Supporting Information

Synthesis of Pyrazolone Fused Benzodiazepines via Rh(III)-Catalyzed [4+3] Annulation of 1-Phenylpyrazolidinones with Propargyl Alcohols

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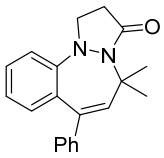
I. General experimental information

Commercial reagents were used without further purification. 1-Phenylpyrazolidinones (**1**),[1,2] propargyl alcohols (**2**, **4**, **6**),[3,4] and $[RhCp^*Cl_2]_2$[5] were prepared based on literature procedures. Melting points were recorded with a micro melting point apparatus and uncorrected. The ^1H NMR spectra were recorded at 400 MHz or 600 MHz. The ^{13}C NMR spectra were recorded at 100 MHz or 150 MHz. The ^{19}F NMR spectra were recorded at 376 MHz. Chemical shifts were expressed in parts per million (δ), and were reported as s (singlet), d (doublet), t (triplet), dd (doublet of doublets), m (multiplet), br s (broad singlet), etc. The coupling constants J were given in Hz. High resolution mass spectra (HRMS) were obtained *via* ESI mode by using a MicrOTOF mass spectrometer. All reactions were monitored by thin layer chromatography (TLC) using silica gel plates (silica gel 60 F254 0.25 mm), and components were visualized by observation under UV light (254 and 365 nm).

II. Experimental procedures and spectroscopic data

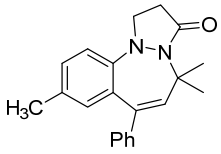
1. Typical procedure for the synthesis of 3a and spectroscopic data of 3a-3ee, 5a-5m and 7a-7q

To a reaction tube equipped with a stir bar were charged with 1-phenylpyrazolidin-3-one (**1a**, 48.7 mg, 0.3 mmol), toluene (2 mL), $[RhCp^*Cl_2]_2$ (4.7 mg, 0.0075 mmol), $Zn(OAc)_2$ (27.5 mg, 0.15 mmol), NaOAc (12.3 mg, 0.15 mmol) and 2-methyl-4-phenylbut-3-yn-2-ol (**2a**, 48.1 mg, 0.3 mmol). The resulting mixture was stirred at 100 °C (oil bath) for 4 h under air. Upon completion, it was cooled to room temperature, filtered through a pad of celite and concentrated under reduced pressure. The residue was purified by silica gel chromatography using petroleum ether/ethyl acetate (3:1) as eluent to afford **3a** (80.5 mg, 88%). **3b-3ee**, **5a-5m** and **7a-7q** were obtained in a similar manner.



5,5-Dimethyl-7-phenyl-1,2-dihydro-3*H*,5*H*-benzo[*c*]pyrazolo[1,2-*a*][1,2]diazepin-3-one (3a)

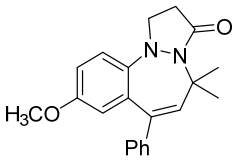
White solid (80.5 mg, 88%), mp 173.2-174.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.67 (s, 6H), 2.77 (t, J = 7.2 Hz, 2H), 4.10 (t, J = 7.2 Hz, 2H), 5.99 (s, 1H), 6.99-7.01 (m, 1H), 7.03-7.07 (m, 1H), 7.18-7.20 (m, 2H), 7.25-7.26 (m, 2H), 7.28-7.33 (m, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 26.9, 33.3, 49.0, 63.1, 116.3, 124.4, 127.4, 127.9, 128.1, 129.3, 132.1, 132.6, 136.5, 139.9, 144.4, 149.6, 173.6. HRMS calcd for $C_{20}H_{21}N_2O$: 305.1648 $[M+H]^+$, found: 305.1647.



5,5,9-Trimethyl-7-phenyl-1,2-dihydro-3*H*,5*H*-benzo[*c*]pyrazolo[1,2-*a*][1,2]diazepin-3-one (3b)

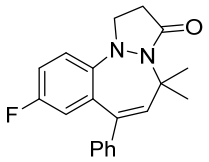
White solid (80.4 mg, 84%), mp 155.3-156.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ1.66 (s, 6H), 2.20 (s, 3H), 2.77 (t, J = 7.6 Hz, 2H), 4.08 (t, J = 7.6 Hz, 2H), 5.99 (s, 1H), 6.80 (s, 1H), 7.07 (d, J = 8.0 Hz, 1H), 7.16 (d, J = 8.4 Hz, 1H), 7.19-7.21 (m, 2H), 7.31-7.33 (m, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 20.8, 26.8, 33.3, 49.0, 62.7,

116.2, 127.3, 128.1, 128.5, 129.2, 132.4, 132.5, 134.0, 136.7, 139.8, 144.3, 147.2, 173.2. HRMS calcd for $C_{21}H_{23}N_2O$: 319.1805 $[M+H]^+$, found: 319.1804.



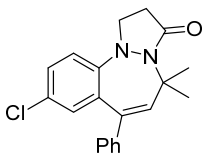
9-Methoxy-5,5-dimethyl-7-phenyl-1,2-dihydro-3*H*,5*H*-benzo[*c*]pyrazolo[1,2-*a*][1,2]diazepin-3-one (3c)

Light yellow solid (70.2 mg, 70%), mp 170.1-172.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.65 (s, 6H), 2.77 (t, J = 7.2 Hz, 2H), 3.65 (s, 3H), 4.06 (t, J = 7.2 Hz, 2H), 6.02 (s, 1H), 6.54 (d, J = 2.4 Hz, 1H), 6.81 (dd, J_1 = 9.2 Hz, J_2 = 2.4 Hz, 1H), 7.18-7.23 (m, 3H), 7.30-7.33 (m, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 26.8, 33.4, 49.1, 55.4, 62.6, 113.1, 117.2, 117.3, 127.5, 128.2, 129.2, 134.0, 136.7, 140.1, 143.1, 143.9, 156.2, 172.9. HRMS calcd for $C_{21}H_{23}N_2O_2$: 335.1754 $[M+H]^+$, found: 335.1754.



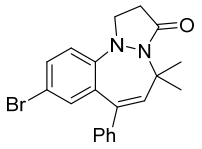
9-Fluoro-5,5-dimethyl-7-phenyl-1,2-dihydro-3*H*,5*H*-benzo[*c*]pyrazolo[1,2-*a*][1,2]diazepin-3-one (3d)

White solid (79.3 mg, 82%), mp 168.0-169.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.67(s, 6H), 2.77 (t, J = 7.2 Hz,2H), 4.08 (t, J = 7.6 Hz, 2H), 6.02 (s, 1H), 6.71 (dd, J_1 = 9.6 Hz, J_2 = 2.8 Hz, 1H), 6.95 (td, J_1 = 8.4 Hz, J_2 = 2.8 Hz, 1H), 7.18-7.23 (m, 3H), 7.32-7.35 (m, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 26.8, 33.2, 49.4, 63.1, 114.3 (d, $^2J_{C\text{-}F}$ = 22.4 Hz), 117.5 (d, $^3J_{C\text{-}F}$ = 8.7 Hz), 118.4 (d, $^2J_{C\text{-}F}$ = 23.2 Hz), 127.6, 128.3, 129.2, 134.6 (d, $^3J_{C\text{-}F}$ = 7.3 Hz), 135.6 (d, $^4J_{C\text{-}F}$ = 2.1 Hz), 141.0, 143.7, 145.8 (d, $^4J_{C\text{-}F}$ = 2.9 Hz), 159.4 (d, $^1J_{C\text{-}F}$ = 242.0 Hz), 173.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ -118.14 – -118.08 (m). HRMS calcd for $C_{20}H_{20}FN_2O$: 323.1554 $[M+H]^+$, found: 323.1553.



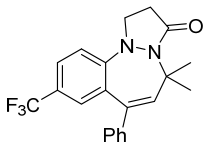
9-Chloro-5,5-dimethyl-7-phenyl-1,2-dihydro-3*H*,5*H*-benzo[*c*]pyrazolo[1,2-*a*][1,2]diazepin-3-one (3e)

White solid (74.1 mg, 73%), mp 179.0-180.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.67 (s, 6H), 2.75 (t, *J* = 7.2 Hz, 2H), 4.07 (t, *J* = 7.2 Hz, 2H), 6.00 (s, 1H), 6.97 (d, *J* = 2.0 Hz, 1H), 7.17-7.23 (m, 4H), 7.32-7.36 (m, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 26.8, 33.1, 49.2, 63.3, 117.5, 127.6, 127.7, 128.4, 129.2, 129.8, 131.7, 134.3, 135.3, 141.2, 143.8, 148.2, 173.6. HRMS calcd for$C_{20}H_{20}ClN_2O$: 339.1259 $[M+H]^+$, found: 339.1242.



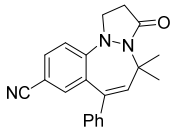
9-Bromo-5,5-dimethyl-7-phenyl-1,2-dihydro-3*H*,5*H*-benzo[*c*]pyrazolo[1,2-*a*][1,2]diazepin-3-one (3f)

White solid (90.5 mg, 79%), mp 177.6-179.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.67 (s, 6H), 2.75 (t, *J* = 7.2 Hz, 2H), 4.07 (t, *J* = 7.2 Hz, 2H), 6.00 (s, 1H), 7.11-7.14 (m, 2H), 7.17-7.19 (m, 2H), 7.33-7.38 (m, 4H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 26.8, 33.1, 49.2, 63.3, 117.5, 117.9, 127.7, 128.4, 129.2, 130.5, 134.60, 134.63, 135.2, 141.3, 143.7, 148.7, 173.6. HRMS calcd for $C_{20}H_{20}BrN_2O$: 383.0754 $[M+H]^+$, found: 383.0751.



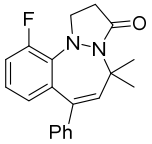
5,5-Dimethyl-7-phenyl-9-(trifluoromethyl)-1,2-dihydro-3*H*,5*H*-benzo[*c*]pyrazolo[1,2-*a*][1,2]diazepin-3-one (3g)

White solid (91.5 mg, 82%), mp 180.3-181.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.69 (s, 6H), 2.77 (t, *J* = 7.2 Hz, 2H), 4.13 (t, *J* = 7.2 Hz, 2H), 6.03 (s, 1H), 7.15-7.17 (m, 2H), 7.26 (s, 1H), 7.33-7.36 (m, 4H), 7.51 (d, *J* = 8.4 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 26.9, 33.0, 49.3, 63.8, 116.4, 123.9 (q, $^{1}J_{C\text{-}F}$ = 270.1 Hz), 124.5 (q, $^{3}J_{C\text{-}F}$ = 3.6 Hz), 126.5 (q, $^{2}J_{C\text{-}F}$ = 32.5 Hz), 127.8, 128.4, 129.17, 129,24 (q, $^{3}J_{C\text{-}F}$ = 3.6 Hz), 132.9, 135.1, 141.6, 143.8, 152.5, 174.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.22 (s). HRMS calcd for $C_{21}H_{20}F_3N_2O$: 373.1522 $[M+H]^+$, found: 373.1523.



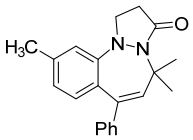
5,5-Dimethyl-3-oxo-7-phenyl-2,3-dihydro-1*H*,5*H*-benzo[*c*]pyrazolo[1,2-*a*][1,2]diazepine-9-carbonitrile (3h)

Light yellow solid (77.4 mg, 78%), mp 185.0-186.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.69 (s, 6H), 2.75 (t, J = 7.2 Hz, 2H), 4.13 (t, J = 7.2 Hz, 2H), 6.00 (s, 1H), 7.12-7.15 (m, 2H), 7.29 (d, J = 1.2 Hz, 1H), 7.31-7.36 (m, 4H), 7.54 (dd, J_1 = 8.4 Hz, J_2 = 1.6 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 26.9, 32.9, 49.3, 64.2, 107.9, 116.8, 118.6, 127.9, 128.6, 129.2, 131.1, 133.3, 134.2, 136.2, 142.2, 143.7, 153.4, 174.4. HRMS calcd for $C_{21}H_{20}N_3O$: 330.1601 $[M+H]^+$, found: 330.1596.



11-Fluoro-5,5-dimethyl-7-phenyl-1,2-dihydro-3*H*,5*H*-benzo[*c*]pyrazolo[1,2-*a*][1,2]diazepin-3-one (3i)

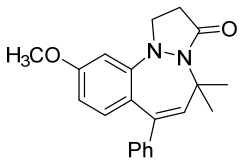
Light yelow solid (62.8 mg, 65%), mp 183.2-184.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.62 (s, 6H), 2.85 (t, J = 7.2 Hz, 2H), 4.11 (t, J = 7.2 Hz, 2H), 6.11 (s, 1H), 6.77-6.79 (m, 1H), 7.00-7.04 (m, 2H), 7.19-7.21 (m, 2H), 7.30-7.33 (m, 3H). ^{13}C{^{1}H} NMR(100 MHz, $CDCl_3$) δ 26.7, 35.0 (d, $^{5}J_{C\text{-}F}$ = 7.2 Hz), 51.6 (d, $^{4}J_{C\text{-}F}$ = 12.3 Hz), 62.4, 116.3 (d, $^{2}J_{C\text{-}F}$ = 24.5 Hz), 125.5 (d, $^{3}J_{C\text{-}F}$ = 9.3 Hz), 127.1 (d, $^{3}J_{C\text{-}F}$ = 2.9 Hz), 127.6, 128.2, 129.0, 136.1 (d, $^{2}J_{C\text{-}F}$ = 10.1 Hz), 137.0 (d, $^{4}J_{C\text{-}F}$ = 2.9 Hz), 137.2(d, $^{4}J_{C\text{-}F}$ = 2.9 Hz), 140.4, 143.9, 153.9 (d, $^{1}J_{C\text{-}F}$ = 243.4 Hz), 174.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ -119.91 (dd, J_1 = 10.9 Hz, J_2 = 5.6 Hz). HRMS calcd for $C_{20}H_{20}FN_2O$: 323.1554 $[M+H]^+$, found: 323.1551.



5,5,10-Trimethyl-7-phenyl-1,2-dihydro-3*H*,5*H*-benzo[*c*]pyrazolo[1,2-*a*][1,2]diazepin-3-one (3j)

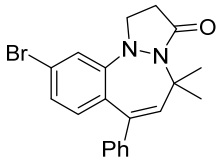
White solid (87.0 mg, 91%), mp 164.7-165.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.66 (s, 6H), 2.39 (s, 3H), 2.78 (t, J = 7.6 Hz, 2H), 4.09 (t, J = 7.6 Hz, 2H), 5.94 (s, 1H), 6.88 (s, 2H), 7.05 (s 1H), 7.18-7.20 (m, 2H), 7.29-7.33 (m, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 21.7, 26.9, 33.3, 48.9, 63.0, 117.1, 125.3, 127.3, 128.1, 129.3, 129.9, 131.9, 136.5, 137.9, 139.1, 144.5, 149.4, 173.5. HRMS calcd for $C_{21}H_{23}N_2O$: 319.1805 $[M+H]^+$, found:

319.1804.



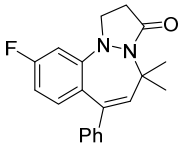
10-Methoxy-5,5-dimethyl-7-phenyl-1,2-dihydro-3*H*,5*H*-benzo[*c*]pyrazolo[1,2-*a*][1,2]diazepin-3-one (3k)

Brown syrup (75.1 mg, 75%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.66 (s, 6H), 2.77 (t, J = 7.2 Hz, 2H), 3.82 (s, 3H), 4.06 (t, J = 7.2 Hz, 2H), 5.86 (s, 1H), 6.60 (dd, J_1 = 8.4 Hz,J_2 = 2.0 Hz, 1H), 6.80 (d, J = 2.4 Hz, 1H), 6.92 (d, J = 8.8 Hz, 1H), 7.19-7.21 (m, 2H), 7.28-7.32 (m, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 26.8, 33.4, 49.1, 55.4, 62.6, 113.1, 117.2, 117.3, 127.5, 128.2, 129.2, 134.0, 136.7, 140.1, 143.1, 143.9, 156.2, 172.9. HRMS calcd for $C_{21}H_{23}N_2O_2$: 335.1754 $[M+H]^+$, found: 335.1754.



10-Bromo-5,5-dimethyl-7-phenyl-1,2-dihydro-3*H*,5*H*-benzo[*c*]pyrazolo[1,2-*a*][1,2]diazepin-3-one (3l)

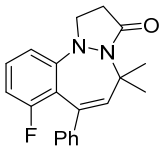
Light yellow solid (99.7 mg, 87%), mp 180.5-181.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.67 (s, 6H), 2.77 (t, J = 7.6 Hz, 2H), 4.07 (t, J = 7.6 Hz, 2H), 5.97 (s, 1H), 6.86 (d, J = 8.4 Hz, 1H), 7.16-7.19 (m, 3H), 7.31-7.33 (m, 3H), 7.38 (s, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 26.8, 33.1, 49.2, 63.3, 117.5, 127.6, 127.7, 128.4, 129.2, 129.8, 131.7, 134.3,135.3, 141.2, 143.8, 148.2, 173.6. HRMS calcd for $C_{20}H_{20}BrN_2O$: 383.0754 $[M+H]^+$, found: 383.0748.



10-Fluoro-5,5-dimethyl-7-phenyl-1,2-dihydro-3*H*,5*H*-benzo[*c*]pyrazolo[1,2-*a*][1,2]diazepin-3-one (3m)

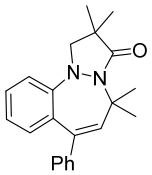
White solid (34.8 mg, 36%), mp 153.8-154.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.67 (s, 6H), 2.77 (t, J = 7.6 Hz, 2H), 4.06 (t, J = 7.6 Hz, 2H), 5.93 (s, 1H), 6.77 (td, J_1 = 8.0 Hz, J_2= 2.4 Hz, 1H), 6.95-6.98 (m, 2H), 7.16-7.18 (m, 2H), 7.30-7.33 (m, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 26.9, 32.9, 49.2, 63.4, 104.1 (d, $^{2}J_{C\text{-}F}$ = 23.8

Hz), 111.3 (d, $^{2}J_{C\text{-}F}$ = 20.9 Hz), 127.5, 128.2, 128.6 (d, $^{4}J_{C\text{-}F}$ = 2.9 Hz), 129.2, 133.6 (d, $^{3}J_{C\text{-}F}$ = 8.7 Hz), 135.5, 139.5, 144.3, 151.2 (d, $^{3}J_{C\text{-}F}$ = 6.5 Hz), 161.7 (d, $^{1}J_{C\text{-}F}$ = 247.0 Hz), 173.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ -112.09 – -112.02 (m). HRMS calcd for $C_{20}H_{20}FN_2O$: 323.1554 $[M+H]^+$, found: 323.1555.



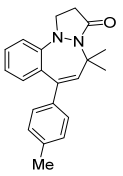
8-Fluoro-5,5-dimethyl-7-phenyl-1,2-dihydro-3*H*,5*H*-benzo[*c*]pyrazolo[1,2-*a*][1,2]diazepin-3-one (3m')

Light yellow solid (32.8 mg, 34%), mp 186.0-188.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.65 (s, 6H), 2.75 (brs, 2H), 4.07 (t, *J* = 7.6 Hz, 2H), 6.22 (s, 1H), 6.84-6.89 (m, 1H), 7.11 (d, *J* = 8.0 Hz, 1H), 7.14-7.17 (m, 2H), 7.27-7.33 (m, 4H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 26.8, 33.1, 49.0, 61.7, 112.4 (d, $^{4}J_{C\text{-}F}$ = 3.3 Hz), 113.1 (d, $^{2}J_{C\text{-}F}$ = 21.9 Hz), 120.8 (d, $^{2}J_{C\text{-}F}$ = 12.0 Hz), 126.7, 127.3, 128.2, 129.1 (d, $^{3}J_{C\text{-}F}$ = 9.9 Hz), 133.2, 141.8, 143.2 (d, $^{4}J_{C\text{-}F}$ = 2.3 Hz), 151.4 (d, $^{3}J_{C\text{-}F}$ = 5.4 Hz), 161.0 (d, $^{1}J_{C\text{-}F}$ = 250.5 Hz), 172.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ -101.96 (dd, J_1 = 9.8 Hz, J_2 = 5.6 Hz). HRMS calcd for $C_{20}H_{20}FN_2O$: 323.1554 $[M+H]^+$, found: 323.1554.



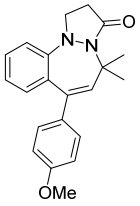
2,2,5,5-Tetramethyl-7-phenyl-1,2-dihydro-3*H*,5*H*-benzo[*c*]pyrazolo[1,2-*a*][1,2]diazepin-3-one (3n)

White solid (80.7 mg, 81%), mp 166.8-167.9 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.32 (s, 6H), 1.68 (s, 6H), 4.03 (s, 2H), 5.93 (s, 1H), 6.97-7.00 (m, 2H), 7.16-7.18 (m, 2H), 7.20-7.23 (m, 1H), 7.28-7.32 (m, 3H), 7.34 (d, *J* = 7.8 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 24.7, 26.8, 42.4, 59.8, 63.8, 117.2, 123.5, 127.0, 127.2, 128.1, 129.4, 131.9, 132.4, 136.4, 139.8, 145.0, 149.7, 180.4. HRMS calcd for $C_{22}H_{25}N_2O$: 333.1961 $[M+H]^+$, found: 333.1959.



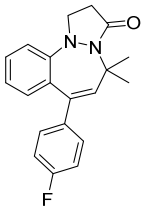
5,5-Dimethyl-7-(*p*-tolyl)-1,2-dihydro-3*H*,5*H*-benzo[*c*]pyrazolo[1,2-*a*][1,2]diazepin-3-one (3o)

White solid (83 mg, 87%), mp 199.1-200.2 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.66 (s, 6H), 2.36 (s, 3H), 2.77 (t, *J* = 7.2 Hz, 2H), 4.09 (t, *J* = 7.2 Hz, 2H), 5.98 (s, 1H), 7.01-7.06 (m, 2H), 7.08 (d, *J* = 8.4 Hz, 2H), 7.12 (d, *J* = 7.8 Hz, 2H), 7.24-7.25 (m, 2H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 21.2, 26.9, 33.3,49.0, 63.0, 116.3, 124.4, 127.8, 128.8, 129.2, 132.1, 132.8, 136.4, 137.1, 139.4, 141.6, 149.5, 173.5. HRMS calcd for $C_{21}H_{23}N_2O$: 319.1805 $[M+H]^+$, found: 319.1807.



7-(4-Methoxyphenyl)-5,5-dimethyl-1,2-dihydro-3*H*,5*H*-benzo[*c*]pyrazolo[1,2-*a*][1,2]diazepin-3-one (3p)

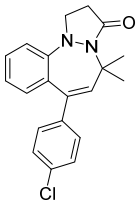
White solid (83.9 mg, 84%), mp 184.5-185.2 °C.^{1}H NMR (600 MHz, $CDCl_3$) δ 1.66 (s, 6H), 2.77 (t, *J* = 7.2 Hz, 2H), 3.81 (s, 3H), 4.09 (t, *J* = 7.2 Hz, 2H), 5.98 (s, 1H), 6.83-6.85 (m, 2H), 7.03-7.07 (m, 2H), 7.10-7.13 (m, 2H), 7.25-7.26 (m, 2H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 26.9, 33.3, 49.0, 55.3, 62.8, 113.5, 116.3, 124.4, 127.8, 130.4, 132.1, 132.9, 136.1, 136.9, 139.0, 149.5, 159.1, 173.3. HRMS calcd for $C_{21}H_{23}N_2O_2$: 335.1754 $[M+H]^+$, found: 335.1760.



7-(4-Fluorophenyl)-5,5-dimethyl-1,2-dihydro-3*H*,5*H*-benzo[*c*]pyrazolo[1,2-*a*][1,2]diazepin-3-one (3q)

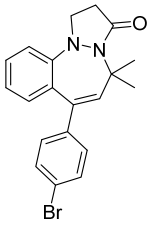
White solid (71.5 mg, 74%), mp 193.0-194.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.67(s, 6H), 2.77 (t, *J* = 7.2 Hz, 2H), 4.10 (t, *J* = 7.2 Hz, 2H), 5.97 (s, 1H), 6.97-7.02 (m, 3H), 7.04-7.08 (m, 1H), 7.14-7.17 (m, 2H), 7.25-7.27 (m, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 26.9, 33.2, 49.0, 63.0, 115.0 (d, $^{2}J_{C\text{-}F}$ = 20.9 Hz), 116.3, 124.5, 128.0, 130.8 (d, $^{3}J_{C\text{-}F}$ = 8.0 Hz), 132.0, 132.4, 135.5, 139.9, 140.4 (d, $^{4}J_{C\text{-}F}$ = 2.8 Hz), 149.6, 162.3 (d, $^{1}J_{C\text{-}F}$ = 244.8 Hz), 173.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.13 – -115.06 (m). HRMS calcd for $C_{20}H_{20}FN_2O$:

323.1554 $[M+H]^+$, found: 323.1557.



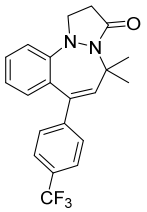
7-(4-Chlorophenyl)-5,5-dimethyl-1,2-dihydro-3*H*,5*H*-benzo[*c*]pyrazolo[1,2-*a*][1,2]diazepin-3-one (3r)

White solid (84.2 mg, 83%), mp 219.6-220.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.66 (s, 6H), 2.77 (t, *J* = 7.2 Hz, 2H), 4.10 (t, *J* = 7.6 Hz, 2H), 5.97 (s, 1H), 6.97 (d, *J* = 7.6 Hz, 1H), 7.05-7.09 (m, 1H), 7.13 (d, *J* = 8.0 Hz, 2H), 7.27-7.29 (m, 4H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 26.8, 33.2, 49.0, 63.1, 116.3, 124.5, 128.1, 128.3, 130.6, 131.9, 132.2, 133.3, 135.4, 140.2, 142.8, 149.6, 173.6. HRMS calcd for$C_{20}H_{20}ClN_2O$: 339.1259 $[M+H]^+$, found: 339.1258.



7-(4-Bromophenyl)-5,5-dimethyl-1,2-dihydro-3*H*,5*H*-benzo[*c*]pyrazolo[1,2-*a*][1,2]diazepin-3-one (3s)

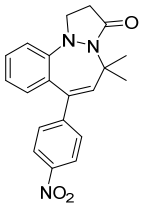
White solid (91.7 mg, 80%), mp 213.2-214.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.66 (s, 6H), 2.77 (t, *J* = 7.6 Hz, 2H), 4.10 (t, *J* = 7.6 Hz, 2H), 5.96 (s, 1H), 6.97 (d, *J* = 7.6 Hz, 1H), 7.04-7.08 (m, 3H), 7.26-7.30 (m, 2H), 7.44 (d, *J* = 8.0 Hz, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 26.8, 33.2, 49.0, 63.1, 116.3, 121.5, 124.5, 128.1, 130.9, 131.3, 131.9, 132.1, 135.4, 140.2, 143.3, 149.6, 173.6. HRMS calcd for $C_{20}H_{20}BrN_2O$: 383.0754 $[M+H]^+$, found: 383.0760.



5,5-Dimethyl-7-(4-(trifluoromethyl)phenyl)-1,2-dihydro-3*H*,5*H*-benzo[*c*]pyrazolo[1,2-*a*][1,2]diazepin-3-on

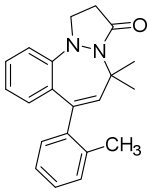
e (3t)

White solid (90.4 mg, 81%), mp 126.4-127.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.68 (s, 6H), 2.78 (t, J = 7.2 Hz, 2H), 4.12 (t, J = 7.2 Hz, 2H), 5.99 (s, 1H), 6.93 (d, J = 7.6 Hz, 1H), 7.05-7.09 (m, 1H), 7.27-7.32 (m, 4H), 7.57 (d, J = 8.0 Hz, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 26.8, 33.2,49.1, 63.3, 116.4, 124.2 (q, $^{1}J_{C\text{-}F}$ = 270.8 Hz), 124.6, 125.1 (q, $^{3}J_{C\text{-}F}$ = 3.6 Hz), 128.2, 129.5 (q, $^{2}J_{C\text{-}F}$ = 31.8 Hz), 129.6, 131.8, 131.9, 135.3, 141.1, 148.0, 149.7, 173.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.40 (s). HRMS calcd for $C_{21}H_{20}F_3N_2O$: 373.1522 $[M+H]^+$, found: 373.1527.



5,5-Dimethyl-7-(4-nitrophenyl)-1,2-dihydro-3*H*,5*H*-benzo[*c*]pyrazolo[1,2-*a*][1,2]diazepin-3-one(3u)

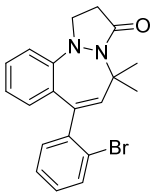
Light yellow solid (68.1 mg, 65%), mp 168.6-170.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.70 (s, 6H), 2.79 (t, J = 7.2 Hz, 2H), 4.12 (t, J = 7.6 Hz, 2H), 6.03 (s, 1H), 6.89-6.91 (m, 1H), 7.07-7.11 (m, 1H), 7.29-7.32 (m, 2H), 7.34-7.31 (m, 2H), 8.16-8.19 (m, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 26.7, 33.2, 49.1, 63.4, 116.5, 123.5, 124.7, 128.5, 130.0, 131.4, 131.8, 134.7, 141.9, 147.1, 149.8, 151.0, 173.8. HRMS calcd for $C_{20}H_{20}N_3O_3$: 350.1499 $[M+H]^+$, found: 350.1497.



5,5-Dimethyl-7-(*o*-tolyl)-1,2-dihydro-3*H*,5*H*-benzo[*c*]pyrazolo[1,2-*a*][1,2]diazepin-3-one (3v)

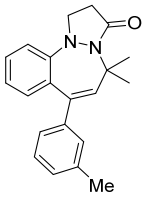
White solid (85.9 mg, 90%), mp 132.8-134.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.69(s, 6H), 1.96 (s, 3H), 2.76 (brs, 2H), 4.11 (t, J = 7.2 Hz, 2H), 5.74 (s, 1H), 6.79 (d, J = 8.0 Hz, 1H), 6.94-6.98 (m, 1H), 7.13-7.16 (m, 2H), 7.17-7.24 (m, 4H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 19.7, 26.9, 33.4, 49.2, 63.8, 115.9, 124.4, 125.7, 127.38, 127.40, 130.1, 130.2, 131.1, 132.3, 135.0, 136.5, 140.4, 144.0, 148.9, 174.6. HRMS calcd for $C_{21}H_{23}N_2O$:

319.1805 $[M+H]^+$, found: 319.1808.



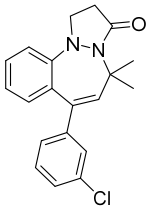
7-(2-Bromophenyl)-5,5-dimethyl-1,2-dihydro-3*H*,5*H*-benzo[*c*]pyrazolo[1,2-*a*][1,2]diazepin-3-one (3w)

White solid (99.7 mg, 87%), mp 177.4-179.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.71 (s, 6H), 2.77 (t, *J* = 7.2 Hz, 2H), 4.13 (t, *J* = 7.2 Hz, 2H), 5.75 (s, 1H), 6.77 (d, *J* = 7.6 Hz, 1H), 6.98-7.02 (m, 1H), 7.16-7.31 (m, 5H), 7.59 (d, *J* = 8.0 Hz, 1H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 26.8, 33.2, 49.0, 63.2, 116.4, 124.6, 127.46, 127.50, 128.1, 129.3, 129.4, 131.9, 132.0, 134.0, 135.3, 140.6, 146.2, 149.6, 173.7. HRMS calcd for $C_{20}H_{20}BrN_2O$: 383.0754 $[M+H]^+$, found: 383.0757.



5,5-Dimethyl-7-(*m*-tolyl)-1,2-dihydro-3*H*,5*H*-benzo[*c*]pyrazolo[1,2-*a*][1,2]diazepin-3-one (3x)

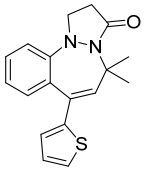
White solid (78.3 mg, 82%), mp 131.1-132.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.67 (s, 6H), 2.33 (s, 3H), 2.77 (t, *J* = 7.6 Hz, 2H), 4.10 (t, *J* = 7.2 Hz, 2H), 5.98 (s, 1H), 6.98-7.02 (m, 3H), 7.04-7.08 (m, 1H), 7.11 (d, *J* = 7.6 Hz, 1H), 7.20 (t, *J* = 7.2 Hz, 1H), 7.25-7.26 (m, 2H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 21.4, 26.9, 33.3, 49.0, 63.0, 116.3, 124.4, 126.4, 127.8, 128.0, 128.1, 129.9, 132.2, 132.7, 136.5, 137.7, 139.7, 144.4, 149.5, 173.5. HRMS calcd for $C_{21}H_{23}N_2O$: 319.1805 $[M+H]^+$, found: 319.1807.



7-(3-Chlorophenyl)-5,5-dimethyl-1,2-dihydro-3*H*,5*H*-benzo[*c*]pyrazolo[1,2-*a*][1,2]diazepin-3-one (3y)

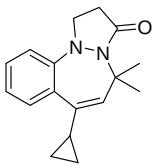
Light yellow solid (74.1 mg, 73%), mp 143.0-144.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.69 (s, 6H), 2.77 (t, *J* =

7.2 Hz, 2H), 4.10 (t, *J* = 7.2 Hz, 2H), 5.97 (s, 1H), 6.98 (d, *J* = 8.0 Hz, 1H), 7.06-7.10 (m, 2H), 7.20 (s, 1H), 7.22-7.28 (m, 4H). $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$) δ 26.8, 33.2, 49.0, 63.2, 116.4, 124.6, 127.46, 127.50, 128.1, 129.3, 129.4, 131.9, 132.0, 134.0, 135.3, 140.6, 146.2, 149.6, 173.7. HRMS calcd for $C_{20}H_{20}ClN_2O$: 339.1259 $[M+H]^+$, found: 339.1258.



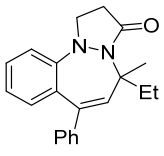
5,5-Dimethyl-7-(thiophen-2-yl)-1,2-dihydro-3*H*,5*H*-benzo[*c*]pyrazolo[1,2-*a*][1,2]diazepin-3-one (3z)

White solid (76.3 mg, 82%), mp 174.0-176.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.64 (s, 6H), 2.76 (t, *J* = 7.2 Hz, 2H), 4.07 (t, *J* = 7.2 Hz, 2H), 6.26 (s, 1H), 6.86 (d, *J* = 3.6 Hz, 1H), 6.97 (t, *J* = 4.0 Hz, 1H), 7.14 (t, *J* = 7.6 Hz, 1H), 7.22 (d, *J* = 5.2 Hz, 1H), 7.25-7.32 (m, 2H), 7.37 (d, *J* = 8.0 Hz, 1H). $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$) δ 26.7, 33.2, 48.8, 62.3, 116.6, 124.7, 124.9, 126.7, 127.0, 128.4, 130.3, 131.7, 132.2, 139.4, 146.7, 149.2, 172.8. HRMS calcd for $C_{18}H_{19}N_2OS$: 311.1213 $[M+H]^+$, found: 311.1218.



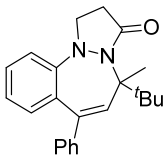
7-Cyclopropyl-5,5-dimethyl-1,2-dihydro-3*H*,5*H*-benzo[*c*]pyrazolo[1,2-*a*][1,2]diazepin-3-one (3aa)

White solid (70.8 mg, 88%), mp 179.0-180.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.61 (q, *J* = 5.2 Hz, 2H), 0.82-0.87 (m, 2H), 1.54 (s, 6H), 1.58-1.62 (m, 1H), 2.73 (t, *J* = 7.2 Hz, 2H), 4.04 (t, *J* = 7.2 Hz, 2H), 5.66 (s, 1H), 7.18-7.26 (m, 3H), 7.90 (d, *J* = 7.6 Hz, 1H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 7.0, 19.2, 27.0, 33.3, 49.0, 62.7, 116.1, 124.6, 127.4, 128.9, 133.5, 134.3, 135.9, 148.4, 173.6. HRMS calcd for $C_{17}H_{21}N_2O$: 269.1648 $[M+H]^+$, found: 269.1649.



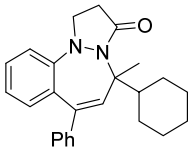
5-Ethyl-5-methyl-7-phenyl-1,2-dihydro-3*H*,5*H*-benzo[*c*]pyrazolo[1,2-*a*][1,2]diazepin-3-one (3bb)

White solid (77.3 mg, 81%), mp 123.5-124.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.86 (t, *J* = 7.2 Hz, 3H), 1.60 (s, 3H), 1.63-1.72 (m, 1H), 2.53-2.62 (m, 1H), 2.68-2.75 (m, 1H), 2.83-2.91 (m, 1H), 4.03-4.10 (m, 1H), 4.14-4.21 (m, 1H), 5.92 (s, 1H), 7.01 (d, *J* = 7.6 Hz, 1H), 7.04-7.08 (m, 1H), 7.19-7.23 (m, 2H), 7.26-7.27 (m, 2H), 7.30-7.34 (m, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 9.0, 26.3, 32.0, 33.3, 48.7, 66.7, 116.4, 124.5, 127.4, 127.8, 128.1, 129.2, 132.0, 133.0, 138.2, 144.4, 149.4, 172.8. HRMS calcd for $C_{21}H_{23}N_2O$: 319.1805 $[M+H]^+$, found: 319.1803.



5-(*tert*-Butyl)-5-methyl-7-phenyl-1,2-dihydro-3*H*,5*H*-benzo[*c*]pyrazolo[1,2-*a*][1,2]diazepin-3-one (3cc)

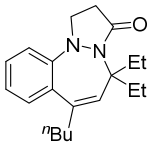
White solid (69.6 mg, 67%), mp 176.2-171.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.16 (s, 9H), 1.74 (s, 3H), 2.49 (dd, J_1 = 16.4 Hz, J_2= 6.4 Hz, 1H), 3.12-3.21 (m, 1H), 4.01 (td, J_1 = 13.6 Hz, J_2 = 6.8 Hz, 1H), 4.22 (dd, J_1 = 12.8 Hz, J_2 = 6.8 Hz, 1H), 6.19 (s, 1H), 6.95 (d, *J* = 7.6 Hz, 1H), 6.97-7.01 (m, 1H), 7.19-7.21 (m, 4H), 7.28-7.35 (m, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 23.1, 27.8, 33.9, 42.7, 47.5, 72.1,115.8, 124.0, 127.1, 127.2, 128.1, 129.5, 131.8, 132.7, 135.9, 137.1, 145.6, 150.1, 174.9. HRMS calcd for $C_{23}H_{27}N_2O$: 347.2118 $[M+H]^+$, found: 347.2114.



5-Cyclohexyl-5-methyl-7-phenyl-1,2-dihydro-3*H*,5*H*-benzo[*c*]pyrazolo[1,2-*a*][1,2]diazepin-3-one (3dd)

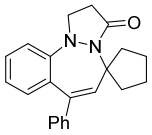
White solid (79.3 mg, 71%), mp 191.5-193.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.92-1.01 (m, 1H), 1.07-1.32 (m, 4H), 1.50-1.53 (m, 1H), 1.61-1.64 (m, 5H), 1.79-1.82 (m, 1H),1.89-1.92 (m, 1H), 2.62-2.73 (m, 2H), 2.85-2.93 (m, 1H), 4.02-4.10 (m, 1H), 4.14-4.21 (m. 1H), 6.05 (s, 1H), 7.00 (d, *J* = 7.6Hz, 1H), 7.04-7.08 (m, 1H), 7.19-7.22 (m, 2H), 7.25-7.27 (m, 2H), 7.31-7.34 (m, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 24.5, 26.3, 26.6,

26.8, 28.0, 28.7, 33.5, 45.4, 48.7, 69.6, 116.5, 124.6, 127.4, 127.7, 128.1, 129.2, 131.9, 133.3, 135.8, 138.0, 144.8, 149.2, 172.5. HRMS calcd for $C_{25}H_{29}N_2O$: 373.2274 $[M+H]^+$, found: 373.2275.



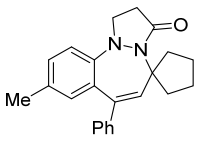
7-Butyl-5,5-diethyl-1,2-dihydro-3*H*,5*H*-benzo[*c*]pyrazolo[1,2-*a*][1,2]diazepin-3-one (3ee)

Yellow solid (77.7 mg, 83%), mp 95.2-96.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.78 (t, *J* = 7.6 Hz, 6H), 0.88 (t, *J* = 7.2 Hz, 3H), 1.26-1.33 (m, 2H), 1.35-1.43 (m, 2H), 1.50-1.59 (m, 2H), 2.30-2.39 (m, 2H), 2.52 (t,*J* = 6.8 Hz, 2H), 2.76 (t, *J* = 7.2 Hz, 2H), 4.05 (t, *J* = 7.2 Hz, 2H), 5.58 (s, 1H), 7.14-7.21 (m, 3H), 7.42 (d, *J* = 7.6 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 8.8, 13.9, 22.3, 31.4, 31.7, 33.3, 38.5, 48.0, 69.5, 117.0, 124.9, 127.1, 128.0, 133.6, 134.2, 136.7, 148.6, 171.8. HRMS calcd for $C_{20}H_{29}N_2O$: 313.2274 $[M+H]^+$, found: 313.2271.



7-Phenyl-1,2-dihydro-3*H*-spiro[benzo[*c*]pyrazolo[1,2-*a*][1,2]diazepine-5,1'-cyclopentan]-3-one (5a)

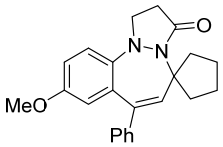
White solid (67.4 mg, 68%), mp 156.0-157.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.70-1.77(m, 2H), 1.82-1.97 (m, 4H), 2.59-2.66 (m, 2H), 2.78 (t, *J* = 7.2 Hz, 2H),4.07 (t, *J* = 7.2 Hz, 2H), 6.15 (s, 1H), 7.00-7.02 (m, 1H), 7.04-7.08 (m, 1H), 7.18-7.21 (m, 2H), 7.24-7.27 (m, 2H), 7.28-7.34 (m, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 24.7, 33.5, 38.2, 48.5, 71.9, 116.8, 124.5, 127.4, 128.0, 128.2, 129.2, 131.9, 133.2, 137.1, 139.4, 144.1, 149.5, 172.3. HRMS calcd for $C_{22}H_{23}N_2O$: 331.1805 $[M+H]^+$, found: 331.1803.



9-Methyl-7-phenyl-1,2-dihydro-3*H*-spiro[benzo[*c*]pyrazolo[1,2-*a*][1,2]diazepine-5,1'-cyclopentan]-3-one (5b)

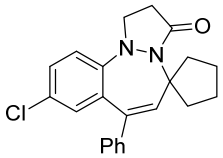
White solid (64.0 mg, 62%), mp 156.8-157.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.69-1.75 (m, 2H), 1.79-1.85 (m,

2H), 1.89-1.94 (m, 2H), 2.21 (s, 3H), 2.58-2.65(m, 2H), 2.78 (t, J = 7.2 Hz, 2H), 4.04 (t, J = 7.2 Hz, 2H), 6.15 (s, 1H), 6.82 (d, J = 1.6 Hz, 1H), 7.06-7.09 (m, 1H), 7.15 (d, J = 8.4 Hz, 1H), 7.19-7.21 (m, 2H), 7.29-7.34 (m, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 20.8, 24.6, 33.6, 38.1, 48.4, 71.4, 116.8, 127.4, 128.1, 128.7, 129.1, 132.1, 133.3, 134.1, 137.5, 139.3, 144.0, 147.2, 171.9. HRMS calcd for $C_{23}H_{25}N_2O$: 345.1961 $[M+H]^+$, found: 345.1962.



9-Methyl-7-phenyl-1,2-dihydro-3*H*-spiro[benzo[*c*]pyrazolo[1,2-*a*][1,2]diazepine-5,1'-cyclopentan]-3-one (5c)

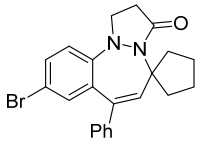
White solid (64.8 mg, 60%), mp 158.4-159.9 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 1.68-1.74 (m, 2H), 1.78-1.83 (m, 2H), 1.90-1.95 (m, 2H), 2.58-2.65 (m, 2H), 2.78 (t, J = 7.2 Hz, 2H), 3.65 (s, 3H), 4.02 (t, J = 7.2 Hz, 2H), 6.18 (s, 1H), 6.55 (d, J = 3.2 Hz, 1H), 6.81 (dd, J_1 = 8.4 Hz, J_2 = 2.8 Hz, 2H), 7.17-7.20 (m, 2H), 7.21-7.23 (m, 2H), 7.28-7.33 (m, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 24.6, 33.6, 38.0, 48.4, 72.0, 113.4, 116.7, 177.9, 127.5, 128.2, 129.1, 134.8, 137.5, 139.6, 143.1, 143.5, 156.4, 171.7. HRMS calcd for $C_{23}H_{25}N_2O_2$: 361.1911 $[M+H]^+$, found: 361.1909.



9-Chloro-7-phenyl-1,2-dihydro-3*H*-spiro[benzo[*c*]pyrazolo[1,2-*a*][1,2]diazepine-5,1'-cyclopentan]-3-one (5d)

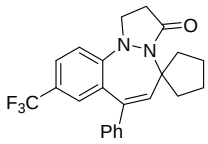
Brown syrup (71.0 mg, 65%). ^1H NMR (400 MHz, $CDCl_3$) δ: 1.71-1.76 (m, 2H), 1.82-1.97 (m, 2H), 2.58-2.64 (m, 2H), 2.76 (t, J = 7.2 Hz, 2H), 4.03 (t, J = 7.2 Hz, 2H), 6.15 (s, 1H), 6.98 (d, J = 2.4 Hz, 1H), 7.16-7.24 (m, 4H), 7.30-7.36 (m, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 24.8, 33.2, 38.3, 48.8, 72.2, 118.0, 127.67, 127.73, 128.4, 129.2, 129.9, 131.5, 134.8, 135.8, 140.7, 143.5, 148.2, 172.4. HRMS calcd for $C_{22}H_{22}ClN_2O$: 365.1415

$[M+H]^+$, found: 365.1411.



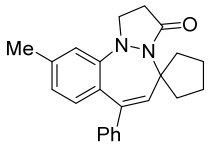
9-Bromo-7-phenyl-1,2-dihydro-3*H*-spiro[benzo[*c*]pyrazolo[1,2-*a*][1,2]diazepine-5,1'-cyclopentan]-3-one (5e)

White solid (77.1 mg, 63%), mp 186.2-187.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.70-1.76 (m, 2H), 1.82-1.95 (m, 4H), 2.58-2.65 (m, 2H), 2.76 (t, *J* = 7.2 Hz, 2H), 4.03 (t, *J* = 7.2 Hz, 2H), 6.15(s, 1H), 7.11-7.13 (m, 2H), 7.17-7.19 (m, 2H), 7.31-7.38 (m, 4H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 24.8, 33.3, 38.3, 48.7, 72.2, 117.6, 118.3, 127.7, 128.4, 129.1, 130.7, 134.4, 135.2, 135.7, 140.8, 143.5, 148.7, 172.4. HRMS calcd for $C_{22}H_{22}BrN_2O$: 409.0910 $[M+H]^+$, found: 409.0906.



7-Phenyl-9-(trifluoromethyl)-1,2-dihydro-3*H*-spiro[benzo[*c*]pyrazolo[1,2-*a*][1,2]diazepine-5,1'-cyclopentan]-3-one (5f)

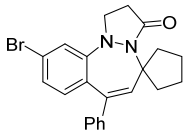
White solid (72.9 mg, 61%), mp 171.0-172.7 °C.^{1}H NMR (400 MHz, $CDCl_3$) δ 1.71-1.80 (m, 2H), 1.88-1.99 (m, 4H), 2.59-2.66 (m, 2H), 2.77 (t, *J* = 7.2 Hz, 2H), 4.10 (t, *J* = 7.2 Hz, 2H), 6.17(s, 1H), 7.15-7.19 (m, 2H), 7.26-7.27 (m, 1H), 7.31-7.37 (m, 4H), 7.51 (dd, J_1 = 8.4 Hz, J_2 = 1.6 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 24.9, 33.2, 38.5, 49.0, 72.8, 116.7, 123.9 (q, $^1J_{C\text{-}F}$ = 270.1 Hz), 124.6 (q, $^3J_{C\text{-}F}$ = 3.6 Hz), 126.4 (q, $^2J_{C\text{-}F}$ = 32.5 Hz), 127.8, 128.4, 129.1, 129.2 (q, $^3J_{C\text{-}F}$ = 4.4 Hz), 133.2, 135.4, 141.0, 143.6, 152.5, 172.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.40 (s). HRMS calcd for $C_{23}H_{22}F_3N_2O$: 399.1679$[M+H]^+$, found: 399.1671.



10-Methyl-7-phenyl-1,2-dihydro-3*H*-spiro[benzo[*c*]pyrazolo[1,2-*a*][1,2]diazepine-5,1'-cyclopentan]-3-one

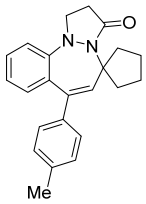
(5g)

White solid (74.3 mg, 72%), mp 146.3-147.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.70-1.75 (m, 2H), 1.80-1.96 (m, 4H), 2.39 (s, 3H), 2.58-2.65 (m, 2H), 2.78 (t, *J* = 7.2 Hz, 2H), 4.06 (t, *J* = 7.2 Hz, 2H), 6.11 (s, 1H), 6.86-6.91 (m, 2H), 7.04 (s, 1H), 7.18-7.20 (m, 2H), 7.26-7.33 (m, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 20.8, 24.6, 33.6, 38.1, 48.4, 71.4, 116.8, 127.4, 128.1, 128.7, 129.1, 132.1, 133.3, 134.1, 137.5, 139.3, 144.0, 147.2, 171.9. HRMS calcd for $C_{23}H_{25}N_2O$: 345.1961 $[M+H]^+$, found: 345.1958.



10-Bromo-7-phenyl-1,2-dihydro-3*H*-spiro[benzo[*c*]pyrazolo[1,2-*a*][1,2]diazepine-5,1'-cyclopentan]-3-one (5h)

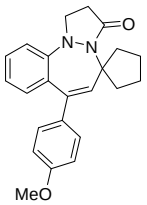
White solid (85.7 mg, 70%), mp 131.3-133.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.71-1.77 (m, 2H), 1.83-1.97 (m, 4H), 2.58-2.65 (m, 2H),2.78 (t, *J* = 7.2 Hz, 2H), 4.04 (t, *J* = 7.2 Hz, 2H), 6.12 (s, 1H), 6.87 (d, *J* = 8.4 Hz, 1H), 7.15-7.19 (m, 3H), 7.29-7.34 (m, 3H), 7.36 (d, *J* = 2.0 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 24.8, 33.2, 38.3, 48.8, 72.4, 120.0, 121.2, 127.5, 127.6, 128.3, 129.2, 132.0, 133.3, 135.9, 140.0, 143.8, 150.8, 172.5. HRMS calcd for $C_{22}H_{22}BrN_2O$: 409.0910 $[M+H]^+$, found: 409.0904.



7-(*p*-Tolyl)-1,2-dihydro-3*H*-spiro[benzo[*c*]pyrazolo[1,2-*a*][1,2]diazepine-5,1'-cyclopentan]-3-one (5i)

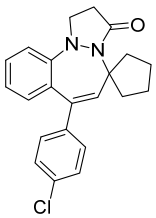
White solid (77.4 mg, 75%), mp 124.2-126.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.68-1.75 (m, 2H), 1.80-1.94 (m, 4H), 2.36 (s, 3H), 2.58-2.65 (m, 2H), 2.78 (t, *J* = 7.2 Hz, 2H), 4.07 (t, *J* = 7.2 Hz, 2H), 6.13 (s, 1H), 7.02-7.13 (m, 6H), 7.23-7.27 (m, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 21.2, 24.7, 33.5, 38.2, 48.5, 71.8, 116.8, 124.5, 128.0, 128.9, 129.0, 131.9, 133.4, 137.0, 137.1, 138.9, 141.2, 149.5, 172.2. HRMS calcd for $C_{23}H_{25}N_2O$:

345.1961 $[M+H]^+$, found: 345.1957.



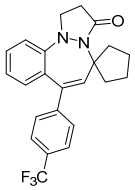
7-(4-Methoxyphenyl)-1,2-dihydro-3*H*-spiro[benzo[*c*]pyrazolo[1,2-*a*][1,2]diazepine-5,1'-cyclopentan]-3-one (5j)

White solid (65.9 mg, 61%), mp 139.1-140.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.68-1.75 (m, 2H), 1.79-1.84 (m, 2H), 1.87-1.96 (m, 2H), 2.58-2.65 (m, 2H), 2.78 (t, J = 7.2 Hz, 2H), 3.82 (s, 3H), 4.07 (t, J = 7.2 Hz, 2H), 6.14 (s, 1H), 6.83-6.86 (m, 2H), 7.03-7.14 (m, 4H), 7.24-7.29 (m, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 24.6, 33.5, 38.1, 48.4, 55.3, 71.5, 113.5, 116.9, 124.6, 128.0, 130.2, 131.8, 133.6, 136.5, 136.9, 138.4, 149.5, 159.1,172.0. HRMS calcd for $C_{23}H_{25}N_2O_2$: 361.1911 $[M+H]^+$, found: 361.1911.



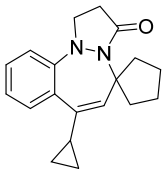
7-(4-Chlorophenyl)-1,2-dihydro-3*H*-spiro[benzo[*c*]pyrazolo[1,2-*a*][1,2]diazepine-5,1'-cyclopentan]-3-one (5k)

White solid (71.2 mg, 65%), mp 152.6-154.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.68-1.75 (m, 2H), 1.81-1.86 (m, 2H), 1.89-1.97 (m, 2H), 2.58-2.65 (m, 2H), 2.78 (t,J = 7.2 Hz, 2H), 4.07 (t, J = 7.2 Hz, 2H), 6.12 (s, 1H), 6.98 (dd, J_1 = 8.0 Hz, J_2 = 1.2 Hz, 1H), 7.07 (td, J_1 = 8.0 Hz, J_2 = 1.6 Hz, 1H), 7.11-7.14 (m, 2H), 7.24-7.29 (m, 4H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 24.8, 33.4, 38.2, 48.5, 72.0, 116.8, 124.6, 128.2, 128.4, 130.5, 131.8, 132.8, 133.3, 136.0, 139.7, 142.6, 149.6, 172.4. HRMS calcd for $C_{22}H_{22}ClN_2O$: 365.1415 $[M+H]^+$, found: 365.1416.



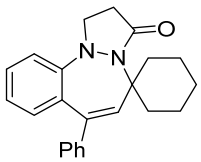
7-(4-(Trifluoromethyl)phenyl)-1,2-dihydro-3*H*-spiro[benzo[*c*]pyrazolo[1,2-*a*][1,2]diazepine-5,1'-cyclopentan]-3-one (5l)

White solid (75.3 mg, 63%), mp 143.9-145.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.71-1.78 (m, 2H), 1.84-1.99 (m, 4H), 2.60-2.67 (m, 2H), 2.79 (t, *J* = 7.2 Hz, 2H), 4.08 (t, *J* = 7.2 Hz, 2H), 6.13 (s, 1H), 6.93-6.95 (m, 1H), 7.05-7.09 (m, 1H), 7.25-7.32 (m, 4H), 7.57 (d, *J* = 8.0 Hz, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 24.8, 33.4, 38.3, 48.7, 72.3, 116.8, 124.2 (q, $^{1}J_{C\text{-}F}$ = 270.1 Hz), 124.6, 125.2 (q, $^{3}J_{C\text{-}F}$ = 3.7 Hz), 128.3, 129.45 (q, $^{2}J_{C\text{-}F}$ = 31.8 Hz), 129.49, 131.8, 132.3, 135.7, 140.7, 147.8, 149.7, 172.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.22 (s). HRMS calcd for $C_{23}H_{22}F_3N_2O$: 399.1679 $[M+H]^+$, found: 399.1674.



7-Cyclopropyl-1,2-dihydro-3*H*-spiro[benzo[*c*]pyrazolo[1,2-*a*][1,2]diazepine-5,1'-cyclopentan]-3-one (5m)

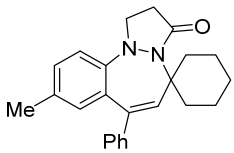
White solid (63.5 mg, 72%), mp 183.6-184.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.59-0.63 (m, 2H), 0.82-0.87 (m, 2H), 1.58-1.74 (m, 5H), 1.81-1.90 (m, 2H), 2.49-2.56 (m, 2H), 2.73 (t, *J* = 7.2 Hz, 2H), 4.01 (t, *J* = 7.2 Hz, 2H), 5.79 (d, *J* = 0.8 Hz, 1H), 7.16-7.18 (m, 1H), 7.20-7.28 (m, 2H), 7.88 (dd, J_1 = 7.6 Hz, J_2 = 1.6 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 7.1, 19.0, 24.7, 33.5, 38.3, 48.6, 71.7, 116.5, 124.6, 127.5, 128.8, 134.0, 134.9, 135.3, 148.4, 172.4. HRMS calcd for $C_{19}H_{23}N_2O$: 295.1805$[M+H]^+$, found: 295.1804.



7-Phenyl-1,2-dihydro-3*H*-spiro[benzo[*c*]pyrazolo[1,2-*a*][1,2]diazepine-5,1'-cyclohexan]-3-one (7a)

White solid (89.8 mg, 87%), mp 162.7-164.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.31-1.40 (m, 1H), 1.56-1.74 (m,

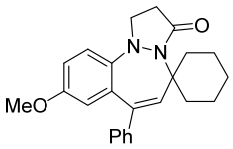
7H), 2.63-2.70 (m, 2H), 2.80 (t, J = 7.2 Hz, 2H), 4.04 (t, J = 7.2 Hz, 2H), 6.62 (s, 1H), 7.04 (d, J = 7.2 Hz, 1H), 7.08-7.12 (m, 1H), 7.20-7.22 (m, 2H), 7.28-7.34 (m, 5H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 23.6, 24.8, 33.5, 34.1, 48.6, 64.8, 120.6, 121.4, 127.8, 128.0, 128.3, 129.0, 132.8, 132.9, 136.1, 137.6, 143.7, 150.7, 171.3. HRMS calcd for $C_{23}H_{25}N_2O$: 345.1961 $[M+H]^+$, found: 345.1952.



9-Methyl-7-phenyl-1,2-dihydro-3*H*-spiro[benzo[*c*]pyrazolo[1,2-*a*][1,2]diazepine-5,1'-cyclohexan]-3-one

(7b)

White solid (91.3 mg, 85%), mp 181.4-183.0 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 1.30-1.36 (m, 1H), 1.55-1.73 (m, 7H), 2.23 (s, 3H), 2.62-2.68 (m, 2H), 2.79 (t, J = 7.6 Hz, 2H), 4.01(t, J = 7.6 Hz, 2H), 6.59 (s,1H), 6.85 (d, J = 1.6 Hz, 1H), 7.09 (dd, J_1 = 8.0 Hz, J_2 = 1.6 Hz, 1H), 7.18 (d, J = 8.4 Hz, 1H), 7.21-7.24 (m, 2H), 7.30-7.35 (m, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 20.8, 23.7, 24.8, 33.8, 33.9, 48.3, 64.0, 117.1, 127.6, 128.2, 129.0, 131.7, 134.0, 134.5, 135.3, 138.9, 144.0, 147.1, 170.8. HRMS calcd for $C_{24}H_{27}N_2O$: 359.2118 $[M+H]^+$, found: 359.2114.

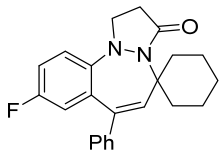


9-Methoxy-7-phenyl-1,2-dihydro-3*H*-spiro[benzo[*c*]pyrazolo[1,2-*a*][1,2]diazepine-5,1'-cyclohexan]-3-one

(7c)

Light yellow solid (86.4 mg, 77%), mp 176.2-177.9 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 1.30-1.37 (m, 1H), 1.54-1.74 (m, 7H), 2.65 (td, J_1 = 12.4 Hz, J_2 = 3.6 Hz, 2H), 2.80 (t, J = 7.6 Hz, 2H), 3.67 (s, 3H), 3.99 (t, J = 7.6 Hz, 2H), 6.58 (d, J = 2.8 Hz, 1H), 6.61 (s, 1H), 6.83 (dd, J_1 = 8.4 Hz, J_2 = 2.8 Hz, 1H), 7.20-7.28 (m, 3H), 7.29-7.34 (m, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 23.7, 24.8, 33.8, 34.0, 48.4, 55.5, 63.9, 113.7, 116.2, 118.3, 127.7, 128.2, 129.0, 135.4, 135.6, 138.8, 143.0, 143.5, 156.6, 170.7. HRMS calcd for $C_{24}H_{27}N_2O_2$:

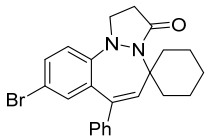
375.2067 $[M+H]^+$, found: 375.2055.



9-Fluoro-7-phenyl-1,2-dihydro-3*H*-spiro[benzo[*c*]pyrazolo[1,2-*a*][1,2]diazepine-5,1'-cyclohexan]-3-one

(7d)

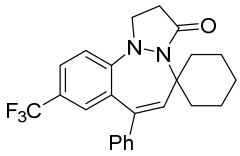
White solid (79.3 mg, 73%), mp 175.3-176.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.30-1.39 (m, 1H), 1.54-1.75 (m, 7H), 2.63-2.69 (m, 2H), 2.80 (t, J = 7.2 Hz, 2H), 4.01 (t, J = 7.2 Hz, 2H), 6.65 (s, 1H), 6.75 (dd, J_1 = 9.6 Hz, J_2 = 2.8 Hz, 1H), 6.96-7.01 (m, 1H), 7.20-7.26 (m, 3H), 7.31-7.36 (m, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 23.6, 24.8, 33.8, 34.0, 48.7, 64.4, 114.9 (d, $^2J_{C\text{-}F}$ = 22.4 Hz), 117.7 (d, $^2J_{C\text{-}F}$ = 22.4 Hz), 118.6 (d, $^3J_{C\text{-}F}$ = 8.7 Hz), 127.8, 128.4, 129.0, 136.0 (d, $^3J_{C\text{-}F}$ = 8.0 Hz), 136.5, 137.8 (d, $^4J_{C\text{-}F}$ = 2.1 Hz), 143.3, 145.7 (d, $^4J_{C\text{-}F}$ = 2.2 Hz), 159.7 (d, $^1J_{C\text{-}F}$ = 242.7 Hz), 171.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ -117.32 – -117.26 (m). HRMS calcd for $C_{23}H_{24}FN_2O$: 363.1867 $[M+H]^+$, found: 363.1861.



9-Bromo-7-phenyl-1,2-dihydro-3*H*-spiro[benzo[*c*]pyrazolo[1,2-*a*][1,2]diazepine-5,1'-cyclohexan]-3-one

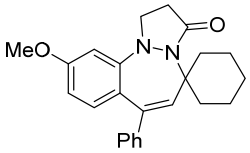
(7e)

Light yellow solid (95.0 mg, 75%), mp214.3-215.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.32-1.39 (m, 1H), 1.54-1.76 (m, 7H), 2.62-2.69 (m, 2H), 2.78 (t, J = 7.2 Hz, 2H), 4.00 (t, J = 7.2 Hz, 2H), 6.64 (s, 1H), 7.15-7.17 (m, 2H), 7.18-7.21 (m, 2H), 7.32-7.36 (m, 3H), 7.39 (dd, J_1 = 8.4 Hz, J_2 = 2.4 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 23.6, 24.8, 33.6, 34.0, 48.6, 64.6, 118.0, 118.9, 127.9, 128.4, 129.0, 131.0, 134.0, 136.0, 136.8, 137.4, 143.4, 148.6, 171.2. HRMS calcd for $C_{23}H_{24}BrN_2O$: 423.1067 $[M+H]^+$, found: 423.1066.



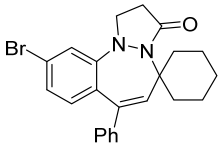
7-Phenyl-9-(trifluoromethyl)-1,2-dihydro-3*H*-spiro[benzo[*c*]pyrazolo[1,2-*a*][1,2]diazepine-5,1'-cyclohexan]-3-one (7f)

White solid (103.9 mg, 84%), mp 202.3-203.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.32-1.42 (m, 1H), 1.56-1.75 (m, 7H), 2.64-2.72 (m, 2H), 2.79 (t, J = 7.6 Hz, 2H), 4.07 (t, J = 7.6 Hz, 2H), 6.70 (s, 1H), 7.16-7.20 (m, 2H), 7.30-7.38 (m, 5H), 7.54 (dd, J_1 = 8.4 Hz, J_2 = 1.6 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 23.5, 24.8, 33.5, 34.2, 48.8, 65.1, 117.4, 123.9 (q, $^{1}J_{C\text{-}F}$ = 270.1 Hz), 125.0 (q, $^{3}J_{C\text{-}F}$ = 3.6 Hz), 126.9 (q, $^{1}J_{C\text{-}F}$ = 32.5 Hz), 128.0, 128.5, 128.7 (q, $^{3}J_{C\text{-}F}$ = 3.6 Hz), 129.0, 134.1, 137.2, 143.6, 152.3, 171.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.22 (s). HRMS calcd for $C_{24}H_{24}F_3N_2O$: 413.1835 $[M+H]^+$, found: 413.1829.



10-Methoxy-7-phenyl-1,2-dihydro-3*H*-spiro[benzo[*c*]pyrazolo[1,2-*a*][1,2]diazepine-5,1'-cyclohexan]-3-one (7g)

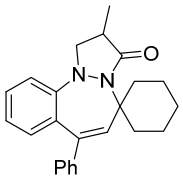
White solid (79.7 mg, 71%), mp 167.6-168.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.34-1.40 (m, 1H), 1.59-1.73 (m, 7H), 2.65 (td, J_1 = 13.2 Hz, J_2 = 4.0 Hz, 2H), 2.79 (t, J = 7.6 Hz, 2H), 3.84 (s, 3H),4.01 (t, J = 7.2 Hz, 2H), 6.49 (s, 1H), 6.65 (dd,J_1 = 8.8 Hz, J_2 = 2.4 Hz, 1H), 6.81 (d, J = 2.4 Hz, 1H), 6.96 (d, J = 8.4 Hz, 1H), 7.20-7.23 (m, 2H), 7.29-7.34 (m, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 23.6, 24.8, 33.6, 33.9, 48.5, 55.5, 64.4, 104.5, 109.1, 126.7, 127.5, 128.2, 129.0, 132.6, 133.7, 138.4, 144.2, 150.7, 159.4, 171.1. HRMS calcd for $C_{24}H_{27}N_2O_2$: 375.2067 $[M+H]^+$, found: 375.2060.



10-Bromo-7-phenyl-1,2-dihydro-3*H*-spiro[benzo[*c*]pyrazolo[1,2-*a*][1,2]diazepine-5,1'-cyclohexan]-3-one

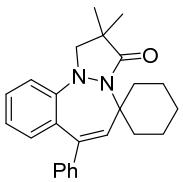
(7h)

White solid (103.8 mg, 82%), mp 157.8-159.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.33-1.39 (m, 1H), 1.54-1.75 (m, 7H), 2.66 (td, J_1 = 13.6 Hz, J_2 = 4.8 Hz, 2H), 2.79 (t, J = 7.2 Hz, 2H), 4.01 (t, J = 7.2 Hz, 2H), 6.62 (s, 1H), 6.91 (d, J = 8.4 Hz, 1H), 7.17-7.19 (m, 2H), 7.22 (dd, J_1 = 8.4 Hz, J_2 = 1.6 Hz, 1H), 7.31-7.34 (m, 3H), 7.40 (d, J = 1.6 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 23.6, 24.8, 33.5, 34.1, 48.6, 64.8, 120.6, 121.4, 127.8, 128.0, 128.3, 129.0, 132.8, 132.9, 136.1, 137.6, 143.7, 150.7, 171.3. HRMS calcd for $C_{23}H_{24}BrN_2O$: 423.1067 $[M+H]^+$, found: 423.1062.



2-Methyl-7-phenyl-1,2-dihydro-3*H*-spiro[benzo[*c*]pyrazolo[1,2-*a*][1,2]diazepine-5,1'-cyclohexan]-3-one (7i)

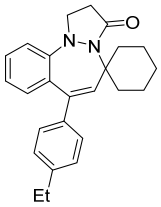
White solid (79.5 mg, 74%), mp 141.3-143.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.24 (d, J = 6.8 Hz, 3H), 1.32-1.82 (m, 7H), 1.97 (d, J = 12.8 Hz, 1H), 2.51 (td, J_1 = 13.2 Hz, J_2 = 4.8 Hz, 1H), 2.82 (td, J_1 = 13.2 Hz, J_2 = 4.4 Hz, 1H), 3.14-3.23 (m, 1H), 3.50 (t, J = 12.8 Hz, 1H), 4.27-4.32 (m, 1H), 6.61 (s, 1H), 7.02-7.10 (m, 2H), 7.20-7.22 (m, 2H), 7.25-7.33 (m, 5H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 13.8, 23.4, 23.8, 24.9, 33.2, 34.7, 37.4, 56.3, 64.5, 117.4, 124.7, 127.5, 128.1, 128.2, 129.1, 131,6, 133.9, 135.5, 138.5, 144.2, 149.5, 173.8. HRMS calcd for $C_{24}H_{27}N_2O$: 359.2118 $[M+H]^+$, found: 359.2118.



2,2-Dimethyl-7-phenyl-1,2-dihydro-3*H*-spiro[benzo[*c*]pyrazolo[1,2-*a*][1,2]diazepine-5,1'-cyclohexan]-3-one (7j)

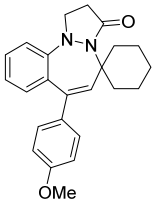
White solid (89.3 mg, 80%), mp 139.8-141.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.27 (s, 6H), 1.41-1.47 (m, 1H), 1.54-1.72 (m, 7H), 2.65-2.71 (m, 2H),3.92 (s, 2H), 6.43 (s, 1H), 6.89-6.97 (m, 2H),7.17-7.19 (m, 2H), 7.21-7.22

(m, 2H), 7.28-7.33 (m, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 23.1, 24.5, 25.2, 33.8, 42.8, 62.2, 63.3, 118.5, 122.7, 127.3, 127.9, 128.2, 129.0, 131.0, 132.4, 136.6, 139.6, 144.5, 150.5, 176.1. HRMS calcd for $C_{25}H_{29}N_2O$: 373.2274 $[M+H]^+$, found: 373.2269.



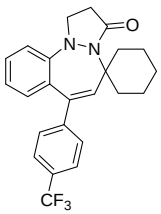
7-(4-Ethylphenyl)-1,2-dihydro-3*H*-spiro[benzo[*c*]pyrazolo[1,2-*a*][1,2]diazepine-5,1'-cyclohexan]-3-one (7k)

White solid (99.4 mg, 89%), mp 133.6-134.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.25 (t, *J* = 7.6 Hz, 3H), 1.32-1.37 (m, 1H), 1.58-1.72 (m, 7H), 2.62-2.69 (m, 4H), 2.80 (t, *J* = 7.2 Hz, 2H),4.04 (t, *J* = 7.6 Hz, 2H), 6.60 (s, 1H),7.06-7.16 (m, 6H), 7.27-7.29 (m, 2H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 15.6, 23.6, 24.8, 28.6, 33.8, 33.9, 48.4, 64.3, 117.2, 124.8, 127.7, 128.2, 129.0, 131.6, 134.2, 134.9, 138.5, 141.4, 143.7, 149.4, 171.1. HRMS calcd for $C_{25}H_{29}N_2O$: 373.2274 $[M+H]^+$, found: 373.2271.



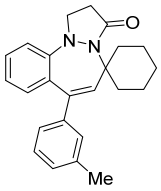
7-(4-Methoxyphenyl)-1,2-dihydro-3*H*-spiro[benzo[*c*]pyrazolo[1,2-*a*][1,2]diazepine-5,1'-cyclohexan]-3-one (7l)

Yellow syrup (86.6 mg, 77%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.32-1.38 (m, 1H), 1.54-1.73 (m, 7H), 2.62-2.68 (m, 2 H), 2.80 (t, *J* = 7.6 Hz, 2H), 3.81 (s, 3H), 4.03 (t, *J* = 7.6 Hz, 2H), 6.57 (s, 1H), 6.83-6.87 (m, 2H), 7.06-7.11 (m, 2H), 7.12-7.16 (m, 2H), 7.26-7.28 (m, 2H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 23.7, 24.8, 33.8, 33.9, 48.3, 55.3, 64.2, 113.6, 117.2, 124.9, 128.3, 130.1, 131.5, 134.2, 134.3, 136.5, 138.3, 149.4, 159.3, 171.0. HRMS calcd for $C_{24}H_{27}N_2O_2$: 375.2067 $[M+H]^+$, found: 375.2059.



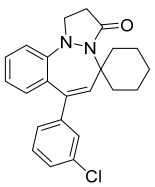
7-(4-(Trifluoromethyl)phenyl)-1,2-dihydro-3*H*-spiro[benzo[*c*]pyrazolo[1,2-*a*][1,2]diazepine-5,1'-cyclohexan]-3-one (7m)

Yellow solid (101.4 mg, 82%), mp 178.4-179.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.31-1.41 (m, 1H), 1.53-1.64 (m, 2H), 1.69-1.76 (m, 5H), 2.68 (td, J_1 = 13.2 Hz, J_2 = 4.4 Hz, 2H), 2.81 (t, J = 7.2 Hz, 2H), 4.05 (t, J = 7.2 Hz, 2H), 6.64 (s, 1H), 6.97-6.99 (m, 1H), 7.09-7.13 (m, 1H), 7.29-7.33 (m, 4H), 7.58 (d, J = 8.0 Hz, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 23.6, 24.8, 33.7, 33.9, 48.5, 64.6, 117.3, 124.2 (q, $^{1}J_{C\text{-}F}$ = 270.2 Hz), 125.0, 125.2 (q, $^{3}J_{C\text{-}F}$ = 3.6 Hz), 128.6, 129.3, 129.6 (q, $^{2}J_{C\text{-}F}$ = 32.5 Hz), 131.3, 133.2, 136.9, 137.4, 147.7, 149.5, 171.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.42 (s). HRMS calcd for $C_{24}H_{24}F_3N_2O$: 413.1835 $[M+H]^+$, found: 413.1833.



7-(*m*-Tolyl)-1,2-dihydro-3*H*-spiro[benzo[*c*]pyrazolo[1,2-*a*][1,2]diazepine-5,1'-cyclohexan]-3-one (7n)

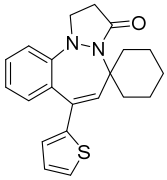
Light yellow solid (92.4 mg, 86%), mp 163.0-164.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.33-1.38 (m, 1H), 1.55-1.74 (m, 7H), 2.33(s, 3H), 2.62-2.70 (m, 2H), 2.80 (t, J = 7.2 Hz, 2H), 4.04 (t, J = 7.6Hz, 2H),6.59 (s, 1H), 6.99-7.05 (m, 3H), 7.08-7.12 (m, 2H), 7.21 (t, J = 7.2 Hz, 1H), 7.26-7.29 (m, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 21.5, 23.6, 24.8, 33.8, 33.9, 48.4, 64.3, 117.2, 124.9, 126.2, 128.1, 128.2, 128.3, 129.7, 131.6, 134.1, 135.2, 137.8, 138.7, 144.1, 149.4, 171.2. HRMS calcd for $C_{24}H_{27}N_2O$: 359.2118 $[M+H]^+$, found: 359.2114.



7-(3-Chlorophenyl)-1,2-dihydro-3*H*-spiro[benzo[*c*]pyrazolo[1,2-*a*][1,2]diazepine-5,1'-cyclohexan]-3-one

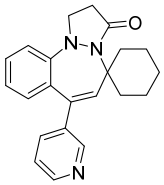
(7o)

White solid (99.8 mg, 88%), mp 157.8-159.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.33-1.40 (m, 1H), 1.53-1.63 (m, 2H), 1.68-1.75 (m, 5H), 2.63-2.69 (m, 2H), 2.80 (t, J = 7.6 Hz, 2H), 4.04 (t, J = 7.6 Hz, 2H), 6.60 (s, 1H),7.02 (d, J = 7.2 Hz, 1H), 7.08-7.14 (m, 2H), 7.18 (d, J = 1.6 Hz, 1H), 7.23-7.32 (m, 4H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 23.6, 24.8, 33.7, 33.9, 48.5, 64.4, 117.3, 125.0, 127.3, 127.7, 128.6, 129.0, 129.5, 131.4, 133.3, 134.1, 136.3, 137.4, 145.9, 149.5, 171.3. HRMS calcd for $C_{23}H_{24}ClN_2O$: 379.1572 $[M+H]^+$, found: 379.1572.



7-(Thiophen-2-yl)-1,2-dihydro-3*H*-spiro[benzo[*c*]pyrazolo[1,2-*a*][1,2]diazepine-5,1'-cyclohexan]-3-one (7p)

White solid (85.4 mg, 81%), mp 153.8-154.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.26-1.38 (m, 1H), 1.50-1.72 (m, 7H), 2.63 (td, J_1 = 12.4 Hz, J_2 = 4.0 Hz, 2H), 2.80 (t, J = 7.6 Hz, 2H), 4.02 (t, J = 7.6 Hz, 2H), 6.80 (s, 1H), 6.86 (dd, J_1 = 3.2 Hz, J_2 = 0.8 Hz,1H), 6.97 (dd, J_1 = 5.2 Hz, J_2 = 3.6 Hz, 1H), 7.16-7.20 (m, 1H), 7.23 (dd, J_1 = 5.2 Hz, J_2 = 1.2 Hz, 1H), 7.27-7.29 (m, 1H), 7.31-7.35 (m, 1H), 7.41 (dd, J_1 = 8.0 Hz, J_2 = 1.6 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 23.6, 24.7, 33.7, 33.8, 48.2, 64.0, 117.4, 125.0, 125.1, 126.6, 127.2, 128.8, 131.2, 132.1, 133.4, 134.8, 146.5, 149.1, 170.7. HRMS calcd for $C_{21}H_{23}N_2OS$: 351.1526 $[M+H]^+$, found: 351.1523.



7-(Pyridin-3-yl)-1,2-dihydro-3*H*-spiro[benzo[*c*]pyrazolo[1,2-*a*][1,2]diazepine-5,1'-cyclohexan]-3-one (7q)

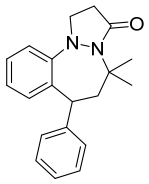
White solid (86.9 mg, 84%), mp 138.2-139.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.34-1.41 (m, 1H), 1.54-1.65 (m, 2H), 1.73-1.76 (m, 5H), 2.68 (td, J_1= 12.8 Hz, J_2 = 4.0 Hz, 2H), 2.81 (t, J = 7.6 Hz, 2H), 4.06 (t, J = 7.6 Hz, 2H), 6.65 (s, 1H), 7.00-7.01 (m, 1H), 7.10-7.14 (m, 1H), 7.23-7.28 (m, 1H), 7.31-7.33 (m, 2H), 7.47 (dt, J_1 = 8.0 Hz, J_2 = 2.0 Hz, 1H), 8.55-8.57 (m, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 23.6, 24.7, 33.7, 34.0, 48.6, 64.7, 117.3,

123.1, 125.1, 128.7, 131.1, 133.0, 135.3, 136.3, 136.9, 139.7, 148.8, 149.5, 149.8, 171.5. HRMS calcd for $C_{22}H_{24}N_3O$: 346.1914 $[M+H]^+$, found: 346.1908.

2. Structural elaborations of 3a

2.1. Synthesis of 8 from 3a

To a solution of **3a** (60.8 mg, 0.2 mmol) in MeOH/DCM (2 mL, 10/3) was added Pd/C (10 wt%, 10 mg). The mixture was stirred at room temperature under H_2 (balloon, 1 atm) for 24 h. Upon completion, it was filtered through a pad of celite and concentrated under reduced pressure. The residue was purified by silica gel chromatography using petroleum ether/ethyl acetate (3:1) as eluent to afford **8** (58.2 mg, 95%).



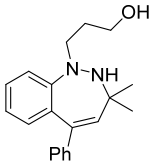
5,5-Dimethyl-7-phenyl-1,2,6,7-tetrahydro-3*H*,5*H*-benzo[*c*]pyrazolo[1,2-*a*][1,2]diazepin-3-one (8)

White solid (58.2 mg, 95%), mp 101.1-102.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.53 (s, 3H), 1.65 (s, 3H), 1.78 (dd, J_1 = 14.4 Hz, J_2 = 4.4 Hz, 1H), 2.42-2.49 (m, 1H), 2.83-2.95 (m, 2H), 3.78-3.86 (m, 1H), 4.12 (ddd, J_1 = 12.8 Hz, J_2 = 7.2 Hz, J_3 = 2.8 Hz, 1H), 4.42 (dd, J_1 = 12.4 Hz, J_2 = 4.0 Hz, 1H), 6.83 (d, J = 7.6 Hz, 1H), 6.89-6.92 (m, 1H), 7.07-7.11 (m, 2H), 7.14-7.21 (m, 3H), 7.27-7.30 (m, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 24.3, 27.2, 33.5, 46.9, 48.6, 48.7, 60.0, 116.4, 124.4, 126.3, 126.7, 128.3, 128.7, 132.6, 136.2, 147.7, 149.3, 173.4. HRMS calcd for $C_{20}H_{23}N_2O$: 307.1805 $[M+H]^+$, found: 307.1805.

2.2. Synthesis of 9 from 3a

To a solution of **3a** (60.8 mg, 0.2mmol) in THF (5 mL) was added $LiAlH_4$ (0.4 mL, 1M) at 0 °C. It was then stirred at room temperature for 2 h. Upon completion, it was quenched with water, concentrated and extracted with EtOAc. The combined organic layers were dried over anhydrous Na_2SO_4, and then concentrated under reduced pressure. The residue was purified by silica gel chromatography using petroleum ether/ethyl acetate (3:1)

as eluent to afford **9** (33.9 mg, 55%).



3-(3,3-Dimethyl-5-phenyl-2,3-dihydro-1*H*-benzo[*c*][1,2]diazepin-1-yl)propan-1-ol (9)

Yellowish syrup (33.9 mg, 55%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.35 (s, 6H), 1.95-2.01 (m, 2H), 3.61-3.64 (m, 4H), 3.80 (t, J = 5.6 Hz, 2H), 6.08 (s, 1H), 6.87 (td, J_1 = 7.2 Hz, J_2 = 0.8 Hz, 1H), 6.92 (dd,J_1 = 8.0 Hz, J_2 = 1.6 Hz, 1H), 7.04 (d, J = 7.6 Hz, 1H), 7.13-7.18 (m, 3H), 7.25-7.33 (m, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 27.8, 30.2, 54.4, 61.5, 62.8, 115.4, 122.3, 126.8, 127.2, 128.0, 129.5, 130.5, 133.3, 136.2, 143.6, 146.0, 151.8. HRMS calcd for $C_{20}H_{25}N_2O$: 309.1961 $[M+H]^+$, found: 309.1962.

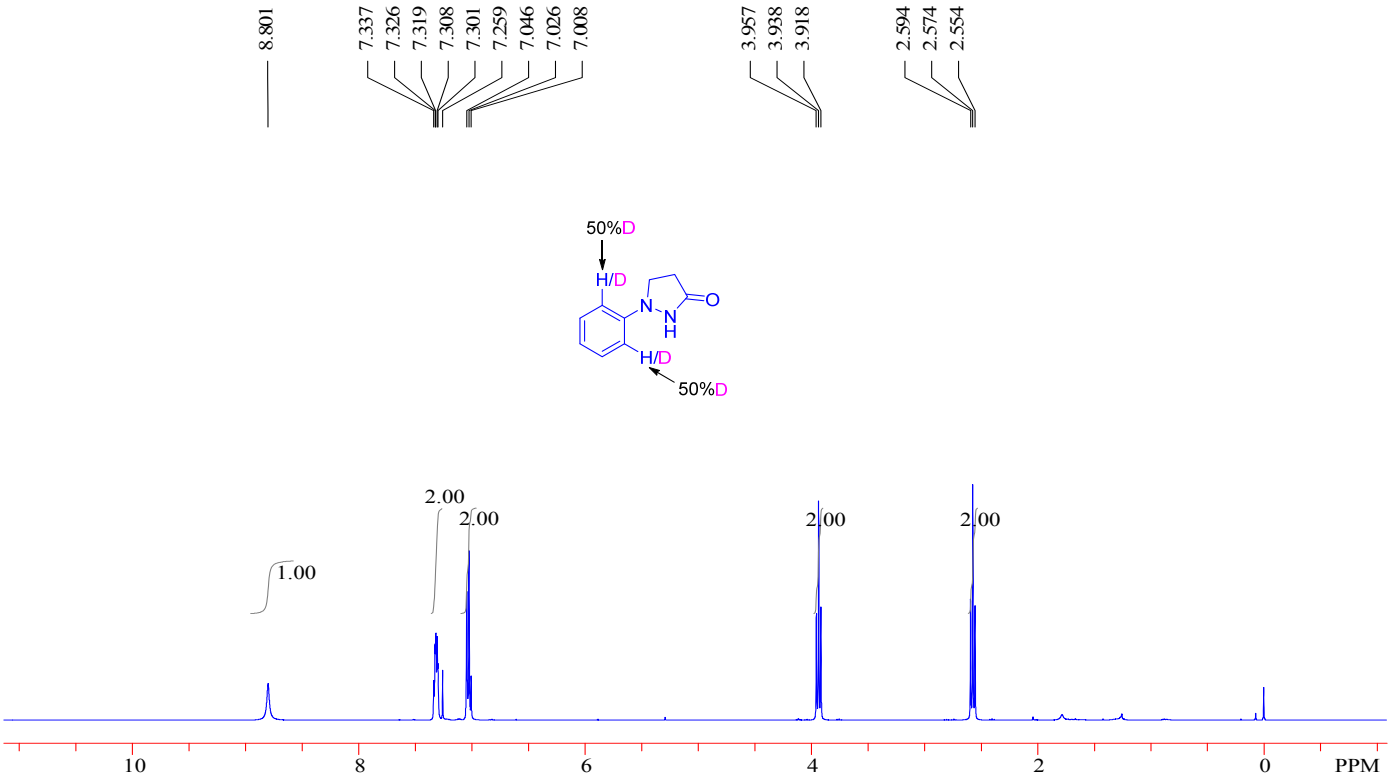
2.3. Gram-scale synthesis of 3a

To a reaction tube equipped with a stir bar were charged with 1-phenylpyrazolidin-3-one (**1a**, 814 mg, 5 mmol), toluene (20 mL), $[RhCp^*Cl_2]_2$ (31 mg, 0.05 mmol), $Zn(OAc)_2$ (460 mg, 2.5 mmol), NaOAc (205 mg, 2.5 mmol) and 2-methyl-4-phenylbut-3-yn-2-ol (**2a**, 801 mg, 5 mmol). The mixture was stirred at 100 °C (oil bath) for 10 h under air. Upon completion, it was cooled to room temperature, filtered through a pad of celite and concentrated under reduced pressure. The residue was purified by silica gel chromatography using petroleum ether/ethyl acetate (3:1) as eluent to afford **3a** (1.16 g, 76%).

III. Mechanism studies

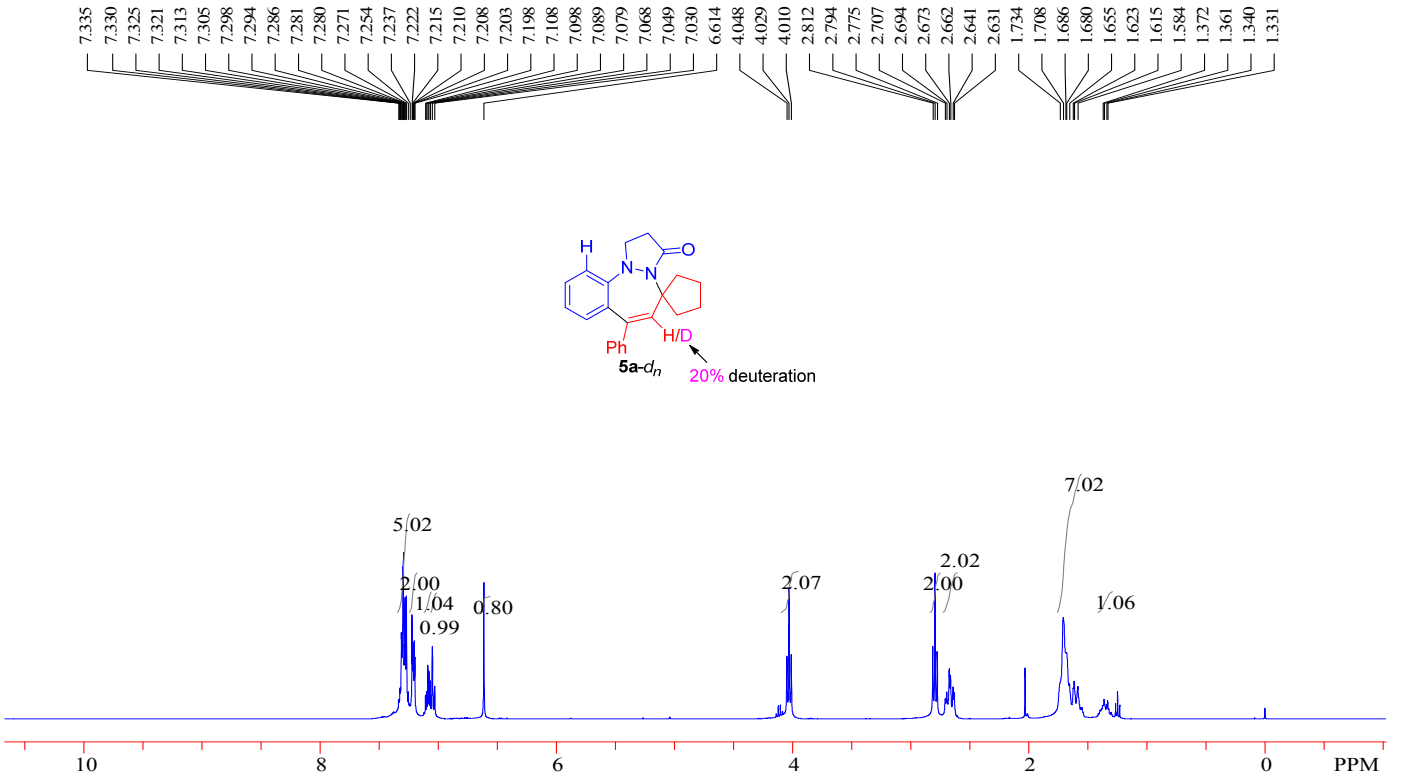
(1) H/D exchange experiments

To a reaction tube equipped with a stir bar were charged with 1-phenylpyrazolidin-3-one (**1a**, 32.4 mg, 0.2 mmol), toluene (2 mL), CD_3OD (0.08 mL, 2 mmol), $[RhCp^*Cl_2]_2$ (3.1 mg, 0.005 mmol), $Zn(OAc)_2$ (18.3 mg, 0.1 mmol) and NaOAc (8.2 mg, 0.1 mmol). The mixture was stirred at 100 °C (oil bath) for 30 min under air. The resulting mixture was cooled to room temperature, concentrated under reduced pressure. The residue was purified by silica gel chromatography using petroleum ether/ethyl acetate (1:1) as eluent to give **1a**-d_n. Upon analyzing the ^{1}H NMR spectrum of the product, the deuteration percentage was determined as 50%.



To a reaction tube equipped with a stir bar were charged with 1-phenylpyrazolidin-3-one (**1a**, 48.7 mg, 0.3 mmol), toluene (2 mL), CD_3OD (0.12 mL, 3 mmol), $[RhCp^*Cl_2]_2$ (4.7 mg, 0.0075 mmol), $Zn(OAc)_2$ (27.5 mg, 0.15 mmol), NaOAc (12.3 mg, 0.15 mmol) and 1-(phenylethynyl)cyclopentan-1-ol (**4a**, 55.8 mg, 0.3 mmol). The mixture was stirred at 100 °C (oil bath) for 30 min under air. The resulting mixture was cooled to room temperature, filtered through a pad of celite and concentrated under reduced pressure. The residue was purified

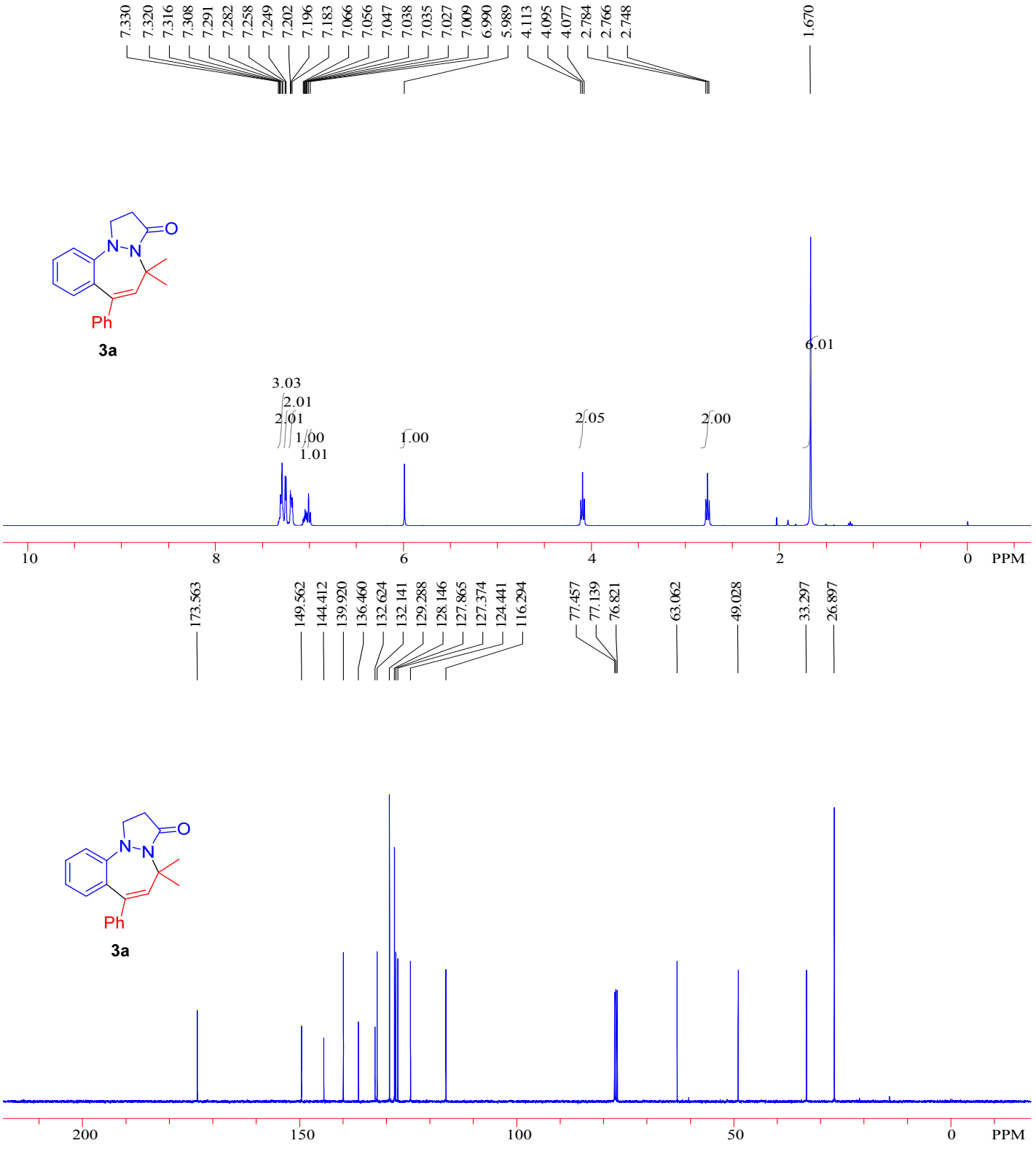
by silica gel chromatography using petroleum ether/ethyl acetate (3:1) as eluent to give **5a-*d*$_n$**. Upon analyzing the ^{1}H NMR spectrum of the product, the deuteration percentage was determined as 20%.

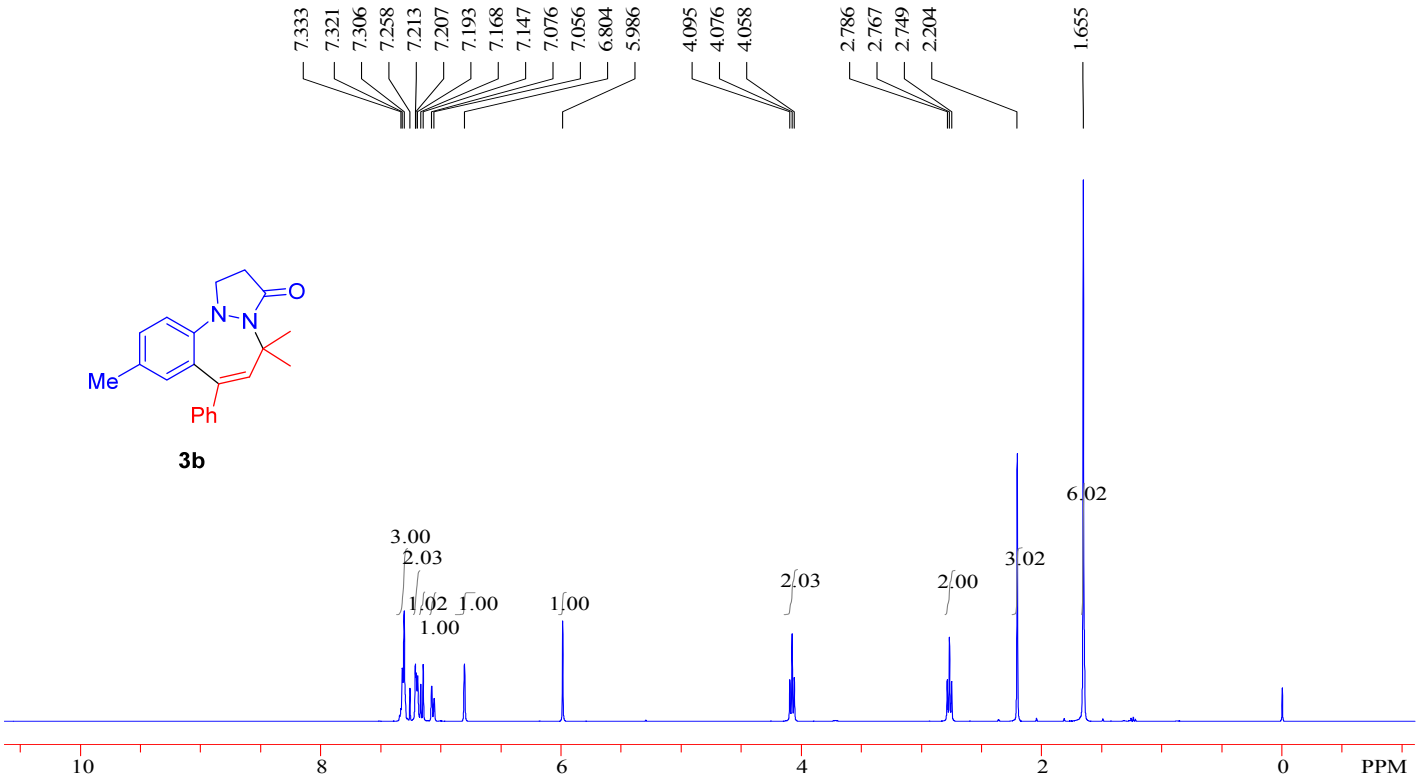


(2) Competition experiment between 1c and 1g

To a reaction tube equipped with a stir bar were charged with 1-(4-methoxyphenyl)pyrazolidin-3-one (**1c**, 57.6 mg, 0.3 mmol), 1-(4-(trifluoromethyl)phenyl)pyrazolidin-3-one **(1g**, 69.0 mg, 0.3 mmol), 2-methyl-4-phenyl-but-3-yn-2-ol (**2a**, 48.1 mg, 0.3 mmol), $[Cp^*RhCl_2]_2$ (4.7 mg, 0.0075 mmol), $Zn(OAc)_2$ (27.5 mg, 0.15 mmol), NaOAc (12.3 mg, 0.15 mmol) and toluene (2 mL). The mixture was stirred at 100 ^{o}C (oil bath) for 4 h. The resulting mixture was cooled to room temperature, filtered through a pad of celite and concentrated under reduced pressure. The residue was purified by silica gel chromatography using petroleum ether/ethyl acetate (3:1) as eluent to afford **3c** (12.0 mg, 12%) and **3g** (81.4 mg, 73%).

IV. Copies of NMR spectra of 3a-3ee

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4.095
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4.058
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2.767
2.749
2.204
1.655
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Ph
3b
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1.02
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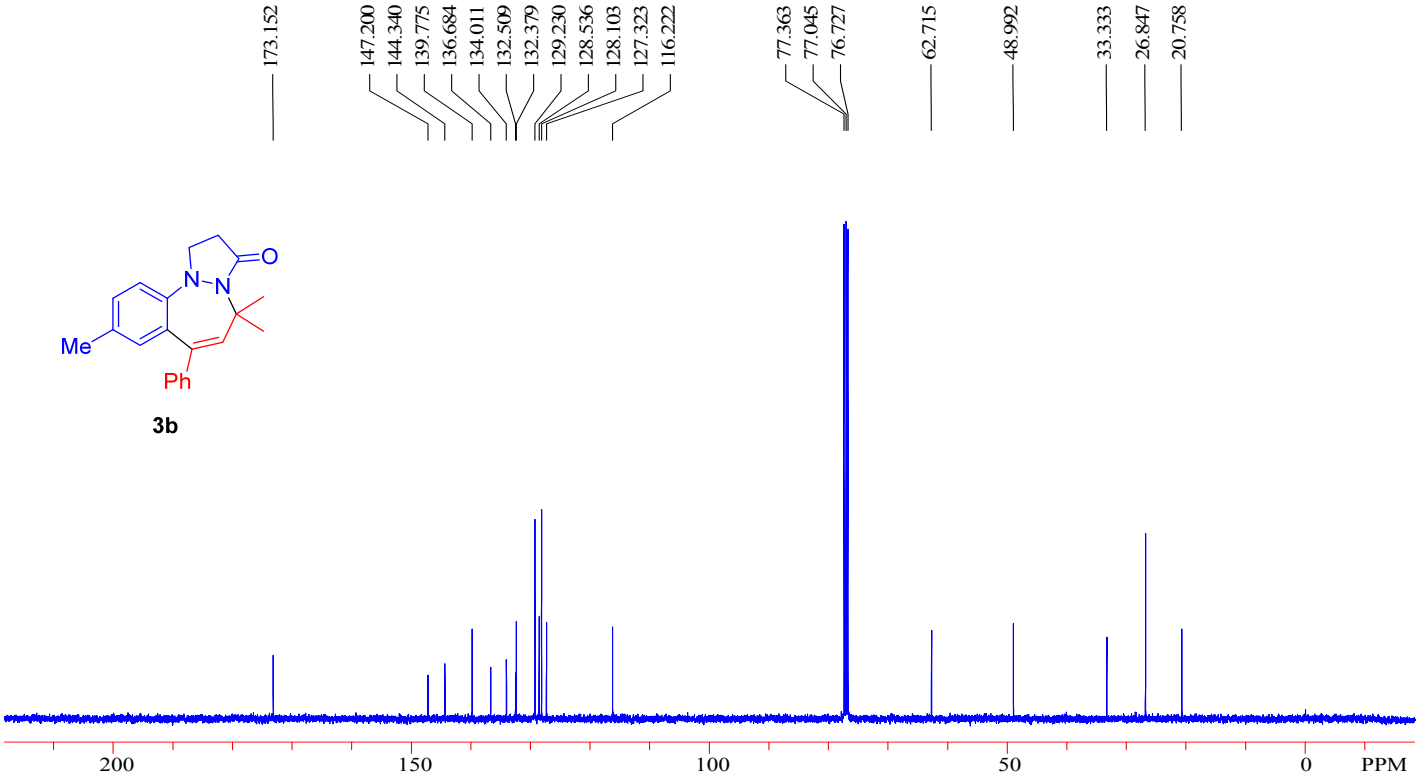
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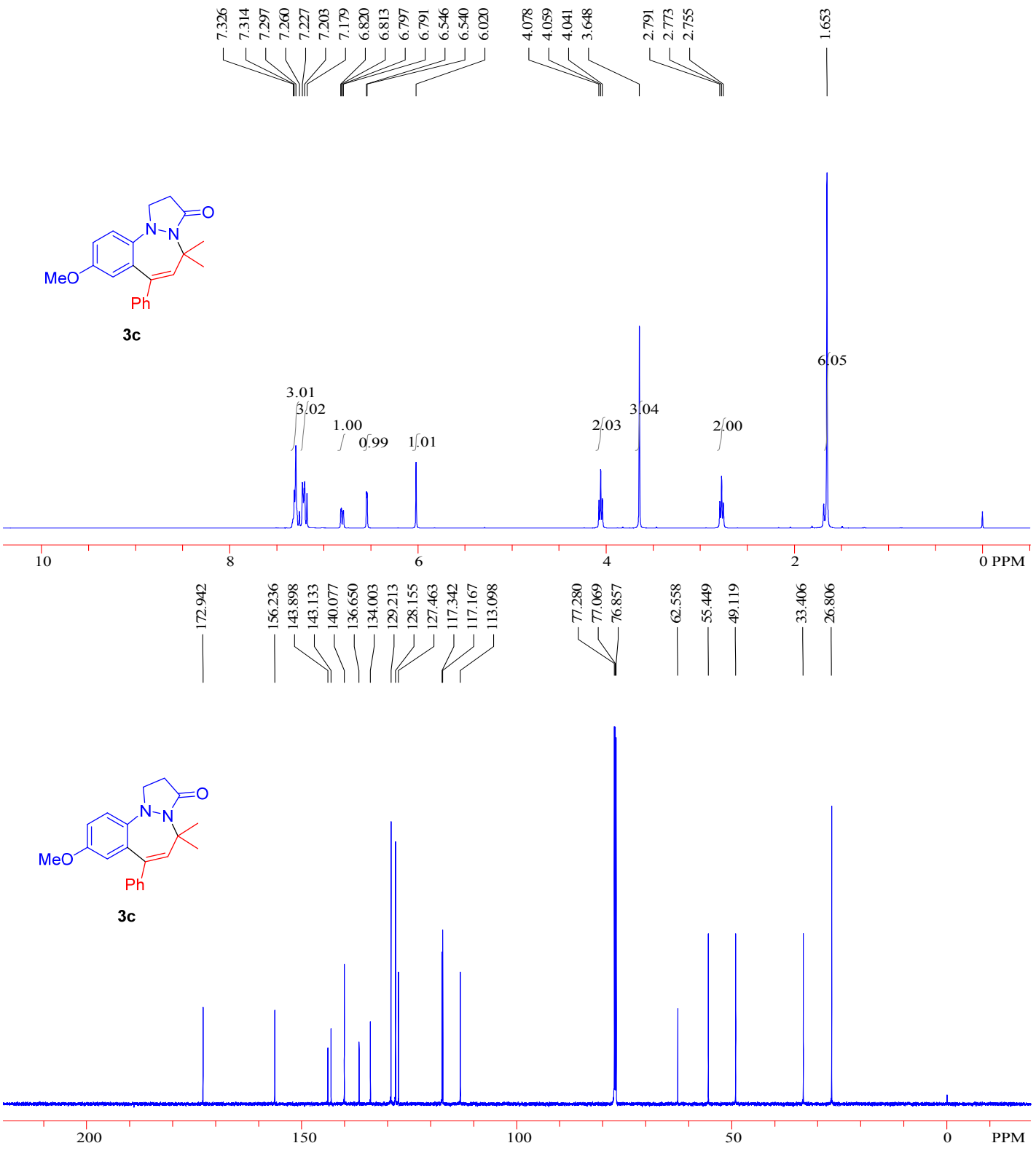
PPM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4.059
4.041
3.648
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3.02
1.00
0.99
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2.03
3.04
2.00
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10
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2
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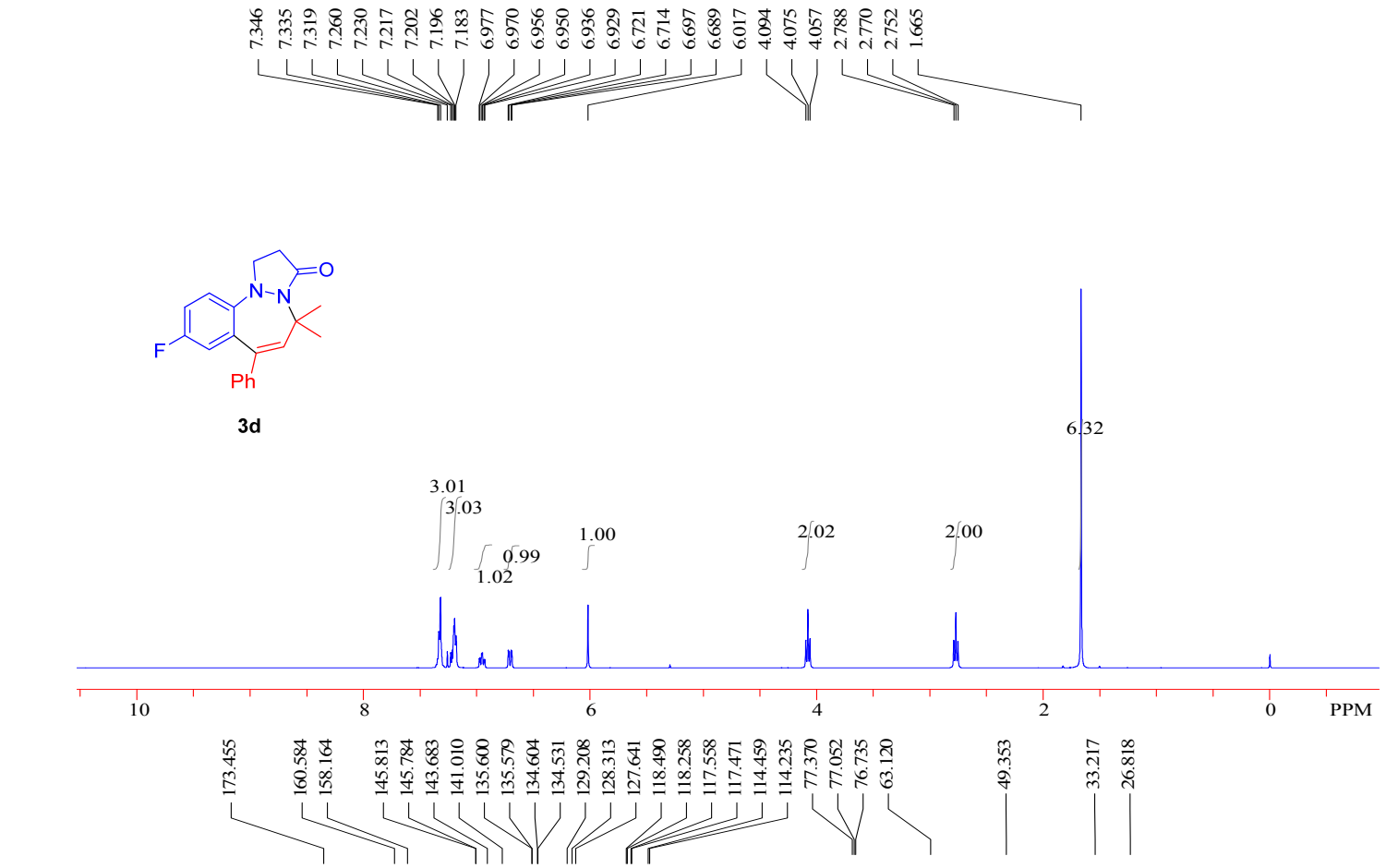
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N
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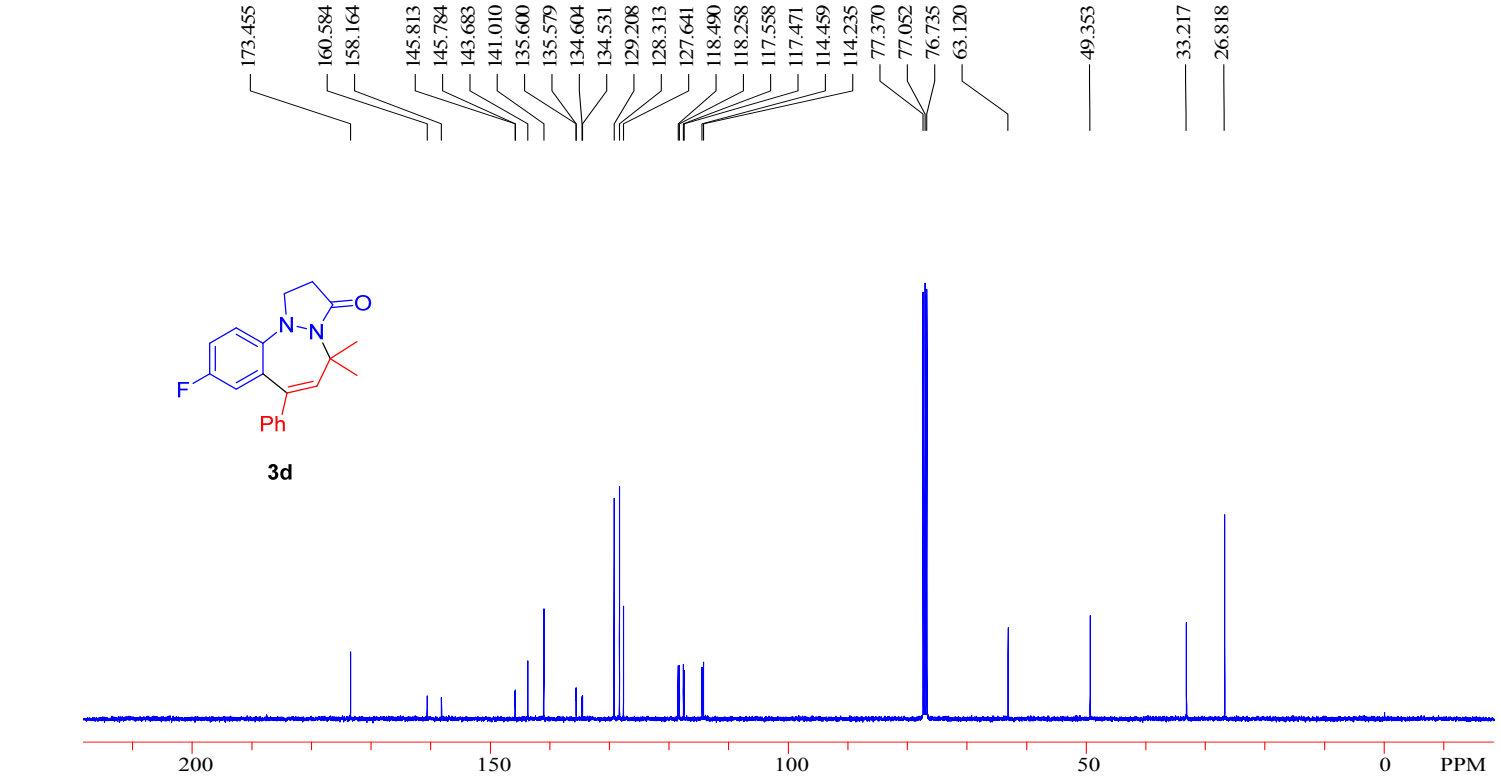
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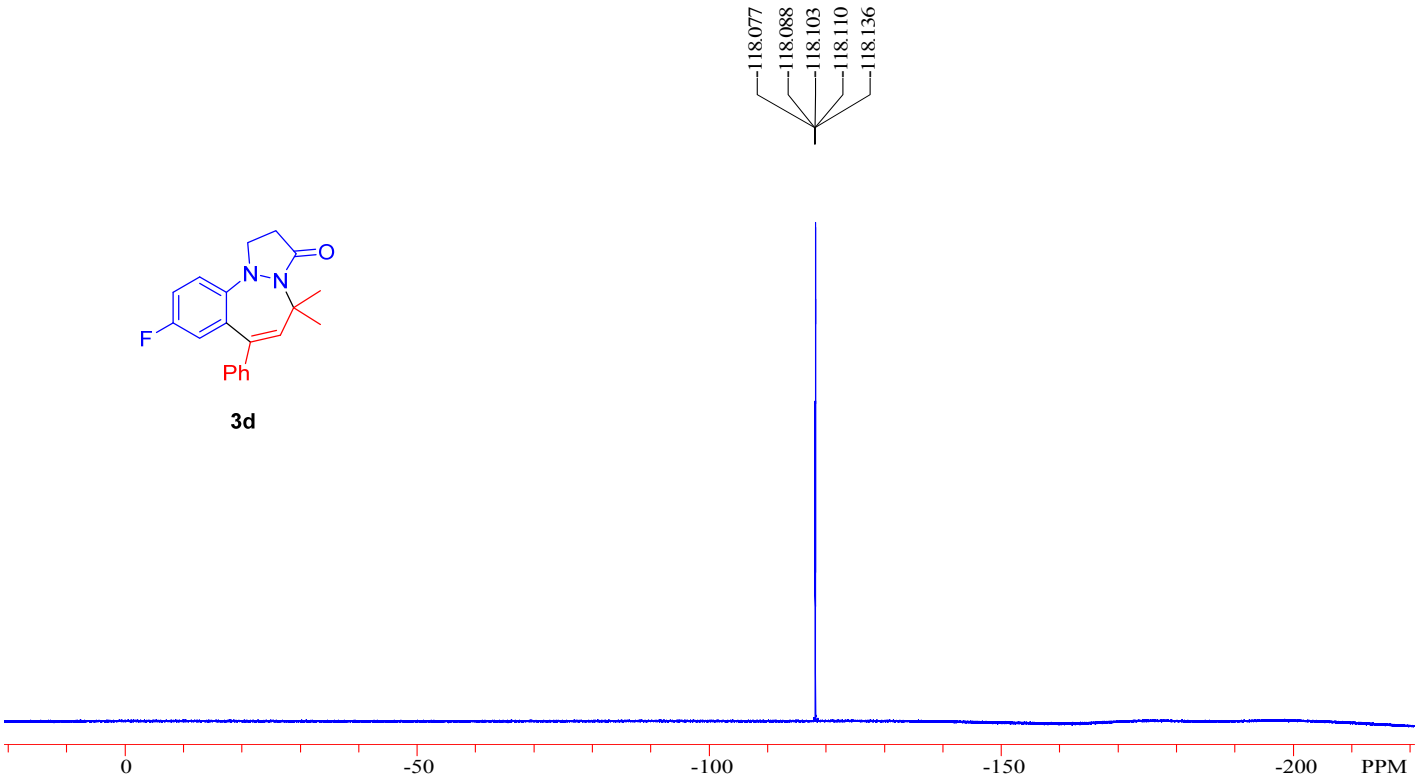
PPM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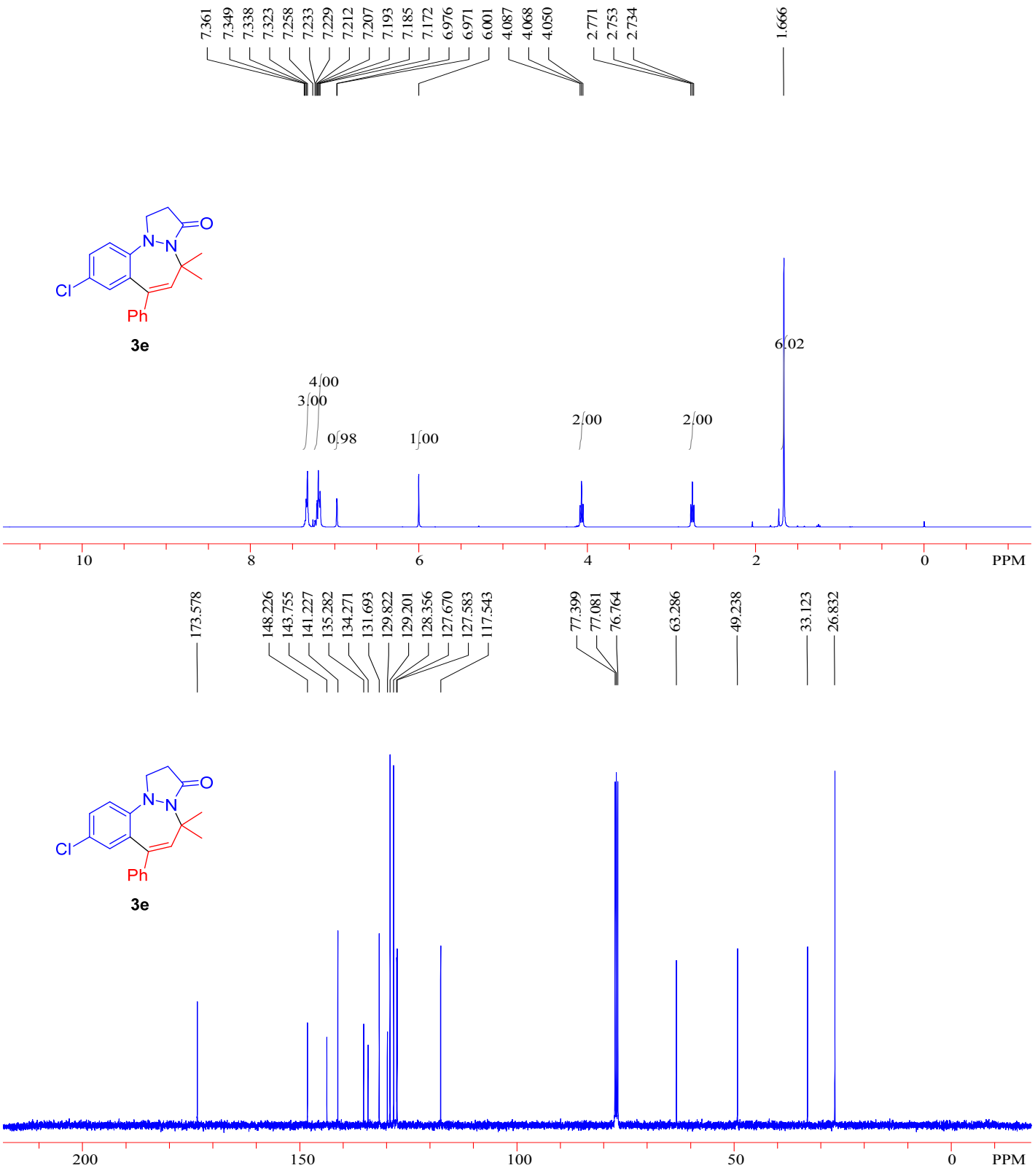
-100
-150
-200
PPM

