Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information

A Highly Diastereoselective One-Pot Ugi/Radical Spirocyclization/Aza-Michael Addition Sequence

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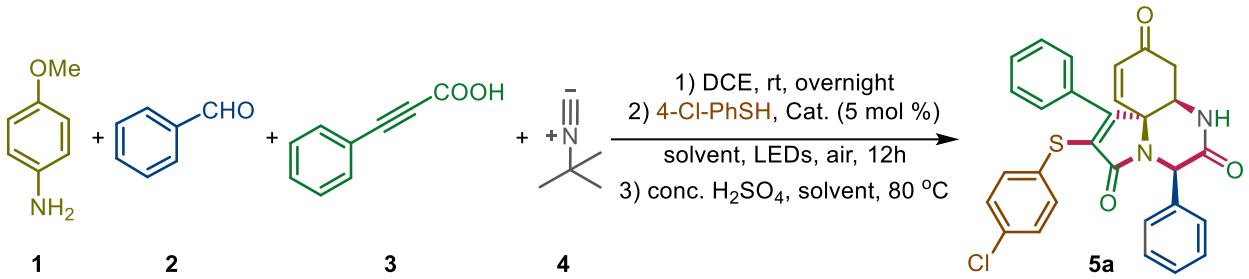
Experimental Section

General Experimental

^{1}H and ^{13}C spectra were recorded on Bruker Avance 400 and 500 MHz spectrophotometers. The chemical shifts (δ ppm) and coupling constants (Hz) are reported in the standard fashion with reference to internal chloroform. High resolution mass measurements were carried out using Micromass Q-ToF ESI instrument using direct inlet mode. Analytical thin-layer chromatography (TLC) was performed on pre-coated 0.2 mm thick Merck 60 F_{245} silica plates and various combinations of diethyl ether and Petroleum ether were used as eluent. Visualization of the spots were accomplished by exposure to UV or iodine vapors. All compounds were purified using silica gel (100-200 mesh) column chromatography and gave spectroscopic data consistent with being ≥95% the assigned structure. Thiols and Thiophenols were purchased from either Sigma-Aldrich and TCI and were used as such without further purification. Aryl diazonium salts[1] and DABSO[2] were prepared as per the previous reports.

Note: A few compounds were found to trap ethyl acetate which could not be removed by prolonged evaporation and azeotropic evaporation. This could be because of the compounds existing as solvates resulting in extra peaks corresponding to ethyl acetate in the NMR spectra.

Optimization table.

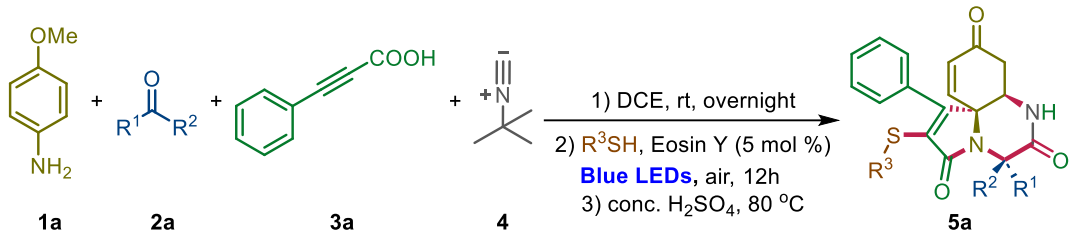


1 **2** **3** **4** **5a**

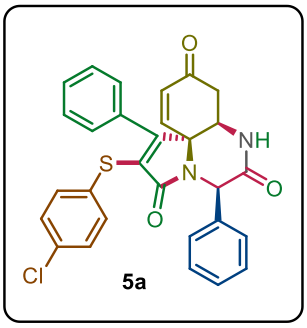
No.	Solvent	Light Source	Catalyst	Results[a]
1	ACN	Blue LEDs	Eosin Y	77% (73%)
2	ACN	Blue LEDs	Eosin B	35%
3	ACN	Blue LEDs	Rhodamin B	27%
4	ACN	Blue LEDs	Rose Bengal	42%
5	Toluene	Blue LEDs	Eosin Y	51%
6	DCM	Blue LEDs	Eosin Y	-
7	**1,2-DCE**	**Blue LEDs**	**Eosin Y**	**82% (77%)**
8	EtOAc	Blue LEDs	Eosin Y	-
9	DMF	Blue LEDs	Eosin Y	39%
10	DMSO	Blue LEDs	Eosin Y	27%
11	1,2-DCE	Green LEDs	Eosin Y	63%
12	1,2-DCE	White LEDs	Eosin Y	-
13[b]	1,2-DCE	-	Eosin Y	-
14[c]	1,2-DCE	Blue LEDs	-	-
15	1,2-DCE	Purple LEDs	-	-

[a]Reaction conditions: **1** (0.2 mmol), **2** (0.2 mmol), **3** (0.2 mmol), **4** (0.2 mmol), DCE (2 mL), rt overnight. **5a** (0.4 mmol), solvent 2 mL, LED's, rt, 12 h. conc. H_2SO_4 (1.0 mmol), 80 °C. [b]without light. [c]Without photocatalyst.

Procedure for the one-pot Ugi-sulfenylative spirocyclization and aza-Michael addition reaction cascade.



In a reaction tube equipped with a magnetic stirring bar was added benzaldehyde **2a** (21 μL, 0.2 mmol, 1.0 equiv) and *p*-anisidine **1a** (24.6 mg, 0.2 mmol, 1.0 equiv) in DCE (2mL) and stirred at rt for 5 mins. Phenylpropiolic acid **3a** (30 mg, 0.2 mmol, 1.0 equiv) and *tert*-butyl isocyanide **4** (22 μL, 0.2 mmol, 1.0 equiv) were added all at once and resulting solution was stirred at room temperature for 12 hrs. After completion of the reaction (TLC control), 4-chlorobenzene thiol **5a** (58 mg, 0.4 mmol, 2.0 equiv) and eosin Y (6.4 mg, 0.01 mmol, 5 mol%) were added, the contents were irradiated under blue LED's at room temperature in air for 12 hrs. To this reaction mixture was added conc. H_2SO_4 (54 μL, 1 mmol, 5.0 equiv) and the contents were heated at 80 ^oC for 8 h. The reaction was then quenched with sat. $NaHCO_3$ solution, extracted with DCM (3 x 5 mL). Combined organics were dried over Na_2SO_4 and concentrated under reduced pressure. Residue was purified by column chromatography with EtOAc in petroleum ether to furnish the desired tricyclic compound **5a** in 77% yield (79 mg) as a pale-yellow solid.



(5R,7aR,11aR)-2-((4-chlorophenyl)thio)-1,5-diphenyl-7a,8-dihydro-3H-pyrrolo[1,2-d]quinoxaline-3,6,9(5H,7H)-trione (5a)

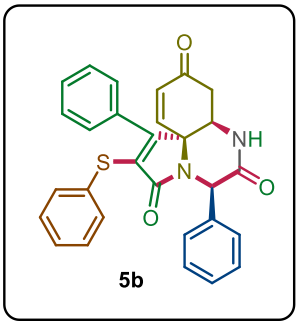
Physical appearance: Yellow solid

R_f: 0.5 (1:1 EtOAc:Petroleum ether boiling range 60-80 ^oC).

^{1}H NMR (500 MHz, DMSO-*d6*): δ 8.53 (s, 1H), 7.35-7.20 (m, 12H), 7.17 (d, *J* = 7.2 Hz, 2H), 6.41 (dd, *J* = 10.1, 2.1 Hz, 1H), 6.11 (d, *J* = 10.2 Hz, 1H), 5.59 (s, 1H), 4.44 (s, 1H), 2.37 (d, *J* = 17.2 Hz, 1H), 1.55 (dd, *J* = 17.2, 3.7 Hz, 1H).

^{13}C NMR (126 MHz, DMSO-*d6*) δ 193.9, 166.4, 165.6, 157.9, 143.8, 137.8, 132.1, 131.7, 131.6, 131.1, 129.7, 129.6, 128.9, 128.53, 128.48, 128.4, 128.3, 64.0, 56.3, 53.7, 39.2.

HRMS (ESI, M+Na^{+}) m/z calcd. for $C_{29}H_{22}ClN_2O_3S$ 536.0937, found 536.0933.



(5R,7aR,11aR)-1,5-diphenyl-2-(phenylselanyl)-7a,8-dihydro-3H-pyrrolo[1,2-d]quinoxaline-3,6,9(5H,7H)-trione (5b)

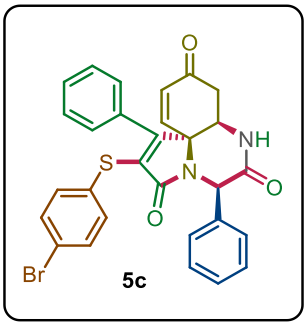
Physical appearance: Pale yellow solid

R_f: 0.5 (1:1 EtOAc:Petroleum ether boiling range 60-80 ºC).

^{1}H NMR (400 MHz, DMSO-*d6*): δ 8.57 (s, 1H), 7.40-7.32 (m, 10H), 7.22-7.18 (m, 5H), 6.42 (dd, *J* = 10.2, 2.0 Hz, 1H), 6.15 (d, *J* = 10.2 Hz, 1H), 5.67 (s, 1H), 4.45 (s, 1H), 2.42 (d, *J* = 16.6 Hz, 1H), 1.59 (dd, *J* = 17.3, 3.8 Hz, 1H).

^{13}C NMR (100 MHz, DMSO-*d6*) δ 193.8, 166.8, 166.4, 159.2, 144.0, 137.9, 132.4, 132.0, 131.8, 129.4, 129.2, 128.5, 128.4, 128.3, 128.2, 128.0, 127.9, 127.8, 127.2, 65.0, 56.3, 53.8, 39.2.

HRMS (ESI, M+Na^{+}) m/z calcd. for $C_{29}H_{22}N_2NaO_3S$ 501.1249, found 501.1244.



(5R,7aR,11aR)-2-((4-bromophenyl)thio)-1,5-diphenyl-7a,8-dihydro-3H-pyrrolo[1,2-d]quinoxaline-3,6,9(5H,7H)-trione (5c)

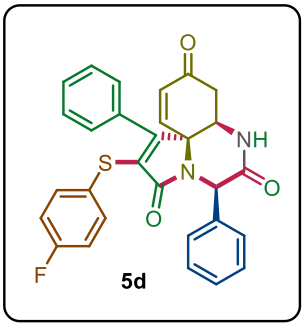
Physical appearance: Yellow solid

R_f: 0.5 (1:1 EtOAc:Petroleum ether boiling range 60-80 ^oC).

^{1}H NMR (500 MHz, DMSO-*d6*): δ 8.60 (s, 1H), 7.42-7.32 (m, 10H), 7.26-7.22 (m, 4H), 6.46 (dd, *J* = 10.1, 1.7 Hz, 1H), 6.17 (d, *J* = 10.1 Hz, 1H), 5.66 (s, 1H), 4.50 (br. s, 1H), 2.44 (d, *J* = 16.6 Hz, 1H), 1.61 (dd, *J* = 17.3, 3.6 Hz, 1H).

^{13}C NMR (126 MHz, DMSO-*d6*) δ 193.7, 166.4, 165.5, 158.1, 143.7, 137.7, 132.1, 131.8, 131.6, 131.3, 129.6, 129.5, 128.5, 128.45, 128.40, 128.2, 127.8, 120.0, 64.0, 56.2, 53.8, 39.1.

HRMS (ESI, M+Na$^+$) m/z calcd. for $C_{29}H_{21}BrN_2NaO_3S$ 579.0354, found 579.0361.



2-((4-fluorophenyl)thio)-1,5-diphenyl-7a,8-dihydro-3H-pyrrolo[1,2-d]quinoxaline-3,6,9(5H,7H)-trione (5d)

Physical appearance: Yellow solid

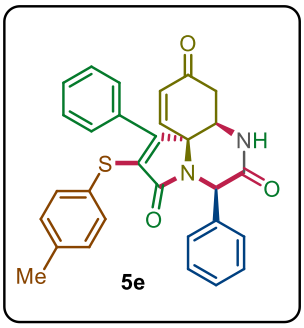
R_f: 0.5 (1:1 EtOAc:Petroleum ether boiling range 60-80 ^oC).

^{1}H NMR (500 MHz, DMSO-*d6*): δ 8.58 (s, 1H), 7.39-7.33 (m, 11H), 7.21 (d, *J* = 7.3 Hz, 2H), 7.07 (t, *J* = 7.5 Hz, 2H), 6.46 (d, *J* = 9.9 Hz, 1H), 6.17 (d, *J* = 9.9 Hz, 1H), 5.65 (s, 1H), 4.48 (s, 1H), 2.42 (d, *J* = 17.2 Hz, 1H), 1.60 (dd, *J* = 17.2, 3.0 Hz, 1H).

^{13}C NMR (126 MHz, DMSO-*d6*) δ 193.8, 166.4, 165.7, 156.3, 143.9, 137.8, 132.6, 132.5, 132.0, 131.6, 130.4, 129.4, 128.5, 128.4, 128.3, 128.1, 127.8, 127.7, 126.9, 116.1, 115.9, 64.0, 56.2, 53.8, 39.1.

^{19}F NMR (470 MHz, $CDCl_3$): δ -112.5.

HRMS (ESI, M+Na$^+$) m/z calcd. for $C_{29}H_{21}FN_2NaO_3S$ 519.1155, found 519.1157.



(5R,7aR,11aR)-1,5-diphenyl-2-(p-tolylthio)-7a,8-dihydro-3H-pyrrolo[1,2-d]quinoxaline-3,6,9(5H,7H)-trione (5e)

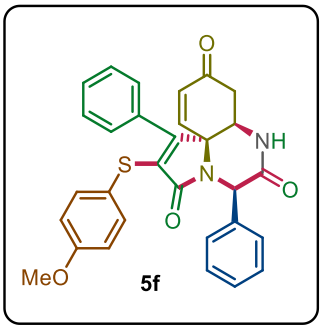
Physical appearance: Brown solid

R_f: 0.5 (1:1 EtOAc: Petroleum ether boiling range 60-80 ^oC).

^{1}H NMR (500 MHz, DMSO-*d6*): δ 8.56 (s, 1H), 7.40-7.33 (m, 8H), 7.22 (d, *J* = 7.5 Hz, 2H), 7.17 (d, *J* = 7.5 Hz, 2H), 7.05 (d, *J* = 7.9 Hz, 2H), 6.44 (d, *J* = 10.0 Hz, 1H), 6.16 (d, *J* = 10.0 Hz, 1H), 5.64 (s, 1H), 4.46 (s, 1H), 2.42 (d, *J* = 17.2 Hz, 1H), 2.24 (s, 3H), 1.61 (dd, *J* = 17.0, 3.4 Hz, 1H).

^{13}C NMR (126 MHz, DMSO-*d6*) δ 193.8, 166.4, 165.7, 157.0, 143.9, 137.8, 136.5, 132.0, 131.7, 130.4, 129.8, 129.6, 129.3, 128.5, 128.4, 128.3, 128.2, 127.8, 63.9, 56.2, 53.8, 39.1, 20.5.

HRMS (ESI, M+Na$^+$) m/z calcd. for $C_{30}H_{24}N_2NaO_3S$ 515.1405, found 515.1400.



(5R,7aR,11aR)-2-((4-methoxyphenyl)thio)-1,5-diphenyl-7a,8-dihydro-3H-pyrrolo[1,2-d]quinoxaline-3,6,9(5H,7H)-trione (5f)

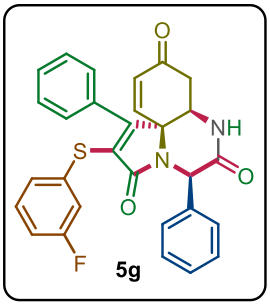
Physical appearance: Pale yellow solid solid

R_f: 0.5 (1:1 EtOAc:Petroleum ether boiling range 60-80 ^oC).

^{1}H NMR (500 MHz, DMSO-*d6*): δ 8.58 (s, 1H), 7.40-7.35 (m, 8H), 7.24 (d, *J* = 8.2 Hz, 2H), 7.18 (d, *J* = 7.5 Hz, 2H), 6.78 (d, *J* = 8.2 Hz, 2H), 6.42 (d, *J* = 10.2 Hz, 1H), 6.14 (d, *J* = 9.6 Hz, 1H), 5.64 (s, 1H), 4.44 (s, 1H), 3.72 (s, 3H), 2.40 (d, *J* = 16.8 Hz, 1H), 1.59 (dd, *J* = 17.3, 3.2 Hz, 1H).

^{13}C NMR (100 MHz, DMSO-*d6*) δ 193.8, 166.4, 165.9, 159.0, 154.8, 144.1, 137.9, 133.0, 132.0, 131.7, 131.3, 129.2, 128.6, 128.5, 128.4, 128.3, 127.8, 121.0, 114.6, 63.8, 56.2, 55.2, 53.8, 39.1.

HRMS (ESI, M+Na$^+$) m/z calcd. for $C_{30}H_{24}N_2NaO_4S$ 531.1354, found 531.1362.



(7aR,11aR)-2-((3-fluorophenyl)thio)-1,5-diphenyl-7a,8-dihydro-3H-pyrrolo[1,2-d]quinoxaline-3,6,9(5H,7H)-trione (5g)

Physical appearance: Pale yellow solid solid

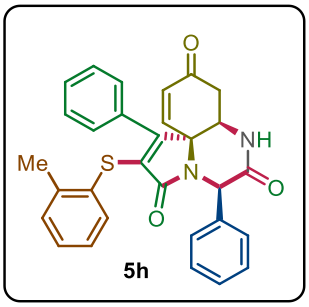
R_f: 0.5 (1:1 EtOAc:Petroleum ether boiling range 60-80 ^{o}C).

^{1}H NMR (500 MHz, DMSO-*d6*): δ 8.58 (s, 1H), 7.39-7.21 (m, 11H), 7.14 (d, *J* = 9.0 Hz, 1H), 7.10 (d, *J* = 8.7 Hz, 1H), 7.01 (d, *J* = 8.7 Hz, 1H), 6.49 (dd, *J* = 10.1, 2.0 Hz, 1H), 6.16 (d, *J* = 10.1 Hz, 1H), 5.64 (s, 1H), 4.50 (s, 1H), 3.72 (s, 3H), 2.40 (d, *J* = 17.2 Hz, 1H), 1.58 (dd, *J* = 17.3, 3.8 Hz, 1H).

^{13}C NMR (125 MHz, DMSO-*d6*) δ 194.3, 166.8, 166.0, 162.5 (d, J^1 = 243.5 Hz), 159.2, 144.3, 138.3, 135.3, 135.2, 132.6, 132.1, 131.2, (d, J^3 = 8.6 Hz), 130.1, 129.6, 129.0, 128.93, 128.87, 128.7, 128.3, 125.3 (d, J^4 = 3.0 Hz), 116.2, 116.0, 114.2, 114.0, 64.6, 56.7, 54.2, 39.6.

^{19}F NMR (470 MHz, $CDCl_3$): δ -111.7.

HRMS (ESI, M+Na$^+$) m/z calcd. for $C_{29}H_{21}FN_2NaO_3S$ 519.1155, found 519.1163.



(5R,7aR,11aR)-1,5-diphenyl-2-(p-tolylthio)-7a,8-dihydro-3H-pyrrolo[1,2-d]quinoxaline-3,6,9(5H,7H)-trione (5h)

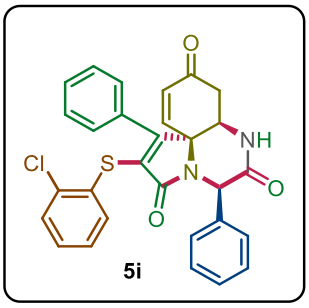
Physical appearance: Brown solid

R_f: 0.5 (1:1 EtOAc: Petroleum ether boiling range 60-80 ^oC).

^{1}H NMR (500 MHz, DMSO-*d6*): δ 8.56 (s, 1H), 7.40-7.33 (m, 8H), 7.22 (d, *J* = 7.5 Hz, 2H), 7.17 (d, *J* = 7.5 Hz, 2H), 7.05 (d, *J* = 7.9 Hz, 2H), 6.44 (d, *J* = 10.0 Hz, 1H), 6.16 (d, *J* = 10.0 Hz, 1H), 5.64 (s, 1H), 4.46 (s, 1H), 2.42 (d, *J* = 17.2 Hz, 1H), 2.24 (s, 3H), 1.61 (dd, *J* = 17.0, 3.4 Hz, 1H).

^{13}C NMR (126 MHz, DMSO-*d6*) δ 193.8, 166.4, 165.7, 157.0, 143.9, 137.8, 136.5, 132.0, 131.7, 130.4, 129.8, 129.6, 129.3, 128.5, 128.4, 128.3, 128.2, 127.8, 63.9, 56.2, 53.8, 39.1, 20.5.

HRMS (ESI, M+Na$^+$) m/z calcd. for $C_{30}H_{24}N_2NaO_3S$ 515.1405, found 515.1411.



(5R,7aR,11aR)-1,5-diphenyl-2-(4-chlorophenylthio)-7a,8-dihydro-3H-pyrrolo[1,2-d]quinoxaline-3,6,9(5H,7H)-trione (5i)

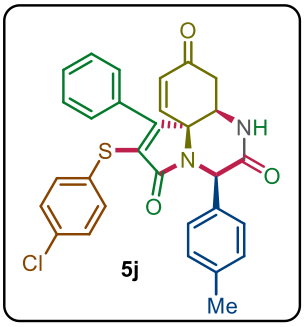
Physical appearance: Brown solid

R_f: 0.5 (1:1 EtOAc: Petroleum ether boiling range 60-80 ^oC).

^{1}H NMR (500 MHz, DMSO-*d6*): δ 8.61 (s, 1H), 7.43-7.33 (m, 10H), 7.26-7.23 (m, 4H), 6.47 (dd, *J* = 10.2, 2.2 Hz, 1H), 6.19 (d, *J* = 10.3 Hz, 1H), 5.67 (s, 1H), 4.54 (br s, 1H), 2.44 (d, *J* = 17.2 Hz, 1H), 1.61 (dd, *J* = 17.4, 3.9 Hz, 1H) ppm.

^{13}C NMR (126 MHz, DMSO-*d6*) δ 194.2, 166.8, 165.9, 159.8, 144.1, 138.2, 132.7, 132.2, 132.1, 131.9, 130.8, 130.2, 130.0, 129.2, 129.0, 128.94, 128.90, 128.6, 128.5, 128.4, 138.3, 64.6, 56.7, 54.2, 39.6 ppm.

HRMS (ESI, M+Na$^+$) m/z calcd. for $C_{29}H_{21}ClN_2NaO_3S$ 535.0859, found 535.0859.



(5R,7aR,11aR)-5-(4-chlorophenyl)-2-((4-chlorophenyl)thio)-1-phenyl-7a,8-dihydro-3H-pyrrolo[1,2-d]quinoxaline-3,6,9(5H,7H)-trione (5j)

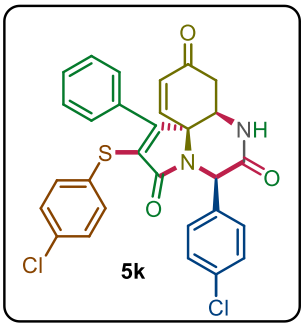
Physical appearance: Yellow solid

R_f: 0.5 (1:1 EtOAc:Petroleum ether boiling range 60-80 ºC).

^{1}H NMR (400 MHz, DMSO-*d6*): δ 8.62 (s, 1H), 7.44 (d, *J* = 8.4 Hz, 2H), 7.40-7.35 (m, 5H), 7.31-7.25 (m, 4H), 7.20 (d, *J* = 6.5 Hz, 2H), 6.50 (dd, *J* = 9.9, 1.1 Hz, 1H), 6.18 (d, *J* = 9.9 Hz, 1H), 5.64 (s, 1H), 4.47 (s, 1H), 3.72 (s, 3H), 2.41 (d, *J* = 16.8 Hz, 1H), 1.59 (dd, *J* = 17.1, 3.4 Hz, 1H).

^{13}C NMR (100 MHz, DMSO-*d6*) δ 193.7, 166.0, 165.6, 158.0, 143.6, 136.7, 132.6, 132.3, 131.7, 131.6, 131.11, 131.06, 130.3, 129.7, 129.6, 128.9, 128.5, 128.4, 128.2, 64.0, 55.5, 53.7, 39.1.

HRMS (ESI, M+Na$^+$) m/z calcd. for $C_{30}H_{23}ClN_2NaO_3S$ 549.1016, found 549.1019.



(5R,7aR,11aR)-5-(4-chlorophenyl)-2-((4-chlorophenyl)thio)-1-phenyl-7a,8-dihydro-3H-pyrrolo[1,2-d]quinoxaline-3,6,9(5H,7H)-trione (5k)

Physical appearance: Yellow solid

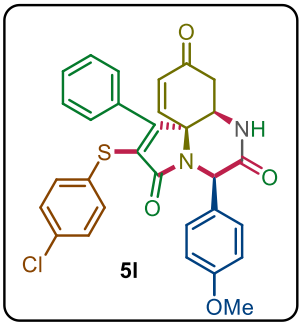
R_f: 0.5 (1:1 EtOAc:Petroleum ether boiling range 60-80 ºC).

^{1}H NMR (400 MHz, DMSO-*d6*): δ 8.62 (s, 1H), 7.44 (d, *J* = 8.4 Hz, 2H), 7.40-7.35 (m, 5H), 7.31-7.25 (m, 4H), 7.20 (d, *J* = 6.5 Hz, 2H), 6.50 (dd, *J* = 9.9, 1.1 Hz, 1H), 6.18 (d, *J* = 9.9 Hz,

1H), 5.64 (s, 1H), 4.47 (s, 1H), 3.72 (s, 3H), 2.41 (d, *J* = 16.8 Hz, 1H), 1.59 (dd, *J* = 17.1, 3.4 Hz, 1H).

^{13}C NMR (100 MHz, DMSO-*d6*) δ 193.7, 166.0, 165.6, 158.0, 143.6, 136.7, 132.6, 132.3, 131.7, 131.6, 131.11, 131.06, 130.3, 129.7, 129.6, 128.9, 128.5, 128.4, 128.2, 64.0, 55.5, 53.7, 39.1.

HRMS (ESI, M+Na$^+$) m/z calcd. for $C_{29}H_{20}Cl_2N_2NaO_3S$ 569.0469, found 569.0478.



(5R,7aR,11aR)-2-((4-chlorophenyl)thio)-5-(4-methoxyphenyl)-1-phenyl-7a,8-dihydro-3H-pyrrolo[1,2-d]quinoxaline-3,6,9(5H,7H)-trione (5l)

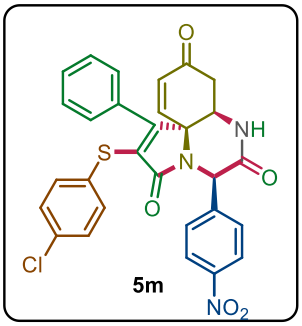
Physical appearance: Yellow solid

R$_f$: 0.5 (1:1 EtOAc:Petroleum ether boiling range 60-80 ^{o}C).

^{1}H NMR (400 MHz, DMSO-*d6*): δ 8.53 (s, 1H), 7.39-7.19 (m, 12H), 6.91 (d, *J* = 8.8 Hz, 2H), 6.40 (dd, *J* = 10.0, 1.7 Hz, 1H), 6.14 (d, *J* = 10.2 Hz, 1H), 5.57 (s, 1H), 4.45 (s, 1H), 3.74 (s, 3H), 2.39 (d, *J* = 16.8 Hz, 1H), 1.56 (dd, *J* = 17.3, 3.4 Hz, 1H).

^{13}C NMR (100 MHz, DMSO-*d6*) δ 193.9, 166.6, 165.4, 158.7, 157.8, 143.9, 132.0, 131.66, 131.60, 131.2, 131.1, 129.85, 129.79, 129.7, 129.6, 128.9, 128.5, 128.3, 113.8, 63.9, 55.6, 55.1, 53.8, 39.2.

HRMS (ESI, M+Na$^+$) m/z calcd. for $C_{30}H_{23}ClN_2NaO_4S$ 565.0965, found 565.0972.



(5R,7aR,11aR)-2-((4-chlorophenyl)thio)-5-(4-nitrophenyl)-1-phenyl-7a,8-dihydro-3H-pyrrolo[1,2-d]quinoxaline-3,6,9(5H,7H)-trione (5m)

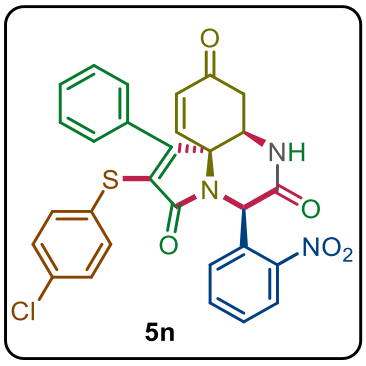
Physical appearance: Yellow solid

R_f: 0.5 (1:1 EtOAc:Petroleum ether boiling range 60-80 ^oC).

^{1}H NMR (400 MHz, DMSO-*d6*): δ 8.76 (s, 1H), 8.30 (d, *J* = 8.5 Hz, 2H), 7.70 (d, *J* = 8.5 Hz, 2H), 7.47-7.20 (m, 12H), 6.60 (d, *J* = 10.0 Hz, 1H), 6.63 (d, *J* = 10.0 Hz, 1H), 5.83 (s, 1H), 4.56 (s, 1H), 2.47 (d, *J* = 16.8 Hz, 1H), 1.67 (dd, *J* = 17.1, 3.4 Hz, 1H) ppm.

^{13}C NMR (100 MHz, DMSO-*d6*) δ 194.0, 166.4, 165.9, 158.6, 147.5, 143.7, 133.1, 132.2, 132.0, 131.6, 131.5, 130.2, 130.1, 129.4, 129.0, 128.9, 128.74, 128.69, 124.1, 64.7, 56.2, 54.1, 39.5 ppm.

HRMS (ESI, M+Na$^+$) m/z calcd. for $C_{29}H_{20}ClN_3NaO_5S$ 580.0710, found 580.0707.



5n

(5R,7aR,11aR)-2-((4-chlorophenyl)thio)-5-(2-nitrophenyl)-1-phenyl-7a,8-dihydro-3H-pyrrolo[1,2-d]quinoxaline-3,6,9(5H,7H)-trione (5n)

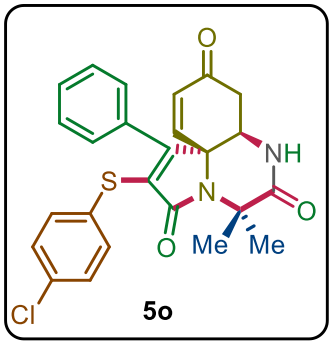
Physical appearance: Yellow solid

R_f: 0.5 (1:1 EtOAc:Petroleum ether boiling range 60-80 ^oC).

^{1}H NMR (500 MHz, DMSO-*d6*): δ 8.61 (s, 1H), 7.99 (d, *J* = 8.0 Hz, 1H), 7.74 (t, *J* = 7.5 Hz, 1H), 7.68 (d, *J* = 7.7 Hz, 1H), 7.61 (t, *J* = 7.7 Hz, 1H), 7.34-7.23 (m, 7H), 6.59 (s, 1H), 6.35 (d, *J* = 10.2 Hz, 1H), 4.61 (s, 1H), 2.41 (d, *J* = 17.5 Hz, 1H), 1.71 (dd, *J* = 17.9, 3.8 Hz, 1H) ppm.

^{13}C NMR (100 MHz, DMSO-*d6*) δ 193.8, 167.6, 165.4, 159.4, 150.7, 143.9, 133.5, 133.3, 132.4, 132.1, 131.6, 131.5, 131.4, 130.7, 130.0, 129.4, 129.3, 129.0, 128.8, 128.7, 125.2, 66.1, 53.8, 53.6, 39.4 ppm.

HRMS (ESI, M+Na$^+$) m/z calcd. for $C_{29}H_{20}ClN_3NaO_5S$ 580.0710, found 580.0717.



(7aR,11aR)-2-((4-chlorophenyl)thio)-5,5-dimethyl-1-phenyl-7a,8-dihydro-3H-pyrrolo[1,2-d]quinoxaline-3,6,9(5H,7H)-trione (5o)

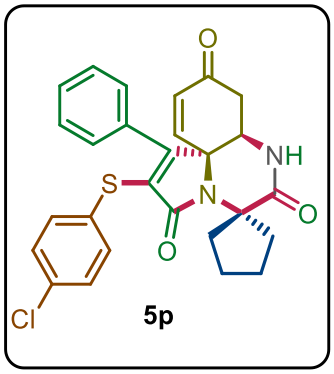
Physical appearance: Yellow solid.

R_f: 0.5 (1:1 EtOAc:Petroleum ether boiling range 60-80 ^oC).

^{1}H NMR (400 MHz, DMSO-*d6*): δ 8.25 (s, 1H), 7.41-7.17 (m, 9H), 6.84 (dd, *J* = 10.0, 2.2 Hz, 1H), 6.30 (d, *J* = 10.0 Hz, 1H), 6.14 (d, *J* = 10.2 Hz, 1H), 4.46 (d, *J* = 2.2 Hz, 1H), 2.36 (d, *J* = 16.2 Hz, 1H), 1.76 (s, 3H), 1.57 (dd, *J* = 17.7, 3.4 Hz, 1H), 1.53 (s, 3H).

^{13}C NMR (100 MHz, DMSO-*d6*) δ 193.7, 172.1, 165.2, 156.3, 145.0, 132.8, 132.2, 132.0, 131.8, 131.2, 129.4, 129.0, 128.6, 128.2, 66.3, 58.6, 52.1, 39.1, 25.6, 23.9.

HRMS (ESI, M+H$^+$) m/z calcd. for $C_{25}H_{22}ClN_2O_3S$ 465.1040, found 465.1049.



(7a'R,11a'R)-2'-((4-chlorophenyl)thio)-1'-phenyl-7a',8'-dihydro-3'H,6'H-spiro[cyclopentane-1,5'-pyrrolo[1,2-d]quinoxaline]-3',6',9'(7'H)-trione (5p)

Physical appearance: Yellow solid.

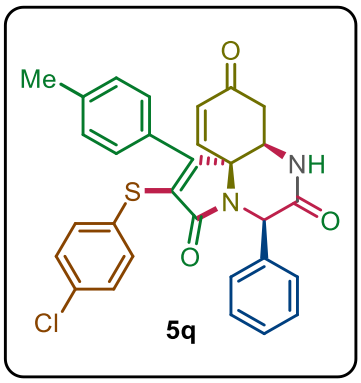
R_f: 0.5 (1:1 EtOAc:Petroleum ether boiling range 60-80 ^oC).

^{1}H NMR (400 MHz, DMSO-*d6*): δ 8.19 (s, 1H), 7.42-7.35 (m, 3H), 7.29 (s, 4H), 7.23-7.16 (m, 2H), 6.85 (d, *J* = 10.3 Hz, 1H), 6.32 (d, *J* = 10.0 Hz, 1H), 4.45 (s, 1H), 2.82-2.77 (m, 1H), 2.38 (d,

J = 17.0 Hz, 1H), 2.21 (t, *J* = 2.2 Hz, 1H), 2.04-1.98 (m, 1H), 1.94-1.89 (m, 3H), 1.82-1.72 (m, 2H), 1.56 (dd, *J* = 17.7, 3.4 Hz, 1H).

^{13}C NMR (100 MHz, DMSO-*d6*) δ 193.7, 174.0, 164.5, 156.2, 144.7, 132.8, 132.0, 131.6, 131.4, 131.0, 129.4, 128.9, 128.6, 128.1, 66.9, 66.3, 52.2, 4.13, 41.2, 37.2, 28.1, 26.3.

HRMS (ESI, M+Na$^+$) m/z calcd. for $C_{27}H_{23}ClN_2NaO_3S$ 513.1016, found 513.1016.



(5R,7aR,11aR)-2-((4-chlorophenyl)thio)-5-phenyl-1-(p-tolyl)-7a,8-dihydro-3H-pyrrolo[1,2-d]quinoxaline-3,6,9(5H,7H)-trione (5q)

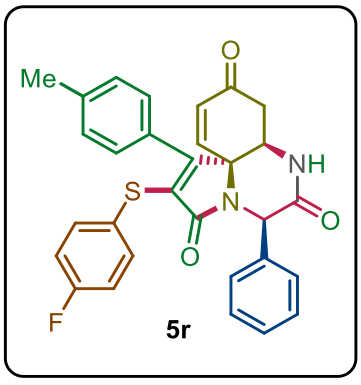
Physical appearance: Yellow solid

R_f: 0.5 (1:1 EtOAc:Petroleum ether boiling range 60-80 ^oC).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44-7.4 (m, 3H), 7.38-7.32 (m, 3H), 7.22-7.19 (m, 2H), 7.16-7.12 (m, 2H), 7.10 (d, *J* = 8.0 Hz, 2H), 6.91 (d, *J* = 8.1 Hz, 2H), 6.16 (d, *J* = 10.0 Hz, 1H), 6.04 (s, 1H), 5.99 (dd, *J* = 10.2, 1.8 Hz, 1H), 4.15 (s, 1H), 2.35 (s, 3H), 2.29 (br s, 1H), 1.93 (dd, *J* = 17.2, 3.7 Hz, 1H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 193.2, 168.2, 166.0, 154.0, 142.9, 140.5, 137.0, 134.3, 133.2, 132.9, 132.3, 129.8, 129.23, 129.20, 129.0, 128.9, 128.6, 128.2, 128.1, 77.4, 63.9, 55.9, 40.5, 21.5 ppm.

HRMS (ESI, M+H$^+$) m/z calcd. for $C_{30}H_{23}ClN_2O_3S$ 527.1198, found 527.1198.



(5R,7aR,11aR)-2-((4-fluorophenyl)thio)-5-phenyl-1-(p-tolyl)-7a,8-dihydro-3H-pyrrolo[1,2-d]quinoxaline-3,6,9(5H,7H)-trione (5r)

Physical appearance: Yellow solid

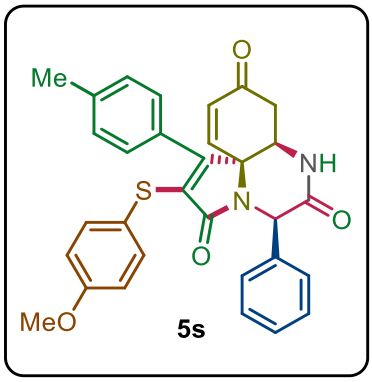
R_f: 0.5 (1:1 EtOAc:Petroleum ether boiling range 60-80 ^oC).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65 (s, 1H), 7.42-7.38 (m, 3H), 7.37-7.31 (m, 3H), 7.30-7.26 (m, 3H), 7.09 (d, *J* = 7.8 Hz, 2H), 6.99-6.84 (m, 4H), 6.14 (d, *J* = 10.1 Hz, 1H), 6.03 (s, 1H), 5.98 (dd, *J* = 10.2, 1.9 Hz, 1H), 4.14 (s, 1H), 2.34 (s, 3H), 2.30 (br s, 1H), 1.90 (dd, *J* = 17.4, 3.5 Hz, 1H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 193.3, 168.4, 166.2, 162.7 (d, J^1= 244.8 Hz), 153.2, 143.0, 140.3, 137.1, 134.6 (d, J^3= 8.2 Hz), 132.89, 132.86, 129.7, 129.0, 128.8, 128.5, 128.2, 128.1, 125.6 (d, J^4 = 3.2 Hz), 116.2 (d, J^2 = 22.4 Hz), 77.36, 63.7, 55.8, 40.4, 21.4 ppm.

^{19}F NMR (470 MHz, $CDCl_3$): δ -112.8 ppm.

HRMS (ESI, M+H^+) m/z calcd. for $C_{30}H_{23}FN_2O_3S$ 511.1498, found 511.1499.



(5R,7aR,11aR)-2-((4-methoxyphenyl)thio)-5-phenyl-1-(p-tolyl)-7a,8-dihydro-3H-pyrrolo[1,2-d]quinoxaline-3,6,9(5H,7H)-trione (5s)

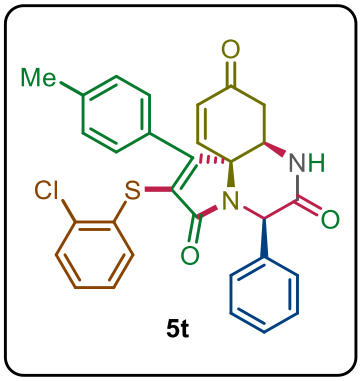
Physical appearance: Yellow solid

R_f: 0.5 (1:1 EtOAc:Petroleum ether boiling range 60-80 ^oC).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43-7.41 (m, 2H), 7.37-7.31 (m, 3H), 7.25 (d, *J* = 8.8 Hz, 2H), 7.06 (d, *J* = 7.7 Hz, 2H), 6.88 (d, *J* = 8.1 Hz, 2H), 6.69 (d, *J* = 9.1 Hz, 2H), 6.12 (d, *J* = 10.2 Hz, 2H), 6.04 (s, 1H), 5.97 (dd, *J* = 10.2, 2.4 Hz, 1H), 4.14 (s, 1H), 3.77 (s, 3H), 2.33 (s, 3H), 2.27 (d, *J* = 17.3 Hz, 1H), 1.92 (dd, *J* = 17.3, 3.8 Hz, 1H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ193.2, 168.0, 166.3, 159.3, 151.6, 143.3, 139.8, 137.0, 134.9, 133.7, 132.5, 129.5, 128.9, 128.7, 128.4, 128.3, 128.2, 120.3, 114.5, 77.2, 63.5, 55.8, 55.3, 40.5, 21.3 ppm.

