Supporting Information

Rhodium(III)-Catalyzed Intramolecular Annulation through C-H Activation: Concise Synthesis of Rosettacin and Oxypalmatime

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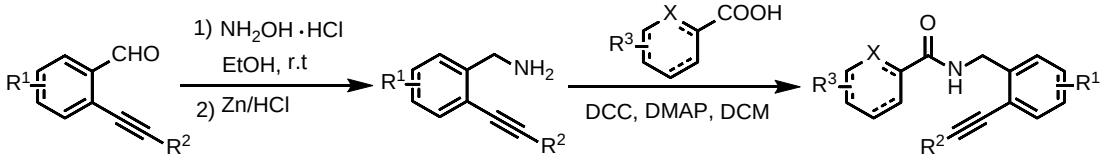
Contents

1. General Information

Commercially available reagents were used without additional purification. Column chromatography was performed with silica gel (70-230 mesh). ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AM (300 or 400 MHz) spectrometer at ambient temperature using $CDCl_3$ as solvent. HRMS (ESI) spectrometry data were acquired on a quadrupole orthogonal acceleration time-of-flight mass spectrometer [Synapt G2 high definition mass spectrometer (HDMS), Waters, Milford, MA]. Samples were infused at 3 μL min^{-1}, and spectra were obtained in the positive ionization mode with a resolution of 15000 [full width at half maximum (FWHM)] with leucine encephalin as lock mass. Melting points were recorded on a Reichert Thermovar apparatus and are uncorrected.

2. Synthesis of the Substrates



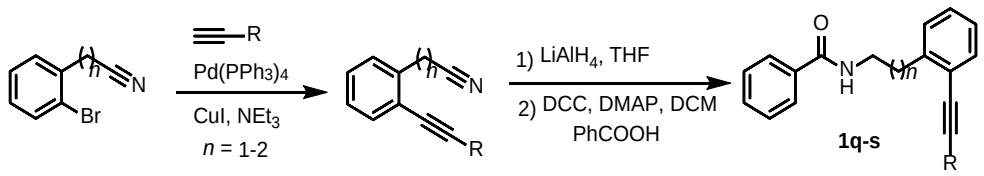
1a-p'1t-z

General Procedure A

A solution of corresponding 2-alkynylbenzaldehyde[1-3] (4 mmol, 1 equiv.) and hydroxylammonium chloride (4.8 mmol, 1.2 equiv.) in ethanol (2.5 mL) was stirred for 60 min. Subsequently, hydrochloric acid (12 M, 1.34 mL, 4 equiv.) and zinc dust (10 mmol, 2.5 equiv.) were slowly added to the solution and the mixture was stirred at room temperature for 30 min. A solution of ammonia (30%, 1.4 mL) and sodium hydroxide (6 M, 3mL) was added dropwise to the resulting slurry, and the mixture was stirred at room temperature for 30 min. Then, the resultant solution was extracted with DCM, dried over Na_2SO_4, and filtered. The solvent was removed under vacuum. The resulting crude primary amine was used in the subsequent step without further purification[4].

Under the protection of argon[5], a solution of the crude primary amine and the corresponding aryl acid (4.4 mmol, 1.1 equiv.) in DCM (2 mL) was cooled to 0 °C.

Then, DMAP (0.4 mmol, 0.1 equiv.) and DCC (4.4 mmol, 1.1 equiv.) in DCM (4 mL) were added dropwise. The mixture was then stirred at room temperature until full consumption of the starting material as monitored by TLC. The crude mixture was filtered and washed with DCM. The filtrate was concentrated and the residue was purified by a silica gel column chromatography (*n*-heptane/ethyl acetate) to afford the product **1a-p**, **1t-1z**.



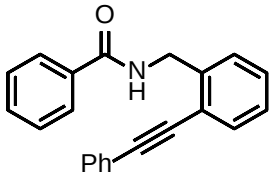
General Procedure B

To a solution of corresponding 2-bromophenylacetonitrile (5.0 mmol, 1 equiv.) and corresponding ethyne (6.0 mmol, 1.2 equiv.) in Et_3N (20 mL) were added $Pd(PPh_3)_4$ (0.25 mmol, 5 mol%) and CuI (0.15 mmol, 3 mol%) at room temperature under argon. Then the reaction mixture was gradually warmed up to 85 ℃ and stirred at the same temperature for 30 h. After cooling down to room temperature, the crude mixture was filtered and extracted with ethyl acetate. The combined organic extracts were washed with water and brine, and dried over Na_2SO_4. The solvent was evaporated under the reduced pressure and the residue was purified by a silica gel column chromatography (*n*-heptane/ethyl acetate) to afford corresponding 2-ethynylphenylacetonitrile [6].

The 2-ethynylphenylacetonitrile, and distilled THF (20 mL) were mixed together, then $LiAlH_4$ (25 mmol, 5 equiv.) was added portion-wise to the solution at 0 °C. The mixture was left under stirring for 24 h at room temperature, then it was hydrolyzed at 0 °C with water to neutralize excess $LiAlH_4$ and extracted with DCM. The combined organic phases were washed with brine, dried over Na_2SO_4 and the solvent was removed under vacuum. The residue was used in the subsequent step without further purification[7].

Under the protection of argon[5], a solution of the crude primary amine and benzoic acid (5.5 mmol, 1.1 equiv.) in DCM (2.5 mL) was cooled to 0 °C. Then, DMAP (0.5 mmol,

0.1 equiv.) and DCC (5.5 mmol, 1.1 equiv.) in DCM (5 mL) were added dropwise. The mixture was then stirred at room temperature until full consumption of the starting material as monitored by TLC. The crude mixture was filtered and washed with DCM. The filtrate was concentrated and the residue was purified by a silica gel column chromatography (*n*-heptane/ethyl acetate) to afford the product **1q-s**.



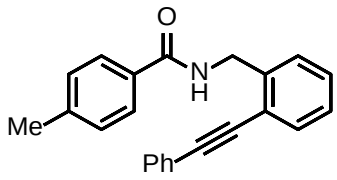
1a

Following **General Procedure A**, **1a** was obtained as a white solid (64%, three steps). Melting point 100-102 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80-7.74 (2H, m), 7.56 (1H, dd, J = 7.3, 1.7 Hz), 7.54-7.50 (2H, m), 7.46-7.42 (2H, m), 7.40-7.32 (5H, m), 7.32-7.24 (2H, m), 6.78 (1H, s), 4.87 (2H, d, J = 5.8 Hz).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.3, 139.7, 134.4, 132.4, 131.5, 131.4, 128.8, 128.64, 128.58, 128.5, 128.4, 127.6, 126.9, 122.8, 122.4, 94.3, 87.1, 43.0.

HRMS (ESI, m/z) calcd for $C_{22}H_{18}NO$ $(M+H)^+$: 312.1383, found: 312.1383.



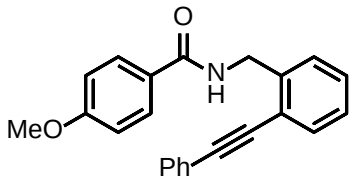
1b

Following **General Procedure A**, **1b** was obtained as a white solid (56%, three steps). Melting point 126-128 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (2H, d, J = 8.1 Hz), 7.56-7.48 (3H, m), 7.42-7.38 (1H, m), 7.35-7.30 (3H, m), 7.29-7.22 (2H, m), 7.14 (2H, d, J = 8.0 Hz), 6.85 (1H, s), 4.84 (2H, d, J = 5.8 Hz), 2.33 (3H, s).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.3, 141.8, 139.8, 132.3, 131.48, 131.45, 129.1, 128.7, 128.5, 128.38, 128.36, 127.4, 126.9, 122.8, 122.3, 94.3, 87.1, 42.8, 21.3.

HRMS (ESI, m/z) calcd for $C_{23}H_{19}NONa$ $(M+Na)^+$: 348.1359, found: 348.1354.



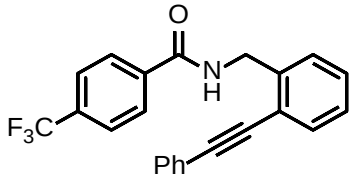
1c

Following **General Procedure A**, **1c** was obtained as a yellow solid (62%, three steps). Melting point 143-145 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (2H, d, J = 8.8 Hz), 7.58-7.50 (3H, m), 7.44 (1H, d, J = 7.2 Hz), 7.37-7.33 (3H, m), 7.33-7.25 (2H, m), 6.87 (2H, d, J = 8.8 Hz), 6.66 (1H, s), 4.85 (2H, d, J = 5.8 Hz), 3.81 (3H, s).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.8, 162.1, 140.0, 132.4, 131.5, 128.8, 128.72, 128.65, 128.6, 128.4, 127.5, 126.7, 122.8, 122.4, 113.7, 94.3, 87.1, 55.3, 42.9.

HRMS (ESI, m/z) calcd for $C_{23}H_{20}NO_2$ $(M+H)^+$: 342.1488, found: 342.1481.



1d

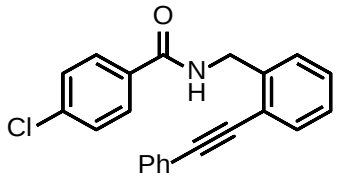
Following **General Procedure A**, **1d** was obtained as a white solid (61%, three steps). Melting point 134-136 ℃.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.85 (2H, d, J = 8.1 Hz), 7.62 (2H, d, J = 8.2 Hz), 7.59-7.55 (1H, m), 7.53-7.49 (2H, m), 7.42 (1H, dd, J = 5.8, 3.2 Hz), 7.37-7.29 (5H, m), 6.86 (1H, s), 4.86 (2H, d, J = 5.8 Hz).

^{13}C NMR (75 MHz, $CDCl_3$) δ 166.0, 139.3, 137.7, 133.3, 132.9, 132.5, 131.5, 128.9, 128.7, 128.5, 127.8, 127.4, 125.6 (d, J = 3.7 Hz), 122.6, 122.5, 121.8, 94.5, 87.0, 43.1.

^{19}F NMR (377 MHz, $CDCl_3$) δ -62.97.

HRMS (ESI, m/z) calcd for $C_{23}H_{16}F_3NONa$ $(M+Na)^+$: 402.1076, found: 402.1078.



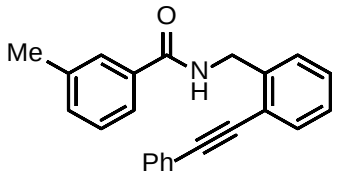
1e

Following **General Procedure A**, **1e** was obtained as a red solid (57%, three steps). Melting point 130-132 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71-7.67 (2H, m), 7.56 (1H, dd, J = 7.1, 1.8 Hz), 7.53-7.49 (2H, m), 7.44-7.40 (1H, m), 7.36-7.29 (7H, m), 6.74 (1H, s), 4.84 (2H, d, J = 5.8 Hz).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.2, 139.5, 137.7, 132.8, 132.5, 131.5, 128.83, 128.76, 128.72, 128.67, 128.5, 128.4, 127.7, 122.7, 122.5, 94.4, 87.0, 43.1.

HRMS (ESI, m/z) calcd for $C_{22}H_{16}ClNONa$ $(M+Na)^+$: 368.0813, found: 368.0810.



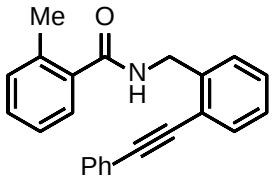
1f

Following **General Procedure A**, **1f** was obtained as a white solid (60%, three steps). Melting point 96-98 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (1H, s), 7.52 (4H, m), 7.40 (1H, d, J = 7.1 Hz), 7.35-7.30 (3H, m), 7.30-7.22 (4H, m), 6.87 (1H, s), 4.84 (2H, d, J = 5.8 Hz), 2.29 (3H, s).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.4, 139.8, 138.2, 134.3, 132.3, 132.1, 131.5, 128.7, 128.5, 128.4, 128.3, 127.6, 127.4, 123.9, 122.7, 122.2, 94.3, 87.1, 42.8, 21.2.

HRMS (ESI, m/z) calcd for $C_{23}H_{19}NONa$ $(M+Na)^+$: 348.1359, found: 348.1352.



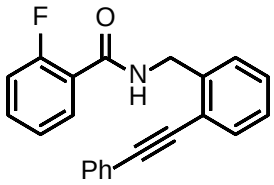
1g

Following **General Procedure A**, **1g** was obtained as a yellow solid (54%, three steps). Melting point 128-130 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58-7.48 (3H, m), 7.44 (1H, d, J = 7.1 Hz), 7.36-7.23 (7H, m), 7.18-7.09 (2H, m), 6.31 (1H, s), 4.82 (2H, d, J = 5.7 Hz), 2.40 (3H, s).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.7, 139.6, 136.2, 136.1, 132.4, 131.5, 130.9, 129.8, 128.8, 128.6, 128.5, 128.4, 127.6, 126.7, 125.6, 122.7, 122.4, 94.3, 87.0, 42.7, 19.7.

HRMS (ESI, m/z) calcd for $C_{23}H_{20}NO$ $(M+H)^+$: 326.1539, found: 326.1537.



1h

Following **General Procedure A**, **1h** was obtained as a yellow solid (62%, three steps). Melting point 84-86 ℃.

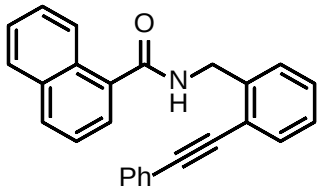
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (1H, td, J = 7.9, 1.2 Hz), 7.59-7.53 (3H, m), 7.46 (2H, dd, J = 13.4, 7.4 Hz), 7.35 (4H, dd, J = 6.9, 4.8 Hz), 7.23 (2H, dd, J = 14.7, 7.2 Hz), 7.11-7.06 (1H, m), 4.90 (2H, d, J = 5.8 Hz).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.1 (d, J = 3.2 Hz), 161.9, 159.4, 139.6, 133.3 (d, J = 9.7 Hz), 132.4, 132.1 (d, J = 2.1 Hz), 131.6, 128.8, 128.5 (d, J = 3.0 Hz), 128.4, 127.6,

124.8 (d, J = 3.3 Hz), 122.9, 122.5, 120.9 (d, J = 11.4 Hz), 116.0 (d, J = 24.8 Hz), 94.4, 86.9, 42.9.

^{19}F NMR (377 MHz, $CDCl_3$) δ -113.34.

HRMS (ESI, m/z) calcd for $C_{22}H_{17}FNO$ $(M+H)^+$: 330.1289, found: 330.1288.



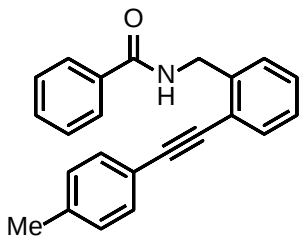
1i

Following **General Procedure A**, **1i** was obtained as a red solid (59%, three steps). Melting point 128-130 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (1H, d, J = 8.2 Hz), 7.80 (3H, dd, J = 12.5, 8.3 Hz), 7.55 (2H, d, J = 6.9 Hz), 7.50 (2H, dd, J = 6.4, 2.8 Hz), 7.47-7.42 (3H, m), 7.30 (5H, dd, J = 6.5, 4.3 Hz), 6.56 (1H, s), 4.90 (2H, d, J = 5.7 Hz).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.2, 139.5, 134.2, 133.5, 132.4, 131.5, 130.5, 130.1, 128.7, 128.6, 128.5, 128.4, 128.1, 127.6, 127.0, 126.3, 125.4, 124.9, 124.6, 122.7, 122.5, 94.4, 87.0, 43.0.

HRMS (ESI, m/z) calcd for $C_{26}H_{19}NONa$ $(M+Na)^+$: 384.1359, found: 384.1361.



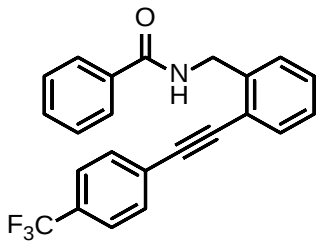
1j

Following **General Procedure A**, **1j** was obtained as a yellow solid (57%, three steps). Melting point 126-128 ℃.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.80-7.74 (2H, m), 7.57-7.52 (1H, m), 7.46-7.39 (5H, m), 7.37 (1H, t, J = 1.6 Hz), 7.31-7.26 (2H, m), 7.15 (2H, dd, J = 8.4, 0.6 Hz), 6.78 (1H, s), 4.86 (2H, d, J = 5.8 Hz), 2.36 (3H, s).

^{13}C NMR (75 MHz, $CDCl_3$) δ 167.2, 139.6, 138.8, 134.4, 132.3, 131.4, 129.2, 128.6, 128.5, 127.6, 126.9, 122.6, 119.6, 94.6, 86.5, 43.0, 21.5.

HRMS (ESI, m/z) calcd for $C_{23}H_{19}NONa$ $(M+Na)^+$: 348.1359, found: 348.1356.



1k

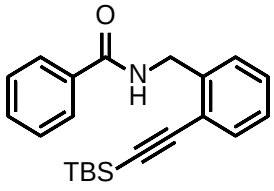
Following **General Procedure A**, **1k** was obtained as a white solid (60%, three steps). Melting point 149-151 ℃.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.80-7.74 (2H, m), 7.65-7.57 (5H, m), 7.50-7.44 (2H, m), 7.43-7.39 (2H, m), 7.38-7.31 (2H, m), 6.61 (1H, s), 4.88 (2H, d, J = 5.7 Hz).

^{13}C NMR (75 MHz, $CDCl_3$) δ 167.3, 139.9, 134.3, 132.7, 131.8, 131.6, 129.4, 128.7, 128.6, 127.7, 126.9, 125.3 (d, J = 3.8 Hz), 121.8, 92.9, 89.3, 42.9.

^{19}F NMR (377 MHz, $CDCl_3$) δ -62.81.

HRMS (ESI, m/z) calcd for $C_{23}H_{16}F_3NONa$ $(M+Na)^+$: 402.1076, found: 402.1074.



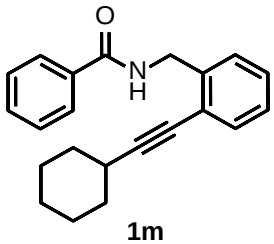
1l

Following **General Procedure A**, **1l** was obtained as a white solid (48%, three steps). Melting point 77-79 ℃.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.83-7.76 (2H, m), 7.47 (5H, m), 7.32-7.22 (2H, m), 6.89 (1H, s), 4.79 (2H, d, J = 6.0 Hz), 1.01 (9H, s), 0.21 (6H, s).

^{13}C NMR (75 MHz, $CDCl_3$) δ 167.1, 140.3, 134.4, 132.8, 131.4, 129.0, 128.7, 128.5, 127.4, 126.9, 122.3, 103.7, 97.9, 42.9, 26.1, 16.6, -4.6.

HRMS (ESI, m/z) calcd for $C_{22}H_{27}NOSiNa$ $(M+Na)^+$: 372.1754, found: 372.1749.



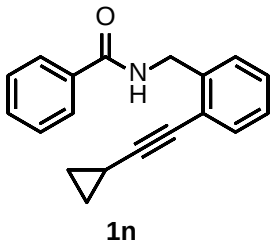
1m

Following **General Procedure A**, **1m** was obtained as a yellow solid (50%, three steps). Melting point 82-84 ℃.

^{1}H NMR (400 MHz, CDCl3) δ 7.80-7.75 (2H, m), 7.51-7.45 (1H, m), 7.45-7.36 (4H, m), 7.27-7.20 (2H, m), 6.74 (1H, s), 4.76 (2H, d, J = 5.8 Hz), 2.64 (1H, ddd, J = 12.7, 8.8, 3.7 Hz), 1.87 (2H, dd, J = 9.7, 3.6 Hz), 1.79-1.66 (2H, m), 1.53 (3H, m), 1.34 (3H, m).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.1, 139.5, 134.5, 132.3, 131.4, 128.6, 128.5, 128.0, 127.4, 126.9, 123.3, 99.7, 78.4, 43.1, 32.7, 29.8, 25.8, 24.8.

HRMS (ESI, m/z) calcd for $C_{22}H_{23}NONa$ $(M+Na)^+$: 340.1672, found: 340.1671.



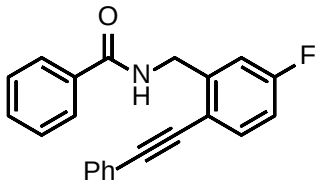
1n

Following **General Procedure A**, **1n** was obtained as a yellow solid (46%, three steps). Melting point 96-98 ℃.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.82-7.75 (2H, m), 7.53-7.43 (2H, m), 7.41 (2H, dd, J = 8.5, 1.9 Hz), 7.38-7.34 (1H, m), 7.27-7.20 (2H, m), 6.70 (1H, s), 4.73 (2H, d, J = 5.8 Hz), 1.48 (1H, tt, J = 8.2, 5.1 Hz), 0.93-0.84 (2H, m), 0.79 (2H, m).

^{13}C NMR (75 MHz, $CDCl_3$) δ 167.1, 139.6, 134.5, 132.4, 131.4, 128.5, 127.9, 127.4, 126.9, 123.1, 98.7, 73.6, 43.0, 8.8, 0.2.

HRMS (ESI, m/z) calcd for $C_{19}H_{17}NONa$ $(M+Na)^+$: 298.1203, found: 298.1196.



1o

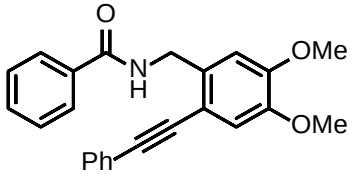
Following **General Procedure A**, **1o** was obtained as a yellow solid (61%, three steps). Melting point 144-146 ℃.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.82-7.75 (2H, m), 7.55-7.44 (5H, m), 7.39 (1H, d, J = 1.5 Hz), 7.37-7.33 (3H, m), 7.15 (1H, dd, J = 9.2, 2.6 Hz), 6.97 (1H, td, J = 8.4, 2.7 Hz), 6.85 (1H, s), 4.85 (2H, d, J = 6.0 Hz).

^{13}C NMR (75 MHz, $CDCl_3$) δ 171.0, 167.5, 164.2, 160.9, 142.5 (d, J = 7.6 Hz), 134.1 (d, J = 10.8 Hz), 133.6, 131.6 (d, J = 13.0 Hz), 130.1, 128.5 (dd, J = 14.0, 3.8 Hz), 127.0, 122.6, 118.2 (d, J = 3.4 Hz), 115.5 (d, J = 22.9 Hz), 114.7 (d, J = 22.0 Hz), 94.0, 86.1, 42.5.

^{19}F NMR (377 MHz, $CDCl_3$) δ -109.78.

HRMS (ESI, m/z) calcd for $C_{22}H_{16}FNONa$ $(M+Na)^+$: 352.1108, found: 352.1105.



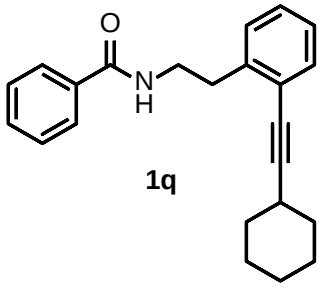
1p

Following **General Procedure A**, **1p** was obtained as a yellow solid (64%, three steps). Melting point 168-170 ℃.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.80-7.73 (2H, m), 7.52-7.43 (3H, m), 7.41-7.32 (5H, m), 7.04 (1H, s), 6.98 (1H, s), 6.73 (1H, d, J = 7.0 Hz), 4.81 (2H, d, J = 5.8 Hz), 3.90 (3H, s), 3.89 (3H, s).

^{13}C NMR (75 MHz, $CDCl_3$) δ 167.2, 149.6, 148.1, 134.4, 133.4, 131.4, 131.4, 128.5, 128.4, 128.4, 126.9, 122.9, 114.5, 114.4, 112.1, 92.7, 87.3, 56.0, 42.8, 30.9.

HRMS (ESI, m/z) calcd for $C_{24}H_{21}NO_3Na$ $(M+Na)^+$: 394.1414, found: 394.1409.



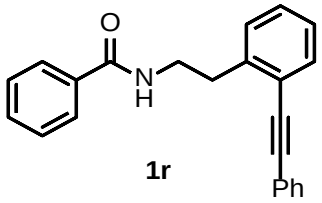
1q

Following **General Procedure B**, **1q** was obtained as a white solid (49%, three steps). Melting point 100-102 ℃.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.74-7.67 (2H, m), 7.50-7.38 (4H, m), 7.25-7.14 (3H, m), 6.31 (1H, s), 3.85-3.70 (2H, m), 3.18-3.06 (2H, m), 2.66-2.51 (1H, m), 1.83 (2H, dd, J = 9.5, 3.4 Hz), 1.72 (2H, dd, J = 9.0, 3.6 Hz), 1.57-1.42 (3H, m), 1.36-1.25 (3H, m).

^{13}C NMR (75 MHz, $CDCl_3$) δ 167.5, 140.7, 134.6, 132.4, 131.3, 129.3, 128.4, 128.0, 126.9, 126.5, 123.7, 98.8, 79.1, 40.8, 33.8, 32.6, 29.7, 25.8, 24.8.

HRMS (ESI, m/z) calcd for $C_{23}H_{25}NONa$ $(M+Na)^+$: 354.1829, found: 354.1829.



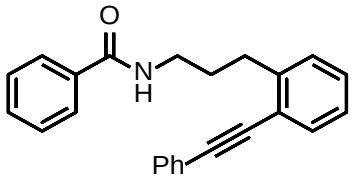
1r

Following **General Procedure B**, **1r** was obtained as a yellow solid (55%, three steps). Melting point 103-105 ℃.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.70-7.64 (2H, m), 7.58-7.48 (3H, m), 7.40 (1H, dt, J = 2.6, 1.8 Hz), 7.34-7.22 (8H, m), 6.40 (1H, s), 3.89-3.77 (2H, m), 3.20 (2H, t, J = 6.5 Hz).

^{13}C NMR (75 MHz, $CDCl_3$) δ 167.5, 141.0, 138.3, 134.5, 132.4, 131.5, 131.2, 129.5, 128.8, 128.43, 128.37, 126.8, 126.6, 122.90, 122.88, 93.4, 87.9, 40.9, 34.0.

HRMS (ESI, m/z) calcd for $C_{23}H_{19}NONa$ $(M+Na)^+$: 348.1359, found: 348.1360.



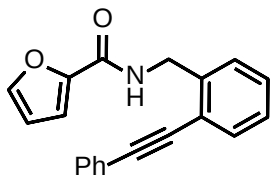
1s

Following **General Procedure B**, **1s** was obtained as a red solid (50%, three steps). Melting point 63-65 ℃.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.67-7.60 (2H, m), 7.53-7.40 (4H, m), 7.32-7.21 (8H, m), 6.38 (1H, s), 3.51 (2H, dd, J = 12.7, 6.7 Hz), 2.97 (2H, t, J = 7.5 Hz), 2.11-1.96 (2H, m).

^{13}C NMR (75 MHz, $CDCl_3$) δ 167.6, 143.3, 134.4, 132.3, 131.4, 131.2, 128.9, 128.7, 128.4, 128.34, 128.29, 126.8, 126.1, 123.1, 122.5, 93.0, 88.0, 39.5, 31.9, 30.4.

HRMS (ESI, m/z) calcd for $C_{24}H_{21}NONa$ $(M+Na)^+$: 362.1516, found: 362.1511.



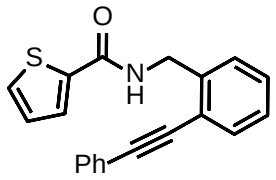
1t

Following **General Procedure A**, **1t** was obtained as a red solid (50%, three steps). Melting point 76-78 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (3H, dd, J = 6.2, 3.6 Hz), 7.46-7.40 (1H, m), 7.38-7.32 (4H, m), 7.32-7.24 (2H, m), 7.11 (1H, d, J = 3.4 Hz), 6.94 (1H, s), 6.46 (1H, dd, J = 3.5, 1.7 Hz), 4.84 (2H, d, J = 6.1 Hz).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.2, 147.9, 143.8, 139.5, 132.3, 131.5, 128.7, 128.5, 128.4, 127.5, 122.8, 122.4, 114.3, 112.1, 94.4, 86.9, 41.9.

HRMS (ESI, m/z) calcd for $C_{20}H_{16}NO_2$ $(M+H)^+$: 302.1175, found: 302.1174.



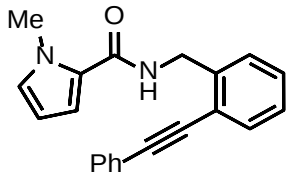
1u

Following **General Procedure A**, **1u** was obtained as a red solid (52%, three steps). Melting point 64-66 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54-7.46 (4H, m), 7.41-7.36 (2H, m), 7.35-7.30 (3H, m), 7.28-7.21 (2H, m), 6.97 (1H, dd, J = 4.8, 3.9 Hz), 6.85 (1H, s), 4.80 (2H, d, J = 5.9 Hz).

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.8, 139.6, 138.7, 132.2, 131.5, 129.9, 128.7, 128.5, 128.4, 128.3, 128.1, 127.5, 127.4, 122.7, 122.2, 94.4, 87.0, 42.6.

HRMS (ESI, m/z) calcd for $C_{20}H_{15}NOSNa$ $(M+Na)^+$: 340.0767, found: 340.0769.



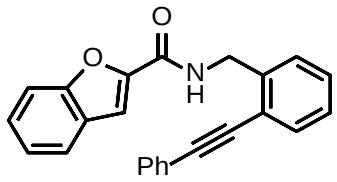
1v

Following **General Procedure A**, **1v** was obtained as a red oil (56%, three steps).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (3H, m), 7.40 (1H, d, J = 7.3 Hz), 7.33 (3H, dd, J = 4.9, 1.8 Hz), 7.26 (2H, m), 6.69-6.64 (1H, m), 6.52 (2H, dd, J = 4.0, 1.7 Hz), 6.02 (1H, dd, J = 3.9, 2.6 Hz), 4.77 (2H, d, J = 6.0 Hz), 3.90 (3H, s).

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.7, 140.2, 132.2, 131.5, 128.7, 128.5, 128.3, 128.1, 127.8, 127.3, 125.5, 122.8, 122.2, 111.5, 107.1, 94.2, 87.1, 41.9, 36.6.

HRMS (ESI, m/z) calcd for $C_{21}H_{18}N_2ONa$ $(M+Na)^+$: 337.1312, found: 337.1313.



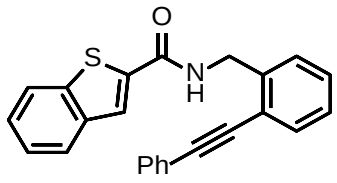
1w

Following **General Procedure A**, **1w** was obtained as a red solid (58%, three steps). Melting point 107-109 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (1H, d, J = 7.8 Hz), 7.61-7.55 (3H, m), 7.46 (2H, d, J = 8.3 Hz), 7.35 (5H, m), 7.33-7.28 (3H, m), 7.26-7.23 (1H, m), 4.89 (2H, d, J = 6.1 Hz).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.6, 154.6, 148.6, 139.3, 132.4, 131.6, 128.8, 128.63, 128.58, 128.4, 127.7, 127.5, 126.8, 123.6, 122.8, 122.6, 122.5, 111.6, 110.5, 94.5, 87.0, 42.2.

HRMS (ESI, m/z) calcd for $C_{24}H_{17}NO_2Na$ $(M+Na)^+$: 374.1152, found: 374.1147.



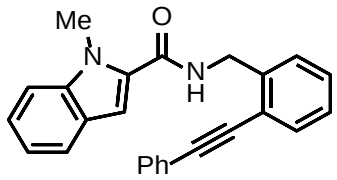
1x

Following **General Procedure A**, **1x** was obtained as a white solid (55%, three steps). Melting point 174-176 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (1H, d, J = 7.9 Hz), 7.73 (2H, d, J = 11.2 Hz), 7.56 (3H, m), 7.45 (1H, d, J = 7.0 Hz), 7.40-7.33 (5H, m), 7.33-7.28 (2H, m), 6.78 (1H, d, J = 5.2 Hz), 4.87 (2H, d, J = 5.9 Hz).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.1, 140.8, 139.4, 139.0, 138.3, 132.5, 131.6, 128.9, 128.7, 128.6, 128.5, 127.7, 126.3, 125.3, 125.0, 124.8, 122.7, 122.6, 122.5, 94.5, 87.0, 43.0.

HRMS (ESI, m/z) calcd for $C_{24}H_{17}NOSNa$ $(M+Na)^+$: 390.0923, found: 390.0918.



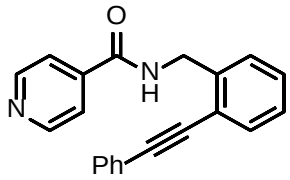
1y

Following **General Procedure A**, **1y** was obtained as a red solid (59%, three steps). Melting point 137-139 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (4H, m), 7.47-7.42 (1H, m), 7.36-7.28 (7H, m), 7.13-7.08 (1H, m), 6.81 (1H, s), 6.77 (1H, t, J = 5.2 Hz), 4.85 (2H, d, J = 5.9 Hz), 4.03 (3H, s).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.3, 139.7, 139.0, 132.5, 131.8, 131.6, 128.8, 128.6, 128.5, 128.5, 127.6, 126.0, 124.0, 122.8, 122.4, 121.7, 120.4, 110.1, 103.8, 94.4, 87.1, 42.5, 31.5.

HRMS (ESI, m/z) calcd for $C_{25}H_{21}N_2O$ $(M+H)^+$: 365.1648, found: 365.1647.



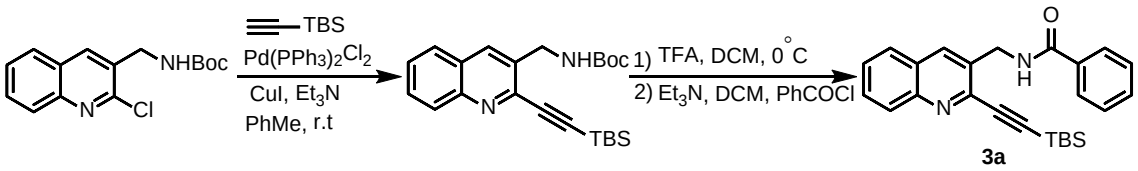
1z

Following **General Procedure A**, **1z** was obtained as a white solid (55%, three steps). Melting point 122-124 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (2H, d, J = 4.6 Hz), 7.59-7.53 (3H, m), 7.50 (2H, dd, J = 6.6, 3.0 Hz), 7.39 (1H, d, J = 6.4 Hz), 7.36-7.32 (3H, m), 7.32-7.27 (2H, m), 7.11 (1H, s), 4.84 (2H, d, J = 5.7 Hz).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.3, 150.4, 141.4, 139.0, 132.5, 131.5, 128.8, 128.7, 128.5, 127.8, 122.6, 122.5, 120.8, 94.5, 86.9, 43.1.

HRMS (ESI, m/z) calcd for $C_{21}H_{16}N_2ONa$ $(M+Na)^+$: 335.1155, found: 335.1151.



To a round-bottom flask equipped with 2-chloroquinoline (5 mmol, 1.0 equiv.), $Pd(PPh_3)_2Cl_2$ (0.25 mmol, 0.05 equiv.) and CuI (0.25 mmol, 0.05 equiv.) was added degassed PhMe (25 mL) under nitrogen. The mixture was added Et_3N (20 mmol, 4.0 equiv.) and (*tert*-butyldimethylsilyl)acetylene (7.5 mmol, 1.5 equiv.). The mixture was stirred at 25 ℃ for 12 h, filtered through a pad of celite, concentrated, and purified by a silica gel column chromatography (*n*-heptane/ethyl acetate) to afford the 2-ethynylquinoline[8].

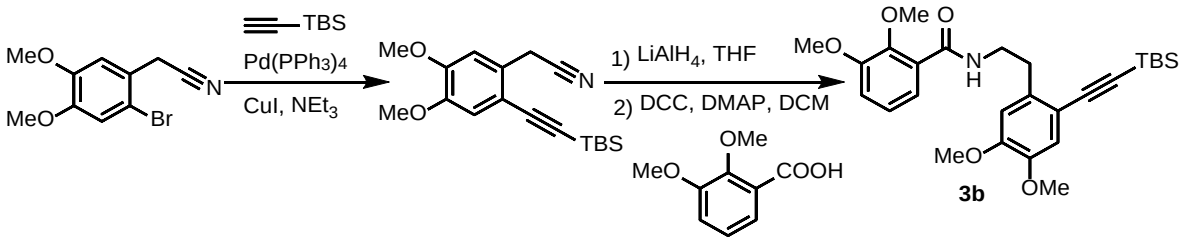
To a solution of 2-ethynylquinoline in DCM (25 mL) was added TFA (5 mL) at 0 ℃. The mixture was stirred at 25 ℃ for 12 h. Then extracted with DCM, the combined organic phases were washed with saturated solution of Na_2CO_3, dried over Na_2SO_4 and the solvent was removed under vacuum. The residue was used in the subsequent step without further purification[8].

To a solution of the crude primary amine in DCM (10 mL) was added Et_3N (2 mL) and benzoyl chloride (5.5 mmol, 1.1 equiv.) at 0 ℃. The mixture was stirred at 25 ℃ for 12 h, then quenched with saturated solution of NH_4Cl. Extracted with DCM, the combined organic phases dried over Na_2SO_4. The solvent was removed under vacuum and the residue was purified by a silica gel column chromatography (*n*-heptane/ethyl acetate) to afford the product **3a** as a yellow solid (50%, three steps)[9]. Melting point 140-142 ℃.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.15 (1H, s), 8.08 (1H, d, J = 8.4 Hz), 7.83-7.77 (2H, m), 7.76-7.65 (2H, m), 7.55-7.46 (2H, m), 7.46-7.38 (2H, m), 7.07 (1H, t, J = 6.0 Hz), 4.92 (2H, d, J = 6.1 Hz), 1.03 (9H, s), 0.26 (6H, s).

^{13}C NMR (75 MHz, $CDCl_3$) δ 167.4, 147.2, 142.6, 135.4, 134.0, 132.6, 131.7, 129.9, 128.9, 128.6, 127.6, 127.5, 127.2, 126.9, 103.0, 98.7, 41.8, 26.2, 16.6, -4.7, -4.7.

HRMS (ESI, m/z) calcd for $C_{25}H_{29}N_2OSi$ (M+H) $^+$: 401.2044, found: 401.2040.



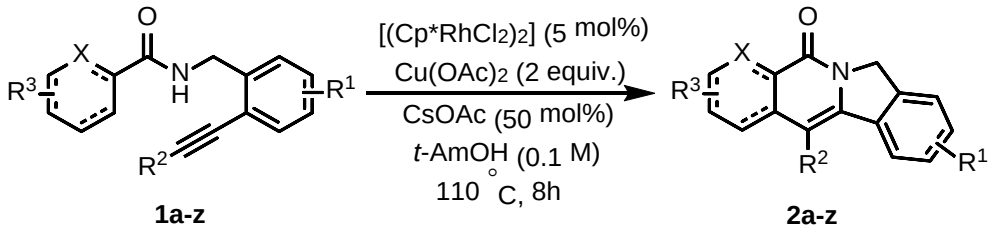
Following **General Procedure B**, **3b** was obtained as a yellow oil (54%, three steps).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (1H, s), 7.71 (1H, d, J = 7.9 Hz), 7.13 (1H, t, J = 8.0 Hz), 7.02 (1H, d, J = 8.0 Hz), 6.97 (1H, s), 6.76 (1H, s), 3.87 (6H, s), 3.82 (3H, s), 3.78 (2H, dd, J = 12.9, 6.6 Hz), 3.70 (3H, s), 3.09 (2H, t, J = 6.9 Hz), 1.00 (9H, s), 0.19 (6H, s).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.1, 152.4, 149.4, 147.4, 147.0, 134.9, 126.5, 124.1, 122.6, 115.2, 114.9, 114.5, 112.2, 104.2, 94.8, 60.9, 55.9, 55.9, 55.8, 39.9, 33.8, 26.0, 16.5, -4.6.

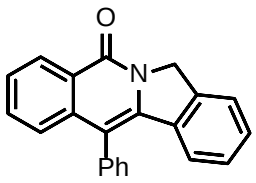
HRMS (ESI, m/z) calcd for $C_{27}H_{38}NO_5Si$ (M+H) $^+$: 484.2514, found: 484.2515.

3. Rhodium(III)-Catalyzed Intramolecular Annulations



1a-z **2a-z**

To a Schlenk flask equipped with a stir bar were added **1a-z** (0.3 mmol), $[Cp^*RhCl_2]_2$ (9.3 mg, 5 mol%), $Cu(OAc)_2$ (109 mg, 2 equiv.), CsOAc (28.8 mg, 50 mol%) and *t*-AmOH (3.0 mL) without any particular precautions to extrude oxygen or moisture. The reaction was stirred for 8 h at 110°C, cooled to room temperature. The solvent was removed in *vacuo* and the remaining residue was purified by a silica gel column chromatography (*n*-heptane/ethyl acetate) to afford the product **2a-z**.



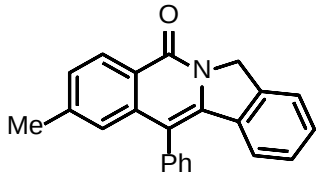
2a

2a was obtained as a red solid (93%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (1H, dd, J = 8.0, 0.9 Hz), 7.57 (4H, m), 7.54-7.46 (2H, m), 7.43-7.37 (2H, m), 7.35 (1H, t, J = 7.5 Hz), 7.23 (1H, d, J = 8.0 Hz), 7.10 (1H, t, J = 7.7 Hz), 6.44 (1H, d, J = 8.0 Hz), 5.24 (2H, s).

^{13}C NMR (101 MHz, $CDCl_3$) δ 160.7, 138.7, 138.4, 138.0, 135.2, 134.3, 131.9, 131.0, 129.4, 129.2, 128.4, 127.8, 127.2, 126.2, 125.1, 124.1, 124.0, 123.0, 114.4, 51.8.

Spectral data was consistent with that previously reported[10].



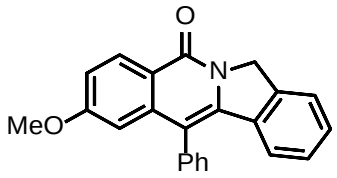
2b

2b was obtained as a yellow solid (75%). Melting point 271-273 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (1H, d, J = 8.2 Hz), 7.62-7.56 (3H, m), 7.49 (1H, s), 7.42-7.37 (2H, m), 7.35-7.28 (2H, m), 7.08 (1H, s), 6.99 (1H, s), 6.39 (1H, d, J = 8.0 Hz), 5.20 (2H, s), 2.36 (3H, s).

^{13}C NMR (101 MHz, $CDCl_3$) δ 160.6, 142.4, 138.8, 138.4, 138.0, 135.3, 134.4, 131.0, 129.3, 129.0, 128.3, 127.81, 127.76, 127.2, 124.8, 123.9, 122.9, 122.0, 114.3, 51.6, 21.9.

HRMS (ESI, m/z) calcd for $C_{23}H_{18}NO$ $(M+H)^+$: 324.1383, found: 324.1382.



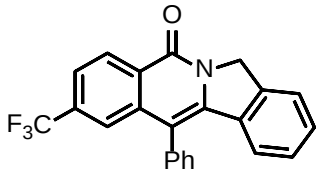
2c

2c was obtained as a yellow solid (95%). Melting point 258-260 ℃.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.49 (1H, d, J = 8.9 Hz), 7.63-7.50 (4H, m), 7.43-7.32 (3H, m), 7.13-7.04 (2H, m), 6.58 (1H, d, J = 2.5 Hz), 6.42 (1H, d, J = 8.0 Hz), 5.23 (2H, s), 3.73 (3H, s).

^{13}C NMR (75 MHz, $CDCl_3$) δ 162.5, 160.4, 140.9, 139.0, 138.3, 135.3, 134.4, 131.0, 129.5, 129.3, 129.2, 128.4, 127.8, 124.0, 123.0, 118.2, 115.0, 114.1, 106.9, 55.2, 51.6.

HRMS (ESI, m/z) calcd for $C_{23}H_{18}NO_2$ $(M+H)^+$: 340.1332, found: 340.1332.



2d

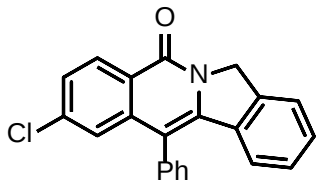
2d was obtained as a yellow solid (83%). Melting point 275-277℃.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.63 (1H, d, J = 8.4 Hz), 7.66-7.60 (4H, m), 7.56-7.47 (2H, m), 7.39 (3H, m), 7.13 (1H, t, J = 7.7 Hz), 6.44 (1H, d, J = 8.0 Hz), 5.22 (2H, s).

^{13}C NMR (75 MHz, $CDCl_3$) δ 159.8, 139.9, 138.7, 138.1, 134.1, 133.84, 133.79, 133.4, 130.9, 129.7, 128.9, 128.3, 128.0, 125.9, 125.5, 124.3, 123.1, 122.3 (d, J = 4.1 Hz), 122.0, 114.0, 51.9.

^{19}F NMR (377 MHz, $CDCl_3$) δ -62.85.

HRMS (ESI, m/z) calcd for $C_{23}H_{15}F_3NO$ $(M+H)^+$: 378.1100, found: 378.1096.



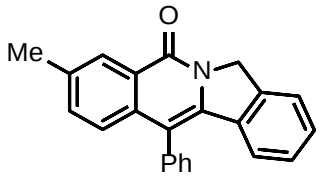
2e

2e was obtained as a red solid (84%). Melting point 283-285 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (1H, d, J = 8.6 Hz), 7.64-7.57 (3H, m), 7.52 (1H, d, J = 7.6 Hz), 7.41-7.34 (4H, m), 7.18 (1H, d, J = 1.7 Hz), 7.11 (1H, t, J = 7.7 Hz), 6.42 (1H, d, J = 8.0 Hz), 5.21 (2H, s).

^{13}C NMR (101 MHz, $CDCl_3$) δ 160.0, 140.1, 139.7, 138.7, 138.2, 134.4, 134.0, 131.0, 129.6, 129.5, 129.0, 128.7, 128.0, 126.6, 124.4, 124.2, 123.0, 122.4, 113.4, 51.8.

HRMS (ESI, m/z) calcd for $C_{22}H_{15}ClNO$ $(M+H)^+$: 344.0837, found: 344.0826.



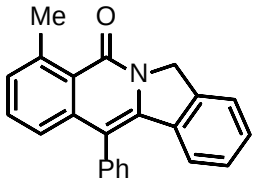
2f

2f was obtained as a yellow solid (82%). Melting point 274-276 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (1H, s), 7.59-7.54 (3H, m), 7.49 (1H, d, J = 7.7 Hz), 7.38 (3H, m), 7.30 (1H, d, J = 7.7 Hz), 7.13 (1H, d, J = 8.3 Hz), 7.08 (1H, t, J = 7.7 Hz), 6.43 (1H, d, J = 8.0 Hz), 5.20 (2H, s), 2.47 (3H, s).

^{13}C NMR (101 MHz, $CDCl_3$) δ 160.5, 137.9, 137.4, 136.4, 136.3, 135.3, 134.4, 133.4, 131.0, 129.3, 128.9, 128.3, 127.7, 126.7, 125.1, 124.0, 123.7, 122.9, 114.4, 51.7, 21.3.

HRMS (ESI, m/z) calcd for $C_{23}H_{17}NONa$ $(M+Na)^+$: 346.1203, found: 346.1200.



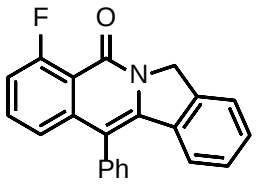
2g

2g was obtained as a yellow solid (96%). Melting point 305-307 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (3H, m), 7.53 (1H, d, J = 7.6 Hz), 7.38 (3H, m), 7.34 (1H, d, J = 7.5 Hz), 7.25 (1H, s), 7.10-7.05 (2H, m), 6.36 (1H, d, J = 8.0 Hz), 5.20 (2H, s), 3.06 (3H, s).

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.6, 141.6, 140.5, 138.2, 138.2, 135.9, 134.5, 131.2, 131.1, 129.5, 129.4, 129.1, 128.3, 127.8, 124.0, 123.6, 123.0, 122.6, 114.4, 51.9, 24.0.

HRMS (ESI, m/z) calcd for $C_{23}H_{17}NONa$ $(M+Na)^+$: 346.1203, found: 346.1211.



2h

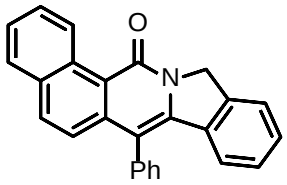
2h was obtained as a yellow solid (92%). Melting point 269-271 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63-7.57 (3H, m), 7.54 (1H, d, J = 7.6 Hz), 7.47 (1H, td, J = 8.1, 5.1 Hz), 7.38 (3H, t, J = 7.7 Hz), 7.12 (2H, dd, J = 13.2, 6.6 Hz), 6.99 (1H, d, J = 8.2 Hz), 6.39 (1H, d, J = 8.0 Hz), 5.23 (2H, s).

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.0, 161.4, 158.1 (d, J = 4.0 Hz), 141.8, 139.5, 138.3, 135.1, 134.1, 132.6 (d, J = 10.1 Hz), 131.1, 129.6, 128.6, 127.9, 124.2, 123.1, 121.1 (d, J = 4.4 Hz), 113.5 (d, J = 2.8 Hz), 113.3 (d, J = 5.7 Hz), 113.0 (d, J = 21.6 Hz), 51.9.

^{19}F NMR (377 MHz, $CDCl_3$) δ -111.38.

HRMS (ESI, m/z) calcd for $C_{22}H_{14}FNONa$ $(M+Na)^+$: 350.0952, found: 350.0952.



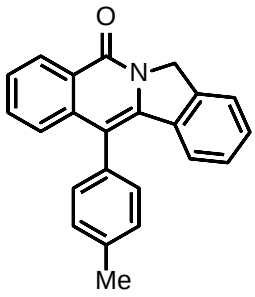
2i

2i was obtained as a yellow solid (91%). Melting point 236-238 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.37 (1H, d, J = 8.7 Hz), 7.83 (1H, d, J = 9.0 Hz), 7.80 (1H, d, J = 7.9 Hz), 7.72-7.69 (1H, m), 7.58 (3H, m), 7.48 (1H, d, J = 7.6 Hz), 7.40 (2H, m), 7.29 (3H, m), 7.07 (1H, t, J = 7.6 Hz), 6.39 (1H, d, J = 7.9 Hz), 5.23 (2H, s).

^{13}C NMR (101 MHz, $CDCl_3$) δ 160.9, 139.8, 139.7, 138.3, 135.7, 134.3, 133.0, 131.9, 131.8, 131.2, 129.4, 129.2, 128.4, 128.2, 127.9, 127.8, 127.4, 126.1, 123.9, 123.1, 122.9, 117.1, 114.6, 52.5.

HRMS (ESI, m/z) calcd for $C_{26}H_{18}NO$ $(M+H)^+$: 360.1383, found: 360.1370.



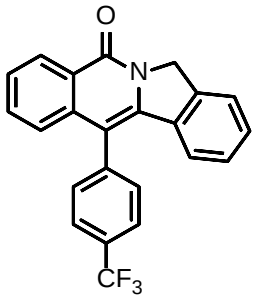
2j

2j was obtained as a yellow solid (95%). Melting point 253-255 ℃.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.57 (1H, dd, J = 7.9, 1.1 Hz), 7.56-7.45 (3H, m), 7.36 (3H, m), 7.26 (3H, m), 7.11 (1H, t, J = 7.6 Hz), 6.52 (1H, d, J = 8.0 Hz), 5.24 (2H, s), 2.52 (3H, s).

^{13}C NMR (75 MHz, $CDCl_3$) δ 160.7, 138.9, 138.3, 138.1, 138.0, 134.4, 132.0, 131.9, 130.8, 130.1, 129.1, 127.8, 127.2, 126.1, 125.2, 124.0, 123.0, 114.5, 51.8, 21.4.

HRMS (ESI, m/z) calcd for $C_{23}H_{18}NO$ $(M+H)^+$: 324.1383, found: 324.1377.



2k

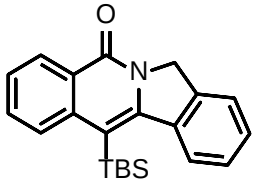
2k was obtained as a red solid (93%). Melting point 254-256 ℃.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.55 (1H, dd, J = 7.9, 1.0 Hz), 7.88 (2H, d, J = 8.0 Hz), 7.61-7.52 (4H, m), 7.51-7.45 (1H, m), 7.40 (1H, dd, J = 10.9, 4.1 Hz), 7.14 (2H, dd, J = 13.0, 7.8 Hz), 6.43 (1H, d, J = 8.0 Hz), 5.22 (2H, s).

^{13}C NMR (75 MHz, $CDCl_3$) δ 160.6, 139.3, 138.5, 138.2, 138.1, 133.9, 132.2, 131.8, 130.9, 130.5, 129.6, 128.0, 127.4, 126.4 (d, J = 3.7 Hz), 124.7, 124.1, 123.7, 123.2, 122.3, 112.7, 51.8.

^{19}F NMR (377 MHz, $CDCl_3$) δ -62.37.

HRMS (ESI, m/z) calcd for $C_{23}H_{15}F_3NO$ $(M+H)^+$: 378.1100, found: 378.1105.



