Hydrazonyl Radical-Participated Tandem Reaction: A Strategy for the Synthesis of Pyrazoline-Functionalized Oxindoles

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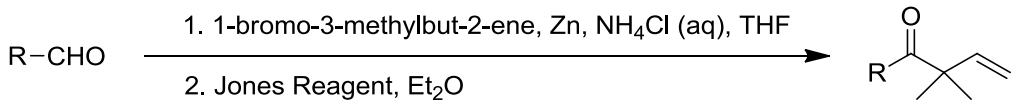
Supporting Information

General:

All reagents were purchased from commercial suppliers and used without further purification. Flash chromatography was carried out with silica gel (200-300 mesh). Analytical TLC was performed with silica gel GF254 plates, and the products were visualized by UV detection. ^{1}H NMR and ^{13}C NMR (400 MHz and 100 MHz, respectively) spectra were recorded in $CDCl_3$. Chemical shifts (δ) are reported in ppm using TMS as internal standard and spin-spin coupling constants (J) are given in Hz. The high resolution mass spectra (HRMS) were measured on a Bruker Daltonics APEX II 47e spectrometer by ESI. Data collections for crystal structure were performed at room temperature (293 K) using Mo $K\alpha$ radiation on a Bruker APEXII diffractometer. Integration of the frames and data reduction was carried out using SAINT. The structure was solved by direct methods using SHELXS-97.

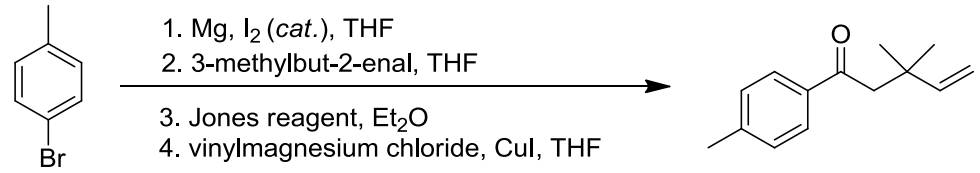
Methods for the synthesis of ketones:[1]



(1) A round bottomed flask charged with a solution of the 3-bromo-2-methylprop-1-ene (2.0 equiv) and the aldehyde (1.0 equiv) in THF/H_2O (1:1) was kept at 0 ^{o}C with stirring. The Zn powder (2.0 equiv) was slowly added to the solution and the resulting suspension was stirred at RT for 24 h as monitored by TLC. 1 N hydrochloride solution was added at 0 ^{o}C. The THF layer was separated from the aqueous layer, which was extracted with diethyl ether for 3 times. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated in vacuo. The crude product was directly used in the next step without further purification.

(2) To the previous prepared mixture was added a solution of Jones reagent (12 mL) and H_2O (12 mL) at 0 ^{o}C. The mixture was stirred at 0 ^{o}C for 1–2 h, H_2O (50 mL) was added, and extracted with Et_2O (300 mL). The organic extracts were washed with

brine (30 mL), dried (Na_2SO_4) and concentrated in vacuo. Purification of the residue was performed by silica gel column chromatography (hexanes–EtOAc 40:1) to give product in about 75% yield.



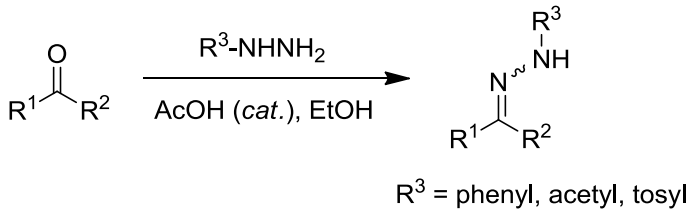
(1) Under Ar atmosphere, a solution of 1-bromo-4-methylbenzene (20 mmol) and THF (20 mL) was slowly added to a mixture of Mg (24 mmol), I_2 (*cat.*) and THF (20 mL). Then the mixture was stirred at reflux for 6 h.

(2) A solution of 3-methylbut-2-enal (22 mmol) and THF (20 mL) was added to the previous prepared solution of Grignard reagent. The mixture was stirred at RT for 2 h as monitored by TLC. The reaction was quenched adding saturated NH_4Cl, and extracted with Et_2O. The organic extracts were washed with brine, dried (Na_2SO_4) and concentrated to 100 mL in vacuo.

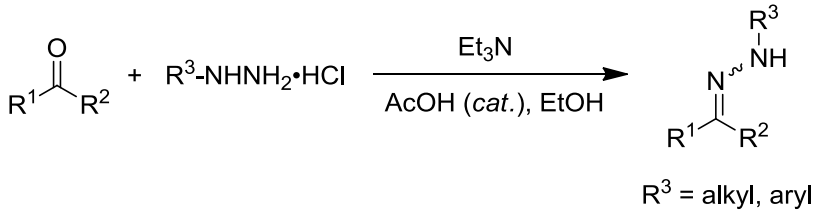
(3) To the previous prepared mixture was added a solution of Jones reagent (12 mL) and H_2O (12 mL) at 0 ^oC. The mixture was stirred at 0 ^oC for 1–2 h, H_2O (50 mL) was added, and extracted with Et_2O (300 mL). The organic extracts were washed with brine (30 mL), dried (Na_2SO_4) and concentrated in vacuo. Purification of the residue was performed by silica gel column chromatography (hexanes–EtOAc 40:1) to give product in 75% yield (2.61 g, 15 mmol).

(4) Under Ar atmosphere, a mixture of the previous prepared 3-methyl-1-(p-tolyl)-but-2-en-1-one (10 mmol), CuI (1 mmol) and THF (20 mL) was cooled to -40 ^oC, and a solution of vinylmagnesium chloride (12 mmol) was added to the mixture. Then the mixture was stirred at RT overnight. The reaction was quenched adding saturated NH_4Cl, and extracted with Et_2O. The organic extracts dried (Na_2SO_4) and concentrated in vacuo. Purification of the residue was performed by silica gel column chromatography (hexanes–EtOAc 100:1) to give product in 60% yield (1.21 g, 6 mmol).

Methods for the synthesis of substituted hydrazones:[1]

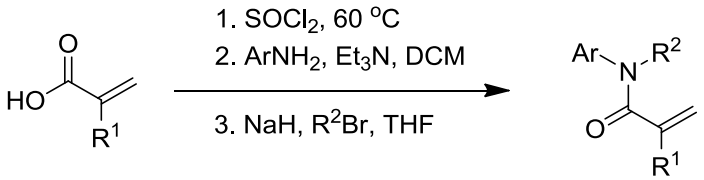


To a solution of the ketone (1.0 equiv) in anhydrous ethanol was added *N*-substituted hydrazines (1.5 equiv) and acetic acid (0.2 equiv). The mixture was stirred at reflux and monitored by TLC. Then the mixture was directly concentrated in vacuo. The crude material was purified by flash chromatography on silica gel to afford the hydrazone in 60–70% yield.



To a solution of the ketone (1.0 mmol) in 2 mL of anhydrous ethanol and acetic acid (0.2 mL) was added a solution of *N*-substituted hydrazine hydrochloride (1.5 mmol) and Et_3N (0.2 mL, 1.5 mmol) in 3mL of ethanol. The reaction mixture was stirred overnight at reflux and monitored by TLC. Then the mixture was directly concentrated in vacuo. The crude material was purified by flash chromatography on silica gel to afford the hydrazone in 45–60% yield.

Methods for the synthesis of substituted amide:[2]



(1) A mixture of acrylic acid (12 mmol) and $SOCl_2$ (14 mmol) was stirred at 60 ^oC for 2 h.

(2) A mixture of arylamine (10 mmol), Et_3N (12 mmol) and DCM (20 mL) was stirred

at 0 ^{o}C, then a solution of the previous prepared acyl chloride and DCM (10 mL) was added slowly into the mixture. And the reaction mixture was stirred at RT and monitored by TLC. The reaction was quenched adding saturated $NaHCO_3$, and extracted with DCM. The organic extracts dried (Na_2SO_4) and concentrated in vacuo. Purification of the residue was performed by silica gel column chromatography (hexanes–EtOAc 5:1) to give product in about 70% yield.

(3) A mixture of acrylamide (8 mmol), and THF (20 mL) was stirred at 0 ^{o}C, NaH (10 mmol) was added slowly to the mixture. Then the reaction mixture was stirred at 0 ^{o}C for 30 min, and R^2Br (10 mmol) was added to the mixture. At last, the mixture was stirred at RT for 2h and monitored by TLC. The reaction was quenched by adding H_2O, and extracted with Et_2O. The organic extracts dried (Na_2SO_4) and concentrated in vacuo. Purification of the residue was performed by silica gel column chromatography (hexanes–EtOAc 10:1) to give product in about 80% yield.

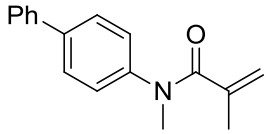
General experimental procedure:

A mixture of *N*-aryl acrylamide **1** (0.5 mmol), hydrazone **2** (1.0 mmol) and DTBP (3.25 mmol) was placed in a 10 mL Schlenk tube and stirred at 100 ^{o}C under argon for 72 h. When the starting materials were consumed completely as monitored by TLC, the reaction mixture was isolated by silica gel column chromatography to give the product in 42–94% yield. The identity and purity of the product was confirmed by ^{1}H and ^{13}C NMR spectroscopic analysis.

Reference:

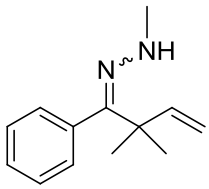
1. X. Y. Duan, X. L. Yang, R. Fang, X. X. Peng, W. Yu and B. Han, *J. Org. Chem.*, 2013, **78**, 10692;
2. L. N. Guo, H. Wang and X. H. Duan, *Chem. Commun.*, 2013, **49**, 7540;

Analytical data for new substrates:



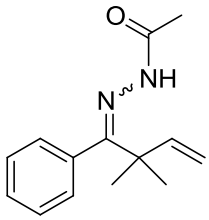
N-([1, 1'-biphenyl]-4-yl)-N-methylmethacrylamide (1i)

Yellow solid, mp 94–95 ^{o}C; R_f = 0.55 (hexanes/ethyl acetate 5:1, twice); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59–7.55 (m, 4H), 7.44 (t, J = 8.0 Hz, 2H), 7.35 (t, J = 7.2 Hz, 1H), 7.20 (d, J = 8.4 Hz, 2H), 5.07 (s, 1H), 5.05 (s, 1H), 3.38 (s, 3H), 1.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.9, 143.7, 140.6, 139.9, 139.6, 128.8, 127.7, 127.5, 126.9, 126.6, 119.4, 37.6, 20.3; ESI-HRMS: *m/z* Calcd for $C_{17}H_{17}NO+H^+$: 252.1383, found 252.1381.



1-(2, 2-dimethyl-1-phenylbut-3-en-1-ylidene)-2-methylhydrazine (2f)

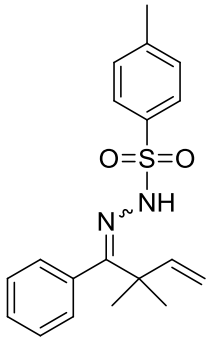
Yellow oil; R_f = 0.40 (hexanes/ethyl acetate 100:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41–7.38 (m, 2H), 7.35-7.40 (m, 1H), 6.77 (dd, J = 6.8 Hz, J = 1.6 Hz, 2H), 5.98 (dd, J = 17.6 Hz, J = 10.4 Hz,1H), 4,99–4.90 (m, 2H), 4.39 (br, 1H), 2.81 (s, 3H), 1.22 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.1, 145.7, 134.3, 128.6, 128.5, 128.0, 111.4, 43.5, 37.7, 25.5; ESI-HRMS: *m/z* Calcd for $C_{13}H_{18}N_2+H^+$: 203.1543, found 203.1540.



N'-(2, 2-dimethyl-1-phenylbut-3-en-1-ylidene) acetohydrazide (2g)

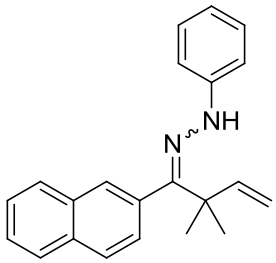
Yellow oil; R_f = 0.35 (hexanes/ethyl acetate 10:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 (br, 1H), 7.44–7.39 (m, 3H), 7.01 (dd, J = 7.6 Hz, J = 1.6 Hz, 2H), 5.92 (dd, J = 18.8 Hz, J = 10.8 Hz, 1H), 5.06–4.96 (m, 2H), 2.30 (s, 3H), 1.26 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.8, 158.3, 144.2, 131.9, 129.1, 129.0, 128.0, 112.8, 44.2,

25.2, 20.4; ESI-HRMS: *m/z* Calcd for $C_{14}H_{18}N_2O+H^+$: 231.1492, found 231.1489.



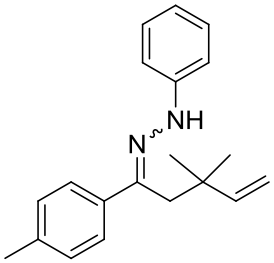
N'-(2,2-dimethyl-1-phenylbut-3-en-1-ylidene)-4-methylbenzenesulfonohydrazide (2h)

White solid, mp 102–103 ^oC; R_f = 0.35 (hexanes/ethyl acetate 5:1); ^1H NMR (400 MHz, $CDCl_3$): δ 7.78 (d, J = 8.4 Hz, 2H), 7.38 (t, J = 3.0 Hz, 3H), 7.33 (d, J = 8.0 Hz, 2H), 6.96 (br, 1H), 6.81 (dd, J = 5.2 Hz, J = 2.8 Hz, 2H), 5.73 (dd, J = 17.6 Hz, J = 10.4 Hz,1H), 4.97–4.82 (m, 2H), 2.46 (s, 3H), 1.16 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.9, 143.9, 143.8, 135.3, 131.4, 129.34, 129.31, 129.1, 127.9, 127.6, 113.1, 44.4, 25.1, 21.6; ESI-HRMS: *m/z* Calcd for $C_{19}H_{22}N_2O_2S+H^+$: 343.1475, found 343.1474.



1-(2, 2-dimethyl-1-(naphthalen-2-yl) but-3-en-1-ylidene)-2-phenylhydrazine (2m)

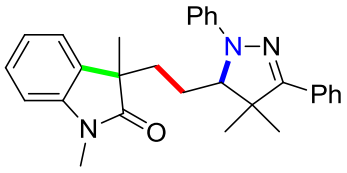
Yellow oil; R_f = 0.55 (hexanes/ethyl acetate 40:1); ^1H NMR (400 MHz, $CDCl_3$): δ 7.92–7.84 (m, 3H), 7.60 (s, 1H), 7.55–7.51 (m, 2H), 7.21–7.13 (m, 3H), 6.91–6.86 (m, 3H), 6.77–6.74 (m, 1H), 6.12-6.04 (m, 1H), 5.05–4.96 (m, 2H), 1.36 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.0, 145.6, 145.3, 133.1, 133.0, 130.9, 129.0, 128.7, 128.2, 128.1, 127.8, 126.7, 126.5, 119.4, 112.6, 112.1, 44.3, 25.7; ESI-HRMS: *m/z* Calcd for $C_{22}H_{22}N_2+H^+$: 315.1856, found 315.1851.



1-(3, 3-dimethyl-1-(p-tolyl) pent-4-en-1-ylidene)-2-phenylhydrazine (2q)

Yellow oil; R_f = 0.60 (hexanes/ethyl acetate 40:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27 (br, 1H), 7.65 (d, *J* = 8.4 Hz, 2H), 7.45 (br, 1H), 7.28–7.21 (m, 6H), 7.19–7.15 (m, 7H), 7.09 (d, *J* = 8.2 Hz, 2H), 7.95 (d, *J* = 8.0 Hz, 1H), 6.85 (t, *J* = 7.2 Hz, 1H), 6.77 (t, *J* = 7.2 Hz, 1H), 5.97–5.90 (m, 1H), 5.82–5.75 (m, 1H), 5.12–5.00 (m, 2H), 4.86–4.76 (m, 2H), 2.76 (s, 2H), 2.63 (s, 2H), 2.39 (s, 3H), 2.36 (s, 3H), 1.09 (s, 6H), 1.01 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.2, 148.1, 145.3, 143.6, 138.5, 137.59, 137.57, 132.5, 129.8, 129.2, 129.1, 128.9, 127.8, 126.1, 119.9, 119.3, 113.0, 112.6, 111.5, 110.0, 50.4, 38.3, 38.1, 37.6, 28.0, 27.2, 21.3, 21.1; ESI-HRMS: *m/z* Calcd for $C_{20}H_{24}N_2$+H^+: 293.2012, found 293.2010.

Analytical data for products:

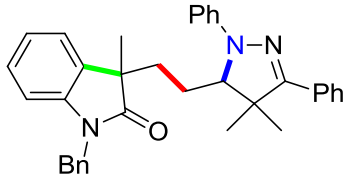


(dr ≈ 1.51:1)

3-(2-(4, 4-dimethyl-1, 3-diphenyl-4, 5-dihydro-1H-pyrazol-5-yl) ethyl)-1, 3-dimethylindolin-2-one (3a)

Yellow oil; (192 mg, 88% yield); R_f = 0.45 (hexanes/acetone 5:1, twice); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (d, *J* = 8.0 Hz, 2H), 7.66 (d, *J* = 8.0 Hz, 2H), 7.39–7.29 (m, 7H), 7.23–7.14 (m, 7H), 7.07–7.01 (m, 3H), 6.91–6.73 (m, 6H), 6.45 (d, *J* = 7.2 Hz, 1H), 3.82 (d, *J* = 6.0 Hz, 1H), 3.61 (d, *J* = 8.0 Hz, 1H), 3.14 (s, 3H), 3.13 (s, 3H), 2.01 (td, *J* = 6.0 Hz, *J* = 4.0 Hz, 1H), 1.82 (td, *J* = 6.0 Hz, *J* = 4.0 Hz, 1H), 1.76 (td, *J* = 8.0 Hz, *J* = 4.0 Hz, 1H), 1.63–1.52 (m, 3H), 1.42 (s, 3H), 1.40 (s, 3H), 1.37 (s, 3H), 1.33 (s, 3H), 1.31 (s, 3H), 1.29–1.25 (m, 2H), 1.20 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 180.4, 180.0, 155.6, 155.2, 144.8, 144.5, 143.4, 143.2, 133.4, 133.1, 132.58, 132.57,

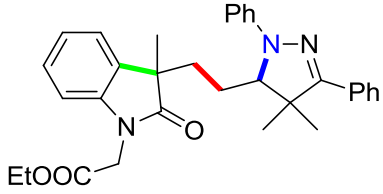
129.1, 128.9, 128.43, 128.35, 128.31, 128.3, 128.0, 127.5, 126.9, 122.8, 122.6, 122.4, 122.3, 119.5, 119.1, 114.4, 114.2, 108.2, 107.7, 72.1, 71.3, 50.0, 49.2, 48.3, 48.2, 34.9, 32.8, 28.09, 28.06, 26.2, 26.1, 24.6, 23.8, 22.3, 22.1, 19.5, 19.2; ESI-HRMS: *m/z* Calcd for $C_{29}H_{31}N_3O+H^+$: 438.2540, found 438.2532.



(dr ≈ 1.79:1)

1-benzyl-3-(2-(4, 4-dimethyl-1, 3-diphenyl-4, 5-dihydro-1H-pyrazol-5-yl) ethyl)-3-methylindolin-2-one (3b)

Yellow oil; (200 mg, 78% yield); R_f = 0.55 (hexanes/acetone 5:1, twice); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (d, *J* = 6.8 Hz, 2H), 7.66 (d, *J* = 6.8 Hz, 2H), 7.40–7.30 (m, 9H), 7.29–7.10 (m, 13H), 7.06–7.00 (m, 5H), 6.93 (d, *J* = 8.0 Hz, 1H), 6.85 (t, *J* = 7.2 Hz, 1H), 6.79 (t, *J* = 7.2 Hz, 2H), 6.68–6.64 (m, 2H), 6.49 (d, *J* = 6.8 Hz, 1H), 4.83 (dd, *J* = 36.0 Hz, *J* = 15.6 Hz, 4H), 3.81 (d, *J* = 5.2 Hz, 1H), 3.62 (dd, *J* = 7.6 Hz, *J* = 3.2 Hz, 1H), 2.07 (td, *J* = 13.0 Hz, *J* = 5.0 Hz, 1H), 1.92 (td, *J* = 13.2 Hz, *J* = 4.3 Hz, 1H), 1.79 (td, *J* = 12.6 Hz, *J* = 3.6 Hz, 1H), 1.65 (td, *J* = 13.2 Hz, *J* = 3.6 Hz, 1H), 1.60–1.42 (m, 2H), 1.41 (s, 3H), 1.39 (s, 3H), 1.38 (s, 3H), 1.35 (s, 3H), 1.32-1.31 (m, 1H), 1.30 (s, 3H), 1.29–1.27 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 180.4, 180.1, 155.5, 155.1, 144.8, 144.5, 142.4, 142.1, 136.1, 136.0, 133.3, 133.0, 132.5, 129.1, 128.8, 128.65, 128.64, 128.34, 128.27, 128.23, 128.19, 127.8, 127.5, 127.4, 127.3, 127.1, 126.85, 126.81, 122.7, 122.6, 122.3, 119.4, 119.1, 114.4, 114.2, 109.1, 108.7, 72.0, 71.1, 49.9, 49.2, 48.19, 48.16, 43.6, 43.5, 34.9, 32.8, 28.0, 27.9, 24.9, 24.0, 22.5, 22.2, 19.3, 19.1; ESI-HRMS: *m/z* Calcd for $C_{35}H_{35}N_3O+H^+$: 514.2853, found 514.2844.

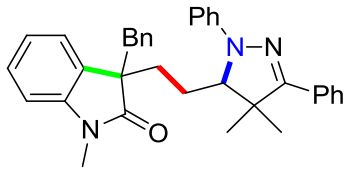


(dr ≈ 1.07:1)

Ethyl 2-(3-(2-(4, 4-dimethyl-1, 3-diphenyl-4, 5-dihydro-1H-pyrazol-5-yl) ethyl)-3-methyl-2-oxoindolin-1-yl) acetate (3c)

Yellow oil; (211 mg, 83% yield); R_f = 0.45 (hexanes/acetone 5:1, twice); ^{1}H NMR

(400 MHz, $CDCl_3$): δ 7.74 (d, J = 7.2 Hz, 2H), 7.67 (dd, J = 8.0 Hz, J = 1.6 Hz, 2H), 7.41–7.32 (m, 7H), 7.23–7.14 (m, 7H), 7.03 (d, J = 8.0 Hz, 2H), 6.92 (d, J = 8.0 Hz, 2H), 6.86–6.78 (m, 3H), 6.66 (d, J = 8.0 Hz, 1H), 6.63 (d, J = 8.0 Hz, 1H), 6.43 (d, J = 7.2 Hz, 1H), 4.56–4.48 (m, 2H), 4.31–4.24 (m, 2H), 4.22–4.07 (m, 4H), 3.86 (d, J = 4.8 Hz, 1H), 3.62 (dd, J = 8.0 Hz, J = 2.8 Hz, 1H), 2.06 (td, J = 12.0 Hz, J = 5.2 Hz, 1H), 1.88–1.79 (m, 2H), 1.68–1.47 (m, 3H), 1.42 (s, 3H), 1.40 (s, 3H), 1.37 (s, 3H), 1.35 (s, 3H), 1.33 (s, 3H), 1.30–1.21 (m, 8H), 1.22 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 180.4, 180.0, 167.6, 167.5, 155.5, 155.2, 144.8, 144.5, 142.0, 141.8, 133.1, 132.8, 132.6, 129.0, 128.8, 128.4, 128.3, 128.22, 128.16, 128.0, 127.4, 126.9, 123.1, 122.9, 122.54, 122.47, 119.4, 119.0, 114.4, 114.1, 108.0, 107.5, 72.1, 71.2, 61.6, 50.0, 49.1, 48.22, 48.21, 41.2, 41.1, 35.0, 32.6, 31.9, 29.7, 28.0, 24.7, 24.0, 22.7, 22.4, 22.0, 19.4, 19.0, 14.1; ESI-HRMS: *m/z* Calcd for $C_{32}H_{35}N_3O_3$+H^+: 510.2751, found 510.2743.

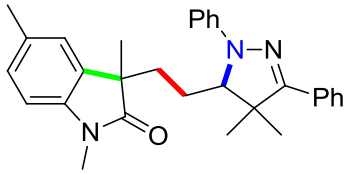


(dr ≈ 1.58:1)

3-benzyl-3-(2-(4, 4-dimethyl-1, 3-diphenyl-4, 5-dihydro-1H-pyrazol-5-yl) ethyl)-1-methylindolin-2-one (3f)

Yellow oil; (167 mg, 65% yield); R_f = 0.25 (hexanes/acetone 5:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (d, J = 8.8 Hz, 2H), 7.67 (dd, J = 8.0 Hz, J = 1.6 Hz, 2H), 7.43–7.31 (m, 7H), 7.21–7.12 (m, 4H), 7.10-6.98 (m, 9H), 6.91 (d, J = 8.0 Hz, 2H), 6.86–6.73 (m, 6H), 6.67 (d, J = 6.8 Hz, 3H), 6.53–6.48 (m, 2H), 6.21 (d, J = 6.8 Hz, 1H), 3.86 (d, J = 8.0 Hz, 1H), 3.63 (dd, J = 8.0 Hz, J = 3.2 Hz, 1H), 3.05–2.79 (m, 10H), 2.21 (td, J = 12.0 Hz, J = 4.0 Hz, 1H), 2.01–1.87 (m, 2H), 1.72–1.55 (m, 3H), 1.47 (s, 3H), 1.42 (s, 3H), 1.40 (s, 3H), 1.36 (s, 3H), 1.26–1.18 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 178.9, 178.5, 155.5, 155.1, 144.7, 144.5, 143.9, 143.6, 135.6, 135.5, 132.53, 132.51, 130.4, 130.2, 129.9, 129.8, 129.0, 128.8, 128.4, 128.3, 128.2, 128.0, 127.44, 127.36, 127.2, 126.85, 126.82, 126.4, 126.3, 123.3, 123.2, 122.2, 122.0, 119.4, 119.1, 114.4, 114.3, 107.8, 107.2, 72.0, 71.4, 54.5, 54.4, 50.0, 49.0, 44.8, 44.3, 33.5, 31.0, 28.0, 27.9, 25.73, 25.69, 22.3, 21.9, 19.4, 19.1; ESI-HRMS: *m/z* Calcd for

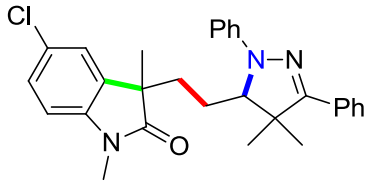
$C_{35}H_{35}N_3O+H^+$: 514.2853, found 514.2846.



(dr ≈ 1.45:1)

3-(2-(4, 4-dimethyl-1, 3-diphenyl-4, 5-dihydro-1H-pyrazol-5-yl) ethyl)-1, 3, 5-trimethylindolin-2-one (3g)

Yellow oil; (194 mg, 86% yield); R_f = 0.35 (hexanes/acetone 5:1, twice); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (d, J = 6.8 Hz, 2H), 7.66 (t, J = 8.0 Hz, J = 1.6 Hz, 2H), 7.41–7.30 (m, 6H), 7.24–7.15 (m, 4H), 7.05–6.96 (m, 5H), 6.90 (d, J = 8.4 Hz, 2H), 6.86–6.78 (m, 2H), 6.65 (dd, J = 8.0 Hz, J = 5.2 Hz, 2H), 6.30 (s, 1H), 3.83 (d, J = 7.2 Hz, 1H), 3.59 (dd, J = 8.4 Hz, J = 2.8 Hz, 1H), 3.13 (s, 3H), 3.12 (s, 3H), 2.35 (s, 3H), 2.17 (s, 3H), 2.06–2.00 (m, 1H), 1.87–1.74 (m, 2H), 1.60–1.49 (m, 2H), 1.43 (m, 3H), 1.41 (s, 3H), 1.37 (s, 3H), 1.34 (s, 3H), 1.31 (s, 3H), 1.29–1.23 (m, 3H), 1.18 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 180.2, 179.9, 155.5, 155.1, 144.7, 144.3, 140.9, 140.7, 133.3, 133.1, 132.49, 132.46, 132.0, 131.9, 128.8, 128.7, 128.3, 128.23, 128.18, 128.15, 128.1, 127.7, 126.8, 123.1, 123.0, 119.4, 119.1, 114.4, 114.1, 107.8, 107.3, 72.1, 71.1, 50.0, 49.0, 48.3, 48.2, 35.0, 32.5, 28.0, 26.1, 26.0, 24.6, 23.9, 22.2, 22.1, 21.1, 19.4, 19.0; ESI-HRMS: *m/z* Calcd for $C_{30}H_{33}N_3O+H^+$: 452.2696, found 452.2687.

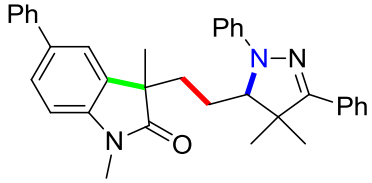


(dr ≈ 1.53:1)

5-chloro-3-(2-(4, 4-dimethyl-1, 3-diphenyl-4, 5-dihydro-1H-pyrazol-5-yl) ethyl)-1, 3-dimethylindolin-2-one (3h)

Yellow oil; (191 mg, 81% yield); R_f = 0.35 (hexanes/acetone 5:1, twice); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (dd, J = 8.0 Hz, J = 4.2 Hz, 2H), 7.70 (dd, J = 8.0 Hz, J = 1.2 Hz, 2H), 7.44–7.18 (m, 14H), 7.08 (d, J = 7.6 Hz, 2H), 6.95–6.91 (m, 2H), 6.85 (t, J = 7.2 Hz, 1H), 6.70 (d, J = 8.4 Hz, 2H), 6.48 (d, J = 2.4 Hz, 1H), 3.87 (d, J = 4.2 Hz, 1H), 3.64 (dd, J = 8.4 Hz, J = 2.4 Hz, 1H), 3.16 (s, 3H), 3.15 (s, 3H), 2.07 (td, J = 13.2 Hz, J = 4.2 Hz, 1H), 1.87 (td, J = 13.2 Hz, J = 4.0 Hz, 1H), 1.75 (td, J = 13.2 Hz,

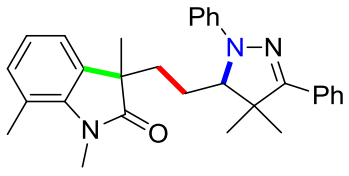
J = 3.2 Hz, 1H), 1.64-1.53 (m, 3H), 1.45 (s, 3H), 1.446 (s, 3H), 1.41 (s, 3H), 1.39 (s, 3H), 1.34 (s, 3H), 1.39–1.28 (m, 2H), 1.22 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 179.8, 179.4, 155.6, 155.2, 144.6, 144.3, 141.9, 141.7, 135.1, 134.9, 132.5, 132.4, 129.0, 128.9, 128.4, 128.31, 128.29, 128.1, 128.0, 127.9, 127.7, 126.9, 122.9, 122.8, 119.8, 119.7, 114.5, 114.1, 109.0, 108.6, 72.2, 71.1, 50.0, 49.2, 48.6, 48.5, 35.0, 32.6, 28.0, 27.9, 26.22, 26.19, 24.5, 23.7, 22.1, 19.5, 19.1; ESI-HRMS: *m/z* Calcd for $C_{29}H_{30}ClN_3O+H^+$: 472.2150, found 472.2144.



(dr ≈ 1.60:1)

3-(2-(4, 4-dimethyl-1, 3-diphenyl-4, 5-dihydro-1H-pyrazol-5-yl) ethyl)-1, 3-dimethyl-5-phenylindolin-2-one (3i)

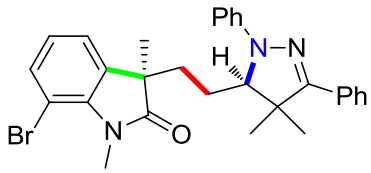
Yellow oil; (210 mg, 82% yield); R_f = 0.50 (hexanes/acetone 5:1, twice); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23 (dd, *J* = 8.0 Hz, *J* = 1.2 Hz, 2H), 7.67 (dd, *J* = 7.6 Hz, *J* = 1.2 Hz, 1H), 7.53 (d, *J* = 7.6 Hz, 2H), 7.47–7.32 (m, 18H), 7.10–7.00 (m, 6H), 6.92 (d, *J* = 8.0 Hz, 2H), 6.83 (t, *J* = 8.0 Hz, 3H), 6.75 (t, *J* = 7.2 Hz, 1H), 6.49 (t, *J* = 7.2 Hz, 1H), 3.83 (d, *J* = 5.2 Hz, 1H), 3.61 (dd, *J* = 8.4 Hz, *J* = 2.4 Hz, 1H), 3.20 (s, 3H), 3.18 (s, 3H), 2.10–2.05 (m, 1H), 1.92–1.81 (m, 1H), 1.70–1.61 (m, 1H), 1.58–1.50 (m, 1H), 1.45 (s, 3H), 1.42 (s, 3H), 1.37 (s, 9H), 1.34–1.26 (m, 7H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 180.4, 180.0, 155.7, 155.2, 144.6, 144.1, 142.7, 142.5, 141.0, 140.86, 136.2, 136.1, 133.9, 133.7, 132.5, 132.4, 128.9, 128.85, 128.78, 128.6, 128.4, 128.3, 128.2, 127.0, 126.9, 126.84, 126.81, 126.5, 121.20, 121.15, 119.5, 119.1, 114.3, 113.8, 108.3, 107.9, 72.1, 71.0, 50.0, 49.1, 48.5, 48.4, 35.0, 32.7, 28.05, 27.95, 26.22, 26.20, 24.6, 24.0, 23.97, 22.2, 19.5, 19.0; ESI-HRMS: *m/z* Calcd for $C_{35}H_{35}N_3O+H^+$: 514.2853, found 514.2845.

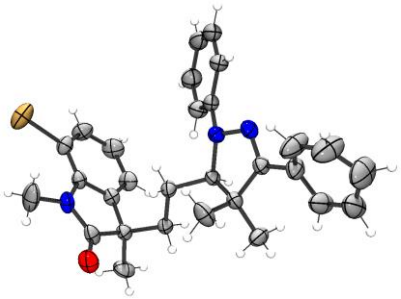


(dr ≈ 1.02:1)

3-(2-(4, 4-dimethyl-1, 3-diphenyl-4, 5-dihydro-1H-pyrazol-5-yl) ethyl)-1, 3, 7-trimethylindolin-2-one (3j)

Yellow oil; (142 mg, 63% yield); R_f = 0.25 (hexanes/acetone 5:1, twice); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (dd, *J* = 8.4 Hz, *J* = 1.6 Hz, 2H), 7.67 (dd, *J* = 8.4 Hz, *J* = 1.2 Hz, 2H), 7.38–7.32 (m, 6H), 7.25–7.15 (m, 5H), 7.04–6.78 (m, 9H), 6.69 (t, *J* = 7.6 Hz, 1H), 6.31 (d, *J* = 6.8 Hz, 1H), 3.81 (dd, *J* = 6.8 Hz, *J* = 1.6 Hz, 1H), 3.59 (dd, *J* = 8.4 Hz, *J* = 2.4 Hz, 1H), 3.42 (s, 3H), 3.417 (s, 3H), 2.53 (s, 3H), 2.52 (s, 3H), 2.03 (td, *J* = 12.8 Hz, *J* = 4.2 Hz, 1H), 1.85 (td, *J* = 13.2 Hz, *J* = 4.4 Hz, 1H), 1.76–1.54 (m, 3H), 1.42 (s, 3H), 1.41 (s, 3H), 1.38 (s, 3H), 1.35 (s, 3H), 1.29 (s, 3H), 1.27–1.20 (m, 3H), 1.18 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 181.0, 181.7, 155.6, 155.2, 144.7, 144.5, 141.1, 140.8, 134.0, 133.7, 132.5, 131.7, 131.2, 129.0, 128.8, 128.4, 128.3, 128.22, 128.19, 126.9, 122.6, 122.4, 120.2, 120.1, 119.7, 119.4, 119.2, 119.1, 114.4, 114.2, 72.1, 71.2, 50.0, 49.2, 47.6, 47.5, 35.2, 33.0, 29.4, 28.04, 28.02, 25.0, 24.3, 22.2, 22.1, 19.5, 19.2, 19.0; ESI-HRMS: *m/z* Calcd for $C_{30}H_{33}N_3O+H^+$: 452.2696, found 452.2689.



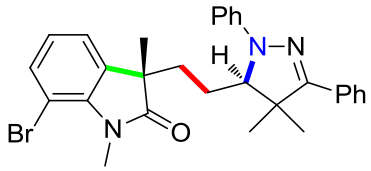


X-ray structure of 3k

(R*)-7-bromo-3-(2-((R*)-4, 4-dimethyl-1, 3-diphenyl-4, 5-dihydro-1H-pyrazol-5-yl) ethyl)-1, 3-dimethylindolin-2-one (3k)

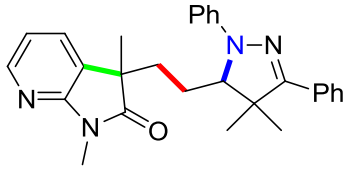
Colorless solid, mp 134–135 ^{o}C; (121 mg, 47% yield); R_f = 0.35 (hexanes/acetone 5:1, twice); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (dd, *J* = 8.0 Hz, *J* = 1.2 Hz, 2H), 7.42–7.33 (m, 3H), 7.24–7.18 (m, 3H), 7.02 (dd, *J* = 8.8 Hz, *J* = 0.8 Hz, 2H), 6.84 (t, *J* = 7.2 Hz, 1H), 6.60 (t, *J* = 7.2 Hz, 1H), 6.25 (dd, *J* = 7.2 Hz, *J* = 1.2 Hz, 1H), 3.86 (d, *J* = 7.2 Hz, 1H), 3.53 (s, 3H), 1.84 (td, *J* = 13.2 Hz, *J* = 4.4 Hz, 1H), 1.51 (td, *J* = 13.2 Hz, *J* = 3.2 Hz, 1H), 1.43 (s, 3H), 1.38 (s, 3H), 1.36–1.21 (m, 2H), 1.20 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 180.6, 155.2, 144.4, 140.3, 136.2, 133.0, 132.4, 129.1, 128.4, 128.3, 126.8, 123.9, 121.2, 119.0, 114.1, 101.9, 71.0, 48.9, 48.0, 32.6, 29.6, 27.9, 25.0, 21.9, 19.0; ESI-HRMS: *m/z* Calcd for $C_{29}H_{30}BrN_3O+H^+$: 516.1645, found

516.1649.



(S*)-7-bromo-3-(2-((R*)-4, 4-dimethyl-1, 3-diphenyl-4, 5-dihydro-1H-pyrazol-5-yl) ethyl)-1, 3-dimethylindolin-2-one (3k')

Yellow oil; (98 mg, 38% yield); R_f = 0.45 (hexanes/acetone 3:1, twice); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 (d, J = 8.0 Hz, 2H), 7.37–7.30 (m, 4H), 7.20 (t, J = 7.6 Hz, 2H), 7.04 (d, J = 7.2 Hz, 1H), 6.93 (d, J = 7.6 Hz, 2H), 6.88 (t, J = 8.0 Hz, 1H), 6.82 (t, J = 7.6 Hz, 1H), 3.63 (dd, J = 8.0 Hz, J = 2.8 Hz, 1H), 3.52 (s, 3H), 2.00 (td, J = 13.2 Hz, J = 4.8 Hz, 1H), 1.71 (td, J = 12.8 Hz, J = 3.6 Hz, 1H), 1.58–1.48 (m, 1H), 1.40 (s, 3H), 1.33 (s, 3H), 1.28 (s, 3H), 1.26-1.23 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 180.3, 155.5, 144.7, 140.6, 136.6, 133.6, 132.5, 128.9, 128.3, 128.2, 126.9, 123.6, 121.3, 119.6, 114.4, 102.6, 71.9, 49.9, 47.9, 35.0, 29.6, 28.0, 24.1, 22.2, 19.4; ESI-HRMS: *m/z* Calcd for $C_{29}H_{30}BrN_3O+H^+$: 516.1645, found 516.1640.

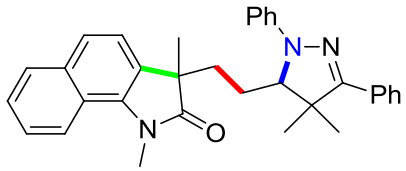


(dr ≈ 1.03:1)

3-(2-(4, 4-dimethyl-1, 3-diphenyl-4, 5-dihydro-1H-pyrazol-5-yl) ethyl)-1, 3-dimethyl-1H-pyrrolo [2, 3-b] pyridin-2(3H)-one (3l)

Yellow oil; (123 mg, 56% yield); R_f = 0.40 (hexanes/ethyl acetate 5:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.13 (dd, J = 5.2 Hz, J = 1.2 Hz, 2H), 7.60 (dd, J = 5.2 Hz, J = 1.2 Hz, 2H), 7.74 (d, J = 7.2 Hz, 2H), 7.66 (d, J = 6.8 Hz, 2H), 7.41–7.31 (m, 7H), 7.24–6.99 (m, 4H), 6.97–6.89 (m, 2H), 6.87–6.81 (m, 3H), 6.66 (dd, J = 7.2 Hz, J = 5.6 Hz, 1H), 6.50 (dd, J = 7.2 Hz, J = 5.2 Hz, 1H), 3.88 (d, J = 5.2 Hz, 1H), 3.69 (dd, J = 7.2 Hz, J = 2.8 Hz, 1H), 3.23 (s, 6H), 1.97–1.93 (m, 1H), 1.86–1.81 (m, 1H), 1.76–1.72 (m, 1H), 1.66–1.50 (m, 2H), 1.49 (s, 3H), 1.45 (s, 3H), 1.40 (s, 3H), 1.37 (s, 3H), 1.33 (s, 3H), 1.30–1.23 (m, 3H), 1.19 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 179.9, 179.6, 156.8, 156.7, 155.6, 155.3, 146.8, 146.3, 144.7, 144.4, 132.4, 129.7, 129.6, 129.1, 128.9, 128.41, 128.37, 128.32, 128.29, 127.8, 127.4, 126.85, 126.83,

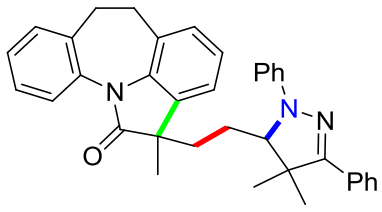
119.6, 119.1, 118.3, 118.0, 114.4, 114.2, 71.8, 71.0, 49.9, 49.0, 48.0, 47.8, 34.2, 32.0, 28.0, 27.9, 25.25, 25.18, 24.1, 23.0, 22.4, 21.9, 19.3, 19.0; ESI-HRMS: *m/z* Calcd for $C_{28}H_{30}N_4O+H^+$: 439.2492, found 439.2489.



