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[3+2] Annulations between Indoles and α, β-Unsaturated Ketones: Access to Pyrrolo[1,2-a]indoles and Model Reactions Toward the Originally Assigned Structure of Yuremamine

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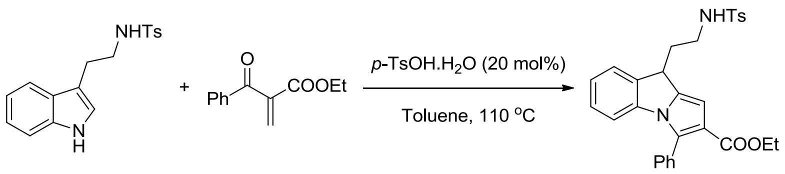
Experimental Procedures

Materials and methods

Unless stated otherwise, reactions were conducted in dry glassware using anhydrous solvents (passed through activated alumina columns) and commercially available reagents were used as received without further purification. Reaction temperatures were controlled using an IKAmag temperature modulator, and unless stated otherwise, reactions were performed at room temperature (rt, approximately 23 ℃). Thin-layer chromatography (TLC) was conducted with plates (GF254) supplied by Yantai Chemicals (China) and visualized using a combination of UV, anisaldehyde, iodine, and potassium permanganate staining. Silica gel (200-300 mesh) supplied by Tsingtao Haiyang Chemicals (China) was used for flash column chromatography. ^{1}H NMR spectra were recorded on Bruker spectrometers (at 400 MHz) and are reported relative to residual solvent signals. Data for ^{1}H NMR spectra are reported as follows: chemical shift (δ ppm), multiplicity, coupling constant (Hz) and integration. Data for ^{13}C NMR spectra are reported in terms of chemical shift. High resolution mass spectra were obtained from the Tsinghua University Mass Spectrometry Facilities.

Experimental Procedures

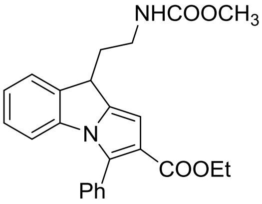
A. General procedure for the [3+2] annulations between indoles and α, β-unsaturated ketones



3a **4a** **5a**

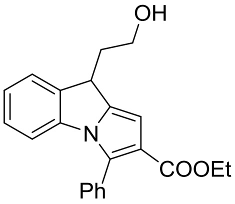
To a solution of **3a** (62.8 mg, 0.2 mmol) and **4a** (49.0 mg, 0.24 mmol) in toluene (1.0 mL) in a sealed tube at room temperature was added *p*-toluenesulfonic acid monohydrate (7.6 mg, 0.04 mmol). The resulting mixture was stirred at 110 ^{o}C for 2 h and then cooled to room temperature. The reaction was concentrated under reduced pressure to afford the crude residue, which was purified directly. Purification by silica gel chromatography (ethyl acetate/petroleum ether = 1:5) afforded the desired product **5a** (87.1 mg, 87% yield) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): 7.78 (d, *J* =

8.4 Hz, 2H), 7.469 (s, 5H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 7.2 Hz, 1H), 7.06 (t, *J* = 7.2 Hz, 1H), 7.01 (t, *J* = 7.2 Hz, 1H), 7.55 (d, *J* = 1.2 Hz, 1H), 7.48 (d, *J* = 7.6 Hz, 1H), 5.12 (d, *J* = 2.8 Hz, 1H), 4.15-4.06 (m, 3H), 3.24-3.10 (m, 2H), 2.43 (s, 3H), 2.27-2.18 (m, 1H), 1.87-1.78 (m, 1H), 1.13 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 164.8, 143.6, 140.0, 138.9, 137.9, 136.8, 131.5, 131.4, 130.7, 129.8, 128.8, 128.0, 127.7, 127.2, 125.1, 124.6, 117.7, 112.4, 104.2, 59.6, 40.6, 37.5, 33.8, 21.6, 14.1; HRMS-ESI (*m*/*z*) $[M+H]^+$ calcd for $C_{29}H_{29}N_2O_4S$, 501.1848; found, 501.1835.



5b

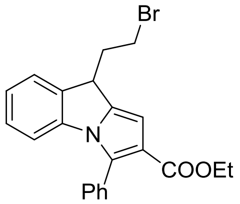
Purification by silica gel chromatography (dichloromethane/ethyl acetate = 50:1) afforded the above compound **5b** (65.4 mg, 81% yield) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): 7.51 (s, 1H), 7.48 (s, 4H), 7.38 (d, *J* = 7.4 Hz, 2H), 7.08 (t, *J* = 7.2 Hz, 1H), 7.02 (t, *J* = 7.6 Hz, 1H), 6.70 (s, 1H), 6.52 (d, *J* = 7.6 Hz, 1H), 5.04 (s, 1H), 4.13 (q, *J* = 7.1 Hz, 2H), 4.09-4.03 (m, 1H), 3.66 (s, 3H), 3.45-3.35 (m, 2H), 2.29-2.24 (m, 1H), 1.92-1.86 (m, 1H), 1.15 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 164.8, 157.2, 140.0, 139.2, 138.3, 131.6, 131.4, 130.7, 128.8, 127.6, 125.1, 124.6, 117.8, 112.4, 104.2, 59.6, 52.1, 38.6, 37.9, 34.0, 14.2; HRMS-ESI (*m*/*z*) $[M+H]^+$ calcd for $C_{24}H_{25}N_2O_4$, 405.1814; found, 405.1796.



5c

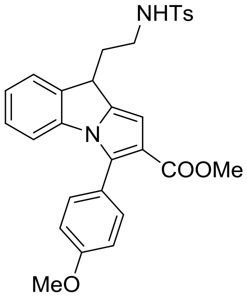
Purification by silica gel chromatography (dichloromethane/ethyl acetate = 25:1) afforded the above compound **5c** (37.2 mg, 54% yield) as a light yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): 7.54-7.48 (m, 5H), 7.41 (d, *J* = 7.2 Hz, 1H), 7.10 (t, *J* = 7.6

Hz, 1H), 7.03 (t, *J* = 8.0 Hz, 1H), 6.68 (s, 1H), 6.53 (d, *J* = 7.6 Hz, 1H), 4.21 (dd, *J* = 4.8, 9.2 Hz, 2H), 4.13 (q, *J* = 7.1 Hz, 2H), 4.01-3.90 (m, 2H), 2.37-2.29 (m, 1H), 1.94-1.86 (m, 1H), 1.13 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 165.0, 140.0, 139.8, 138.7, 131.6, 131.3, 130.7, 128.7, 127.5, 125.1, 124.5, 117.7, 112.4, 104.1, 60.2, 59.6, 37.1, 36.6, 14.1; HRMS-ESI (*m*/*z*) $[M+H]^+$ calcd for $C_{22}H_{22}NO_3$, 348.16; found, 348.1588.



5d

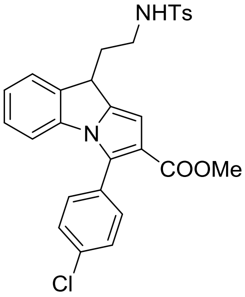
Purification by silica gel chromatography (dichloromethane/petroleum ether = 1:2) afforded the above compound **5d** (65.6 mg, 80% yield) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): 7.55-7.50 (m, 5H), 7.39 (d, *J* = 7.6 Hz, 1H), 7.12 (t, *J* = 7.6 Hz, 1H), 7.05 (t, *J* = 7.6 Hz, 1H), 6.72 (s, 1H), 6.55 (d, *J* = 8.0 Hz, 1H), 4.27 (dd, *J* = 4.8, 9.2 Hz, 1H), 4.16 (q, *J* = 7.1 Hz, 2H), 3.72-3.60 (m, 2H), 2.59-2.51 (m, 1H), 2.22-2.13 (m, 1H), 1.16 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 164.7, 140.1, 138.7, 137.3, 131.6, 131.3, 130.7, 130.7, 128.8, 128.1, 127.8, 125.1, 117.9, 112.1, 104.4, 59.6, 39.0, 36.8, 30.4, 14.2; HRMS-ESI (*m*/*z*) $[M+H]^+$ calcd for $C_{22}H_{21}NO_2Br$, 410.0756; found, 410.0748.



5e

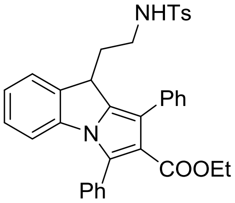
Purification by silica gel chromatography (ethyl acetate/petroleum ether =1:5) afforded the above compound **5e** (61.3 mg, 59% yield) as a light yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): 7.77 (d, *J* = 8.0 Hz, 2H), 7.40 (d, *J* = 7.6 Hz, 2H), 7.32 (d, *J*

= 8.0 Hz, 2H), 7.28 (d, *J* = 6.8 Hz, 1H), 7.09-7.00 (m, 4H), 6.57 (t, *J* = 7.2 Hz, 1H), 6.50 (d, *J* = 1.2 Hz, 1H), 4.83 (t, *J* = 2.0 Hz, 1H), 4.07 (dd, *J* = 4.4, 8.4 Hz, 1H), 3.90 (s, 3H), 3.69 (s, 3H), 3.23-3.09 (m, 2H), 2.43 (s, 3H), 2.26-2.18 (m, 1H), 1.88-1.79 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): 165.2, 160.0, 143.6, 140.0, 138.8, 137.6, 136.8, 131.9, 131.7, 129.8, 127.7, 127.1, 125.0, 124.6, 123.2, 117.1, 113.6, 112.5, 104.1, 55.3, 50.9, 40.6, 37.5, 33.8, 21.6; HRMS-ESI (*m*/*z*) $[M+H]^+$ calcd for $C_{29}H_{29}N_2O_5S$, 517.1797; found, 517.1777.



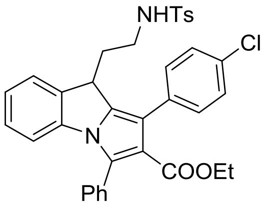
5f

Purification by silica gel chromatography (ethyl acetate/petroleum ether = 1:5) afforded the above compound **5f** (64.4 mg, 62% yield) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): 7.77 (d, *J* = 8.0 Hz, 2H), 7.47-7.42 (m, 4H), 7.33-7.29 (m, 3H), 7.12-7.04 (m, 2H), 6.55 (d, *J* = 8.0 Hz, 1H), 6.53 (s, 1H), 4.79 (t, *J* = 6.0 Hz, 1H), 4.09 (dd, *J* = 4.4, 4.4 Hz, 1H), 3.69 (s, 3H), 3.23-3.09 (m, 2H), 2.44 (s, 3H), 2.27-2.17 (m, 1H), 1.89-1.79 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): 164.9, 143.7, 139.8, 138.8, 138.2, 136.7, 135.0, 132.1, 130.2, 129.9, 129.6, 128.4, 127.8, 127.2, 125.2, 124.8, 117.6, 112.3, 104.3, 51.0, 40.6, 37.5, 33.8, 21.6; HRMS-ESI (*m*/*z*) $[M+H]^+$ calcd for $C_{28}H_{26}N_2O_4SCl$, 521.1302; found, 521.1279.



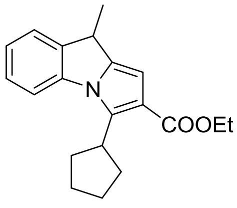
5g

Purification by silica gel chromatography (ethyl acetate/petroleum ether = 1:5) afforded the above compound **5g** (84.3 mg, 73% yield) as a light yellow solid. ^{1}H NMR (400 MHz, CDCl$_3$): 7.66-7.20 (m, 15H), 7.13-6.99 (m, 2H), 6.48 (d, J = 7.6 Hz, 1H), 4.38 (t, J = 6.0 Hz, 1H), 3.04-3.86 (m, 3H), 2.73-2.63 (m, 1H), 2.59-2.49 (m, 1H), 2.42 (s, 3H), 1.99-1.89 (m, 1H), 1.85-1.75 (m, 1H), 0.84 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, CDCl$_3$): 164.7, 143.3, 139.9, 138.5, 136.8, 235.6, 135.0, 131.72, 131.68, 130.7, 129.6, 129.5, 128.8, 128.12, 128.07, 127.9, 127.0, 126.9, 125.2, 124.7, 120.0, 116.5, 112.6, 59.5, 40.2, 37.7, 32.6, 21.5, 13.6; HRMS-ESI (*m*/*z*) [M+H]$^+$ calcd for $C_{35}H_{33}N_2O_4S$, 577.2161; found, 577.2159.



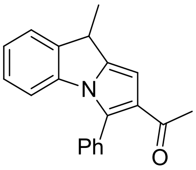
5h

Purification by silica gel chromatography (ethyl acetate/petroleum ether = 1:5) afforded the above compound **5h** (77.0 mg, 63% yield) as a light yellow solid. ^{1}H NMR (400 MHz, CDCl$_3$): 7.63-7.41 (m, 7H), 7.39-7.24 (m, 7H), 7.10 (t, J = 7.4 Hz, 1H), 7.05 (t, J = 7.6 Hz, 1H), 6.46 (d, J = 7.8 Hz, 1H), 4.37 (t, J = 5.6 Hz, 1H), 4.08 (t, J = 6.2 Hz, 1H), 4.10-3.86 (m, 2H), 2.72-2.62 (m, 1H), 2.62-2.46 (m, 1H), 2.43 (s, 3H), 1.96-1.81 (m, 2H), 0.86 (t, J = 7.1 Hz); ^{13}C NMR (100 MHz, CDCl$_3$): 164.6, 143.4, 139.8, 138.2, 136.7, 135.6, 133.4, 132.7, 131.9, 131.6, 130.8, 129.7, 128.9, 128.2, 128.1, 128.0, 127.0, 125.2, 124.9, 118.8, 116.3, 112.6, 59.6, 40.1, 37.8, 32.2, 21.5, 13.6; HRMS-ESI (*m*/*z*)) [M+H]$^+$ calcd for $C_{35}H_{32}N_2O_4SCl$, 611.1771; found, 611.1759.



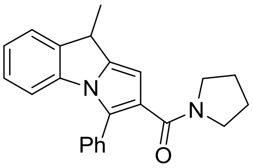
5i

Purification by silica gel chromatography (ethyl acetate/petroleum ether = 1:20) afforded the above compound **5i** (44.5 mg, 72% yield) as a brown oil. ^{1}H NMR (400 MHz, $CDCl_3$): 7.49 (d, 1H, *J* = 8.0 Hz), 7.39 (d, *J* = 7.2 Hz, 1H), 7.33 (t, *J* = 7.6 Hz, 1H), 7.18 (t, *J* = 7.6 Hz, 1H), 6.51 (d, *J* = 1.6 Hz, 1H), 4.29 (q, *J* = 7.2 Hz, 2H), 3.96 (q, *J* = 14.4 Hz, 1H), 2.17-2.03 (m, 7H), 2.02-1.81 (m, 2H), 1.50 (d, *J* = 7.2 Hz, 3H), 1.38 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 165.6, 141.7, 140.7, 140.5, 137.2, 127.4, 125.0, 124.1, 116.2, 113.5, 102.9, 59.5, 36.8, 34.6, 30.9, 26.2, 26.2, 19.4, 14.6; HRMS-ESI (*m*/*z*) [M+H] $^+$ calcd for $C_{20}H_{24}NO_2$, 310.1807; found, 310.1799.



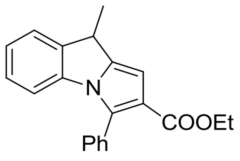
5j

Purification by silica gel chromatography (dichloromethane/petroleum ether = 1: 1) afforded the above compound **5j** (41.8 mg, 72% yield) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): 7.84 (d, *J* = 6.9 Hz, 2H), 7.41-7.20 (m, 5H), 7.32 (t, *J* = 8.0 Hz, 1H), 7.21 (t, *J* = 7.2 Hz, 1H), 6.28 (s, 1H), 4.01 (q, *J* = 7.2 Hz, 1H), 2.91 (s, 3H), 1.49 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 192.8, 141.6, 140.8, 140.1, 139.7, 131.1, 129.9, 129.2, 128.0, 127.8, 125.1, 124.6, 124.5, 112.3, 104.5, 35.0, 19.4, 12.7; HRMS-ESI (*m*/*z*) [M+H]$^+$ calcd for $C_{20}H_{18}NO$, 288.1388; found, 288.1381.



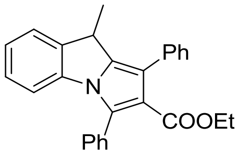
5k

Purification by silica gel chromatography (dichloromethane/ethyl acetate = 4:1) afforded the above compound **5k** (55.0 mg, 73% yield) as a light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): 7.54 (d, *J* = 6.8 Hz, 2H), 7.50-7.30 (m, 4H), 7.15-7.02 (m, 2H), 6.94 (t, *J* = 4.8 Hz, 1H), 6.32 (s, 1H), 4.04 (q, *J* = 6.8 Hz, 1H), 3.60-3.40 (m, 2H), 3.15-3.00 (m, 1H), 3.00-2.85 (m, 1H), 1.83-1.55 (m, 4H), 1.54 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 166.7, 142.2, 141.2, 140.5, 131.7, 129.9, 128.4, 128.1, 127.2, 125.6, 124.7, 123.8, 123.7, 111.9, 101.6, 48.2, 45.6, 35.1, 25.9, 24.3, 19.1; HRMS-ESI (*m*/*z*) $[M+H]^+$ calcd for $C_{23}H_{23}N_2O$, 343.181; found, 343.1801.



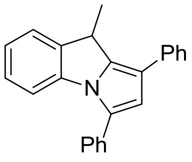
5l

Purification by silica gel chromatography (ethyl acetate/petroleum ether = 1:20) afforded the above compound **5l** (54.2 mg, 85% yield) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): 7.60-7.47 (m, 5H), 7.38 (d, *J* = 7.8 Hz, 1H), 7.11 (t, *J* = 7.2 Hz, 1H), 7.03 (t, *J* = 8.0 Hz, 1H), 6.67 (d, *J* = 1.2 Hz, 1H), 6.56 (d, *J* = 8.0 Hz, 1H), 4.16 (q, *J* = 7.1 Hz, 2H), 4.08 (q, *J* = 7.2 Hz, 1H), 1.57 (d, *J* = 7.2 Hz, 3H), 1.17 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 164.9, 141.3, 141.0, 139.9, 131.7, 131.1, 130.8, 128.7, 128.0, 127.4, 124.8, 124.4, 117.7, 112.3, 102.9, 59.5, 35.0, 19.2, 14.2; HRMS-ESI (*m*/*z*) $[M+H]^+$ calcd for $C_{21}H_{20}NO_2$, 318.1494; found, 318.1486.



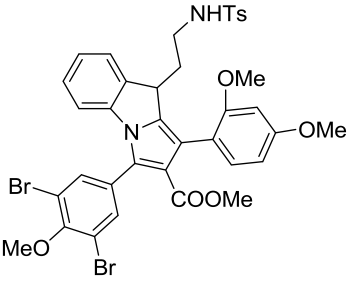
5m

Purification by silica gel chromatography (dichloromethane/petroleum ether = 1:3) afforded the above compound **5m** (69.7 mg, 89% yield) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): 7.66-7.44(m, 7H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.36 (t, *J* = 7.2 Hz, 2H), 7.12 (t, *J* = 7.2 Hz, 1H), 7.05 (t, *J* = 7.6 Hz, 1H), 6.56 (d, *J* = 8.0 Hz, 1H), 4.31 (q, *J* = 6.8 Hz, 1H), 4.09-3.91 (m, 2H), 1.37 (d, *J* = 7.2 Hz, 3H), 0.90 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 165.0, 141.2, 139.7, 138.3, 134.9, 132.0, 131.1, 130.9, 129.6, 128.7, 128.1, 127.8, 127.4, 126.5, 124.8, 124.5, 119.5, 116.5, 112.4, 59.5, 35.5, 17.8, 13.7; HRMS-ESI (*m*/*z*) $[M+H]^+$ calcd for $C_{27}H_{24}NO_2$, 394.1807; found, 394.1796.