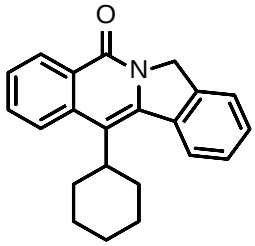
2l

2l was obtained as a red oil (82%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.54 (1H, dd, J = 8.0, 1.5 Hz), 8.15 (1H, d, J = 7.2 Hz), 7.96 (1H, d, J = 8.4 Hz), 7.62 (2H, m), 7.47 (3H, m), 5.21 (2H, s), 1.32 (9H, s), 0.39 (6H, s).

^{13}C NMR (75 MHz, $CDCl_3$) δ 161.1, 149.3, 142.2, 139.1, 135.1, 130.6, 129.7, 129.6, 127.1, 126.5, 126.3, 125.7, 124.5, 123.1, 108.3, 51.9, 29.7, 19.4, 2.1.

HRMS (ESI, m/z) calcd for $C_{22}H_{26}NOSi$ $(M+H)^+$: 348.1778, found: 348.1774.



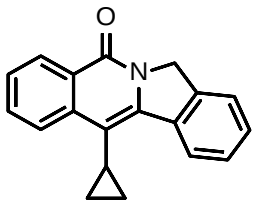
2m

2m was obtained as a red solid (79%). Melting point 151-153 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (1H, dd, J = 8.0, 1.2 Hz), 8.24 (1H, d, J = 8.4 Hz), 8.03 (1H, d, J = 7.4 Hz), 7.71-7.63 (1H, m), 7.60 (1H, d, J = 6.8 Hz), 7.53-7.44 (3H, m), 5.18 (2H, s), 3.81 (1H, tt, J = 12.6, 3.3 Hz), 2.43-2.29 (2H, m), 2.01 (2H, d, J = 13.0 Hz), 1.90 (3H, d, J = 12.0 Hz), 1.60-1.44 (3H, m).

^{13}C NMR (101 MHz, $CDCl_3$) δ 160.3, 138.6, 138.1, 137.6, 135.1, 130.8, 128.9, 128.2, 127.8, 125.8, 125.1, 124.5, 123.5, 118.7, 51.7, 39.0, 31.2, 27.5, 26.1.

HRMS (ESI, m/z) calcd for $C_{22}H_{22}NO$ $(M+H)^+$: 316.1696, found: 316.1692.



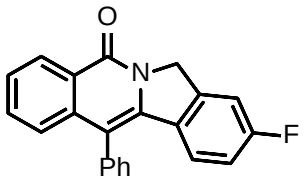
2n

2n was obtained as a yellow solid (96%). Melting point 196-198 ℃.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.48 (1 H, dd, J = 8.0, 1.1 Hz), 8.39-8.32 (1 H, m), 8.28 (1 H, d, J = 8.3 Hz), 7.72-7.64 (1 H, m), 7.55-7.42 (4 H, m), 5.12 (2 H, s), 2.12-1.97 (1 H, m), 1.36-1.28 (2 H, m), 0.70-0.60 (2 H, m).

^{13}C NMR (75 MHz, $CDCl_3$) δ 160.4, 141.0, 139.2, 138.2, 134.3, 131.4, 129.0, 127.6, 127.2, 125.8, 125.7, 124.8, 124.2, 122.8, 113.4, 51.7, 10.7, 7.9.

HRMS (ESI, m/z) calcd for $C_{19}H_{16}NO$ $(M+H)^+$: 274.1226, found: 274.1231.



2o

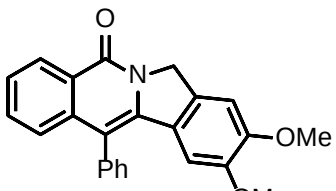
2o was obtained as a yellow solid (90%). Melting point 188-190 ℃.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.54 (1H, dd, J = 7.9, 1.5 Hz), 7.61-7.48 (5H, m), 7.41-7.37 (2H, m), 7.22 (2H, d, J = 7.6 Hz), 6.81 (1H, td, J = 8.8, 2.2 Hz), 6.38 (1H, dd, J = 8.8, 5.0 Hz), 5.22 (2H, s).

^{13}C NMR (75 MHz, $CDCl_3$) δ 164.9, 161.6, 160.6, 140.2 (d, J = 9.4 Hz), 138.7, 137.5, 135.0, 132.1, 131.0, 130.5 (d, J = 2.6 Hz), 129.5, 128.5, 126.7 (d, J = 73.3 Hz), 125.7 (d, J = 9.0 Hz), 125.1, 123.9, 115.6 (d, J = 22.9 Hz), 114.0, 110.4 (d, J = 24.0 Hz), 51.5.

^{19}F NMR (377 MHz, $CDCl_3$) δ -110.32.

HRMS (ESI, m/z) calcd for $C_{22}H_{14}FNONa$ $(M+Na)^+$: 350.0952, found: 350.0937.



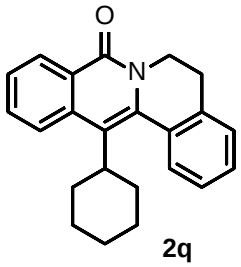
2p

2p was obtained as a yellow solid (91%). Melting point 202-204 ℃.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.54 (1H, dd, J = 8.0, 1.0 Hz), 7.63-7.52 (4H, m), 7.45 (3H, m), 7.27-7.23 (1H, m), 6.98 (1H, s), 5.88 (1H, s), 5.14 (2H, s), 3.91 (3H, s), 3.41 (3H, s).

^{13}C NMR (75 MHz, $CDCl_3$) δ 160.7, 150.6, 148.8, 138.8, 138.7, 135.3, 131.9, 131.6, 131.1, 129.2, 128.2, 127.2, 126.5, 125.7, 124.7, 123.5, 112.6, 106.0, 105.1, 56.1, 55.2, 51.6.

HRMS (ESI, m/z) calcd for $C_{24}H_{20}NO_3$ $(M+H)^+$: 370.1438, found: 370.1432.



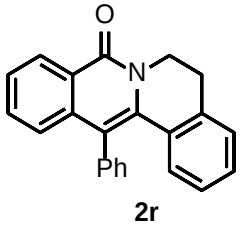
2q

2q was obtained as a yellow solid (68%). Melting point 118-120 ℃.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.57 (1H, dd, J = 8.0, 1.4 Hz), 8.29 (1H, d, J = 8.4 Hz), 7.65 (1H, ddd, J = 8.5, 7.1, 1.6 Hz), 7.58-7.53 (1H, m), 7.50-7.44 (1H, m), 7.38-7.29 (3H, m), 4.23 (2H, s), 3.48-3.32 (1H, m), 2.90 (2H, t, J = 5.8 Hz), 2.37 (2H, dd, J = 23.2, 11.3 Hz), 1.86 (4H, d, J = 11.1 Hz), 1.39-1.22 (4H, m).

^{13}C NMR (75 MHz, $CDCl_3$) δ 161.2, 139.3, 136.4, 135.6, 131.5, 130.9, 129.4, 128.9, 128.5, 127.1, 126.1, 125.9, 125.74, 125.65, 120.3, 42.0, 41.8, 32.4, 29.7, 27.1, 26.1.

HRMS (ESI, m/z) calcd for $C_{23}H_{24}NO$ $(M+H)^+$: 330.1852, found: 330.1850.



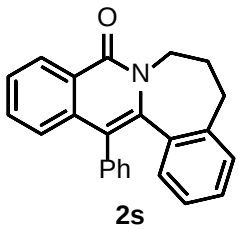
2r

2r was obtained as a yellow solid (77%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.62-8.46 (1H, m), 7.54-7.37 (5H, m), 7.35-7.30 (1H, m), 7.27-7.11 (4H, m), 6.81 (2H, m), 4.51-4.19 (2H, m), 3.04-2.88 (2H, m).

^{13}C NMR (75 MHz, $CDCl_3$) δ 161.6, 138.3, 137.7, 137.3, 134.6, 131.9, 131.0, 130.4, 128.9, 128.3, 127.7, 127.5, 126.9, 126.6, 125.5, 124.8, 117.8, 41.5, 29.6.

Spectral data was consistent with that previously reported[10].



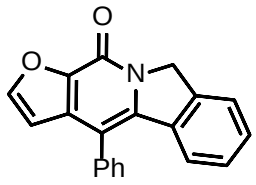
2s

2s was obtained as a yellow solid (70%). Melting point 245-247 ℃.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.63-8.52 (1H, m), 7.58-7.39 (4H, m), 7.38-7.31 (1H, m), 7.26-7.13 (3H, m), 7.10-7.01 (1H, m), 6.92-6.80 (2H, m), 6.60 (1H, d, J = 7.6 Hz), 5.19 (1H, dd, J = 13.5, 5.2 Hz), 3.08 (1H, td, J = 13.2, 4.9 Hz), 2.85-2.64 (2H, m), 2.40 (1H, tdd, J = 16.0, 5.9, 2.7 Hz), 1.93-1.77 (1H, m).

^{13}C NMR (75 MHz, $CDCl_3$) δ 161.4, 140.8, 138.7, 137.1, 136.7, 133.9, 132.3, 131.9, 131.1, 128.9, 128.7, 128.0, 127.5, 126.9, 126.5, 125.7, 125.3, 124.7, 118.1, 41.5, 29.8, 28.6.

HRMS (ESI, m/z) calcd for $C_{24}H_{19}NONa$ $(M+Na)^+$: 360.1359, found: 360.1356.



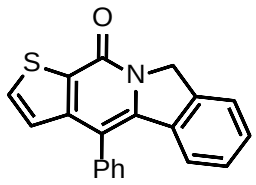
2t

2t was obtained as a red solid (50%). Melting point 190-192℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (1H, d, J = 1.9 Hz), 7.55 (4H, m), 7.48 (2H, m), 7.37 (1H, t, J = 7.4 Hz), 7.15 (1H, t, J = 7.7 Hz), 6.91 (1H, d, J = 8.0 Hz), 6.47 (1H, d, J = 1.9 Hz), 5.25 (2H, s).

^{13}C NMR (101 MHz, $CDCl_3$) δ 154.2, 137.8, 135.8, 135.1, 134.9, 134.4, 131.4, 130.3, 128.9, 127.9, 127.9, 127.6, 123.0, 122.7, 121.5, 112.5, 101.9, 51.2.

HRMS (ESI, m/z) calcd for $C_{20}H_{13}NO_2Na$ $(M+Na)^+$: 322.0839, found: 322.0840.



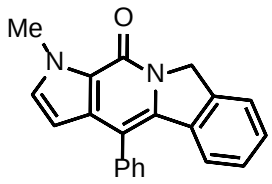
2u

2u was obtained as a yellow solid (60%). Melting point 259-261 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (1H, d, J = 5.1 Hz), 7.55 (4H, m), 7.45 (2H, d, J = 7.4 Hz), 7.37 (1H, t, J = 7.5 Hz), 7.13 (1H, t, J = 7.6 Hz), 6.92 (1H, d, J = 5.2 Hz), 6.71 (1H, d, J = 7.9 Hz), 5.25 (2H, s).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.9, 147.8, 140.1, 138.1, 135.4, 134.1, 132.8, 130.4, 129.24, 129.15, 128.5, 127.9, 127.3, 124.3, 123.5, 123.1, 113.6, 51.7.

HRMS (ESI, m/z) calcd for $C_{20}H_{14}NOS$ $(M+H)^+$: 316.0791, found: 316.0786.



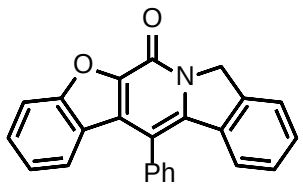
2v

2v was obtained as a yellow solid (54%). Melting point 282-284 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (6H, m), 7.29 (1H, t, J = 7.4 Hz), 7.10 (1H, t, J = 7.6 Hz), 6.99 (1H, d, J = 2.8 Hz), 6.81 (1H, d, J = 8.0 Hz), 6.03 (1H, d, J = 2.8 Hz), 5.17 (2H, s), 4.26 (3H, s).

^{13}C NMR (101 MHz, $CDCl_3$) δ 154.2, 137.8, 135.8, 135.1, 134.9, 134.4, 131.4, 130.3, 128.9, 127.93, 127.88, 127.6, 123.0, 122.7, 121.5, 112.5, 101.9, 51.2, 35.8.

HRMS (ESI, m/z) calcd for $C_{21}H_{17}N_2O$ $(M+H)^+$: 313.1335, found: 313.1335.



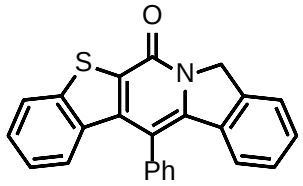
2w

2w was obtained as a red solid (76%). Melting point 358-360 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66-7.64 (3H, m), 7.60-7.54 (4H, m), 7.47 (1H, d, J = 8.0 Hz), 7.38 (1H, t, J = 7.5 Hz), 7.16-7.08 (2H, m), 6.83 (1H, d, J = 7.9 Hz), 6.73 (1H, d, J = 8.0 Hz), 5.31 (2H, s).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.2, 152.4, 142.0, 139.5, 138.3, 134.5, 134.0, 130.3, 129.9, 129.6, 129.0, 128.5, 128.0, 123.5, 123.3, 123.2, 123.2, 122.8, 112.8, 112.7, 111.4, 52.2.

HRMS (ESI, m/z) calcd for $C_{24}H_{16}NO_2$ $(M+H)^+$: 350.1175, found: 350.1173.



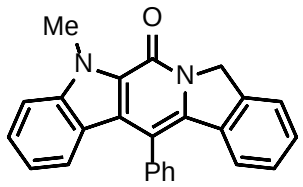
2x

2x was obtained as a green solid (78%). Melting point 306-308 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (1H, d, J = 8.1 Hz), 7.66 (3H, d, J = 6.2 Hz), 7.58-7.50 (3H, m), 7.38 (2H, dd, J = 14.9, 7.5 Hz), 7.13-7.06 (2H, m), 6.81 (1H, d, J = 8.4 Hz), 6.40 (1H, d, J = 8.0 Hz), 5.27 (2H, s).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.1, 142.6, 141.2, 141.0, 138.0, 135.8, 135.5, 134.4, 130.7, 129.9, 129.1, 129.1, 128.0, 127.9, 127.2, 125.6, 124.3, 123.7, 123.4, 123.1, 114.3, 51.8.

HRMS (ESI, m/z) calcd for $C_{24}H_{16}NOS$ $(M+H)^+$: 366.0947, found: 366.0953.



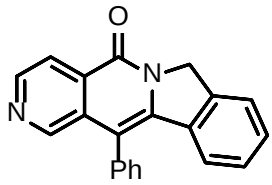
2y

2y was obtained as a yellow solid (94%). Melting point 304-306 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (3H, m), 7.53 (2H, dd, J = 6.5, 3.0 Hz), 7.48 (1H, d, J = 7.6 Hz), 7.40 (2H, d, J = 5.0 Hz), 7.26 (1H, dd, J = 13.6, 6.1 Hz), 7.09 (1H, t, J = 7.6 Hz), 6.94 (1H, ddd, J = 8.0, 5.4, 2.6 Hz), 6.79 (1H, d, J = 8.1 Hz), 6.57 (1H, d, J = 7.9 Hz), 5.16 (2H, s), 4.34 (3H, s).

^{13}C NMR (101 MHz, $CDCl_3$) δ 154.4, 141.2, 137.4, 136.0, 134.9, 134.8, 130.4, 129.4, 128.5, 127.8, 127.7, 126.3, 125.8, 125.3, 123.0, 122.7, 122.5, 121.8, 119.7, 113.4, 109.8, 51.6, 31.2.

HRMS (ESI, m/z) calcd for $C_{25}H_{19}N_2O$ $(M+H)^+$: 363.1492, found: 363.1484.



2z

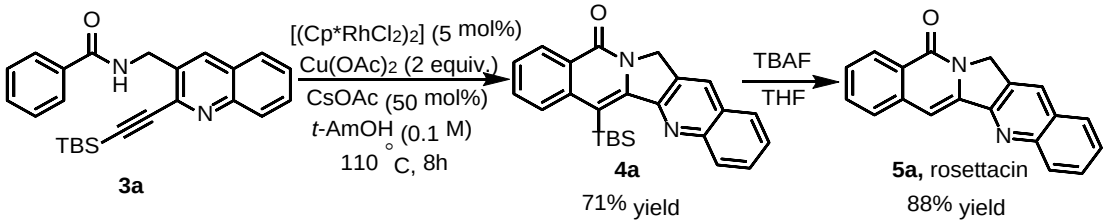
2z was obtained as a yellow solid (43%). Melting point 236-238 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (2H, d, J = 5.7 Hz), 8.29 (1H, d, J = 5.2 Hz), 7.65-7.60 (3H, m), 7.56 (1H, d, J = 7.6 Hz), 7.47-7.38 (3H, m), 7.15 (1H, t, J = 7.7 Hz), 6.54 (1H, d, J = 8.0 Hz), 5.27 (2H, s).

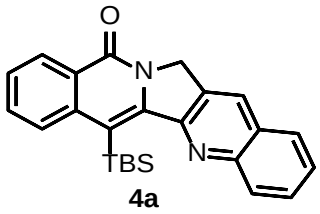
^{13}C NMR (101 MHz, $CDCl_3$) δ 159.6, 149.1, 145.6, 140.1, 137.9, 133.8, 133.4, 132.9, 130.9, 129.8, 129.6, 128.9, 128.5, 128.2, 124.3, 123.1, 119.3, 112.7, 52.0.

HRMS (ESI, m/z) calcd for $C_{21}H_{15}N_2O$ $(M+H)^+$: 311.1179, found: 311.1181.

4. Synthesis of Rosettacin and Oxypalmatime



To a Schlenk flask equipped with a stir bar were added **3a** (0.6 mmol), $[Cp^*RhCl_2]_2$ (18.6 mg, 5 mol%), $Cu(OAc)_2$ (218 mg, 2 equiv.), CsOAc (57.6 mg, 50 mol%) and *t*-AmOH (6.0 mL) without any particular precautions to extrude oxygen or moisture. The reaction was stirred for 8 h at 110°C, cooled to room temperature. The solvent was removed in *vacuo* and the remaining residue was purified by a silica gel column chromatography (*n*-heptane/ethyl acetate) to afford the product **4a** as a yellow solid (71%). Melting point 212-214 ℃.



4a

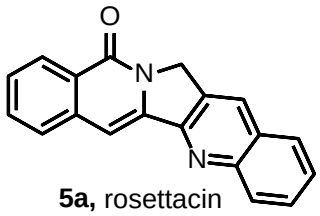
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.60 (1H, dd, J = 8.0, 1.2 Hz), 8.26 (2H, d, J = 8.6 Hz), 8.14 (1H, d, J = 8.4 Hz), 7.86 (1H, d, J = 8.3 Hz), 7.80-7.66 (2H, m), 7.62-7.50 (2H, m), 5.32 (2H, s), 1.35 (9H, d, J = 1.9 Hz), 0.52 (6H, d, J = 2.0 Hz).

^{13}C NMR (75 MHz, $CDCl_3$) δ 161.0, 154.2, 147.6, 146.1, 141.9, 130.8, 130.3, 129.8, 129.61, 129.57, 129.2, 129.0, 127.8, 127.3, 127.2, 126.5, 125.6, 112.3, 49.1, 29.4, 19.2, 2.8, 2.7.

HRMS (ESI, m/z) calcd for $C_{25}H_{27}N_2OSi$ $(M+H)^+$: 399.1887, found: 399.1888.

A 25 mL round-bottomed flask equipped with a stirring bar is charged with **4a** (0.4 mmol), *tetra*-*n*-butylammonium fluoride (TBAF, 1 M in THF, 0.8 mL, 0.8 mmol) and 2 mL of anhydrous THF. Then allowed to stir at 60°C for 12 h. The solvent was removed

and the residue purified by a silica gel column chromatography (*n*-heptane/ethyl acetate) to afford the product **5a** as a yellow solid (88%)[11].

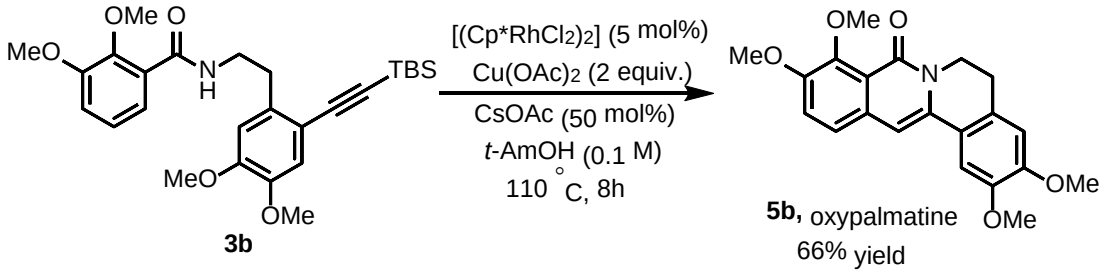


5a, rosettacin

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.51 (1H, d, J = 8.0 Hz), 8.26 (1H, s), 8.18 (1H, d, J = 8.5 Hz), 7.85 (1H, d, J = 8.2 Hz), 7.78-7.69 (3H, m), 7.61 (1H, s), 7.55 (2H, ddd, J = 8.2, 5.0, 1.5 Hz), 5.32 (2H, d, J = 0.8 Hz).

^{13}C NMR (75 MHz, $CDCl_3$) δ 161.0, 153.6, 148.8, 139.9, 137.5, 132.4, 130.7, 130.2, 129.4, 128.8, 128.0, 128.0, 127.5, 127.3, 126.0, 101.1, 49.4.

Spectral data was consistent with that previously reported[8].



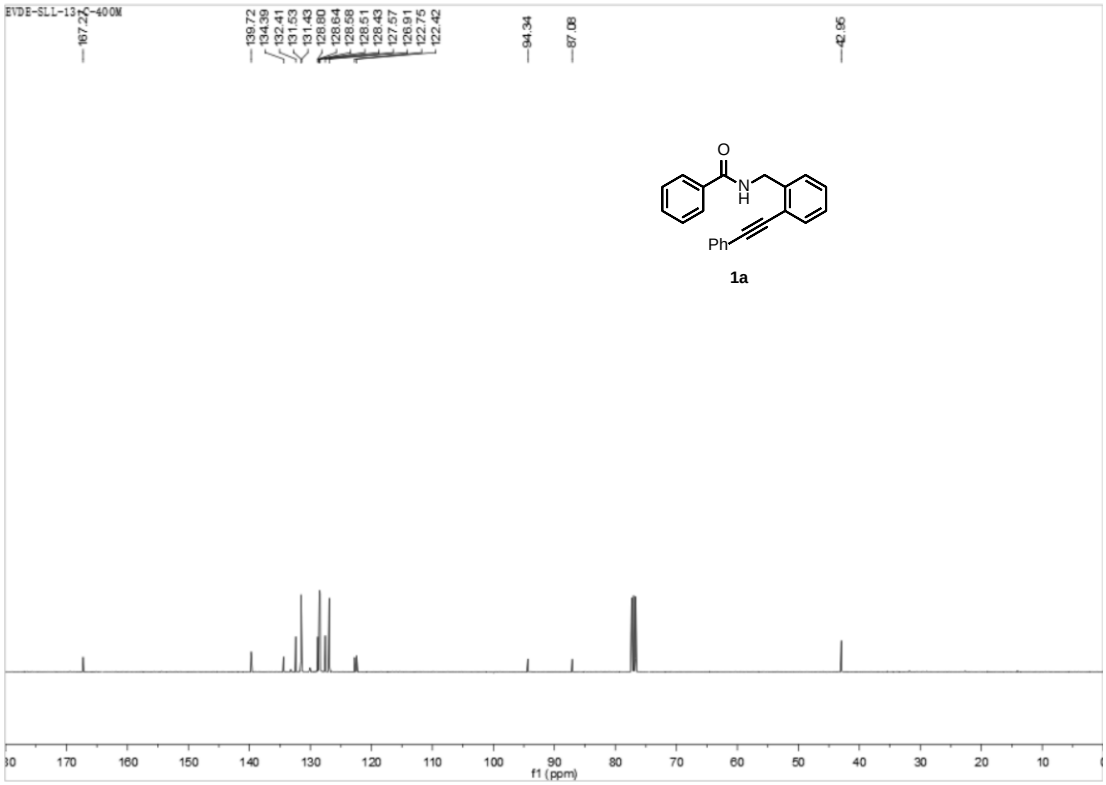
To a Schlenk flask equipped with a stir bar were added **3b** (0.6 mmol), $[Cp^*RhCl_2]_2$ (18.6 mg, 5 mol%), $Cu(OAc)_2$ (218 mg, 2 equiv.), CsOAc (57.6 mg, 50 mol%) and *t*-AmOH (6.0 mL) without any particular precautions to extrude oxygen or moisture. The reaction was stirred for 8 h at 110°C, cooled to room temperature. The solvent was removed in *vacuo* and the remaining residue was purified by a silica gel column chromatography (*n*-heptane/ethyl acetate) to afford the product **5b** as a yellow solid (66%).

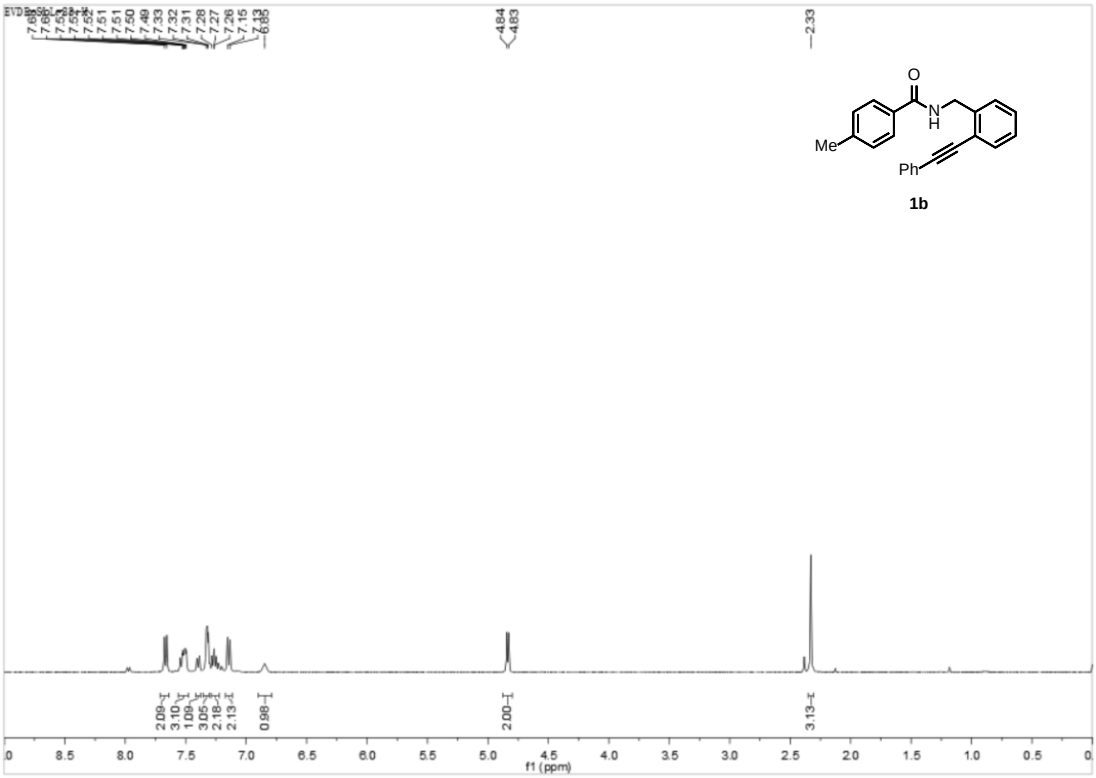
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (2H, d, J = 3.1 Hz), 7.23 (1H, s), 6.74 (2H, d, J = 9.2 Hz), 4.31 (2H, s), 4.02 (3H, s), 3.98 (3H, s), 3.94 (6H, d, J = 4.3 Hz), 2.92 (2H, t, J = 5.6 Hz).

^{13}C NMR (101 MHz, $CDCl_3$) δ 160.1, 151.2, 150.0, 149.4, 148.3, 135.5, 132.3, 128.4, 122.2, 122.1, 119.2, 118.9, 110.4, 107.4, 100.8, 61.5, 56.7, 56.1, 55.9, 39.3, 28.1.

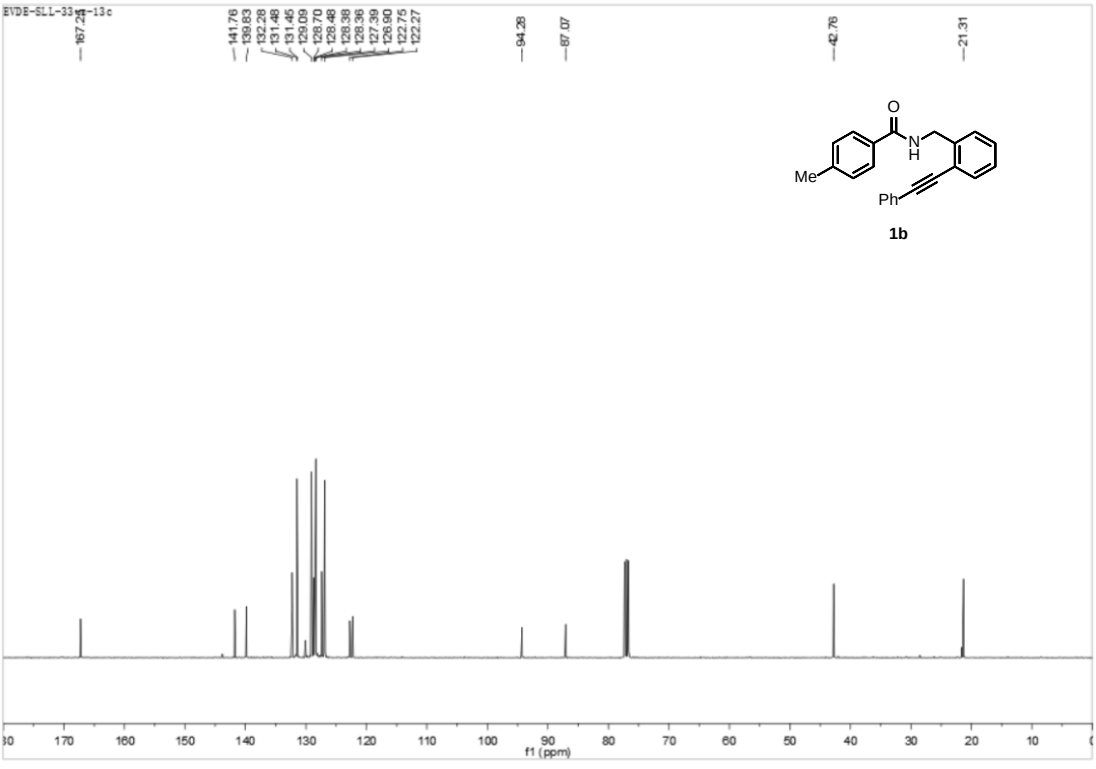
Spectral data was consistent with that previously reported[8].

4. NMR Spectra




7.68
7.66
7.53
7.52
7.51
7.51
7.50
7.49
7.33
7.32
7.31
7.28
7.27
7.26
7.15
7.13
6.88
4.84
4.83
2.33
O
N
H
Me
Ph
2.09
3.10
1.00
3.05
2.18
2.13
0.98
2.00
3.13
f1 (ppm)

1b


EVDE-SLL-33
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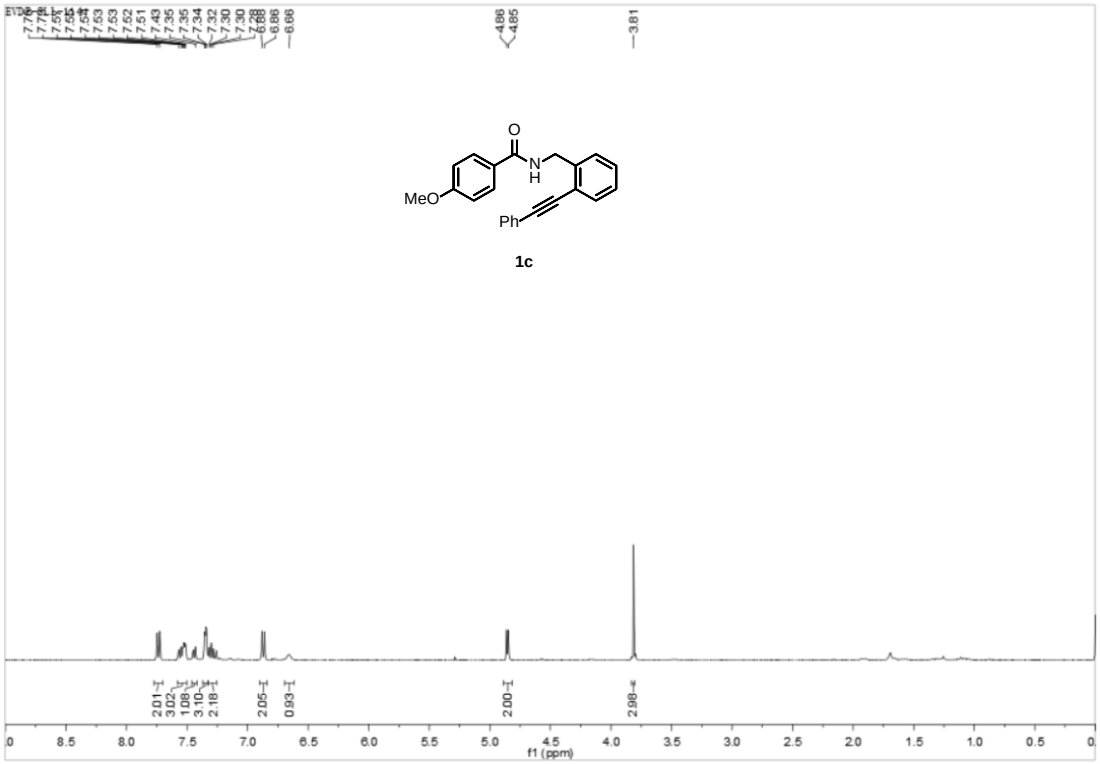
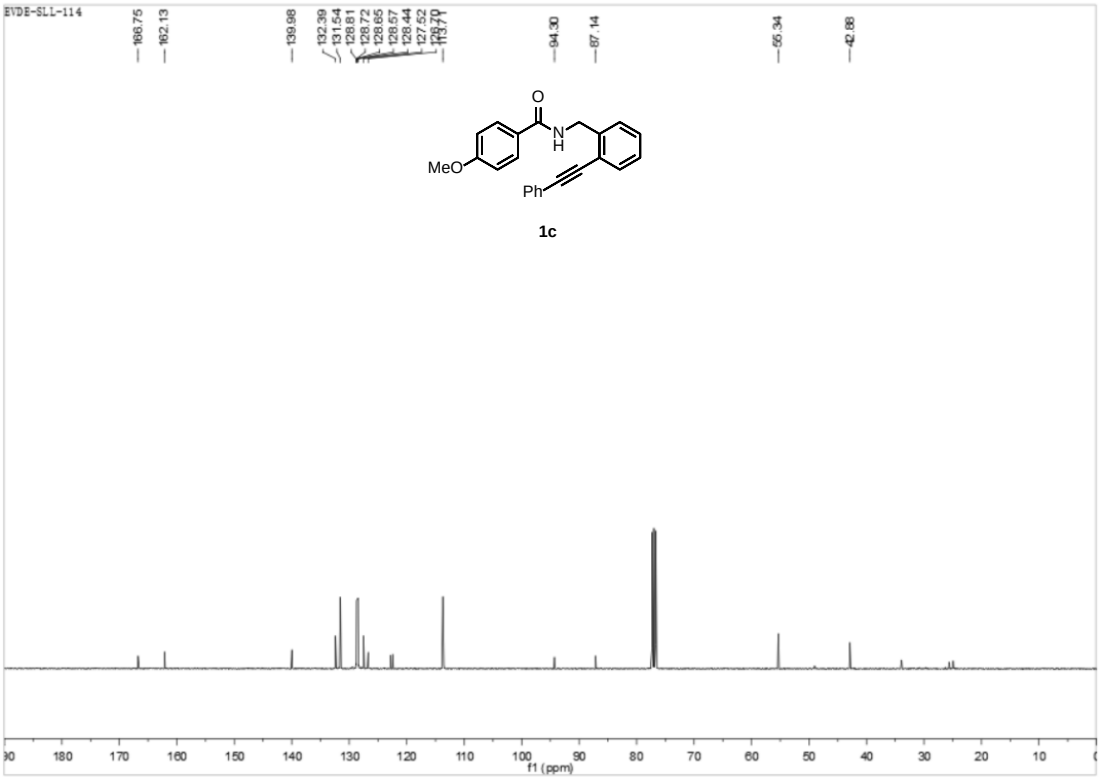
132.28
131.46
131.45
129.09
128.70
128.48
128.38
128.36
127.39
126.90
122.75
122.27
94.29
87.07
42.76
21.31
O
N
H
Me
Ph
f1 (ppm)

1b


4.86
4.85
3.81
O
N
H
MeO
Ph
2.01
3.02
1.08
3.10
2.18
2.05
0.93
2.00
2.98
f1 (ppm)

1c


EVDB-SLL-114
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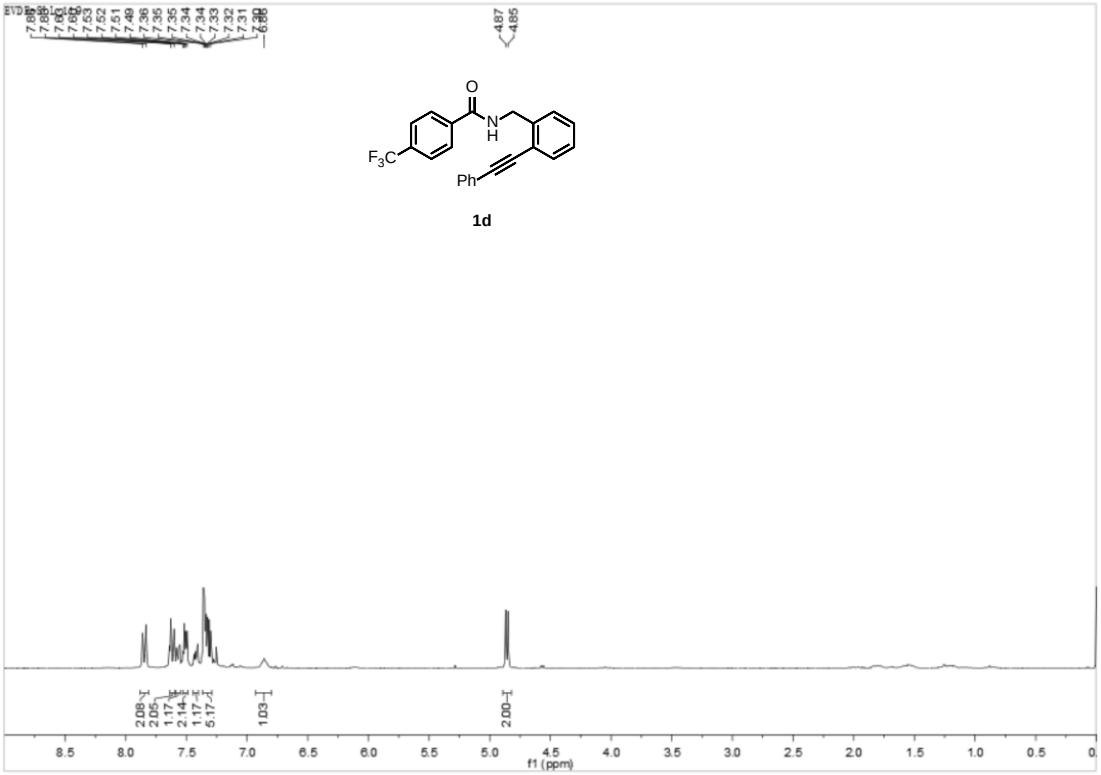
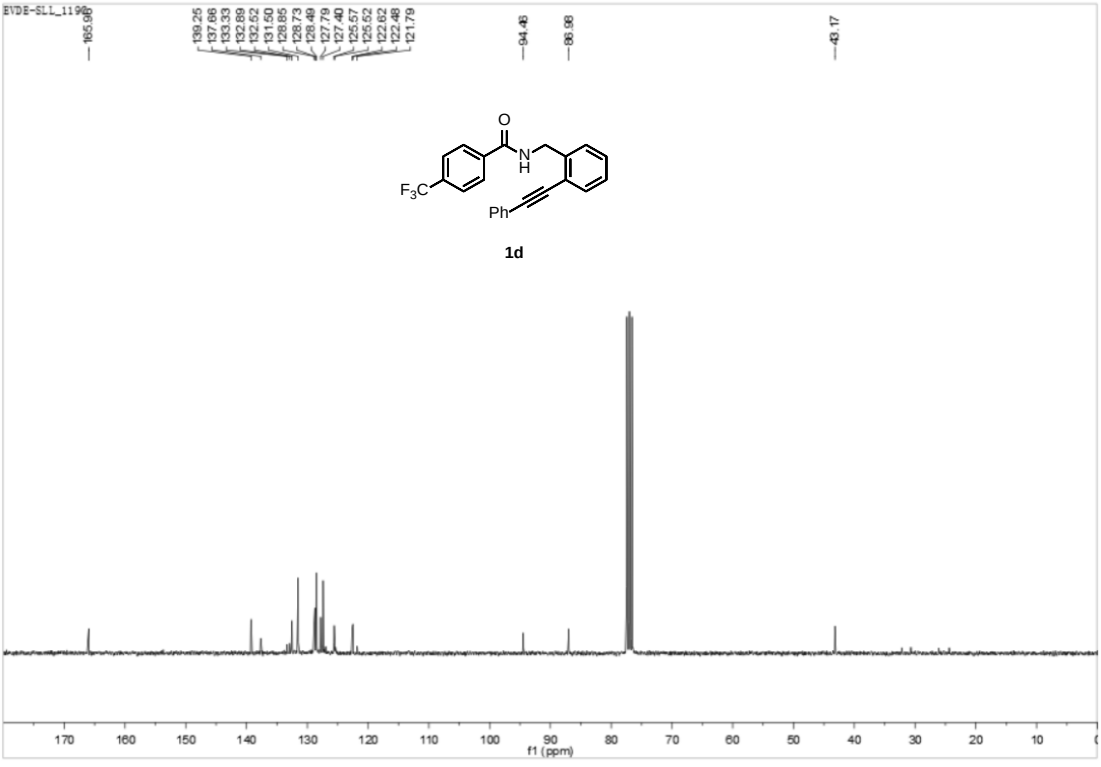
132.39
131.54
128.81
128.72
128.65
128.57
128.44
127.52
94.30
87.14
55.34
42.88
O
N
H
MeO
Ph
f1 (ppm)

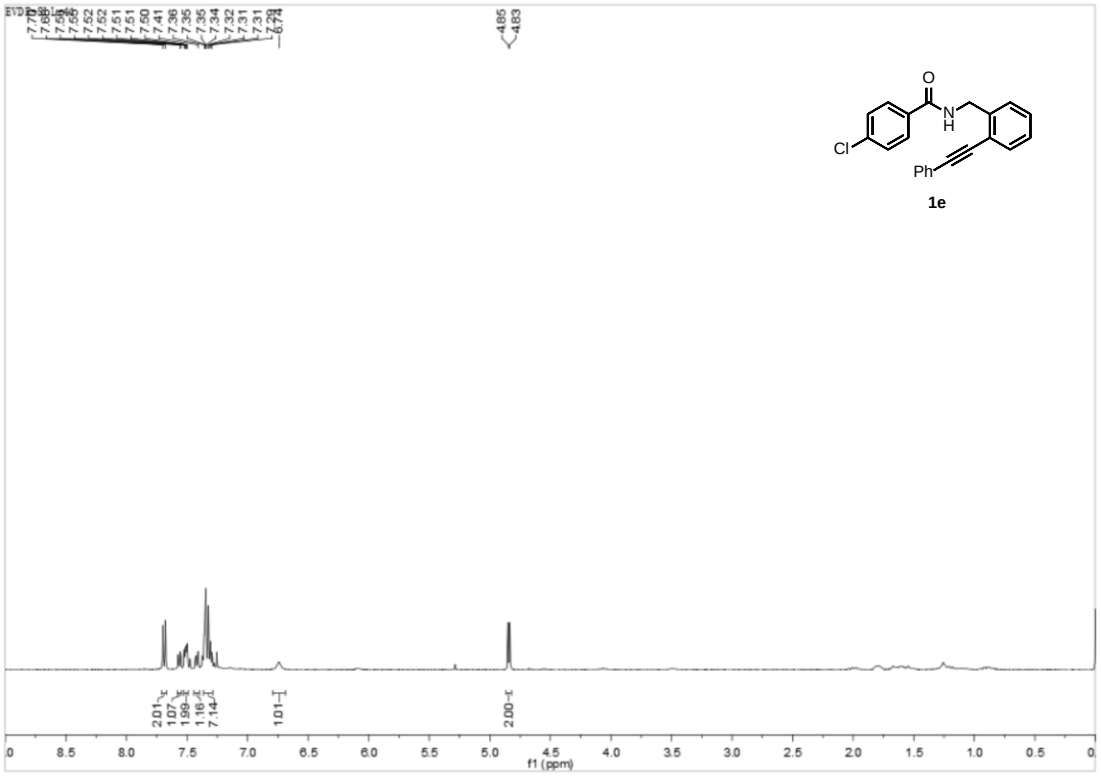
1c


O
N
H
F_3C
Ph
1d
f1 (ppm)


O
N
H
F_3C
Ph
1d
f1 (ppm)


EVDE-SLL-119F
-62.97
O
N
H
F3C
Ph
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)

1d


7.70
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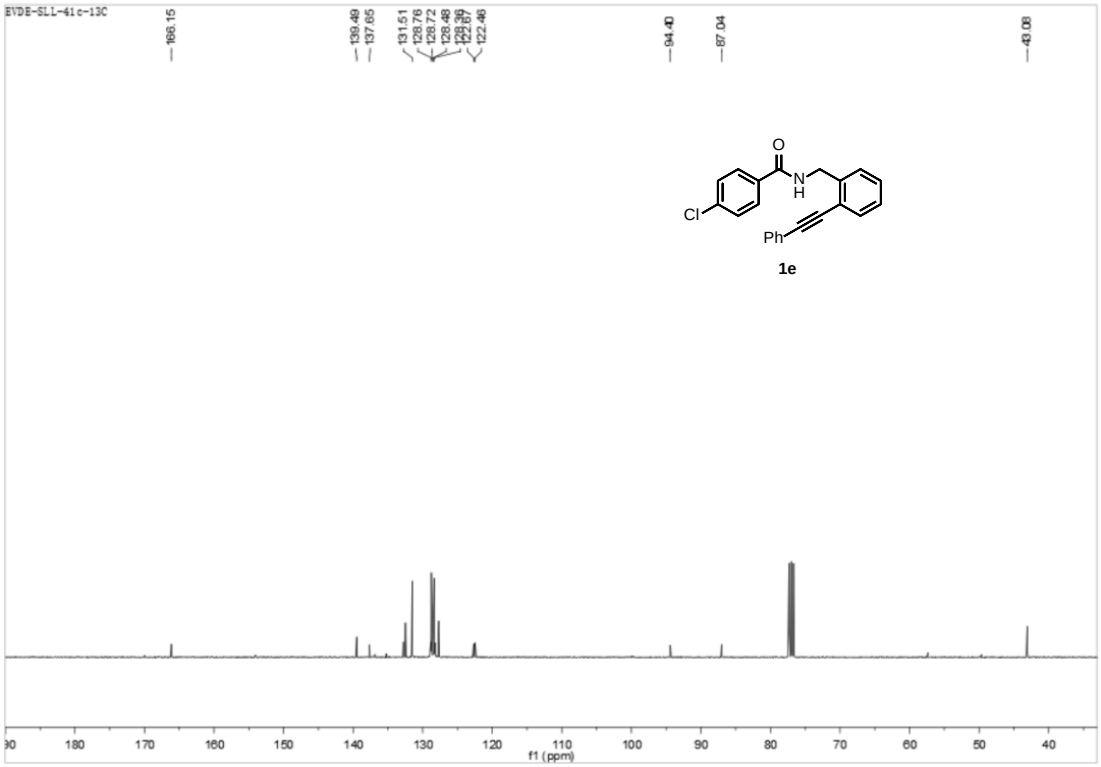
7.52
7.52
7.51
7.51
7.50
7.41
7.36
7.35
7.35
7.34
7.32
7.31
7.31
7.29
7.74
4.85
4.83
O
N
H
Cl
Ph
2.01
1.07
1.99
1.16
7.14
1.01
2.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

1e


EVDE-SLL-41c-13C
166.15
139.49
137.65
131.51
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128.48
122.46
94.40
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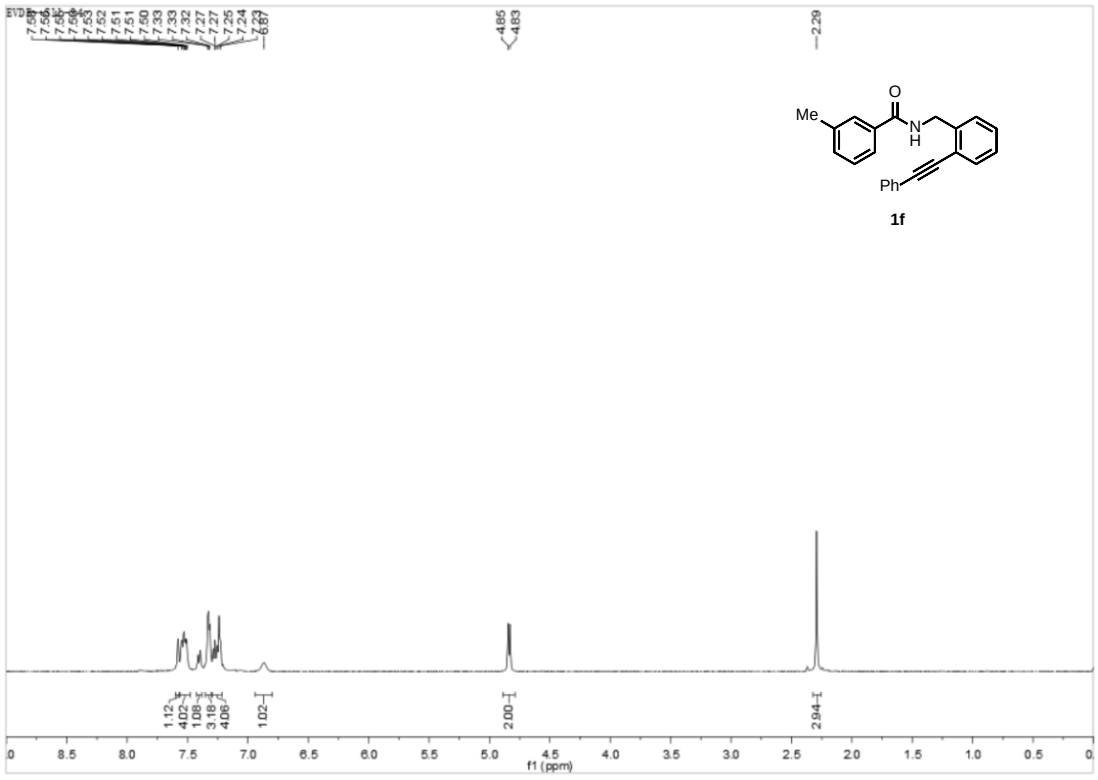
O
N
H
Cl
Ph
f1 (ppm)

1e


4.85
4.83
2.29
O
N
H
Me
Ph
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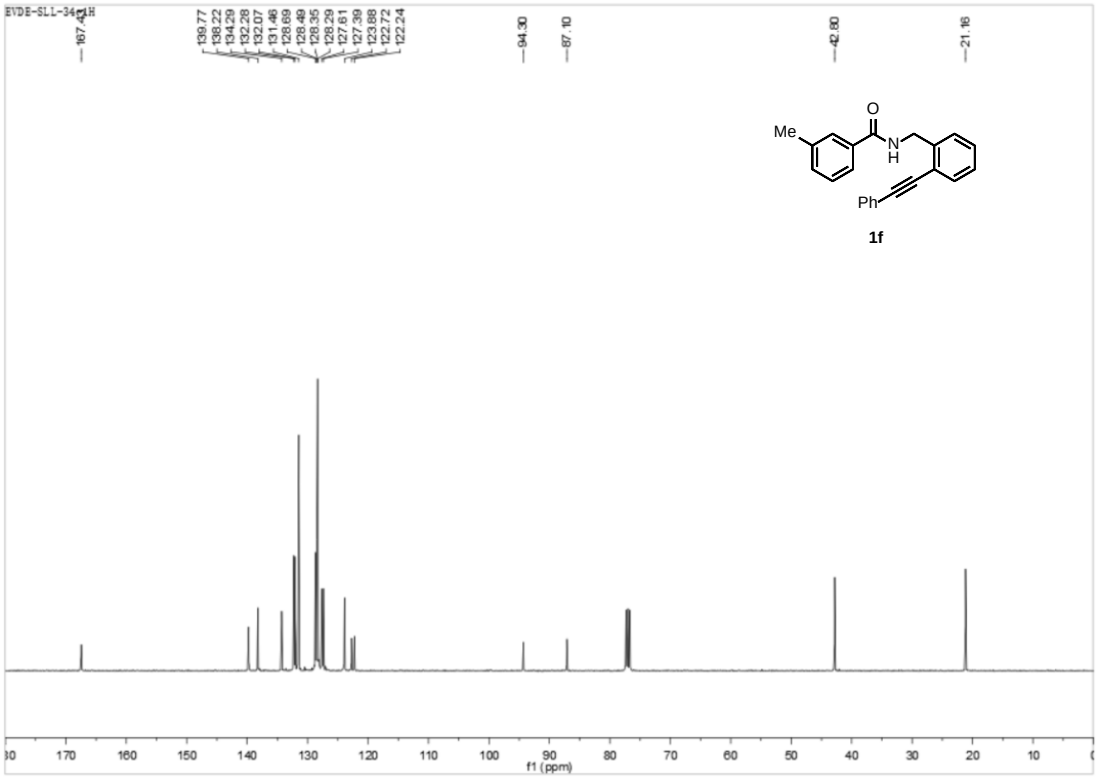
4.02
1.08
3.18
4.06
1.02
2.00
2.94
f1 (ppm)

