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Supporting Information

"Novel oxoisochromene synthesis via chemoselective O-H insertion of 1,3-dicarbonyl compounds and subsequent Pd-catalyzed intramolecular Heck reaction"

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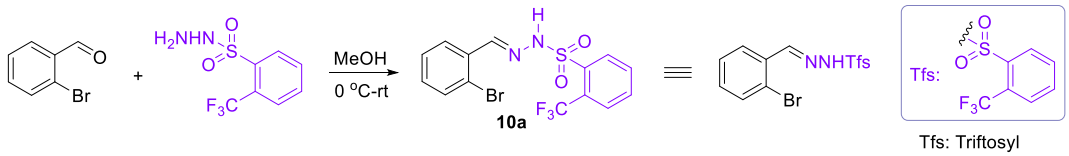
Contents:

General Experimental: Unless otherwise mentioned, all chemicals received from commercial sources were used without purification. All commercial grade solvents were used without any purification. Anhydrous solvents were obtained following standard procedures. Column chromatography was performed on 100-200 mesh silica gel using gradient mixture of ethyl acetate in hexanes. ^{1}H and ^{13}C NMR spectra were recorded on Jeol JNM-ECS spectrometer at operating frequencies of 500 MHz (^{1}H) or 125 MHz (^{13}C) and Bruker Avance Neo spectrometer at operating frequencies of 600 MHz (^{1}H) or 150 MHz (^{13}C) as indicated in the individual spectrum using TMS as an internal standard. HRMS spectra were recorded on SCIEX G2-SQ ToF (Waters, USA) mass spectrometer. Thin layer chromatography was performed on aluminum plates (silica gel 60 PF_{254}, 0.25 mm) purchased from Merck. The multiplicity in ^{1}H NMR spectra is presented as s for singlet, d for doublet, dd for doublet of doublet, t for triplet, dt for doublet of triplets, apt for aparently triplate, q for quartet, ABq for AB type quartet and m for multiplet.

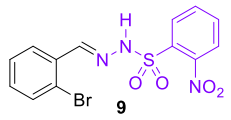
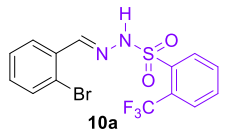
Starting material preparation: 2-Bromoarybenzaldehydes were either purchased from commercial sources or prepared in the laboratory following reported procedures.[1] Arylsulfonylhydrazides were either obtained from commercial sources or prepared in the laboratory using commercially available arylsulfonylchlorides following reported procedure.[2]

Preparation of *N*-sulfonylarylhydrazones:

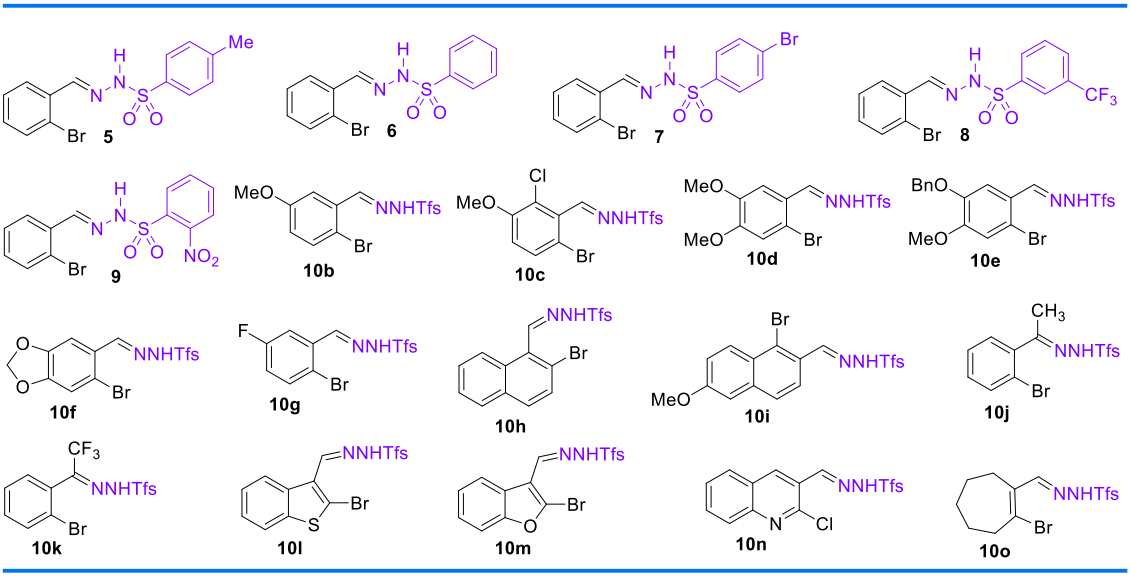


Tfs: Triftosyl

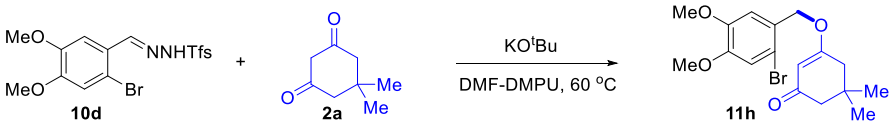
To the vigorously stirred solution of 2-bromobenzaldehyde (925 mg, 5.0 mmol) in MeOH (5.0 mL) at 0 °C was added *N*-2-(trifluoromethyl) benzenesulfonylhydrazide (1.20 g, 5.0 mmol). Then ice-water bath was removed and the reaction mixture was stirred at rt for 5 hours. TLC analysis indicated completed conversion. Then solvent evaporated and the crude product was recrystallized from hot THF to obtain pure *N*-sulfonylhydrazone **10a** as white crystalline solid (1.71 g, 84% yield).

 **9**	Compound **9**: **^{1}H NMR** (DMSO-d_6, 500 MHz) δ 12.5 (brs, 1H, NH), 8.17 (dd, *J* = 4.0, 8.0 Hz, 1H), 8.10 (dd, *J* = 4.0, 8.0 Hz, 1H), 8.00-7.97 (m, 2H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.73 (d, *J* = 8.5 Hz, 1H), 7.48 (apt, *J* = 8.0 Hz, 1H), 7.42 (apt, *J* = 9.5 Hz, 1H); **^{13}C NMR** (DMSO-d_6, 125 MHz) δ 147.8, 146.0, 135.0, 133.2, 132.7, 132.2, 132.1, 130.8, 130.6, 128.2, 127.0, 124.6, 123.4.
 **10a**	Compound **10a**: **^{1}H NMR** ($CDCl_3$+ DMSO-d_6, 600 MHz) δ 8.32 (d, *J* = 4.8 Hz, 1H), 8.21 (dd, *J* = 4.2, 8.4 Hz, 1H), 7.81 (apt, *J* = 6.6 Hz, 1H), 7.71-7.62 (m, 3H), 7.46-7.41 (m, 1H), 7.18 (dd, *J* = 4.8, 7.8 Hz, 1H), 7.14-7.09 (m, 1H); **^{13}C NMR** ($CDCl_3$ + DMSO-d_6, 150 MHz) δ 145.2 (q, $J_{C\text{-}F}$ = 4.6 Hz), 138.0, 132.6, 132.5, 132.5 (2C), 132.0, 131.9, 130.8, 127.8 (q, $J_{C\text{-}F}$ = 6.6 Hz), 127.4 (q, $J_{C\text{-}F}$ = 33.0 Hz), 127.2, 127.1, 123.5, 122.5 (q, $J_{C\text{-}F}$ = 272.4 Hz).

The following *N*-sulfonylhydrazones were synthesized following the procedure described above:

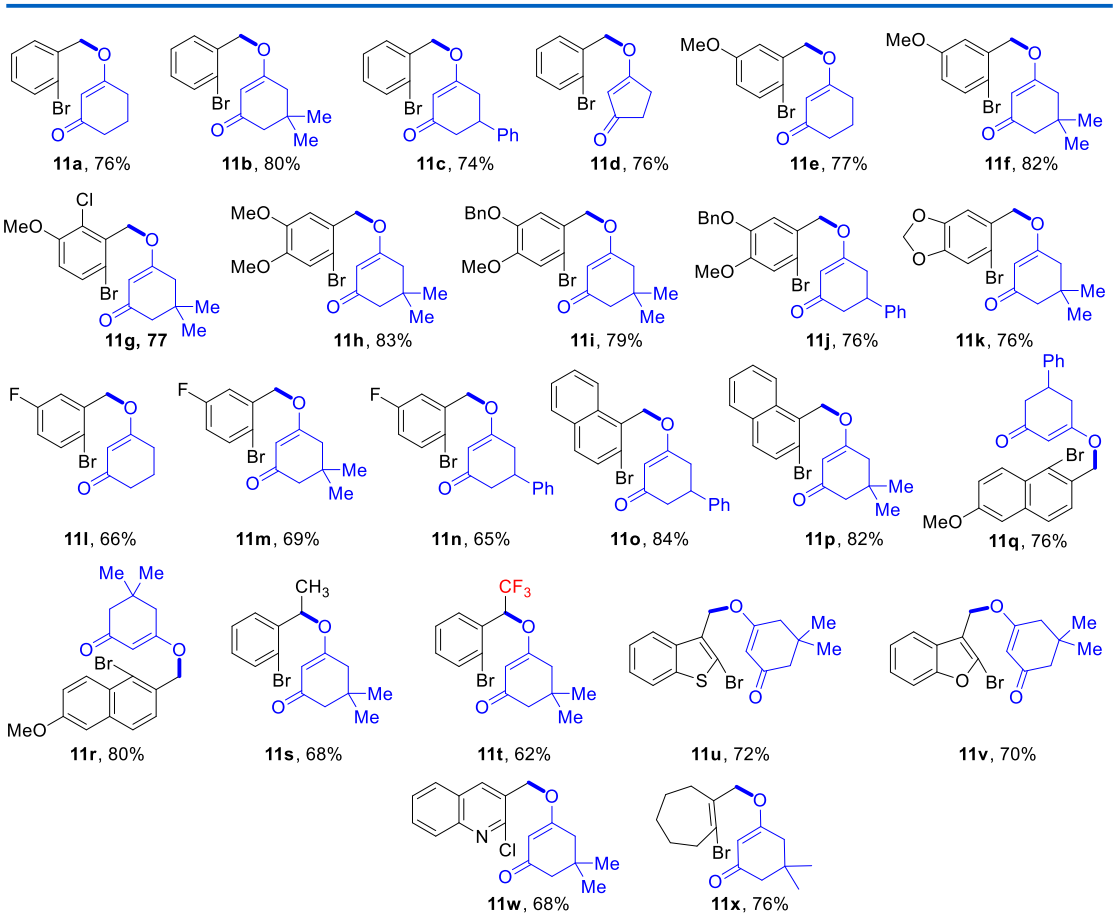


Experimental procedure for chemoselective *O*-alkylation of 1,3-diketone:

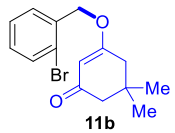
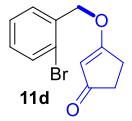
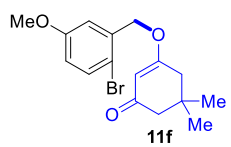
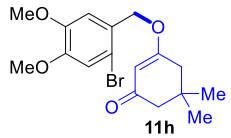


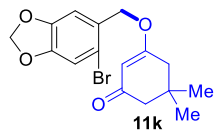
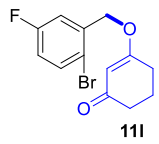
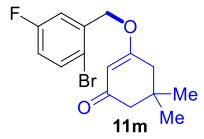
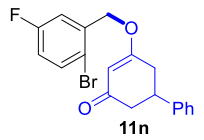
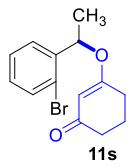
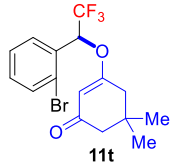
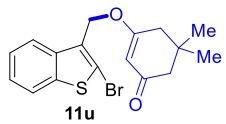
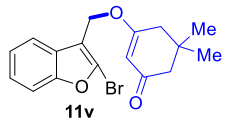
To a stirred solution of dimedone **2a** (56.1 mg, 0.40 mmol) in dry DMF-DMPU (4:1, 0.80 mL) under nitrogen atmosphere was added KO^{t}Bu (45.0 mg, 0.40 mmol) at rt. The mixture was then stirred at 60 °C for 15 minutes. Then, solid *N*-triftosylhydrazone **10a** (93.5 mg, 0.20 mmol) was added in portions over 2 minutes. The resulting mixture was stirred at 60 °C for 15 minutes and then cooled to rt. The reaction mixture was then diluted with ethyl acetate (25 mL) and extracted with brine (3 x 10 mL). Organic layer was dried over Na_2SO_4 and evaporated. The crude product was purified by silica gel column chromatography using 10% ethyl acetate in hexanes as eluent to obtain vinyl ether **11h** (61.3 mg, 83% yield) as light brown oil.

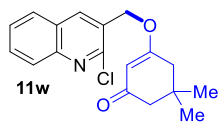
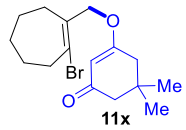
The following vinyl ethers were synthesized according to the procedure described above:



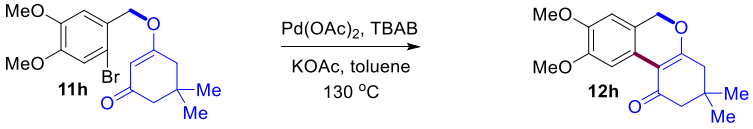
Analytical data of selected vinyl ethers:

 11b	Compound **11b**: 47.1 mg, 76% yield; white solid, mp 105-106 °C; purified using 10% ethyl acetate in hexanes as eluent; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 7.52 (d, *J* = 7.0 Hz, 1H), 7.35 (d, *J* = 8.0 Hz, 1H), 7.27 (apt, *J* = 8.0 Hz, 1H), 7.14 (apt, *J* = 8.0 Hz, 1H), 5.42 (s, 1H), 4.90 (s, 2H), 2.31 (s, 2H), 2.17 (s, 2H), 1.03 (s, 6H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 199.4, 175.5, 134.4, 132.9, 129.8, 129.1, 127.6, 122.8, 102.4, 69.8, 50.7, 42.7, 32.6, 28.3.
 11d	Compound **11d**: 39.8 mg, 76% yield; white solid, mp 43-45 °C; purified using 10% ethyl acetate in hexanes as eluent; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 7.55 (d, *J* = 8.0 Hz, 1H), 7.38 (d, *J* = 6.5 Hz, 1H), 7.29 (apt, *J* = 8.0 Hz, 1H), 7.17 (apt, *J* = 8.0 Hz, 1H), 5.36 (s, 1H), 5.03 (s, 2H), 2.62 (apt, *J* = 2.5 Hz, 2H), 2.41 (apt, *J* = 2.5 Hz, 2H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 205.7, 189.4, 133.9, 133.0, 130.2, 129.5, 127.7, 123.1, 105.7, 72.9, 34.1, 28.4.
 11f	Compound **11f**: 55.7 mg, 82% yield; light yellow solid, mp 79-81°C; purified using 10% ethyl acetate in hexanes as eluent; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 7.39 (d, *J* = 8.0 Hz, 1H), 6.90 (s, 1H), 6.70 (dd, *J* = 3.0, 9.0 Hz, 1H), 5.40 (s, 1H), 4.86 (s, 2H), 3.73 (s, 3H), 2.32 (s, 2H), 2.17 (s, 2H), 1.03 (s, 6H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 199.4, 175.4, 159.1, 135.3, 133.4, 115.1, 114.9, 112.8, 102.5, 69.7, 55.5, 50.7, 42.7, 32.5, 28.3, 21.9; **HRMS** (ESI-TOF) calculated for $C_{16}H_{20}BrO_3$ $[M+H]^+$: 339.0596 found 339.0606.
 11h	Compound **11h**: 61.3 mg, 83% yield; white solid, mp 85-87°C; purified using 10% ethyl acetate in hexanes as eluent; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 6.97 (s, 1H), 6.83 (s, 1H), 5.41 (s, 1H), 4.82 (s, 2H), 3.80 (s, 6H), 2.28 (s, 2H), 2.16 (s, 2H), 1.02 (s, 6H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 199.4, 175.5, 149.7, 148.5, 126.2, 115.5, 113.7, 112.3,

	102.3, 69.9, 56.2, 56.0, 50.7, 42.7, 32.5, 28.2; **HRMS** (ESI-TOF) calculated for $C_{17}H_{22}BrO_4$ $[M+H]^+$: 370.0701 found 370.0711.
 **11k**	Compound **11i**: 53.8 mg, 76% yield; white solid, mp 65-67°C; purified using 10% ethyl acetate in hexanes as eluent; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 6.96 (s, 1H), 6.81 (s, 1H), 5.93 (s, 2H), 5.39 (s, 1H), 4.80 (s, 2H), 2.28 (s, 2H), 2.17 (s, 2H), 1.02 (s, 6H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 199.4, 175.4, 148.5, 147.6, 127.5, 113.8, 113.0, 109.1, 102.4, 102.0, 69.9, 50.7, 42.7, 32.5, 28.3; **HRMS** (ESI-TOF) calculated for $C_{16}H_{18}BrO_4$ $[M+H]^+$: 353.0388 found 353.0393.
 **11l**	Compound **11l**: 39.5 mg, 66% yield; white solid, mp 65-67°C; purified using 10% ethyl acetate in hexanes as eluent; purified using 15% ethyl acetate in hexanes as eluent; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 7.45 (dd, J = 3.0, 8.5 Hz, 1H), 7.11 (dd, J = 3.0, 6.5, Hz, 1H), 6.86 (dt, J = 2.5, 8.0 Hz, 1H), 5.39 (s, 1H), 4.84 (s, 2H), 2.45 (apt, J = 7.0 Hz, 2H), 2.30 (apt, J = 8.0 Hz, 2H), 1.99-1.93 (m, 2H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 199.4, 176.6, 162.0 (d, J_{C-F} = 246.2 Hz), 136.5 (d, J_{C-F} = 6.6 Hz), 133.9 (d, J_{C-F} = 8.2 Hz), 116.6 (d, J_{C-F} = 21.6 Hz), 116.0, 115.7 (d, J_{C-F} = 23.2 Hz), 103.7, 68.9, 36.6, 28.7, 21.0; **HRMS** (ESI-TOF) calculated for $C_{13}H_{13}BrFO_2$ $[M+H]^+$: 299.0083 found 299.0093.
 **11m**	Compound **11m**: 45.2 mg, 69% yield; white solid, mp 70-72 °C ; purified using 15% ethyl acetate in hexanes as eluent; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 7.46 (dd, J = 5.0, 9.0, Hz, 1H), 7.11 (dd, J = 3.0, 9.0 Hz, 1H), 6.88 (dt, J = 2.5, 9.0, Hz, 1H), 5.40 (s, 1H), 4.87 (s, 2H), 2.33 (s, 2H), 2.18 (s, 2H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 199.3, 175.0, 162.0 (d, J_{C-F} = 246.2 Hz), 136.7(d, J_{C-F} = 8.2 Hz), 134.1 (d, J_{C-F} = 6.6 Hz), 116.7 (d, J_{C-F} = 23.3 Hz), 116.0, 115.7 (d, J_{C-F} = 24.8 Hz), 102.7, 69.1, 50.7, 42.7, 32.6, 28.3; **HRMS** (ESI-TOF) calculated for $C_{15}H_{17}BrFO_2$ $[M+H]^+$: 327.0396 found 327.0405.
 **11n**	Compound **11n**: 48.7 mg, 65% yield; white solid; mp 75-77 °C; purified using 10% ethyl acetate in hexanes as eluent; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 7.50 (dd, J = 8.0, 9.0 Hz, 1H), 7.33 (apt, J = 6.5 Hz, 2H), 7.27-7.23 (m, 3H), 7.15 (dd, J = 8.0, 2.5 Hz, 1H), 6.94-6.89 (m, 1H), 5.54 (s, 1H), 4.94 (s, 2H), 3.40 (m, 1H), 2.79-2.53 (m, 4H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 198.3, 175.6, 162.0 (d, J_{C-F} = 246 Hz), 142.3, 136.4, (d, J_{C-F} = 8.3 Hz), 133.9 (d, J_{C-F} = 8.2 Hz), 128.7, 127.0, 126.5, 116.7 (d, J_{C-F} = 21.6 Hz), 116.0, 115.7 (d, J_{C-F} = 23.2 Hz), 103.5, 69.2, 43.7, 39.1, 36.2; **HRMS** (ESI-TOF) calculated for $C_{19}H_{17}BrFO_2$ $[M+H]^+$: 375.0396 found 375.0392.
 **11s**	Compound **11s**: 40.2 mg, 68% yield; yellow solid, mp 79-81°C; purified using 10% acetone in hexanes as eluent; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 7.52 (d, J = 8.0 Hz, 1H), 7.33-7.27 (m, 2H), 7.14 (apt, J = 8.0 Hz, 1H), 5.51 (q, J = 6.5 Hz, 1H), 5.14 (s, 1H), 2.51-2.42 (m, 2H), 2.32-2.23 (m, 2H), 2.01-1.91 (m, 2H), 1.57 (d, J = 7.0 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 199.5, 175.8, 140.4, 132.9, 129.3, 128.0, 126.0, 121.3, 104.8, 75.4, 36.6, 29.1, 21.9, 21.1; **HRMS** (ESI-TOF) calculated for $C_{14}H_{16}BrO_2$ $[M+H]^+$: 295.0333 found 295.0322.
 **11t**	Compound **11t**: 46.7 mg, 62% yield; white solid, mp 62-64 °C; purified using 10% ethyl acetate in hexanes as eluent; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 7.56 (d, J = 8.0 Hz, 1H), 7.39 (d, J = 8.0 Hz, 1H), 7.30 (apt, J = 8.0 Hz, 1H), 7.22 (apt, J = 8.0 Hz, 1H), 5.80 (dd, J = 6.5 Hz, 1H), 5.06 (s, 1H), 2.34 (ABq, J = 17.5 Hz, 2H), 2.09 (ABq, J = 16.0 Hz, 2H), 1.02 (s, 3H), 0.92 (s, 3H); **^{13}CNMR** ($CDCl_3$, 125 MHz) δ 198.7, 172.4, 133.4, 131.7, 130.2, 128.6, 128.1, 124.3, 122.7 (q, J_{C-F} = 279.1 Hz), 104.3, 75.6 (q, J_{C-F} = 33.2 Hz), 50.6, 42.5, 32.5, 28.2, 27.9; **HRMS** (ESI-TOF) calculated for $C_{16}H_{17}BrF_3O_2$ $[M+H]^+$: 377.0364 found 377.0342.
 **11u**	Compound **11u**: 52.6 mg, 72% yield; white solid, mp 242-244 °C; purified using 15% ethyl acetate in hexanes as eluent; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 7.68 (d, J = 8.0 Hz, 1H), 7.63 (d, J = 6.5 Hz, 1H), 7.34-7.28 (m, 2H), 5.55 (s, 1H), 5.04 (s, 2H), 2.24 (s, 2H), 2.12 (s, 2H), 1.01 (s, 6H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 199.3, 175.4, 155.5, 129.1, 127.3, 125.0, 123.7, 119.0, 114.3, 111.2, 102.2, 61.6, 50.7, 42.7, 32.5, 28.2; **HRMS** (ESI-TOF) calculated for $C_{17}H_{18}BrO_2S$ $[M+H]^+$: 365.0211 found 365.0218.
 **11v**	Compound **11v**: 48.9 mg, 70% yield; white solid, mp 242-244 °C; purified using 15% ethyl acetate in hexanes as eluent; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 7.46 (d, J = 6.5 Hz, 1H), 7.39 (d, J = 8.0 Hz, 1H), 7.24 (apt, J = 8.0 Hz, 1H), 7.20 (apt, J = 8.0 Hz, 1H), 5.48 (s, 1H), 4.92 (s, 2H), 2.25 (s, 2H), 2.16 (s, 2H), 1.01 (s, 6H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 199.3, 175.4, 155.5, 129.1, 127.3, 125.0, 123.7, 119.0, 114.3, 111.2, 102.2,

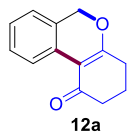
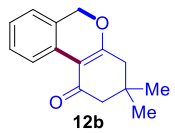
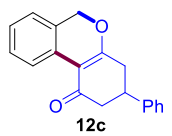
	61.6, 50.7, 42.7, 32.5, 28.2; **HRMS** (ESI-TOF) calculated for $C_{17}H_{18}BrO_3$ $[M+H]^+$: 349.0439 found 349.0451.
 **11w**	Compound **11w**: 43.1 mg, 68% yield; white solid, mp 168-170 °C; purified using 20% ethyl acetate in hexanes as eluent; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 8.15 (s, 1H), 7.97 (d, *J* = 9.0 Hz, 1H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.69 (apt, *J* = 8.0 Hz, 1H), 7.53 (apt, *J* = 7.5 Hz, 1H), 5.49 (s, 1H), 5.04 (s, 2H), 2.37 (s, 2H), 2.20 (s, 2H), 1.02 (s, 6H); **^{13}CNMR** ($CDCl_3$, 125 MHz**)** δ 199.2, 175.0, 148.9, 147.3, 137.3, 130.9, 128.4, 127.6, 127.5, 127.0, 126.9, 102.6, 66.9, 50.7, 42.7, 32.6, 28.3; **HRMS** (ESI) calculated for $C_{18}H_{19}ClNO_2$ $[M+H]^+$: 316.1106 found 316.1102.
 **11x**	Compound **11x**: 49.1 mg, 75% yield; white solid, mp 62-64°C; purified using 10% ethyl acetate in hexanes as eluent; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 5.39 (s, 1H), 4.52 (s, 2H), 2.80 (apt, *J* = 5.0 Hz, 2H), 2.31-2.27 (m, 1H), 2.21 (s, 2H), 1.78-1.74 (m, 2H), 1.62-1.57 (m, 2H), 1.53-1.49 (m, 2H), 1.50 (s, 6H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 199.4, 175.7, 135.8, 126.8, 102.1, 73.1, 50.7, 42.7, 41.4, 32.4, 31.2, 30.3, 28.2, 25.4, 25.1; **HRMS** (ESI) calculated for $C_{16}H_{24}BrO_2$ $[M+H]^+$: 327.0959 found 327.0941.

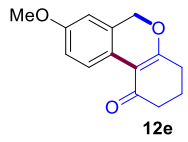
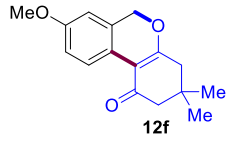
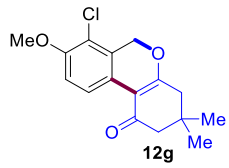
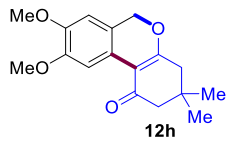
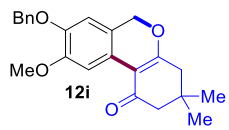
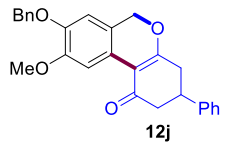
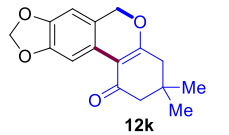
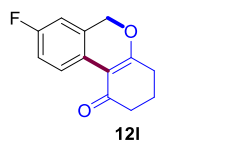
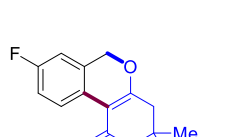
Experimental procedure for intramolecular Heck reaction:

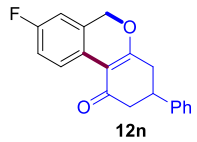
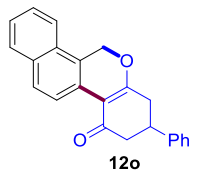
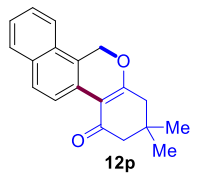
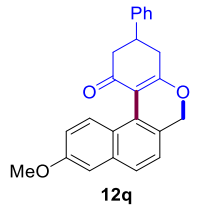
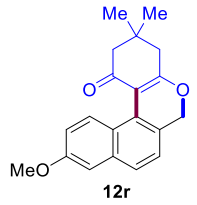
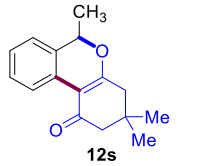
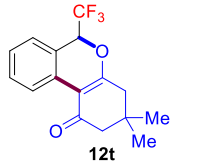
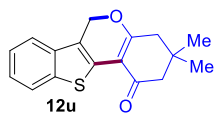


A 35 mL pressure tube fitted with a magnetic stir bar and nitrogen inlet was charged with vinyl ether **11h** (36.9 mg, 0.10 mmol), KOAc (24.5 mg, 0. 25 mmol), tetra-*n*-butylammonium bromide (32.3 mg, 0.10 mmol), $Pd(OAc)_2$ (2.3 mg, 0.010 mmol) and toluene (1.0 mL). The mixture was purged briefly with nitrogen, sealed with Teflon® screw cap and placed in a pre-heated oil bath at 130 °C. After stirring for 3 hours, the reaction mixture was cooled to rt, diluted with ethyl acetate (15 mL), washed with brine (2 x 10 mL), dried over Na_2SO_4 and evaporated. The crude product was purified by silica gel column chromatography using 15% ethyl acetate in hexanes as eluent to obtain compound **12h** (19.1 mg, 66% yield) as light brown oil.

Analytical data for synthesized tricyclic oxoisochromenes:

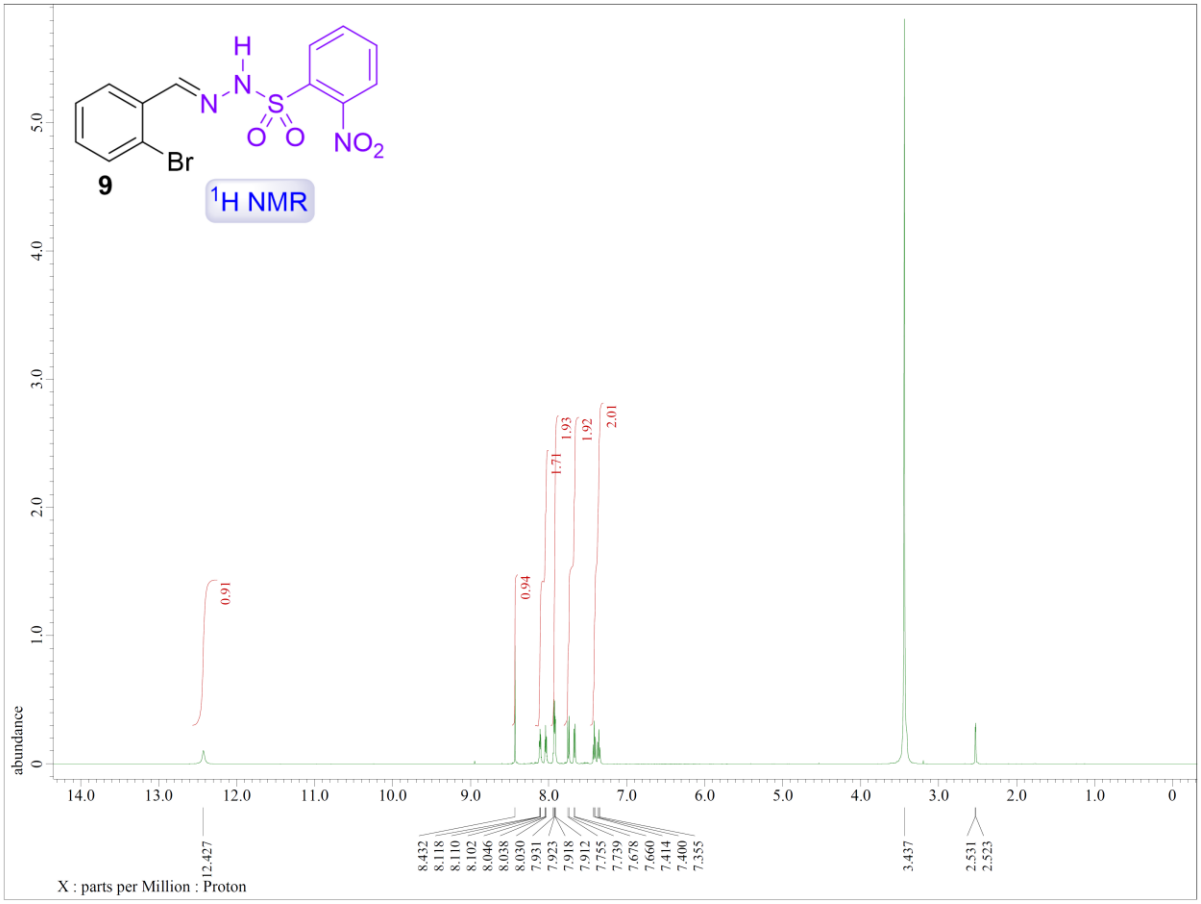
 **12a**	Compound **12a**: 18.1 mg, 90% yield; light yellow oil; purified using 5% ethyl acetate in hexanes as eluent; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 8.29 (d, *J* = 7.5 Hz, 1H), 7.32 (apt, *J* = 6.5 Hz, 1H), 7.20 (apt, *J* = 7.5 Hz, 1H), 7.02 (d, *J* = 7.5 Hz, 1H), 5.11 (s, 2H), 2.59-2.51 (m, 4H), 2.03-1.96 (m, 2H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 196.4, 174.1, 128.8, 128.5, 126.8, 124.8, 123.6, 113.3, 69.5, 38.2, 28.8, 20.0.
 **12b**	Compound **12b**: 21.0 mg, 92% yield; yellow oil; purified using 5% ethyl acetate in hexanes as eluent; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 8.39 (d, *J* = 8.5 Hz, 1H), 7.31 (apt, *J* = 7.5 Hz, 1H), 7.20 (apt, *J* = 7.5 Hz, 1H), 7.02 (d, *J* = 6.5 Hz, 1H), 5.12 (s, 2H), 2.43 (s, 2H), 2.40 (s, 2H), 1.10 (s, 2H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 196.3, 172.5, 128.5, 127.6, 126.8, 126.7, 124.6, 123.6, 111.7, 69.4, 52.1, 42.5, 29.7, 28.2; **HRMS** (ESI-TOF) calculated for $C_{15}H_{17}O_2$ $[M+H]^+$: 229.1228 found 229.1248.
 **12c**	Compound **12c**: 24.3 mg, 88% yield; light brown oil; purified using 5% ethyl acetate in hexanes as eluent; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 8.39 (d, *J* = 8.5 Hz, 1H), 7.31 (apt, *J* = 7.5 Hz, 1H), 7.20 (apt, *J* = 7.5 Hz, 1H), 7.02 (d, *J* = 6.5 Hz, 1H), 5.12 (s, 2H), 2.43 (s, 2H), 2.40 (s, 2H), 1.10 (s, 2H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 196.3, 172.5, 128.5, 127.6, 126.8, 126.7, 124.6, 123.6, 111.7, 69.4, 52.1, 42.5, 29.7, 28.2; **HRMS** (ESI-TOF) calculated for $C_{19}H_{17}O_2$ $[M+H]^+$: 277.1228 found 277.1228.
 **12d**	Compound **12d**: 13.1 mg, 70% yield; brown solid, mp 150-152 °C; purified using 10% ethyl acetate in hexanes as eluent; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 8.04 (d, *J* = 6.5 Hz, 1H), 7.22 (apt, *J* = 8.0 Hz, 1H), 7.13 (apt, *J* = 8.0 Hz, 1H), 6.94 (d, *J* = 8.0 Hz, 1H), 5.40 (s, 2H), 2.58 (apt, *J* = 5.5 Hz, 2H)), 2.51 (apt, *J* = 2.5 Hz, 2H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 200.7, 185.1, 128.7, 127.6, 126.5, 125.3, 123.5, 122.0, 71.9, 34.2, 25.9.