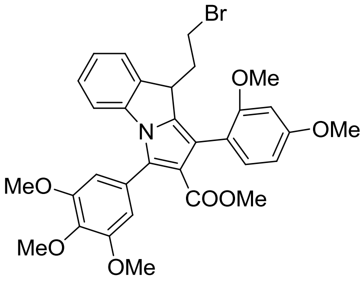
5n

Purification by silica gel chromatography (ethyl acetate/petroleum ether = 1:20) afforded the above compound **5n** (49.4 mg, 90% yield) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): 7.73-7.64(m, 4H), 7.60-7.40 (m, 6H), 7.29 (t, *J* = 7.6 Hz, 1H), 7.25-7.05 (m, 3H), 6.66 (s, 1H), 4.52 (q, *J* = 7.2 Hz, 1H), 1.61 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 141.2, 140.4, 138.7, 135.5, 132.9, 129.1, 128.7, 128.7, 128.4, 127.6, 127.3, 126.1, 125.6, 124.7, 123.4, 118.3, 112.9, 111.9, 36.2, 17.3; HRMS-ESI (*m*/*z*) $[M+H]^+$ calcd for $C_{24}H_{20}N$, 322.1596; found, 322.1587.



5o

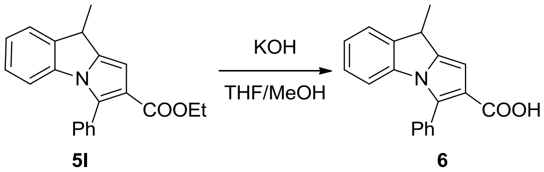
Purification by silica gel chromatography (dichloromethane/ethyl acetate =20:1) afforded the above compound **5o** (92.1 mg, 57% yield) as a light yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): 7.85 (s, 1H), 7.63 (s, 1H), 7.51 (d, *J* = 7.6 Hz, 2H), 7.45-7.05 (m, 7H), 6.65-6.45 (m, 3H), 4.27 (t, *J* = 5.6 Hz, 2H), 4.01 (t, *J* = 5.6 Hz, 1H), 4.01 (s, 3H), 3.89 (s, 3H), 3.76 (s, 3H), 3.49 (s, 3H), 2.85-2.65 (m, 1H), 2.60-2.45 (m, 1H), 2.40 (s, 3H), 2.05-1.90 (m, 1H), 1.85-1.70 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): 165.0, 160.5, 158.1, 154.4, 143.2, 139.8, 137.0, 137.0, 134.8, 131.1, 130.1, 129.6, 127.9, 127.4, 126.9, 125.2, 124.8, 118.0, 117.5, 116.1, 115.7, 112.2, 104.3, 98.9, 60.9, 55.6, 55.4, 50.8, 40.1, 37.9, 32.3, 21.5; HRMS-ESI (*m*/*z*) $[M+H]^+$ calcd for $C_{37}H_{35}N_2O_7SBr_2$, 809.0532; found, 809.0516.



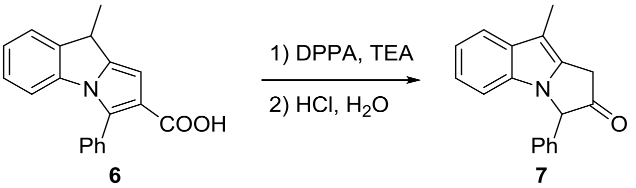
5p

Camphorsulfonic acid (20 mol%) was used as the catalyst. Purification by silica gel chromatography (petroleum ether/ethyl acetate = 8:1) afforded the above compound **5p** (52.4 mg, 42% yield) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): 7.41-7.36 (m, 1H), 7.29-7.24 (m, 1H), 7.15-7.05 (m, 2H), 7.92 (s, 1H), 7.68 (s, 1H), 6.64-6.50 (m, 3H), 4.38 (t, *J* = 5.6 Hz, 1H), 3.97 (s, 3H), 3.91 (s, 3H), 3.88 (s, 3H), 3.83 (s, 3H), 3.81 (s, 3H), 3.50 (s, 3H), 3.11 (t, *J* = 7.6 Hz, 2H), 2.35-2.15 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): 165.5, 160.2, 157.9, 152.8, 140.1, 138.4, 138.2, 135.8, 131.3, 130.7, 127.9, 126.8, 125.1, 124.5, 117.3, 115.9, 115.3, 112.6, 108.1, 107.8, 104.1, 98.5, 61.1, 56.3, 55.6, 55.4, 50.8, 39.7, 35.9, 30.4; HRMS-ESI (*m*/*z*) $[M+H]^+$ calcd for $C_{32}H_{33}NO_7Br$, 622.144; found, 622.1433.

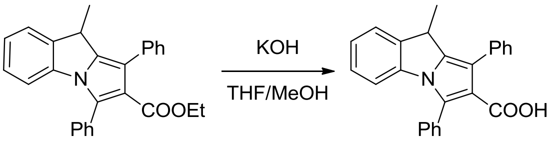
B. Model reactions via Curtius rearrangement



To a solution of **5l** (317 mg, 1.0 mmol) in THF/methanol (5.0 mL/5.0 mL) was added KOH (280 mg, 5.0 mmol). After stirring at reflux for overnight, the reaction was concentrated under reduced pressure. The residue was extracted with ethyl acetate (3 x 30 mL) in the presence of brine (20 mL). The combined organic layers were dried over anhydrous sodium sulfate, and concentrated under reduced pressure. The crude residue was purified by silica gel chromatography (ethyl acetate/petroleum ether = 1:5) to afford the product **6** (202 mg, 70% yield) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): 7.65-7.40 (m, 5H), 7.37 (d, *J* = 7.2 Hz, 1H), 7.11 (t, *J* = 7.6 Hz, 1H), 7.02 (t, *J* = 7.6 Hz, 1H), 6.66 (s, 1H), 6.48 (d, *J* = 8.0 Hz, 1H), 4.06 (q, *J* = 7.2 Hz, 1H), 1.55 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 170.1, 141.4, 141.2, 139.8, 132.0, 131.3, 130.8, 130.7, 128.8, 128.2, 127.4, 124.8, 124.6, 116.7, 112.4, 103.6, 34.9, 19.1; HRMS-ESI (*m*/*z*) $[M+H]^+$ calcd for $C_{19}H_{16}NO_2$, 290.1181; found, 290.1174.



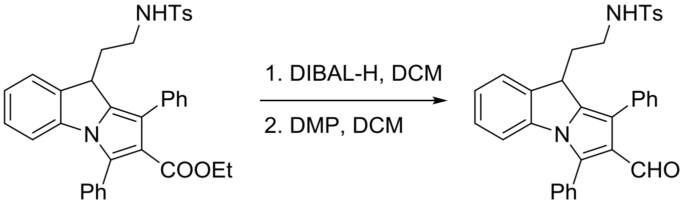
To a stirred solution of **6** (86.7 mg, 0.3 mmol) and Et_3N (0.125 m1, 0.9 mmol) in THF (2.5 mL) at room temperature was added diphenylphosphoryl azide (0.097 ml, 0.45 mmol) dropwise. The resulting mixture was stirred for 3 h at room temperature. HCl (2 M, 1mL) was added to the reaction and the resulting mixture was heated to reflux for 2 h (Caution! N_2 was generated!). The solution was cooled to room temperature, quenched with saturated K_2CO_3 solution and extracted with ethyl acetate (3 x 20 mL). The combined organic layers were washed with brine, dried over anhydrous sodium sulfate. The solvent was evaporated under reduced pressure and the residue was purified by silica gel chromatography (ethyl acetate/petroleum ether = 10:1) to afford the product **7** (70 mg, 89% yield) as light pink solid. ^{1}H NMR (400 MHz, $CDCl_3$): 7.63 (d, *J* = 7.9 Hz, 2H), 7.31-7.38 (m, 3H), 7.22-7.02 (m, 4H), 6.90 (d, *J* = 8.4 Hz, 1H), 5.48 (s, 1H), 3.74 (s, 2H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 207.9, 134.9, 133.5, 132.4, 131.3, 129.1, 128.6, 126.4, 121.5, 119.9, 118.9, 110.5, 104.3, 67.1, 35.2, 9.1; HRMS-ESI (*m*/*z*) $[M+H]^+$ calcd for $C_{18}H_{16}NO$, 262.1232; found, 262.1230.



5m **8**

The compound **8** was prepared by following the same procedure as that for the synthesis of **6**. Purification by silica gel chromatography (ethyl acetate/petroleum ether = 1:5) afforded **8** (370 mg, 90% yield) as a brown oil. ^{1}H NMR (400 MHz, $CDCl_3$): 10.45 (s, 1H), 7.70-7.20 (m, 11H), 7.12 (t, *J* = 6.4 Hz, 1H), 7.08 (t, *J* = 8.0 Hz, 1H), 6.41 (d, *J* = 8.0 Hz, 1H), 4.27 (q, *J* = 7.2 Hz, 1H), 1.29 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 168.9, 141.2, 139.5, 138.6, 134.5, 132.1, 131.6, 130.7, 129.5, 128.8, 128.2, 127.9, 127.4, 126.5, 124.7, 124.7, 119.8, 114.9, 112.5, 35.4, 17.5; HRMS-ESI (*m*/*z*) $[M+H]^+$ calcd for $C_{25}H_{20}NO_2$, 366.1494; found, 366.1485.

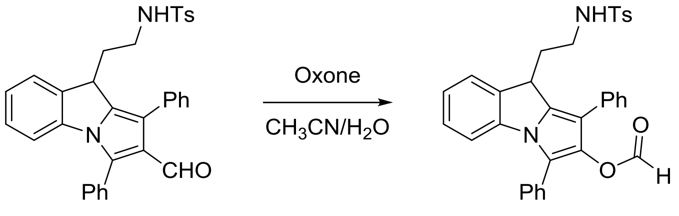
C. Model reactions via Baeyer-Villiger oxidation



5g **10**

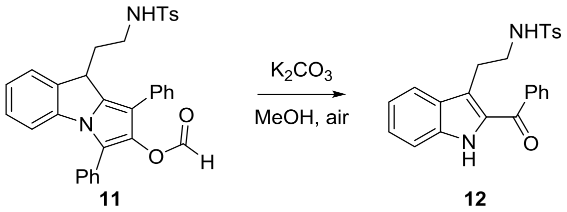
To a solution of **5g** (577 mg, 1.0 mmol) in dichloromethane (10.0 mL) at -50 ^oC was added DIBAL-H (1.5 M in toluene, 2.3 mL) dropwise. After being stirred at -50 ^oC for 2 h, the reaction was quenched with water (2 mL). Saturated aqueous potassium sodium tatrate (20 mL) was added to the reaction, and the mixture was stirred vigorously at room temperature until the mixture became clear. The mixture was extracted with dichloromethane (3x20 mL). The combined organic layers were washed with brine and dried over anhydrous sodium sulfate. The solvent was evaporated under reduced pressure to afford the crude residue, which was used for next step without further purification.

To a solution of the crude residue in dichloromethane (200 mL) was added Dess-Martin periodinane (636 mg, 1.5 mmol). The resulting mixture was stirred at room temperature for 5 min under N_2 atmosphere. Upon completion, the reaction was quenched by the addition of saturated aqueous $NaHSO_3$ (15 mL) and extracted with ethyl acetate (2 x 300 mL). The combined organic layers were washed with saturated aqueous $NaHCO_3$, brine and dried over anhydrous sodium sulfate. The solvent was evaporated under reduced pressure and the residue was purified by silica gel chromatography (ethyl acetate/dichloromethane = 1:50) to afford the product **10** (341 mg, 64% yield) as light yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): 7.80-7.45 (m, 9H), 7.45-7.30 (m, 4H), 7.24 (d, J = 8.0 Hz, 2H), 7.20-7.05 (m, 2H), 6.71 (d, J = 7.6 Hz, 1H), 4.48 (t, J = 6.0 Hz, 1H), 4.00 (t, J = 6.4 Hz, 1H), 2.75-2.65 (m, 1H), 2.60-2.50 (m, 1H), 2.42 (s, 3H), 2.05-1.93 (m, 1H), 1.92-1.80 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): 186.6, 143.4, 139.3, 138.8, 136.8, 136.7, 136.3, 133.4, 131.0, 130.9, 129.6, 129.5, 129.1, 128.6, 128.3, 128.0, 127.3, 127.0, 125.5, 125.4, 124.2, 119.3, 113.0, 40.2, 37.6, 32.4, 21.5; HRMS-ESI (*m*/*z*) $[M+H]^+$ calcd for $C_{33}H_{29}N_2O_3S$, 533.1899; found, 533.1888.

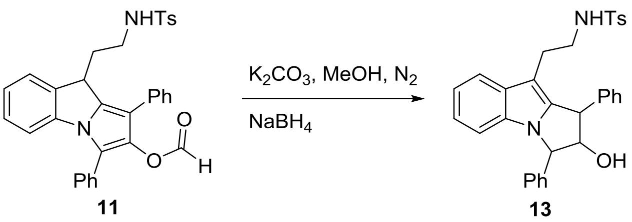


10 **11**

To a solution of **10** (327.6 mg, 0.6 mmol) in dry DMF (5 mL) under N_2 atmosphere was added Oxone (738 mg, 1.2 mmol). When **10** was fully consumed by TLC, the reaction was filtered through a pad of celite® and washed with toluene (2 x 15 mL). The organic layer was separated and evaporated under reduced pressure. The resulting crude residue was purified by preparative silica gel chromatography (ethyl acetate/petroleum ether = 1: 5) to afford **11** (250 mg, 69% yield) as a light yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): 8.03 (s, 1H), 7.67-7.38 (m, 11H), 7.35-7.25 (m, 2H), 7.20 (d, J = 7.6 Hz, 2H), 7.16-7.00 (m, 2H), 6.87 (d, J = 6.8 Hz, 1H), 4.53 (t, J = 5.2 Hz, 1H), 4.14 (d, J = 5.2 Hz, 1H), 2.80-2.52 (m, 2H), 2.40 (s, 3H), 2.15-1.90 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): 160.0, 143.3, 140.8, 136.8, 136.6, 133.8, 132.8, 132.2, 130.0, 129.6, 129.0, 128.8, 128.7, 128.5, 127.9, 127.8, 127.0, 126.9, 124.9, 124.0, 118.8, 112.4, 112.0, 40.2, 39.1, 31.6, 21.5; HRMS-ESI (*m*/*z*) $[M+H]^+$ calcd for $C_{33}H_{29}N_2O_4S$, 549.1848; found, 549.1844.



To a solution of **11** (100.0 mg, 0.18 mmol) in methanol (5 mL) was added K_2CO_3. After stirring at room temperature for 1 h, the reaction was quenched with water. Methanol was evaporated under reduced pressure and the aqueous phase was extracted with ethyl acetate (3 x 15 mL). The combined organics were washed with brine and dried over anhydrous sodium sulfate. The solvent was evaporated under reduced pressure and the residue was purified by silica gel chromatography (ethyl acetate/petroleum ether = 1:5) to afford the product **12** (42.7 mg, 57% yield) as light yellow oil. ^1H NMR (400 MHz, $CDCl_3$): 8.63 (s, 1H), 7.73 (d, *J* = 7.6 Hz, 2H), 7.70-7.50 (m, 6H), 7.37 (s, 2H), 7.20-7.10 (m, 1H), 7.06 (d, *J* = 8.0 Hz, 2H), 5.65 (t, *J* = 4.8 Hz, 1H), 3.28 (q, *J* = 6.0 Hz, 2H), 3.12 (t, *J* = 6.4 Hz, 2H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 188.9, 142.7, 138.3, 136.8, 136.5, 132.7, 131.7, 129.3, 129.1, 128.8, 127.6, 126.8, 126.6, 121.6, 121.0, 120.7, 112.2, 43.8, 24.7, 21.4; HRMS-ESI (*m*/*z*) $[M+H]^+$ calcd for $C_{24}H_{23}N_2O_3S$, 419.1429; found, 419.1426.



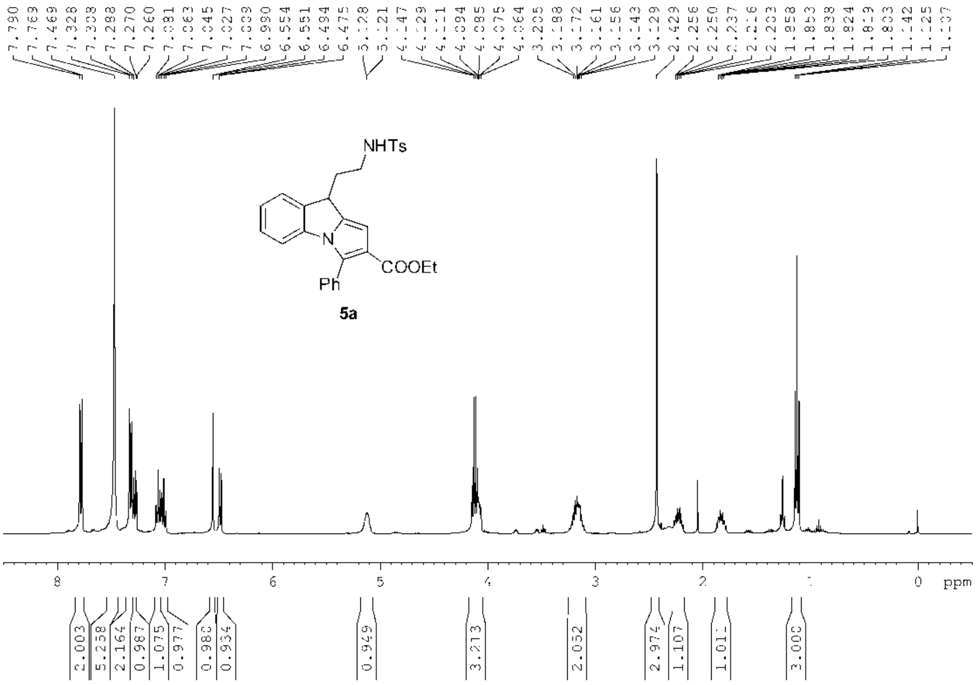
To a solution of **11** (250.0 mg, 0.45 mmol) in methanol (5 mL) at room temperature under N_2 atmosphere was added K_2CO_3 (61.4 mg, 0.45 mmol). After stirring at room temperature for 1 h, $NaBH_4$ (33.8 mg, 0.89 mmol) was added and the mixture was stirred for additional 30 min. The reaction was quenched with water. Methanol was evaporated under reduced pressure and the aqueous phase was extracted with ethyl acetate (3x30 ml). The combined organics were washed with brine and dried over anhydrous sodium sulfate. The solvent was evaporated in vacuum and the residue was purified by silica gel chromatography (ethyl acetate/dichloromethane = 1/50) to afford the product **13** (193.2 mg, 81% yield, dr = 2:1:2) as white solid.

