Supporting Information

Synthesis of cyclohexylidenehydrazines-fused polycyclics via photocatalytic radical cascade reaction of 2-ethynylaldehyde hydrazones

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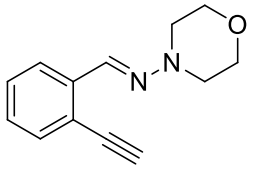
General Information: All reactions were carried out under Ar atmosphere unless otherwise noted. All catalysts and solvents were obtained from commercial suppliers. Reactions were monitored by TLC on silica gel plates (GF254), and the analytical thin-layer chromatography (TLC) was performed on precoated, glass-backed silica gel plates. ^{1}H NMR, ^{13}C NMR spectra and ^{19}F NMR spectra were recorded on 400 MHz spectrometer at room temperature. Chemical shifts (δ) are reported in ppm downfield from tetramethylsilane. High resolution mass spectra were obtained on a high–resolution mass spectrometer in the ESI mode.

General procedures for the synthesis of starting 2-ethynylhydrazones.[1,2]

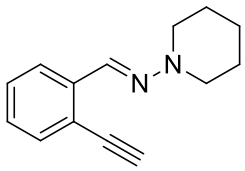
1) To a solution of the corresponding 2-bromobenzaldehyde (2 mmol, 1 equiv), $PdCl_2(PPh_3)_2$ (2 mol%), and CuI (2 mol%) in NEt_3 (0.25 M) was added the trimethylsilylacetylene (1.2 equiv). The resulting mixture was heated under Ar atmosphere at 50 ℃ for 6-18 hours. After the reaction was finished, the crude mixture was purified by silica gel column chromatography (hexane/EtOAc = 10/1).

2) 2-alkynylbenzaldehyde derivatives in methanol (10 mL) was reacted with K_2CO_3 (0.1 equiv), the crude mixture was purified by silica gel column chromatography (hexane/EtOAc = 10/1).

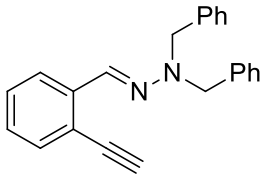
3) A mixture of hydrazine (1.2 equiv), 2-alkynylbenzaldehyde derivatives (1 equiv) and anhydrous $MgSO_4$ (5 equiv) in CH_2Cl_2 (10 mL) was stirred overnight at room temperature. After filtration of $MgSO_4$, CH_2Cl_2 was removed under reduced pressure and the residue was subjected to column chromatography to give the desired product.



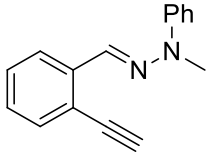
*(E)-N-(2-ethynylbenzylidene)morpholin-4-amine (**1a**).* Yellow solid; (0.36g, 85%); mp: 78-80 ºC; R_f = 0.35 (petroleum ether/ethyl acetate 10:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.06 (s, 1H), 7.95 (d, *J* = 8.0 Hz, 1H), 7.49-7.47 (m, 1H), 7.35-7.31 (m, 1H), 7.24-7.20 (m, 1H), 3.90 (t, *J* = 4.8 Hz, 4H), 3.33 (s, 1H), 3.22 (t, *J* = 4.8 Hz, 4H) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 137.5, 134.0, 133.0, 129.0, 127.7, 124.2, 120.5, 82.1, 81.4, 66.4, 51.7 ppm. ESI-HRMS: m/z Calcd for $C_{13}H_{14}N_2O+H^+$:215.1179, found 215.1176.



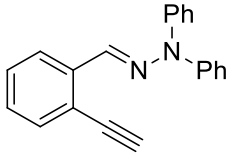
*(E)-N-(2-ethynylbenzylidene)piperidin-1-amine (**1b**).* Yellow oil; (0.356 g, 84%); R_f = 0.45 (petroleum ether/ethyl acetate 20:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.99 (s, 1H), 7.94 (d, *J* = 7.6 Hz, 1H), 7.46-7.44 (m, 1H), 7.32-7.29 (m, 1H), 7.19-7.15 (m, 1H), 3.32 (s, 1H), 3.20 (t, *J* = 6.0 Hz, 4H), 1.79-1.73 (m, 4H), 1.58-1.52 (m, 2H) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 138.4, 132.9, 132.2, 129.0, 127.1, 124.0, 120.0, 81.8, 81.6, 51.9, 25.1, 24.1 ppm. ESI-HRMS: m/z Calcd for $C_{14}H_{16}N_2+H^+$:213.1386, found 213.1389.



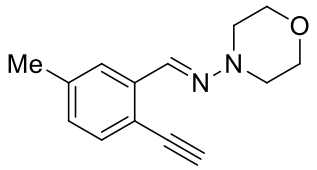
*(E)-1,1-dibenzyl-2-(2-ethynylbenzylidene)hydrazine (**1c**).* Yellow solid; (0.52 g, 81%); mp: 135-137 °C; R_f = 0.35 (petroleum ether/ethyl acetate 10:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.95 (dd, *J* = 7.6 Hz, *J* = 0.4 Hz, 1H), 7.67 (s, 1H), 7.37-7.35 (m, 1H), 7.31-7.28 (m, 9H), 7.26-7.23 (m, 2H), 7.13-7.09 (m, 1H), 3.89 (t, *J* = 4.8 Hz, 4H), 4.55 (s, 3H), 3.00 (s, 1H) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 138.8, 137.5, 132.6, 130.3, 128.8, 127.7, 127.2, 126.5, 123.5, 119.6, 81.6, 81.3, 58.2 ppm; ESI-HRMS: m/z Calcd for $C_{23}H_{20}N_2$+H^+:325.1699, found 325.1697.



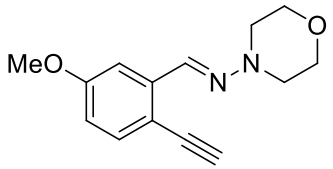
*(E)-2-(2-ethynylbenzylidene)-1-methyl-1-phenylhydrazine (**1d**).* Yellow solid; (0.346 g, 74%); mp: 136-138 °C; R_f = 0.47 (petroleum ether/ethyl acetate 20:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.10-8.08 (m, 1H), 7.95 (s, 1H), 7.50-7.48 (m, 1H), 7.41-7.38 (m, 2H), 7.35-7.30 (m, 3H), 7.24-7.17 (m, 1H), 6.97-6.93 (m, 1H), 3.45 (s, 3H), 3.37 (s, 1H) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 147.1, 138.4, 130.01, 129.99, 129.0, 127.1, 124.3, 120.9, 120.1, 115.5, 82.0, 81.7, 33.2 ppm. ESI-HRMS: m/z Calcd for $C_{16}H_{14}N_2$+H^+:235.1230, found 235.1233.



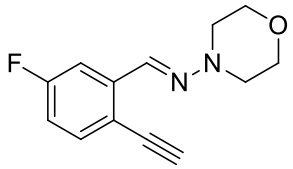
*(E)-2-(2-ethynylbenzylidene)-1,1-diphenylhydrazine (**1e**).* Yellow solid; (0.45 g, 76%); mp: 148-150 °C; R_f = 0.48 (petroleum ether/ethyl acetate 20:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.13 (d, *J* = 8.0 Hz, 1H), 7.68 (s, 1H), 7.44-7.34 (m, 6H), 7.24-7.16 (m, 7H), 3.02 (s, 1H) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 143.5, 137.8, 133.9, 132.8, 129.8, 128.9, 127.5, 124.6, 124.5, 122.4, 120.5, 81.7, 81.0 ppm; ESI-HRMS: m/z Calcd for $C_{21}H_{16}N_2$+H^+:297.1386, found 297.1385.



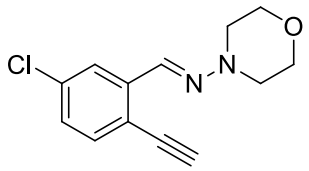
*(E)-N-(2-ethynyl-5-methylbenzylidene)morpholin-4-amine (**1f**).* Yellow solid; (0.374 g, 82%); mp: 85-87 °C; R_f = 0.33 (petroleum ether/ethyl acetate 10:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.04 (s, 1H), 7.61 (s, 1H), 7.37 (d, *J* = 7.6 Hz, 1H), 7.05-7.03 (m, 1H), 3.90 (t, *J* = 4.8 Hz, 4H), 3.39 (s, 1H), 3.22 (t, *J* = 4.8 Hz, 4H) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 139.1, 137.2, 134.3, 132.9, 128.9, 124.6, 117.8, 81.6, 81.4, 66.4, 51.7, 21.5 ppm. ESI-HRMS: m/z Calcd for $C_{14}H_{16}N_2O$+H^+:229.1335, found 229.1337.



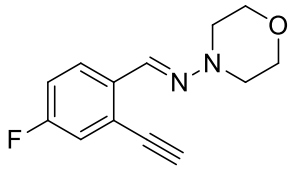
*(E)-N-(2-ethynyl-5-methoxybenzylidene)morpholin-4-amine (**1g**).* Yellow solid; (0.356 g, 73%); mp: 89-91 °C; R_f = 0.31 (petroleum ether/ethyl acetate 10:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.02 (s, 1H), 7.46 (d, *J* = 2.8 Hz, 1H), 7.39 (d, *J* = 8.4 Hz,, 1H), 6.80-6.78 (m, 1H), 3.90 (t, *J* = 4.8 Hz, 4H), 3.84 (s, 1H), 3.26 (s, 1H), 3.22 (t, *J* = 4.8 Hz, 4H) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 160.1, 139.1, 134.3, 133.8, 111.5, 113.1, 107.6, 81.5, 80.8, 66.4, 55.3, 51.7 ppm. ESI-HRMS: m/z Calcd for $C_{14}H_{16}N_2O_2$+H^+:245.1285, found 245.1287.



*(E)-N-(2-ethynyl-5-fluorobenzylidene)morpholin-4-amine (**1h**).* Yellow solid; (0.362 g, 78%); mp: 83-85 °C; R_f = 0.35 (petroleum ether/ethyl acetate 10:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.95 (d, *J* = 2.0 Hz, 1H), 7.65-7.62 (m, 1H), 7.46-7.43 (m, 1H), 6.94-6.89 (m, 1H), 3.89 (t, *J* = 4.8 Hz, 4H), 3.30 (s, 3H), 3.23 (t, *J* = 4.8 Hz, 4H) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 162.9 (d, *J* = 248.7 Hz), 140.2 (d, *J* = 8.7 Hz), 134.8 (d, *J* = 8.7 Hz), 133.2, 116.3, 115.1 (d, *J* = 23.1 Hz), 110.7 (d, *J* = 23.1 Hz), 81.7, 80.5, 66.3, 51.5 ppm; ^{19}F NMR (376 MHz, $CDCl_3$): -109.66 ppm. ESI-HRMS: m/z Calcd for $C_{13}H_{13}FN_2O$+H^+:233.1085, found 233.1083.

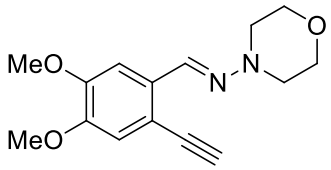


*(E)-N-(5-chloro-2-ethynylbenzylidene)morpholin-4-amine (**1i**).* Yellow solid; (0.4 g, 81%); mp: 91-93 °C; R_f = 0.31 (petroleum ether/ethyl acetate 10:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.94 (d, *J* = 2.4 Hz, 1H), 7.92 (s, 1H), 7.39 (d, *J* = 8.4 Hz, 1H), 7.18-7.16 (m, 1H), 3.89 (t, *J* = 4.8 Hz, 4H), 3.36 (s, 3H), 3.23 (t, *J* = 4.8 Hz, 4H) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 139.2, 135.3, 134.1, 131.9, 127.7, 124.2, 118.6, 82.9, 80.5, 66.3, 51.5 ppm. ESI-HRMS: m/z Calcd for $C_{13}H_{13}ClN_2O$+H^+:249.0789, found 249.0791.

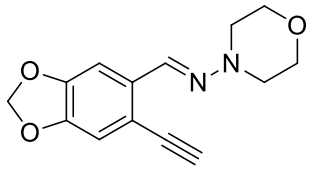


*(E)-N-(2-ethynyl-4-fluorobenzylidene)morpholin-4-amine (**1j**).* Yellow solid; (0.357 g, 77%); mp: 88-90 °C; R_f = 0.34 (petroleum ether/ethyl acetate 10:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.98 (s, 1H), 7.95-7.92 (m, 1H), 7.17-7.14 (m, 1H), 7.07-7.02 (m, 1H), 3.89 (t, *J* = 4.8 Hz, 4H), 3.37 (s, 3H), 3.20 (t, *J* = 4.8 Hz, 4H) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 161.8 (d, *J*=246.7 Hz), 134.1, 132.9, 126.3 (d, *J* = 8.7 Hz), 121.8 (d, *J* = 9.1 Hz), 119.1 (d, *J* = 23.1 Hz), 116.9 ((d, *J* = 22.5 Hz),

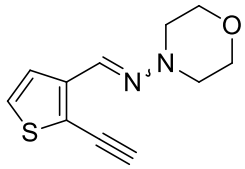
83.0, 80.2, 66.4, 51.7 ppm; δ ^{19}F NMR (376 MHz, $CDCl_3$): -113.64 ppm. ESI-HRMS: m/z Calcd for $C_{13}H_{13}FN_2O+H^+$:233.1085, found 233.1087.



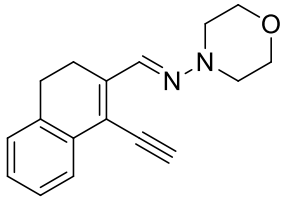
(E)-N-(2-ethynyl-4,5-dimethoxybenzylidene)morpholin-4-amine ***(1k)***. Yellow solid; (0.462 g, 84 %); mp: 103-105 °C; R_f = 0.30 (petroleum ether/ethyl acetate 10:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.02 (s, 1H), 7.46 (s, 1H), 6.93 (s, 1H), 3.94 (s, 3H), 3.90 (t, *J* = 4.8 Hz, 4H), 3.89(s, 3H), 3.28 (s, 1H), 3.22 (t, *J* = 4.8 Hz, 4H) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 150.1， 148.9，134.5, 131.6, 114.4, 113.1, 106.2, 81.4, 80.9, 66.5, 55.93, 55.89， 51.89 ppm. ESI-HRMS: m/z Calcd for $C_{15}H_{18}N_2O_3+H^+$:275.1390, found 275.1393.



(E)-N-((6-ethynylbenzo[d][1,3]dioxol-5-yl)methylene)morpholin-4-amine ***(1l)***. Yellow solid; (0.408 g, 79%); mp: 122-123 °C; R_f = 0.31 (petroleum ether/ethyl acetate 10:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.00 (s, 1H), 7.41 (s, 1H), 6.88 (s, 1H), 5.97 (s, 2H), 3.89 (t, *J* = 4.8 Hz, 4H), 3.26 (s, 3H), 3.18 (t, *J* = 4.8 Hz, 4H) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 148.9, 147.3, 133.6, 114.4, 111.7, 104.0, 101.5, 81.4, 80.9, 66.4, 51.8 ppm. ESI-HRMS: m/z Calcd for $C_{14}H_{14}N_2O_3+H^+$:259.1077, found 259.1010.



N-((2-ethynylthiophen-3-yl)methylene)morpholin-4-amine ***(1m)***. Yellow solid; (0.317 g, 72%); R_f = 0.35 (petroleum ether/ethyl acetate 10:1); (Z/E mixture; 0.36:1); Major: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.46 (d, *J* = 1.2 Hz, 1H), 7.43-7.42 (m, 1H), 7.11 (d, *J* = 5.2 Hz, 1H), 3.92 (t, *J* = 4.8 Hz, 4H), 3.42 (s, 1H), 2.82 (t, *J* = 4.8 Hz, 4H) ppm; Minor: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.88 (s, 1H), 7.08 (d, *J* = 0.4 Hz, 1H), 7.01 (d, *J* = 5.2 Hz, 1H), 3.88 (t, *J* = 4.8 Hz, 4H), 3.29 (s, 1H), 3.19 (t, *J* = 4.8 Hz, 4H) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 151.5, 134.2, 131.4, 130.1, 129.5, 129.4, 126.4, 124.4, 83.1, 81.3, 66.4 66.3, 54.9, 51.5 ppm; ESI-HRMS: m/z Calcd for $C_{11}H_{12}N_2OS+H^+$:221.0743, found 221.0746.

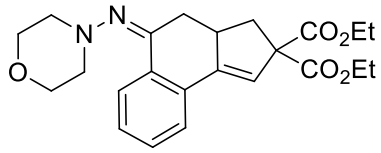


(E)-N-((1-ethynyl-3,4-dihydronaphthalen-2-yl)methylene)morpholin-4-amine ***(1n)***. Yellow solid; (0.426 g, 80%); mp: 132-135 °C; R_f = 0.31 (petroleum ether/ethyl acetate 10:1); ^{1}H NMR (400

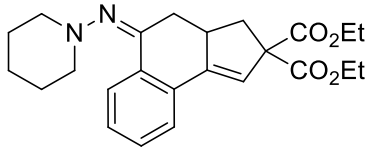
MHz, $CDCl_3$): δ = 8.04 (s, 1H), 7.67 (dd, *J* = 8.0 Hz, *J* = 0.8 Hz, 1H), 7.26-7.22 (m, 1H), 7.20-7.12 (m, 2H), 3.87 (t, *J* = 4.8 Hz, 4H), 3.53 (s, 1H), 3.18 (t, *J* = 4.8 Hz, 4H), 2.83-2.73 (m, 4H) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 148.9, 143.1 135.9, 135.7, 133.3, 127.6, 127.2, 126.6, 125.4, 118.5, 81.4, 79.6, 66.4, 51.5, 27.1, 22.3 ppm. ESI-HRMS: m/z Calcd for $C_{17}H_{18}N_2O+H^+$:267.1492, found 267.1495.

General Procedure for the visible-light photoredox-Catalyzed Cascade Annulation of Unsaturated α-Bromocarbonyls with hydrazones

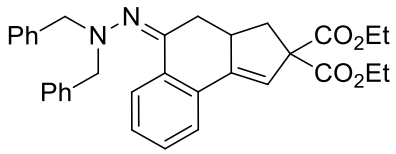
An oven-dried Schlenk tube (10 mL) was equipped with a magnetic stir bar, **1** (0.1 mmol), *fac*-Ir(ppy)$_3$ (0.02 equiv, 0.002 mmol), **2** (2 equiv, 0.2 mmol), Na_2HPO_4 (2 equiv, 0.2 mmol). The flask was evacuated and backfilled with Ar for 3 times. 1 mL CH_2Cl_2 was added with syringe under Ar. The tube was placed at a distance (app.5 cm) from 33w fluorescent light bulb, and the resulting solution was stirred at ambient temperature under visible-light irradiation. After the reaction was finished, the solvent was concentrated in vacuo and the residue was purified by chromatography on silica gel to afford the corresponding products **3**.



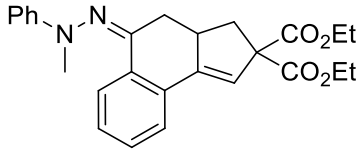
*(Z)-diethyl 5-(morpholinoimino)-3,3a,4,5-tetrahydro-2H-cyclopenta[a]naphthalene-2,2-dicarboxylate (**3aa**)*. Yellow solid; (36.7 mg, 89%); mp: 145-146 °C; R_f = 0.32 (petroleum ether/ethyl acetate 3:1); ^1H NMR (400 MHz, $CDCl_3$): δ = 8.11-8.09 (m, 1H), 7.63-7.61 (m, 1H), 7.38-7.34 (m, 1H), 7.32-7.27 (m, 1H), 6.22 (d, *J* = 2.4 Hz, 1H), 4.27-4.14 (m, 4H), 3.90-3.83 (m, 4H), 3.82-3.77 (m, 1H), 3.25-3.22 (m, 1H), 3.04-2.99 (m, 1H), 2.93-2.88 (m, 2H), 2.83-2.78 (m, 2H), 2.07 (dd, *J* = 12.8 Hz, *J* = 8.0 Hz, 1H), 1.95 (t, *J* = 9.6 Hz, 1H), 1.31-1.24 (m, 6H) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 171.3, 170.3, 161.4, 145.1, 132.6, 131.7, 130.0, 128.8, 125.7, 125.2, 120.1, 62.23, 62.16, 61.67, 61.65, 55.3, 42.0, 39.3, 33.7, 14.08, 14.05 ppm. ESI-HRMS: m/z Calcd for $C_{23}H_{28}N_2O_5+H^+$:413.2071, found 413.2074.



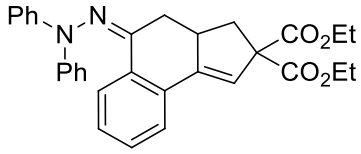
*(Z)-diethyl 5-(piperidin-1-ylimino)-3,3a,4,5-tetrahydro-2H-cyclopenta[a]naphthalene-2,2-dicarboxylate (**3ba**)*. Yellow oil; (34.0 mg, 83%); R_f = 0.35 (petroleum ether/ethyl acetate 3:1); ^1H NMR (400 MHz, $CDCl_3$): δ = 8.09 (dd, *J* = 8.0Hz, *J* = 1.2 Hz, 1H), 7.61 (d, *J* = 0.8 Hz, 1H), 7.59-7.26 (m, 2H), 6.02 (d, *J* = 2.4 Hz, 1H), 4.27-4.14 (m, 4H), 3.79-3.75 (m, 1H), 3.28-3.19 (m, 1H), 3.03-2.98 (m, 1H), 2.84-2.79 (m, 2H), 2.76-2.70 (m, 2H), 2.07 (dd, *J* = 13.2 Hz, *J* = 8.4 Hz, 1H), 1.95 (t, *J* = 14.0 Hz, 1H), 1.78-1.65 (m, 4H), 1.52-1.46 (m, 2H), 1.31-1.24 (m, 6H) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 171.4, 170.4, 160.2, 145.3, 133.0, 131.5, 129.6, 128.7, 125.7, 125.1, 119.8, 66.1, 61.62, 61.60, 56.4, 42.1, 39.4, 33.7, 25.3, 23.9, 14.07, 14.04 ppm. ESI-HRMS: m/z Calcd for $C_{24}H_{30}N_2O_4+H^+$:411.2278, found 411.2275.



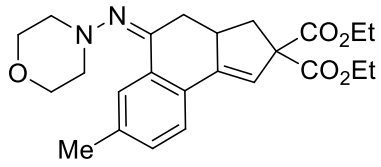
*(Z)-diethyl 5-(2,2-dibenzylhydrazono)-3,3a,4,5-tetrahydro-2H-cyclopenta[a]naphthalene-2,2-dicarboxylate (**3ca**).* Yellow solid; (45.4 mg, 87%); mp: 123-125 °C; R_f = 0.35 (petroleum ether/ethyl acetate 3:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.06 (dd, *J* = 7.6 Hz, *J* = 1.2 Hz, 1H), 7.54 (dd, *J* = 7.6 Hz, *J* = 1.2 Hz, 1H), 7.34-7.32 (m, 4H), 7.30-7.22 (m, 5H), 7.21-7.18 (m, 2H), 6.11 (d, *J* = 2.4 Hz, 1H), 4.24-4.12 (m, 4H), 4.00-3.92 (m, 4H), 3.84 (dd, *J* = 14.0 Hz, *J* = 5.2 Hz, 1H), 2.82 (dd, *J* = 12.8 Hz, *J* = 7.2 Hz, 1H), 2.54-2.45 (m, 1H), 1.86 (dd, *J* = 13.2 Hz, *J* = 7.2 Hz, 1H), 1.49 (d, *J* = 10.0 Hz, 1H), 1.31-1.23 (m, 6H) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 171.4, 170.3, 165.7, 145.2, 138.6, 132.5, 131.8, 130.0, 129.4, 128.6, 128.1, 127.0, 126.0, 125.1, 119.8, 66.0, 62.1, 61.6, 41.7, 39.3, 34.2, 14.09 ppm. ESI-HRMS: m/z Calcd for $C_{33}H_{34}N_2O_4$+H^+:523.2591, found 523.5294.



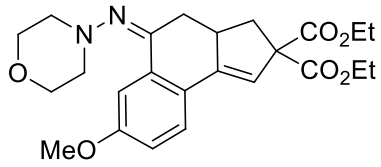
*(Z)-diethyl 5-(2-methyl-2-phenylhydrazono)-3,3a,4,5-tetrahydro-2H-cyclopenta[a]naphthalene-2,2-dicarboxylate (**3da**).* Yellow solid; (36.7 mg, 85%); mp: 133-135 °C; R_f = 0.33 (petroleum ether/ethyl acetate 3:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.29 (dd, *J* = 8.0 Hz, *J* = 0.8 Hz, 1H), 7.65 (dd, *J* = 8.0 Hz, *J* = 0.8 Hz, 1H), 7.42-7.38 (m, 1H), 7.36-7.32 (m, 1H), 7.29-7.25 (m, 2H), 6.97 (dd, *J* = 8.8 Hz, *J* = 0.8 Hz, 2H), 6.91 (t, *J* = 5.4 Hz, 1H), 6.24 (d, *J* = 2.4 Hz, 1H), 4.26-4.14 (m, 4H), 3.59 (dd, *J* = 15.2 Hz, *J* = 5.6 Hz, 1H), 3.28-3.21 (m, 1H), 3.18 (s, 3H), 2.96 (dd, *J* = 13.2 Hz, *J* = 7.6 Hz, 1H), 2.06-1.98 (m, 2H), 1.30-1.24 (m, 6H) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 171.3, 170.3, 163.1, 151.2, 145.0, 132.4, 131.9, 130.2, 128.9, 128.8, 126.0, 125.3, 120.29, 120.26, 115.5, 66.2, 61.7, 43.3, 41.9, 39.2, 34.8, 14.06 ppm. ESI-HRMS: m/z Calcd for $C_{26}H_{28}N_2O_4$+H^+:433.2122, found 433.2125.



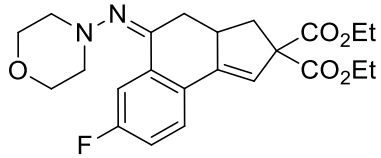
*(Z)-diethyl 5-(2,2-diphenylhydrazono)-3,3a,4,5-tetrahydro-2H-cyclopenta[a]naphthalene-2,2-dicarboxylate (**3ea**).* Yellow solid; (42.0 mg, 85%); mp: 113-115 °C; R_f = 0.33 (petroleum ether/ethyl acetate 3:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.38 (d, *J* = 8.0 Hz, 1H), 7.62 (d, *J* = 7.2 Hz, 1H), 7.40-7.25 (m, 6H), 7.11-7.04 (m, 5H), 6.19 (d, *J* = 2.0 Hz, 1H), 4.24-4.10 (m, 4H), 3.40 (dd, *J* = 7.6 Hz, *J* = 1.6 Hz, 1H), 3.23-3.16 (m, 1H), 2.88 (dd, *J* = 13.2 Hz, *J* = 7.2 Hz, 1H), 1.82 (dd, *J* = 13.2 Hz, *J* = 8.4 Hz, 1H), 1.56-1.49 (m, 1H), 1.26-1.24 (m, 6H) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 171.2, 170.2, 161.8, 148.4, 144.7, 132.5, 131.7, 130.0, 129.1, 128.8, 126.2, 125.3, 123.3, 121.3, 120.1, 66.1, 61.64, 61.58, 41.5, 39.3, 34.7, 14.02 ppm. ESI-HRMS: m/z Calcd for $C_{31}H_{30}N_2O_4$+H^+:495.2278, found 495.2275.



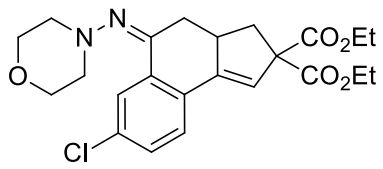
*(Z)-diethyl 7-methyl-5-(morpholinoimino)-3,3a,4,5-tetrahydro-2H-cyclopenta[a]naphthalene-2,2-dicarboxylate (**3fa**).* Yellow solid; (40.2 mg, 91%); mp: 133-135 °C; R_f = 0.33 (petroleum ether/ethyl acetate 3:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.89 (s, 1H), 7.52 (d, *J* = 8.0 Hz, 1H), 7.19-7.17 (m, 1H), 6.16 (d, *J* = 2.4 Hz, 1H), 4.26-4.14 (m, 4H), 3.91-3.82 (m, 4H), 3.81-3.77 (m, 1H), 3.26-3.17 (m, 1H), 3.03-2.98 (m, 1H), 2.93-2.88 (m, 2H), 2.83-2.78 (m, 2H), 2.36 (s, 3H), 2.04 (dd, *J* = 13.2 Hz, *J* = 8.4 Hz, 1H), 1.93 (t, *J* = 14.0 Hz, 1H), 1.31-1.24 (m, 6H) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 171.4, 170.4, 161.8, 145.0, 138.8, 132.3, 131.1, 129.1, 125.7, 125.2, 119.1, 66.2, 66.1, 61.6, 55.3, 42.1, 39.3, 33.6, 21.4, 14.04, 14.01 ppm. ESI-HRMS: m/z Calcd for $C_{24}H_{31}N_2O_5$+H^+:427.2227, found 427.2229.



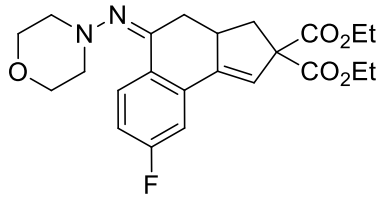
*(Z)-diethyl 7-methoxy-5-(morpholinoimino)-3,3a,4,5-tetrahydro-2H-cyclopenta[a]naphthalene-2,2-dicarboxylate (**3ga**).* Yellow solid; (40.7 mg, 92%); mp: 123-124 °C; R_f = 0.31 (petroleum ether/ethyl acetate 3:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.59 (d, *J* = 2.8 Hz, 1H), 7.54 (d, *J* = 8.4 Hz, 1H), 6.95-6.92 (m, 1H), 6.08 (d, *J* = 2.4 Hz, 1H), 4.26-4.13 (m, 4H), 3.91-3.82 (m, 4H), 3.79-3.74 (m, 1H), 3.25-3.16 (m, 1H), 3.02-2.97 (m, 1H), 2.94-2.88 (m, 2H), 2.83-2.78 (m, 2H), 2.04 (dd, *J* = 13.2 Hz, *J* = 8.4 Hz, 1H), 1.92 (t, *J* = 14.0 Hz, 1H), 1.31-1.24 (m, 6H) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 171.5, 170.5, 161.3, 159.8, 144.6, 133.9, 126.8, 125.0, 118.0, 117.9, 108.3, 66.2, 66.0, 61.6, 55.4, 55.3, 42.1, 39.2, 33.6, 14.05, 14.02 ppm. ESI-HRMS: m/z Calcd for $C_{24}H_{30}N_2O_6$+H^+:443.2177, found 443.2179.



