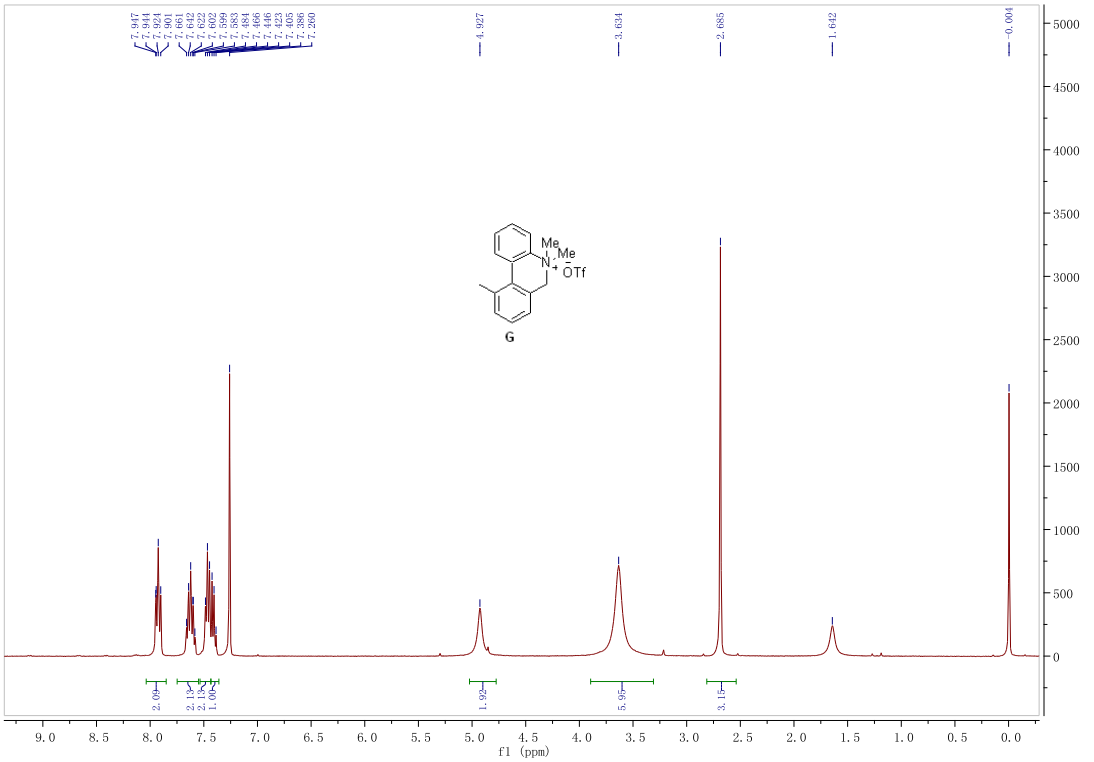
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7.924
7.901
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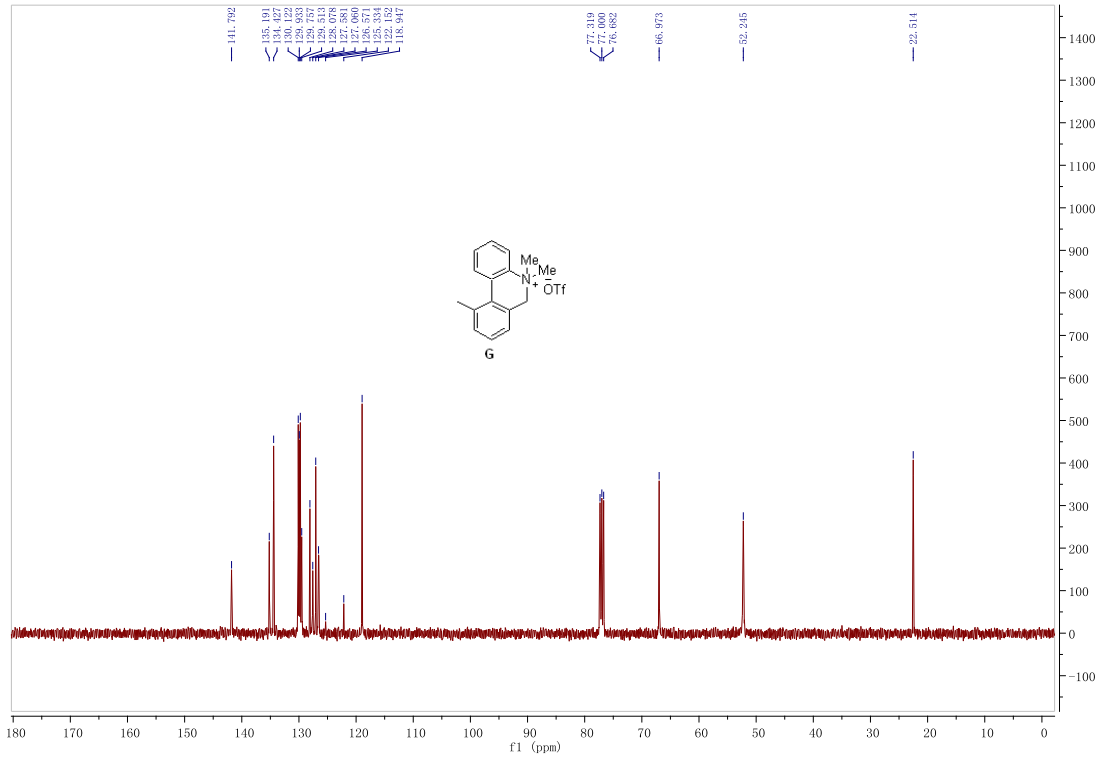
7.642
7.622
7.602
7.599
7.583
7.484
7.466
7.446
7.423
7.405
7.396
7.280
4.927
3.634
2.685
1.642
-0.004
Me
Me
N+
OTf
G
2.09
2.13
2.15
1.00
1.92
5.96
3.15
f1 (ppm)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135.191
134.427
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128.753
128.078
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125.934
125.182
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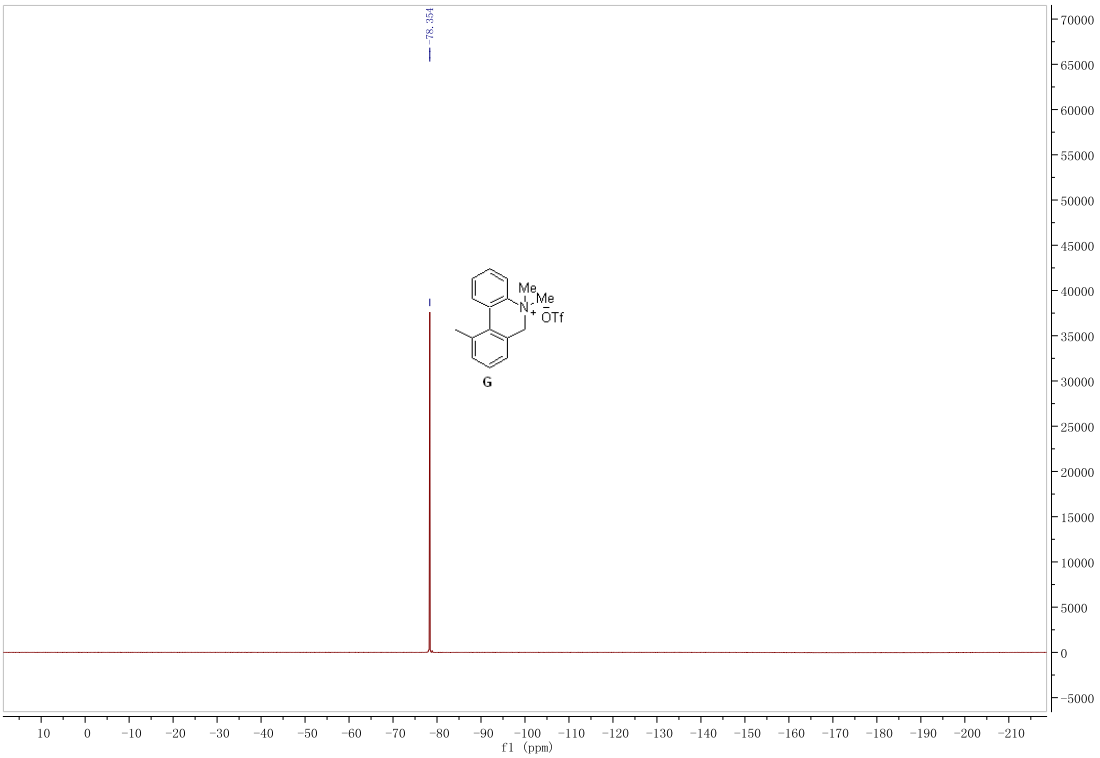
77.000
76.682
66.973
52.245
22.514
Me
Me
N+
OTf
G
f1 (ppm)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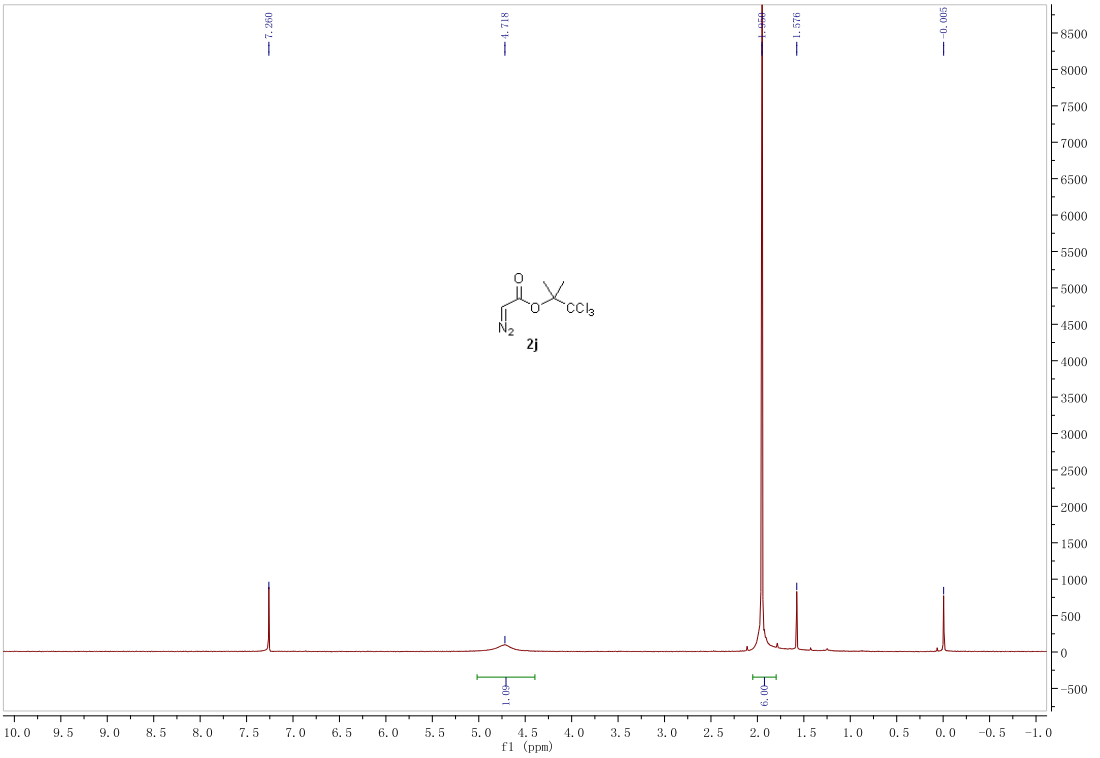
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O
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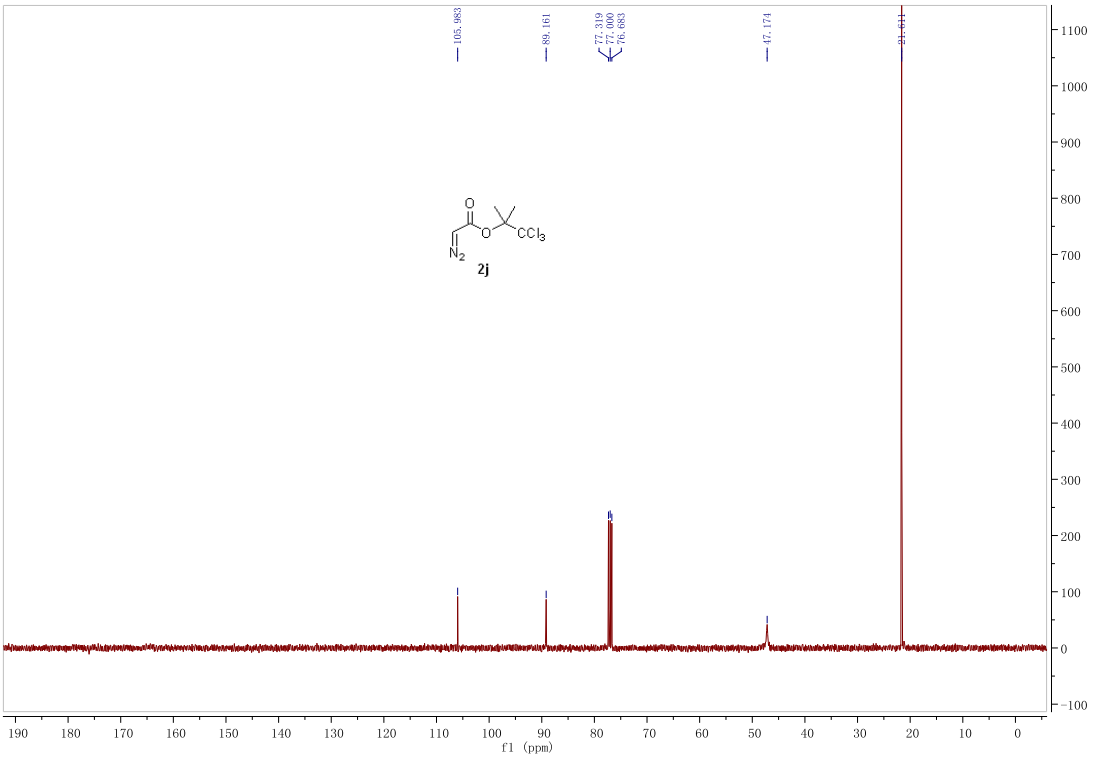
CCl3
N2
2j
1.09
6.00
f1 (ppm)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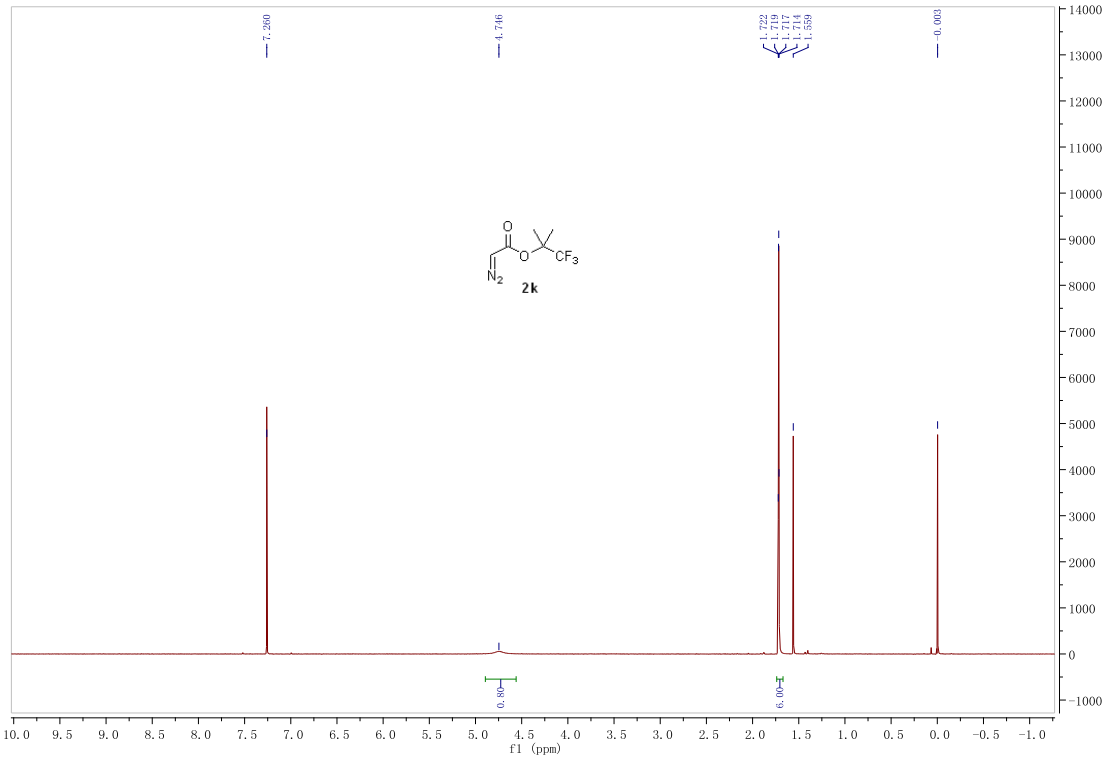
77.319
77.000
76.683
47.174
21.611
2j
f1 (ppm)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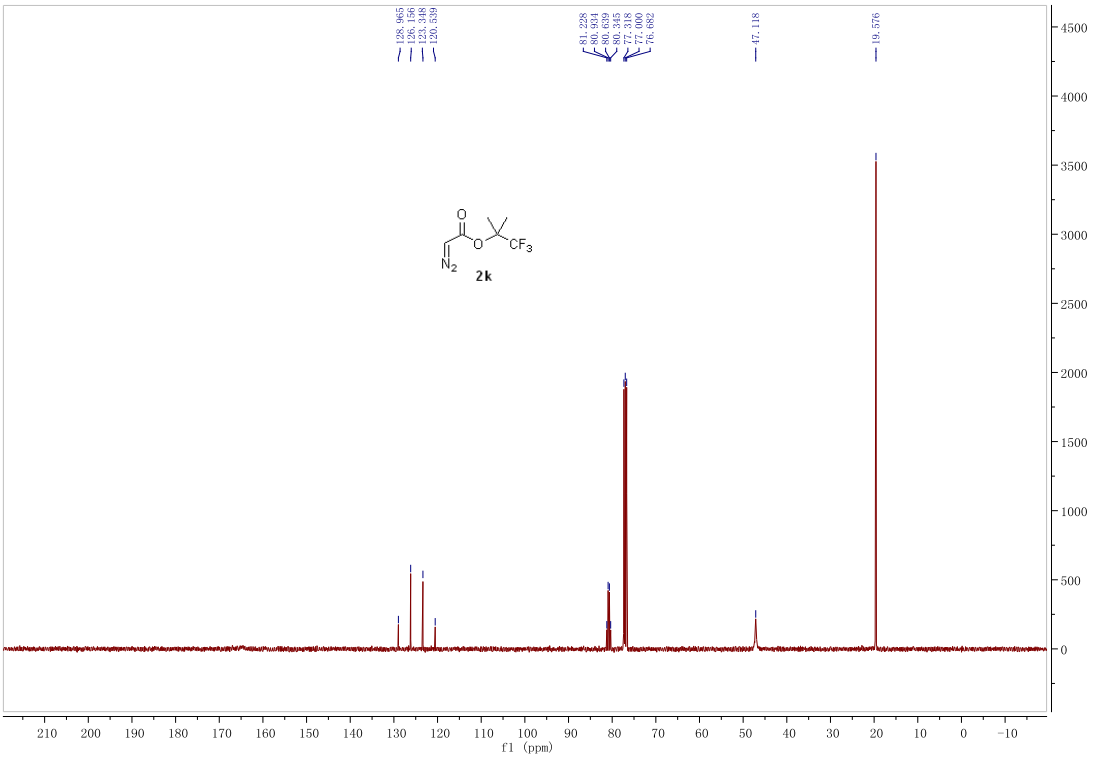
1.714
1.559
-0.003
2k
0.89
6.00
f1 (ppm)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80.345
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77.000
76.682
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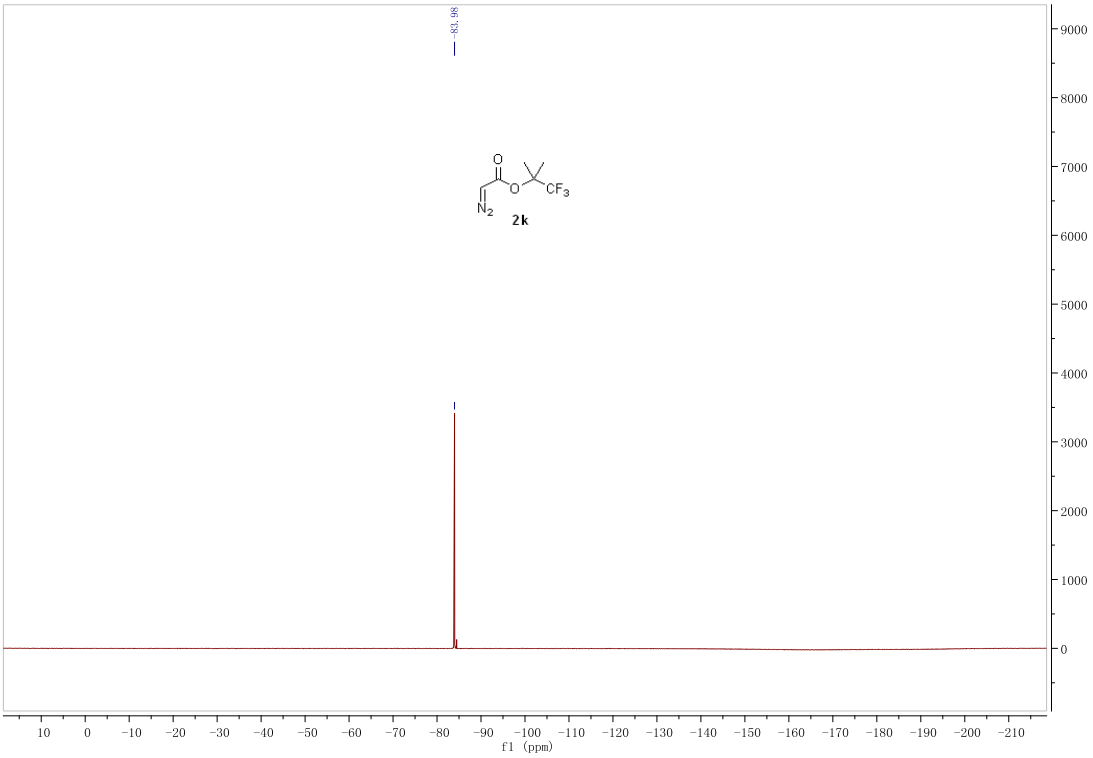
2k
f1 (ppm)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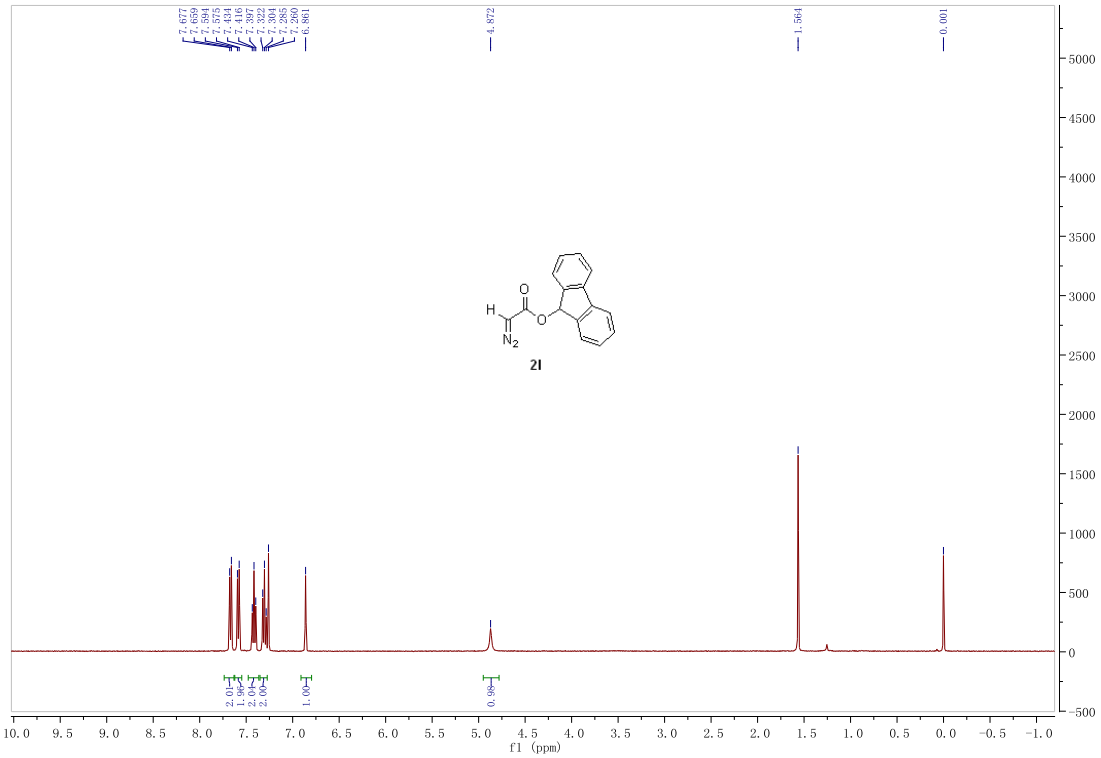
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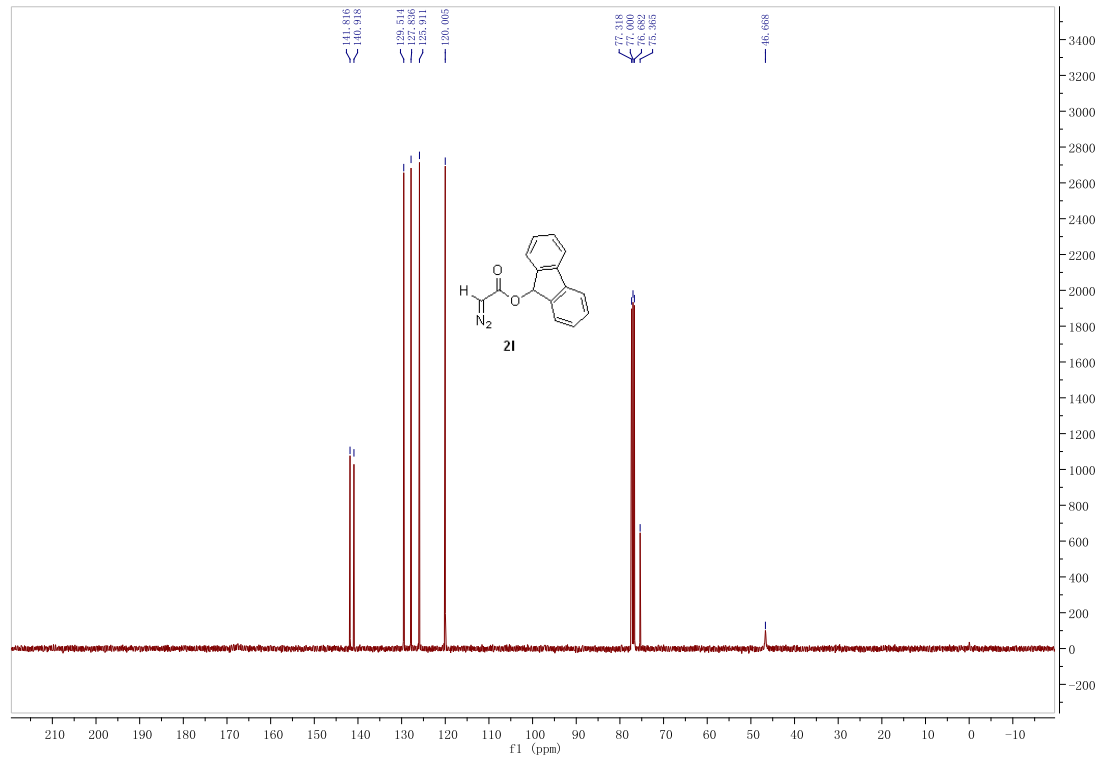
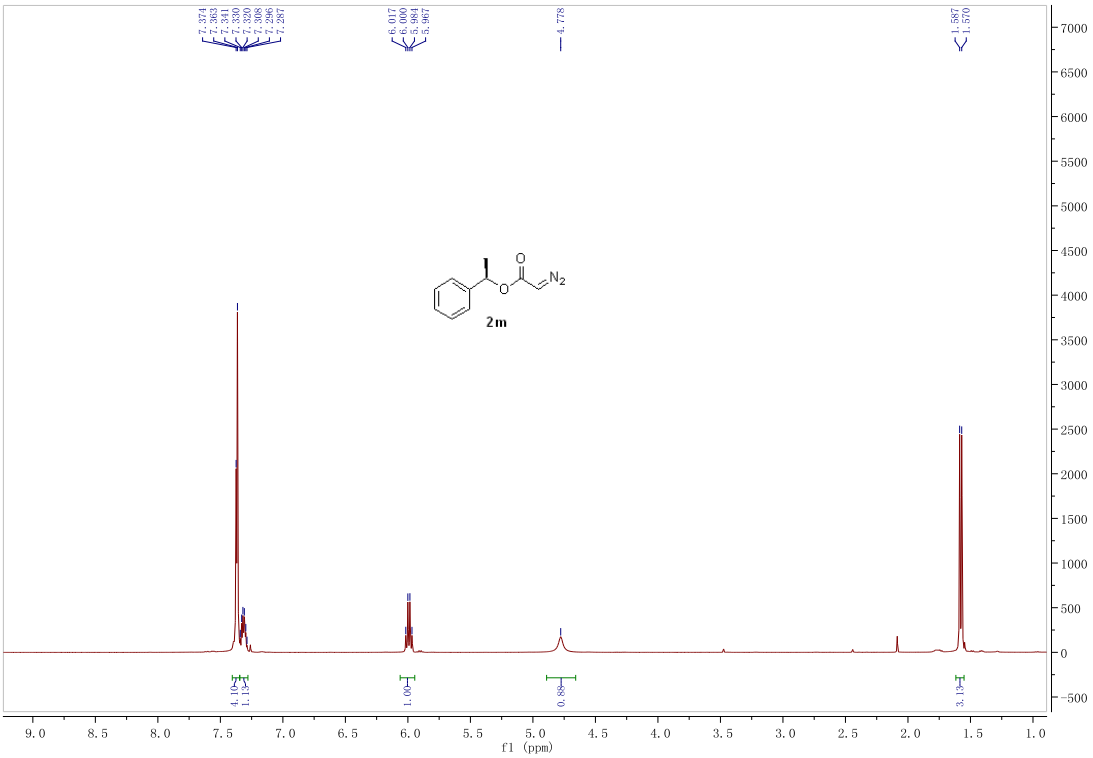
7.659
7.594
7.575
7.434
7.416
7.397
7.322
7.304
7.285
7.269
6.861
4.872
1.564
0.001
2.01
1.96
2.07
2.00
1.00
0.99
2I
f1 (ppm)