1f


EVDE-SLL-34-1H
167.41
139.77
138.22
134.29
132.28
132.07
131.46
128.69
128.49
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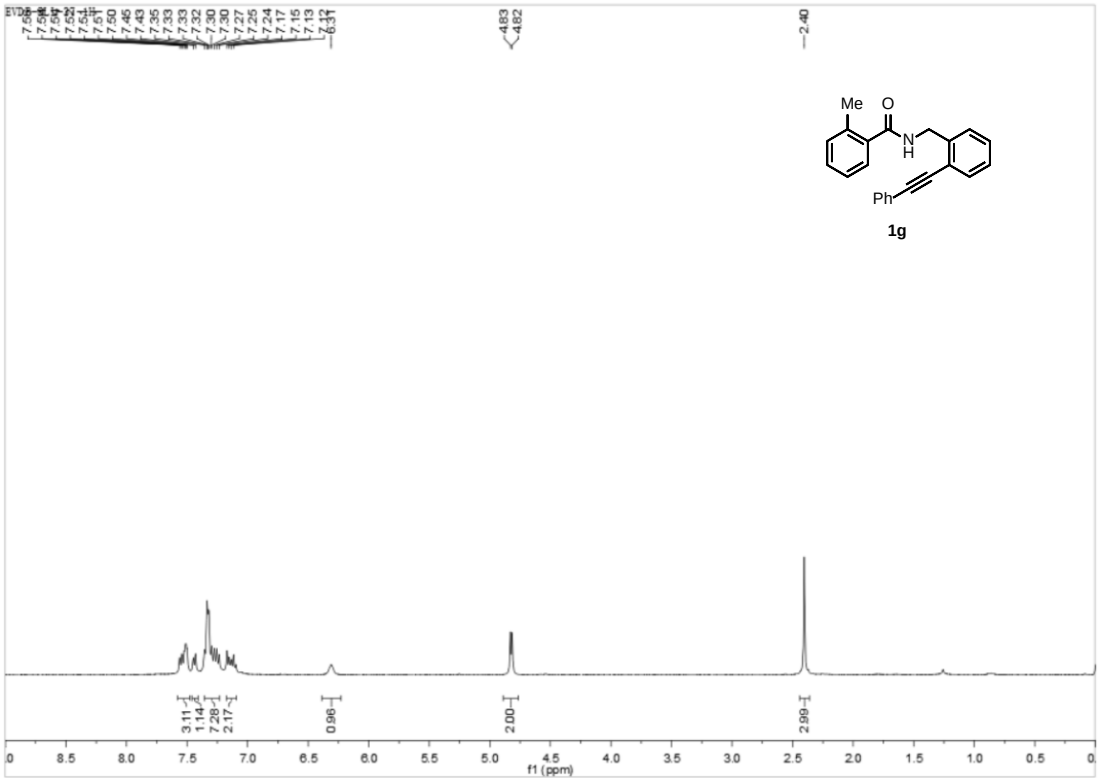
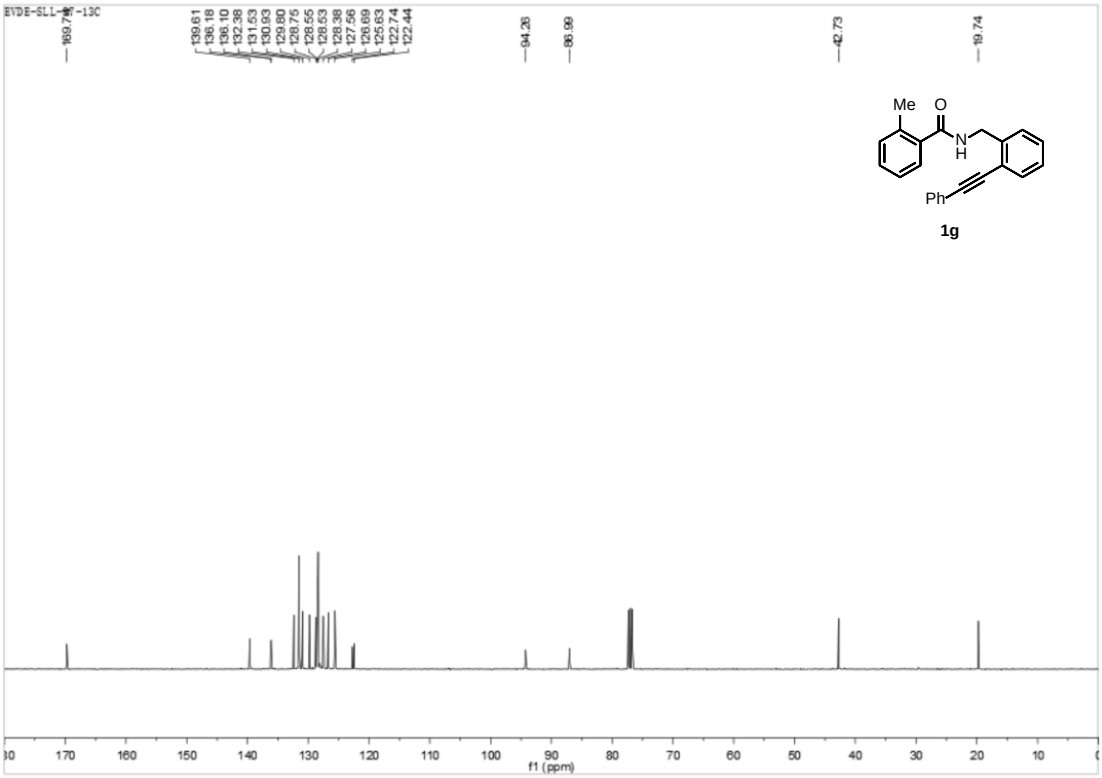
128.29
127.61
127.39
123.88
122.72
122.24
94.30
87.10
42.80
21.16
Me
O
N
H
Ph
f1 (ppm)

1f


7.51
7.50
7.45
7.43
7.35
7.33
7.32
7.30
7.27
7.25
7.24
7.17
7.15
7.13
6.31
4.83
4.82
2.40
Me
O
N
H
Ph
3.11
1.14
7.28
2.17
0.96
2.00
2.99
f1 (ppm)

1g


EVDE-SLL-13C
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139.61
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131.53
130.93
129.80
128.75
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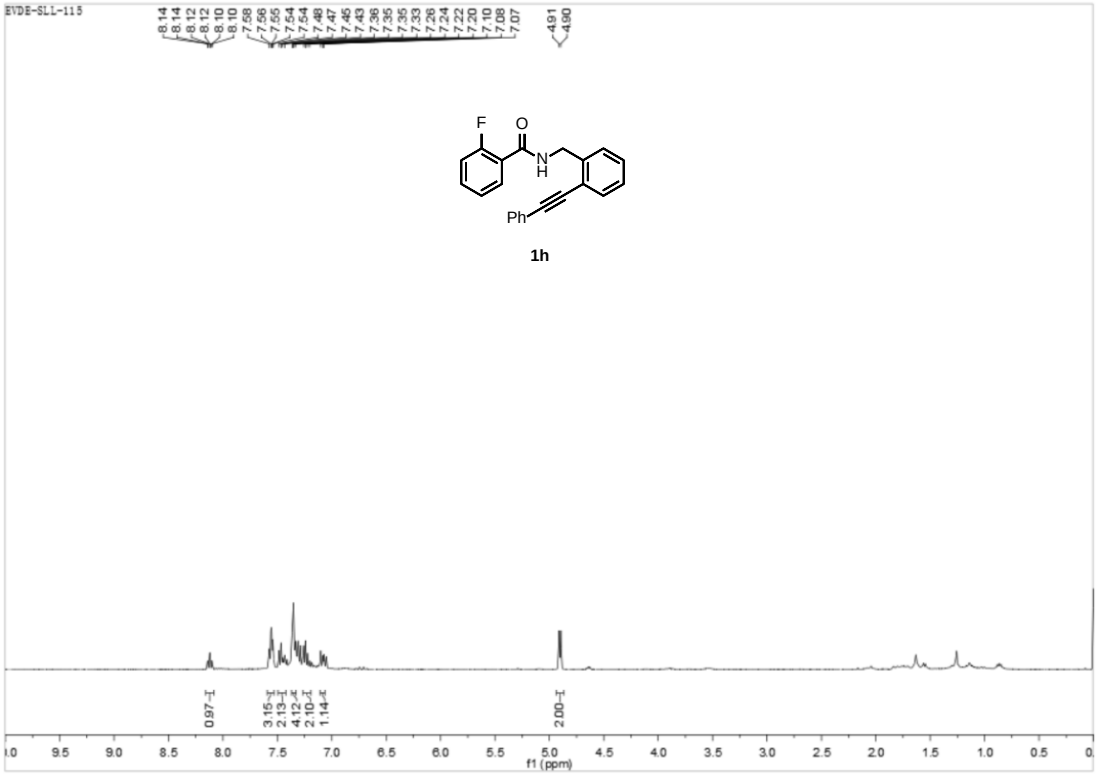
128.38
127.56
126.69
125.63
122.74
122.44
94.28
86.99
42.73
19.74
Me
O
N
H
Ph
f1 (ppm)

1g


EVDE-SLL-115
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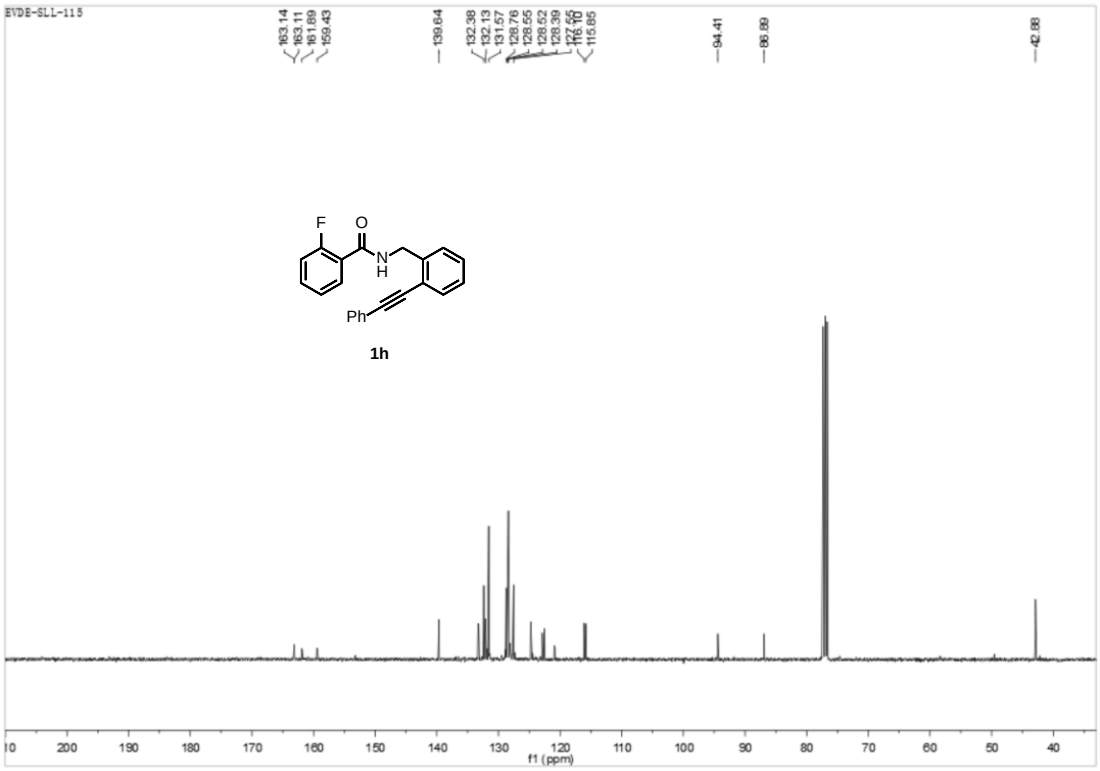
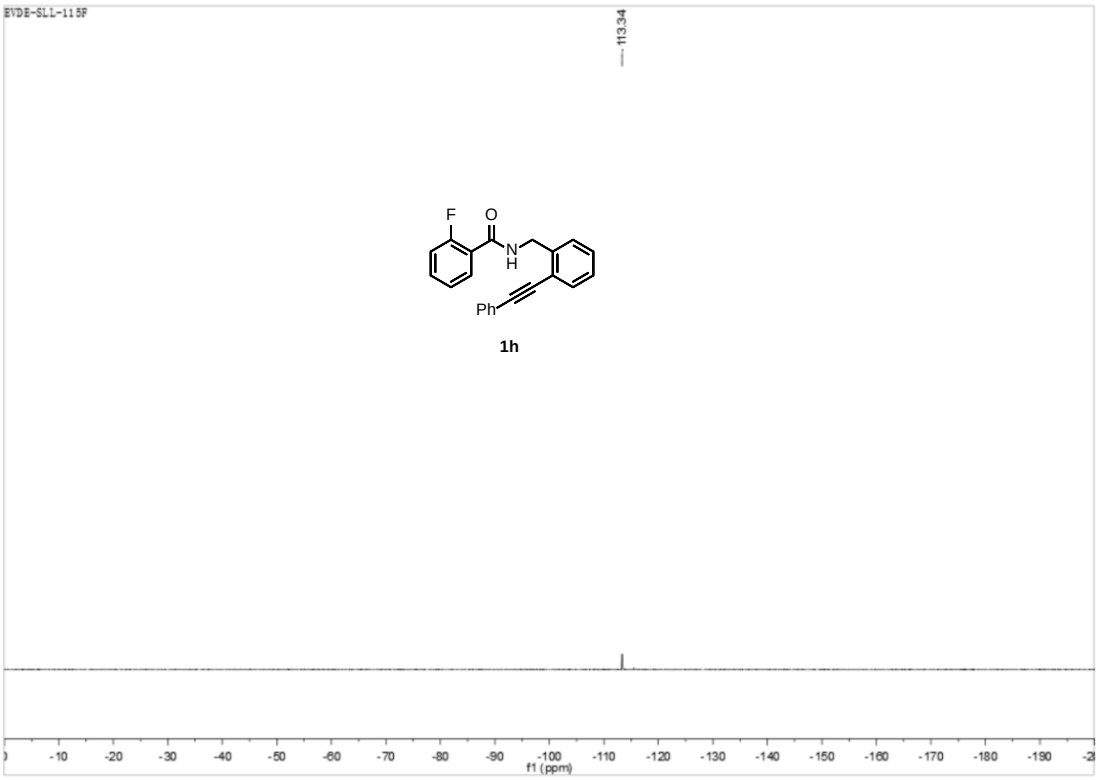
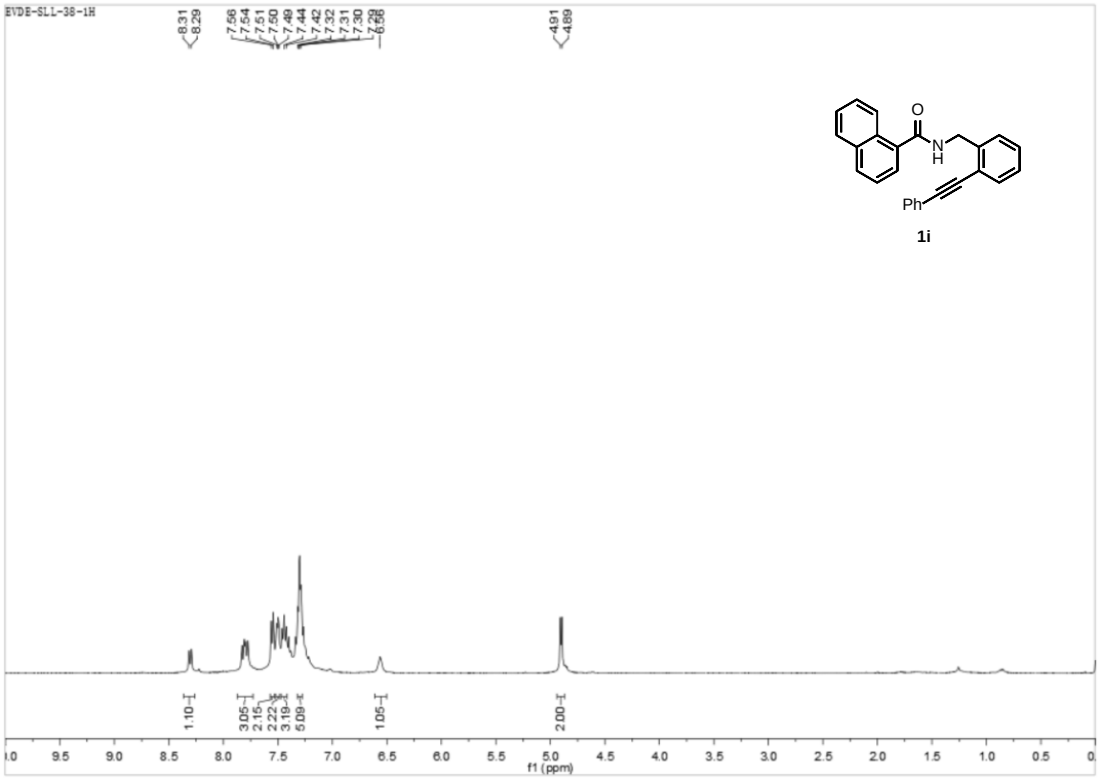
8.14
8.12
8.12
8.10
8.10
7.58
7.56
7.55
7.54
7.54
7.48
7.47
7.45
7.43
7.36
7.35
7.35
7.33
7.26
7.24
7.22
7.20
7.10
7.08
7.07
4.91
4.90
F
O
N
H
Ph
0.97
3.15
2.13
4.12
2.10
1.14
2.00
f1 (ppm)

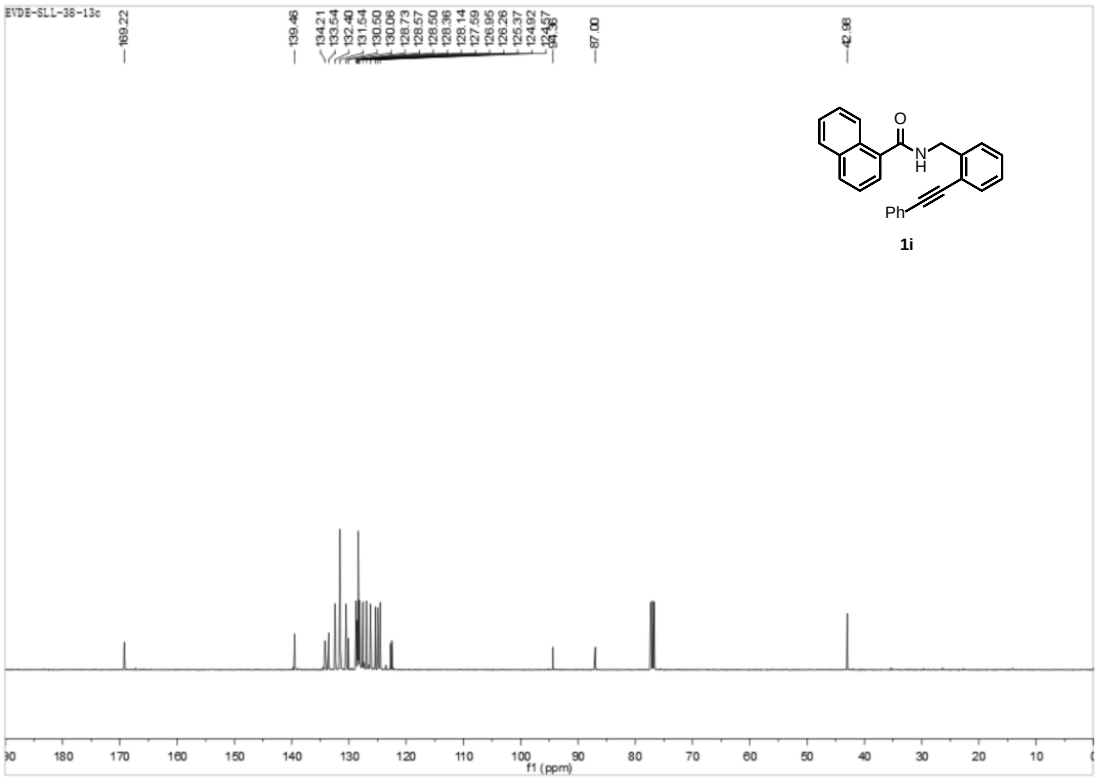
1h


EVDE-SLL-115
163.14
163.11
161.89
159.43
139.64
132.38
132.13
131.57
128.76
128.55
128.52
128.39
116.15
115.85
94.41
86.89
42.88
F
O
N
H
Ph
1h
f1 (ppm)

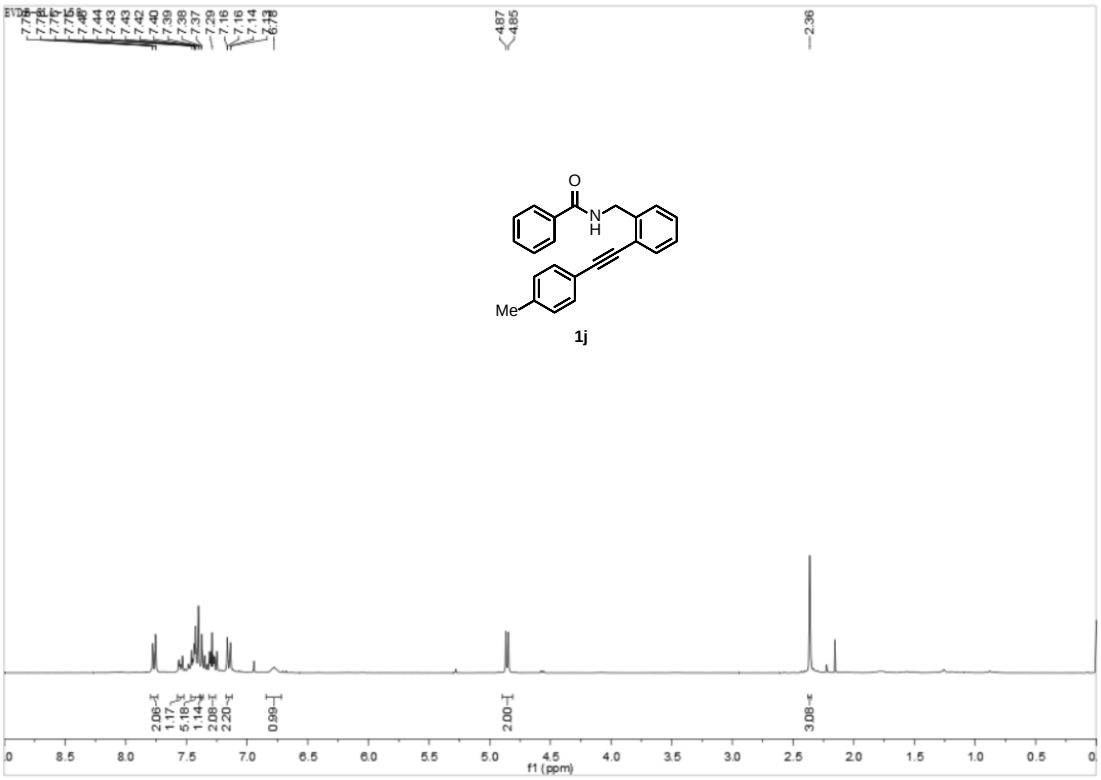

EVDE-SLL-115F
113.34
F
O
N
H
Ph
1h
f1 (ppm)

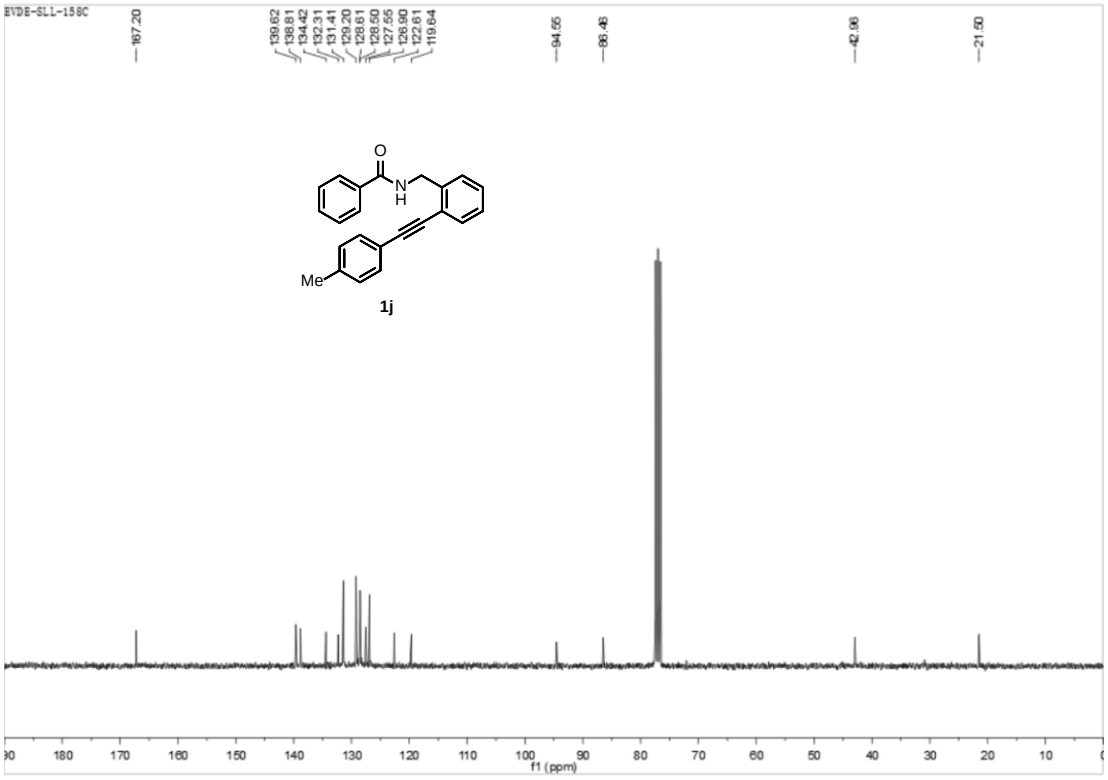

EVDE-SLL-38-1H
8.31
8.29
7.56
7.54
7.51
7.50
7.49
7.44
7.42
7.32
7.31
7.30
7.29
6.56
4.91
4.89
O
N
H
Ph
1.10
3.05
2.15
2.22
3.19
5.09
1.05
2.00
f1 (ppm)

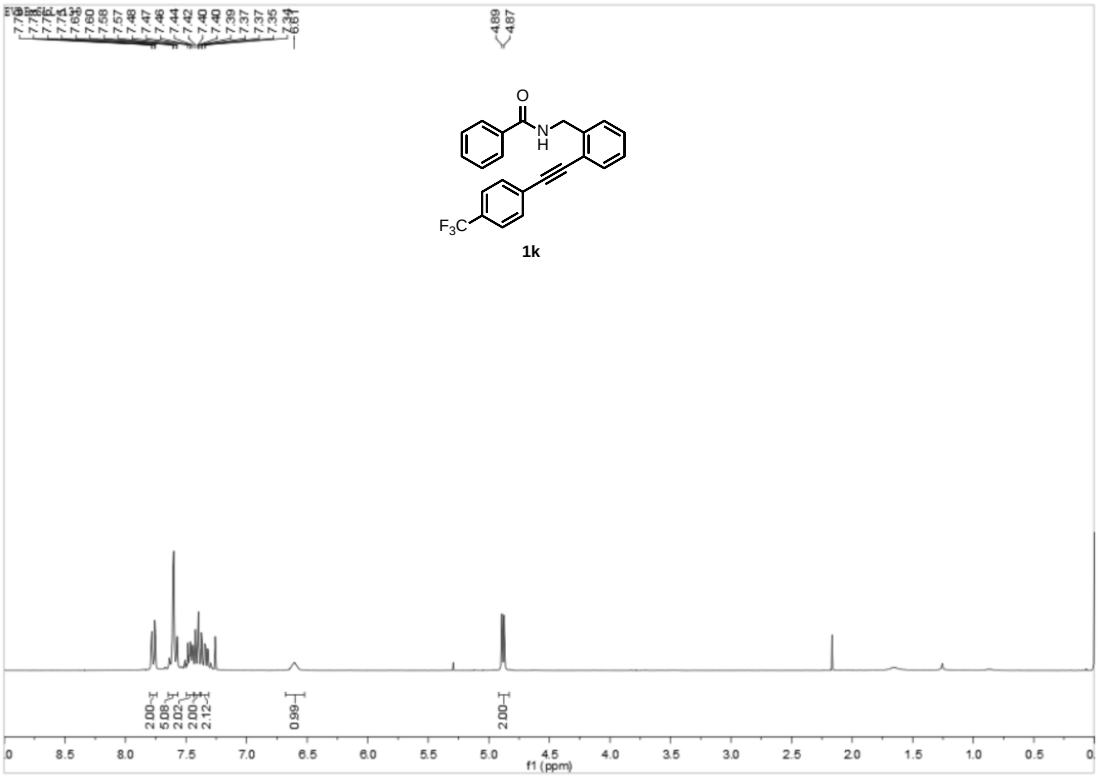
1i

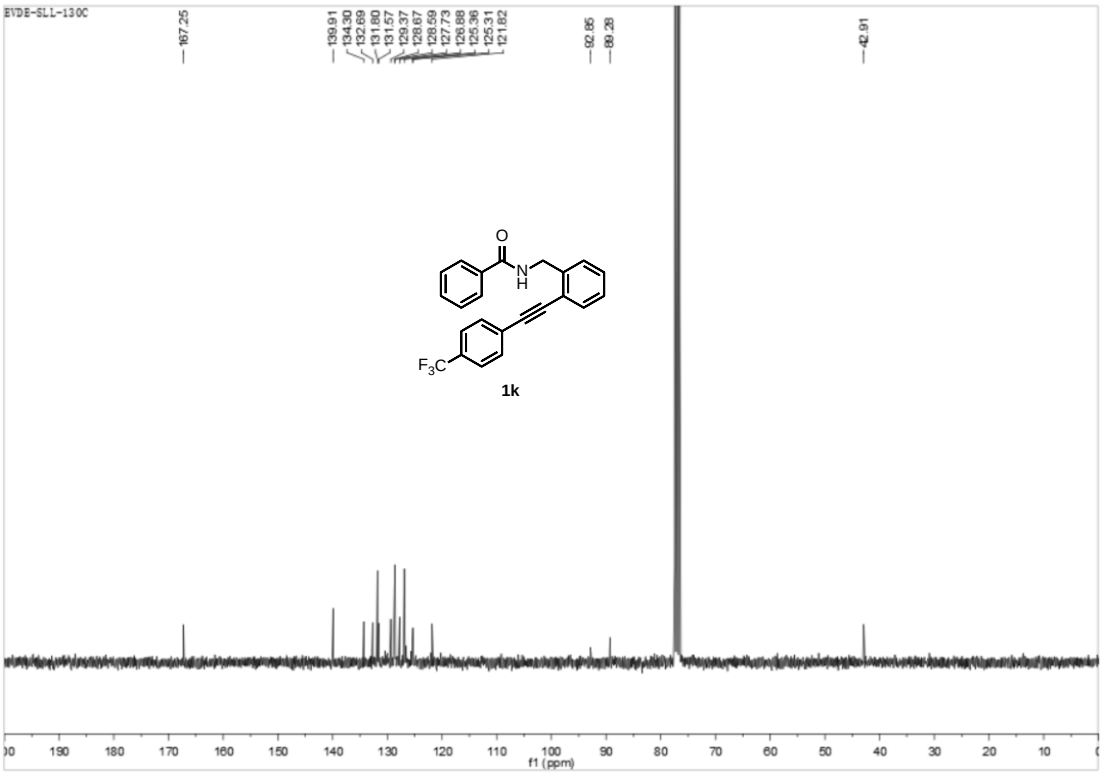

EVDE-SLL-38-13c
169.22
139.46
134.21
133.54
132.40
131.54
130.50
130.06
128.73
128.57
128.50
128.36
128.14
127.59
126.95
126.26
125.37
124.92
94.30
87.00
42.96
O
N
H
Ph
f1 (ppm)

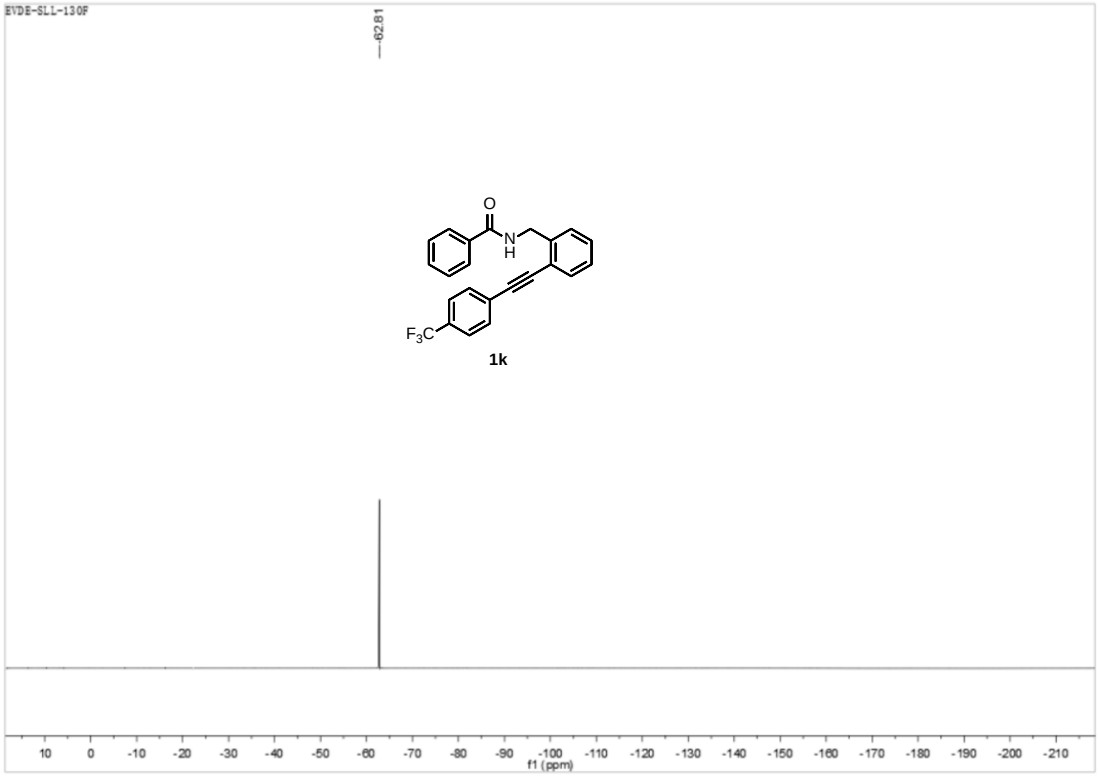
1i

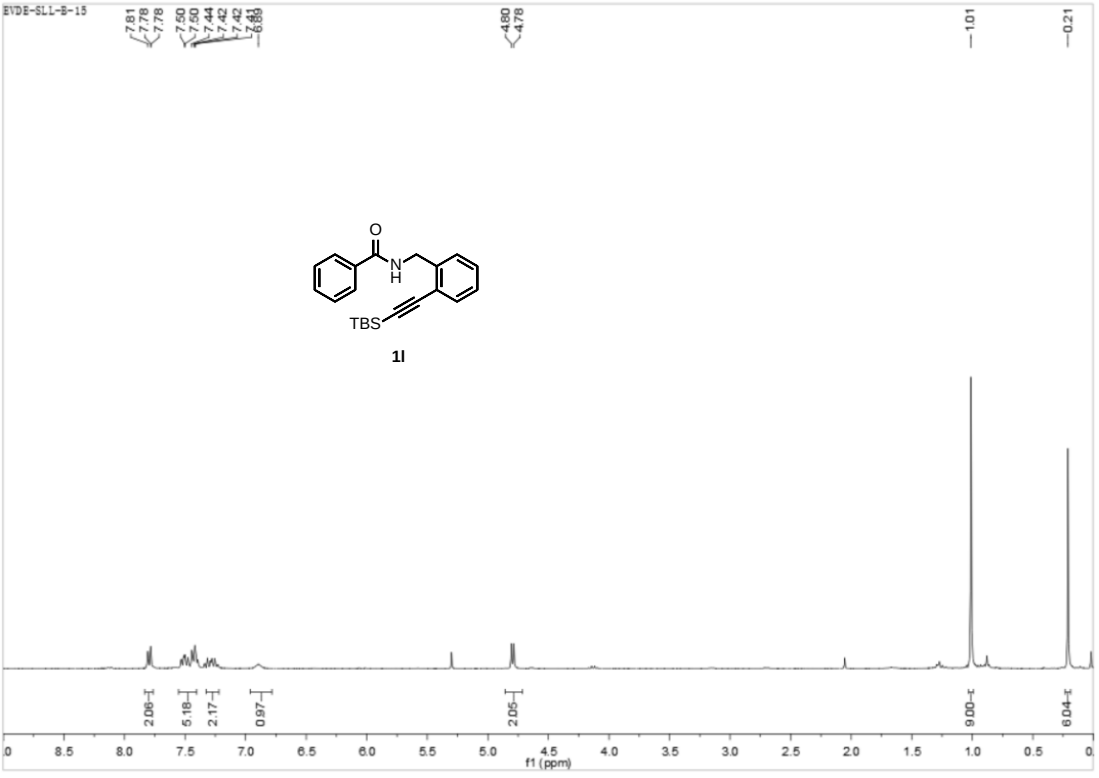

O
N
H
Me
1j
f1 (ppm)

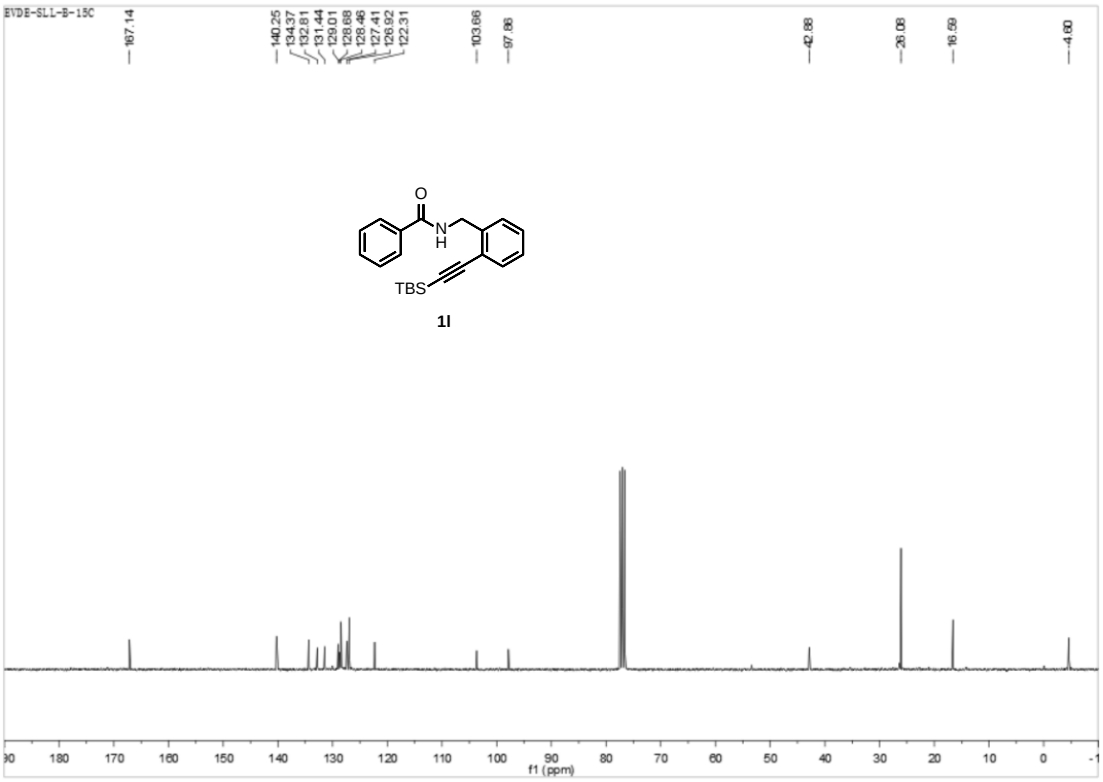

EVDE-SLL-158C
O
N
H
Me
1j
f1 (ppm)


O
N
H
F3C
1k
f1 (ppm)


EVDE-SLL-130C
O
N
H
F3C
1k
f1 (ppm)


EVDE-SLL-130F
-62.81
O
N
H
F3C
1k
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)

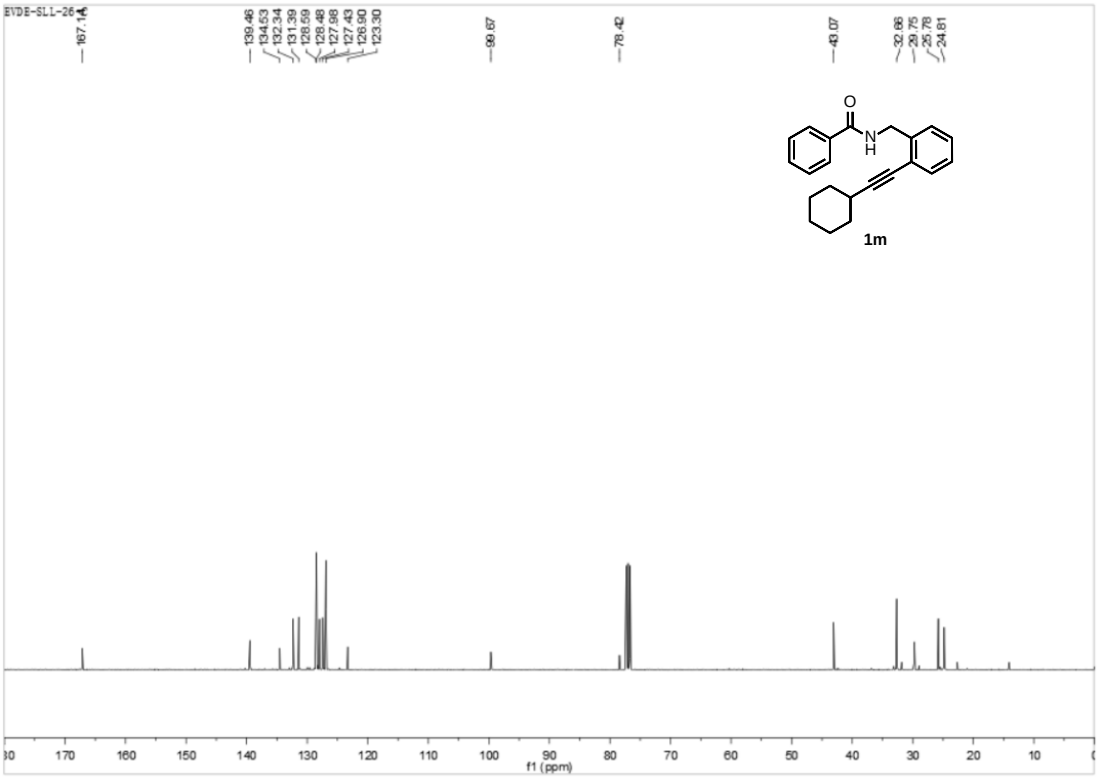

EVDE-SLL-B-15
7.81
7.78
7.78
7.50
7.50
7.44
7.42
7.42
6.88
4.80
4.78
1.01
0.21
O
N
H
TBS
1l
2.06
5.18
2.17
0.97
2.05
9.00
6.04
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

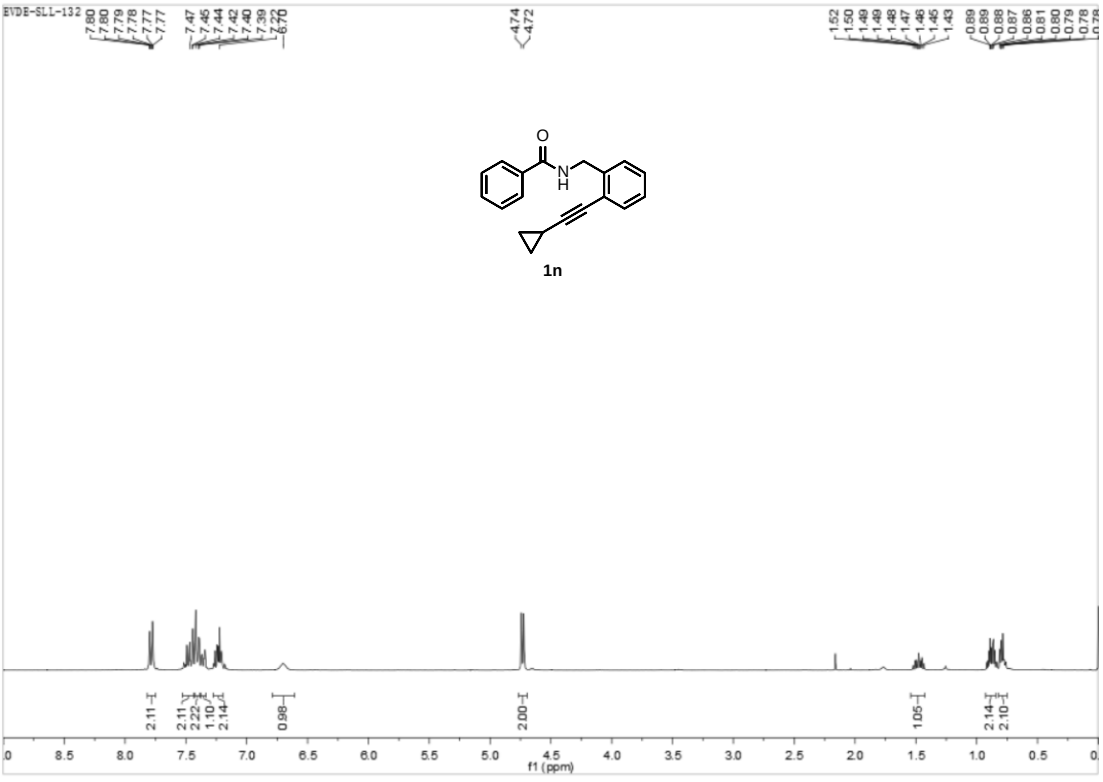

EVDE-SLL-B-15C
167.14
140.25
134.37
132.81
131.44
129.01
128.68
128.46
127.41
126.92
122.31
103.66
97.86
42.88
26.08
16.69
-4.60
O
N
H
TBS
f1 (ppm)

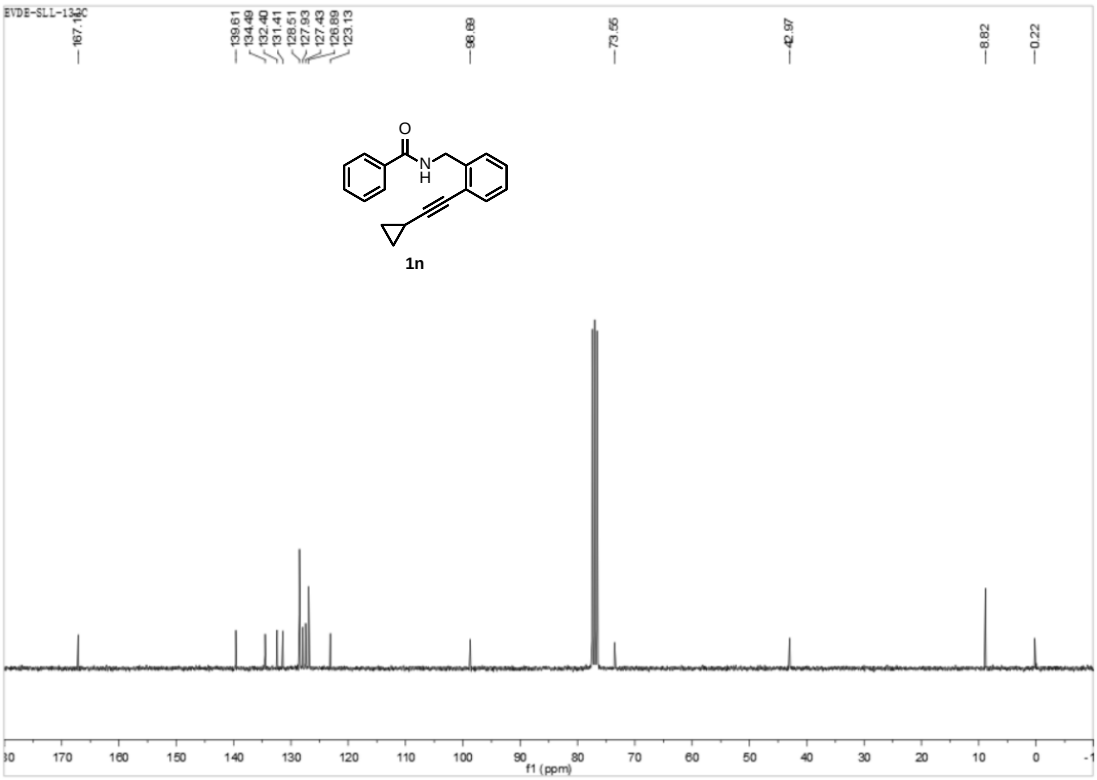
1l


EVDE-SLL-26-H
7.79
7.77
7.76
7.43
7.42
7.41
7.41
7.41
7.23
6.74
4.76
4.75
2.67
2.66
2.65
2.64
2.63
2.61
2.61
1.88
1.87
1.86
1.85
1.74
1.73
1.73
1.72
1.71
1.56
1.54
1.52
1.51
1.50
1.37
1.36
1.35
1.34
O
N
H
1.96
1.10
4.14
2.10
0.93
2.00
0.98
2.05
2.19
3.12
3.07
f1 (ppm)

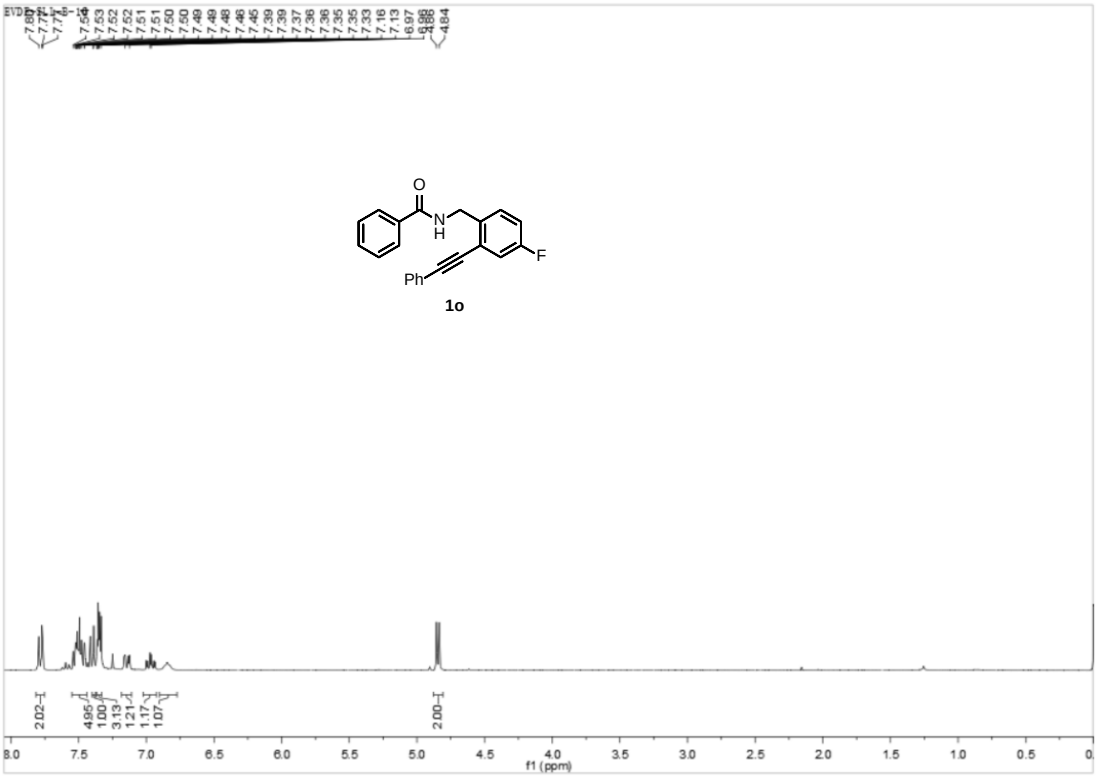
1m


EVDE-SLL-264
167.14
139.46
134.53
132.34
131.39
128.59
128.48
127.98
127.43
126.90
123.30
99.67
78.42
43.07
32.66
29.75
25.78
24.81
O
N
H
1m
f1 (ppm)