1st isomer: ^{1}H NMR (400 MHz, $CDCl_3$): 7.56 (d, J = 7.9 Hz, 2H), 7.42-7.29 (m, 11H), 7.22 (d, J = 7.8 Hz, 2H), 7.04 (t, J = 7.4 Hz, 1H), 6.98 (t, J = 7.8 Hz, 1H), 6.66 (d, J = 8.0 Hz, 2H), 5.49 (d, J = 5.2 Hz, 2H), 4.99-4.92 (m, 1H), 4.68 (d, J = 6.0 Hz, 2H), 4.17 (t, J = 5.9 Hz, 1H), 3.14-2.97 (m, 2H), 2.75-2.65 (m, 1H), 2.61-2.50 (m, 1H), 2.42 (s, 3H), 1.25 (d, J = 5.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): 143.1, 141.6, 137.0, 135.1, 133.8, 132.9, 132.5, 130.0, 129.5, 128.8, 128.6, 128.6, 128.5, 127.9, 127.0, 121.0, 119.6, 118.5, 111.0, 103.6, 78.3, 65.8, 49.3, 42.9, 24.4, 21.5; HRMS-ESI (m/z) $[M+H]^+$ calcd for $C_{32}H_{31}N_2O_3S$, 523.2055; found, 523.2052.

2nd isomer: ^{1}H NMR (400 MHz, $CDCl_3$): 7.60 (d, J = 8.0 Hz, 2H), 7.44 (d, J = 7.5 Hz, 2H), 7.41-7.29 (m, 6H), 7.21 (d, J = 8.0 Hz, 2H), 7.14-6.99 (m, 6H), 6.79 (d, J = 8.0 Hz, 1H), 5.24 (d, J = 4.4 Hz, 1H), 4.78-4.70 (m, 1H), 4.68 (d, J = 6.5 Hz, 1H), 4.30 (t, J = 6.0 Hz, 1H), 3.13-2.98 (m, 2H), 2.82-2.72 (m, 1H), 2.72-2.62 (m, 1H), 2.42 (s, 3H), 1.81 (d, J = 6.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): 141.1, 137.6, 137.0, 135.3, 132.5, 31.9, 129.6, 129.4, 129.1, 129.1, 128.4, 128.2, 127.0, 126.7, 121.3, 119.5, 118.7, 110.7, 103.5, 84.9, 67.2, 47.5, 43.0, 24.8, 21.5; HRMS-ESI (m/z) $[M+H]^+$ calcd for $C_{32}H_{31}N_2O_3S$, 523.2055; found, 523.2056.

3rd isomer: ^{1}H NMR (400 MHz, $CDCl_3$): 7.59 (d, J = 7.8 Hz, 1H), 7.40-7.27 (m, 7H), 7.25-7.20 (m, 2H), 7.20-7.14 (m, 2H), 7.12-6.90 (m, 6H), 5.65 (d, J = 6.5 Hz, 1H), 4.85-4.76 (m, 1H), 4.37 (t, J = 6.7 Hz, 1H), 4.26 (d, J = 6.4 Hz, 1H), 3.10-2.93 (m, 2H), 2.72-2.61 (m, 1H), 2.59-2.49 (m, 1H), 2.09 (d, J = 8.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): 143.2, 140.5, 139.1, 137.0, 134.6, 132.4, 131.8, 129.6, 129.0, 128.9, 128.6, 128.2, 127.8, 127.6, 127.1, 121.4, 119.6, 118.8, 110.5, 103.7, 84.6, 63.0, 51.1, 43.1, 24.4, 21.6; HRMS-ESI (*m*/*z*) $[M+H]^+$ calcd for $C_{32}H_{31}N_2O_3S$, 523.2055; found, 523.2056.

NMR Spectra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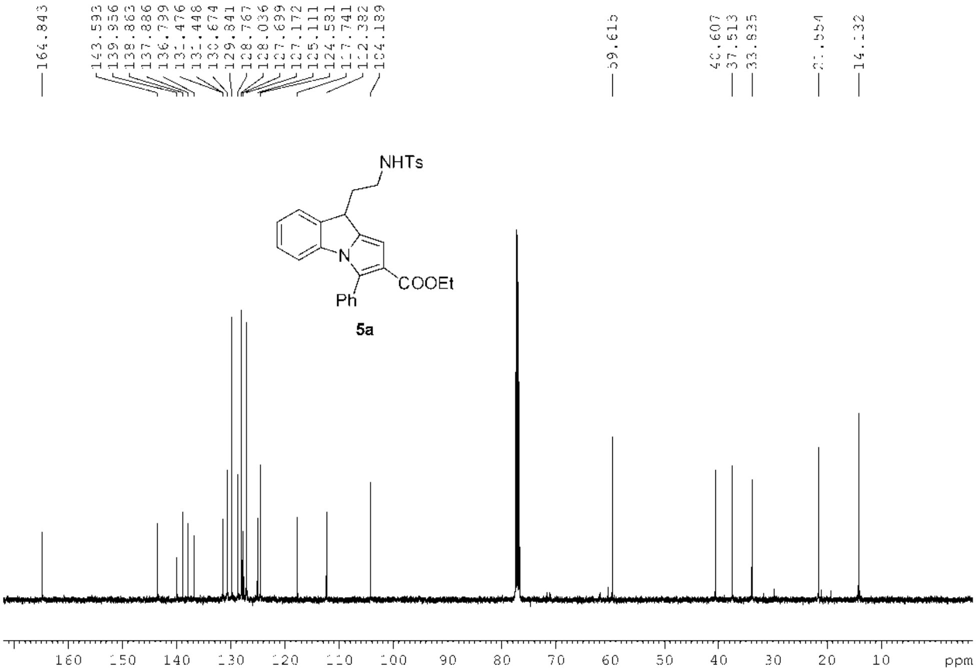
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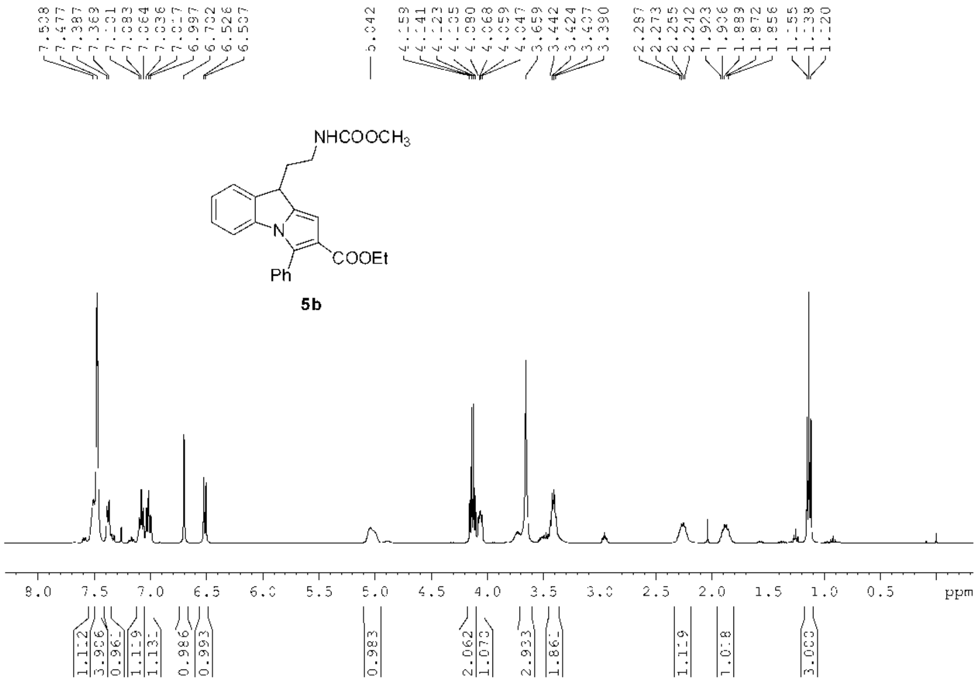
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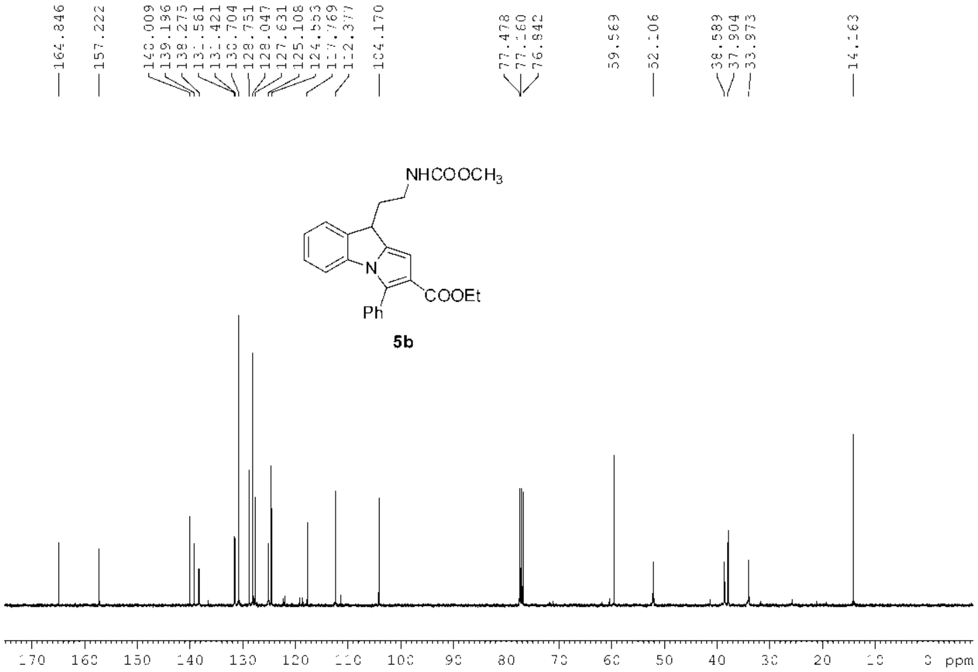
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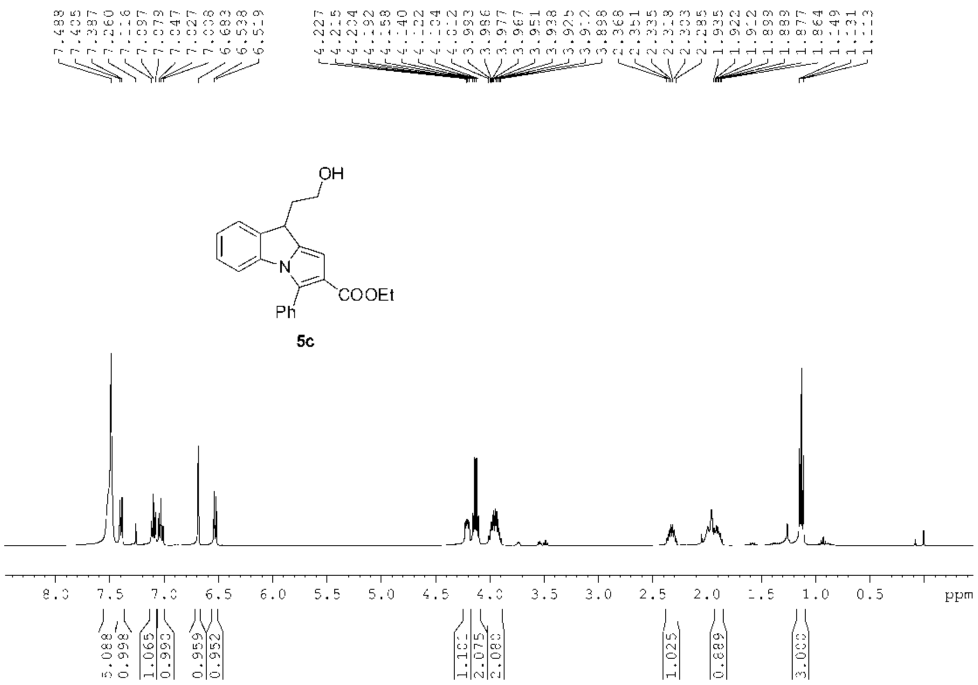
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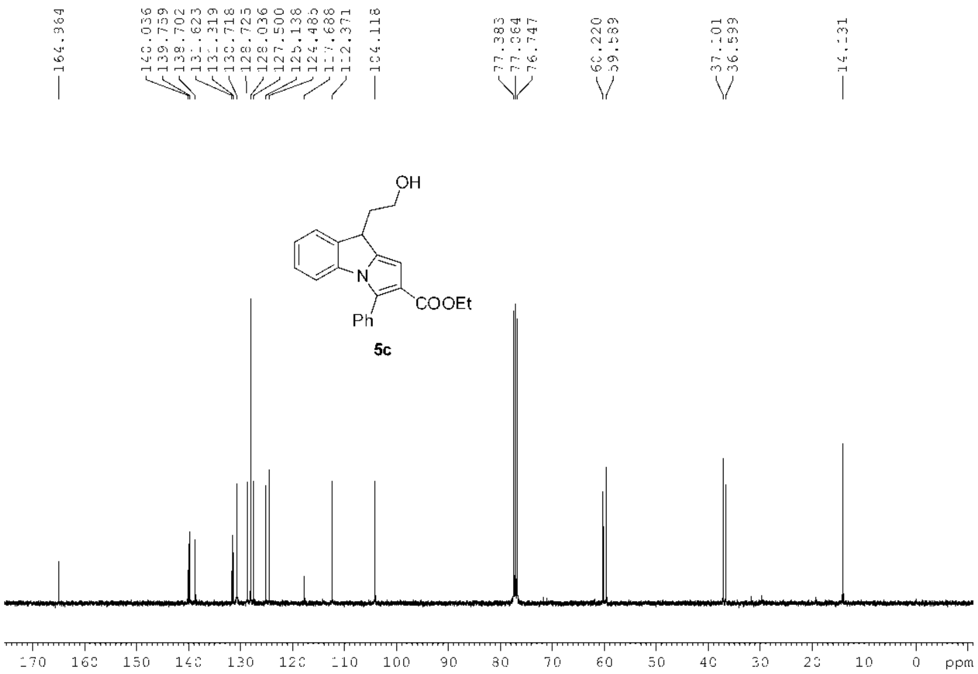
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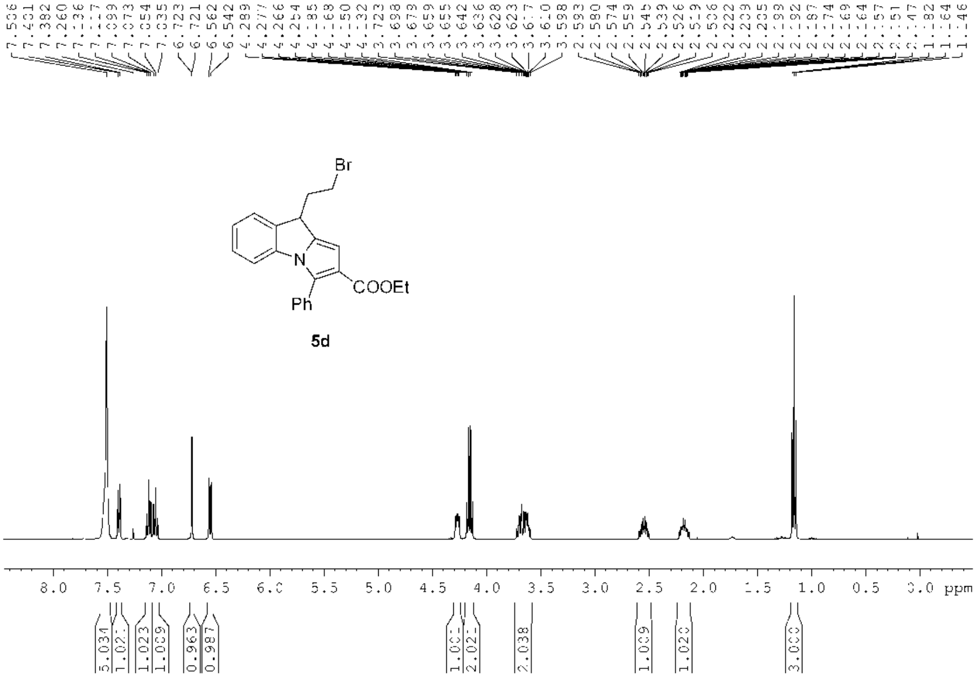
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2.574
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2.519
2.506
2.222
2.209
2.205
2.199
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2.187
2.174
2.169
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2.157
2.151
2.147
1.182
1.164
1.146
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N
COOEt
Ph
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6.0
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3.0
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2.0
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1.0
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0.0
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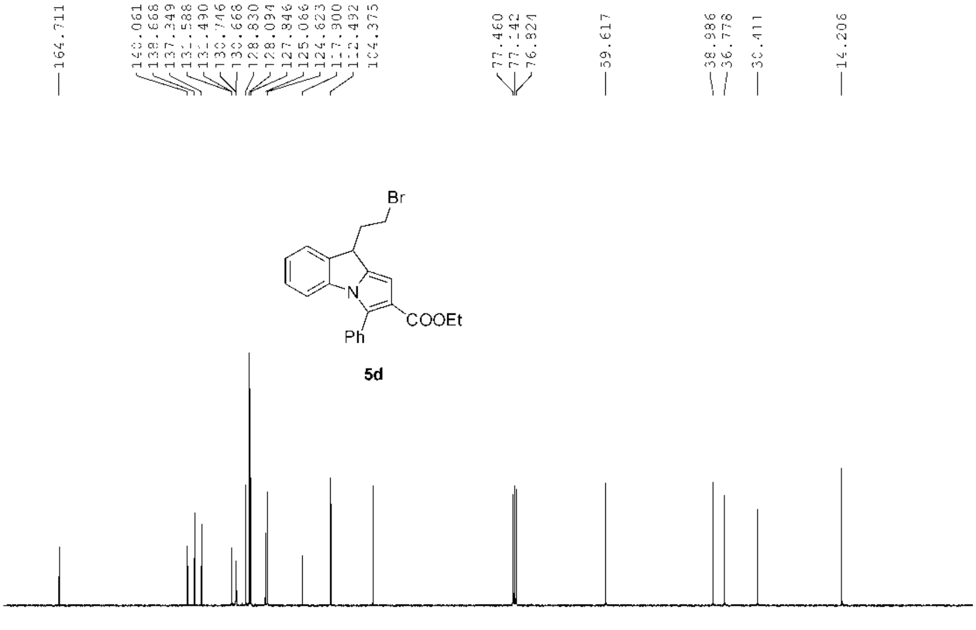
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38.986
36.778
30.411
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Br
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COOEt
Ph
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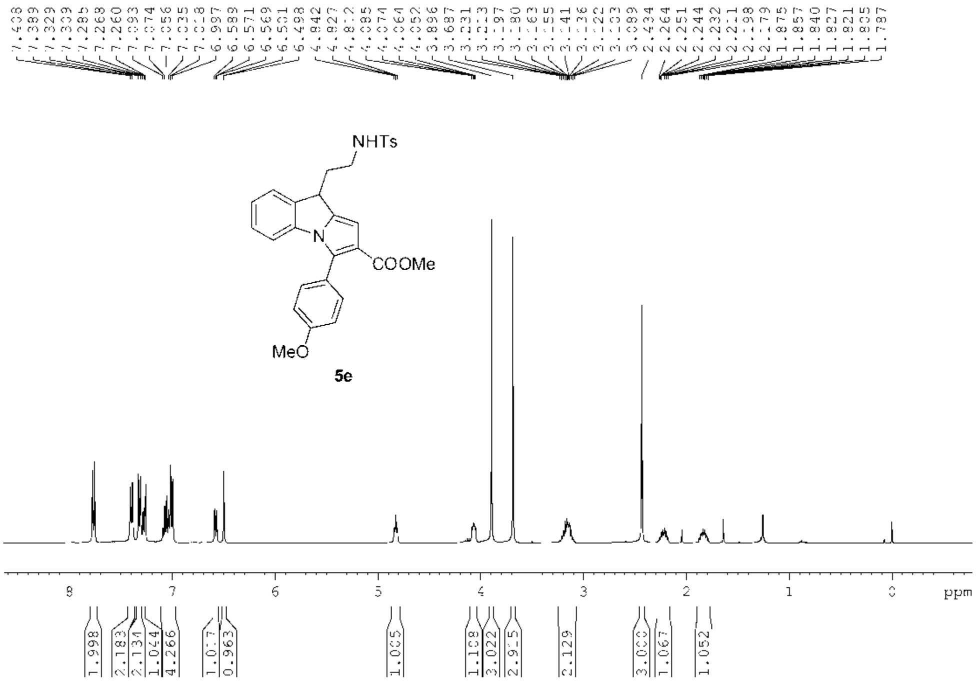
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6.501
6.498
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4.812
4.085
4.074
4.064
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3.896
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3.197
3.180
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3.155
3.141
3.136
3.122
3.103
3.089
2.434
2.264
2.251
2.244
2.232
2.211
2.198
2.179
1.875
1.857
1.840
1.827
1.821
1.805
1.787
NHTs
N
COOMe
MeO
5e
8
7
6
5
4
3
2
1
0
ppm
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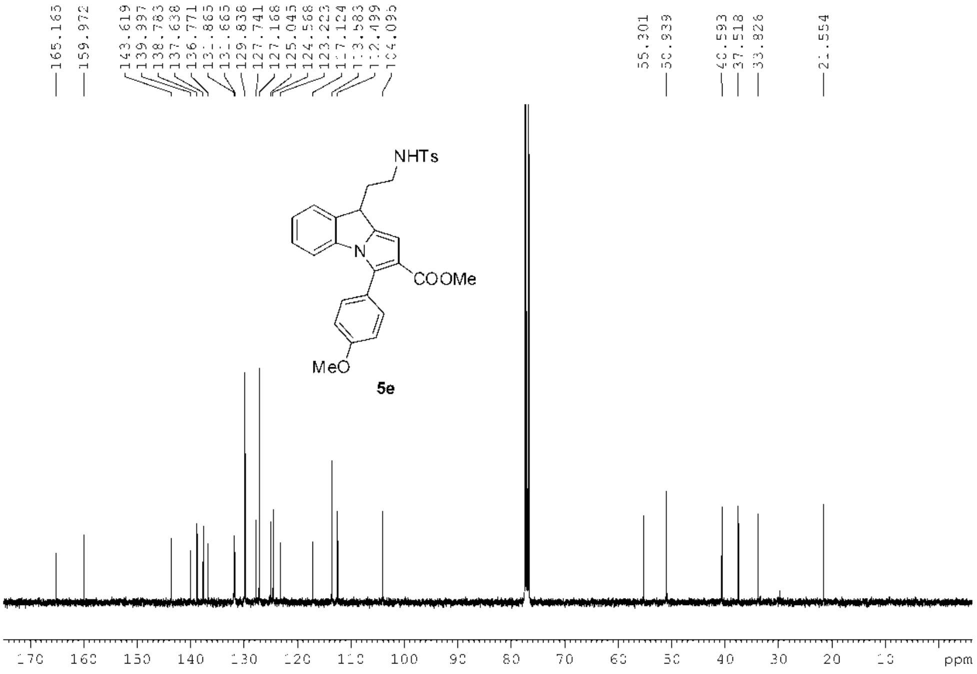
1.052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104.095
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50.939
40.593
37.518
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21.554
NHTs
N
COOMe
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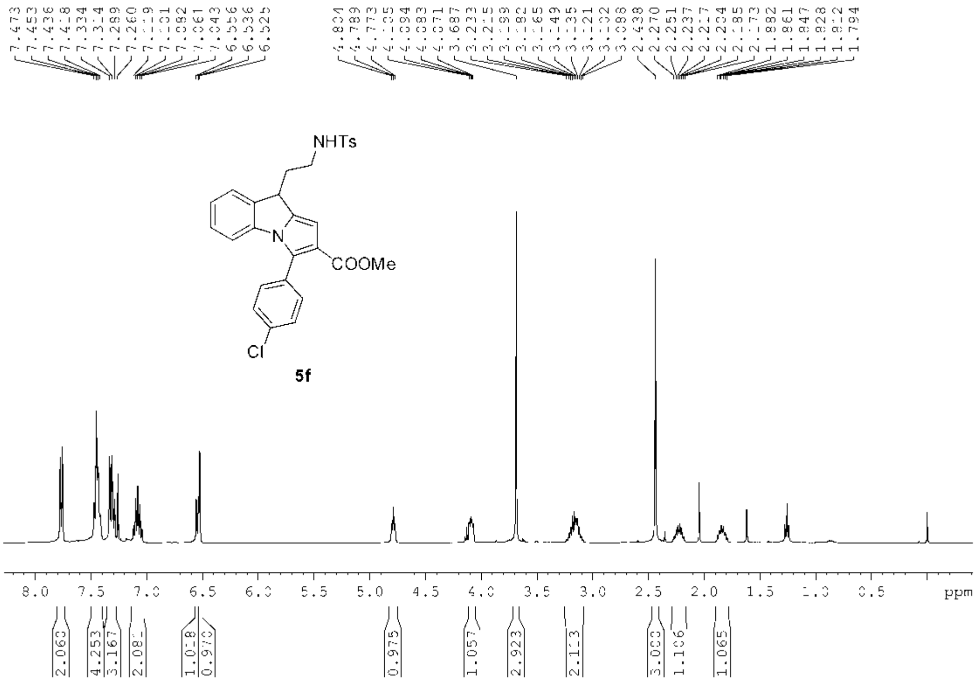
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6.525
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4.789
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4.094
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4.071
3.687
3.233
3.215
3.199
3.182
3.165
3.149
3.135
3.121
3.102
3.088
2.438
2.270
2.251
2.237
2.217
2.204
2.185
2.173
1.882
1.861
1.847
1.828
1.812
1.794
NHTs
N
COOMe
Cl
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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
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ppm
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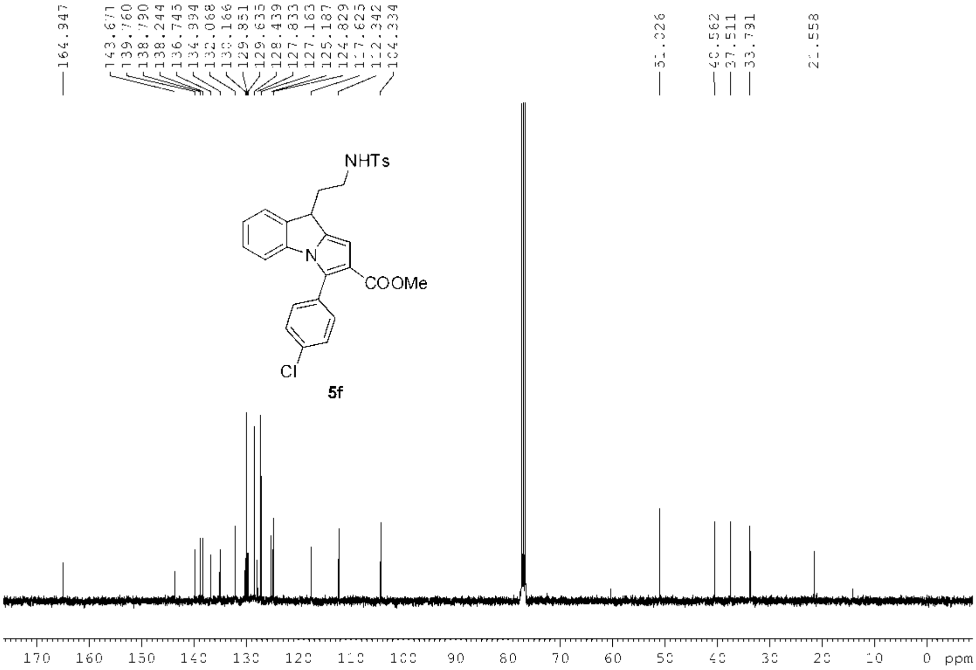
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127.163
125.187
124.829
117.625
112.342
104.334
51.026
40.562
37.511
33.791
21.558
NHTs
N
COOMe
Cl
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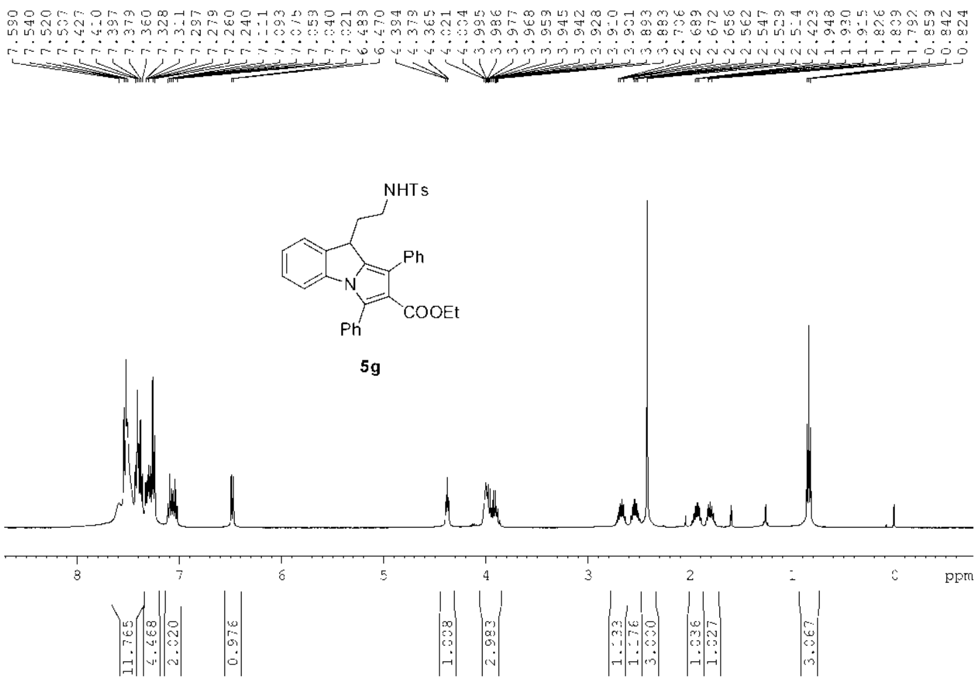
ppm