141.816
140.918
129.514
127.826
125.911
120.005
77.318
77.000
76.682
75.365
46.668
2I
f1 (ppm)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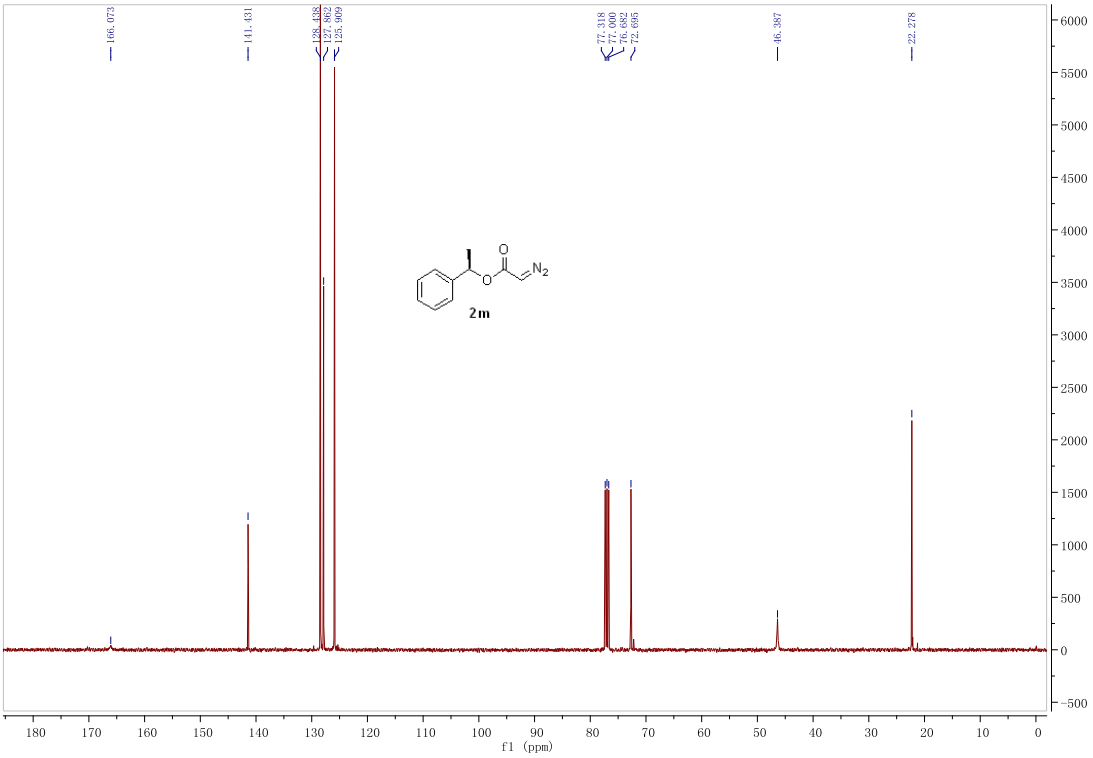
7.363
7.341
7.330
7.320
7.308
7.296
7.287
6.017
6.000
5.984
5.967
4.778
1.587
1.570
2m
4.10
1.15
1.00
0.88
3.13
f1 (ppm)