(dr ≈ 1.10:1)

3-(2-(4, 4-dimethyl-1, 3-diphenyl-4, 5-dihydro-1H-pyrazol-5-yl) ethyl)-1, 3-dimethyl-1H-benzo[g]indol-2(3H)-one (3m)

Yellow oil; (185 mg, 76% yield); R_f = 0.40 (hexanes/ethyl acetate 5:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 (d, *J* = 6.8 Hz, 2H), 7.70 (d, *J* = 7.6 Hz, 1H), 7.65 (d, *J* = 1.6 Hz, 1H), 7.63–7.53 (m, 2H), 7.47–7.30 (m, 13H), 7.24–7.02 (m, 6H), 6.88–6.84 (m, 3H), 6.80 (d, *J* = 8.0 Hz, 2H), 6.73 (t, *J* = 7.2 Hz, 1H), 6.65 (d, *J* = 7.2 Hz, 1H), 3.87 (d, *J* = 5.2 Hz, 1H), 3.57 (dd, *J* = 8.4 Hz, *J* = 2.8 Hz, 1H), 3.46 (s, 3H), 3.44 (s, 3H), 2.54 (td, *J* = 12.0 Hz, *J* = 4.0 Hz, 1H), 2.38 (td, *J* = 12.0 Hz, *J* = 4.0 Hz, 1H), 1.91 (td, *J* = 16.0 Hz, *J* = 3.2 Hz, 1H), 1.76 (td, *J* = 12.8 Hz, *J* = 4.0 Hz, 1H), 1.69–1.53 (m, 2H), 1.47 (s, 3H), 1.44 (s, 3H), 1.40 (s, 3H), 1.37 (s, 3H), 1.32 (s, 6H), 1.26 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.2, 172.8, 155.5, 155.3, 144.5, 144.4, 137.5, 136.9, 136.5, 133.2, 133.1, 132.6, 132.5, 130.4, 129.0, 128.7, 128.54, 128.51, 128.3, 128.22, 128.17, 128.1, 127.3, 126.9, 126.8, 126.3, 126.1, 126.0, 125.4, 122.44, 125.40, 122.36, 122.3, 119.7, 119.5, 119.2, 118.9, 114.3, 114.0, 108.3, 108.0, 72.0, 71.2, 50.0, 49.1, 47.51, 47.47, 40.7, 36.5, 32.9, 31.2, 29.53, 29.50, 28.0, 27.9, 23.22, 23.17, 19.4, 18.9; ESI-HRMS: *m/z* Calcd for $C_{33}H_{33}N_3O+H^+$: 488.2696, found 488.2687.

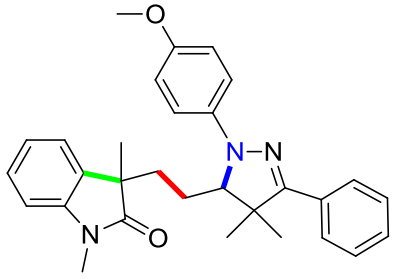


(dr ≈ 1.40:1)

7-(2-(4, 4-dimethyl-1, 3-diphenyl-4, 5-dihydro-1H-pyrazol-5-yl) ethyl)-7-methyl-11, 12-dihydrobenzo [6, 7] azepino [3, 2, 1-hi] indol-6(7H)-one (3n)

Yellow oil; (189 mg, 72% yield); R_f = 0.50 (hexanes/acetone 5:1, twice); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (d, *J* = 7.2 Hz, 3H), 7.67 (d, *J* = 7.2 Hz, 3H), 7.40–7.28 (m, 7H), 7.25–7.12 (m, 9H), 7.07–7.01 (m, 3H), 7.00–6.98 (m, 2H), 6.95–6.87 (m, 3H),

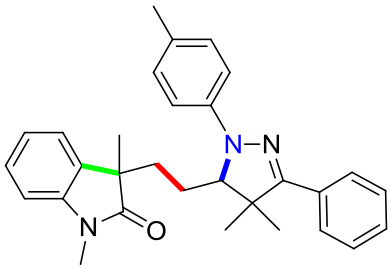
6.86–6.79 (m, 2H), 6.75 (t, *J* = 7.4 Hz, 1H), 6.36 (d, *J* = 6.0 Hz, 1H), 3.88 (d, *J* = 6.0 Hz, 1H), 3.66 (d, *J* = 6.0 Hz, 1H), 2.97–2.87 (m, 8H), 2.15 (td, *J* = 12.8 Hz, *J* = 4.8 Hz, 1H), 1.99 (t, *J* = 11.2 Hz, 1H), 1.80 (t, *J* = 12.8 Hz, 1H), 1.70–1.45 (m, 5H), 1.41 (s, 6H), 1.38 (s, 3H), 1.36 (s, 3H), 1.32 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 181.0, 180.5, 155.4, 155.1, 144.7, 144.4, 140.4, 140.1, 136.62, 136.59, 136.1, 136.0, 133.6, 133.2, 132.5, 129.8, 129.5, 129.3, 129.1, 128.9, 128.4, 128.3, 128.24, 128.19, 126.8, 126.5, 126.4, 126.3, 126.2, 125.8, 124.7, 124.6, 122.5, 122.4, 120.02, 119.99, 119.4, 119.1, 114.4, 114.2, 72.0, 71.2, 49.8, 49.2, 47.9, 33.9, 33.8, 33.6, 33.5, 28.0, 27.9, 22.4, 22.1, 19.4, 19.1; ESI-HRMS: *m/z* Calcd for $C_{36}H_{35}N_3O+H^+$: 526.2853, found 526.2840.



(dr ≈ 1.61:1)

3-(2-(1-(4-methoxyphenyl)-4, 4-dimethyl-3-phenyl-4, 5-dihydro-1H-pyrazol-5-yl) ethyl)-1, 3-dimethylindolin-2-one (3o)

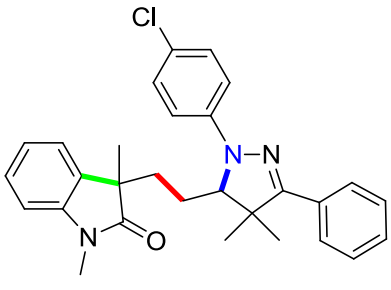
Yellow oil; (198 mg, 85% yield); R_f = 0.30 (hexanes/acetone 5:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (d, *J* = 6.8 Hz, 2H), 7.68 (dd, *J* = 8.0 Hz, *J* = 1.6 Hz, 2H), 7.41–7.32 (m, 7H), 7.30–7.16 (m, 2H), 7.10 (dd, *J* = 7.2 Hz, *J* = 0.8 Hz, 1H), 7.00 (dd, *J* = 6.8 Hz, *J* = 2.4 Hz, 2H), 6.91–6.78 (m, 9H), 6.57 (d, *J* = 6.8 Hz, 1H), 3.85 (s, 3H), 3.80 (s, 3H), 3.71 (dd, *J* = 8.4 Hz, *J* = 2.0 Hz, 1H), 3.43 (d, *J* = 8.4 Hz, 1H), 3.19 (s, 3H), 3.18 (s, 3H), 2.02 (td, *J* = 16.0 Hz, *J* = 4.0 Hz, 1H), 1.88 (td, *J* = 16.0 Hz, *J* = 4.0 Hz, 1H), 1.78–1.47 (m, 4H), 1.44 (s, 3H), 1.41 (s, 3H), 1.40 (s, 3H), 1.34 (s, 3H), 1.31 (s, 3H), 1.29–1.275 (m, 2H), 1.25(s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 180.2, 180.0, 155.6, 154.8, 154.2, 153.6, 143.3, 143.1, 139.5, 139.0, 133.3, 133.1, 132.59, 132.56, 128.26, 128.18, 128.0, 127.9, 127.4, 126.74, 126.69, 122.5, 122.4, 122.22, 122.21, 117.8, 116.4, 114.4, 114.2, 108.0, 107.6, 73.7, 72.2, 55.6, 55.5, 49.9, 49.1, 48.24, 48.15, 35.0, 33.0, 27.4, 27.2, 26.04, 255.99, 24.3, 23.7, 22.05, 22.00, 19.2, 19.1; ESI-HRMS: *m/z* Calcd for $C_{30}H_{33}N_3O_2+H^+$: 468.2646, found 468.2639.



(dr ≈ 1.17:1)

3-(2-(4, 4-dimethyl-3-phenyl-1-(p-tolyl)-4, 5-dihydro-1H-pyrazol-5-yl) ethyl)-1, 3-dimethylindolin-2-one (3p)

Yellow oil; (167 mg, 74% yield); R_f = 0.55 (hexanes/acetone 5:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71 (d, *J* = 6.8 Hz, 2H), 7.65 (d, *J* = 6.4 Hz, 2H), 7.39–7.29 (m, 6H), 7.24–7.14 (m, 3H), 7.08–6.98 (m, 5H), 6.93 (d, *J* = 8.4Hz, 2H), 6.83–6.74 (m, 5H), 6.47 (d, *J* = 6.8 Hz, 1H), 3.76 (dd, *J* = 6.4 Hz, *J* = 1.6 Hz, 1H), 3.53 (dd, *J* = 8.0 Hz, *J* = 3.2 Hz, 1H), 3.16 (s, 3H), 3.15 (s, 3H), 2.33 (s, 3H), 2.26 (s, 3H), 2.00 (td, *J* = 13.2 Hz, *J* = 5.2 Hz, 1H), 1.84 (td, *J* = 13.2 Hz, *J* = 3.6 Hz, 1H), 1.75 (td, *J* = 13.2 Hz, *J* = 3.6 Hz, 1H), 1.68–1.51 (m, 2H), 1.40 (s, 3H), 1.396 (s, 3H), 1.37 (s, 3H), 1.32 (s, 3H), 1.31 (s, 3H), 1.29–1.23 (m, 3H), 1.21 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 180.3, 180.0, 155.3, 154.7, 143.3, 143.1, 142.8, 142.4, 133.4, 133.1, 132.63, 132.60, 129.5, 129.4, 129.0, 128.4, 128.3, 128.2, 128.08, 128.06, 127.9, 127.4, 126.81, 126.79, 122.51, 122.48, 122.34, 122.26, 115.0, 114.5, 108.1, 107.6, 72.5, 71.6, 49.9, 49.1, 48.3, 48.1, 34.9, 32.8, 29.6, 27.8, 26.1, 26.0, 24.5, 23.7, 22.3, 22.1, 20.54, 20.51, 19.4, 19.1; ESI-HRMS: *m/z* Calcd for $C_{30}H_{33}N_3O+H^+$: 452.2696, found 452.2690.

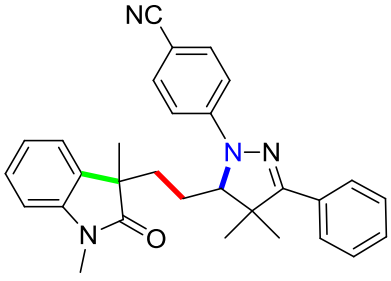


(dr ≈ 1.36:1)

3-(2-(1-(4-chlorophenyl)-4, 4-dimethyl-3-phenyl-4, 5-dihydro-1H-pyrazol-5-yl) ethyl)-1, 3-dimethylindolin-2-one (3q)

Yellow oil; (212 mg, 90% yield); R_f = 0.30 (hexanes/acetone 5:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71 (dd, *J* = 8.0 Hz, *J* = 1.6 Hz, 2H), 7.75 (dd, *J* = 8.0 Hz, *J* = 1.6 Hz, 2H), 7.41–7.32 (m, 6H), 7.28–7.24 (m, 2H), 7.19 (td, *J* = 7.6 Hz, *J* = 1.2 Hz, 1H), 7.16–7.07 (m, 6H), 6.93 (dd, *J* = 7.2 Hz, *J* = 2.8 Hz, 2H), 6.87 (t, *J* = 8.2 Hz, 1H), 6.80–6.75 (m, 3H), 6.44 (d, *J* = 7.2 Hz, 1H), 3.79 (d, *J* = 4.8 Hz, 1H), 3.57 (dd, *J* =

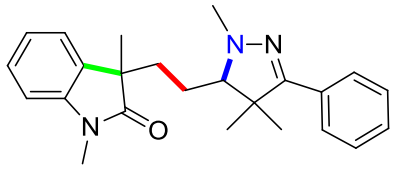
8.0 Hz, *J* = 2.4 Hz, 1H), 3.15 (s, 3H), 3.147 (s, 3H), 2.04 (td, *J* = 12.0 Hz, *J* = 4.0 Hz, 1H), 1.86 (td, *J* = 12.0 Hz, *J* = 4.0 Hz, 1H), 1.76 (td, *J* = 12.0 Hz, *J* = 4.0 Hz, 1H), 1.63–1.50 (m, 3H), 1.42 (s, 3H), 1.39 (s, 3H), 1.37 (s, 3H), 1.33 (s, 3H), 1.31 (s, 3H), 1.29–1.24 (m, 2H), 1.20 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 180.1, 179.8, 156.0, 155.9, 143.3, 143.2, 143.0, 133.2, 132.9, 132.2, 128.9, 128.7, 128.5, 128.4, 128.3, 128.0, 127.5, 126.9, 124.0, 123.7, 122.7, 122.5, 122.11, 122.07, 115.3, 115.2, 108.1, 107.6, 72.0, 71.2, 50.1, 49.2, 48.2, 48.1, 34.7, 32.6, 28.0, 27.9, 26.1, 26.0, 24.5, 23.7, 22.1, 21.8, 19.4, 19.0; ESI-HRMS: *m/z* Calcd for $C_{29}H_{30}ClN_3O+H^+$: 472.2150, found 472.2141.



(dr ≈ 1.30:1)

4-(5-(2-(1, 3-dimethyl-2-oxoindolin-3-yl) ethyl)-4, 4-dimethyl-3-phenyl-4, 5-dihydro-1H-pyrazol-1-yl) benzonitrile (3r)

Yellow oil; (204 mg, 94% yield); R_f = 0.30 (hexanes/acetone 5:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (dd, *J* = 8.0 Hz, *J* = 4.4 Hz, 2H), 7.66 (dd, *J* = 8.0 Hz, *J* = 4.4 Hz, 2H), 7.45–7.37 (m, 10H), 7.29 (d, *J* = 7.6 Hz, 1H), 7.23–7.07 (m, 3H), 6.97 (d, *J* = 8.8 Hz, 2H), 6.86–6.77 (m, 5H), 6.47 (d, *J* = 7.2 Hz, 1H), 3.87 (d, *J* = 4.8 Hz, 1H), 3.69 (dd, *J* = 8.0 Hz, *J* = 2.4 Hz, 1H), 3.16 (s, 3H), 3.14 (s, 3H), 2.01 (td, *J* = 12.0 Hz, *J* = 4.0 Hz, 1H), 1.84 (td, *J* = 12.0 Hz, *J* = 4.0 Hz, 1H), 1.71 (td, *J* = 12.0 Hz, *J* = 4.0 Hz, 1H), 1.61–1.48 (m, 3H), 1.46 (s, 3H), 1.39 (s, 3H), 1.38 (s, 6H), 1.34 (s, 3H), 1.33–1.25 (m, 1H), 1.21 (s, 3H), 1.19–1.05 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 179.9, 179.6, 158.4, 158.2, 146.8, 146.6, 143.3, 143.0, 133.3, 133.2, 133.0, 132.6, 131.42, 131.39, 129.1, 129.0, 128.5, 128.4, 128.1, 127.7, 127.05, 127.01, 122.6, 122.5, 122.0, 121.8, 120.3, 113.1, 112.7, 108.2, 107.8, 100.0, 99.9, 71.1, 70.5, 50.2, 49.4, 48.1, 48.0, 34.4, 32.4, 28.4, 28.3, 26.1, 26.0, 24.4, 23.7, 22.2, 21.8, 19.1, 18.8; ESI-HRMS: *m/z* Calcd for $C_{30}H_{30}N_4O+H^+$: 463.2492, found 463.2485.

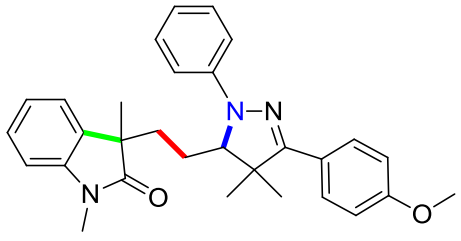


(dr ≈ 1.06:1)

1, 3-dimethyl-3-(2-(1, 4, 4-trimethyl-3-phenyl-4, 5-dihydro-1H-pyrazol-5-yl) ethyl) indolin-2-one (3s)

(Major) Yellow oil; (53 mg, 28% yield); R_f = 0.25 (hexanes/acetone 5:1, twice); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57 (dd, J = 8.0 Hz, J = 1.6 Hz, 2H), 7.33–7.29 (m, 4H), 7.20 (d, J = 7.2 Hz, 1H), 7.09 (t, J = 7.2 Hz, 1H), 6.87 (d, J = 8.0 Hz, 1H), 3.24 (s, 3H), 2.75 (s, 3H), 2.46 (dd, J = 8.0 Hz, J = 4.0 Hz, 1H), 2.05 (td, J = 12.4 Hz, J = 4.8 Hz, 1H), 1.93 (td, J = 12.8 Hz, J = 4.4 Hz, 1H), 1.40 (s, 3H), 1.31 (s, 3H), 1.26–1.14 (m, 1H) , 0.99 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 180.2, 158.1, 143.4, 133.4, 132.7, 128.18, 128.16, 128.0, 126.9, 122.6, 122.2, 108.1, 78.1, 50.2, 48.4, 41.8, 35.3, 26.1, 25.7, 23.8, 22.0, 18.4; ESI-HRMS: *m/z* Calcd for $C_{24}H_{29}N_3O+H^+$: 376.2383, found 376.2381.

(Minor) Yellow oil; (50 mg, 27% yield); R_f = 0.30 (hexanes/acetone 5:1, twice); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58 (dd, J = 8.4 Hz, J = 1.4 Hz, 2H), 7.35–7.27 (m, 4H), 7.20 (d, J = 6.4 Hz, 1H), 7.10 (td, J = 7.2 Hz, 0.8 Hz, 1H), 6.87 (d, J = 8.0 Hz, 1H), 3.24 (s, 3H), 2.69 (s, 3H), 2.42 (dd, J = 8.0 Hz, J = 4.4 Hz, 1H), 2.13 (td, J = 13.2 Hz, J = 4.8 Hz, 1H), 1.85 (td, J = 13.2 Hz, J = 4.0 Hz, 1H), 1.40 (s, 3H), 1.34 (s, 3H), 1.32–1.22 (m, 2H) , 1.07 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 180.2, 158.4, 143.4, 133.3, 132.7, 128.22, 128.18, 127.9, 127.0, 122.6, 122.3, 108.1, 78.5, 50.3, 48.4, 41.9, 35.5, 26.2, 25.6, 23.9, 22.0, 18.4; ESI-HRMS: *m/z* Calcd for $C_{24}H_{29}N_3O+H^+$: 376.2383, found 376.2385.

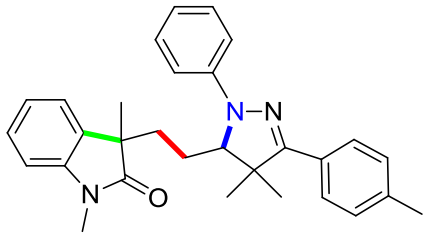


(dr ≈ 1.57:1)

3-(2-(3-(4-methoxyphenyl)-4, 4-dimethyl-1-phenyl-4, 5-dihydro-1H-pyrazol-5-yl) ethyl)-1, 3-dimethylindolin-2-one (3v)

Yellow oil; (184 mg, 79% yield); R_f = 0.35 (hexanes/acetone 5:1, twice); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 (d, J = 8.8 Hz, 2H), 7.61 (d, J = 8.4 Hz, 2H), 7.23–7.15 (m,

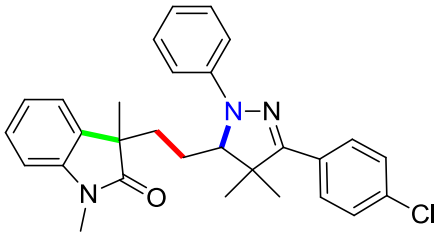
6H), 7.08–6.99 (m, 4H), 6.94–6.74 (m, 11H), 6.47 (d, *J* = 8.8 Hz, 1H), 3.84 (s, 3H), 3.82 (s, 3H), 3.78 (dd, *J* = 9.2 Hz, *J* = 5.2 Hz, 1H), 3.56 (dd, *J* = 8.0 Hz, *J* = 2.8 Hz, 1H), 3.15 (s, 6H), 2.06–1.99 (m, 1H), 1.88–1.81 (m, 1H), 1.80–1.72 (m, 1H), 1.64–1.56 (m, 1H), 1.43 (, 3H), 1.40 (s, 3H), 1.39 (s, 3H), 1.35 (s, 3H), 1.32 (s, 3H), 1.29–1.23 (m, 4H), 1.21 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 180.3, 180.0, 159.8, 159.7, 155.5, 155.2, 145.0, 144.7, 143.3, 143.1, 133.4, 133.1, 129.0, 128.8, 128.2, 127.9, 127.4, 125.1, 125.0, 122.7, 122.5, 122.3, 122.2, 119.2, 118.8, 114.3, 114.1, 113.84, 113.75, 108.1, 107.6, 71.9, 71.0, 55.3, 55.2, 50.0, 49.2, 48.2, 48.1, 34.9, 32.8, 28.00, 27.96, 26.1, 26.1, 24.5, 23.7, 22.3, 22.0, 19.6, 19.2; ESI-HRMS: *m/z* Calcd for $C_{30}H_{33}N_3O_2$+H^+: 468.2646, found 468.2640.



(dr ≈ 1.62:1)

3-(2-(4, 4-dimethyl-1-phenyl-3-(p-tolyl)-4, 5-dihydro-1H-pyrazol-5-yl) ethyl)-1, 3-dimethylindolin-2-one (3w)

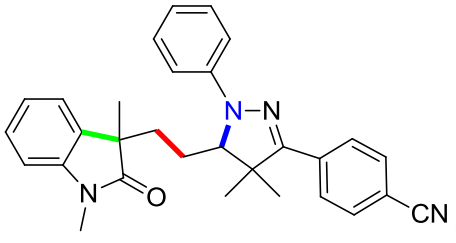
Yellow oil; (156 mg, 69% yield); R_f = 0.40 (hexanes/acetone 5:1, twice); ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.62 (d, *J* = 8.4 Hz, 2H), 7.56 (d, *J* = 8.4 Hz, 2H), 7.23–7.14 (m, 10H), 7.07 (d, *J* = 7.2 Hz, 1H), 7.02 (d, *J* = 8.0 Hz, 3H), 6.92 (d, *J* = 8.0 Hz, 2H), 6.86–6.74 (m, 5H), 6.47 (d, *J* = 7.2 Hz, 1H), 3.79 (d, *J* = 5.6 Hz, 1H), 3.58 (dd, *J* = 8.4 Hz, *J* = 2.8 Hz, 1H), 3.14 (s, 6H), 2.38 (s, 3H), 2.35 (s, 3H), 2.02 (td, *J* = 13.2 Hz, *J* = 5.2 Hz, 1H), 1.89–1.72 (m, 2H), 1.64–1.45 (m, 2H), 1.43 (s, 3H), 1.41 (s, 3H), 1.39 (s, 3H), 1.36 (s, 3H), 1.32 (s, 3H), 1.31–1.23 (m, 3H), 1.20 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 180.3, 180.0, 155.6, 155.3, 144.8, 144.6, 143.3, 143.1, 138.2, 138.1, 133.4, 133.1, 129.62, 129.59, 129.05, 129.0, 128.97, 128.8, 127.9, 127.4, 126.8, 122.7, 122.5, 122.3, 122.2, 119.2, 118.9, 114.3, 114.1, 108.0, 107.6, 72.0, 71.1, 50.0, 49.2, 48.2, 48.1, 34.9, 32.8, 28.01, 27.97, 26.05, 26.02, 24.5, 23.7, 22.2, 22.0, 21.22, 21.19, 19.5, 19.1; ESI-HRMS: *m/z* Calcd for $C_{30}H_{33}N_3O$+H^+: 452.2696, found 452.2691.



(dr ≈ 1.49:1)

3-(2-(3-(4-chlorophenyl)-4, 4-dimethyl-1-phenyl-4, 5-dihydro-1H-pyrazol-5-yl) ethyl)-1, 3-dimethylindolin-2-one (3x)

Yellow oil; (170 mg, 72% yield); R_f = 0.30 (hexanes/acetone 5:1, twice); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 (d, *J* = 8.8 Hz, 2H), 7.60 (d, *J* = 8.4 Hz, 2H), 7.34 (d, *J* = 8.4 Hz, 2H), 7.30 (d, *J* = 8.4 Hz, 2H), 7.25–7.14 (m, 6H), 7.08–7.00 (m, 3H), 6.90–6.74 (m, 8H), 6.46 (d, *J* = 7.2 Hz, 1H), 3.82 (d, *J* = 5.2 Hz, 1H), 3.61 (dd, *J* = 8.4 Hz, *J* = 2.4 Hz, 1H), 3.145 (s, 3H), 3.140 (s, 3H), 2.02 (td, *J* = 12.8 Hz, *J* = 7.6 Hz, 1H), 1.82 (td, *J* = 13.2 Hz, *J* = 8.8 Hz, 1H), 1.74 (td, *J* = 12.4 Hz, *J* = 3.6 Hz, 1H), 1.61–1.41 (m, 3H), 1.38 (s, 3H), 1.35 (s, 3H), 1.32 (s, 3H), 1.31 (s, 3H), 1.28 (s, 3H), 1.27–1.23 (m, 2H), 1.20 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 180.2, 179.9, 154.2, 153.9, 144.4, 144.2, 143.3, 143.1, 134.05, 134.01, 133.3, 133.0, 131.0, 129.1, 128.9, 128.6, 128.5, 128.0, 127.5, 122.7, 122.5, 122.3, 122.2, 119.7, 119.4, 114.5, 114.2, 108.1, 107.6, 72.1, 71.3, 49.8, 49.0, 48.2, 48.1, 34.8, 32.7, 27.94, 27.90, 26.09, 26.06, 24.5, 23.7, 22.2, 22.0, 19.4, 19.1; ESI-HRMS: *m/z* Calcd for $C_{29}H_{30}ClN_3O+H^+$: 472.2150, found 472.2141.

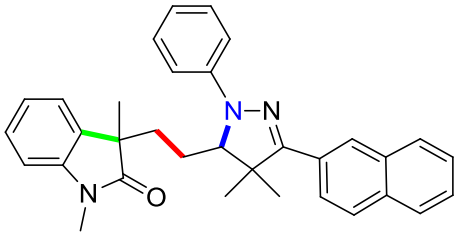


(dr ≈ 1.40:1)

4-(5-(2-(1, 3-dimethyl-2-oxoindolin-3-yl) ethyl)-4, 4-dimethyl-1-phenyl-4, 5-dihydro-1H-pyrazol-3-yl) benzonitrile (3y)

Yellow oil; (173 mg, 75% yield); R_f = 0.30 (hexanes/acetone 3:1, twice); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 (d, *J* = 8.8 Hz, 2H), 7.79 (d, *J* = 8.8 H, 2H), 7.51 (d, *J* = 16.0 Hz, *J* = 8.8 Hz, 4H), 7.72–7.14 (m, 7H), 7.08–7.03 (m, 3H), 6.93–6.75 (m, 7H), 6.45 (d, *J* = 7.2 Hz, 1H), 3.89 (d, *J* = 5.2 Hz, 1H), 3.70 (dd, *J* = 8.4 Hz, *J* = 2.4 Hz, 1H), 3.15 (s, 3H), 3.14 (s, 3H), 2.04–1.98 (m, 1H), 1.86–1.81 (m, 1H), 1.79–1.73 (m, 1H), 1.58–1.51 (m, 1H), 1.45 (s, 3H), 1.41 (s, 3H), 1.37 (s, 3H), 1.36 (s, 3H) 1.31 (s,

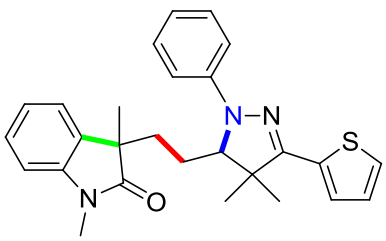
3H), 1.30–1.22 (m, 4H), 1.20 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 180.1, 179.8, 152.5, 152.3, 143.6, 143.5, 143.2, 143.0, 137.0, 133.2, 132.8, 132.1, 132.03, 131.96, 129.1, 128.9, 128.0, 127.5, 126.6, 122.7, 122.6, 122.5, 122.14, 122.12, 120.2, 120.0, 118.92, 118.88, 114.5, 114.4, 110.84, 110.79, 108.1, 107.7, 72.4, 71.7, 49.4, 48.6, 48.1, 48.0, 34.7, 32.5, 27.94, 27.89, 26.1, 26.0, 24.5, 23.7, 22.12, 22.07, 19.3, 19.0; ESI-HRMS: *m/z* Calcd for $C_{30}H_{30}N_4O+H^+$: 463.2492, found 463.2488.



(dr ≈ 1.38:1)

3-(2-(4, 4-dimethyl-3-(naphthalen-2-yl)-1-phenyl-4, 5-dihydro-1H-pyrazol-5-yl) ethyl)-1, 3-dimethylindolin-2-one (3z)

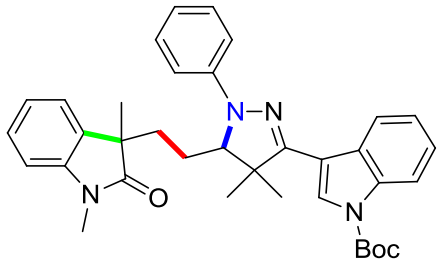
Yellow oil; (144 mg, 59% yield); R_f = 0.30 (hexanes/acetone 5:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09 (s, 1H), 8.04 (s, 1H), 8.00 (dd, *J* = 8.8 Hz, *J* = 1.6 Hz, 1H), 7.93 (dd, *J* = 8.8 Hz, *J* = 1.6 Hz, 1H), 7.87–7.78 (m, 6H), 7.51–7.45 (m, 4H), 7.24–7.16 (m, 7H), 7.06 (dd, *J* = 8.4 Hz, *J* = 4.0 Hz, 3H), 6.95 (d, *J* = 8.0 Hz, 2H), 6.89–6.75 (m, 5H), 6.48 (d, *J* = 7.2 Hz, 1H), 3.87 (d, *J* = 5.2 Hz, 1H), 3.67 (dd, *J* = 8.0 Hz, *J* = 2.4 Hz, 1H), 3.15 (s, 3H), 3.147 (s, 3H), 2.08 (td, *J* = 12.0 Hz, *J* = 4.8 Hz, 1H), 1.92 (td, *J* = 12.0 Hz, *J* = 4.0 Hz, 1H), 1.85–1.63 (m, 2H), 1.61 (s, 3H), 1.57 (s, 3H), 1.52 (s, 3H), 1.48 (s, 3H), 1.47 (s, 3H), 1.45–1.26 (m, 4H), 1.24 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 180.3, 180.0, 155.1, 154.8, 144.5, 144.3, 143.3, 143.1, 133.3, 133.14, 133.06, 133.0, 130.0, 129.9, 129.1, 128.9, 128.24, 128.21, 127.93, 127.87, 127.59, 127.56, 127.4, 126.24, 126.22, 126.18, 125.19, 125.16, 125.15, 122.7, 122.5, 122.3, 122.2, 119.5, 119.2, 114.4, 114.2, 108.1, 107.6, 72.1, 71.3, 49.9, 49.1, 48.2, 48.1, 34.8, 32.7, 29.6, 28.2, 28.1, 26.0, 24.5, 23.7, 22.1, 19.7, 19.4, 14.1; ESI-HRMS: *m/z* Calcd for $C_{33}H_{33}N_3O+H^+$: 488.2696, found 488.2690.



(dr ≈ 1.21:1)

3-(2-(4, 4-dimethyl-1-phenyl-3-(thiophen-2-yl)-4, 5-dihydro-1H-pyrazol-5-yl) ethyl)-1, 3-dimethylindolin-2-one (3aa)

Yellow oil; (200 mg, 86% yield); R_f = 0.35 (hexanes/acetone 5:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29–7.14 (m, 12H), 7.08–6.98 (m, 5H), 6.88–6.74 (m, 6H), 6.50 (d, *J* = 7.6 Hz, 1H), 3.82 (d, *J* = 5.2 Hz, 1H), 3.61 (dd, *J* = 8.8 Hz, *J* = 2.4 Hz, 1H), 3.15 (s, 6H), 2.04 (td, *J* = 12.0 Hz, *J* = 5.2 Hz, 1H), 1.88 (td, *J* = 12.0 Hz, *J* = 4.4 Hz, 1H), 1.77 (td, *J* = 12.0 Hz, *J* = 4.8 Hz, 1H), 1.64–1.51 (m, 2H), 1.49 (s, 3H), 1.47 (s, 3H), 1.40 (s, 3H), 1.39 (s, 3H), 1.34 (s, 3H), 1.32–1.23 (m, 3H), 1.22 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 180.4, 180.0, 151.3, 151.0, 144.5, 144.2, 143.4, 143.2, 135.72, 135.68, 133.4, 133.1, 129.1, 128.9, 128.0, 127.5, 127.4, 127.3, 125.8, 124.6, 124.5, 122.7, 122.6, 122.4, 122.3, 119.6, 119.3, 114.5, 114.3, 108.2, 107.7, 71.9, 71.0, 50.2, 49.4, 48.3, 48.2, 35.0, 32.8, 29.7, 28.0, 27.9, 26.1, 24.5, 23.8, 22.4, 22.2, 19.7, 19.3; ESI-HRMS: *m/z* Calcd for $C_{27}H_{29}N_3OS+Na^+$: 466.1924, found 466.1917.

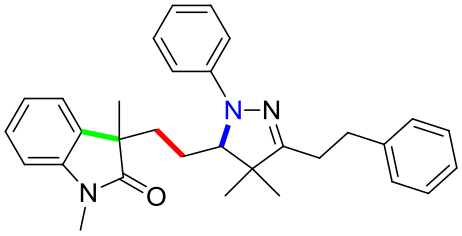


(dr ≈ 1.31:1)

tert-butyl 3-(5-(2-(1, 3-dimethyl-2-oxoindolin-3-yl) ethyl)-4, 4-dimethyl-1-phenyl-4, 5-dihydro-1H-pyrazol-3-yl)-1H-indole-1-carboxylate (3ab)

Yellow oil; (190 mg, 66% yield); R_f = 0.30 (hexanes/acetone 5:1, twice); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.51 (d, *J* = 6.8 Hz, 1H), 8.42 (d, *J* = 7.2 Hz, 1H), 8.13–8.09 (m, 2H), 7.88 (s, 1H), 7.84 (s, 1H), 7.39–7.32 (m, 4H), 7.28–7.15 (m, 9H), 7.08–7.05 (m, 3H), 6.95 (d, *J* = 8.0 Hz, 1H), 6.88–6.73 (m, 4H), 6.47 (d, *J* = 7.2 Hz, 1H), 3.80 (d, *J* = 6.0 Hz, 1H), 3.60 (d, *J* = 6.0 Hz, 1H), 3.14 (s, 3H), 3.13 (s, 3H), 2.05 (td, *J* = 13.2 Hz, *J* = 5.2 Hz, 1H), 1.91–1.76 (m, 3H), 1.76 (s, 9H), 1.71 (s, 9H), 1.70–1.58 (m, 2H), 1.52 (s, 3H), 1.43 (s, 3H), 1.41 (s, 3H), 1.35 (s, 3H), 1.32 (s, 3H), 1.26–1.23 (s, 2H), 1.17 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 180.3, 180.0, 151.2, 150.9, 149.6, 144.8, 144.6, 143.3, 143.1, 135.2, 135.1, 133.4, 133.1, 129.2, 129.1, 128.9, 127.9, 127.4, 125.0, 123.5, 123.4, 123.1, 122.7, 122.5, 122.3, 122.2, 119.2, 119.0, 114.8, 114.7, 114.2, 114.1, 112.9, 112.8, 108.1, 107.6, 84.24, 84.21, 70.6, 69.7, 50.5, 49.7, 48.3,

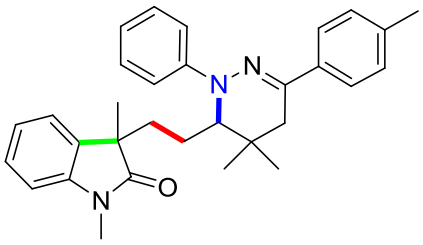
48.2, 35.0, 32.7, 28.2, 28.1, 26.10, 26.06, 24.6, 23.8, 22.2, 22.1, 20.0, 19.6; ESI-HRMS: *m/z* Calcd for $C_{36}H_{40}N_4O_3$+H^+: 577.3173, found 577.3161.



(dr ≈ 1.26:1)

3-(2-(4, 4-dimethyl-3-phenethyl-1-phenyl-4, 5-dihydro-1H-pyrazol-5-yl) ethyl)-1, 3-dimethylindolin-2-one (3ac)

Yellow oil; (188 mg, 81% yield); R_f = 0.35 (hexanes/acetone 5:1, twice); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29–7.08 (m, 18H), 6.91 (d, *J* = 8.8 Hz, 2H), 6.87 (d, *J* = 7.6 Hz, 1H), 6.82–6.76 (m, 6H), 6.60 (d, *J* = 7.2 Hz, 1H), 3.56 (d, *J* = 6.0 Hz, 1H), 3.30 (dd, *J* = 9.2 Hz, *J* = 2.8 Hz, 1H), 3.16 (s, 3H), 3.15 (s, 3H), 3.05–2.95 (m, 4H), 2.54–2.44 (m, 4H), 2.02 (td, *J* = 13.2 Hz, *J* = 5.2 Hz, 1H), 1.83–1.70 (m, 2H), 1.64–1.56 (m, 2H), 1.34 (s, 3H), 1.32–1.26 (m, 2H), 1.24 (s, 3H), 1.21–1.16 (m, 1H), 1.12 (s, 3H), 1.10 (s, 3H), 1.07 (s, 3H), 1.06 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 180.3, 180.1, 159.2, 158.6, 146.0, 145.5, 143.4, 143.1, 141.99, 141.96, 133.3, 133.1, 129.0, 128.7, 128.4, 128.3, 127.9, 127.5, 125.9, 122.6, 122.5, 122.4, 122.2, 119.0, 118.6, 114.4, 114.0, 108.1, 107.7, 70.6, 69.3, 50.5, 49.8, 48.24, 48.22, 35.0, 33.2, 32.6, 32.5, 28.0, 27.96, 26.7, 26.1, 26.0, 24.4, 23.8, 22.5, 22.3, 18.7, 18.3; ESI-HRMS: *m/z* Calcd for $C_{31}H_{35}N_3O$+H^+: 466.2853, found 466.2845.