HRMS (ESI, M+H$^+$) m/z calcd. for $C_{31}H_{26}N_2O_4S$ 545.1511, found 545.1511.



(5R,7aR,11aR)-2-((2-chlorophenyl)thio)-5-phenyl-1-(p-tolyl)-7a,8-dihydro-3H-pyrrolo[1,2-d]quinoxaline-3,6,9(5H,7H)-trione (5t)

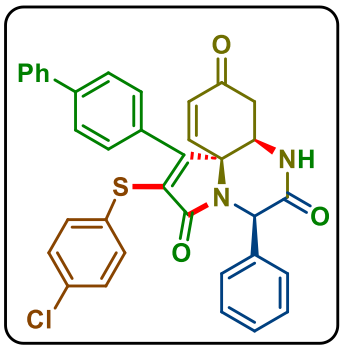
Physical appearance: Yellow solid

R_f: 0.5 (1:1 EtOAc:Petroleum ether boiling range 60-80 ^oC).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (s, 1H), 7.41-7.39 (m, 2H), 7.35-7.30 (m, 3H), 7.26-7.24 (m, 2H), 7.12 (td, *J* = 7.5, 1.5 Hz, 1H), 7.06-7.03 (m, 3H), 6.93 (d, *J* = 8.1 Hz, 2H), 6.12 (d, *J* = 10.3 Hz, 1H), 6.02 (s, 1H), 5.96 (dd, *J* = 10.8, 1.8 Hz, 1H), 4.14 (s, 1H), 2.33 (d, *J* = 17.7 Hz, 1H), 2.28 (s, 3H), 1.89 (dd, *J* = 17.4, 3.7 Hz, 1H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) 193.3, 168.3, 165.7, 153.7, 142.9, 140.2, 137.0, 135.7, 133.1, 132.8, 131.2, 130.0, 129.6, 129.0, 128.8, 128.7, 128.4, 128.0, 127.8, 127.0, 63.7, 56.1, 55.8, 40.3, 21.3 ppm.

HRMS (ESI, M+H$^+$) m/z calcd. for $C_{30}H_{23}ClN_2O_3S$ 527.1202, found 527.1202.



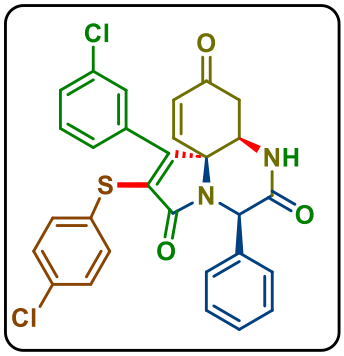
(5R,7aR,11aR)-1-([1,1'-biphenyl]-4-yl)-5-phenyl-2-(phenylthio)-7a,8-dihydro-3H-pyrrolo[1,2-d]quinoxaline-3,6,9(5H,7H)-trione (5u)

Physical appearance: Brown solid

R_f: 0.5 (1:1 EtOAc:Petroleum ether boiling range 60-80 ^oC).

^{1}H NMR (500 MHz, DMSO): δ 8.59 (s, 1H), 7.67 (d, *J* = 7.1 Hz, 4H), 7.45 (t, *J* = 7.5 Hz, 3H), 7.37 (t, *J* = 3.5 Hz, 3H), 7.35-7.32 (m, 3H), 7.30 (d, *J* = 5.4 Hz, 2H), 7.28 (d, *J* = 3.2 Hz, 2H), 6.49 (dd, *J* = 10.1, 1.9 Hz, 1H), 6.19 (d, *J* = 10.2 Hz, 1H), 5.64 (s, 1H), 4.52 (s, 1H), 1.73 (dd, *J* = 17.2 Hz, 3.5 Hz, 1H) ppm

^{13}C NMR (101 MHz, DMSO): 194.1, 166.9, 166.6, 158.5, 144.2, 140.9, 139.1, 138.1, 132.2, 131.6, 130.1, 129.3, 129.2, 129.0, 128.7, 128.6, 128.5, 128.1, 128.0, 127.3, 126.9, 126.7, 126.6, 65.2, 56.4, 56.2, 54.0.



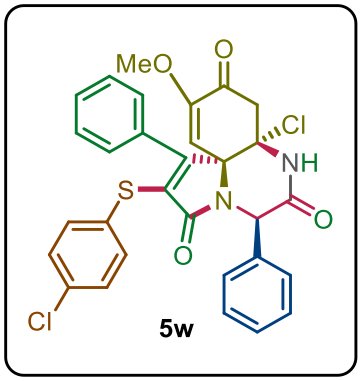
(5R,7aR,11aR)-1-(3-chlorophenyl)-2-((4-chlorophenyl)thio)-5-phenyl-7a,8-dihydro-3H-pyrrolo[1,2-d]quinoxaline-3,6,9(5H,7H)-trione (5v)

Physical appearance: Brown solid

R_f: 0.5 (1:1 EtOAc:Petroleum ether boiling range 60-80 ^{o}C).

^{1}H NMR (500 MHz, DMSO): δ 8.61 (s, 1H), 7.95 (d, *J* = 8.5 Hz, 1H), 7.58 (d, *J* = 8.5 Hz, 1H), 7.45 (d, *J* = 8.2 Hz, 2H), 7.38 (d, *J* = 6.8 Hz, 2H), 7.36 – 7.30 (m, 4H), 7.28 (d, *J* = 8.7 Hz, 1H), 7.23 (d, *J* = 8.1 Hz, 1H), 6.47 (dd, *J* = 10.2, 2.2 Hz, 1H), 6.17 (d, *J* = 10.1 Hz, 1H), 5.64 (s, 1H), 4.51 (s, 1H), 1.67 (dd, *J* = 17.4, 3.9 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 193.8, 166.5, 166.4, 165.5, 155.6, 143.9, 137.9, 137.7, 134.5, 132.0, 132.2, 131.7, 131.2, 130.7, 130.5, 130.3, 129.7, 128.9, 128.8, 128.7, 128.6, 128.5, 64.1, 56.3, 53.7.



(5R,7aS,11aR)-7a-chloro-2-((4-chlorophenyl)thio)-10-methoxy-1,5-diphenyl-7a,8-dihydro-3H-pyrrolo[1,2-d]quinoxaline-3,6,9(5H,7H)-trione (5w)

Physical appearance: Yellow solid

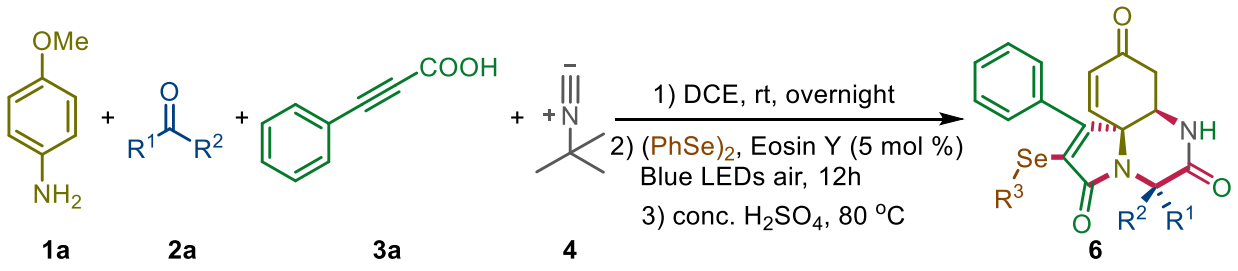
R_f: 0.5 (1:1 EtOAc:Petroleum ether boiling range 60-80 ^oC).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40-7.35 (m, 3H), 7.33-7.29 (m, 5H), 7.17 (d, *J* = 8.6 Hz, 2H), 7.10 (d, *J* = 8.6 Hz, 2H), 6.87 (d, *J* = 7.1 Hz, 2H), 6.46 (s, 1H), 6.15 (s, 1H), 5.51 (s, 1H), 4.35 (d, *J* = 3.2 Hz, 1H), 3.91 (d, *J* = 3.2 Hz, 1H), 2.96 (s, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ185.0, 166.3, 166.1, 165.7, 152.0, 135.7, 134.3, 133.4, 133.1, 130.4, 130.3, 129.5, 129.1, 128.8, 128.5, 128.4, 128.3, 127.5, 105.4, 65.4, 60.7, 59.4, 56.1, 56.0 ppm.

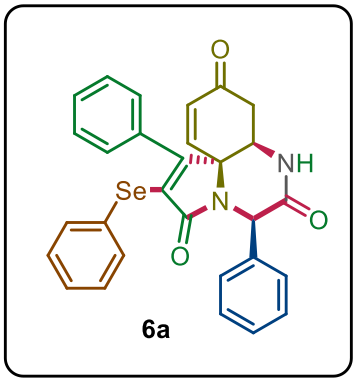
HRMS (ESI, M+H$^+$) m/z calcd. for $C_{30}H_{22}Cl_2N_2O_4S$ 599.0580, found 599.0580.

Procedure for the one-pot Ugi-selenylative spirocyclization and aza-Michael addition reaction cascade.



In a reaction tube equipped with a magnetic stirring bar was added benzaldehyde **2a** (21 μL, 0.2 mmol, 1.0 equiv) and *p*-anisidine **1a** (24.6 mg, 0.2 mmol, 1.0 equiv) in DCE (2mL) and stirred at rt for 5 mins. Phenylpropiolic acid **3a** (30 mg, 0.2 mmol, 1.0 equiv) and *tert*-butyl isocyanide **4** (22 μL, 0.2 mmol, 1.0 equiv) were added all at once and resulting solution was stirred at room

temperature for 12 hrs. After completion of the reaction (TLC control), solvent was removed and diphenyl diselenide (124 mg, 0.4 mmol, 2.0 equiv) was added, the contents were dissolved in MeCN (2 mL) and irradiated under blue LED's at room temperature under O_2 atmosphere for 24 hrs. Then again solvent was evaporated and the residue was diluted with DCE (2 mL). To this reaction mixture was added conc. H_2SO_4 (54 μL, 1 mmol, 5.0 equiv) and the contents were heated at 80 ^oC for 8 h. The reaction was then quenched with sat. $NaHCO_3$ solution, extracted with DCM (3 x 5 mL). Combined organics were dried over Na_2SO_4 and concentrated under reduced pressure. Residue was purified by column chromatography with EtOAc in petroleum ether to furnish the desired tricyclic compound **6a** in 72% yield (79 mg) as a pale-yellow solid.



6a

(5R,7aR,11aR)-1,5-diphenyl-2-(phenylselanyl)-7a,8-dihydro-3H-pyrrolo[1,2-d]quinoxaline-3,6,9(5H,7H)-trione (6a)

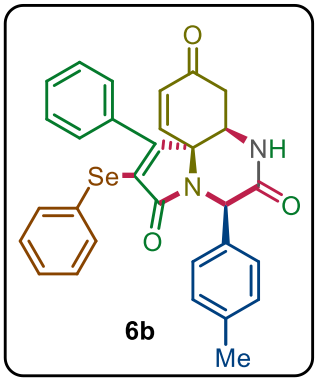
R_f: 0.5 (1:1 EtOAc:Petroleum ether boiling range 60-80 ^oC).

^{1}H NMR (400 MHz, DMSO-*d6*): δ 8.57 (s, 1H), 7.40-7.32 (m, 10H), 7.22-7.18 (m, 5H), 6.42 (dd, *J* = 10.2, 2.0 Hz, 1H), 6.15 (d, *J* = 10.2 Hz, 1H), 5.67 (s, 1H), 4.45 (s, 1H), 2.42 (d, *J* = 16.6 Hz, 1H), 1.59 (dd, *J* = 17.3, 3.8 Hz, 1H).

^{13}C NMR (100 MHz, DMSO-*d6*) δ 193.8, 166.8, 166.4, 159.2, 144.0, 137.9, 132.4, 132.0, 131.8, 129.4, 129.2, 128.5, 128.4, 128.3, 128.2, 128.0, 127.9, 127.8, 127.2, 65.0, 56.3, 53.8, 39.2.

^{77}Se NMR (95 MHz, DMSO-*d6*) δ 286.6.

HRMS (ESI, M+H$^+$) m/z calcd. for $C_{29}H_{23}N_2O_3Se$ 527.0866, found 527.0866.



(5R,7aR,11aR)-1-phenyl-2-(phenylselanyl)-5-(p-tolyl)-7a,8-dihydro-3H-pyrrolo[1,2-d]quinoxaline-3,6,9(5H,7H)-trione (6b)

Physical appearance: Yellow solid

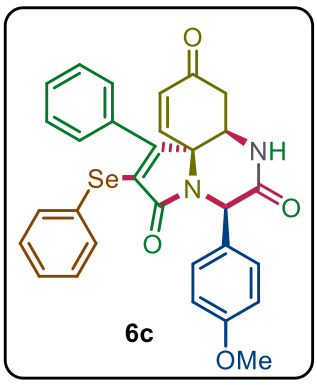
R_f: 0.5 (1:1 EtOAc:Petroleum ether boiling range 60-80 ^oC).

^{1}H NMR (500 MHz, DMSO-*d6*): δ 8.54 (s, 1H), 7.39-7.32 (m, 5H), 7.24-7.16 (m, 9H), 6.40 (dd, *J* = 10.4, 2.0 Hz, 1H), 6.14 (d, *J* = 10.1 Hz, 1H), 5.62 (s, 1H), 4.44 (s, 1H), 2.40 (d, *J* = 16.9 Hz, 1H),2.30 (s, 3H), 1.59 (dd, *J* = 17.2, 3.8 Hz, 1H).

^{13}C NMR (100 MHz, DMSO-*d6*) δ 193.8, 166.5, 159.2, 144.0, 137.0, 135.0, 132.4, 131.9, 131.7, 129.4, 129.2, 128.9, 128.4, 128.3, 128.2, 128.0, 127.9, 127.2, 64.9, 55.9, 53.8, 39.2, 20.7.

^{77}Se NMR (95 MHz, DMSO-*d6*) δ 284.7.

HRMS (ESI, M+Na$^+$) m/z calcd. for $C_{30}H_{24}N_2NaO_3Se$ 563.0850, found 563.0855.



(5R,7aR,11aR)-2-((phenyl)selanyl)-5-(4-methoxyphenyl)-1-phenyl-7a,8-dihydro-3H-pyrrolo[1,2-d]quinoxaline-3,6,9(5H,7H)-trione (6c)

Physical appearance: Yellow solid

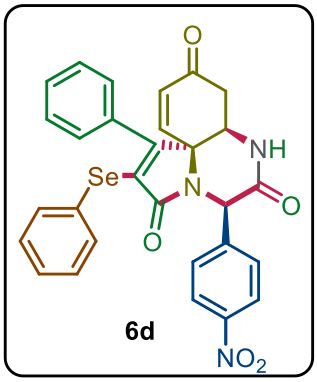
R_f: 0.5 (1:1 EtOAc:Petroleum ether boiling range 60-80 ^oC).

^{1}H NMR (400 MHz, DMSO-*d6*): δ 8.53 (s, 1H), 7.39-7.19 (m, 12H), 6.91 (d, *J* = 8.8 Hz, 2H), 6.40 (dd, *J* = 10.0, 1.7 Hz, 1H), 6.14 (d, *J* = 10.2 Hz, 1H), 5.57 (s, 1H), 4.45 (s, 1H), 3.74 (s, 3H), 2.39 (d, *J* = 16.8 Hz, 1H), 1.56 (dd, *J* = 17.3, 3.4 Hz, 1H).

^{13}C NMR (100 MHz, DMSO-*d6*) δ 193.9, 166.6, 165.4, 158.7, 157.8, 143.9, 132.0, 131.66, 131.60, 131.2, 131.1, 129.85, 129.79, 129.7, 129.6, 128.9, 128.5, 128.3, 113.8, 63.9, 55.6, 55.1, 53.8, 39.2.

^{77}Se NMR (95 MHz, DMSO-*d6*) δ 289.7.

HRMS (ESI, M+Na^{+}) m/z calcd. for $C_{30}H_{24}N_2NaO_4Se$ 579.0799, found 579.0793.



(5R,7aR,11aR)-2-((phenyl)selanyl)-5-(4-nitrophenyl)-1-phenyl-7a,8-dihydro-3H-pyrrolo[1,2-d]quinoxaline-3,6,9(5H,7H)-trione (6d)

Physical appearance: Yellow solid

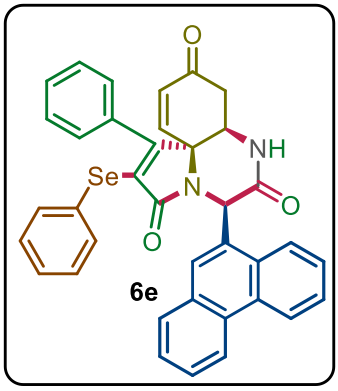
R_f: 0.5 (1:1 EtOAc:Petroleum ether boiling range 60-80 ^{o}C).

^{1}H NMR (400 MHz, DMSO-*d6*): δ 8.66 (s, 1H), 8.24 (d, *J* = 8.8 Hz, 2H), 7.63 (d, *J* = 8.8 Hz, 2H), 7.36-7.30 (m, 5H),7.19-7.14 (m, 6H), 6.55 (dd, *J* = 10.2, 2.1 Hz, 1H), 6.17 (d, *J* = 10.2 Hz, 1H), 5.76 (s, 1H), 4.45 (s, 1H), 2.39 (d, *J* = 16.5 Hz, 1H), 1.58 (dd, *J* = 17.4, 3.7 Hz, 1H).

^{13}C NMR (100 MHz, DMSO-*d6*) δ 193.7, 167.2, 165.6, 159.4, 147.0, 144.9, 143.5, 132.5, 132.4, 131.9, 131.8, 129.8, 129.5, 129.2, 128.4, 128.2, 128.0, 127.8, 127.3, 123.6, 65.2, 55.8, 53.7, 39.1.

^{77}Se NMR (95 MHz, DMSO-*d6*) δ 287.1.

HRMS (ESI, M+Na^{+}) m/z calcd. for $C_{29}H_{21}N_3NaO_5Se$ 595.0544, found 595.0539.



(5R,7aR,11aR)-2-((phenyl)selanyl)-5-(4-methoxyphenyl)-1-phenyl-7a,8-dihydro-3H-pyrrolo[1,2-d]quinoxaline-3,6,9(5H,7H)-trione (6e)

Physical appearance: Yellow solid

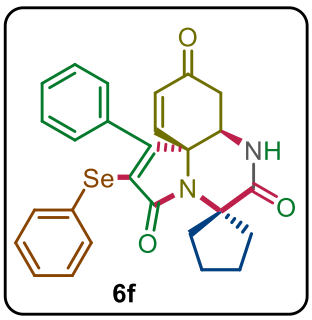
R_f: 0.5 (1:1 EtOAc:Petroleum ether boiling range 60-80 ^oC).

^{1}H NMR (400 MHz, DMSO-*d6*): δ 8.53 (s, 1H), 7.39-7.19 (m, 12H), 6.91 (d, *J* = 8.8 Hz, 2H), 6.40 (dd, *J* = 10.0, 1.7 Hz, 1H), 6.14 (d, *J* = 10.2 Hz, 1H), 5.57 (s, 1H), 4.45 (s, 1H), 3.74 (s, 3H), 2.39 (d, *J* = 16.8 Hz, 1H), 1.56 (dd, *J* = 17.3, 3.4 Hz, 1H).

^{13}C NMR (100 MHz, DMSO-*d6*) δ 193.9, 166.6, 165.4, 158.7, 157.8, 143.9, 132.0, 131.66, 131.60, 131.2, 131.1, 129.85, 129.79, 129.7, 129.6, 128.9, 128.5, 128.3, 113.8, 63.9, 55.6, 55.1, 53.8, 39.2.

^{77}Se NMR (95 MHz, DMSO-*d6*) δ 289.7.

HRMS (ESI, M+Na$^+$) m/z calcd. for $C_{37}H_{26}N_2NaO_3Se$ 649.1006, found 649.1002.



(7a'R,11a'R)-1'-phenyl-2'-(phenylselanyl)-7a',8'-dihydro-3'H,6'H-spiro[cyclopentane-1,5'-pyrrolo[1,2-d]quinoxaline]-3',6',9'(7'H)-trione (6f)

Physical appearance: Yellow solid

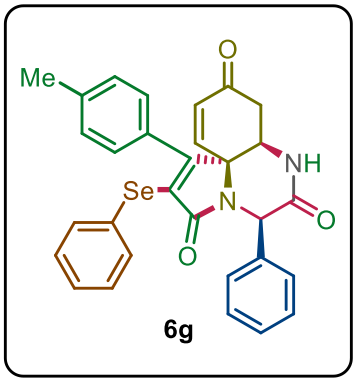
R_f: 0.5 (1:1 EtOAc: Petroleum ether boiling range 60-80 ^oC).

^{1}H NMR (400 MHz, DMSO-*d6*): δ 8.25 (s, 1H), 7.41-7.17 (m, 9H), 6.84 (dd, *J* = 10.0, 2.2 Hz, 1H), 6.30 (d, *J* = 10.0 Hz, 1H), 6.14 (d, *J* = 10.2 Hz, 1H), 4.46 (d, *J* = 2.2 Hz, 1H), 2.36 (d, *J* = 16.2 Hz, 1H), 1.76 (s, 3H), 1.57 (dd, *J* = 17.7, 3.4 Hz, 1H), 1.53 (s, 3H).

^{13}C NMR (100 MHz, DMSO-*d6*) δ 193.7, 172.1, 165.2, 156.3, 145.0, 132.8, 132.2, 132.0, 131.8, 131.2, 129.4, 129.0, 128.6, 128.2, 66.3, 58.6, 52.1, 39.1, 25.6, 23.9.

^{77}Se NMR (95 MHz, DMSO-*d6*) δ 289.9.

HRMS (ESI, M+H^{+}) m/z calcd. for $C_{27}H_{25}N_2O_3Se$ 505.1030, found 505.1030.



(5R,7aR,11aR)-5-phenyl-2-(phenylselanyl)-1-(p-tolyl)-7a,8-dihydro-3H-pyrrolo[1,2-d]quinoxaline-3,6,9(5H,7H)-trione (6g)

Physical appearance: Yellow solid

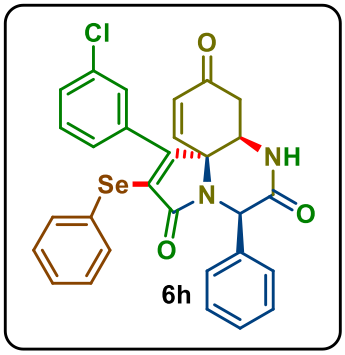
R_f: 0.5 (1:1 EtOAc:Petroleum ether boiling range 60-80 ^{o}C).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41 (d, *J* = 7.6 Hz, 2H), 7.35-7.30 (m, 5H), 7.21-7.17 (m, 2H), 7.11-7.08 (m, 2H), 7.00 (d, *J* = 8.1 Hz, 2H), 6.83 (d, *J* = 8.1 Hz, 2H), 6.10 (d, *J* = 10.1 Hz, 1H), 6.04 (s, 1H), 5.95 (dd, *J* = 10.2, 1.9 Hz, 1H), 4.12 (br s, 1H), 2.29 (s, 3H), 1.88 (dd, *J* = 17.4, 3.8 Hz, 1H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ193.2, 168.1, 167.2, 155.9, 143.1, 139.9, 137.1, 134.2, 132.6, 130.2, 129.5, 129.0, 128.90, 128.88, 128.7, 128.4, 128.0, 127.8, 126.6, 64.8, 56.3, 55.7, 40.5, 21.3 ppm.

^{77}Se NMR (76 MHz, $CDCl_3$) δ 308.7.

HRMS (ESI, M+Na^{+}) m/z calcd. for $C_{30}H_{24}N_2O_3Se$ 541.1037, found 541.1037.



(5R,7aR,11aR)-1-(3-chlorophenyl)-5-phenyl-2-(phenylthio)-7a,8-dihydro-3H-pyrrolo[1,2-d]quinoxaline-3,6,9(5H,7H)-trione (6h)

Physical appearance: Brown solid

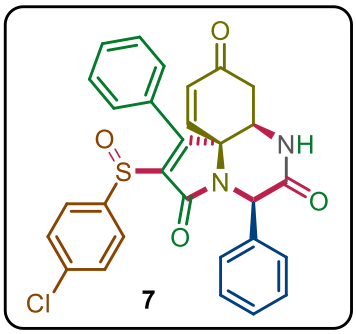
R_f: 0.5 (1:1 EtOAc:Petroleum ether boiling range 60-80 ^oC).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 (s, 1H), 7.40 (d, *J* = 6.4 Hz, 2H), 7.31 (d, *J* = 19.1 Hz, 2H), 7.29 (d, *J* = 18.6 Hz, 2H), 7.18 (t, *J* = 7.4 Hz, 1H), 7.11 (d, *J* = 8.3 Hz, 2H), 7.07 (*J* = d, 7.6 Hz, 2H), 6.82 (d, *J* = 8.2 Hz, 2H), 6.04 (s, 1H) 6.10 (d, *J* = 10.2 Hz, 1H). 5.93 (d, *J* = 10.1 Hz, 1H), 4.12 (br. s, 1H), 2.32 (d, *J* = 17.3 Hz, 1H), 1.82 (dd, *J* = 17.4 Hz, 3.2 Hz, 1H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ 192.8, 168.5, 167.0, 153.0, 142.9, 137.0, 135.9, 134.9, 132.7, 132.0, 130.1, 129.5, 129.22, 129.2, 129.0, 128.8, 128.5, 128.4, 125.7, 64.9, 56.4, 55.5, 40.4

^{77}Se NMR (95 MHz, DMSO-*d6*): δ 323.56

HRMS (ESI, M+H^+) m/z calcd. for $C_{29}H_{21}ClN_2O_3Se$ 561.0479, found 561.0487.



(7aR,11aS)-2-((R)-(4-chlorophenyl)sulfinyl)-1,5-diphenyl-7a,8-dihydro-3H-pyrrolo[1,2-d]quinoxaline-3,6,9(5H,7H)-trione (7)

In a reaction tube equipped with a magnetic stirring bar was dissolved sulfide **5a** (100 mg, 0.20 mmol) in DCM (4 mL) followed by addition of *m*-CPBA 60% suspension in water (60 mg, 0.21 mmol, 1.05 equiv.) at 0 ^oC and the resulting solution was allowed to stir at room temperature for

4 hrs. The reaction was then quenched with careful addition of saturated aqueous sodium bicarbonate solution further extraction with DCM (4 x 10 mL), drying over sodium sulfate and concentration under reduced pressure gave the crude product. The crude material on column chromatography with ethyl acetate in petroleum ether yielded the corresponding sulfoxide **7** in 89% yield (94 mg).

Physical appearance: Yellow solid

R_f: 0.5 (1:1 EtOAc: Petroleum ether boiling range 60-80 ^oC).

^{1}H NMR (400 MHz, DMSO-*d6*): δ 8.60 (s, 1H), 7.71 (d, *J* = 8.6 Hz, 2H), 7.68 (d, *J* = 8.6 Hz, 2H), 7.58-7.51 (m, 3H), 7.43-7.28 (m, 7H), 6.43 (dd, *J* = 10.1, 2.0 Hz, 1H), 6.23 (d, *J* = 10.1 Hz, 1H), 5.58 (s, 1H), 4.55 (s, 1H), 2.43 (d, *J* = 17.6 Hz, 1H), 1.59 (dd, *J* = 17.0, 4.0 Hz, 1H).

^{13}C NMR (100 MHz, DMSO-*d6*) δ 194.0, 166.6, 163.5, 162.4, 143.0, 140.8, 137.9, 137.7, 136.4, 133.2, 130.7, 130.1, 129.7, 129.6, 129.0, 128.9, 128.8, 128.4, 127.3, 64.6, 56.5, 53.5, 39.4.

HRMS (ESI, M+H$^+$) m/z calcd. for $C_{29}H_{22}ClN_2O_4S$ 529.0989, found 529.0989.

Crystal data and structure refinement

Single crystal of suitable for structural studies was obtained by slow evaporation of a mixture of ethyl acetate and hexanes. Crystals of suitable size were tested for single crystallinity using Leica DM-EP polarizing microscope. X-ray data collection was performed with Bruker AXS (Kappa Apex 2) CCD Diffractometer equipped with graphite monochromated Mo (Kα) (λ = 0.7107 Å) radiation. Crystal fixed at the tip of the glass fibre was mounted on the goniometer head and was optically centered. The automatic cell determination routine, with 32 frames (frame width 0.5°) at three different orientaions of the detector was employed to collect reflections and the program APEX- SAINT was used for finding the unit cell parameters. Four–fold redundancy per reflection was utilized for achieving good absorption correction using multi-scan procedure. Besides absorption, Lorentz polarization and decay correction were applied during data reduction. The program SADABS was used for absorption correction using multi-scan procedure.

The structure was solved using SHELXS-97 and refined by full-matrix least square techniques using SHELXL-97. All hydrogens were fixed at chemically meaningful positions and riding model refinement was applied.

Crystal data and structure refinement for compound **5c** ***CCDC: 2298650***

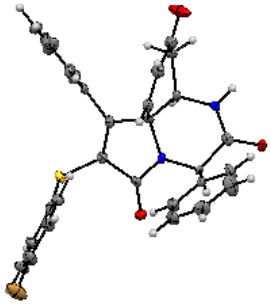
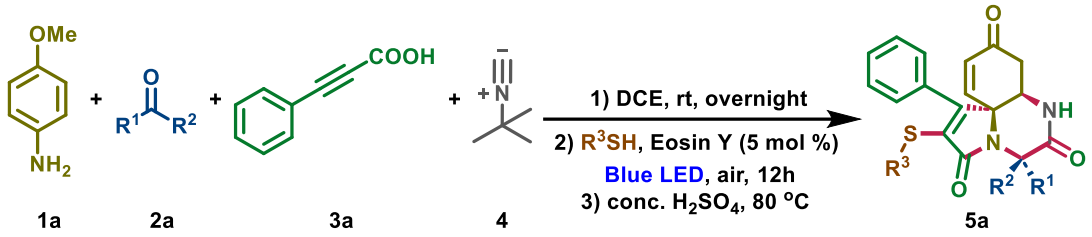
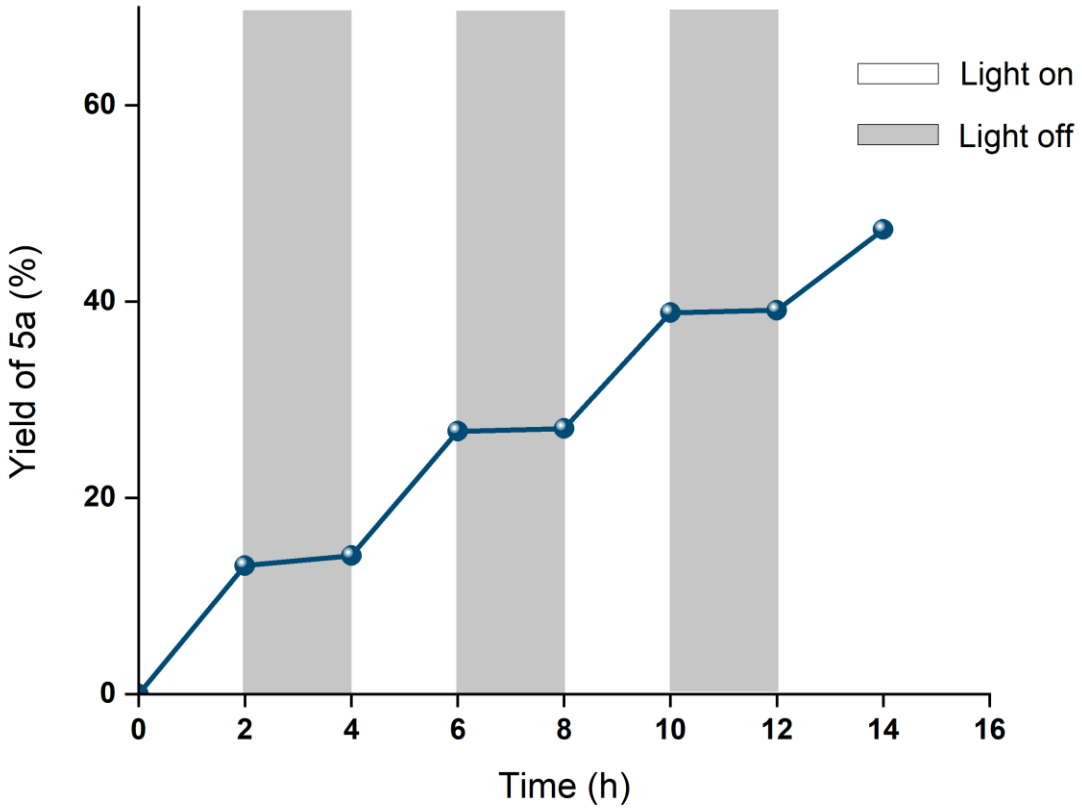


Table 1 Crystal data and structure refinement for cmrv-sk-969_mo.	
Identification code	**cmrv-sk-969**_mo
Empirical formula	$C_{116}H_{84}Br_4N_8O_{12}S_4$
Formula weight	2229.79
Temperature/K	150.0
Crystal system	triclinic
Space group	P-1
a/Å	13.7999(4)
b/Å	15.4016(4)
c/Å	27.5518(8)
α/°	87.085(2)
β/°	81.887(2)
γ/°	82.628(2)
Volume/Å^3	5746.1(3)
Z	2
ρ_{calc}g/cm^3	1.289
μ/mm^{-1}	1.534
F(000)	2272.0
Crystal size/mm^3	0.201 × 0.109 × 0.062
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.004 to 50
Index ranges	-16 ≤ h ≤ 16, -18 ≤ k ≤ 18, -32 ≤ l ≤ 32
Reflections collected	110890
Independent reflections	20233 [R_{int} = 0.0958, R_{sigma} = 0.0742]
Data/restraints/parameters	20233/0/1297
Goodness-of-fit on F^2	1.031
Final R indexes [I>=2σ (I)]	R_1 = 0.0701, wR_2 = 0.1801
Final R indexes [all data]	R_1 = 0.1060, wR_2 = 0.2101
Largest diff. peak/hole / e Å^{-3}	3.34/-0.86

Light on/off experiment



To study the necessity of continuous irradiation with visible light for the progress of.the reaction, a reaction was carried out with succesive irradiation and blank periods. The following standard reaction procedure was followed: In a reaction tube equipped with a magnetic stirring bar was added benzaldehyde **2a** (21 μL, 0.2 mmol, 1.0 equiv) and *p*-anisidine **1a** (24.6 mg, 0.2 mmol, 1.0 equiv) in DCE (2mL) and stirred at rt for 5 mins. Phenylpropiolic acid **3a** (30 mg, 0.2 mmol, 1.0 equiv) and *tert*-butyl isocyanide **4** (22 μL, 0.2 mmol, 1.0 equiv) were added all at once and resulting solution was stirred at room temperature for 12 hrs. After completion of the reaction (TLC control), 4-chlorothiophenol **5a** (58 mg, 0.4 mmol, 2.0 equiv) and eosin Y (6.4 mg, 0.01 mmol, 5 mol%) were added, the contents were irradiated under blue LED's at room temperature in air for corresponding intervals. Then ^{1}H NMR of the sample was taken to determine the yields of the corresponding spirocyclized product with 1,3,5-trimethoxybenzene as an internal standard. The grey boxes represent the periods in which the reaction tube was covered (dark period). These findings highlighted the importance of blue LEDs irradiation for the success of spirocyclization at room temperature, while showing that constant irradiation is required for effective product formation.



Quantum Yield measurement for Ugi/Radical Spirocyclization/Aza-Michael product

Determination of the photon flux

The photon flux of a single blue LED (40 W, λ_{max} = 454 nm) was determined by ferrioxalate actinometry following a literature procedure. For this purpose, the following two solutions were prepared:

Solution A:

Potassium ferrioxalate hydrate (737 mg, 1.50 mmol) was dissolved in aq. H_2SO_4 (0.05 M, 10 mL) to afford a 0.15 M ferrioxalate solution.

Solution B:

1,10-Phenanthroline monohydrate (20 mg, 0.10 mmol), and NaOAc (2.71 g, 41.3 mmol) were dissolved in aq. H_2SO_4 (0.5 M, 20 mL).

Notice: Solution A was prepared in the dark and both solutions were stored in the dark to avoid external irradiation prior to the actinometry. The following procedure was performed in a darkened lab.

First, the photon flux of the 454 nm LED was determined. For this, solution A (1.0 mL) was filled in a reaction tube and irradiated for 60 s, at λ_{max} = 454 nm. After irradiation, solution B (175 µL) was added to the same reaction tube, and the mixture was stirred in the dark for 1 h to ensure coordination of Fe(II)- ions by phenanthroline. The solution was poured into a quartz cuvette and the absorption of the solution was measured at 510 nm. Sample preparation and measurement were repeated two more times. In a similar way a non-irradiated control sample was prepared, measured for absorbance at 510 nm, which was repeated twice. The average of the absorption of the both irradiated and radiated samples were calculated and were used to calculate the conversion factor n applying eq. 1.

$$n(\mathrm{Fe}^{+2}) = \frac{V \Delta A(510nm)}{l.\varepsilon} \quad (1)$$

V refers to the total volume (0.001175 L) of the solution (after addition of solution B), *ΔA* is the average difference in absorption of irradiated and non-irradiated samples between at 510 nm, *l* is the path length (1.0 cm) of the cuvette, and *ε* is the molar extinction coefficient of the ferrioxalate actinometer at 510 nm (11,100 L mol−1 cm−1). The photon flux (Φ_q) is calculated using eq. 2.

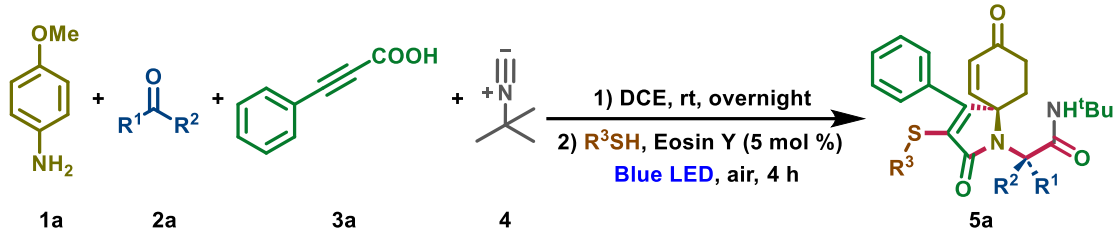
$$\Phi q = \frac{n(Fe^{+2})}{\Phi_F t.f} \quad (2)$$

Φ_F refers to the quantum yield for the ferrioxalate actinometer (0.92 at λ_{ex} = 468 nm), *t* is the irradiation time for solution A (60 s), and *f* is the fraction of light absorbed at λ_{ex} = 454 nm by the ferrioxalate actinometer. This value is calculated using eq. 3, where *A*(454 nm) is the absorption of the ferrioxalate solution at 454 nm. A measured absorbance value of 1.00753 at 454 nm indicates the fraction of absorbed light (*f*) to be around 0.9.

$$f = 1 - 10^{-A(454nm)} \quad (3)$$

Thus, the average photon flux was calculated to be 2.73×10^{-9} Einsteins s^{-1}.

Determination of Quantum Yield of Ugi/Radical Spirocyclization/Aza-Michael product

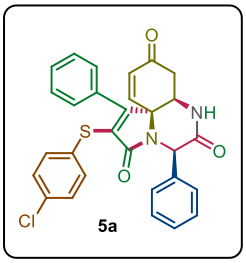


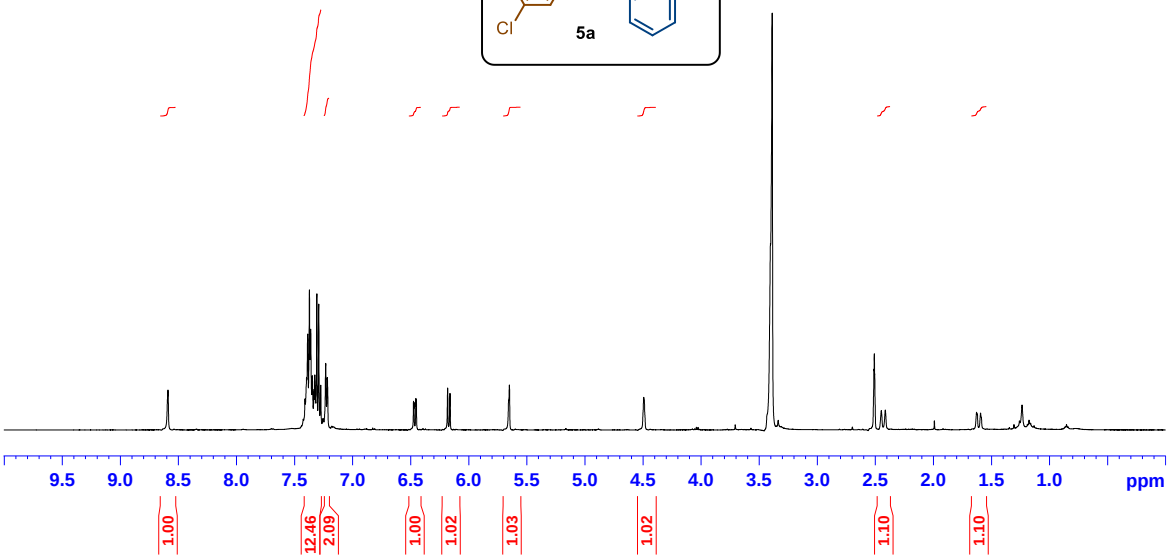
To an oven-dried reaction tube was added *p*-anisidine **1a** (24.63 mg, 0.2 mmol, 1.0 equiv.), benzaldehyde **2a** (21.22 mg, 0.2 mmol, 1 equiv.), 3-phenylpropiolic acid **3a** (29.22 mg, 0.2 mmol, 1 equiv.), tert-butyl isocyanide **4a** (16.26 mg, 0.2 mmol, 1 equiv.), 4-chlorothiophenol **5a** (57.66 mg, 0.4 mmol, 2 equiv.), Eosin Y (6.91 mg, 0.01 mmol, 5 mol%) and DCE (2 mL). The tube was sealed and placed 2 cm away from the blue LED. After irradiation for 4 hours, the yield of the product was determined by ^{1}H NMR using *1,3,5-trimethoxybenzene* as the internal standard. Thus, the average yield was calculated to be 15% (0.03 mmol). The quantum yield (Φ) of the reaction was determined using eq. 4, where the photon flux (Φ_q) is 2.73×10^{-9} Einsteins s^{-1} (see above), t is the reaction time (4 h = 14400 s) and f_R is the fraction of light absorbed by the reaction mixture (indicated in eq. 3; A_{Rct} (454 nm) = 0.97) determined using eq. 4.

$$\Phi = \frac{n(product)}{\Phi q.t.f_R} \qquad (4)$$

Thus, the quantum yield (Φ) of the product was determined to be: Φ = 0.85, suggesting that a photo-induced reaction has occurred.

