Electronic Supplementary Material (ESI) for ChemComm.

Acid Promoted Radical-Chain Difunctionalization of Styrenes with Stabilized Radicals and (N,O)-Nucleophiles

Sensheng Liu, and Martin Klussmann*

Contents

General experimental details

Unless otherwise indicated, all reagents and solvents were purchased from commercial distributors and used as received. Solvents (hexanes, ethyl acetate) used for column chromatography were of technical grade and used after distillation in a rotary evaporator.

Benzoyl peroxide (BPO) 75% remainder H_2O and Hexafluorophosphoric acid solution (HPF_6, 55% wt. in H_2O) from Sigma-Aldrich, used directly without further purification.

TLC was used to check the reactions for full conversion and was performed on Macherey-Nagel Polygram Sil G/UV254 thin layer plates. TLC spots were visualized by UV-light irradiation.

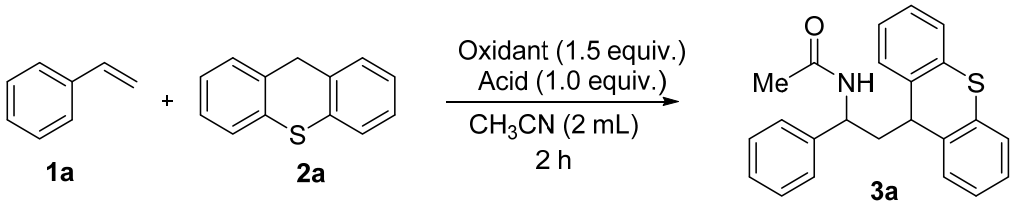
Flash column chromatography was carried out using Merck Silica Gel 60 (40-63 µm). Yields refer to pure isolated compounds.

^{1}H and ^{13}C NMR spectra were measured with Bruker AV 500 spectrometer. All chemical shifts are given in ppm downfield relative to TMS and were referenced to the solvent residual peaks.[1] ^{1}H NMR chemical shifts are designated using the following abbreviations as well as their combinations: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. For ^{13}C NMR data the following abbreviations are used: p = primary (CH_3), s = secondary (CH_2), t = tertiary (CH), q = quaternary (C).

High resolution mass spectra were recorded with a Bruker APEX III FTICR-MS or a Finnigan SSQ 7000 quadrupole MS or a Finnigan MAT 95 double focusing sector field MS instrument.

The three electrode system was controlled by using a potentiostat/galvanostat (BioLogic VSP, France). Two platinized Pt wire as a counter and working electrode with a Ag/AgCl electrode as a reference were used. The cyclic voltammetry (CV) was conducted from -1 V to 0.5 V with a scan rate of 100 mV/s.

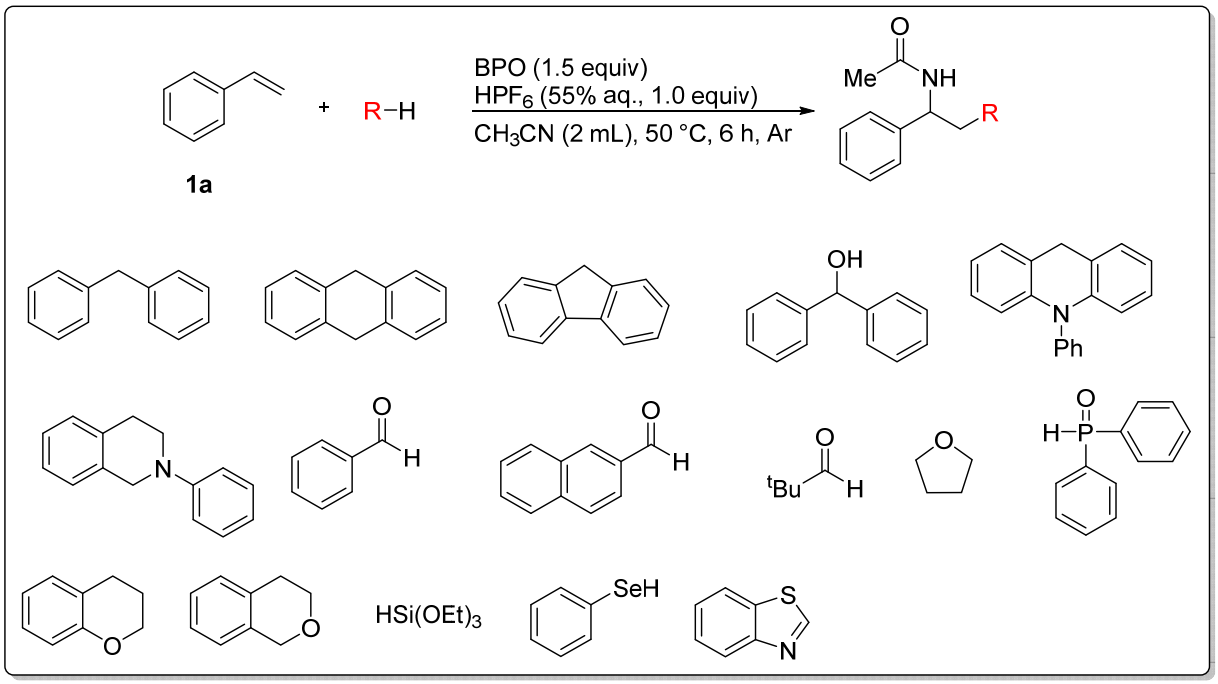
Optimization of reaction conditions[a]



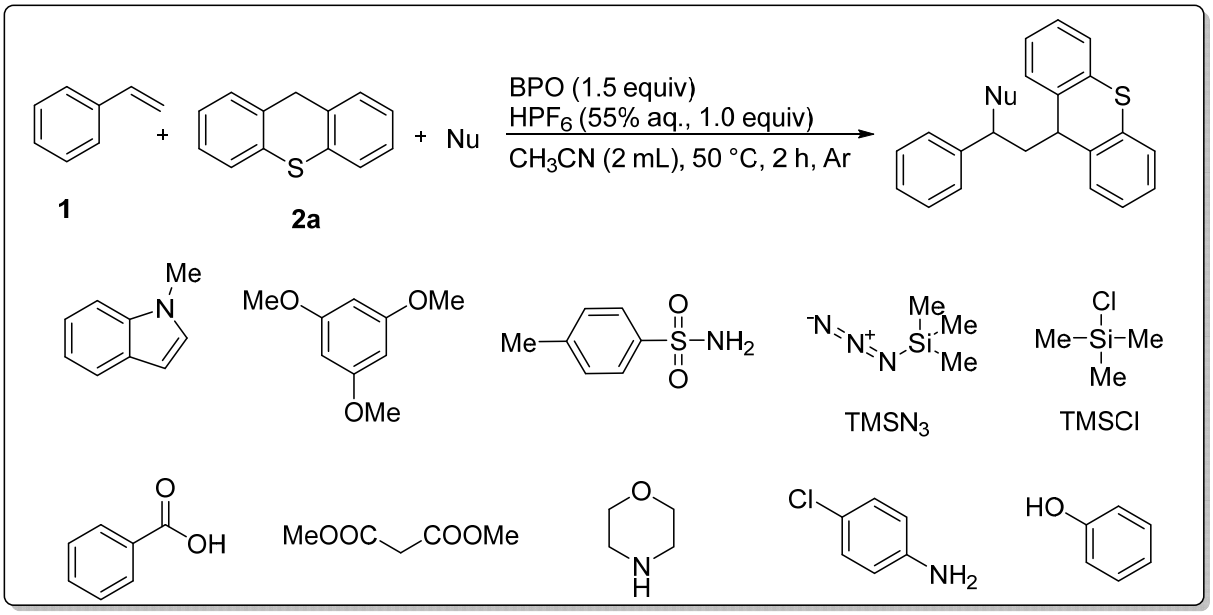
Entry	Oxidant	Equiv.	Acid	Equiv.	Additive	T/°C	Yield (%)[b]
1	BPO	(1.5 equiv.)	HCl (aq., 38%)	1.0	-	50	7
2	BPO	(1.5 equiv.)	CF_3COOH[c]	1.0	-	50	11
3	BPO	(1.5 equiv.)	H_2SO_4 (aq., 55%)	1.0	-	50	25
4	BPO	(1.5 equiv.)	HBF_4 (aq., 48%)	1.0	-	50	39
5	BPO	(1.5 equiv.)	$HClO_4$ (aq., 70%)	1.0	-	50	51
6	BPO	(1.5 equiv.)	TfOH[c]	1.0	-	50	47
7	BPO	(1.5 equiv.)	HPF_6 (aq., 55%)	1.0	-	50	88
8	BPO	(1.5 equiv.)	-	-	$NaPF_6$ (1.0 equiv.)	50	< 5
9	DTBP	(1.5 equiv.)	HPF_6 (aq., 55%)	1.0	-	50	0
10	TBPB	(1.5 equiv.)	HPF_6 (aq., 55%)	1.0	-	50	0
11	TBHP	(1.5 equiv.)	HPF_6 (aq., 55%)	1.0	-	50	0
12	BPO	(1.5 equiv.)	HPF_6 (aq., 55%)	1.0	-	100	35
13	BPO	(1.5 equiv.)	HPF_6 (aq., 55%)	1.0	-	r.t.	25
14	BPO	(1.5 equiv.)	HPF_6 (aq., 55%)	0.5	-	50	16
15	BPO	(1.5 equiv.)	HPF_6 (aq., 55%)	0.1	-	50	20
16	BPO	(1.5 equiv.)	-	-	-	50	0
17	BPO	(1.0 equiv.)	HPF_6 (aq., 55%)	1.0	-	50	40
18	BPO	(0.5 equiv.)	HPF_6 (aq., 55%)	1.0	-	50	18
19	-	-	HPF_6 (aq., 55%)	1.0	-	50	0
20[d]	BPO	(1.5 equiv.)	HPF_6 (aq., 55%)	1.0	-	50	91 (88)

[a] **1a** (0.2 mmol), **2a** (0.4 mmol, 2.0 equiv.), Oxidant (0.3 mmol, 1.5 equiv.), Acid (0.2 mmol, 1.0 equiv.) and CH_3CN (2 mL), for 2 hours. [b] Yields were determined by **^{1}H NMR** spectroscopic analysis of the crude reaction mixture relative to the internal standard CH_3NO_2, yield of isolated product in parentheses. [c] H_2O (0.2 mmol, 1.0 equiv.) was added. [d] Degassed, under argon.

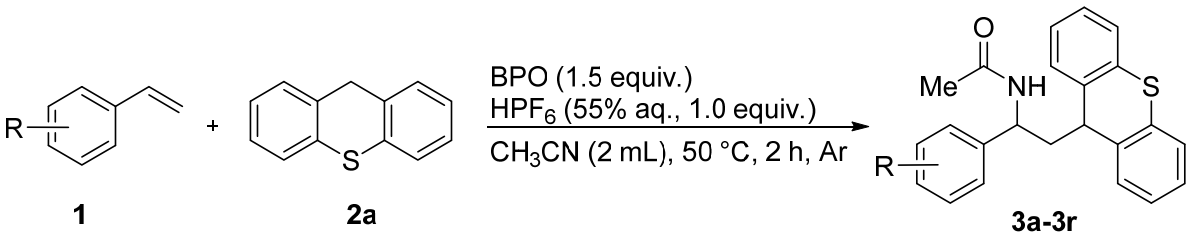
Failed examples for Hydrogen donors



Failed examples for Nucleophiles



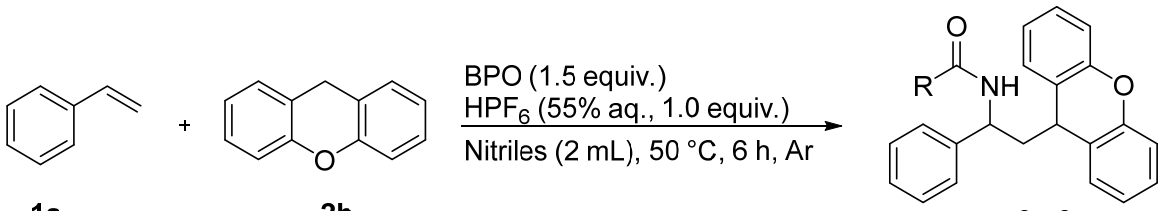
General procedure A: synthesis of *N*-(1-phenyl-2-(9*H*-thioxanthen-9-yl)ethyl)acetamides.



1 **2a** **3a-3r**

Under argon atmosphere, the thioxanthene **2a** (0.4 mmol, 2.0 equiv.), BPO (0.3 mmol, 1.5 equiv.) were added into a 10 mL glass tube. Then CH_3CN (2 mL), alkenes **1** (0.2 mmol), HPF_6 (55% aq., 0.2 mmol, 1.0 equiv.) were added. The reaction mixture was stirred at 50 °C for 2 h under Ar atmospheres. After the reaction was fully completed, the mixture was cooled to room temperature and concentrated under reduced pressure to give a crude product. The residue was further purified by silica gel column with *iso*-hexane/ethyl acetate (from 10:1 to 1:1) to give the desired products **3a**-**3r** (*trans*-**3q** and *trans*-**3r** need 6 h).

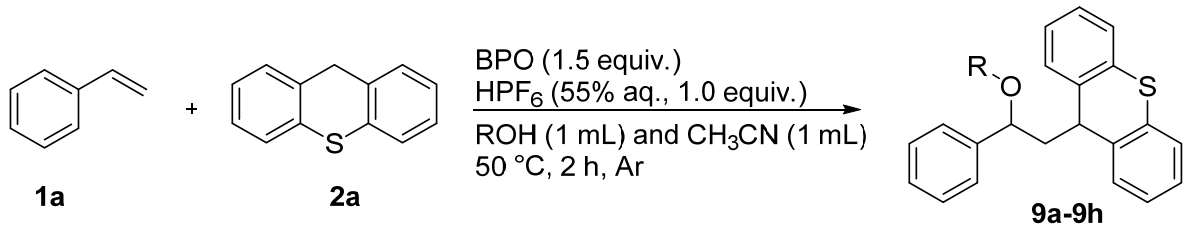
General procedure B: synthesis of *N*-(1-phenyl-2-(9*H*-xanthene-9-yl)ethyl)amides.



1a **2b** **3s-3x**

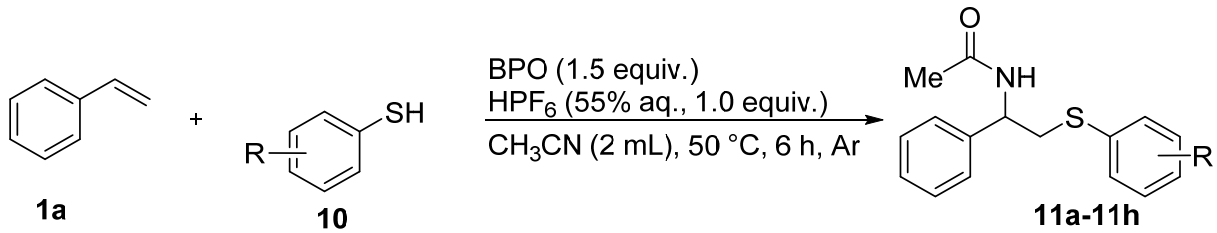
Under argon atmosphere, the xanthene **2b** (0.4 mmol, 2.0 equiv.), BPO (0.3 mmol, 1.5 equiv.) were added into a 10 mL glass tube. Then nitriles (2 mL), styrene **1a** (0.2 mmol), HPF_6 (55% aq., 0.2 mmol, 1.0 equiv.) were added. The reaction mixture was stirred at 50 °C for 6 h under Ar atmospheres. After the reaction was fully completed, the mixture was cooled to room temperature and concentrated under reduced pressure to give a crude product. The residue was further purified by silica gel column with *iso*-hexane/ethyl acetate (from 10:1 to 1:1) to give the desired products **3s-3x** .

General procedure C: synthesis of 9-(2-methoxy-2-phenylethyl)-9*H*-thioxanthenes.



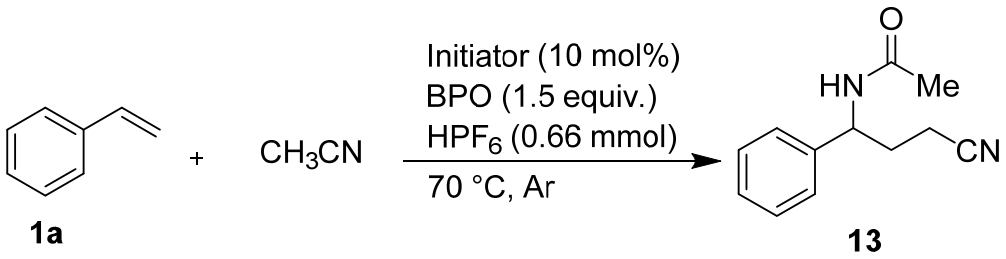
Under argon atmosphere, the thioxanthene **2a** (0.4 mmol, 2.0 equiv), BPO (0.3 mmol, 1.5 equiv) were added into a 10 mL glass tube. Then CH_3CN (1 mL), alcohols (1 mL), styrene **1a** (0.2 mmol), HPF_6 (55% aq., 0.2 mmol, 1.0 equiv) were added. The reaction mixture was stirred at 50 °C for 2 h under Ar atmospheres. After the reaction was fully completed, the mixture was cooled to room temperature and concentrated under reduced pressure to give a crude product. The residue was further purified by silica gel column with *iso*-hexane/ethyl acetate (100:1) to give the desired products **9a-9h**.

General procedure D: synthesis of 9-(2-methoxy-2-phenylethyl)-9*H*-thioxanthene *N*-(1-phenyl-2-(phenylthio)ethyl)acetamides



Under argon atmosphere, the thiophenols **10** (0.4 mmol, 2.0 equiv.), BPO (0.3 mmol, 1.5 equiv.) were added into a 10 mL glass tube. Then CH_3CN (1 mL), alcohols (1 mL), styrene **1a** (0.2 mmol), HPF_6 (55% aq., 0.2 mmol, 1.0 equiv.) were added. The reaction mixture was stirred at 50 °C for 6 h under Ar atmospheres. After the reaction was fully completed, the mixture was cooled to room temperature and concentrated under reduced pressure to give a crude product. The residue was further purified by silica gel column with *iso*-hexane/ethyl acetate (from 10:1 to 2:1) to give the desired products **5a-5h**.

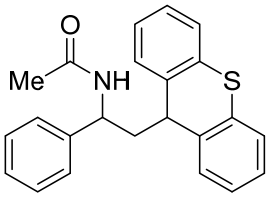
General procedure E: synthesis of *N*-(3-cyano-1-phenylpropyl)acetamide



Under argon atmosphere, BPO (0.75 mmol, 1.5 equiv., three portions every 2 hours) were added into a 10 mL glass tube. Then CH_3CN (30 mL), styrene **1a** (0.5 mmol), HPF_6 (55% aq., 0.66 mmol, 1.32 equiv.) and a *N*,*N*-dimethylaniline derivative as initiator (10 mol%, 0.05 mmol) were added. The reaction mixture was stirred at 70 °C for 18 h under Ar atmospheres. After the reaction was fully completed, the mixture was cooled to room temperature and concentrated under reduced pressure to give a crude product. The residue was further purified by silica gel column with *iso*-hexane/ethyl acetate (from 10:1 to 1:1) to give the desired products **13**.

Characterization Data

***N*-(1-phenyl-2-(9*H*-thioxanthen-9-yl)ethyl)acetamide** (**3a**, unreported product)



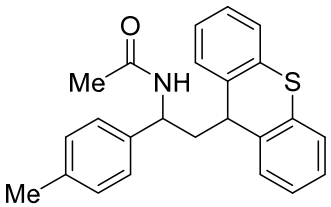
Following the general procedure **A**, white solid (65.3 mg, 91%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36-7.32 (m, 2H), 7.24-7.09 (m, 11H), 5.39 (d, J = 12.5 Hz, 1H), 4.85-4.80 (m, 1H), 4.07-4.00 (m, 1H), 2.20-2.09 (m, 2H), 1.80 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 168.99, 142.05, 137.66, 137.62, 132.53, 132.32, 128.97, 128.71, 128.68, 127.42, 127.23, 127.10, 126.79, 126.77, 126.71, 126.60, 51.63, 46.77, 38.02, 23.46.

HRMS (ESIpos) (m/z): M^+ calculated for $C_{23}H_{21}NOSNa$ 382.123605; found 382.123850.

***N*-(2-(9*H*-thioxanthen-9-yl)-1-(*p*-tolyl)ethyl)acetamide** (**3b**, unreported product)



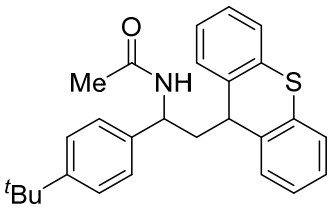
Following the general procedure **A**, white solid (62.0 mg, 83%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36-7.31 (m, 1H), 7.20-7.10 (m, 7H), 7.04 (s, 4H), 5.35 (d, J = 8.5 Hz, 1H), 4.78 (dd, J = 15.5 Hz, 7.5 Hz, 1H), 4.05 (dd, J = 15.0 Hz, 5.0 Hz, 1H), 2.24 (s, 3H), 2.14 (t, J = 7.5 Hz, 2H), 1.79 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 168.89, 139.04, 137.78, 137.65, 137.12, 132.54, 132.35, 129.39, 128.93, 128.72, 127.23, 127.07, 126.67, 126.59, 51.31, 46.69, 37.93, 23.49, 21.06.

HRMS (ESIpos) (m/z): M^+ calculated for $C_{24}H_{23}NOSNa$ 396.139255; found 396.139160.

***N*-(1-(4-(*tert*-butyl)phenyl)-2-(9*H*-thioxanthen-9-yl)ethyl)acetamide** (**3c**, unreported product)



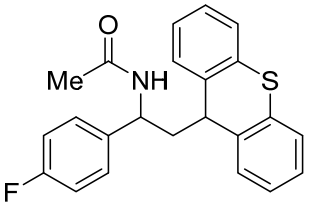
Following the general procedure **A**, white solid (51.4 mg, 62%).

^{1}H NMR (500 MHz, DMSO-d_6) δ 8.42 (d, J = 8.5 Hz, 1H), 7.49 (dd, J = 6.5 Hz, 4.0 Hz, 1H), 7.44 (d, J = 7.0 Hz, 1H), 7.40 (d, J = 6.5 Hz, 1H), 7.32-7.23 (m, 7H), 7.00 (d, J = 8.0 Hz, 2H), 4.45-4.40 (m, 1H), 4.18 (dd, J = 9.5 Hz, 4.5 Hz, 1H), 2.09-2.04 (m, 1H), 1.92 (s, 3H), 1.85-1.78 (m, 1H), 1.22 (s, 9H).

^{13}C NMR (125 MHz, DMSO-d_6) δ 168.95, 149.42, 141.14, 138.65, 137.14, 131.87, 131.72, 129.89, 129.13, 127.35, 127.22, 127.18, 127.11, 126.29, 125.48, 50.28, 45.69, 39.13, 34.55, 31.58, 23.26.

HRMS (ESIpos) (m/z): M^+ calculated for $C_{27}H_{29}NOSNa$ 438.186205; found 438.186910.

***N*-(1-(4-fluorophenyl)-2-(9*H*-thioxanthen-9-yl)ethyl)acetamide** (**3d**, unreported product)



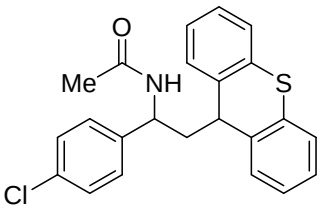
Following the general procedure **A**, white solid (72.4 mg, 96%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36-7-33 (m, 2H), 7.17-7.09 (m, 8H), 6.90 (t, J = 10.0 Hz, 2H), 5.35 (d, J = 5.0 Hz, 1H), 4.81-4.76 (m, 1H), 4.01 (t, 2H, J = 10.0 Hz, 1H), 2.15-2.11 (m, 2H), 1.80 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 169.05, 162.92, 160.97, 137.92 (d, J = 3.75 Hz, 1C), 137.46 (d, J = 8.75 Hz, 1C), 133.46, 132.52, 132.29, 130.12, 128.92, 128.66, 128.45, 128.26, 128.19, 127.28, 127.16, 126.86 (d, J = 3.75 Hz, 1C), 126.78, 115.57, 115.40, 51.09, 46.85, 37.92, 23.42.

HRMS (ESIpos) (m/z): M^+ calculated for $C_{23}H_{20}FNOSNa$ 400.114184; found 400.114170.

***N*-(1-(4-chlorophenyl)-2-(9*H*-thioxanthen-9-yl)ethyl)acetamide** (**3e**, unreported product)



Following the general procedure **A**, white solid (66.0 mg, 84%).

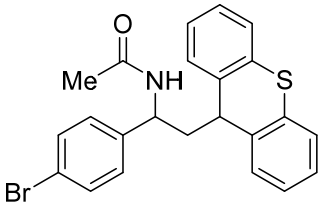
^{1}H NMR (500 MHz, DMSO-d_6) δ 8.53 (d, J = 5.0 Hz, 1H), 7.55-7.54 (m, 1H), 7.50 (dd, J = 5.0 Hz, 2.5 Hz, 1H), 7.45 (dd, J = 5.0 Hz, 1.5 Hz, 1H), 7.38-7.28 (m, 7H), 7.15 (d, J = 8.5 Hz, 2H), 4.48-4.41 (m, 1H), 4.25 (dd, J = 10.0 Hz, 5.5 Hz, 1H), 2.12-2.08 (m, 1H), 1.98 (s, 3H), 1.92-1.86 (m, 1H).

^{13}C NMR (125 MHz, DMSO-d_6) δ 169.10, 143.08, 138.40, 136.97, 131.88, 131.73, 131.63, 129.84, 129.20, 128.76, 128.51, 127.42, 127.40, 127.37, 127.30, 127.24, 127.17, 50.24, 45.58, 38.76, 23.20.

HRMS (ESIpos) (m/z): M^+ calculated for $C_{23}H_{20}ClNOSNa$ 416.084633; found 416.084760.

***N*-(1-(4-bromophenyl)-2-(9*H*-thioxanthen-9-yl)ethyl)acetamide** (**3f**, unreported product)

Following the general procedure **A**, white solid (70.8 mg, 81%).

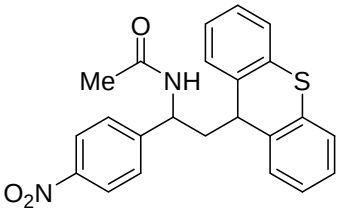


^{1}H NMR (500 MHz, DMSO-d_6) δ 8.53 (d, J = 5.0 Hz, 1H), 7.55-7.53 (m, 1H), 7.50 (d, J = 8.5 Hz, 3H), 7.45 (dd, J = 7.5 Hz, 1.0 Hz, 1H), 7.38-7.28 (m, 5H), 7.09 (d, J = 8.5 Hz, 2H), 4.46-4.41 (m, 1H), 4.25 (dd, J = 9.5 Hz, 5.0 Hz, 1H), 2.14-2.08 (m, 1H), 1.97 (s, 3H), 1.92-1.85 (m, 1H).

^{13}C NMR (125 MHz, DMSO-d_6) δ 169.11, 143.51, 138.39, 136.96, 131.88, 131.73, 131.67, 129.84, 129.20, 128.89, 127.43, 127.41, 127.37, 127.30, 127.24, 127.17, 120.12, 50.31, 45.57, 38.69, 23.20.

HRMS (ESIpos) (m/z): M^+ calculated for $C_{23}H_{20}BrNOSNa$ 460.034131; found 460.034780.

***N*-(1-(4-nitrophenyl)-2-(9*H*-thioxanthen-9-yl)ethyl)acetamide** (**3g**, unreported product)



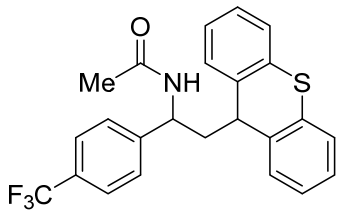
Following the general procedure **A**, light yellow solid (8.0 mg, 10%).

^{1}H NMR (500 MHz, DMSO-d_6) δ 8.69 (d, J = 8.0 Hz, 1H), 8.81 (d, J = 8.5 Hz, 2H), 7.57-7.55 (m, 1H), 7.50 (t, J = 16.5 Hz, 8.0 Hz, 2H), 7.40-7.30 (m, 7H), 4.56-4.51 (m, 1H), 4.34 (dd, J = 10.0 Hz, 5.0 Hz, 1H), 2.18-2.12 (m, 1H), 2.01 (s, 3H), 1.94-1.88 (m, 1H).

^{13}C NMR (125 MHz, DMSO-d_6) δ 169.37, 151.87, 146.76, 138.27, 136.67, 131.90, 131.77, 129.89, 129.22, 127.86, 127.53, 127.47, 127.42, 127.36, 127.25, 127.21, 124.12, 50.78, 45.49, 38.33, 23.15.

HRMS (ESIpos) (m/z): M^+ calculated for $C_{23}H_{20}N_2O_3SNa$ 427.108684; found 427.109200.

***N*-(2-(9*H*-thioxanthen-9-yl)-1-(4-(trifluoromethyl)phenyl)ethyl)acetamide** (**3h**, unreported product)



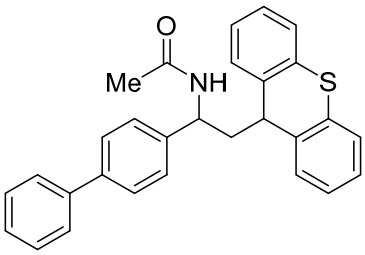
Following the general procedure **A**, white solid (25.6 mg, 30%).

^{1}H NMR (500 MHz, DMSO-d_6) δ 8.64 (d, J = 8.0 Hz, 1H), 7.67 (d, J = 8.0 Hz, 2H), 7.56-7.55 (m, 1H), 7.50-7.47 (m, 2H), 7.37-7.30 (m, 7H), 4.54-4.50 (m, 1H), 4.31 (dd, J = 10.0 Hz, 5.0 Hz, 1H), 2.18-2.14 (m, 1H), 2.00 (s, 3H), 1.92-1.87 (m, 1H).

^{13}C NMR (125 MHz, DMSO-d_6) δ 169.27, 148.88, 138.38, 136.79, 131.88, 131.75, 129.89, 129.20, 127.48, 127.44, 127.39, 127.32, 127.23, 127.18, 125.78, 125.74, 125.71, 50.72, 45.55, 38.61, 23.17.

HRMS (ESIneg) (m/z): H^- calculated for $C_{24}H_{20}F_3NOS$ 426.114497; found 426.115170.

***N*-(1-([1,1'-biphenyl]-4-yl)-2-(9*H*-thioxanthen-9-yl)ethyl)acetamide** (**3i**, unreported product)



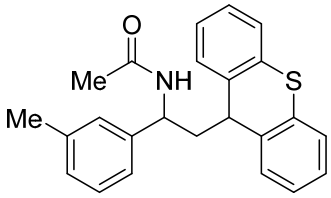
Following the general procedure **A**, white solid (69.6 mg, 80%).

^{1}H NMR (500 MHz, DMSO-d_6) δ 8.50 (d, J = 8.0 Hz, 1H), 7.60 (d, J = 7.0 Hz, 2H), 7.55 (d, J = 8.0 Hz, 2H), 7.51-7.49 (m, 1H), 7.46-7.42 (m, 4H), 7.35-7.24 (m, 6H), 7.71 (d, J = 8.0 Hz, 2H), 4.51-4.46 (m, 1H), 4.23 (dd, J = 10.0 Hz, 5.0 Hz, 1H), 2.15-2.10 (m, 1H), 1.59 (s, 3H), 1.91-1.85 (m, 1H).

^{13}C NMR (125 MHz, DMSO-d_6) δ 169.06, 143.34, 140.37, 139.11, 138.55, 137.11, 131.89, 131.75, 129.89, 129.34, 129.19, 127.75, 127.40, 127.37, 127.27, 127.23, 127.21, 127.15, 127.01, 50.46, 45.68, 39.01, 23.27.

HRMS (ESIpos+neg) (m/z): M^+ calculated for $C_{29}H_{25}NOSNa$ 458.154905; found 458.154970.

***N*-(2-(9*H*-thioxanthen-9-yl)-1-(*m*-tolyl)ethyl)acetamide** (**3j**, unreported product)



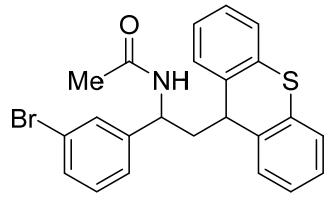
Following the general procedure **A**, white solid (50.0 mg, 63%).

^{1}H NMR (500 MHz, DMSO-d_6) δ 8.43 (d, J = 8.5 Hz, 1H), 7.50-7.48 (m, 1H), 7.45-7.39 (m, 2H), 7.33-7.23 (m, 5H), 7.14 (t, J = 7.5 Hz 1H), 6.98 (d, J = 7.5 Hz, 1H), 6.88-6.86 (m, 2H), 4.42-4.40 (m, 1H), 4.18 (dd, J = 10.0 Hz, 5.0 Hz, 1H), 2.24 (s, 3H), 2.09-2.03 (m, 1H), 1.93 (s, 3H), 1.85-1.79 (m, 1H).

^{13}C NMR (125 MHz, DMSO-d_6) δ 168.95, 144.10, 138.62, 137.81, 137.10, 131.86, 131.71, 129.89, 129.17, 128.69, 127.78, 127.37, 127.24, 127.22, 127.19, 127.13, 123.71, 50.58, 45.66, 39.19, 23.28, 21.49.

HRMS (ESIpos) (m/z): M^+ calculated for $C_{24}H_{23}NOSNa$ 396.139256; found 396.139410.

***N*-(1-(3-bromophenyl)-2-(9*H*-thioxanthen-9-yl)ethyl)acetamide** (**3k**, unreported product)



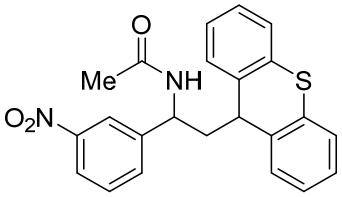
Following the general procedure **A**, white solid (67.3 mg, 77%).

^{1}H NMR (500 MHz, DMSO-d_6) δ 8.55 (d, J = 8.5 Hz, 1H), 7.55-7.53 (m, 1H), 7.50 (dd, J = 7.5 Hz, 1.0 Hz, 1H), 7.47-7.41 (m, 2H), 7.38-7.25 (m, 7H), 7.10 (d, J = 7.5 Hz, 1H), 4.48-4.39 (m, 1H), 4.28 (dd, J = 9.5 Hz, 5.0 Hz, 1H), 2.14-2.08 (m, 1H), 2.04 (s, 3H), 1.92-1.86 (m, 1H).

^{13}C NMR (125 MHz, DMSO-d_6) δ 169.17, 146.97, 138.43, 136.86, 131.90, 131.76, 131.06, 130.08, 129.85, 129.22, 129.17, 127.44, 127.42, 127.38, 127.29, 127.22, 127.16, 125.83, 122.12, 50.49, 45.63, 38.80, 23.22.

HRMS (ESIpos) (m/z): M^+ calculated for $C_{23}H_{20}BrNOSNa$ 460.034131; found 460.033700.

***N*-(1-(3-nitrophenyl)-2-(9*H*-thioxanthen-9-yl)ethyl)acetamide** (**3l**, unreported product)



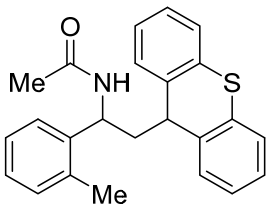
Following the general procedure **A**, light yellow solid (26.6 mg, 33%).

^{1}H NMR (500 MHz, DMSO-d_6) δ 8.64 (d, J = 8.0 Hz, 1H), 8.05-8.63 (m, 1H), 7.94 (s, 1H), 7.56-7.42 (m, 5H), 7.32-7.25 (m, 5H), 4.56-4.51 (m, 1H), 4.29 (dd, J = 10.0 Hz, 5.5 Hz, 1H), 2.15-2.09 (m, 1H), 1.94 (s, 3H), 1.92-1.88 (m, 1H).

^{13}C NMR (125 MHz, DMSO-d_6) δ 169.30, 148.30, 146.30, 138.31, 136.75, 133.66, 131.91, 131.79, 130.41, 129.85, 129.22, 127.47, 127.43, 127.40, 127.34, 127.24, 127.19, 122.28, 121.15, 50.61, 45.57, 38.43, 23.18.

HRMS (ESIpos) (m/z): M^+ calculated for $C_{23}H_{20}N_2O_3SNa$ 427.108684; found 427.109450.

***N*-(2-(9*H*-thioxanthen-9-yl)-1-(*o*-tolyl)ethyl)acetamide** (**3m**, unreported product)



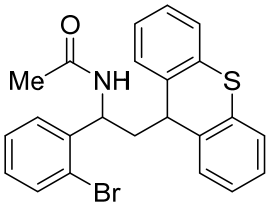
Following the general procedure **A**, white solid (57.4 mg, 77%).

^{1}H NMR (500 MHz, DMSO-d_6) δ 8.57 (d, J = 8.5 Hz, 1H), 7.50-7.48 (m, 1H), 7.43 (d, J = 7.0 Hz, 1H), 7.42 (d, J = 5.0 Hz, 1H), 7.34-7.29 (m, 4H), 7.26-7.20 (m, 2H), 7.10 (t, J = 7.5 Hz, 1H), 7.04-7.00 (m, 1H), 6.97 (d, J = 10.0 Hz, 1H), 4.71-4.67 (m, 1H), 4.25 (dd, J = 11.0 Hz, 3.5 Hz, 1H), 2.20-1.97 (m, 4H), 1.70 (s, 3H), 1.62-1.56 (m, 1H).

^{13}C NMR (125 MHz, DMSO-d_6) δ 169.11, 142.90, 138.74, 136.57, 134.12, 131.74, 131.66, 130.39, 130.28, 129.04, 127.50, 127.41, 127.24, 127.15, 127.07, 127.00, 126.69, 126.45, 125.22, 46.93, 45.82, 38.62, 23.26, 18.01.

HRMS (ESIpos) (m/z): M^+ calculated for $C_{24}H_{23}NOSNa$ 396.139255; found 396.139960.

***N*-(1-(2-bromophenyl)-2-(9*H*-thioxanthen-9-yl)ethyl)acetamide** (**3n**, unreported product)



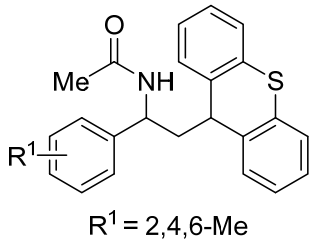
Following the general procedure **A**, white solid (62.0 mg, 71%).

^{1}H NMR (500 MHz, DMSO-d_6) δ 8.69 (d, J = 7.5 Hz, 1H), 7.48-7.45 (m, 2H), 7.41-7.39 (m, 2H), 7.34-7.28 (m, 6H), 7.25-7.21 (m, 1H), 7.08 (td, J = 15.0 Hz, 7.5 Hz, 2.5 Hz, 1H), 4.81-4.76 (m, 1H), 4.31 (dd, J = 11.5 Hz, 4.0 Hz, 1H), 2.22-2.16 (m, 1H), 2.02 (s, 3H), 1.49-1.43 (m, 1H).

^{13}C NMR (125 MHz, DMSO-d_6) δ 169.17, 146.97, 138.43, 136.86, 131.90, 131.76, 131.06, 130.08, 129.85, 129.22, 129.17, 127.44, 127.42, 127.38, 127.29, 127.22, 127.16, 125.83, 122.12, 50.49, 45.63, 38.80, 23.22.

HRMS (ESIpos) (m/z): M^+ calculated for $C_{23}H_{20}BrNOSNa$ 460.034131; found 460.034720.

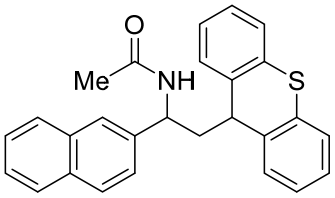
***N*-(1-mesityl-2-(9H-thioxanthen-9-yl)ethyl)acetamide** (**3o**, unreported product)



Following the general procedure **A**, white solid (61.5 mg, 75%).

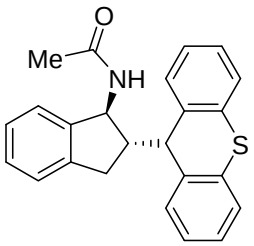
^{1}H NMR (500 MHz, DMSO-d_6) δ 8.42 (d, J = 8.5 Hz, 1H), 7.50-7.48 (m, 1H), 7.44 (dd, J = 8.0 Hz, 1.5 Hz, 1H), 7.40 (dd, J = 10.0 Hz, 5.0 Hz, 1H), 7.33-7.24 (m, 7H), 7.00 (d, J = 8.5 Hz, 2H), 4.45-4.42 (m, 1H), 4.18 (dd, J = 9.5 Hz, 4.5 Hz, 1H), 2.10-2.04 (m, 1H), 1.92 (s, 3H), 1.84-1.78 (m, 1H), 1.22 (s, 9H).
^{13}C NMR (125 MHz, DMSO-d_6) δ 168.93, 149.43, 141.14, 138.65, 137.14, 131.86, 131.72, 129.89, 129.13, 127.36, 127.22, 127.19, 127.12, 126.26, 125.49, 50.27, 45.68, 39.13, 34.56, 31.58, 23.26.
HRMS (ESIpos) (m/z): M^+ calculated for $C_{26}H_{27}NOSNa$.170555; found 424.170840424.

