Supporting Information

Brønsted Base-Catalyzed Reductive Cyclization of Alkynyl *α*-Iminoesters through Auto-Tandem Catalysis

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Contents

General Information

Unless otherwise noted, the reactions were carried out with dried glassware under argon atmosphere. ^{1}H NMR spectra were recorded on a JEOL JNM-ECA600 (600 MHz) spectrometer. Chemical shifts are reported in ppm from the solvent resonance or tetramethylsilane (TMS) as the internal standard ($CDCl_3$: 7.26 ppm, TMS: 0.00 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz) and integration. ^{13}C NMR spectra were recorded on a JEOL JNM-ECA600 (150 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from the solvent resonance as the internal standard ($CDCl_3$: 77.0 ppm). Analytical thin layer chromatography (TLC) was performed on Merck precoated TLC plates (silica gel 60 GF_{254}, 0.25 mm). Flash column chromatography was performed on silica gel 60N (spherical, neutral, 40-50 μm; Kanto Chemical Co., Inc.). High resolution mass spectra analysis was performed on a Bruker Daltonics solariX 9.4T FT-ICR-MS spectrometer at Research and Analytical Center for Giant Molecules, Graduate School of Science, Tohoku University.

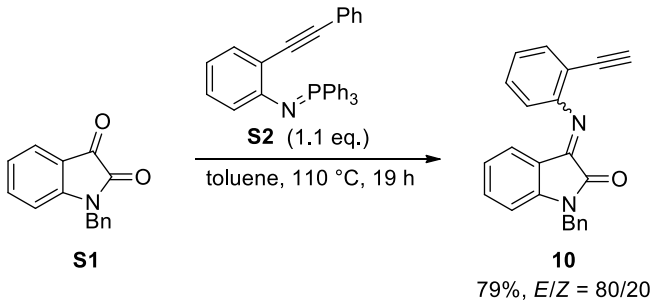
Materials: Unless otherwise noted, materials were purchased from Wako Pure Chemical Industries, Ltd., Tokyo Chemical Industry Co., LTD., Aldrich Inc., and other commercial suppliers and were used without purification. Dichloromethane, tetrahydrofuran and toluene were supplied from Kanto Chemical Co., Inc. as “Dehydrated solvent system”. Other solvents were purchased from commercial suppliers as dry solvents, and used under argon atmosphere.

Experimental Procedure

Procedure for Preparation of *N*-(2-Alkynylaryl)-α-iminoesters 1.

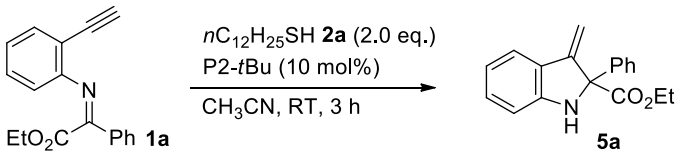
N-(2-Alkynylaryl)-α-iminoesters **1** were prepared by aza-Wittig reaction of the corresponding α-ketoesters with iminophosphoranes according to the method described in our previous report.[S1] The major isomer of each iminoester was assigned as *Z* isomer by analogy with compounds reported in literature.[S2]

Procedure for Preparation of Oxindole 10.



A solution of *N*-benzyl isatin (**S1**, 0.47 g, 2.0 mmol) and iminophosphorane **S2** (0.83 g, 2.2 mmol) in toluene (7.5 mL) was heated at 110 °C for 19 h. The mixture was cooled to room temperature and then concentrated under reduced pressure. The residue was purified by silica gel column chromatography (hexane/AcOEt = 3:1) followed by recrystallization from a mixture of AcOEt and hexane to afford oxindole **10** (*E*/*Z* = 80/20, 0.53 g, 1.6 mmol, 79%) as an orange solid. The major isomer was assigned as *E* isomer by analogy with compounds reported in literature.[S3]

General Procedure for Brønsted Base-Catalyzed Reductive Cyclization of Alkynyl α-Iminoesters.



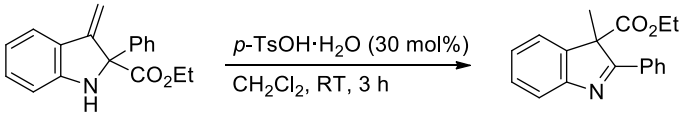
The reaction of **1a** with 1-dodecanethiol (**2a**) is representative (Table 1, entry 14). To a solution of **1a** (28 mg, 0.10 mmol) and 1-dodecanethiol (**2a**, 48 μL, 0.20 mmol) in acetonitrile (1.0 mL) was added a solution of P2-*t*Bu in THF (2.0 M, 5.0 μL, 0.010 mmol) at room temperature. The resulting mixture was stirred at that temperature for 3 h. The reaction was then quenched with sat. aq. NH_4Cl, and the product was extracted with AcOEt for three times. The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. The purification of the crude mixture by column chromatography (hexane/AcOEt = 20:1 to 10:1) provided **5a** (23 mg, 0.082 mmol, 82%) as a colorless oil.

(S1) Kondoh, A.; Terada, M. *Chem. Eur. J.* **2018**, *15*, 3998.
(S2) Curto, J. M.; Dickstein, J. S.; Berritt, S.; Kozlowski, M. S. *Org. Lett.* **2014**, *16*, 1948.
(S3) Aslam, N. A.; Babu, S. A.; Rani, S.; Mahajan, S.; Solanki, J.; Yasuda, M.; Baba, A. *Eur. J. Org. Chem.* **2015**, 4168.

Lager scale reaction

To a solution of **1a** (1.0 g, 3.6 mmol) and 1-dodecanethiol (**2a**, 1.7 mL, 7.2 mmol) in acetonitrile (18 mL) was added a solution of P2-*t*Bu in THF (2.0 M, 0.18 mL, 0.36 mmol) at room temperature. The resulting mixture was stirred at that temperature for 3 h. The reaction was then quenched with sat. aq. NH_4Cl, and the product was extracted with AcOEt for three times. The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. The purification of the crude mixture by column chromatography (hexane/AcOEt = 20:1 to 10:1) provided **5a** (0.87 g, 3.1 mmol, 86%) as a colorless oil.

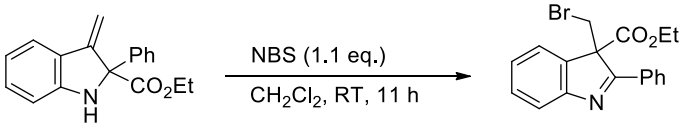
Procedure for Transformation of 5a into 12 (Scheme 8a).



5a **12** 85%

To a solution of **5a** (24 mg, 0.087 mmol) in CH_2Cl_2 (1.5 mL) was added *p*-TsOH·H_2O (4.9 mg, 0.026 mmol). The resulting mixture was stirred at room temperature for 3 h. The reaction was quenched with sat. aq. $NaHCO_3$, and the product was extracted with CH_2Cl_2 for three times. The combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The crude mixture was purified by column chromatography (hexane/AcOEt = 20:1 to 10:1) to provide **12** (21 mg, 0.074 mmol, 85%) as a pale yellow oil.

Procedure for Transformation of 5a into 13 (Scheme 8b).

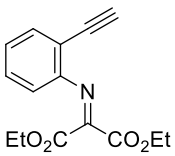


5a **13** 83%

To a solution of **5a** (24 mg, 0.087 mmol) in CH_2Cl_2 (1.5 mL) was added NBS (18 mg, 0.10 mmol). The resulting mixture was stirred at room temperature for 11 h and then concentrated under reduced pressure. The residue was purified by column chromatography (hexane/AcOEt = 20:1 to 10:1) to provide **13** (26 mg, 0.072 mmol, 83%) as a pale yellow solid.

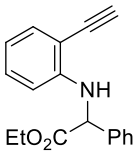
Analytical Data

Diethyl 2-(2-ethynylphenyl)iminomalonate (1h):



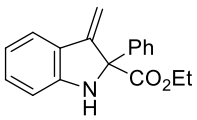
Yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.03 (t, J = 7.2 Hz, 3H), 1.42 (t, J = 7.2 Hz, 3H), 3.25 (s, 1H), 4.14 (q, J = 7.2 Hz, 2H), 4.46 (q, J = 7.2 Hz, 2H), 6.80 (d, J = 7.8 Hz, 1H), 7.14 (dd, J = 7.8, 7.8 Hz, 1H), 7.30 (dd, J = 7.8, 7.8 Hz, 1H), 7.50 (d, J = 7.8 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 13.6, 14.0, 62.1, 63.0, 79.6, 82.8, 112.8, 117.6, 125.7, 129.1, 133.1, 150.1, 153.3, 161.0; IR (ATR): 3279, 2984, 2939, 1739, 1475, 1316, 1243, 1069, 794 cm^{-1}; HRMS (ESI) Calcd for $C_{15}H_{15}NO_4$ $[M+Na]^+$ 296.0893, Found 296.0894.

Ethyl 2-(2-ethynylphenyl)amino-2-phenylacetate (3a):



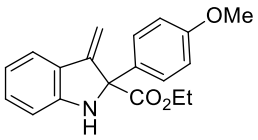
White solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.22 (t, J = 7.2 Hz, 3H), 3.51 (s, 1H), 4.15 (dq, J = 10.8, 7.2 Hz, 1H), 4.24 (dq, J = 10.8, 7.2 Hz, 1H), 5.10 (d, J = 5.4 Hz, 1H), 6.03 (brd, J = 5.4 Hz, 1H), 6.30 (d, J = 8.4 Hz, 1H), 6.61 (dd, J = 7.8, 7.2 Hz, 1H), 7.05 (dd, J = 7.8, 7.2 Hz, 1H), 7.30 (t, J = 7.2 Hz, 1H), 7.33-7.37 (m, 3H), 7.50 (d, J = 7.2 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 14.0, 60.4, 61.9, 80.3, 83.2, 107.1, 110.5, 117.0, 127.1, 128.3, 128.8, 130.1, 132.6, 137.3, 147.3, 171.2; IR (ATR): 3392, 3247, 2986, 2917, 1725, 1572, 1506, 1328, 1176, 794 cm^{-1}; HRMS (ESI) Calcd for $C_{18}H_{17}NO_2$ $[M+Na]^+$ 302.1152, Found 302.1152; m.p. 105.7-106.5 °C.

2-Ethoxycarbonyl-3-methylene-2-phenylindoline (5a):



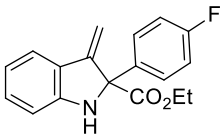
23 mg, 82% yield; colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.28 (t, J = 7.2 Hz, 3H), 4.28 (m, 2H), 5.17 (brs, 1H), 5.27 (s, 1H), 5.76 (s, 1H), 6.78 (d, J = 7.8 Hz, 1H), 6.81 (dd, J = 7.8, 7.2 Hz, 1H), 7.16 (dd, J = 7.8, 7.8 Hz, 1H), 7.30 (tt, J = 7.2, 1.2 Hz, 1H), 7.35 (dd, J = 7.8, 7.2 Hz, 2H), 7.37 (d, J = 7.8 Hz, 1H), 7.46 (dd, J = 7.8, 1.2 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 14.0, 62.3, 75.5, 107.2, 110.9, 119.6, 120.9, 125.5, 126.3, 127.8, 128.6, 130.3, 142.3, 147.2, 150.5, 172.3; IR (ATR): 3375, 3060, 2981, 2931, 1727, 1606, 1469, 1232, 795 cm^{-1}; HRMS (ESI) Calcd for $C_{18}H_{17}NO_2$ $[M+Na]^+$ 302.1152, Found 302.1152.

2-Ethoxycarbonyl-2-(4-methoxyphenyl)-3-methyleneindoline (5b):



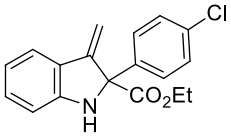
24 mg, 76% yield; pale yellow oil;^{1}H NMR (600 MHz, $CDCl_3$) δ 1.28 (t, J = 7.2 Hz, 3H), 3.79 (s, 3H), 4.22-4.31 (m, 2H), 5.14 (brs, 1H), 5.26 (s, 1H), 5.74 (s, 1H), 6.76 (d, J = 7.8 Hz, 1H), 6.77 (dd, J = 7.8, 7.2 Hz, 1H), 6.87 (d, J = 9.0 Hz, 2H), 7.15 (dd, J = 7.8, 7.8 Hz, 1H), 7.37 (d, J = 7.2 Hz, 1H), 7.38 (d, J = 9.0 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 14.0, 55.3, 62.2, 75.1, 107.0, 110.9, 113.9, 119.5, 120.9, 125.5, 127.6, 130.3, 134.5, 147.5, 150.4, 159.1, 172.5; IR (ATR): 3381, 2981, 2934, 1727, 1606, 1509, 1469, 1249, 1032, 795 cm^{-1}; HRMS (ESI) Calcd for $C_{19}H_{19}NO_3$ $[M+Na]^+$ 332.1257, Found 332.1257.

2-Ethoxycarbonyl-2-(4-fluorophenyl)-3-methyleneindoline (5c):



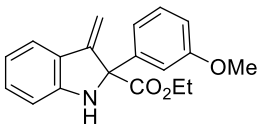
23 mg, 79% yield; colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.28 (t, J = 7.2 Hz, 3H), 4.23-4.32 (m, 2H), 5.18 (brs, 1H), 5.24 (s, 1H), 5.75 (s, 1H), 6.78 (d, J = 7.8 Hz, 1H), 6.81 (dd, J = 7.8, 7.2 Hz, 1H), 7.02 (dd, J = 9.0, 9.0 Hz, 2H), 7.17 (dd, J = 7.8, 7.2 Hz, 1H), 7.37 (d, J = 7.2 Hz, 1H), 7.45 (dd, J = 9.0, 5.4 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 14.0, 62.4, 74.9, 107.2, 111.1, 115.4 (d, J = 21.6 Hz), 119.8, 120.9, 125.4, 128.2 (d, J = 7.2 Hz), 130.4, 138.1, 147.3, 150.3, 162.3 (d, J = 245.6 Hz), 172.1; IR (ATR): 3382, 2982, 2919, 1728, 1604, 1506, 1469, 1226, 1086, 765 cm^{-1}; HRMS (ESI) Calcd for $C_{18}H_{16}FNO_2$ $[M+Na]^+$ 320.1057, Found 320.1057.

2-(4-Chlorophenyl)-2-ethoxycarbonyl-3-methyleneindoline (5d):



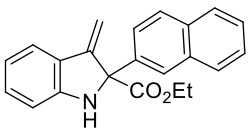
28 mg, 89% yield; colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.28 (t, J = 7.2 Hz, 3H), 4.22-4.32 (m, 2H), 5.17 (brs, 1H), 5.24 (s, 1H), 5.75 (s, 1H), 6.78 (d, J = 7.8 Hz, 1H), 6.82 (dd, J = 7.2, 7.2 Hz, 1H), 7.17 (dd, J = 7.8, 7.2 Hz, 1H), 7.31 (d, J = 9.0 Hz, 2H), 7.36 (d, J = 7.2 Hz, 1H), 7.42 (d, J = 9.0 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 14.0, 62.5, 74.9, 107.2, 111.1, 119.9, 120.9, 125.3, 127.8, 128.7, 130.4, 133.7, 140.8, 147.1, 150.3, 171.9; IR (ATR): 3377, 2981, 2925, 1727, 1607, 1469, 1233, 1092, 795 cm^{-1}; HRMS (ESI) Calcd for $C_{18}H_{16}ClNO_2$ $[M+Na]^+$ 336.0762, Found 336.0762.

2-Ethoxycarbonyl-2-(3-methoxyphenyl)-3-methyleneindoline (5e):



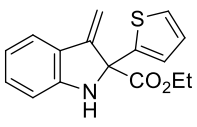
26 mg, 85% yield; pale yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.28 (t, J = 7.2 Hz, 3H), 3.78 (s, 3H), 4.23-4.31 (m, 2H), 5.16 (brs, 1H), 5.30 (s, 1H), 5.76 (s, 1H), 6.78 (d, J = 7.8 Hz, 1H), 6.81 (dd, J = 7.8, 7.2 Hz, 1H), 6.84 (ddd, J = 7.8, 2.4, 1.2 Hz, 1H), 7.03-7.06 (m, 2H), 7.16 (dd, J = 7.8, 7.2 Hz, 1H), 7.27 (dd, J = 7.8, 7.8 Hz, 1H), 7.37 (d, J = 7.8 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 14.0, 55.2, 62.3, 75.4, 107.2, 110.9, 112.4, 113.0, 118.5, 119.6, 120.9, 125.5, 129.6, 130.3, 143.7, 146.9, 150.4, 159.7, 172.2; IR (ATR): 3376, 2980, 2937, 1728, 1605, 1469, 1234, 1091, 876, 795 cm^{-1}; HRMS (ESI) Calcd for $C_{19}H_{19}NO_3$ $[M+Na]^+$ 332.1257, Found 332.1257.

2-Ethoxycarbonyl-3-methylene-2-(2-naphthyl)indoline (5f):



25 mg, 77% yield; colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.29 (t, J = 7.2 Hz, 3H), 4.31 (q, J = 7.2 Hz, 2H), 5.26 (brs, 1H), 5.31 (s, 1H), 5.80 (s, 1H), 6.80 (d, J = 8.4 Hz, 1H), 6.83 (dd, J = 7.8, 7.2 Hz, 1H), 7.17 (dd, J = 7.8, 7.2 Hz, 1H), 7.41 (d, J = 7.8 Hz, 1H), 7.44-7.49 (m, 2H), 7.53-7.56 (m 1H), 7.78-7.83 (m, 3H), 7.88 (d, J = 0.6 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 14.0, 62.4, 75.6, 107.4, 110.0, 119.7, 120.9, 124.6, 125.0, 125.6, 126.3 (2C), 127.5, 128.3, 128.5, 130.3, 132.8, 133.0, 139.4, 147.1, 150.5, 172.3; IR (ATR): 3377, 3055, 2981, 1727, 1607, 1469, 1233, 1088, 795 cm^{-1}; HRMS (ESI) Calcd for $C_{22}H_{19}NO_2$ $[M+Na]^+$ 352.1308, Found 352.1308.

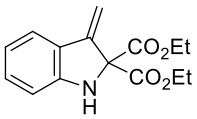
2-Ethoxycarbonyl-3-methylene-2-(2-thienyl)indoline (5g):



22 mg, 76% yield; pale yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.31 (t, J = 7.2 Hz, 3H), 4.23-4.32 (m, 2H), 5.38 (brs, 1H), 5.44 (s, 1H), 5.70 (s, 1H), 6.82 (dd, J = 7.8, 7.2 Hz, 1H), 6.83

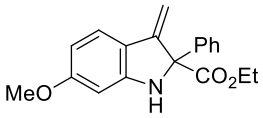
(d, *J* = 8.4 Hz, 1H), 6.99 (dd, *J* = 4.2, 4.2 Hz, 1H), 7.18 (d, *J* = 8.4, 7.2 Hz, 1H), 7.24 (d, *J* = 4.2 Hz, 2H), 7.34 (d, *J* = 7.8 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 13.9, 62.8, 72.7, 106.8, 112.3, 120.1, 121.1, 124.2, 125.0, 125.5, 127.2, 130.3, 146.8, 147.3, 150.4, 171.2; IR (ATR): 3364, 2980, 2922, 1727, 1607, 1469, 1315, 1227, 1089, 1016, 795 cm^{-1}; HRMS (ESI) Calcd for $C_{16}H_{15}NO_2S$ $[M+Na]^+$ 308.0716, Found 308.0716.

2,2-Di(ethoxycarbonyl)-3-methyleneindoline (5h):



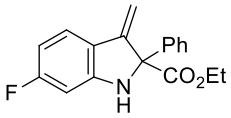
24 mg, 88% yield; colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.29 (t, *J* = 7.2 Hz, 6H), 4.27 (q, *J* = 7.2 Hz, 4H), 5.10 (brs, 1H), 5.55 (s, 1H), 5.80 (s, 1H), 6.80 (d, *J* = 8.4 Hz, 1H), 6.82 (dd, *J* = 7.8, 7.2 Hz, 1H), 7.14 (dd, *J* = 8.4, 7.2 Hz, 1H), 7.34 (d, *J* = 7.8 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 13.9, 62.5, 74.9, 107.7, 111.5, 120.3, 120.8, 125.6, 130.2, 142.0, 150.4, 168.5; IR (ATR): 3376, 2982, 2938, 1736, 1608, 1470, 1251, 1208, 1098, 795 cm^{-1}; HRMS (ESI) Calcd for $C_{15}H_{17}NO_4$ $[M+Na]^+$ 298.1050, Found 298.1050.

2-Ethoxycarbonyl-6-methoxy-3-methylene-2-phenylindoline (5i):



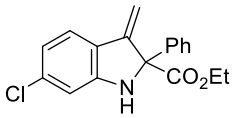
26 mg, 85% yield; pale yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.28 (t, *J* = 7.2 Hz, 3H), 3.78 (s, 3H), 4.24-4.32 (m, 2H), 5.12 (s, 1H), 5.16 (brs, 1H), 5.58 (s, 1H), 6.32 (d, *J* = 2.4 Hz, 1H), 6.38 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.27 (d, *J* = 8.4 Hz, 1H), 7.29 (t, *J* = 7.2 Hz, 1H), 7.34 (dd, *J* = 7.8, 7.2 Hz, 2H), 7.44 (d, *J* = 7.8 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 14.0, 55.4, 62.3, 76.1, 96.1, 104.5, 106.3, 118.6, 121.7, 126.3, 127.7, 128.6, 142.3, 146.6, 152.0, 162.3, 172.4; IR (ATR): 3377, 2980, 1728, 1615, 1498, 1234, 1163, 1092, 795 cm^{-1}; HRMS (ESI) Calcd for $C_{19}H_{19}NO_3$ $[M+Na]^+$ 332.1257, Found 332.1257.