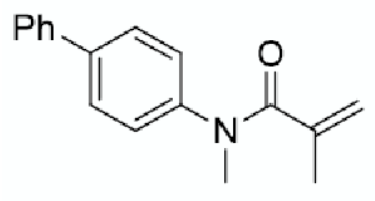


(dr ≈ 1.05:1)

3-(2-(4, 4-dimethyl-2-phenyl-6-(p-tolyl)-2, 3, 4, 5-tetrahydropyridazin-3-yl) ethyl)-1, 3-dimethylindolin-2-one (5)

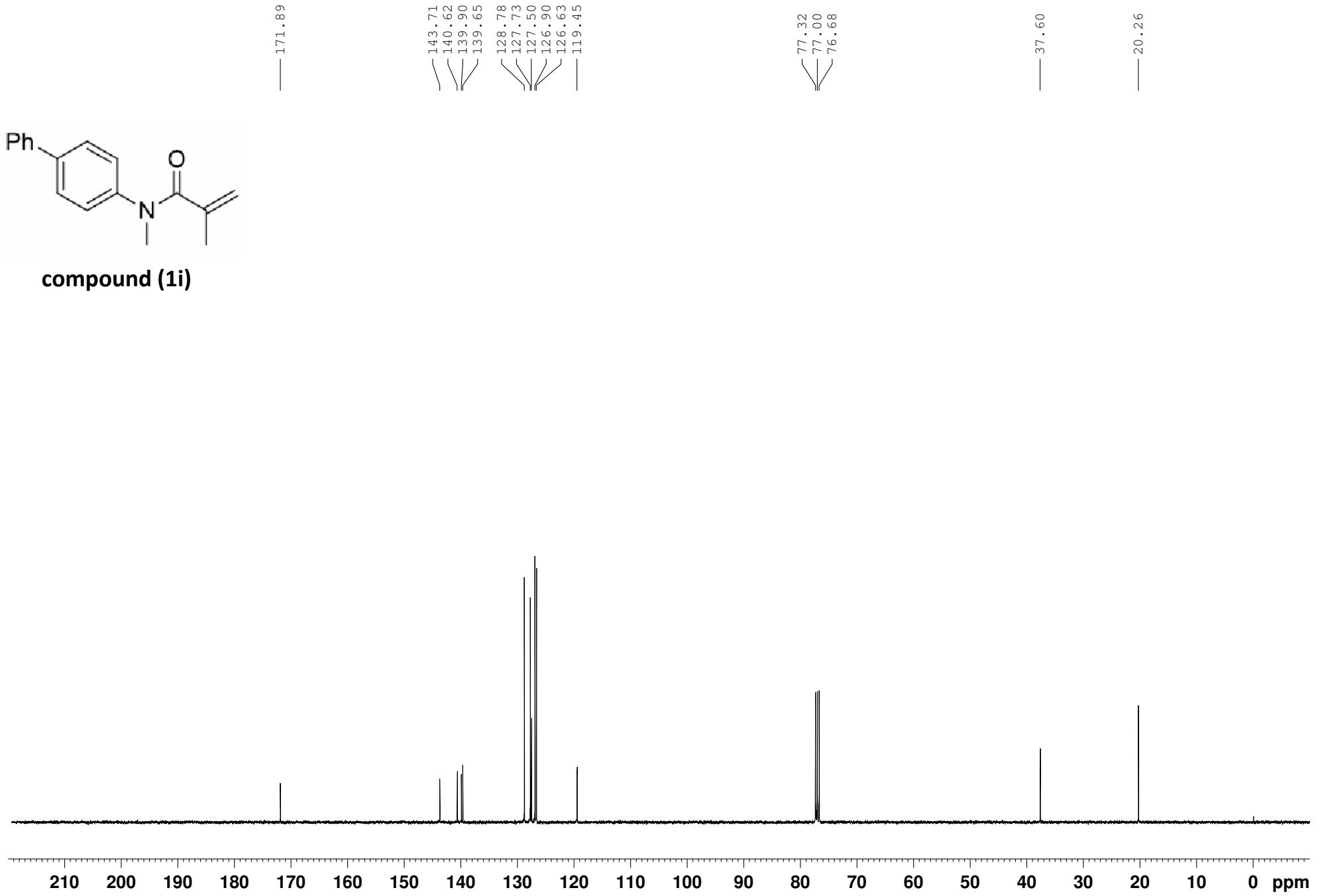
Yellow oil; (98 mg, 42% yield); R_f = 0.35 (hexanes/acetone 5:1, twice); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 (d, *J* = 8.4 Hz, 2H), 7.61 (d, *J* = 8.4 Hz, 2H), 7.31–7.27 (m, 5H), 7.24–7.10 (m, 9H), 7.00–6.92 (m, 3H), 6.88–6.73 (m, 5H), 3.56 (t, *J* = 6.2 Hz, 1H), 3.50 (t, *J* = 5.4 Hz, 1H), 3.16 (s, 3H), 3.12 (s, 3H), 2.36 (s, 6H), 2.27 (d, *J* = 2.8 Hz,

2H), 2.15 (d, J = 3.6 Hz, 2H), 2.08–1.98 (m, 2H), 1.86–1.77 (m, 2H), 1.58–1.25 (m, 4H), 1.26 (s, 6H), 1.05 (s, 3H), 1.04 (s, 3H), 0.82 (s, 3H), 0.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 180.3, 180.0, 147.7, 147.4, 143.1, 143.0, 139.4, 138.5, 137.3, 136.1, 135.9, 133.6, 133.0, 129.0, 128.9, 128.85, 128.78, 127.7, 127.6, 124.4, 122.6, 122.4, 122.29, 122.27, 119.3, 119.2, 114.0, 113.9, 107.9, 107.8, 60.92, 60.87, 48.4, 48.0, 36.3, 36.2, 33.2, 33.0, 30.33, 30.27, 28.3, 28.0, 27.2, 27.1, 26.1, 25.1, 24.9, 24.4, 23.4, 21.1; ESI-HRMS: *m/z* Calcd for $C_{31}H_{35}N_3O+H^+$: 466.2853, found 466.2846.

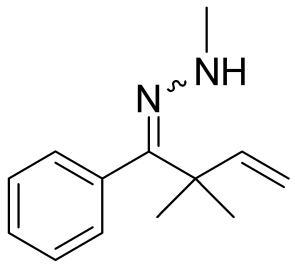

Ph
O
N

compound (1i)

7.589
7.586
7.571
7.550
7.457
7.439
7.419
7.369
7.351
7.332
7.256
7.207
7.186
5.073
5.049
3.377
1.806
0.000
11
10
9
8
7
6
5
4
3
2
1
0
ppm
4.09
2.04
1.05
2.02
1.03
1.00
3.02
3.03


171.89
143.71
140.62
139.90
139.65
128.78
127.73
127.50
126.90
126.63
119.45
77.32
77.00
76.68
37.60
20.26
Ph
O
N
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

compound (1i)


NH
N

compound (2f)

7.414
7.411
7.407
7.393
7.390
7.378
7.375
7.347
7.343
7.340
7.331
7.325
7.318
7.310
7.306
7.303
7.255
7.051
7.047
7.042
7.030
7.027
6.016
5.989
5.972
5.946
4.988
4.985
4.961
4.958
4.951
4.948
4.907
4.905
4.393
2.812
1.220
0.000
11
10
9
8
7
6
5
4
3
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1
0
ppm
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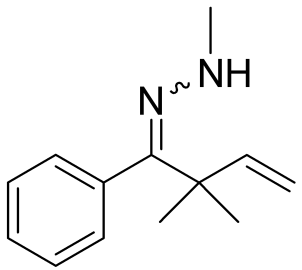
1.24
2.02
1.00
2.10
0.90
3.02
6.23


NH
N

compound (2f)

154.08
145.74
134.29
128.64
128.54
127.97
111.43
77.32
77.00
76.68
43.51
37.74
25.53
210
200
190
180
170
160
150
140
130
120
110
100
90
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60
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10
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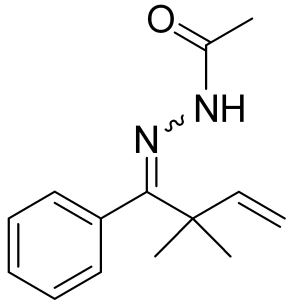
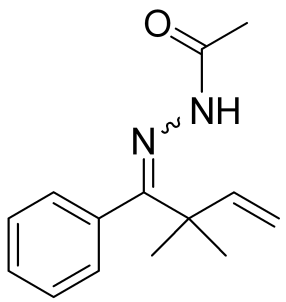

O
NH
N

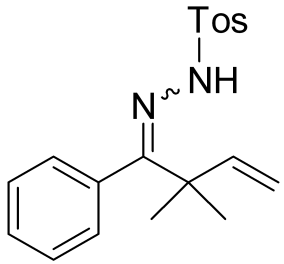
compound (2g)

7.895
7.445
7.438
7.423
7.405
7.390
7.278
7.026
7.022
7.007
7.003
5.960
5.933
5.916
5.889
5.065
5.063
5.038
5.037
5.008
4.965
2.305
1.264
0.000
11
10
9
8
7
6
5
4
3
2
1
0
ppm
0.99
3.34
2.14
1.02
2.20
3.00
6.11


O
NH
N

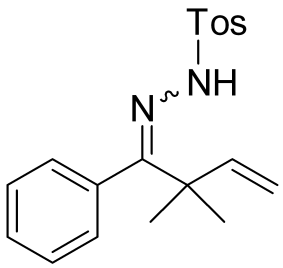
compound (2g)

172.82
158.32
144.15
131.91
129.10
129.00
127.99
112.84
77.32
77.00
76.68
44.15
25.18
20.42
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


Tos
NH
N

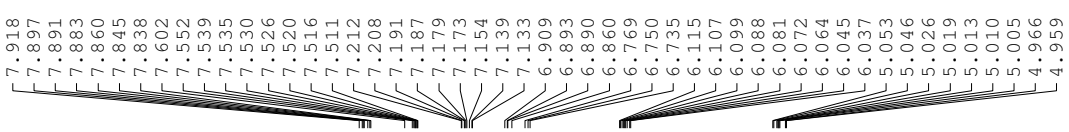
compound (2h)

7.788
7.767
7.389
7.381
7.374
7.340
7.320
7.266
6.957
6.817
6.814
6.808
6.801
5.765
5.738
5.721
5.695
4.971
4.945
4.860
4.817
2.456
1.158
0.000
11
10
9
8
7
6
5
4
3
2
1
0
ppm
2.20
3.02
2.25
1.01
2.41
1.00
2.05
3.07
6.19


Tos
NH
N

compound (2h)

162.93
143.88
143.85
135.29
131.42
129.34
129.31
129.11
127.87
127.63
113.12
77.32
77.00
76.68
44.40
25.14
21.57
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


7.918
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7.891
7.883
7.860
7.845
7.838
7.602
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7.539
7.535
7.530
7.526
7.520
7.516
7.511
7.212
7.208
7.191
7.187
7.179
7.173
7.154
7.139
7.133
6.909
6.893
6.890
6.860
6.769
6.750
6.735
6.115
6.107
6.099
6.088
6.081
6.072
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6.045
6.037
5.053
5.046
5.026
5.019
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5.010
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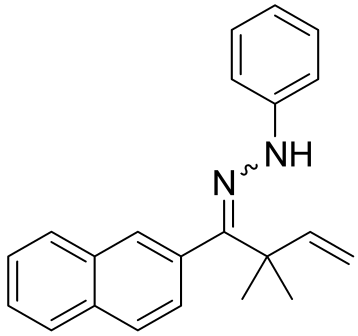
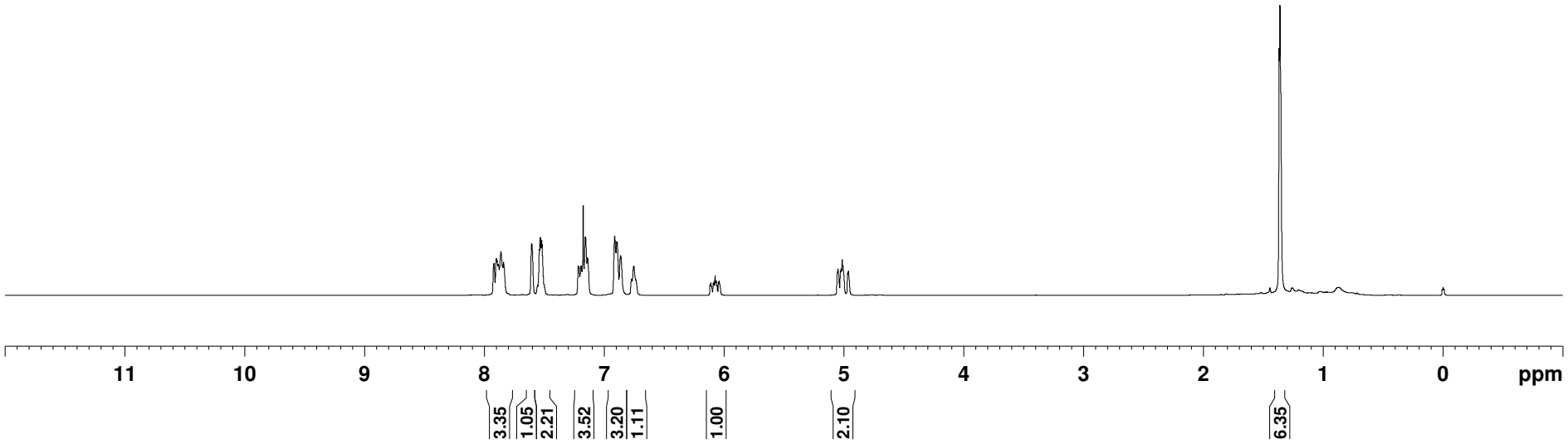
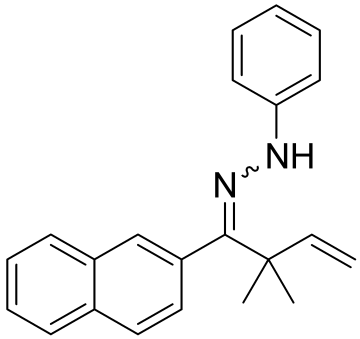
0.000
-0.009


NH
N

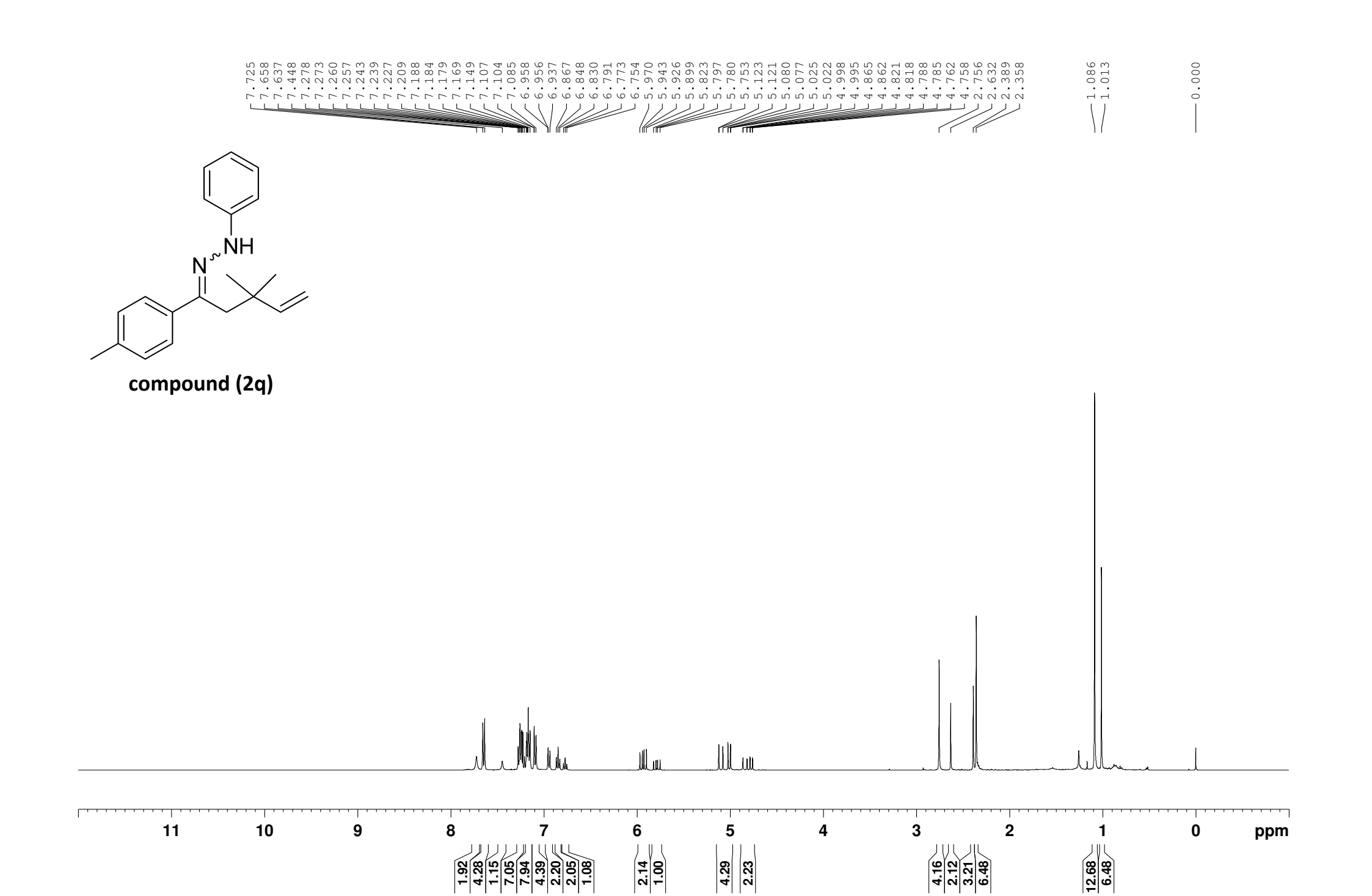
compound (2m)


11
10
9
8
7
6
5
4
3
2
1
0
ppm
3.35
1.05
2.21
3.52
3.20
1.11
1.00
2.10
6.35

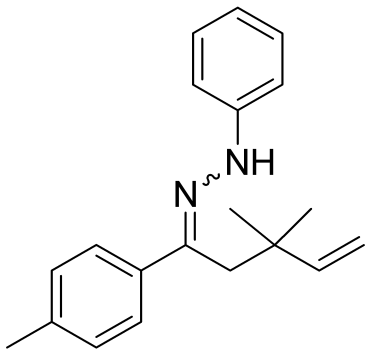

NH
N

compound (2m)

152.03
145.55
145.30
133.13
132.96
130.92
129.05
128.70
128.21
128.07
127.79
126.71
126.50
119.37
112.55
112.06
77.32
77.00
76.68
44.30
25.70
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


7.725
7.658
7.637
7.448
7.278
7.273
7.260
7.257
7.243
7.239
7.227
7.209
7.188
7.184
7.179
7.169
7.149
7.107
7.104
7.085
6.958
6.956
6.937
6.867
6.848
6.830
6.791
6.773
6.754
5.970
5.943
5.926
5.899
5.823
5.797
5.780
5.753
5.123
5.121
5.080
5.077
5.025
5.022
4.998
4.995
4.865
4.862
4.821
4.818
4.788
4.785
4.762
4.758
2.756
2.632
2.389
2.358
1.086
1.013
0.000
NH
N
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.92
4.28
1.15
7.05
7.94
4.39
2.20
2.05
1.08
2.14
1.00
4.29
2.23
4.16
2.12
3.21
6.48
12.68
6.48

compound (2q)



compound (2q)

148.21
148.14
145.28
143.57
138.50
137.59
137.57
132.46
129.81
129.17
129.10
128.89
127.81
126.09
119.86
119.26
112.98
112.62
111.48
109.95

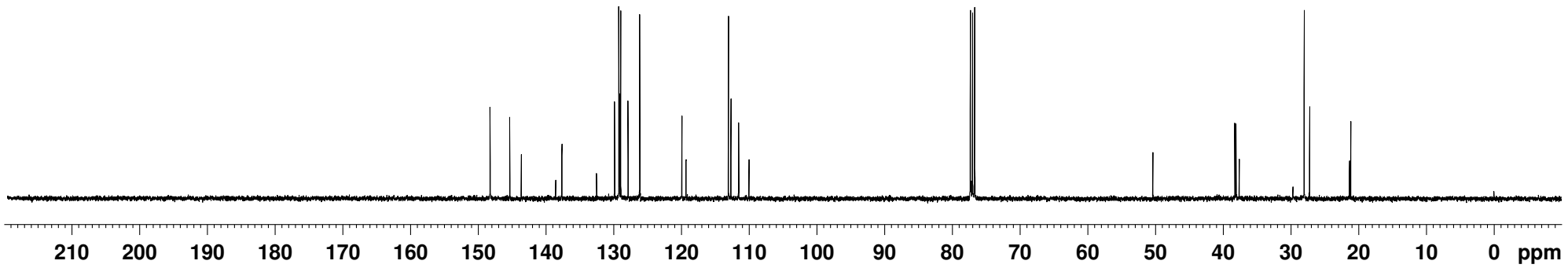
77.31
77.00
76.68

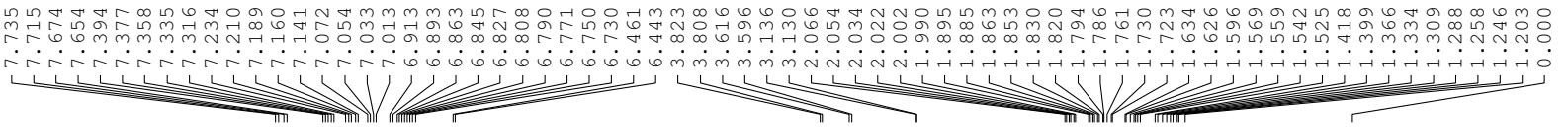
50.36

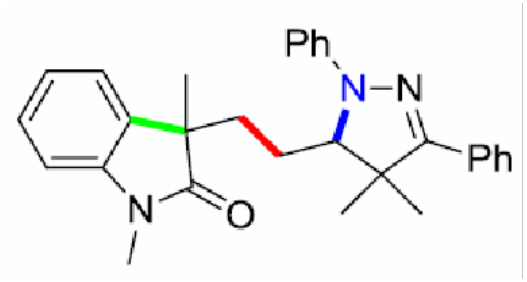
38.26
38.08
37.60

28.02
27.21

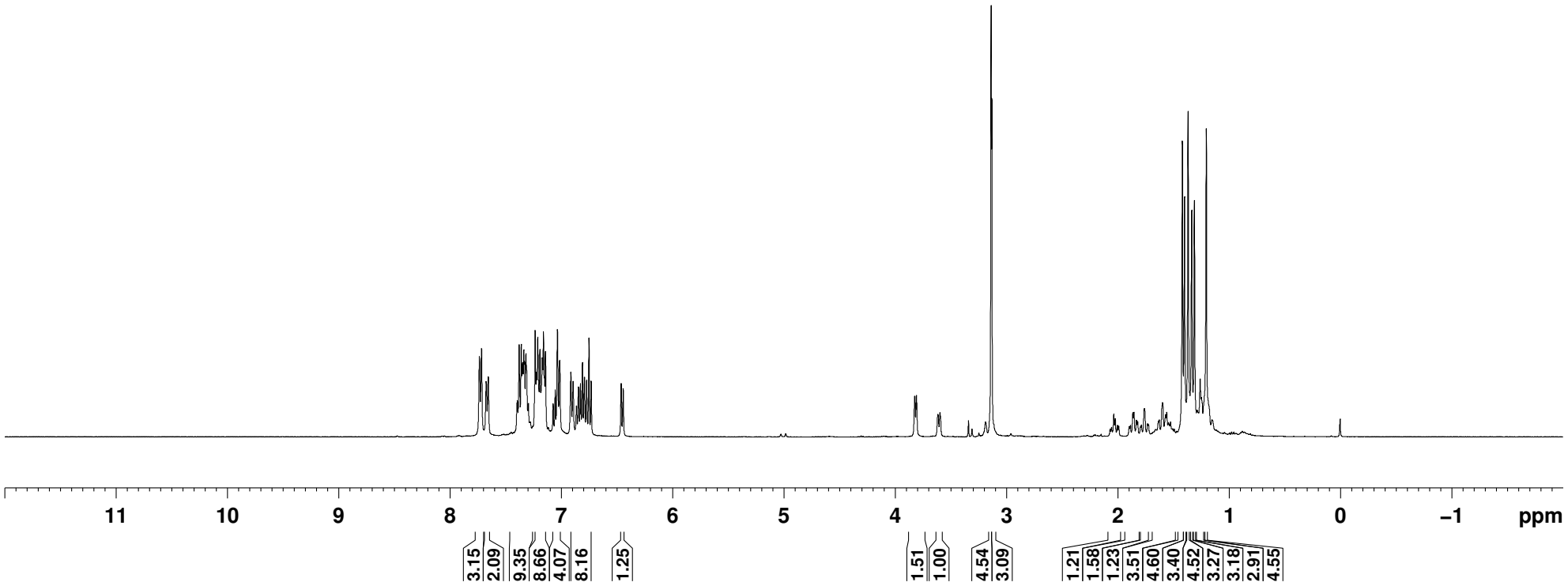
21.33
21.14

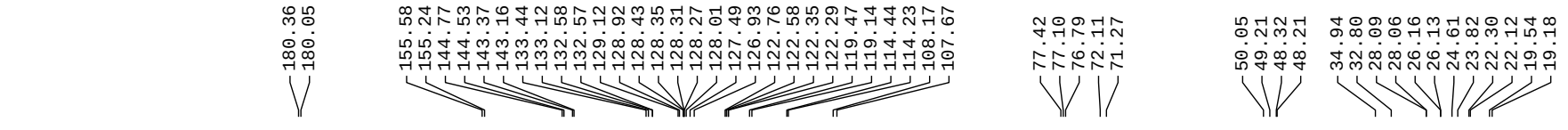


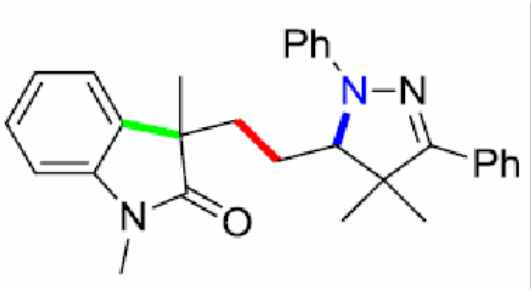

7.735
7.715
7.674
7.654
7.394
7.377
7.358
7.335
7.316
7.234
7.210
7.189
7.160
7.141
7.072
7.054
7.033
7.013
6.913
6.893
6.863
6.845
6.827
6.808
6.790
6.771
6.750
6.730
6.461
6.443
3.823
3.808
3.616
3.596
3.136
3.130
2.066
2.054
2.034
2.022
2.002
1.990
1.895
1.885
1.863
1.853
1.830
1.820
1.794
1.786
1.761
1.730
1.723
1.634
1.626
1.596
1.569
1.559
1.542
1.525
1.418
1.399
1.366
1.334
1.309
1.288
1.258
1.246
1.203
0.000


Ph
N–N
Ph
N
O

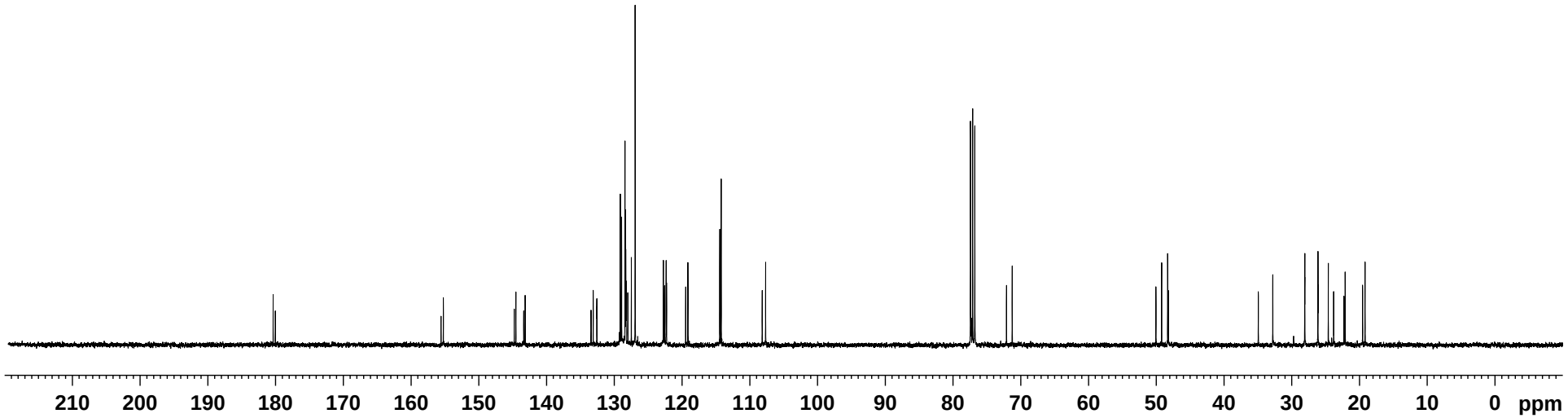
compound (3a)

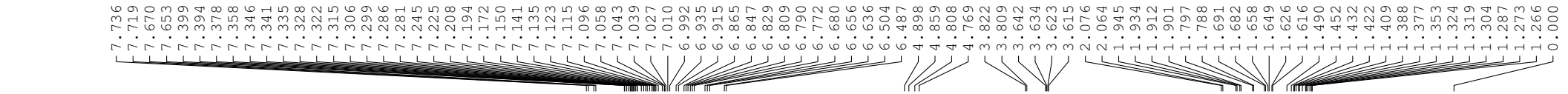

11
10
9
8
7
6
5
4
3
2
1
0
–1
ppm
3.15
2.09
9.35
8.66
4.07
8.16
1.25
1.51
1.00
4.54
3.09
1.21
1.58
1.23
3.51
4.60
3.40
4.52
3.27
3.18
2.91
4.55

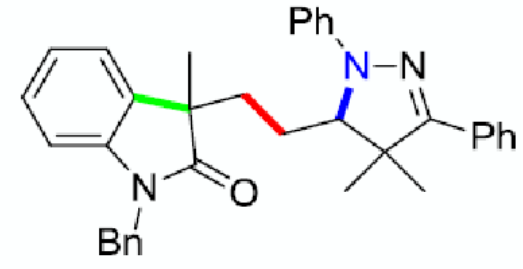

180.36
180.05
155.58
155.24
144.77
144.53
143.37
143.16
133.44
133.12
132.58
132.57
129.12
128.92
128.43
128.35
128.31
128.27
128.01
127.49
126.93
122.76
122.58
122.35
122.29
119.47
119.14
114.44
114.23
108.17
107.67
77.42
77.10
76.79
72.11
71.27
50.05
49.21
48.32
48.21
34.94
32.80
28.09
28.06
26.16
26.13
24.61
23.82
22.30
22.12
19.54
19.18


Ph
N
N
Ph
N
O

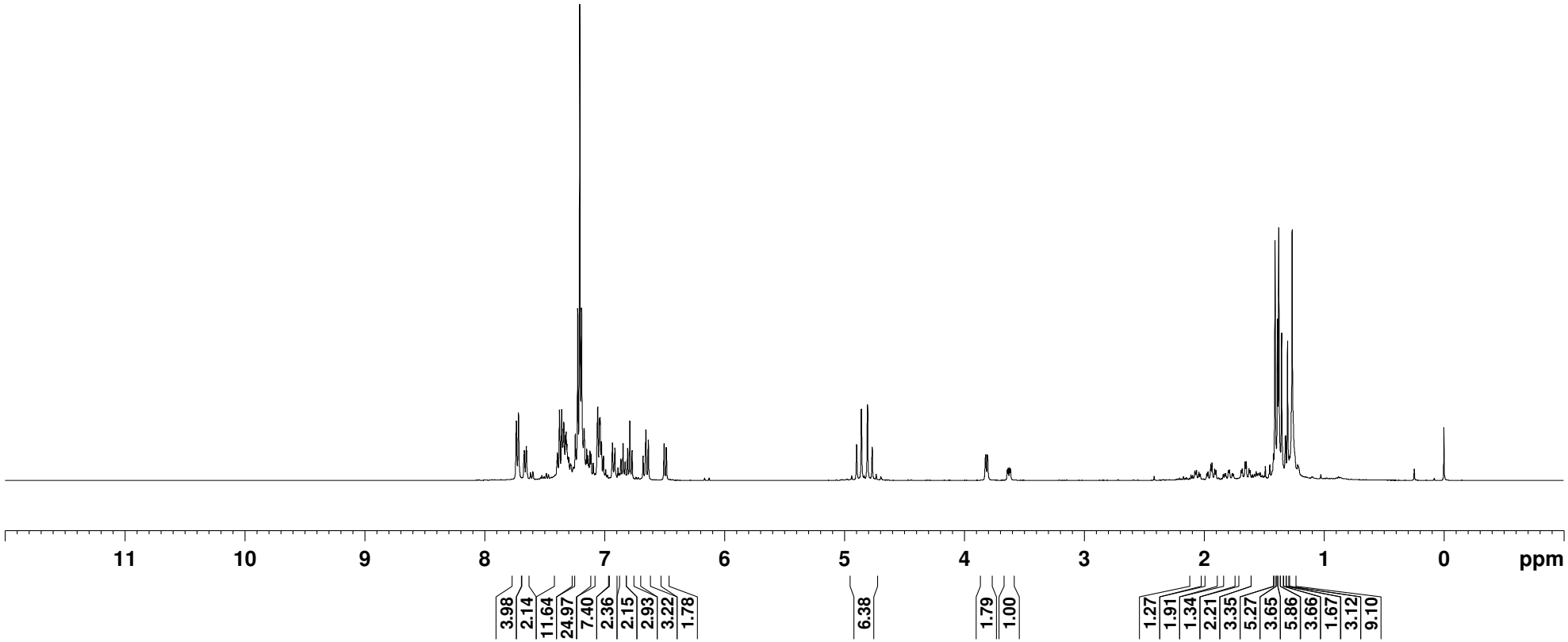
compound (3a)

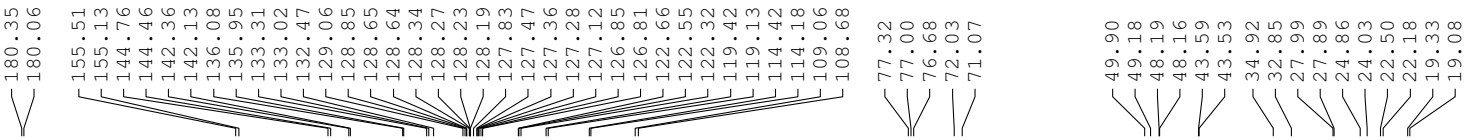

210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

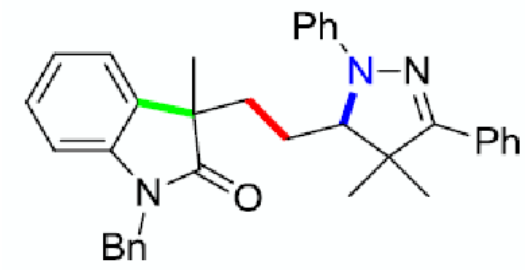

7.736
7.719
7.670
7.653
7.399
7.394
7.378
7.358
7.346
7.341
7.335
7.328
7.322
7.315
7.306
7.299
7.286
7.281
7.245
7.225
7.208
7.194
7.172
7.150
7.141
7.135
7.123
7.115
7.096
7.058
7.043
7.039
7.027
7.010
6.992
6.935
6.915
6.865
6.847
6.829
6.809
6.790
6.772
6.680
6.656
6.636
6.504
6.487
4.898
4.859
4.808
4.769
3.822
3.809
3.642
3.634
3.623
3.615
2.076
2.064
1.945
1.934
1.912
1.901
1.797
1.788
1.691
1.682
1.658
1.649
1.626
1.616
1.490
1.452
1.432
1.422
1.409
1.388
1.377
1.353
1.324
1.319
1.304
1.287
1.273
1.266
0.000


Ph
N–N
Ph
N
O
Bn

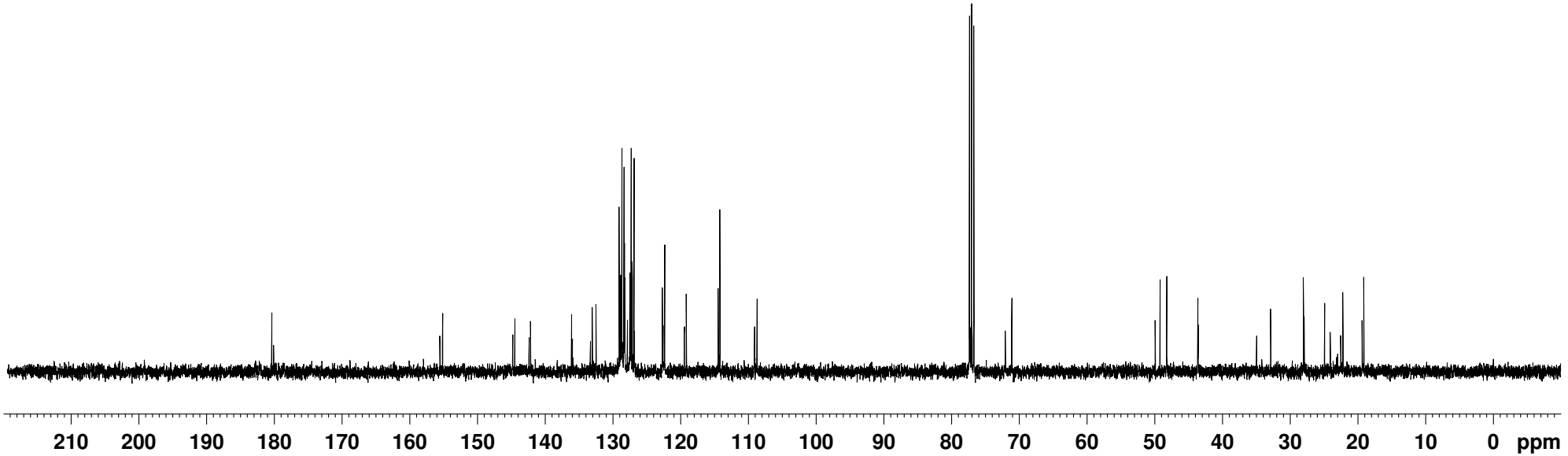
compound (3b)

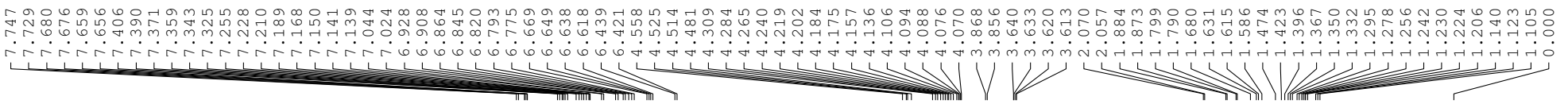

11
10
9
8
7
6
5
4
3
2
1
0
ppm
3.98
2.14
11.64
24.97
7.40
2.36
2.15
2.93
3.22
1.78
6.38
1.79
1.00
1.27
1.91
1.34
2.21
3.35
5.27
3.65
5.86
3.66
1.67
3.12
9.10


180.35
180.06
155.51
155.13
144.76
144.46
142.36
142.13
136.08
135.95
133.31
133.02
132.47
129.06
128.85
128.65
128.64
128.34
128.27
128.23
128.19
127.83
127.47
127.36
127.28
127.12
126.85
126.81
122.66
122.55
122.32
119.42
119.13
114.42
114.18
109.06
108.68
77.32
77.00
76.68
72.03
71.07
49.90
49.18
48.19
48.16
43.59
43.53
34.92
32.85
27.99
27.89
24.86
24.03
22.50
22.18
19.33
19.08


Ph
N
N
Ph
N
O
Bn

compound (3b)


210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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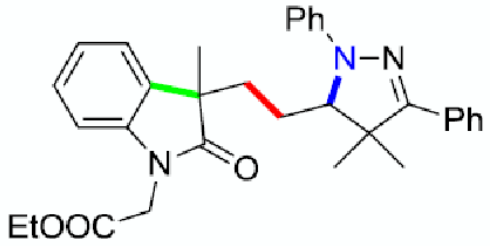
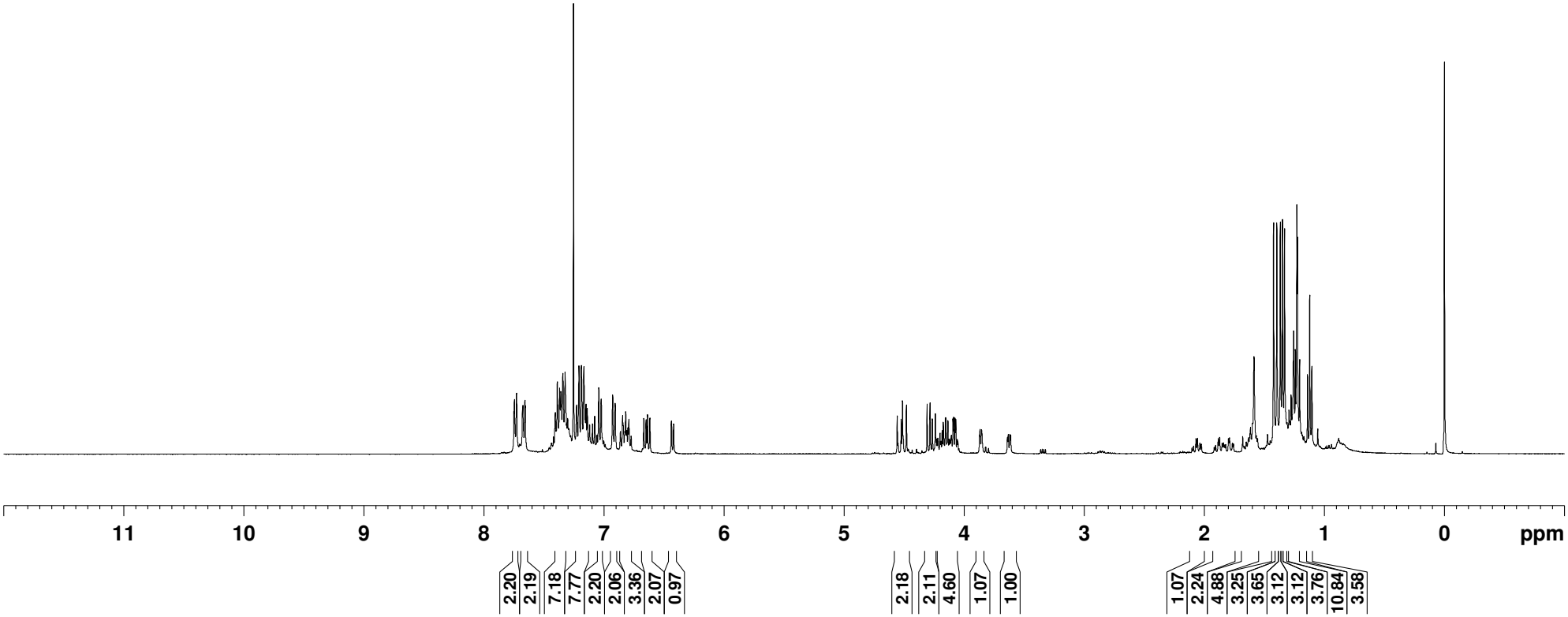
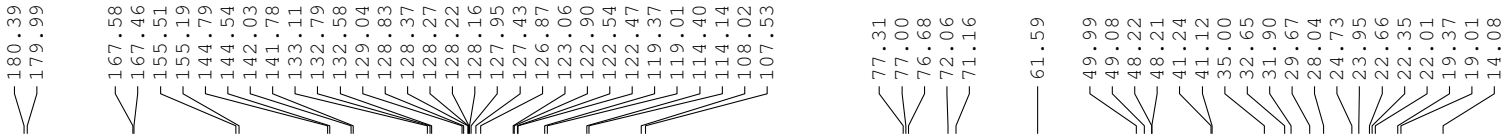
7.656
7.406
7.390
7.371
7.359
7.343
7.325
7.255
7.228
7.210
7.189
7.168
7.150
7.141
7.139
7.044
7.024
6.928
6.908
6.864
6.845
6.820
6.793
6.775
6.669
6.649
6.638
6.618
6.439
6.421
4.558
4.525
4.514
4.481
4.309
4.284
4.265
4.240
4.219
4.202
4.184
4.175
4.157
4.136
4.106
4.094
4.088
4.076
4.070
3.868
3.856
3.640
3.633
3.620
3.613
2.070
2.057
1.884
1.873
1.799
1.790
1.680
1.631
1.615
1.586
1.474
1.423
1.396
1.367
1.350
1.332
1.295
1.278
1.256
1.242
1.230
1.224
1.206
1.140
1.123
1.105
0.000