5f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7.279
7.260
7.240
7.111
7.093
7.075
7.059
7.040
7.021
6.489
6.470
4.394
4.379
4.365
4.021
4.004
3.995
3.986
3.977
3.968
3.959
3.945
3.942
3.928
3.910
3.901
3.893
3.883
2.706
2.689
2.672
2.656
2.562
2.547
2.529
2.514
2.423
1.948
1.930
1.915
1.826
1.809
1.792
0.859
0.842
0.824
NHTs
Ph
N
COOEt
Ph
5g
8
7
6
5
4
3
2
1
0
ppm
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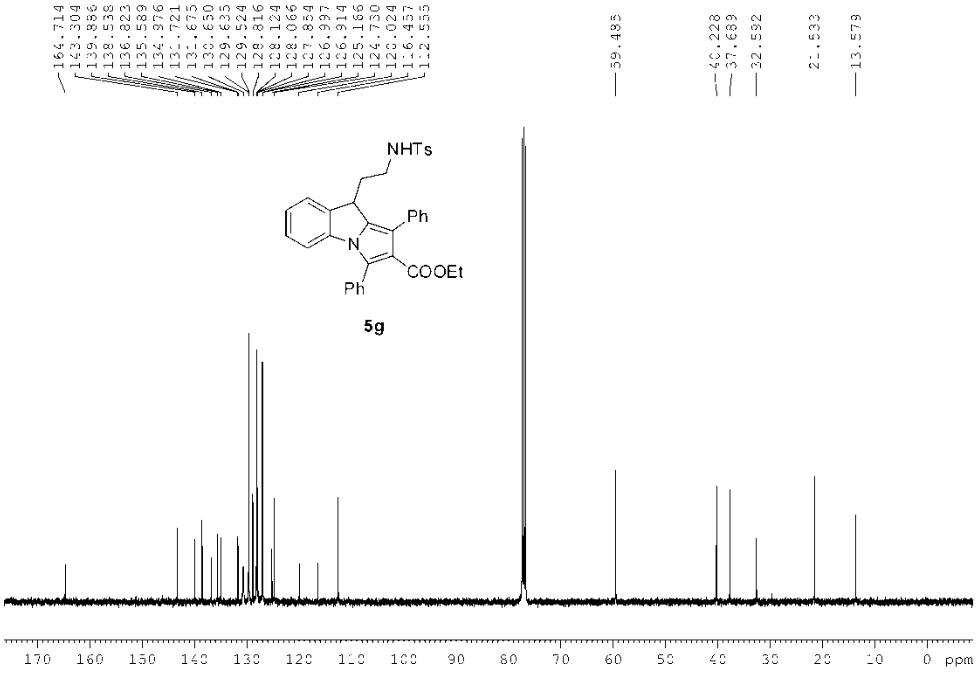
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128.816
128.124
128.066
127.854
126.997
126.914
125.166
124.730
120.024
116.457
112.555
59.485
40.228
37.689
32.592
21.533
13.579
NHTs
Ph
N
COOEt
Ph
5g
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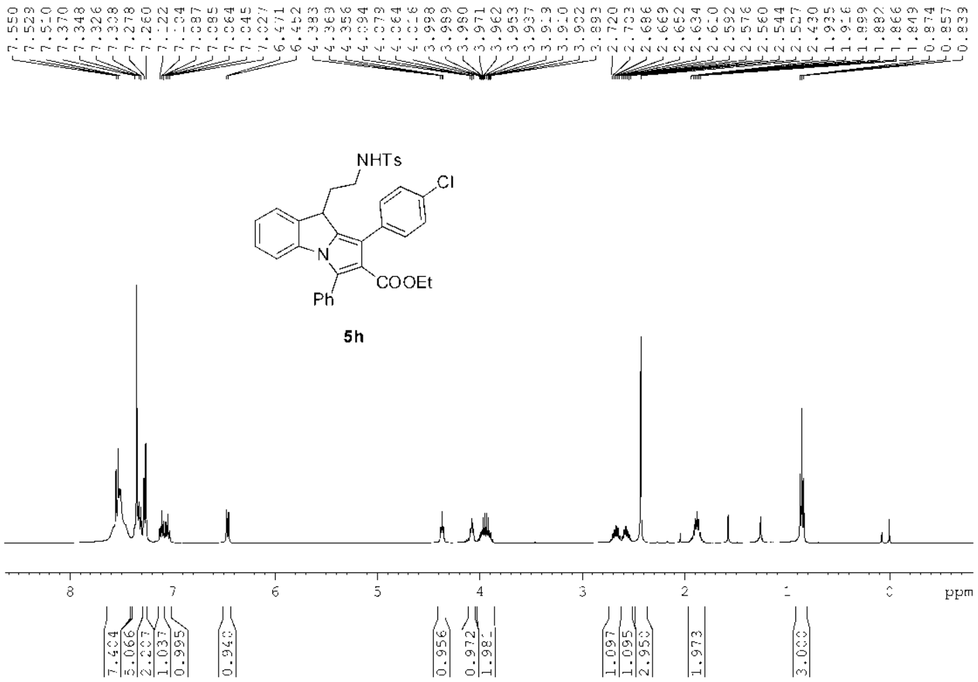
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7.085
7.064
7.045
7.027
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6.452
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4.369
4.356
4.094
4.079
4.064
4.016
3.998
3.989
3.980
3.971
3.962
3.953
3.937
3.919
3.910
3.902
3.893
2.720
2.703
2.686
2.669
2.652
2.634
2.610
2.592
2.576
2.560
2.544
2.527
2.430
1.935
1.916
1.899
1.882
1.866
1.849
0.874
0.857
0.839
NHTs
Cl
N
COOEt
Ph
5h
8
7
6
5
4
3
2
1
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ppm
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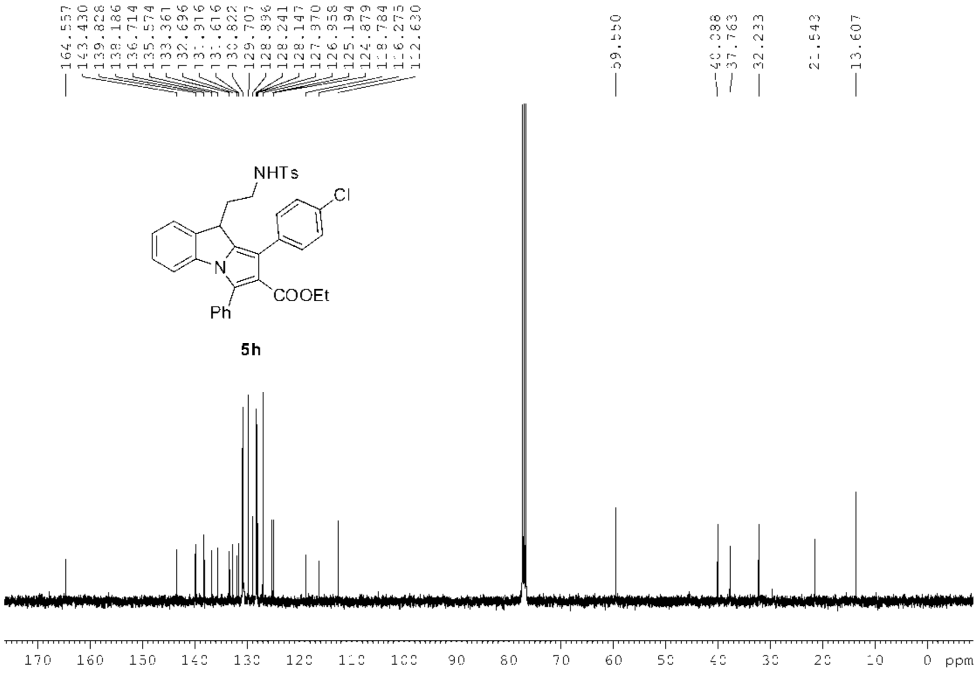
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128.147
127.370
126.958
125.194
124.879
118.784
116.275
112.630
59.550
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37.763
32.233
21.543
13.607
NHTs
Cl
N
COOEt
Ph
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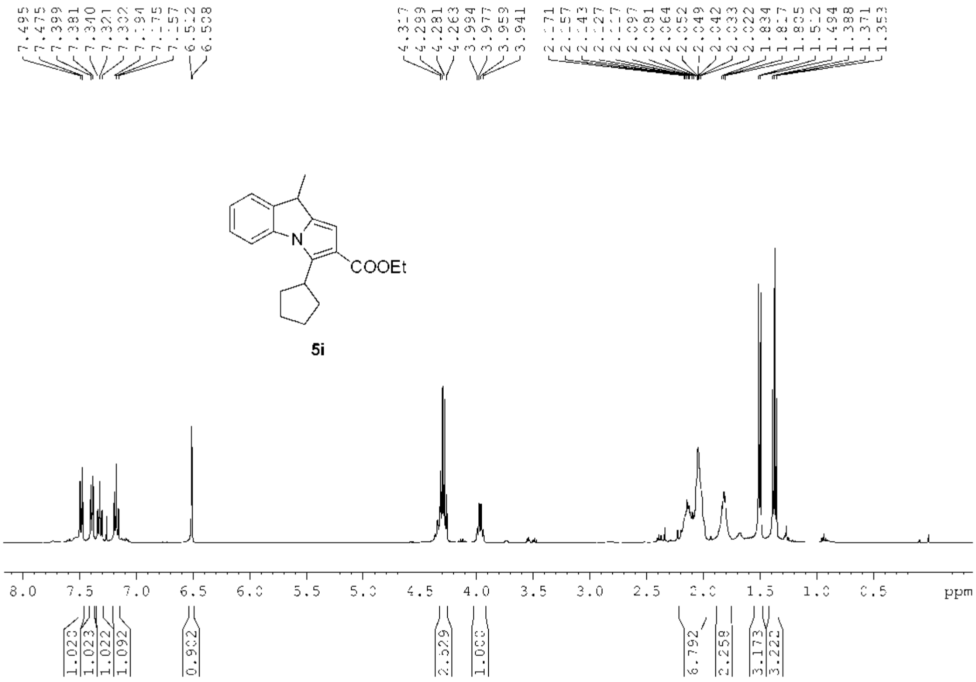
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4.281
4.263
3.994
3.977
3.959
3.941
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2.157
2.143
2.127
2.117
2.097
2.081
2.064
2.052
2.049
2.042
2.033
2.022
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1.817
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1.512
1.494
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1.371
1.353
COOEt
N
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6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
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1.0
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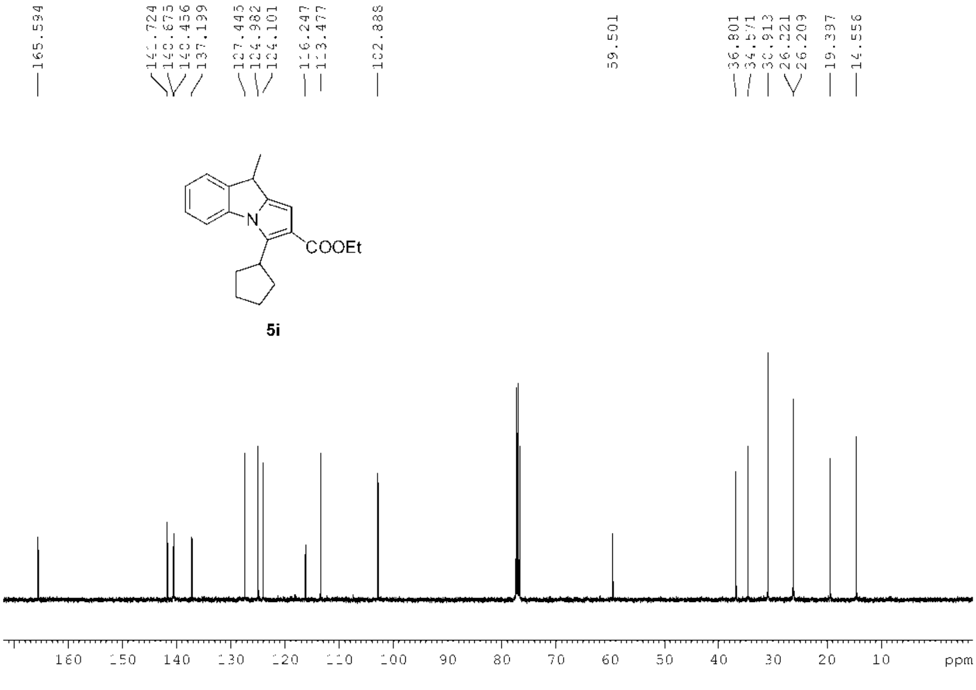
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30.913
26.221
26.209
19.397
14.556
COOEt
N
5i
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