2-Ethoxycarbonyl-6-fluoro-3-methylene-2-phenylindoline (5j):



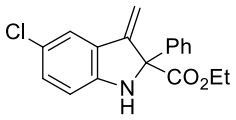
23 mg, 78% yield; pale yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.28 (t, *J* = 7.2 Hz, 3H), 4.24-4.33 (m, 2H), 5.22 (s, 2H), 5.67 (s, 1H), 6.44 (dd, *J* = 9.6, 1.2 Hz, 1H), 6.46-6.51 (m, 1H), 7.28 (dd, *J* = 8.4, 5.4 Hz, 1H), 7.31 (t, *J* = 7.2 Hz, 1H), 7.36 (dd, *J* = 7.8, 7.2 Hz, 2H), 7.43 (d, *J* = 7.8 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 14.0, 62.4, 76.1, 98.1 (d, *J* = 26.0 Hz), 106.45 (d, *J* = 20.1 Hz), 106.54, 121.4, 121.9 (d, *J* = 11.4 Hz), 126.2, 127.9, 128.6, 141.9, 145.9, 151.7 (d, *J* = 11.4 Hz), 165.0 (d, *J* = 244.2 Hz), 172.0; IR (ATR): 3063, 2982, 2923, 1730, 1618, 1494, 1235, 1092, 795 cm^{-1}; HRMS (ESI) Calcd for $C_{18}H_{16}FNO_2$ $[M+Na]^+$ 320.1057, Found 320.1057.

6-Chloro-2-ethoxycarbonyl-3-methylene-2-phenylindoline (5k):



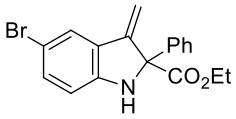
19 mg, 62% yield; pale yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.28 (t, *J* = 7.2 Hz, 3H), 4.24-4.32 (m, 2H), 5.20 (brs, 1H), 5.27 (s, 1H), 5.73 (s, 1H), 6.74 (d, *J* = 1.8 Hz, 1H), 6.76 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.26 (d, *J* = 7.8 Hz, 1H), 7.31 (t, *J* = 7.2 Hz, 1H), 7.35 (dd, *J* = 7.8, 7.2 Hz, 2H), 7.43 (d, *J* = 7.8 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 14.0, 62.4, 75.8, 107.7, 110.8, 119.6, 121.7, 124.0, 126.2, 128.0, 128.7, 135.8, 141.8, 145.9, 151.2, 171.9; IR (ATR): 3379, 2980, 2922, 1727, 1601, 1447, 1314, 1233, 1092, 795 cm^{-1}; HRMS (ESI) Calcd for $C_{18}H_{16}ClNO_2$ $[M+Na]^+$ 336.0762, Found 336.0762.

5-Chloro-2-ethoxycarbonyl-3-methylene-2-phenylindoline (5l):



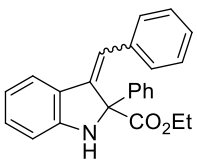
22 mg, 69% yield; pale yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.28 (t, J = 7.2 Hz, 3H), 4.24-4.32 (m, 2H), 5.16 (brs, 1H), 5.31 (s, 1H), 5.75 (s, 1H), 6.68 (d, J = 7.8 Hz, 1H), 7.10 (dd, J = 8.4, 1.8 Hz, 1H), 7.31 (t, J = 7.2 Hz, 1H), 7.32 (d, J = 1.8 Hz, 1H), 7.35 (dd, J = 7.8, 7.8 Hz, 2H), 7.42 (d, J = 7.8 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 14.0, 62.5, 76.0, 108.6, 111.8, 120.9, 124.6, 126.2, 127.1, 127.9, 128.7, 130.0, 141.8, 146.1, 148.9, 172.0; IR (ATR): 3377, 2981, 2922, 1731, 1472, 1235, 1091, 881, 794 cm^{-1}; HRMS (ESI) Calcd for $C_{18}H_{16}ClNO_2$ $[M+Na]^+$ 336.0762, Found 336.0762.

5-Bromo-2-ethoxycarbonyl-3-methylene-2-phenylindoline (5m):



28 mg, 78% yield; pale yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.28 (t, J = 7.2 Hz, 3H), 4.24-4.32 (m, 2H), 5.16 (brs, 1H), 5.30 (s, 1H), 5.75 (s, 1H), 6.64 (d, J = 8.4 Hz, 1H), 7.24 (dd, J = 8.4, 1.8 Hz, 1H), 7.29-7.32 (m,1H), 7.35 (dd, J = 7.8, 7.2 Hz, 2H), 7.40-7.43 (m, 2H), 7.46 (d, J = 1.8 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 14.0, 62.5, 75.9, 108.6, 111.6, 112.2, 123.8, 126.2, 127.6, 128.0, 128.7, 132.8, 141.8, 146.0, 149.3, 171.9; IR (ATR): 3375, 2981, 2923, 1730, 1601, 1470, 1446, 1234, 1092, 795 cm^{-1}; HRMS (ESI) Calcd for $C_{18}H_{16}BrNO_2$ $[M+Na]^+$ 380.0257, Found 380.0257.

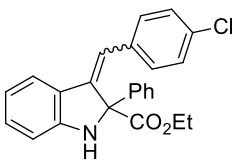
3-Benzylidene-2-ethoxycarbonyl-2-phenylindoline (5n):



Z/E = 88/12

30 mg, 85% yield; pale yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) Z isomer: δ 1.01 (t, J = 7.2 Hz, 3H), 4.07 (dq, J = 11.4, 7.2 Hz, 1H), 4.18 (dq, J = 11.4, 7.2 Hz, 1H), 4.97 (brs, 1H), 6.71 (d, J = 8.4 Hz, 1H), 6.87 (dd, J = 8.4, 7.8 Hz, 1H), 6.98-7.10 (m, 5H), 7.15 (t, J = 7.8 Hz, 1H), 7.20-7.28 (m, 4H), 7.38-7.43 (m, 2H), 7.53 (d, J = 7.8 Hz, 1H); E isomer: δ 1.33 (t, J = 7.2 Hz, 3H), 4.27-4.39 (m, 2H), 5.18 (brs, 1H), 6.55 (dd, J = 7.8, 7.2 Hz, 1H), 6.63 (s, 1H), 6.76 (d, J = 7.8 Hz, 1H), 7.09 (dd, J = 8.4, 7.2 Hz, 1H), 7.14 (d, J = 8.4 Hz, 1H), 7.22-7.43 (m, 8H), 7.50 (d, J = 7.2 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) Z isomer: δ 13.7, 62.2, 76.1, 110.8, 120.0, 120.1, 123.2, 126.7, 126.9, 127.4, 127.5, 127.9, 128.4, 129.4, 129.9, 135.5, 139.3, 139.5, 149.7, 172.0; E isomer: δ 14.1, 62.3, 77.2, 110.8, 119.0, 123.9, 124.0, 126.9, 127.2, 127.8, 128.1, 128.3, 128.6, 129.4, 130.1, 137.4, 140.3, 142.8, 151.8, 172.8; IR (ATR): 3376, 3054, 2980, 2921, 1727, 1601, 1470, 1235, 1090, 795 cm^{-1}; HRMS (ESI) Calcd for $C_{24}H_{21}NO_2$ $[M+Na]^+$ 378.1465, Found 378.1465.

3-(4-Chloro)benzylidene-2-ethoxycarbonyl-2-phenylindoline (5o):

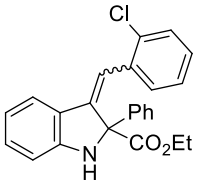


Z/E = 66/34

35 mg, 89% yield; yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) Z isomer: δ 1.08 (t, J = 7.2 Hz, 3H), 4.13 (dq, J = 10.2, 7.2 Hz, 1H), 4.23 (dq, J = 10.2, 7.2 Hz, 1H), 5.03 (brs, 1H), 6.71 (d, J = 7.8 Hz, 1H), 6.87 (dd, J = 7.8, 7.2 Hz, 1H), 6.95-7.02 (m, 4H), 7.16 (dd, J = 7.8, 7.2 Hz, 1H), 7.17 (s, 1H), 7.20-7.40 (m, 5H), 7.50 (d, J = 7.8 Hz, 1H); E isomer: δ 1.32 (t, J = 7.2 Hz, 3H), 4.27-4.38 (m, 2H), 5.19 (brs, 1H), 6.53 (s, 1H), 6.58 (dd, J = 7.8, 7.2 Hz, 1H), 6.77 (d, J = 8.4 Hz, 1H), 7.09-7.13 (m, 2H), 7.20-7.40 (m, 7H), 7.48 (d, J = 7.8 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 13.8, 14.1, 62.3, 62.4, 76.3, 77.2, 110.7, 110.8, 119.1, 120.0, 120.1, 121.8, 123.6, 123.8, 125.4, 126.8, 127.4, 127.5, 127.7, 127.9, 128.0, 128.5, 128.6 (2C),

129.8, 130.1, 130.4, 130.8, 132.4, 132.9, 134.0, 135.8, 139.4, 140.1, 141.2, 142.6, 149.9, 152.0, 172.0, 172.6; IR (ATR): 3377, 3060, 2981, 1726, 1601, 1469, 1314, 1232, 1092, 1013, 795 cm^{-1}; HRMS (ESI) Calcd for $C_{24}H_{20}ClNO_2$ $[M+Na]^+$ 412.1075, Found 412.1075.

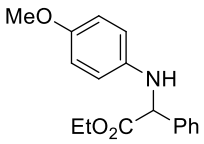
3-(2-Chloro)benzylidene-2-ethoxycarbonyl-2-phenylindoline (5p):



Z/*E* = 30/70

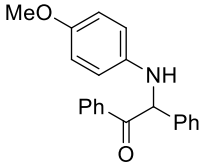
35 mg, 91% yield; yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) *Z* isomer: δ 1.15 (t, *J* = 7.2 Hz, 3H), 4.16 (dq, *J* = 10.8, 7.2 Hz, 1H), 4.24 (dq, *J* = 10.8, 7.2 Hz, 1H), 5.07 (brs, 1H), 6.74 (d, *J* = 7.8 Hz, 1H), 6.79 (dd, *J* = 7.8, 7.2 Hz, 1H), 6.89 (dd, *J* = 7.8, 7.2 Hz, 1H), 6.95-6.99 (m, 2H), 7.12-7.28 (m, 5H), 7.42-7.46 (m, 2H), 7.51-7.56 (m, 2H); *E* isomer: δ 1.34 (t, *J* = 7.2 Hz, 3H), 4.31-4.39 (m, 2H), 5.24 (brs, 1H), 6.55 (dd, *J* = 7.8, 7.2 Hz, 1H), 6.61 (s, 1H), 6.77 (d, *J* = 7.8 Hz, 1H), 6.92 (d, *J* = 7.8 Hz, 1H), 7.10 (dd, *J* = 7.8, 7.2 Hz, 1H), 7.12-7.27 (m, 3H), 7.32 (t, *J* = 7.2 Hz, 1H), 7.38 (dd, *J* = 7.8, 7.2 Hz, 2H), 7.52 (d, *J* = 7.2 Hz, 2H), 7.52-7.55 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 13.8, 14.1, 62.3, 62.5, 76.2, 77.2, 110.5, 111.0, 119.2, 119.9, 120.1, 120.7, 123.7, 123.9, 124.0, 125.4, 126.5, 126.6, 127.0, 127.1, 127.4, 127.7, 127.9, 128.0, 128.5, 128.6, 128.8, 129.6, 130.2, 130.3, 130.47, 130.51, 133.6, 134.0, 134.4, 135.9, 140.3, 141.4, 141.9, 142.6, 150.0, 152.0, 172.1, 172.8; IR (ATR): 3377, 3060, 2979, 1726, 1604, 1470, 1311, 1234, 1091, 795 cm^{-1}; HRMS (ESI) Calcd for $C_{24}H_{20}ClNO_2$ $[M+Na]^+$ 412.1075, Found 412.1075.

Ethyl 2-(4-methoxyphenyl)amino-2-phenylacetate (7a)[S4]:



24 mg, 85% yield; yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.21 (t, *J* = 7.2 Hz, 3H), 3.70 (s, 3H), 4.13 (dq, *J* = 10.8, 7.2 Hz, 1H), 4.22 (dq, *J* = 10.8, 7.2 Hz, 1H), 4.67 (brs, 1H), 5.00 (s, 1H), 6.53 (d, *J* = 9.0 Hz, 2H), 6.72 (d, *J* = 9.0 Hz, 2H), 7.30 (t, *J* = 7.2 Hz, 1H), 7.35 (dd, *J* = 7.2, 7.2 Hz, 2H), 7.49 (d, *J* = 7.2 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 14.0, 55.7, 61.67, 61.69, 114.7, 114.8, 127.2, 128.1, 128.8, 137.9, 140.2, 152.4, 172.0.

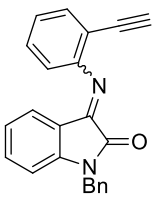
2-(4-Methoxyphenyl)amino-1,2-diphenylethanone (9a)[S5]:



30 mg, 93% yield; yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.70 (s, 3H), 5.10 (brs, 1H), 5.97 (s, 1H), 6.63 (d, *J* = 9.0 Hz, 2H), 6.72 (d, *J* = 9.0 Hz, 2H), 7.20 (t, *J* = 7.8 Hz, 1H), 7.27 (dd, *J* = 7.8, 7.8 Hz, 2H), 7.42 (dd, *J* = 7.8, 7.8 Hz, 2H), 7.43 (d, *J* = 7.8 Hz, 2H), 7.52 (t, *J* = 7.8 Hz, 1H), 7.98 (d, *J* = 7.8 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 55.7, 63.7, 114.8, 115.0, 128.0, 128.1, 128.6, 128.8, 129.0, 133.4 (2C), 135.2, 137.9, 140.4, 152.3.

(S4) Qian, C.; Chen, J.; Fu, M.; Zhu, S.; Chen, W.-H.; Jiang, H.; Zeng, W. *Org. Biomol. Chem.* **2013**, *11*, 6013.
(S5) Chen, H.; Fan, G.; Li, S.; Mao, K.; Lin, Y. *Tetrahedron Lett.* **2014**, *55*, 1593.

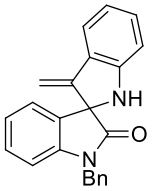
1-Benzyl-3-(2-ethynylphenyl)iminoindolin-2-one (10):



E/*Z* = 80/20

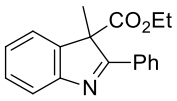
0.53 g, 79%; Orange solid; ^{1}H NMR (600 MHz, $CDCl_3$) major isomer: δ 3.07 (s, 1H), 5.02 (s, 2H), 6.51 (d, *J* = 7.8 Hz, 1H), 6.74 (d, *J* = 8.4 Hz, 2H), 6.99 (d, *J* = 7.8 Hz, 1H), 7.20 (dd, *J* = 7.8, 7.2 Hz, 1H), 7.24 (dd, *J* = 7.8, 7.2 Hz, 1H), 7.24-7.40 (m, 5H), 7.41 (dd, *J* = 7.8, 7.2 Hz, 1H), 7.59 (d, *J* = 7.2 Hz, 1H); minor isomer: δ 3.07 (s, 1H), 4.83 (s, 2H), 6.73 (d, *J* = 7.2 Hz, 1H), 6.99 (d, *J* = 7.8 Hz, 1H), 7.08-7.14 (m, 2H), 7.24-7.40 (m, 7H), 7.54 (d, *J* = 7.2 Hz, 1H), 7.80 (d, *J* = 7.2 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 43.6, 44.0, 79.9, 81.06, 81.10, 82.2, 109.8, 110.3, 110.9, 111.1, 116.2, 117.5, 118.1, 120.9, 122.9, 123.3, 123.5, 124.4, 124.8, 126.1, 127.4, 127.5, 127.87, 127.90, 128.8, 128.9, 129.4, 129.9, 133.0, 133.6, 134.1, 134.3, 135.1, 135.2, 146.3, 147.0, 152.0, 152.5, 153.5, 155.1, 157.4, 163.1; IR (ATR): 3290, 3062, 2922, 1731, 1609, 1468, 1353, 1097, 795 cm^{-1}; HRMS (ESI) Calcd for $C_{23}H_{16}N_2O$ $[M+Na]^+$ 359.1155, Found 359.1155; m.p. 126.0-126.7 °C.

1-Benzyl-3'-methylene-2,3'-spirobi[indolin]-2-one (11):



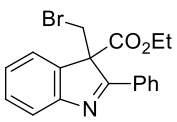
29 mg, 87% yield; pale brown oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.46 (brs, 1H), 4.52 (s, 1H), 4.72 (d, *J* = 15.6 Hz, 1H), 5.07 (d, *J* = 15.6 Hz, 1H), 5.41 (s, 1H), 6.79 (d, *J* = 7.8 Hz, 1H), 6.83 (d, *J* = 7.8 Hz, 1H), 6.86 (dd, *J* = 7.8, 7.8 Hz, 1H), 7.03 (dd, *J* = 7.8, 7.2 Hz, 1H), 7.18-7.24 (m, 3H), 7.25-7.37 (m, 5H), 7.40 (d, *J* = 7.2 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 44.0, 71.9, 102.4, 109.3, 111.2, 119.9, 121.5, 123.5, 124.2, 125.7, 127.5, 127.8, 128.8, 129.4, 130.5, 132.3, 135.7, 142.8, 149.1, 152.4, 176.7; IR (ATR): 3355, 3061, 2924, 1718, 1609, 1467, 1347, 1173, 795 cm^{-1}; HRMS (ESI) Calcd for $C_{23}H_{18}N_2O$ $[M+Na]^+$ 361.1311, Found 361.1312.

3-Ethoxycarbonyl-3-methyl-2-phenyl-3*H*-indole (12)[S6]:



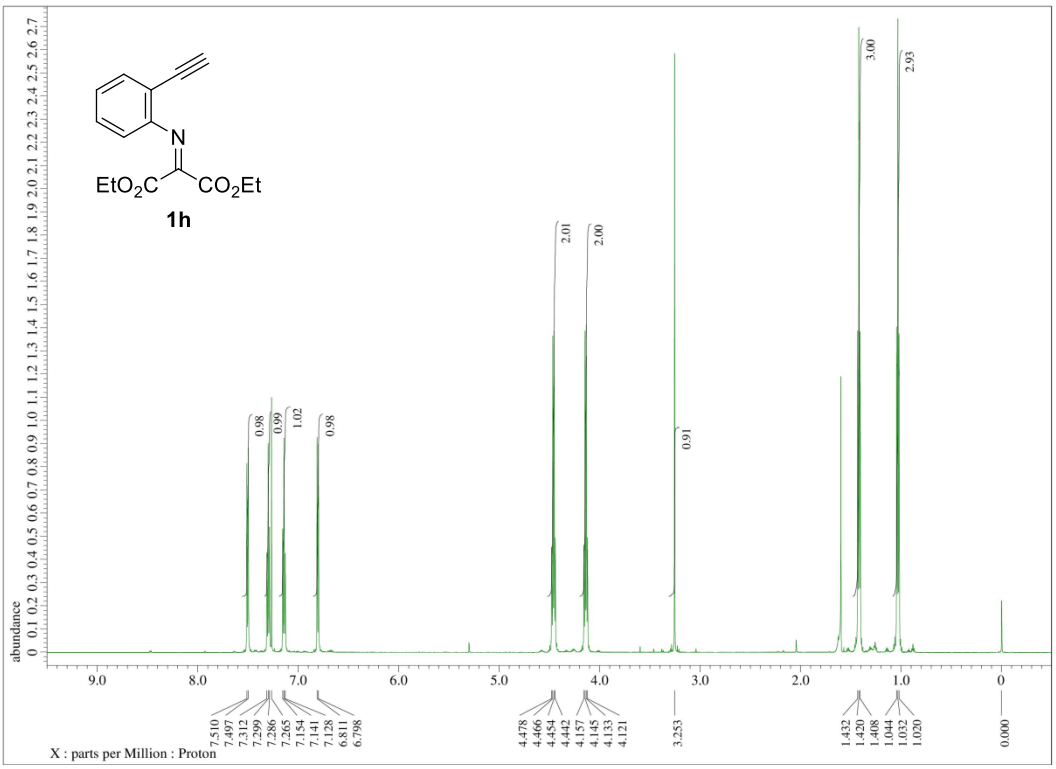
24 mg, 85% yield; pale yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 0.98 (t, *J* = 7.2 Hz, 3H), 1.72 (s, 3H), 3.99 (dq, *J* = 10.8, 7.2 Hz, 1H), 4.13 (dq, *J* = 10.8, 7.2 Hz, 1H), 7.27 (dd, *J* = 7.2, 7.2 Hz, 1H), 7.40 (d, *J* = 7.2 Hz, 1H), 7.43 (dd, *J* = 7.8, 7.2 Hz, 1H), 7.46-7.52 (m, 3H), 7.72 (d, *J* = 7.8 Hz, 1H), 7.96-7.98 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 13.7, 21.0, 61.8, 62.0, 121.1, 121.3, 126.3, 128.3, 128.7, 129.0, 131.1, 132.0, 141.7, 154.9, 171.5, 178.0.