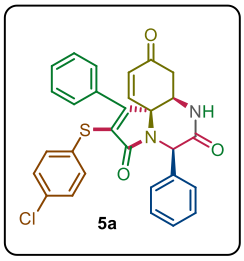
CMRV-SK-968-1H



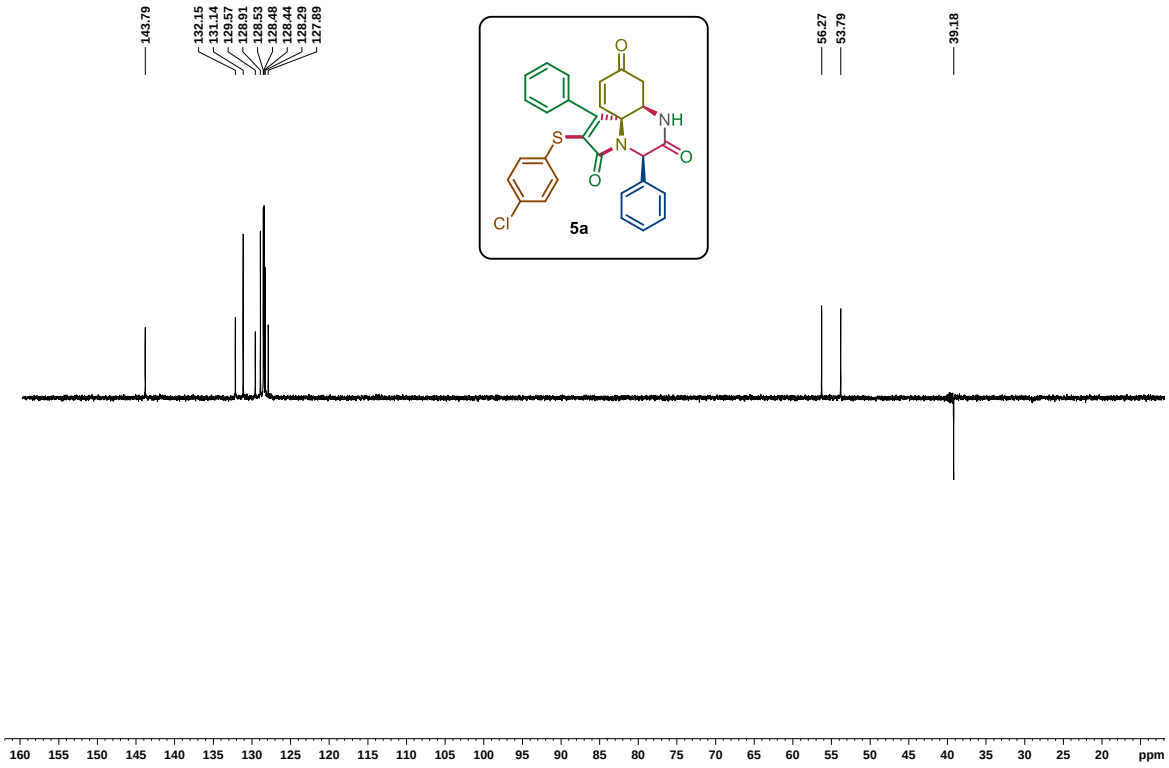


CMRV-SK-968-13C

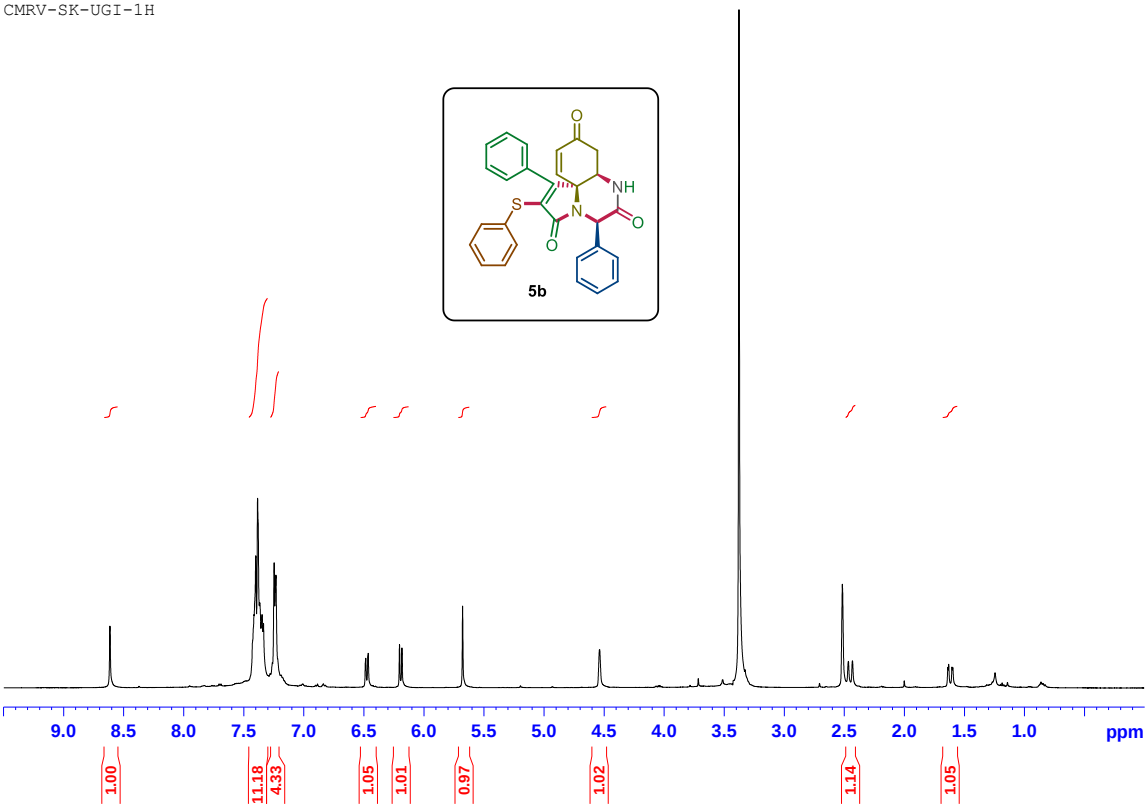
193.80
166.40
165.59
157.91
143.79
137.77
132.14
131.68
131.60
131.13
129.72
129.56
128.90
128.53
128.48
128.44
128.28
127.88
64.05
56.26
53.78



CMRV-SK-968-DEPT



CMRV-SK-UGI-1H



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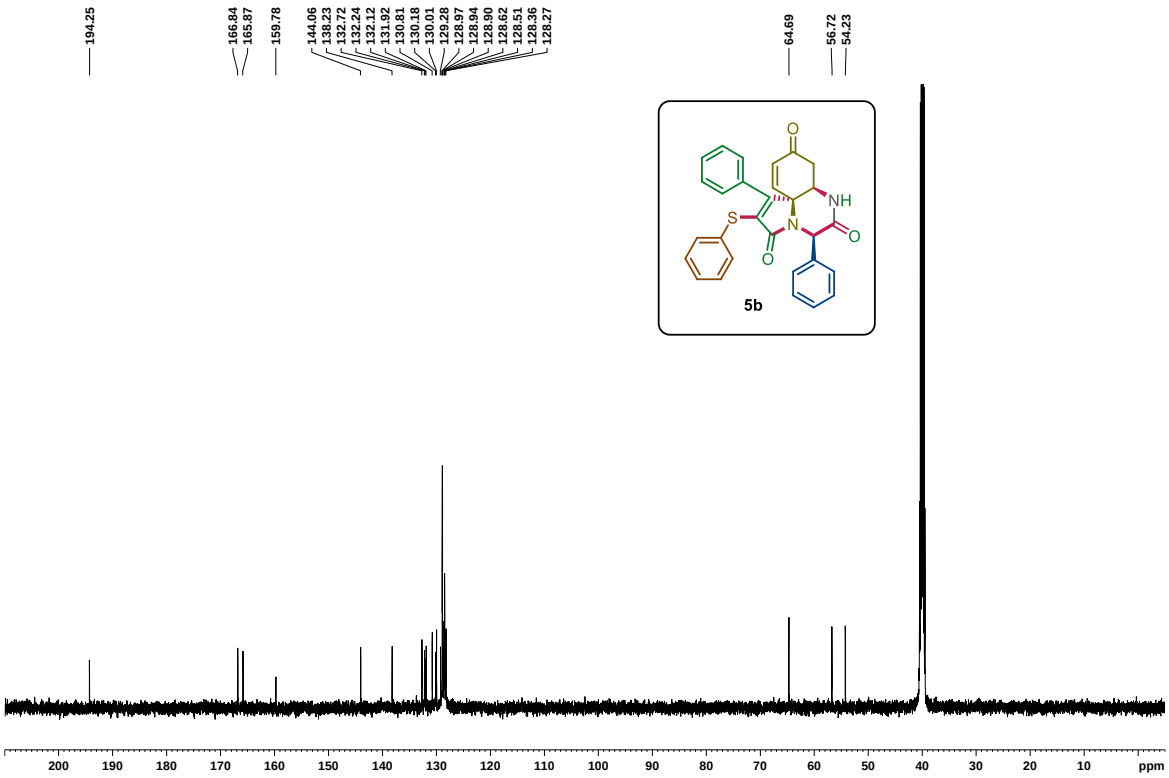

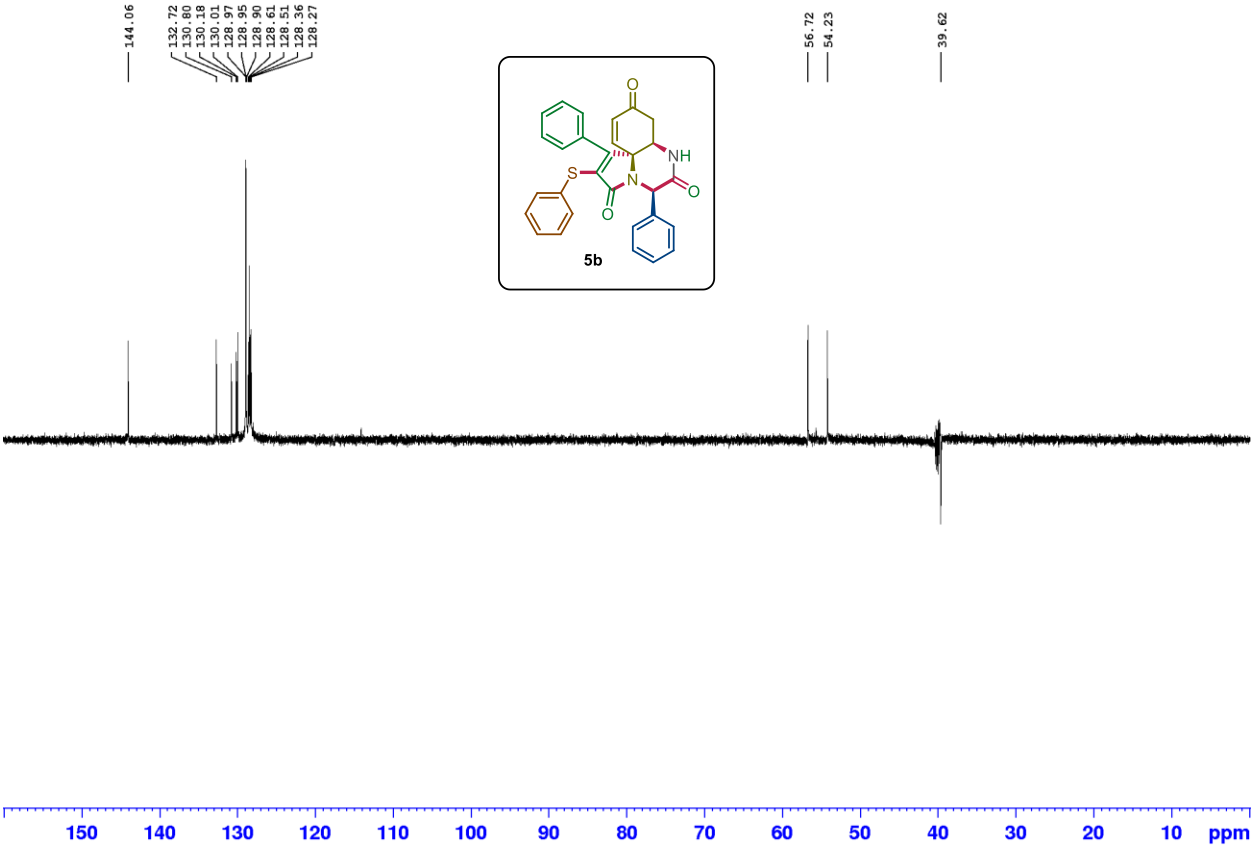
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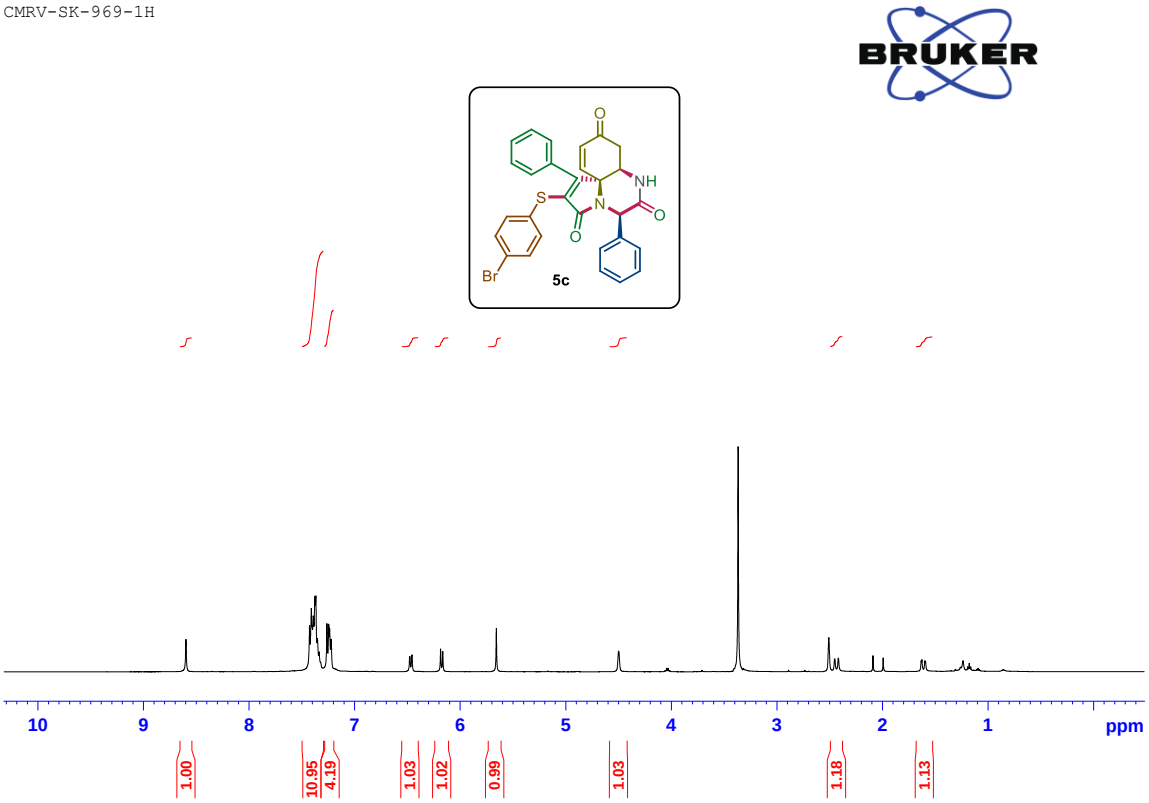
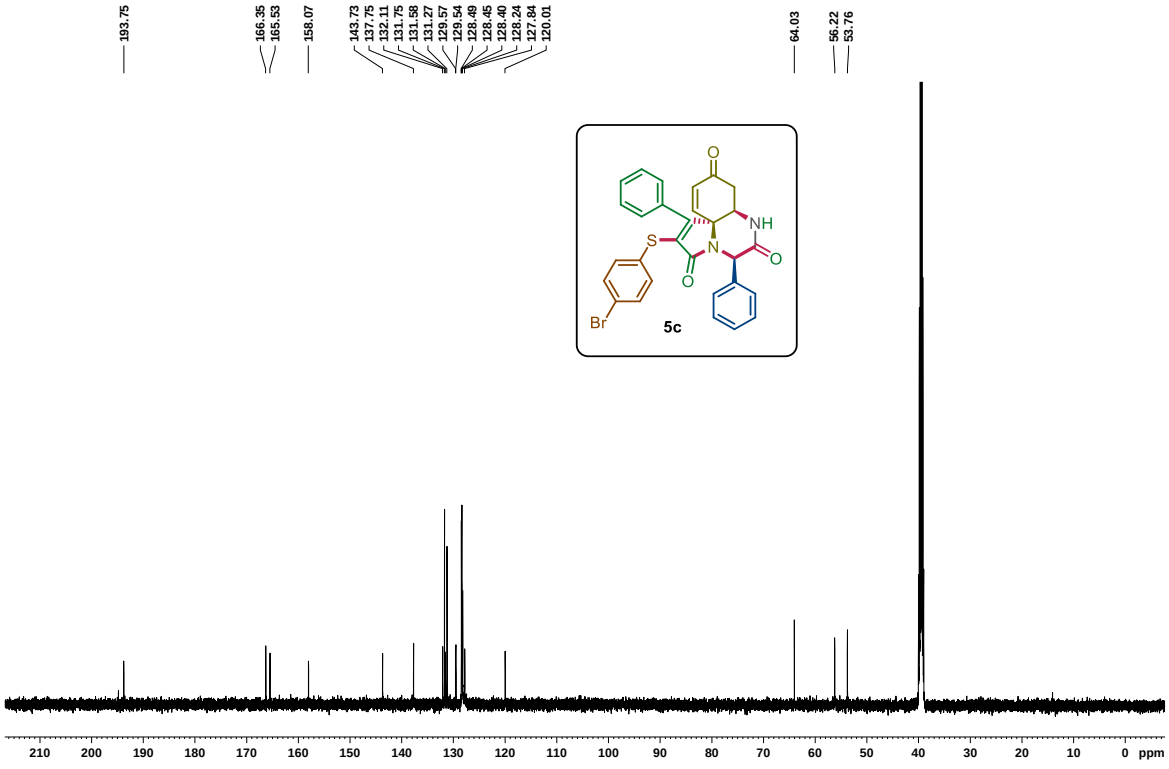
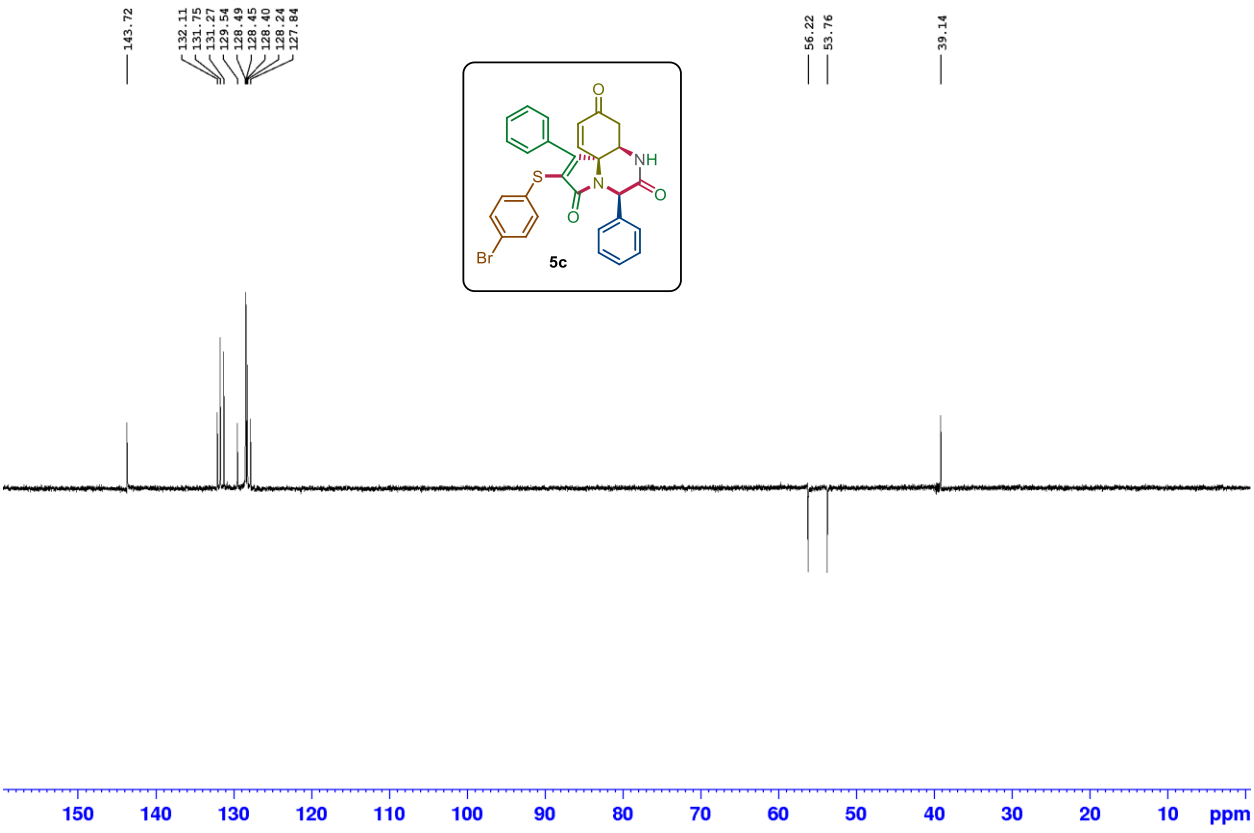
132.72
130.80
130.18
130.01
128.97
128.95
128.90
128.61
128.51
128.36
128.27
56.72
54.23
39.62
O
NH
S
N
O
O
5b
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

CMRV-SK-969-1H



CMRV-SK-969-13C

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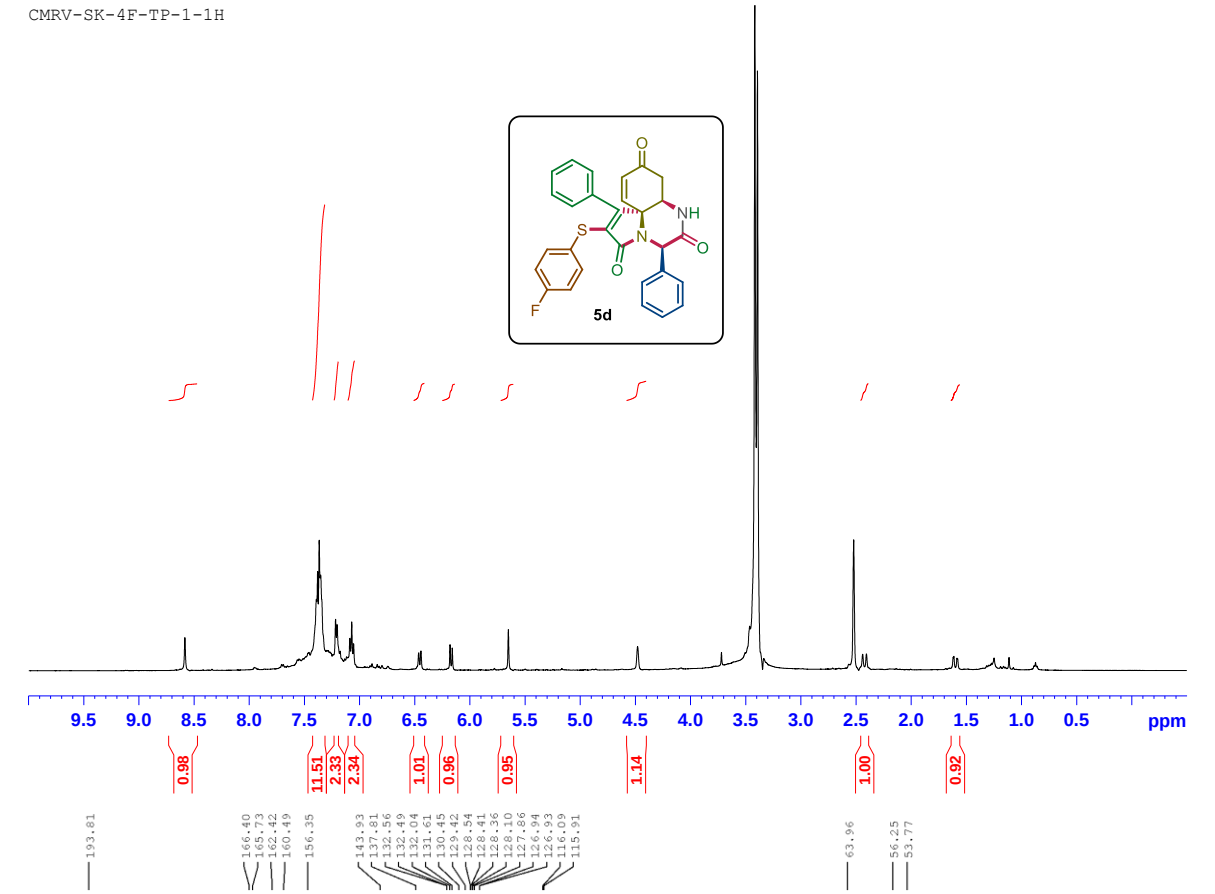
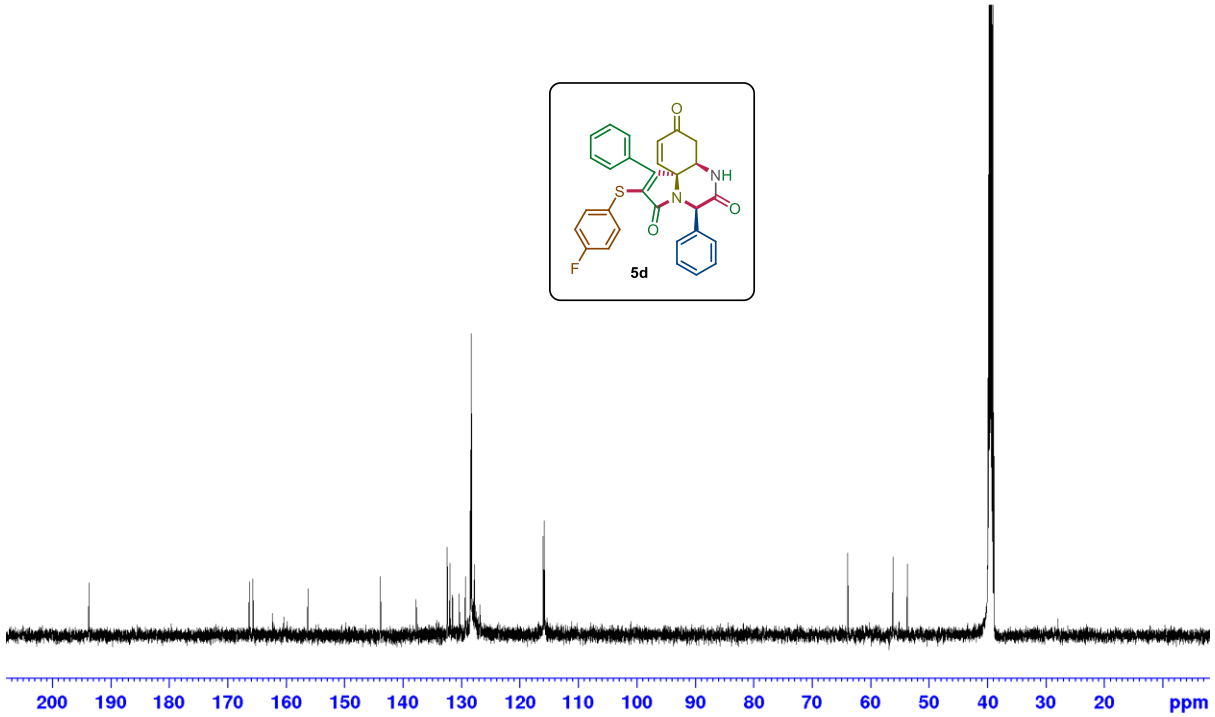
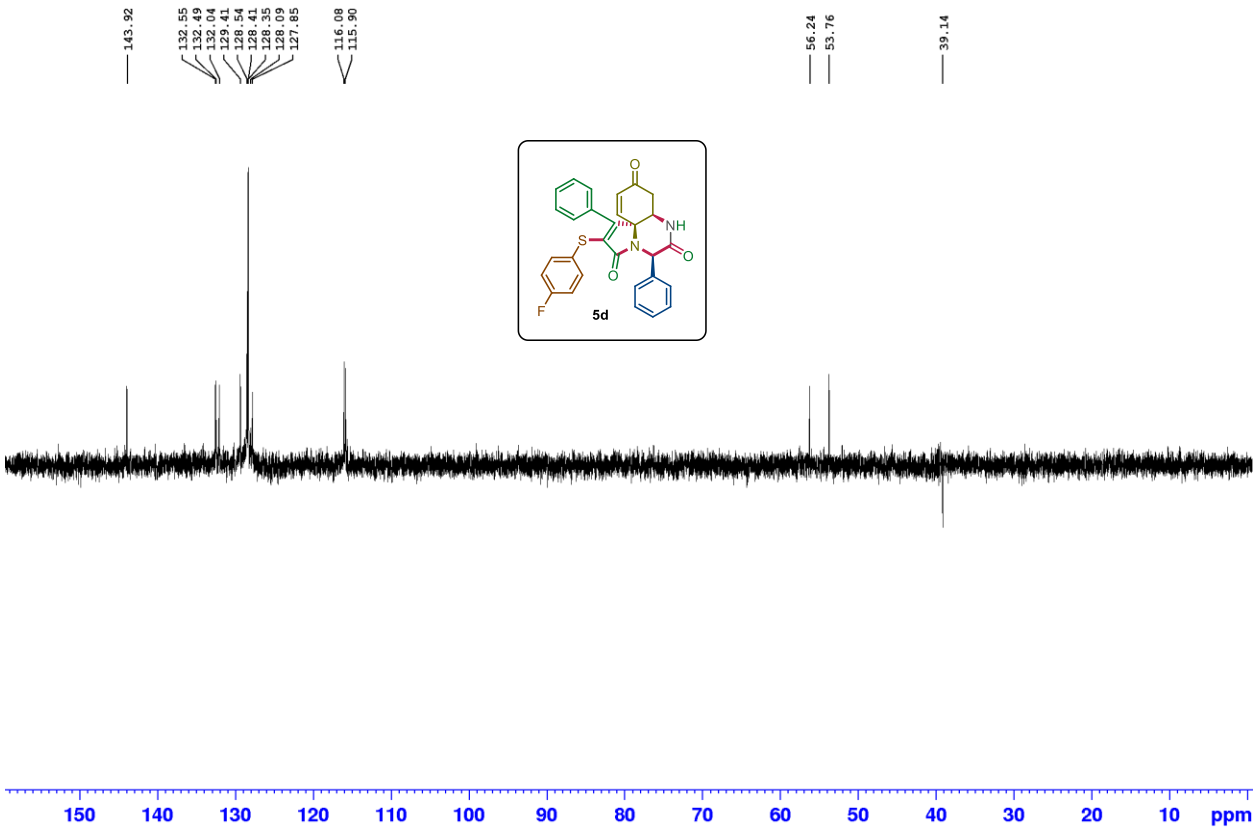
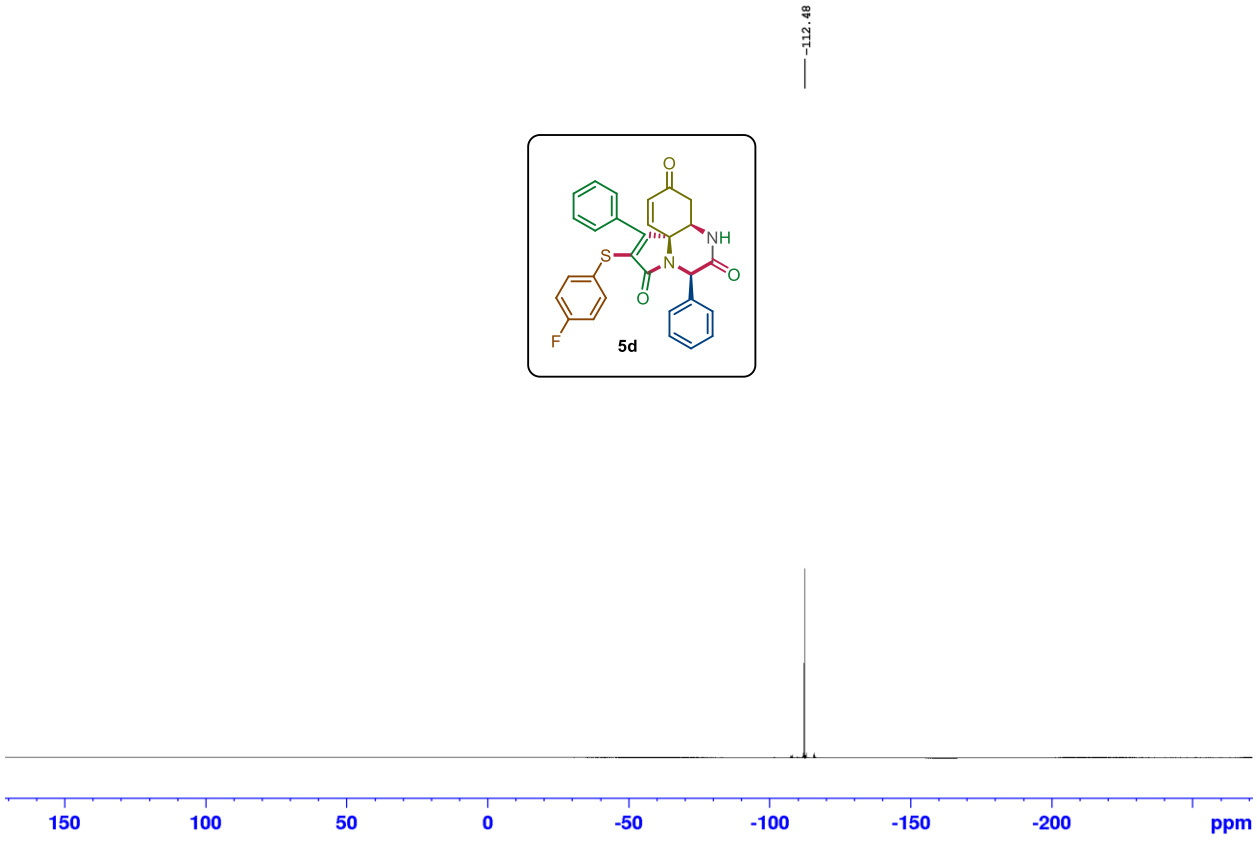
131.75
131.27
129.54
128.49
128.45
128.40
128.24
127.84
56.22
53.76
39.14
O
NH
S
N
O
O
Br
5c
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

CMRV-SK-4F-TP-1-1H






143.92
132.55
132.49
132.04
129.41
128.54
128.41
128.35
128.09
127.85
116.08
115.90
56.24
53.76
39.14
5d
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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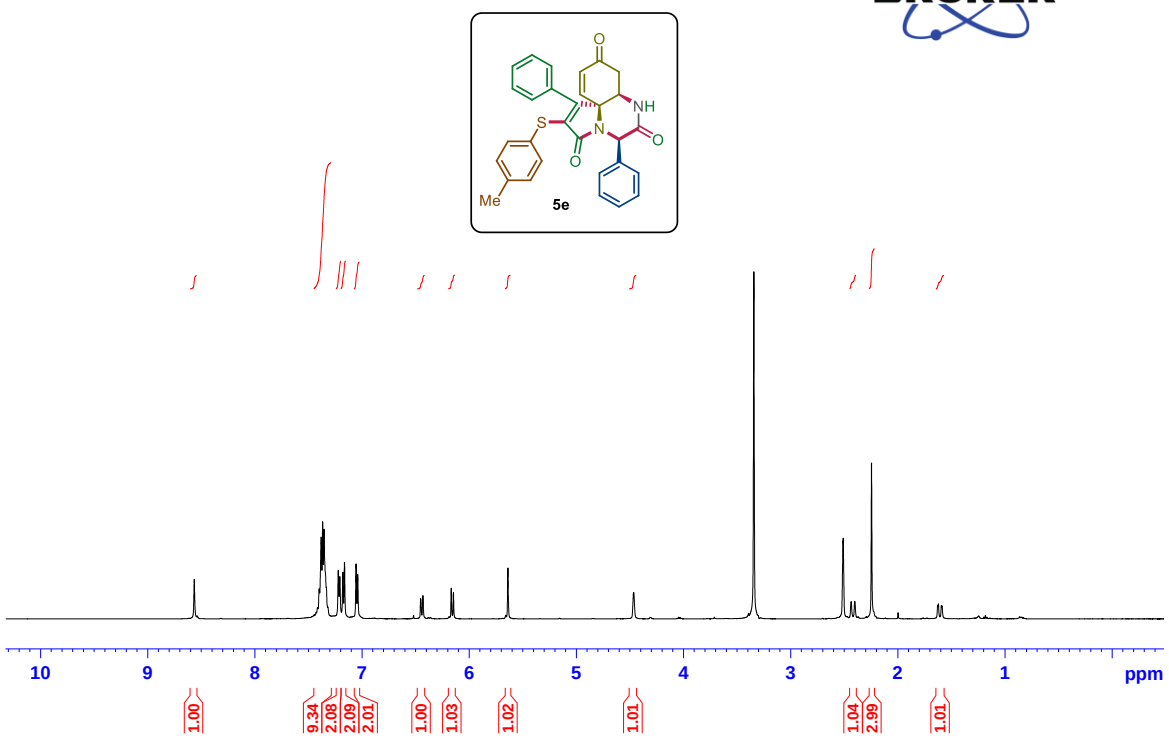
-50
-100
-150
-200
ppm

CMRV-SK-972-1H



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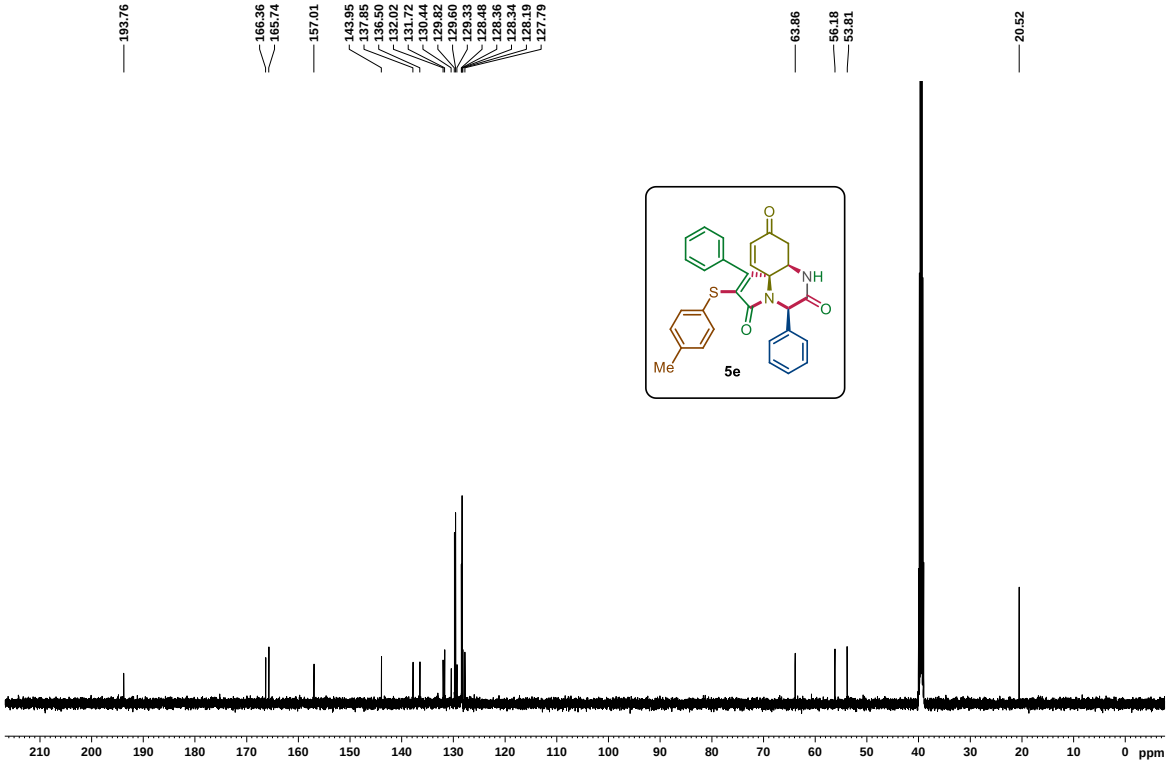