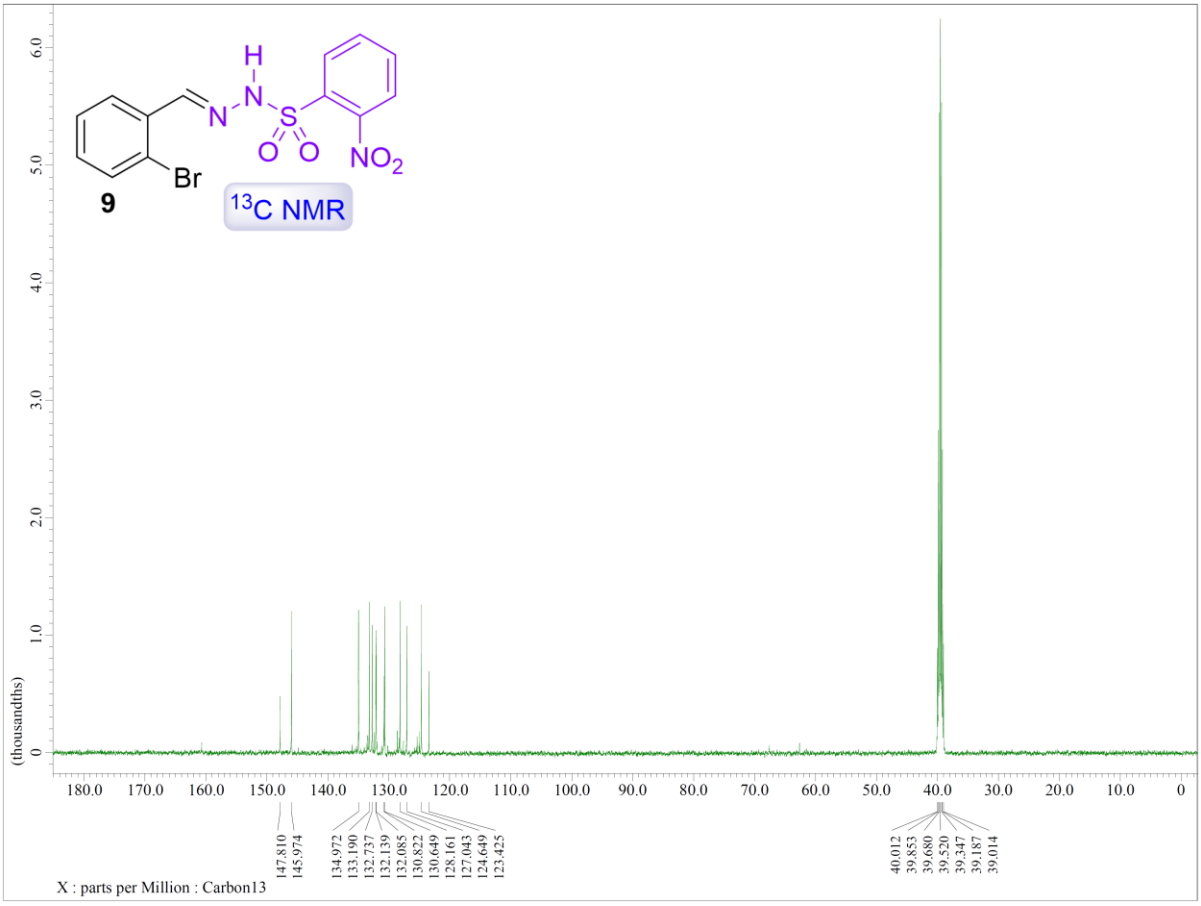
 **12e**	Compound **12e**: 15.7 mg, 68% yield; white solid, mp 75-76 °C; purified using 15% ethyl acetate in hexanes as eluent eluent; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 8.27 (d, *J* = 8.5 Hz, 1H), 6.85 (dd, *J* = 7.5, 1.5 Hz, 1H), 6.57 (s, 1H), 5.08 (s, 2H), 3.80 (s, 3H), 2.57-2.50 (m, 4H), 2.02-1.96 (m, 2H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 196.5, 172.4, 158.5, 128.7, 126.3, 120.5, 113.1, 109.8, 69.3, 55.3, 38.2, 29.7, 28.7, 20.1.
 **12f**	Compound **12f**: 18.1 mg, 70% yield; white oil; purified using 10% ethyl acetate in hexanes as eluent; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 8.33 (d, *J* = 9.0 Hz, 1H), 6.83 (dd, *J* = 6.5, 2.5 Hz, 1H), 6.56 (s, 1H), 5.08 (s, 2H), 3.78 (s, 3H), 2.40 (s, 2H), 2.37 (s, 2H), 1.08 (s, 6H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 196.5, 170.8, 158.5, 128.5, 126.0, 120.4, 113.0, 109.8, 69.3, 55.3, 52.1, 42.4, 30.9, 28.2, 28.2; **HRMS** (ESI) calculated for $C_{16}H_{19}O_3$ $[M+H]^+$: 259.1334 found 259.1341.
 **12g**	Compound **12g**: 19.1 mg, 65% yield; white solid, mp 120-122°C; purified using 10% ethyl acetate in hexanes as eluent; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 8.29 (d, *J* = 8.0 Hz, 1H), 6.81 (d, *J* = 9.0 Hz, 1H), 5.23 (s, 1H), 3.83 (s, 1H), 2.35 (s, 1H), 2.32 (s, 1H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 196.2, 171.0, 153.8, 126.5, 124.6, 123.8, 121.5, 117.9, 111.1, 110.4, 66.3, 56.3, 56.2, 52.2, 42.4, 31.4, 28.1; **HRMS** (ESI-TOF) calculated for $C_{16}H_{17}ClO_3$ $[M+H]^+$: 293.0944 found 293.0925.
 **12h**	Compound **12h**: 19.0 mg, 66% yield; light yellow oil; purified using 15% ethyl acetate in hexanes as eluent; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 8.13 (s, 1H), 6.54 (s, 1H), 5.09 (s, 2H), 3.93 (s, 3H), 3.86 (s, 3H), 2.42 (s, 2H), 2.39 (s, 2H), 1.10 (s, 6H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 196.7, 171.4, 148.7, 147.8, 120.7, 118.7, 108.5, 107.1, 69.1, 56.0, 56.0, 52.2, 42.5, 31.5, 29.7, 28.2; **HRMS** (ESI-TOF) calculated for $C_{17}H_{21}O_4$ $[M+H]^+$: 289.1440 found 289.1443.
 **12i**	Compound **12i**: 30 mg, 70% yield; white solid, mp 125-127 °C; purified using 15% ethyl acetate in hexanes as eluent; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 8.14 (s, 1H), 7.42 (d, *J* = 8.0 Hz, 1H) 7.36 (apt, *J* = 8.0 Hz, 1H), 7.30 (d, *J* = 8.0 Hz, 1H), 6.54 (s, 1H), 5.13 (s, 2H), 5.01 (s, 2H), 3.93 (s, 3H), 2.41 (s, 2H), 2.39 (s, 2H), 1.09 (s, 6H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 196.6, 171.6, 149.5, 146.8, 137.1, 128.5, 127.8, 127.2, 121.4, 118.7, 111.3, 110.2, 108.9, 71.3, 69.0, 56.0, 52.2, 42.3, 28.2; **HRMS** (ESI-TOF) calculated for $C_{23}H_{25}O_4$ $[M+H]^+$: 365.1753 found 365.1748.
 **12j**	Compound **12j**: 30.9 mg, 75% yield; white solid, mp 102-104 °C; purified using 10% ethyl acetate in hexanes as eluent; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 8.14 (s, 1H), 7.35 (m, 5H), 6.54 (s, 1H), 5.13 (s, 2H), 5.01 (s, 2H), 3.93 (s, 3H), 2.41 (s, 2H), 2.39 (s, 2H), 1.09 (s, 6H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 196.6, 171.6, 149.5, 146.8, 137.1, 128.5, 127.8, 127.2, 121.4, 118.7, 111.3, 110.2, 108.9, 71.3, 69.0, 56.0, 52.2, 42.3, 31.5, 28.2; **HRMS** (ESI) calculated for $C_{27}H_{25}O_4$ $[M+H]^+$: 413.1753 found 413.1763.
 **12k**	Compound **12k**: 20.4 mg, 75% yield; white solid, mp 155-157°C; purified using 10% ethyl acetate in hexanes as eluent; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 7.89 (s, 1H), 6.43 (s, 1H), 5.84 (s, 2H), 4.92 (s, 2H), 2.32 (s, 2H), 2.29 (s, 2H), 1.00 (s, 6H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 196.2, 171.4, 147.6, 146.1, 121.9, 120.1, 111.8, 106.1, 104.4, 101.0, 69.3, 52.1, 42.3, 31.4, 28.1; **HRMS** (ESI-TOF) calculated for $C_{16}H_{17}O_4$ $[M+H]^+$: 273.1127 found 273.1131.
 **12l**	Compound **12l**: 15.1 mg, 69% yield; off-white solid, mp 97-99 °C; purified using 10% ethyl acetate in hexanes as eluent; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 8.32 (dd, *J* = 2.5, 6.5 Hz, 1H), 6.99 (dt, *J* = 6.5, 9.5 Hz, 1H), 6.73 (dd, *J* = 2.0, 9.0 Hz, 1H), 5.09 (s, 2H), 2.56 (apt, *J* = 5.5, 6.5 Hz, 2H), 2.53 (apt, *J* = 5.5, 8.0 Hz, 2H), 2.02-1.99 (m, 2H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 196.2, 173.3, 161.5 (d, $J_{C\text{-}F}$ = 244.2 Hz), 129.0 (d, $J_{C\text{-}F}$ = 6.6 Hz), 126.8 (d, $J_{C\text{-}F}$ = 8.3 Hz), 123.8, 115.0 (d, $J_{C\text{-}F}$ = 20.2 Hz), 112.4, 110.7 (d, $J_{C\text{-}F}$ = 23.2 Hz), 68.8, 38.1, 28.7, 20.0.
 **12m**	Compound **12m**: 16.0 mg, 65% yield; light yellow oil; purified using 7% ethyl acetate in hexanes as eluent; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 8.33 (dd, *J* = 8.0, 5.5 Hz, 1H), 6.91 (dt, *J* = 3.0, 8.0 Hz, 1H), 6.65 (dd, *J* = 8.0, 2.5 Hz, 1H), 5.01 (s, 1H), 2.34 (s, 2H), 2.31 (s, 2H), 1.01 (s, 6H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 196.2, 171.8, 161.5 (d, $J_{C\text{-}F}$ = 244.2 Hz), 128.8 (d, $J_{C\text{-}F}$ = 8.2 Hz), 126.5 (d, $J_{C\text{-}F}$ = 6.6 Hz), 123.7, 114.9 (d, $J_{C\text{-}F}$ = 20.2 Hz), 111.1, 110.7 (d, $J_{C\text{-}F}$ = 23.3 Hz), 68.8, 52.0, 42.3, 31.4, 28.1; **HRMS** (ESI-TOF) calculated for $C_{15}H_{16}FO_2$ $[M+H]^+$: 247.1134 found 247.1128.

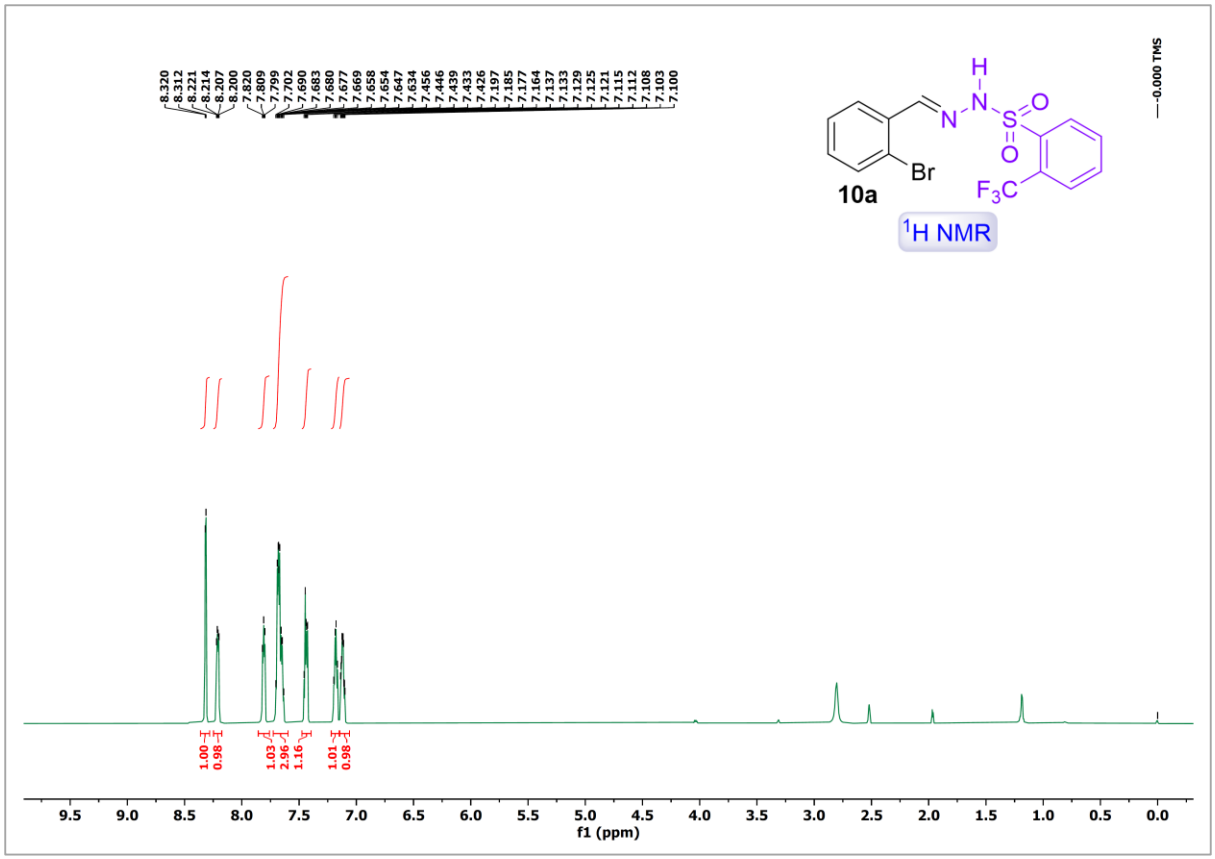
 **12n**	Compound **12n**: 18.3 mg, 62% yield; white solid, mp 180-182 °C; purified using 10% ethyl acetate in hexanes as eluent; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 8.31 (dd, *J* = 6.5Hz, 1H), 7.28 (apt, *J* = 8.0 Hz, 2H), 7.20 (apt, *J* = 9.5 Hz, 3H), 6.95 (dt, *J* = 7.5 Hz, 1H), 6.69 (dd, *J* = 2.5, 8.0 Hz,1H), 5.07 (ABq, *J* = 13.5 Hz, 2H), 3.37-3.28 (m, 1H), 2.79-2.67 (m, 4H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 195.4, 172.4, 161.9 (d, J_{C-F} = 246.1 Hz), 142.2, 128.9 (d, J_{C-F} = 6.7 Hz), 128.8, 127.1, 126.8 (d, J_{C-F} = 6.6 Hz), 126.6, 123.6, 115.1 (d, J_{C-F} = 21.6 Hz), 112.2, 110.8 (d, J_{C-F} = 23.3 Hz), 69.0, 45.1, 38.1, 36.2; **HRMS** (ESI-TOF) calculated for $C_{19}H_{16}FO_2$ $[M+H]^+$: 295.1134 found 295.1149.
 **12o**	Compound **12o**: 23.5 mg, 72% yield; yellow solid, mp 205-207 °C; purified using 10% ethyl acetate in hexanes as eluent **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 8.47 (d, *J* = 9.5 Hz, 1H), 7.75 (apt, *J* = 9.5 Hz, 2H), 7.63 (d, *J* = 8.0 Hz, 1H), 7.42 (apt, *J* = 8.0 Hz, 1H), 7.36 (apt, *J* = 8.0 Hz, 1H), 7.28 (apt, *J* = 8.0 Hz, 2H), 7.22-7.16 (m, 3H), 5.61 (ABq, *J* = 13.5 Hz, 2H), 3.39-3.32 (m, 1H), 2.75 (m, 4H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 195.3, 173.2, 142.4, 132.7, 128.8, 128.7, 128.3, 128.0, 127.1, 126.6, 126.4, 125.5, 125.3, 123.2, 121.6, 120.5, 112.8, 66.5, 45.3, 38.1, 36.3; **HRMS** (ESI-TOF) calculated for $C_{23}H_{19}O_2$ $[M+H]^+$: 327.1385 found 327.1381.
 **12p**	Compound **12p**: 20.6 mg, 74% yield; orange solid, mp 107-109 °C; purified using 10% ethyl acetate in hexanes as eluent; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 8.59 (d, *J* = 8.0 Hz, 1H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.81 (d, *J* = 9.0 Hz, 1H) , 7.72 (d, *J* = 8.0 Hz, 1H), 7.49 (apt, *J* = 8.0 Hz, 1H), 7.43 (apt, *J* = 8.0 Hz, 1H), 5.66 (s, 2H), 2.50 (s, 2H), 2.44 (s, 2H), 1.13 (s, 6H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 196.2, 172.6, 132.6, 128.6, 128.3, 127.9, 126.3, 125.1, 123.1, 121.6, 120.3, 111.8 , 66.2, 52.2, 42.5, 31.5, 28.2; **HRMS** (ESI-TOF) calculated for $C_{19}H_{19}O_2$ $[M+H]^+$: 279.1385 found 279.1393.
 **12q**	Compound 12q: 24.2 mg, 68% yield; light yellow solid, mp 150-160 °C; purified using 15% ethyl acetate in hexanes as eluent; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 7.71 (d, *J* = 9.5 Hz, 1H), 7.69 (d, *J* = 9.5 Hz, 1H), 7.38 (apt, 2H, *J* = 8.0 Hz), 7.31 (m, 3H), 7.18 (d, *J* =8.0 Hz, 1H), 7.14 (d, *J* =3.0 Hz, 1H), 7.11 (d, *J* = 3.0 Hz, 1H), 5.20 (ABq, *J* = 12.0 Hz, 2H), 3.92 (s, 3H), 3.56 (m, 1H), 2.91 (m, 4H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 193.8, 175.9, 157.3, 142.1, 135.8, 128.8, 128.8, 127.3, 127.1, 126.8, 125.1, 124.0, 123.2, 122.5, 118.0, 117.3, 106.2, 71.4, 55.3, 44.7, 37.4, 36.4; **HRMS** (ESI-TOF) calculated for $C_{24}H_{21}O_3$ $[M+H]^+$: 357.1490 found 357.1478.
 **12r**	Compound **12r**: 19.8 mg, 64% yield; light brown solid, mp 115-117 °C; purified using 15% ethyl acetate in hexanes as eluent; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 7.66 (d, *J* = 9.0 Hz, 2H), 7.17 (d, *J* = 8.0 Hz, 1H), 7.11 (m, 2H), 5.13 (s, 2H), 3.91 (s, 3H), 2.55 (s, 4H), 1.23 (s, 6H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 194.7, 175.0, 157, 135.8, 128.8, 127.0, 125.1, 123.3, 122.5, 117.9, 116.6, 71.2, 55.2, 51.5, 42.2, 30.1, 28.3; **HRMS** (ESI-TOF) calculated for $C_{20}H_{21}O_3$ $[M+H]^+$: 309.1490 found 309.1487.
 **12s**	Compound **12s**: 18.9 mg, 78% yield; white solid, mp 198-200 °C; purified using 15% ethyl acetate in hexanes as eluent; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 8.35 (d, *J* = 8.0 Hz, 1H), 7.31 (apt, *J* = 8.0 Hz, 1H), 7.22 (apt, *J* = 8.0 Hz, 1H), 7.03 (d, *J* = 7.5 Hz, 1H), 5.29 (q, *J* = 8.0 Hz, 1H), 2.54 (m, 4H), 2.00 (m, 2H), 1.61 (d, *J* = 6.5 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 196.3, 172.7, 131.5, 128.1, 127.0, 124.9, 123, 112.3, 75.5, 38.4, 29.7, 29.4, 20.1; **HRMS** (ESI-TOF) calculated for $C_{16}H_{19}O_2$ $[M+H]^+$: 243.1385 found 243.1388.
 **12t**	Compound **12t**: 22.3 mg, 75% yield; yellow solid, mp 110-115 °C; purified using 5% ethyl acetate in hexanes as eluent; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 8.55 (d, *J* = 8.0 Hz, 1H), 7.36 (apt, *J* = 8.0 Hz, 1H), 7.21 (apt, *J* = 8.0 Hz, 1H), 7.06 (d, *J* = 8.0 Hz, 1H), 5.48 (dd, *J* = 6.5, 8.0 Hz, 1H), 2.49-2.29 (m, 4H), 1.07 (s, 3H), 1.02 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 196.3, 169.3, 130.3, 127.3, 127.1, 126.5, 125.3, 123.0 (q, J_{C-F} = 284 Hz), 120.3, 110.4, 75.4 (q, J_{C-F} = 33.1 Hz), 52.4, 42.4, 29.7, 28.8, 27.4; **HRMS** (ESI-TOF) calculated for $C_{16}H_{16}F_3O_2$ $[M+H]^+$: 297.1102 found 297.1112.
 **12u**	Compound **12u**: 18.8 mg, 66% yield; yellow solid, mp 110-115 °C; purified using 5% ethyl acetate in hexanes as eluent; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 7.79 (d, *J* = 8.0 Hz, 1H), 7.34 (d, *J* = 8.0 Hz, 1H), 7.27 (apt, *J* = 8.0 Hz, 1H), 7.21 (apt, *J* = 8.0 Hz, 1H), 5.63 (s,2H), 2.39 (s, 2H), 2.32 (s, 2H), 1.05 (s, 6H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 193.9, 170.8, 141.1, 134.6, 127.2, 124.2, 123.6, 122.7, 119.4, 117.1, 108.7, 68.2, 50.1, 42.0, 32.3, 28.4; **HRMS** (ESI-TOF) calculated for $C_{17}H_{17}O_2S$ $[M+H]^+$: 285.0949 found 285.0957.

References:

1. (a) Zhou, F.; Zhou, L.; Jing, P.; Sun, M.; Deng, G.; Liang, Y.; Yang, Y. *Org. Lett.* **2022**, *24*, 1400-1404; (b) Kong, H.-H.; Zhu, C.; Deng, S.; Xu, G.; Zhao, R.; Yao, C.; Xiang, H.-M.; Zhao, C.; Qi, X.; Xu, H. *J. Am. Chem. Soc.* **2022**, *144*, 21347-21355; (c) Nitti, A.; Osw, P.; Calcagno, G.; Botta, C.; Etkind, S. I.; Bianchi, G.; Po, R.; Swager, T. M.; Pasini, D. *Org. Lett.* **2020**, *22*, 3263-3267.
2. (a) Ning, X.; Chen, Y.; Hu, F.; Xia, Y. *Org. Lett.* **2021**, *23*, 8348-8352; (b) Li, X.; Song, J.-N.; Karmakar, S.; Lu, Y.; Lv, Y.; Liao, P.; Liu, Z. *Chem. Commun.* **2022**, *58*, 13783-13786.
3. (a) Muimhneachain, E.O.; Pardo, L. M.; Bateman, L.M.; Rao Khandavilli, U. B.; Lawrence, S. E.; McGlacken, G. P. *Adv. Synth. Catal.* **2017**, *359*, 1529-1534; (b) Mao, Z.; Zhu, X.; Wan, Y. *Catal. Lett*. **2015**, *145*, 1612-1620; (c) Sudheendran, K.; Malakar, C.C.; Conrad, J.; Beifuss, U. *J. Org. Chem.* **2012**, *77*, 10194-10210.