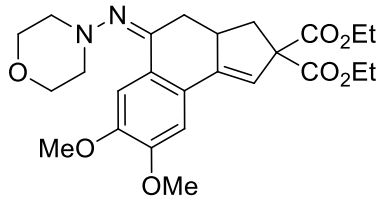
*(Z)-diethyl 7-fluoro-5-(morpholinoimino)-3,3a,4,5-tetrahydro-2H-cyclopenta[a]naphthalene-2,2-dicarboxylate (**3ha**).* Yellow solid; (37.4 mg, 87%); mp: 146-148 °C; R_f = 0.38 (petroleum ether/ethyl acetate 3:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.78 (dd, *J* = 10.0 Hz, *J* = 2.4 Hz, 1H), 7.59 (dd, *J* = 8.4 Hz, *J* = 5.6 Hz, 1H), 7.08-7.03 (m, 1H), 6.15 (d, *J* = 2.0 Hz, 1H), 4.27-4.14 (m, 4H), 3.91-3.81 (m, 4H), 3.75 (dd, *J* = 14.4 Hz, *J* = 5.2 Hz, 1H), 3.26-3.17 (m, 1H), 3.11 (dd, *J* = 13.2 Hz, *J* = 7.2 Hz, 1H), 2.94- 2.89 (m, 2H), 2.82-2.77 (m, 2H), 2.07 (dd, *J* = 13.2 Hz, *J* = 8.4 Hz, 1H), 1.94 (t, *J* = 14.0 Hz, 1H), 1.31-1.24 (m, 6H) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 171.2, 170.2, 162.8 (d, *J* = 246.7 Hz), 160.1, 144.0, 134.8 (d, *J* = 7.5 Hz), 128.0, 127.3 (d, *J* = 8.3 Hz), 119.7, 117.4 (d, *J* = 23.5 Hz), 111.8 (d, *J* = 17.8 Hz), 66.1, 61.7, 55.2, 41.9, 39.1, 33.5, 14.04, 14.01 ppm; ^{19}F NMR (376 MHz, $CDCl_3$): -111.44 ppm. ESI-HRMS: m/z Calcd for $C_{23}H_{27}FN_2O_5$+H^+:431.1977, found 431.1979.



*(Z)-diethyl 7-chloro-5-(morpholinoimino)-3,3a,4,5-tetrahydro-2H-cyclopenta[a]naphthalene-2,2-dicarboxylate (**3ia**).* Yellow solid; (36.1 mg, 81%); mp: 167-169 °C; R_f = 0.38 (petroleum ether/ethyl acetate 3:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.08 (d, *J* = 2.0 Hz, 1H), 7.54 (d, *J* = 8.4 Hz, 1H), 7.32-7.29 (m, 1H), 6.21 (d, *J* = 2.4 Hz, 1H), 4.27-4.14 (m, 4H), 3.91-3.81 (m, 4H), 3.77-3.73 (m, 1H), 3.26-3.17 (m, 1H), 3.04-2.99 (m, 1H), 2.94-2.89 (m, 2H), 2.83-2.78 (m, 2H), 2.06 (dd, *J* = 13.2 Hz, *J* = 8.4 Hz, 1H), 1.92 (t, *J* = 14.0 Hz, 1H), 1.31-1.24 (m, 6H) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 171.2, 170.1, 159.9, 144.0, 134.8, 134.0, 130.03, 129.96, 126.7, 125.5, 120.7, 66.2, 61.7, 55.3, 41.8, 39.2, 33.5, 14.03 ppm. ESI-HRMS: m/z Calcd for $C_{23}H_{27}ClN_2O_5$+H^+:447.1681, found 447.1683.

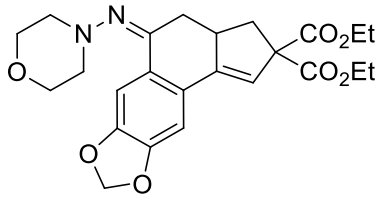


*(Z)-diethyl 8-fluoro-5-(morpholinoimino)-3,3a,4,5-tetrahydro-2H-cyclopenta[a]naphthalene-2,2-dicarboxylate (**3ja**).* Yellow solid; (37.0 mg, 86%); mp: 142-144 °C; R_f = 0.39 (petroleum ether/ethyl acetate 3:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.11 (dd, *J* = 8.8 Hz, *J* = 6.0 Hz, 1H), 7.26 (dd, *J* = 9.2 Hz, *J* = 2.4 Hz, 1H), 7.01-6.96 (m, 1H), 6.22 (d, *J* = 2.0 Hz, 1H), 4.27-4.15 (m, 4H), 3.90-3.84 (m, 4H), 3.82-3.77 (m, 1H), 3.27-3.22 (m, 1H), 3.02 (dd, *J* = 13.2 Hz, *J* = 7.2 Hz, 1H), 2.91- 2.86 (m, 2H), 2.81-2.76 (m, 2H), 2.07 (dd, *J* = 13.2 Hz, *J* = 8.4 Hz, 1H), 1.93 (t, *J* = 14.0 Hz, 1H), 1.31-1.25 (m, 6H) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 171.2, 170.2, 162.8 (d, *J* = 246.7 Hz), 160.1, 144.0, 134.8 (d, *J* = 7.5 Hz), 128.0, 127.3 (d, *J* = 8.3 Hz), 119.7, 117.4 (d, *J* = 23.5 Hz), 111.8 (d, *J* = 17.8 Hz), 66.1, 61.7, 55.2, 41.9, 39.1, 33.5, 14.04, 14.01 ppm; ^{19}F NMR (376 MHz, $CDCl_3$): -110.86 ppm. ESI-HRMS: m/z Calcd for $C_{23}H_{27}FN_2O_5$+H^+:431.1977, found 431.1975.

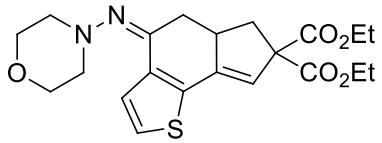


*(Z)-diethyl 7,8-dimethoxy-5-(morpholinoimino)-3,3a,4,5-tetrahydro-2H-cyclopenta[a]naphthalene-2,2-dicarboxylate (**3ka**).* Yellow solid; (39.2 mg, 83%); mp: 178-181 °C; R_f = 0.31 (petroleum ether/ethyl acetate 3:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.60 (s, 1H), 7.02 (s, 1H), 6.16 (d, *J* = 2.4 Hz, 1H), 4.28-4.13 (m, 4H), 3.96 (s, 3H), 3.94 (s, 3H), 3.88-3.84 (m, 4H), 3.82-3.77 (m, 1H), 3.26-3.17 (m, 1H), 3.02-2.96 (m, 1H), 2.91-2.86 (m, 2H), 2.81-2.76 (m, 2H), 2.04 (dd, *J* = 13.2 Hz, *J* = 8.4 Hz, 1H), 1.92 (t, *J* = 14.0 Hz, 1H), 1.32-1.25 (m, 6H) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 171.4, 170.4, 161.3, 150.9, 149.7, 145.1, 126.1, 125.4, 118.1, 107.1, 106.6, 66.3, 66.0, 61.6, 55.9, 55.3, 42.1, 39.3, 33.5, 14.06, 14.03 ppm. ESI-HRMS: m/z Calcd for $C_{25}H_{32}N_2O_7$+H^+:473.2282, found

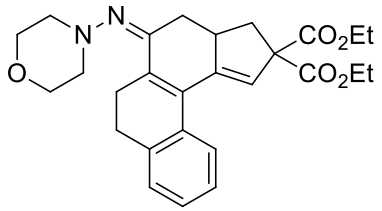
473.2285.



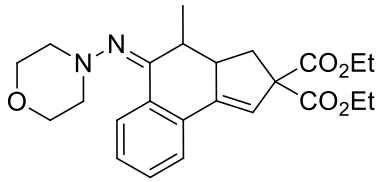
*(Z)-diethyl 5-(morpholinoimino)-3,3a,4,5-tetrahydro-2H-cyclopenta[5,6]naphtho[2,3-d][1,3]dioxole-2,2-dicarboxylate (**3la**).* Yellow solid; (37.4 mg, 82%); mp: 166-168 °C; R_f = 0.35 (petroleum ether/ethyl acetate 3:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.57 (s, 1H), 7.01 (s, 1H), 7.32-7.29 (m, 1H), 6.05 (d, *J* = 2.4 Hz, 1H), 5.97 (dd, *J* = 5.2 Hz, *J* = 1.2 Hz, 2H), 4.27-4.14 (m, 4H), 3.89-3.80 (m, 4H), 3.78-3.74 (m, 1H), 3.23-3.14 (m, 1H), 3.01-2.96 (m, 1H), 2.89-2.84 (m, 2H), 2.79-2.74 (m, 2H), 2.04 (dd, *J* = 13.2 Hz, *J* = 8.4 Hz, 1H), 1.90 (t, *J* = 14.0 Hz, 1H), 1.31-1.24 (m, 6H) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 171.4, 170.4, 161.2, 149.5, 148.6, 145.0, 127.9, 127.1, 118.8, 105.0, 104.2, 101.4, 66.2, 65.9, 61.6, 55.3, 41.9, 39.2, 33.4, 14.05, 14.03 ppm. ESI-HRMS: m/z Calcd for $C_{24}H_{28}N_2O_7$+H^+:457.1969, found 457.1971.



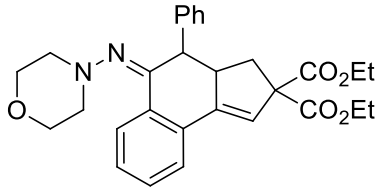
*(Z)-diethyl 4-(morpholinoimino)-5a,6-dihydro-4H-indeno[4,5-b]thiophene-7,7(5H)-dicarboxylate (**3ma**).* Yellow solid; (31.3 mg, 75%); mp: 131-133 °C; R_f = 0.37 (petroleum ether/ethyl acetate 3:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.27 (d, *J* = 5.2 Hz, 1H), 7.15 (d, *J* = 5.2 Hz, 1H), 5.98 (d, *J* = 2.4 Hz, 1H), 4.27-4.14 (m, 4H), 3.88-3.79 (m, 4H), 3.70 (dd, *J* = 15.2 Hz, *J* = 5.6 Hz, 1H), 2.97 (dd, *J* = 13.2 Hz, *J* = 7.2 Hz, 1H), 2.91-2.86 (m, 1H), 2.83-2.76 (m, 2H), 2.79-2.74 (m, 2H), 2.01 (dd, *J* = 13.2 Hz, *J* = 9.2 Hz, 1H), 1.99 (t, *J* = 4.8 Hz, 1H), 1.30-1.24 (m, 6H) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 171.1, 170.2, 160.1 , 142.2, 139.1, 132.8, 128.1, 123.4, 120.4, 66.6, 61.7, 55.0, 42.7, 39.6, 38.8, 14.04 ppm; ESI-HRMS: m/z Calcd for $C_{21}H_{26}N_2O_5S$+H^+:419.1635, found 419.1638.



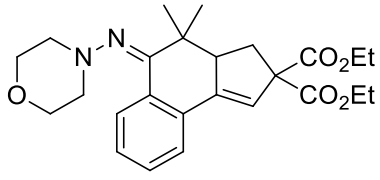
*(Z)-diethyl 5-(morpholinoimino)-3,3a,4,5,6,7-hexahydro-2H-cyclopenta[c]phenanthrene-2,2-dicarboxylate (**3na**).* Yellow solid; (35.3 mg, 76%); mp: 111-113 °C; R_f = 0.37 (petroleum ether/ethyl acetate 3:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.65 (dd, *J* = 6.4 Hz, *J* = 1.2 Hz, 1H), 7.24-7.22 (m, 3H), 6.07 (d, *J* = 1.2 Hz, 1H), 4.29-4.16 (m, 4H), 3.88-3.81 (m, 4H), 3.67 (dd, *J* =15.2 Hz, *J* = 6.4 Hz, 1H), 3.20-3.16 (m, 1H), 3.15-3.09 (m, 1H), 2.90-2.85 (m, 3H), 2.76-2.67 (m, 4H), 2.35-2.26 (m, 1H), 2.17 (dd, *J* = 13.6 Hz, *J* = 7.6 Hz, 1H), 2.04-1.96 (m, 1H), 1.33-1.24 (m, 6H) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 171.2, 171.1, 162.9, 143.0, 138.7, 136.0, 133.4, 133.2, 127.8, 127.5, 126.5, 126.1, 123.5, 66.8, 66.3, 61.72, 61.68, 55.2, 42.9, 37.8, 34.6, 28.0, 22.9, 14.12, 14.06 ppm; ESI-HRMS: m/z Calcd for $C_{27}H_{32}N_2O_5$+H^+:465.2384, found 465.2387.



*(Z)-diethyl 4-methyl-5-(morpholinoimino)-3,3a,4,5-tetrahydro-2H-cyclopenta[a]naphthalene-2,2-dicarboxylate (**3ab**).* Yellow solid; (31.1 mg, 73%); dr= 5:1; mp: 134-136 °C; R_f = 0.35 (petroleum ether/ethyl acetate 3:1); ^{1}H NMR (400 MHz, $CDCl_3$) date of the major isomer: δ = 8.00 (dd, *J* = 8.0 Hz, *J* = 1.2 Hz, 1H), 7.64 (d, *J* = 7.6 Hz, 1H), 6.29 (d, *J* = 2.0 Hz, 1H), 4.33-4.08 (m, 4H), 3.89-3.81 (m, 4H), 3.79 (dd, *J* = 8.0 Hz, *J* = 1.2 Hz, 1H), 3.44-3.35 (m, 1H), 2.85-2.82 (m, 4H), 2.78-2.76 (m, 1H), 2.77 (dd, *J* = 13.6 Hz, *J* = 8.8 Hz, 1H), 1.34-1.22 (m, 6H), 0.88 (d, *J* = 6.8 Hz, 1H) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 171.4, 170.5, 169.2, 142.8, 131.4, 130.0, 129.0, 126.8, 124.8, 121.5, 66.2, 61.7, 61.6, 56.0, 55.3, 46.3, 33.7, 32.03, 14.05, 11.5 ppm. ESI-HRMS: m/z Calcd for $C_{24}H_{30}N_2O_5$+H^+:427.2227, found 427.2225.

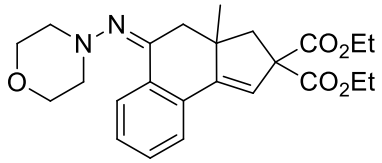


*(Z)-diethyl 5-(morpholinoimino)-4-phenyl-3,3a,4,5-tetrahydro-2H-cyclopenta[a]naphthalene-2,2-dicarboxylate (**3ac**).* Yellow solid; (17.1 mg, 35%); dr= 4:1; mp: 188-189 °C; R_f = 0.32 (petroleum ether/ethyl acetate 3:1); ^{1}H NMR (400 MHz, $CDCl_3$) date of the major isomer: δ = 8.17 (dd, *J* = 8.0 Hz, *J* = 1.2 Hz, 1H), 7.56 (dd, *J* = 8.0 Hz, *J* = 1.2 Hz, 1H), 7.48-7.34 (m, 3H), 7.27-7.24 (m, 2H), 7.18-7.13 (m, 3H), 6.14 (d, *J* = 2.4 Hz, 1H), 4.32-4.08 (m, 4H), 3.85-3.74 (m, 1H), 3.45-3.40 (m, 2H), 3.35-3.30 (m, 2H), 3.29-3.24 (m, 1H), 2.76 (dd, *J* = 13.6 Hz, *J* = 7.6 Hz, 1H), 2.54-2.49 (m, 2H), 2.31 (dd, *J* = 14.0 Hz, *J* = 7.6 Hz, 1H), 2.20-2.18 (m, 2H), 1.31-1.21 (m, 6H) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 171.4, 170.5, 169.2, 142.8, 131.4, 130.0, 129.0, 126.8, 124.8, 121.5, 66.2, 61.7, 61.6, 56.0, 55.3, 46.3, 33.7, 32.03, 14.05, 11.5 ppm. ESI-HRMS: m/z Calcd for $C_{29}H_{32}N_2O_5$+H^+:489.2384, found 489.2387.

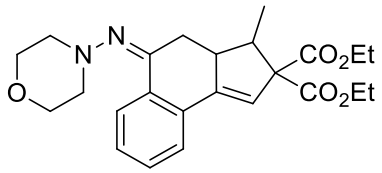


*(Z)-diethyl 4,4-dimethyl-5-(morpholinoimino)-3,3a,4,5-tetrahydro-2H-cyclopenta[a]naphthalene-2,2-dicarboxylate (**3ad**).* Yellow solid; (40.0 mg, 91%); mp: 133-135 °C; R_f = 0.34 (petroleum ether/ethyl acetate 3:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.65-8.62 (m, 1H), 7.69-7.67 (m, 1H), 7.31-7.24 (m, 2H), 6.29 (d, *J* = 2.8 Hz, 1H), 4.31-4.11 (m, 4H), 3.71-3.69 (m, 4H), 3.10-3.05 (m, 1H), 2.84-2.79 (m, 2H), 2.76-2.73 (m, 1H), 2.73-2.68 (m, 2H), 2.13 (dd, *J* = 13.2 Hz, *J* = 9.6 Hz, 2H), 1.31-1.25 (m, 6H), 1.19 (s, 3H), 0.79 (s, 3H) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 171.4, 170.4, 161.5, 144.2, 130.9, 129.5, 129.2, 128.1, 124.8, 121.3, 66.3, 65.4, 61.64, 61.57, 55.1, 53.3, 41.3, 33.0,

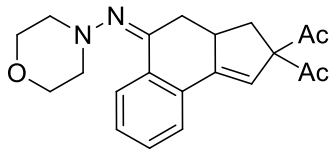
24.1, 18.5, 14.04 ppm. ESI-HRMS: m/z Calcd for $C_{25}H_{32}N_2O_5$+H^+:441.2384, found 441.2387.



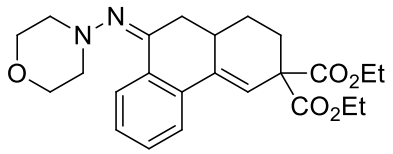
*(Z)-diethyl 3a-methyl-5-(morpholinoimino)-3,3a,4,5-tetrahydro-2H-cyclopenta[a]naphthalene-2,2-dicarboxylate (**3ae**).* Yellow solid; (35.4 mg, 83%); mp: 114-115 °C; R_f = 0.35 (petroleum ether/ethyl acetate 3:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.14 (dd, *J* = 8.0 Hz, *J* = 0.8 Hz, 1H), 7.60 (dd, *J* = 7.6 Hz, *J* = 0.8 Hz, 1H), 7.39-7.34 (m, 1H), 7.32-7.28 (m, 1H), 6.07 (s, 1H), 4.29-4.19 (m, 4H), 3.90-3.81 (m, 4H), 3.78 (d, *J* = 14.4 Hz, 1H), 2.91-2.86 (m, 2H), 2.81-2.76 (m, 2H), 2.73 (d, *J* = 13.6 Hz, 1H), 2.45 (d, *J* = 13.6 Hz, 2H), 2.17 (d, *J* = 14.8 Hz, 1H), 1.31-1.26 (m, 6H), 1.11 (s, 3H) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 171.4, 170.9, 161.2, 149.3, 131.7, 131.7, 131.0, 130.1, 128.6, 125.8, 125.5, 119.0, 62.2, 61.8, 61.7, 46.3, 46.2, 40.9, 25.2, 14.03 ppm. ESI-HRMS: m/z Calcd for $C_{24}H_{30}N_2O_5$+H^+:427.2227, found 427.2229.



*(Z)-diethyl 3-methyl-5-(morpholinoimino)-3,3a,4,5-tetrahydro-2H-cyclopenta[a]naphthalene-2,2-dicarboxylate (**3af**).* Yellow solid; (30.7 mg, 72%); dr= 3:1; mp: 128-129 °C; R_f = 0.35 (petroleum ether/ethyl acetate 3:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.01 (dd, *J* = 8.0 Hz, *J* = 0.8 Hz, 1H), 7.64 (d, *J* = 7.6 Hz, 1H), 7.36 (dd, *J* = 7.6 Hz, *J* = 1.2 Hz, 1H), 7.29 (dd, *J* = 7.6 Hz, *J* = 0.8 Hz, 1H), 6.29 (d, *J* = 2.0 Hz, 1H), 4.28-4.12 (m, 4H), 3.89-3.84 (m, 4H), 3.82-3.78 (m, 1H), 3.68 (t, *J* = 4.4 Hz, 1H), 3.41-3.35 (m, 1H), 2.87-2.82 (m, 4H), 2.80-2.76 (m, 1H), 2.27 (dd, *J* = 13.6 Hz, *J* = 8.8 Hz, 1H), 1.31-1.25 (m, 6H), 0.88 (d, *J* = 7.6 Hz, 3H) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 171.4, 170.5, 169.2, 142.8, 131.4, 130.0, 129.0, 126.8, 124.8, 121.5, 66.2, 61.7, 61.6, 56.0, 46.3, 33.7, 32.0, 14.08, 14.05, 11.5 ppm. ESI-HRMS: m/z Calcd for $C_{24}H_{30}N_2O_5$+H^+:427.2227, found 427.2224.

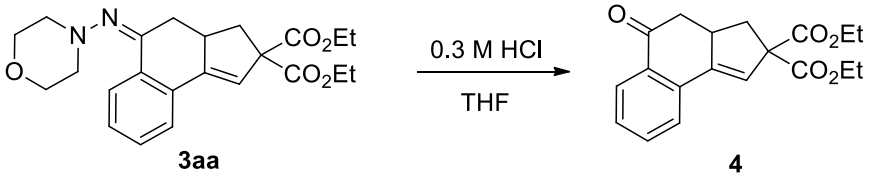


*(Z)-1,1'-(5-(morpholinoimino)-3,3a,4,5-tetrahydro-2H-cyclopenta[a]naphthalene-2,2-diyl)diethanone (**3ag**).* Yellow solid; (30.3 mg, 86%); mp: 134-135 °C; R_f = 0.39 (petroleum ether/ethyl acetate 3:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.11 (dd, *J* = 7.6 Hz, *J* = 0.8 Hz, 1H), 7.62 (dd, *J* = 7.6 Hz, *J* = 0.8 Hz, 1H), 7.40-7.35 (m, 1H), 7.33-7.29 (m, 1H), 6.39 (d, *J* = 2.0 Hz, 1H), 3.91-3.83 (m, 4H), 3.82-3.80 (m, 1H), 3.17-3.11 (m, 1H), 3.10-3.04 (m, 1H), 2.93-2.88 (m, 2H), 2.83-2.78 (m, 1H), 2.22 (s, 3H), 2.20 (s, 3H), 1.95-1.87 (m, 2H) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 205.8, 203.4, 161.1, 145.9, 132.6, 131.3, 130.0, 129.0, 125.9, 125.0, 119.6, 126.0, 80.5, 66.2, 55.3, 41.8, 37.1, 33.7, 27.1, 27.0 ppm. ESI-HRMS: m/z Calcd for $C_{21}H_{24}N_2O_3$+H^+:353.1860, found 353.1863.



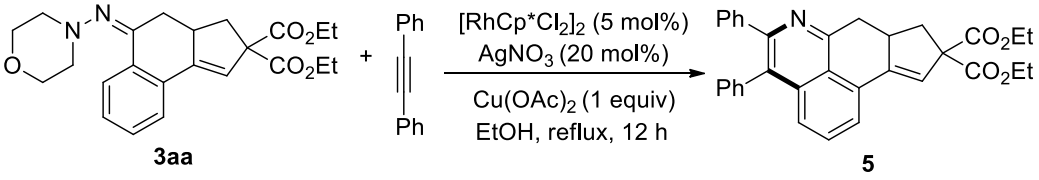
*(Z)-diethyl 9-(morpholinoimino)-1,9,10,10a-tetrahydrophenanthrene-3,3(2H)-dicarboxylate (**3ai**).* Yellow solid; (32.0 mg, 75%); mp:167-169 °C; R_f = 0.40 (petroleum ether/ethyl acetate 3:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.17 (dd, *J* = 8.0 Hz, *J* = 1.2 Hz, 1H), 7.66 (dd, *J* = 8.0 Hz, *J* = 1.2 Hz, 1H), 7.38-7.34 (m, 1H), 7.30-7.28 (m, 1H), 6.53 (s, 1H), 4.30-4.12 (m, 4H), 3.91-3.81 (m, 4H), 3.56 (dd, *J* = 15.2 Hz, *J* = 4.8 Hz, 1H), 3.19 (t, *J* = 4.8, 1H), 2.94-2.89 (m, 2H), 2.81-2.76 (m, 2H), 2.59-2.47 (m, 1H), 2.13-2.04 (m, 1H), 1.98-1.83 (m, 2H), 1.64-1.55 (m, 2H), 1.32-1.24 (m, 6H), ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 171.0, 170.3, 160.9, 139.0, 136.0, 132.0, 130.1, 128.2, 125.1, 124.6, 119.3, 66.2, 61.7, 61.6, 55.2, 34.3, 34.0, 27.39, 27.35, 14.03 ppm. ESI-HRMS: m/z Calcd for $C_{24}H_{30}N_2O_5$+H^+:427.2227, found 427.2225.

Synthetic Utility of Methodology.[3]



3aa **4**

3aa (41.2 mg, 0.10 mmol) was added to a 1/1 mixture of HCl 0.3N/THF. The resulting solution was stirred at room temperature and monitored by TLC. After **3aa** was used up, extracted with DCM and washed with aq $NaHCO_3$. The organic layer was dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by flash chromatography (silica gel, petroleum ether /ethyl acetate 20/1) to afford **4** (27.9 mg, 85%) as colourless oil. *diethyl 5-oxo-3,3a,4,5-tetrahydro-2H-cyclopenta[a]naphthalene-2,2-dicarboxylate (**4**).* Yellow oil; (26.6 mg, 81%); R_f = 0.47 (petroleum ether/ethyl acetate 10:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.01 (dd, *J* = 8.0 Hz, *J* = 1.2 Hz, 1H), 7.70 (d, *J* = 7.2 Hz, 1H), 7.58-7.54 (m, 1H), 7.44-7.40 (m, 1H), 6.37 (d, *J* = 2.0 Hz, 1H), 4.29-4.15 (m, 4H), 3.58-3.48 (m, 1H), 3.09-2.98 (m, 1H), 2.54-2.47 (m, 1H), 2.11 (dd, *J* = 13.2 Hz, *J* = 8.4 Hz, 1H), 1.32-1.26 (m, 6H), ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 197.0, 171.0, 170.0, 143.7, 135.1, 133.7, 131.1, 129.1, 127.3, 125.5, 122.4, 66.3, 42.3, 39.2, 14.03 ppm. ESI-HRMS: m/z Calcd for $C_{19}H_{20}O_5$+H^+:329.1384, found 329.1397.



3aa **5**

To a Schlenk tube were added diphenylacetylene (0.1 mmol), **3aa** (0.15 mmol), [($RhCp^*Cl_2$)$_2$] (5 mol %), $AgNO_3$ (20 mol %), $Cu(OAc)_2$ (0.1 mmol), and anhydrous EtOH (1 mL). Then the tube was charged with argon, and the reaction mixture was stirred under reflux for the indicated time until complete consumption of the starting material was achieved as monitored by TLC. After the reaction was finished, the reaction mixture was diluted with diethyl ether, and washed with brine. The aqueous phase was re-extracted with diethyl ether. The combined organic extracts were dried over $MgSO_4$ and concentrated in vacuum, and the resulting residue was purified by silica gel column chromatography (silica gel, petroleum ether /ethyl acetate 20/1) to afford **5** (38.2 mg, 76%)

as yellow solid. *diethyl 4,5-diphenyl-7a,8-dihydrobenzo[de]cyclopenta[g]quinoline-9,9(7H)-dicarboxylate (5).* Yellow solid; (38.2 mg, 76%); mp:127-129 °C; R_f = 0.45 (petroleum ether/ethyl acetate 10:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.84 (dd, *J* = 7.6 Hz, *J* = 2.4 Hz, 1H), 7.62-7.56 (m, 2H), 7.37-7.33 (m, 5H), 7.25-7.17 (m, 5H), 6.46 (d, *J* = 2.0 Hz, 1H), 4.31-4.17 (m, 4H), 3.75 (dd, *J* = 15.6 Hz, *J* = 6.0 Hz, 1H), 3.64-3.56 (m, 1H), 3.21 (dd, *J* = 13.6 Hz, *J* = 7.6 Hz, 1H), 3.08 (dd, *J* = 13.6 Hz, *J* = 13.2 Hz, 1H), 2.25 (dd, *J* = 13.6 Hz, *J* = 8.0 Hz, 1H), 1.34-1.30 (m, 6H), ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 171.3, 170.5, 157.1, 149.9, 145.2, 140.8, 137.4, 136.1, 133.7, 131.3, 130.2, 130.0, 129.0, 128.24, 128.2, 127.6, 127.3, 127.2, 127.0, 126.3, 125.5, 122.7, 122.4, 121.5, 66.3, 61.74, 61.71, 45.7, 42.3, 41.5, 39.5, 39.2, 14.1 ppm. ESI-HRMS: m/z Calcd for $C_{33}H_{29}NO_4$+H^+:504.2169, found 504.2167.

