Support Information – New. J. Chem.

Three-Component [3+2] Cycloaddition for Regio- and Diastereoselective Synthesis of Spirooxindole-Pyrrolidines

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Content

1. General information

All commercially available chemical reagents and solvents were purchased from Sigma-Aldrich, and Oakwood. ^{1}H-NMR (400 MHz) and ^{13}C-NMR spectra (101 MHz) were detected on Agilent NMR spectrometers. LC-MS were performed on an Agilent 2100 LC with 6130 quadrupole MS spectrometers. A linear gradient from 25:75 (v/v) MeOH/water to 100% MeOH over 7.0 min at a flow rate of 0.7 mL/min was used as a mobile phase. UV detections were conducted at 210 nm and 254 nm. Low resolution mass spectra were recorded in APCI (atmospheric pressure chemical ionization). A C18 column (5.0 μm, 6.0 x 50 mm) was used for the separation from Agela. The high-resolution mass spectra were obtained on a Waters Micromass GCT Premier. All products were purified on Agela Flash System with Venusil PrepG C18 column (10 μm, 120 Å, 21.2 mm x 250 mm).

2. General procedure for products

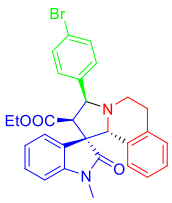
General procedure I for one-pot synthesis of compound 1, 5 and 6.

To a solution of cyclic amines **2** (1.3 mmol), aldehydes **3** (1.1 mmol), and olefinic oxindoles **4** (1.0 mmol) in 4 mL of EtOH was added BzOH (0.5 mmol). The reaction solution was stirred at 125 ºC for 30 mins under microwave heating. Upon the completion of the reaction as monitored by LC-MS, the reaction mixture was evaporated to remove solvents, and the concentrated reaction solution was isolated by Agela Flash System to give product **1**, **5** and **6**.

General procedure II for one-pot synthesis of compound 7a.

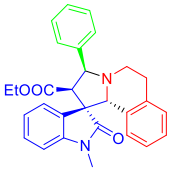
To a solution of THIQ **2a** (1.3 mmol), 2-azidobenzaldehyde or 2-nitrobenzaldehyde (1.1 mmol), and olefinic oxindoles **4a** (1.0 mmol) in 4 mL of EtOH was added BzOH (0.5 mmol). The reaction solution was stirred at 125 ºC for 30 mins under microwave heating. Upon the completion of the reaction as monitored by LC-MS, the reaction mixture was added to 1 mL of H_2O, Fe (2.5 mmol) and AcOH (3.0 mmol) *in situ*, then stirred at 85 ºC for 6 h. the concentrated reaction solution was isolated by Agela Flash System to give product **7a**.

3. Characterization of products

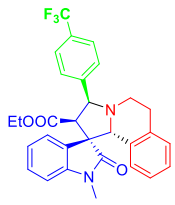


*Compound **1a**:* white solid (63% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, J = 8.5 Hz, 2H), 7.49 (d, J = 8.6 Hz, 2H), 7.07 (td, J = 7.7, 1.2 Hz, 1H), 6.90 (ddt, J = 14.3, 7.6, 4.5 Hz, 3H), 6.76 – 6.68 (m, 3H), 6.39 (d, J = 7.8 Hz, 1H), 5.29 (s, 1H), 4.90 (d, J = 9.1 Hz, 1H), 3.77 (d, J = 9.1 Hz, 1H), 3.54 (ddd, J = 14.3, 9.0, 3.6 Hz, 2H), 3.35 (s, 3H), 3.00 – 2.91 (m, 2H), 2.76 (ddd, J = 12.7, 11.3, 3.2 Hz, 1H), 2.56 – 2.49 (m, 1H), 0.62 (t, J = 7.1 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 175.2, 168.3, 143.4, 135.1,

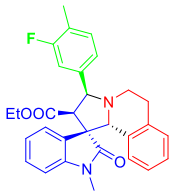
130.1, 129.3, 128.8, 126.2, 125.9, 122.1, 121.2, 107.8, 67.2, 65.9, 60.6, 56.5, 26.5, 13.5. HRMS (ESI-TOF, *m/z*): $[M+H]^+$ calcd. for $C_{29}H_{27}BrN_2O_3$ 531.1283, found: 531.1279.



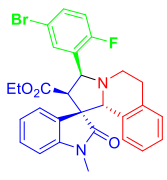
Compound ***1b****:* white solid (66% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 – 7.63 (m, 2H), 7.40 – 7.27 (m, 5H), 7.12 – 7.01 (m, 3H), 6.93 – 6.88 (m, 1H), 6.86 – 6.79 (m, 1H), 6.13 (d, J = 7.7 Hz, 1H), 4.28 – 4.22 (m, 2H), 3.62 (d, J = 9.6 Hz, 1H), 3.58 – 3.48 (m, 2H), 3.24 – 3.14 (m, 4H), 3.06 (ddd, J = 10.9, 6.4, 1.9 Hz, 1H), 2.68 (d, J = 16.2 Hz, 1H), 2.38 (td, J = 11.0, 4.1 Hz, 1H), 0.59 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.4, 169.9, 144.1, 139.5, 135.6, 134.8, 130.2, 129.3, 128.8, 128.6, 128.6, 127.9, 126.7, 125.5, 124.2, 122.7, 122.6, 107.9, 72.9, 69.7, 61.7, 60.2, 57.2, 46.2, 29.8, 26.4, 13.4. HRMS (ESI-TOF, *m/z*): $[M+H]^+$ calcd. for $C_{29}H_{28}N_2O_3$ 453.2178, found: 453.2181.



Compound ***1c****:* white solid (72% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, J = 8.1 Hz, 2H), 7.64 (d, J = 8.0 Hz, 2H), 7.09 (td, J = 7.7, 1.2 Hz, 1H), 6.98 – 6.87 (m, 3H), 6.75 (ddd, J = 10.5, 8.5, 4.4 Hz, 3H), 6.41 (d, J = 7.7 Hz, 1H), 5.34 (s, 1H), 5.01 (d, J = 9.2 Hz, 1H), 3.81 (d, J = 9.2 Hz, 1H), 3.63 – 3.49 (m, 2H), 3.36 (s, 3H), 3.02 – 2.92 (m, 2H), 2.81 (ddd, J = 12.7, 11.2, 3.1 Hz, 1H), 2.56 (dd, J = 12.5, 3.3 Hz, 1H), 0.64 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.4, 168.8, 145.8, 143.8, 135.5, 135.0, 128.8, 128.6, 128.2, 127.3, 126.1, 125.8, 125.4, 125.0, 124.9, 122.2, 107.5, 67.9, 67.9, 66.2, 61.0, 60.4, 60.1, 43.9, 27.1, 26.7, 26.7, 13.4. HRMS (ESI-TOF, *m/z*): $[M+H]^+$ calcd. for $C_{30}H_{27}F_3N_2O_3$ 521.2052, found: 521.2050.

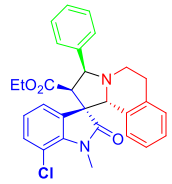


Compound ***1d****:* white solid (60% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.59 (m, 1H), 7.37 – 7.27 (m, 2H), 7.22 – 6.98 (m, 6H), 6.76 (dd, J = 10.5, 4.3 Hz, 2H), 6.01 (d, J = 7.7 Hz, 1H), 5.57 – 5.51 (m, 2H), 3.82 – 3.70 (m, 2H), 3.31 (dd, J = 6.4, 0.4 Hz, 1H), 3.22 – 3.12 (m, 1H), 3.04 – 2.98 (m, 2H), 2.82 (d, J = 2.5 Hz, 3H), 2.44 (d, J = 15.1 Hz, 1H), 2.26 (d, J = 1.5 Hz, 3H), 0.81 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.47, 169.05, 144.3, 137.9, 134.9, 130.8, 129.0, 128.5, 127.2, 126.1, 125.6, 125.2, 124.3, 123.3, 122.9, 107.9, 67.9, 66.9, 60.9, 60.2, 57.0, 44.7, 26.2, 13.6. HRMS (ESI-TOF, *m/z*): $[M+H]^+$ calcd. for $C_{30}H_{29}FN_2O_3$ 485.2240, found: 485.2235.

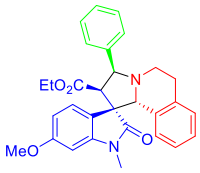


Compound ***1e****:* white solid (39% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (dd, J = 7.4, 0.8 Hz, 1H), 7.38 (dd, J = 6.3, 2.6 Hz, 1H), 7.31 (d, J = 7.2 Hz, 1H), 7.22 – 7.09 (m, 5H), 7.02 (td, J = 7.6, 1.0 Hz, 1H), 6.69 (dd, J = 9.7, 8.7 Hz, 1H), 6.57 (d, J = 7.7 Hz, 1H), 5.51 (d, J = 7.6 Hz, 1H), 5.01 (s, 1H), 3.86 – 3.79 (m, 1H), 3.77 (d, J = 7.6 Hz, 1H), 3.67 – 3.60 (m, 1H), 3.14 – 3.04 (m, 4H), 3.02 – 2.88 (m, 3H), 2.45 (d, J = 15.7 Hz, 1H), 0.61 (t, J = 7.1 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 175.2, 170.4, 143.7, 138.9, 134.5, 131.6, 128.7, 128.6, 126.9, 126.7, 126.3, 126.2, 126.1, 125.3, 121.9, 116.0, 107.3, 60.6, 60.4, 59.2, 59.0, 43.6, 26.4, 23.3, 13.4. HRMS (ESI-TOF, *m/z*): $[M+H]^+$ calcd. for $C_{29}H_{26}BrFN_2O_3$

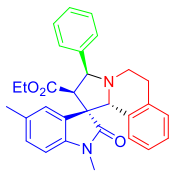
549.1189, found: 549.1193.



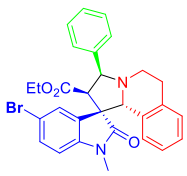
Compound 1f: white solid (77% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (dd, J = 7.3, 1.2 Hz, 1H), 7.28 (d, J = 7.4 Hz, 1H), 7.23 – 7.13 (m, 2H), 7.13 – 7.01 (m, 7H), 6.94 – 6.88 (m, 1H), 5.47 (d, J = 7.3 Hz, 1H), 4.68 (s, 1H), 3.90 (dd, J = 10.7, 7.1 Hz, 1H), 3.70 (dt, J = 6.8, 3.2 Hz, 2H), 3.42 (s, 3H), 3.06 (tdd, J = 13.8, 4.7, 2.1 Hz, 2H), 2.99 – 2.90 (m, 1H), 2.37 (d, J = 16.1 Hz, 1H), 0.71 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.4, 170.5, 139.4, 139.2, 134.9, 134.5, 130.4, 129.7, 128.8, 127.9, 127.7, 127.6, 126.9, 126.7, 126.1, 124.9, 122.7, 114.6, 71.4, 61.3, 60.7, 59.3, 58.9, 43.0, 29.7, 22.8, 13.4. HRMS (ESI-TOF, *m/z*): $[M+H]^+$ calcd. for $C_{29}H_{27}ClN_2O_3$ 487.1788, found: 487.1791.