9
1H NMR
abundance
X : parts per Million : Proton


9
13C NMR
(thousandths)
X : parts per Million : Carbon13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8.312
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8.207
8.200
7.820
7.809
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7.702
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7.680
7.677
7.669
7.658
7.654
7.647
7.634
7.456
7.446
7.439
7.433
7.426
7.197
7.185
7.177
7.164
7.137
7.133
7.129
7.125
7.121
7.115
7.112
7.108
7.103
7.100
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^{1}H NMR
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0.98
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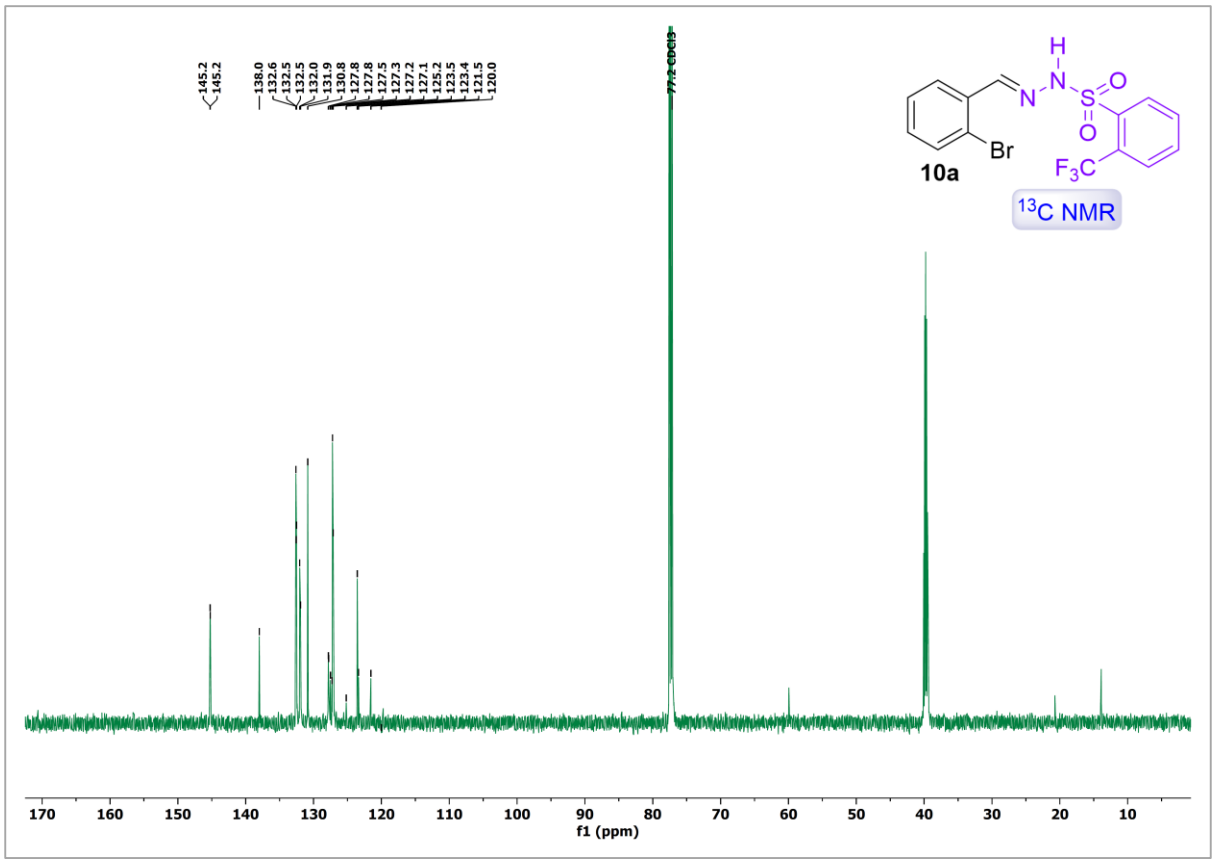
2.96
1.16
1.01
0.98
f1 (ppm)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145.2
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132.5
132.0
131.9
130.8
127.8
127.8
127.5
127.3
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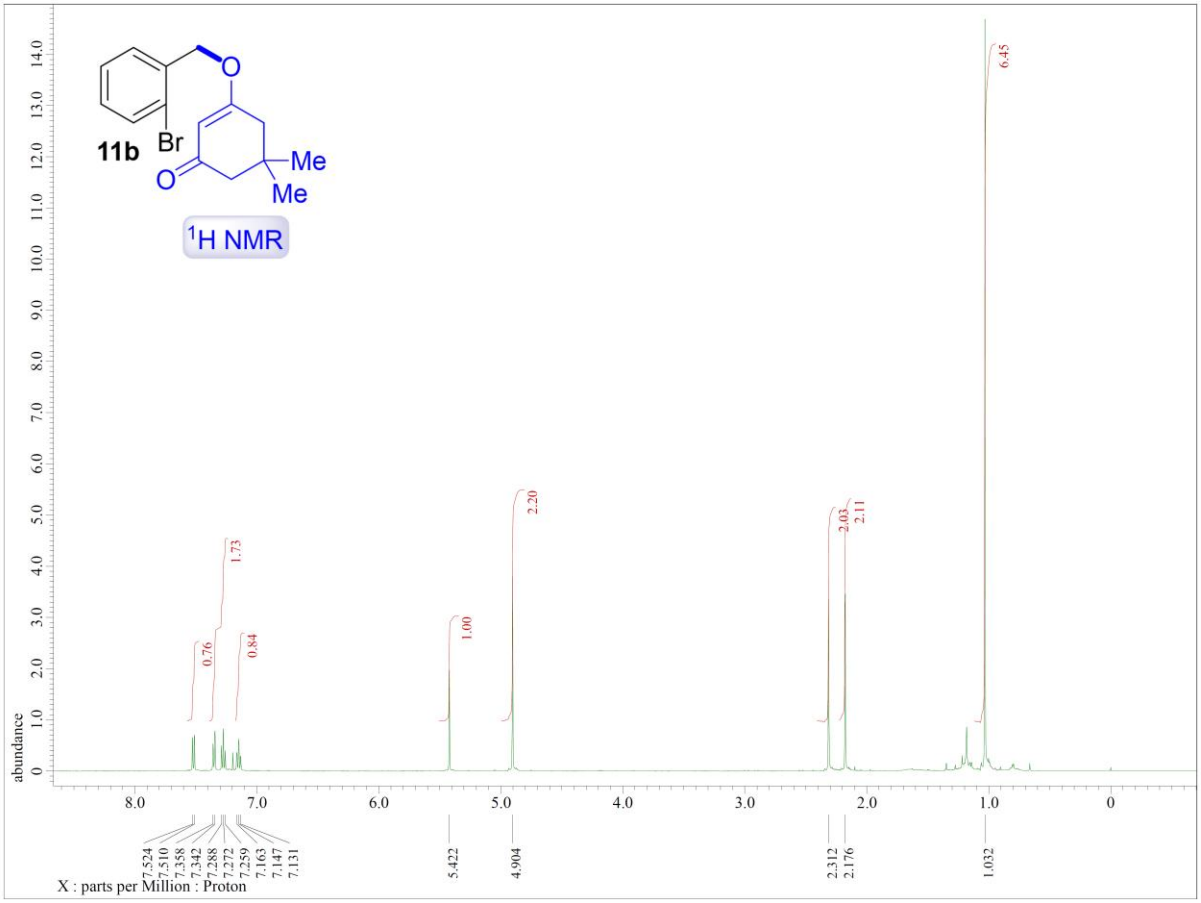
120.0
77.2 CDCl3
10a
^{13}C NMR
f1 (ppm)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O
Me
Me
1H NMR
abundance
X : parts per Million : Proton
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2.11
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7.510
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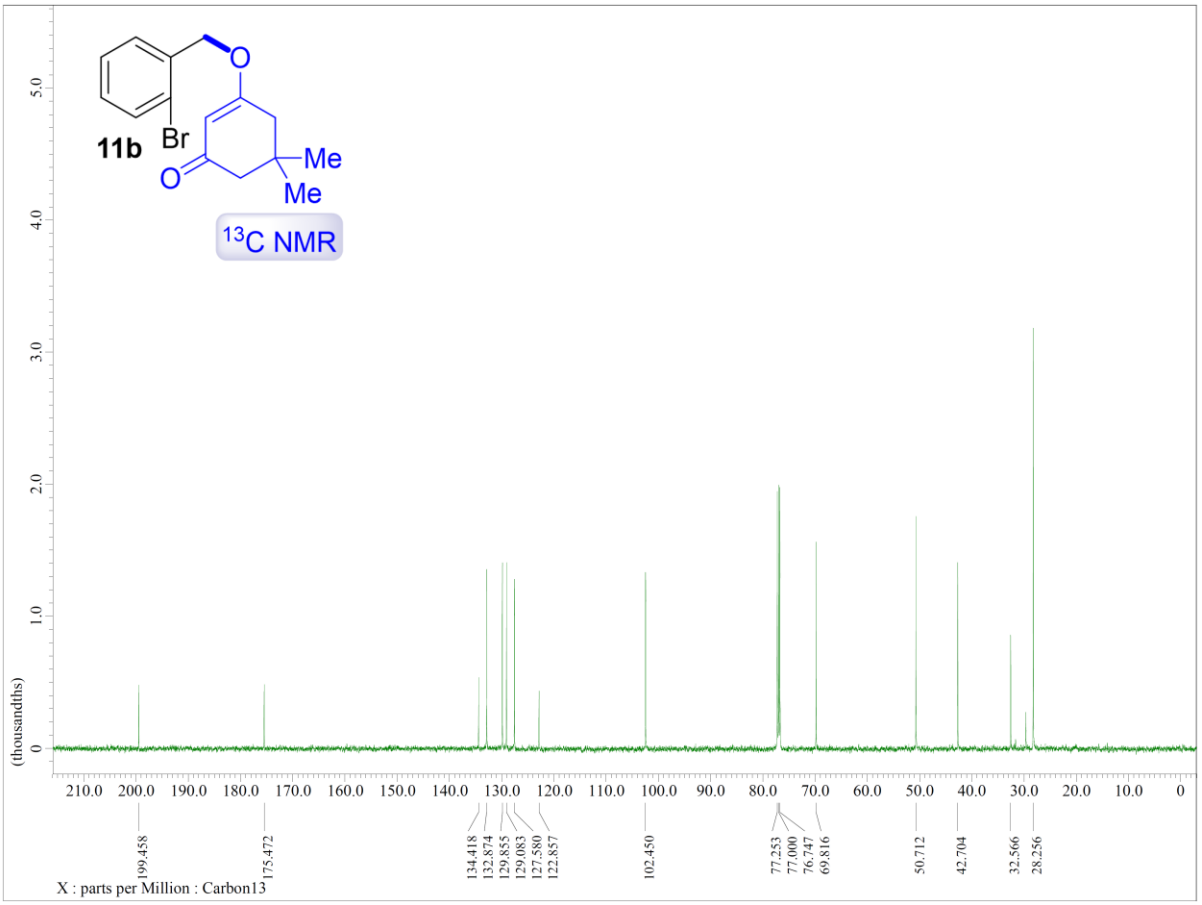
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Br
O
O
Me
Me
13C NMR
(thousandths)
X : parts per Million : Carbon13
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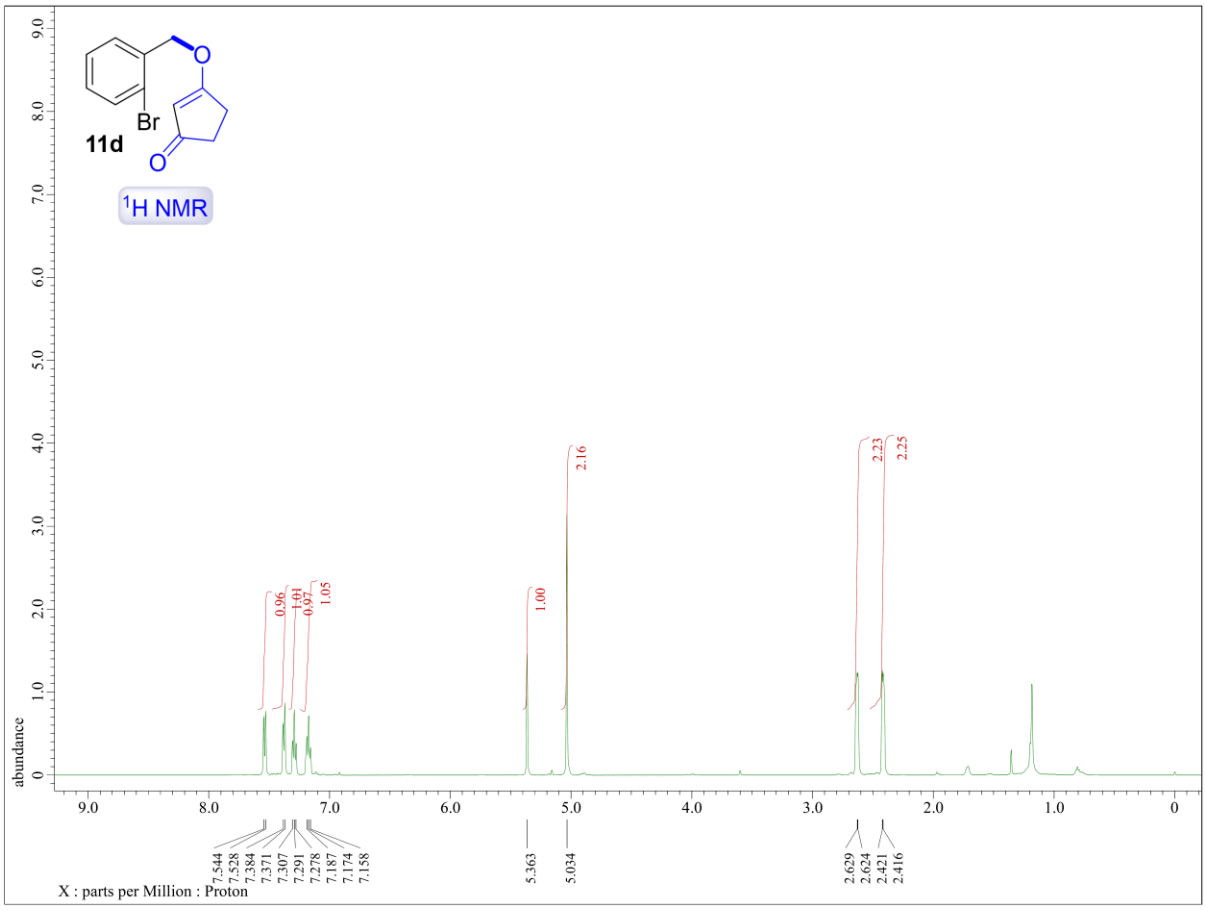
11d
Br
O
O
1H NMR
abundance
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4.0
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2.0
1.0
0
0.96
1.01
0.97
1.05
1.00
2.16
2.23
2.25
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7.371
7.307
7.291
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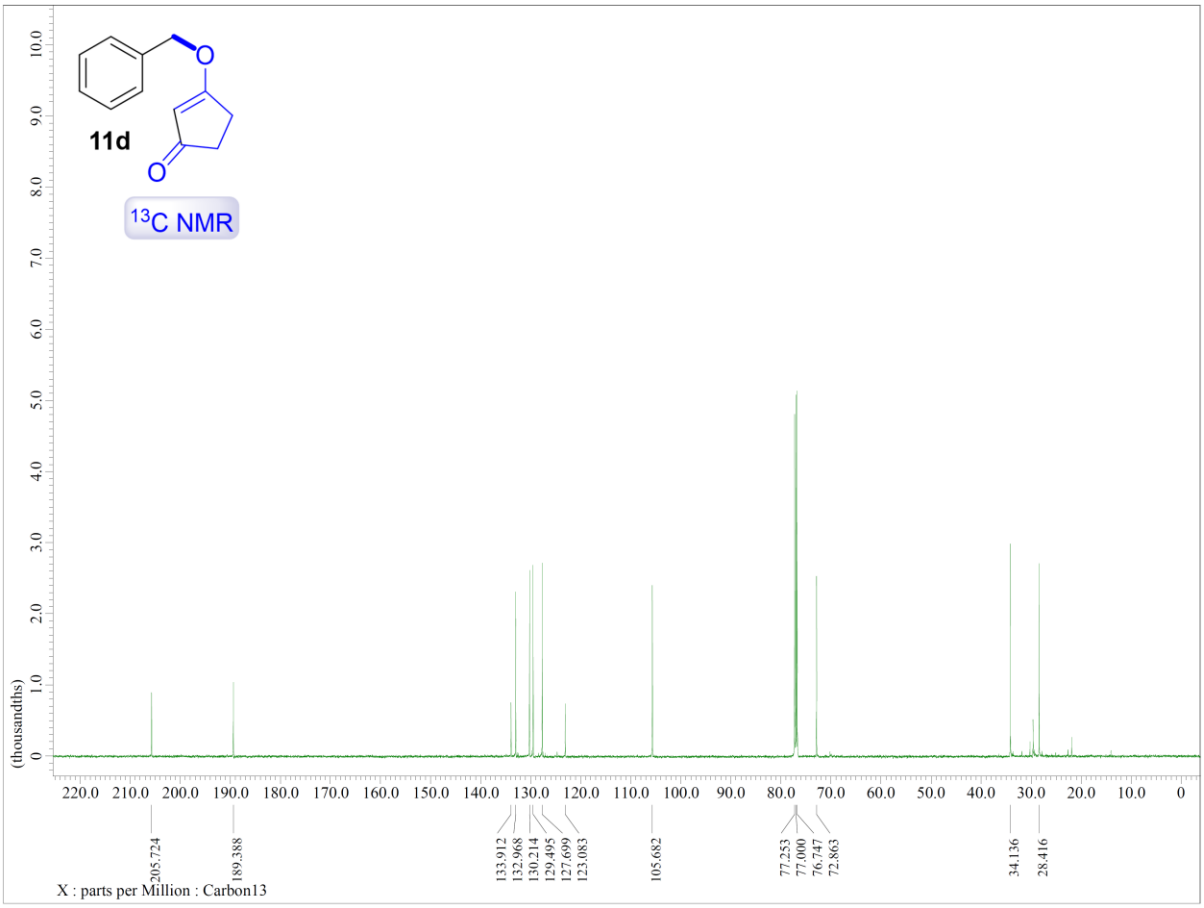
X : parts per Million : Proton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O
13C NMR
(thousandths)
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4.0
3.0
2.0
1.0
0
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210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
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80.0
70.0
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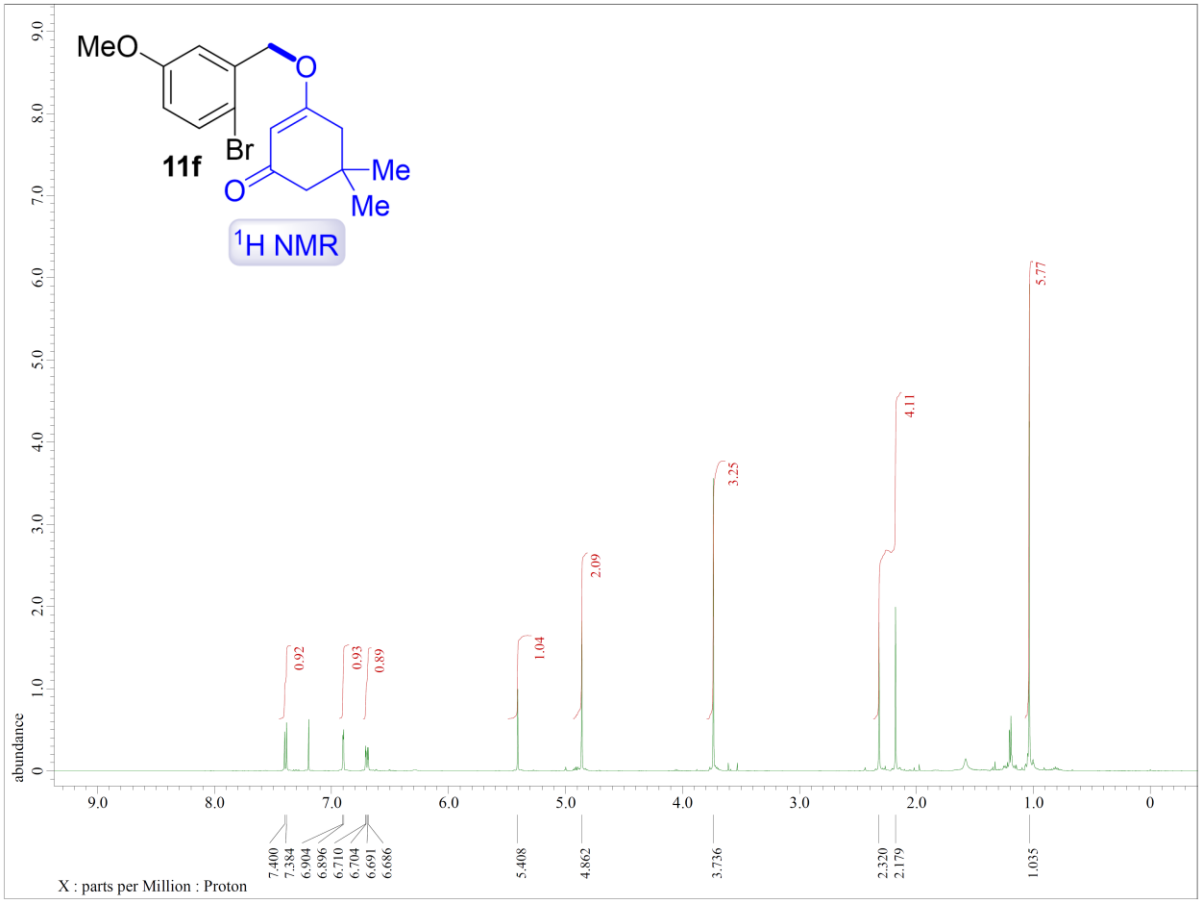
X : parts per Million : Carbon13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11f
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1H NMR
abundance
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4.0
3.0
2.0
1.0
0
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0.93
0.89
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2.09
3.25
4.11
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7.384
6.904
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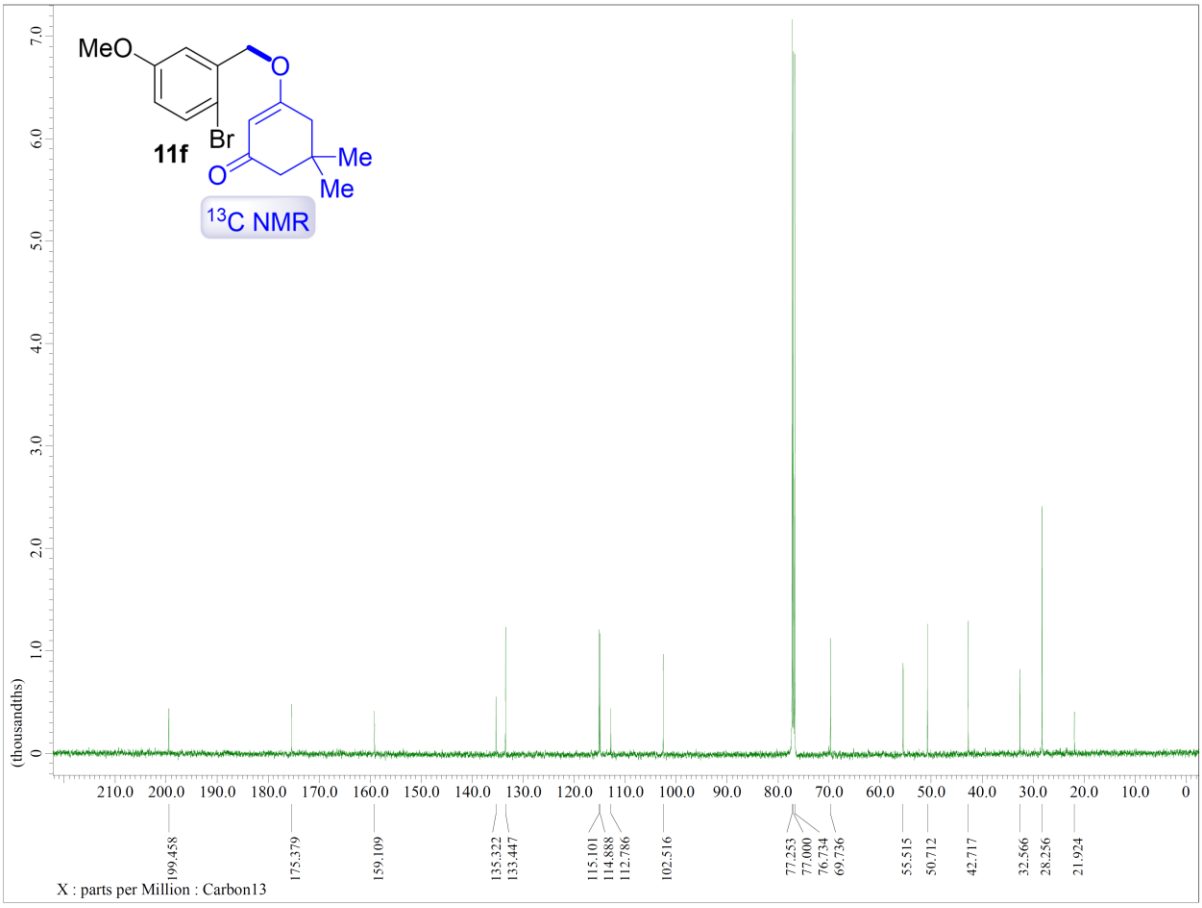
X : parts per Million : Proton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Br
11f
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Me
Me
13C NMR
(thousandths)
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30.0
20.0
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112.786
102.516
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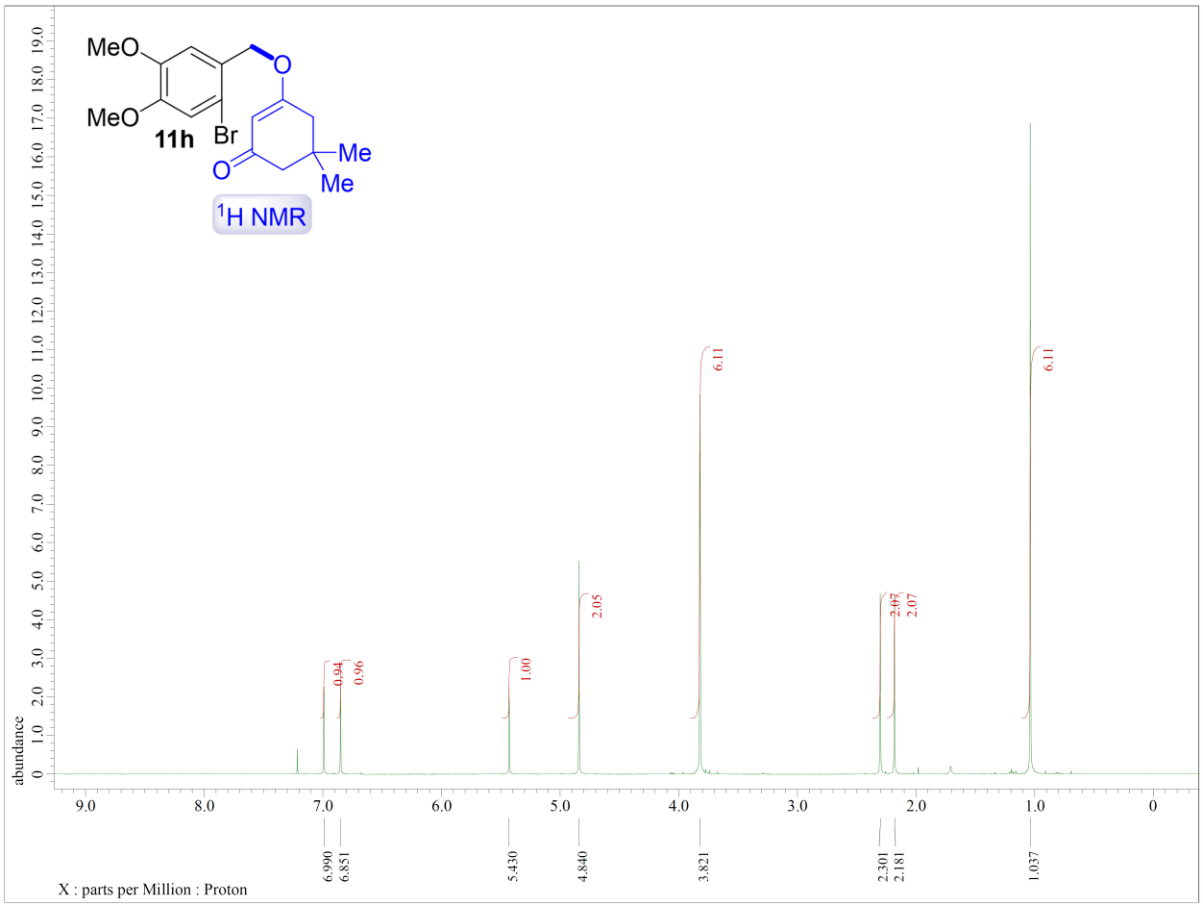
X : parts per Million : Carbon13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11h
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O
Me
Me
1H NMR
abundance
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2.07
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0.96
6.11
9.0
8.0
7.0
6.0
5.0
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2.0
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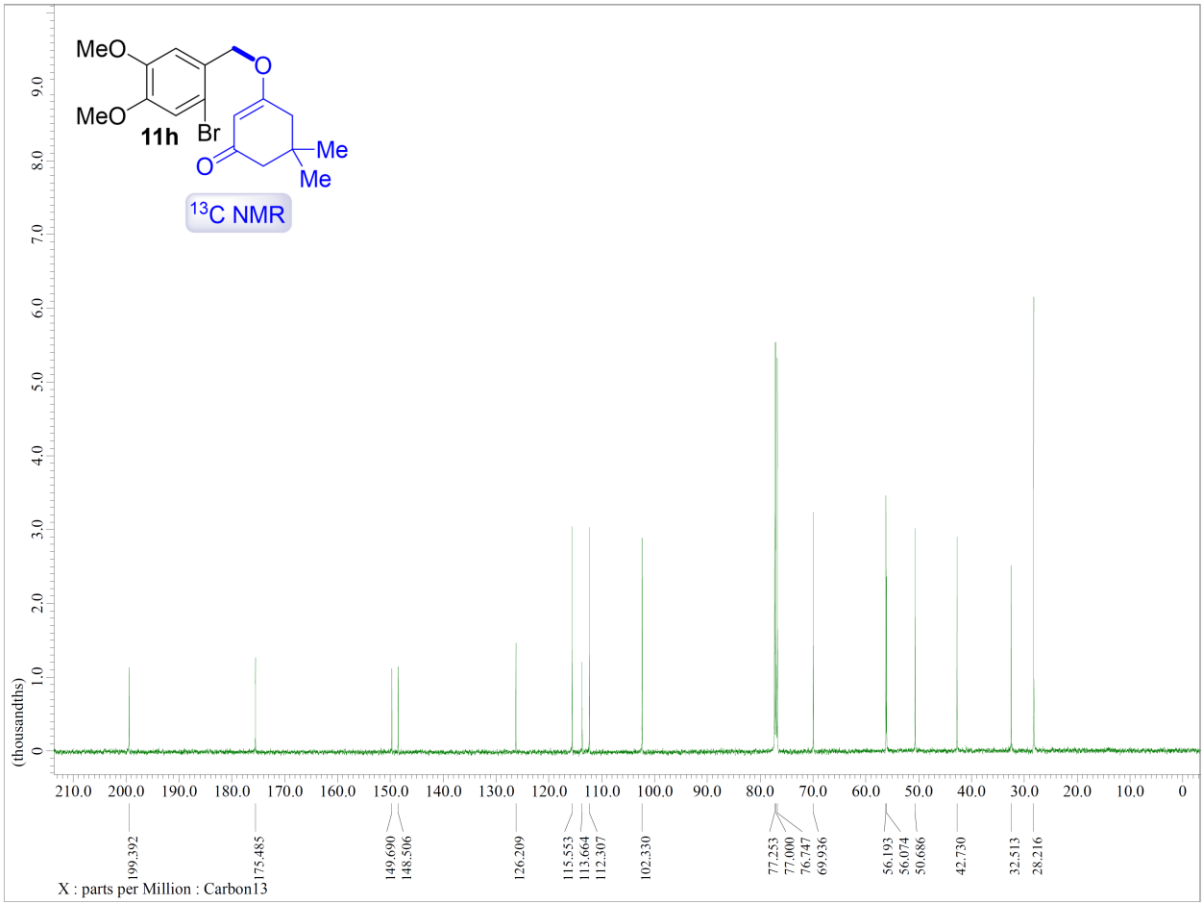
X : parts per Million : Proton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MeO
11h
Br
O
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Me
Me
13C NMR
(thousandths)
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102.330
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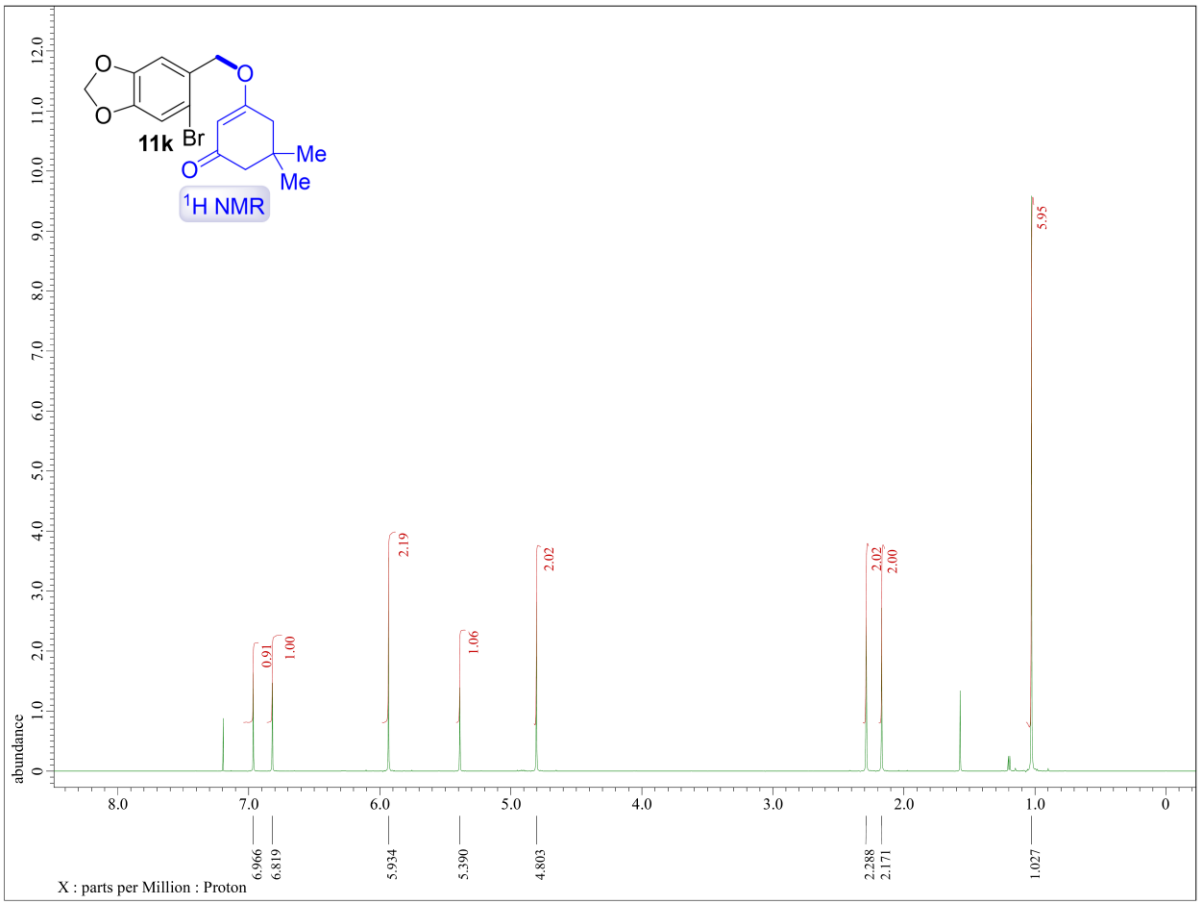
X : parts per Million : Carbon13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Br
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O
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Me
Me
1H NMR
abundance
X : parts per Million : Proton
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2.00
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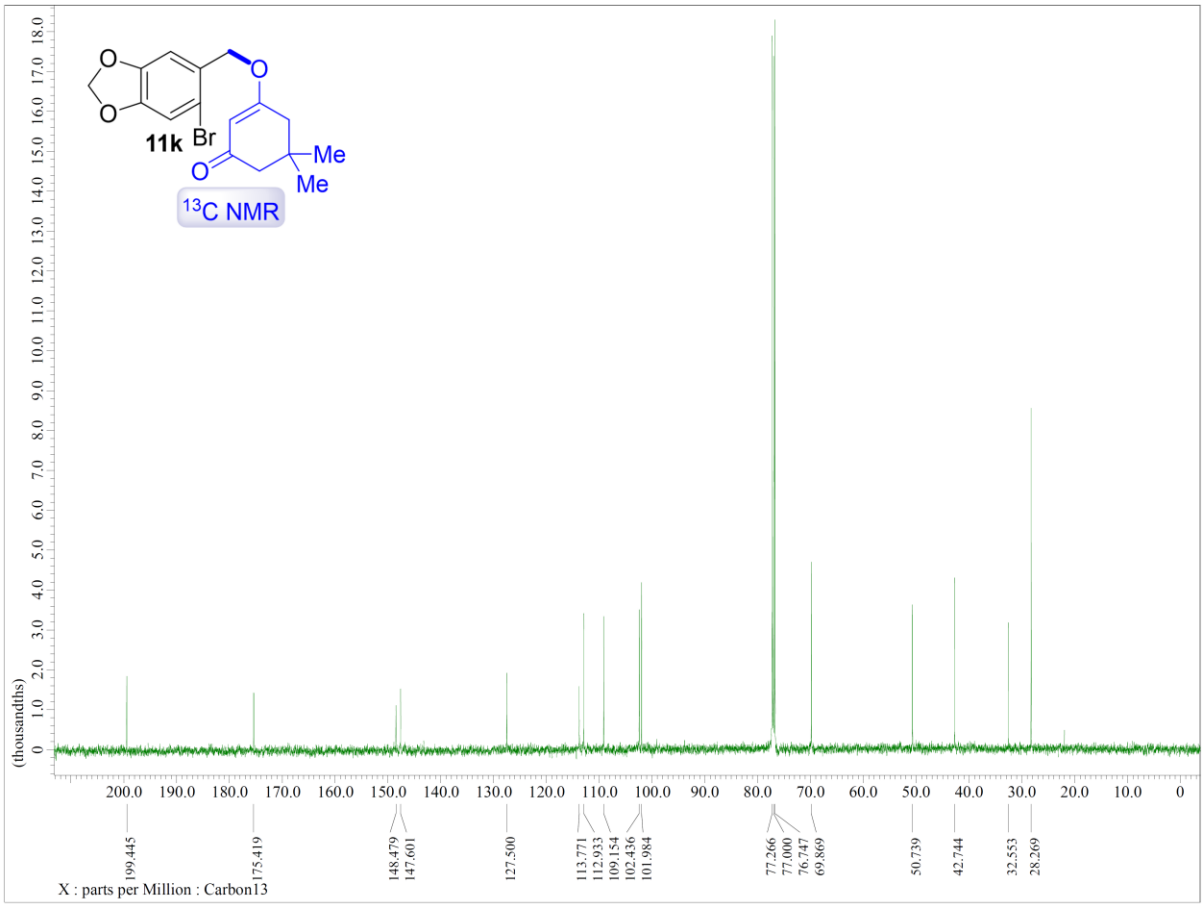
11k
Br
O
O
O
Me
Me
13C NMR
(thousandths)
X : parts per Million : Carbon13
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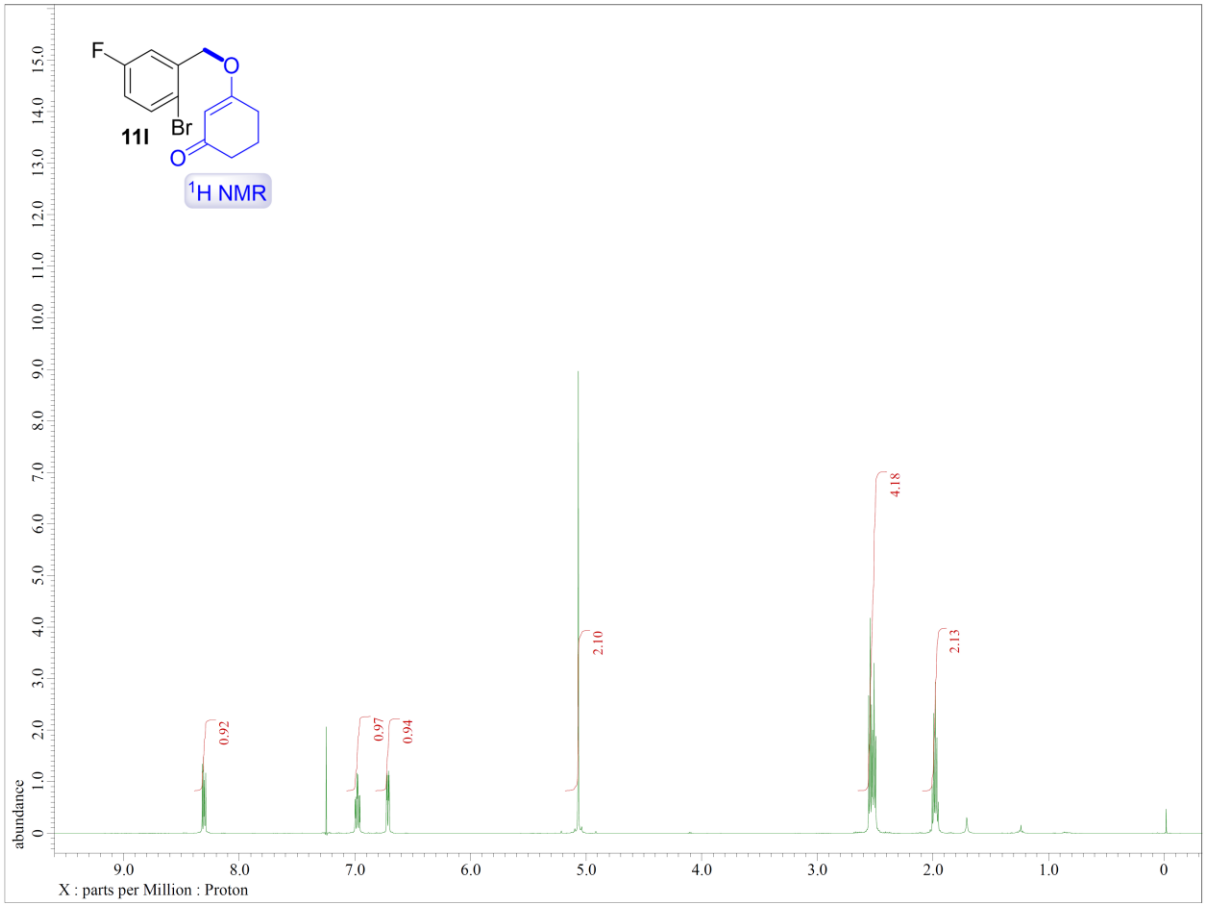
F
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11l
Br
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1H NMR
abundance
X : parts per Million : Proton
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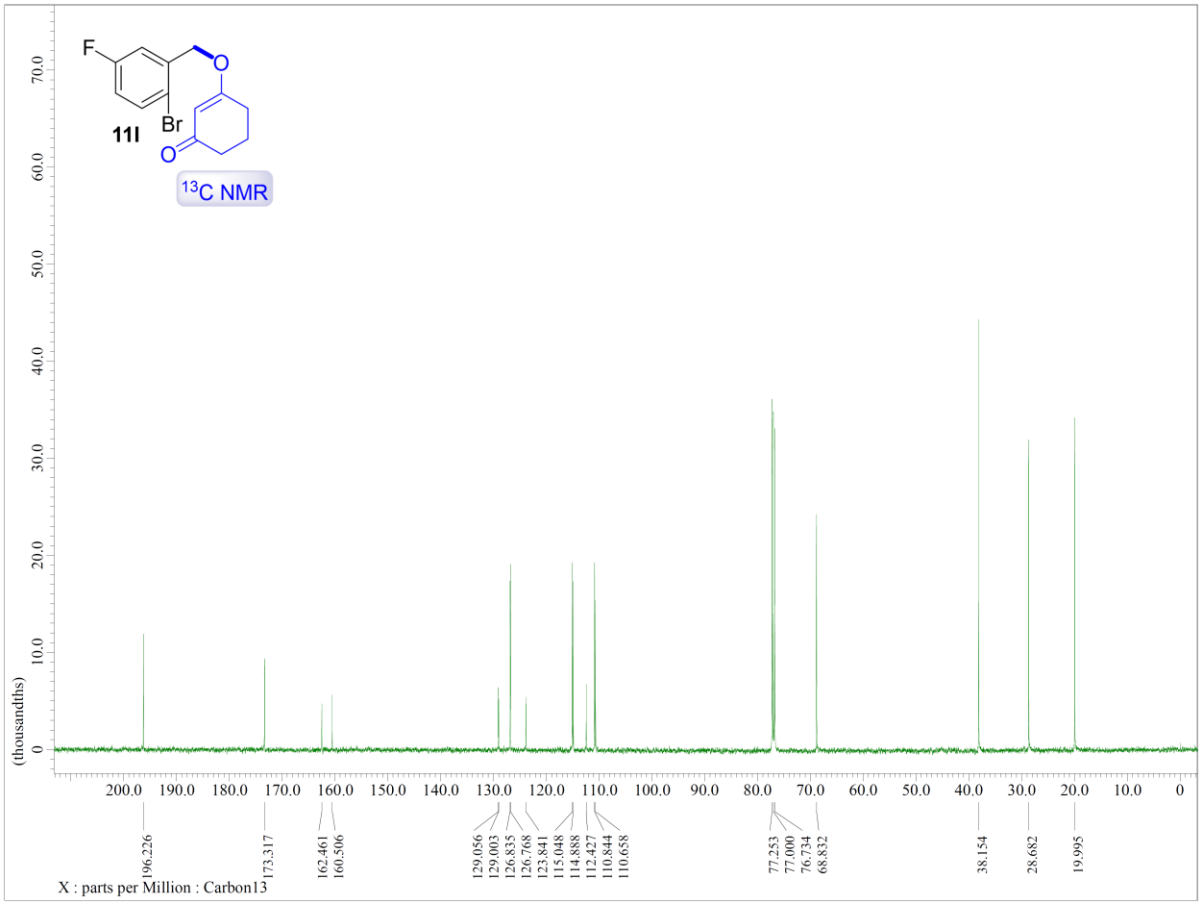
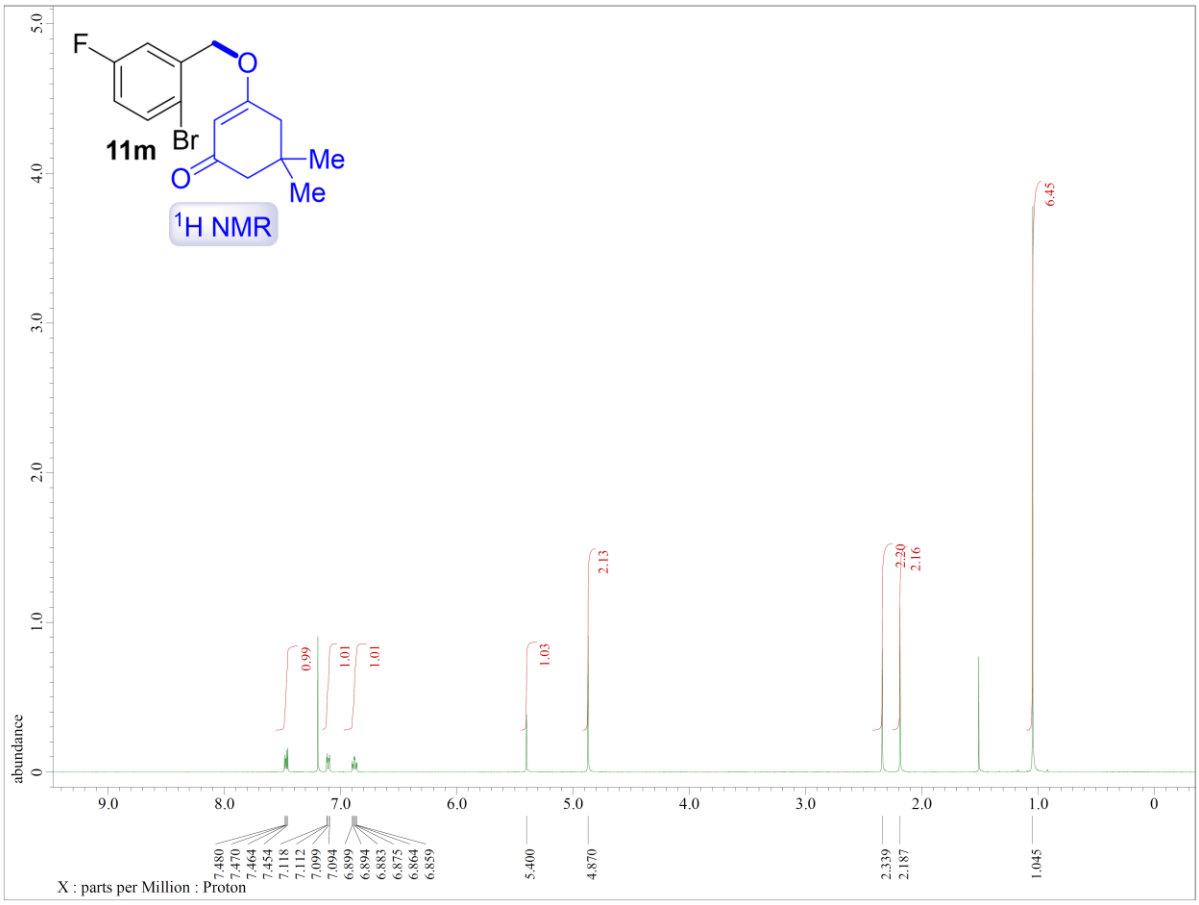
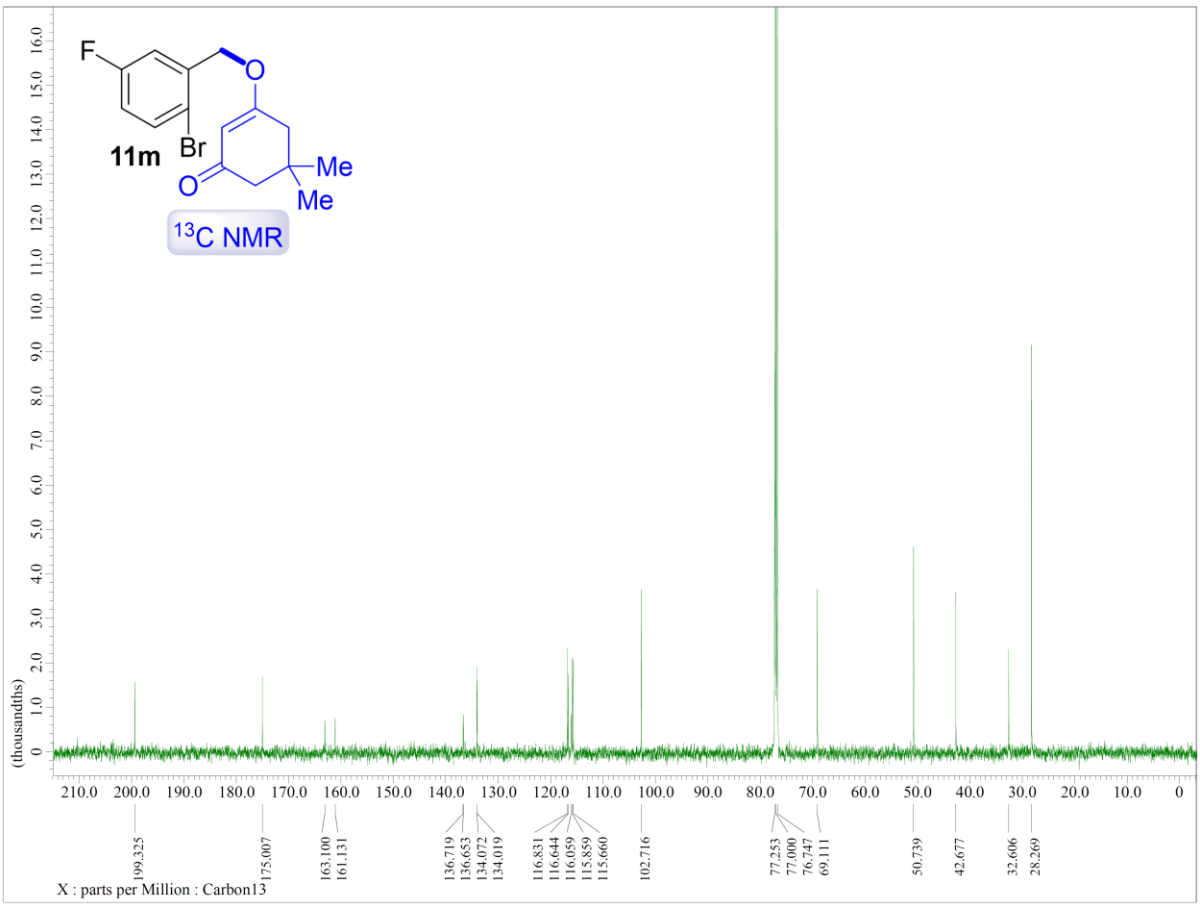
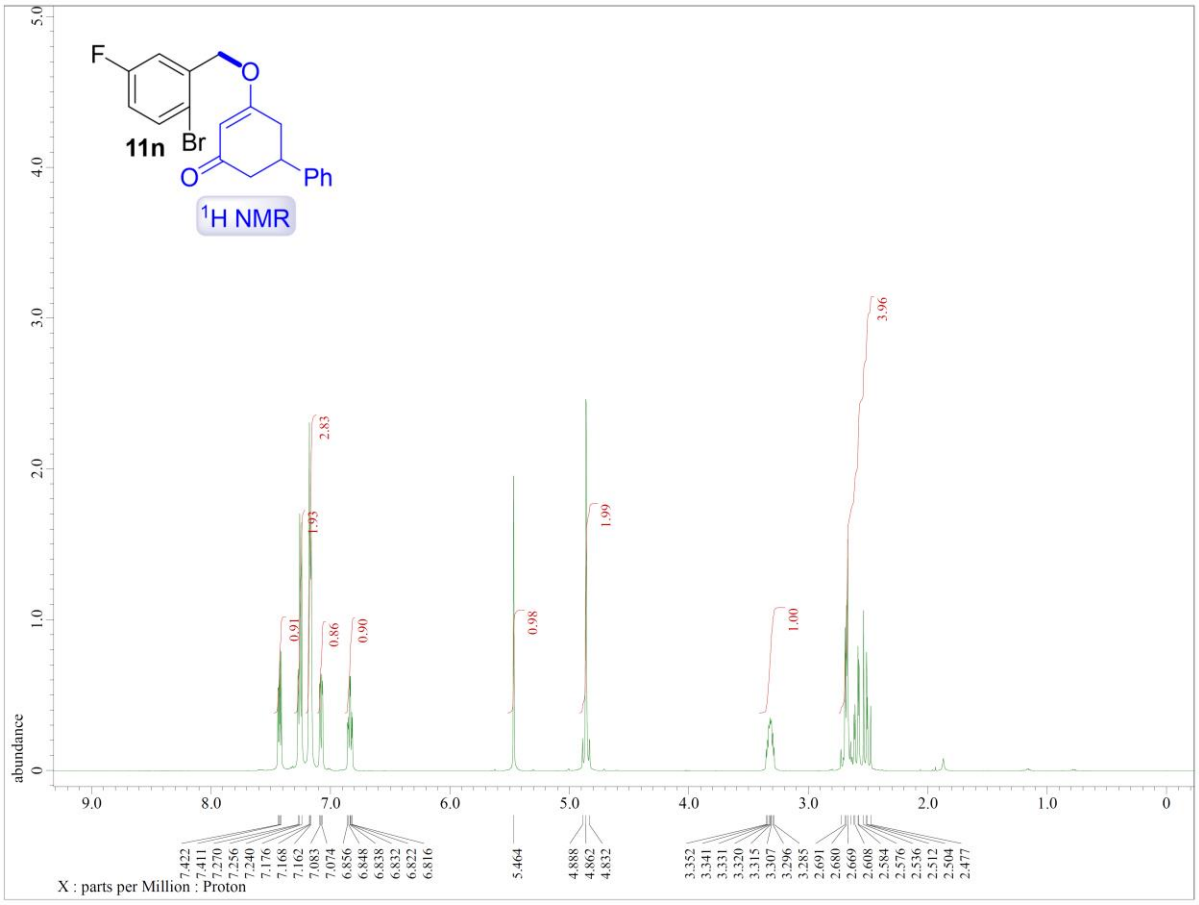
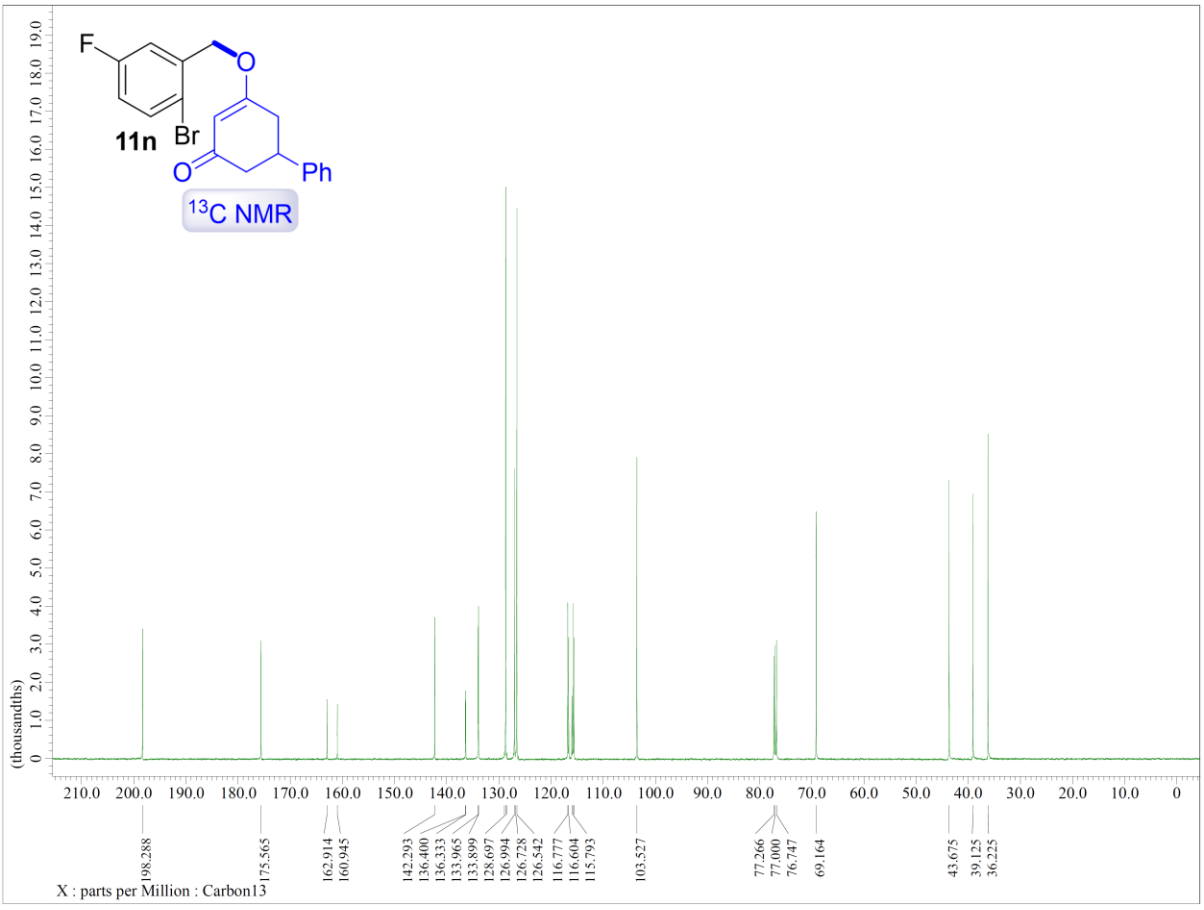
4.18
2.13