166.073
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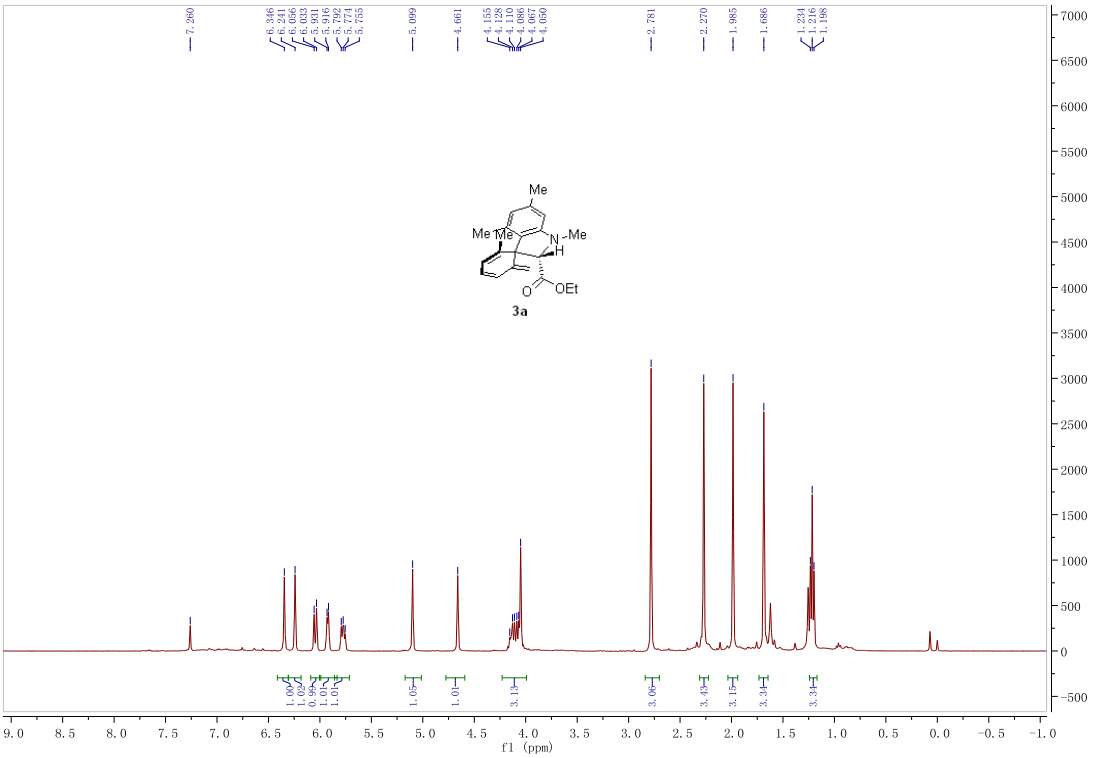
128.438
127.892
125.909
77.318
77.000
76.682
72.685
46.387
22.278
2m
f1 (ppm)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6.346
6.241
6.036
6.033
5.931
5.916
5.792
5.774
5.755
5.099
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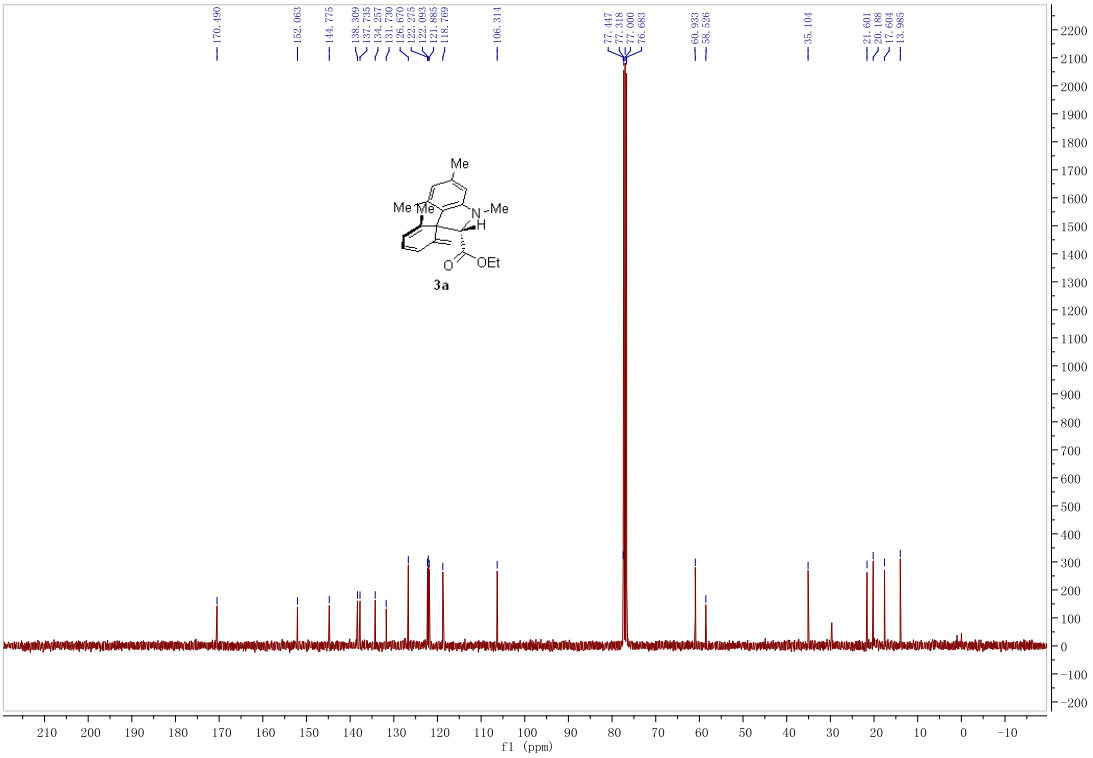
4.155
4.128
4.110
4.086
4.067
4.050
2.781
2.270
1.985
1.686
1.234
1.216
1.198
Me
Me Me
N-Me
H
O
OEt
3a
f1 (ppm)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106.314
77.447
77.318
77.000
76.683
60.933
58.526
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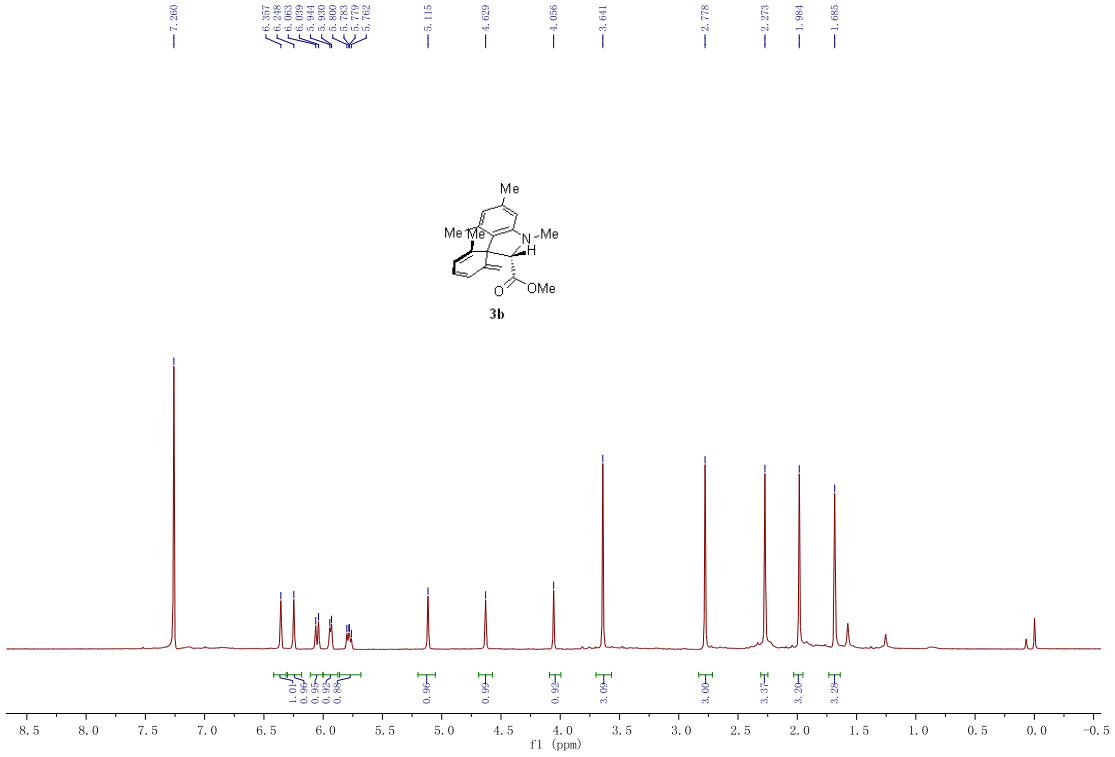
20.188
17.604
15.985
Me
Me Me
N-Me
H
O
OEt
3a
f1 (ppm)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6.039
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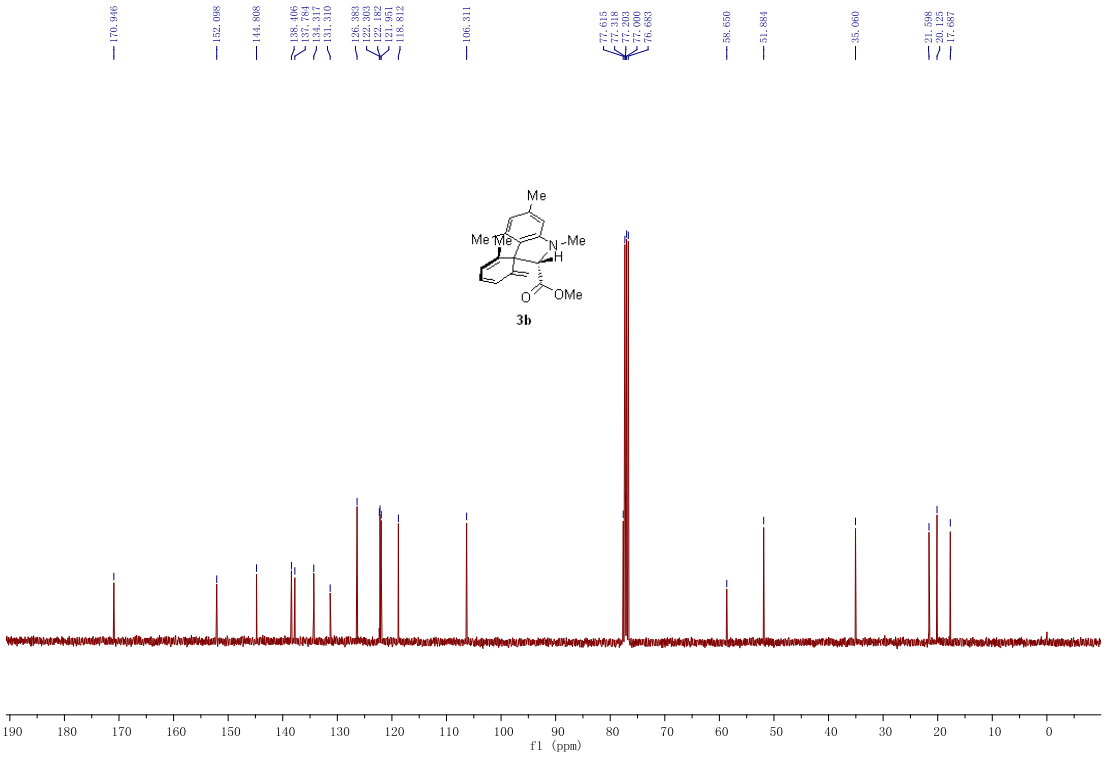
5.800
5.793
5.779
5.762
5.115
4.629
4.056
3.641
2.778
2.273
1.984
1.685
Me
Me
Me
N
Me
H
O
OMe
3b
1.01
0.96
0.97
0.95
0.88
0.96
0.99
0.92
3.09
3.00
3.37
3.20
3.28
f1 (ppm)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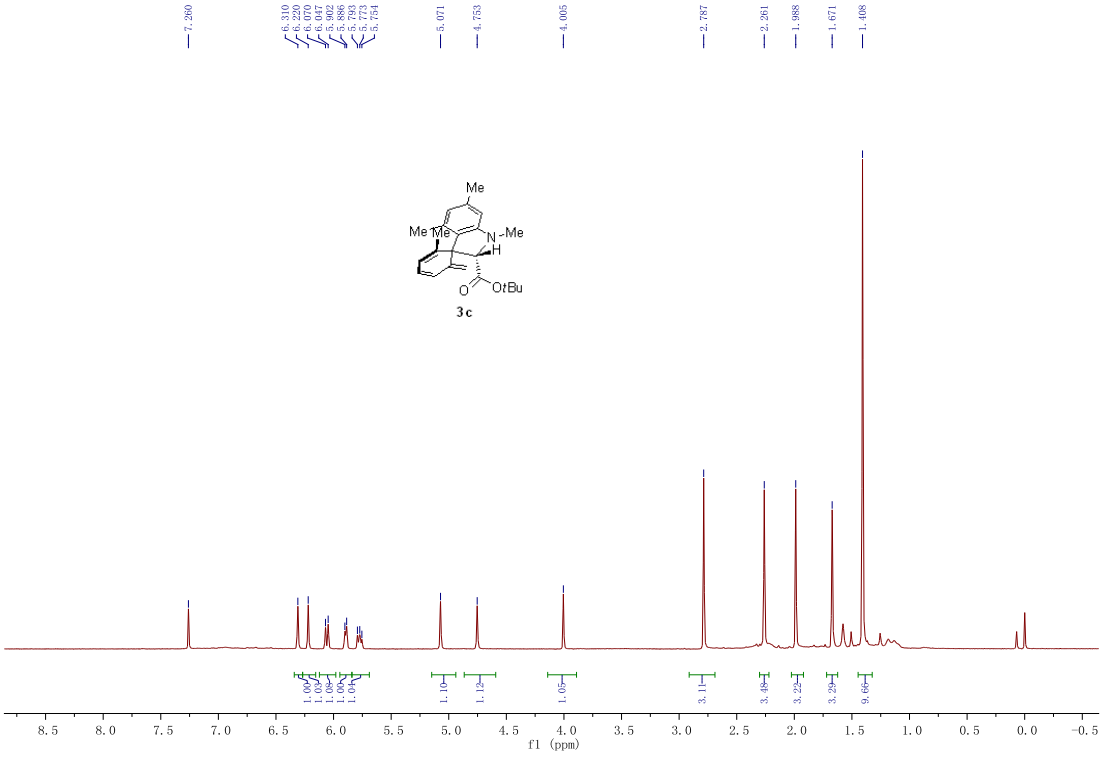
126.383
122.303
122.182
121.991
118.812
106.311
77.615
77.318
77.203
77.000
76.683
58.650
51.884
35.060
21.598
20.125
17.687
Me
Me
Me
N
Me
H
O
OMe
3b
f1 (ppm)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5.896
5.793
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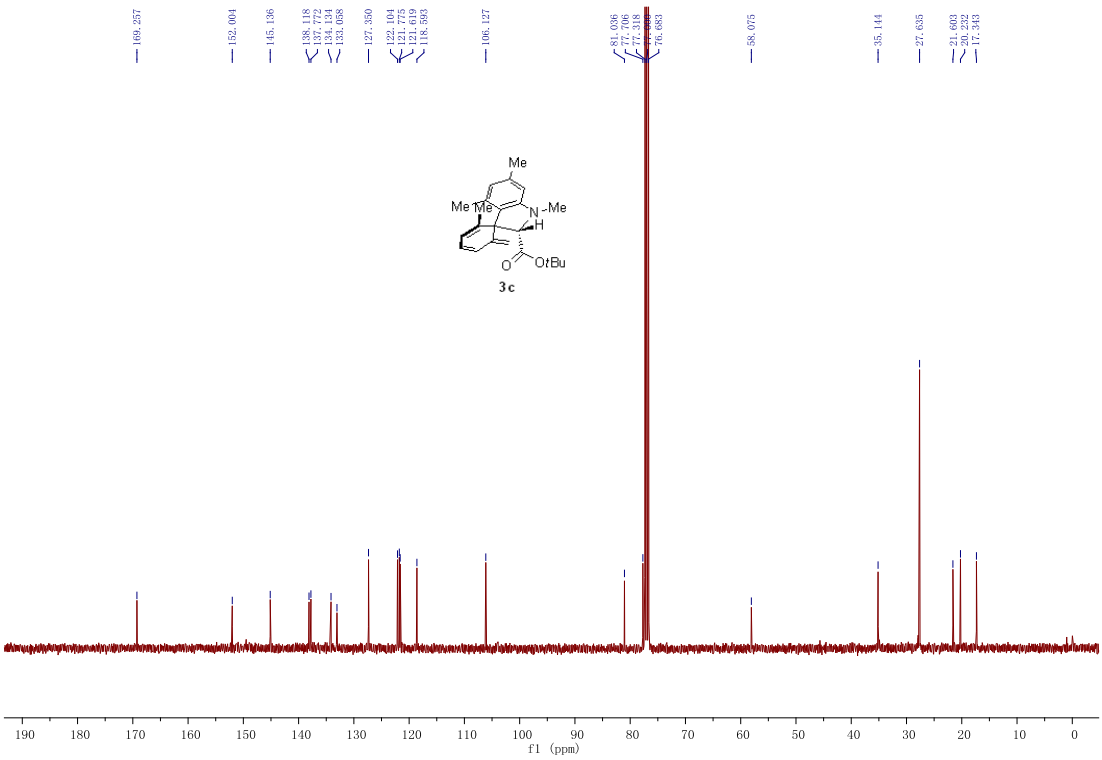
5.071
4.753
4.005
2.787
2.261
1.988
1.671
1.408
Me
Me Me
N-Me
H
O
OtBu
3c
1.00
1.03
1.06
1.06
1.04
1.10
1.13
1.05
3.11
3.46
3.23
3.29
9.66
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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81.036
77.706
77.388
77.069
76.683
58.075
35.144
27.635
21.603
20.232
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Me
Me Me
N-Me
H
O
OtBu
3c
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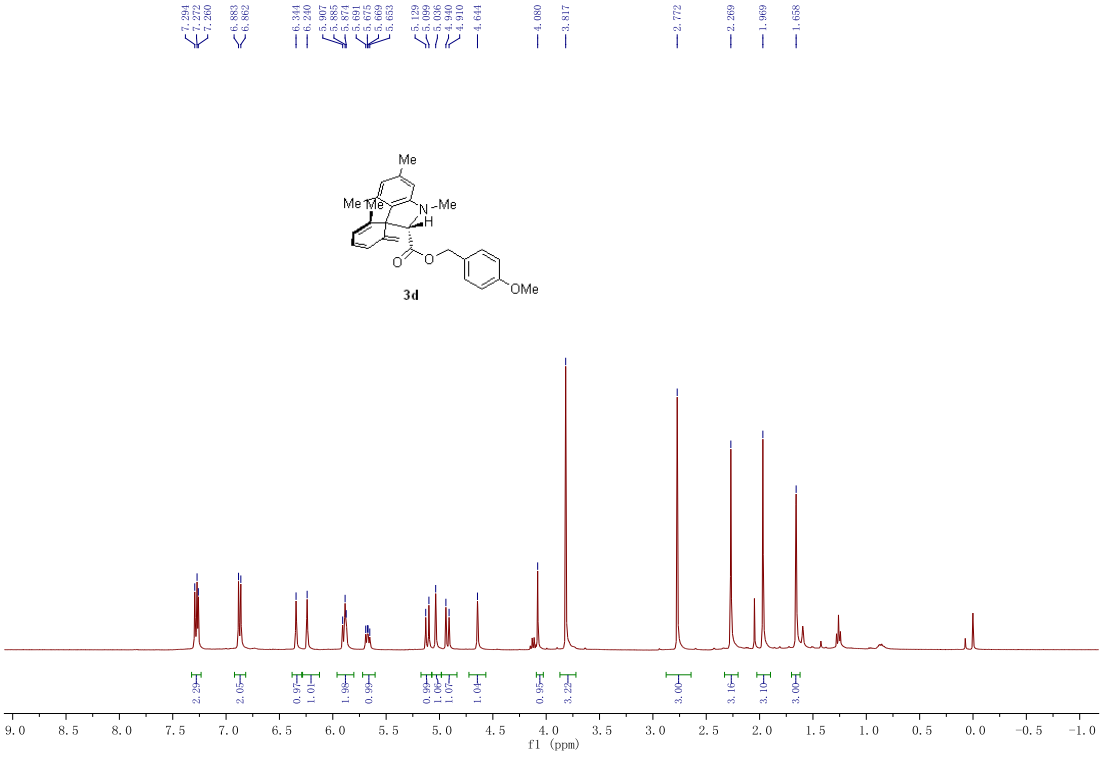
f1 (ppm)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5.669
5.633
5.129
5.094
5.036
4.940
4.910
4.644
4.080
3.817
2.772
2.269
1.969
1.658
Me
Me
Me
N
Me
H
O
O
OMe
3d
2.29
2.05
0.97
1.01
1.98
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1.07
1.04
0.95
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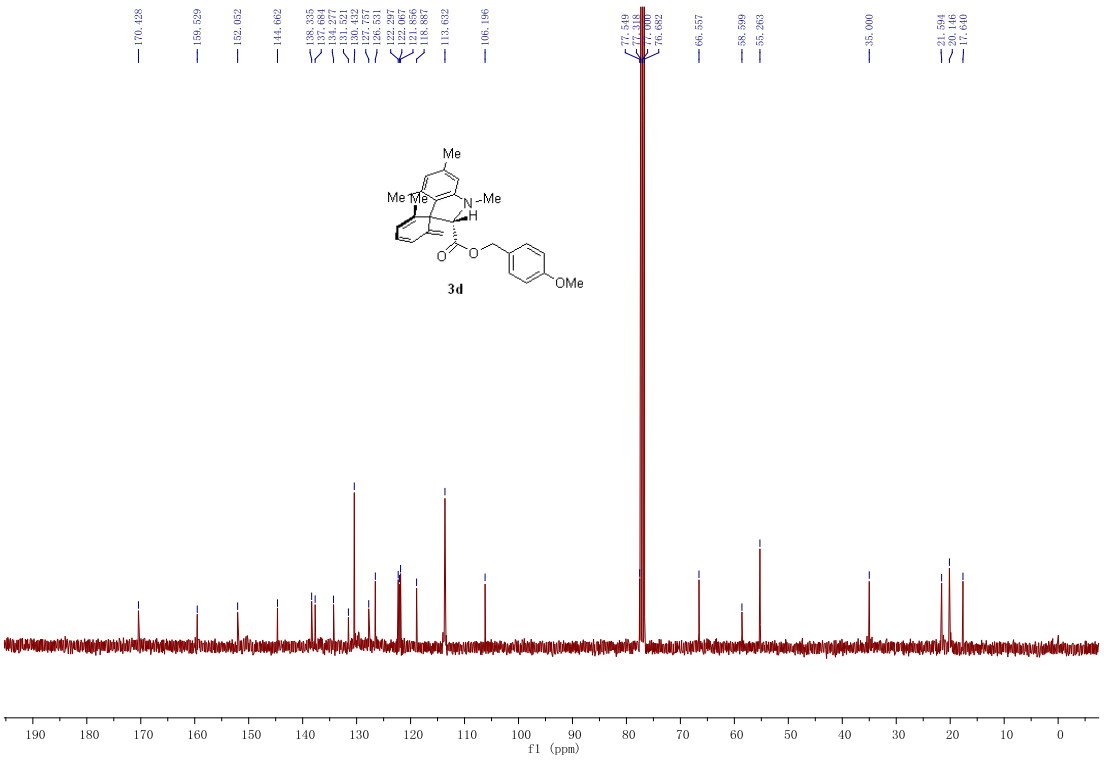
3.00
3.16
3.10
3.00
f1 (ppm)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122.067
121.856
118.887
113.632
106.196
77.549
77.318
77.000
76.682
66.557
58.599
55.263
35.000
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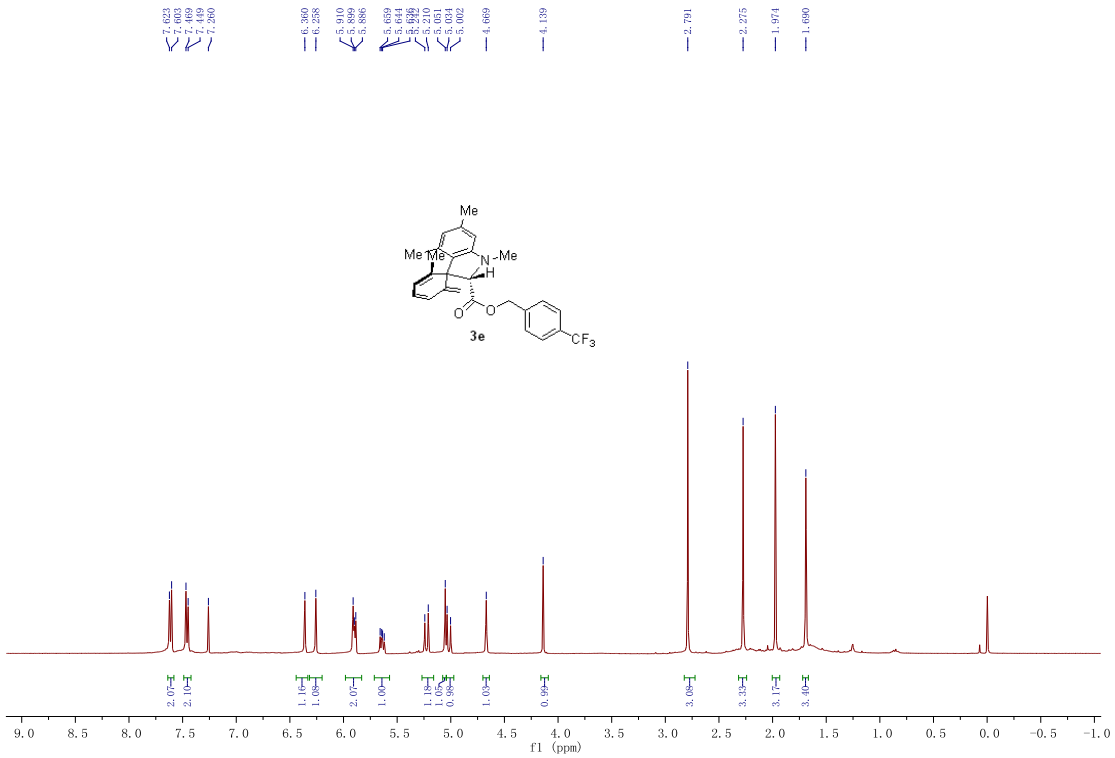
20.146
17.640
Me
Me
Me
N
Me
H
O
O
OMe
3d
f1 (ppm)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5.899
5.886
5.639
5.614
5.232
5.210
5.051
5.034
5.002
4.669
4.139
2.791
2.275
1.974
1.690
Me
Me
Me
N
Me
H
O
O
CF3
3e
2.07
2.10
1.14
1.06
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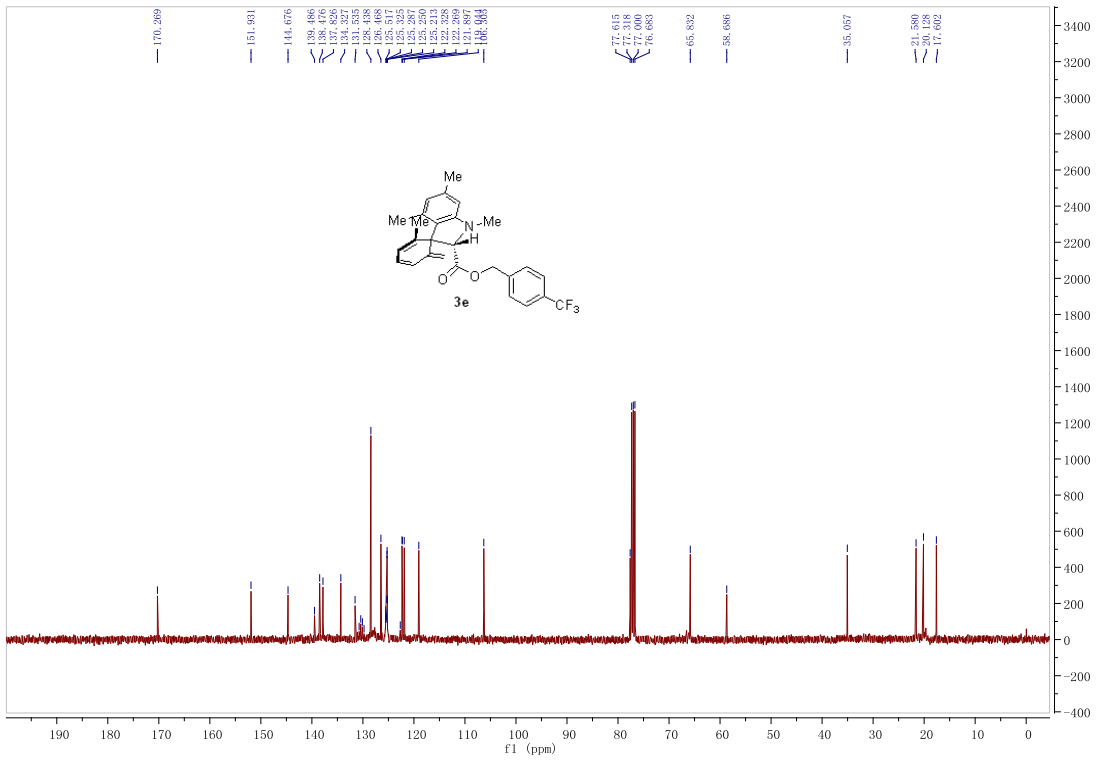
3.33
3.17
3.40
f1 (ppm)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131.555
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125.335
125.287
125.250
125.213
122.328
122.069
121.897
118.944
118.583
77.615
77.318
77.000
76.683
65.832
58.686
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20.128
17.602
Me
Me
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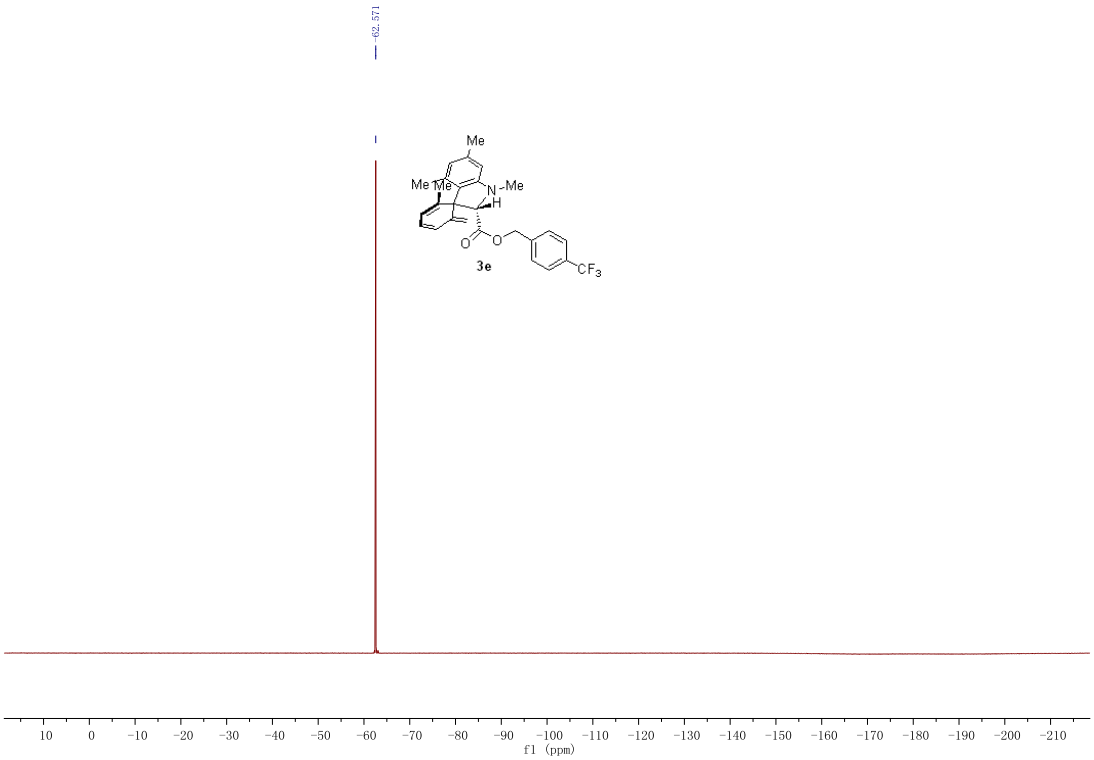
N
Me
H
O
O
CF3
3e
f1 (ppm)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Me Me
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O
O
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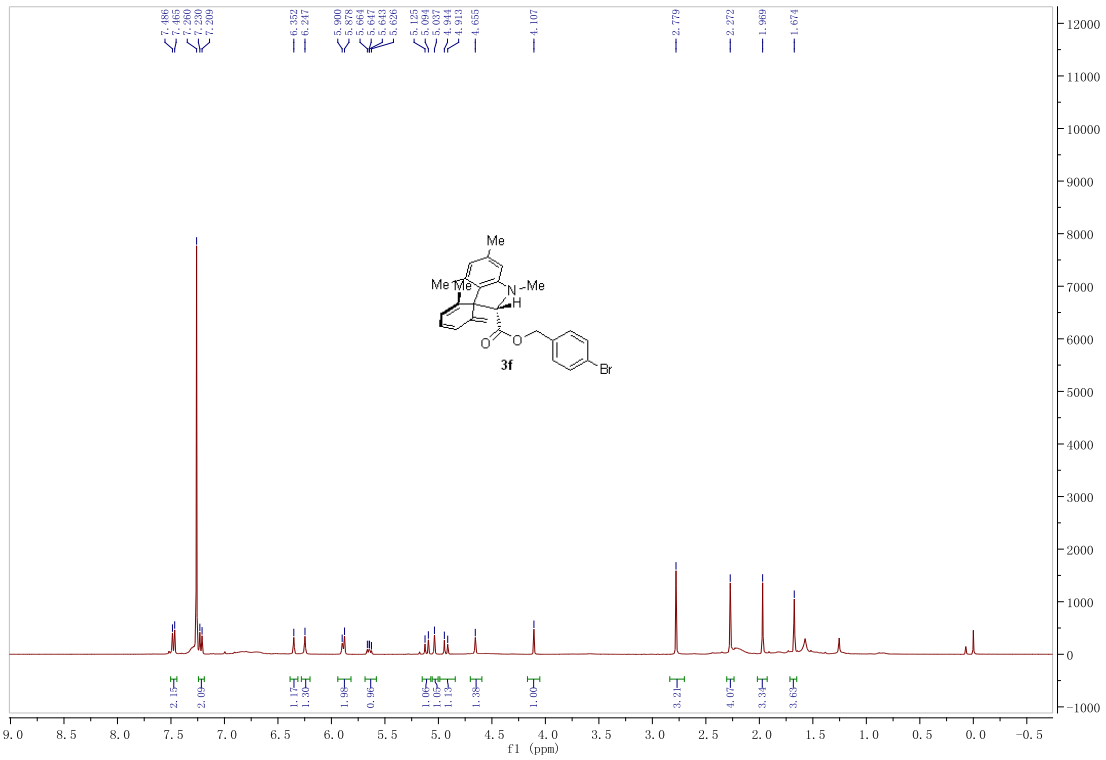
3e
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)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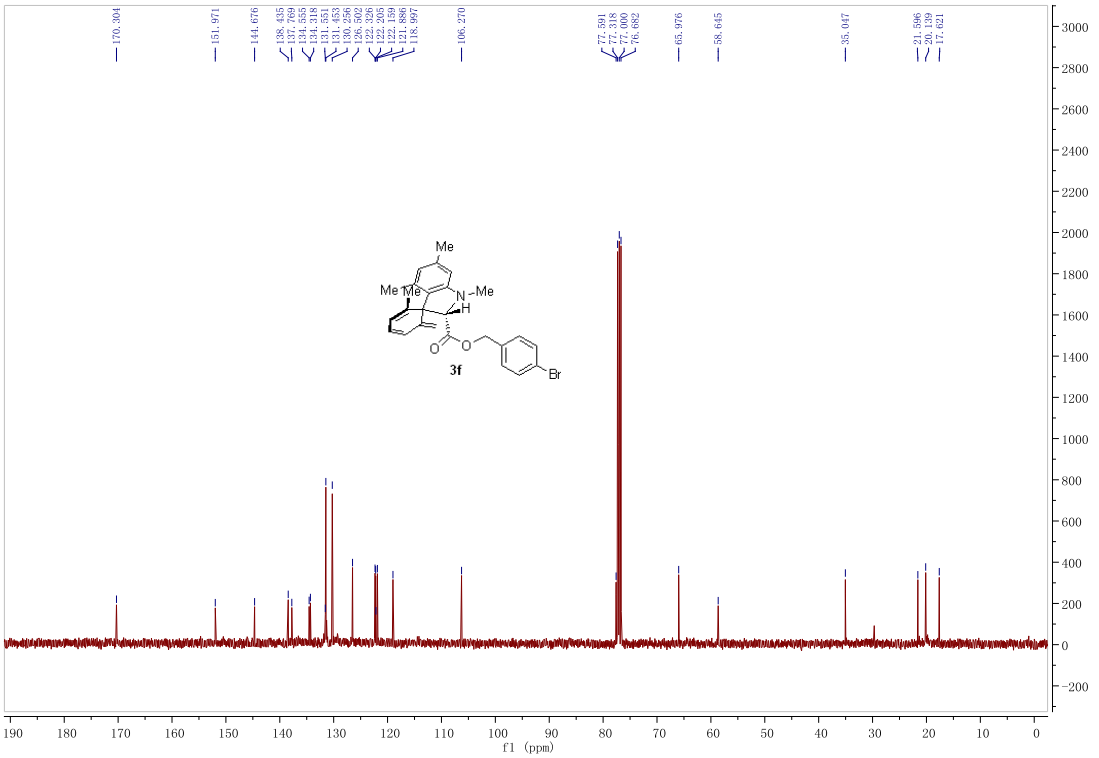
5.125
5.094
5.037
4.944
4.913
4.655
4.107
2.779
2.272
1.969
1.674
Me
Me Me
N-Me
H
O
O
Br
3f
2.15
2.09
1.17
1.30
1.99
0.96
1.08
1.05
1.13
1.38
1.00
3.21
4.07
3.34
3.63
12000 11000 10000 9000 8000 7000 6000 5000 4000 3000 2000 1000 0 -1000
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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122.265
122.159
121.886
118.997
106.270
77.591
77.318
77.000
76.682
65.976
58.645
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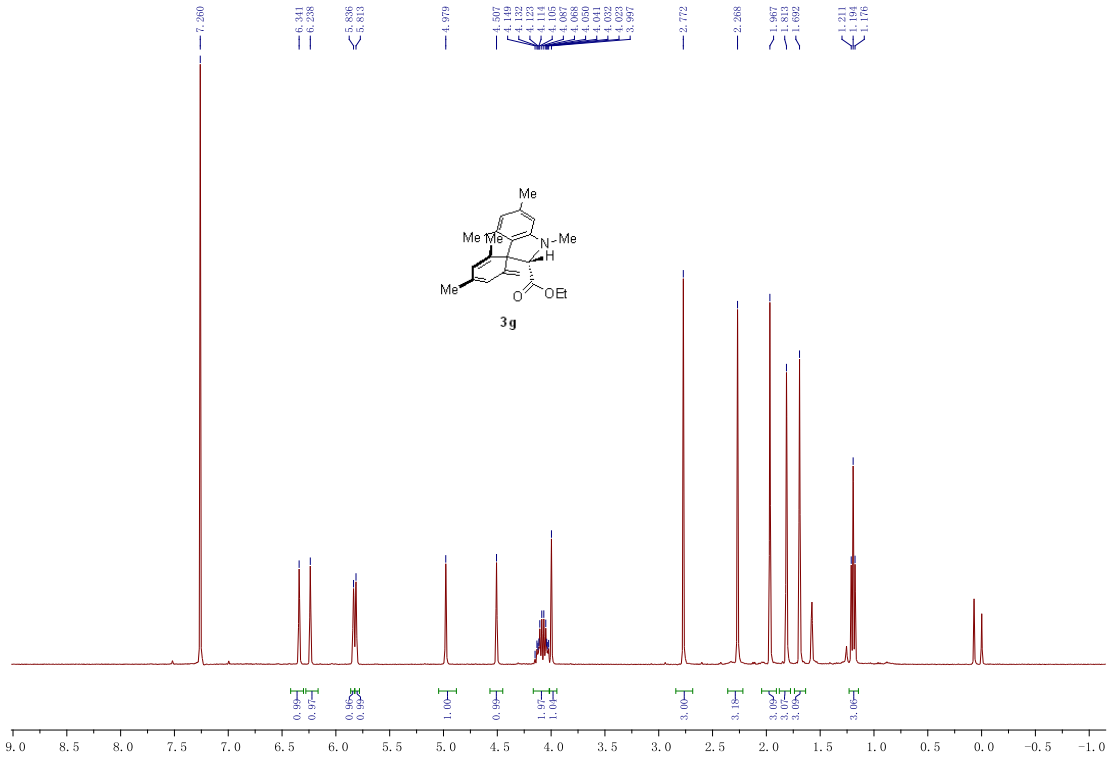
20.139
17.621
Me
Me Me
N-Me
H
O
O
Br
3f
f1 (ppm)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4.114
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4.087
4.068
4.060
4.041
4.032
4.023
3.997
2.772
2.268
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1.211
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N-Me
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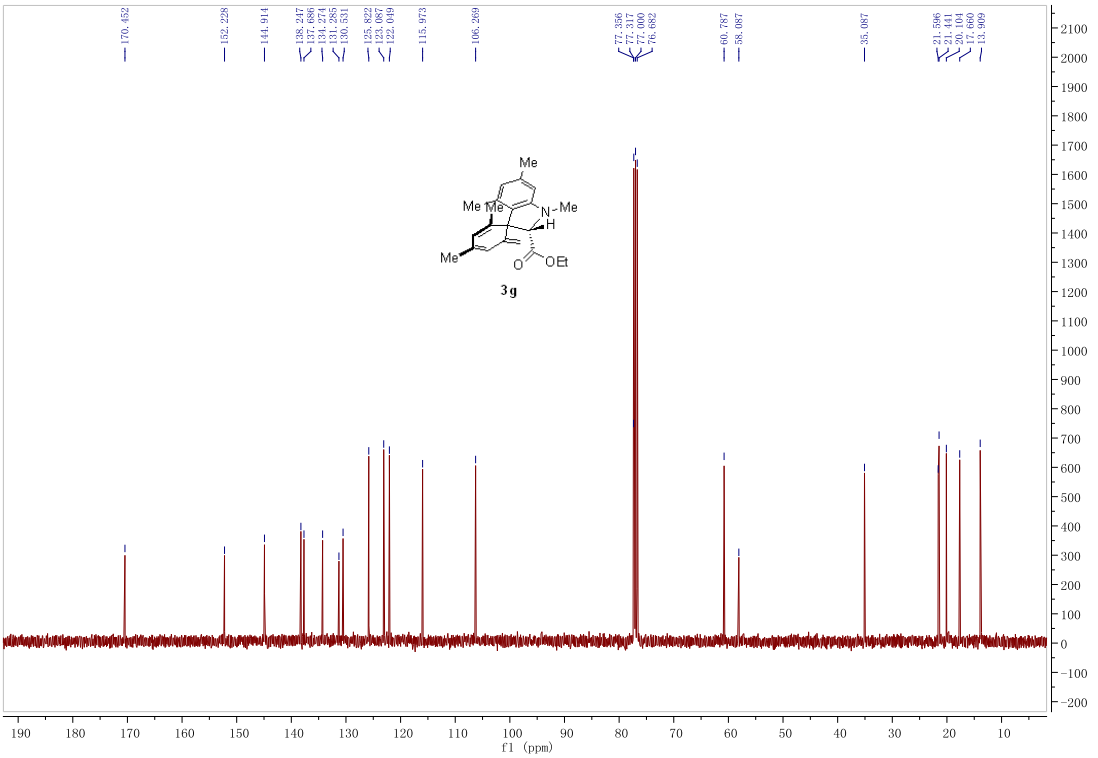
O
OEt
3g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77.356
77.317
77.000
76.682
60.787
58.087
35.087
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17.660
13.909
Me
Me
Me
N-Me
H
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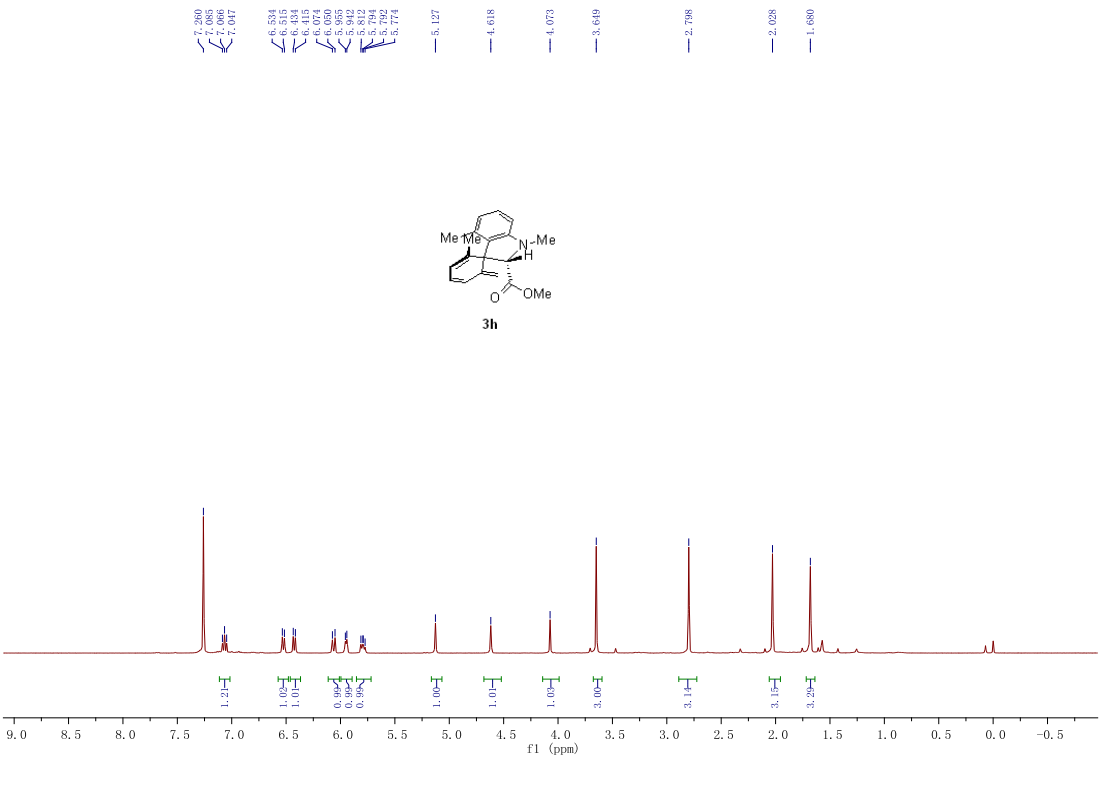
O
OEt
3g
f1 (ppm)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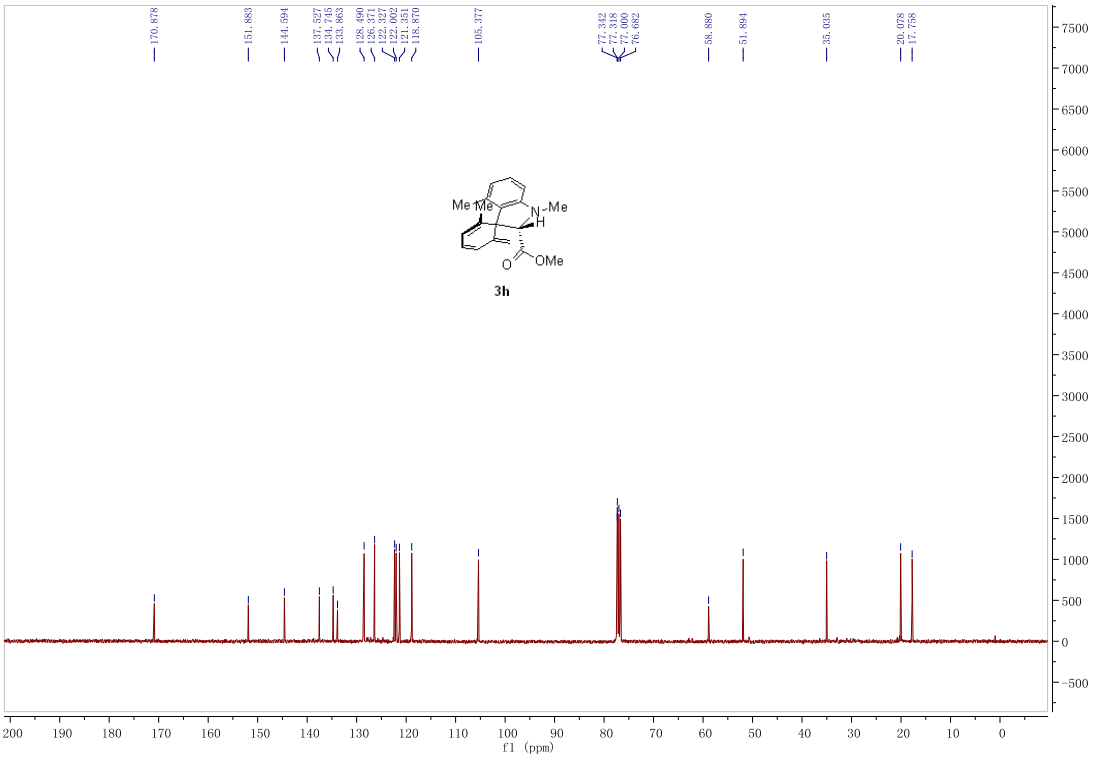
2.798
2.028
1.680
Me
Me
N-Me
H
O
OMe
3h
1.21
1.02
1.01
0.99
0.99
1.00
1.01
1.03
3.00
3.14
3.15
3.29
f1 (ppm)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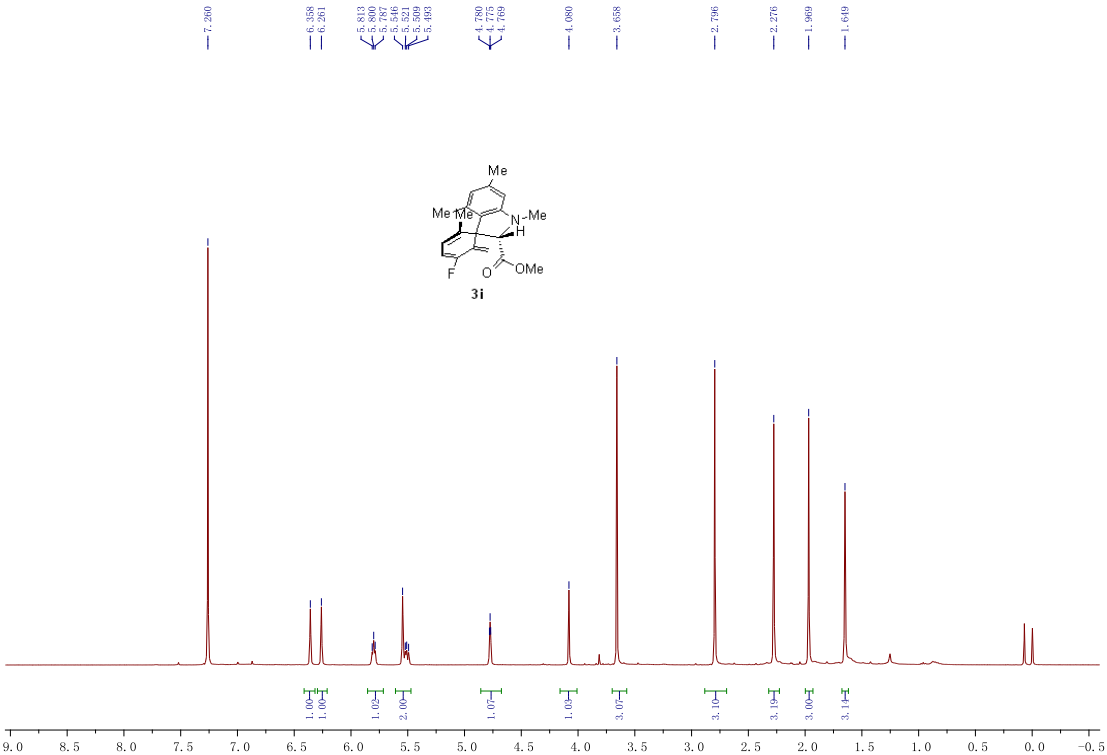
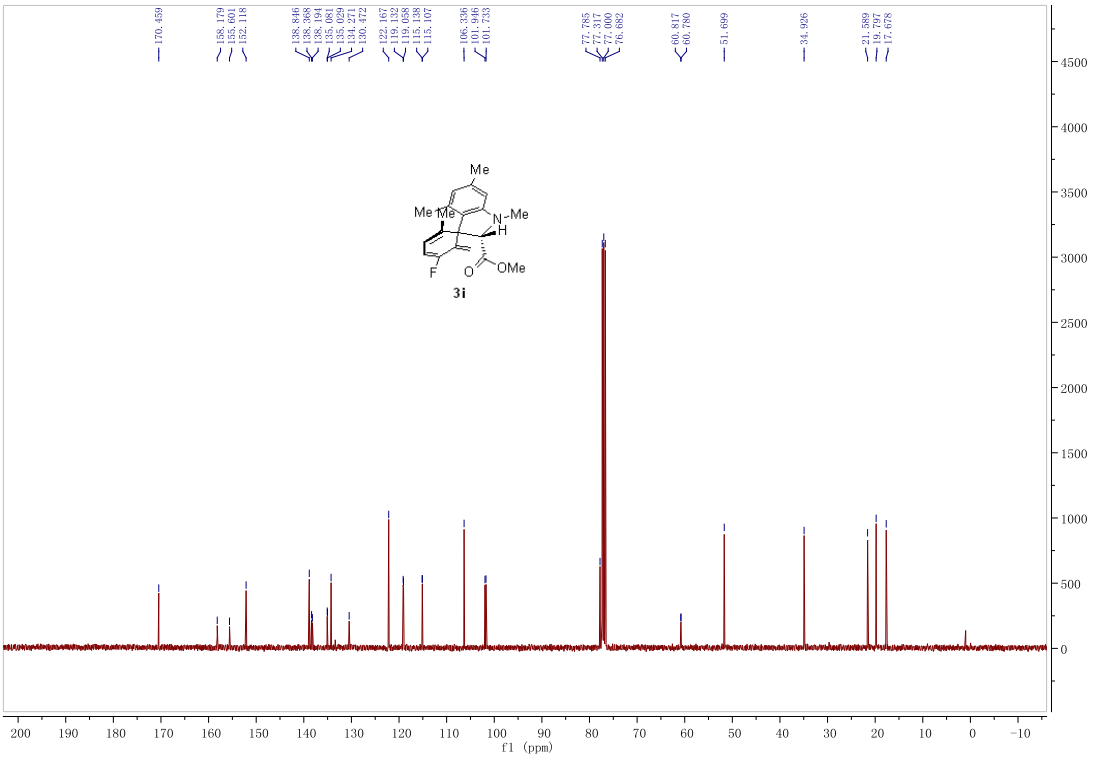
151.883
144.594
137.527
134.745
133.863
128.490
126.371
122.337
122.002
121.351
118.870
105.377
77.342
77.318
77.000
76.662
58.880
51.894
35.035
20.078
17.758
Me
Me
N-Me
H
O
OMe
3h
f1 (ppm)