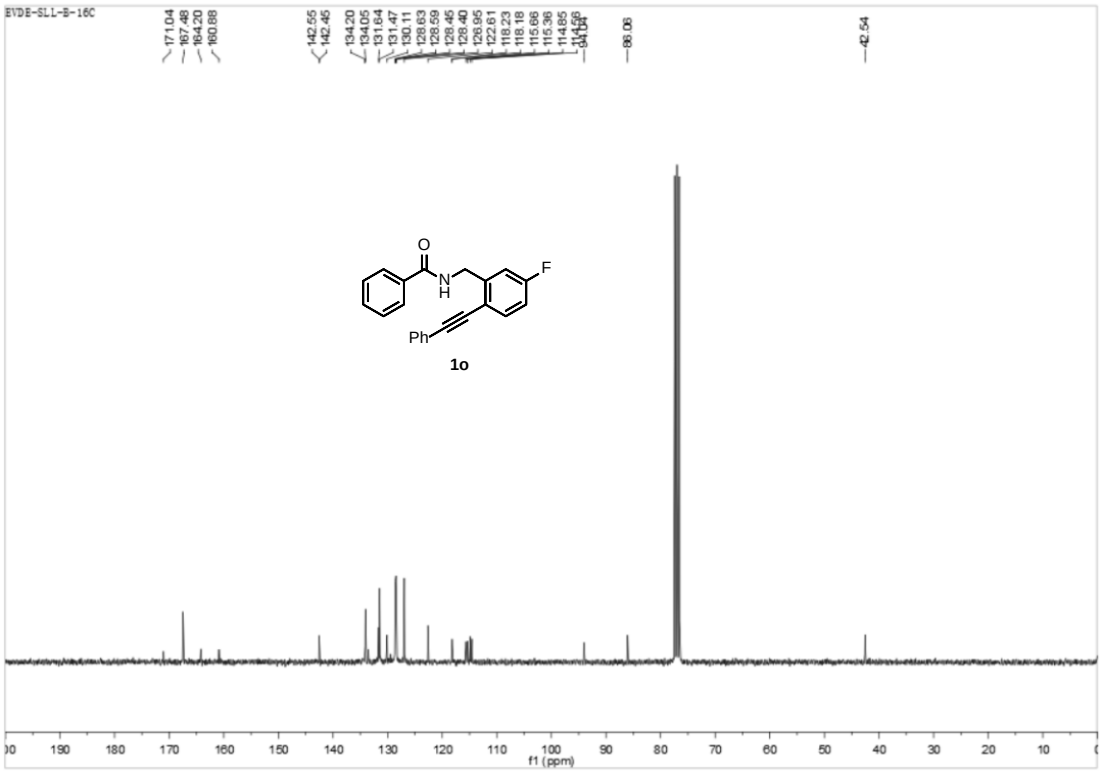

EVDE-SLL-132
7.80
7.80
7.79
7.78
7.77
7.77
7.47
7.46
7.44
7.42
7.40
7.39
7.27
6.70
4.74
4.72
1.52
1.50
1.49
1.49
1.48
1.47
1.46
1.45
1.43
0.89
0.89
0.88
0.87
0.86
0.81
0.80
0.79
0.78
2.11
2.11
2.22
1.10
2.14
0.98
2.00
1.05
2.14
2.10
O
N
H
1n
f1 (ppm)

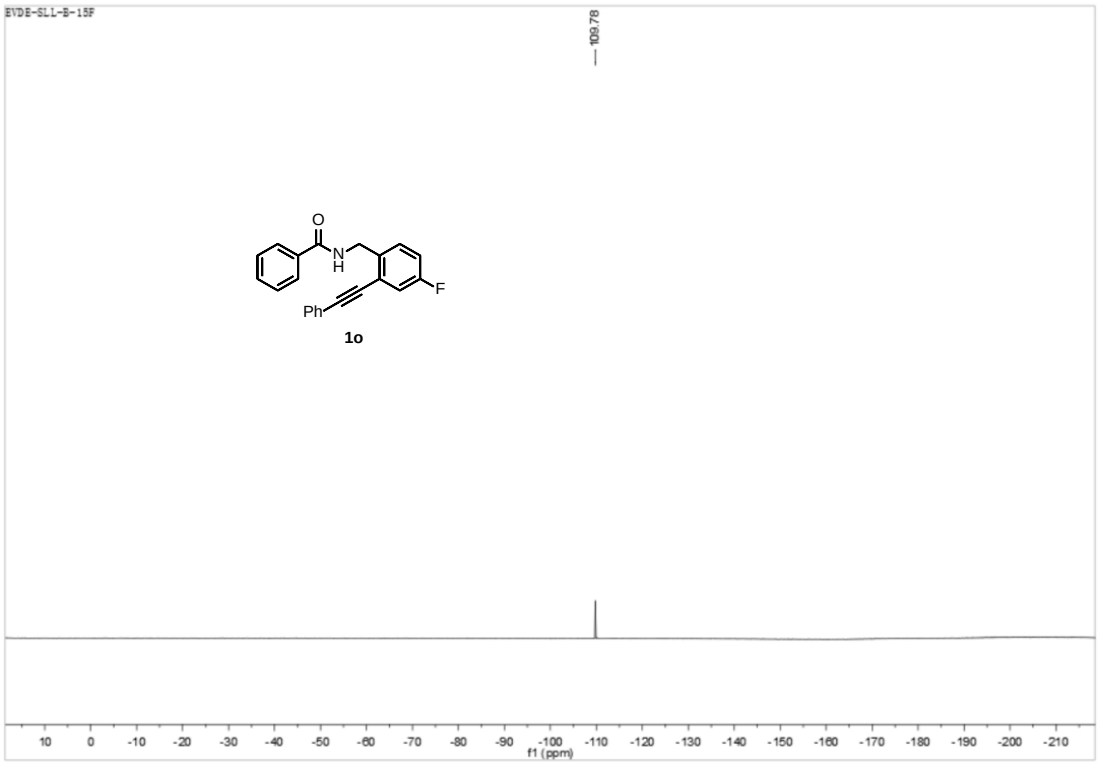

EVDE-SLI-13C
167.10
139.61
134.49
132.40
131.41
128.51
127.93
127.43
126.89
123.13
98.89
73.55
42.97
8.82
0.22
O
N
H
f1 (ppm)

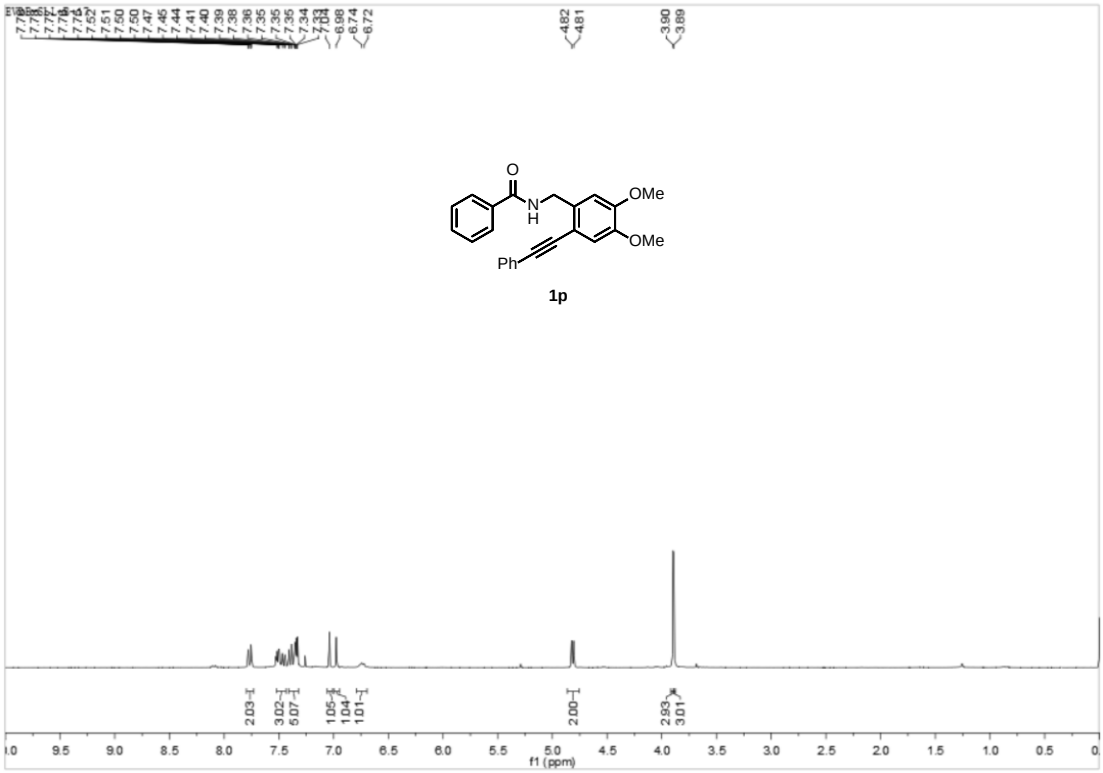
1n

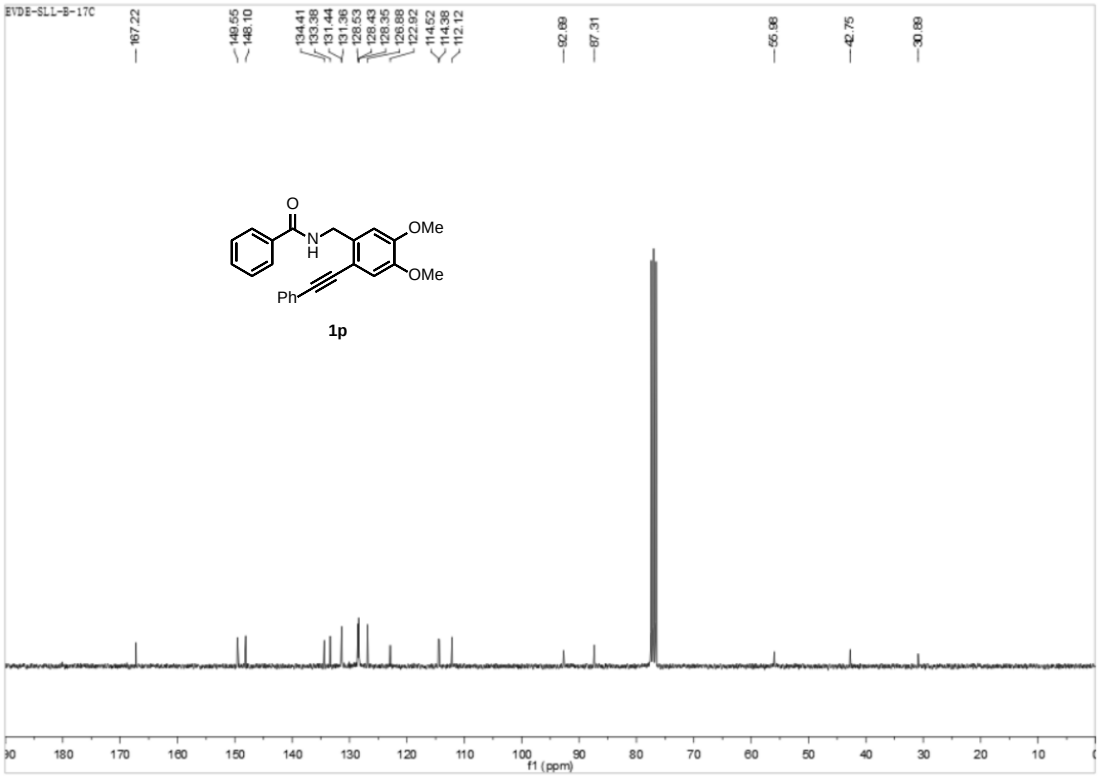

7.89
7.77
7.71
7.54
7.53
7.52
7.52
7.51
7.51
7.50
7.50
7.49
7.49
7.48
7.46
7.45
7.39
7.39
7.37
7.36
7.36
7.35
7.35
7.33
7.16
7.13
6.97
6.96
4.88
4.84
2.02
4.95
1.00
3.13
1.21
1.17
1.07
2.00
O
N
H
F
Ph
f1 (ppm)

1o

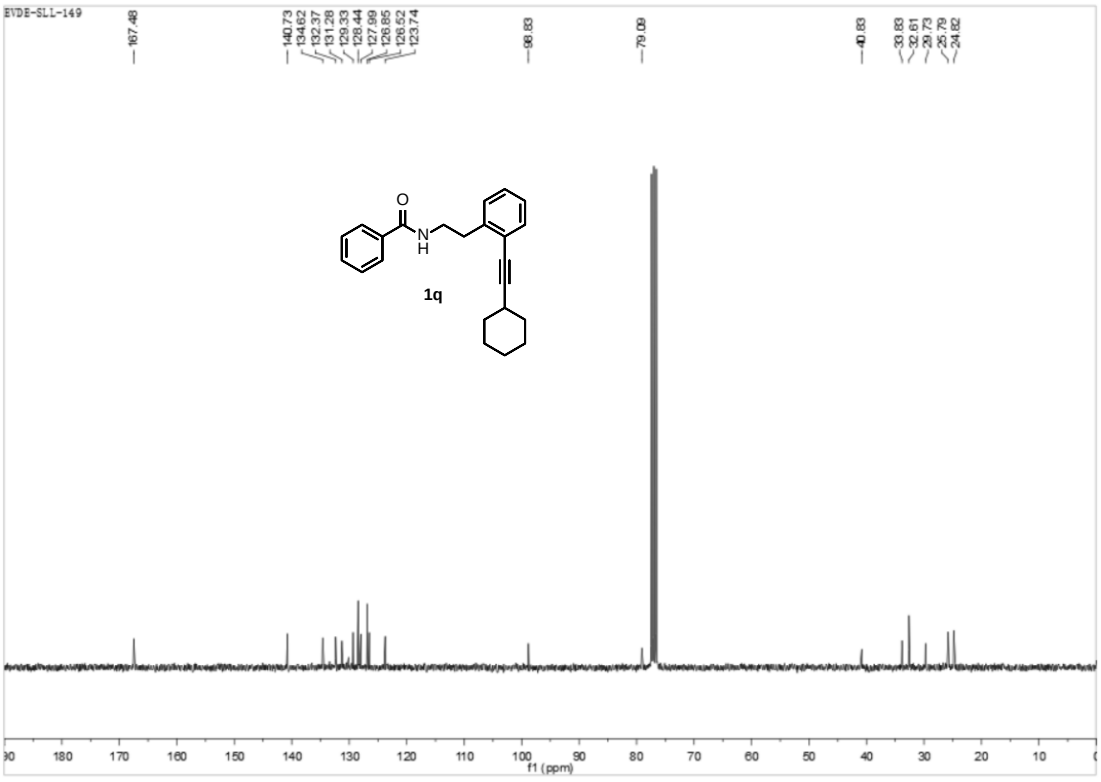

EVDE-SLL-B-16C
171.04
167.48
164.20
160.88
142.55
142.45
134.20
134.05
131.64
131.47
130.11
128.63
128.59
128.45
128.40
126.95
122.61
118.23
118.18
115.66
115.36
114.85
94.04
86.06
42.54
O
N
H
F
Ph
1o
f1 (ppm)

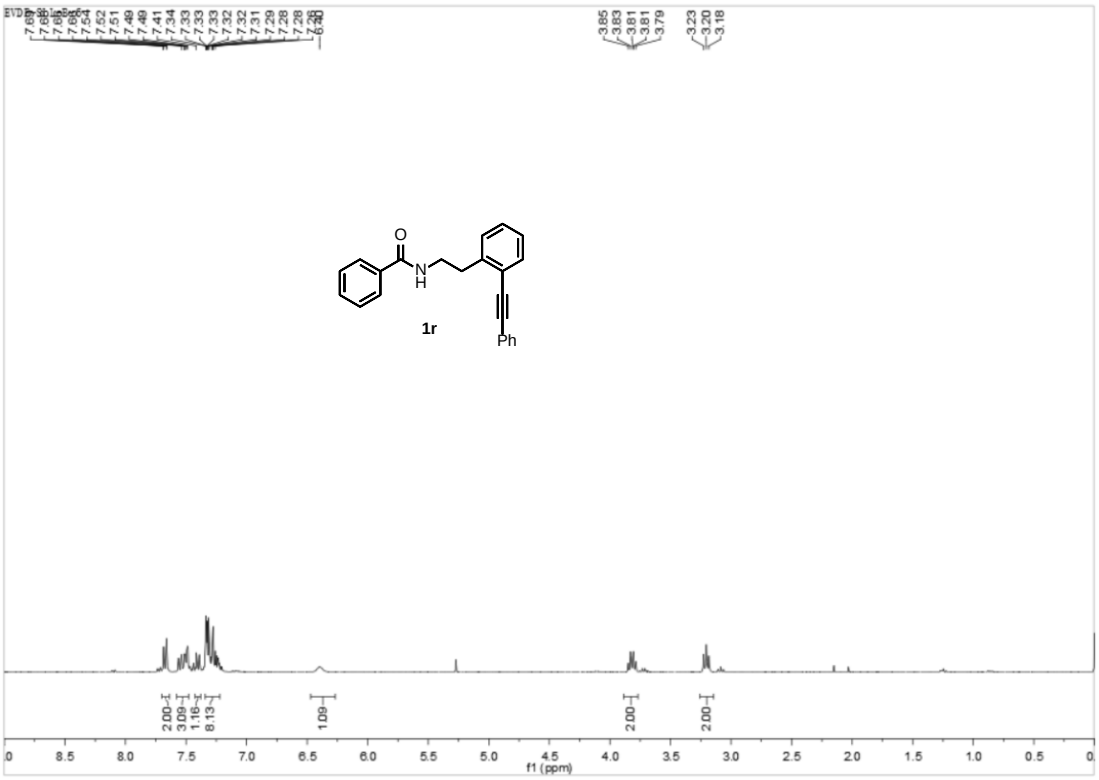

EVDE-SLL-B-15F
109.78
O
N
H
F
Ph
1o
f1 (ppm)

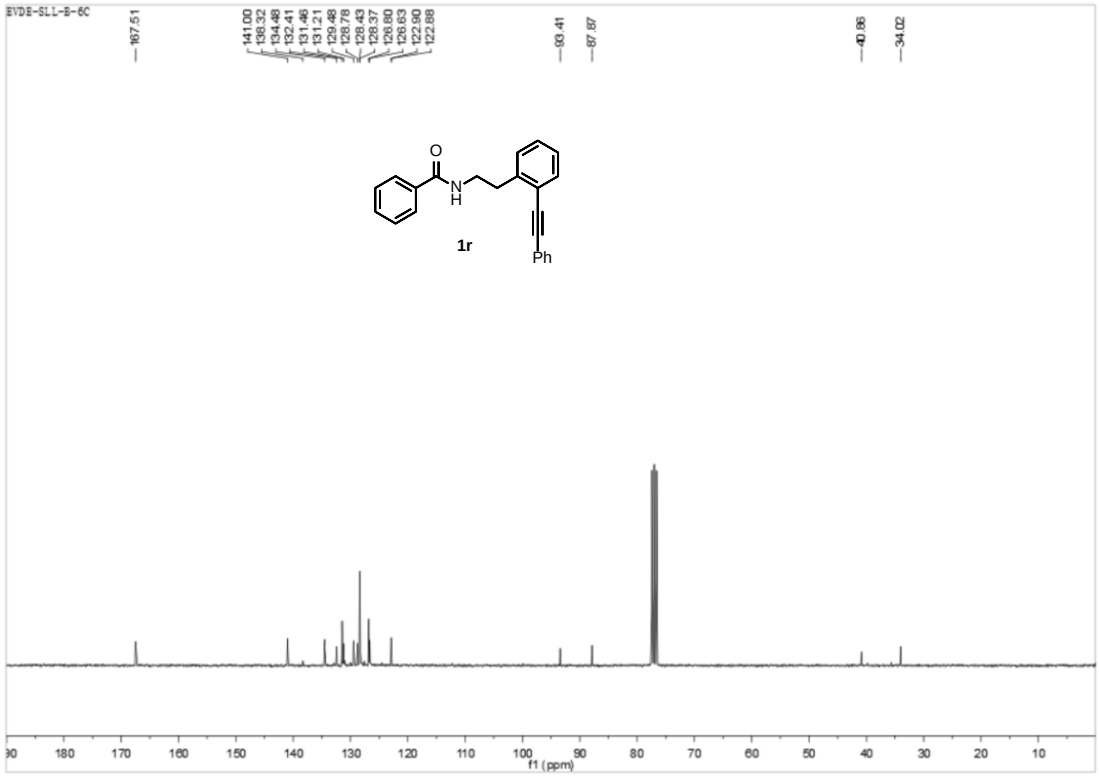

O
N
H
OMe
OMe
Ph
1p
f1 (ppm)

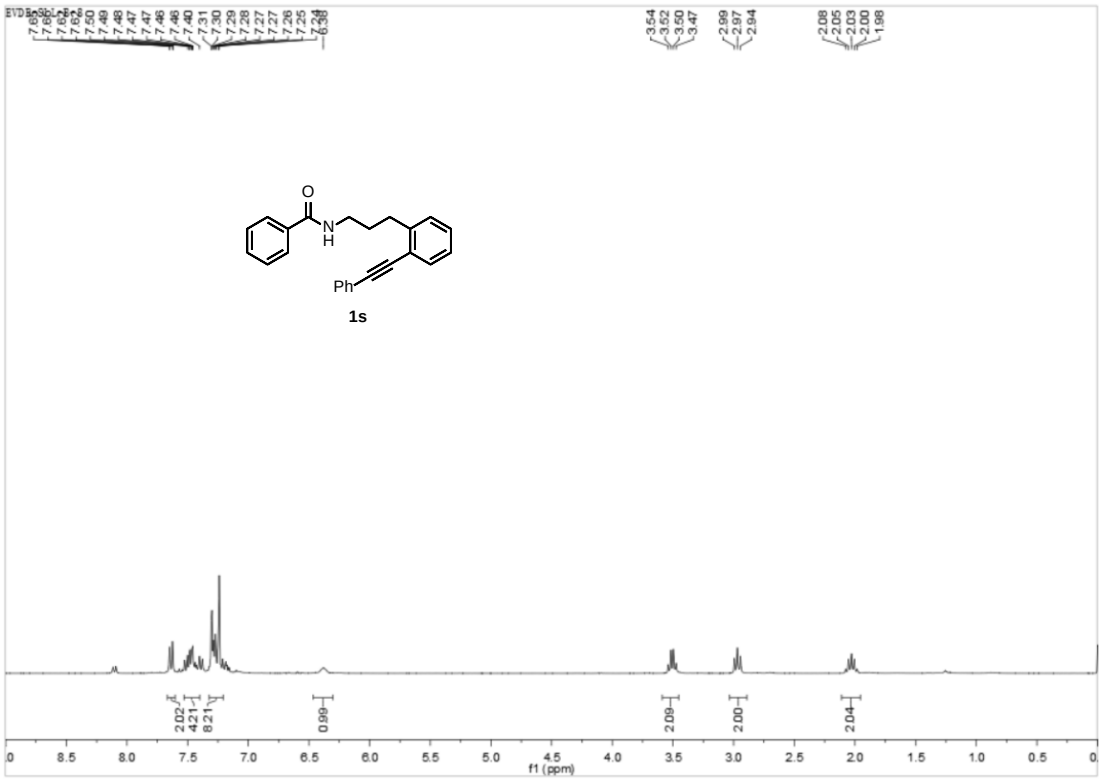

EVDE-SLL-B-17C
O
N
H
OMe
OMe
Ph
1p
f1 (ppm)

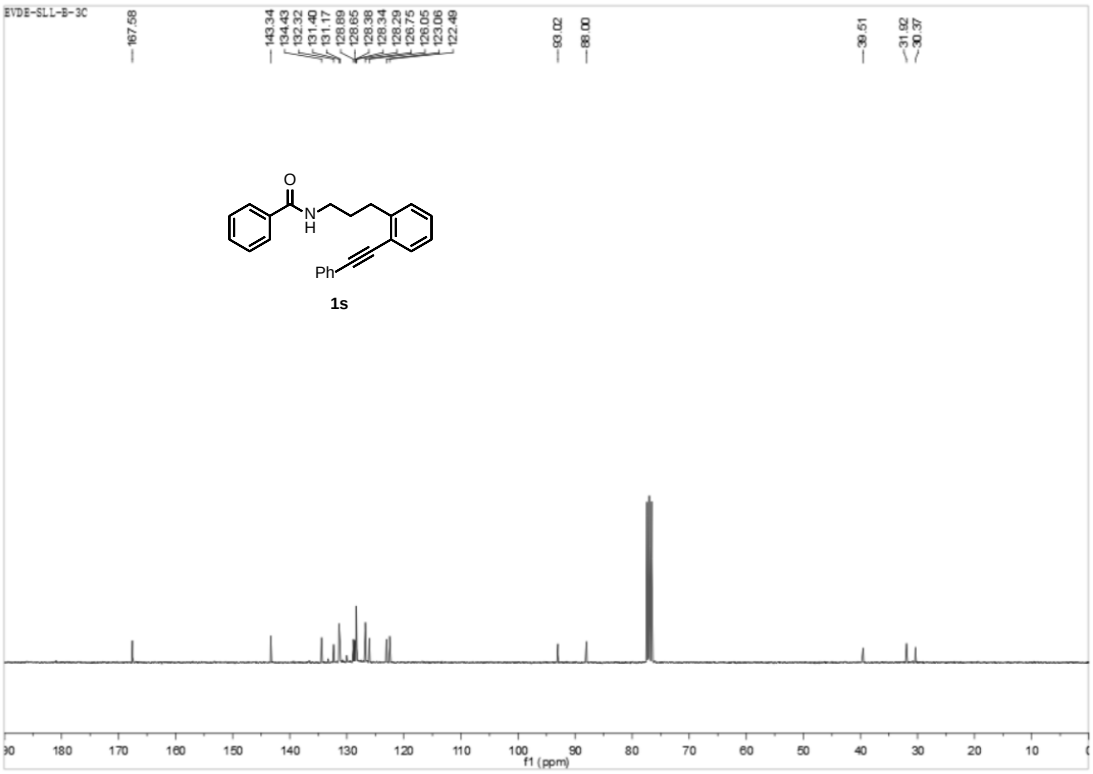

1q
f1 (ppm)

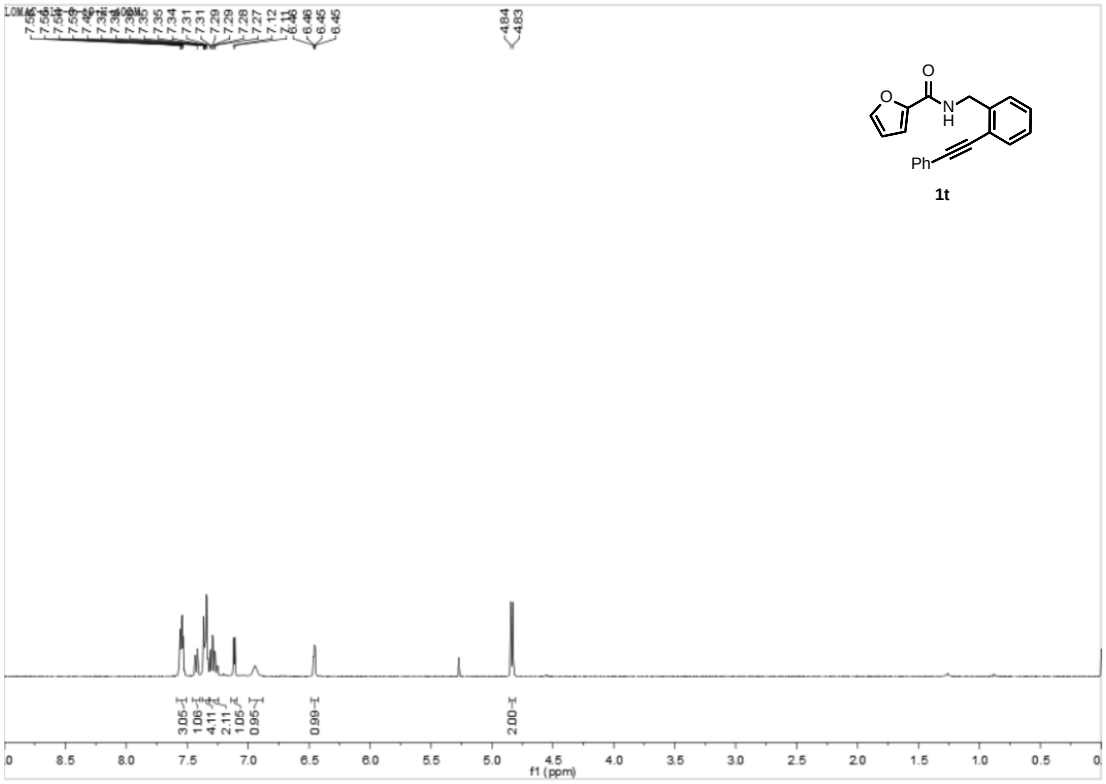

EVDE-SLL-149
1q
f1 (ppm)


O
N
H
Ph
1r
f1 (ppm)

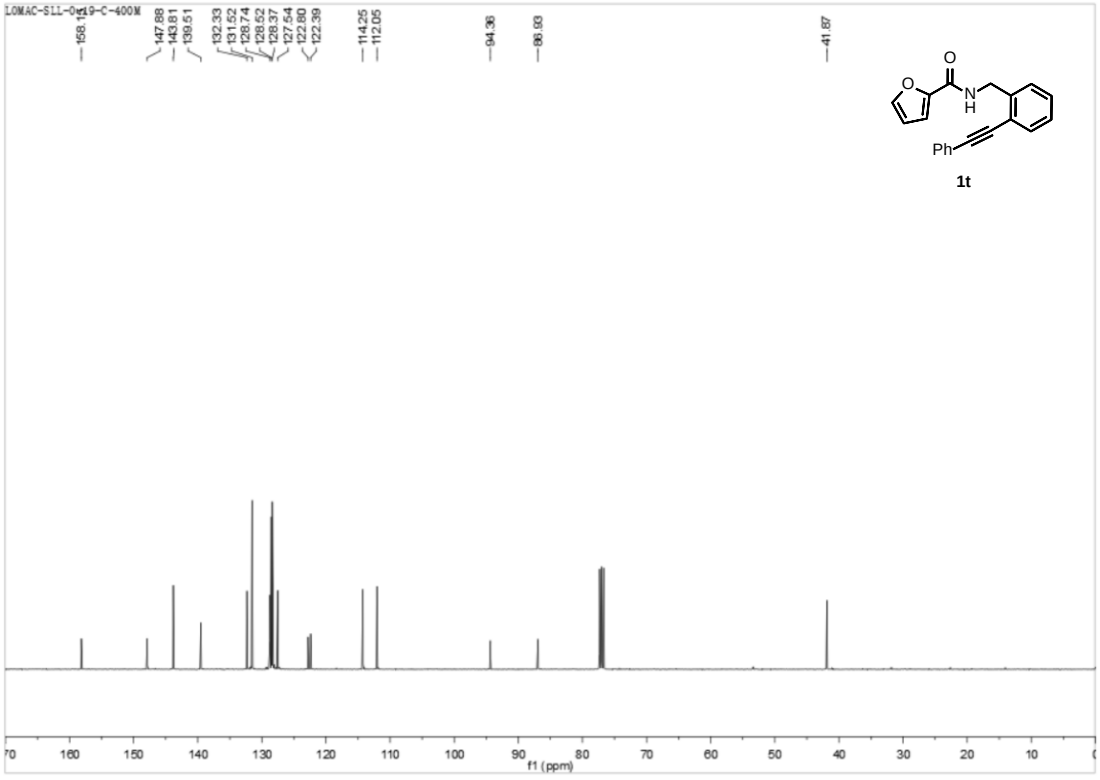

O
N
H
Ph
1r
f1 (ppm)


O
N
H
Ph
1s
f1 (ppm)

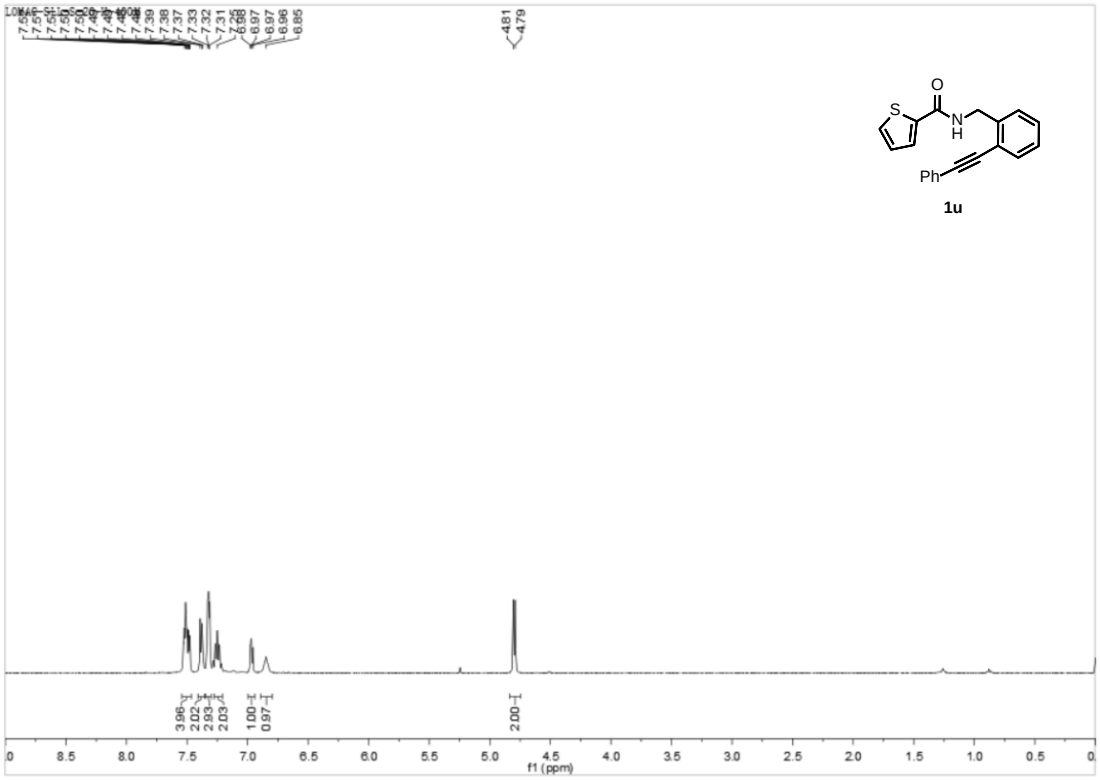

O
N
H
Ph
1s
f1 (ppm)


4.84
4.83
3.05
1.08
4.11
2.11
1.05
0.95
0.99
2.00
f1 (ppm)
O
O
N
H
Ph

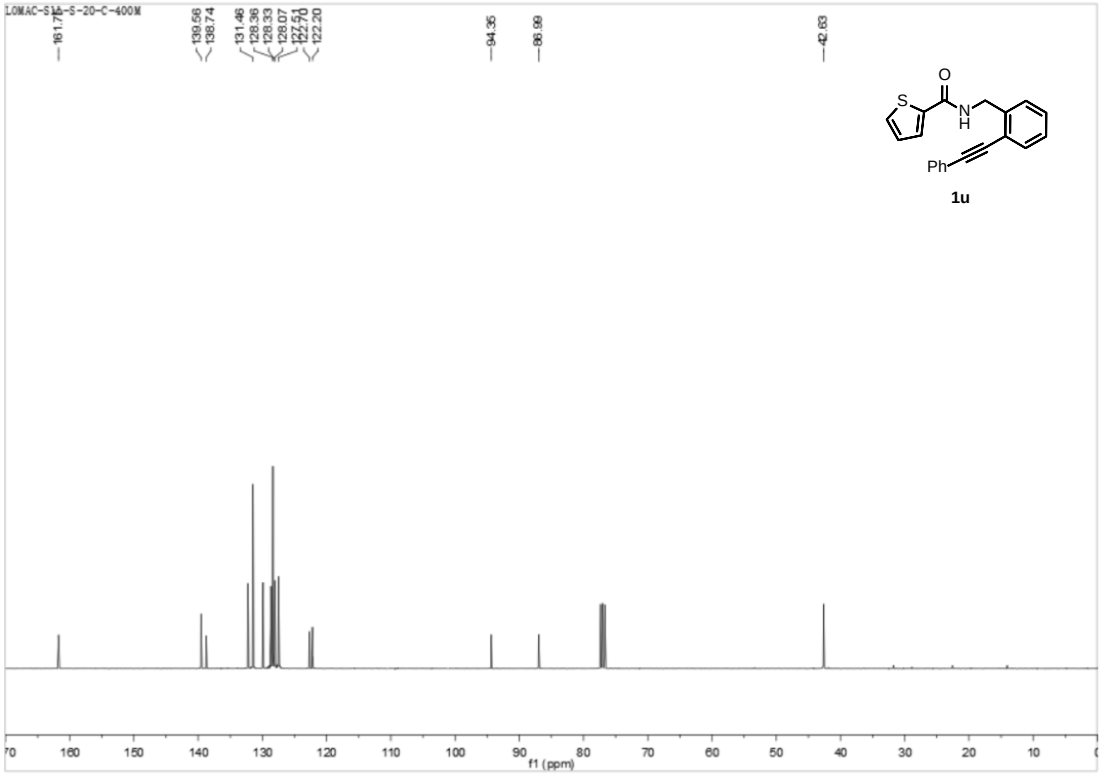
1t


158.19
147.88
143.81
139.51
132.33
131.52
128.74
128.52
128.37
127.54
122.80
122.39
114.25
112.05
94.36
86.93
41.87
f1 (ppm)
O
O
N
H
Ph

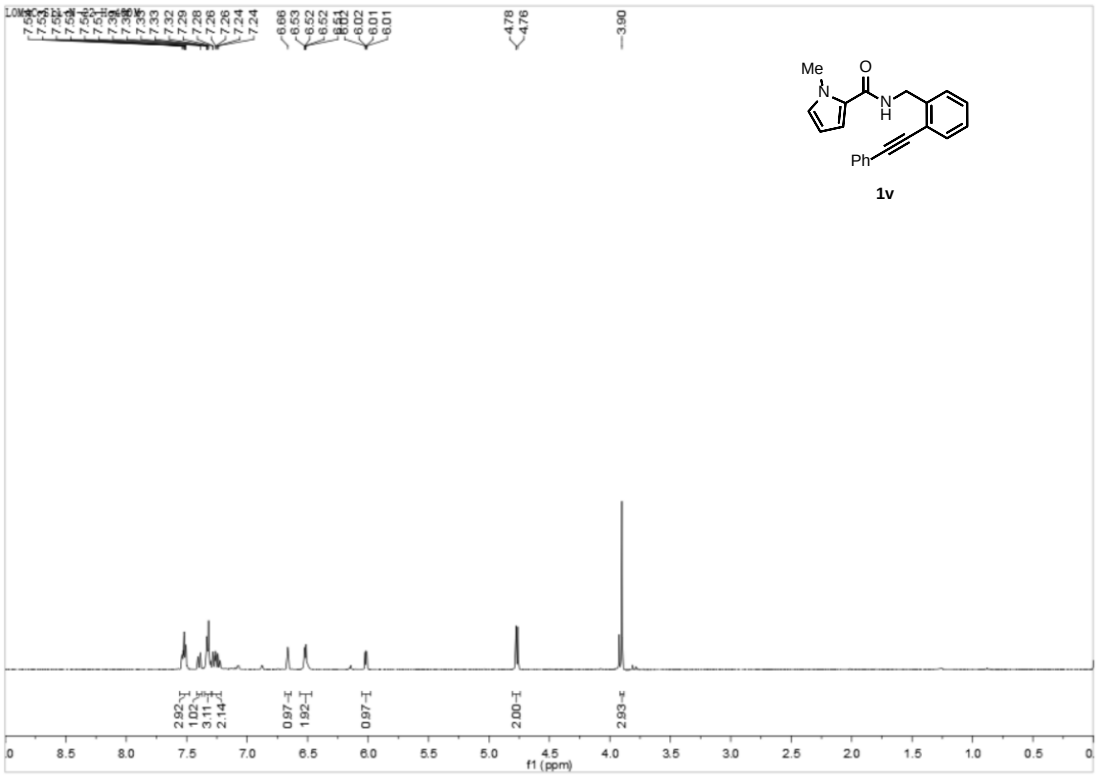
1t

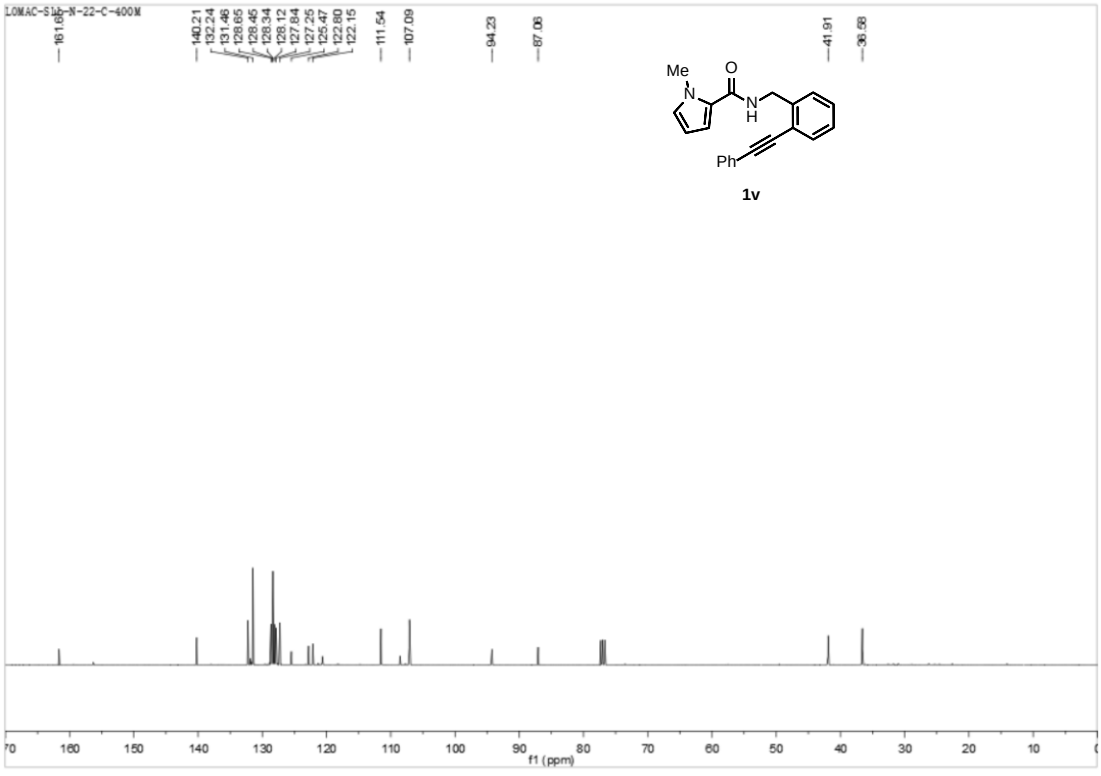

4.81
4.79
3.96
2.02
2.93
2.03
1.00
0.97
2.00
f1 (ppm)
O
S
N
H
Ph

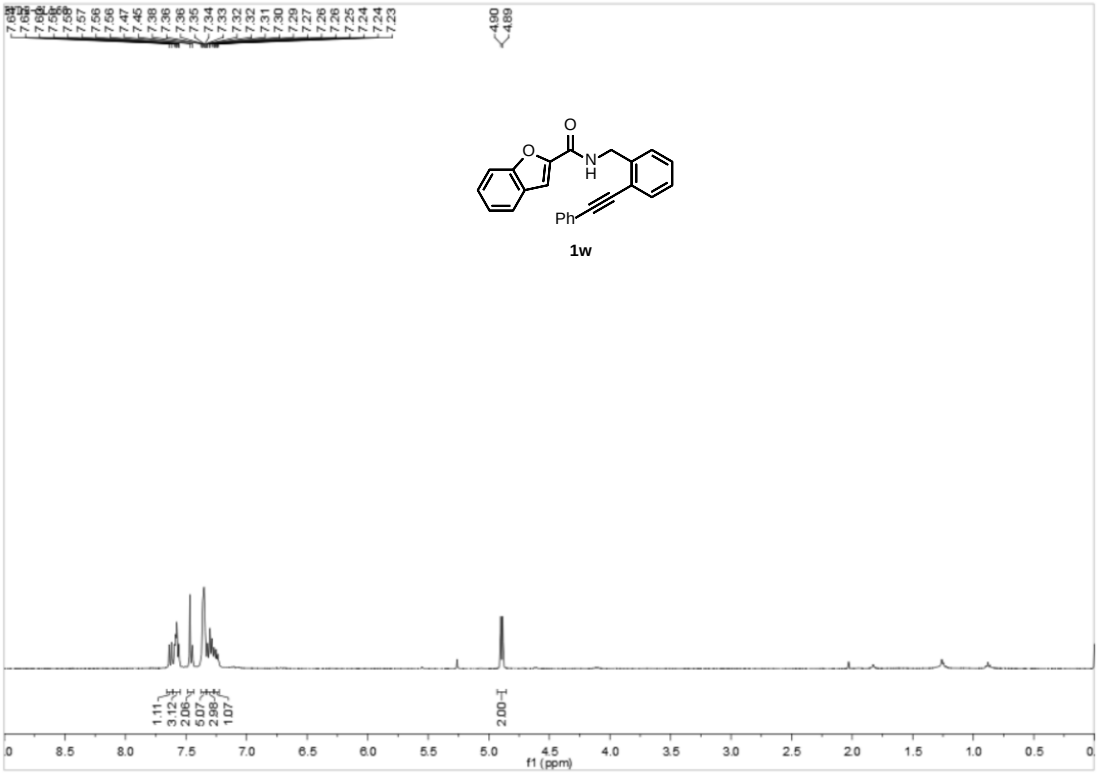
1u

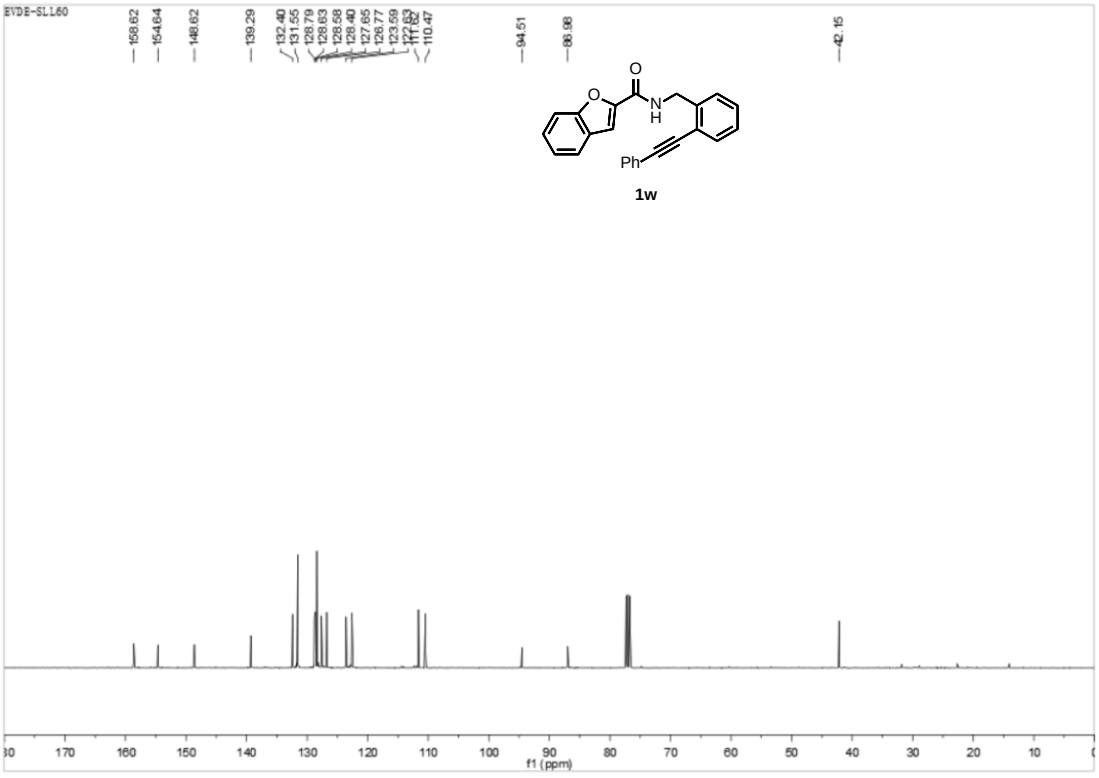

161.75
139.66
138.74
131.46
128.36
128.33
128.07
94.36
86.99
42.63
122.20
f1 (ppm)
O
S
N
H
Ph

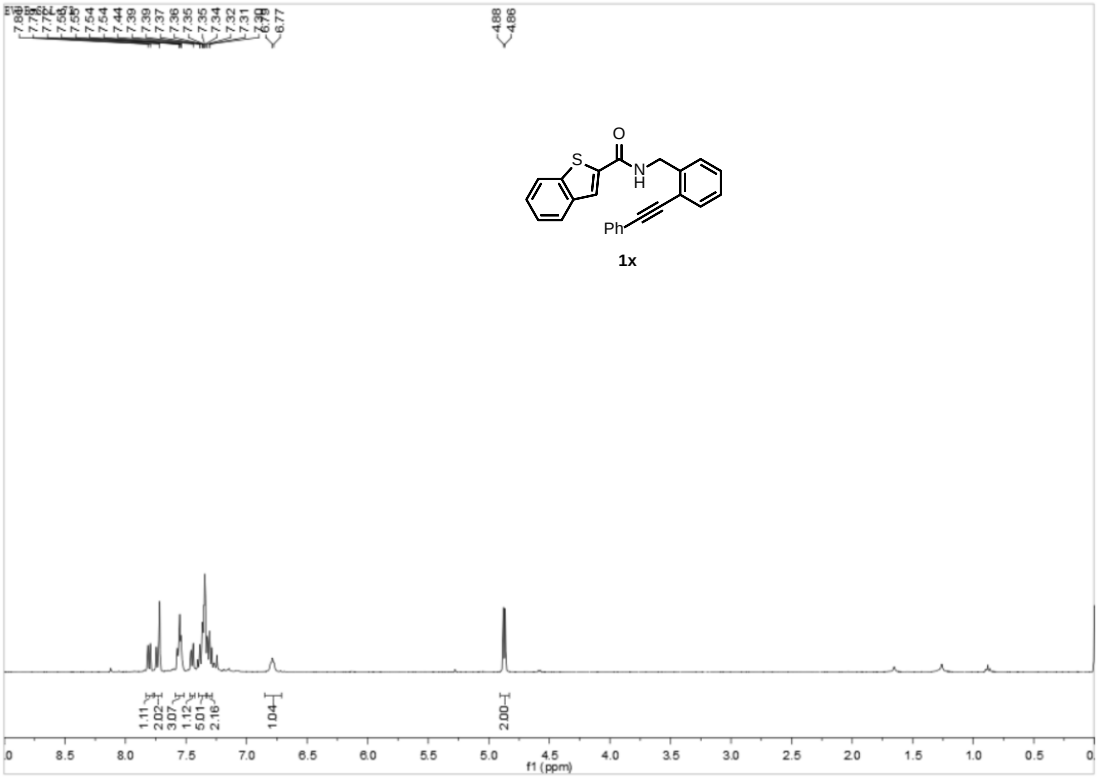
1u


Me
O
N
H
Ph
1v
f1 (ppm)

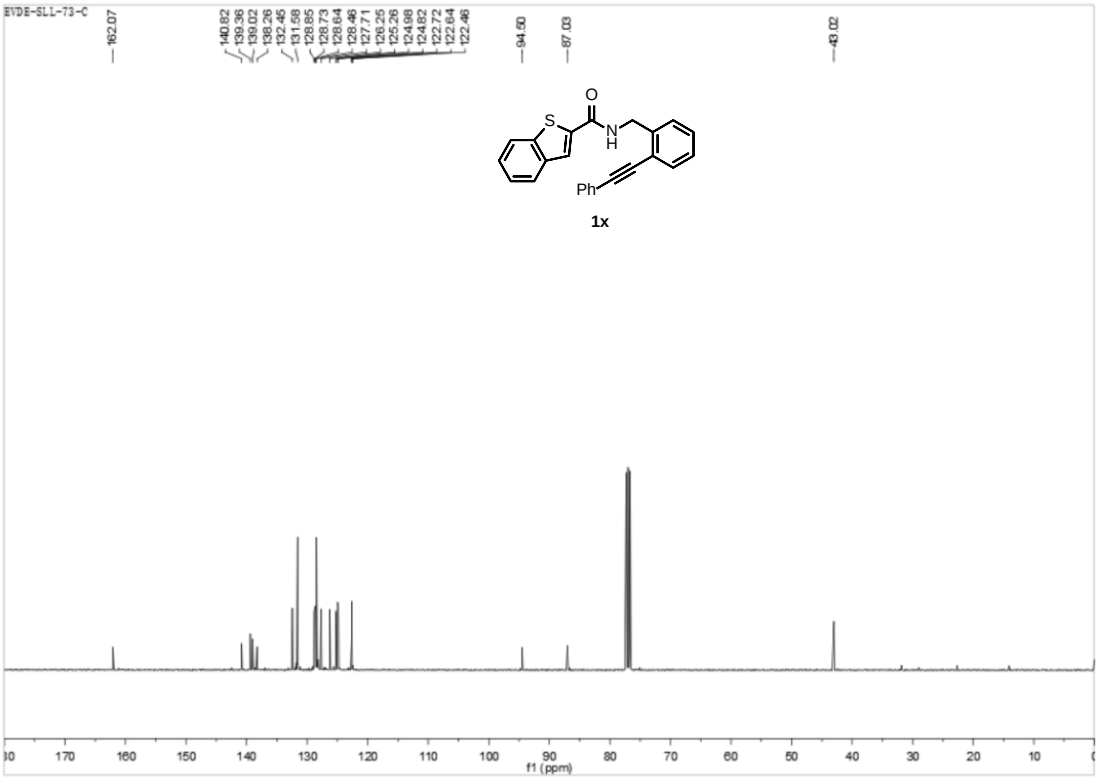

Me
O
N
H
Ph
1v
f1 (ppm)