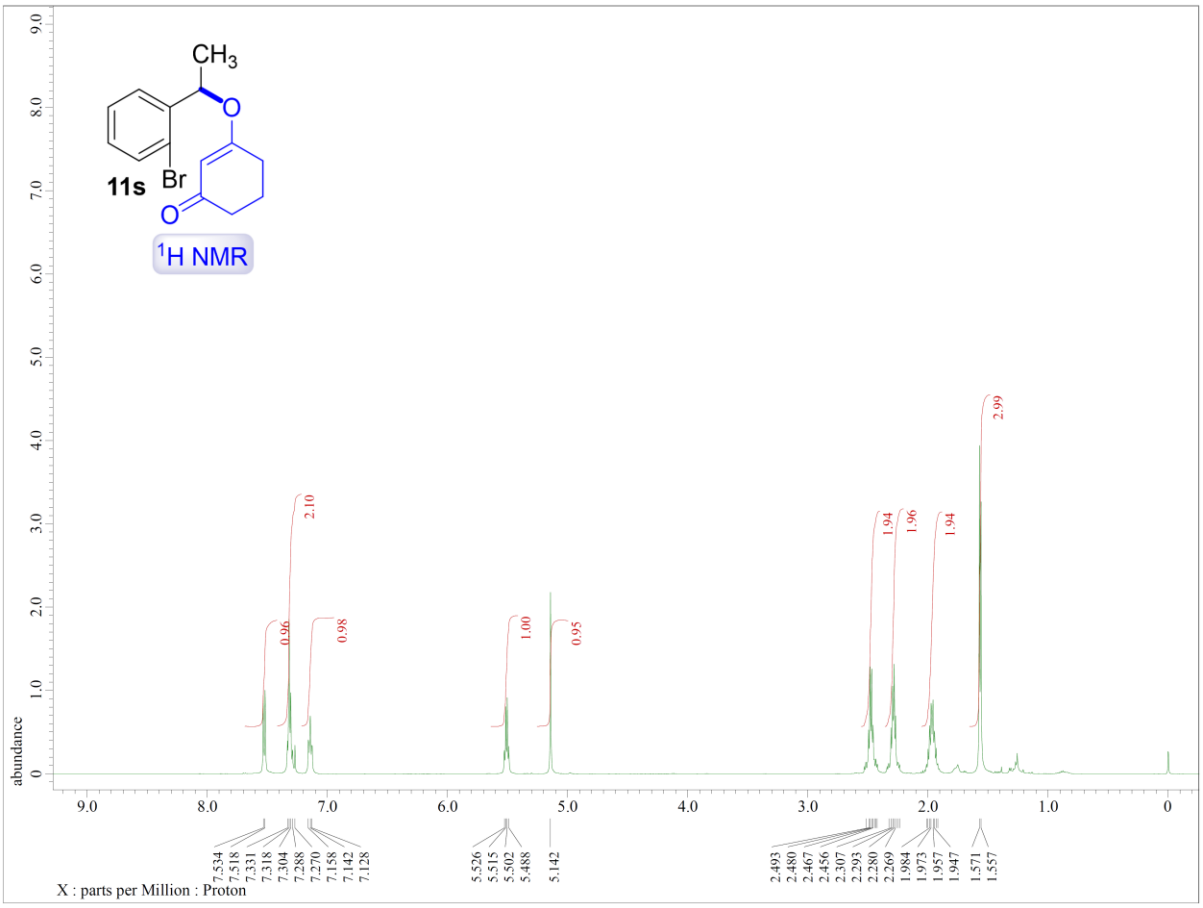

F
O
11l
Br
O
13C NMR
(thousandths)
X : parts per Million : Carbon13
196.226
173.317
162.461
160.506
129.056
129.003
126.835
126.768
123.841
115.048
114.888
112.427
110.844
110.658
77.253
77.000
76.734
68.832
38.154
28.682
19.995

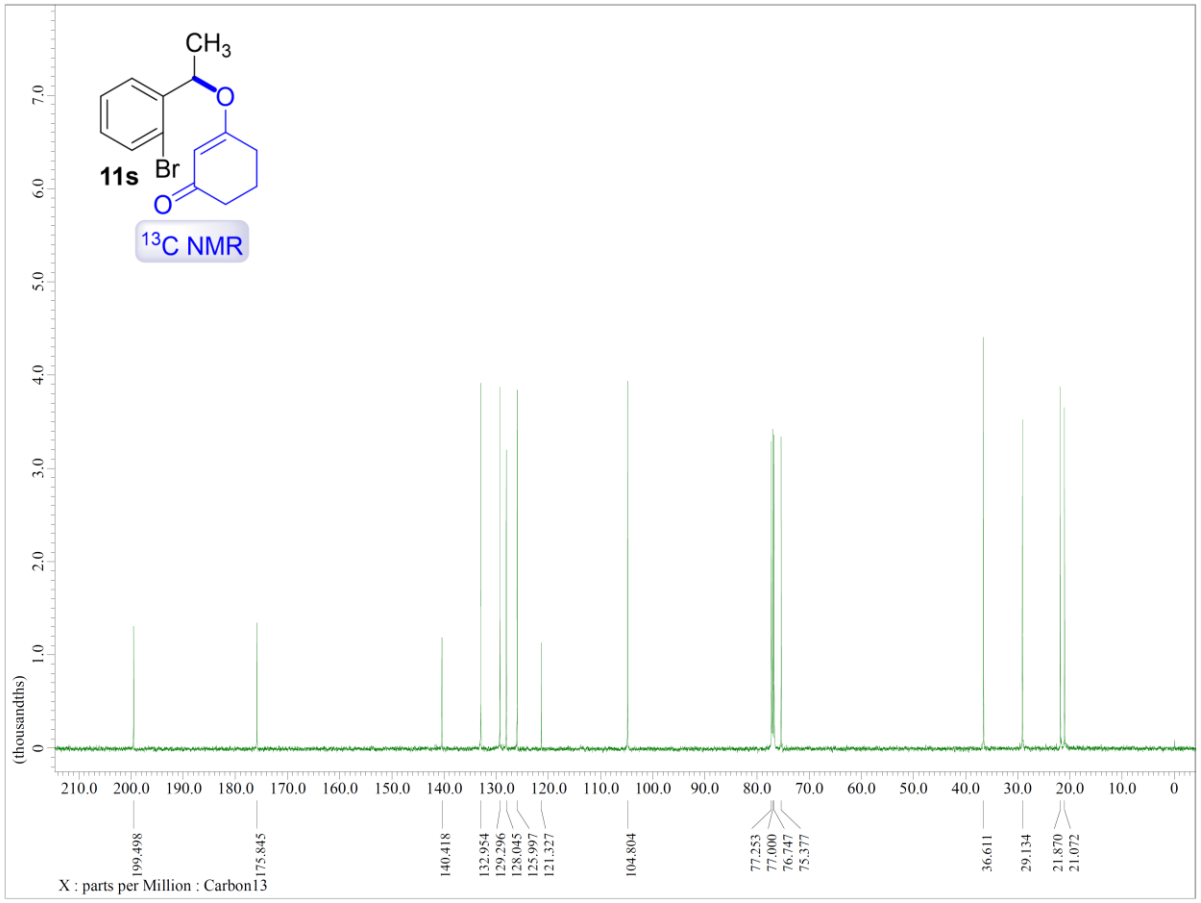

F
O
Br
11m
O
Me
Me
1H NMR
abundance
6.45
2.13
2.20
2.16
0.99
1.01
1.01
1.03
7.480
7.470
7.464
7.454
7.118
7.112
7.099
7.094
6.899
6.894
6.883
6.875
6.864
6.859
5.400
4.870
2.339
2.187
1.045
X : parts per Million : Proton

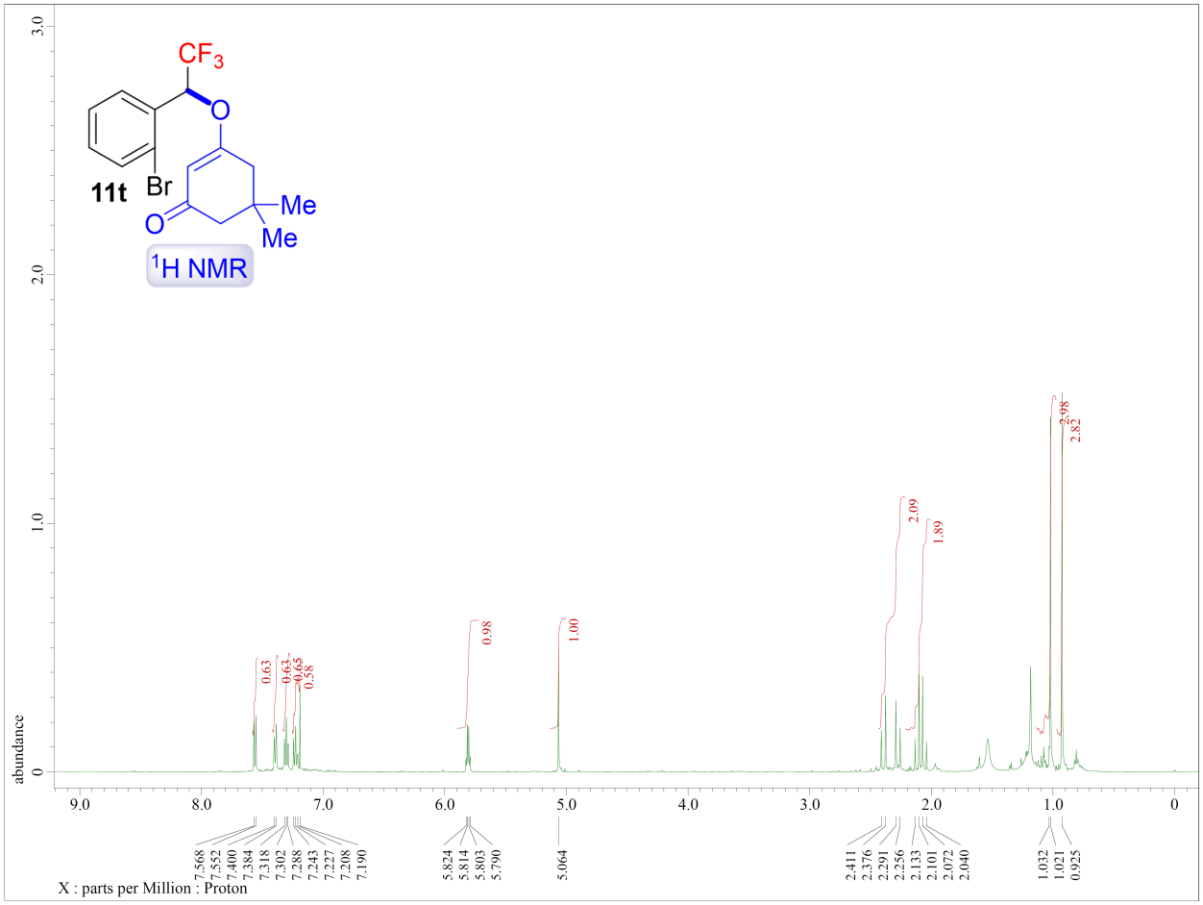

F
O
Br
11m
O
Me
Me
13C NMR
(thousandths)
199.325
175.007
163.100
161.131
136.719
136.653
134.072
134.019
116.831
116.644
116.059
115.859
115.660
102.716
77.253
77.000
76.747
69.111
50.739
42.677
32.606
28.269
X : parts per Million : Carbon13

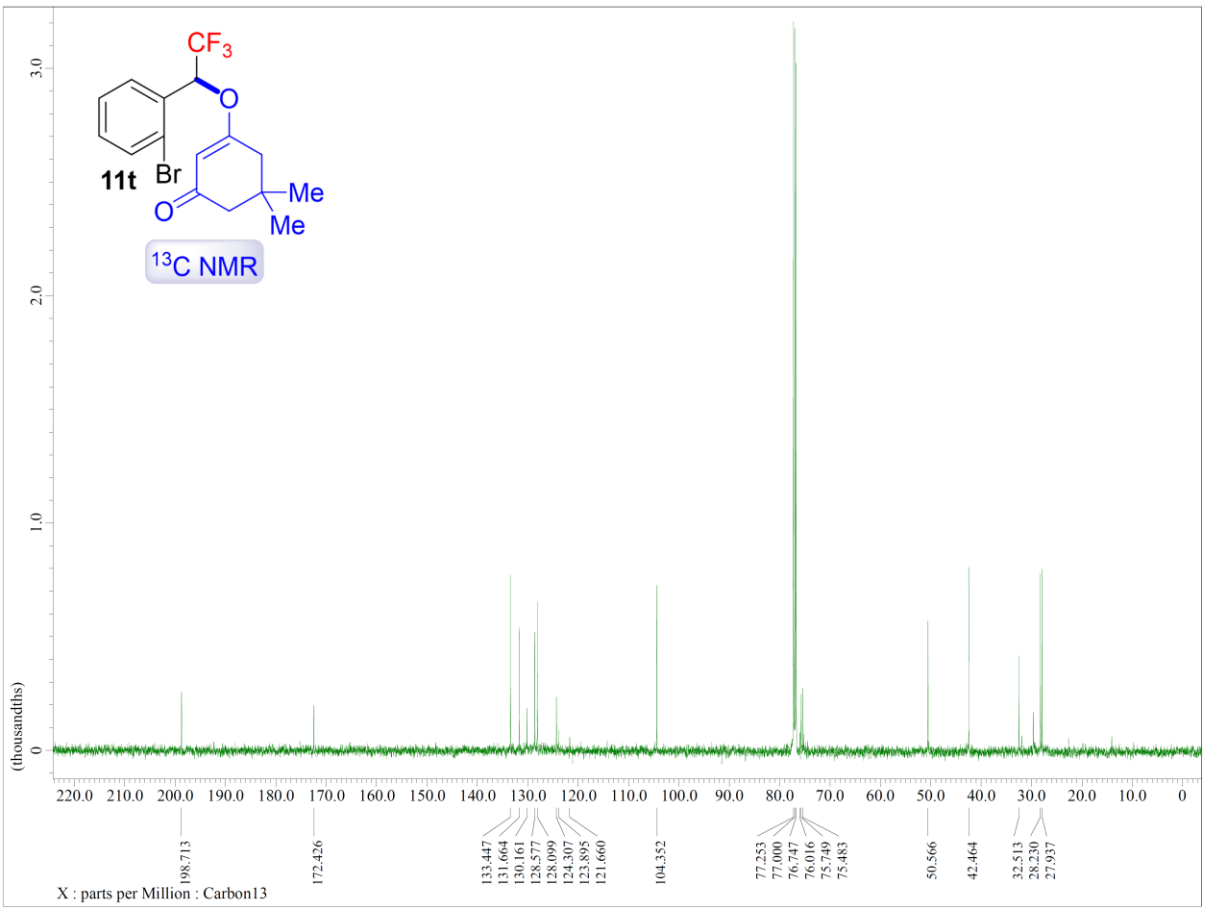

F
O
11n Br
O
Ph
1H NMR
abundance
X : parts per Million : Proton

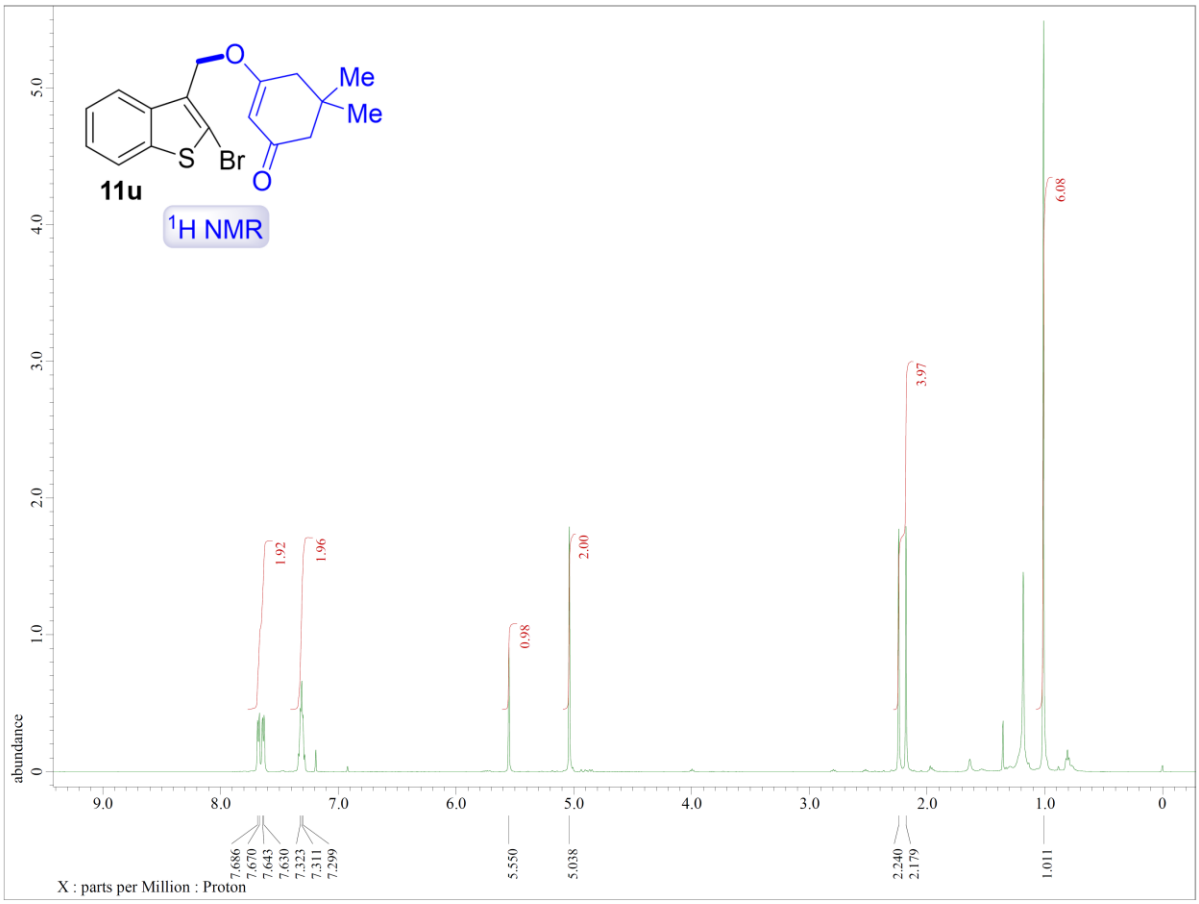

F
O
11n Br
O
Ph
13C NMR
(thousandths)
X : parts per Million : Carbon13

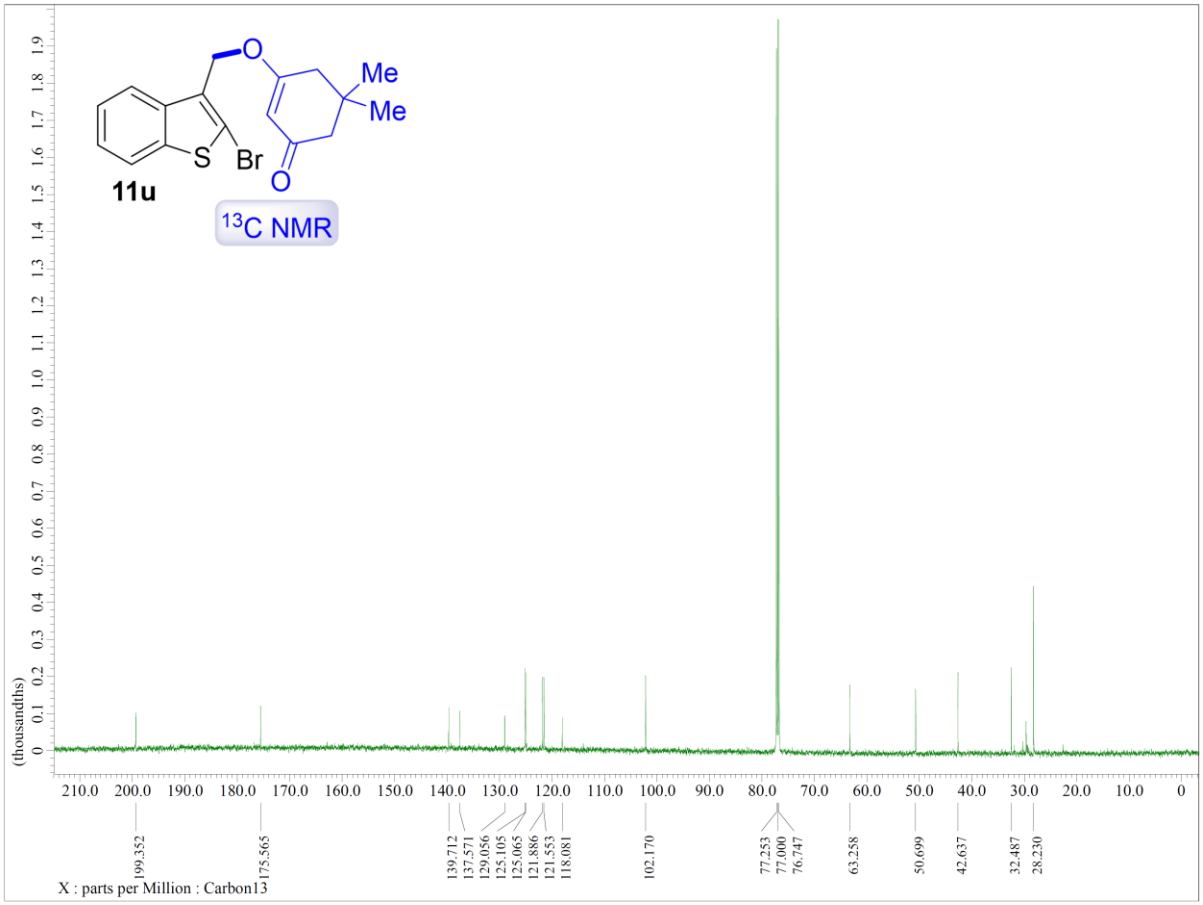

CH3
O
11s Br
O
1H NMR
abundance
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
2.99
2.10
1.94
1.96
1.94
0.96
0.98
1.00
0.95
7.534
7.518
7.331
7.318
7.304
7.288
7.270
7.158
7.142
7.128
5.526
5.515
5.502
5.488
5.142
2.493
2.480
2.467
2.456
2.307
2.293
2.280
2.269
1.984
1.973
1.957
1.947
1.571
1.557
X : parts per Million : Proton

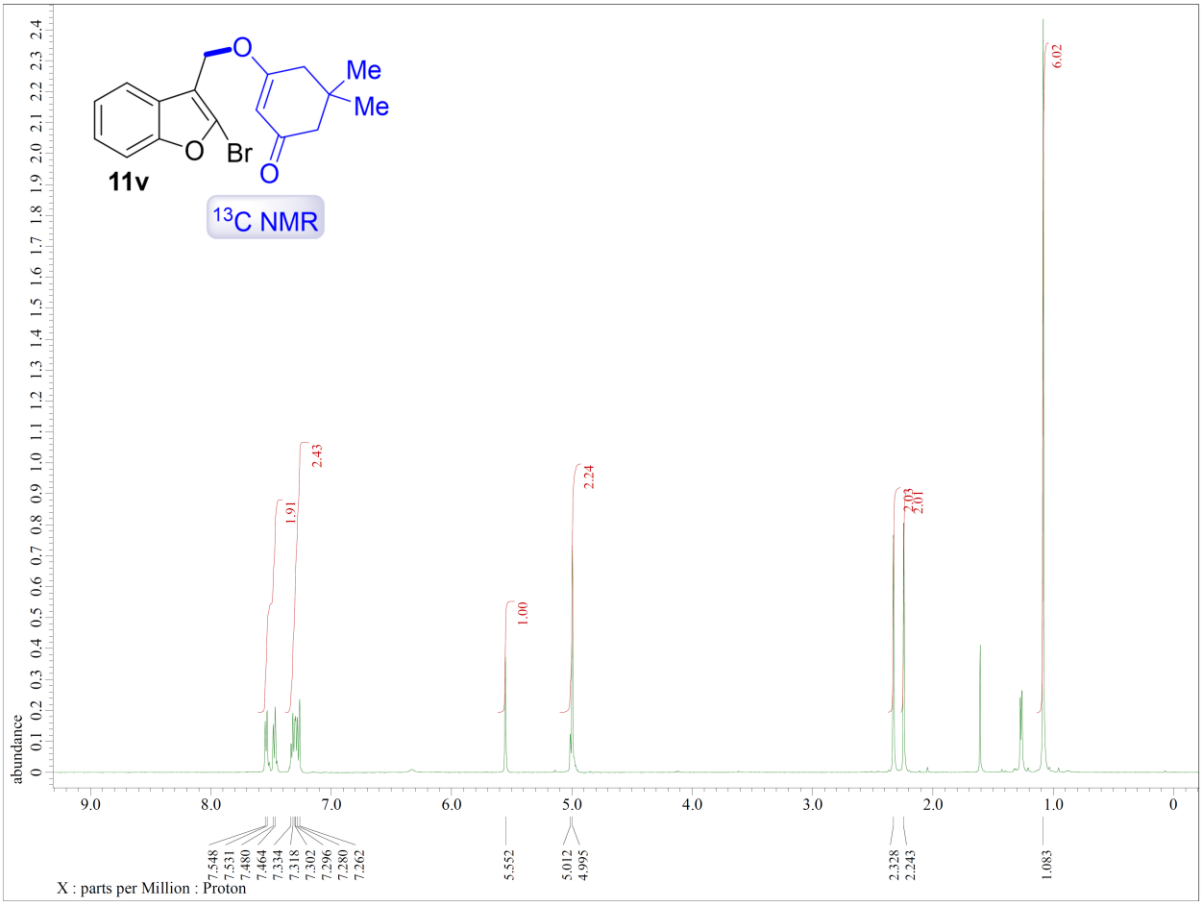

CH3
O
11s Br
O
13C NMR
(thousandths)
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
199.498
175.845
140.418
132.954
129.296
128.045
125.997
121.327
104.804
77.253
77.000
76.747
75.377
36.611
29.134
21.870
21.072
X : parts per Million : Carbon13

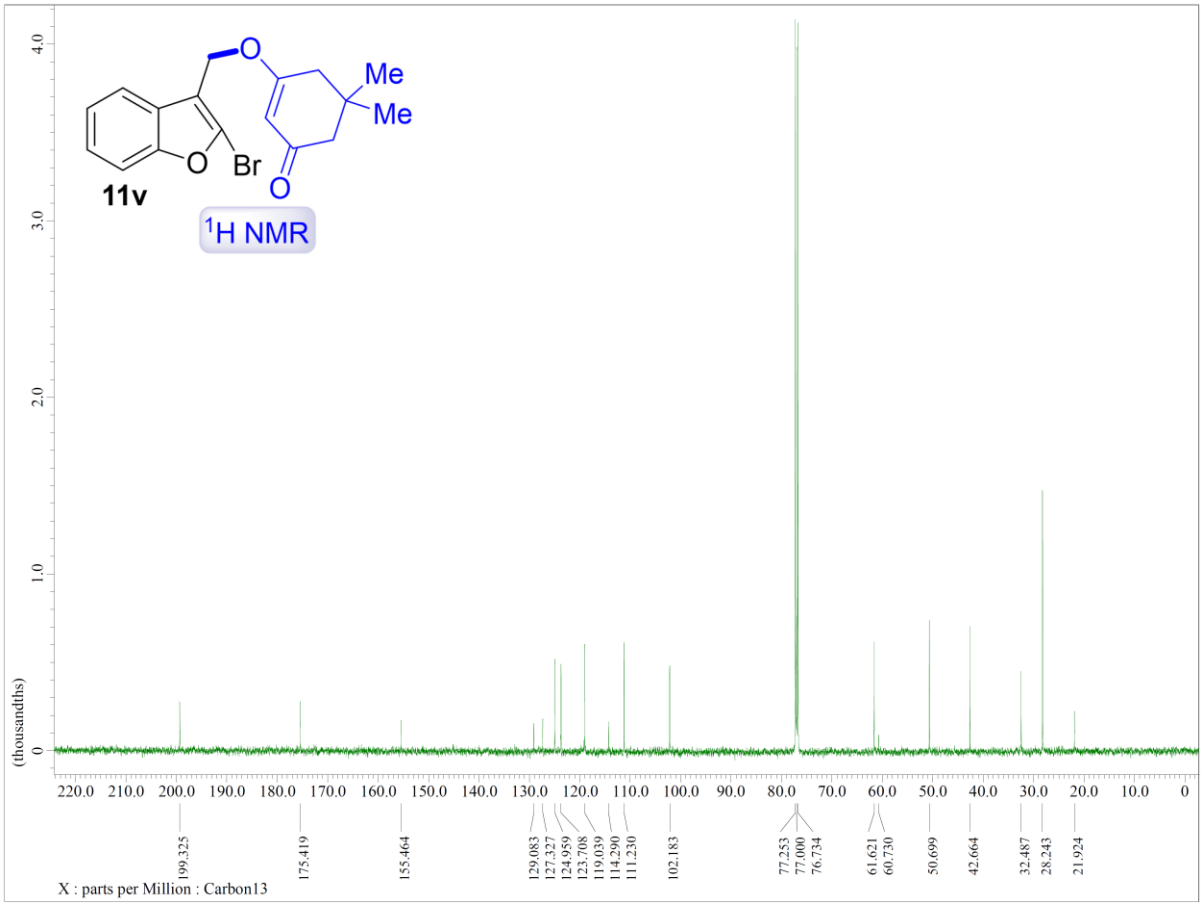

CF3
O
11t Br
O
Me
Me
1H NMR
abundance
3.0
2.0
1.0
0
0.63
0.63
0.65
0.58
0.98
1.00
2.09
1.89
3.98
2.82
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.568
7.552
7.400
7.384
7.318
7.302
7.288
7.243
7.227
7.208
7.190
5.824
5.814
5.803
5.790
5.064
2.411
2.376
2.291
2.256
2.133
2.101
2.072
2.040
1.032
1.021
0.925
X : parts per Million : Proton

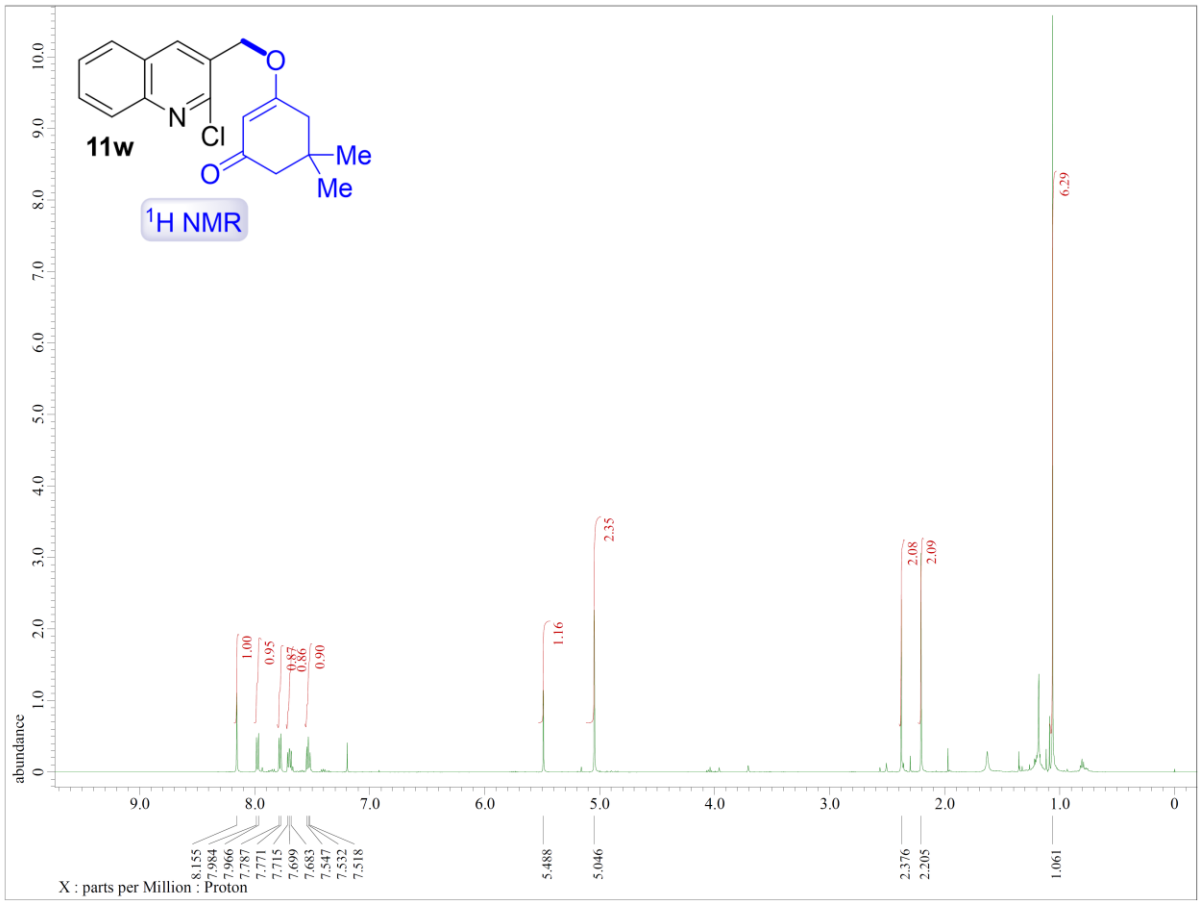

CF3
O
11t Br
O
Me
Me
13C NMR
(thousandths)
3.0
2.0
1.0
0
220.0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
198.713
172.426
133.447
131.664
130.161
128.577
128.099
124.307
123.895
121.660
104.352
77.253
77.000
76.747
76.016
75.749
75.483
50.566
42.464
32.513
28.230
27.937
X : parts per Million : Carbon13

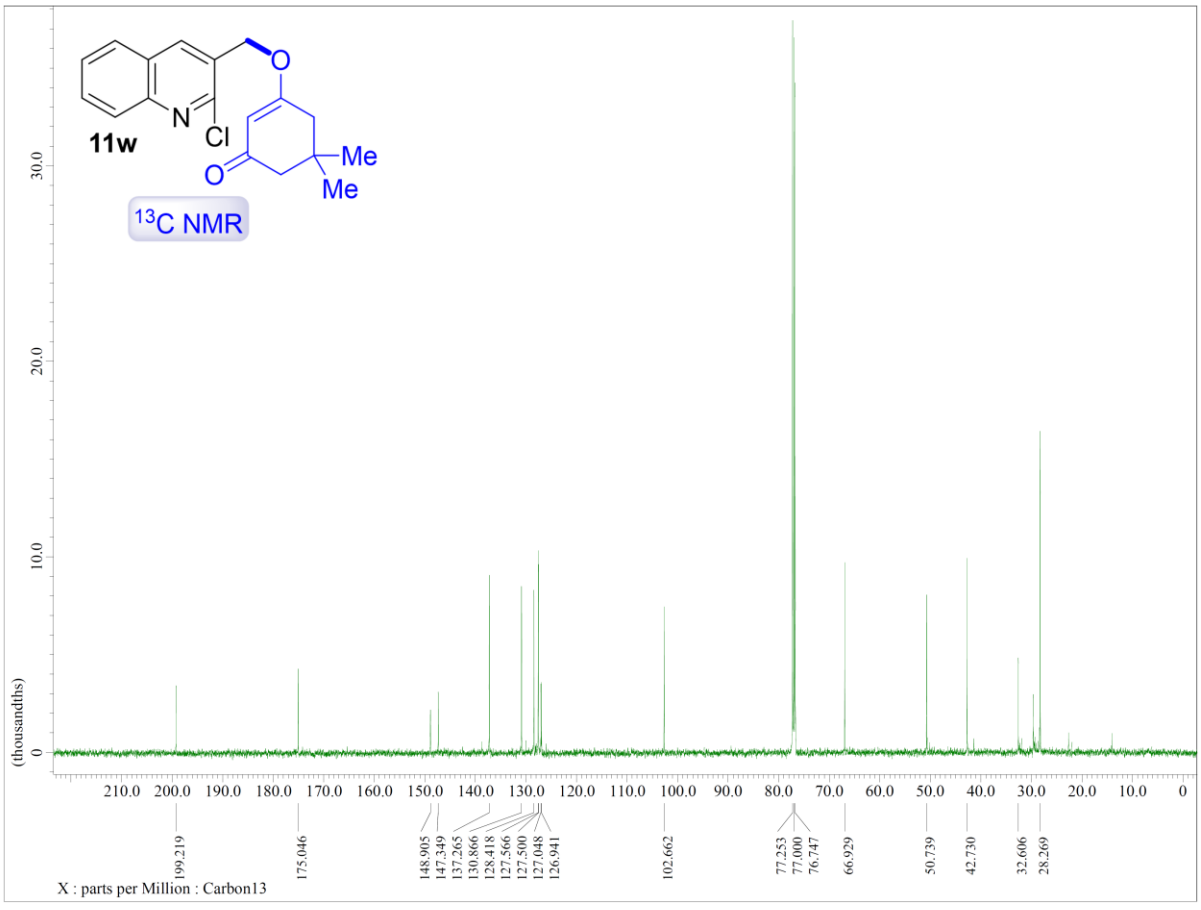

11u
1H NMR
abundance
X : parts per Million : Proton

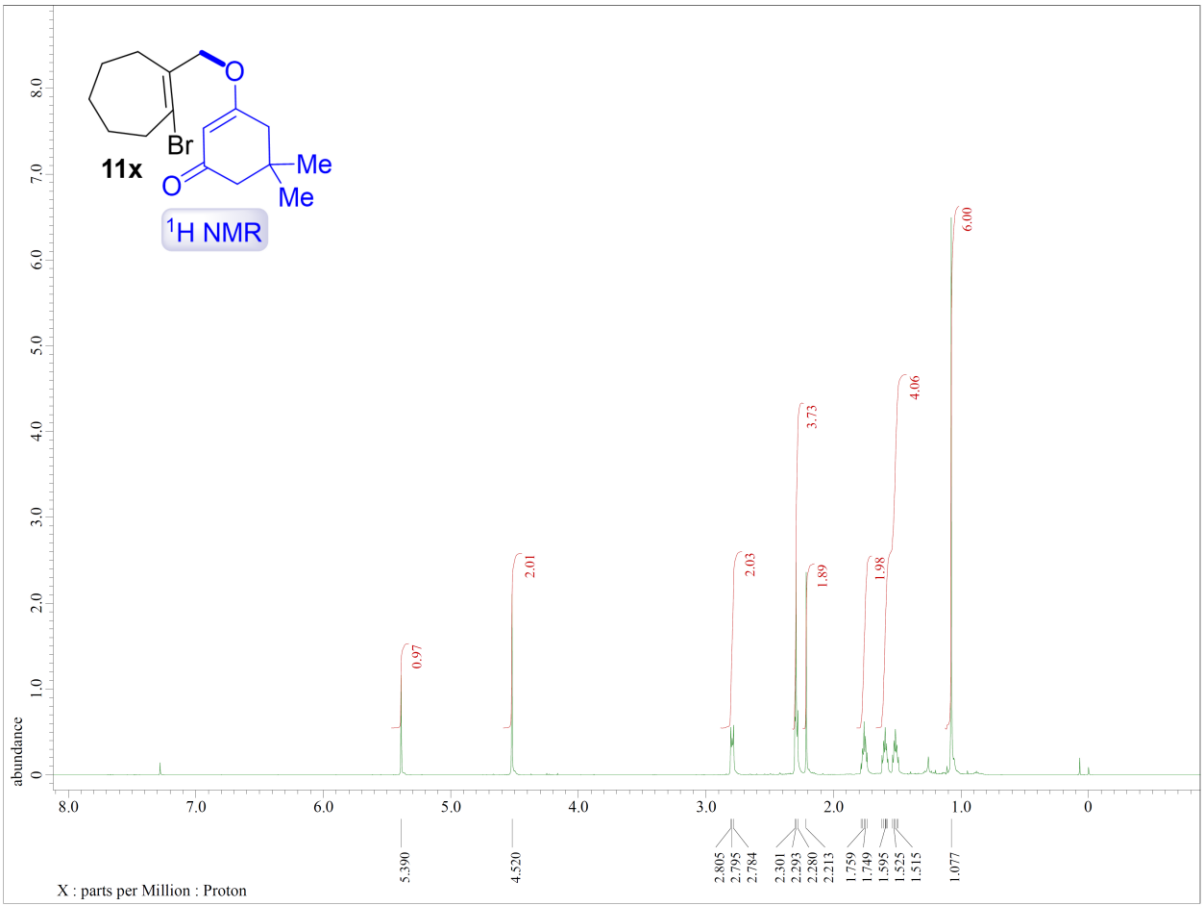

11u
13C NMR
(thousandths)
X : parts per Million : Carbon13

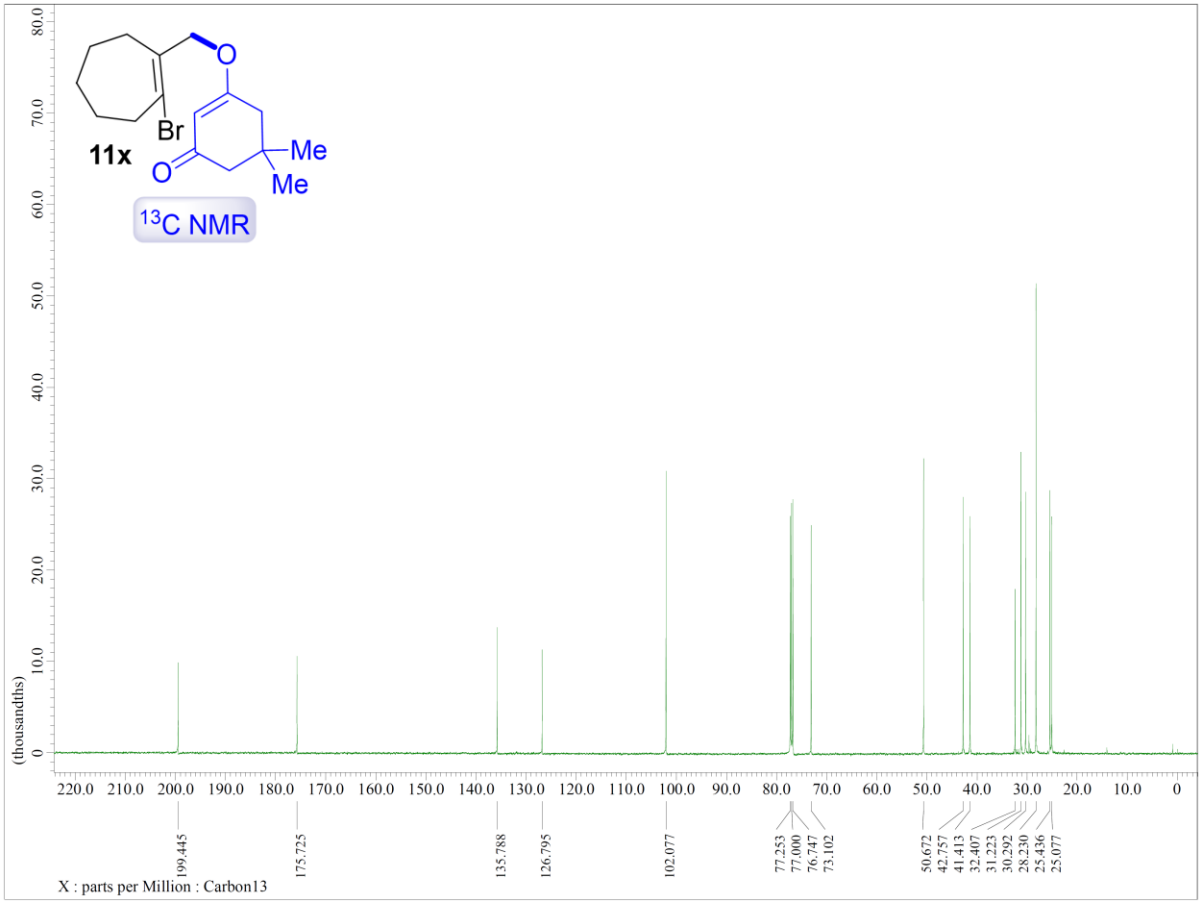

11v
13C NMR
Me
Me
O
Br
O
abundance
X : parts per Million : Proton
6.02
2.43
2.24
1.91
1.00
2.03
2.01
7.548
7.531
7.480
7.464
7.334
7.318
7.302
7.296
7.280
7.262
5.552
5.012
4.995
2.328
2.243
1.083