Reference

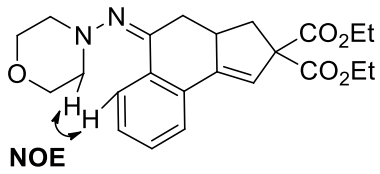
1. S. Bhunia, K.-C. Wang, R.-S. Liu, *Angew. Chem. Int. Ed.* **2008**, *47*, 5063.

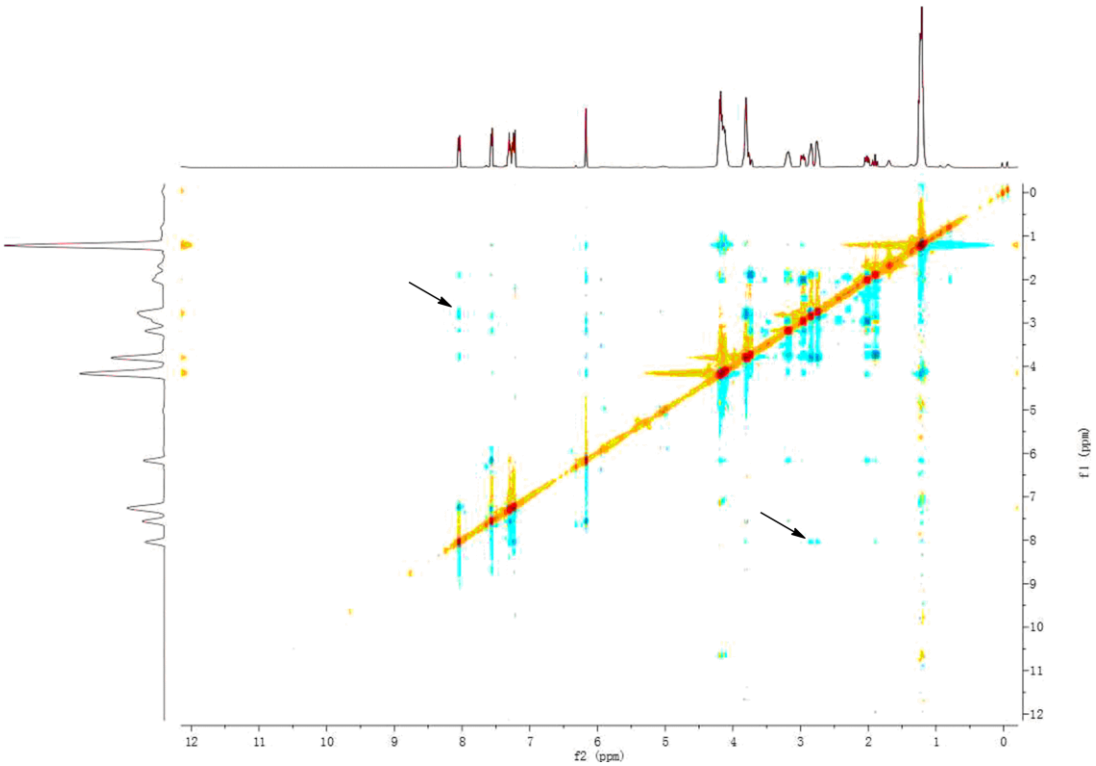
2. A. Ros, R. Lopez-Rodriguez, B. Estepa, E. Alvarez, R. Fernandez, J. M. Lassaletta, *J. Am. Chem. Soc.* **2012**, *134*, 4573.

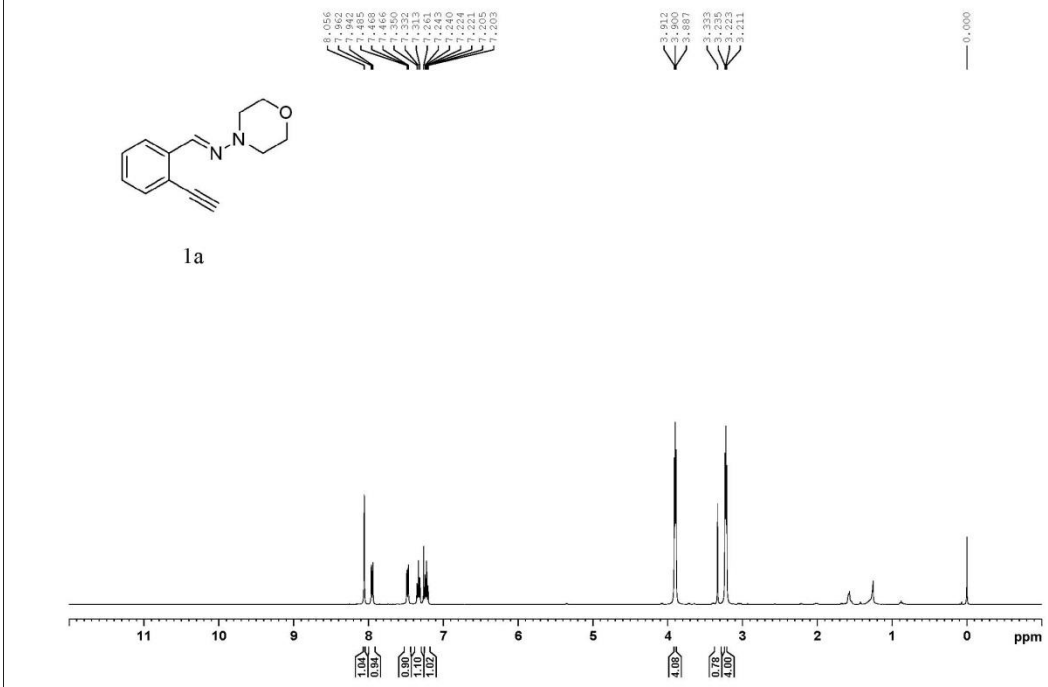
3. X.-C. Huang, X.-H. Yang, R.-J. Song, J.-H. Li, *J. Org. Chem.* **2014**, *79*, 1025.

Determination of the geometry of the CN double bond

NOESY



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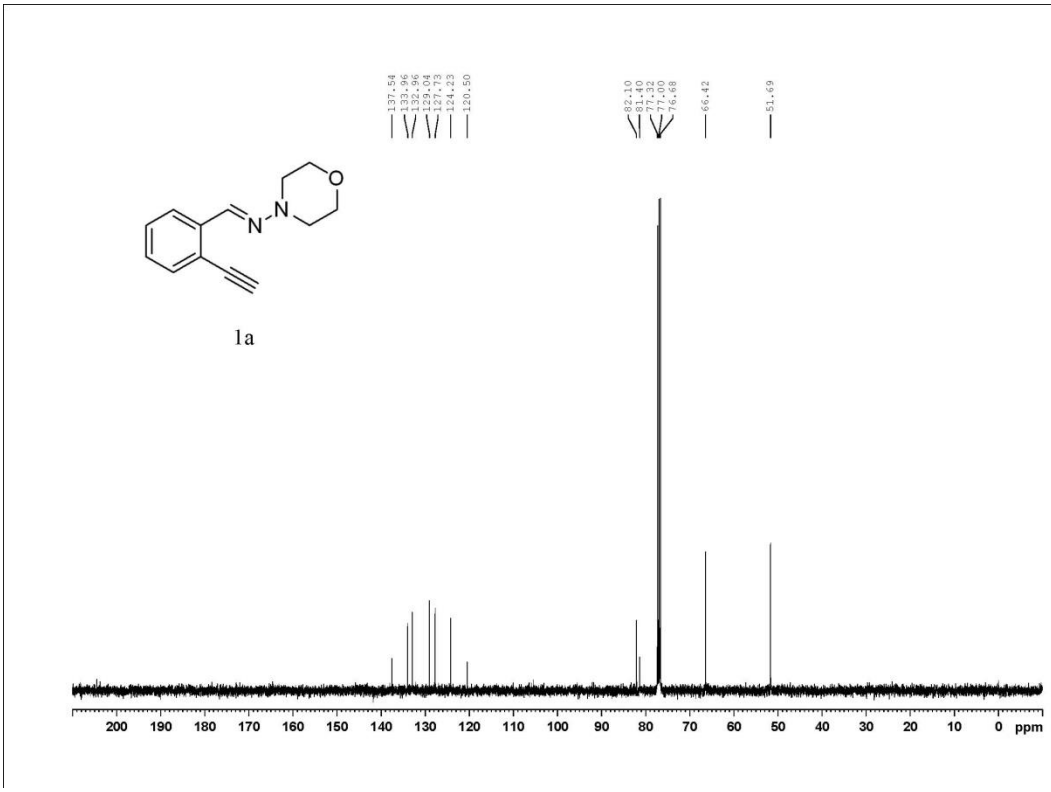
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100
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80
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60
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20
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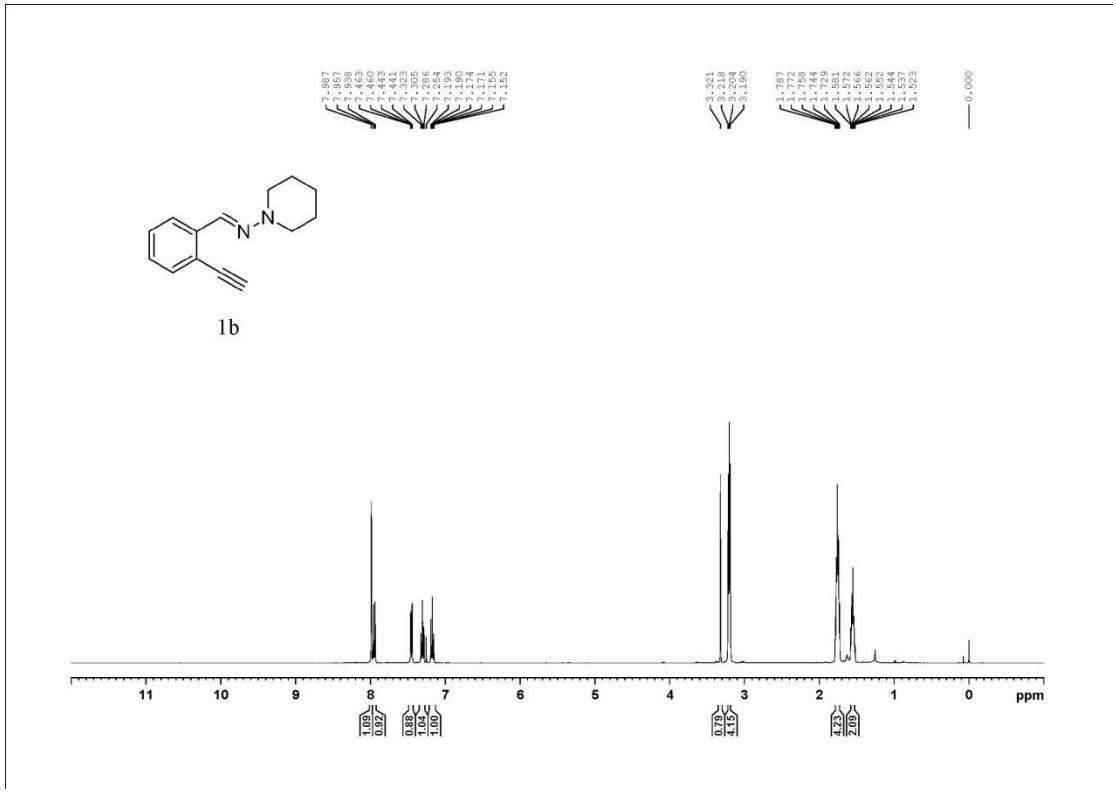
0
ppm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7.957
7.938
7.463
7.460
7.443
7.441
7.323
7.305
7.286
7.254
7.193
7.190
7.174
7.171
7.155
7.152
3.321
3.218
3.204
3.190
1.787
1.772
1.758
1.744
1.729
1.681
1.572
1.566
1.562
1.552
1.544
1.537
1.523
0.000
N
N
1b
11
10
9
8
7
6
5
4
3
2
1
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ppm
1.09
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1.00
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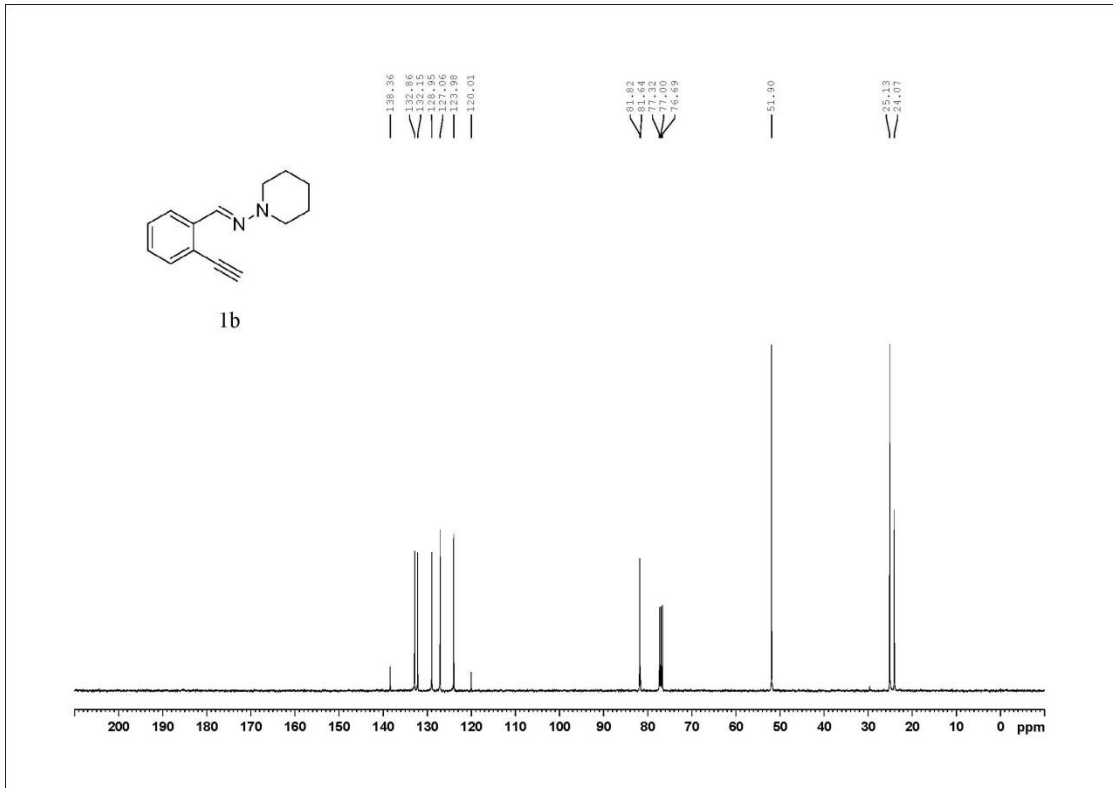
4.23
2.00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132.86
132.15
129.85
127.06
123.98
120.01
81.82
81.64
77.32
77.00
76.69
51.90
25.13
24.07
N
N
1b
200
190
180
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150
140
130
120
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100
90
80
70
60
50
40
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20
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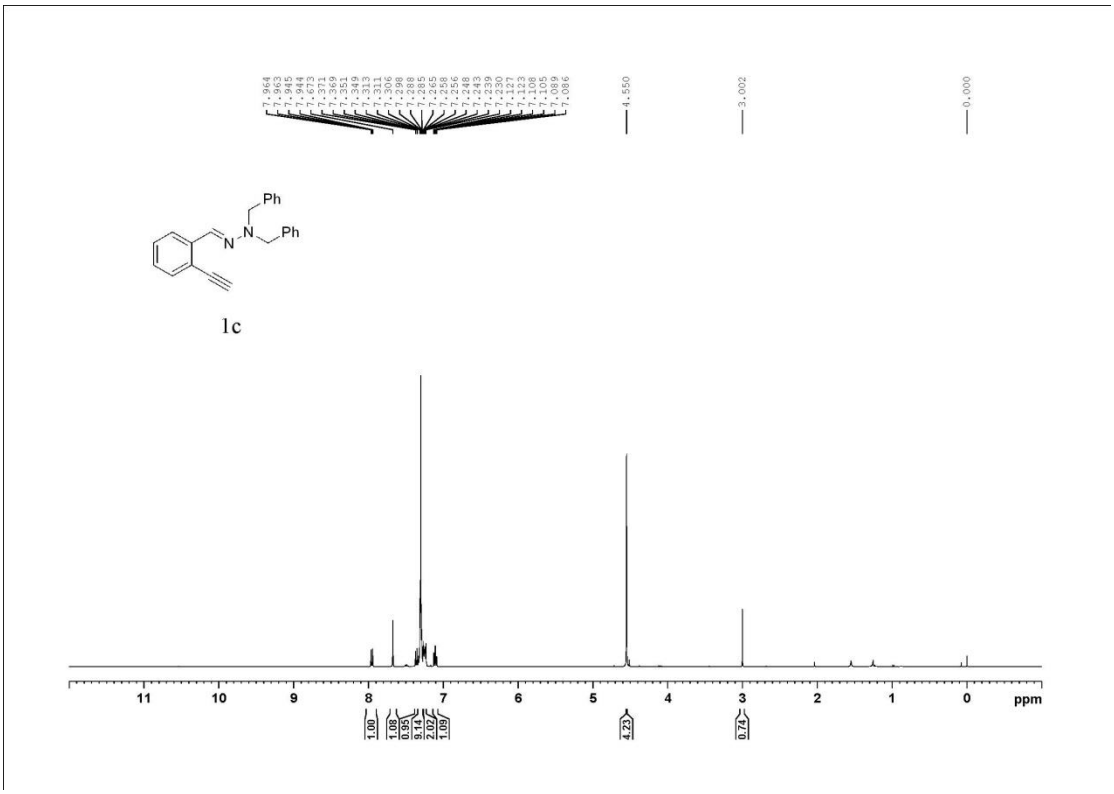
0
ppm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7.945
7.944
7.673
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7.369
7.351
7.349
7.313
7.311
7.306
7.298
7.288
7.285
7.265
7.258
7.256
7.248
7.243
7.239
7.230
7.127
7.123
7.108
7.105
7.089
7.086
4.550
3.002
0.000
Ph
N
Ph
1c
11
10
9
8
7
6
5
4
3
2
1
0
ppm
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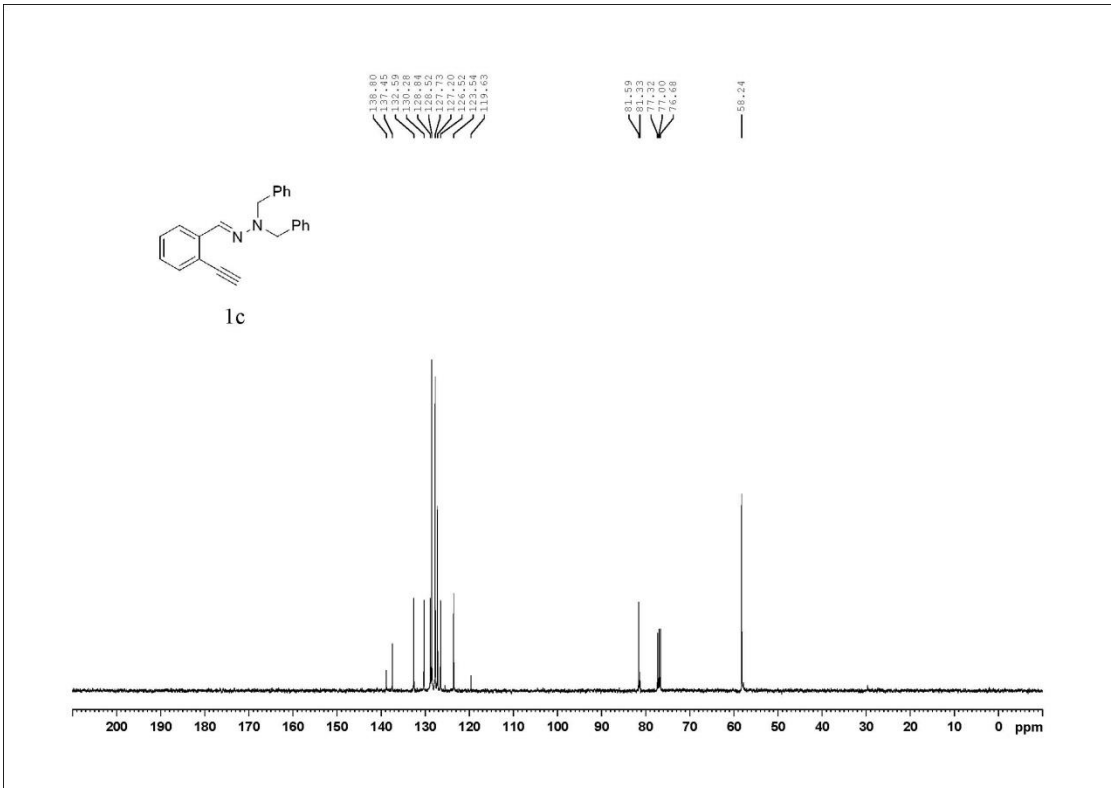
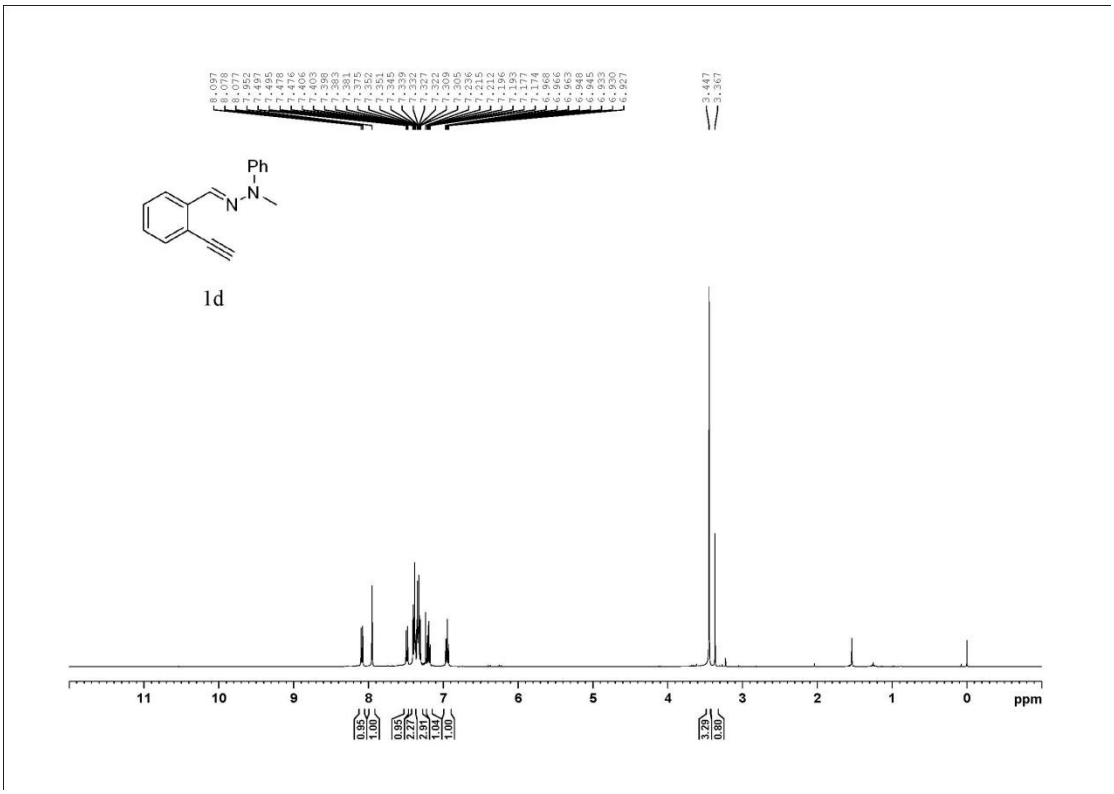
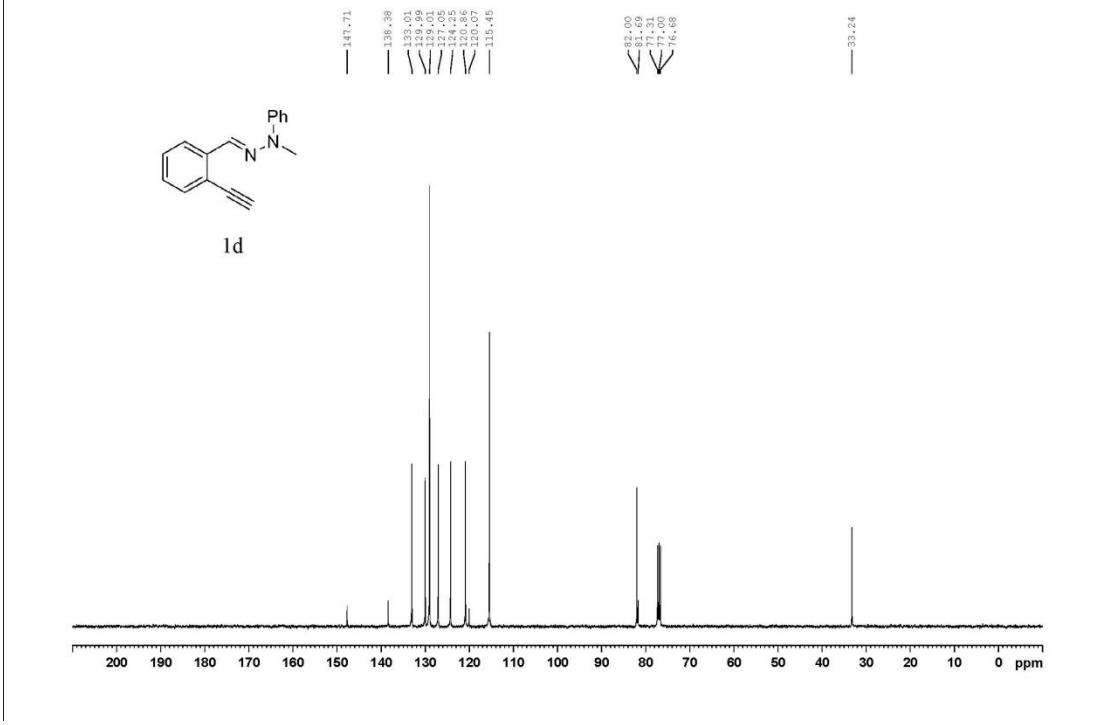
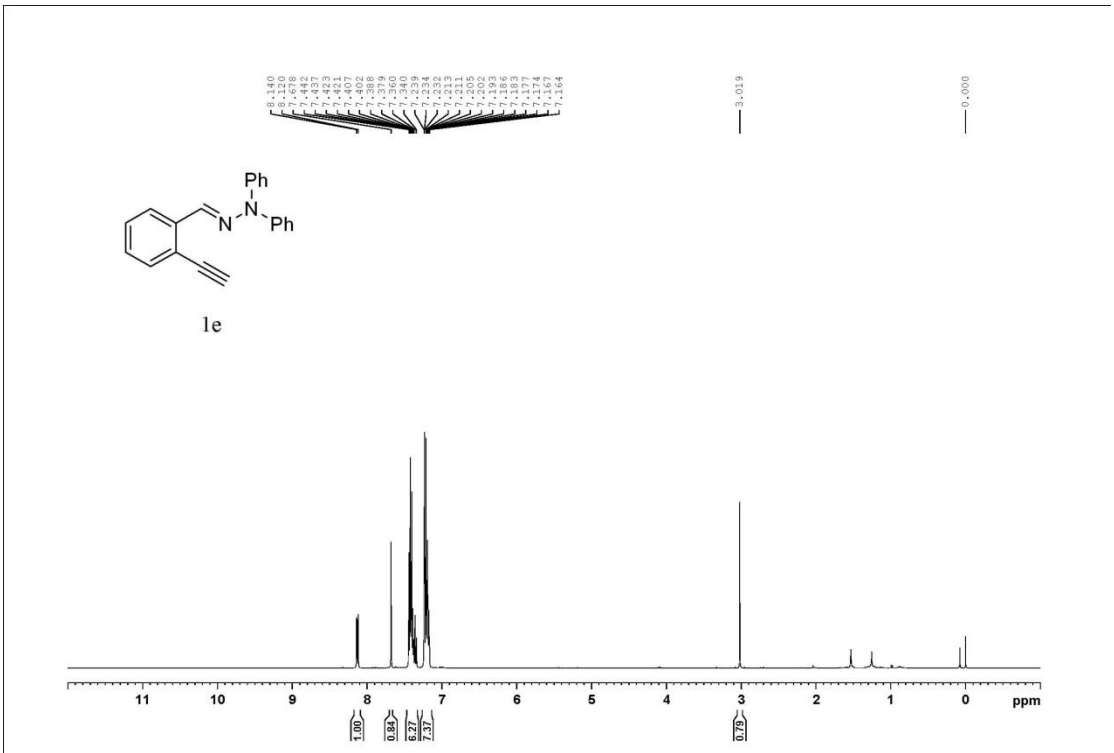
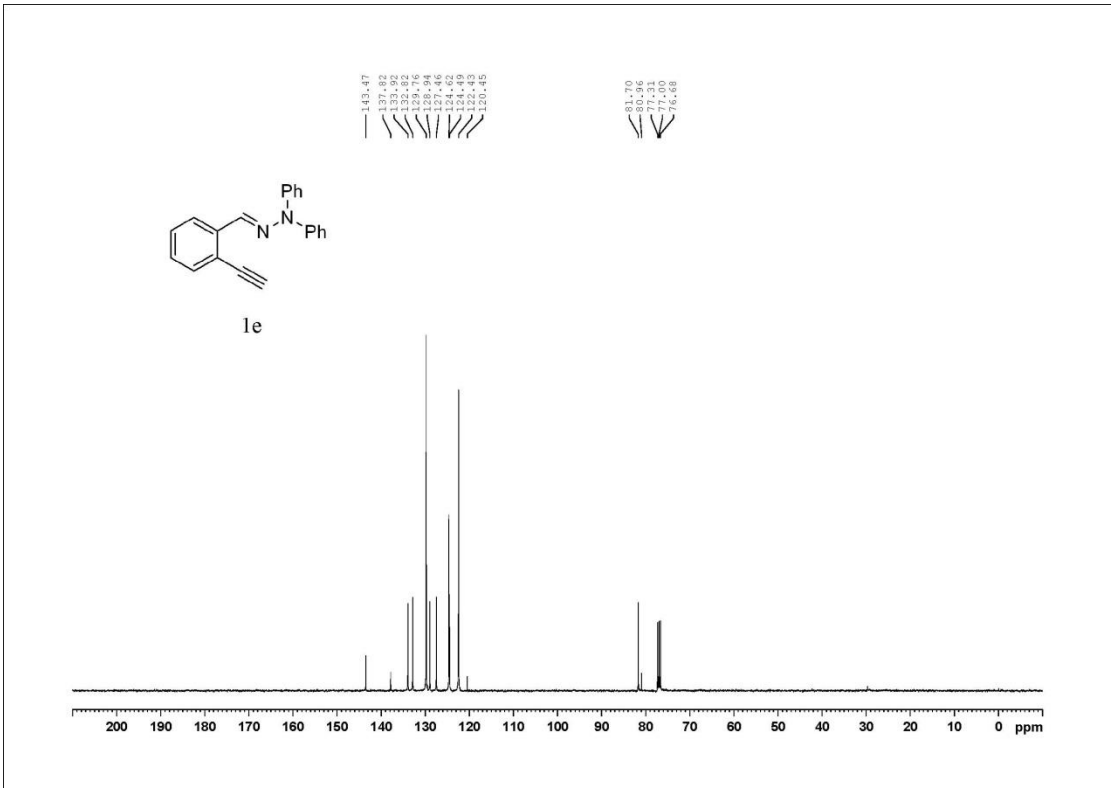
1.08
0.95
9.14
2.07
1.09
4.23
0.74