1w
f1 (ppm)

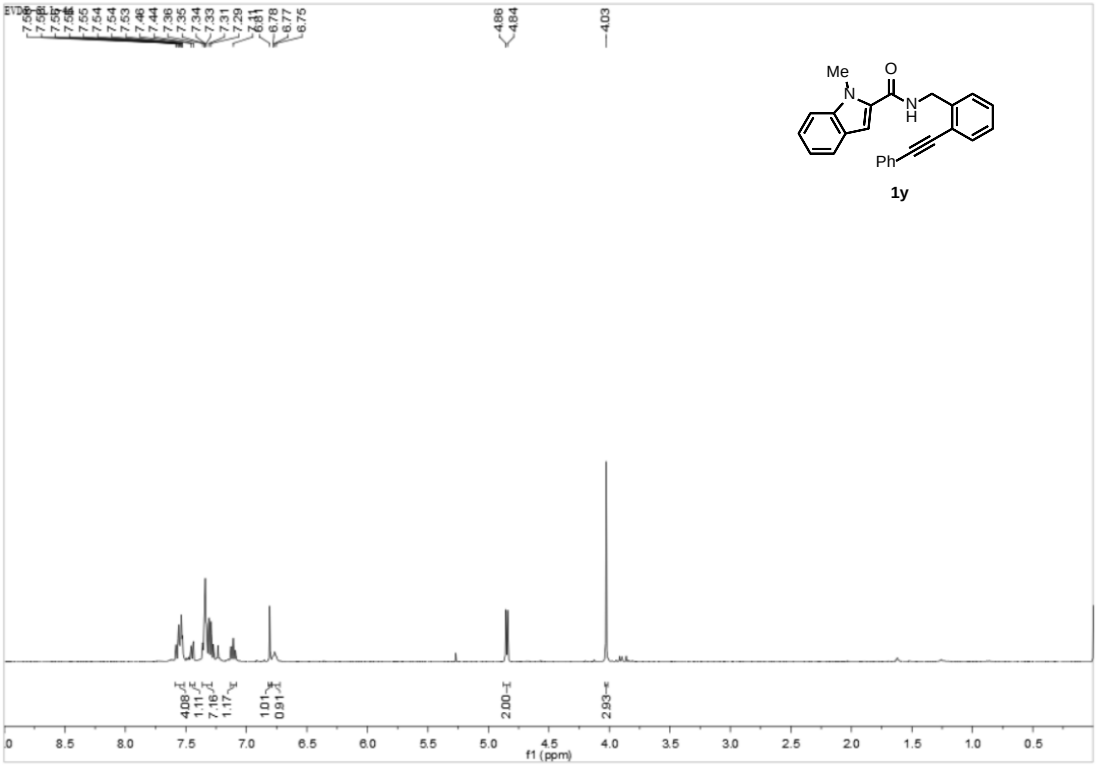

EVDE-SLL60
1w
f1 (ppm)

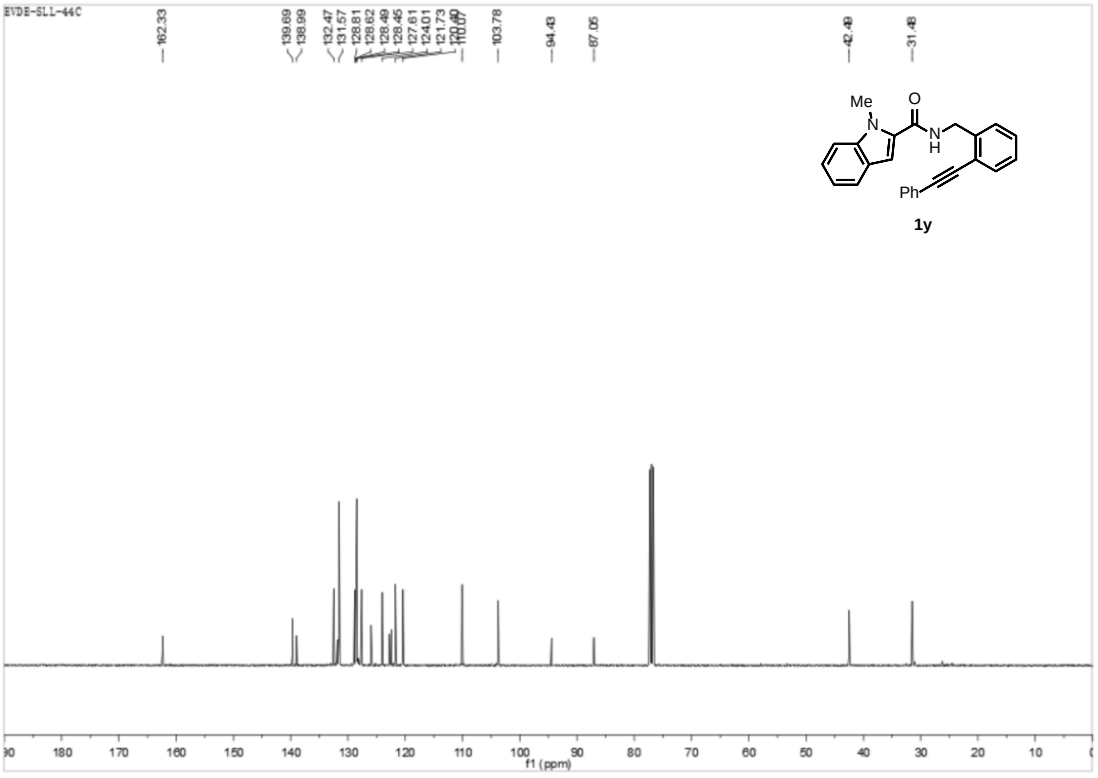

7.89
7.78
7.77
7.56
7.55
7.54
7.54
7.44
7.39
7.39
7.37
7.36
7.35
7.35
7.34
7.32
7.31
7.30
6.78
6.77
4.88
4.86
O
S
N
H
Ph
1.11
2.02
3.07
1.12
5.01
2.16
1.04
2.00
f1 (ppm)

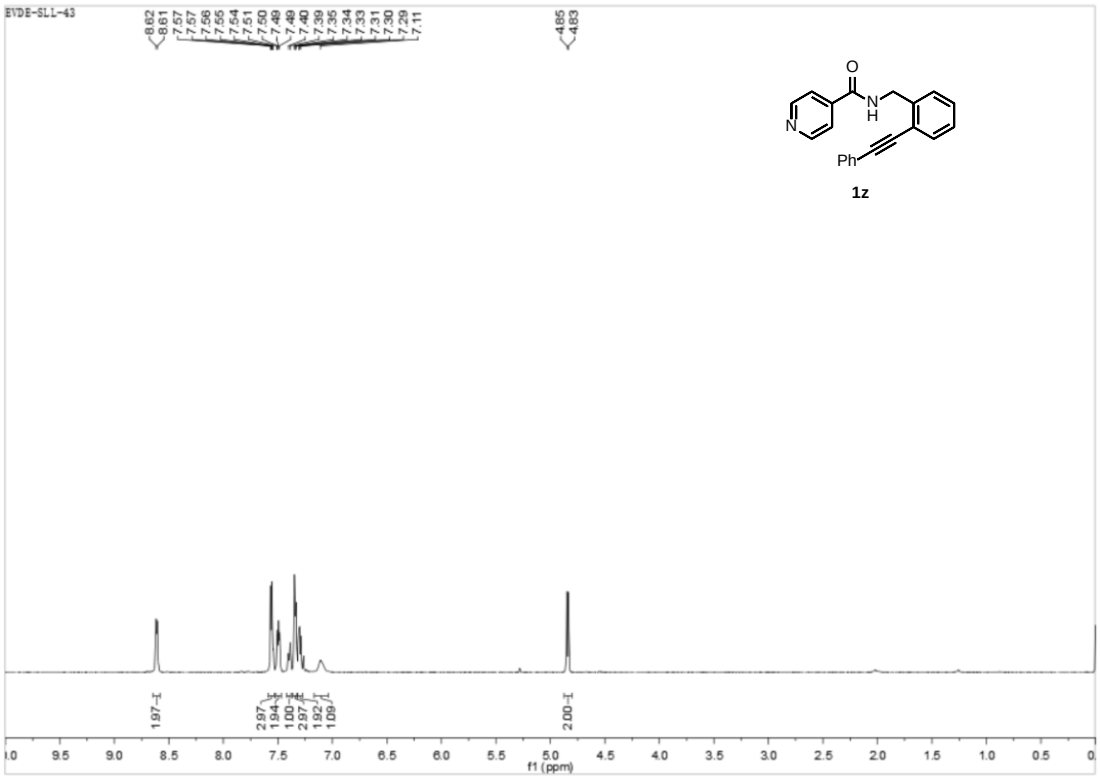
1x


EVDE-SLL-73-C
162.07
140.92
139.36
139.02
138.26
132.45
131.58
128.85
128.73
128.64
128.46
127.71
126.25
125.26
124.98
124.82
122.72
122.64
122.46
94.50
87.03
43.02
O
S
N
H
Ph
f1 (ppm)

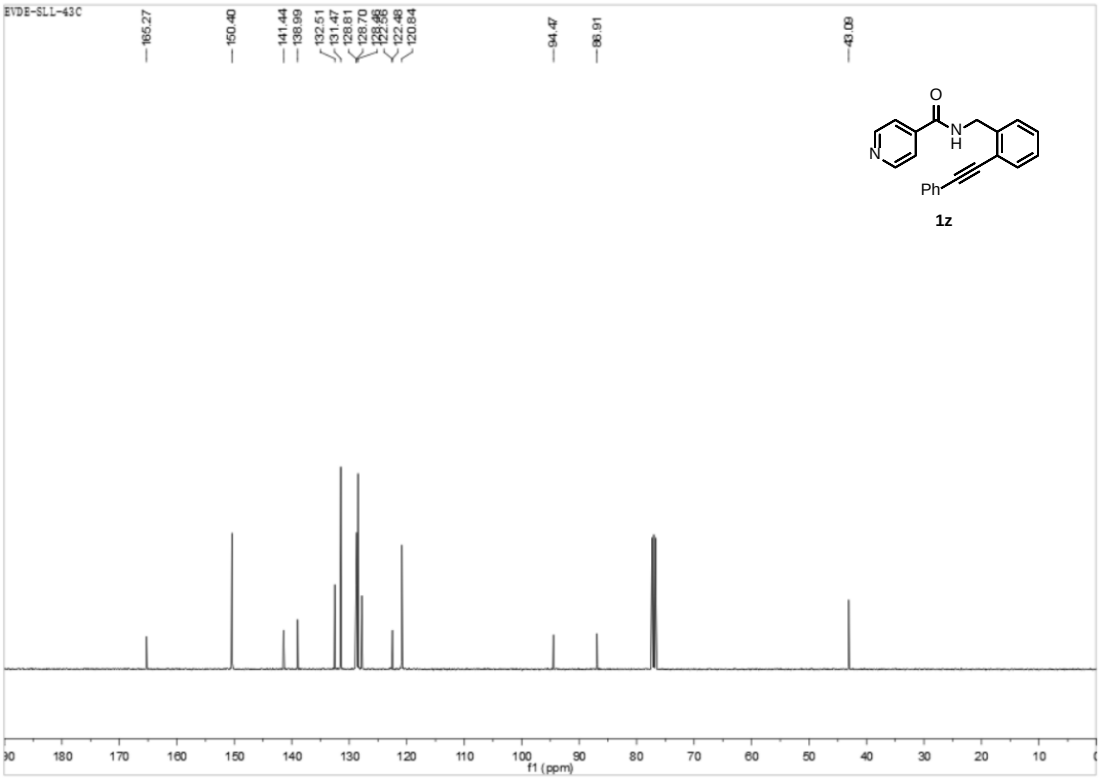
1x


Me
O
N
H
N
Ph
1y
4.86
4.84
4.03
4.08
1.11
7.16
1.17
1.01
0.91
2.00
2.93
f1 (ppm)

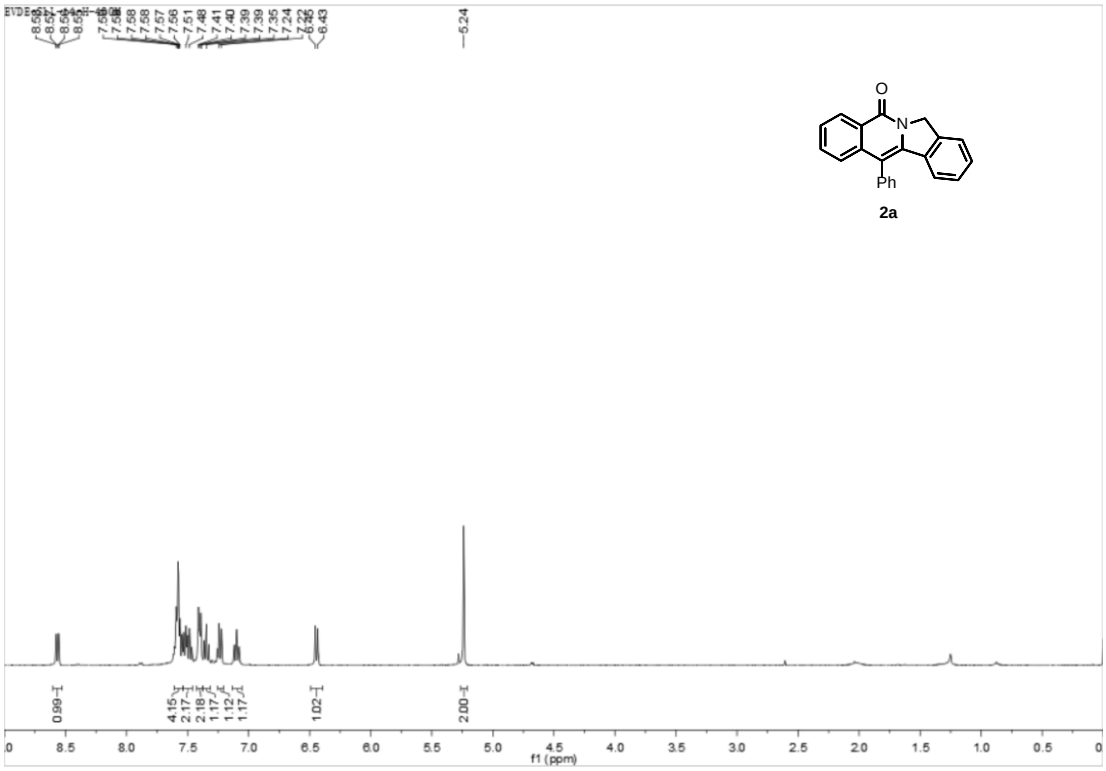

EVDE-SLL-44C
162.33
139.69
138.99
132.47
131.57
128.81
128.62
128.49
128.45
127.61
124.01
121.73
110.07
103.78
94.43
87.05
42.49
31.48
Me
O
N
H
N
Ph
1y
f1 (ppm)

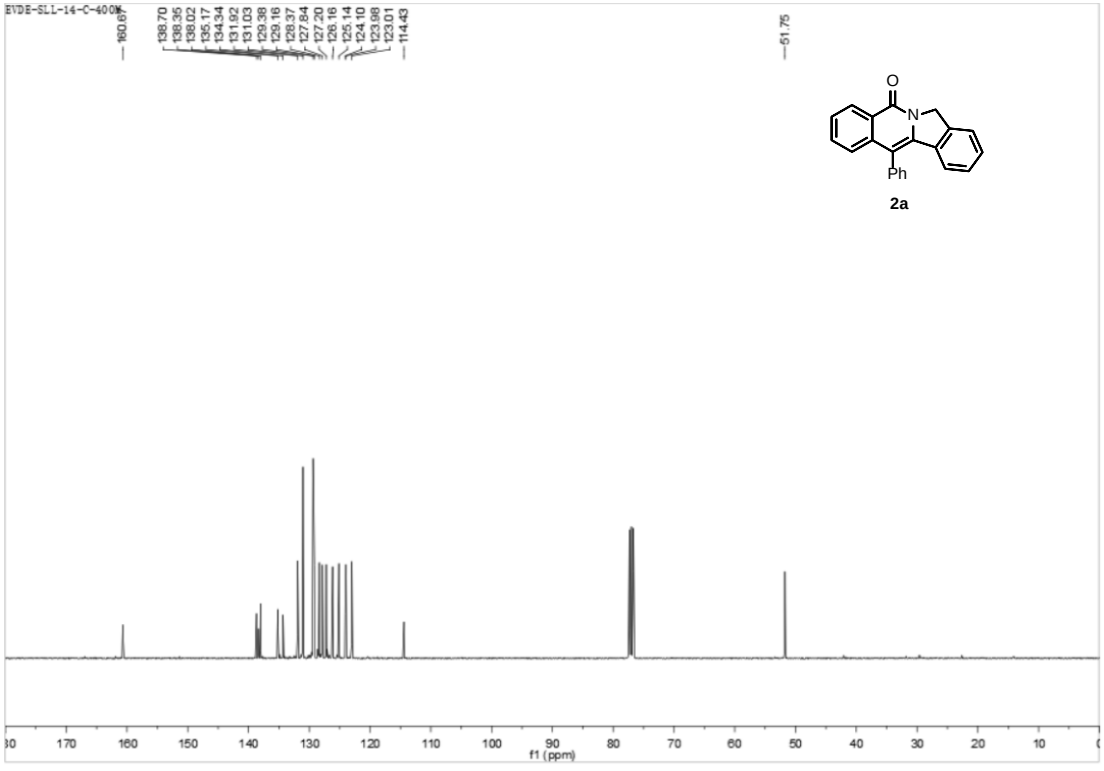

EVDE-SLL-43
8.62
8.61
7.57
7.57
7.56
7.55
7.54
7.51
7.50
7.49
7.48
7.40
7.39
7.35
7.34
7.33
7.31
7.30
7.29
7.11
4.86
4.83
1.97
2.97
1.94
1.00
2.97
1.92
1.09
2.00
f1 (ppm)
O
N
H
N
Ph

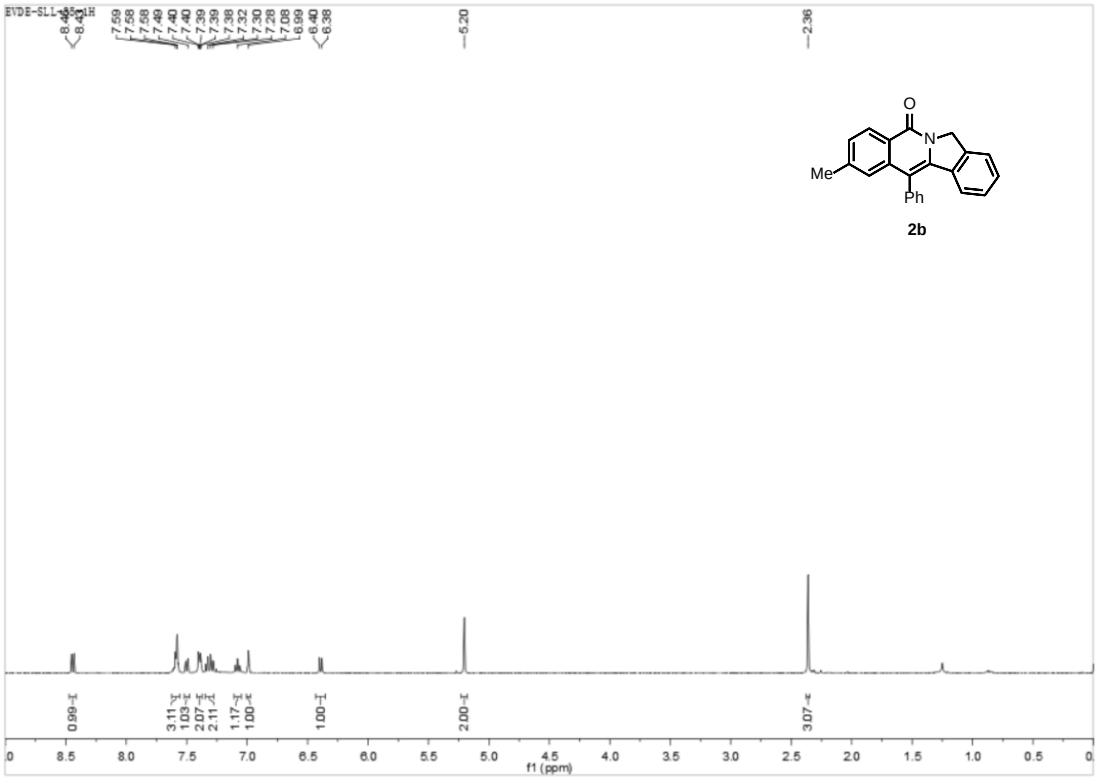
1z


EVDE-SLL-43C
165.27
150.40
141.44
138.99
132.51
131.47
128.81
128.70
122.48
120.84
94.47
86.91
43.09
f1 (ppm)
O
N
H
N
Ph

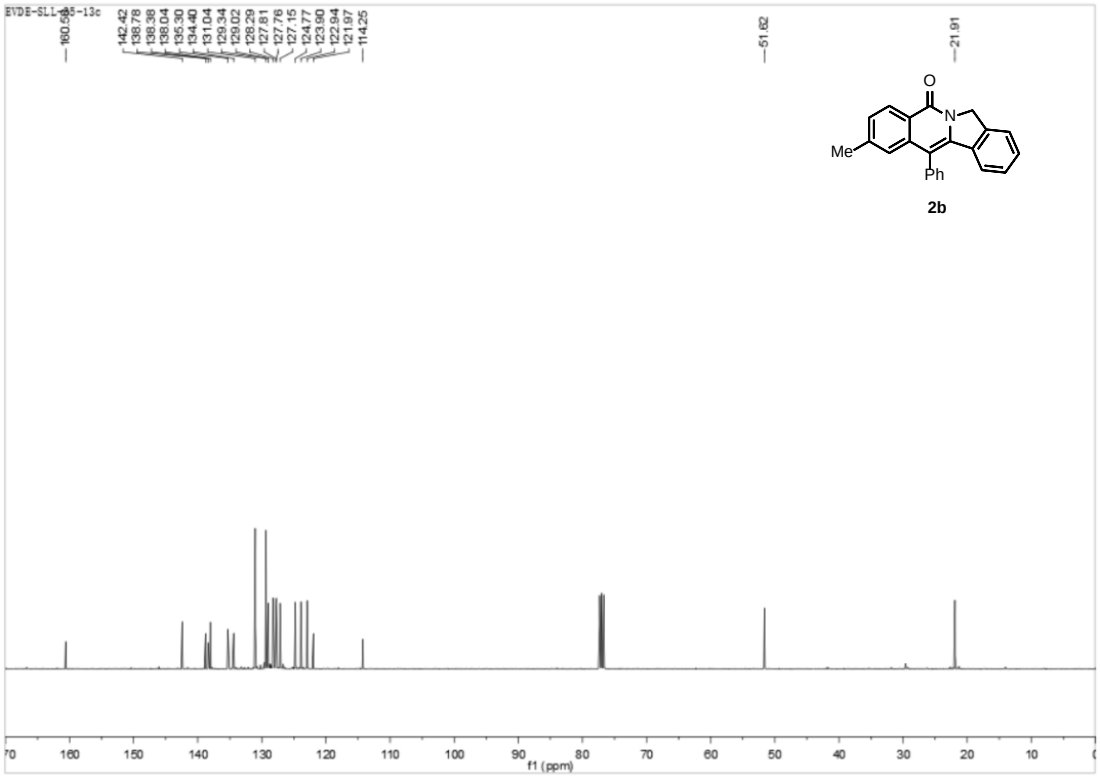
1z


5.24
O
N
Ph
2a
0.99
4.15
2.17
2.18
1.17
1.12
1.17
1.02
2.00
f1 (ppm)

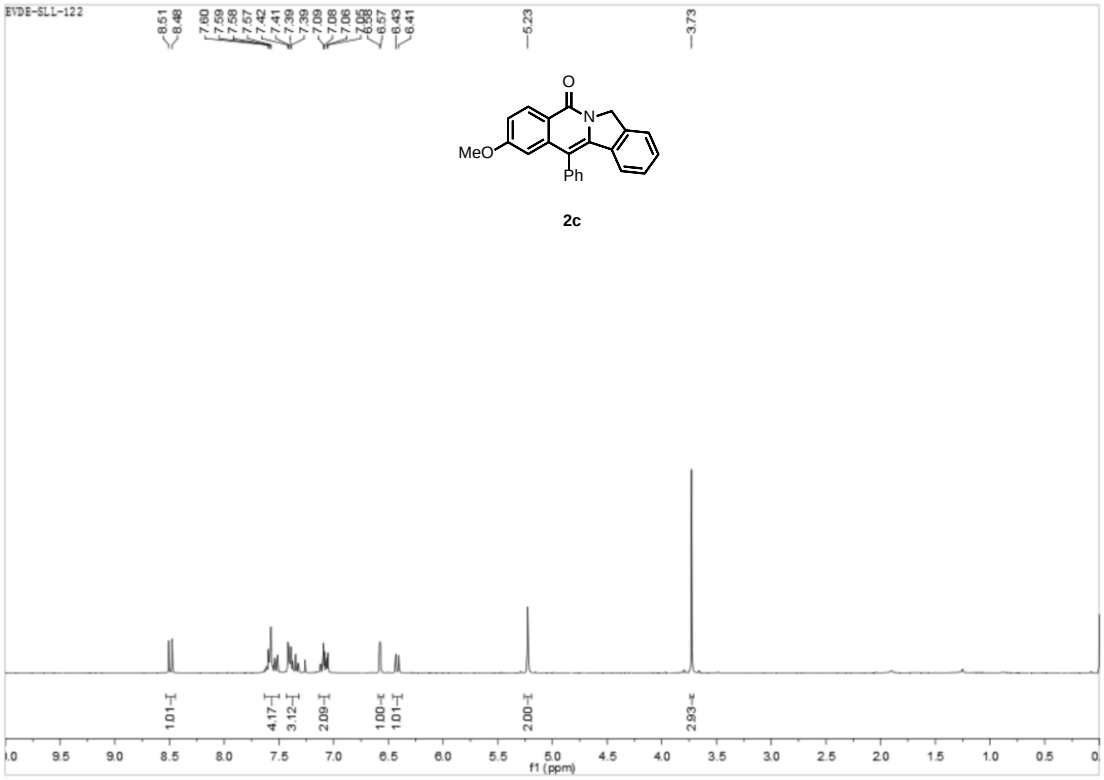

160.67
138.70
138.35
138.02
135.17
134.34
131.92
131.03
129.38
129.16
128.37
127.84
127.20
126.16
125.14
124.10
123.98
123.01
114.43
51.75
O
N
Ph
2a
f1 (ppm)


8.46
8.45
7.59
7.58
7.58
7.49
7.40
7.40
7.39
7.39
7.38
7.32
7.30
7.28
7.08
6.99
6.40
6.38
5.20
2.36
O
N
Me
Ph
0.99
3.11
1.03
2.07
2.11
1.17
1.00
1.00
2.00
3.07
f1 (ppm)

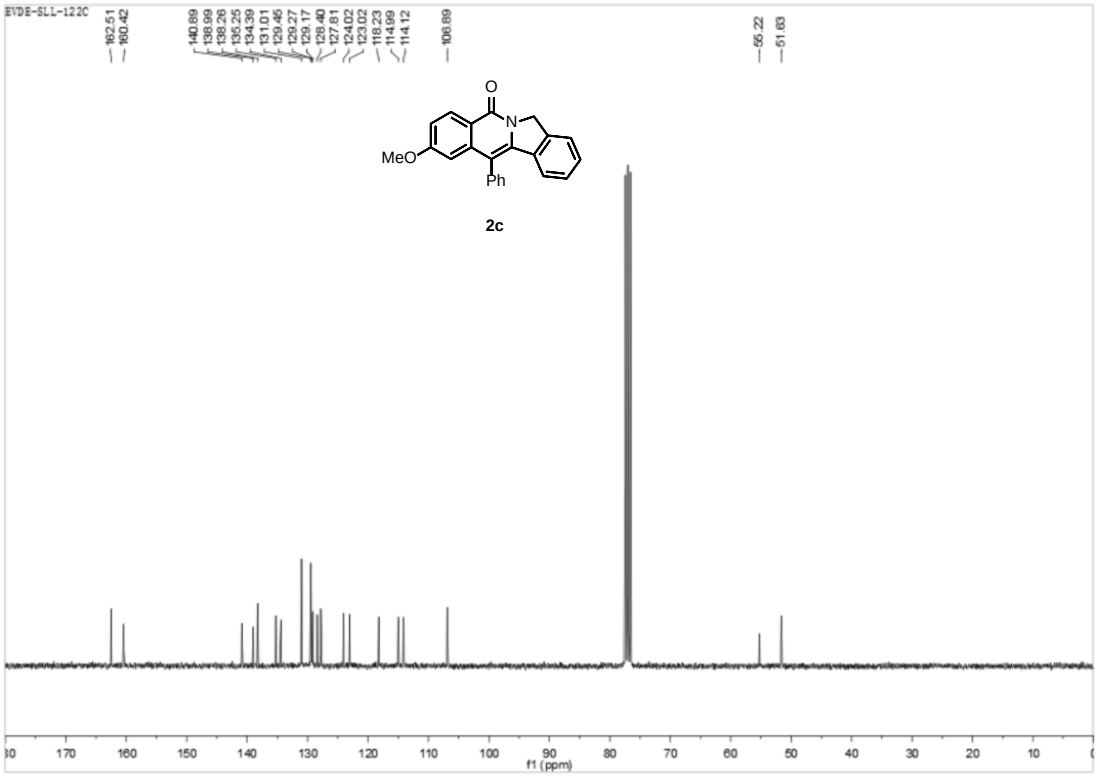
2b


160.56
142.42
138.78
138.38
138.04
135.30
134.40
131.04
129.34
129.02
128.29
127.81
127.76
127.15
124.77
123.90
122.94
121.97
114.25
51.82
21.91
O
N
Me
Ph
f1 (ppm)

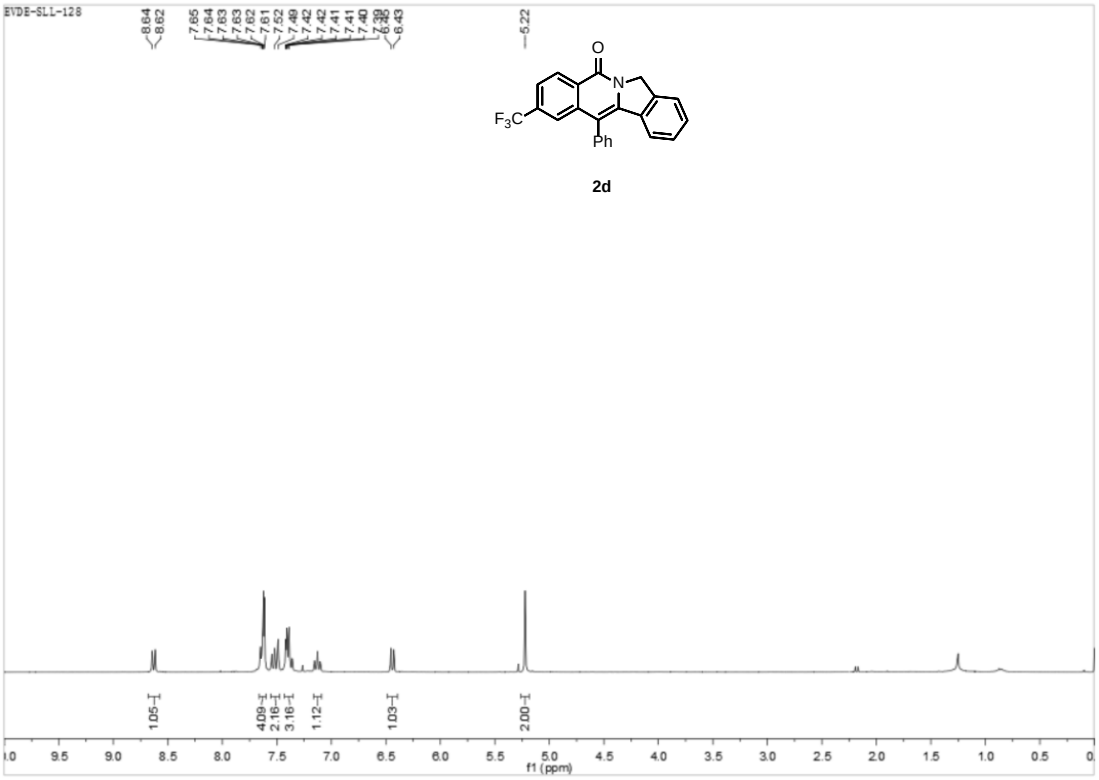
2b


EVDE-SLL-122
8.51
8.48
7.60
7.59
7.58
7.57
7.42
7.41
7.39
7.39
7.09
7.08
7.06
7.05
6.58
6.57
6.43
6.41
5.23
3.73
O
N
MeO
Ph
1.01
4.17
3.12
2.09
1.00
1.01
2.00
2.93
f1 (ppm)

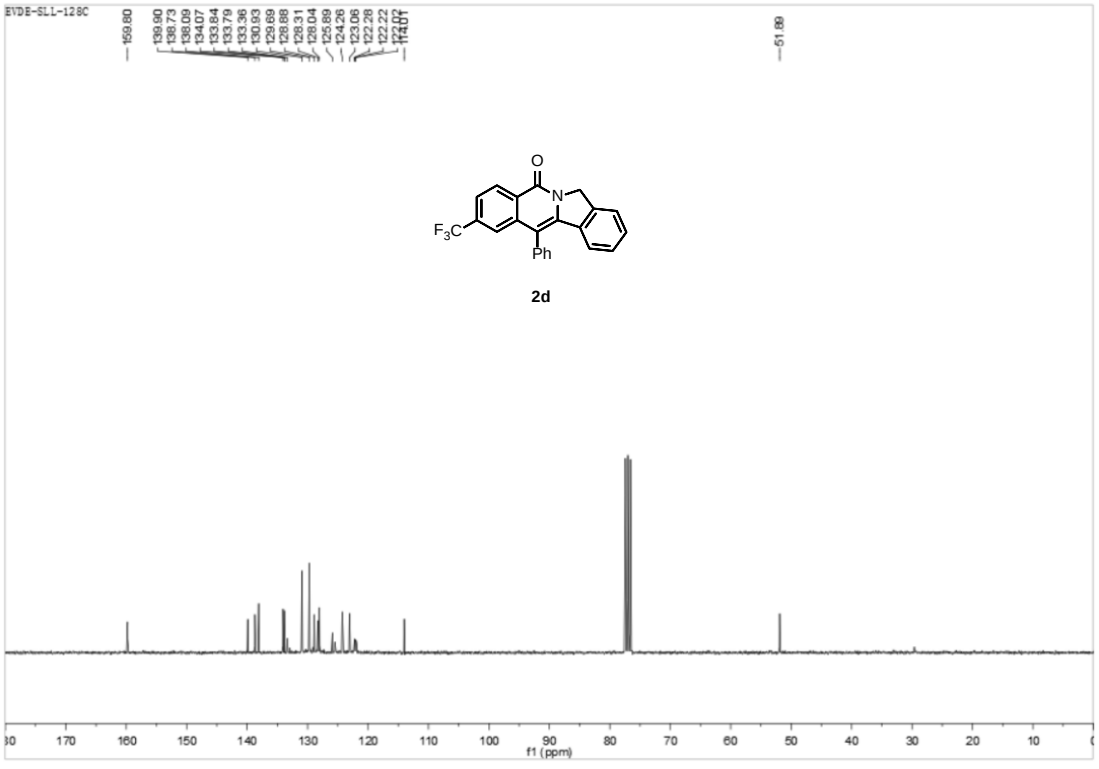
2c


EVDE-SLL-122C
162.51
160.42
140.89
138.99
138.26
135.25
134.39
131.01
129.46
129.27
129.17
128.40
127.81
124.02
123.02
118.23
114.99
114.12
106.89
55.22
51.63
O
N
MeO
Ph
f1 (ppm)

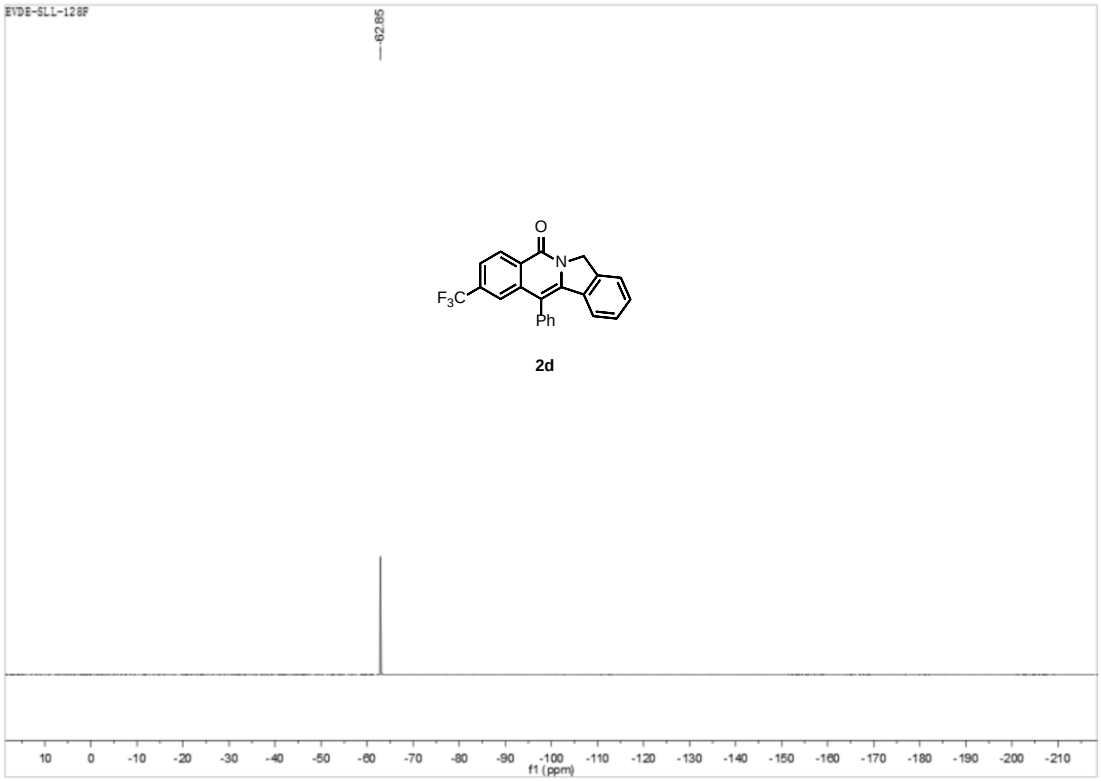
2c


EVDE-SLL-128
8.64
8.62
7.65
7.64
7.63
7.63
7.62
7.61
7.52
7.49
7.42
7.42
7.41
7.41
7.40
6.43
5.22
O
N
F3C
Ph
1.05
4.09
2.16
3.16
1.12
1.03
2.00
f1 (ppm)

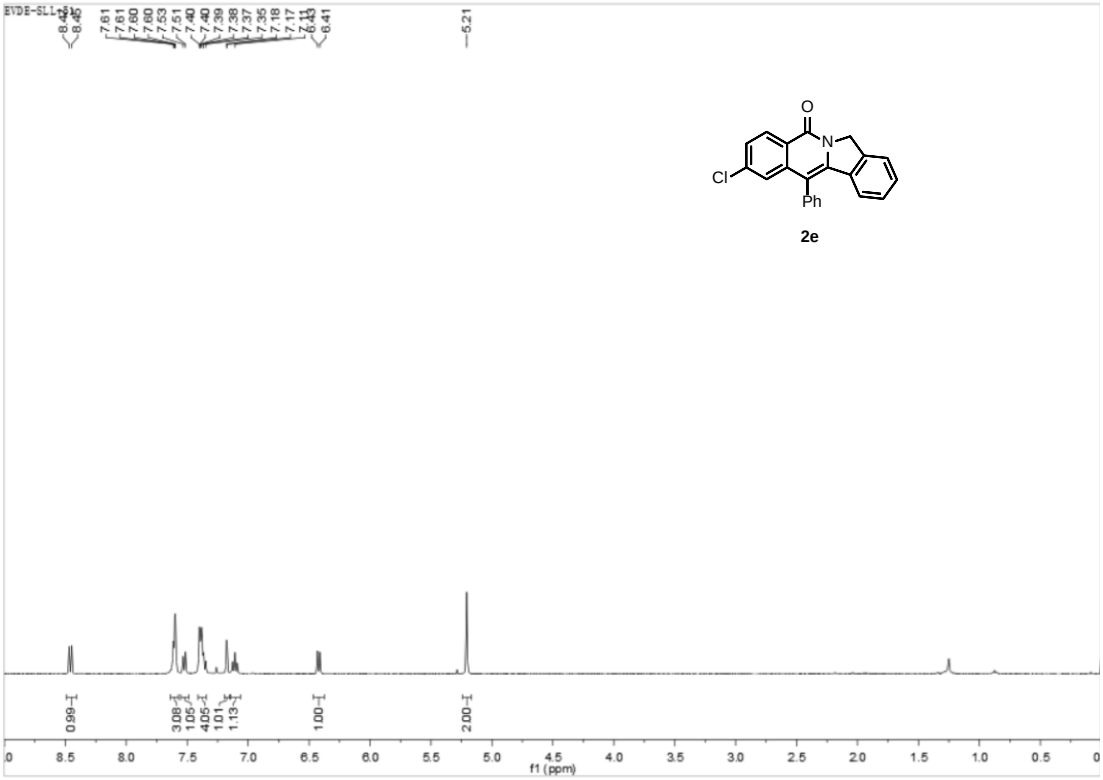
2d


EVDE-SLL-128C
159.80
139.90
138.73
138.09
134.07
133.84
133.79
133.36
130.93
129.89
128.88
128.31
128.04
125.89
124.26
123.06
122.28
122.22
51.89
O
N
F3C
Ph
f1 (ppm)

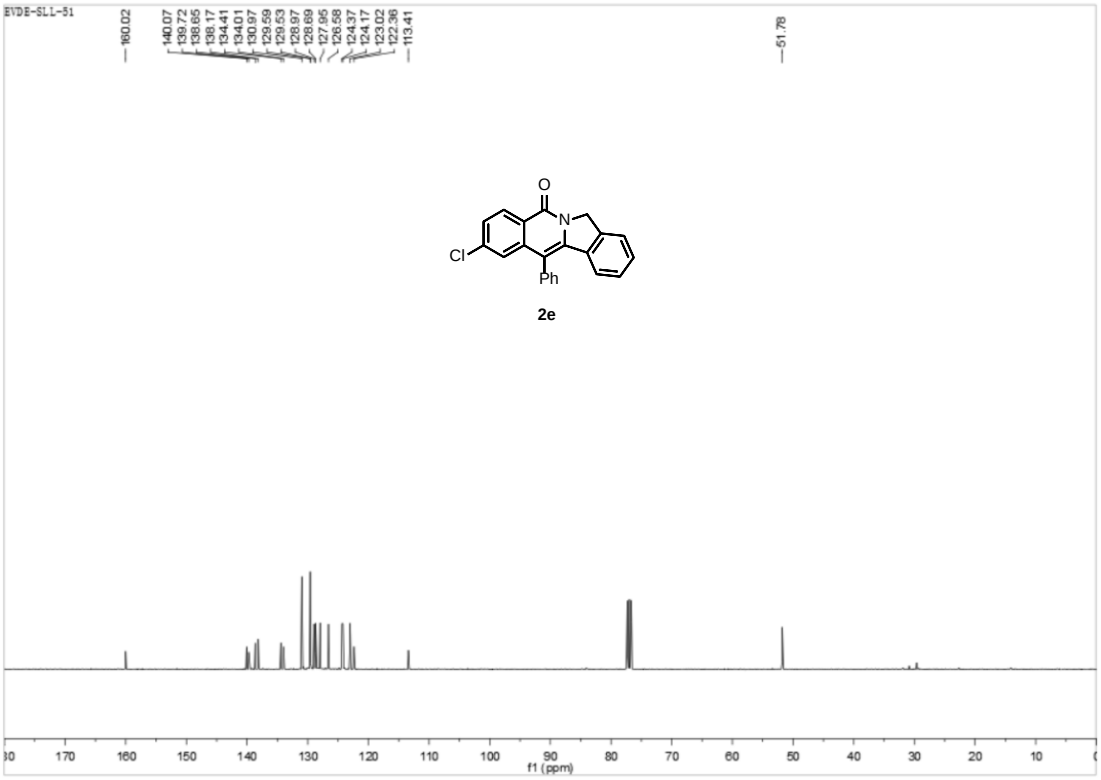
2d


EVDE-SLL-128F
-62.65
O
N
F3C
Ph
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)

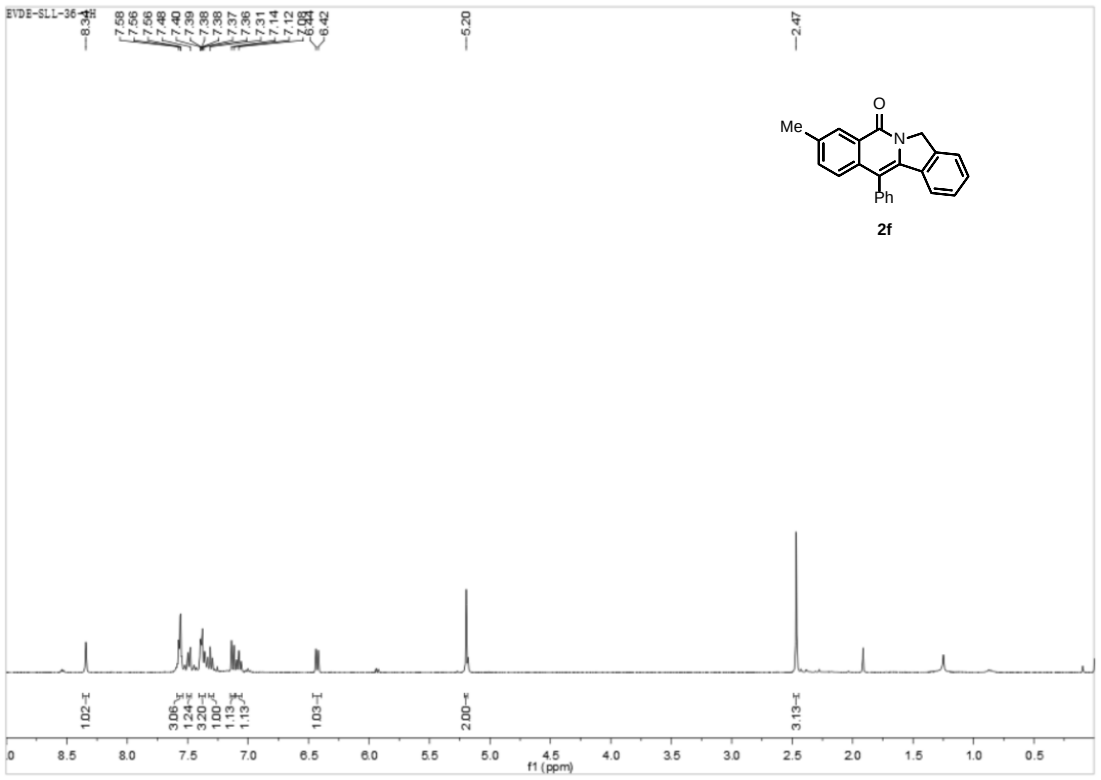
2d


8.42
8.40
7.61
7.61
7.60
7.60
7.53
7.51
7.40
7.39
7.38
7.37
7.35
7.19
7.17
7.13
6.43
6.41
-5.21
O
N
Cl
Ph
0.99
3.08
1.06
4.06
1.01
1.13
1.00
2.00
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
f1 (ppm)

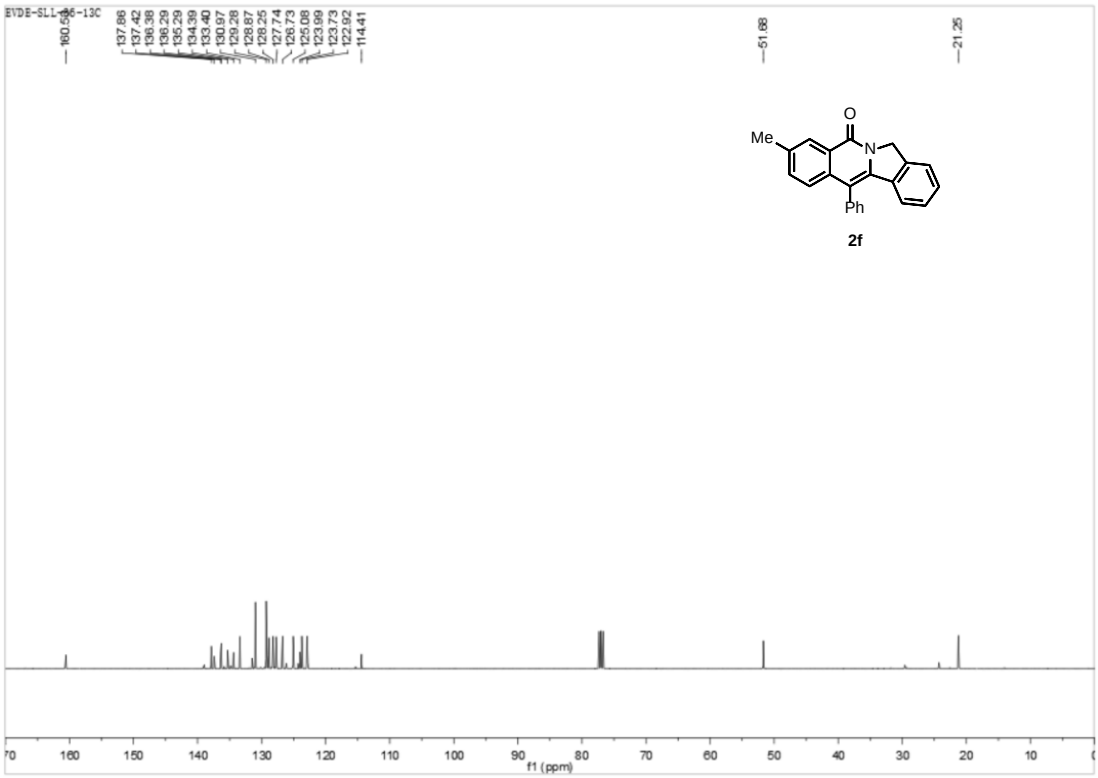
2e


EVDE-SLL-51
160.02
140.07
139.72
138.65
138.17
134.41
134.01
130.97
129.59
129.53
128.97
128.89
127.95
126.58
124.37
124.17
123.02
122.36
113.41
51.78
O
N
Cl
Ph
f1 (ppm)

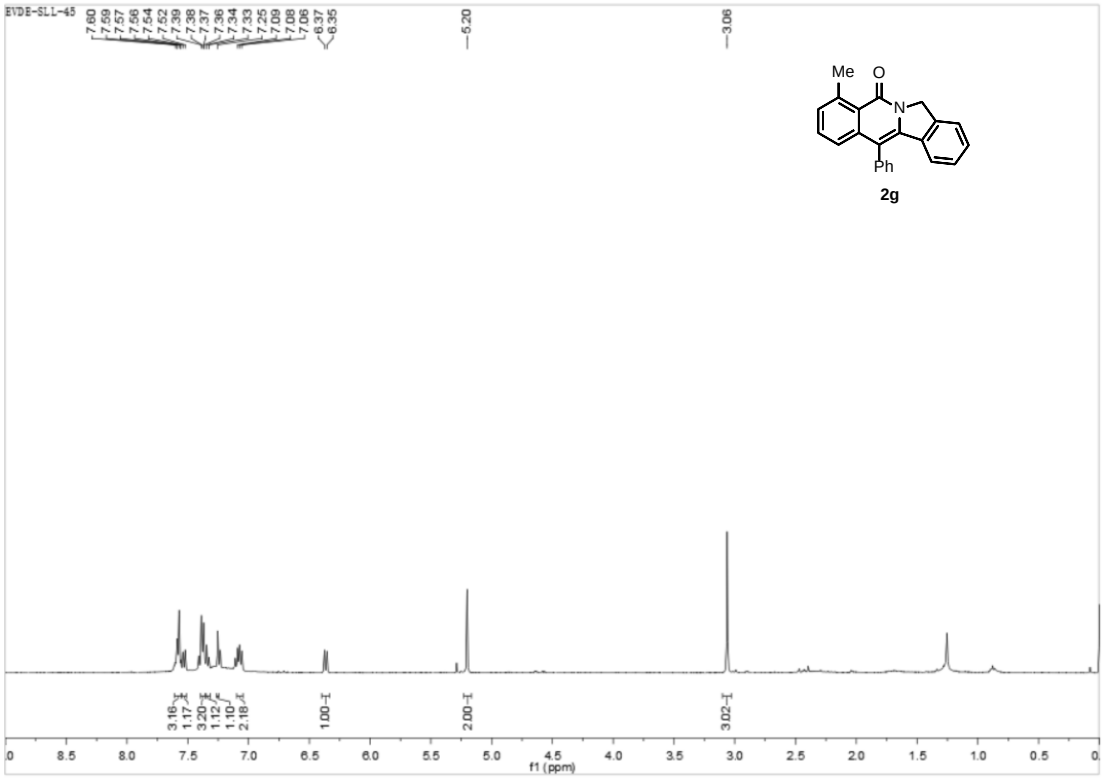
2e


EVDE-SLL-36-1H
8.34
7.59
7.56
7.56
7.48
7.40
7.39
7.38
7.38
7.37
7.36
7.31
7.14
7.12
7.08
6.44
6.42
5.20
2.47
1.02
3.06
1.24
3.20
1.00
1.13
1.13
1.03
2.00
3.13
O
N
Me
Ph
f1 (ppm)