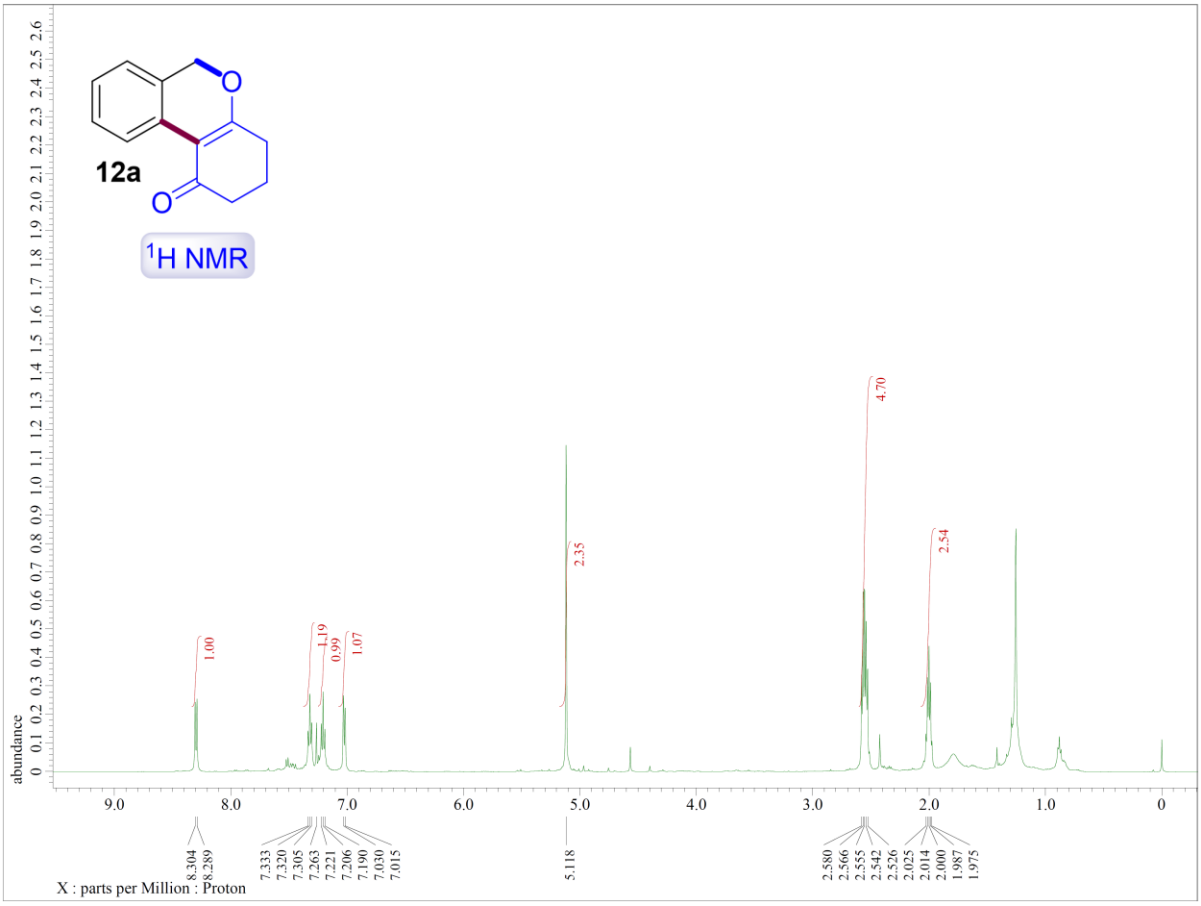

11v
1H NMR
Me
Me
O
Br
O
(thousandths)
X : parts per Million : Carbon13
199.325
175.419
155.464
129.083
127.327
124.959
123.708
119.039
114.290
111.230
102.183
77.253
77.000
76.734
61.621
60.730
50.699
42.664
32.487
28.243
21.924

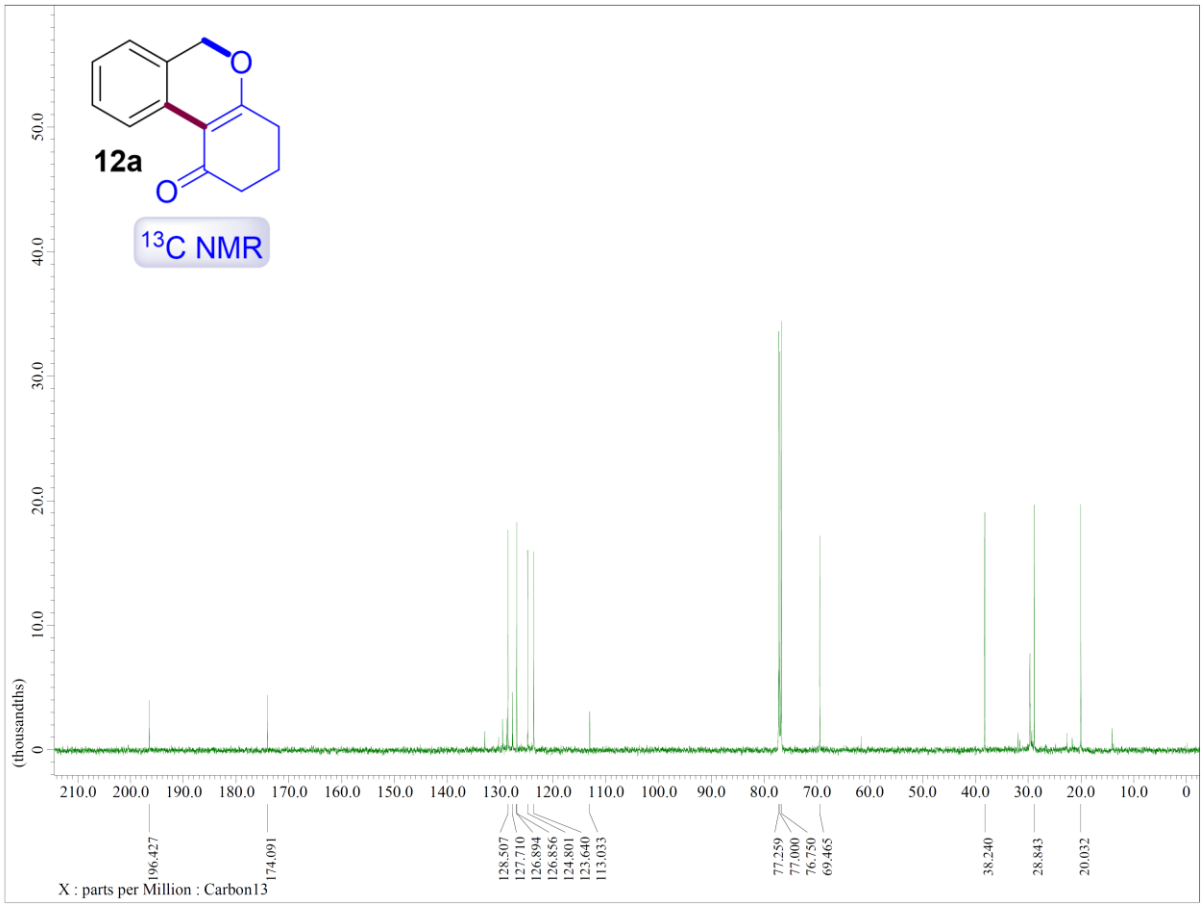

11w
Cl
N
O
O
Me
Me
1H NMR
abundance
X : parts per Million : Proton

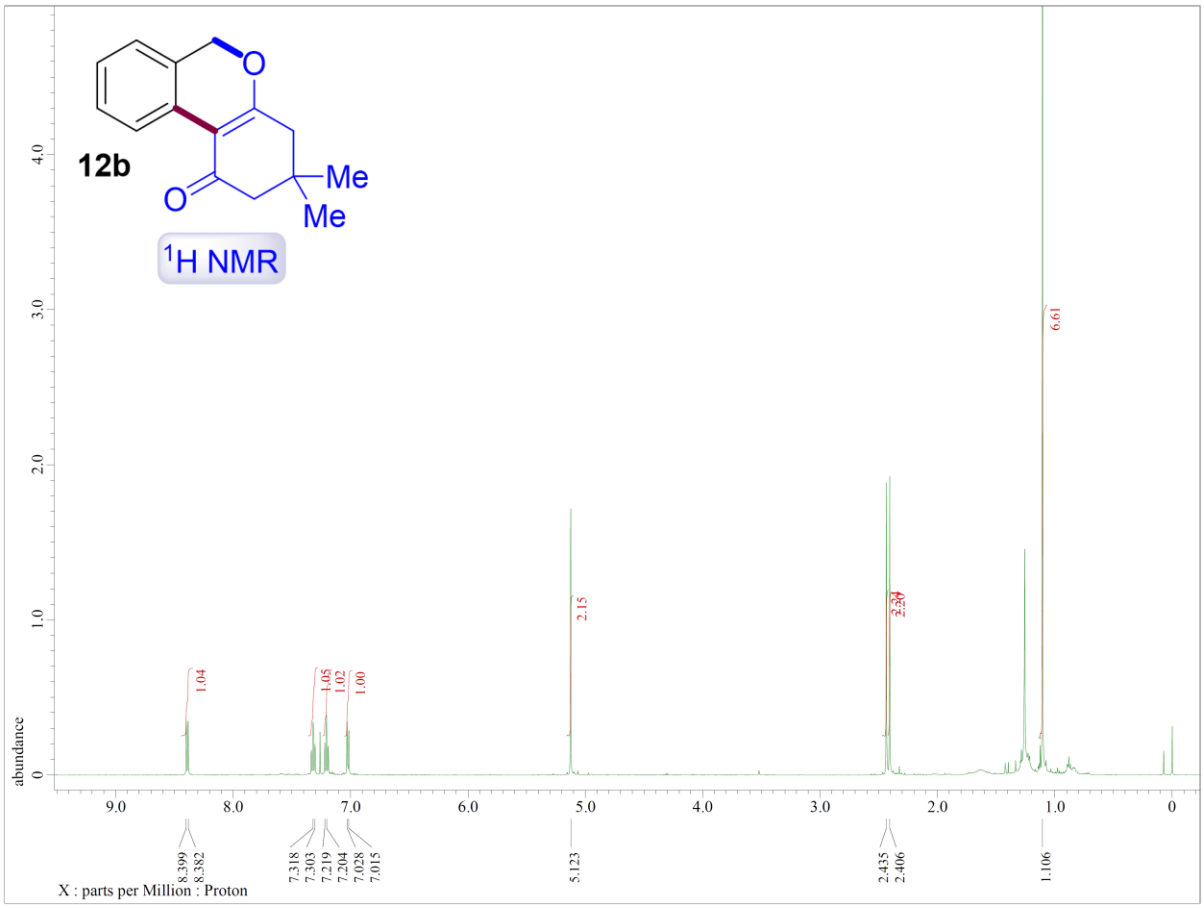

11w
Cl
N
O
O
Me
Me
13C NMR
(thousandths)
X : parts per Million : Carbon13

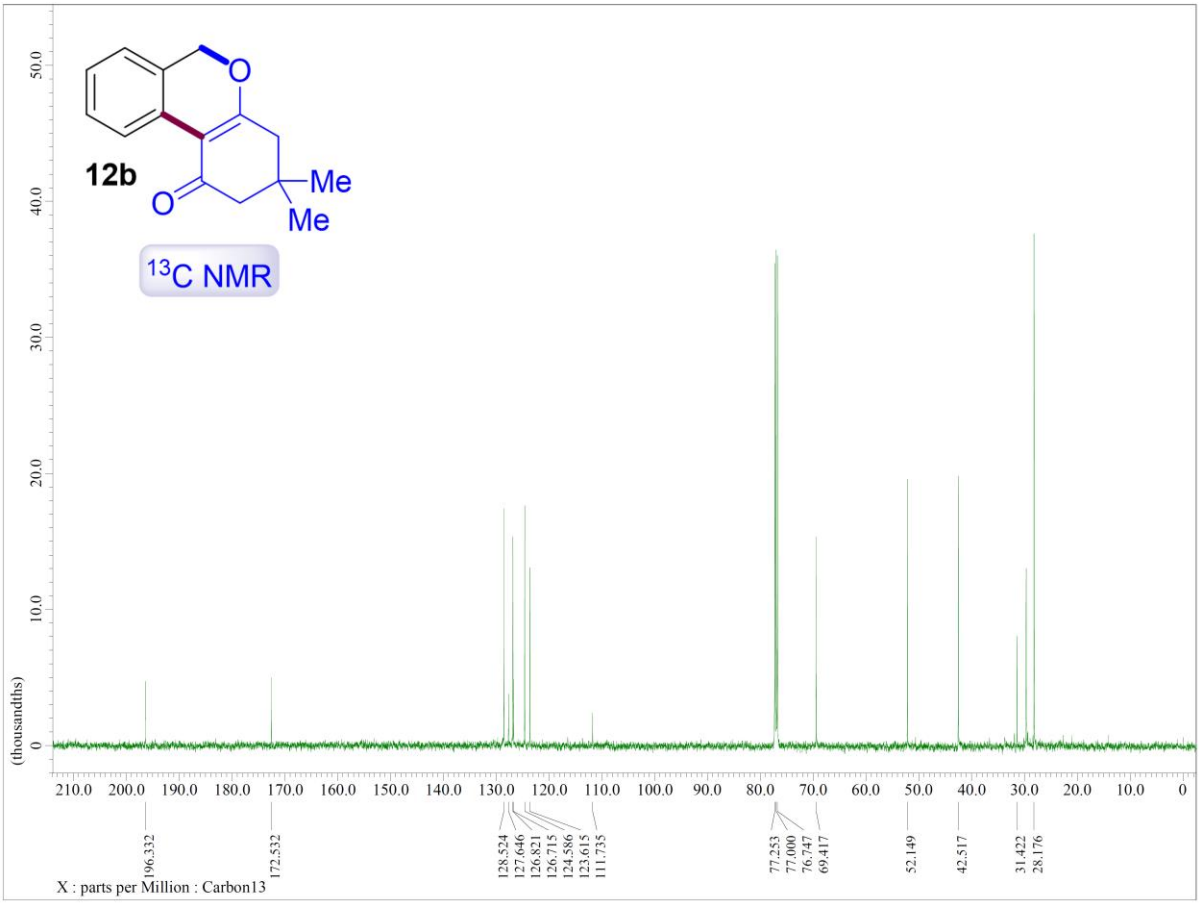

11x
Br
O
O
Me
Me
1H NMR
abundance
X : parts per Million : Proton
0.97
2.01
2.03
3.73
1.89
1.98
4.06
6.00
5.390
4.520
2.805
2.795
2.784
2.301
2.293
2.280
2.213
1.759
1.749
1.595
1.525
1.515
1.077

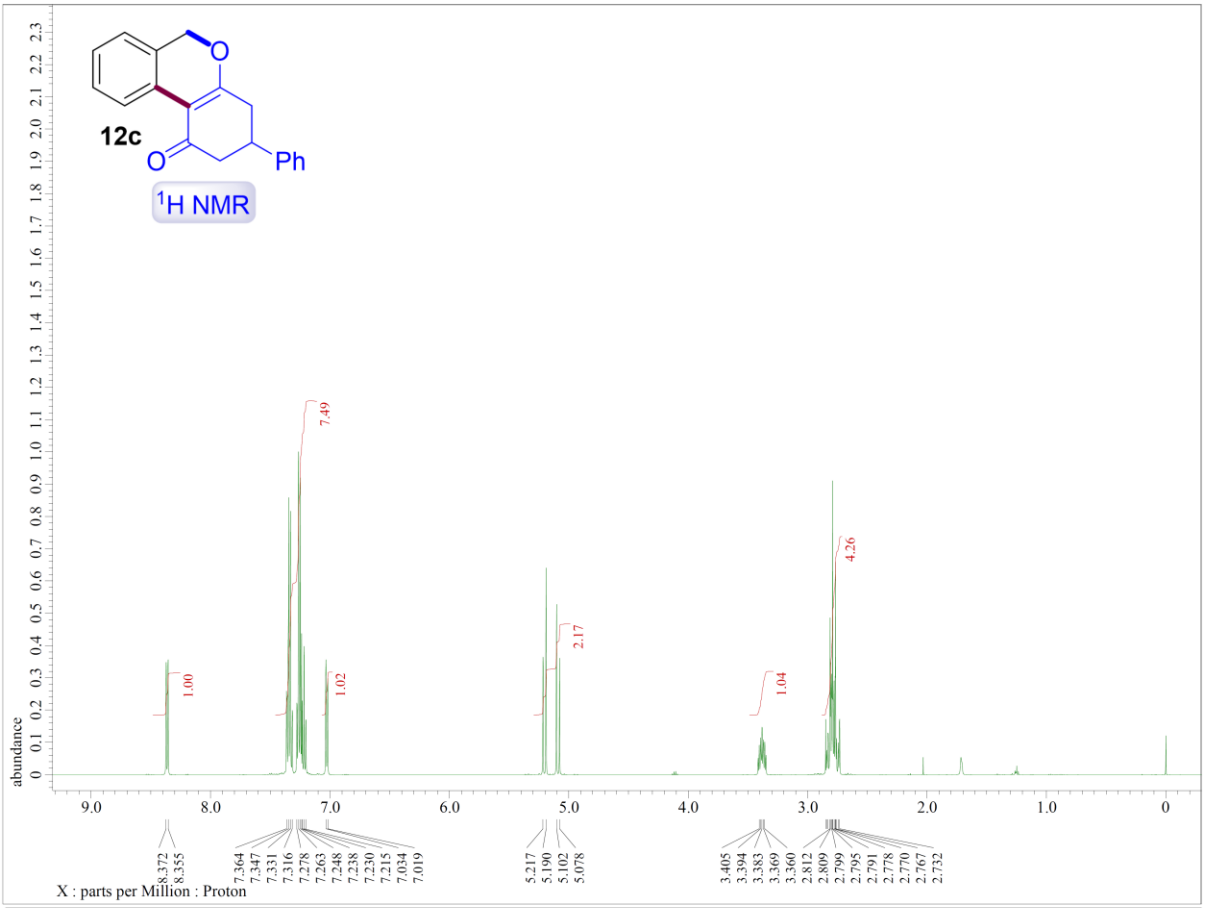

11x
Br
O
O
Me
Me
13C NMR
(thousandths)
X : parts per Million : Carbon13
199.445
175.725
135.788
126.795
102.077
77.253
77.000
76.747
73.102
50.672
42.757
41.413
32.407
31.223
30.292
28.230
25.436
25.077

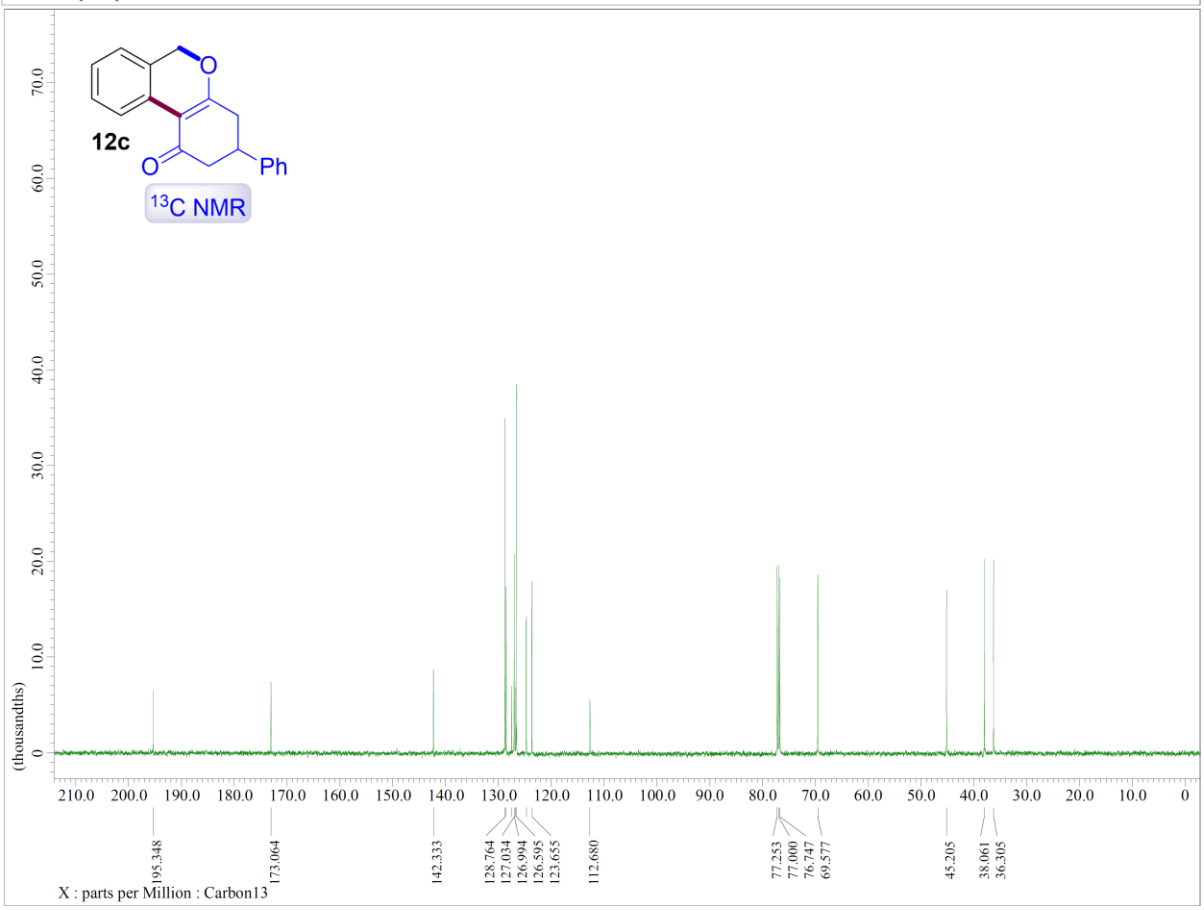

12a
^{1}H NMR
abundance
X : parts per Million : Proton
1.00
1.19
0.99
1.07
2.35
4.70
2.54
8.304
8.289
7.333
7.320
7.305
7.263
7.221
7.206
7.190
7.030
7.015
5.118
2.580
2.566
2.555
2.542
2.526
2.025
2.014
2.000
1.987
1.975

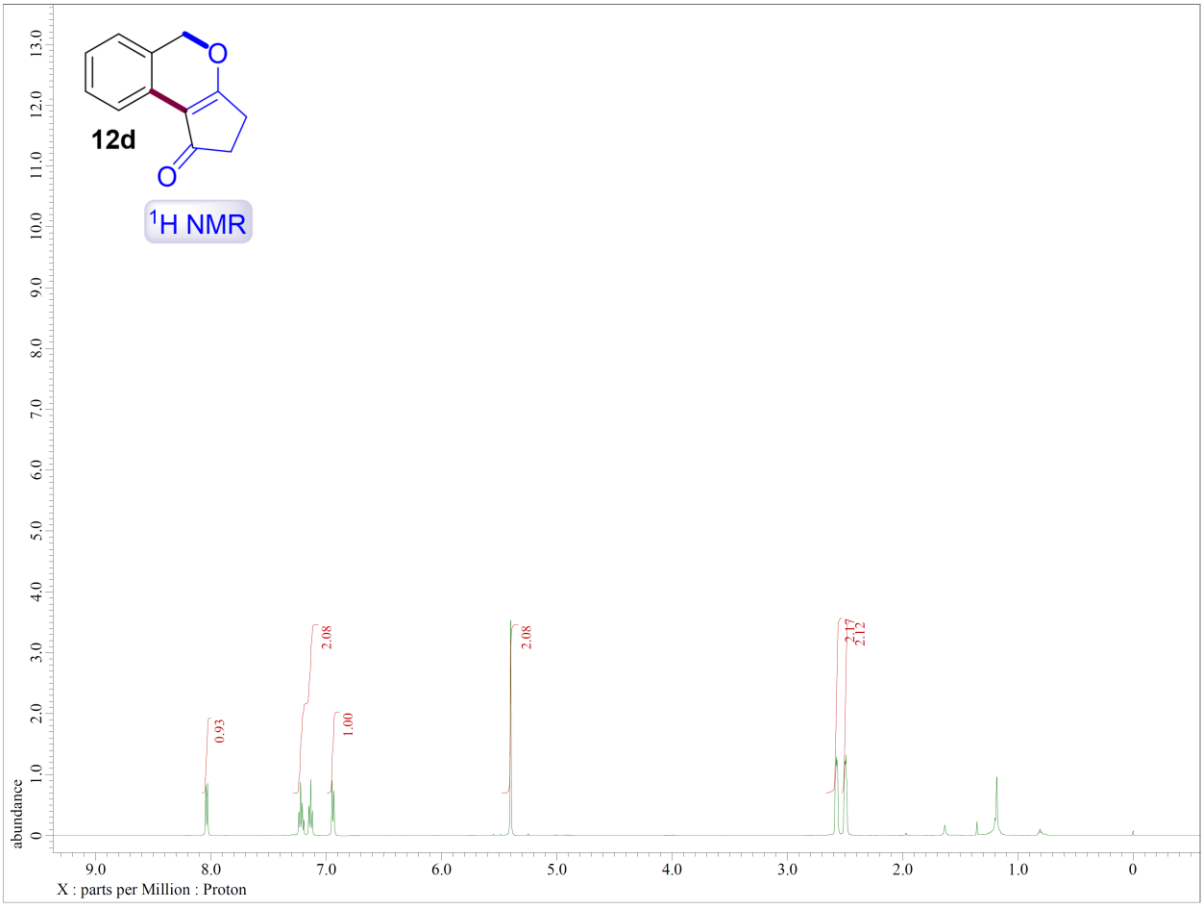

12a
^{13}C NMR
(thousandths)
X : parts per Million : Carbon13
196.427
174.091
128.507
127.710
126.894
126.856
124.801
123.640
113.033
77.259
77.000
76.750
69.465
38.240
28.843
20.032

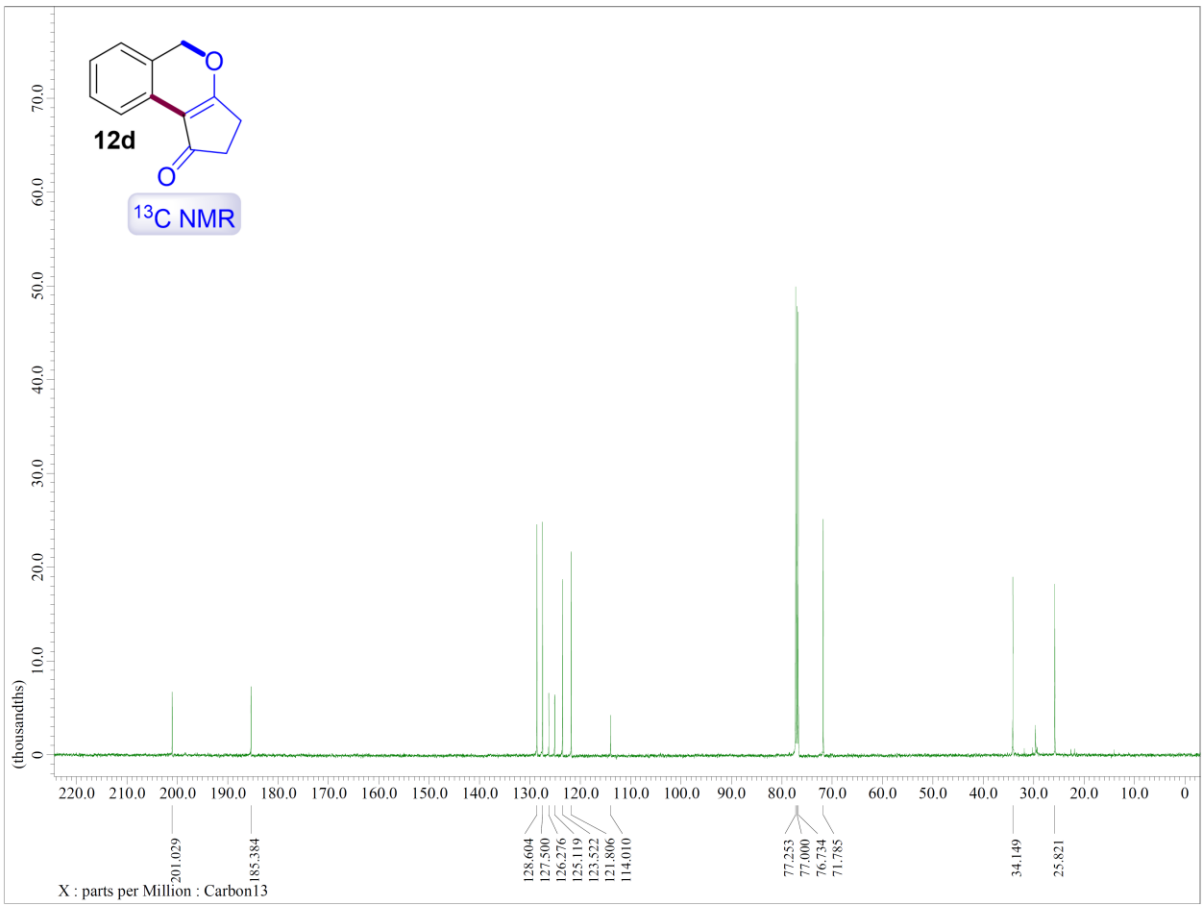

12b
Me
Me
O
O
1H NMR
abundance
X : parts per Million : Proton
1.04
1.05
1.02
1.00
2.15
2.24
6.61
8.399
8.382
7.318
7.303
7.219
7.204
7.028
7.015
5.123
2.435
2.406
1.106

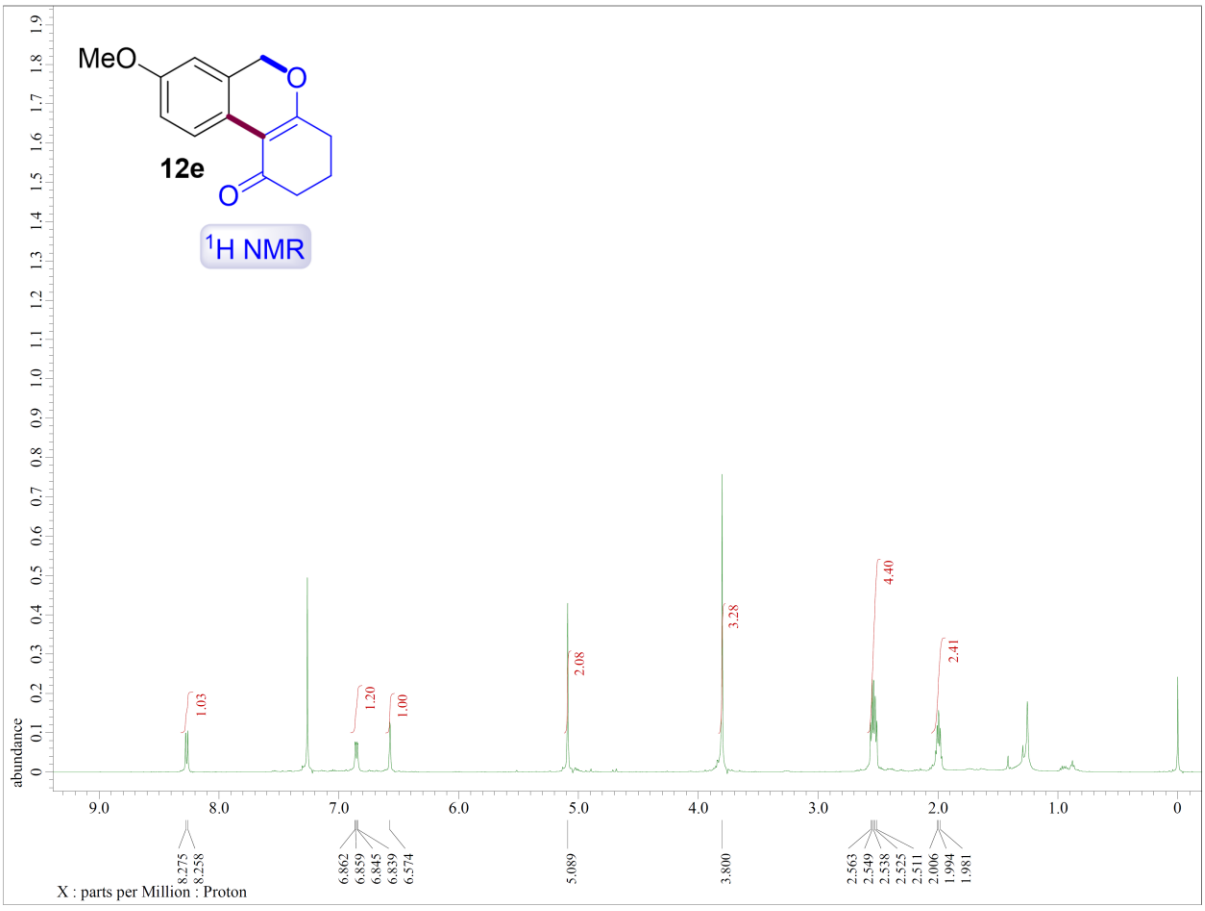

12b
Me
Me
O
O
13C NMR
(thousandths)
X : parts per Million : Carbon13
196.332
172.532
128.524
127.646
126.821
126.715
124.586
123.615
111.735
77.253
77.000
76.747
69.417
52.149
42.517
31.422
28.176