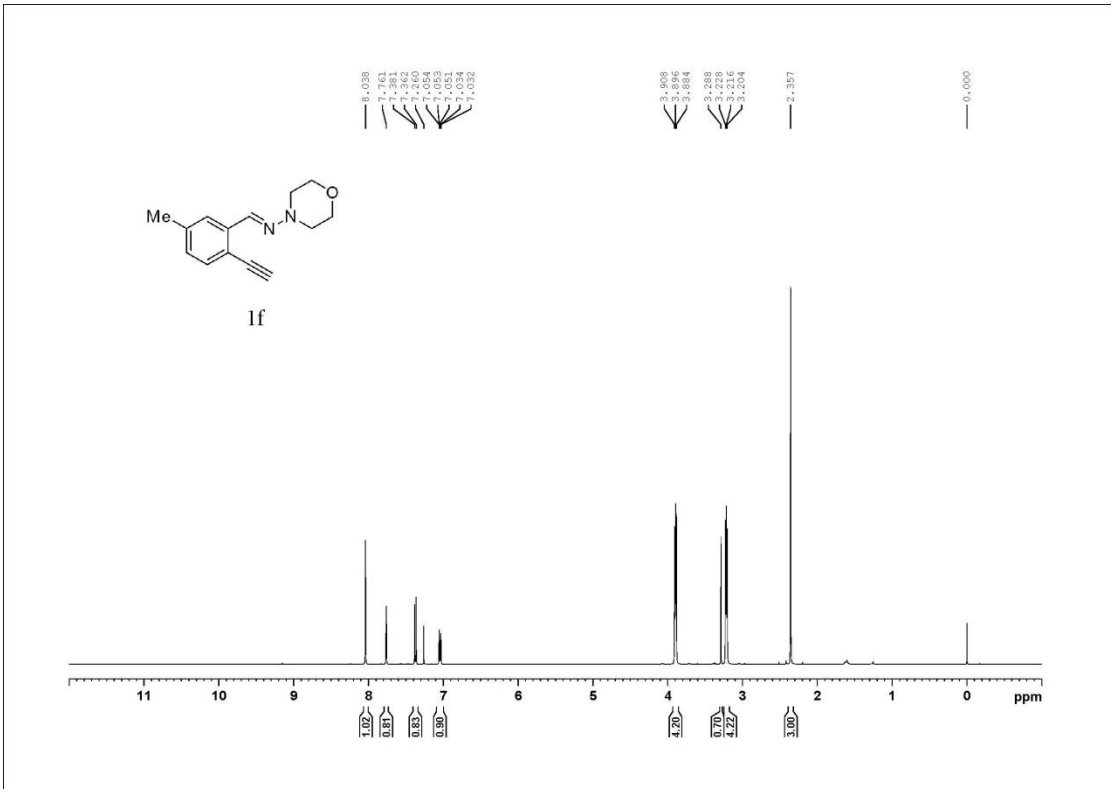

138.80
137.45
132.59
130.28
128.84
128.52
127.73
127.20
126.52
123.54
119.63
81.59
81.53
77.32
77.00
76.68
58.24
Ph
N
Ph
1c
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

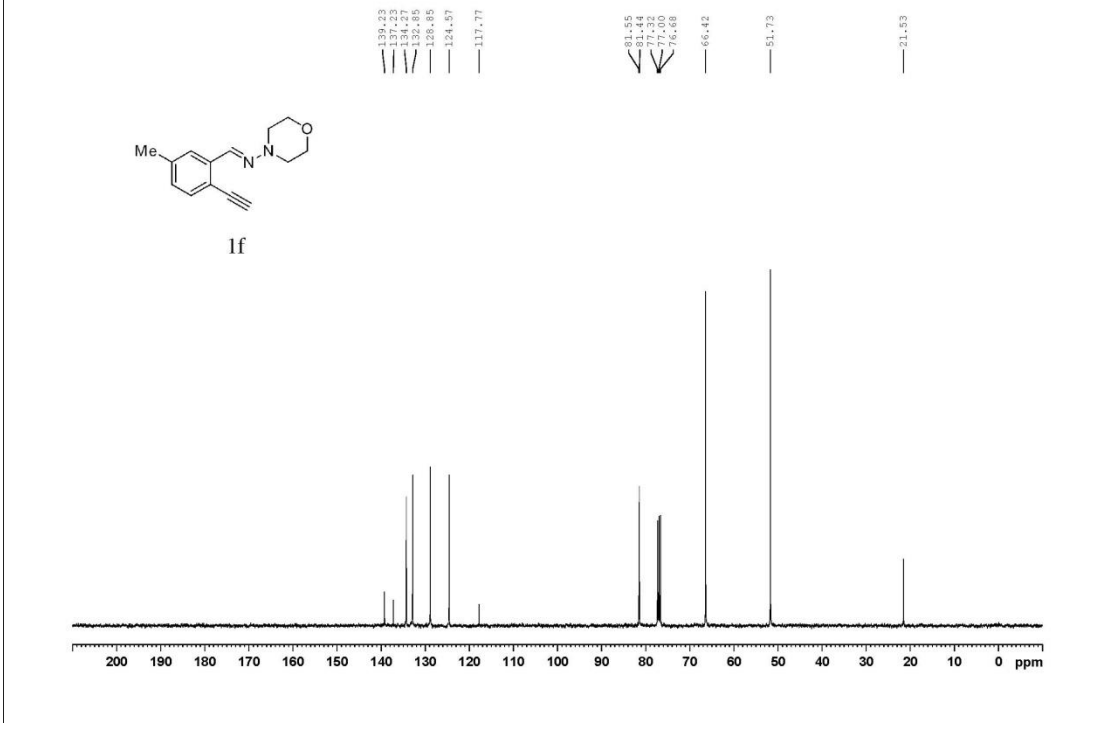

Ph
N
N
1d
ppm

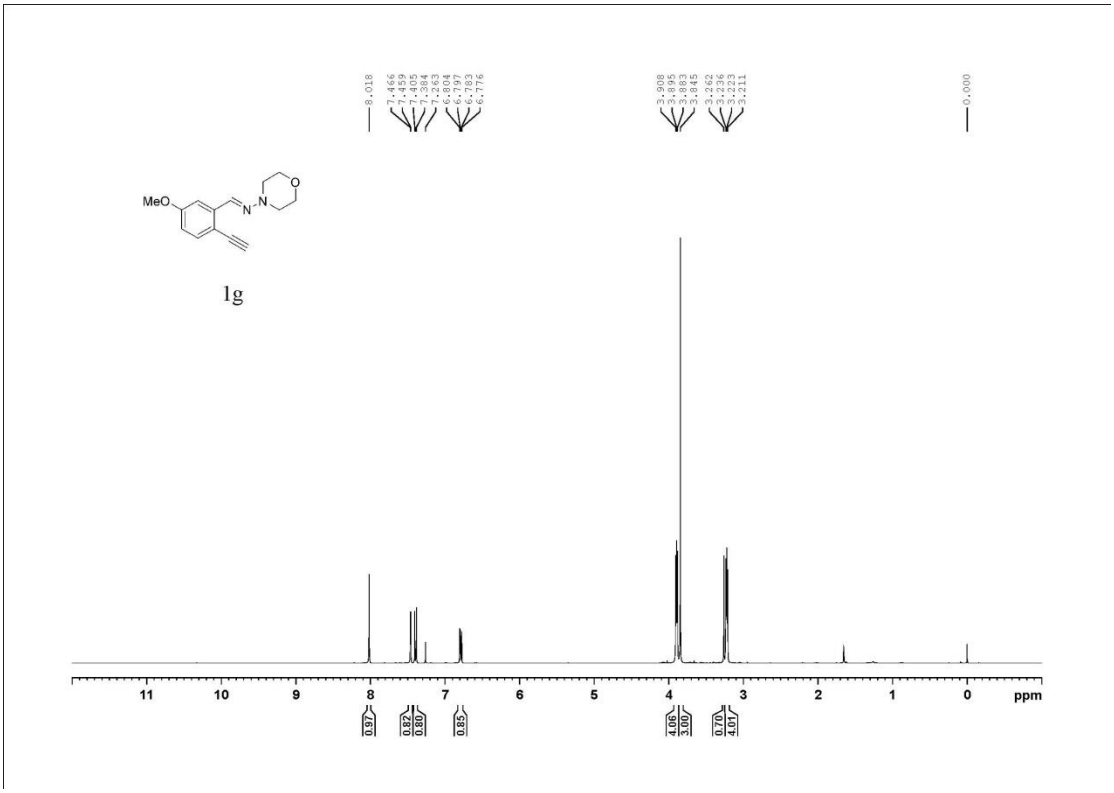

Ph
N
N
1d
ppm


8.140
8.120
7.678
7.492
7.437
7.423
7.421
7.407
7.402
7.388
7.379
7.360
7.340
7.239
7.234
7.232
7.213
7.211
7.205
7.202
7.193
7.186
7.183
7.177
7.174
7.167
7.164
3.019
0.000
Ph
N
N
Ph
1e
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
0.84
6.27
7.37
0.79

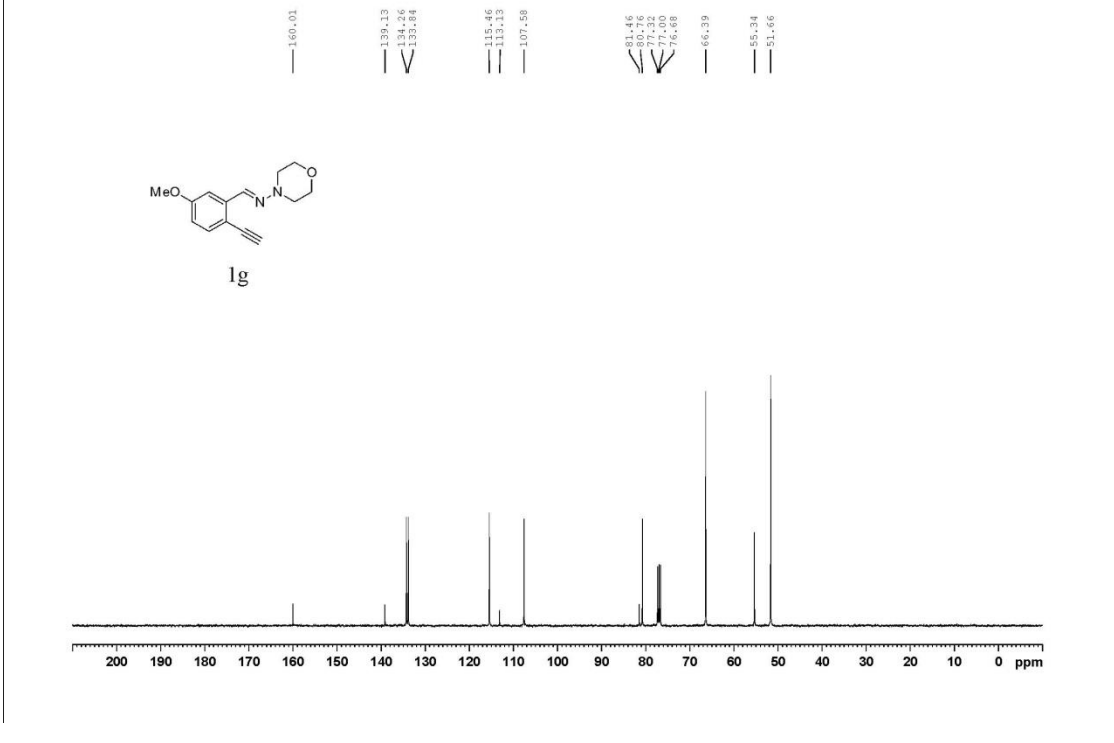

143.47
137.82
133.92
132.62
129.76
128.94
127.46
124.62
124.49
122.43
120.45
81.70
80.96
77.31
77.00
76.68
Ph
N
N
Ph
1e
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


8.038
7.761
7.381
7.362
7.360
7.054
7.053
7.051
7.034
7.032
3.908
3.896
3.884
3.288
3.228
3.216
3.204
2.357
0.000
Me
O
N
N
1f
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.02
0.81
0.83
0.90
4.20
0.70
4.22
3.00

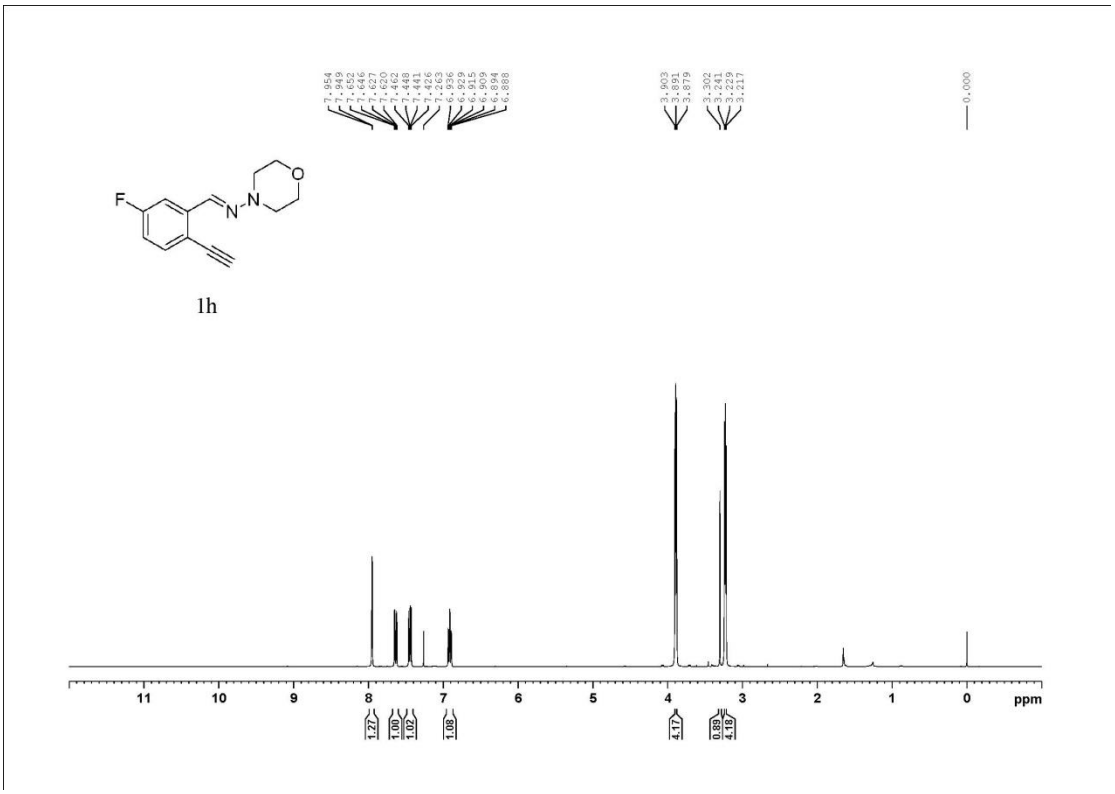

139.23
137.23
134.27
132.85
126.85
124.57
117.77
81.55
81.44
77.32
77.00
76.68
66.42
51.73
21.53
Me
O
N
N
1f
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

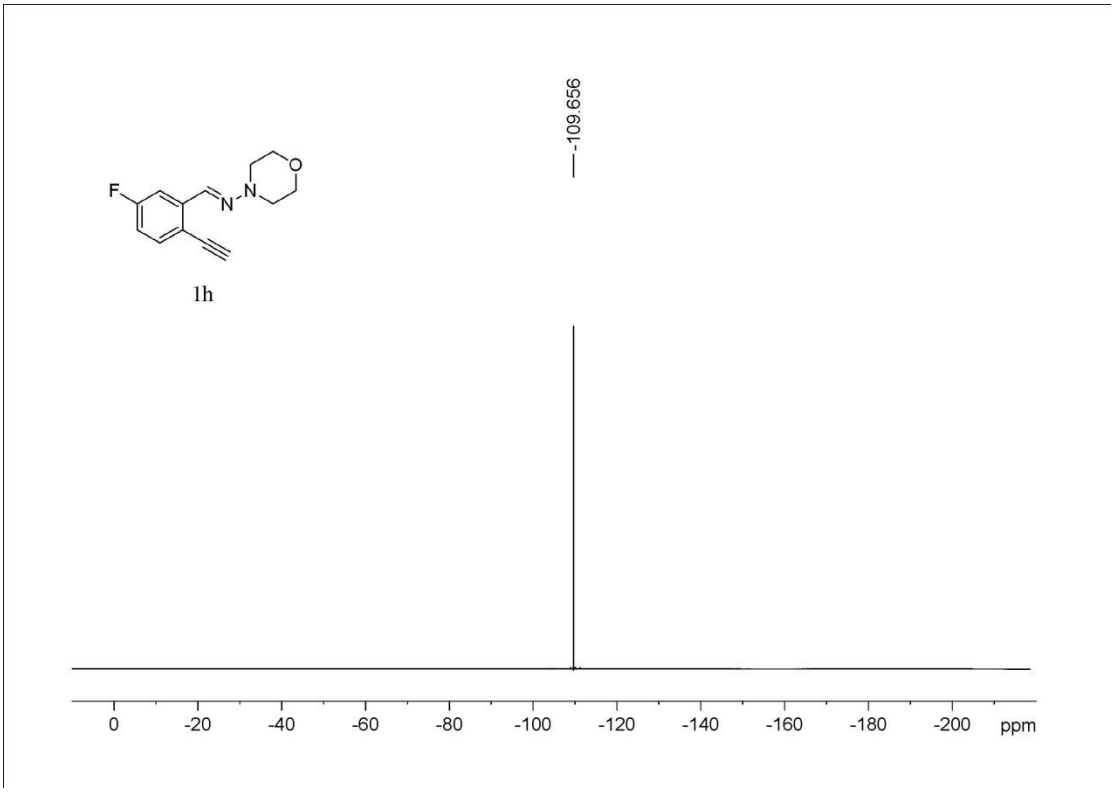

8.018
7.466
7.459
7.405
7.384
7.263
6.804
6.797
6.783
6.776
3.908
3.895
3.883
3.845
3.262
3.236
3.223
3.211
0.000
MeO
N
O
11
10
9
8
7
6
5
4
3
2
1
0
ppm
0.97
0.82
0.80
0.85
4.06
3.00
0.70
4.01

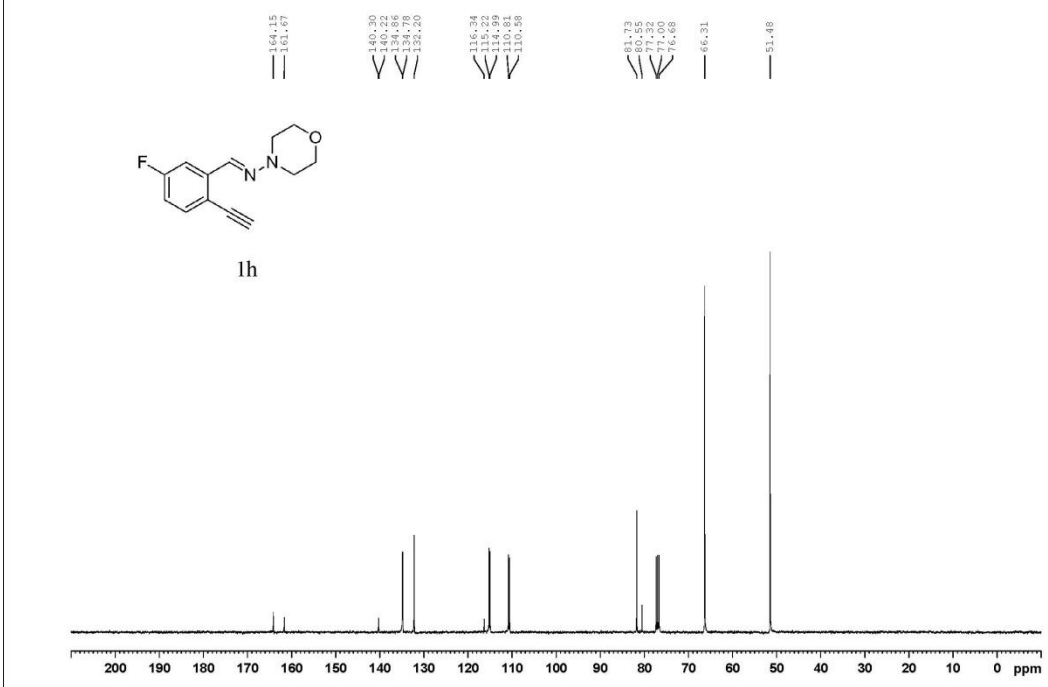
1g


160.01
139.13
134.26
133.84
115.46
113.13
107.58
81.46
80.76
77.32
77.00
76.68
66.39
55.34
51.66
MeO
N
O
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

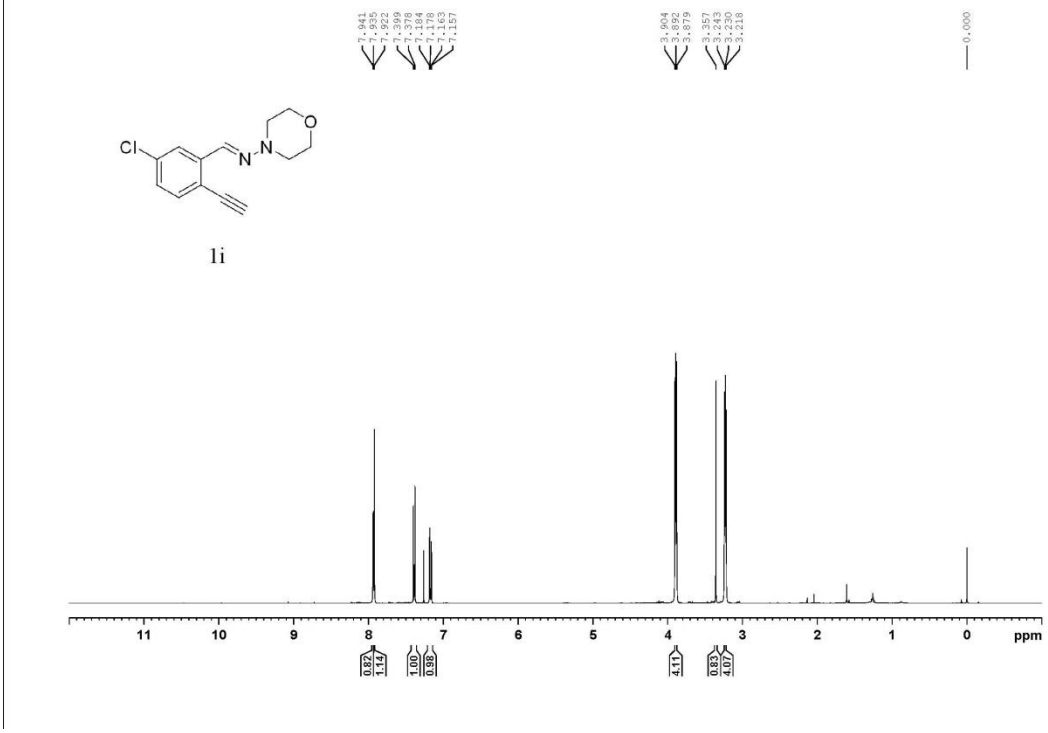
1g


7.954
7.949
7.652
7.646
7.627
7.620
7.462
7.448
7.441
7.426
7.263
6.936
6.929
6.915
6.909
6.894
6.888
3.903
3.891
3.879
3.302
3.241
3.229
3.217
0.000
F
N
O
1h
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.27
1.00
1.02
1.08
4.17
0.89
4.18

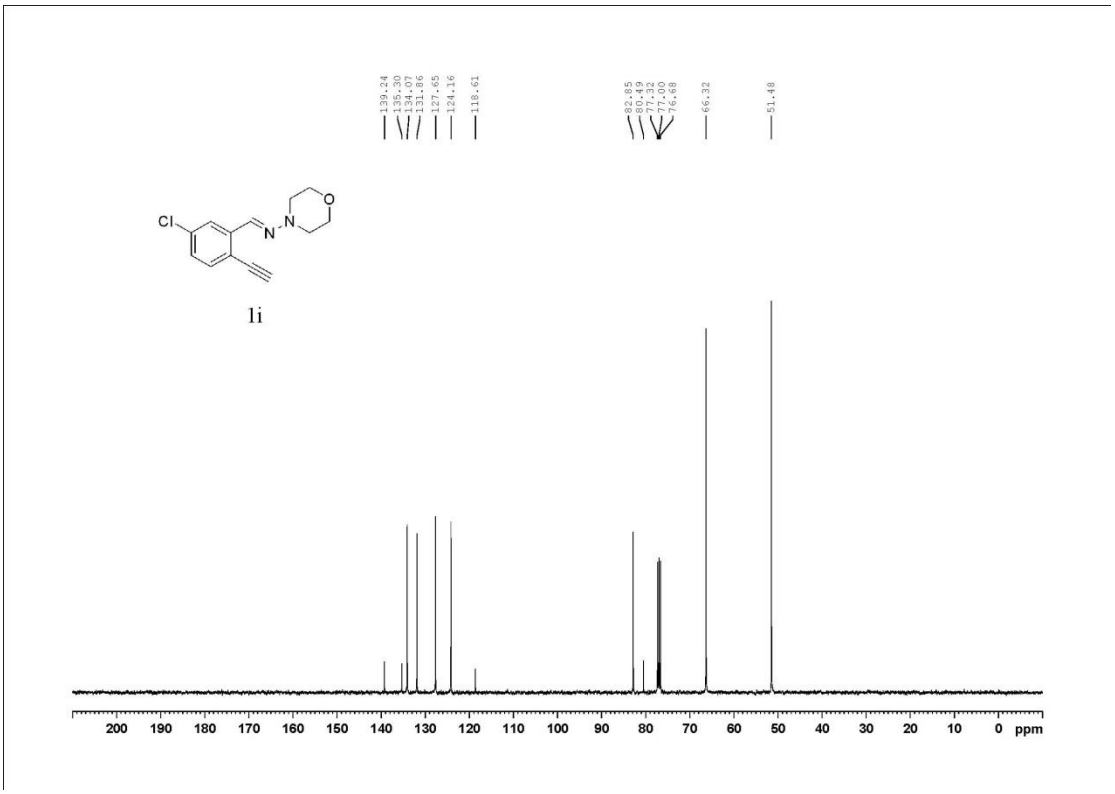

-109.656
F
N
O
1h
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm


164.15
161.67
140.30
140.22
134.86
134.78
132.20
116.34
116.22
114.99
110.81
110.58
81.73
80.55
77.32
77.00
76.68
66.31
51.48
F
N
O
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

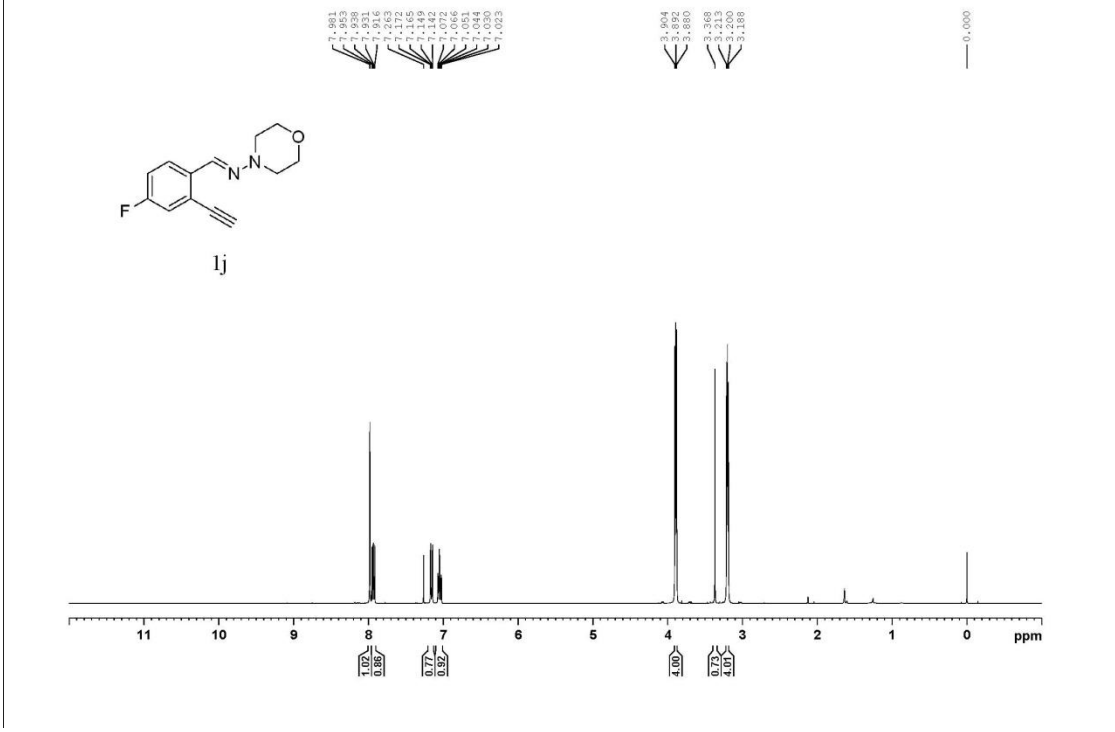
1h


7.941
7.935
7.922
7.399
7.378
7.184
7.178
7.163
7.157
3.904
3.892
3.879
3.357
3.243
3.230
3.218
0.000
Cl
N
O
11 10 9 8 7 6 5 4 3 2 1 0 ppm
0.82
1.14
1.00
0.98
4.11
0.83
4.07