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7.523
7.505
7.478
7.459
7.441
7.420
7.401
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7.324
7.225
7.207
7.188
6.276
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4.019
4.001
3.983
2.912
1.503
1.485
N
Ph
O
5j
8
7
6
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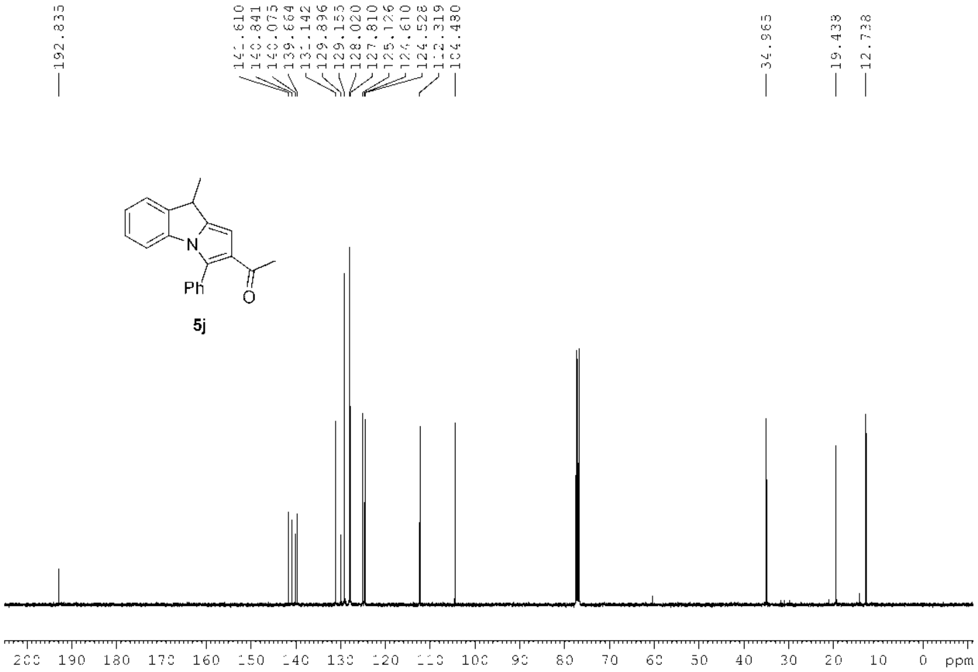
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112.319
104.430
34.965
19.438
12.738
N
Ph
O
5j
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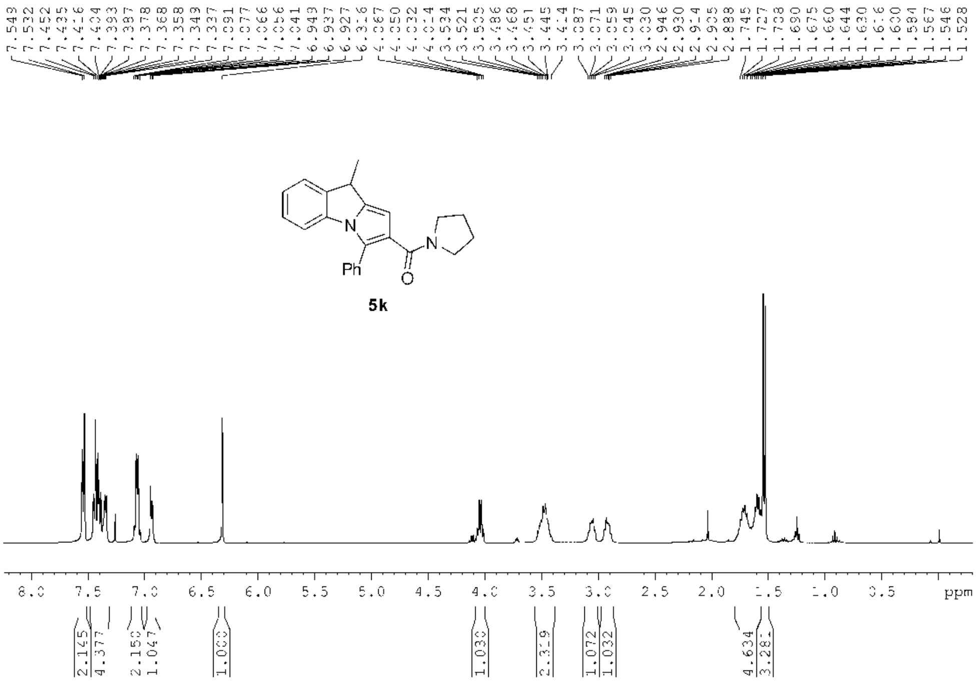
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7.056
7.041
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6.927
6.316
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4.032
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3.059
3.045
3.030
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2.930
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2.905
2.888
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1.616
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1.584
1.567
1.546
1.528
N
Ph
O
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6.5
6.0
5.5
5.0
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4.0
3.5
3.0
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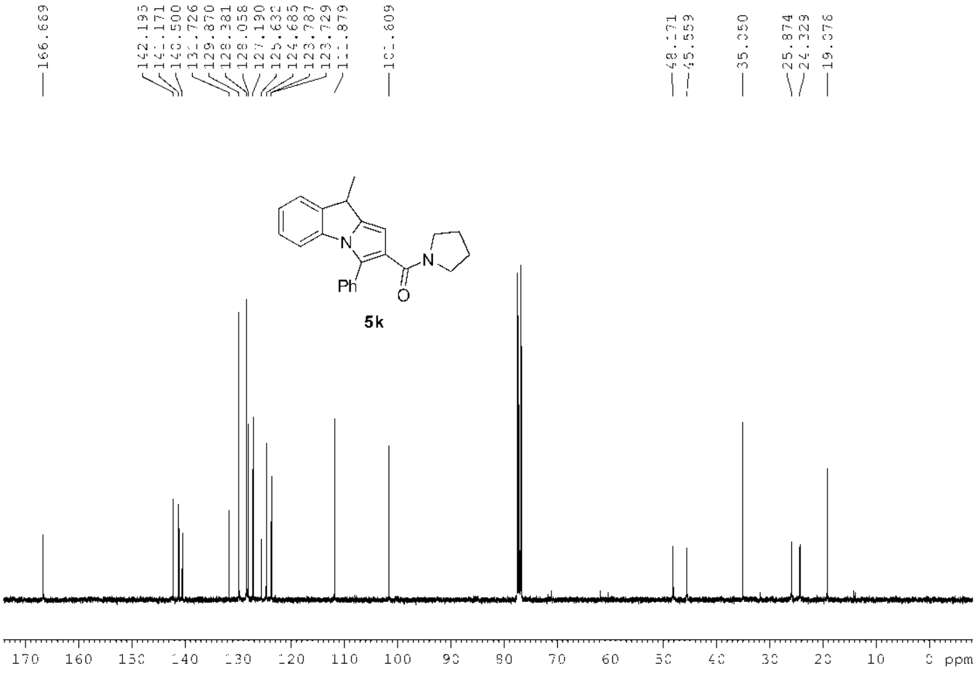
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123.729
111.879
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48.171
45.559
35.050
25.874
24.329
19.076
N
Ph
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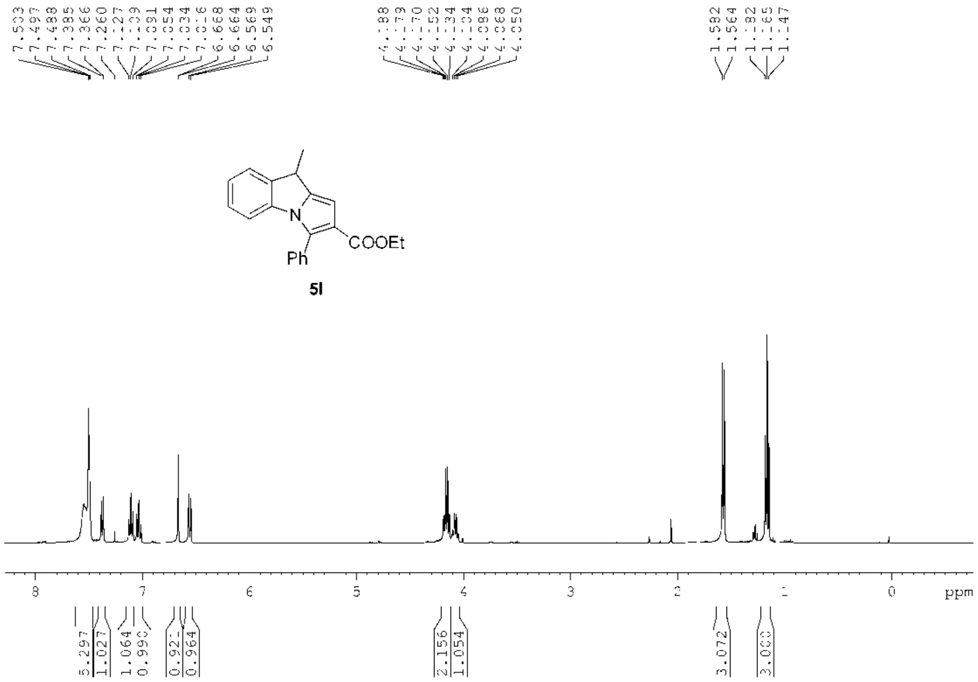
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6.549
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4.104
4.086
4.068
4.050
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1.165
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COOEt
Ph
5l
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4
3
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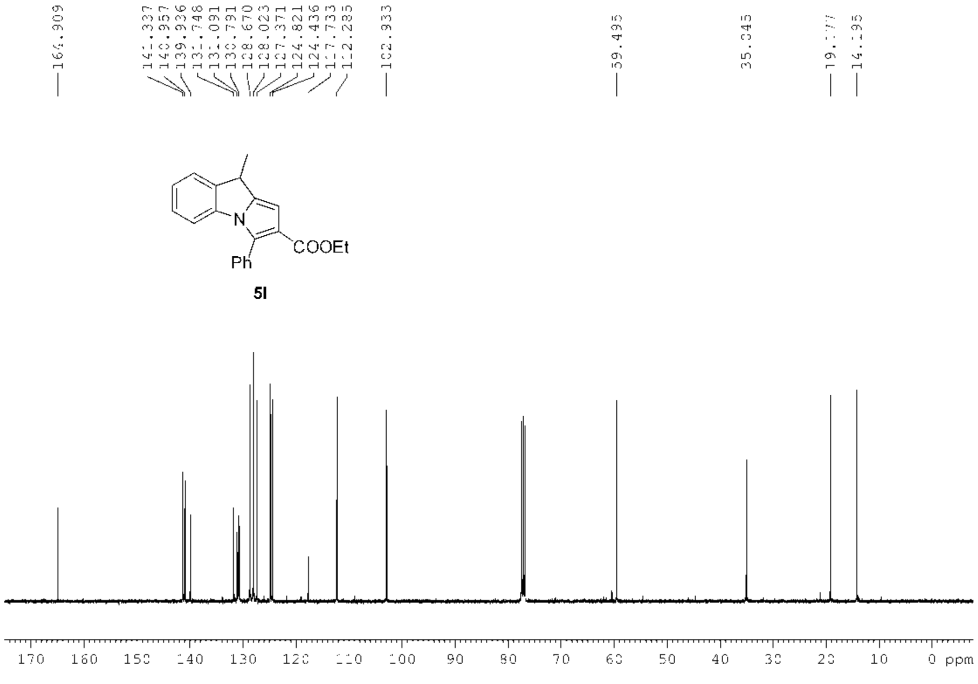
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59.495
35.045
19.177
14.195
N
COOEt
Ph
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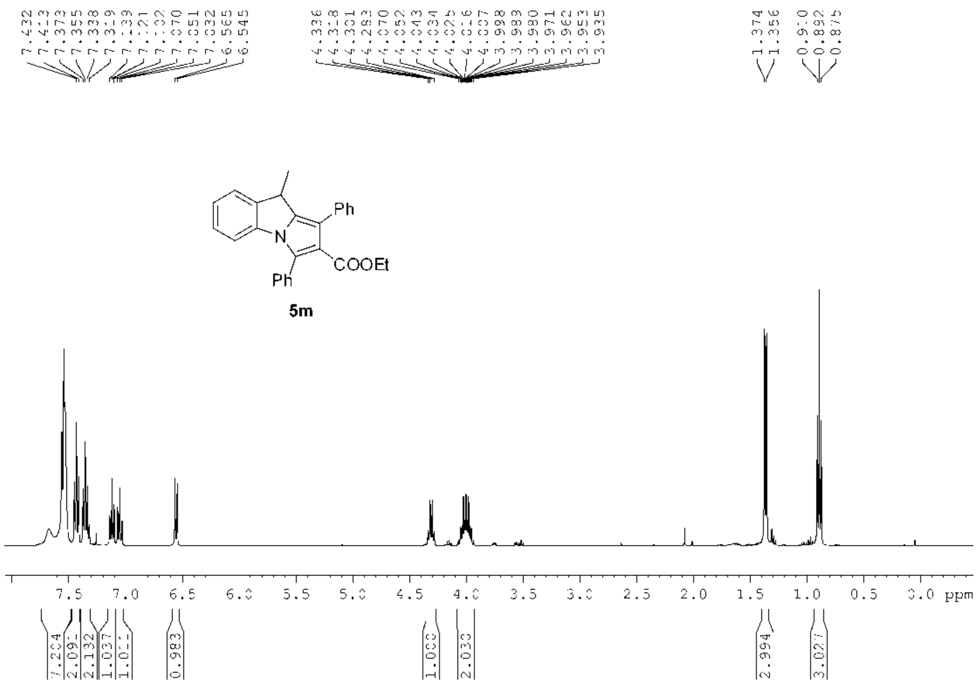
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6.545
4.336
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0.875
Ph
N
COOEt
Ph
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6.0
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5.0
4.5
4.0
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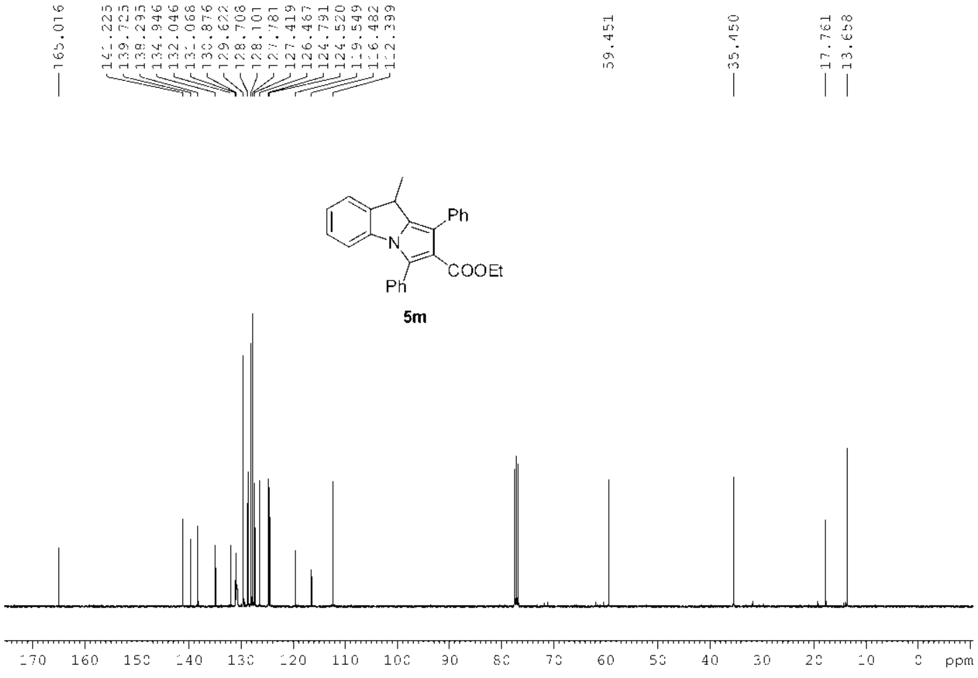
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124.791
124.520
119.549
116.482
112.399
59.451
35.450
17.761
13.658
Ph
N
COOEt
Ph
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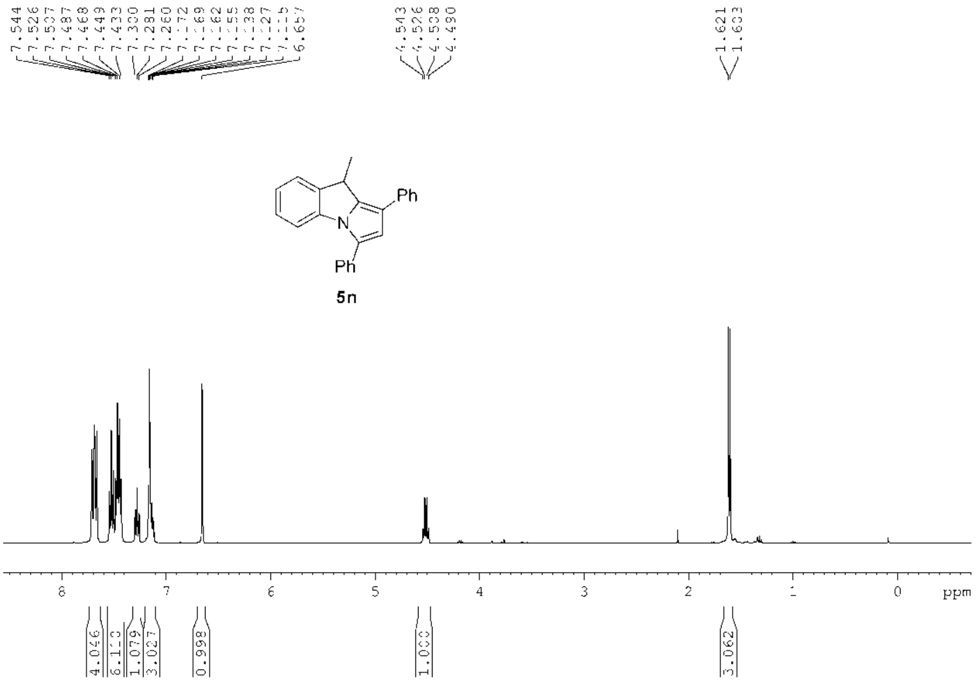
5m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7.162
7.155
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7.127
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6.657
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4.526
4.508
4.490
1.621
1.603
Ph
N
Ph
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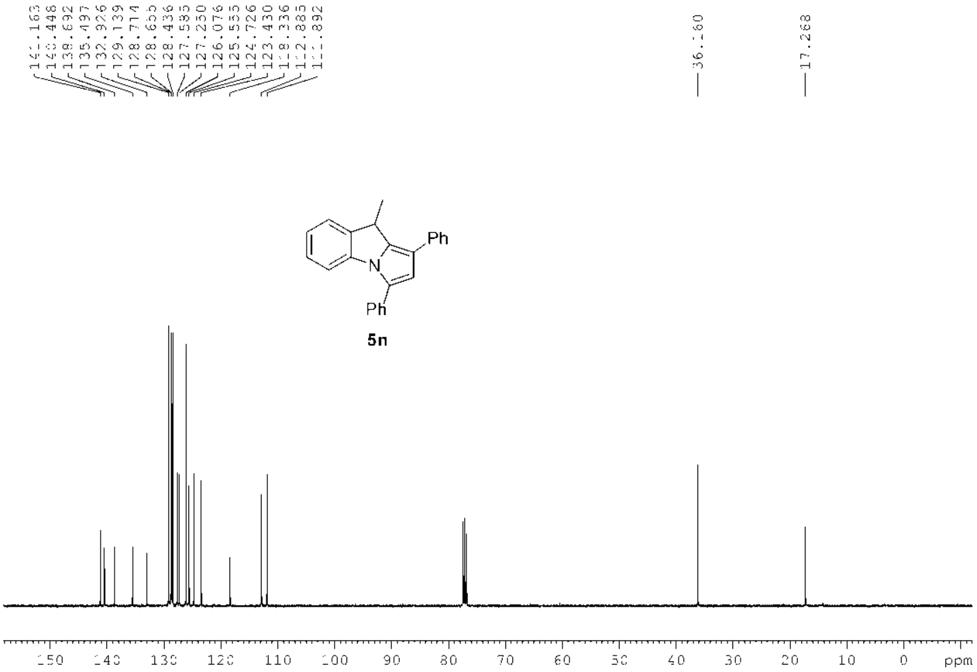
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127.250
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125.555
124.726
123.430
118.336
112.885
111.892
36.160
17.268
Ph
N
Ph
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140
130
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20
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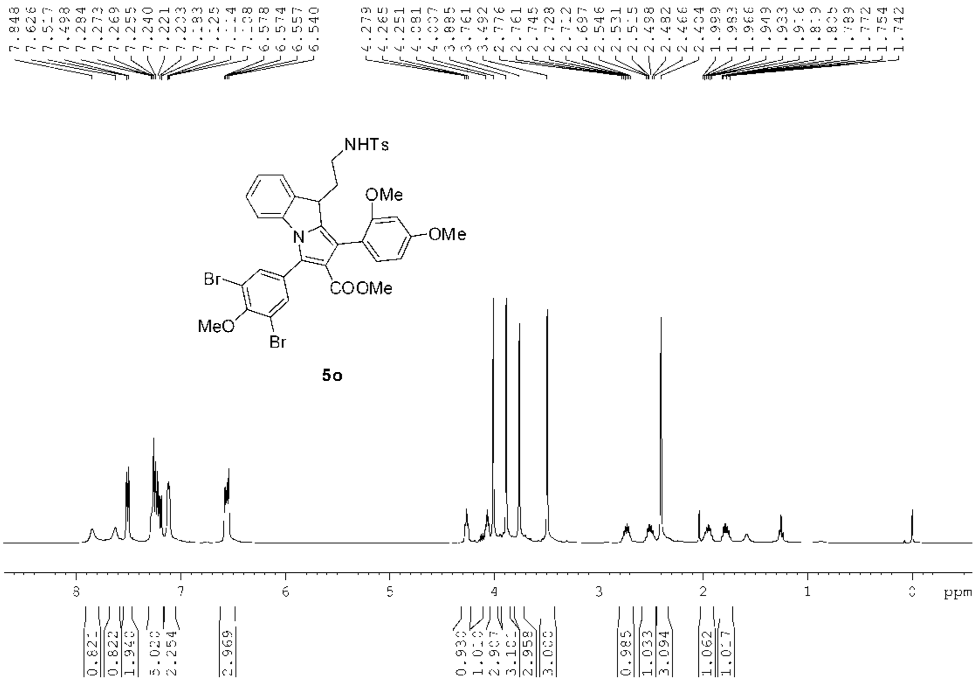
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7.114
7.108
6.578
6.574
6.557
6.540
4.279
4.265
4.251
4.081
4.007
3.885
3.761
3.492
2.776
2.761
2.745
2.728
2.712
2.697
2.546
2.531
2.515
2.498
2.482
2.466
2.404
1.999
1.983
1.966
1.949
1.933
1.916
1.819
1.805
1.789
1.772
1.754
1.742
NHTs
OMe
N
OMe
Br
COOMe
MeO
Br
8
7
6
5
4
3
2
1
0
ppm
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0.822
1.940
5.020
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2.969
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3.101
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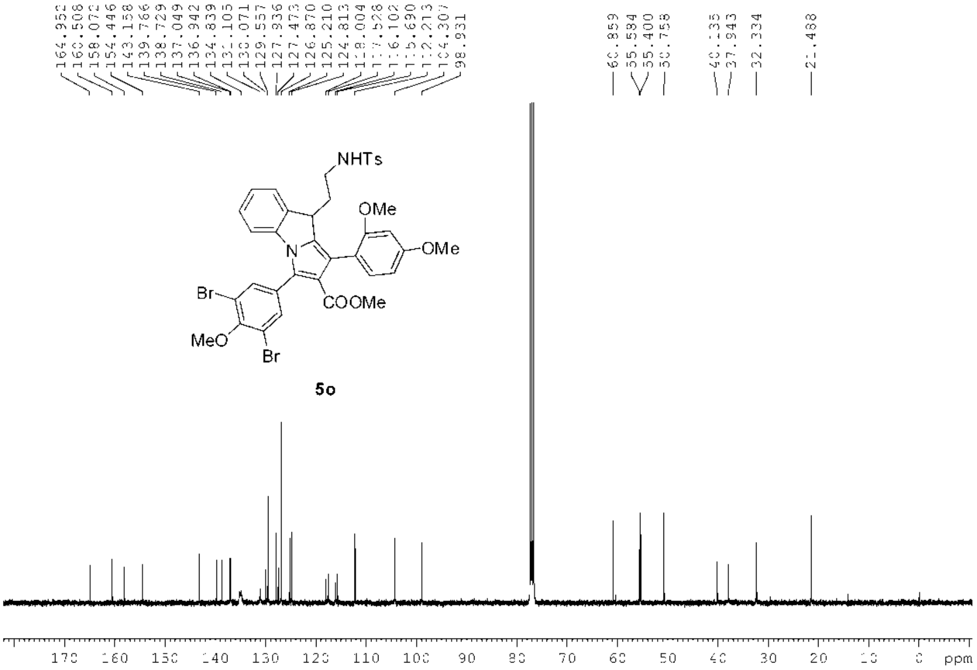
1.062
1.017