***N*-(1-(naphthalen-2-yl)-2-(9*H*-thioxanthen-9-yl)ethyl)acetamide** (**3p**, unreported product)



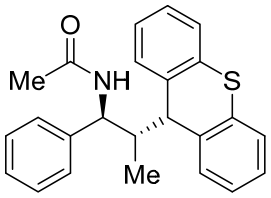
Following the general procedure **A**, white solid (59.7 mg, 73%).
^{1}H NMR (500 MHz, DMSO-d_6) δ 8.62 (d, J = 8.5 Hz, 1H), 7.91-7.86 (m, 3H), 7.57-7.48 (m, 6H), 7.38-7.29 (m, 6H), 4.69-4.64 (m, 1H), 4.30 (dd, J = 9.5 Hz, 5.0 Hz, 1H), 2.28-2.21 (m, 1H), 2.04-1.98 (m, 4H).
^{13}C NMR (125 MHz, DMSO-d_6) δ 169.12, 141.52, 138.57, 137.11, 133.26, 132.48, 131.91, 131.77, 129.92, 129.25, 128.51, 128.11, 127.86, 127.42, 127.39, 127.28, 127.23, 127.19, 126.58, 126.12, 125.25, 124.93, 50.83, 45.66, 38.83, 23.30.
HRMS (ESIpos) (m/z): M^+ calculated for $C_{27}H_{23}NOSNa$ 432.139255; found 432.139730.

***trans*-*N*-(2-(9*H*-thioxanthen-9-yl)-2,3-dihydro-1*H*-inden-1-yl)acetamide** (*trans*-**3q**, unreported product)



Following the general procedure **A** (reaction time for 6 hours), white solid (22.2 mg, 30%).
^{1}H NMR (500 MHz, DMSO-d_6) δ 7.69 (d, J = 9.0 Hz, 1H), 7.59 (dd, J = 7.5 Hz, 2.0 Hz, 1H), 7.52 (dd, J = 6.5 Hz, 1.5 Hz, 1H), 7.50-7.48 (m, 1H), 7.44 (dd, J = 7.0 Hz, 2.0 Hz, 1H), 7.37-7.31 (m, 2H), 7.30-7.24 (m, 2H), 7.16-7.12 (m, 3H), 7.00-7.98 (m, 1H), 5.33 (t, J = 9.0 Hz, 1H), 4.45 (d, J = 9.0 Hz, 1H), 2.93-2.86 (m, 1H), 2.79-2.74 (m, 1H), 2.39-2.34 (m, 1H), 1.56 (s, 3H).
^{13}C NMR (125 MHz, DMSO-d_6) δ 168.90, 144.77, 140.73, 137.22, 132.48, 131.97, 130.30, 129.83, 127.59, 127.24, 127.13, 126.95, 126.91, 126.84, 124.53, 123.78, 57.29, 51.70, 47.42, 35.39, 22.76.
HRMS (ESIpos) (m/z): M^+ calculated for $C_{24}H_{21}NOSNa$ 394.123605; found 394.124240.

***trans*-*N*-(1-phenyl-2-(9*H*-thioxanthen-9-yl)propyl)acetamide** (*trans*-**3r**, unreported product)



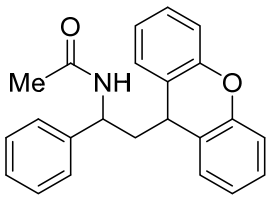
Following the general procedure **A** (reaction time for 6 hours), white solid (36.5 mg, 49%).

^{1}H NMR (500 MHz, DMSO-d_6) δ 8.09 (d, J = 8.5 Hz, 1H), 7.57-7.55 (m, 1H), 7.48 (dd, J = 7.5 Hz, 1.5 Hz, 1H), 7.37-7.35 (m, 2H), 7.31-7.21 (m, 6H), 7.12 (t, J = 7.5 Hz, 1H), 7.09-6.87 (m, 2H), 4.58 (dd, J = 8.5 Hz, 2.5 Hz, 1H), 4.07 (d, J = 10.0 Hz, 1H), 2.41-2.37 (m, 1H), 2.11 (s, 3H), 0.44 (d, J = 7.5 Hz, 3H).

^{13}C NMR (125 MHz, DMSO-d_6) δ 169.90, 143.46, 137.71, 137.67, 132.47, 130.56, 128.49, 127.62, 127.46, 127.23, 127.10, 126.97, 126.78, 126.60, 126.12, 53.48, 51.76, 37.80, 23.23, 12.08.

HRMS (ESIpos) (m/z): M^+ calculated for $C_{24}H_{23}NOSNa$ 396.1392563; found 96.139390.

***N*-(1-phenyl-2-(9*H*-xanthen-9-yl)ethyl)acetamide** (**3s**, unreported product)



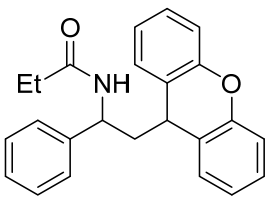
Following the general procedure **B**, white solid (63.1 mg, 92%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24 (d, J = 7.5 Hz, 1H), 7.20-7.10 (m, 8H), 7.08-6.99 (m, 4H), 5.40 (d, J = 8.5 Hz, 1H), 4.95-4.90 (m, 1H), 3.98 (dd, J = 7.0 Hz, 5.5 Hz, 1H), 2.13-2.05 (m, 2H), 1.79 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 169.06, 152.39, 152.29, 142.25, 128.68, 128.66, 128.21, 127.90, 127.34, 126.41, 125.25, 124.98, 123.50, 123.44, 116.78, 116.62, 50.82, 46.67, 36.86, 23.40.

HRMS (ESIpos) (m/z): M^+ calculated for $C_{23}H_{21}NO_2Na$ 366.146448; found 366.146620.

***N*-(1-phenyl-2-(9*H*-xanthen-9-yl)ethyl)propionamide** (**3t**, unreported product)



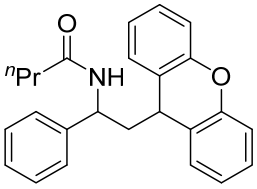
Following the general procedure **B**, white solid (51.4 mg, 72%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26 (dd, J = 7.5 Hz, 1.5 Hz, 1H), 7.21-7.09 (m, 8H), 7.06-6.99 (m, 4H), 5.35 (d, J = 8.0 Hz, 1H), 4.98-4.93 (m, 1H), 3.96 (t, J = 6.5 Hz, 1H), 2.11-1.97 (m, 4H), 1.01 (t, J = 7.5 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 172.74, 152.38, 152.27, 142.28, 133.60, 130.16, 128.68, 128.46, 128.20, 127.88, 127.33, 126.43, 125.32, 125.08, 123.50, 123.42, 116.77, 116.60, 50.66, 46.76, 36.85, 29.67, 9.63.

HRMS (ESIpos+neg) (m/z): $[M+H]^+$ calculated for $C_{24}H_{24}NO_2Na$ 358.180154; found 358.179870.

***N*-(1-phenyl-2-(9*H*-xanthen-9-yl)ethyl)butyramide** (**3u**, unreported product)



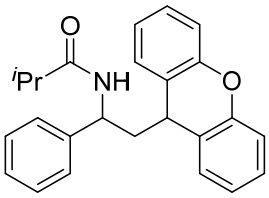
Following the general procedure **B**, white solid (60.1 mg, 81%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.45 (d, J = 8.5 Hz, 1H), 7.40 (dd, J = 7.5 Hz, 6.0 Hz, 1H), 7.35-7.29 (m, 5H), 7.23-7.16 (m, 7H), 4.90-4.80 (m, 1H), 4.07 (dd, J = 9.5 Hz, 4.0 Hz, 1H), 2.27-2.18 (m, 2H), 2.07-2.04 (m, 1H), 1.85-1.70 (m, 1H), 1.66-1.60 (m, 2H), 0.94 (t, J = 7.5 Hz, 3H).

^{13}C NMR (125 MHz, DMSO-d_6) δ 171.97, 152.09, 152.03, 144.08, 129.60, 129.05, 128.75, 128.46, 128.23, 127.11, 126.55, 125.13, 124.05, 123.79, 116.81, 116.53, 49.82, 47.98, 37.95, 36.25, 19.27, 14.15.

HRMS (ESIpos+neg) (m/z): $[M+H]^+$ calculated for $C_{25}H_{26}NO_2$ 372.195804; found 372.195770.

***N*-(1-phenyl-2-(9*H*-xanthen-9-yl)ethyl)*iso*-butyramide** (**3v**, unreported product)



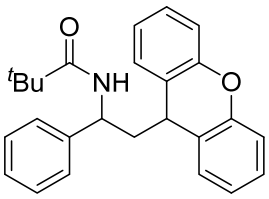
Following the general procedure **B**, white solid (30.4 mg, 41%).

^{1}H NMR (500 MHz, DMSO-d_6) δ 8.35 (d, J = 8.5 Hz, 1H), 7.40 (dd, J = 7.5 Hz, 2.0 Hz, 1H), 7.32-7.26 (m, 1H), 7.25-7.23 (m, 4H), 7.17-7.10 (m, 7H), 4.81-4.76 (m, 1H), 4.01 (dd, J = 9.5 Hz, 4.0 Hz, 1H), 2.06-2.00 (m, 1H), 1.99-1.74 (m, 1H), 1.12 (d, J = 6.5 Hz, 3H), 1.01 (d, J = 6.5 Hz, 3H).

^{13}C NMR (125 MHz, DMSO-d_6) δ 175.97, 152.09, 152.03, 144.12, 129.59, 129.06, 128.78, 128.47, 128.24, 127.09, 126.56, 126.48, 125.14, 124.05, 123.81, 116.81, 116.54, 49.64, 48.06, 36.29, 34.58, 20.30, 19.87.

HRMS (ESIpos) (m/z): M^+ calculated for $C_{25}H_{25}NO_2Na$ 394.177747; found 394.177150.

***N*-(1-phenyl-2-(9*H*-xanthen-9-yl)ethyl)pivalamide** (**3w**, unreported product)



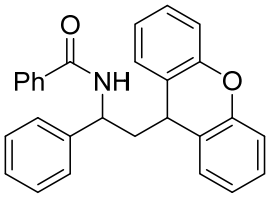
Following the general procedure **B**, white solid (39.2 mg, 51%).

^{1}H NMR (500 MHz, DMSO-d_6) δ 8.01 (d, J = 7.5 Hz, 1H), 7.46 (dd, J = 8.0 Hz, 2.0 Hz, 1H), 7.37-7.34 (m, 1H), 7.33-7.28 (m, 4H), 7.22-7.16 (m, 7H), 4.91-4.88 (m, 1H), 4.02 (dd, J = 10.0 Hz, 4.0 Hz, 1H), 2.27-2.21 (m, 1H), 1.85-1.80 (m, 1H), 1.24 (s, 9H).

^{13}C NMR (125 MHz, DMSO-d_6) δ 177.34, 152.09, 152.03, 144.34, 129.60, 129.20, 128.69, 128.44, 128.22, 126.98, 126.61, 126.46, 125.21, 123.99, 123.80, 116.83, 116.50, 49.87, 47.73, 38.65, 36.42, 27.90.

HRMS (ESIpos+neg) (m/z): $[M+H]^+$ calculated for $C_{26}H_{27}NO_2$ 386.211454; found 386.210940.

***N*-(1-phenyl-2-(9*H*-xanthen-9-yl)ethyl)benzamide** (**3x**, unreported product)



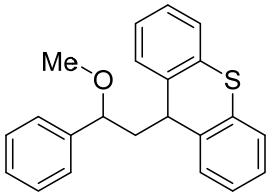
Following the general procedure **B**, white solid (32.4 mg, 40%).

^{1}H NMR (500 MHz, DMSO-d_6) δ 8.94 (d, J = 8.5 Hz, 1H), 7.90-7.88 (m, 2H), 7.56-7.39 (m, 5H), 7.2-7.20 (m, 7H), 7.17-7.11 (m, 4H), 5.04-5.00 (m, 1H), 4.12 (dd, J = 9.5 Hz, 4.5 Hz, 1H), 2.36-2.30 (m, 1H), 1.90-1.85 (m, 1H).

^{13}C NMR (125 MHz, DMSO-d_6) δ 166.46, 152.14, 152.01, 144.05, 134.99, 131.71, 129.60, 129.21, 128.79, 128.71, 128.67, 128.65, 128.44, 128.24, 127.89, 127.82, 127.21, 126.75, 126.50, 126.44, 125.16, 123.99, 123.82, 116.82, 116.53, 50.76, 47.34, 36.49.

HRMS (ESIpos+neg) (m/z): $[M+Na]^+$ calculated for $C_{28}H_{23}NO_2Na$ 428.162098; found 428.162020.

9-(2-methoxy-2-phenylethyl)-9*H*-thioxanthene (**9a**, unreported product)



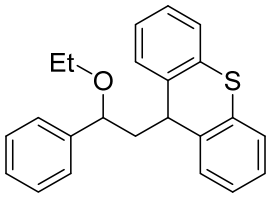
Following the general procedure **C**, white solid (58.6 mg, 91%).

^{1}H NMR (500 MHz, DMSO-d_6) δ 7.51 (dd, J = 7.5 Hz, 1.5 Hz, 1H), 7.43 (dd, J = 8.0 Hz, 1.5 Hz, 1H), 7.41-7.34 (m, 7H), 7.28-7.23 (m, 2H), 7.11-7.10 (m, 2H), 4.43 (dd, J = 10.5 Hz, 5.5 Hz, 1H), 4.07 (dd, J = 10.5 Hz, 3.5 Hz, 1H), 3.08 (s, 3H), 2.01-1.95 (m, 1H), 1.81-1.76 (m, 1H).

^{13}C NMR (125 MHz, DMSO-d_6) δ 141.85, 138.77, 137.04, 131.89, 129.90, 129.01, 128.94, 128.07, 127.50, 127.44, 127.19, 127.11, 126.80, 80.67, 56.17, 45.29, 40.80.

HRMS (ESIpos) (m/z): M^+ calculated for $C_{22}H_{20}OSNa$ 355.112707; found 355.112750.

9-(2-ethoxy-2-phenylethyl)-9*H*-thioxanthene (**9b**, unreported product)



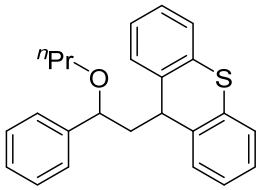
Following the general procedure **C**, colorless oil (50.5 mg, 73%).

^{1}H NMR (500 MHz, DMSO-d_6) δ 7.51 (dd, J = 7.5 Hz, 1.5 Hz, 1H), 7.43 (dd, J = 7.5 Hz, 1.5 Hz, 1H), 7.40-7.22 (m, 9H), 7.11-7.10 (m, 2H), 4.43 (dd, J = 10.5 Hz, 5.5 Hz, 1H), 3.76 (dd, J = 10.0 Hz, 3.0 Hz, 1H), 3.21-3.13 (m, 2H), 2.00-1.95 (m, 1H), 1.80-1.75 (m, 1H), 1.16 (t, J = 6.5 Hz, 3H).

^{13}C NMR (125 MHz, DMSO-d_6) δ 142.57, 138.84, 137.13, 131.95, 131.93, 129.87, 128.99, 128.89, 127.91, 127.50, 127.47, 127.40, 127.20, 127.14, 127.07, 126.61, 79.01, 63.73, 45.44, 40.91, 15.79.

HRMS (EI) (m/z): calculated for $C_{23}H_{22}OS$ 346.139138; found 346.139318.

9-(2-phenyl-2-propoxyethyl)-9*H*-thioxanthene (**9c**, unreported product)



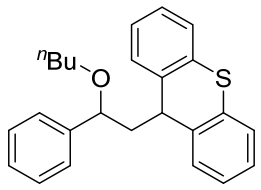
Following the general procedure **C**, colorless oil (67.0 mg, 93%).

^{1}H NMR (500 MHz, DMSO-d_6) δ 7.52-7.50 (m, 1H), 7.44 (dd, J = 7.5 Hz, 1.5 Hz, 1H), 7.40 (dd, J = 7.5 Hz, 1.5 Hz, 1H), 7.36-7.34 (m, 2H), 7.32-7.27 (m, 4H), 7.25-7.21 (m, 2H), 7.11-7.09 (m, 2H), 4.43 (dd, J = 10.5 Hz, 4.5 Hz, 1H), 3.76 (dd, J = 10.0 Hz, 3.0 Hz, 1H), 3.10 (t, J = 6.5 Hz, 2H), 2.01-1.95 (m, 1H), 1.81-1.75 (m, 1H), 1.60-1.53 (m, 2H), 0.93 (t, J = 7.0 Hz, 3H).

^{13}C NMR (125 MHz, DMSO-d_6) δ 142.58, 138.85, 137.14, 131.93, 131.90, 129.83, 128.99, 128.89, 127.92, 127.53, 127.50, 127.42, 127.21, 127.16, 127.09, 126.64, 79.10, 70.03, 45.45, 41.03, 23.20, 11.31.

HRMS (ESIpos) (m/z): M^+ calculated for $C_{24}H_{24}OSNa$ 383.144007; found 383.144320.

9-(2-butoxy-2-phenylethyl)-9*H*-thioxanthene (**9d**, unreported product)



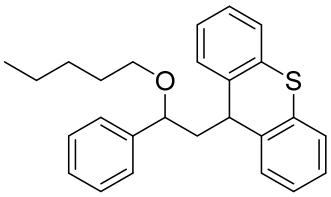
Following the general procedure **C**, Colorless oil (68.8 mg, 92%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37-7.35 (m, 1H), 7.28-7.26 (m, 3H), 7.18-7.05 (m, 9H), 4.41 (dd, J = 11.0 Hz, 4.5 Hz, 1H), 3.70 (dd, J = 10.5 Hz, 3.0 Hz, 1H), 3.21-3.17 (m, 1H), 3.12-3.07 (m, 1H), 2.14-2.09 (m, 1H), 1.80-1.74 (m, 1H), 1.59-1.52 (m, 2H); 1.43-1.36 (m, 2H), 0.89 (t, J = 7.0 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 142.71, 138.98, 137.10, 132.56, 132.39, 129.60, 128.51, 128.25, 127.28, 127.20, 126.83, 126.68, 126.60, 126.46, 126.38, 126.15, 79.21, 68.32, 45.71, 40.82, 32.33, 19.71, 14.08.

HRMS (EI) (m/z): calculated for $C_{25}H_{26}OS$ 374.170438; found 374.170248.

9-(2-(pentyloxy)-2-phenylethyl)-9*H*-thioxanthene (**9e**, unreported product)



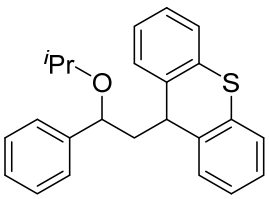
Following the general procedure **C**, Colorless oil (65.1 mg, 84%).

^{1}H NMR (500 MHz, DMSO-d_6) δ 7.57-7.55 (m, 1H), 7.48 (dd, J = 7.5 Hz, 1.5 Hz, 1H), 7.44 (dd, J = 7.5 Hz, 1.5 Hz, 1H), 7.40-7.31 (m, 6H), 7.30-7.25 (m, 2H), 7.16-7.14 (m, 2H), 4.46 (dd, J = 10.5 Hz, 5.5 Hz, 1H), 3.80 (dd, J = 10.0 Hz, 3.5 Hz, 1H), 3.17 (t, J = 6.5 Hz, 2H), 2.05-2.00 (m, 1H), 1.86-1.80 (m, 1H), 1.61-1.57 (m, 2H), 1.42-1.31 (m, 5H), 0.94 (t, J = 7.5 Hz, 3H).

^{13}C NMR (125 MHz, DMSO-d_6) δ 142.58, 138.83, 137.16, 133.70, 131.96, 131.91, 129.78, 129.51, 129.22, 128.97, 128.88, 127.92, 127.53, 127.49, 127.42, 127.21, 127.16, 127.05, 126.64, 79.13, 68.31, 45.46, 41.01, 29.58, 28.45, 22.43, 14.38.

HRMS (ESIpos) (m/z): M^+ calculated for $C_{26}H_{28}OSNa$ 411.175307; found 411.175940.

9-(2-isopropoxy-2-phenylethyl)-9*H*-thioxanthene (**9f**, unreported product)



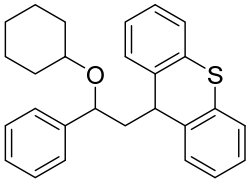
Following the general procedure **C**, colorless oil (49.6 mg, 69%).

^{1}H NMR (500 MHz, DMSO-d_6) δ 7.55 (dd, J = 7.5 Hz, 1.5 Hz, 1H), 7.47 (dd, J = 7.5 Hz, 1.0 Hz, 1H), 7.44-7.41 (m, 2H), 7.39-7.25 (m, 7H), 7.14-7.16 (m, 2H), 4.40 (dd, J = 10.0 Hz, 5.0 Hz, 1H), 4.05 (dd, J = 9.5 Hz, 3.0 Hz, 1H), 3.41-3.39 (m, 1H), 2.06-2.00 (m, 1H), 1.82-1.77 (m, 1H), 1.16 (d, J = 6.0 Hz, 3H), 1.05 (d, J = 6.0 Hz, 3H).

^{13}C NMR (125 MHz, DMSO-d_6) δ 143.36, 139.06, 137.37, 131.99, 131.95, 130.00, 128.93, 128.85, 127.85, 127.57, 127.49, 127.39, 127.24, 127.11, 126.98, 126.71, 76.05, 68.55, 45.40, 41.36, 23.91, 21.66.

HRMS (EI) (m/z): calculated for $C_{24}H_{24}OS$ 360.154787; found 360.154395.

9-(2-(cyclohexyloxy)-2-phenylethyl)-9*H*-thioxanthene (**9g**, unreported product)



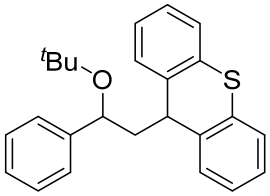
Following the general procedure **C**, colorless oil (22.4 mg, 28%).

^{1}H NMR (500 MHz, DMSO-d_6) δ 7.50 (dd, J = 7.0 Hz, 1.0 Hz, 1H), 7.43 (dd, J = 7.5 Hz, 1.5 Hz, 1H), 7.39-7.34 (m, 2H), 7.33-7.24 (m, 5H), 7.23-7.20 (m, 2H), 7.12-7.10 (m, 2H), 4.35 (dd, J = 10.0 Hz, 4.5 Hz, 1H), 4.09 (dd, J = 9.5 Hz, 3.0 Hz, 1H), 3.08-3.04 (m, 1H), 2.01-1.95 (m, 1H), 1.90-1-87 (m, 1H), 1.78-1.71 (m, 2H), 1.61-1.56 (m, 2H), 1.45-1.42 (m, 1H), 1.35-1.30 (m, 1H), 1.25-1.03 (m, 4H).

^{13}C NMR (125 MHz, DMSO-d_6) δ 143.59, 139.11, 137.51, 132.00, 131.93, 129.82, 129.51, 129.17, 128.88, 128.84, 127.81, 127.60, 127.51, 127.37, 127.24, 127.12, 127.03, 126.64, 75.93, 74.77, 45.44, 41.62, 33.72, 31.79, 25.78, 24.28, 24.19.

HRMS (EI) (m/z): calculated for $C_{27}H_{28}OS$ 400.186088; found 400.185978.

9-(2-(tert-butoxy)-2-phenylethyl)-9*H*-thioxanthene (**9h**, unreported product)



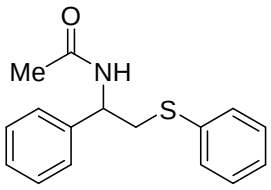
Following the general procedure **C**, colorless oil (30.0 mg, 40%).

^{1}H NMR (500 MHz, DMSO-d_6) δ 7.42-7.37 (m, 2H), 7.24-7.14 (m, 11H), 4.19 (dd, J = 7.0 Hz, 5.5 Hz, 1H), 3.99 (dd, J = 7.5 Hz, 6.0 Hz, 1H), 1.92-1.82 (m, 2H), 0.92 (s, 9H).

^{13}C NMR (125 MHz, DMSO-d_6) δ 145.65, 138.95, 138.57, 132.18, 132.13, 129.06, 128.93, 128.72, 127.54, 127.48, 127.36, 127.32, 127.20, 127.16, 127.11, 126.86, 74.35, 72.08, 45.23, 42.29, 29.13.

HRMS (EI) (m/z): calculated for $C_{25}H_{26}OS$ 374.170438; found 374.170366.

***N*-(1-phenyl-2-(phenylsulfinyl)ethyl)acetamide** (**11a**, CAS: 98289-63-5)



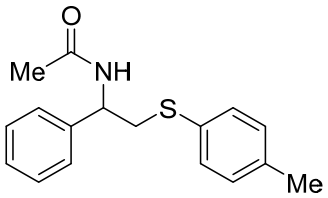
Following the general procedure **D**, light yellow oil (35.0 mg, 61%).

^{1}H NMR (500 MHz, DMSO-d_6) δ 8.46 (d, J = 8.0 Hz, 1H), 7.37-7.31 (m, 8H), 7.28-7.25 (m, 1H), 7.22-7.19 (m, 1H), 4.94 (dd, J = 15.5 Hz, 7.5 Hz, 1H), 3.27 (d, J = 7.0 Hz, 2H), 1.85 (s, 3H).

^{13}C NMR (125 MHz, DMSO-d_6) δ 169.09, 142.24, 136.41, 129.71, 129.53, 129.02, 128.81, 128.74, 127.69, 127.23, 126.25, 52.34, 38.90, 23.10.

HRMS (ESIpos) (m/z): $[M-H]^-$ calculated for $C_{16}H_{17}NOS$ 270.095811; found 270.095880.

***N*-(1-phenyl-2-(*p*-tolylthio)ethyl)acetamide** (**11b**, CAS: 1820957-34-3)



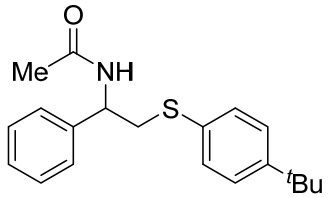
Following the general procedure **D**, colorless oil (25.6 mg, 45%).

^{1}H NMR (500 MHz, DMSO-d_6) δ 8.44 (d, J = 8.5 Hz, 1H), 7.49-7.25 (m, 7H), 7.14 (d, J = 8.0 Hz, 1H), 4.90 (dd, J = 15.0 Hz, 7.5 Hz, 1H), 3.32 (d, J = 7.5 Hz, 2H), 2.82 (s, 3H), 1.85 (s, 3H).

^{13}C NMR (125 MHz, DMSO-d_6) δ 169.09, 142.36, 135.98, 133.31, 132.54, 130.18, 129.65, 129.02, 128.79, 127.63, 127.19, 52.32, 39.00, 23.11, 21.01.

HRMS (ESIpos) (m/z): M^+ calculated for $C_{17}H_{19}NOSNa$ 308.107956; found 308.107750.

***N*-(2-((4-(tert-butyl)phenyl)thio)-1-phenylethyl)acetamide** (**11c**, unreported product)



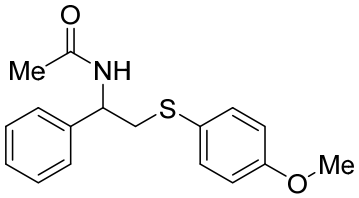
Following the general procedure **D**, colorless oil (35.1 mg, 54%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25-7.18 (m, 9H), 5.87 (d, J = 7.5 Hz, 1H), (m, 7H), 5.13 (dd, J = 13.5 Hz, 6.0 Hz, 1H), 3.31-3.21 (m, 2H), 1.87 (s, 3H), 1.22 (s, 9H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 169.53, 149.96, 140.35, 131.85, 130.14, 130.11, 128.72, 128.42, 127.79, 126.58, 126.17, 53.06, 40.24, 34.50, 31.25, 23.28.

HRMS (ESIpos) (m/z): M^+ calculated for $C_{20}H_{25}OSNa$ 350.154905; found 350.154770.

***N*-(2-((4-methoxyphenyl)thio)-1-phenylethyl)acetamide** (**11d**, CAS: 141248-72-8)



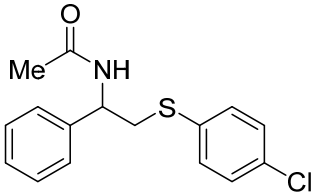
Following the general procedure **D**, colorless oil (30.1 mg, 50%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28-7.22 (m, 4H), 7.20-7.15 (m, 3H), 5.93 (d, J = 8.0 Hz, 1H), 5.02 (dd, J = 13.5 Hz, 7.0 Hz, 1H), 3.71 (s, 3H), 3.19-3.11 (s, 3H), 1.90 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 169.50, 159.25, 140.51, 133.64, 128.71, 127.74, 126.56, 125.42, 114.77, 55.35, 52.95, 41.81, 23.33.

HRMS (ESIpos) (m/z): [M] calculated for $C_{17}H_{19}NO_2S$ 301.113110; found 301.113101.

***N*-(2-((4-chlorophenyl)thio)-1-phenylethyl)acetamide** (**11e**, CAS: 1883670-31-2)

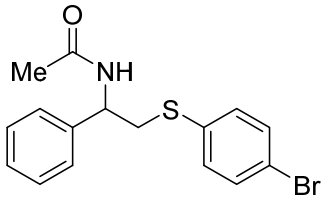


Following the general procedure **D**, colorless oil (24.7 mg, 42%).

^{1}H NMR (500 MHz, DMSO-d_6) δ 8.45 (d, J = 7.5 Hz, 1H), 7.37 (s, 4H), 7.35-7.31 (m, 4H), 7.28-7.25 (m, 4H), 7.28-7.25 (m, 1H), 4.95-4.91 (m, 1H), 3.30-3.24 (m, 2H), 1.84 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 169.12, 142.06, 130.89, 130.47, 129.40, 128.82, 127.74, 127.25, 52.20, 38.93, 23.08.

HRMS (ESIpos) (m/z): M^+ calculated for $C_{16}H_{16}ClNOSNa$ 328.053333; found 328.052790.



***N*-(2-((4-bromophenyl)thio)-1-phenylethyl)acetamide** (**11f**, CAS: 1883670-32-3)

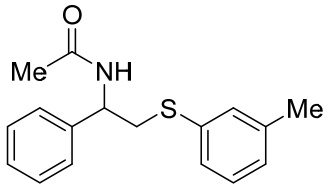
Following the general procedure **D**, colorless oil (34.3 mg, 49%).

^{1}H NMR ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32-7.34 (m, 2H), 7.28-7.25 (m, 2H), 7.27-7.22 (m, 1H), 7.19-7.17 (m, 2H), 7.16-7.14 (m, 2H), 5.80 (d, J = 7.5 Hz, 1H), 5.09 (dd, J = 14.0 Hz, 7.0 Hz, 1H), 3.37 (dd, J = 13.5 Hz, 6.5 Hz, 1H), 3.20 (dd, J = 13.5 Hz, 6.5 Hz, 1H), 1.92 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 169.50, 139.80, 132.06, 131.19, 128.88, 128.09, 126.70, 120.36, 52.94, 39.45, 23.34.

HRMS (ESIpos) (m/z): M^+ calculated for $C_{16}H_{16}BrNOSNa$ 372.002830; found 372.002510.

***N*-(1-phenyl-2-(*m*-tolylthio)ethyl)acetamide** (**11g**, CAS: 1883670-29-8)



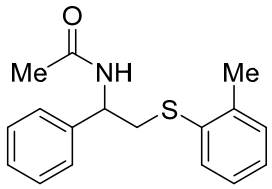
Following the general procedure **D**, colorless oil (30.2 mg, 53%).

^{1}H NMR (500 MHz, DMSO-d_6) δ 8.45 (d, J = 8.0 Hz, 1H), 7.34-7.31 (m, 4H), 7.27-7.25 (m, 1H), 7.20 (t, J = 7.5 Hz, 1H), 7.16-7.13 (m, 2H), 7.01-7.00 (m, 1H), 4.96-4.93 (m, 1H), 3.26 (d, J = 7.5 Hz, 2H), 2.28 (s, 3H), 1.85 (s, 3H).

^{13}C NMR (125 MHz, DMSO-d_6) δ 169.10, 142.25, 138.84, 136.19, 129.71, 129.43, 129.12, 129.02, 128.80, 127.69, 127.24, 126.98, 125.70, 52.40, 38.82, 23.09, 21.35.

HRMS (ESIpos) (m/z): M^+ calculated for $C_{17}H_{19}NOSNa$ 308.107955; found 308.107310.

***N*-(1-phenyl-2-(o-tolylthio)ethyl)acetamide** (**11h**, CAS: 1820957-37-6)



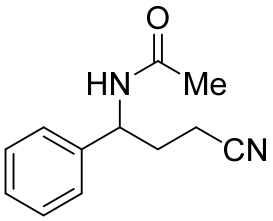
Following the general procedure **D**, colorless oil (20.1 mg, 39%).

^{1}H NMR (500 MHz, DMSO-d_6) δ 8.47 (d, J = 8.0 Hz, 1H), 7.39-7.37 (m, 1H), 7.36-7.31 (m, 4H), 7.28-7.25 (m, 1H), 7.16-7.13 (m, 1H), 7.21-7.18 (m, 2H), 7.13-7.10 (m, 1H), 4.94 (dd, J = 15.5 Hz, 7.5 Hz, 1H), 3.26 (d, J = 1.0 Hz, 2H), 2.25 (s, 3H), 1.86 (s, 3H).

^{13}C NMR (125 MHz, DMSO-d_6) δ 169.09, 142.30, 136.98, 135.60, 130.46, 128.81, 128.01, 127.70, 127.21, 127.13, 126.04, 52.32, 38.55, 23.10, 20.41.

HRMS (ESIpos) (m/z): M^+ calculated for $C_{17}H_{19}NOSNa$ 308.107955; found 308.107620.

***N*-(3-cyano-1-phenylpropyl)acetamide** (**13**, CAS: 2127514-83-2)



Following the general procedure **E**, using *p*-bromo-*N*,*N*-dimethylaniline as initiator; isolated as a white solid (48.5 mg, 48%).

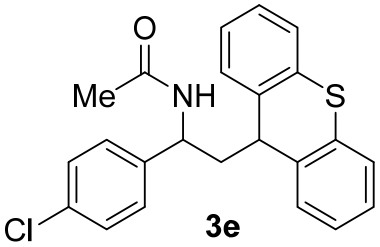
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38-7.35 (m, 2H), 7.32-7.30 (m, 1H), 7.27-7.26 (m, 2H), 5.90 (d, J = 8.0 Hz, 1H), 5.04 (dd, J = 15.5 Hz, 8.0 Hz, 1H), 2.37-2.31 (m, 2H), 2.27-2.22 (m, 1H), 2.15-2.10 (m, 1H), 1.99 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 169.85, 139.83, 129.21, 128.34, 126.55, 119.26, 52.90, 31.66, 23.37, 14.54.

HRMS (ESIpos) (m/z): M^+ calculated for $C_{12}H_{14}N_2O$ 202.110063; found 202.109890.

X-ray study

Single crystals of **3e** were crystallized from CH_3CN.



3e

Table 1. Crystal data and structure refinement.

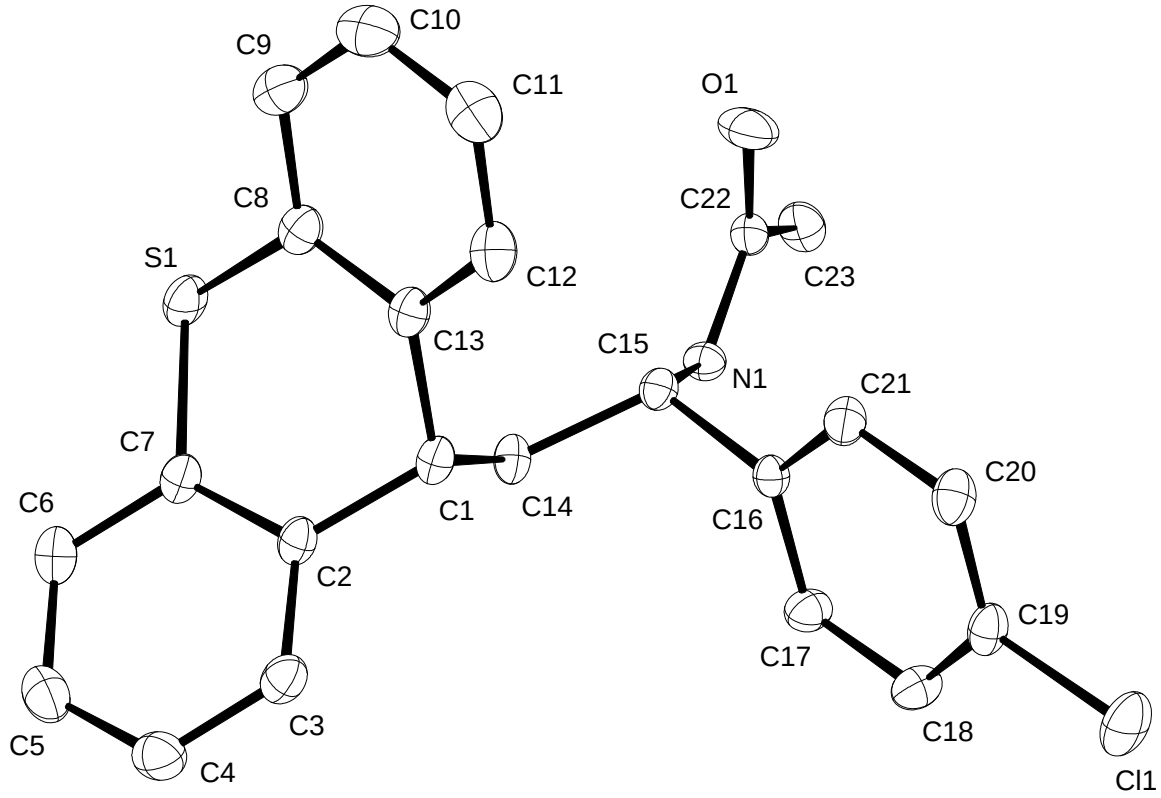
Identification code	CCDC 1957001	
Empirical formula	$C_{23}H_{20}ClNOS$	
Color	colourless	
Formula weight	393.91 $g \cdot mol^{-1}$	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	MONOCLINIC	
Space group	**$P2_1/n$, (no. 14)**	
Unit cell dimensions	a = 13.3178(19) Å	α= 90°.
	b = 9.6266(14) Å	β= 106.661(5)°.
	c = 15.545(2) Å	γ= 90°.
Volume	1909.2(5) $Å^3$	
Z	4	
Density (calculated)	1.370 $Mg \cdot m^{-3}$	
Absorption coefficient	0.322 mm^{-1}	
F(000)	824 e	

Crystal size	0.128 x 0.100 x 0.040 mm^3	
θ range for data collection	2.381 to 31.679°.	
Index ranges	$-19 \leq h \leq 19$, $-14 \leq k \leq 14$, $-22 \leq l \leq 22$	
Reflections collected	53315	
Independent reflections	6405 [$R_{int} = 0.0286$]	
Reflections with $I>2\sigma(I)$	5548	
Completeness to $\theta = 25.242°$	99.9 %	
Absorption correction	Gaussian	
Max. and min. transmission	0.99 and 0.96	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6405 / 0 / 257	
Goodness-of-fit on F^2	1.035	
Final R indices [$I>2\sigma(I)$]	$R_1 = 0.0343$	$wR^2 = 0.0889$
R indices (all data)	$R_1 = 0.0413$	$wR^2 = 0.0930$
Largest diff. peak and hole	0.5 and -0.3 $e \cdot Å^{-3}$	

Table 2. Bond lengths [Å] and angles [°].