Ph
N–N
Ph
N
O
EtOOC

compound (3c)


11
10
9
8
7
6
5
4
3
2
1
0
ppm
2.20
2.19
7.18
7.77
2.20
2.06
3.36
2.07
0.97
2.18
2.11
4.60
1.07
1.00
1.07
2.24
4.88
3.25
3.65
3.12
3.12
3.76
10.84
3.58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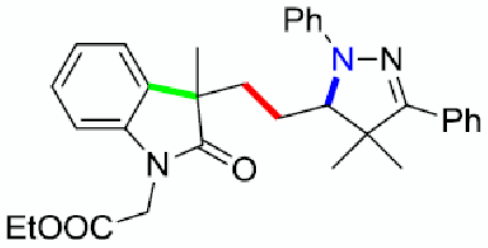
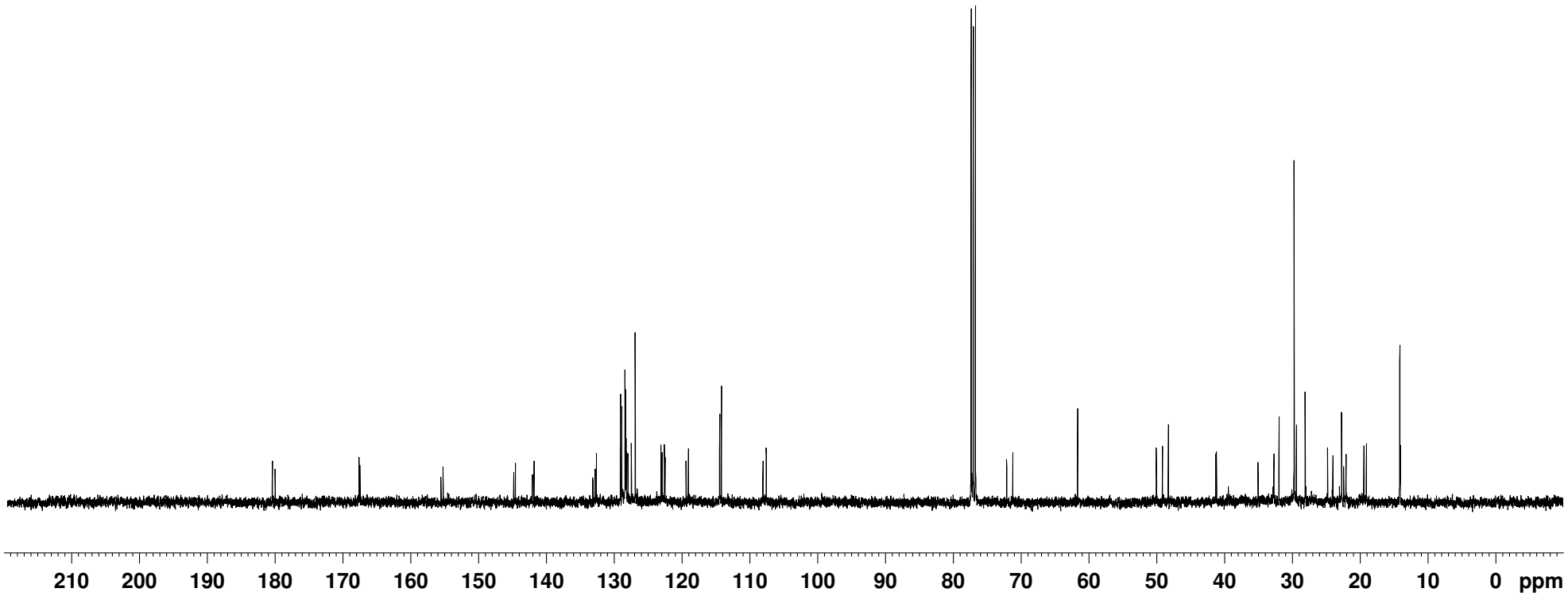
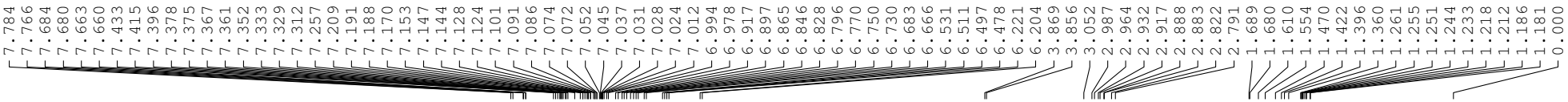
179.99
167.58
167.46
155.51
155.19
144.79
144.54
142.03
141.78
133.11
132.79
132.58
129.04
128.83
128.37
128.27
128.22
128.16
127.95
127.43
126.87
123.06
122.90
122.54
122.47
119.37
119.01
114.40
114.14
108.02
107.53
77.31
77.00
76.68
72.06
71.16
61.59
49.99
49.08
48.22
48.21
41.24
41.12
35.00
32.65
31.90
29.67
28.04
24.73
23.95
22.66
22.35
22.01
19.37
19.01
14.08


Ph
N–N
Ph
N
O
EtOOC

compound (3c)


210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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7.660
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7.415
7.396
7.378
7.375
7.367
7.361
7.352
7.333
7.329
7.312
7.257
7.209
7.191
7.188
7.170
7.153
7.147
7.144
7.128
7.124
7.101
7.091
7.086
7.074
7.072
7.052
7.045
7.037
7.031
7.028
7.024
7.012
6.994
6.978
6.917
6.897
6.865
6.846
6.828
6.796
6.770
6.750
6.730
6.683
6.666
6.531
6.511
6.497
6.478
6.221
6.204
3.869
3.856
3.052
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2.964
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2.917
2.888
2.883
2.822
2.791
1.689
1.680
1.610
1.554
1.470
1.422
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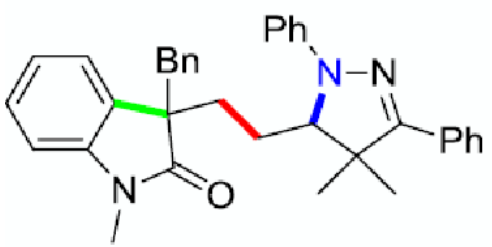
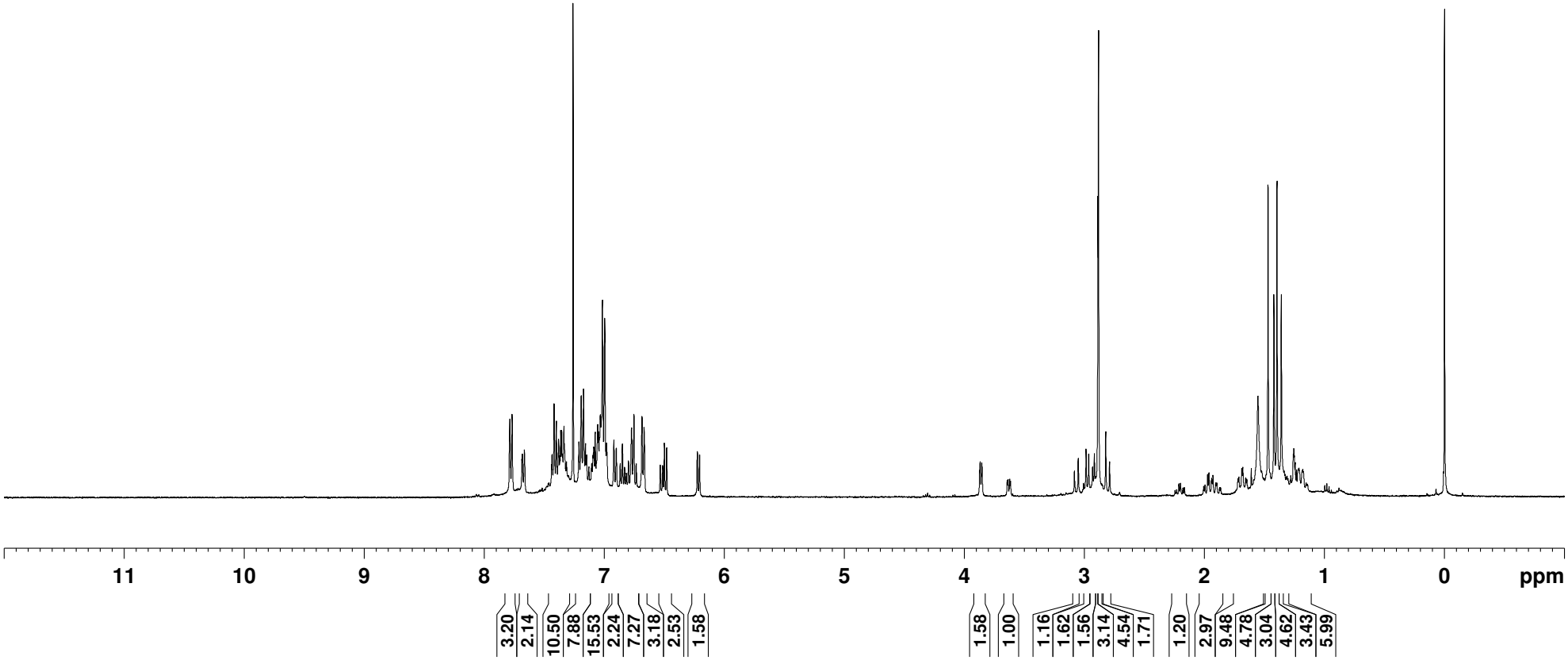
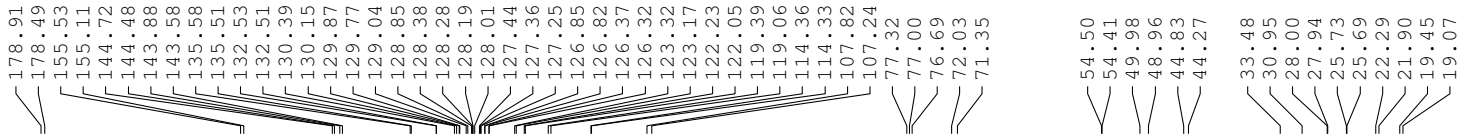
1.360
1.261
1.255
1.251
1.244
1.233
1.218
1.212
1.186
1.181
0.000


Ph
Bn
N–N
Ph
N
O

compound (3f)


11
10
9
8
7
6
5
4
3
2
1
0
ppm
3.20
2.14
10.50
7.88
15.53
2.24
7.27
3.18
2.53
1.58
1.58
1.00
1.16
1.62
1.56
3.14
4.54
1.71
1.20
2.97
9.48
4.78
3.04
4.62
3.43
5.99


178.91
178.49
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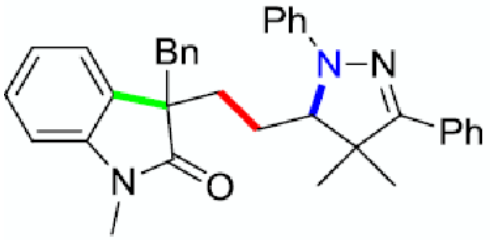
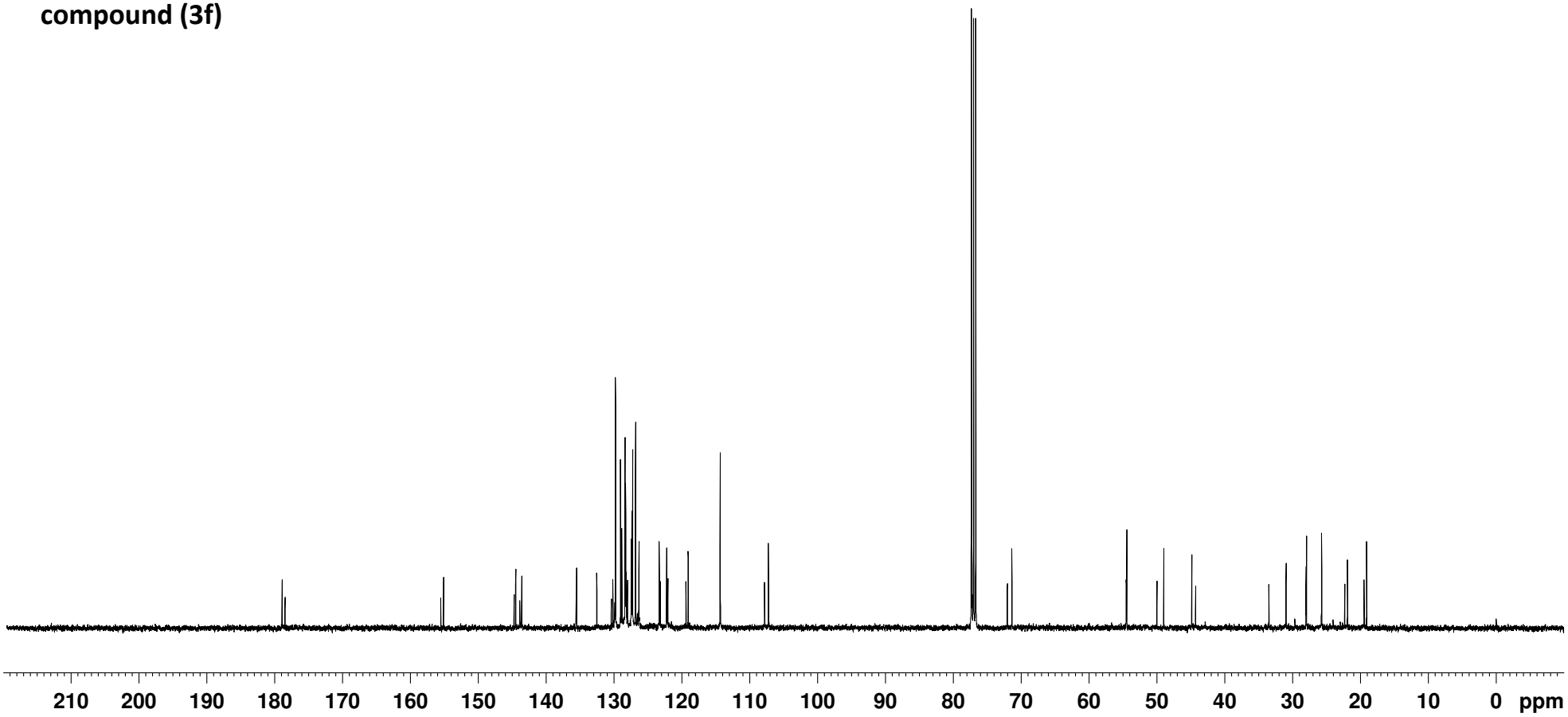
155.11
144.72
144.48
143.88
143.58
135.58
135.51
132.53
132.51
130.39
130.15
129.87
129.77
129.04
128.85
128.38
128.28
128.19
128.01
127.44
127.36
127.25
126.85
126.82
126.37
126.32
123.32
123.17
122.23
122.05
119.39
119.06
114.36
114.33
107.82
107.24
77.32
77.00
76.69
72.03
71.35
54.50
54.41
49.98
48.96
44.83
44.27
33.48
30.95
28.00
27.94
25.73
25.69
22.29
21.90
19.45
19.07


Ph
Bn
N–N
Ph
N
O

compound (3f)


210
200
190
180
170
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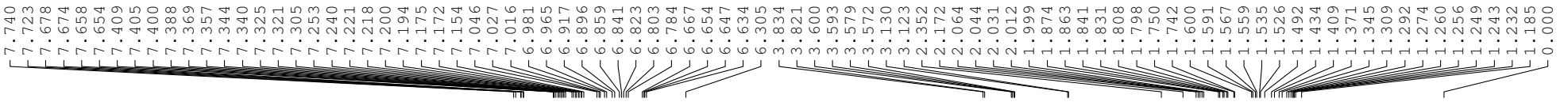
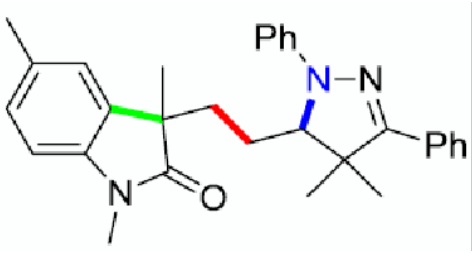
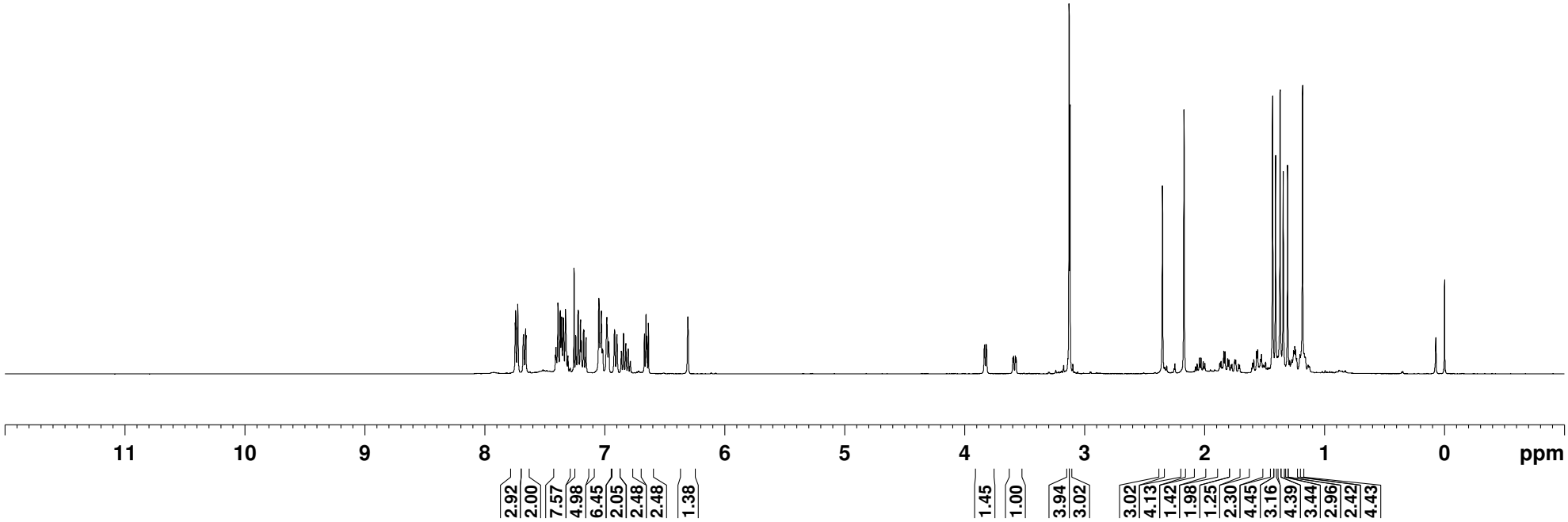
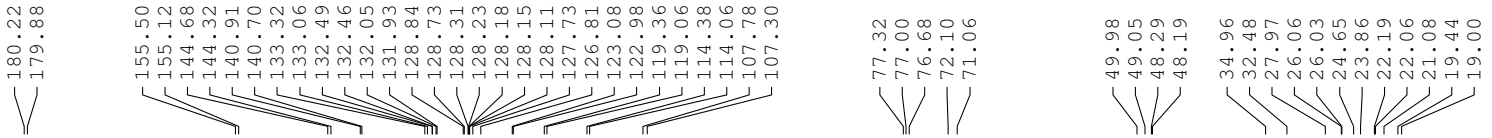
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

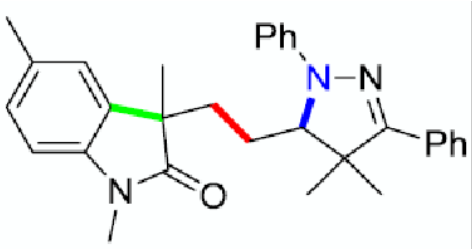

7.740
7.723
7.678
7.674
7.658
7.654
7.409
7.405
7.400
7.388
7.369
7.357
7.344
7.340
7.325
7.321
7.305
7.253
7.240
7.221
7.218
7.200
7.194
7.175
7.172
7.154
7.046
7.027
7.016
6.981
6.965
6.917
6.896
6.859
6.841
6.823
6.803
6.784
6.667
6.654
6.647
6.634
6.305
3.834
3.821
3.600
3.593
3.579
3.572
3.130
3.123
2.352
2.172
2.064
2.044
2.031
2.012
1.999
1.874
1.863
1.841
1.831
1.808
1.798
1.750
1.742
1.600
1.591
1.567
1.559
1.535
1.526
1.492
1.434
1.409
1.371
1.345
1.309
1.292
1.274
1.260
1.256
1.249
1.243
1.232
1.185
0.000


Ph
N–N
Ph
N
O

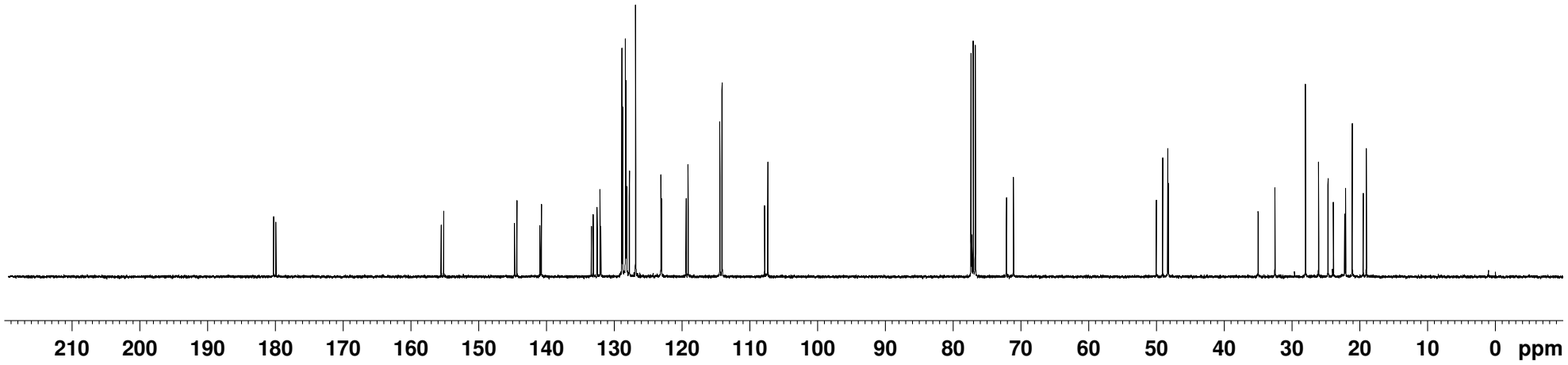
compound (3g)


11
10
9
8
7
6
5
4
3
2
1
0
ppm
2.92
2.00
7.57
4.98
6.45
2.05
2.48
2.48
1.38
1.45
1.00
3.94
3.02
3.02
4.13
1.42
1.98
1.25
2.30
4.45
3.16
4.39
3.44
2.96
2.42
4.43


180.22
179.88
155.50
155.12
144.68
144.32
140.91
140.70
133.32
133.06
132.49
132.46
132.05
131.93
128.84
128.73
128.31
128.23
128.18
128.15
128.11
127.73
126.81
123.08
122.98
119.36
119.06
114.38
114.06
107.78
107.30
77.32
77.00
76.68
72.10
71.06
49.98
49.05
48.29
48.19
34.96
32.48
27.97
26.06
26.03
24.65
23.86
22.19
22.06
21.08
19.44
19.00


Ph
N
N
Ph
N
O

compound (3g)


210
200
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140
130
120
110
100
90
80
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60
50
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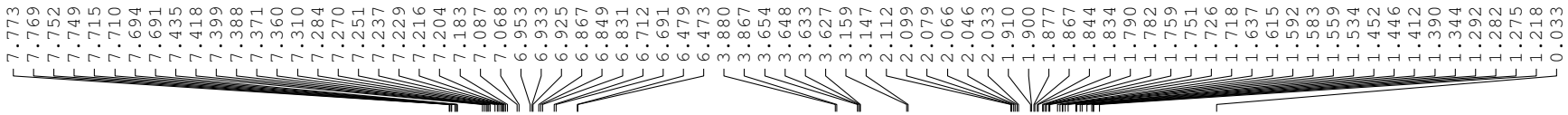
30
20
10
0
ppm


7.773
7.769
7.752
7.749
7.715
7.710
7.694
7.691
7.435
7.418
7.399
7.388
7.371
7.360
7.310
7.284
7.270
7.251
7.237
7.229
7.216
7.204
7.183
7.087
7.068
6.953
6.933
6.925
6.867
6.849
6.831
6.712
6.691
6.479
6.473
3.880
3.867
3.654
3.648
3.633
3.627
3.159
3.147
2.112
2.099
2.079
2.066
2.046
2.033
1.910
1.900
1.877
1.867
1.844
1.834
1.790
1.782
1.759
1.751
1.726
1.718
1.637
1.615
1.592
1.583
1.559
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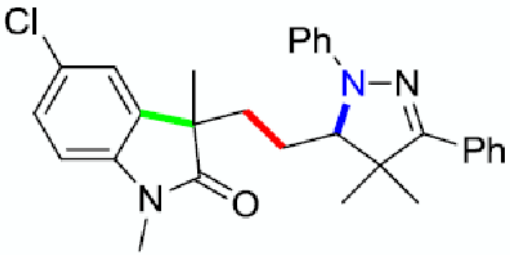
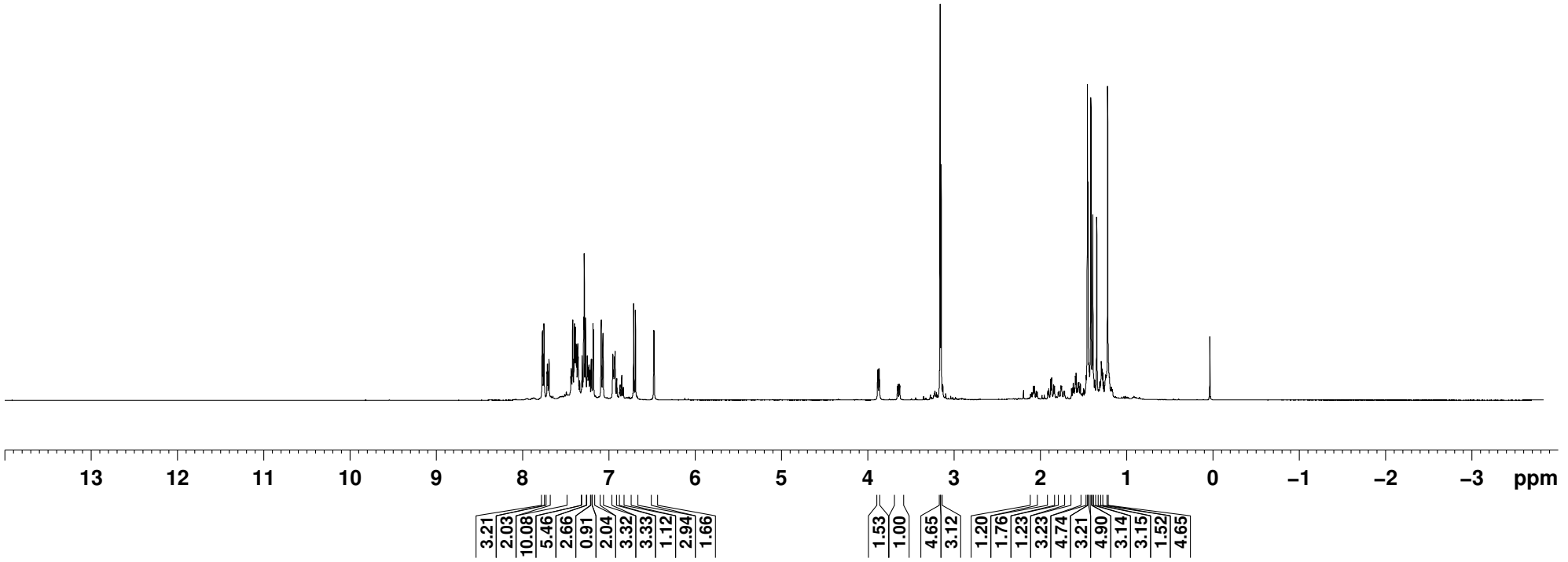
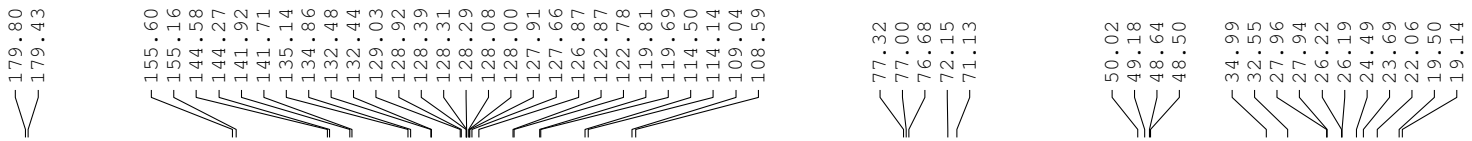
1.344
1.292
1.282
1.275
1.218
0.033


Cl
Ph
N–N
Ph
N
O

compound (3h)


13
12
11
10
9
8
7
6
5
4
3
2
1
0
–1
–2
–3
ppm
3.21
2.03
10.08
5.46
2.66
0.91
2.04
3.32
3.33
1.12
2.94
1.66
1.53
1.00
4.65
3.12
1.20
1.76
1.23
3.23
4.74
3.21
4.90
3.14
3.15
1.52
4.65


179.80
179.43
155.60
155.16
144.58
144.27
141.92
141.71
135.14
134.86
132.48
132.44
129.03
128.92
128.39
128.31
128.29
128.08
128.00
127.91
127.66
126.87
122.87
122.78
119.81
119.69
114.50
114.14
109.04
108.59
77.32
77.00
76.68
72.15
71.13
50.02
49.18
48.64
48.50
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27.96
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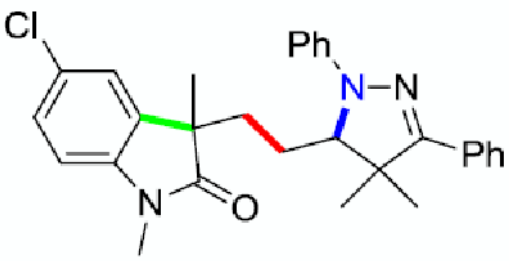
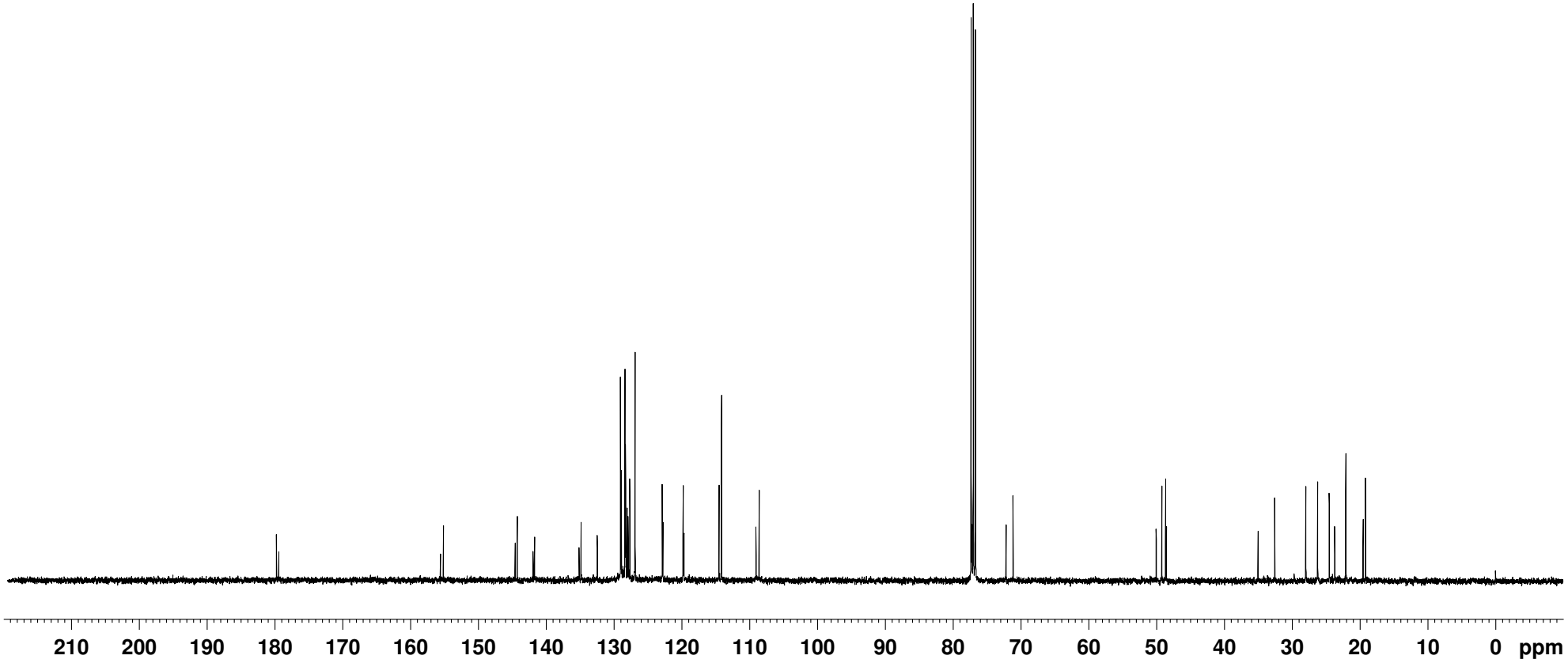
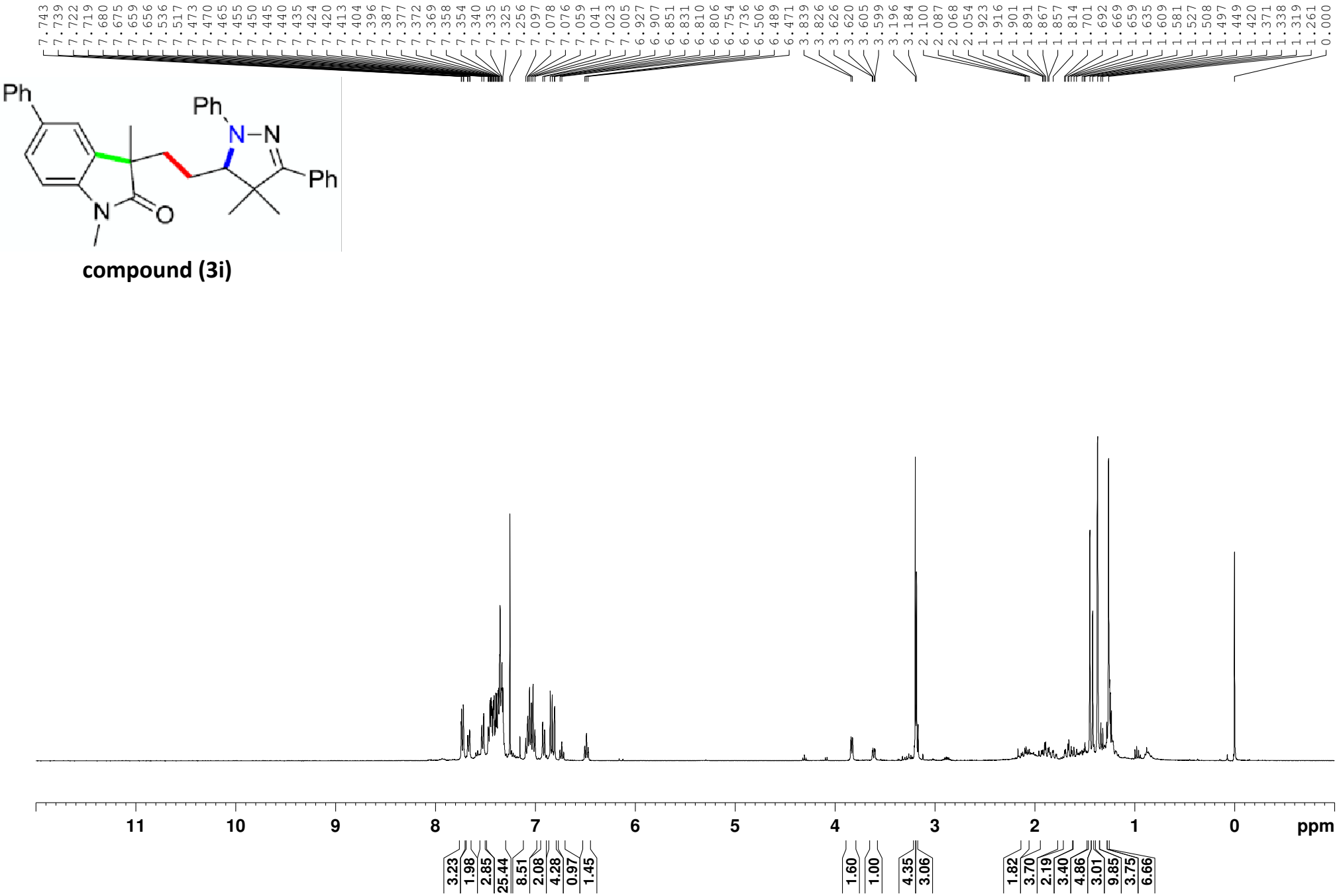
26.22
26.19
24.49
23.69
22.06
19.50
19.14

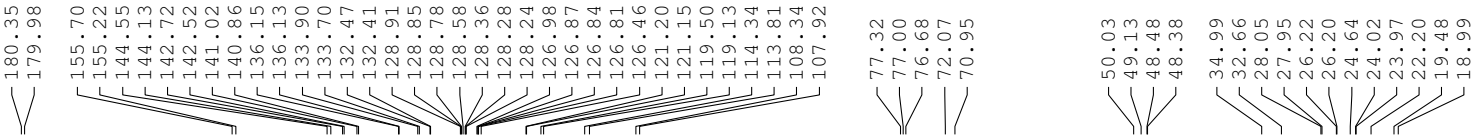

Cl
Ph
N–N
Ph
N
O

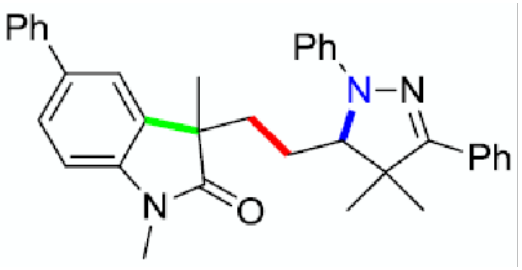
compound (3h)


210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

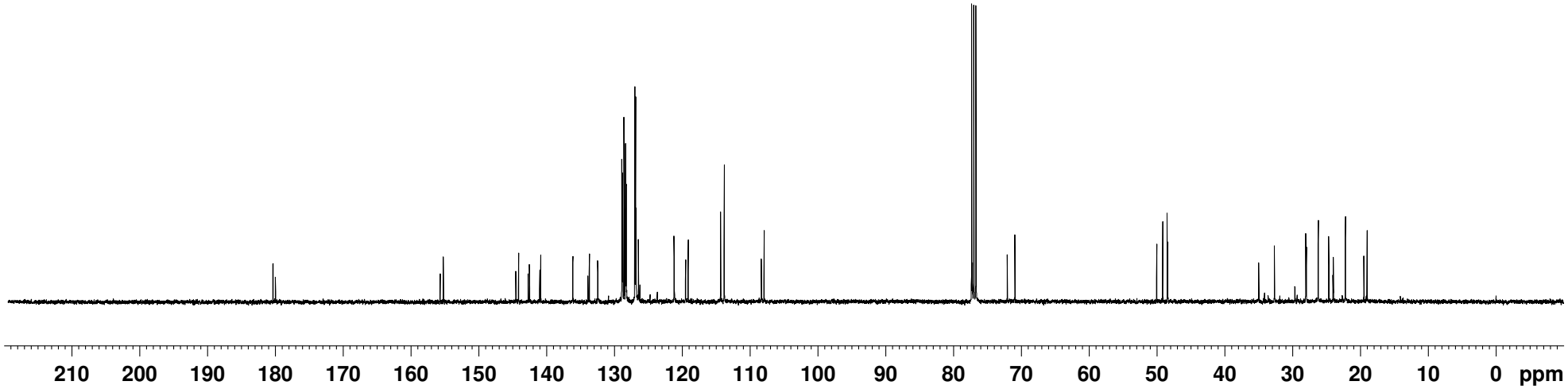

7.743 7.739 7.722 7.719 7.680 7.675 7.659 7.656 7.536 7.517 7.473 7.470 7.465 7.455 7.450 7.445 7.440 7.435 7.424 7.420 7.413 7.404 7.396 7.387 7.377 7.372 7.369 7.358 7.354 7.340 7.335 7.325 7.256 7.097 7.078 7.076 7.059 7.041 7.023 7.005 6.927 6.907 6.851 6.831 6.810 6.806 6.754 6.736 6.506 6.489 6.471 3.839 3.826 3.626 3.620 3.605 3.599 3.196 3.184 2.100 2.087 2.068 2.054 1.923 1.916 1.901 1.891 1.867 1.857 1.814 1.701 1.692 1.669 1.659 1.635 1.609 1.581 1.527 1.508 1.497 1.449 1.420 1.371 1.338 1.319 1.261 0.000
Ph
Ph
N–N
Ph
N
O
11 10 9 8 7 6 5 4 3 2 1 0 ppm
3.23 1.98 2.85 25.44 8.51 2.08 4.28 0.97 1.45
1.60 1.00 4.35 3.06
1.82 3.70 2.19 3.40 4.86 3.01 9.85 3.75 6.66