5o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129.557
127.936
127.473
126.870
125.210
124.813
118.004
117.526
116.102
115.690
112.213
104.307
98.931
60.859
55.534
55.400
50.758
40.135
37.943
32.334
21.488
NHTs
OMe
N
OMe
Br
COOMe
MeO
Br
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160
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130
120
110
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90
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70
60
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40
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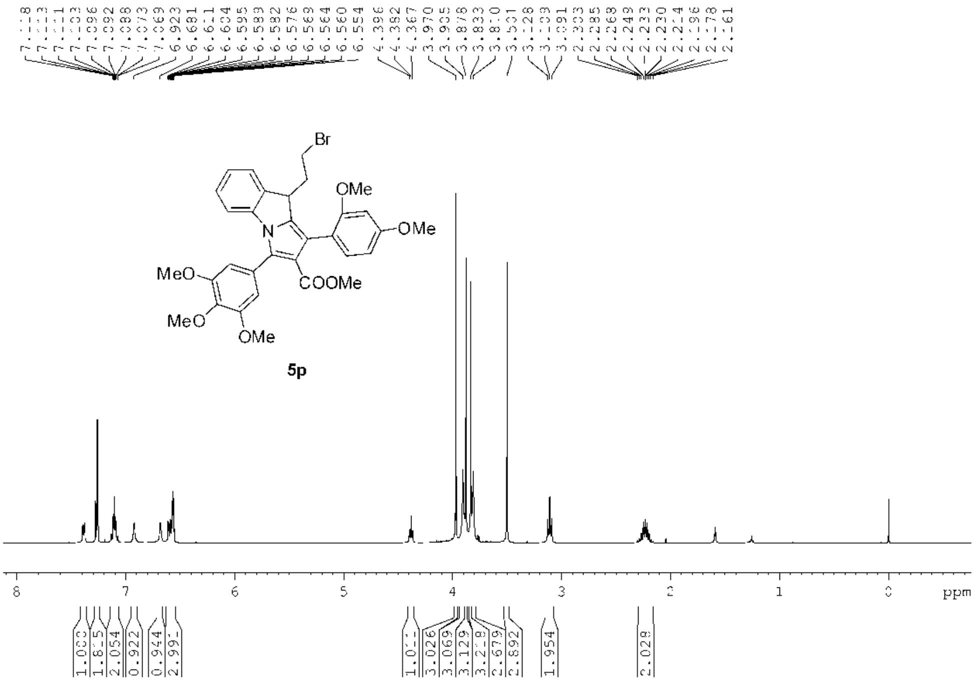
0
ppm

5o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7.092
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6.681
6.611
6.604
6.595
6.589
6.582
6.576
6.569
6.564
6.560
6.554
4.396
4.382
4.367
3.970
3.905
3.878
3.833
3.810
3.501
3.128
3.109
3.091
2.303
2.285
2.268
2.249
2.233
2.230
2.214
2.196
2.178
2.161
Br
OMe
OMe
N
MeO
COOMe
MeO
OMe
5p
8
7
6
5
4
3
2
1
0
ppm
1.000
1.815
2.054
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1.011
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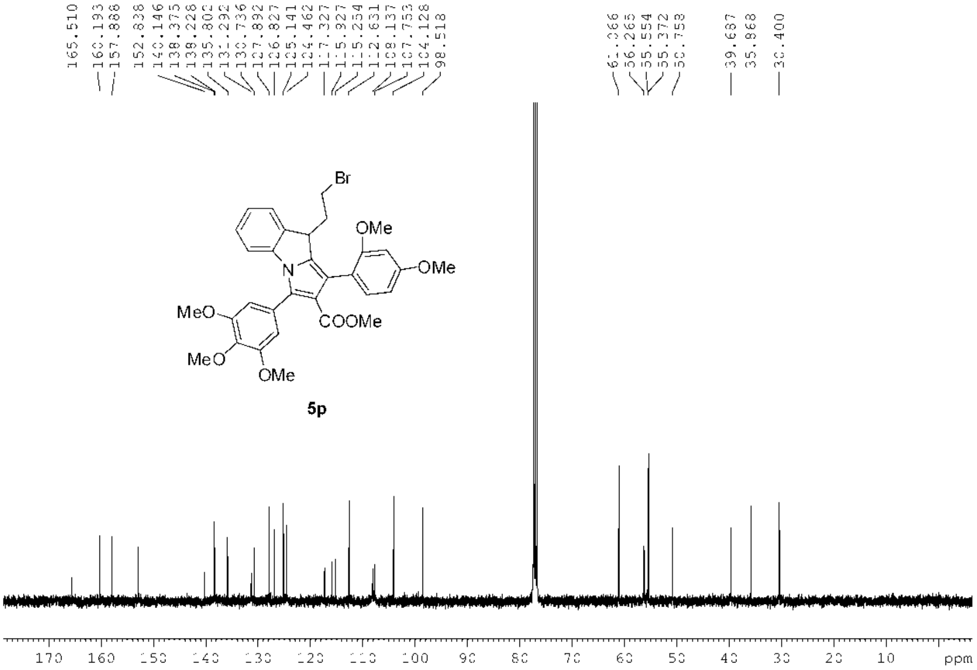
1.954
2.028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135.802
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125.141
124.462
117.327
115.927
115.254
112.631
108.137
107.753
104.128
98.518
61.066
56.265
55.554
55.372
50.753
39.687
35.868
30.400
Br
OMe
N
OMe
MeO
COOMe
MeO
OMe
5p
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160
150
140
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120
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30
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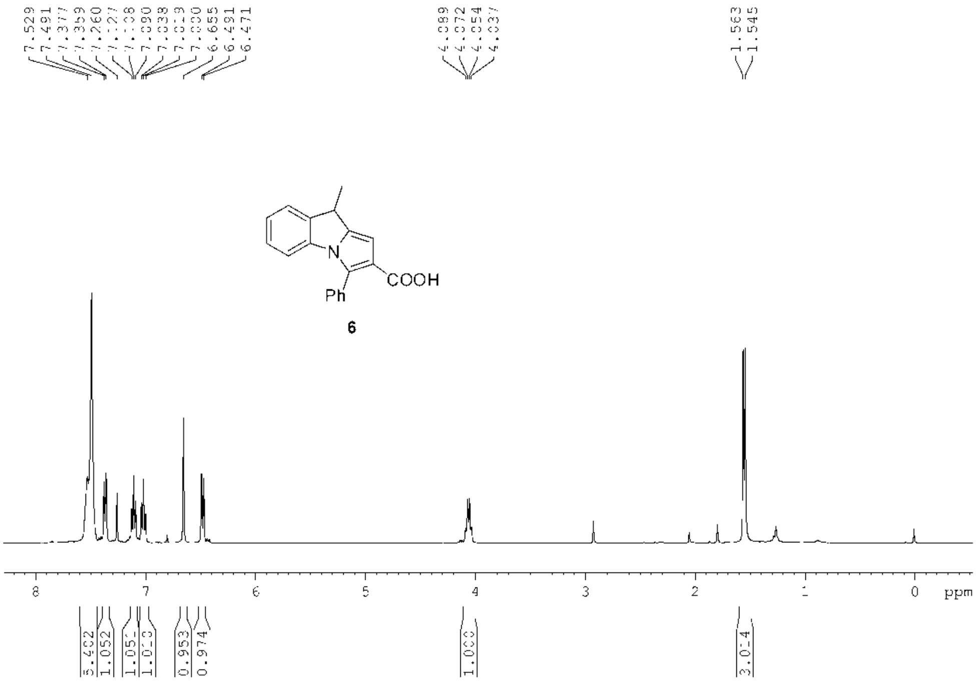
10
ppm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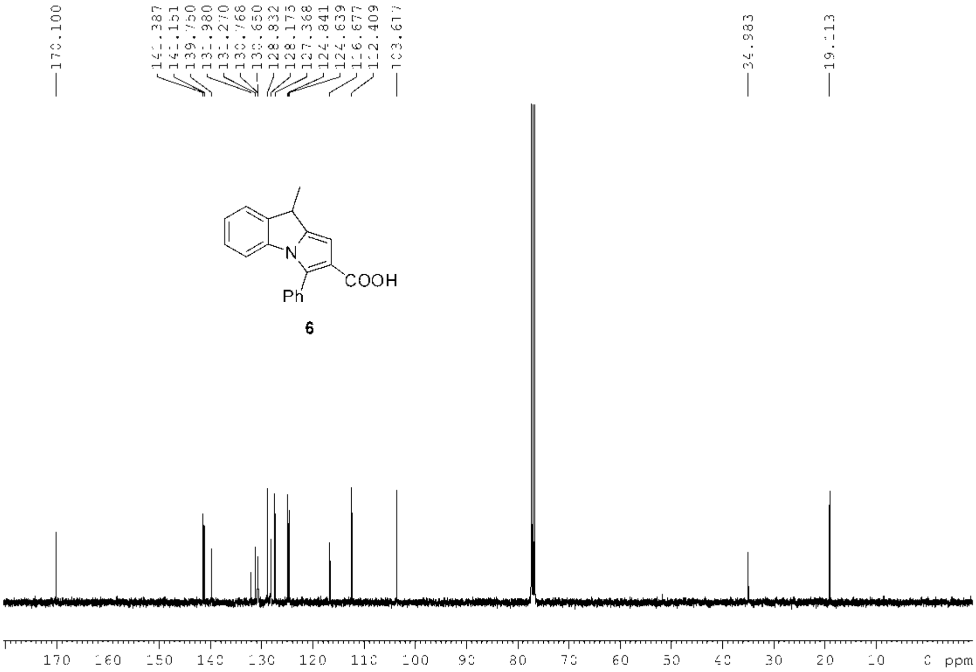
7.491
7.377
7.359
7.260
7.127
7.108
7.090
7.038
7.019
7.000
6.655
6.491
6.471
4.089
4.072
4.054
4.037
1.563
1.545
COOH
Ph
N
6
8
7
6
5
4
3
2
1
0
ppm
5.402
1.052
1.051
1.013
0.953
0.974
1.000
3.014