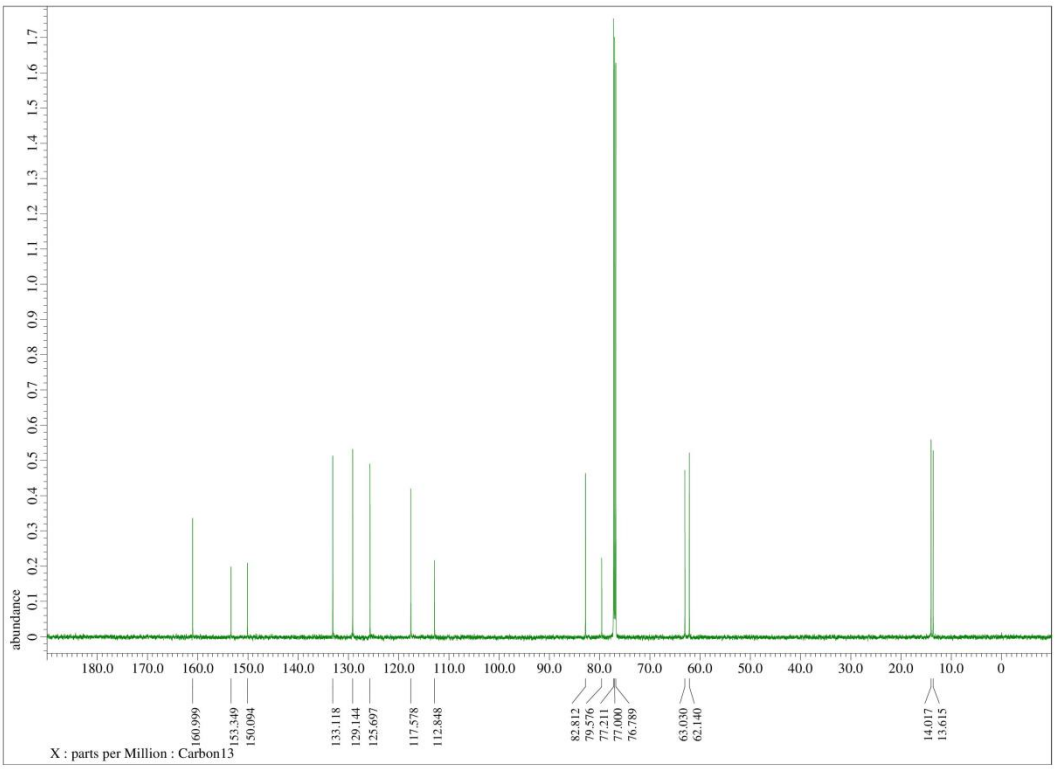
3-(Bromomethyl)-3-ethoxycarbonyl-2-phenyl-3*H*-indole (13):

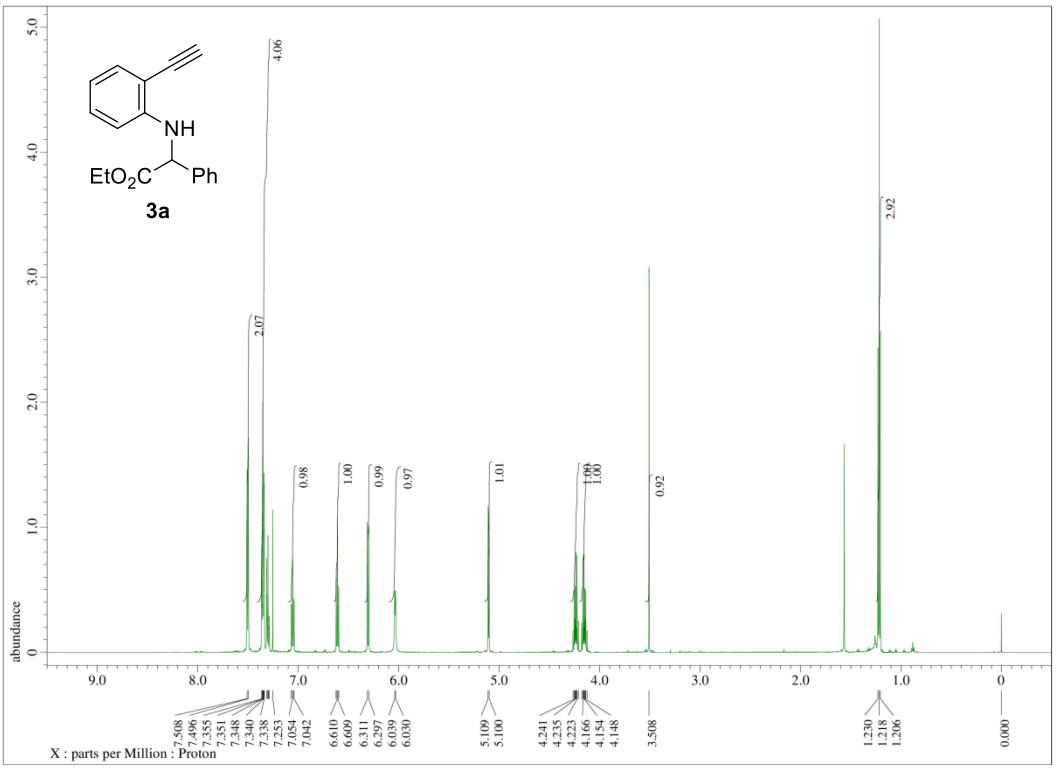


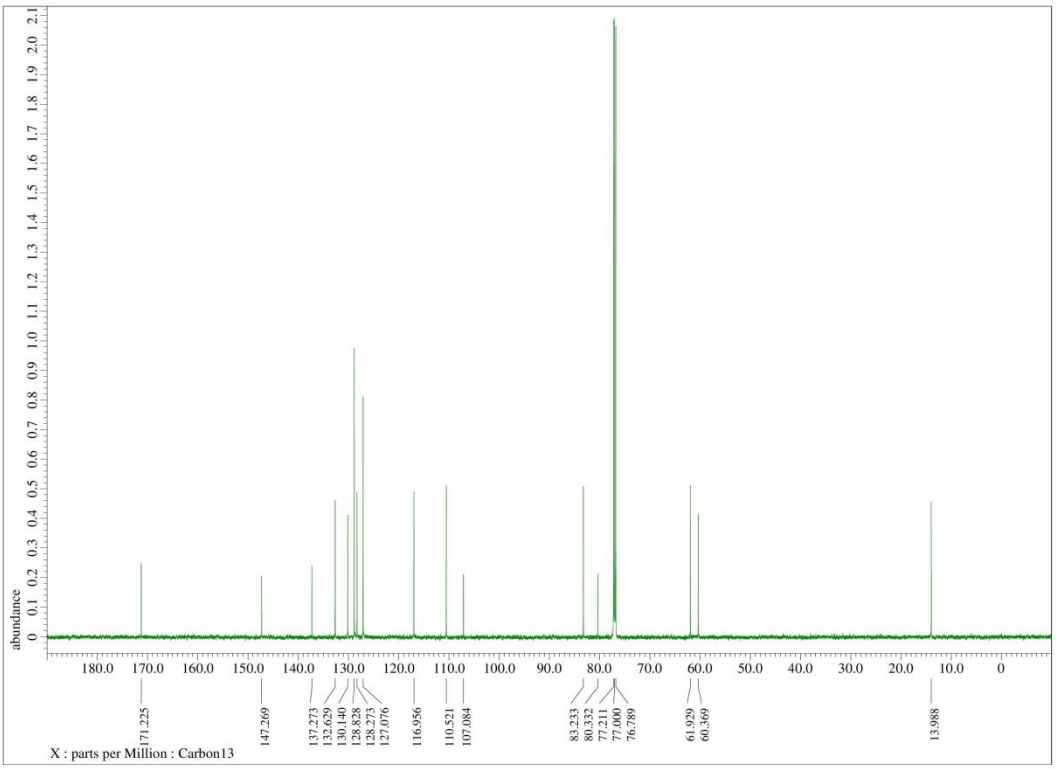
30 mg, 83% yield; pale yellow solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.02 (t, *J* = 7.2 Hz, 3H), 4.04 (dq, *J* = 10.8, 7.2 Hz, 1H), 4.06 (d, *J* = 10.8 Hz, 1H), 4.17 (dq, *J* = 10.8, 7.2 Hz, 1H), 4.26 (d, *J* = 10.8 Hz, 1H), 7.33 (dd, *J* = 7.8, 7.2 Hz, 1H), 7.40 (d, *J* = 7.2 Hz, 1H), 7.47-7.55 (m, 4H), 7.75 (d, *J* = 7.8 Hz, 1H), 7.91-7.94 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 13.7, 32.0, 62.5, 66.5, 121.2, 121.3, 126.6, 127.9, 129.4, 129.9, 131.4, 131.8, 137.8, 156.0, 169.4, 174.3; IR (ATR): 3063, 2980, 2920, 1724, 1538, 1445, 1230, 1091, 761 cm^{-1}; HRMS (ESI) Calcd for $C_{18}H_{16}BrNO_2$ $[M+Na]^+$ 380.0257, Found 380.0257; m.p. 65.7-66.7 °C.

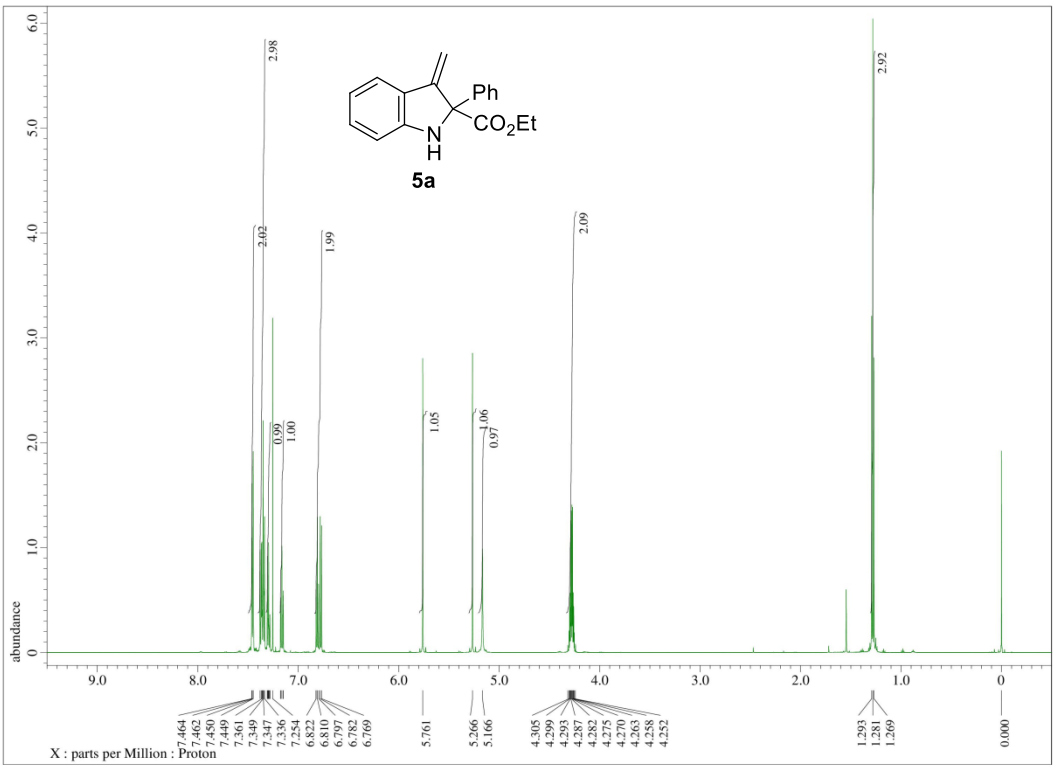
(S6) He, Z.; Li, H.; Li, Z. *J. Org. Chem.* **2010**, *75*, 4636.