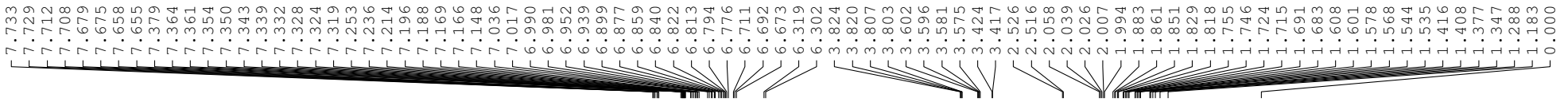
compound (3i)


180.35
179.98
155.70
155.22
144.55
144.13
142.72
142.52
141.02
140.86
136.15
136.13
133.90
133.70
132.47
132.41
128.91
128.85
128.78
128.58
128.36
128.28
128.24
126.98
126.87
126.84
126.81
126.46
121.20
121.15
119.50
119.13
114.34
113.81
108.34
107.92
77.32
77.00
76.68
72.07
70.95
50.03
49.13
48.48
48.38
34.99
32.66
28.05
27.95
26.22
26.20
24.64
24.02
23.97
22.20
19.48
18.99


Ph
Ph
N
N
Ph
N
O

compound (3i)


210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


7.733
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7.712
7.708
7.679
7.675
7.658
7.655
7.379
7.364
7.361
7.354
7.350
7.343
7.339
7.332
7.328
7.324
7.319
7.253
7.236
7.214
7.196
7.188
7.169
7.166
7.148
7.036
7.017
6.990
6.981
6.952
6.939
6.899
6.877
6.859
6.840
6.822
6.813
6.794
6.776
6.711
6.692
6.673
6.319
6.302
3.824
3.820
3.807
3.803
3.602
3.596
3.581
3.575
3.424
3.417
2.526
2.516
2.058
2.039
2.026
2.007
1.994
1.883
1.861
1.851
1.829
1.818
1.755
1.746
1.724
1.715
1.691
1.683
1.608
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1.578
1.568
1.544
1.535
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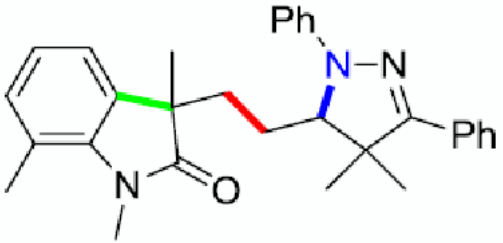
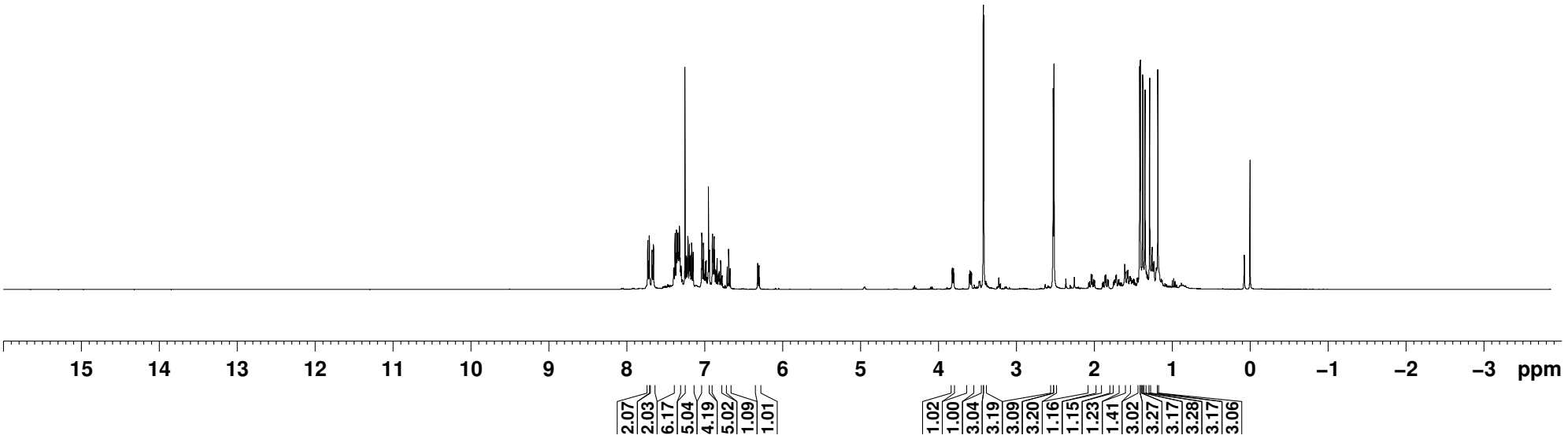
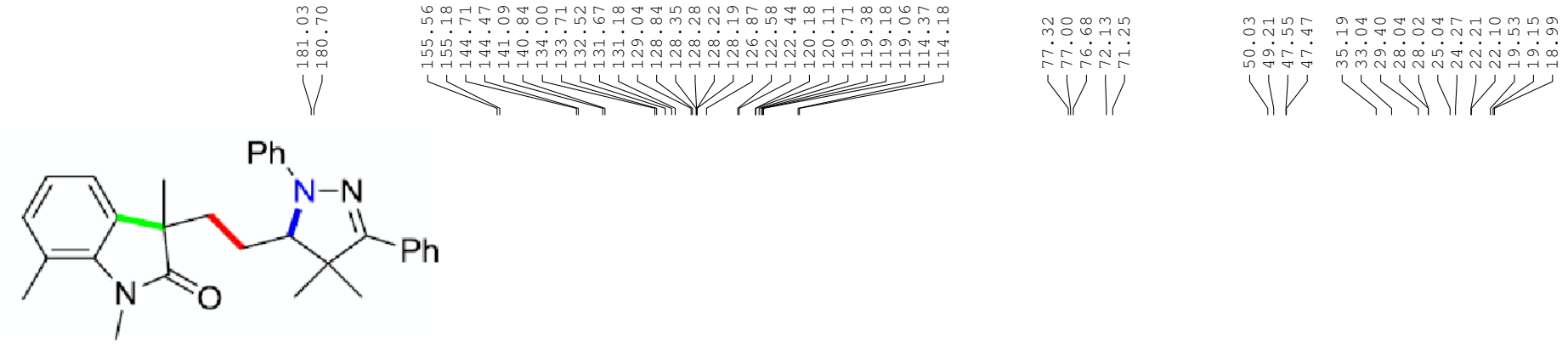
1.408
1.377
1.347
1.288
1.183
0.000

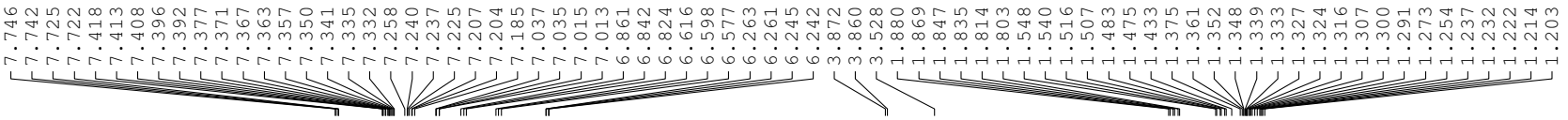

Ph
N
N
Ph
N
O

compound (3j)


15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
−1
−2
−3
ppm
2.07
2.03
6.17
5.04
4.19
5.02
1.09
1.01
1.02
1.00
3.04
3.19
3.09
3.20
1.16
1.15
1.23
1.41
3.02
3.27
3.17
3.28
3.17
3.06


181.03
180.70
155.56
155.18
144.71
144.47
141.09
140.84
134.00
133.71
132.52
131.67
131.18
129.04
128.84
128.35
128.28
128.22
128.19
126.87
122.58
122.44
120.18
120.11
119.71
119.38
119.18
119.06
114.37
114.18
77.32
77.00
76.68
72.13
71.25
50.03
49.21
47.55
47.47
35.19
33.04
29.40
28.04
28.02
25.04
24.27
22.21
22.10
19.53
19.15
18.99
Ph
N–N
Ph
N
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

compound (3j)


7.746
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7.725
7.722
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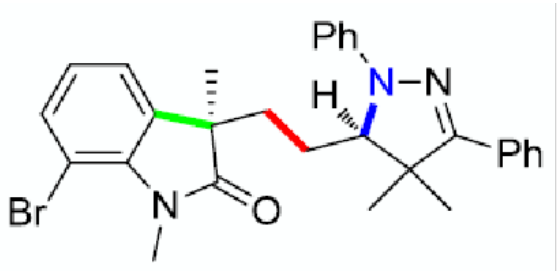
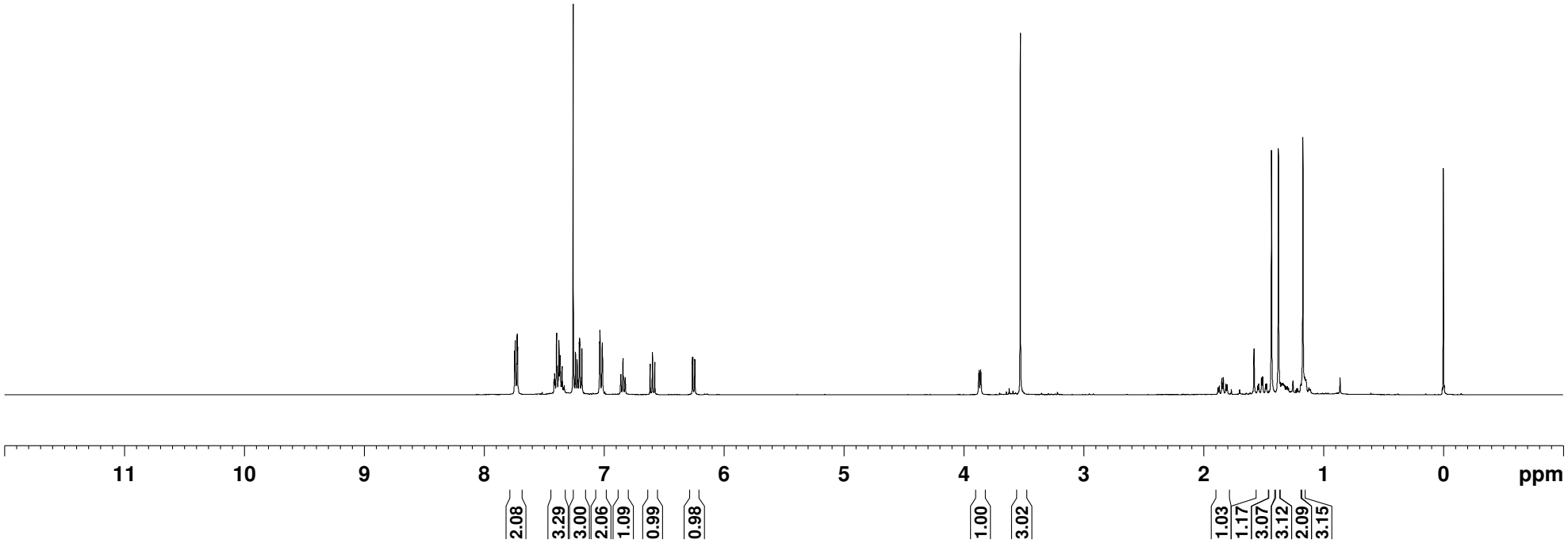
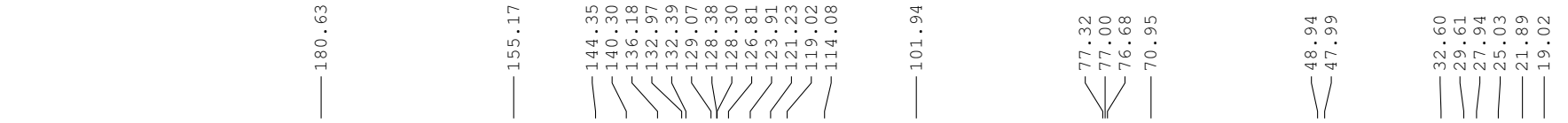
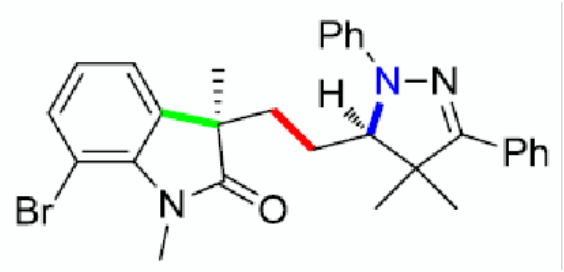
7.413
7.408
7.396
7.392
7.377
7.371
7.367
7.363
7.357
7.350
7.341
7.335
7.332
7.258
7.240
7.237
7.225
7.207
7.204
7.185
7.037
7.035
7.015
7.013
6.861
6.842
6.824
6.616
6.598
6.577
6.263
6.261
6.245
6.242
3.872
3.860
3.528
1.880
1.869
1.847
1.835
1.814
1.803
1.548
1.540
1.516
1.507
1.483
1.475
1.433
1.375
1.361
1.352
1.348
1.339
1.333
1.327
1.324
1.316
1.307
1.300
1.291
1.273
1.254
1.237
1.232
1.222
1.214
1.203


Ph
N–N
H
Ph
Br
N
O

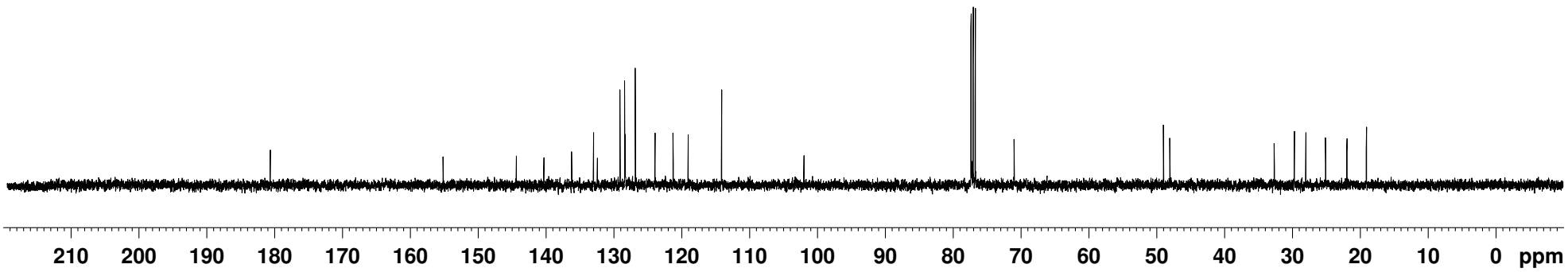
compound (3k)

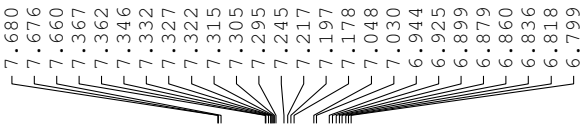

11
10
9
8
7
6
5
4
3
2
1
0
ppm
2.08
3.29
3.00
2.06
1.09
0.99
0.98
1.00
3.02
1.03
1.17
3.07
3.12
2.09
3.15


180.63
155.17
144.35
140.30
136.18
132.97
132.39
129.07
128.38
128.30
126.81
123.91
121.23
119.02
114.08
101.94
77.32
77.00
76.68
70.95
48.94
47.99
32.60
29.61
27.94
25.03
21.89
19.02


Ph
N–N
H
Ph
Br
N
O

compound (3k)


210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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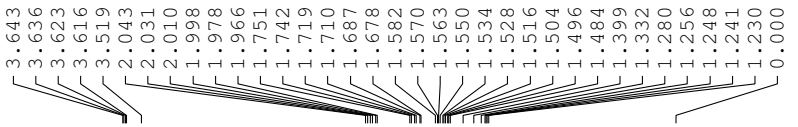
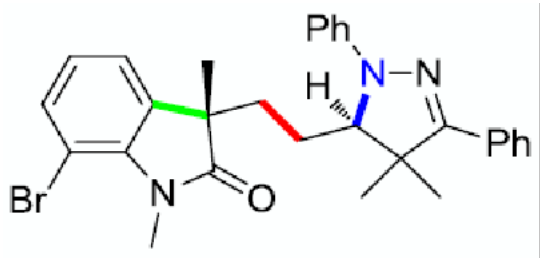
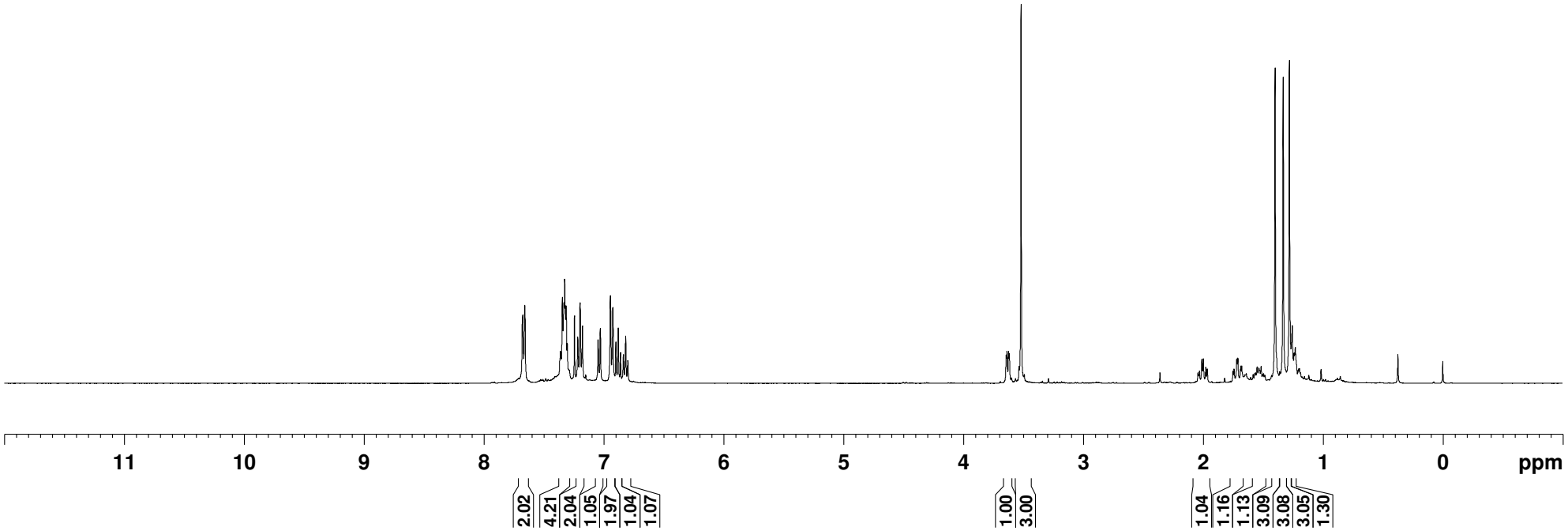
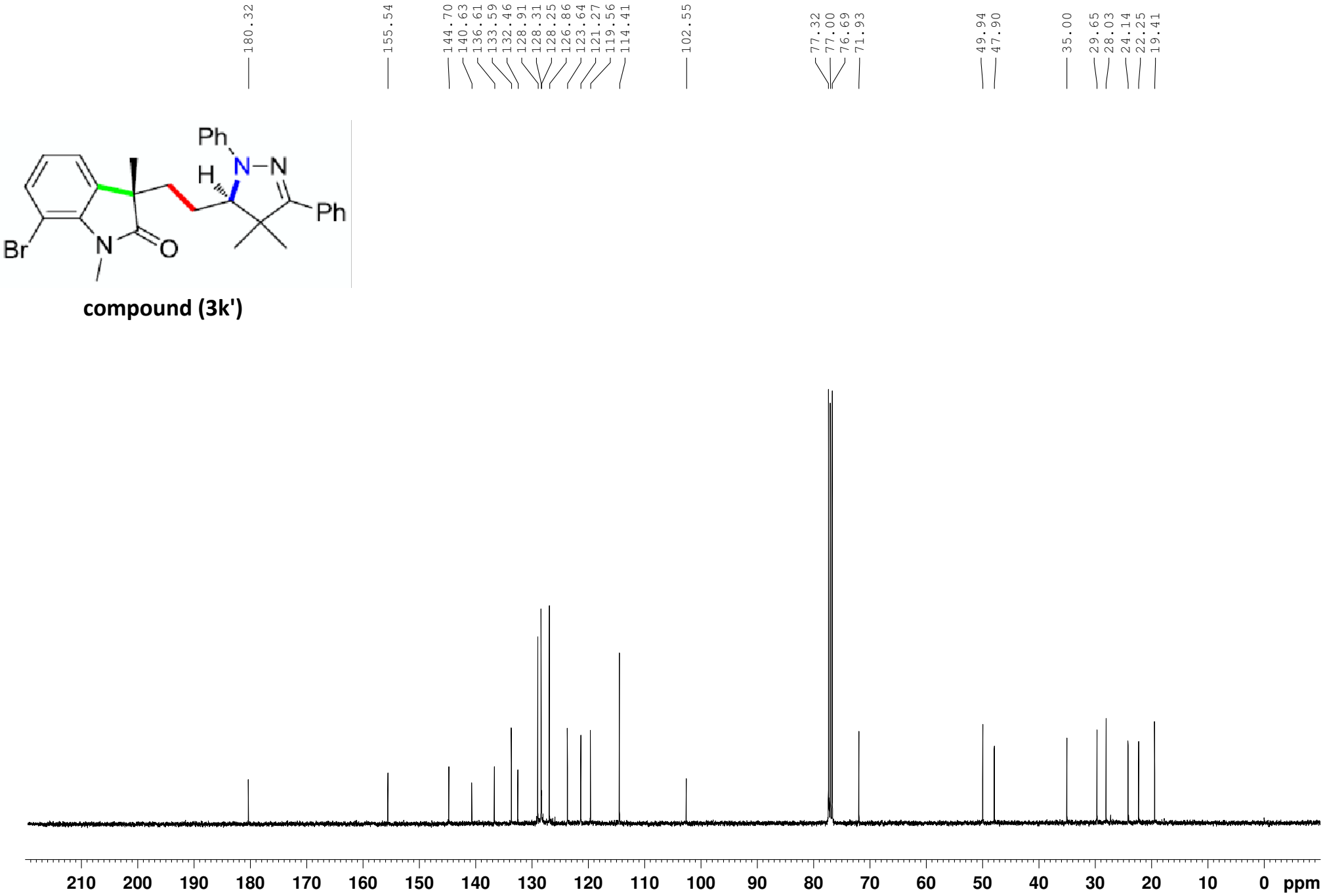
7.676
7.660
7.367
7.362
7.346
7.332
7.327
7.322
7.315
7.305
7.295
7.245
7.217
7.197
7.178
7.048
7.030
6.944
6.925
6.899
6.879
6.860
6.836
6.818
6.799


3.643
3.636
3.623
3.616
3.519
2.043
2.031
2.010
1.998
1.978
1.966
1.751
1.742
1.719
1.710
1.687
1.678
1.582
1.570
1.563
1.550
1.534
1.528
1.516
1.504
1.496
1.484
1.399
1.332
1.280
1.256
1.248
1.241
1.230
0.000

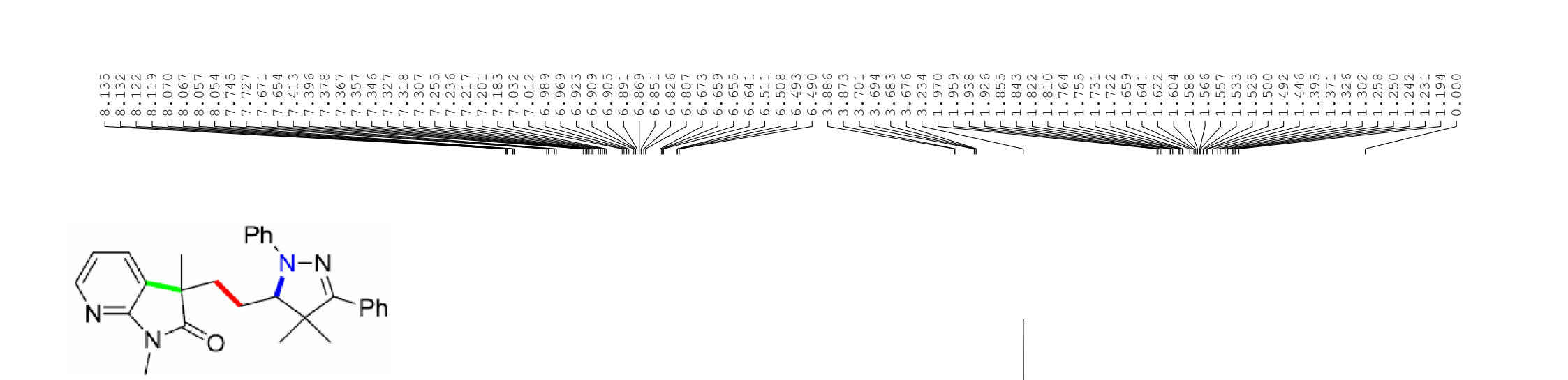

Ph
H
N–N
Ph
Br
N
O

compound (3k')


11
10
9
8
7
6
5
4
3
2
1
0
ppm
2.02
4.21
2.04
1.05
1.97
1.04
1.07
1.00
3.00
1.04
1.16
1.13
3.09
3.08
3.05
1.30

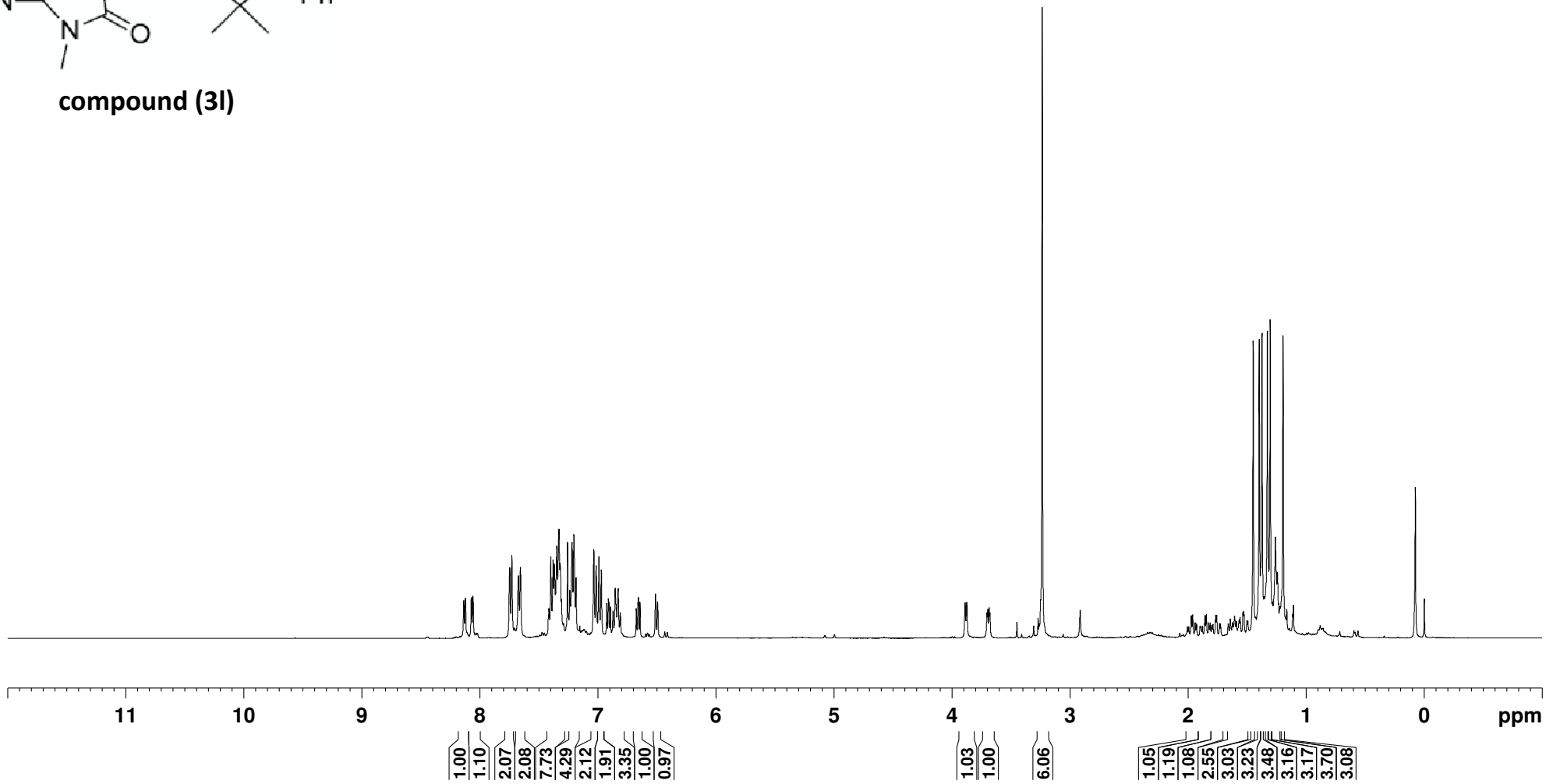

180.32
155.54
144.70
140.63
136.61
133.59
132.46
128.91
128.31
128.25
126.86
123.64
121.27
119.56
114.41
102.55
77.32
77.00
76.69
71.93
49.94
47.90
35.00
29.65
28.03
24.14
22.25
19.41
Ph
H
N–N
Ph
Br
N
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

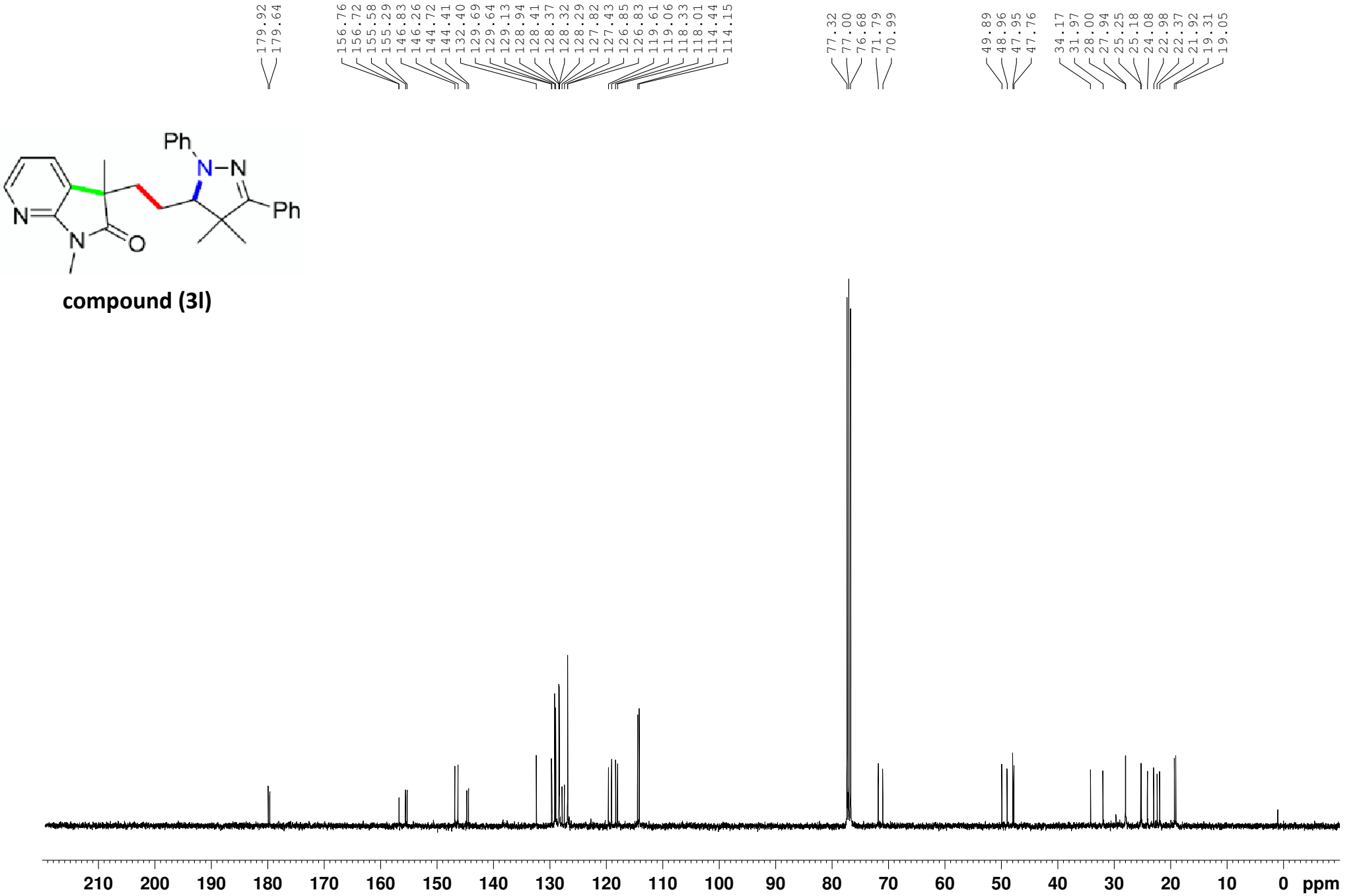
compound (3k')


8.135
8.132
8.122
8.119
8.070
8.067
8.057
8.054
7.745
7.727
7.671
7.654
7.413
7.396
7.378
7.367
7.357
7.346
7.327
7.318
7.307
7.255
7.236
7.217
7.201
7.183
7.032
7.012
6.989
6.969
6.923
6.909
6.905
6.891
6.869
6.851
6.826
6.807
6.673
6.659
6.655
6.641
6.511
6.508
6.493
6.490
3.886
3.873
3.701
3.694
3.683
3.676
3.234
1.970
1.959
1.938
1.926
1.855
1.843
1.822
1.810
1.764
1.755
1.731
1.722
1.659
1.641
1.622
1.604
1.588
1.566
1.557
1.533
1.525
1.500
1.492
1.446
1.395
1.371
1.326
1.302
1.258
1.250
1.242
1.231
1.194
0.000

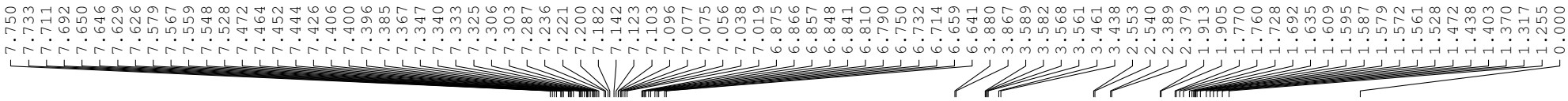
Ph
N–N
Ph
N
N
O

compound (3l)


11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.10
2.07
2.08
7.73
4.29
2.12
1.91
3.35
1.00
0.97
1.03
1.00
6.06
1.05
1.19
1.08
2.55
3.03
3.23
3.48
3.16
3.17
3.70
3.08


179.92
179.64
156.76
156.72
155.58
155.29
146.83
146.26
144.72
144.41
132.40
129.69
129.64
129.13
128.94
128.41
128.37
128.32
128.29
127.82
127.43
126.85
126.83
119.61
119.06
118.33
118.01
114.44
114.15
77.32
77.00
76.68
71.79
70.99
49.89
48.96
47.95
47.76
34.17
31.97
28.00
27.94
25.25
25.18
24.08
22.98
22.37
21.92
19.31
19.05
Ph
N–N
Ph
N
N
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

compound (3l)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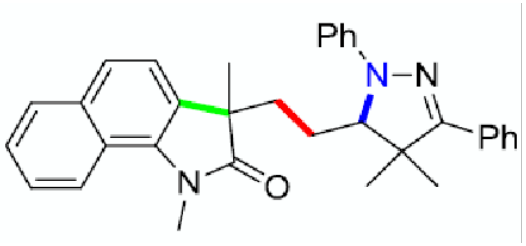
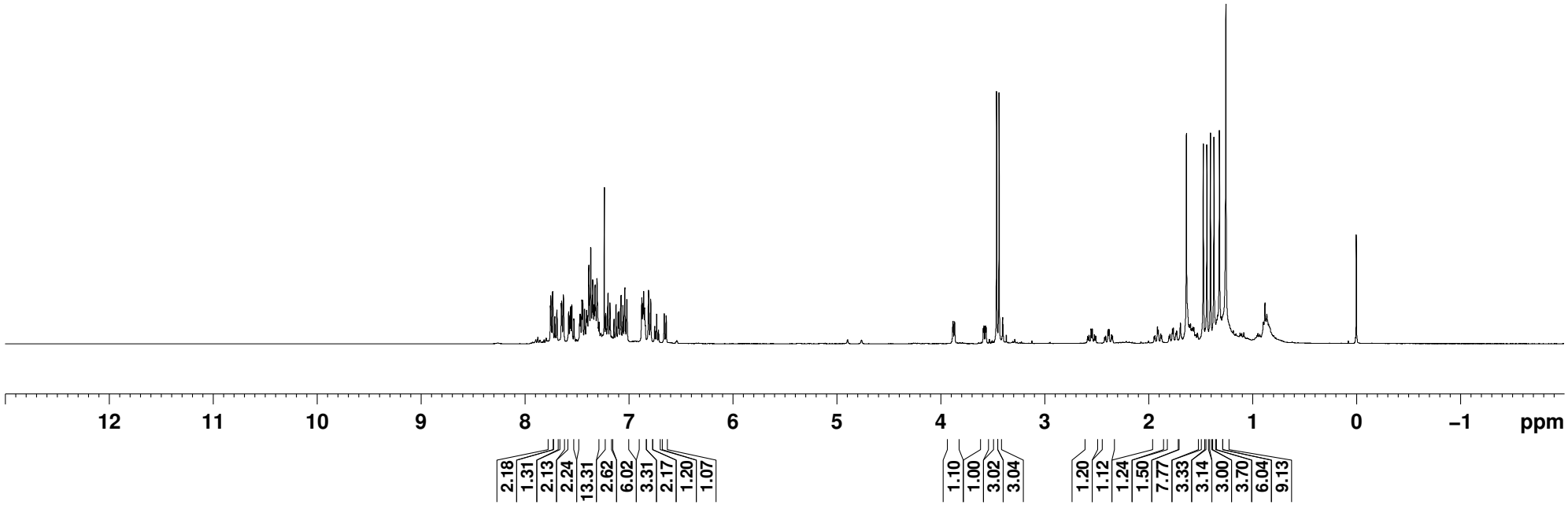
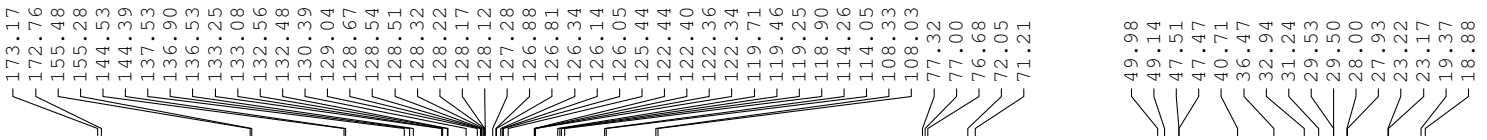
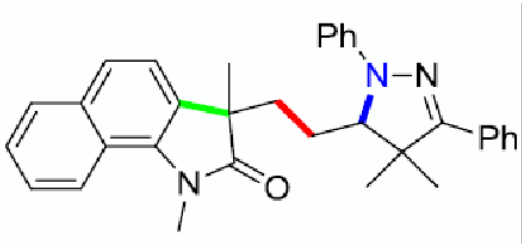
7.733
7.711
7.692
7.650
7.646
7.629
7.626
7.579
7.567
7.559
7.548
7.528
7.472
7.464
7.452
7.444
7.426
7.406
7.400
7.396
7.385
7.367
7.347
7.340
7.333
7.325
7.306
7.303
7.287
7.236
7.221
7.200
7.182
7.142
7.123
7.103
7.096
7.077
7.075
7.056
7.038
7.019
6.875
6.866
6.857
6.848
6.841
6.810
6.790
6.750
6.732
6.714
6.659
6.641
3.880
3.867
3.589
3.582
3.568
3.561
3.461
3.438
2.553
2.540
2.389
2.379
1.913
1.905
1.770
1.760
1.728
1.692
1.635
1.609
1.595
1.587
1.579
1.572
1.561
1.528
1.472
1.438
1.403
1.370
1.317
1.255
0.000


Ph
N–N
Ph
N
O

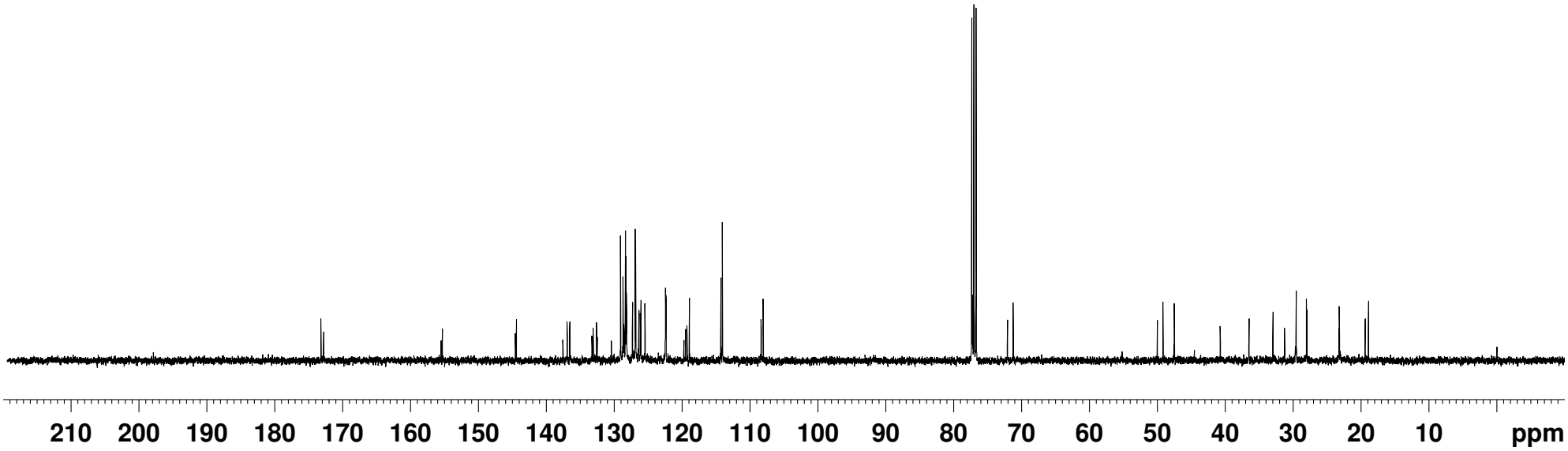
compound (3m)

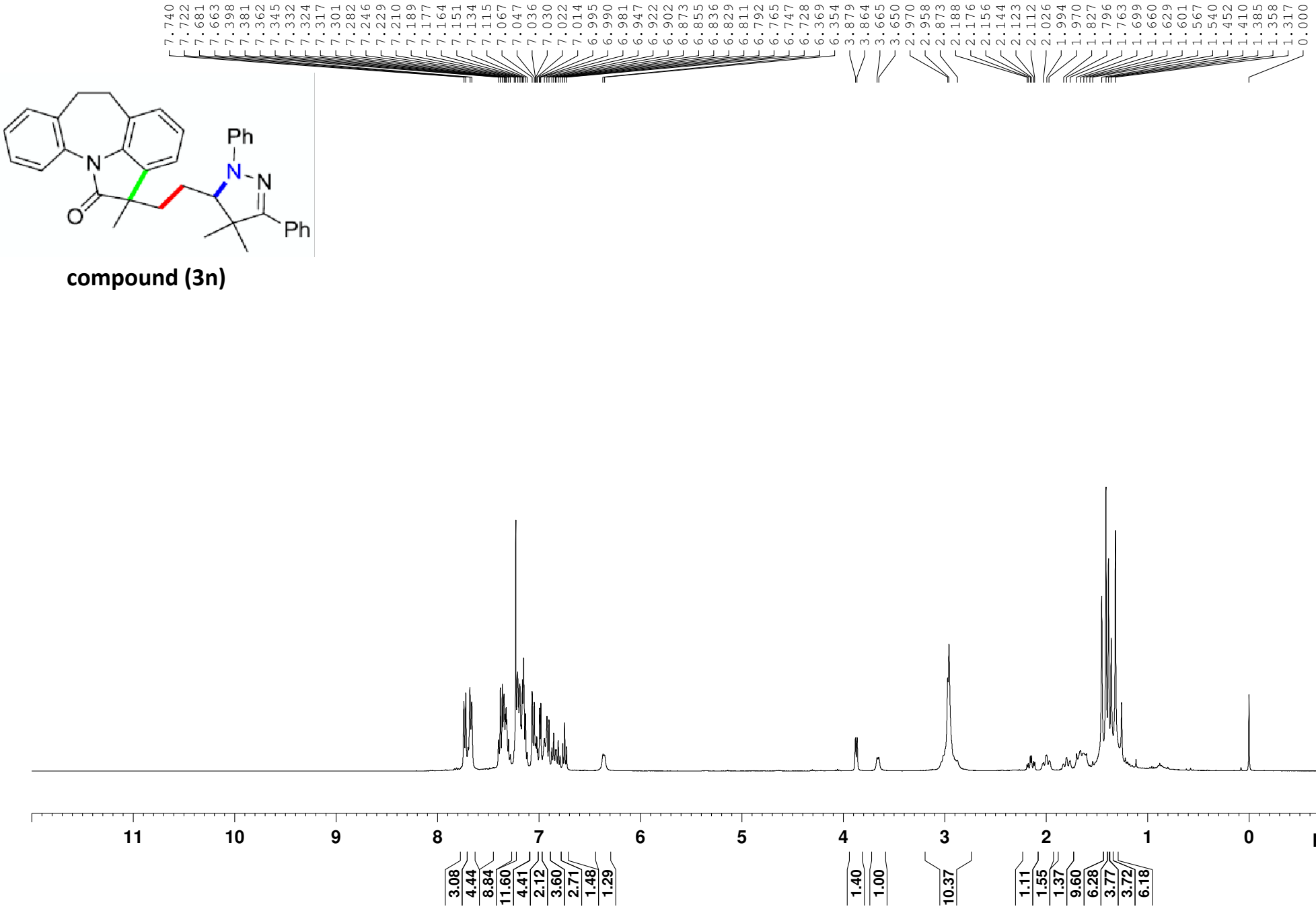

12
11
10
9
8
7
6
5
4
3
2
1
0
–1
ppm
2.18
1.31
2.13
2.24
13.31
2.62
6.02
3.31
2.17
1.20
1.07
1.10
1.00
3.02
3.04
1.20
1.12
1.24
1.50
7.77
3.33
3.14
3.00
3.70
6.04
9.13


173.17
172.76
155.48
155.28
144.53
144.39
137.53
136.90
136.53
133.25
133.08
132.56
132.48
130.39
129.04
128.67
128.54
128.51
128.32
128.22
128.17
128.12
127.28
126.88
126.81
126.34
126.14
126.05
125.44
122.44
122.40
122.36
122.34
119.71
119.46
119.25
118.90
114.26
114.05
108.33
108.03
77.32
77.00
76.68
72.05
71.21
49.98
49.14
47.51
47.47
40.71
36.47
32.94
31.24
29.53
29.50
28.00
27.93
23.22
23.17
19.37
18.88

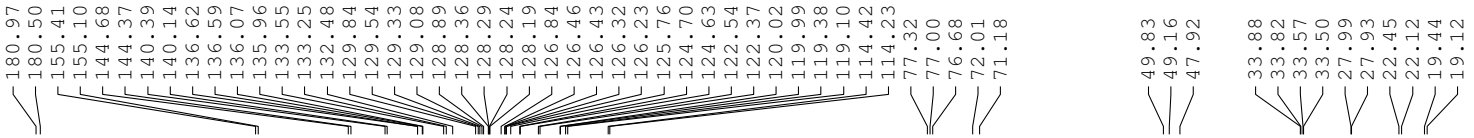

Ph
N–N
Ph
N
O

compound (3m)


210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


7.740
7.722
7.681
7.663
7.398
7.381
7.362
7.345
7.332
7.324
7.317
7.301
7.282
7.246
7.229
7.210
7.189
7.177
7.164
7.151
7.134
7.115
7.067
7.047
7.036
7.030
7.022
7.014
6.995
6.990
6.981
6.947
6.922
6.902
6.873
6.855
6.836
6.829
6.811
6.792
6.765
6.747
6.728
6.369
6.354
3.879
3.864
3.665
3.650
2.970
2.958
2.873
2.188
2.176
2.156
2.144
2.123
2.112
2.026
1.994
1.970
1.827
1.796
1.763
1.699
1.660
1.629
1.601
1.567
1.540
1.452
1.410
1.385
1.358
1.317
0.000
Ph
N
N
N
O
Ph
11
10
9
8
7
6
5
4
3
2
1
0
ppm
3.08
4.44
8.84
11.60
4.41
2.12
3.60
2.71
1.48
1.29
1.40
1.00
10.37
1.11
1.55
1.37
9.60
6.28
3.77
3.72
6.18

compound (3n)


180.97
180.50
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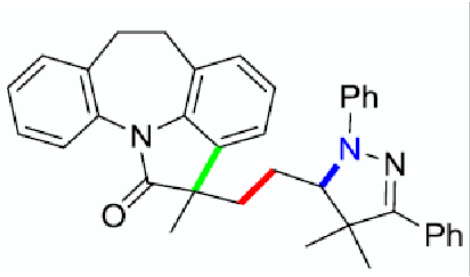
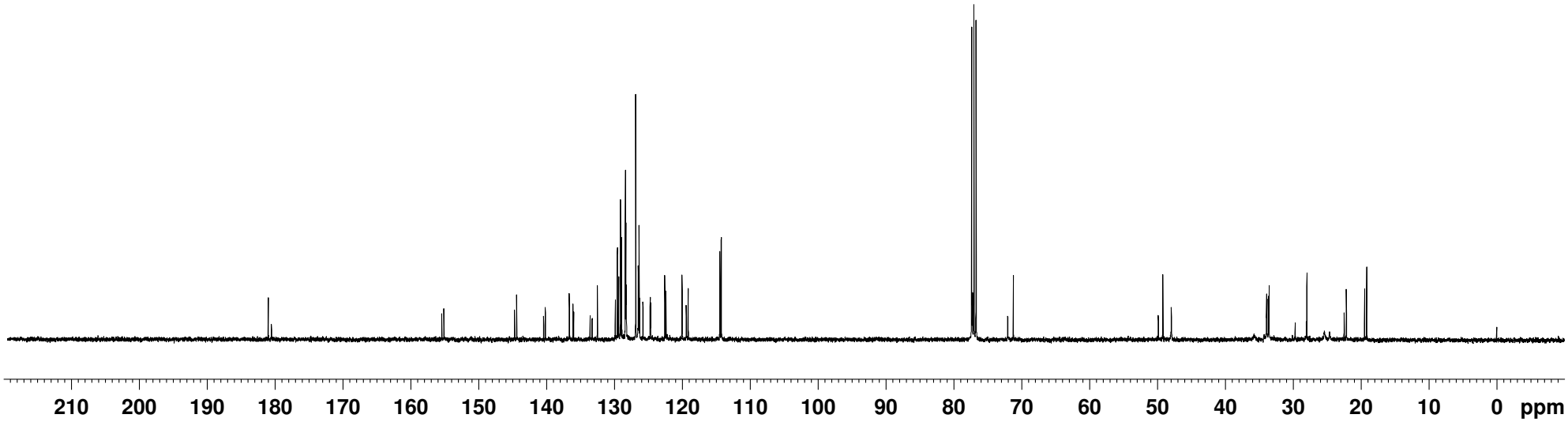
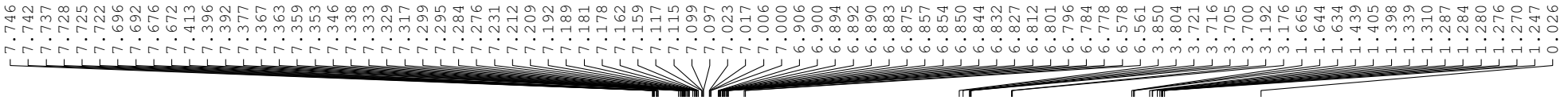
155.10
144.68
144.37
140.39
140.14
136.62
136.59
136.07
135.96
133.55
133.25
132.48
129.84
129.54
129.33
129.08
128.89
128.36
128.29
128.24
128.19
126.84
126.46
126.43
126.32
126.23
125.76
124.70
124.63
122.54
122.37
120.02
119.99
119.38
119.10
114.42
114.23
77.32
77.00
76.68
72.01
71.18
49.83
49.16
47.92
33.88
33.82
33.57
33.50
27.99
27.93
22.45
22.12
19.44
19.12


Ph
N
N
N
O
Ph

compound (3n)


210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


7.746
7.742
7.737
7.728
7.725
7.722
7.696
7.692
7.676
7.672
7.413
7.396
7.392
7.377
7.367
7.363
7.359
7.353
7.346
7.338
7.333
7.329
7.317
7.299
7.295
7.284
7.276
7.231
7.212
7.209
7.192
7.189
7.181
7.178
7.162
7.159
7.117
7.115
7.099
7.097
7.023
7.017
7.006
7.000
6.906
6.900
6.894
6.892
6.890
6.883
6.875
6.857
6.854
6.850
6.844
6.832
6.827
6.812
6.801
6.796
6.784
6.778
6.578
6.561
3.850
3.804
3.721
3.716
3.705
3.700
3.192
3.176
1.665
1.644
1.634
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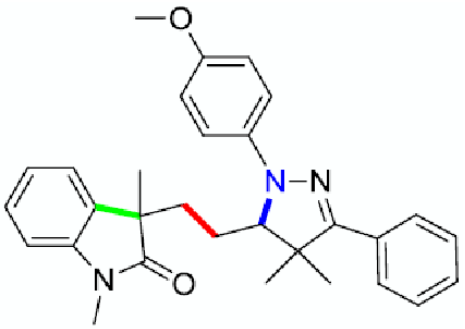
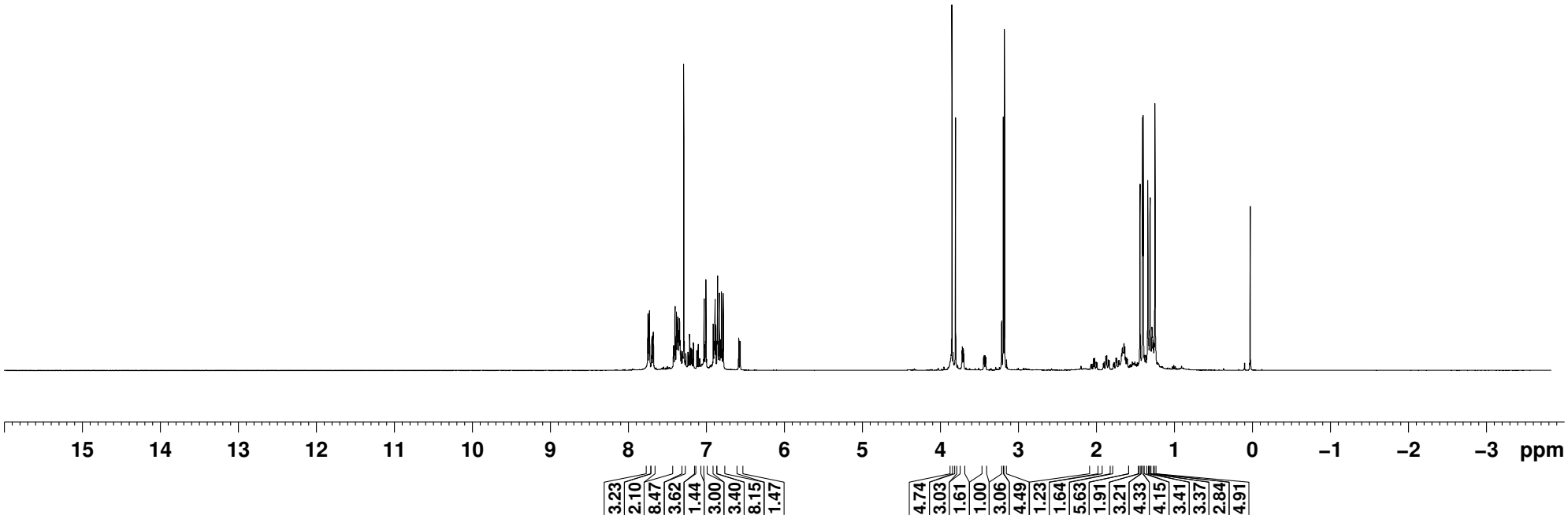
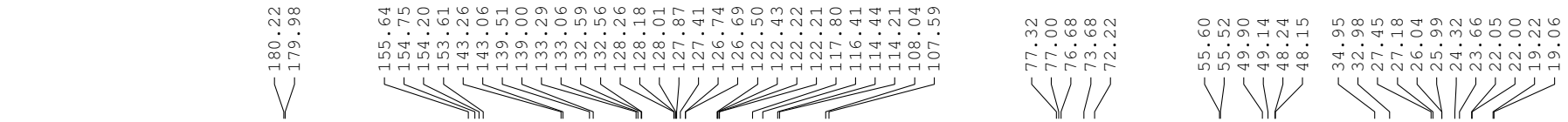
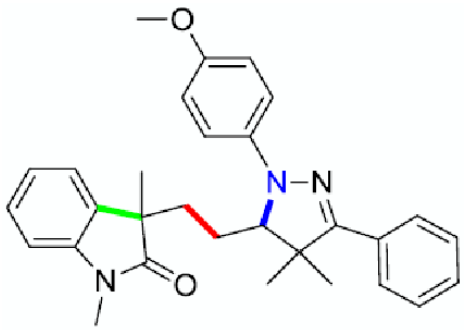
1.405
1.398
1.339
1.310
1.287
1.284
1.280
1.276
1.270
1.247
0.026


O
N–N
N
O

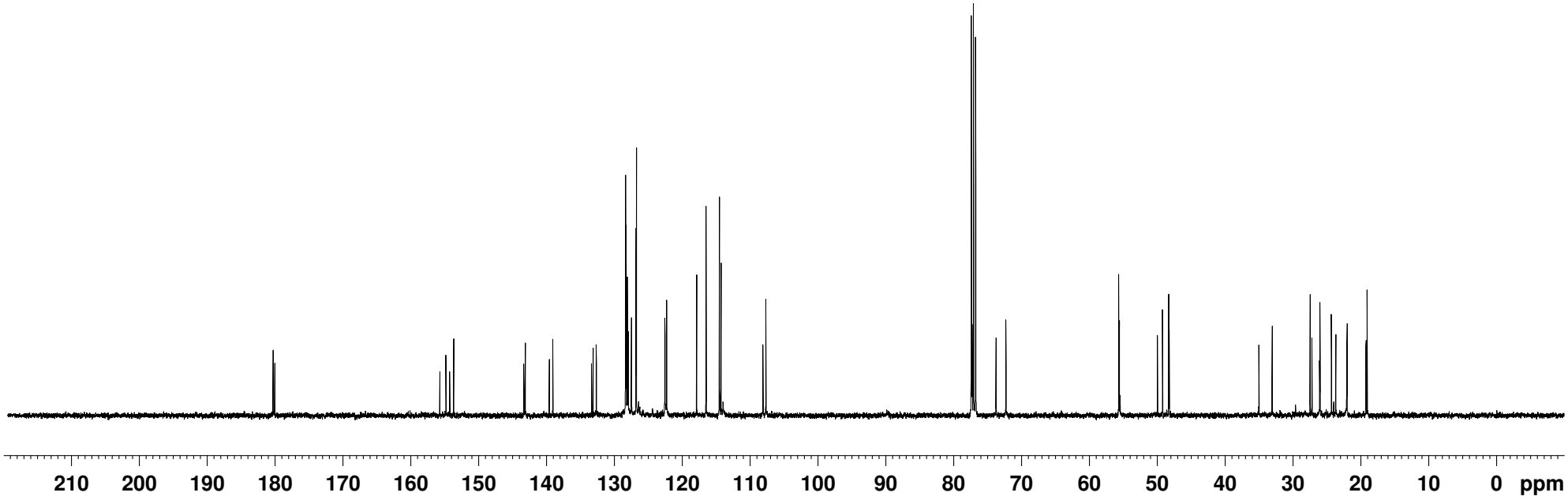
compound (3o)


15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
–1
–2
–3
ppm
3.23
2.10
8.47
3.62
1.44
3.00
3.40
8.15
1.47
4.74
3.03
1.61
1.00
3.06
4.49
1.23
1.64
5.63
1.91
3.21
4.33
4.15
3.41
3.37
2.84
4.91


180.22
179.98
155.64
154.75
154.20
153.61
143.26
143.06
139.51
139.00
133.29
133.06
132.59
132.56
128.26
128.18
128.01
127.87
127.41
126.74
126.69
122.50
122.43
122.22
122.21
117.80
116.41
114.44
114.21
108.04
107.59
77.32
77.00
76.68
73.68
72.22
55.60
55.52
49.90
49.14
48.24
48.15
34.95
32.98
27.45
27.18
26.04
25.99
24.32
23.66
22.05
22.00
19.22
19.06


O
N
N
O

compound (3o)


210
200
190
180
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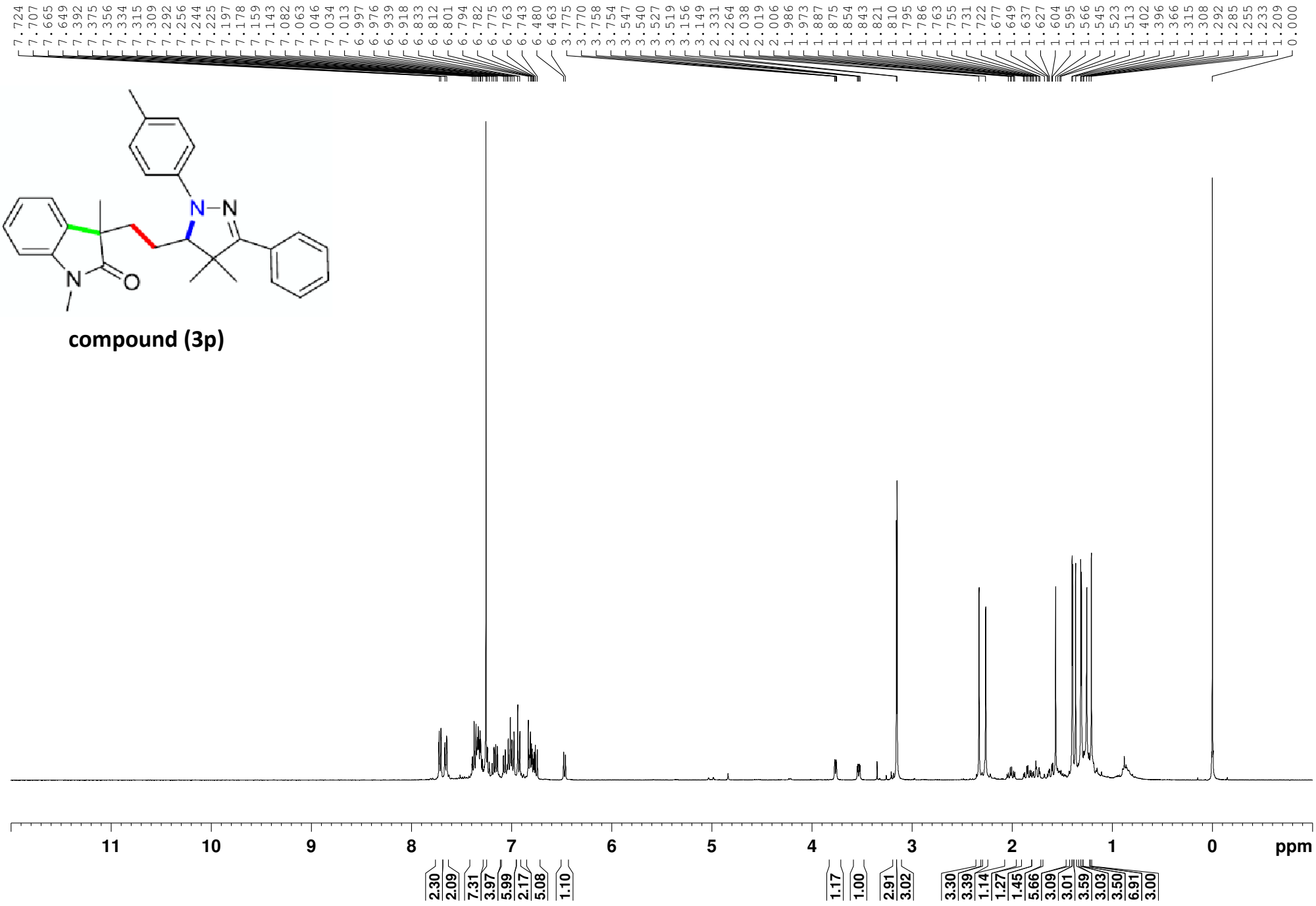
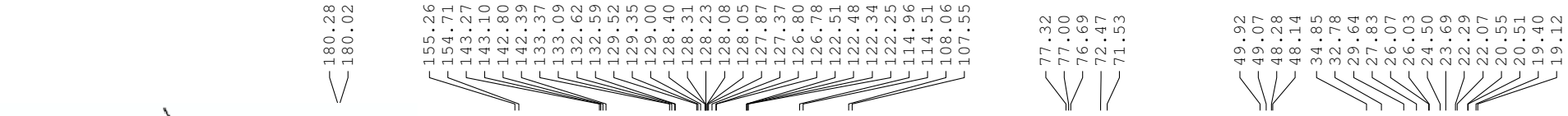
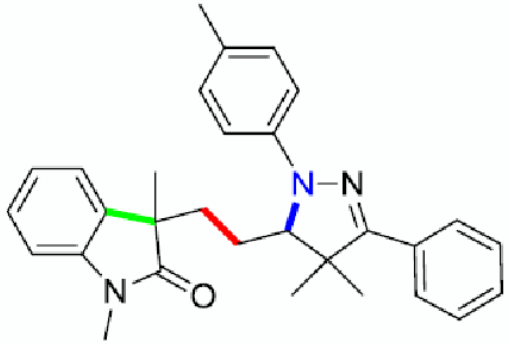
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

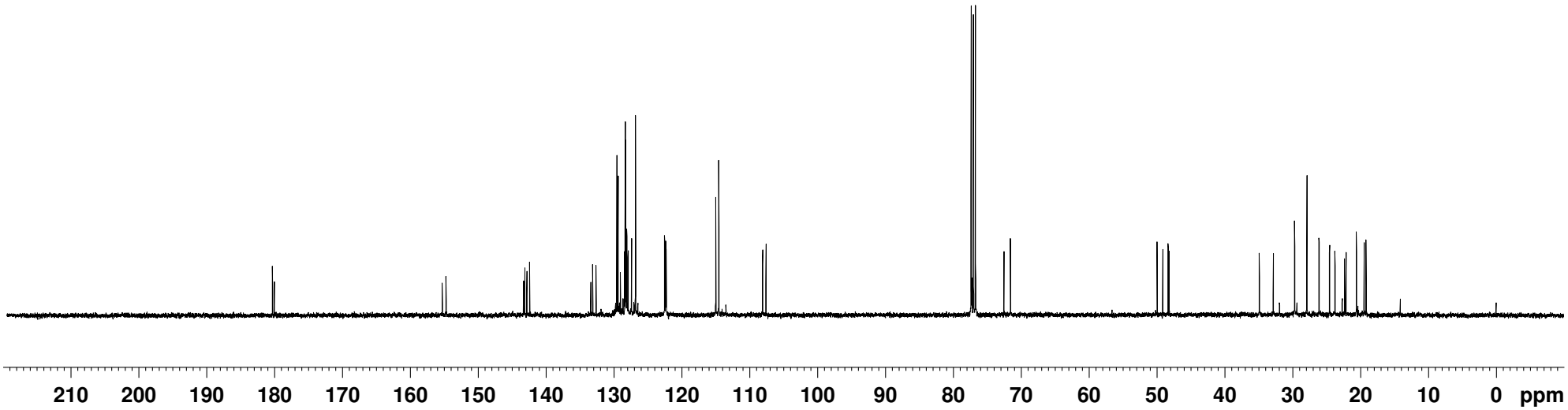

7.724 7.707 7.665 7.649 7.392 7.375 7.356 7.334 7.315 7.309 7.292 7.256 7.244 7.225 7.197 7.178 7.159 7.143 7.082 7.063 7.046 7.034 7.013 6.997 6.976 6.939 6.918 6.833 6.812 6.801 6.794 6.782 6.775 6.763 6.743 6.480 6.463 3.775 3.770 3.758 3.754 3.547 3.540 3.527 3.519 3.156 3.149 2.331 2.264 2.038 2.019 2.006 1.986 1.973 1.887 1.875 1.854 1.843 1.821 1.810 1.795 1.786 1.763 1.755 1.731 1.722 1.677 1.649 1.637 1.627 1.604 1.595 1.566 1.545 1.523 1.513 1.402 1.396 1.366 1.315 1.308 1.292 1.285 1.255 1.233 1.209 0.000
N–N
N
O
11 10 9 8 7 6 5 4 3 2 1 0 ppm
2.30 2.09 7.31 3.97 5.99 2.17 5.08 1.10
1.17 1.00 2.91 3.02
3.30 3.39 1.14 1.27 1.45 5.66 3.09 3.01 3.59 3.03 3.50 6.91 3.00

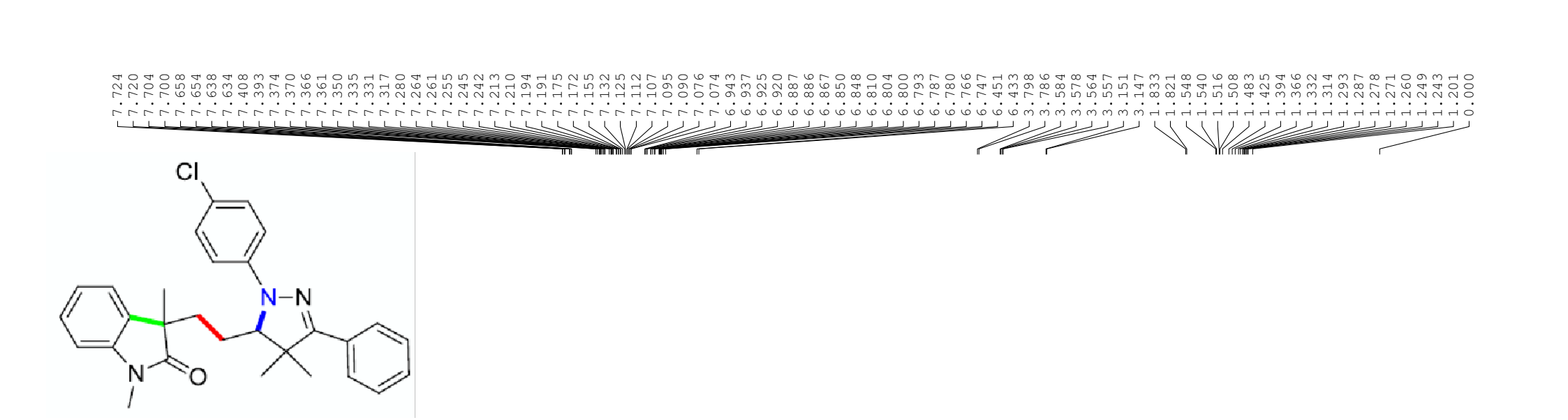
compound (3p)


180.28
180.02
155.26
154.71
143.27
143.10
142.80
142.39
133.37
133.09
132.62
132.59
129.52
129.35
129.00
128.40
128.31
128.23
128.08
128.05
127.87
127.37
126.80
126.78
122.51
122.48
122.34
122.25
114.96
114.51
108.06
107.55
77.32
77.00
76.69
72.47
71.53
49.92
49.07
48.28
48.14
34.85
32.78
29.64
27.83
26.07
26.03
24.50
23.69
22.29
22.07
20.55
20.51
19.40
19.12


N
N
N
O

compound (3p)


210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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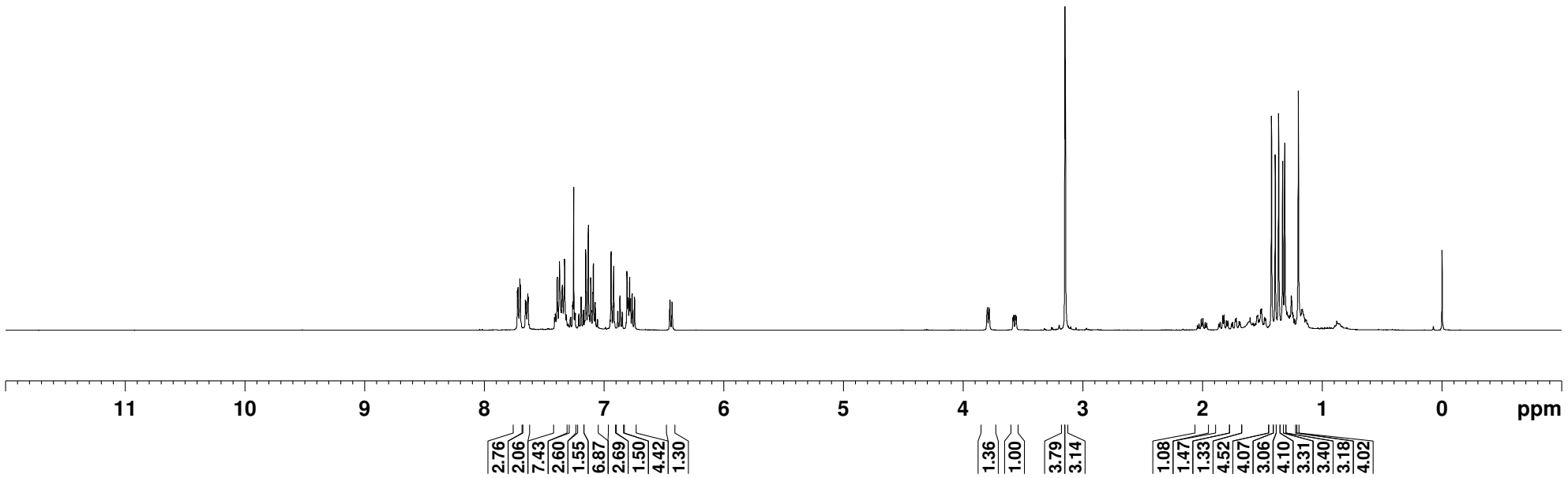
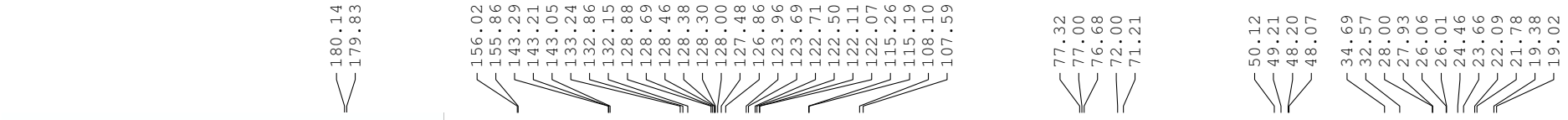
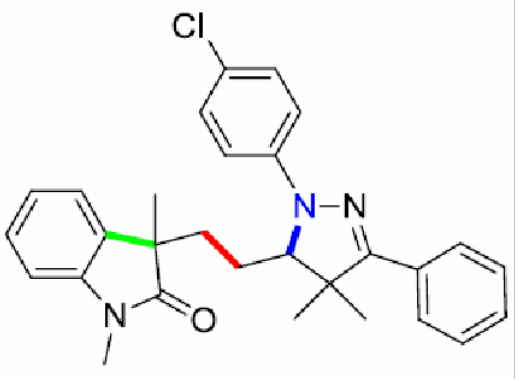
7.720
7.704
7.700
7.658
7.654
7.638
7.634
7.408
7.393
7.374
7.370
7.366
7.361
7.350
7.335
7.331
7.317
7.280
7.264
7.261
7.255
7.245
7.242
7.213
7.210
7.194
7.191
7.175
7.172
7.155
7.132
7.125
7.112
7.107
7.095
7.090
7.076
7.074
6.943
6.937
6.925
6.920
6.887
6.886
6.867
6.850
6.848
6.810
6.804
6.800
6.793
6.787
6.780
6.766
6.747
6.451
6.433
3.798
3.786
3.584
3.578
3.564
3.557
3.151
3.147
1.833
1.821
1.548
1.540
1.516
1.508
1.483
1.425
1.394
1.366
1.332
1.314
1.293
1.287
1.278
1.271
1.260
1.249
1.243
1.201
0.000

Cl
N–N
N
O

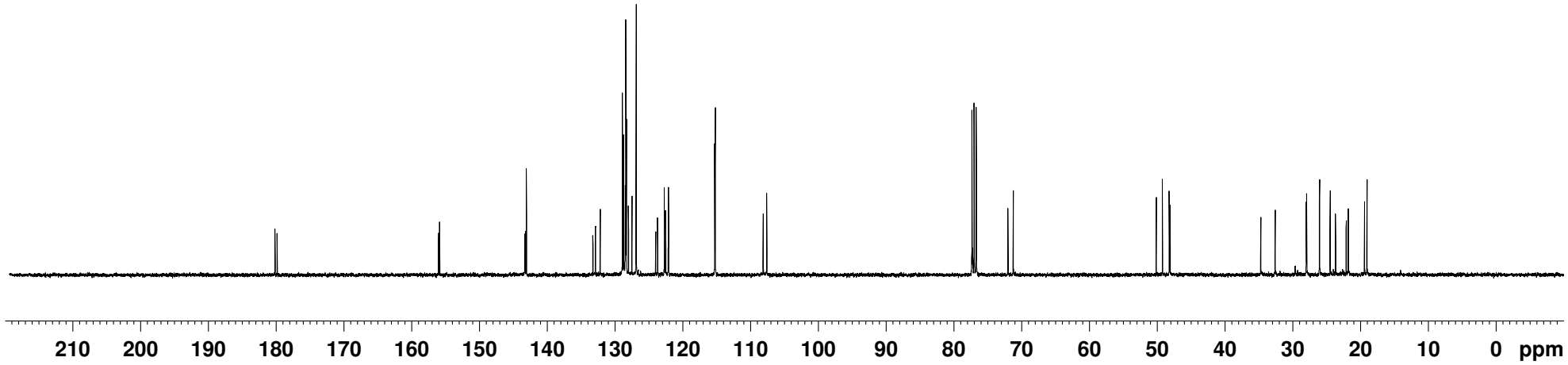
compound (3q)

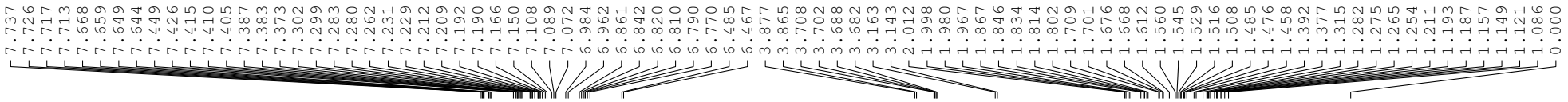

11
10
9
8
7
6
5
4
3
2
1
0
ppm
2.76
2.06
7.43
2.60
1.55
6.87
2.69
1.50
4.42
1.30
1.36
1.00
3.79
3.14
1.08
1.47
1.33
4.52
4.07
3.06
4.10
3.31
3.40
3.18
4.02


180.14
179.83
156.02
155.86
143.29
143.21
143.05
133.24
132.86
132.15
128.88
128.69
128.46
128.38
128.30
128.00
127.48
126.86
123.96
123.69
122.71
122.50
122.11
122.07
115.26
115.19
108.10
107.59
77.32
77.00
76.68
72.00
71.21
50.12
49.21
48.20
48.07
34.69
32.57
28.00
27.93
26.06
26.01
24.46
23.66
22.09
21.78
19.38
19.02


Cl
N
N
O

compound (3q)


210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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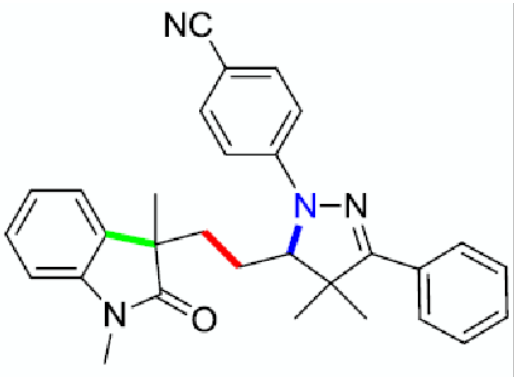
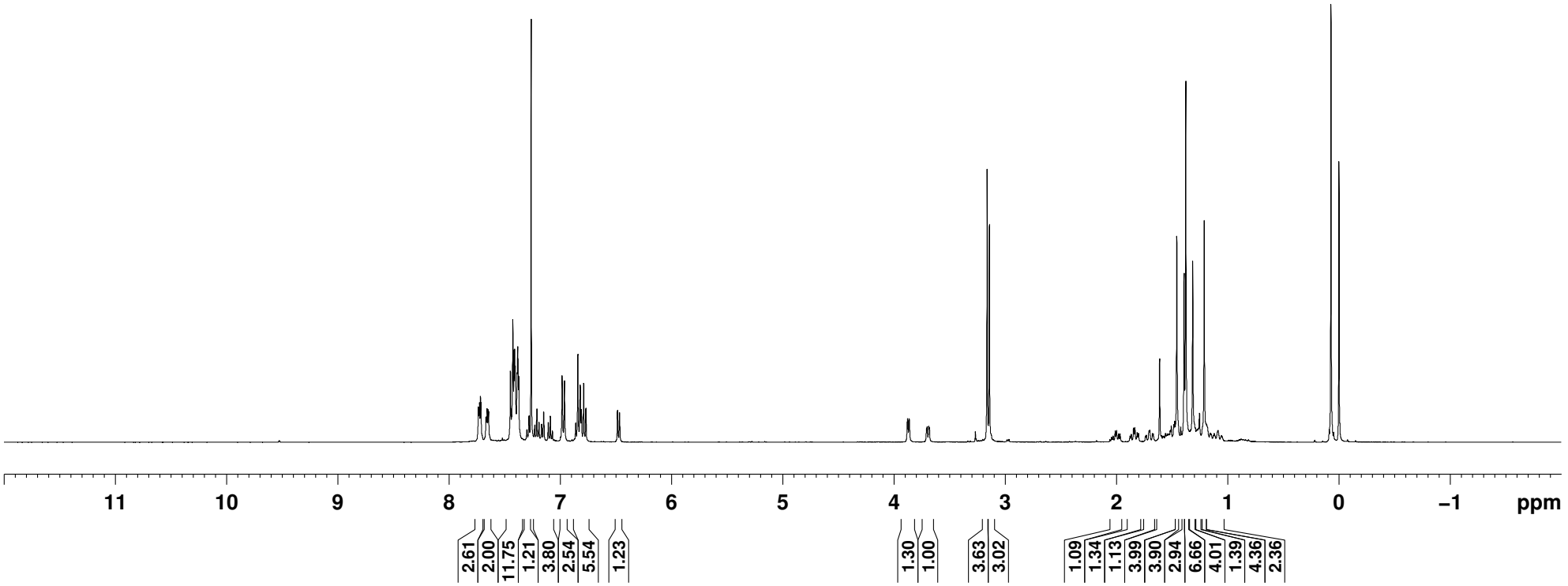
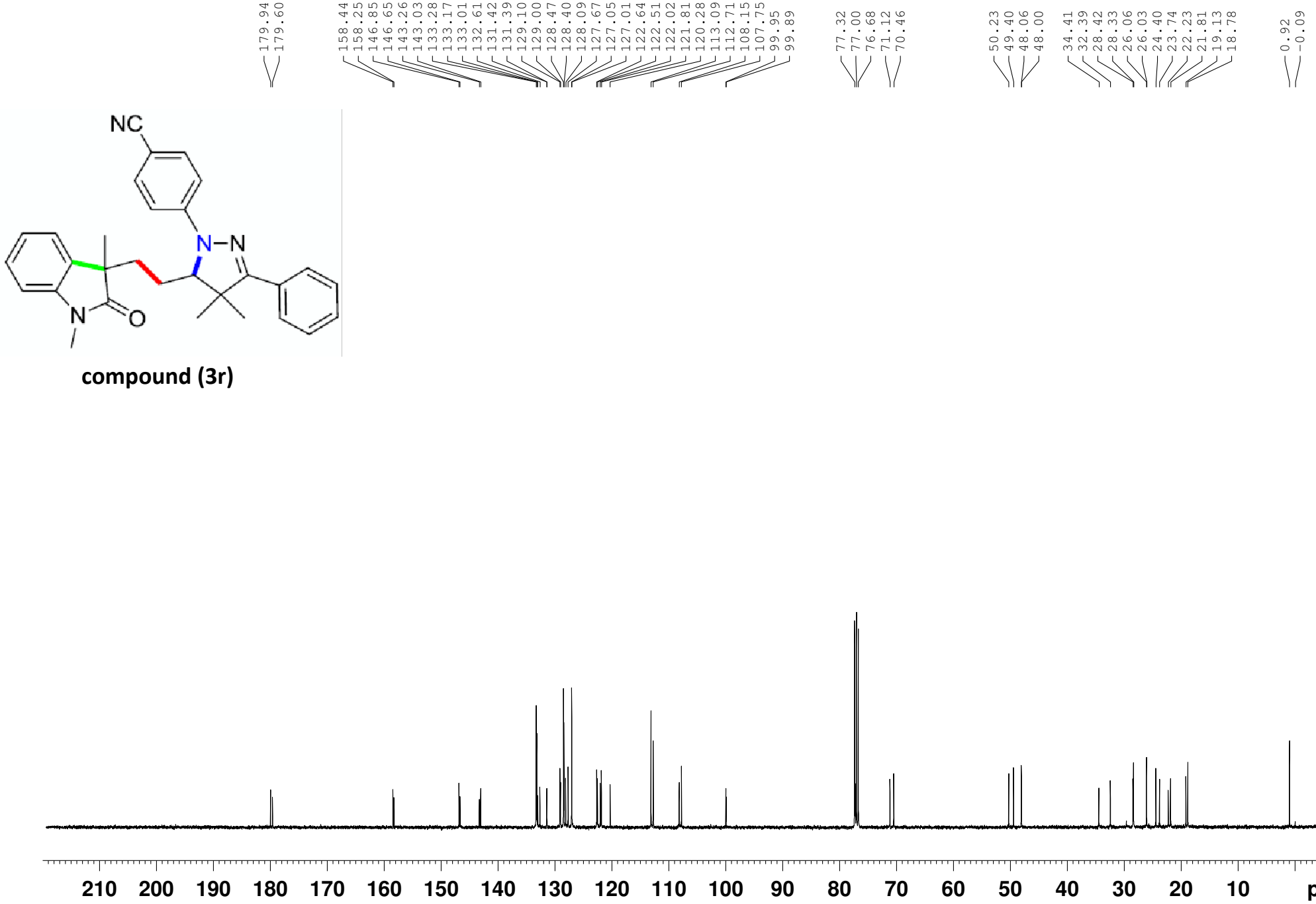
7.726
7.717
7.713
7.668
7.659
7.649
7.644
7.449
7.426
7.415
7.410
7.405
7.387
7.383
7.373
7.302
7.299
7.283
7.280
7.262
7.231
7.229
7.212
7.209
7.192
7.190
7.166
7.150
7.108
7.089
7.072
6.984
6.962
6.861
6.842
6.820
6.810
6.790
6.770
6.485
6.467
3.877
3.865
3.708
3.702
3.688
3.682
3.163
3.143
2.012
1.998
1.980
1.967
1.867
1.846
1.834
1.814
1.802
1.709
1.701
1.676
1.668
1.612
1.560
1.545
1.529
1.516
1.508
1.485
1.476
1.458
1.392
1.377
1.315
1.282
1.275
1.265
1.254
1.211
1.193
1.187
1.157
1.149
1.121
1.086
0.000

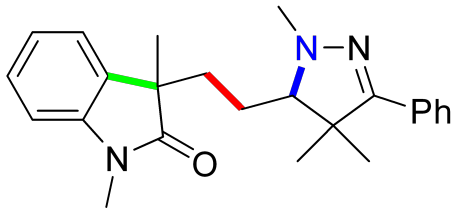

NC
N–N
N
O

compound (3r)

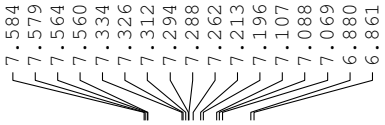

11
10
9
8
7
6
5
4
3
2
1
0
–1
ppm
2.61
2.00
11.75
1.21
3.80
2.54
5.54
1.23
1.30
1.00
3.63
3.02
1.09
1.34
1.13
3.99
3.90
2.94
6.66
4.01
1.39
4.36
2.36

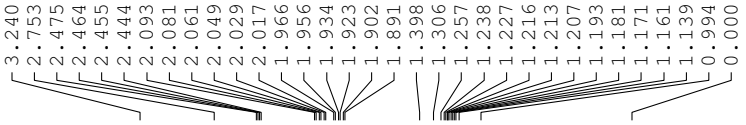

179.94
179.60
158.44
158.25
146.85
146.65
143.26
143.03
133.28
133.17
133.01
132.61
131.42
131.39
129.10
129.00
128.47
128.40
128.09
127.67
127.05
127.01
122.64
122.51
122.02
121.81
120.28
113.09
112.71
108.15
107.75
99.95
99.89
77.32
77.00
76.68
71.12
70.46
50.23
49.40
48.06
48.00
34.41
32.39
28.42
28.33
26.06
26.03
24.40
23.74
22.23
21.81
19.13
18.78
0.92
-0.09
NC
N–N
N
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

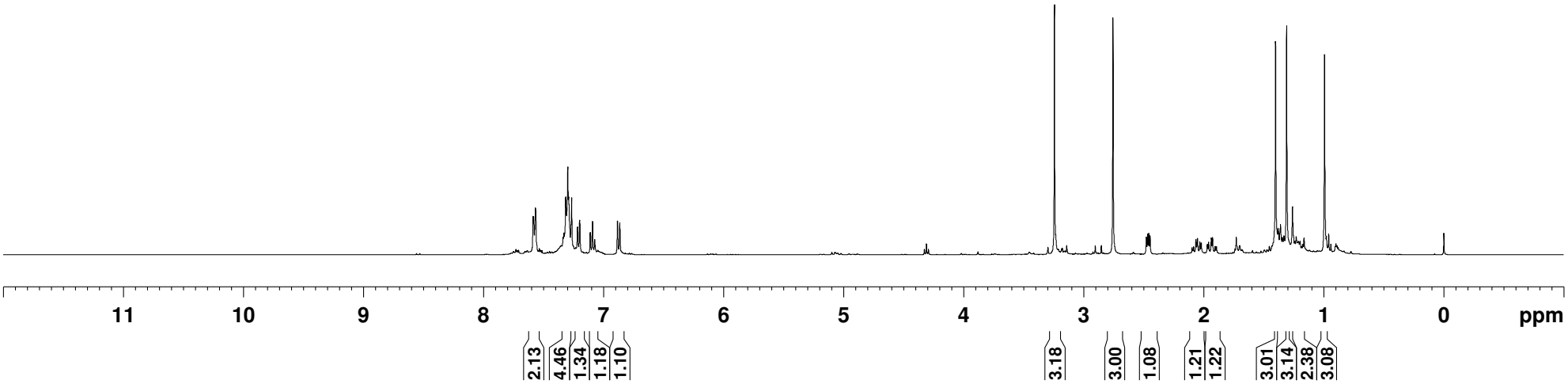
compound (3r)



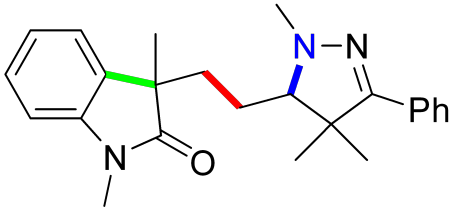
compound (3s)
major



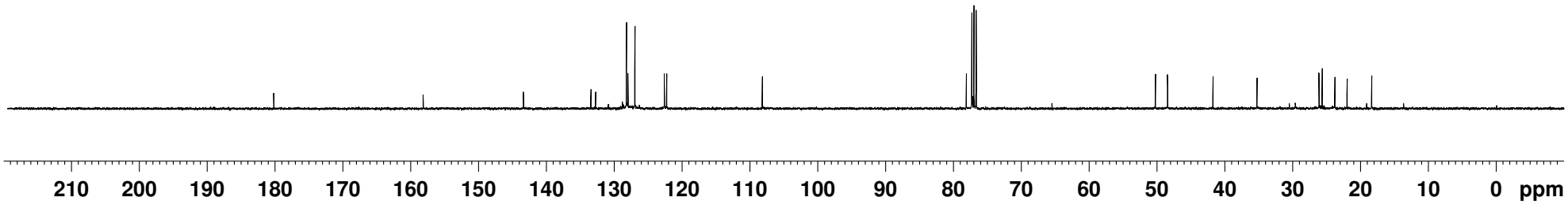


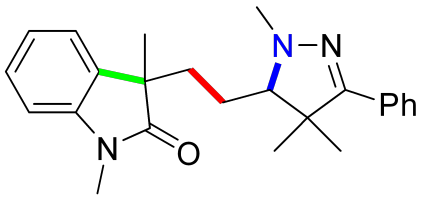


180.18
158.14
143.35
133.42
132.71
128.18
128.16
127.95
126.93
122.59
122.24
108.14
78.12
77.32
77.00
76.68
50.25
48.45
41.77
35.27
26.14
25.66
23.79
21.99
18.37

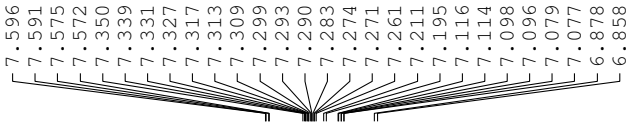


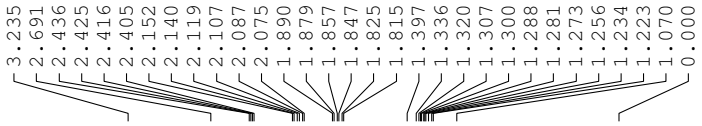
compound (3s)
major

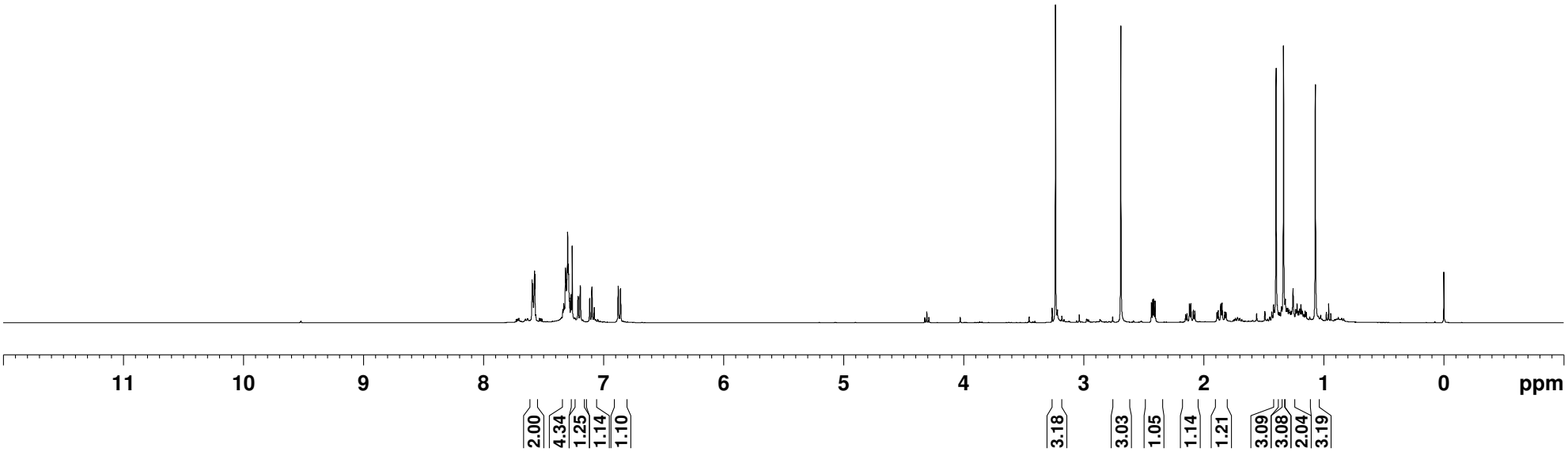


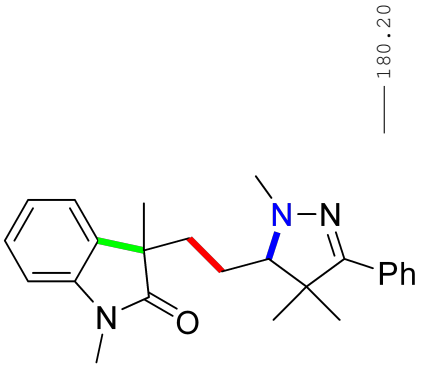


compound (3s)
minor

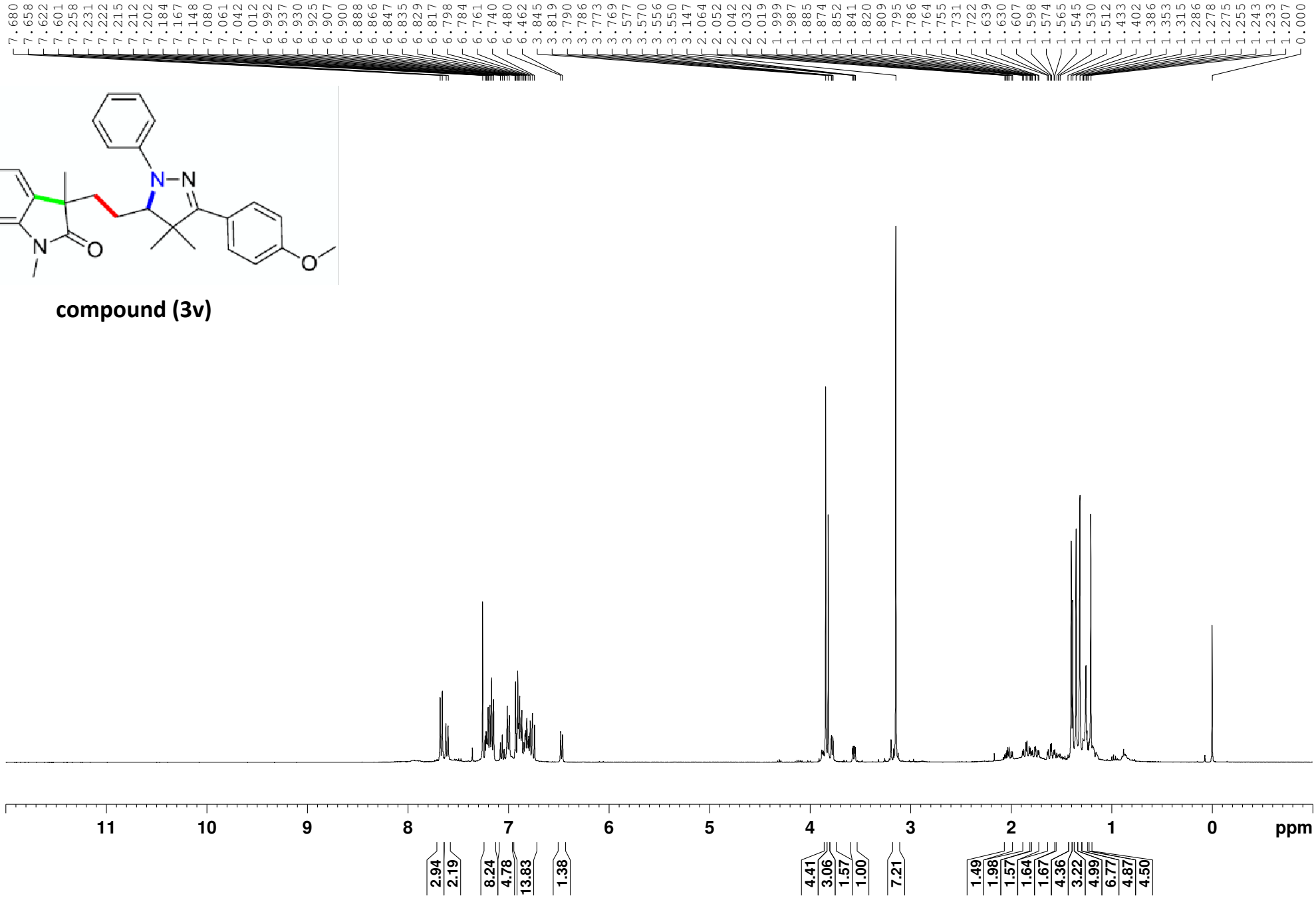








compound (3s)
minor


7.680
7.658
7.622
7.601
7.258
7.231
7.222
7.215
7.212
7.202
7.184
7.167
7.148
7.080
7.061
7.042
7.012
6.992
6.937
6.930
6.925
6.907
6.900
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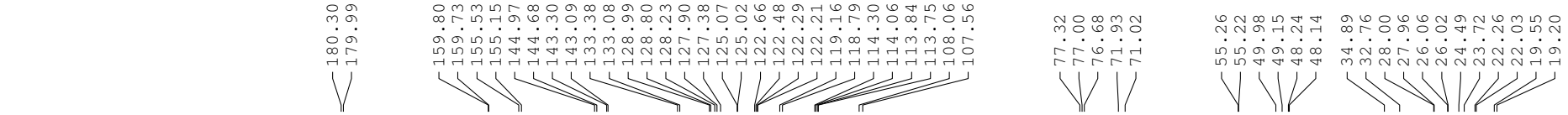
6.866
6.847
6.835
6.829
6.817
6.798
6.784
6.761
6.740
6.480
6.462
3.845
3.819
3.790
3.786
3.773
3.769
3.577
3.570
3.556
3.550
3.147
2.064
2.052
2.042
2.032
2.019
1.999
1.987
1.885
1.874
1.852
1.841
1.820
1.809
1.795
1.786
1.764
1.755
1.731
1.722
1.639
1.630
1.607
1.598
1.574
1.565
1.545
1.530
1.512
1.433
1.402
1.386
1.353
1.315
1.286
1.278
1.275
1.255
1.243
1.233
1.207
0.000
N–N
N
O
O
11
10
9
8
7
6
5
4
3
2
1
0
ppm
2.94
2.19
8.24
4.78
13.83
1.38
4.41
3.06
1.57
1.00
7.21
1.49
1.98
1.57
1.64
1.67
4.36
3.22
4.99
6.77
4.87
4.50

compound (3v)


180.30
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159.80
159.73
155.53
155.15
144.97
144.68
143.30
143.09
133.38
133.08
128.99
128.80
128.23
127.90
127.38
125.07
125.02
122.66
122.48
122.29
122.21
119.16
118.79
114.30
114.06
113.84
113.75
108.06
107.56
77.32
77.00
76.68
71.93
71.02
55.26
55.22
49.98
49.15
48.24
48.14
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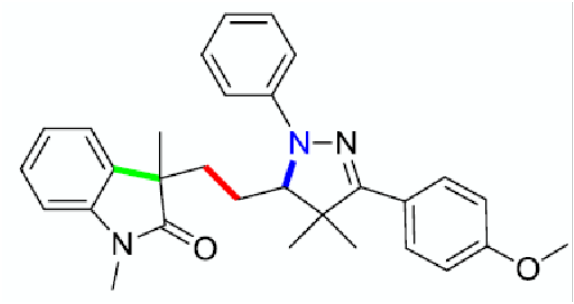
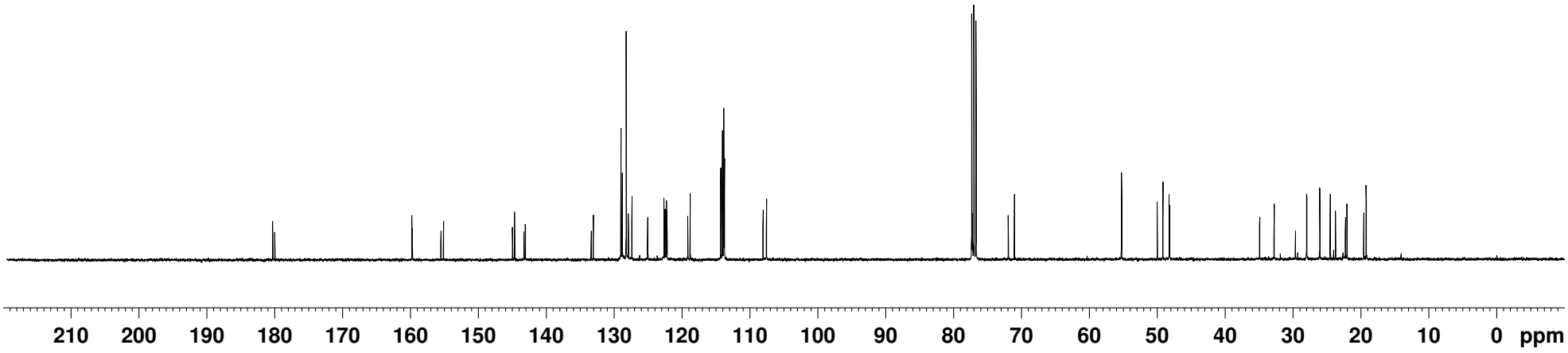
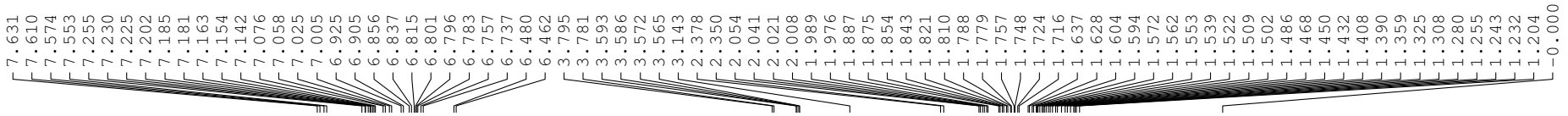
28.00
27.96
26.06
26.02
24.49
23.72
22.26
22.03
19.55
19.20


N–N
N
O
O

compound (3v)


210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


7.631
7.610
7.574
7.553
7.255
7.230
7.225
7.202
7.185
7.181
7.163
7.154
7.142
7.076
7.058
7.025
7.005
6.925
6.905
6.856
6.837
6.815
6.801
6.796
6.783
6.757
6.737
6.480
6.462
3.795
3.781
3.593
3.586
3.572
3.565
3.143
2.378
2.350
2.054
2.041
2.021
2.008
1.989
1.976
1.887
1.875
1.854
1.843
1.821
1.810
1.788
1.779
1.757
1.748
1.724
1.716
1.637
1.628
1.604
1.594
1.572
1.562
1.553
1.539
1.522
1.509
1.502
1.486
1.468
1.450
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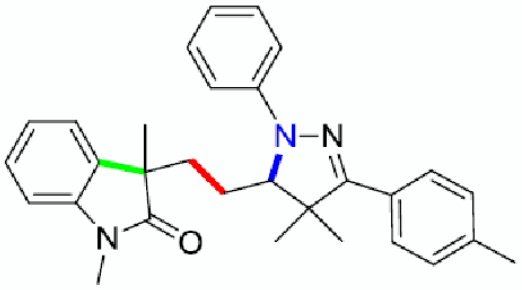
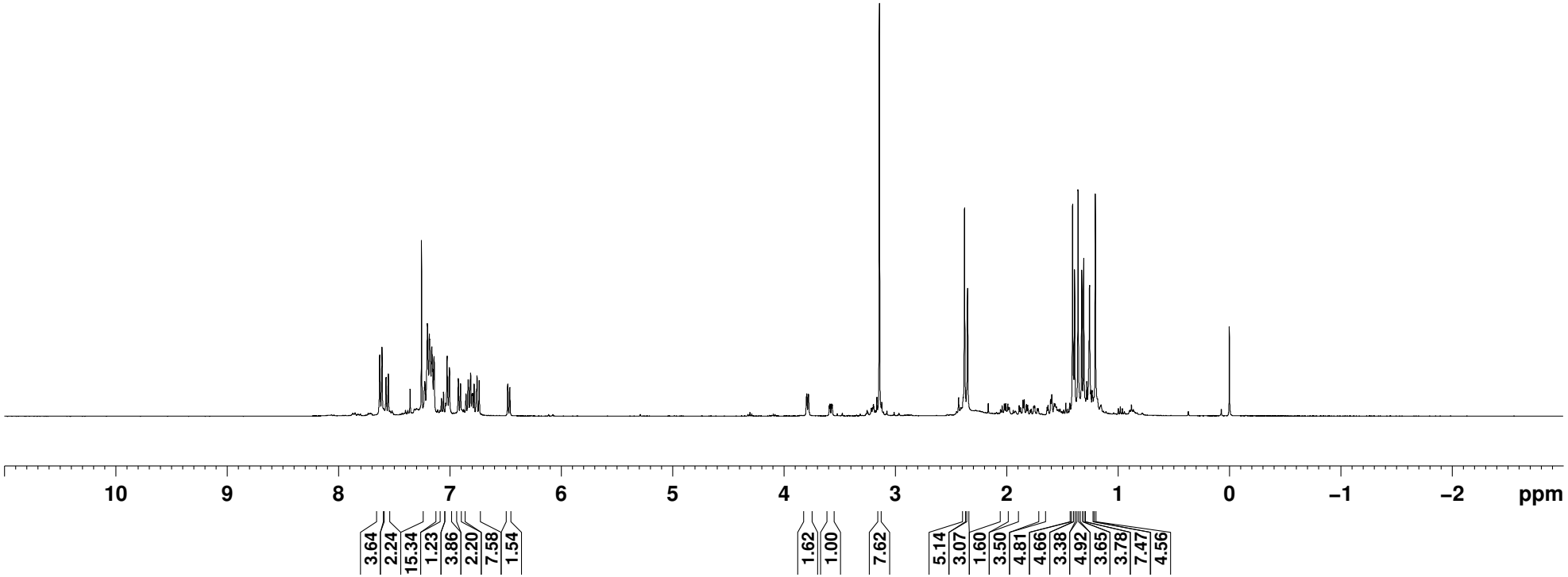
1.204
0.000


N–N
N
O

compound (3w)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–2
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3.86
2.20
7.58
1.54
1.62
1.00
7.62
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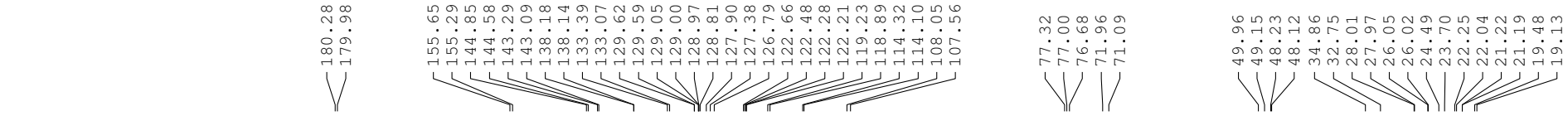
3.50
4.81
4.66
3.38
4.92
3.65
3.78
7.47
4.56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133.07
129.62
129.59
129.05
129.00
128.97
128.81
127.90
127.38
126.79
122.66
122.48
122.28
122.21
119.23
118.89
114.32
114.10
108.05
107.56
77.32
77.00
76.68
71.96
71.09
49.96
49.15
48.23
48.12
34.86
32.75
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26.02
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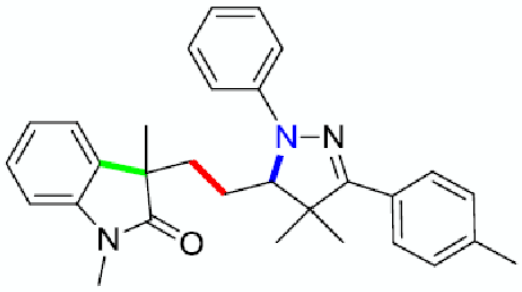
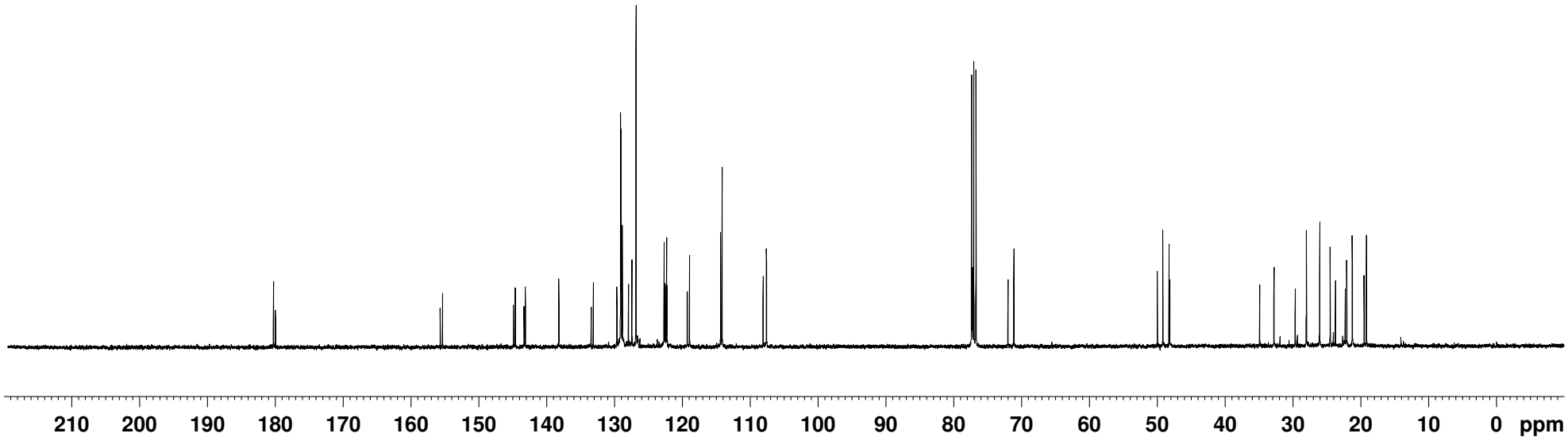
23.70
22.25
22.04
21.22
21.19
19.48
19.13


N–N
N
O

compound (3w)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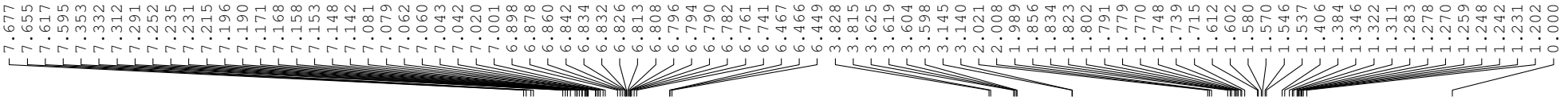
ppm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7.252
7.235
7.231
7.215
7.196
7.190
7.171
7.168
7.158
7.153
7.148
7.142
7.081
7.079
7.062
7.060
7.043
7.042
7.020
7.001
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6.878
6.860
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6.834
6.832
6.826
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6.808
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6.794
6.790
6.782
6.761
6.741
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6.466
6.449
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3.815
3.625
3.619
3.604
3.598
3.145
3.140
2.021
2.008
1.989
1.856
1.834
1.823
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1.791
1.779
1.770
1.748
1.739
1.715
1.612
1.602
1.580
1.570
1.546
1.537
1.406
1.384
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1.259
1.248
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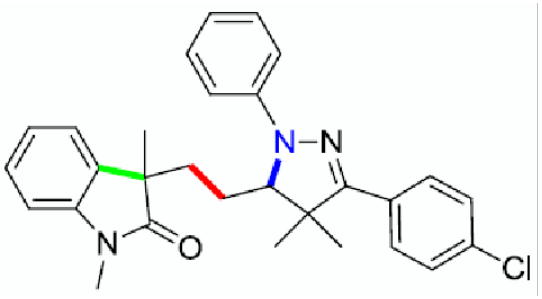
0.000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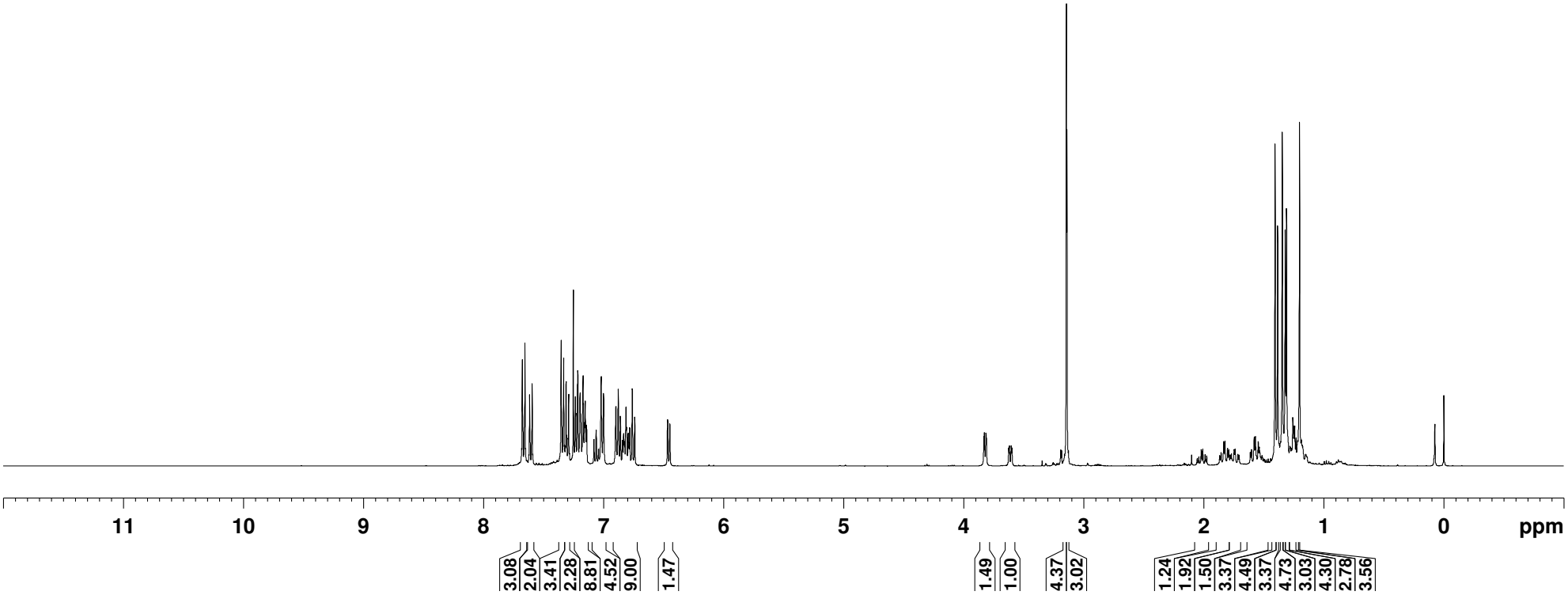
N
O
N
Cl

compound (3x)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8
7
6
5
4
3
2
1
0
ppm
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2.04
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2.28
8.81
4.52
9.00
1.47
1.49
1.00
4.37
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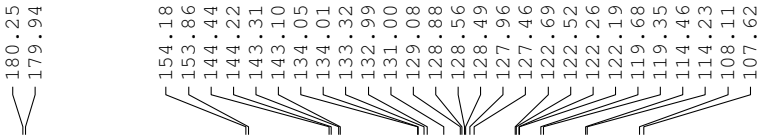
1.50
3.37
4.49
3.37
4.73
3.03
4.30
2.78
3.56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144.22
143.31
143.10
134.05
134.01
133.32
132.99
131.00
129.08
128.88
128.56
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127.96
127.46
122.69
122.52
122.26
122.19
119.68
119.35
114.46
114.23
108.11
107.62
77.31
77.00
76.68
72.14
71.31
49.79
48.98
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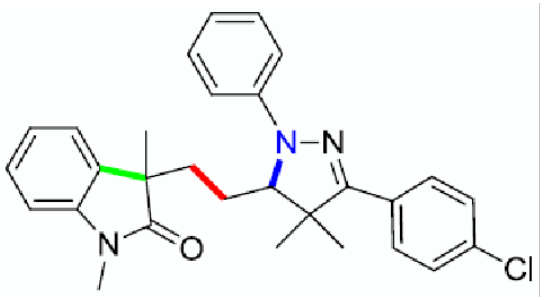
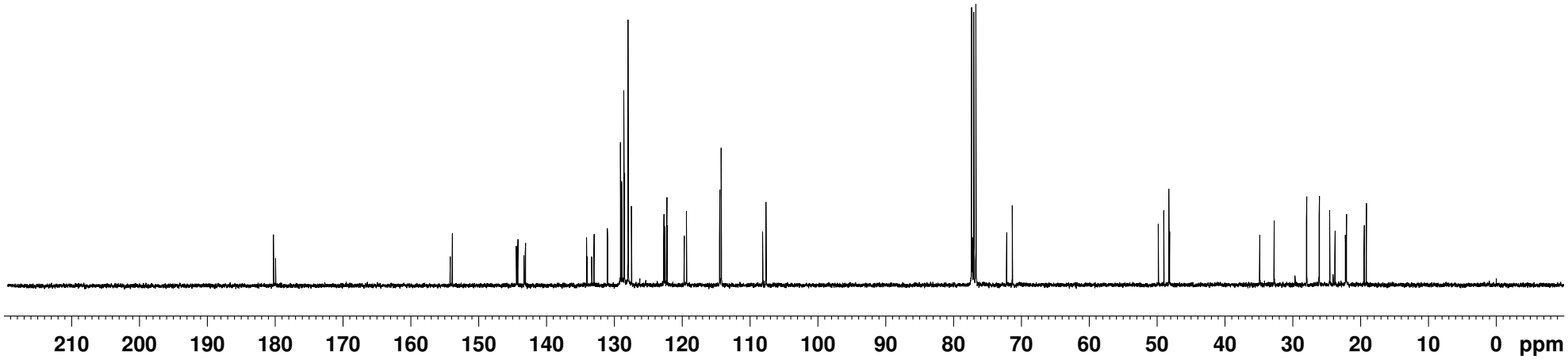
24.51
23.74
22.19
22.05
19.44
19.11


N
N
O
Cl

compound (3x)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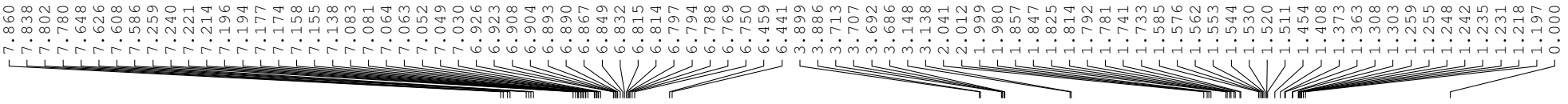
ppm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7.608
7.586
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7.240
7.221
7.214
7.196
7.194
7.177
7.174
7.158
7.155
7.138
7.083
7.081
7.064
7.063
7.052
7.049
7.030
6.926
6.923
6.908
6.904
6.893
6.890
6.867
6.849
6.832
6.815
6.814
6.797
6.794
6.788
6.769
6.750
6.459
6.441
3.899
3.886
3.713
3.707
3.692
3.686
3.148
3.138
2.041
2.012
1.999
1.980
1.857
1.847
1.825
1.814
1.792
1.781
1.741
1.733
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1.576
1.562
1.553
1.544
1.530
1.520
1.511
1.454
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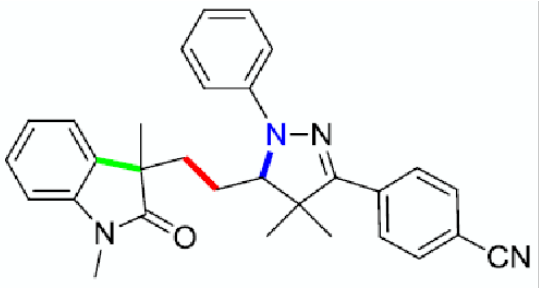
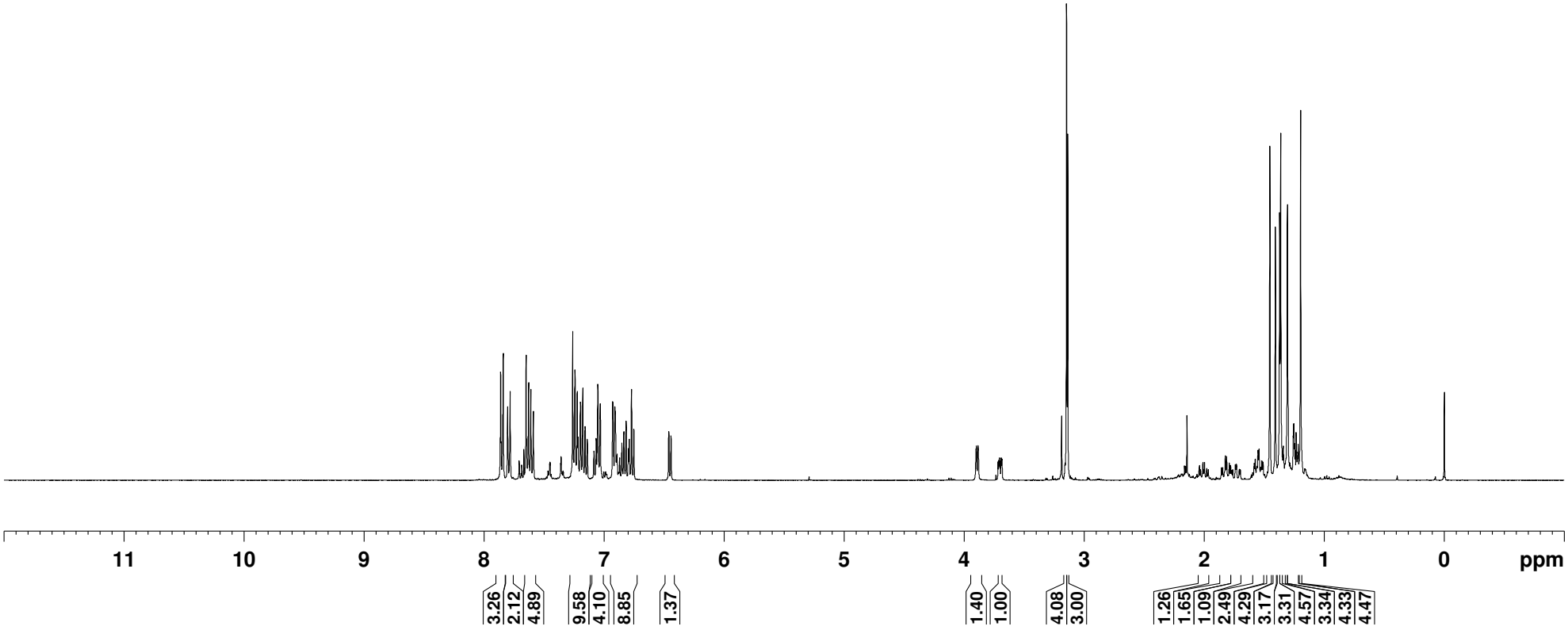

N–N
N
O
CN

compound (3y)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3
2
1
0
ppm
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9.58
4.10
8.85
1.37
1.40
1.00
4.08
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1.09
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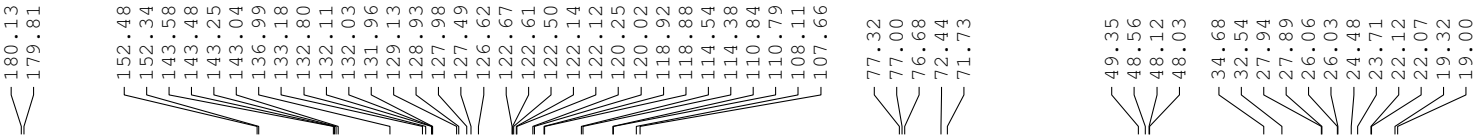
3.17
3.31
4.57
3.34
4.33
4.47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132.03
131.96
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127.98
127.49
126.62
122.67
122.61
122.50
122.14
122.12
120.25
120.02
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118.88
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77.00
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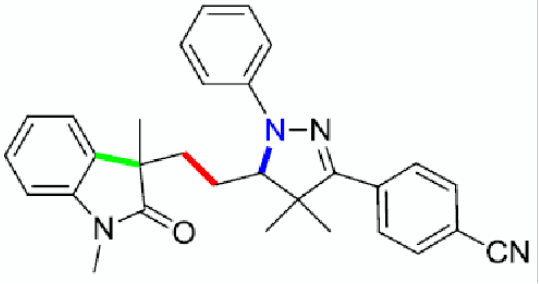
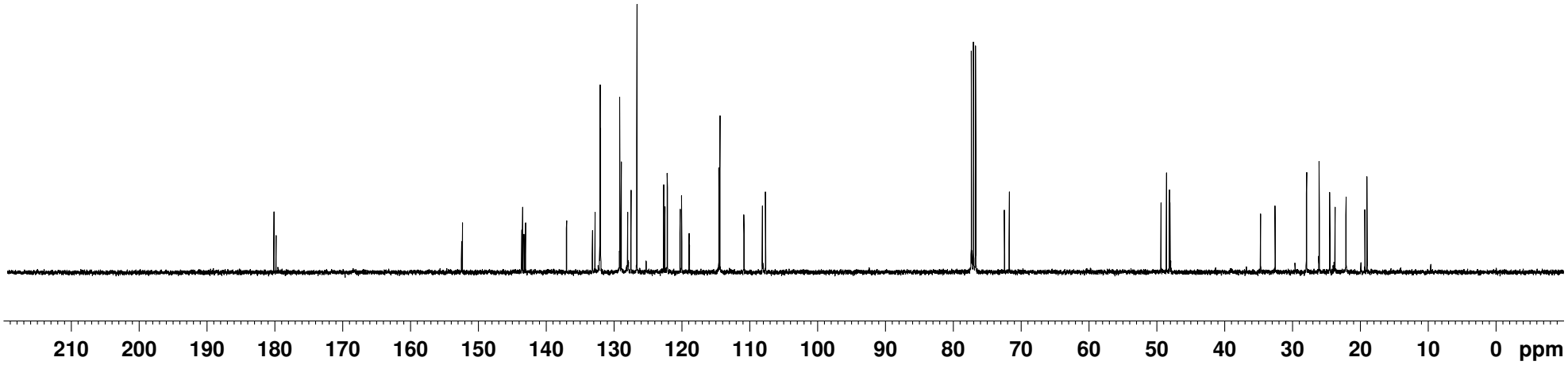
19.32
19.00


N–N
N
O
CN

compound (3y)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70
60
50
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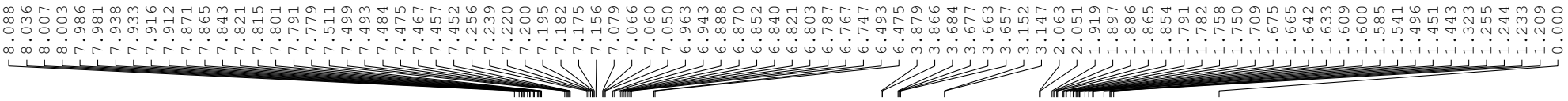
30
20
10
0
ppm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7.467
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7.452
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7.079
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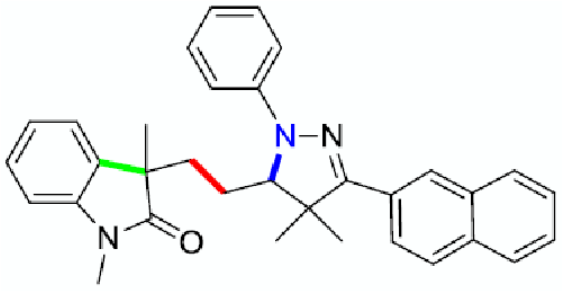
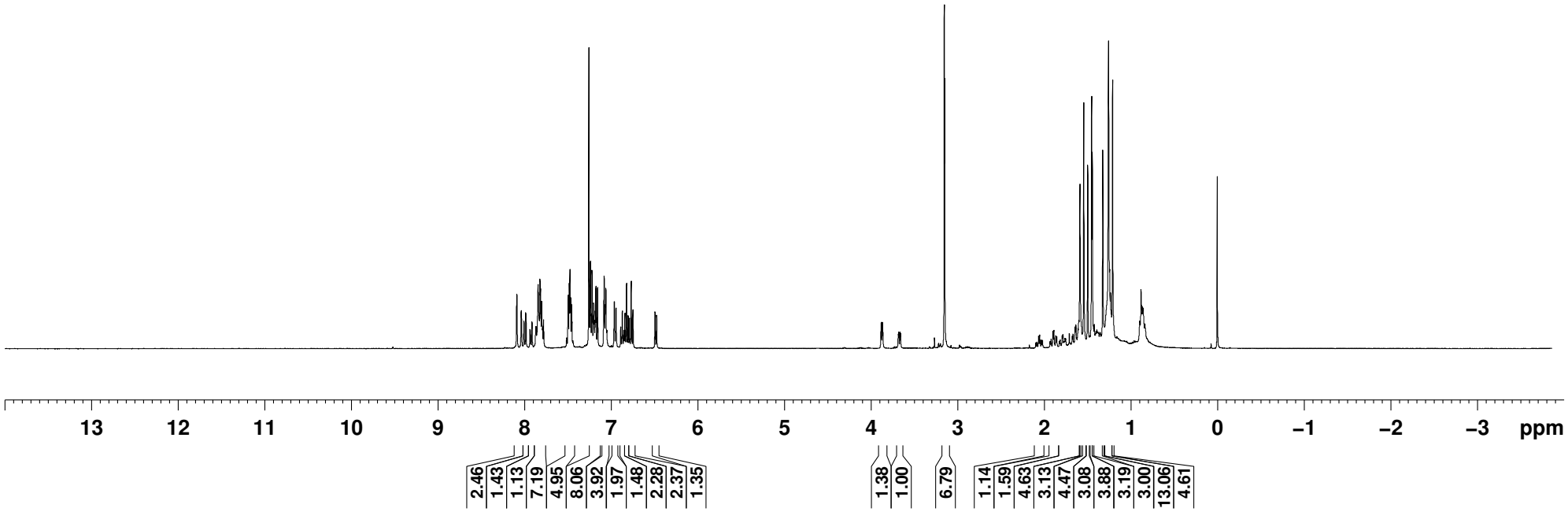

N–N
N
O

compound (3z)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–1
–2
–3
ppm
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1.43
1.13
7.19
4.95
8.06
3.92
1.97
1.48
2.28
2.37
1.35
1.38
1.00
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3.08
3.88
3.19
3.00
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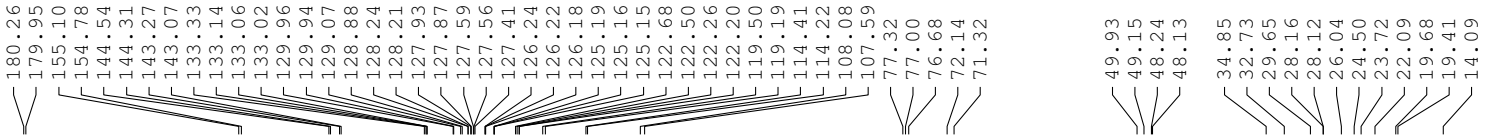
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114.22
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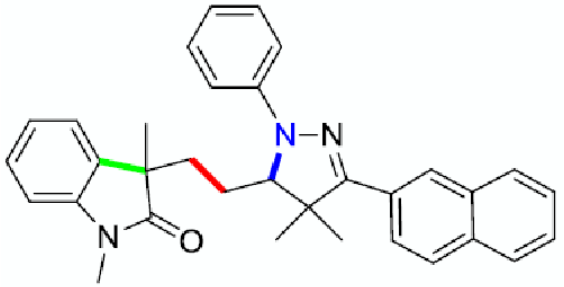
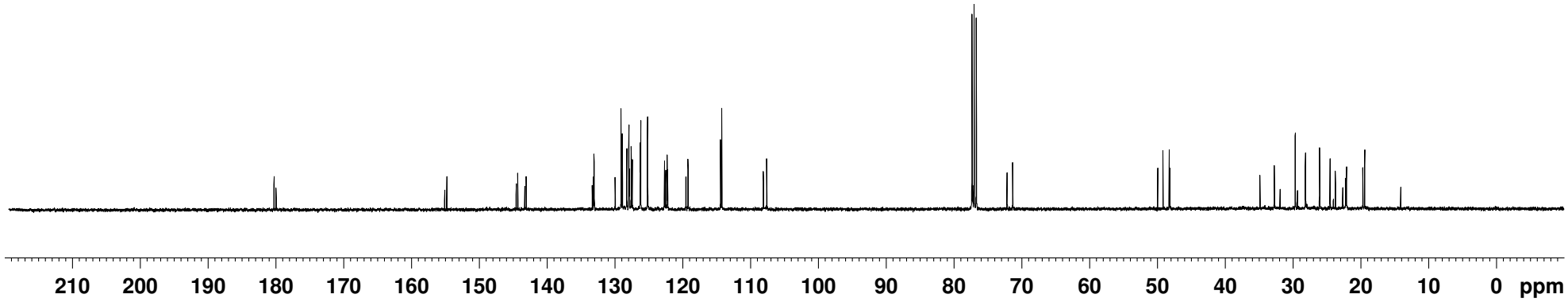

N–N
N
O

compound (3z)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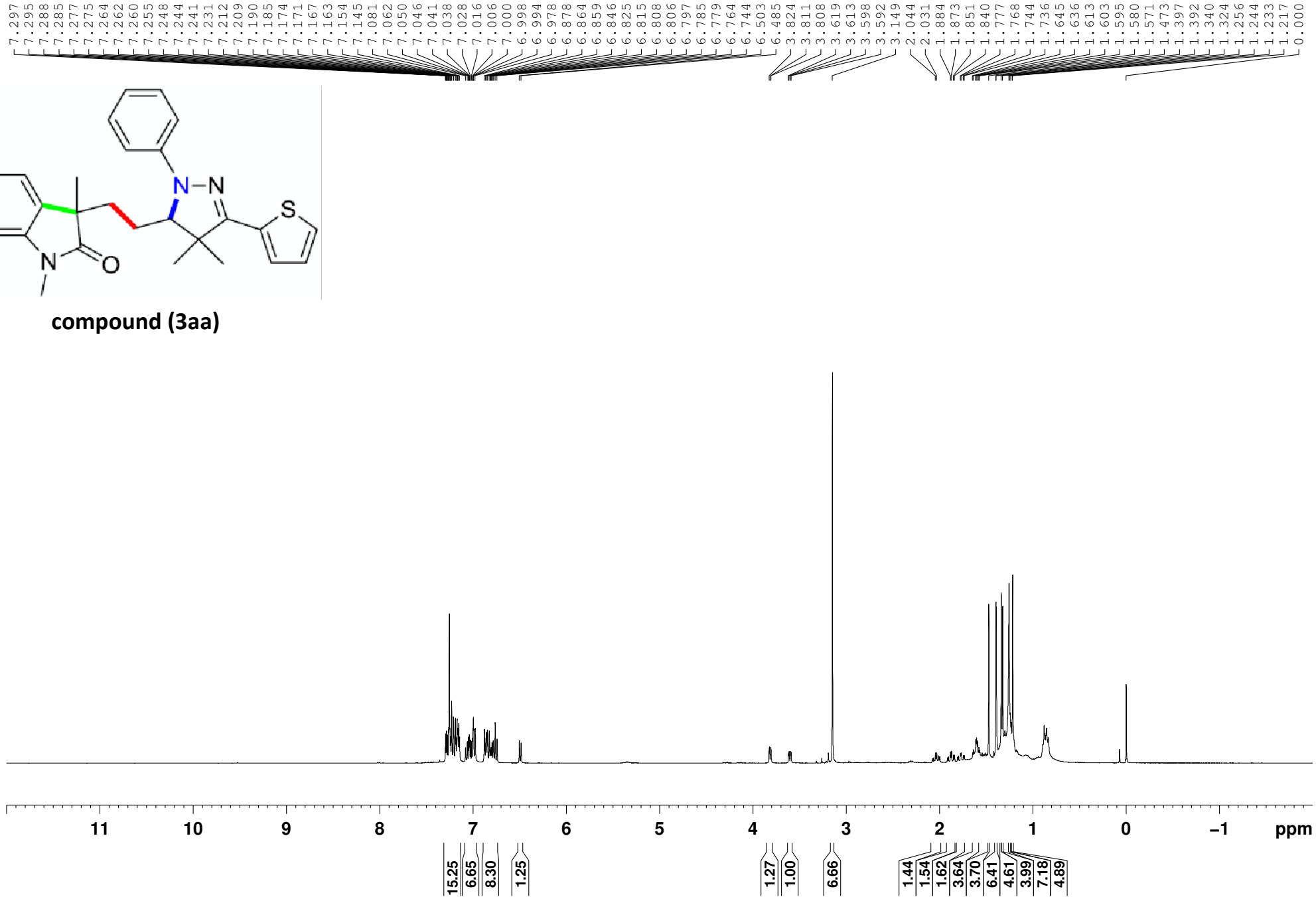
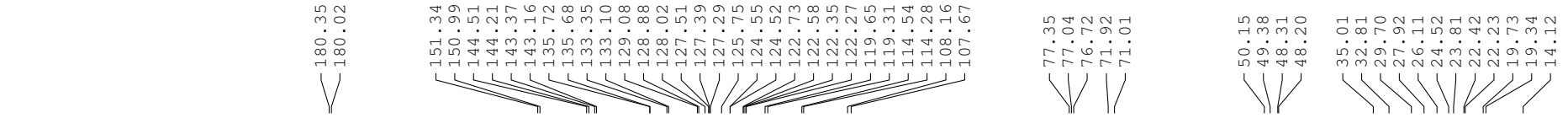
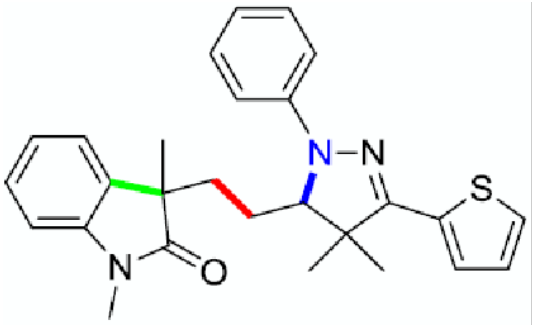
ppm



compound (3aa)





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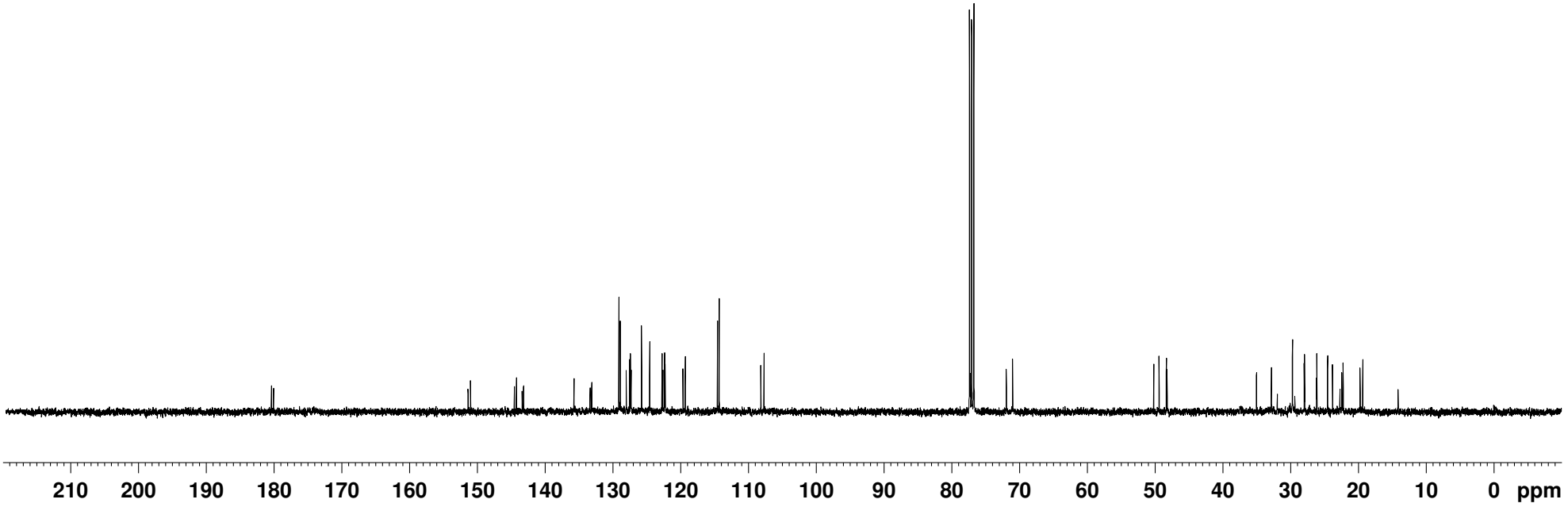
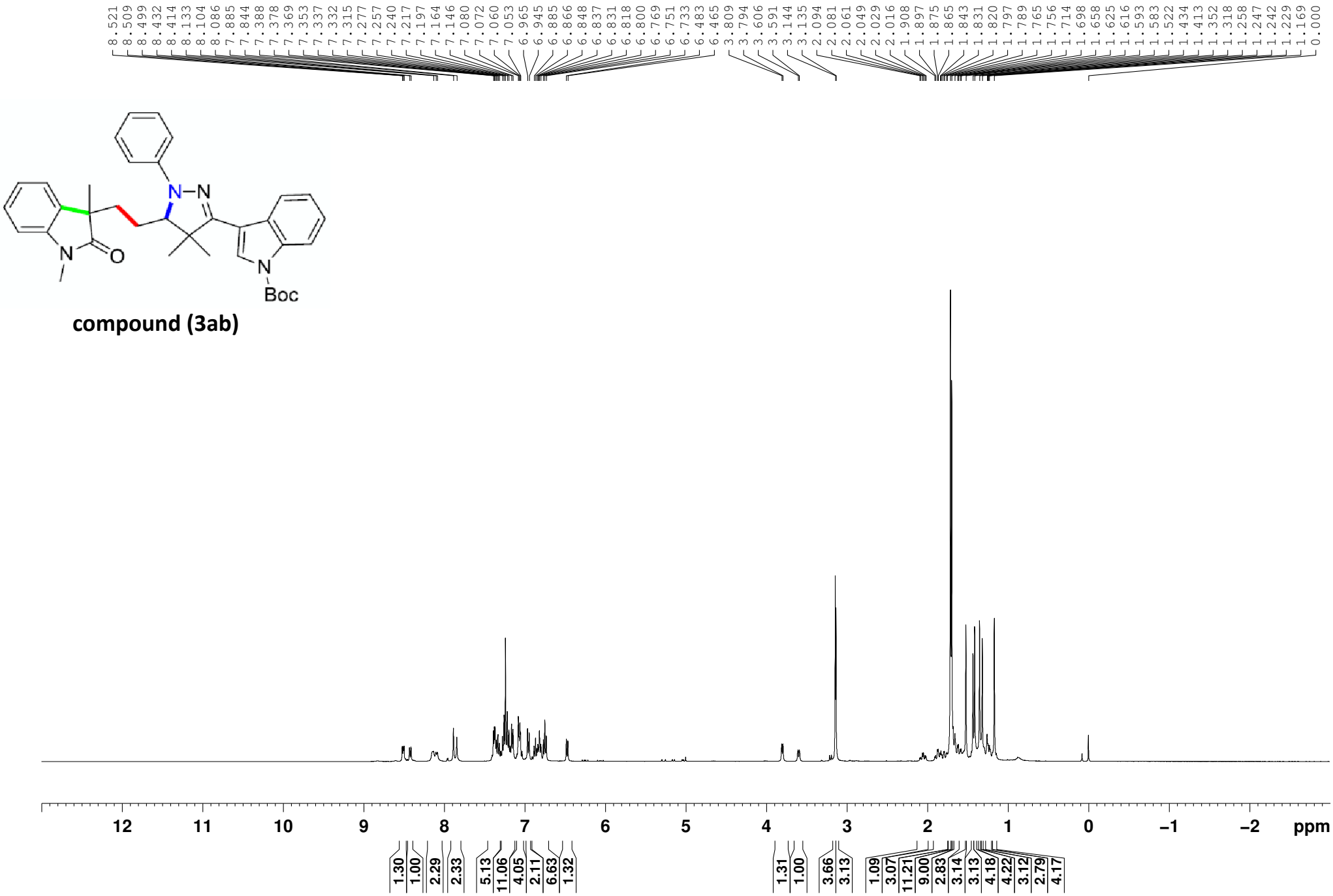
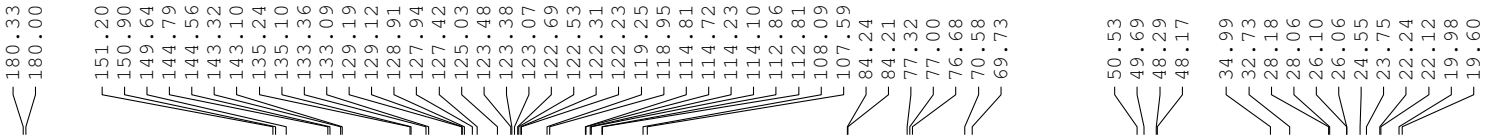
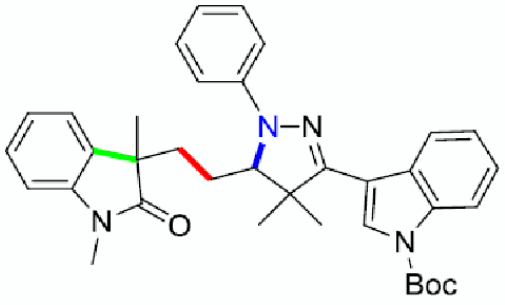


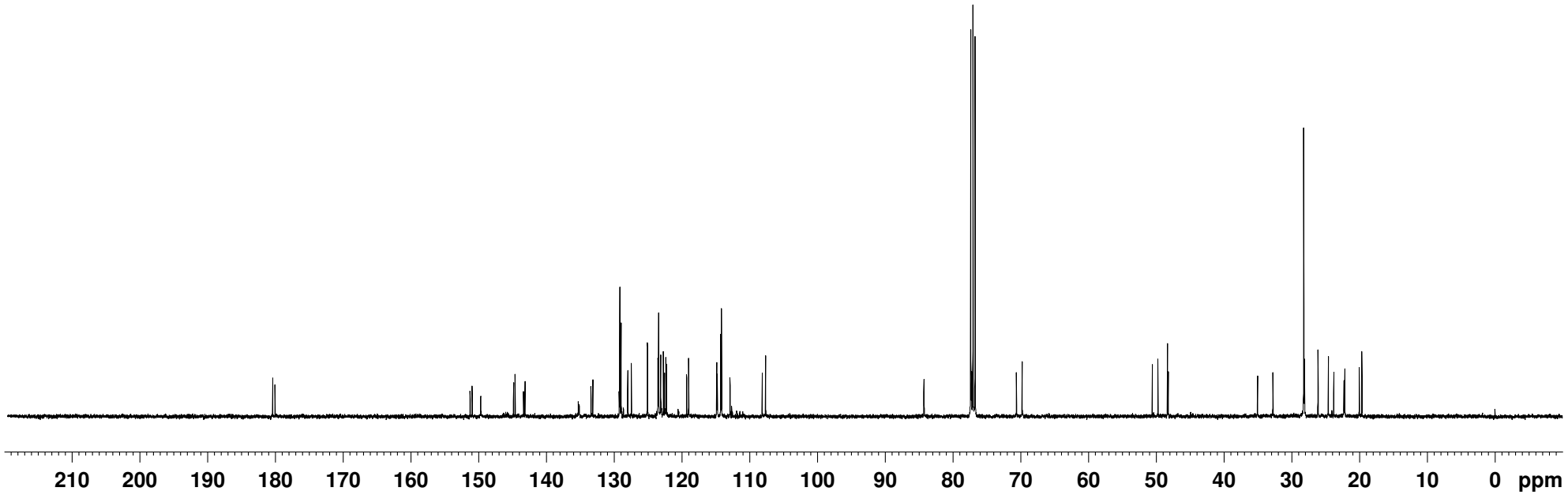


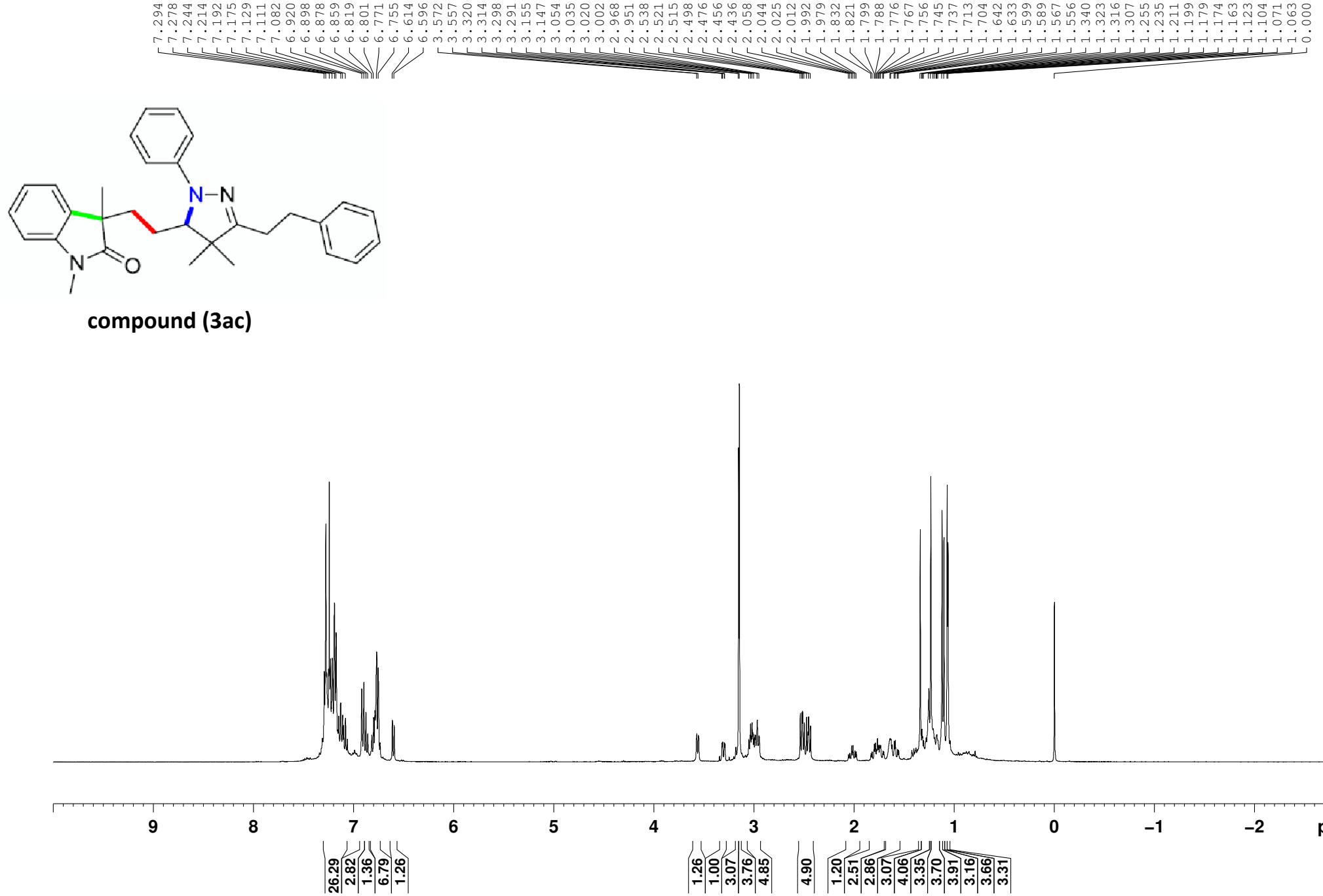
compound (3ab)



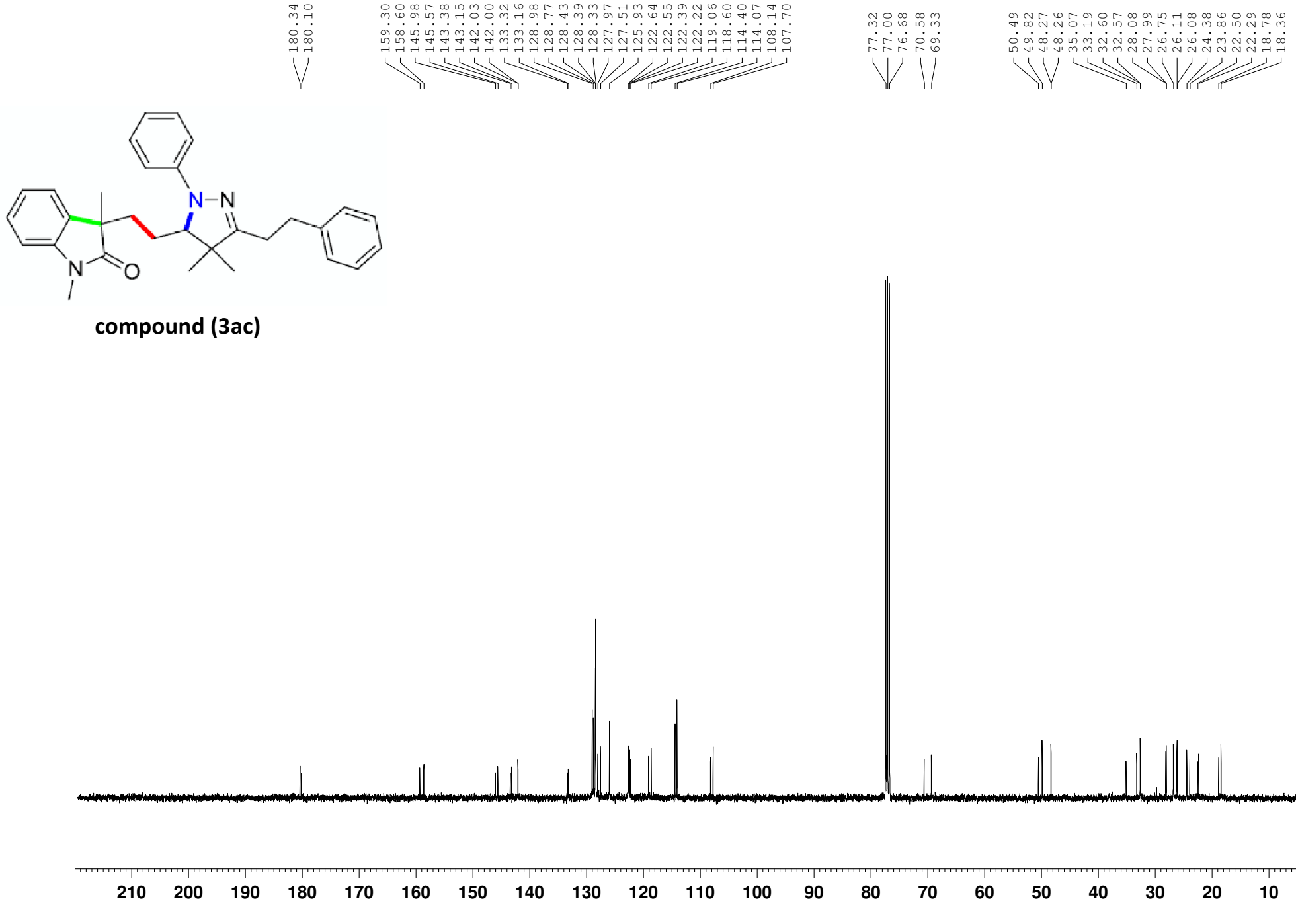


compound (3ab)

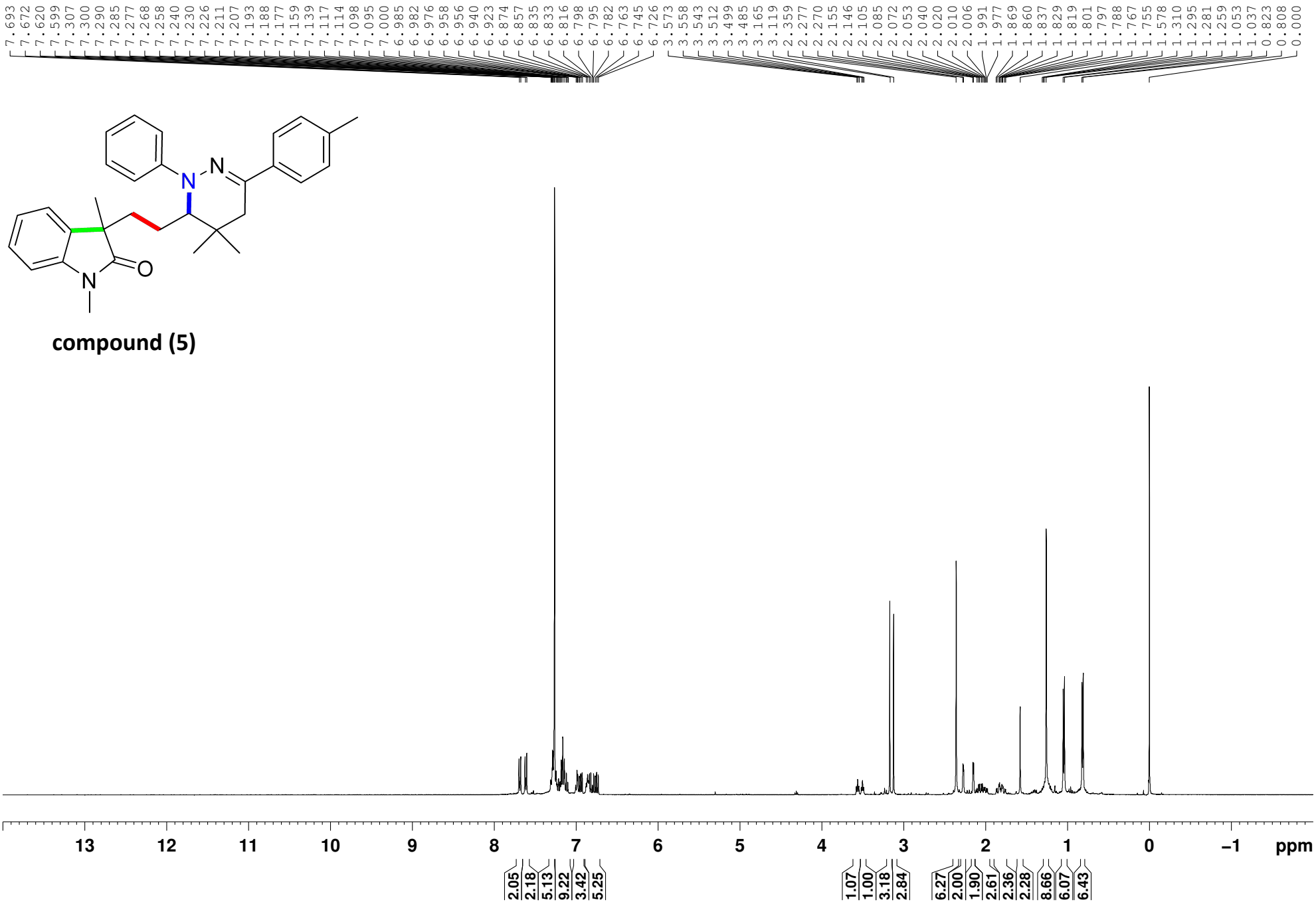




compound (3ac)



compound (3ac)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7.211
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7.159
7.139
7.117
7.114
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7.095
7.000
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1.259
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N
N
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compound (5)
13
12
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7
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3
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1
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–1
ppm
2.05
2.18
5.13
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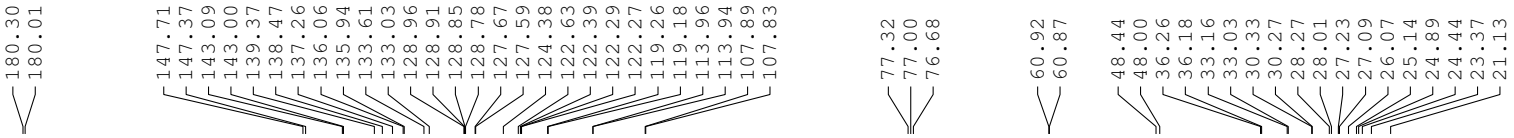
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127.59
124.38
122.63
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122.29
122.27
119.26
119.18
113.96
113.94
107.89
107.83
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77.00
76.68
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60.87
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48.00
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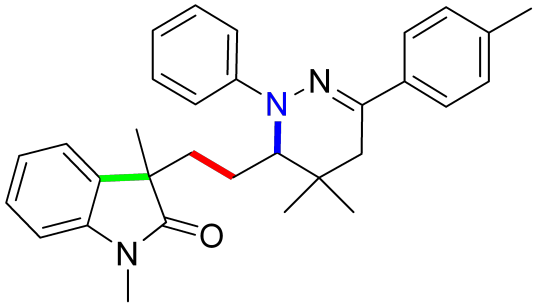
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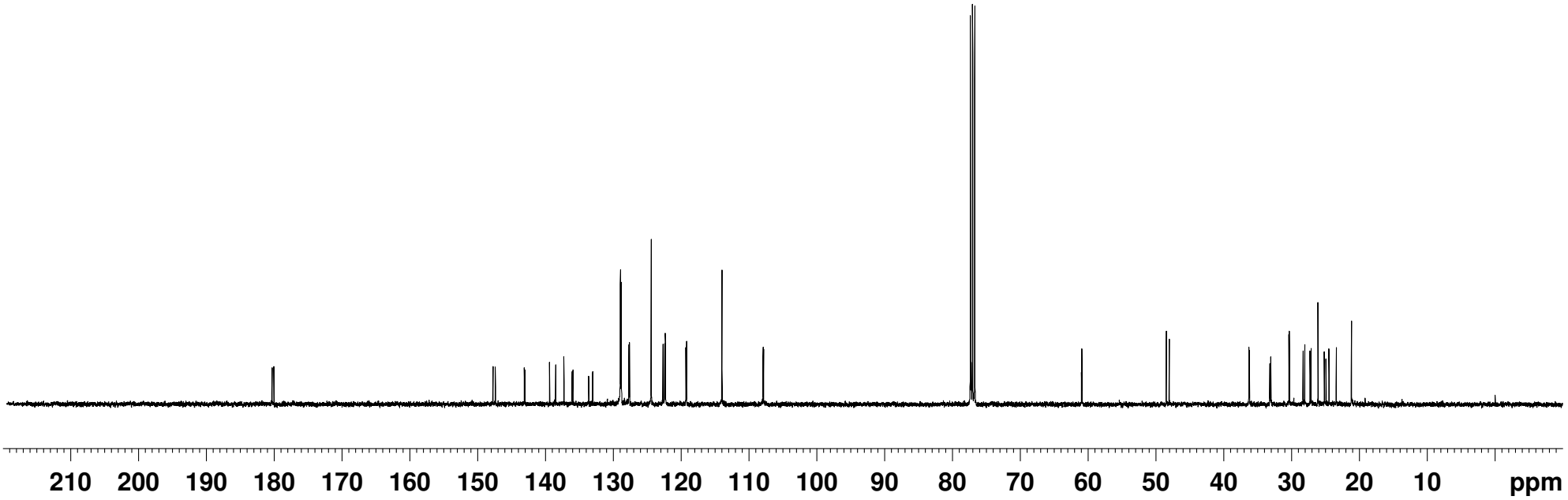
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ppm