170.100
141.387
141.151
139.750
131.980
131.270
130.768
130.650
128.832
128.175
127.368
124.841
124.639
116.677
112.409
103.617
34.983
19.113
COOH
Ph
N
6
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160
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140
130
120
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100
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80
70
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20
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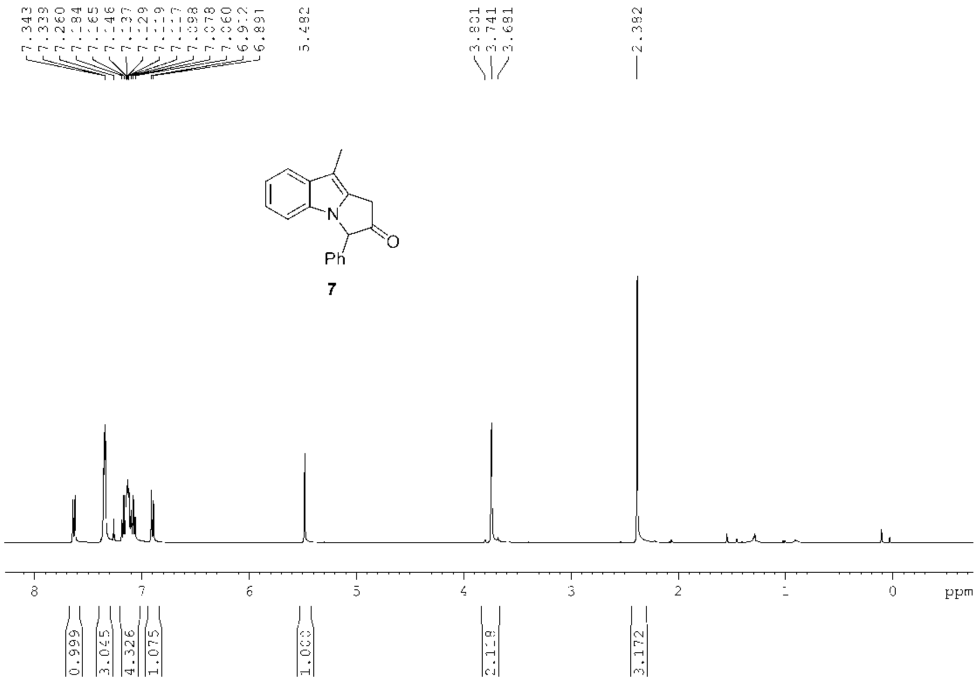
ppm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7.339
7.260
7.184
7.165
7.146
7.137
7.129
7.119
7.117
7.098
7.078
7.060
6.912
6.891
5.482
3.801
3.741
3.681
2.382
N
O
Ph
7
8
7
6
5
4
3
2
1
0
ppm
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1.000
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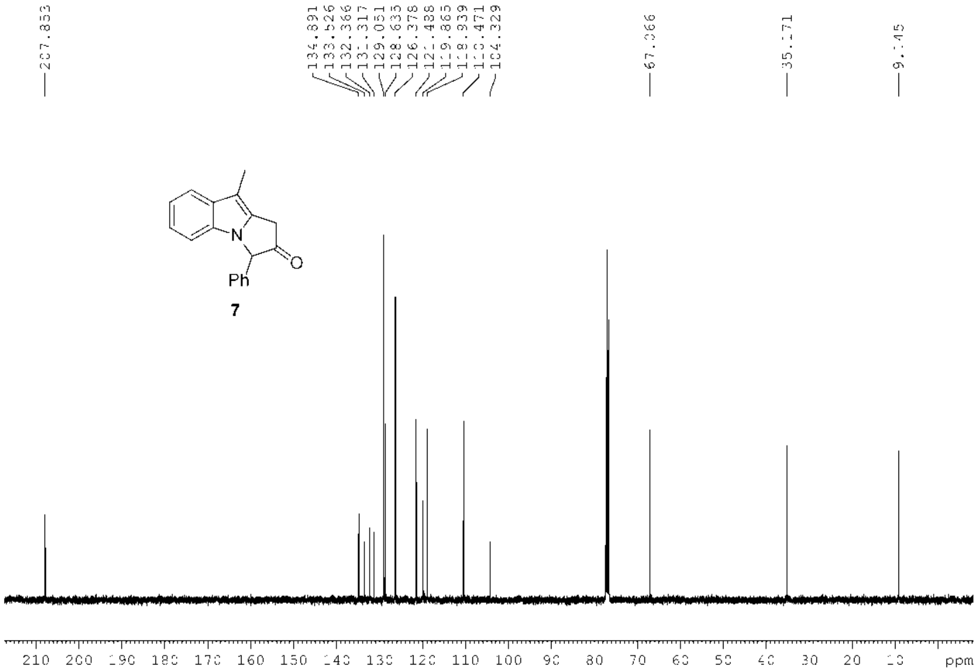
3.172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118.939
110.471
104.329
67.066
35.171
9.145
N
O
Ph
7
210
200
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150
140
130
120
110
100
90
80
70
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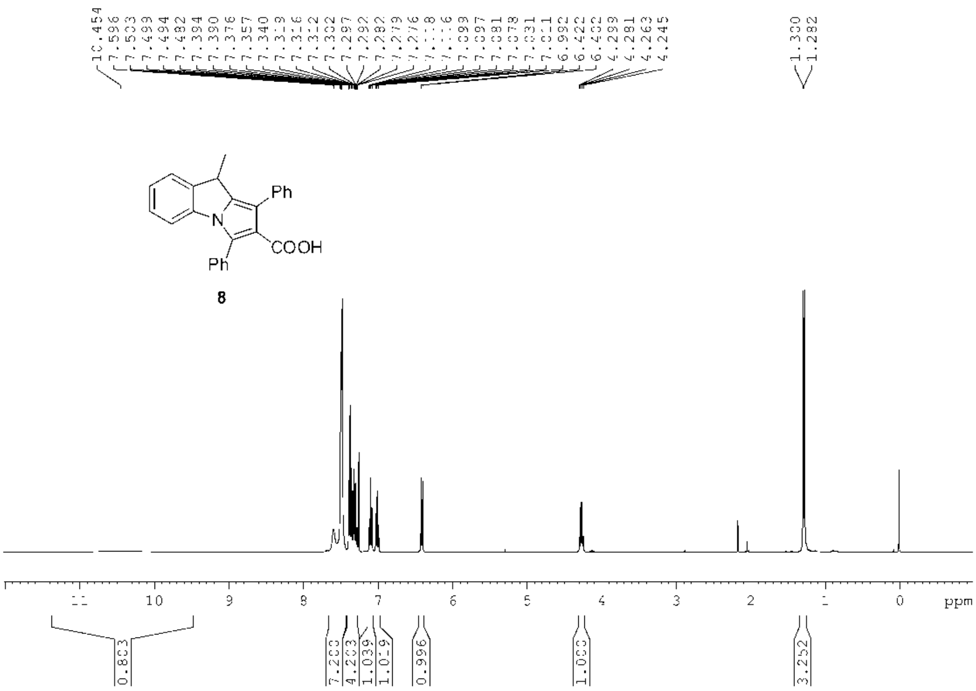
30
20
10
ppm


8

10.454
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7.503
7.499
7.494
7.482
7.394
7.390
7.376
7.357
7.340
7.319
7.316
7.312
7.302
7.297
7.292
7.282
7.279
7.276
7.118
7.116
7.099
7.097
7.081
7.078
7.031
7.011
6.992
6.422
6.403
4.299
4.281
4.263
4.245
1.300
1.282
Ph
N
COOH
Ph
11
10
9
8
7
6
5
4
3
2
1
0
ppm
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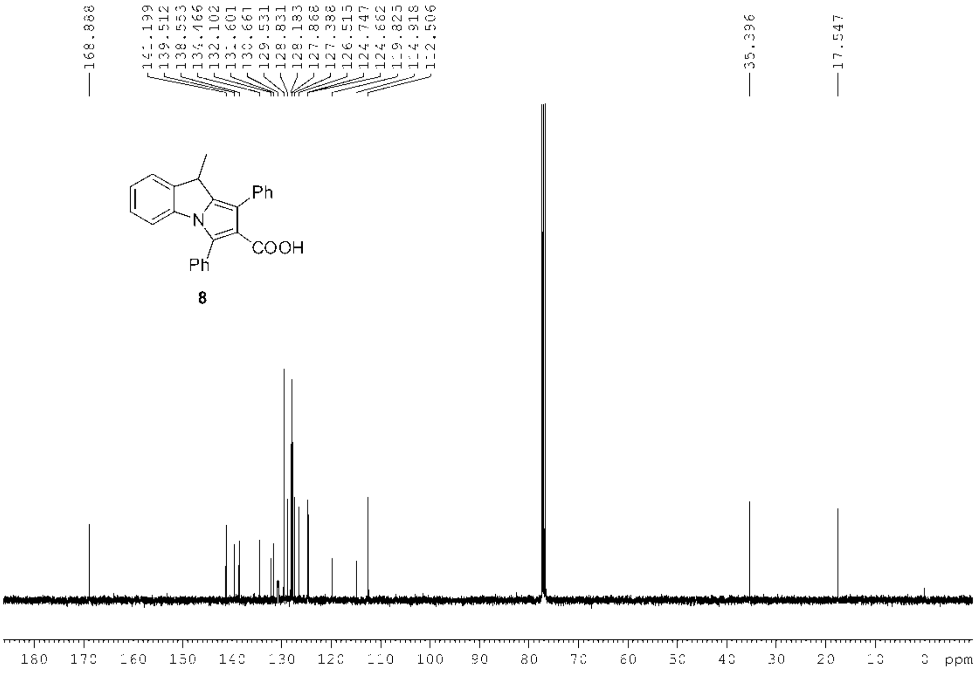
4.203
1.039
1.019
0.996
1.083
3.252