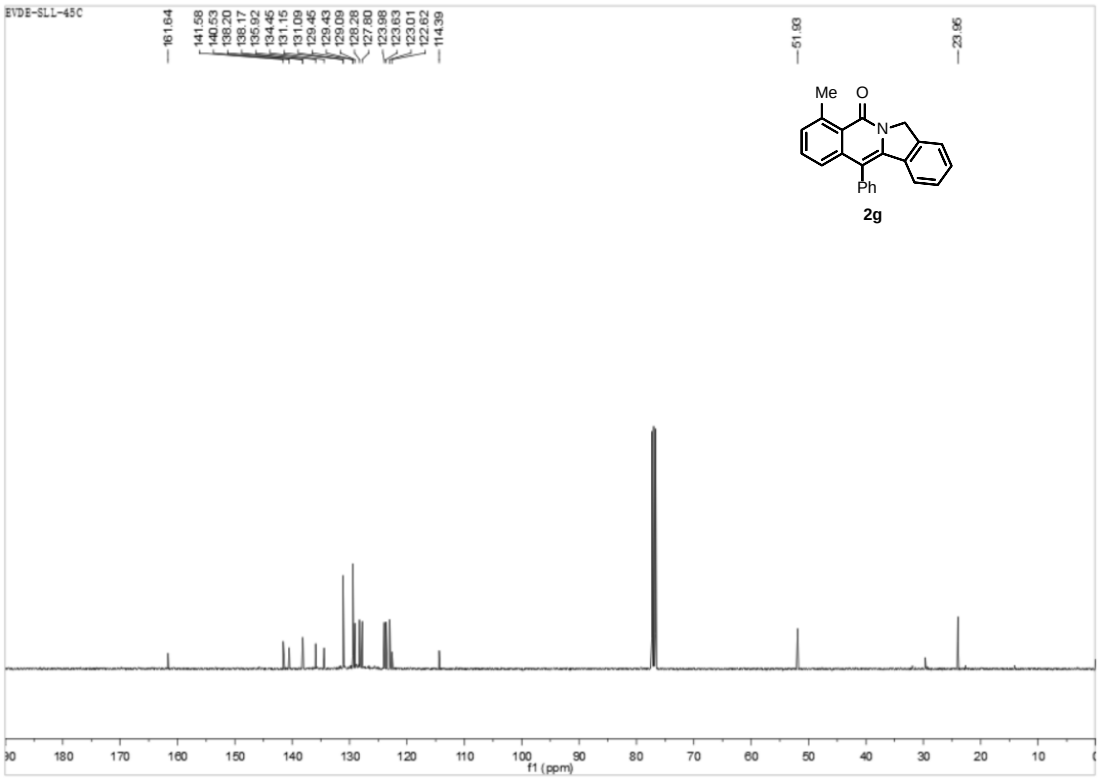
2f


160.68
137.86
137.42
136.98
136.29
135.29
134.39
133.40
130.97
129.29
128.87
128.25
127.74
126.73
125.08
123.99
123.73
122.92
114.41
51.68
21.25
O
Me
N
Ph
f1 (ppm)

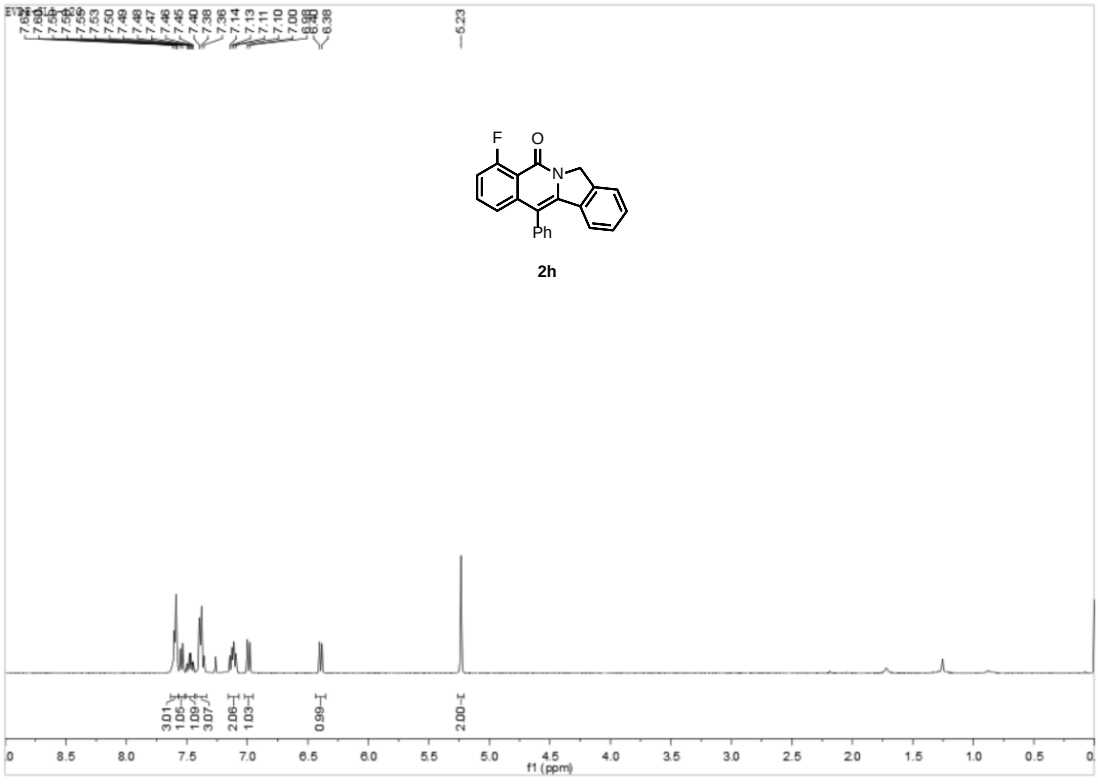
2f


7.60
7.59
7.57
7.56
7.54
7.52
7.39
7.38
7.37
7.36
7.34
7.33
7.25
7.09
7.08
7.06
6.37
6.35
5.20
3.06
Me
O
N
Ph
3.16
1.17
3.20
1.12
1.10
2.18
1.00
2.00
3.02
f1 (ppm)

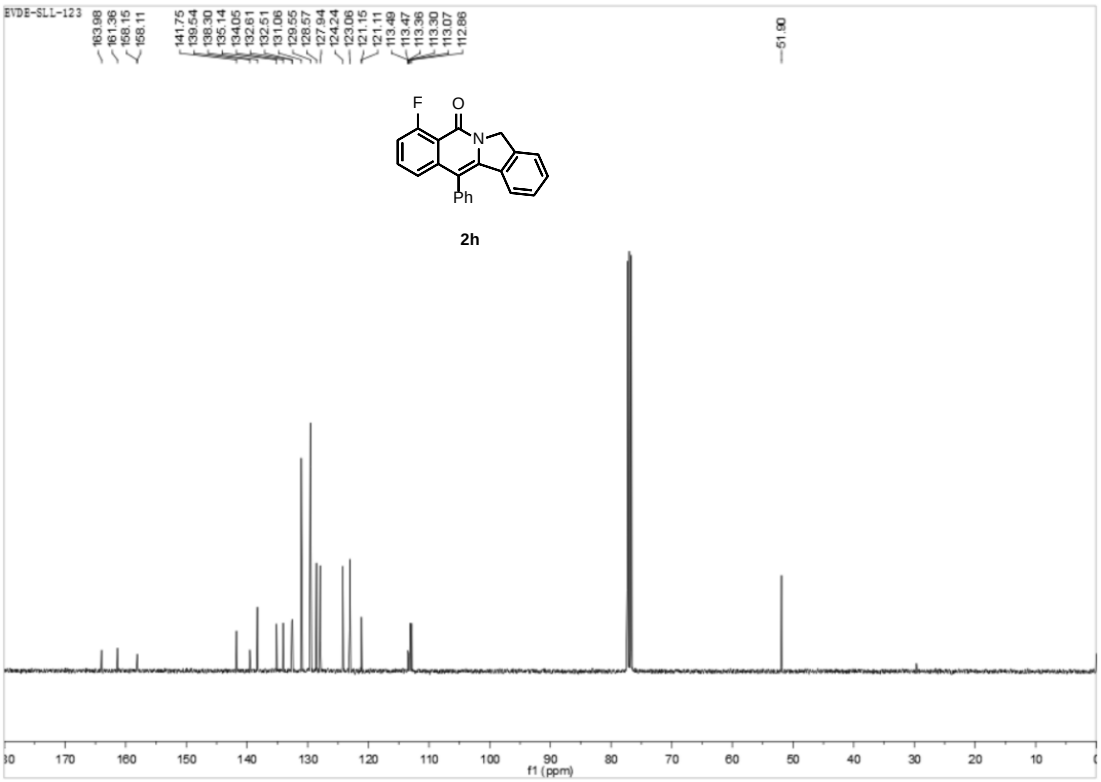
2g


EVDE-SLL-45C
161.64
141.58
140.53
138.20
138.17
135.92
134.45
131.15
131.09
129.45
129.43
129.09
128.28
127.80
123.98
123.63
123.01
122.62
114.39
51.93
29.95
Me
O
N
Ph
f1 (ppm)

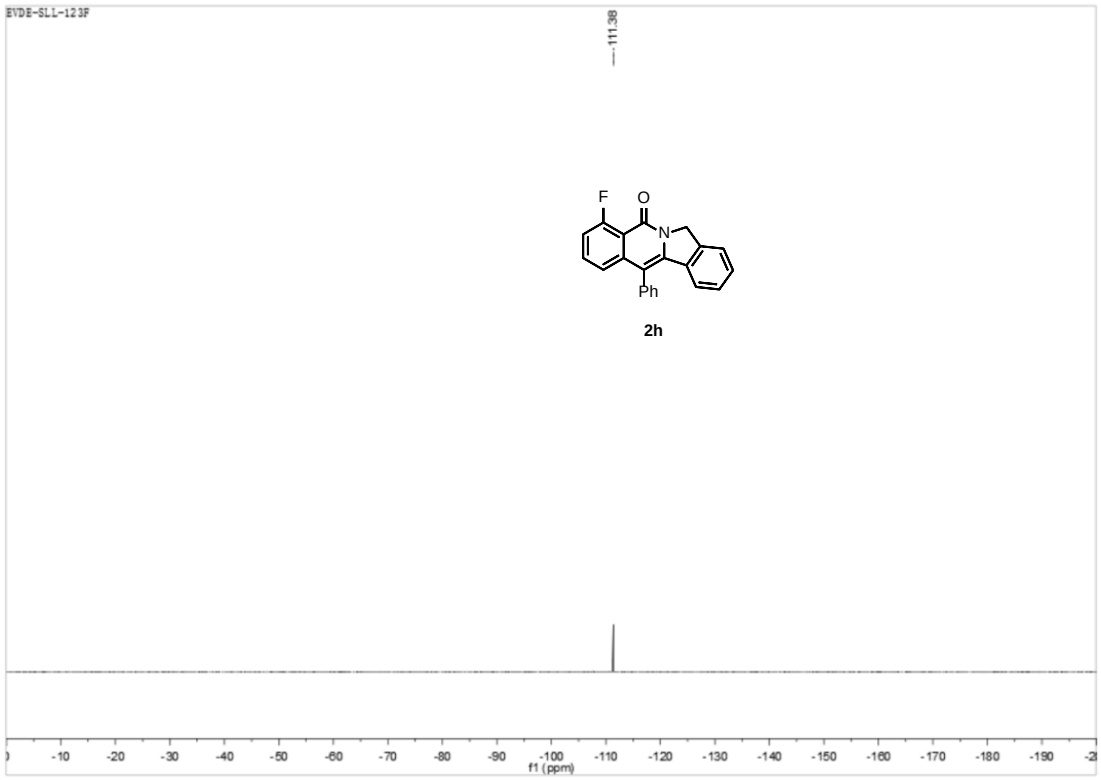
2g


7.60
7.59
7.55
7.53
7.50
7.49
7.48
7.47
7.46
7.45
7.40
7.38
7.36
7.14
7.13
7.11
7.10
7.00
6.98
6.96
6.38
5.23
F
O
N
Ph
3.01
1.05
1.09
3.07
2.06
1.03
0.99
2.00
f1 (ppm)

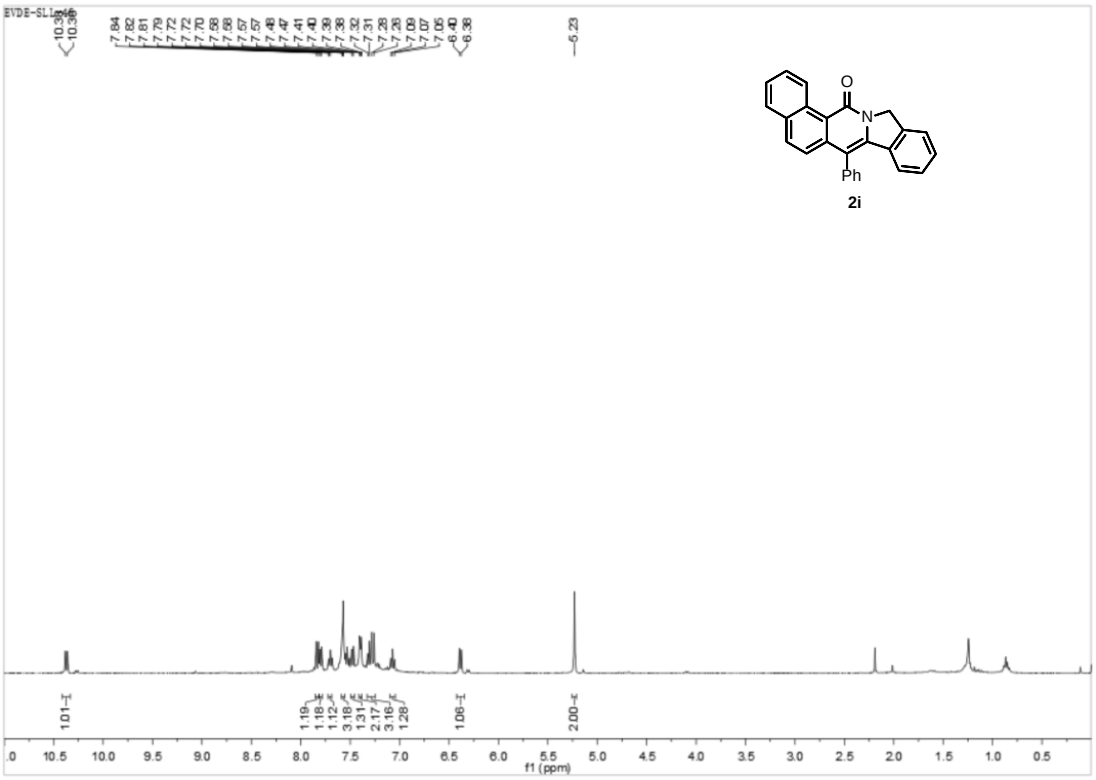
2h

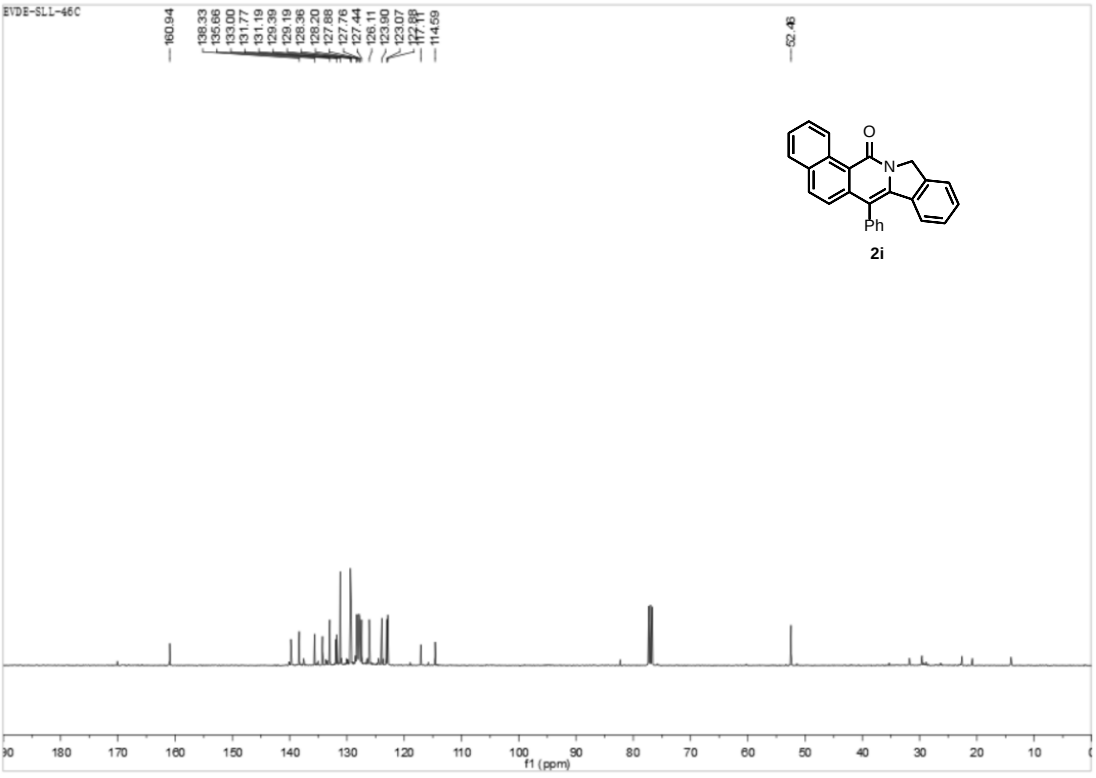

EVDE-SLL-123
163.98
161.36
158.15
158.11
141.75
139.54
138.30
135.14
134.05
132.61
132.51
131.06
129.55
128.57
127.94
124.24
123.06
121.15
121.11
113.49
113.47
113.36
113.30
113.07
112.86
51.90
F
O
N
Ph
f1 (ppm)

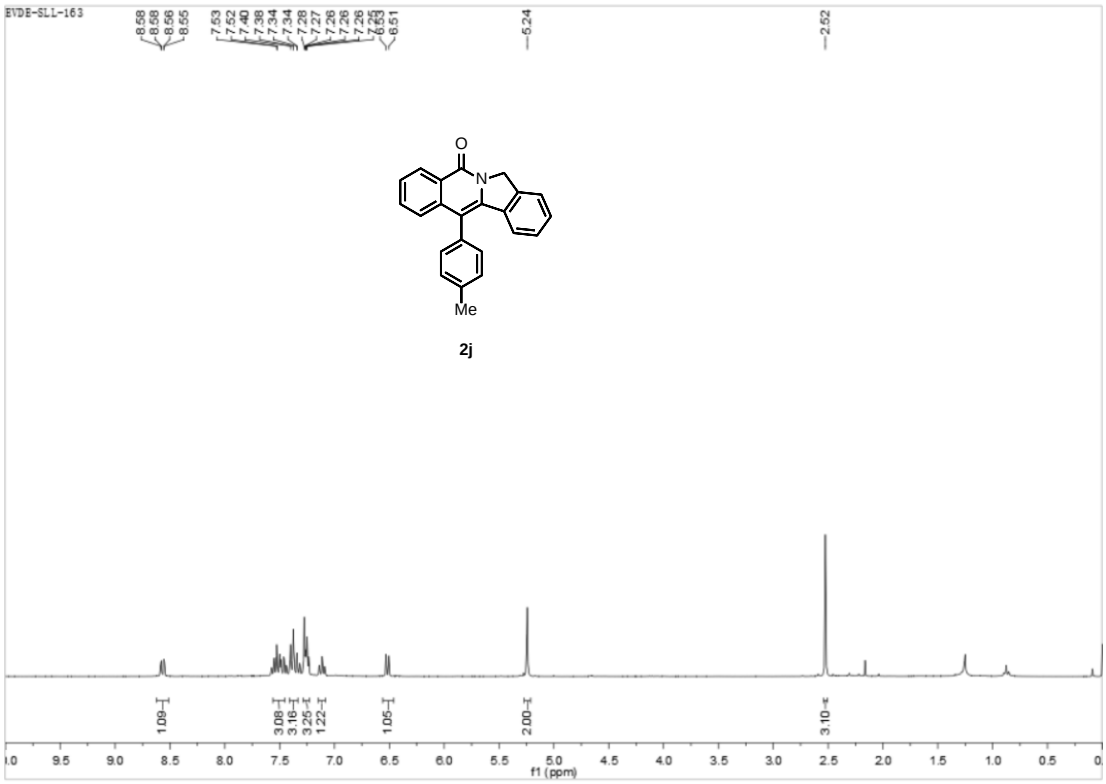
2h


EVDE-SLL-123F
111.38
F
O
N
Ph
f1 (ppm)

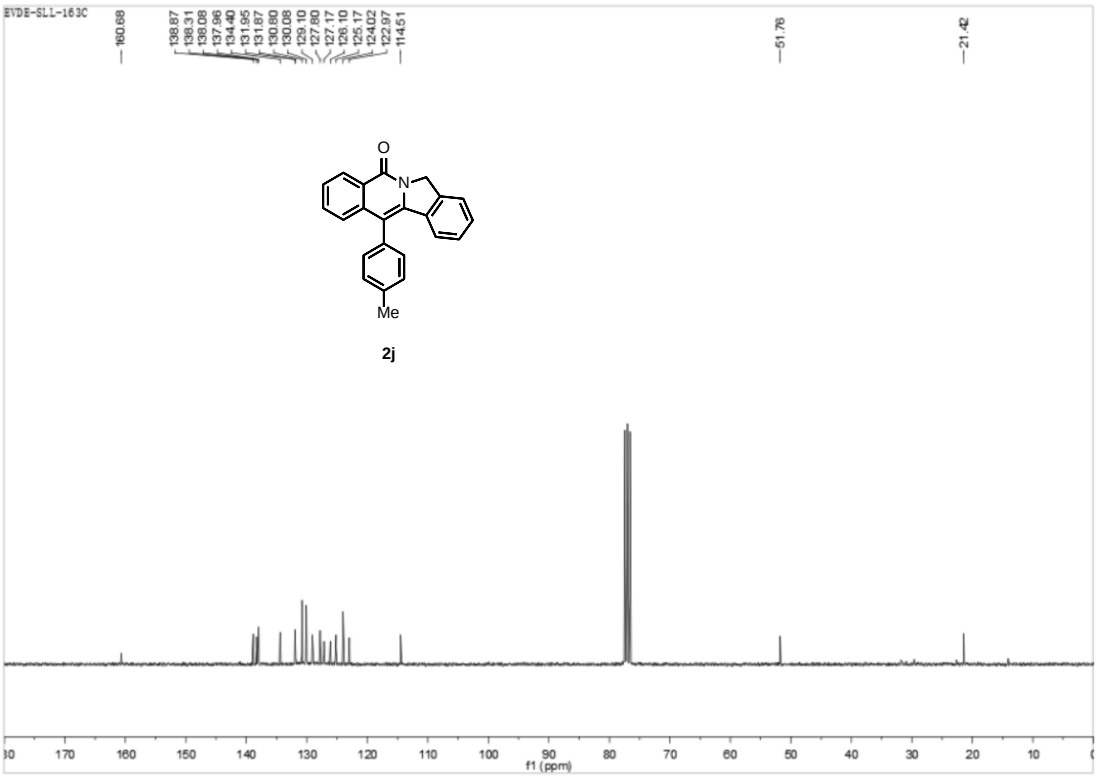
2h


EVDE-SLI-46
10.38
10.36
7.84
7.82
7.81
7.79
7.72
7.72
7.70
7.58
7.58
7.57
7.57
7.48
7.47
7.41
7.40
7.39
7.38
7.32
7.31
7.28
7.28
7.07
7.05
6.40
6.38
6.23
O
N
Ph
2i
1.01
1.19
1.18
1.12
3.18
1.31
2.17
3.16
1.28
1.06
2.00
f1 (ppm)

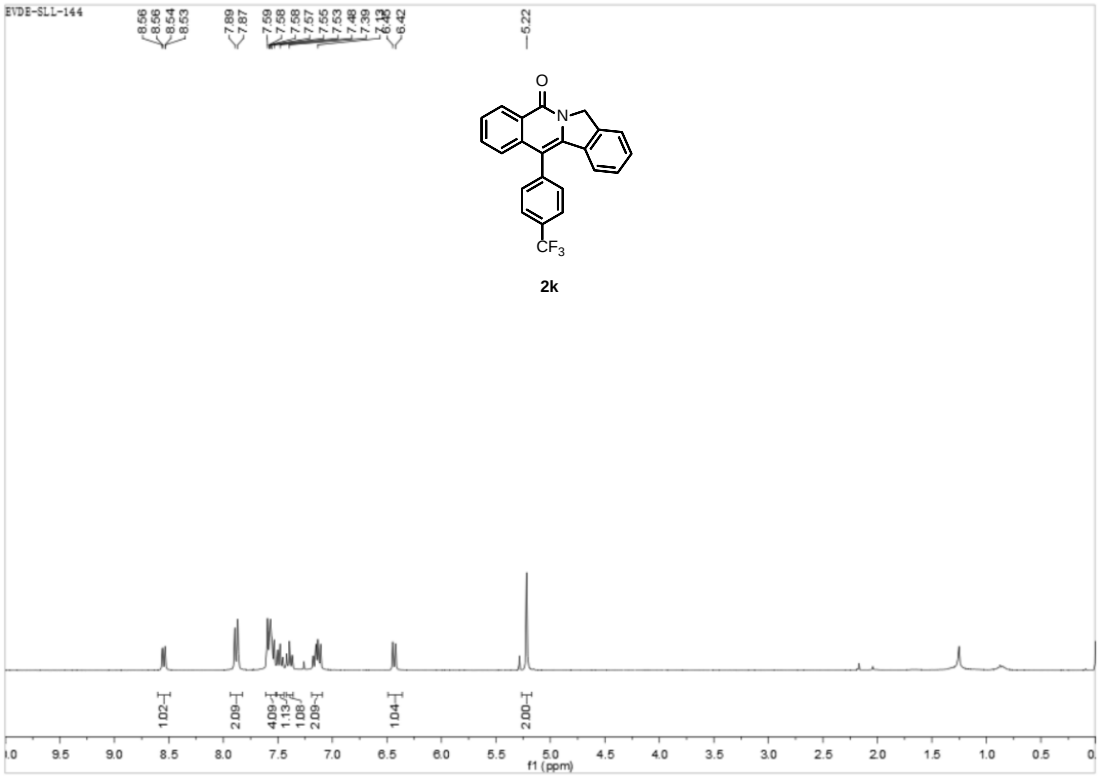

EVDE-SLI-46C
160.94
138.33
135.66
133.00
131.77
131.19
129.39
129.19
128.36
128.20
127.88
127.76
127.44
126.11
123.90
123.07
114.59
52.48
O
N
Ph
2i
f1 (ppm)


EVDE-SLL-163
8.58
8.58
8.56
8.55
7.53
7.52
7.40
7.38
7.34
7.34
7.28
7.27
7.26
7.26
7.26
7.25
6.53
6.51
5.24
2.52
O
N
Me
1.09
3.08
3.16
3.25
1.22
1.05
2.00
3.10
f1 (ppm)

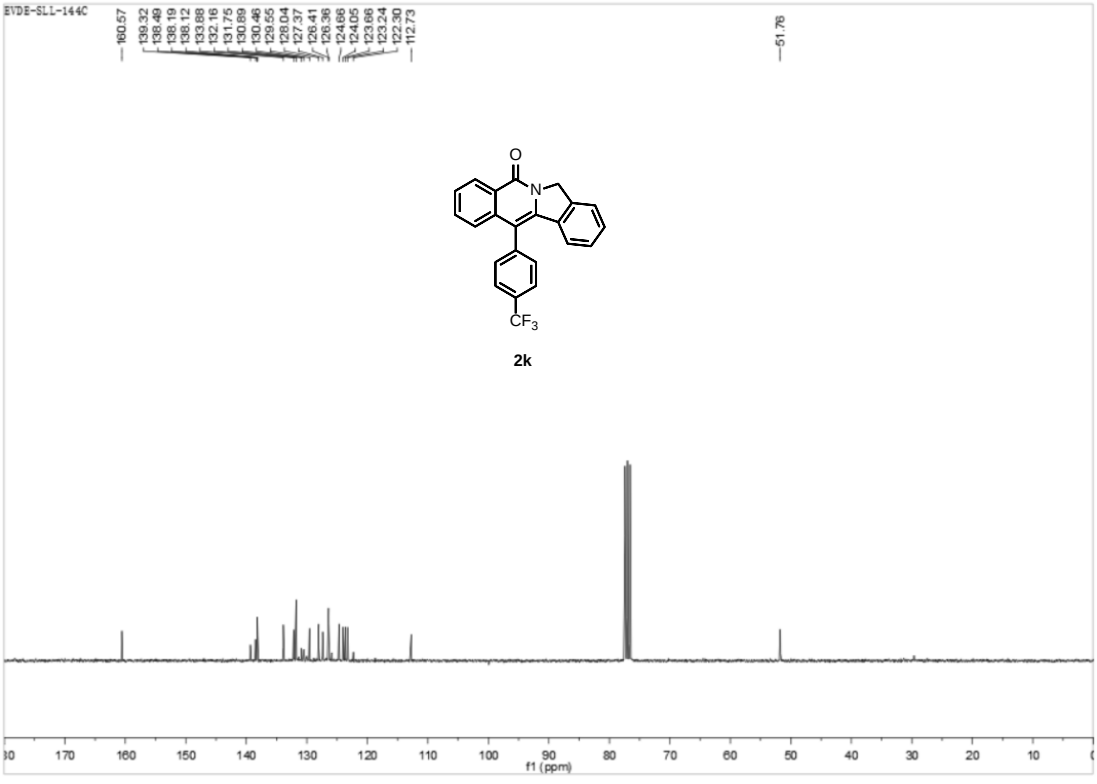
2j


EVDE-SLL-163C
160.68
138.87
138.31
138.08
137.96
134.40
131.95
131.87
130.60
130.08
129.10
127.60
127.17
126.10
125.17
124.02
122.97
114.51
51.76
21.42
O
N
Me
f1 (ppm)

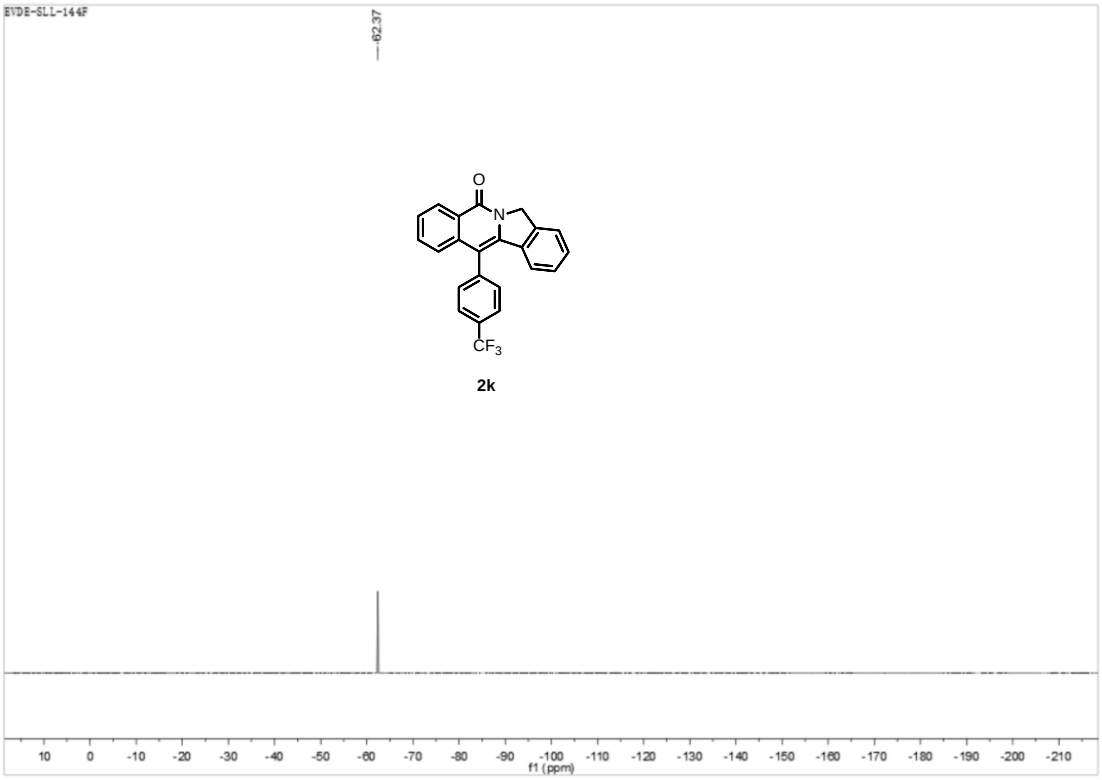
2j


EVDE-SLL-144
8.56
8.56
8.54
8.53
7.89
7.87
7.59
7.58
7.58
7.57
7.55
7.53
7.48
7.39
6.42
5.22
O
N
CF3
1.02
2.09
4.09
1.13
1.08
2.09
1.04
2.00
f1 (ppm)

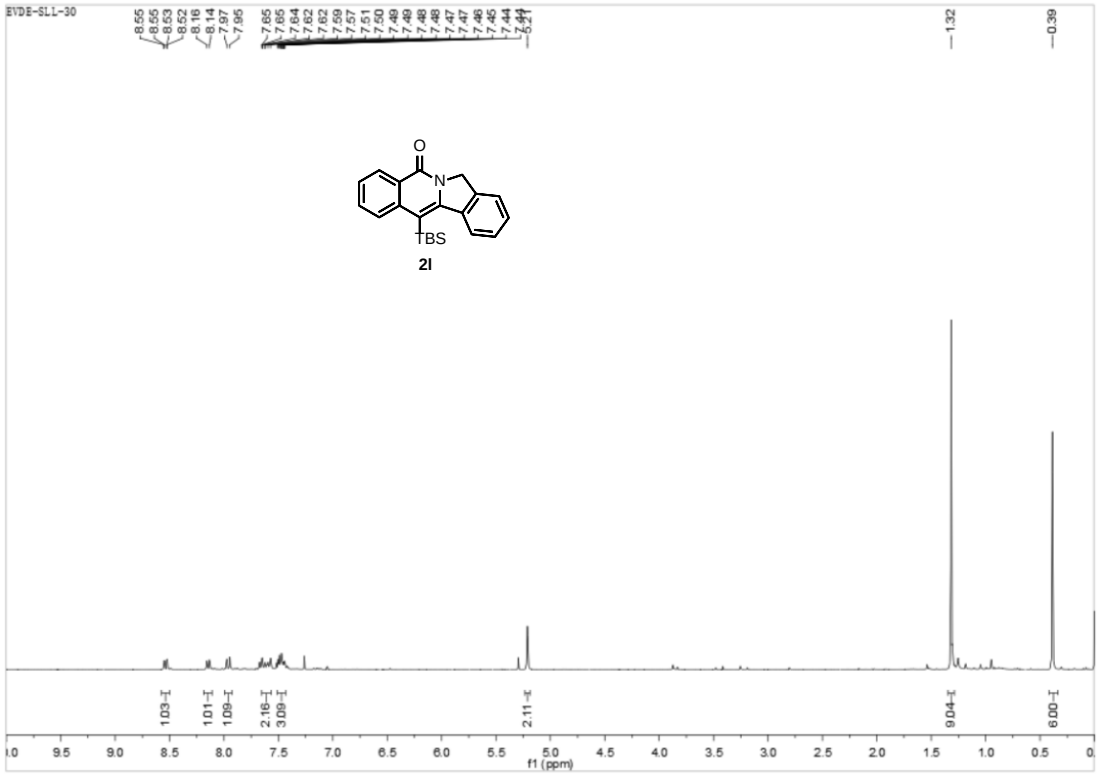
2k


EVDE-SLL-144C
160.57
139.32
138.49
138.19
138.12
133.88
132.16
131.75
130.89
130.46
129.55
126.04
127.37
126.41
126.36
124.66
124.05
123.66
123.24
122.30
112.73
51.76
O
N
CF3
f1 (ppm)

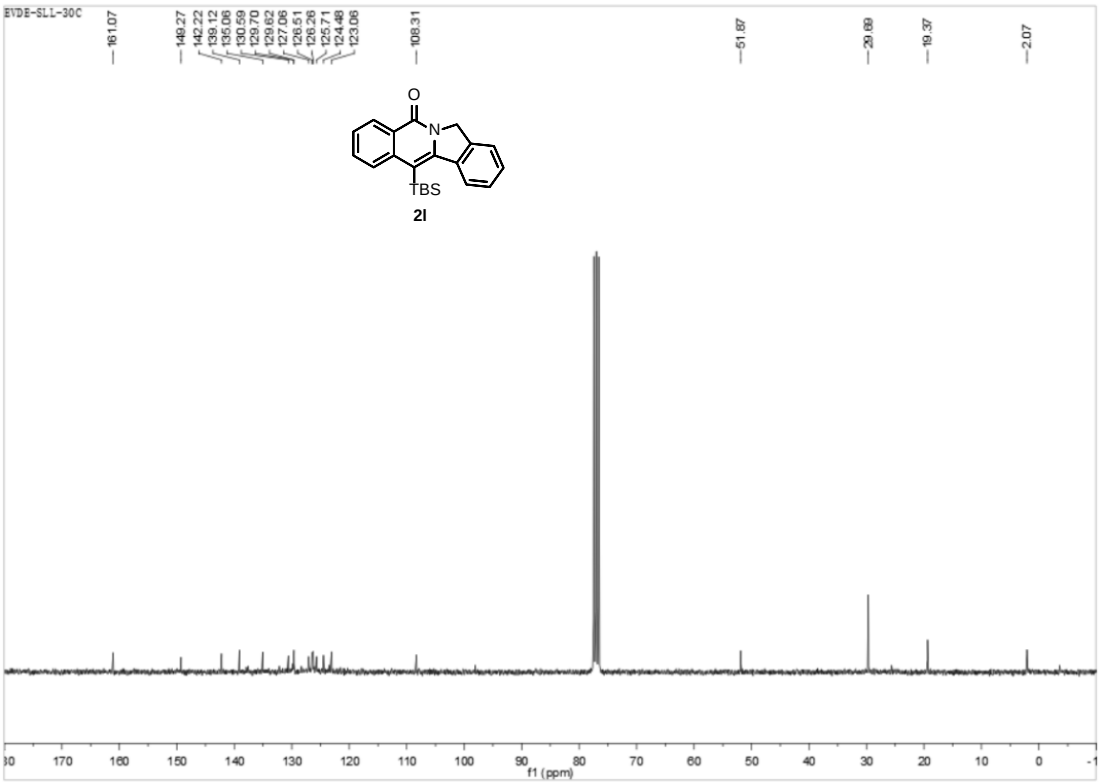
2k


EVDE-SLL-144F
-62.37
O
N
CF3
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)

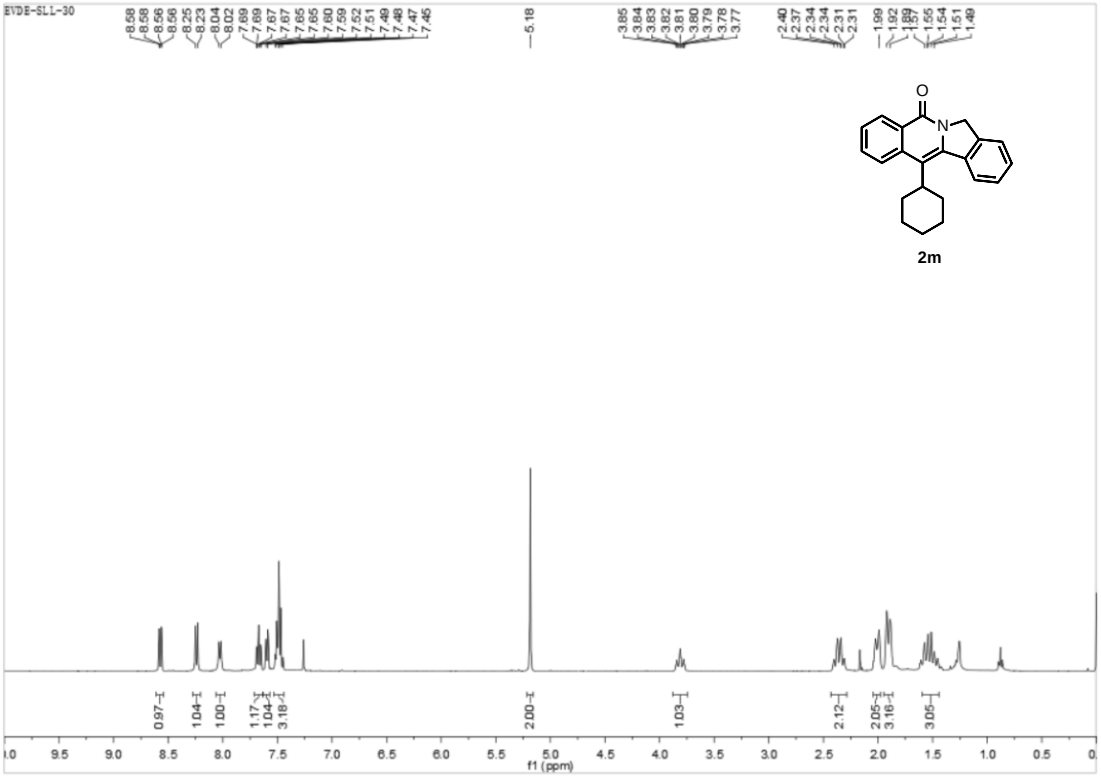
2k


EVDE-SLL-30
8.56
8.55
8.53
8.52
8.16
8.14
7.97
7.96
7.65
7.64
7.62
7.59
7.57
7.51
7.50
7.49
7.48
7.47
7.46
7.45
7.44
5.21
1.32
0.39
O
N
TBS
1.03
1.01
1.09
2.16
3.09
2.11
9.04
6.00
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
f1 (ppm)

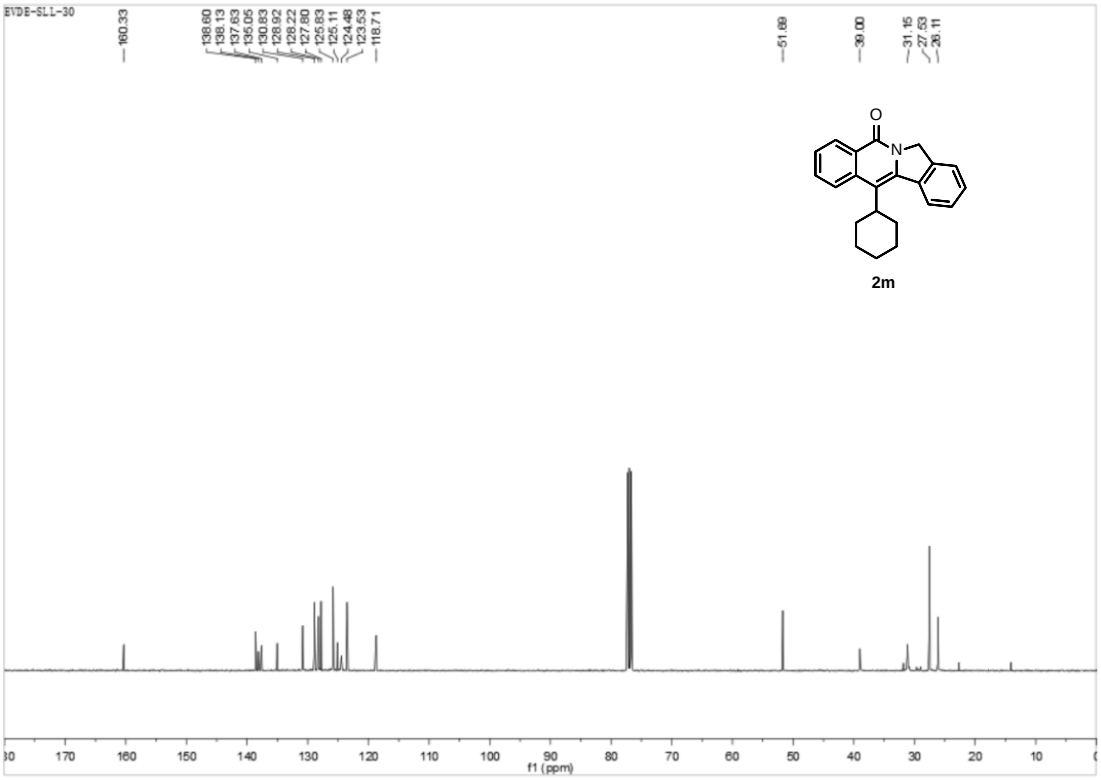
2l

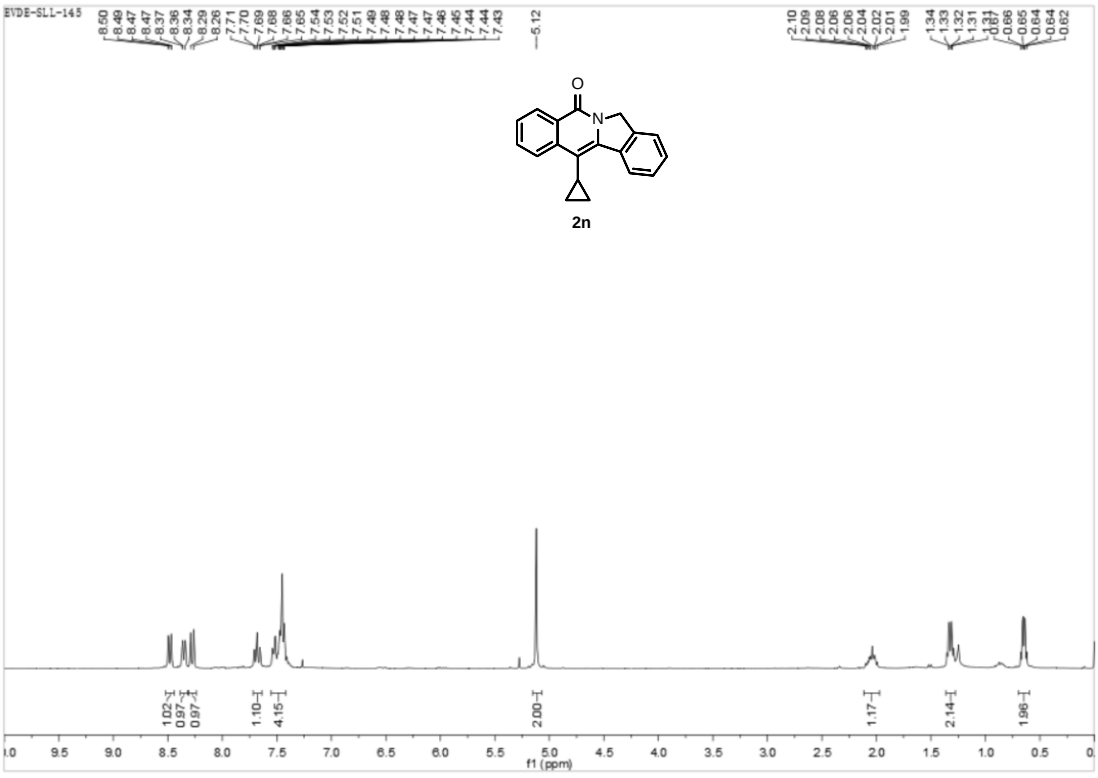

EVDE-SLL-30C
161.07
149.27
142.22
139.12
135.06
130.59
129.70
129.62
127.06
126.51
126.26
125.71
124.48
123.06
108.31
51.87
29.69
19.37
2.07
O
N
TBS
f1 (ppm)

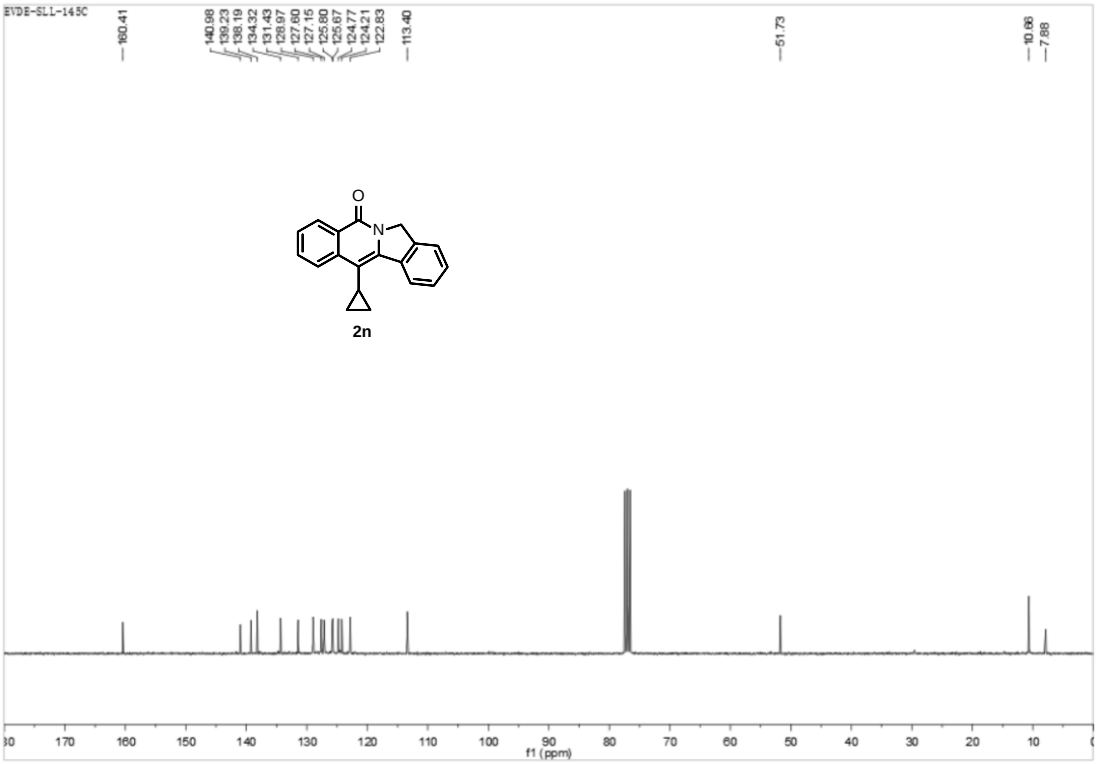
2l

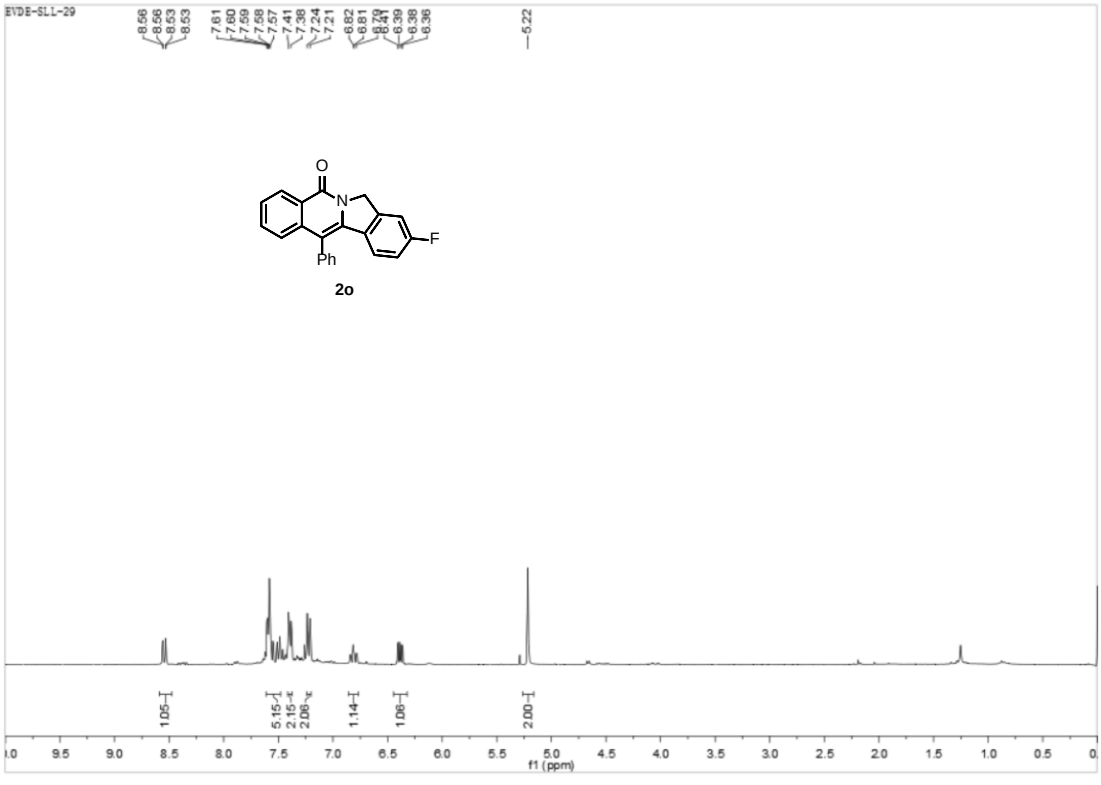

EVDE-SLL-30
8.58
8.58
8.56
8.56
8.25
8.23
8.04
8.02
7.69
7.69
7.67
7.67
7.65
7.65
7.60
7.59
7.52
7.51
7.49
7.48
7.47
7.45
5.18
3.85
3.84
3.83
3.82
3.81
3.80
3.79
3.78
3.77
2.40
2.37
2.34
2.34
2.31
2.31
1.99
1.92
1.89
1.89
1.55
1.54
1.51
1.49
O
N
0.97
1.04
1.00
1.17
1.04
3.18
2.00
1.03
2.12
2.05
3.16
3.05
f1 (ppm)