Cl(1)-C(19)	1.7418(10)	S(1)-C(7)	1.7638(11)
S(1)-C(8)	1.7666(11)	O(1)-C(22)	1.2366(13)
N(1)-C(15)	1.4632(13)	N(1)-C(22)	1.3377(13)
C(1)-C(2)	1.5095(14)	C(1)-C(13)	1.5111(14)
C(1)-C(14)	1.5479(14)	C(2)-C(3)	1.3946(15)
C(2)-C(7)	1.3983(13)	C(3)-C(4)	1.3911(16)
C(4)-C(5)	1.3894(17)	C(5)-C(6)	1.3869(17)
C(6)-C(7)	1.3965(15)	C(8)-C(9)	1.3941(16)
C(8)-C(13)	1.4003(14)	C(9)-C(10)	1.3849(18)
C(10)-C(11)	1.3900(19)	C(11)-C(12)	1.3878(17)
C(12)-C(13)	1.3959(15)	C(14)-C(15)	1.5312(13)
C(15)-C(16)	1.5184(13)	C(16)-C(17)	1.3978(13)
C(16)-C(21)	1.3905(14)	C(17)-C(18)	1.3893(14)
C(18)-C(19)	1.3837(15)	C(19)-C(20)	1.3793(16)
C(20)-C(21)	1.3931(15)	C(22)-C(23)	1.5063(15)
C(7)-S(1)-C(8)	100.13(5)	C(22)-N(1)-C(15)	122.68(8)
C(2)-C(1)-C(13)	111.05(8)	C(2)-C(1)-C(14)	108.92(8)
C(13)-C(1)-C(14)	111.19(8)	C(3)-C(2)-C(1)	121.46(9)
C(3)-C(2)-C(7)	118.43(9)	C(7)-C(2)-C(1)	120.08(9)
C(4)-C(3)-C(2)	121.16(10)	C(5)-C(4)-C(3)	119.71(11)
C(6)-C(5)-C(4)	120.06(10)	C(5)-C(6)-C(7)	119.98(10)
C(2)-C(7)-S(1)	121.05(8)	C(6)-C(7)-S(1)	118.34(8)
C(6)-C(7)-C(2)	120.60(10)	C(9)-C(8)-S(1)	118.34(8)
C(9)-C(8)-C(13)	120.77(10)	C(13)-C(8)-S(1)	120.89(8)
C(10)-C(9)-C(8)	120.06(11)	C(9)-C(10)-C(11)	119.95(11)
C(12)-C(11)-C(10)	119.76(11)	C(11)-C(12)-C(13)	121.35(10)
C(8)-C(13)-C(1)	120.18(9)	C(12)-C(13)-C(1)	121.76(9)
C(12)-C(13)-C(8)	118.05(10)	C(15)-C(14)-C(1)	113.85(8)
N(1)-C(15)-C(14)	108.99(8)	N(1)-C(15)-C(16)	109.44(7)
C(16)-C(15)-C(14)	113.53(8)	C(17)-C(16)-C(15)	120.63(8)
C(21)-C(16)-C(15)	120.59(9)	C(21)-C(16)-C(17)	118.68(9)

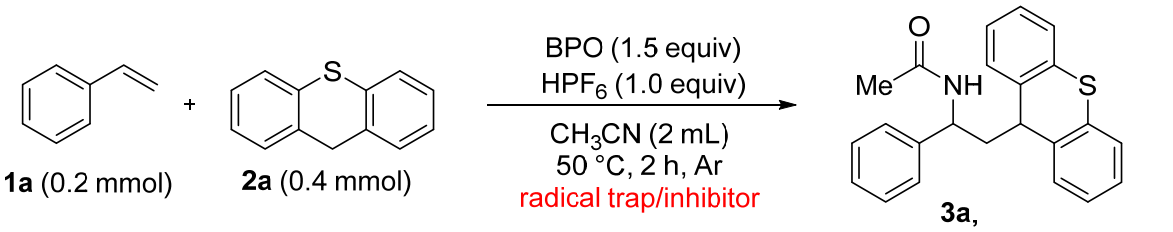
C(18)-C(17)-C(16)	121.00(9)	C(19)-C(18)-C(17)	118.73(10)
C(18)-C(19)-Cl(1)	119.27(8)	C(20)-C(19)-Cl(1)	118.97(8)
C(20)-C(19)-C(18)	121.75(9)	C(19)-C(20)-C(21)	118.89(10)
C(16)-C(21)-C(20)	120.94(10)	O(1)-C(22)-N(1)	123.02(10)
O(1)-C(22)-C(23)	121.39(9)	N(1)-C(22)-C(23)	115.59(9)



ORTEP diagram of the X-ray structure of **3e**. Displacement ellipsoids are drawn at the 50% probability level.

Mechanistic studies:

Radical trapping experiment:

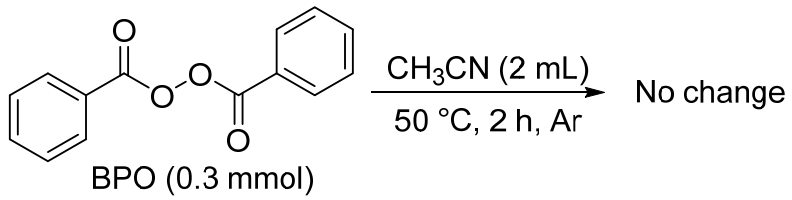


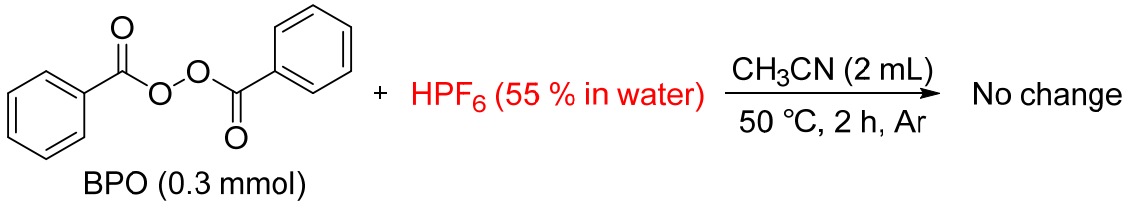
TEMPO: 15%
2,4,6-tri-*tert*-butylphenol: 10%

Under the optimization reaction condition, TEMPO or 2,4,6-tri-*tert*-butylphenol (3.0 equiv.) were added. After the reaction was fully completed, the mixture was cooled to room temperature and concentrated under reduced pressure to give a crude product. Yields were determined by ^{1}H NMR spectroscopic analysis of the crude reaction mixture relative to the internal standard CH_3NO_2. TEMPO and 2,4,6-tri-*tert*-butylphenol reduced the yield significantly, which proves that this reaction might go through the radical procedure.

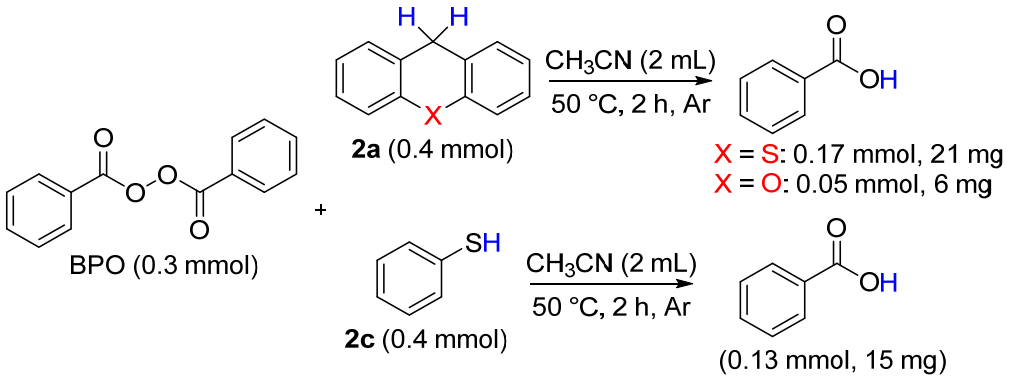
Investigation of the initiation step:

These experiments were performed in a Schlenk tube under Ar and analyze directly without any workup. Yields were determined by ^{1}H NMR spectroscopic analysis of the crude reaction mixture relative to the internal standard CH_3NO_2.

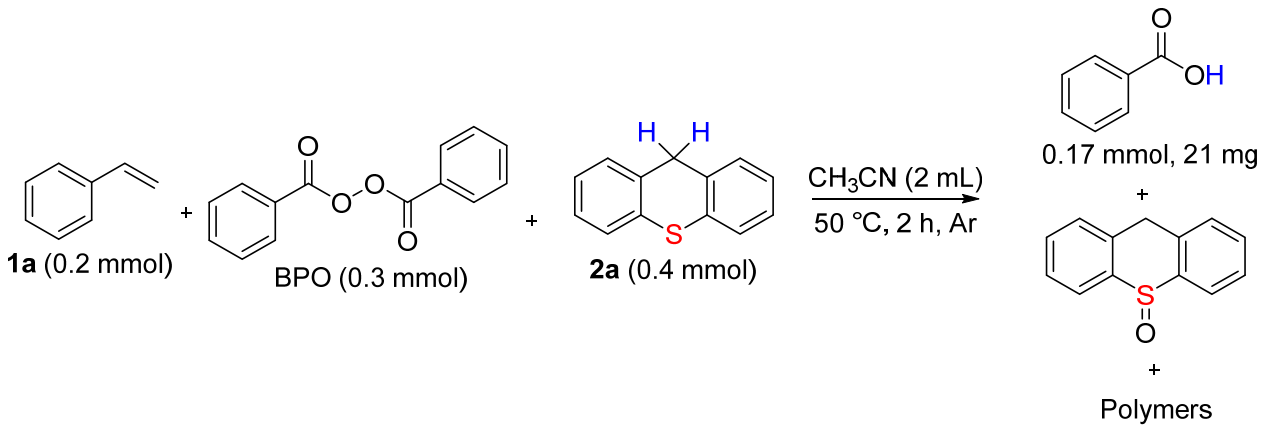




BPO with or without acid in acetonitrile at 50 °C for 2 h did not change, this acid apparently does not affect the decomposition of BPO.

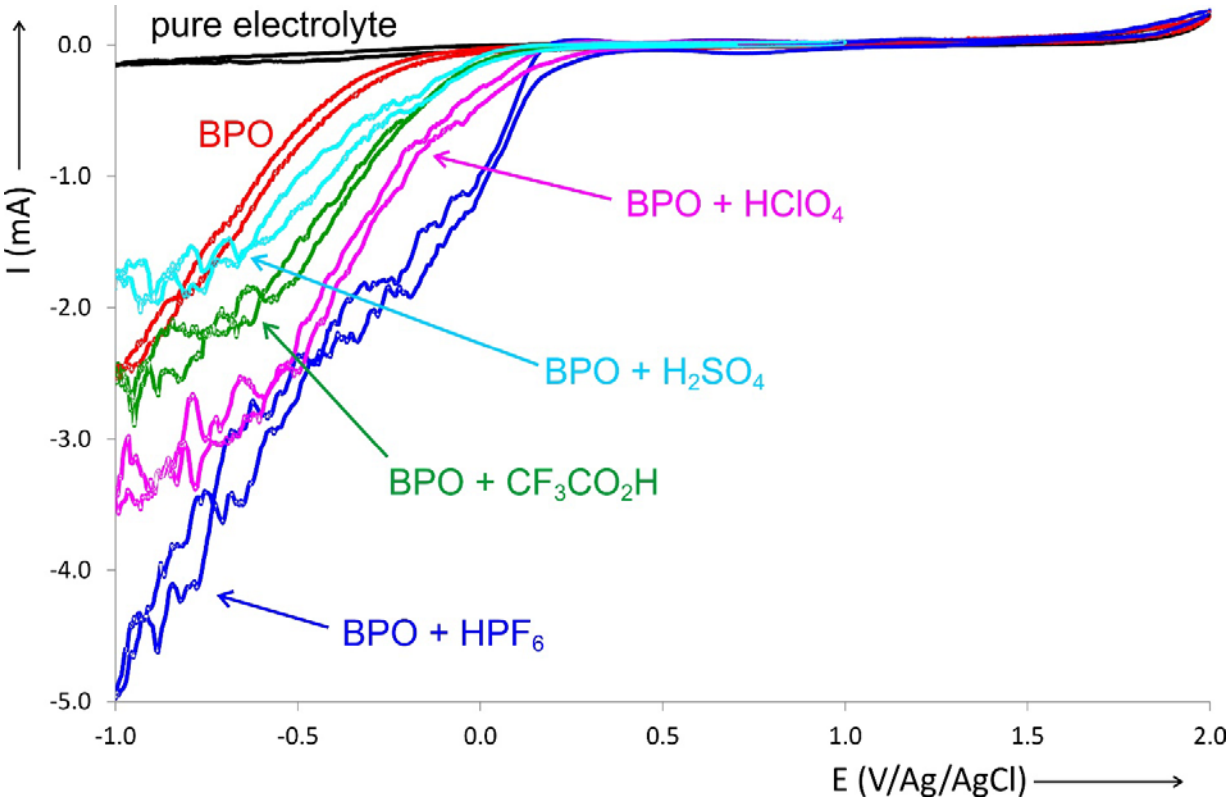


In the presence of thioxanthene, xanthene or thiolphenols, benzoic acid was formed in significant amounts under these conditions, indicating that thioxanthene, xanthene and thiolphenols can accelerate the peroxide decomposition.



In the absence of acid, the product was not formed, indicating that the electron transfer (ET) steps are facilitated by the effect of acid.

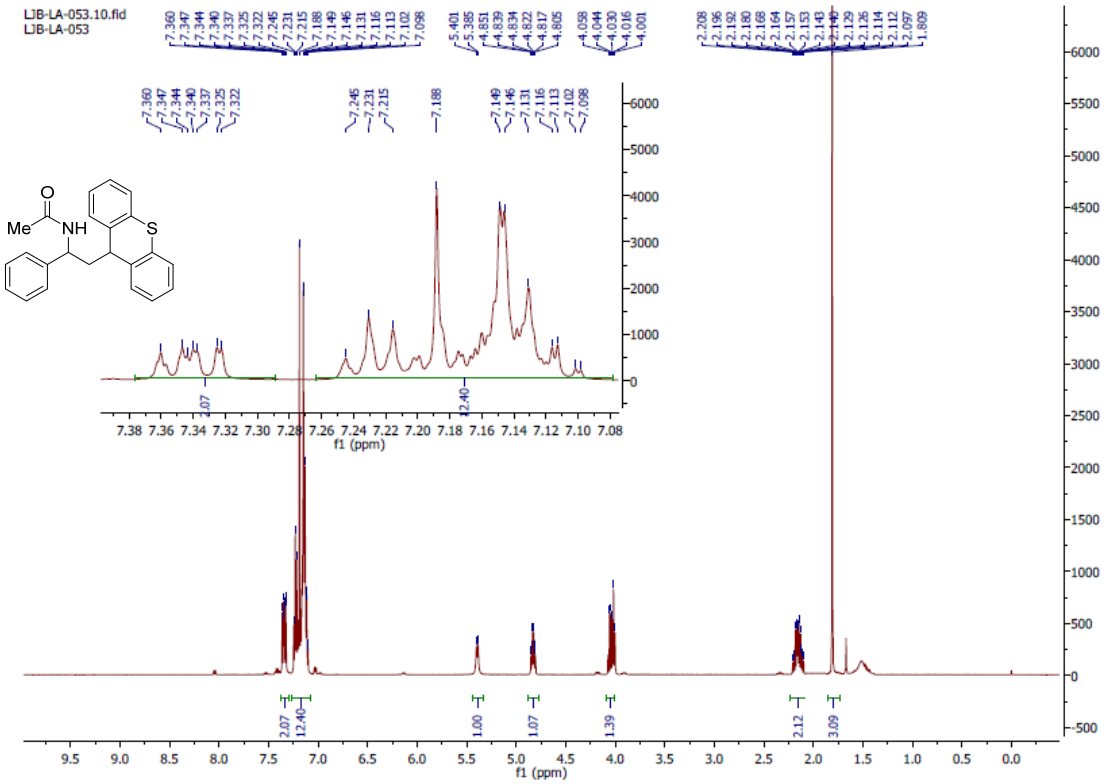
Cyclic Voltammetry of BPO in the presence of different acids

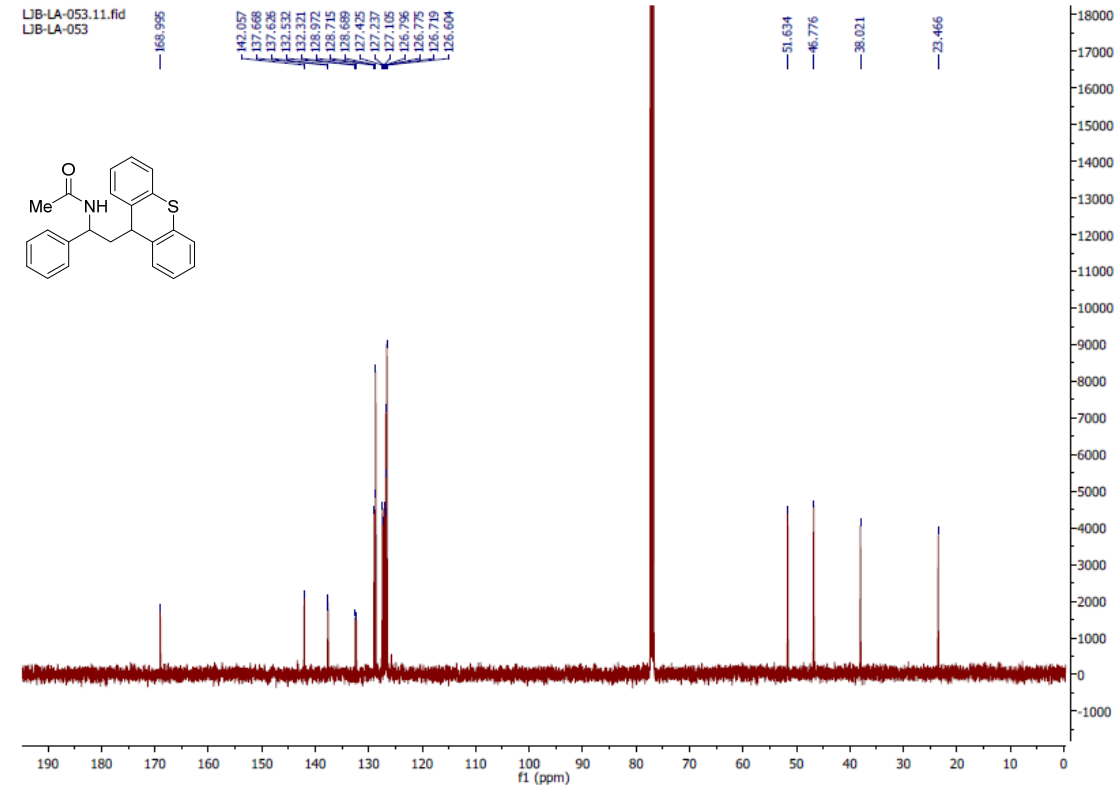


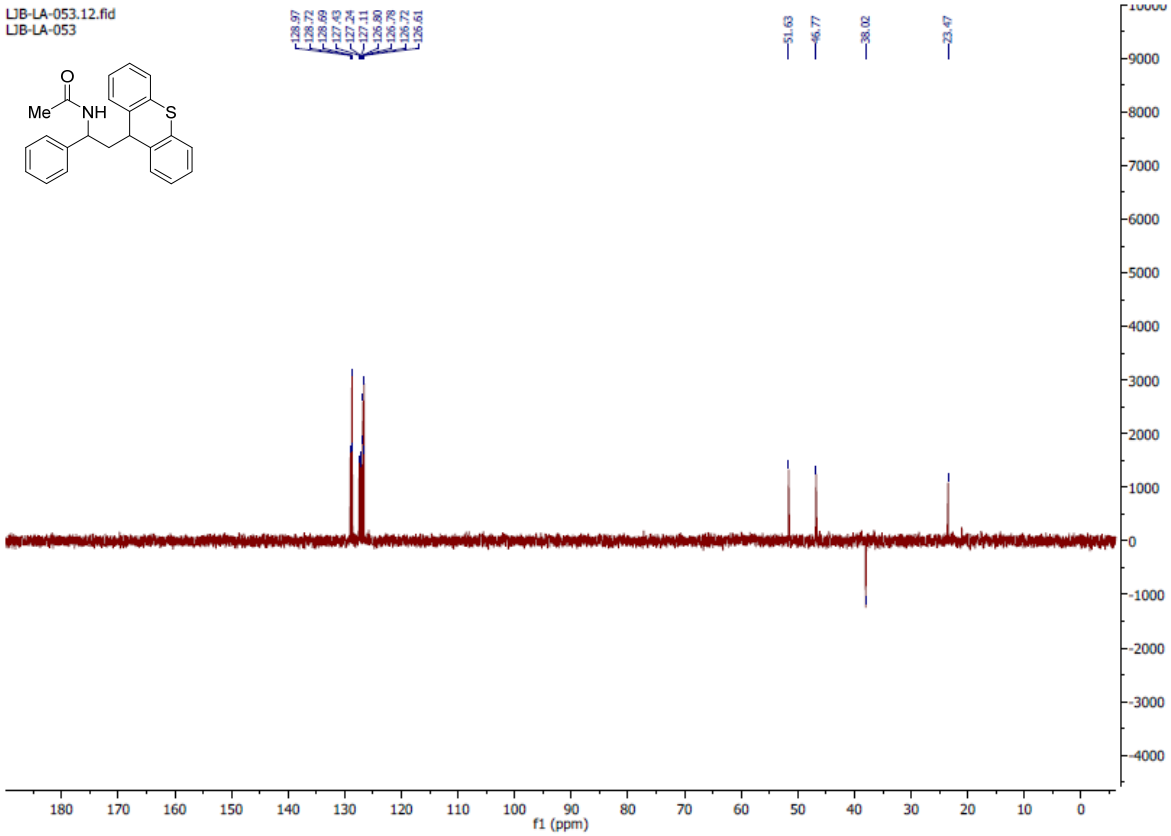
Cyclic voltammograms showing the effect of acid addition on the reduction potential of BPO. Two platinized Pt wires as a counter and working electrode with a Ag/AgCl electrode as a reference were used. The cyclic voltammetry (CV) was conducted from -1.0 V to 2.0 V with a scan rate of 100 mV/s. BPO (0.3 mmol), acid (0.2 mmol), tBu_4NPF_6 (0.1 M) in CH_3CN, under a stream of Ar.

The BPO can be reduced at -345 mV. With the addition of the HPF_6, the reduction process becomes much easier. The reduction potential of the BPO is shifted by around 470 mV, which means the acid addition is favorable for the BPO reduction. Other acid like H_2SO_4, $HClO_4$ and CF_3COOH induce a smaller shift. Apparently, the shift in the reduction potential of BPO is connected with the pKa of the acid.