7.260
6.358
6.261
5.813
5.800
5.787
5.546
5.521
5.509
5.493
4.780
4.775
4.769
4.080
3.658
2.796
2.276
1.969
1.649
Me
Me
Me
N-Me
H
F
O
OMe
3i
1.00
1.00
1.02
2.00
1.07
1.03
3.07
3.10
3.19
3.00
3.14
f1 (ppm)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158.179
155.601
152.118
138.846
138.388
138.194
135.081
135.074
134.271
130.472
122.167
119.152
119.038
115.138
115.107
106.336
101.946
101.733
77.785
77.317
77.000
76.682
60.817
60.780
51.699
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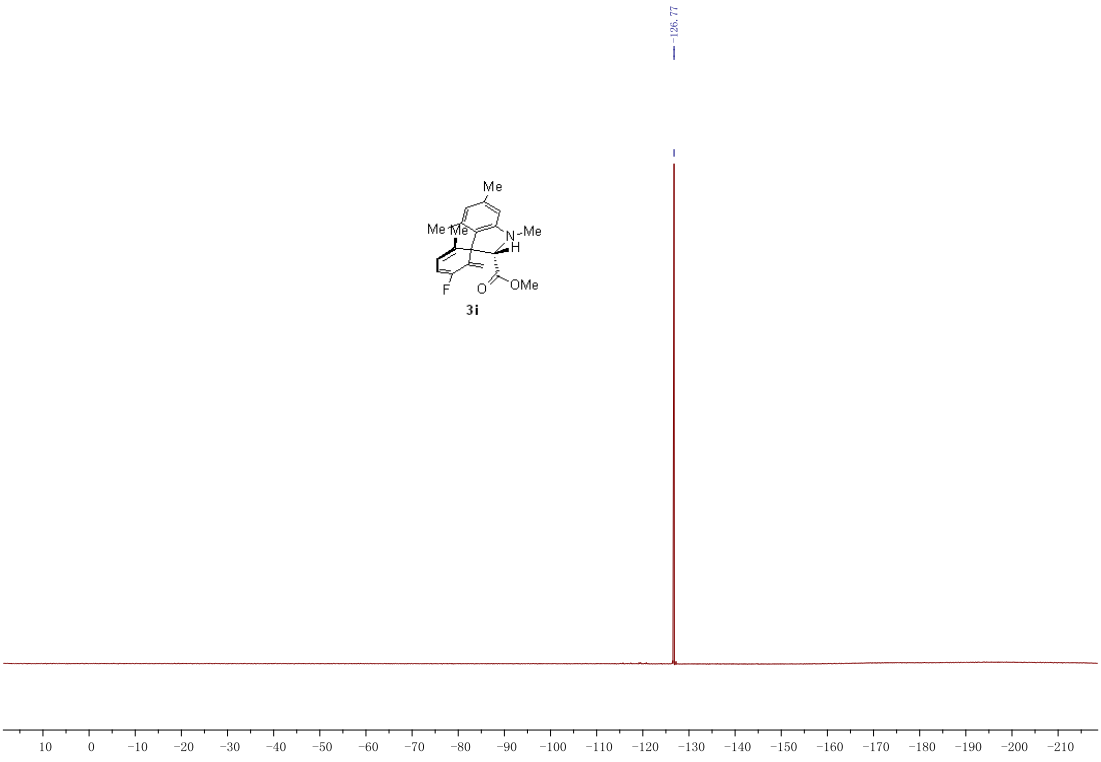
Me
Me
Me
N-Me
H
F
O
OMe
3i
f1 (ppm)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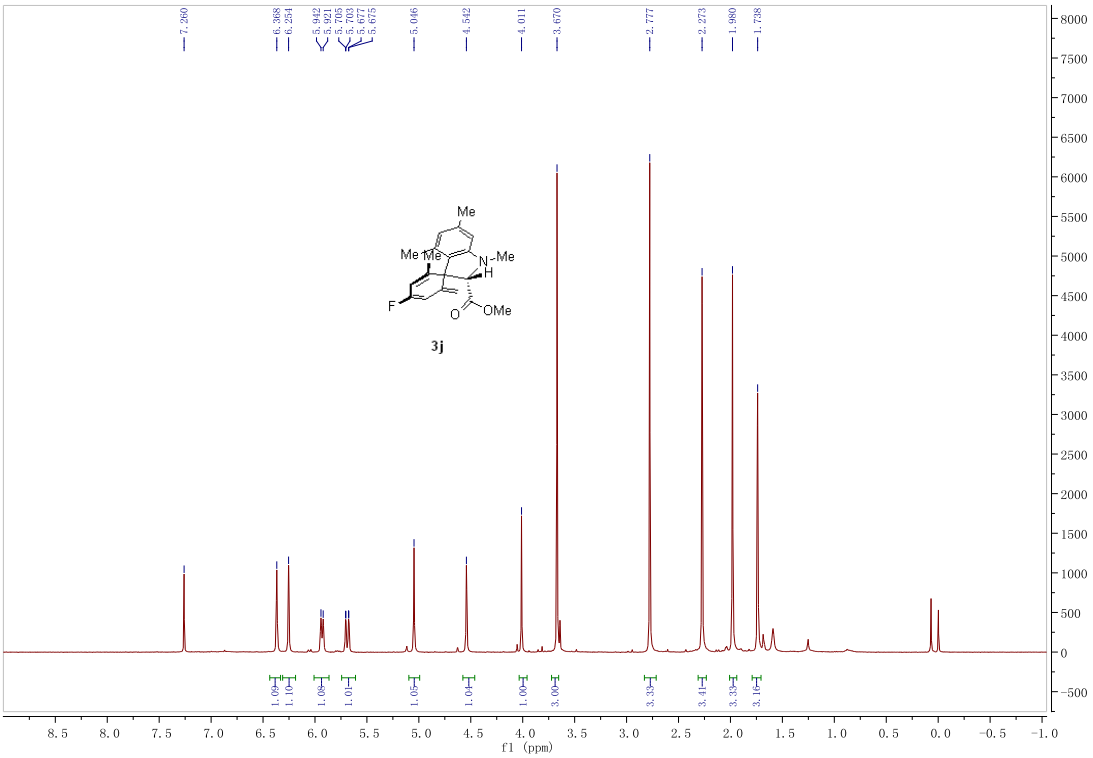
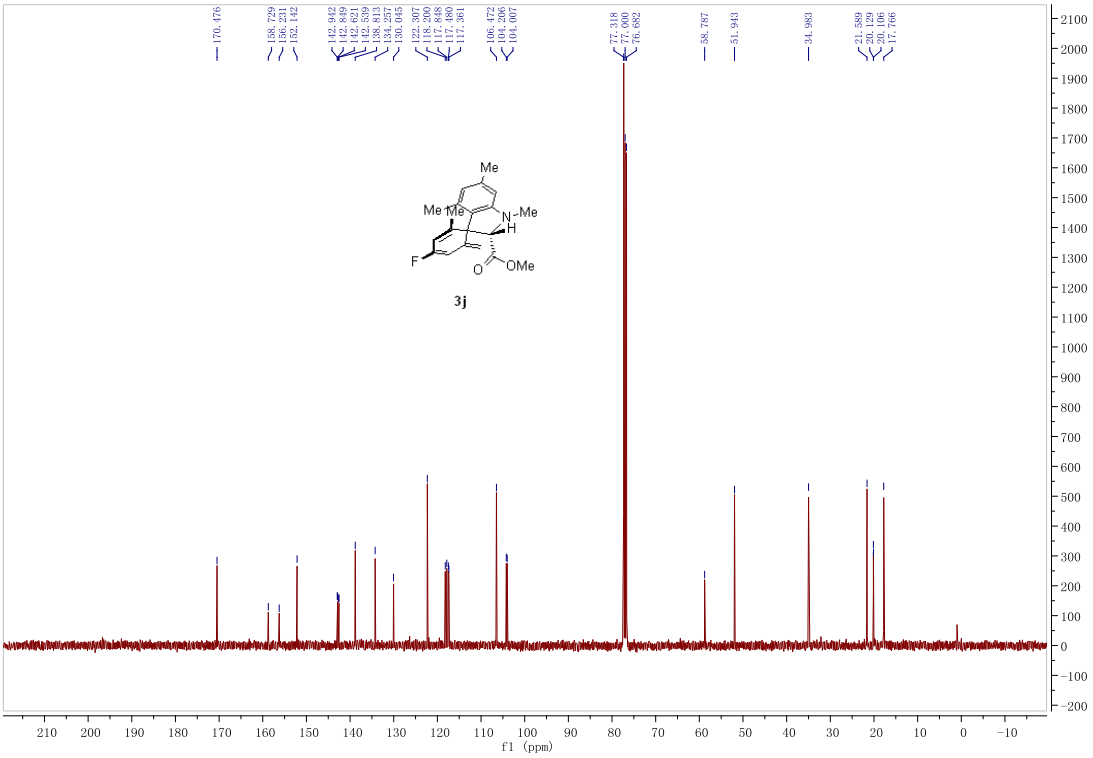
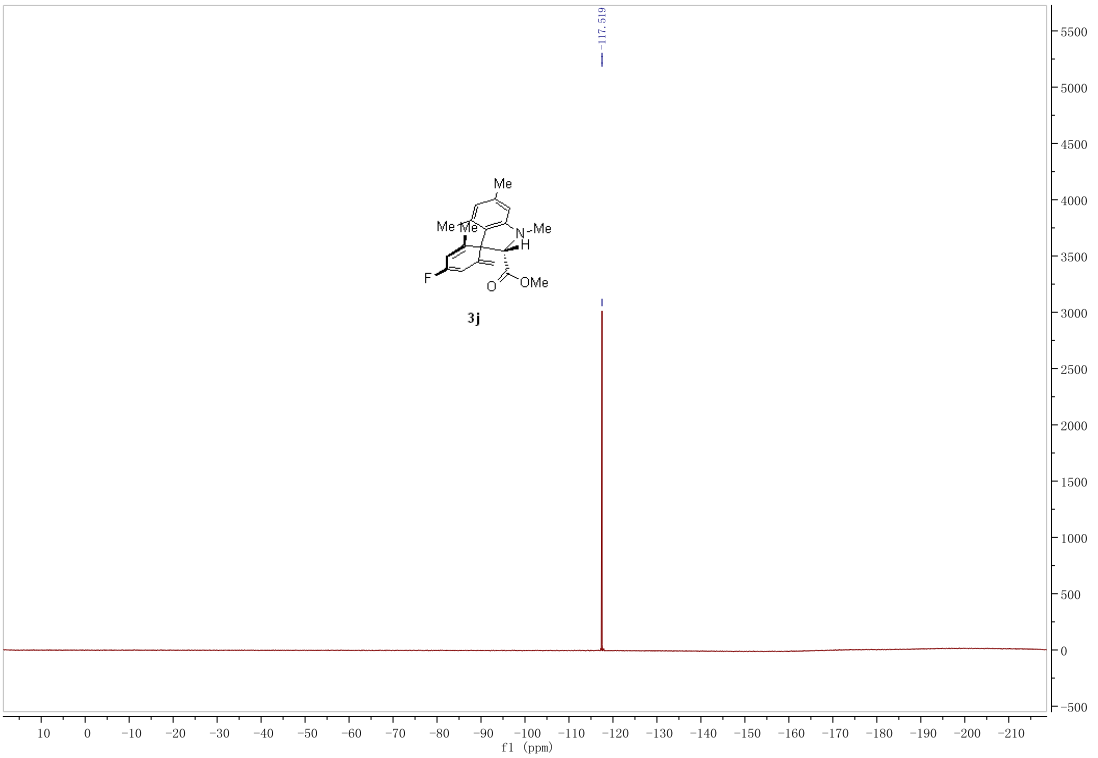
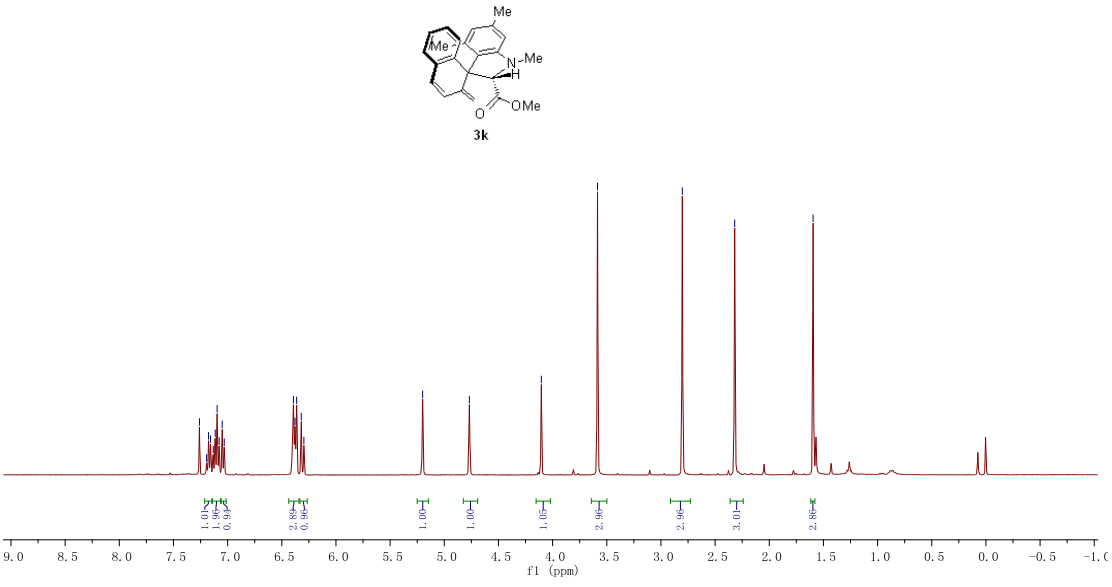
Me
Me
Me
N-Me
H
F
O
OMe
3i

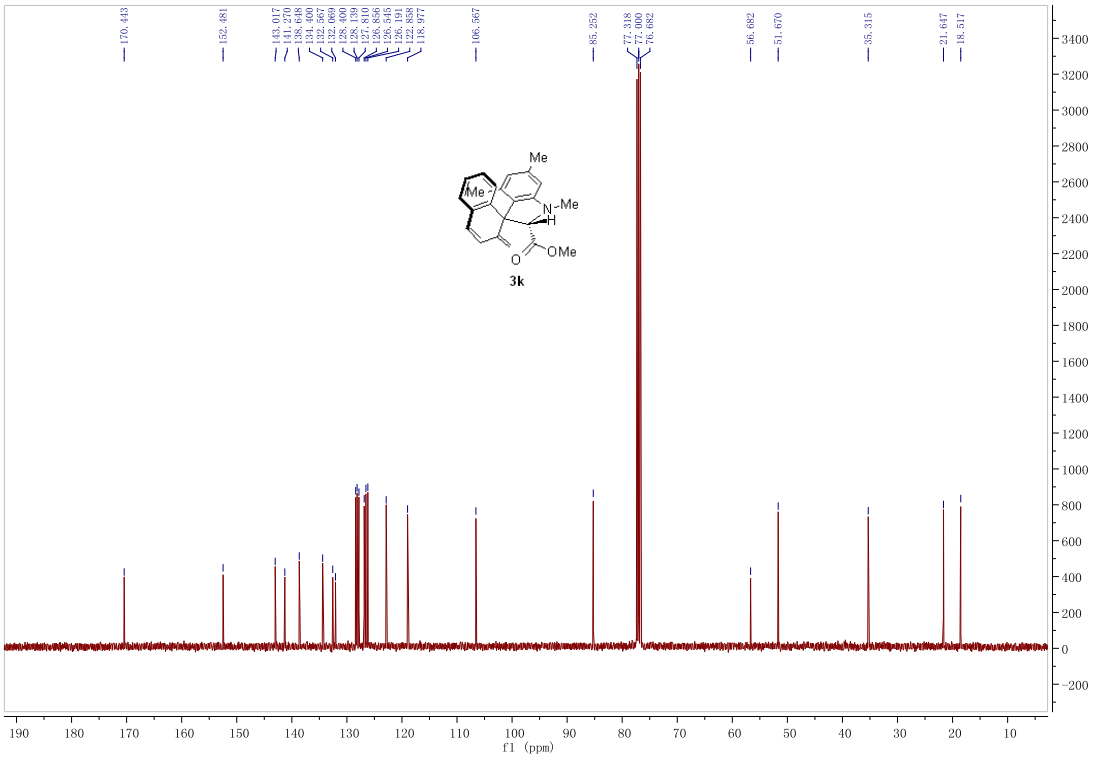

7.260
6.388
6.254
5.942
5.921
5.705
5.703
5.677
5.675
5.046
4.542
4.011
3.670
2.777
2.273
1.980
1.738
Me
Me
Me
N-Me
H
F
O
OMe
3j
f1 (ppm)


170.476
158.729
156.231
152.142
142.942
142.889
142.621
142.539
138.813
134.257
130.045
122.307
118.200
117.886
117.480
117.361
106.472
104.206
104.007
77.318
77.000
76.682
58.787
51.943
34.983
21.589
20.129
20.106
17.766
Me
Me
Me
N-Me
H
F
O
OMe
3j
f1 (ppm)

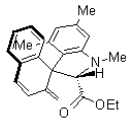

-117.519
Me
Me
Me
N-Me
H
F
O
OMe
3j
f1 (ppm)

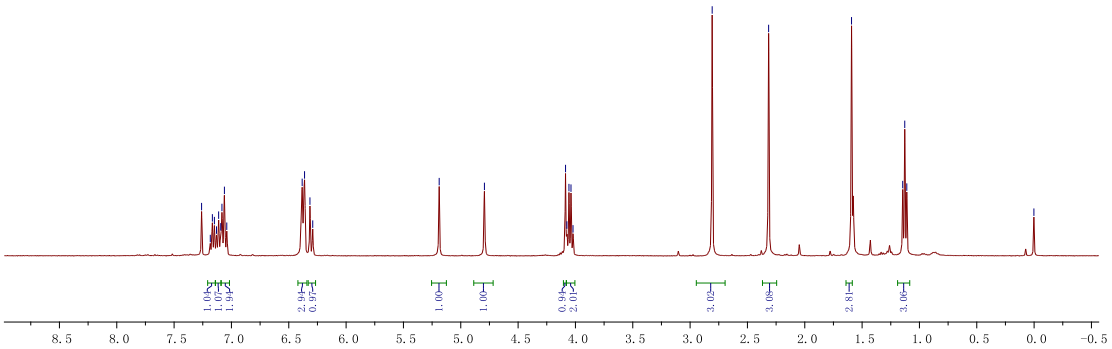

7.260
7.144
7.176
7.158
7.133
7.115
7.097
7.078
7.050
7.031
6.393
6.378
6.362
6.320
6.296
5.200
4.789
4.104
3.586
2.803
2.319
1.595

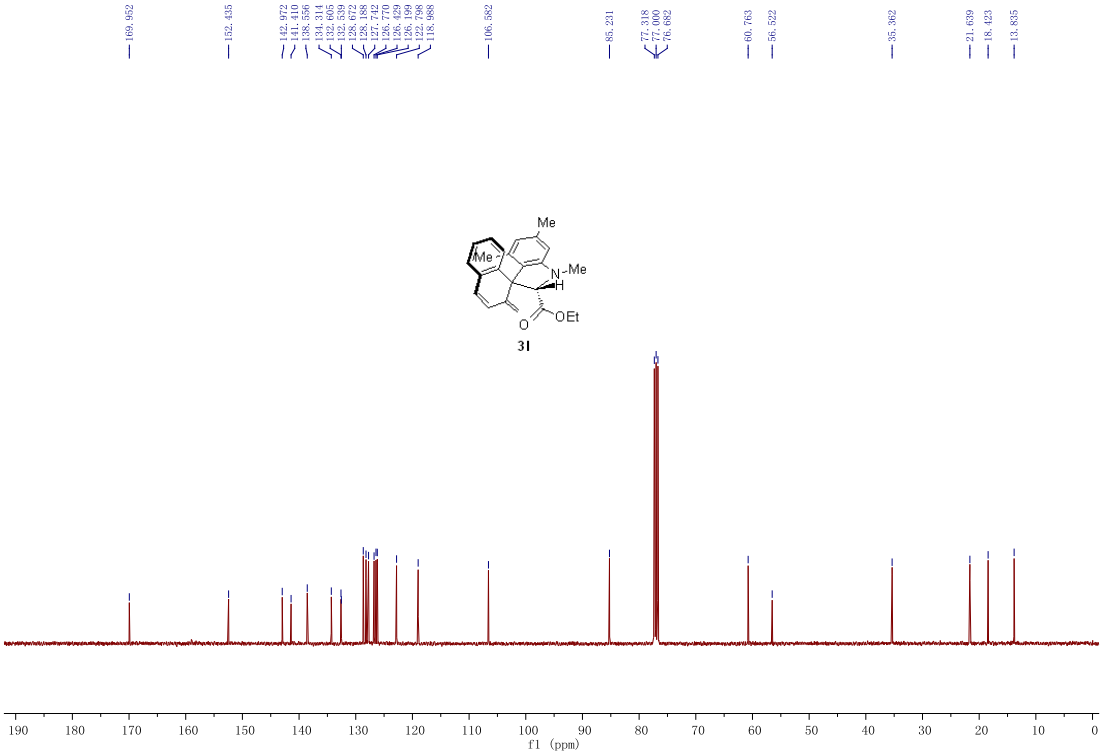

Me
Me
N-Me
H
O
OMe
3k
1.01
1.94
0.94
2.89
0.90
1.00
1.00
1.05
2.96
2.96
3.01
2.88
f1 (ppm)

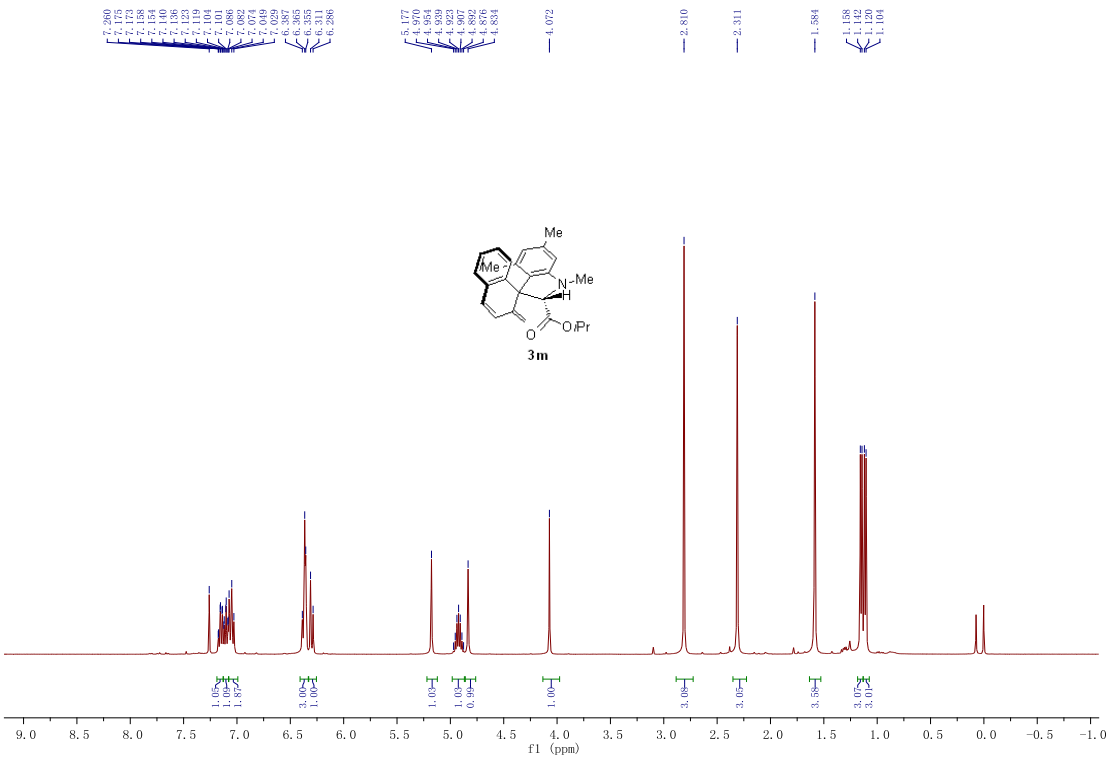

170.443
162.481
143.017
141.270
138.648
134.400
132.567
132.069
128.400
128.134
127.810
126.856
126.545
126.191
122.858
118.977
106.567
85.252
77.318
77.000
76.682
56.682
51.670
35.315
21.647
18.517
Me
Me
N-Me
H
O
OMe
3k
f1 (ppm)


7.260
7.184
7.166
7.149
7.130
7.112
7.093
7.082
7.061
7.041
6.383
6.362
6.315
6.291
5.188
4.794
4.086
4.075
4.057
4.039
4.021
2.807
2.315
1.592
1.146
1.128
1.110
0.002


Me
Me
N-Me
H
O
OEt
3l


1.00
1.07
1.94
2.04
0.97
1.00
1.00
0.91
2.01
3.02
3.08
2.81
3.06


169.952
152.435
142.972
141.410
138.556
134.314
132.605
132.534
128.672
128.188
127.742
126.770
126.459
126.199
122.798
118.988
106.582
85.231
77.318
77.000
76.682
60.763
56.522
35.362
21.639
18.423
13.835
Me
Me
N-Me
H
O
OEt
3l
f1 (ppm)


7.260
7.175
7.173
7.138
7.154
7.140
7.136
7.125
7.119
7.104
7.101
7.086
7.082
7.074
7.049
7.029
6.365
6.355
6.311
6.286
5.177
4.970
4.954
4.938
4.923
4.907
4.892
4.876
4.854
4.072
2.810
2.311
1.584
1.158
1.142
1.120
1.104
Me
Me
N-Me
H
O
OiPr
3m
1.05
1.09
1.87
3.00
1.00
1.03
1.03
0.99
1.00
3.08
3.05
3.58
3.07
3.01
f1 (ppm)


169.384
152.323
143.073
141.536
138.461
134.245
133.147
132.537
129.045
128.245
127.661
126.672
126.377
126.215
122.664
118.941
106.477
85.380
77.318
77.000
76.682
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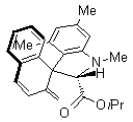
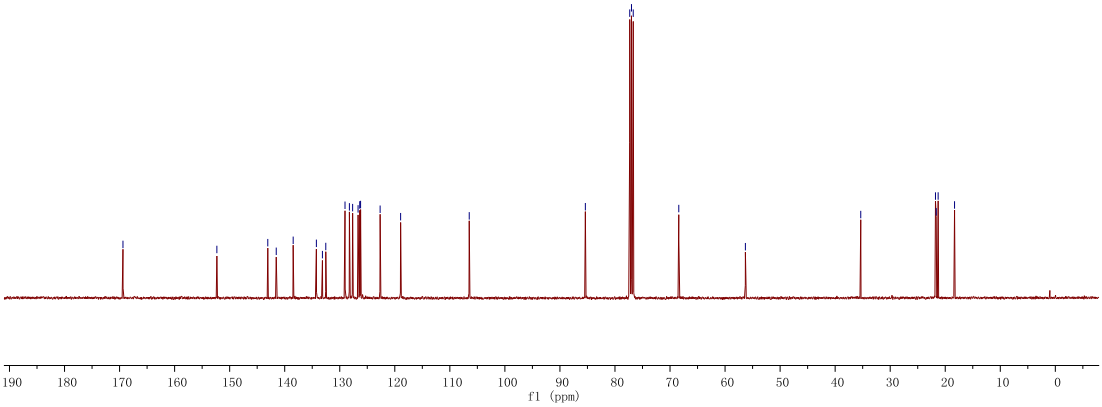
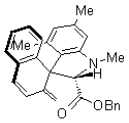
56.306
35.350
21.773
21.638
21.288
18.309


Me
Me
N
Me
H
O
O
iPr

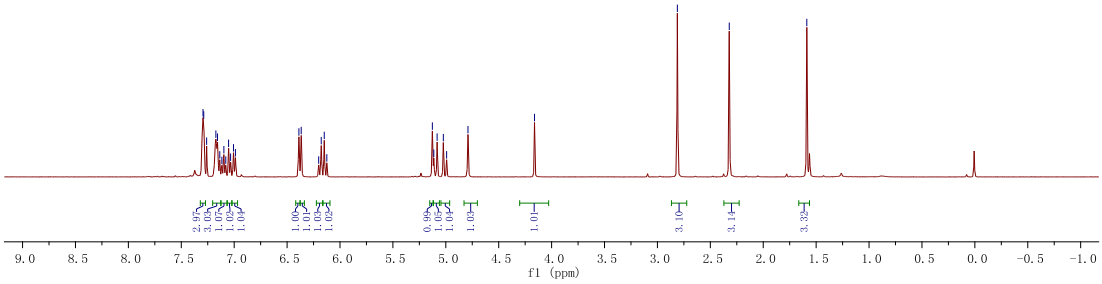
3m

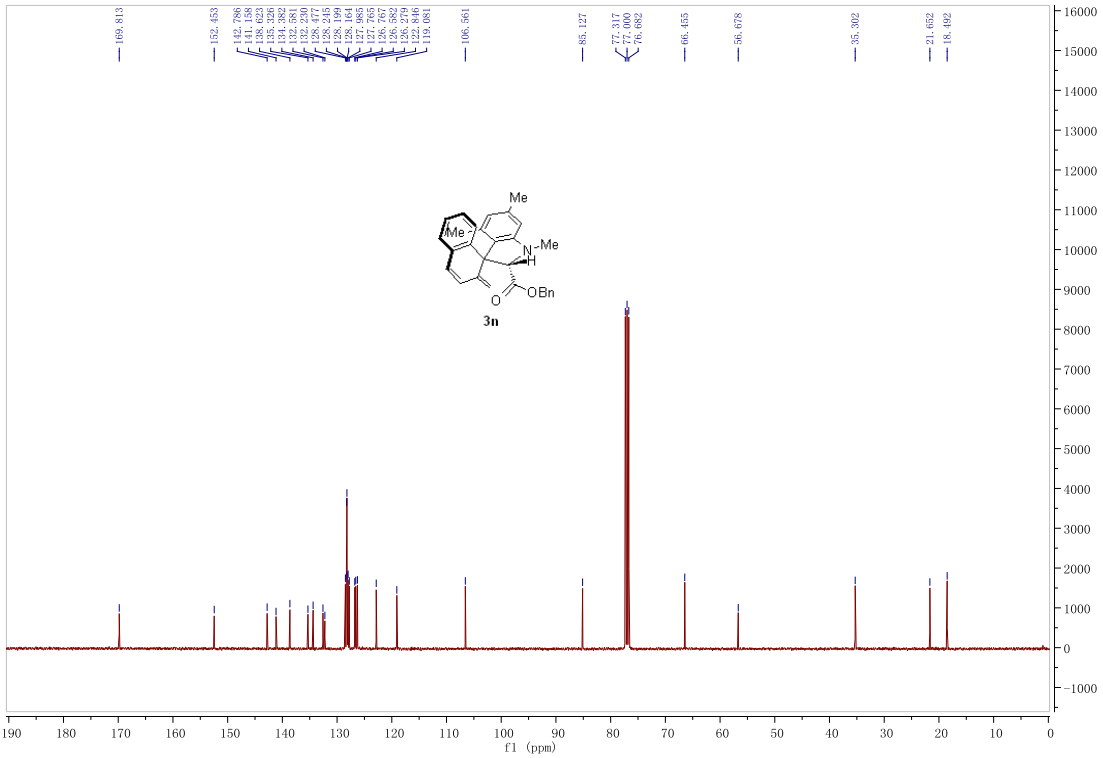

190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.295
7.288
7.260
7.173
7.138
7.136
7.116
7.097
7.093
7.053
7.034
7.007
6.988
6.986
6.367
6.201
6.177
6.149
6.125
5.127
5.113
5.082
5.023
4.962
4.790
4.162
2.812
2.321
1.588