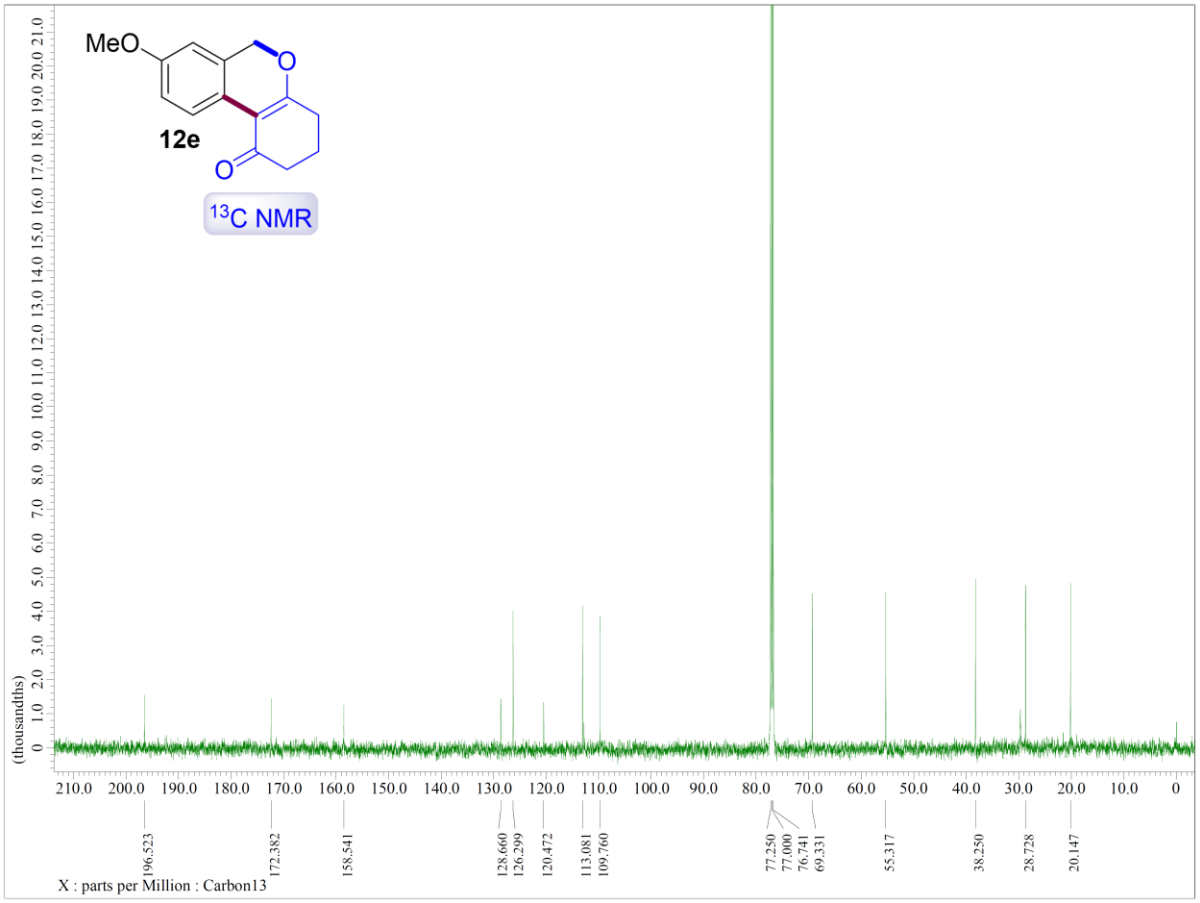

12c
Ph
^{1}H NMR
abundance
X : parts per Million : Proton

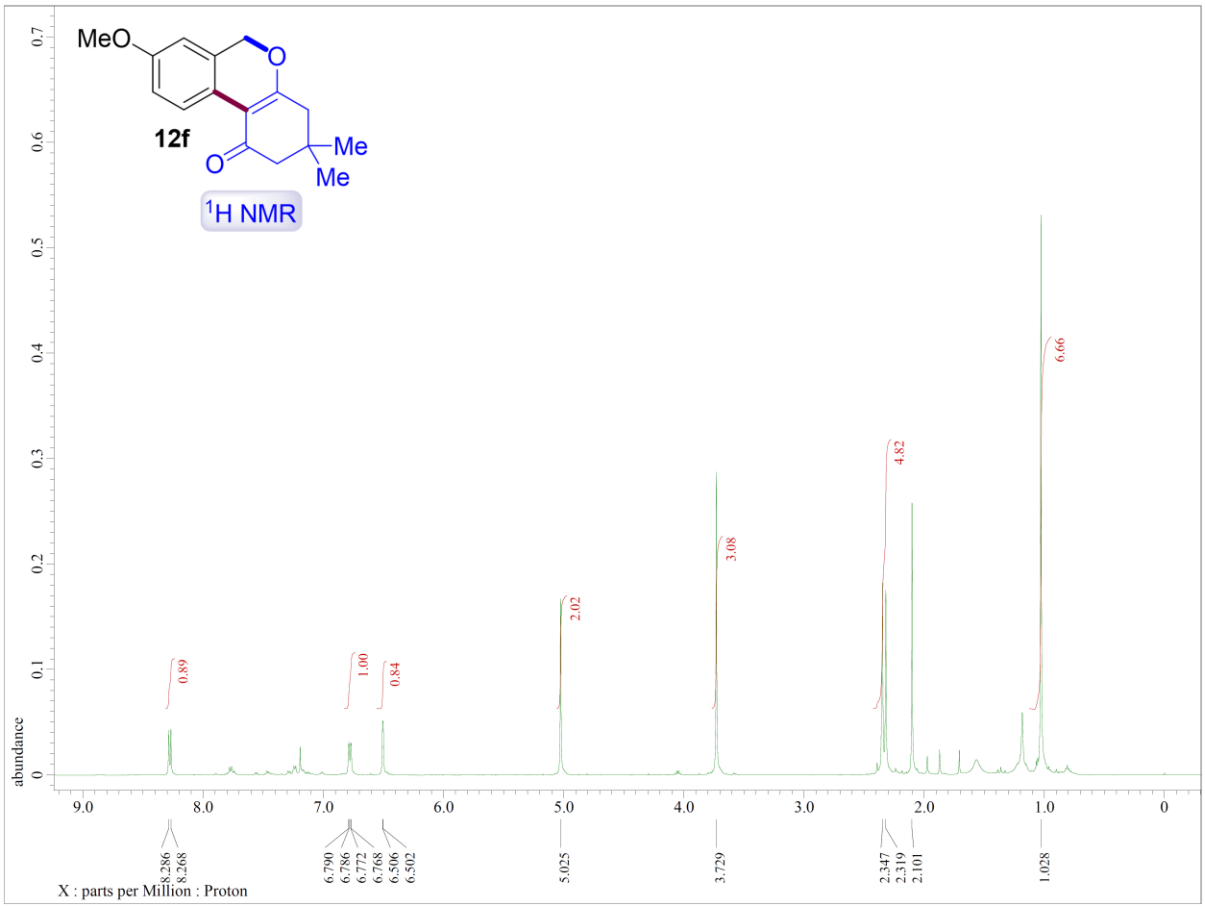

12c
Ph
^{13}C NMR
(thousandths)
X : parts per Million : Carbon13

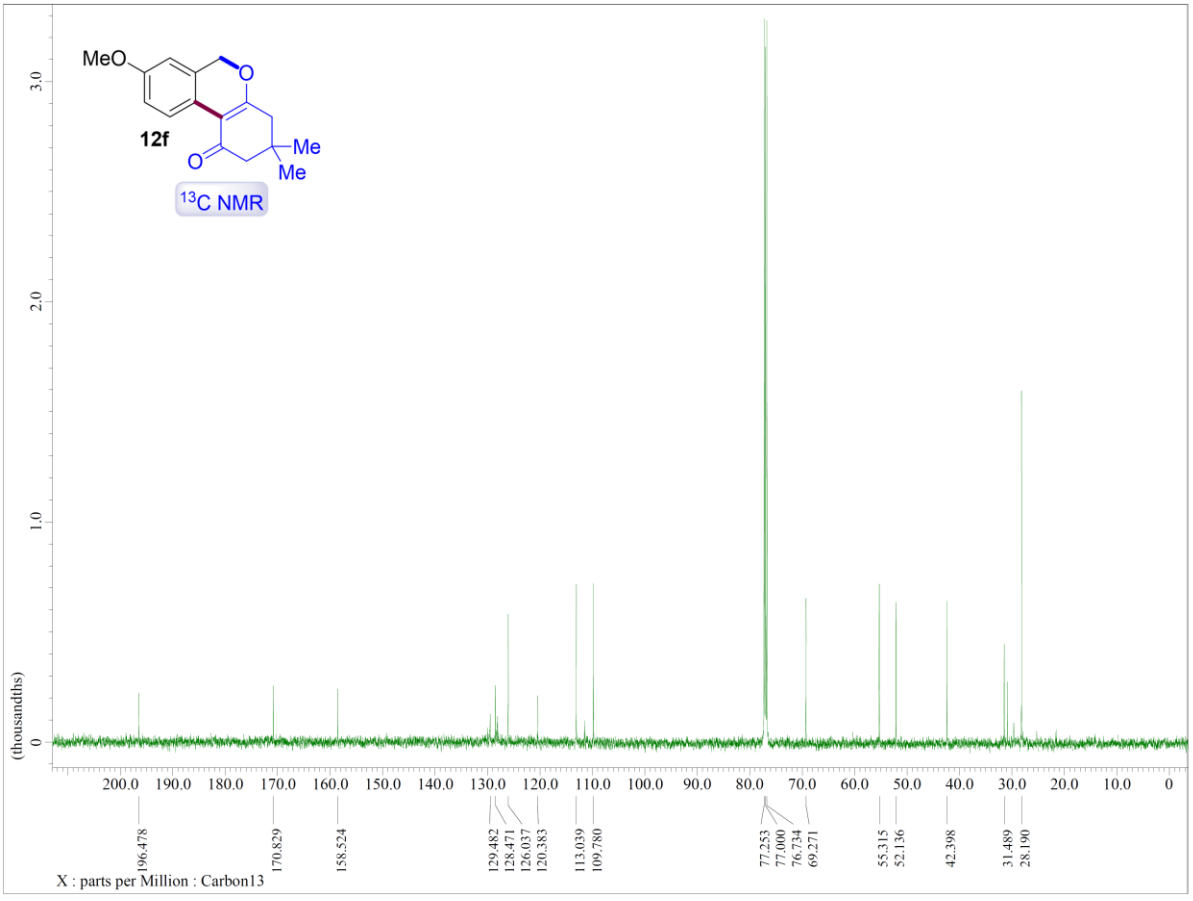

12d
1H NMR
abundance
0.93
2.08
1.00
2.08
2.17
2.12
X : parts per Million : Proton

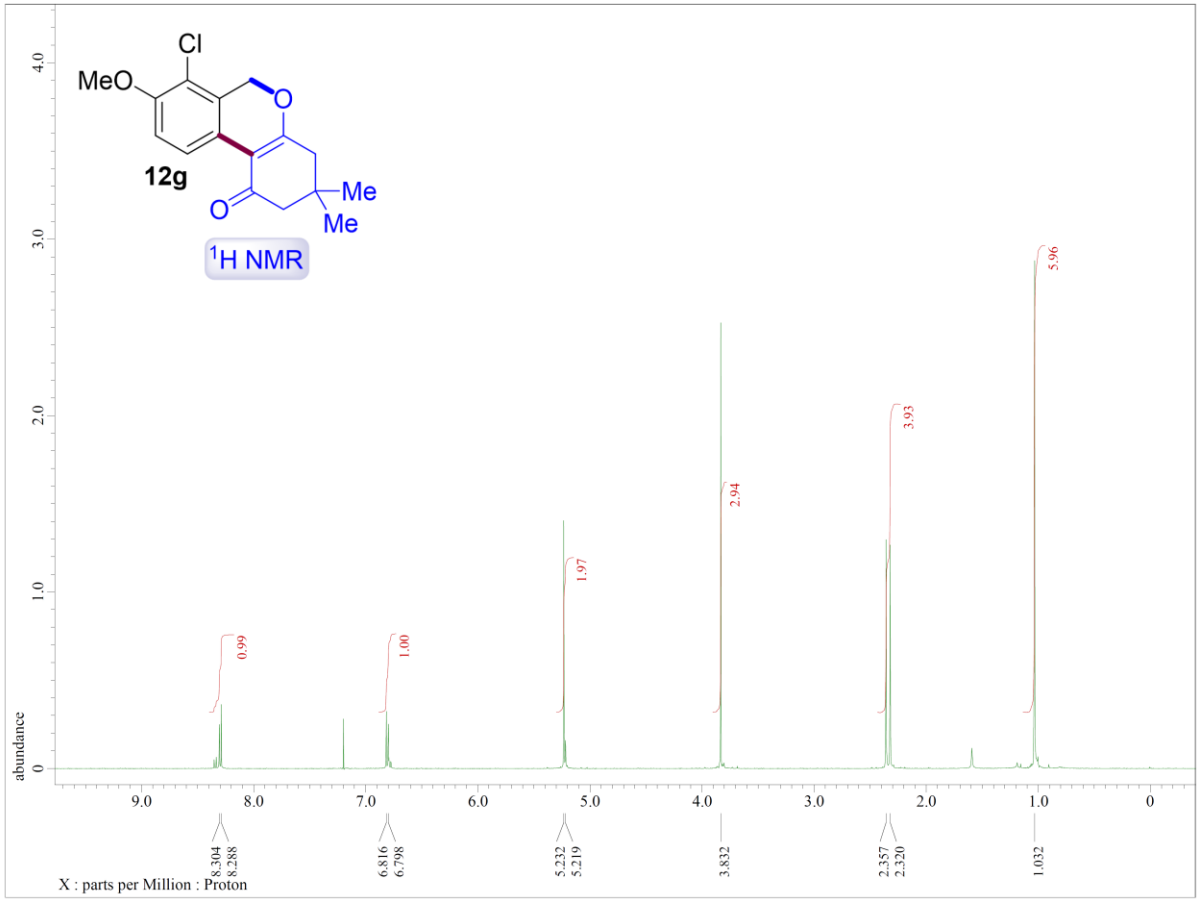

12d
13C NMR
(thousandths)
201.029
185.384
128.604
127.590
126.276
125.119
123.522
121.806
114.010
77.253
77.000
76.734
71.785
34.149
25.821
X : parts per Million : Carbon13

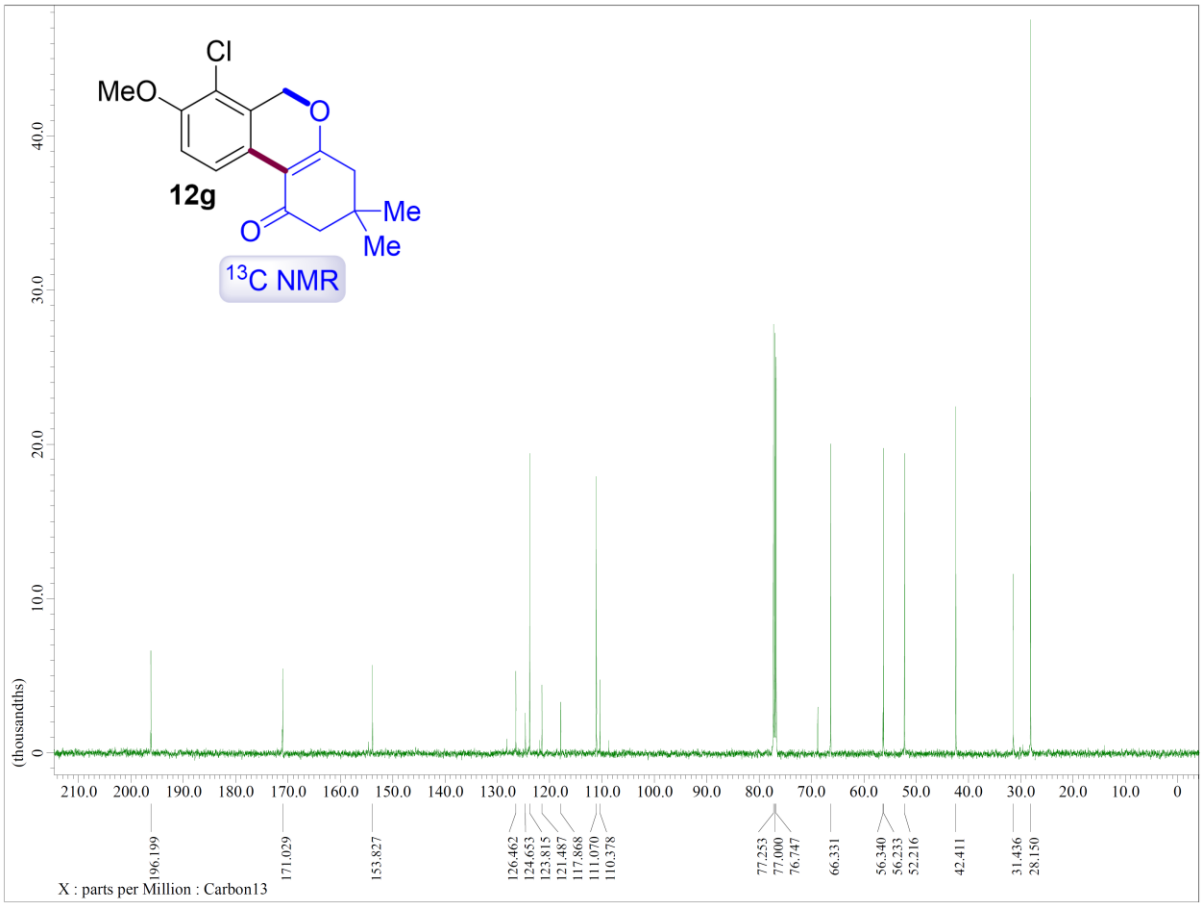

MeO
O
12e
O
1H NMR
abundance
1.03
1.20
1.00
2.08
3.28
4.40
2.41
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
8.275
8.258
6.862
6.859
6.845
6.839
6.574
5.089
3.800
2.563
2.549
2.538
2.525
2.511
2.006
1.994
1.981
X : parts per Million : Proton

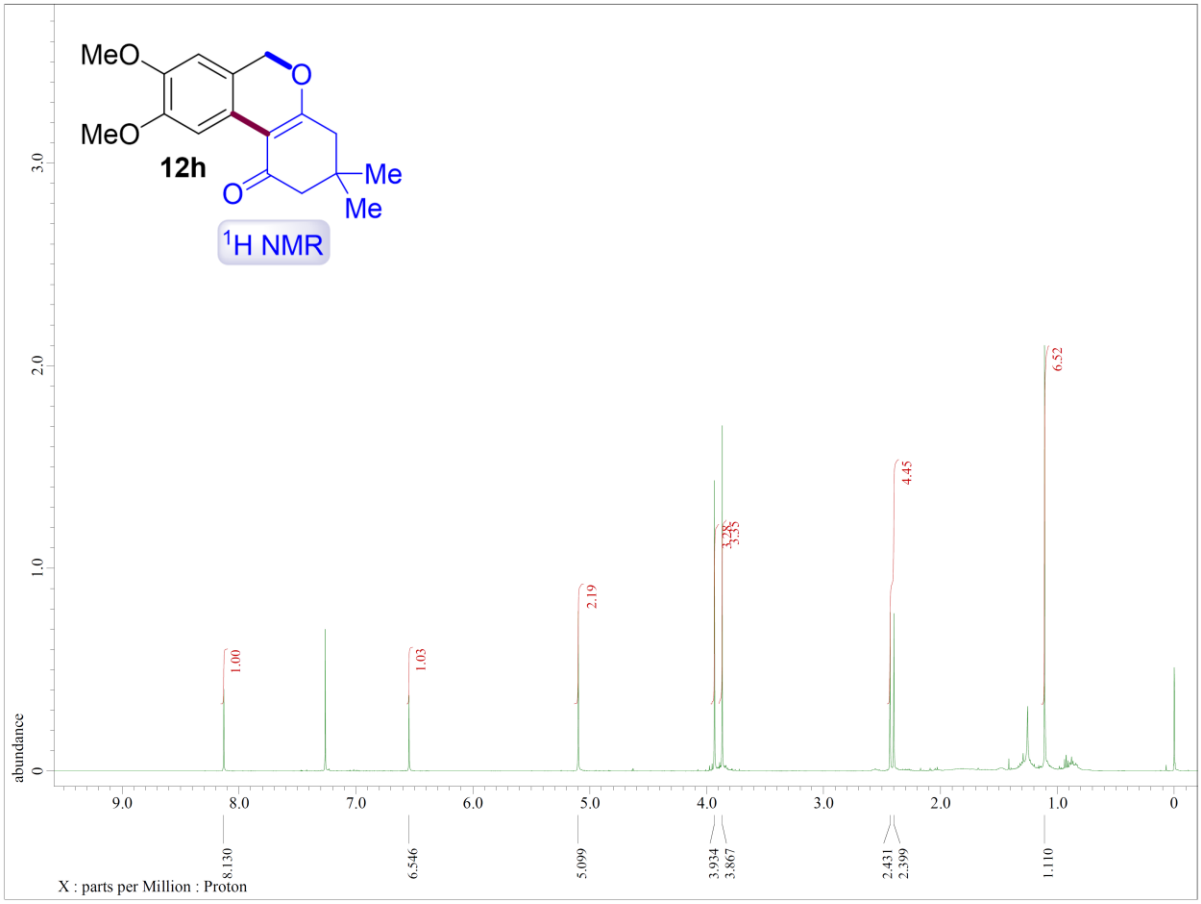

MeO
O
12e
O
13C NMR
(thousandths)
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
196.523
172.382
158.541
128.660
126.299
120.472
113.081
109.760
77.250
77.000
76.741
69.331
55.317
38.250
28.728
20.147
X : parts per Million : Carbon13

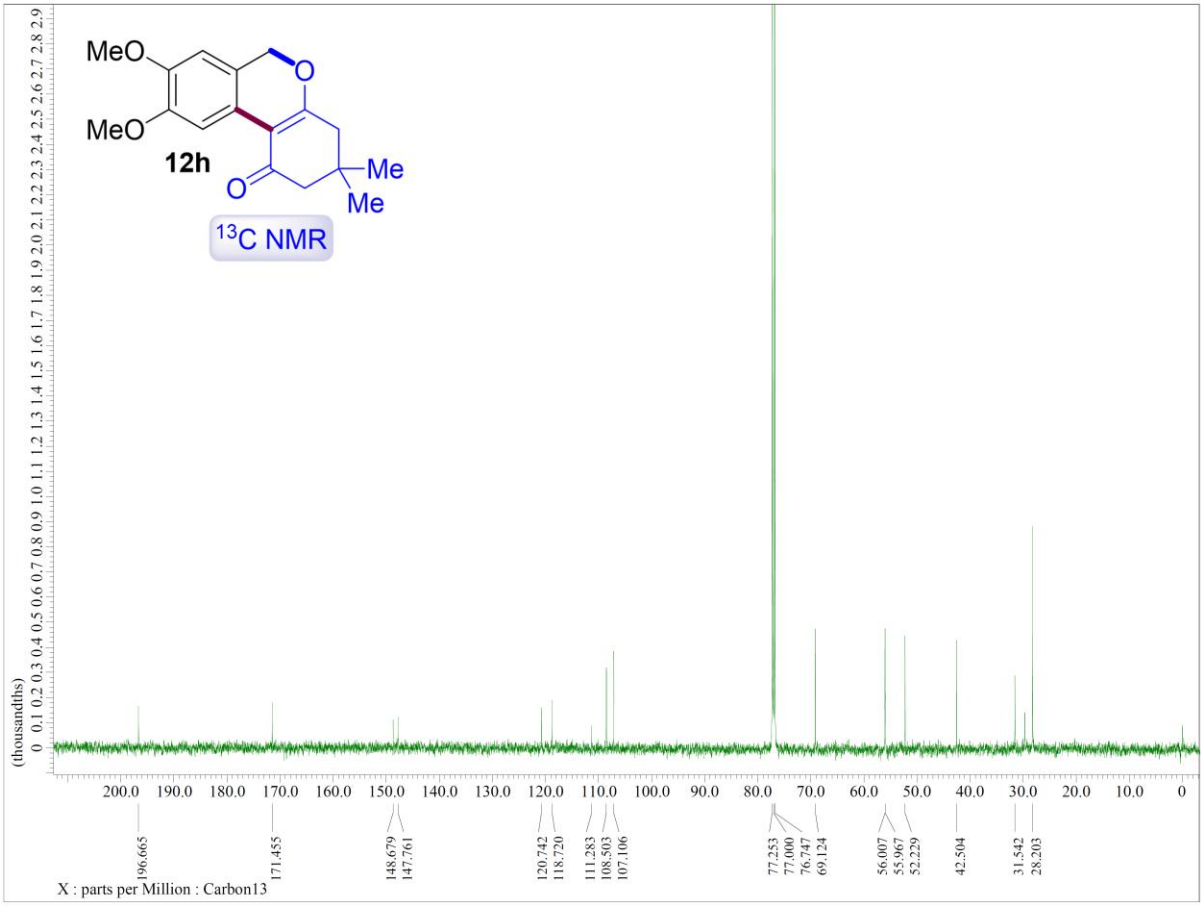

MeO
O
12f
O
Me
Me
1H NMR
abundance
0.89
1.00
0.84
2.02
3.08
4.82
6.66
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
8.286
8.268
6.790
6.786
6.772
6.768
6.506
6.502
5.025
3.729
2.347
2.319
2.101
1.028
X : parts per Million : Proton

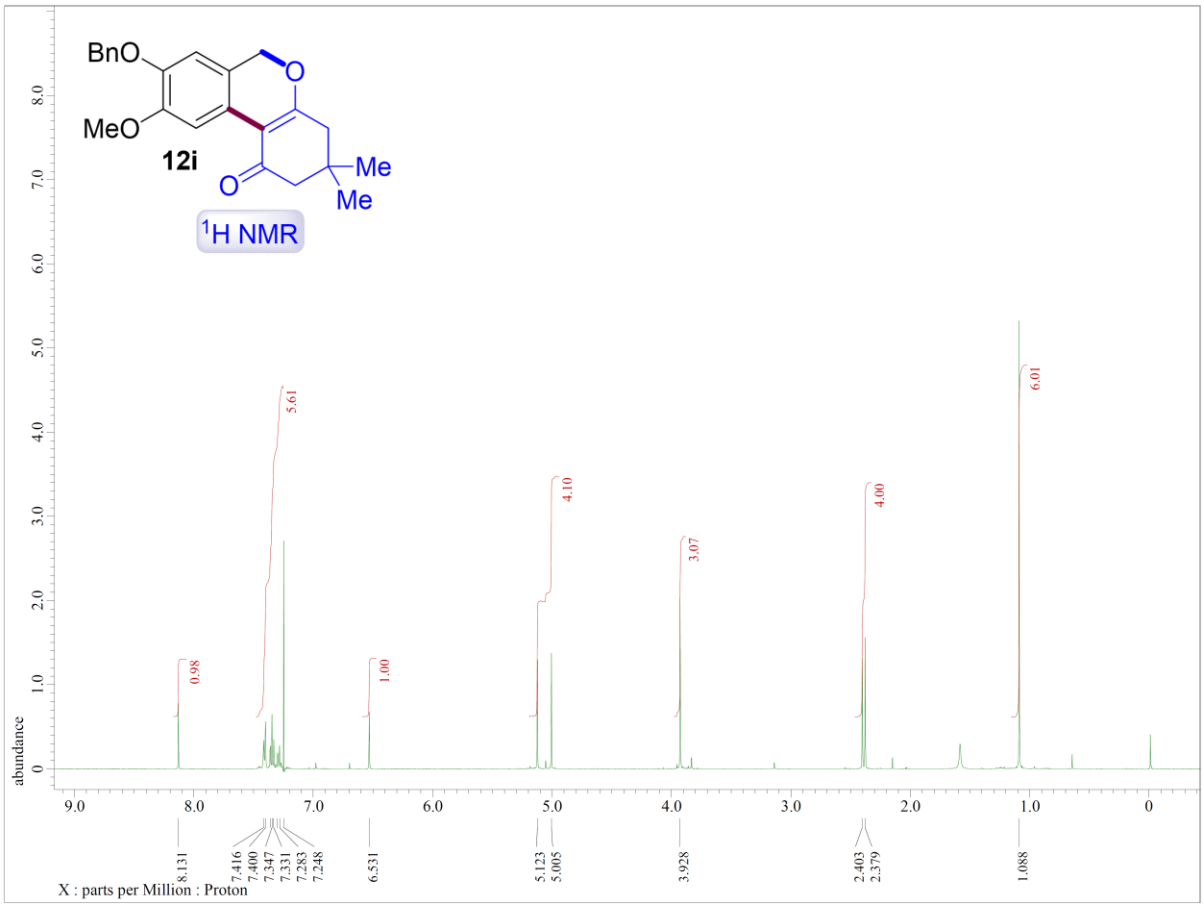

MeO
O
12f
O
Me
Me
13C NMR
(thousandths)
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
196.478
170.829
158.524
129.482
128.471
126.037
120.383
113.039
109.780
77.253
77.000
76.734
69.271
55.315
52.136
42.398
31.489
28.190
X : parts per Million : Carbon13

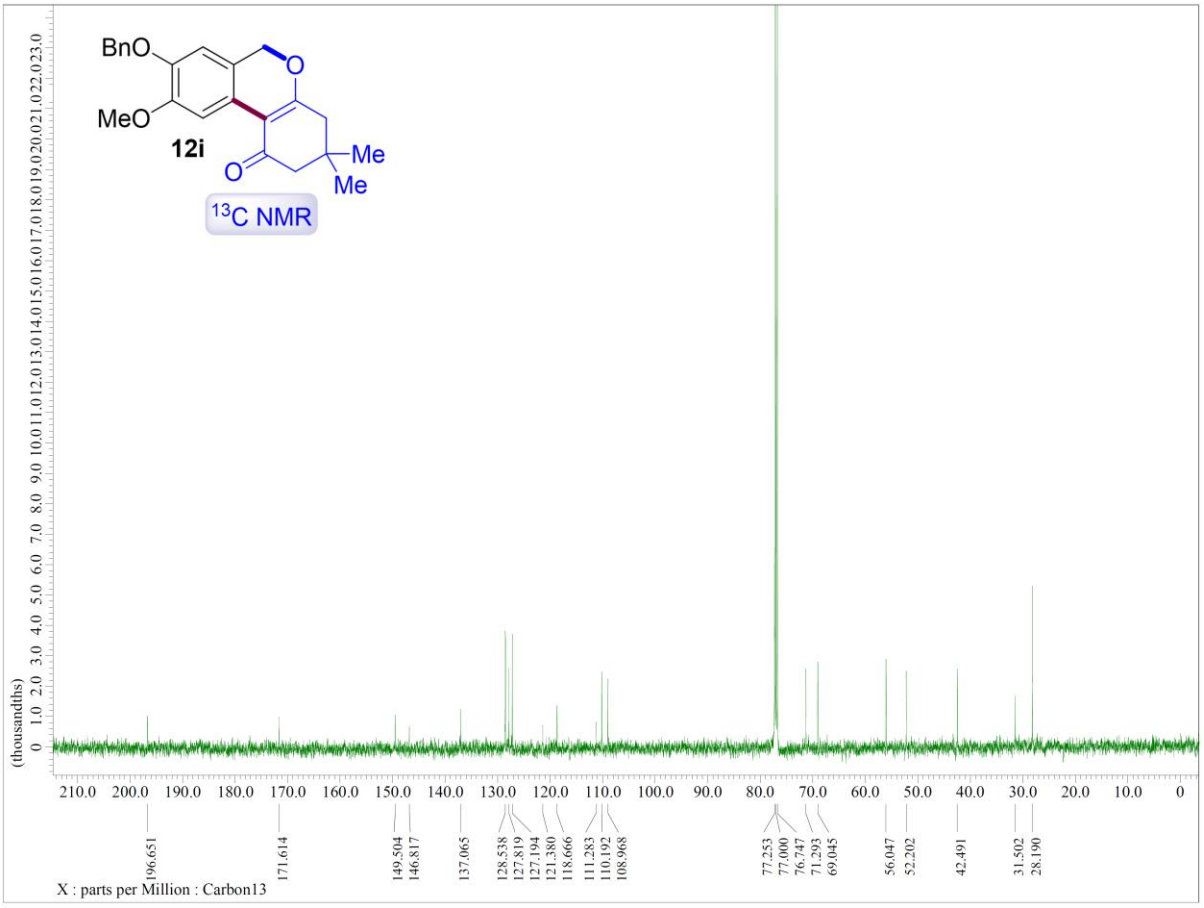

Cl
MeO
O
12g
O
Me
Me
1H NMR
abundance
4.0
3.0
2.0
1.0
0
0.99
1.00
1.97
2.94
3.93
5.96
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
8.304
8.288
6.816
6.798
5.232
5.219
3.832
2.357
2.320
1.032
X : parts per Million : Proton

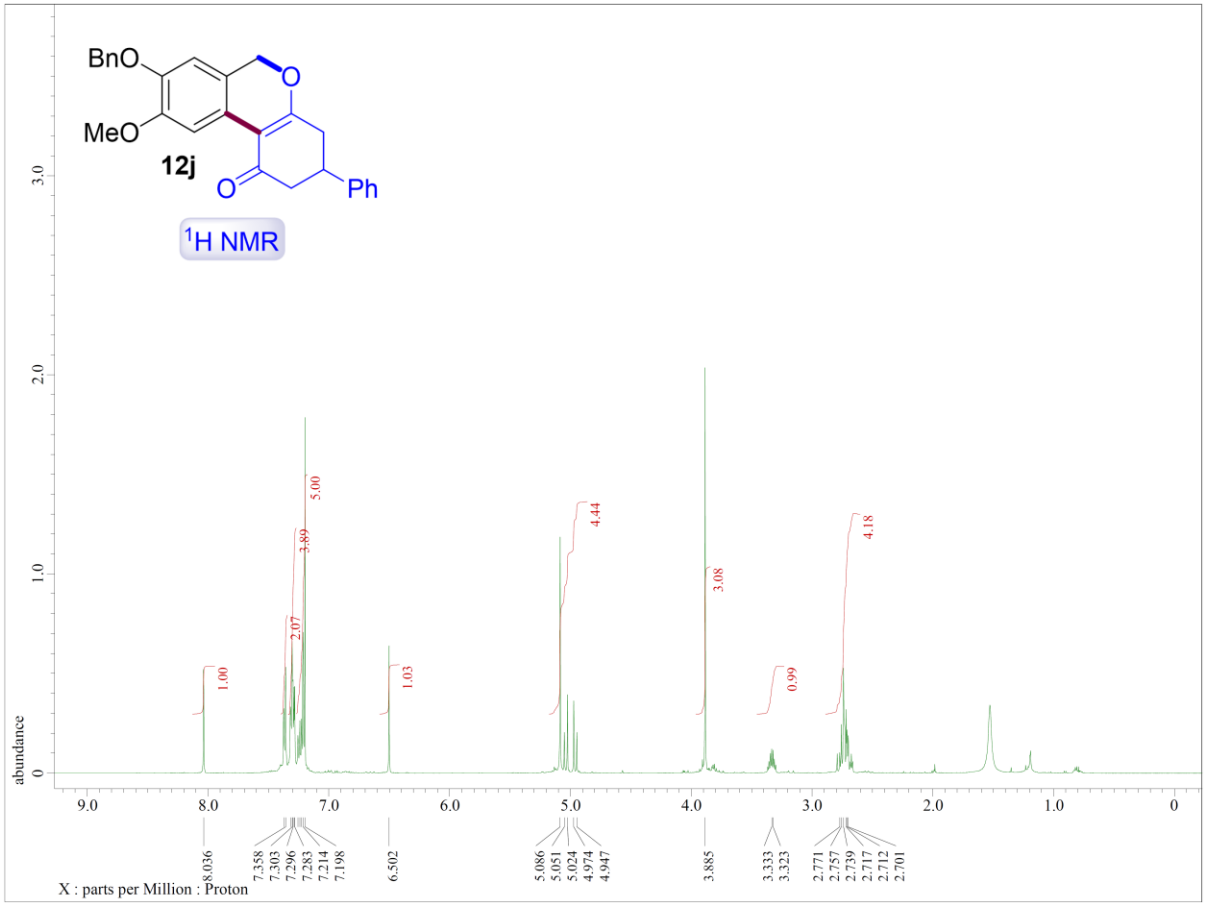

Cl
MeO
O
12g
O
Me
Me
13C NMR
(thousandths)
40.0
30.0
20.0
10.0
0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
196.199
171.029
153.827
126.462
124.653
123.815
121.487
117.868
111.070
110.378
77.253
77.000
76.747
66.331
56.340
56.233
52.216
42.411
31.436
28.150
X : parts per Million : Carbon13

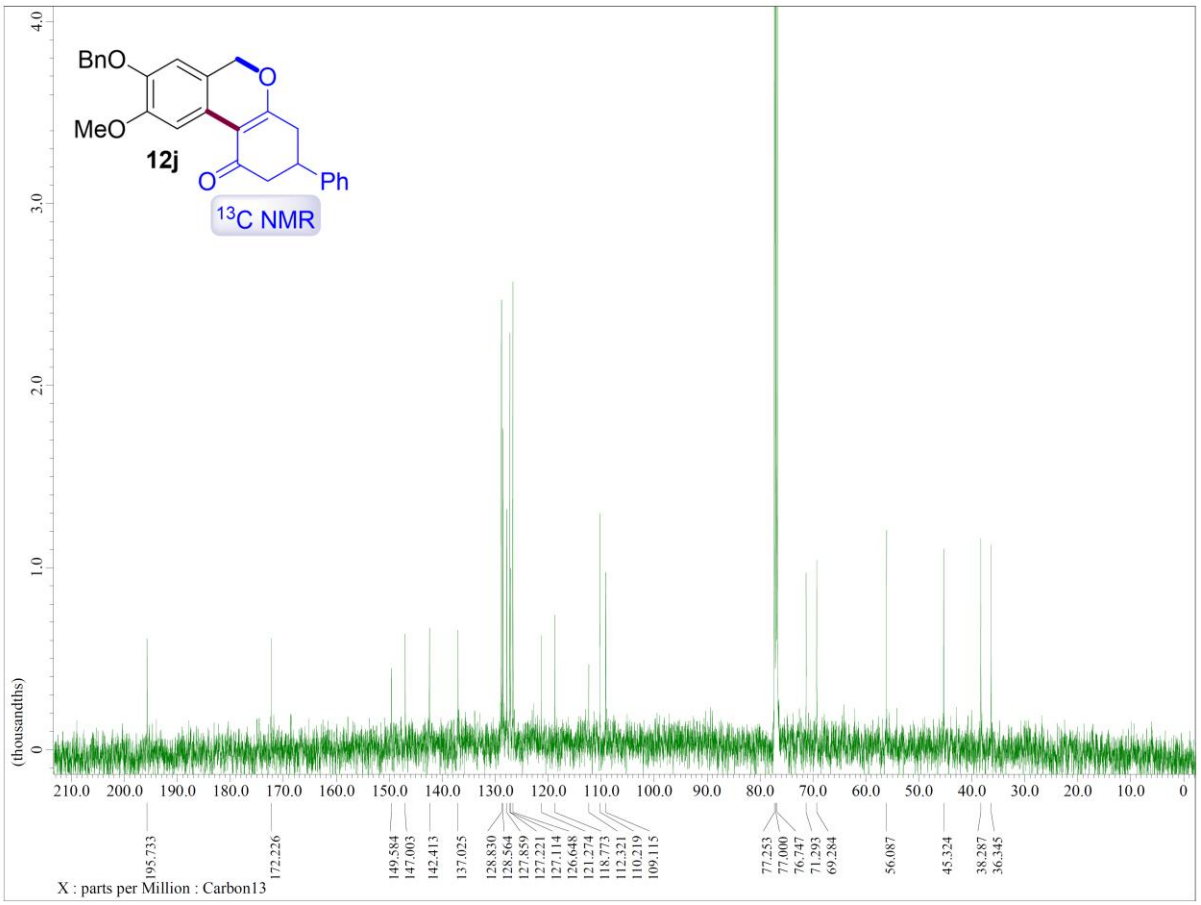

MeO
MeO
O
12h
O
Me
Me
1H NMR
abundance
X : parts per Million : Proton

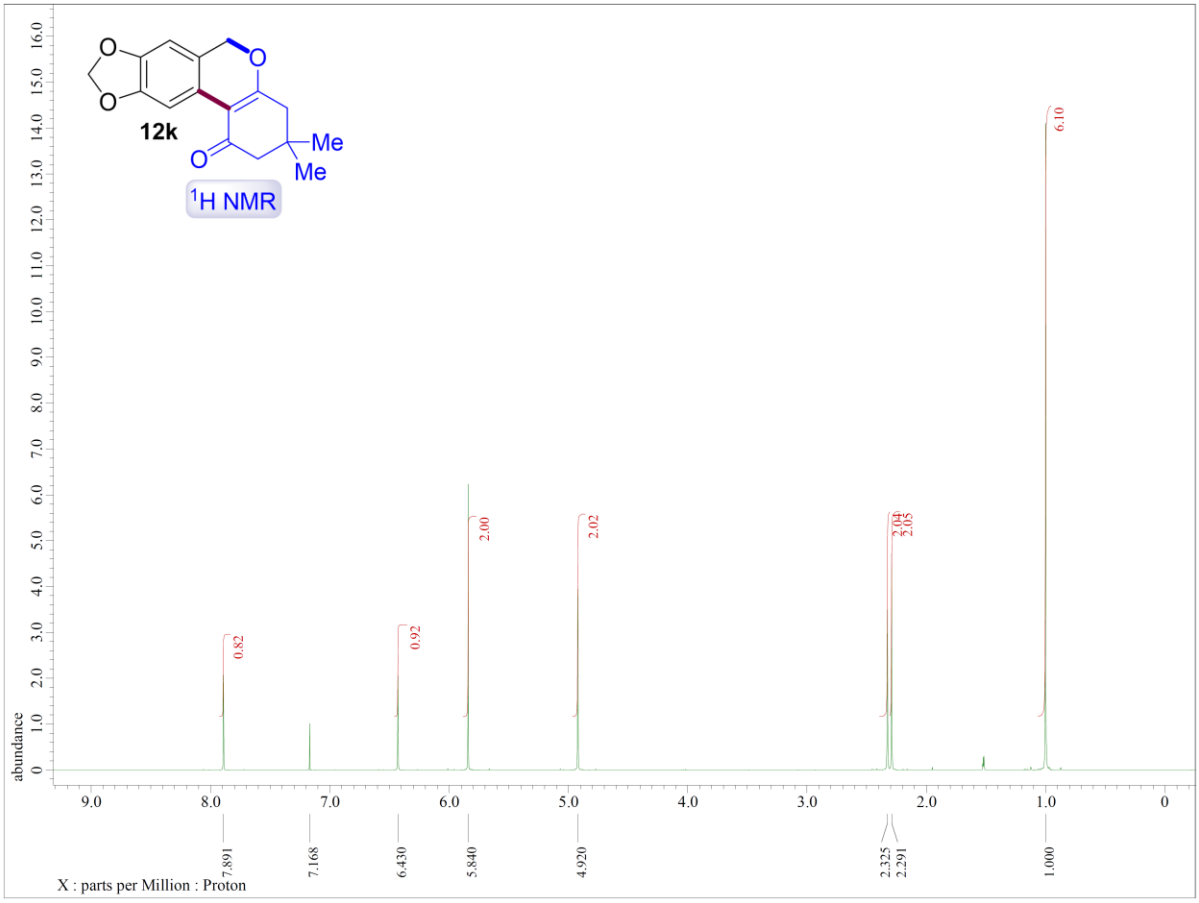

MeO
MeO
O
12h
O
Me
Me
13C NMR
(thousandths)
X : parts per Million : Carbon13

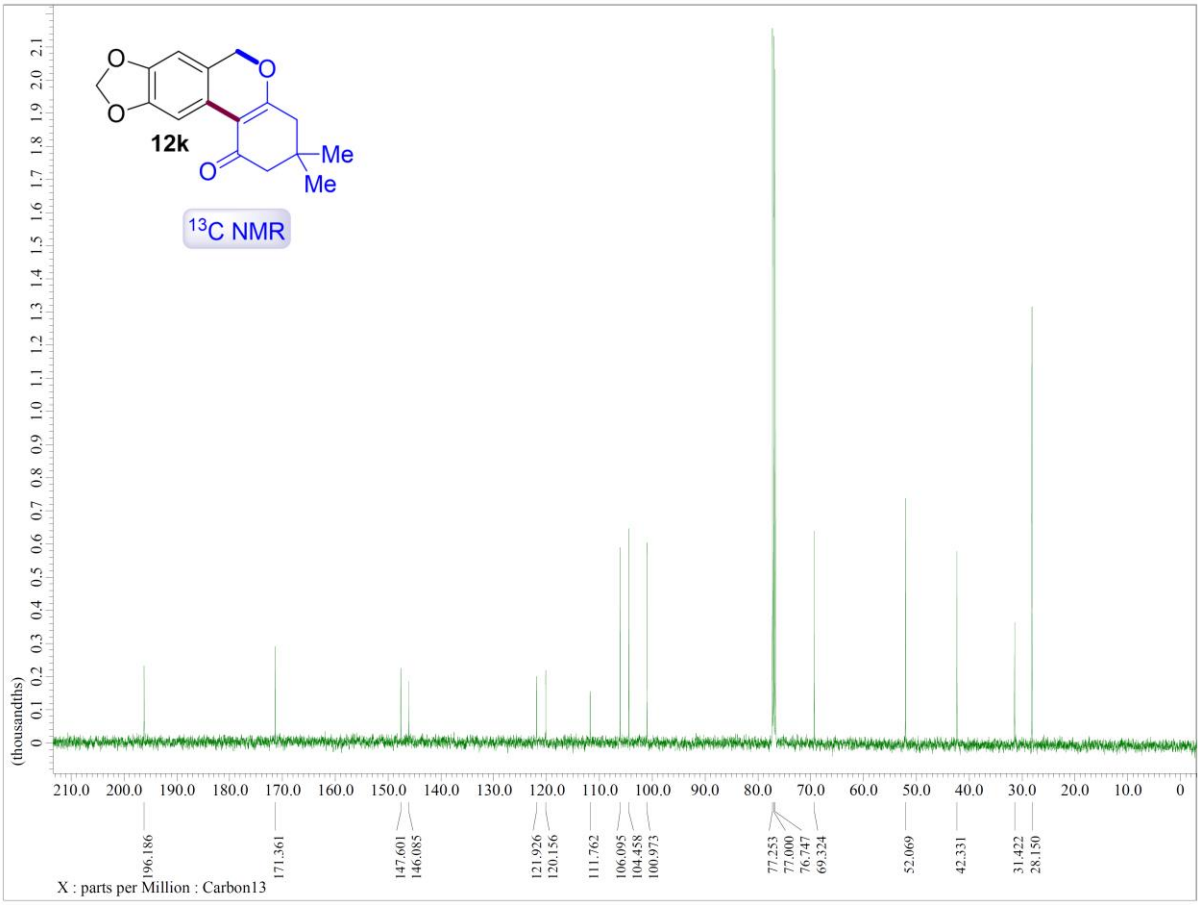

BnO
MeO
12i
O
Me
Me
O
1H NMR
abundance
0.98
5.61
1.00
4.10
3.07
4.00
6.01
X : parts per Million : Proton
8.131
7.416
7.400
7.347
7.331
7.283
7.248
6.531
5.123
5.005
3.928
2.403
2.379
1.088