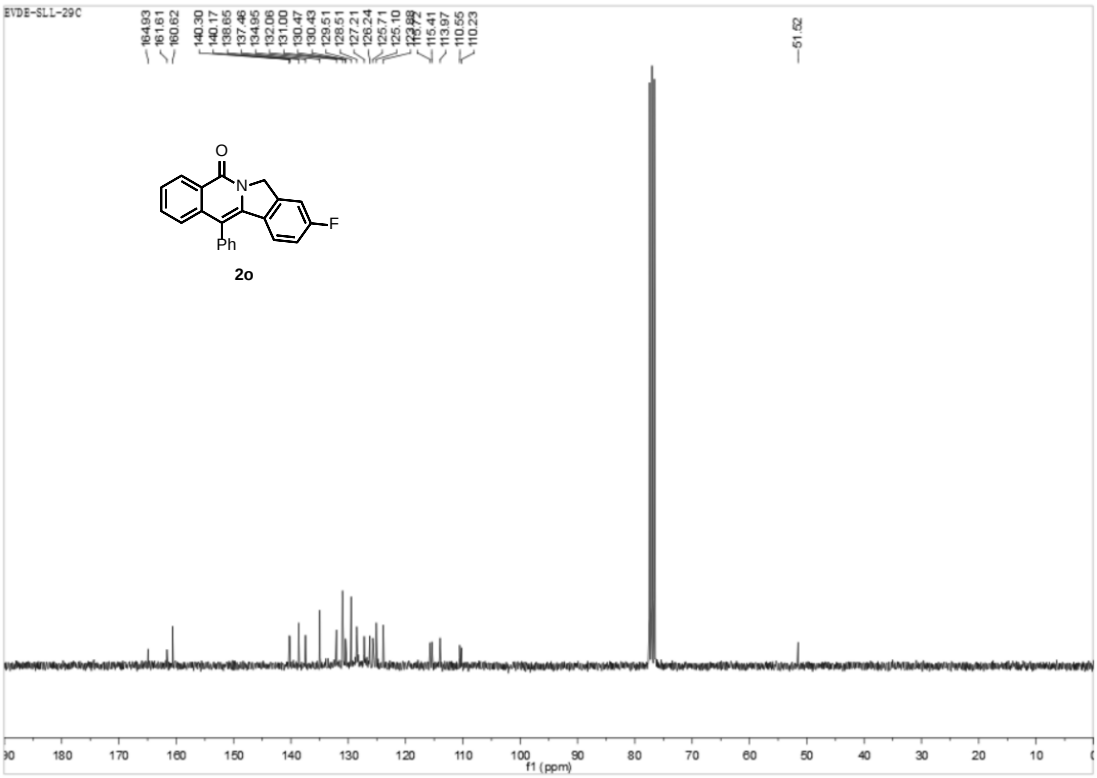
2m

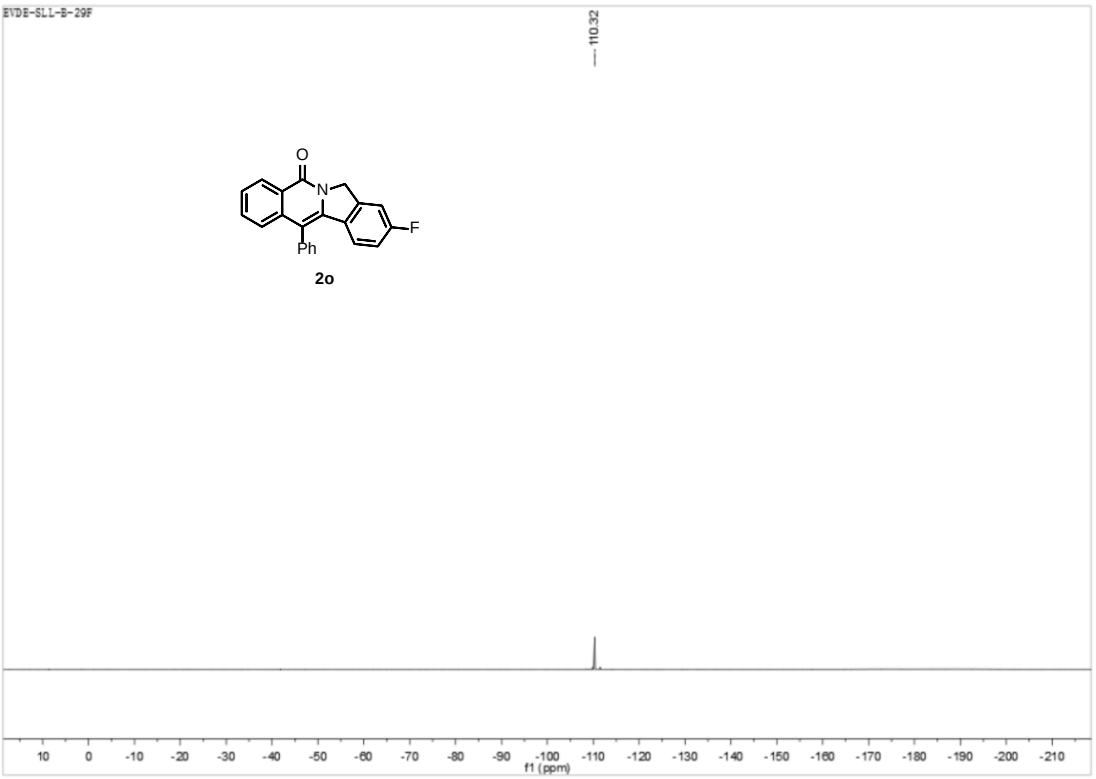

EVDE-SLL-30
160.33
138.60
136.13
137.63
136.05
130.83
129.92
129.22
127.80
125.63
125.11
124.48
123.53
118.71
51.69
39.00
31.15
27.53
26.11
O
N
2m
f1 (ppm)

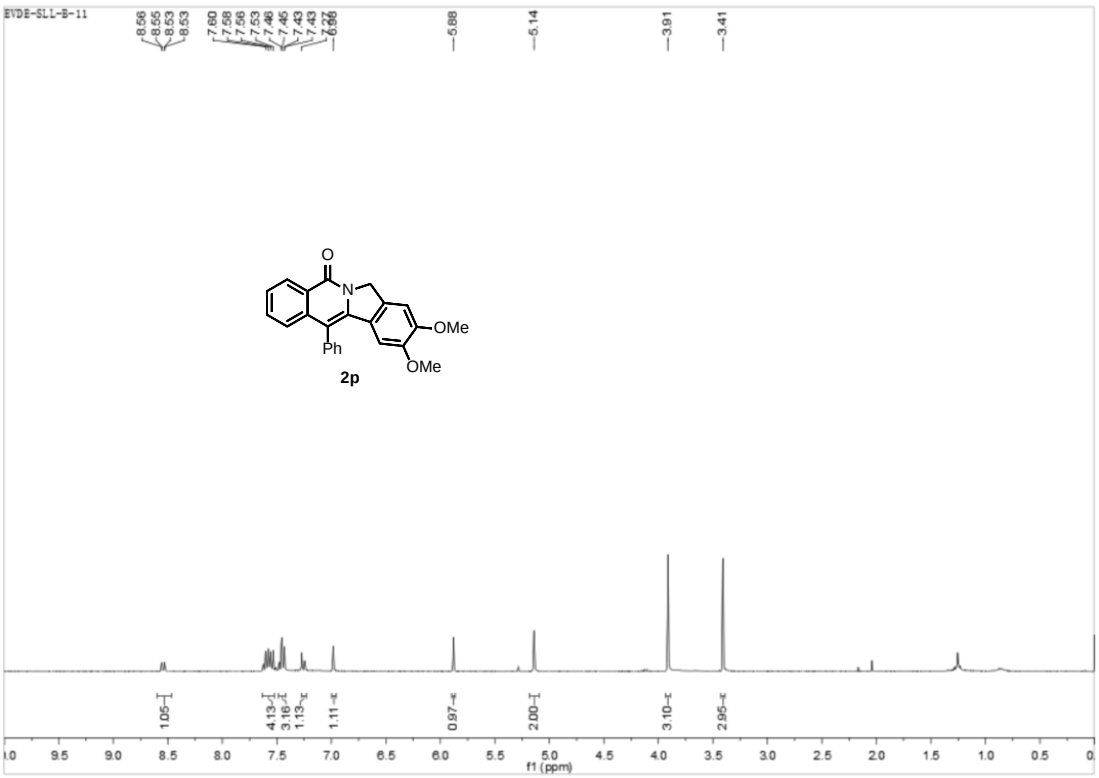

EVDE-SLL-145
8.50
8.49
8.47
8.47
8.37
8.36
8.34
8.29
8.26
7.71
7.70
7.69
7.68
7.66
7.65
7.64
7.53
7.52
7.51
7.49
7.48
7.48
7.47
7.47
7.46
7.45
7.44
7.44
7.43
5.12
2.10
2.09
2.08
2.06
2.04
2.02
2.01
1.99
1.34
1.33
1.32
1.31
0.67
0.66
0.65
0.64
0.64
0.62
1.02
0.97
0.97
1.10
4.15
2.00
1.17
2.14
1.96
O
N
2n
f1 (ppm)

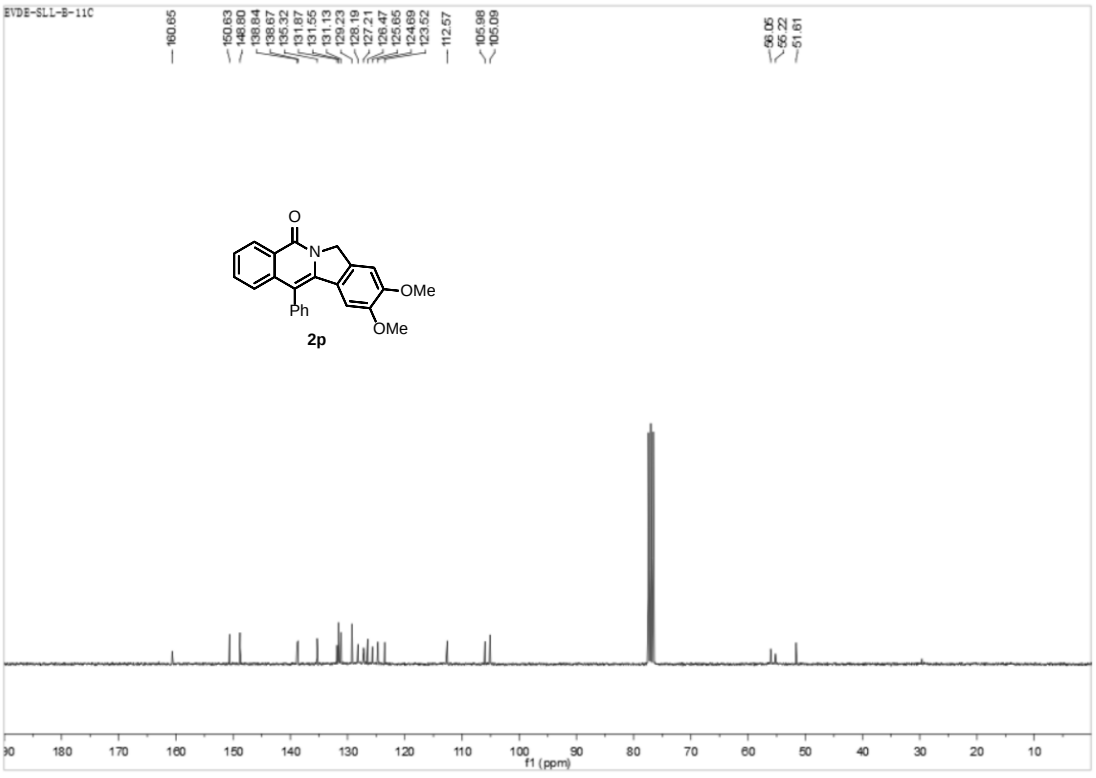

EVDE-SLL-145C
160.41
140.98
139.23
138.19
134.32
131.43
128.97
127.60
127.15
125.80
125.67
124.77
124.21
122.83
113.40
51.73
10.66
7.88
O
N
2n
f1 (ppm)

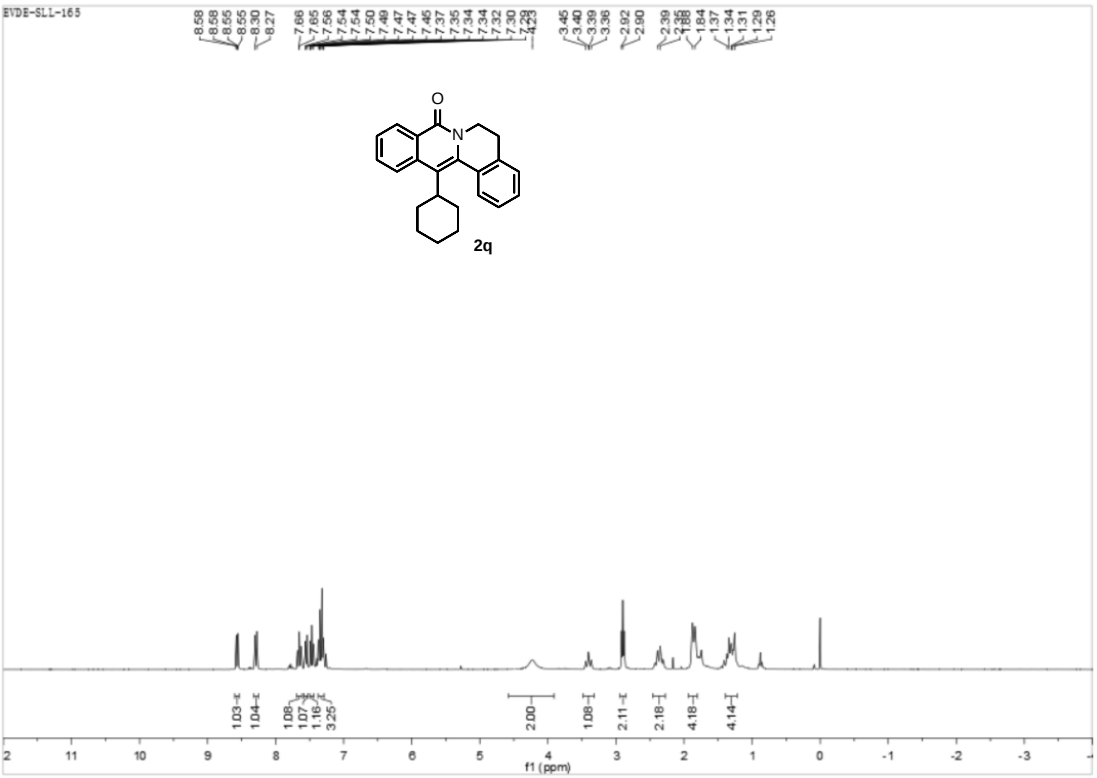

EVDE-SLL-29
8.56
8.56
8.53
8.53
7.61
7.60
7.59
7.58
7.57
7.41
7.38
7.24
7.21
6.82
6.81
6.39
6.38
6.36
5.22
O
N
F
Ph
2o
1.05
5.15
2.15
2.06
1.14
1.06
2.00
f1 (ppm)

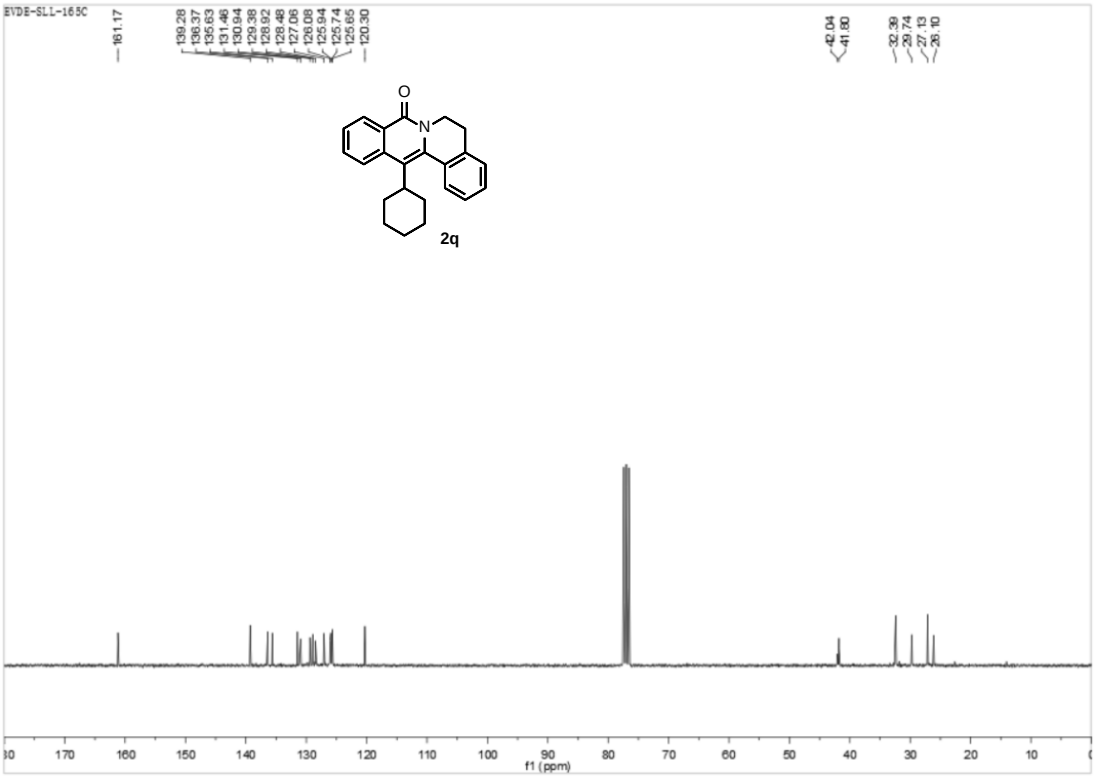

EVDE-SLL-29C
164.93
161.61
160.62
140.30
140.17
138.65
137.46
134.95
132.06
131.00
130.47
130.43
129.51
128.51
127.21
126.24
125.71
125.10
115.41
113.97
110.55
110.23
51.52
O
N
F
Ph
2o
f1 (ppm)

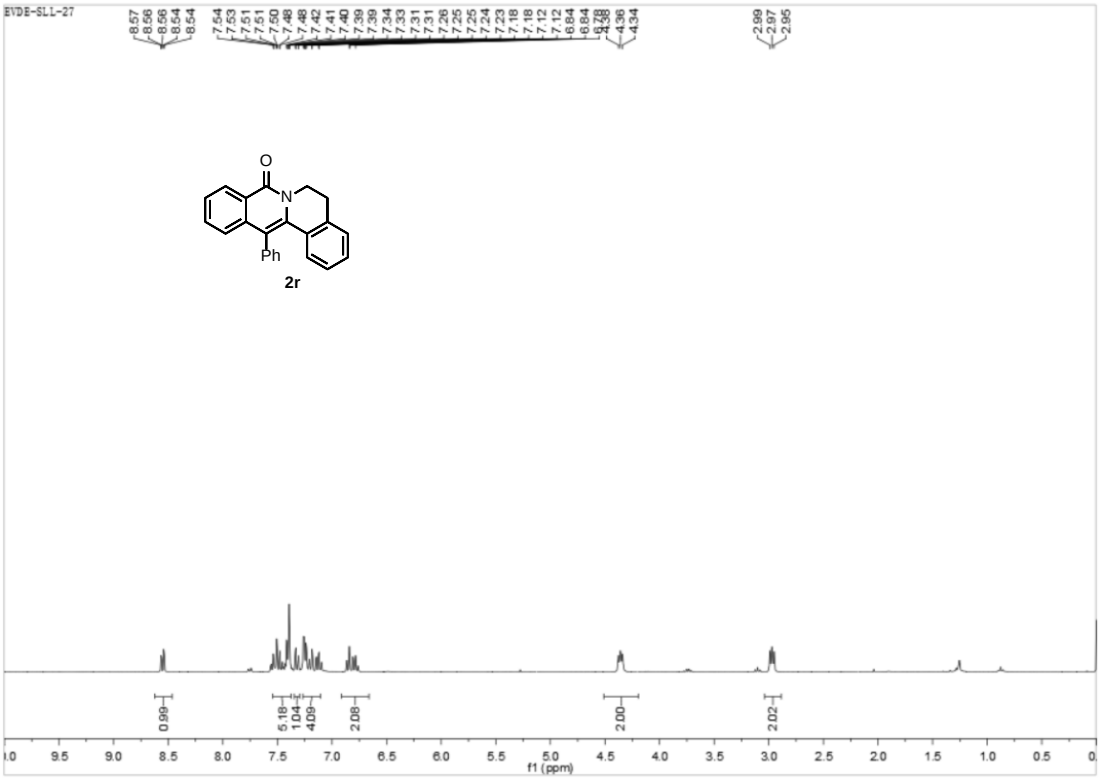

EVDE-SLL-B-29F
110.32
O
N
F
Ph
2o
f1 (ppm)

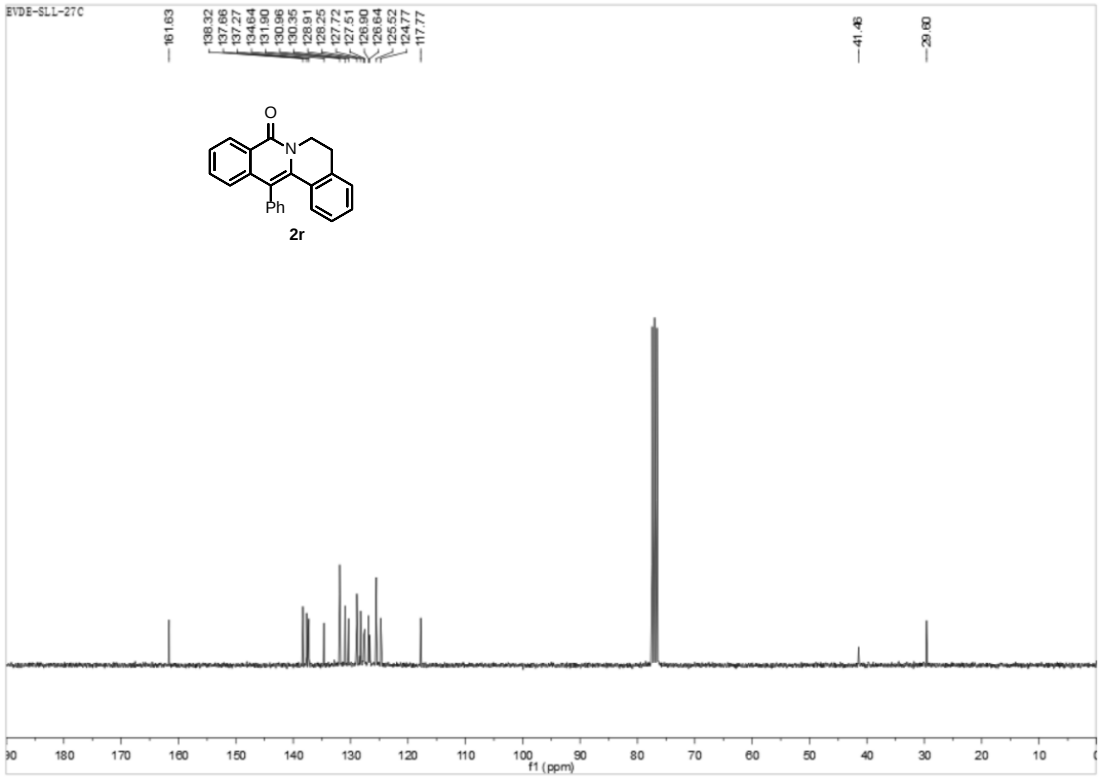

EVDE-SLL-B-11
8.56
8.55
8.53
8.53
7.60
7.58
7.56
7.53
7.46
7.45
7.43
7.43
7.27
6.86
5.88
5.14
3.91
3.41
O
N
OMe
Ph
OMe
2p
1.05
4.13
3.16
1.13
1.11
0.97
2.00
3.10
2.95
f1 (ppm)

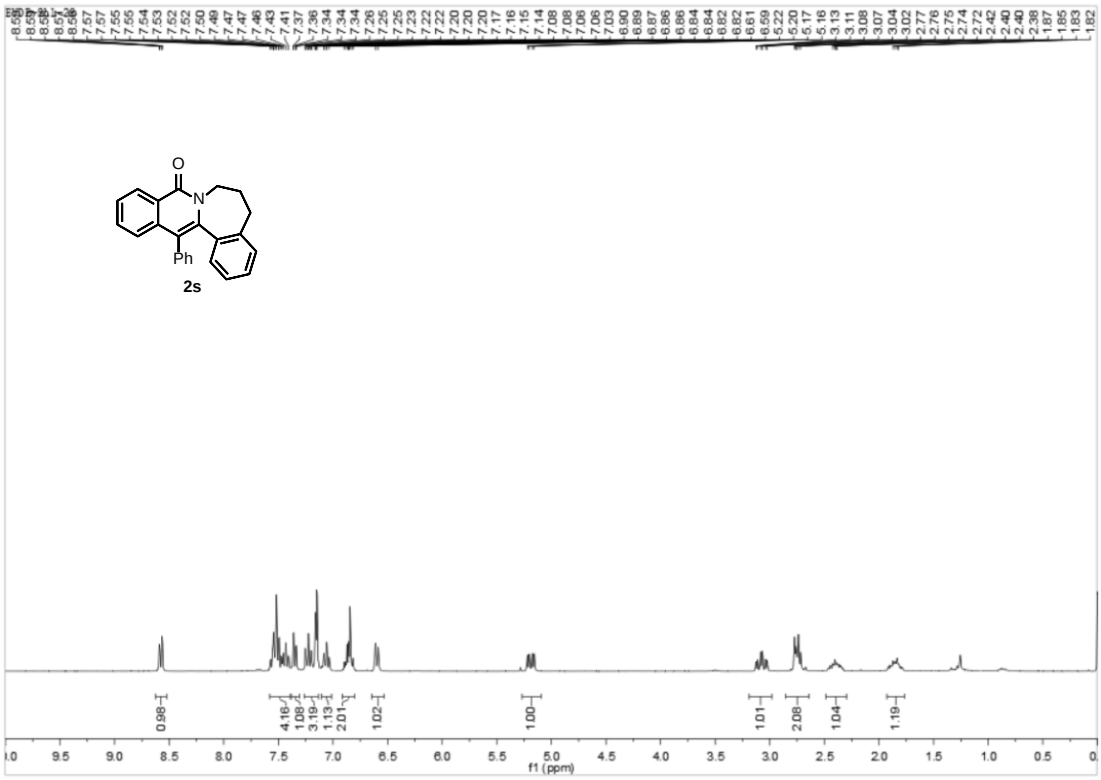

EVDE-SLL-B-11C
160.65
150.63
148.80
138.84
138.67
135.32
131.97
131.55
131.13
129.23
128.19
127.21
126.47
125.65
124.69
123.52
112.57
105.98
105.09
66.05
55.22
51.61
O
N
OMe
Ph
OMe
2p
f1 (ppm)

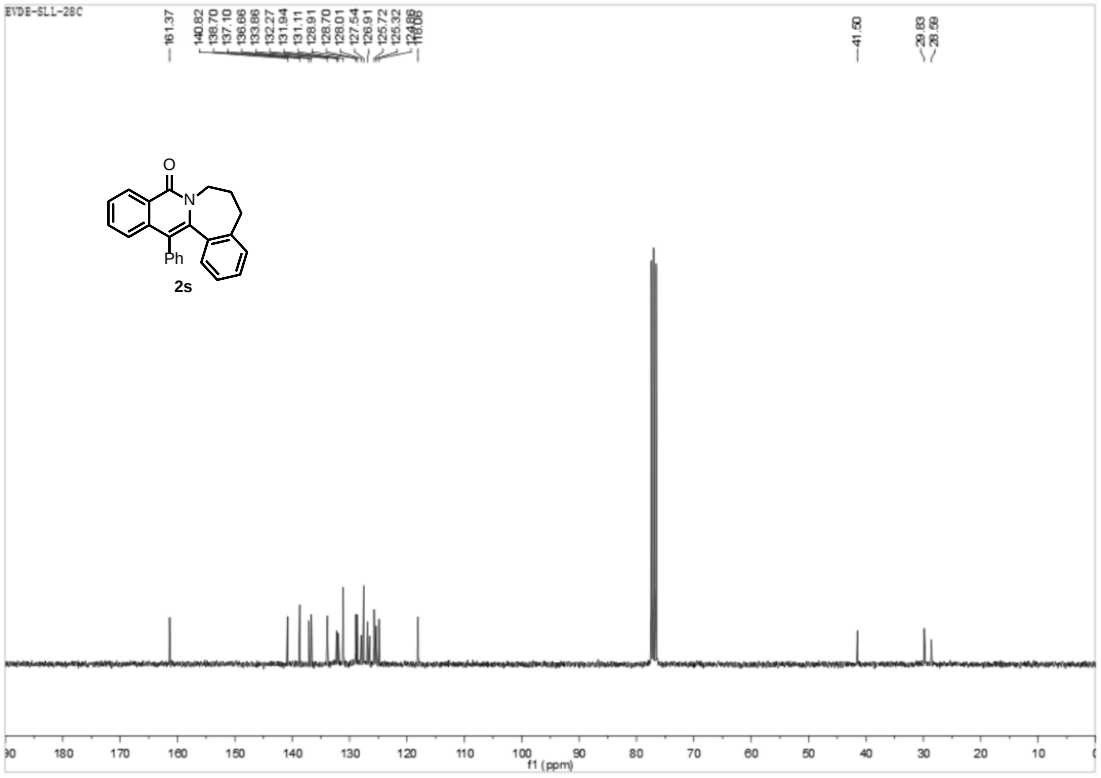

EVDE-SLI-165
8.58
8.58
8.55
8.55
8.30
8.27
7.66
7.65
7.56
7.54
7.54
7.50
7.49
7.47
7.47
7.46
7.37
7.35
7.34
7.34
7.32
7.30
7.29
7.23
3.45
3.40
3.39
3.36
2.92
2.90
2.39
2.35
1.88
1.84
1.37
1.34
1.31
1.29
1.26
O
N
2q
1.03
1.04
1.08
1.07
1.18
3.25
2.00
1.08
2.11
2.18
4.18
4.14
f1 (ppm)

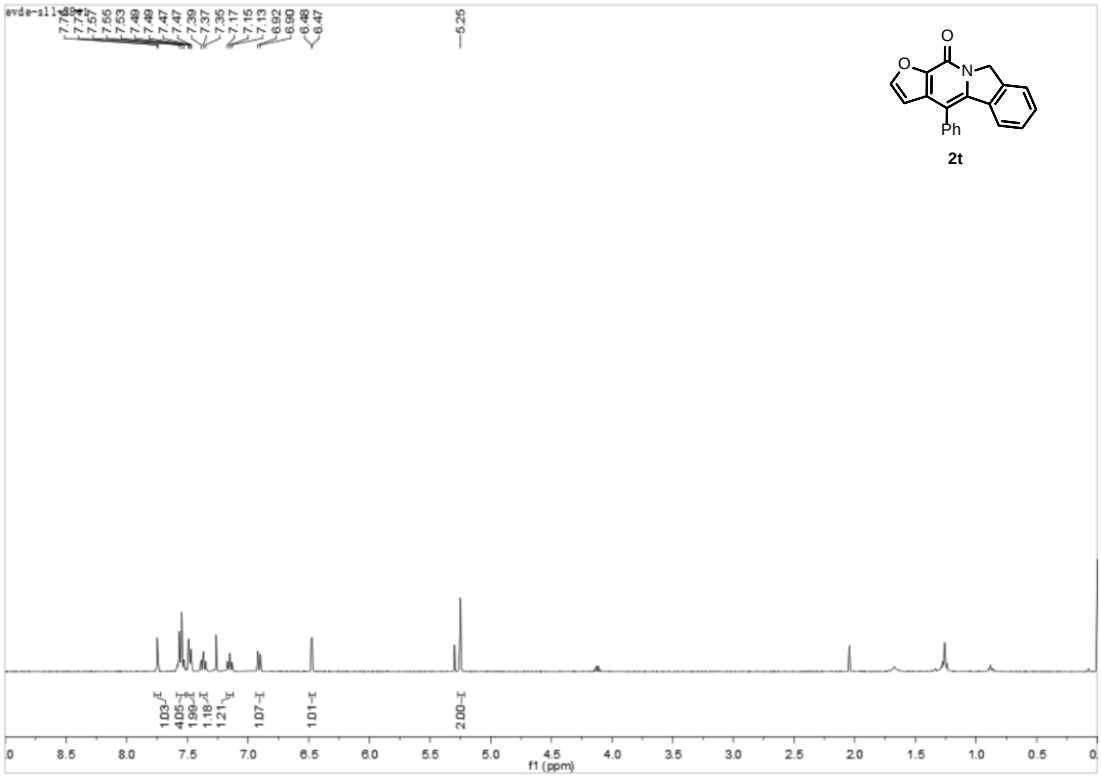

EVDE-SLI-165C
161.17
139.28
136.37
135.63
131.46
130.94
129.38
128.92
128.48
127.06
126.08
125.94
125.74
125.65
120.30
42.04
41.80
32.39
29.74
27.13
26.10
O
N
2q
f1 (ppm)

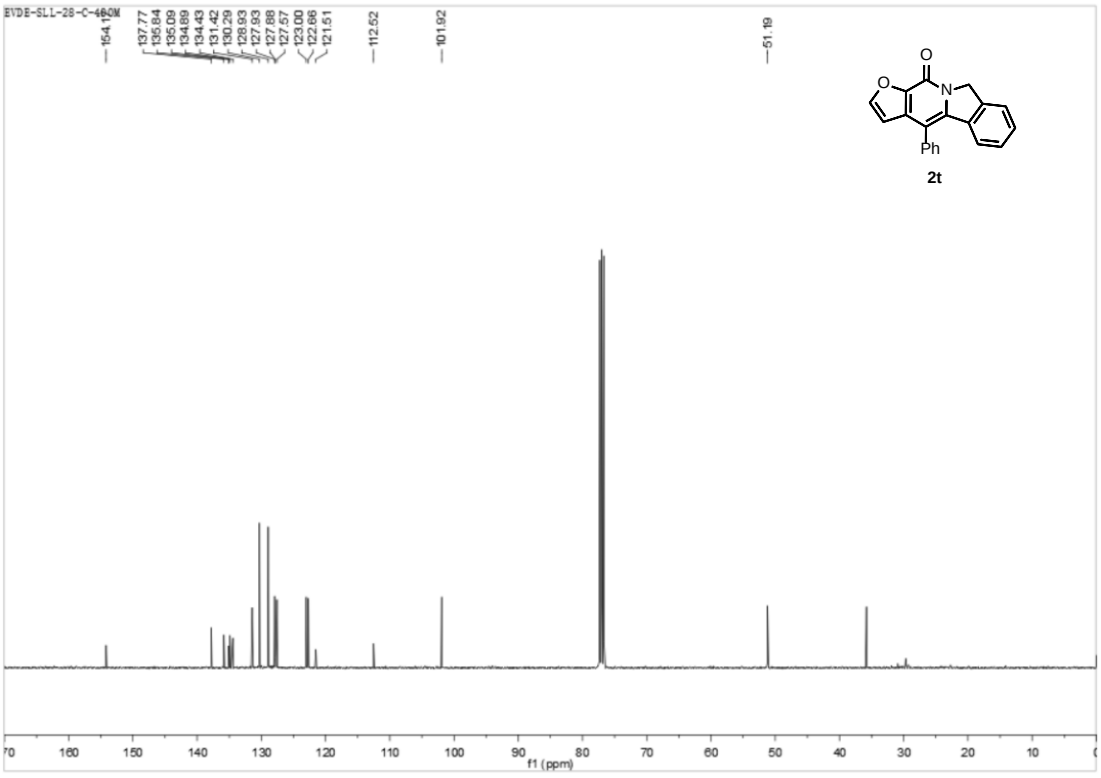

EVDE-SLL-27
8.57
8.56
8.56
8.54
8.54
7.54
7.53
7.51
7.51
7.50
7.48
7.48
7.42
7.41
7.40
7.39
7.39
7.34
7.33
7.31
7.31
7.26
7.25
7.24
7.23
7.18
7.12
6.84
6.84
4.38
4.36
4.34
2.99
2.97
2.95
O
N
Ph
2r
0.99
5.18
1.04
4.09
2.08
2.00
2.02
f1 (ppm)

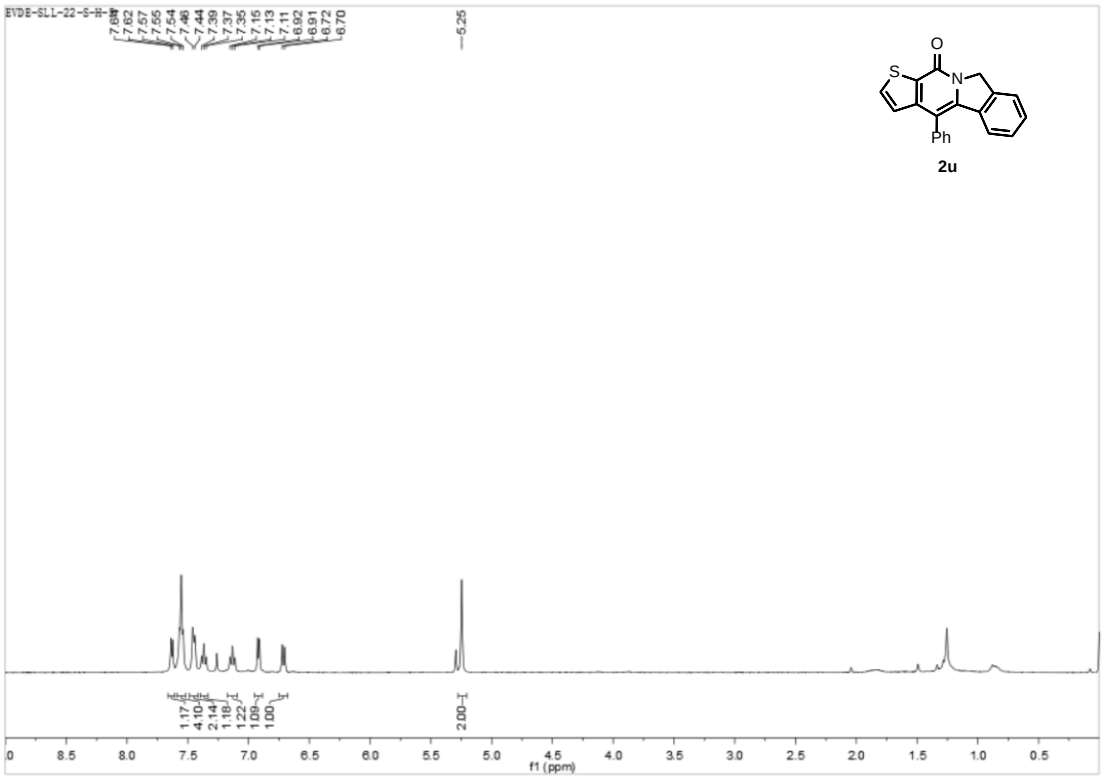

EVDE-SLL-27C
161.63
138.32
137.66
137.27
134.64
131.90
130.96
130.35
128.91
128.25
127.72
127.51
126.90
126.64
125.52
124.77
117.77
41.46
29.00
O
N
Ph
2r
f1 (ppm)


O
N
Ph
2s
0.98
4.16
1.08
3.19
1.13
2.01
1.02
1.00
1.01
2.08
1.04
1.19
f1 (ppm)


EVDE-SLL-28C
O
N
Ph
2s
f1 (ppm)

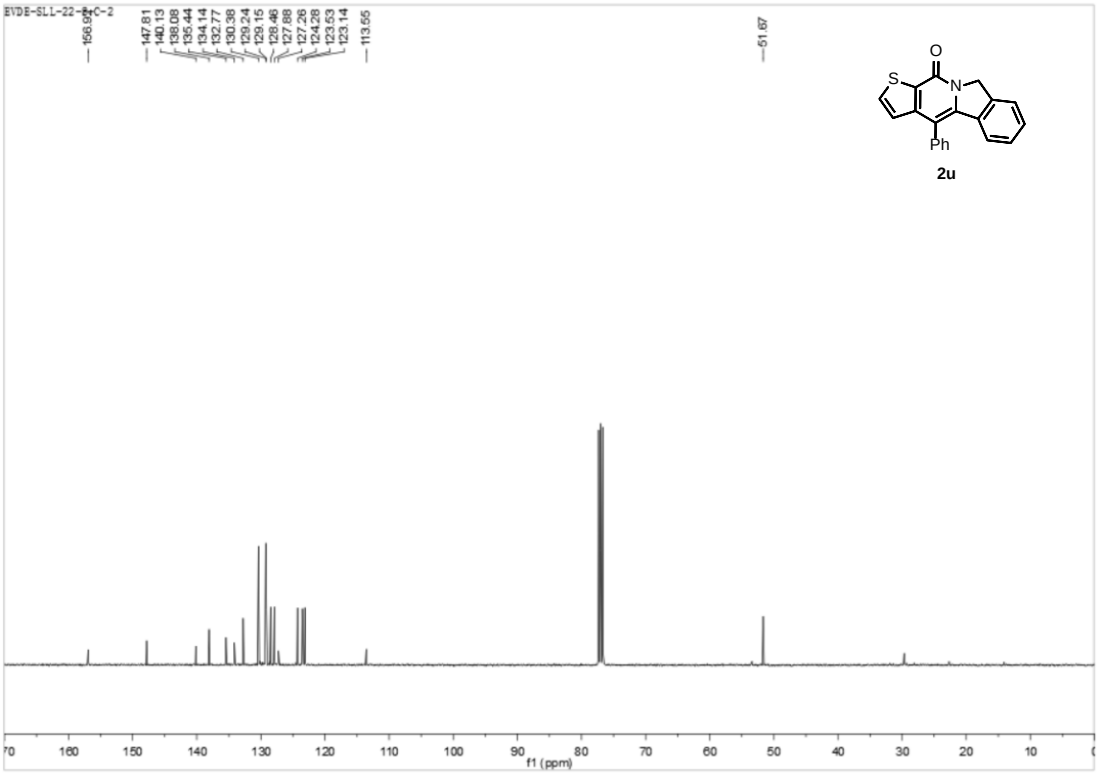

7.76
7.74
7.67
7.65
7.53
7.49
7.48
7.47
7.47
7.39
7.37
7.35
7.17
7.15
7.13
6.92
6.90
6.48
6.47
5.25
1.03
4.05
1.99
1.18
1.21
1.07
1.01
2.00
f1 (ppm)
O
O
N
Ph
2t


EVDE-SLL-28-C-400M
154.10
137.77
135.84
135.09
134.89
134.43
131.42
130.29
128.93
127.93
127.88
127.57
123.00
122.66
121.51
112.52
101.92
51.19
f1 (ppm)
O
O
N
Ph
2t


7.62
7.57
7.55
7.54
7.46
7.44
7.39
7.37
7.35
7.15
7.13
7.11
6.92
6.91
6.72
6.70
5.25
1.17
4.10
2.14
1.18
1.22
1.09
1.00
2.00
f1 (ppm)

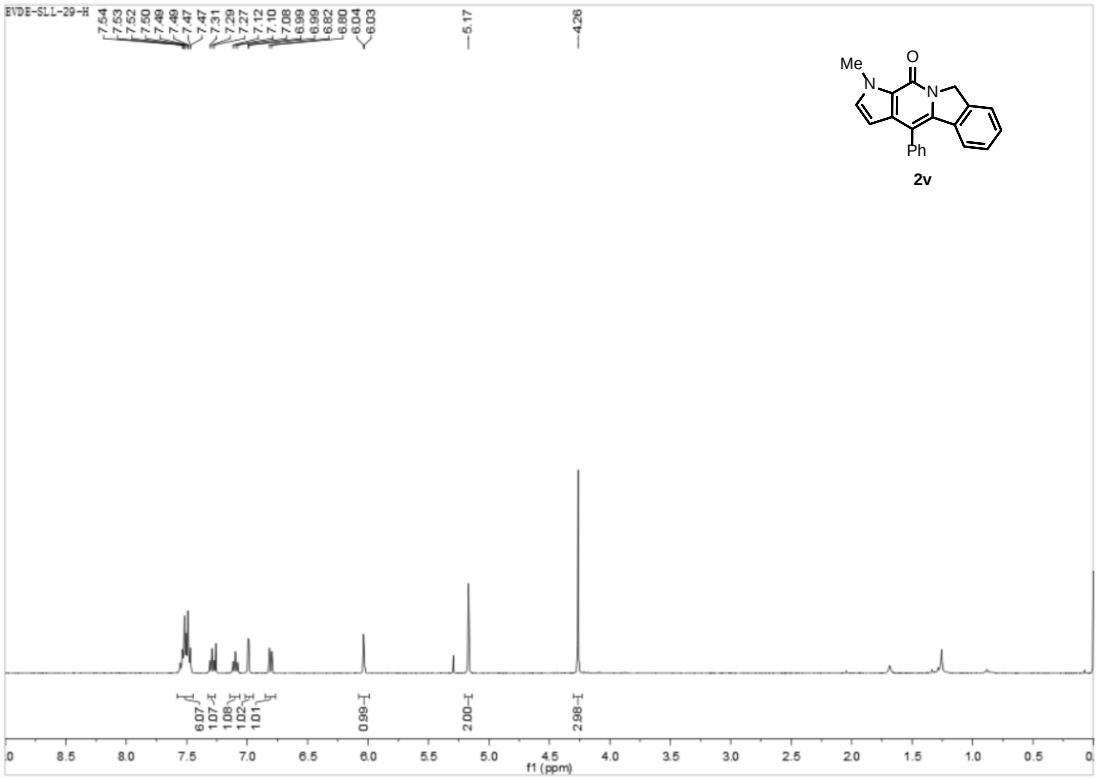
O
S
N
Ph

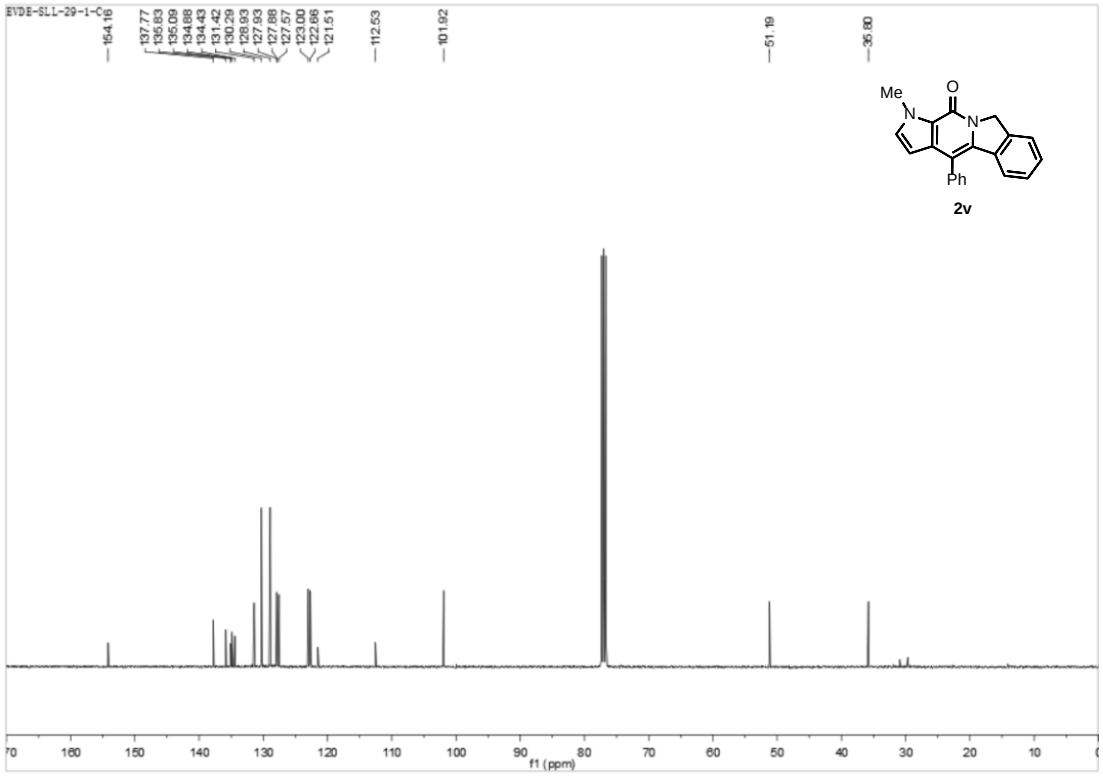
2u

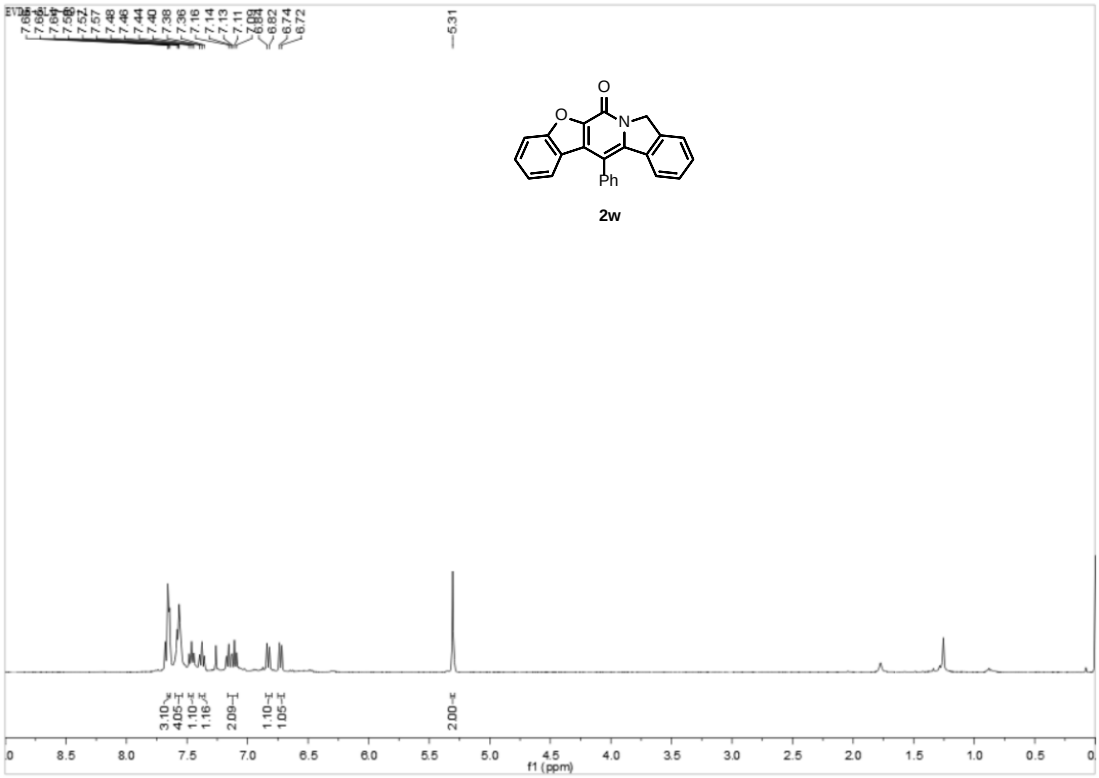

156.92
147.81
140.13
138.08
135.44
134.14
132.77
130.38
129.24
129.15
128.46
127.88
127.26
124.28
123.53
123.14
113.55
51.67
f1 (ppm)

O
S
N
Ph

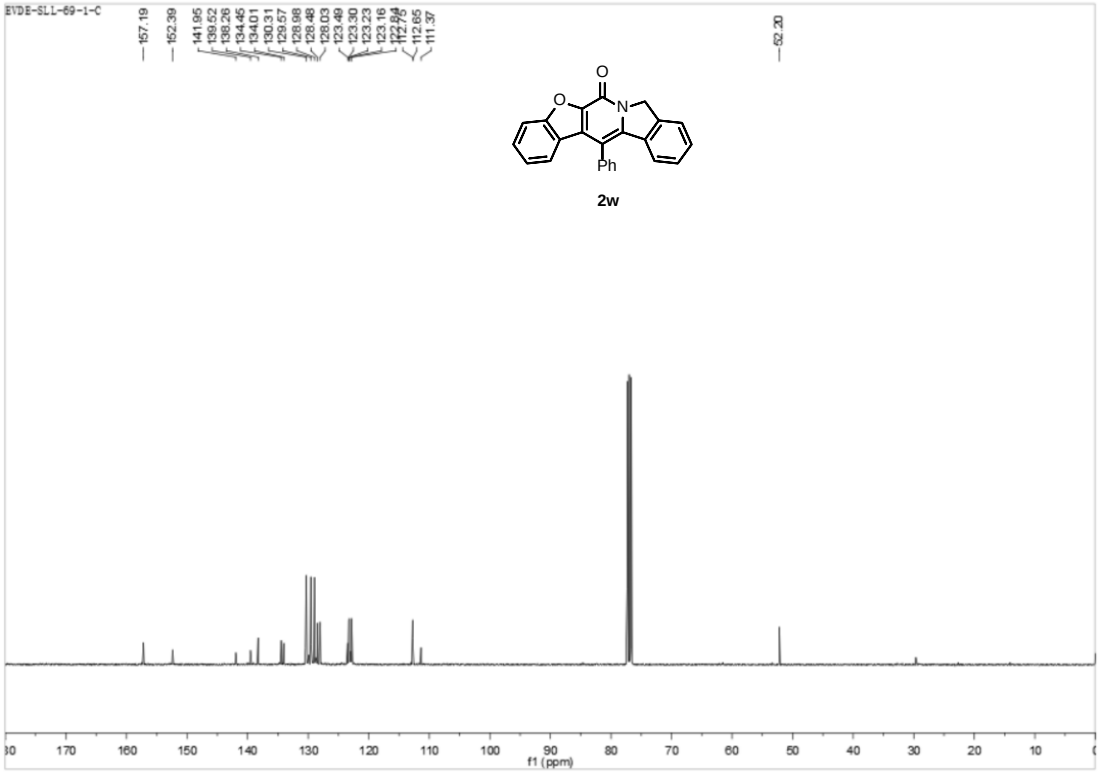
2u


EVDE-SLL-29-H
7.54
7.53
7.52
7.50
7.49
7.49
7.47
7.47
7.31
7.29
7.27
7.12
7.10
7.08
6.99
6.99
6.82
6.80
6.04
6.03
5.17
4.26
Me
N
O
N
Ph
2v
6.07
1.07
1.08
1.02
1.01
0.99
2.00
2.98
f1 (ppm)

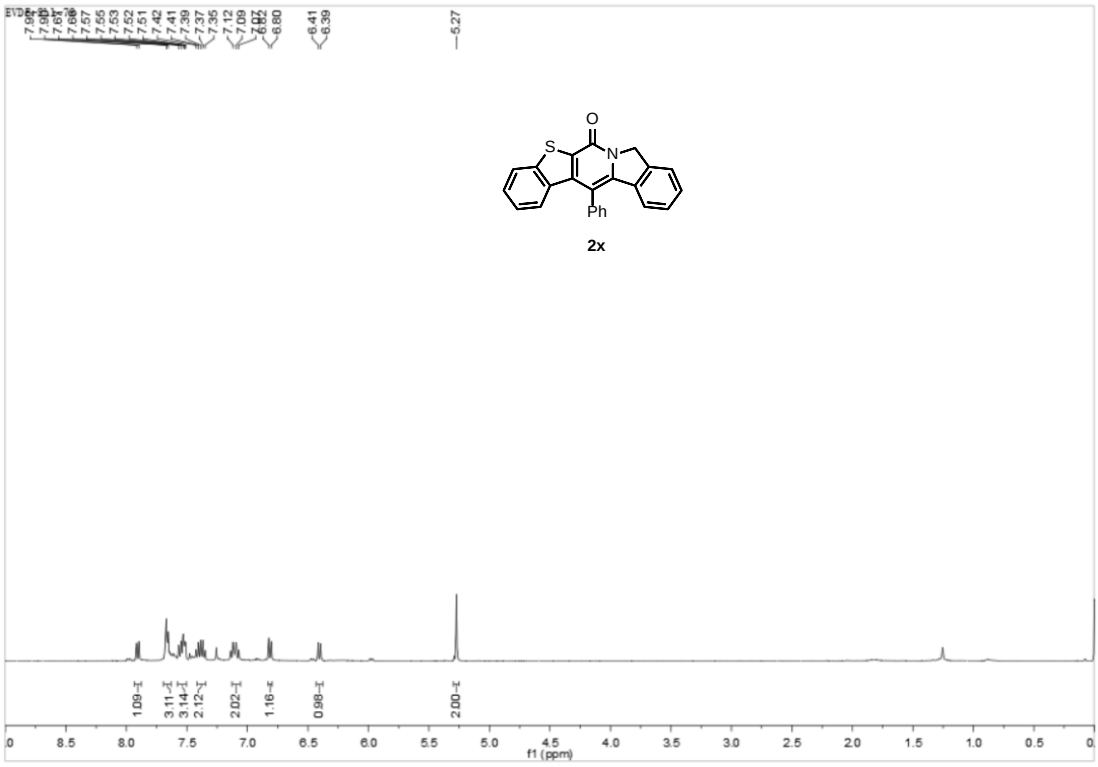

EVDE-SLL-29-1-C
154.16
137.77
135.83
135.09
134.88
134.43
131.42
130.29
128.93
127.93
127.88
127.57
123.00
122.66
121.51
112.53
101.92
51.19
36.80
Me
N
O
N
Ph
2v
f1 (ppm)


O
O
N
Ph
5.31
3.10
4.05
1.10
1.18
2.09
1.10
1.05
2.00
f1 (ppm)

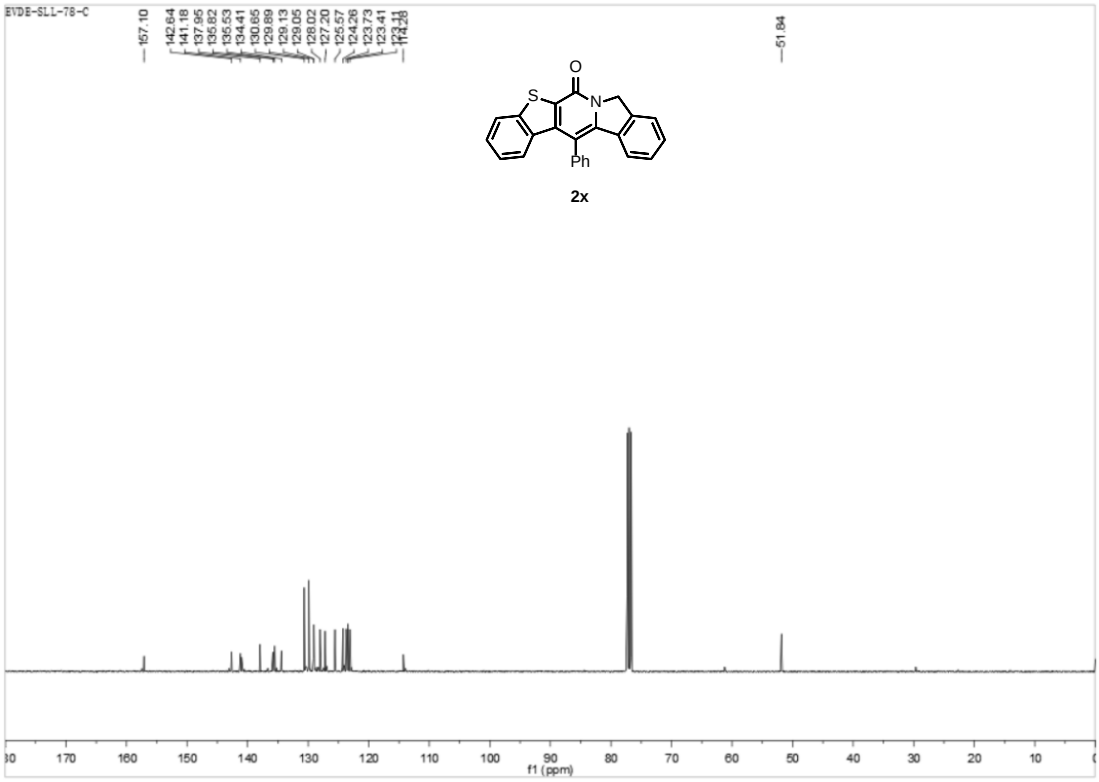
2w


EVDE-SLL-69-1-C
157.19
152.39
141.95
139.52
138.26
134.45
134.01
130.31
129.57
128.98
128.48
128.03
123.49
123.30
123.23
123.16
112.73
112.65
111.37
52.20
O
O
N
Ph
f1 (ppm)

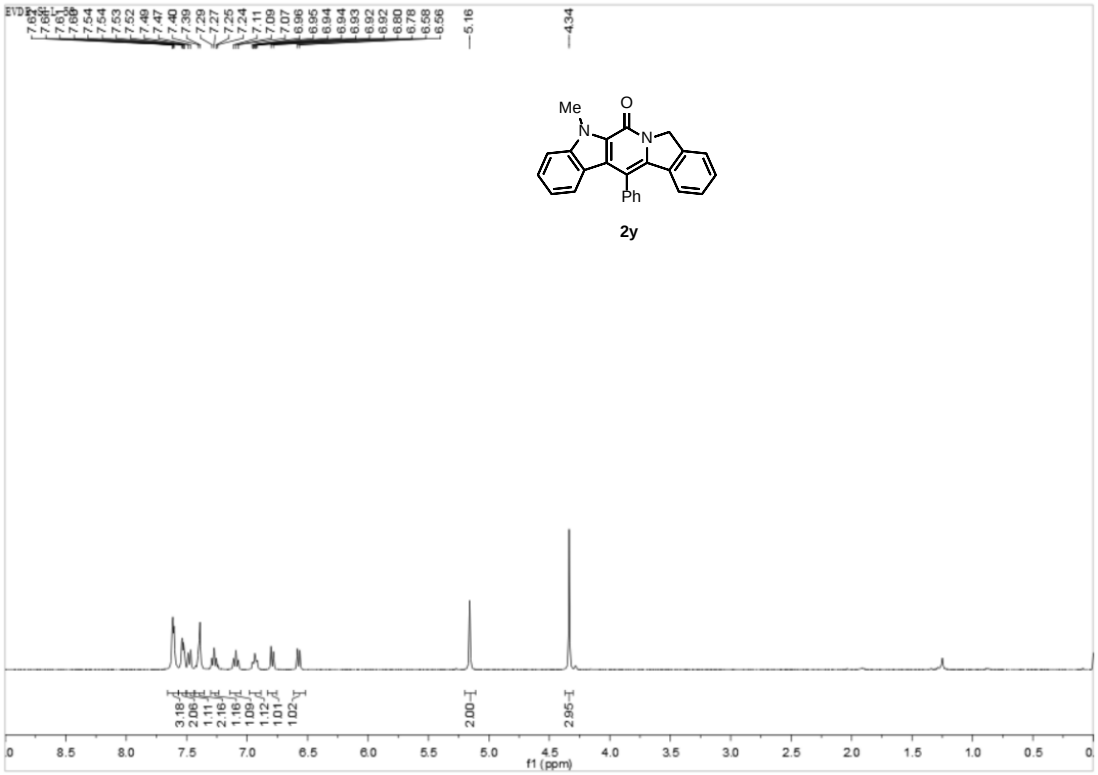
2w


7.95
7.93
7.91
7.81
7.80
7.57
7.55
7.53
7.52
7.51
7.42
7.41
7.39
7.37
7.35
7.12
7.09
6.82
6.80
6.41
6.39
5.27
O
S
N
Ph
1.09
3.11
3.14
2.12
2.02
1.16
0.98
2.00
f1 (ppm)

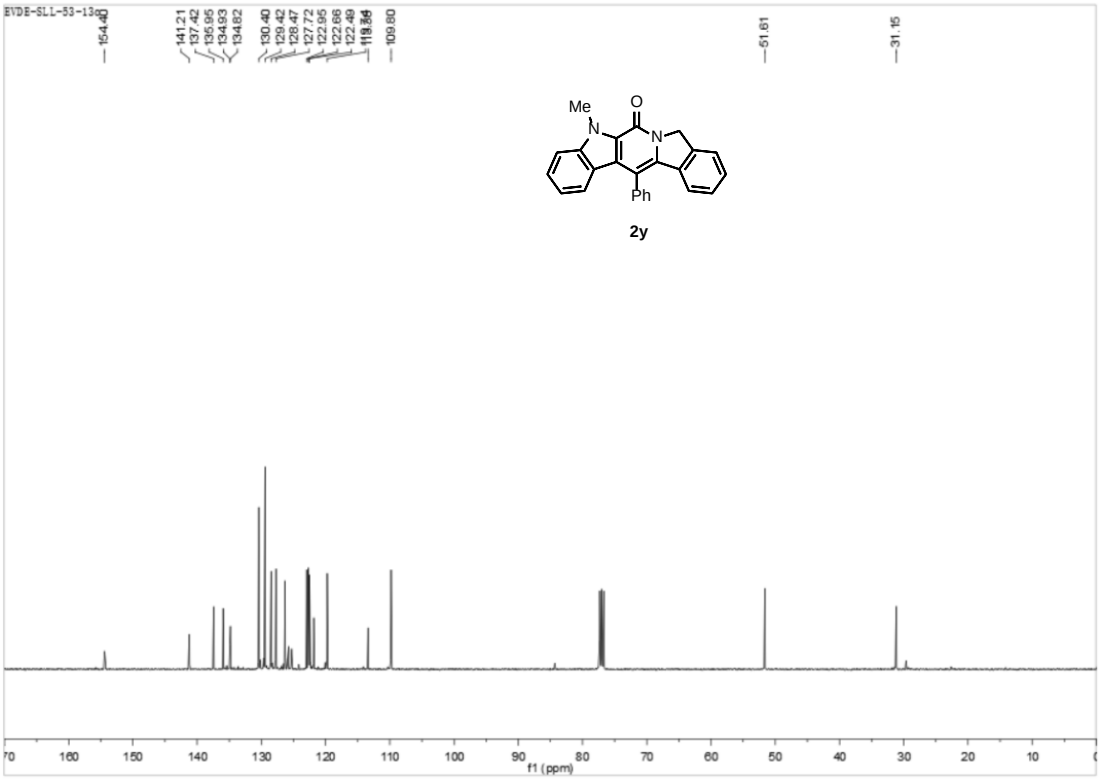
2x


EVDE-SLL-78-C
157.10
142.64
141.18
137.95
135.82
135.53
134.41
130.65
129.89
129.13
129.05
128.02
127.20
125.57
124.26
123.73
123.41
51.84
O
S
N
Ph
f1 (ppm)

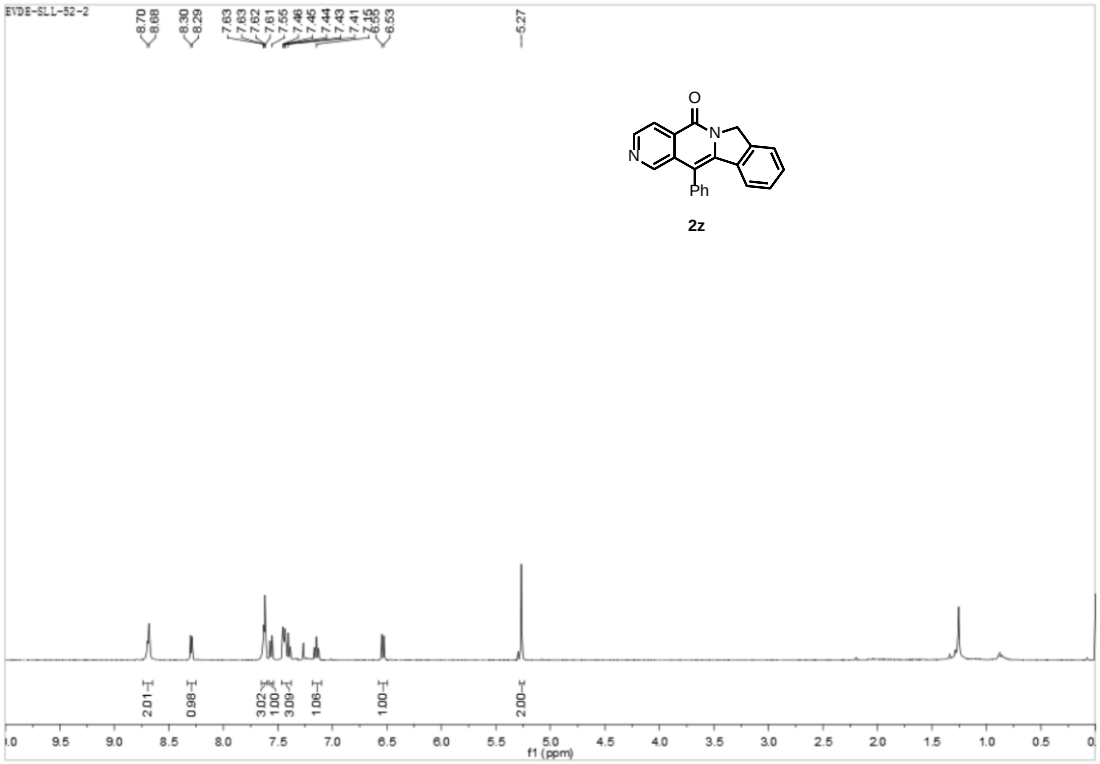
2x

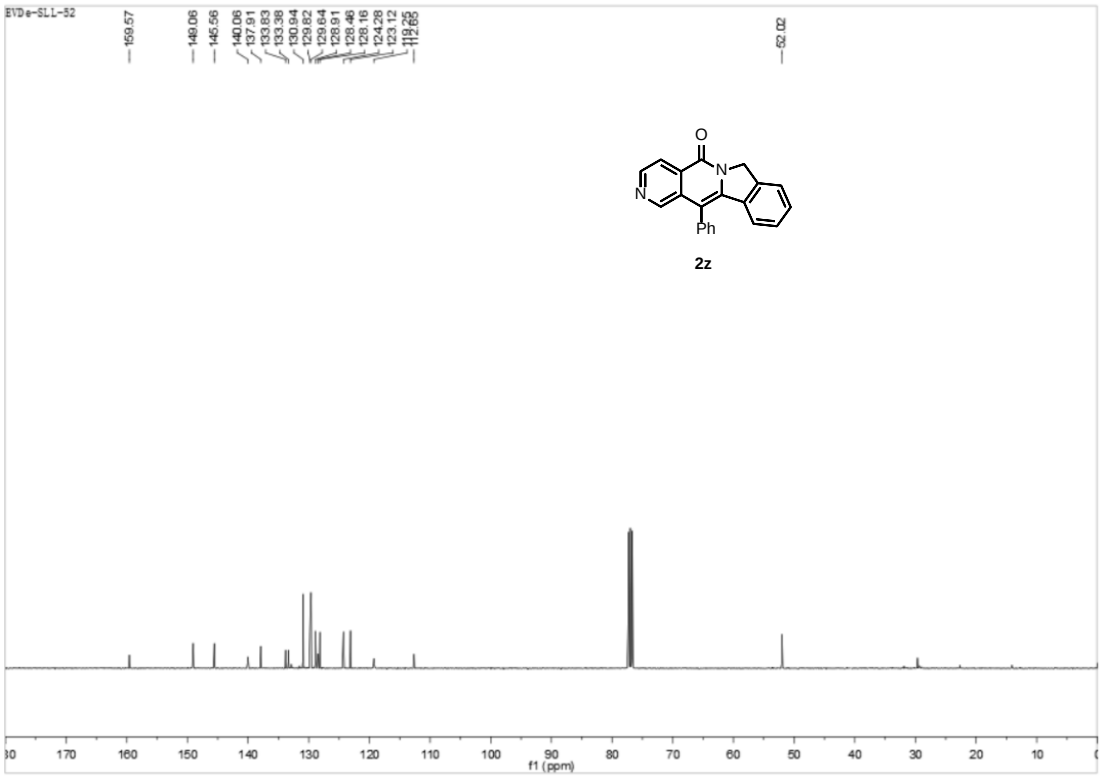

Me
O
N
N
Ph
5.16
4.34
2.00
2.95
f1 (ppm)

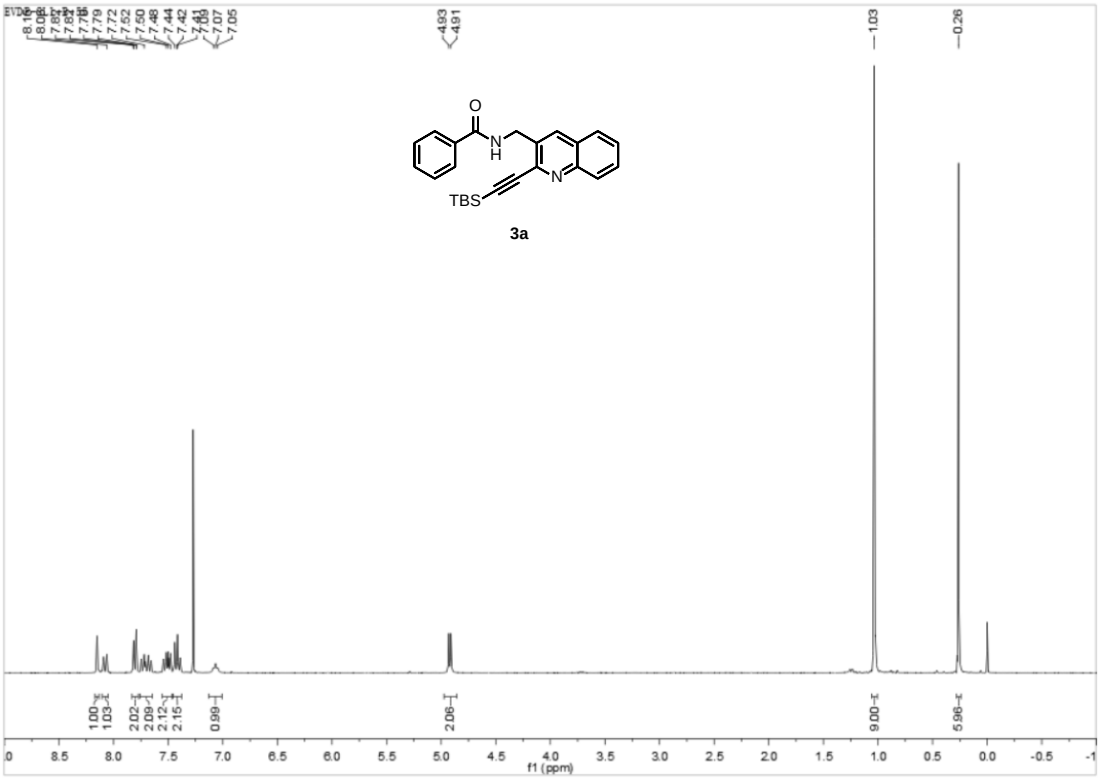
2y

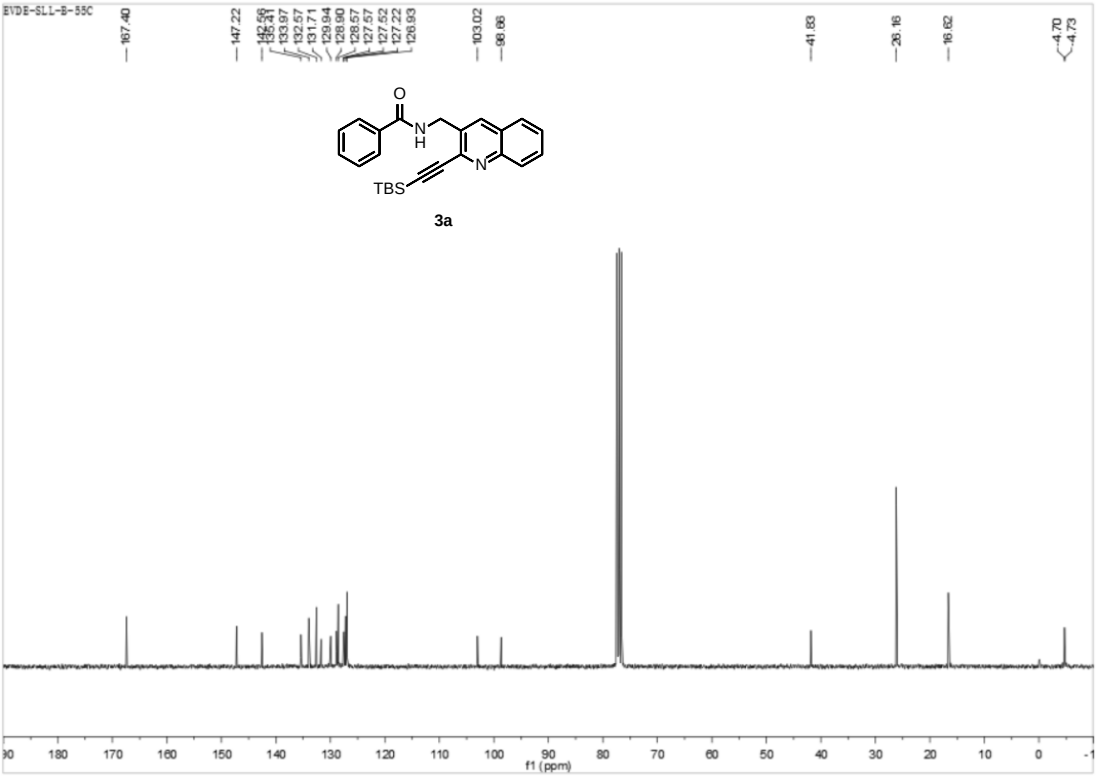

Me
O
N
N
Ph
154.40
141.21
137.42
135.96
134.93
134.62
130.40
129.42
128.47
127.72
122.95
122.66
122.49
109.80
51.61
31.15
f1 (ppm)

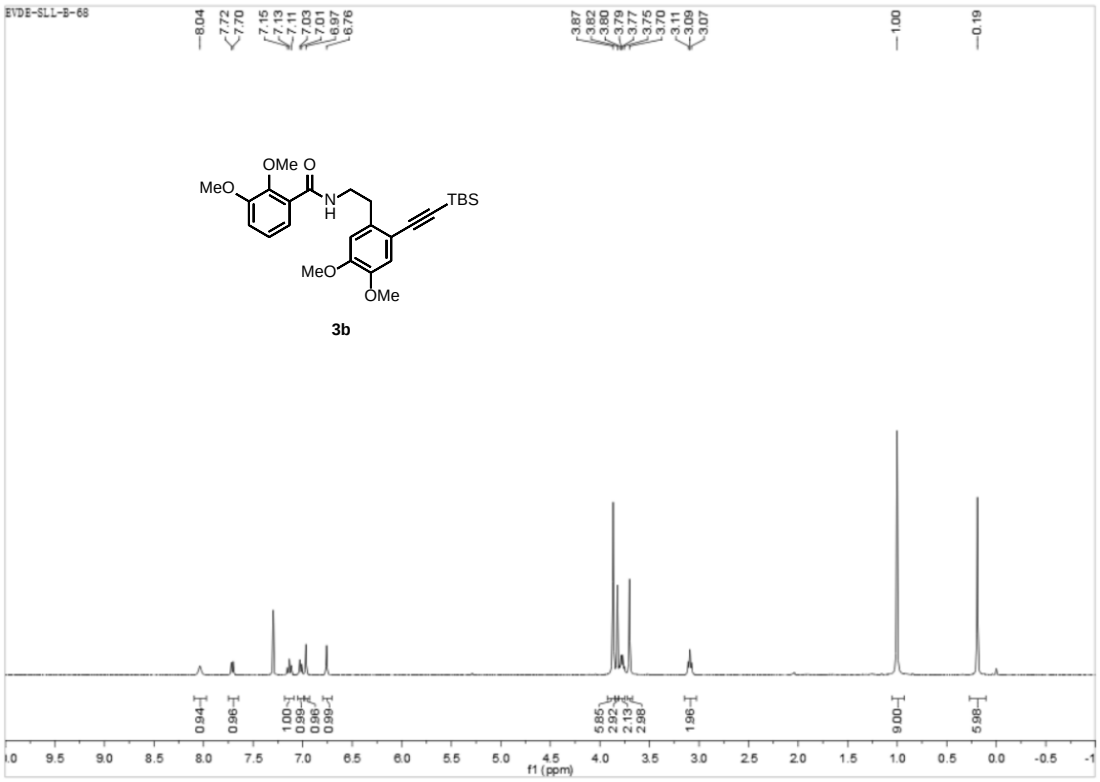
2y


EVDE-SLL-52-2
8.70
8.68
8.30
8.29
7.63
7.63
7.62
7.61
7.55
7.46
7.45
7.44
7.43
7.41
7.15
6.55
6.53
5.27
O
N
N
Ph
2z
2.01
0.98
3.02
1.00
3.09
1.06
1.00
2.00
f1 (ppm)

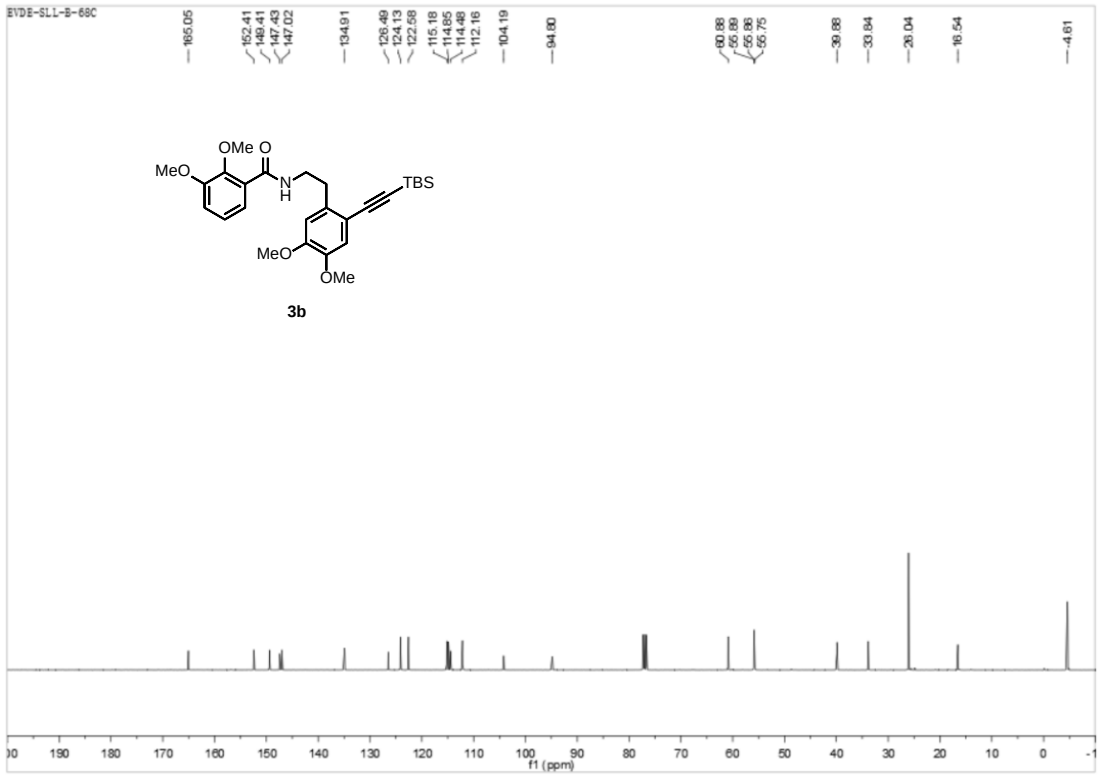

EVDe-SLL-52
159.57
149.06
145.56
140.06
137.91
133.93
133.38
130.94
129.62
129.64
128.91
128.46
128.16
124.28
123.12
52.02
O
N
N
Ph
2z
f1 (ppm)


4.93
4.91
1.03
0.26
TBS
3a
1.00
1.03
2.02
2.09
2.12
2.15
0.99
2.06
9.00
5.96
f1 (ppm)

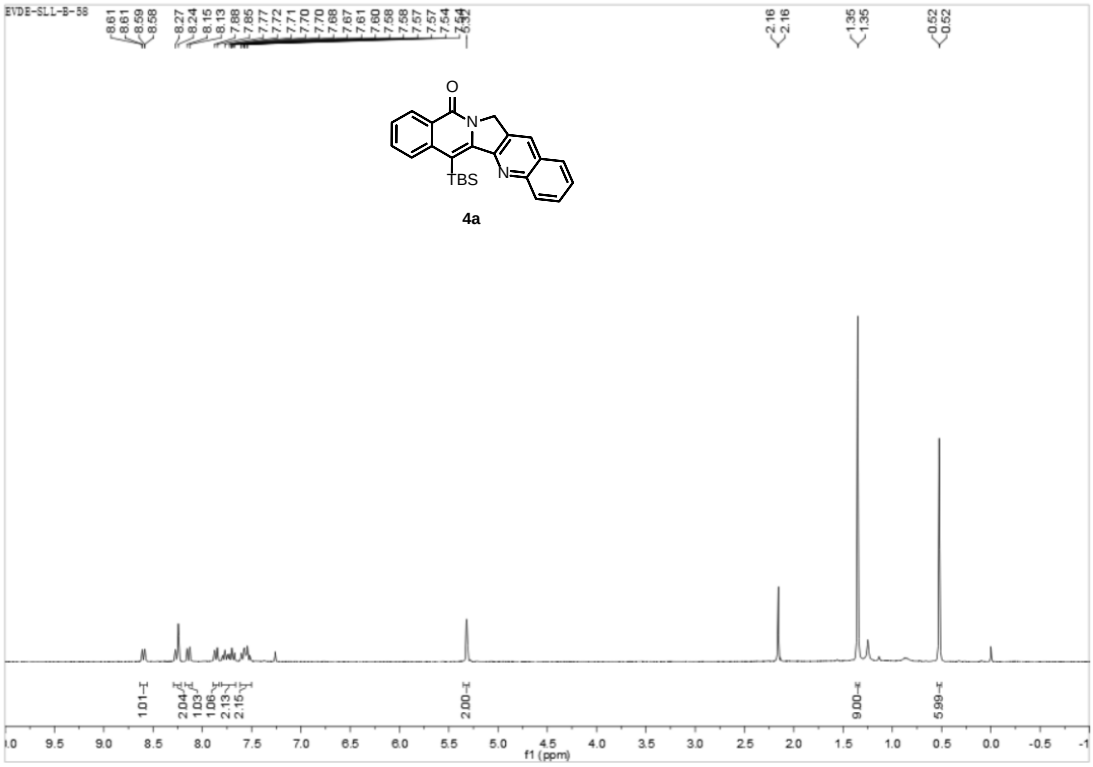

EVDE-SLL-B-55C
167.40
147.22
103.02
98.86
41.83
26.16
16.62
-4.70
-4.73
TBS
3a
f1 (ppm)


EVDE-SLL-B-68
8.04
7.72
7.70
7.15
7.13
7.11
7.03
7.01
6.97
6.76
3.87
3.82
3.80
3.79
3.77
3.75
3.70
3.11
3.09
3.07
1.00
0.19
OMe O
MeO
N
H
TBS
MeO
OMe
0.94
0.96
1.00
0.99
0.96
0.99
5.85
2.92
2.13
2.98
1.96
9.00
5.98
f1 (ppm)

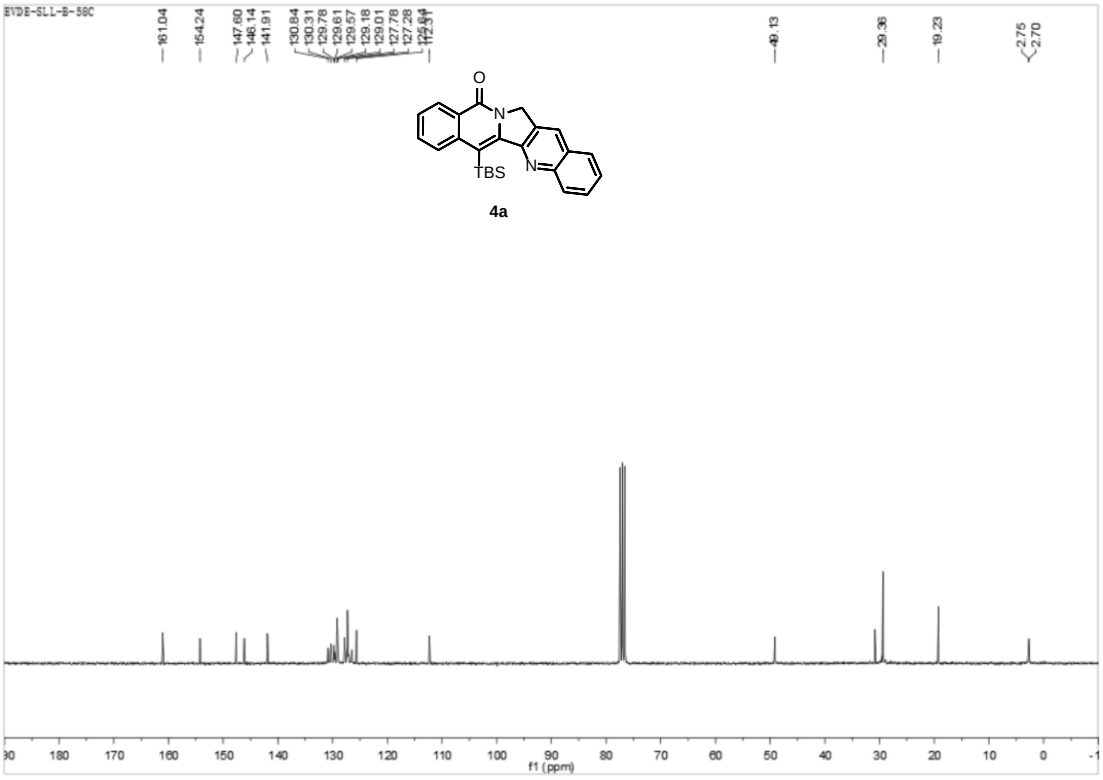
3b


EVDE-SLL-B-68C
165.05
152.41
149.41
147.43
147.02
134.91
126.49
124.13
122.58
115.18
114.85
114.48
112.16
104.19
94.80
60.88
55.89
55.86
55.75
39.88
33.84
26.04
16.54
-4.61
OMe O
MeO
N
H
TBS
MeO
OMe
f1 (ppm)

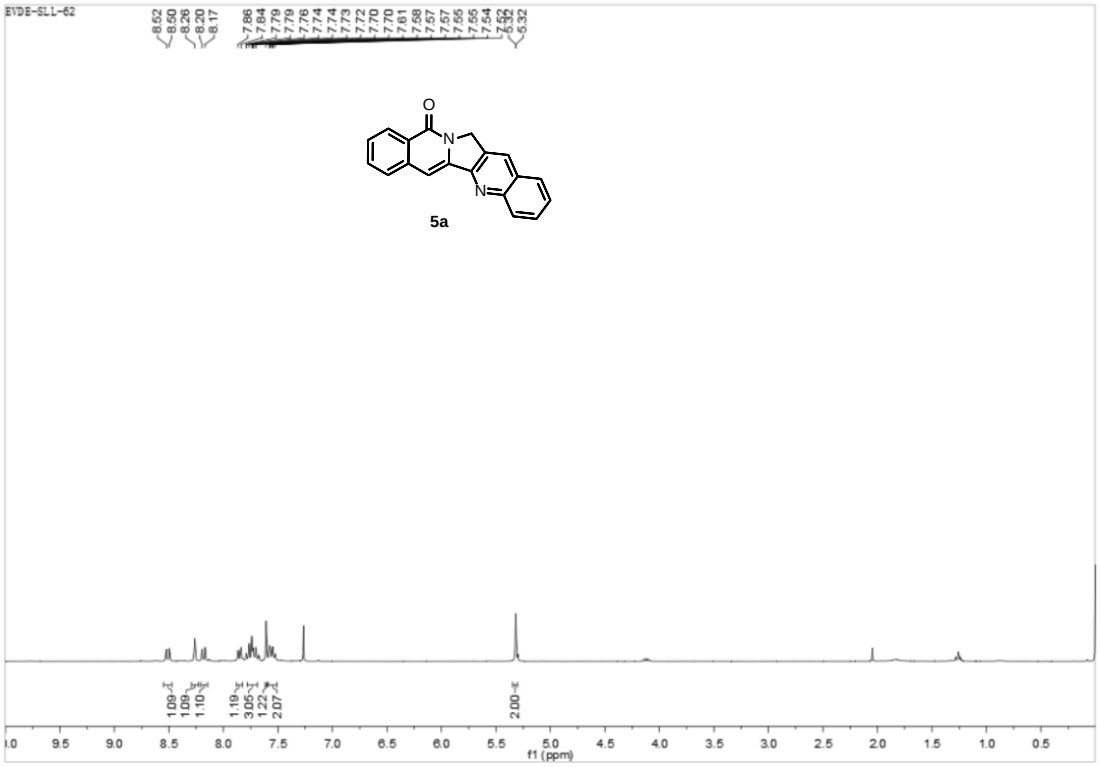
3b

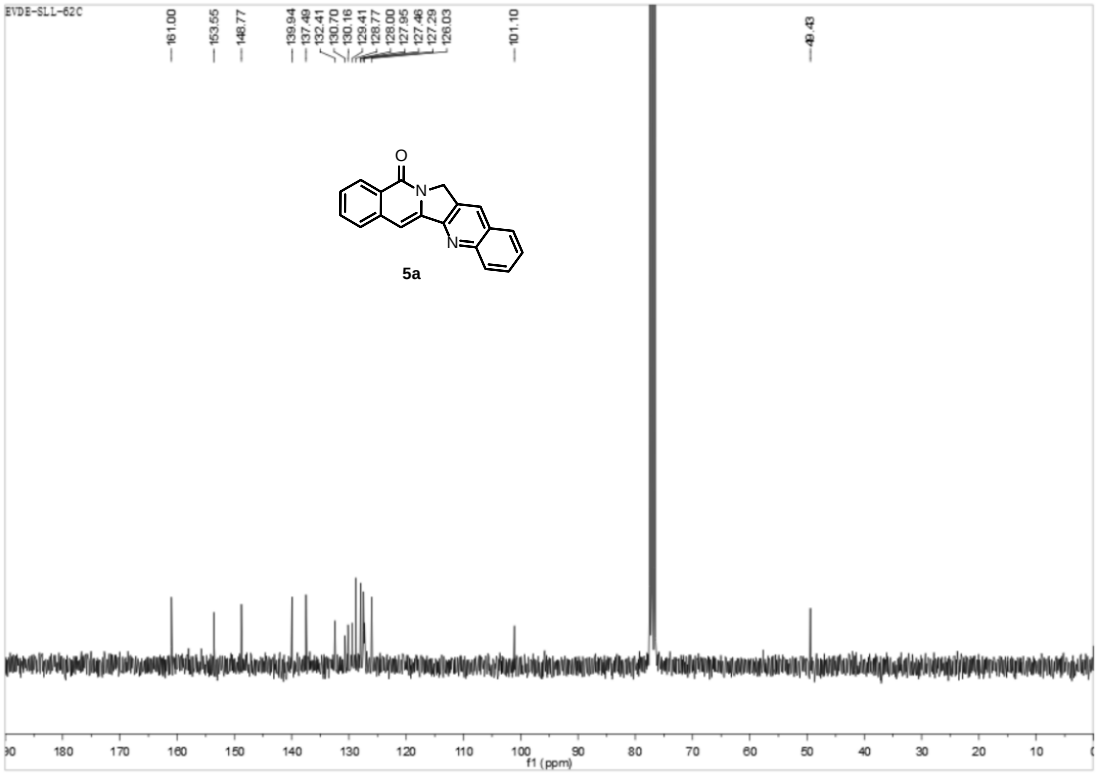

EVDE-SLL-B-58
8.61
8.61
8.59
8.58
8.27
8.24
8.15
8.13
7.88
7.85
7.77
7.72
7.71
7.70
7.70
7.68
7.67
7.61
7.60
7.58
7.58
7.57
7.57
7.54
7.54
5.32
2.16
2.16
1.35
1.35
0.52
0.52
O
N
TBS
N
1.01
2.04
1.03
1.06
2.13
2.15
2.00
9.00
5.99
f1 (ppm)

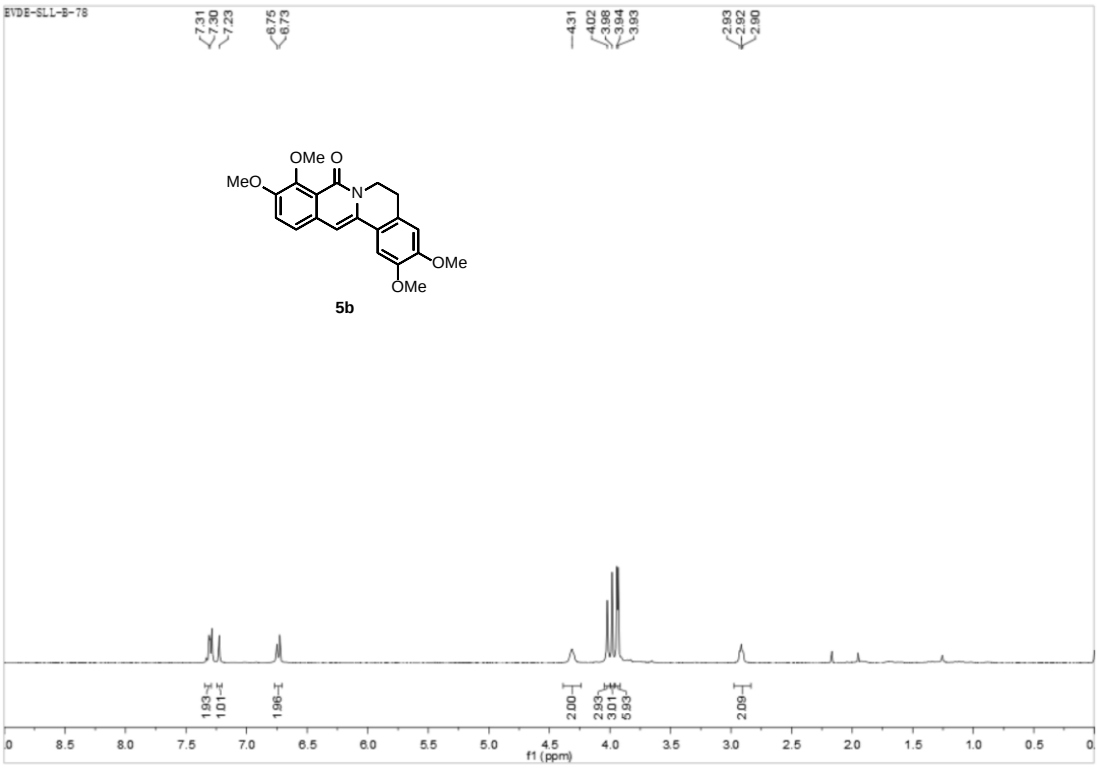
4a


EVDE-SLL-B-58C
161.04
154.24
147.60
146.14
141.91
130.84
130.31
129.78
129.61
129.57
129.18
129.01
127.78
127.28
112.61
112.31
49.13
29.36
19.23
2.75
2.70
O
N
TBS
N
f1 (ppm)

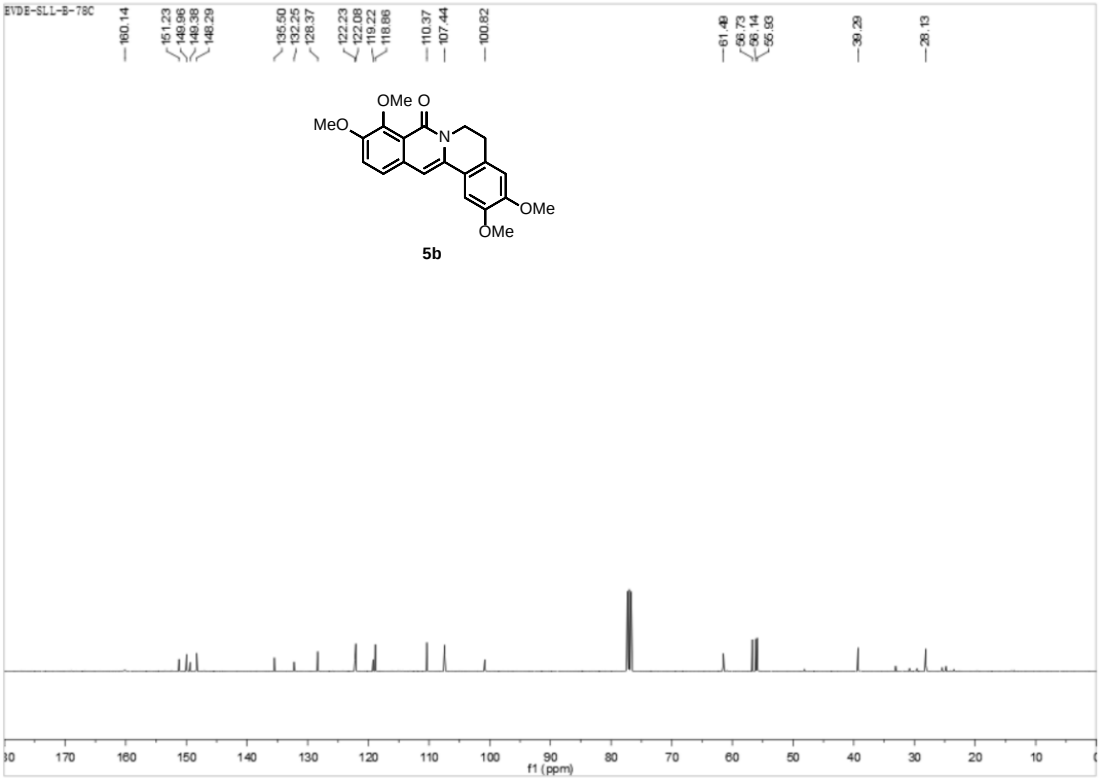
4a


EVDE-SLL-62
8.52
8.50
8.26
8.20
8.17
7.86
7.84
7.79
7.78
7.76
7.74
7.74
7.73
7.72
7.70
7.70
7.61
7.58
7.57
7.57
7.55
7.55
7.54
5.32
5.32
O
N
N
5a
1.09
1.09
1.10
1.19
3.05
1.22
2.07
2.00
f1 (ppm)


EVDE-SLL-62C
161.00
153.55
148.77
139.94
137.49
132.41
130.70
130.16
129.41
128.77
128.00
127.95
127.46
127.29
126.03
101.10
49.43
O
N
N
5a
f1 (ppm)


EVDE-SLL-B-78
7.31
7.30
7.23
6.75
6.73
4.31
4.02
3.98
3.94
3.93
2.93
2.92
2.90
OMe O
MeO
N
OMe
OMe
1.93
1.01
1.96
2.00
2.93
3.01
5.93
2.09
f1 (ppm)

5b


EVDE-SLL-B-78C
160.14
151.23
148.96
148.38
148.29
135.50
132.25
128.37
122.23
122.08
119.22
118.86
110.37
107.44
100.82
61.49
56.73
56.14
55.93
39.29
28.13
OMe O
MeO
N
OMe
OMe
f1 (ppm)

5b

5. References

1. P. C. Too and S. Chiba, *Chem. Commun.*, 2012, **48**, 7634-7636.

2. Y. H. Yang, W. X. Dai, Y. Z. Zhang, J. L. Petersen and K. K. Wang, *Tetrahedron*, 2006, **62**, 4364-4371.

3. J. H. Park, S. V. Bhilare and S. W. Youn, *Org. Lett.*, 2011, **13**, 2228-2231.

4. M. A. Ayedi, Y. L. Bigot, H. Ammar, S. Abid, R. E. Gharbi and M. Delmas, *Synthetic Communications*, 2013, **43**, 2127-2133.

5. J. Xuan, C. G. Daniliuc and A. Studer, *Org. Lett.*, 2016, **18**, 6372-6375.

6. X. You, X. Xie and Y. H. Liu, *Chem. Eur. J.*, 2016, **22**, 16765-16769.

7. L. A. Aronica, G. Albano, L. Giannotti and E. Meucci, *Eur. J. Org. Chem.*, 2017, 955-963.

8. K. Li, J. Ou and S. Gao, *Angew. Chem. Int. Ed.*, 2016, **55**, 14778-14783.

9. C. Ge, X. Zhang, P. Zhang, F. Guo and Q. Liu, *Inorganic Chemistry Communications*, 2003, **6**, 1061-1064.

10. W. Wei, Y. Liu, L. Ye, R. Lei, X. Zhang and M. Yan, *Org. Biomol. Chem.*, 2015, **13**, 817–824.

11. X.-X. Xu, Y. Liu and C.-M. Park, *Angew. Chem. Int. Ed.*, 2012, **51**, 9372-9376.