1i


139.24
135.30
134.07
131.86
127.65
124.16
118.61
80.85
80.48
77.32
77.00
76.68
66.32
51.48
Cl
N
O
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

1i


7.981
7.963
7.938
7.931
7.916
7.253
7.172
7.165
7.149
7.142
7.072
7.066
7.051
7.044
7.030
7.023
3.904
3.892
3.880
3.368
3.213
3.200
3.188
0.000
F
N
O
11 10 9 8 7 6 5 4 3 2 1 0 ppm
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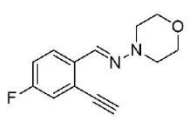
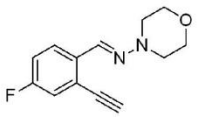
0.86
0.77
0.82
4.00
0.73
4.01

1j



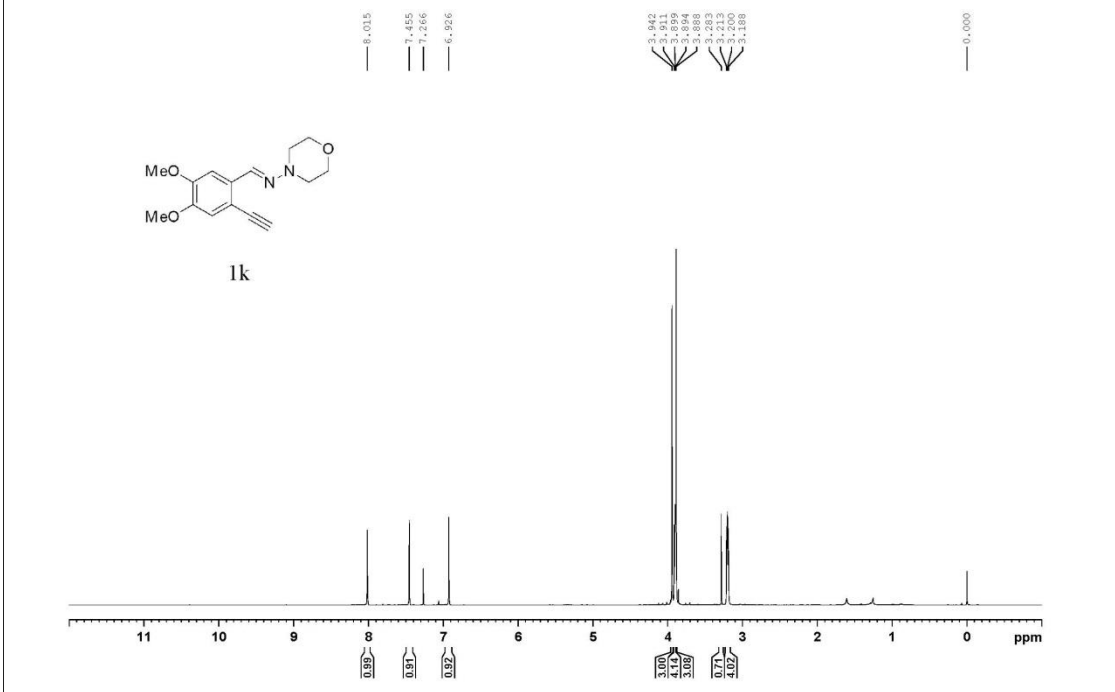
1j

-113.640
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm

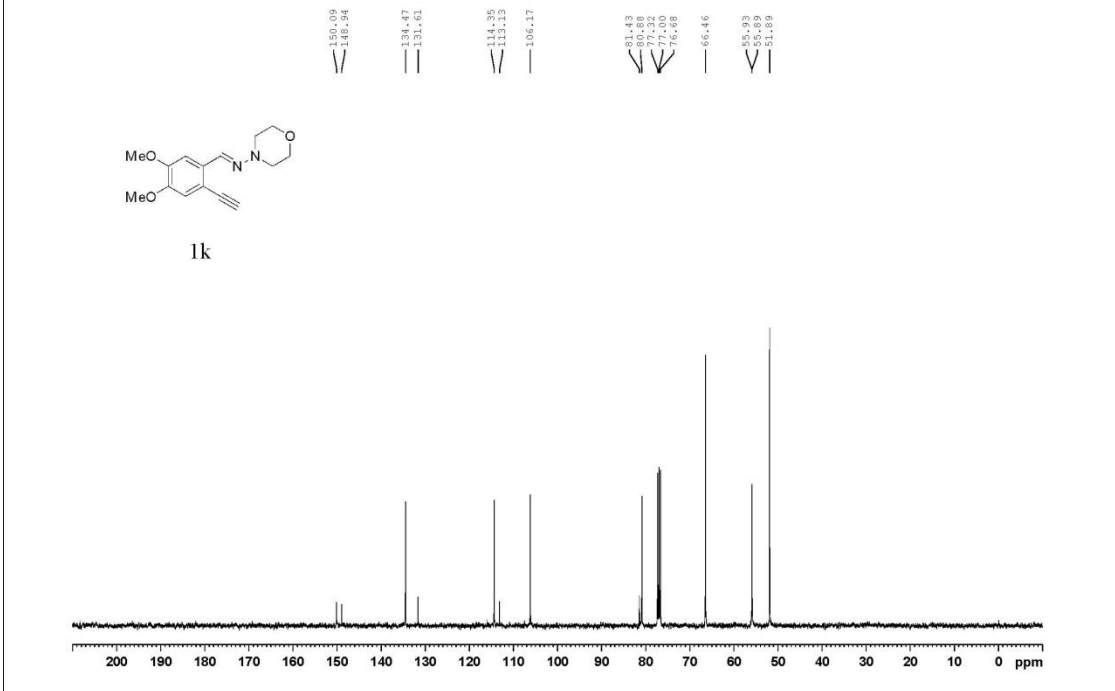


1j

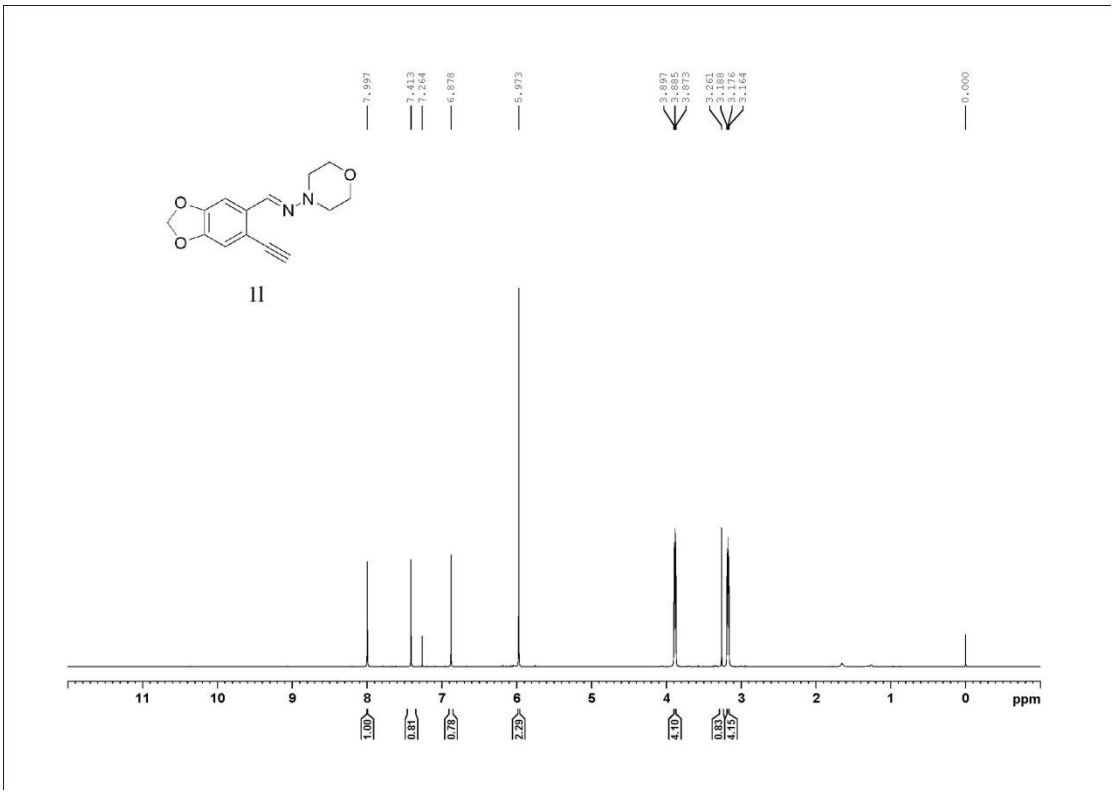
163.03
160.57
134.05
132.93
126.33
126.25
121.98
121.79
119.18
118.95
117.05
116.83
83.01
80.22
77.32
77.00
76.68
66.38
51.68
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

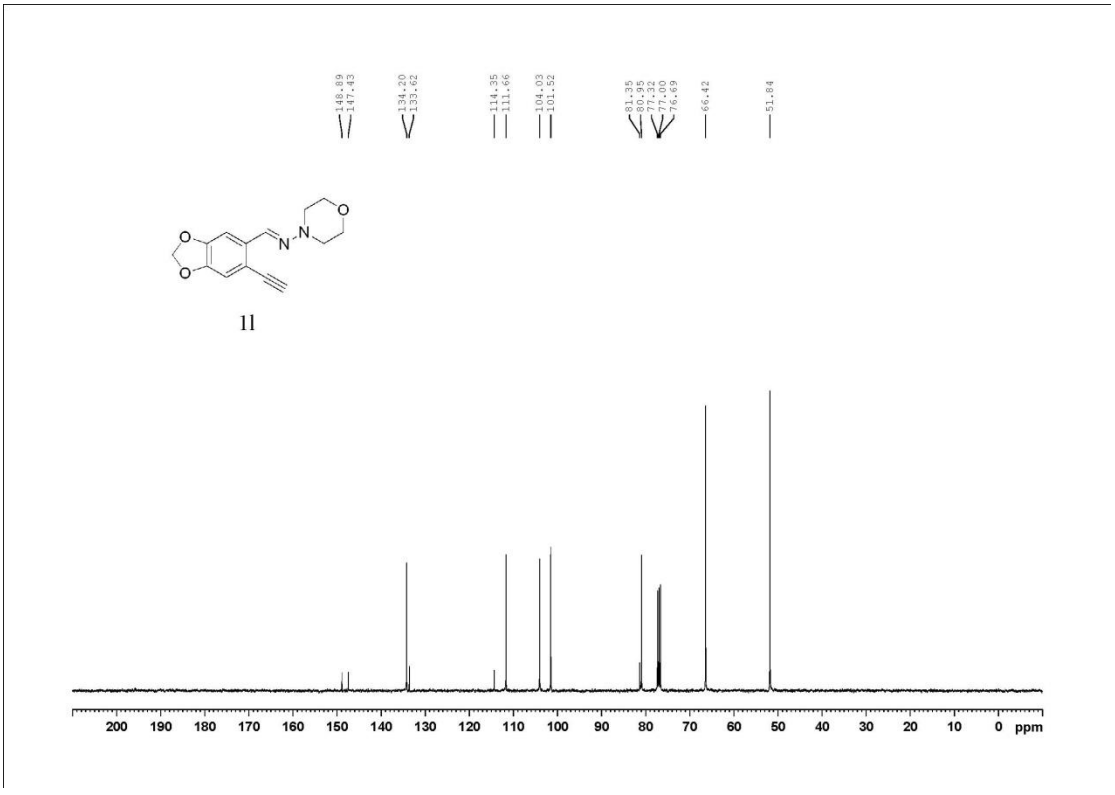

8.015
7.455
7.266
6.926
3.942
3.911
3.899
3.894
3.888
3.283
3.213
3.200
3.188
0.000
MeO
MeO
O
N
N
11
10
9
8
7
6
5
4
3
2
1
0
ppm
0.99
0.91
0.92
3.00
4.14
3.08
0.71
4.02

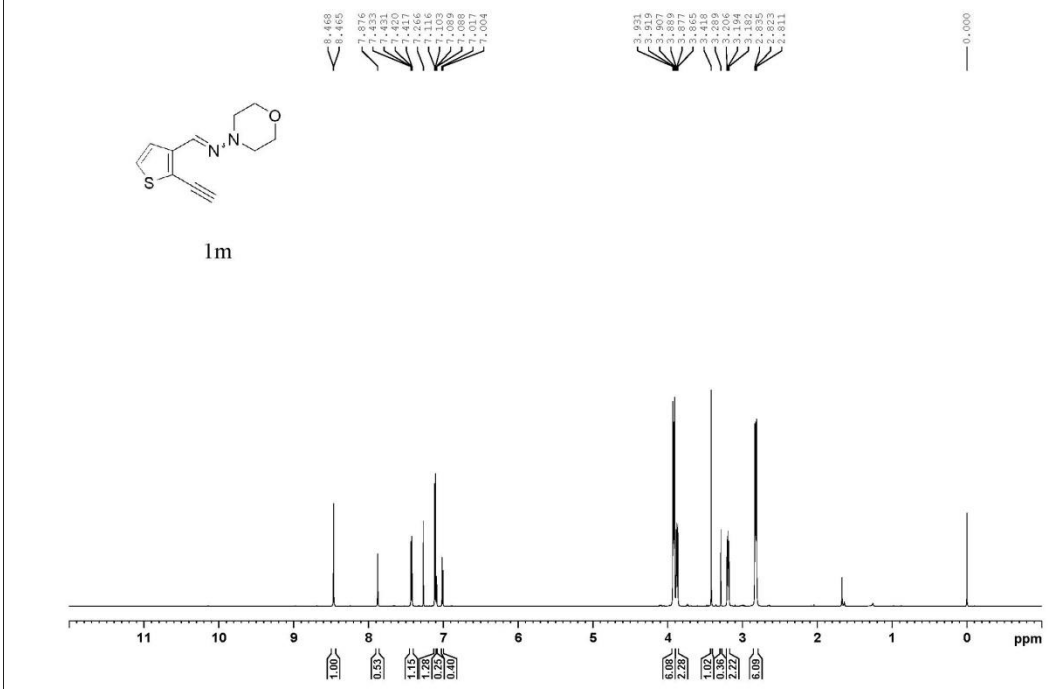
1k


150.09
148.94
134.47
131.61
114.35
113.13
106.17
81.43
80.88
77.32
77.00
76.68
66.46
55.93
55.89
51.89
MeO
MeO
O
N
N
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

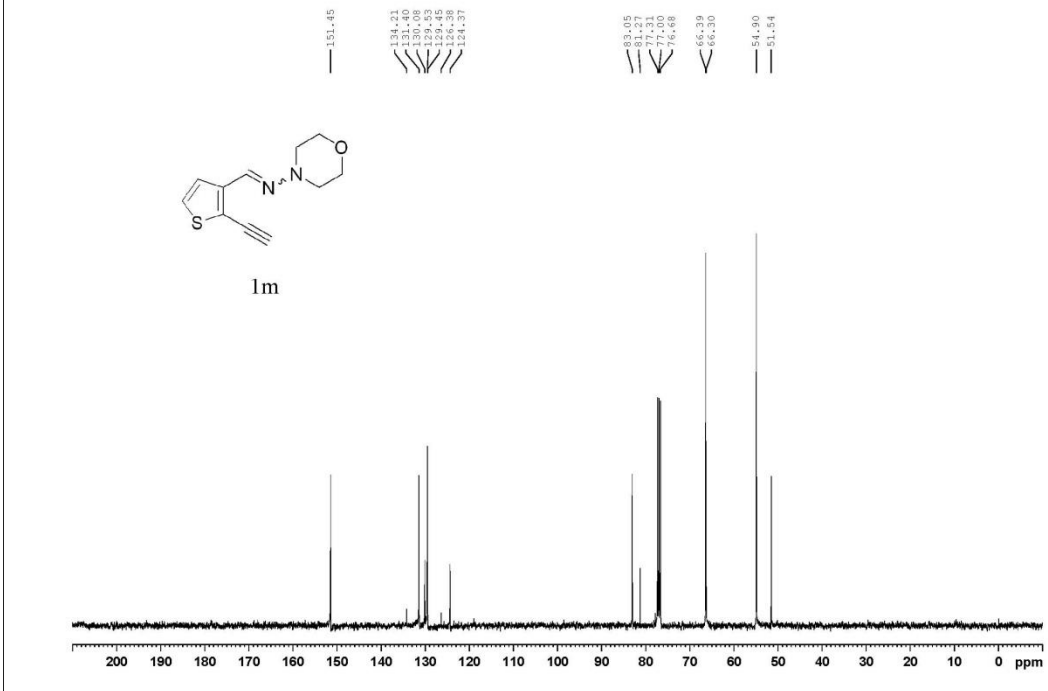
1k


7.997
7.413
7.264
6.878
5.973
3.897
3.885
3.873
3.261
3.188
3.176
3.164
0.000
O
O
N
O
N
11
ppm
1.00
0.81
0.78
2.29
4.10
0.83
4.15

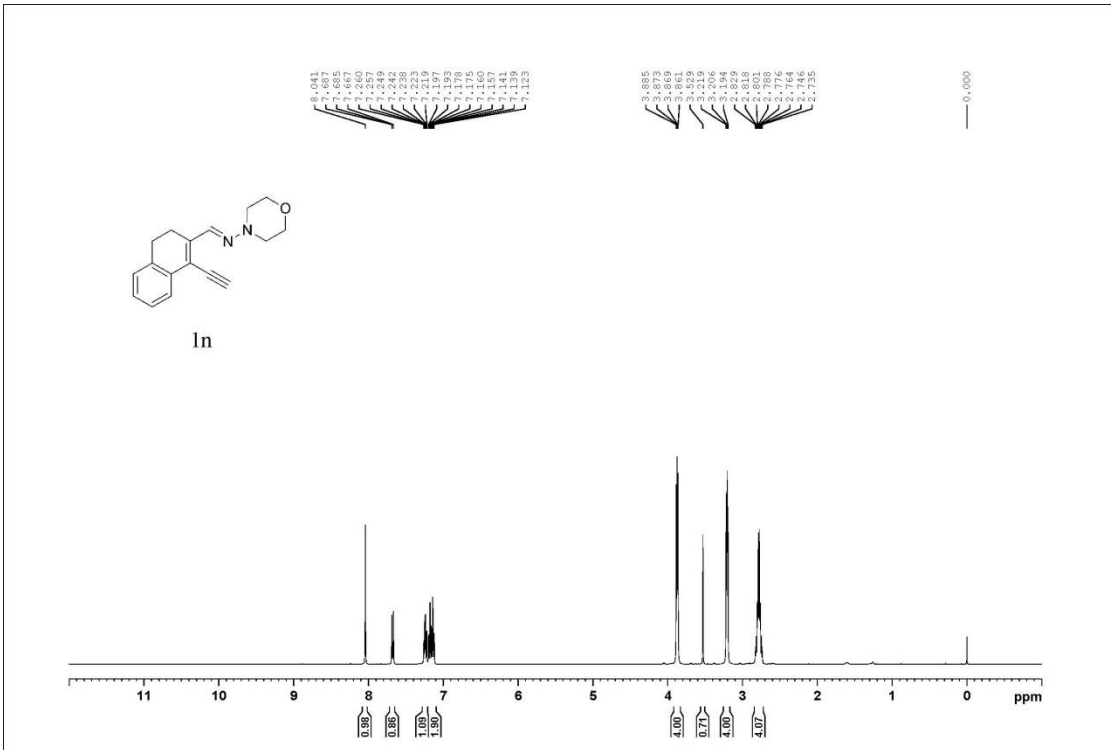

148.89
147.43
134.20
133.62
114.35
111.66
104.03
101.52
81.35
80.55
77.32
77.00
76.69
66.42
51.84
O
O
N
O
N
11
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


8.468
8.465
7.676
7.435
7.431
7.420
7.417
7.116
7.113
7.103
7.089
7.088
7.077
7.004
3.931
3.919
3.907
3.889
3.877
3.865
3.418
3.289
3.206
3.194
3.182
2.835
2.823
2.811
0.000
O
N
S
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
0.53
1.15
1.28
0.25
0.40
6.08
2.29
1.02
0.36
2.27
6.09

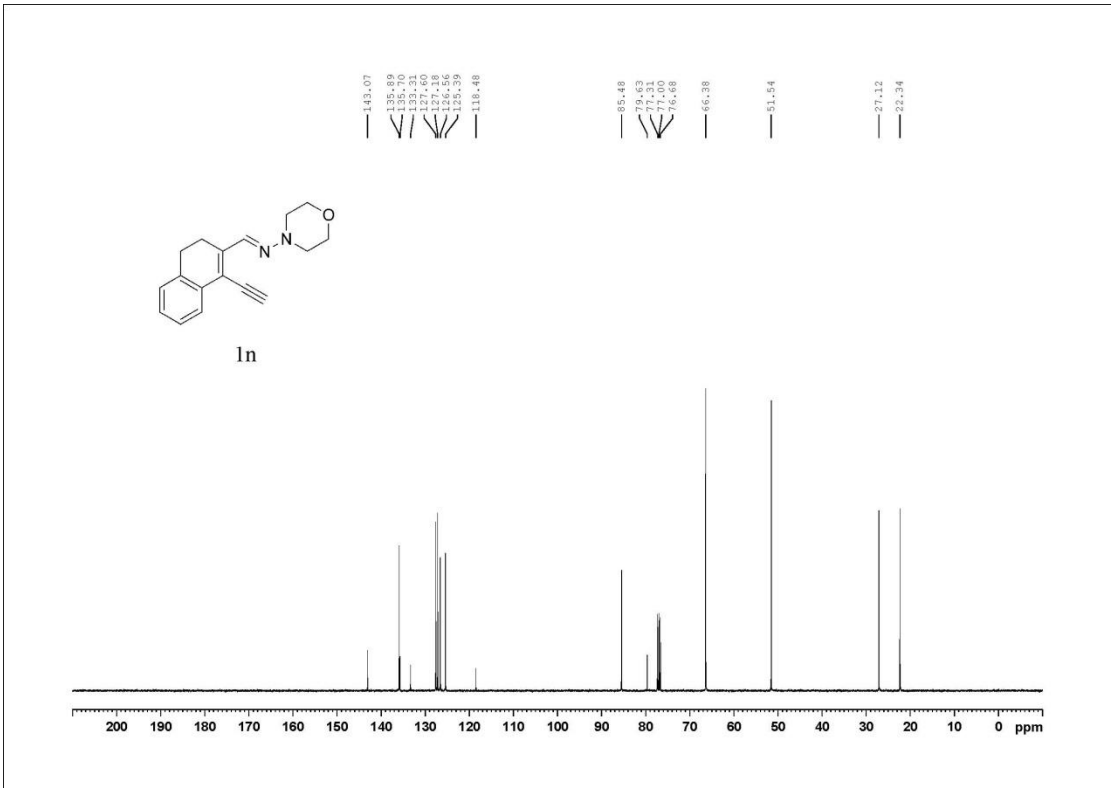
1m


151.45
134.21
131.40
130.08
129.53
128.45
126.38
124.37
83.05
81.27
77.31
77.00
76.68
66.39
66.30
54.90
51.54
O
N
S
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

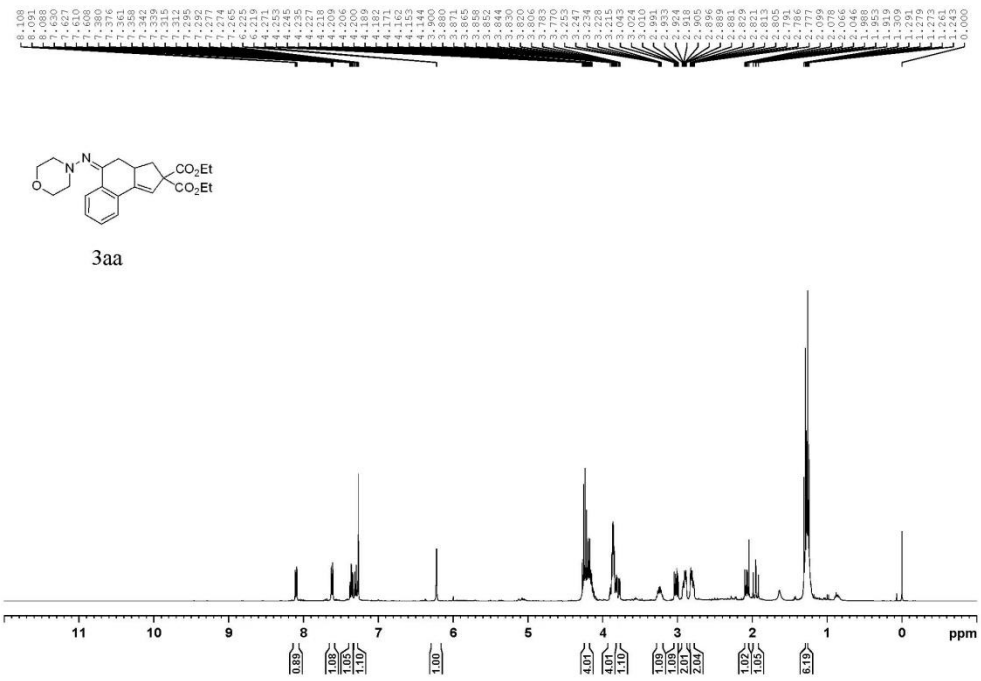
1m

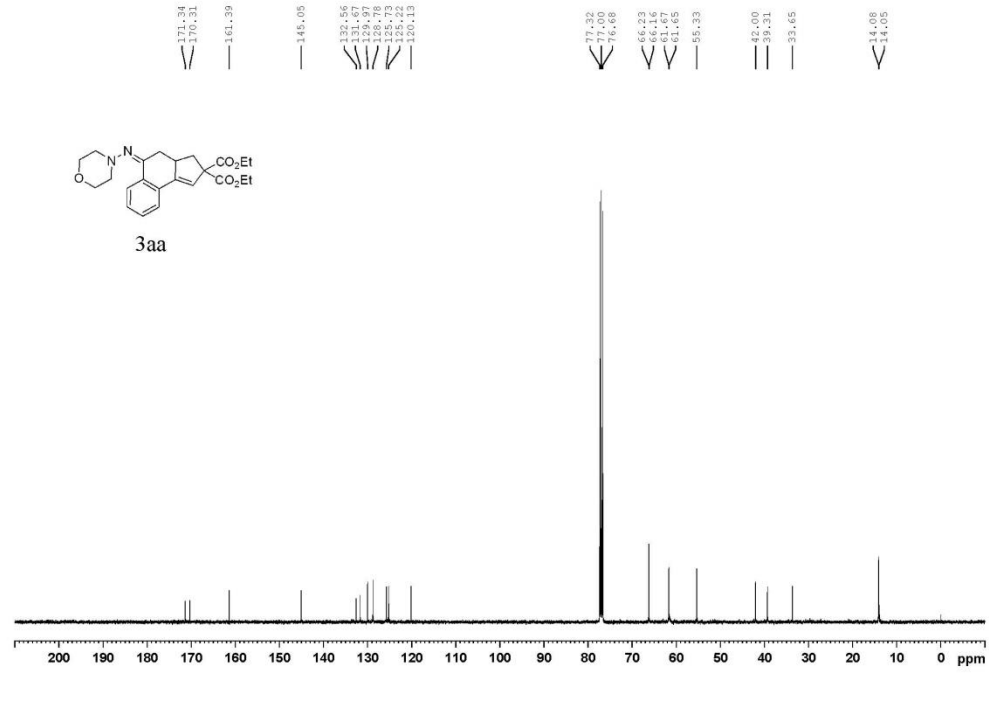

8.041
7.687
7.685
7.667
7.660
7.257
7.249
7.242
7.233
7.223
7.219
7.197
7.193
7.178
7.175
7.160
7.157
7.141
7.139
7.123
3.885
3.873
3.869
3.861
3.529
3.219
3.206
3.194
2.829
2.818
2.801
2.788
2.776
2.764
2.746
2.735
0.000
11
10
9
8
7
6
5
4
3
2
1
0
ppm
0.98
0.88
1.09
1.90
4.00
0.71
4.00
4.07