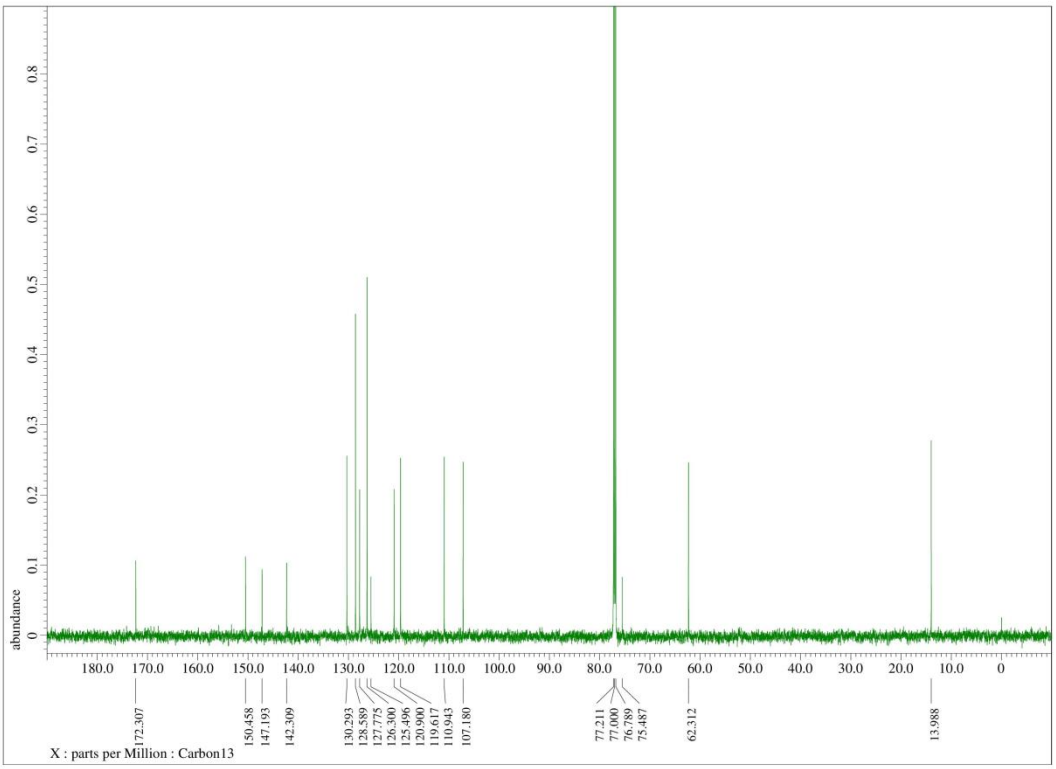

1h
abundance
X : parts per Million : Proton

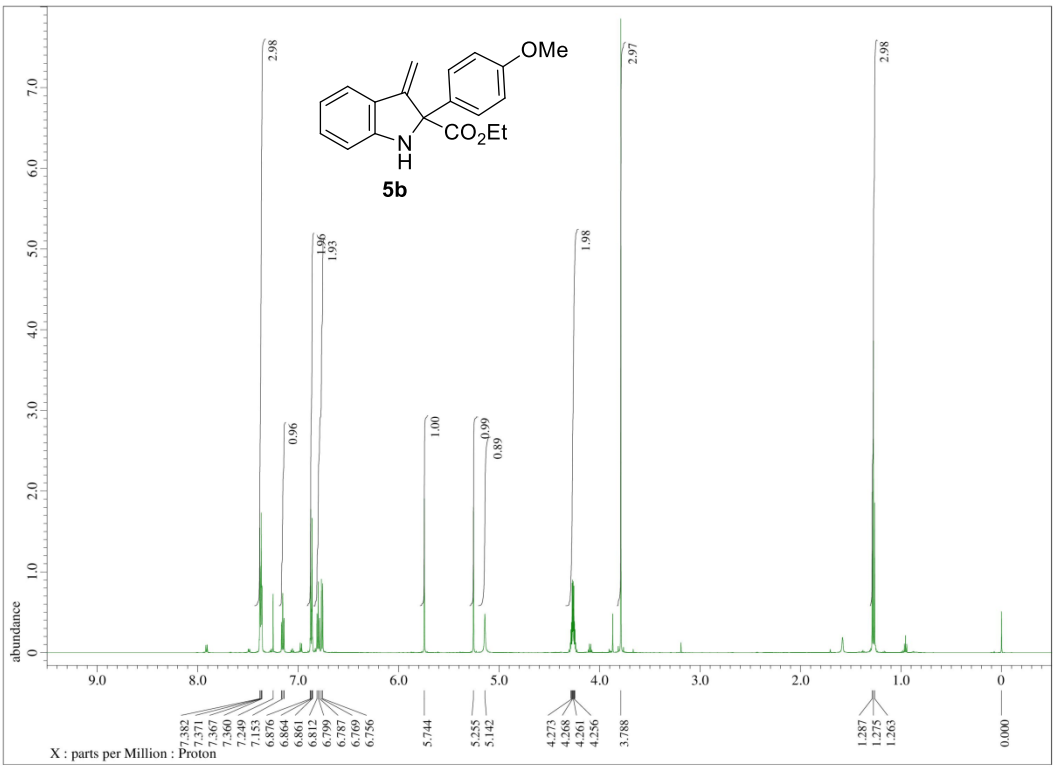

abundance
X : parts per Million : Carbon13

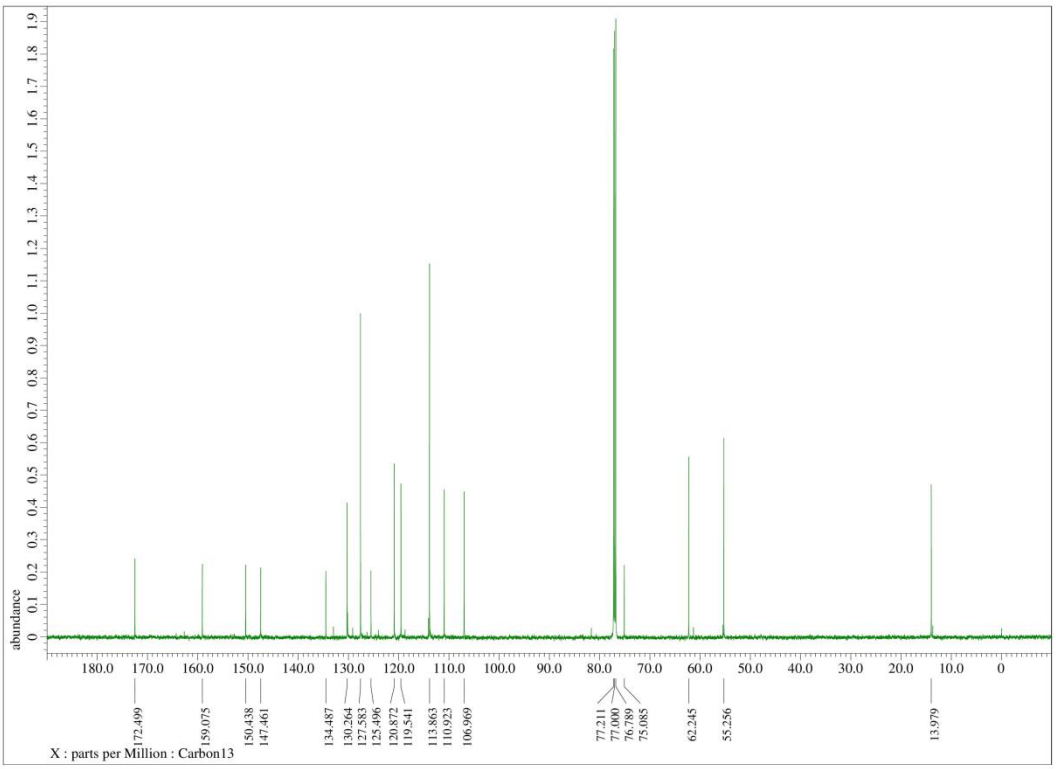

NH
EtO2C
Ph
3a
abundance
X : parts per Million : Proton

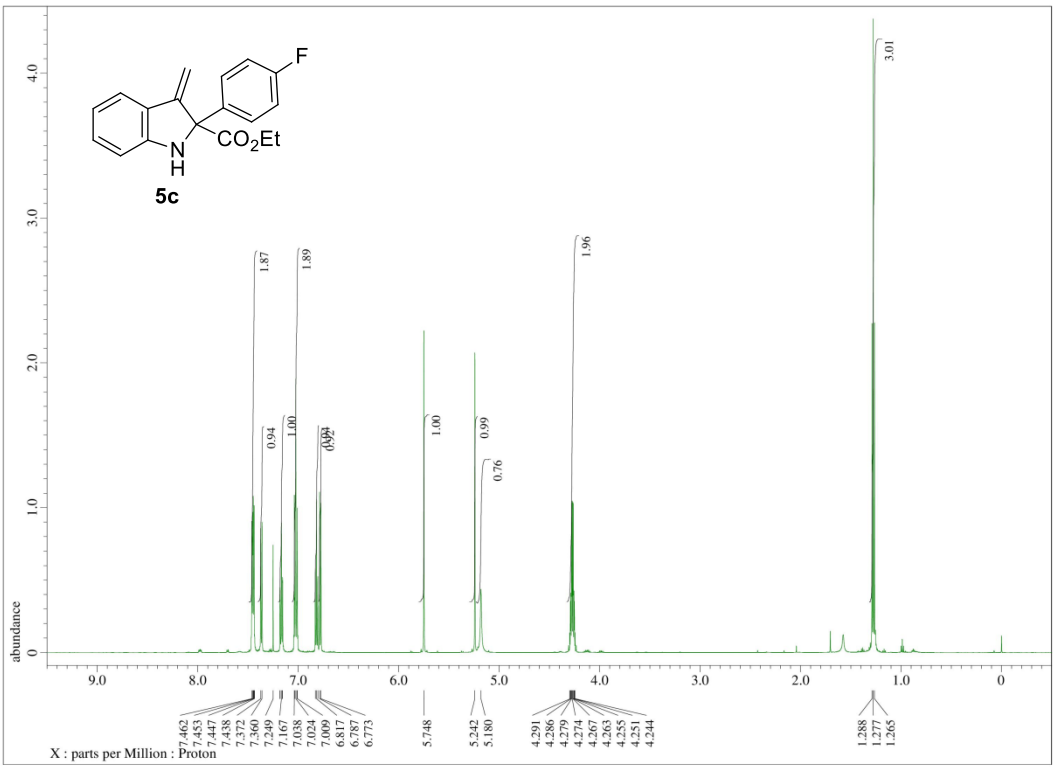

abundance
X : parts per Million : Carbon13

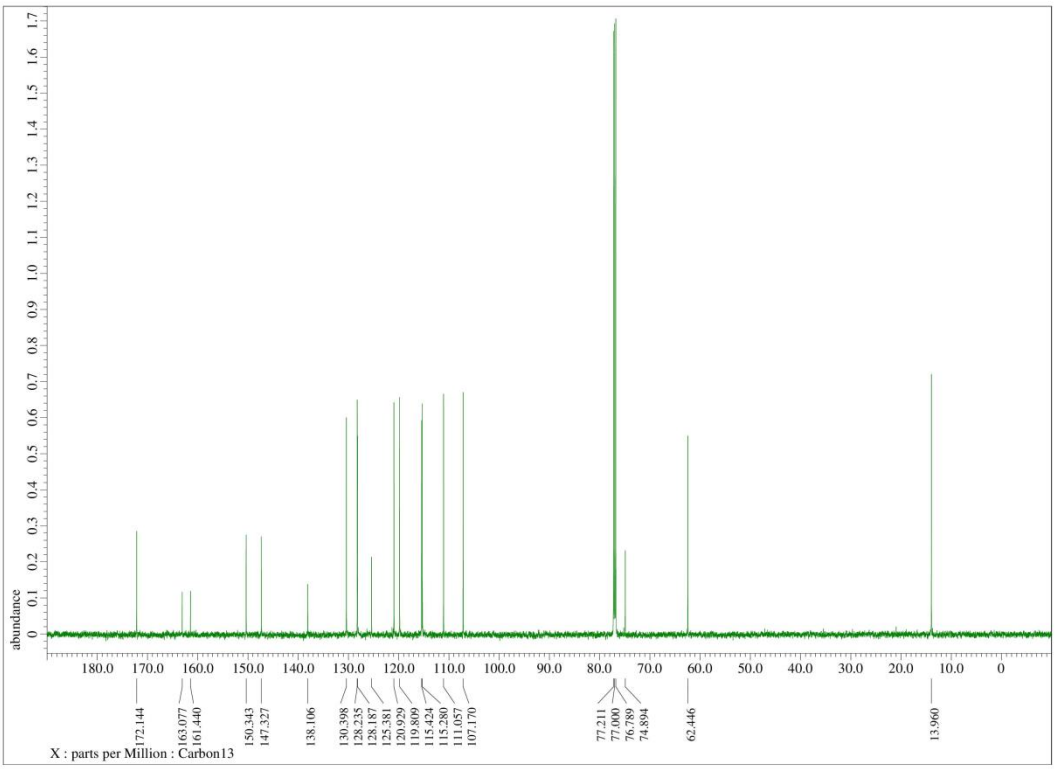

Ph
CO2Et
N
H
5a
abundance
X : parts per Million : Proton

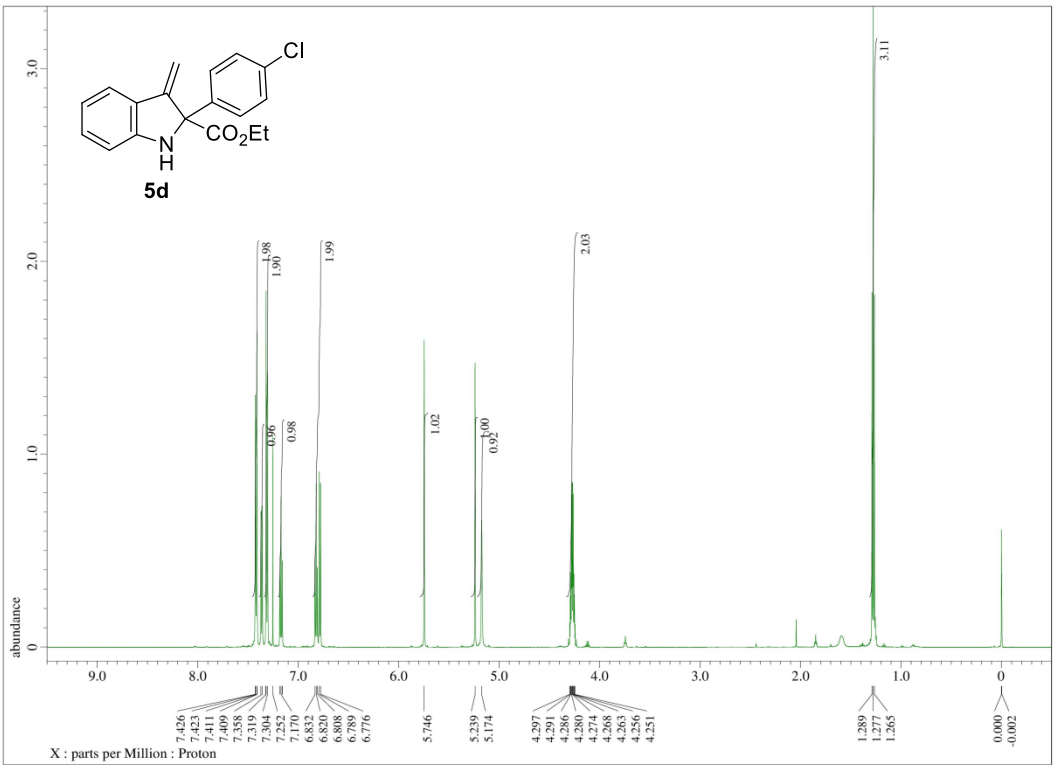

abundance
X : parts per Million : Carbon13

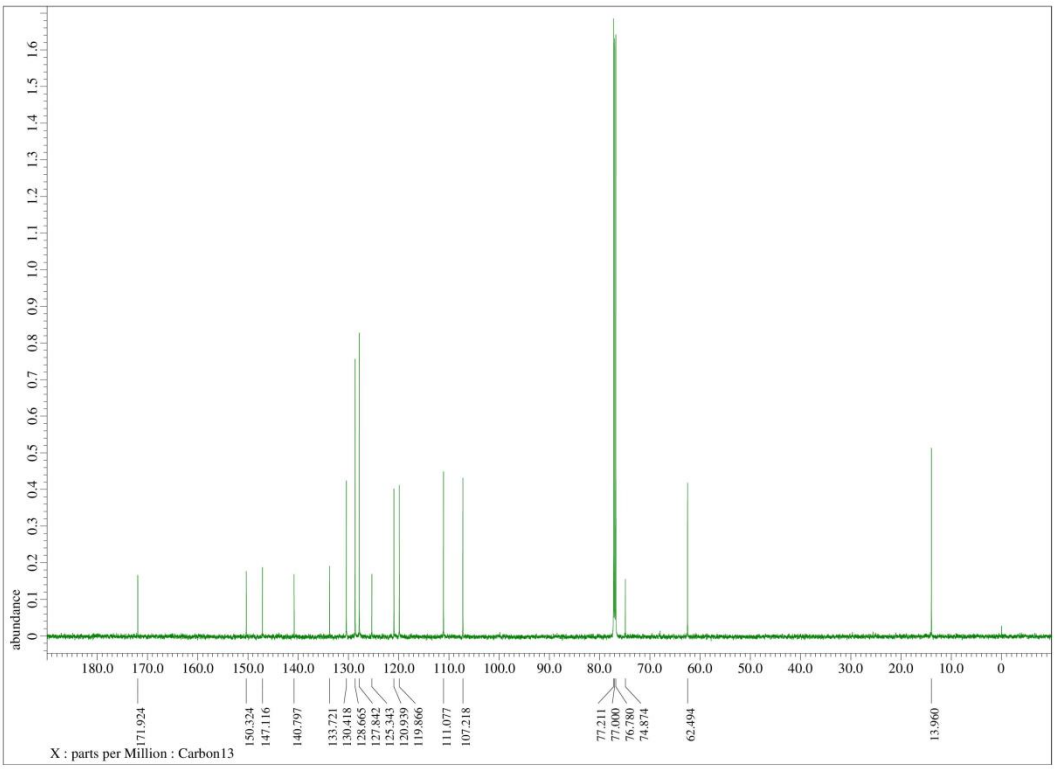

OMe
CO2Et
N
H
5b
abundance
X : parts per Million : Proton

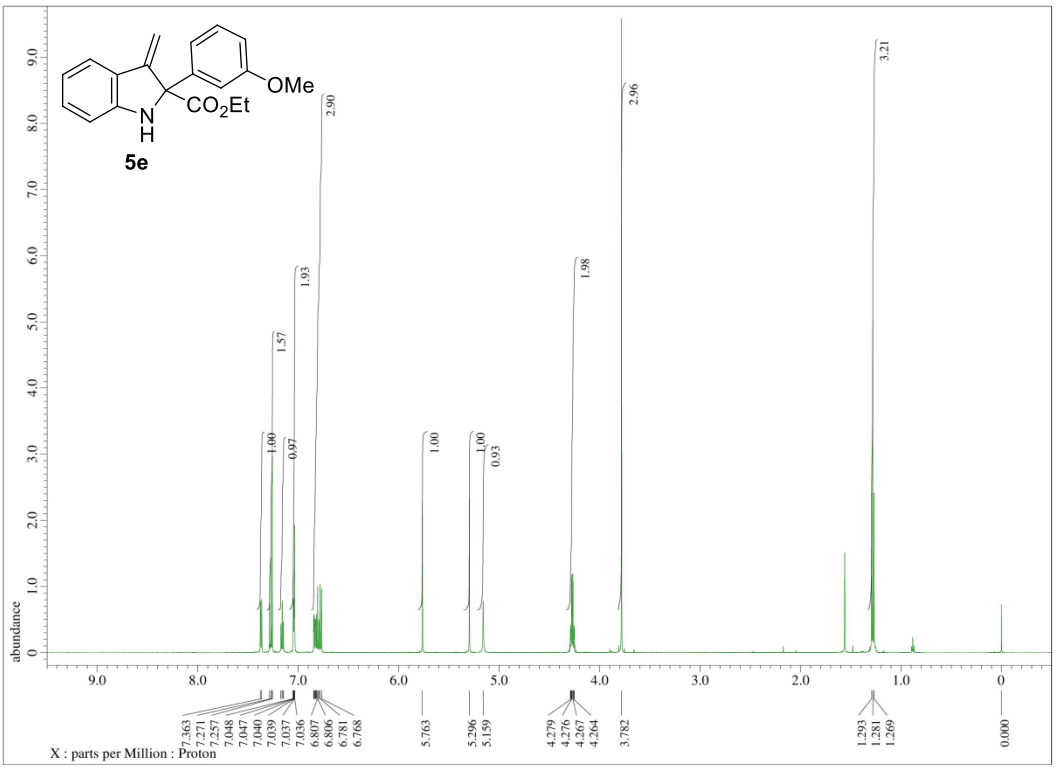

abundance
X : parts per Million : Carbon13

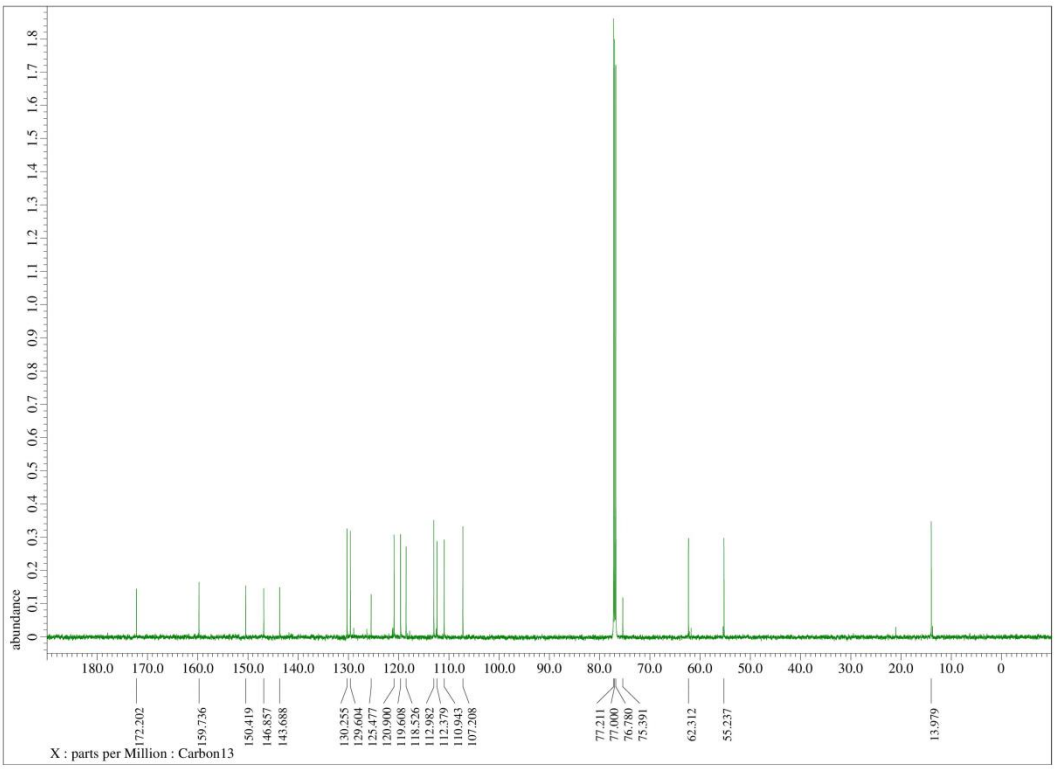

F
CO2Et
N
H
5c
abundance
X : parts per Million : Proton

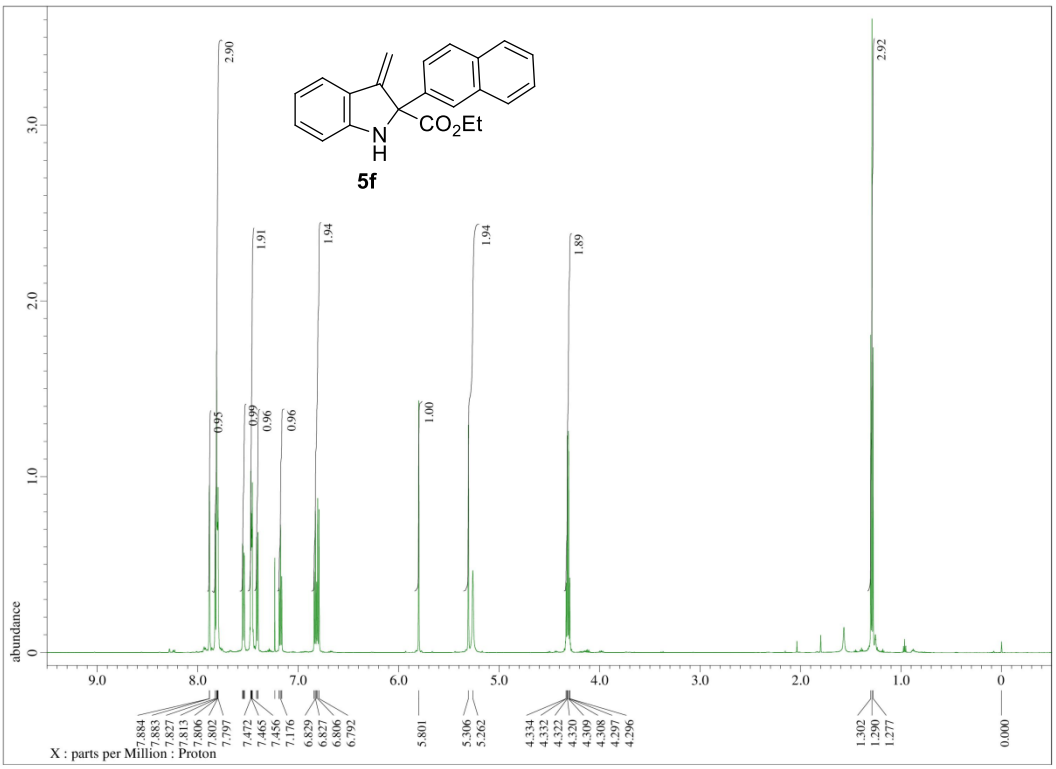

abundance
X : parts per Million : Carbon13

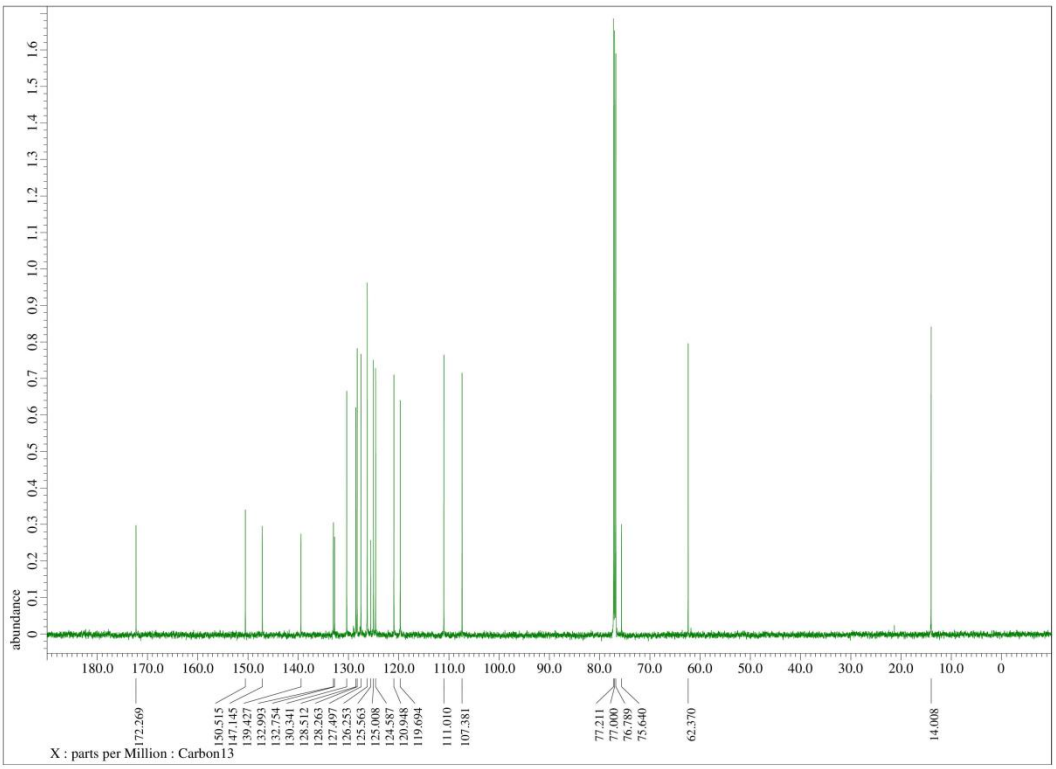

Cl
CO2Et