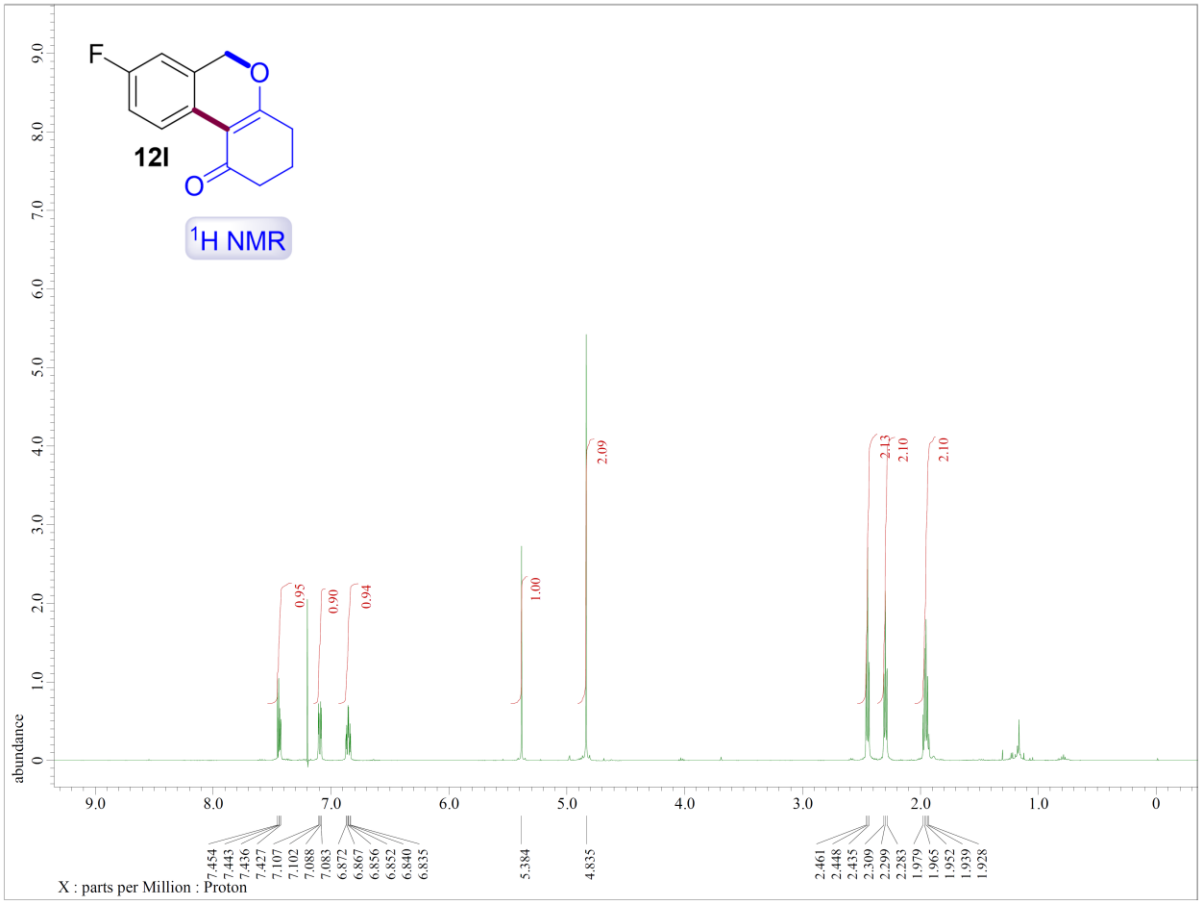

BnO
MeO
12i
O
Me
Me
O
13C NMR
(thousandths)
X : parts per Million : Carbon13
196.651
171.614
149.504
146.817
137.065
128.538
127.819
127.194
121.380
118.666
111.283
110.192
108.968
77.253
77.000
76.747
71.293
69.045
56.047
52.202
42.491
31.502
28.190

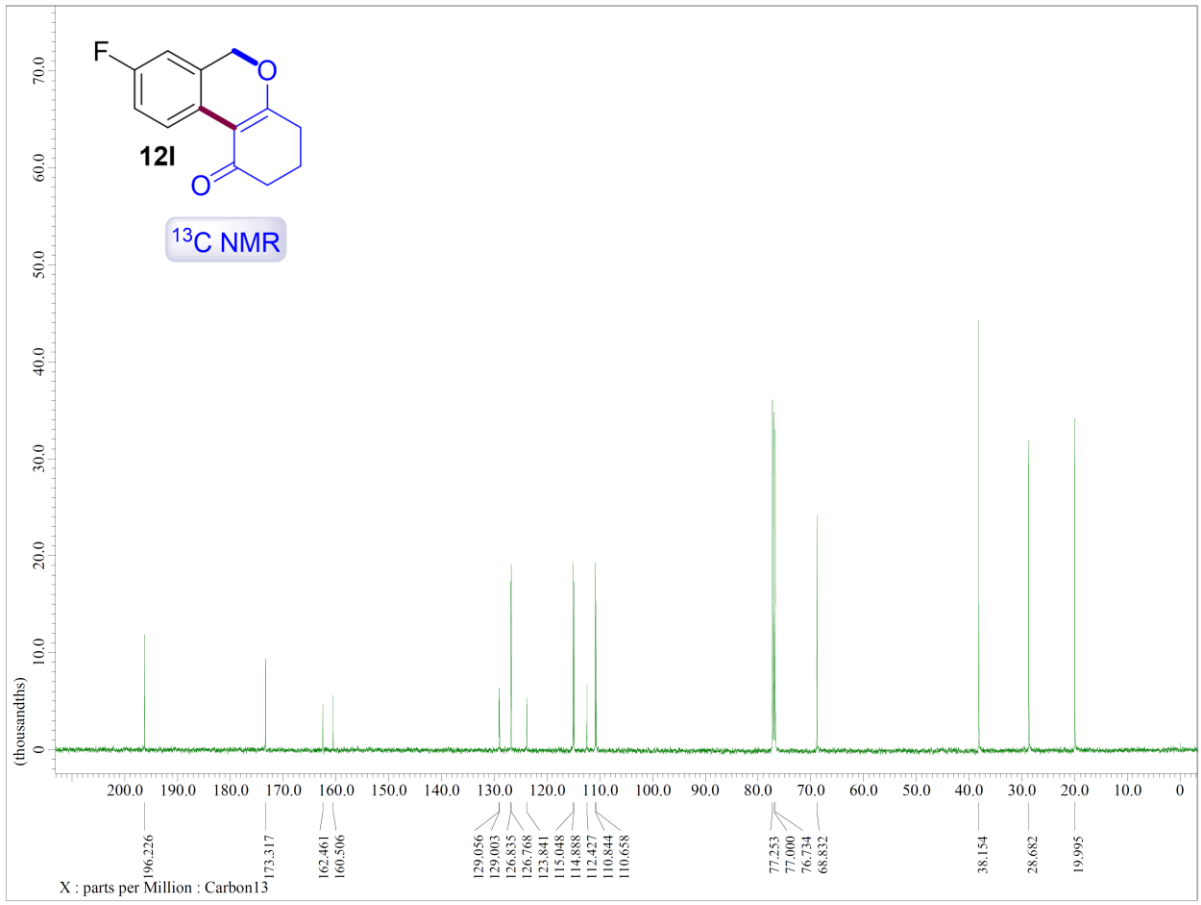

BnO
MeO
12j
O
O
Ph
1H NMR
abundance
X : parts per Million : Proton

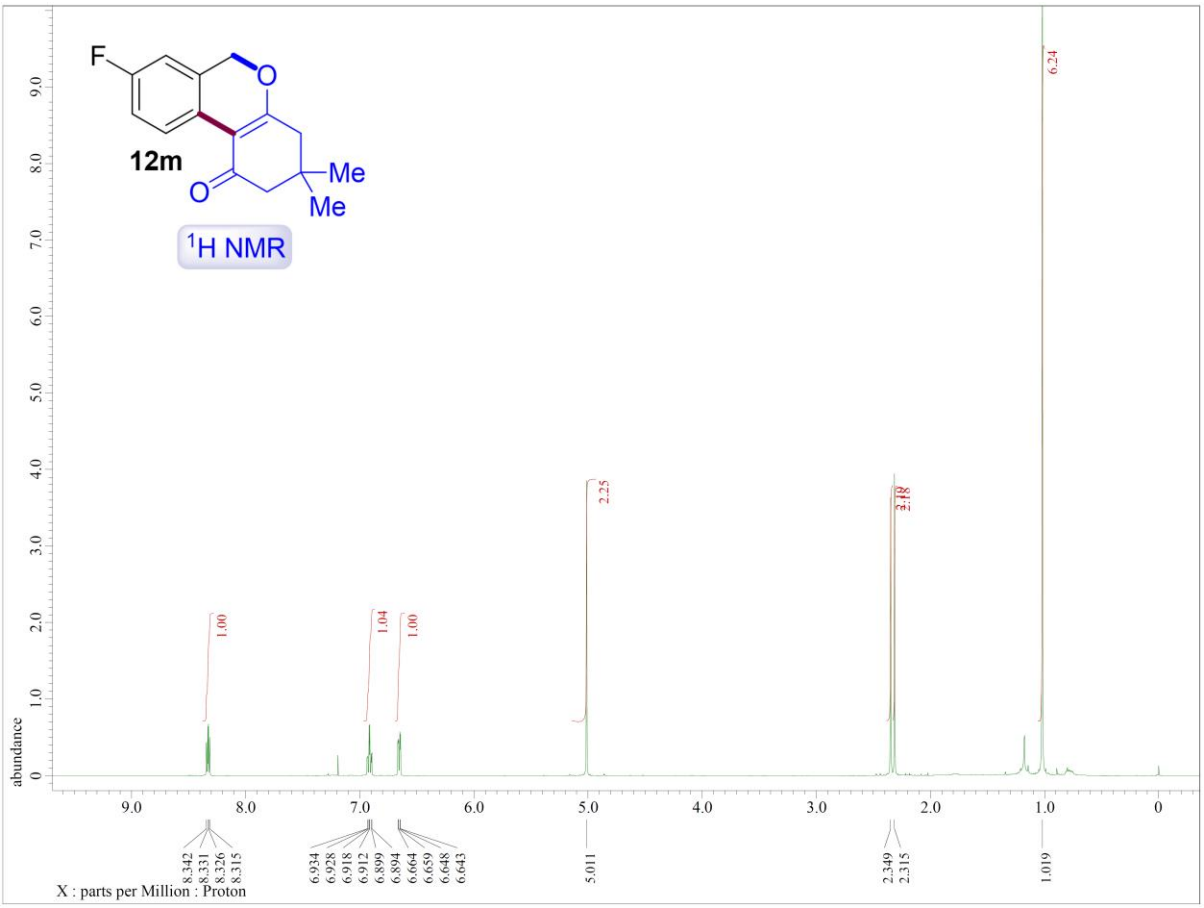

BnO
MeO
12j
O
O
Ph
13C NMR
(thousandths)
X : parts per Million : Carbon13

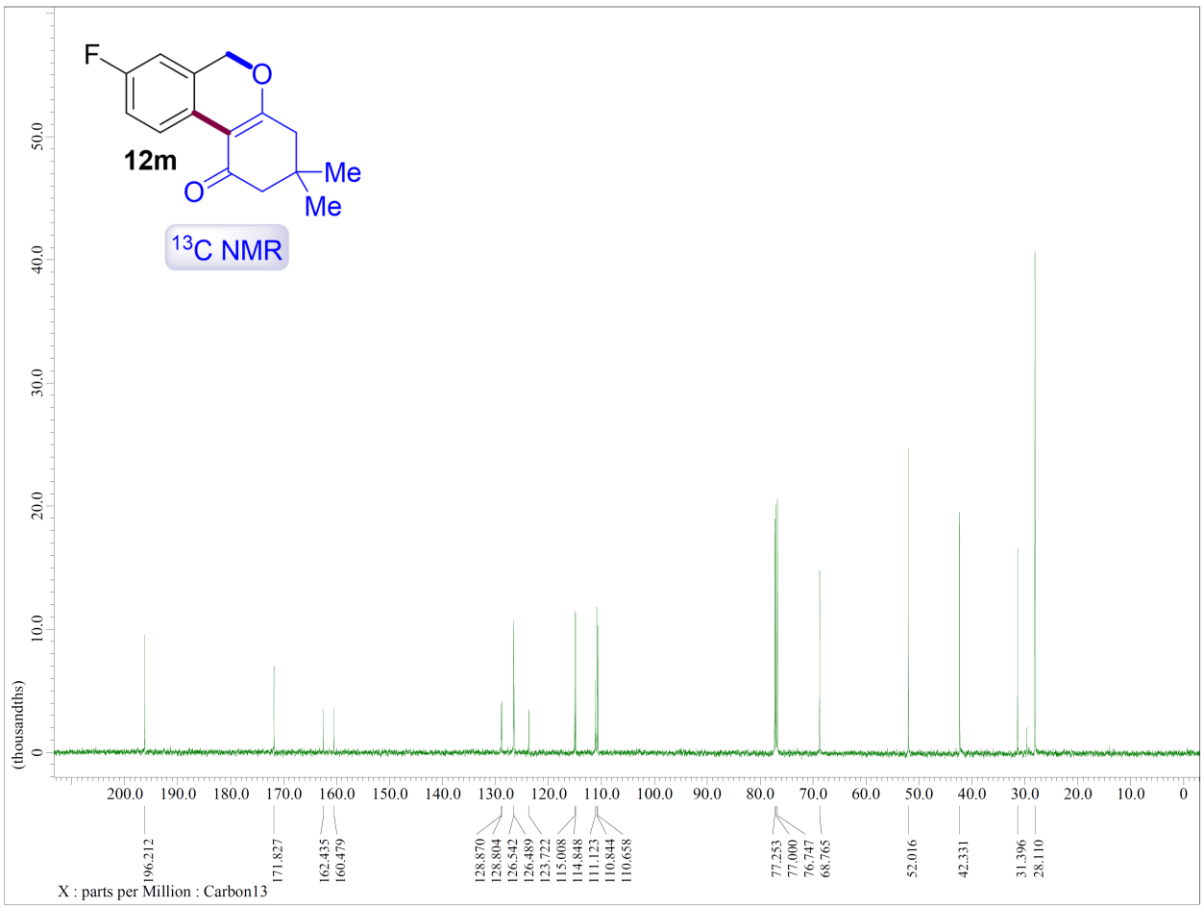

12k
Me
Me
1H NMR
abundance
0.82
0.92
2.00
2.02
2.03
6.10
X : parts per Million : Proton
7.891
7.168
6.430
5.840
4.920
2.325
2.291
1.000

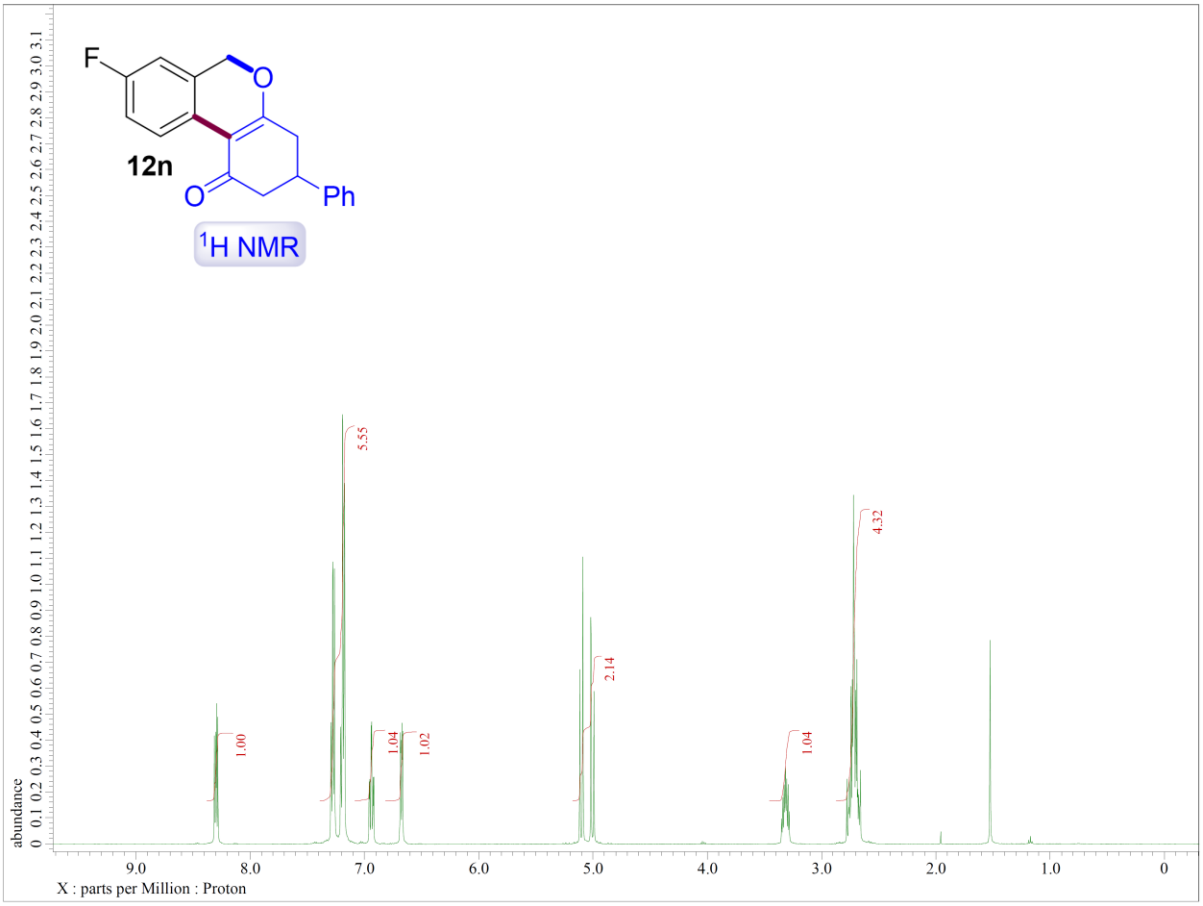

12k
Me
Me
13C NMR
(thousandths)
X : parts per Million : Carbon13
196.186
171.361
147.601
146.085
121.926
120.156
111.762
106.095
104.458
100.973
77.253
77.000
76.747
69.324
52.069
42.331
31.422
28.150

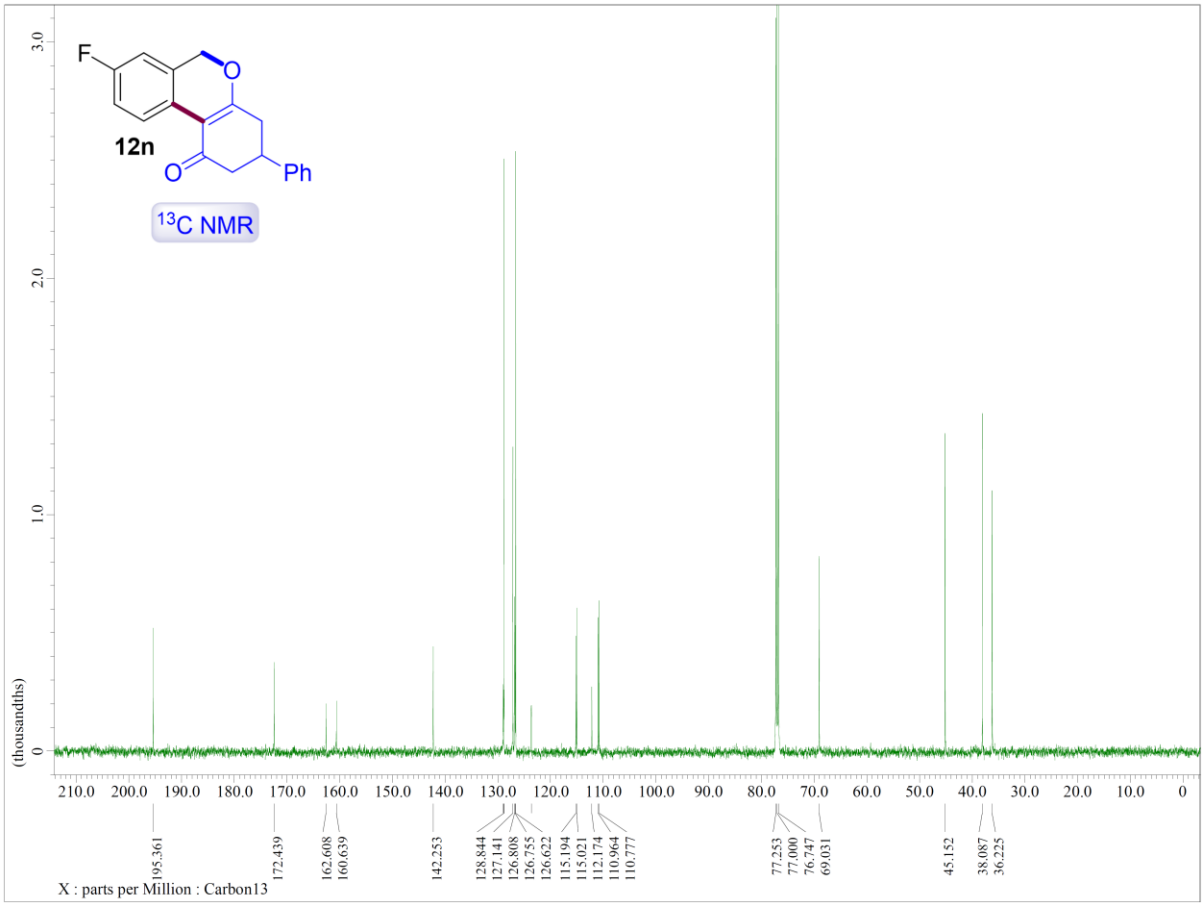

F
O
O
12l
1H NMR
abundance
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
0.95
0.90
0.94
1.00
2.09
2.13
2.10
2.10
7.454
7.443
7.436
7.427
7.107
7.102
7.088
7.083
6.872
6.867
6.856
6.852
6.840
6.835
5.384
4.835
2.461
2.448
2.435
2.309
2.299
2.283
1.979
1.965
1.952
1.939
1.928
X : parts per Million : Proton

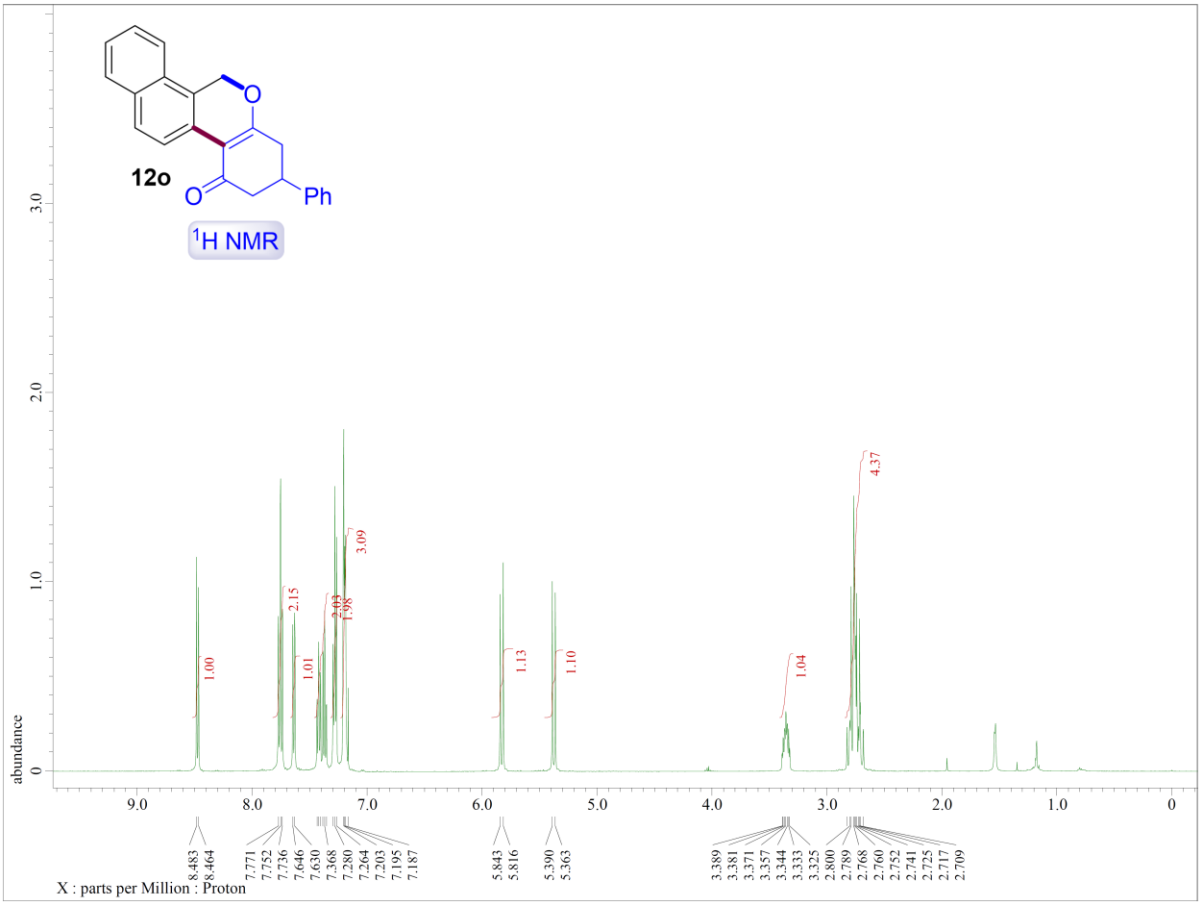

F
O
O
12l
13C NMR
(thousandths)
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
196.226
173.317
162.461
160.506
129.056
129.003
126.835
126.768
123.841
115.048
114.888
112.427
110.844
110.658
77.253
77.000
76.734
68.832
38.154
28.682
19.995
X : parts per Million : Carbon13

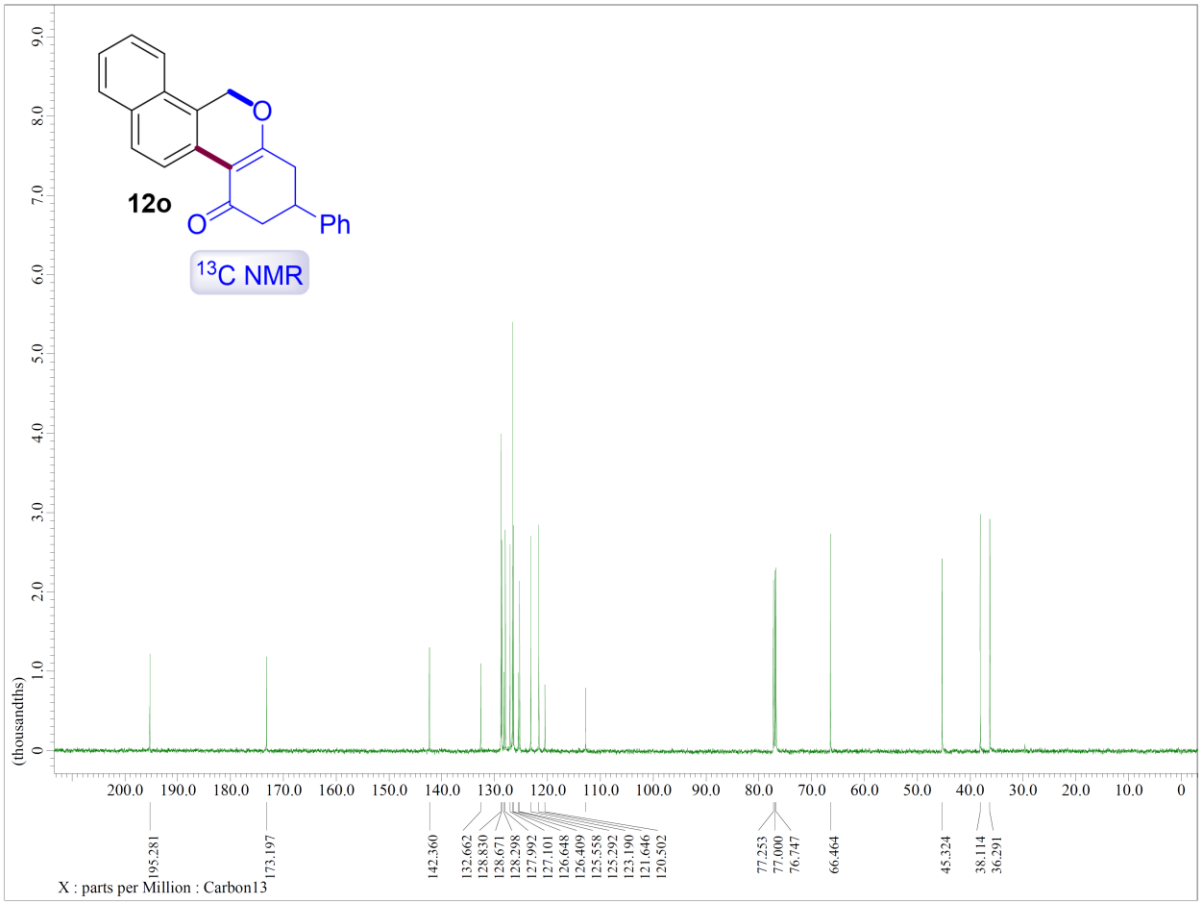

F
O
12m
O
Me
Me
1H NMR
abundance
X : parts per Million : Proton
6.24
2.25
1.00
1.04
1.00
8.342
8.331
8.326
8.315
6.934
6.928
6.918
6.912
6.899
6.894
6.664
6.659
6.648
6.643
5.011
2.349
2.315
1.019

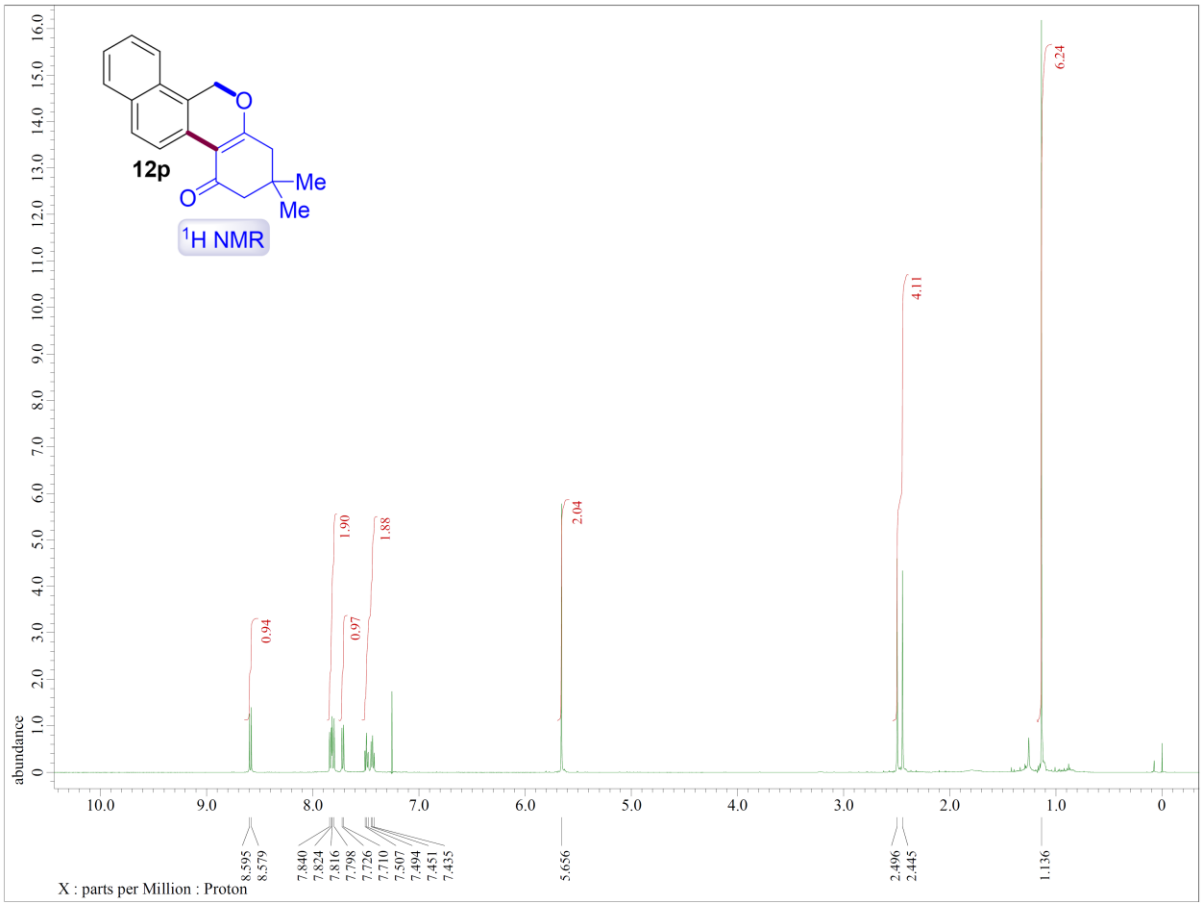

F
O
12m
O
Me
Me
13C NMR
(thousandths)
X : parts per Million : Carbon13
196.212
171.827
162.435
160.479
128.870
128.804
126.542
126.489
123.722
115.008
114.848
111.123
110.844
110.658
77.253
77.000
76.747
68.765
52.016
42.331
31.396
28.110

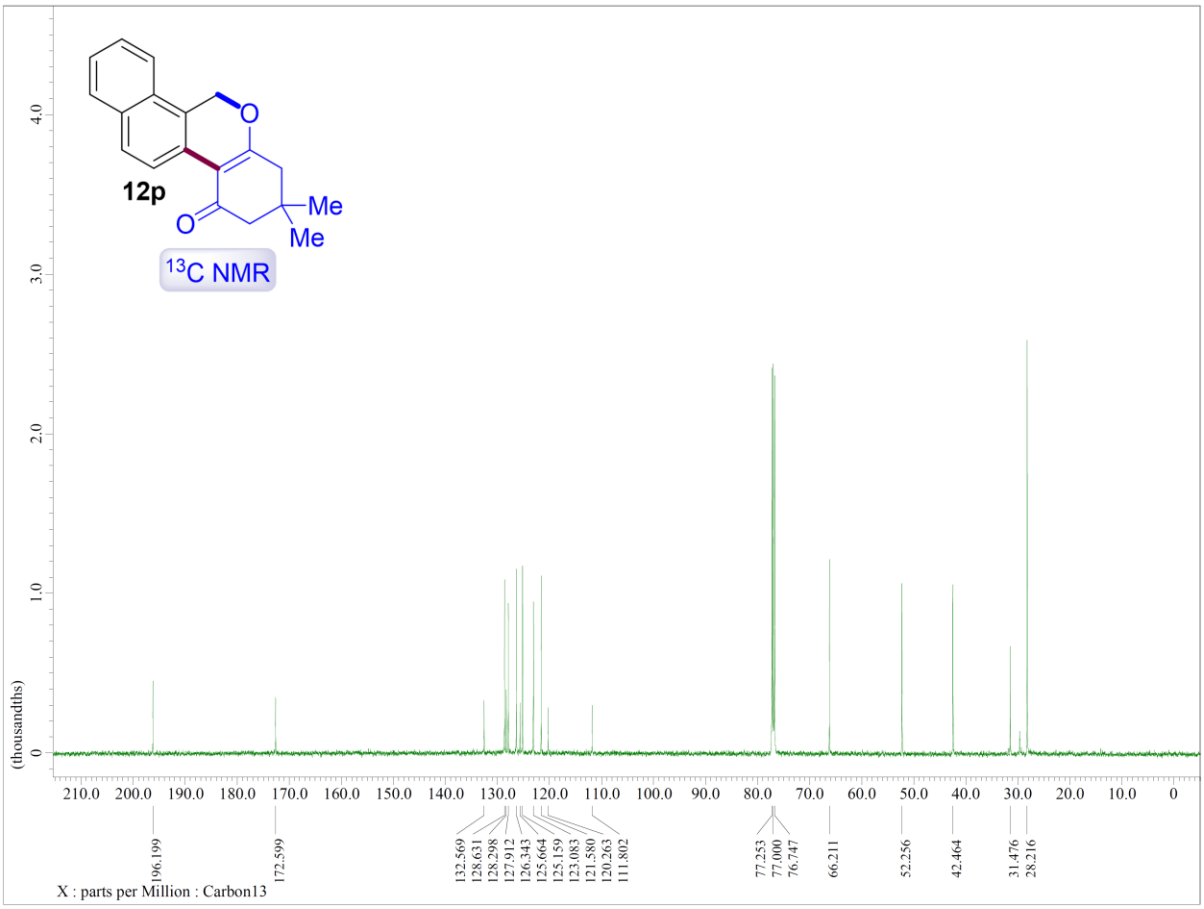

F
O
12n
O
Ph
1H NMR
abundance
X : parts per Million : Proton
1.00
5.55
1.04
1.02
2.14
1.04
4.32