8

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138.553
134.465
132.102
131.601
130.661
129.531
128.831
128.183
127.868
127.338
126.515
124.747
124.662
119.825
114.918
112.506
35.396
17.547
Ph
N
COOH
Ph
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170
160
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140
130
120
110
100
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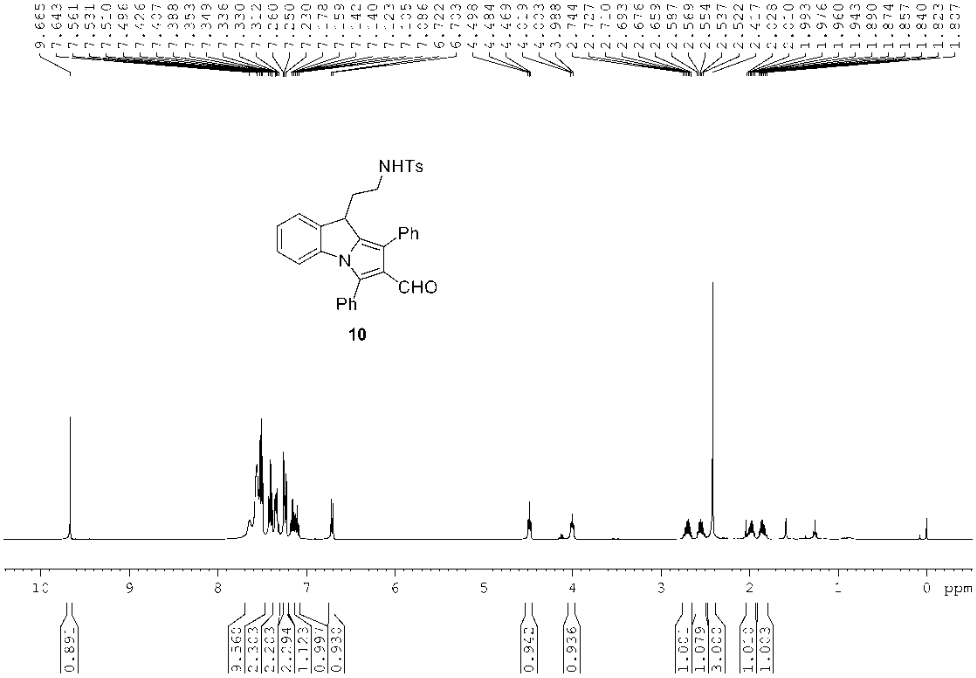
80
70
60
50
40
30
20
10
0
ppm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7.407
7.388
7.353
7.349
7.336
7.330
7.312
7.260
7.250
7.230
7.178
7.159
7.142
7.140
7.123
7.105
7.086
6.722
6.703
4.498
4.484
4.469
4.019
4.003
3.988
2.744
2.727
2.710
2.693
2.676
2.659
2.597
2.569
2.554
2.537
2.522
2.417
2.028
2.010
1.993
1.976
1.960
1.943
1.890
1.874
1.857
1.840
1.823
1.807
NHTs
Ph
N
CHO
Ph
10
10
9
8
7
6
5
4
3
2
1
0 ppm
0.891
9.560
2.303
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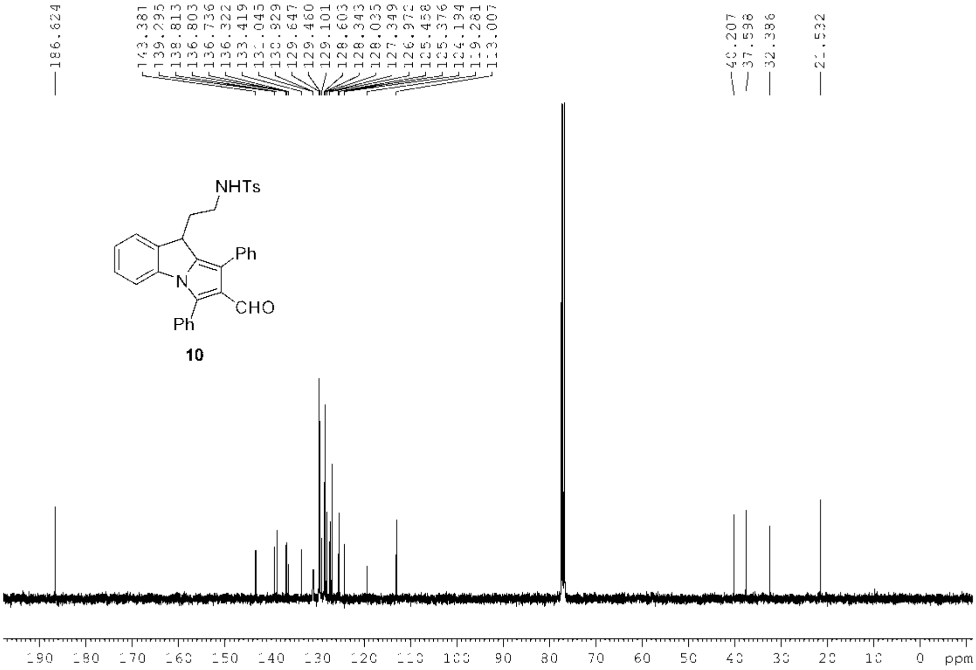
2.294
1.123
0.997
0.930
0.942
0.936
1.001
1.079
3.000
1.010
1.003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133.419
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129.460
129.101
128.603
128.343
128.035
127.349
126.972
125.458
125.376
124.194
119.281
113.007
40.207
37.598
32.386
21.532
NHTs
Ph
N
CHO
Ph
10
190
180
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150
140
130
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110
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80
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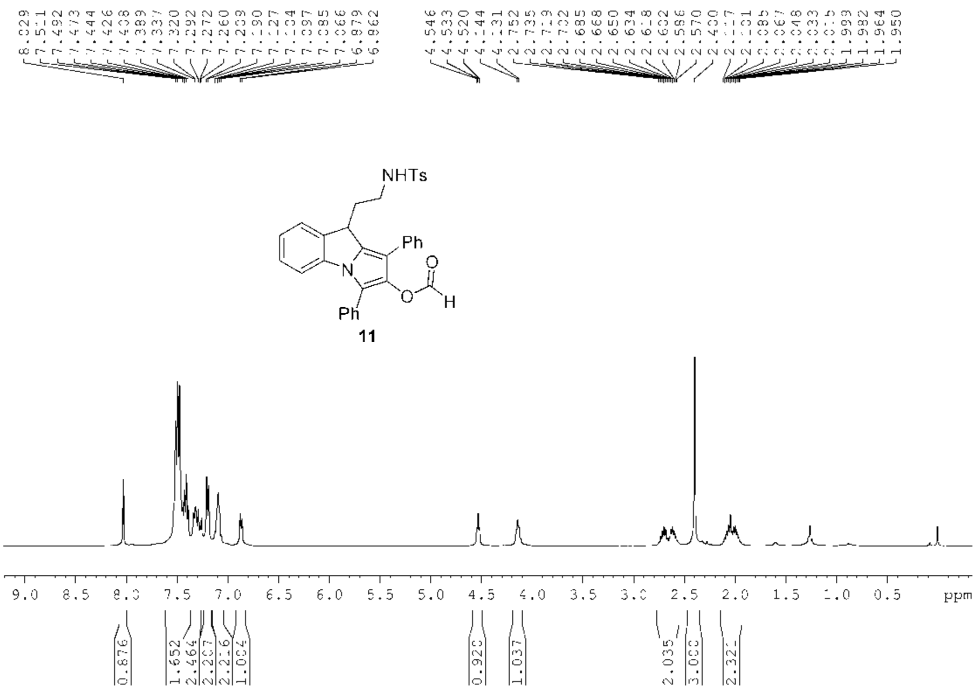
20
10
0 ppm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7.389
7.337
7.320
7.292
7.272
7.260
7.209
7.190
7.127
7.104
7.097
7.085
7.066
6.979
6.962
4.546
4.533
4.520
4.144
4.131
2.752
2.735
2.719
2.702
2.685
2.668
2.650
2.634
2.618
2.602
2.586
2.570
2.400
2.117
2.101
2.085
2.067
2.048
2.033
2.015
1.999
1.982
1.964
1.950
NHTs
Ph
O
O
H
N
Ph
11
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
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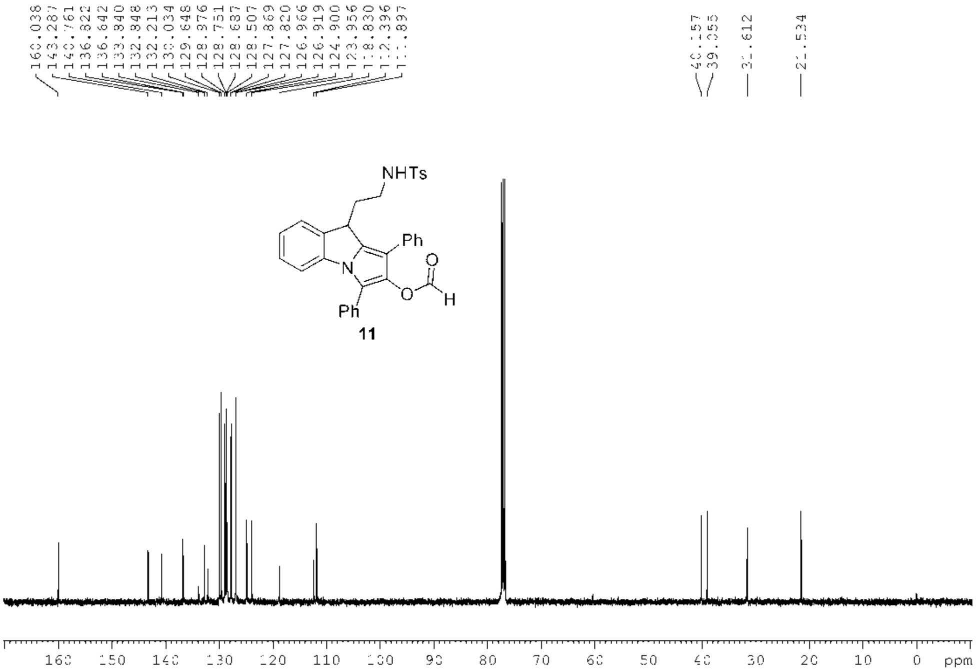
2.321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132.848
132.213
130.034
129.648
128.976
128.751
128.637
128.507
127.869
127.820
126.966
126.919
124.900
123.956
118.830
112.396
111.897
40.157
39.055
31.612
21.534
NHTs
Ph
O
O
H
N
Ph
11
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140
130
120
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60
50
40
30
20
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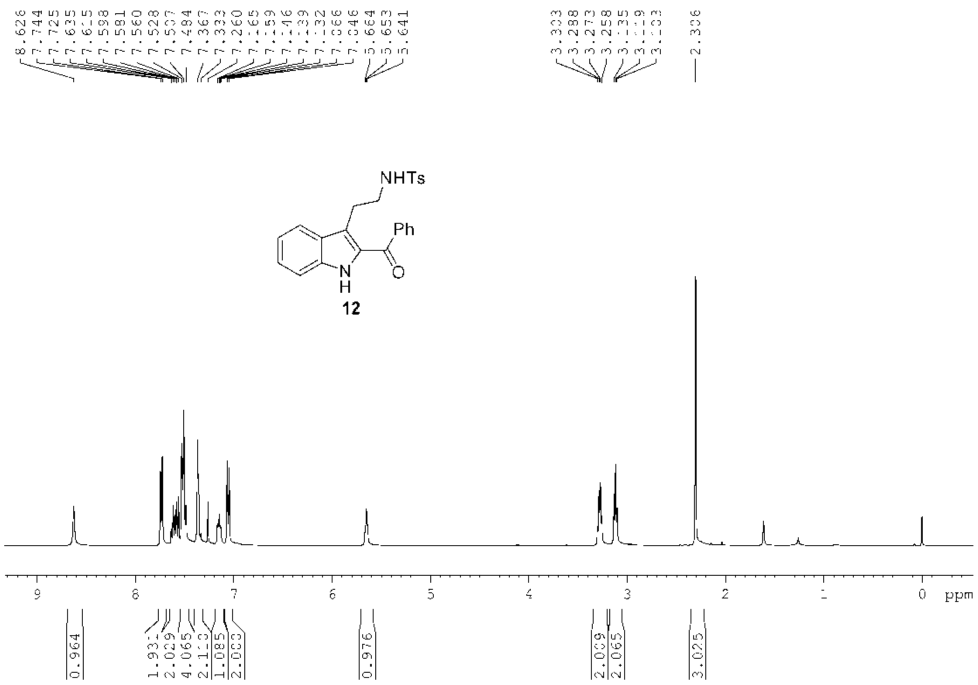
0
ppm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7.725
7.635
7.615
7.598
7.581
7.560
7.528
7.507
7.484
7.367
7.333
7.260
7.165
7.159
7.146
7.139
7.132
7.066
7.046
5.664
5.653
5.641
3.303
3.288
3.273
3.258
3.135
3.119
3.103
2.306
NHTs
Ph
N
H
O
12
9
8
7
6
5
4
3
2
1
0
ppm
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4.065
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1.085
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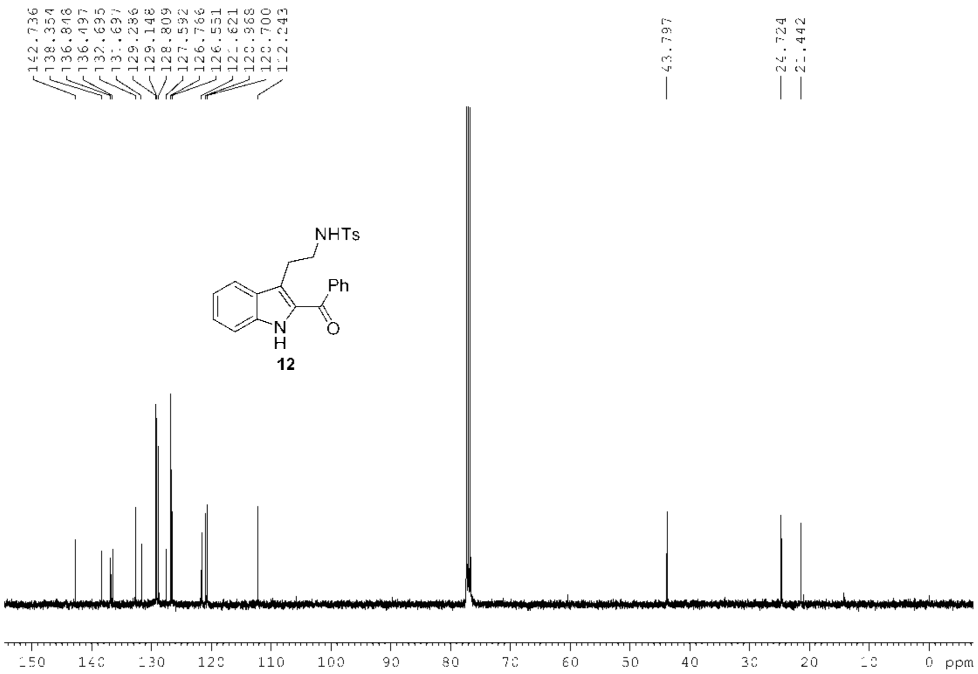
2.065
3.025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129.148
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127.592
126.766
126.551
121.621
120.968
120.700
112.243
43.797
24.724
21.442
NHTs
Ph
N
H
O
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140
130
120
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100
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80
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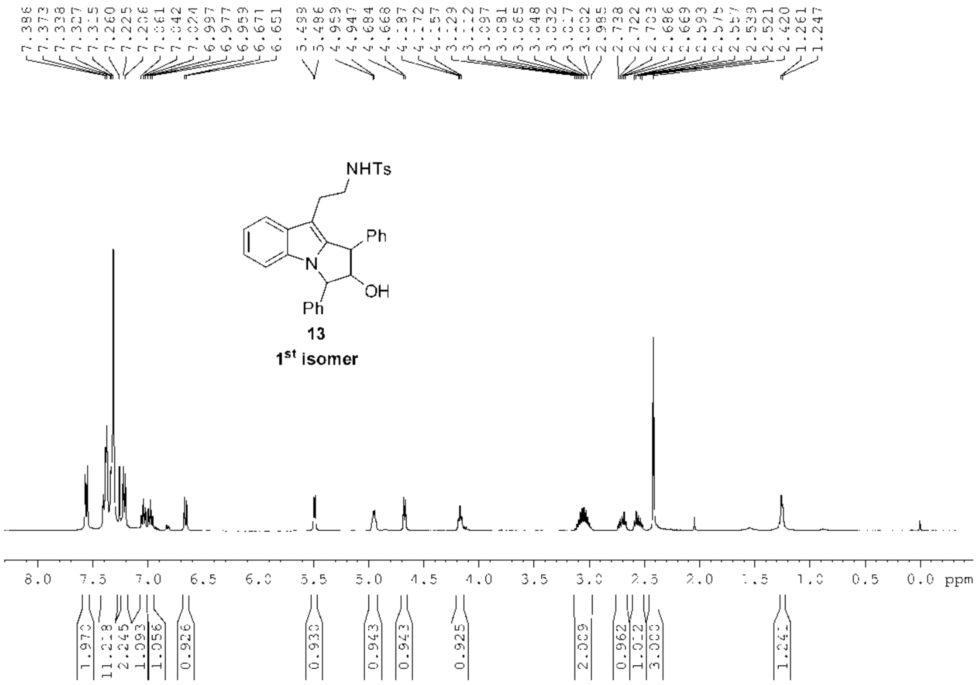
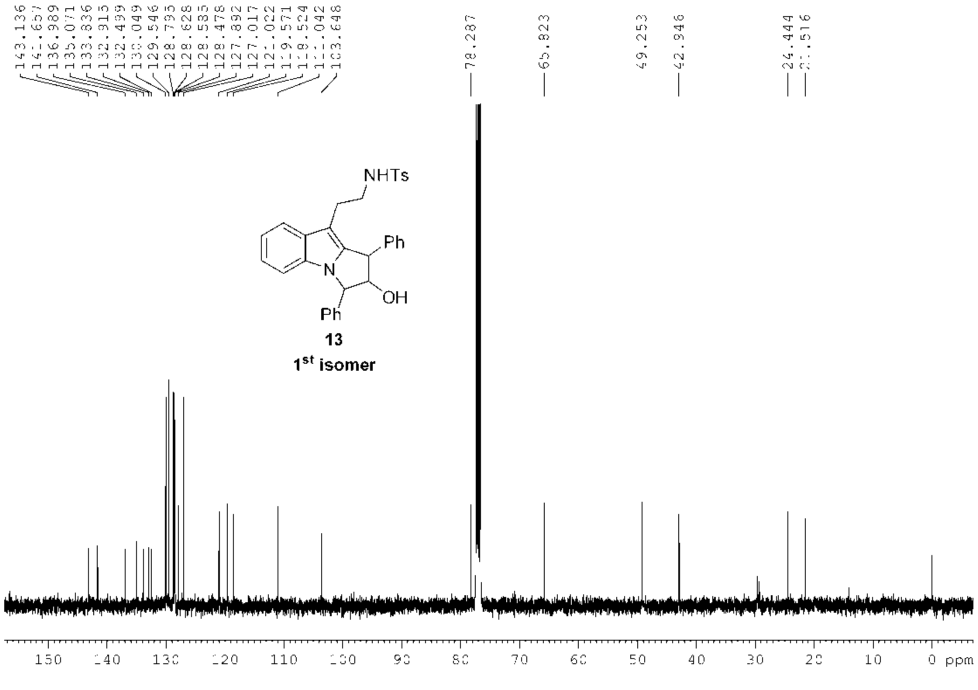
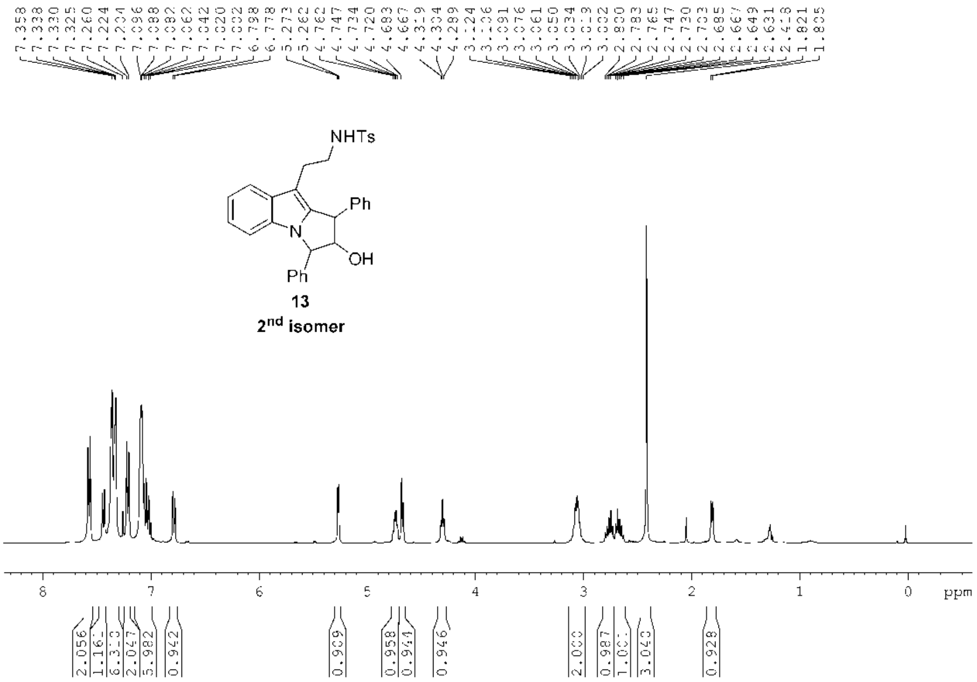
0
ppm



13
1st isomer



13
1st isomer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7.082
7.062
7.042
7.020
7.002
6.798
6.778
5.273
5.262
4.762
4.747
4.734
4.720
4.683
4.667
4.319
4.304
4.289
3.124
3.106
3.091
3.076
3.061
3.050
3.034
3.019
3.002
2.800
2.783
2.765
2.747
2.730
2.703
2.685
2.667
2.649
2.631
2.418
1.821
1.805
NHTs
Ph
N
OH
Ph
13
2nd isomer
8
7
6
5
4
3
2
1
0
ppm
2.056
1.161
6.313
2.047
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0.909
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0.946
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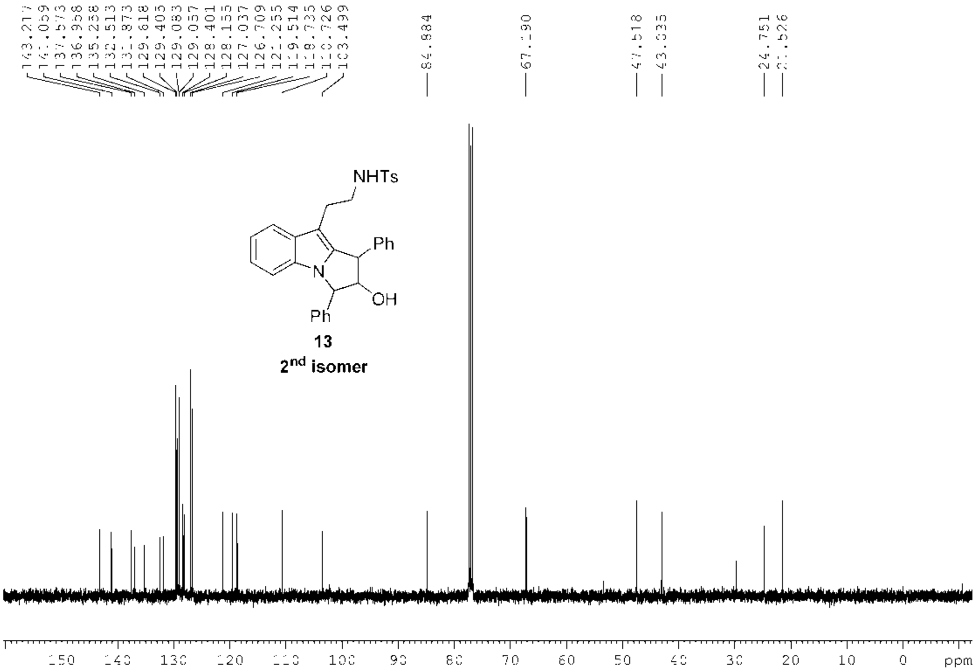
1.001
3.040
0.928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129.618
129.405
129.083
129.057
128.401
128.155
127.037
126.709
121.255
119.514
118.735
110.726
103.499
84.884
67.190
47.518
43.035
24.751
21.526
NHTs
Ph
N
OH
Ph
13
2nd isomer
150
140
130
120
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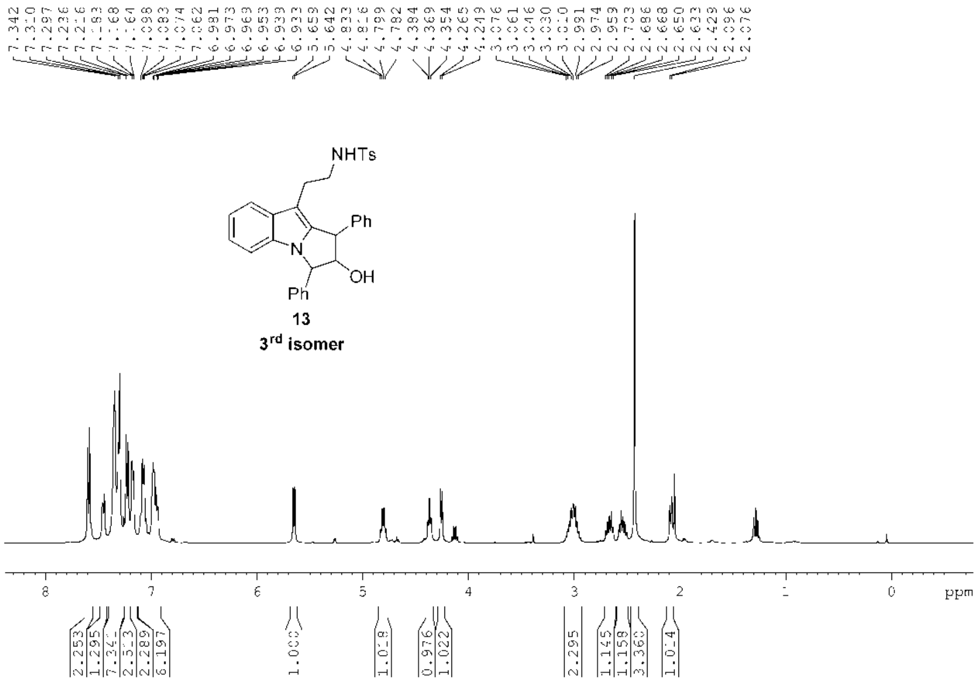
100
90
80
70
60
50
40
30
20
10
0
ppm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7.236
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7.183
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7.164
7.098
7.083
7.074
7.062
6.981
6.973
6.969
6.953
6.939
6.933
5.659
5.642
4.833
4.816
4.799
4.782
4.384
4.369
4.354
4.265
4.249
3.076
3.061
3.046
3.030
3.010
2.991
2.974
2.959
2.703
2.686
2.668
2.650
2.633
2.429
2.096
2.076
NHTs
Ph
N
OH
Ph
13
3rd isomer
8
7
6
5
4
3
2
1
0
ppm
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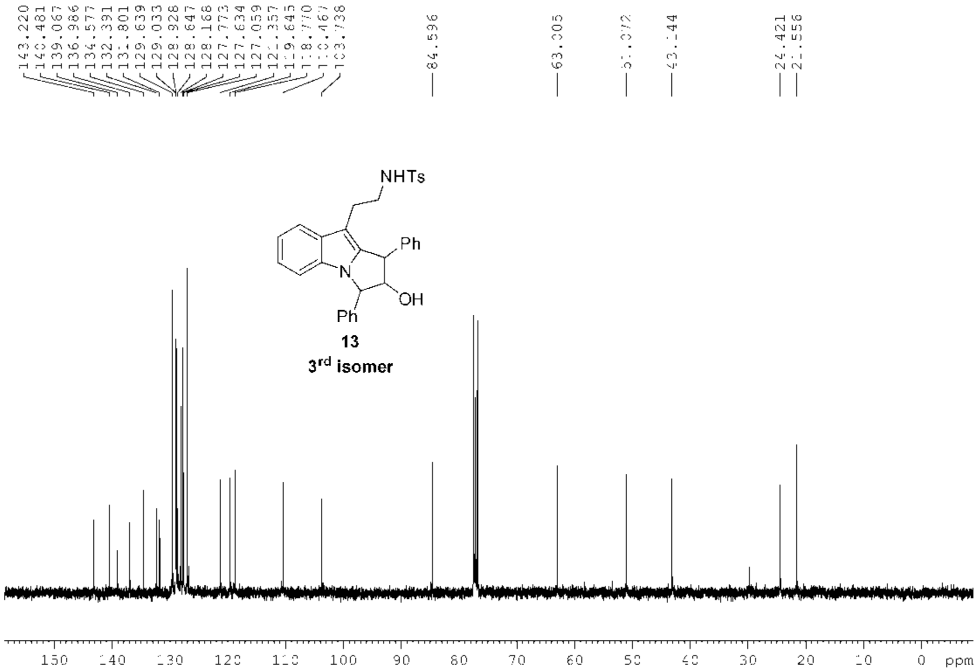
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128.168
127.773
127.634
127.059
121.357
119.645
118.770
110.467
103.738
84.596
63.305
51.072
43.144
24.421
21.556
NHTs
Ph
N
OH
Ph
13
3rd isomer
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm