Supporting Information

Hydrazine-Directed Rh(III) Catalyzed (4+2) Annulation with Sulfoxonium Ylides: Synthesis and Photophysical Properties of Dihydrocinnolines

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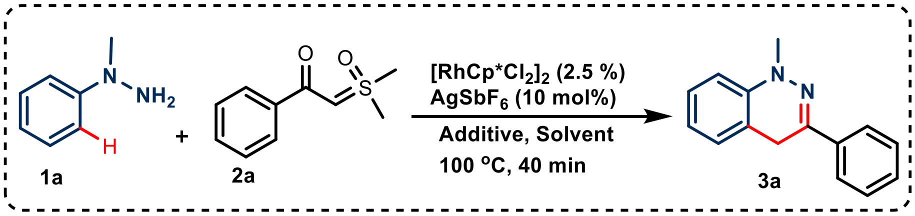
1. General Information:

All chemicals were obtained from commercial sources and were used as received unless otherwise noted. Sulfoxonium ylides[1]and N-Methyl Phenyl hydrazines[2]were synthesized according to literature reports. All the anhydrous solvents required were purchased from Sigma Aldrich.Reactions were monitored using precoated Aluminum supported silica gel 60 F254 TLC (thin layer chromatography) plates (Merck) and are visualized by UV light at 254 nm. The final product was purified using column chromatography (100-200 mesh silica gel purchased from Merck). ^{1}H NMR (400 MHz), ^{19}F NMR (376 MHz), and ^{13}C NMR (101 MHz) spectra were recorded on the Bruker AVANCE NEO 400 MHz spectrometer. Deuterated chloroform, DMSO-d_6 were used as solvents, and Chemical shifts (δ) for ^{1}Hand ^{13}C-NMR spectra are given in ppm relative to tetramethylsilane (TMS) [δ 7.27 for ^{1}H (chloroform-d), δ 77.0 for ^{13}C (chloroform-d); δ 2.50 for ^{1}H (DMSO-d_6), δ 39.52 for ^{13}C (DMSO-d_6)], ^{19}F-NMR spectra are not externally calibrated and chemical shifts is given relative to CCl_3F as received from the automatic data processing. Abbreviations used in the NMR follow-up experiments: br, broad; s, singlet; d, doublet; t, triplet; q, quartet; sep, septet; dd, doublet of doublet; m, multiplet. All fluorescent spectra were recorded by using an FP-8500 spectroflourometer (JASCO) and Cary 3500UV-Visible spectrometer (Agilent).High resolution mass spectra (HRMS) was obtained from Orbitrap Elite HybridIon Trap-Orbitrap (Thermofischer scientific, Newington, NH, USA) Mass Spectrometer in electrospray ionization mode (ESI+).

2. Experimental Section:

2.1. General procedure for the optimization

Table S1: Optimization of reaction conditions.[a]

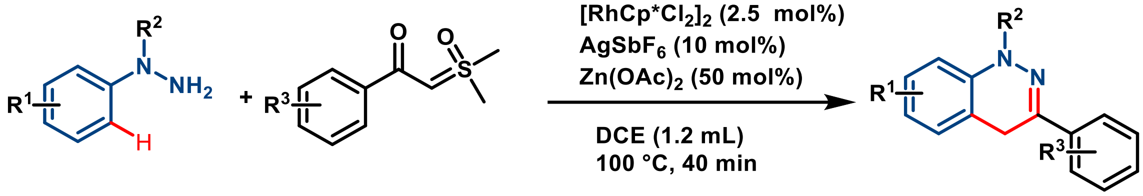


Entry	Additive (equiv)	Solvent	Yield (%)[b]
1	NaOAc (1.0)	ACN	40
2	NaOAc (1.0)	MeOH	20
3	NaOAc (1.0)	TFE	trace
4	NaOAc (1.0)	Dioxane	trace
5[c]	NaOAc (1.0)	DCE	55
6[d]	NaOAc (1.0)	DCE	61
7[e]	NaOAc (1.0)	DCE	72 (78)
8[f]	NaOAc (1.0)	DCE	trace
9[g]	NaOAc (1.0)	DCE	n.d
10[h]	NaOAc (1.0)	DCE	n.d
11[i]	NaOAc (1.0)	DCE	n.d
12	LiOAc (1.0)	DCE	40
13	KOAc (1.0)	DCE	50
14	$Cu(OAc)_2$ (1.0)	DCE	15
15	$Zn(OAc)_2$ (0.2)	DCE	70
16	$Zn(OAc)_2$ (0.5)	DCE	82 (87)
17	$Zn(OAc)_2$ (0.7)	DCE	73
18	AcOH (1.0)	DCE	31
19	PivOH (1.0)	DCE	45
20	_	DCE	16

[a]Reaction conditions: 1a (0.25 mmol) and 2a (0.37 mmol), $[RhCp^*Cl_2]_2$ (2.5 mol %), $AgSbF_6$ (10 mol %) and additive in solvent (1.2 mL) at 100 °C for 40 min Yields are based on crude ^1H NMR (internal standard: 1,1,2,2 tetrachloroethane). [c]Reaction run at 80 °C. [d]Reaction run at 90 °C. [e]Reaction run at 100 °C. [f]Reaction with $[RuCl_2(p\text{-cymene})]_2$ (5 mol %). [g]Reaction with $[CoCp^*(CO_2)I_2]$. [h]Without $AgSbF_6$. [i]Reaction without $[RhCp^*Cl_2]_2$ (2.5 mol %).

To a 15 ml dry pressure tube containing a Teflon coated stir bar were added N-methyl phenyl hydrazine **1a** (10 mg, 0.082 mmol), sulfoxonium ylide **2a** (24 mg, 0.123 mmol), $[Cp^*RhCl_2]_2$ catalyst (1.26 mg, 2.5 mol %), $AgSbF_6$ (2.8 mg, 10 mol%), additive and the corresponding solvent. The tube was then sealed after flushing with argon and placed on a preheated oil bath at 100 °C.The reaction mixture was then stirred at the same temperature for 40 min. After completion of the reaction (monitored by TLC), the reaction mixture was cooled to room temperature, diluted with DCM and solvents removed under reduced pressure. The crude products was analyzed on ^{1}H NMR to find the yield.

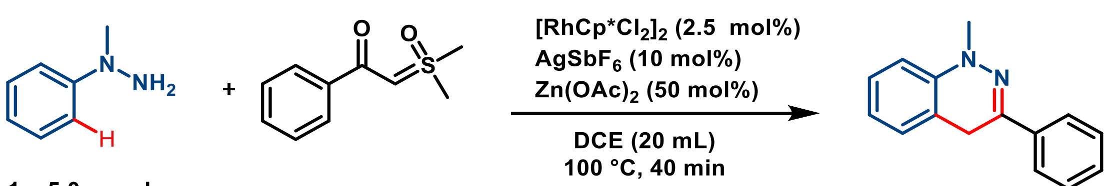
2.2. General procedure for the preparation of compounds 3a-3s, 4a-4m & 6a-6d.



To a 15 ml of pressure seal tube containing a Teflon coated stir bar were added the corresponding N-alkyl aryl hydrazine derivative (1 equiv, 0.25 mmol), sulfoxonium ylide (1.5 equiv, 0.37 mmol), $Zn(OAc)_2$ (22.5 mg, 0.12 mmol), $[Cp*RhCl_2]_2$ (3.86 mg, 2.5 mol %), $AgSbF_6$ (8.6 mg, 10 mol%) followed by the addition of DCE (1.2 mL) as solvent. The tube was then sealed after flushing with argon and placed on a preheated oil bath at 100 °C. The reaction mixture was then stirred at the same temperature for 40 min. After completion of the reaction (monitored by TLC), the reaction mixture was cooled to room temperature, diluted with DCM and the solvents removed under reduced pressure. The crude products were then purified on Column chromatography with 100-200 mesh size silica gel using ethyl acetate/hexane solvent system to afford the desired products.

2.3. Scale up reaction

Same procedure as described in **section 2b** was followed for the 5.0 mmol scale reaction.



1a, 5.0 mmol

2a, 7.5 mmol

3a, 0.81g, 74%

2.4. Photophysical properties of compound 3a, 3c, 3j, 3m, 3q, 3r.

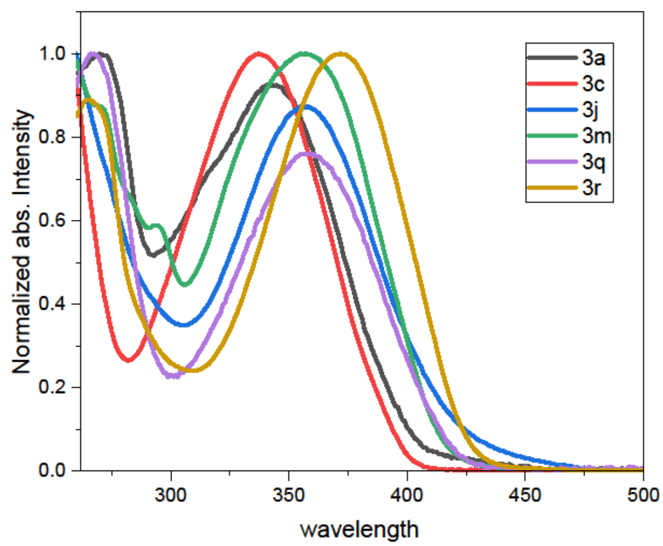


Figure S1: Normalized UV absorption of compound **3a, 3c, 3j, 3m, 3q** and **3r** dispersed in dichloromethane medium (1×10^{-5} M).

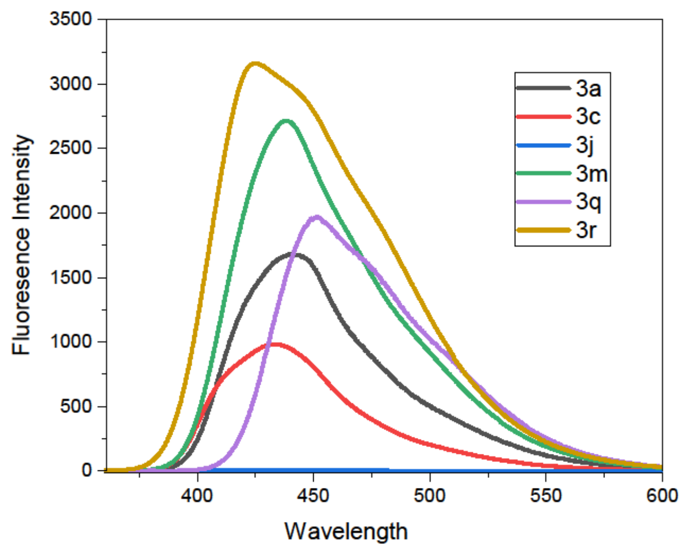


Figure S2: Photoluminescent spectra of compound **3a, 3c, 3j 3m, 3q** and **3r** dispersed in dichloromethane medium (1×10^{-5} M).

Compounds	λ_{abs} (nm)^{a}	λem (nm)^{a,b}	ϕ_F
3a	343	441	0.49
3c	336	432	0.15
3j	357	442	0.02
3m	358	438	0.69
3q	360	452	0.94
3r	372	434	0.85

[a.] Concentration of 1×10^{-5} M in DCM.

Measurement of fluorescence quantum yield (ΦF)

Fluorescence quantum yields (ΦF) of our synthesized dihydrocinnolines derivatives were calculated using 2-aminopyridine (0.1 M H_2SO_4 solution) as a standard (Φ= 0.60). Emission spectra of compounds **3** were recorded from 350 nm to 600 nm with excitation at their absorption maximum. Quantum yields were calculated according to equation (1), in which Φ_{ref} is the quantum yield of the reference, A_{sample} and A_{ref} are the areas under the emission spectra of the sample 3 and the reference, respectively, and OD_{ref} and OD_{sample} are the absorbance of the reference and the sample 3, respectively, measured at the excitation wavelength; n_{sample} and n_{ref} are the refractive indices of the sample 3 and the reference, respectively, in solution.

$$\varphi_{sample} = \varphi_{ref}\left(\frac{A_{sample}}{A_{ref}}\right) \times \left(\frac{OD_{ref}}{OD_{sample}}\right) \times \left(\frac{n_{ref}}{n_{sample}}\right)$$

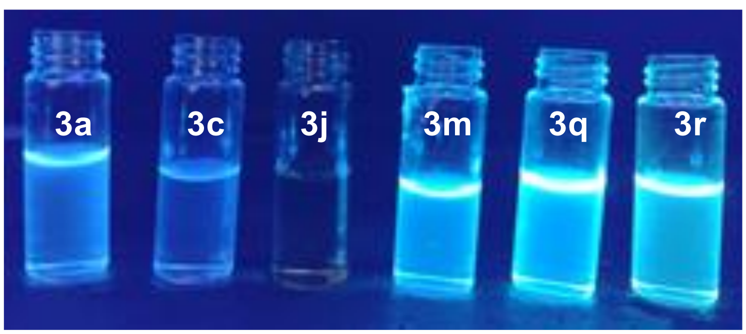
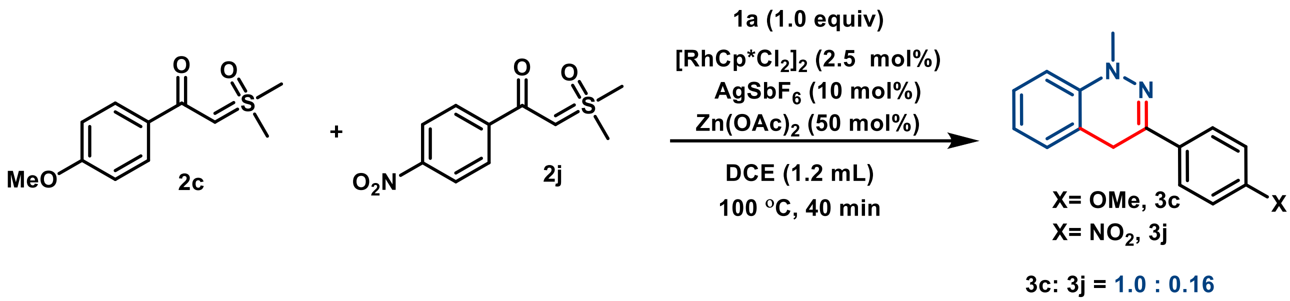
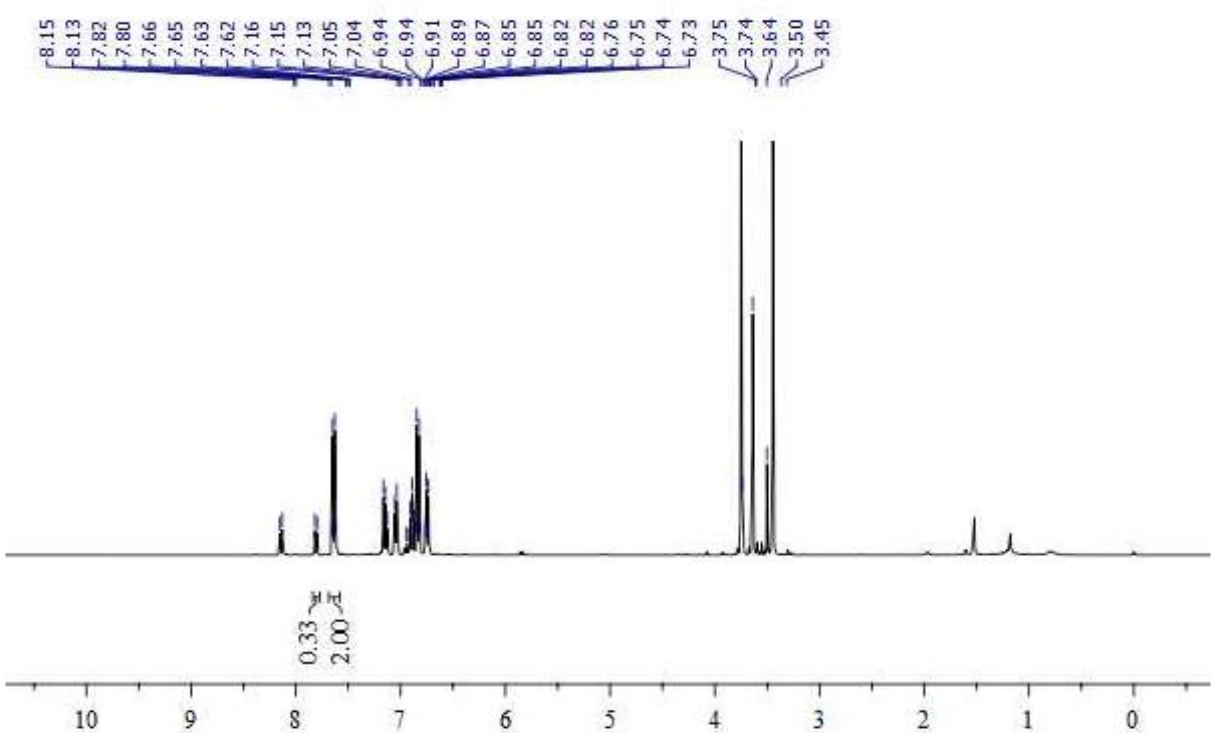


Figure S3: Compounds **3** in DCM (1×10^{-5} M) under UV Irradiation at 365 nm.

2.5. Intermolecular Competition Experiment:



To a dried seal tube containing a Teflon coated stir bar were added **2c** (42 mg, 0.185 mmol), **2j** (45 mg, 0.185 mmol), N-methyl phenyl hydrazine, **1a** (30 mg, 0.25 mmol), $[Cp^*RhCl_2]_2$ (3.86 mg, 2.5 mol %), $AgSbF_6$ (8.45 mg, 10 mol%) followed by DCE (1.2 mL). The tube sealed after flushing with argon and placed with preheated oil bath at 100 °C, and the reaction mixture was stirred at the same temperature for 40 min. After completion of the reaction (monitored by TLC), the reaction mixture was cooled to room temperature, diluted with DCM and solvent removed under reduced pressure. The crude products were purified on Column chromatography on 100-200 silica gel and ratio of products **3c** and **3j** was measured by ^{1}H NMR analysis which was found by **1.0:0.16**.



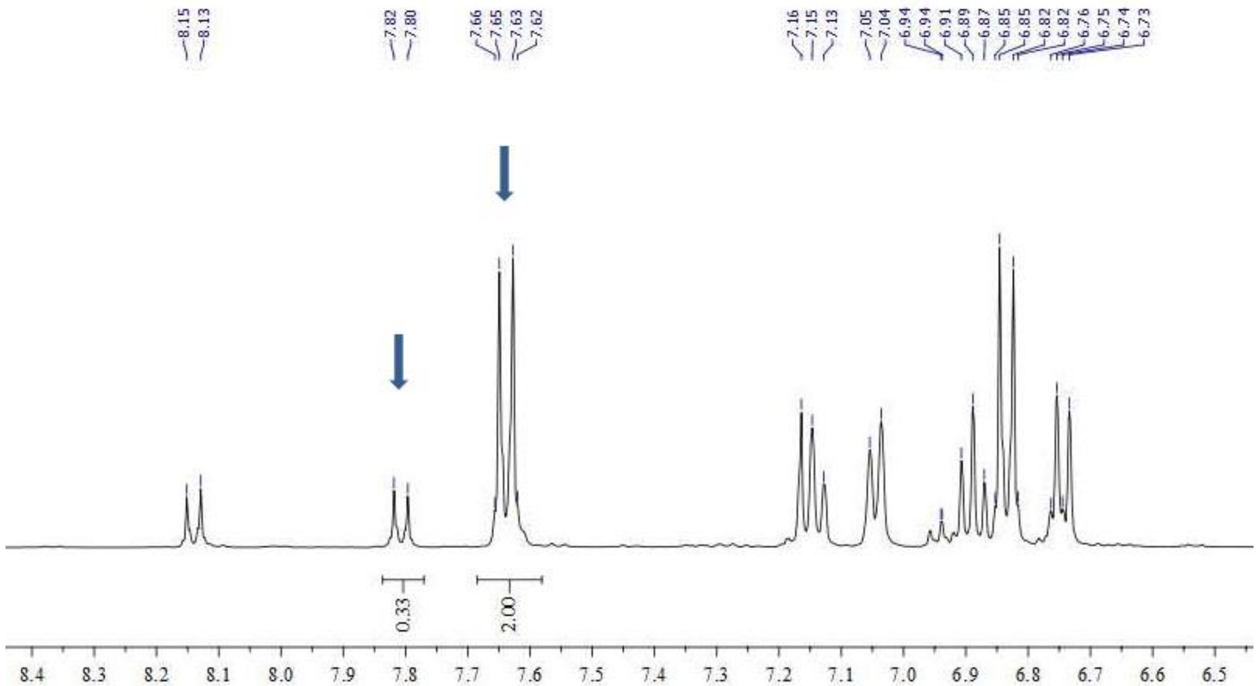
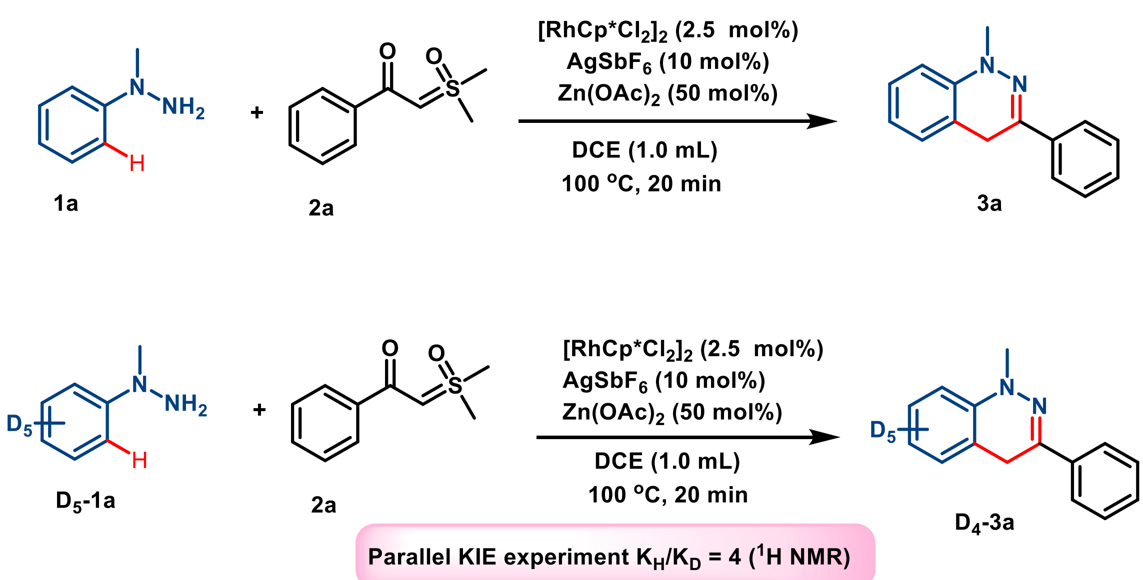


Figure S4. ^{1}H NMR for intermolecular competition experiment between **3c** and **3j.**

2.6 Kinetic Isotope Effect Experiments:

a) Parallel experiment:



N-methyl phenyl hydrazine **1a (**20 mg, 0.16 mmol) and N-methyl phenyl hydrazine **D5 -1a** (21 mg, 0.16 mmol) were added to the two separate seal tubes with magnetic stir bar followed by sulfoxonium ylide, **2a** (48 mg, 0.25 mmol), $[Cp^*RhCl_2]_2$ catalyst (2.5 mg, 2.5 mol %), $AgSbF_6$

(5.5 mg, 10 mol%) and DCE (1.0 mL) in both the test tubes. The tube was then sealed after flushing with argon and placed in a preheated oil bath at 100 ^{o}C and the reaction mixture was stirred at the same temperature for 20 min. The reaction mixture was then cooled to room temperature, diluted with DCM and the solvents were then removed under reduced pressure. The crude products were purified on column chromatography on 100-200 silica gel to afford the desired **3a** and **[D$_4$]-3a.** The KIE value for parallel experiment was found to be 4.0. ($K_H/K_D = 4$) based on the ^{1}H NMR analysis.

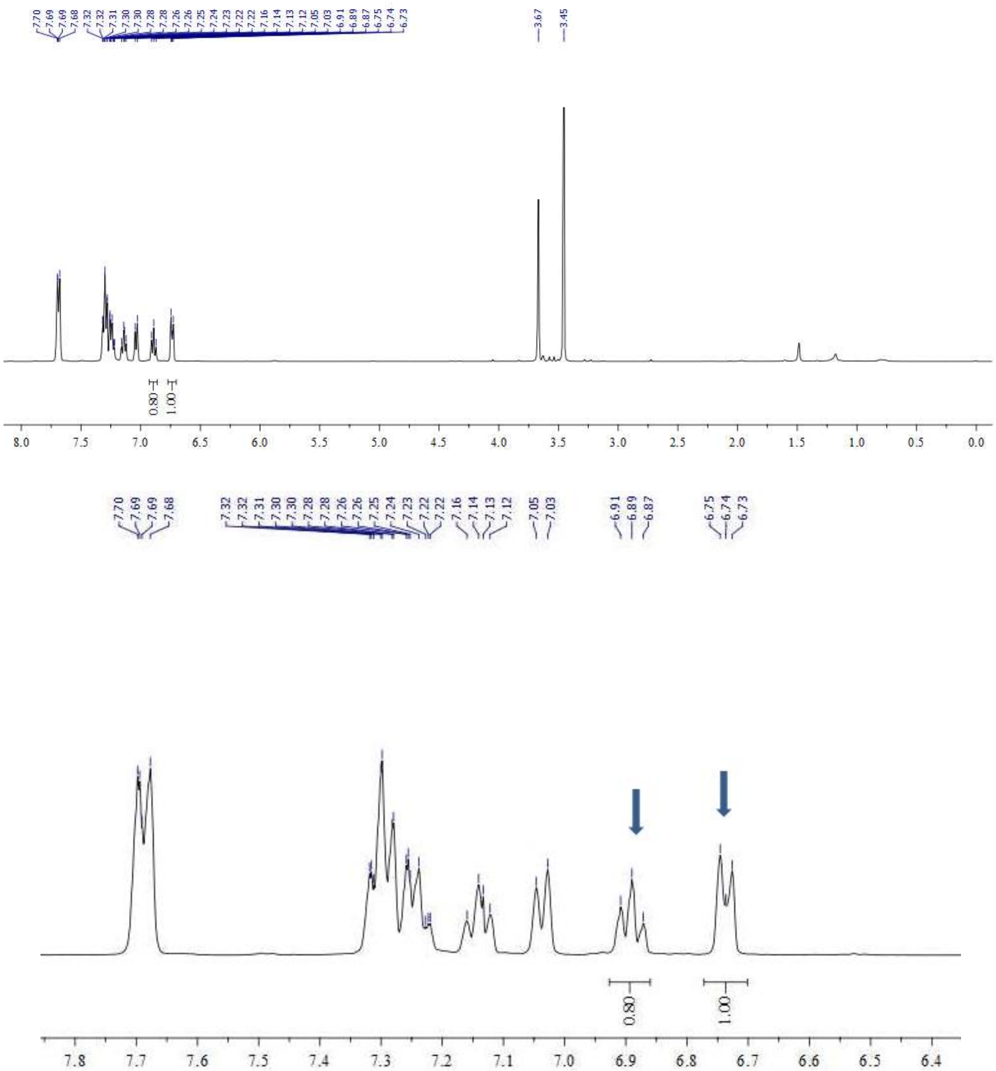
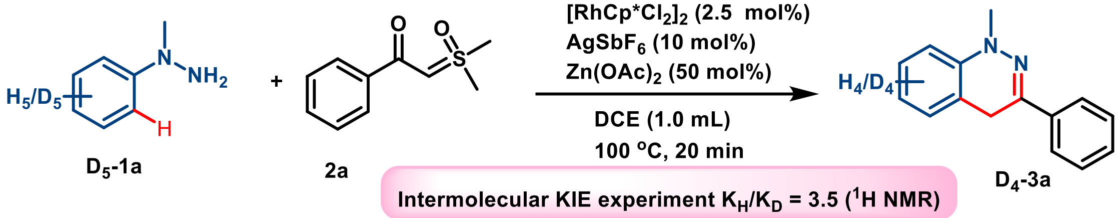


Figure S5. ^{1}H NMR for KIE study **(Parallel experiment)**

b) Intermolecular KIE experiment

To a dried seal tube containing a Teflon coated magnetic stir bar, phenyl N-methyl hydrazine **1a (**20 mg, 0.16 mmol), Phenyl N-methyl hydrazine **D$_5$ -1a** (21 mg, 0.16 mmol) were added followed by sulfoxonium ylide **2a** (48 mg, 0.25 mmol), $[Cp^*RhCl_2]_2$ (2.5 mg, 2.5 mol %), $AgSbF_6$ (5.5 mg, 10 mol%) and

DCE (1.0 mL) as solvent. The tube was sealed after flushing with argon and placed in a preheated oil bath at 100 °C, and the reaction mixture was stirred at the same temperature for 20 min. The reaction mixture was cooled to room temperature, diluted with DCM and the solvent was removed under reduced pressure. The crude products were purified on column chromatography on 100-200 silica gel to afford the desired **products 3a** and **[D4]-3a.** The KIE value for the intermolecular experiment was found to be 3.5 (K_H/K_D = 3.5) based on the ^{1}H NMR analysis.



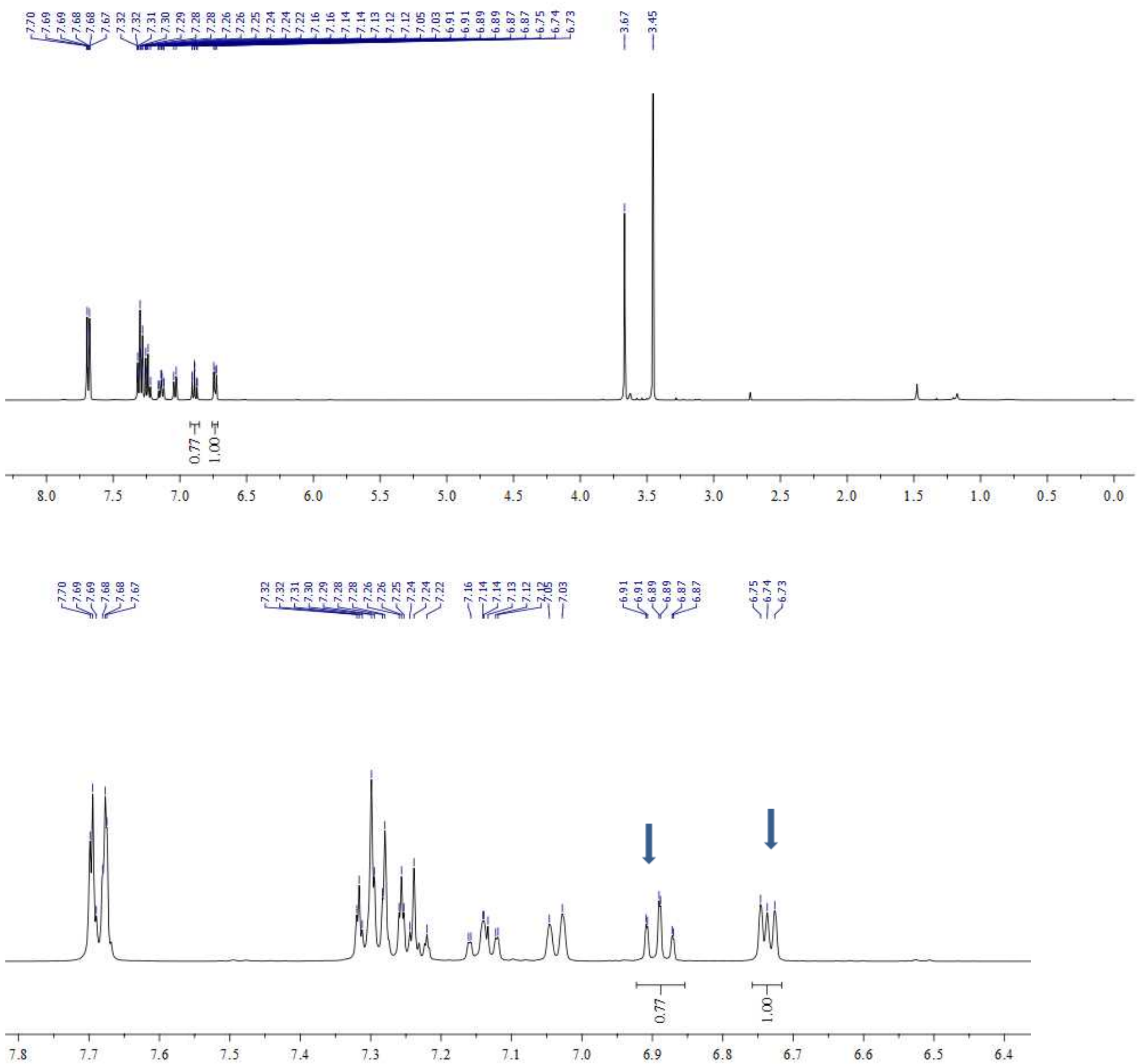
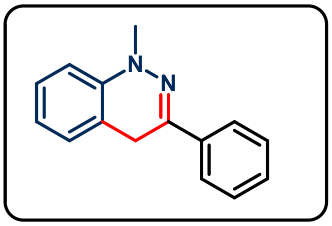


Figure S6. ^{1}H NMR for intermolecular KIE study.

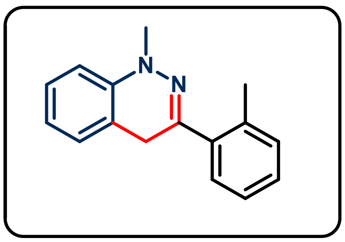
3. Analytical data of compounds

1-Methyl-3-phenyl-1,4-dihydrocinnoline (3a)



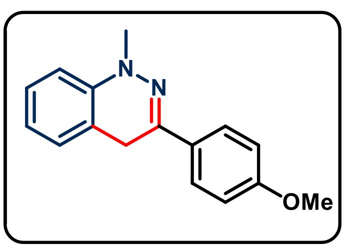
Yellow semi solid(0.25 mmol scale, 45.5 mg, 82%);**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.79 (m, 2H), 7.41 (m, 3H), 7.14 (d, *J* = 7.0 Hz, 1H), 7.14 (d, *J* = 7.0 Hz, 1H), 6.99 (m, 1H), 6.84 (d, *J* = 8.0 Hz, 1H), 3.77 (s, 2H), 3.56 (s, 3H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.01, 140.02, 136.88, 128.34, 127.74, 127.32, 125.36, 121.92, 118.12, 110.14, 76.68, 40.94, 27.86.**HR-MS** (ESI) m/z calcd for $C_{15}H_{15}N_2^+$ [M+H$^+$]: 222.1157, found: 223.1222.

1-methyl-3-(o-tolyl)-1,4-dihydrocinnoline(3b)



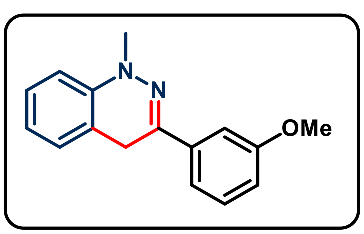
Greenish yellow semi solid(0.25 mmol scale, 46.6 mg, 79%);**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35 – 7.31 (m, 1H), 7.08 (dd, *J* = 7.3, 0.8 Hz, 1H), 6.99 (m, 1H), 6.86 (d, *J* = 8.1 Hz, 1H), 3.57 (s, 2H), 3.49 (s, 3H), 2.38 (s, 3H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.24, 142.04, 137.77, 136.02, 130.85, 128.40, 128.14, 127.17, 125.86, 122.05, 118.47, 110.09, 40.79, 32.04, 20.70. **HR-MS** (ESI) m/z calcd for $C_{16}H_{15}N_2^+$ [M-H$^+$] 235.1235, found: 235.1233.

3-(4-methoxyphenyl)-1-methyl-1,4-dihydrocinnoline(3c)



Yellow semi solid(0.25 mmol scale, 44 mg, 70%);**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.7 Hz, 2H), 7.25 – 7.18 (m, 1H), 7.11 (d, *J* = 7.0 Hz, 1H), 7.02 – 6.87 (m, 3H), 6.81 (d, *J* = 8.0 Hz, 1H), 3.82 (s, 3H), 3.71 (s, 2H), 3.51 (s, 3H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.93, 141.26, 140.13, 129.64, 127.65, 127.23, 126.77, 121.66, 118.16, 113.72, 113.47, 110.04, 55.30, 40.89, 27.98. **HR-MS** (ESI) m/z calcd for $C_{16}H_{17}N_2O^+$ [M+H$^+$]: 253.1335, found: 253.1336.

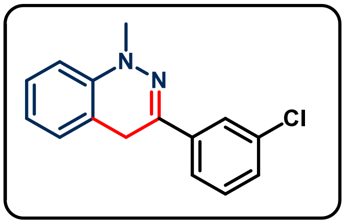
3-(3-methoxyphenyl)-1-methyl-1,4-dihydrocinnoline (3d)



Yellow semi solid(0.25 mmol scale, 34 mg, 68%);**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.45 – 7.32 (m, 3H), 7.29 (s, 2H), 7.17 (d, *J* = 6.9 Hz, 1H), 7.08 – 6.99 (m, 1H), 6.94 (dd, *J* = 5.3, 1.4 Hz, 1H), 6.87

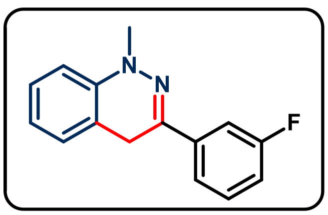
(d, J = 8.0 Hz, 1H), 3.90 (s, 3H), 3.80 (s, 2H), 3.59 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 159.66 (s), 140.89 (s), 139.67 (s), 138.34, 129.27, 127.75, 127.31, 121.93, 118.10, 117.93 , 114.27, 110.57, 110.14, 55.27, 40.94, 27.8.**HR-MS** (ESI) m/z calcd for $C_{16}H_{17}N_2O^+$ [M+H$^+$] 253.1335, found: 253.1334.

3-(3-chlorophenyl)-1-methyl-1,4-dihydrocinnoline (3e)



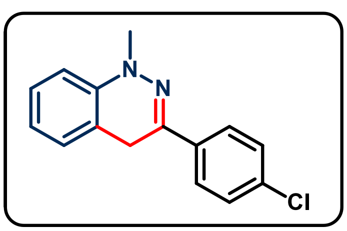
Pale yellow semi solid(0.25 mmol scale, 40 mg, 62%);**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.70 (s, 1H), 7.56 (dd, J = 4.6, 1.8 Hz, 1H), 7.27 – 7.12 (m, 3H), 7.05 (d, J = 6.9 Hz, 1H), 6.95 – 6.86 (m, 1H), 6.75 (d, J = 8.0 Hz, 1H), 3.67 (s, 2H), 3.47 (s, 3H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 140.49, 138.75, 137.94, 134.45, 129.52, 128.15, 127.88, 127.49, 125.34, 123.26, 122.21, 117.72, 110.30, 40.99, 27.45.**HR-MS** (ESI) m/z calcd for $C_{15}H_{14}ClN_2^+$ [M+H$^+$]: 257.0840, found: 257.0845.

3-(3-fluorophenyl)-1-methyl-1,4-dihydrocinnoline(3f)



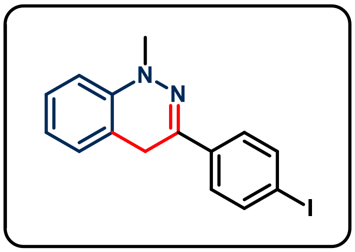
Yellow semi solid (0.25 mmol scale, 37.2 mg, 62%);**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.62 – 7.49 (m, 2H), 7.38 (dd, J = 14.0, 8.0 Hz, 1H), 7.27 (d, J = 10.9 Hz, 2H), 7.17 (d, J = 7.0 Hz, 1H), 7.06 (m), 6.87 (d, J = 8.0 Hz, 1H), 3.79 (s, 2H), 3.59 (s, 3H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 164.21, 161.78, 140.52, 139.30, 139.22(d, J = 7.8 Hz), 138.15(d, J = 2.9 Hz), 129.76(d, J = 8.2 Hz), 129.68, 127.86, 127.47, 122.16, 120.79(d, J = 2.5 Hz), 117.77, 115.18, 114.96, 112.16, 111.93, 110.29, 40.98, 27.51.**HR-MS** (ESI) m/z calcd for $C_{15}H_{14}FN_2^+$ [M+H$^+$] 241.1141.found: 241.1136

3-(4-chlorophenyl)-1-methyl-1,4-dihydrocinnoline(3g)



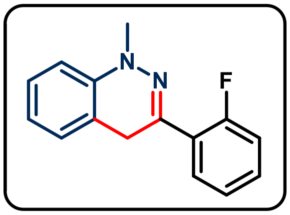
Pale yellow semi solid(0.25 mmol scale, 41 mg, 64%);**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.75 (d, J = 8.7 Hz, 2H), 7.39 (d, J = 8.7 Hz, 2H), 7.26 (s, 2H), 7.17 (d, J = 7.0 Hz, 1H), 7.09 – 6.96 (m, 1H), 6.87 (d, J = 8.0 Hz, 1H), 3.78 (s, 2H), 3.58 (s, 3H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 140.65, 138.46, 135.37, 134.12, 128.48, 127.83, 127.46, 126.52, 122.10, 117.79, 110.26, 40.97, 27.53.**HR-MS** (ESI) m/z calcd for $C_{15}H_{12}ClN_2^+$[M-H$^+$]: 255.0689, found: 255.0684.

3-(4-iodophenyl)-1-methyl-1,4-dihydrocinnoline (3h)



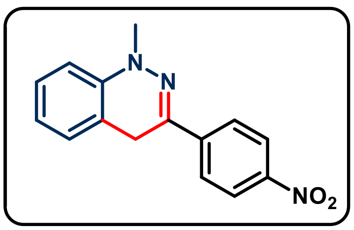
Yellow semi solid (0.25 mmol scale, 59.2 mg, 68%);^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 – 7.66 (m, 2H), 7.59 – 7.44 (m, 2H), 7.30 – 7.20 (m, 1H), 7.13 (d, *J* = 7.3 Hz, 1H), 7.00 (m, 1H), 6.83 (d, *J* = 8.1 Hz, 1H), 3.74 (s, 2H), 3.55 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.48, 138.35, 137.33, 136.36, 127.83, 127.44, 126.92, 122.10, 117.73, 110.24, 94.03, 40.97, 27.25. **HR-MS** (ESI) m/z calcd for $C_{15}H_{12}N_2I^+$ [M+H$^+$]: 347.0045, found: 347.0040.

3-(2-fluorophenyl)-1-methyl-1,4-dihydrocinnoline (3i)



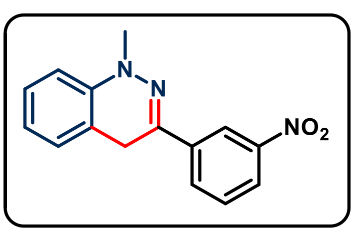
Yellow semi solid (0.25 mmol scale, 40 mg, 66%);**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.65 (m, 1H), 7.34 (dd, *J* = 9.2, 3.2 Hz, 1H), 7.31 – 7.23 (m, 1H), 7.20 – 7.08 (m, 3H), 7.07 – 7.01 (m, 1H), 6.89 (d, *J* = 8.1 Hz, 1H), 3.80 (s, 2H), 3.57 (s, 3H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.49, 160.01, 141.64, 139.30, 130.10 (d, J = 8.5 Hz), 129.66 (d, J = 3.7 Hz), 125.62 (d, J = 11.9 Hz),127.50, 127.22, 125.68, 124.20 (d, J = 3.4 Hz), 122.38, 118.43, 116.18, 115.96, 110.10, 40.88, 31.18 (d, J = 7.2 Hz).**HR-MS** (ESI) m/z calcd for $C_{15}H_{14}FN_2^+$ [M+H$^+$]: 241.1141, found: 241.1136.

1-methyl-3-(4-nitrophenyl)-1,4-dihydrocinnoline (3j)



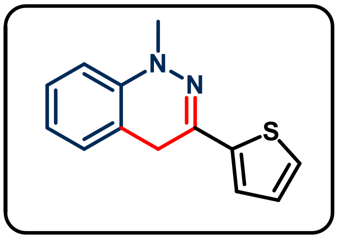
Orange solid(0.25 mmol scale, 36 mg, 54%)mp 200-210 ^{o}C;**^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.25 – 8.18 (m, 2H), 7.89 (d, J = 9.0 Hz, 2H), 7.29 – 7.20 (m, 1H), 7.13 (d, J = 7.3 Hz, 1H), 7.01 (m, 1H), 6.83 (d, J = 8.1 Hz, 1H), 3.82 (s, 2H), 3.58 (s, 3H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 147.04, 142.96, 139.54, 135.95, 128.14, 127.77, 125.33, 123.65, 122.85, 117.39, 110.63, 41.18, 26.88.**HR-MS** (ESI) m/z calcd for $C_{15}H_{12}N_3O_2^+$ [M-H$^+$]: 266.0930, found:266.0925.

1-methyl-3-(3-nitrophenyl)-1,4-dihydrocinnoline(3k)



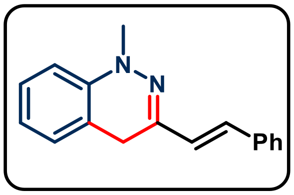
Red solid(0.25 mmol scale, 30.04 mg, 45%)mp190-200^{o}C;**^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.52 (t, *J* = 2.0 Hz, 1H), 8.11 – 8.01 (m, 2H), 7.47 (t, *J* = 8.0 Hz, 1H), 7.23 – 7.16 (m, 1H), 7.09 (d, *J* = 7.3 Hz, 1H), 6.95 (m, 1H), 6.78 (d, *J* = 8.1 Hz, 1H), 3.76 (s, 2H), 3.51 (s, 3H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 148.52, 139.94, 138.71, 136.21, 130.66, 129.15, 128.07, 127.71, 122.57, 122.53, 119.81, 117.32, 110.52, 41.09, 27.09.**HR-MS** (ESI) m/z calcd for $C_{15}H_{14}N_3O_2^+$ [M+H$^+$] 268.1086, found: 268.1081.

1-methyl-3-(thiophen-2-yl)-1,4-dihydrocinnoline(3l)



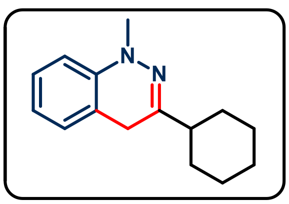
Yellow semi solid(0.25 mmol scale, 47.8 mg, 84%);**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.15 (m, 3H), 7.04 (d, *J* = 7.0 Hz, 1H), 6.94 (dd, *J* = 5.0, 3.7 Hz, 1H), 6.89 (m, 1H), 6.73 (d, *J* = 8.0 Hz, 1H), 3.68 (s, 2H), 3.43 (s, 3H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 142.51, 140.79, 136.22, 127.81, 127.41, 127.09, 126.07, 124.17, 121.87, 117.72, 110.47, 40.86, 28.16.**HR-MS** (ESI) m/z calcd for $C_{13}H_{12}N_2S^+$ [M+H$^+$]: 229.0794, found: 229.0802.

(E)-1-methyl-3-styryl-1,4-dihydrocinnoline(3m)



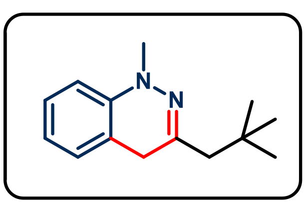
Yellow solid(0.25 mmol scale, 44.7 mg, 72%) mp 220-225 ^{o}C;**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 7.5 Hz, 2H), 7.33 (t, *J* = 7.6 Hz, 2H), 7.23 (m, 2H), 7.13 (d, *J* = 7.3 Hz, 1H), 6.98 (dd, *J* = 15.8, 9.0 Hz, 2H), 6.81 (s, 1H), 6.78 (d, *J* = 7.1 Hz, 1H), 3.65 (s, 2H), 3.49 (s, 3H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.25, 140.46, 136.92, 129.85, 128.72, 128.0, 127.84, 127.39, 127.35, 126.63, 122.02, 117.95, 110.44, 40.80, 25.80.**HR-MS** (ESI) m/z calcd for $C_{17}H_{17}N_2^+$[M+H$^+$] 249.1392.found: 249.1374.

3-Cyclohexyl-1-methyl-1,4-dihydrocinnoline(3n)



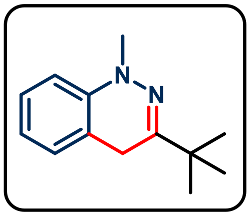
Yellow semi solid(0.25 mmol scale, 41 mg, 67%);**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.21 (t, *J* = 7.1 Hz, 1H), 7.07 (d, *J* = 6.8 Hz, 1H), 7.00 – 6.91 (m, 1H), 6.80 (d, *J* = 8.0 Hz, 1H), 3.39 (s, 3H), 3.21 (s, 2H), 2.32 (t, *J* = 10.0 Hz, 1H), 1.81 (d, *J* = 7.0 Hz, 4H), 1.71 (d, *J* = 11.9 Hz, 1H), 1.41 – 1.25 (m, 5H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.93, 143.00, 126.98, 126.94, 121.40, 118.87, 109.98, 44.89, 40.48, 30.19, 28.5, 26.08, 26.03. **HR-MS** (ESI) m/z calcd for $C_{15}H_{21}N_2^+$ [M+H$^+$]: 229.1705, found: 229.1700.

1-methyl-3-neopentyl-1,4-dihydrocinnoline (3o)



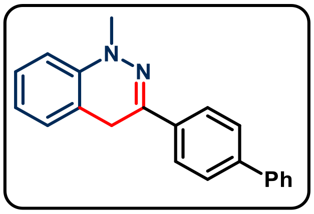
Yellow semi solid(0.25 mmol scale, 36.8 mg, 68%);**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.16 (dd, *J* = 14.3, 7.0 Hz, 1H), 6.98 (d, *J* = 6.8 Hz, 1H), 6.90 (m, 1H), 6.75 (d, *J* = 8.0 Hz, 1H), 3.34 (s, 3H), 3.15 (s, 2H), 2.20 (s, 2H), 0.91 (s, 9H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 146.07, 142.83, 126.88, 126.77, 121.64, 118.82, 109.91, 49.81, 40.50, 33.46, 31.88, 29.93.**HR-MS** (ESI) m/z calcd for $C_{14}H_{21}N_2^+$ [M+H$^+$]: 217.1705, found: 217.1669.

3-(tert-butyl)-1-methyl-1,4-dihydrocinnoline(3p)



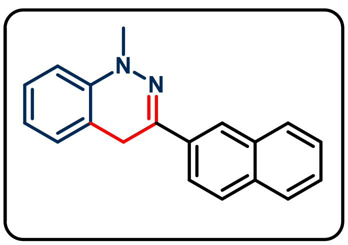
Yellow semi solid(0.25 mmol scale, 36.9 mg, 73%);**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.22 (t, *J* = 7.1 Hz, 1H), 7.10 (d, *J* = 6.7 Hz, 1H), 6.96 (dd, *J* = 7.3, 6.5 Hz, 1H), 6.81 (d, *J* = 8.0 Hz, 1H), 3.40 (s, 3H), 3.21 (s, 2H), 1.18 (s, 9H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 152.91, 143.11, 126.85, 126.82, 121.29, 119.63, 109.89, 40.63, 36.83, 29.69, 27.69.**HR-MS** (ESI) m/z calcd for $C_{13}H_{17}N_2^+$ [M-H$^+$]: 201.1392, found: 201.1386.

3-([1,1'-biphenyl]-4-yl)-1-methyl-1,4-dihydrocinnoline (3q)



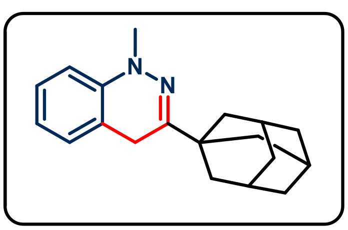
Yellow semi solid (0.25 mmol scale, 46.2 mg, 62%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90 – 7.83 (m, 2H), 7.65 (d, *J* = 7.4 Hz, 4H), 7.47 (t, *J* = 7.5 Hz, 2H), 7.37 (t, *J* = 7.3 Hz, 1H), 7.26 (t, *J* = 7.7 Hz, 1H), 7.17 (d, *J* = 7.3 Hz, 1H), 7.01 (t, *J* = 7.4 Hz, 1H), 6.86 (d, *J* = 8.1 Hz, 1H), 3.82 (s, 2H), 3.59 (s, 3H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 140.94, 140.90, 140.61, 139.49, 135.82, 128.78, 127.79, 127.37, 127.34, 126.99, 126.98, 125.72, 121.95, 118.06, 110.17, 40.98, 27.74.**HR-MS** (ESI) m/z calcd for $C_{21}H_{19}N_2^+$ [M+H$^+$]: 299.1548, found: 299.1543.

1-methyl-3-(naphthalen-2-yl)-1,4-dihydrocinnoline (3r)



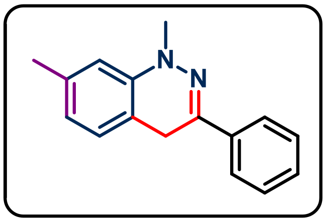
Yellow solid (0.25 mmol scale, 37.4 mg, 55%) mp 240-245 ^{o}C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.13 (dd, *J* = 8.7, 1.8 Hz, 1H), 8.06 (s, 1H), 7.91 (d, *J* = 2.4 Hz, 1H), 7.84 (d, *J* = 8.6 Hz, 2H), 7.54 – 7.44 (m, 2H), 7.29 – 7.24 (m, 1H), 7.20 (d, *J* = 6.8 Hz, 1H), 7.02 (m, 1H), 6.87 (d, *J* = 8.1 Hz, 1H), 3.92 (s, 2H), 3.61 (s, 3H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 140.74, 139.45, 134.32, 133.31, 133.26, 128.29, 127.90, 127.88, 127.64, 127.38, 126.20, 126.14, 124.23, 123.35, 121.9, 118.11, 110.22, 77.32, 41.05, 27.47.**HR-MS** (ESI) m/z calcd for $C_{19}H_{19}N_2^+$ [M+H$^+$]: 275.1544, found: 275.1543.

3-(adamantan-1-yl)-1-methyl-1,4-dihydrocinnoline (3s)



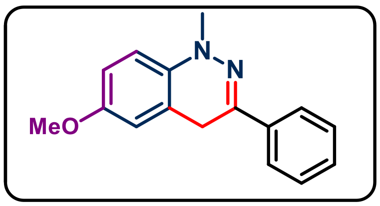
Yellow semi solid (0.25 mmol scale, 29.4 mg, 42%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.25 – 7.19 (m, 1H), 7.10 (d, *J* = 6.7 Hz, 1H), 6.96 (m, 1H), 6.82 (d, *J* = 8.0 Hz, 1H), 3.42 (s, 3H), 3.20 (s, 2H), 2.06 (s, 3H), 1.83 (d, *J* = 2.7 Hz, 6H), 1.75 (q, *J* = 12.1 Hz, 6H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 153.24, 143.29, 126.83, 126.73, 121.30, 119.54, 109.83, 40.60, 39.65, 38.65, 36.86, 28.26, 26.37. **HR-MS** (ESI) m/z calcd for $C_{19}H_{23}N_2^+$ [M-H$^+$] 279.1861, found: 279.1841.

1,7-dimethyl-3-phenyl-1,4-dihydrocinnoline (4a)



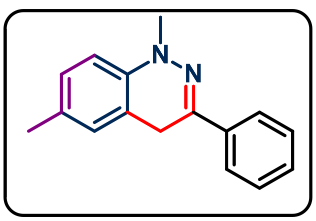
Yellow semi solid (0.25 mmol scale, 36.5 mg, 62%) mp 170-175 ^{o}C;**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.78 (dd, *J* = 5.3, 3.3 Hz, 2H), 7.37 (m, 3H), 7.02 (d, *J* = 7.5 Hz, 1H), 6.81 (d, *J* = 7.5 Hz, 1H), 6.66 (s, 1H), 3.74 (s, 2H), 3.55 (s, 3H), 2.37 (s, 3H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 140.84, 140.05, 137.07, 137.01, 128.31, 128.26, 128.03, 127.56, 125.31, 122.61, 115.19, 110.89, 40.96, 27.47, 21.56.**HR-MS** (ESI) m/z calcd for$C_{16}H_{15}N_2^+$ [M-H^+] 235.1235, found: 235.1230.

6-methoxy-1-methyl-3-phenyl-1,4-dihydrocinnoline (4b)



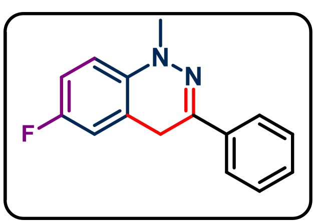
Pale yellow semi solid (0.25 mmol scale, 44.7 mg, 71%);**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.77 (dd, *J* = 5.3, 3.3 Hz, 2H), 7.43 – 7.29 (m, 3H), 6.82 – 6.76 (m, 2H), 6.73 (d, *J* = 1.8 Hz, 1H), 3.79 (s, 3H), 3.76 (s, 2H), 3.53 (s, 3H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 155.22, 138.65, 137.02, 135.38, 128.32, 128.15, 125.21, 119.67, 113.26, 112.55, 111.18, 55.67, 41.26, 28.12.**HR-MS** (ESI) m/z calcd for $C_{16}H_{17}N_2O^+$ [M+H^+] 253.1341, found: 235.1335.

1,6-dimethyl-3-phenyl-1,4-dihydrocinnoline (4c)



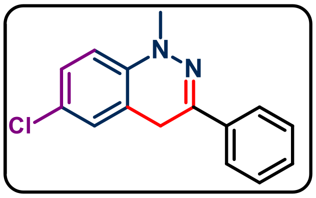
Yellow solid (0.25 mmol scale, 43 mg, 73%);**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.1 Hz, 2H), 7.42 – 7.31 (m, 3H), 7.04 (d, *J* = 8.1 Hz, 1H), 6.96 (s, 1H), 6.74 (d, *J* = 8.2 Hz, 1H), 3.74 (s, 2H), 3.53 (s, 3H), 2.31 (s, 3H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 139.62, 138.89, 137.05, 131.42, 128.30, 128.20, 127.76, 125.80, 125.28, 118.17, 110.14, 41.04, 27.81, 20.58. **HR-MS** (ESI) m/z calcd for$C_{16}H_{15}N_2^+$ [M-H^+] 235.1235, found: 235.1231.

6-fluoro-1-methyl-3-phenyl-1,4-dihydrocinnoline (4d)



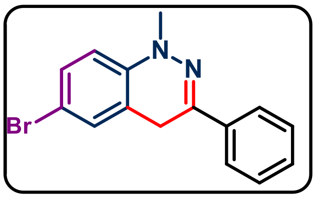
Yellow solid (0.25 mmol scale, 43.2 mg, 72%) mp190-195^{o}C;**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81 – 7.73 (m, 2H), 7.44 – 7.31 (m, 3H), 6.94 (m, 1H), 6.88 (dd, *J* = 8.5, 2.8 Hz, 1H), 6.76 (dd, *J* = 8.8, 4.6 Hz, 1H), 3.75 (s, 2H), 3.53 (s, 3H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.67, 157.29, 138.95, 137.54 (d, J = 1.7 Hz), 137.53,136.58, 128.42 (d, J = 7.6 Hz), 128.37, 125.31, 119.95 (d, J = 7.9 Hz),, 114.40, 114.17, 113.76, 113.53, 111.09 (d, J = 8.0 Hz), 41.27, 27.97.**HR-MS** (ESI) m/z calcd for$C_{15}H_{12}FN_2^+$ [M-H^+] 239.0985, found: 239.0989.

6-Chloro-1-methyl-3-phenyl-1,4-dihydrocinnoline(4e)



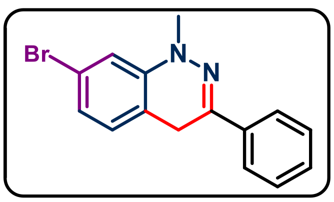
Pale yellow semi solid (0.25 mmol scale, 49.4 mg, 77%);**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.80 – 7.73 (m, 2H), 7.38 (m, 3H), 7.18 (dd, *J* = 8.5, 2.0 Hz, 1H), 7.11 (s, 1H), 6.74 (d, *J* = 8.6 Hz, 1H), 3.74 (s, 2H), 3.53 (s, 3H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 139.69, 139.54, 136.47, 128.58, 128.40, 127.48, 127.15, 126.51, 125.33, 119.78, 111.27, 41.05, 27.64. **HR-MS** (ESI) m/z calcd for $C_{15}H_{12}ClN_2^+$ [M-H$^+$] 255.0689, found: 255.0679.

6-bromo-1-methyl-3-phenyl-1,4-dihydrocinnoline (4f)



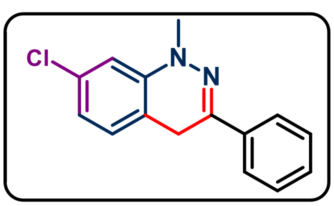
Yellow semi solid (0.25 mmol scale, 54.8 mg, 73%);**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81 – 7.74 (m, 2H), 7.43 – 7.30 (m, 4H), 7.25 (dd, *J* = 2.9, 1.9 Hz, 1H), 6.69 (d, *J* = 8.6 Hz, 1H), 3.74 (s, 2H), 3.52 (s, 3H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 139.97, 139.84, 136.47, 130.33, 130.07, 128.61, 128.40, 125.34, 120.19, 113.77, 111.69, 40.99, 27.54.**HR-MS** (ESI) m/z calcd for $C_{15}H_{12}BrN_2^+$ [M-H$^+$] 299.0184, found: 299.0175.

7-bromo-1-methyl-3-phenyl-1,4-dihydrocinnoline (4g)



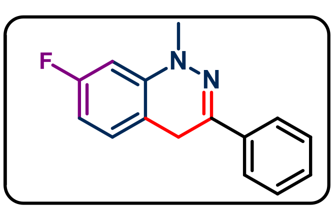
Yellow semi solid (0.25 mmol scale, 63 mg, 84%);**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81 – 7.73 (m, 2H), 7.45 – 7.30 (m, 3H), 7.04 (d, *J* = 8.0 Hz, 1H), 6.94 (dd, *J* = 8.0, 1.9 Hz, 1H), 6.81 (d, *J* = 1.9 Hz, 1H), 3.73 (s, 2H), 3.52 (s, 3H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.77, 140.53, 136.46, 133.02, 128.66, 128.39, 125.39, 121.54, 116.42, 110.34, 40.91, 27.31.**HR-MS** (ESI) m/z calcd for$C_{15}H_{12}BrN_2^+$ [M-H$^+$] 299.0184, found: 299.0183.

7-chloro-1-methyl-3-phenyl-1,4-dihydrocinnoline(4h)



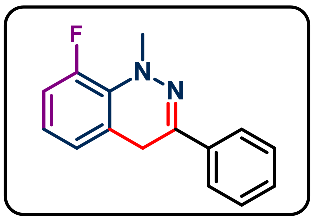
Pale yellow semi solid (0.25 mmol scale, 58 mg, 90%);**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.79 – 7.73 (m, 2H), 7.45 – 7.32 (m, 3H), 7.08 (m, 1H), 6.97 (dd, *J* = 10.0, 4.9 Hz, 2H), 3.71 (s, 2H), 3.52 (s, 3H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 142.00, 140.52, 136.43, 128.98, 128.68, 128.40, 125.40, 124.48, 120.95, 116.95, 113.15, 40.91, 27.39.**HR-MS** (ESI) m/z calcd for $C_{15}H_{12}ClN_2^+$ [M-H$^+$] 255.0689, found: 255.0679.

7-fluoro-1-methyl-3-phenyl-1,4-dihydrocinnoline(4i)



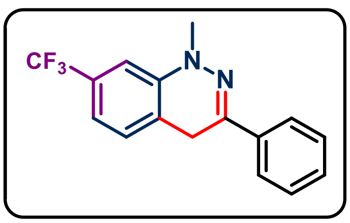
Yellow semi solid (0.25mmol scale, 43.2 mg, 72%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.83 – 7.77 (m, 2H), 7.41 (m, 3H), 7.16 (dd, *J* = 14.6, 8.2 Hz, 1H), 6.74 – 6.65 (m, 1H), 6.56 (d, *J* = 8.3 Hz, 1H), 3.82 (s, 2H), 3.54 (s, 3H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 161.39, 158.97, 141.72 (d, J = 7.4 Hz), 138.96, 136.68, 128.55, 128.35,127.77, 127.82 (d, J = 9.9 Hz), 125.27 (d, J = 19.8 Hz), 107.91, 107.69, 105.72, 41.30, 20.51 (d, J = 3.8 Hz).**^{19}F NMR** (377 MHz, $CDCl_3$) δ -119.94.**HR-MS** (ESI) m/z calcd for $C_{15}H_{14}FN_2^+$ [M+H$^+$] 241.1141, found: 241.1136.

8-Fluoro-1-methyl-3-phenyl-1,4-dihydrocinnoline(4j)



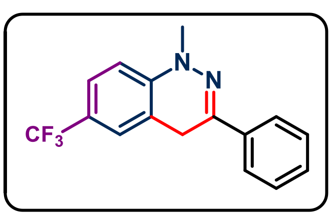
Yellow semi solid (0.25mmol scale,38 mg, 63%);**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 6.9 Hz, 2H), 7.48 – 7.31 (m, 3H), 7.00 – 6.83 (m, 3H), 3.81 (d, *J* = 7.3 Hz, 3H), 3.70 (s, 2H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.33, 147.91, 140.86, 136.34, 128.91 (d, J = 8.0 Hz), 128.63,123.30 (d, J = 2.8 Hz), 125.45, 123.31, 123.28, 122.02 (d, J = 8.0 Hz), 121.72 (d, J = 3.3 Hz), 115.31, 115.08, 44.15, 27.82 (d, J = 3.0 Hz).**^{19}F NMR** (377 MHz, $CDCl_3$) δ -127.03. **HR-MS** (ESI) m/z calcd for $C_{15}H_{12}FN_2^+$ [M-H$^+$] 239.0985, found: 239.0979.

1-methyl-3-phenyl-7-(trifluoromethyl)-1,4-dihydrocinnoline(4k)



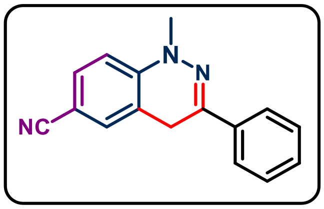
Yellow semi solid (0.25 mmol scale, 47.1 mg, 65%);**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81 – 7.75 (m, 2H), 7.44 – 7.35 (m, 3H), 7.23 (s, 2H), 7.03 (s, 1H), 3.80 (s, 2H), 3.58 (s, 3H).**^{13}C NMR** (101 MHz, CDCl3) δ 141.14, 140.22, 136.26, 129.69, 128.80, 128.45, 128.09, 125.47, 121.74, 118.41 (q, J = 3.9 Hz), 118.39, 106.73, 106.69, 40.87, 27.82.**^{19}F NMR** (377 MHz, CDCl3) δ -62.48. **HR-MS** (ESI) m/z calcd for$C_{16}H_{14}F_3N_2^+$ [M+H$^+$] 291.1109, found: 291.1104.

1-methyl-3-phenyl-6-(trifluoromethyl)-1,4-dihydrocinnoline(4l)



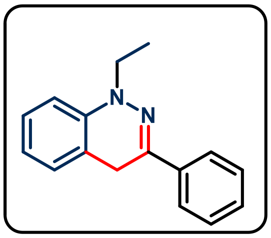
Yellow semi solid (0.25 mmol scale, 60.9 mg, 84%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.82 – 7.75 (m, 2H), 7.48 (d, *J* = 8.4 Hz, 1H), 7.41 (m, 4H), 6.85 (d, *J* = 8.5 Hz, 1H), 3.81 (s, 2H), 3.58 (s, 3H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.06, 140.58, 136.18, 128.88, 128.45,125.85, 125.45, 124.83 (q, J = 21.2, 3.7 Hz), 123.67, 123.25 (d, J = 18.8 Hz), 118.04, 109.74, 40.91, 27.60. **^{19}F NMR** (377 MHz, $CDCl_3$) δ -61.40. **HR-MS** (ESI) m/z calcd for$C_{16}H_{14}F_3N_2^+$ [M+H$^+$] 291.1109, found: 291.1100

1-methyl-3-phenyl-1,4-dihydrocinnoline-6-carbonitrile (4m)



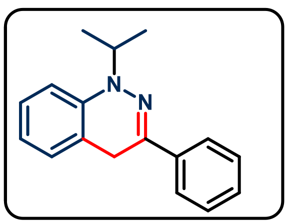
Yield (0.25 mmol scale, 40.8 mg, 66%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 – 7.70 (m, 2H), 7.49 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.46 – 7.34 (m, 4H), 6.79 (d, *J* = 8.5 Hz, 1H), 3.78 (s, 2H), 3.56 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.27, 141.09, 135.75, 131.97, 131.57, 129.14, 128.4, 125.43, 119.53, 118.21, 110.09, 103.86, 40.78 , 27.14.**HR-MS** (ESI) m/z calcd for$C_{16}H_{14}F_3N_2^+$ [M+H$^+$] 248.1182, found: 248.1181

1-ethyl-3-phenyl-1,4-dihydrocinnoline(6a)



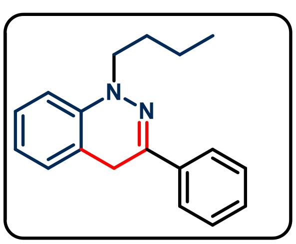
Yellow semi solid (0.25 mmol scale, 37.2 mg, 63%);**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.82 – 7.77 (m, 2H), 7.40 (dd, *J* = 8.1, 6.6 Hz, 2H), 7.36 – 7.28 (m, 2H), 7.25 – 7.19 (m, 1H), 7.14 (d, *J* = 6.9 Hz, 1H), 6.96 (dd, *J* = 7.7, 7.1 Hz, 1H), 6.86 (d, *J* = 8.2 Hz, 1H), 3.96 (q, *J* = 7.1 Hz, 2H), 3.77 (s, 2H), 1.41 (t, *J* = 7.1 Hz, 3H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 139.65, 139.37, 137.19, 128.39, 128.31, 128.28, 127.32, 125.37, 121.60, 118.29, 110.46, 47.04, 27.82, 12.46.**HR-MS** (ESI) m/z calcd for $C_{16}H_{15}N_2^+$ [M-H$^+$] 235.1235, found: 235.1230

1-isopropyl-3-phenyl-1,4-dihydrocinnoline(6b)



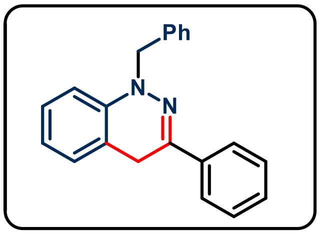
Yellow semi solid (0.25mmol scale, 41.5 mg, 67%);**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.74 (dd, *J* = 8.3, 1.2 Hz, 2H), 7.33 – 7.28 (m, 2H), 7.27 – 7.21 (m, 1H), 7.15 – 7.10 (m, 1H), 7.07 – 7.03 (m, 1H), 4.33 (hept, *J* = 12.8, 6.4 Hz, 1H), 3.64 (s, 2H), 1.35 (d, *J* = 6.4 Hz, 6H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 139.86, 138.96, 137.32, 128.26, 128.24, 128.06, 127.13, 125.28, 121.16, 118.67, 110.53, 49.57, 27.74, 20.10.**HR-MS** (ESI) m/z calcd for$C_{17}H_{17}N_2^+$ [M+H$^+$] 249.1392, found: 249.1386.

1-butyl-3-phenyl-1,4-dihydrocinnoline(6c)



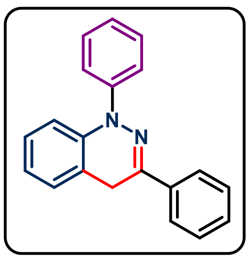
Yellow semi solid (0.25mmol scale,44 mg, 66%);**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.78 (dd, *J* = 11.1, 3.8 Hz, 2H), 7.40 (t, *J* = 7.4 Hz, 2H), 7.33 (dd, *J* = 8.6, 5.9 Hz, 1H), 7.21 (t, *J* = 8.2 Hz, 1H), 7.12 (d, *J* = 7.2 Hz, 1H), 6.94 (t, *J* = 7.3 Hz, 1H), 6.83 (t, *J* = 6.9 Hz, 1H), 3.91 – 3.84 (t, 2H), 3.78 (s, 2H), 1.89 – 1.79 (m, 2H), 1.48 (m,*J* = 14.8, 7.4 Hz, 2H), 1.00 (t, *J* = 7.4 Hz, 3H).^{13}**C NMR** (101 MHz, $CDCl_3$) δ 139.59, 138.63, 137.13, 128.28, 128.19, 128.14, 127.21, 125.21, 121.43, 117.97, 110.29, 52.29, 29.35, 27.57, 20.26, 13.98. **HR-MS** (ESI) m/z calcd for $C_{19}H_{23}N_2^+$ [M-H$^+$] 263.1548, found: 263.1543

1-benzyl-3-phenyl-1,4-dihydrocinnoline (6d)



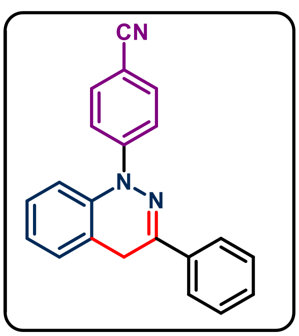
Yellow semi solid (0.25mmol scale,62 mg, 83%);^{1}**H NMR** (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.0 Hz, 2H), 7.34 – 7.27 (m, 4H), 7.27 – 7.18 (m, 4H), 7.14 (dd, *J* = 8.3, 6.0 Hz, 2H), 7.04 – 6.93 (m, 2H), 6.81 (t, *J* = 7.4 Hz, 1H), 6.59 (d, *J* = 8.2 Hz, 1H), 5.07 (s, 2H), 3.77 (s, 2H).^{13}**C NMR** (101 MHz, $CDCl_3$) δ 139.26, 139.03, 138.20, 136.94, 128.50,128.31, 128.12, 127.26, 126.95, 126.93, 125.24, 121.80, 117.66, 111.08, 57.14, 27.39.**HR-MS** (ESI) m/z calcd for $C_{21}H_{19}N_2^+$ [M+H$^+$] 299.1548, found: 299.1539

1,3-Diphenyl-1,4-dihydrocinnoline (6e)



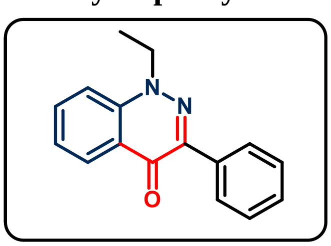
Greenish semi solid (0.25 mmol scale, 54.5 mg, 78%);^{1}**H NMR** (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.0 Hz, 2H), 7.56 (d, *J* = 7.5 Hz, 2H), 7.43 – 7.29 (m, 5H), 7.21 – 7.13 (m, 2H), 7.05 – 6.94 (m, 2H), 6.84 (d, *J* = 7.9 Hz, 1H), 3.80 (s, 2H).^{13}**C NMR** (101 MHz, $CDCl_3$) δ 143.34, 141.11, 139.24, 135.54, 128.12, 127.76, 127.36, 126.97, 125.86, 124.83, 124.22, 123.35, 122.05, 117.92, 111.40, 27.37.**HR-MS** (ESI) m/z calcd for $C_{20}H_{17}N_2^+$ [M+H$^+$] 285.1392, found:285.1386

4-(3-phenylcinnolin-1(4H)-yl)benzonitrile (8a)



Yellow semi solid (0.25 mmol scale, 55 mg, 71%);^{1}**H NMR** (400 MHz, $CDCl_3$) δ 7.91 – 7.82 (m, 2H), 7.56 (dd, *J* = 8.5, 1.1 Hz, 2H), 7.53 – 7.44 (m, 4H), 7.45 – 7.40 (m, 3H), 7.34 (dd, *J* = 8.6, 1.6 Hz, 2H), 6.85 (d, *J* = 8.6 Hz, 1H), 3.89 (s, 2H).^{13}**C NMR** (101 MHz, $CDCl_3$) δ 143.14. 142.98, 135.52, 132.10, 131.35, 129.51, 129.48, 128.54, 126.52, 125.92, 124.85, 118.97, 112.57, 105.15, 27.75.**HR-MS** (ESI) m/z calcd for $C_{21}H_{16}N_3^+$ [M+H$^+$] 310.1344, found: 310.1339

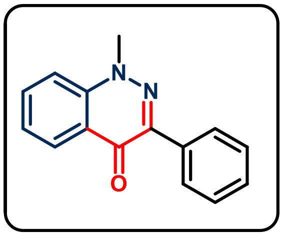
1-methyl-3-phenylcinnolin-4(1H)-one (9a)



Greenish yellow solid (0.25 mmol scale, 56.4 mg, 91%), mp 210-220 ^{o}C;^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (dd, *J* = 8.2, 1.4 Hz, 1H), 8.23 – 8.14 (m, 2H), 7.73 (m, 1H), 7.53 – 7.37 (m, 5H), 4.56 (q, *J* = 7.2

Hz, 2H), 1.58 (t, J = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.83, 145.86, 140.11, 134.65, 133.44, 128.64, 128.54, 128.03, 126.94, 125.48, 124.51, 114.62, 50.93, 13.77.**HR-MS** (ESI) m/z calcd for $C_{16}H_{15}N_2O^+$ [M+H$^+$] 251.1184, found: 251.1179

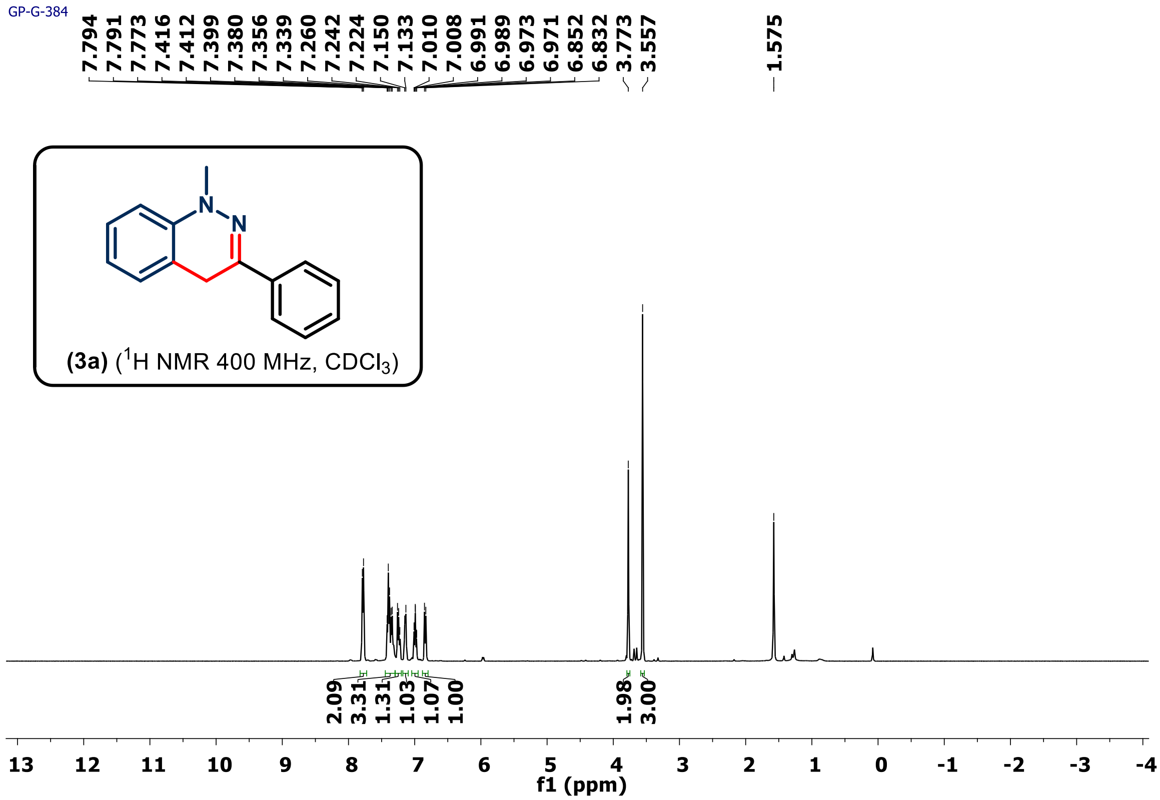
1-methyl-3-phenylcinnolin-4(1H)-one (9b)

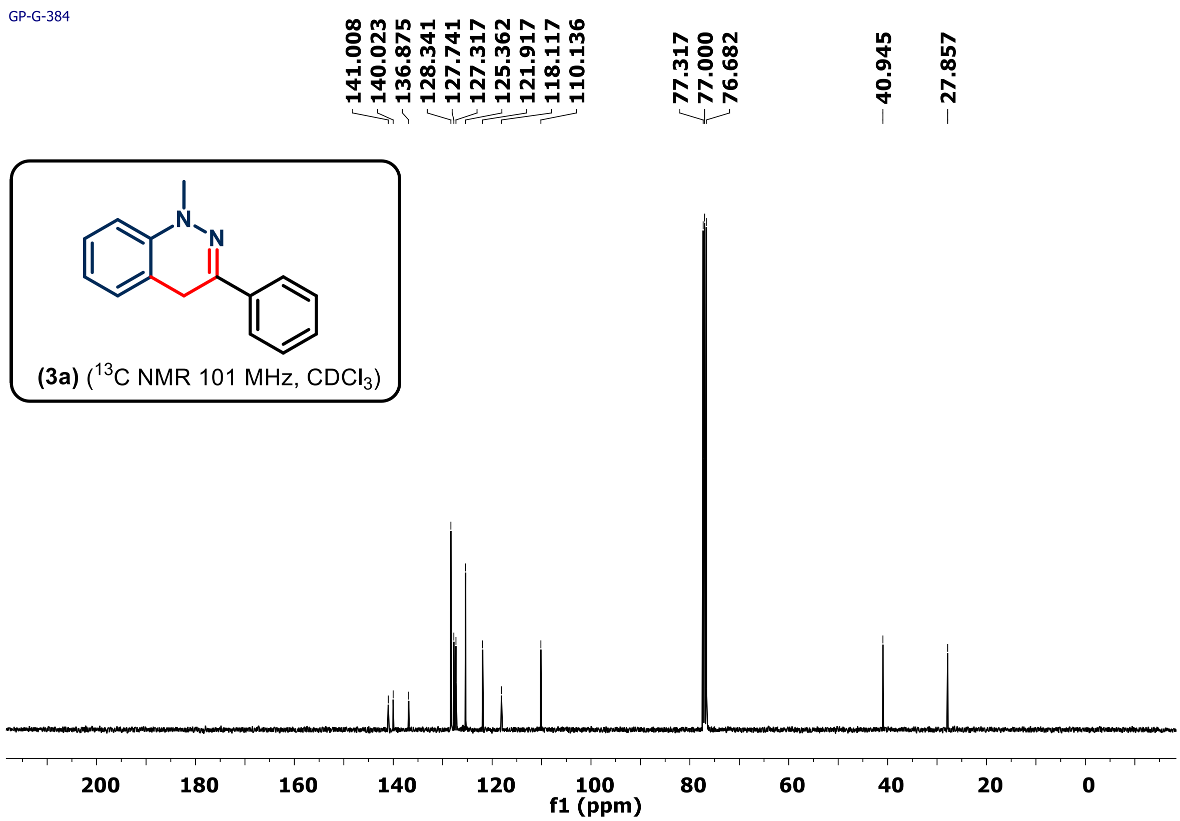


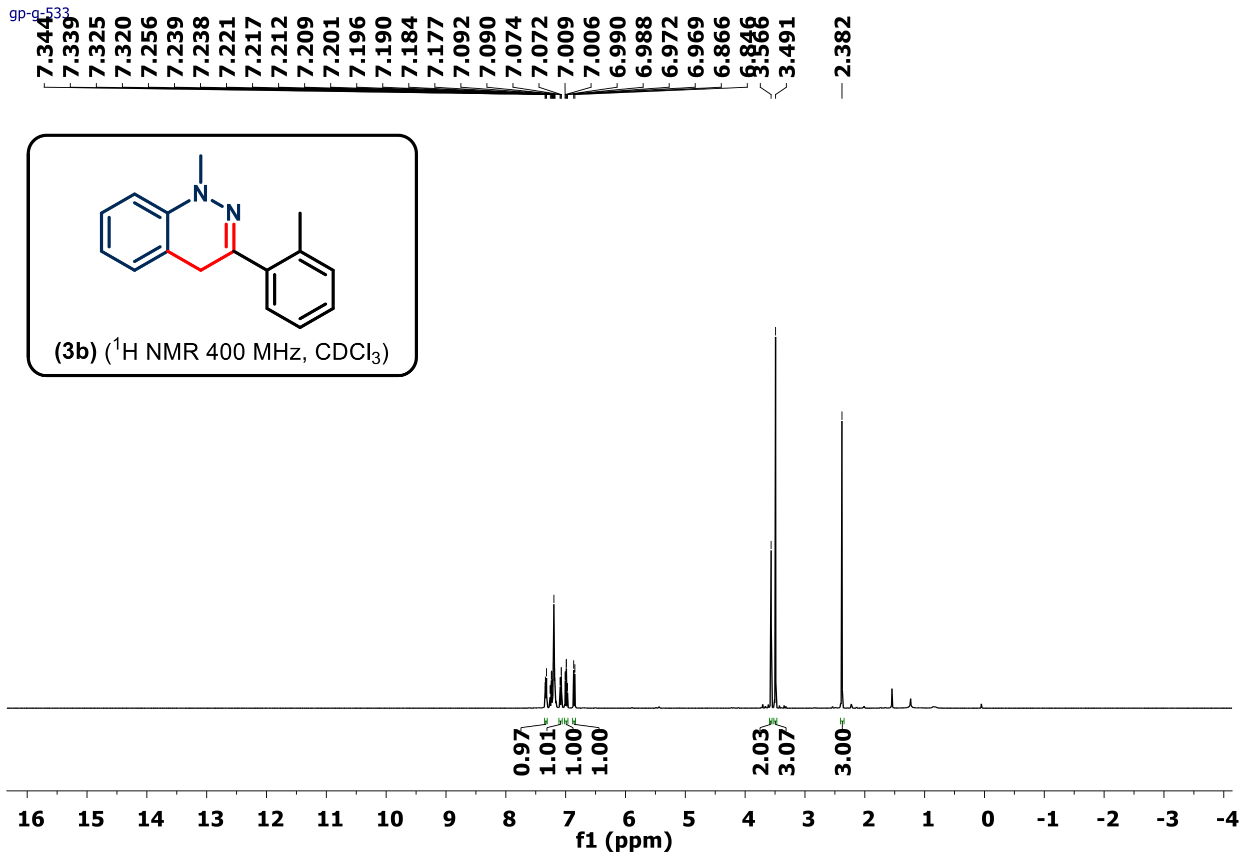
Greenish yellow solid (0.25mmol scale, 51.9mg, 88%)mp 200-205^{o}C;**^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.50 – 8.43 (m, 1H), 8.21 – 8.09 (m, 2H), 7.75 (m, 1H), 7.50 – 7.35 (m, 5H), 4.19 (s, 3H). **^{13}C NMR** (101 MHz, CDCl3) δ 169.98, 145.94, 140.98, 134.47, 133.55, 128.69, 128.50, 128.05, 126.68, 125.17, 124.73, 114.76, 43.85.**HR-MS** (ESI) m/z calcd for $C_{15}H_{13}N_2O^+$ [M+H$^+$]237.1028, found: 237.1022.

4. References

1. (a) R. M. P. Dias and A. C. B. Burtoloso, *Org. Lett.*, 2016, **18**, 3034–3037. (b) M. Barday, C. Janot, N. R. Halcovitch, J. Muir and C. Aïssa, *Angew. Chemie Int. Ed.*, 2017, **56**, 13117–13121.
2. (a) T. Leischner, L. Artús Suarez, A. Spannenberg, K. Junge, A. Nova and M. Beller, *Chem. Sci.*, 2019, **10**, 10566–10576. (b) P. Chaudhary, S. Gupta, N. Muniyappan, S. Sabiah and J. Kandasamy, *Green Chem.*, 2016, **18**, 2323–2330. (c) L. Zhang, J. Chen, X. Chen, X. Zheng, J. Zhou, T. Zhong, Z. Chen, Y.-F. Yang, X. Jiang, Y.-B. She and C. Yu, *Chem. Commun.*, 2020, **56**, 7415–7418. (d) P. Chaudhary, S. Gupta, P. Sureshbabu, S. Sabiah and J. Kandasamy, *Green Chem.*, 2016, **18**, 6215–6221. (e) Y. Huang, P. Y. Choy, J. Wang, M.-K. Tse, R. W.-Y. Sun, A. S.-C. Chan and F. Y. Kwong, *J. Org. Chem.*, 2020, **85**, 14664–14673.


GP-G-384
7.794
7.791
7.773
7.416
7.412
7.399
7.380
7.356
7.339
7.260
7.242
7.224
7.150
7.133
7.010
7.008
6.991
6.989
6.973
6.971
6.852
6.832
3.773
3.557
1.575
N
N
(3a) (1H NMR 400 MHz, CDCl3)
2.09
3.31
1.31
1.03
1.07
1.00
1.98
3.00
13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)


GP-G-384
141.008
140.023
136.875
128.341
127.741
127.317
125.362
121.917
118.117
110.136
77.317
77.000
76.682
40.945
27.857
N
N
(3a) (13C NMR 101 MHz, CDCl3)
200 180 160 140 120 100 80 60 40 20 0
f1 (ppm)



gp-g-533
7.344
7.339
7.325
7.320
7.256
7.239
7.238
7.221
7.217
7.212
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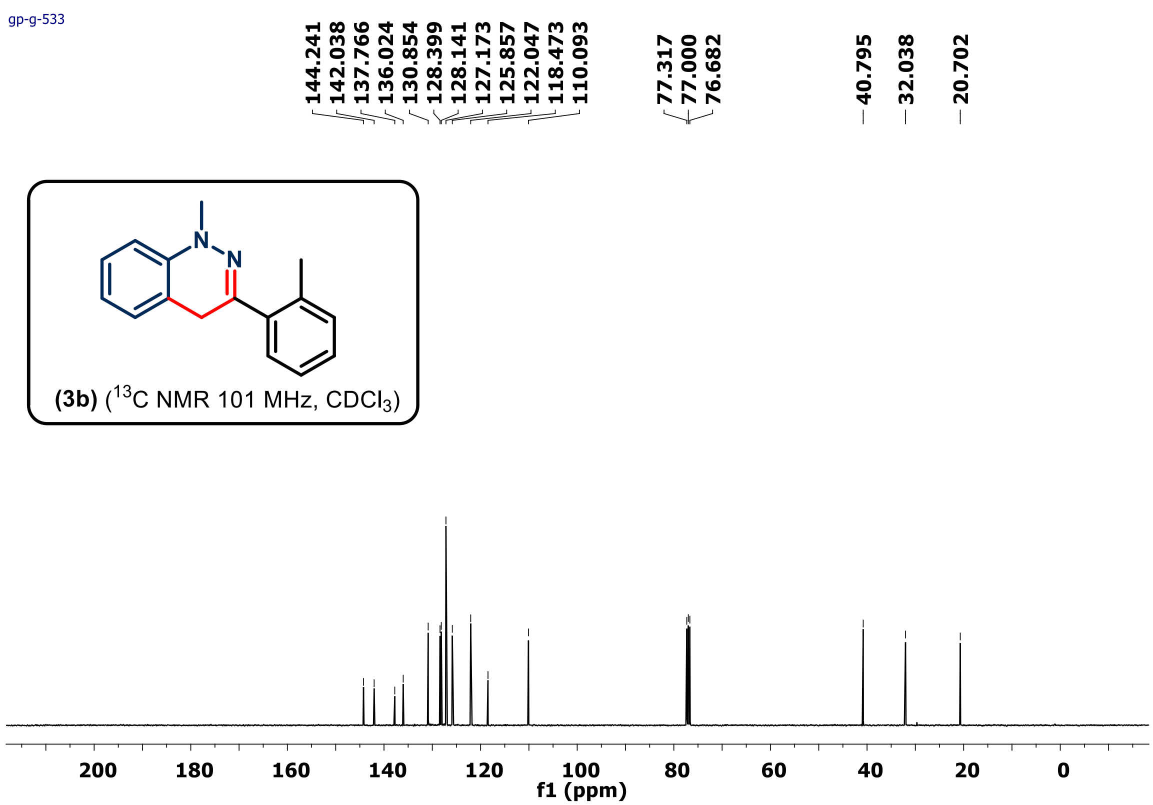
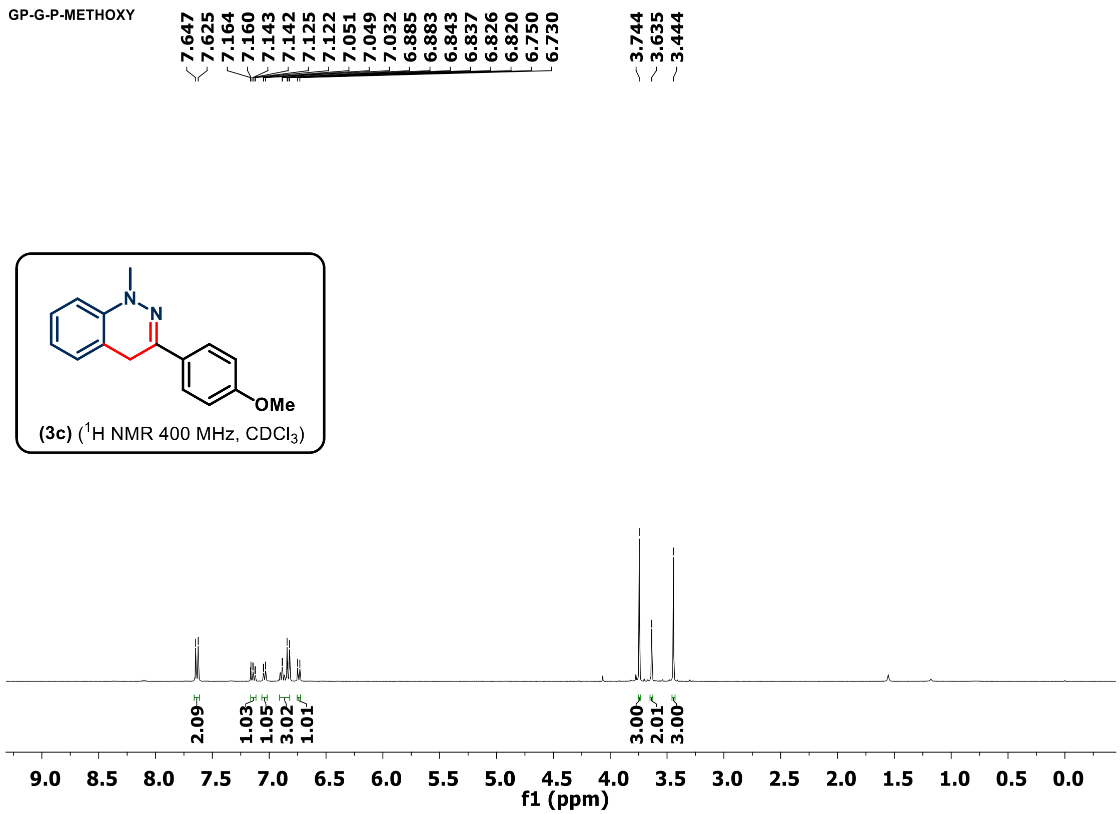
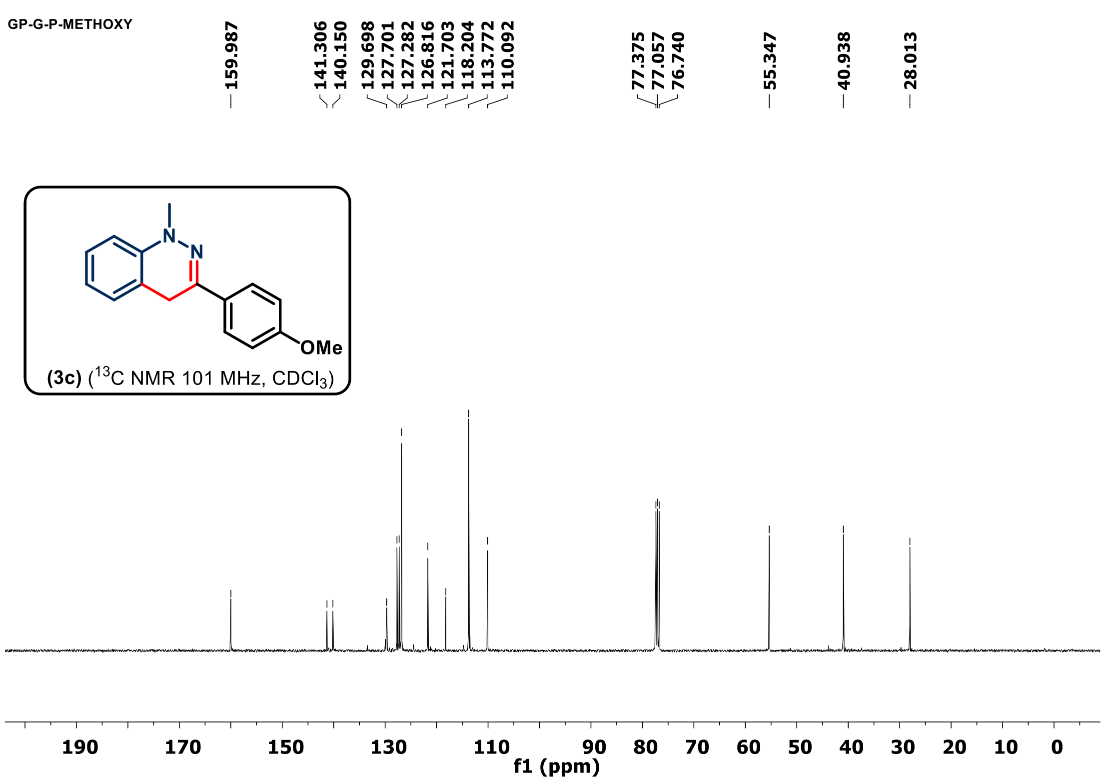
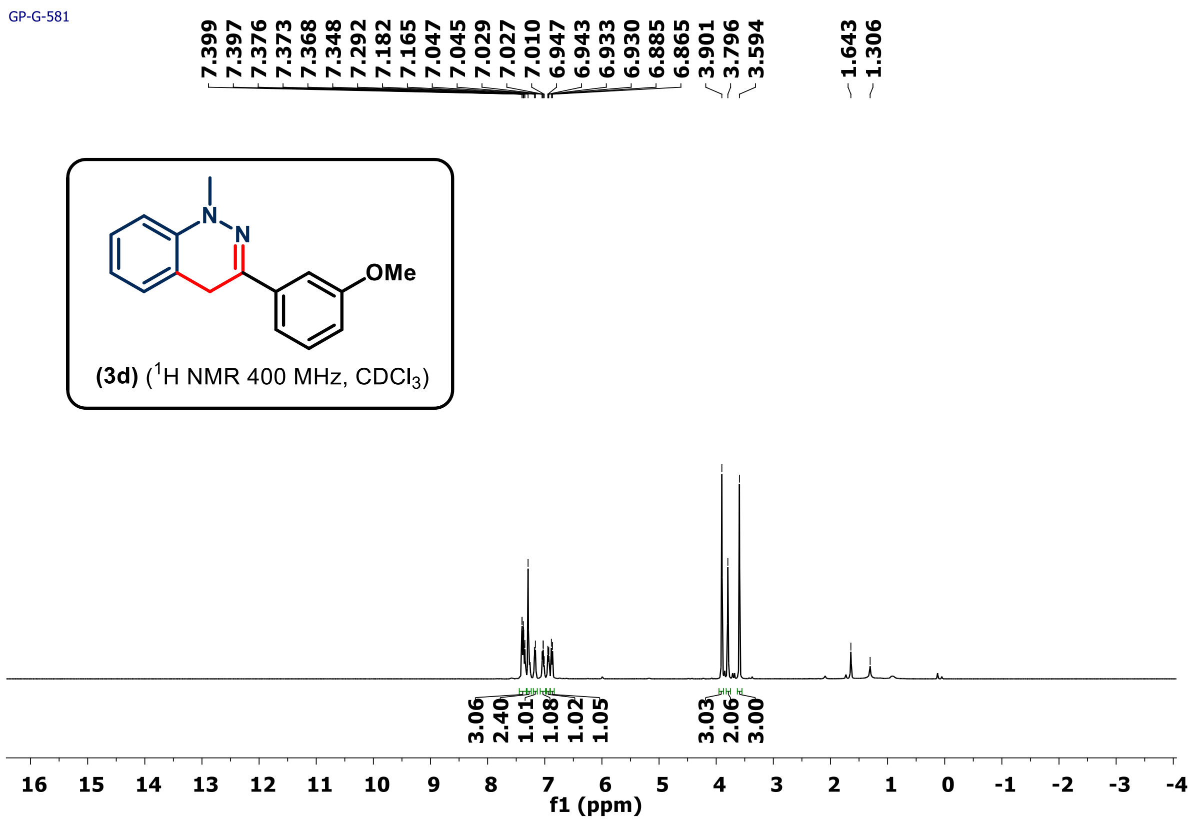
7.201
7.196
7.190
7.184
7.177
7.092
7.090
7.074
7.072
7.009
7.006
6.990
6.988
6.972
6.969
6.866
6.846
3.566
3.491
2.382
N
N
(3b) (^{1}H NMR 400 MHz, $CDCl_3$)
0.97
1.01
1.00
1.00
2.03
3.07
3.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)

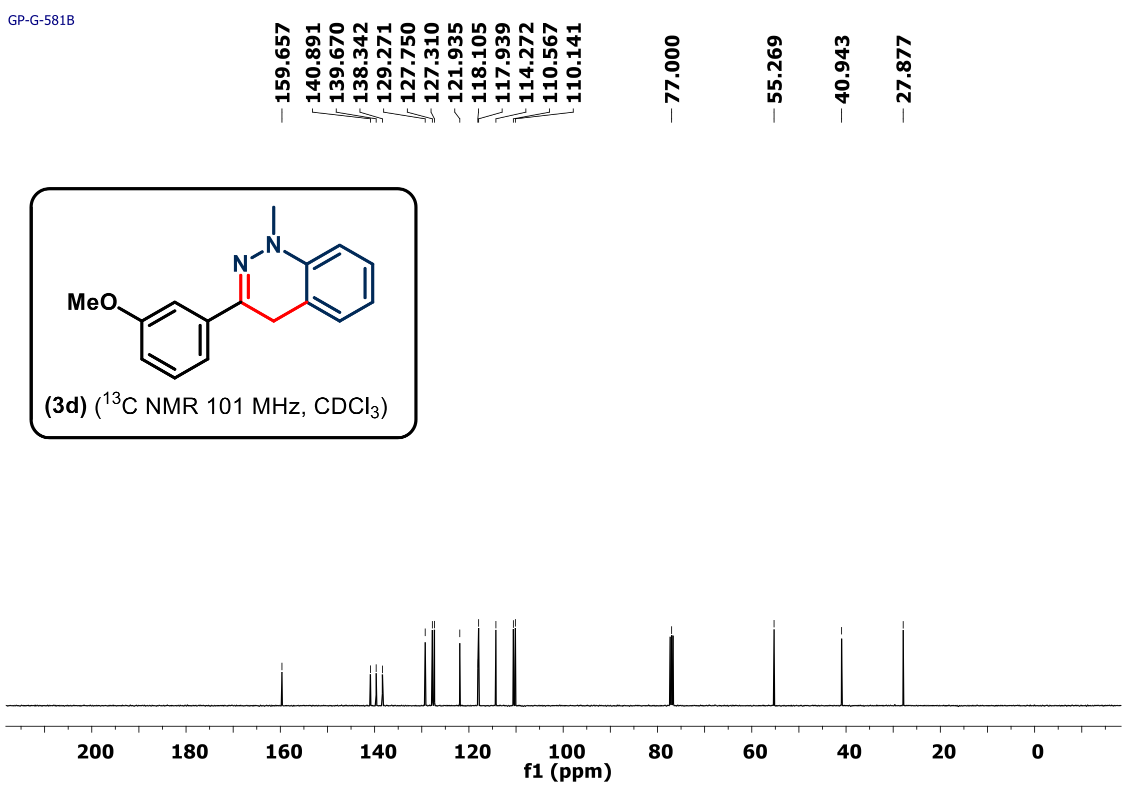


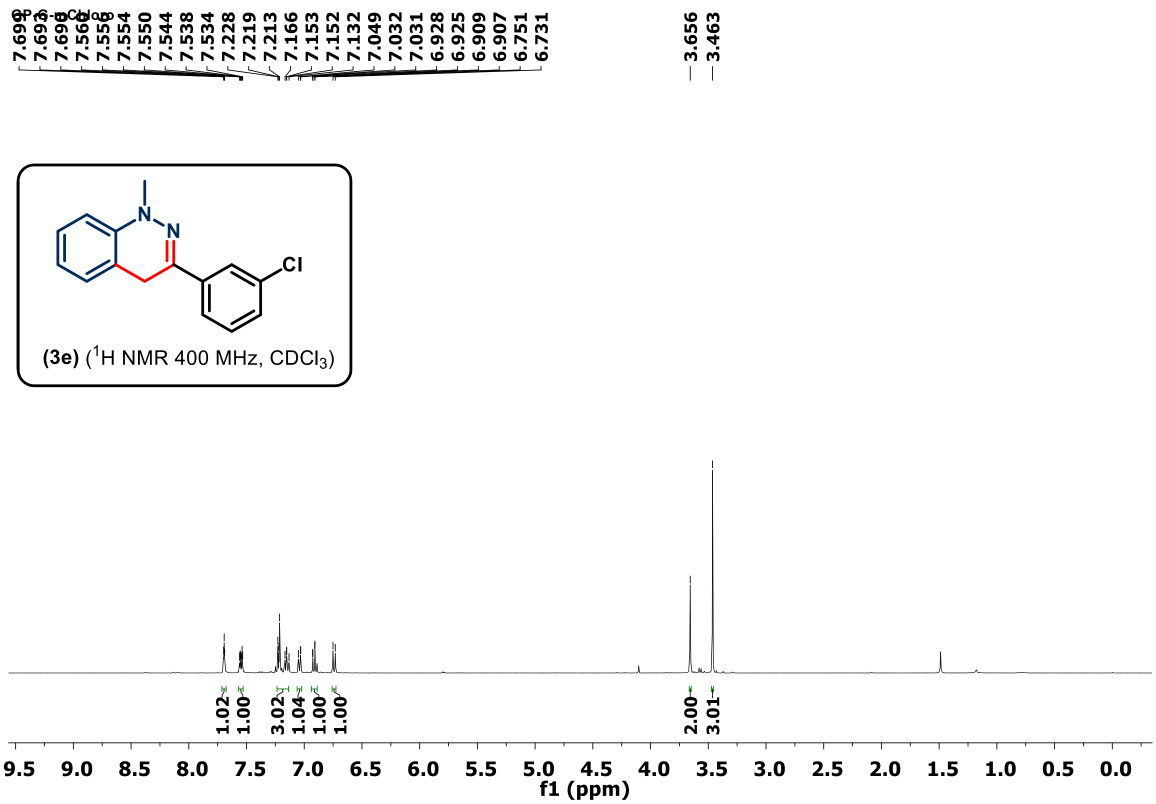
gp-g-533
144.241
142.038
137.766
136.024
130.854
128.399
128.141
127.173
125.857
122.047
118.473
110.093
77.317
77.000
76.682
40.795
32.038
20.702
N
N
(3b) (^{13}C NMR 101 MHz, $CDCl_3$)
200 180 160 140 120 100 80 60 40 20 0
f1 (ppm)

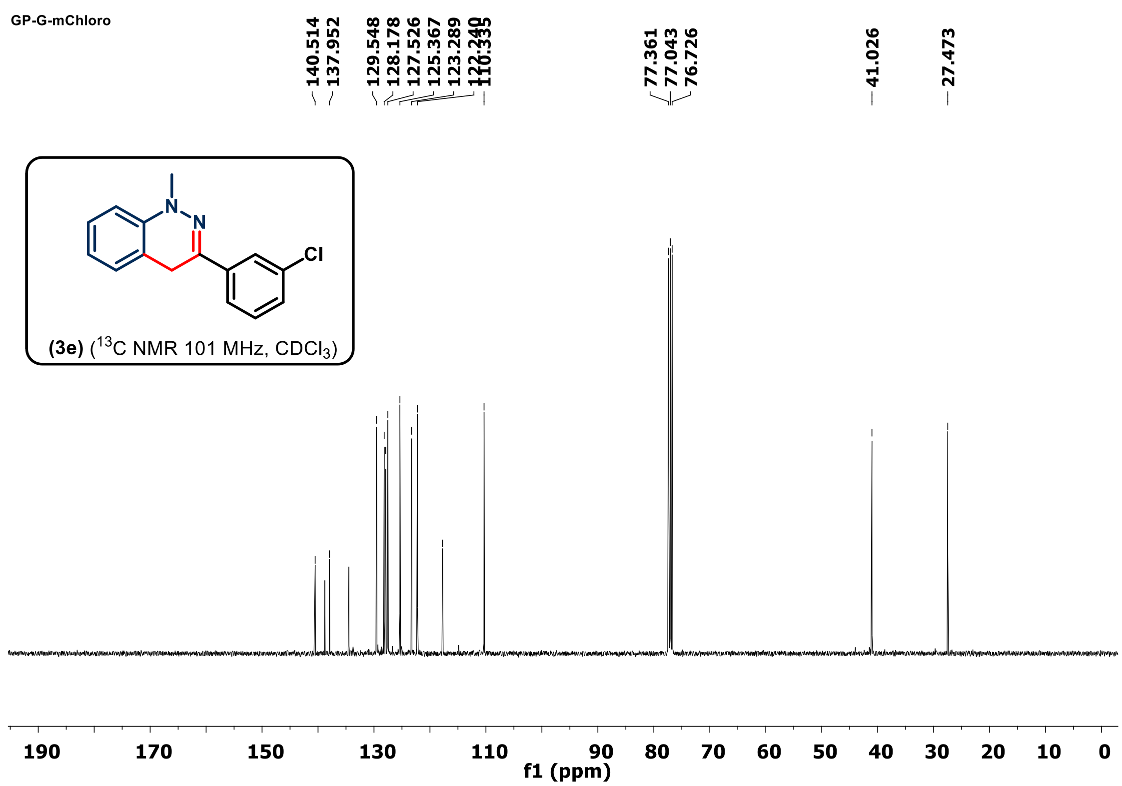

GP-G-P-METHOXY
7.647
7.625
7.164
7.160
7.143
7.142
7.125
7.122
7.051
7.049
7.032
6.885
6.883
6.843
6.837
6.826
6.820
6.750
6.730
3.744
3.635
3.444
N
N
OMe
(3c) (^{1}H NMR 400 MHz, CDCl$_3$)
2.09
1.03
1.05
3.02
1.01
3.00
2.01
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

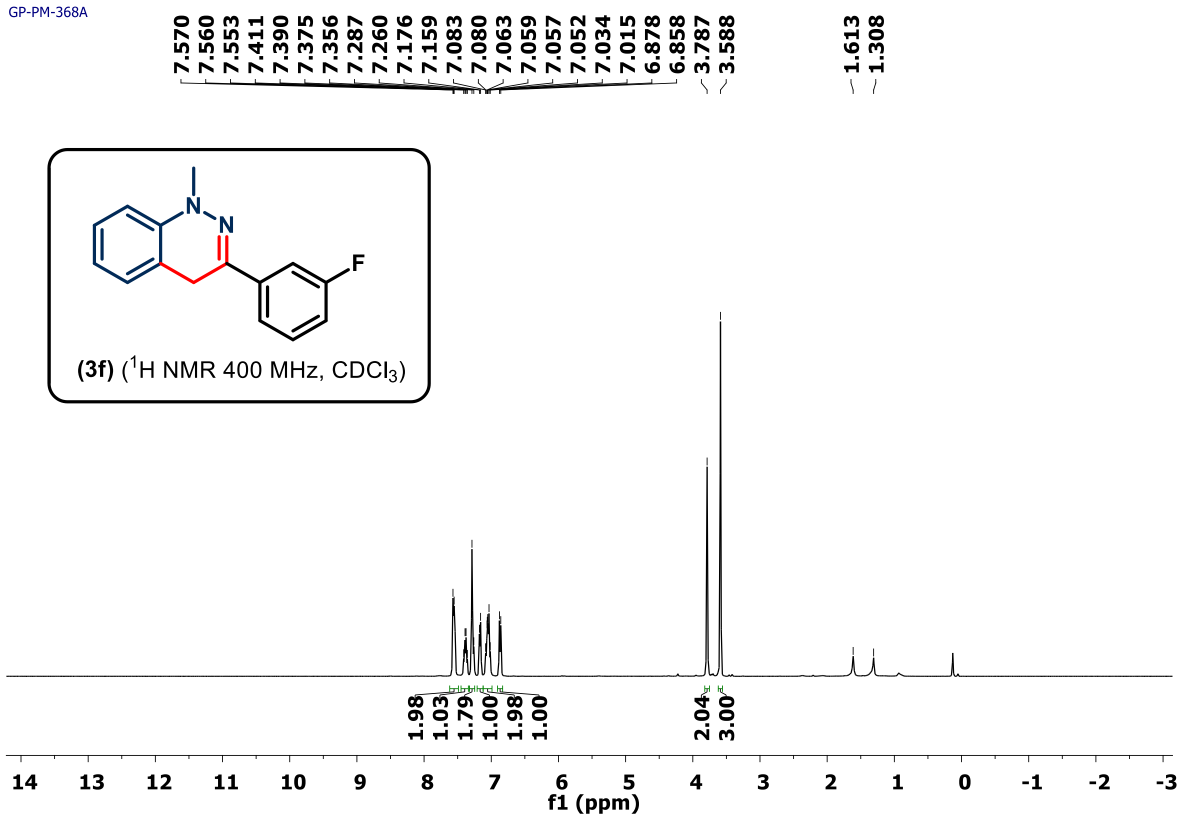

GP-G-P-METHOXY
159.987
141.306
140.150
129.698
127.701
127.282
126.816
121.703
118.204
113.772
110.092
77.375
77.057
76.740
55.347
40.938
28.013
N
N
OMe
(3c) (^{13}C NMR 101 MHz, CDCl$_3$)
190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

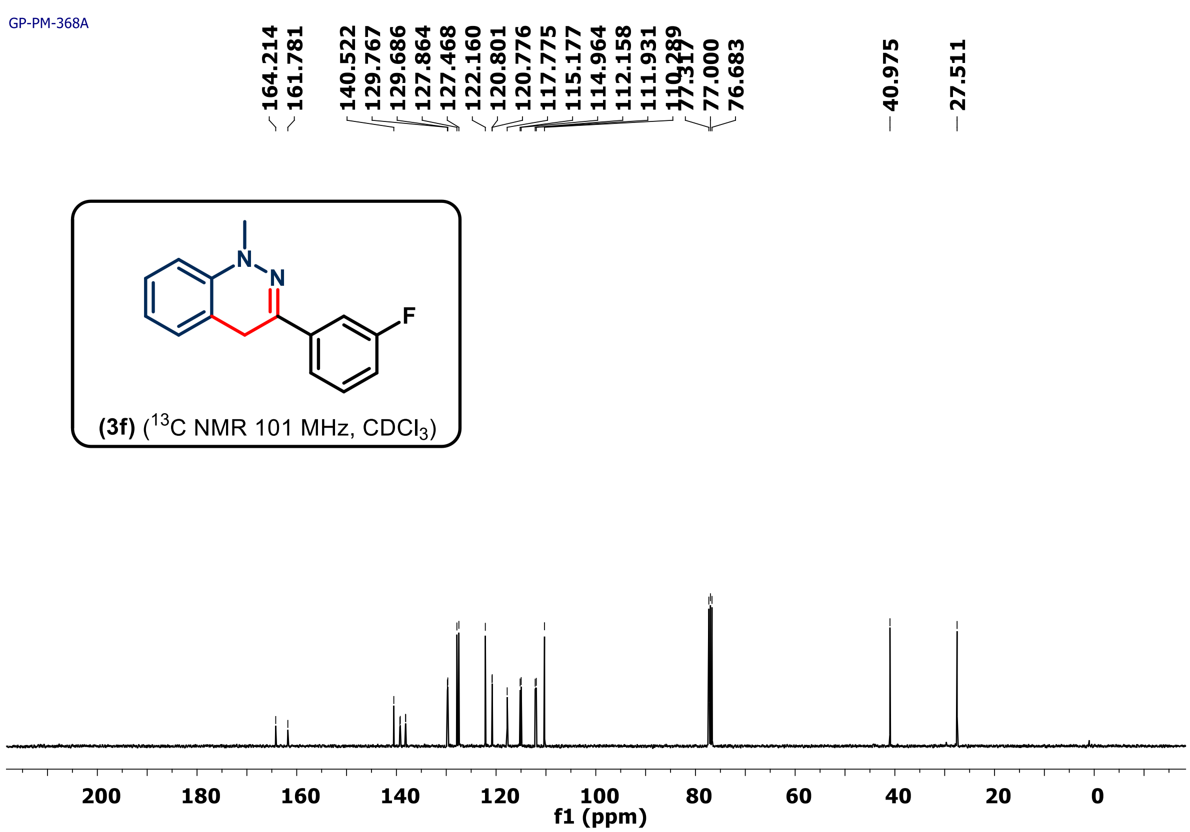

GP-G-581
7.399 7.397 7.376 7.373 7.368 7.348 7.292 7.182 7.165 7.047 7.045 7.029 7.027 7.010 6.947 6.943 6.933 6.930 6.885 6.865 3.901 3.796 3.594 1.643 1.306
N
N
OMe
(3d) (1H NMR 400 MHz, CDCl3)
3.06 2.40 1.01 1.08 1.02 1.05 3.03 2.06 3.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)

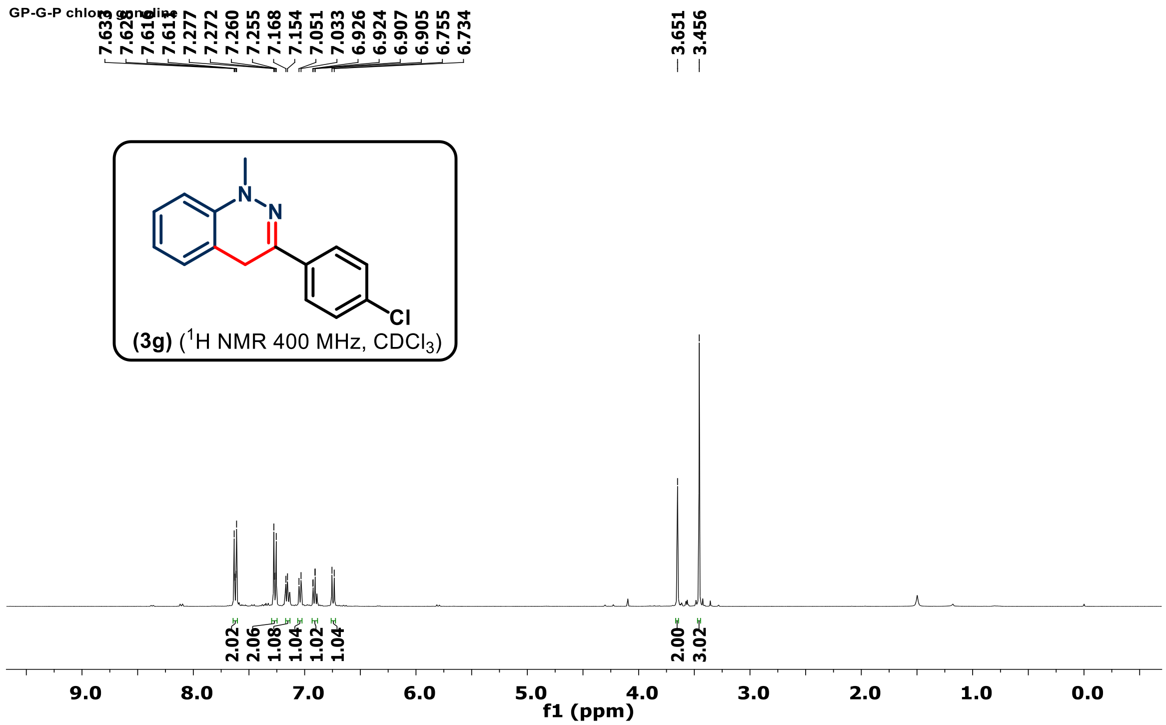

GP-G-581B
159.657 140.891 139.670 138.342 129.271 127.750 127.310 121.935 118.105 117.939 114.272 110.567 110.141 77.000 55.269 40.943 27.877
N
N
MeO
(3d) (13C NMR 101 MHz, CDCl3)
200 180 160 140 120 100 80 60 40 20 0
f1 (ppm)


GP-G-mChloro
7.560 7.556 7.554 7.550 7.544 7.538 7.534 7.228 7.219 7.213 7.166 7.153 7.152 7.132 7.049 7.032 7.031 6.928 6.925 6.909 6.907 6.751 6.731
3.656
3.463
N
N
Cl
(3e) (^{1}H NMR 400 MHz, $CDCl_3$)
1.02 1.00 3.02 1.04 1.00 1.00
2.00 3.01
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

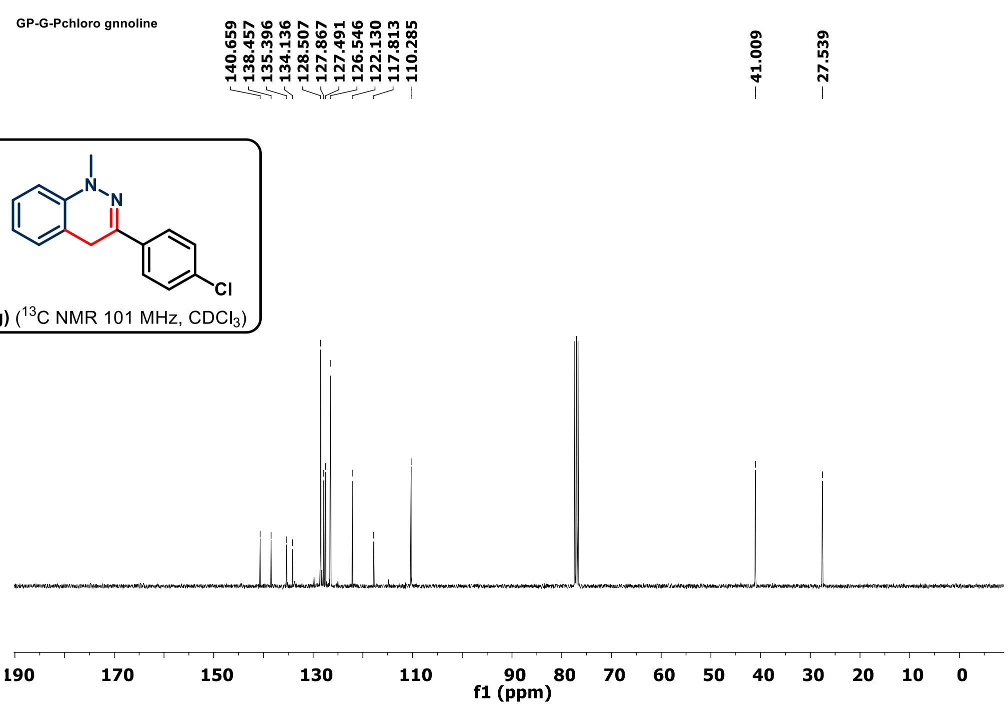

GP-G-mChloro
140.514 137.952 129.548 128.178 127.526 125.367 123.289 122.240 110.335
77.361 77.043 76.726
41.026
27.473
N
N
Cl
(3e) (^{13}C NMR 101 MHz, $CDCl_3$)
190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


GP-PM-368A
7.570
7.560
7.553
7.411
7.390
7.375
7.356
7.287
7.260
7.176
7.159
7.083
7.080
7.063
7.059
7.057
7.052
7.034
7.015
6.878
6.858
3.787
3.588
1.613
1.308
(3f) (^{1}H NMR 400 MHz, CDCl$_3$)
1.98
1.03
1.79
1.00
1.98
1.00
2.04
3.00
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

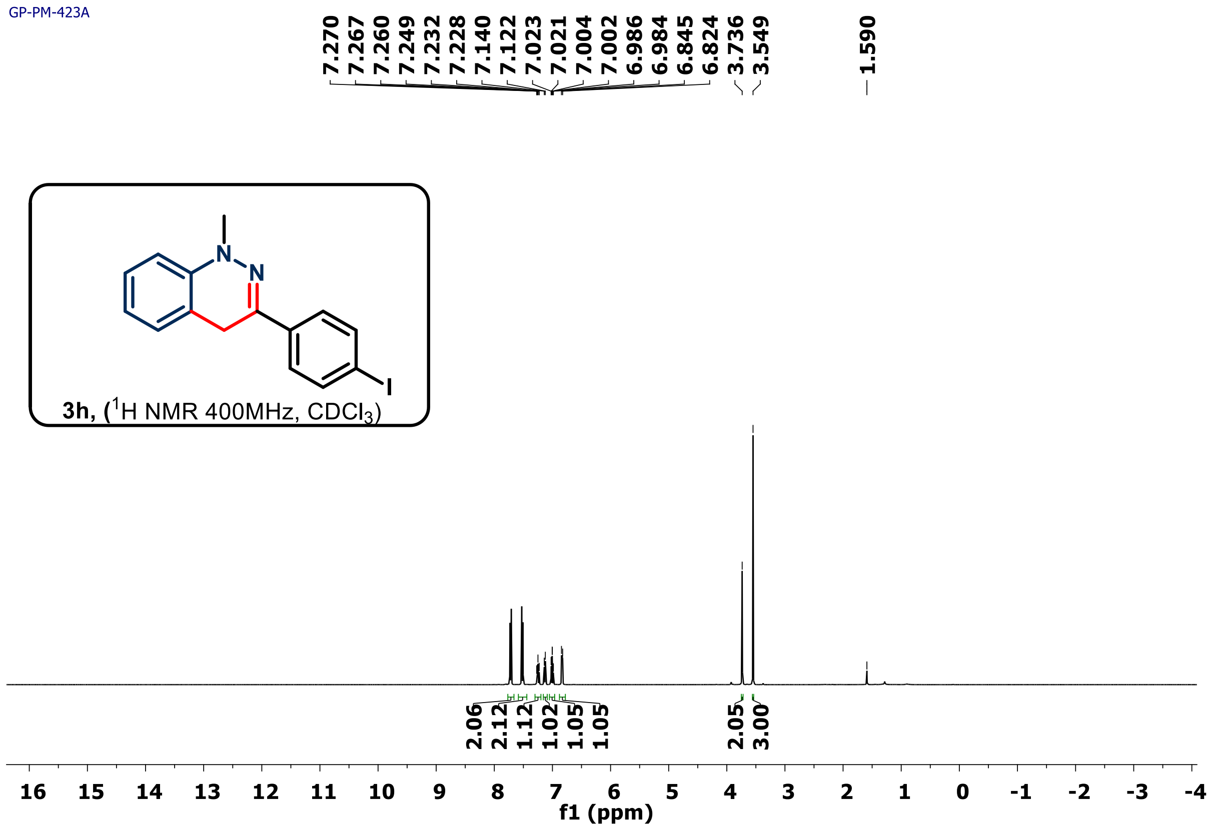

GP-PM-368A
164.214
161.781
140.522
129.767
129.686
127.864
127.468
122.160
120.801
120.776
117.775
115.177
114.964
112.158
111.931
110.289
77.317
77.000
76.683
40.975
27.511
(3f) (^{13}C NMR 101 MHz, CDCl$_3$)
200 180 160 140 120 100 80 60 40 20 0
f1 (ppm)

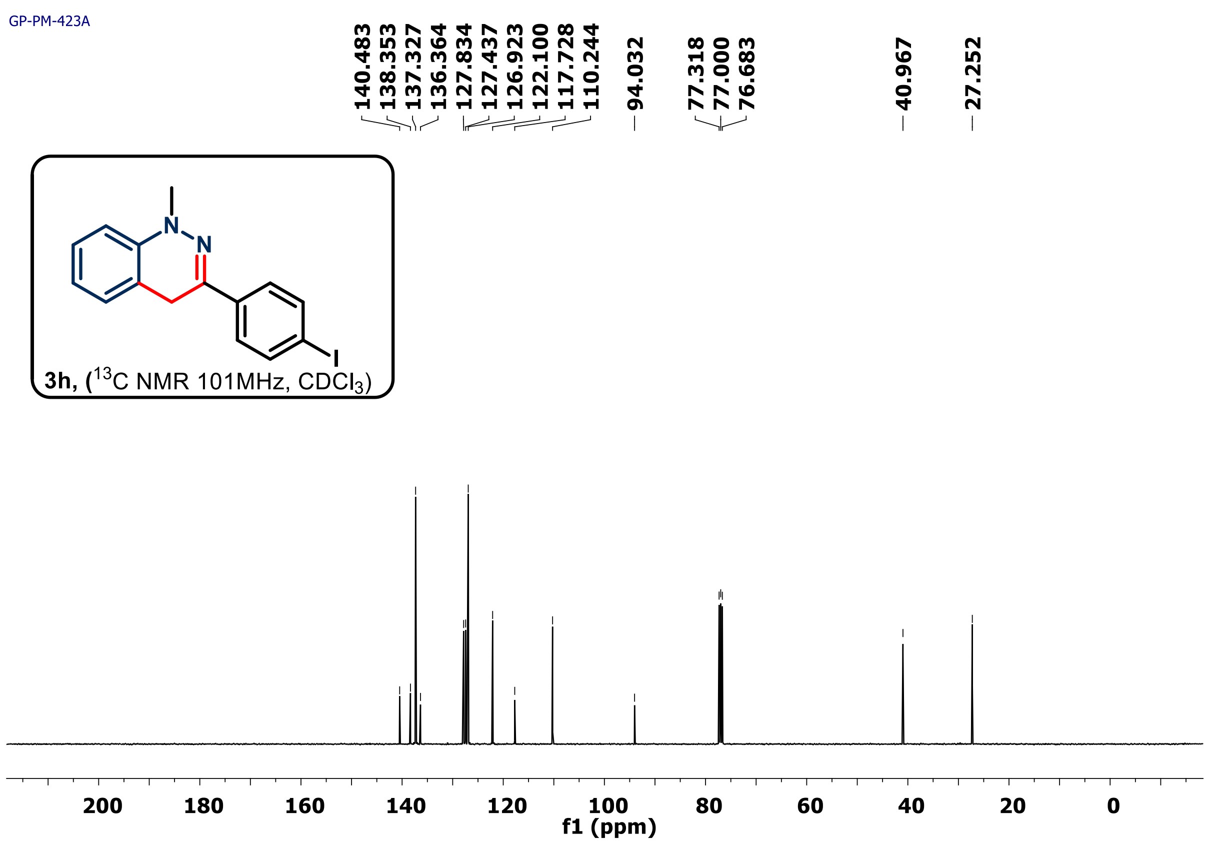


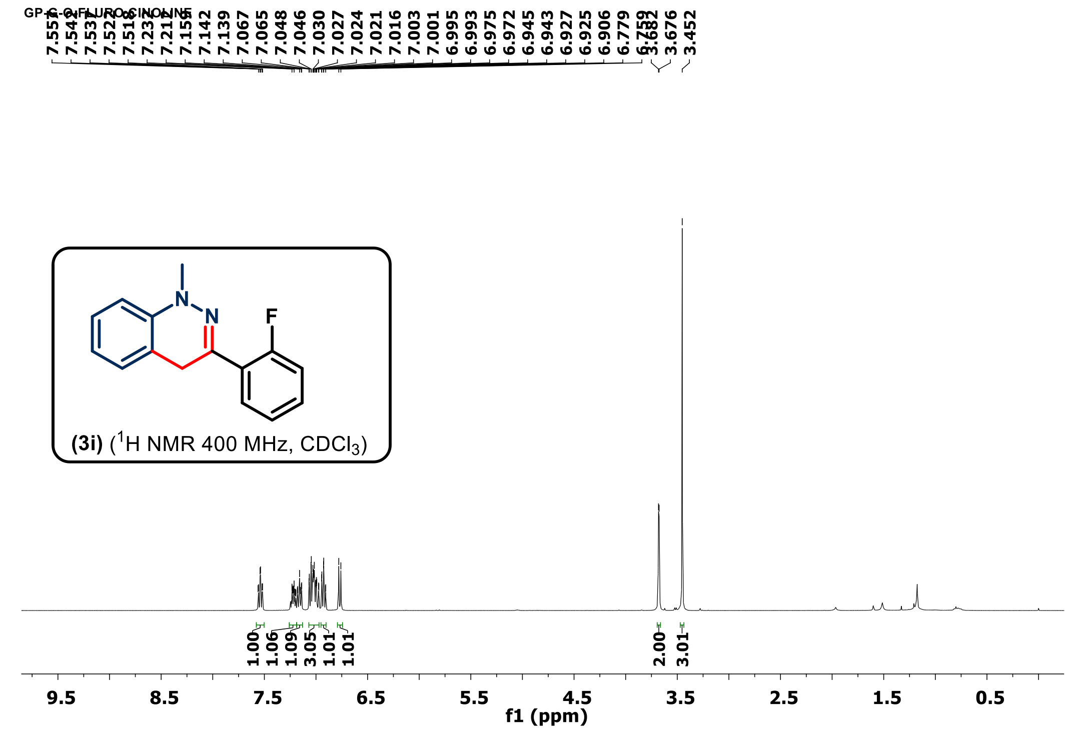
GP-G-P chloro gnnoline
7.630
7.628
7.610
7.611
7.277
7.272
7.260
7.255
7.168
7.154
7.051
7.033
6.926
6.924
6.907
6.905
6.755
6.734
3.651
3.456
(3g) (^{1}H NMR 400 MHz, $CDCl_3$)
2.02
2.06
1.08
1.04
1.02
1.04
2.00
3.02
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

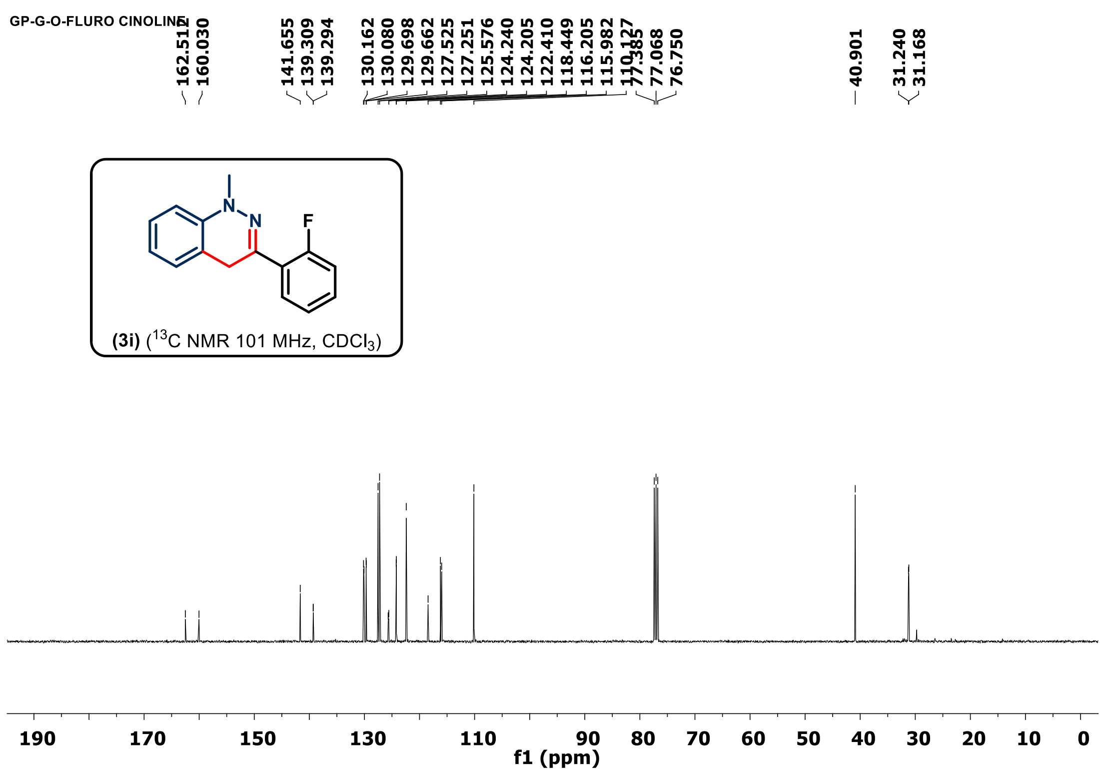


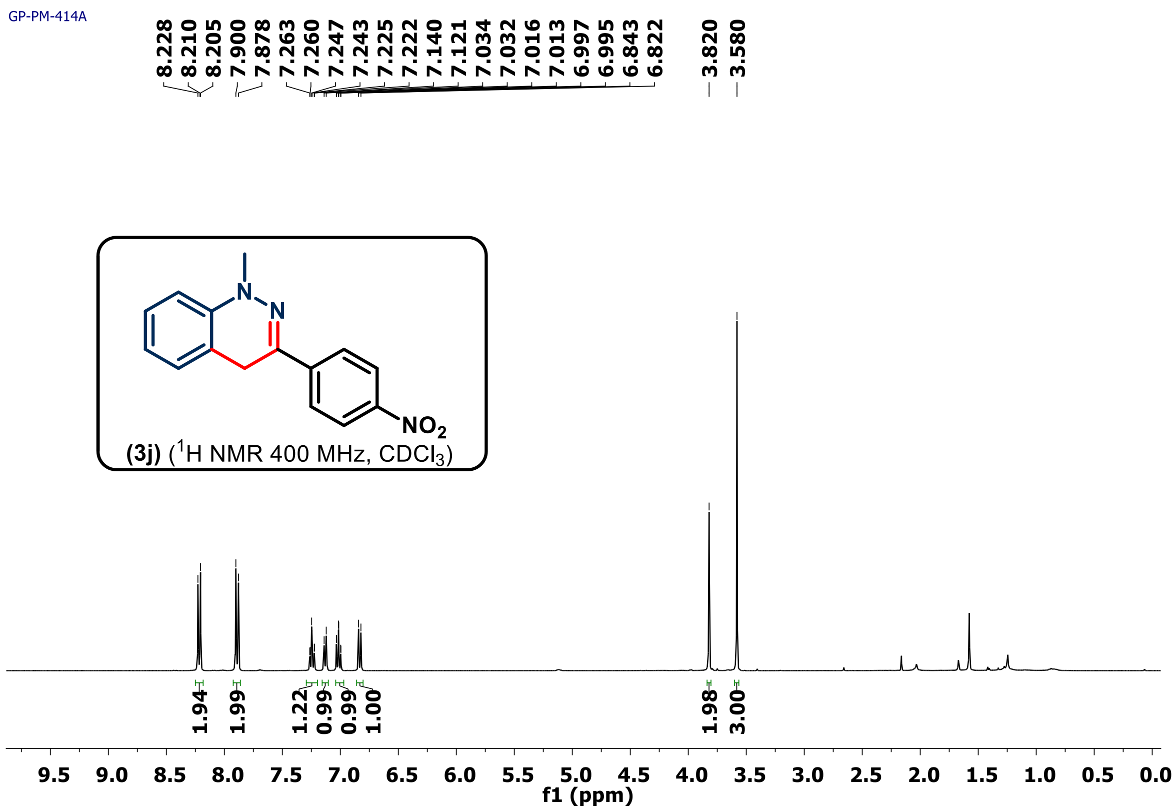
GP-G-Pchloro gnnoline
140.659
138.457
135.396
134.136
128.507
127.867
127.491
126.546
122.130
117.813
110.285
41.009
27.539
(3g) (^{13}C NMR 101 MHz, $CDCl_3$)
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

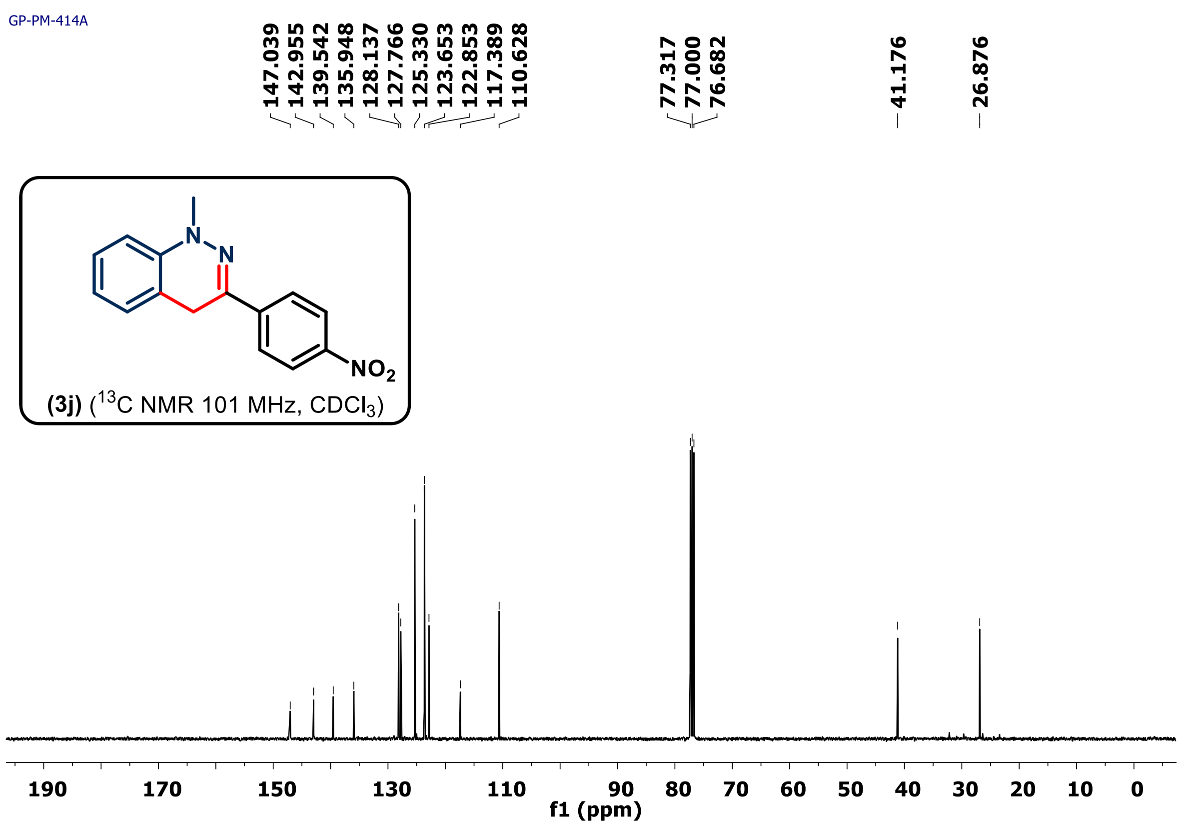

GP-PM-423A
7.270 7.267 7.260 7.249 7.232 7.228 7.140 7.122 7.023 7.021 7.004 7.002 6.986 6.984 6.845 6.824 3.736 3.549
1.590
N
N
I
3h, (1H NMR 400MHz, CDCl3)
2.06 2.12 1.12 1.02 1.05 1.05
2.05 3.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)

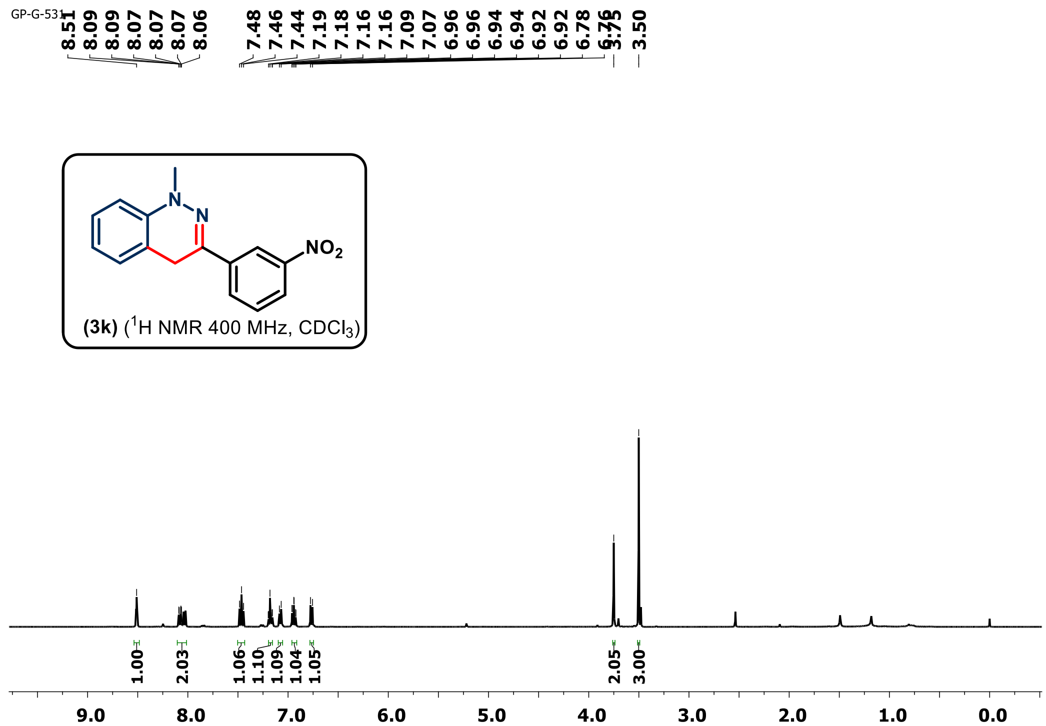

GP-PM-423A
140.483 138.353 137.327 136.364 127.834 127.437 126.923 122.100 117.728 110.244
94.032
77.318 77.000 76.683
40.967
27.252
N
N
I
3h, (13C NMR 101MHz, CDCl3)
200 180 160 140 120 100 80 60 40 20 0
f1 (ppm)

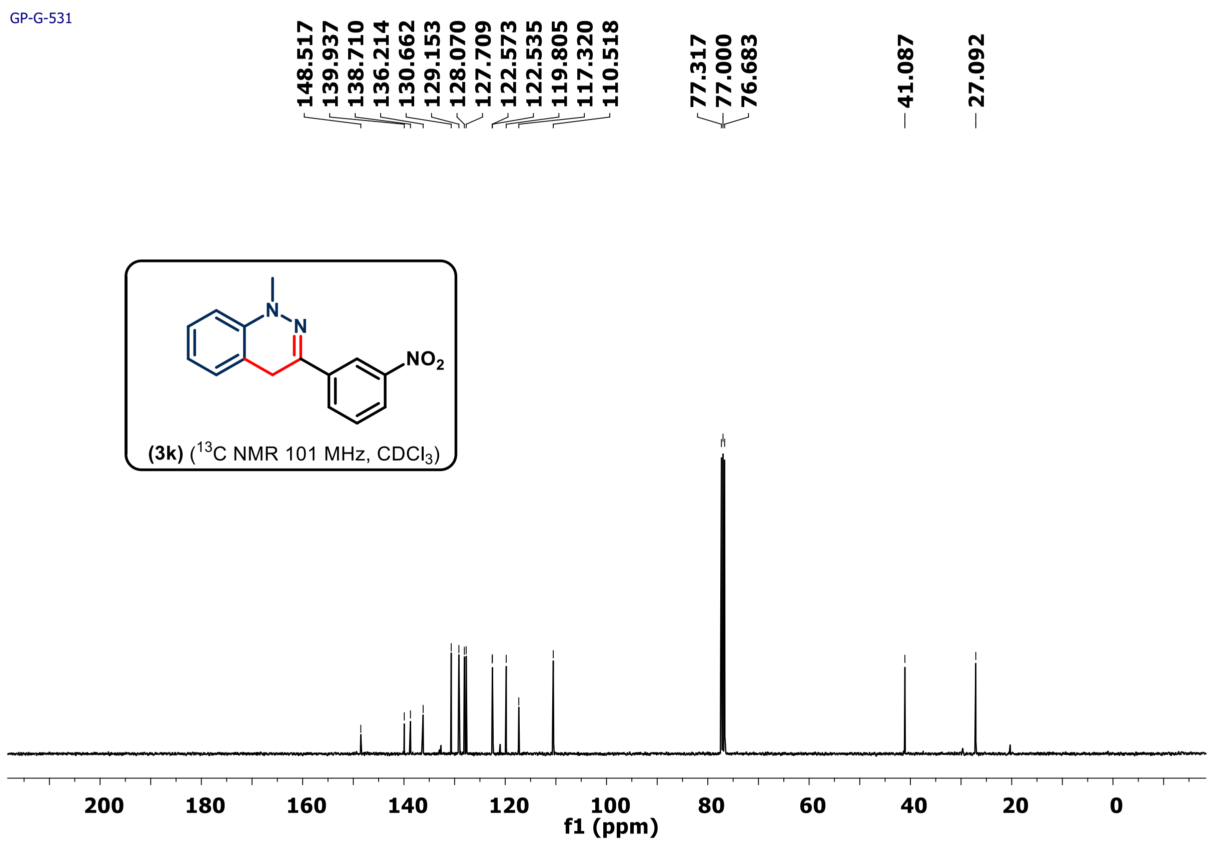

GP-G-O-FLURO CINOLINE
(3i) (^{1}H NMR 400 MHz, CDCl$_3$)
f1 (ppm)

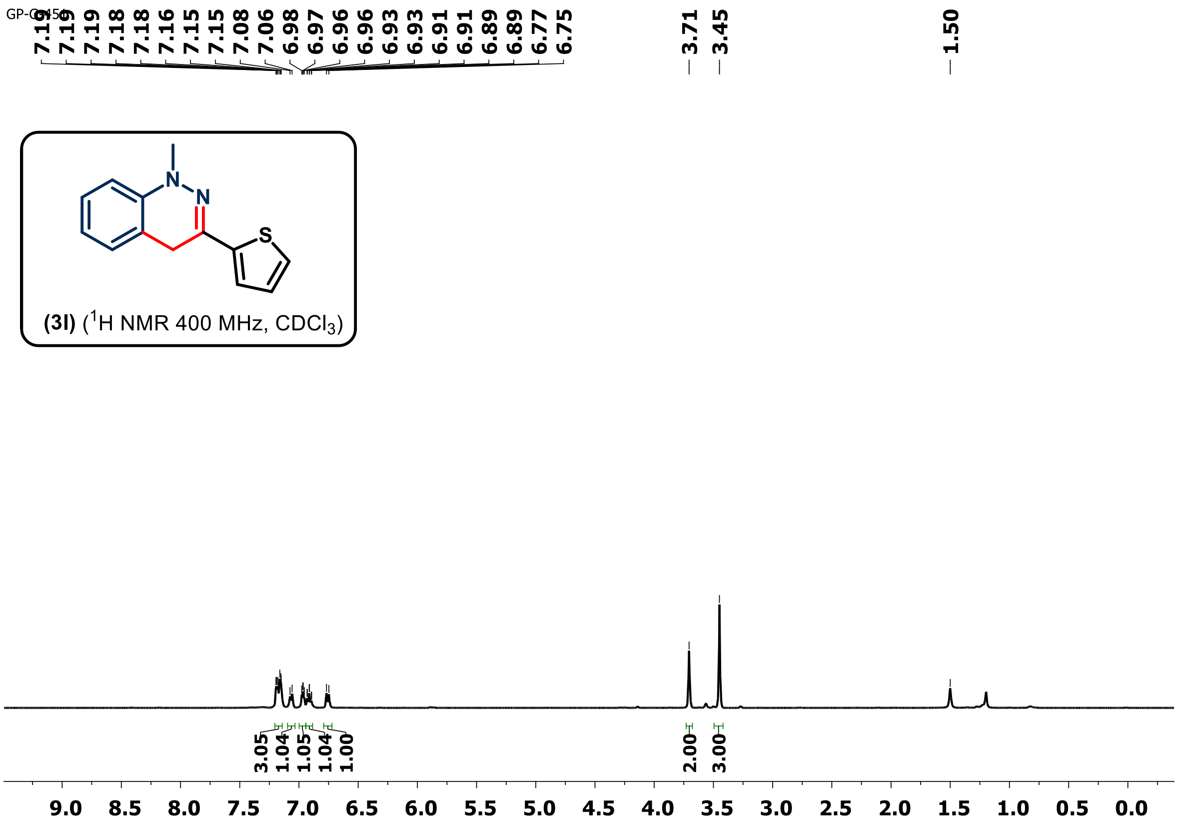

GP-G-O-FLURO CINOLINE
162.512
160.030
141.655
139.309
139.294
130.162
130.080
129.698
129.662
127.525
127.251
125.576
124.240
124.205
122.410
118.449
116.205
115.982
110.127
77.385
77.068
76.750
40.901
31.240
31.168
(3i) (^{13}C NMR 101 MHz, CDCl$_3$)
f1 (ppm)


GP-PM-414A
8.228
8.210
8.205
7.900
7.878
7.263
7.260
7.247
7.243
7.225
7.222
7.140
7.121
7.034
7.032
7.016
7.013
6.997
6.995
6.843
6.822
3.820
3.580
N
N
NO2
(3j) (1H NMR 400 MHz, CDCl3)
1.94
1.99
1.22
0.99
0.99
1.00
1.98
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

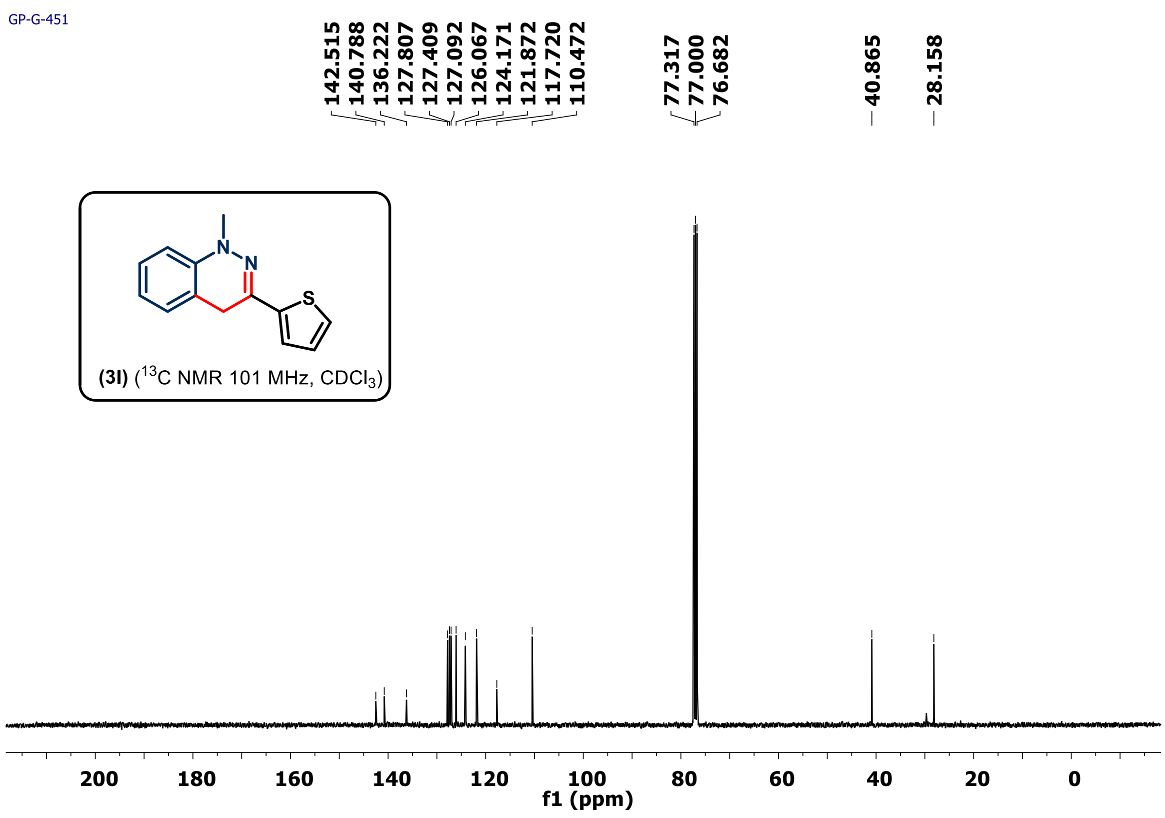

GP-PM-414A
147.039
142.955
139.542
135.948
128.137
127.766
125.330
123.653
122.853
117.389
110.628
77.317
77.000
76.682
41.176
26.876
N
N
NO2
(3j) (13C NMR 101 MHz, CDCl3)
190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


GP-G-531
8.51
8.09
8.09
8.07
8.07
8.07
8.06
7.48
7.46
7.44
7.19
7.18
7.16
7.16
7.09
7.07
6.96
6.96
6.94
6.92
6.92
6.78
6.76
3.75
3.50
NO2
(3k) (1H NMR 400 MHz, CDCl3)
1.00
2.03
1.06
1.10
1.09
1.04
1.05
2.05
3.00
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

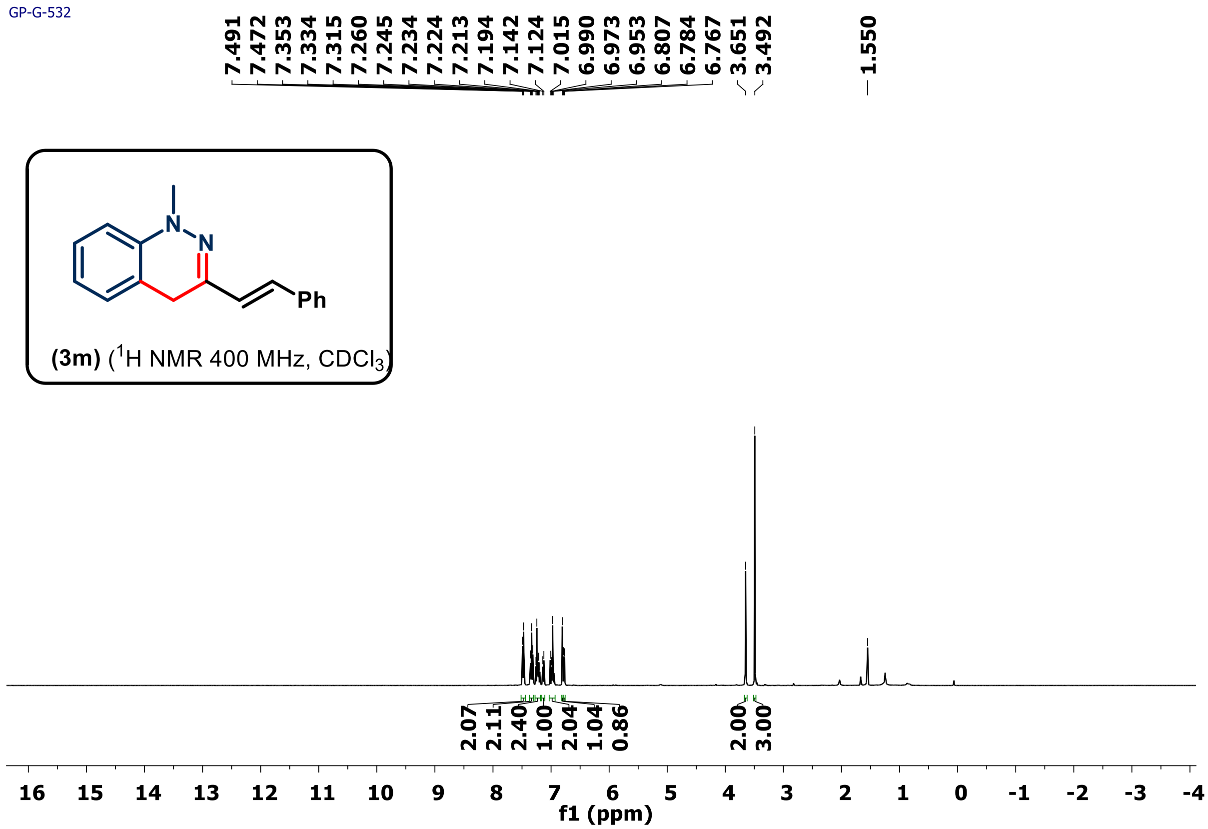

GP-G-531
148.517
139.937
138.710
136.214
130.662
129.153
128.070
127.709
122.573
122.535
119.805
117.320
110.518
77.317
77.000
76.683
41.087
27.092
NO2
(3k) (13C NMR 101 MHz, CDCl3)
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

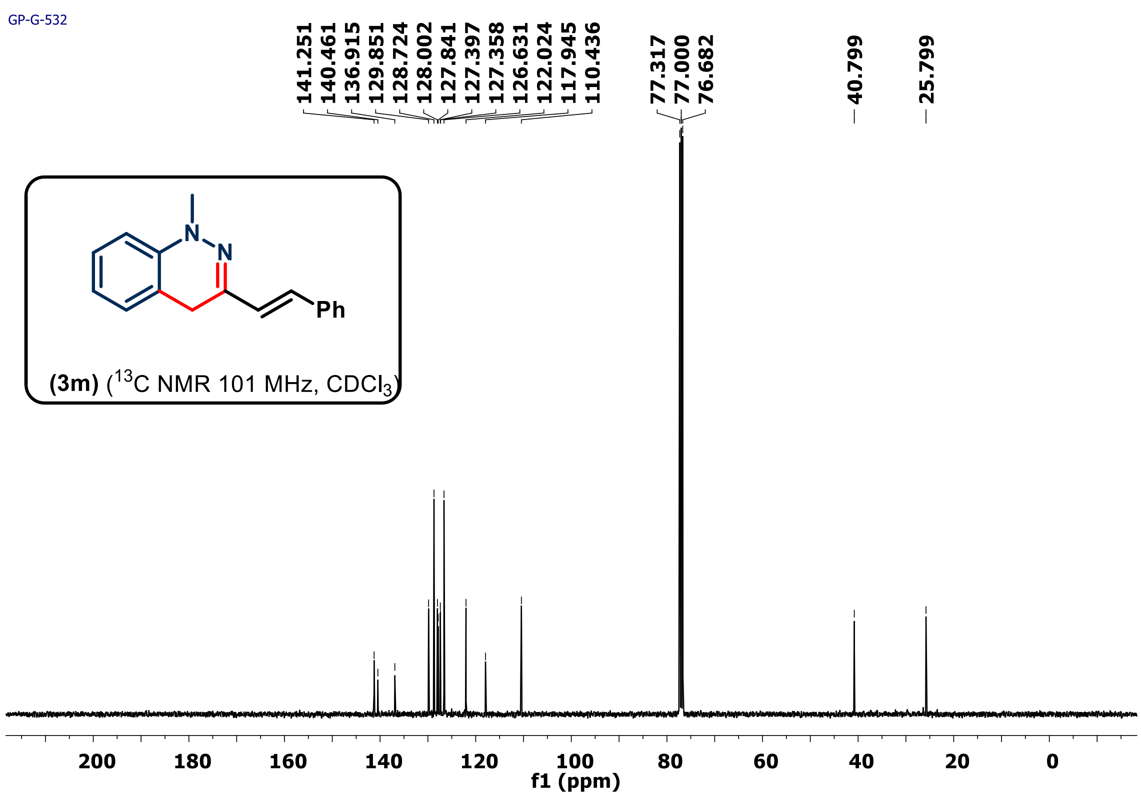


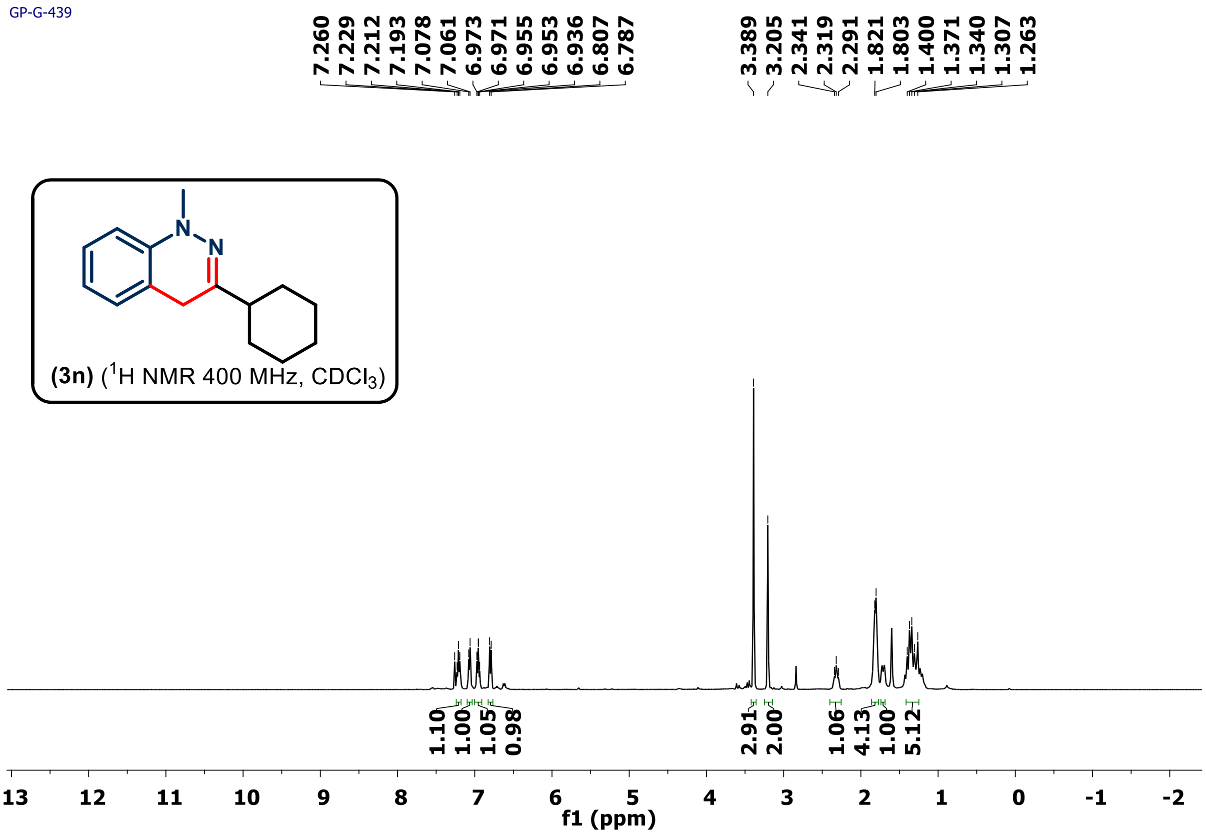
GP-G-450
7.19 7.19 7.19 7.18 7.18 7.16 7.15 7.15 7.08 7.06 6.98 6.97 6.96 6.96 6.93 6.93 6.91 6.91 6.89 6.89 6.77 6.75
3.71
3.45
1.50
(3l) (1H NMR 400 MHz, CDCl3)
3.05 1.04 1.05 1.04 1.00
2.00 3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

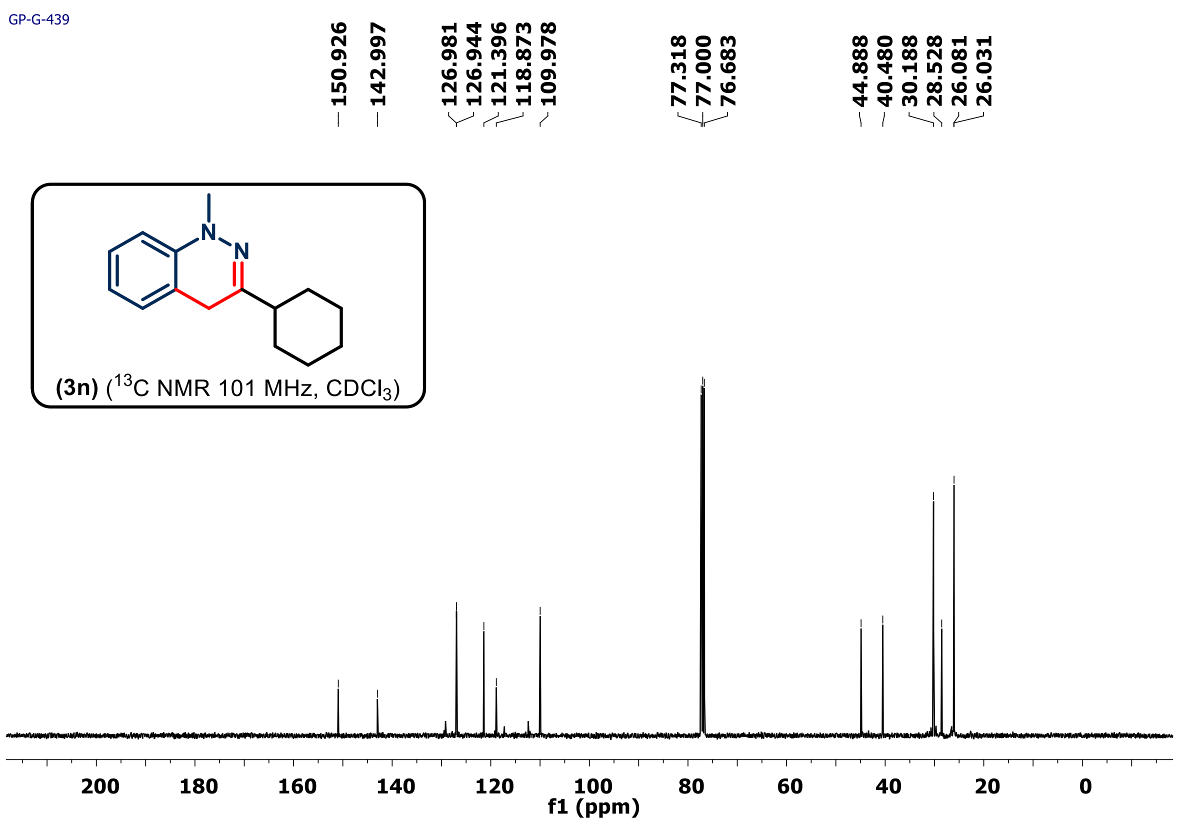


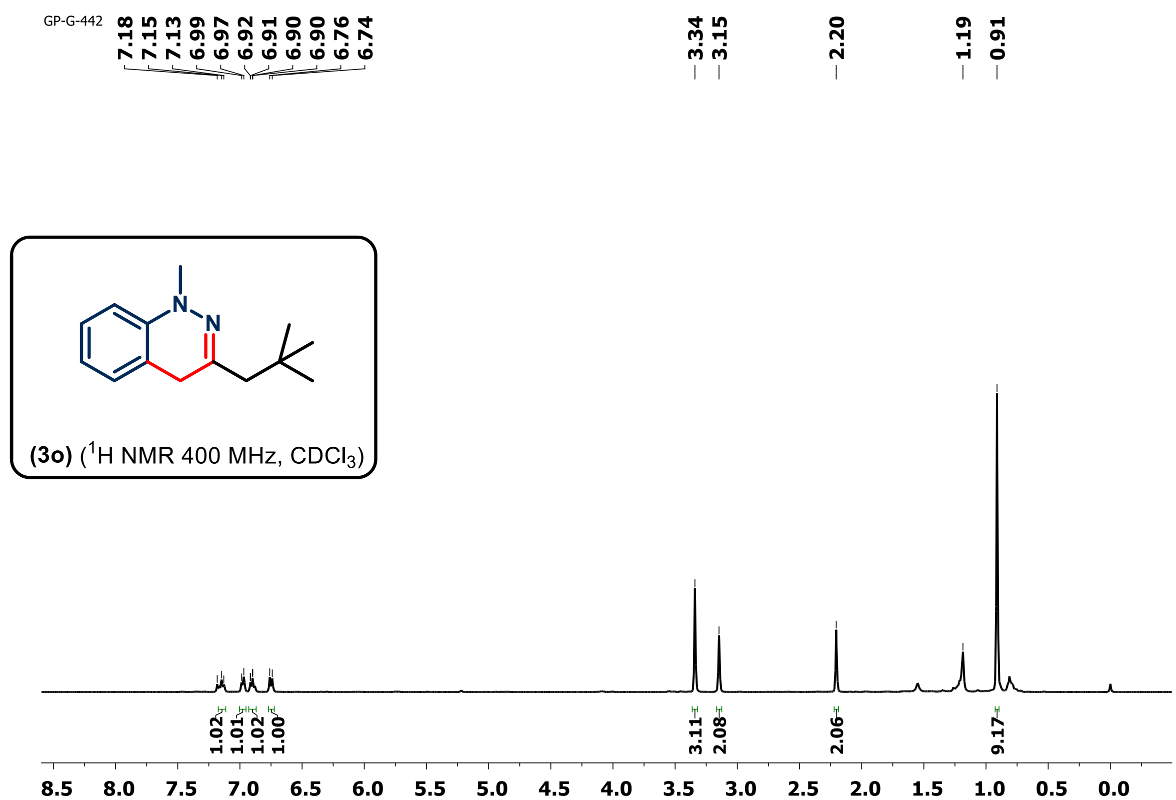
GP-G-451
142.515 140.788 136.222 127.807 127.409 127.092 126.067 124.171 121.872 117.720 110.472
77.317 77.000 76.682
40.865
28.158
(3l) (13C NMR 101 MHz, CDCl3)
200 180 160 140 120 100 80 60 40 20 0
f1 (ppm)

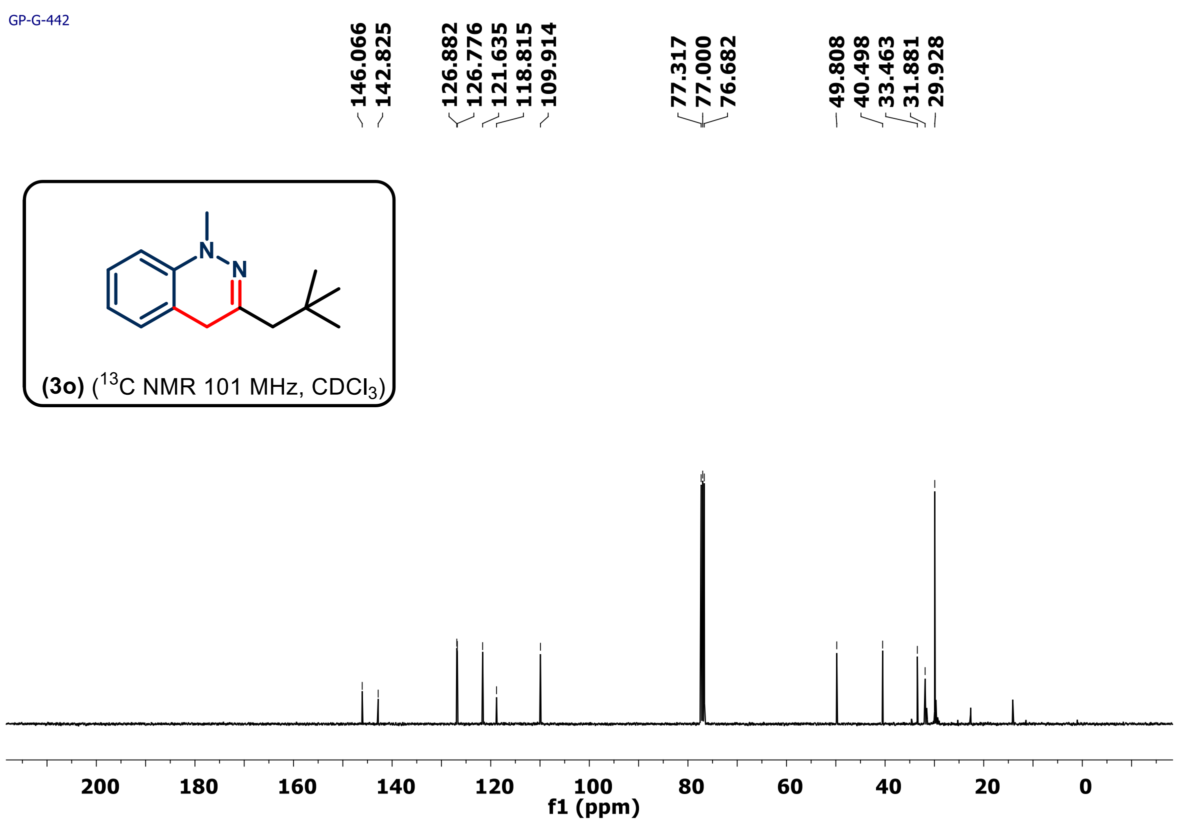

GP-G-532
7.491
7.472
7.353
7.334
7.315
7.260
7.245
7.234
7.224
7.213
7.194
7.142
7.124
7.015
6.990
6.973
6.953
6.807
6.784
6.767
3.651
3.492
1.550
Ph
(3m) (1H NMR 400 MHz, CDCl3)
2.07
2.11
2.40
1.00
2.04
1.04
0.86
2.00
3.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)

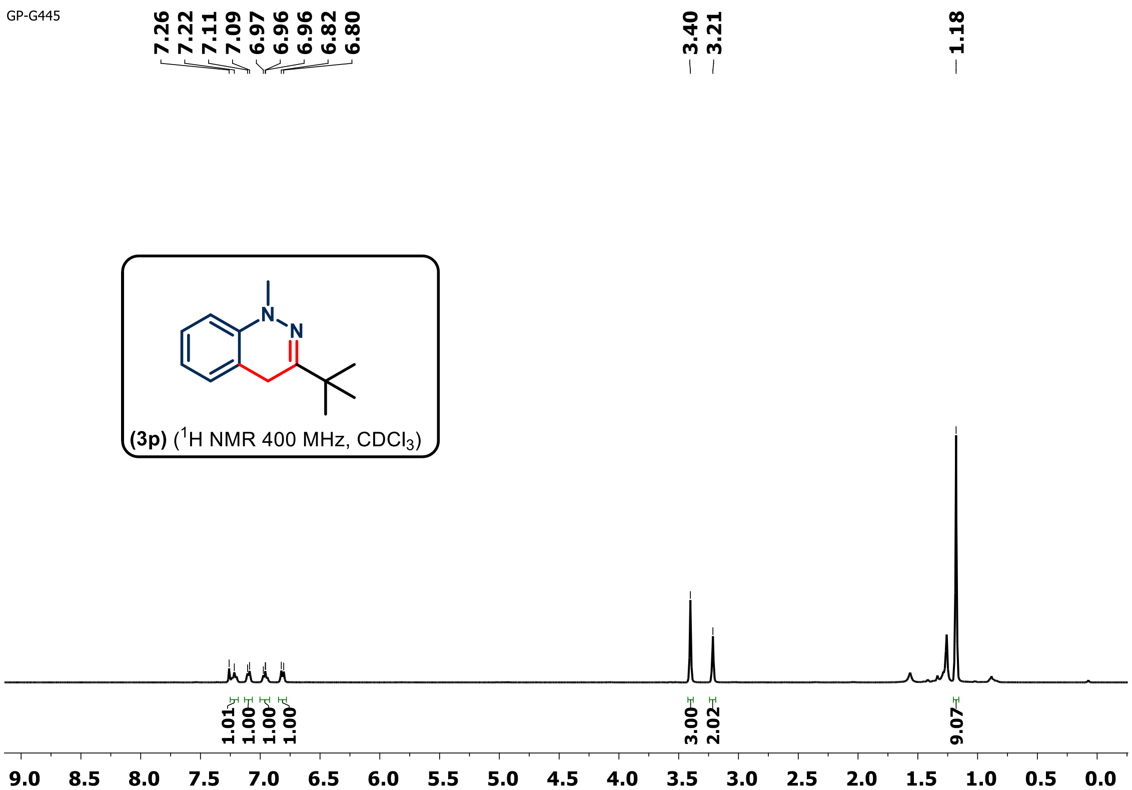

GP-G-532
141.251
140.461
136.915
129.851
128.724
128.002
127.841
127.397
127.358
126.631
122.024
117.945
110.436
77.317
77.000
76.682
40.799
25.799
Ph
(3m) (13C NMR 101 MHz, CDCl3)
200 180 160 140 120 100 80 60 40 20 0
f1 (ppm)

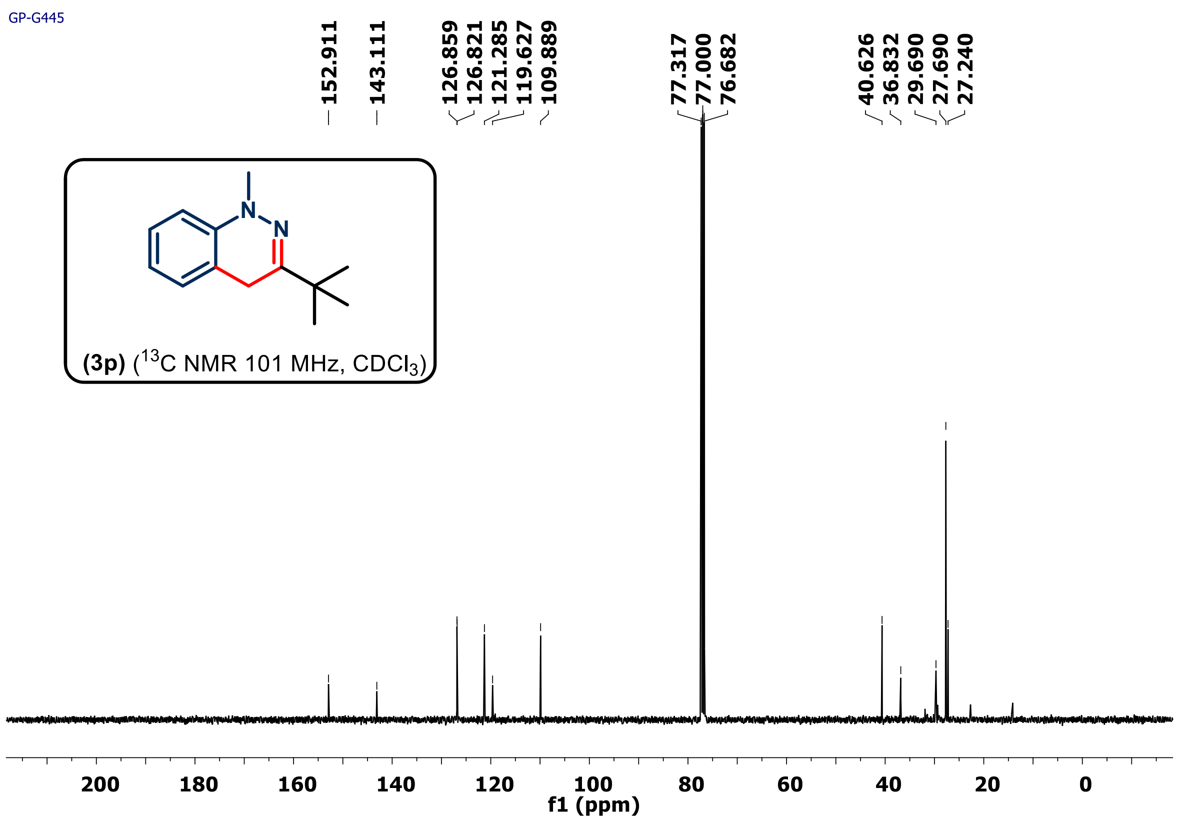

GP-G-439
7.260
7.229
7.212
7.193
7.078
7.061
6.973
6.971
6.955
6.953
6.936
6.807
6.787
3.389
3.205
2.341
2.319
2.291
1.821
1.803
1.400
1.371
1.340
1.307
1.263
(3n) (1H NMR 400 MHz, CDCl3)
1.10
1.00
1.05
0.98
2.91
2.00
1.06
4.13
1.00
5.12
f1 (ppm)

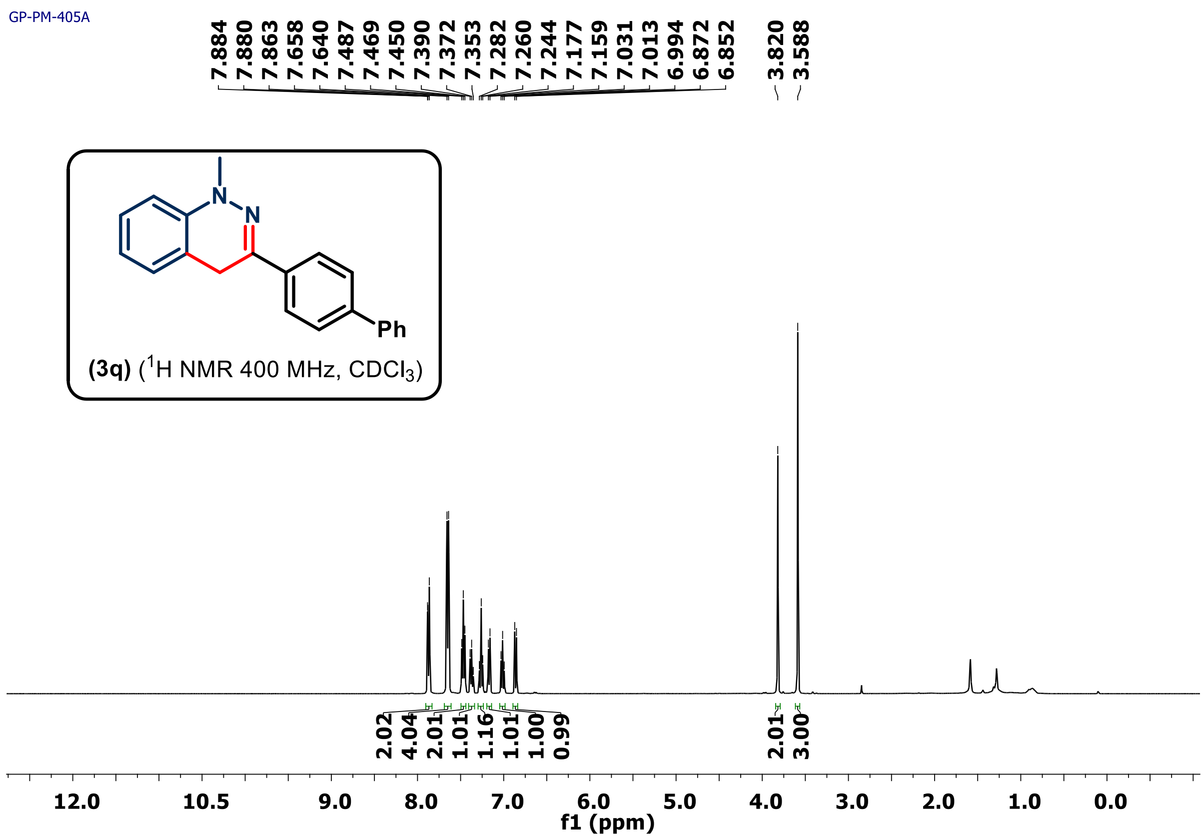

GP-G-439
150.926
142.997
126.981
126.944
121.396
118.873
109.978
77.318
77.000
76.683
44.888
40.480
30.188
28.528
26.081
26.031
(3n) (13C NMR 101 MHz, CDCl3)
f1 (ppm)

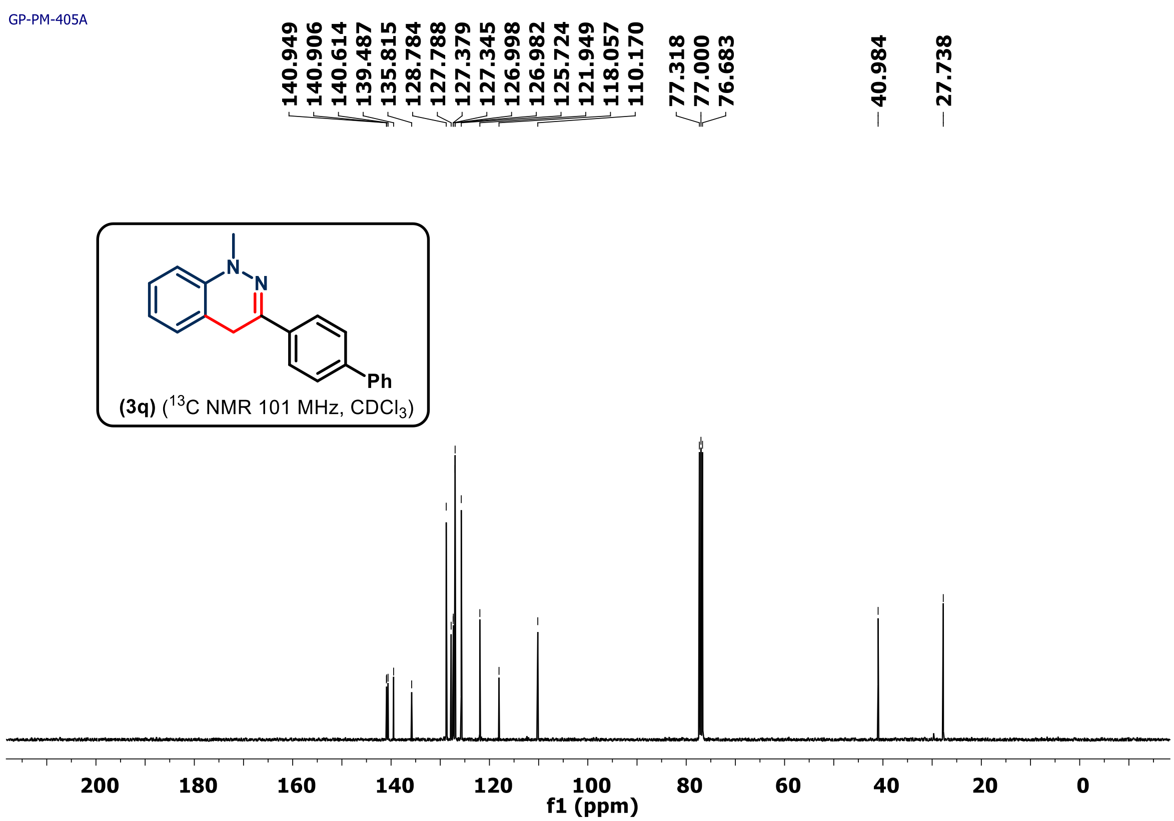

GP-G-442
7.18
7.15
7.13
6.99
6.97
6.92
6.91
6.90
6.90
6.76
6.74
3.34
3.15
2.20
1.19
0.91
N
N
(3o) (^{1}H NMR 400 MHz, $CDCl_3$)
1.02
1.01
1.02
1.00
3.11
2.08
2.06
9.17
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

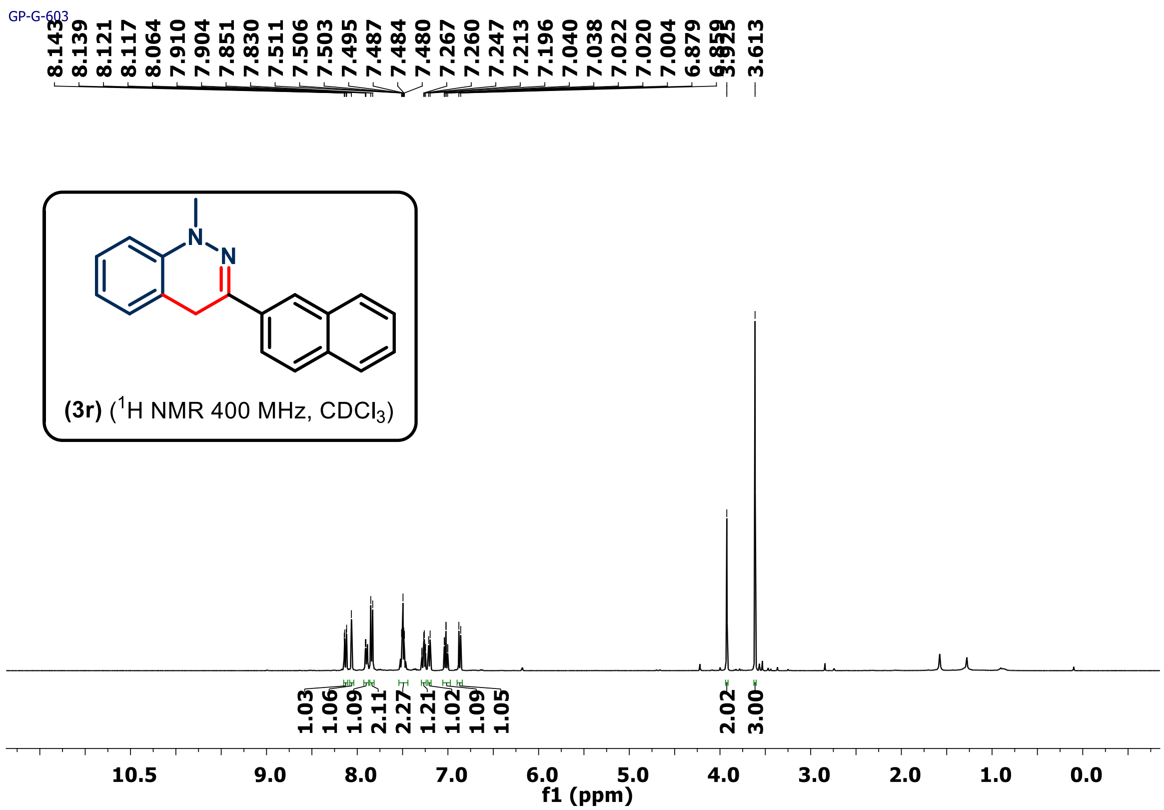

GP-G-442
146.066
142.825
126.882
126.776
121.635
118.815
109.914
77.317
77.000
76.682
49.808
40.498
33.463
31.881
29.928
N
N
(3o) (^{13}C NMR 101 MHz, $CDCl_3$)
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

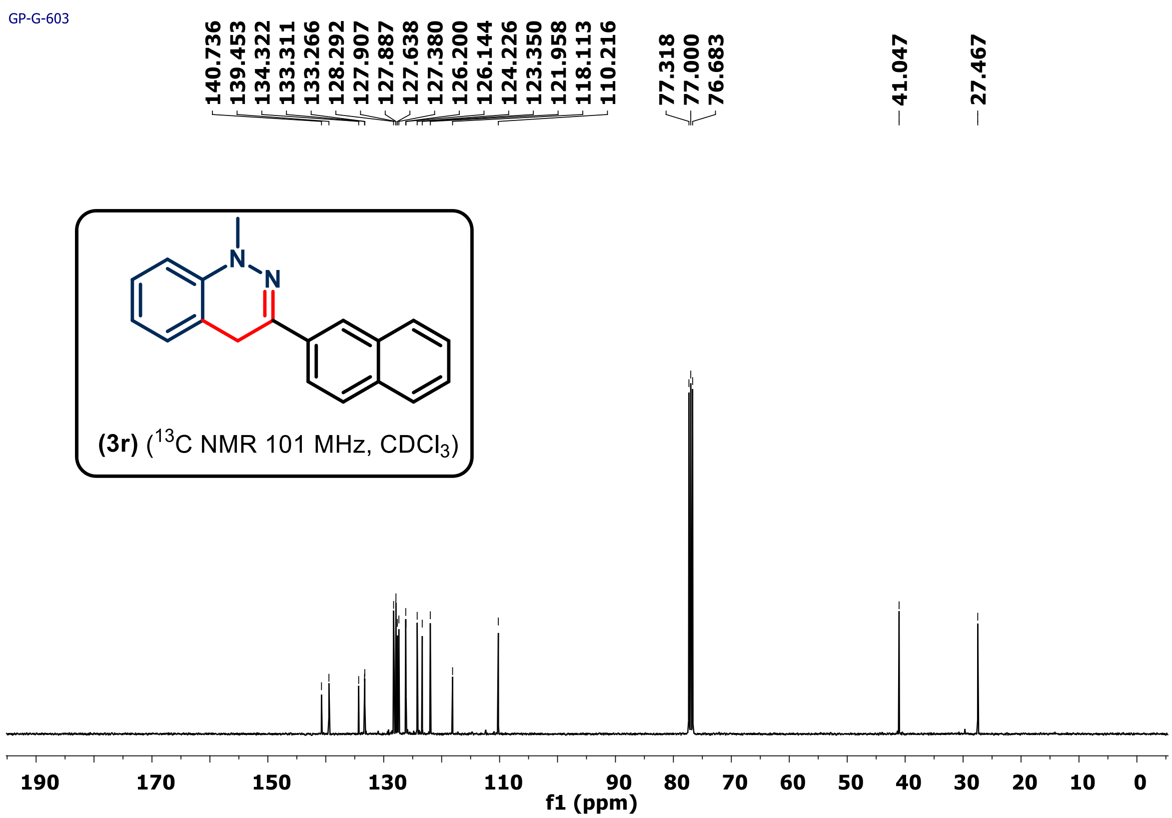

GP-G445
7.26
7.22
7.11
7.09
6.97
6.96
6.96
6.82
6.80
3.40
3.21
1.18
(3p) (1H NMR 400 MHz, CDCl3)
1.01
1.00
1.00
1.00
3.00
2.02
9.07
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

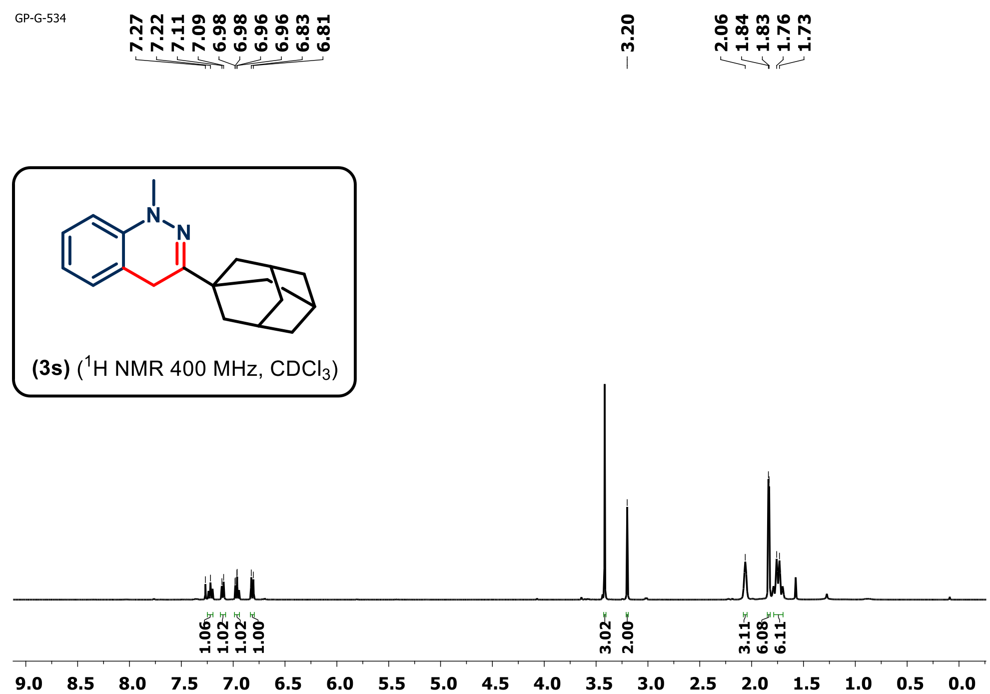

GP-G445
152.911
143.111
126.859
126.821
121.285
119.627
109.889
77.317
77.000
76.682
40.626
36.832
29.690
27.690
27.240
(3p) (13C NMR 101 MHz, CDCl3)
200 180 160 140 120 100 80 60 40 20 0
f1 (ppm)

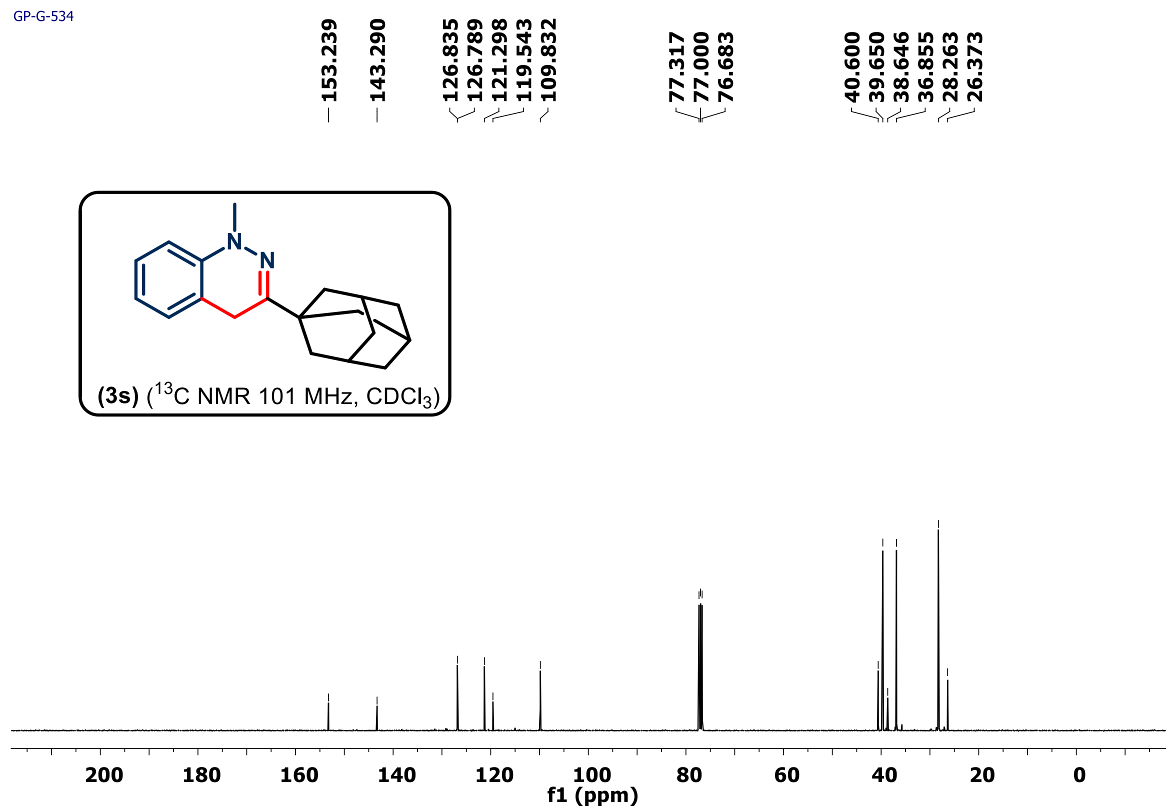

GP-PM-405A
7.884
7.880
7.863
7.658
7.640
7.487
7.469
7.450
7.390
7.372
7.353
7.282
7.260
7.244
7.177
7.159
7.031
7.013
6.994
6.872
6.852
3.820
3.588
N
N
Ph
(3q) (^{1}H NMR 400 MHz, CDCl$_3$)
2.02
4.04
2.01
1.01
1.16
1.01
1.00
0.99
2.01
3.00
12.0
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

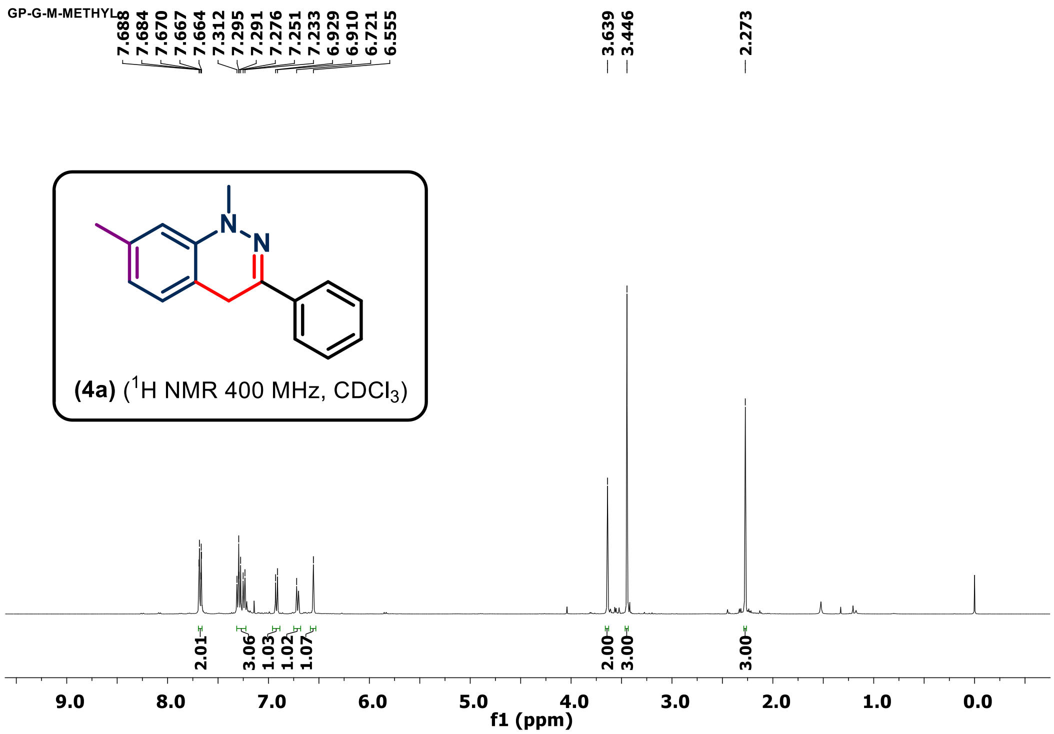

GP-PM-405A
140.949
140.906
140.614
139.487
135.815
128.784
127.788
127.379
127.345
126.998
126.982
125.724
121.949
118.057
110.170
77.318
77.000
76.683
40.984
27.738
N
N
Ph
(3q) (^{13}C NMR 101 MHz, CDCl$_3$)
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

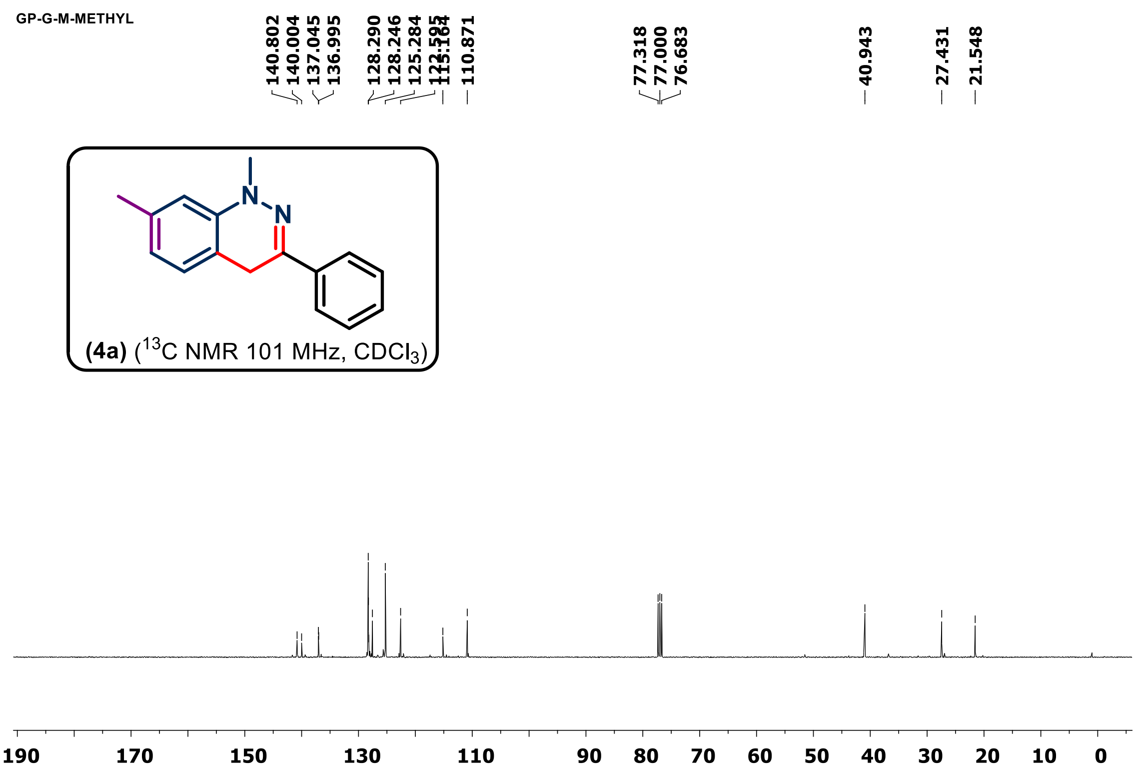

GP-G-603
8.143
8.139
8.121
8.117
8.064
7.910
7.904
7.851
7.830
7.511
7.506
7.503
7.495
7.487
7.484
7.480
7.267
7.260
7.247
7.213
7.196
7.040
7.038
7.022
7.020
7.004
6.879
6.859
3.925
3.613
N
N
(3r) (1H NMR 400 MHz, CDCl3)
1.03
1.06
1.09
2.11
2.27
1.21
1.02
1.09
1.05
2.02
3.00
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

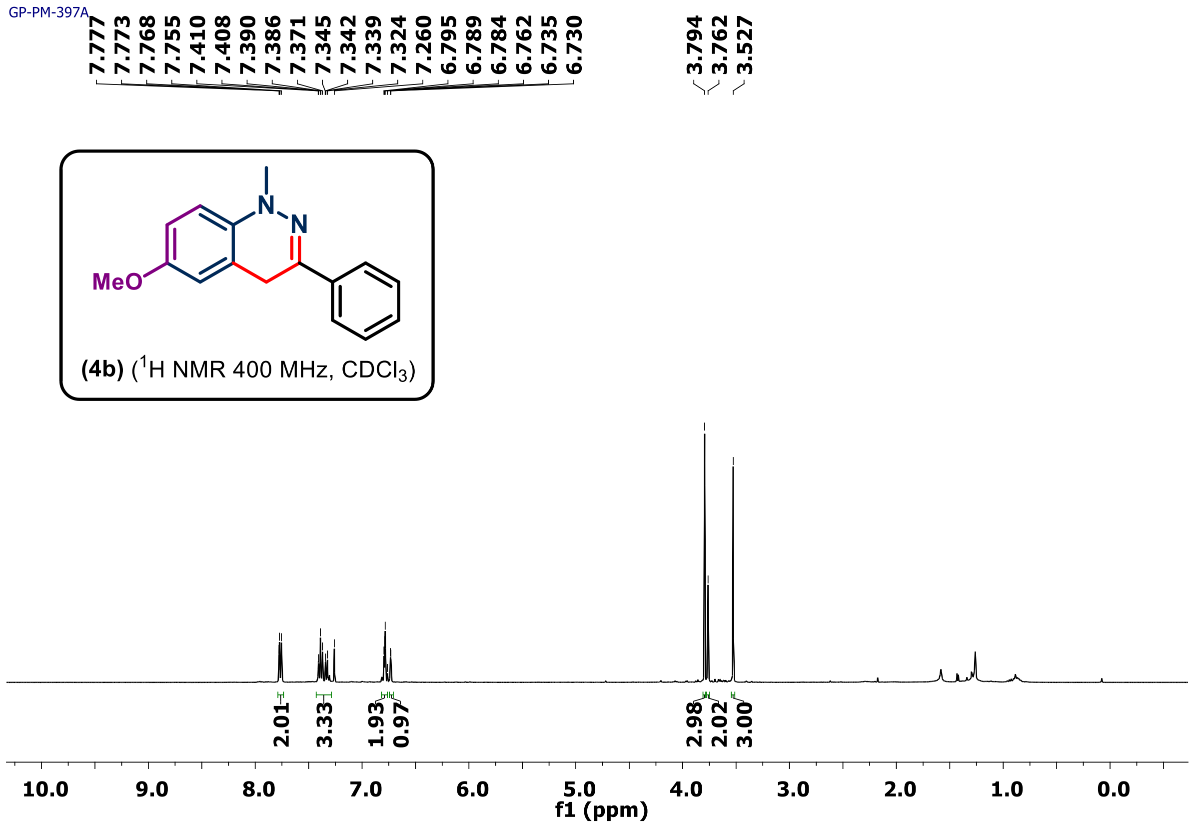

GP-G-603
140.736
139.453
134.322
133.311
133.266
128.292
127.907
127.887
127.638
127.380
126.200
126.144
124.226
123.350
121.958
118.113
110.216
77.318
77.000
76.683
41.047
27.467
N
N
(3r) (13C NMR 101 MHz, CDCl3)
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

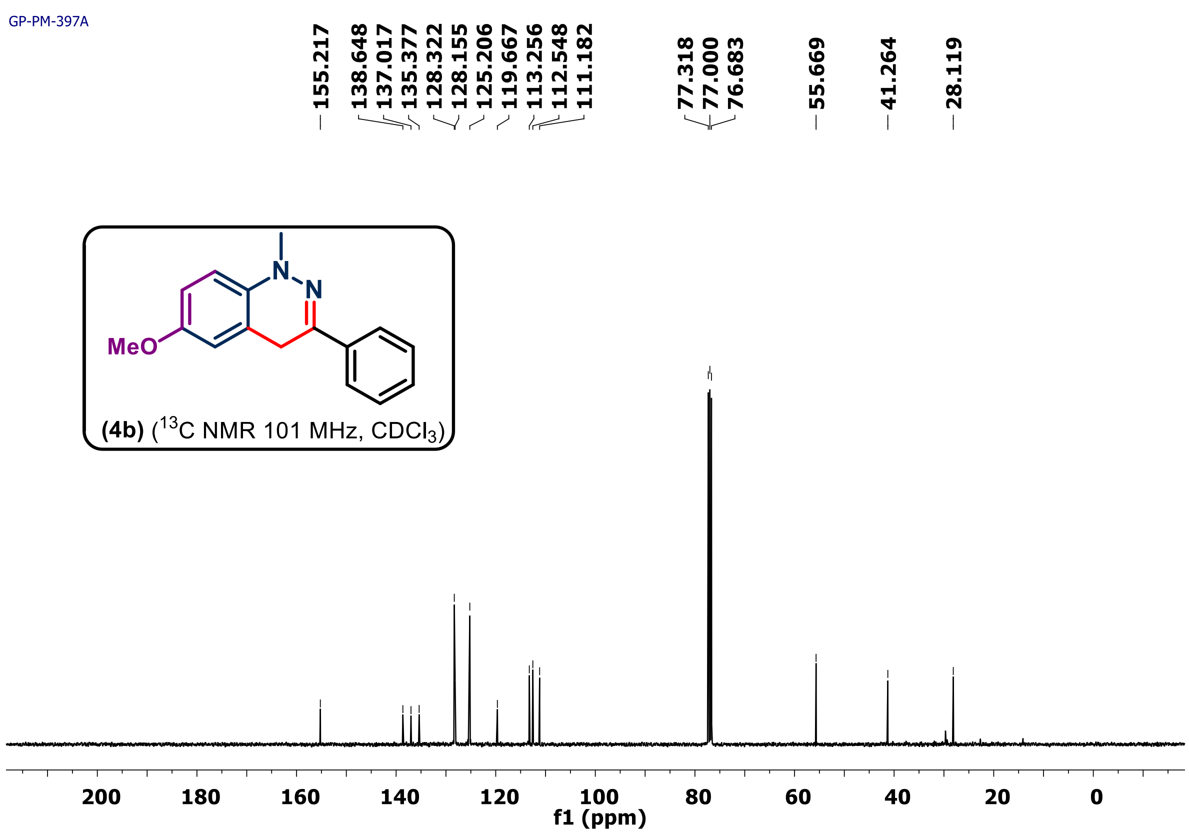

GP-G-534
7.27 7.22 7.11 7.09 6.98 6.98 6.96 6.96 6.83 6.81
3.20
2.06 1.84 1.83 1.76 1.73
(3s) (^{1}H NMR 400 MHz, $CDCl_3$)
1.06 1.02 1.02 1.00
3.02 2.00
3.11 6.08 6.11
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

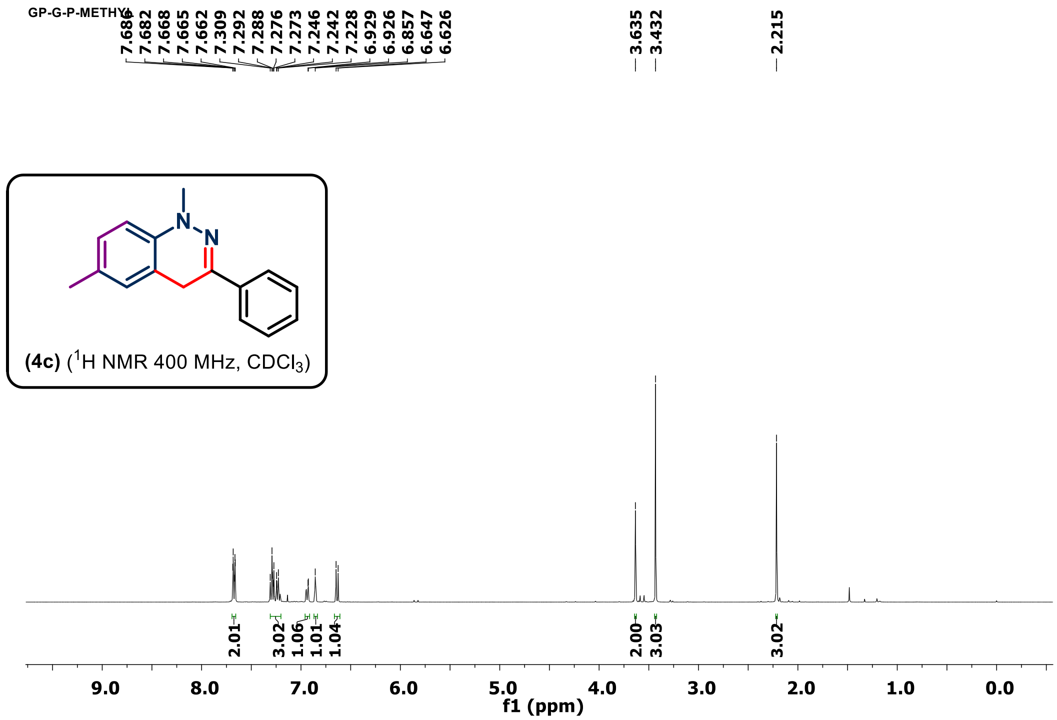

GP-G-534
153.239
143.290
126.835 126.789 121.298 119.543 109.832
77.317 77.000 76.683
40.600 39.650 38.646 36.855 28.263 26.373
(3s) (^{13}C NMR 101 MHz, $CDCl_3$)
200 180 160 140 120 100 80 60 40 20 0
f1 (ppm)

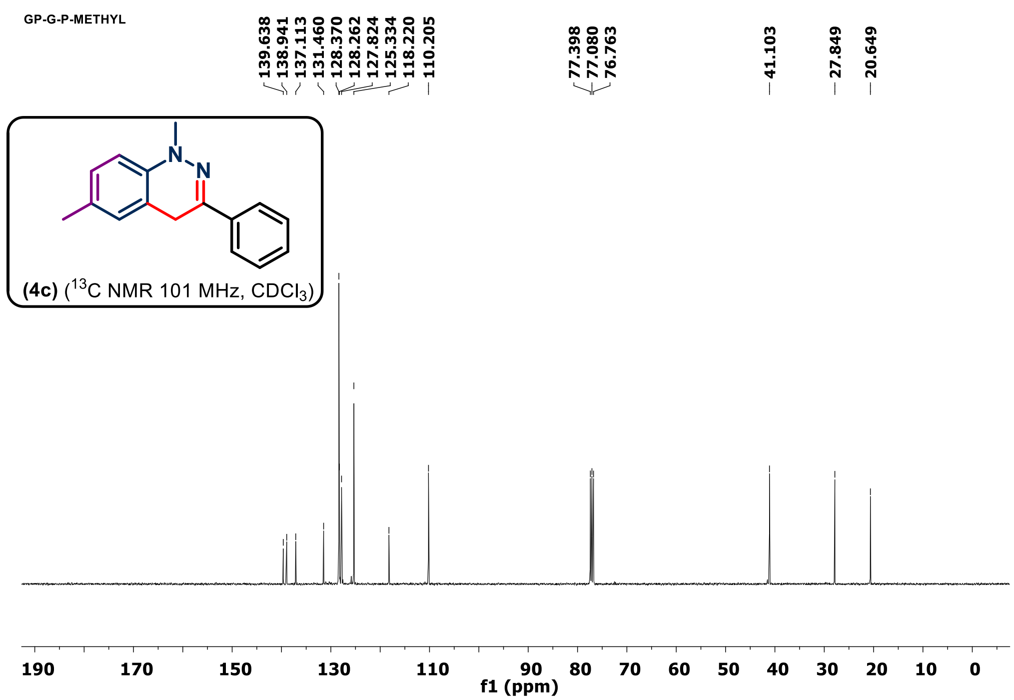

GP-G-M-METHYL
7.688
7.684
7.670
7.667
7.664
7.312
7.295
7.291
7.276
7.251
7.233
6.929
6.910
6.721
6.555
3.639
3.446
2.273
(4a) (^{1}H NMR 400 MHz, $CDCl_3$)
2.01
3.06
1.03
1.02
1.07
2.00
3.00
3.00
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

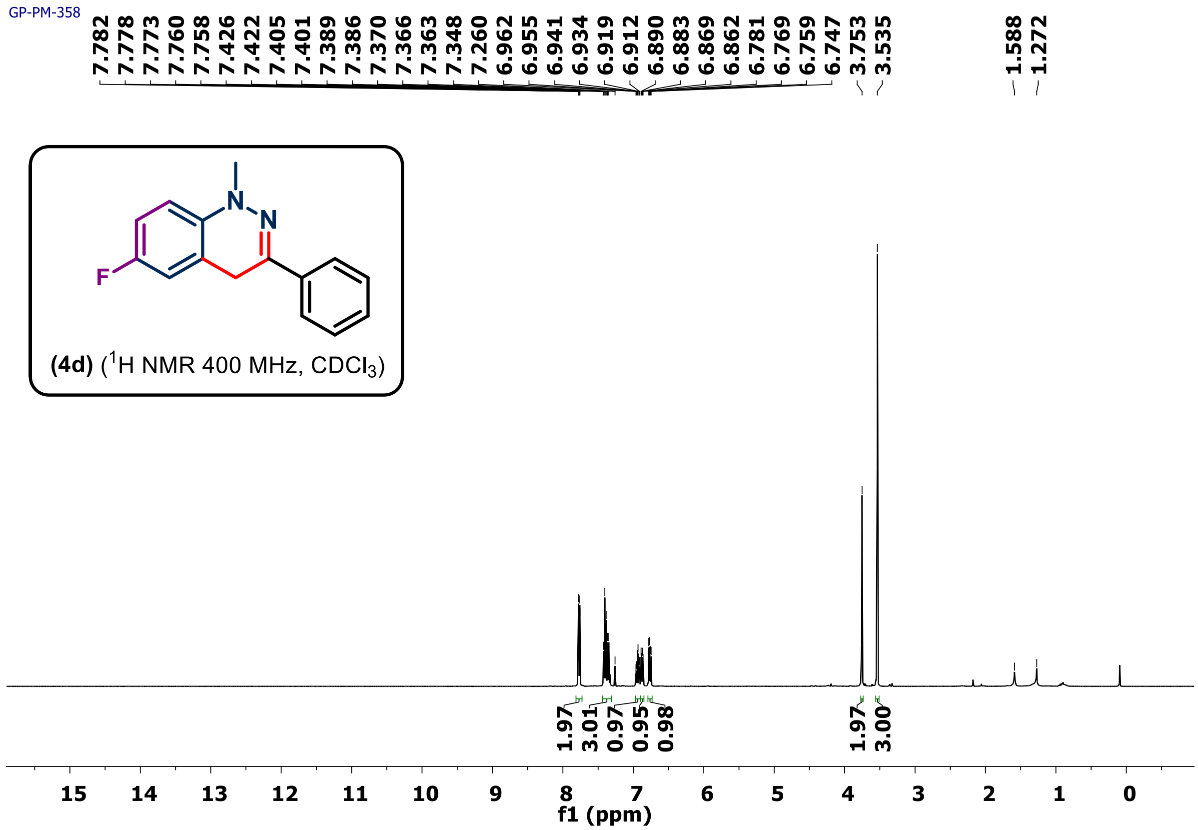

GP-G-M-METHYL
140.802
140.004
137.045
136.995
128.290
128.246
125.284
110.871
77.318
77.000
76.683
40.943
27.431
21.548
(4a) (^{13}C NMR 101 MHz, $CDCl_3$)
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

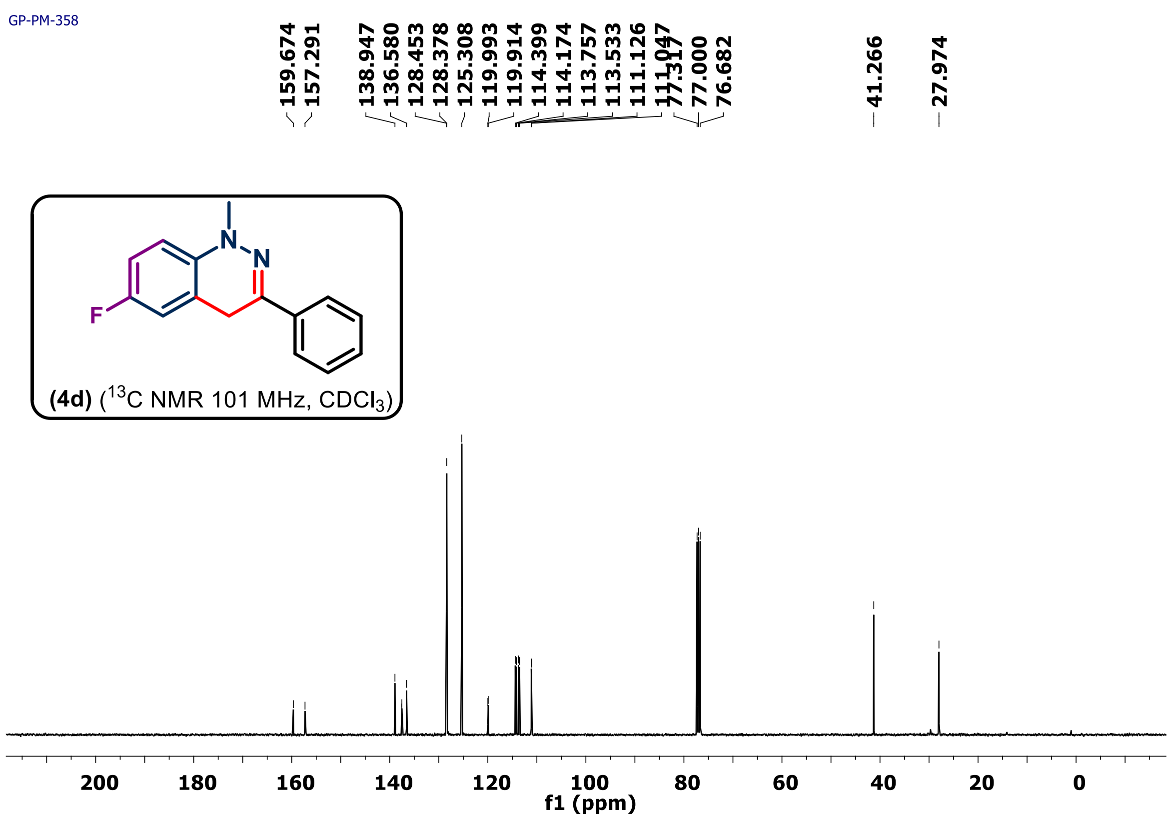

GP-PM-397A
7.777
7.773
7.768
7.755
7.410
7.408
7.390
7.386
7.371
7.345
7.342
7.339
7.324
7.260
6.795
6.789
6.784
6.762
6.735
6.730
3.794
3.762
3.527
N
N
MeO
(4b) (^{1}H NMR 400 MHz, $CDCl_3$)
2.01
3.33
1.93
0.97
2.98
2.02
3.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

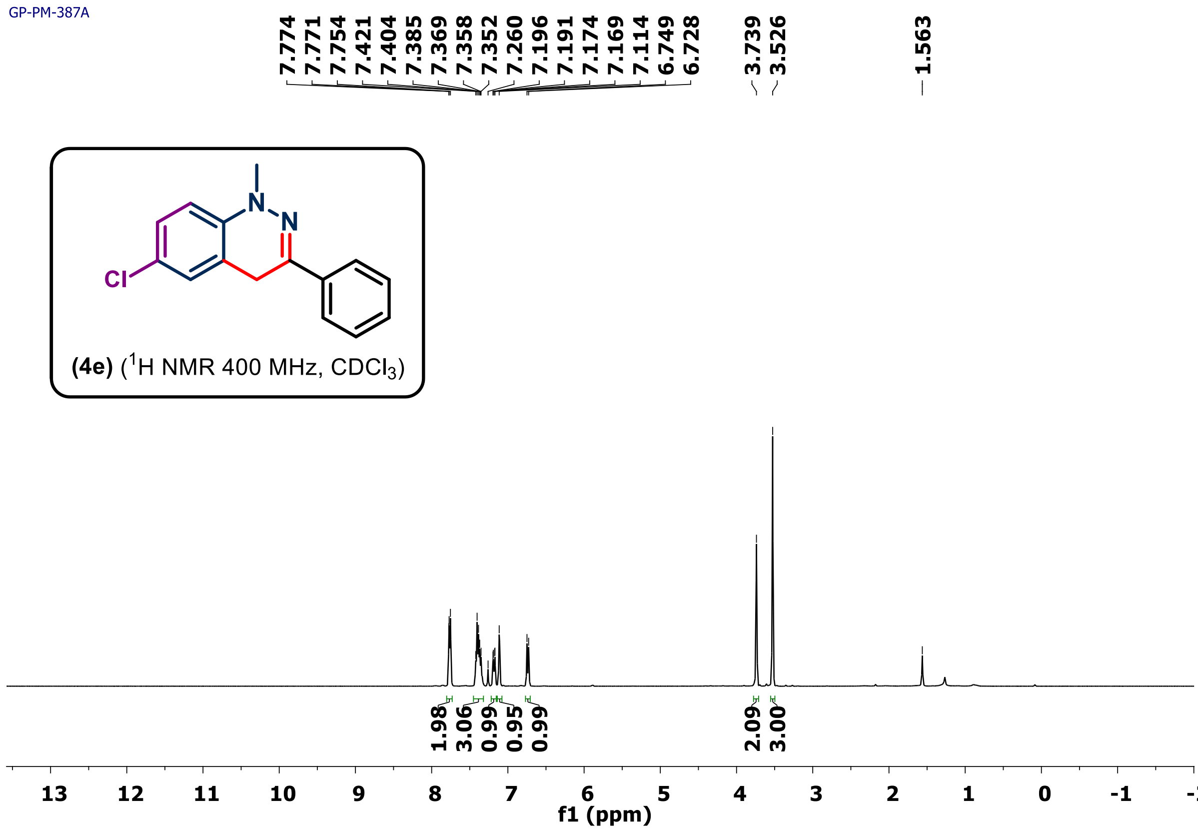

GP-PM-397A
155.217
138.648
137.017
135.377
128.322
128.155
125.206
119.667
113.256
112.548
111.182
77.318
77.000
76.683
55.669
41.264
28.119
N
N
MeO
(4b) (^{13}C NMR 101 MHz, $CDCl_3$)
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

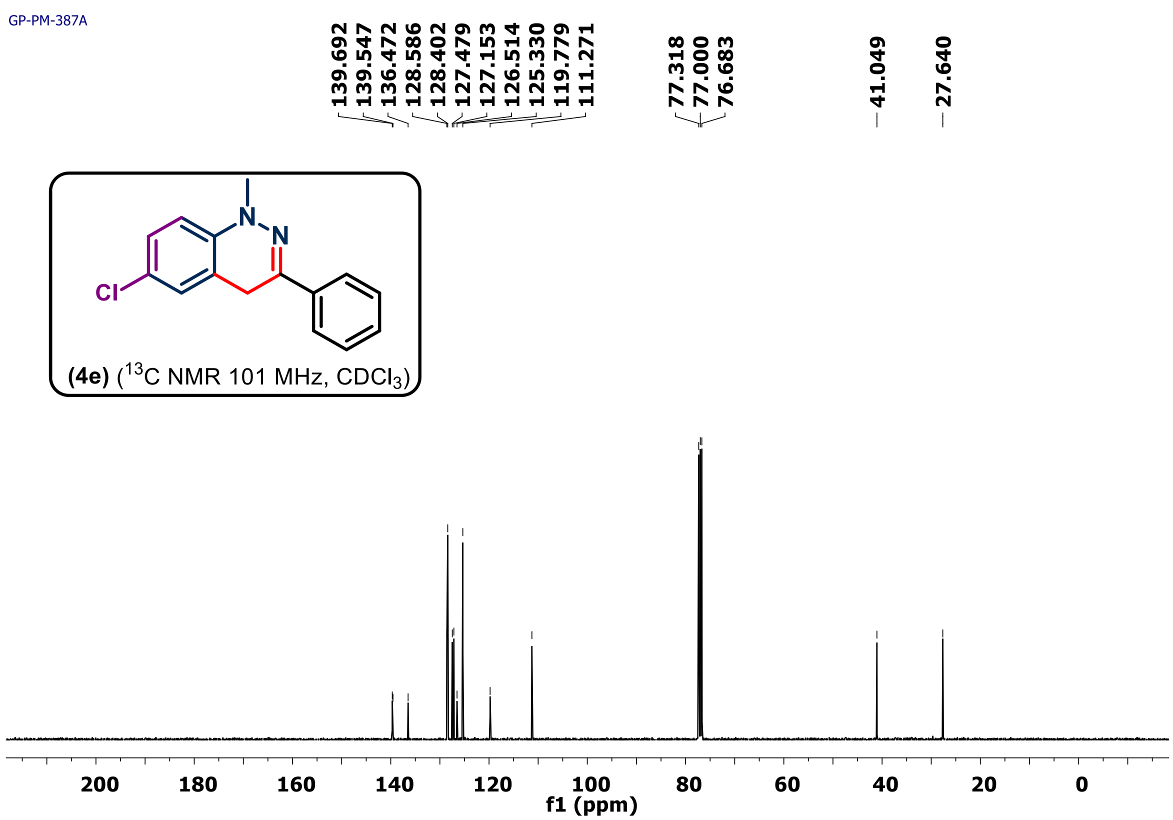

GP-G-P-METHYL
7.686
7.682
7.668
7.665
7.662
7.309
7.292
7.288
7.276
7.273
7.246
7.242
7.228
6.929
6.926
6.857
6.647
6.626
3.635
3.432
2.215
(4c) (^{1}H NMR 400 MHz, $CDCl_3$)
2.01
3.02
1.06
1.01
1.04
2.00
3.03
3.02
9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
f1 (ppm)

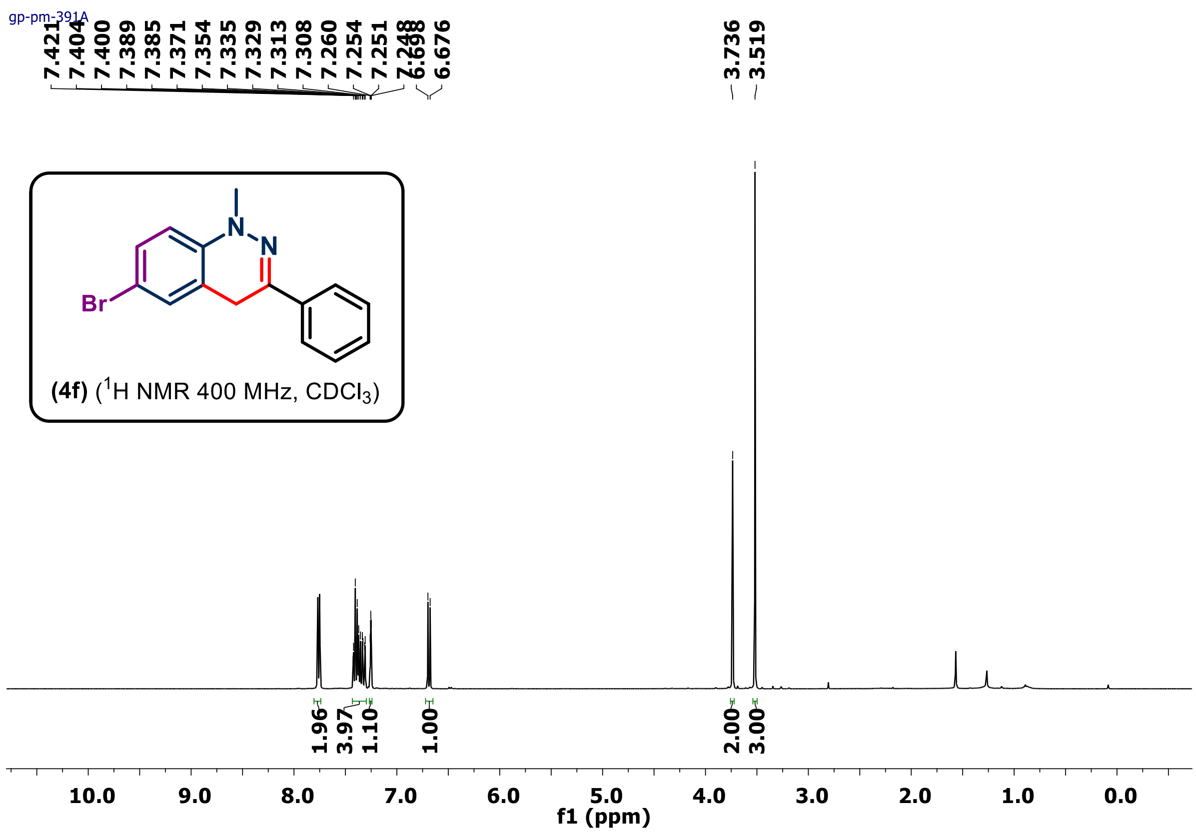

GP-G-P-METHYL
139.638
138.941
137.113
131.460
128.370
128.262
127.824
125.334
118.220
110.205
77.398
77.080
76.763
41.103
27.849
20.649
(4c) (^{13}C NMR 101 MHz, $CDCl_3$)
190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

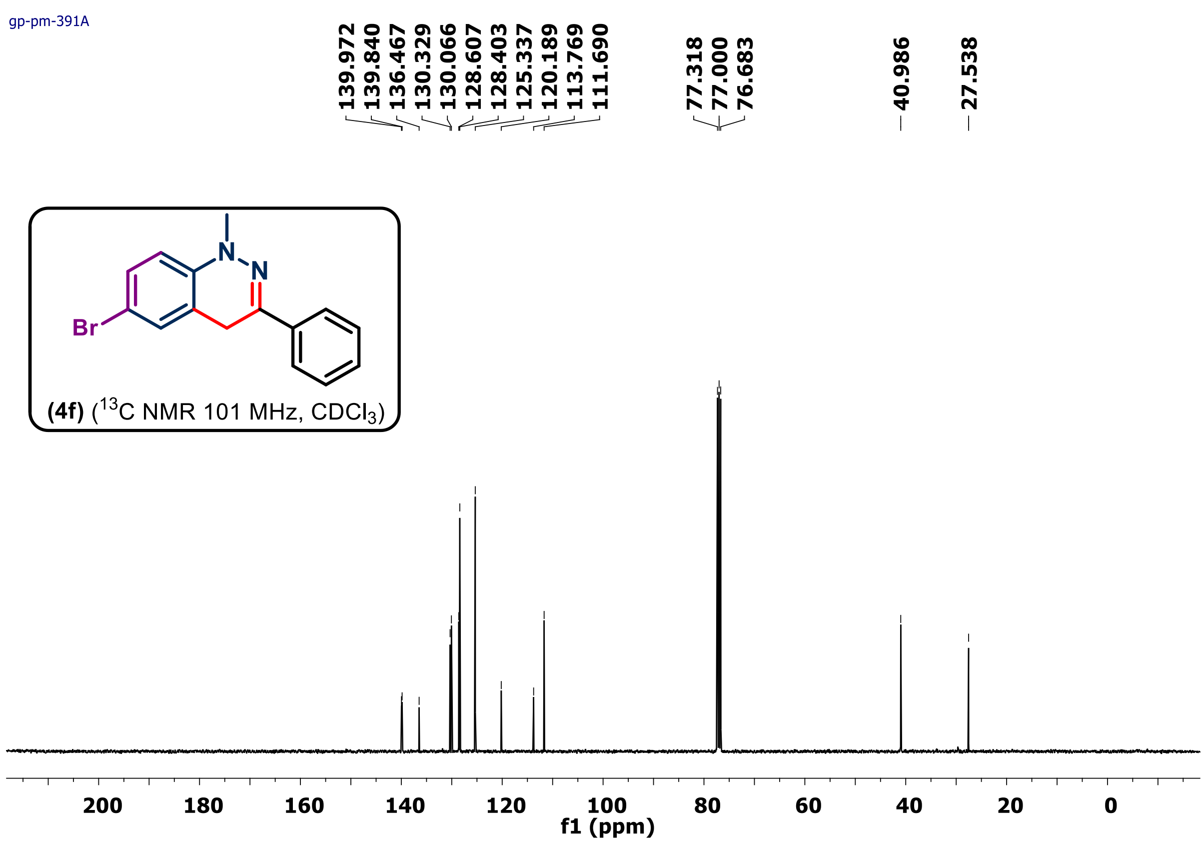

GP-PM-358
7.782 7.778 7.773 7.760 7.758 7.426 7.422 7.405 7.401 7.389 7.386 7.370 7.366 7.363 7.348 7.260 6.962 6.955 6.941 6.934 6.919 6.912 6.890 6.883 6.869 6.862 6.781 6.769 6.759 6.747 3.753 3.535
1.588 1.272
F
N
N
(4d) (1H NMR 400 MHz, CDCl3)
1.97 3.01 0.97 0.95 0.98
1.97 3.00
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)

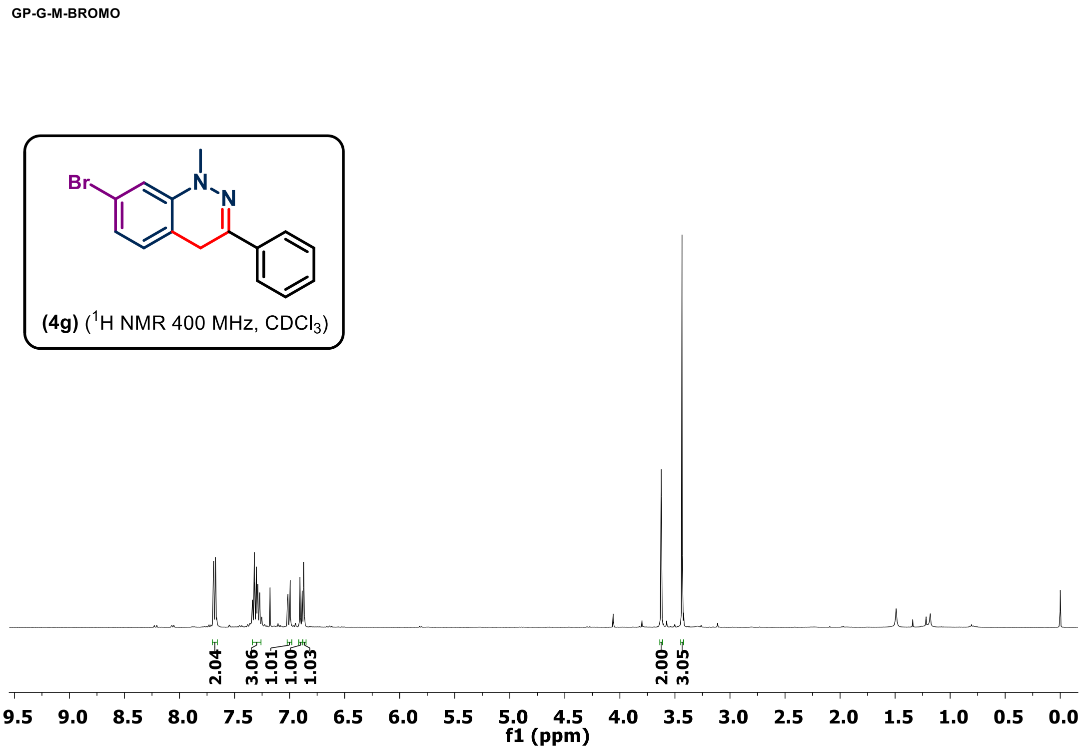

GP-PM-358
159.674 157.291
138.947 136.580 128.453 128.378 125.308 119.993 119.914 114.399 114.174 113.757 113.533 111.126 111.047 77.317 77.000 76.682
41.266
27.974
F
N
N
(4d) (13C NMR 101 MHz, CDCl3)
200 180 160 140 120 100 80 60 40 20 0
f1 (ppm)

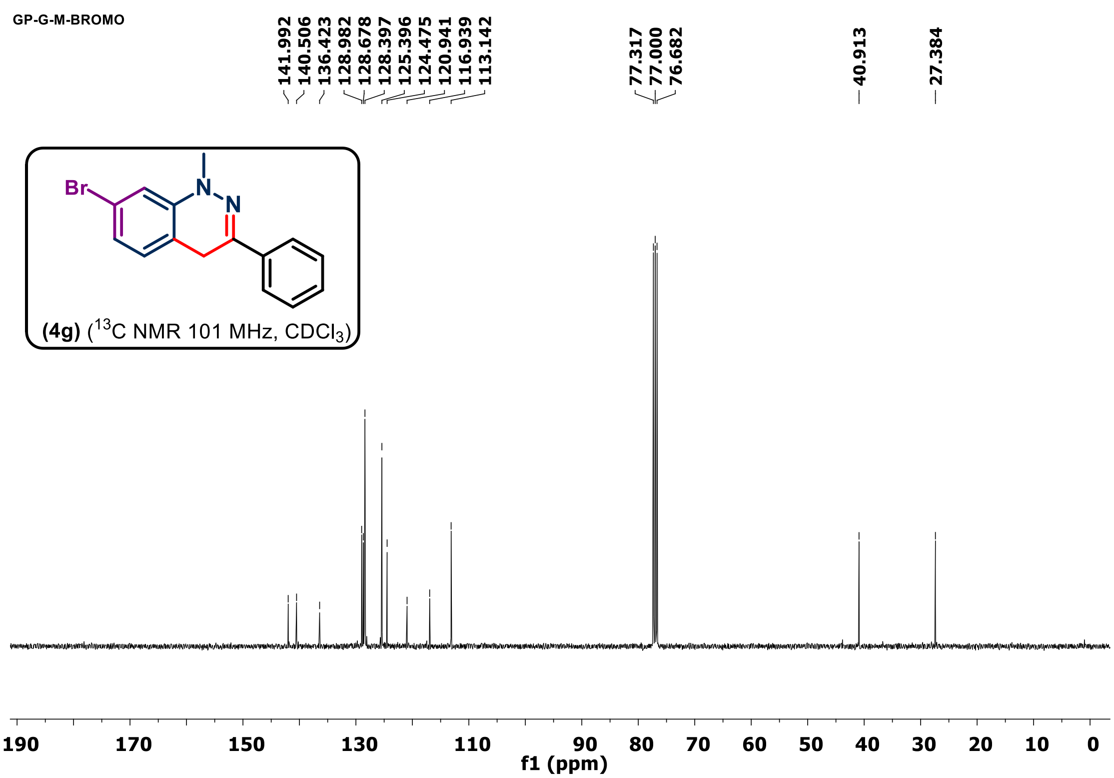

GP-PM-387A
7.774
7.771
7.754
7.421
7.404
7.385
7.369
7.358
7.352
7.260
7.196
7.191
7.174
7.169
7.114
6.749
6.728
3.739
3.526
1.563
Cl
N
N
(4e) (^{1}H NMR 400 MHz, $CDCl_3$)
1.98
3.06
0.99
0.95
0.99
2.09
3.00
13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2
f1 (ppm)

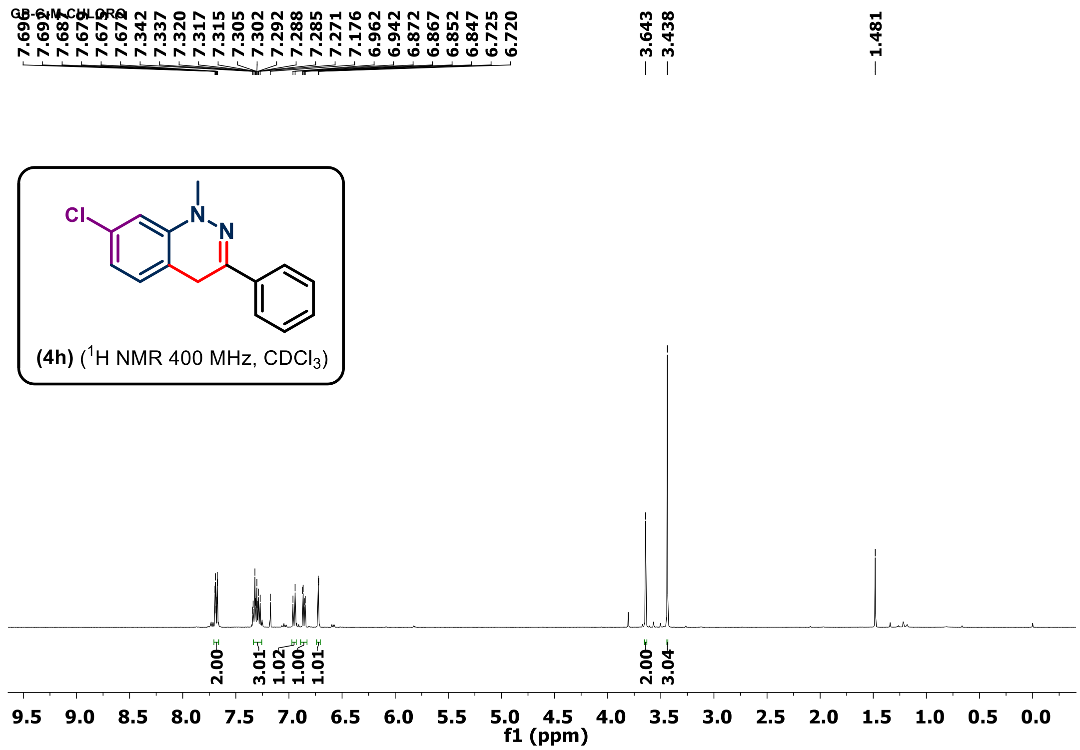

GP-PM-387A
139.692
139.547
136.472
128.586
128.402
127.479
127.153
126.514
125.330
119.779
111.271
77.318
77.000
76.683
41.049
27.640
Cl
N
N
(4e) (^{13}C NMR 101 MHz, $CDCl_3$)
200 180 160 140 120 100 80 60 40 20 0
f1 (ppm)

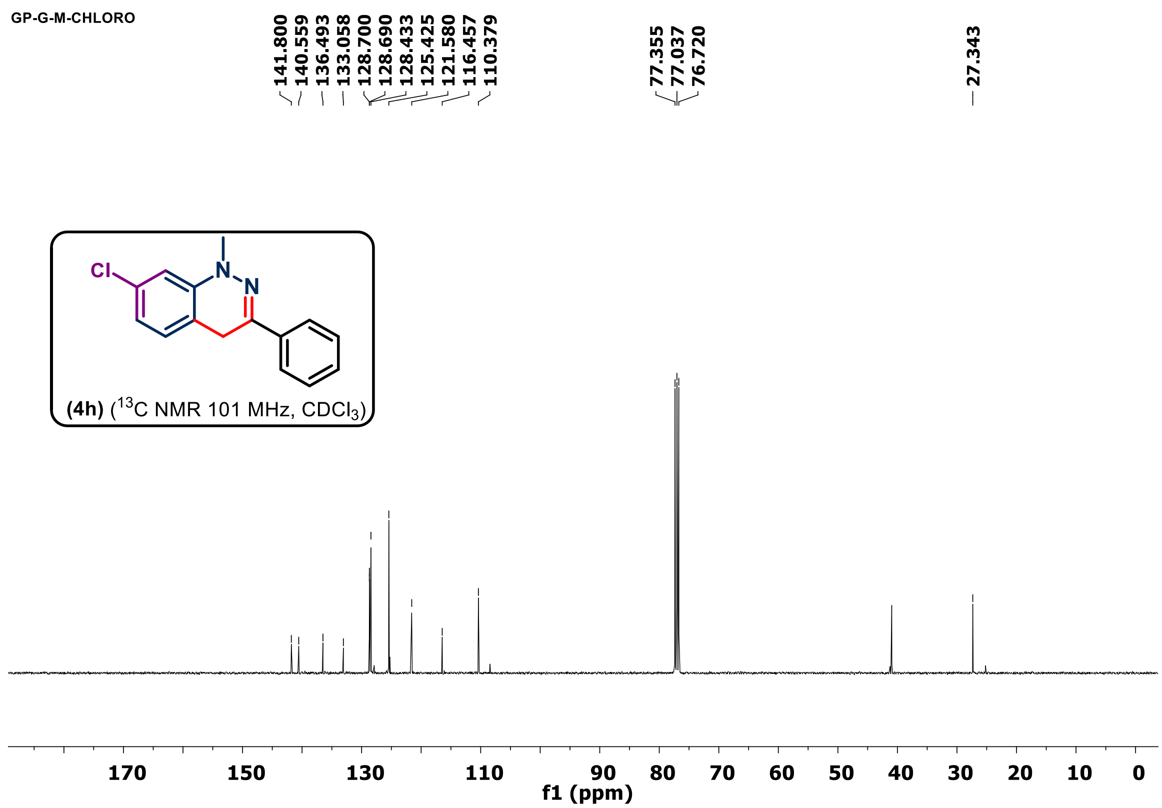

gp-pm-391A
7.421
7.404
7.400
7.389
7.385
7.371
7.354
7.335
7.329
7.313
7.308
7.260
7.254
7.251
7.248
6.698
6.676
3.736
3.519
Br
N
N
(4f) (1H NMR 400 MHz, CDCl3)
1.96
3.97
1.10
1.00
2.00
3.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

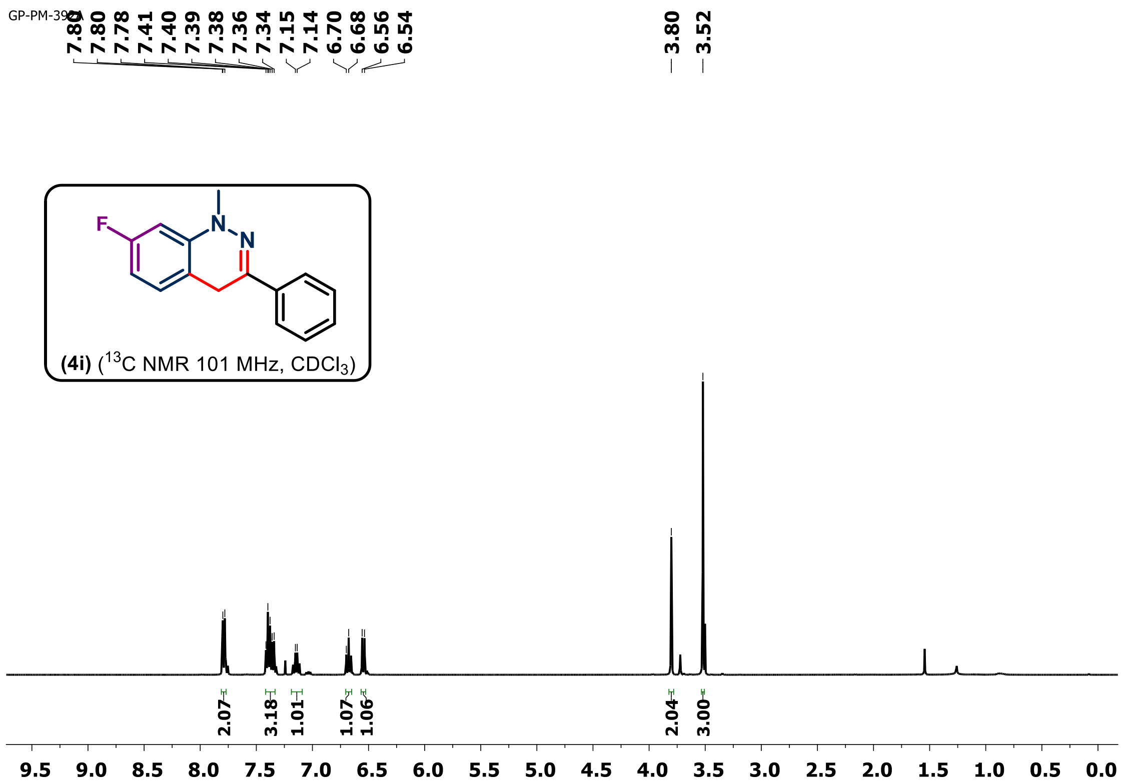

gp-pm-391A
139.972
139.840
136.467
130.329
130.066
128.607
128.403
125.337
120.189
113.769
111.690
77.318
77.000
76.683
40.986
27.538
Br
N
N
(4f) (13C NMR 101 MHz, CDCl3)
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

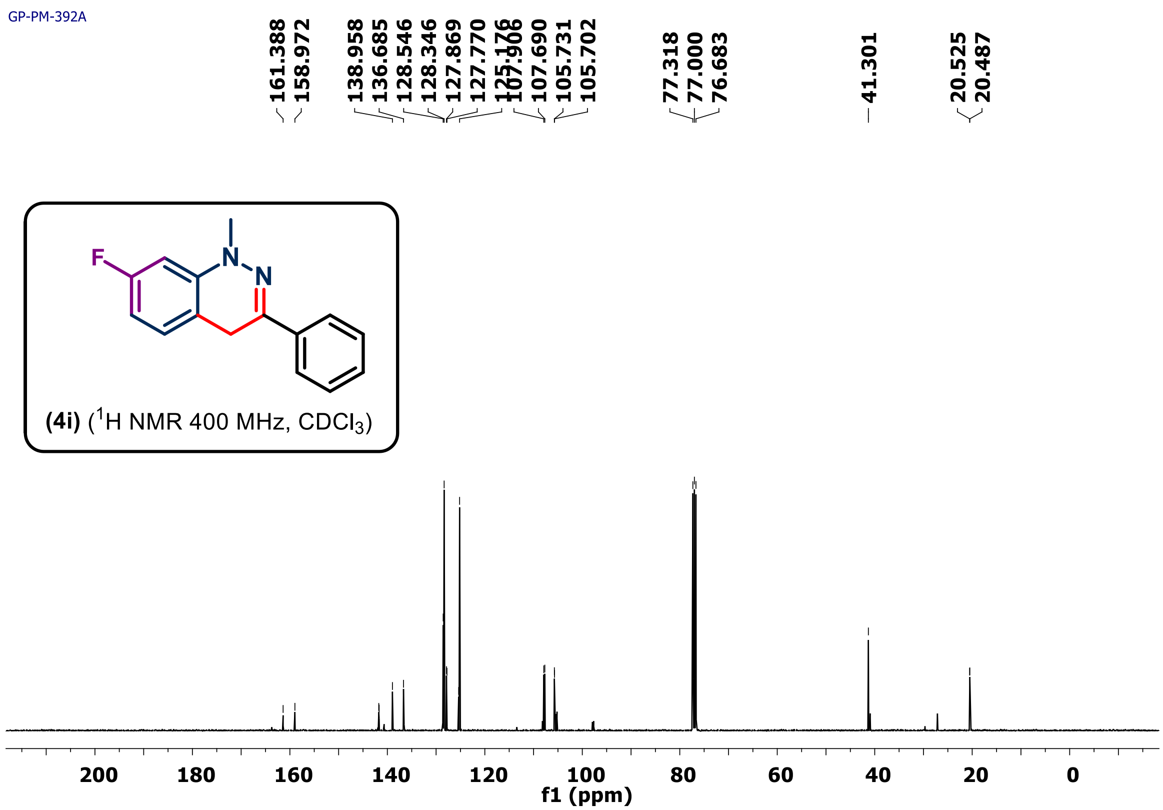

GP-G-M-BROMO
Br
N
N
(4g) (1H NMR 400 MHz, CDCl3)
2.04
3.06
1.01
1.00
1.03
2.00
3.05
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

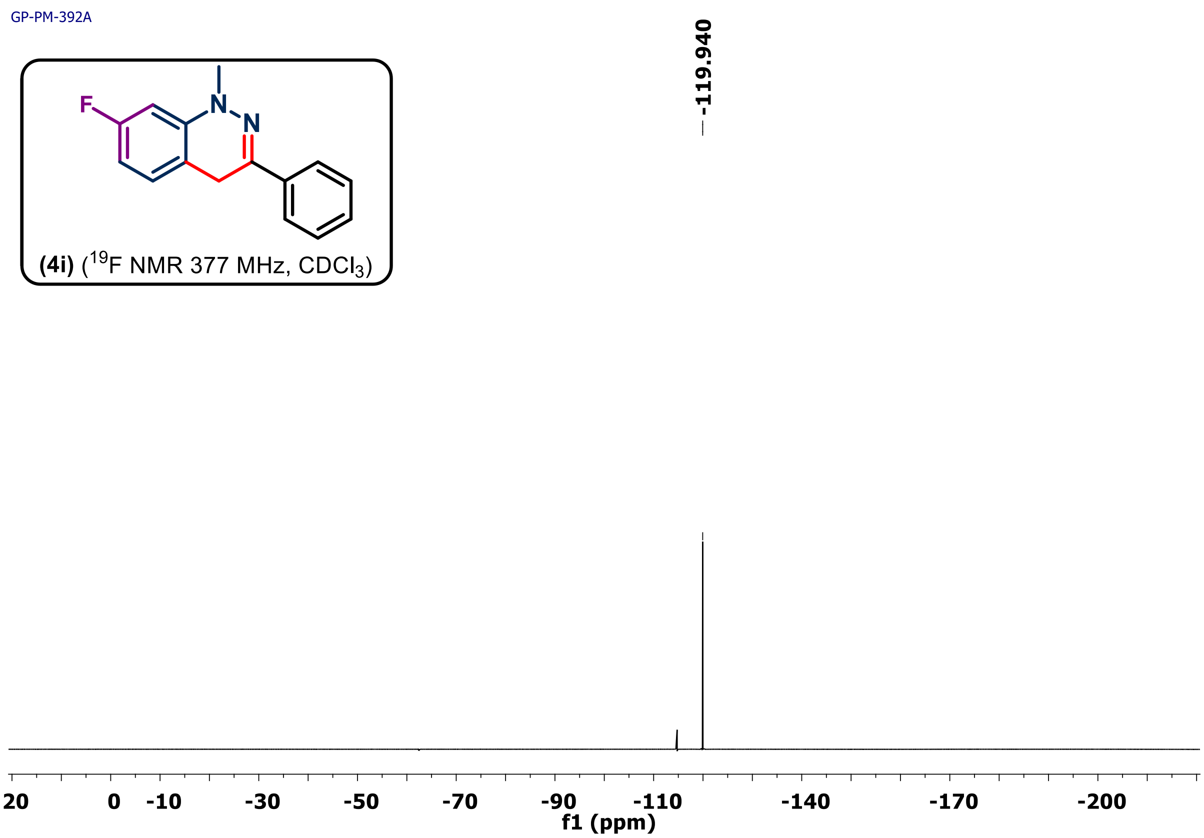

GP-G-M-BROMO
141.992
140.506
136.423
128.982
128.678
128.397
125.396
124.475
120.941
116.939
113.142
77.317
77.000
76.682
40.913
27.384
Br
N
N
(4g) (13C NMR 101 MHz, CDCl3)
190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

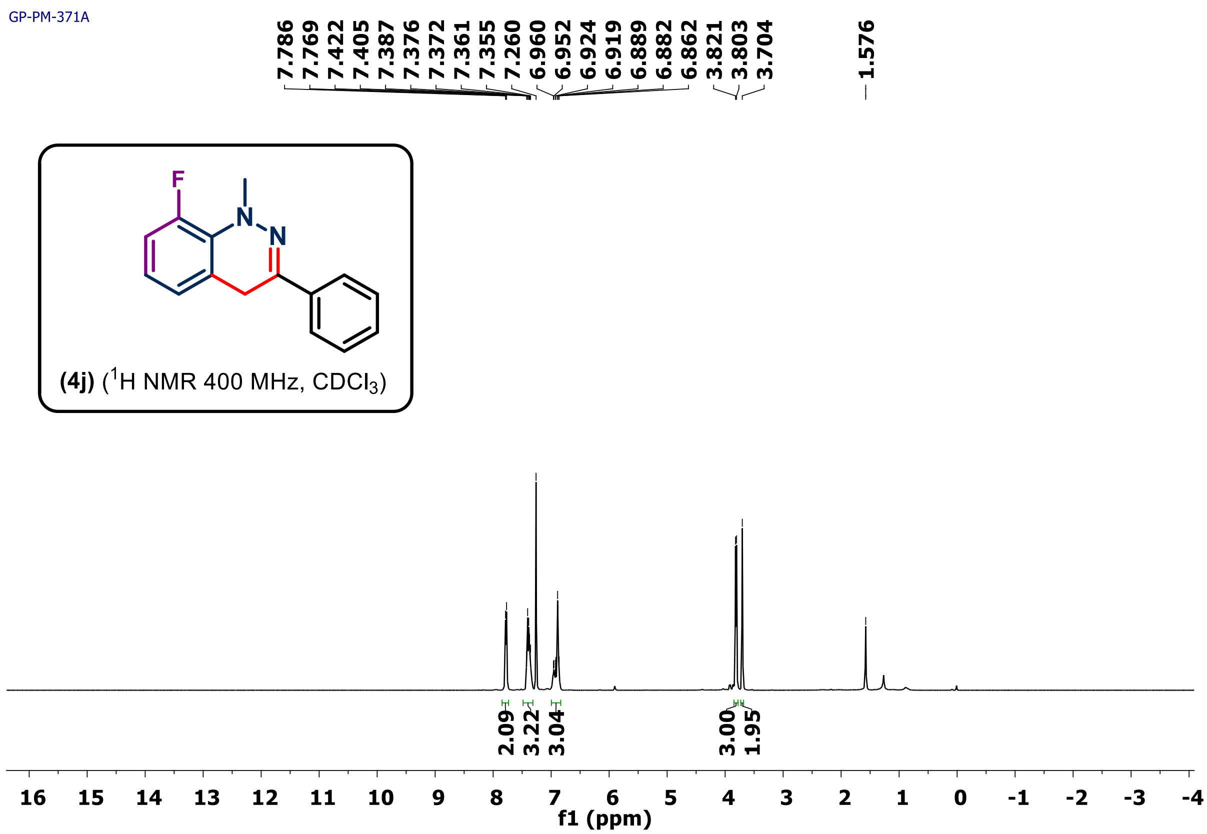

GP-G-M-CHLORO
7.696
7.691
7.687
7.679
7.675
7.671
7.342
7.337
7.320
7.317
7.315
7.305
7.302
7.292
7.288
7.285
7.271
7.176
6.962
6.942
6.872
6.867
6.852
6.847
6.725
6.720
3.643
3.438
1.481
Cl
N
N
(4h) (¹H NMR 400 MHz, CDCl₃)
2.00
3.01
1.02
1.00
1.01
2.00
3.04
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

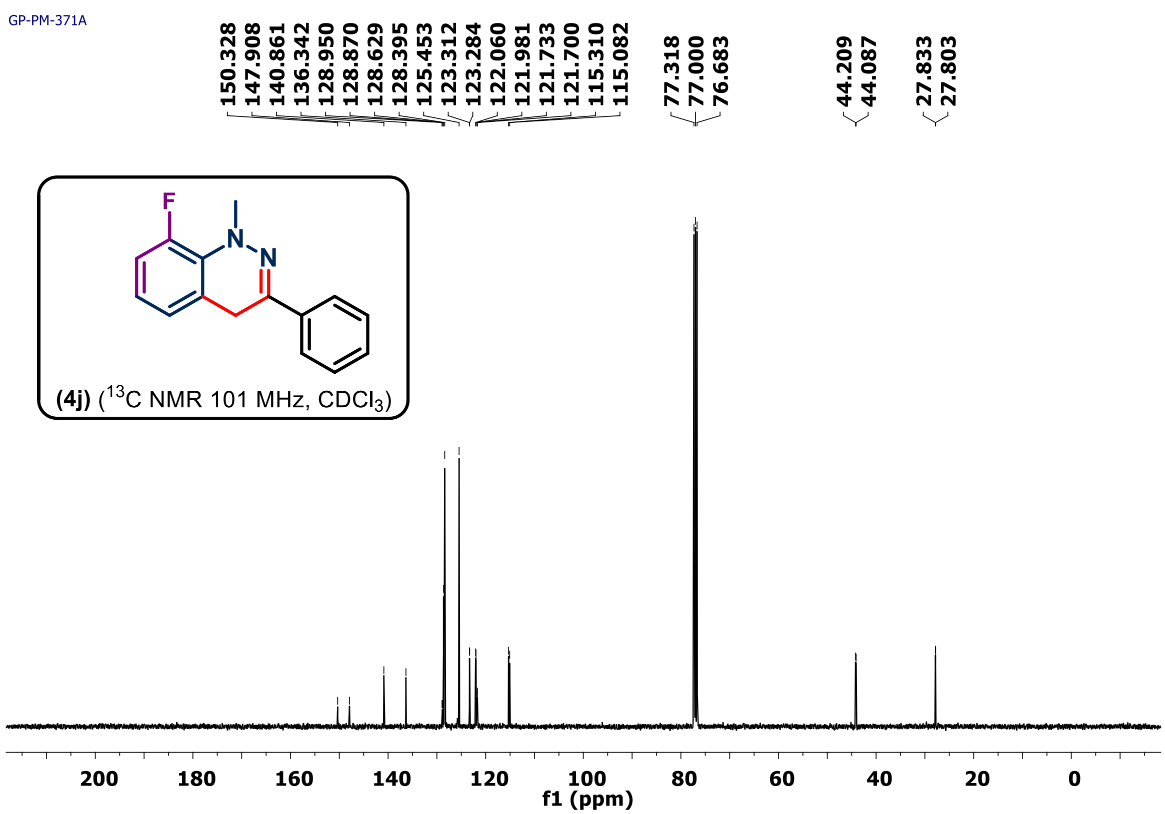

GP-G-M-CHLORO
141.800
140.559
136.493
133.058
128.700
128.690
128.433
125.425
121.580
116.457
110.379
77.355
77.037
76.720
27.343
Cl
N
N
(4h) (¹³C NMR 101 MHz, CDCl₃)
170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


GP-PM-392A
7.80
7.80
7.78
7.41
7.40
7.39
7.38
7.36
7.34
7.15
7.14
6.70
6.68
6.56
6.54
3.80
3.52
F
N
N
(4i) (13C NMR 101 MHz, CDCl3)
2.07
3.18
1.01
1.07
1.06
2.04
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

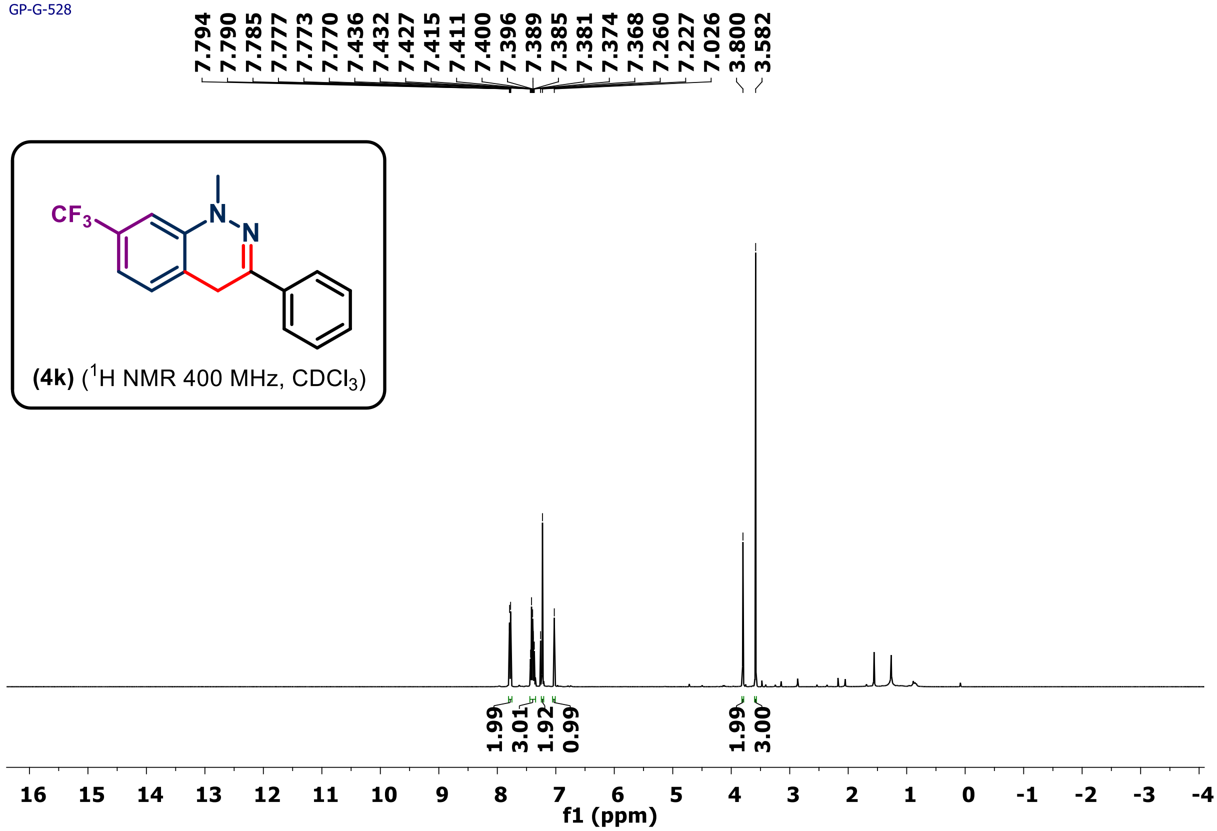

GP-PM-392A
161.388
158.972
138.958
136.685
128.546
128.346
127.869
127.770
125.176
107.906
107.690
105.731
105.702
77.318
77.000
76.683
41.301
20.525
20.487
F
N
N
(4i) (1H NMR 400 MHz, CDCl3)
200 180 160 140 120 100 80 60 40 20 0
f1 (ppm)


GP-PM-392A
-119.940
F
N
N
(4i) (^{19}F NMR 377 MHz, $CDCl_3$)
20
0
-10
-30
-50
-70
-90
-110
-140
-170
-200
f1 (ppm)

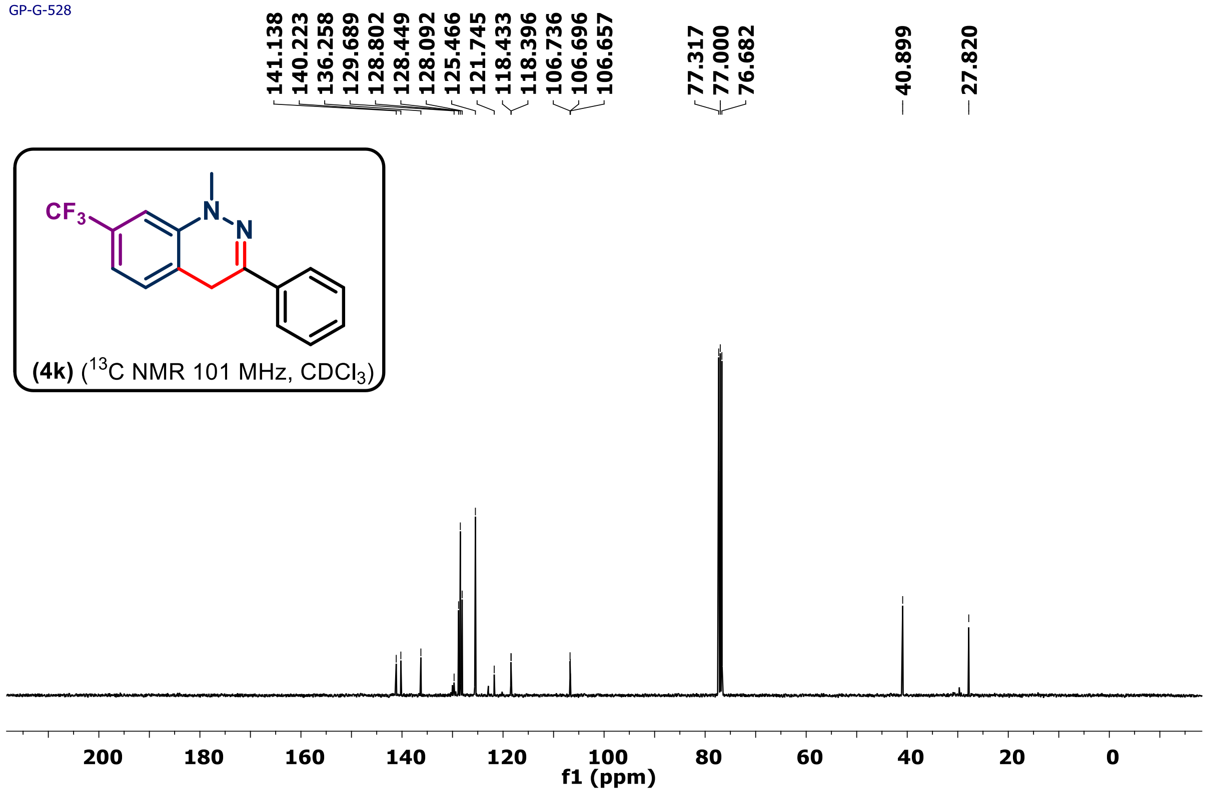

GP-PM-371A
7.786
7.769
7.422
7.405
7.387
7.376
7.372
7.361
7.355
7.260
6.960
6.952
6.924
6.919
6.889
6.882
6.862
3.821
3.803
3.704
1.576
F
N
N
(4j) (1H NMR 400 MHz, CDCl3)
2.09
3.22
3.04
3.00
1.95
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)


GP-PM-371A
150.328
147.908
140.861
136.342
128.950
128.870
128.629
128.395
125.453
123.312
123.284
122.060
121.981
121.733
121.700
115.310
115.082
77.318
77.000
76.683
44.209
44.087
27.833
27.803
F
N
N
(4j) (13C NMR 101 MHz, CDCl3)
200 180 160 140 120 100 80 60 40 20 0
f1 (ppm)

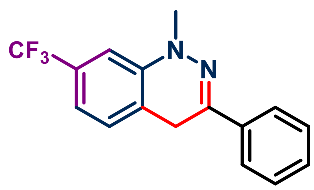
GP-G-528



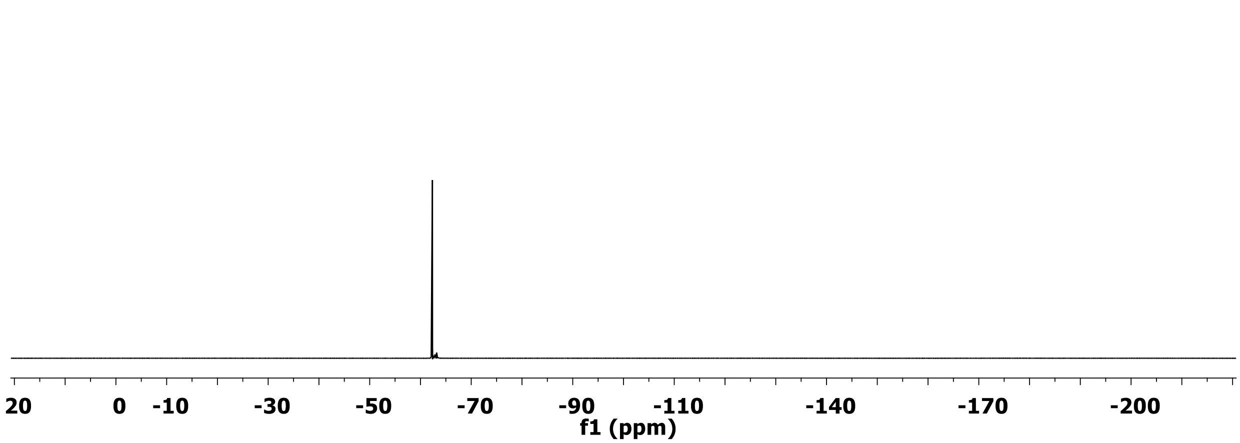
GP-G-528

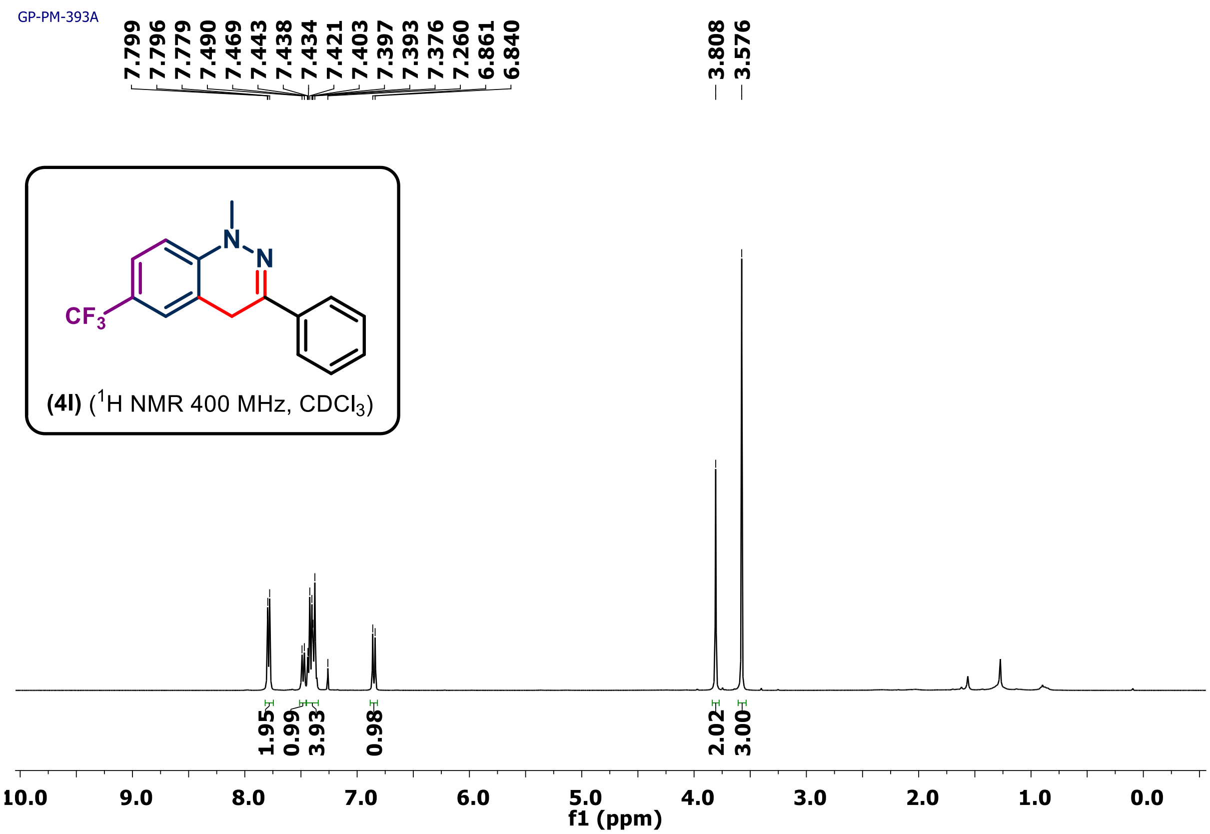


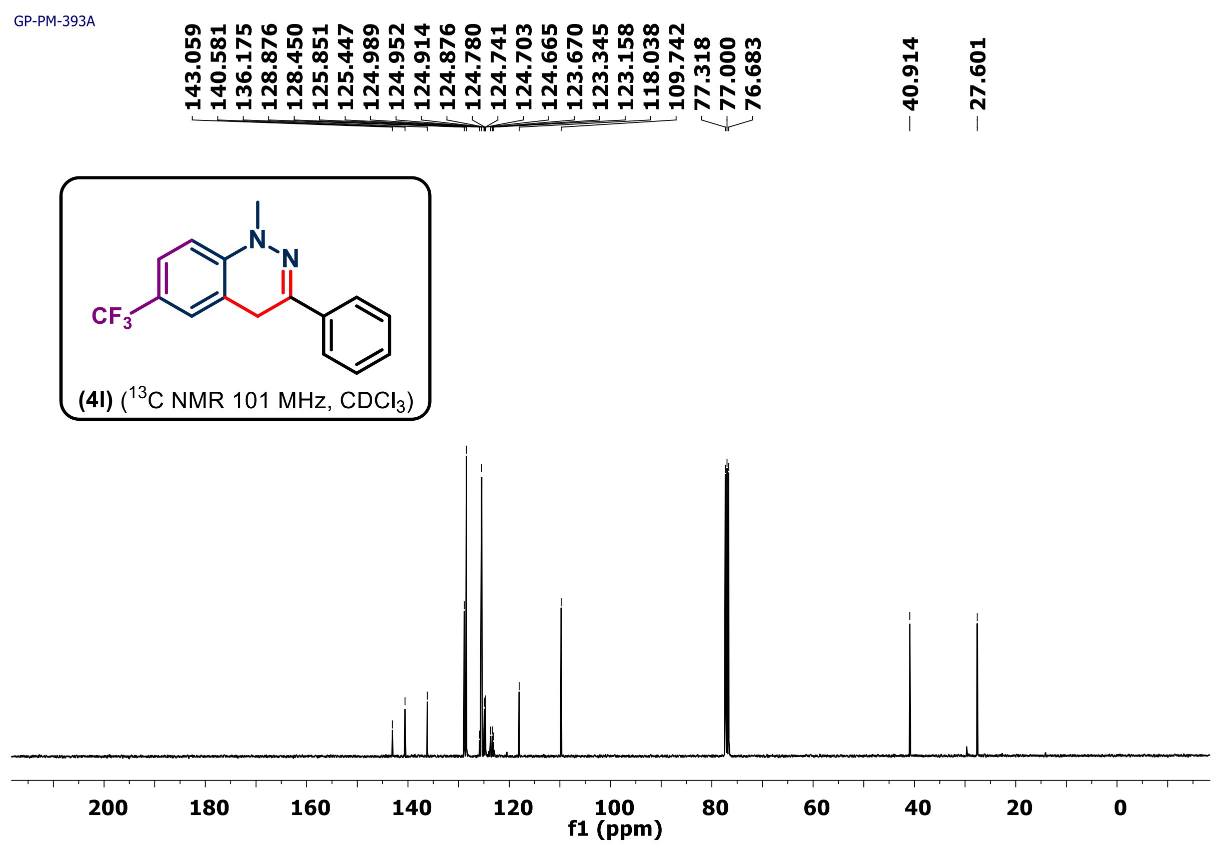
GP-G-528

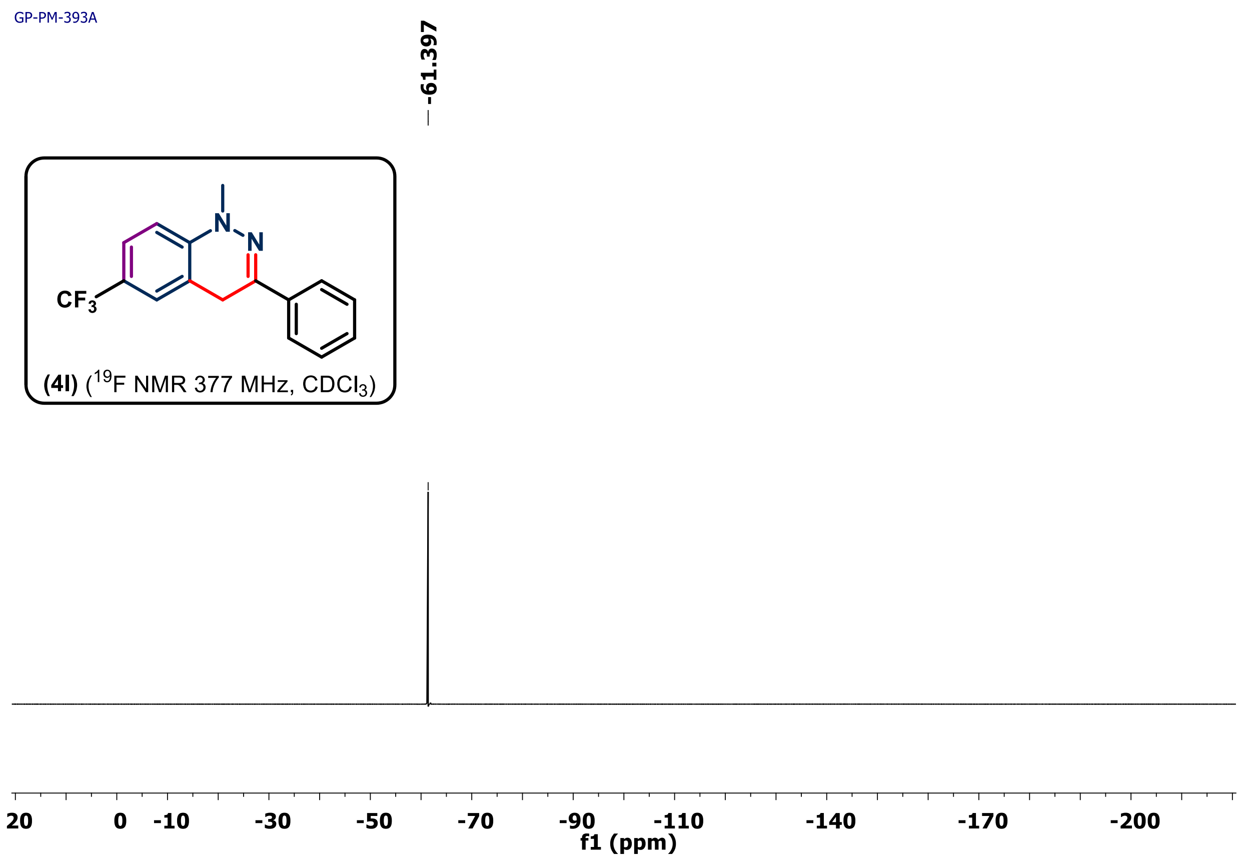


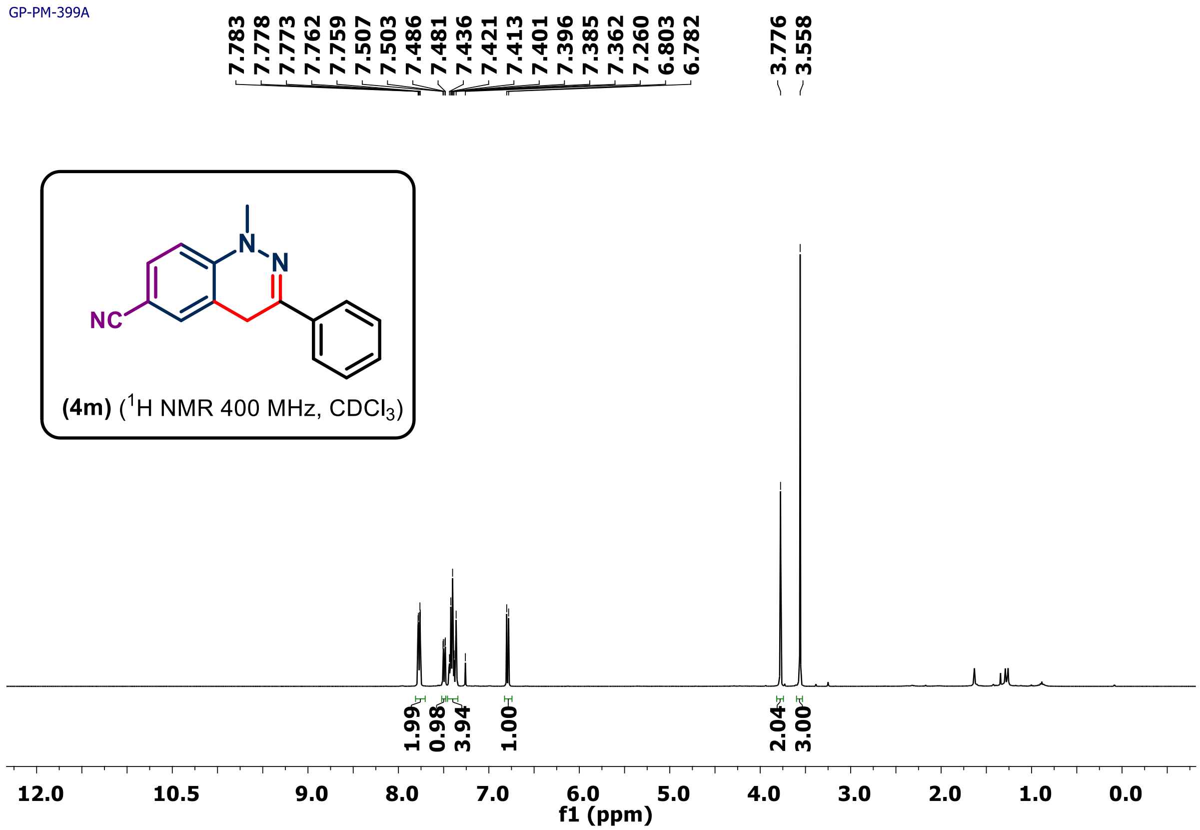
(4k) (^{19}F NMR 377 MHz, $CDCl_3$)

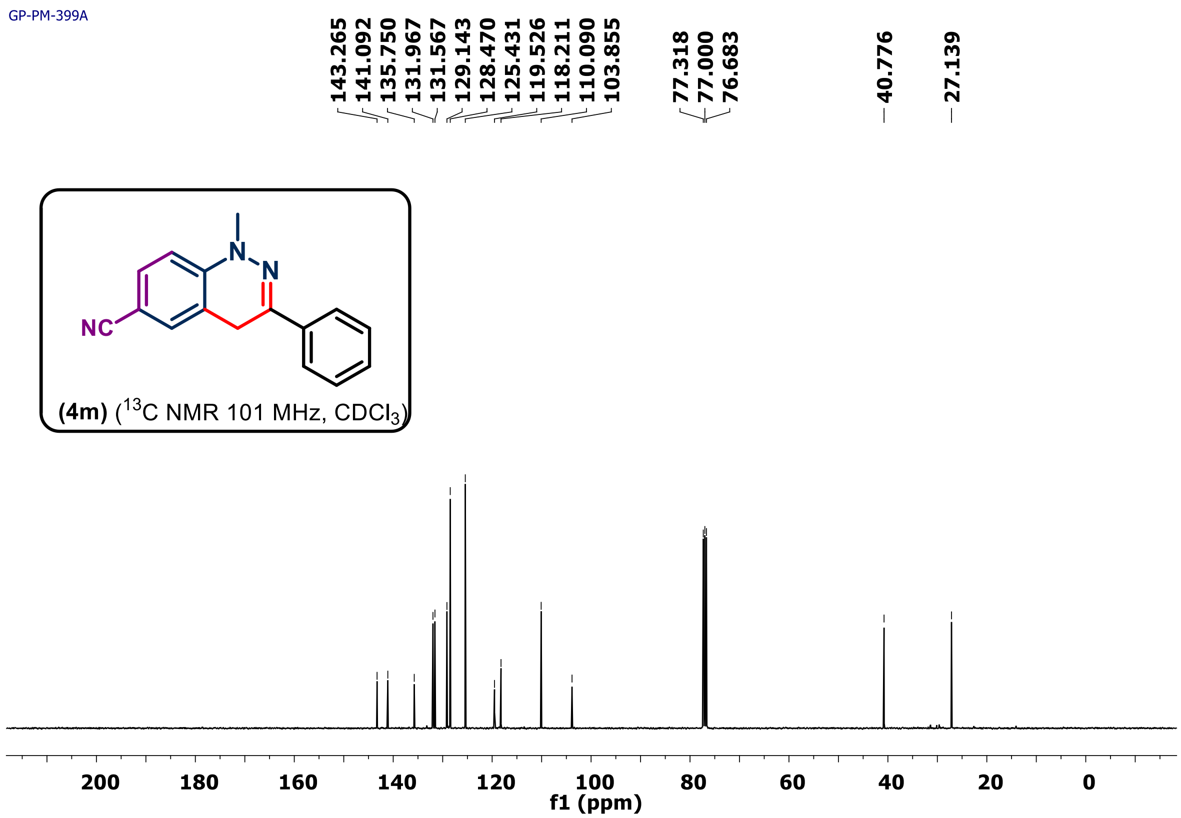


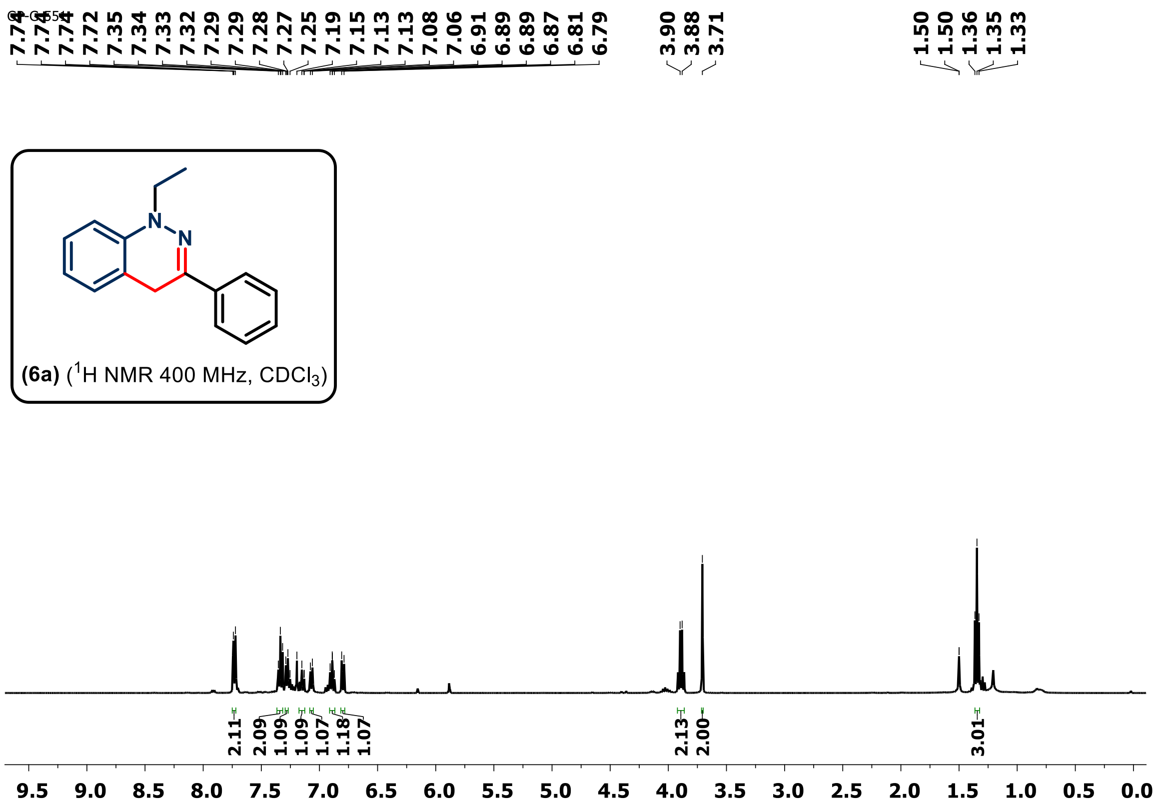

GP-PM-393A
7.799 7.796 7.779 7.490 7.469 7.443 7.438 7.434 7.421 7.403 7.397 7.393 7.376 7.260 6.861 6.840
3.808 3.576
CF3
N
N
(4l) (1H NMR 400 MHz, CDCl3)
1.95 0.99 3.93 0.98 2.02 3.00
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
f1 (ppm)

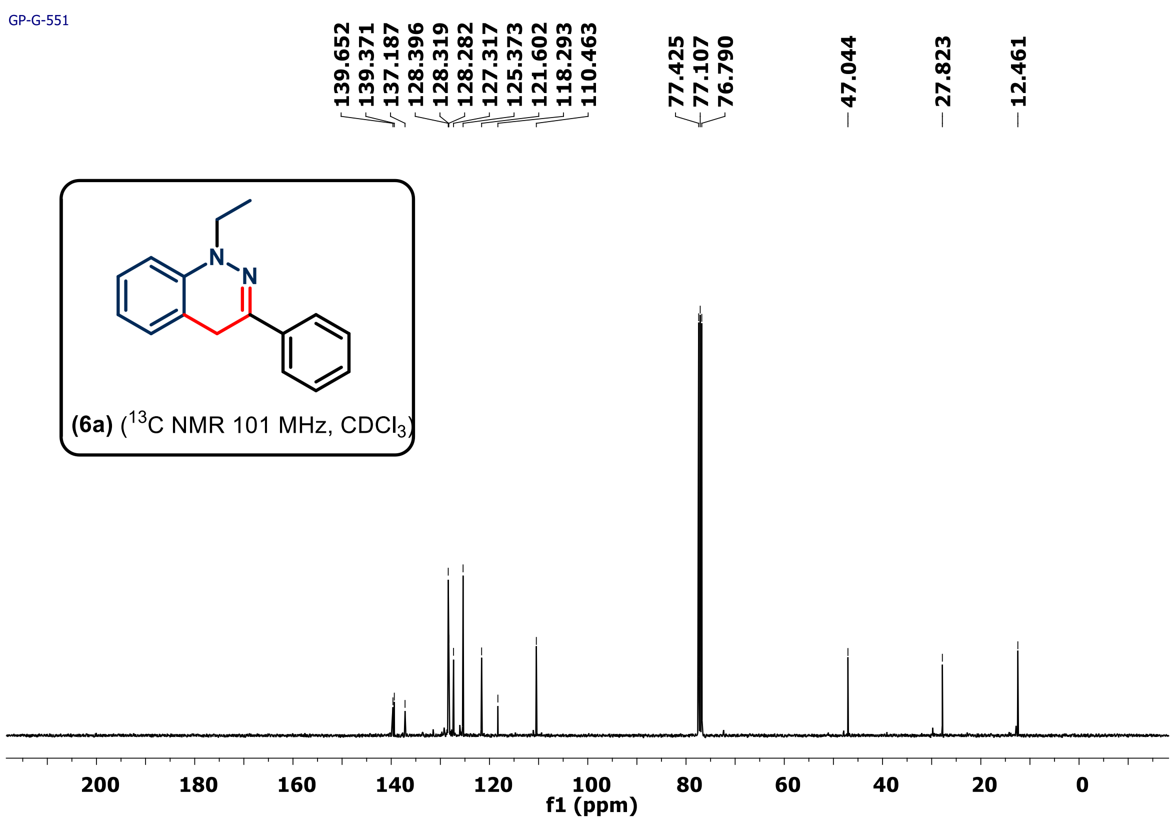

GP-PM-393A
143.059 140.581 136.175 128.876 128.450 125.851 125.447 124.989 124.952 124.914 124.876 124.780 124.741 124.703 124.665 123.670 123.345 123.158 118.038 109.742
77.318 77.000 76.683
40.914
27.601
CF3
N
N
(4l) (13C NMR 101 MHz, CDCl3)
200 180 160 140 120 100 80 60 40 20 0
f1 (ppm)

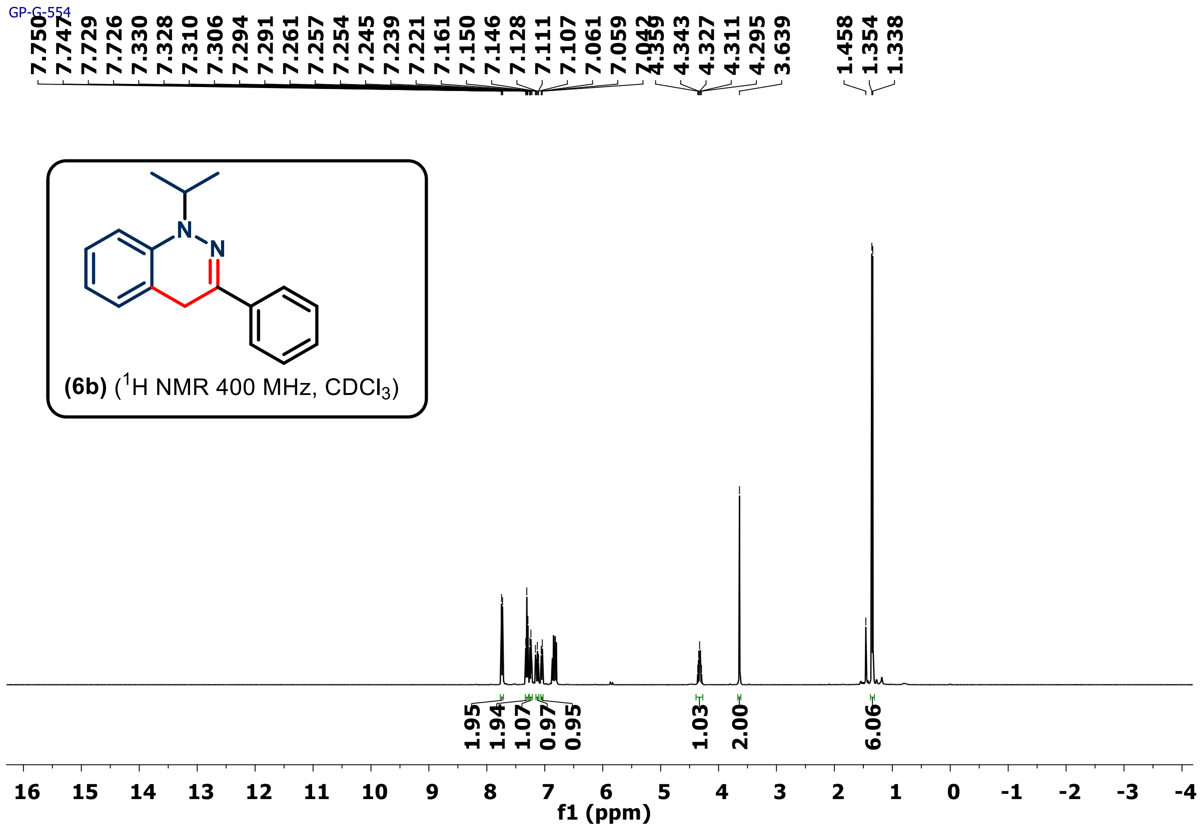

GP-PM-393A
-61.397
CF3
N
N
(4l) (19F NMR 377 MHz, CDCl3)
20
0
-10
-30
-50
-70
-90
-110
-140
-170
-200
f1 (ppm)

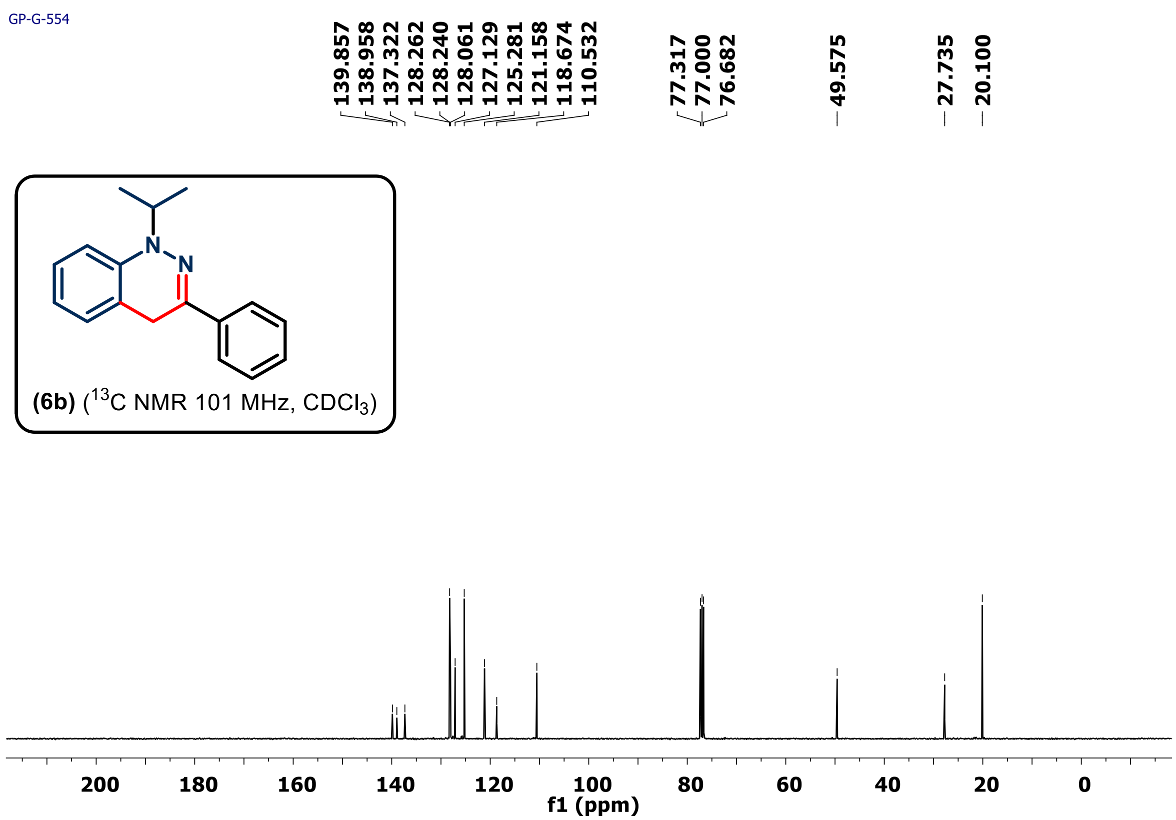

GP-PM-399A
7.783
7.778
7.773
7.762
7.759
7.507
7.503
7.486
7.481
7.436
7.421
7.413
7.401
7.396
7.385
7.362
7.260
6.803
6.782
3.776
3.558
NC
N
N
(4m) (1H NMR 400 MHz, CDCl3)
1.99
0.98
3.94
1.00
2.04
3.00
12.0
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

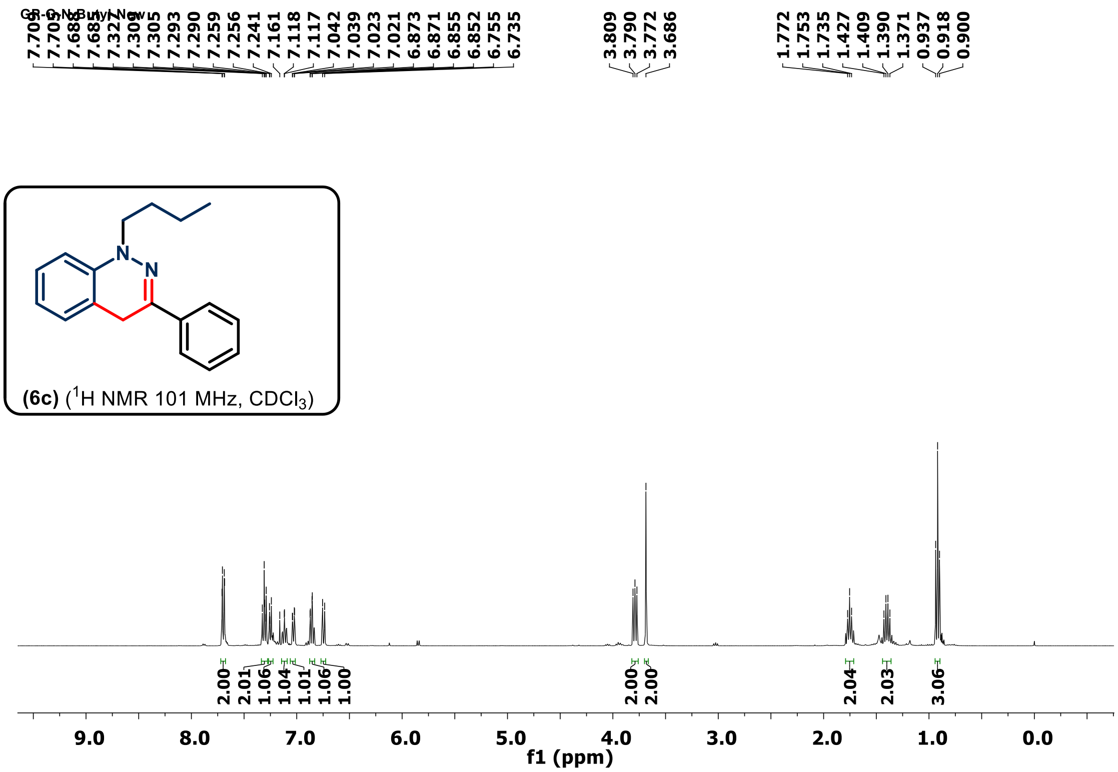

GP-PM-399A
143.265
141.092
135.750
131.967
131.567
129.143
128.470
125.431
119.526
118.211
110.090
103.855
77.318
77.000
76.683
40.776
27.139
NC
N
N
(4m) (13C NMR 101 MHz, CDCl3)
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

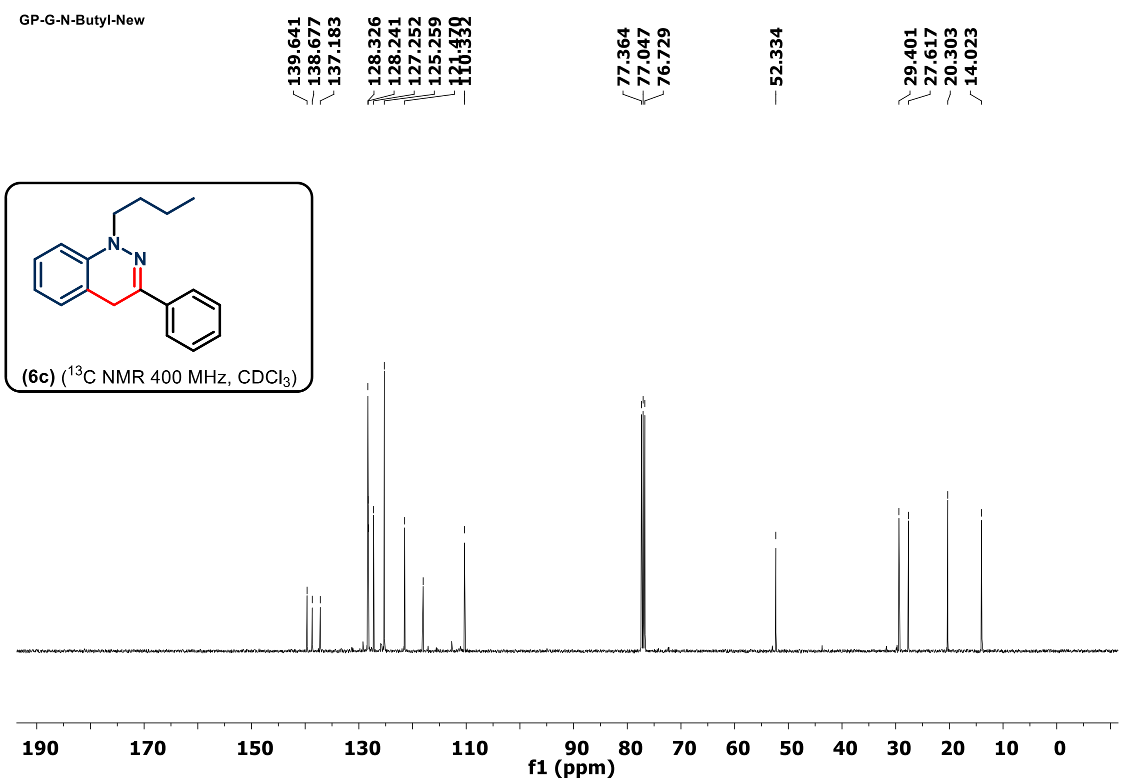

GP-G-551
7.74 7.74 7.74 7.72 7.35 7.34 7.33 7.32 7.29 7.29 7.28 7.27 7.25 7.19 7.15 7.13 7.13 7.08 7.06 6.91 6.89 6.89 6.87 6.81 6.79
3.90 3.88 3.71
1.50 1.50 1.36 1.35 1.33
N
N
(6a) (1H NMR 400 MHz, CDCl3)
2.11 2.09 1.09 1.09 1.07 1.18 1.07
2.13 2.00
3.01
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

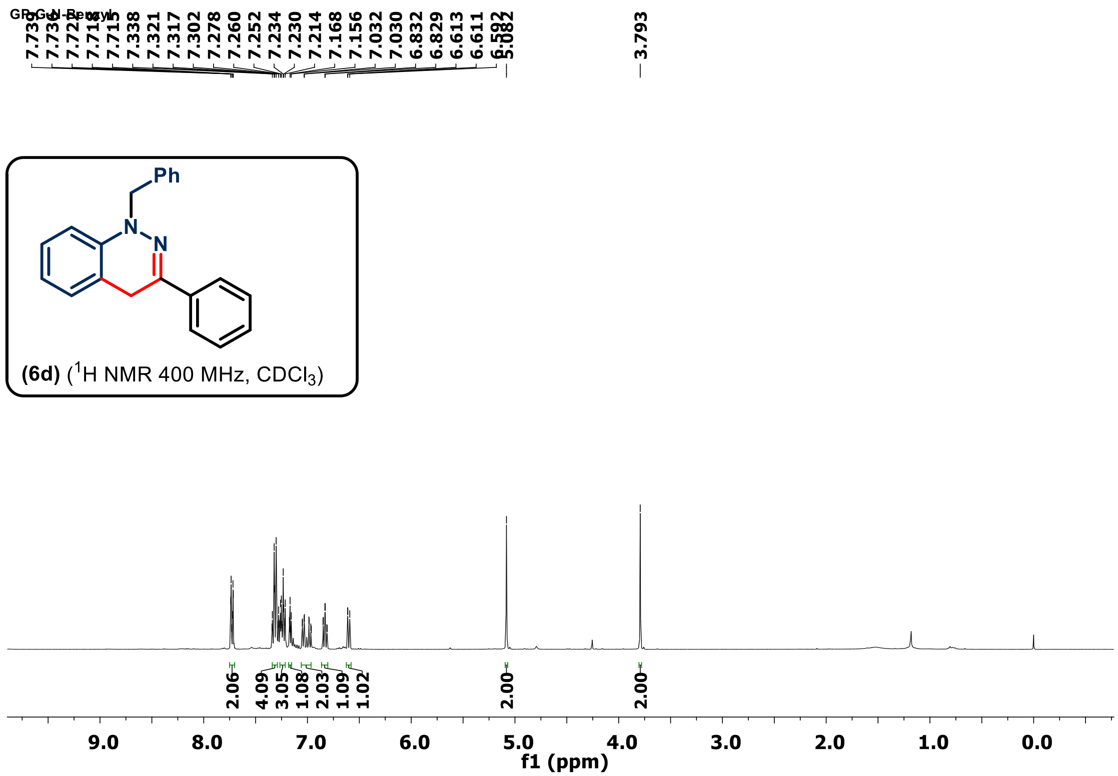

GP-G-551
139.652 139.371 137.187 128.396 128.319 128.282 127.317 125.373 121.602 118.293 110.463
77.425 77.107 76.790
47.044
27.823
12.461
N
N
(6a) (13C NMR 101 MHz, CDCl3)
200 180 160 140 120 100 80 60 40 20 0
f1 (ppm)


GP-G-554
7.750 7.747 7.729 7.726 7.330 7.328 7.310 7.306 7.294 7.291 7.261 7.257 7.254 7.245 7.239 7.221 7.161 7.150 7.146 7.128 7.111 7.107 7.061 7.059 7.042 4.359 4.343 4.327 4.311 4.295 3.639 1.458 1.354 1.338
N
N
(6b) (1H NMR 400 MHz, CDCl3)
1.95 1.94 1.07 0.97 0.95 1.03 2.00 6.06
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)

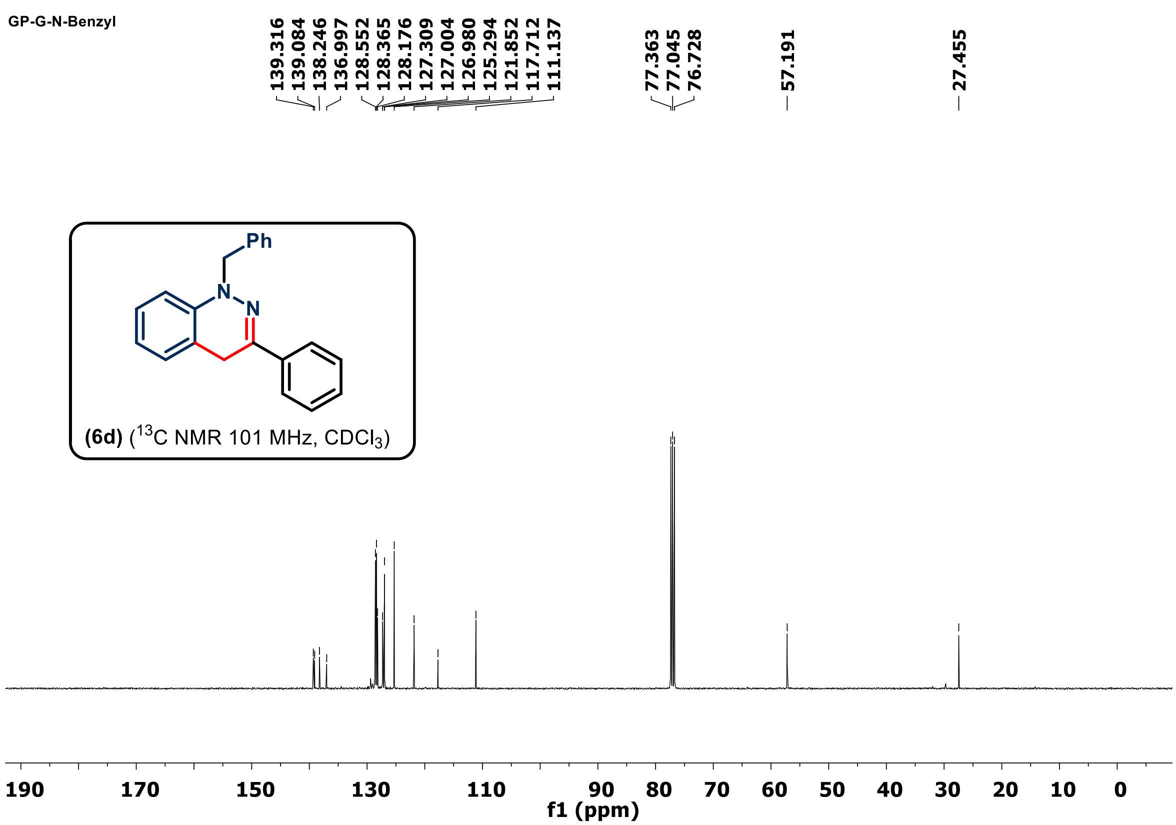

GP-G-554
139.857 138.958 137.322 128.262 128.240 128.061 127.129 125.281 121.158 118.674 110.532 77.317 77.000 76.682 49.575 27.735 20.100
N
N
(6b) (13C NMR 101 MHz, CDCl3)
200 180 160 140 120 100 80 60 40 20 0
f1 (ppm)


GP-G-N-Butyl-New
7.705 7.703 7.686 7.683 7.322 7.309 7.305 7.293 7.290 7.259 7.256 7.241 7.161 7.118 7.117 7.042 7.039 7.023 7.021 6.873 6.871 6.855 6.852 6.755 6.735
3.809 3.790 3.772 3.686
1.772 1.753 1.735 1.427 1.409 1.390 1.371 0.937 0.918 0.900
(6c) (^{1}H NMR 101 MHz, $CDCl_3$)
2.00 2.01 1.06 1.04 1.01 1.06 1.00
2.00 2.00
2.04 2.03 3.06
9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
f1 (ppm)

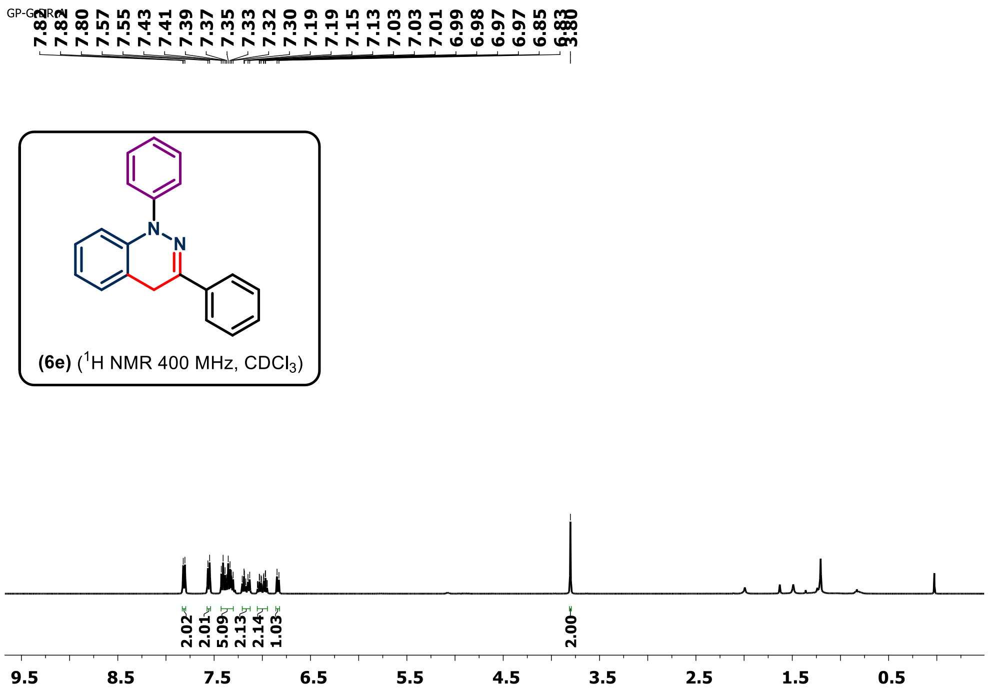

GP-G-N-Butyl-New
139.641 138.677 137.183 128.326 128.241 127.252 125.259 121.470 110.332
77.364 77.047 76.729
52.334
29.401 27.617 20.303 14.023
(6c) (^{13}C NMR 400 MHz, $CDCl_3$)
190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

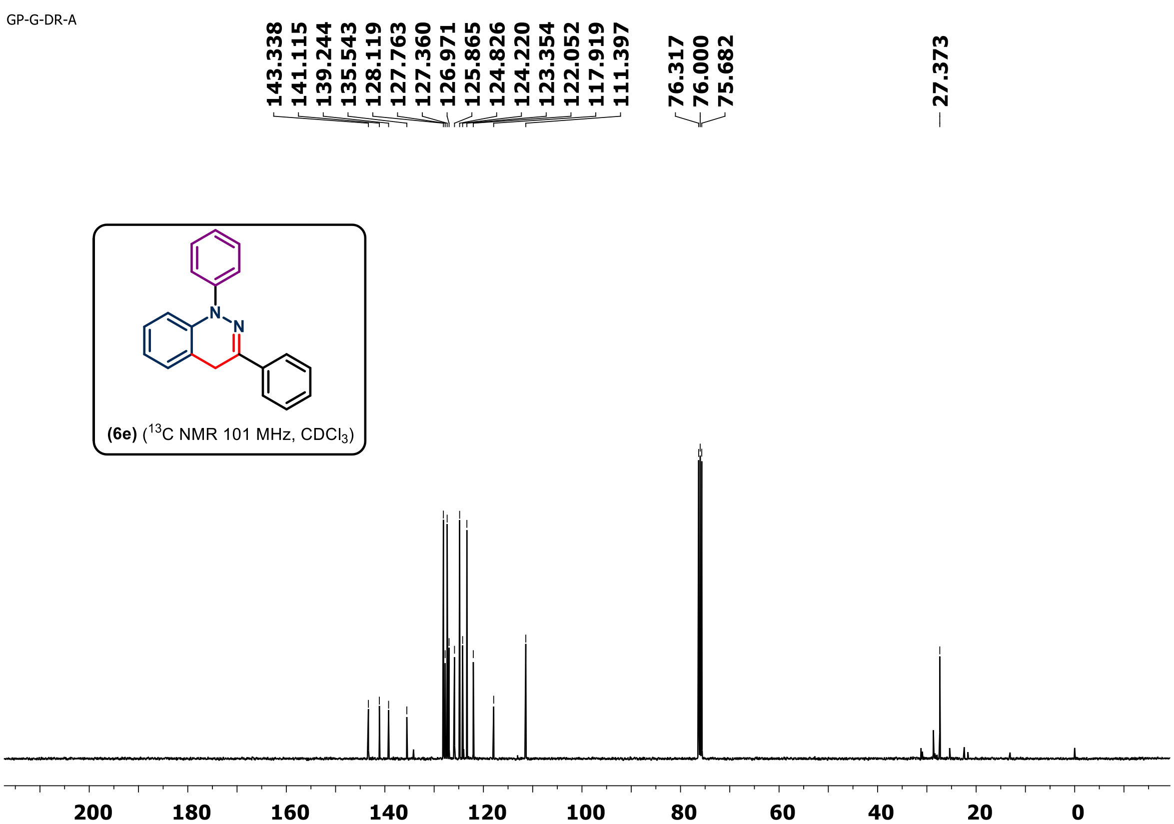


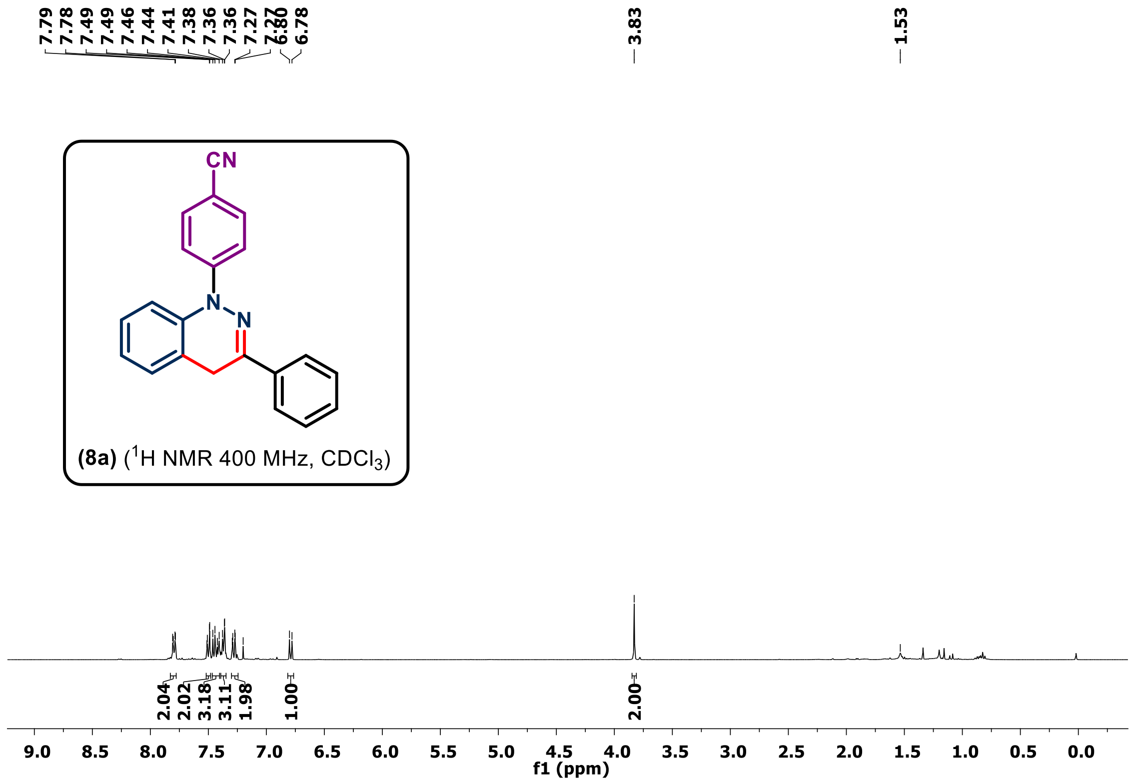
GP-G-N-Benzyl
7.338
7.321
7.317
7.302
7.278
7.260
7.252
7.234
7.230
7.214
7.168
7.156
7.032
7.030
6.832
6.829
6.613
6.611
5.082
3.793
Ph
N
N
(6d) (^{1}H NMR 400 MHz, CDCl$_3$)
2.06
4.09
3.05
1.08
2.03
1.09
1.02
2.00
2.00
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

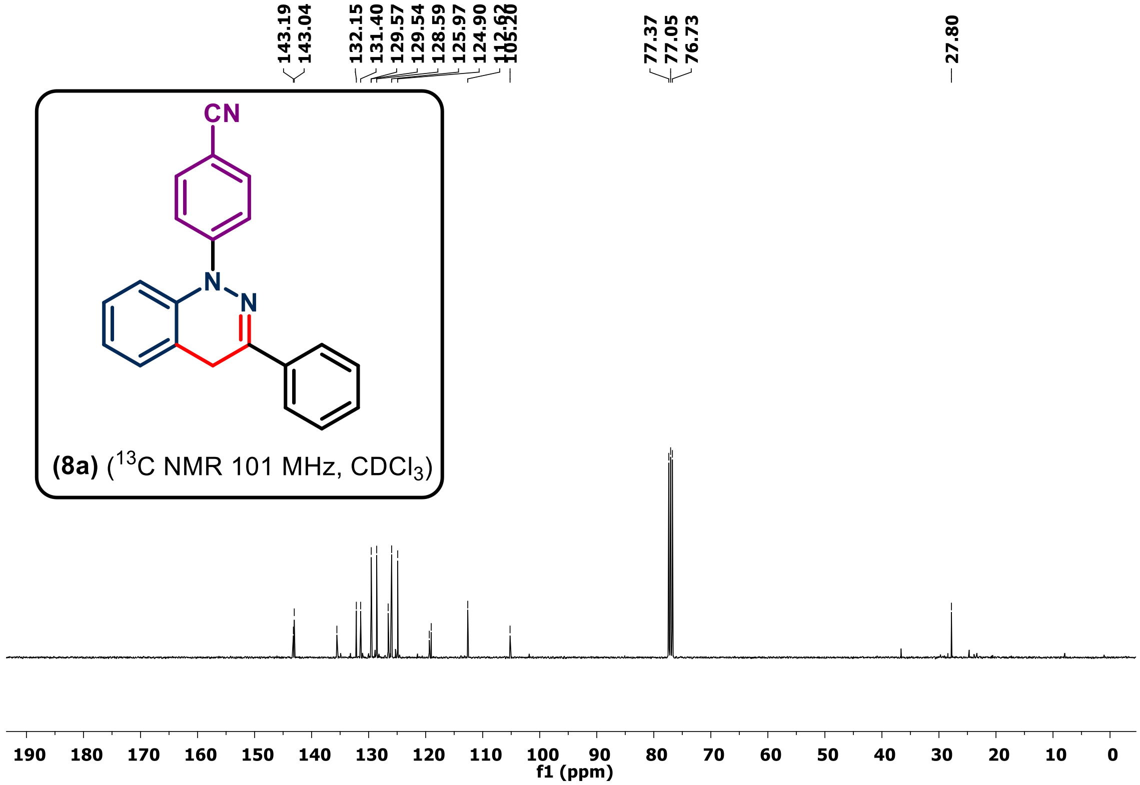


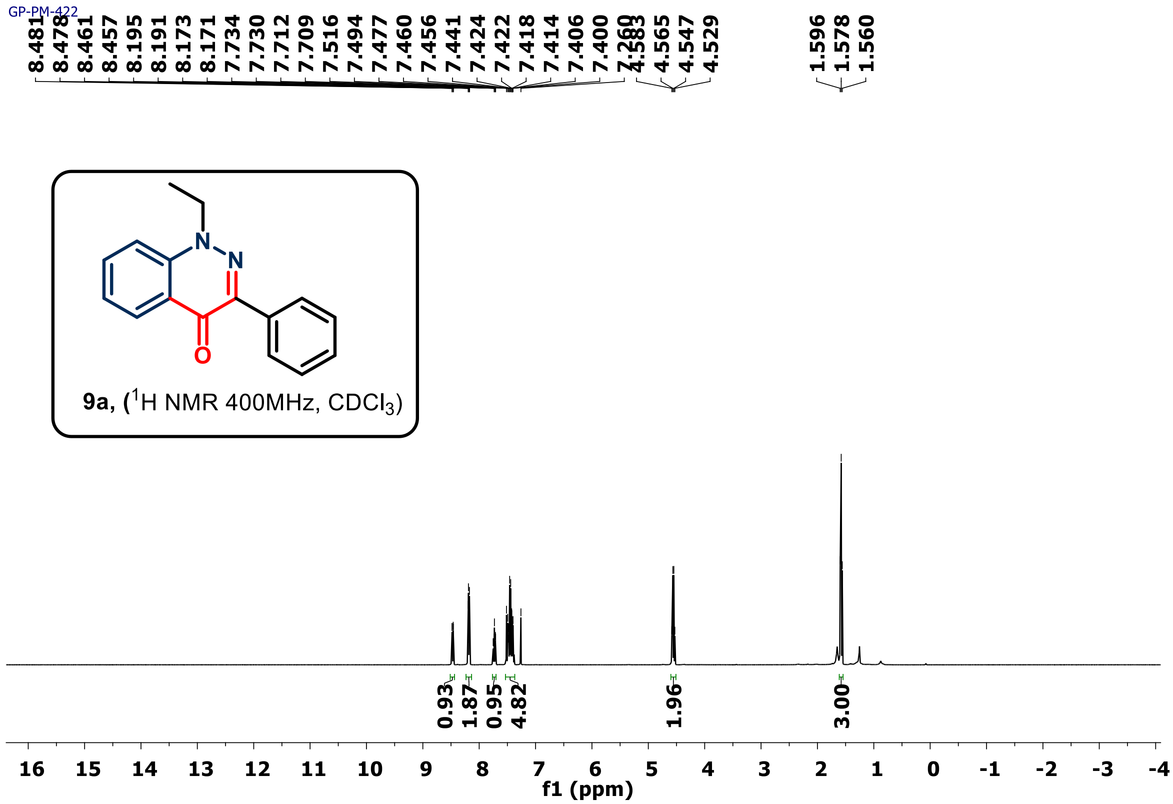
GP-G-N-Benzyl
139.316
139.084
138.246
136.997
128.552
128.365
128.176
127.309
127.004
126.980
125.294
121.852
117.712
111.137
77.363
77.045
76.728
57.191
27.455
Ph
N
N
(6d) (^{13}C NMR 101 MHz, CDCl$_3$)
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

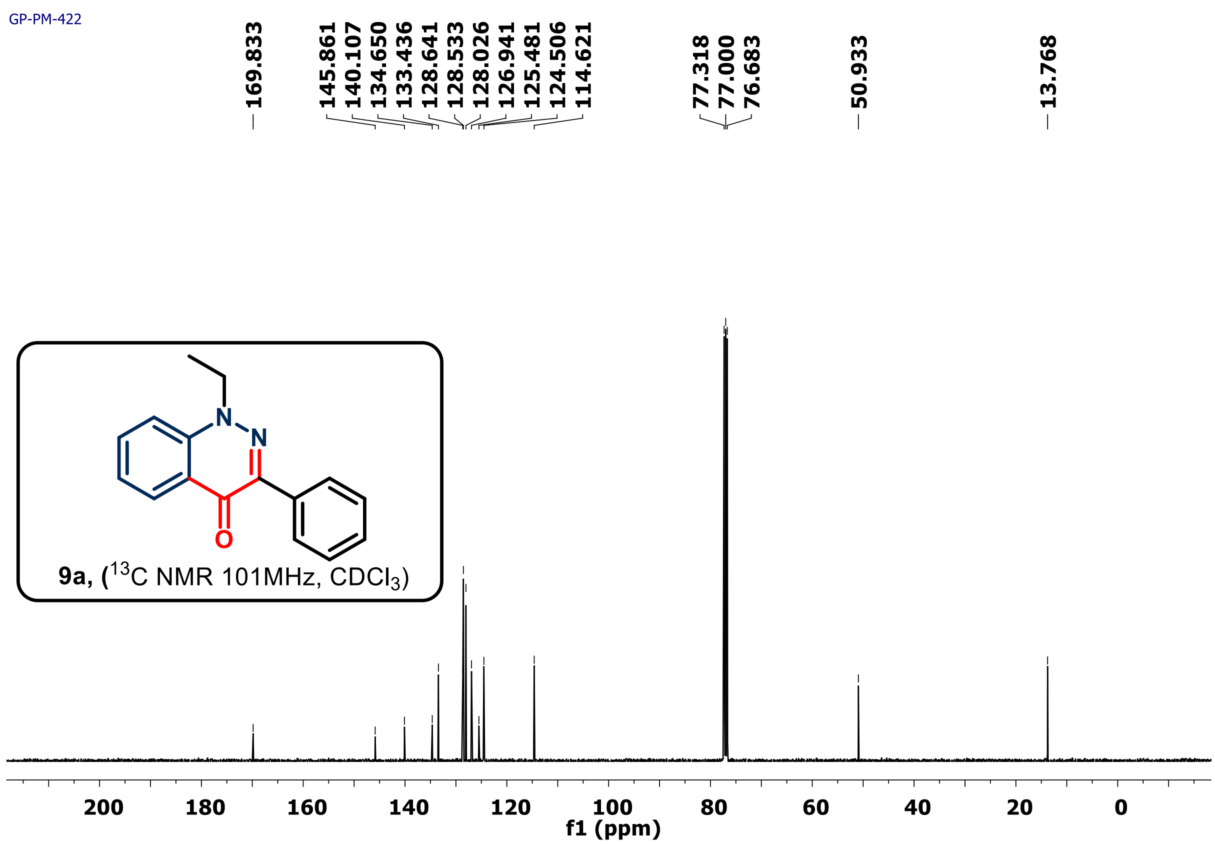

7.82
7.82
7.80
7.57
7.55
7.43
7.41
7.39
7.37
7.35
7.33
7.32
7.30
7.19
7.19
7.15
7.13
7.03
7.03
7.01
6.99
6.98
6.97
6.97
6.85
6.83
3.80
(6e) (^{1}H NMR 400 MHz, CDCl$_3$)
2.02
2.01
5.09
2.13
2.14
1.03
2.00
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5

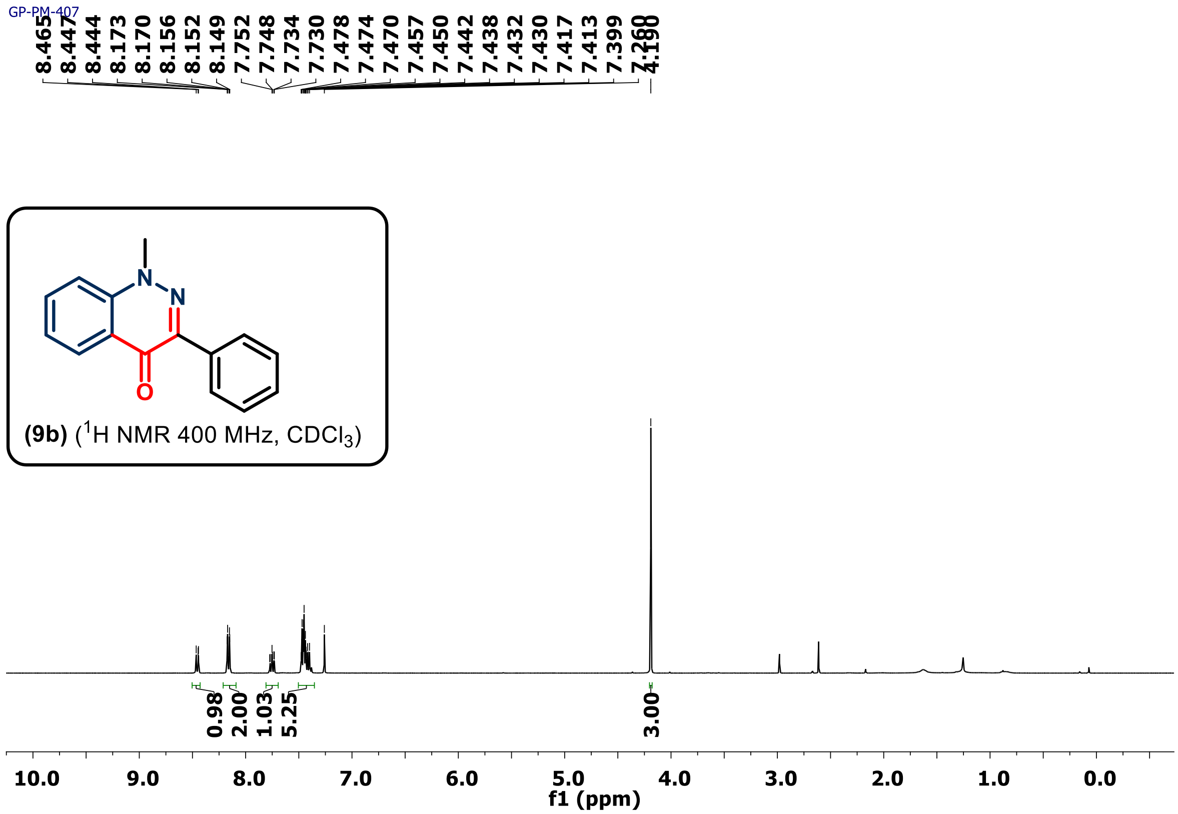

GP-G-DR-A
143.338
141.115
139.244
135.543
128.119
127.763
127.360
126.971
125.865
124.826
124.220
123.354
122.052
117.919
111.397
76.317
76.000
75.682
27.373
(6e) (^{13}C NMR 101 MHz, CDCl$_3$)
200
180
160
140
120
100
80
60
40
20
0

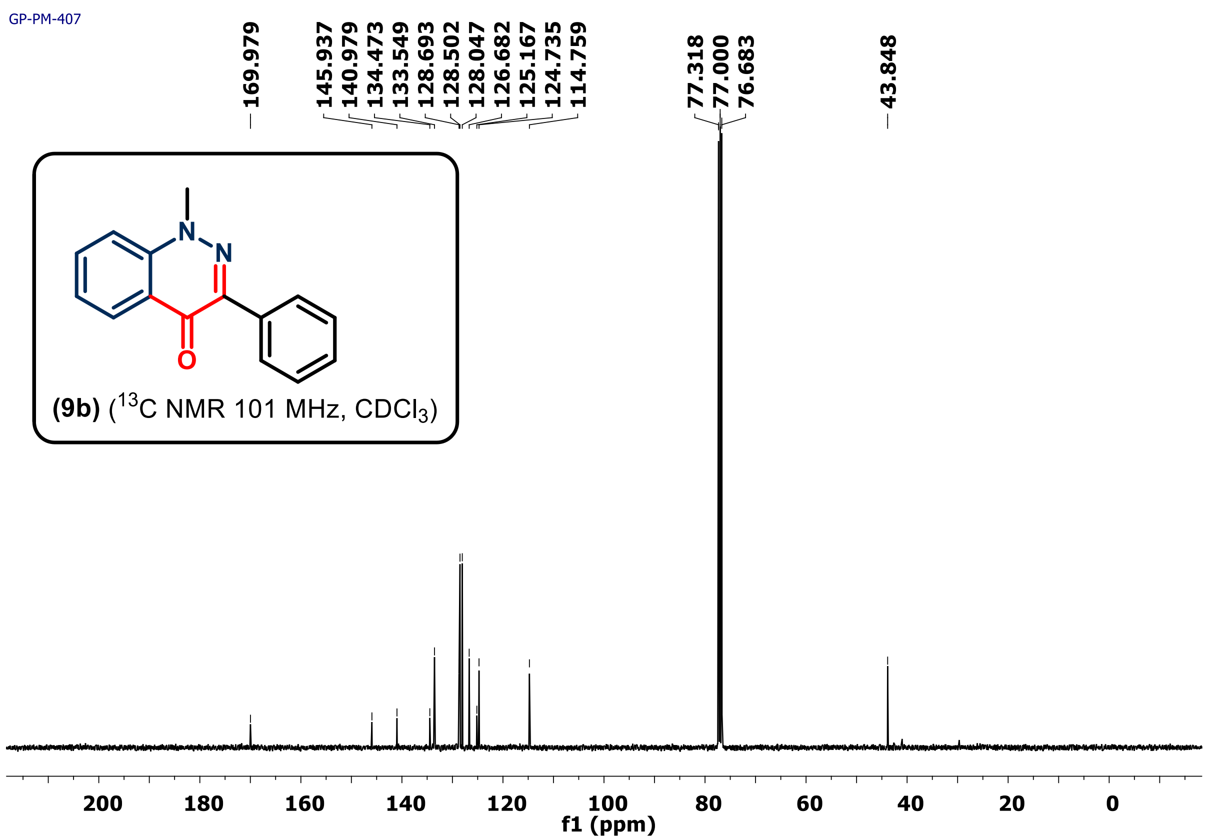

7.79
7.78
7.49
7.49
7.46
7.44
7.41
7.38
7.36
7.36
7.27
7.27
6.80
6.78
3.83
1.53
CN
N
N
(8a) (^{1}H NMR 400 MHz, $CDCl_3$)
2.04
2.02
3.18
3.11
1.98
1.00
2.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


143.19
143.04
132.15
131.40
129.57
129.54
128.59
125.97
124.90
112.62
105.20
77.37
77.05
76.73
27.80
CN
N
N
(8a) (^{13}C NMR 101 MHz, $CDCl_3$)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


GP-PM-422
8.481
8.478
8.461
8.457
8.195
8.191
8.173
8.171
7.734
7.730
7.712
7.709
7.516
7.494
7.477
7.460
7.456
7.441
7.424
7.422
7.418
7.414
7.406
7.400
7.260
4.583
4.565
4.547
4.529
1.596
1.578
1.560
9a, (1H NMR 400MHz, CDCl3)
0.93
1.87
0.95
4.82
1.96
3.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)


GP-PM-422
169.833
145.861
140.107
134.650
133.436
128.641
128.533
128.026
126.941
125.481
124.506
114.621
77.318
77.000
76.683
50.933
13.768
9a, (13C NMR 101MHz, CDCl3)
200 180 160 140 120 100 80 60 40 20 0
f1 (ppm)


GP-PM-407
8.465 8.447 8.444 8.173 8.170 8.156 8.152 8.149 7.752 7.748 7.734 7.730 7.478 7.474 7.470 7.457 7.450 7.442 7.438 7.432 7.430 7.417 7.413 7.399 7.260 4.190
(9b) (1H NMR 400 MHz, CDCl3)
0.98 2.00 1.03 5.25 3.00
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
f1 (ppm)


GP-PM-407
169.979
145.937 140.979 134.473 133.549 128.693 128.502 128.047 126.682 125.167 124.735 114.759
77.318 77.000 76.683
43.848
(9b) (13C NMR 101 MHz, CDCl3)
200 180 160 140 120 100 80 60 40 20 0
f1 (ppm)