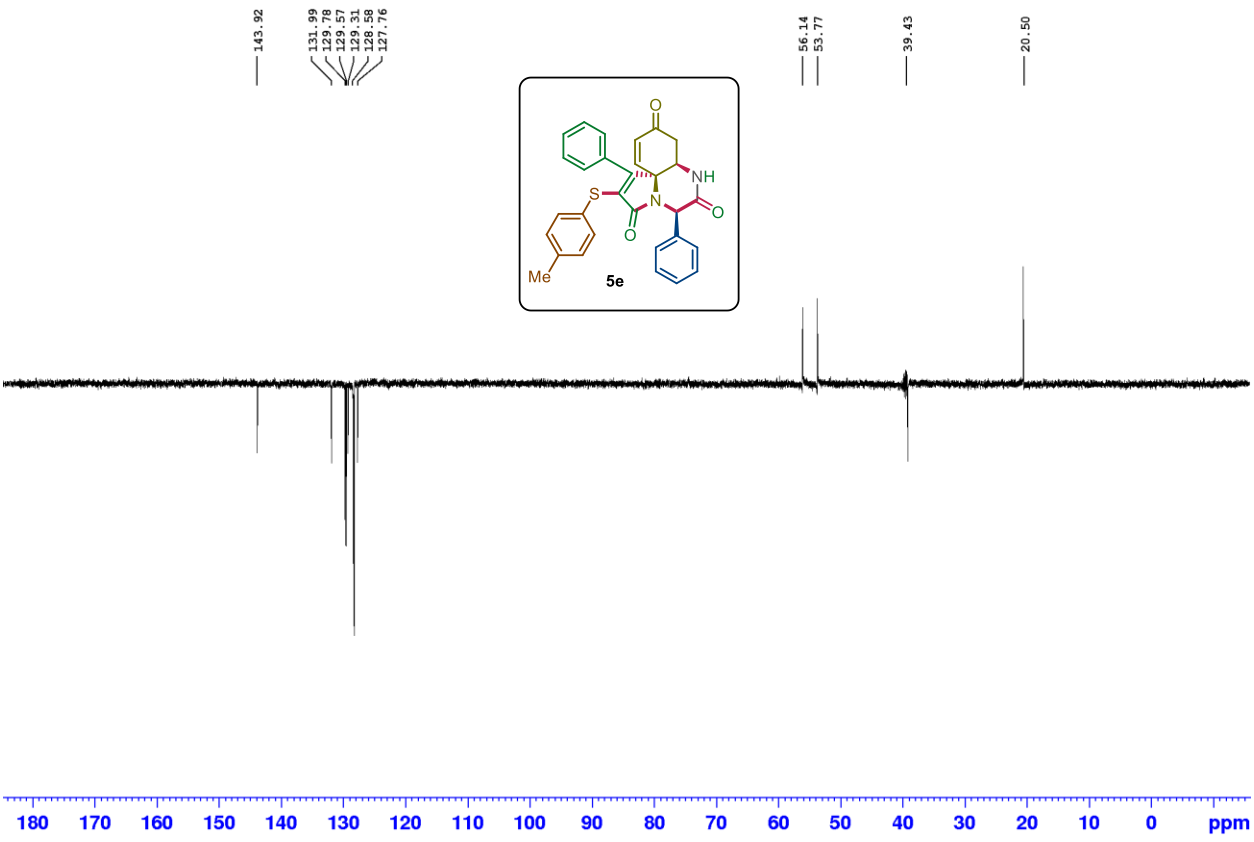
143.92
131.99
129.78
129.57
129.31
128.58
127.76
56.14
53.77
39.43
20.50
O
NH
S
N
O
O
Me
5e
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170
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150
140
130
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110
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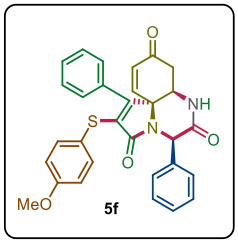
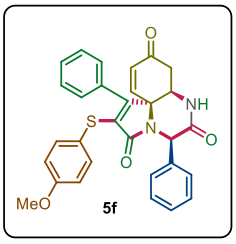
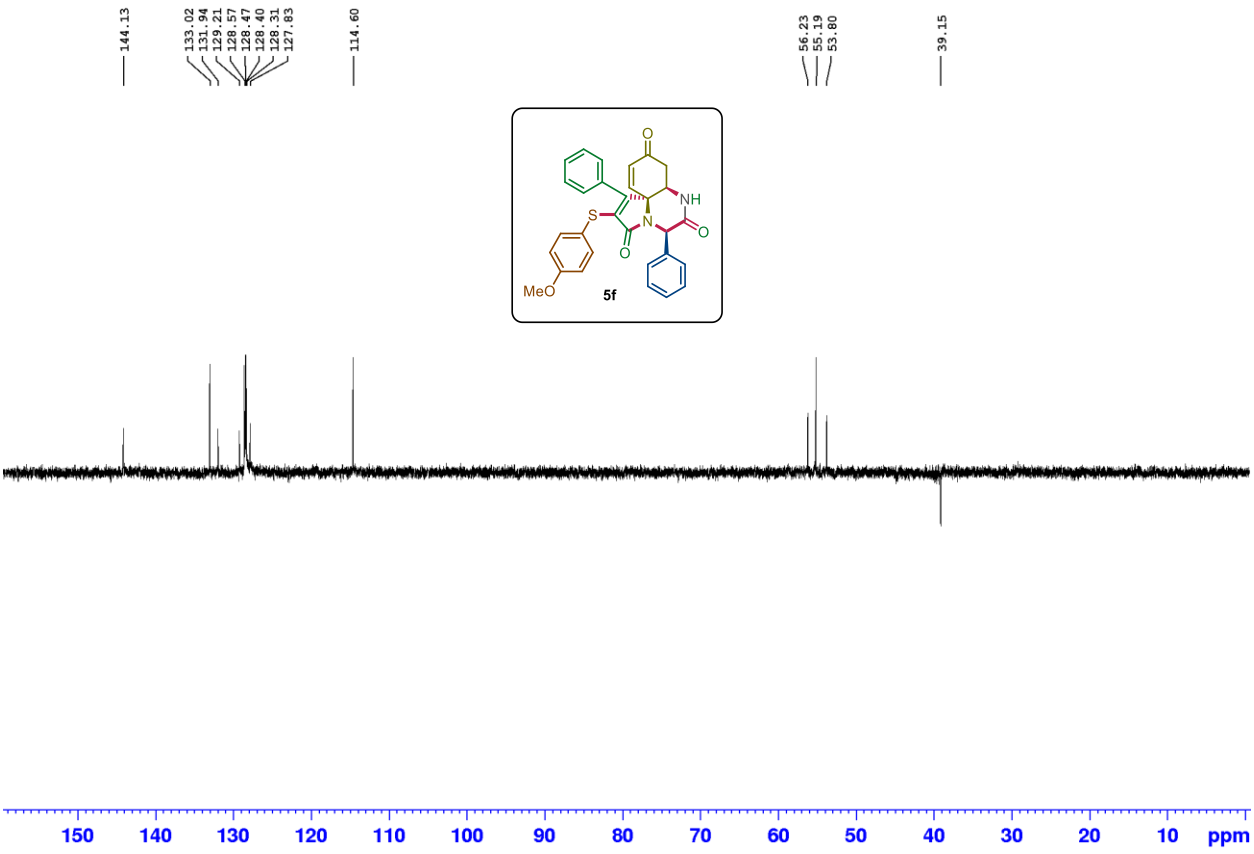
90
80
70
60
50
40
30
20
10
0
ppm



CMRV-SK-1009-13C

193.84
166.44
165.94
158.97
154.82
144.14
137.92
133.04
131.96
131.70
131.33
129.22
128.58
128.49
128.42
128.33
127.84
121.01
114.62
63.82
56.24
55.20
53.82

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133.02
131.94
129.21
128.57
128.47
128.40
128.31
127.83
114.60
56.23
55.19
53.80
39.15
O
NH
S
N
O
O
MeO
5f
150
140
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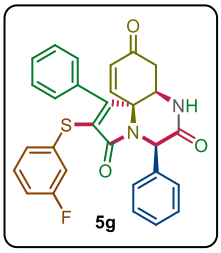
120
110
100
90
80
70
60
50
40
30
20
10
ppm

CMRV-SK-1012-1H



CMRV-SK-1012-13C

194.29
166.85
166.00
163.76
161.32
159.17
144.29
138.26
135.33
135.25
132.59
132.09
131.20
131.12
130.09
129.65
128.98
128.94
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125.30
125.27
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115.96
114.21
114.00
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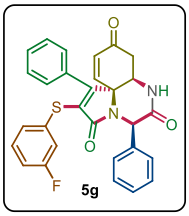
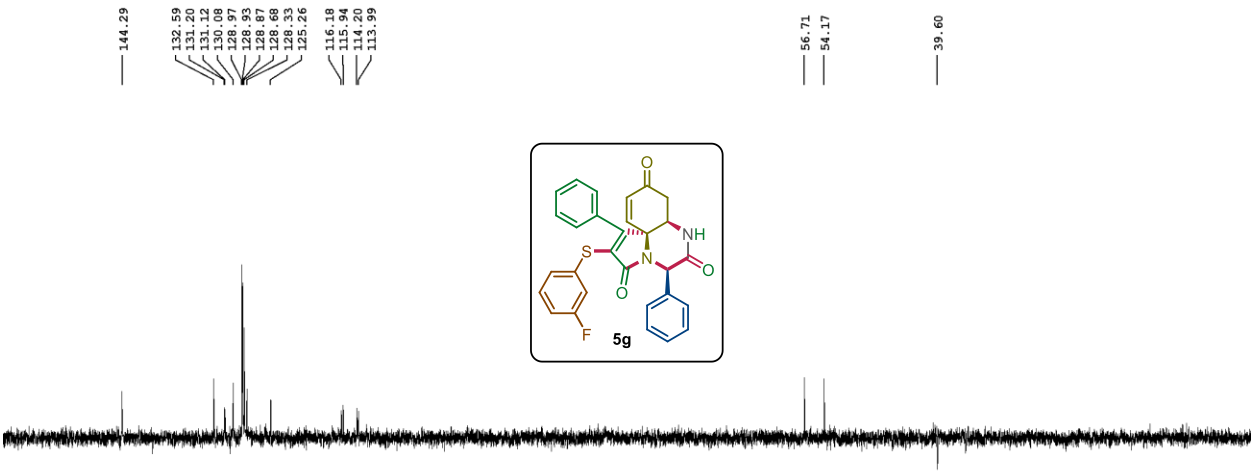
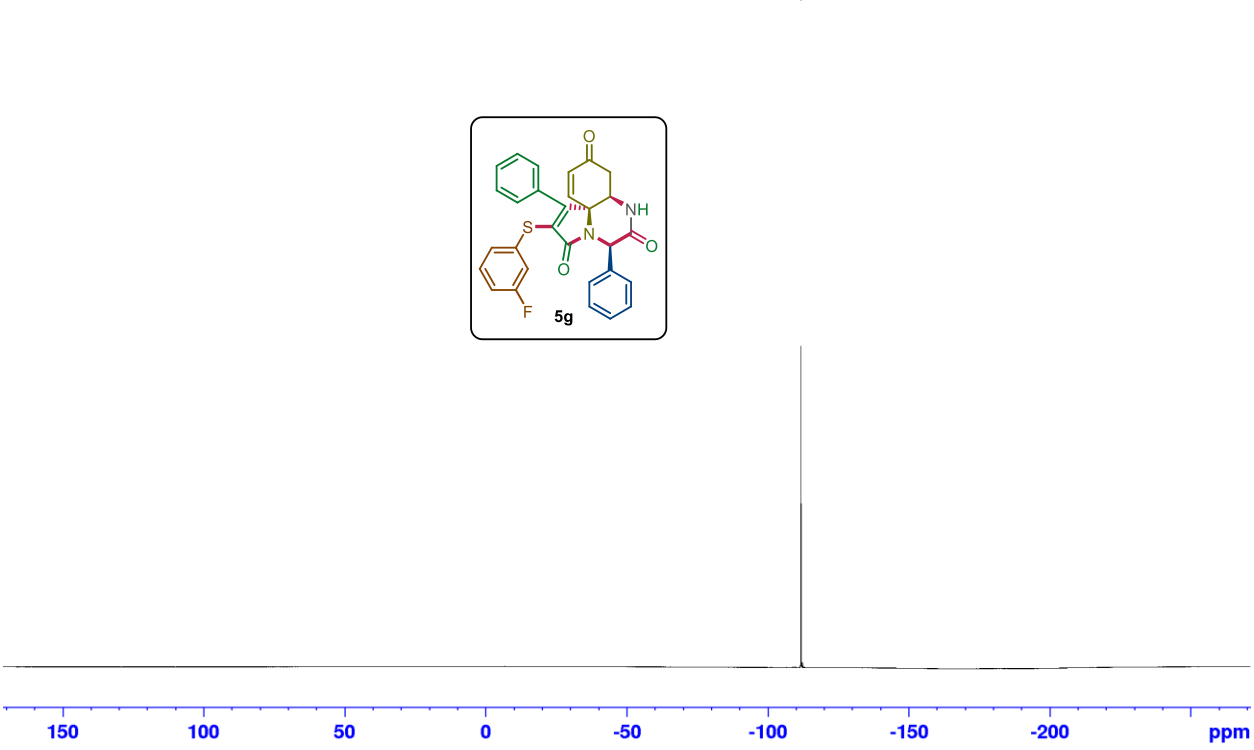
56.71
54.17





CMRV-AC-459-19F



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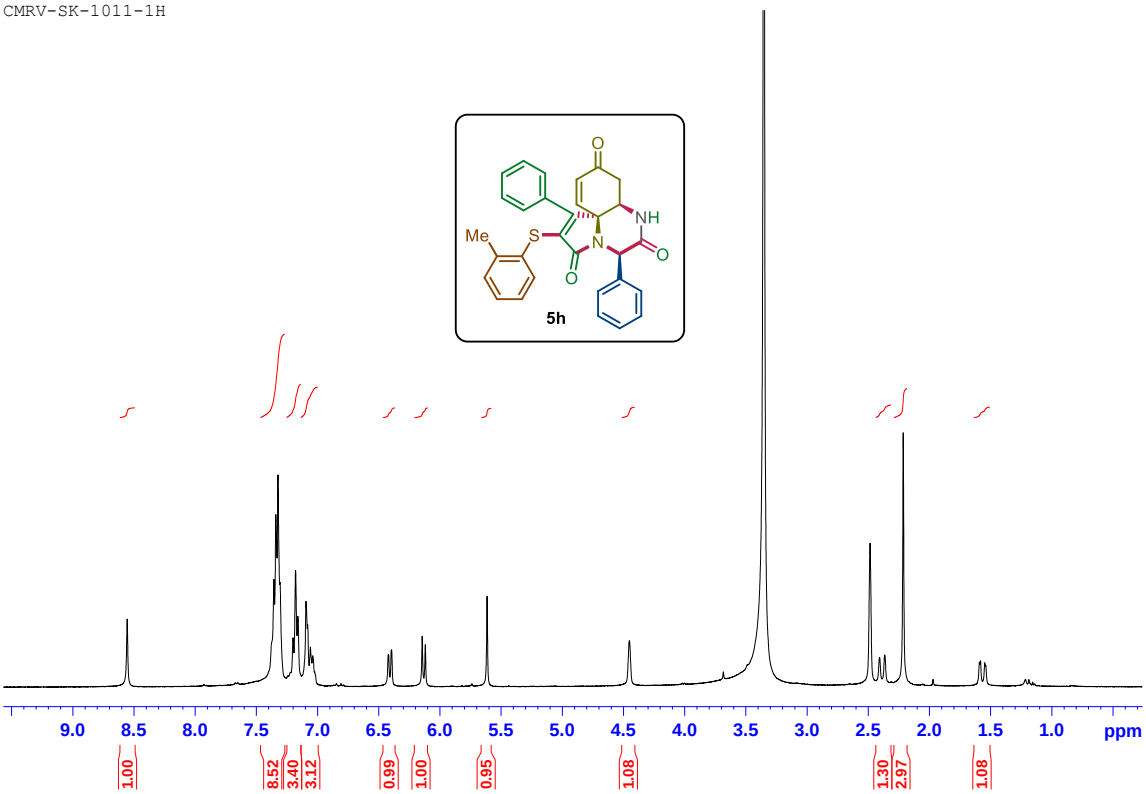

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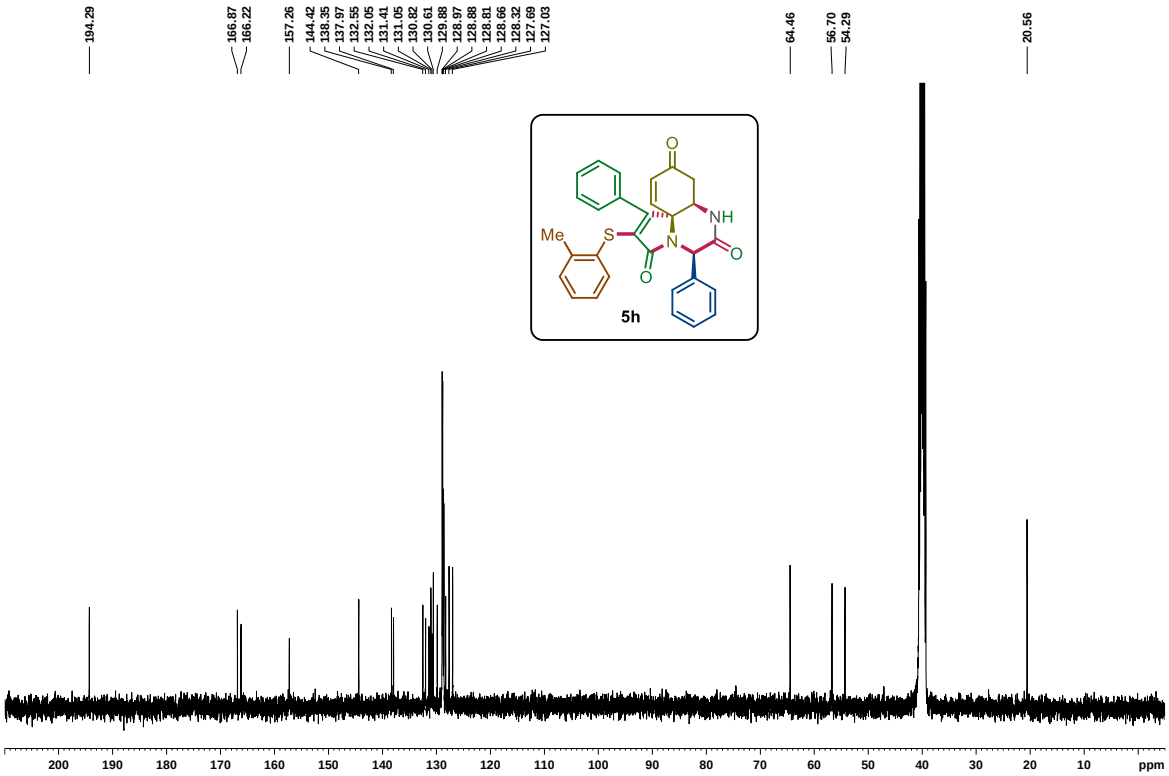

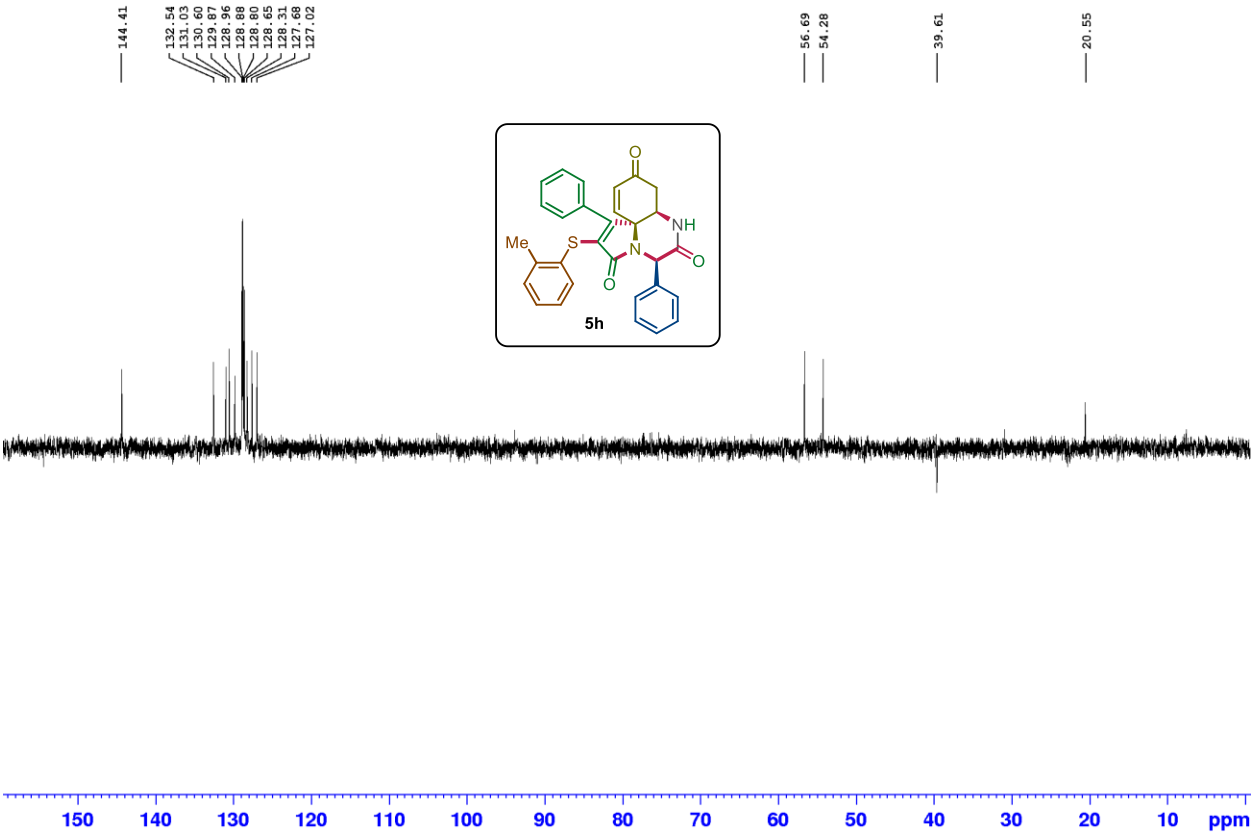
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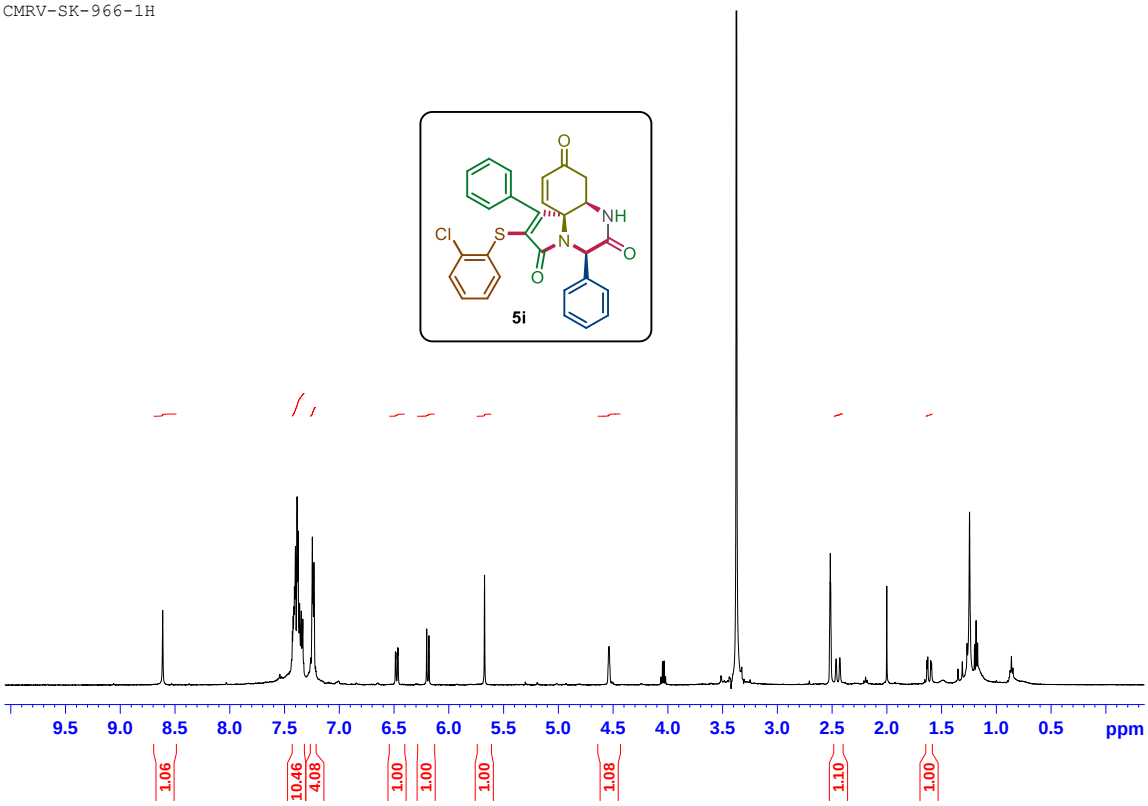
129.87
128.96
128.88
128.80
128.65
128.31
127.68
127.02
56.69
54.28
39.61
20.55
O
NH
Me
S
N
O
O
5h
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

CMRV-SK-966-1H



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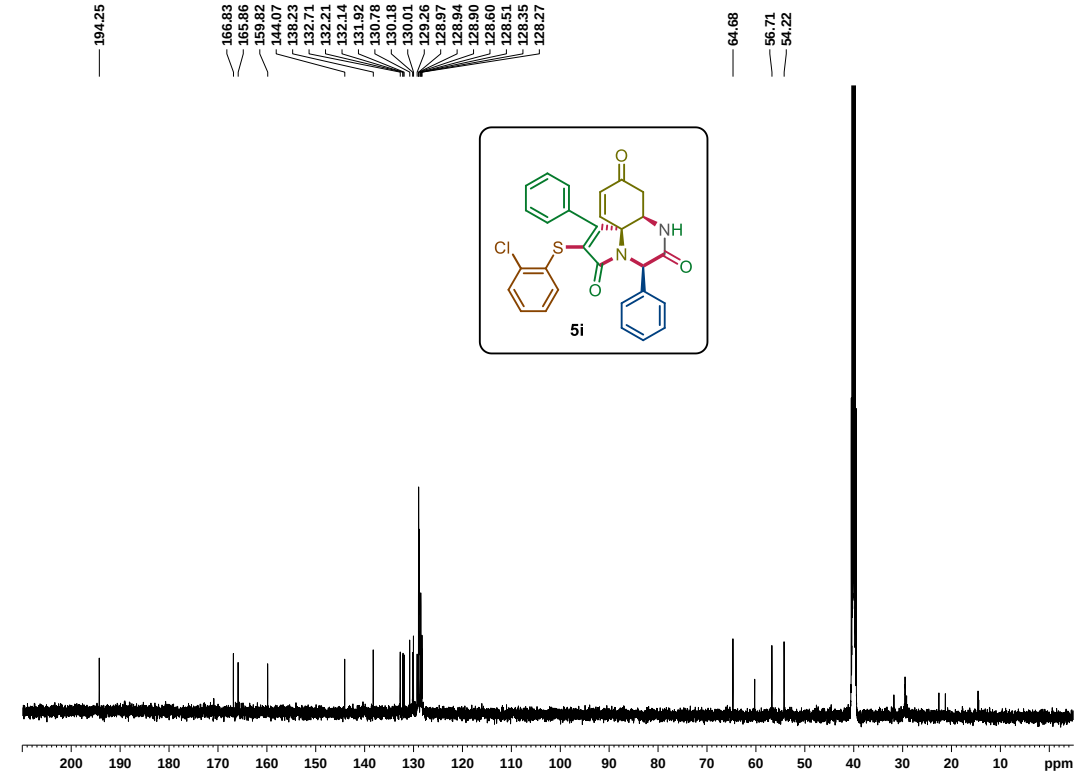

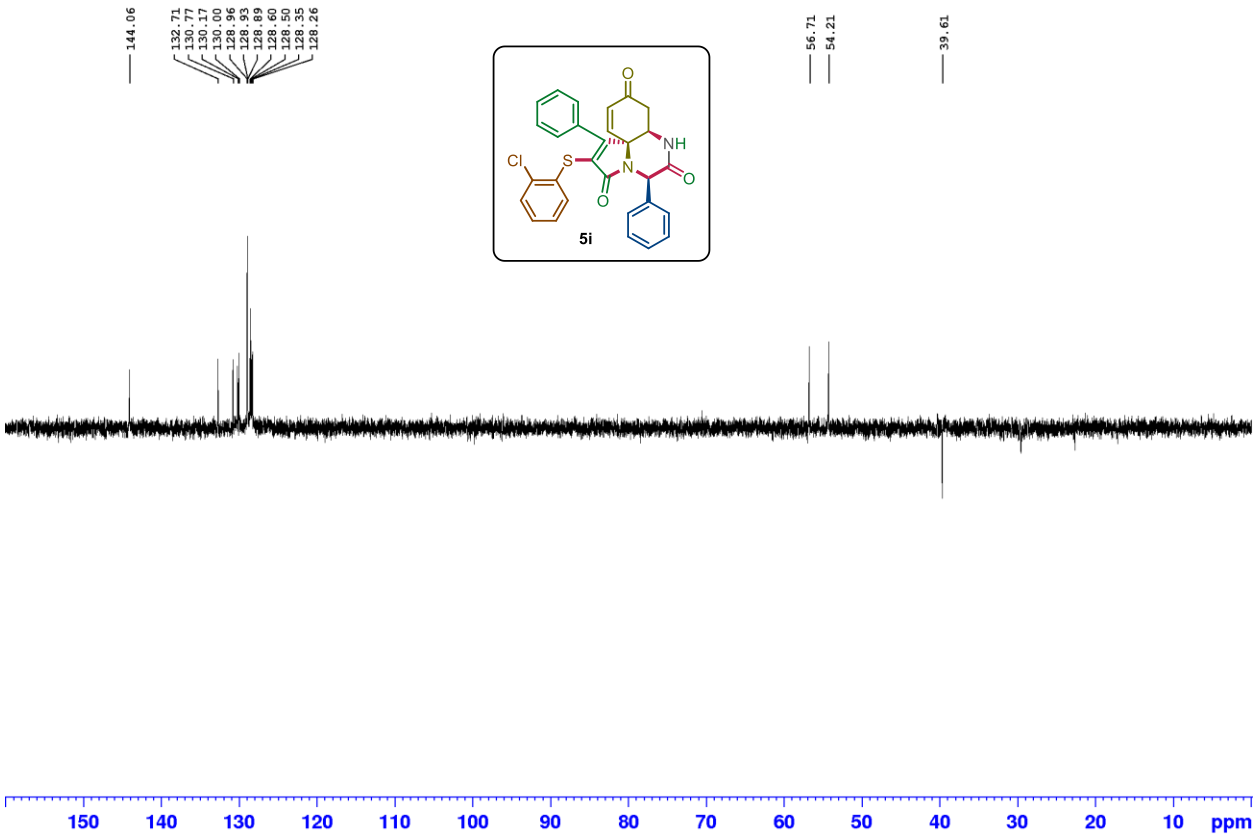
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132.71
130.77
130.17
130.00
128.96
128.93
128.89
128.60
128.50
128.35
128.26
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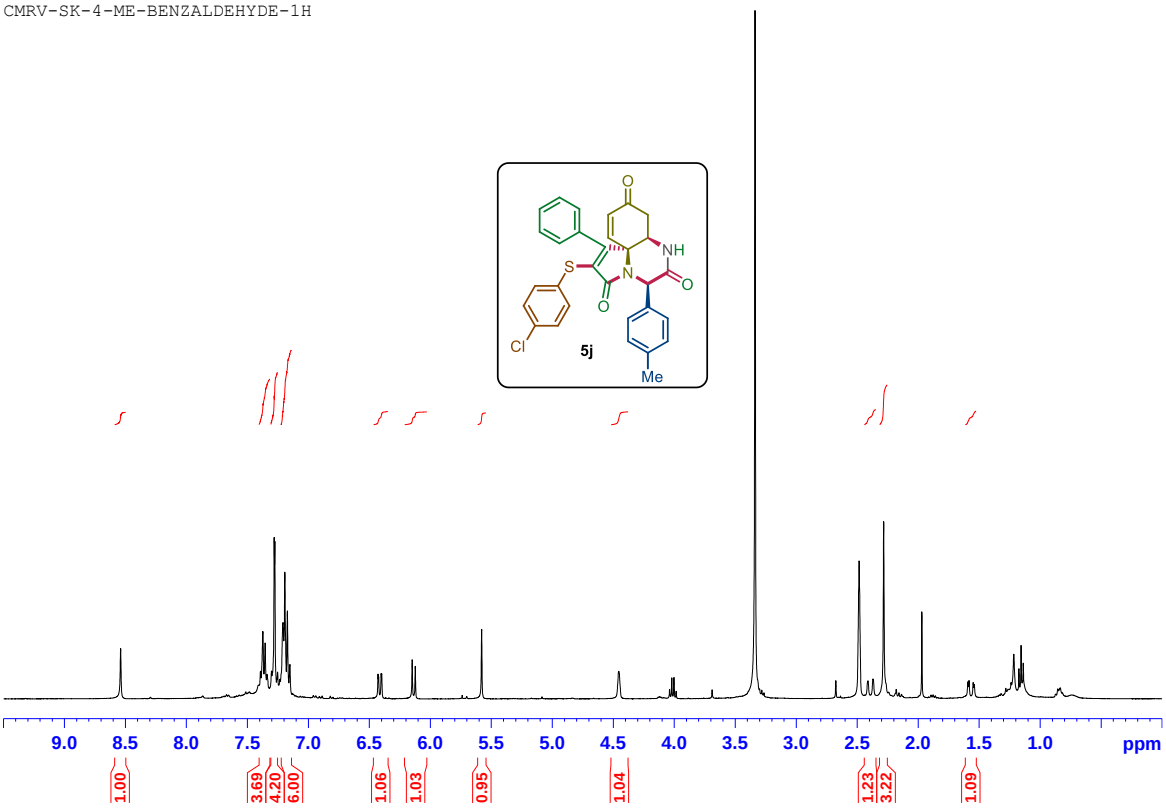
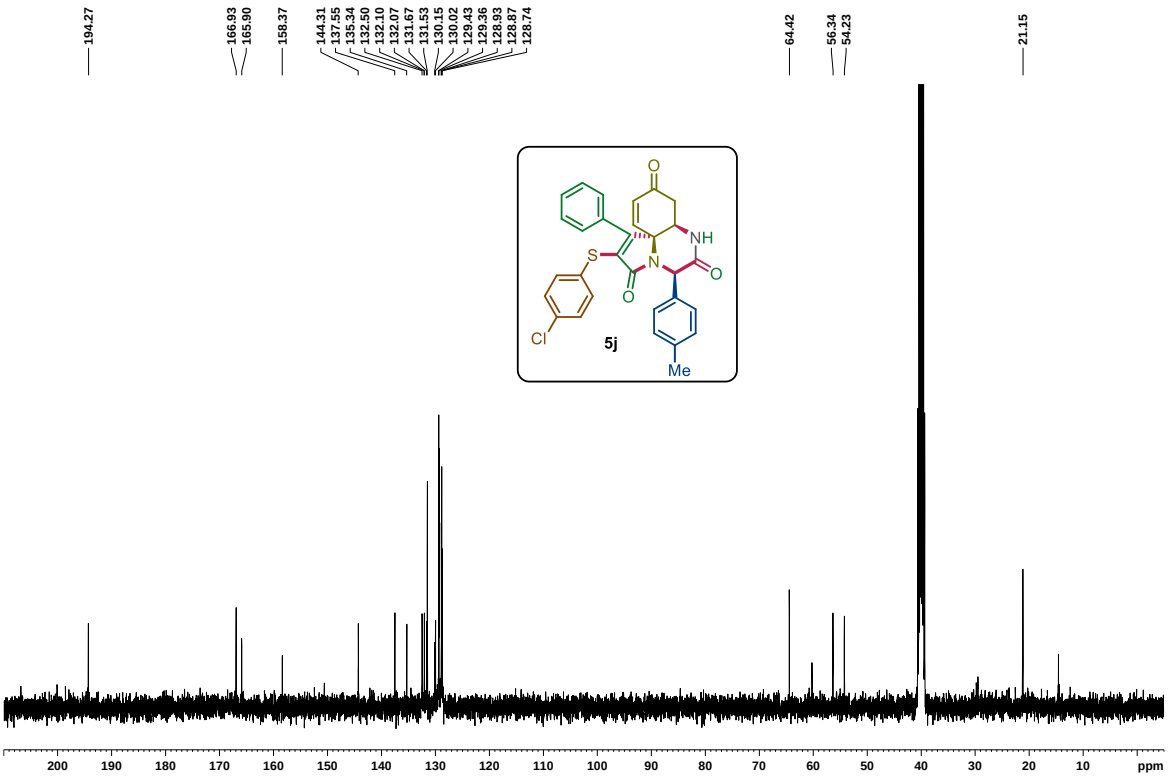
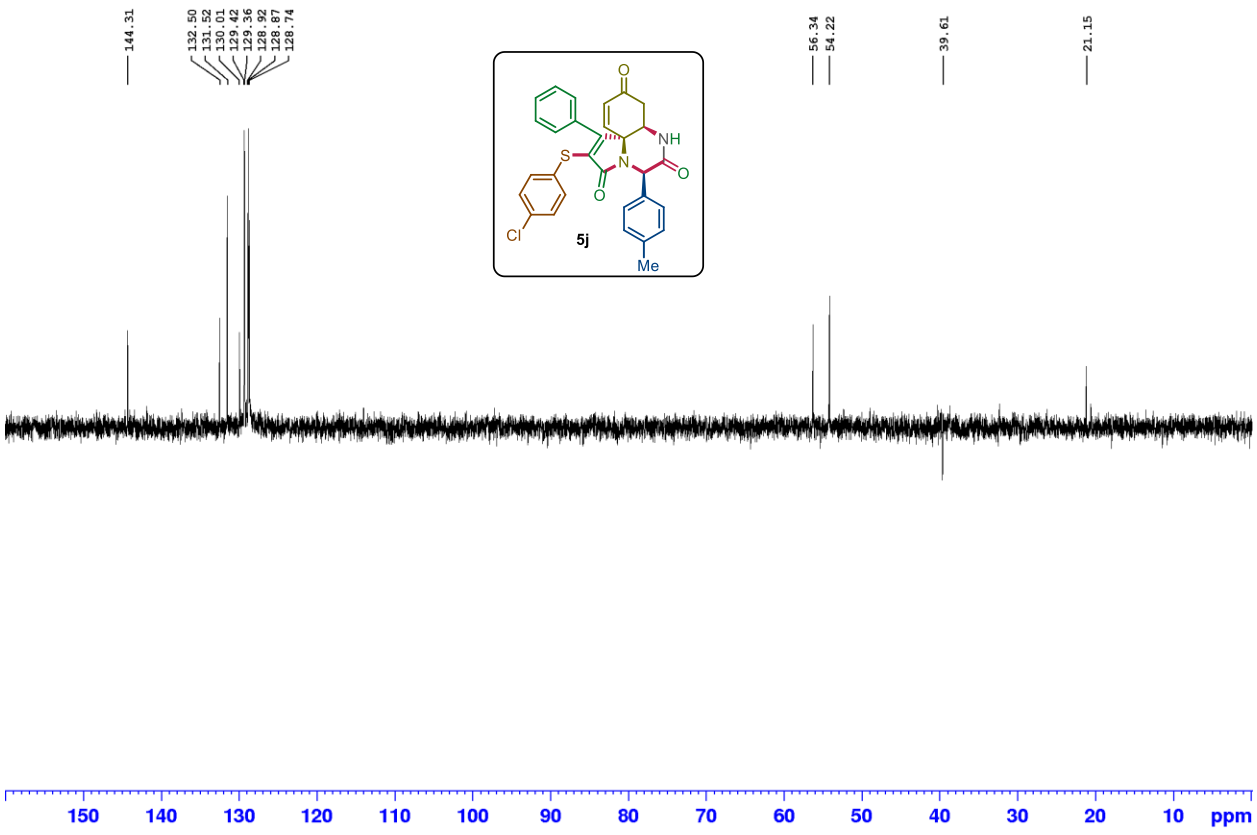
54.21
39.61
O
NH
Cl
S
N
O
O
5i
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

CMRV-SK-4-ME-BENZALDEHYDE-1H

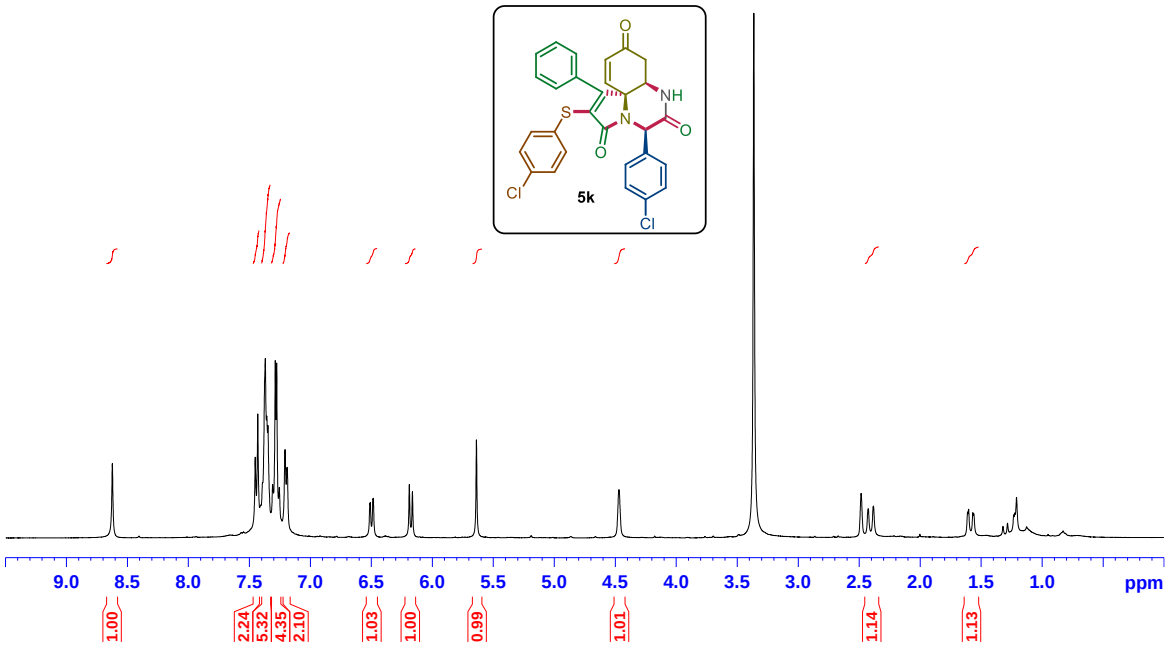


CMRV-SK-4-ME-BENZALDEHYDE-13C




144.31
132.50
131.52
130.01
129.42
129.36
128.92
128.87
128.74
56.34
54.22
39.61
21.15
O
NH
S
N
O
O
Cl
Me
5j
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

CMRV-SK-1016-1H



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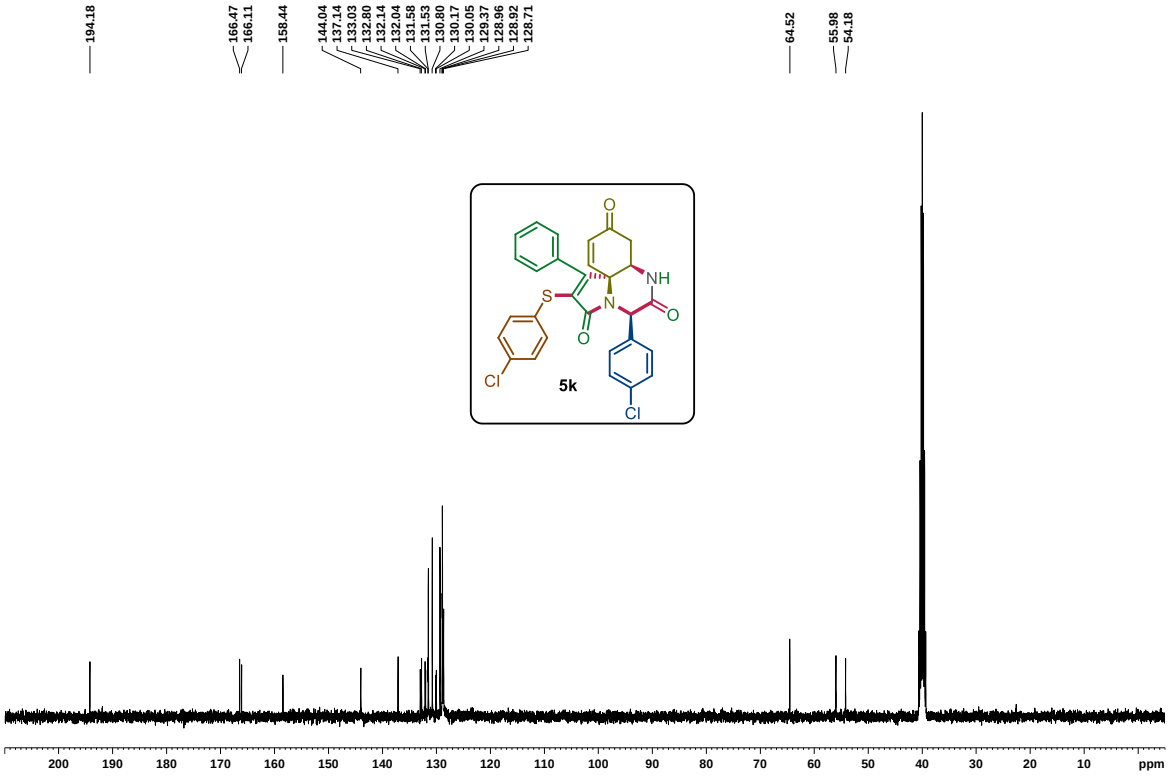

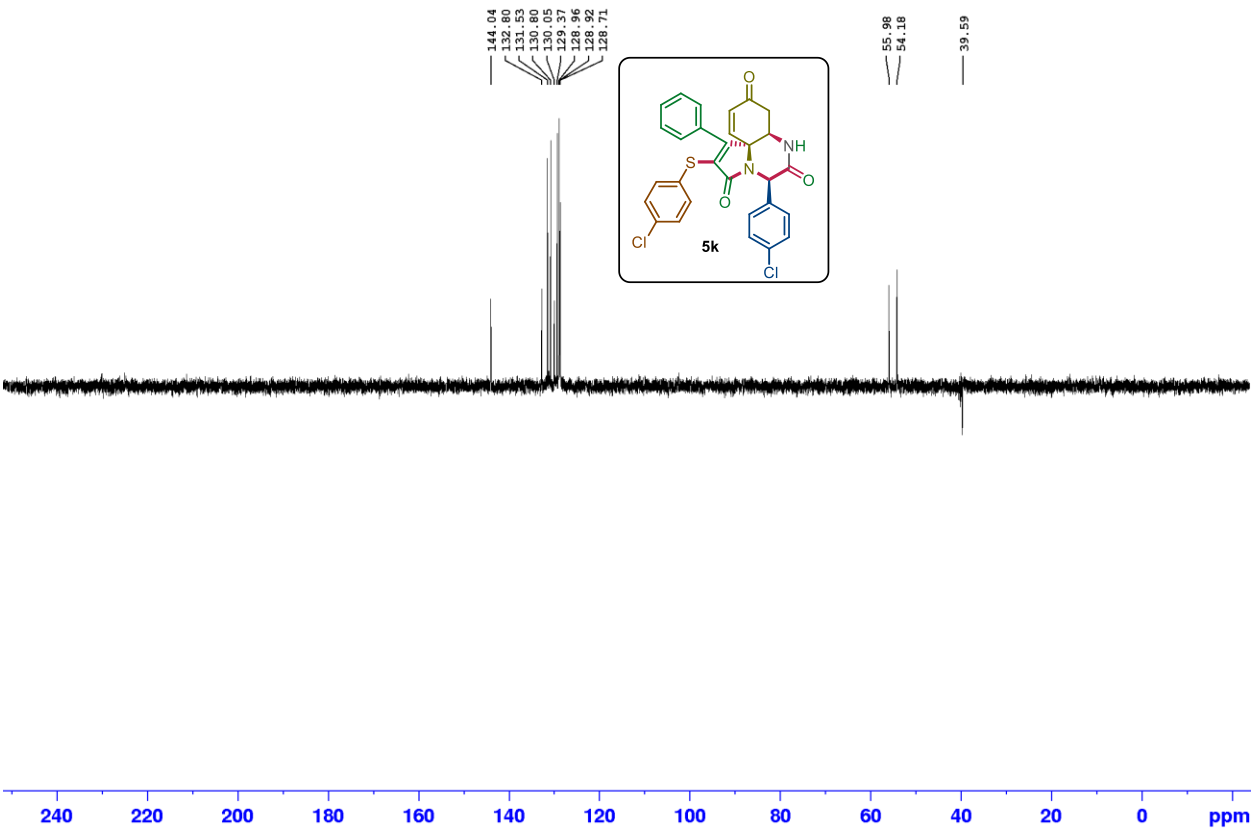
144.04
132.80
131.53
130.80
130.05
129.37
128.96
128.92
128.71
55.98
54.18
39.59
O
NH
S
N
O
O
Cl
Cl
5k
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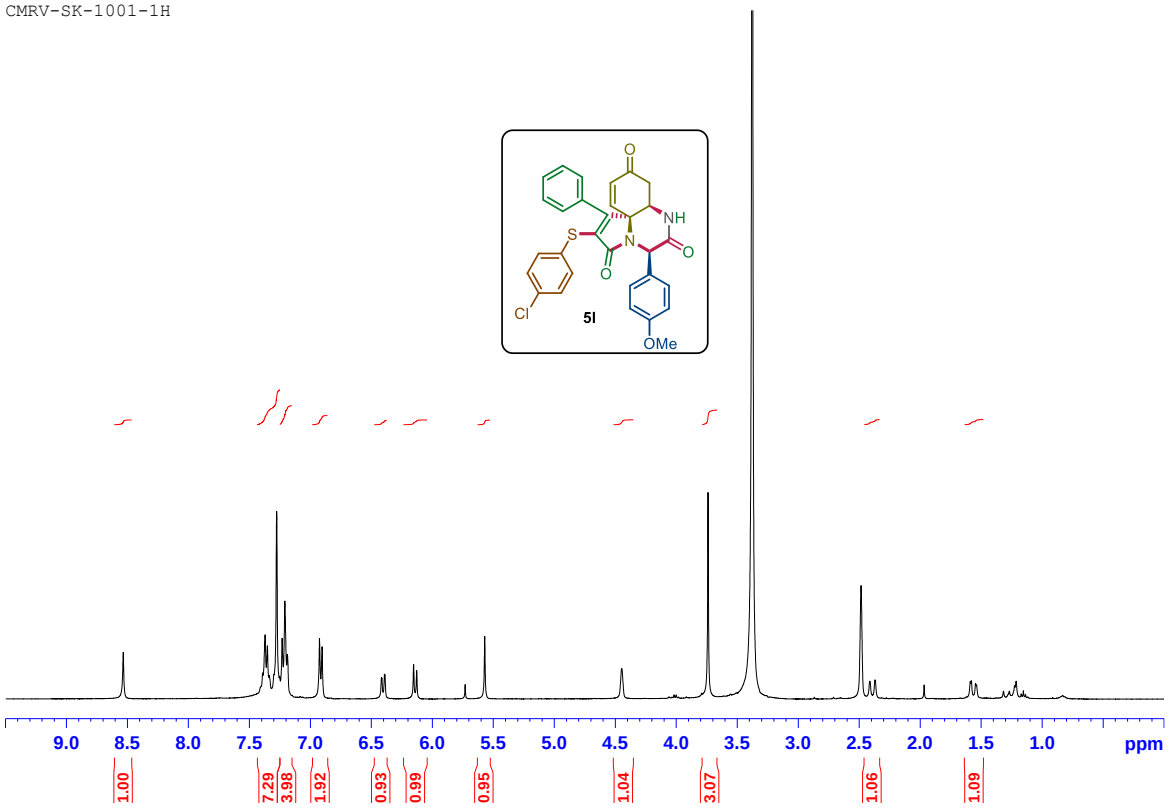
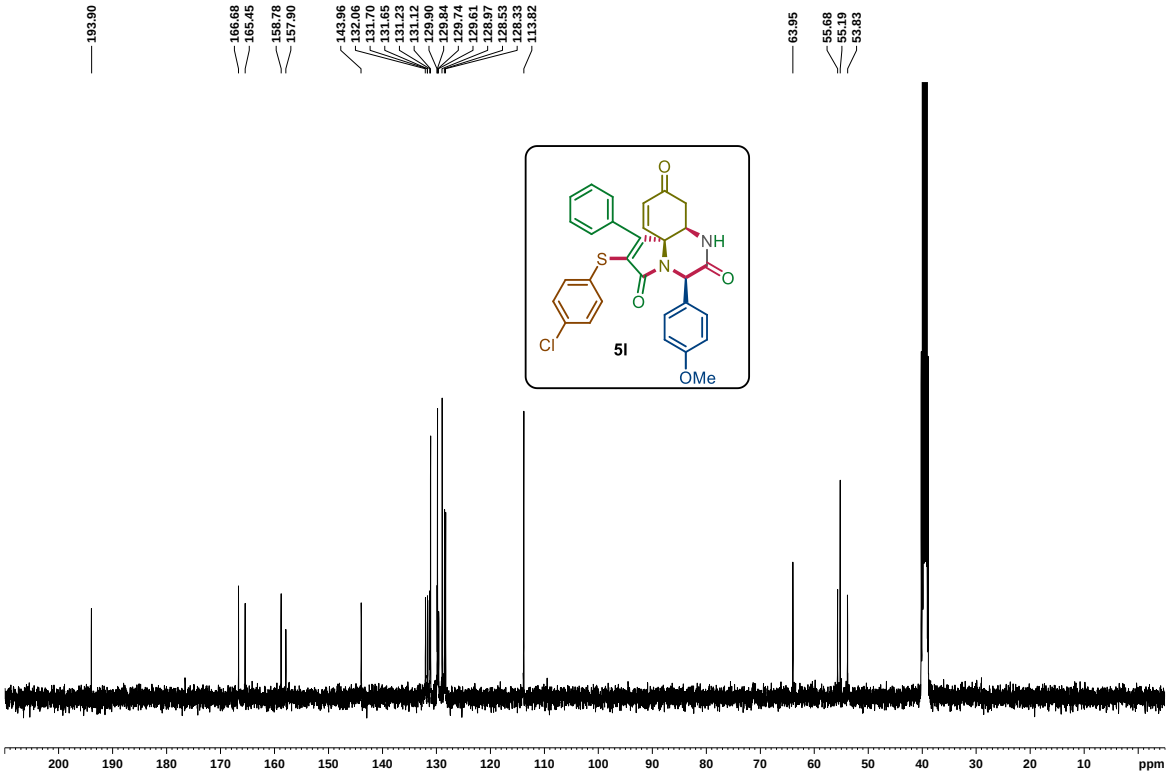
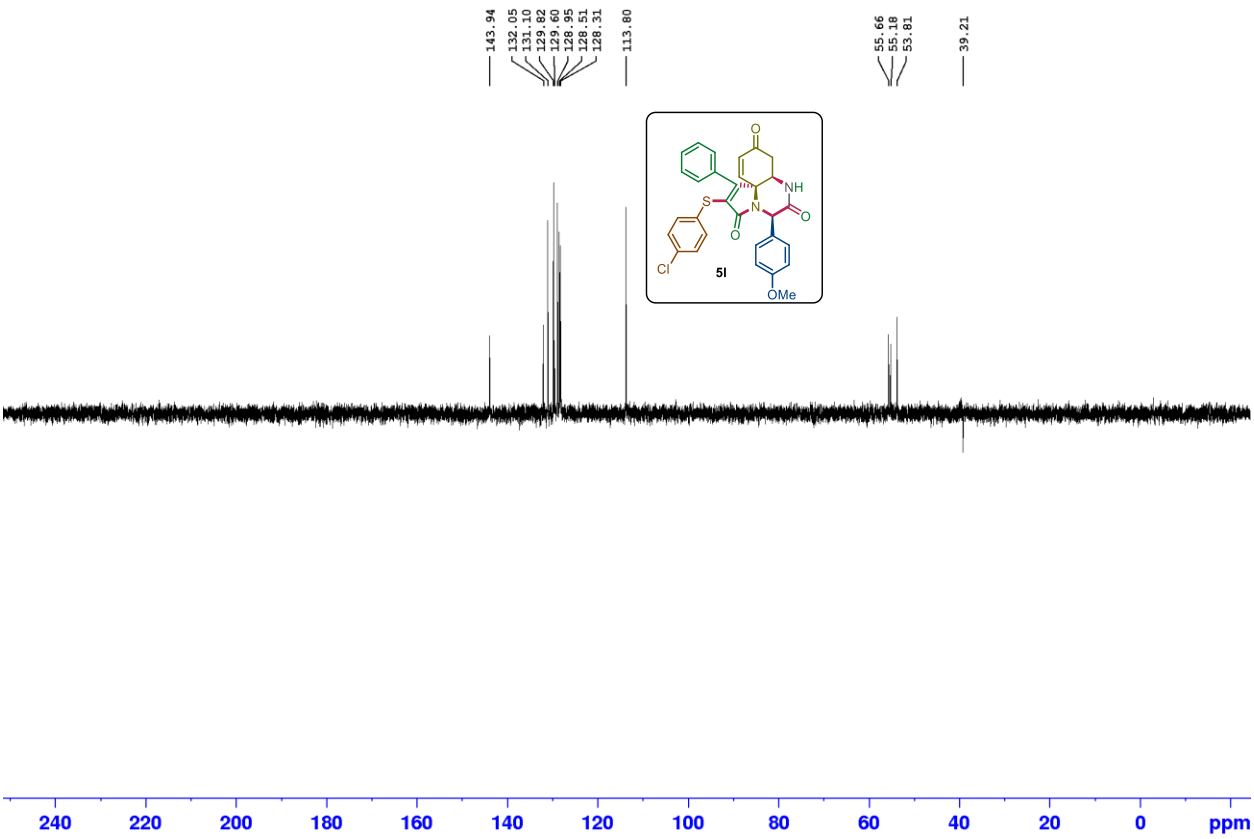
220
200
180
160
140
120
100
80
60
40
20
0
ppm

CMRV-SK-1001-1H



CMRV-SK-1001-13C

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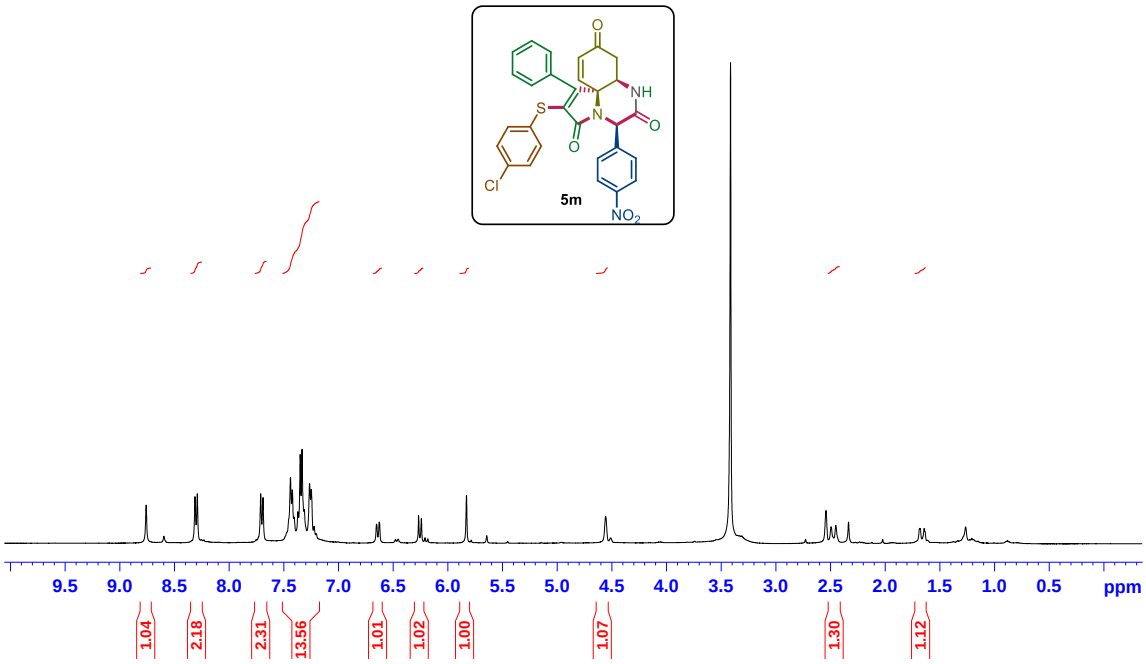
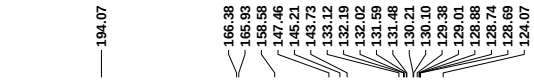
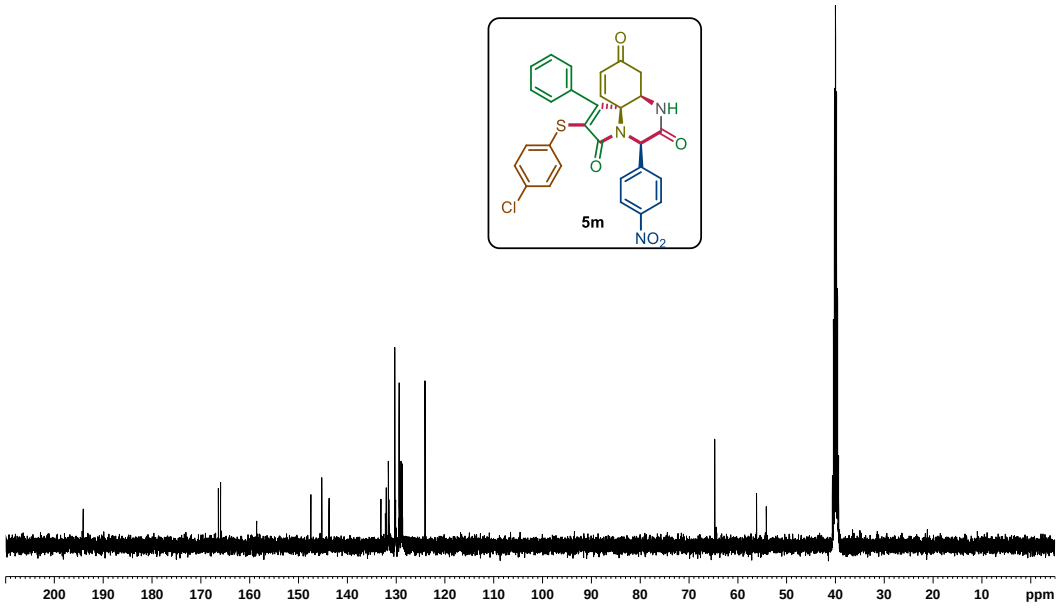
132.05
131.10
129.82
129.60
128.95
128.51
128.31
113.80
55.66
55.18
53.81
39.21
O
NH
S
N
O
O
Cl
5l
OMe
240
220
200
180
160
140
120
100
80
60
40
20
0
ppm

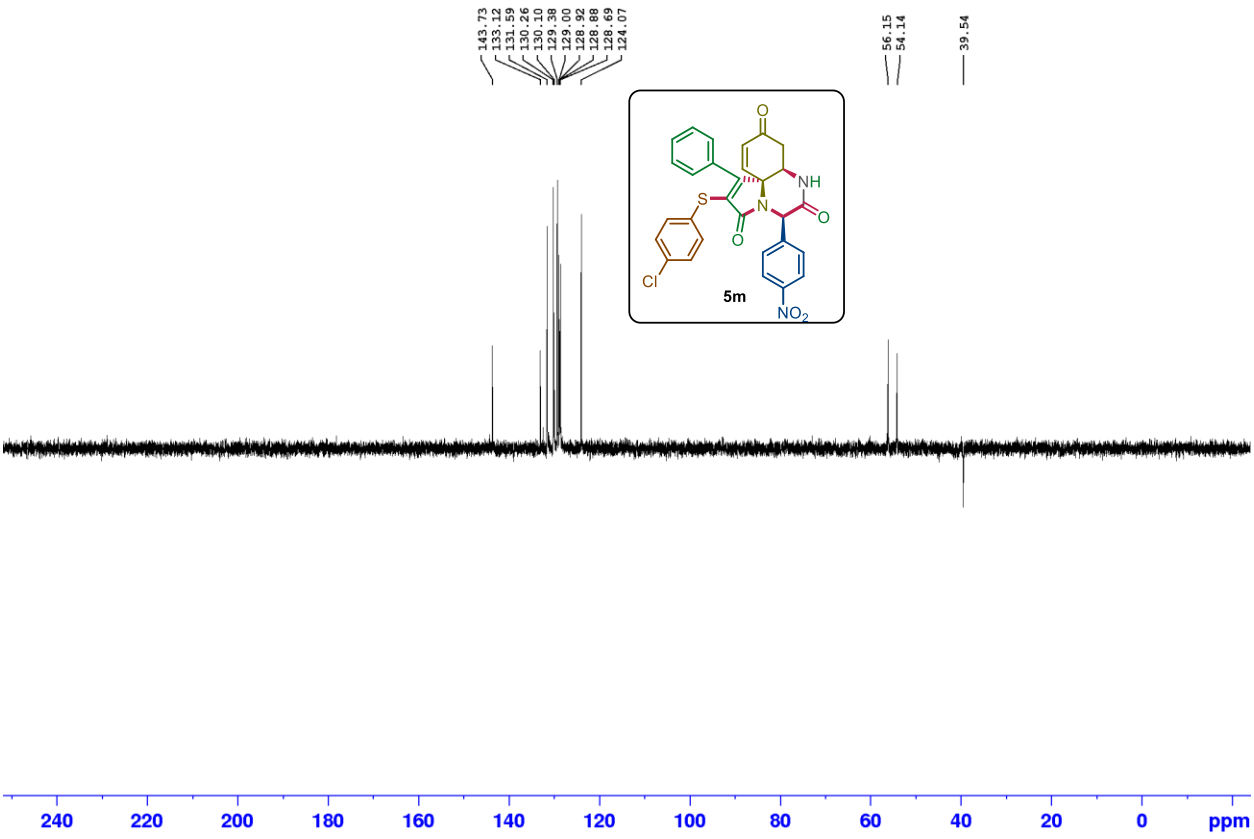
CMRV-SK-1031-1H



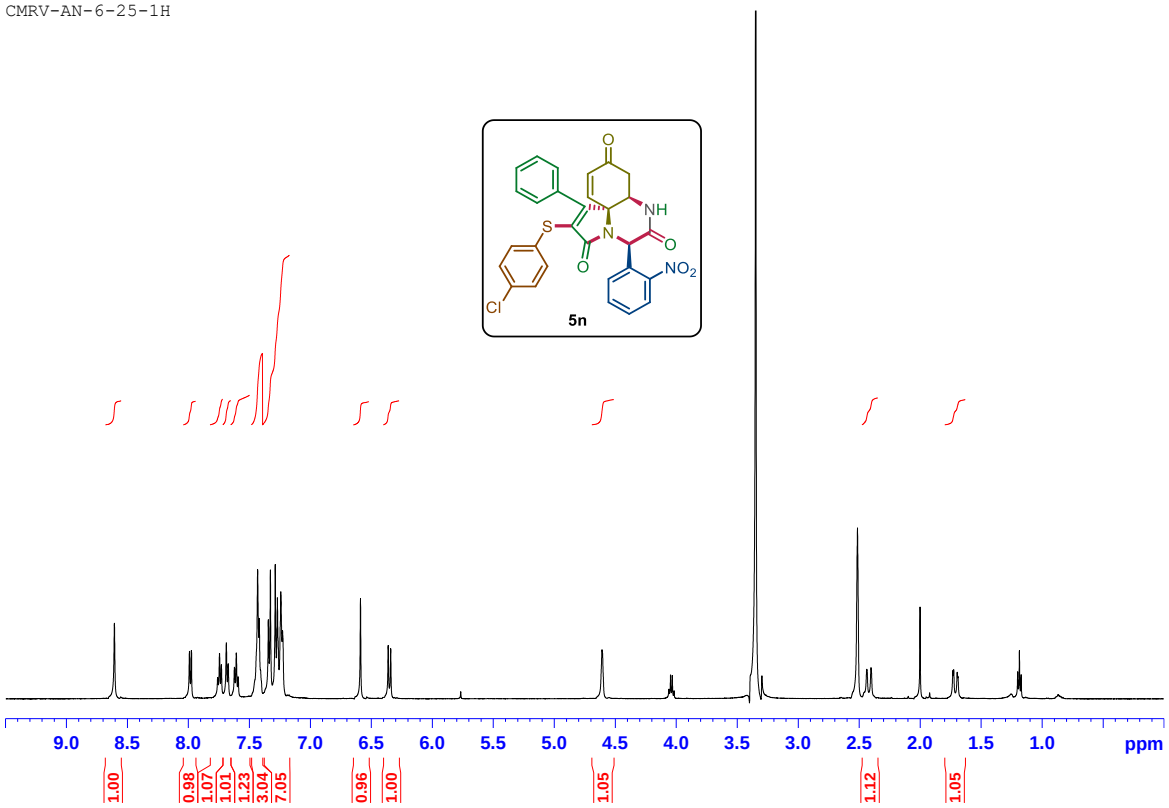
CMRV-SK-1031-13C



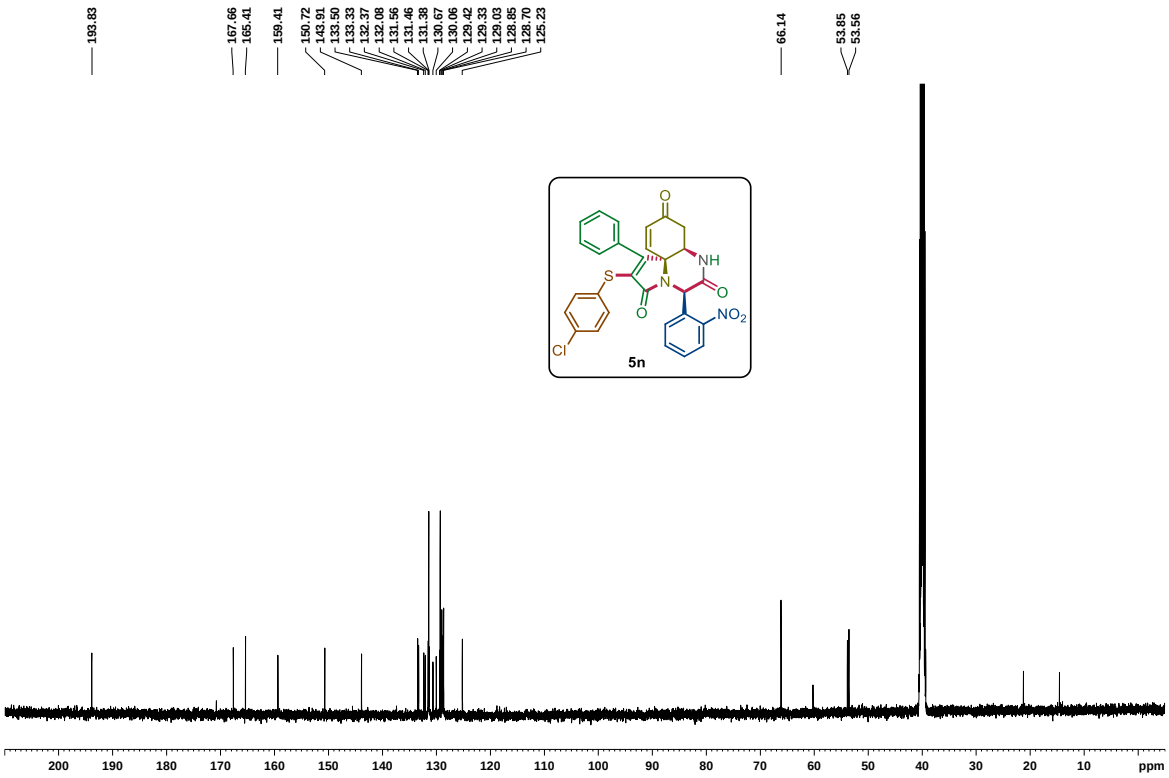


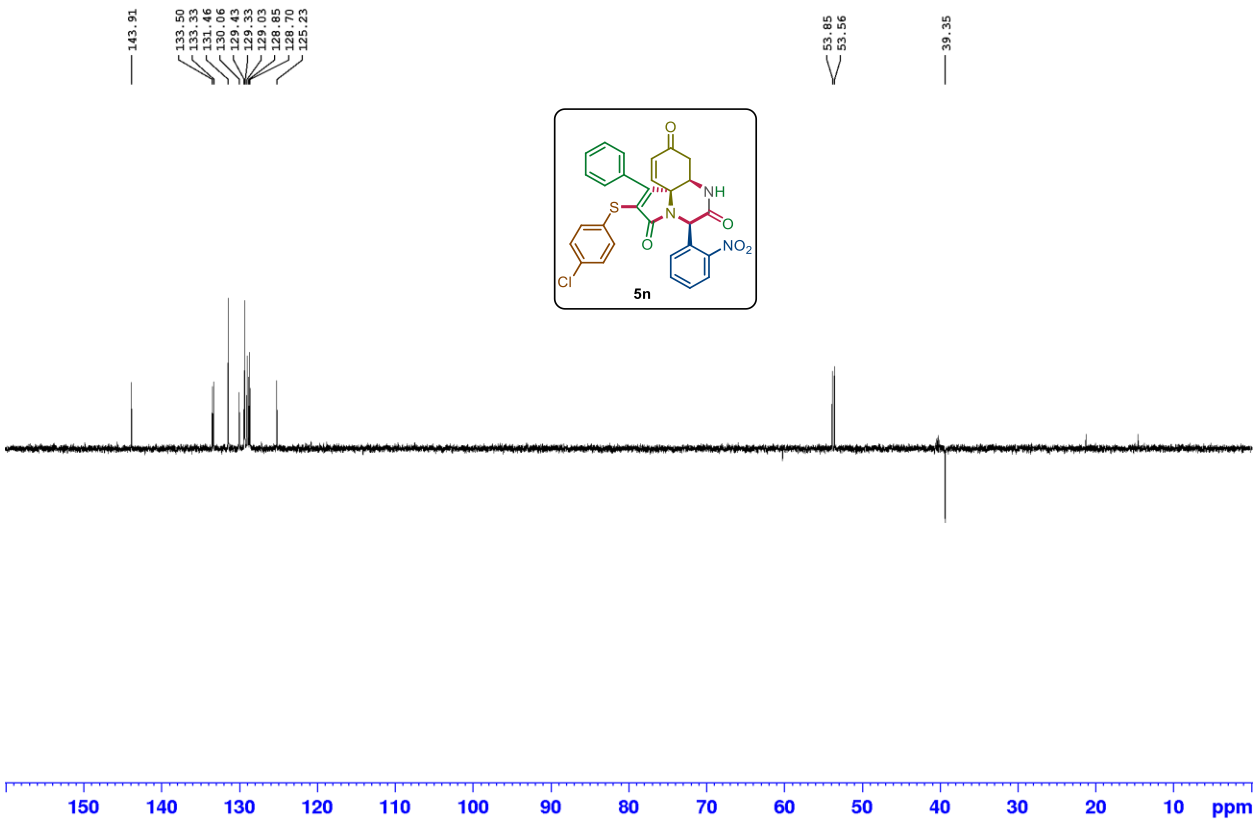

143.73
133.12
131.59
130.26
130.10
129.38
129.00
128.92
128.88
128.69
124.07
56.15
54.14
39.54
O
NH
S
N
O
O
Cl
5m
NO2
240
220
200
180
160
140
120
100
80
60
40
20
0
ppm

CMRV-AN-6-25-1H

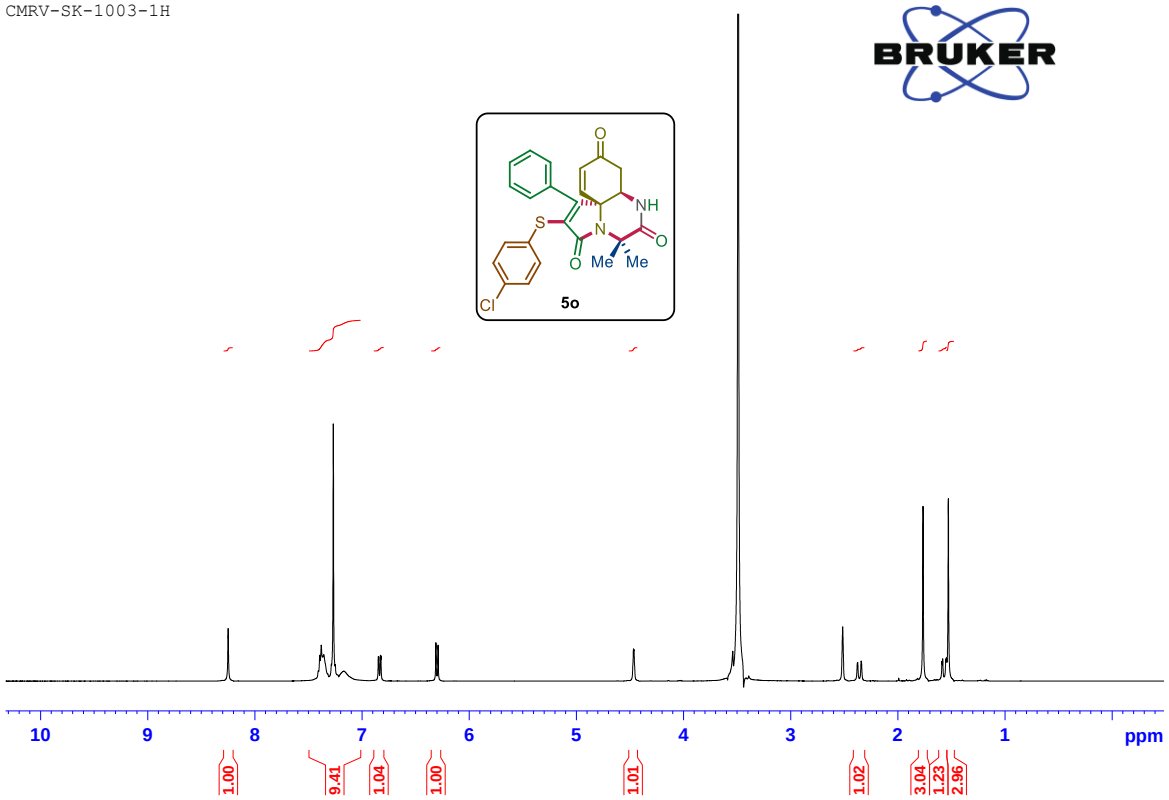


CMRV-AN-6-25-13C

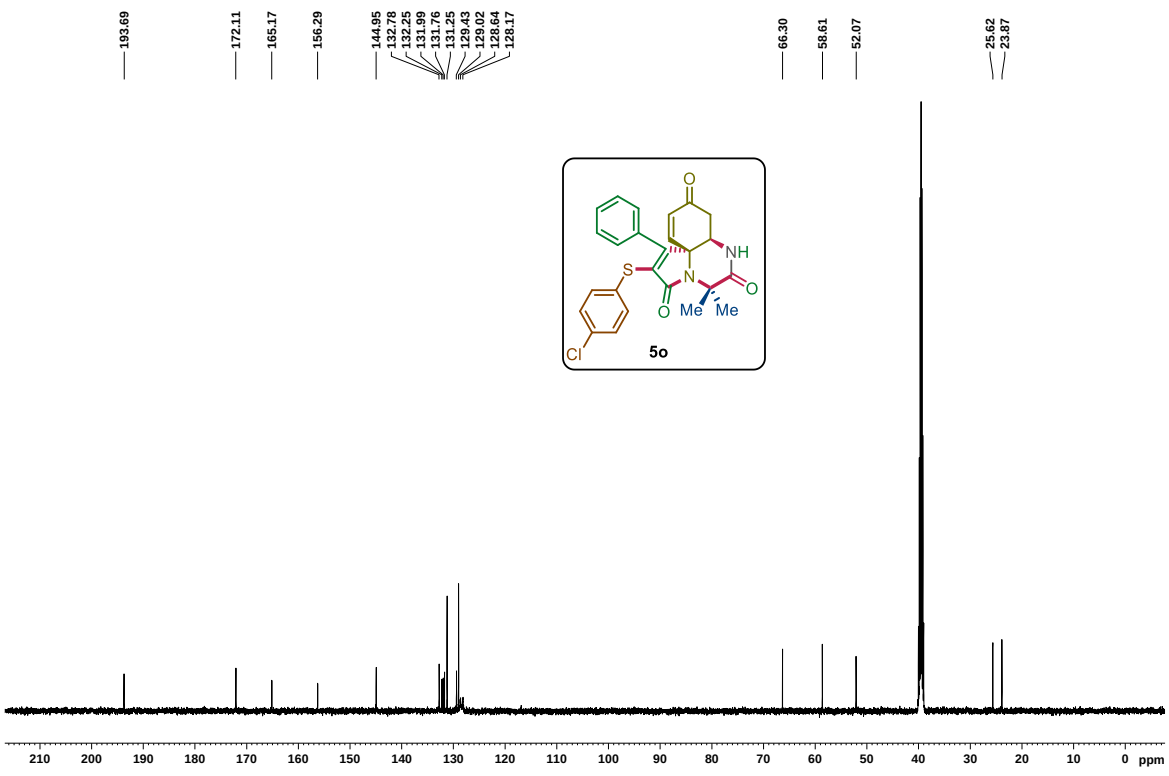


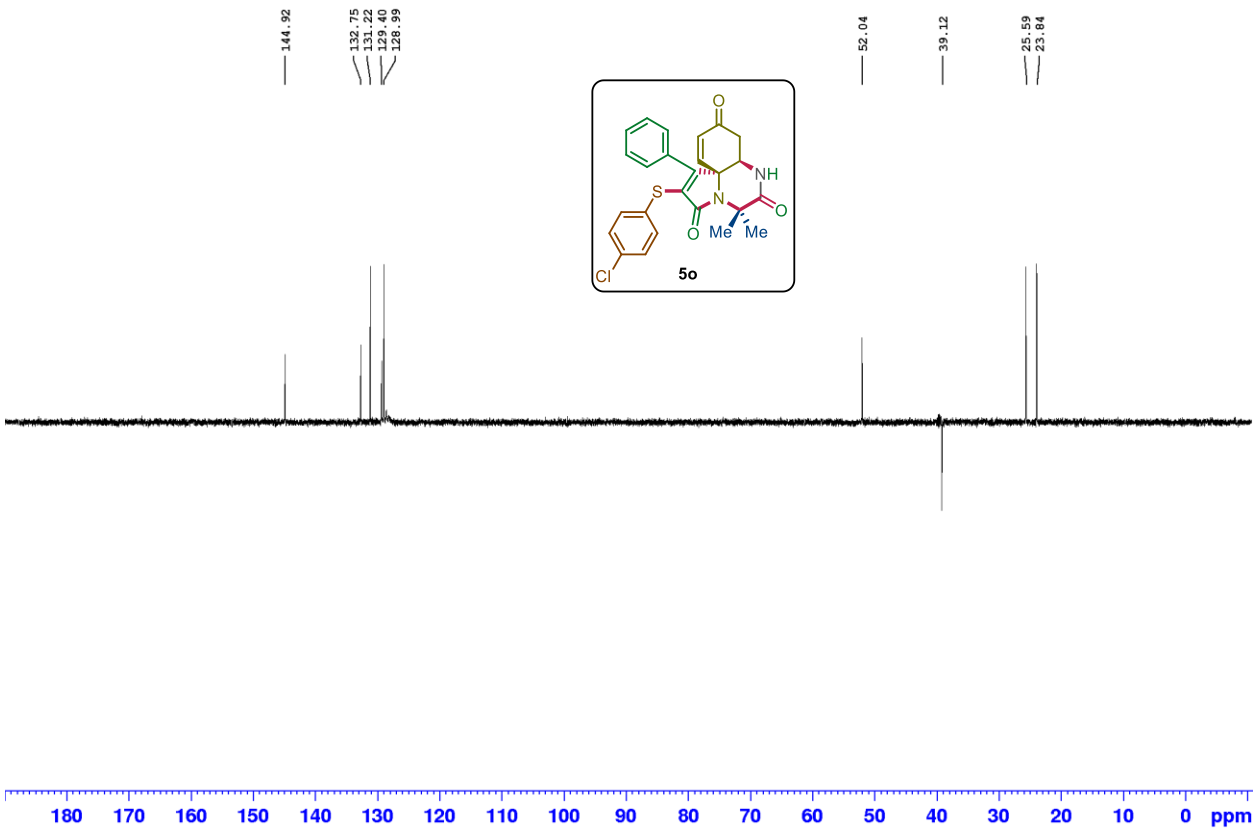

143.91
133.50
133.33
131.46
130.06
129.43
129.33
129.03
128.85
128.70
125.23
53.85
53.56
39.35
O
NH
S
N
O
O
NO2
Cl
5n
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

CMRV-SK-1003-1H

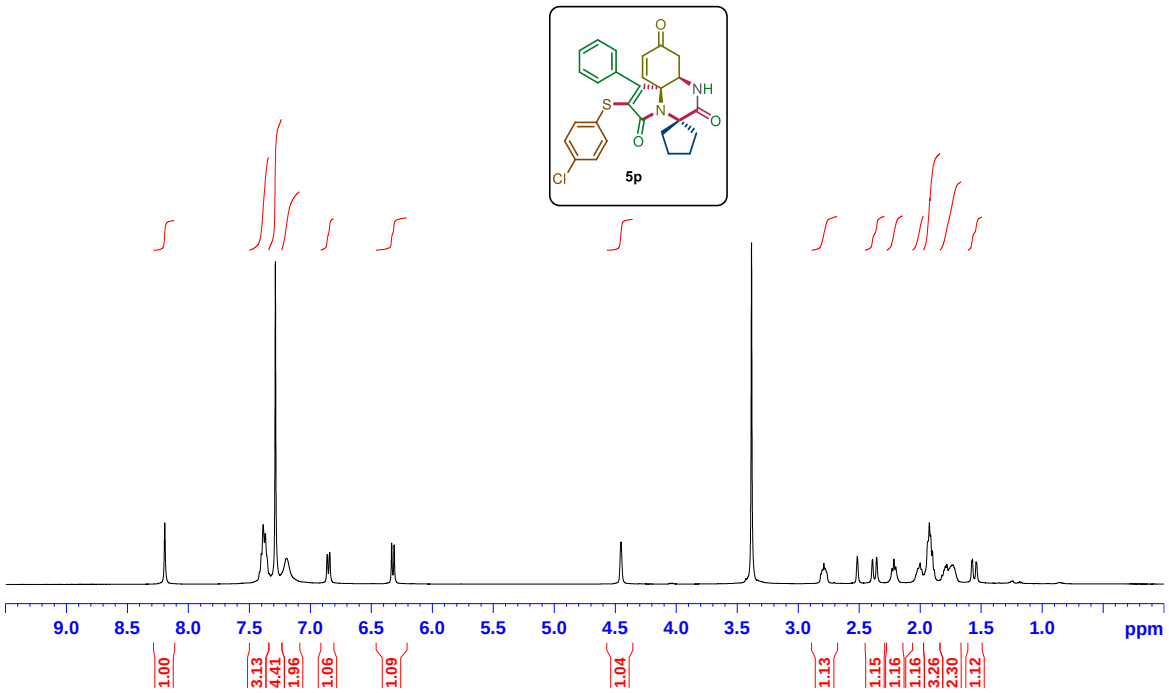


CMRV-SK-1003-13C

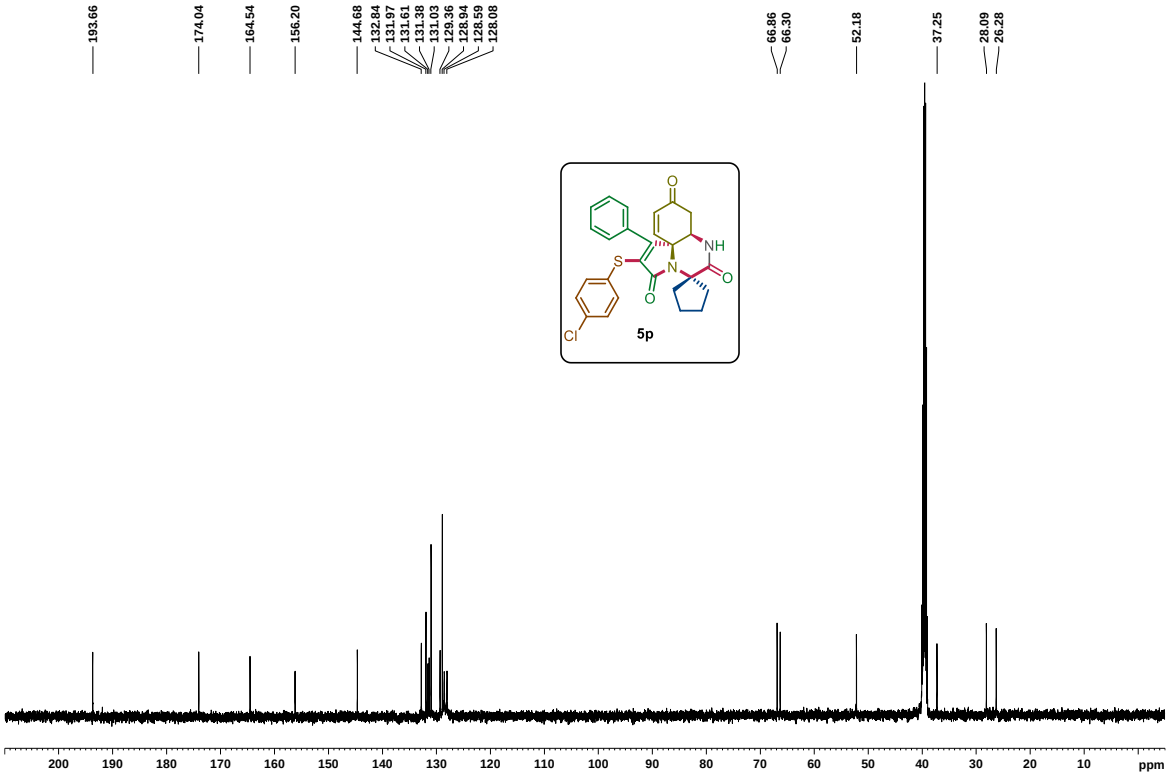


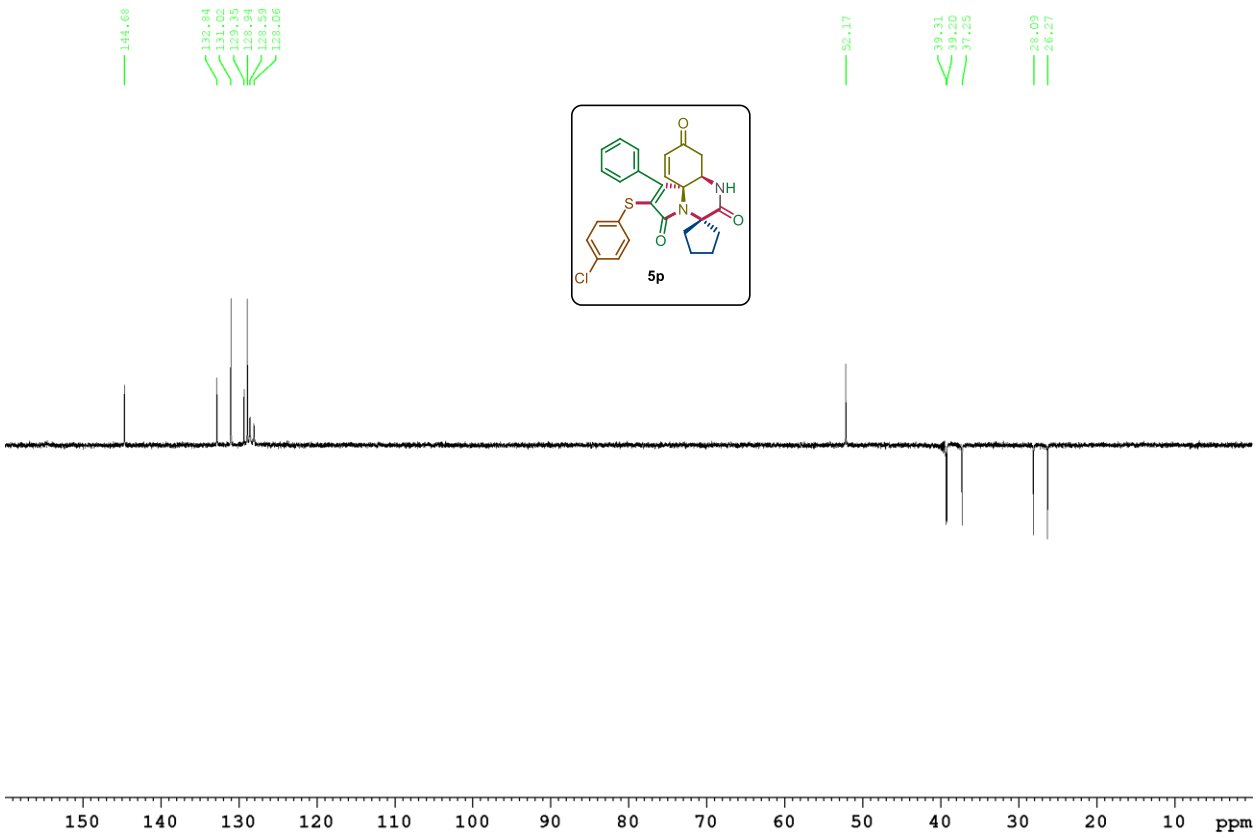

144.92
132.75
131.22
129.40
128.99
52.04
39.12
25.59
23.84
O
NH
S
N
O
O
Me
Me
Cl
5o
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

CMRV-SK-1019-1H

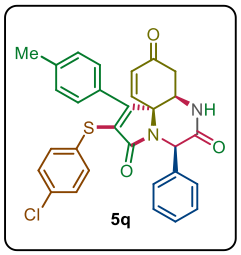


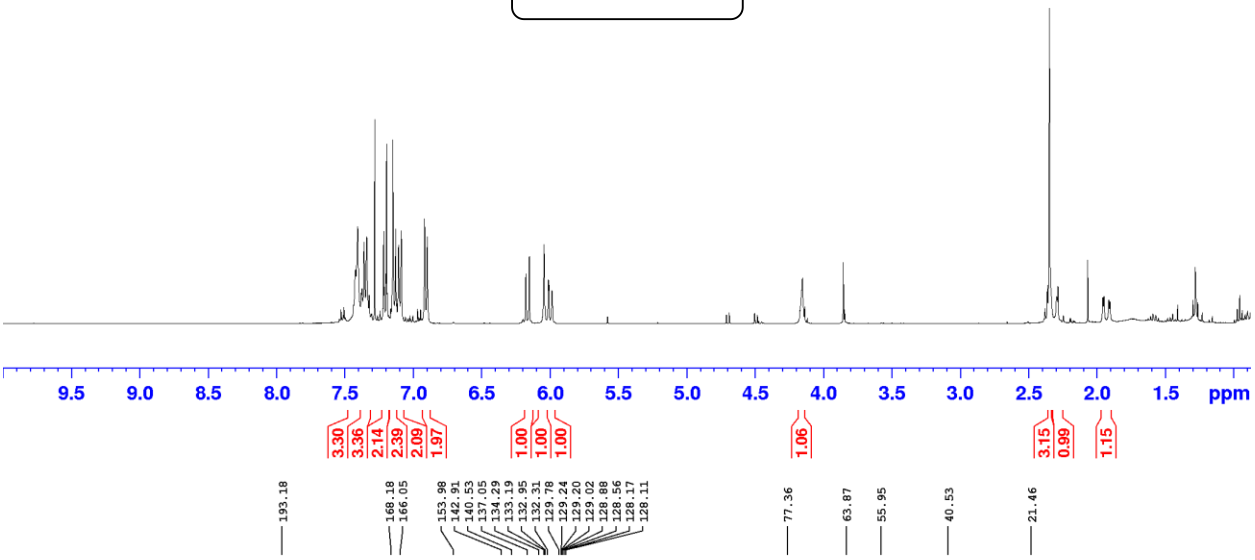
CMRV-SK-1019-13C

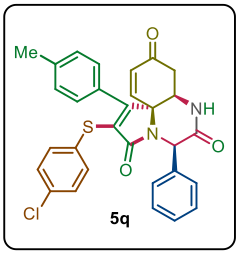


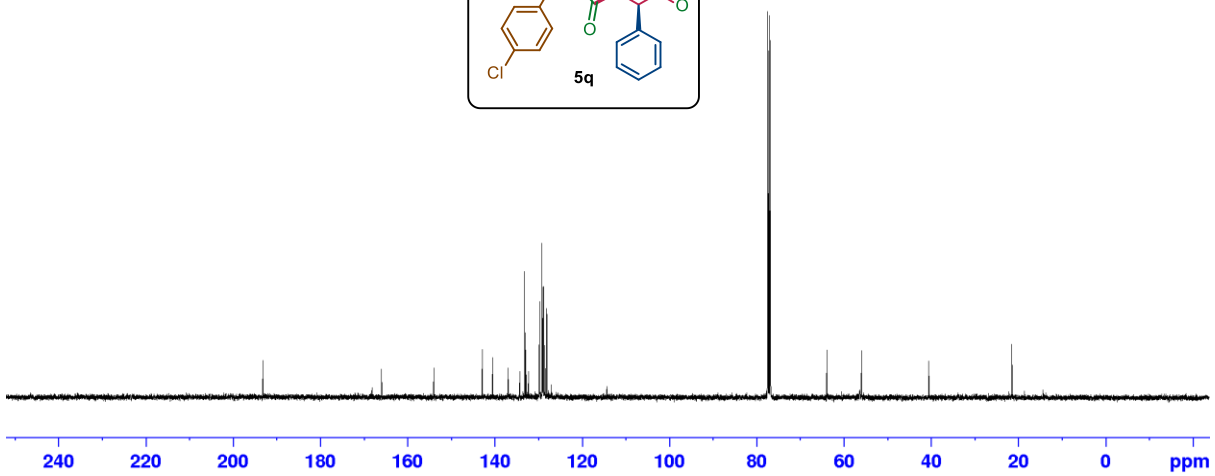

144.68
132.84
131.02
129.35
128.94
128.59
128.06
52.17
39.31
39.20
37.25
28.09
26.27
O
NH
S
N
O
O
Cl
5p
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

CMRV-AC-506-1H

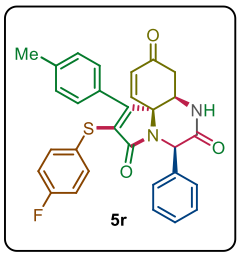


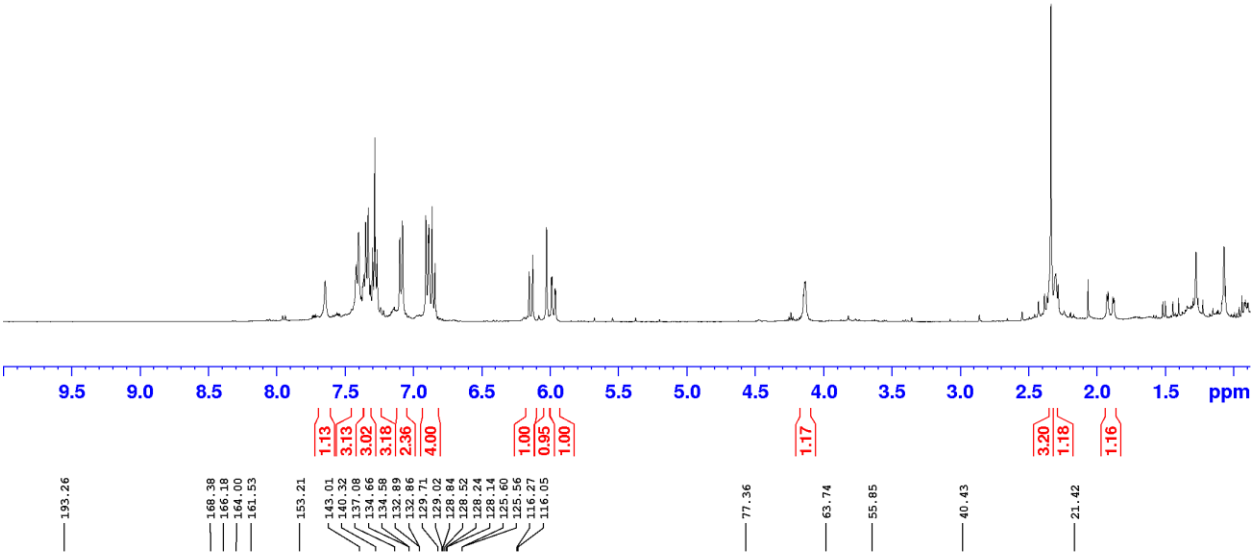


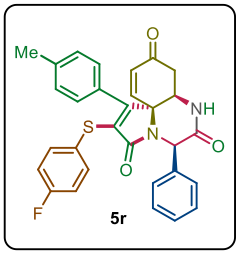


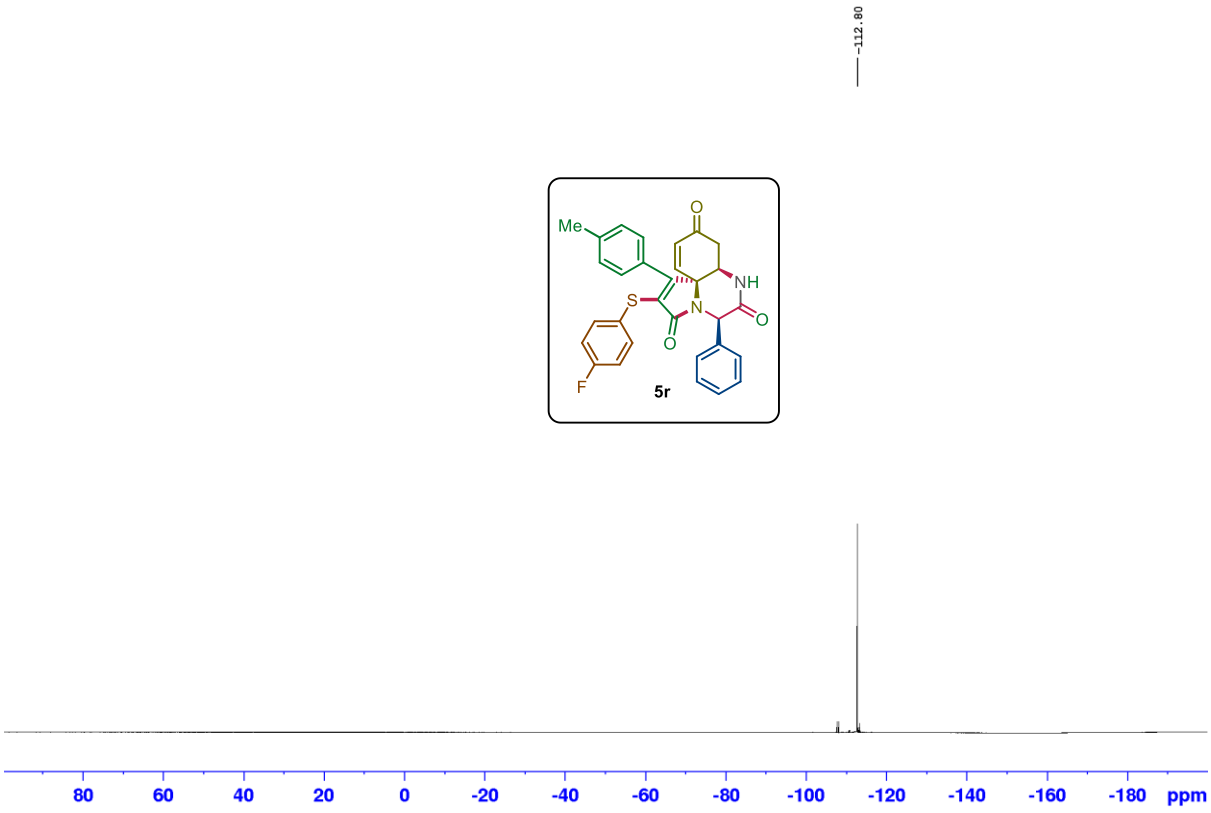


CMRV-AC-525-1H

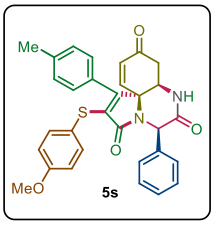


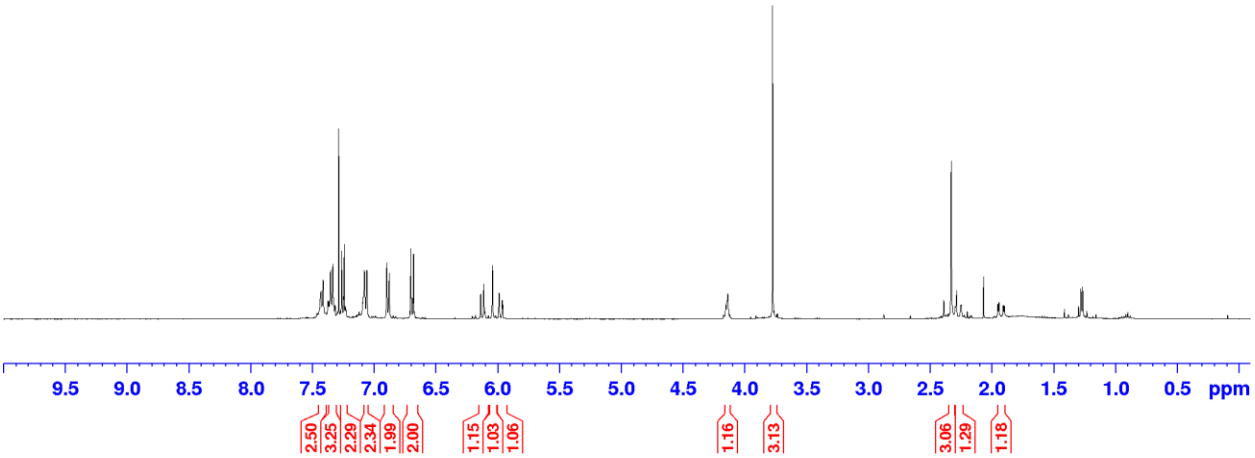




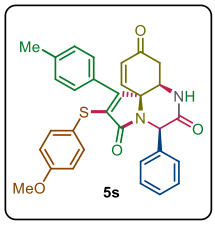

-112.80
Me
O
NH
S
N
O
O
F
5r
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm

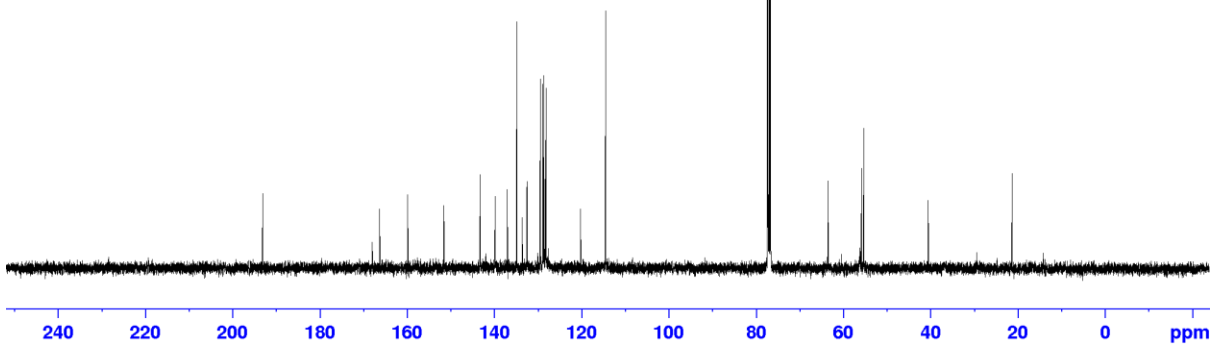
CMRV-AC-524-1H

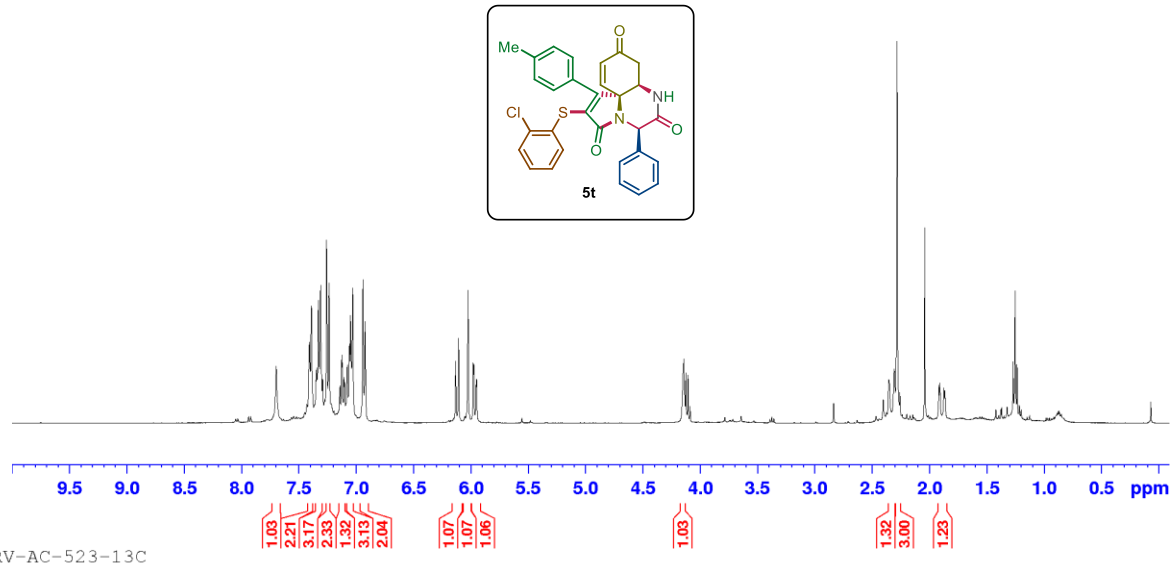




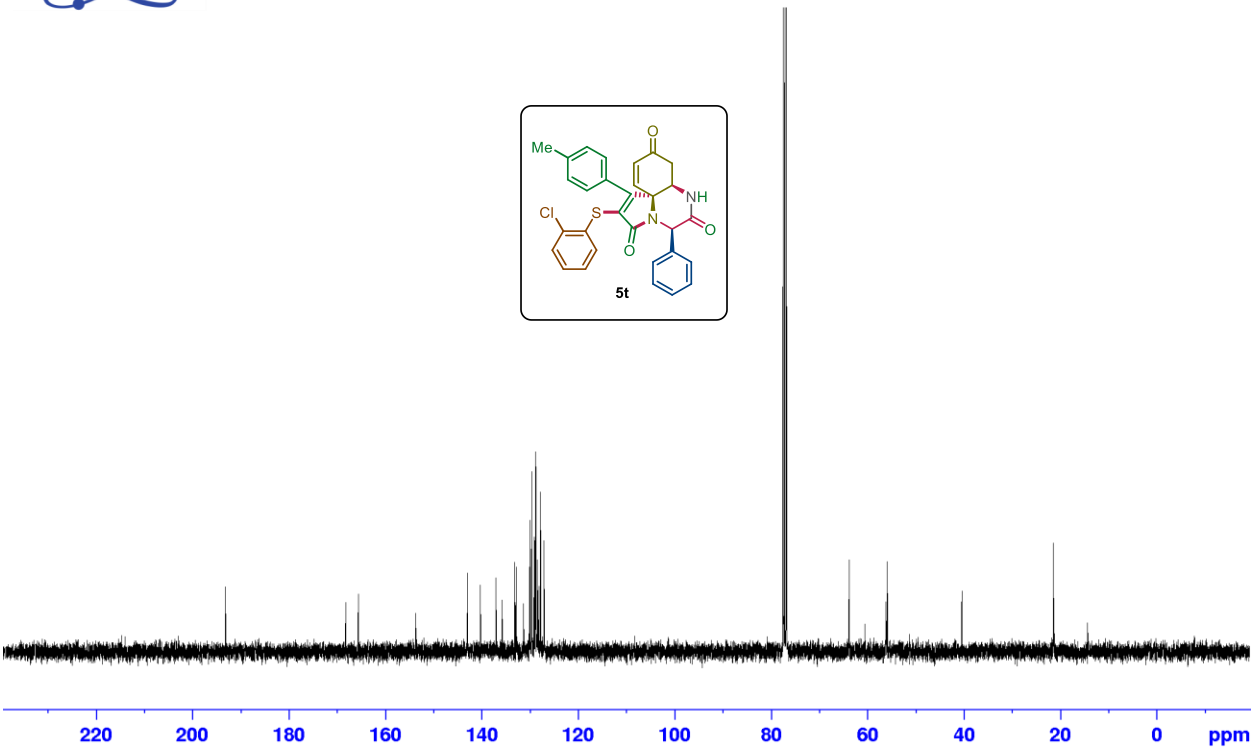
193.16
168.01
166.30
159.90
151.57
143.28
139.82
137.05
134.89
133.66
132.54
129.50
128.91
128.71
128.37
128.28
128.18
120.26
114.48
77.24
63.55
55.84
55.30
40.54
21.31



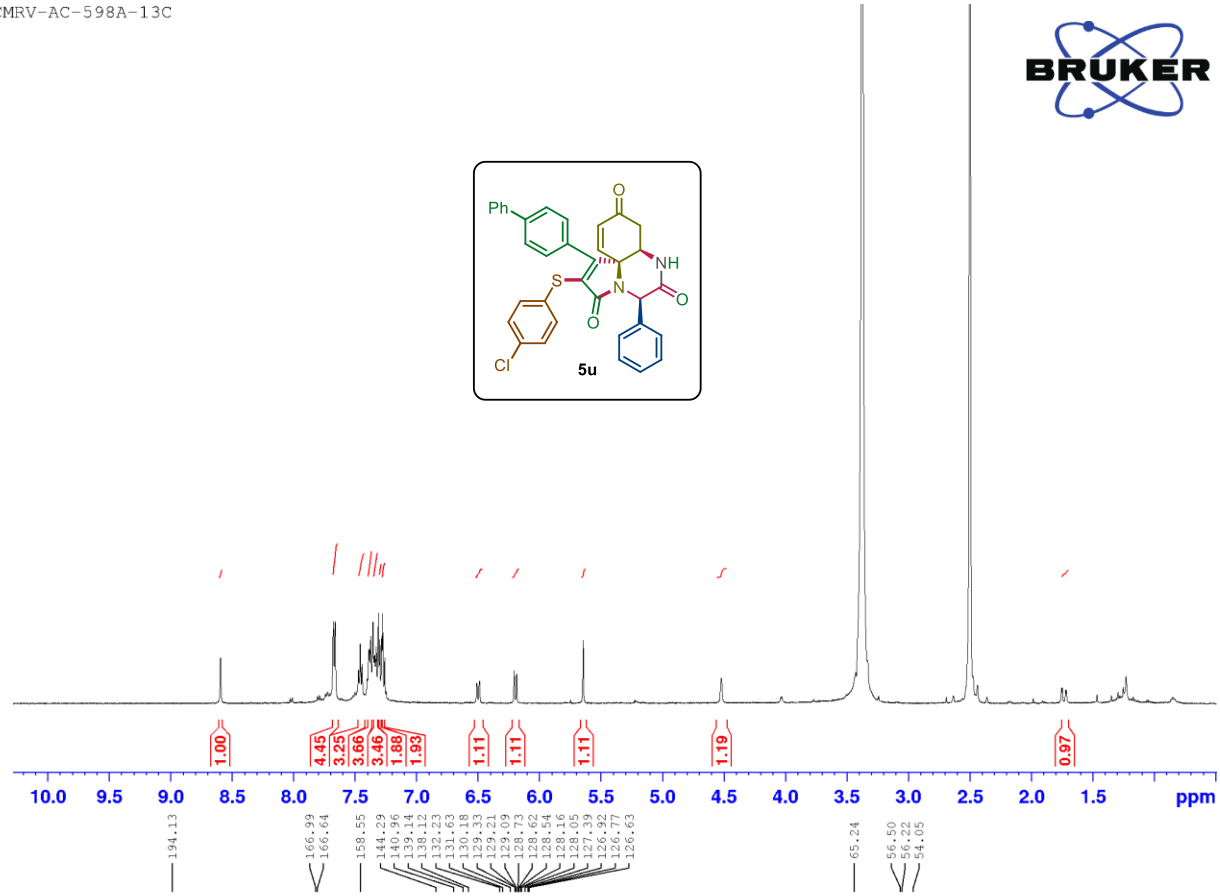


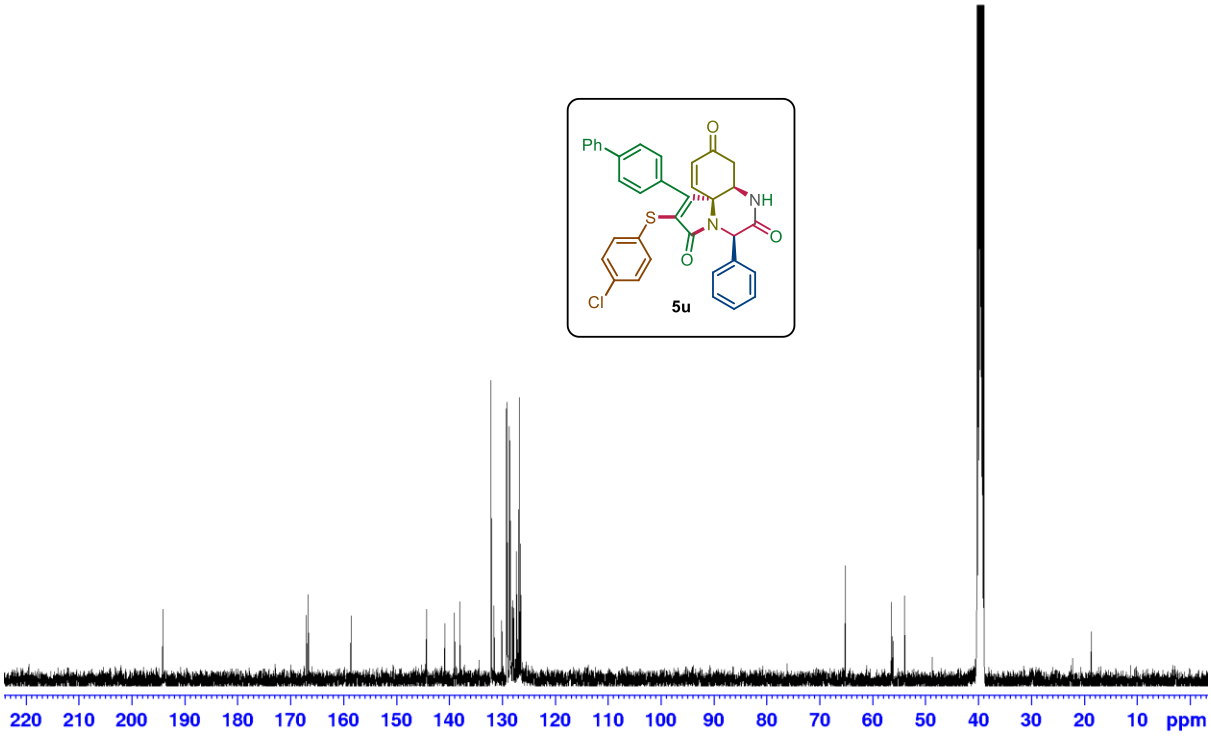


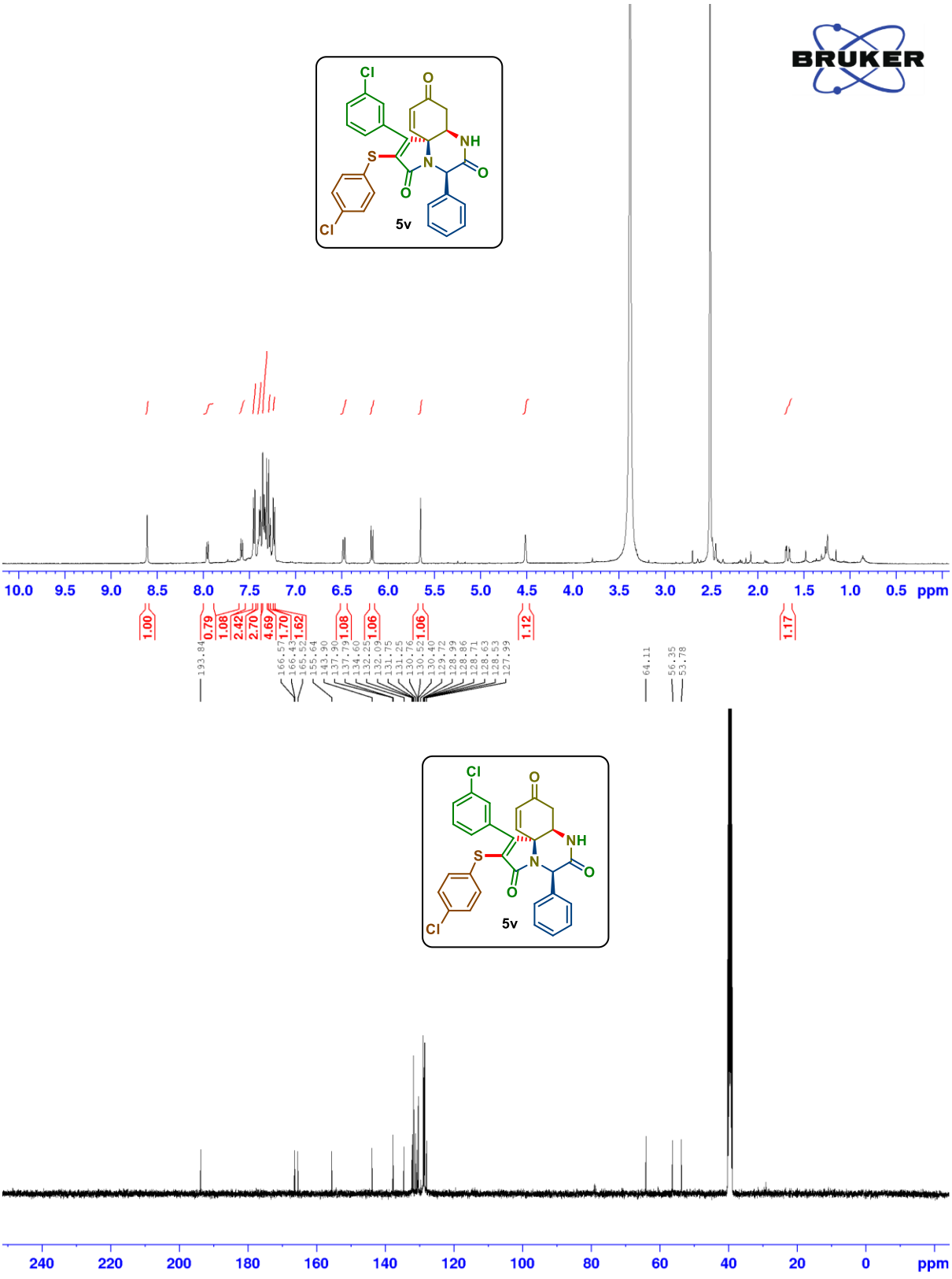
CMRV-AC-523-13C

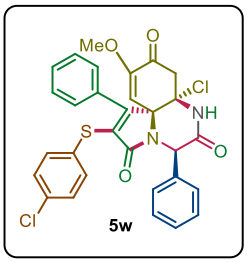


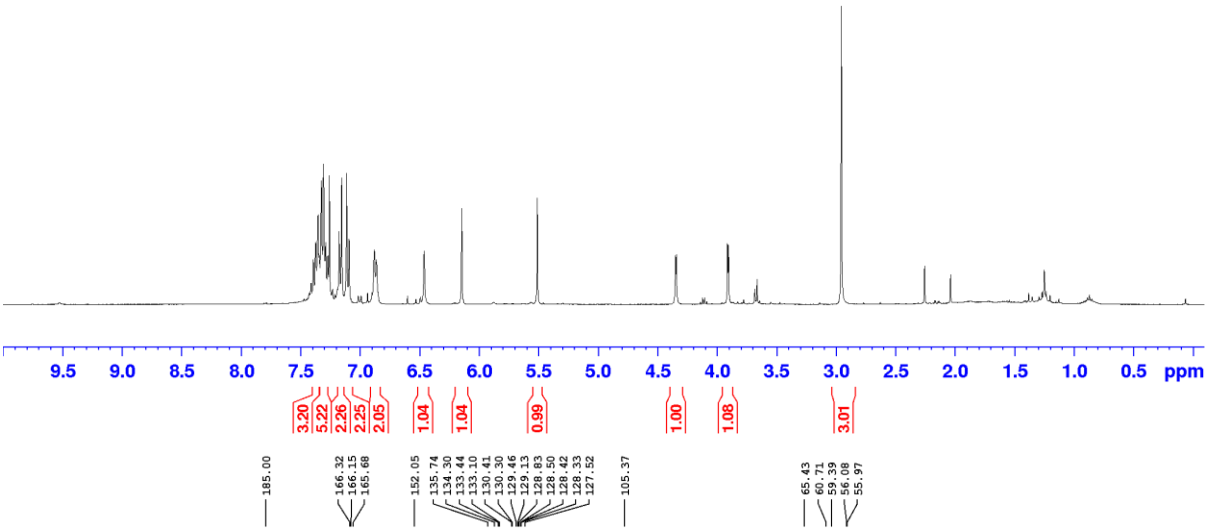
CMRV-AC-598A-13C



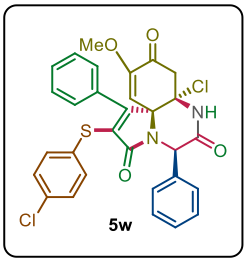



Cl
O
NH
S
N
O
O
Cl
5v
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.00 0.79 1.06 2.42 2.70 4.69 1.70 1.62 1.08 1.06 1.06 1.12 1.17
193.84
166.57
166.43
165.64
165.54
143.94
137.90
137.79
134.60
132.25
132.03
131.75
131.25
130.76
130.52
130.40
129.72
128.99
128.86
128.71
128.63
128.53
127.99
64.11
56.35
53.78
240 220 200 180 160 140 120 100 80 60 40 20 0 ppm

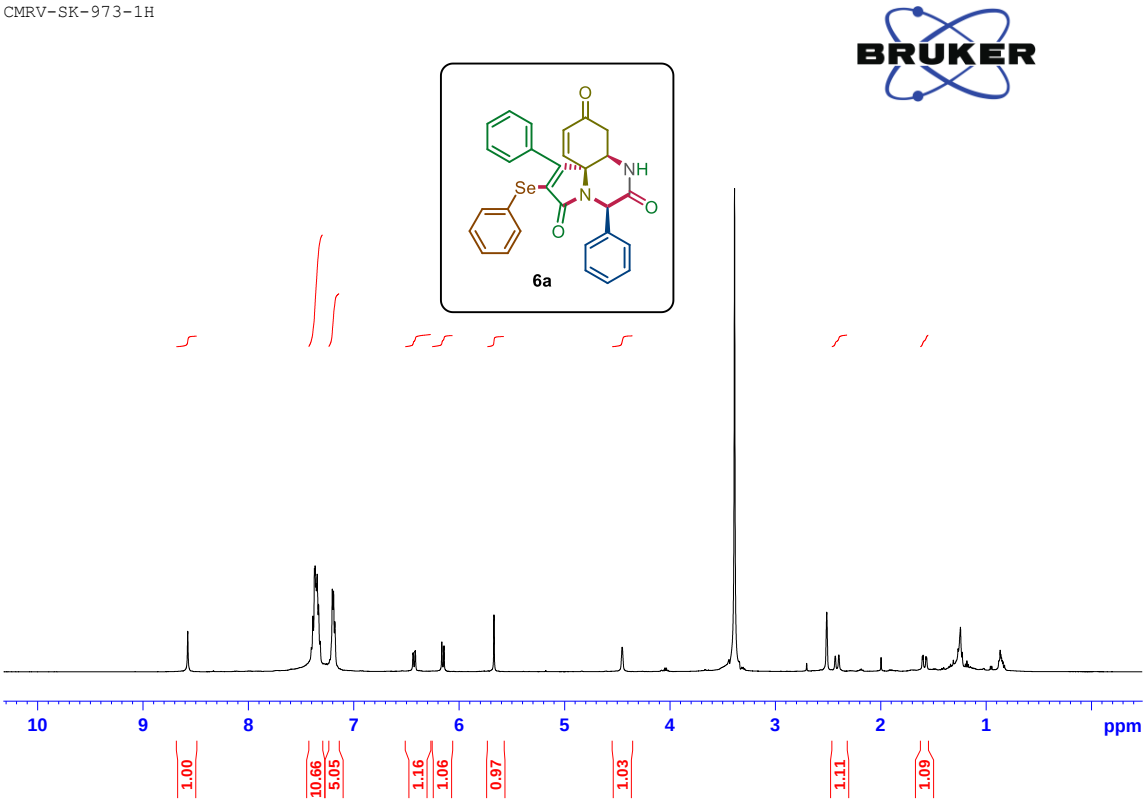




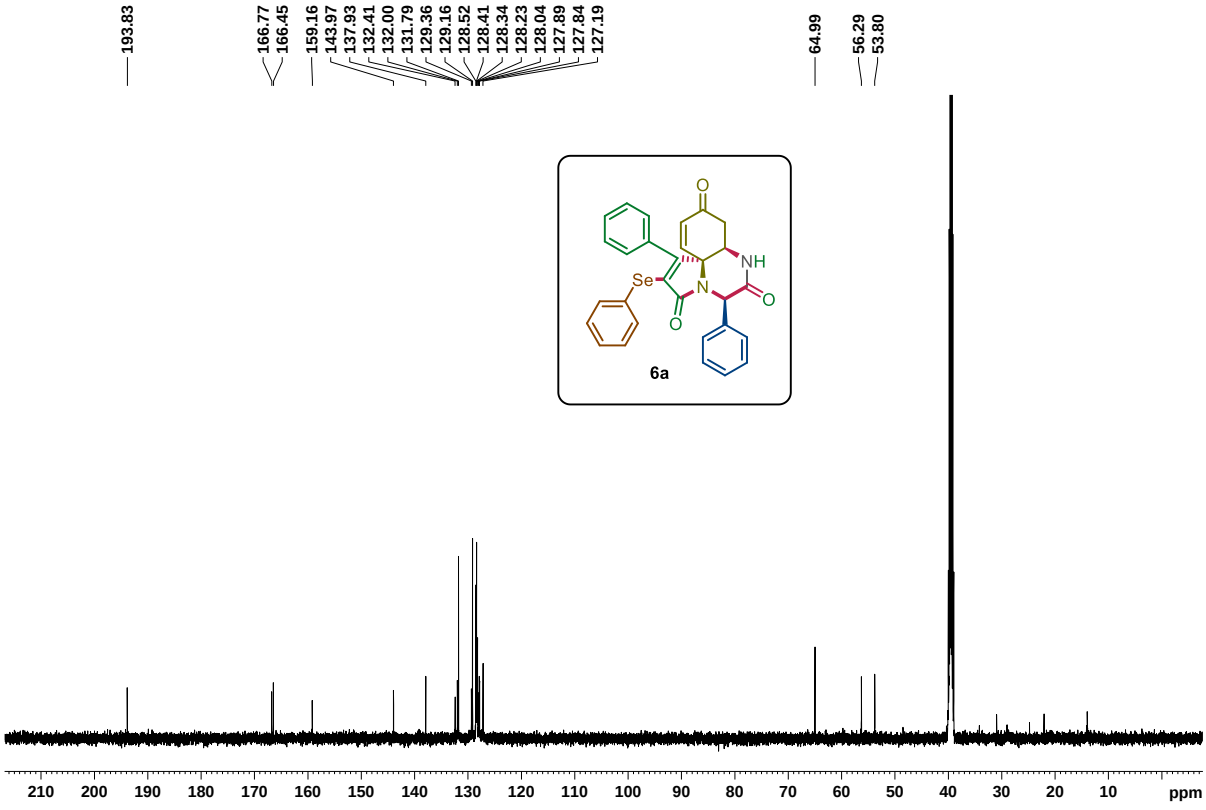
185.00
166.32
166.15
165.68
152.05
135.74
134.30
133.44
133.10
130.41
130.30
129.46
129.13
128.83
128.50
128.42
128.33
127.52
105.37
65.43
60.71
59.39
56.08
55.97

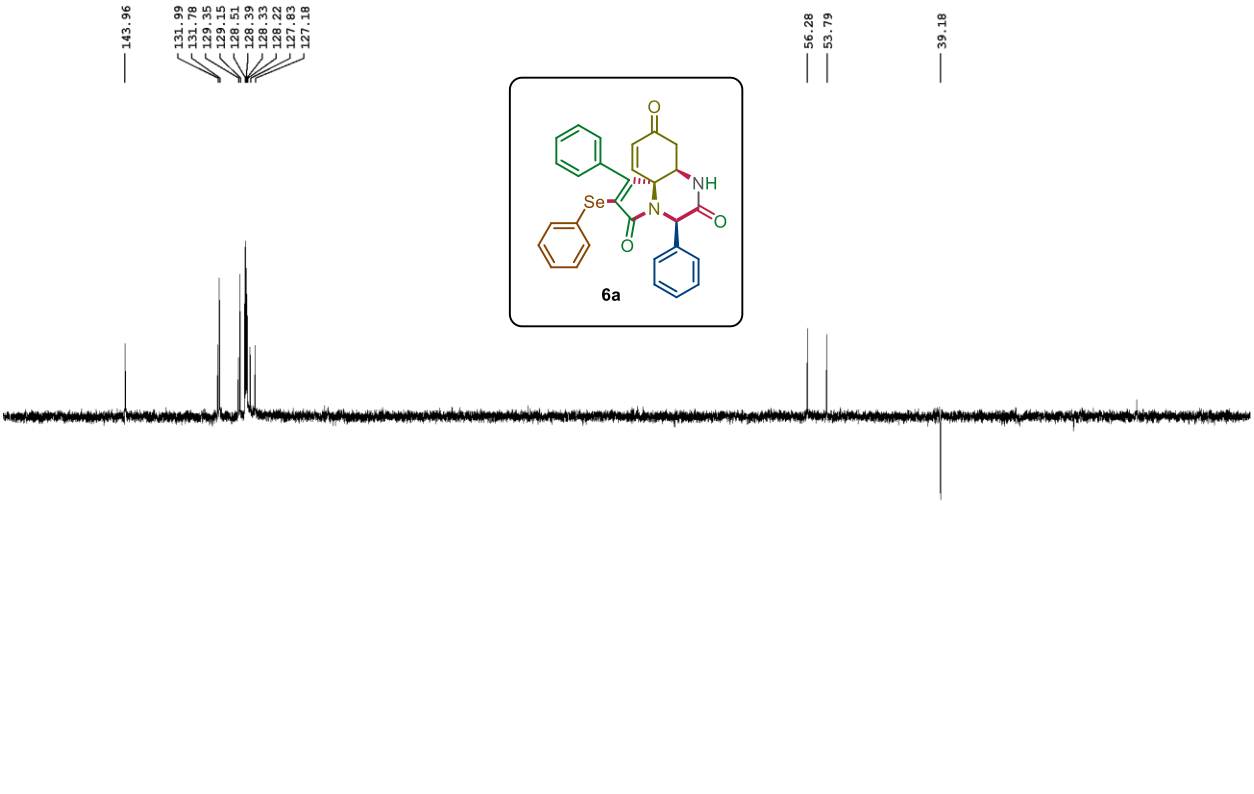


CMRV-SK-973-1H



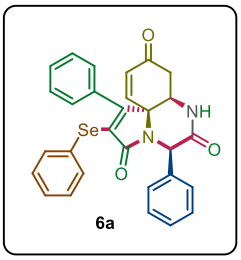
CMRV-SK-973-13C

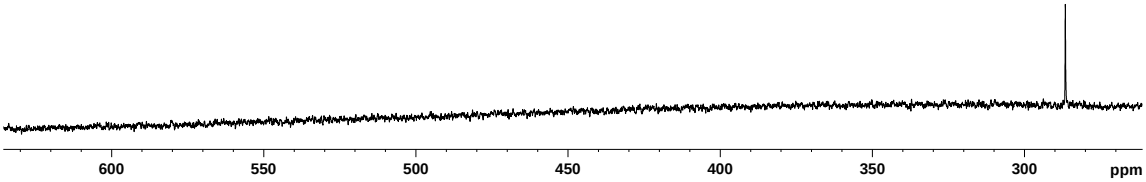




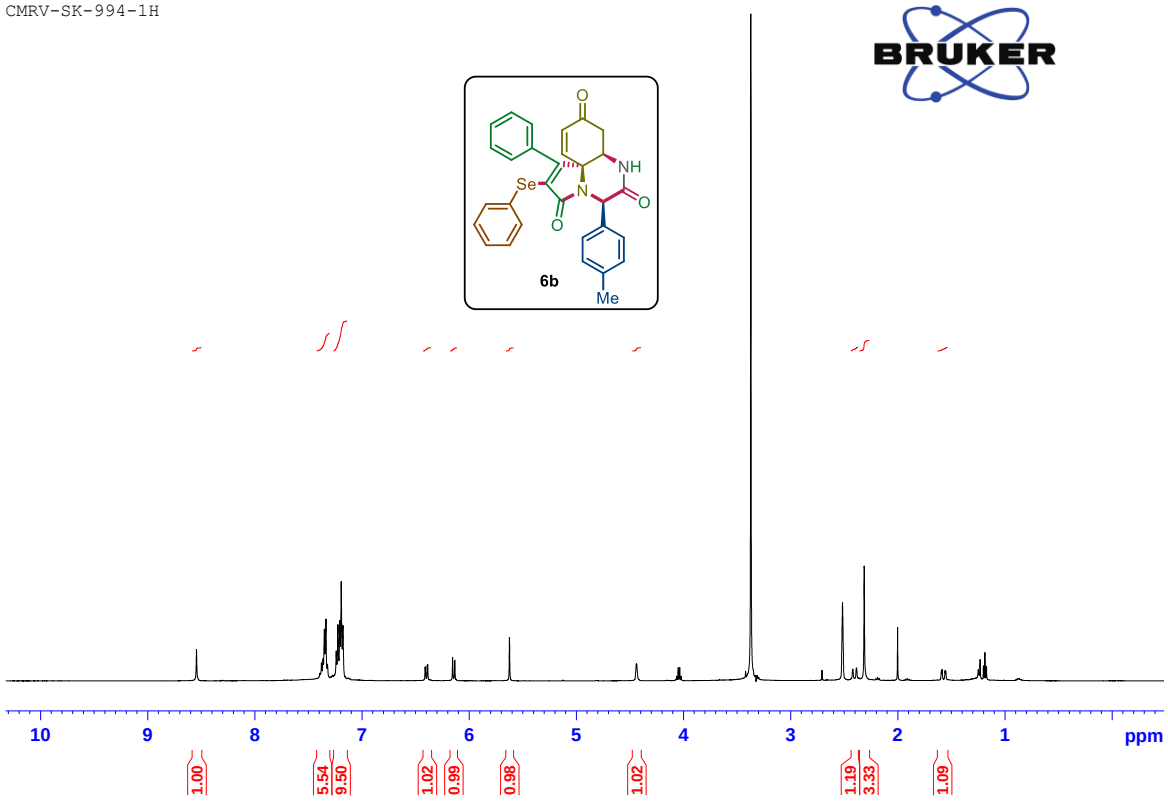
CMRV-SK-973-77Se

286.57

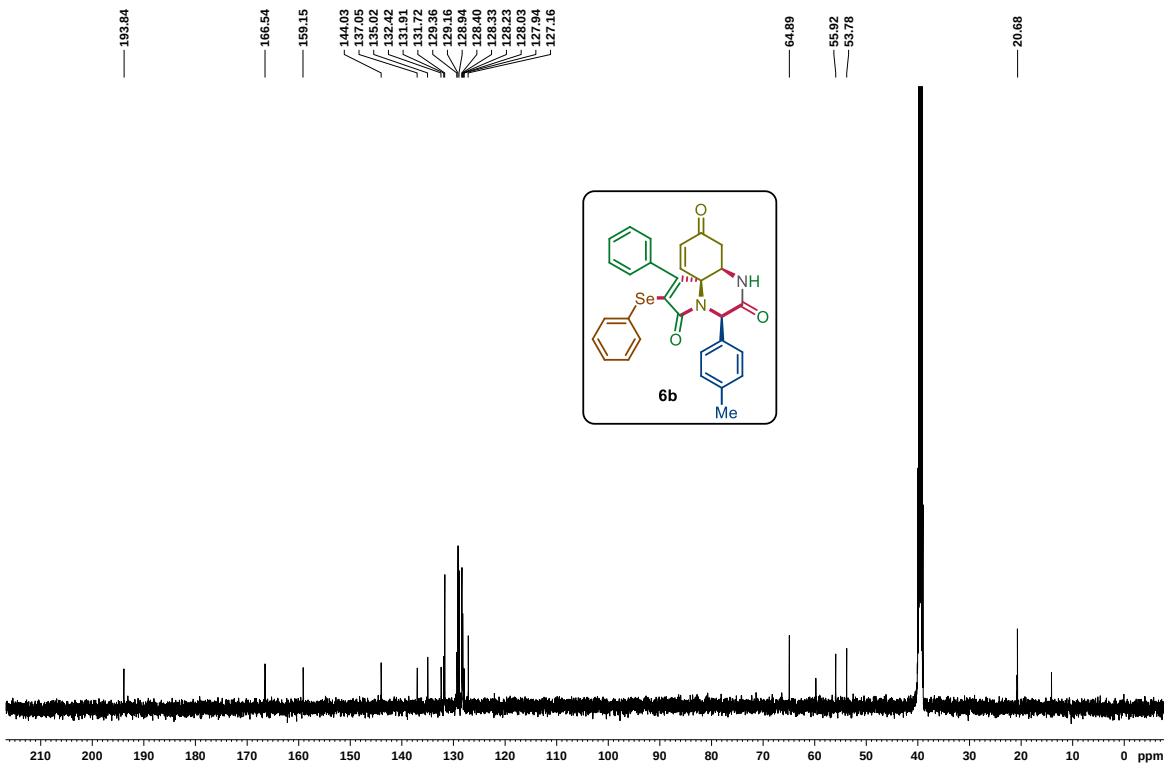


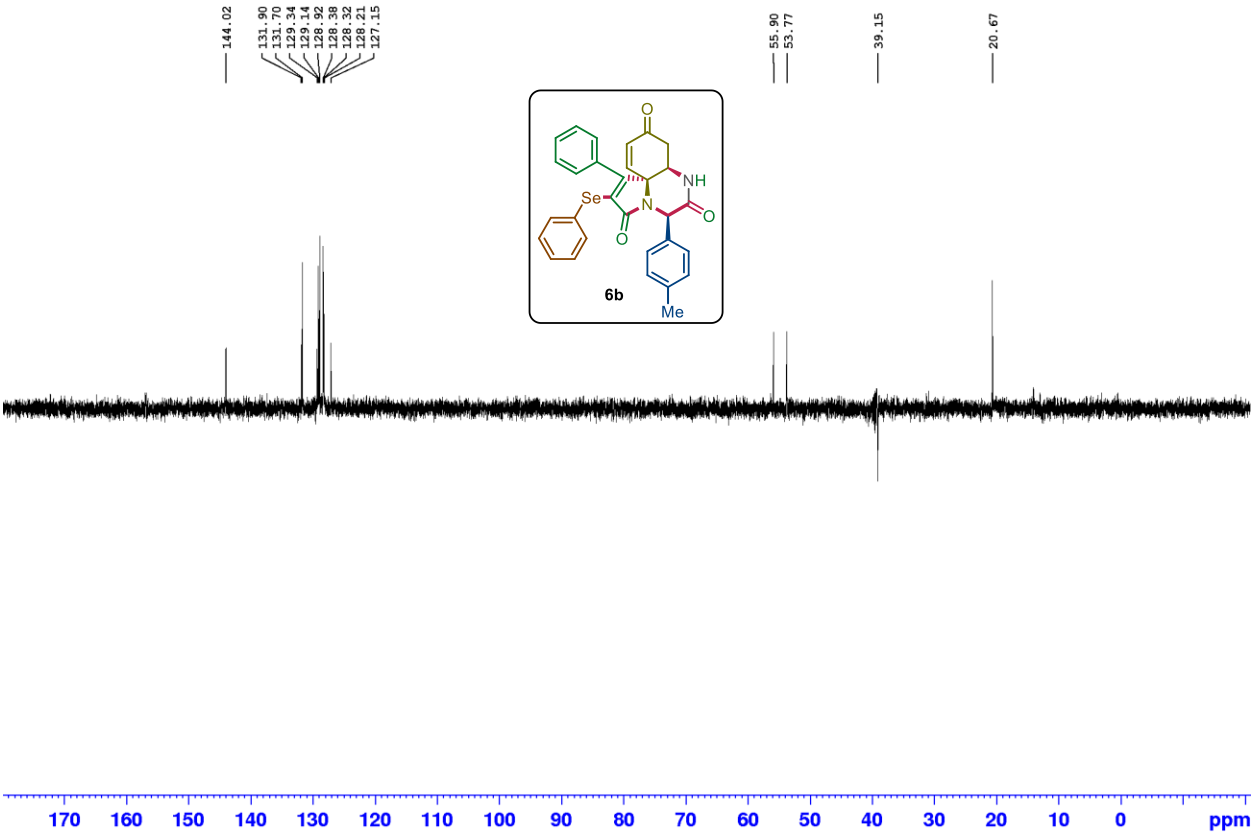


CMRV-SK-994-1H

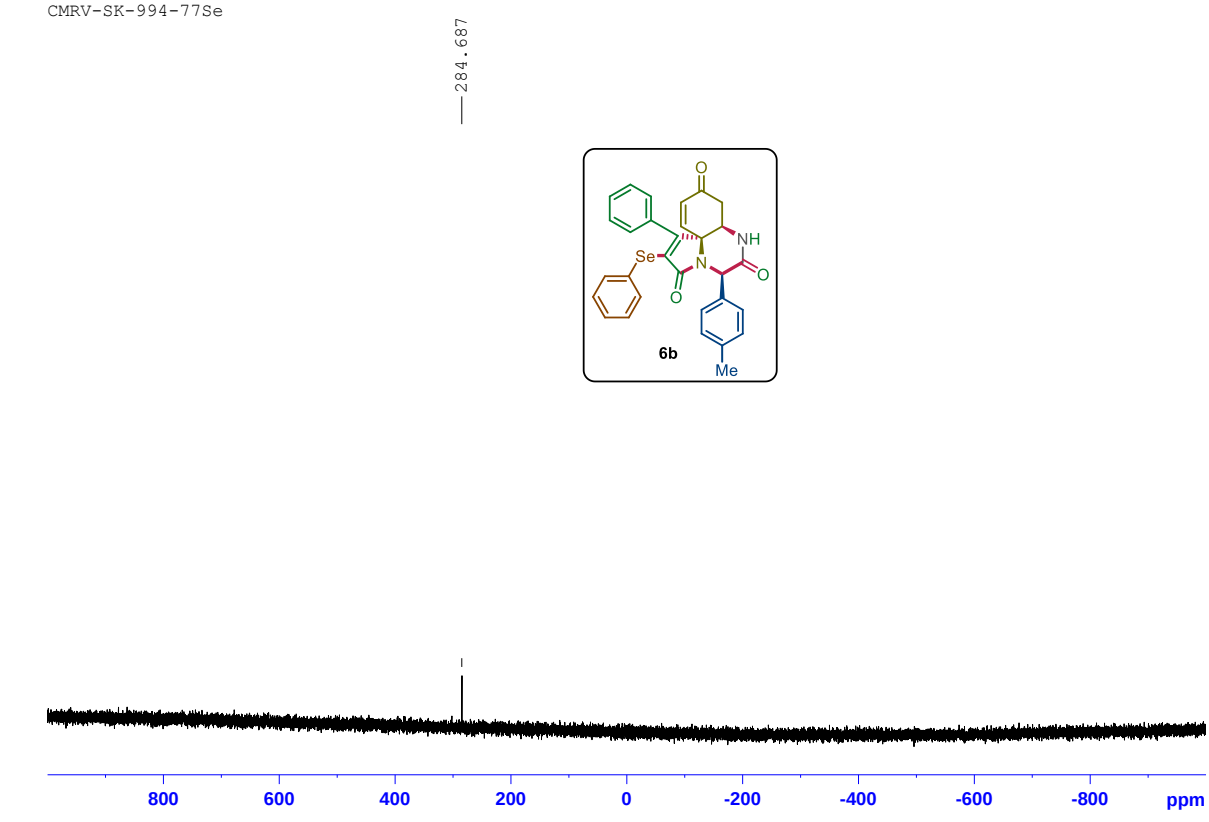


CMRV-SK-994-13C

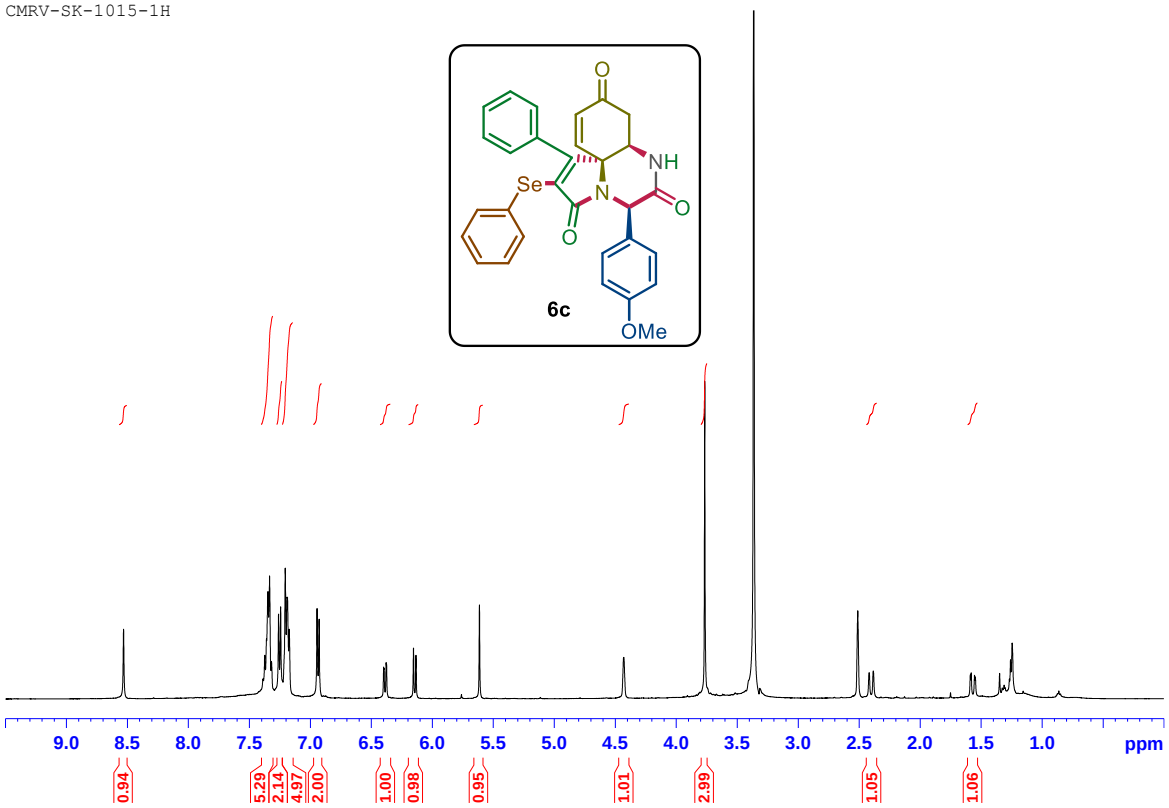




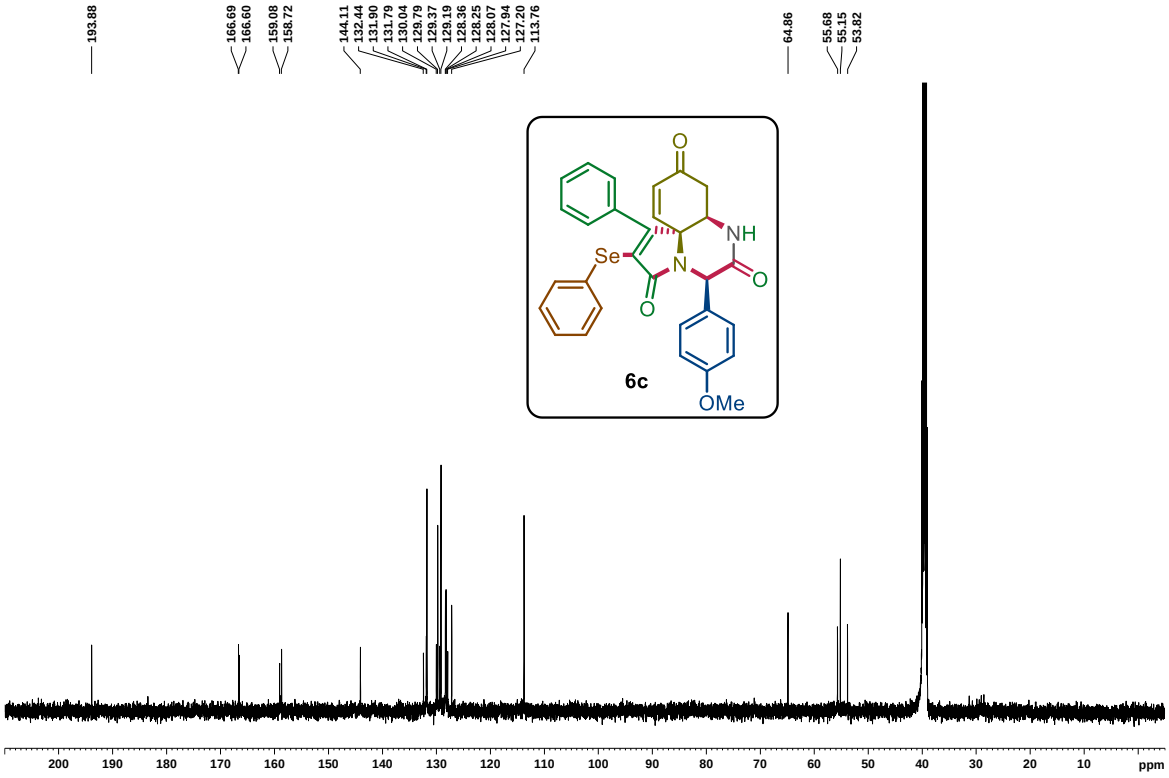
CMRV-SK-994-77Se

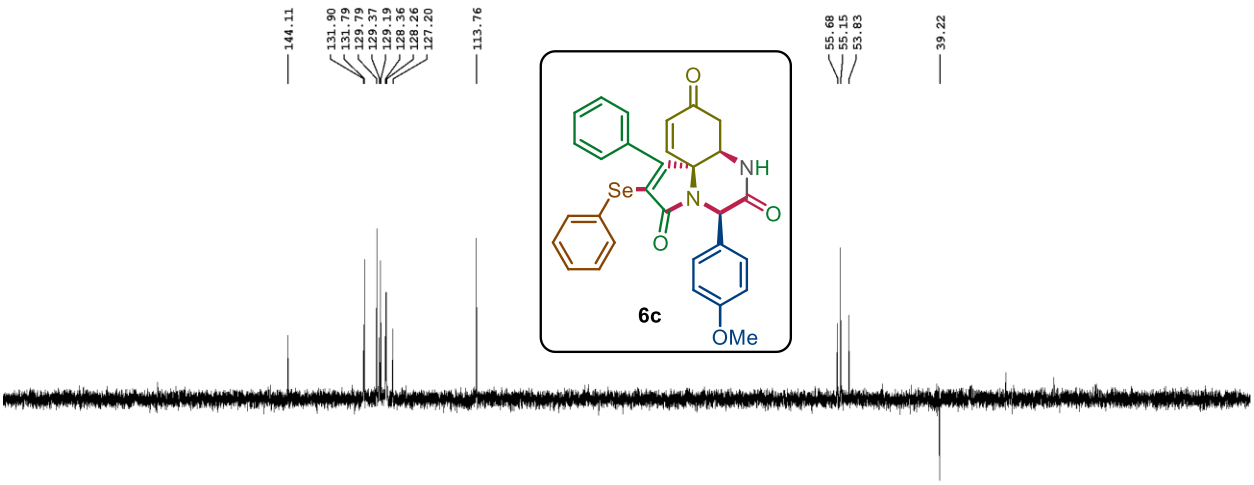


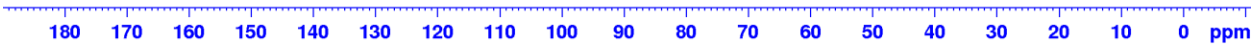
CMRV-SK-1015-1H



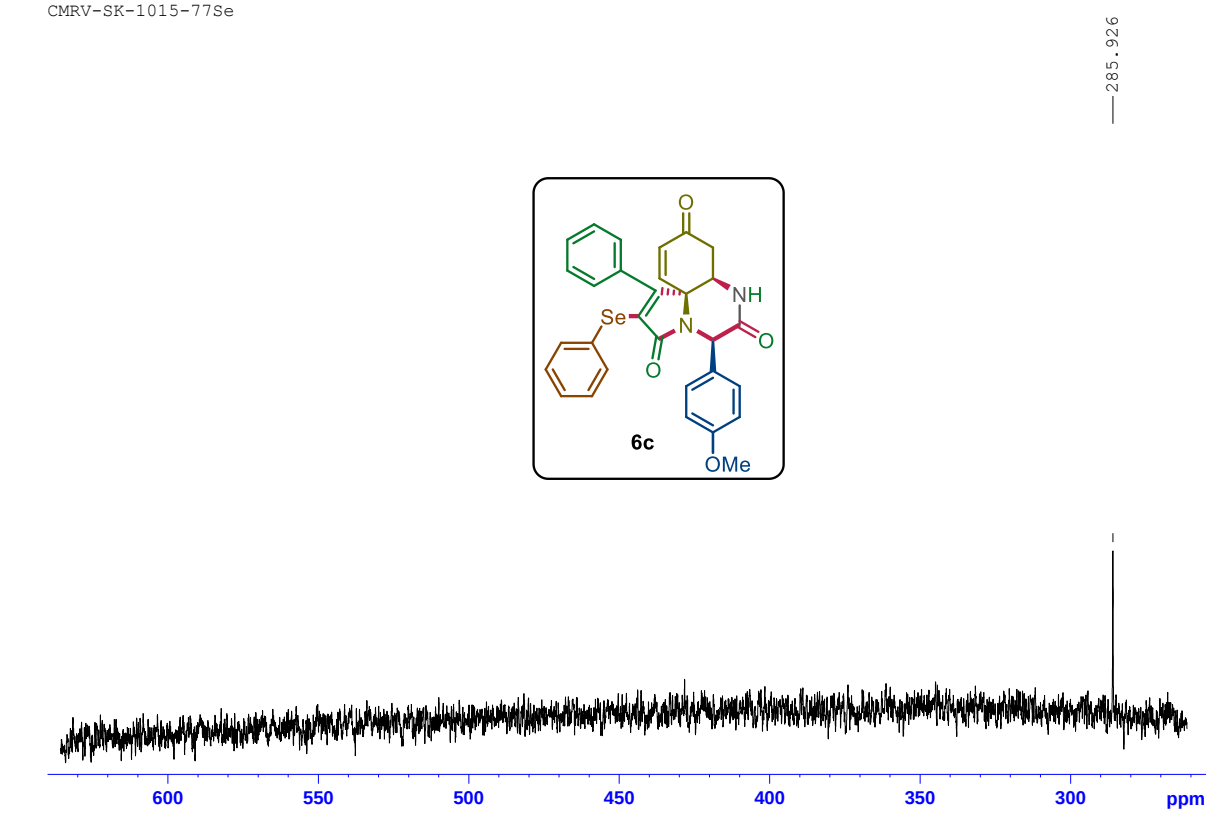
CMRV-SK-1015-13C



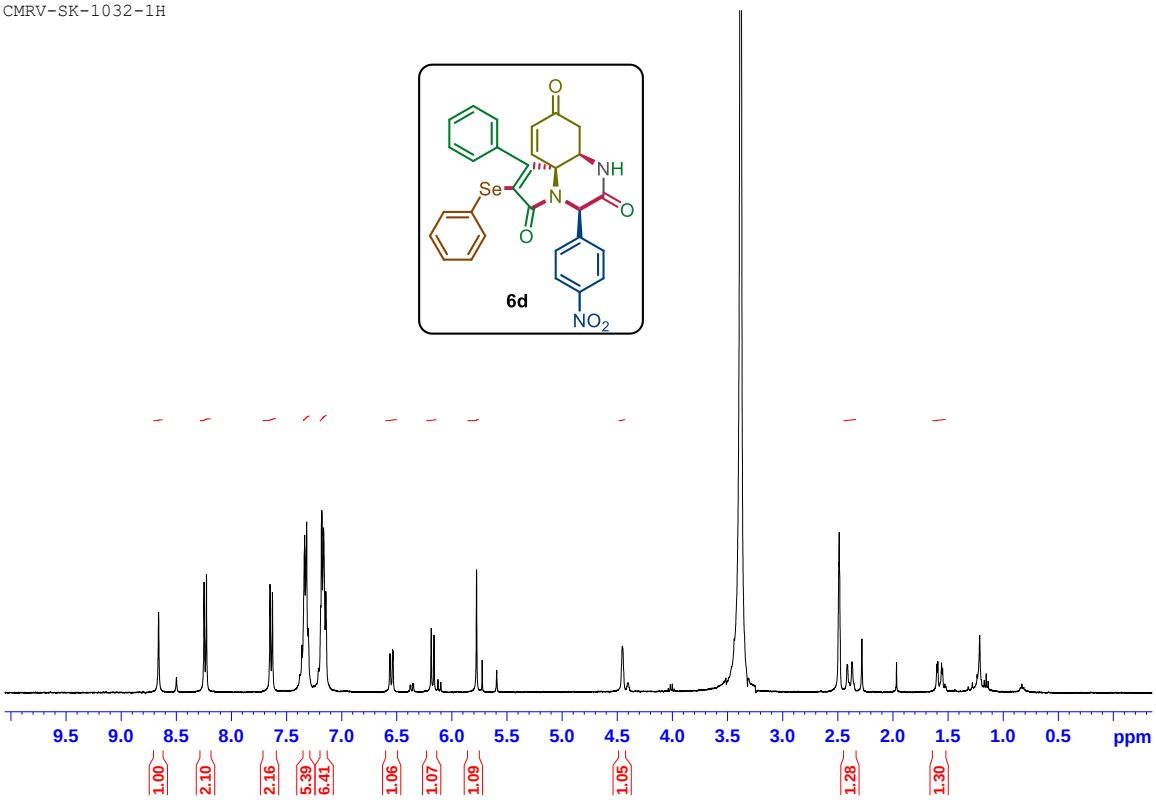




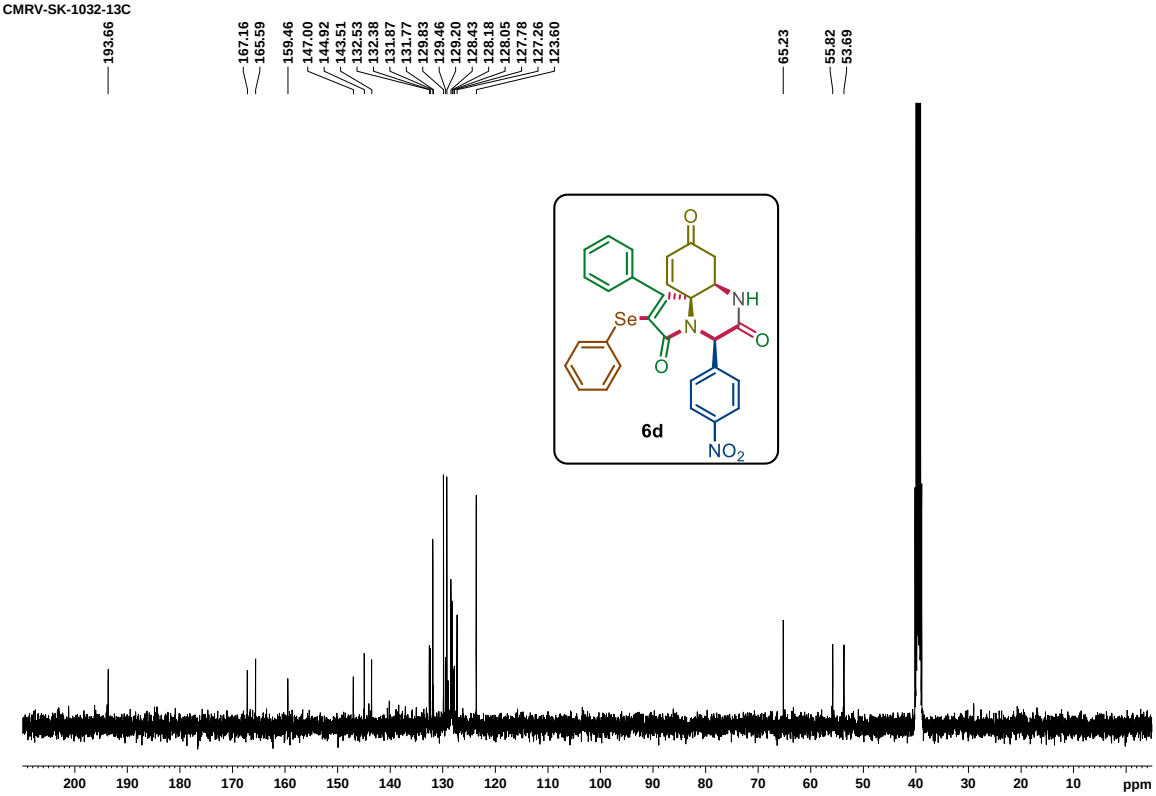
CMRV-SK-1015-77Se



CMRV-SK-1032-1H

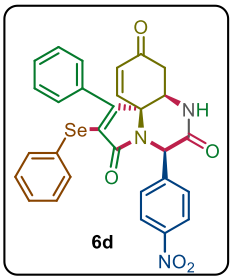


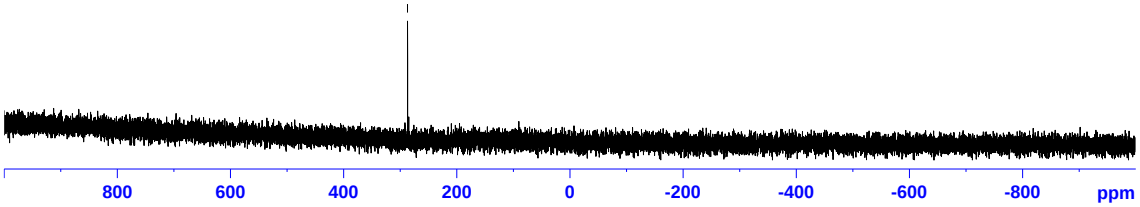
CMRV-SK-1032-13C



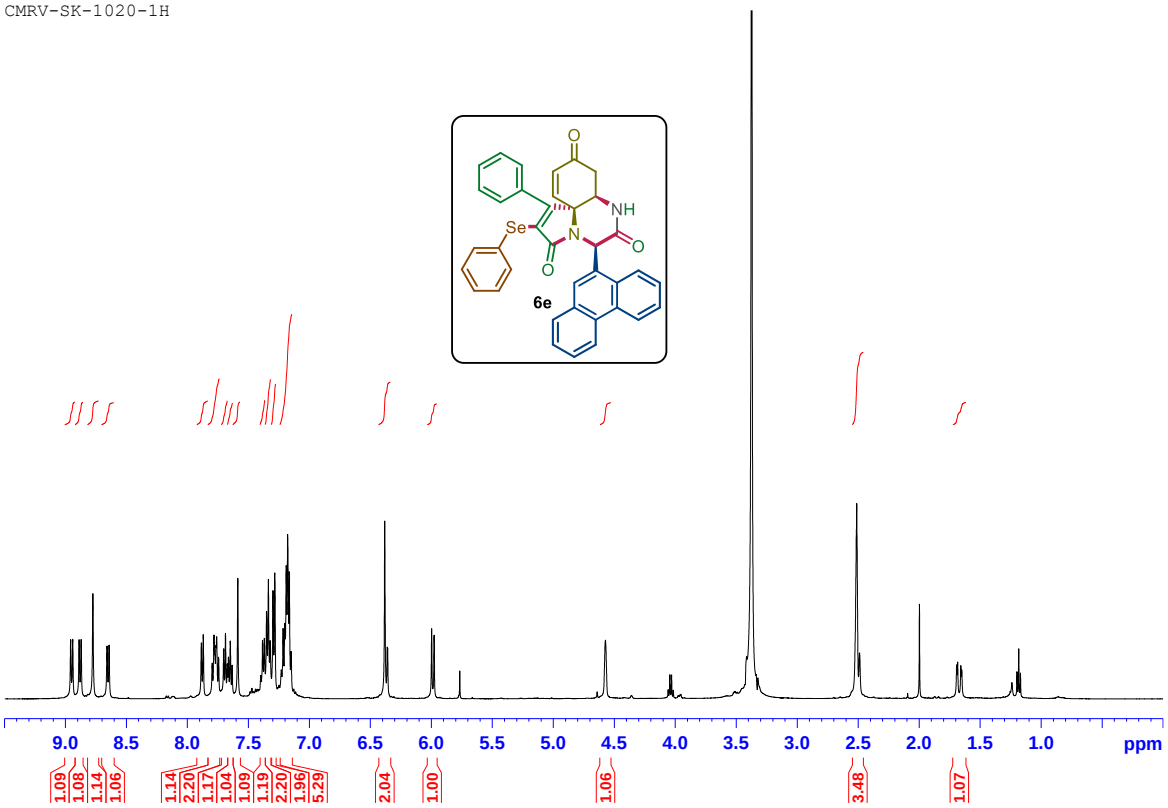
CMRV-SK-1032-77Se

287.085

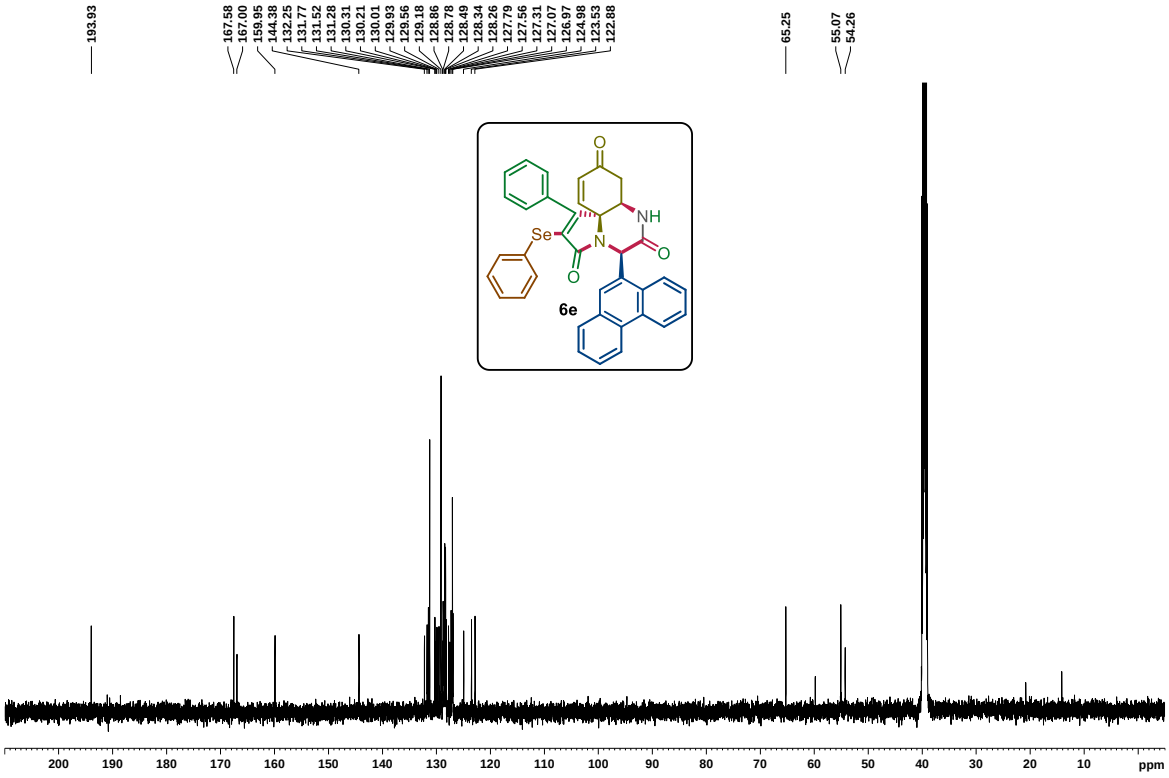


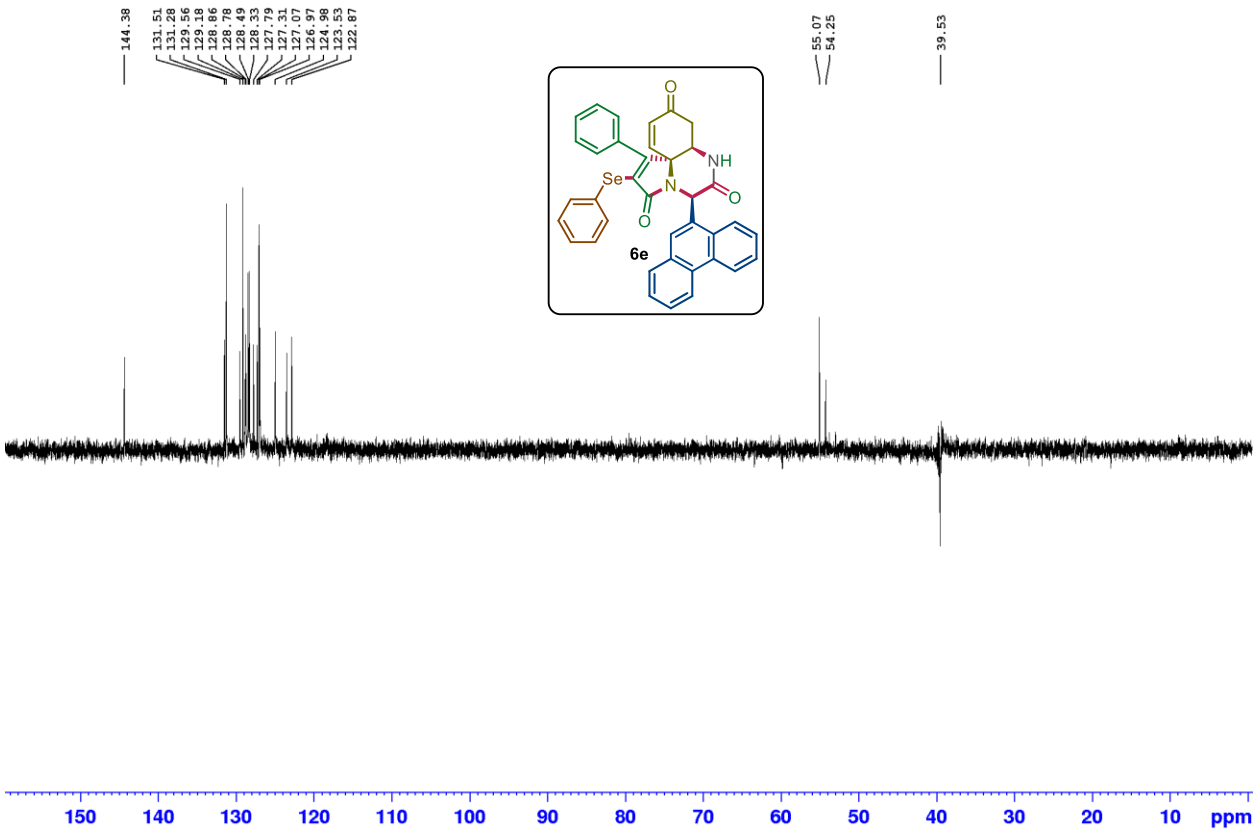


CMRV-SK-1020-1H



CMRV-SK-1020-13C





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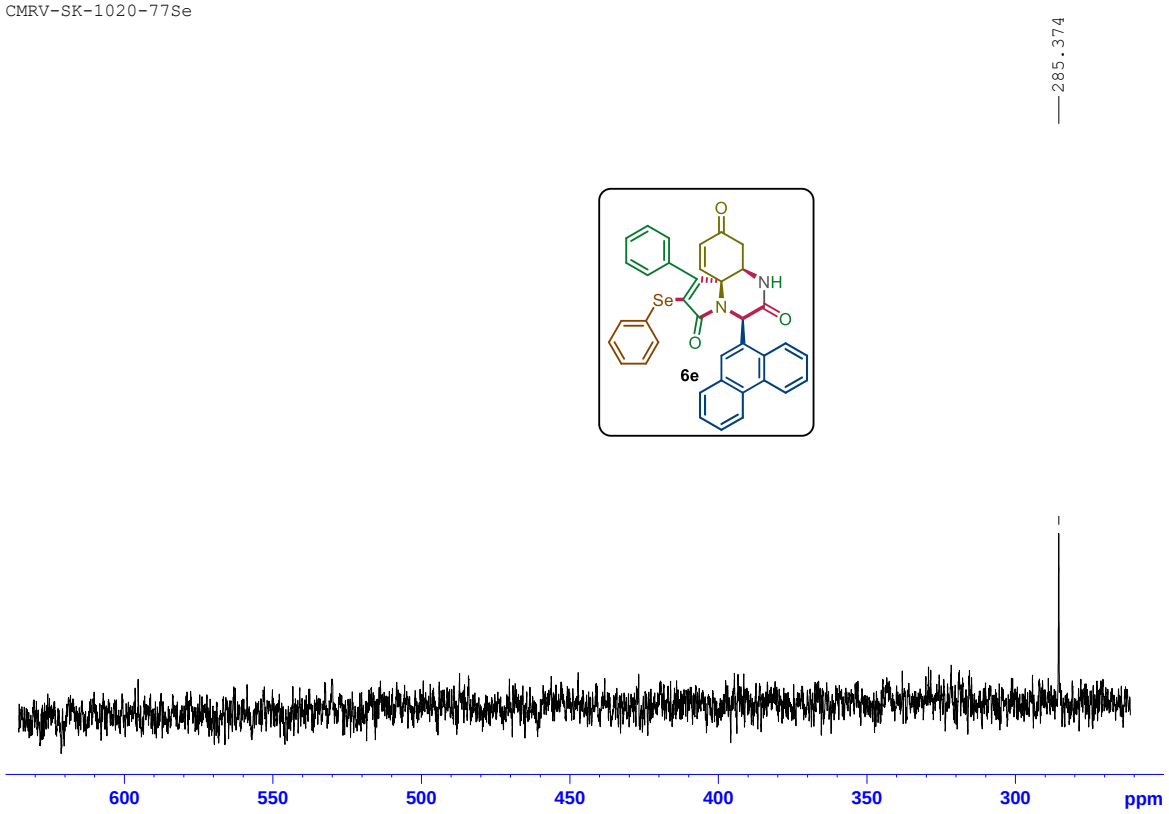

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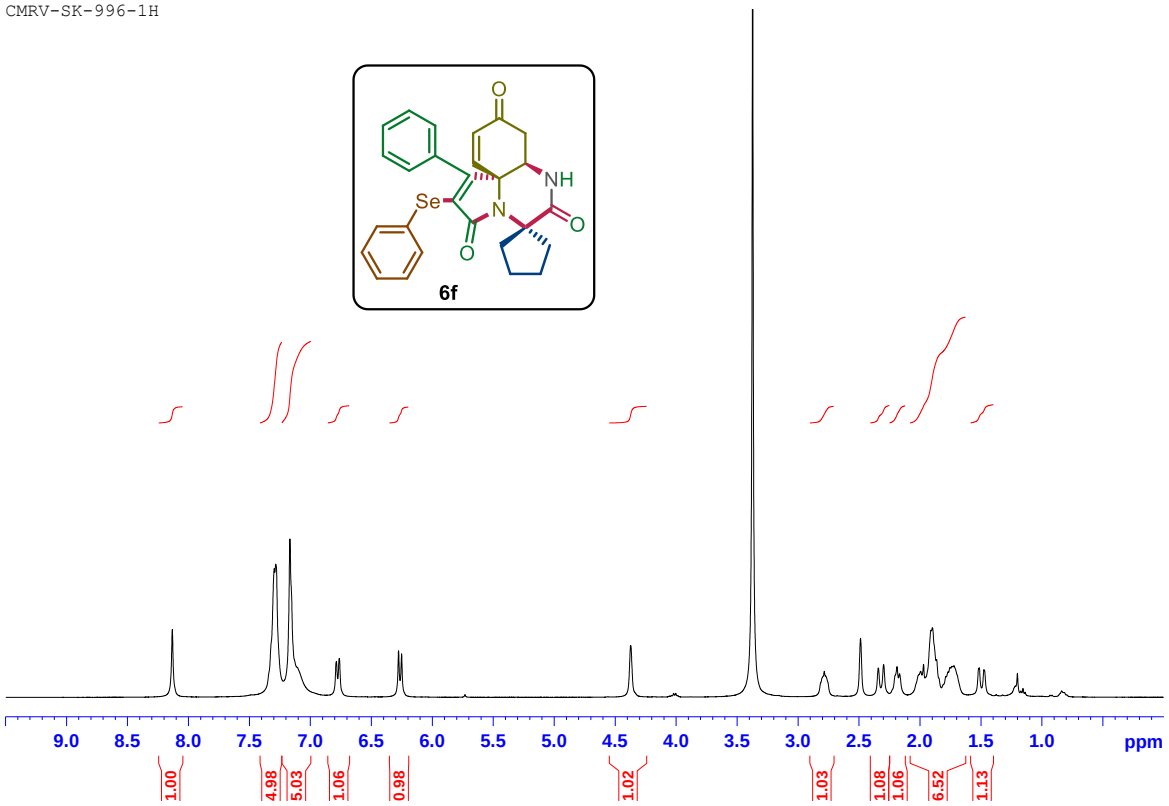

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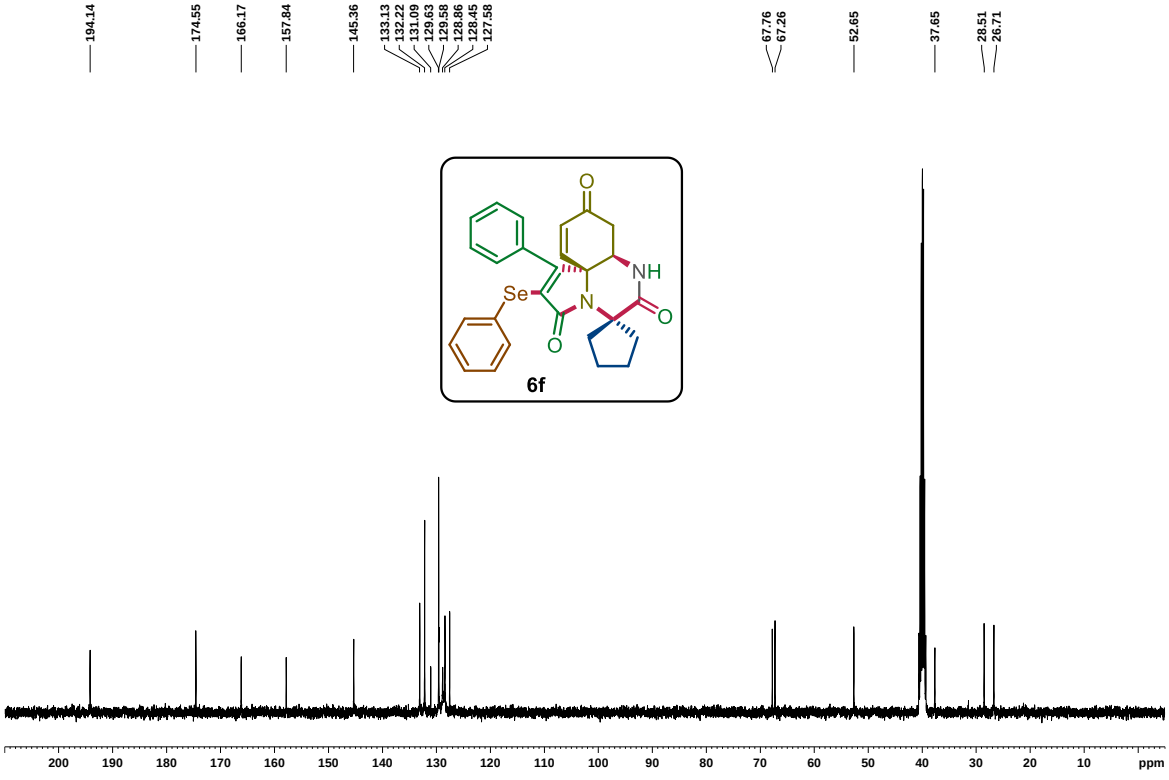

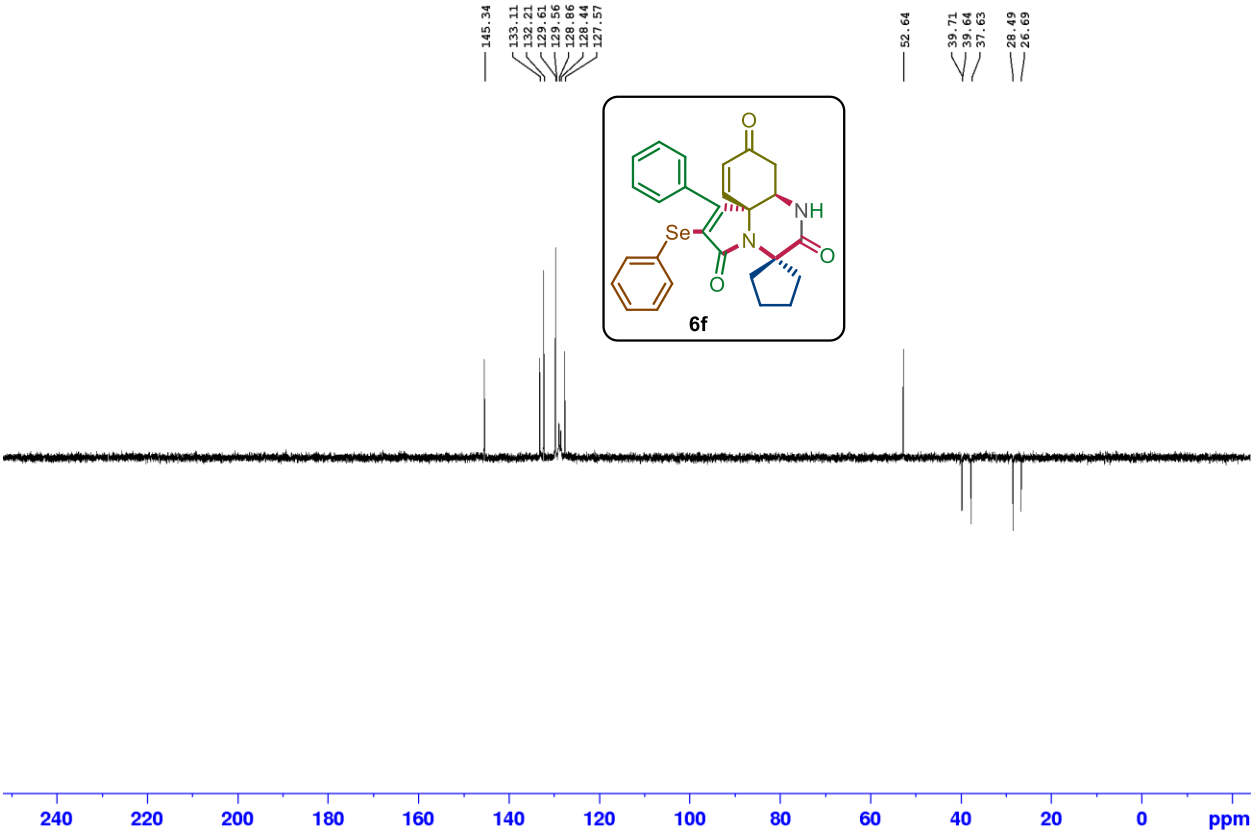

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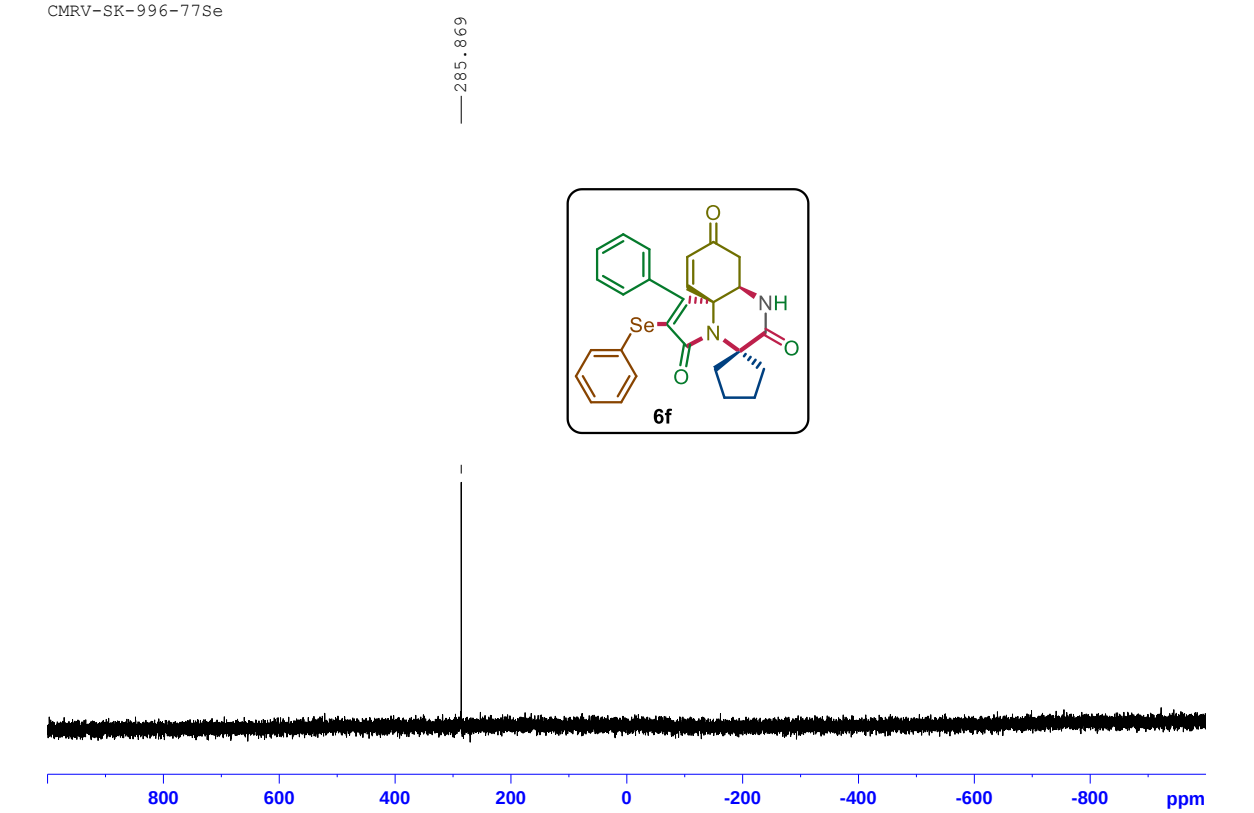

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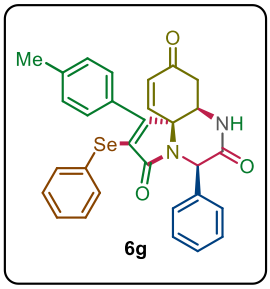

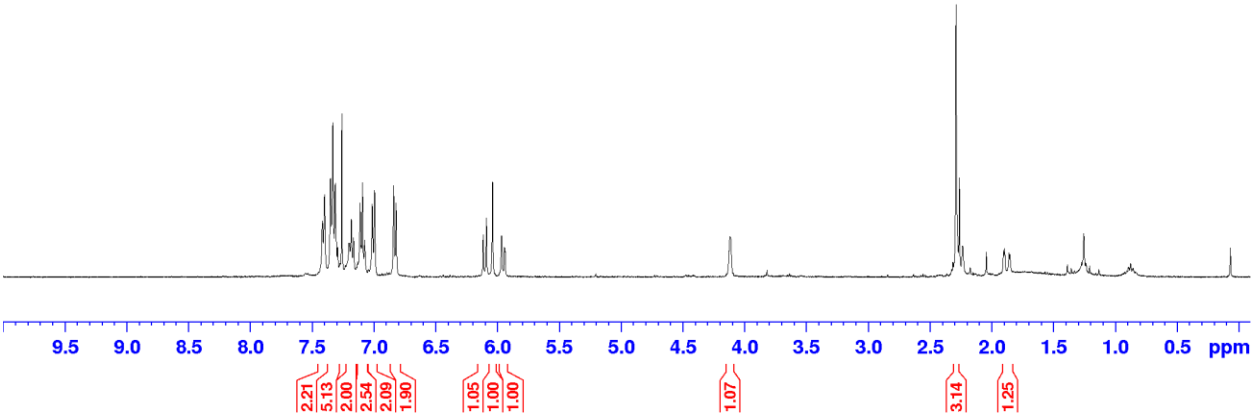

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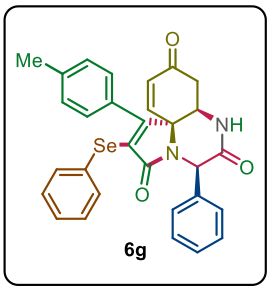

CMRV-AC-510-77SE

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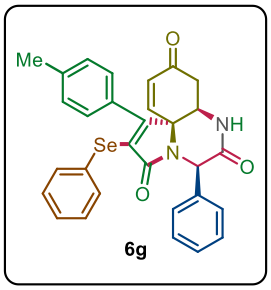

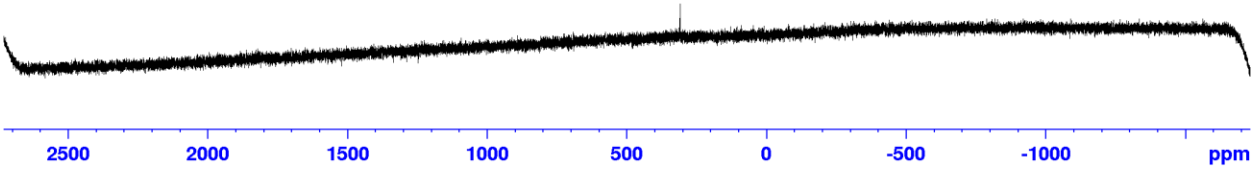

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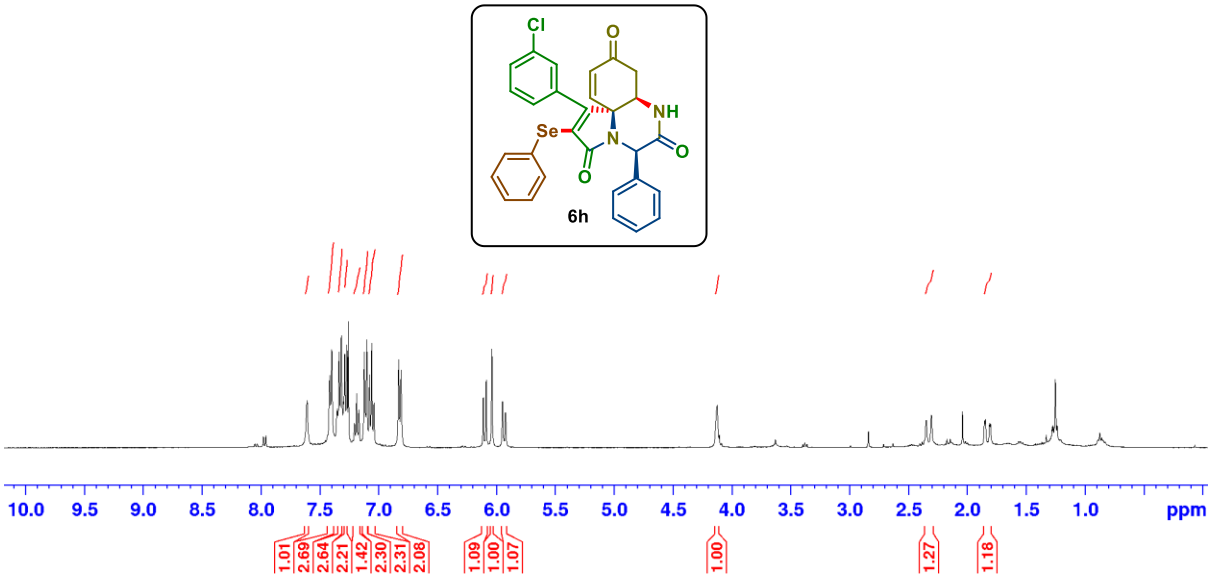

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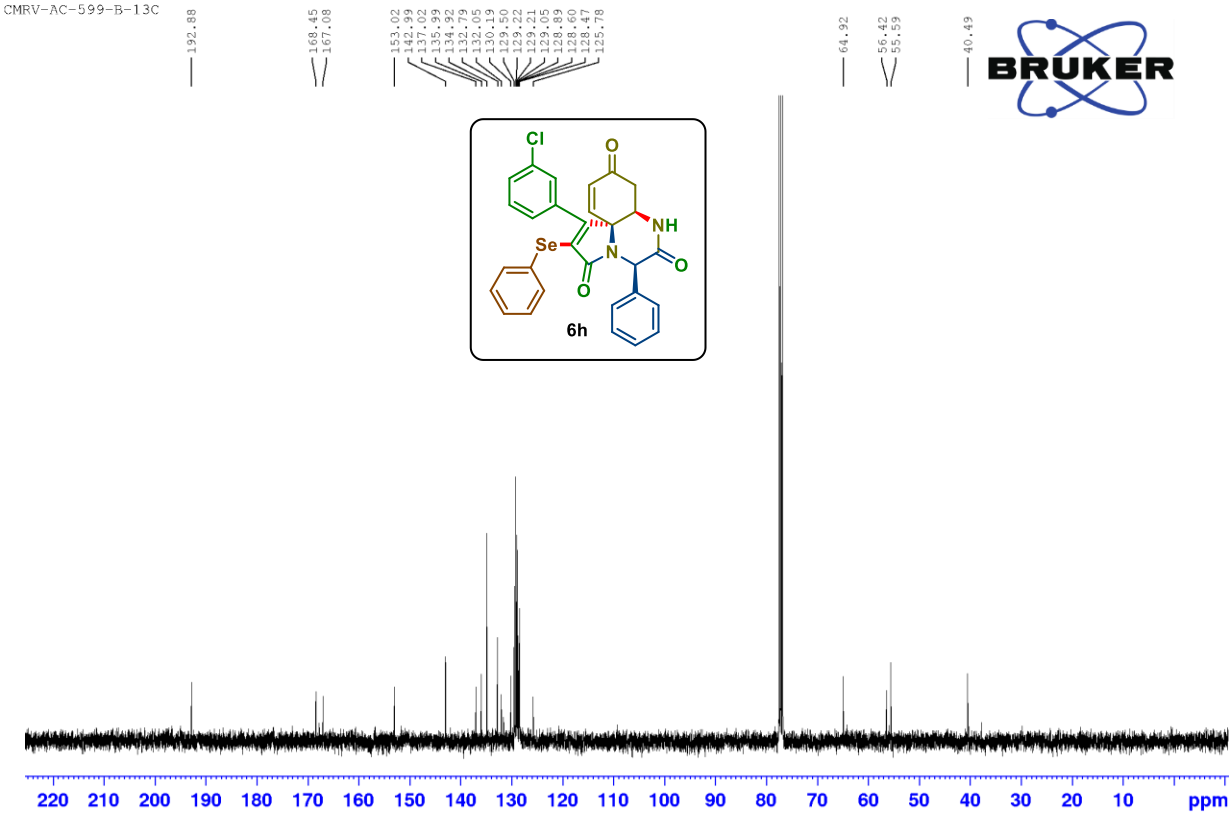

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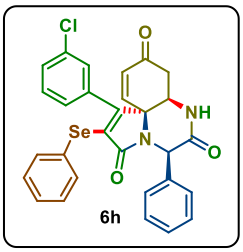

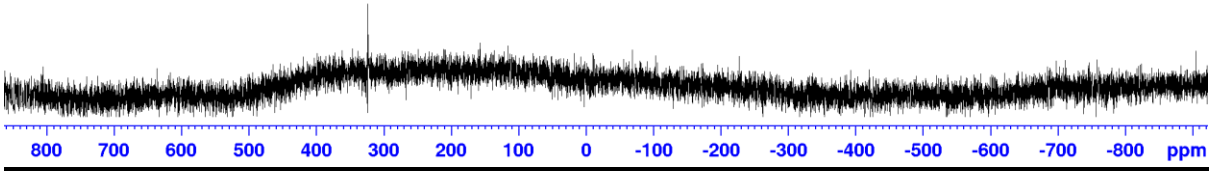

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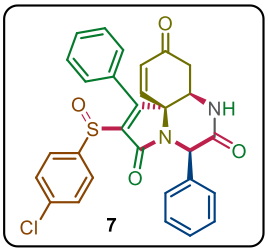

CMRV-SK-1014-13C

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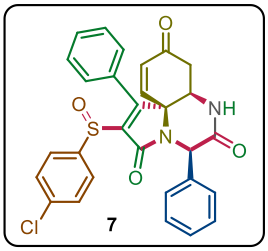

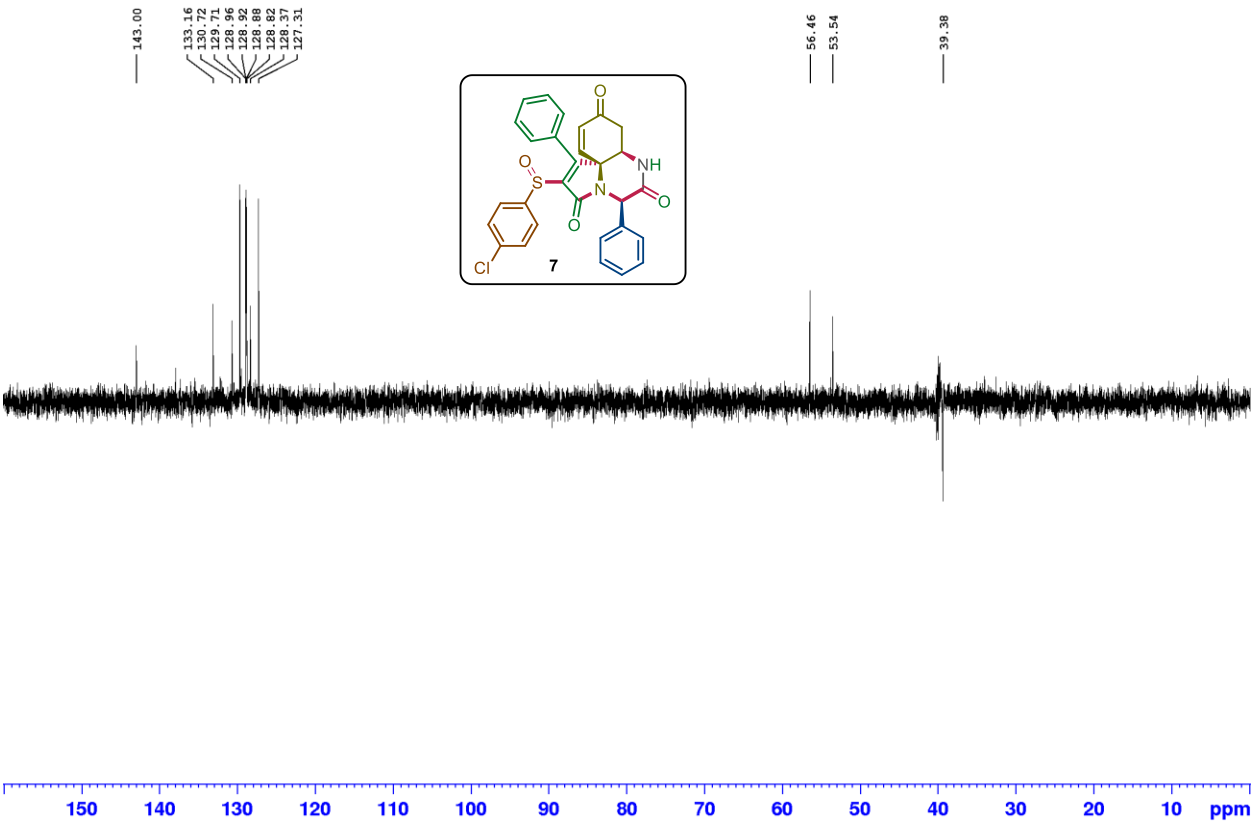
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