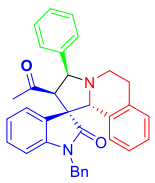
*Compound **1g**:* off-white solid (73% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 – 7.63 (m, 2H), 7.40 – 7.34 (m, 2H), 7.31 (dt, J = 9.6, 4.3 Hz, 1H), 7.06 (t, J = 4.3 Hz, 2H), 6.97 (d, J = 2.5 Hz, 1H), 6.89 (dd, J = 8.4, 2.5 Hz, 1H), 6.85 – 6.79 (m, 2H), 6.15 (d, J = 7.7 Hz, 1H), 4.27 – 4.18 (m, 2H), 3.81 (s, 3H), 3.61 (dd, J = 15.4, 8.3 Hz, 3H), 3.24 – 3.16 (m, 1H), 3.15 (s, 3H), 3.05 (ddd, J = 10.9, 6.3, 1.8 Hz, 1H), 2.67 (d, J = 16.5 Hz, 1H), 2.37 (td, J = 11.1, 4.1 Hz, 1H), 0.63 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.2, 169.9, 155.9, 139.5, 137.6, 135.5, 134.7, 131.4, 129.3, 128.6, 128.6, 127.9, 126.7, 125.5, 113.6, 111.3, 108.3, 73.1, 69.8, 61.6, 60.2, 57.6, 46.2, 29.8, 26.4, 13.4. HRMS (ESI-TOF, *m/z*): $[M+H]^+$ calcd. for $C_{30}H_{30}N_2O_4$ 483.2284, found: 483.2280.



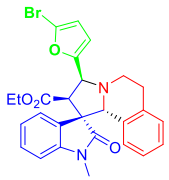
*Compound **1h**:* white solid (53% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (dd, J = 1.2, 0.5 Hz, 1H), 7.31 (d, J = 7.4 Hz, 1H), 7.18 (dtd, J = 16.2, 7.3, 1.2 Hz, 2H), 7.12 – 7.01 (m, 6H), 6.89 (ddd, J = 7.9, 1.7, 0.8 Hz, 1H), 6.36 (d, J = 7.9 Hz, 1H), 5.50 (d, J = 7.4 Hz, 1H), 4.66 (s, 1H), 3.82 (dt, J = 14.2, 7.1 Hz, 1H), 3.70 – 3.61 (m, 2H), 3.13 – 3.03 (m, 2H), 3.02 – 2.92 (m, 4H), 2.35 (s, 3H), 0.62 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.9, 170.7, 141.2, 139.5, 135.5, 134.7, 131.2, 128.7, 128.3, 127.9, 127.5, 127.3, 127.0, 126.8, 126.9, 126.7, 125.9, 106.8, 71.2, 61.6, 60.5, 59.0, 43.2, 26.2, 22.9, 21.2, 13.4. HRMS (ESI-TOF, *m/z*): $[M+H]^+$ calcd. for $C_{30}H_{30}N_2O_3$ 467.2335, found: 467.2340.



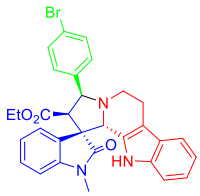
*Compound **1i**:* white solid (57% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, J = 2.0 Hz, 1H), 7.30 (d, J = 7.4 Hz, 1H), 7.25 – 7.22 (m, 1H), 7.22 – 7.13 (m, 2H), 7.09 (d, J = 19.8 Hz, 6H), 6.36 (d, J = 8.3 Hz, 1H), 5.47 (d, J = 7.2 Hz, 1H), 4.65 (s, 1H), 3.93 – 3.86 (m, 1H), 3.75 – 3.67 (m, 2H), 3.15 – 3.03 (m, 2H), 3.01 (s, 3H), 2.97 – 2.89 (m, 1H), 2.38 (d, J = 16.2 Hz, 1H), 0.68 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.4, 170.3, 142.6, 139.2, 134.8, 134.4, 131.0, 129.1, 128.8, 127.9, 127.6, 126.9, 126.7, 126.1, 114.6, 108.4, 71.1, 61.7, 60.7, 58.9, 43.0, 26.3, 22.9, 13.5. HRMS (ESI-TOF, *m/z*): $[M+H]^+$ calcd. for $C_{29}H_{27}BrN_2O_3$ 531.1283, found: 531.1279.



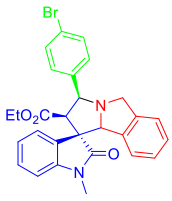
Compound ***1j****:* white solid (55% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.52 (m, 1H), 7.22 – 7.09 (m, 7H), 7.08 – 6.98 (m, 7H), 6.82 (dd, J = 7.9, 1.6 Hz, 2H), 6.41 – 6.36 (m, 1H), 5.64 (d, J = 7.0 Hz, 1H), 5.01 (d, J = 15.8 Hz, 1H), 4.73 (s, 1H), 4.58 (d, J = 15.8 Hz, 1H), 3.85 (d, J = 6.9 Hz, 1H), 3.10 – 2.90 (m, 3H), 2.36 (d, J = 16.1 Hz, 1H), 1.62 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 204.2, 176.2, 142.0, 139.7, 135.0, 134.8, 134.4, 128.8, 128.5, 128.4, 127.9, 127.7, 127.5, 127.4, 126.9, 126.5, 125.9, 125.8, 122.5, 108.7, 72.7, 67.5, 61.4, 57.7, 43.0, 28.9, 22.7. HRMS (ESI-TOF, *m/z*): $[M+H]^+$ calcd. for $C_{34}H_{30}N_2O_2$ 499.2386, found: 499.2390.



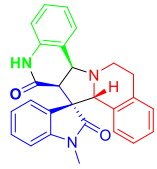
Compound ***1k****:* white solid (68% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.53 (m, 1H), 7.28 – 7.24 (m, 2H), 7.22 – 7.16 (m, 2H), 7.12 (d, J = 7.5 Hz, 1H), 7.05 (td, J = 7.6, 1.0 Hz, 1H), 6.70 (d, J = 7.7 Hz, 1H), 5.95 (d, J = 3.3 Hz, 1H), 5.79 (dd, J = 3.3, 0.6 Hz, 1H), 5.42 (d, J = 7.5 Hz, 1H), 4.70 (s, 1H), 3.86 – 3.78 (m, 1H), 3.68 – 3.59 (m, 2H), 3.17 (s, 3H), 3.12 – 3.00 (m, 3H), 2.49 – 2.42 (m, 1H), 0.65 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.3, 170.2, 152.7, 143.7, 138.7, 134.5, 128.8, 128.6, 126.9, 126.7, 126.1, 122.2, 120.8, 111.0, 107.3, 65.5, 60.6, 59.6, 58.7, 43.7, 26.5, 23.0, 13.4. HRMS (ESI-TOF, *m/z*): $[M+H]^+$ calcd. for $C_{27}H_{25}BrN_2O_4$ 521.1076, found: 521.1072.



Compound ***5a****:* white solid (79% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.50 (m, 4H), 7.44 (dt, J = 6.8, 3.3 Hz, 1H), 7.18 – 7.13 (m, 1H), 7.03 (dtd, J = 7.1, 3.6, 1.2 Hz, 2H), 6.98 (tdd, J = 5.6, 3.2, 1.5 Hz, 1H), 6.86 – 6.83 (m, 1H), 6.75 – 6.64 (m, 3H), 5.26 (d, J = 1.4 Hz, 1H), 4.86 (d, J = 10.0 Hz, 1H), 3.73 (dd, J = 10.0, 1.1 Hz, 1H), 3.48 (ddd, J = 7.2, 3.1, 1.1 Hz, 2H), 3.39 (d, J = 1.1 Hz, 3H), 3.07 – 3.00 (m, 1H), 2.94 – 2.85 (m, 2H), 2.62 – 2.54 (m, 1H), 0.60 (td, J = 7.1, 1.1 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 177.9, 168.5, 143.5, 139.5, 136.1, 131.7, 131.0, 130.3, 128.8, 126.8, 126.7, 125.8, 122.7, 121.8, 121.8, 119.4, 118.2, 111.2, 110.6, 107.7, 64.8, 64.3, 61.3, 60.2, 58.4, 43.6, 27.0, 17.5, 13.4. HRMS (ESI-TOF, *m/z*): $[M+H]^+$ calcd. for $C_{31}H_{28}BrN_3O_3$ 570.1392, found: 570.1388.