N
H
5d
abundance
X : parts per Million : Proton

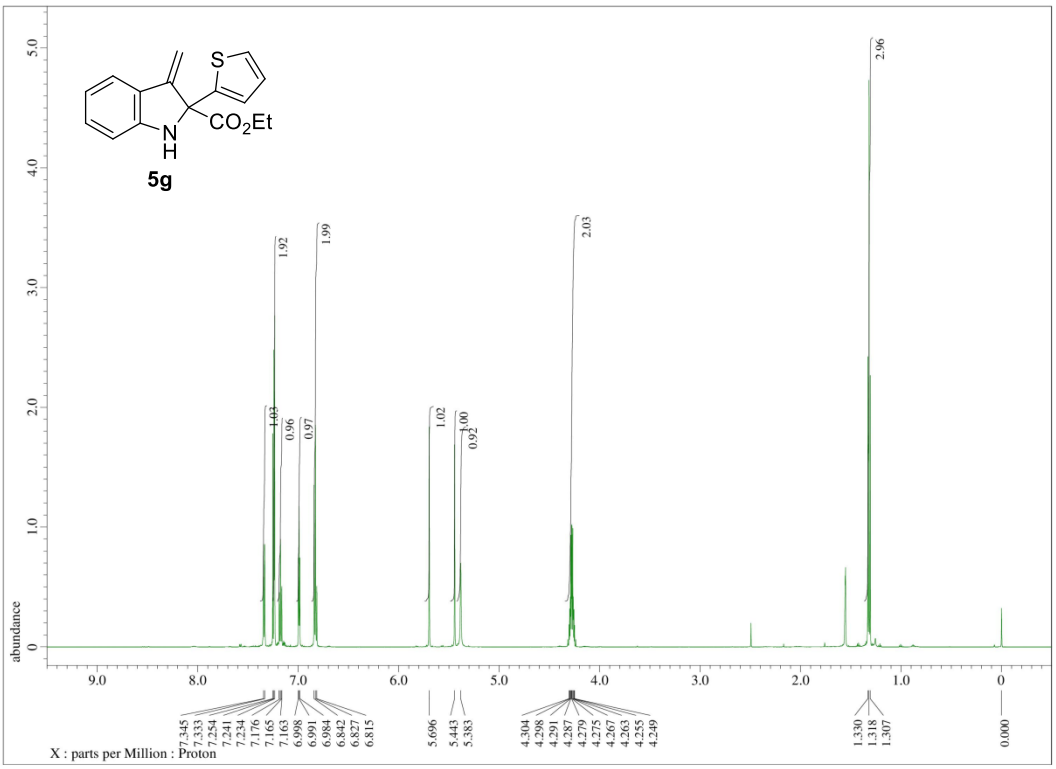

abundance
X : parts per Million : Carbon13

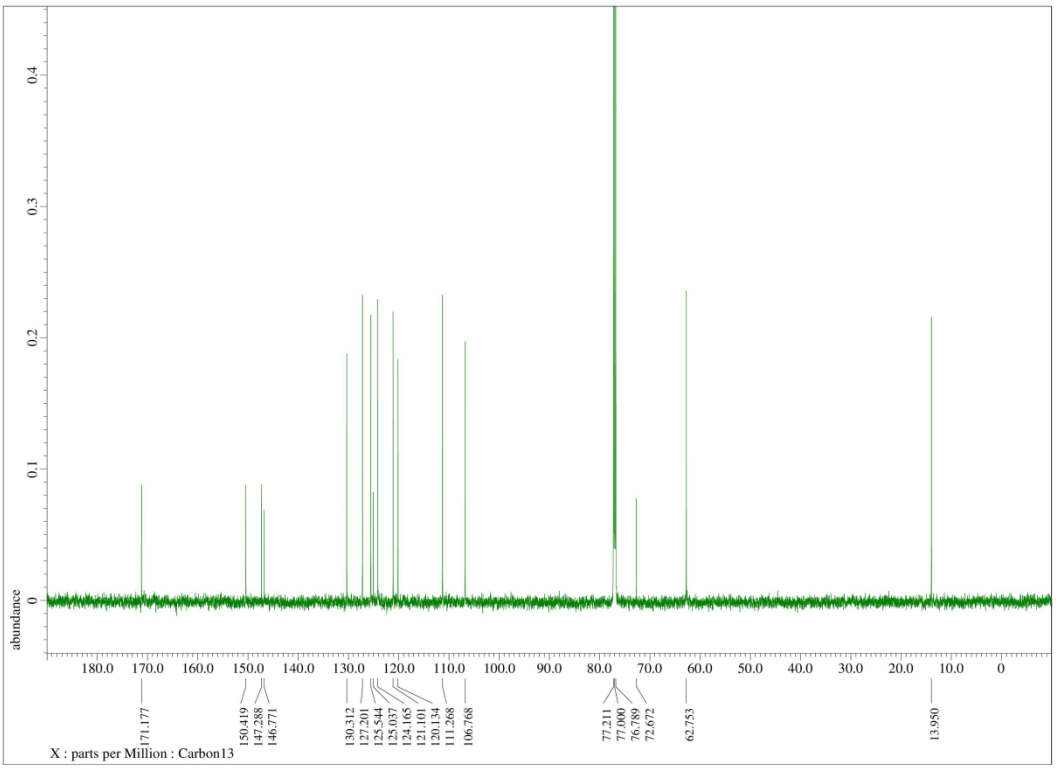

OMe
CO2Et
N
H
5e
abundance
X : parts per Million : Proton

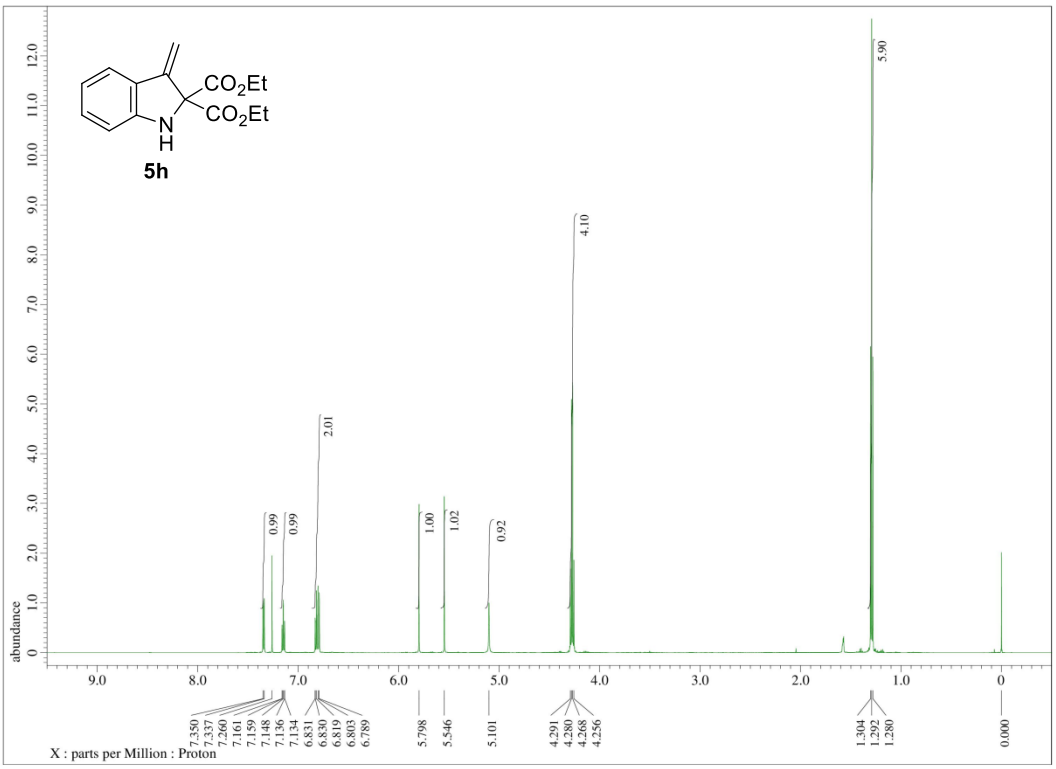

abundance
X : parts per Million : Carbon13

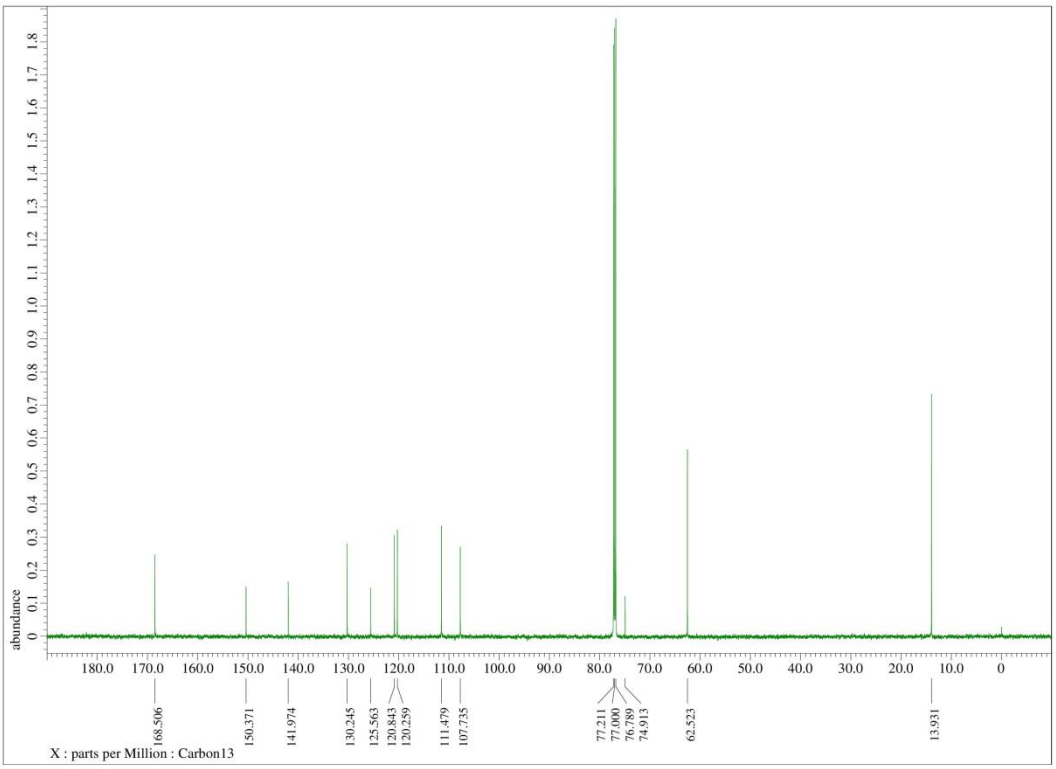

5f
abundance
X : parts per Million : Proton

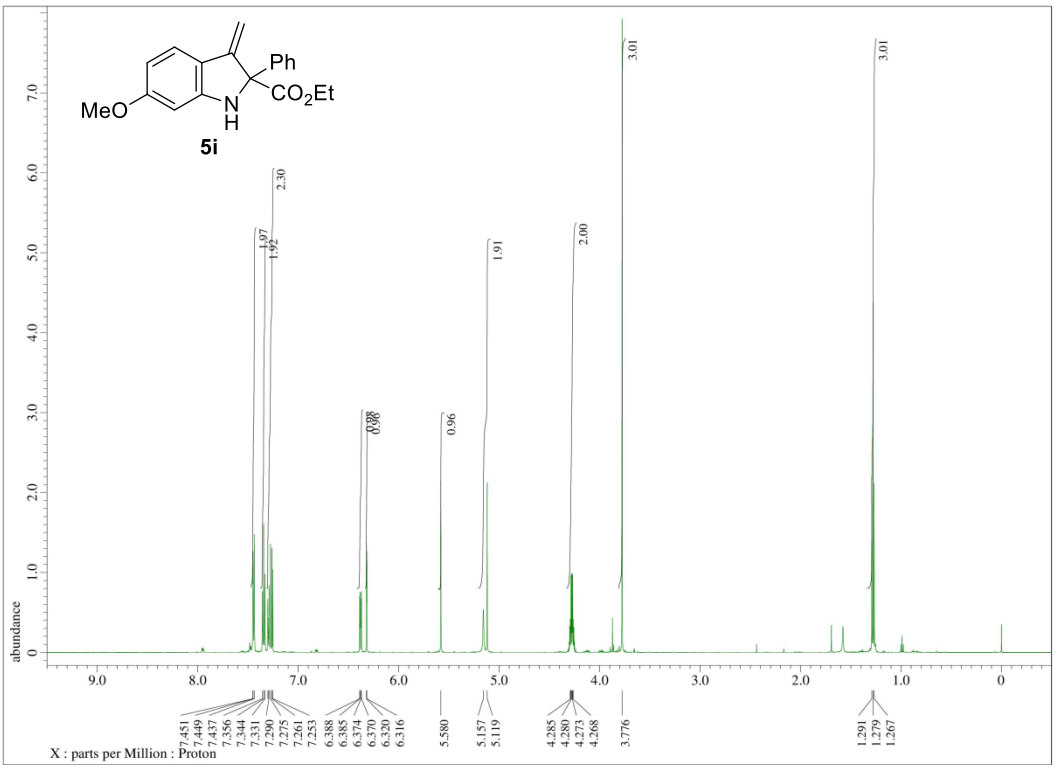

abundance
X : parts per Million : Carbon13

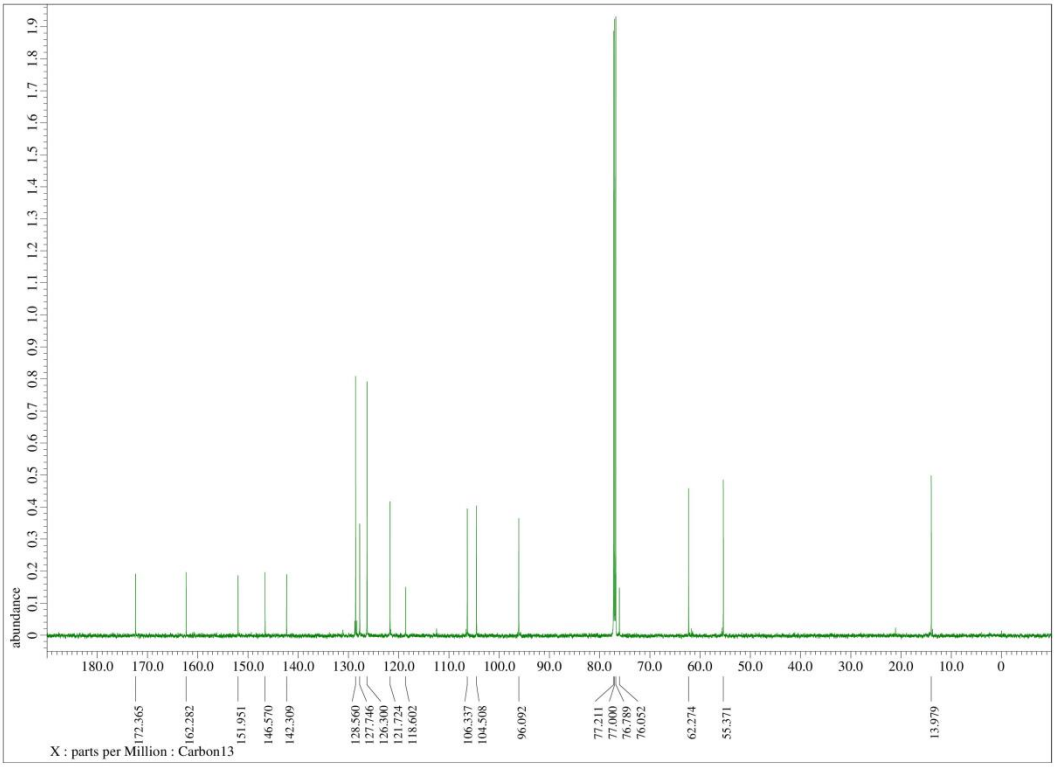

S
CO2Et
N
H
5g
abundance
X : parts per Million : Proton

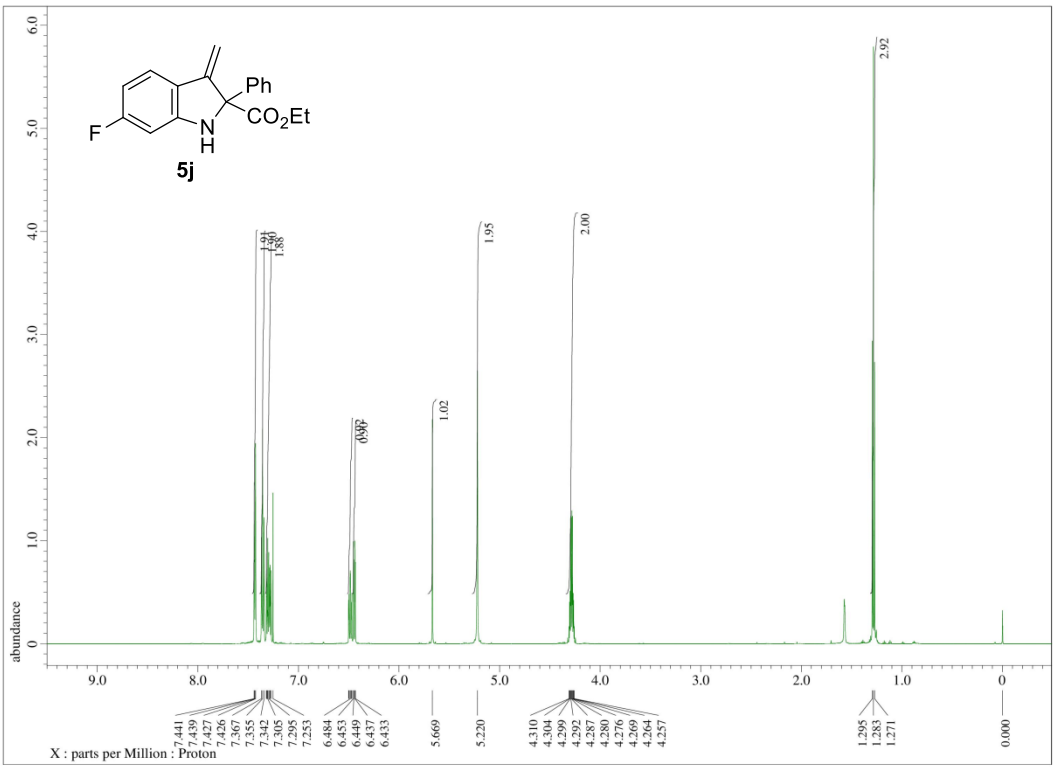

abundance
X : parts per Million : Carbon13

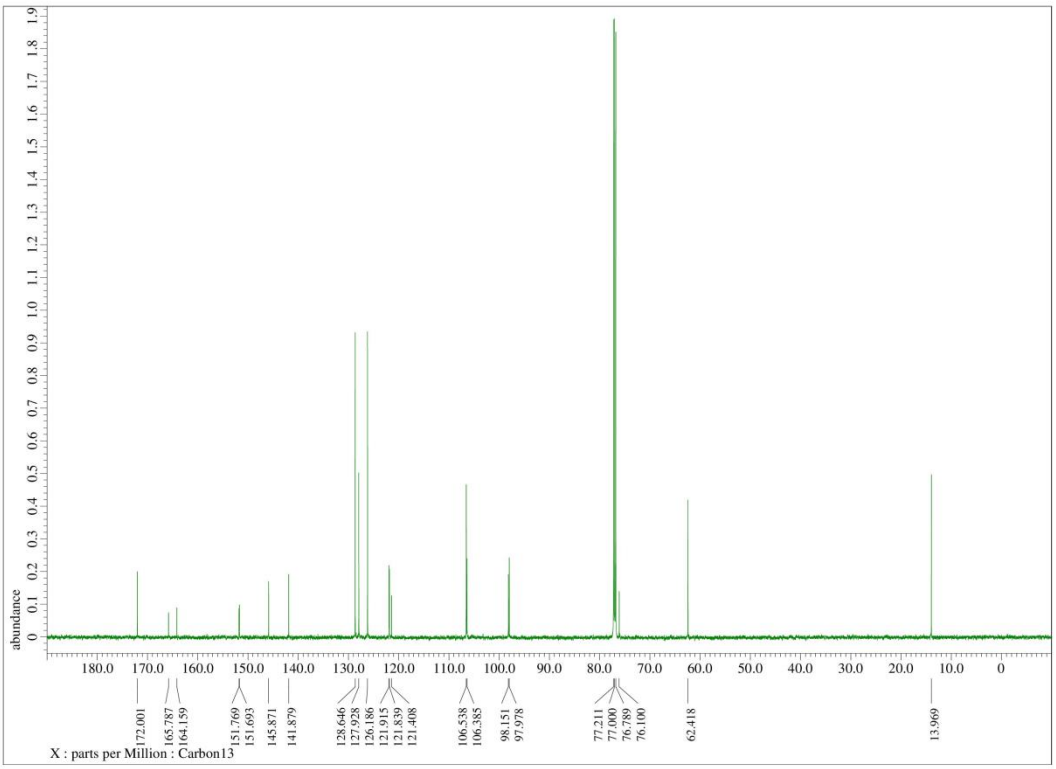

CO2Et
CO2Et
N
H
5h
abundance
X : parts per Million : Proton
5.90
4.10
2.01
0.99
0.99
1.00
1.02
0.92
7.350
7.337
7.260
7.161
7.159
7.148
7.136
7.134
6.831
6.830
6.819
6.803
6.789
5.798
5.546
5.101
4.291
4.280
4.268
4.256
1.304
1.292
1.280
0.000