3d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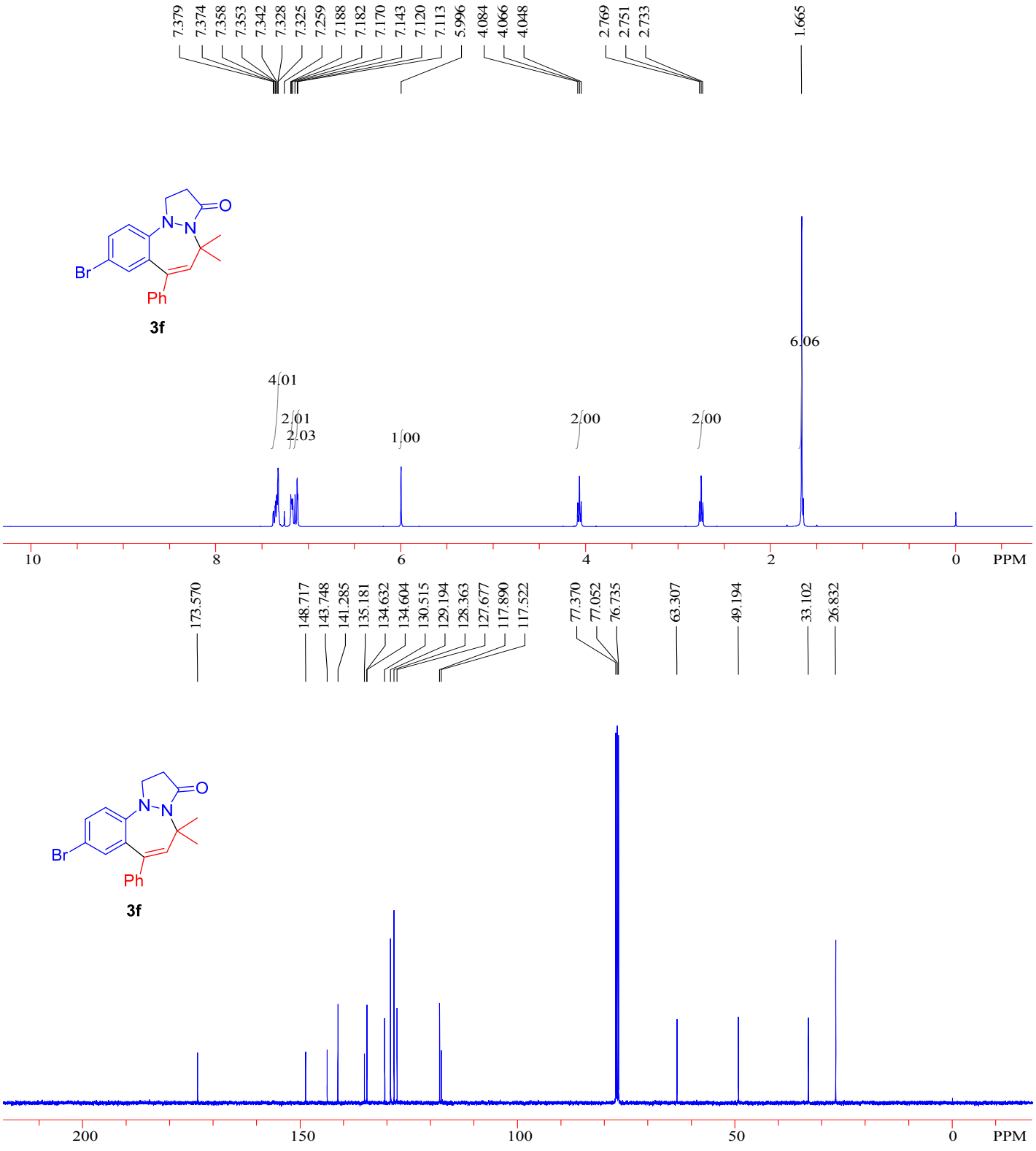
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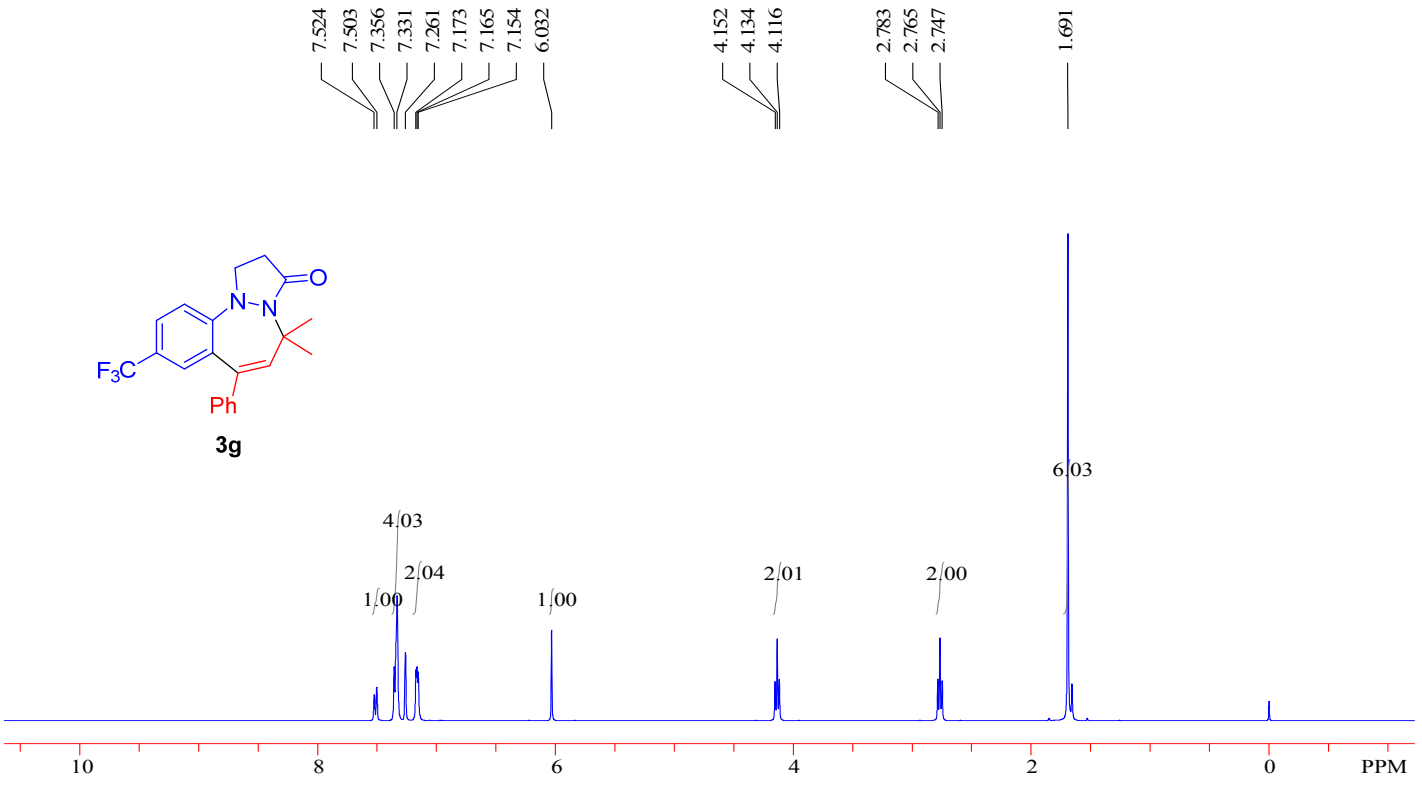
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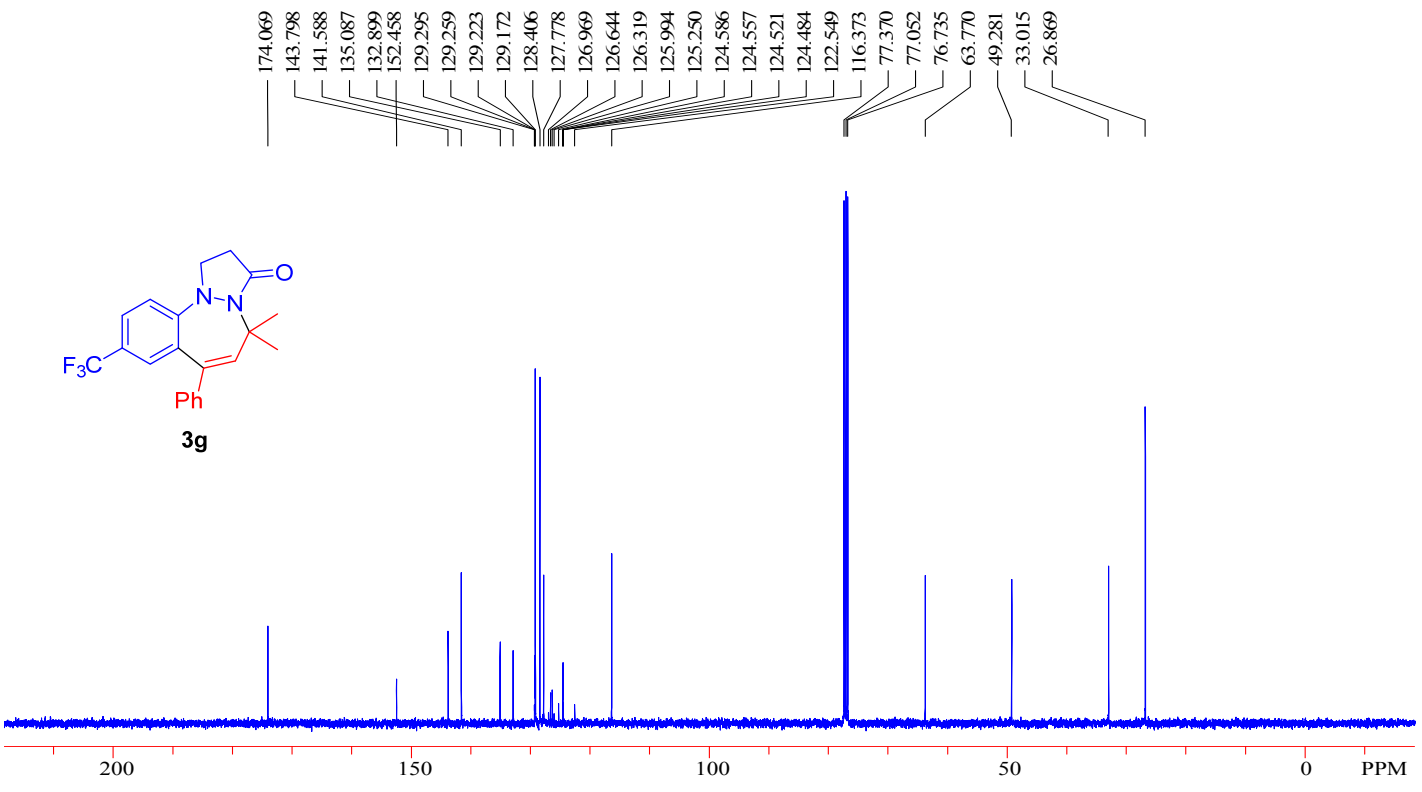
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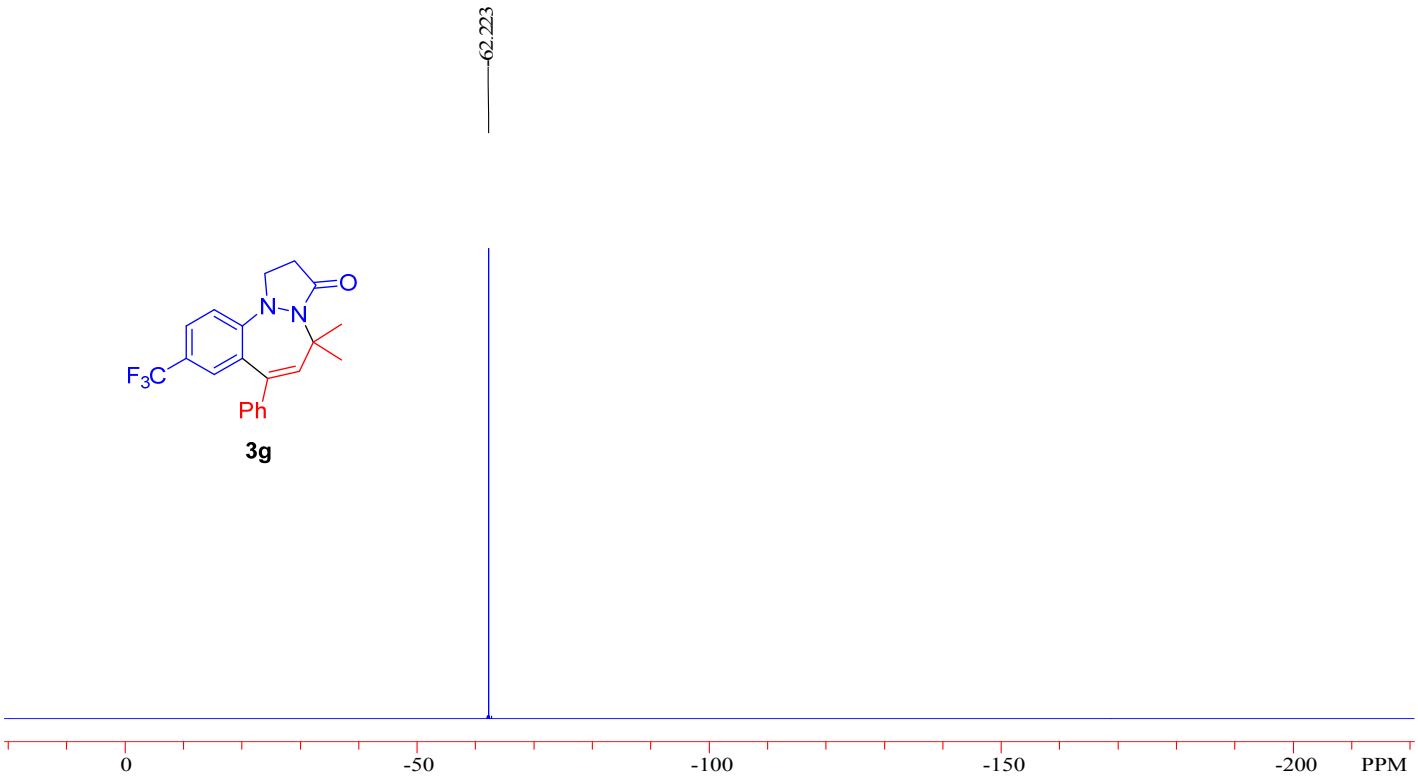

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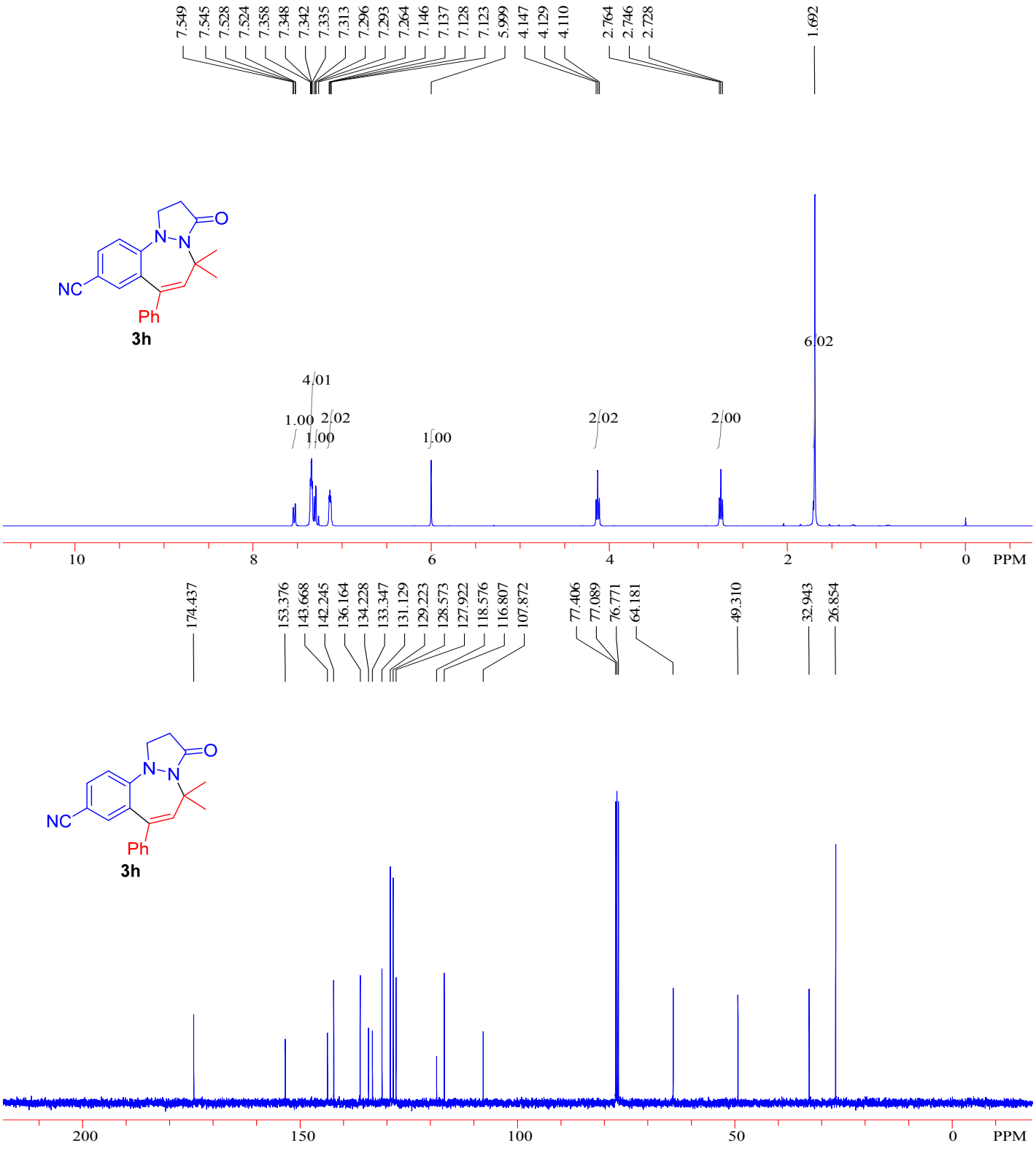
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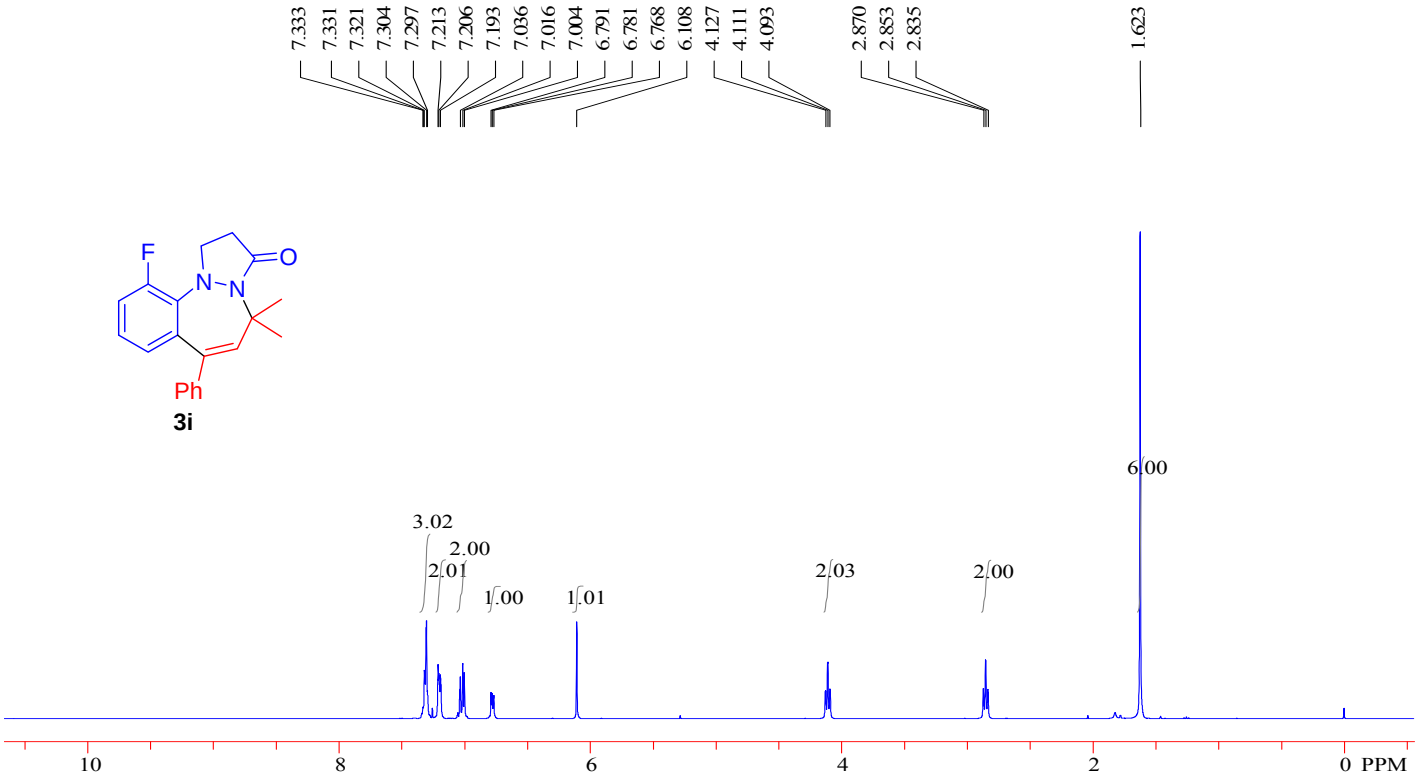
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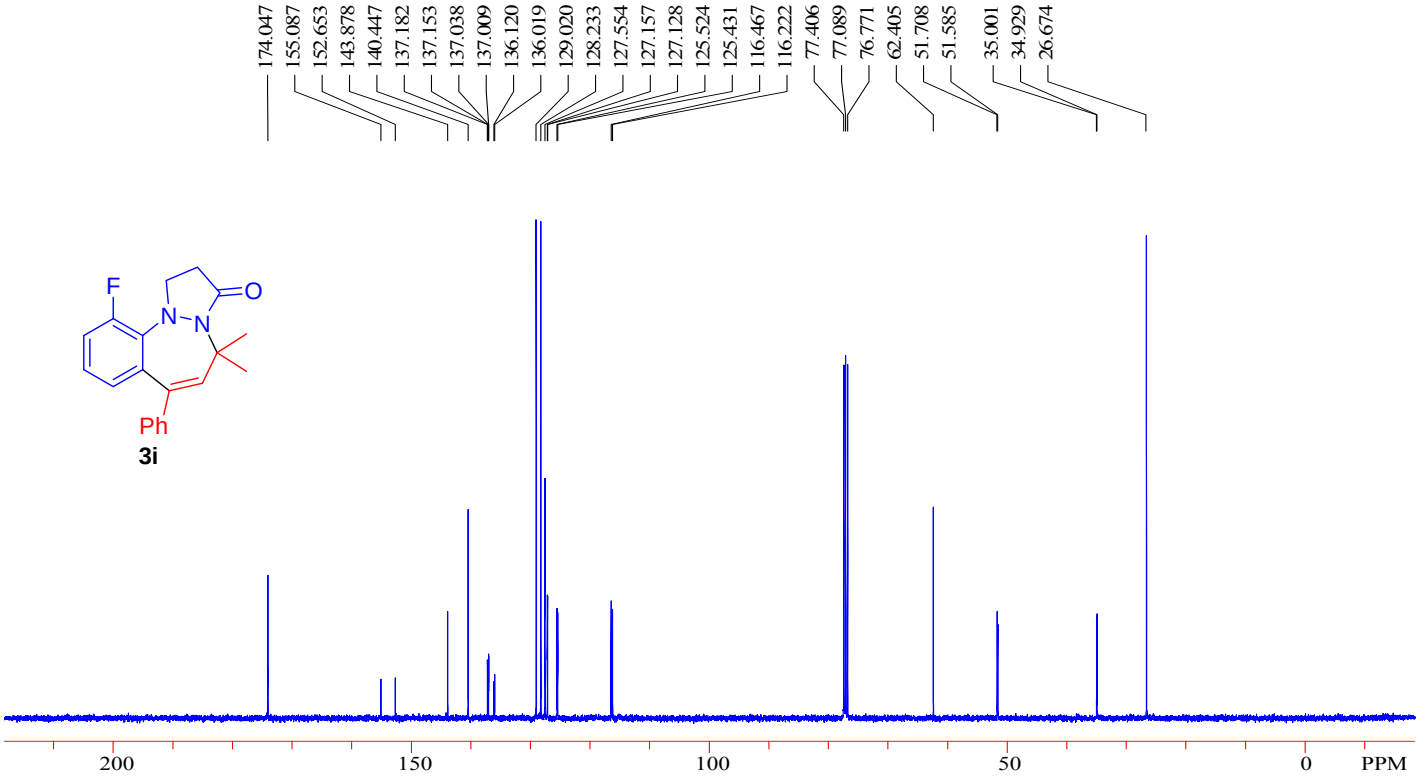
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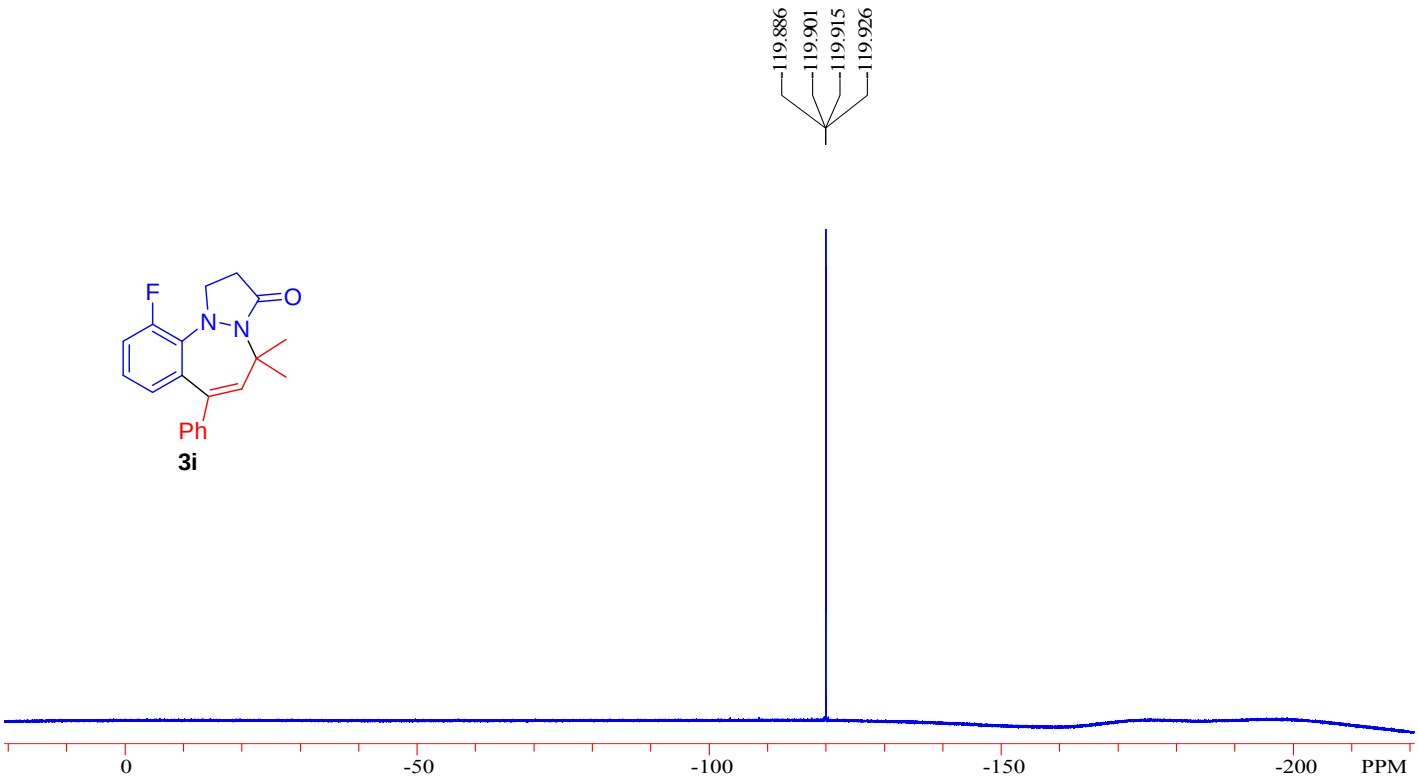

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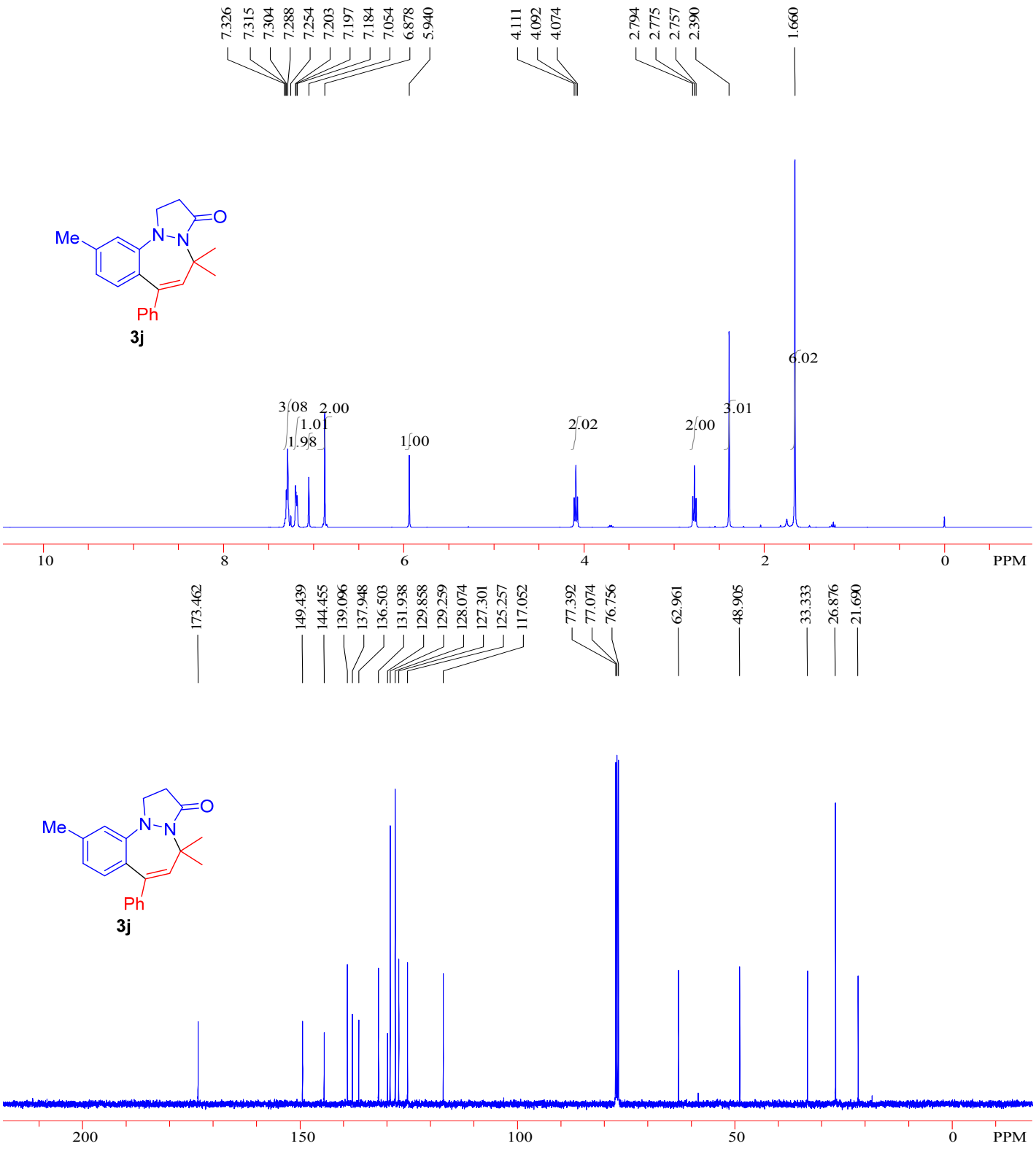
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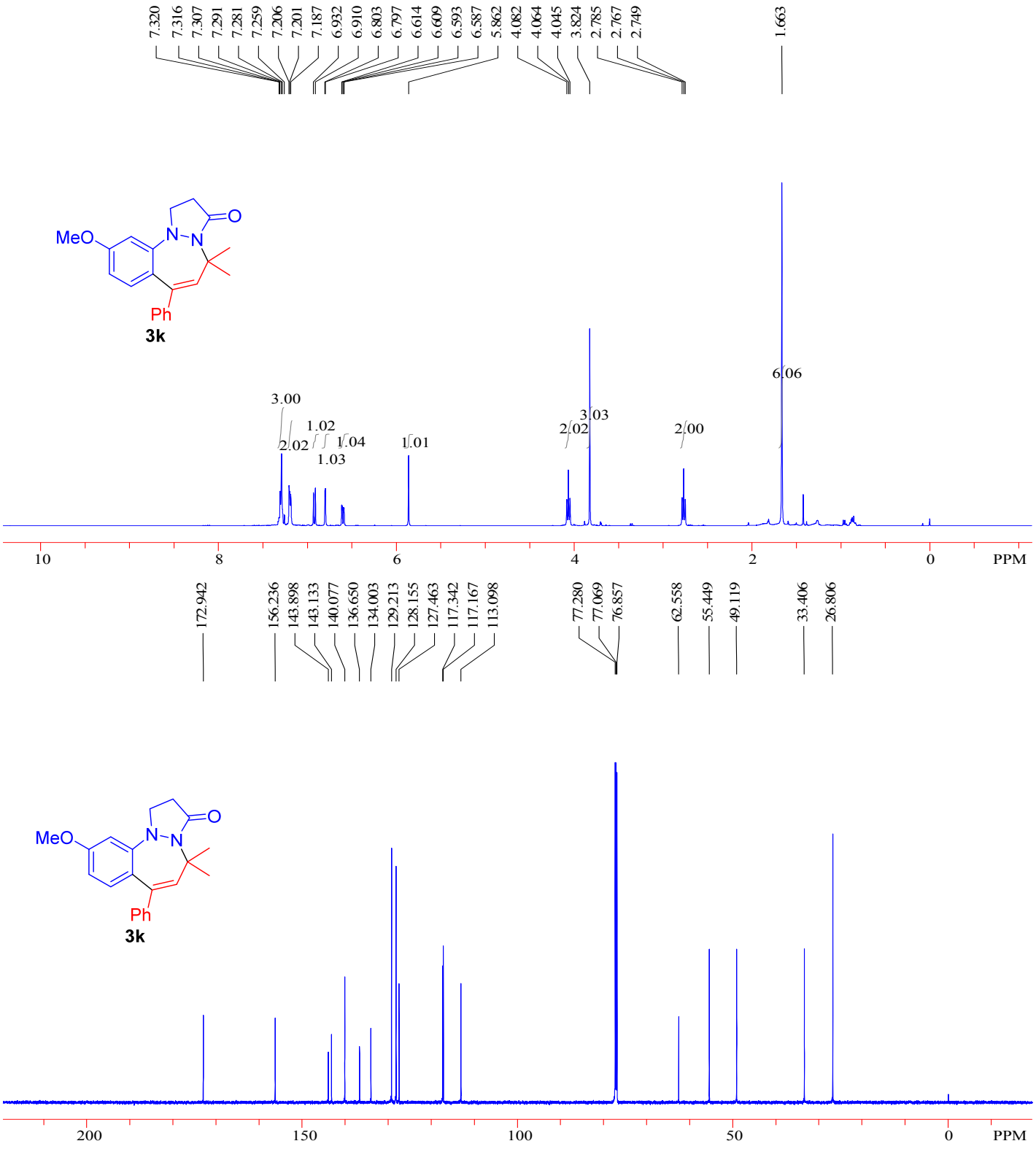
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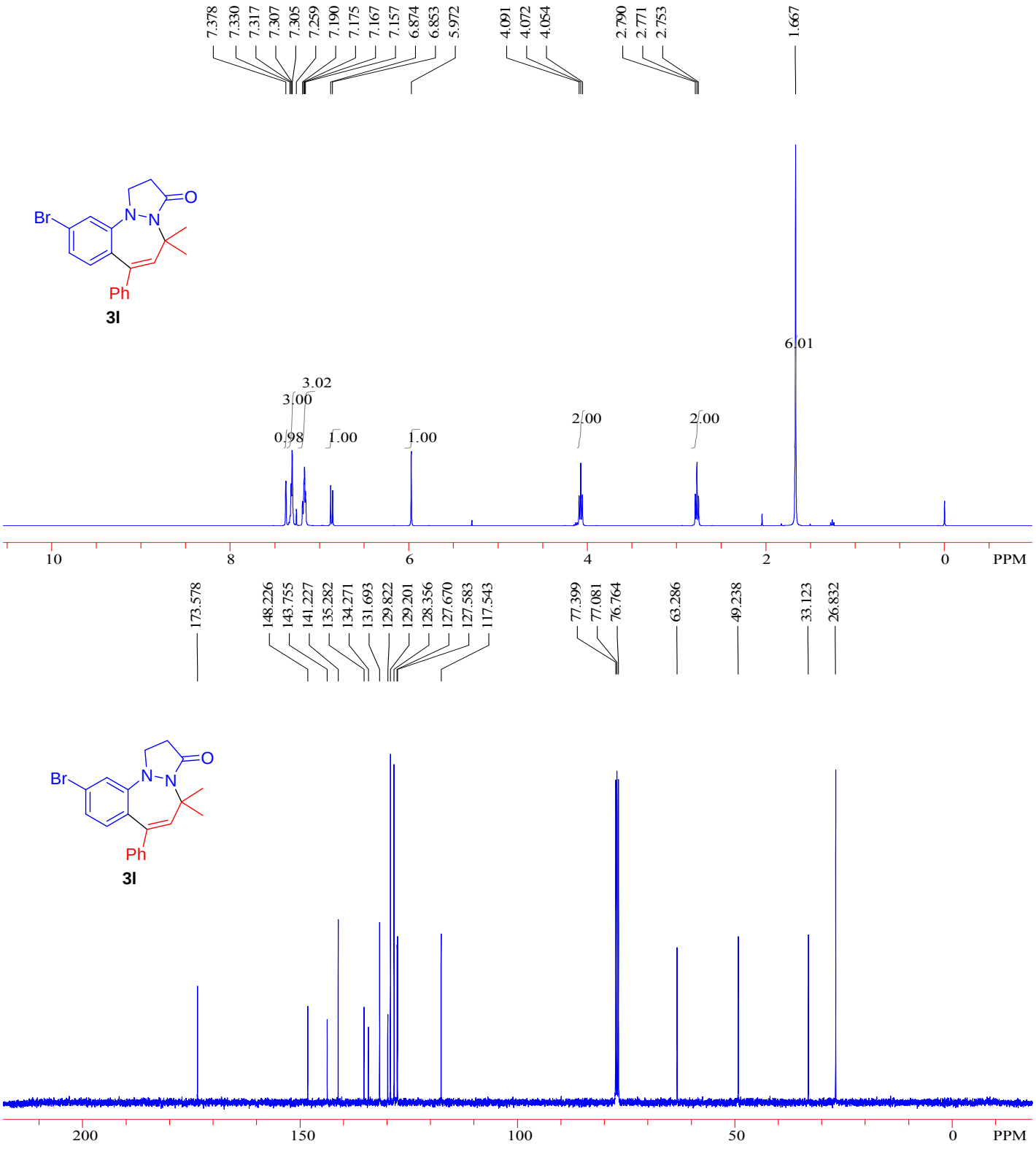
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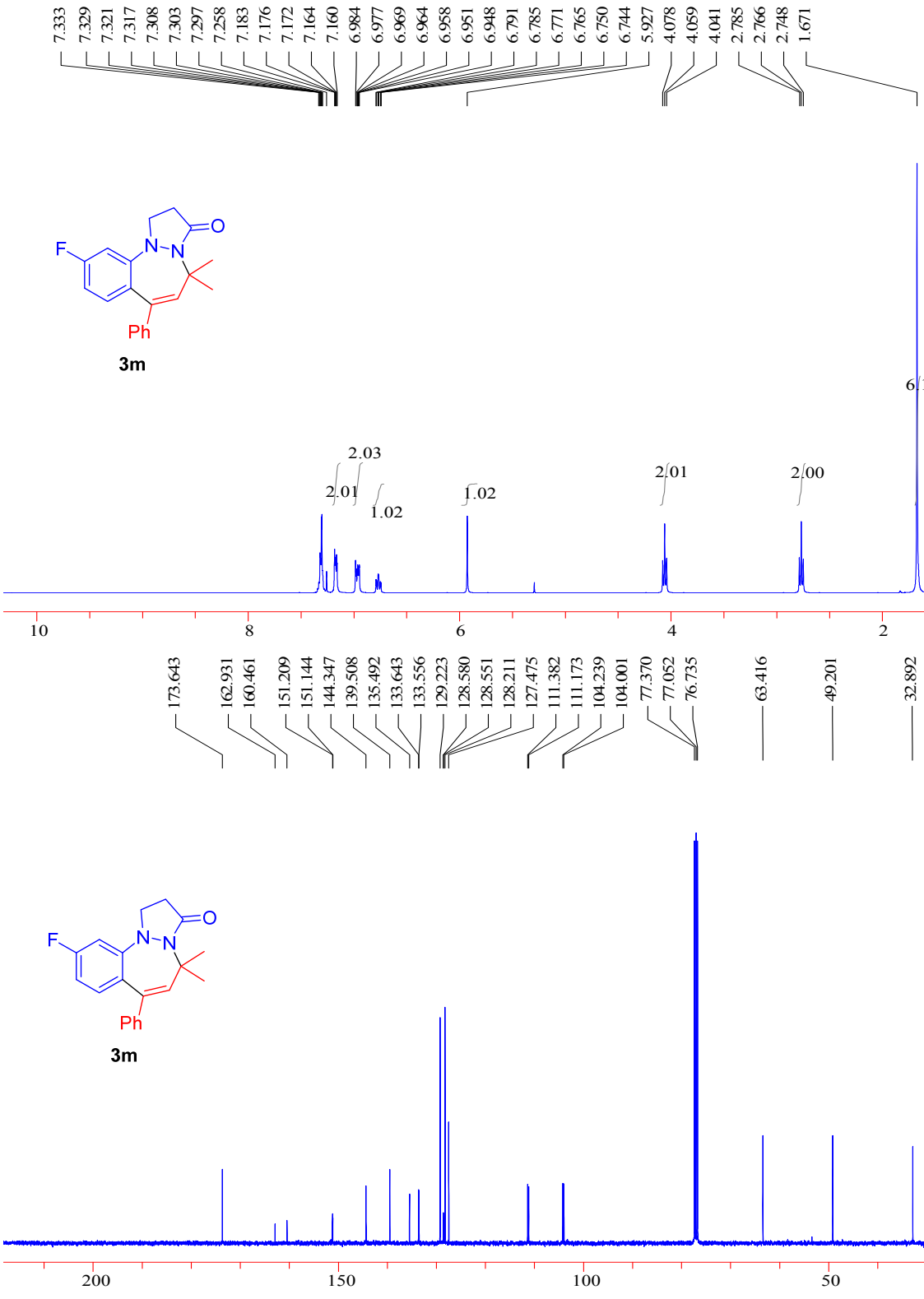
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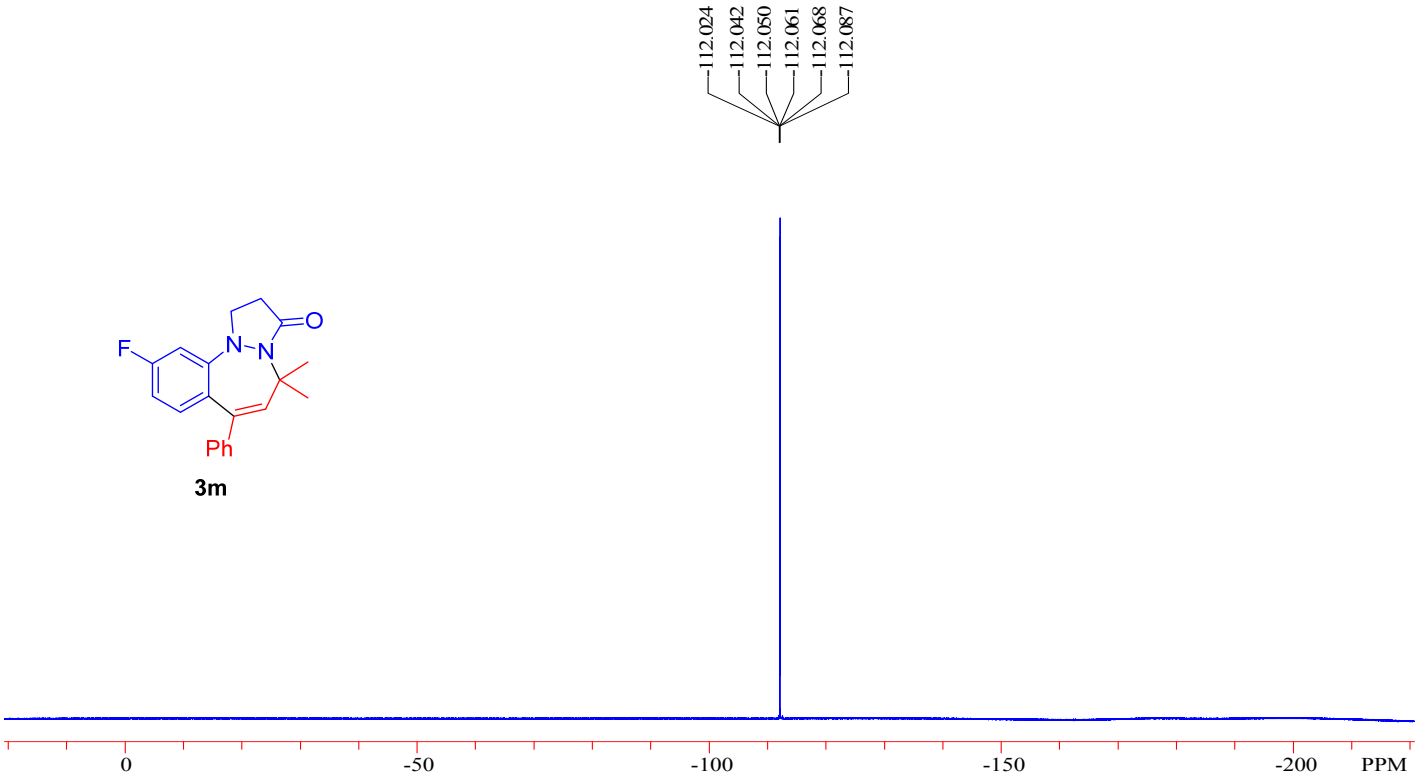
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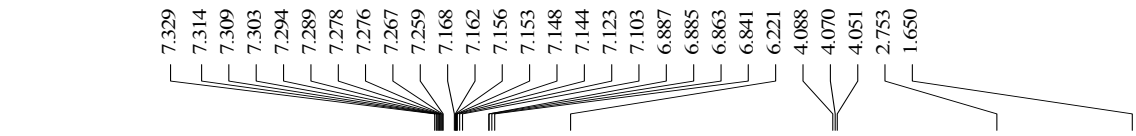
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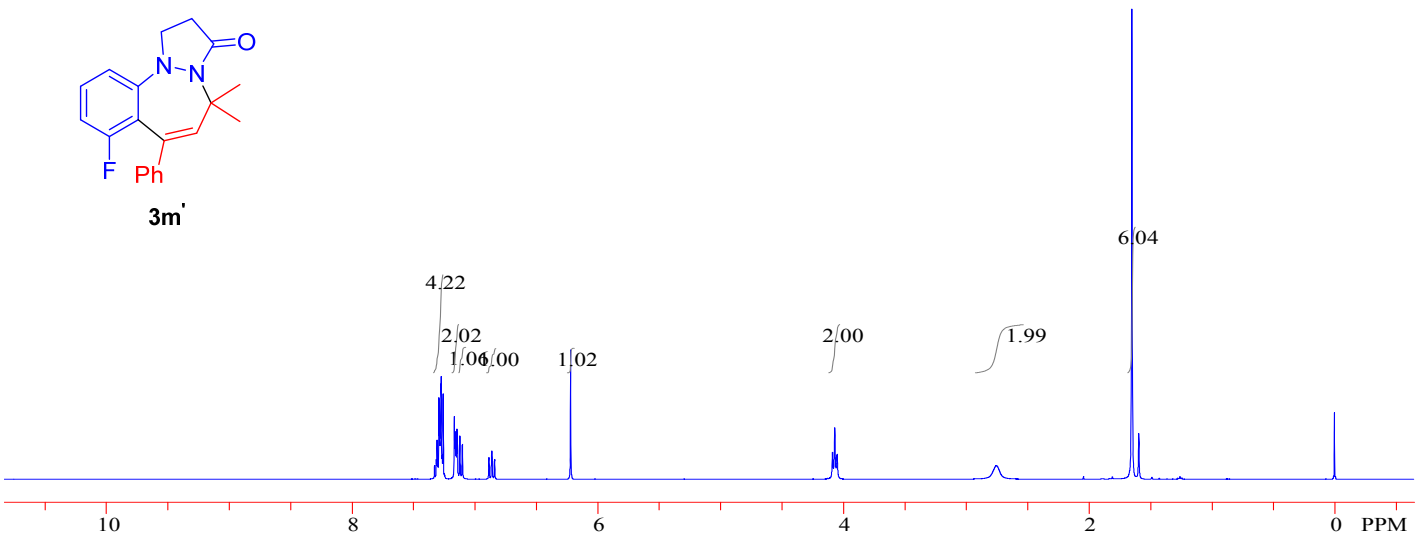
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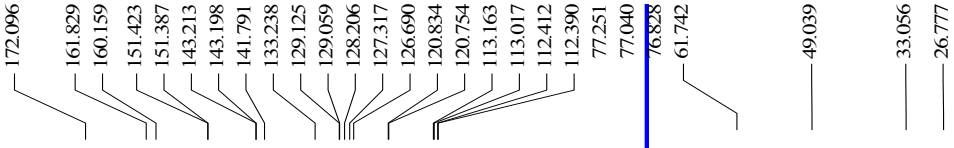
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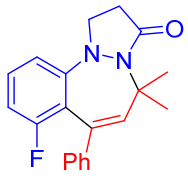
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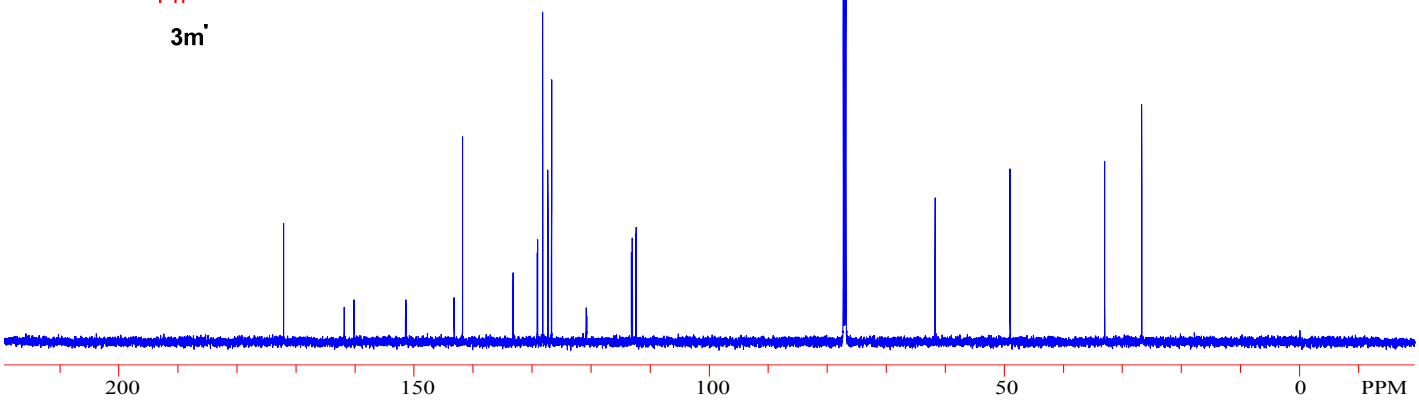
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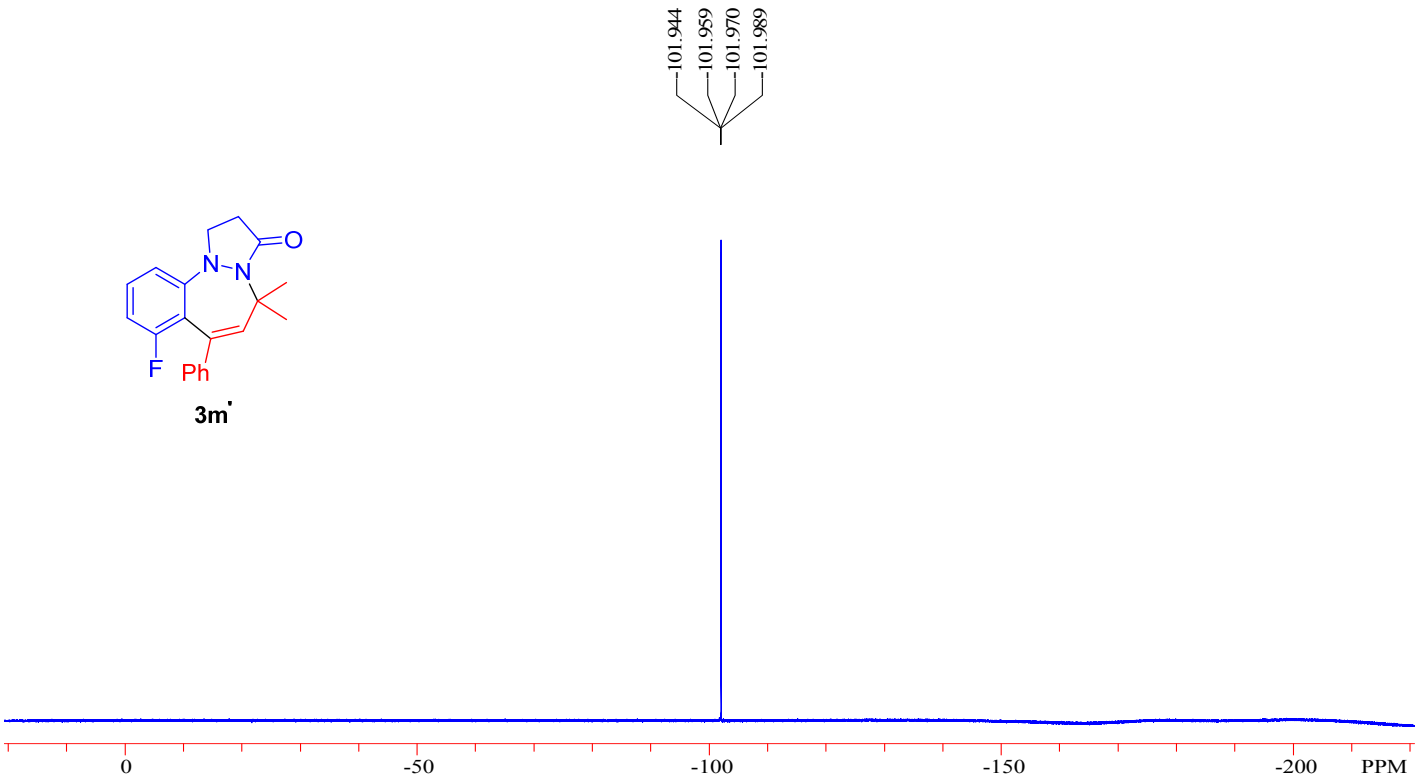

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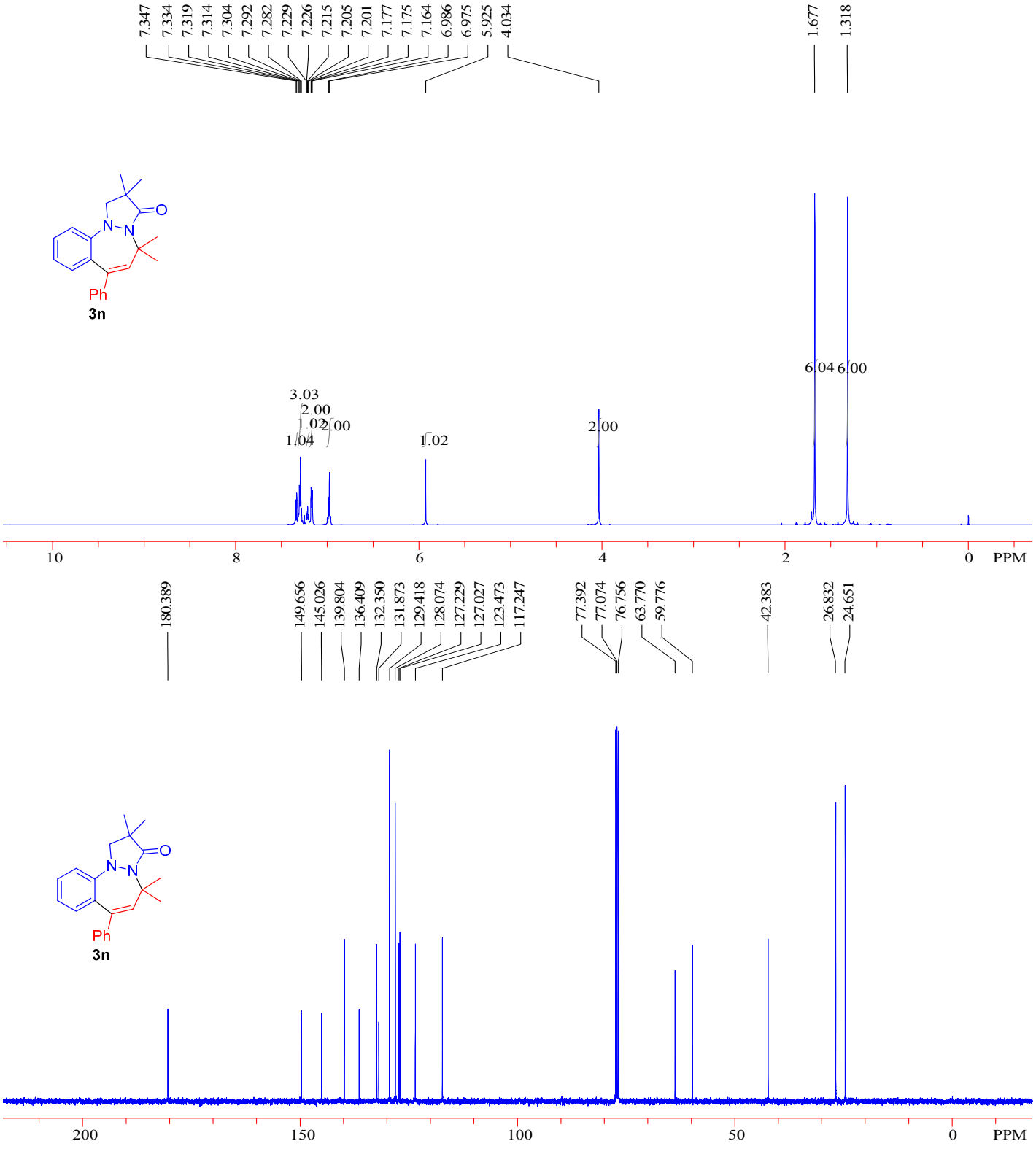
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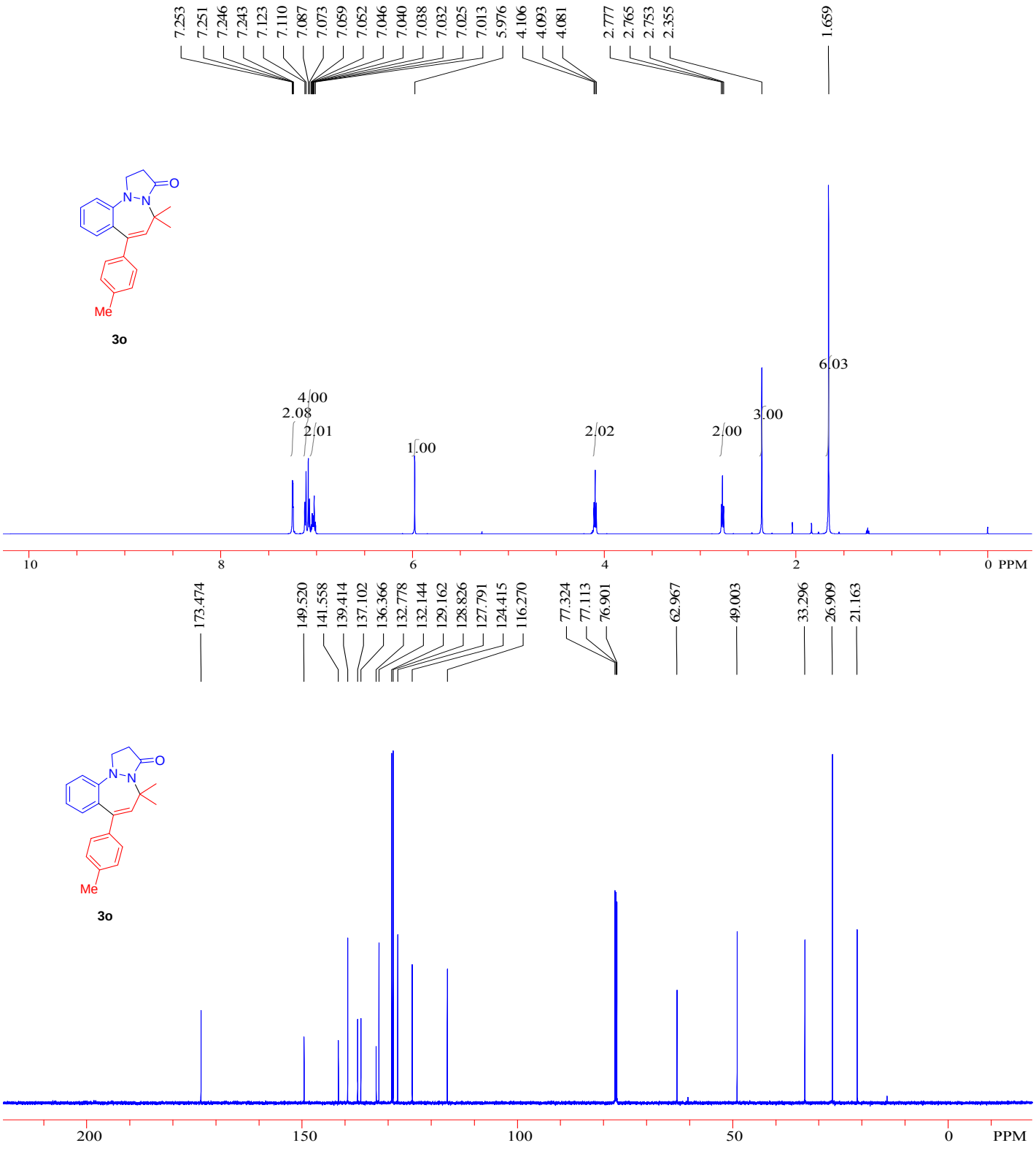
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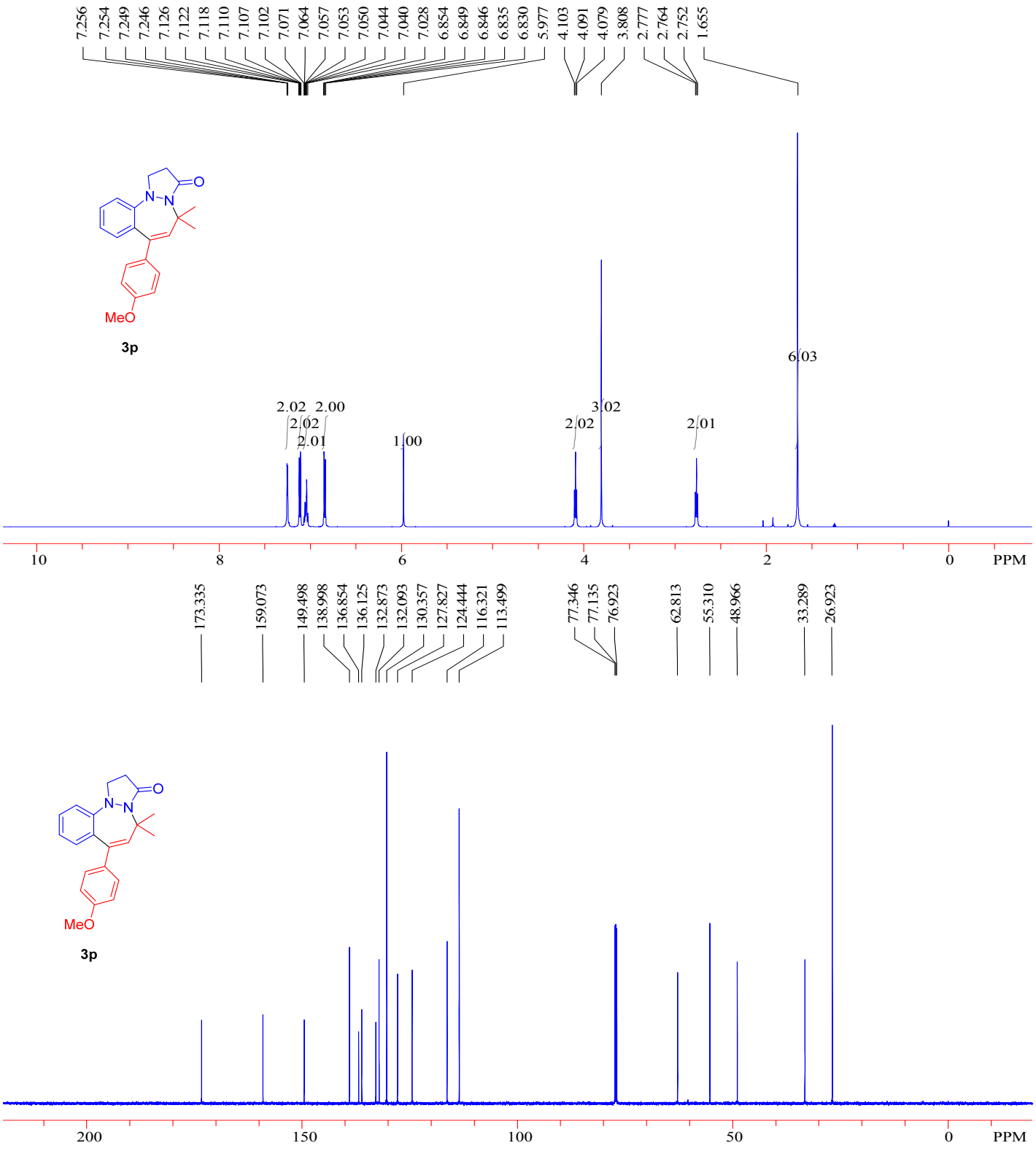
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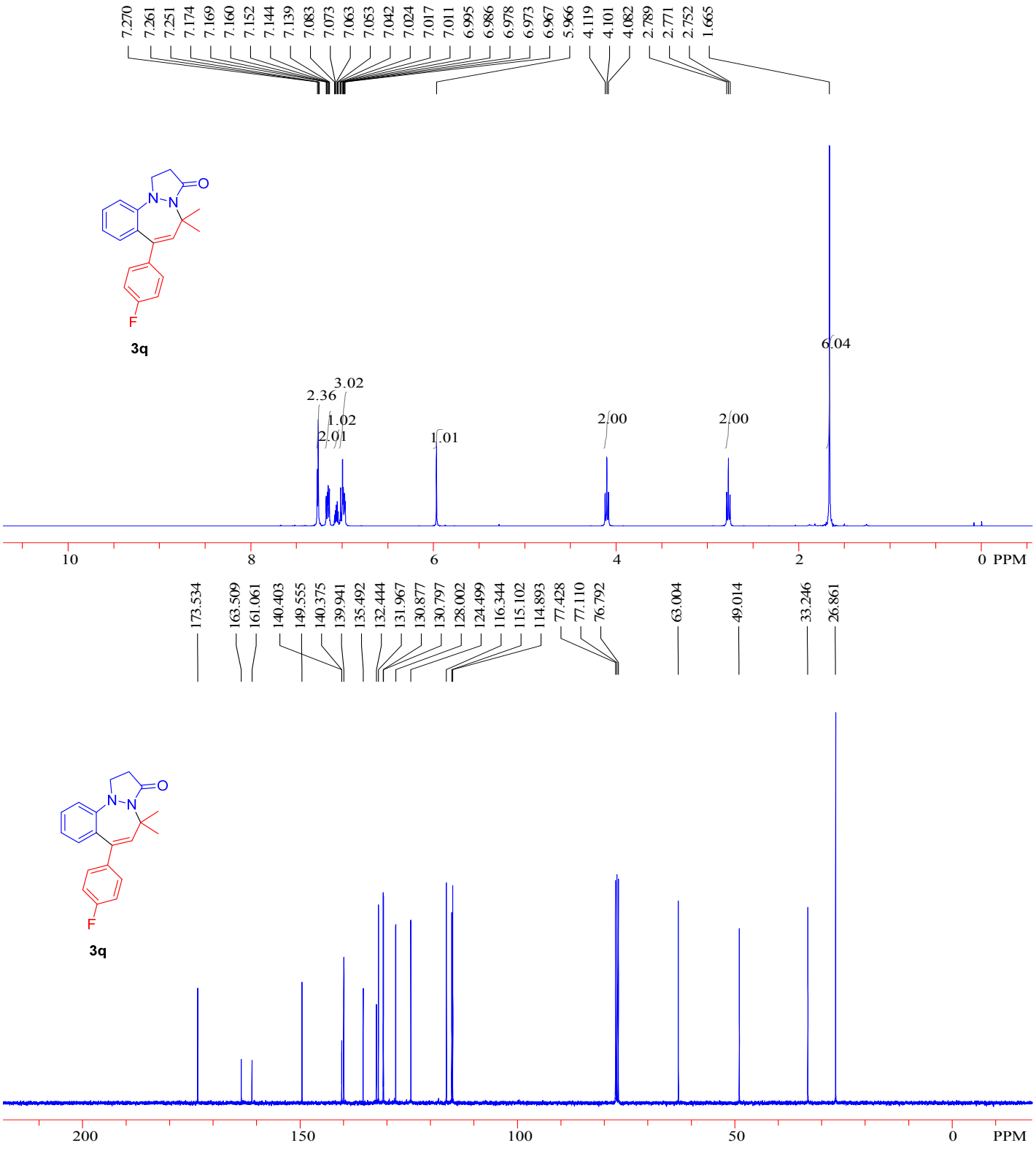
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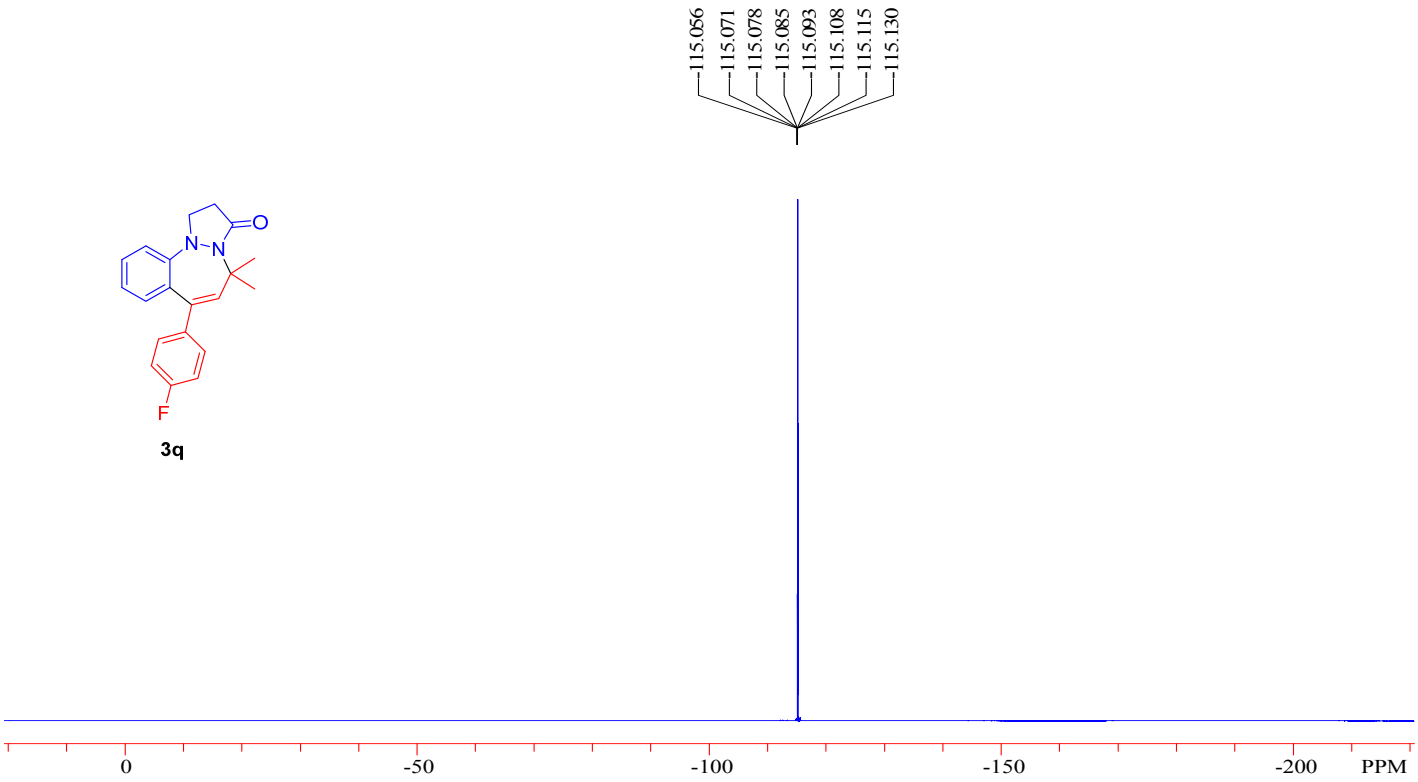
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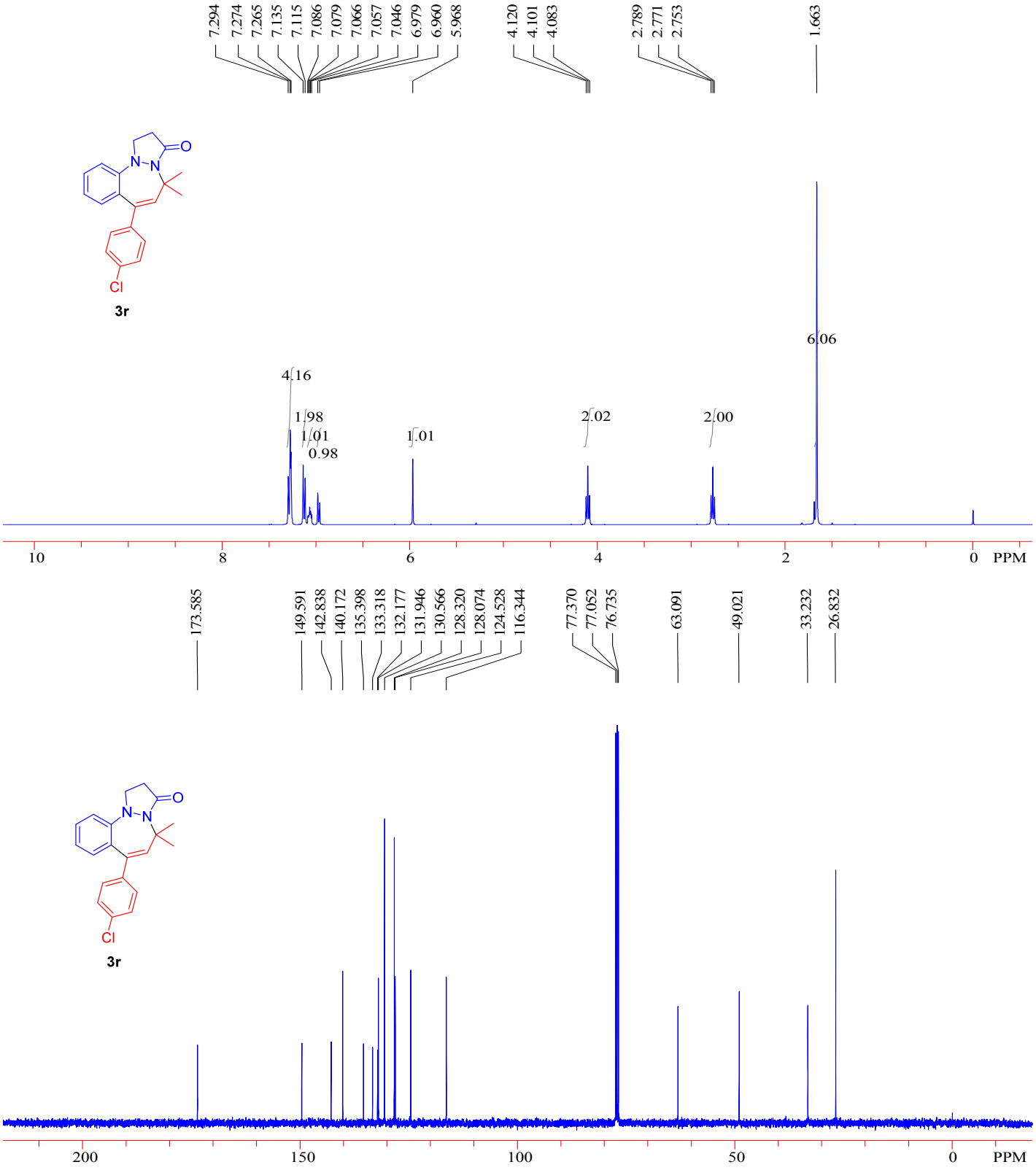
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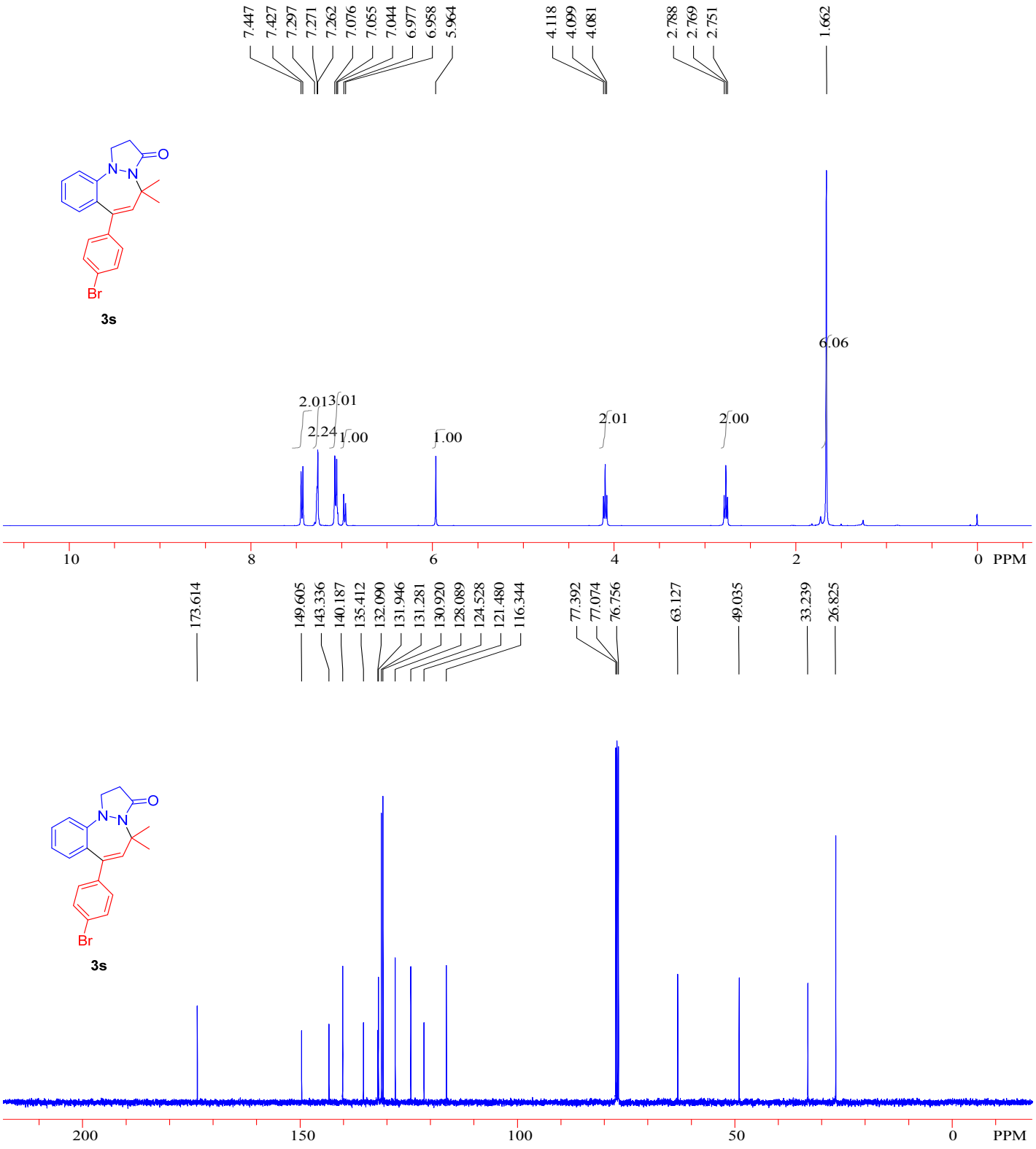
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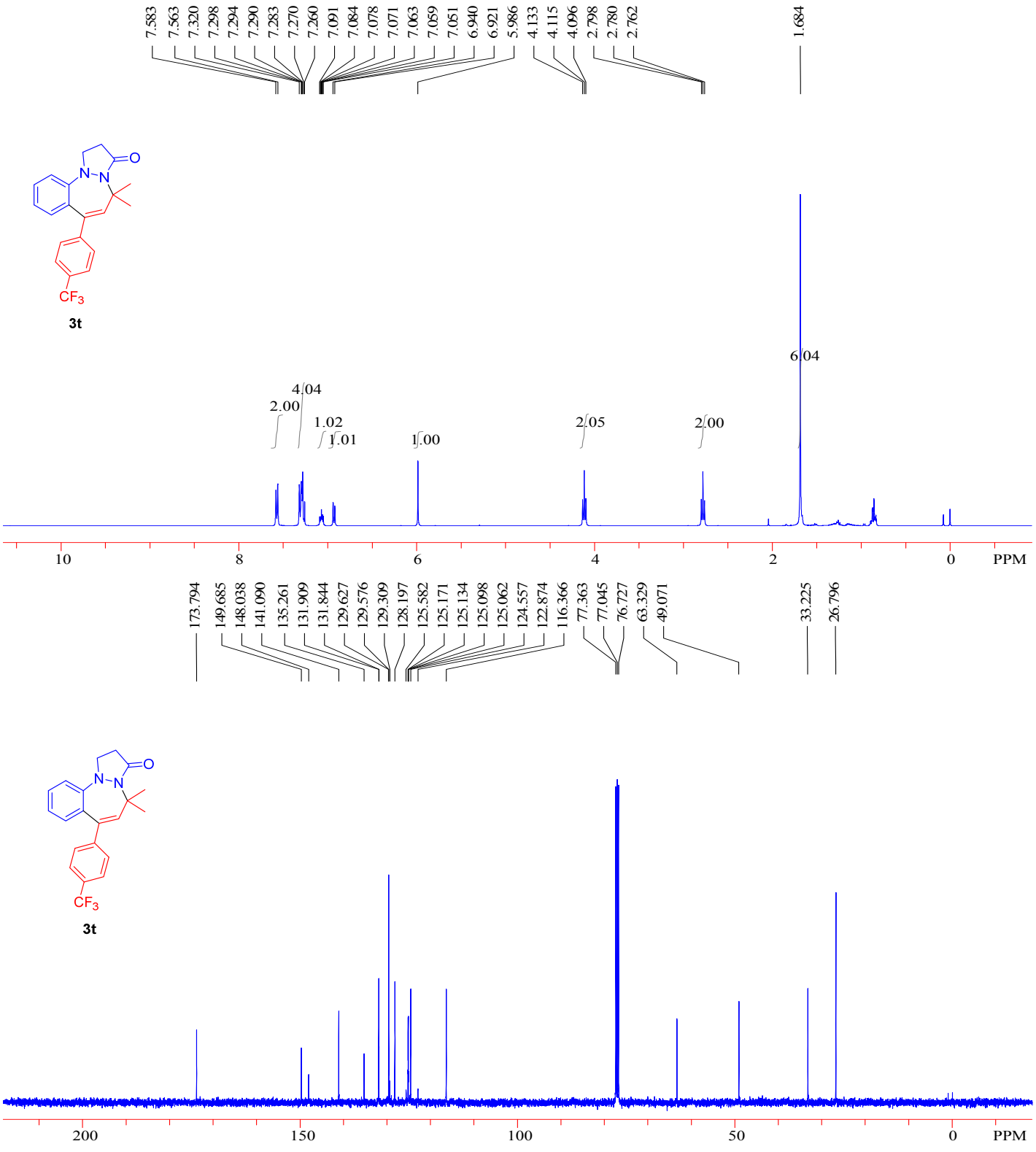
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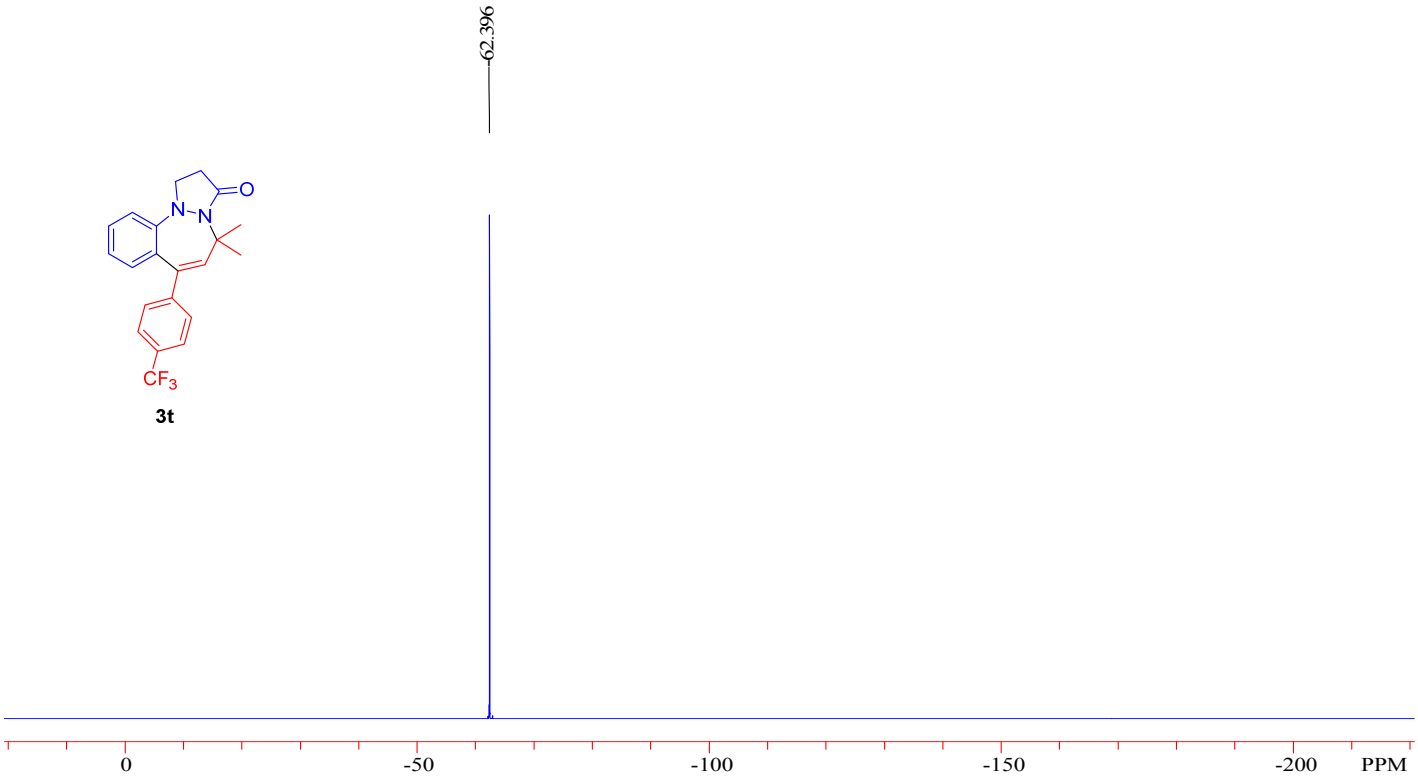

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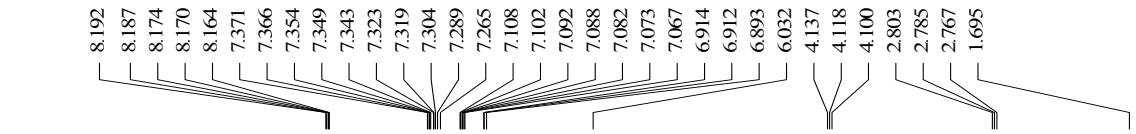
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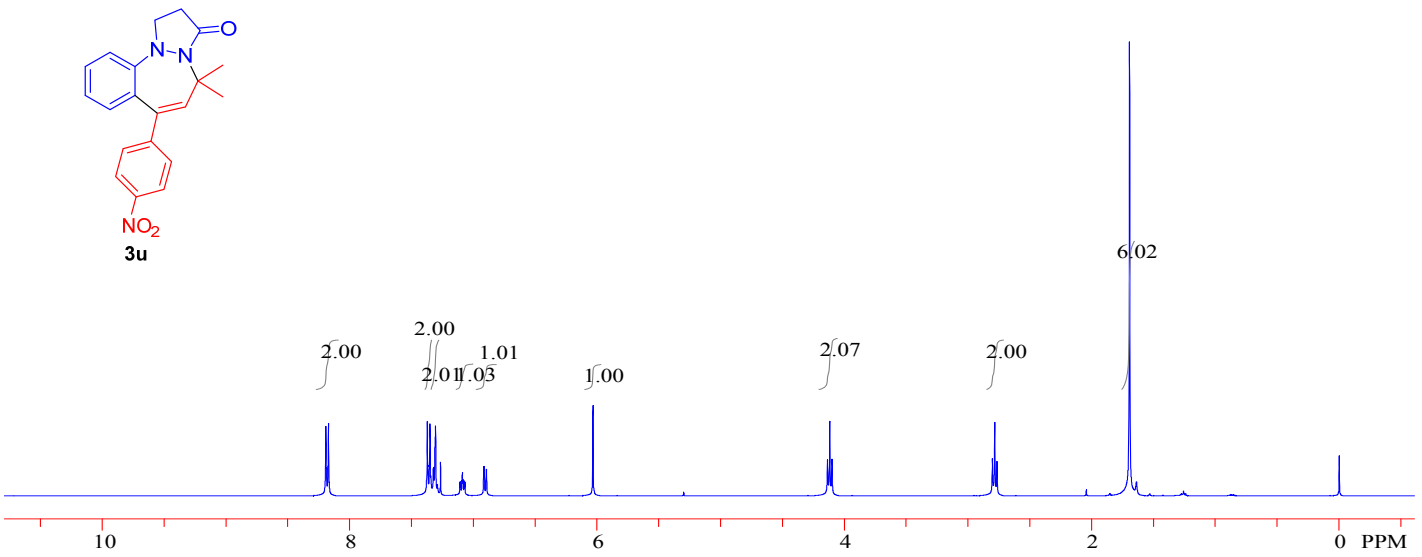
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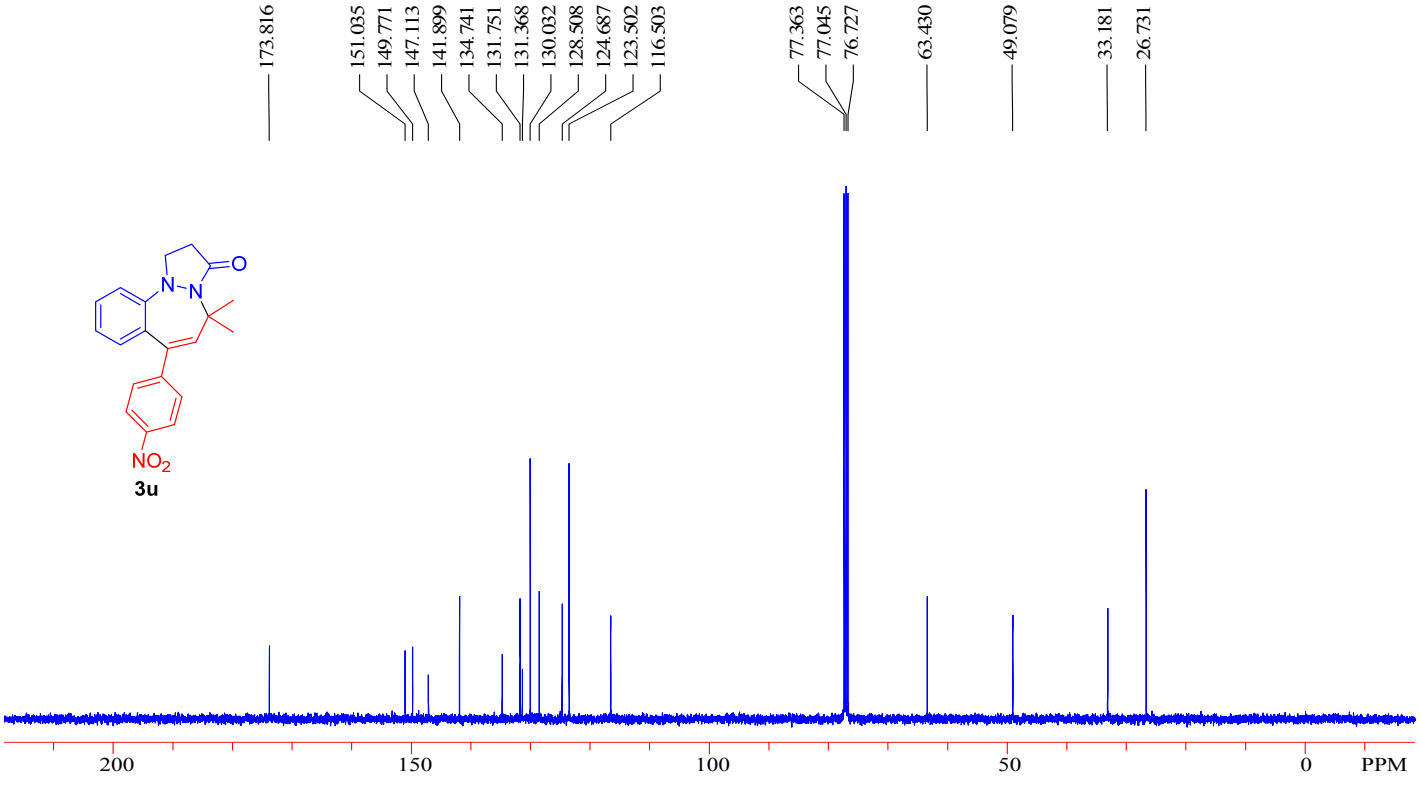
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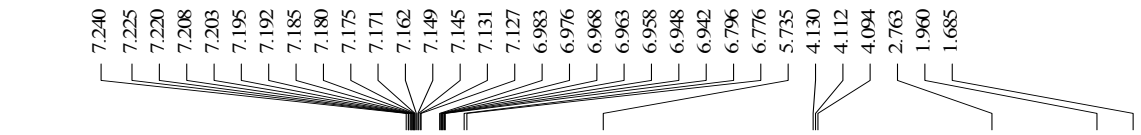
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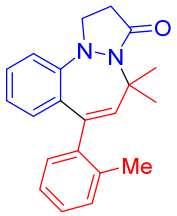
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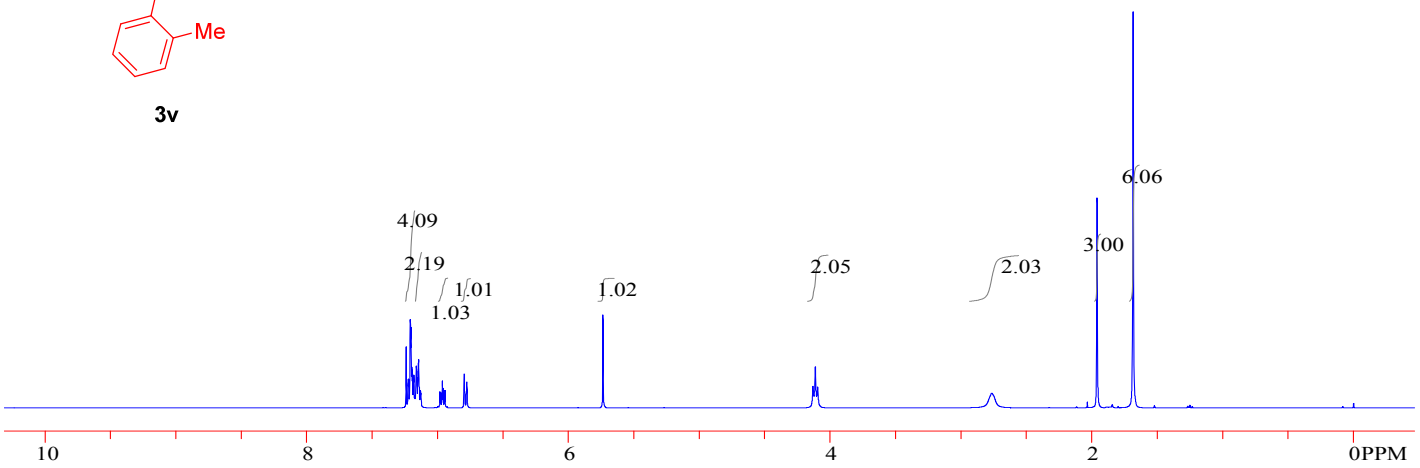
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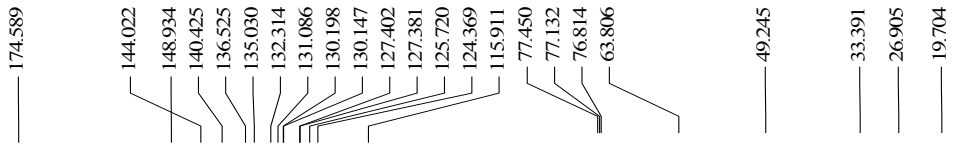
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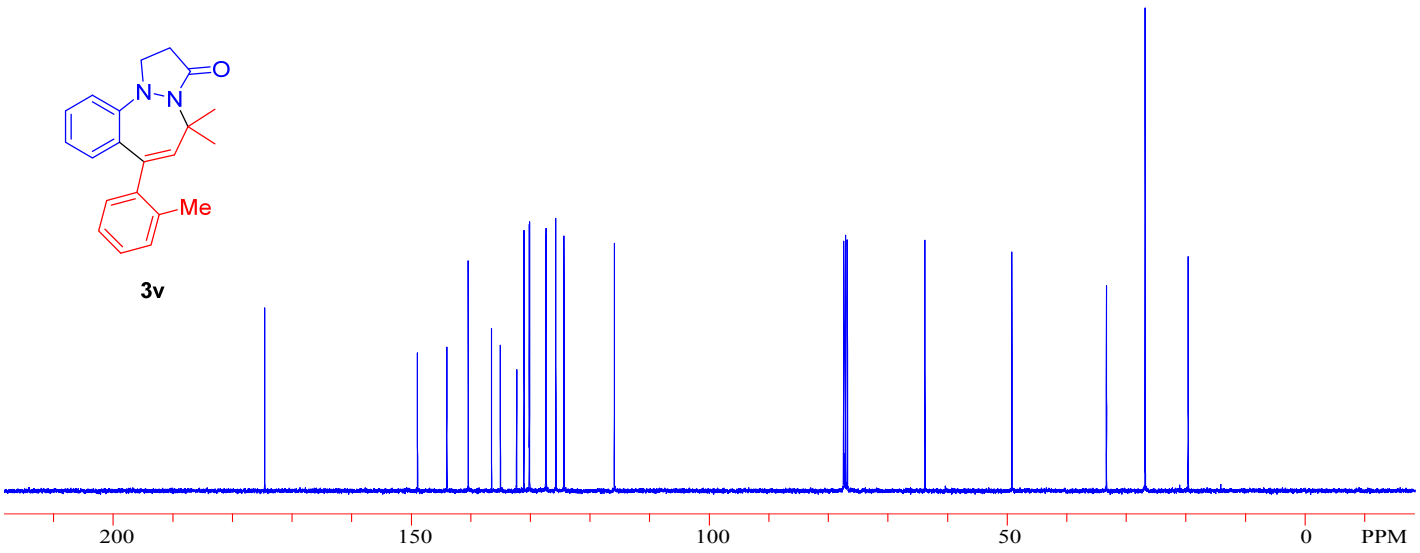
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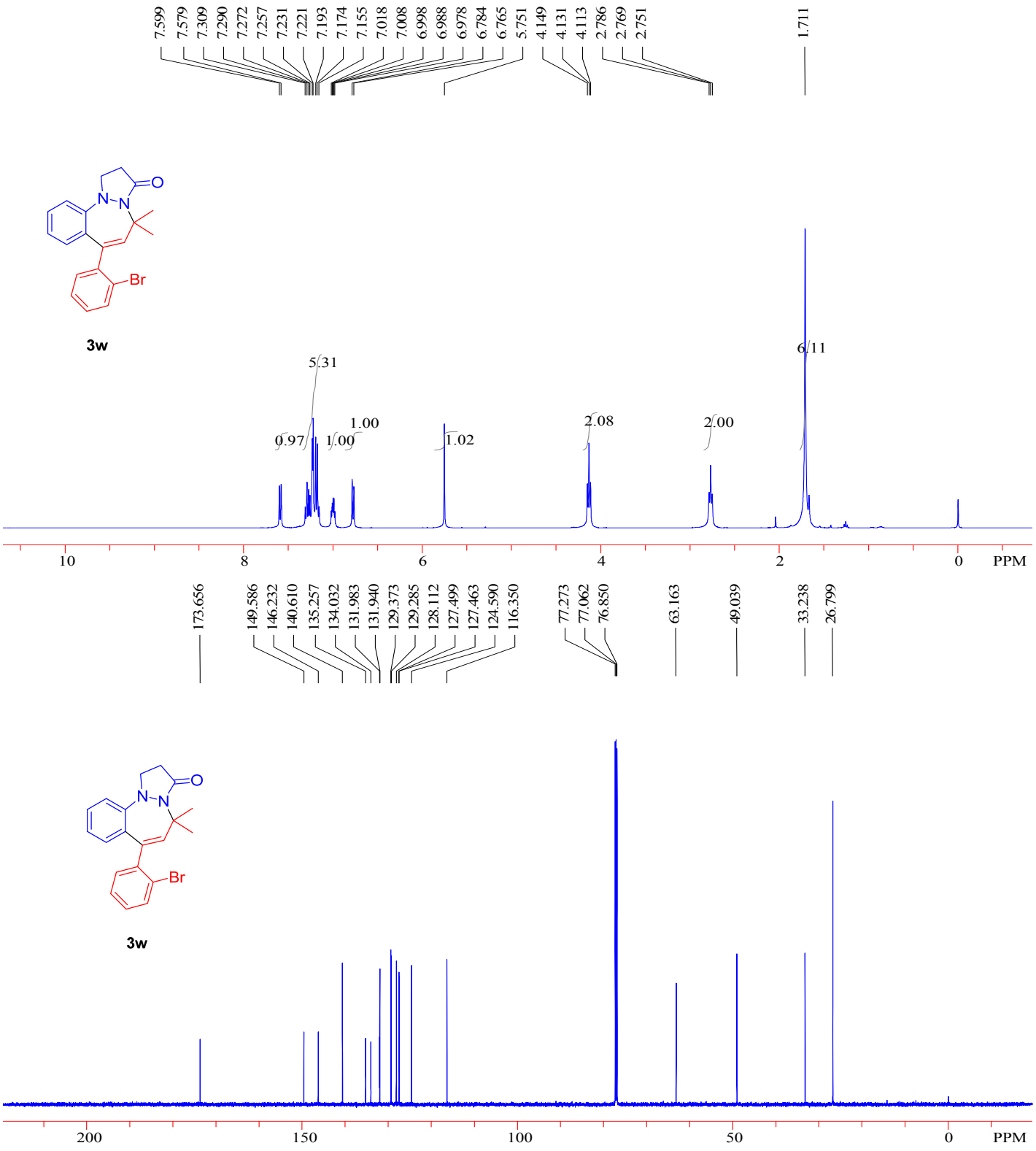
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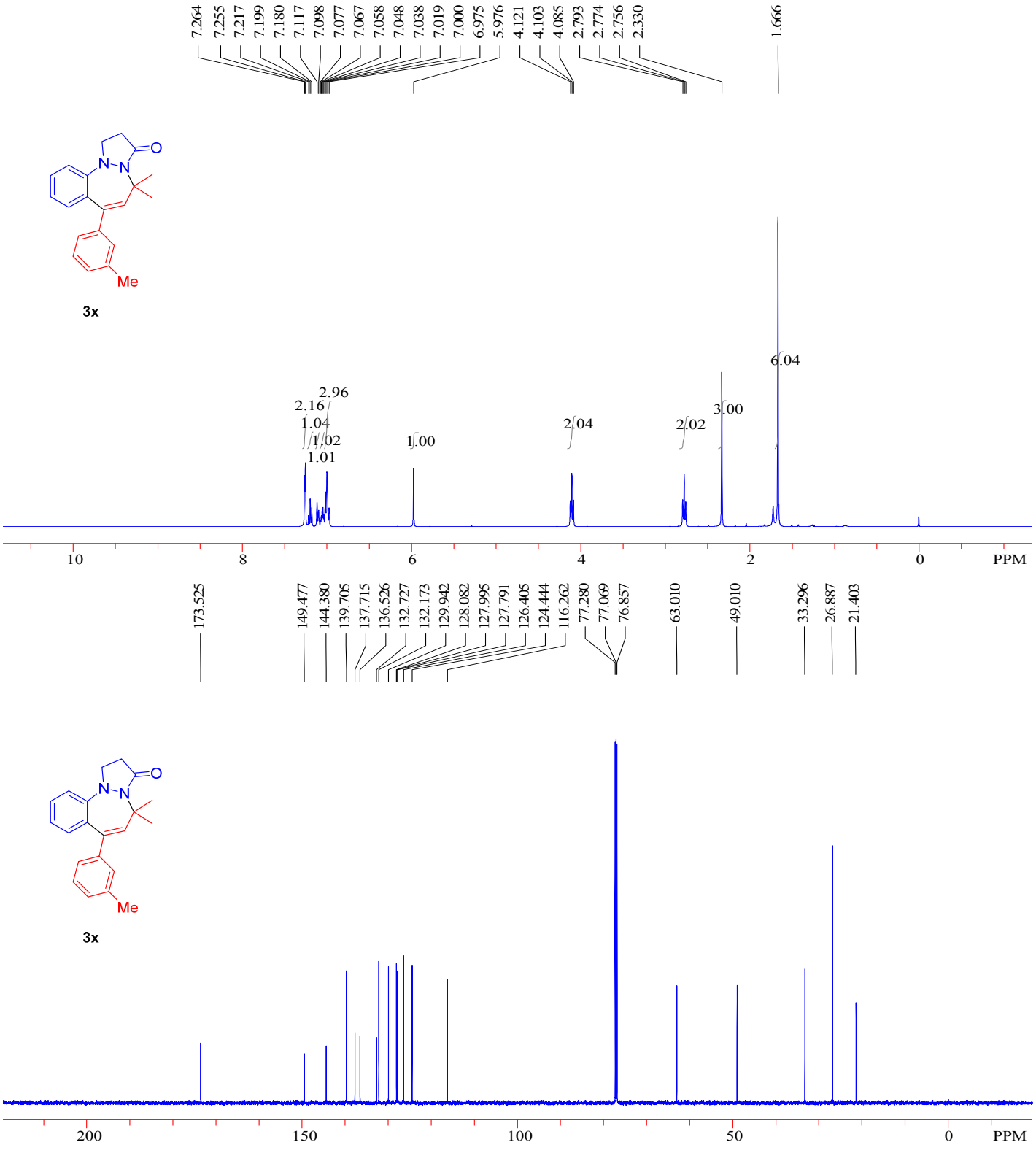
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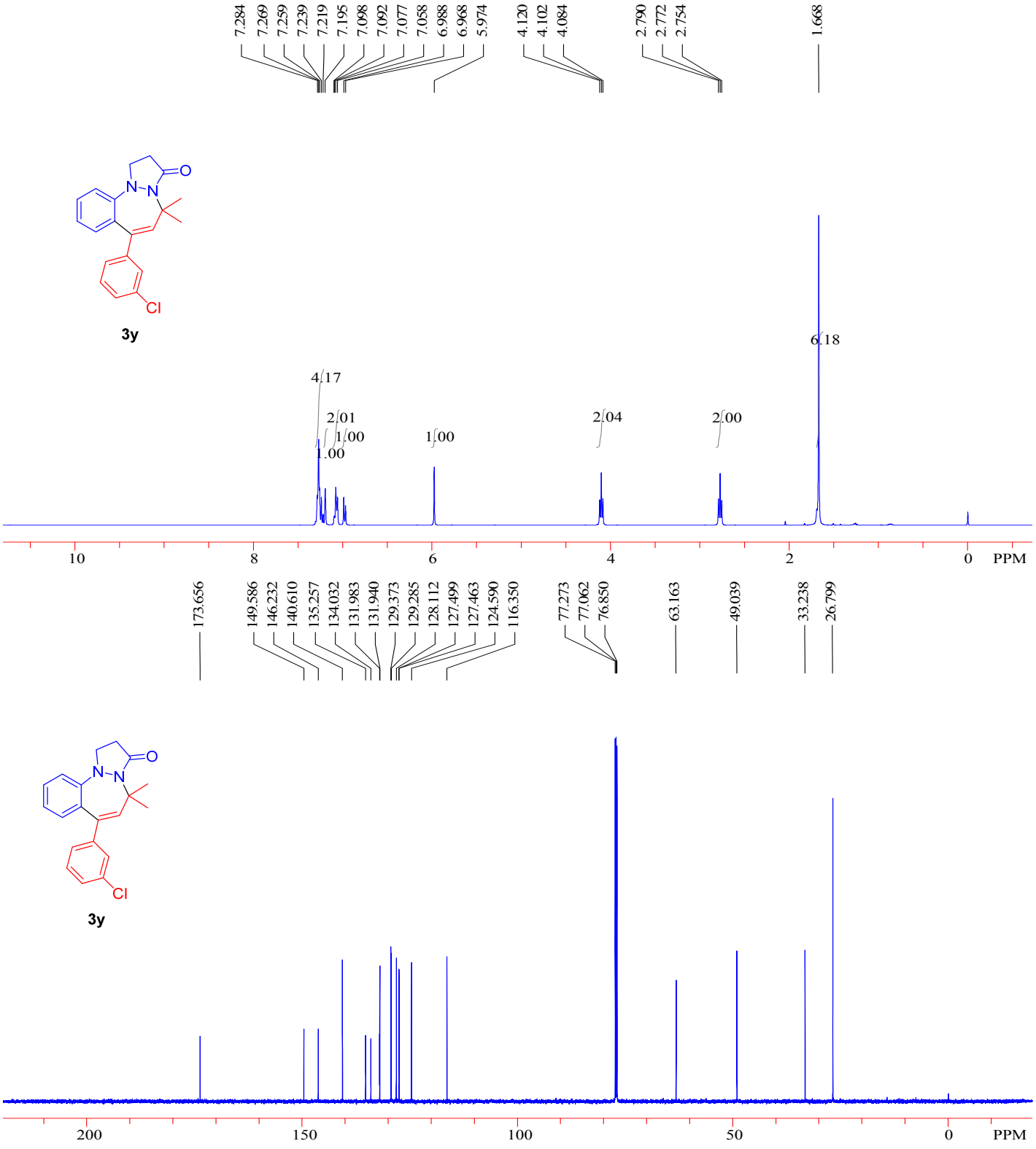
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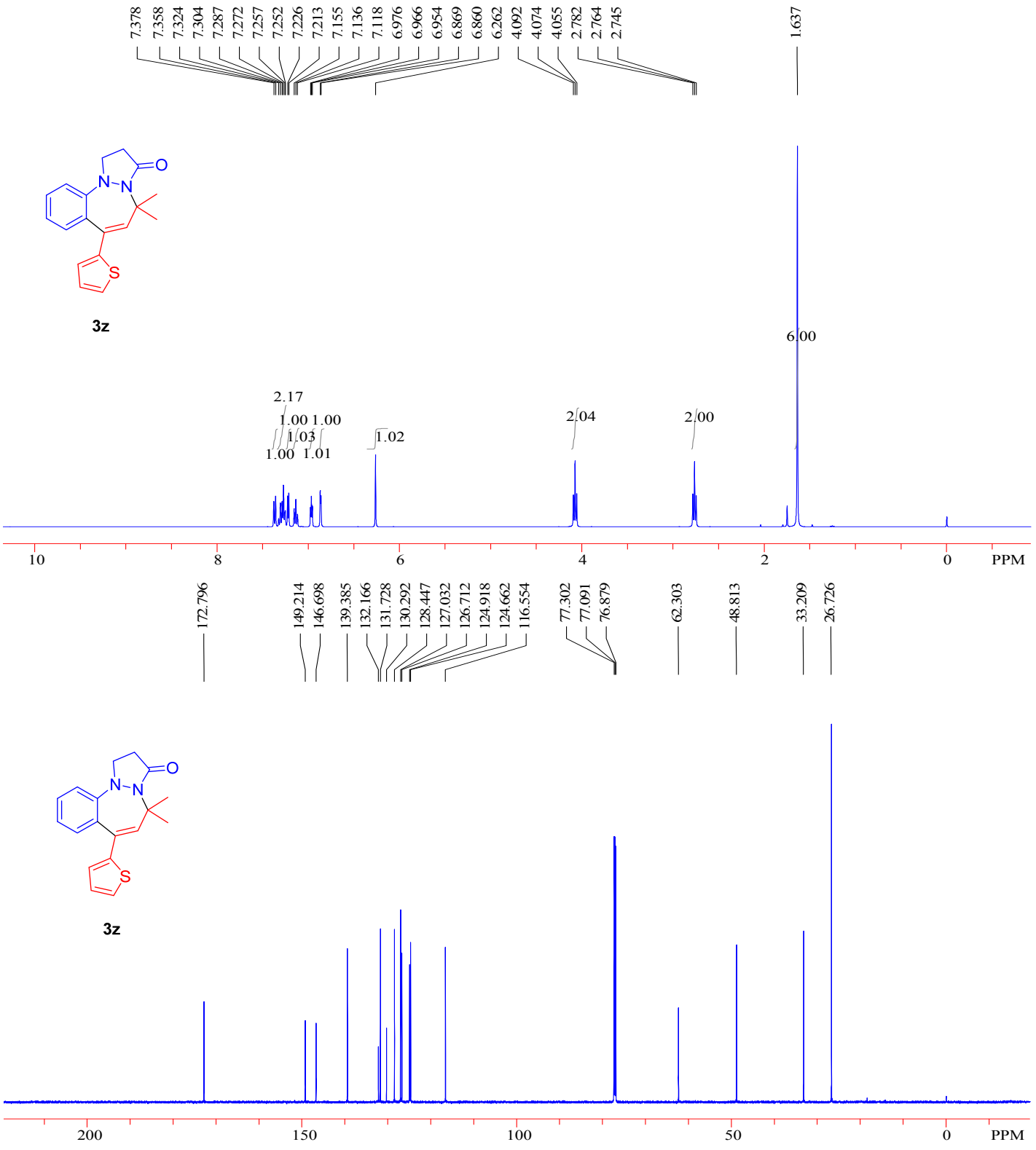
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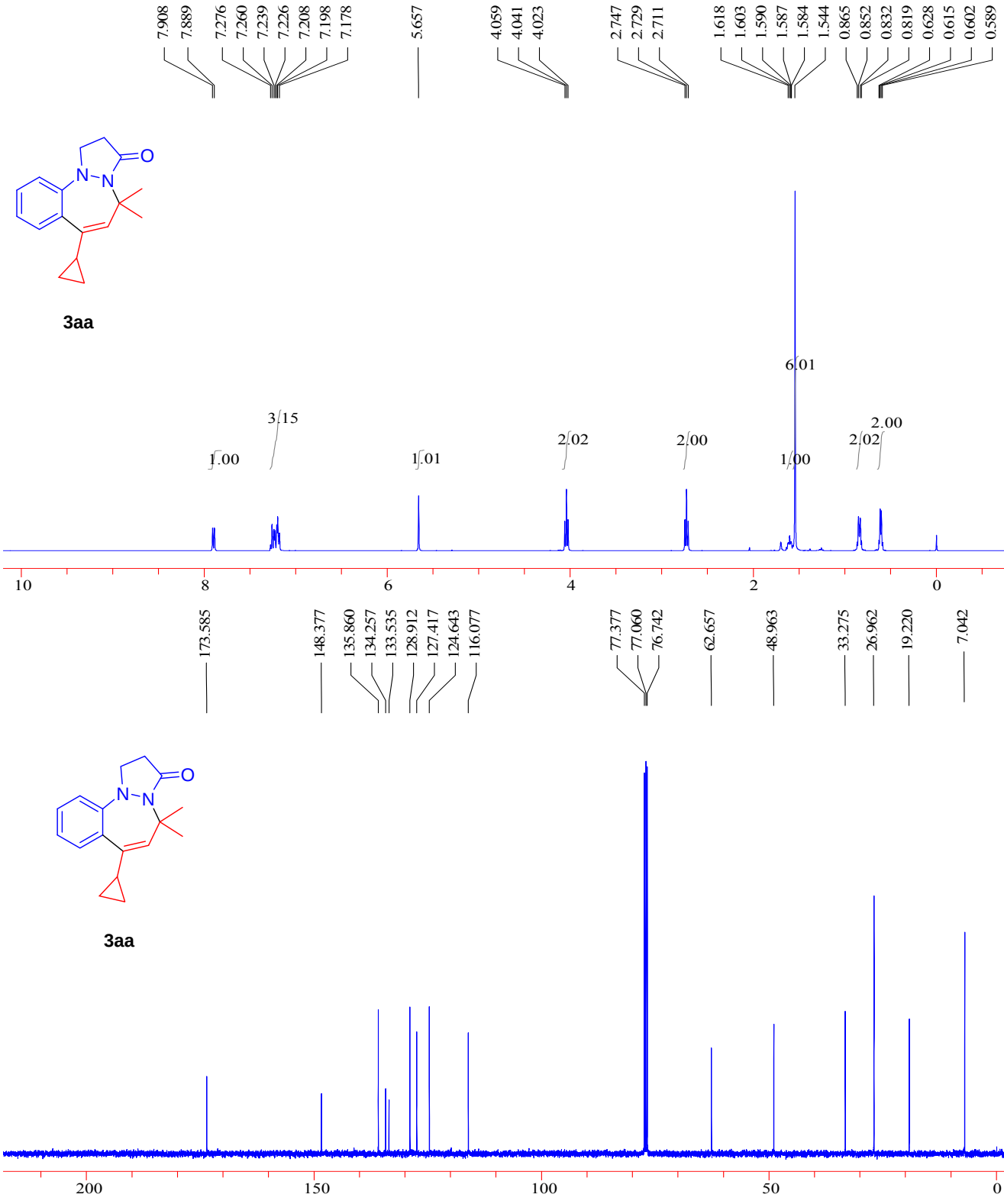
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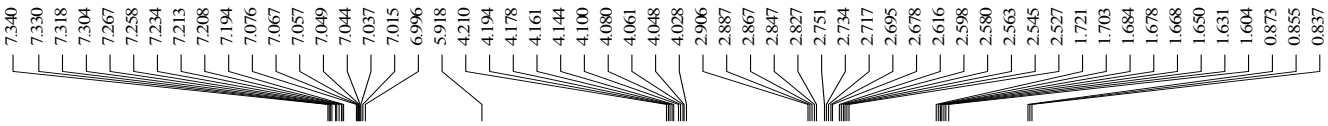
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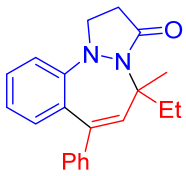
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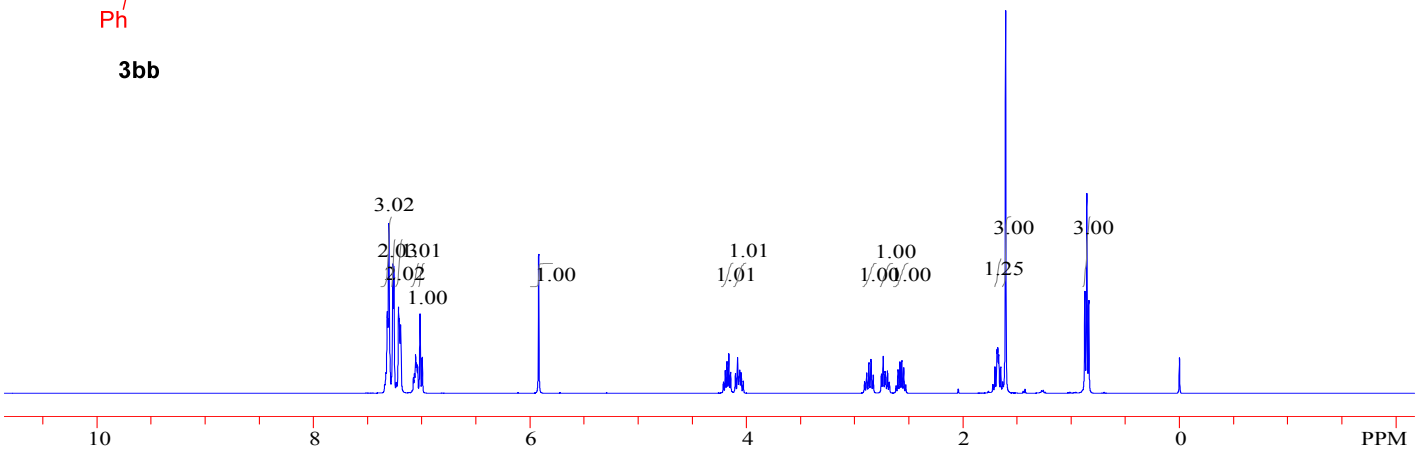
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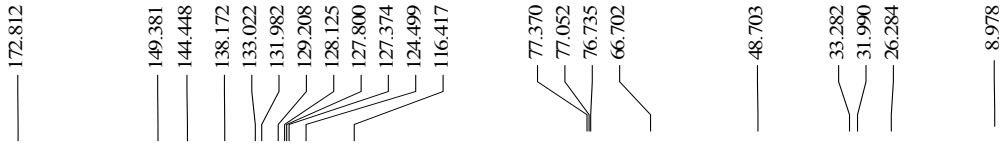
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Ph

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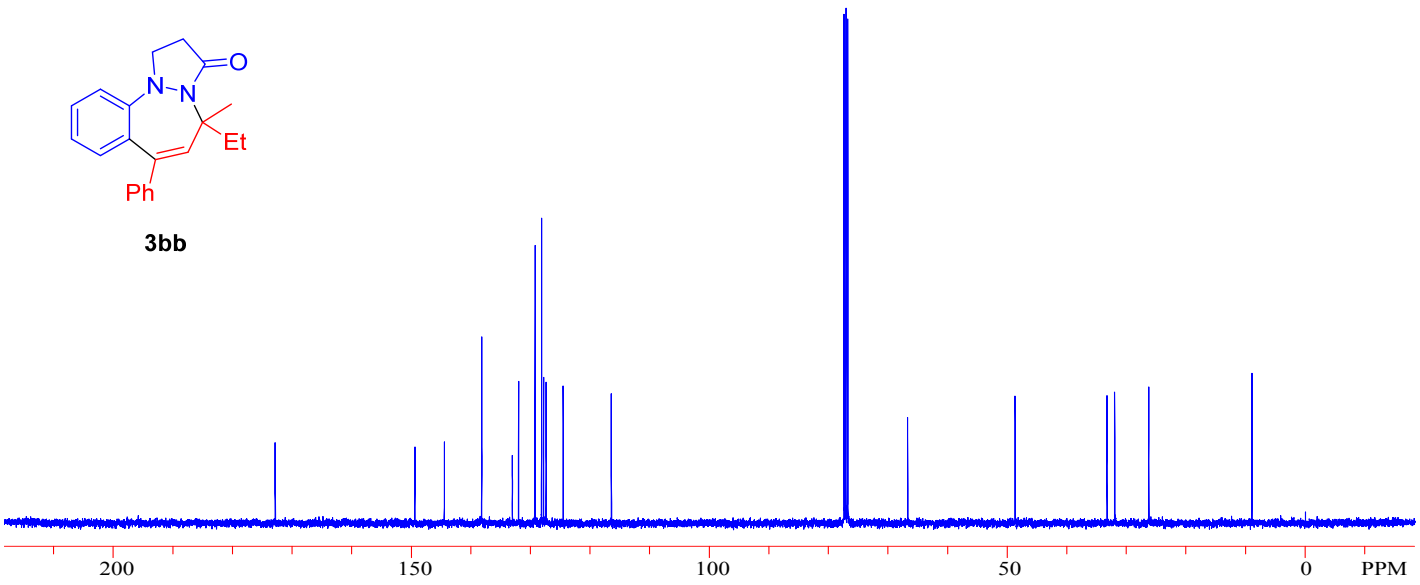
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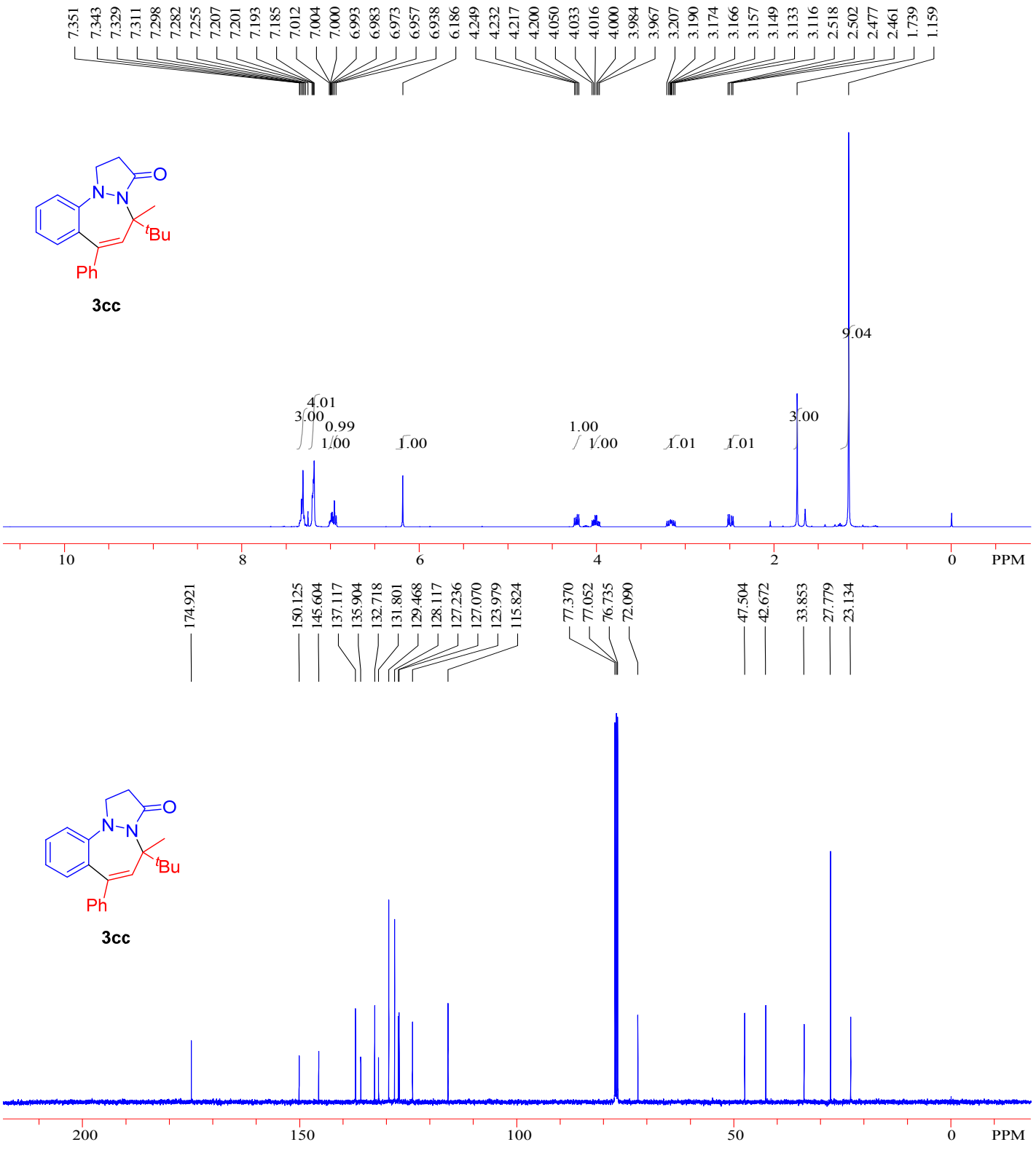
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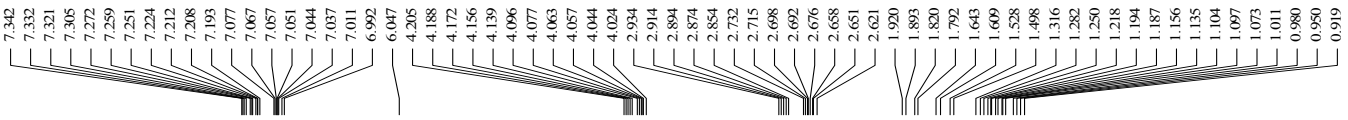
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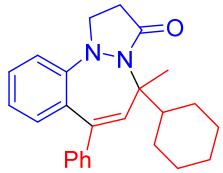
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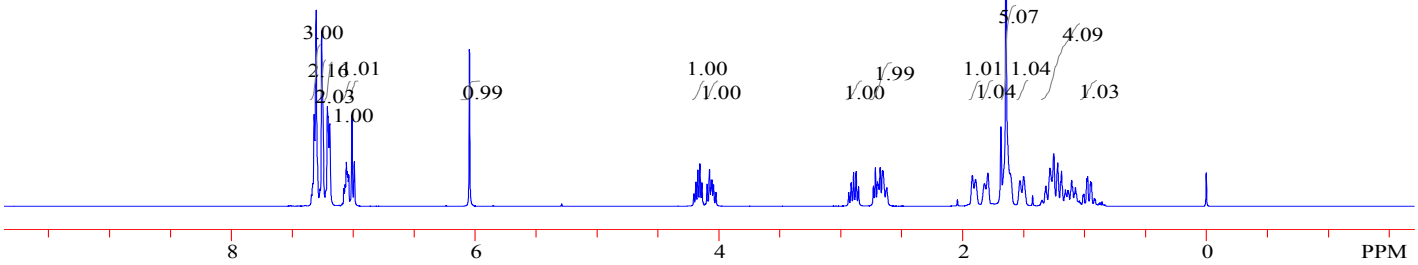
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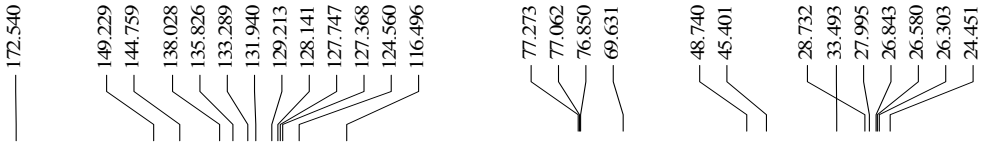
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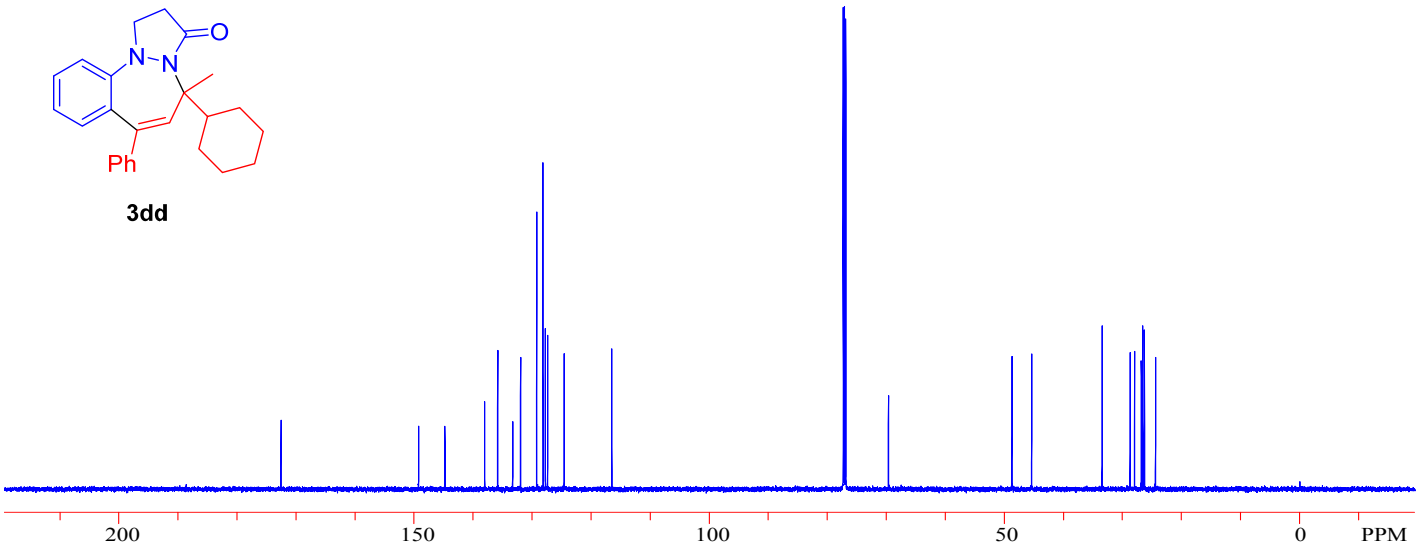
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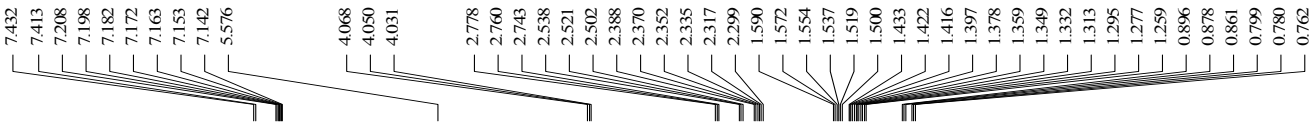
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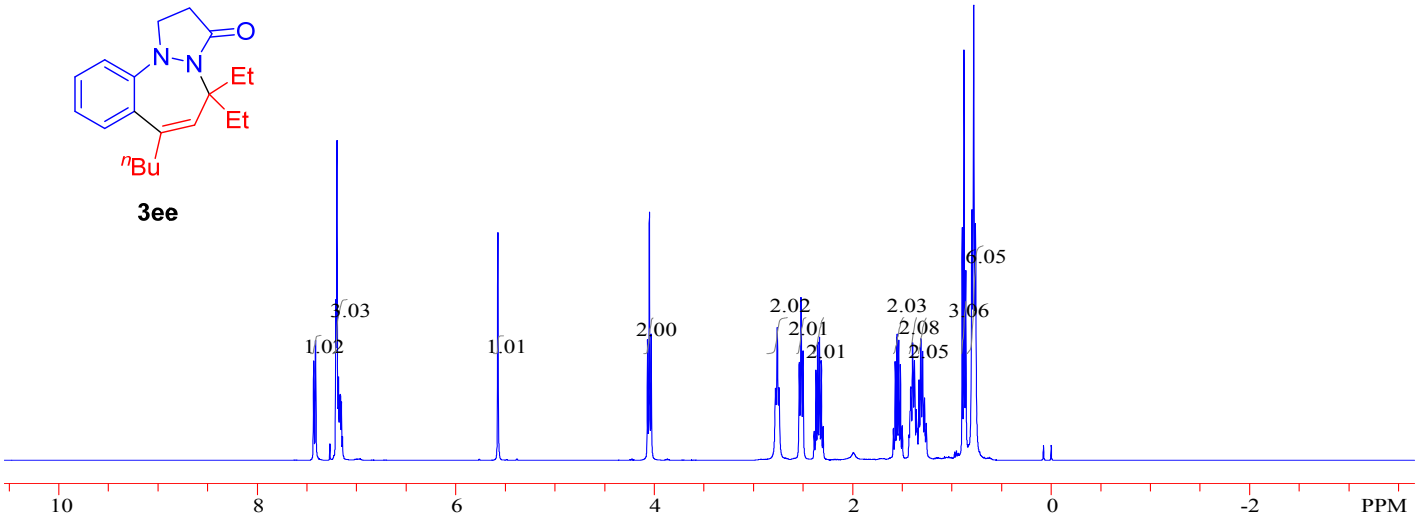
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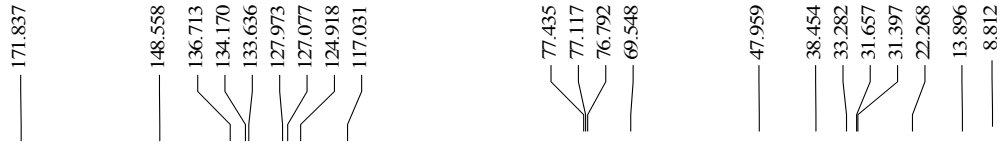
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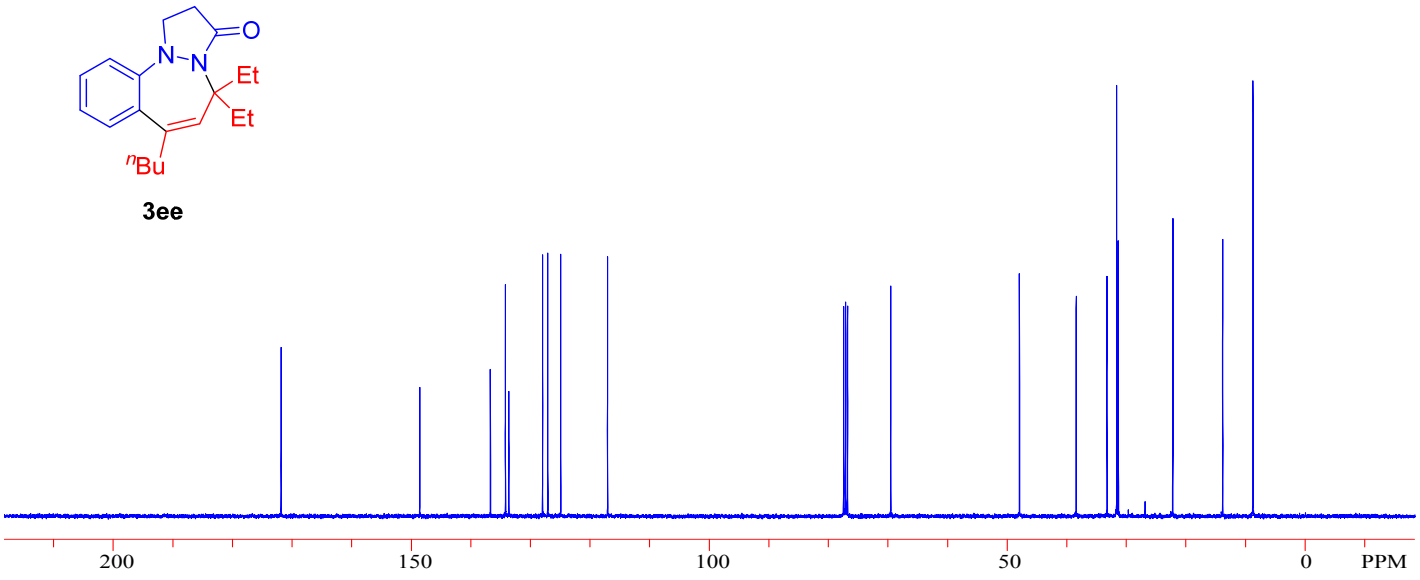
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Et
Et
nBu
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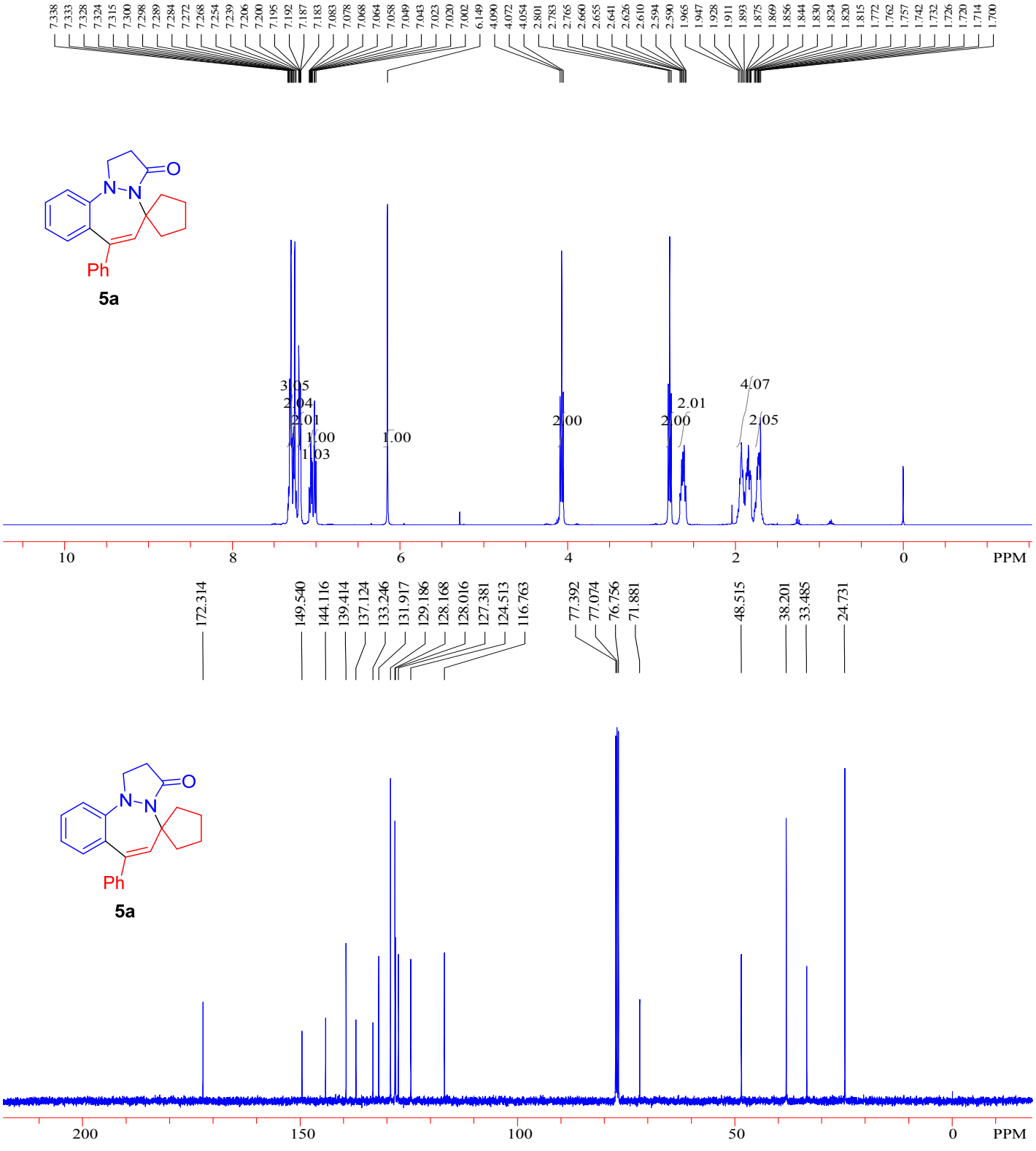
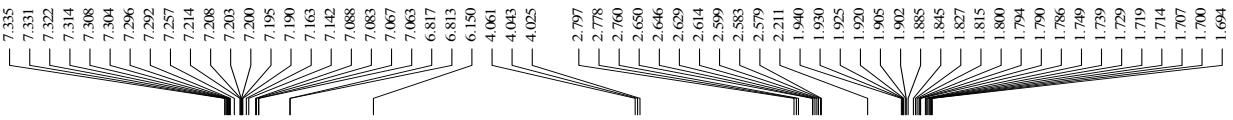
PPM

V. Copies of NMR spectra of 5a-5m

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6.150
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4.043
4.025
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1.694

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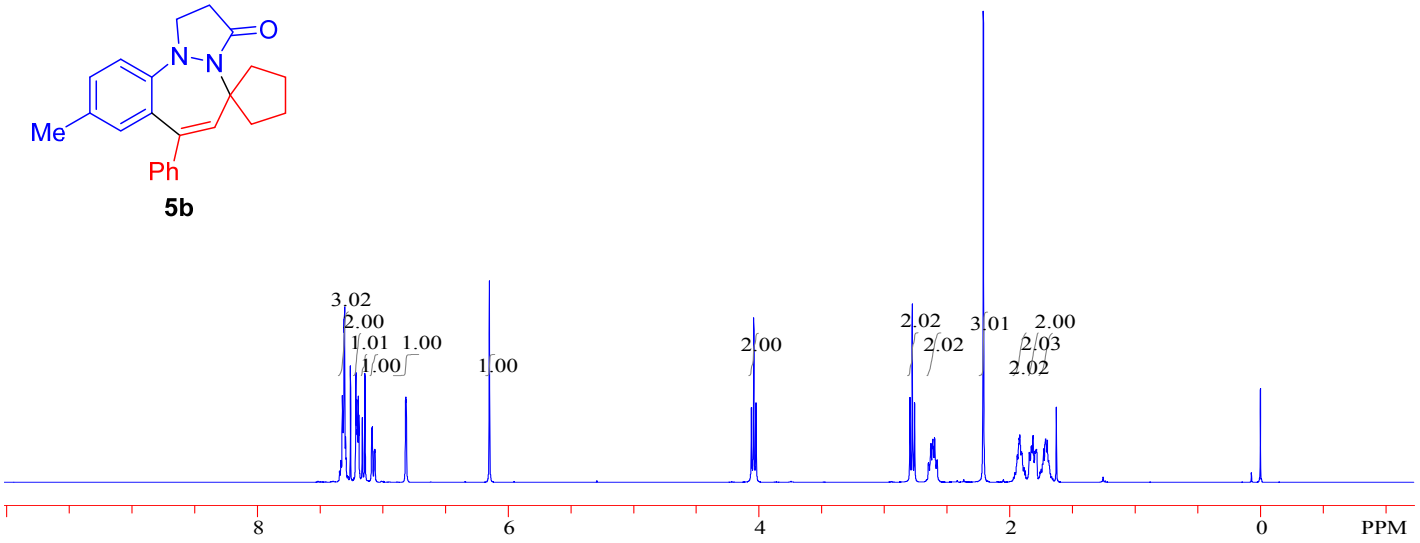
N
Me
Ph

5b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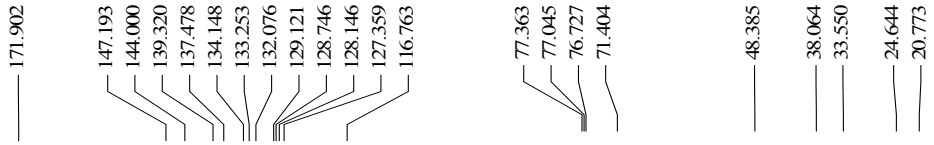
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132.076
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77.363
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71.404
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38.064
33.550
24.644
20.773

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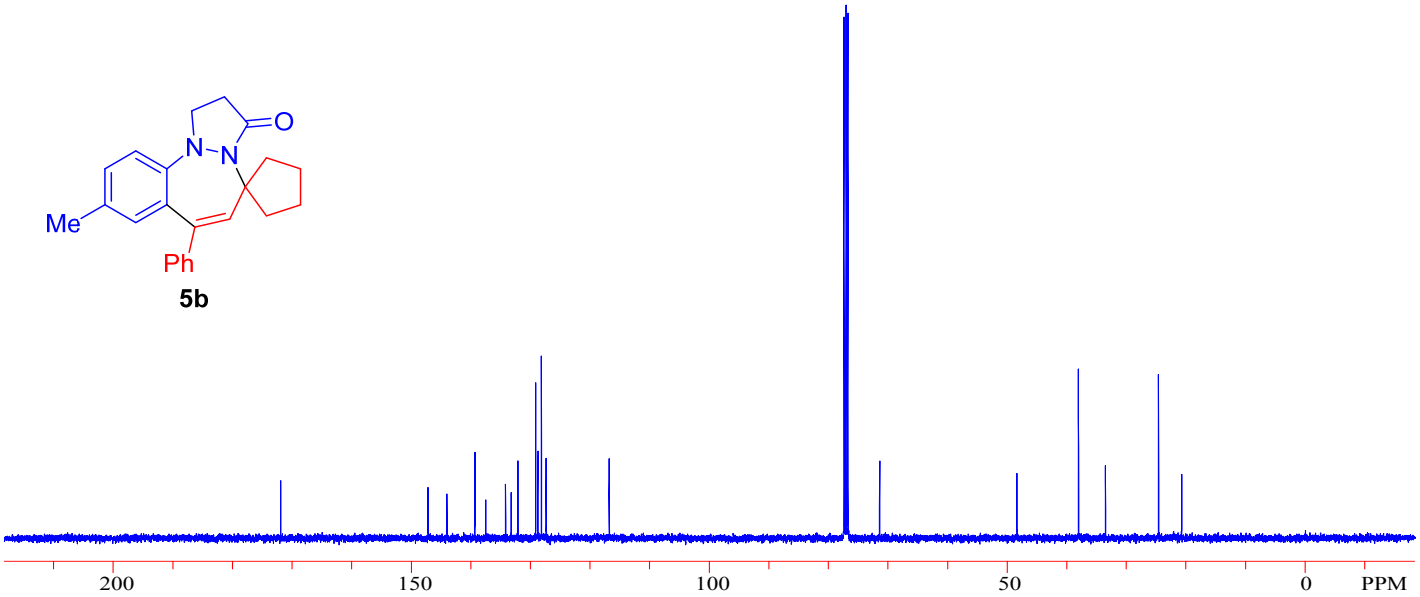
N
Me
Ph

5b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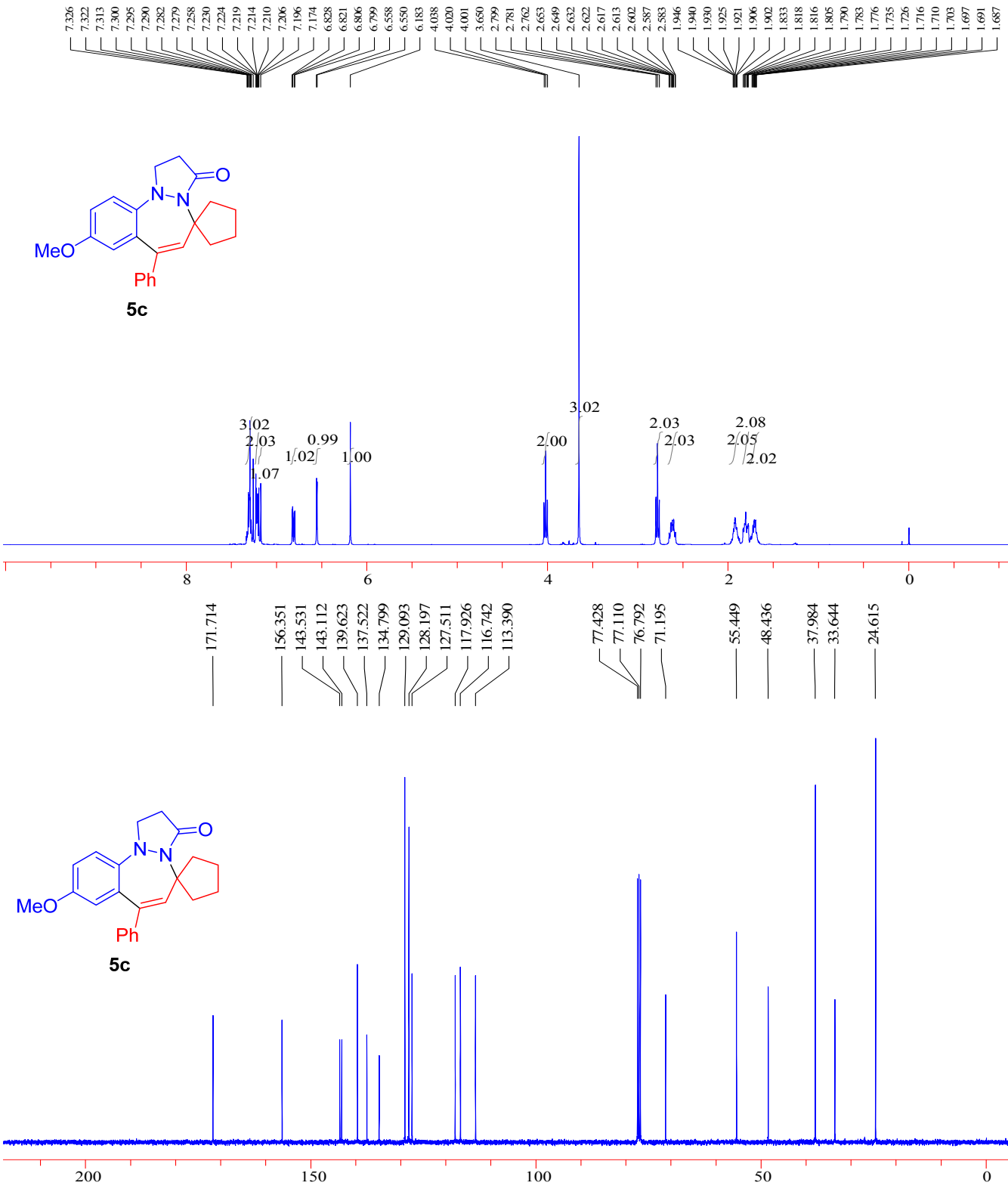
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MeO
Ph
5c
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2.05
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77.110
76.792
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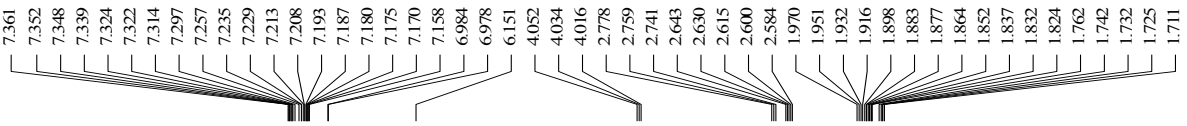
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7.180
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7.170
7.158
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4.016
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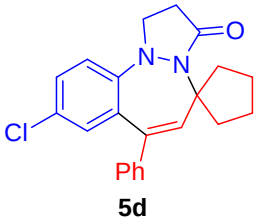
1.711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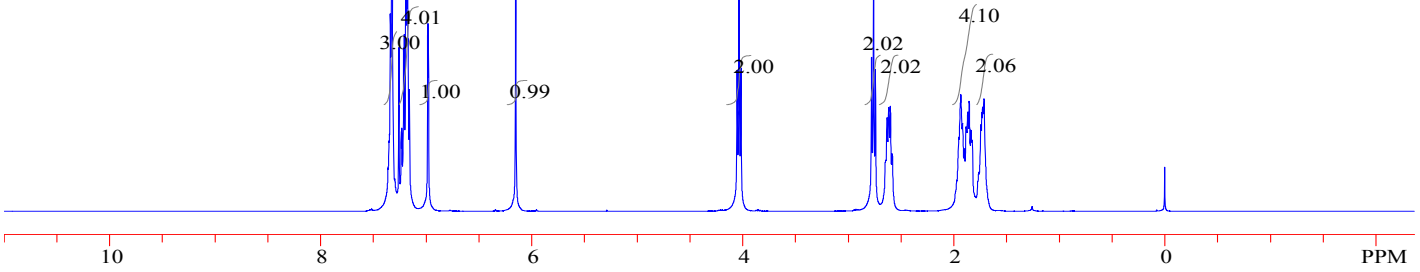
Cl
Ph

5d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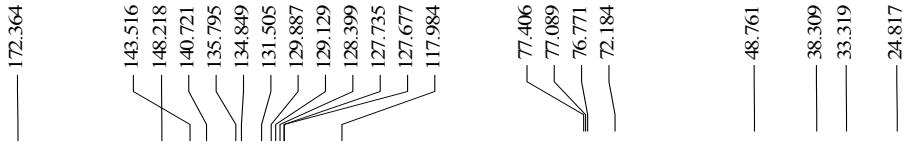
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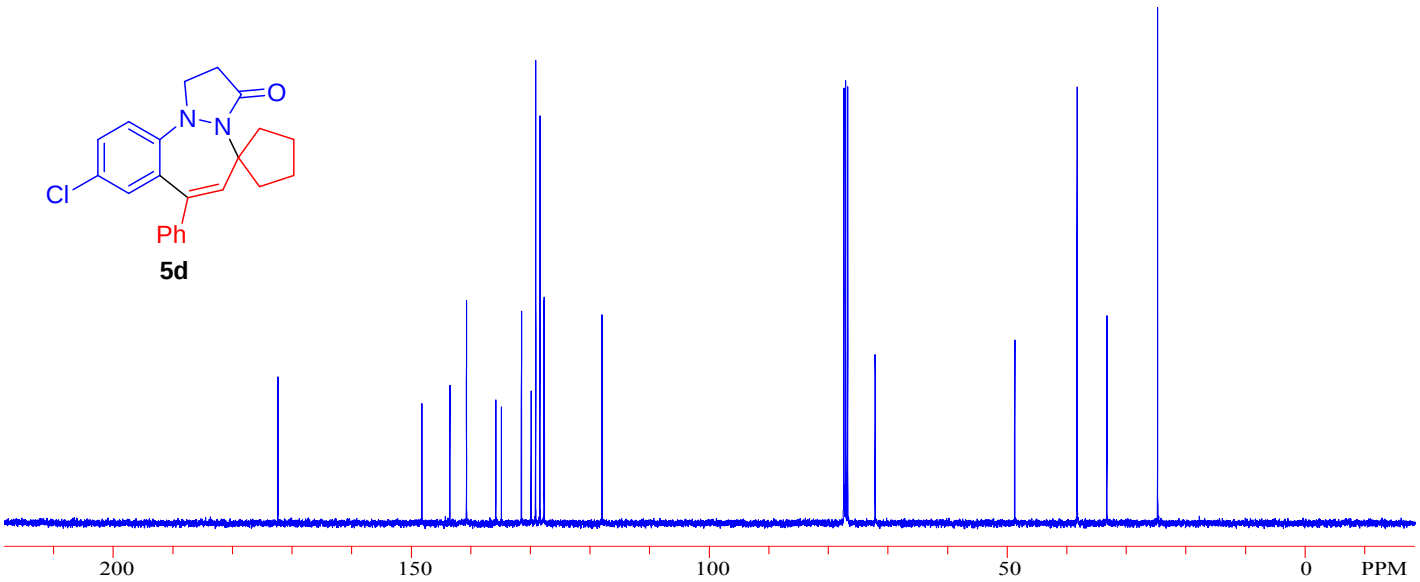
N
Cl
Ph

5d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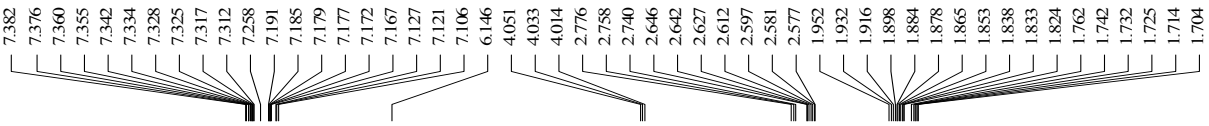
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7.177
7.172
7.167
7.127
7.121
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4.014
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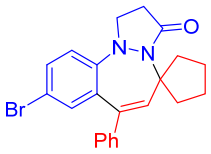
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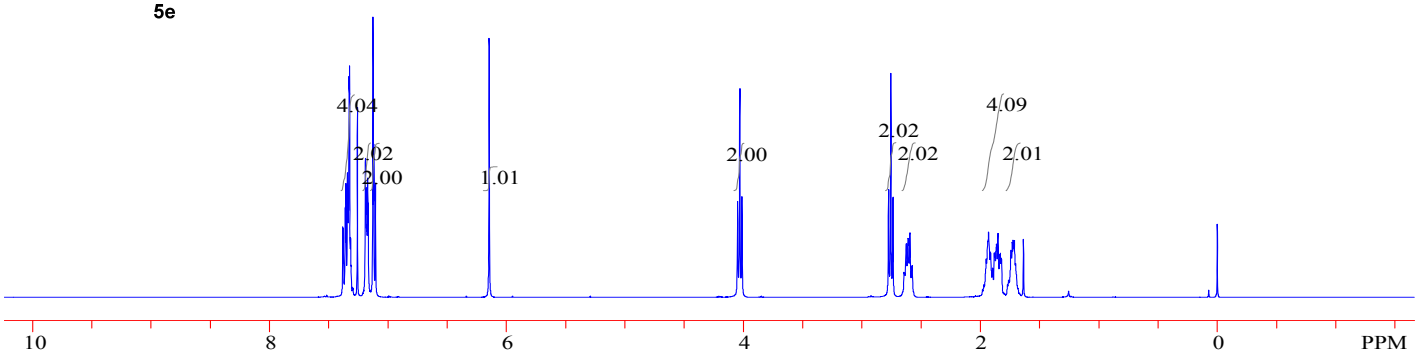
Br
Ph

5e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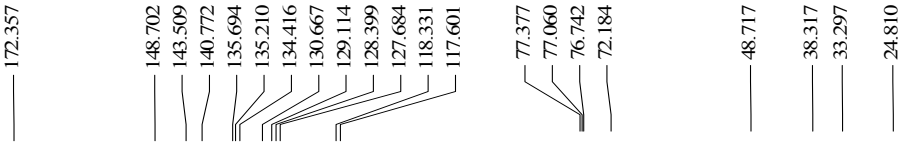
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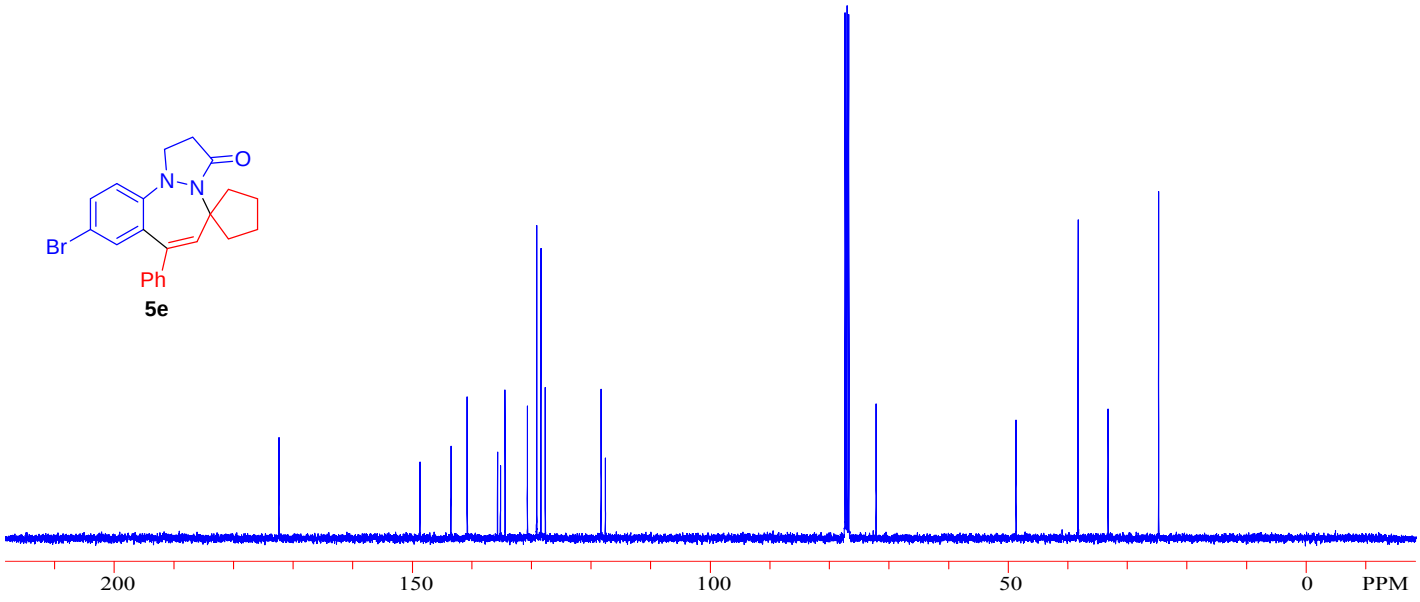
N
Br
Ph

5e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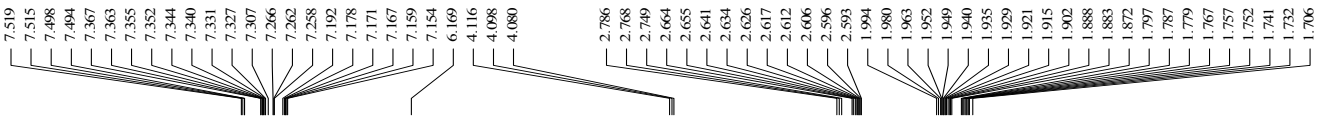
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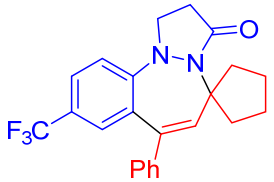
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F3C
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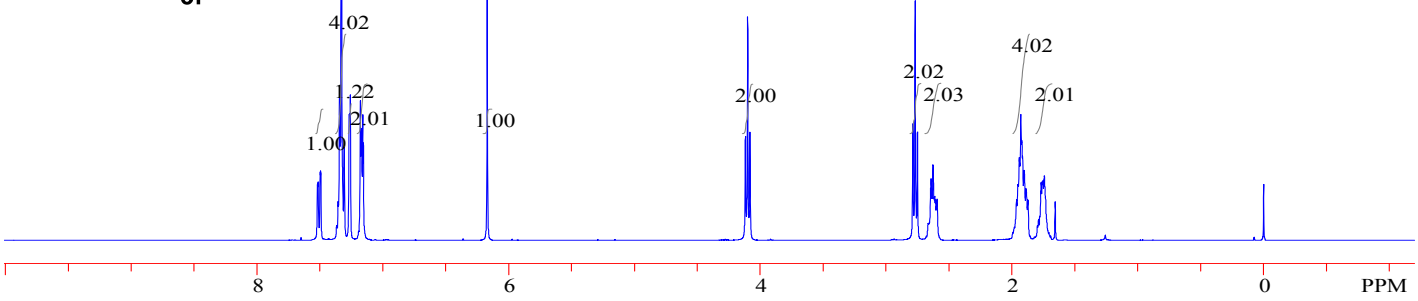
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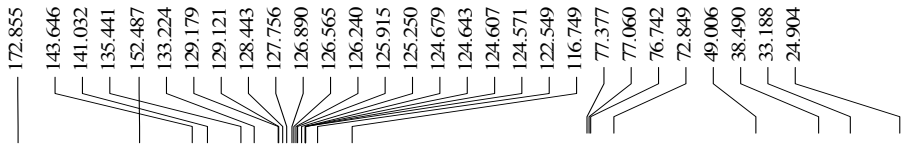
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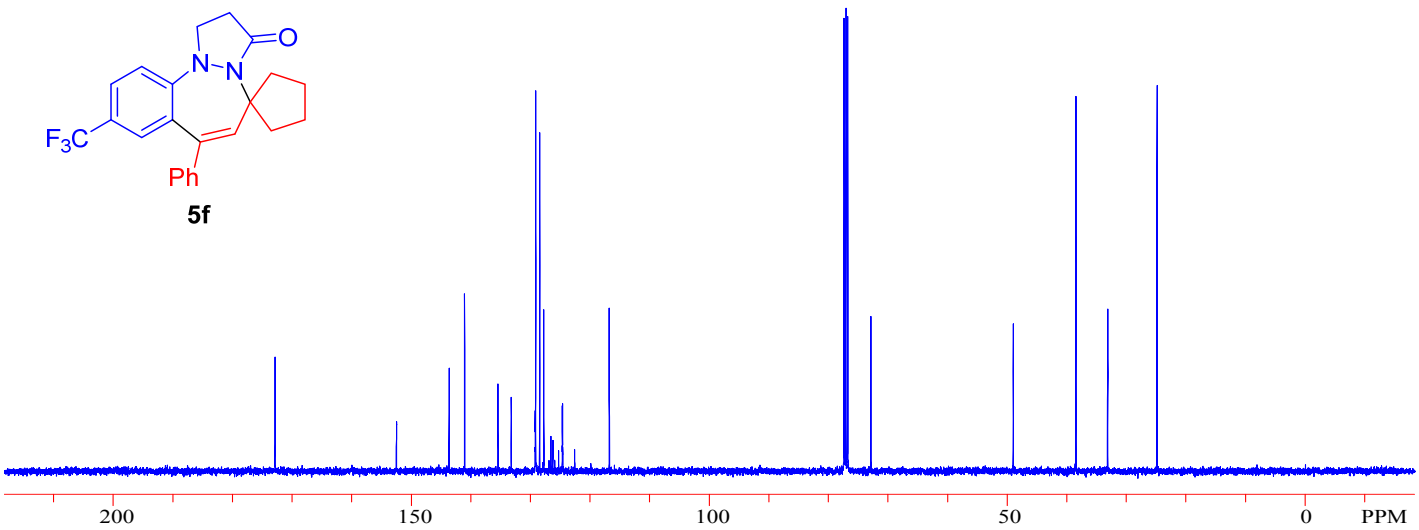
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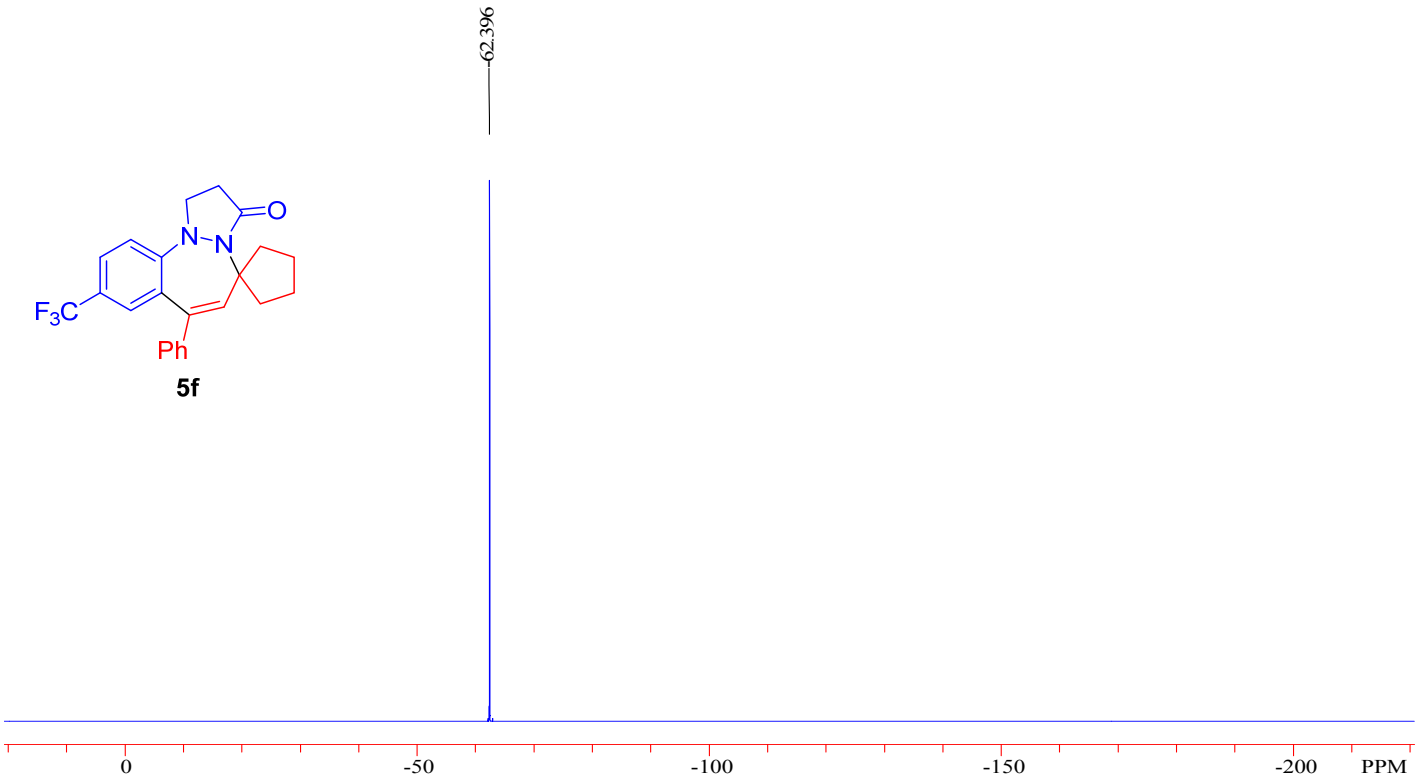

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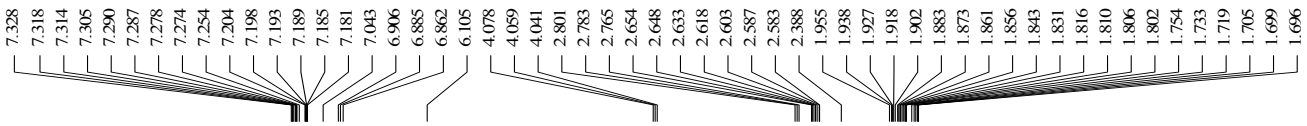
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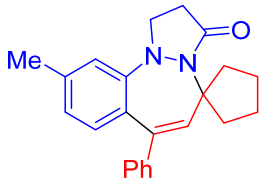
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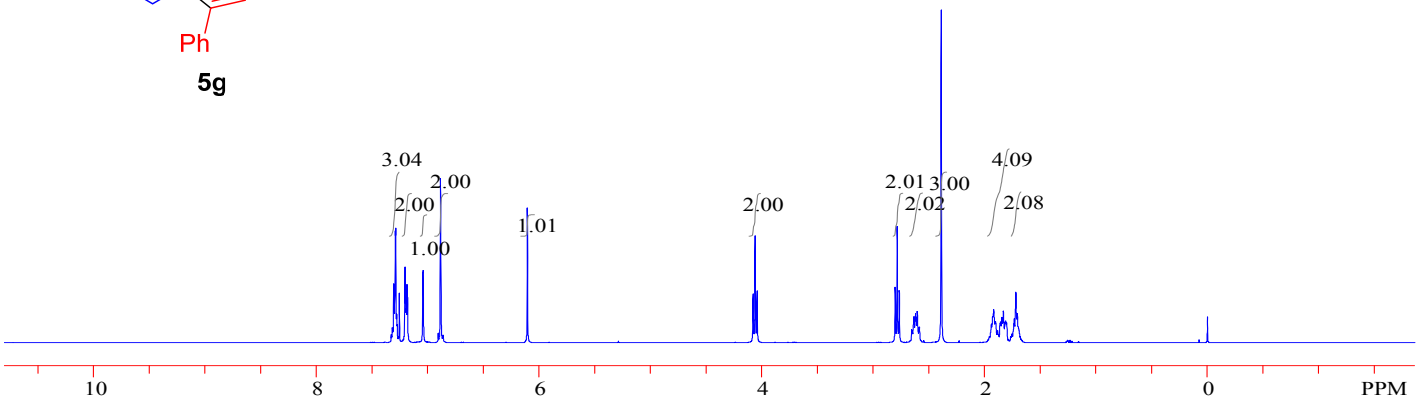
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2
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PPM


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Me
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N
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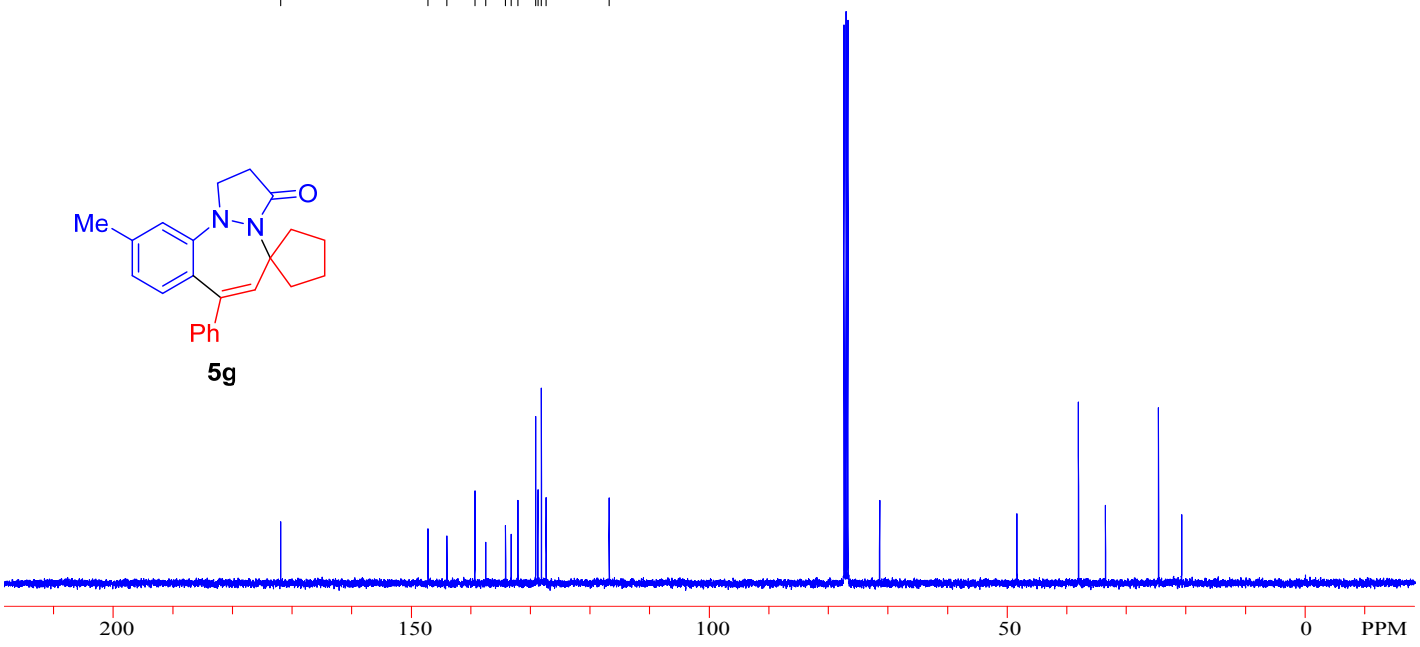
Ph

5g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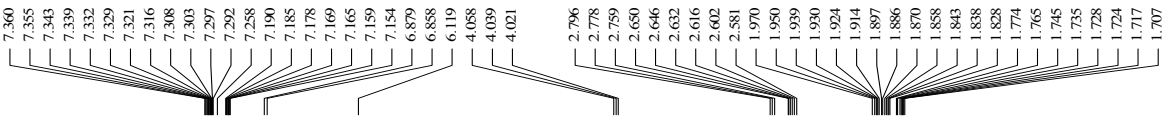
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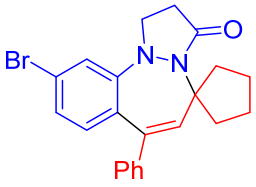
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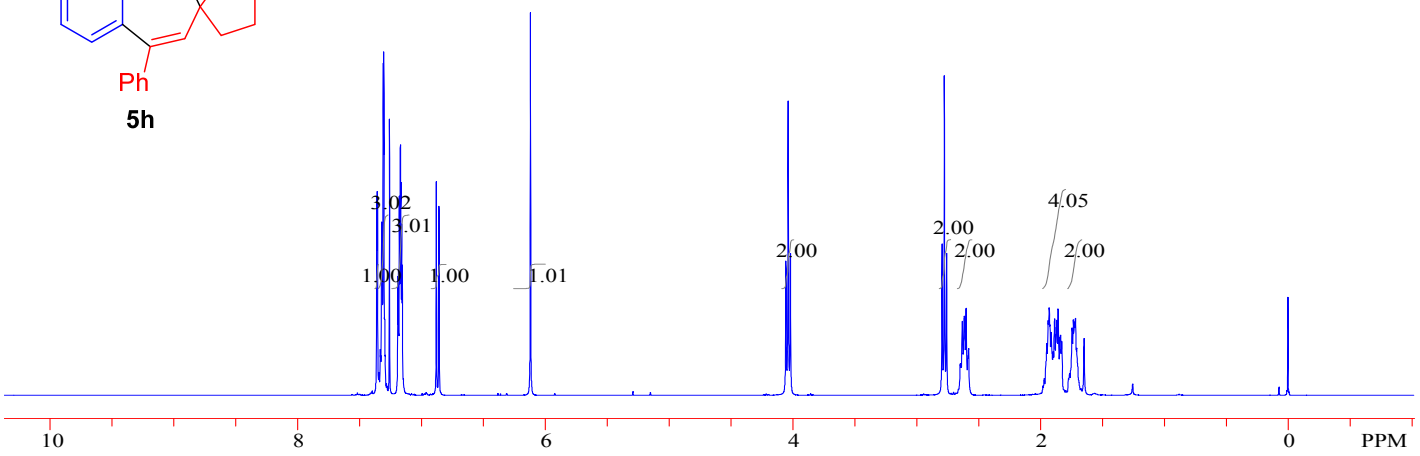
5h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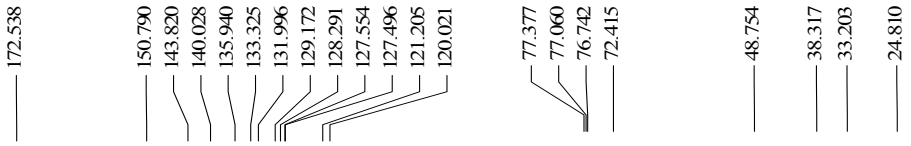
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Br
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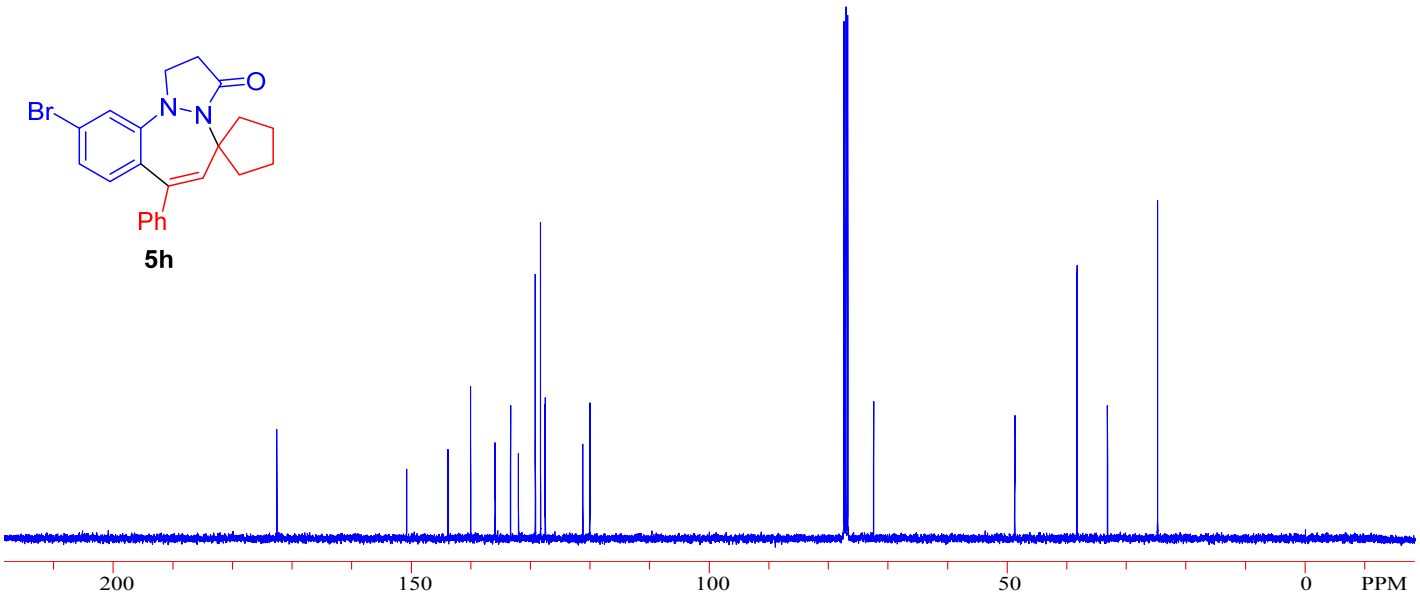
N
O
Ph

5h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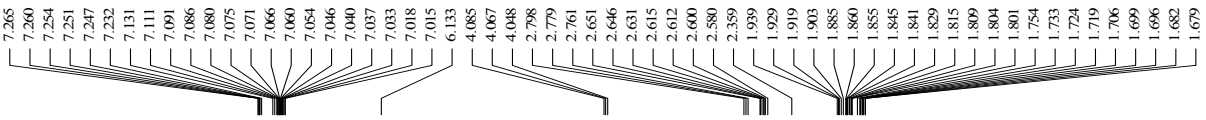
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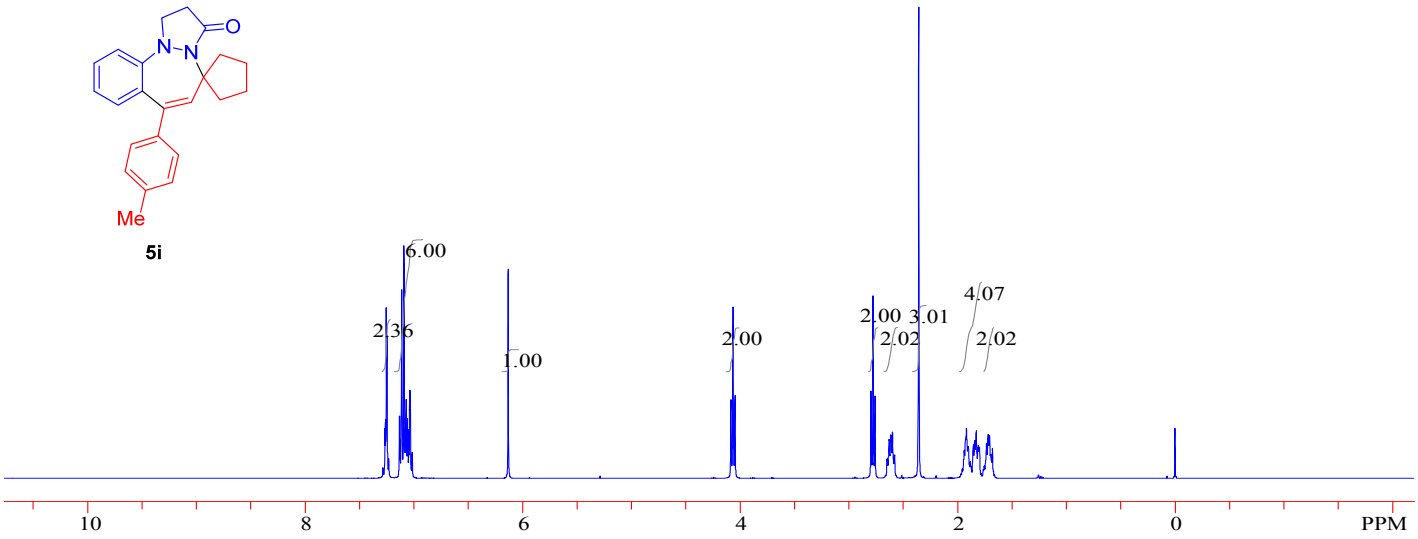
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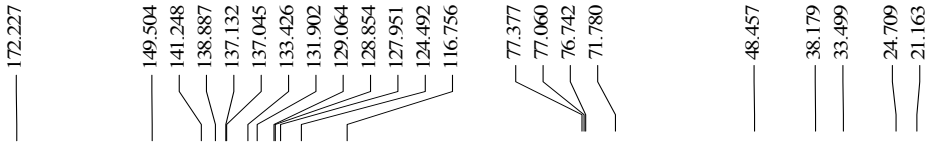
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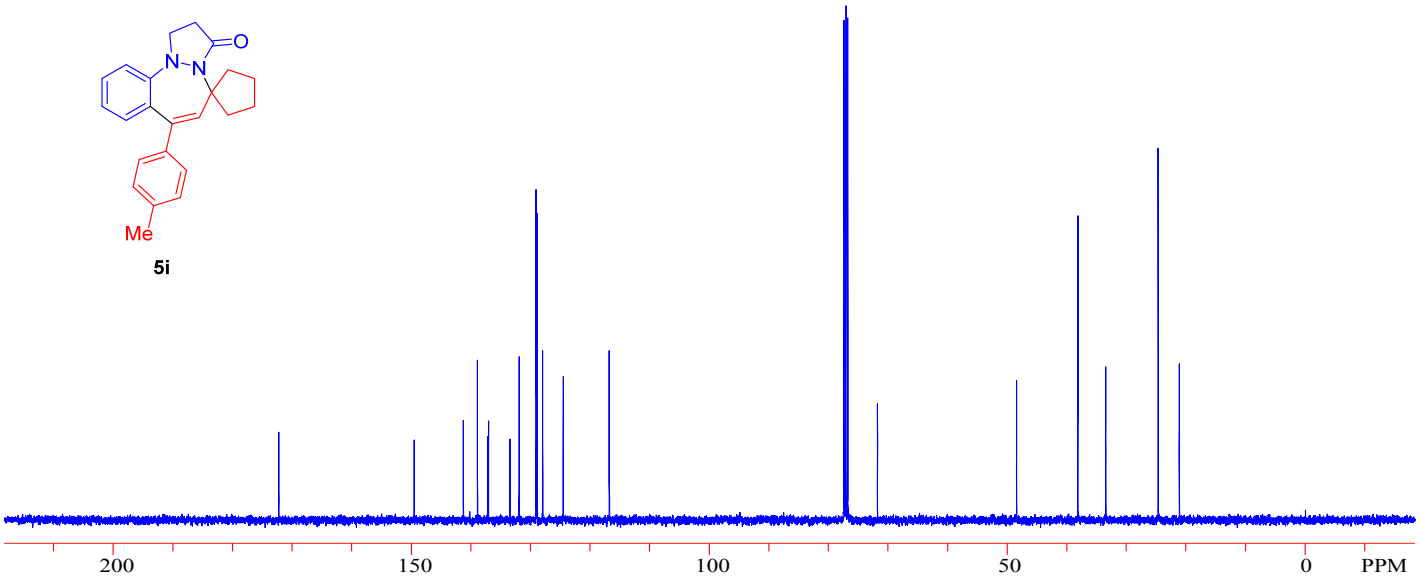
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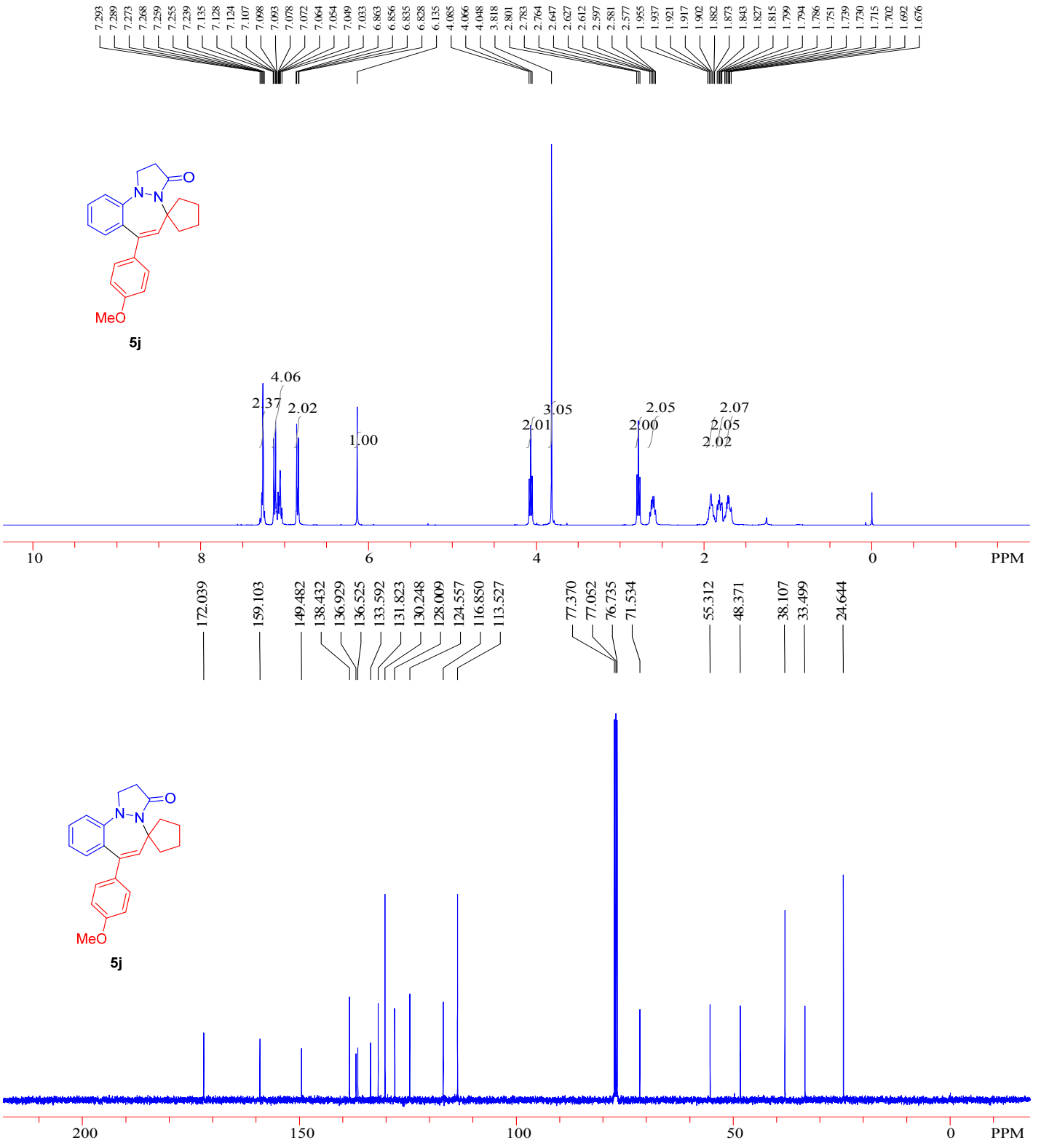
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7.124
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4.066
4.048
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1.715
1.702
1.692
1.676
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N
N
MeO
5j
4.06
2.37
2.02
1.00
2.01
3.05
2.00
2.05
2.02
2.05
2.07
10
8
6
4
2
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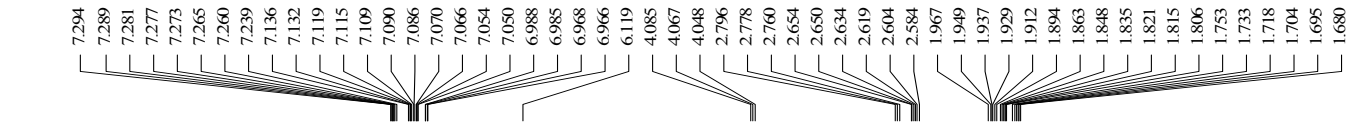
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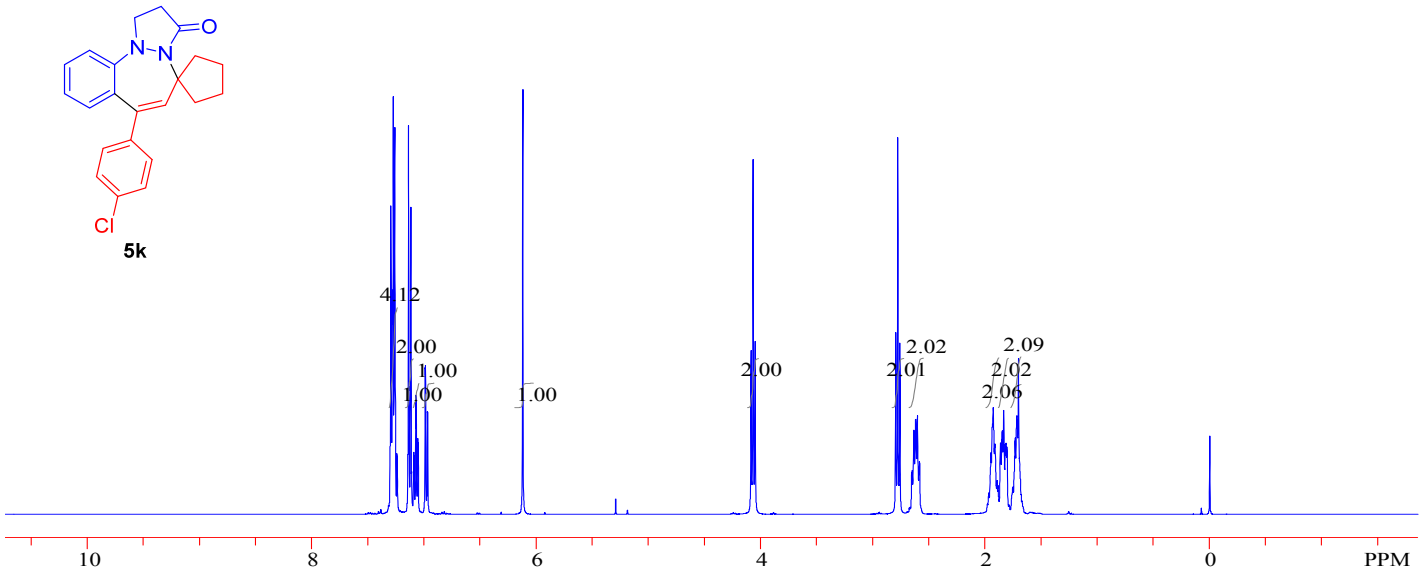
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10
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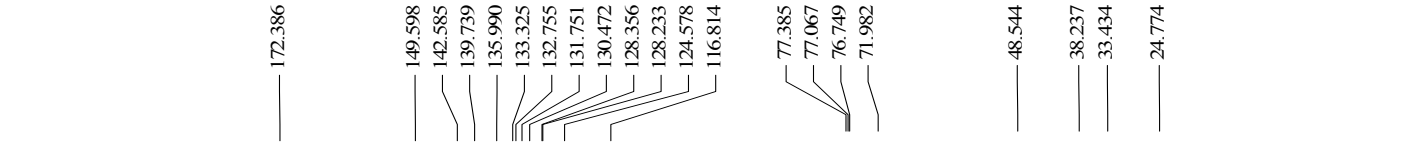
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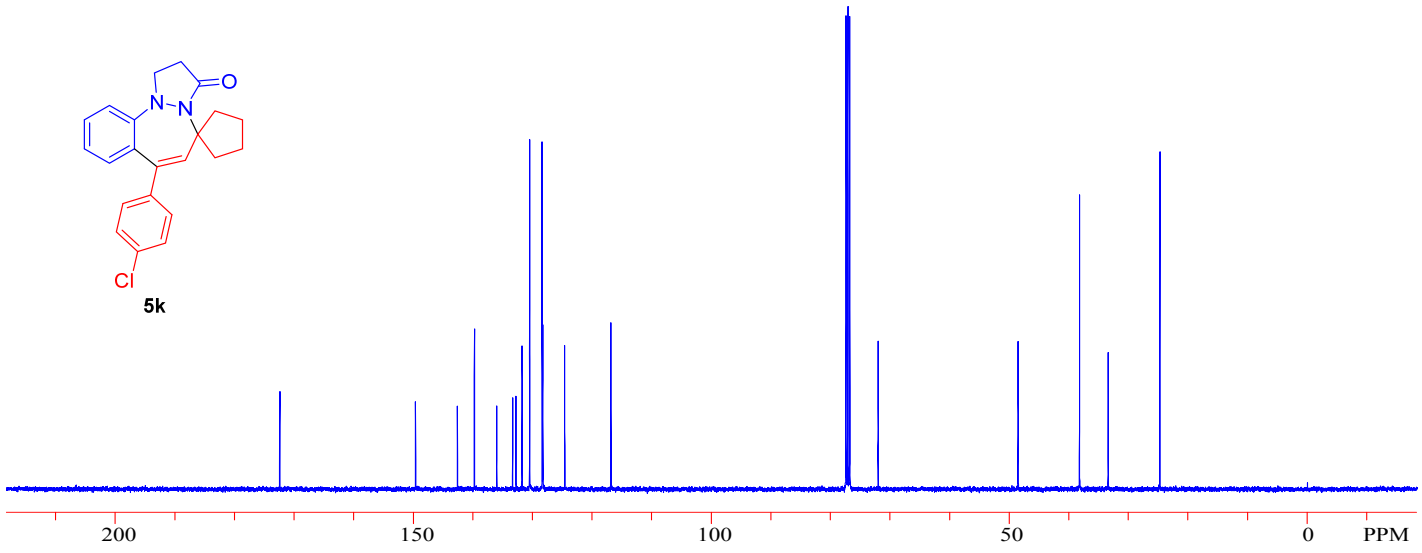
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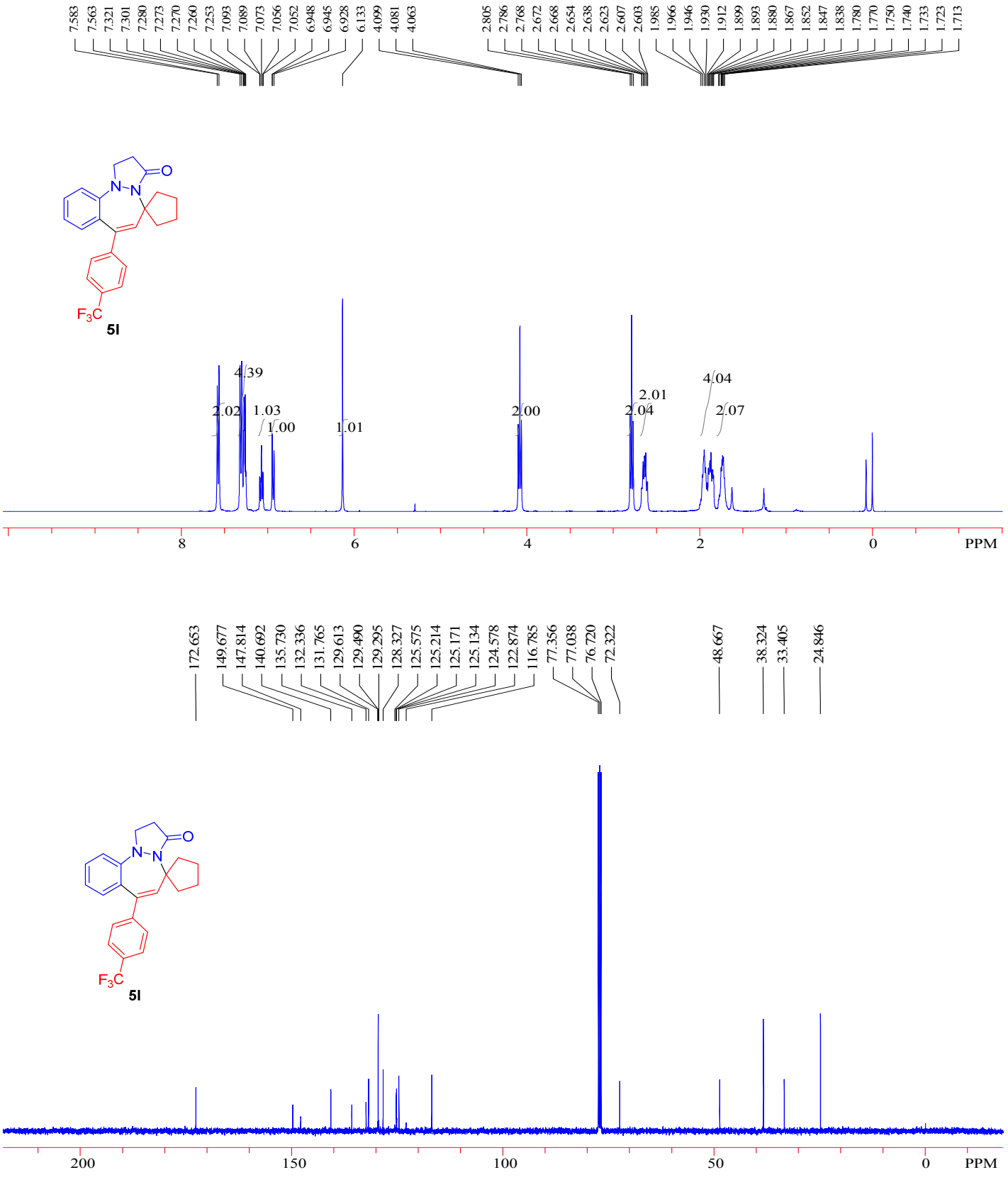
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1.852
1.847
1.838
1.780
1.770
1.750
1.740
1.733
1.723
1.713
O
N
N
F3C
5l
4.39
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1.03
1.00
1.01
2.00
2.01
2.04
4.04
2.07
8
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77.038
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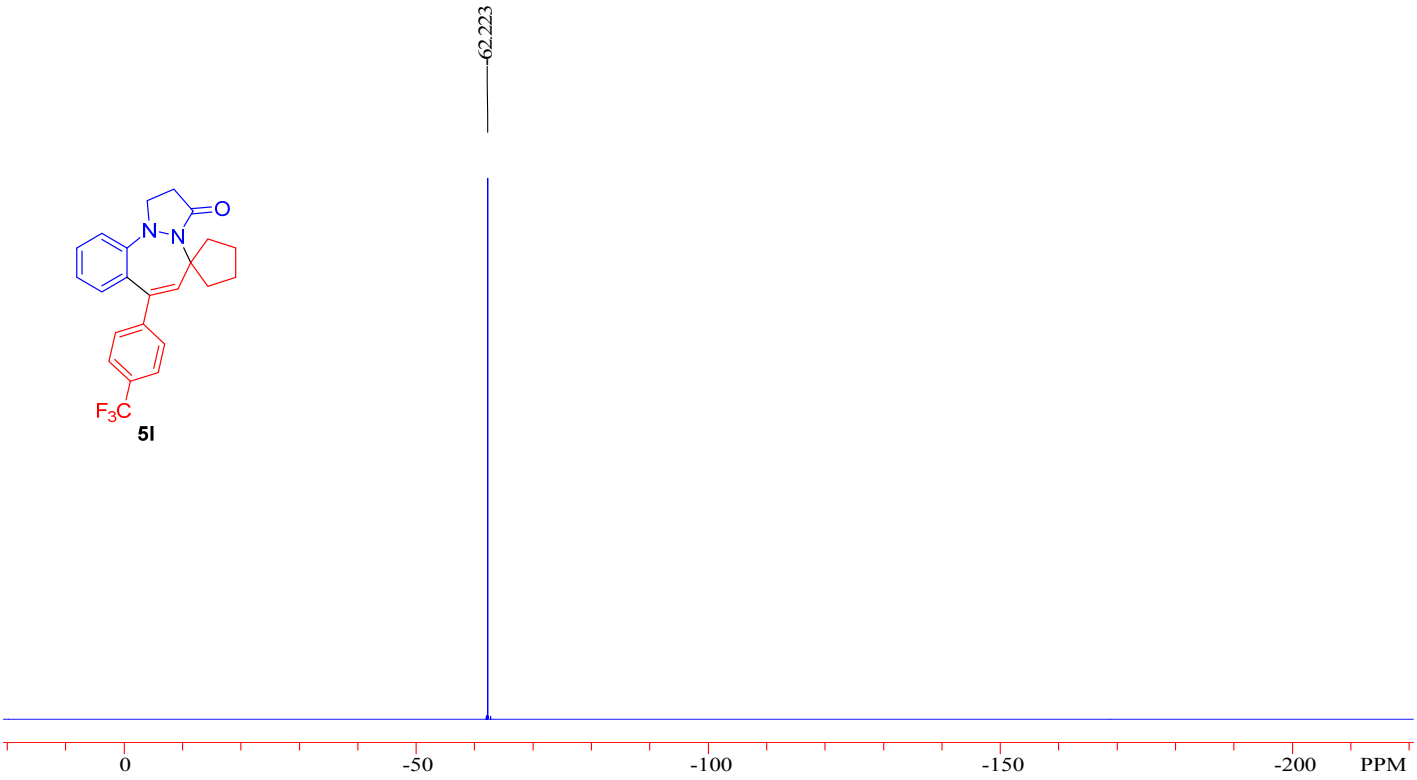

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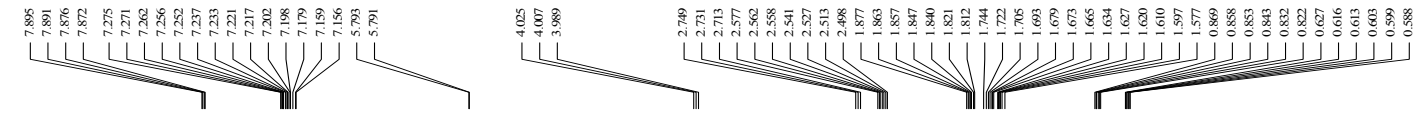
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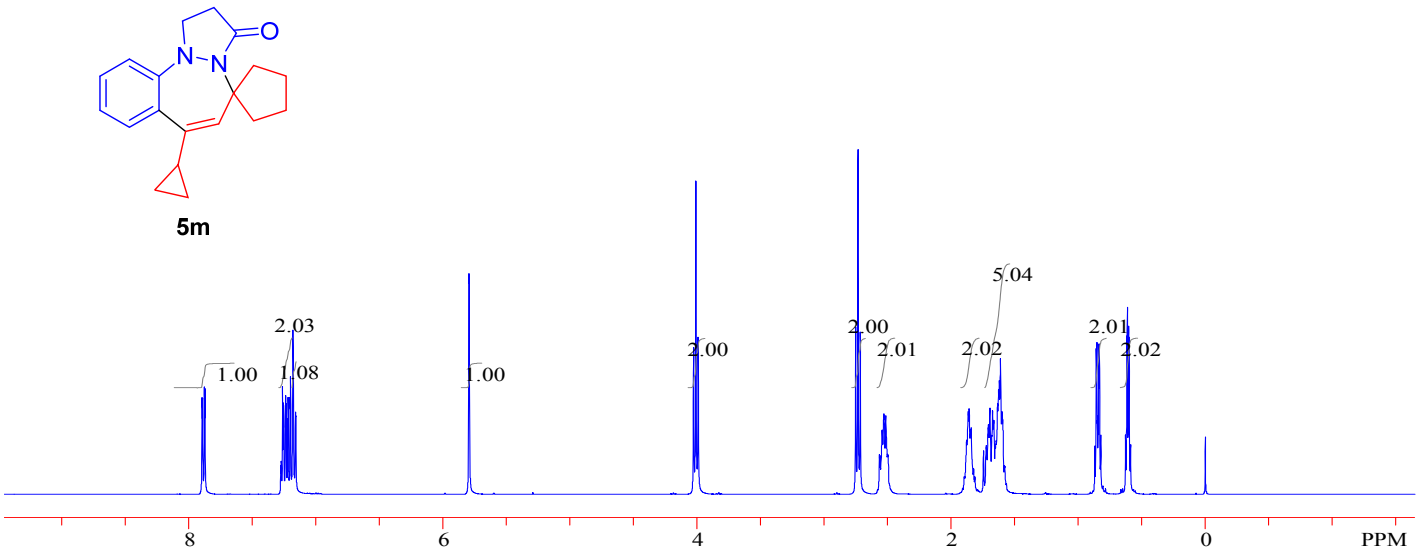
0.822
0.627
0.616
0.613
0.603
0.599
0.588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2.02
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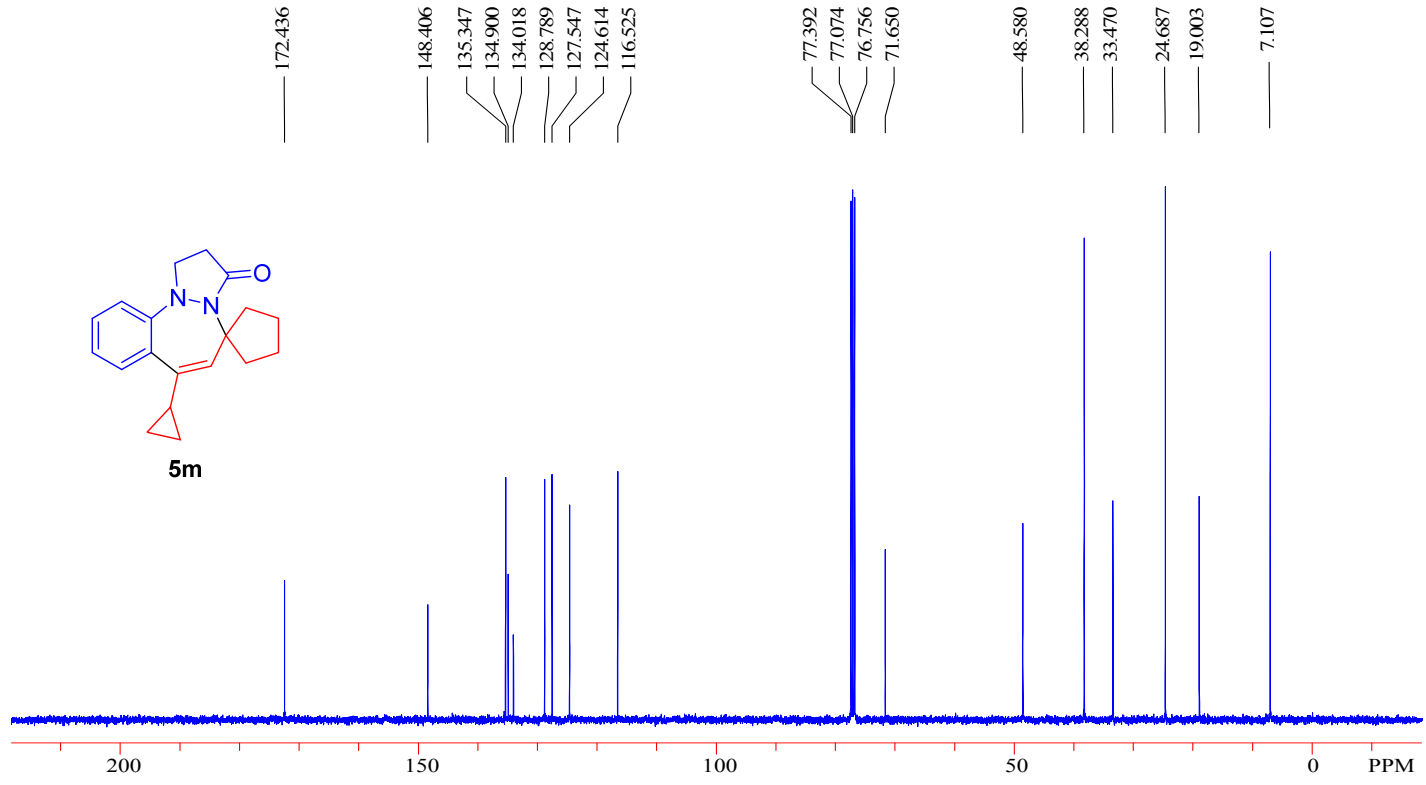
PPM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71.650
48.580
38.288
33.470
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O
N
N
5m
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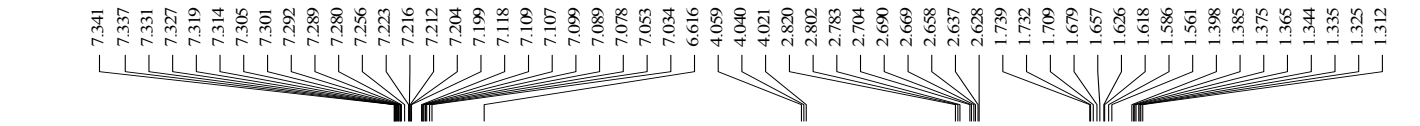
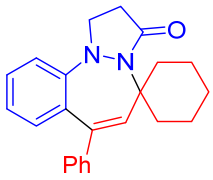
50
0
PPM

V. Copies of NMR spectra of 7a-7q





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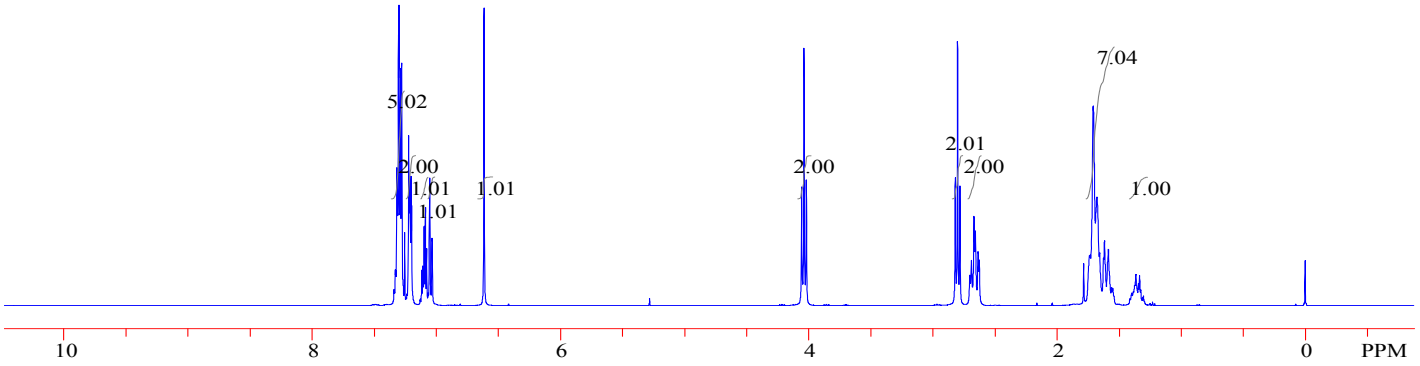

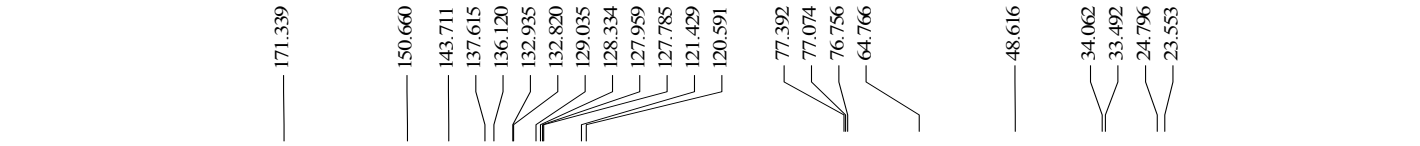

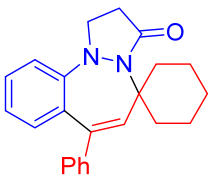

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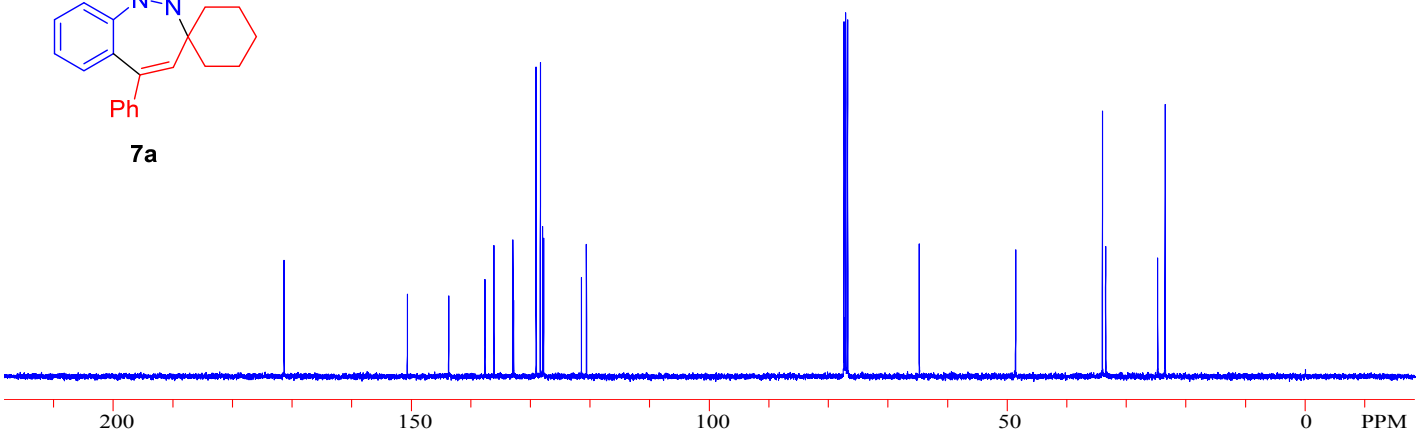

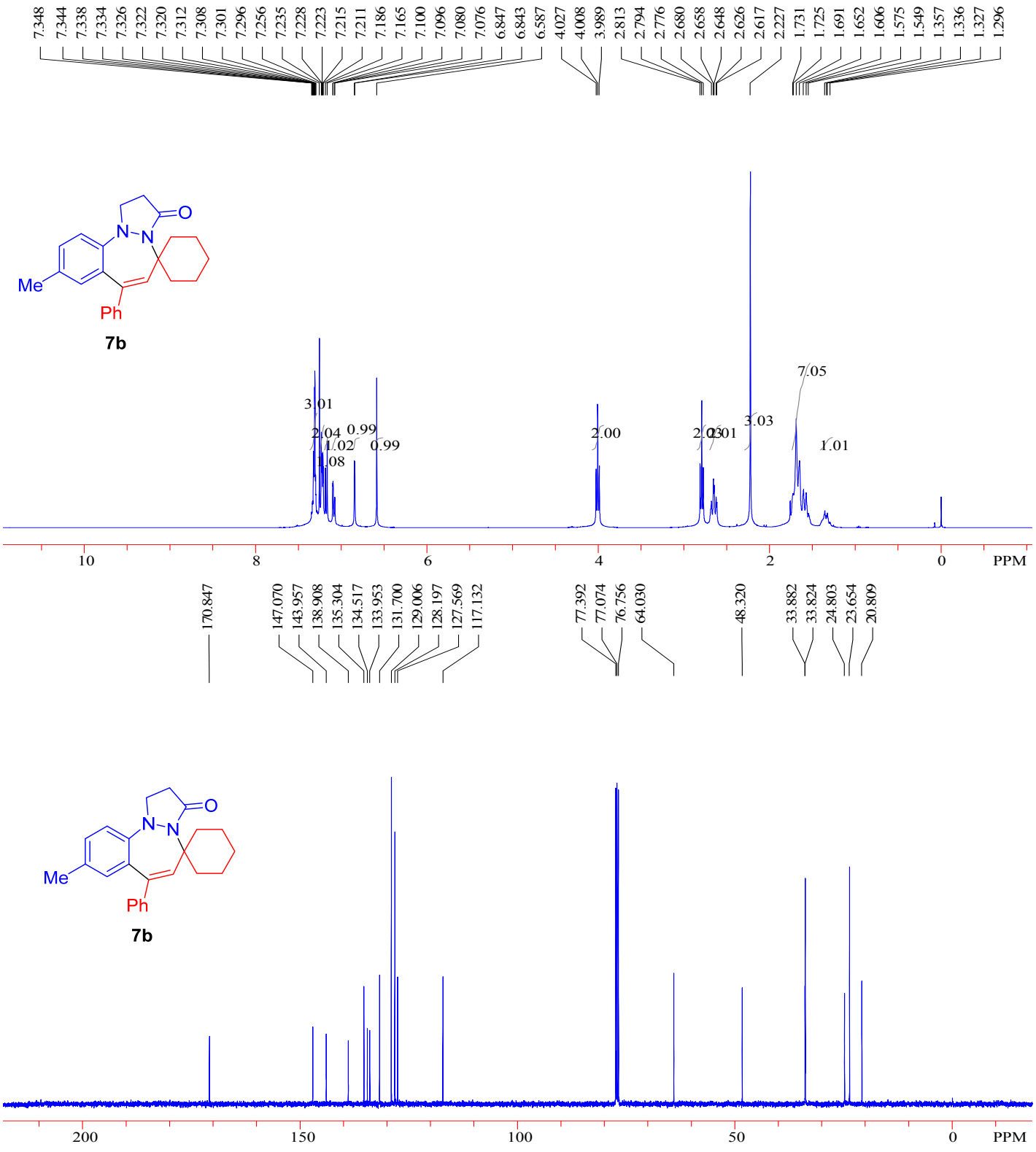
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7.080
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6.843
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4.027
4.008
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1.327
1.296
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N
Me
Ph
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Ph
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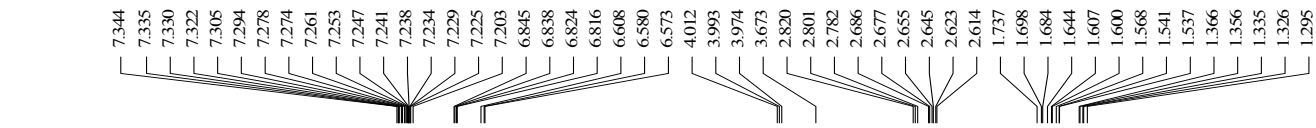
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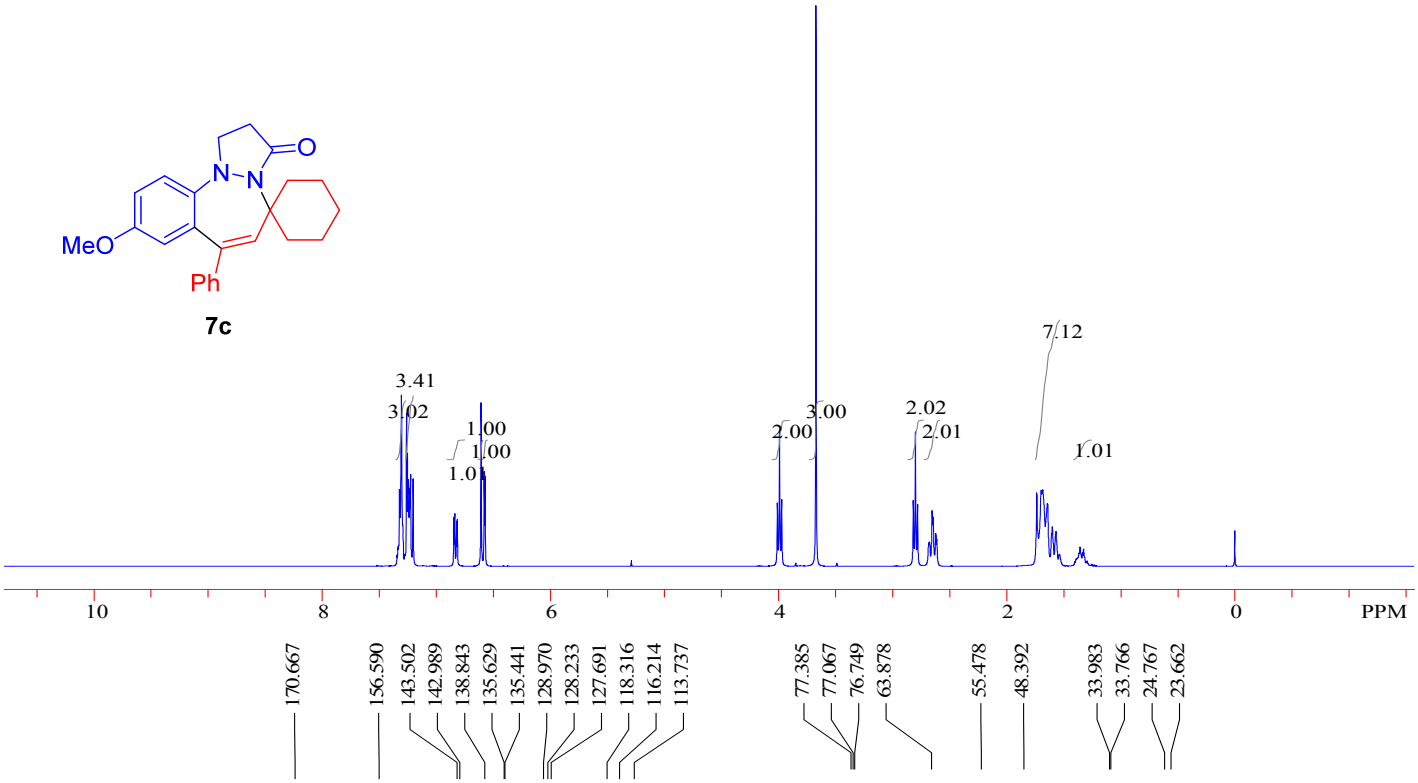
N
MeO
Ph

7c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10
8
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4
2
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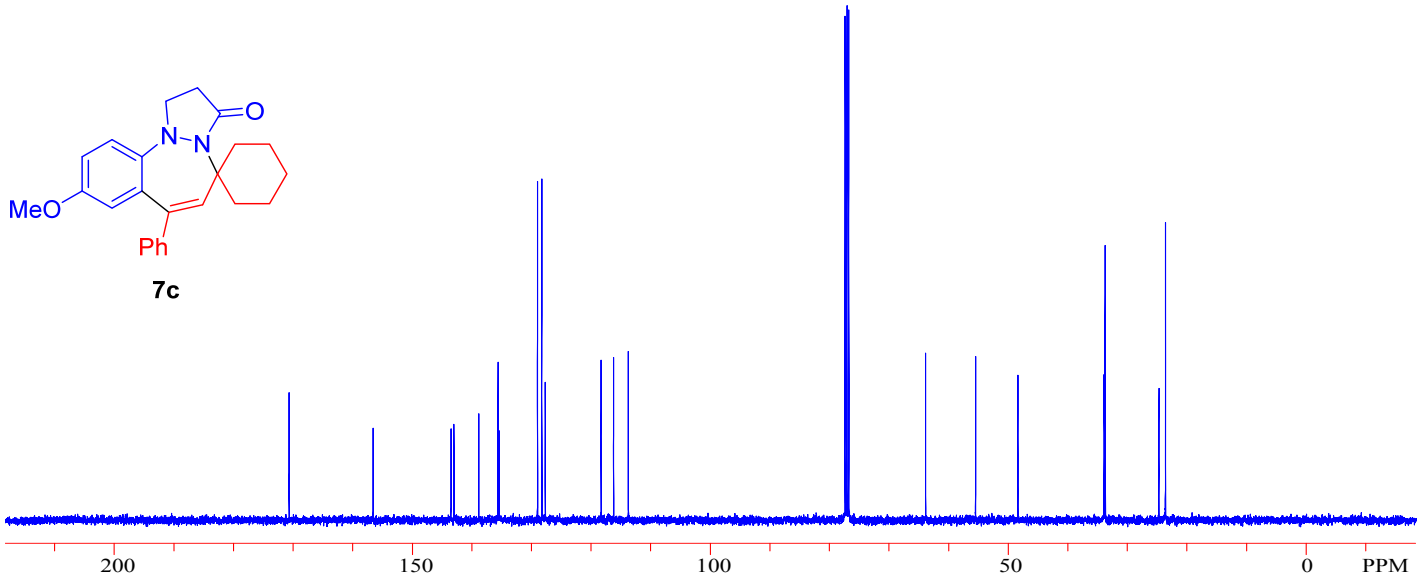
Ph

7c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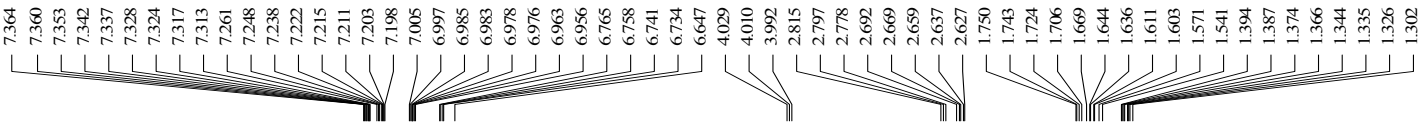
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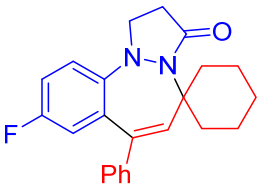
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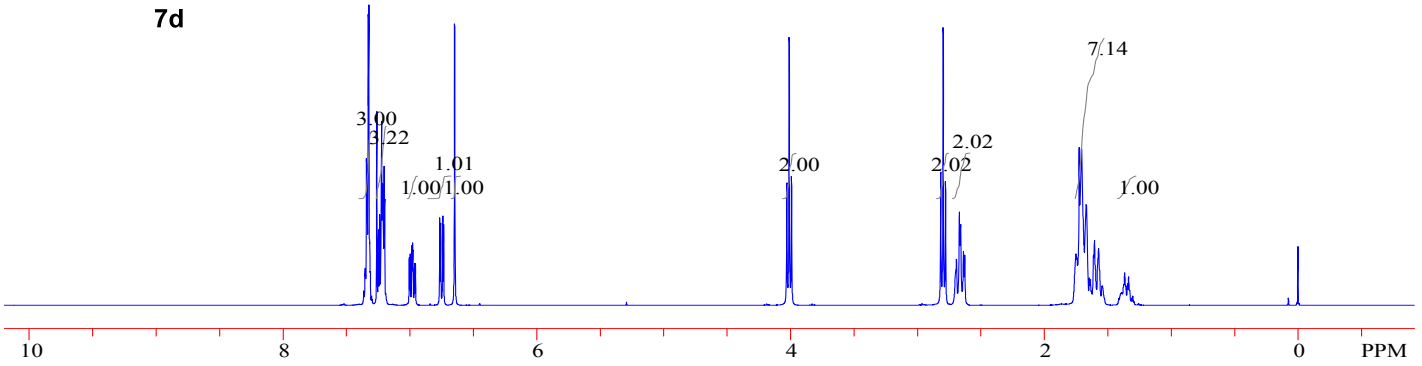
Ph

7d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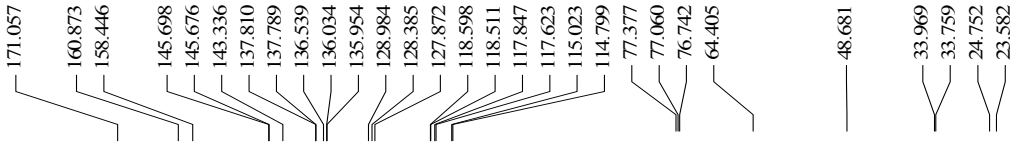
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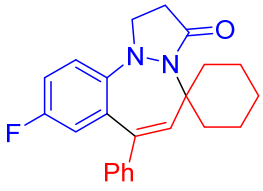
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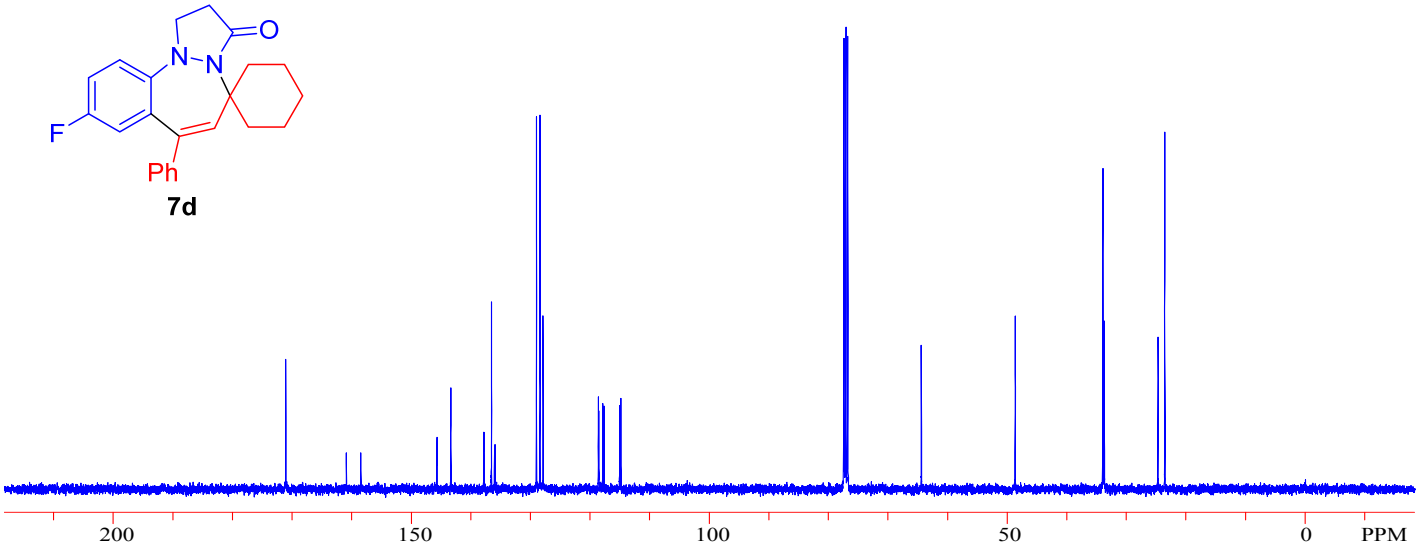
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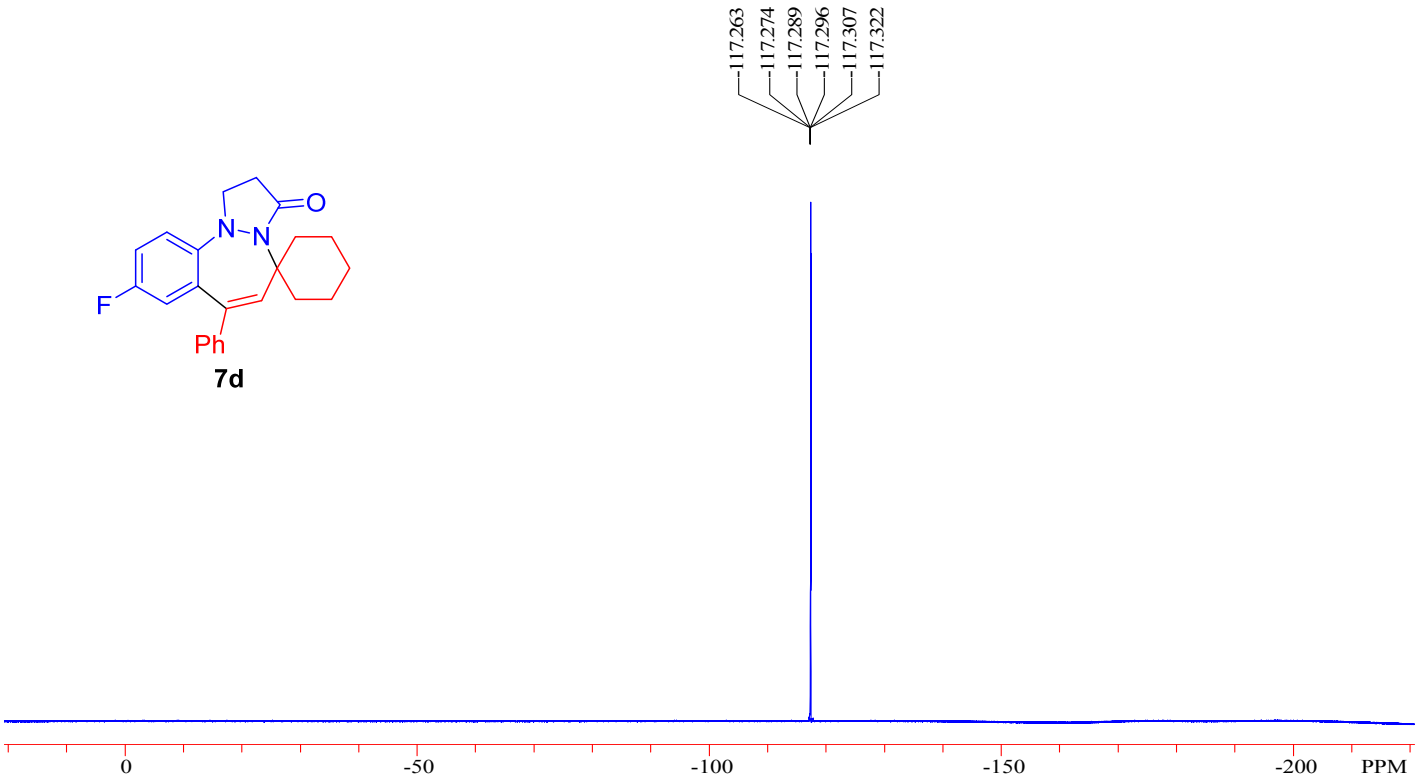
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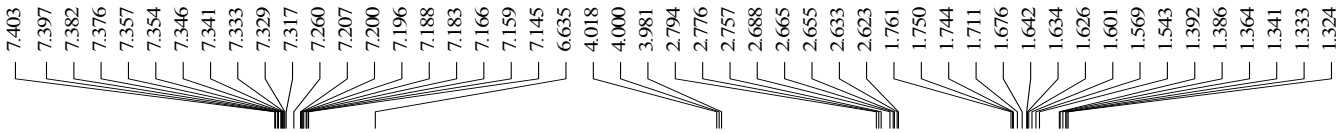
PPM

7d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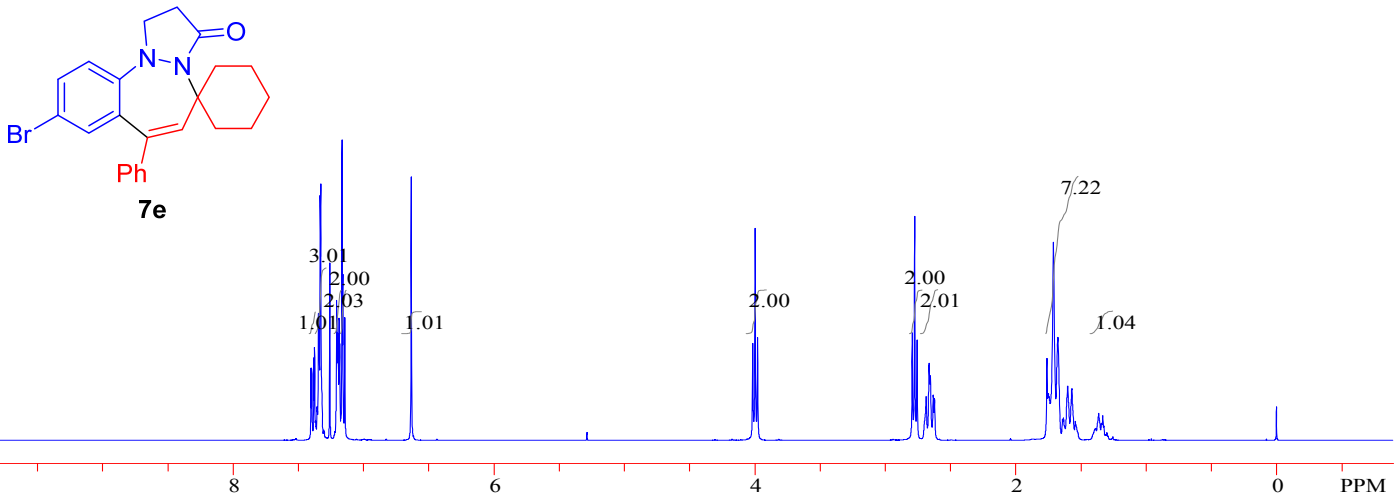
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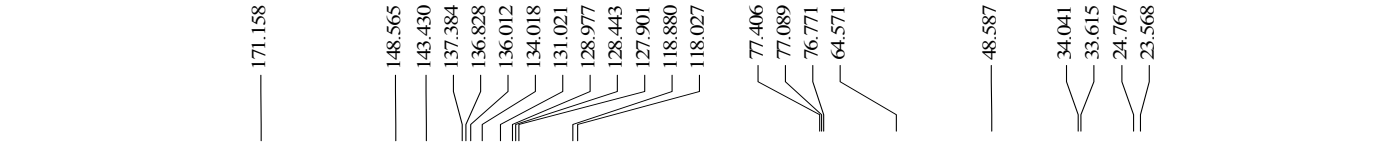
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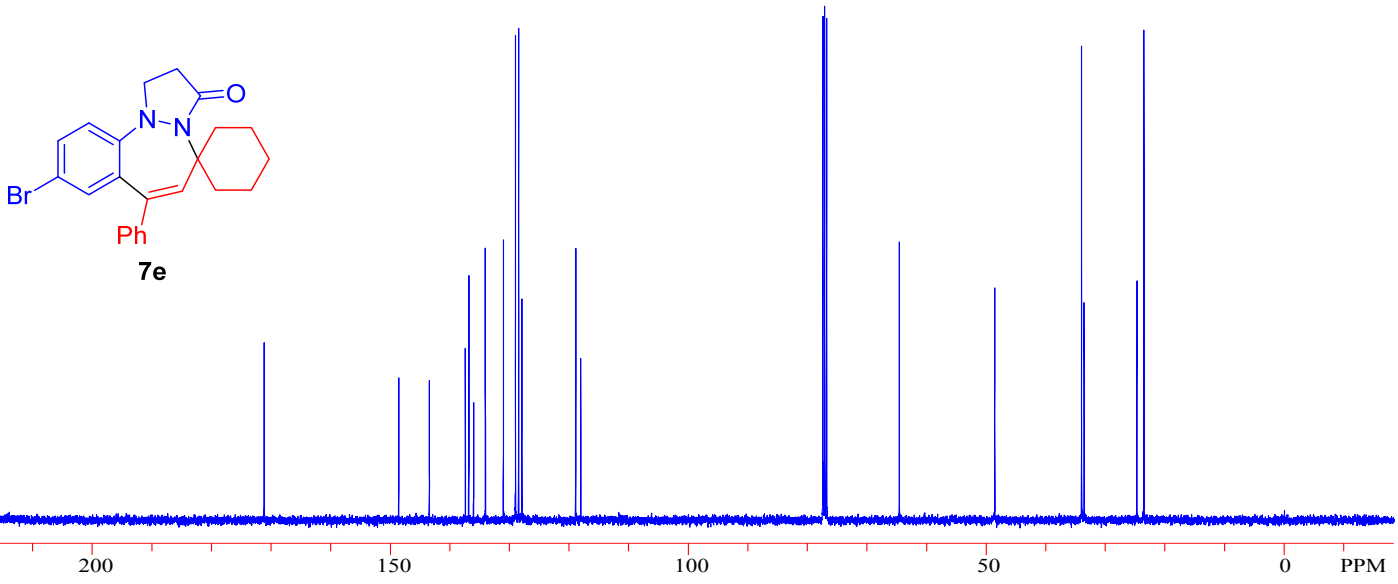
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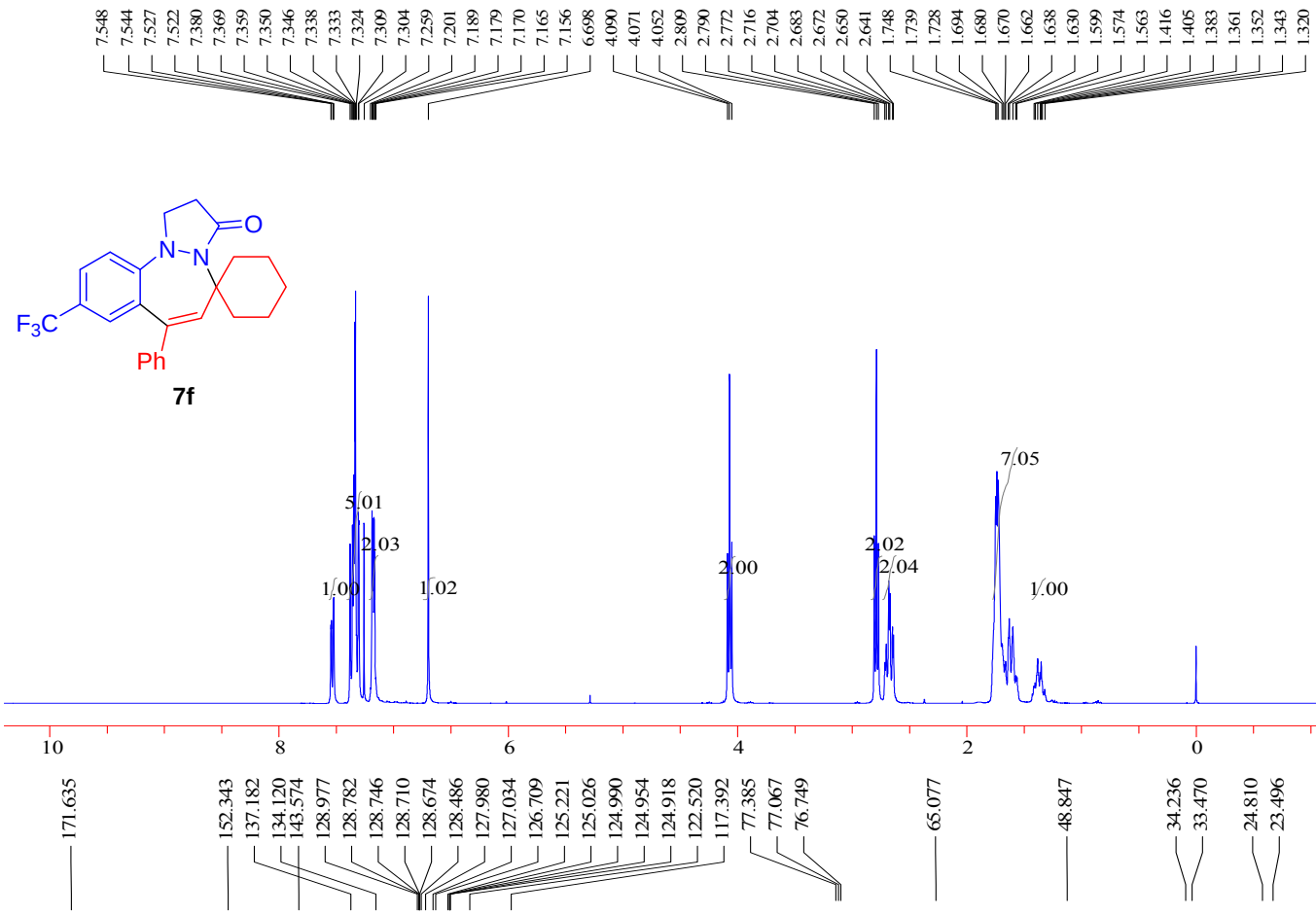
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Ph
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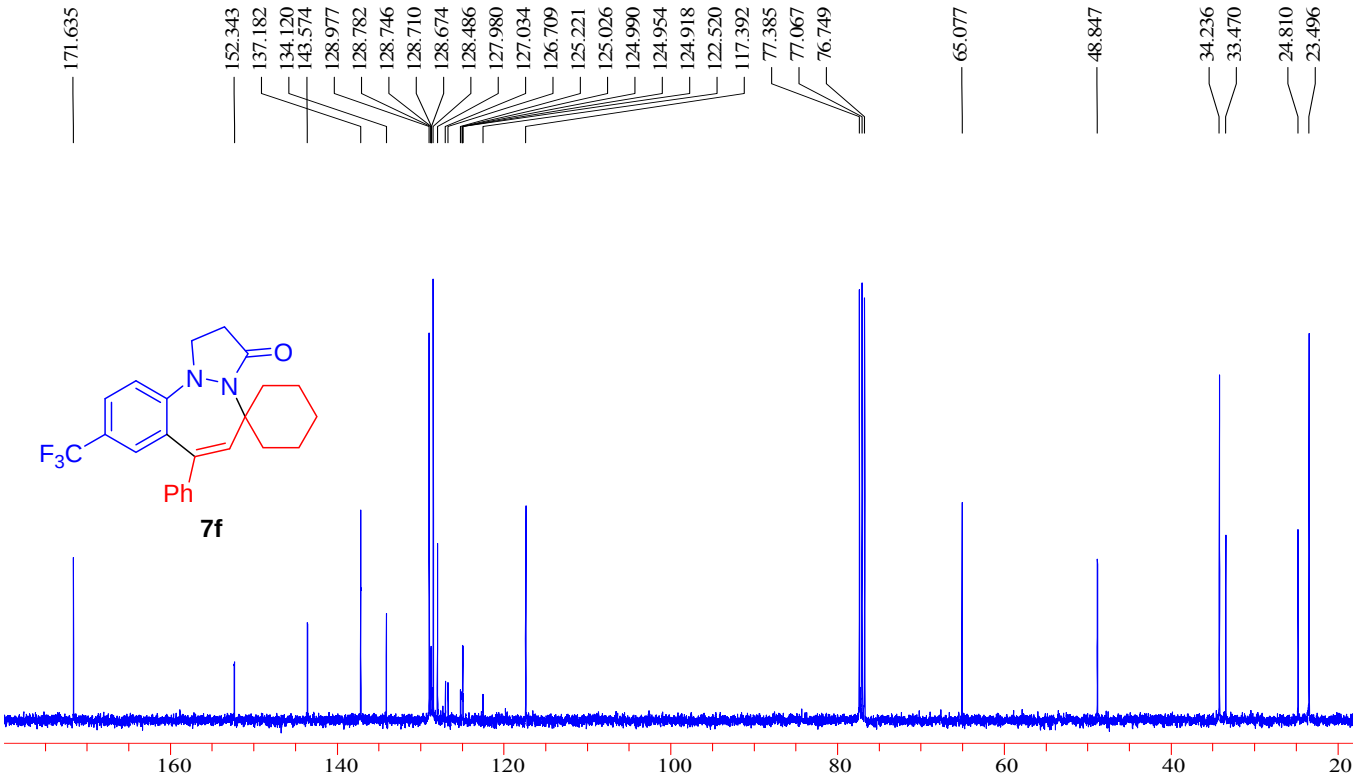
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65.077
48.847
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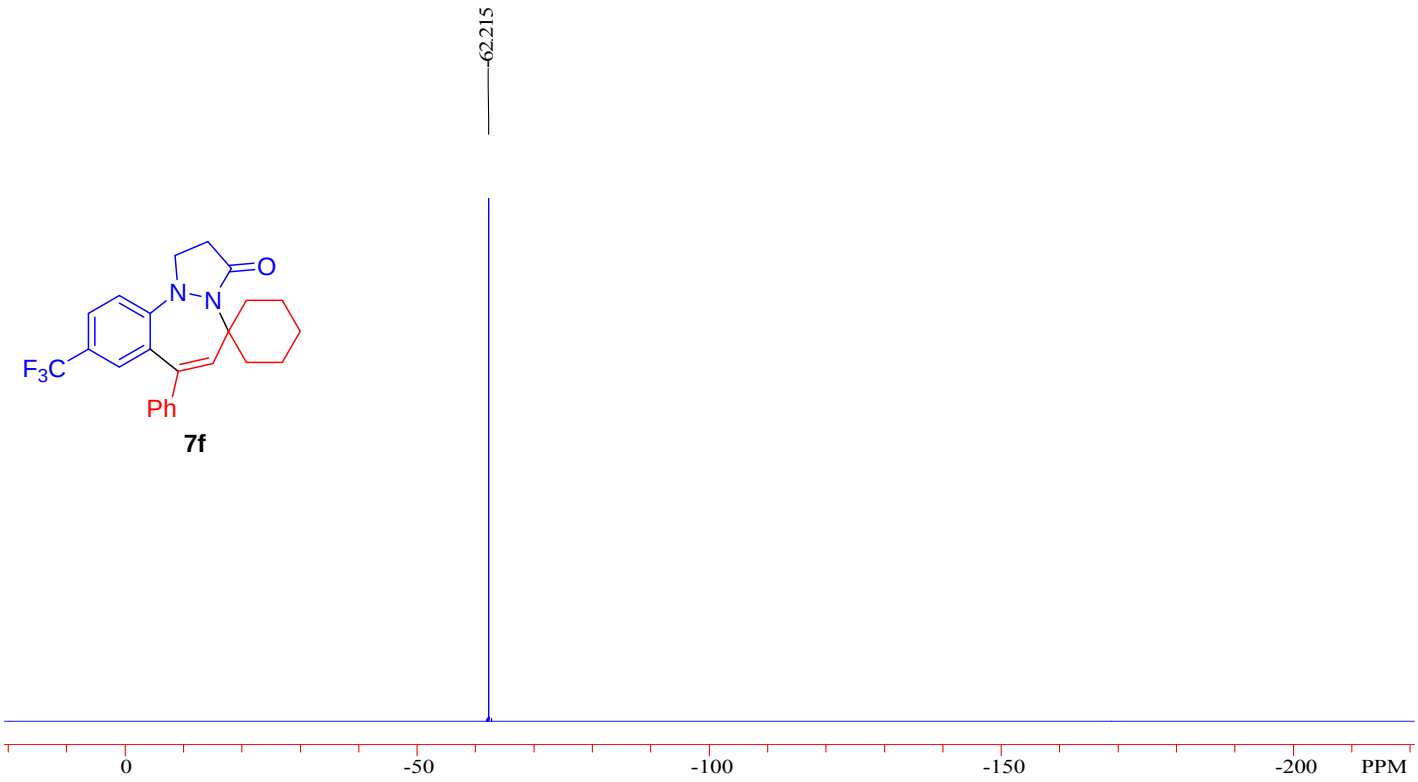

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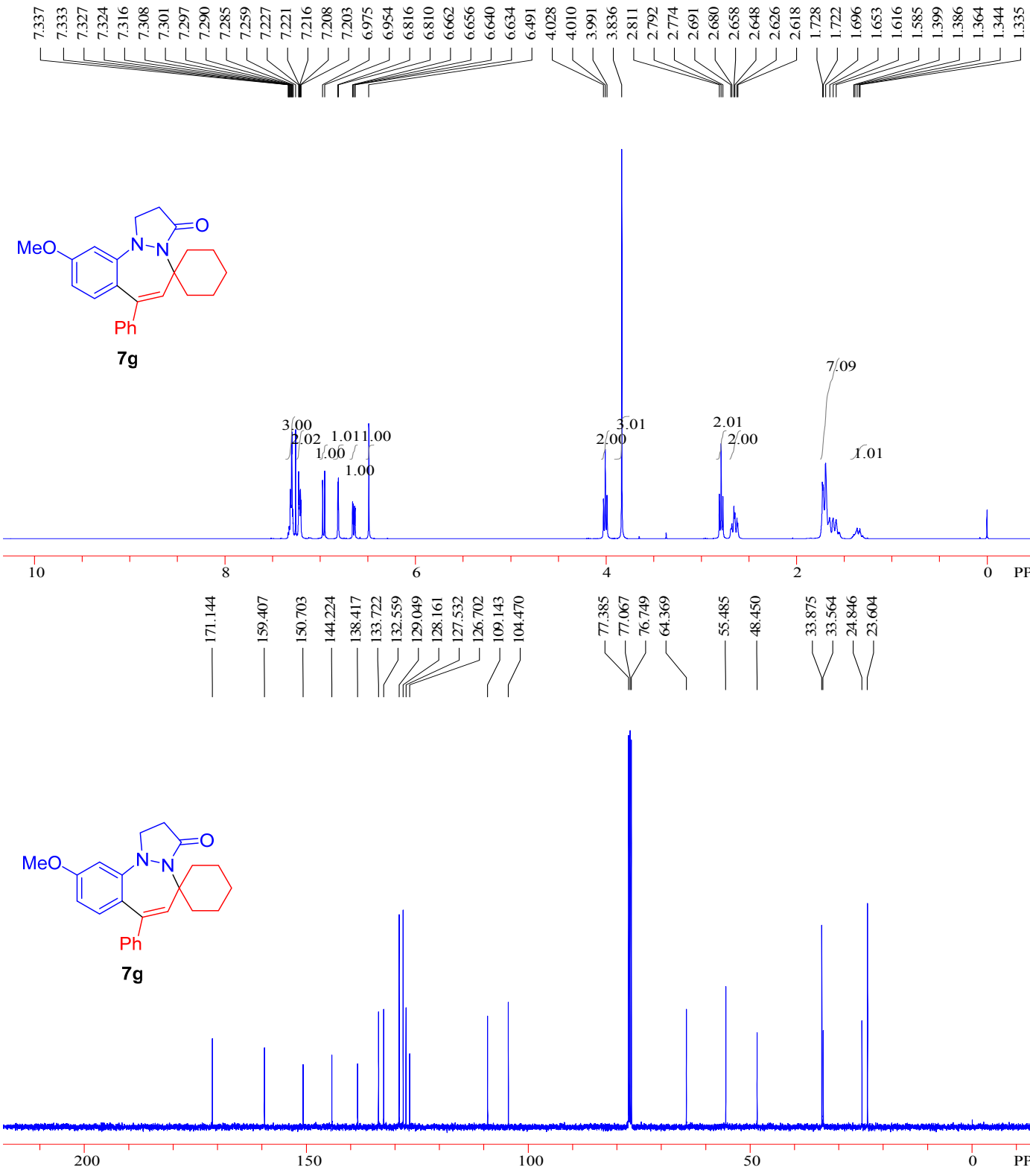
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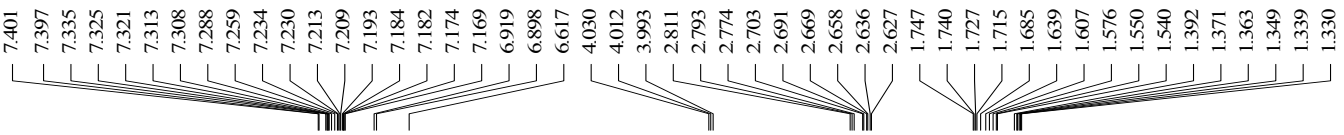
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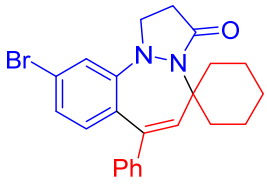
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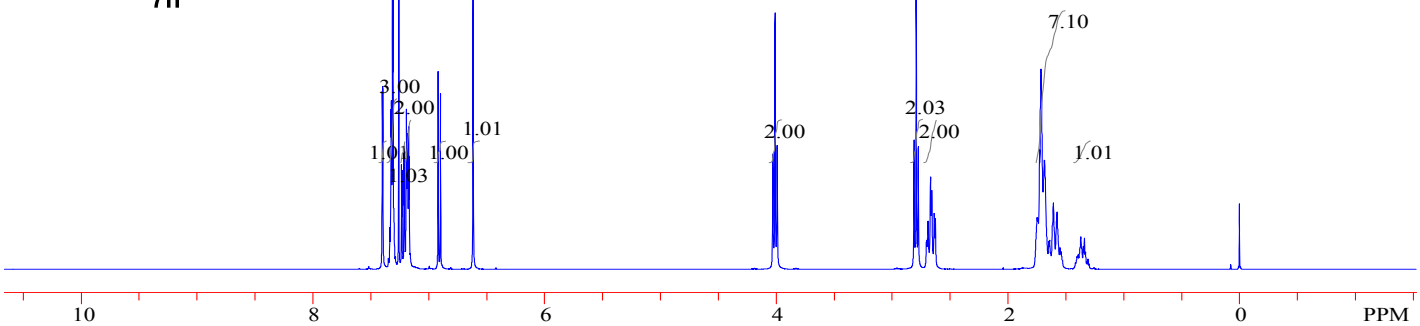
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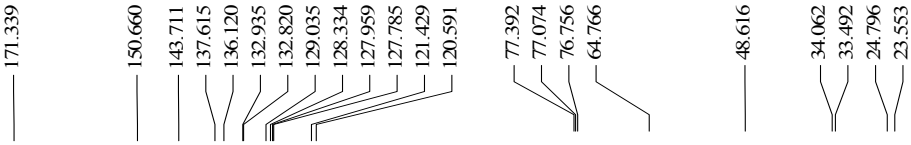
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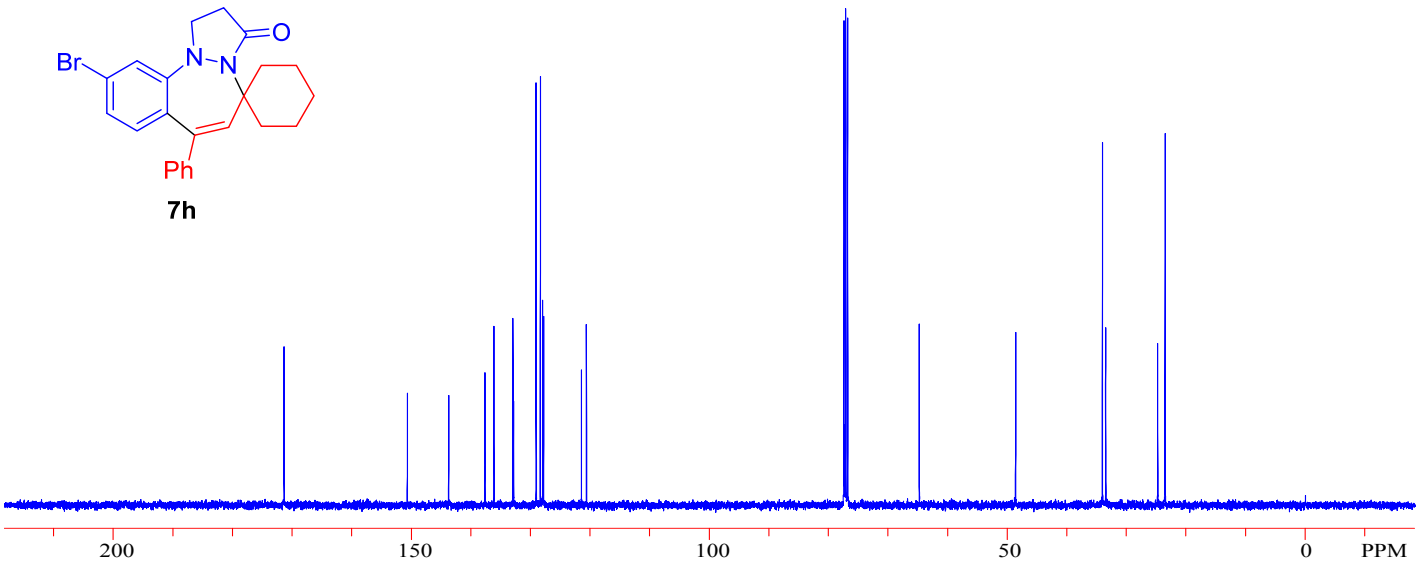
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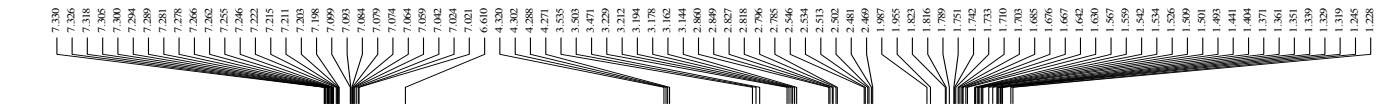
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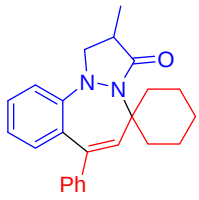
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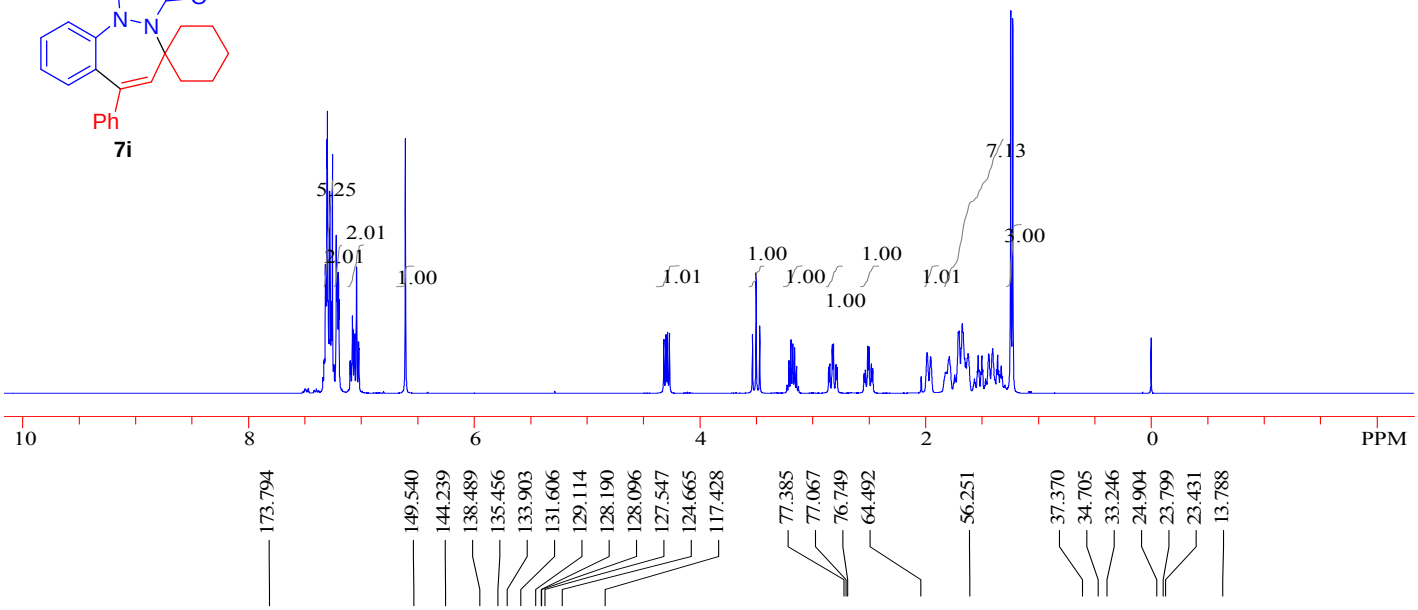
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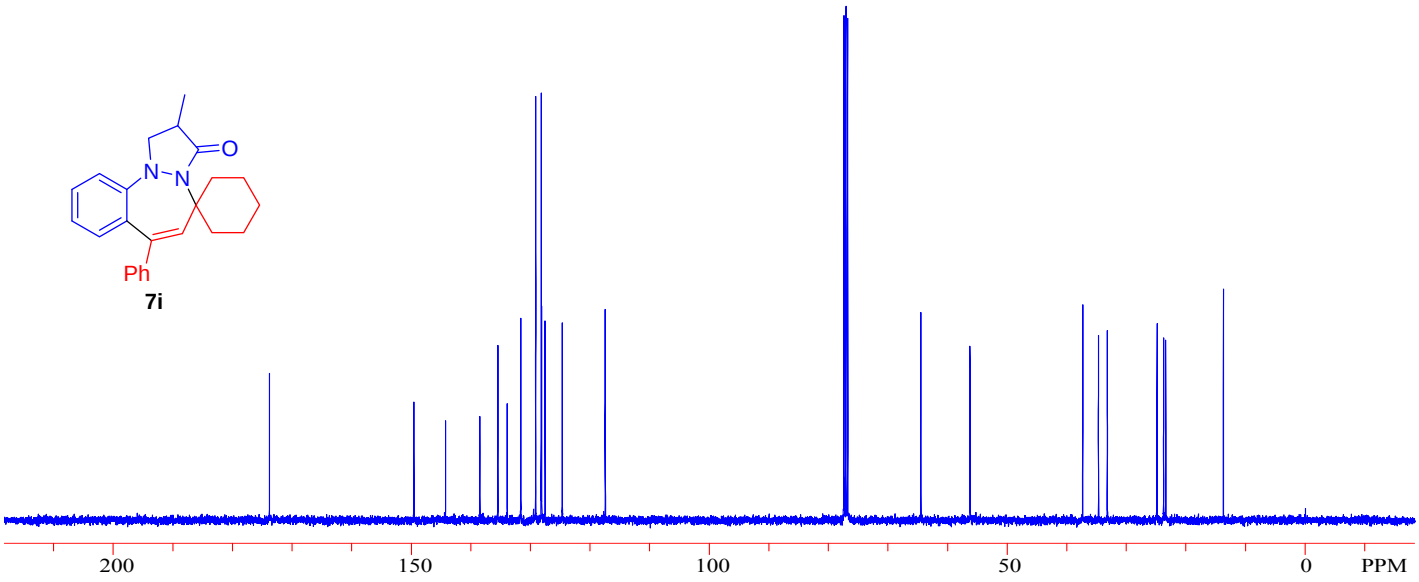
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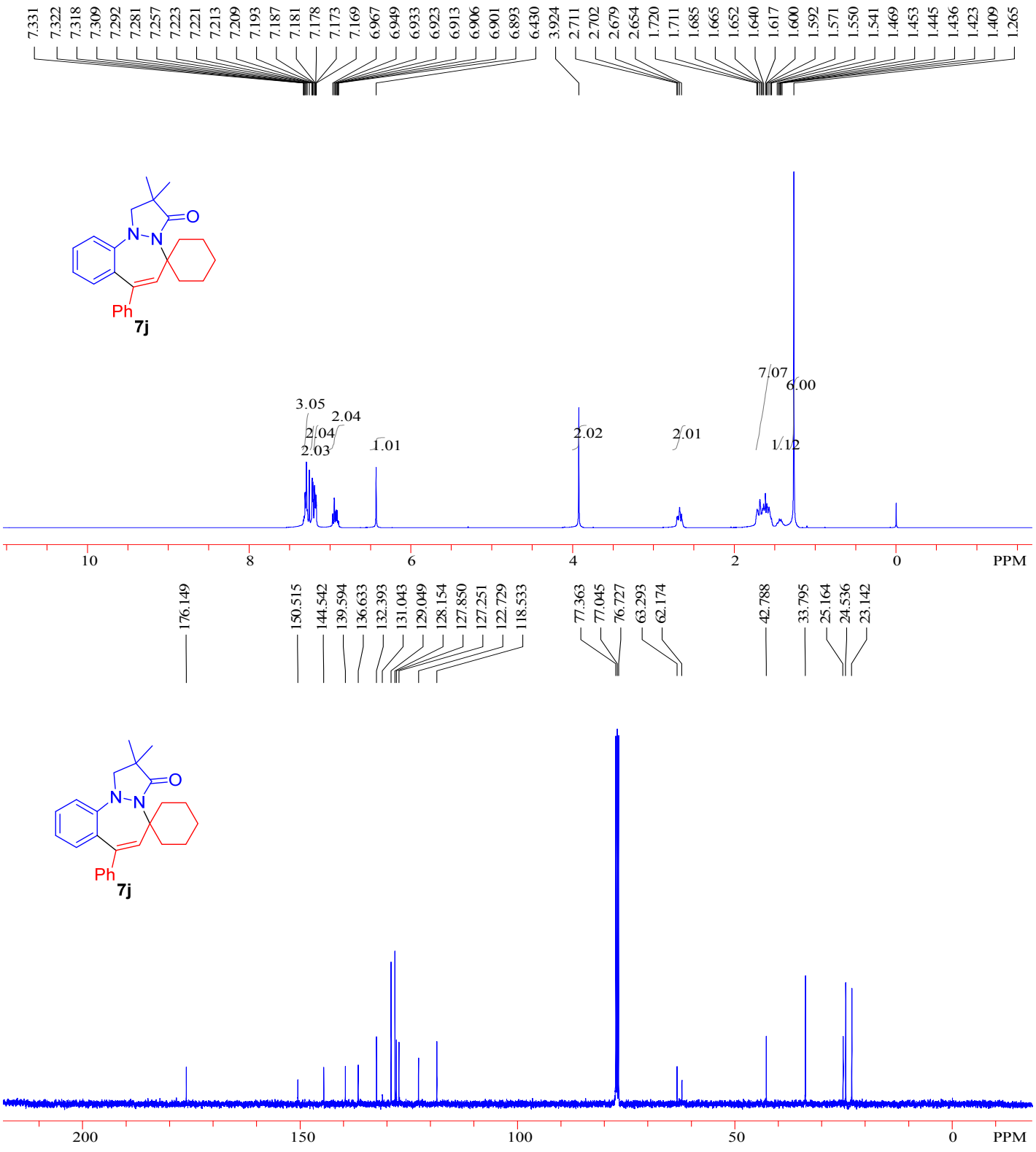
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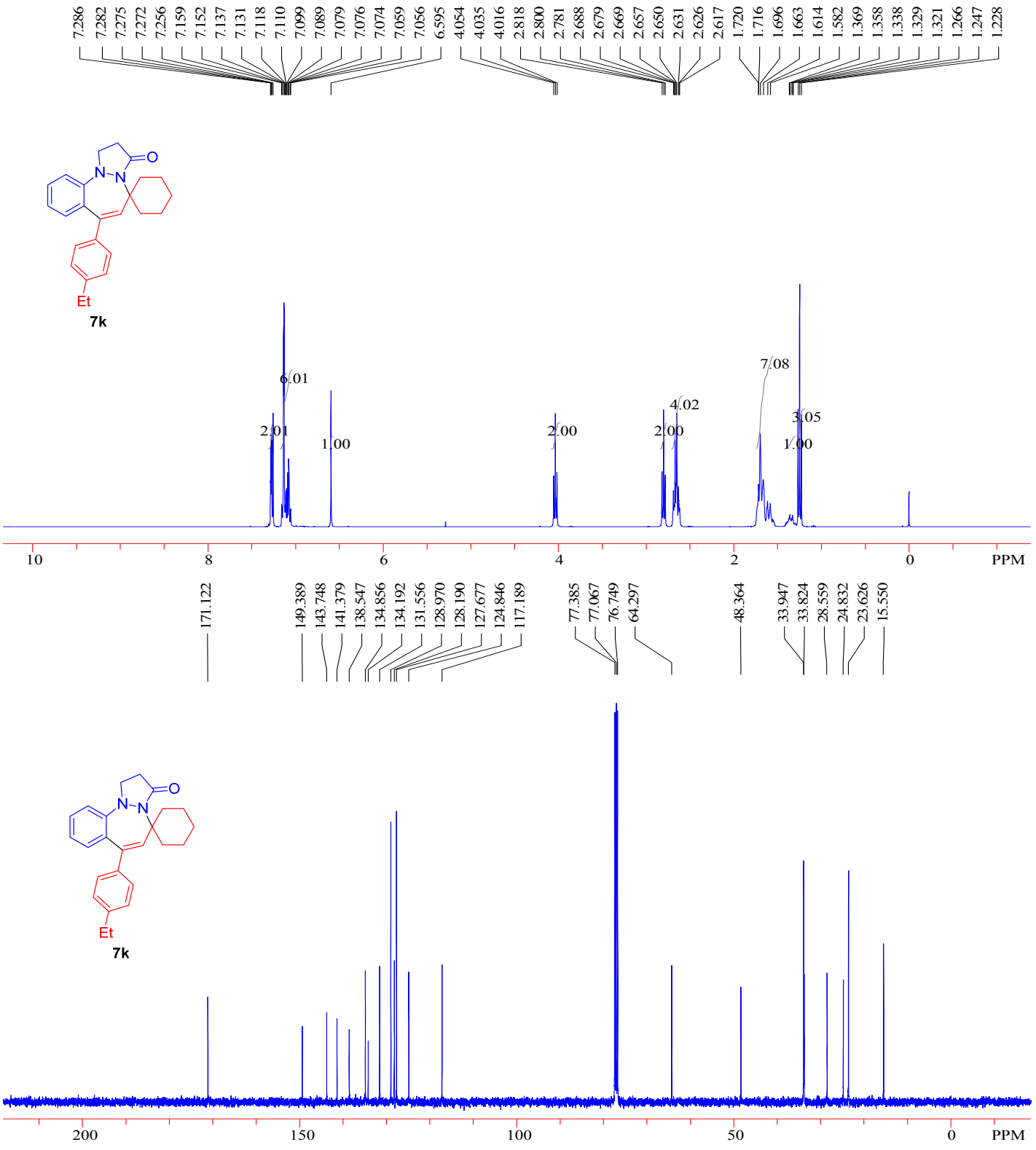
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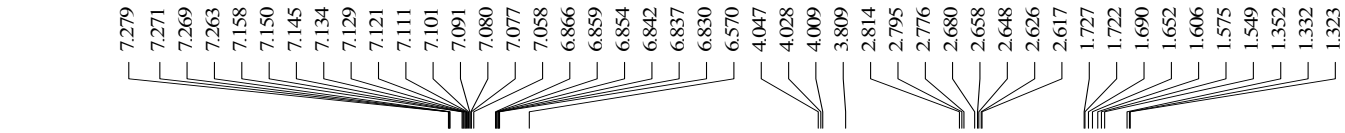
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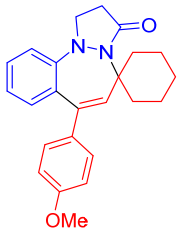
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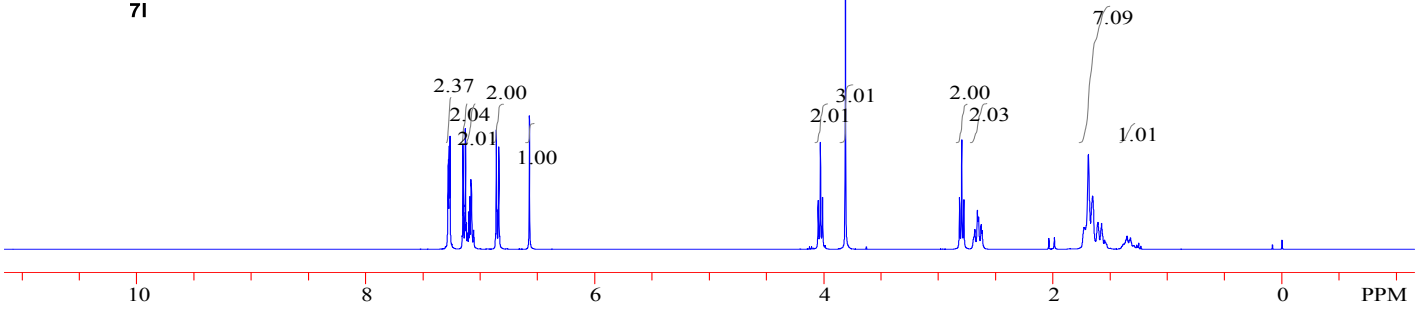
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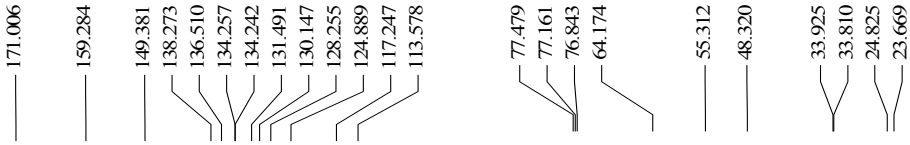
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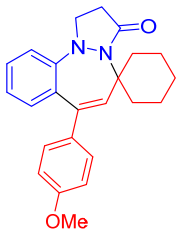
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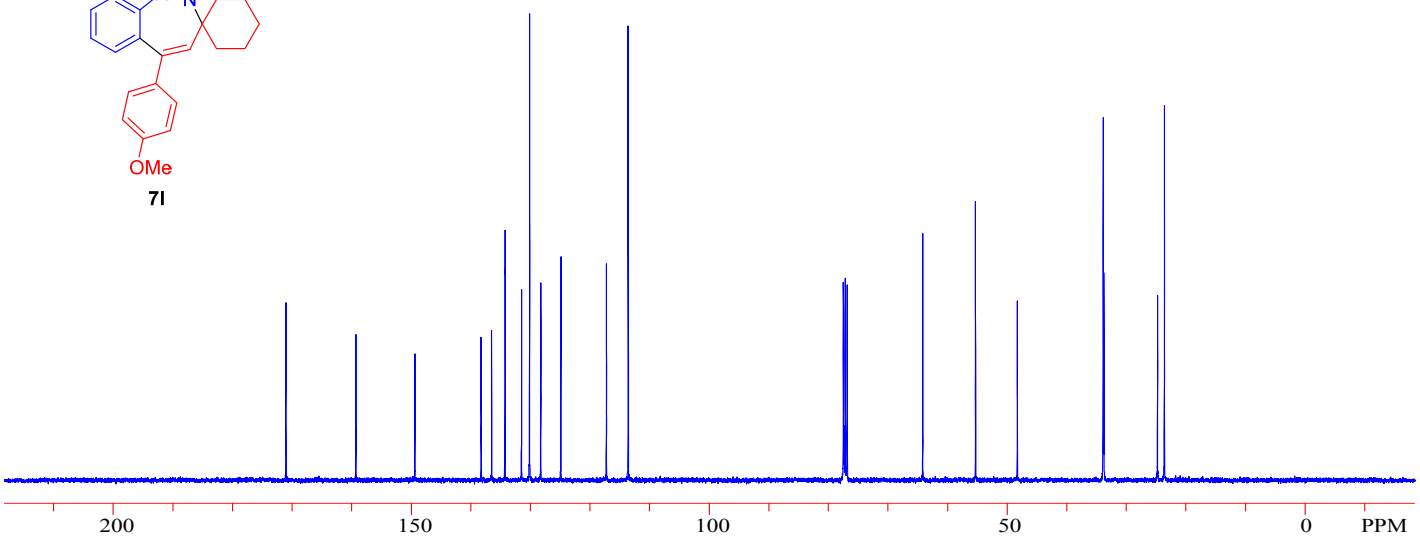
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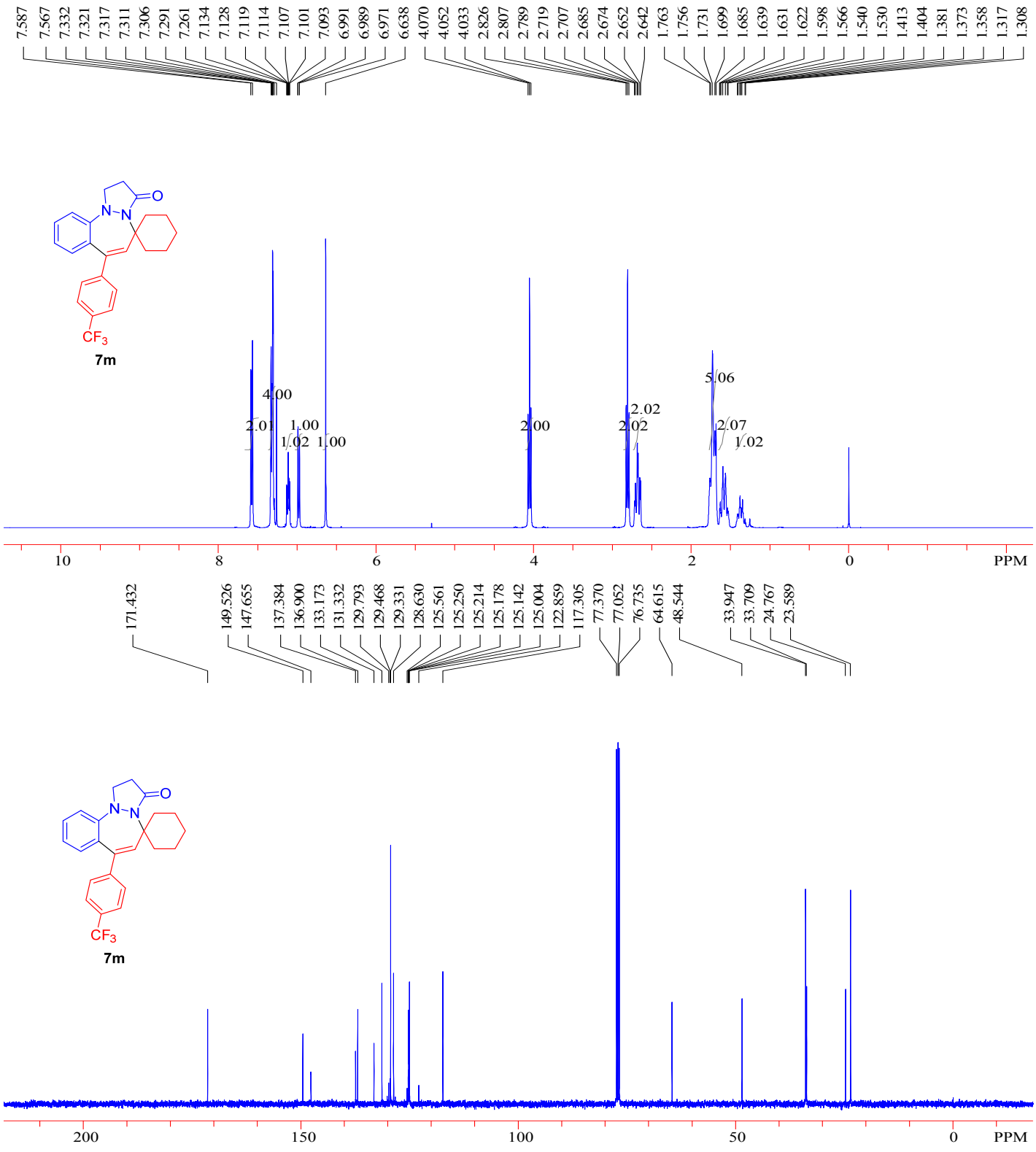
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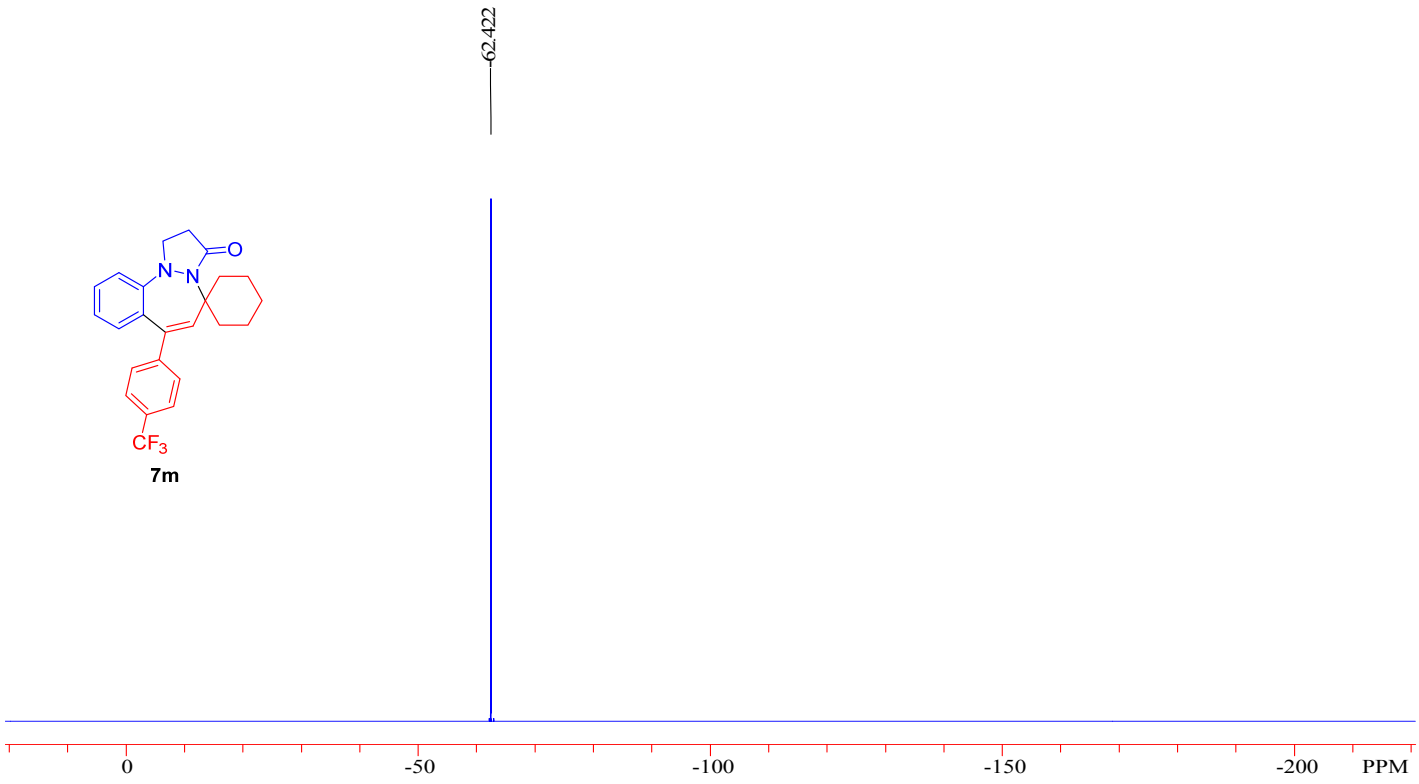

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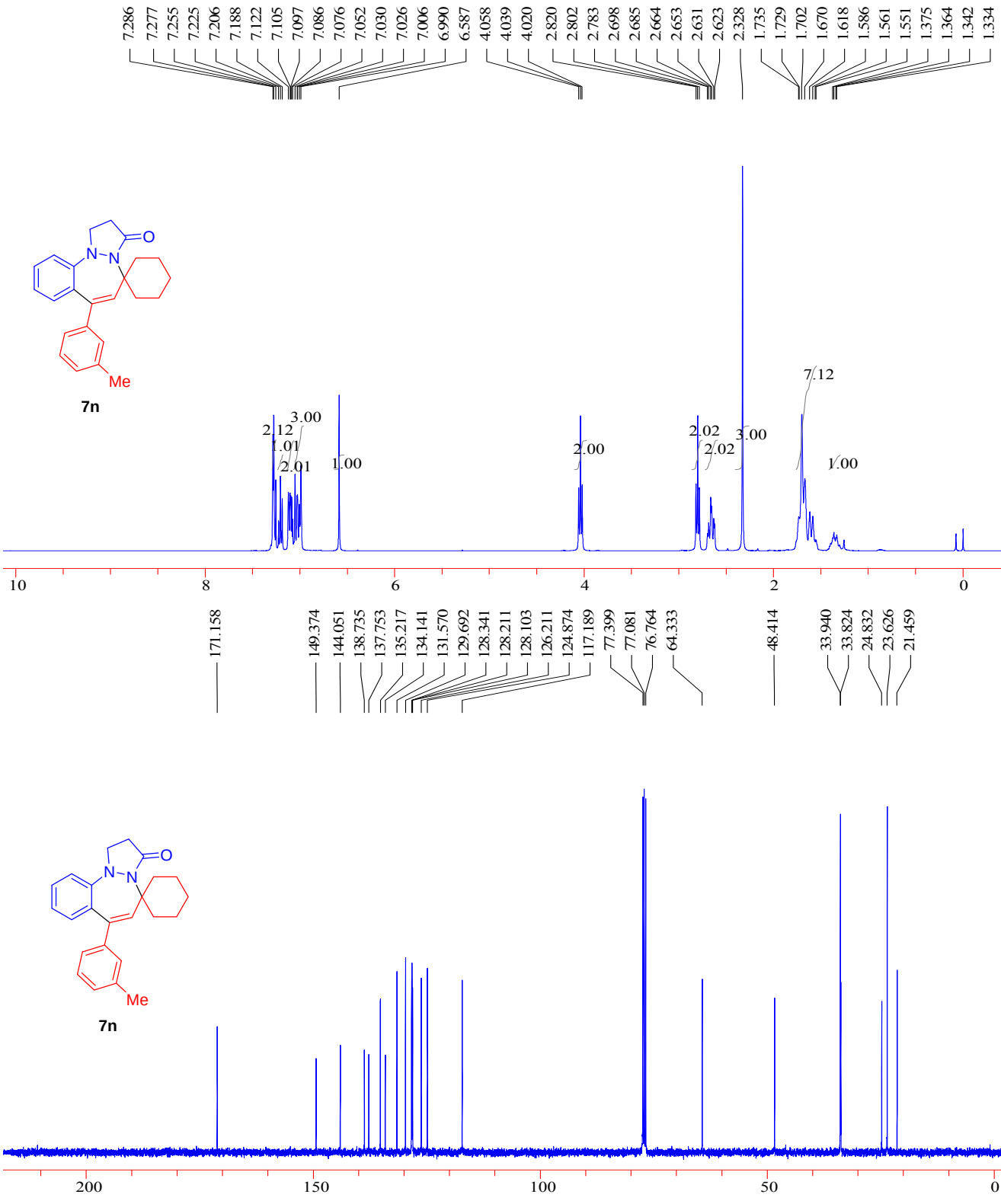
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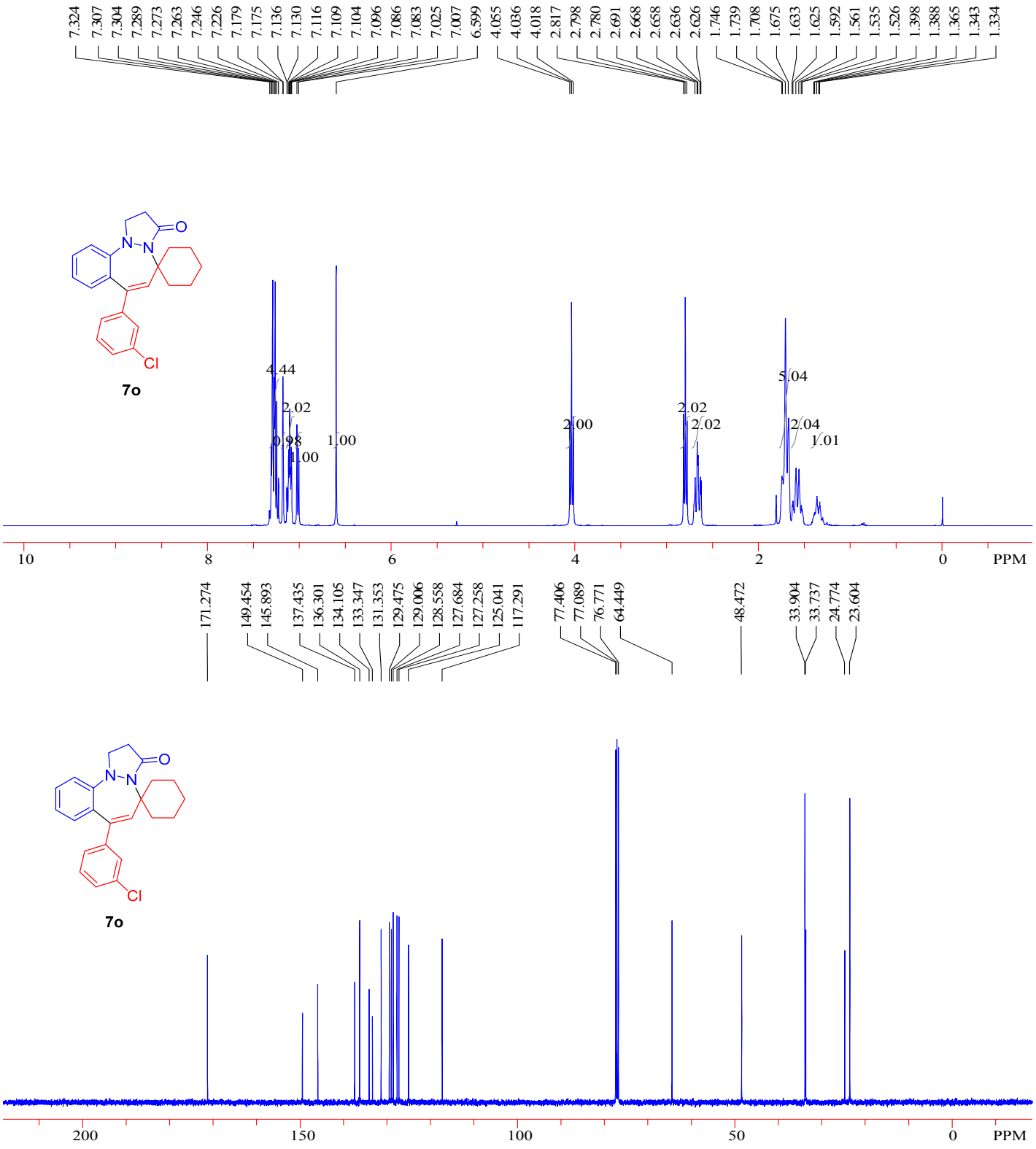
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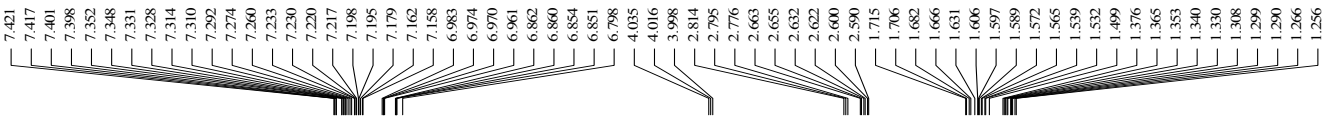
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7.230
7.220
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7.195
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7.158
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6.974
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6.851
6.798
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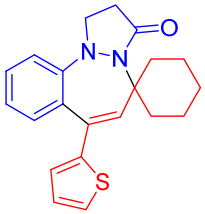

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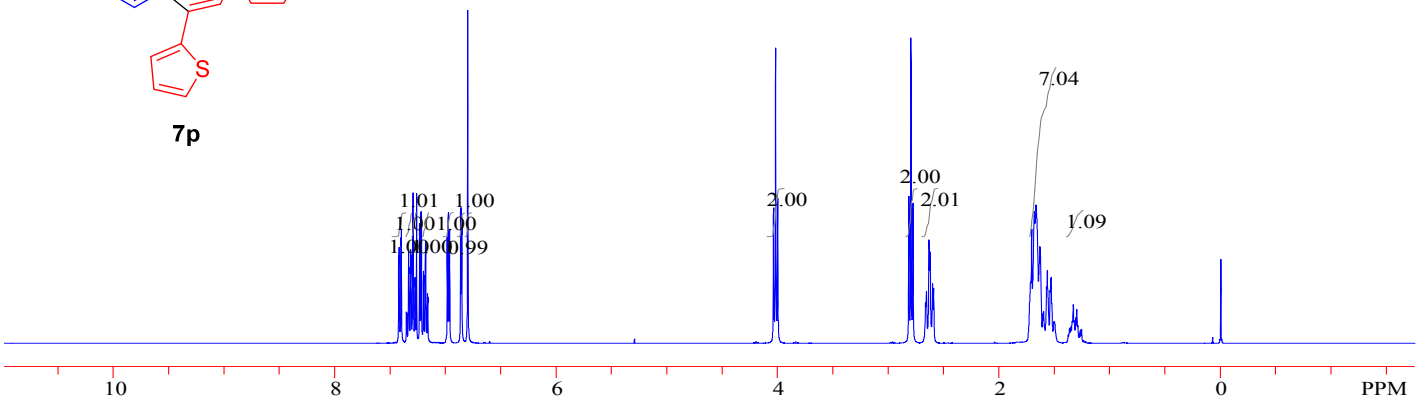
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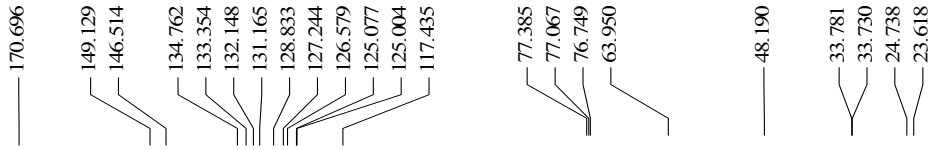
PPM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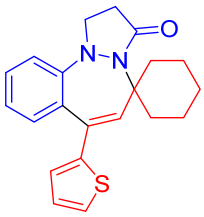
23.618



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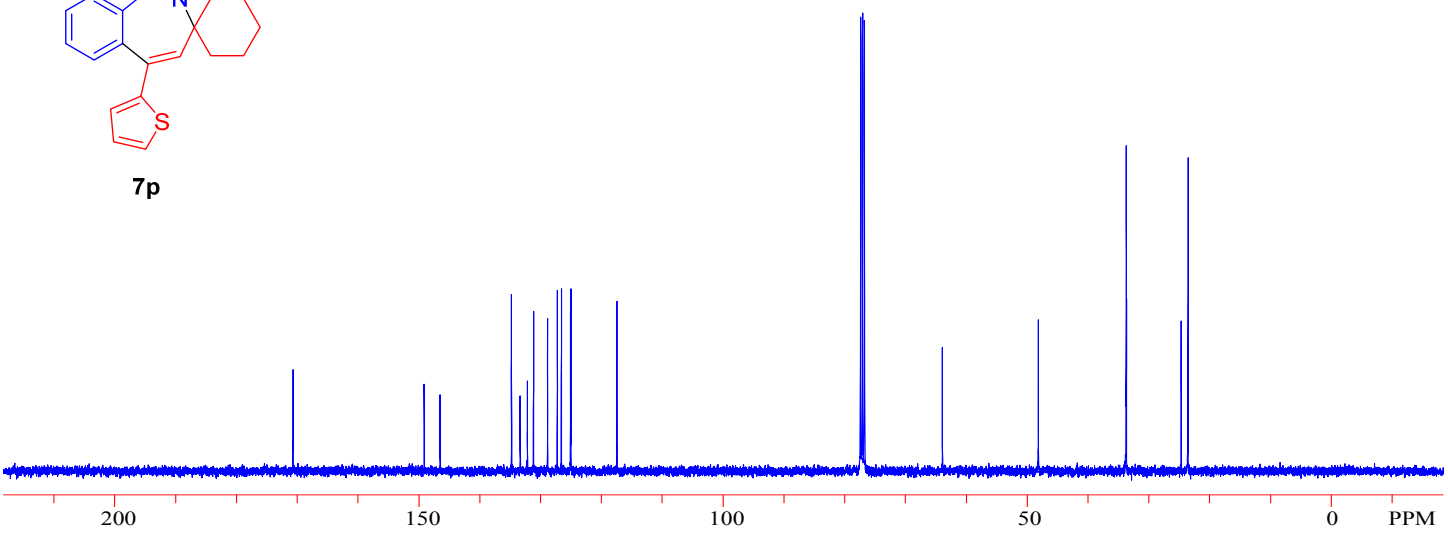
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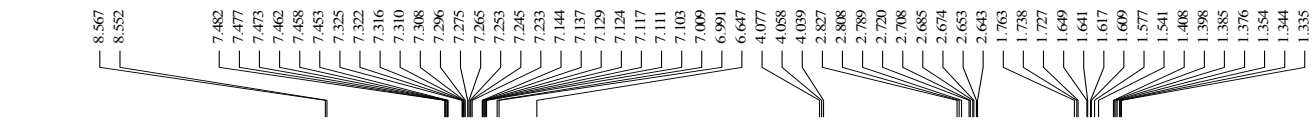
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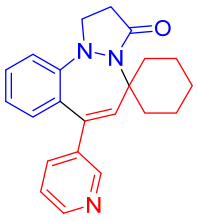
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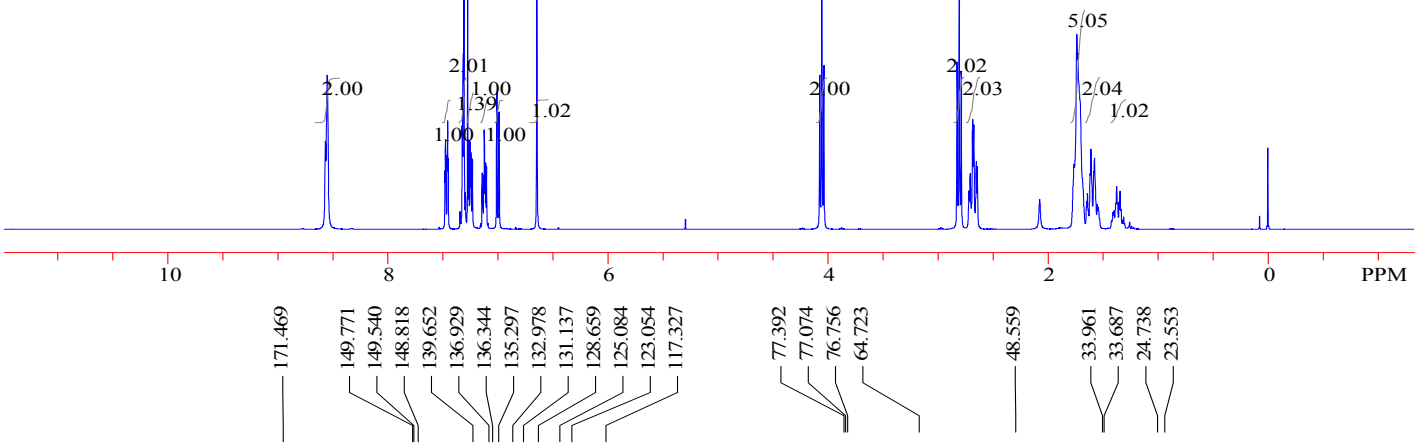
N

7q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10
8
6
4
2
0
PPM

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136.344
135.297
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131.137
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125.084
123.054
117.327
77.392
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48.559
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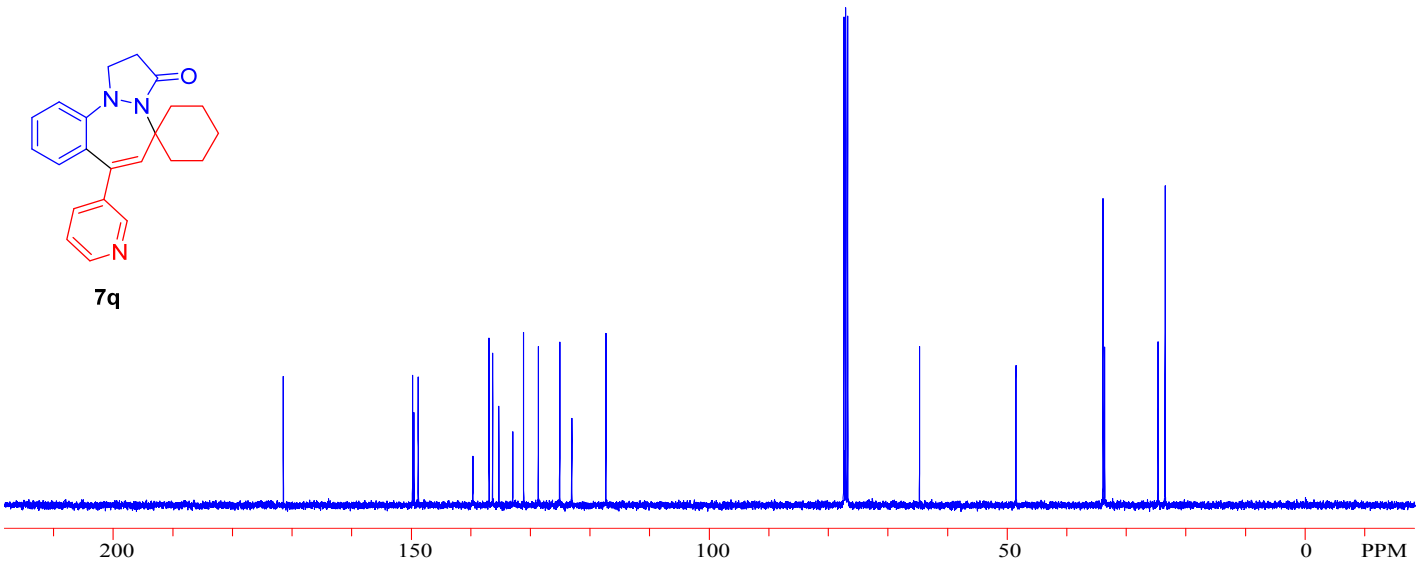
24.738
23.553

O
N
N
N

7q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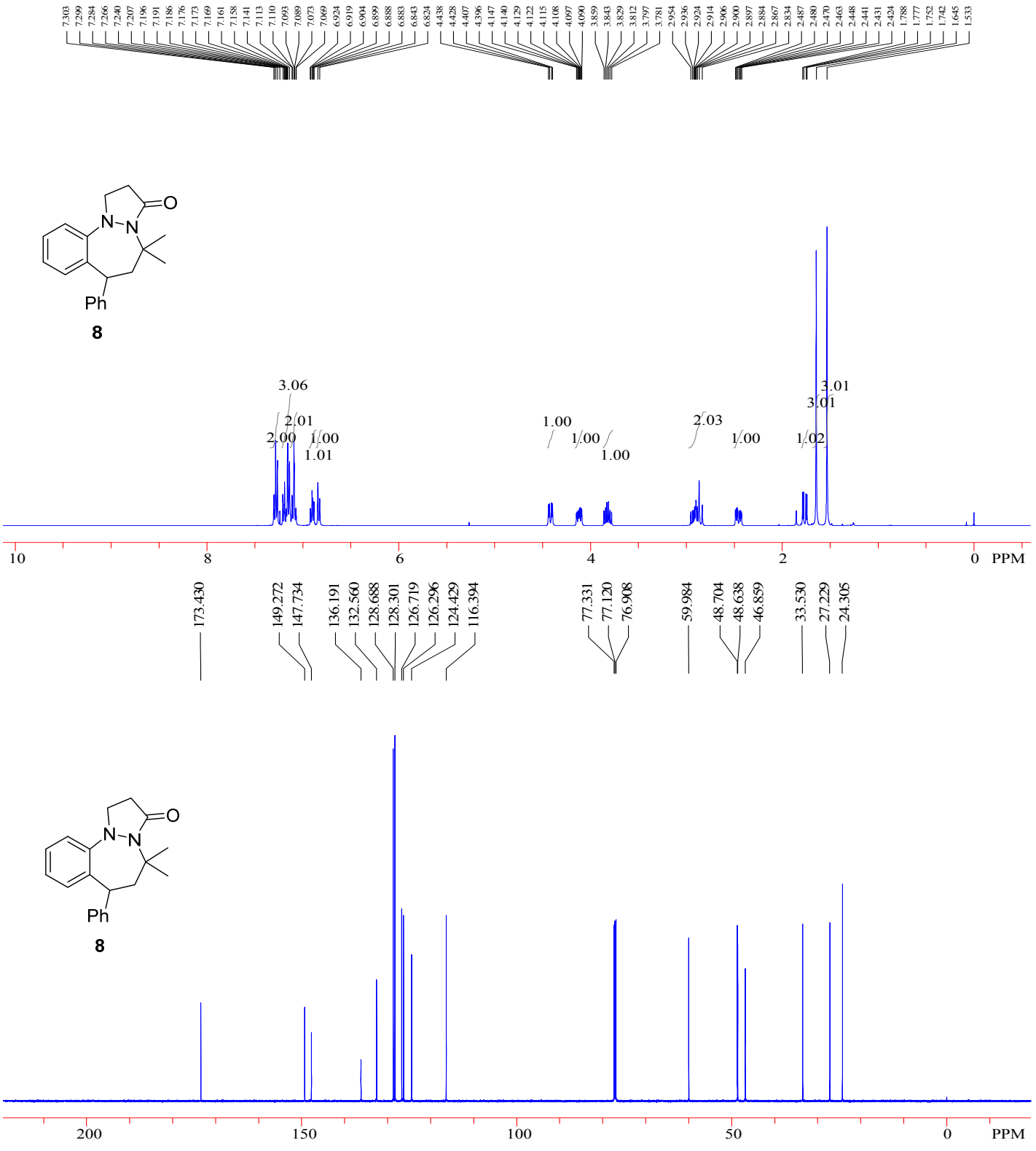
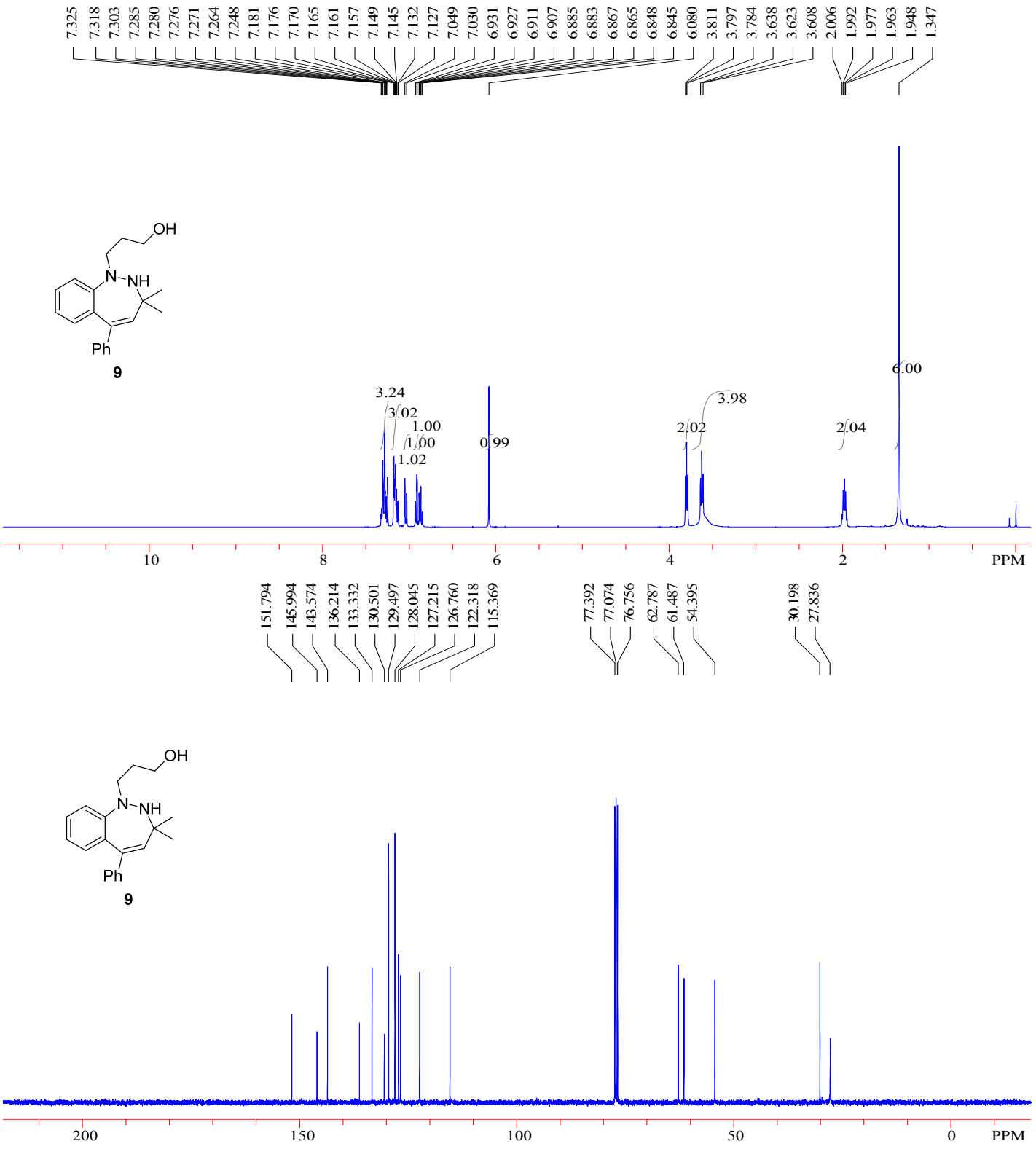
50
0
PPM

VII. Copies of NMR spectra of 8 and 9

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VIII. X-ray crystal structure and data of 3a

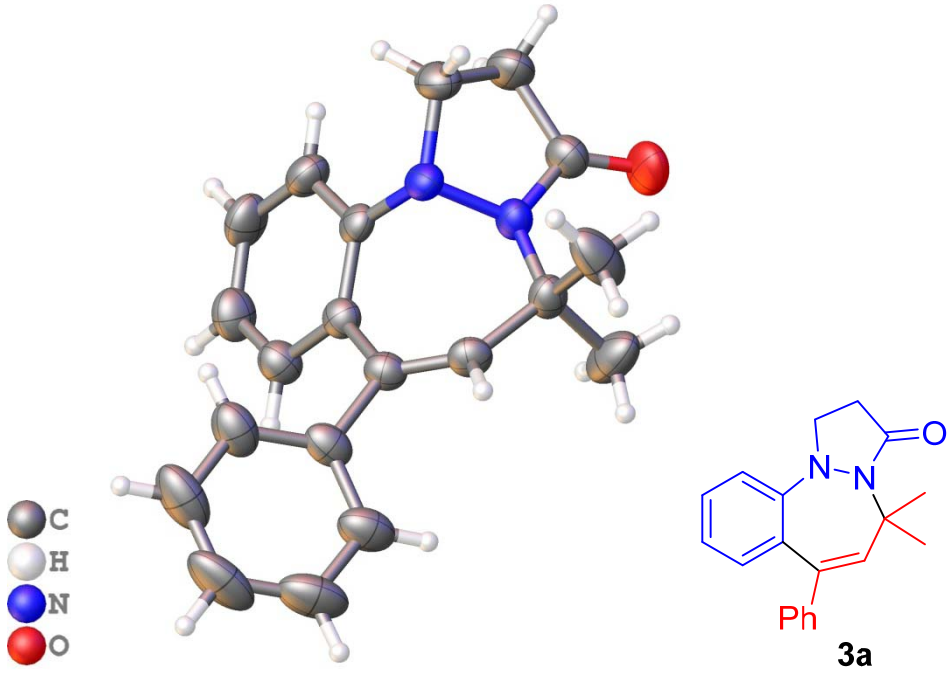

Fig. S1 X-ray structure of **3a** with 50% ellipsoid probability

X-ray structure determination. Single crystals suitable for X-ray diffraction were obtained by slow evaporation of the solvent from a petroleum ether/ethyl acetate (3:1) solution of **3a**.Crystal data collection and refinement parameters of **3a** are summarized in Table S1. Intensity data were collected at 299 K on a SuperNova Dualdiffractometer using mirror-monochromatedCuKα radiation, λ = 1.54184 Å. The data were corrected for decay, Lorentz, and polarization effects as well as absorption and beam corrections based on the multi-scan technique. The structure was solved by a combination of direct methods in SHELXTL and the difference Fourier technique, and refined by full-matrix least-squares procedures. Nonhydrogen atoms were refined with anisotropic displacement parameters. The H-atoms were either located or calculated and subsequently treated with a riding model.

Table S1 Crystallographic data and structure refinement results of **3a**

Empirical formula	$C_{20}H_{20}N_2O$
Formula weight	304.38
Temp, K	299.04(10)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a, Å	7.01650(10)
b, Å	12.2287(2)
c, Å	19.4244(4)
α (°)	90
β (°)	90
γ (°)	90
Volume, Å^3	1666.67(5)
Z	4
d_{calc}, g cm^{-3}	1.213
λ, Å	1.54184
μ, mm^{-1}	0.591
No. of data collected	4511
No. of unique data	2906
R_{int}	0.0155
Goodness-of-fit on F^2	1.092
R_1, wR_2 ($I > 2\sigma(I)$)	0.0407, 0.1033
R_1, wR_2 (all data)	0.0435, 0.1058

IX. X-ray crystal structure and data of 5a

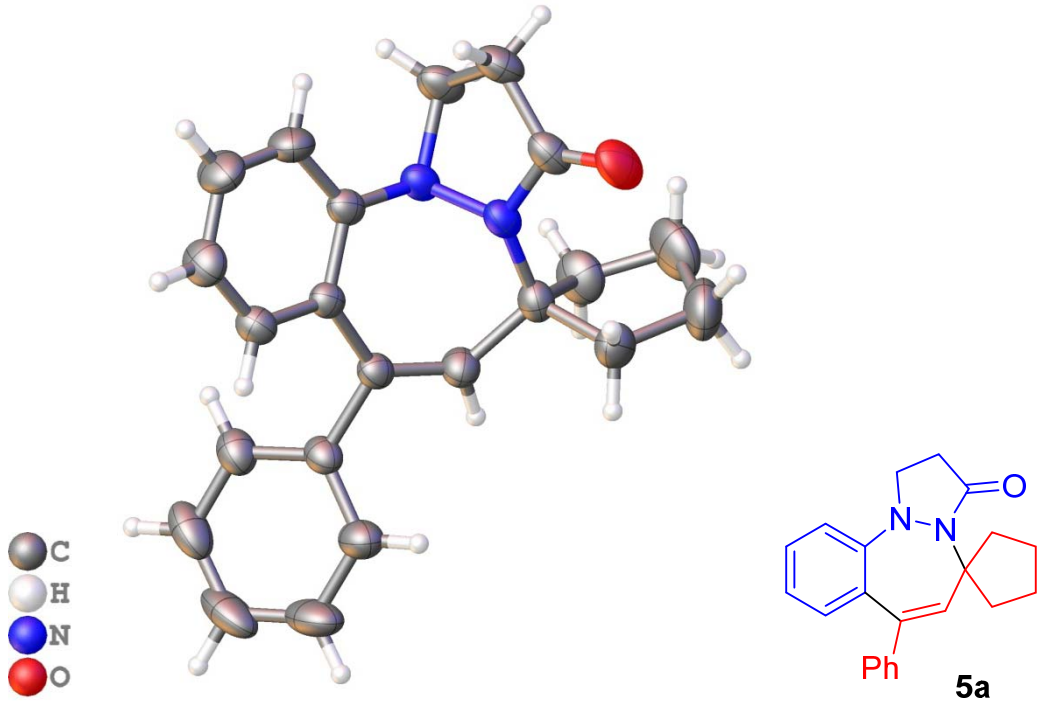

Fig. S2 X-ray structure of **5a** with 50% ellipsoid probability

X-ray structure determination. Single crystals suitable for X-ray diffraction were obtained by slow evaporation of the solvent from a petroleum ether/ethyl acetate (1:3) solution of **5a**. Crystal data collection and refinement parameters of **5a** are summarized in Table S2. Intensity data were collected at 283 K on a SuperNova Dual diffractometer using mirror-monochromated MoKα radiation, λ = 0.71073 Å. The data were corrected for decay, Lorentz, and polarization effects as well as absorption and beam corrections based on the multi-scan technique. The structure was solved by a combination of direct methods in SHELXTL and the difference Fourier technique, and refined by full-matrix least-squares procedures. Nonhydrogen atoms were refined with anisotropic displacement parameters. The H-atoms were either located or calculated and subsequently treated with a riding model.

Table S2 Crystallographic data and structure refinement results of **5a**

Empirical formula	$C_{22}H_{22}N_2O$
Formula weight	330.41
Temp, K	283 (2)
Crystal system	monoclinic
Space group	$P2_1/n$
a, Å	7.6394(5)
b, Å	22.9296(11)
c, Å	10.4410(6)
α (°)	90
β (°)	104.958(6)
γ (°)	90
Volume, Å^3	1766.96(18)
Z	4
d_{calc}, g cm^{-3}	1.242
λ, Å	0.71073
μ, mm^{-1}	0.077
No. of data collected	13029
No. of unique data	4177
R_{int}	0.0397
Goodness-of-fit on F^2	1.045
R_1, wR_2 ($I > 2\sigma(I)$)	0.0581, 0.1318
R_1, wR_2 (all data)	0.0815, 0.1467

X. References

(1) C. Yang, F. Song, J. Chen and Y. Huang, *Adv. Synth. Catal*., 2017, **359**, 3496-3502.

(2) Z. Zhang, H. Jiang and Y. Huang, *Org. Lett.,* 2014, **16**, 5976-5979.

(3) P. K. R. Panyam and T. Gandhi, *Adv. Synth. Catal*., 2017, **359**, 1144-1151.

(4) K. Feng, Y. Ban, P. Yuan, W. Lei, Q. Liu and R. Fang, *Org. Lett.,* 2019, **21**, 3131-3135.

(5) K.-i. Fujita,Y. Takahashi, M. Owaki, K. Yamamoto and R. Yamaguchi, *Org. Lett*., 2004, **6**, 2785-2788.