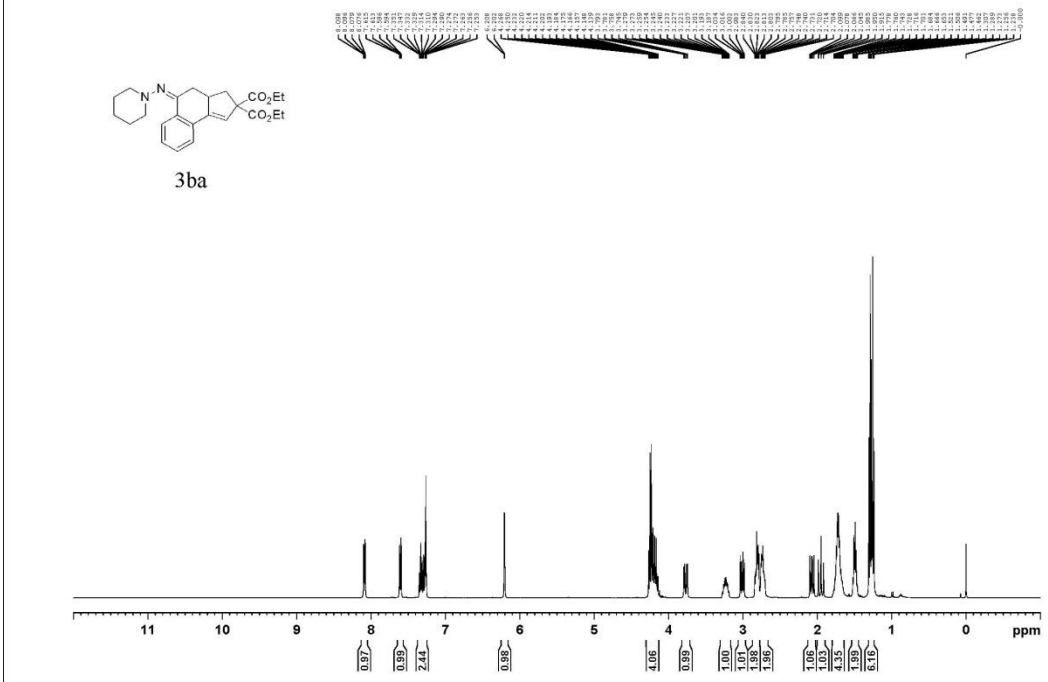
1n


143.07
135.89
135.70
133.31
127.60
127.18
126.56
126.39
116.48
85.48
79.63
77.31
77.00
76.68
66.38
51.54
27.12
22.34
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

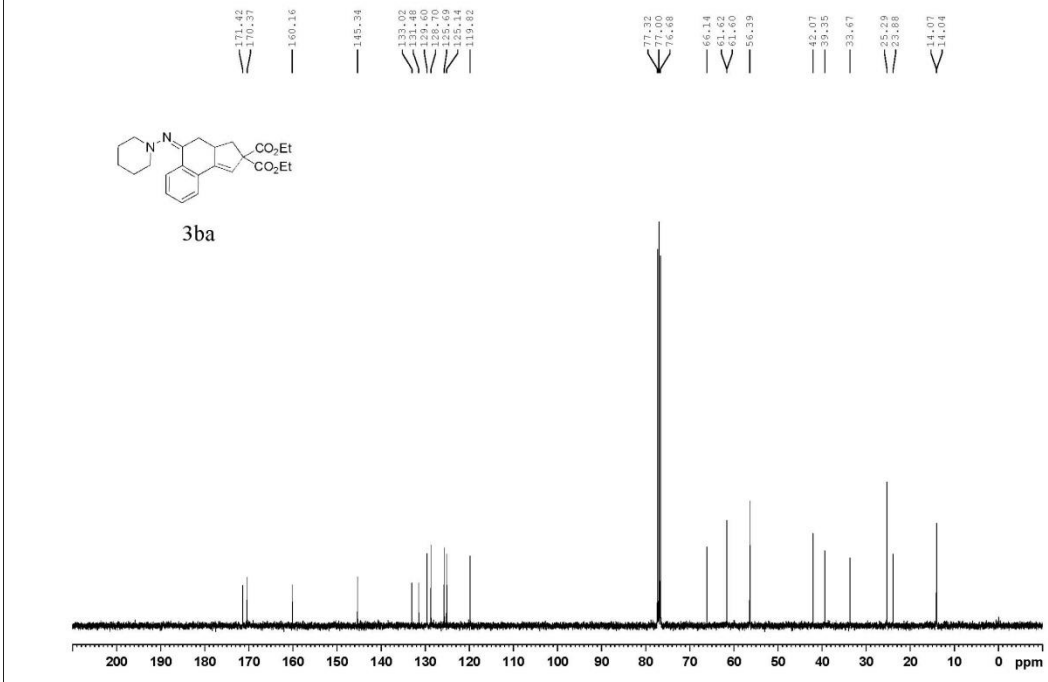
1n


CO2Et
CO2Et
3aa
11
10
9
8
7
6
5
4
3
2
1
0
ppm

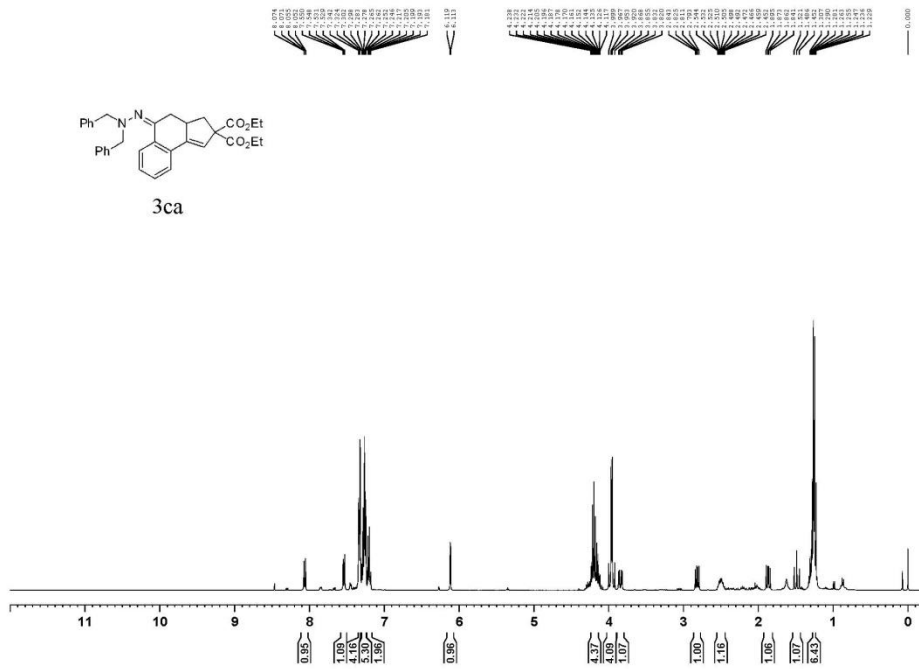

CO2Et
CO2Et
3aa
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


CO2Et
CO2Et
11
10
9
8
7
6
5
4
3
2
1
0
ppm
0.97
0.98
2.44
0.98
4.06
0.99
1.00
1.07
1.98
1.96
1.06
1.02
4.35
1.99
6.16

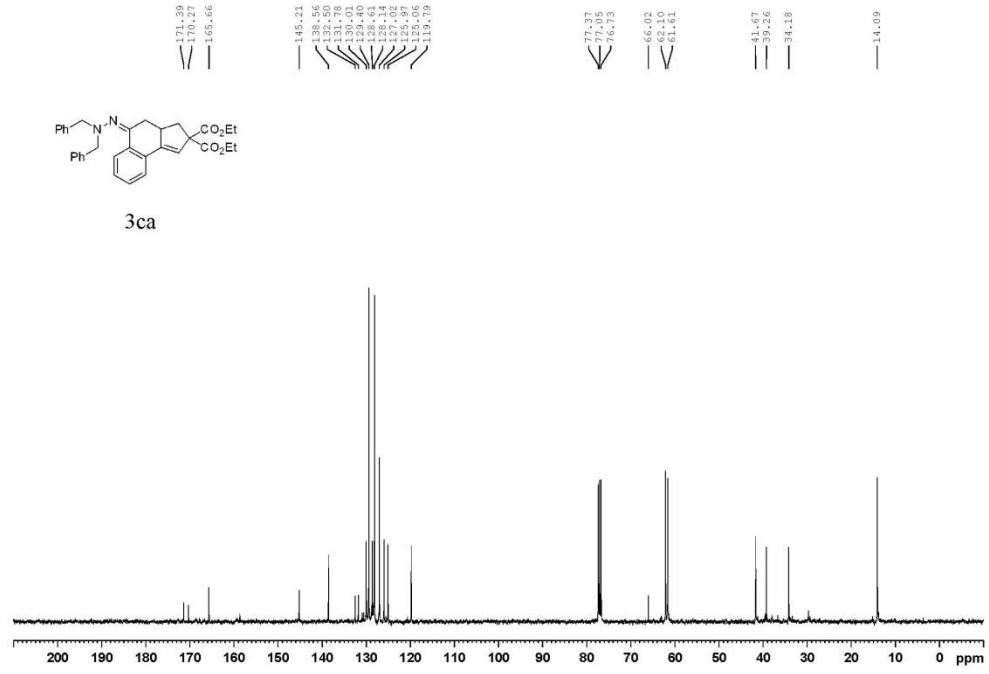
3ba


171.42
170.37
160.16
145.34
133.02
131.48
129.60
128.70
125.69
125.14
119.82
77.32
77.00
76.68
66.14
61.62
61.60
56.39
42.07
39.35
33.67
25.29
23.88
14.07
14.04
CO2Et
CO2Et
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

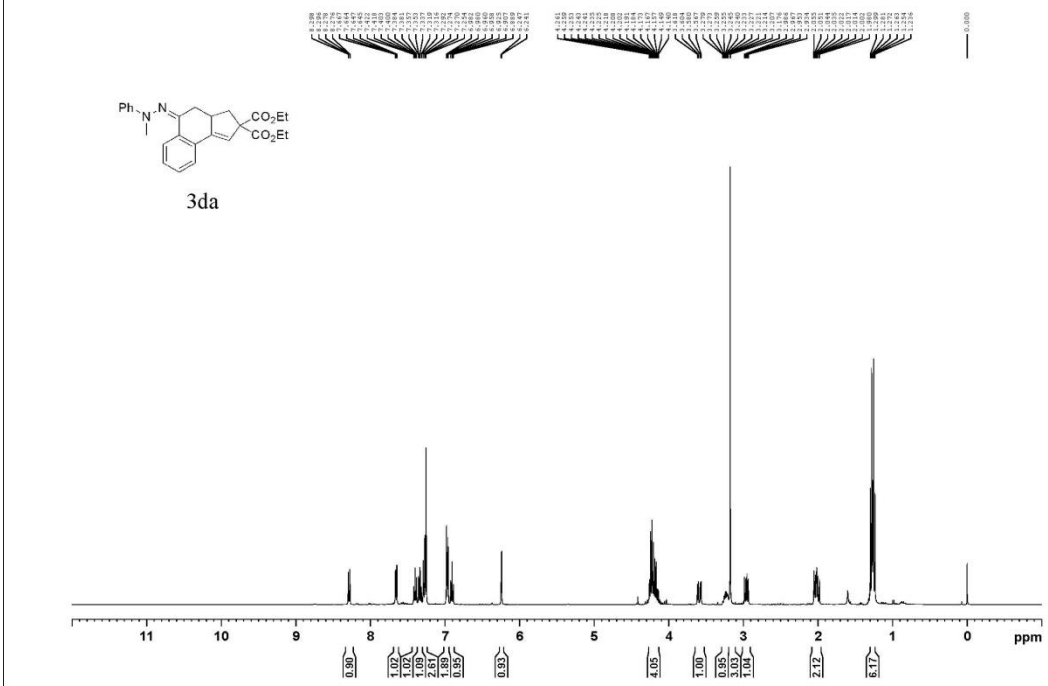
3ba


Ph
N
Ph
CO2Et
CO2Et
11
10
9
8
7
6
5
4
3
2
1
0
ppm
0.95
1.09
4.16
5.30
1.96
0.96
4.37
4.09
4.07
1.00
1.16
1.06
1.07
6.43

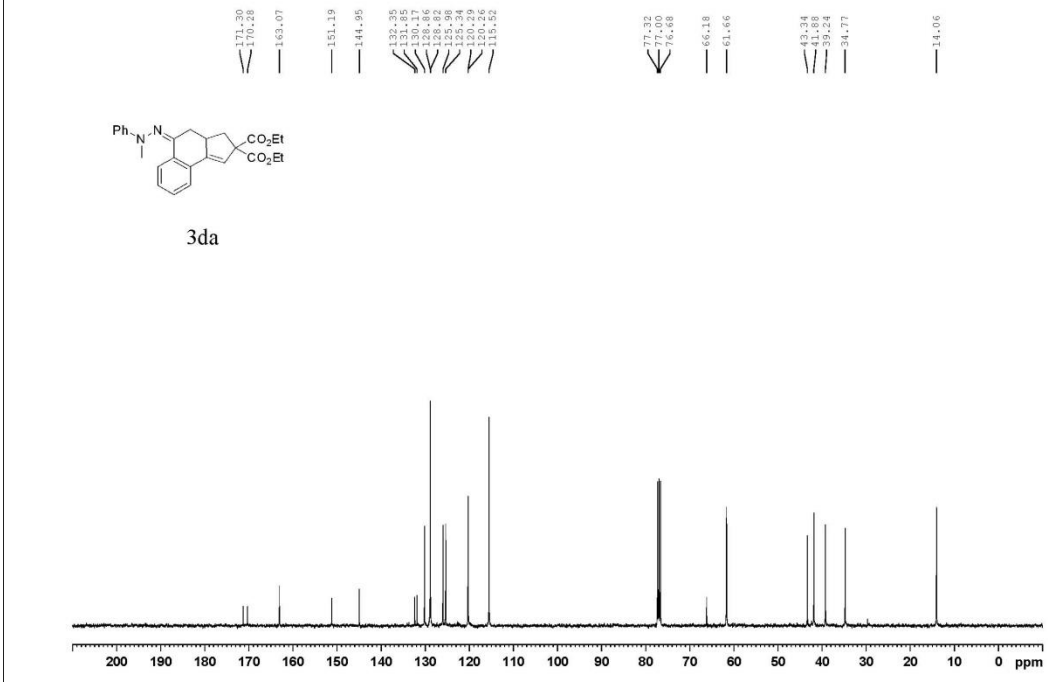
3ca


171.39
170.27
165.66
145.21
138.56
132.50
131.78
130.01
129.40
128.61
128.14
127.02
125.97
125.06
119.79
77.37
77.05
76.73
66.02
62.10
61.61
41.67
39.26
34.18
14.09
Ph
N
Ph
CO2Et
CO2Et
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

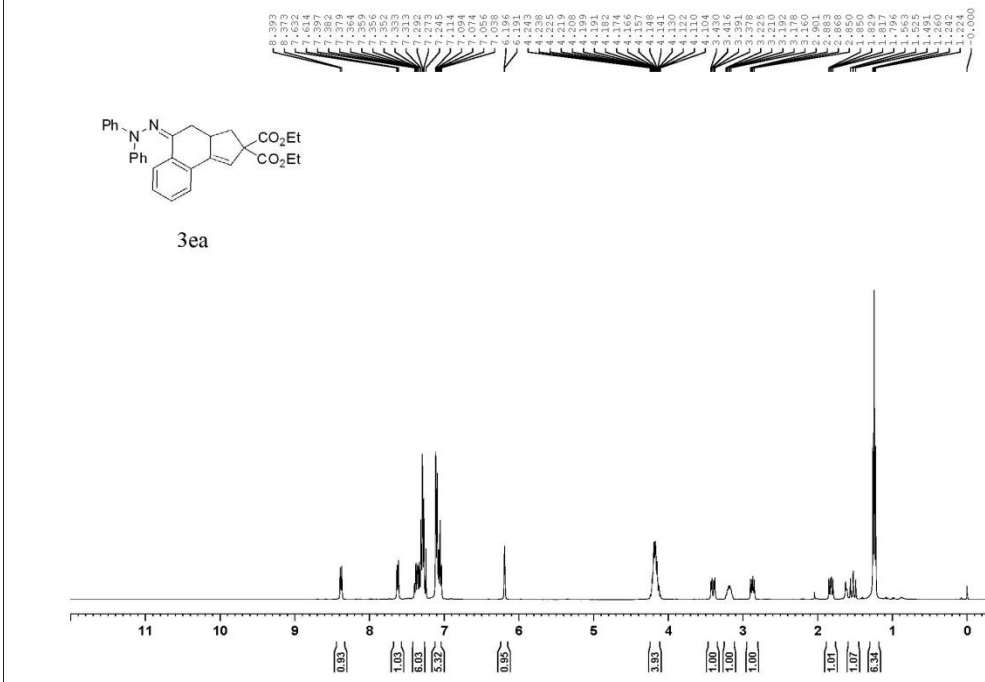
3ca


Ph
N
N
CO2Et
CO2Et
11
10
9
8
7
6
5
4
3
2
1
0
ppm
0.90
1.02
1.02
1.09
2.61
1.89
0.85
0.93
4.05
1.00
0.95
3.03
1.04
2.12
6.17

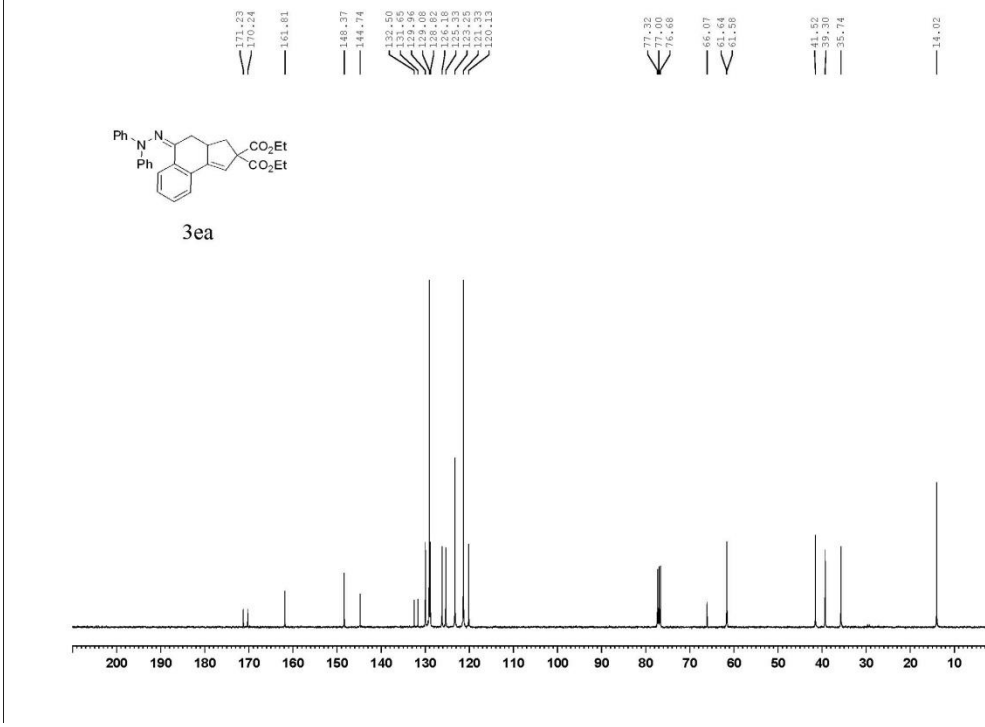
3da


171.30
170.28
163.07
151.19
144.95
132.35
131.85
130.17
128.86
128.82
125.98
125.34
120.29
120.26
115.52
77.32
77.00
76.68
66.18
61.66
43.34
41.88
39.24
34.77
14.06
Ph
N
N
CO2Et
CO2Et
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

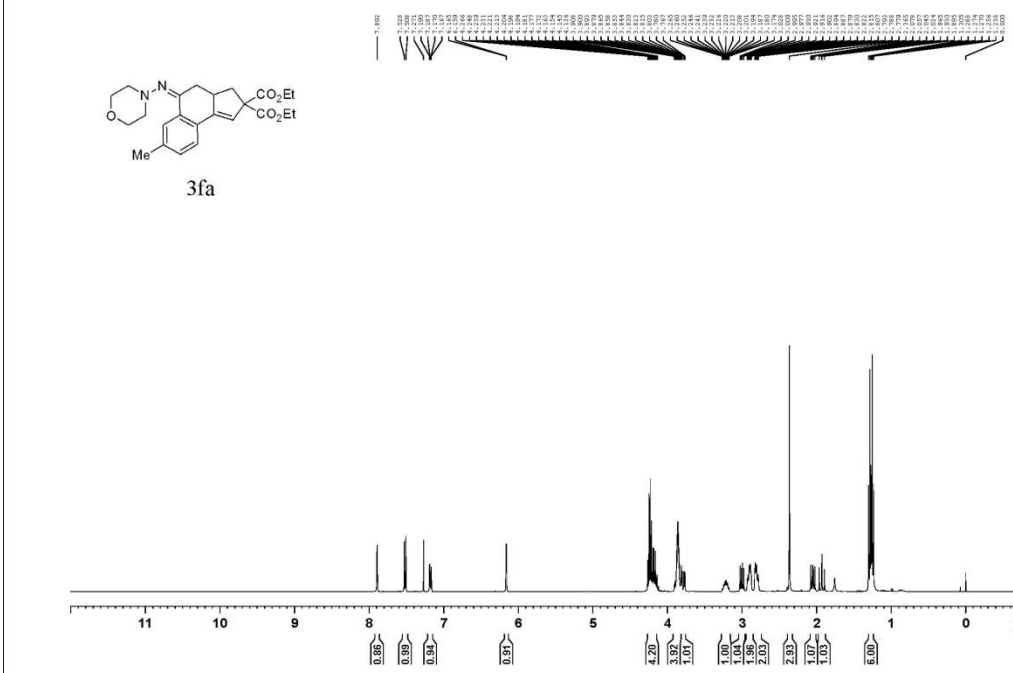
3da


8.393
8.373
7.632
7.614
7.387
7.382
7.379
7.364
7.356
7.352
7.333
7.313
7.272
7.245
7.114
7.094
7.074
7.056
7.038
6.196
6.191
4.233
4.238
4.225
4.219
4.208
4.199
4.191
4.182
4.174
4.167
4.157
4.148
4.141
4.130
4.122
4.110
4.104
3.430
3.416
3.391
3.378
3.225
3.210
3.192
3.178
3.160
2.901
2.883
2.868
2.850
1.850
1.829
1.817
1.796
1.568
1.525
1.491
1.260
1.222
1.224
0.000
Ph
N
N
Ph
CO2Et
CO2Et
11
10
9
8
7
6
5
4
3
2
1
0
ppm
0.93
1.03
6.05
5.32
0.95
3.83
1.00
1.00
1.00
1.01
1.07
6.34

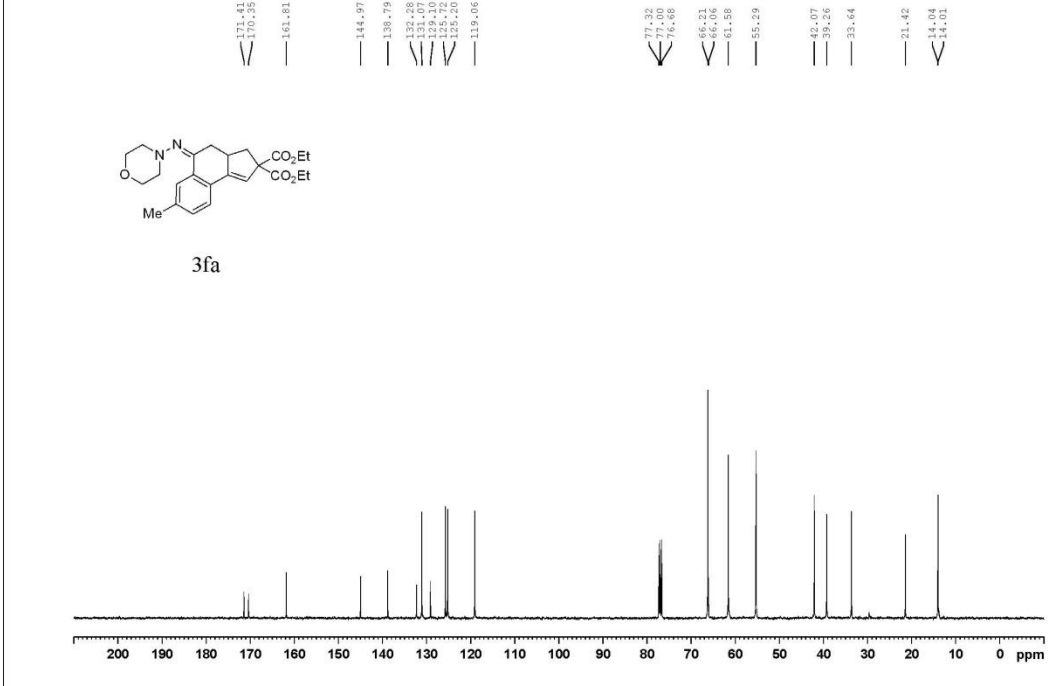
3ea


171.23
170.24
161.81
148.37
144.74
132.50
131.65
129.96
129.08
128.82
126.18
125.33
123.25
121.33
120.13
77.32
77.00
76.68
66.07
61.64
61.58
41.52
39.30
35.74
14.02
Ph
N
N
Ph
CO2Et
CO2Et
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

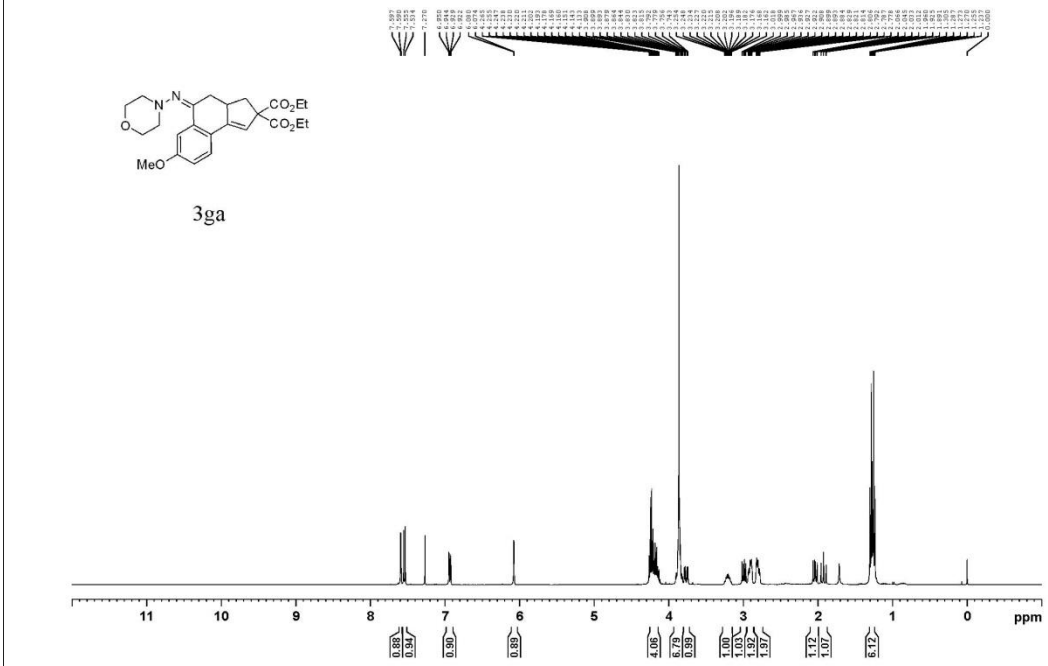
3ea


CO2Et
CO2Et
Me
11
10
9
8
7
6
5
4
3
2
1
0
ppm

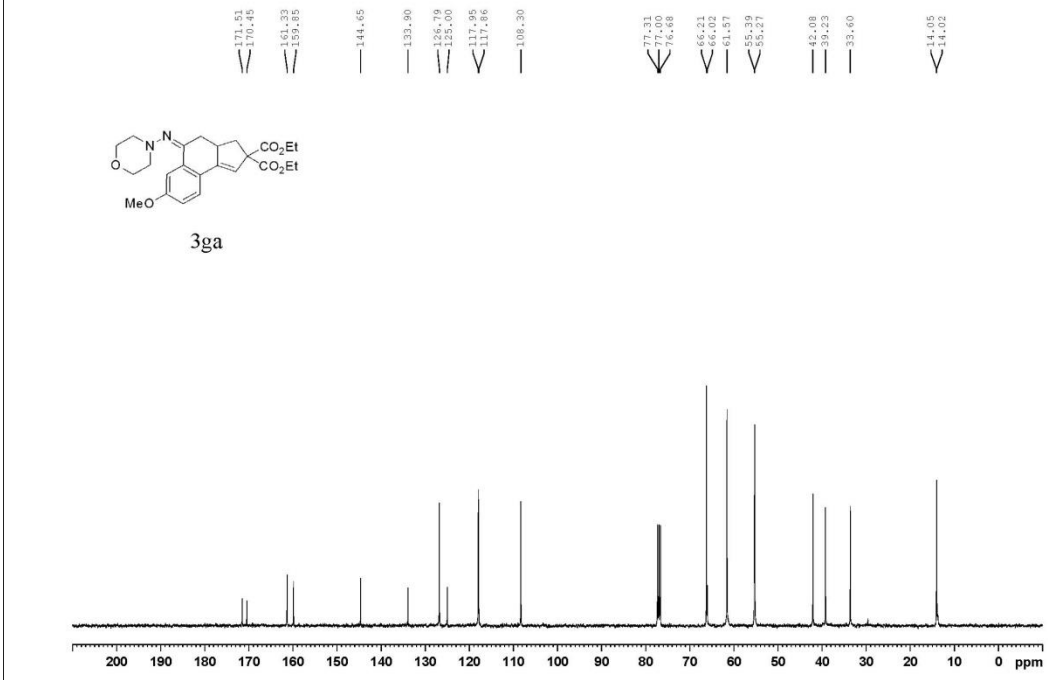
3fa


171.41
170.35
161.81
144.97
138.79
132.28
131.07
129.10
127.22
125.20
119.06
77.32
77.00
76.68
66.21
66.06
61.58
55.29
42.07
39.26
33.64
21.42
14.04
14.01
CO2Et
CO2Et
Me
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