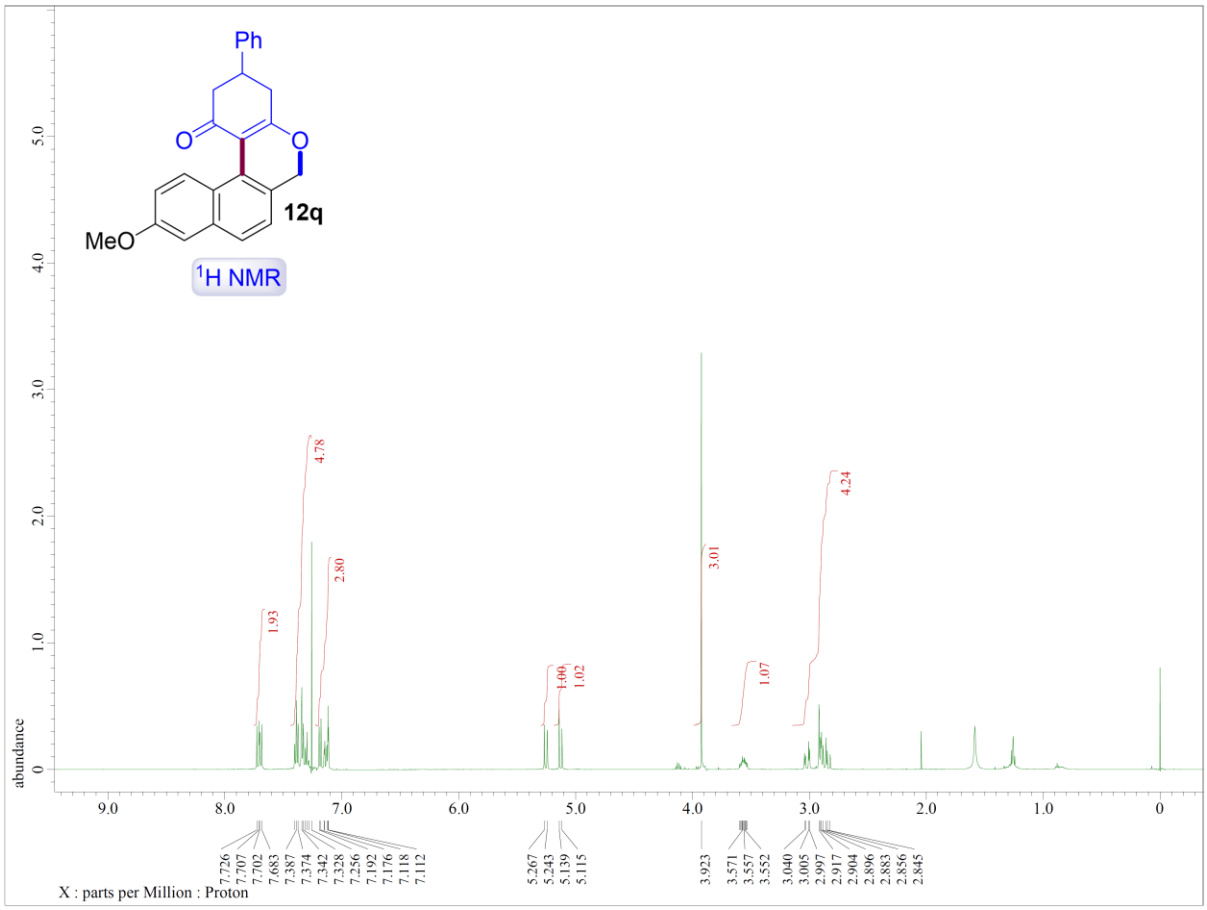

F
O
12n
O
Ph
13C NMR
(thousandths)
X : parts per Million : Carbon13
195.361
172.439
162.608
160.639
142.253
128.844
127.141
126.808
126.755
126.622
115.194
115.021
112.174
110.964
110.777
77.253
77.000
76.747
69.031
45.152
38.087
36.225

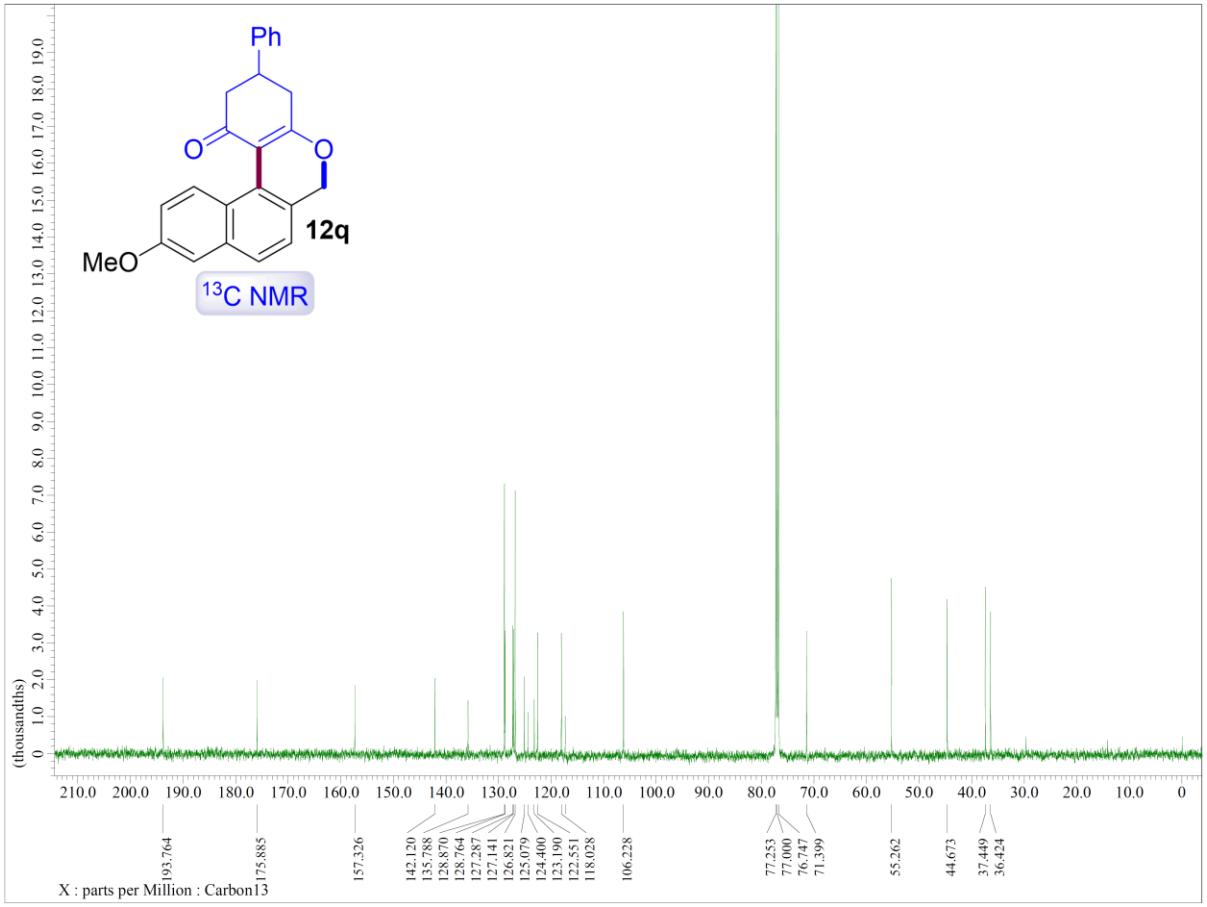

12o
Ph
O
O
^{1}H NMR
abundance
X : parts per Million : Proton

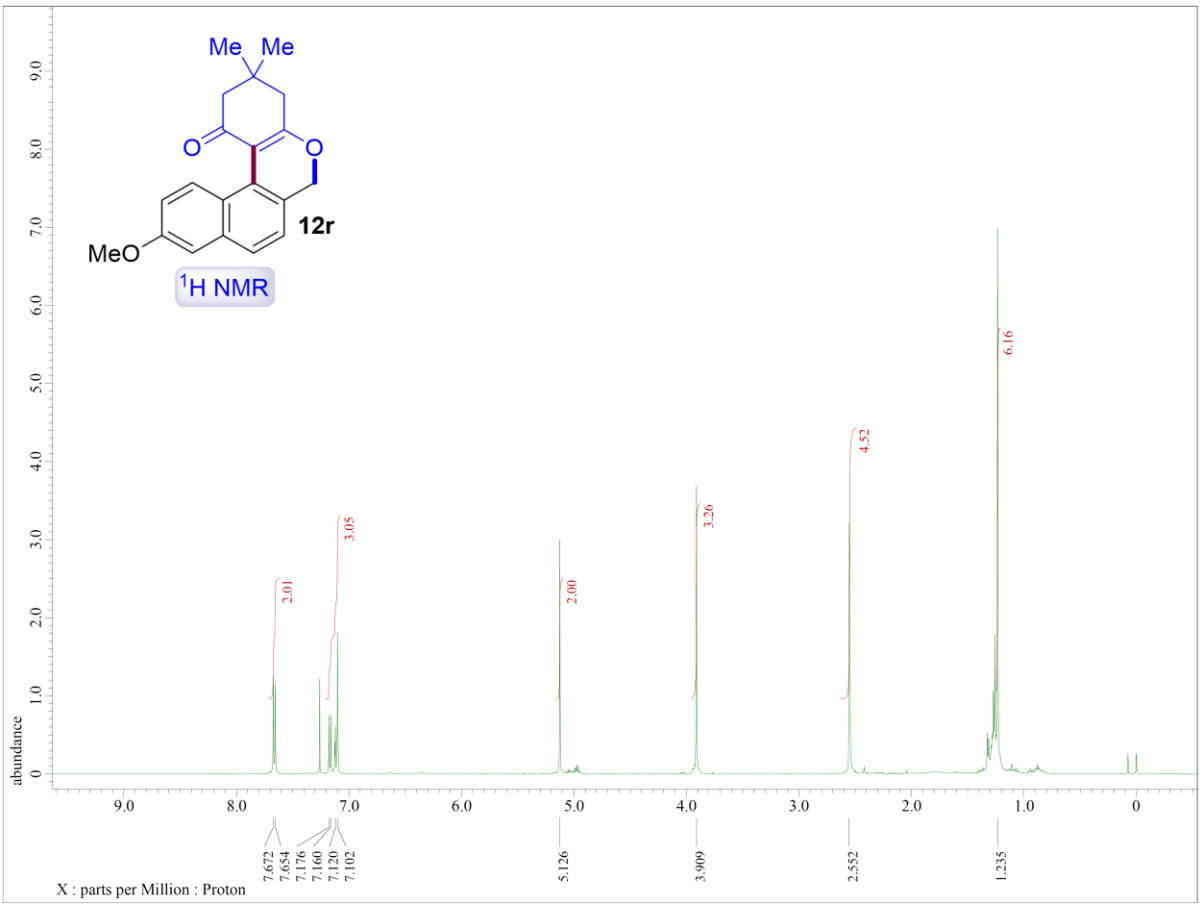

12o
Ph
O
O
^{13}C NMR
(thousandths)
X : parts per Million : Carbon13

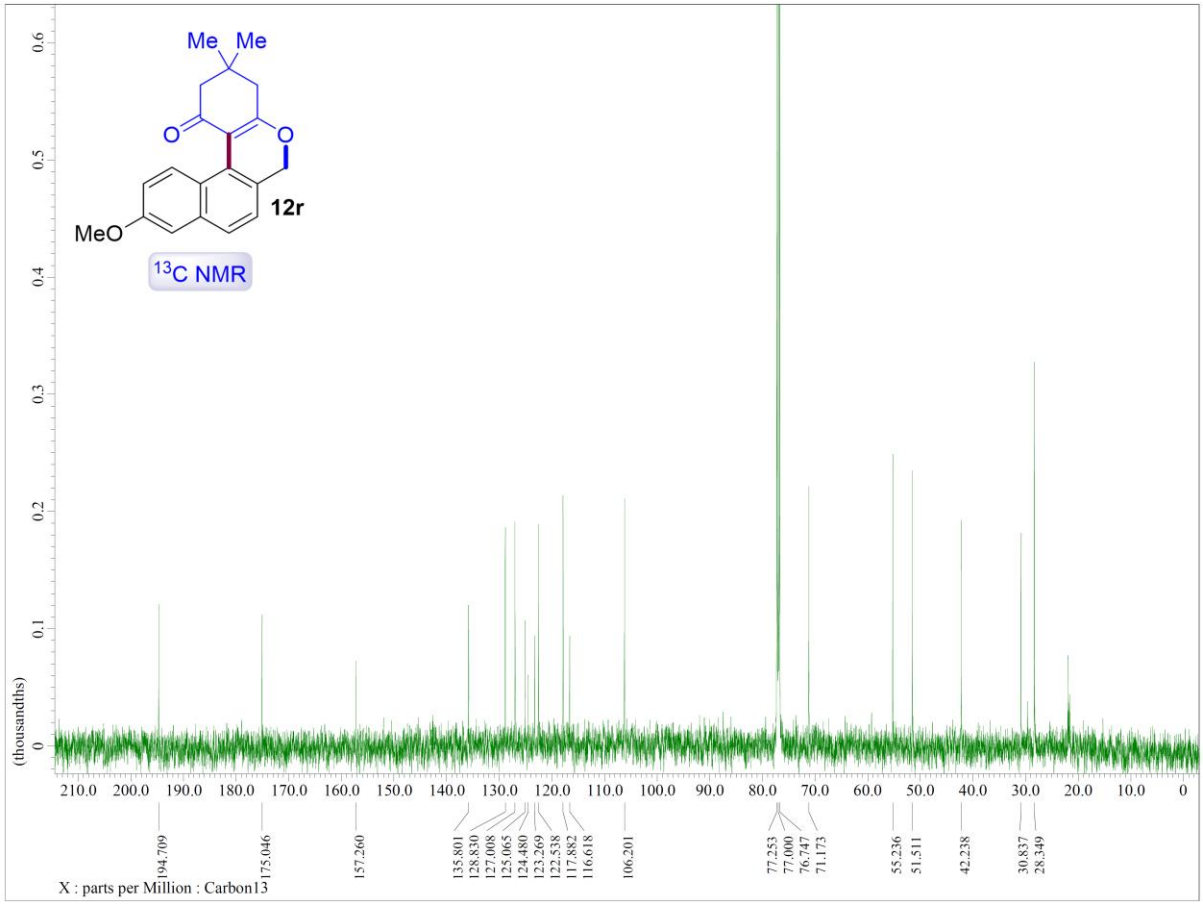

12p
Me
Me
O
O
1H NMR
abundance
X : parts per Million : Proton
6.24
4.11
2.04
1.90
1.88
0.97
0.94
8.595
8.579
7.840
7.824
7.816
7.798
7.726
7.710
7.507
7.494
7.451
7.435
5.656
2.496
2.445
1.136

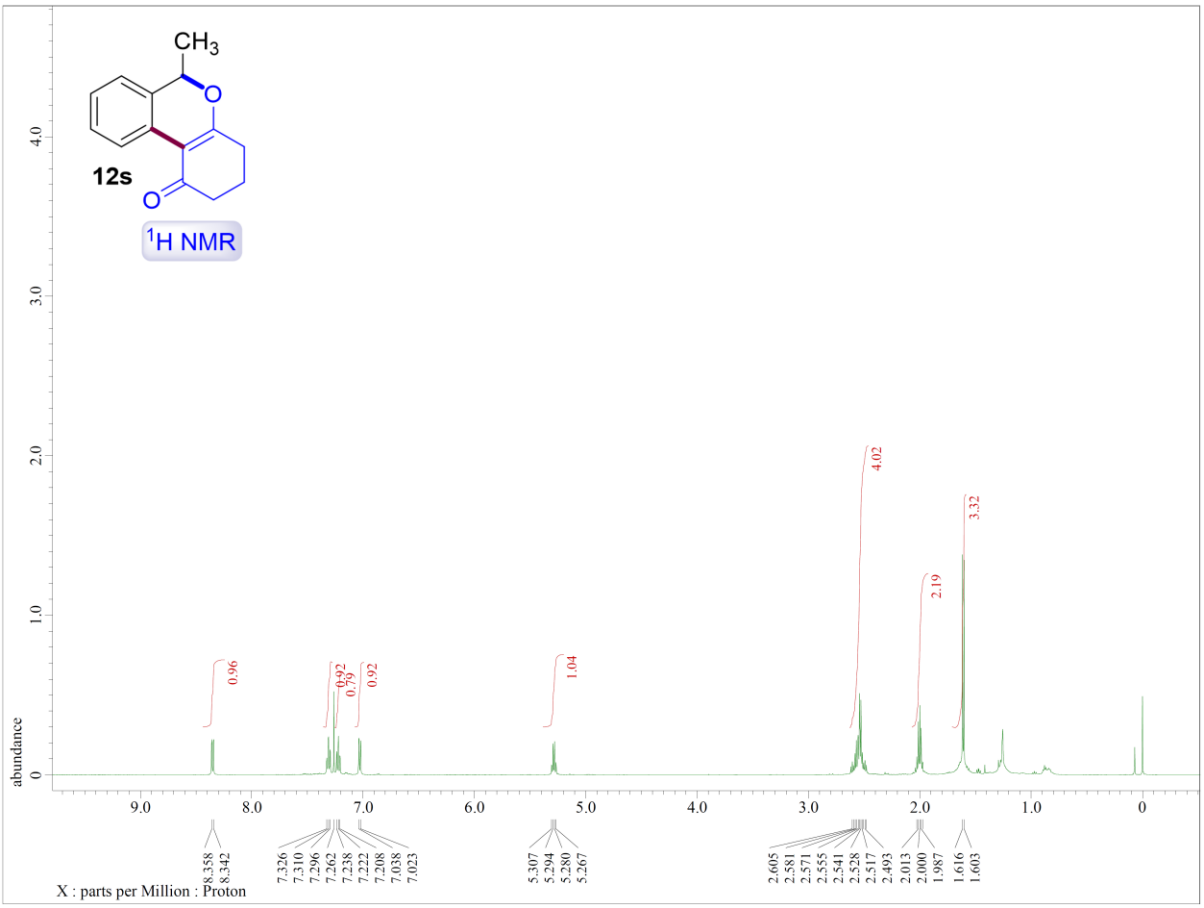

12p
Me
Me
O
O
13C NMR
(thousandths)
X : parts per Million : Carbon13
196.199
172.599
132.569
128.631
128.298
127.912
126.343
125.664
125.159
123.083
121.580
120.263
111.802
77.253
77.000
76.747
66.211
52.256
42.464
31.476
28.216

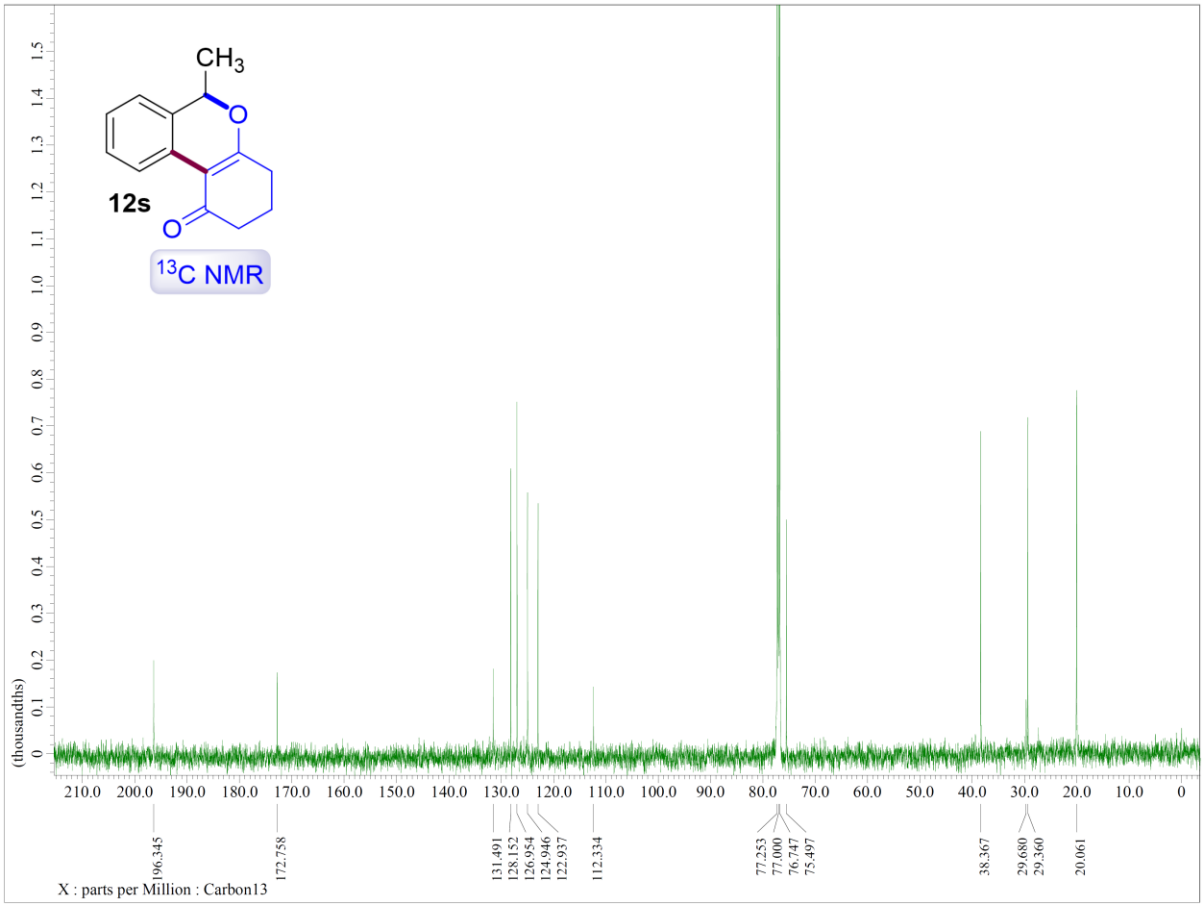

Ph
O
O
MeO
12q
1H NMR
abundance
4.78
2.80
1.93
1.00
1.02
3.01
1.07
4.24
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.726
7.707
7.702
7.683
7.387
7.374
7.342
7.328
7.256
7.192
7.176
7.118
7.112
5.267
5.243
5.139
5.115
3.923
3.571
3.557
3.552
3.040
3.005
2.997
2.917
2.904
2.896
2.883
2.856
2.845
X : parts per Million : Proton

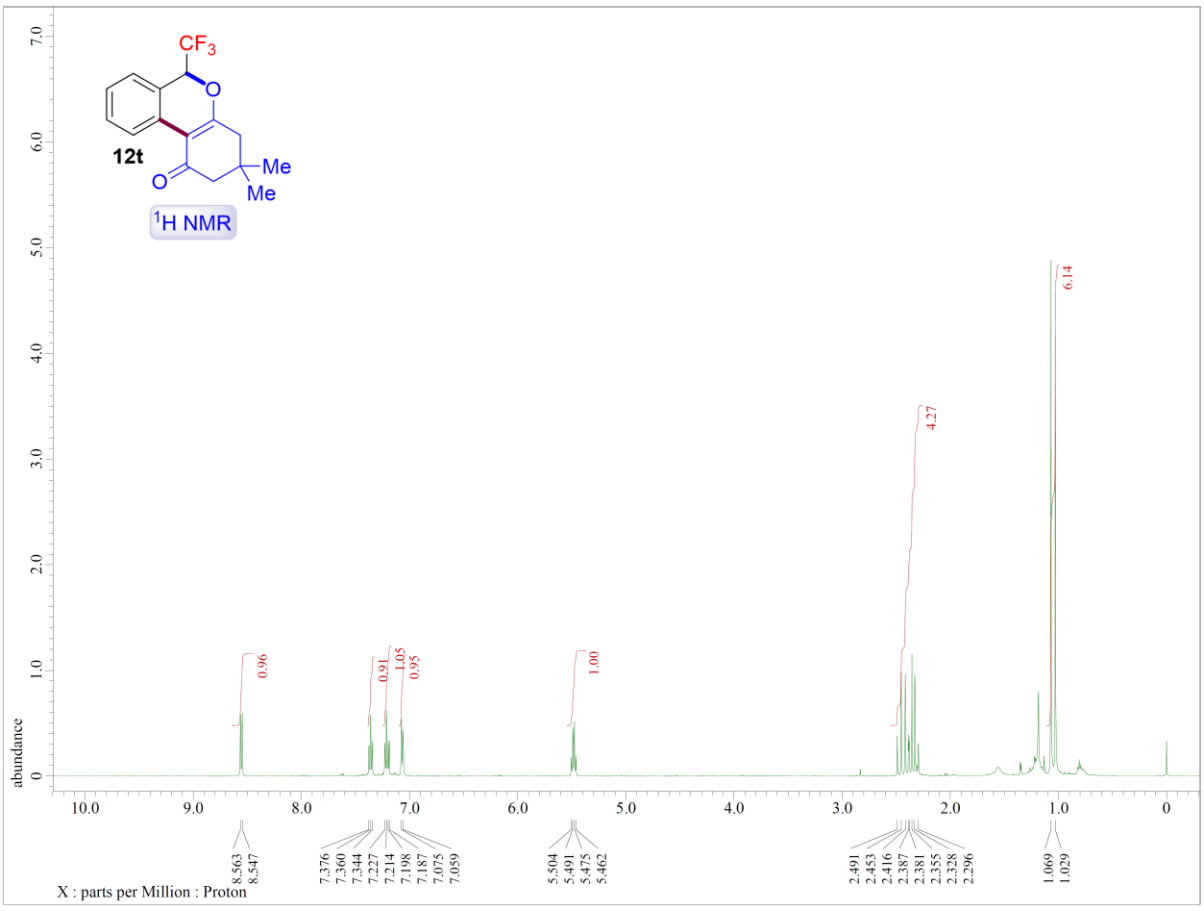

Ph
O
O
MeO
12q
13C NMR
(thousandths)
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
193.764
175.885
157.326
142.120
135.788
128.870
128.764
127.287
127.141
126.821
125.079
124.400
123.190
122.551
118.028
106.228
77.253
77.000
76.747
71.399
55.262
44.673
37.449
36.424
X : parts per Million : Carbon13

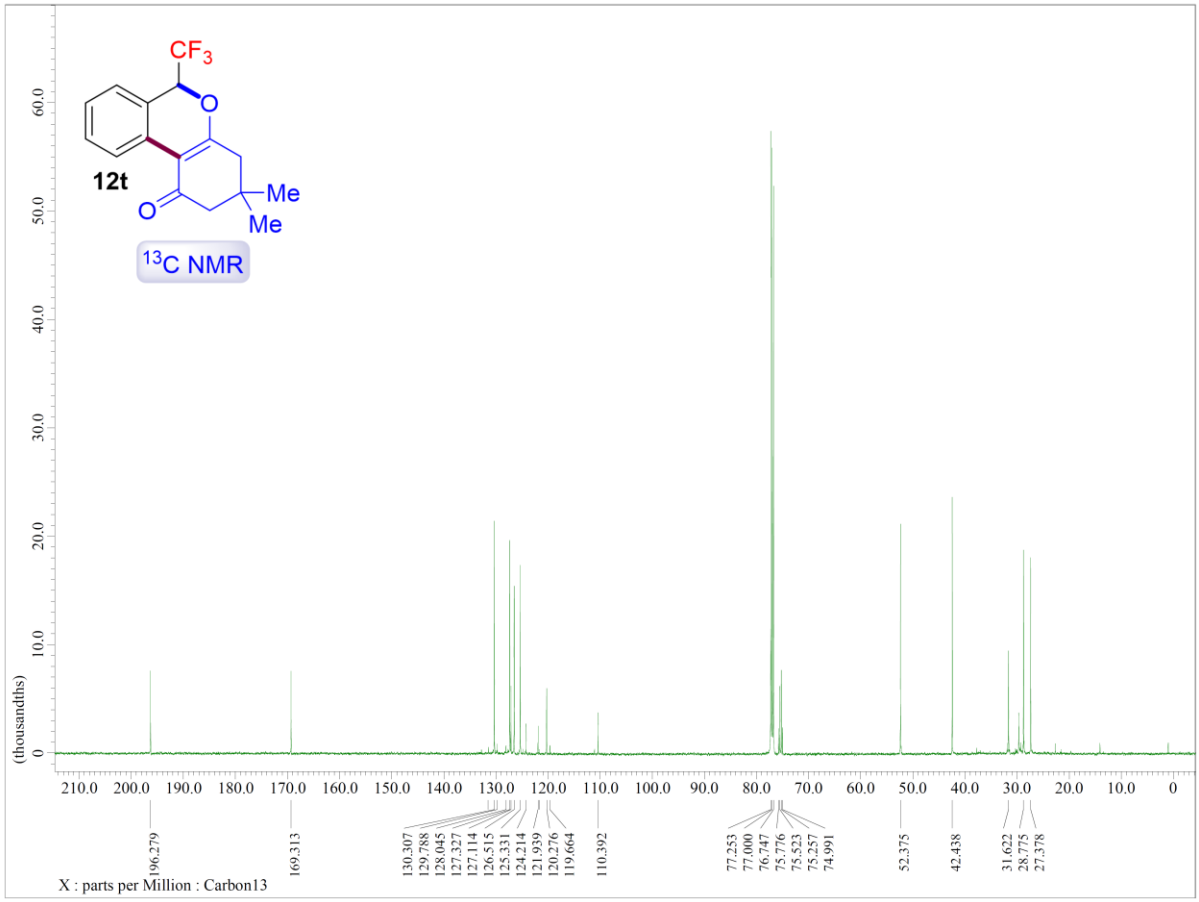

Me Me
O
O
MeO
12r
1H NMR
abundance
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
2.01
3.05
2.00
3.26
4.52
6.16
7.672
7.654
7.176
7.160
7.120
7.102
5.126
3.909
2.552
1.235
X : parts per Million : Proton

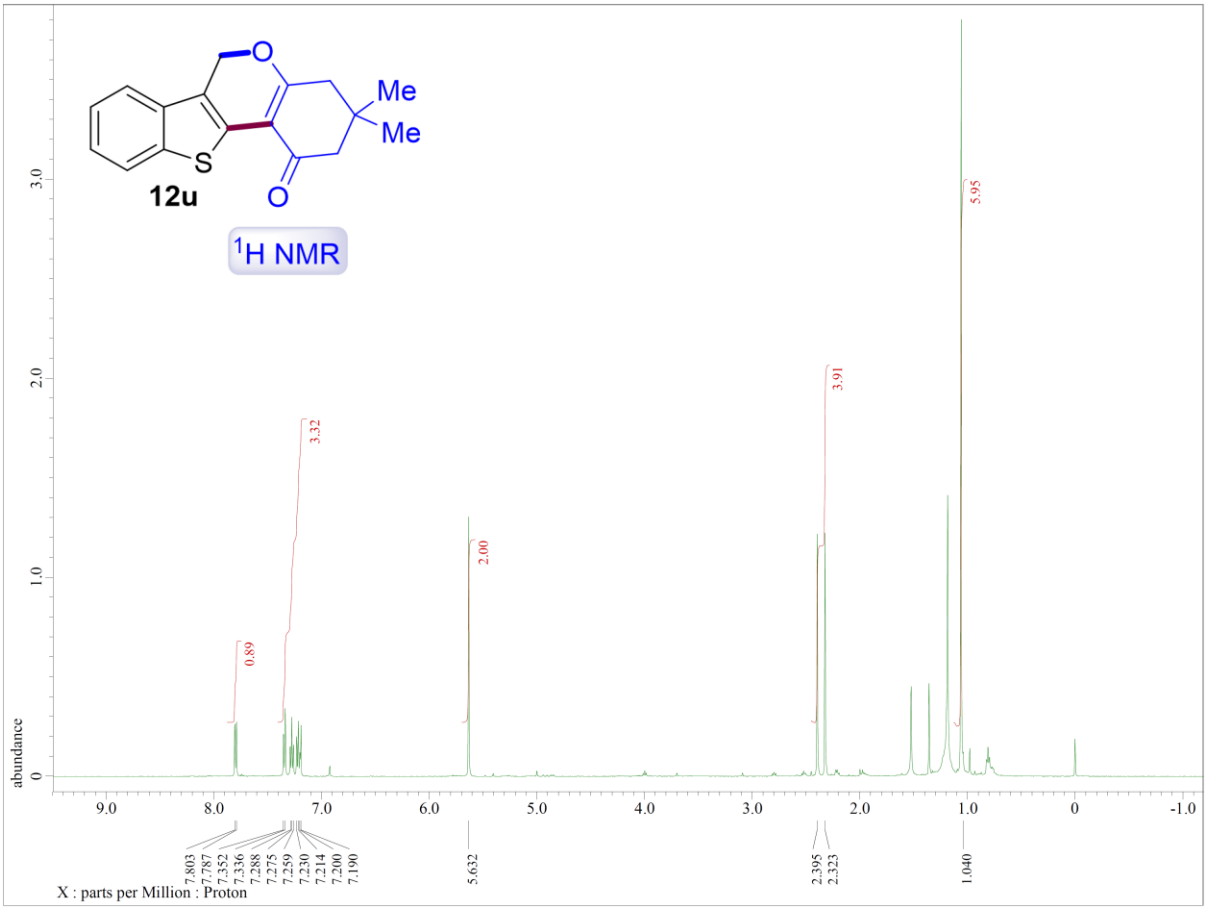

Me Me
O
O
MeO
12r
13C NMR
(thousandths)
0.6
0.5
0.4
0.3
0.2
0.1
0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
194.709
175.046
157.260
135.801
128.830
127.008
125.065
124.480
123.269
122.538
117.882
116.618
106.201
77.253
77.000
76.747
71.173
55.236
51.511
42.238
30.837
28.349
X : parts per Million : Carbon13

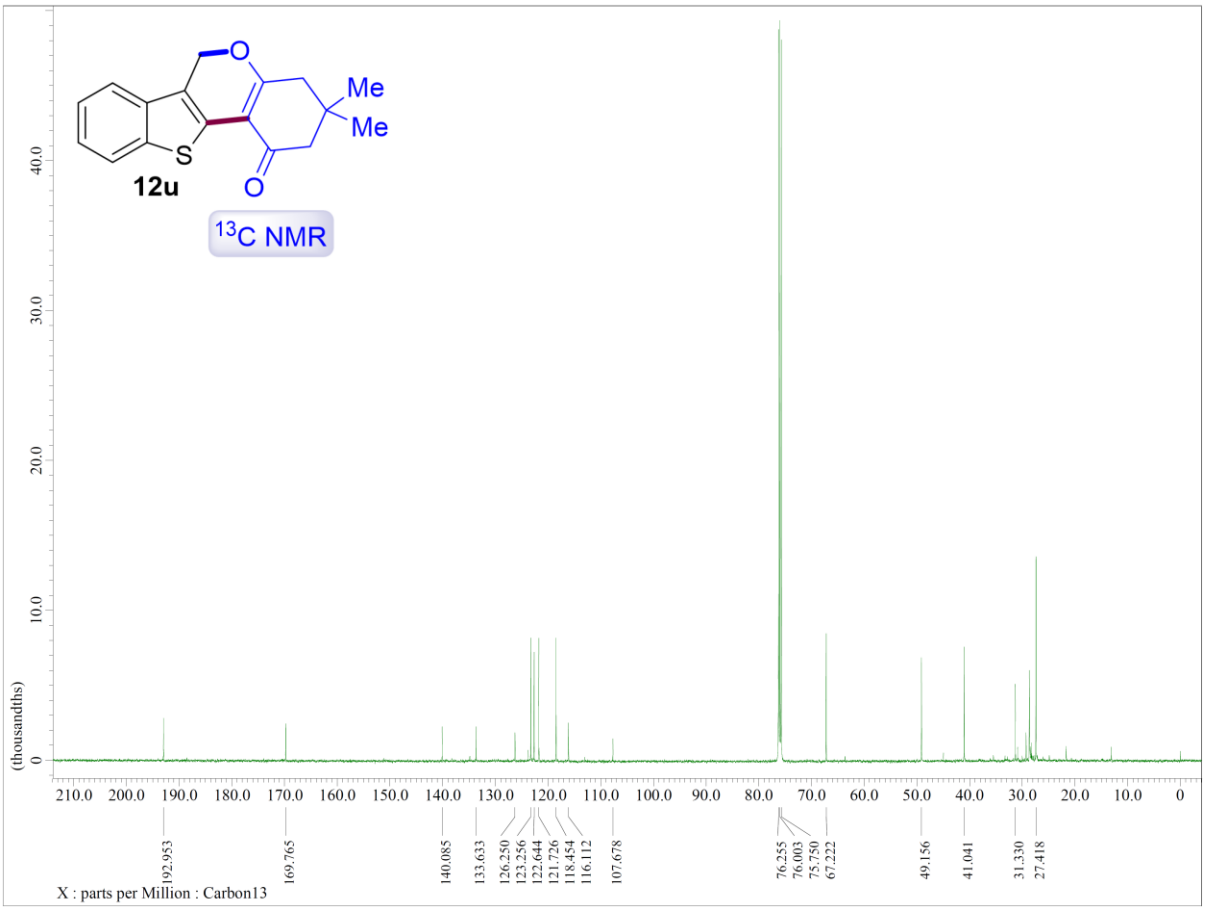

CH3
O
12s
O
1H NMR
abundance
4.0
3.0
2.0
1.0
0
0.96
0.92
0.79
0.92
1.04
4.02
2.19
3.32
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
8.358
8.342
7.326
7.310
7.296
7.262
7.238
7.222
7.208
7.038
7.023
5.307
5.294
5.280
5.267
2.605
2.581
2.571
2.555
2.541
2.528
2.517
2.493
2.013
2.000
1.987
1.616
1.603
X : parts per Million : Proton


CH3
O
12s
O
13C NMR
(thousandths)
1.5
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
196.345
172.758
131.491
128.152
126.954
124.946
122.937
112.334
77.253
77.000
76.747
75.497
38.367
29.680
29.360
20.061
X : parts per Million : Carbon13


CF3
O
12t
O
Me
Me
1H NMR
abundance
6.14
4.27
0.96
0.91
1.05
0.95
1.00
X : parts per Million : Proton


CF3
O
12t
O
Me
Me
13C NMR
(thousandths)
X : parts per Million : Carbon13


O
Me
Me
S
O
12u
1H NMR
abundance
3.0
2.0
1.0
0
0.89
3.32
2.00
3.91
5.95
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
7.803
7.787
7.352
7.336
7.288
7.275
7.259
7.230
7.214
7.200
7.190
5.632
2.395
2.323
1.040
X : parts per Million : Proton


O
Me
Me
S
O
12u
13C NMR
(thousandths)
40.0
30.0
20.0
10.0
0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
192.953
169.765
140.085
133.633
126.250
123.256
122.644
121.726
118.454
116.112
107.678
76.255
76.003
75.750
67.222
49.156
41.041
31.330
27.418
X : parts per Million : Carbon13