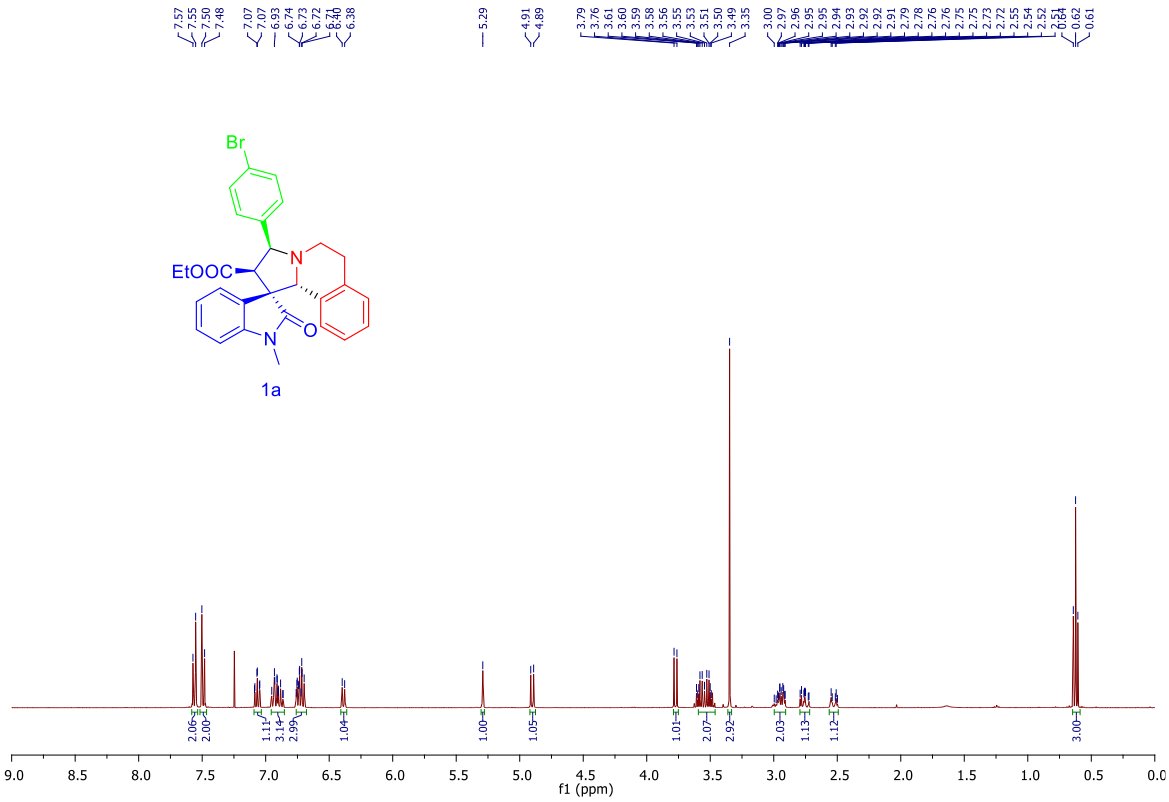


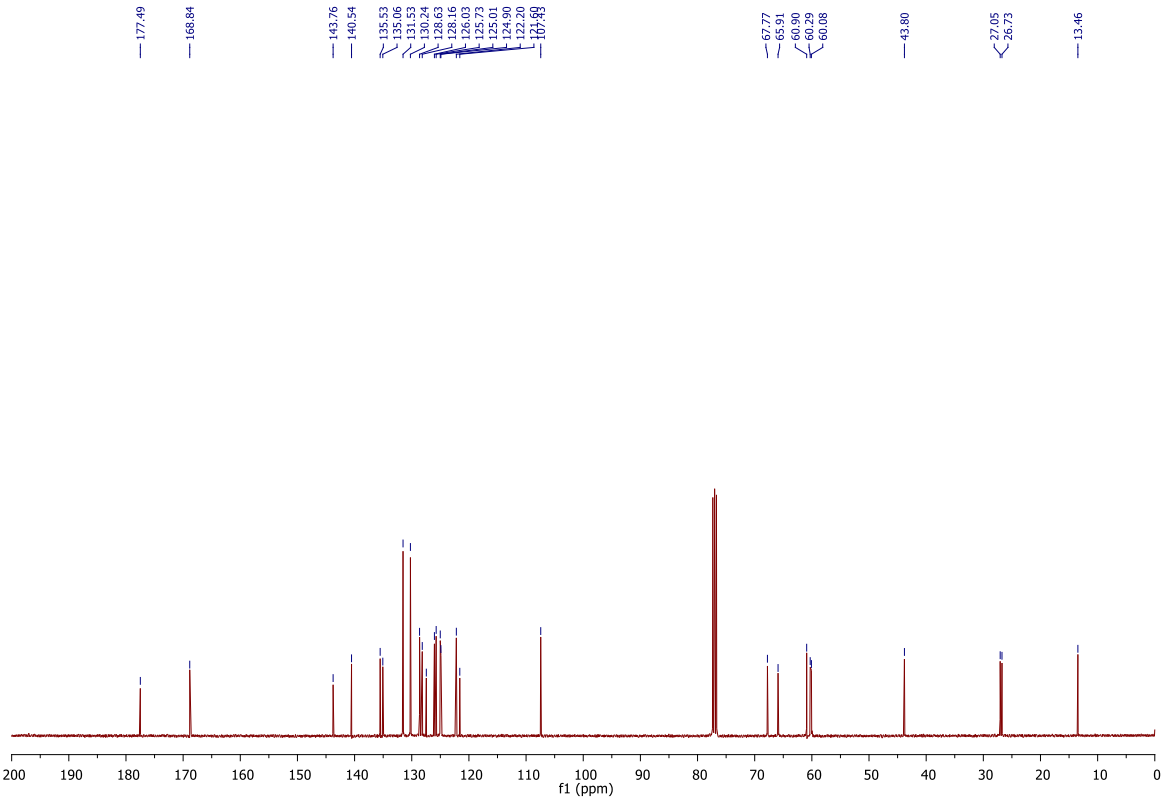
Compound ***6a****:* white solid (46% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 – 7.55 (m, 2H), 7.49 (d, J = 8.5 Hz, 2H), 7.16 – 7.01 (m, 3H), 6.91 – 6.83 (m, 1H), 6.82 – 6.67 (m, 1H), 6.58 (ddd, J = 7.6, 1.3, 0.5 Hz, 1H), 6.52 – 6.38 (m, 1H), 5.53 (d, J = 3.0 Hz, 1H), 4.73 (d, J = 10.5 Hz, 1H), 4.55 – 4.37 (m, 1H), 4.15 (dd, J = 14.5, 3.2 Hz, 1H), 3.88 (d, J = 10.5 Hz, 1H), 3.77 – 3.48 (m, 1H), 3.34 (s, 3H), 0.65 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.4, 169.5, 144.2, 141.2, 139.9, 137.7, 131.1, 129.1, 129.0, 128.2, 126.6, 125.9, 124.7, 123.0, 122.5, 120.7, 120.6, 108.1, 78.6, 71.9, 61.5, 60.5, 60.1, 60.0, 59.6, 25.8, 13.7. HRMS (ESI-TOF, *m/z*): $[M+H]^+$ calcd. for $C_{28}H_{25}BrN_2O_3$ 517.1127, found: 517.1131.

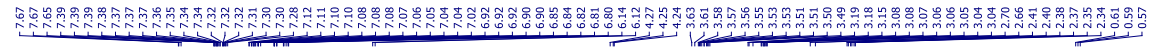


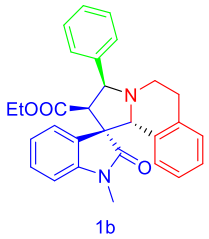
Compound ***7a****:* white solid (NO_2 32%, N_3 51% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (s, 1H), 7.84 (dt, J = 7.7, 1.4 Hz, 1H), 7.31 (dddd, J = 7.9, 7.4, 1.6, 0.9 Hz, 1H), 7.23 – 7.09 (m, 3H), 7.08 – 7.01 (m, 1H), 6.84 (td, J = 7.6, 1.0 Hz, 1H), 6.79 – 6.67 (m, 3H), 6.22 (ddd, J = 7.5, 1.2, 0.5 Hz, 1H), 5.85 – 5.79 (m, 1H), 4.81 (d, J = 8.0 Hz, 1H), 4.49 (s, 1H), 4.15 (d, J = 8.1 Hz, 1H), 3.99 (ddd, J = 12.3, 9.9, 3.4 Hz, 1H), 3.48 (s, 1H), 3.21 (ddd, J = 16.5, 11.8, 5.8 Hz, 1H), 3.14 – 3.08 (m, 1H), 2.92 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.5, 168.6, 144.2, 136.5, 134.5, 132.5, 129.6, 129.3, 128.7, 127.5, 127.1, 125.4, 124.3, 122.9, 122.6, 115.5, 108.0, 71.6, 71.6, 67.19, 65.9, 53.8, 46.0, 29.8, 26.3. HRMS (ESI-TOF, *m/z*): $[M+H]^+$ calcd. for $C_{27}H_{23}N_3O_2$ 422.1869, found: 422.1873.

4. NMR Spectra of Products

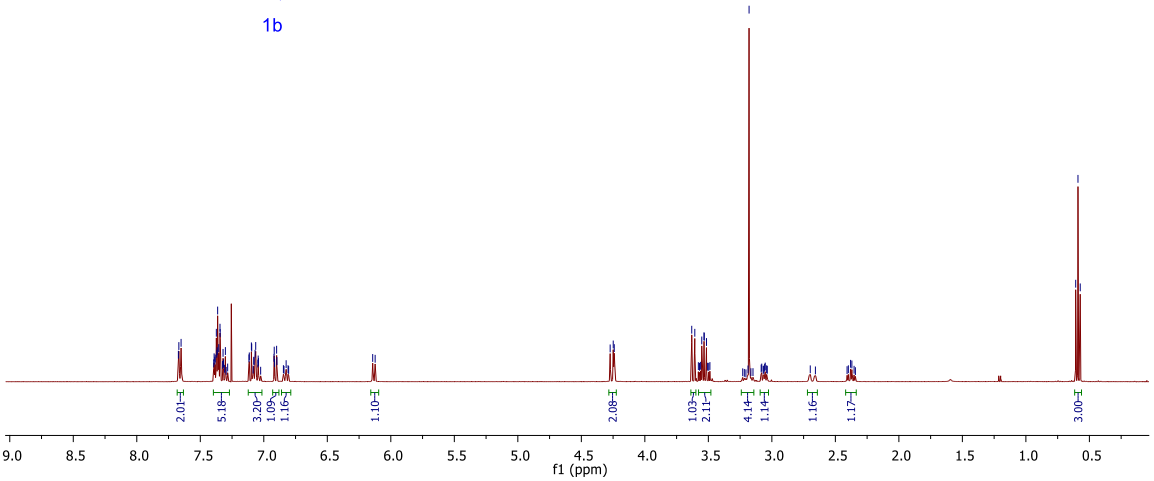







EtOOC
N
O
N

1b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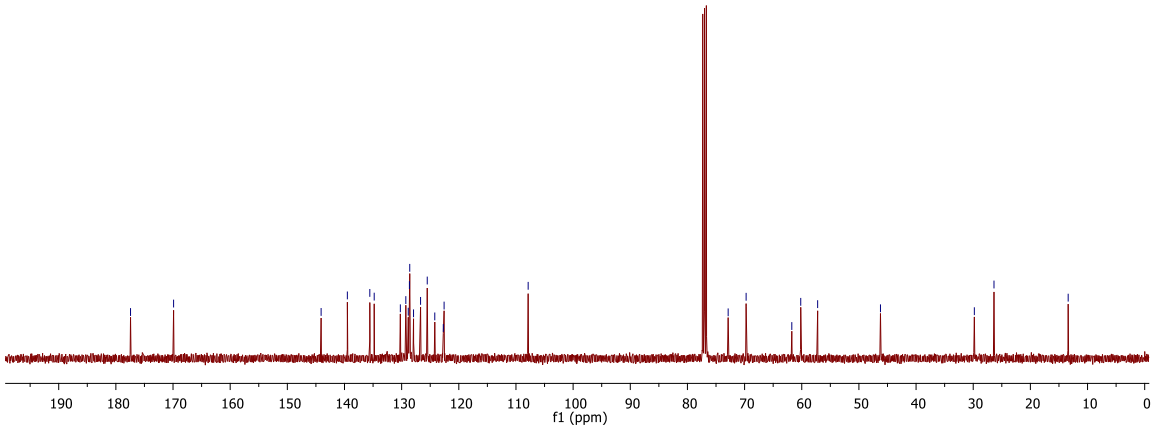
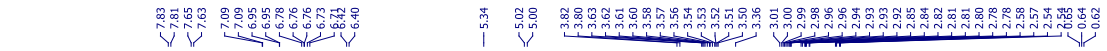
5.18
3.20
1.09
1.16
1.10
2.08
1.03
2.11
4.14
1.14
1.16
1.17
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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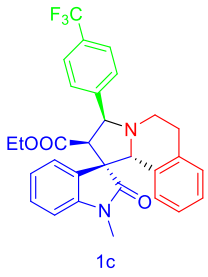
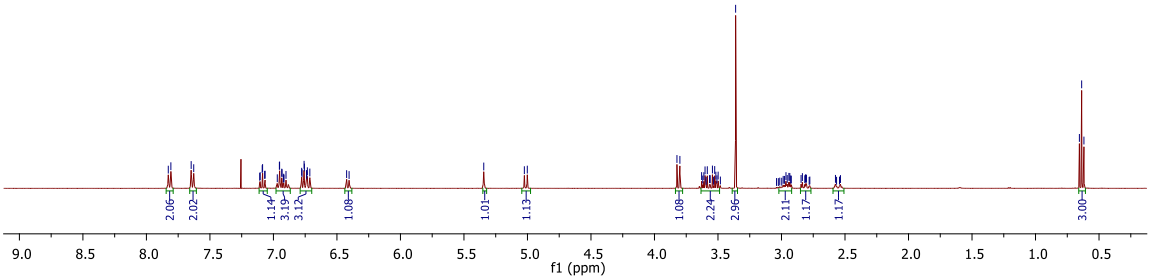
7.81
7.65
7.63
7.09
7.09
6.95
6.95
6.78
6.76
6.76
6.73
6.41
6.40
5.34
5.02
5.00
3.82
3.80
3.63
3.62
3.61
3.60
3.58
3.57
3.56
3.54
3.53
3.52
3.51
3.50
3.36
3.01
3.00
2.99
2.98
2.96
2.96
2.94
2.93
2.93
2.92
2.85
2.84
2.82
2.81
2.81
2.80
2.78
2.78
2.58
2.57
2.54
0.64
0.62


F3C
EtOOC
N
N
O

1c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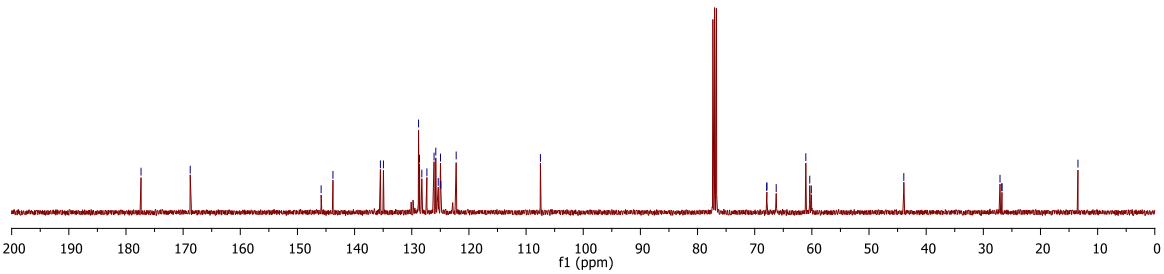
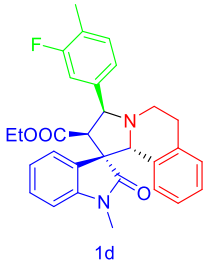
2.02
1.14
3.19
3.12
1.08
1.01
1.13
1.08
2.24
2.96
2.11
1.17
1.17
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

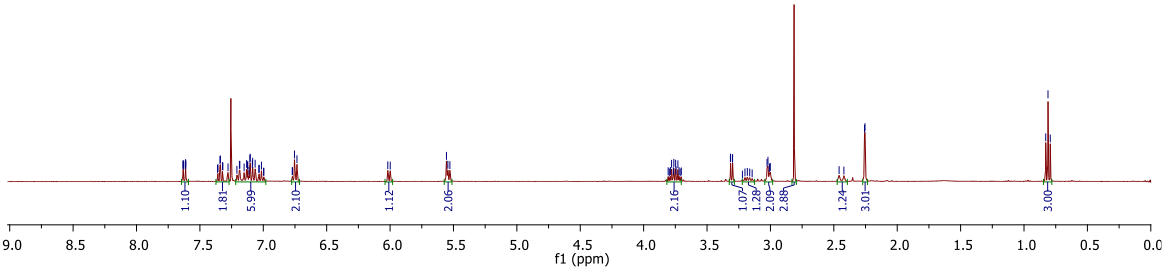

177.37
168.76
145.85
143.79
135.49
134.96
128.81
128.65
128.24
127.35
126.10
125.80
125.37
124.97
124.91
122.23
107.49
67.90
67.87
66.24
61.05
60.37
60.09
43.91
27.08
26.76
26.74
13.44


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


7.63
7.63
7.63
7.62
7.61
7.61
7.61
7.34
7.34
7.11
7.10
6.77
6.75
6.73
6.02
6.00
5.56
5.54
5.53
3.81
3.80
3.79
3.78
3.77
3.76
3.75
3.74
3.73
3.72
3.71
3.70
3.32
3.31
3.30
3.30
3.03
3.02
3.01
2.42
2.26
2.25
0.83
0.81
0.79


F
EtOOC
N
N
O

1d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2.10
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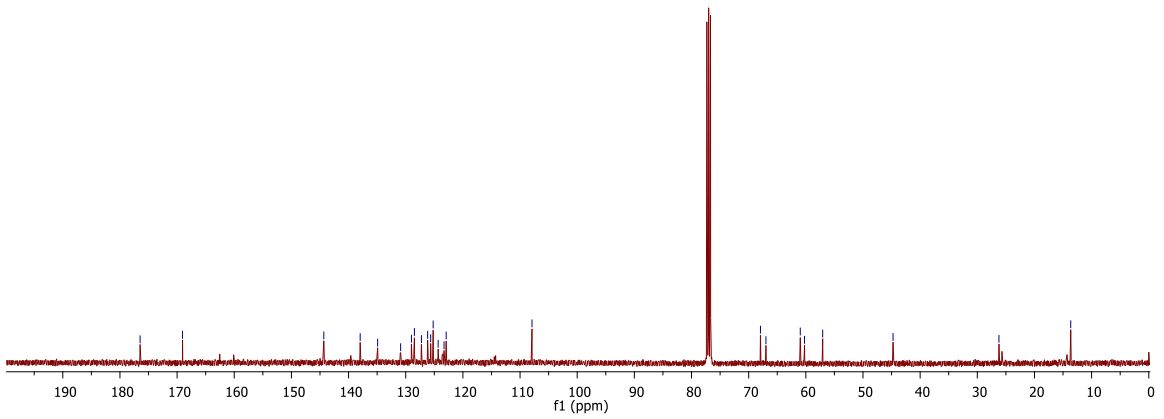
2.06
2.16
1.07
1.28
2.09
2.88
1.24
3.01
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


176.47
169.05
144.33
137.97
134.92
130.89
129.00
128.48
127.25
126.17
125.63
125.20
124.33
123.30
122.93
107.91
67.94
66.98
60.97
60.23
57.05
44.74
26.21
13.65


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


7.50
7.50
7.48
7.48
7.30
7.21
7.20
7.18
7.17
7.15
7.15
7.14
7.13
7.12
7.11
7.04
7.04
7.02
7.02
6.72
6.69
6.69
6.67
6.58
6.56
5.52
5.50
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3.84
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3.82
3.81
3.79
3.78
3.76
3.68
3.66
3.64
3.63
3.63
3.62
3.09
3.06
2.98
2.96
2.94
2.94
2.93
2.47
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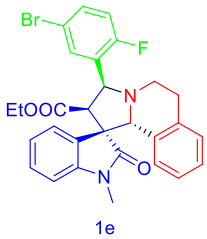
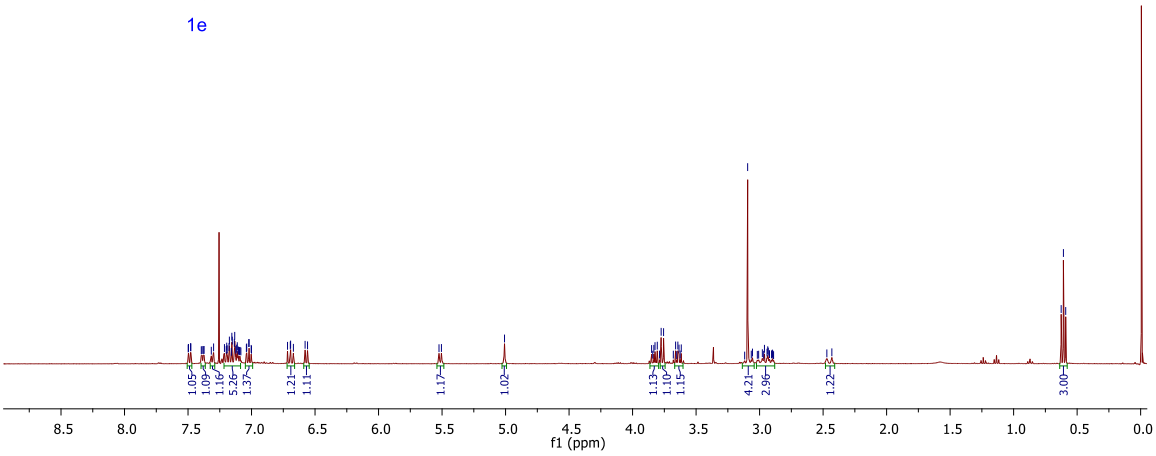
0.61
0.59


Br
F
EtOOC
N
N
O

1e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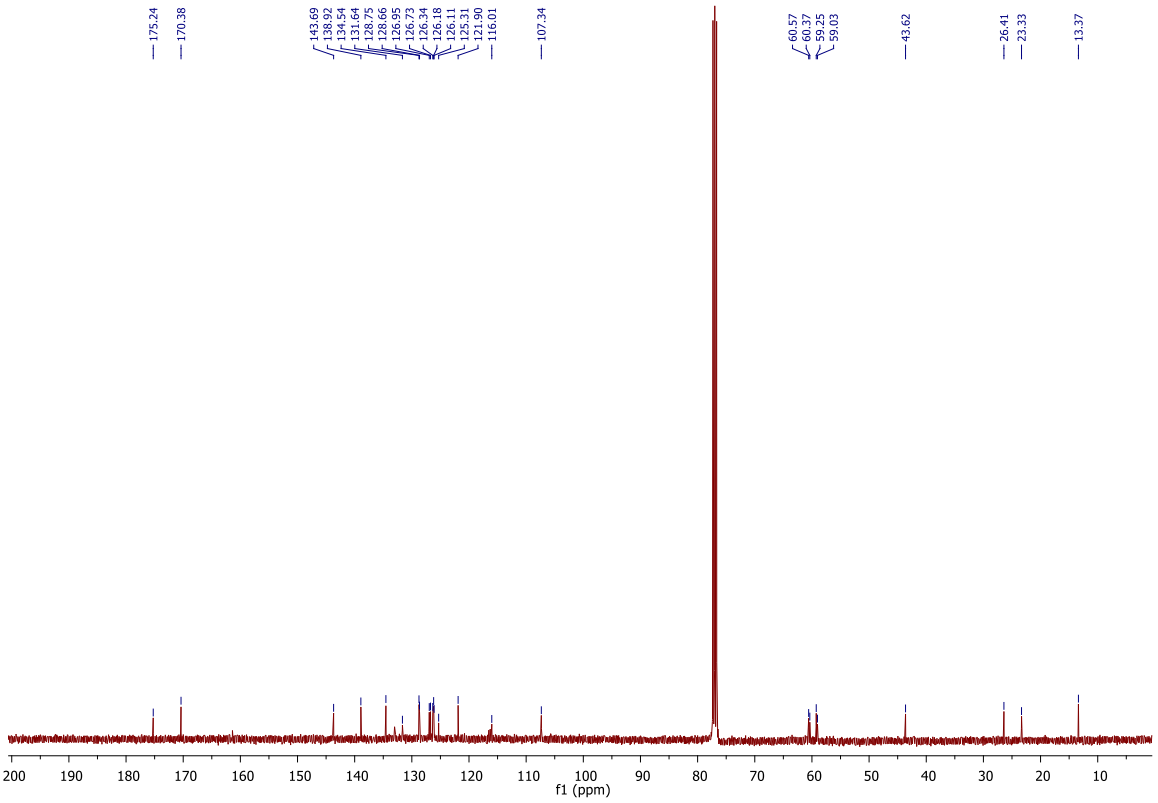
1.09
1.16
5.26
1.37
1.21
1.11
1.17
1.02
1.13
1.19
1.15
4.21
2.96
1.22
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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170.38
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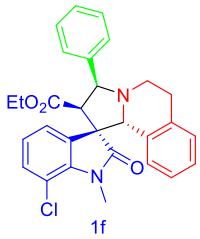
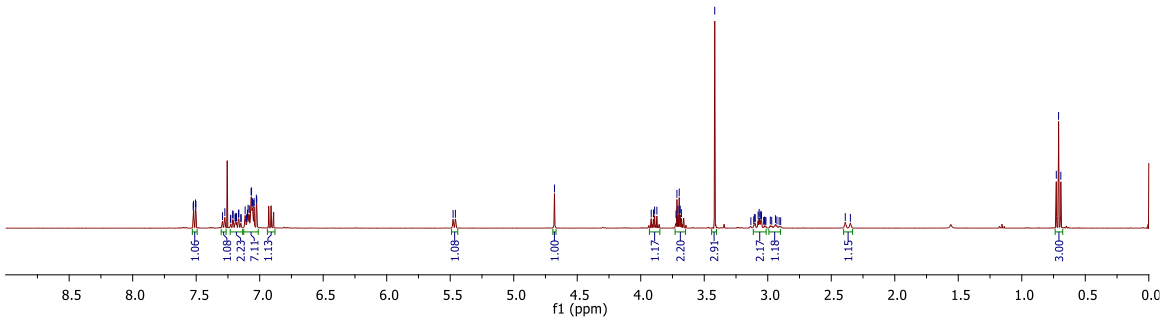
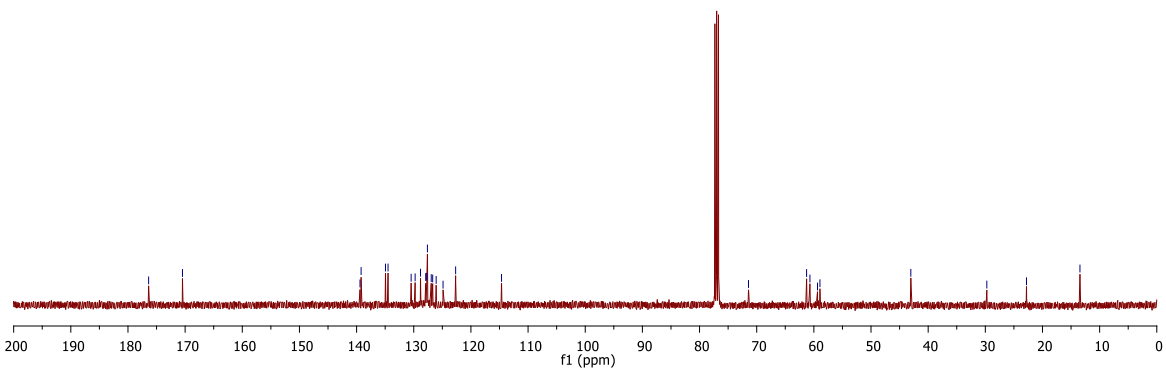
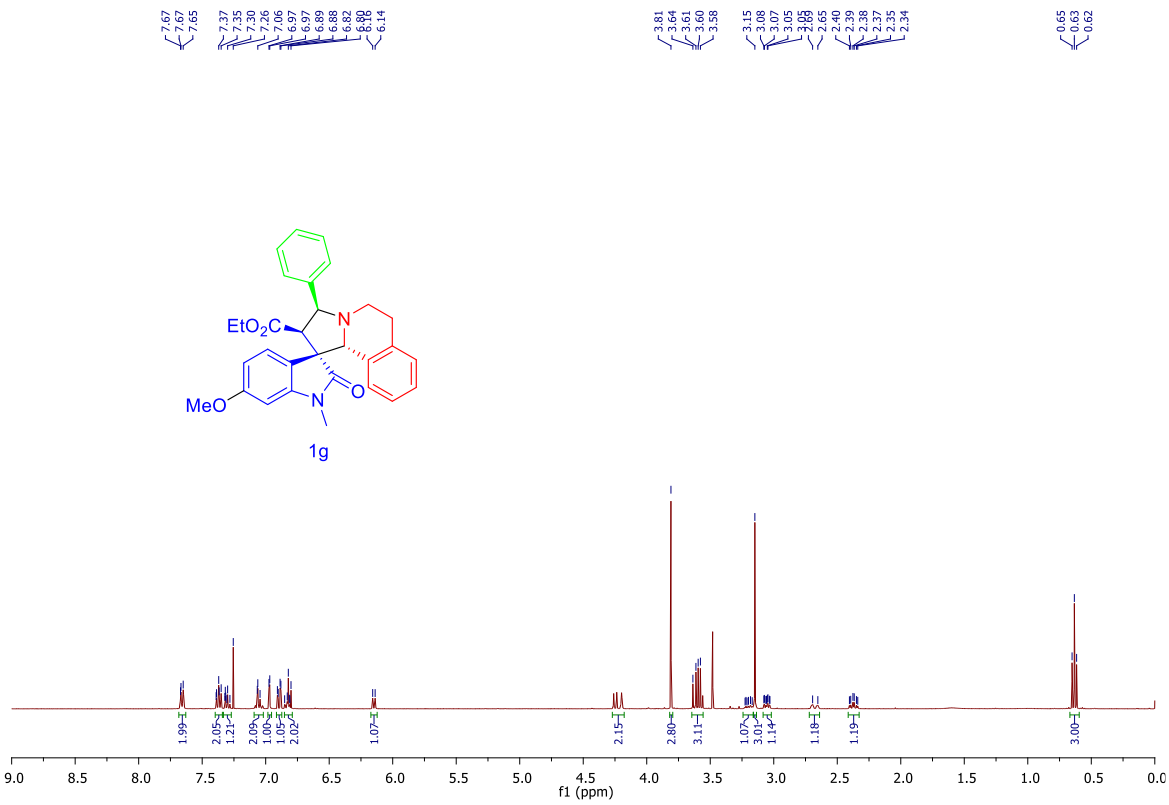
131.64
128.75
128.66
126.95
126.73
126.34
126.18
126.11
125.31
121.90
116.01
107.34
60.57
60.37
59.25
59.03
43.62
26.41
23.33
13.37
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)



1f



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6.97
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6.80
6.14
3.81
3.64
3.61
3.60
3.58
3.15
3.08
3.07
3.05
2.65
2.40
2.39
2.38
2.37
2.35
2.34
0.65
0.63
0.62
EtO2C
N
MeO
N
O
1g
1.99
2.05
1.21
2.09
1.00
1.05
2.02
1.07
2.15
2.80
3.11
1.07
3.01
1.14
1.18
1.19
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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3.5
3.0
2.5
2.0
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1.0
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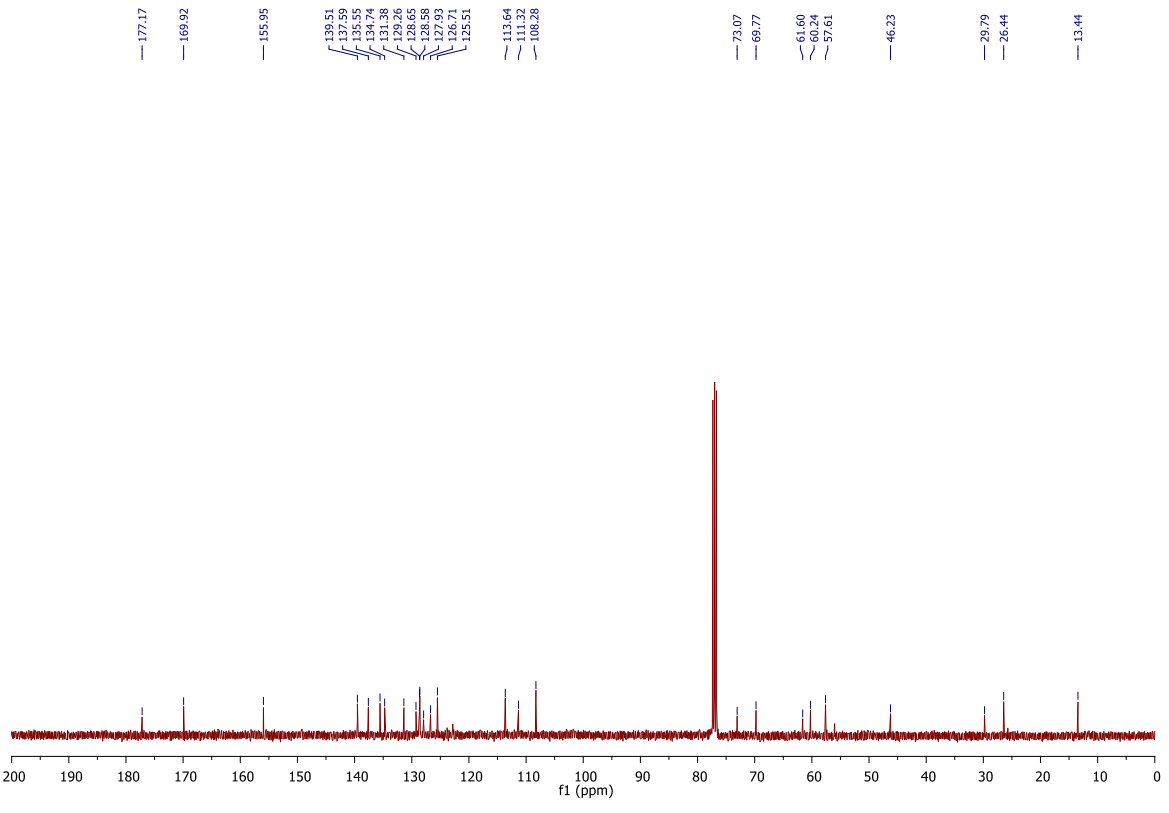
0.0
f1 (ppm)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129.26
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128.58
127.93
126.71
125.51
113.64
111.32
108.28
73.07
69.77
61.60
60.24
57.61
46.23
29.79
26.44
13.44
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.39
7.39
7.39
7.39
7.20
7.21
7.16
7.11
7.09
7.08
7.07
7.06
7.05
7.04
7.03
7.03
7.02
7.02
6.90
6.88
6.88
6.37
6.35
5.51
5.49
4.66
3.86
3.84
3.83
3.81
3.70
3.69
3.68
3.67
3.65
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3.12
3.11
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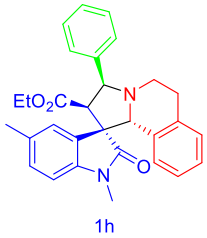
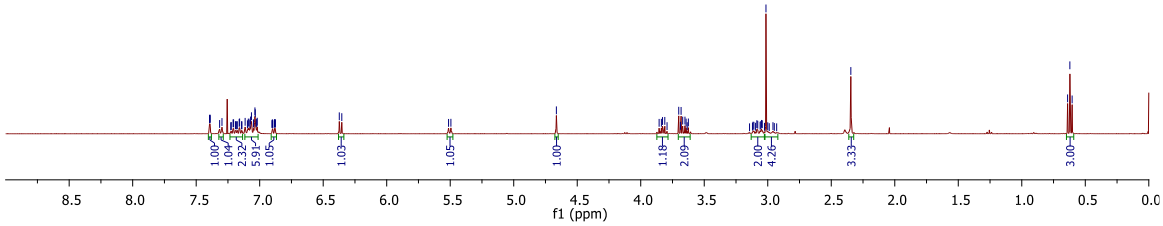
3.08
3.06
3.05
3.05
3.04
3.01
2.35
0.64
0.62
0.60


EtO2C
N
O
N

1h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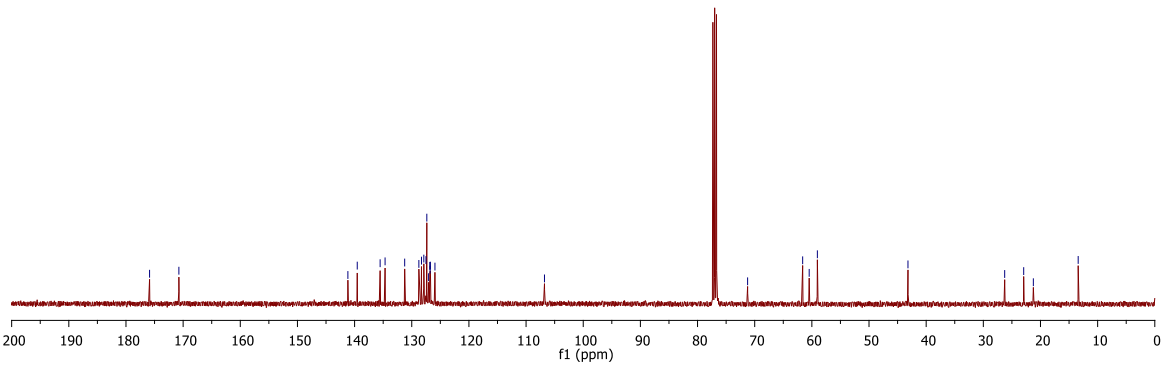
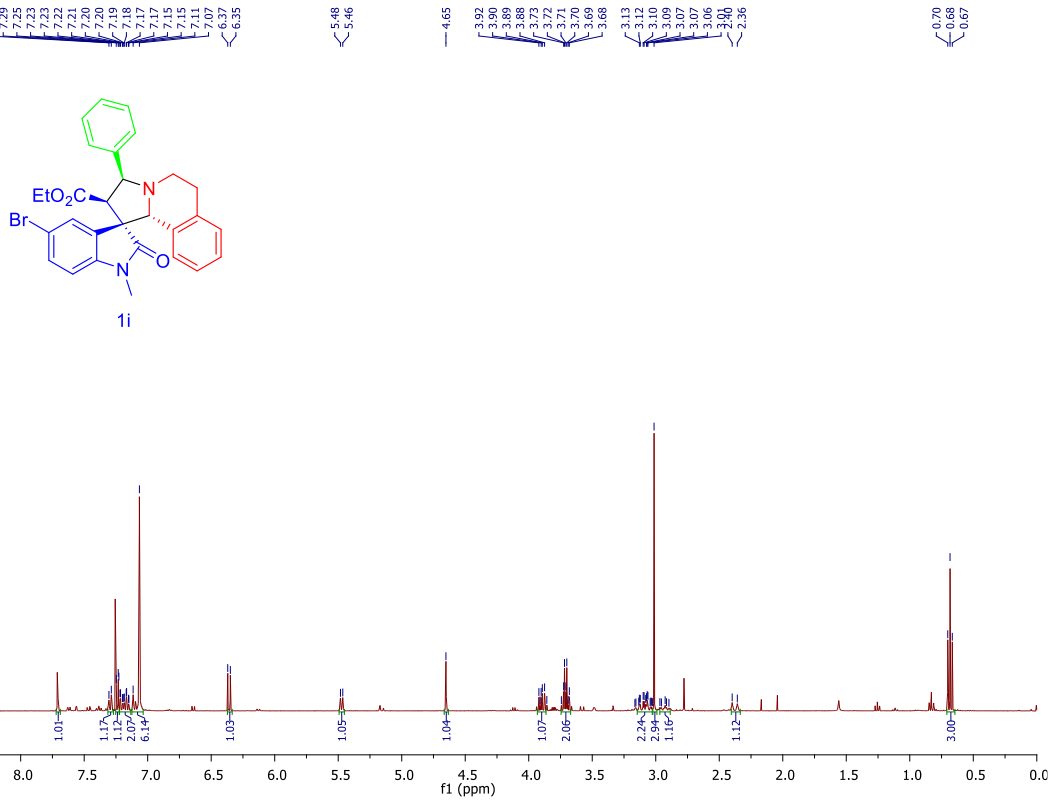
1.03
1.05
1.00
1.18
2.09
2.00
4.26
3.33
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


175.87
170.74
141.18
139.54
135.53
134.67
131.24
128.76
128.30
127.89
127.51
127.36
127.05
126.85
126.79
126.74
125.94
106.78
71.24
61.61
60.47
59.03
43.18
26.26
22.94
21.25
13.40


200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.22
7.21
7.20
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7.19
7.18
7.17
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7.15
7.15
7.11
7.07
6.37
6.35
5.48
5.46
4.65
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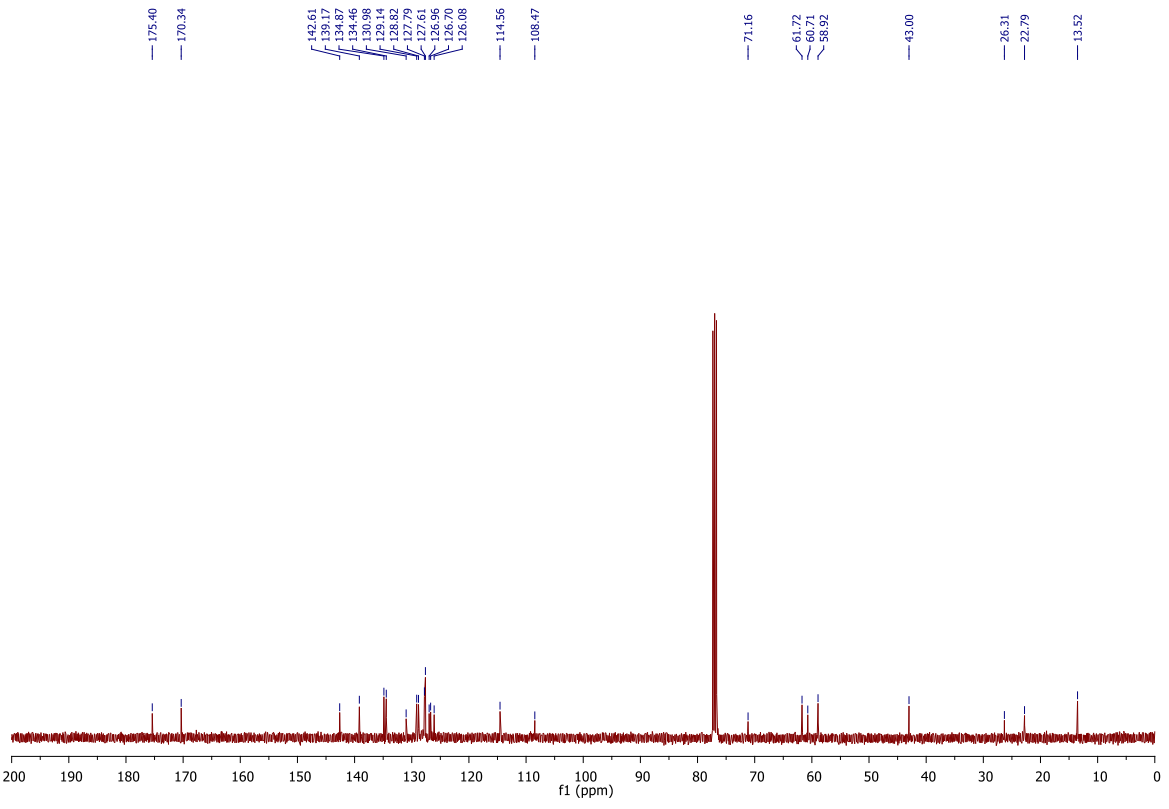
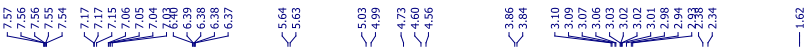
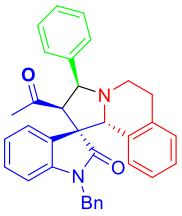
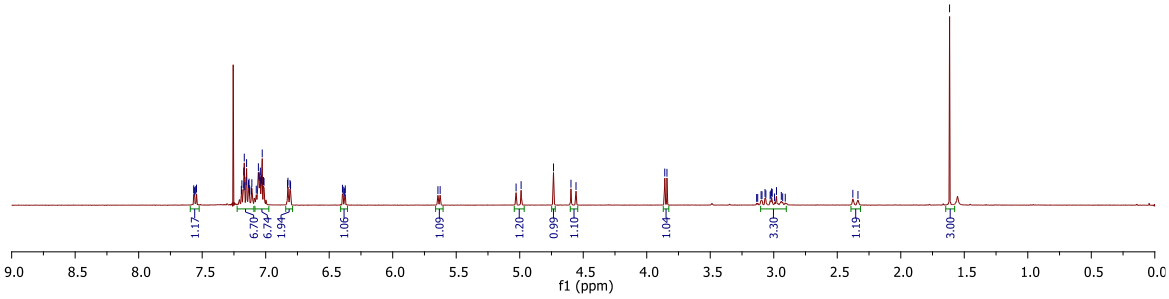
3.90
3.89
3.88
3.73
3.72
3.71
3.70
3.69
3.68
3.13
3.12
3.10
3.09
3.07
3.07
3.06
3.01
2.40
2.36
0.70
0.68
0.67
EtO2C
Br
N
O
N
1i
1.01
1.17
1.12
2.07
6.14
1.03
1.05
1.04
1.07
2.06
2.24
2.94
1.16
1.12
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

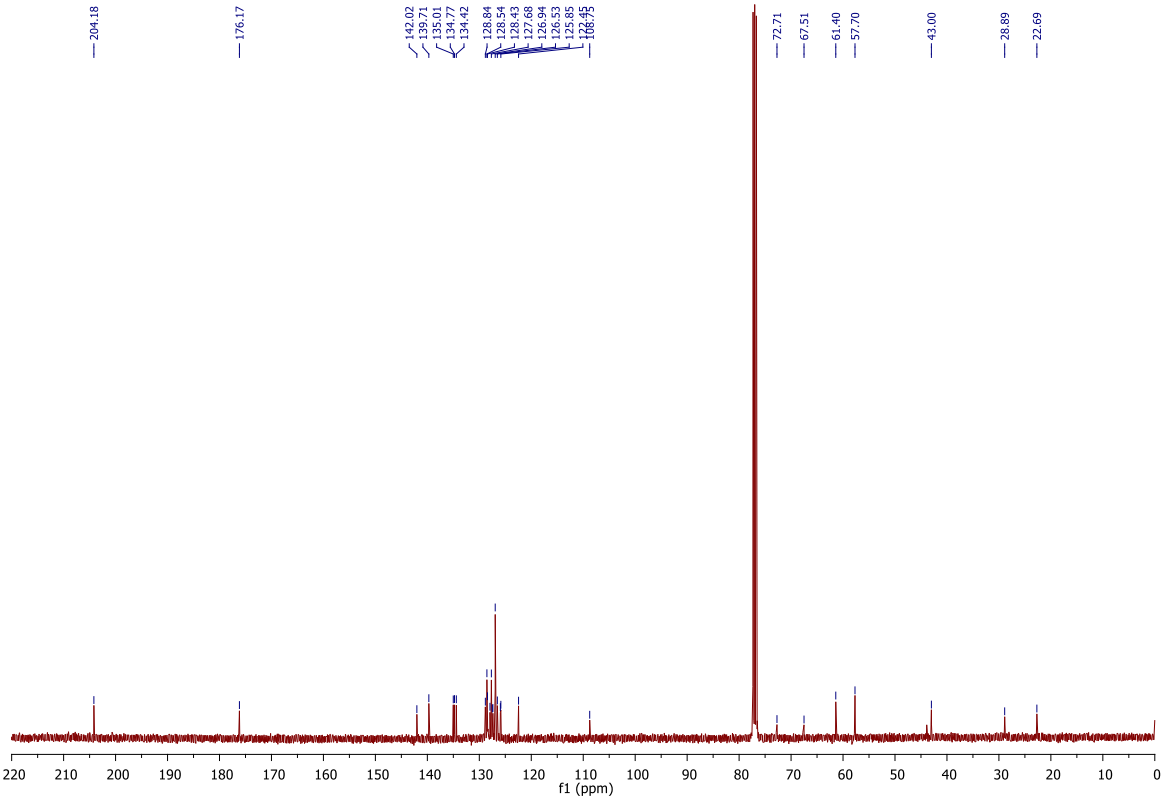

175.40
170.34
142.61
139.17
134.87
134.46
130.98
129.14
128.82
127.79
127.61
126.96
126.70
126.08
114.56
108.47
71.16
61.72
60.71
58.92
43.00
26.31
22.79
13.52
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

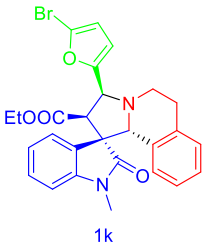

7.57
7.56
7.56
7.55
7.54
7.17
7.17
7.15
7.06
7.05
7.04
6.40
6.39
6.38
6.38
6.37
5.64
5.63
5.03
4.99
4.73
4.60
4.56
3.86
3.84
3.10
3.09
3.07
3.06
3.03
3.02
3.02
3.01
2.98
2.94
2.93
2.38
2.34
1.62


O
N
O
N
Bn

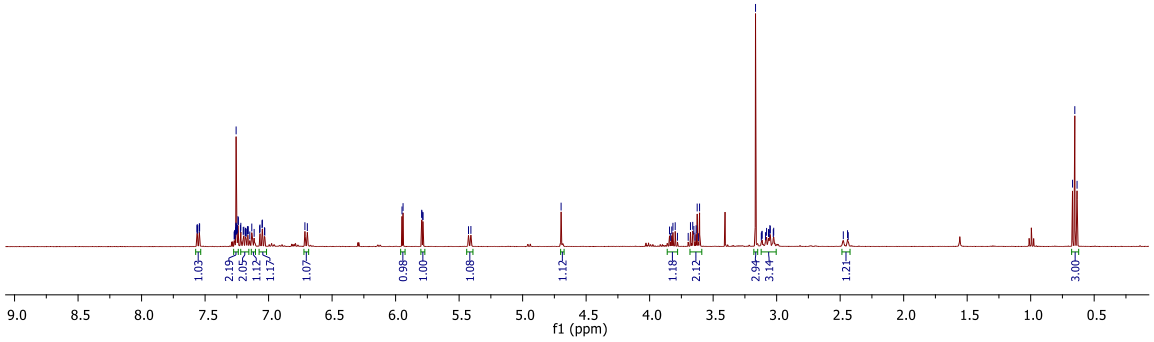
1j

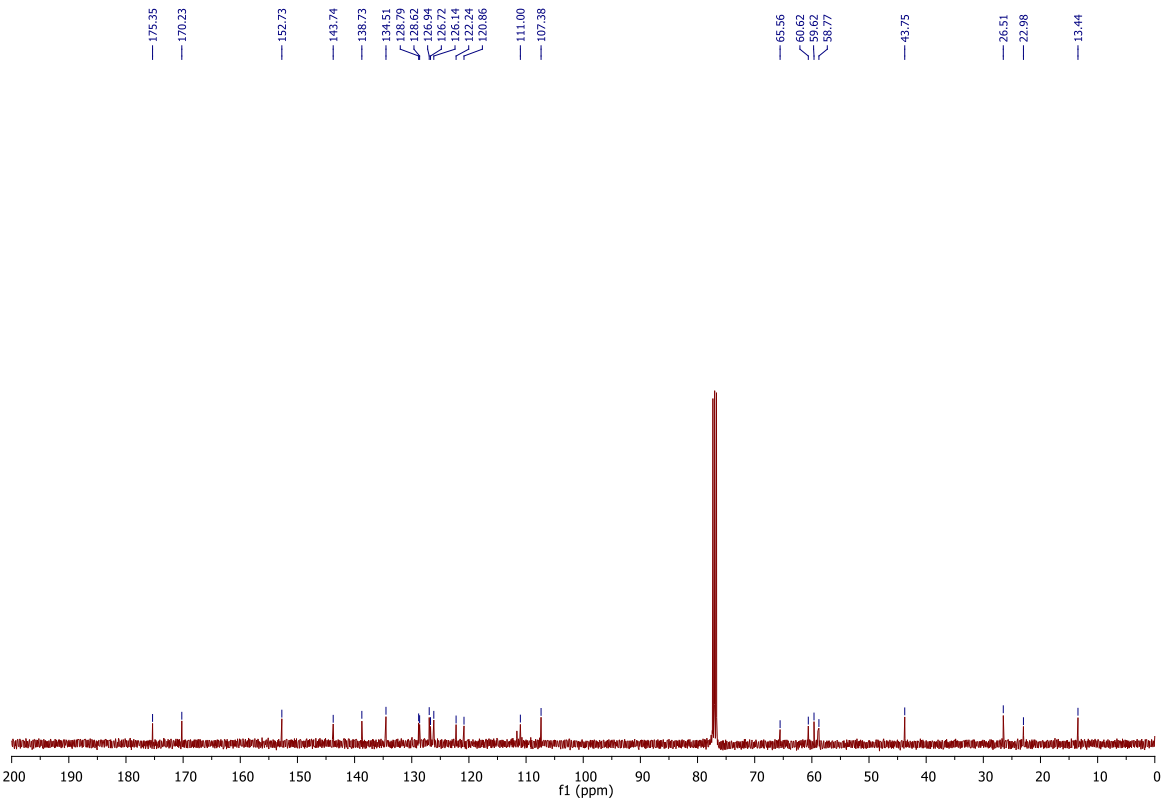

1.17
6.70
6.74
1.94
1.06
1.09
1.20
0.99
1.10
1.04
3.30
1.19
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

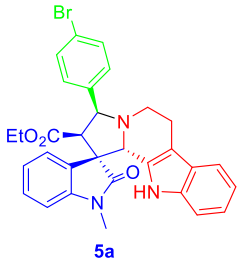

204.18
176.17
142.02
135.71
135.01
134.77
134.42
128.84
128.54
128.43
127.68
126.94
126.53
125.85
72.71
67.51
61.40
57.70
43.00
28.89
22.69
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Br
O
EtOOC
N
O
N

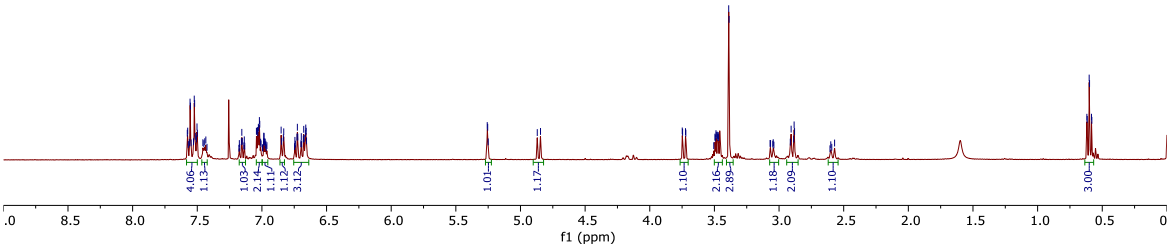
1k

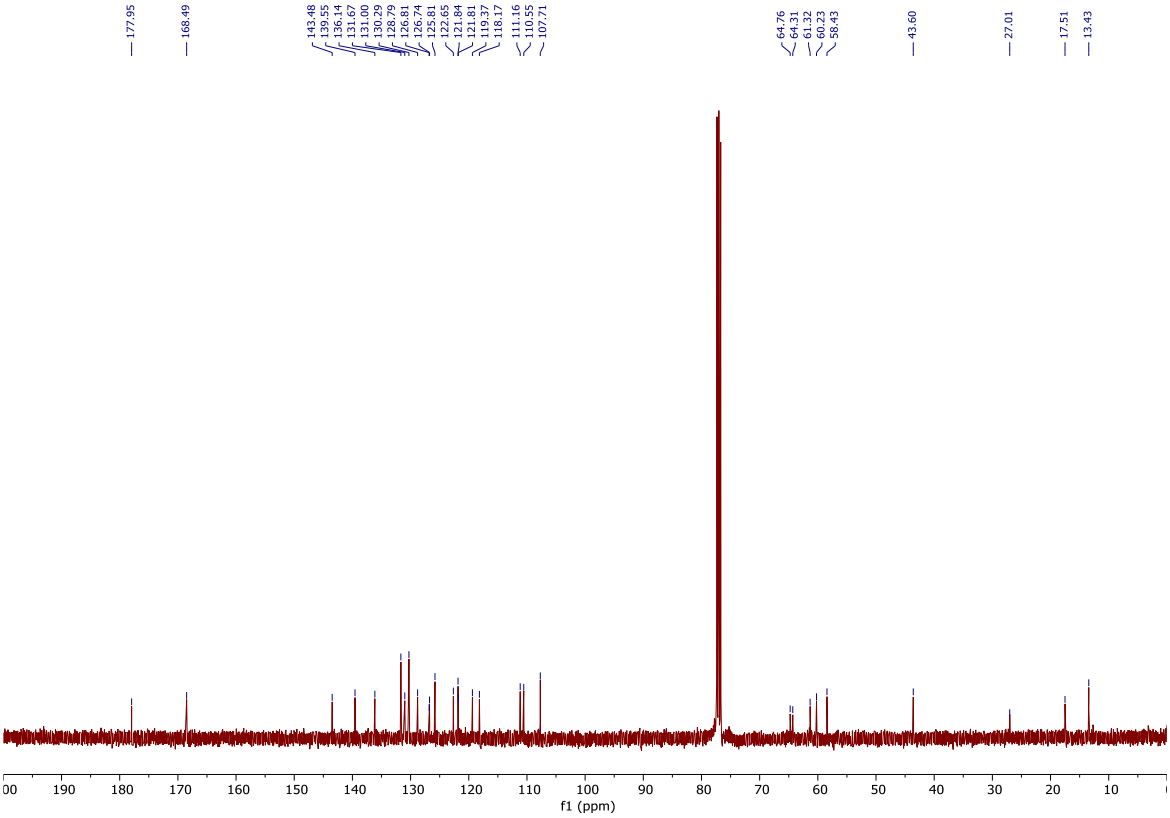

1.03
2.19
2.05
1.12
1.17
1.07
0.98
1.00
1.08
1.12
1.18
2.12
2.94
3.14
1.21
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

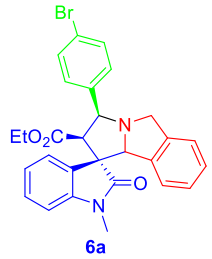

175.35
170.23
152.73
143.74
138.73
134.51
128.79
128.62
126.94
126.72
126.14
122.24
120.86
111.00
107.38
65.56
60.62
59.62
58.77
43.75
26.51
22.98
13.44
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Br
EtO2C
N
O
HN
N

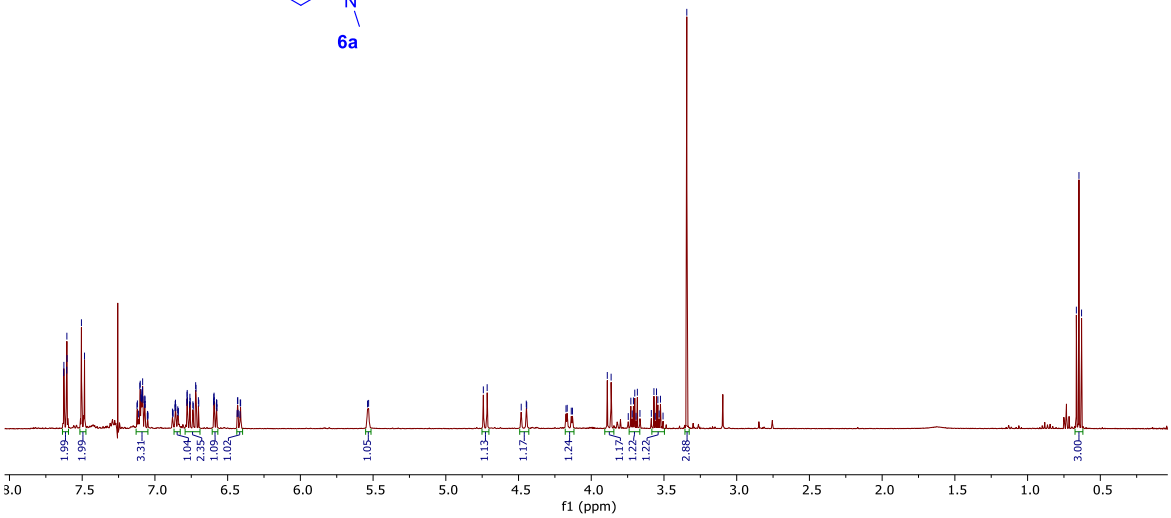
5a


4.06
1.13
1.03
2.14
1.11
1.12
3.12
1.01
1.17
1.10
2.16
2.89
1.18
2.09
1.10
3.00
f1 (ppm)

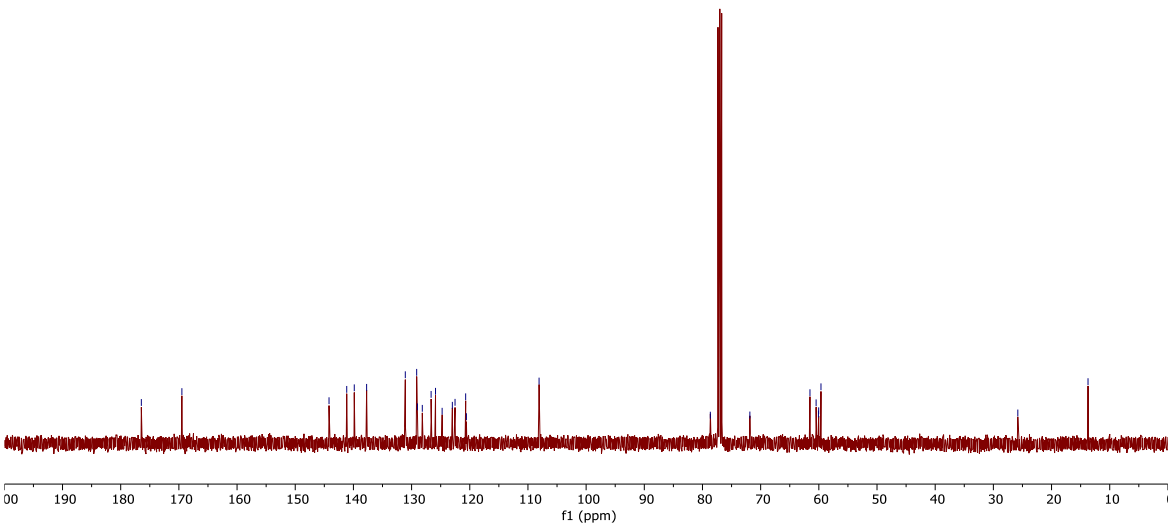

177.95
168.49
143.48
139.55
136.14
131.67
131.00
130.29
128.79
126.81
126.74
125.81
122.65
121.84
121.81
119.37
118.17
111.16
110.55
107.71
64.76
64.31
61.32
60.23
58.43
43.60
27.01
17.51
13.43
f1 (ppm)

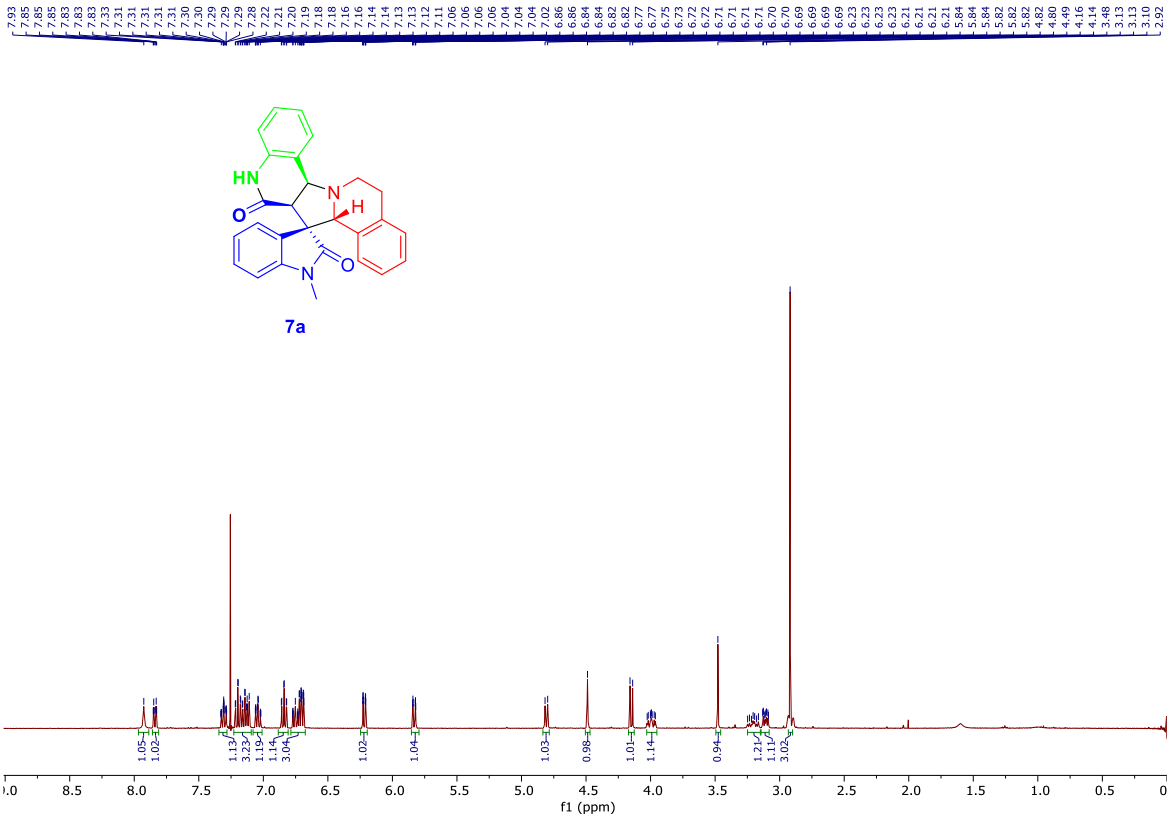

Br
EtO2C
N
O
N

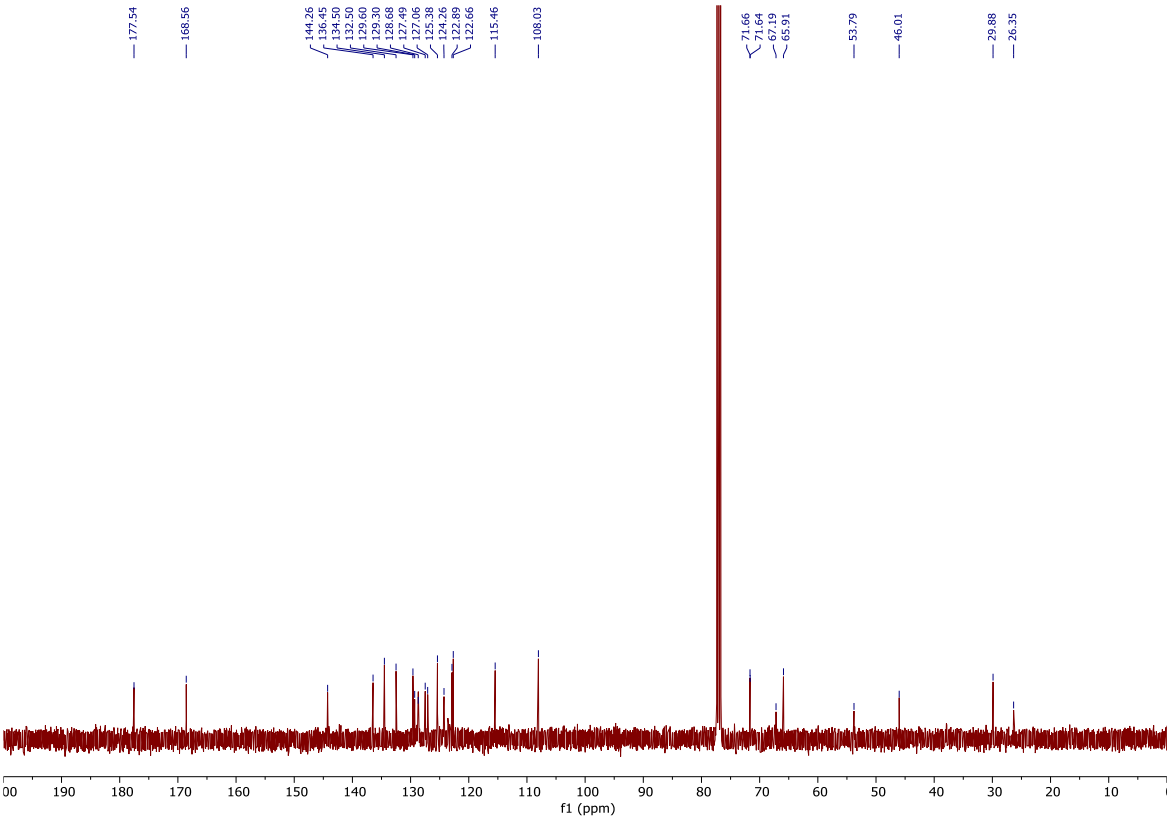
6a


1.99
1.99
3.31
1.04
2.35
1.05
1.02
1.05
1.13
1.17
1.24
1.17
1.22
1.23
2.88
3.00
f1 (ppm)

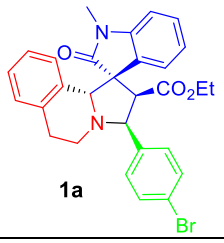

176.45
169.48
144.19
141.15
139.85
137.73
131.08
129.13
129.00
128.16
126.64
125.89
124.75
122.99
122.53
120.71
120.58
108.09
78.65
71.86
61.53
60.47
60.07
60.03
59.63
25.80
13.73


f1 (ppm)

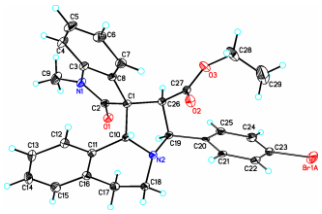

HN
O
N
H
N
O
7a
f1 (ppm)


177.54
168.56
144.26
136.45
134.50
132.50
129.60
129.30
128.68
127.49
127.06
125.38
124.26
122.89
122.66
115.46
108.03
71.66
71.64
67.19
65.91
53.79
46.01
29.88
26.35
f1 (ppm)

5. X-Ray Report of 1a



1a



Cell	a=10.4594 (6)	b=10.8089(8)	c=13.2837(8)
	α=101.462 (5)	β=112.148 (5)	γ=105.775 (6)
Temperature	173K (2)		
	Calculated	Reported	
Volume	1259.83(17)	1259.83(15)	
Space group	P-1	P-1	
Hall group	-P 1	-P 1	
Moiety	C_{29} H_{27}Br N_2 O_3	C_{29} H_{27}Br N_2 O_3	
Sum formula	C_{29} H_{27}Br N_2 O_3	C_{29} H_{27}Br N_2 O_3	
Z	2	2	
μ (mm^{-1})	2.490	2.490	
F000	548.0	548.0	
F000’	548.04		
Nref	4924	4792	
Tmin,Tmax	0.523,0.706	0.683,1.000	
Tmin’	0.474		
CCDC 2098307			
Ellipsoid contour probability		30%	