Me
Me
N
Me
H
O
O
Bn

3n


2.97
3.05
1.07
1.09
1.07
1.00
1.02
1.03
1.02
0.98
1.02
1.04
1.03
1.01
3.10
3.14
3.32
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)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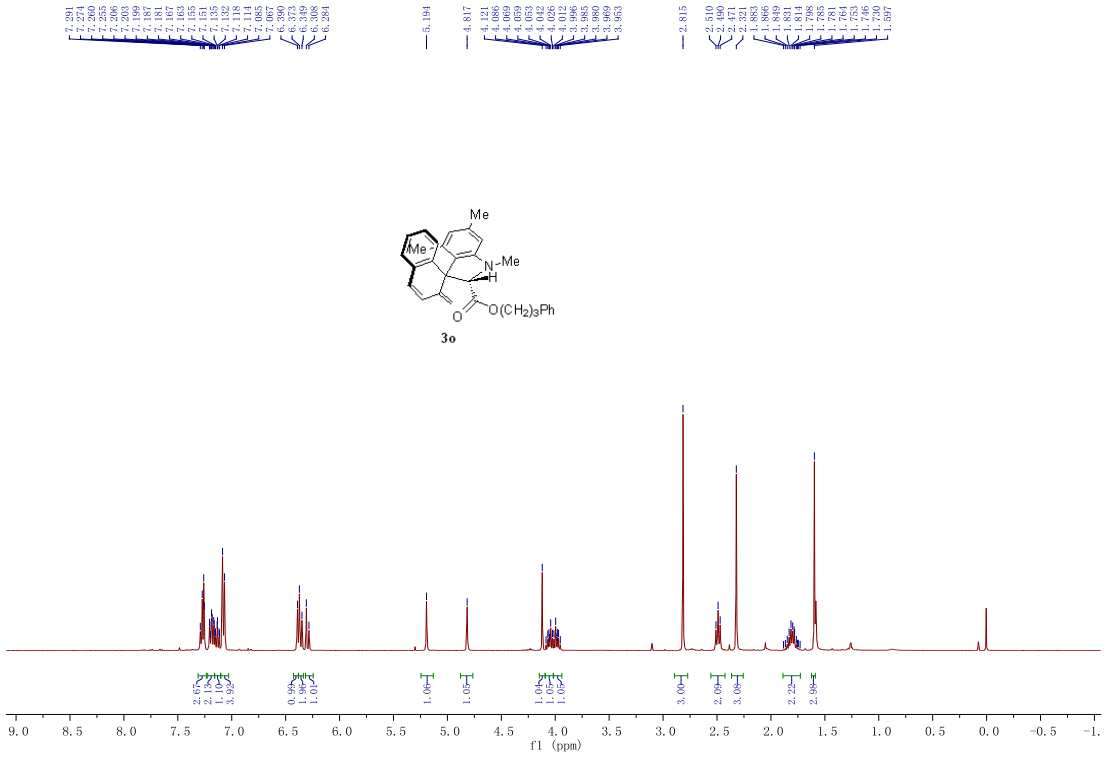
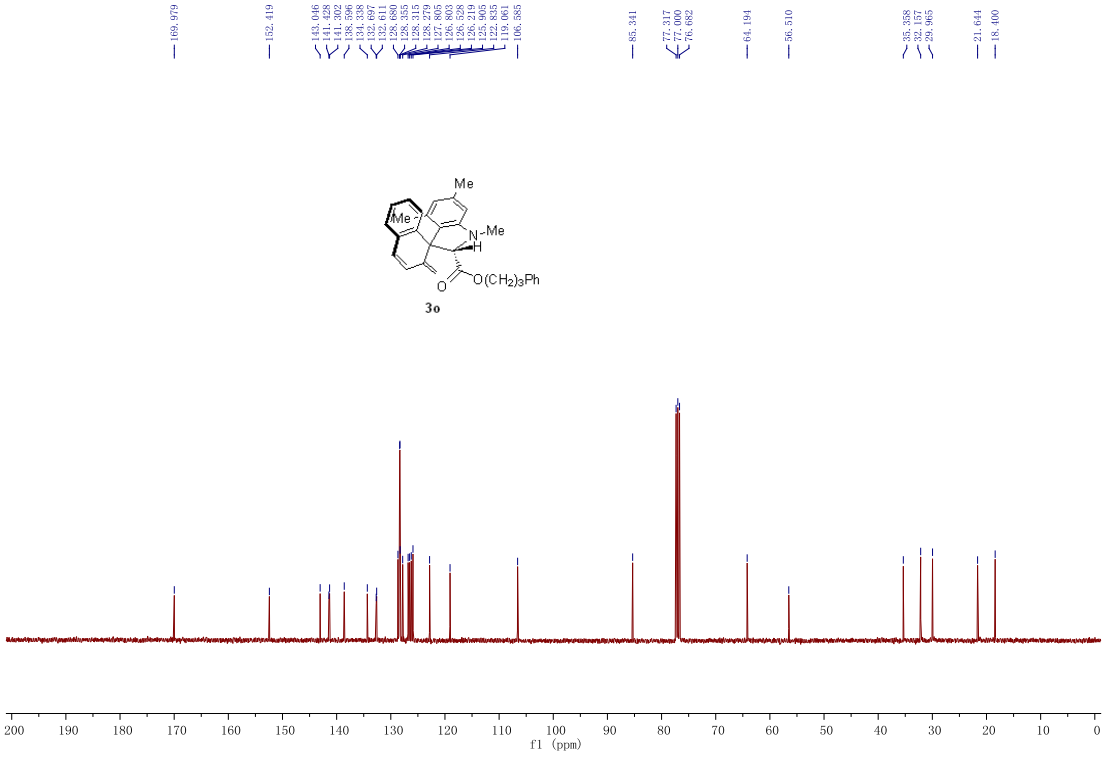
142.786
141.438
138.623
135.326
134.382
132.581
132.230
128.477
128.245
128.199
128.164
127.985
127.765
126.767
126.582
126.279
122.846
119.084
106.561
85.127
77.317
77.000
76.682
66.455
56.678
35.302
21.652
18.492
Me
Me
N-Me
H
OBn
O
3n
f1 (ppm)


7.291
7.274
7.260
7.255
7.206
7.203
7.199
7.187
7.181
7.167
7.163
7.155
7.151
7.135
7.132
7.118
7.114
7.085
7.067
6.390
6.373
6.349
6.308
6.284
5.194
4.817
4.421
4.086
4.069
4.059
4.053
4.042
4.026
4.012
3.996
3.985
3.969
3.949
3.953
2.815
2.510
2.490
2.471
2.321
1.883
1.866
1.849
1.831
1.814
1.798
1.785
1.781
1.764
1.753
1.746
1.730
1.697
Me
Me
N-Me
H
O(CH2)3Ph
O
3o
f1 (ppm)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141.428
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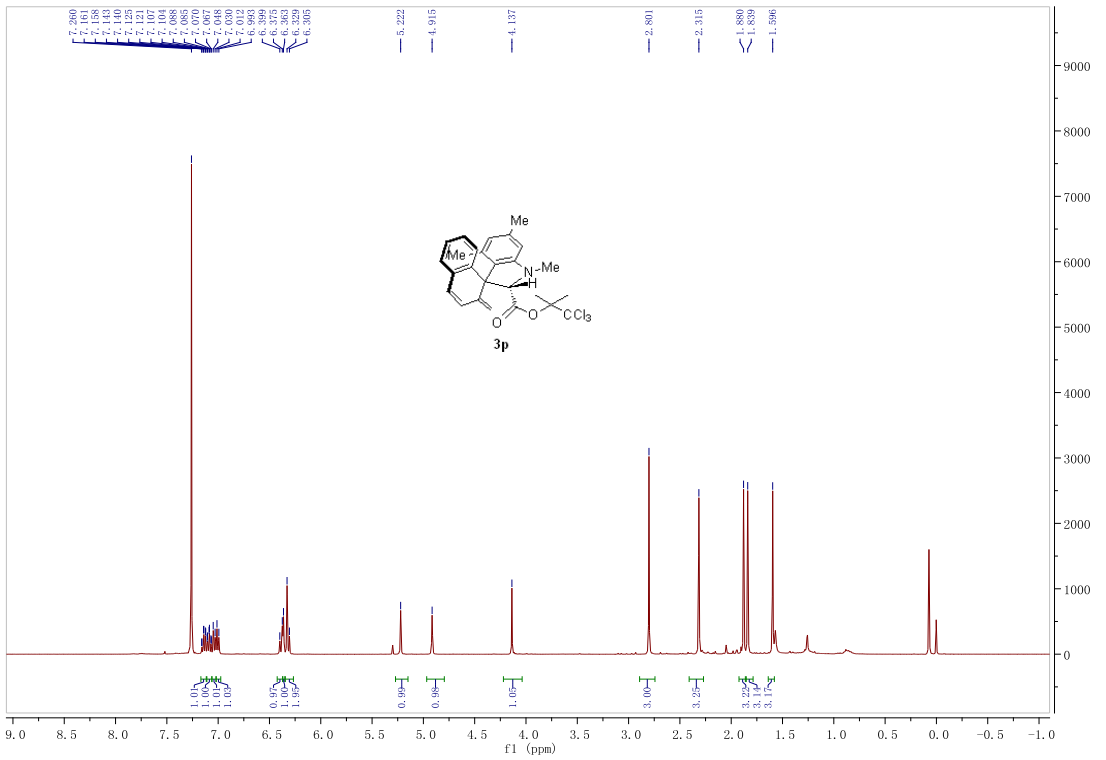
138.596
134.338
132.697
132.611
128.680
128.355
128.315
128.279
127.805
126.803
126.528
126.419
125.965
122.835
119.061
106.585
85.341
77.317
77.000
76.682
64.194
56.510
35.358
32.577
29.965
21.644
18.400
Me
Me
N-Me
H
O
O(CH2)3Ph
3o
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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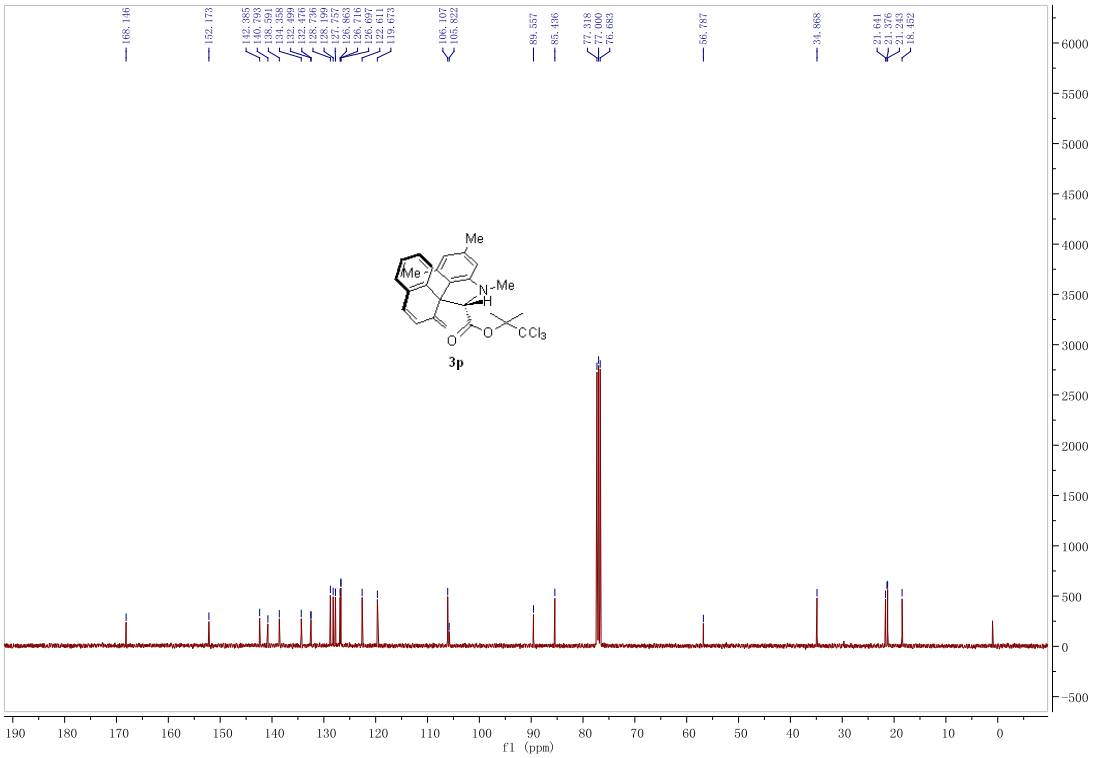
7.161
7.138
7.143
7.140
7.125
7.121
7.107
7.104
7.084
7.085
7.070
7.067
7.048
7.030
7.012
6.993
6.399
6.375
6.363
6.329
6.305
5.222
4.915
4.137
2.801
2.315
1.880
1.839
1.596
Me
Me
N-Me
H
O
O
CCl3
3p
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
−1.0
f1 (ppm)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140.793
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134.338
132.499
132.476
128.736
128.199
127.757
126.863
126.716
126.697
122.611
119.673
106.107
105.822
89.557
85.436
77.318
77.000
76.683
56.787
34.868
21.641
21.376
21.243
18.462
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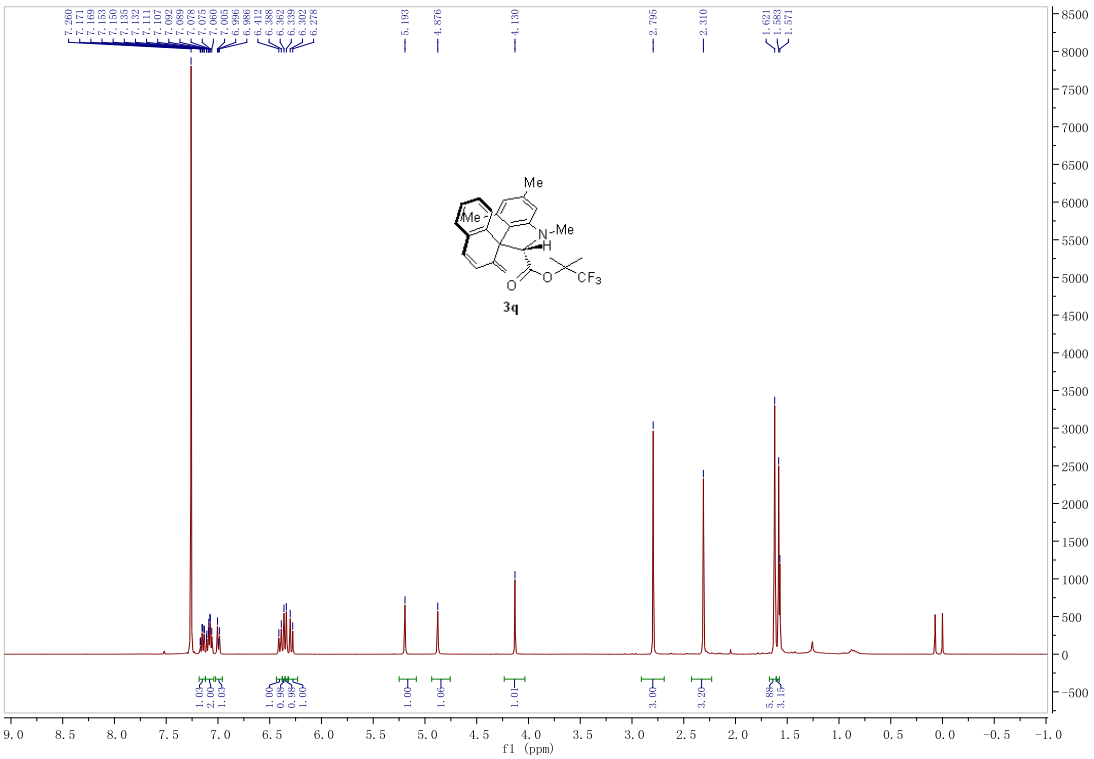
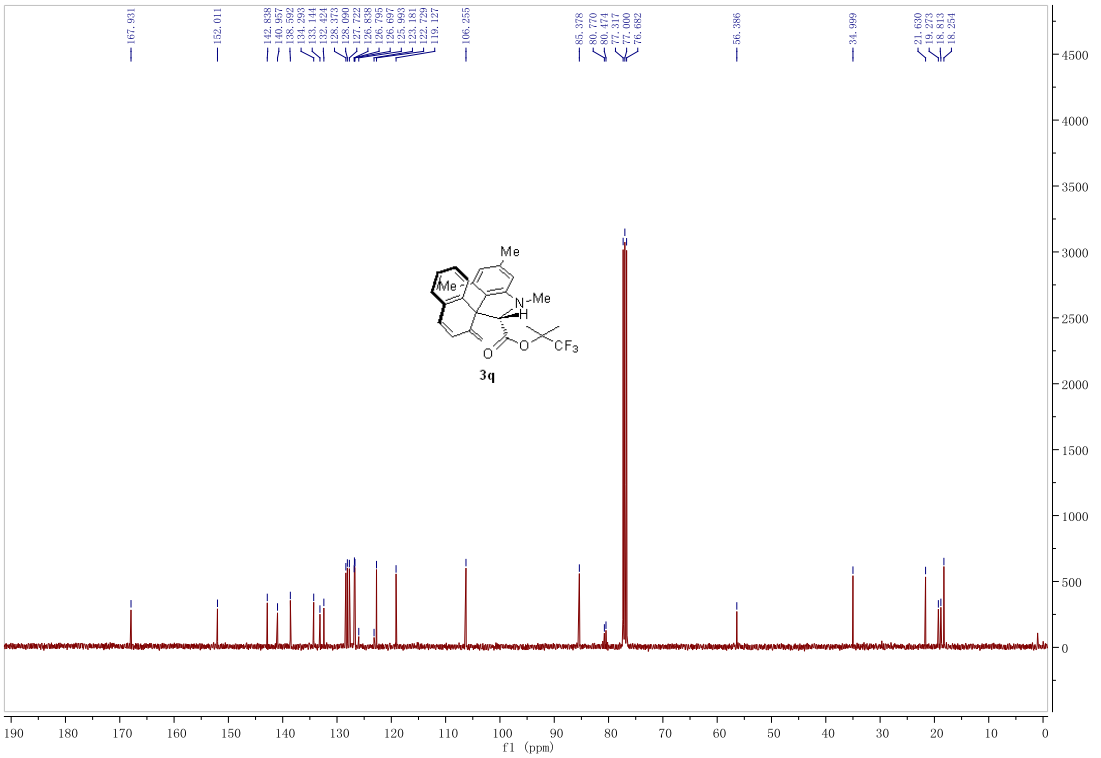
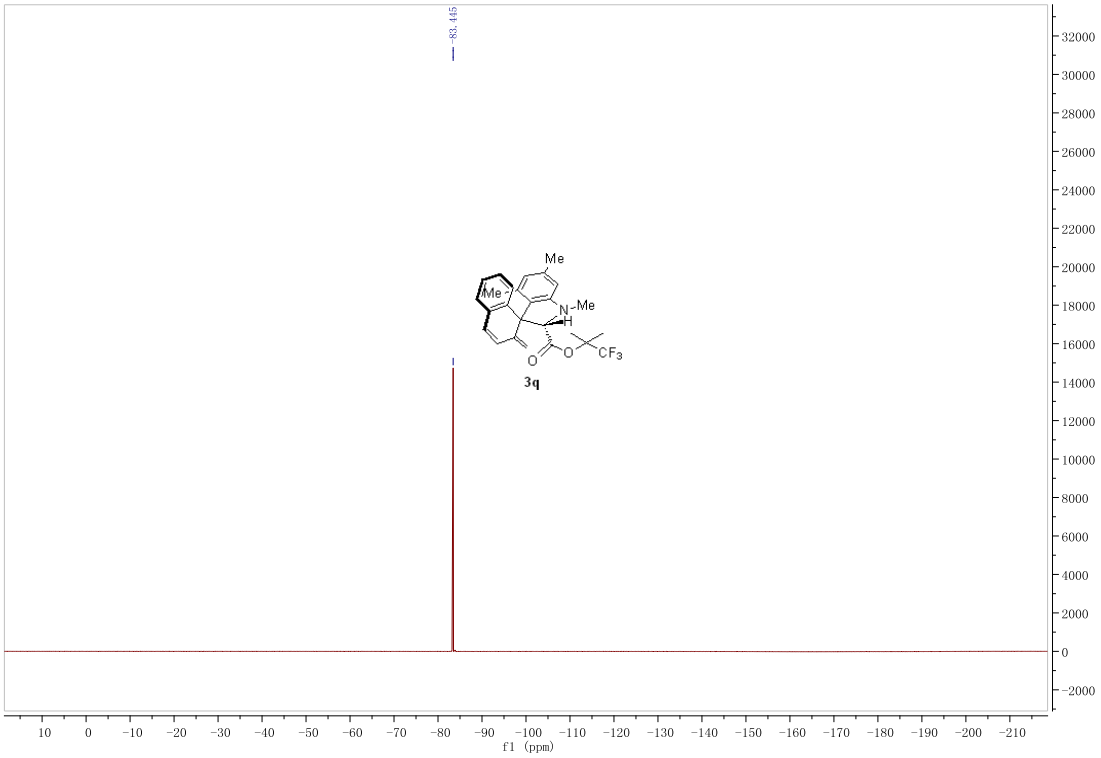
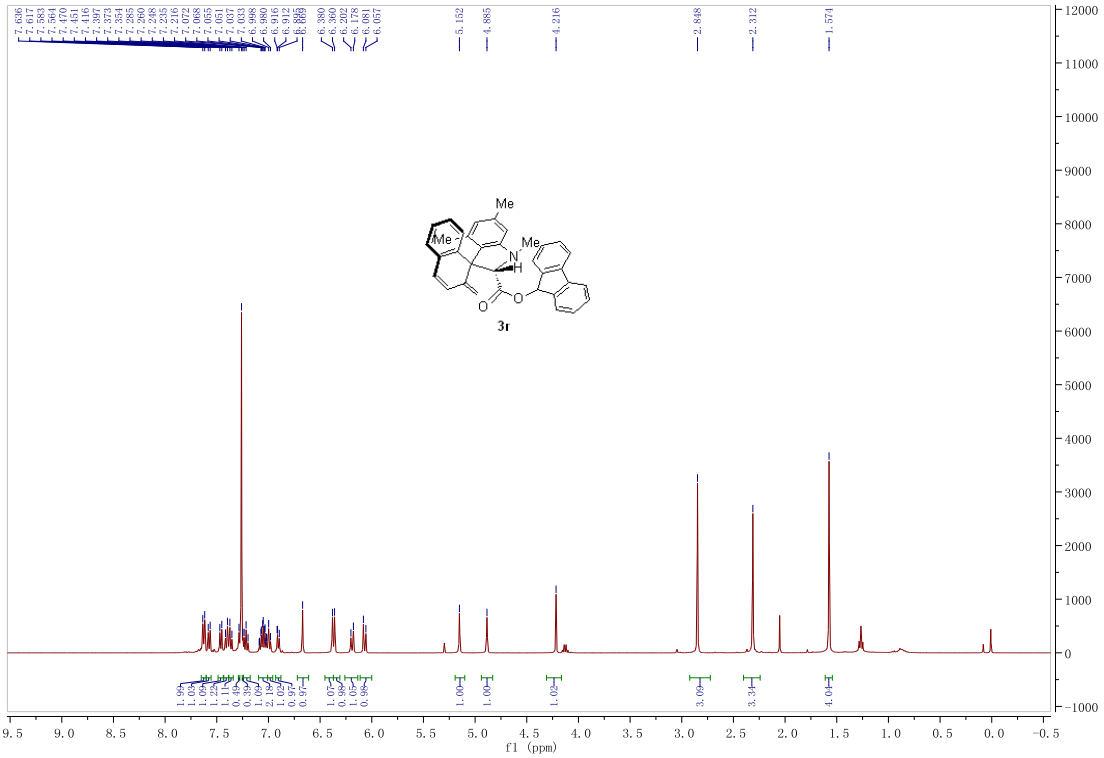
N-Me
H
O
O
CCl3
3p
f1 (ppm)


7.260
7.171
7.169
7.153
7.150
7.135
7.132
7.111
7.110
7.092
7.089
7.078
7.075
7.060
7.005
6.996
6.986
6.612
6.388
6.362
6.339
6.302
6.276
5.193
4.876
4.130
2.796
2.310
1.624
1.583
1.571
Me
Me
N-Me
H
O
O
CF3
3q
f1 (ppm)


167.931
152.011
142.838
140.957
138.592
131.293
130.144
128.373
128.090
127.732
126.795
126.697
125.993
122.729
119.127
106.255
85.378
80.770
80.471
77.317
77.000
76.682
56.386
34.999
21.630
19.273
18.813
18.254
Me
Me
N-Me
H
O
O
CF3
3q
f1 (ppm)


-83.445
Me
Me
N-Me
H
O
O
CF3
3q
f1 (ppm)