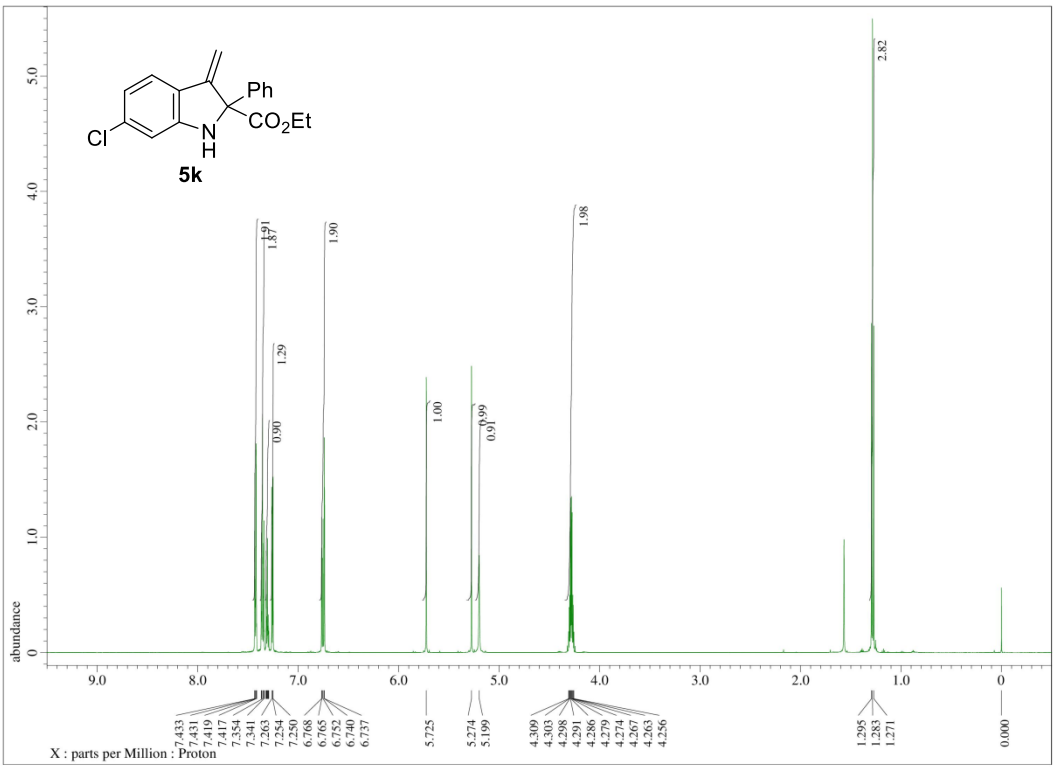

abundance
X : parts per Million : Carbon13
168.506
150.371
141.974
130.245
125.563
120.843
120.259
111.479
107.735
77.211
77.000
76.789
74.913
62.523
13.931