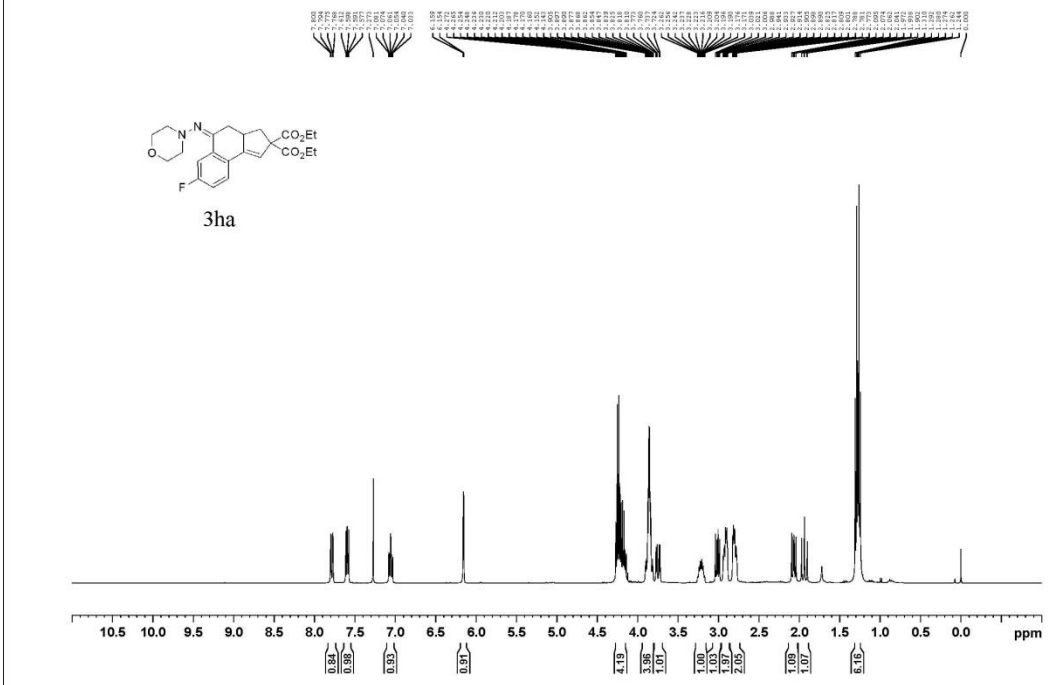
3fa

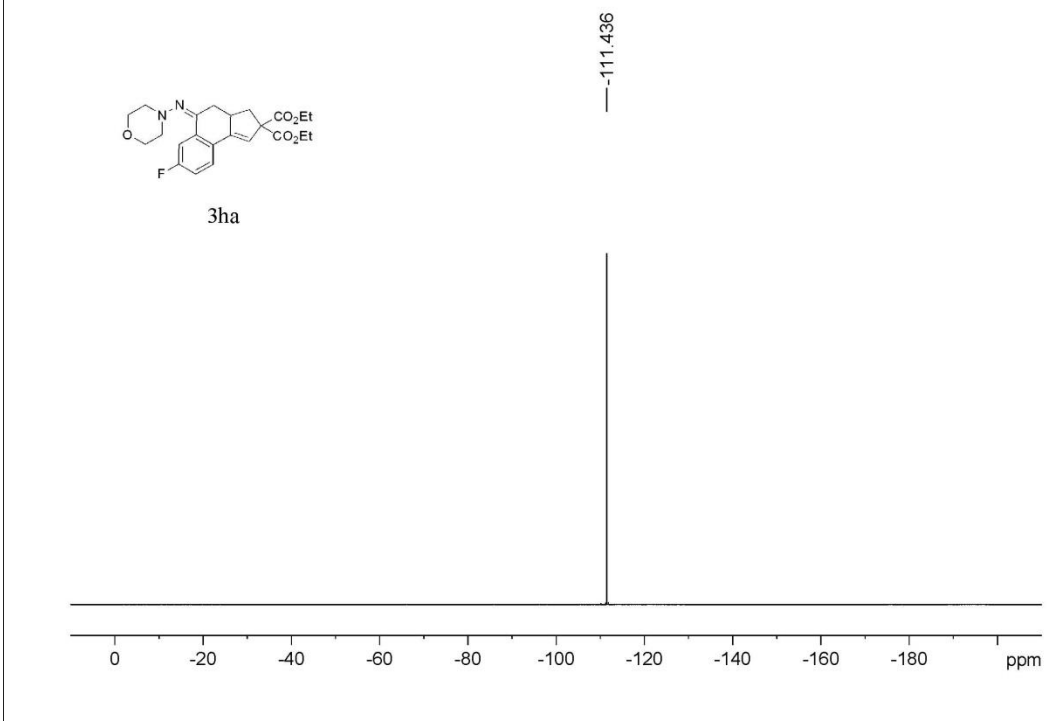

CO2Et
CO2Et
MeO
11
10
9
8
7
6
5
4
3
2
1
0
ppm

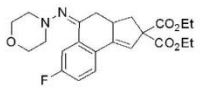
3ga


171.51
170.45
161.33
159.85
144.65
133.90
126.79
126.00
117.95
117.86
108.30
77.31
77.00
76.68
66.21
66.02
61.57
55.39
55.27
42.08
39.23
33.60
14.05
14.02
CO2Et
CO2Et
MeO
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

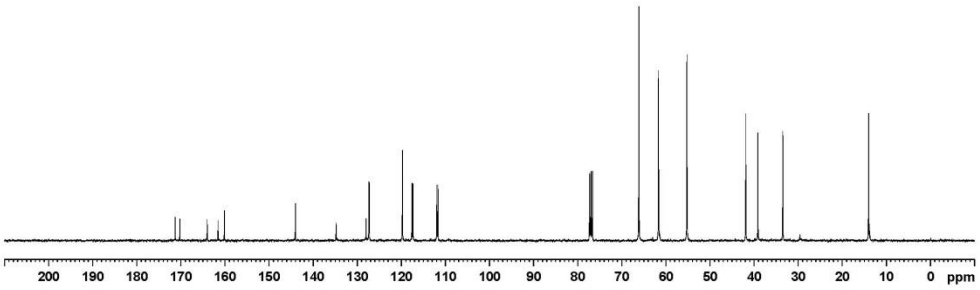
3ga

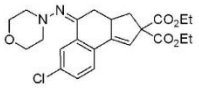

CO2Et
CO2Et
F
3ha
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
0.84 0.98 0.93 0.91 4.19 3.98 1.01 1.00 1.03 1.97 2.05 1.09 1.07 6.16


-111.436
CO2Et
CO2Et
F
3ha
0 -20 -40 -60 -80 -100 -120 -140 -160 -180 ppm

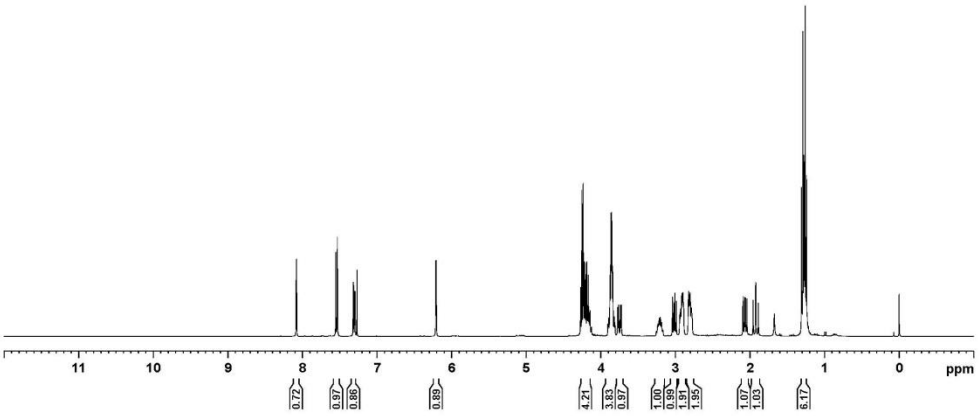


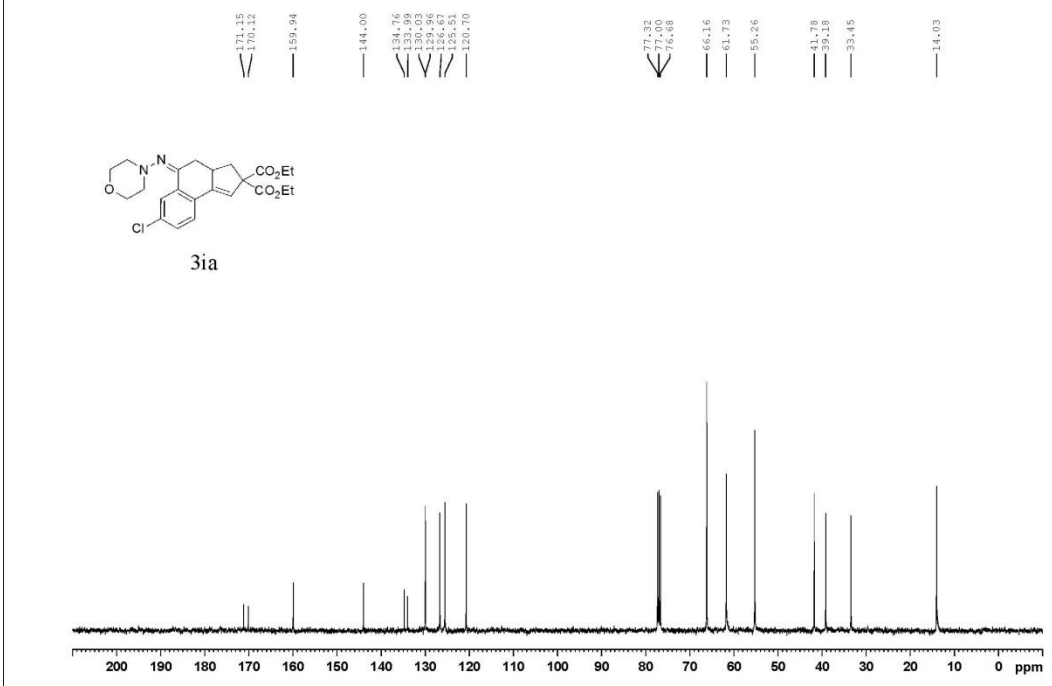
3ha



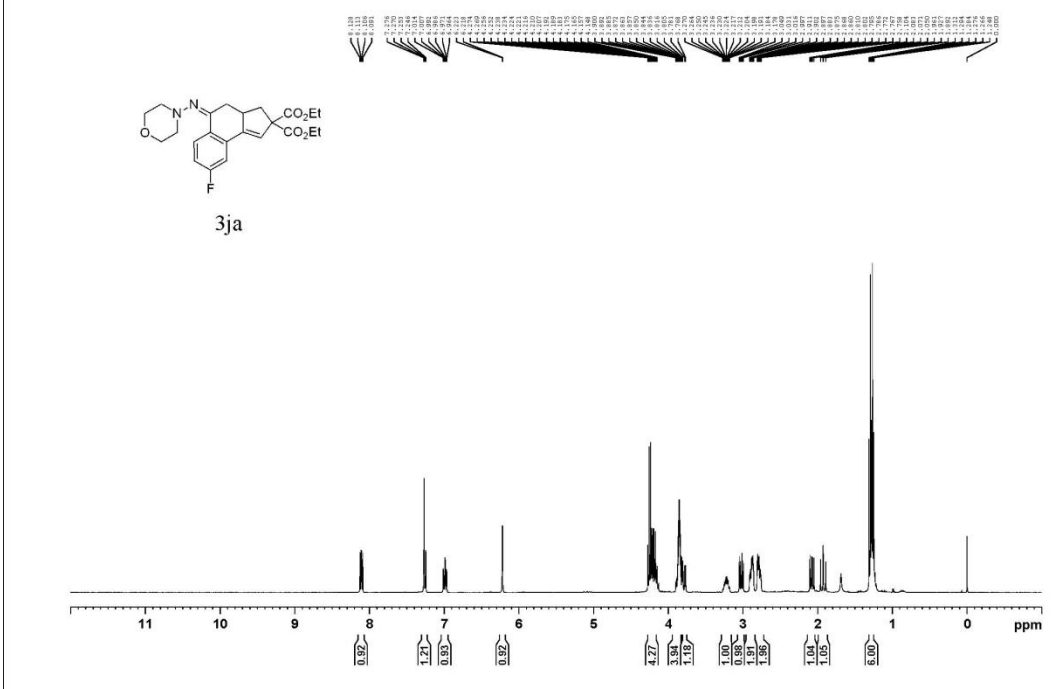


3ia

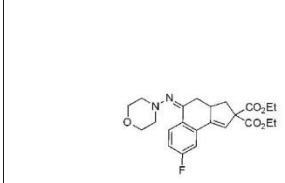



171.15
170.12
159.94
144.00
134.76
133.99
130.03
129.96
126.67
125.51
120.70
77.32
77.00
76.68
66.16
61.73
55.26
41.78
39.18
33.45
14.03
CO2Et
CO2Et
Cl
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

3ia


CO2Et
CO2Et
F
11 10 9 8 7 6 5 4 3 2 1 0 ppm
0.92
1.21
0.83
0.92
4.27
3.84
1.18
1.00
0.98
1.91
1.86
1.04
1.65
6.00

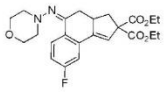
3ja



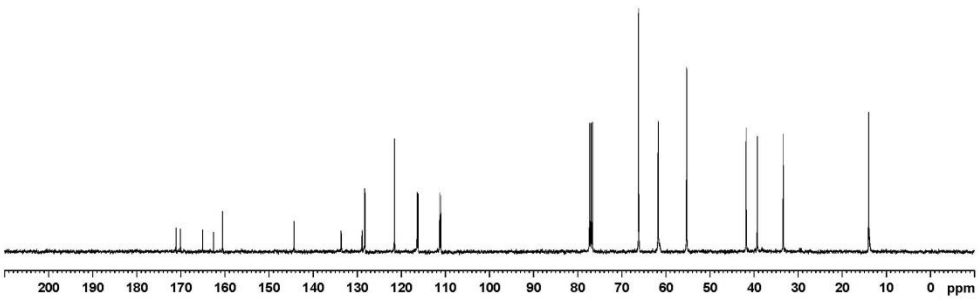
3ja

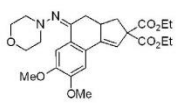
-110.857
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm


171.09
170.05
165.05
162.57
160.51
144.30
133.66
133.58
128.90
128.30
128.22
121.53
116.41
116.19
111.28
111.06
77.31
77.00
76.68
66.19
61.77
61.74
55.30
41.80
39.29
33.40
14.04
14.02

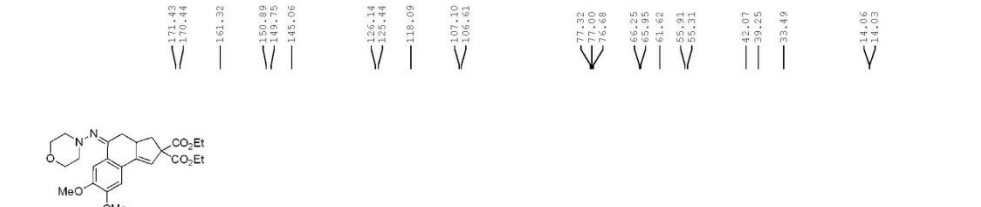


3ja

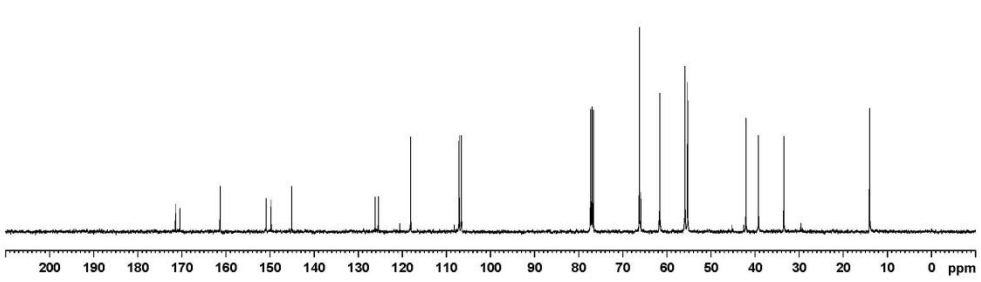

200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

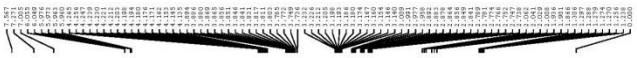


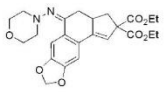
3ka



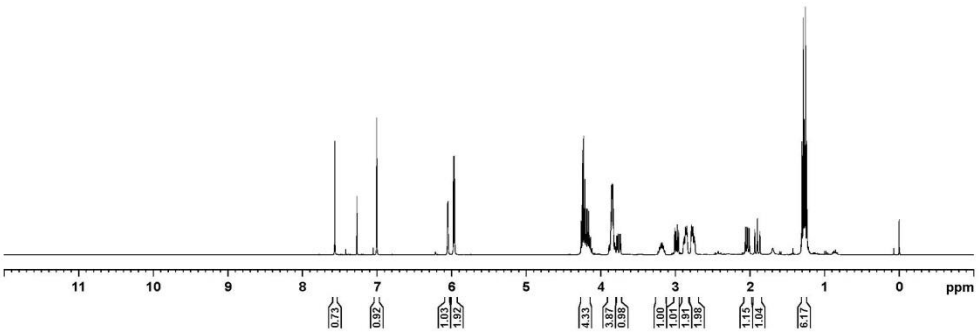
3ka

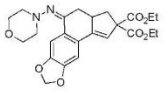




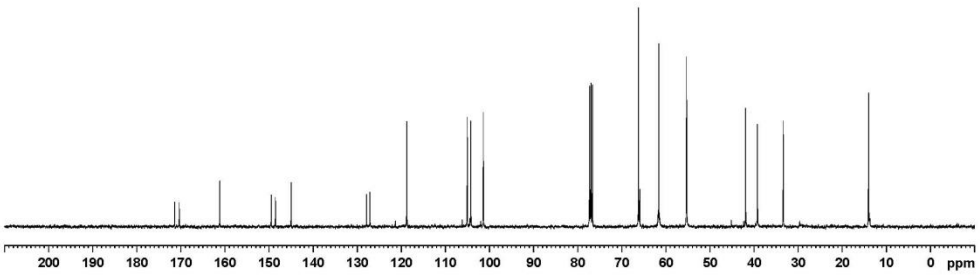


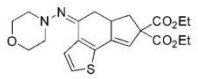
3la



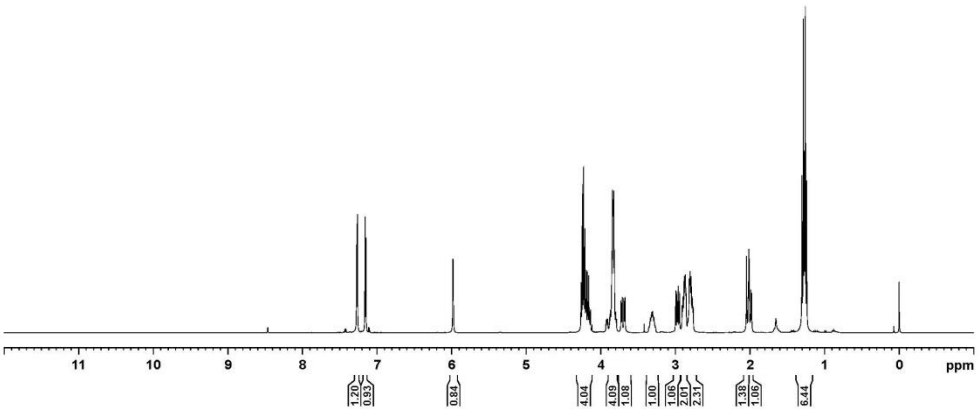


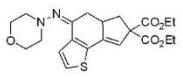
3la



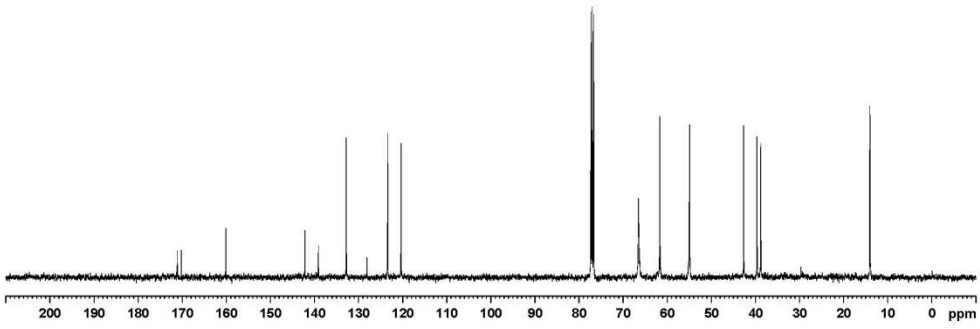


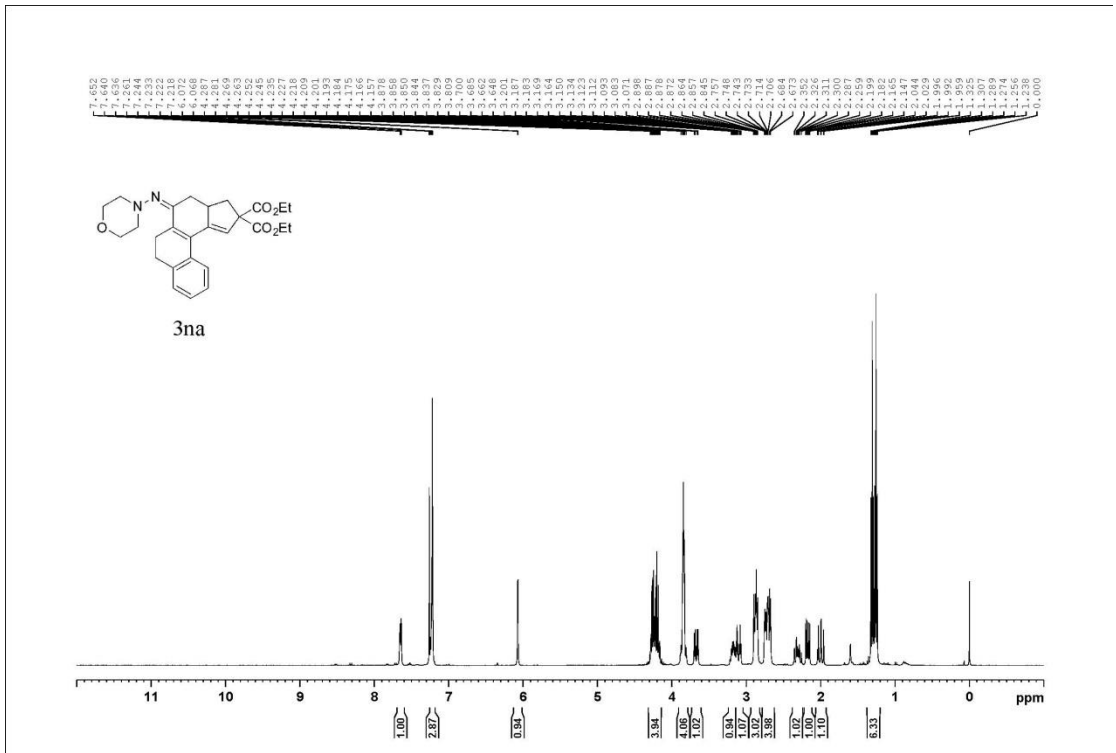
3ma

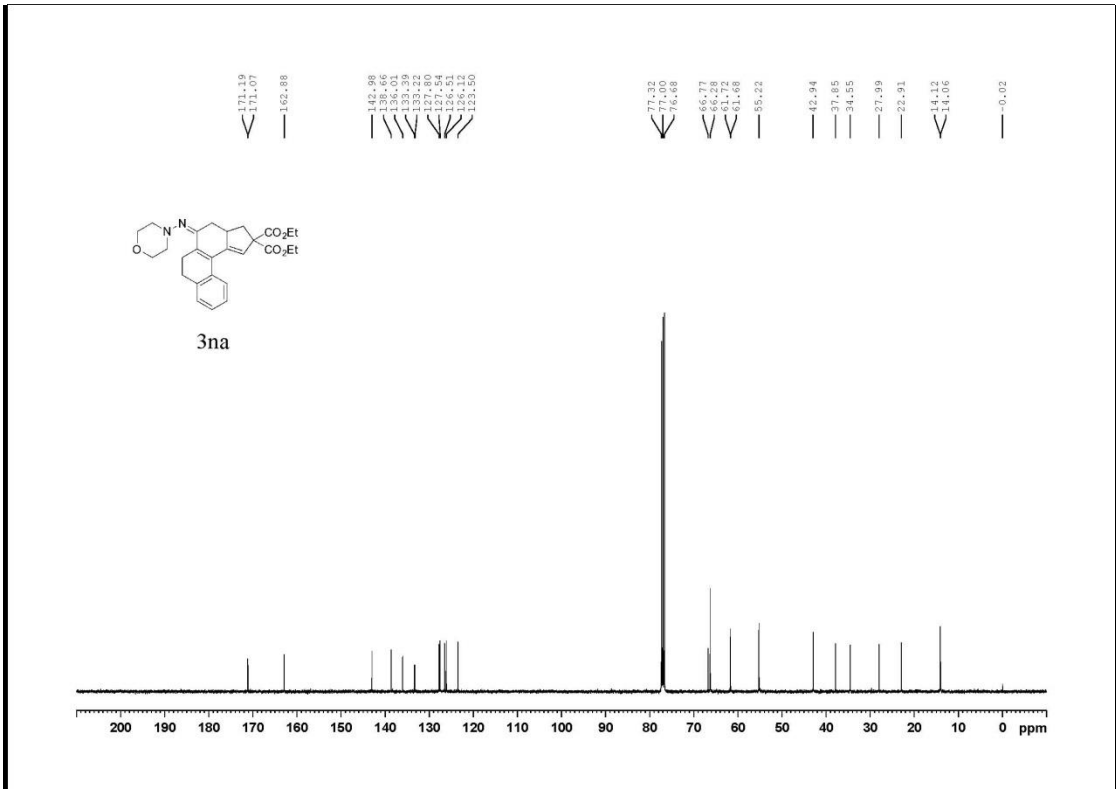


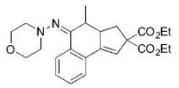


3ma

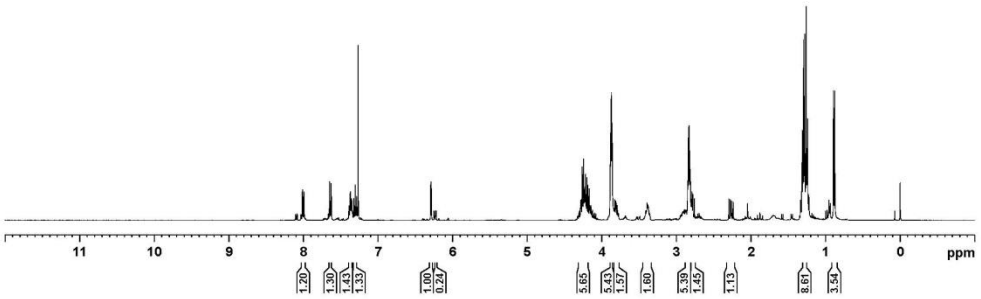



CO2Et
CO2Et
3na
ppm

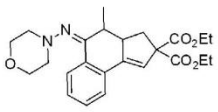

CO2Et
CO2Et
3na
ppm



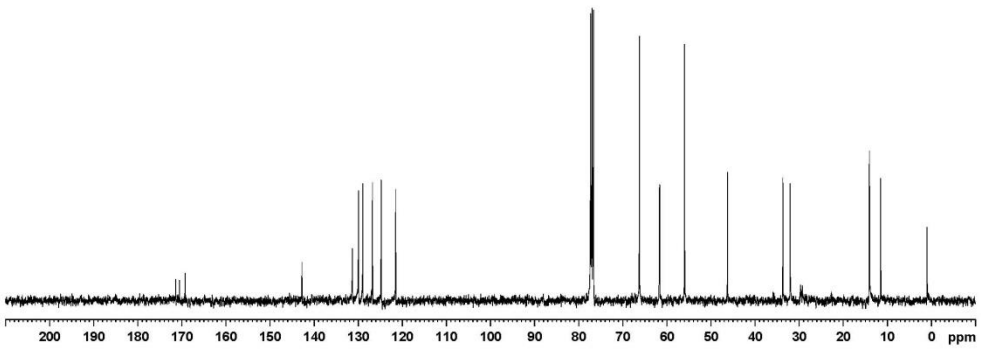
3ab

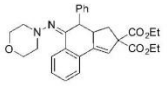

11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.20
1.30
1.43
1.33
1.00
0.24
5.65
5.43
1.57
1.60
5.39
1.45
1.13
8.61
3.54


171.38
170.50
169.20
142.76
131.35
129.97
128.68
126.78
124.81
121.50
77.31
77.00
76.68
66.24
61.72
61.63
55.99
46.26
33.70
32.03
14.05
11.90
0.99