7.636
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7.397
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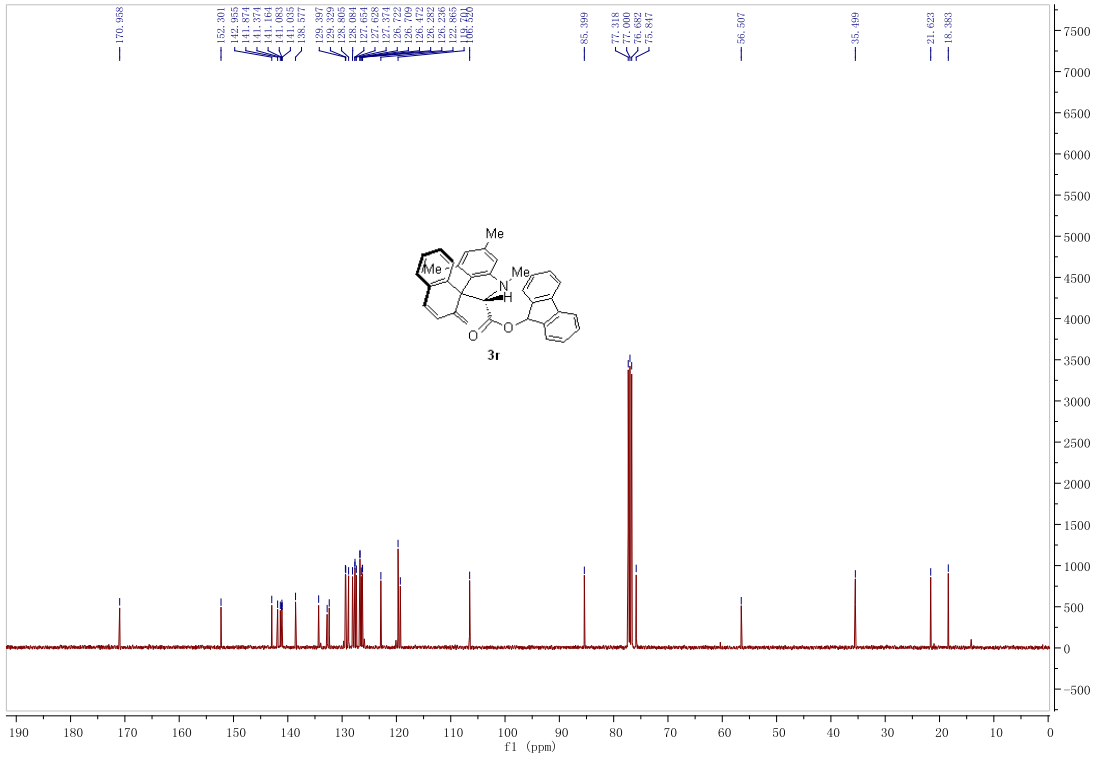
7.260
7.248
7.235
7.216
7.072
7.068
7.055
7.051
7.037
7.033
6.998
6.980
6.916
6.912
6.895
6.889
6.380
6.369
6.202
6.178
6.081
6.057
5.152
4.885
4.216
2.848
2.312
1.574
Me
Me
Me
N
H
O
O
3r
1.99
1.04
1.04
1.23
1.11
0.49
0.94
0.94
2.18
1.02
0.97
0.97
1.07
0.98
1.05
0.98
1.00
1.00
1.02
3.09
3.34
4.04
f1 (ppm)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128.084
127.654
127.628
127.573
126.722
126.709
126.472
126.282
126.205
122.865
120.520
85.399
77.318
77.000
76.682
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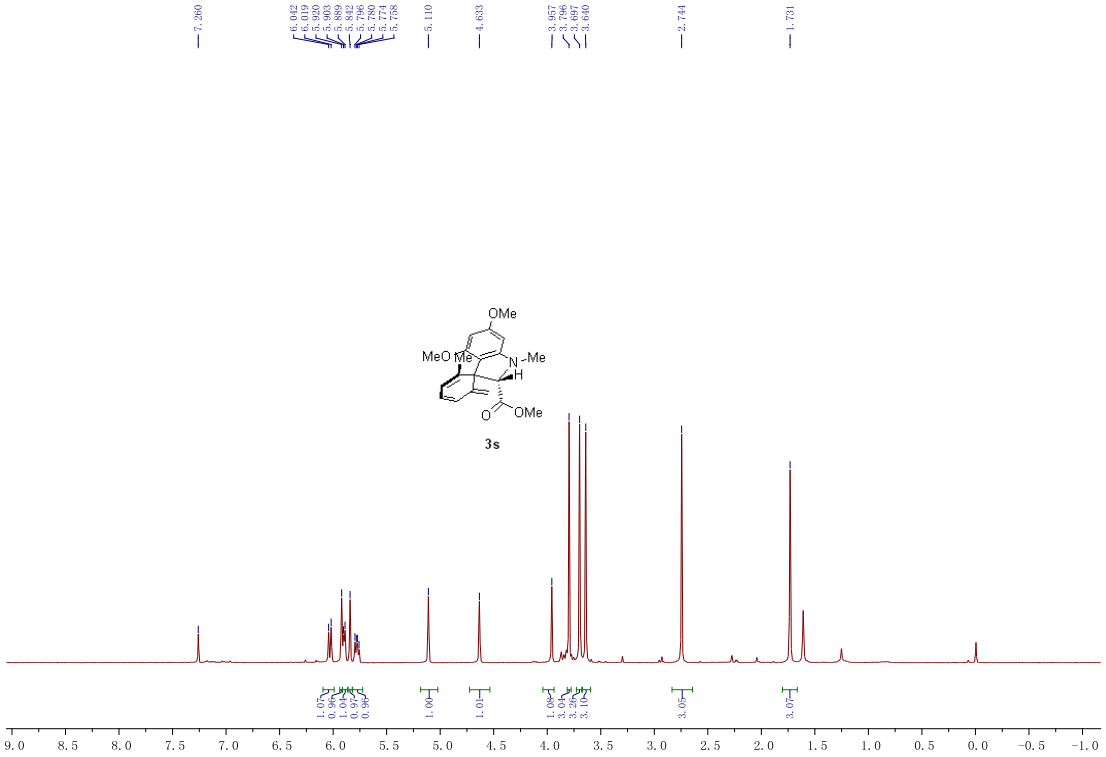
35.499
21.623
18.383
Me
Me
Me
N
H
O
O
3r
f1 (ppm)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6.019
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5.889
5.842
5.796
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5.774
5.758
5.110
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3.957
3.796
3.697
3.640
2.744
1.731
OMe
MeO
Me
N
Me
H
O
OMe
3s
1.07
0.96
1.04
0.97
0.96
1.00
1.01
1.08
3.04
3.26
3.10
3.05
3.07
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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3.0
2.5
2.0
1.5
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0.5
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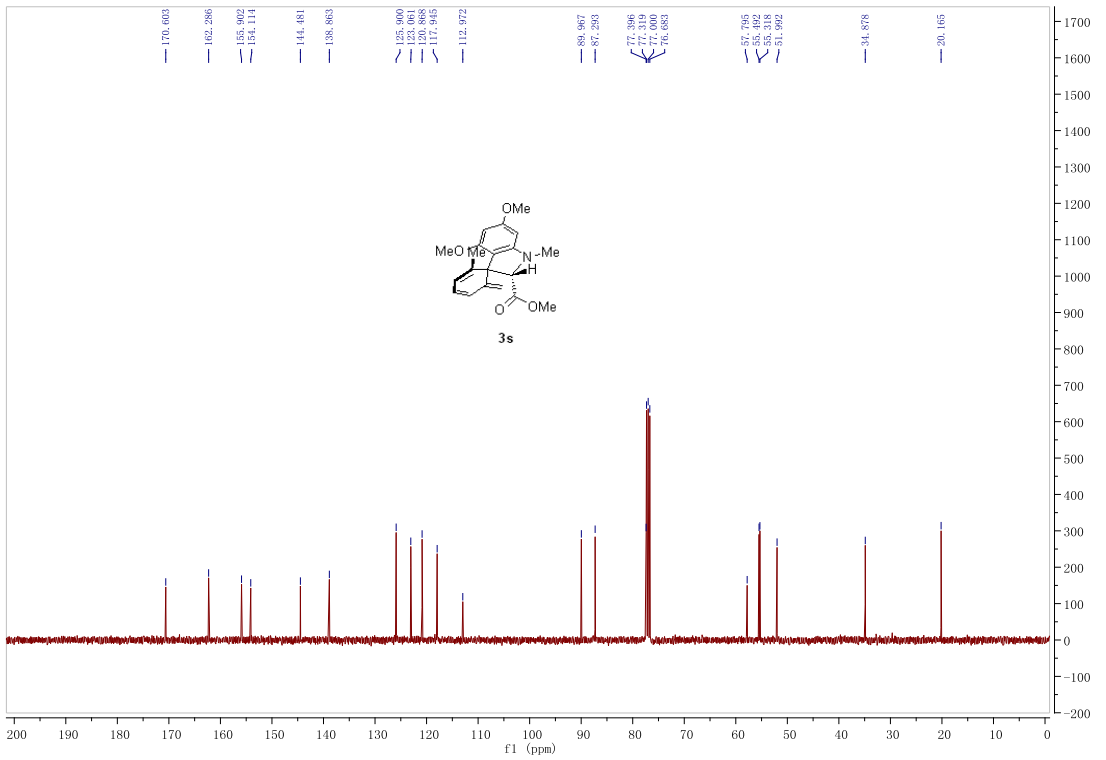
−1.0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123.061
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117.945
112.972
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87.283
77.396
77.319
77.000
76.683
57.795
55.492
55.318
51.992
34.878
20.165
OMe
MeO
Me
N
Me
H
O
OMe
3s
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
−100
−200
200
190
180
170
160
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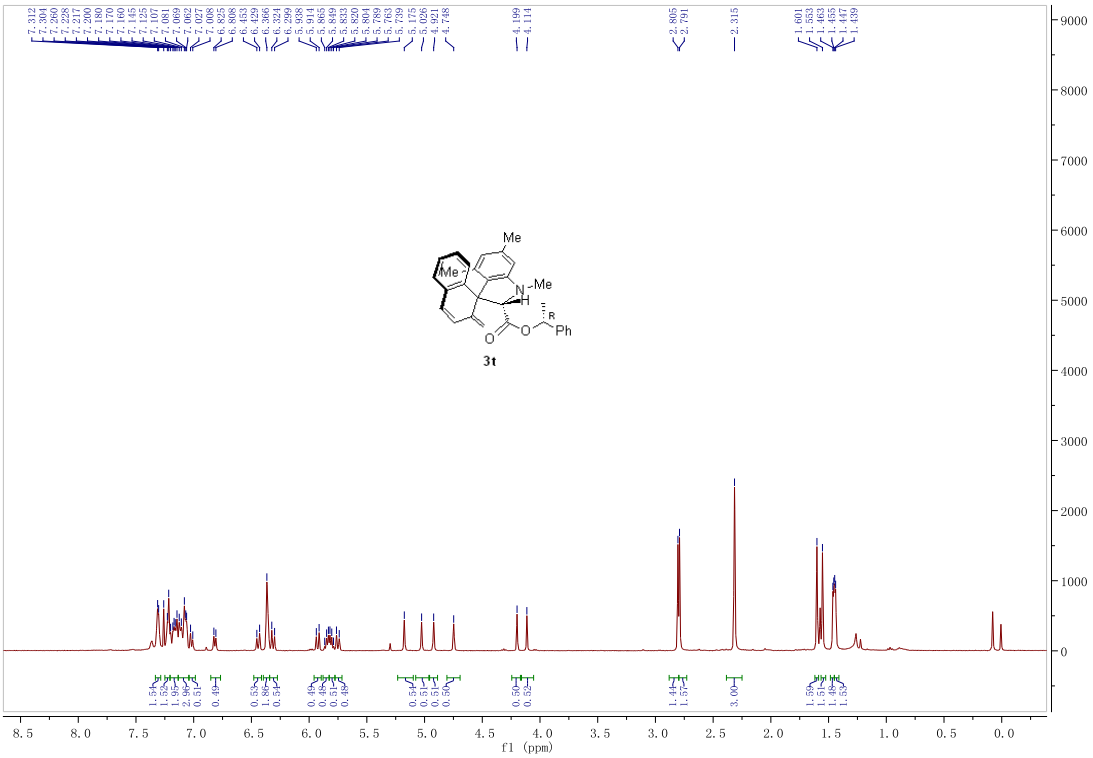
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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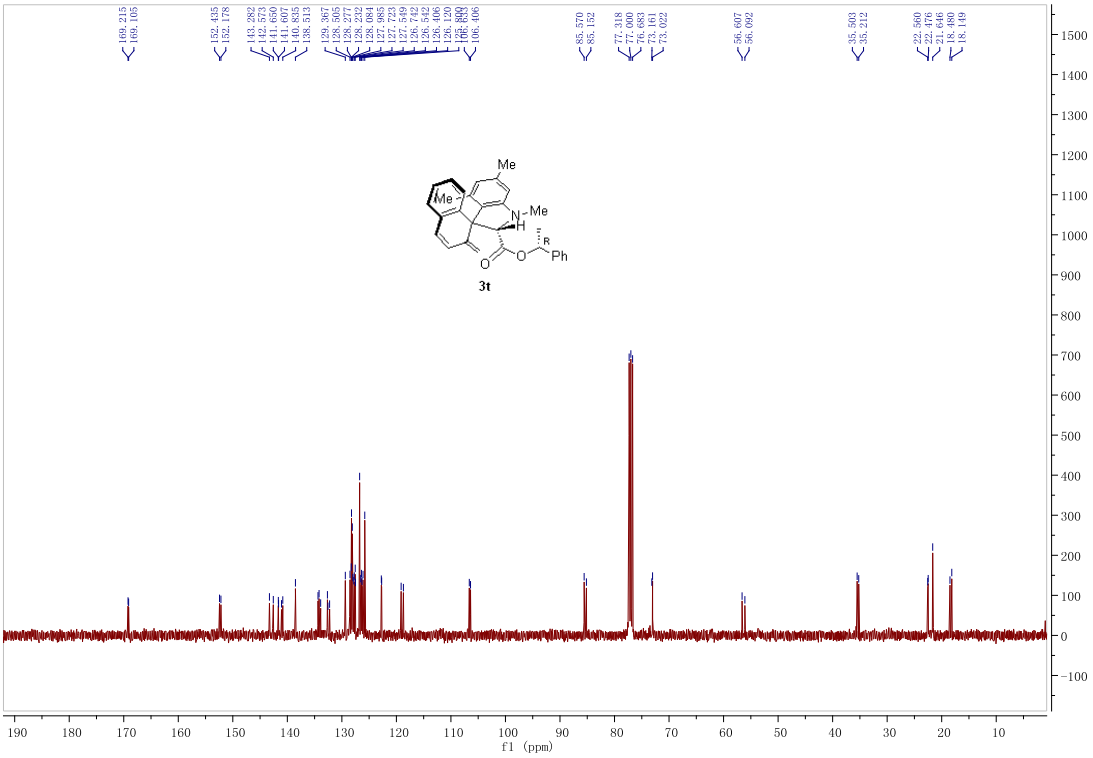
Me
N
Me
H
R
Ph
O
O
3t
f1 (ppm)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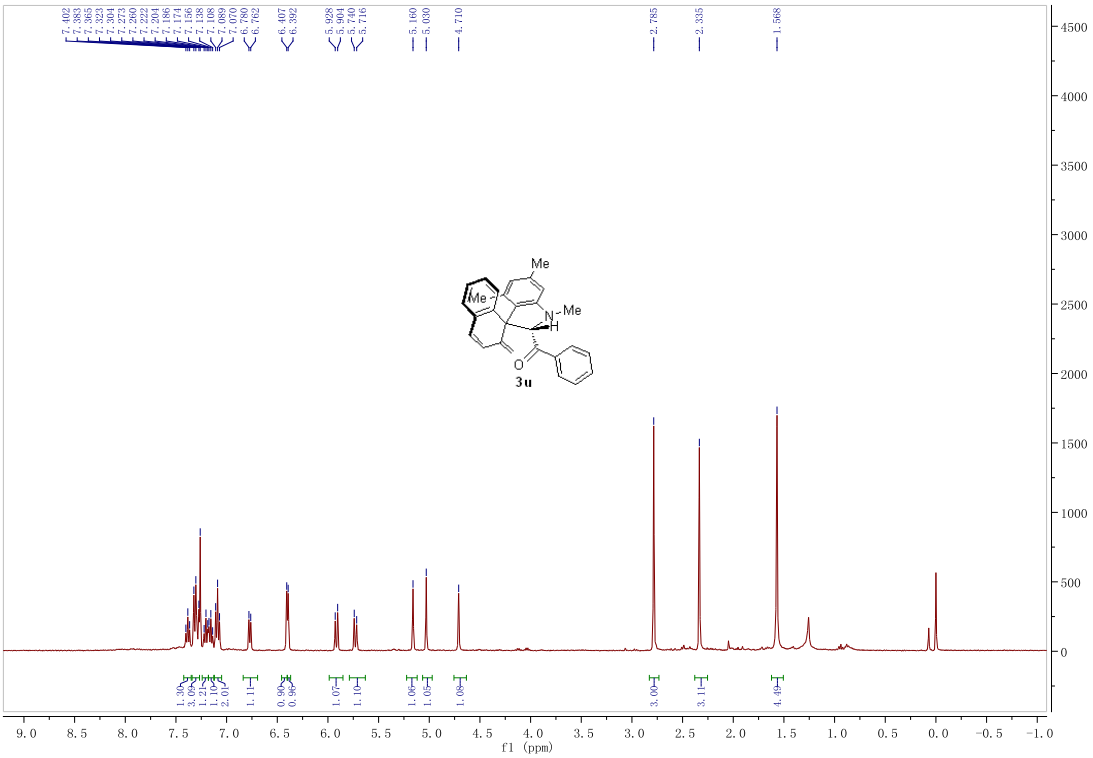
Me
N
Me
H
R
Ph
O
O
3t
f1 (ppm)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7.222
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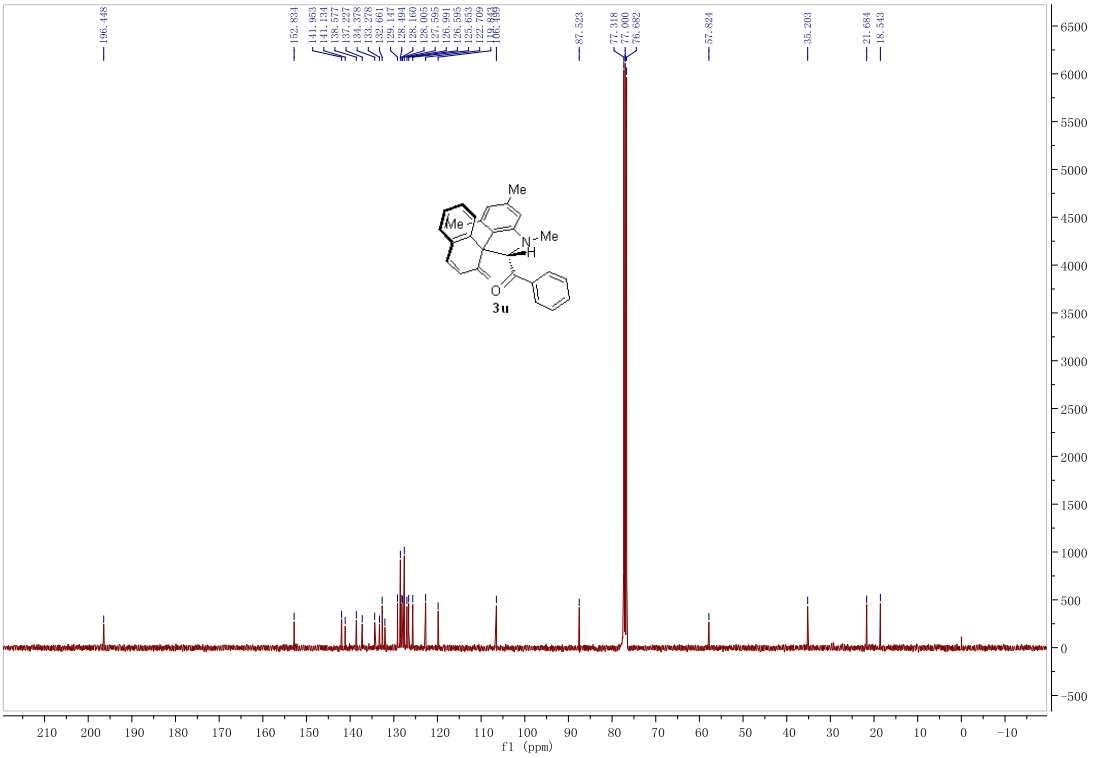
7.174
7.156
7.138
7.108
7.089
7.070
6.789
6.762
6.407
6.392
5.928
5.904
5.740
5.716
5.160
5.030
4.710
2.785
2.335
1.568
Me
Me
N
Me
H
O
3u
f1 (ppm)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133.228
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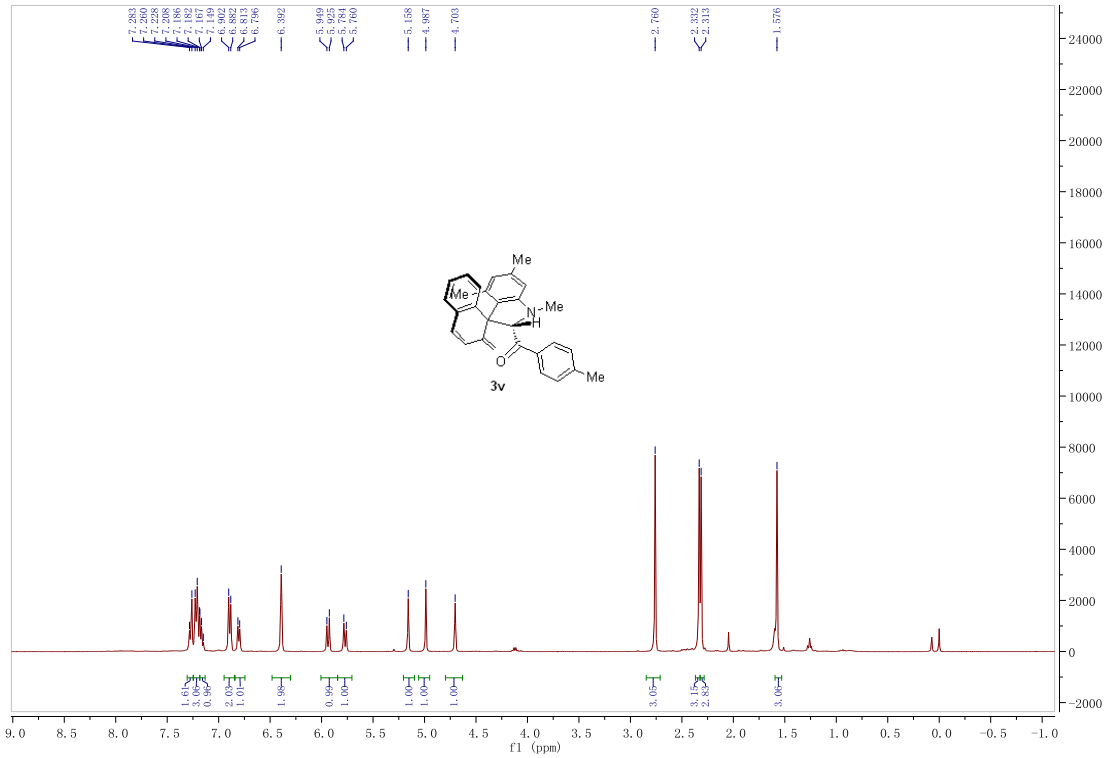
128.060
127.806
127.595
126.991
126.595
125.653
123.709
87.523
77.318
77.000
76.682
57.824
35.203
21.684
18.543
Me
Me
N
Me
H
O
3u
f1 (ppm)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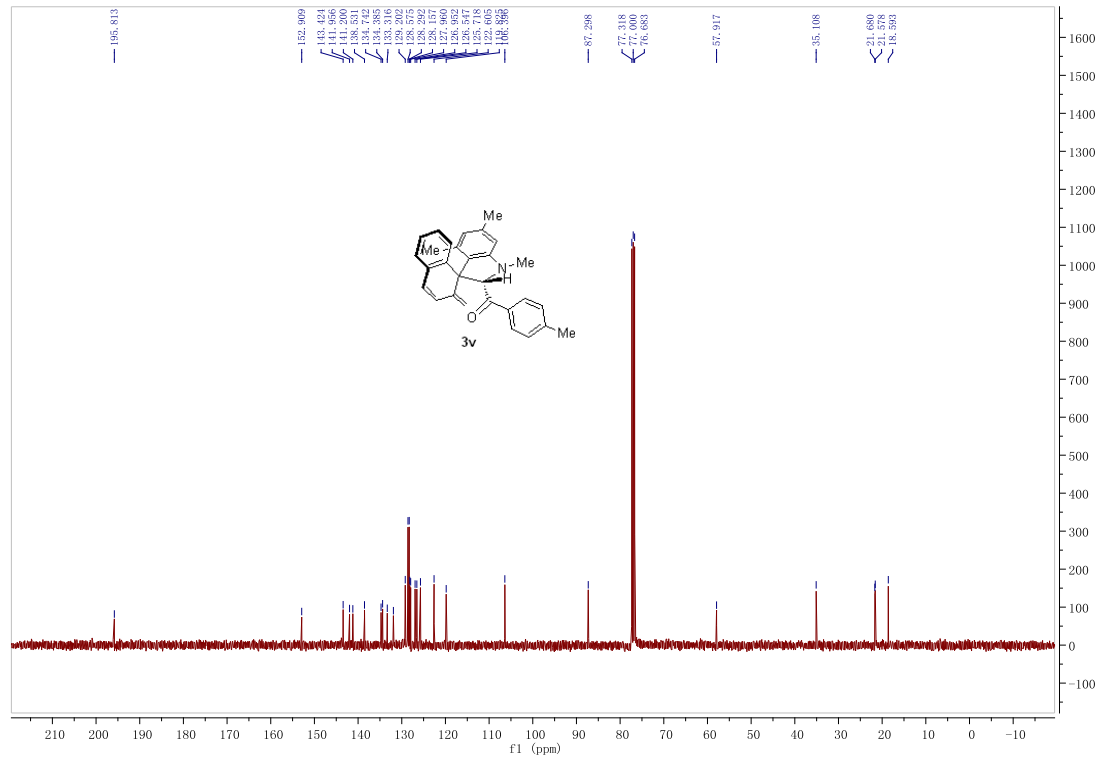
7.228
7.208
7.186
7.182
7.167
7.149
6.902
6.882
6.813
6.796
6.392
5.949
5.925
5.784
5.760
5.158
4.987
4.703
2.760
2.332
2.313
1.576
Me
Me
N
H
O
Me
3v
f1 (ppm)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141.200
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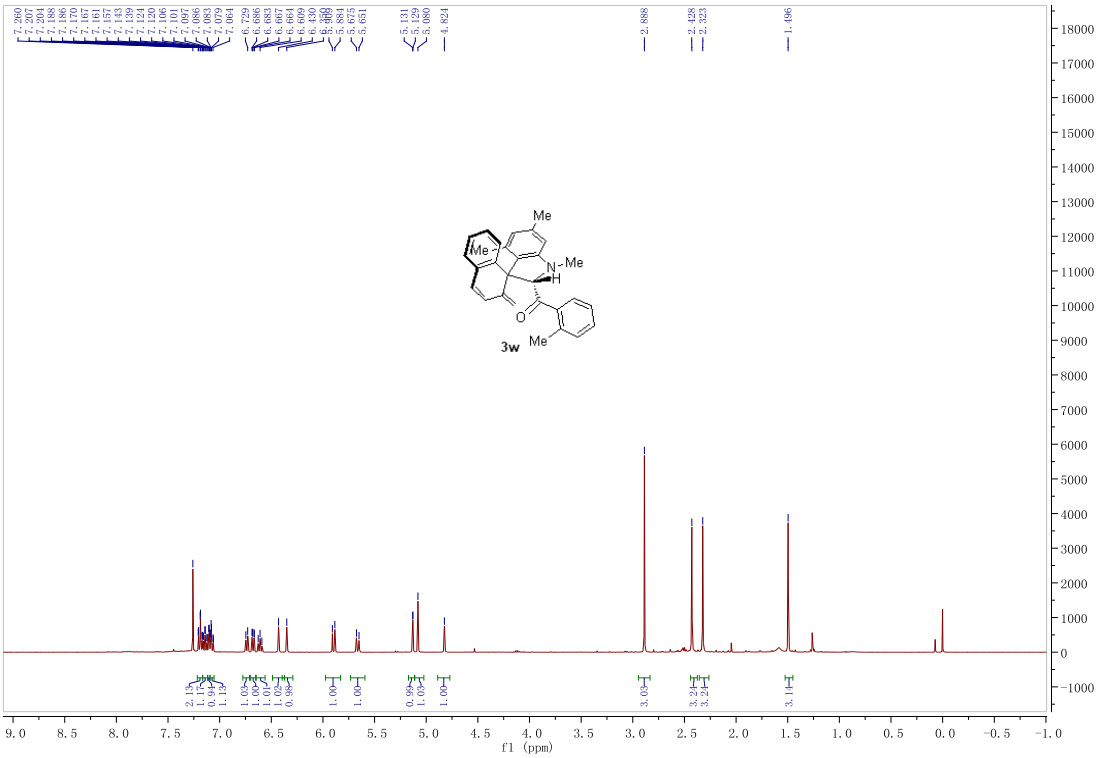
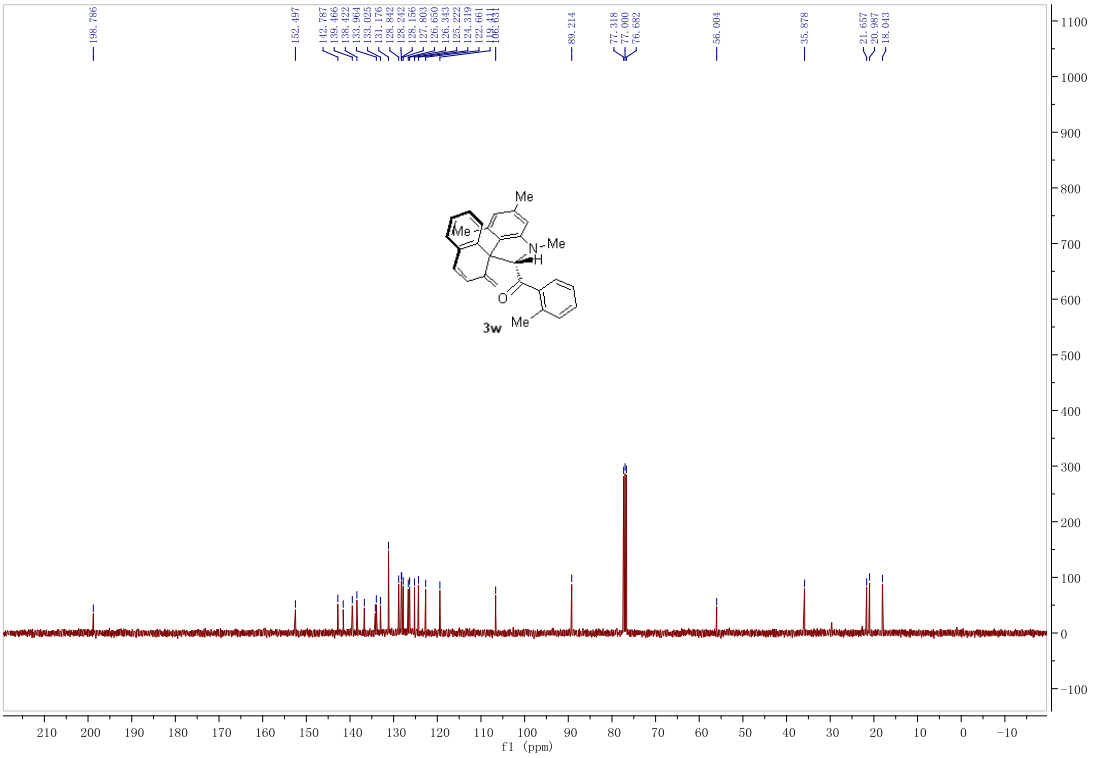
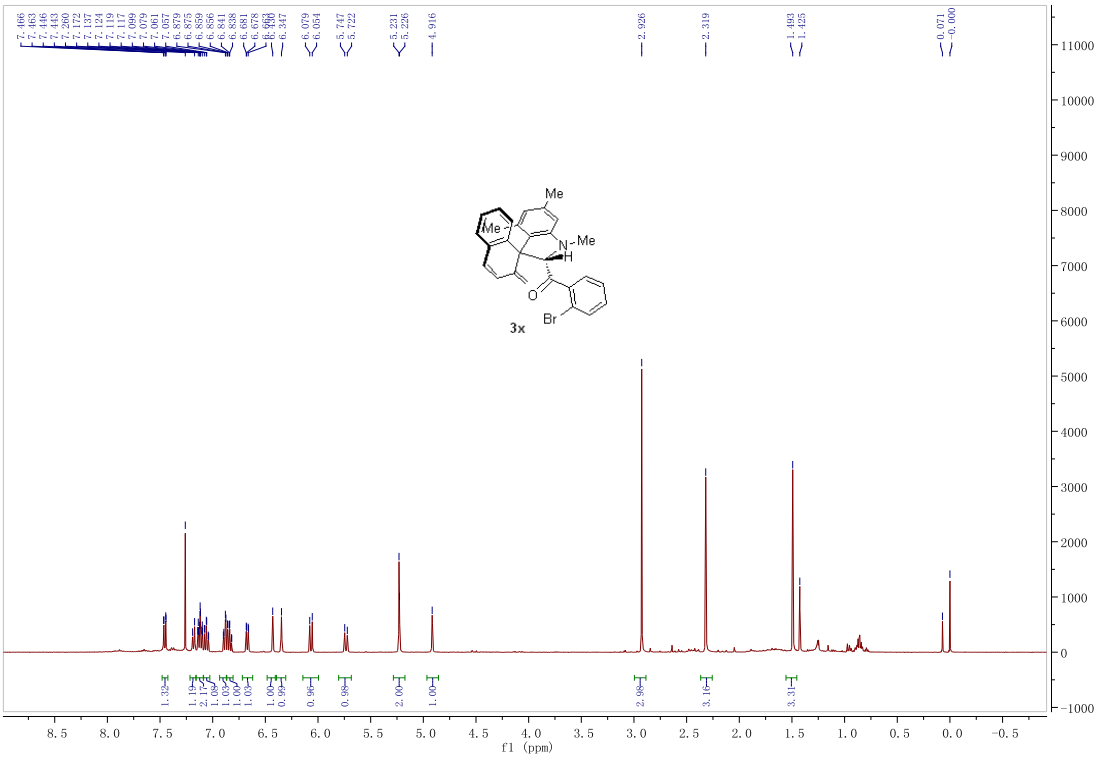
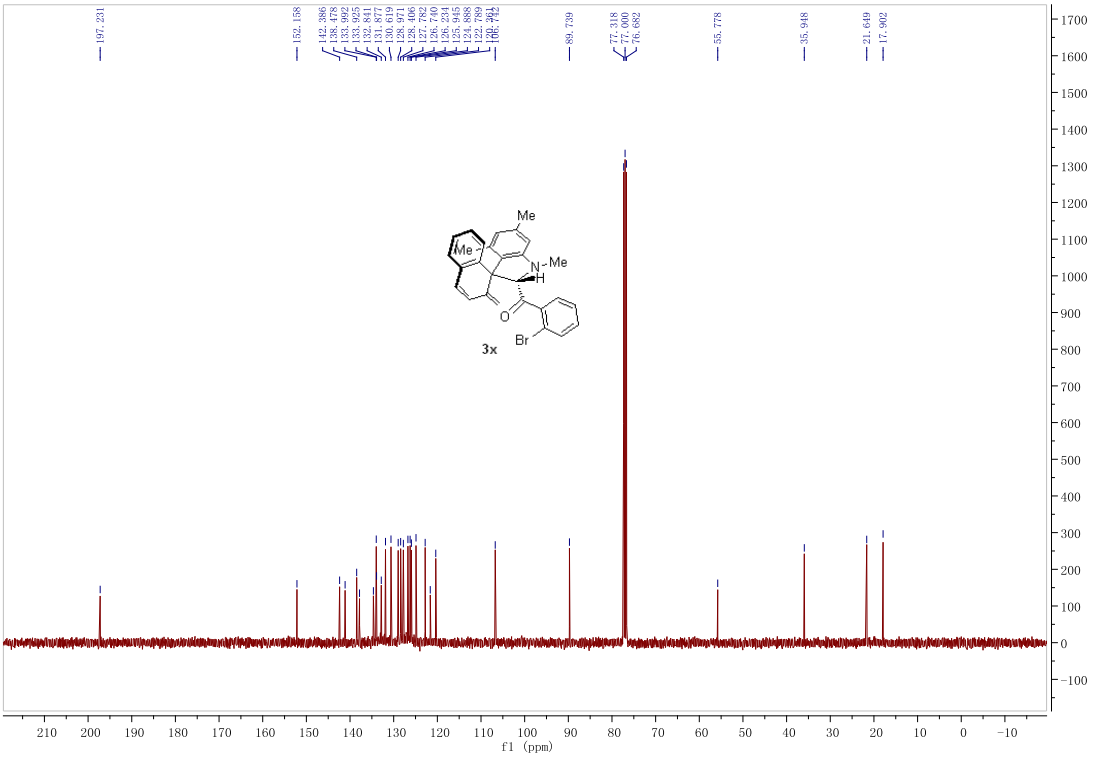
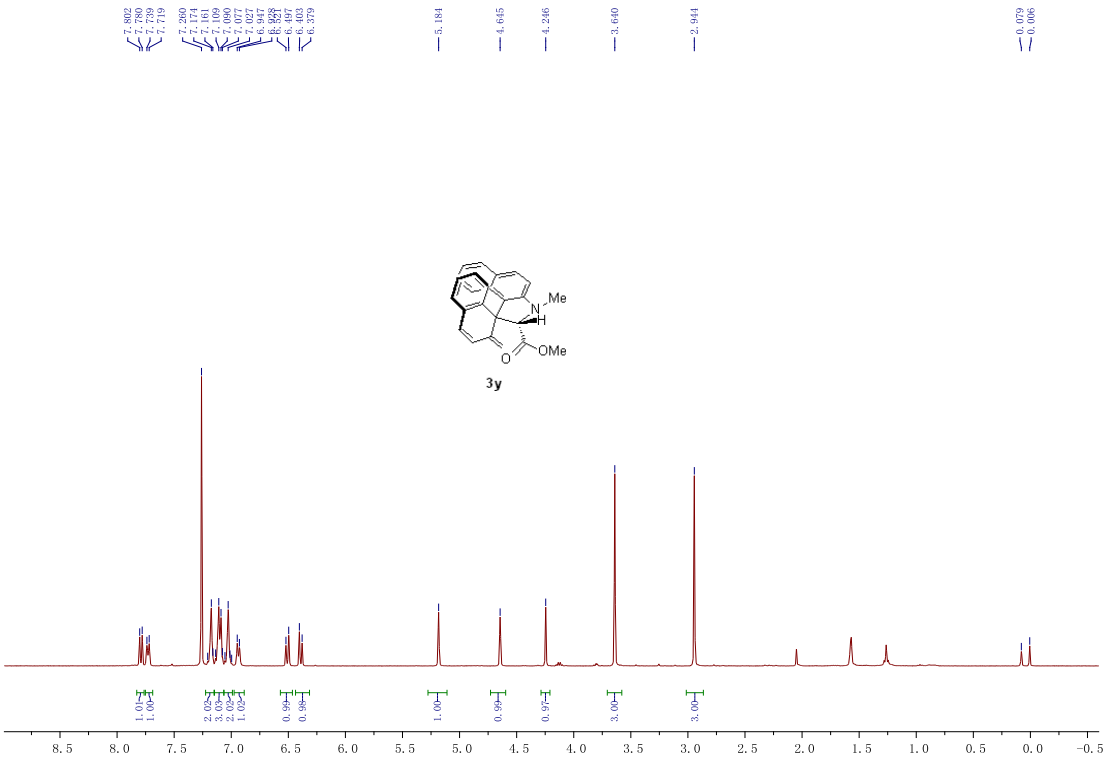
134.368
133.316
129.202
128.575
128.292
128.157
127.960
126.952
126.547
125.718
123.665
87.298
77.318
77.000
76.683
57.917
35.108
21.680
21.578
18.393
Me
Me
N
H
O
Me
3v
f1 (ppm)


Me
Me
N-Me
H
O
Me
3w
f1 (ppm)


Me
Me
N-Me
H
O
Me
3w
f1 (ppm)


Me
Me
N
Me
H
O
Br
3x
f1 (ppm)


Me
Me
N
Me
H
O
Br
3x
f1 (ppm)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7.161
7.109
7.089
7.077
7.027
6.947
6.497
6.493
6.379
5.184
4.645
4.246
3.640
2.944
0.079
0.006
Me
N
H
OMe
O
3y
1.01
1.00
2.02
3.03
2.05
1.02
0.99
0.96
1.00
0.99
0.97
3.00
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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3.5
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2.5
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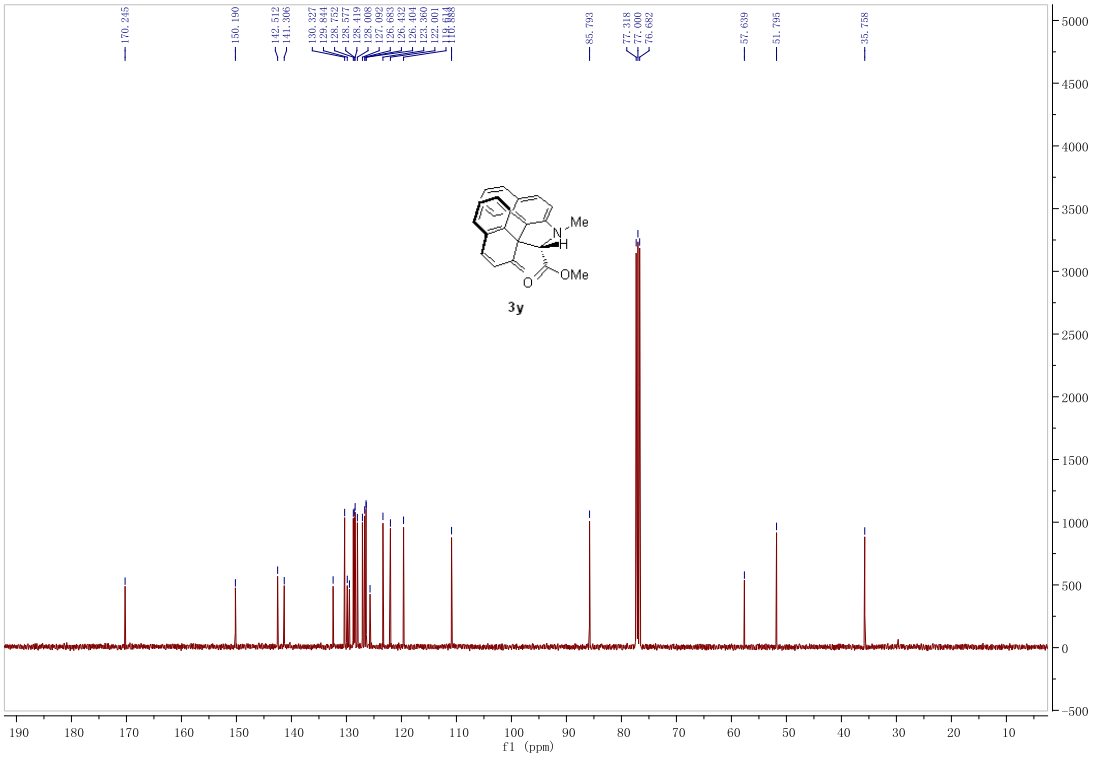
0.0
-0.5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141.306
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128.577
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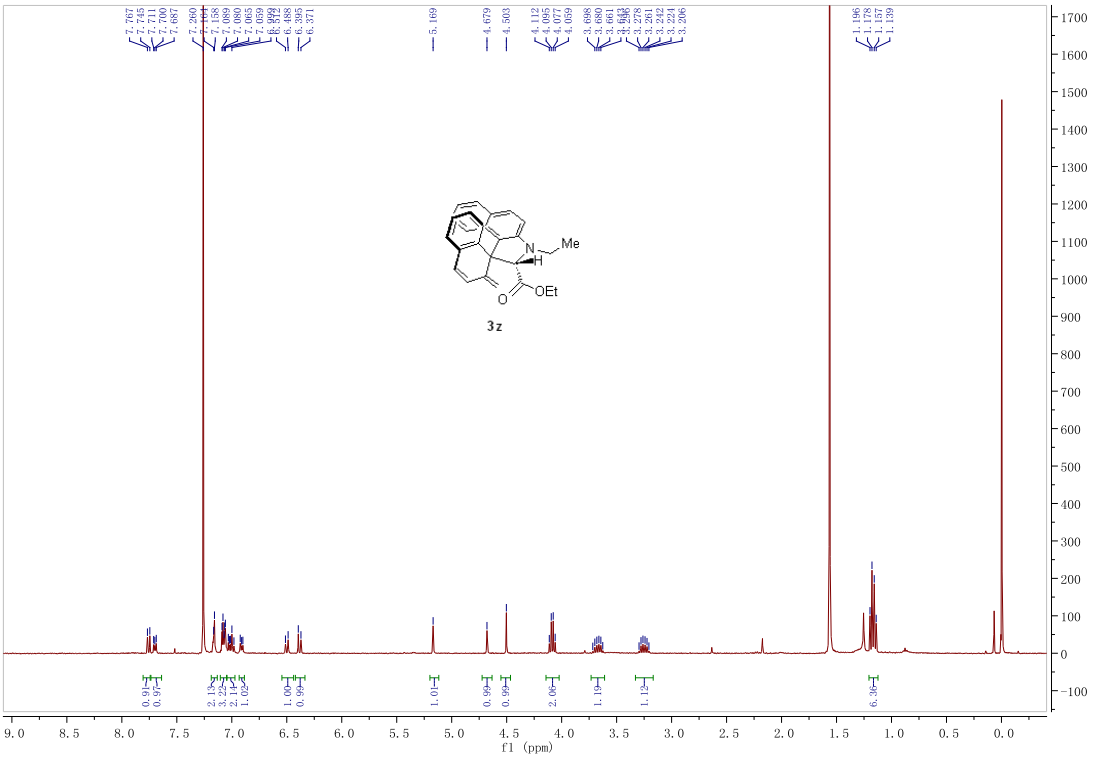
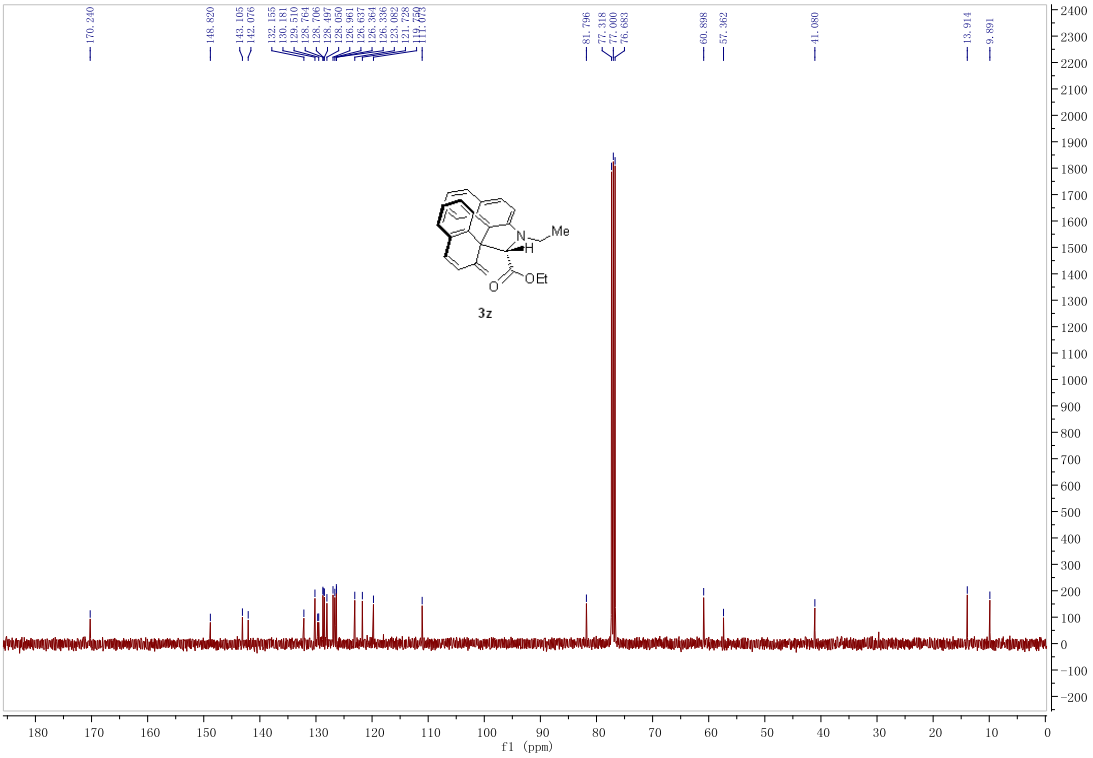
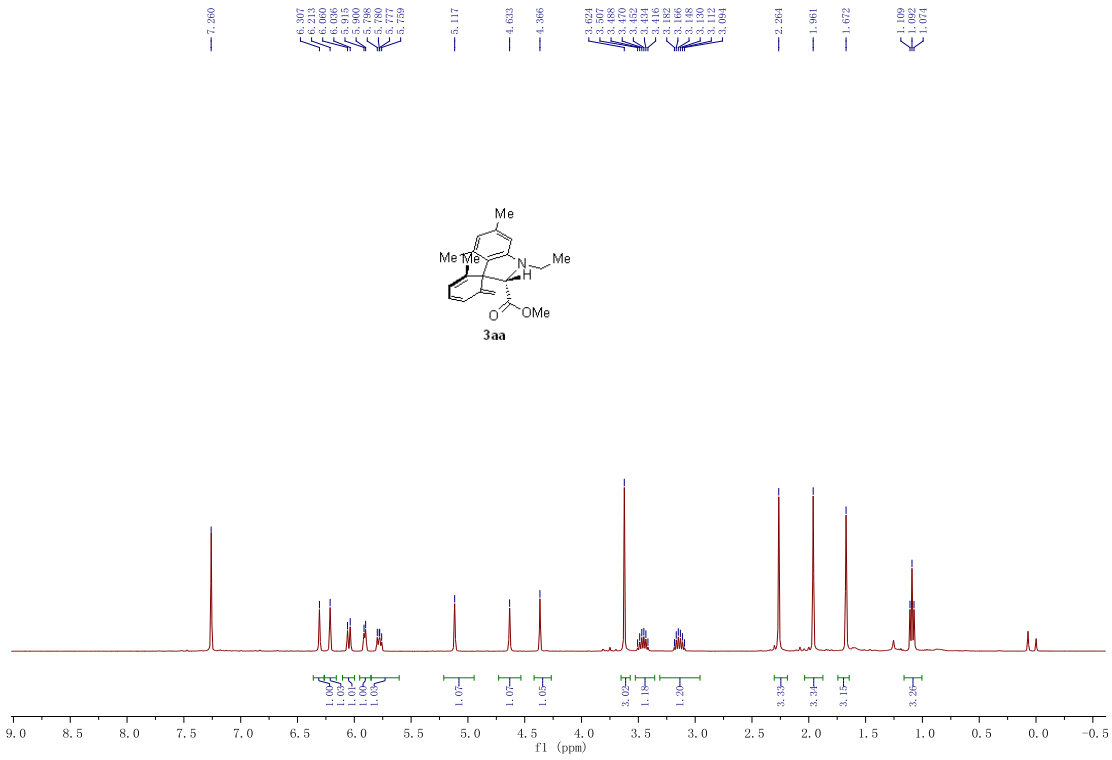
128.108
127.092
126.683
126.432
125.640
125.360
122.001
85.793
77.318
77.000
76.682
57.639
51.795
35.758
Me
N
H
OMe
O
3y
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


Me
N
H
OEt
O
3z
f1 (ppm)


Me
N
H
OEt
O
3z
f1 (ppm)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5.798
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5.777
5.759
5.117
4.633
4.366
3.624
3.507
3.488
3.470
3.452
3.434
3.416
3.182
3.166
3.148
3.130
3.112
3.094
2.264
1.961
1.672
1.109
1.092
1.074
Me
Me
Me
N
H
Me
O
OMe
3aa
1.00
1.02
1.01
1.06
1.05
1.07
1.07
1.05
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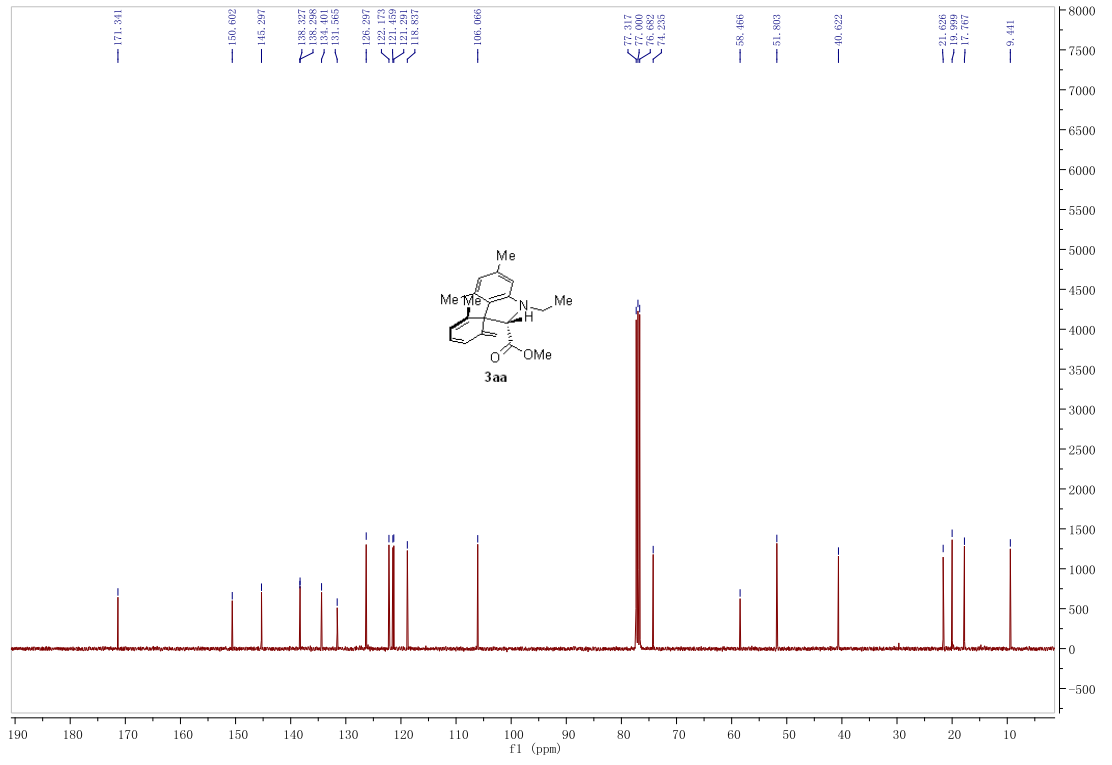
1.20
3.33
3.34
3.15
3.26
f1 (ppm)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121.499
121.291
118.837
106.066
77.317
77.000
76.682
74.235
58.466
51.803
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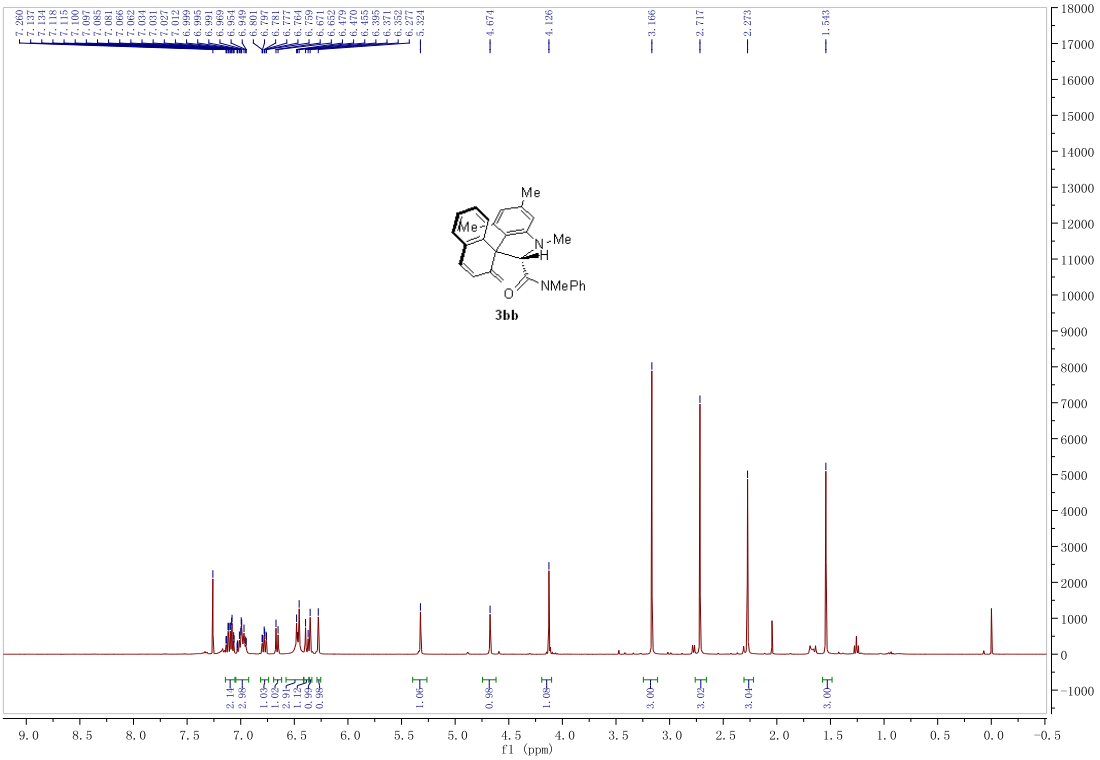
21.626
19.999
17.767
9.441
Me
Me
Me
N
H
Me
O
OMe
3aa
f1 (ppm)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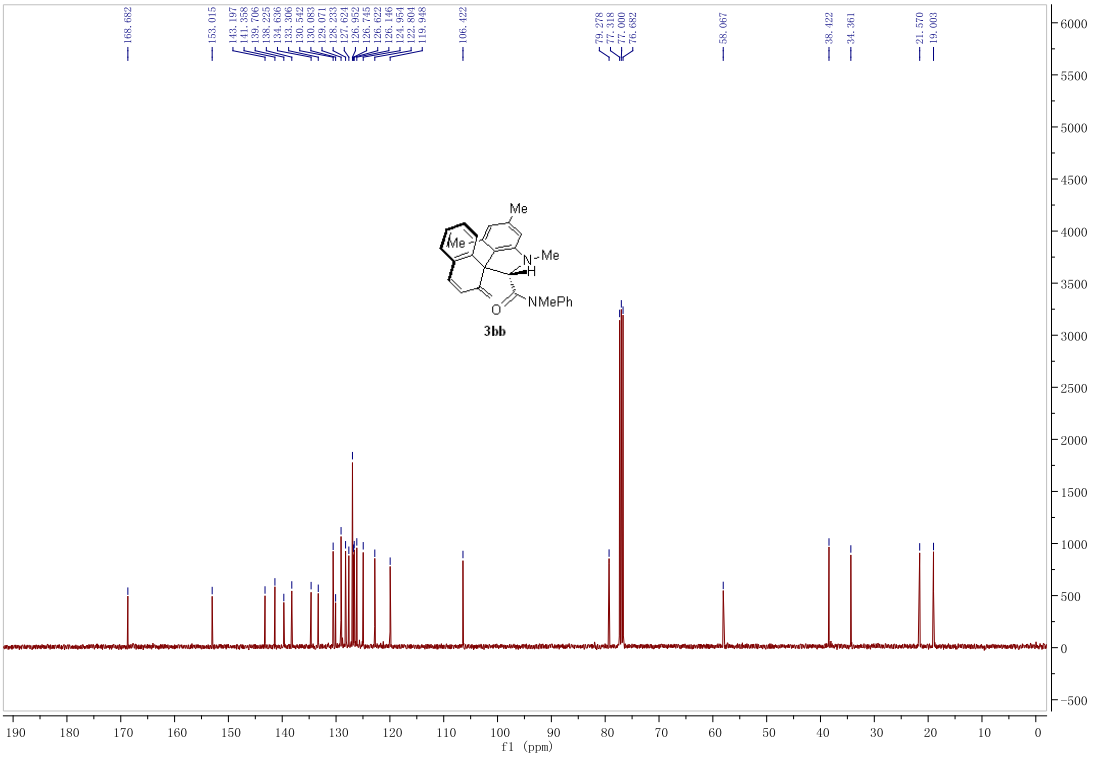
Me
N
Me
H
O
NMePh
3bb
f1 (ppm)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Me
N
Me
H
O
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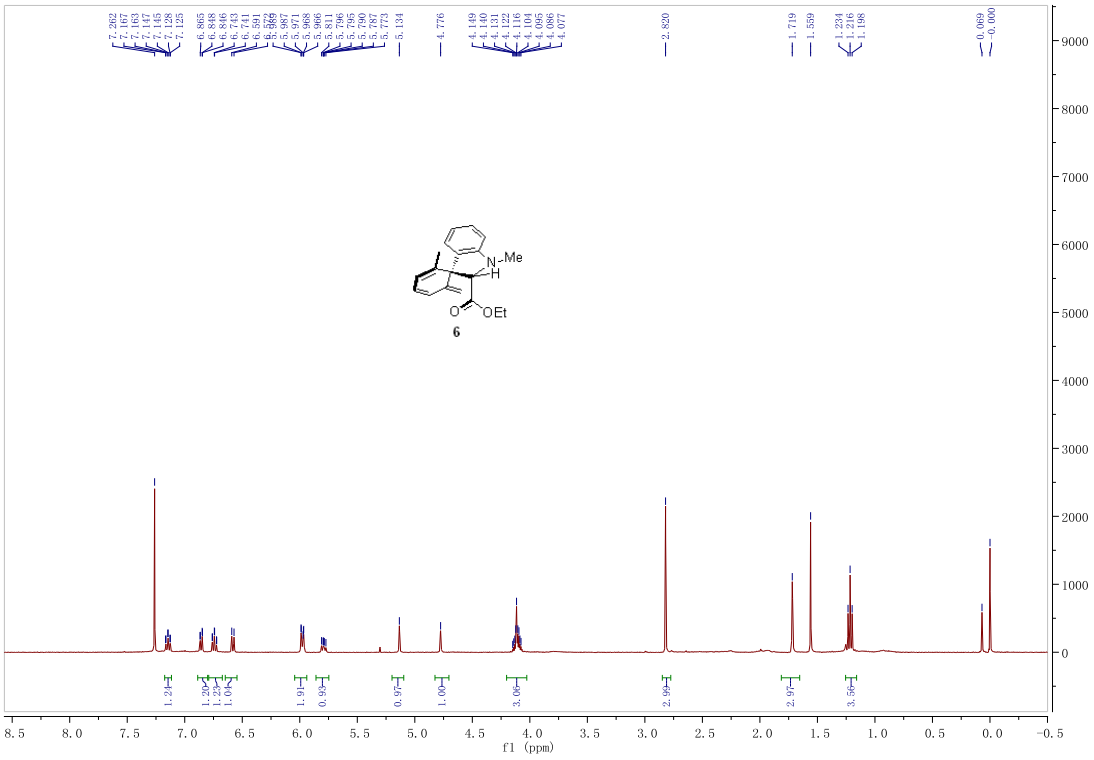
3bb
f1 (ppm)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6.846
6.743
6.741
6.591
6.589
5.989
5.987
5.971
5.968
5.966
5.791
5.788
5.795
5.790
5.787
5.773
5.134
4.776
4.149
4.140
4.131
4.122
4.116
4.104
4.095
4.086
4.077
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1.719
1.559
1.234
1.216
1.198
0.069
-0.000
N-Me
H
O
OEt
6
1.24
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1.23
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0.97
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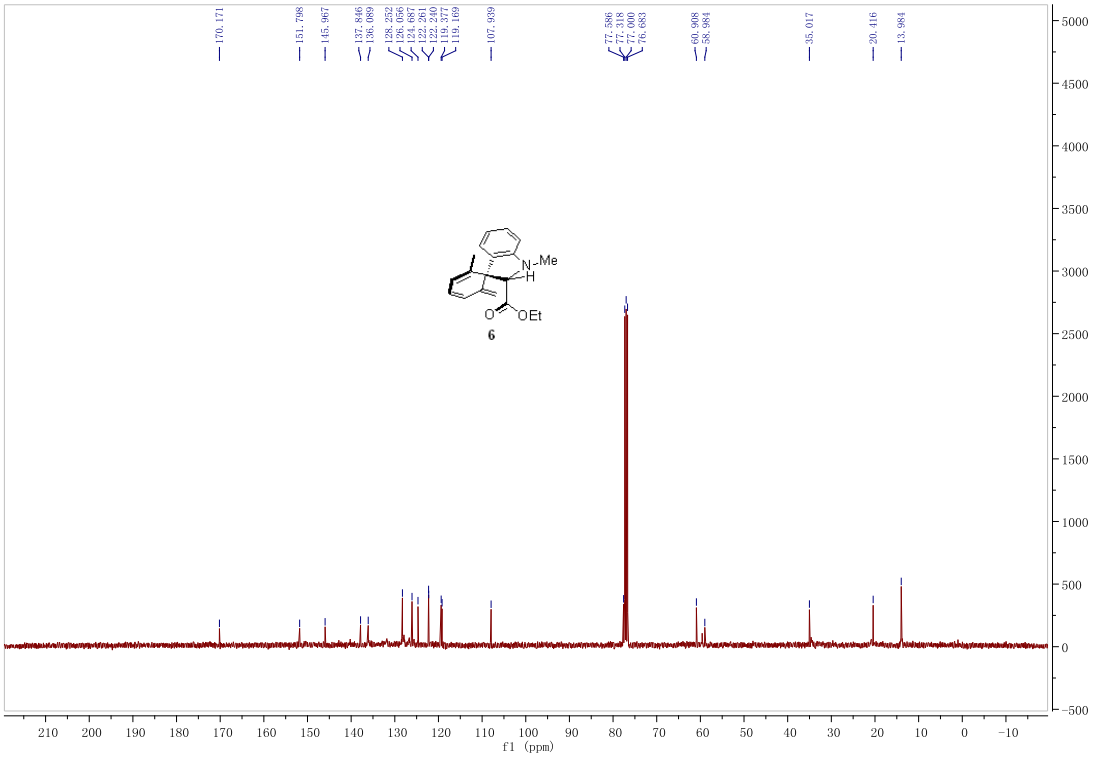
2.99
2.97
3.56
f1 (ppm)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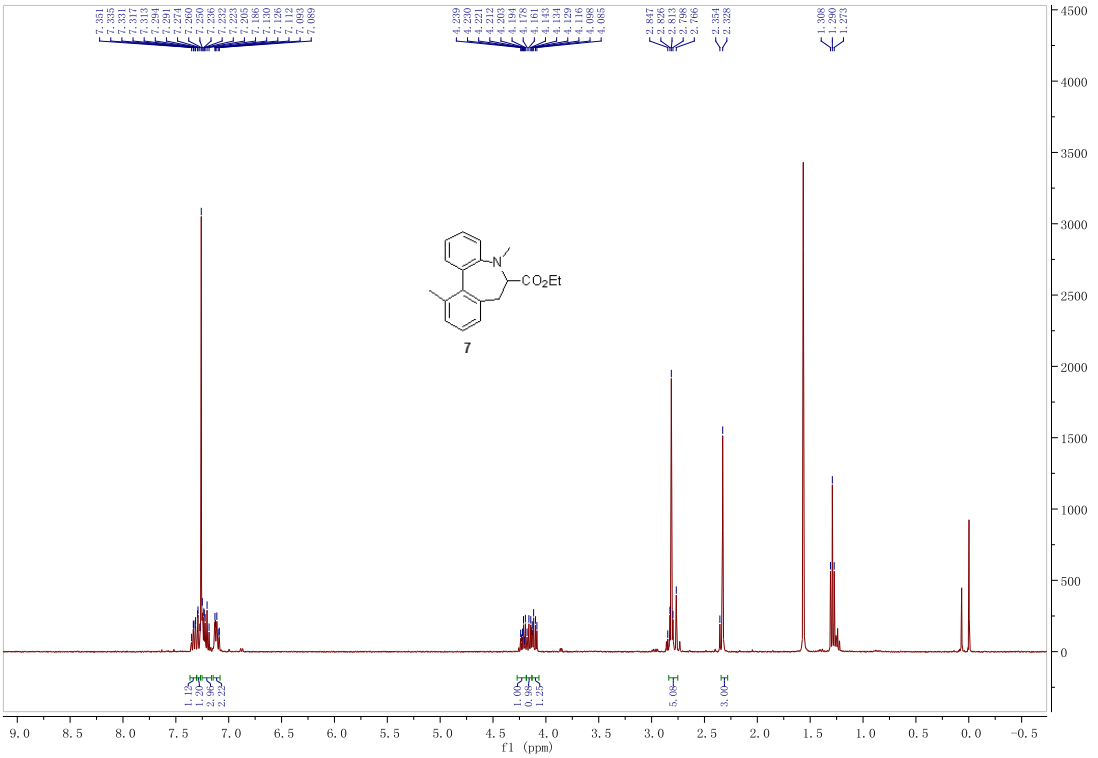
107.939
77.586
77.318
77.000
76.683
60.908
58.984
35.017
20.416
13.984
N-Me
H
O
OEt
6
f1 (ppm)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7.093
7.089
4.239
4.220
4.221
4.212
4.203
4.194
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4.115
4.098
4.085
2.847
2.835
2.813
2.798
2.766
2.354
2.328
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1.290
1.273
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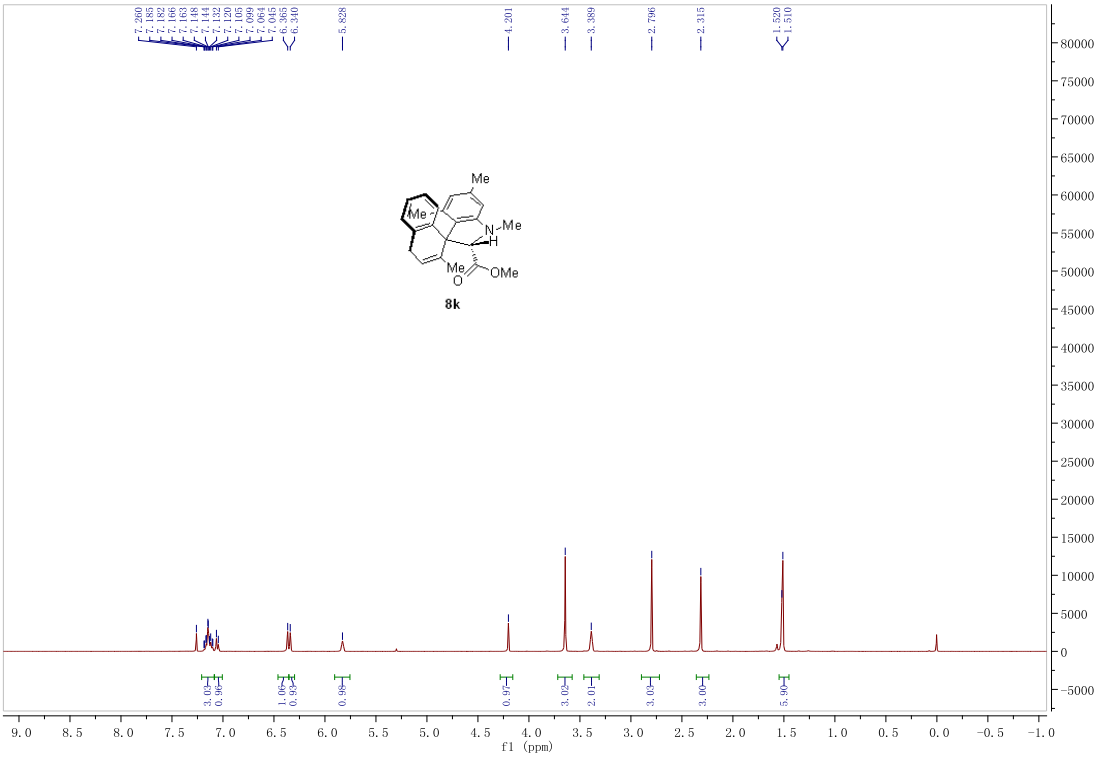
3.00
f1 (ppm)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7.045
6.958
6.340
5.828
4.201
3.644
3.389
2.796
2.315
1.520
1.510
Me
Me
N-Me
H
Me
O
OMe
8k
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3.03
3.00
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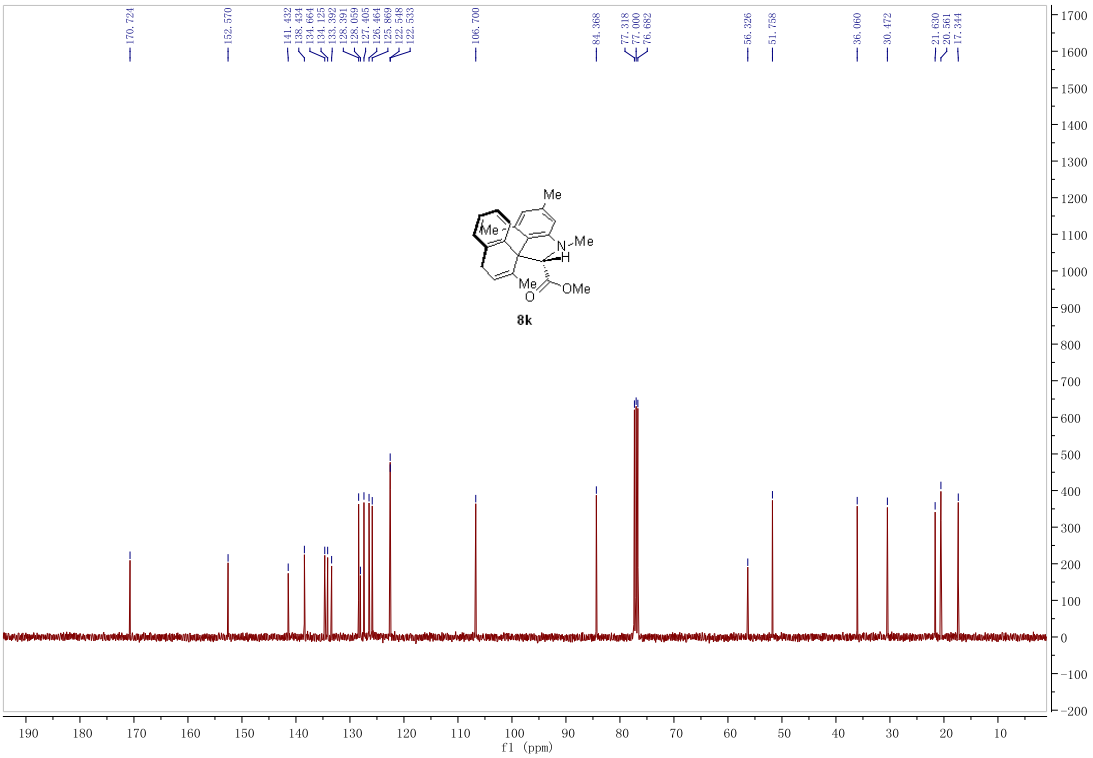
f1 (ppm)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127.405
126.464
125.869
122.548
122.535
106.700
84.368
77.318
77.000
76.682
56.326
51.758
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21.630
20.561
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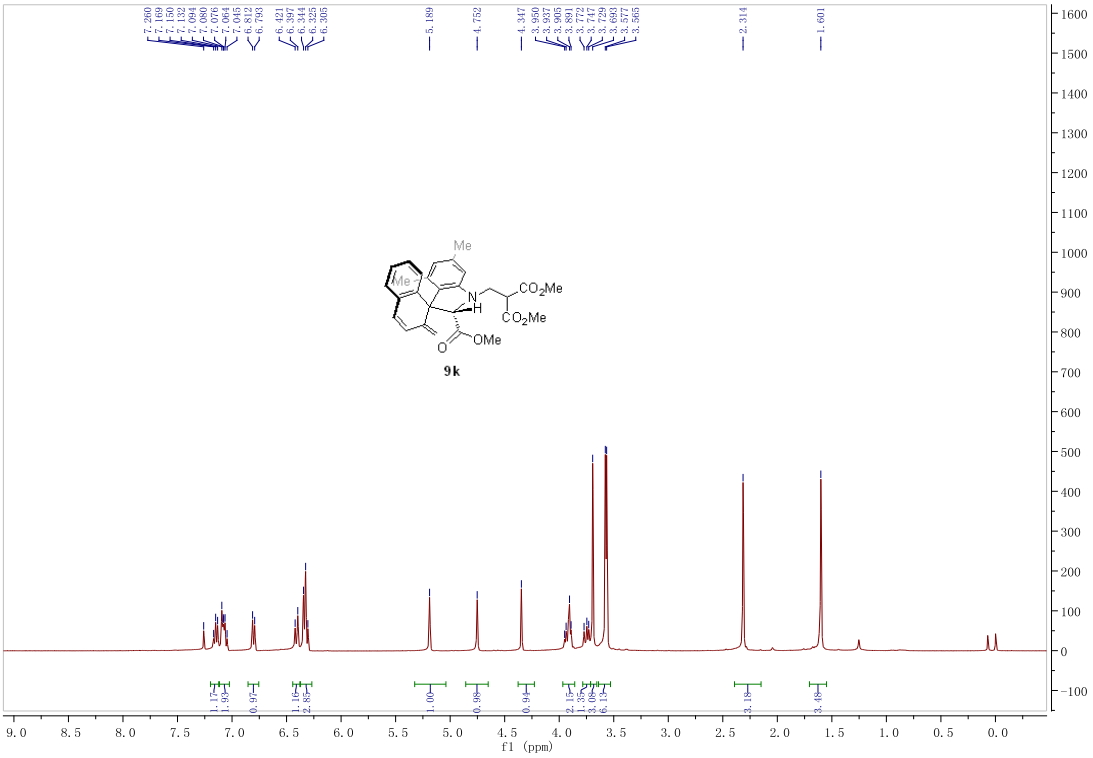
Me
N
H
Me
O
OMe
8k
f1 (ppm)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7.169
7.150
7.132
7.094
7.080
7.066
7.064
7.045
6.812
6.793
6.421
6.397
6.344
6.325
6.305
5.189
4.752
4.347
3.950
3.937
3.906
3.891
3.772
3.747
3.729
3.693
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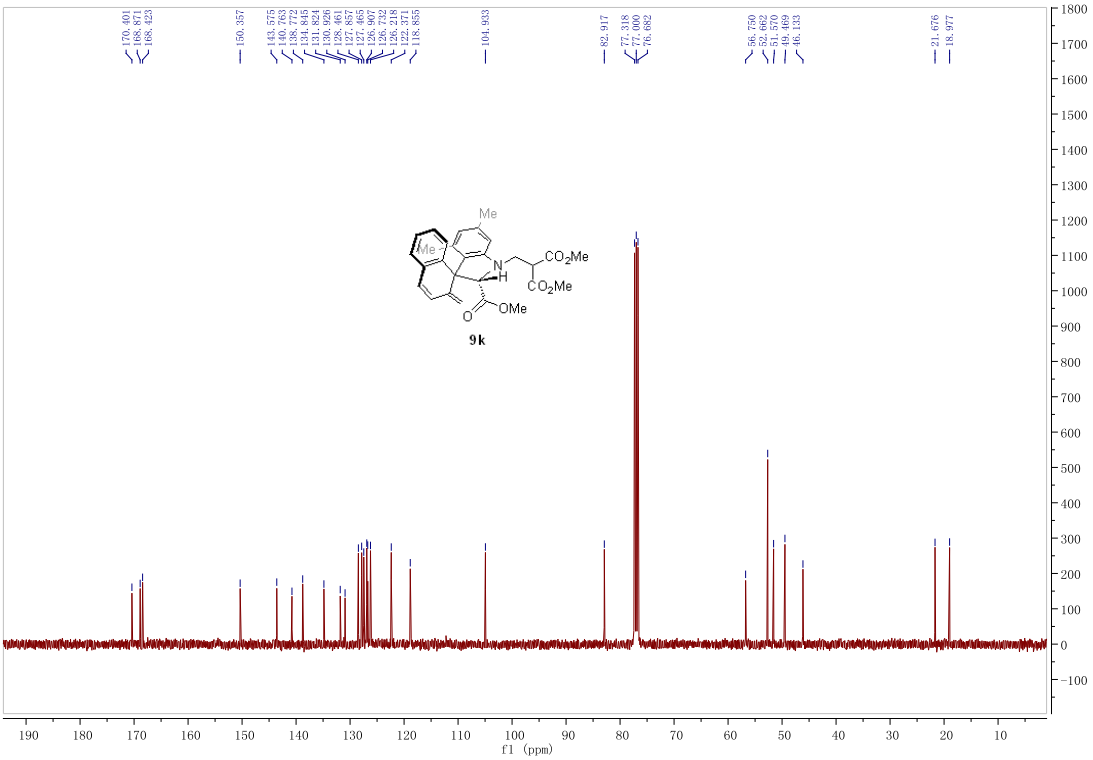
CO2Me
CO2Me
O
OMe
9k
f1 (ppm)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126.772
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104.933
82.917
77.318
77.000
76.682
56.750
52.662
51.570
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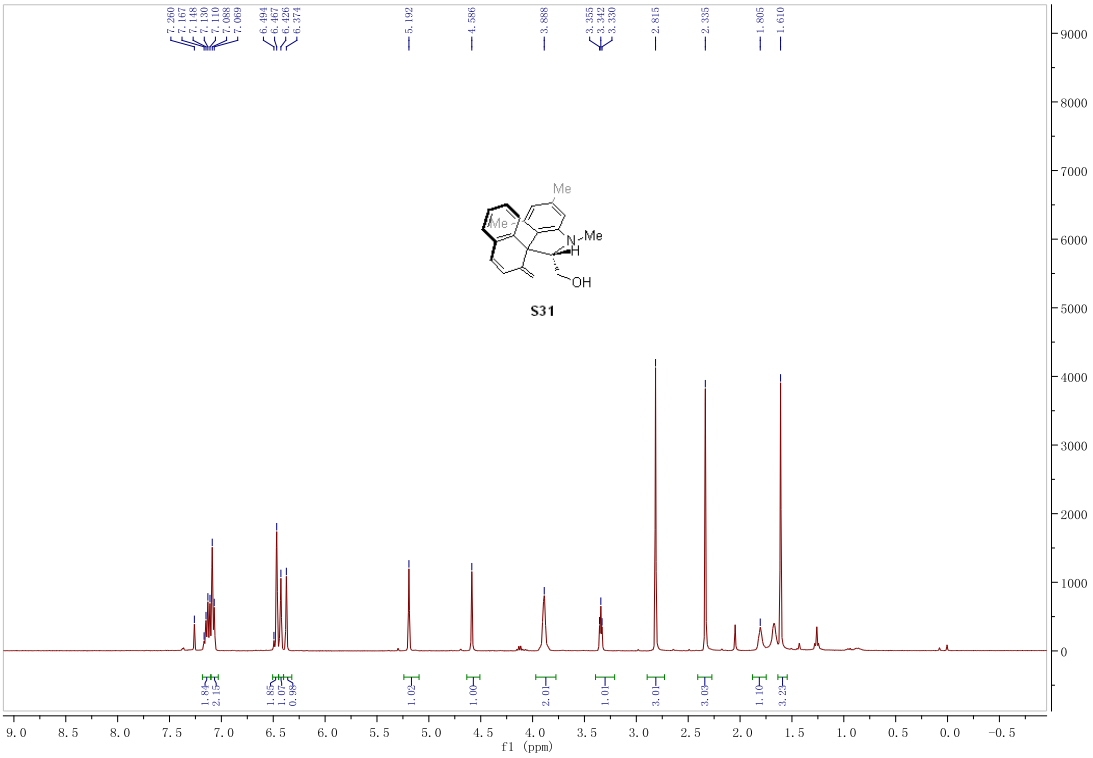
Me
N
H
CO2Me
CO2Me
O
OMe
9k
f1 (ppm)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6.426
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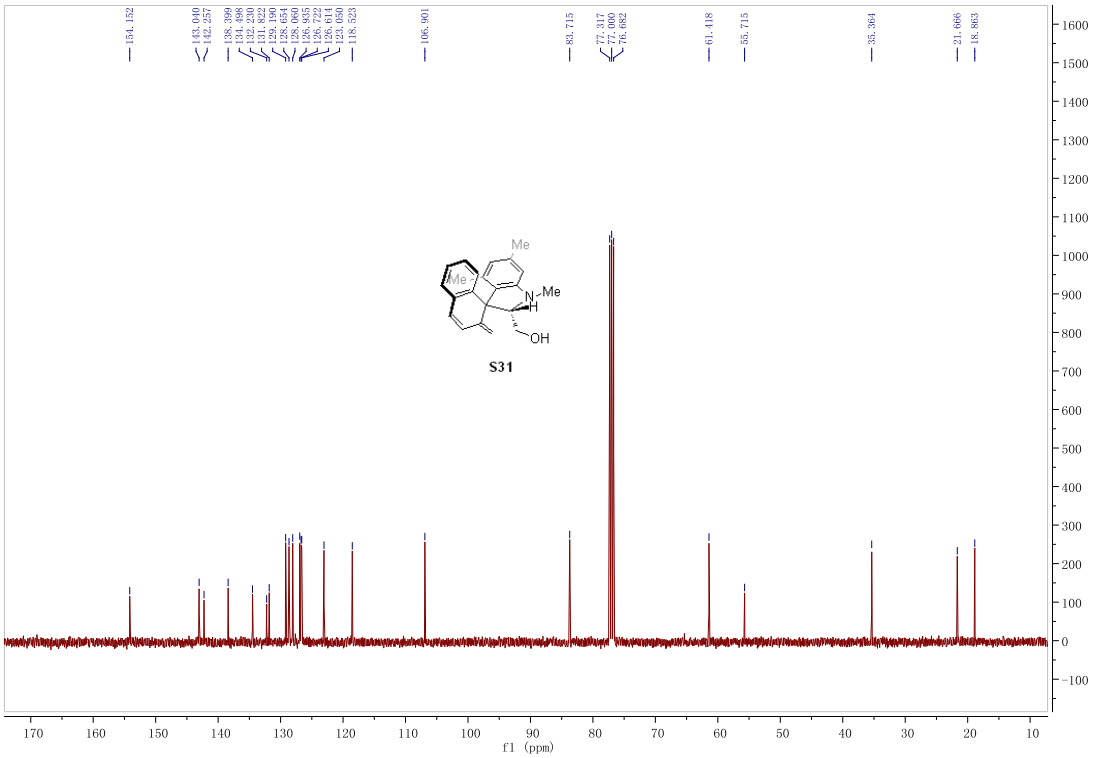
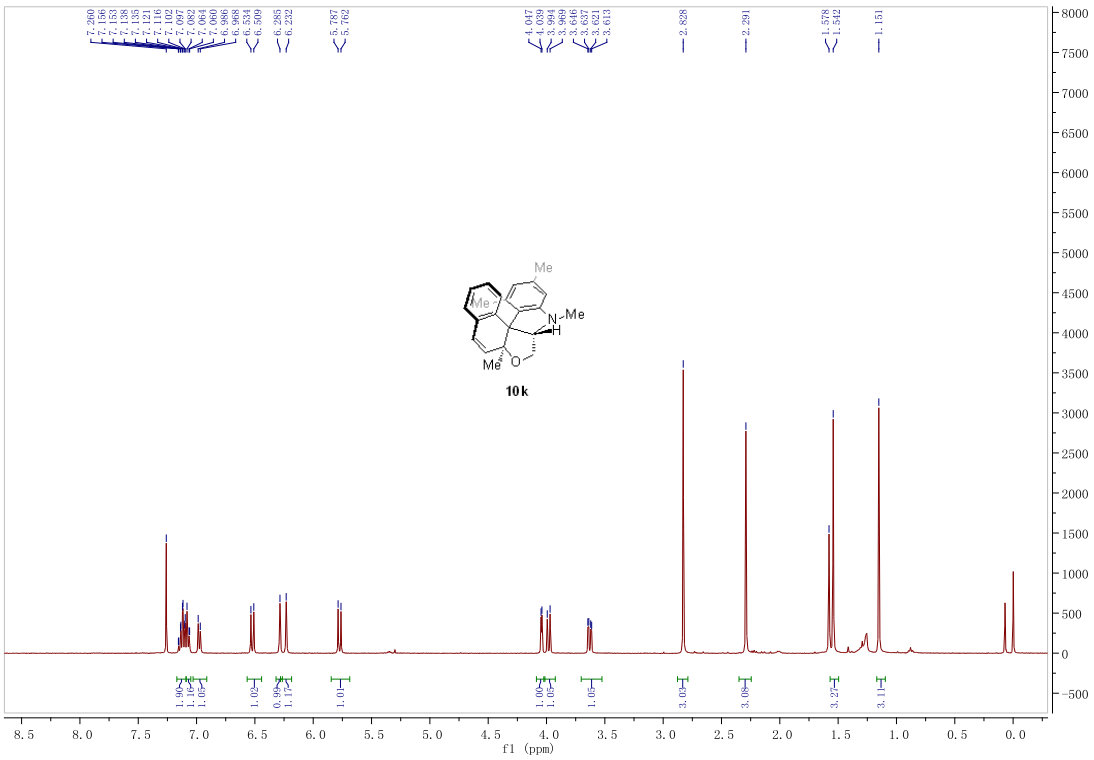
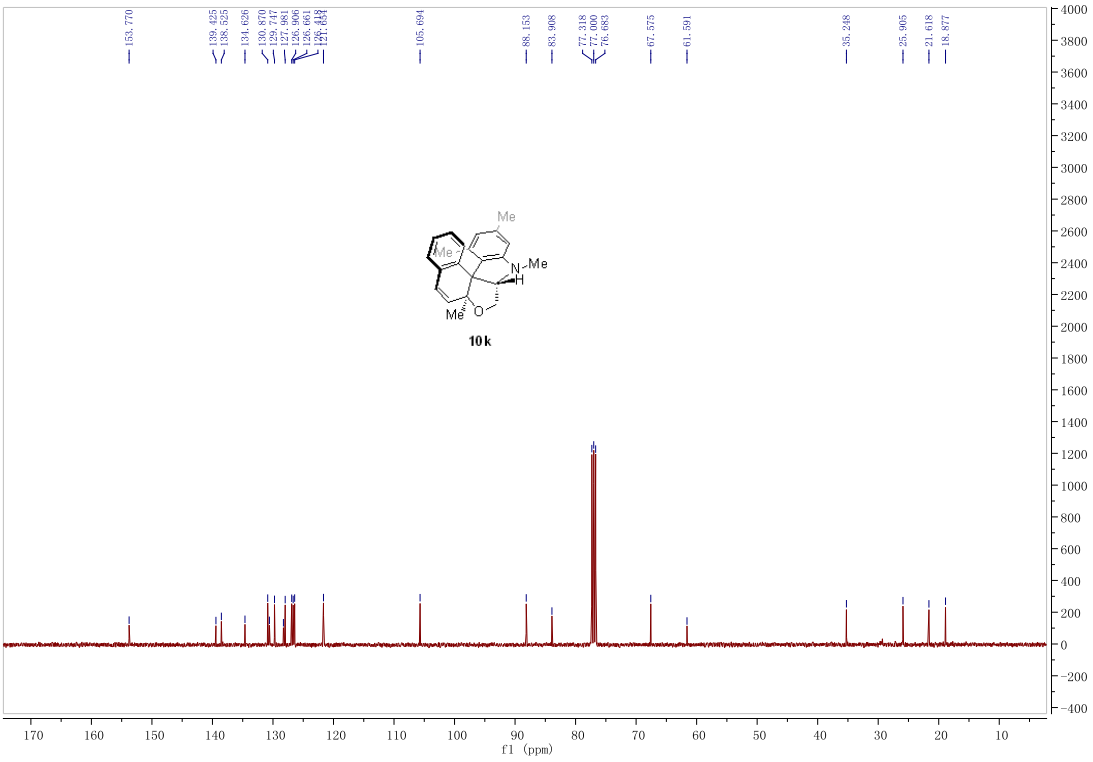
4.586
3.888
3.355
3.342
3.330
2.815
2.335
1.805
1.610
Me
Me
N
H
Me
OH
S31
1.88
2.15
1.85
1.07
0.89
1.02
1.00
2.01
1.01
3.01
3.03
1.10
3.23
f1 (ppm)


154.152
143.040
142.257
138.399
134.498
132.230
131.822
129.590
128.454
128.060
126.935
126.722
126.614
123.658
118.523
106.901
83.715
77.317
77.000
76.682
61.418
55.715
35.364
21.666
18.863
Me
Me
N-Me
H
OH
S31
f1 (ppm)


7.160
7.153
7.138
7.133
7.121
7.115
7.102
7.097
7.082
7.064
7.060
6.986
6.968
6.534
6.509
6.285
6.232
5.787
5.762
4.047
4.039
3.964
3.959
3.646
3.637
3.621
3.613
2.828
2.291
1.578
1.542
1.151
Me
Me
N-Me
H
Me
O
10k
f1 (ppm)


153.770
139.425
138.525
134.626
130.870
129.747
127.981
126.906
126.661
125.448
125.104
105.694
88.153
83.908
77.318
77.000
76.683
67.575
61.591
35.248
25.905
21.618
18.877
Me
Me
N
Me
H
Me
O
10k
4000
3800
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
-400
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)