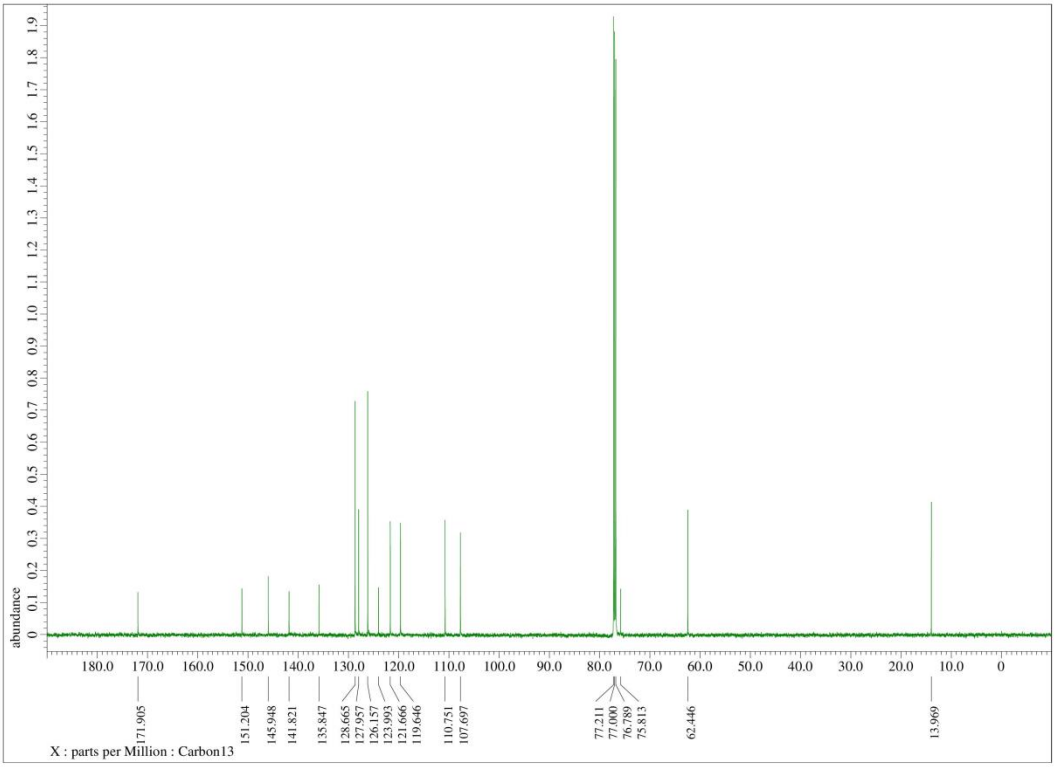

MeO
Ph
CO2Et
N
H
5i
abundance
X : parts per Million : Proton

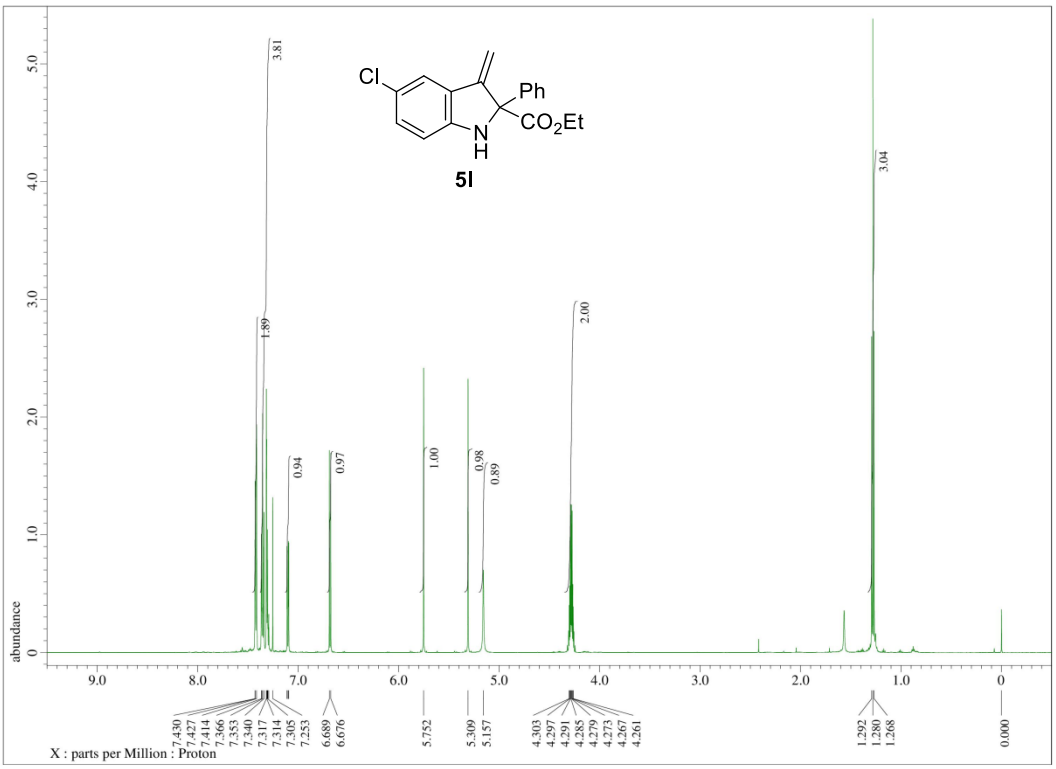

abundance
X : parts per Million : Carbon13

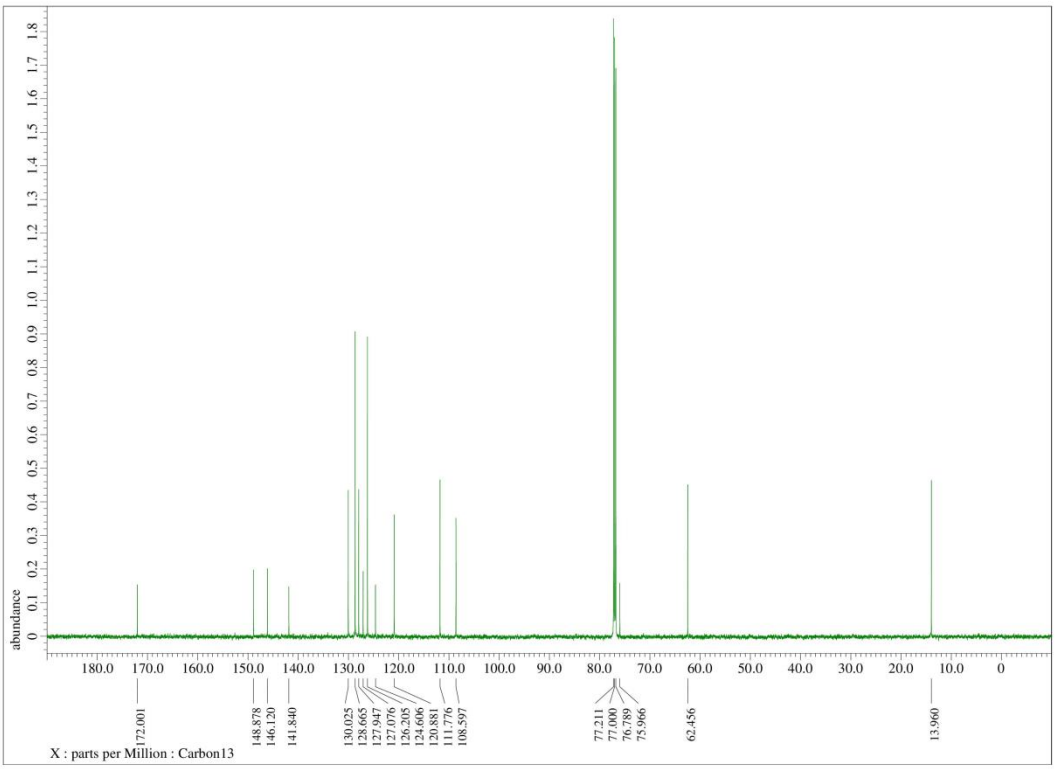

Ph
CO2Et
F
N
H
5j
abundance
X : parts per Million : Proton

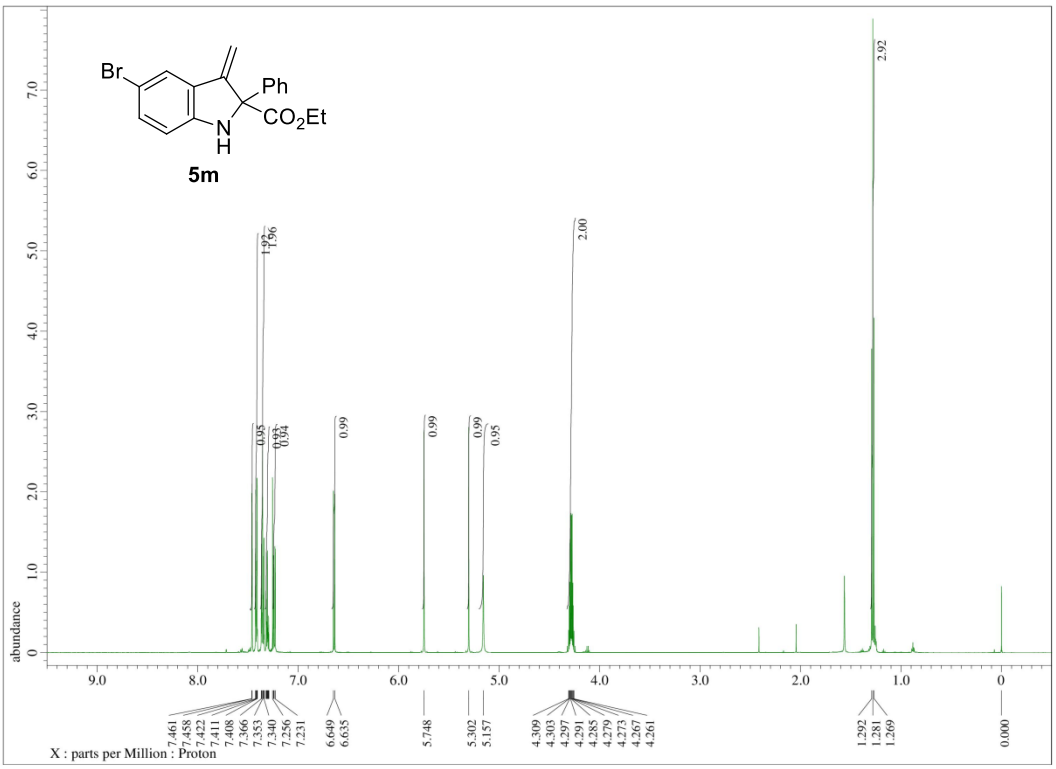

abundance
X : parts per Million : Carbon13

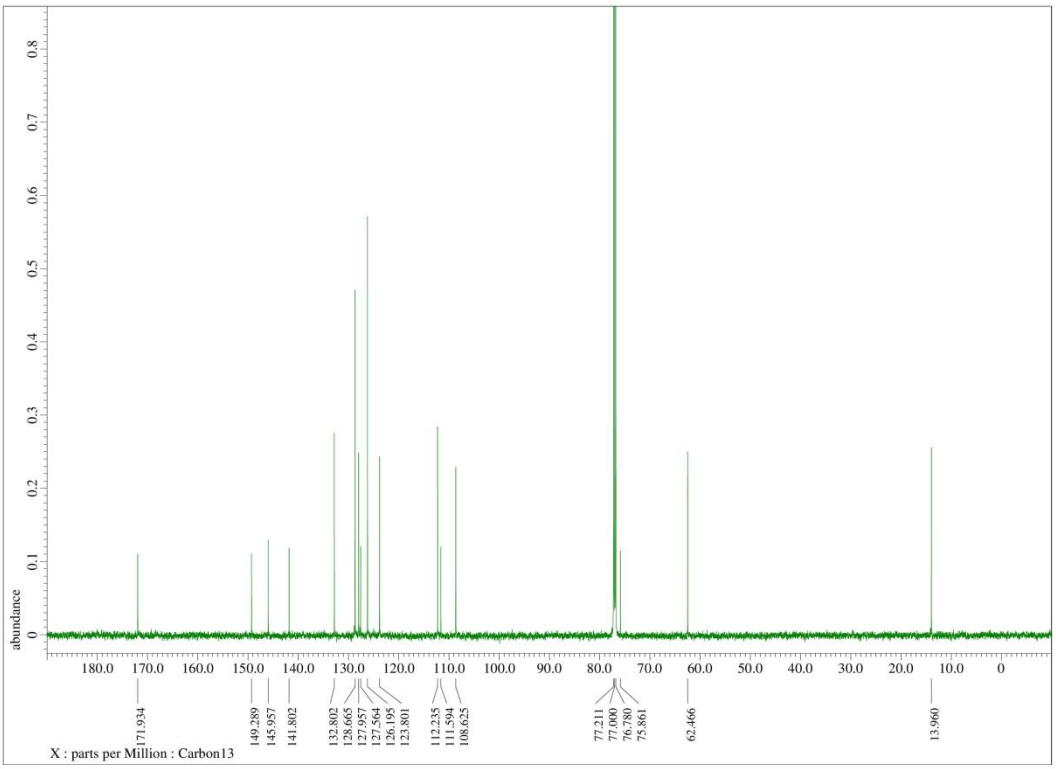

Ph
CO2Et
Cl
N
H
5k
abundance
X : parts per Million : Proton

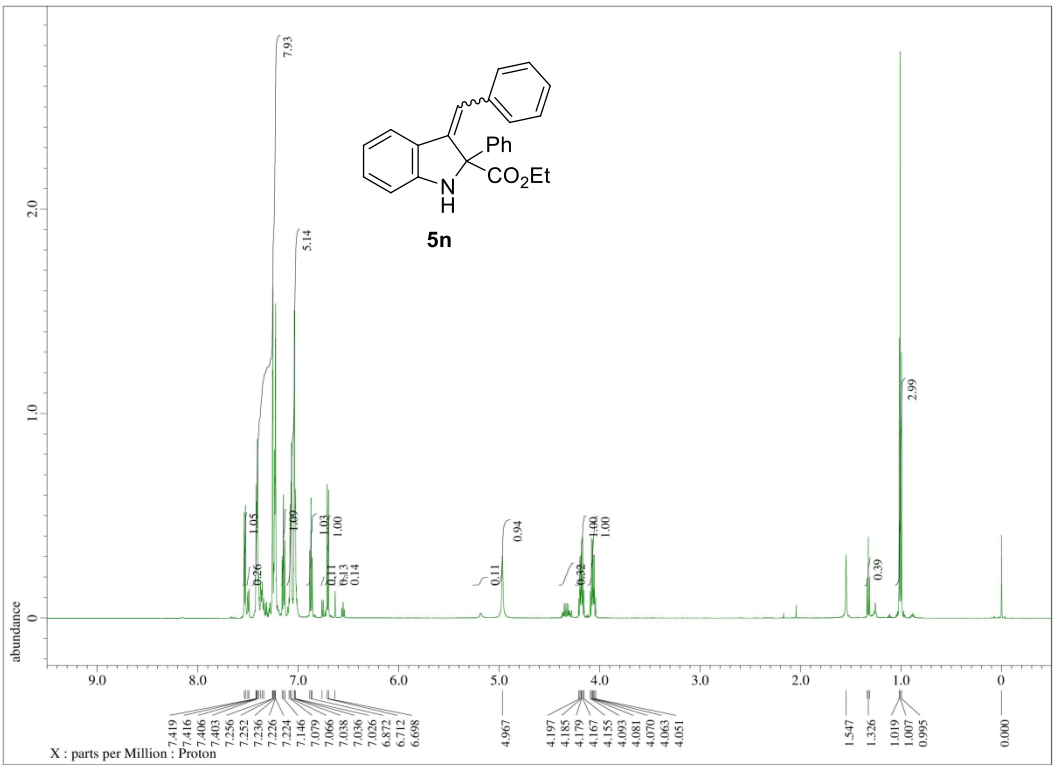

abundance
X : parts per Million : Carbon13

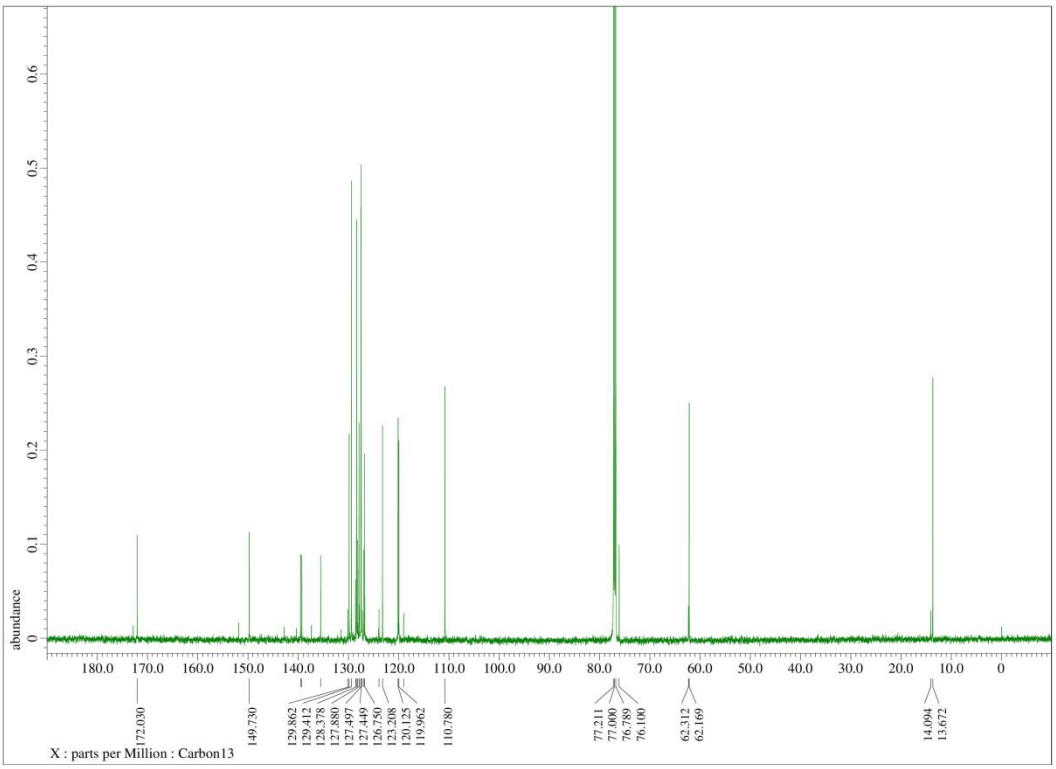

Cl
Ph
CO2Et
N
H
5l
abundance
X : parts per Million : Proton

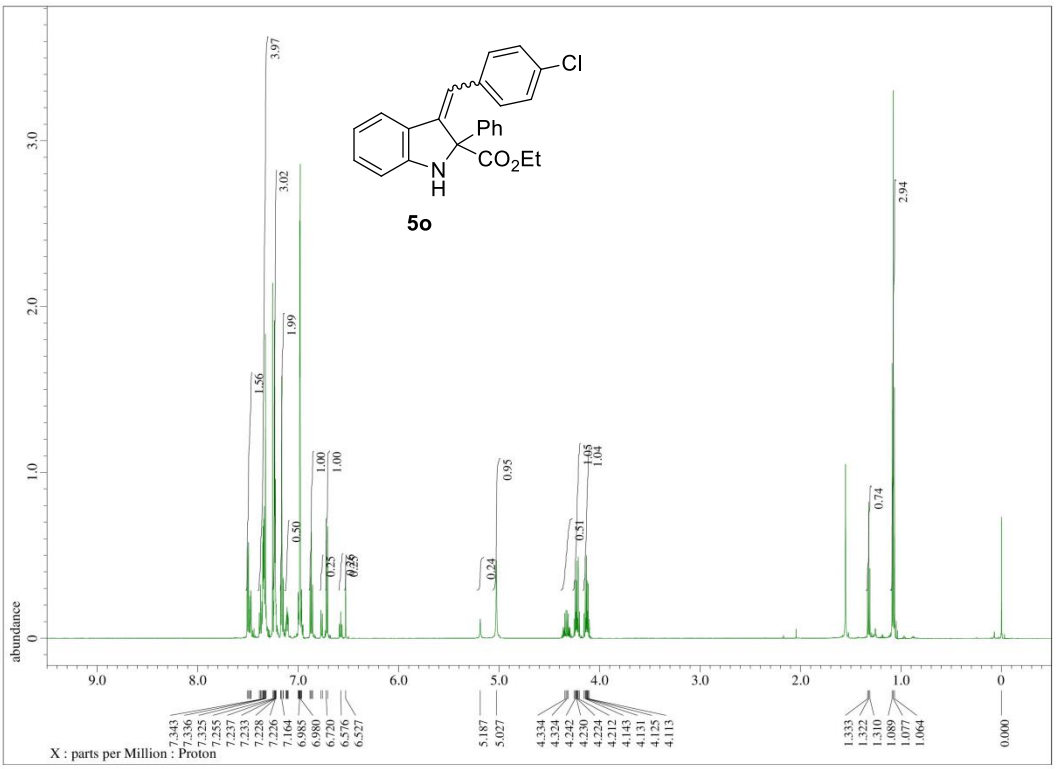

abundance
X : parts per Million : Carbon13

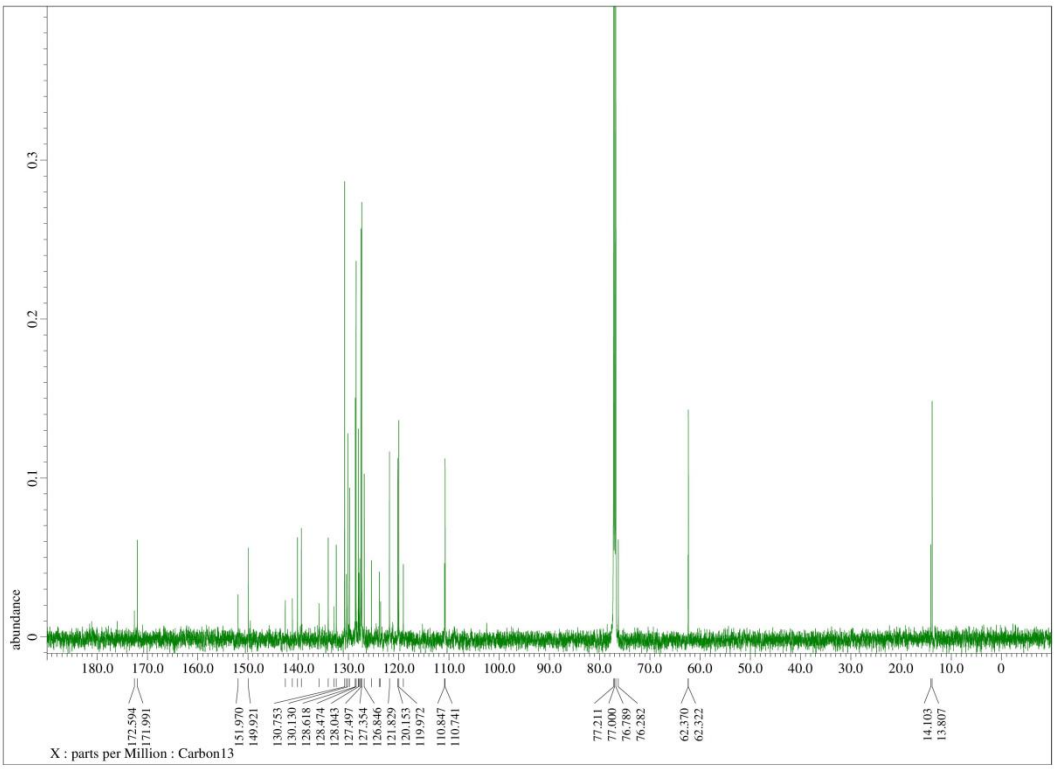

Br
Ph
CO2Et
N
H
5m
abundance
X : parts per Million : Proton

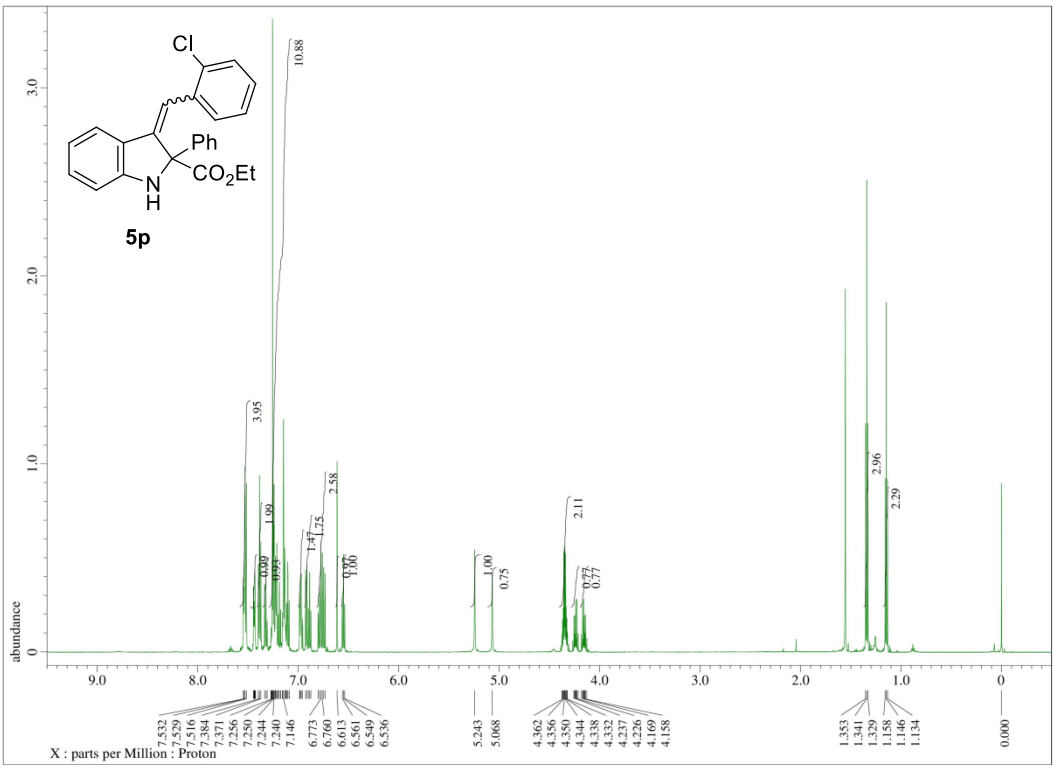

abundance
X : parts per Million : Carbon13

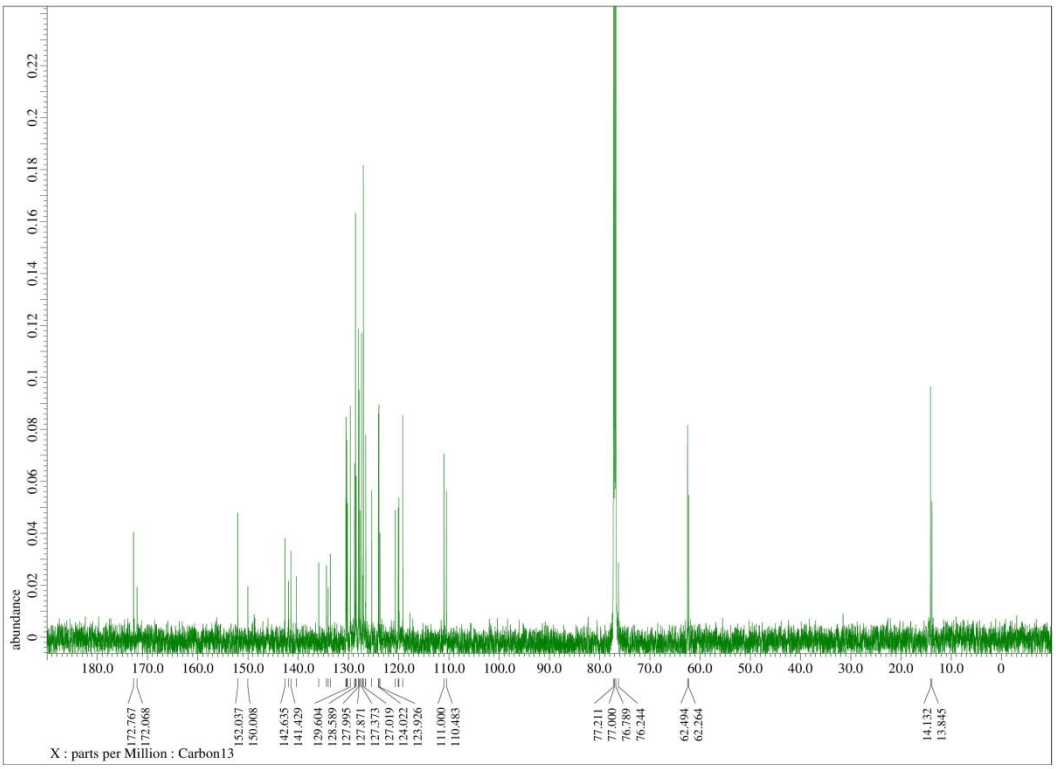

Ph
CO2Et
N
H
5n
abundance
X : parts per Million : Proton

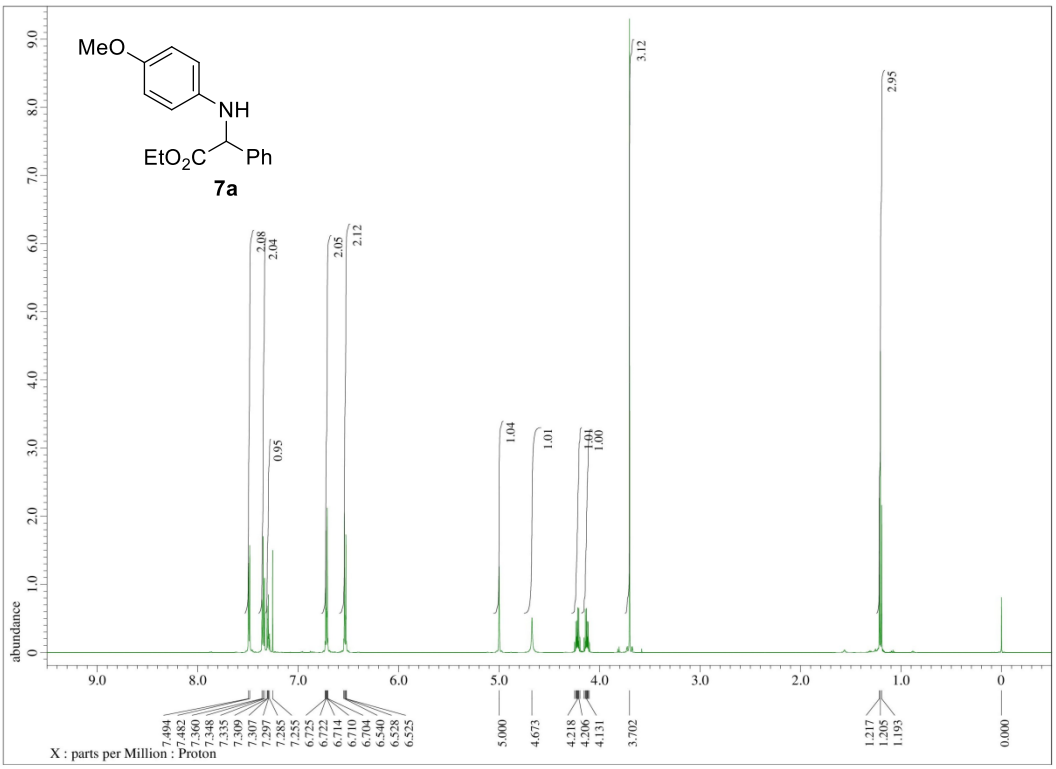

abundance
X : parts per Million : Carbon13

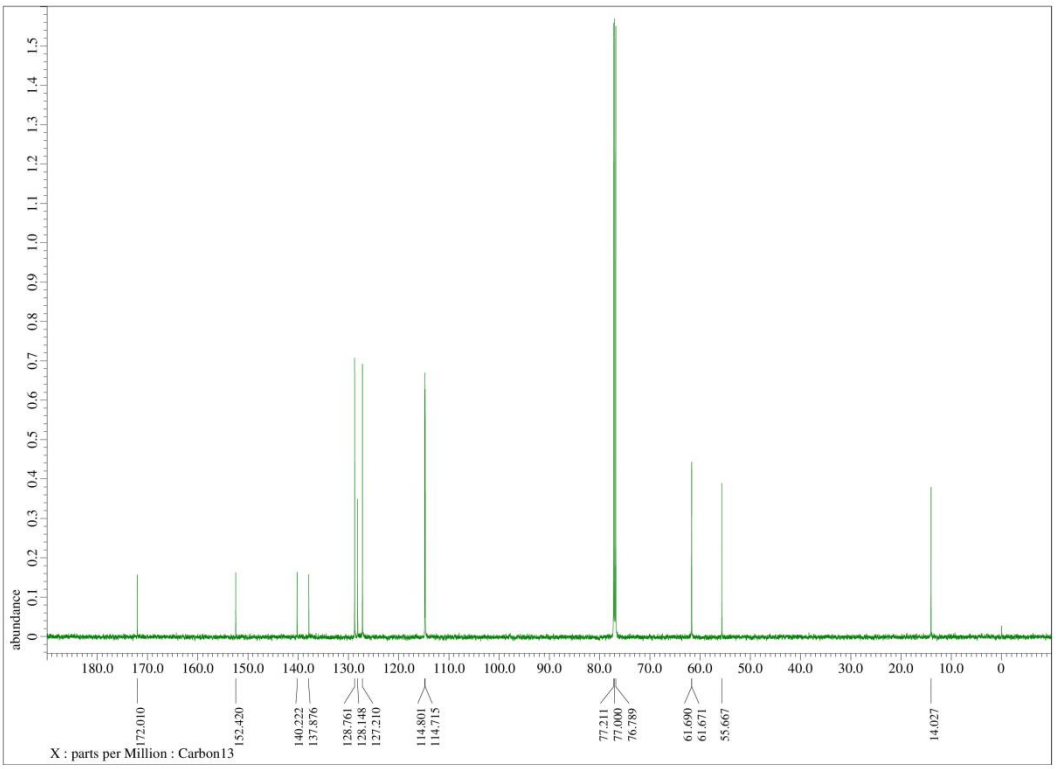

Cl
Ph
CO2Et
N
H
5o
abundance
X : parts per Million : Proton

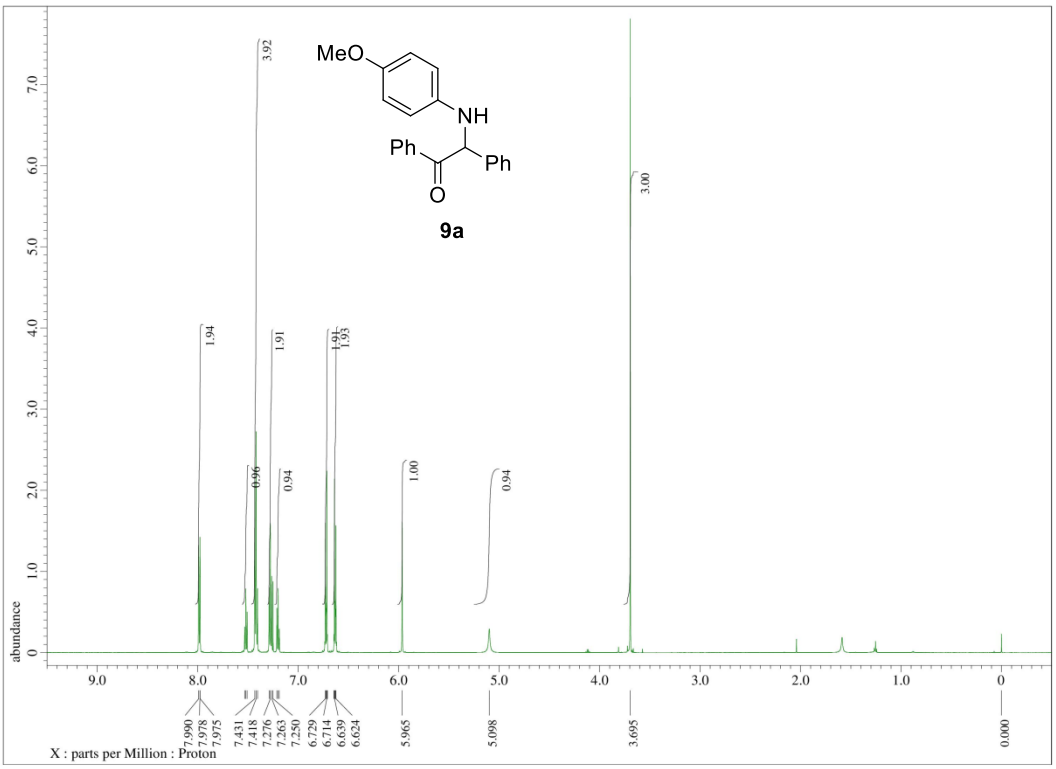

abundance
X : parts per Million : Carbon13

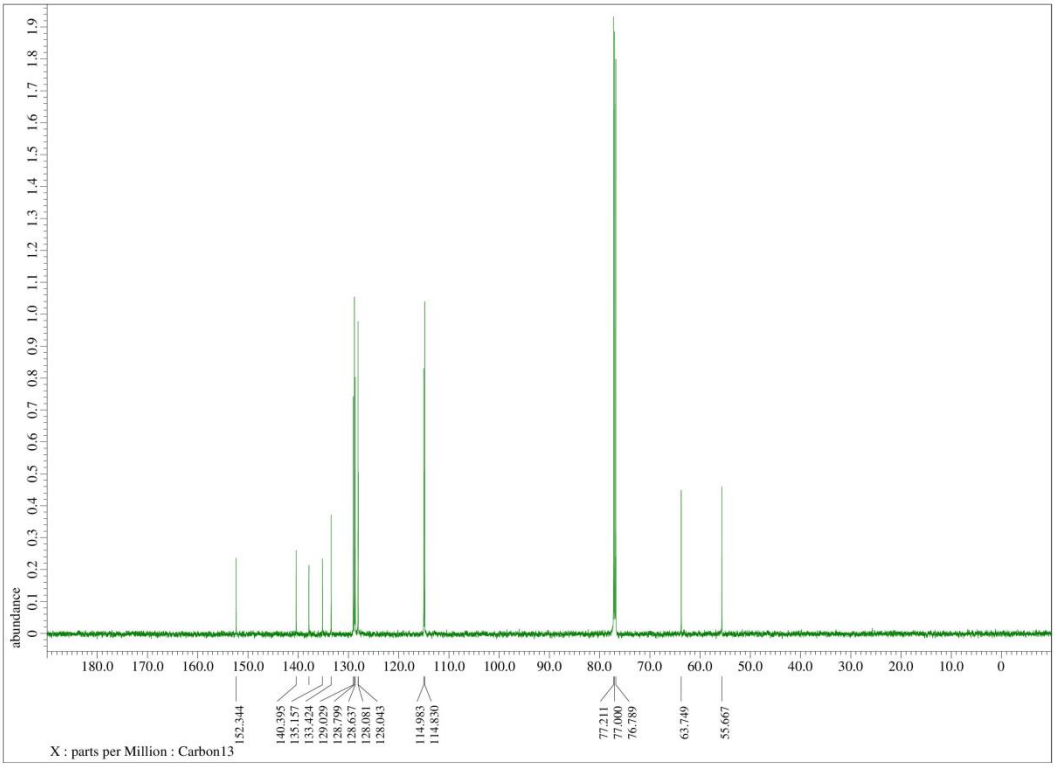

Cl
Ph
CO2Et
N
H
5p
abundance
X : parts per Million : Proton

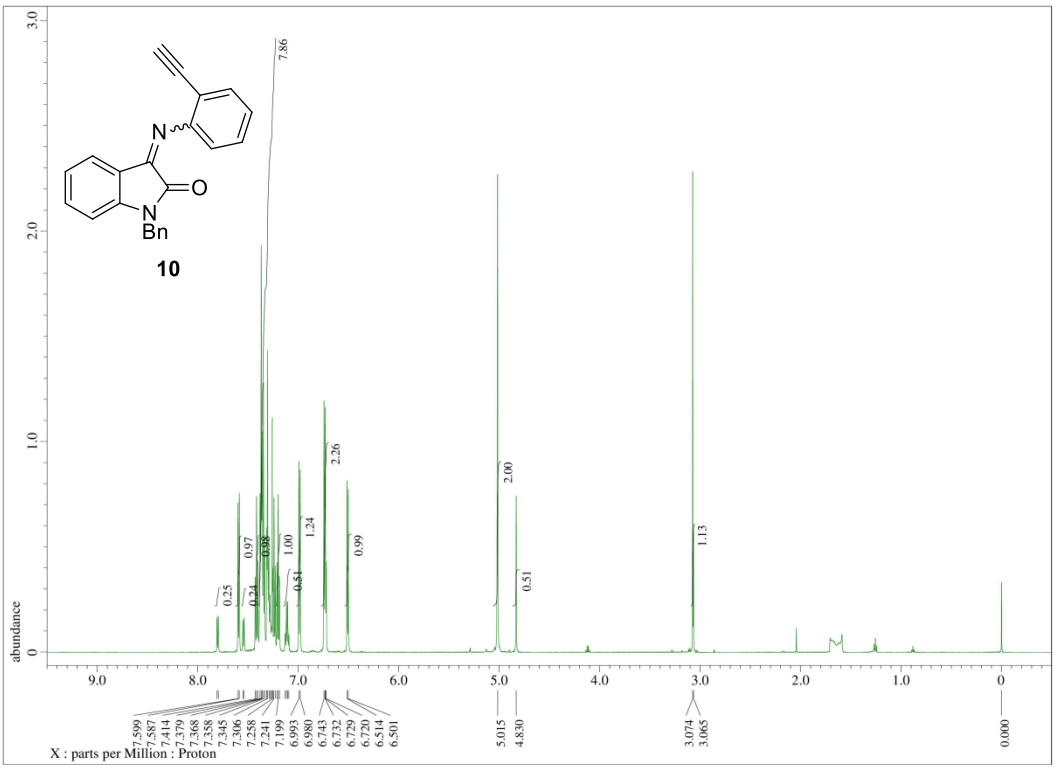

abundance
X : parts per Million : Carbon13

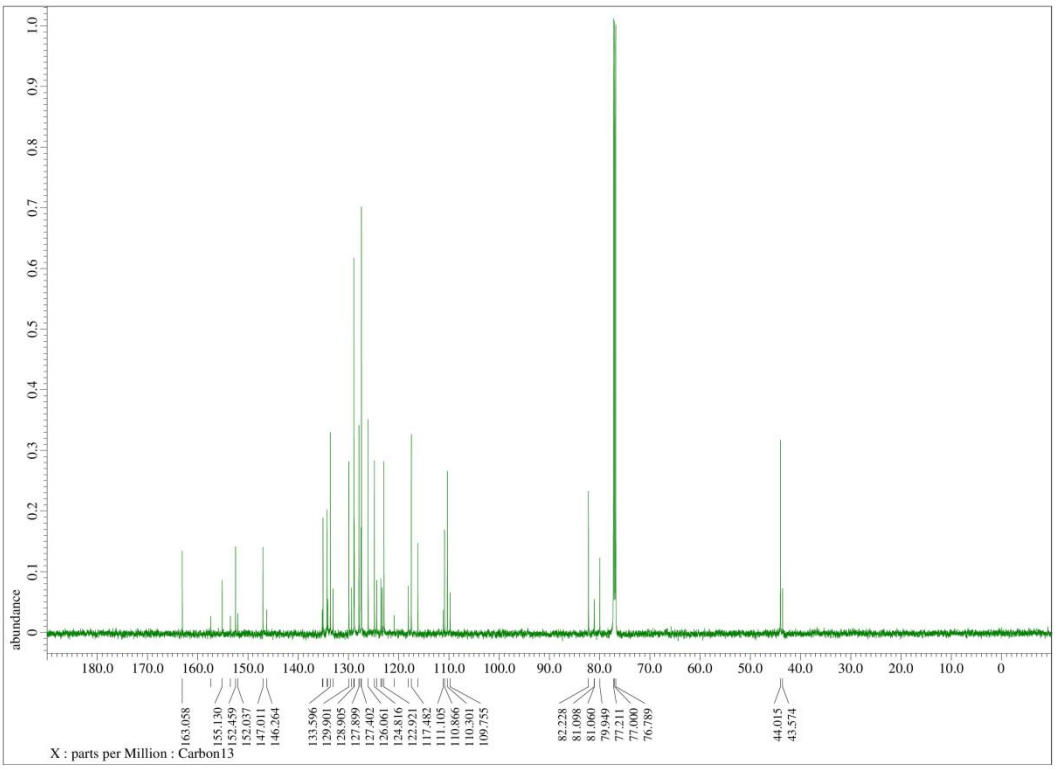

MeO
NH
EtO2C
Ph
7a
abundance
X : parts per Million : Proton

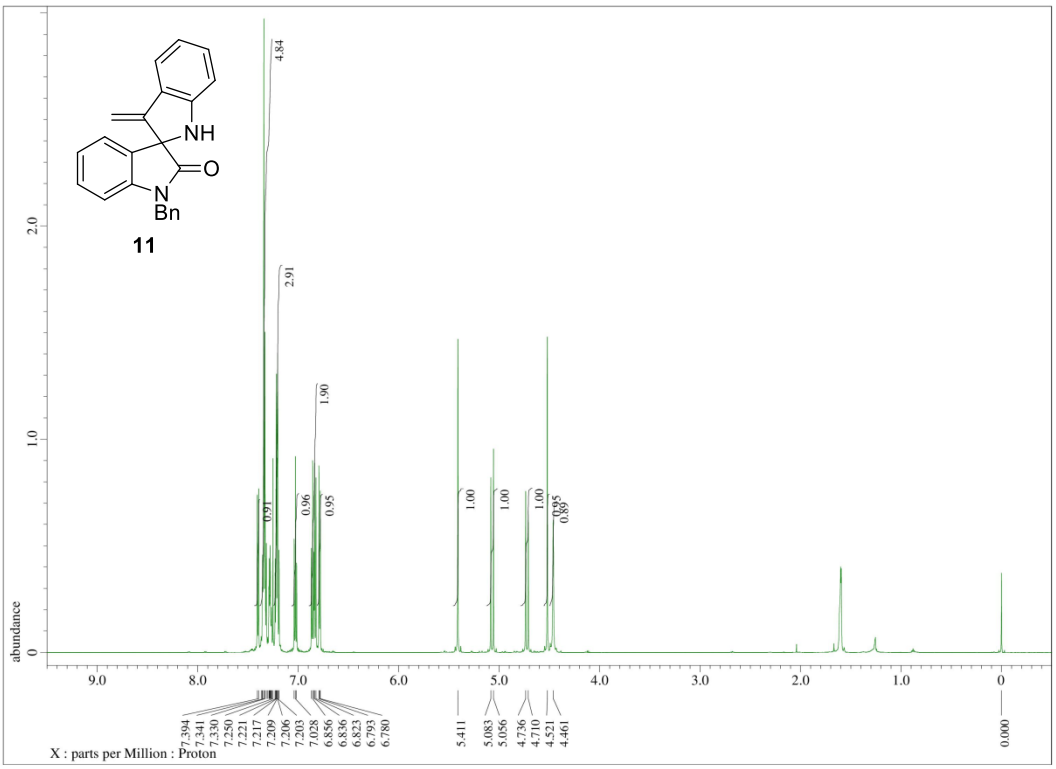

abundance
X : parts per Million : Carbon13

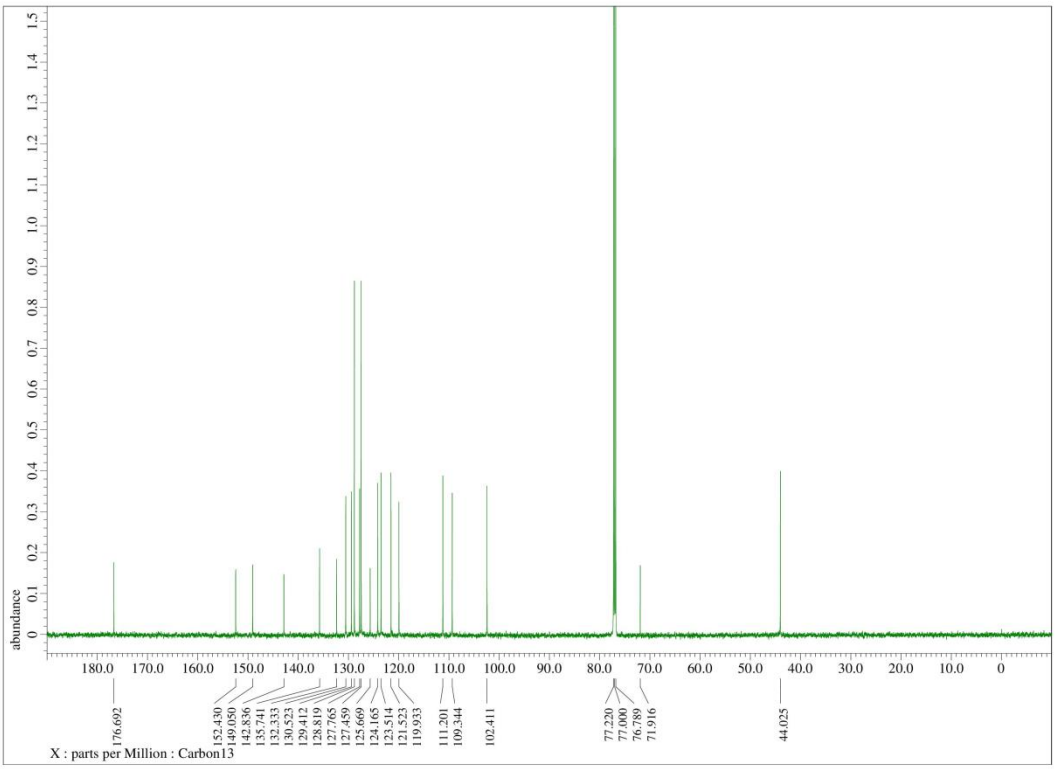

MeO
NH
Ph
Ph
O
9a
abundance
X : parts per Million : Proton

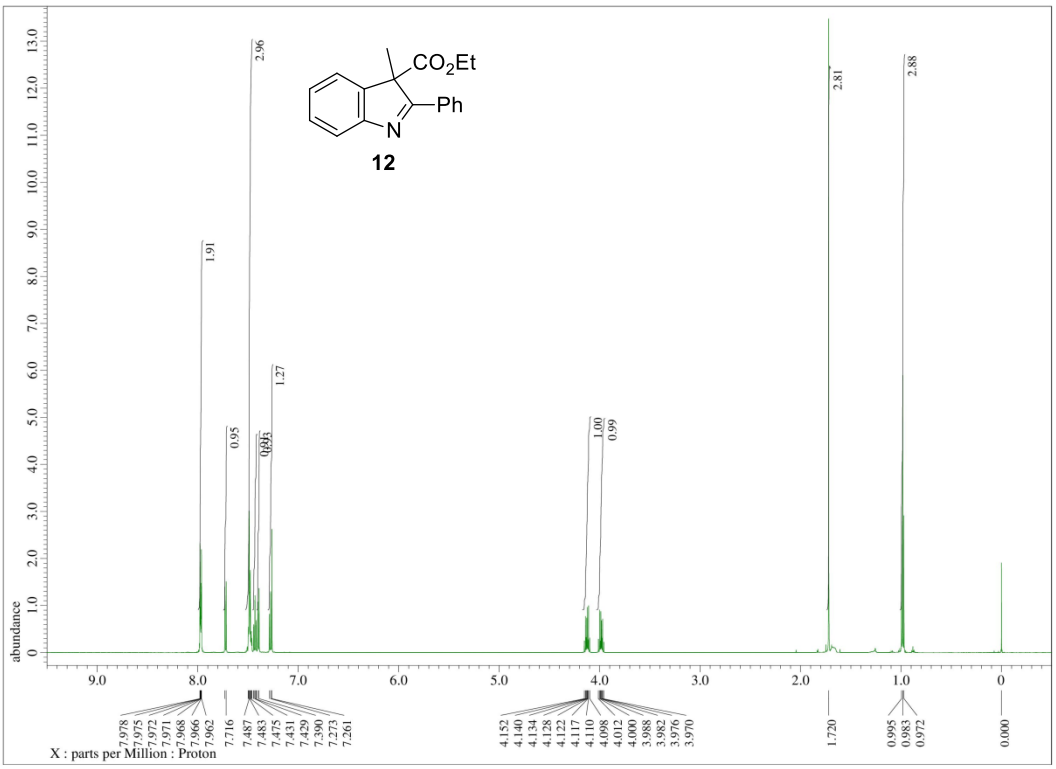

abundance
X : parts per Million : Carbon13

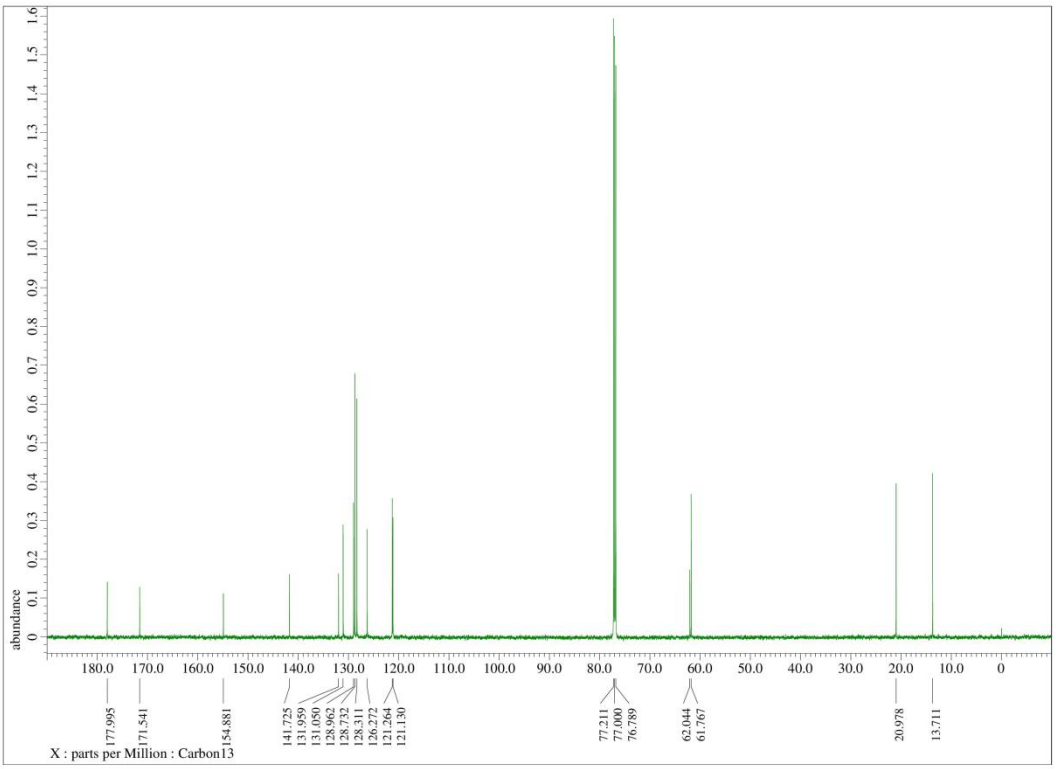

10
abundance
X : parts per Million : Proton

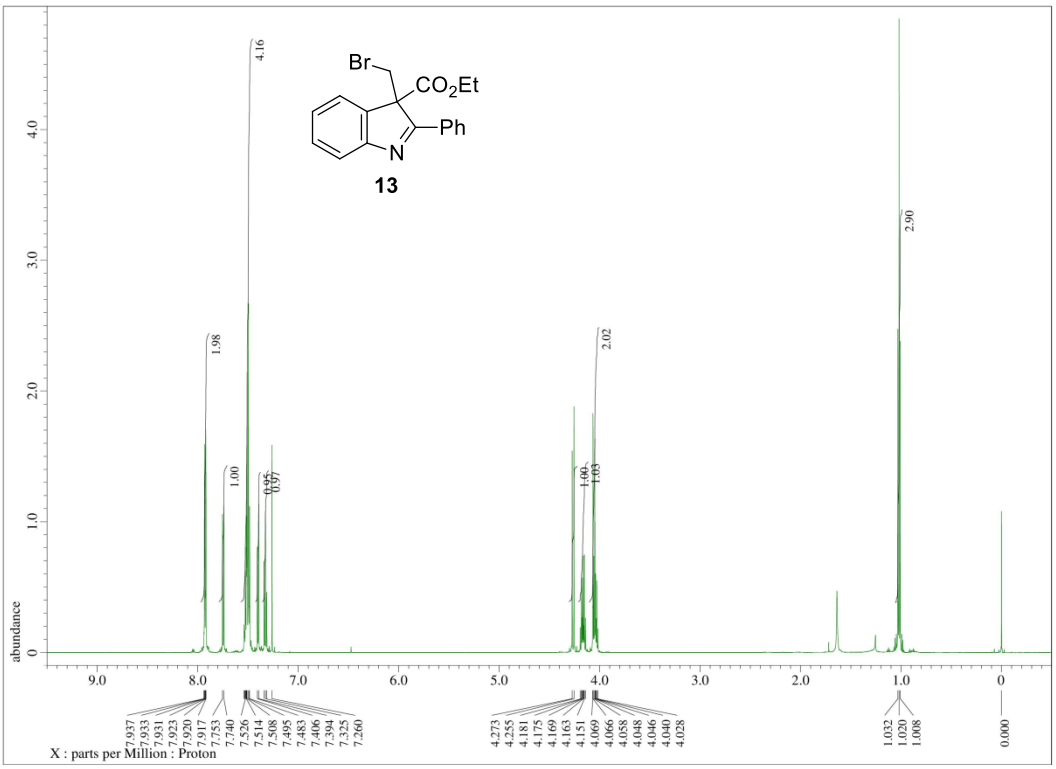

abundance
X : parts per Million : Carbon13

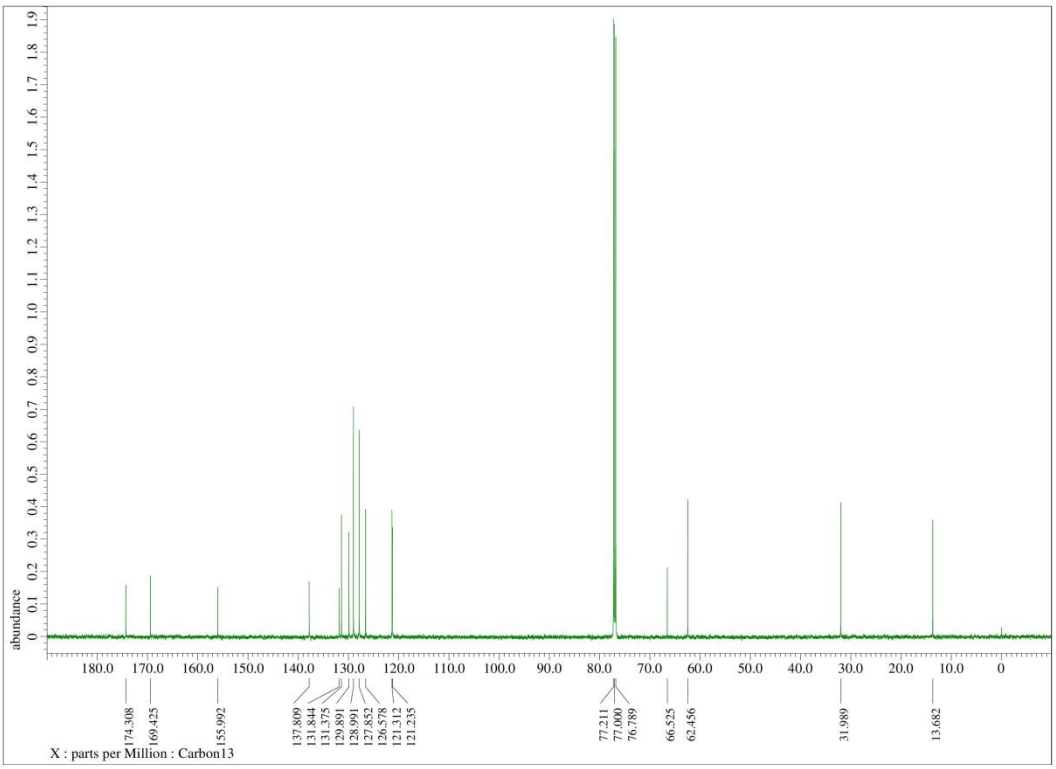

NH
O
N
Bn
11
abundance
X : parts per Million : Proton


abundance
X : parts per Million : Carbon13


CO2Et
Ph
N
12
abundance
X : parts per Million : Proton


abundance
X : parts per Million : Carbon13


Br
CO2Et
Ph
N
13
4.16
2.90
1.98
2.02
1.00
0.96
0.97
1.00
1.03
abundance
X : parts per Million : Proton


abundance
X : parts per Million : Carbon13