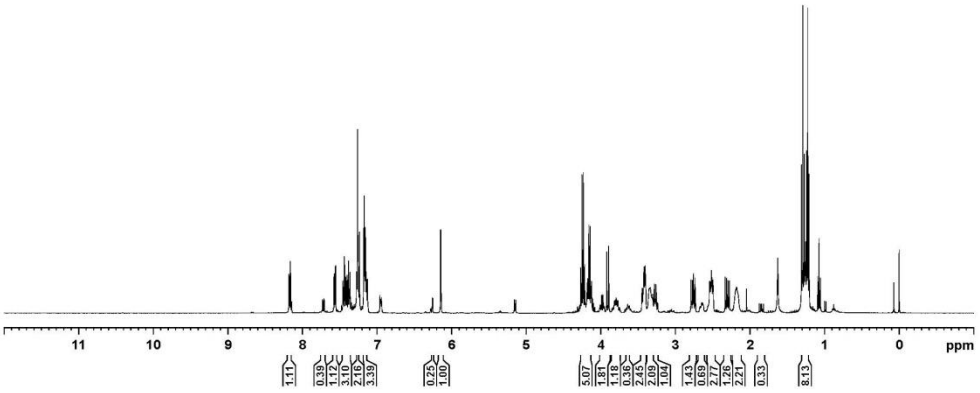


3ab

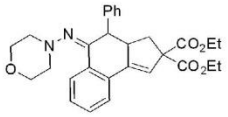

200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


Ph
N
O
CO2Et
CO2Et

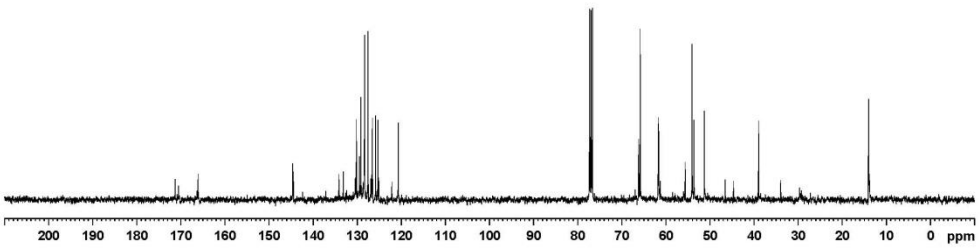
3ac

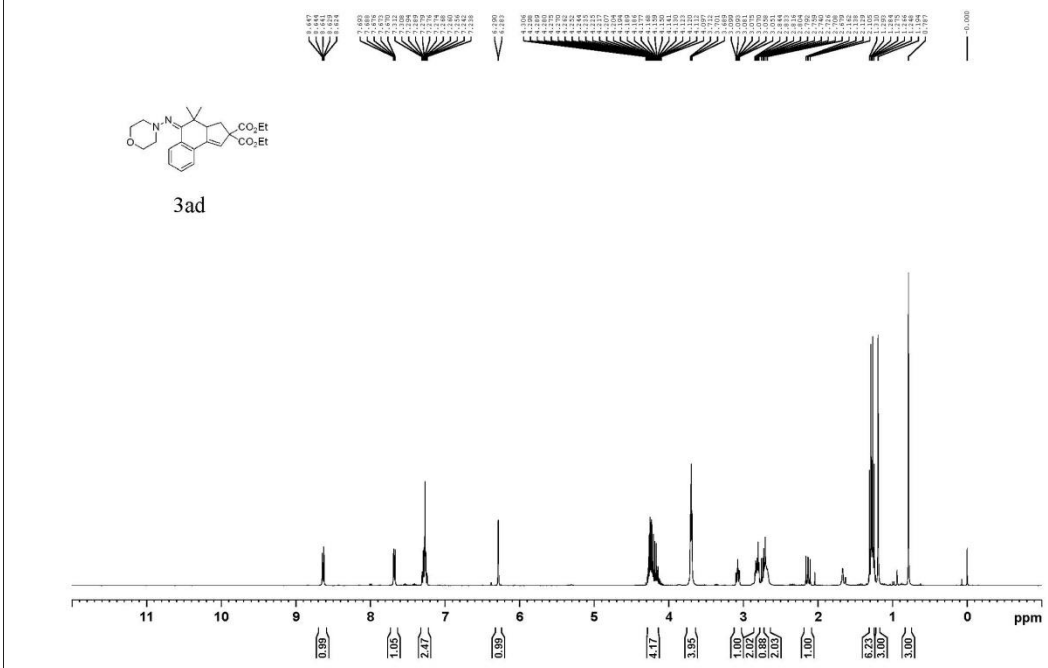

11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.11
0.30
1.12
3.10
2.16
3.39
0.25
1.00
5.07
1.85
1.16
0.38
2.45
2.09
1.04
1.43
0.69
2.77
2.76
2.21
0.33
8.13


171.26
170.53
166.08
144.63
144.47
134.15
133.17
130.42
130.18
129.49
129.14
128.67
128.42
128.31
127.53
126.92
126.73
126.54
125.91
125.31
125.13
122.14
120.69
77.32
77.00
76.69
66.17
65.84
61.75
61.66
55.64
54.08
53.65
51.28
38.98
14.07
14.01

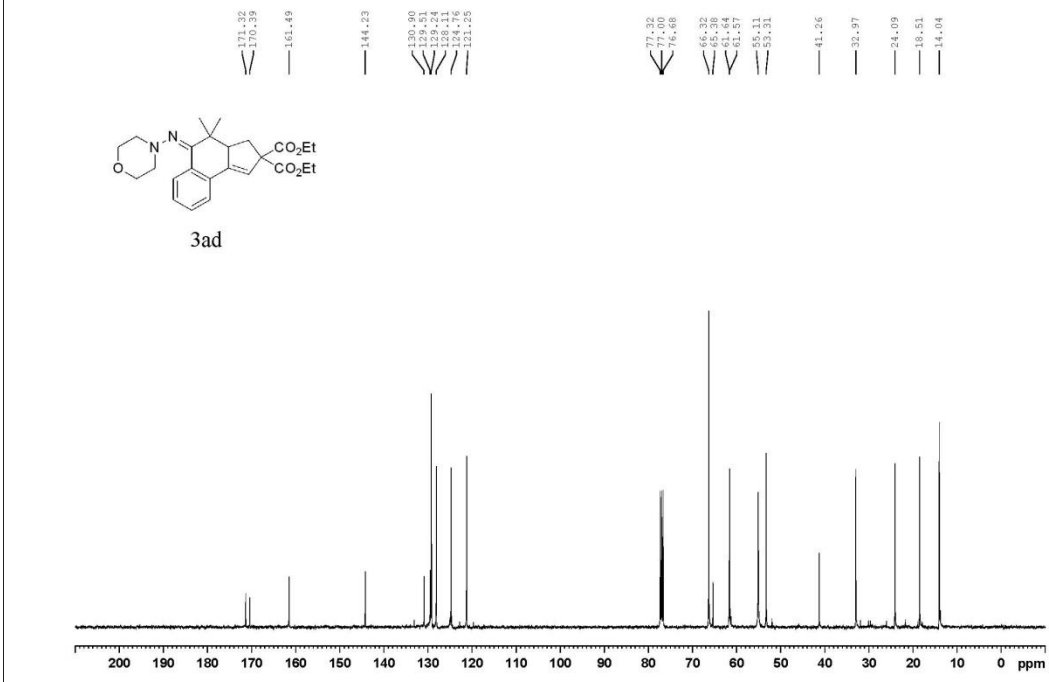

Ph
N
O
CO2Et
CO2Et

3ac

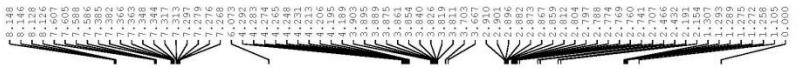

200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

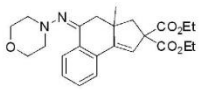

CO2Et
CO2Et
11
10
9
8
7
6
5
4
3
2
1
0
ppm
0.99
1.05
2.47
0.98
4.17
3.95
1.00
2.02
0.88
2.03
1.00
6.23
3.00
3.00

3ad

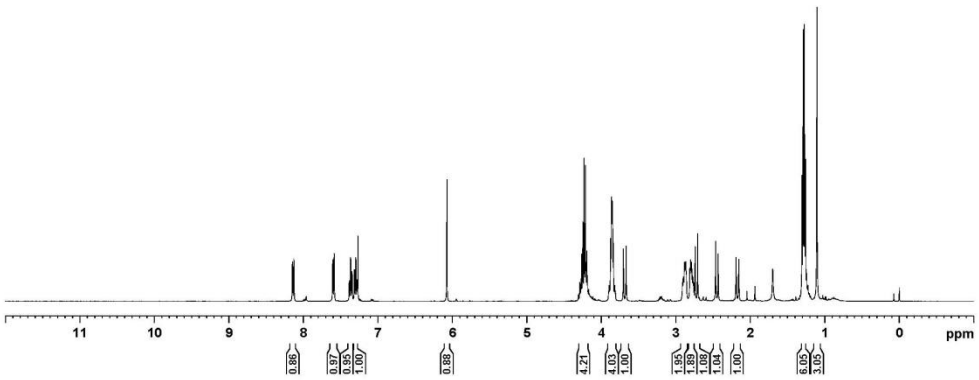

171.32
170.39
161.49
144.23
130.90
129.51
129.24
128.11
124.76
121.25
77.32
77.00
76.68
66.32
65.38
61.44
61.07
55.11
53.31
41.26
32.97
24.09
18.51
14.04
CO2Et
CO2Et
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

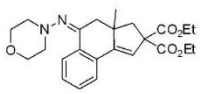
3ad



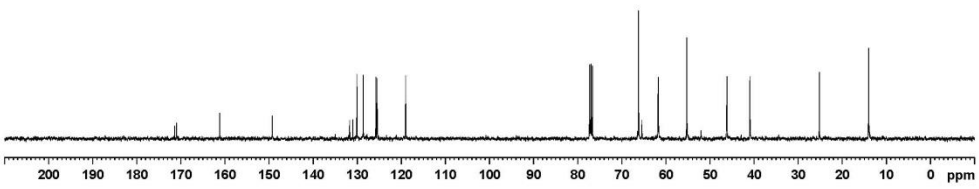


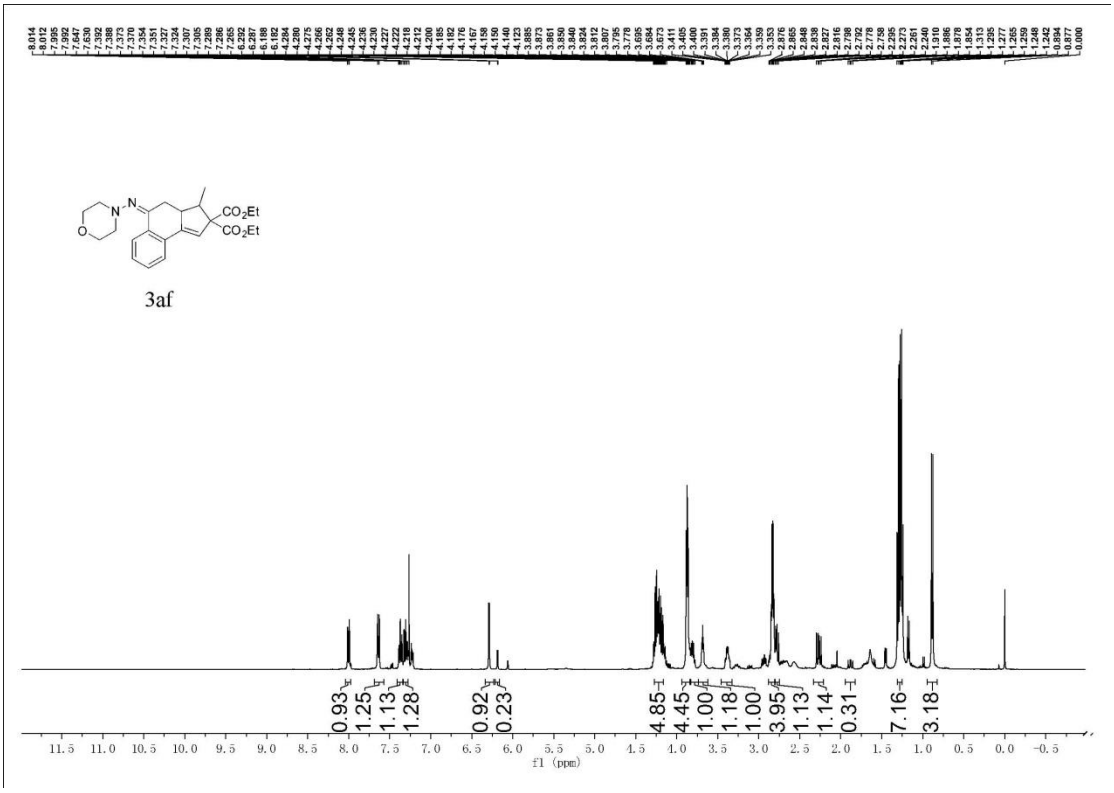
3ae


11
10
9
8
7
6
5
4
3
2
1
0
ppm
0.86
0.97
0.95
1.00
0.88
4.21
4.03
1.00
1.95
1.89
1.08
1.04
1.00
6.05
3.05

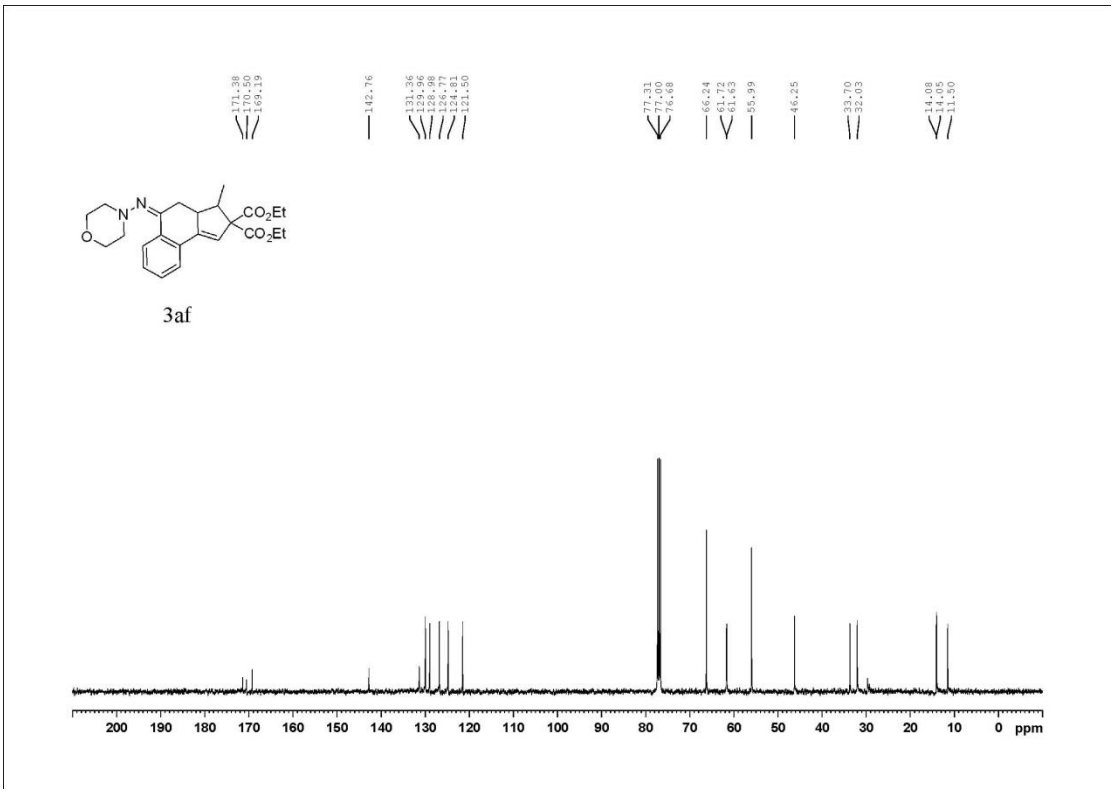


3ae

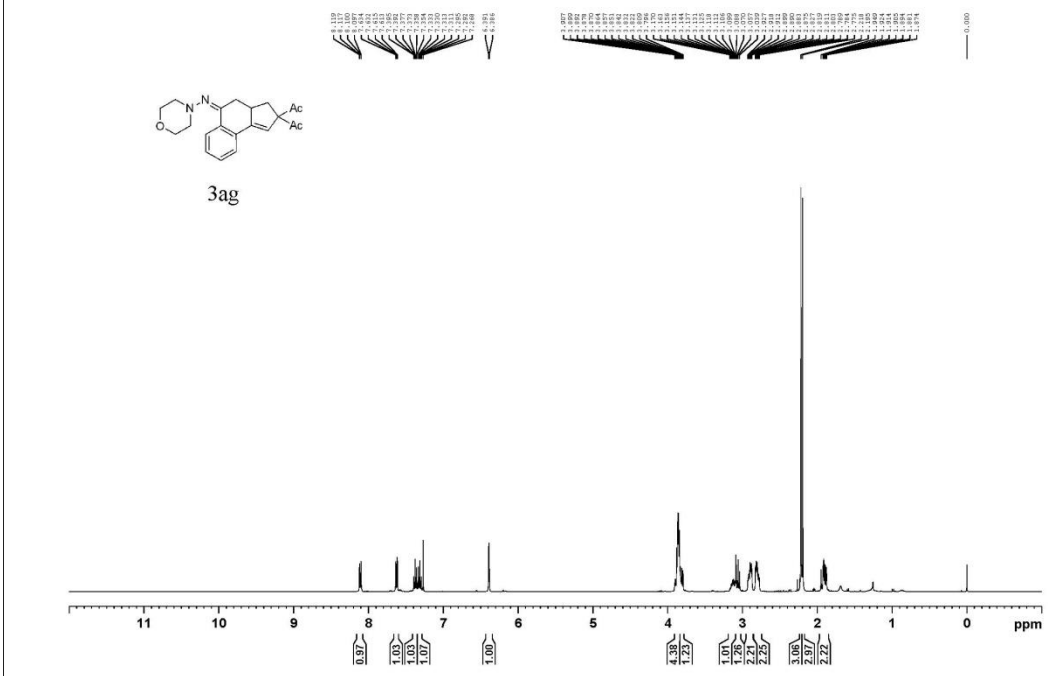

200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

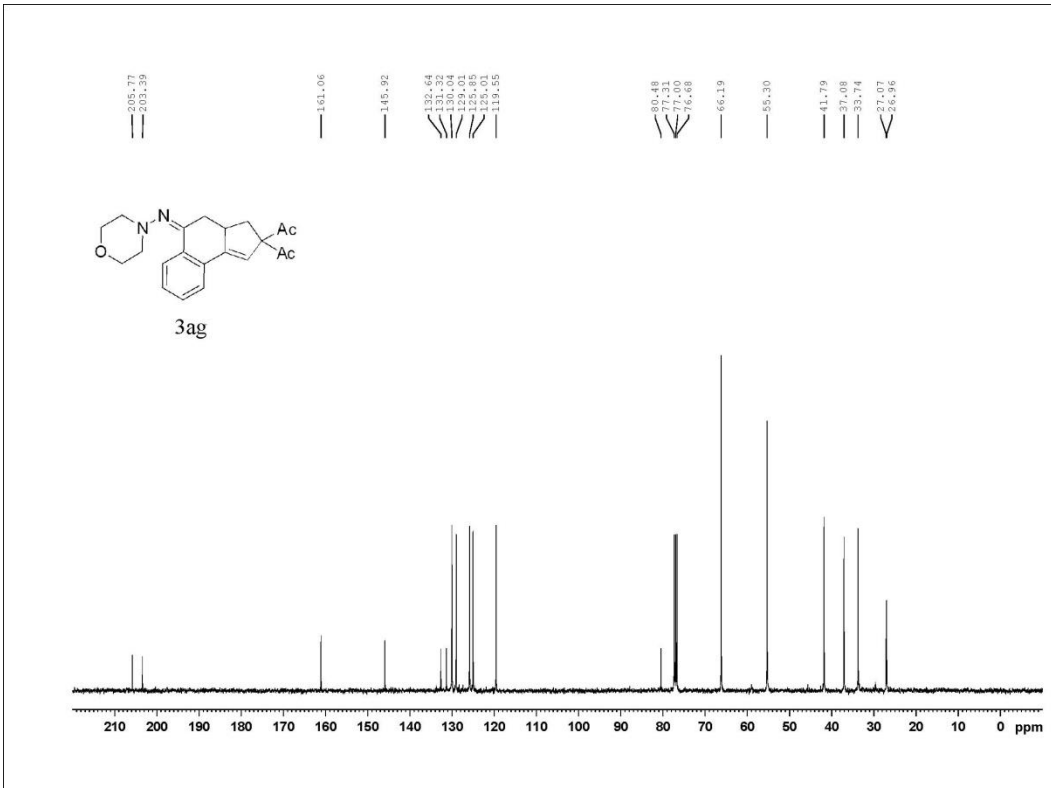

CO2Et
CO2Et
0.93
1.25
1.13
1.28
0.92
0.23
4.85
4.45
1.00
1.18
1.00
3.95
1.13
1.14
0.31
7.16
3.18
f1 (ppm)

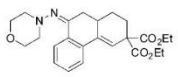
3af


CO2Et
CO2Et
ppm

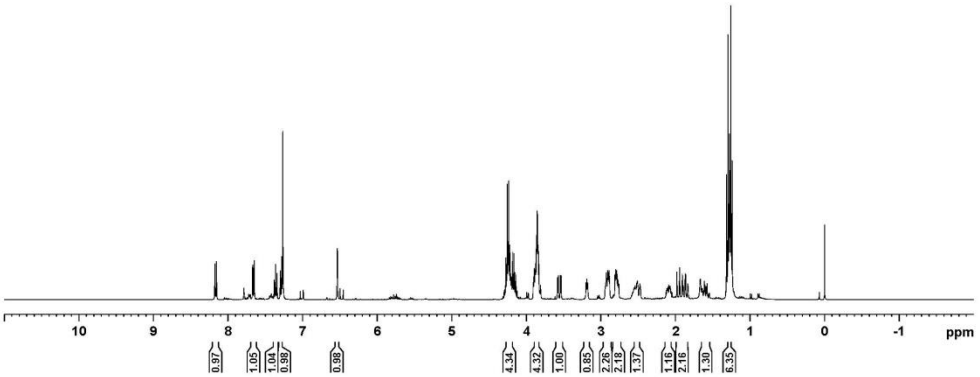
3af


Ac
Ac
3ag
11
10
9
8
7
6
5
4
3
2
1
0
ppm

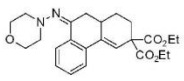

205.77
203.39
161.06
145.92
132.64
131.32
130.04
129.01
128.85
125.01
119.55
80.48
77.31
77.00
76.68
66.19
55.30
41.79
37.08
33.74
27.07
26.96
Ac
Ac
3ag
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm



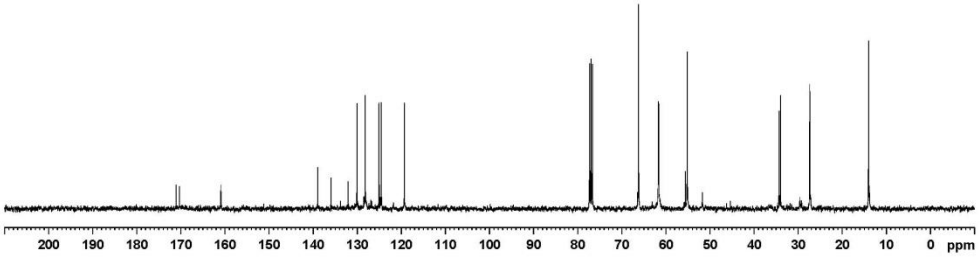
3ai

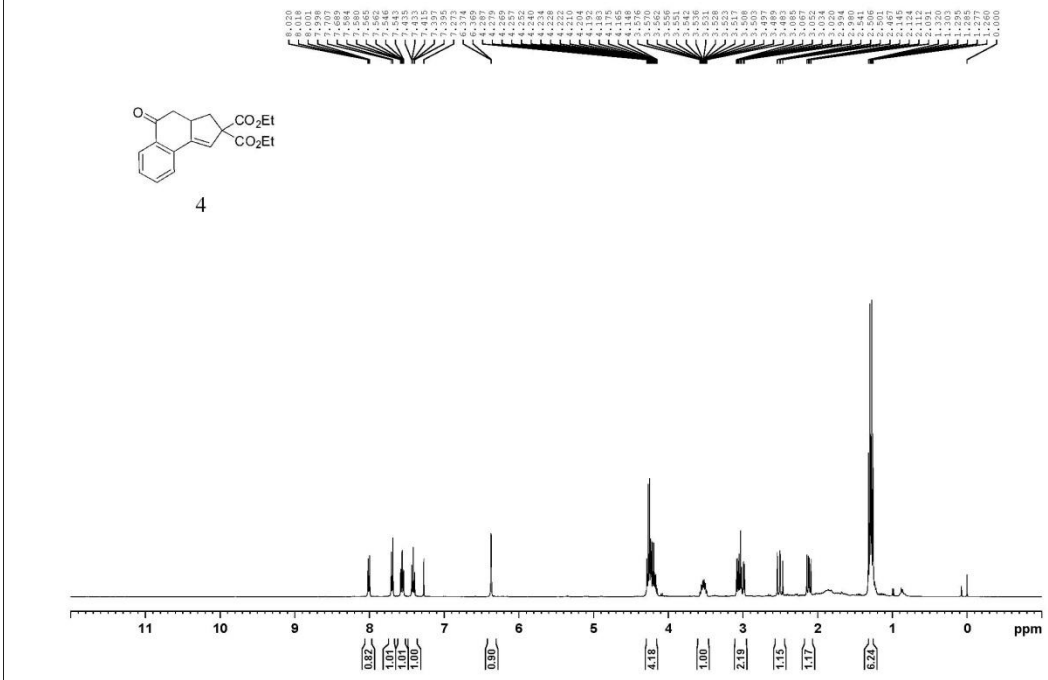

10
9
8
7
6
5
4
3
2
1
0
-1
ppm
0.97
1.05
1.04
0.98
0.98
4.34
4.32
1.00
0.85
2.28
2.18
1.37
1.16
2.16
1.30
6.35

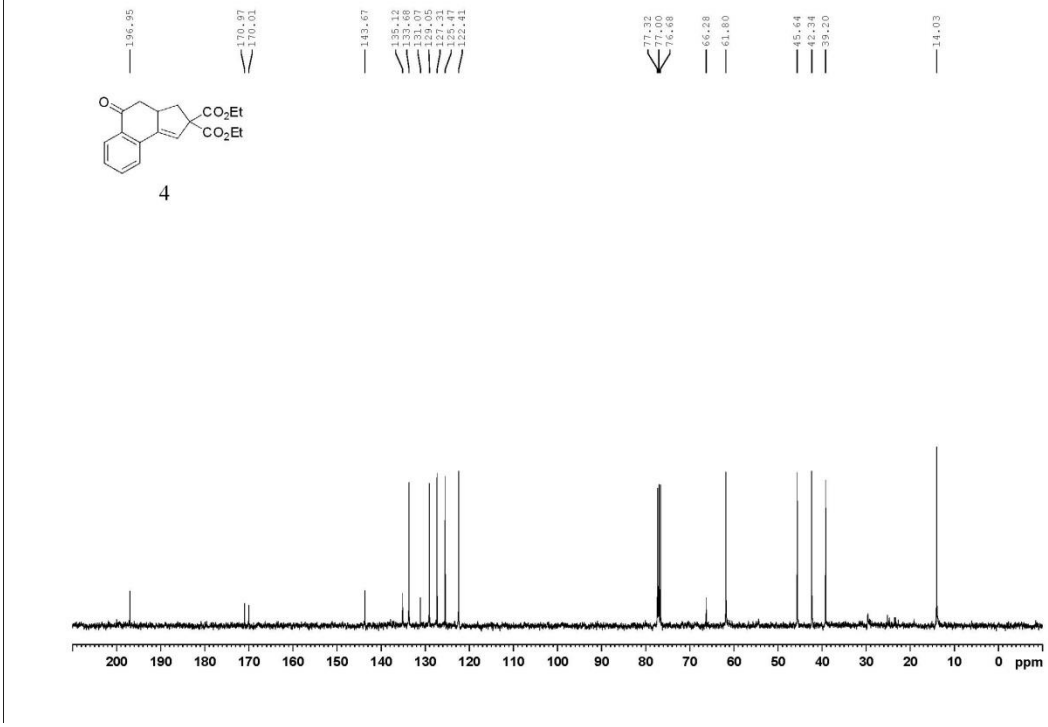

171.03
170.33
160.92
138.96
135.97
132.04
130.05
128.20
125.05
124.45
119.30
77.32
77.00
76.68
66.20
61.71
61.62
55.16
34.32
34.01
27.39
27.35
14.03

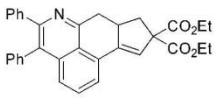


3ai

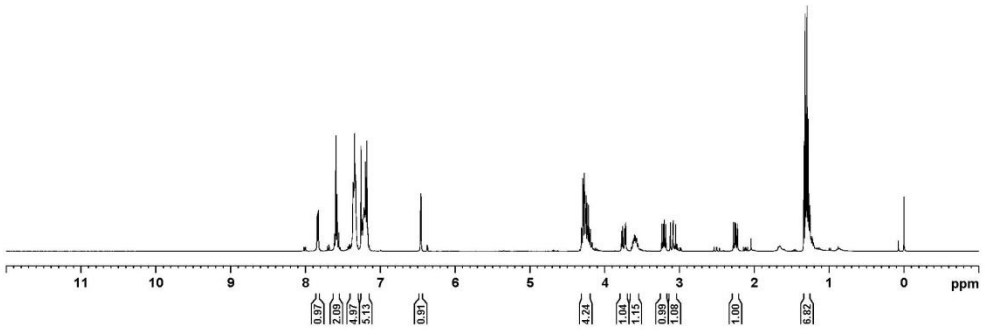

200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

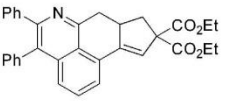

CO2Et
CO2Et
4
ppm


CO2Et
CO2Et
4
ppm

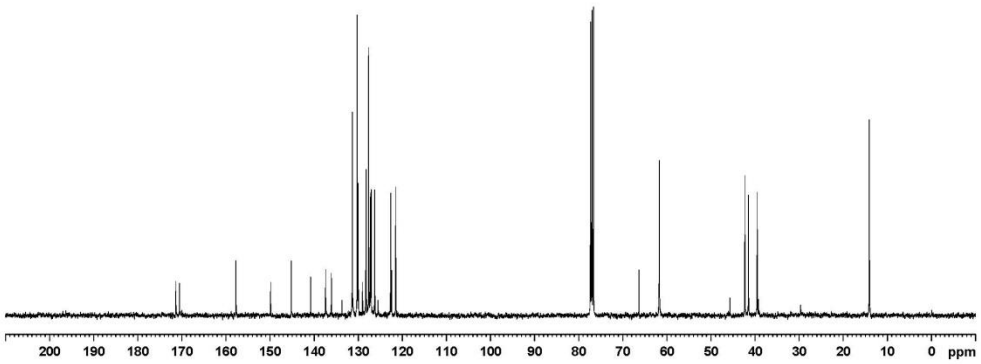

Ph
N
Ph
CO2Et
CO2Et

5


11
10
9
8
7
6
5
4
3
2
1
0
ppm
0.97
2.09
4.97
5.13
0.91
4.24
1.04
1.15
0.89
1.08
1.00
6.82


Ph
N
Ph
CO2Et
CO2Et

5


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