^{1}H, ^{13}C and DEPT 135 NMR Spectra of the Products



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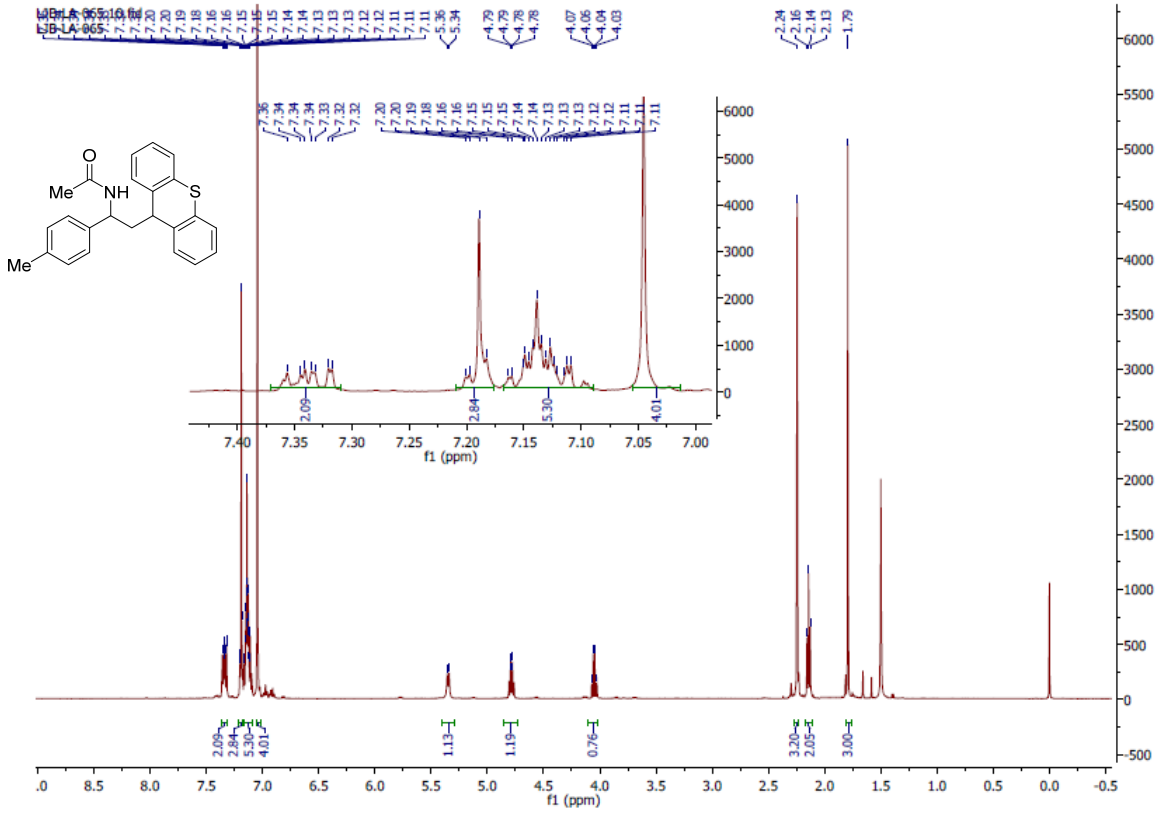
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S
Me
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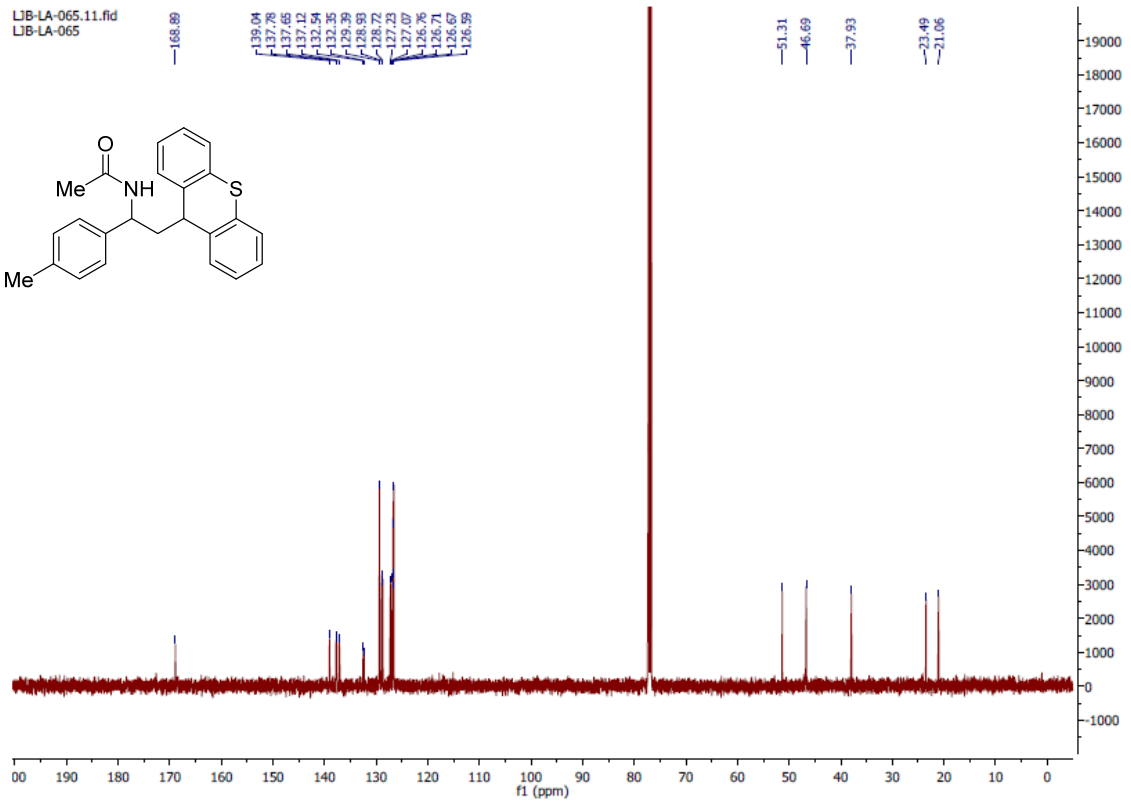
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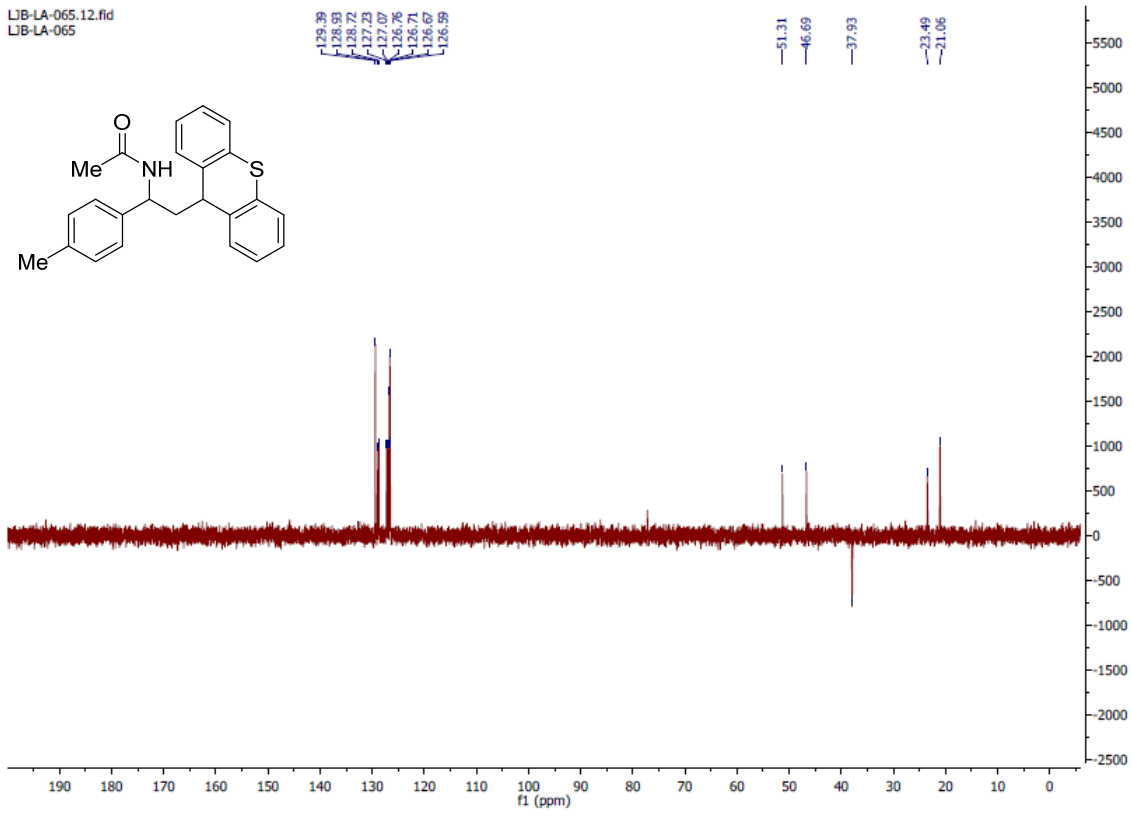
S
Me
f1 (ppm)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46.69
37.93
23.49
21.06
O
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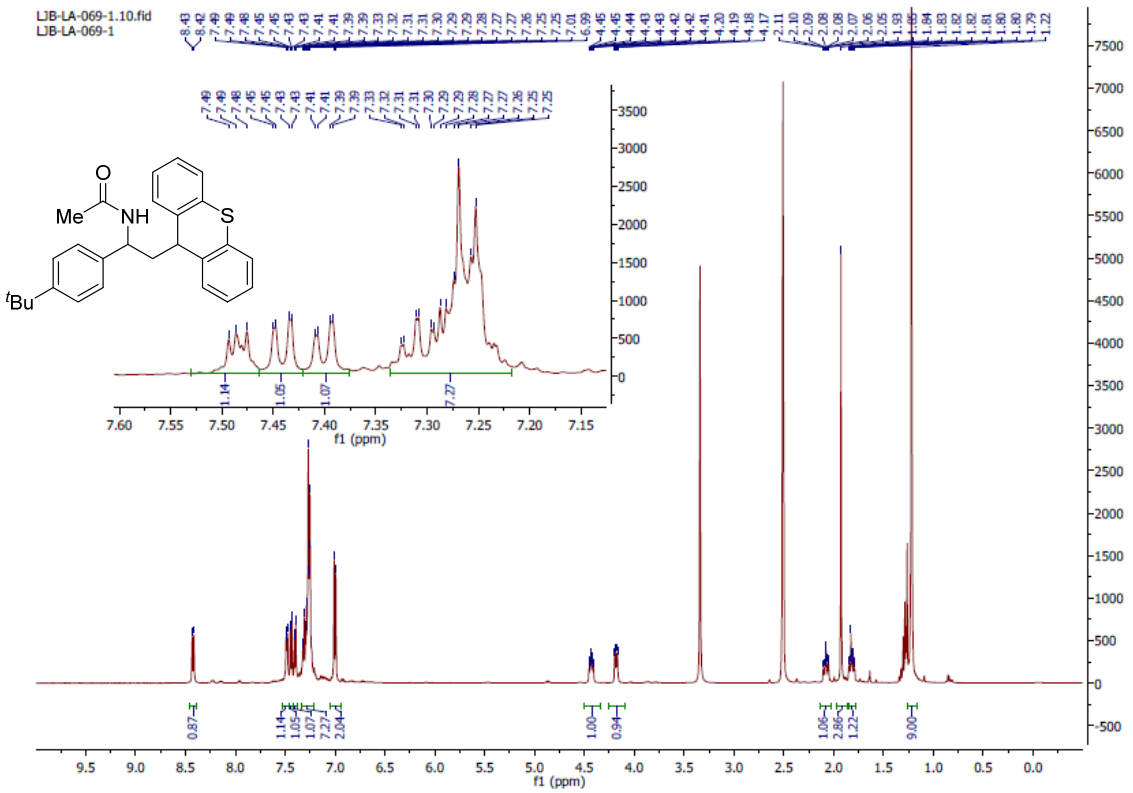
NH
S
Me
f1 (ppm)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O
S
tBu
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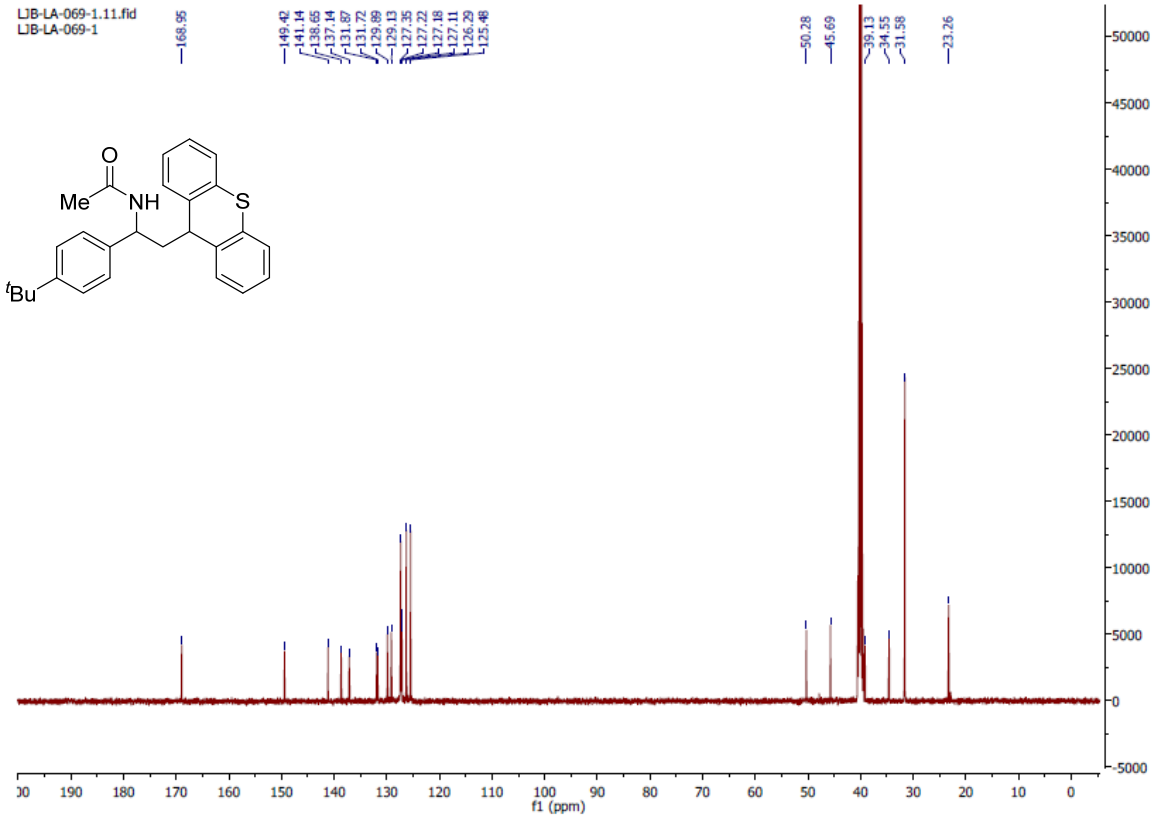
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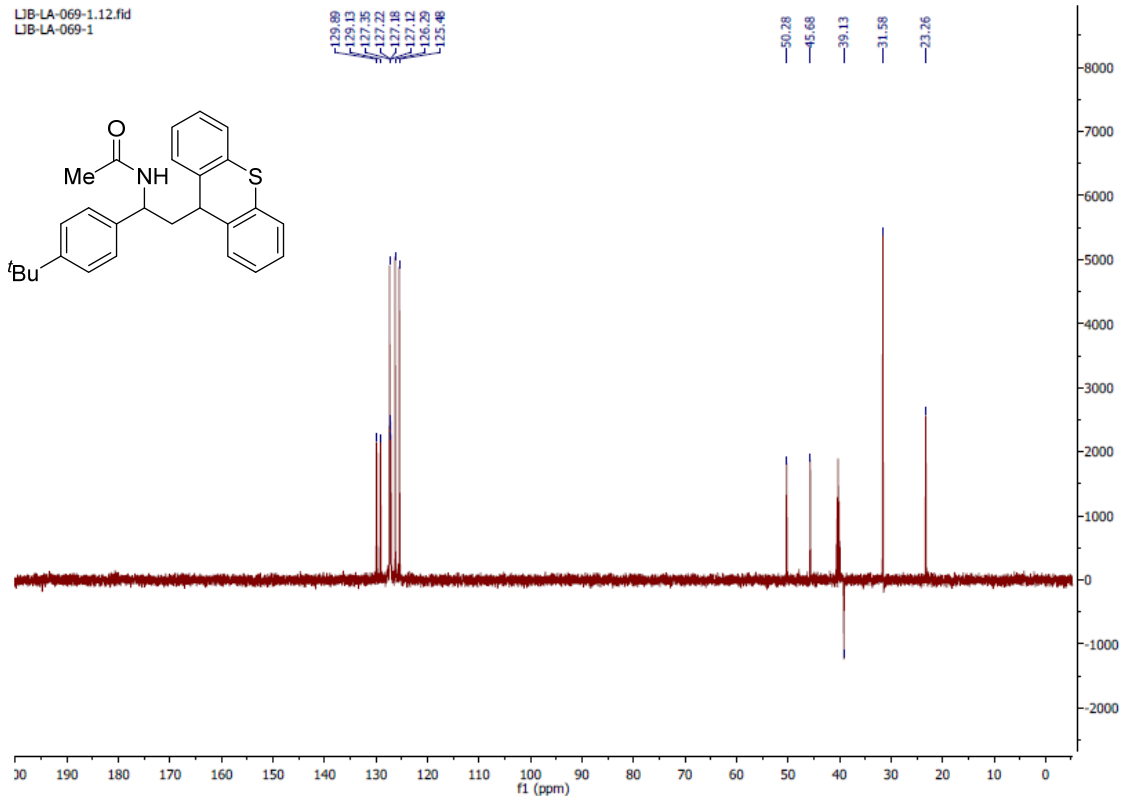
O
S
tBu
f1 (ppm)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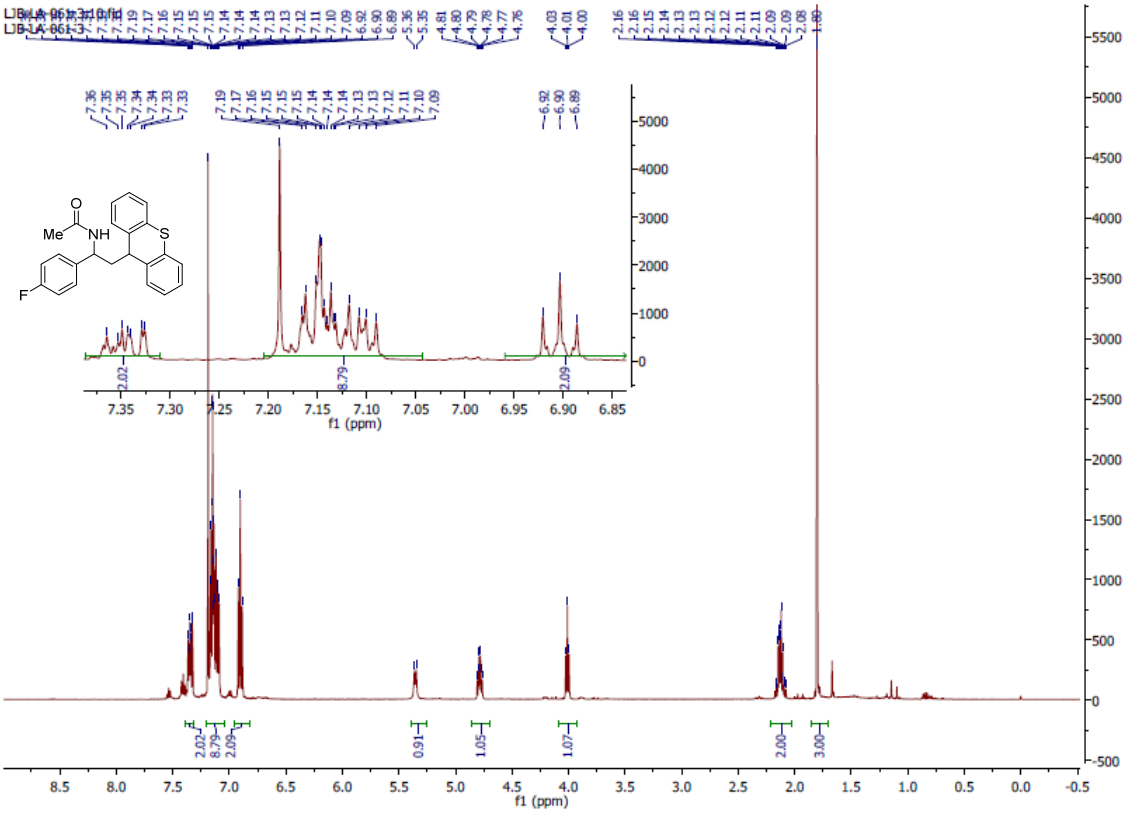
31.58
23.26
O
Me
NH
S
tBu
f1 (ppm)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S
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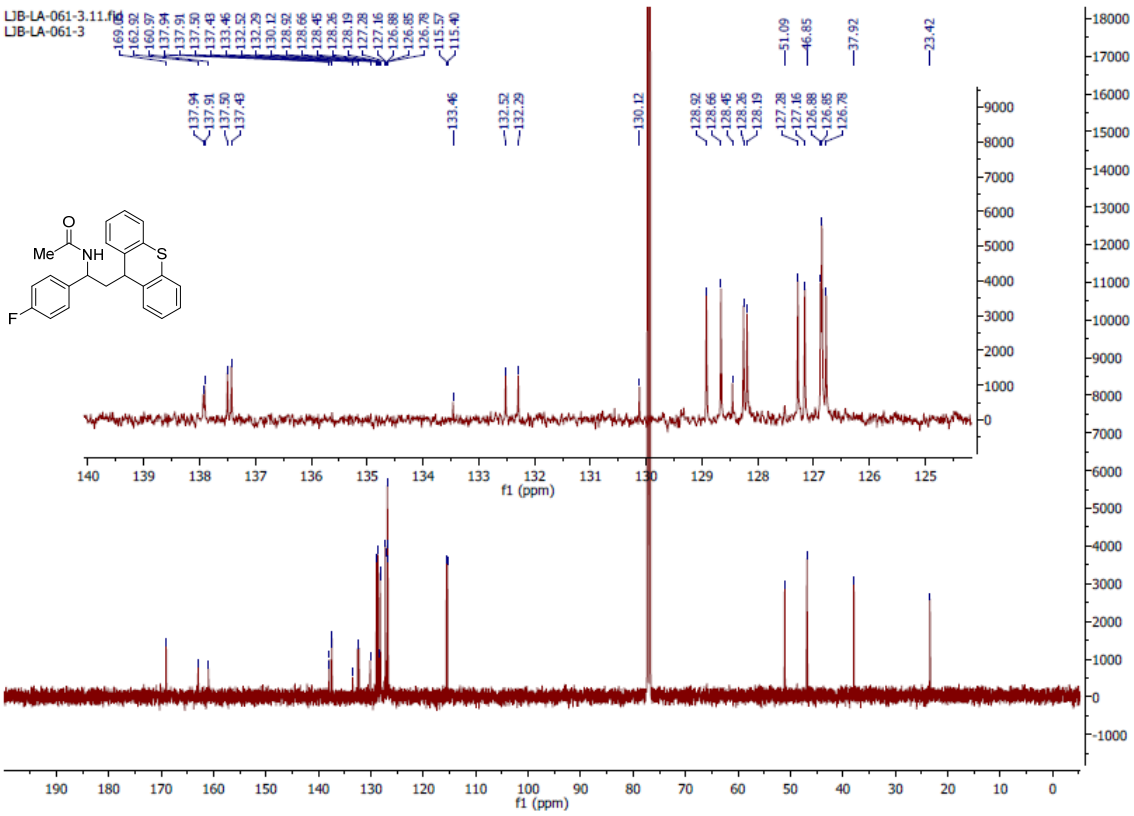
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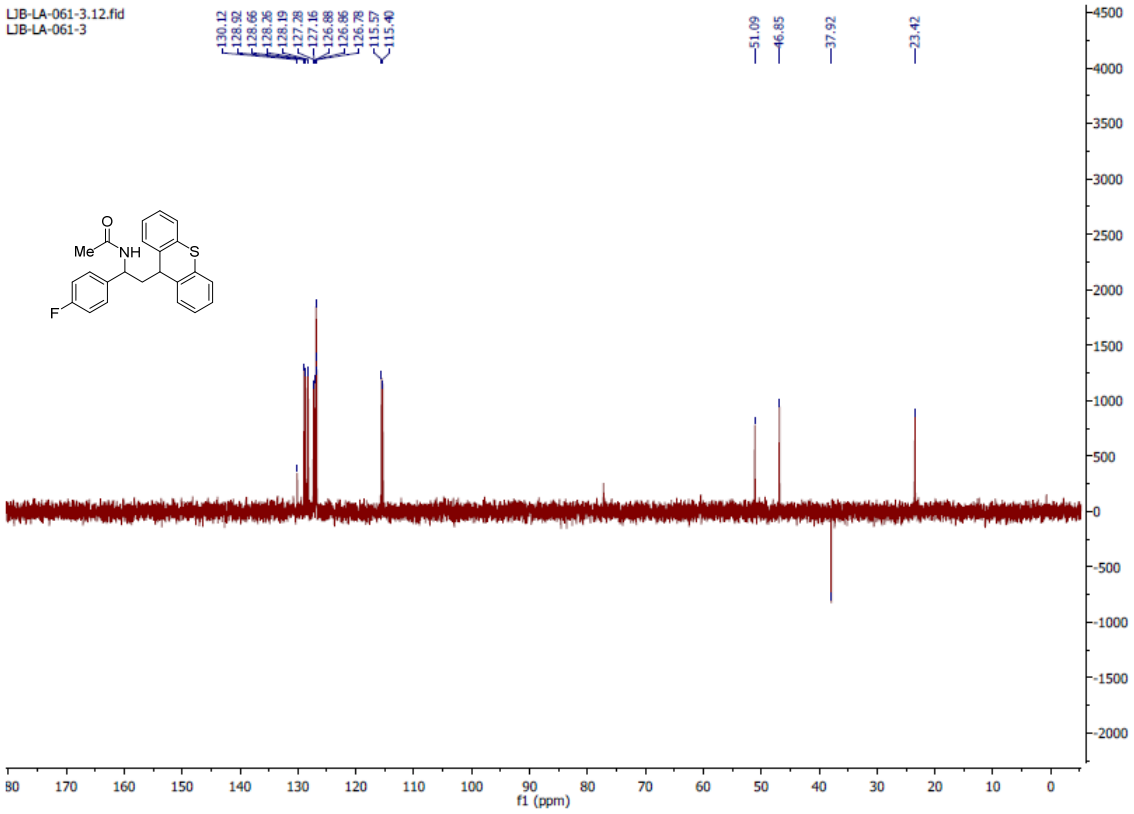
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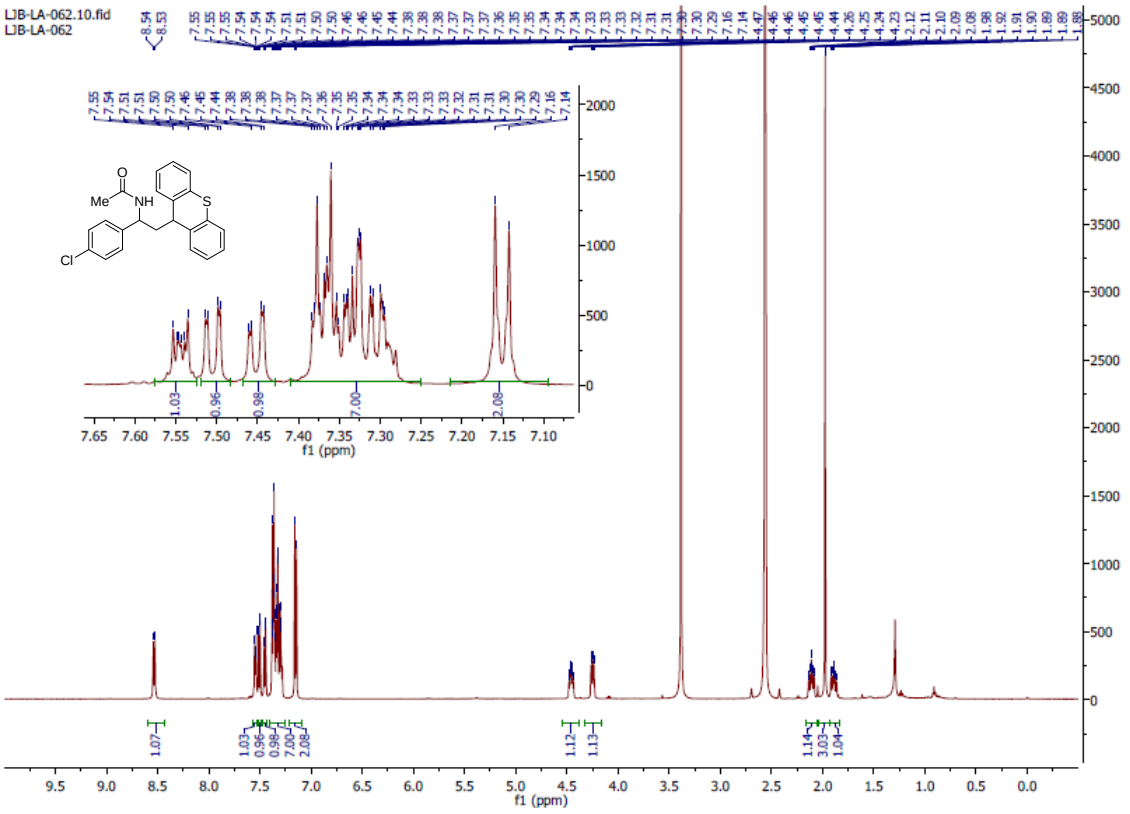
F
f1 (ppm)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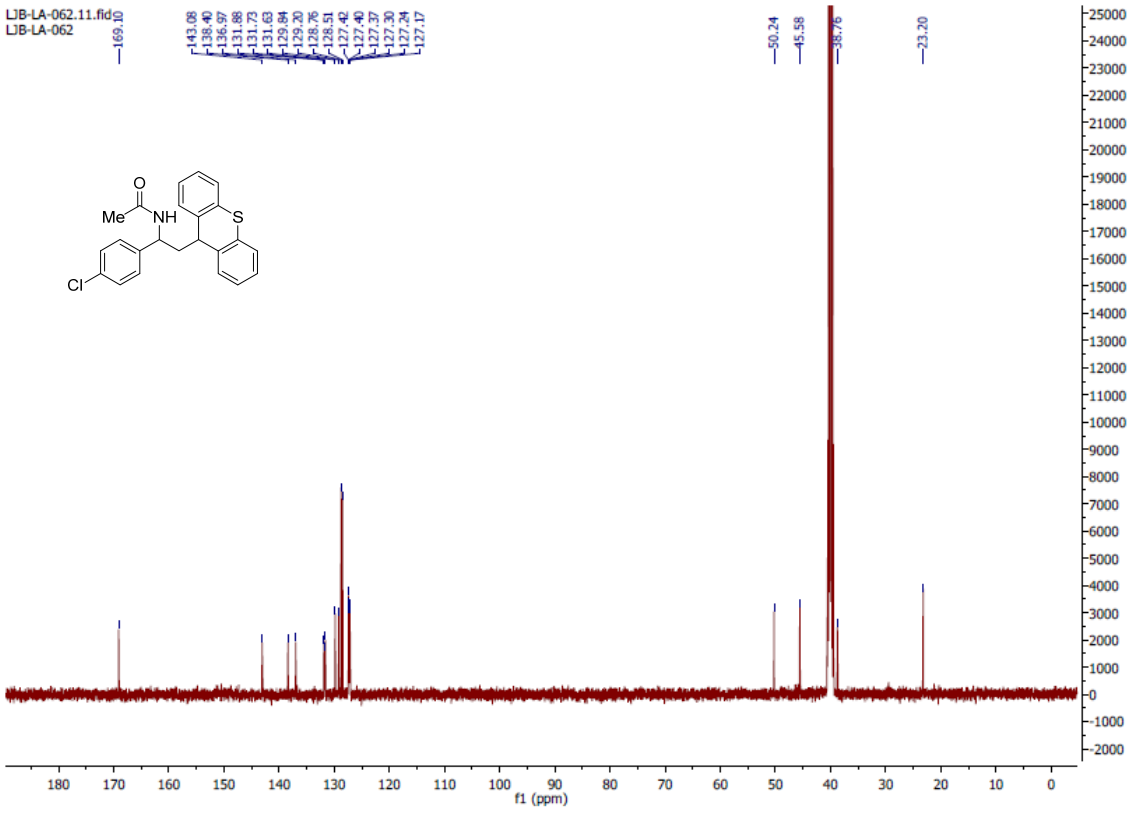
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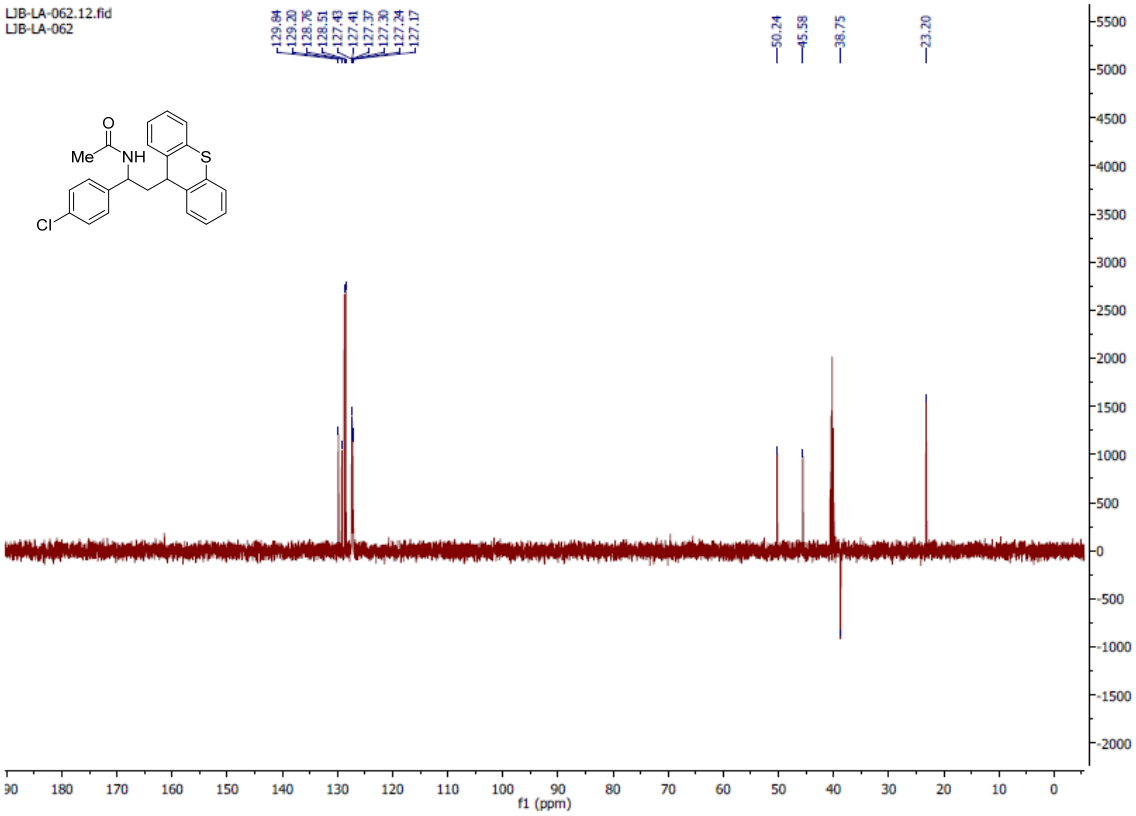
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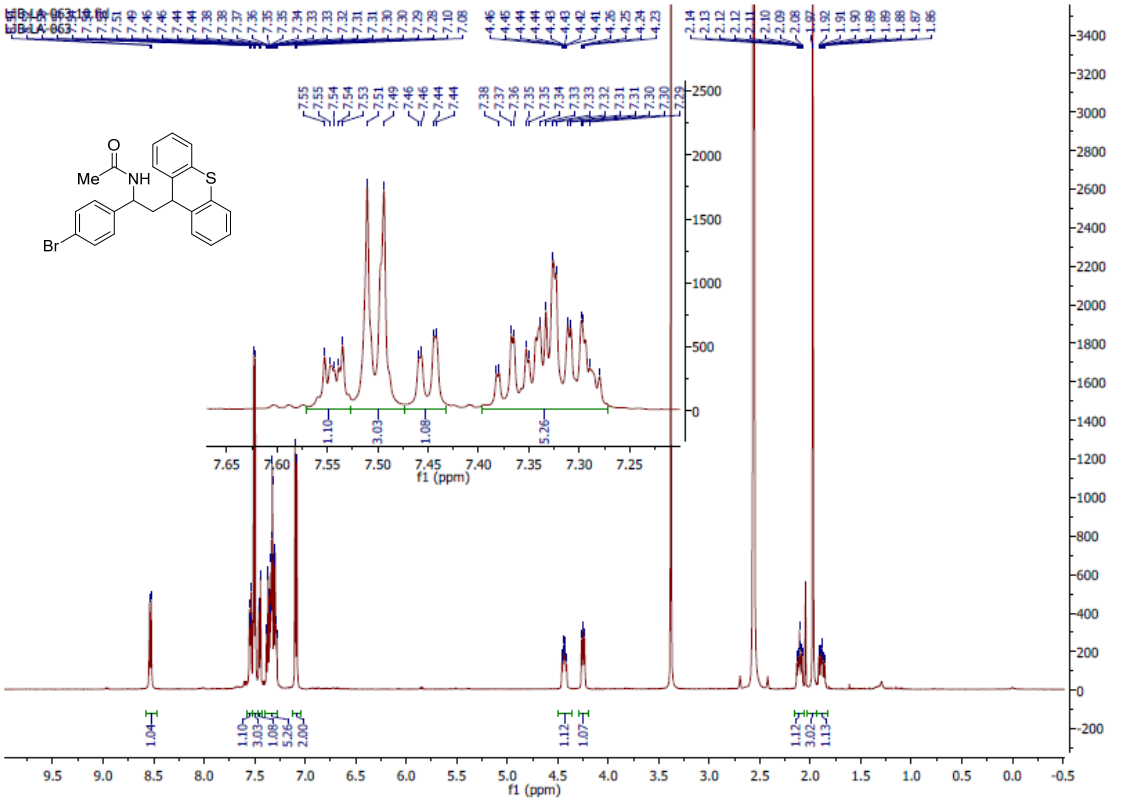
S
Cl
f1 (ppm)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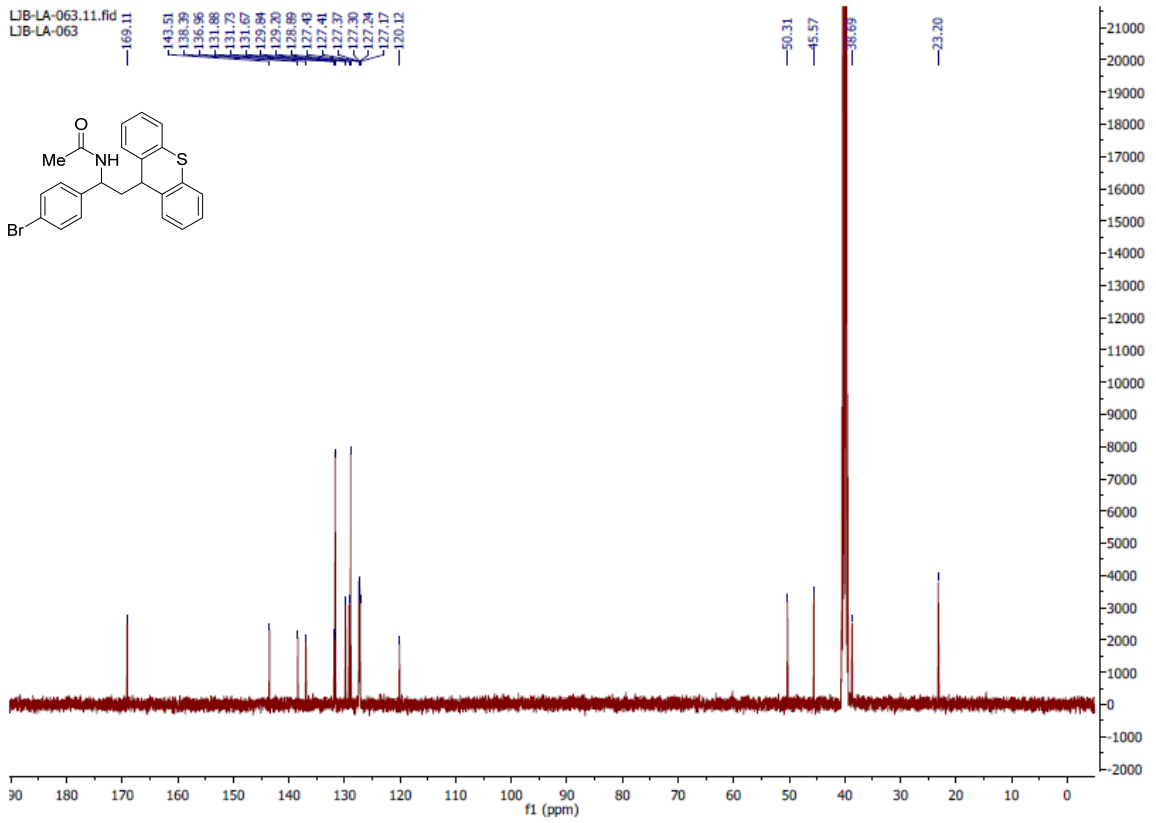
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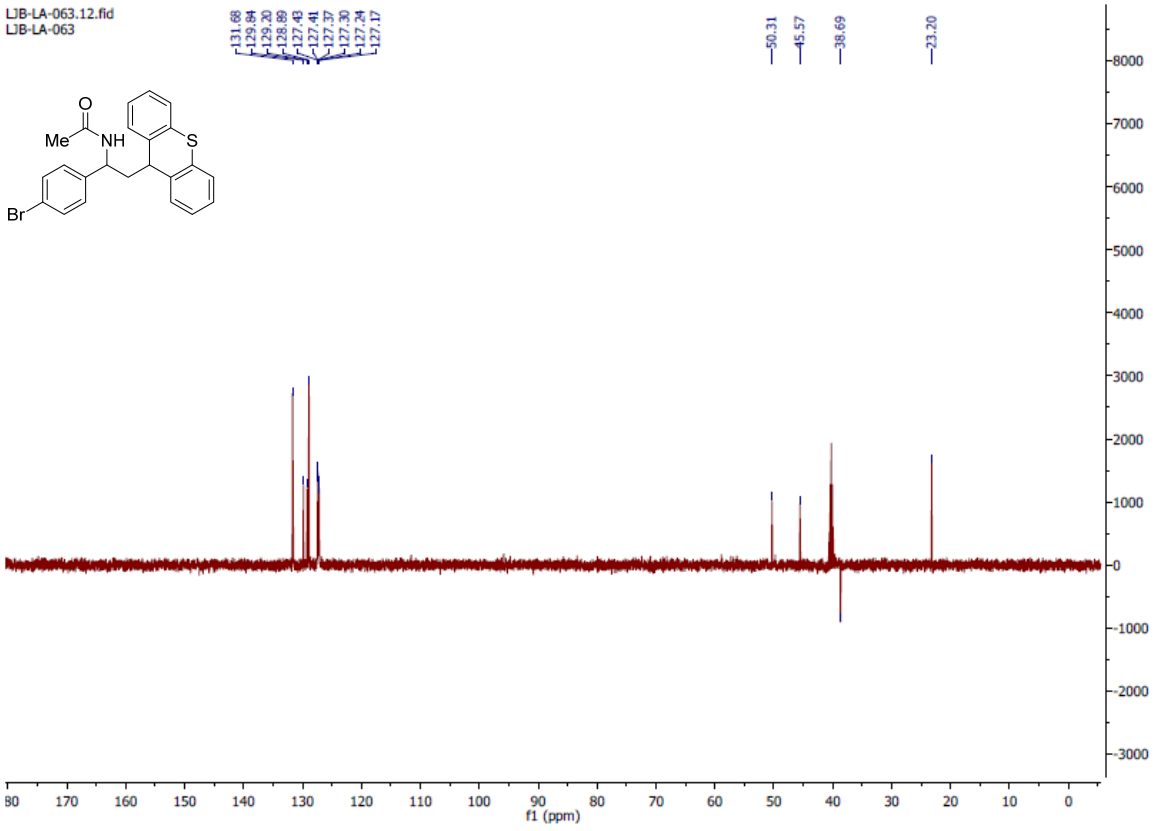
Me
NH
O
S
Br
f1 (ppm)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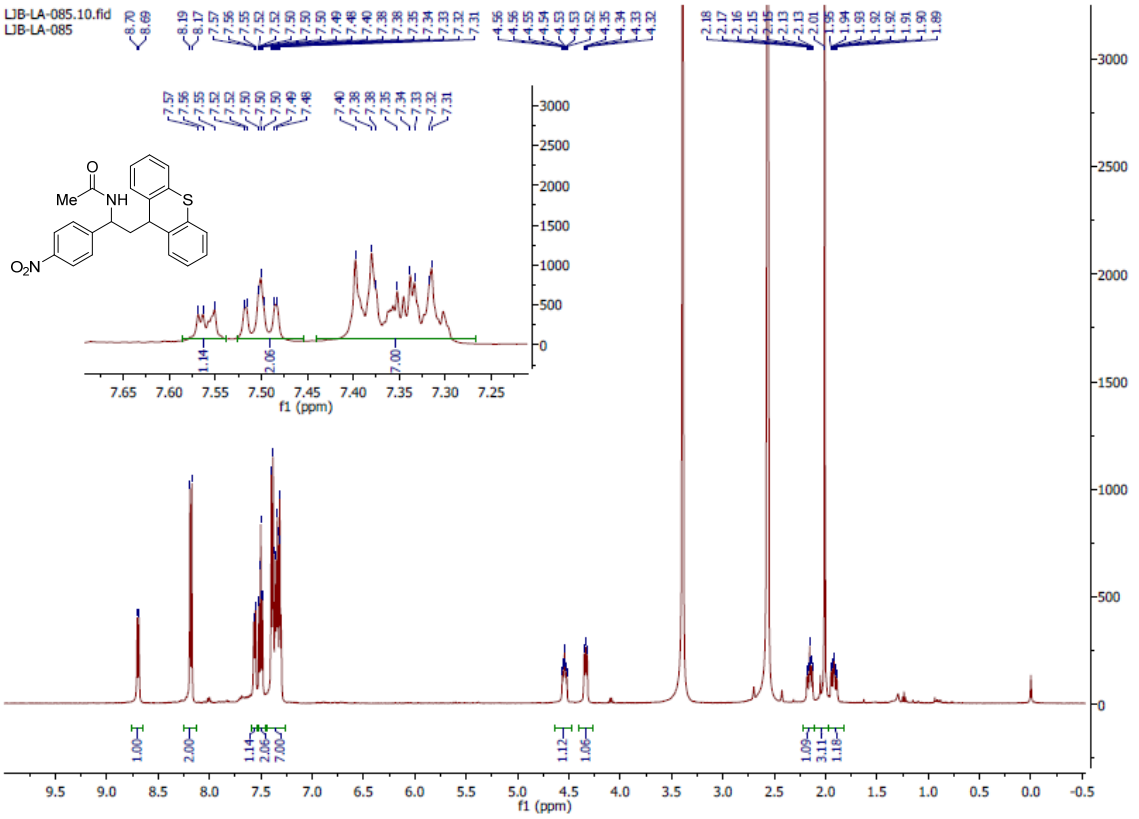
f1 (ppm)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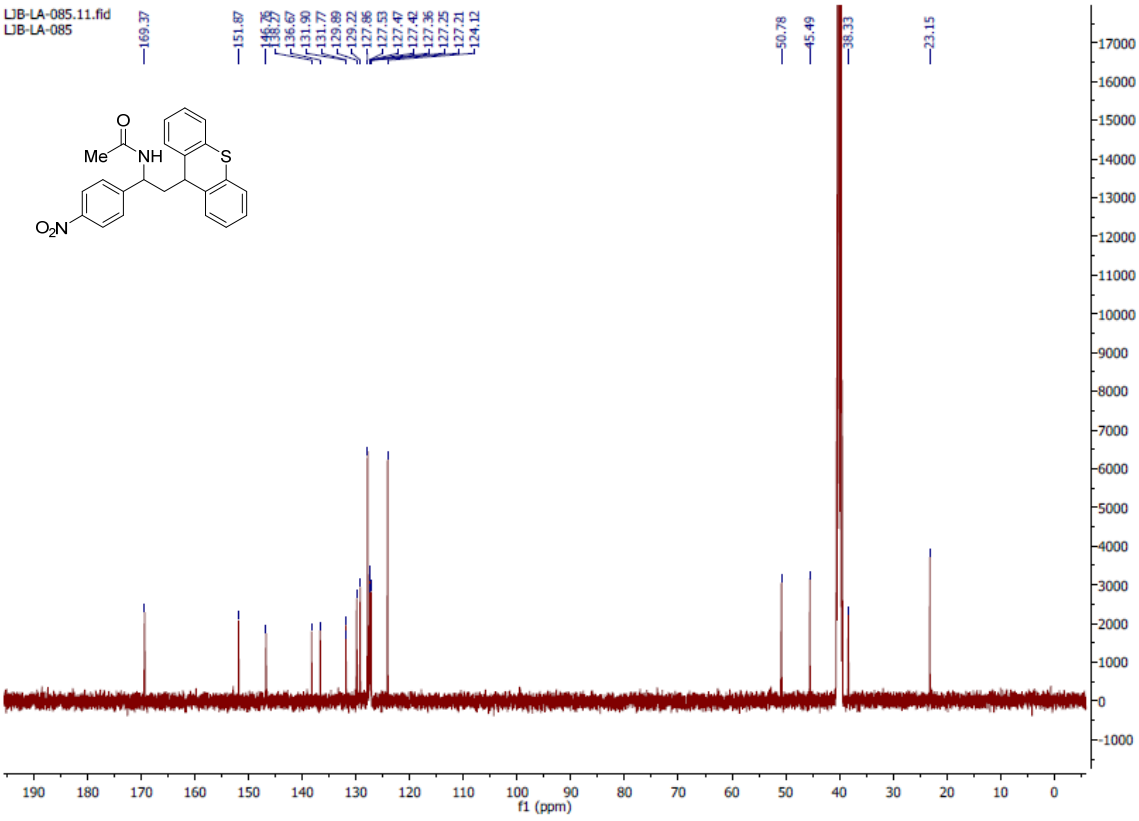
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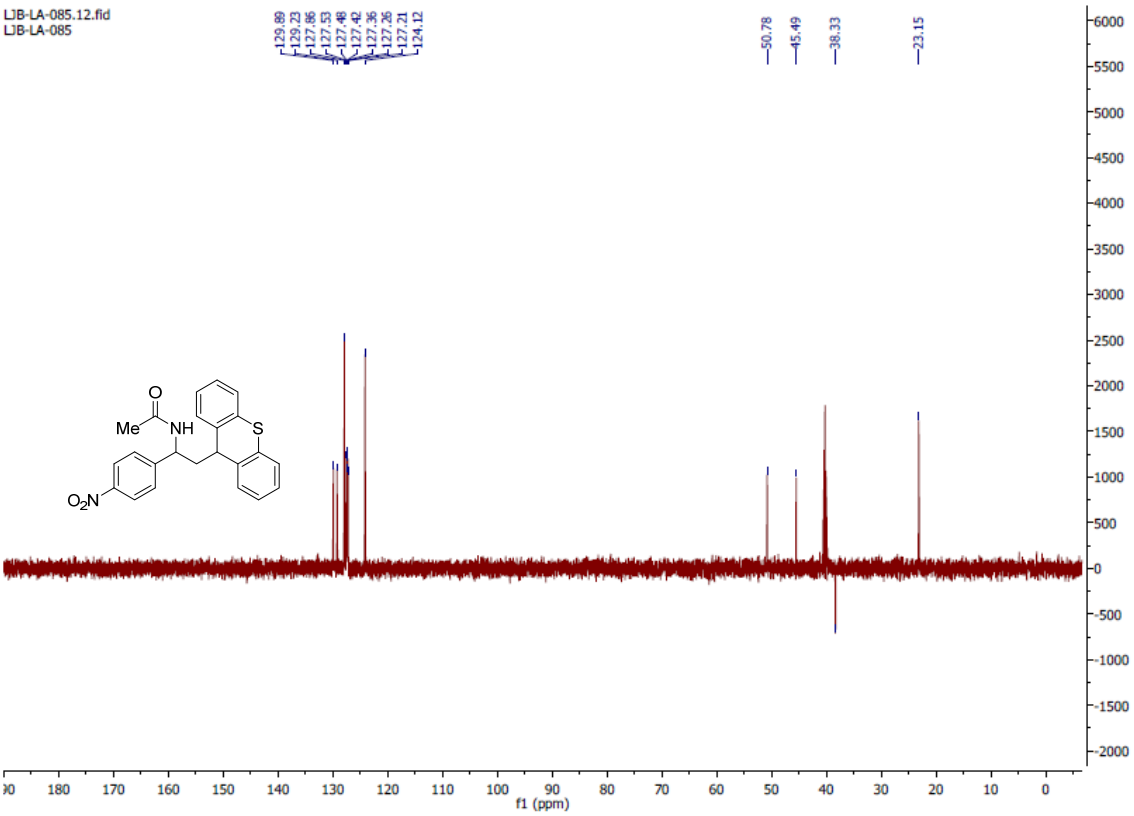
O
S
O2N
f1 (ppm)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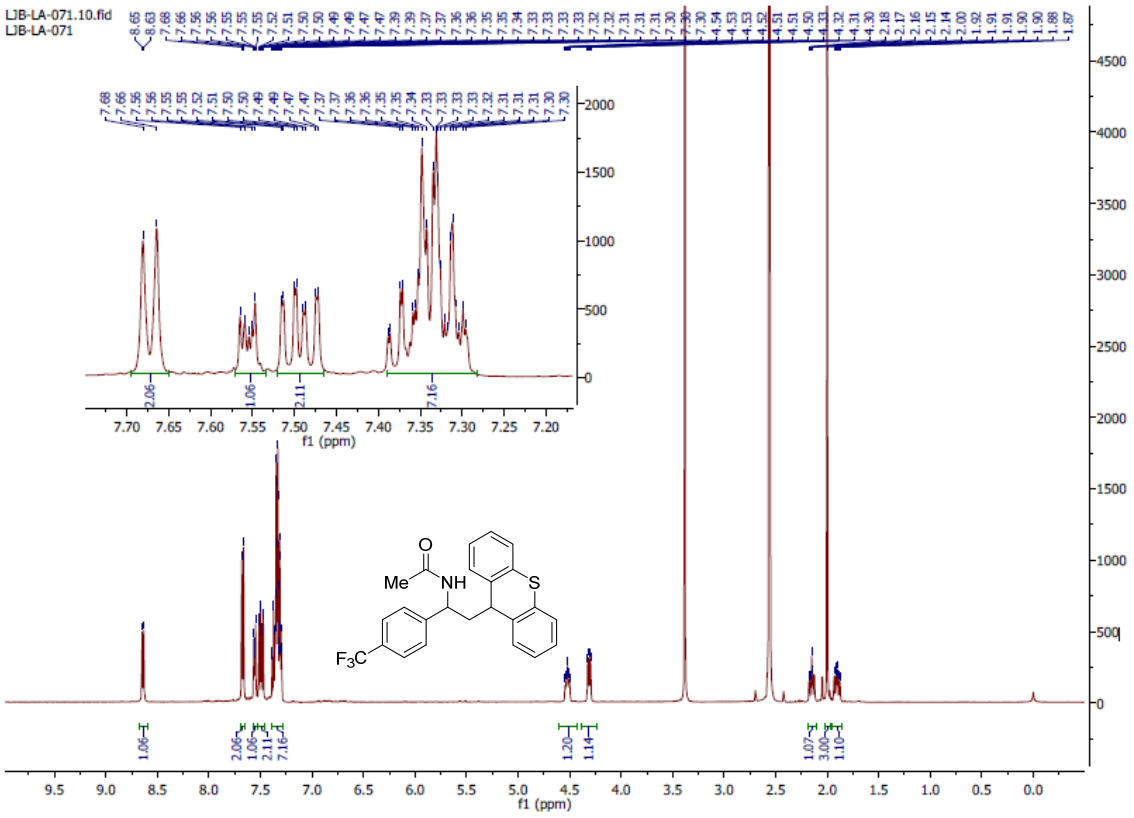
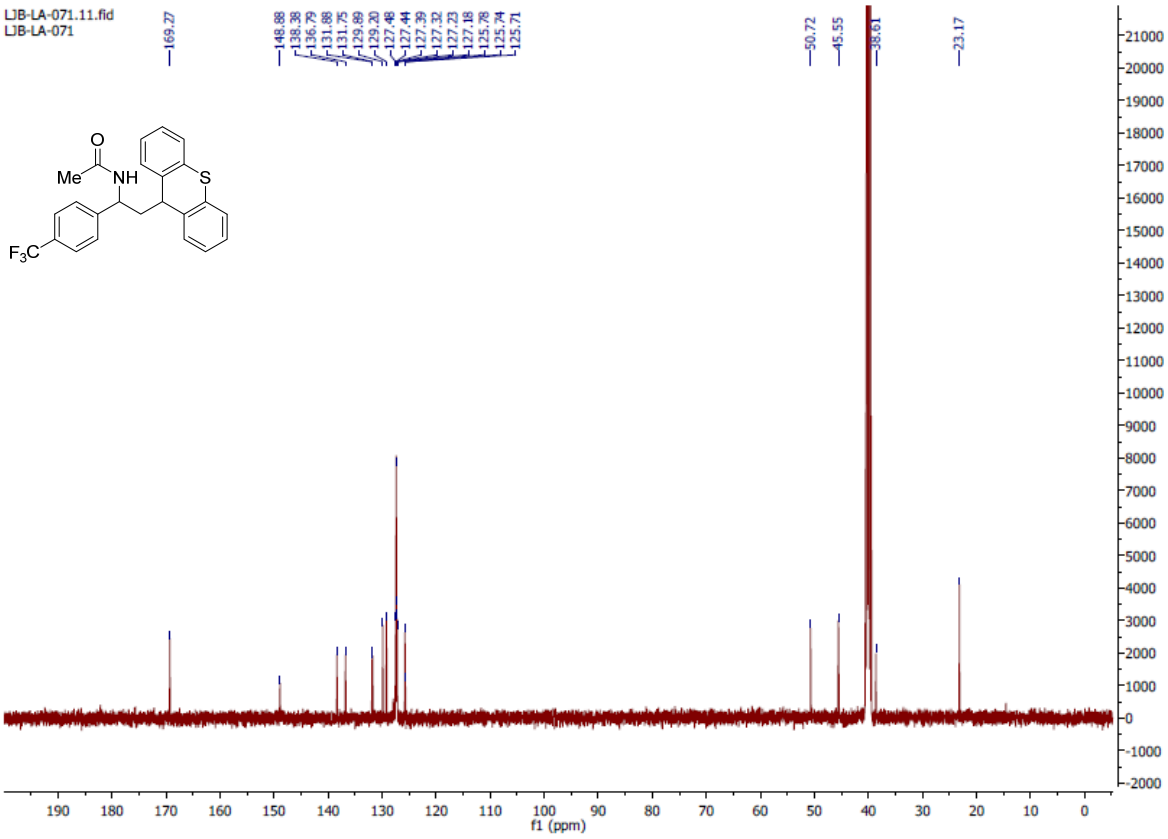
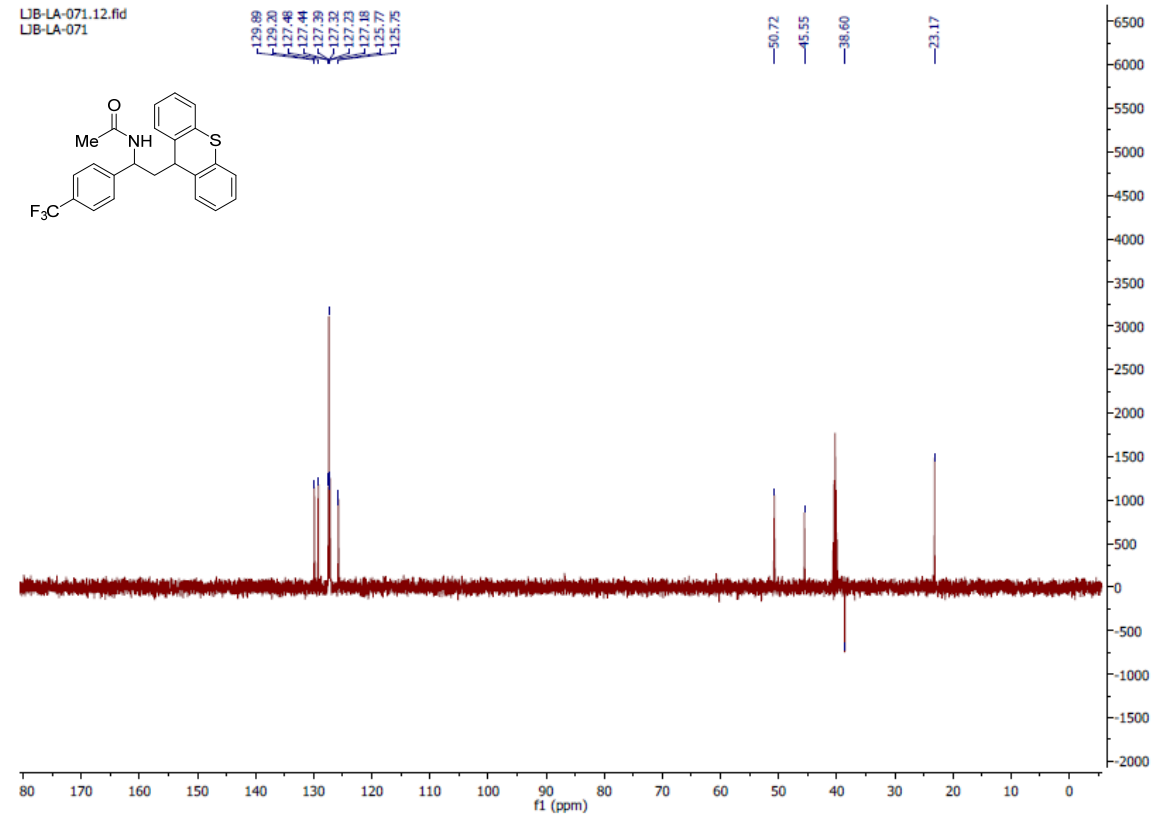
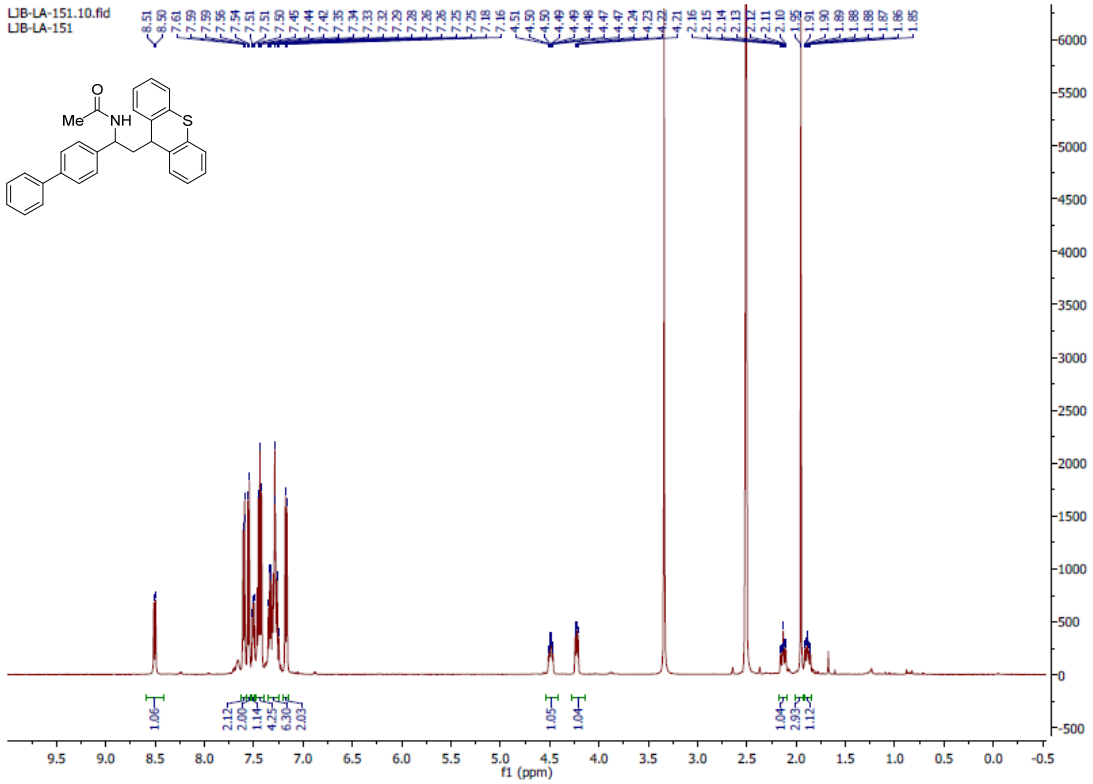
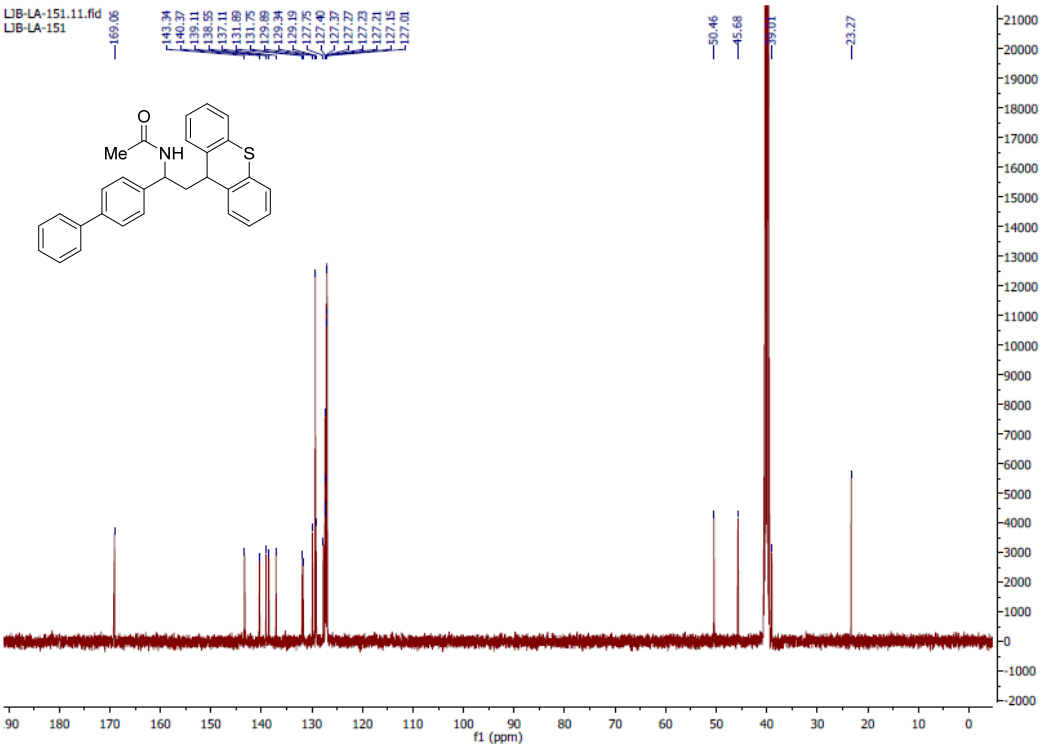
45.49
38.33
23.15
Me
NH
O
S
O2N
f1 (ppm)

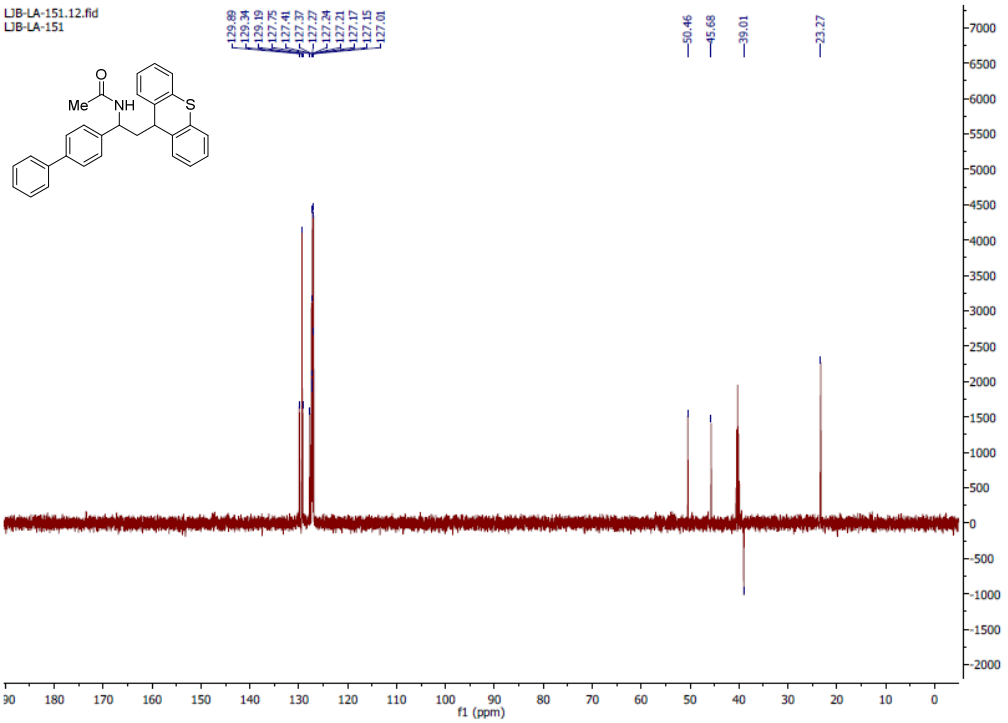

LJB-LA-071.10.fid
LJB-LA-071
f1 (ppm)
Me
NH
O
S
F3C

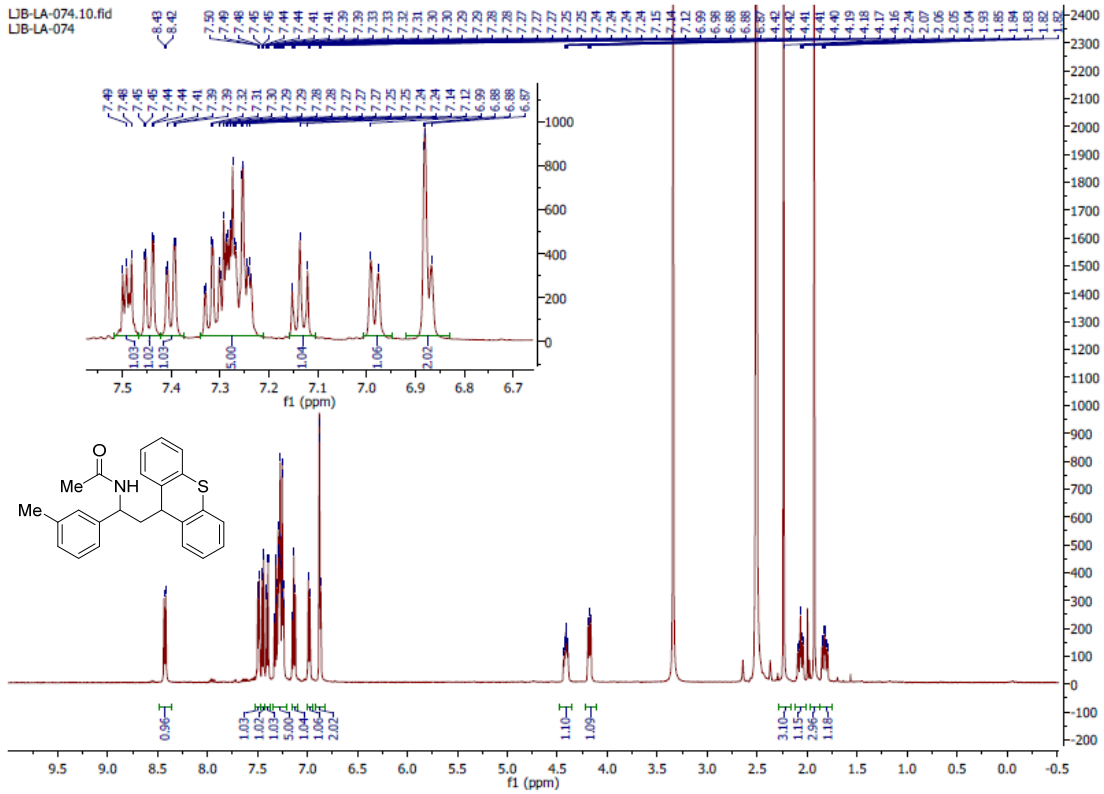

LJB-LA-071.11.fid
LJB-LA-071
169.27
148.88
138.38
136.79
131.88
131.75
129.89
129.20
127.48
127.44
127.39
127.32
127.23
127.18
125.78
125.74
125.71
50.72
45.55
38.61
23.17
O
Me
NH
S
F3C
f1 (ppm)

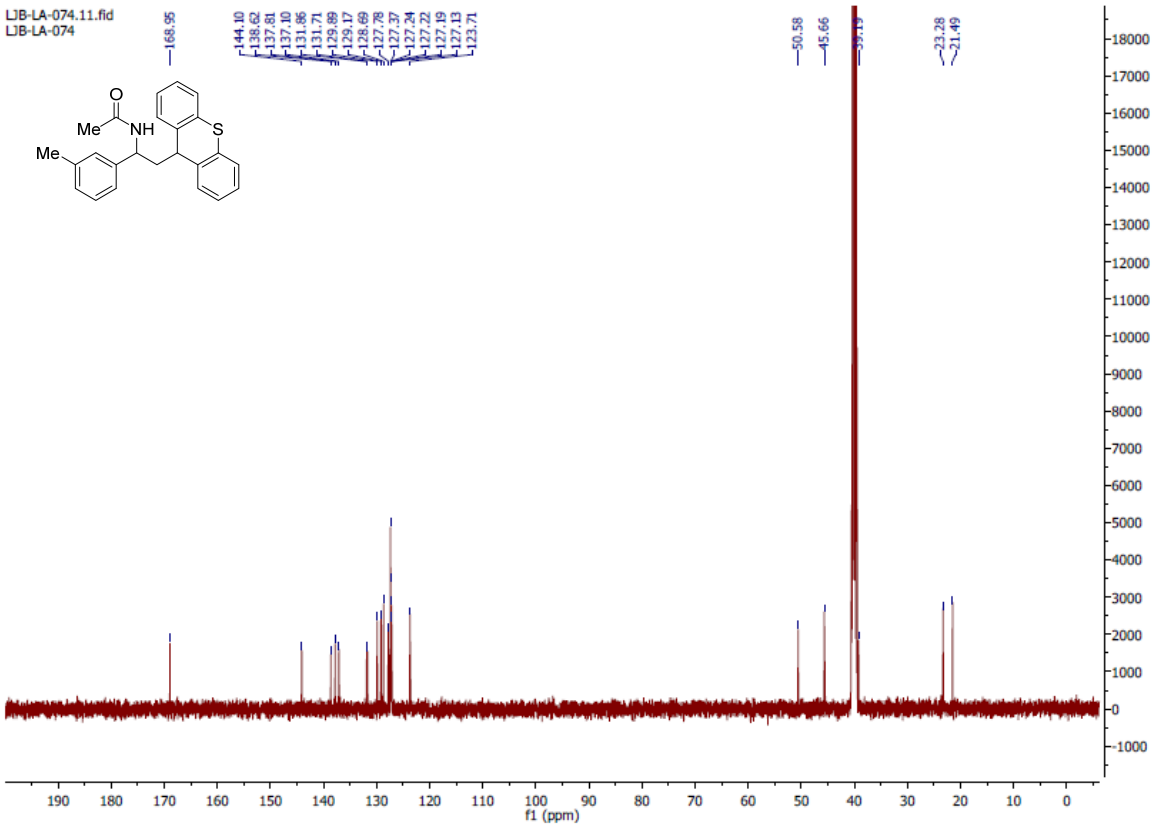

LJB-LA-071.12.fid
LJB-LA-071
129.89
129.20
127.48
127.44
127.39
127.32
127.23
127.18
125.77
125.75
50.72
45.55
38.60
23.17
O
Me
NH
S
F3C
f1 (ppm)

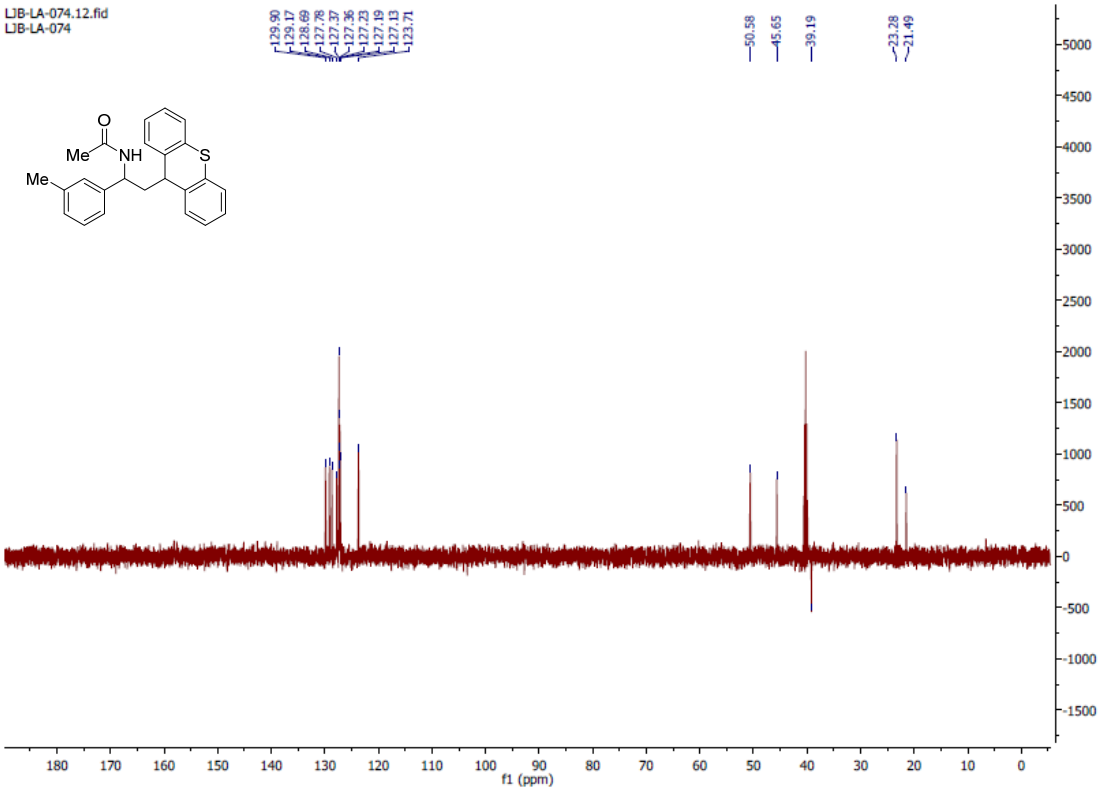

LJB-LA-151.10.fid
LJB-LA-151
Me
NH
O
S
f1 (ppm)


LJB-LA-151.11.fid
LJB-LA-151
Me
NH
O
S
f1 (ppm)

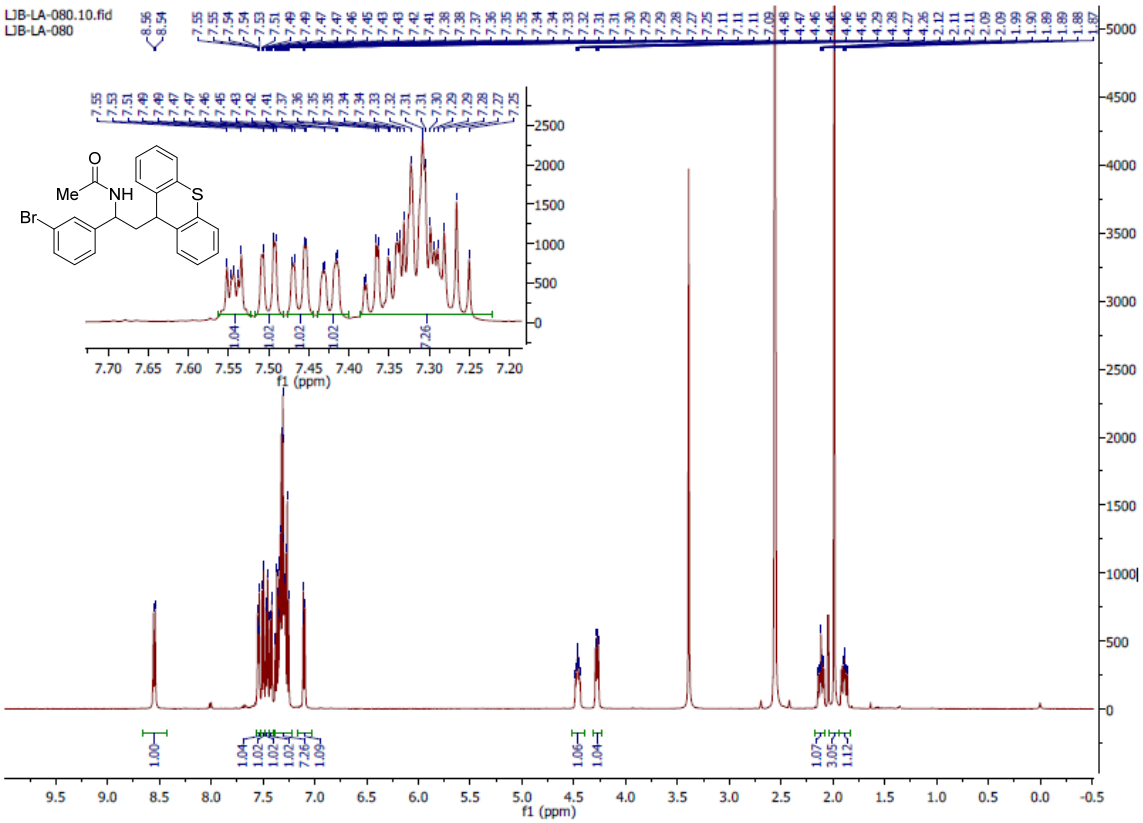

LJB-LA-151.12.fid
LJB-LA-151
129.89
129.34
129.19
127.75
127.41
127.37
127.27
127.24
127.21
127.17
127.15
127.01
50.46
45.68
39.01
23.27
Me
NH
S
f1 (ppm)

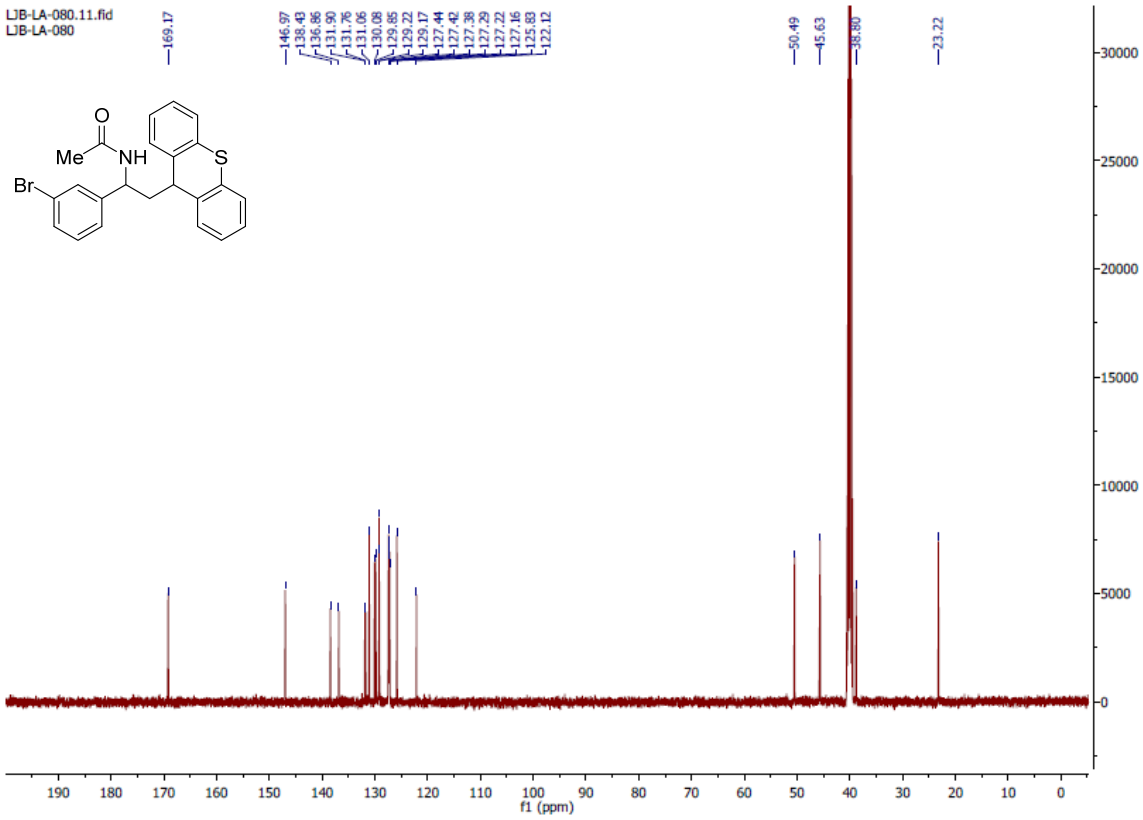

LJB-LA-074.10.fid
LJB-LA-074
8.43
8.42
1.03
1.02
1.03
5.00
1.04
1.06
2.02
0.96
1.10
1.09
3.10
1.15
2.96
1.18
Me
NH
S
Me
f1 (ppm)

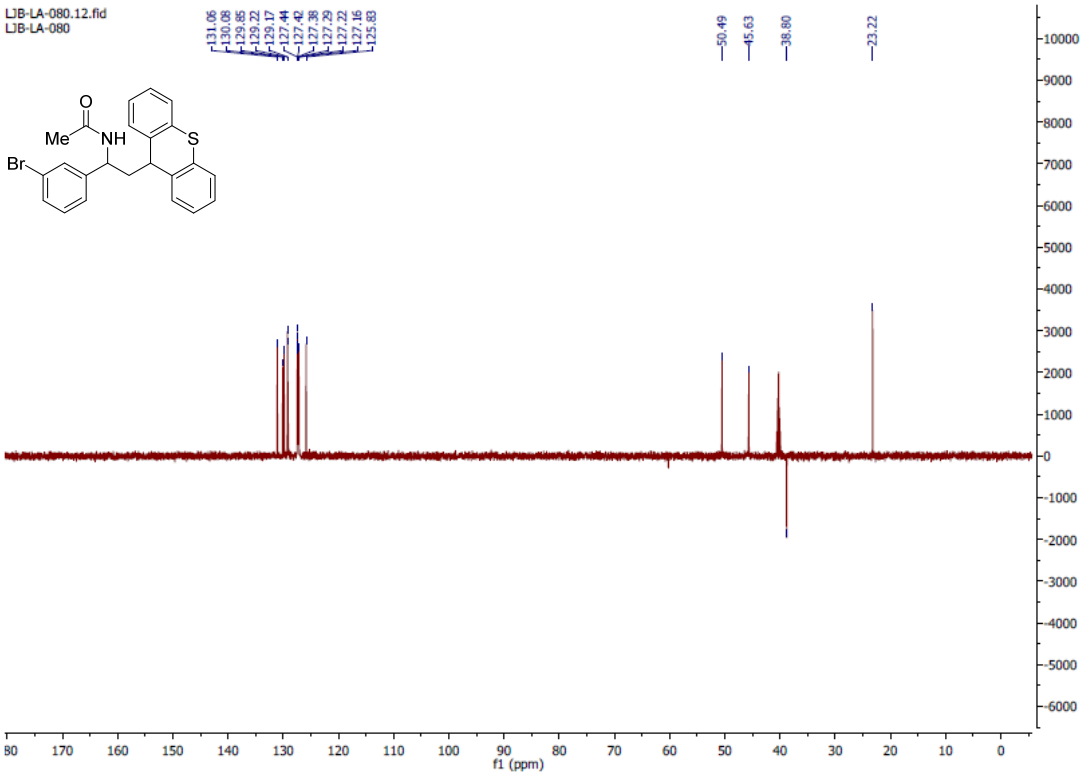

LJB-LA-074.11.fid
LJB-LA-074
168.95
144.10
138.62
137.81
137.10
131.86
131.71
129.89
129.17
128.69
127.78
127.37
127.24
127.22
127.19
127.13
123.71
50.58
45.66
39.19
23.28
21.49
O
Me
NH
S
Me
f1 (ppm)

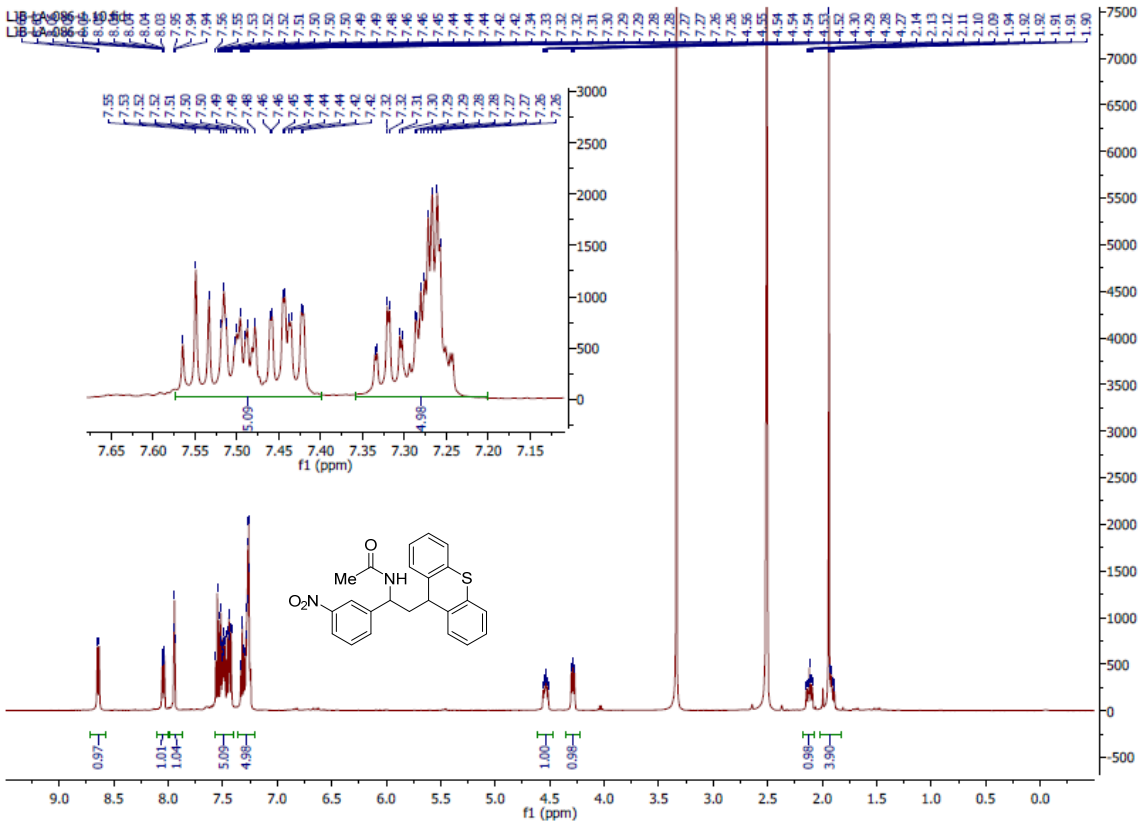

LJB-LA-074.12.fid
LJB-LA-074
129.90
129.17
128.69
127.78
127.37
127.36
127.23
127.19
127.13
123.71
50.58
45.65
39.19
23.28
21.49
O
Me
NH
S
Me
f1 (ppm)

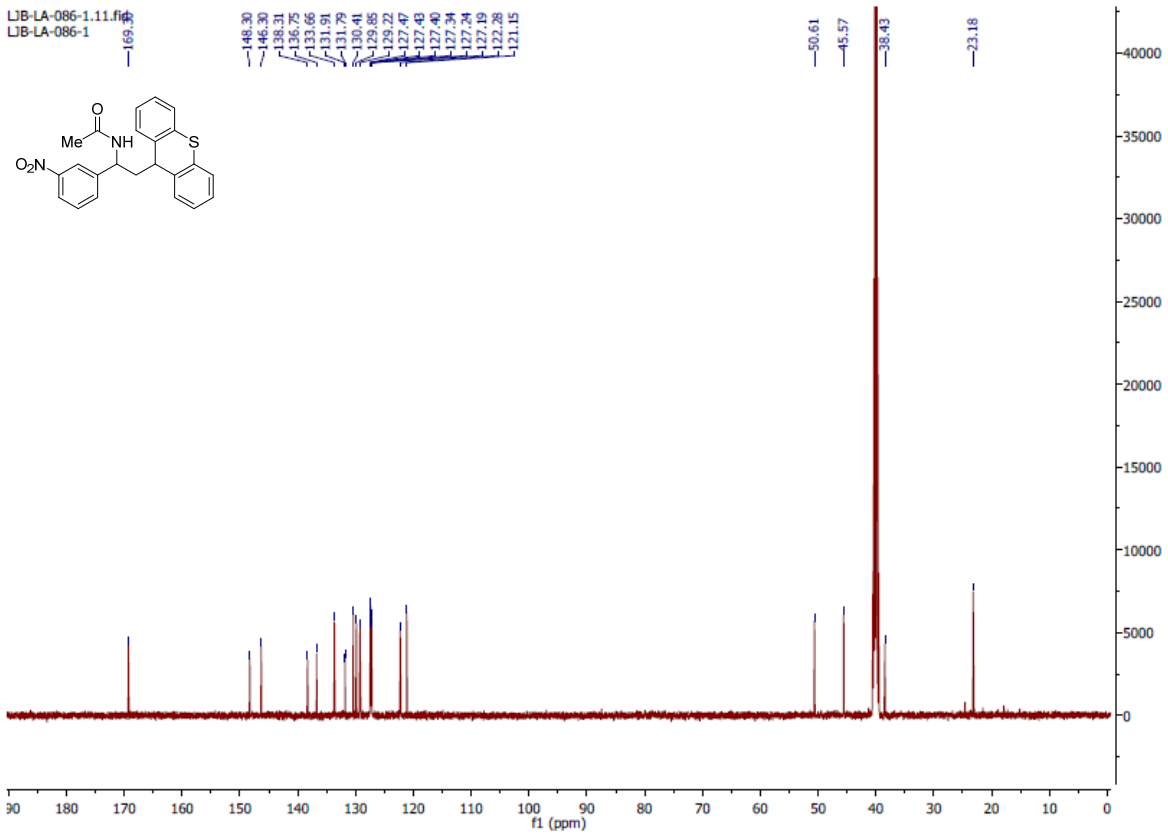
V

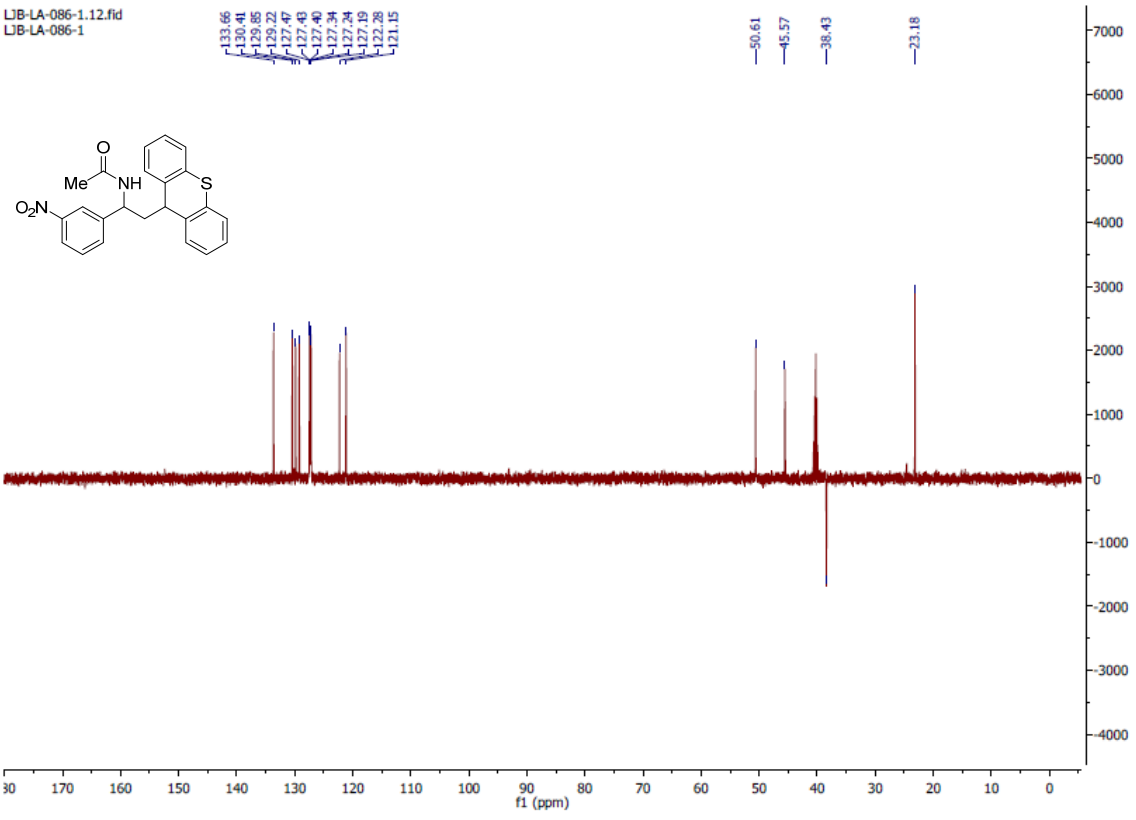

LJB-LA-080.10.fid
LJB-LA-080
Me
NH
O
S
Br
f1 (ppm)

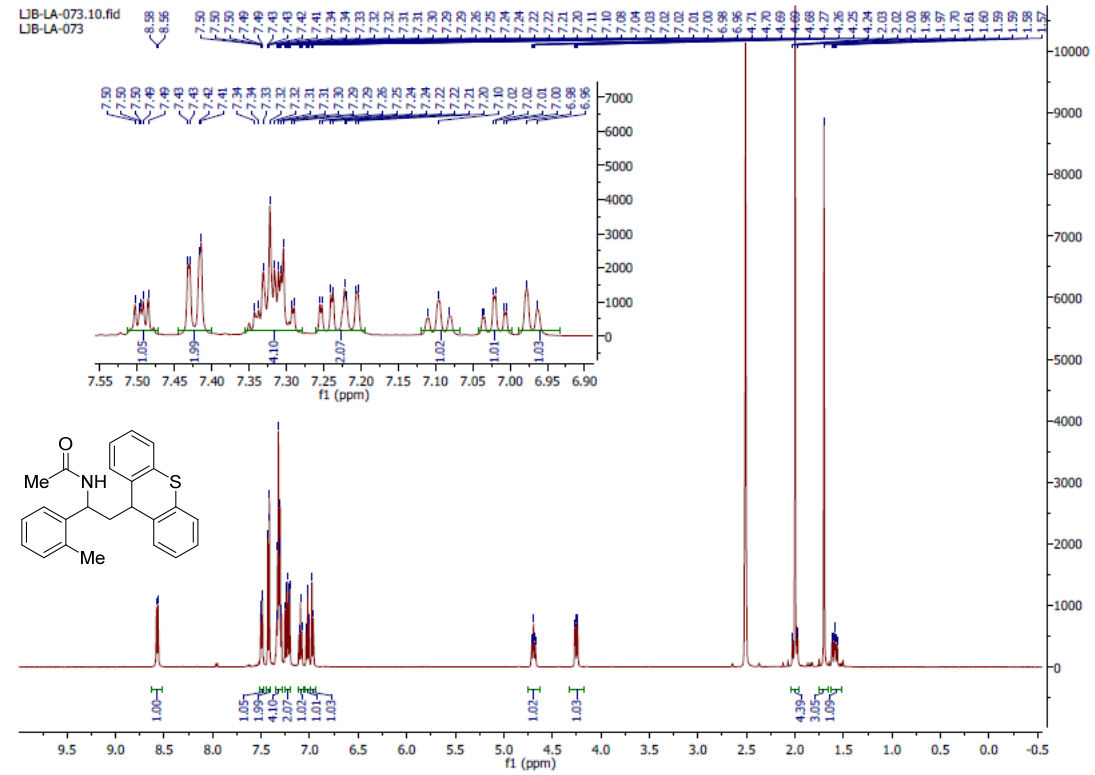

LJB-LA-080.11.fid
LJB-LA-080
Me
NH
O
S
Br
f1 (ppm)

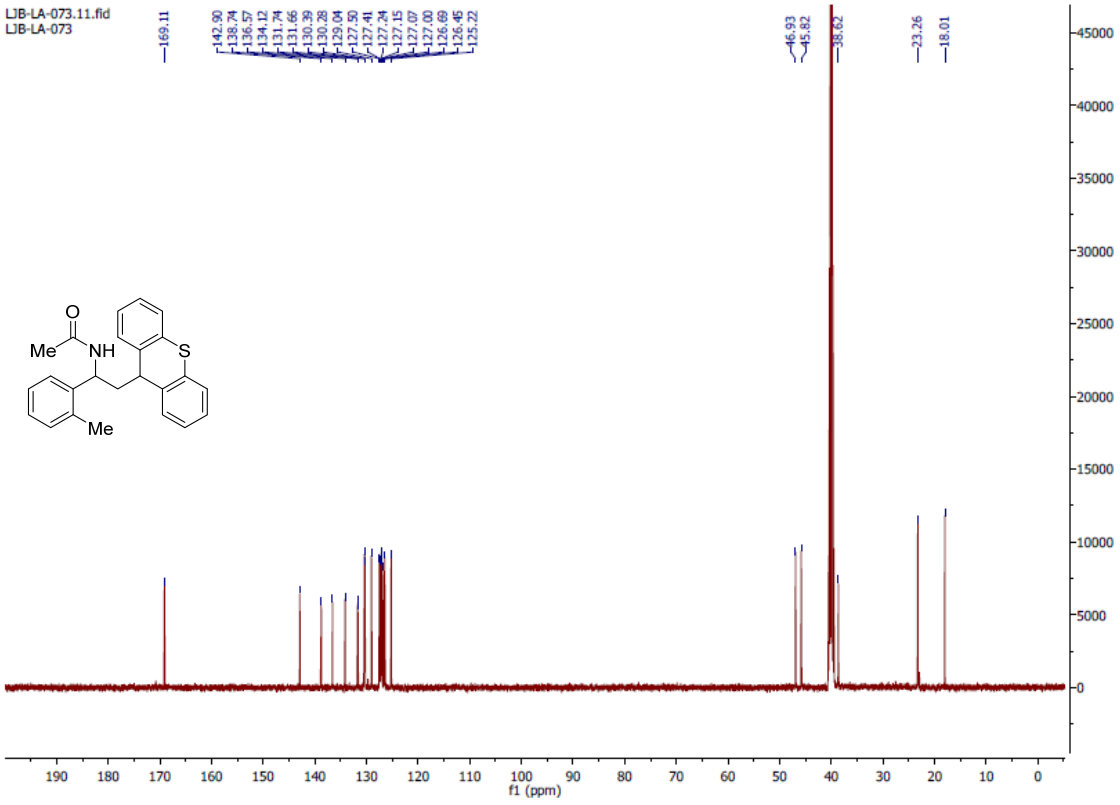

LJB-LA-080.12.fid
LJB-LA-080
131.06
130.08
129.85
129.22
129.17
127.44
127.42
127.38
127.29
127.22
127.16
125.83
50.49
45.63
38.80
23.22
Me
NH
O
S
Br
f1 (ppm)

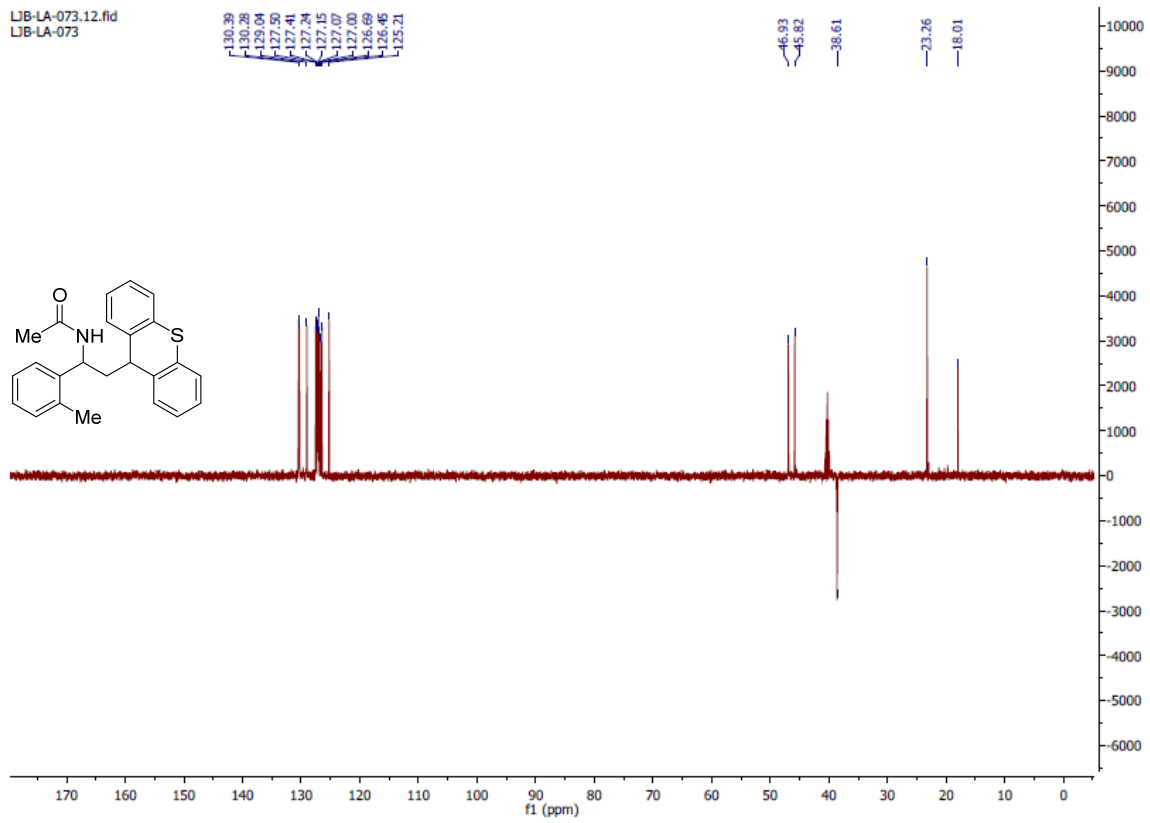

5.09
4.98
f1 (ppm)
Me
NH
O
S
O2N
0.97
1.01
1.04
5.09
4.98
1.00
0.98
0.98
3.90
f1 (ppm)

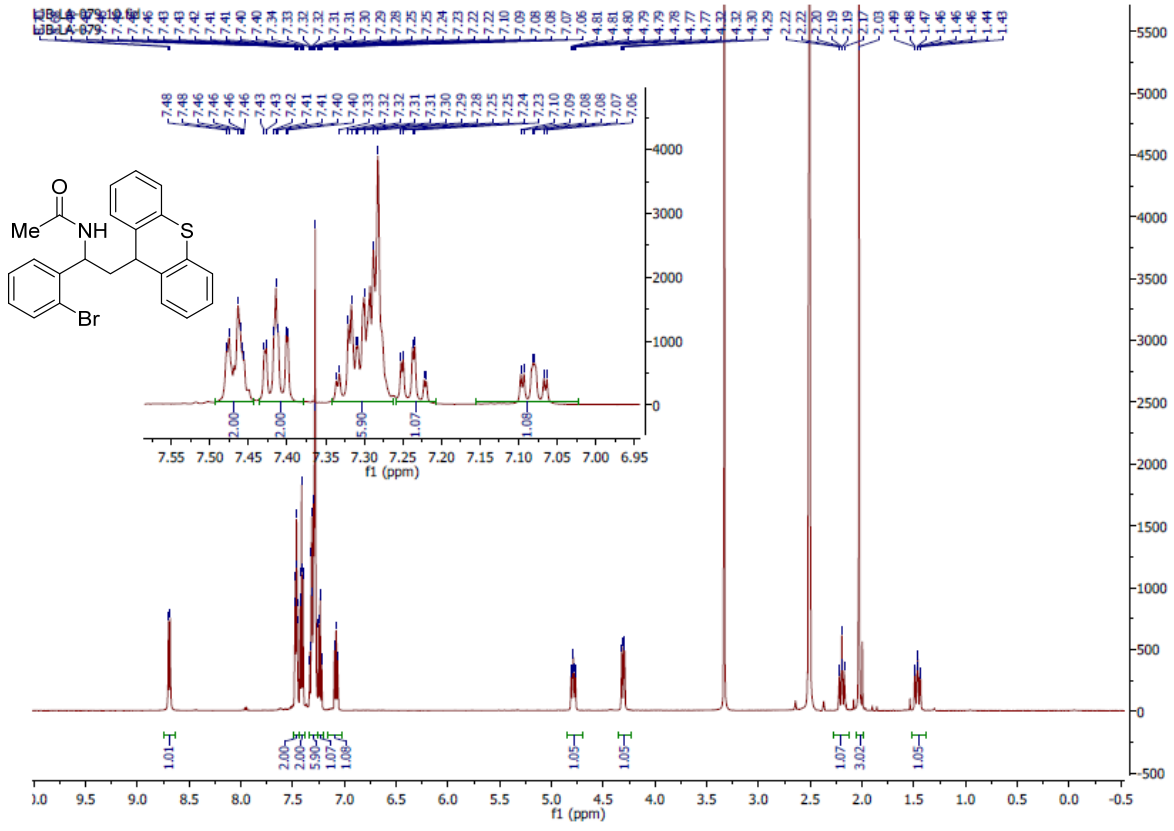

LJB-LA-086-1.11.fid
LJB-LA-086-1
169.30
148.30
146.30
138.31
136.75
133.66
131.91
131.79
130.41
129.85
129.22
127.47
127.43
127.40
127.34
127.24
127.19
122.28
121.15
50.61
45.57
38.43
23.18
Me
NH
S
O2N
f1 (ppm)

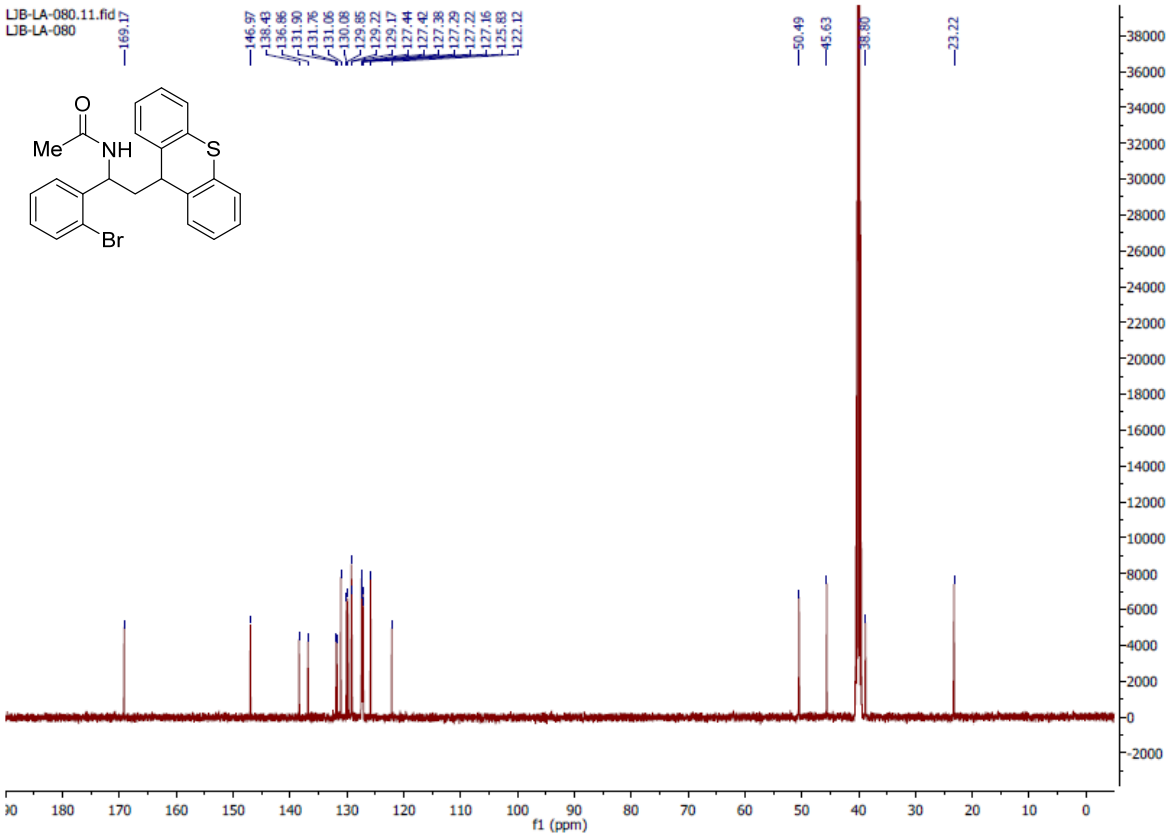

LJB-LA-086-1.12.fid
LJB-LA-086-1
133.66
130.41
129.85
129.22
127.47
127.43
127.40
127.34
127.24
127.19
122.28
121.15
50.61
45.57
38.43
23.18
Me
NH
S
O2N
f1 (ppm)

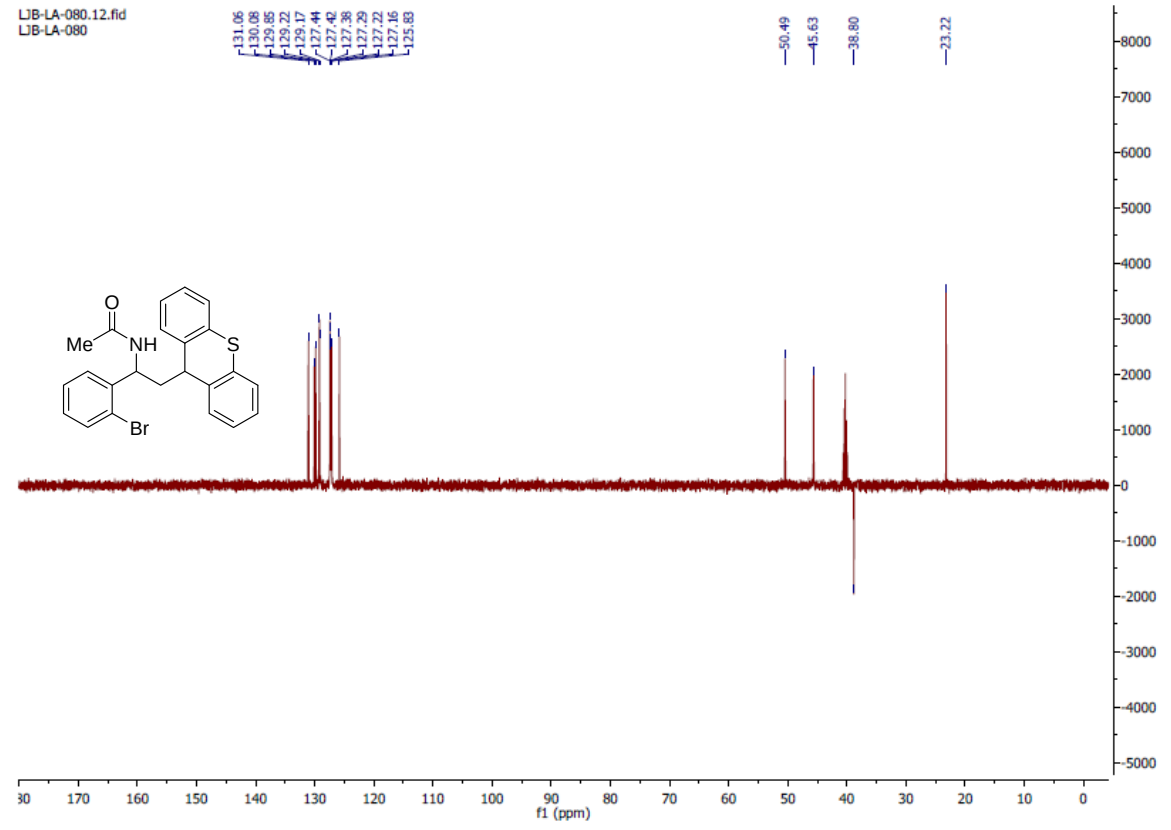

LJB-LA-073.10.fid
LJB-LA-073
f1 (ppm)

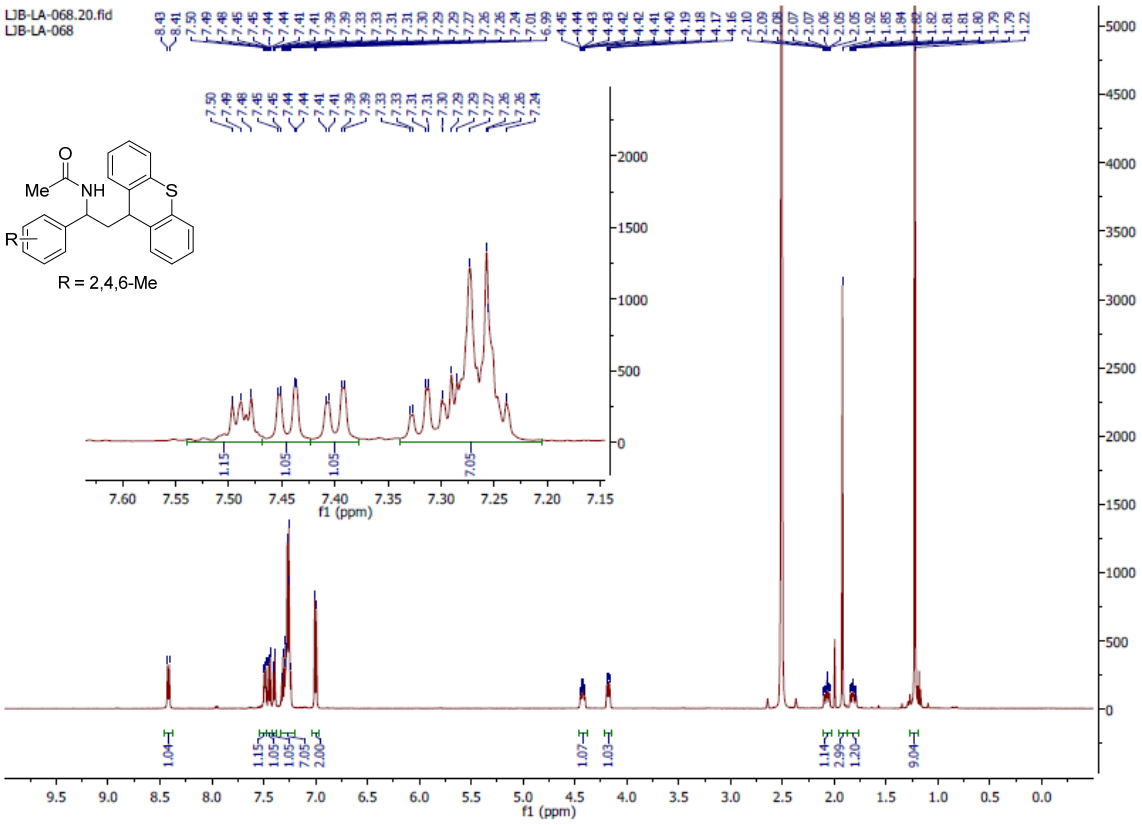

LJB-LA-073.11.fid
LJB-LA-073
f1 (ppm)

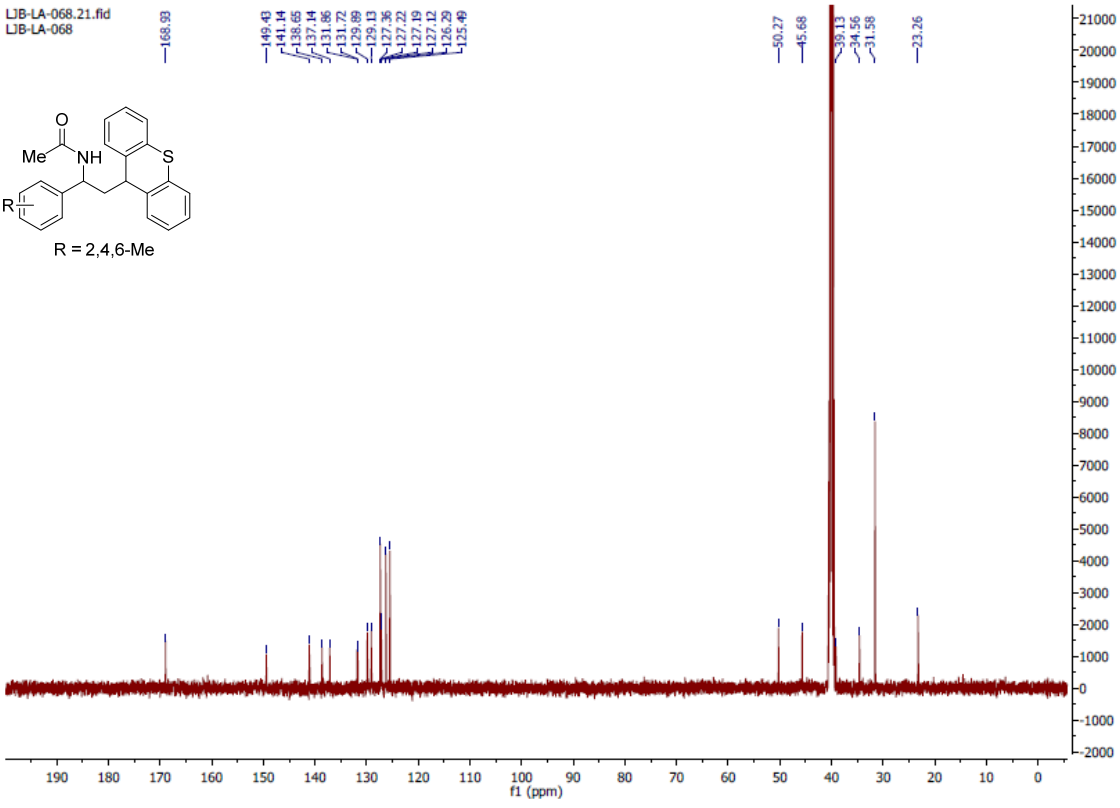

LJB-LA-073.12.fid
LJB-LA-073
130.39
130.28
129.04
127.50
127.41
127.24
127.15
127.07
127.00
126.69
126.45
125.21
46.93
45.82
38.61
23.26
18.01
Me
NH
S
Me
f1 (ppm)

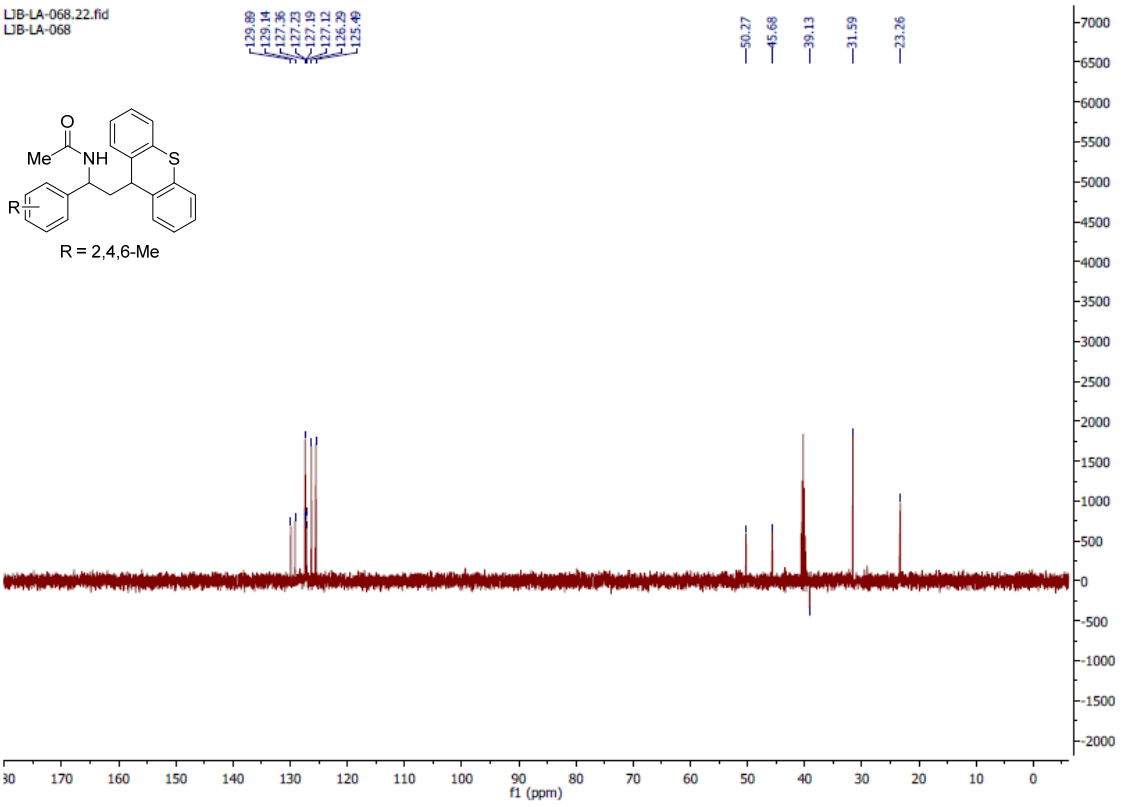

LJB-LA-079
Me
NH
S
Br
f1 (ppm)

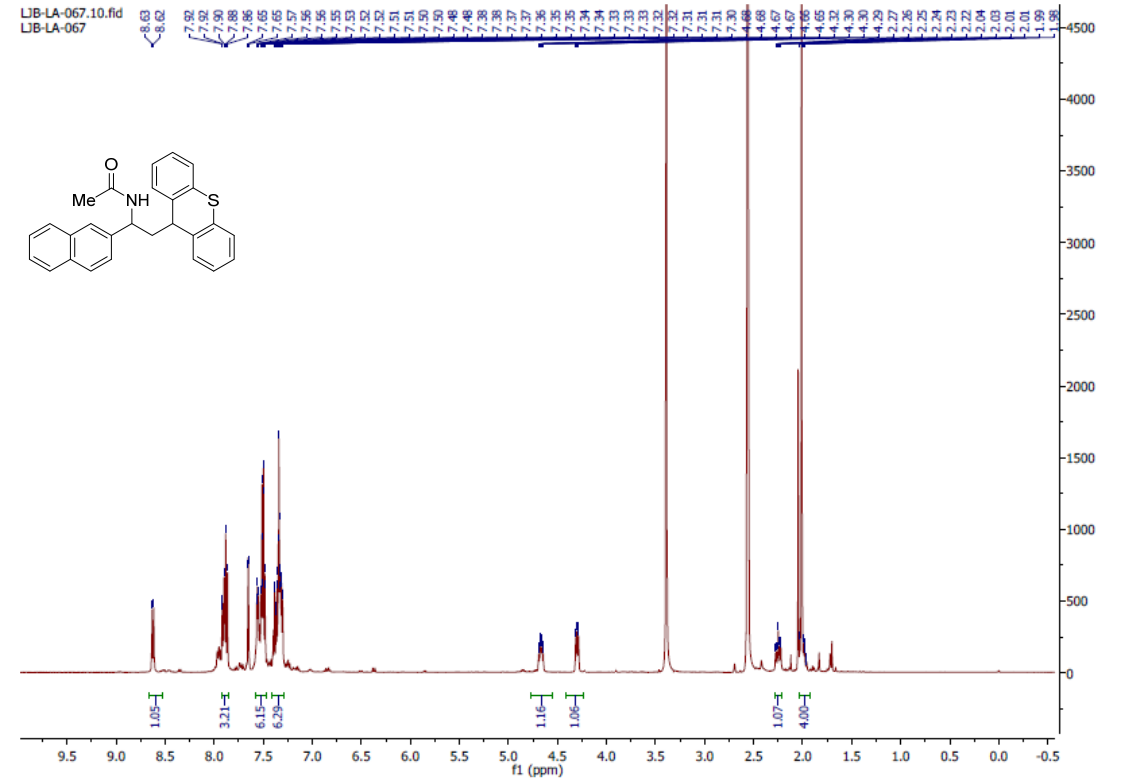

LJB-LA-080.11.fid
LJB-LA-080
169.17
146.97
138.43
136.86
131.90
131.76
131.06
130.08
129.85
129.22
129.17
127.44
127.42
127.38
127.29
127.22
127.16
125.83
122.12
50.49
45.63
38.80
23.22
O
Me
NH
S
Br
f1 (ppm)

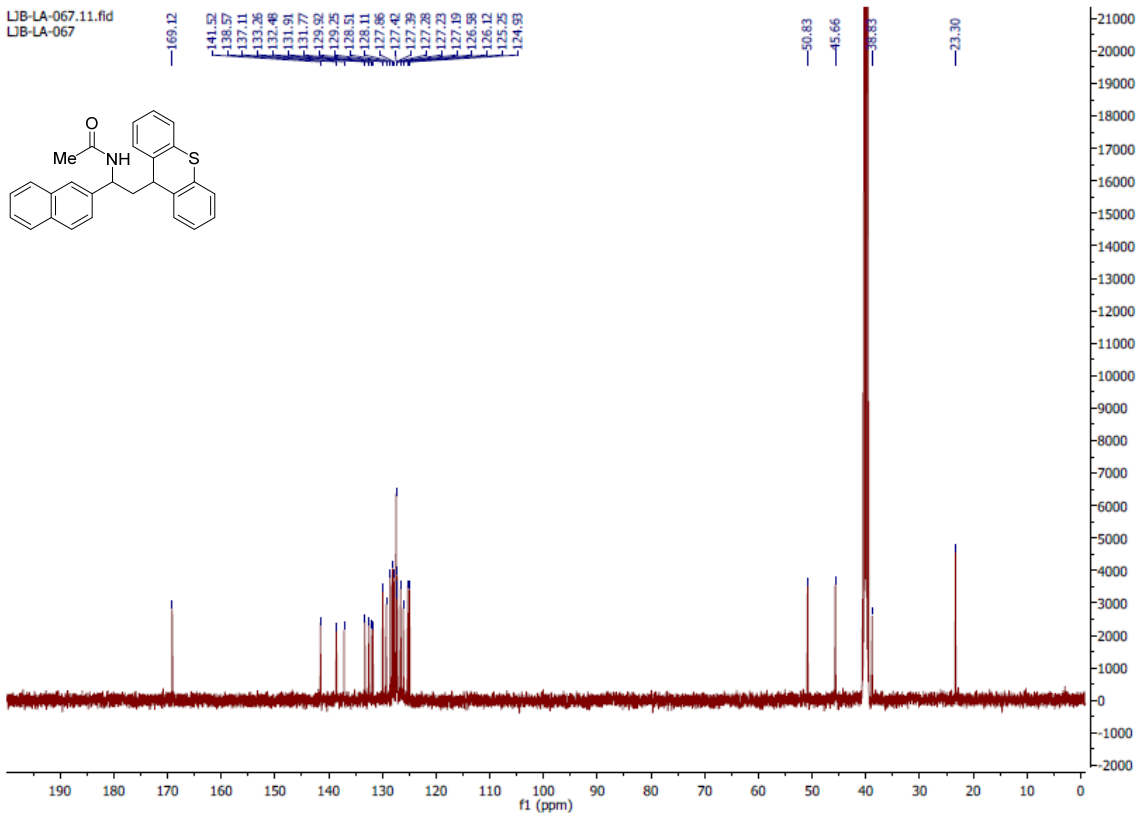

LJB-LA-080.12.fid
LJB-LA-080
131.06
130.08
129.85
129.22
129.17
127.44
127.42
127.38
127.29
127.22
127.16
125.83
50.49
45.63
38.80
23.22
O
Me
NH
S
Br
f1 (ppm)

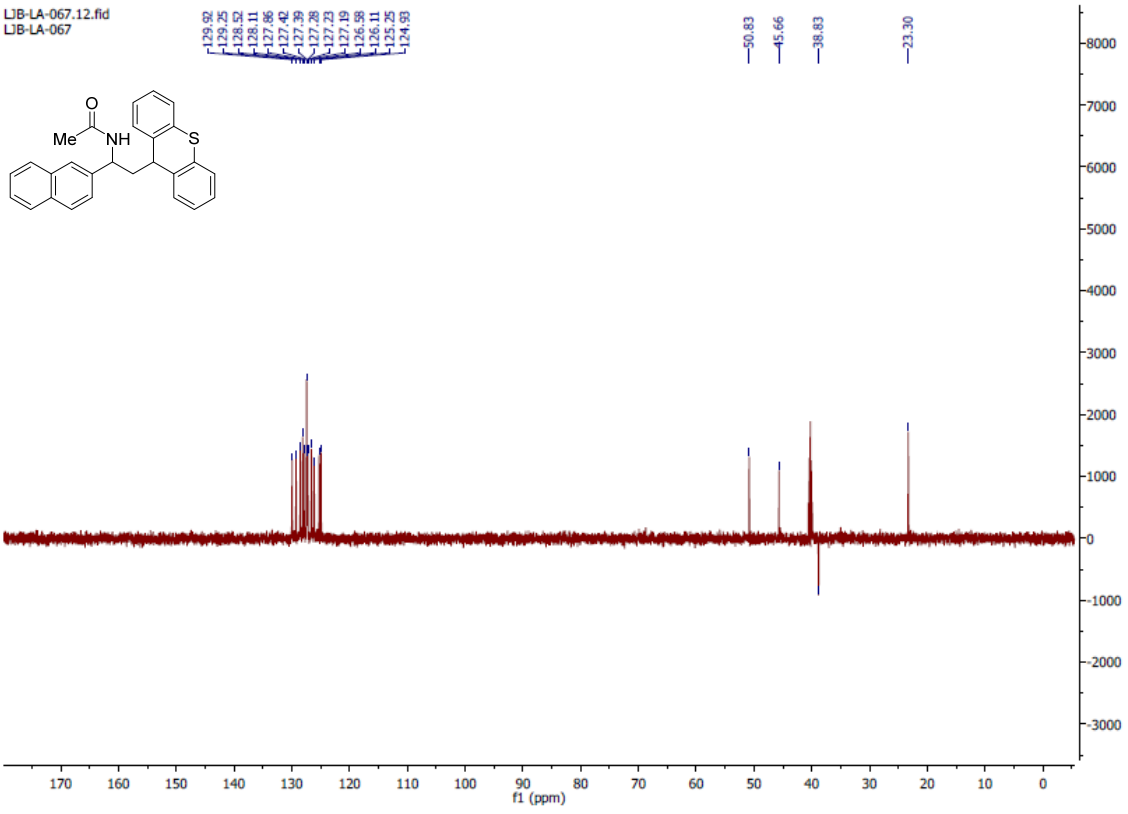

LJB-LA-068.20.fid
LJB-LA-068
Me
NH
O
S
R
R = 2,4,6-Me
f1 (ppm)

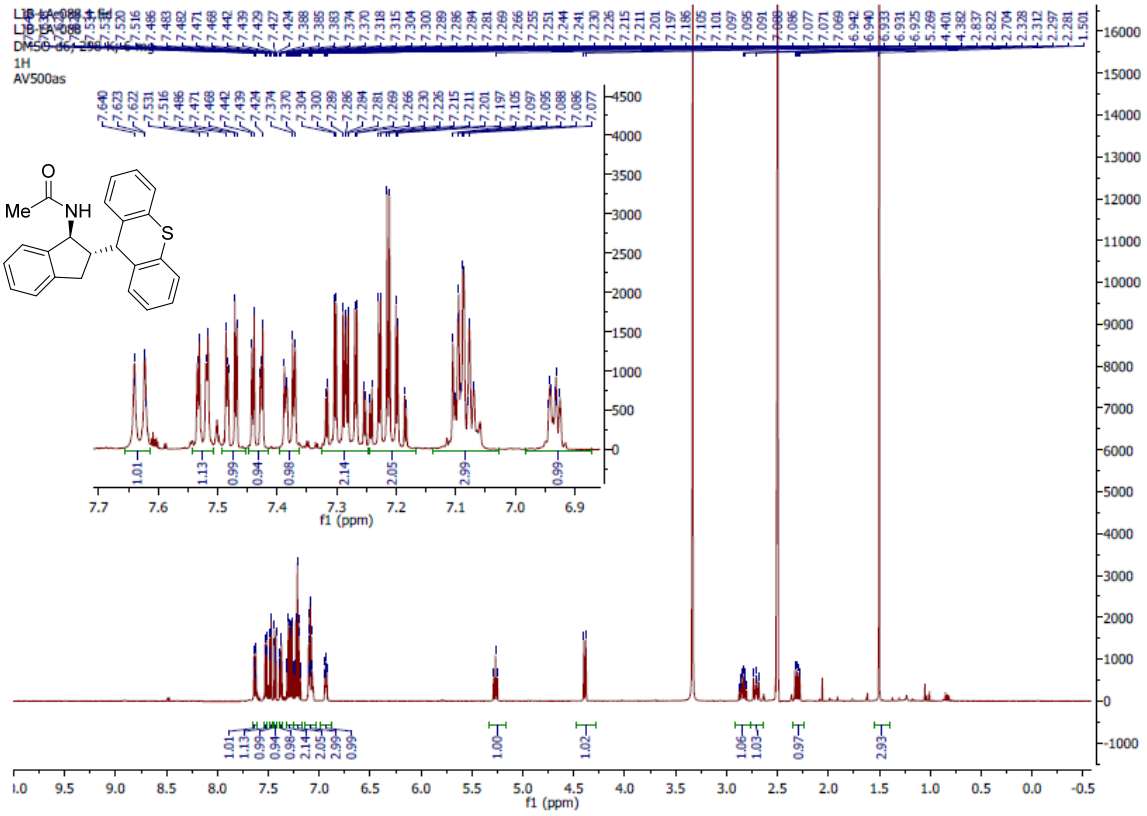

LJB-LA-068.21.fid
LJB-LA-068
Me
NH
O
S
R
R = 2,4,6-Me
f1 (ppm)

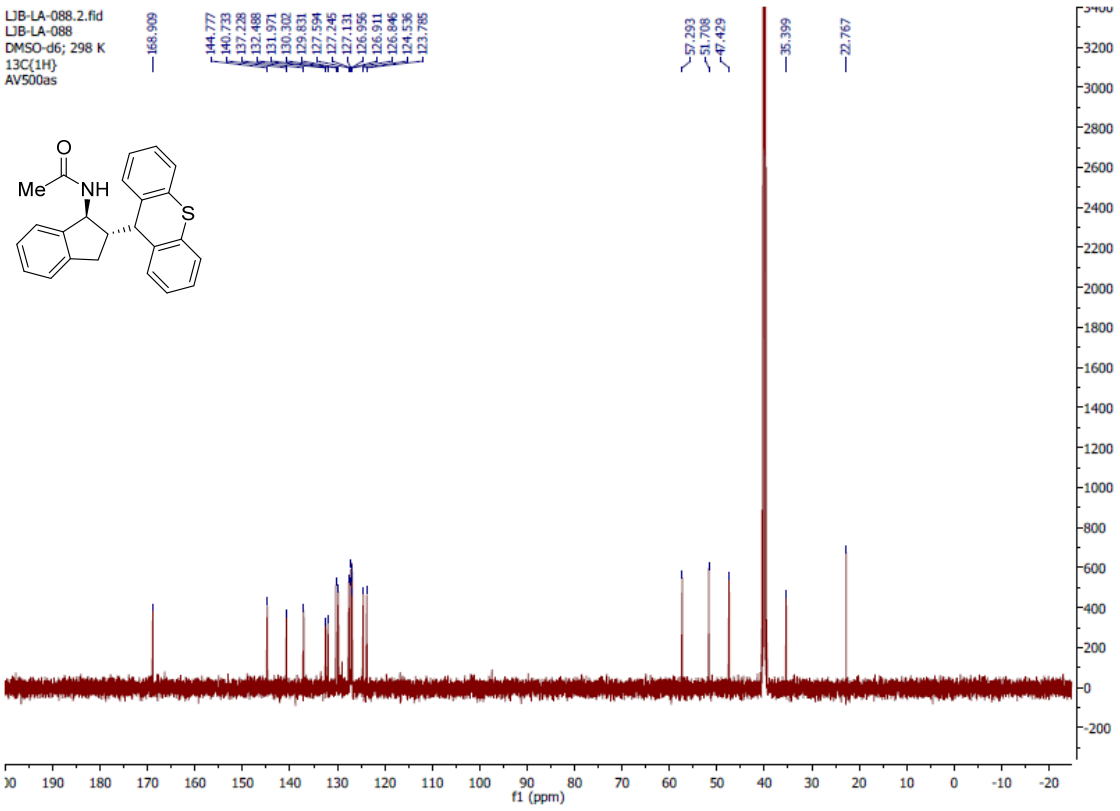

LJB-LA-068.22.fid
LJB-LA-068
129.89
129.14
127.36
127.23
127.19
127.12
126.29
125.49
50.27
45.68
39.13
31.59
23.26
O
Me
NH
S
R
R = 2,4,6-Me
f1 (ppm)

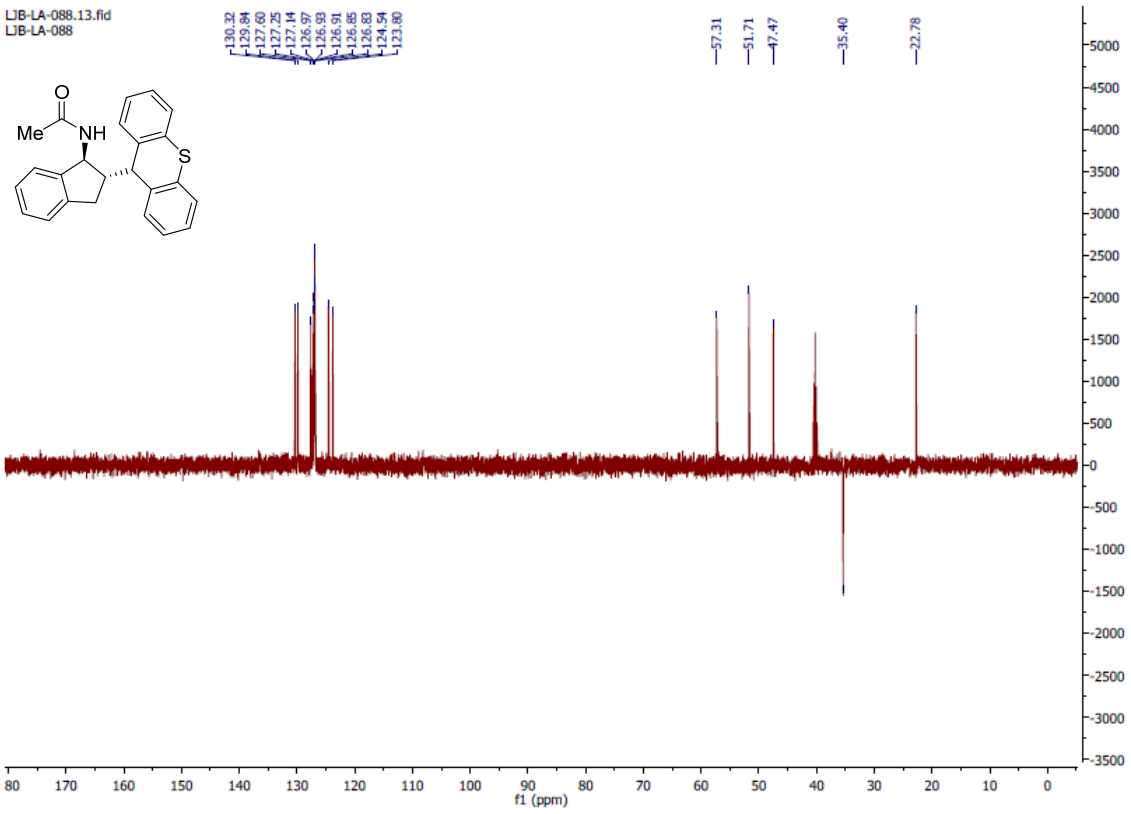

LJB-LA-067.10.fid
LJB-LA-067
8.63
8.62
O
Me
NH
S
1.05
3.21
6.15
6.29
1.16
1.06
1.07
4.00
f1 (ppm)

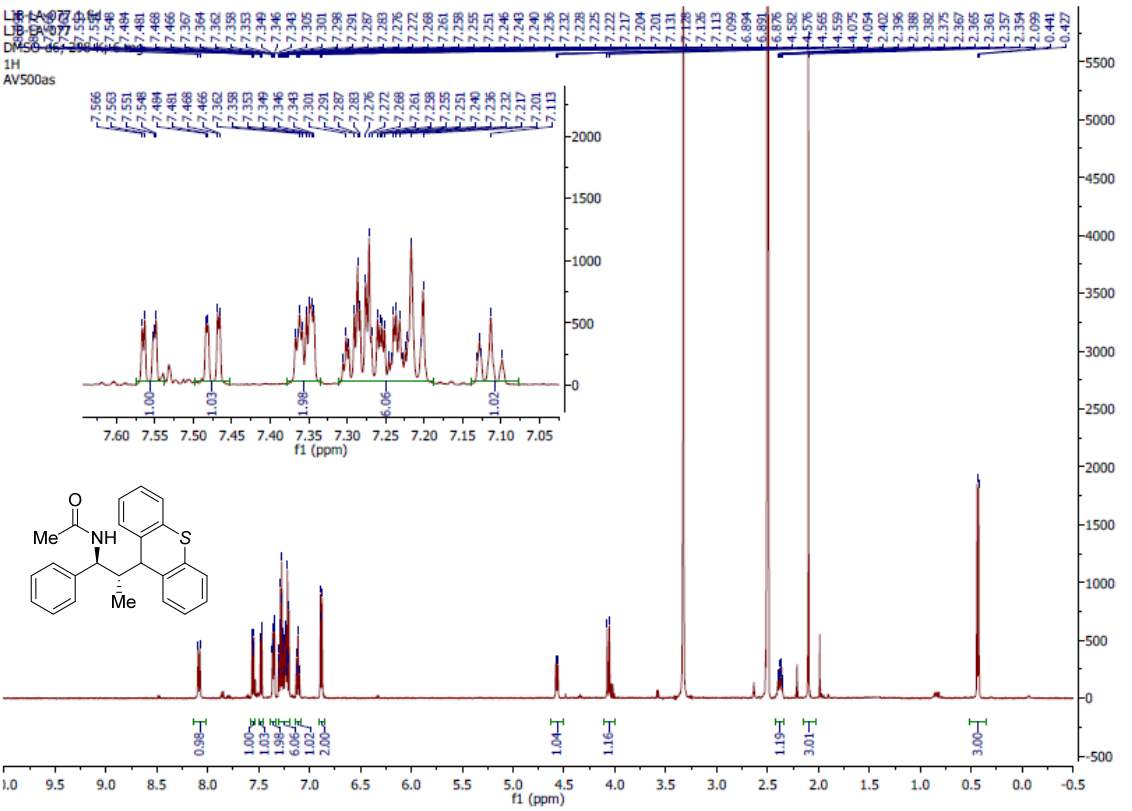

LJB-LA-067.11.fid
LJB-LA-067
169.12
141.52
138.57
137.11
133.26
132.48
131.91
131.77
129.92
129.25
128.51
128.11
127.86
127.42
127.39
127.28
127.23
127.19
126.58
126.12
125.25
124.93
50.83
45.66
38.83
23.30
Me
NH
S
O
f1 (ppm)

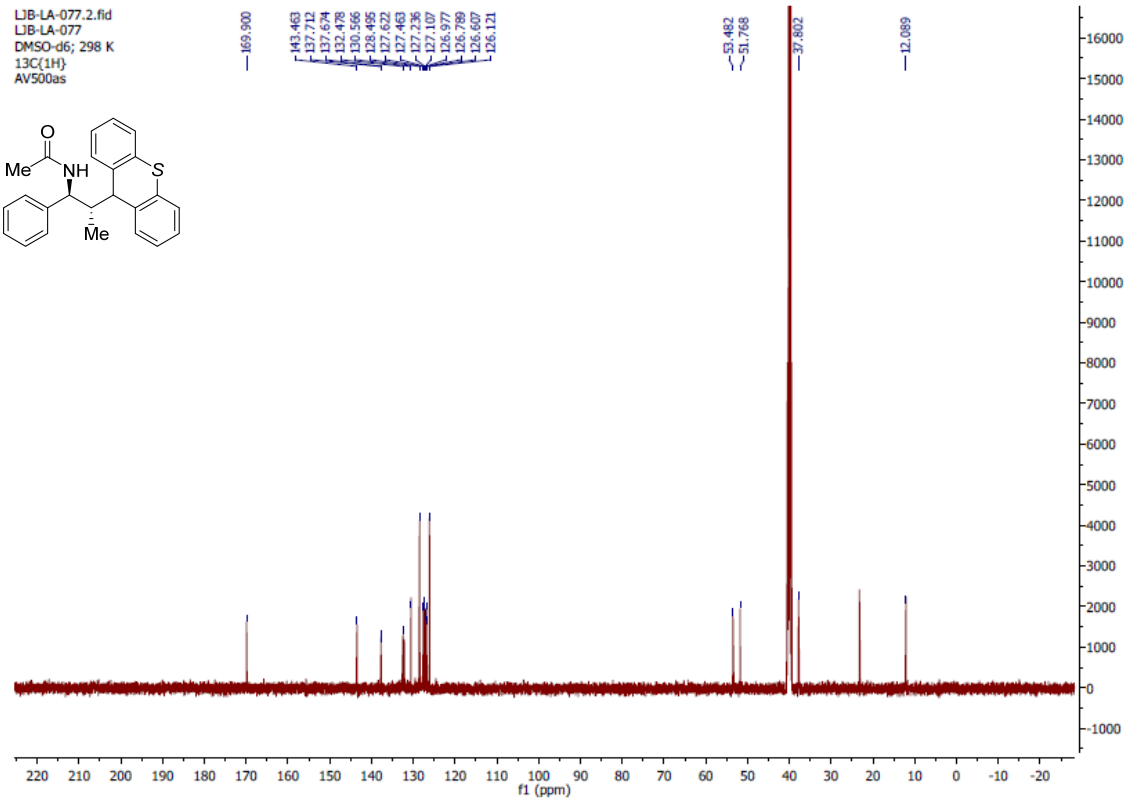

LJB-LA-067.12.fid
LJB-LA-067
129.92
129.25
128.52
128.11
127.86
127.42
127.39
127.28
127.23
127.19
126.58
126.11
125.25
124.93
50.83
45.66
38.83
23.30
Me
NH
S
O
f1 (ppm)

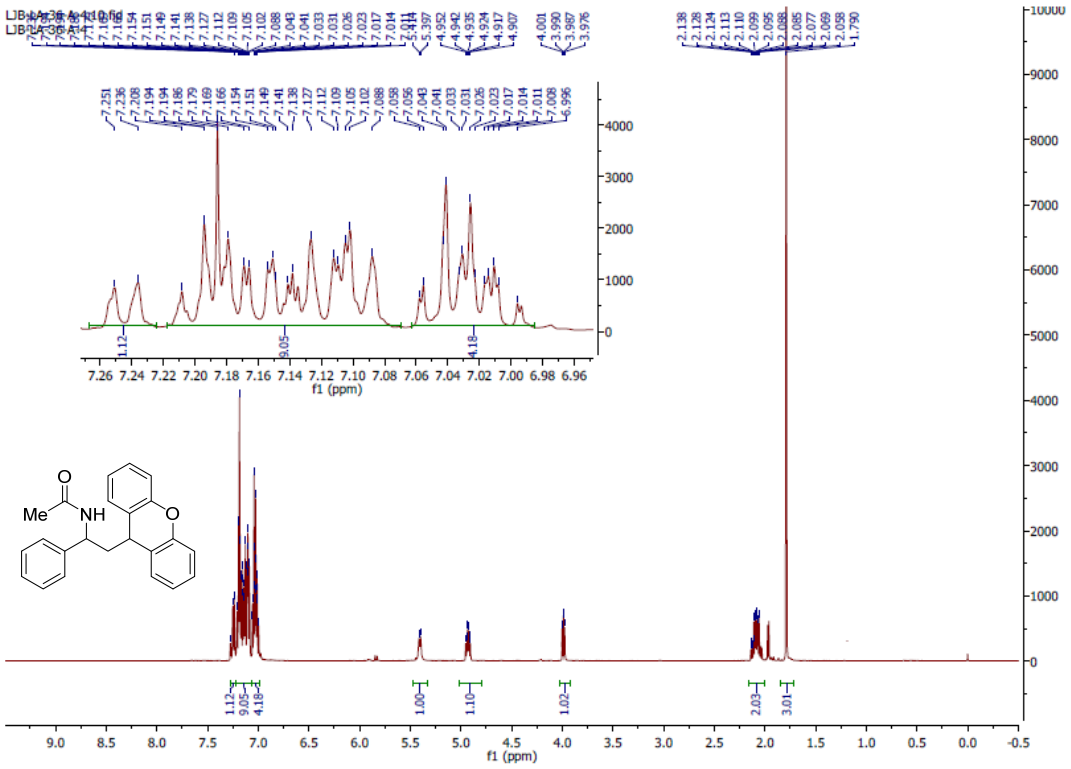

LJB-LA-088.1.fid
LJB-LA-088
DMSO-d6; 298 K
1H
AV500as
Me
NH
O
S
f1 (ppm)

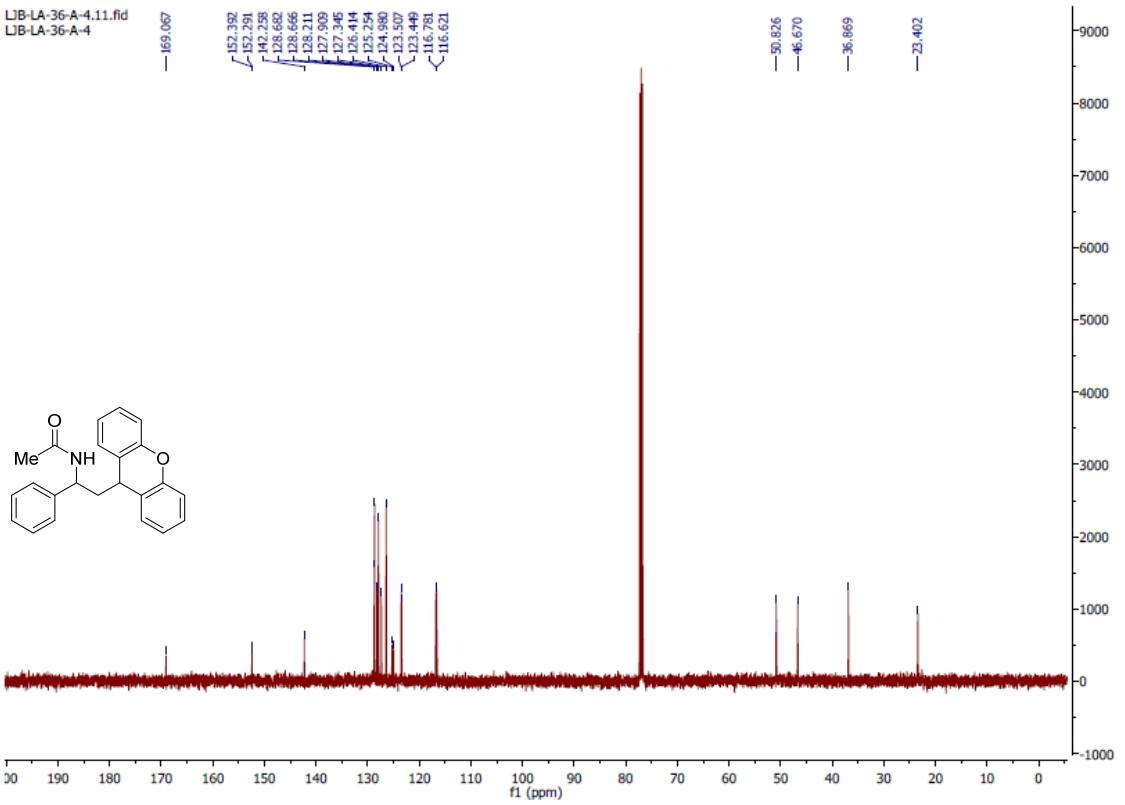

LJB-LA-088.2.fid
LJB-LA-088
DMSO-d6; 298 K
13C{1H}
AV500as
Me
NH
O
S
f1 (ppm)

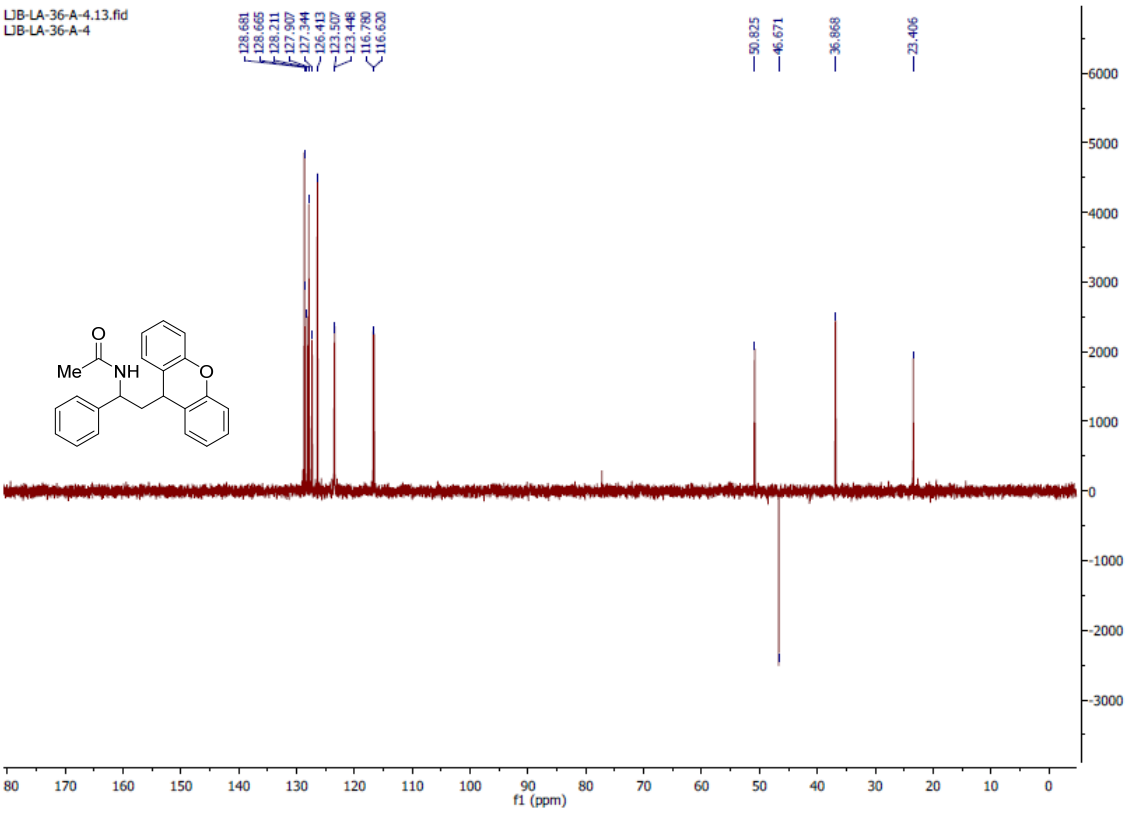

LJB-LA-088.13.fid
LJB-LA-088
130.32
129.84
127.60
127.25
127.14
126.97
126.93
126.91
126.85
126.83
124.54
123.80
57.31
51.71
47.47
35.40
22.78
Me
NH
S
f1 (ppm)

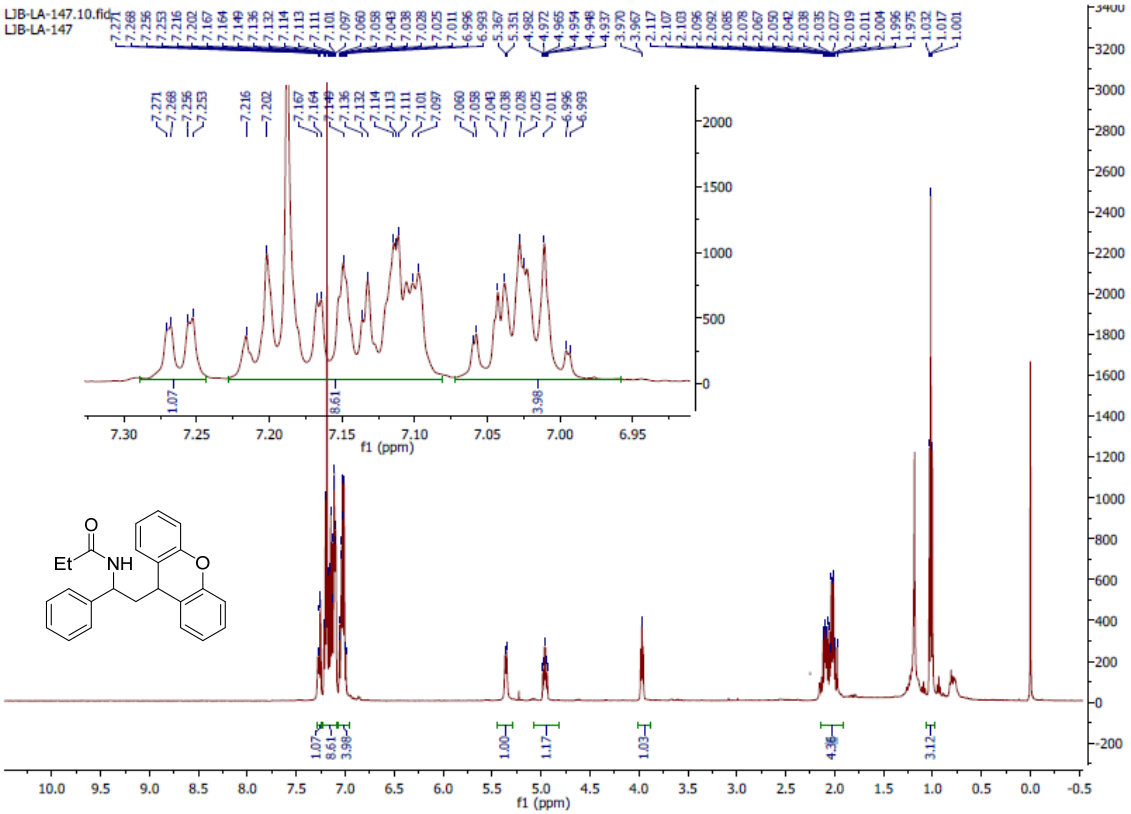

1H
AV500as
Me
NH
S
Me
f1 (ppm)

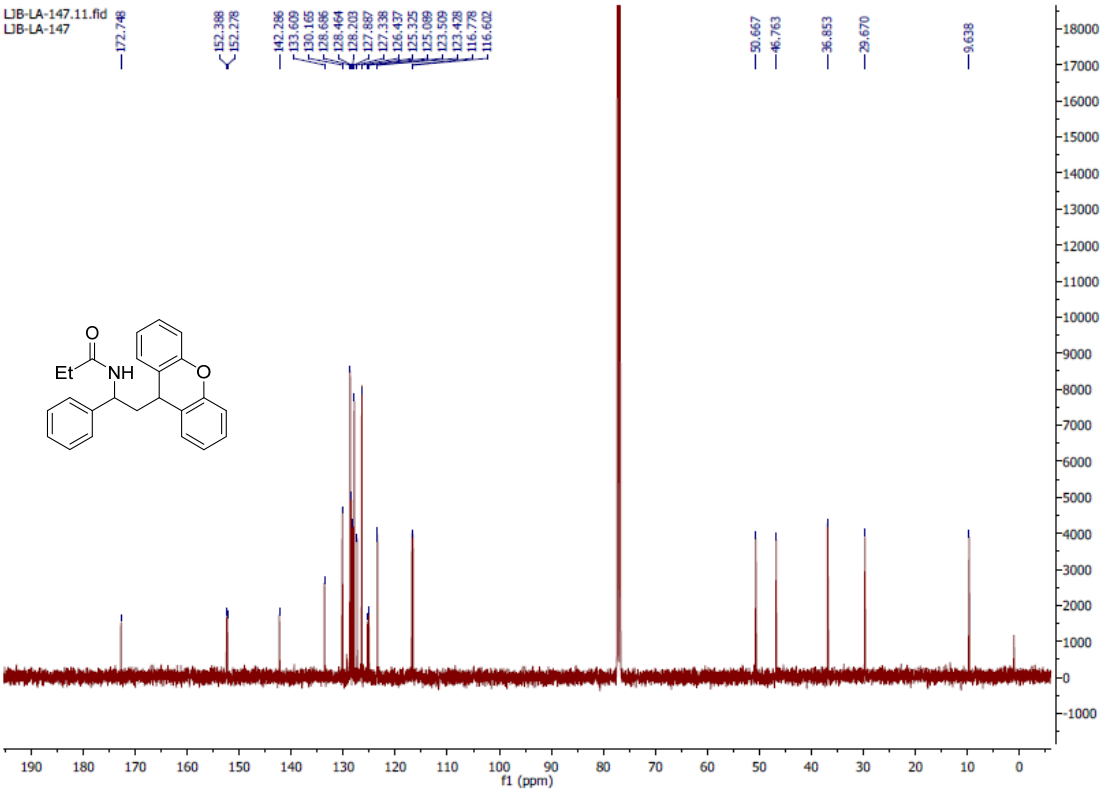

LJB-LA-077.2.fid
LJB-LA-077
DMSO-d6; 298 K
13C{1H}
AV500as
169.900
143.463
137.712
137.674
132.478
130.566
128.495
127.622
127.463
127.236
127.107
126.977
126.789
126.607
126.121
53.482
51.768
37.802
12.089
Me
NH
S
Me
f1 (ppm)

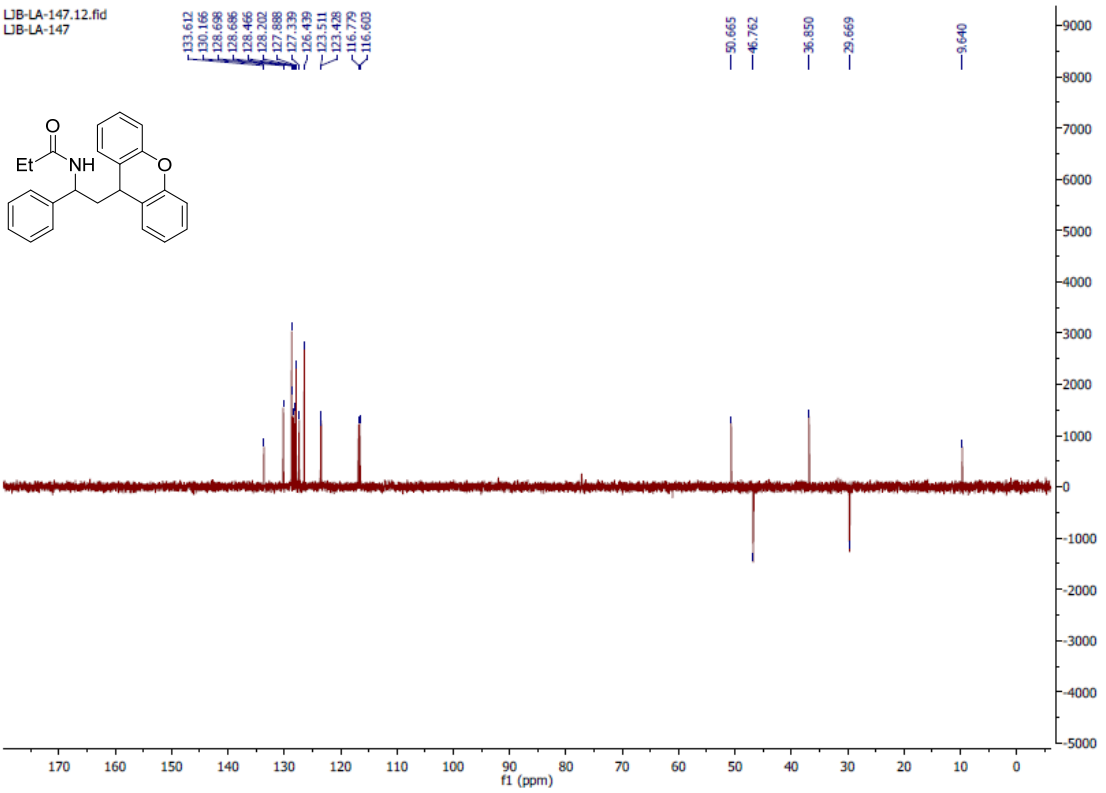

7.26 7.24 7.22 7.20 7.18 7.16 7.14 7.12 7.10 7.08 7.06 7.04 7.02 7.00 6.98 6.96
f1 (ppm)
1.12
9.05
4.18
1.00
1.10
1.02
2.03
3.01
Me
NH
O
f1 (ppm)

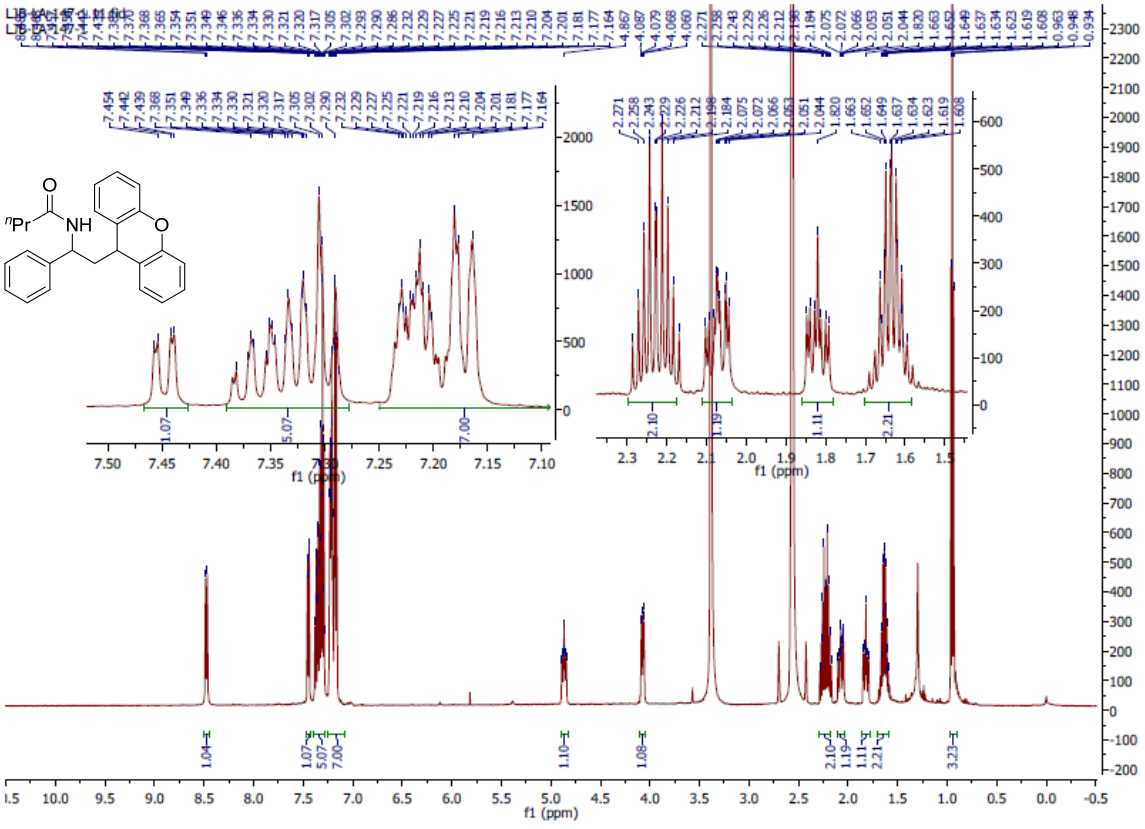

LJB-LA-36-A-4.11.fid
LJB-LA-36-A-4
169.067
152.392
152.291
142.258
128.682
128.666
128.211
127.909
127.345
126.414
125.254
124.980
123.507
123.449
116.781
116.621
50.826
46.670
36.869
23.402
Me
NH
O
f1 (ppm)

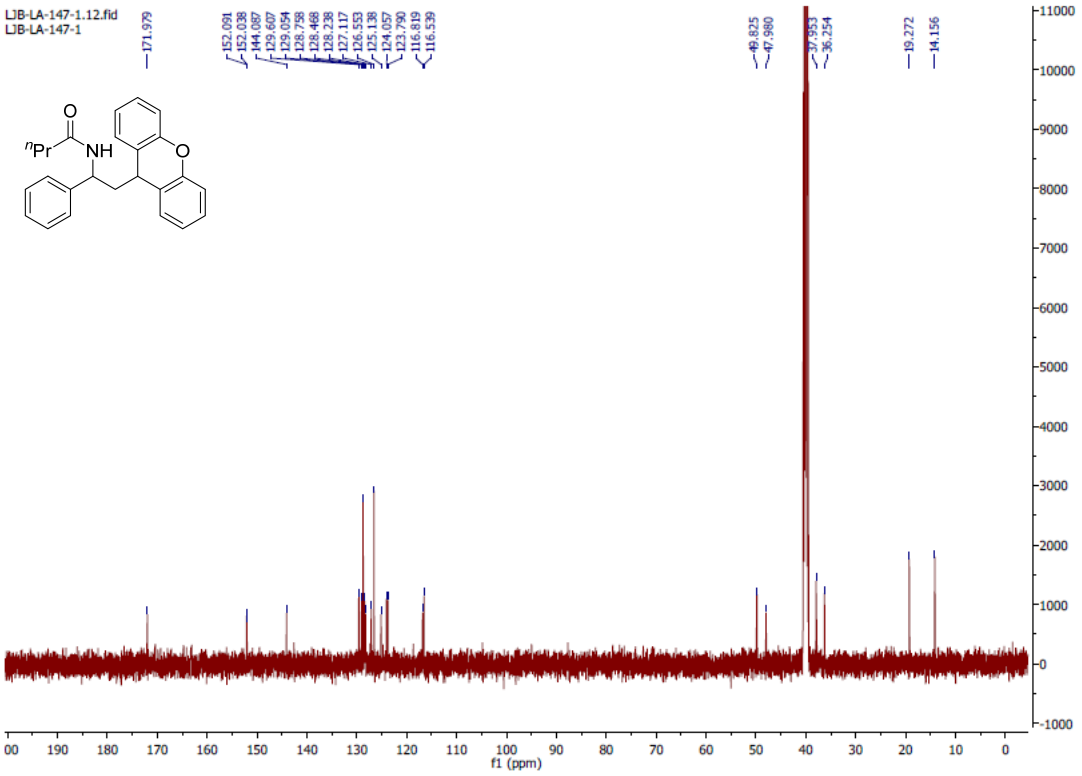

LJB-LA-36-A-4.13.fid
LJB-LA-36-A-4
128.681
128.665
128.211
127.907
127.344
126.413
123.507
123.448
116.780
116.620
50.825
46.671
36.868
23.406
Me
NH
O
f1 (ppm)

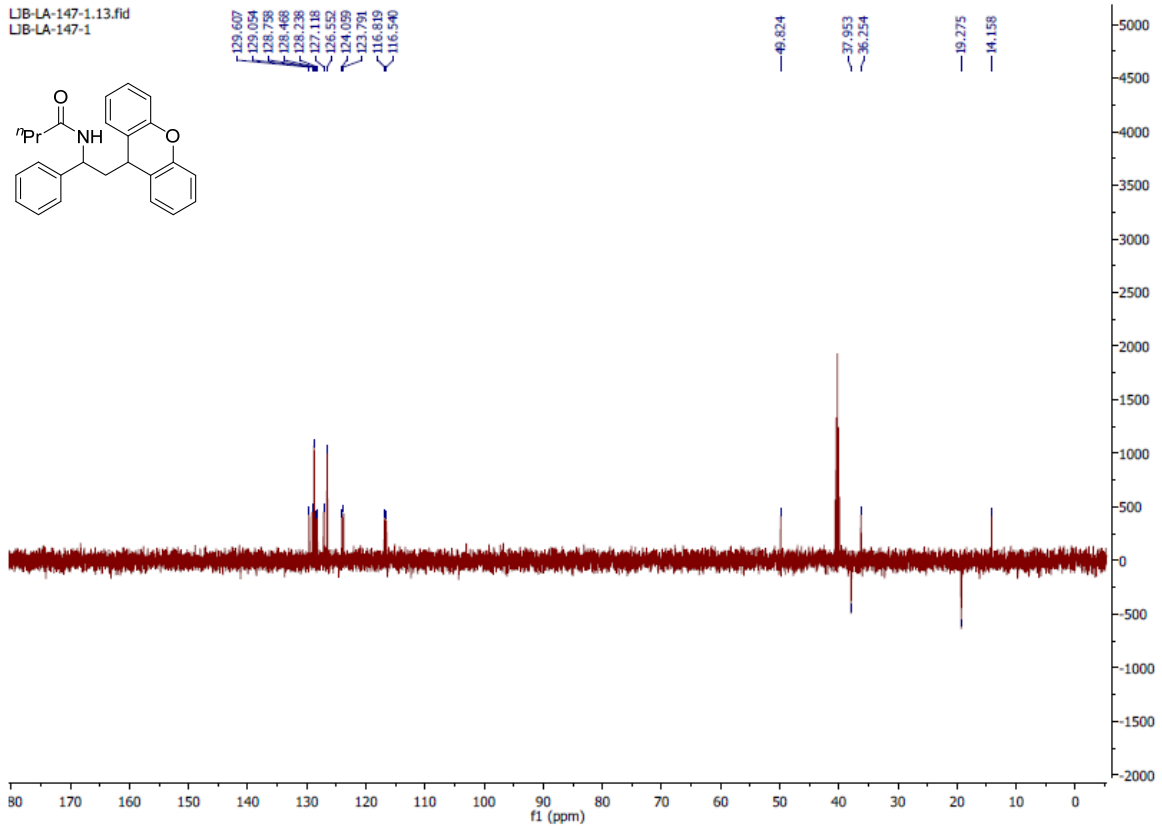

LJB-LA-147.10.fid
LJB-LA-147
Et
NH
O
f1 (ppm)

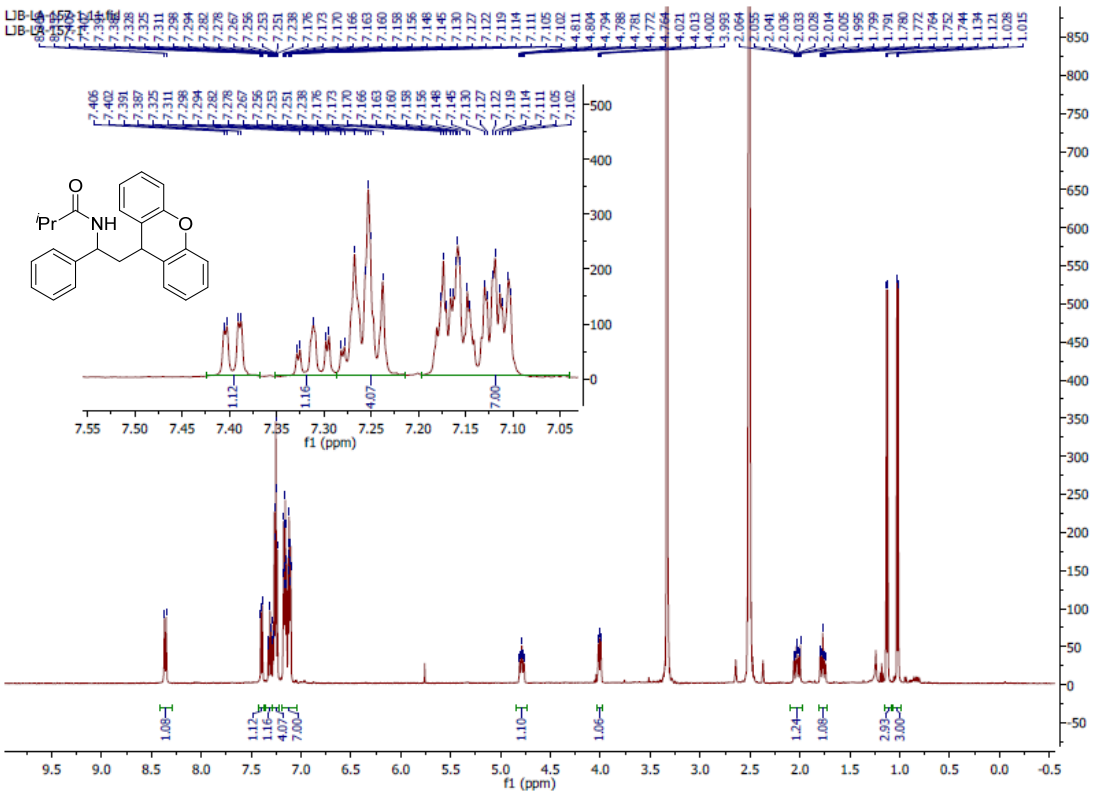

LJB-LA-147.11.fid
LJB-LA-147
Et
NH
O
f1 (ppm)

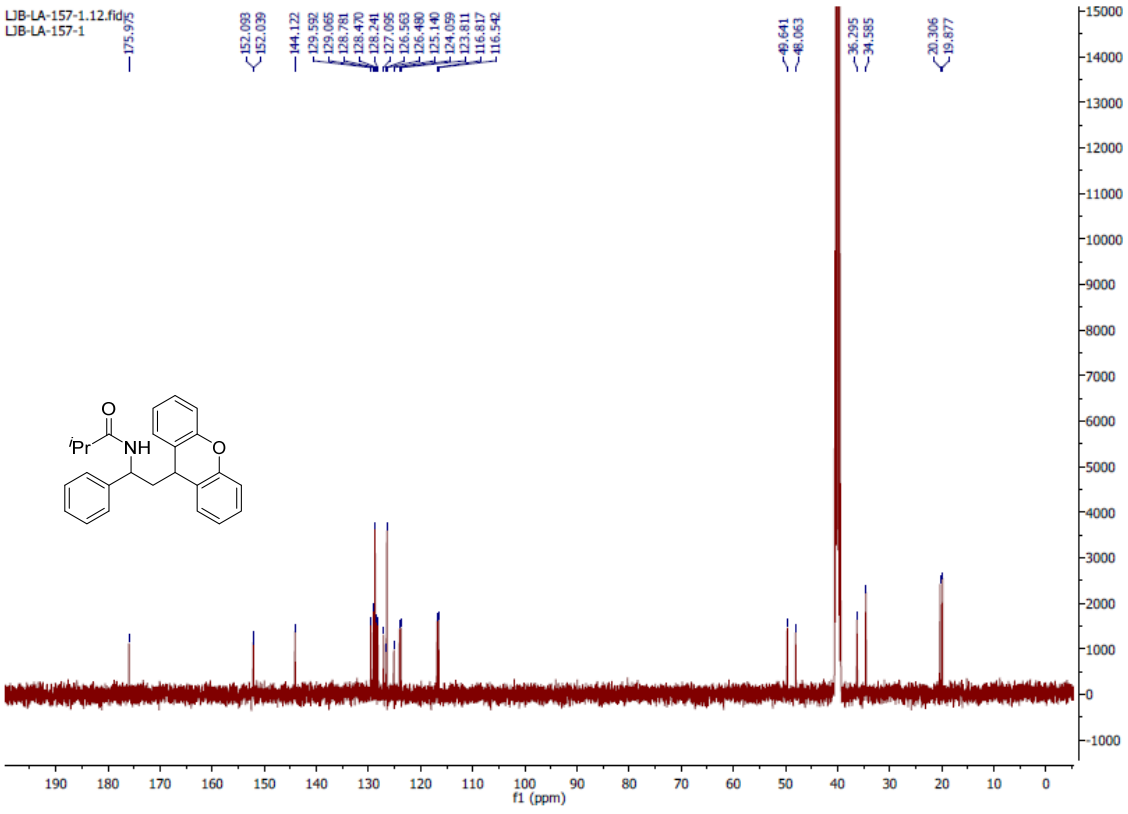

LJB-LA-147.12.fid
LJB-LA-147
133.612
130.166
128.698
128.686
128.466
128.202
127.888
127.339
126.439
123.511
123.428
116.779
116.603
50.665
46.762
36.850
29.669
9.640
O
Et
NH
O
f1 (ppm)

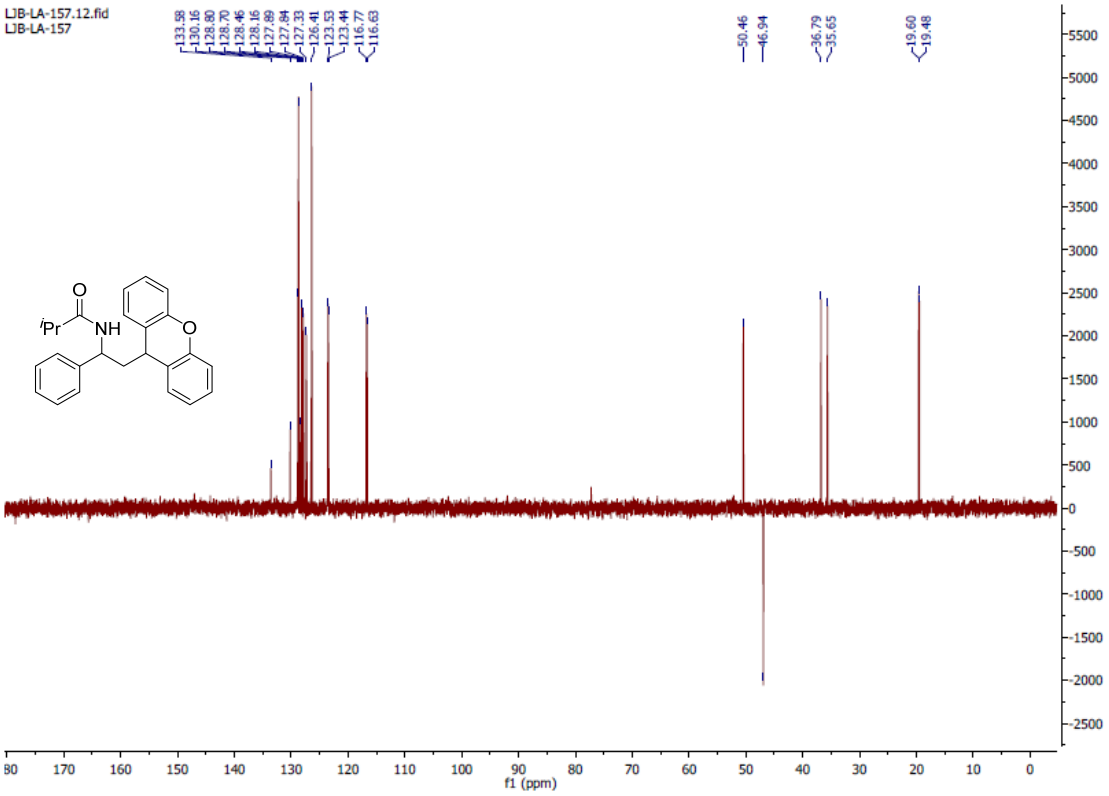

O
nPr
NH
O
1.07
5.07
7.00
2.10
1.19
1.11
2.21
1.04
1.10
1.08
3.23
f1 (ppm)

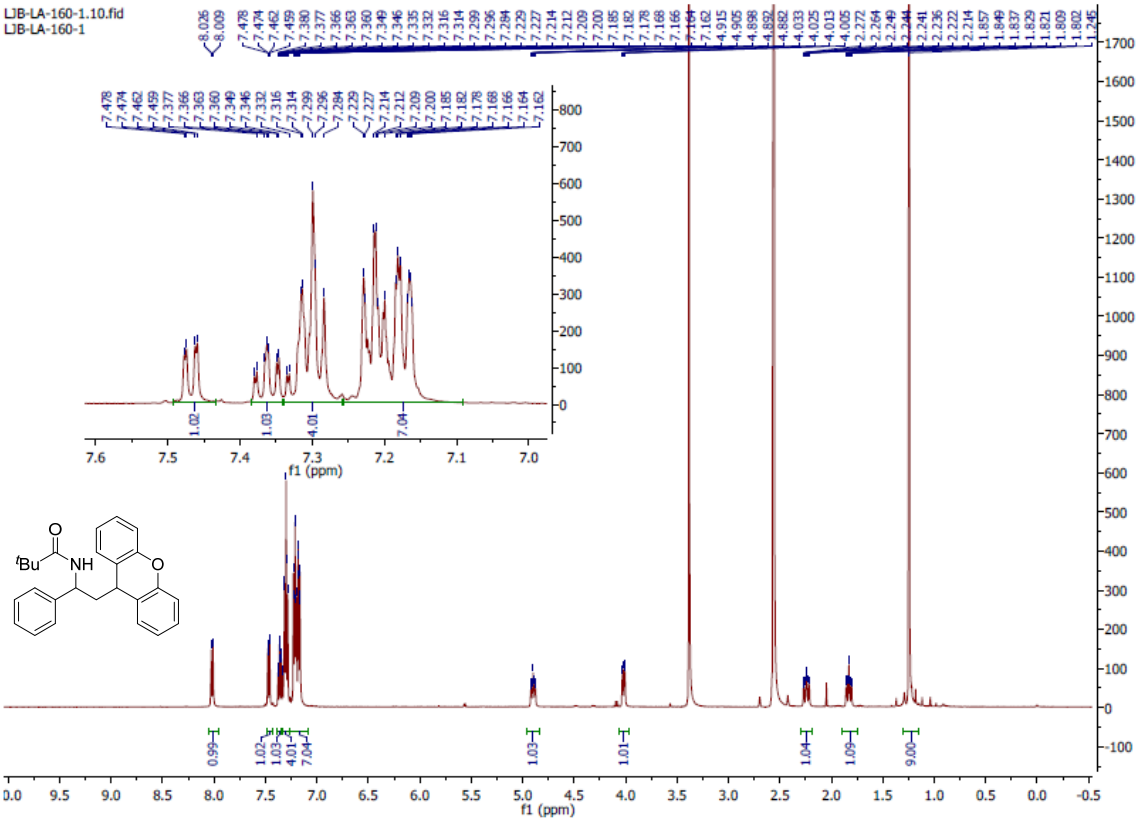

LJB-LA-147-1.12.fid
LJB-LA-147-1
171.979
152.091
152.038
144.087
129.607
129.054
128.758
128.468
128.238
127.117
126.553
125.138
124.057
123.790
116.819
116.539
49.825
47.980
37.953
36.254
19.272
14.156
nPr
NH
O
O
f1 (ppm)

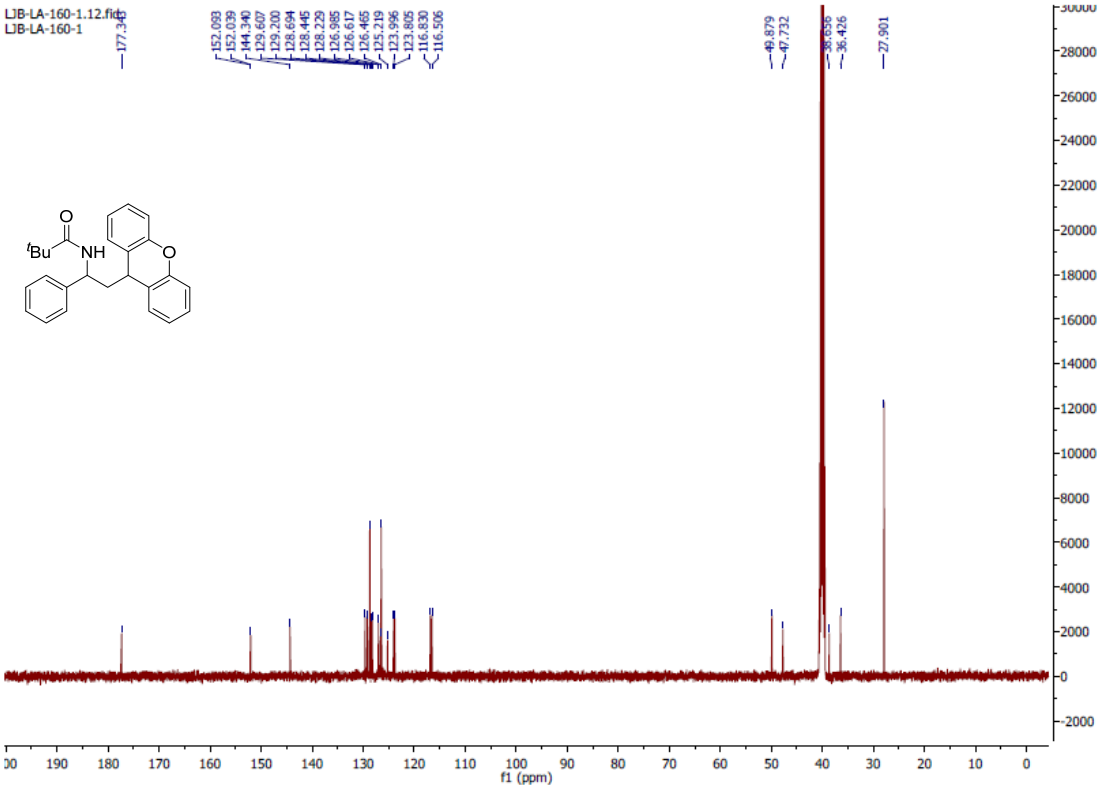

LJB-LA-147-1.13.fid
LJB-LA-147-1
129.607
129.054
128.758
128.468
128.238
127.118
126.552
124.059
123.791
116.819
116.540
49.824
37.953
36.254
19.275
14.158
nPr
NH
O
O
f1 (ppm)

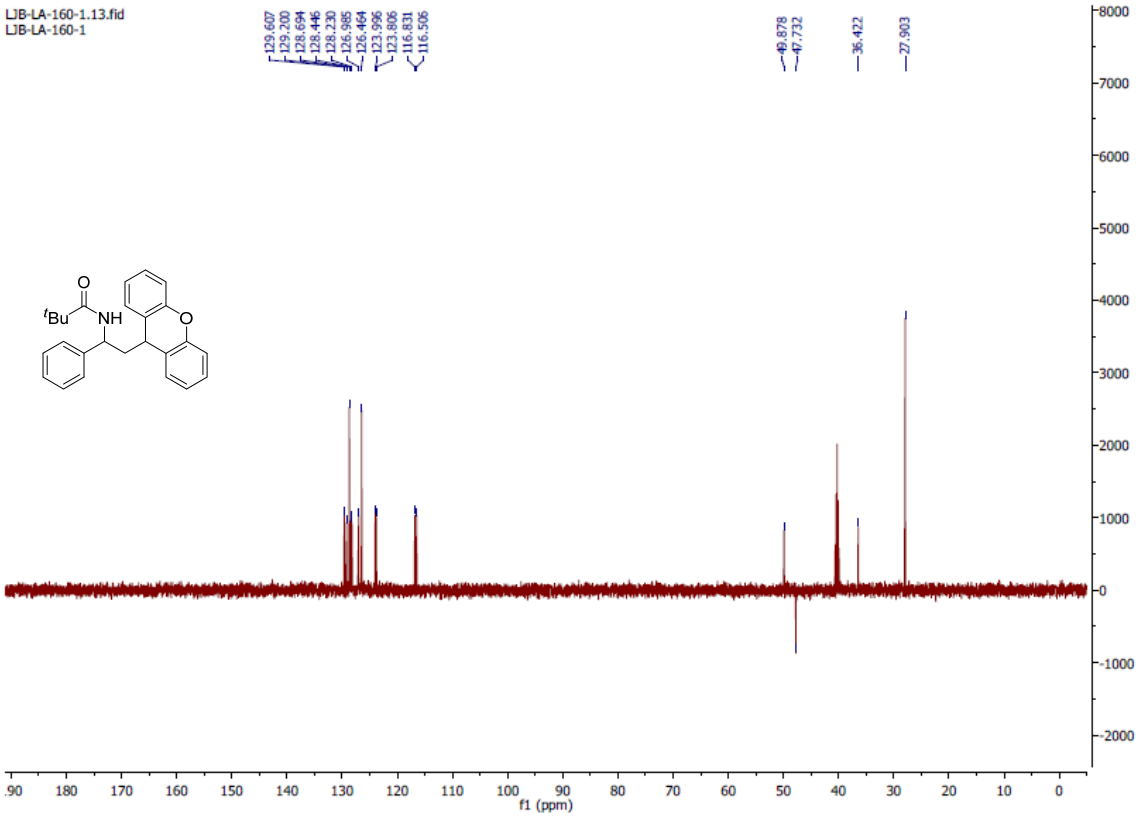

LJB-LA-157-1.14.fid
LJB-LA-157-1
O
iPr
NH
O
f1 (ppm)

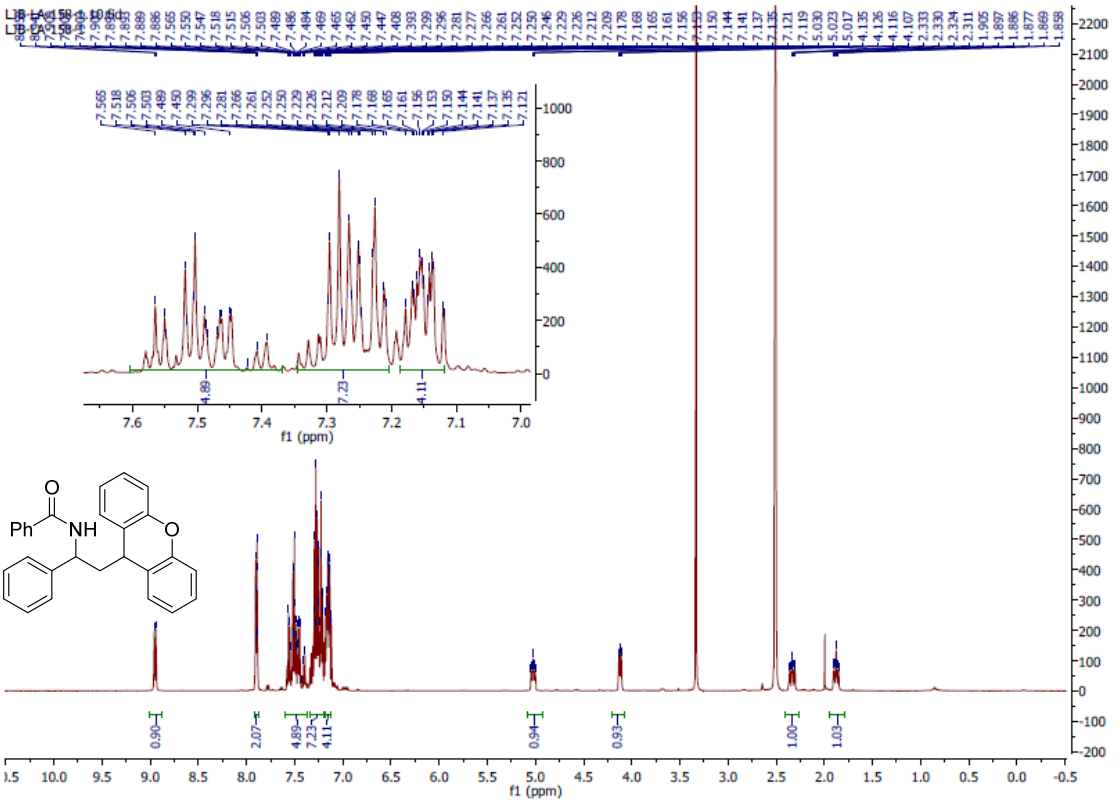

LJB-LA-157-1.12.fid
LJB-LA-157-1
O
iPr
NH
O
f1 (ppm)

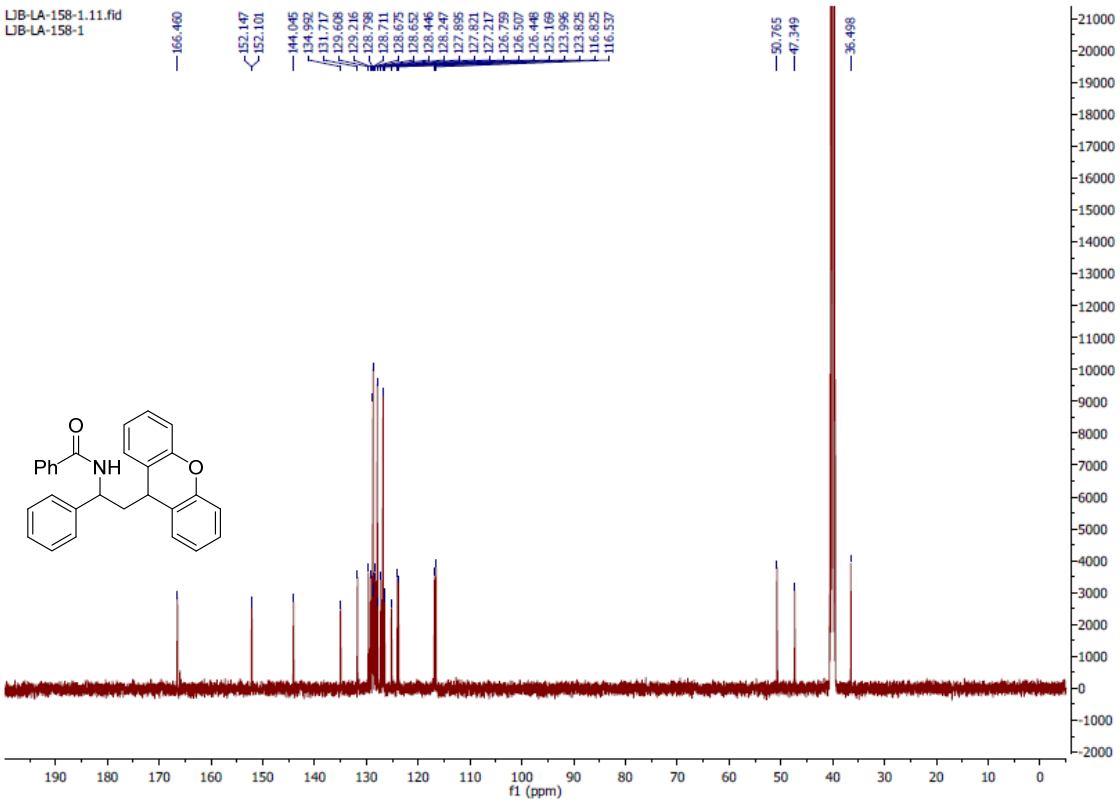

LJB-LA-157.12.fid
LJB-LA-157
f1 (ppm)

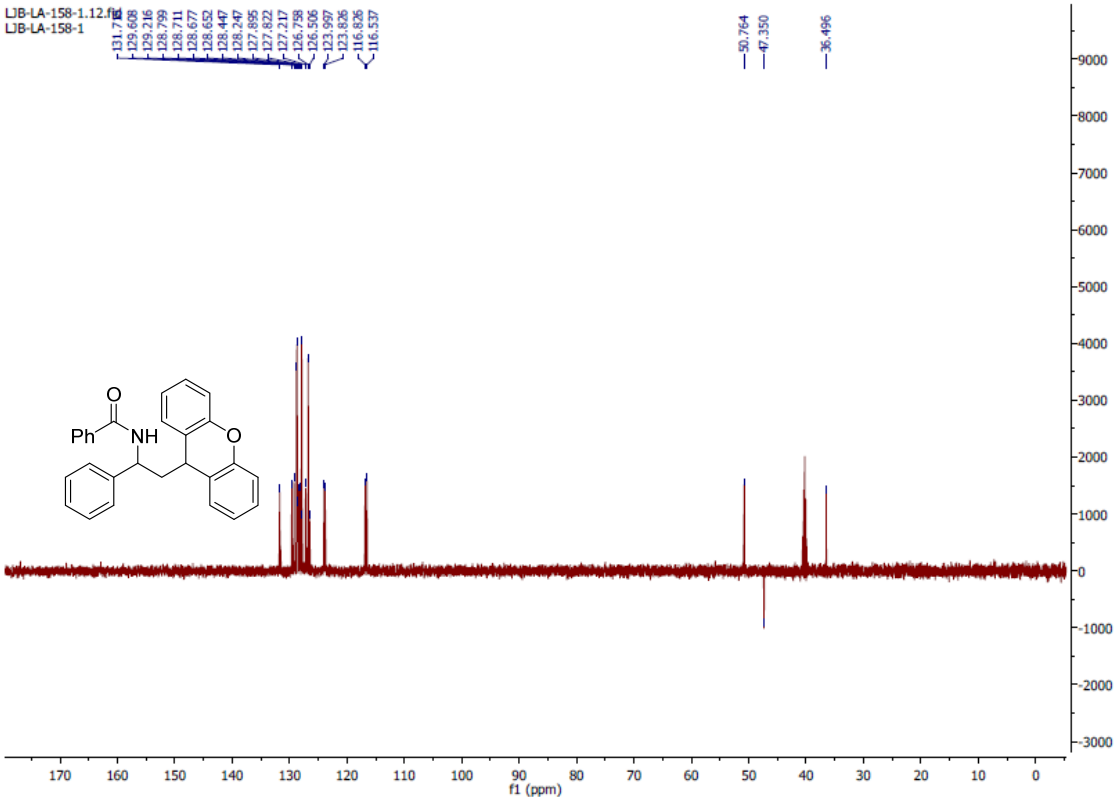

LJB-LA-160-1.10.fid
LJB-LA-160-1
f1 (ppm)

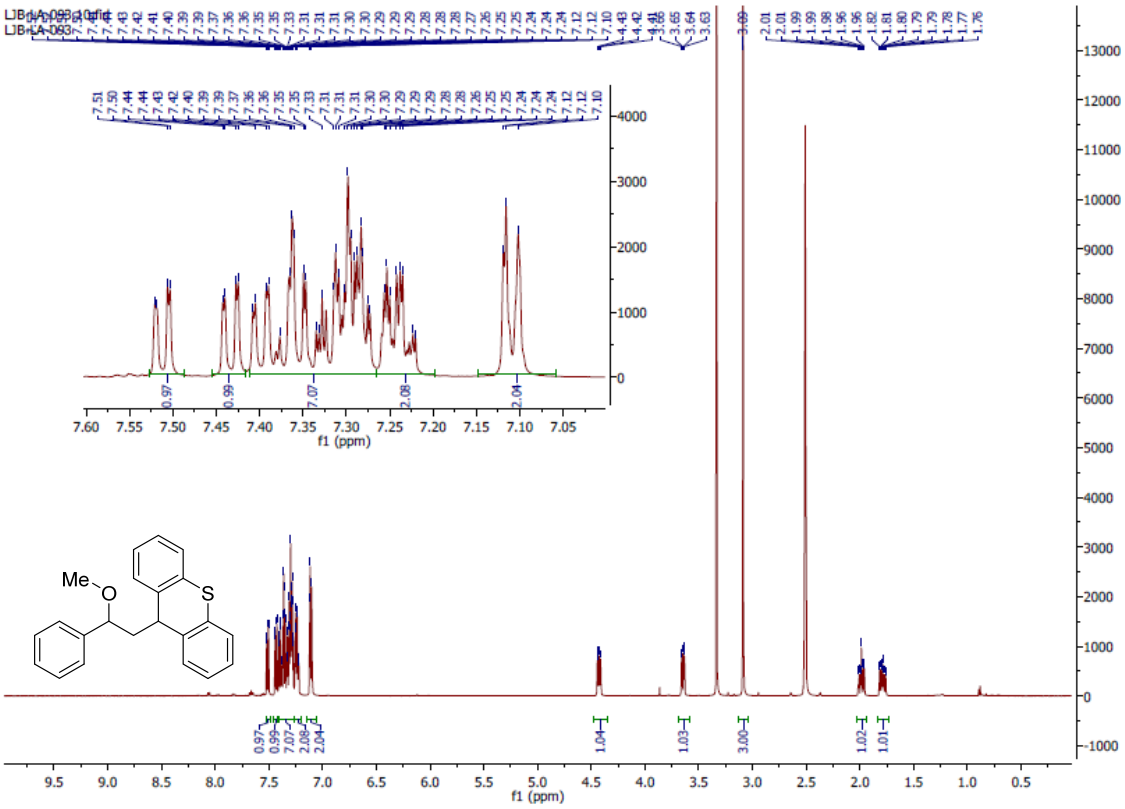

LJB-LA-160-1.12.fid
LJB-LA-160-1
177.348
152.093
152.039
144.340
129.607
129.200
128.694
128.445
128.229
126.985
126.617
126.465
125.219
123.996
123.805
116.830
116.506
49.879
47.732
36.426
27.901
tBu
NH
O
f1 (ppm)

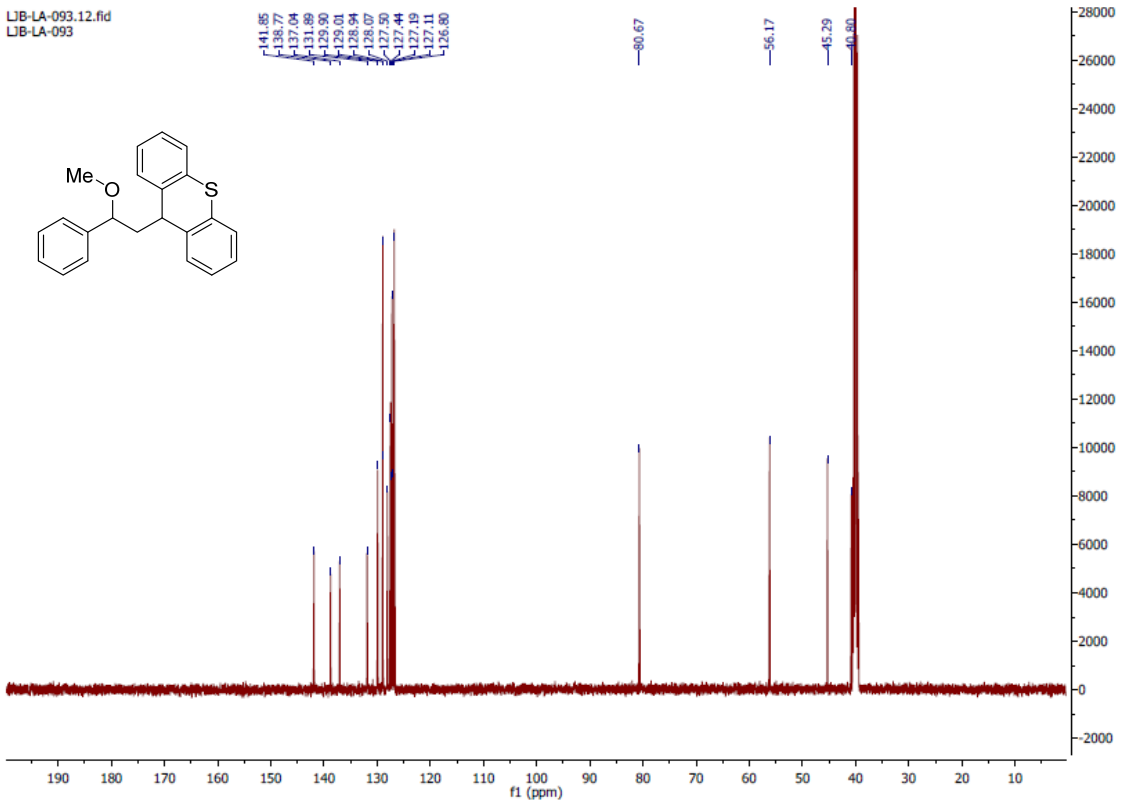

LJB-LA-160-1.13.fid
LJB-LA-160-1
129.607
129.200
128.694
128.446
128.230
126.985
126.464
123.996
123.806
116.831
116.506
49.878
47.732
36.422
27.903
tBu
NH
O
f1 (ppm)

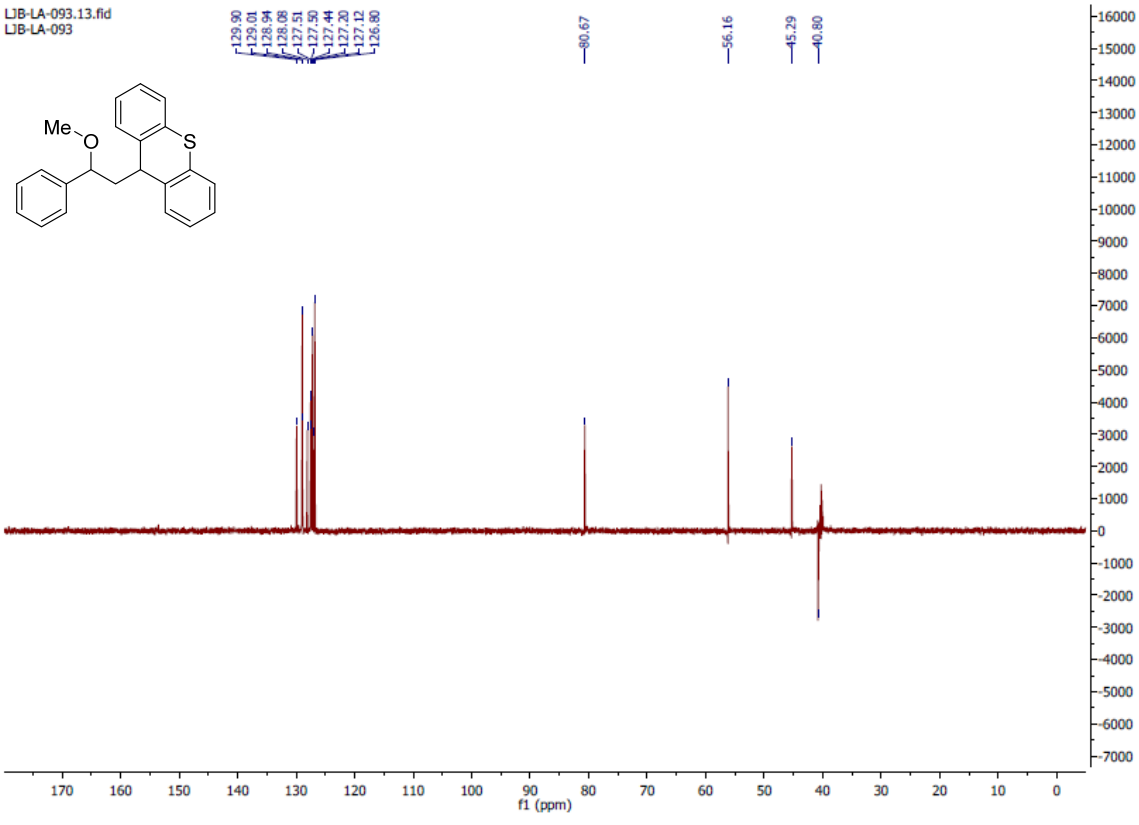

LJB-LA-158-1.10.fid
LJB-LA-158-1
O
Ph
NH
O
f1 (ppm)

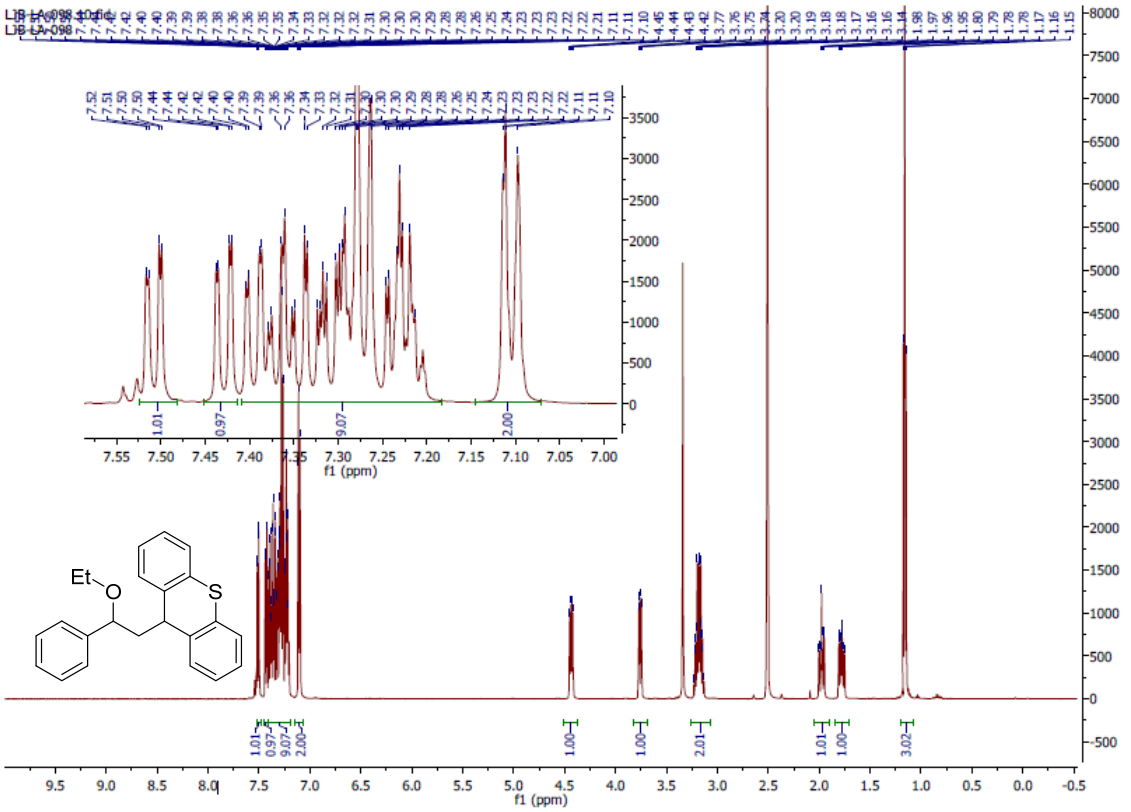

LJB-LA-158-1.11.fid
LJB-LA-158-1
O
Ph
NH
O
f1 (ppm)

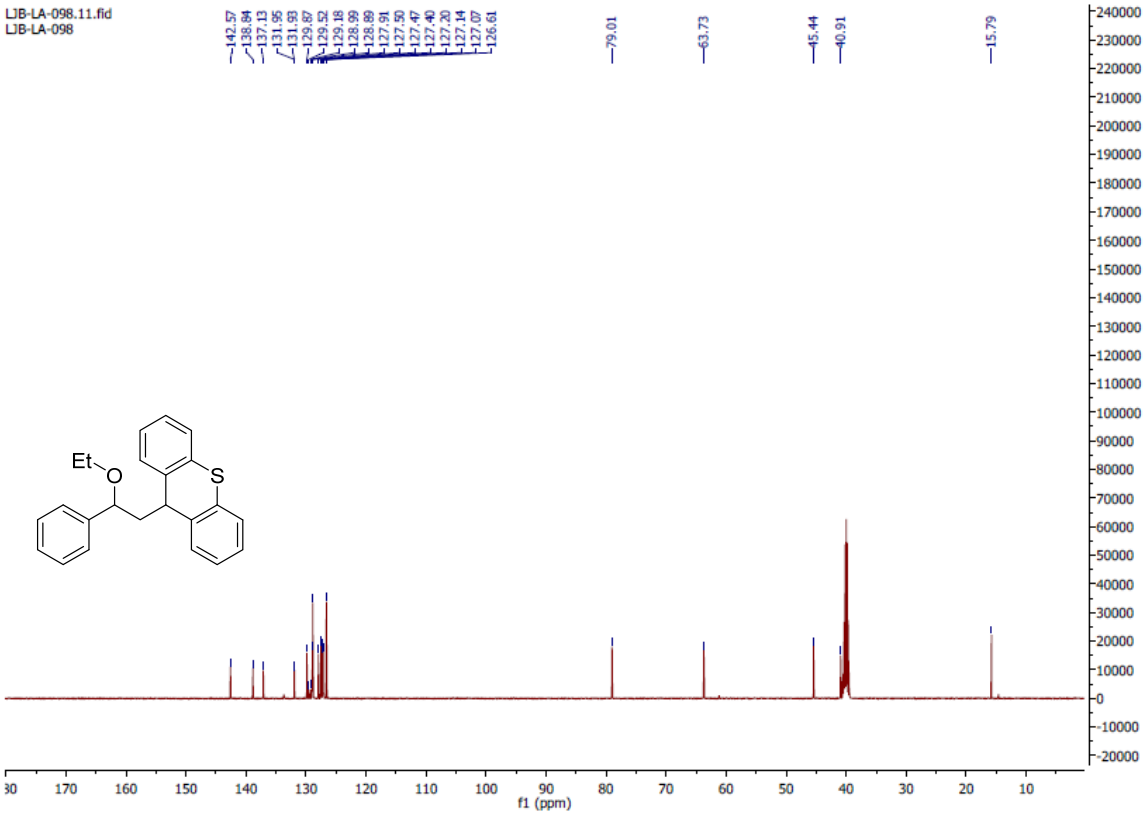

LJB-LA-158-1.12.fid
LJB-LA-158-1
131.788
129.608
129.216
128.799
128.711
128.677
128.652
128.447
128.247
127.895
127.822
127.217
126.758
126.506
123.997
123.826
116.826
116.537
50.764
47.350
36.496
O
Ph
NH
O
f1 (ppm)

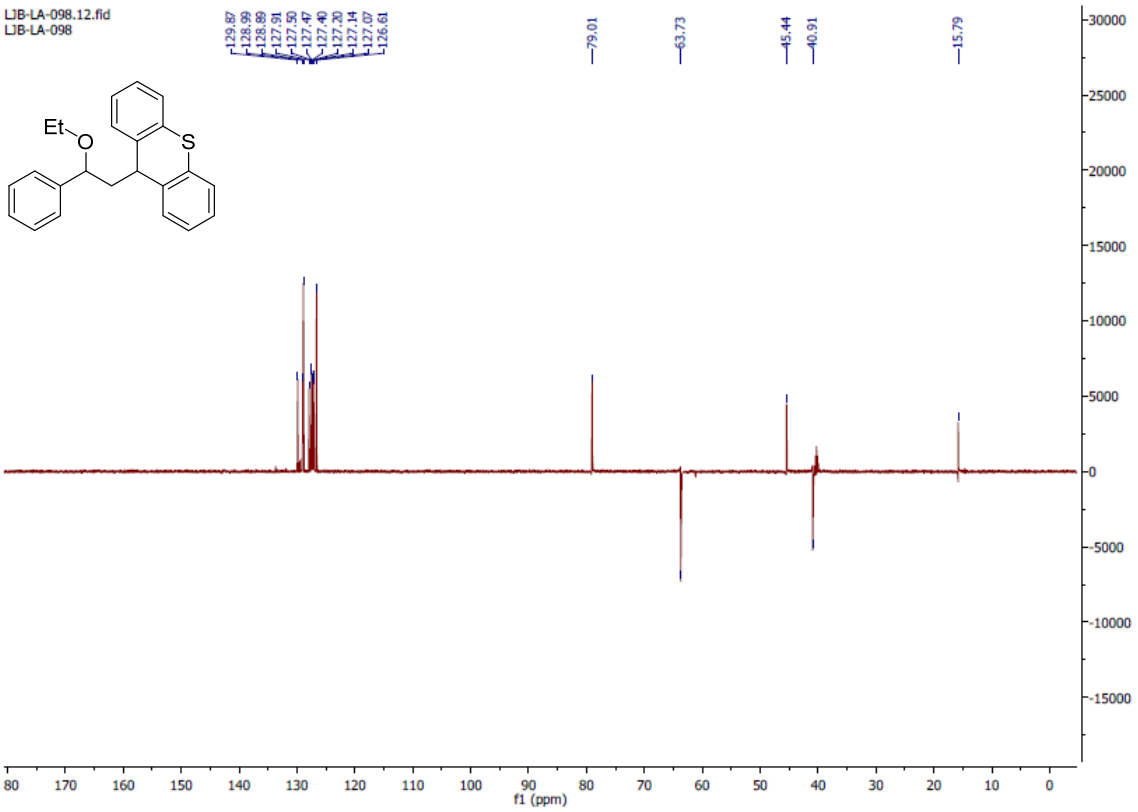

LJB-LA-093
LJB-LA-093
Me
O
S
0.97
0.99
7.07
2.08
2.04
1.04
1.03
3.00
1.02
1.01
f1 (ppm)

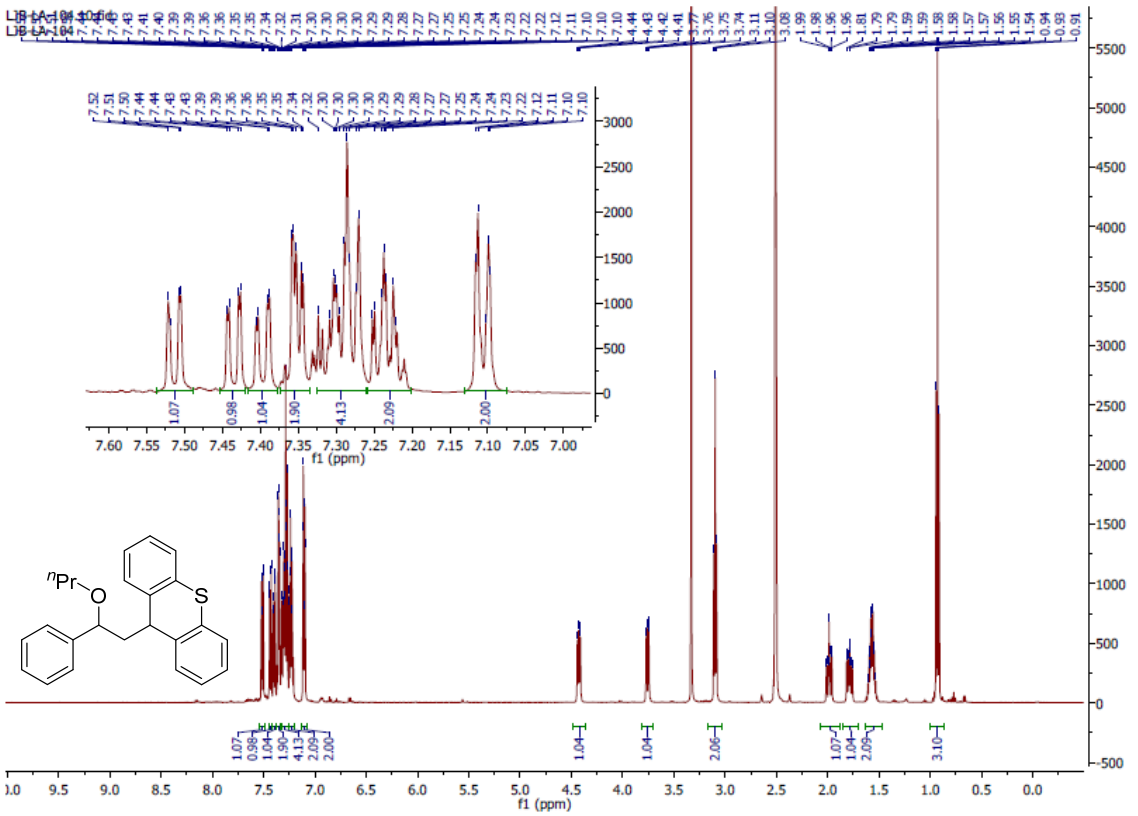

LJB-LA-093.12.fid
LJB-LA-093
141.85
138.77
137.04
131.89
129.90
129.01
128.94
128.07
127.50
127.44
127.19
127.11
126.80
80.67
56.17
45.29
40.80
Me
O
S
f1 (ppm)

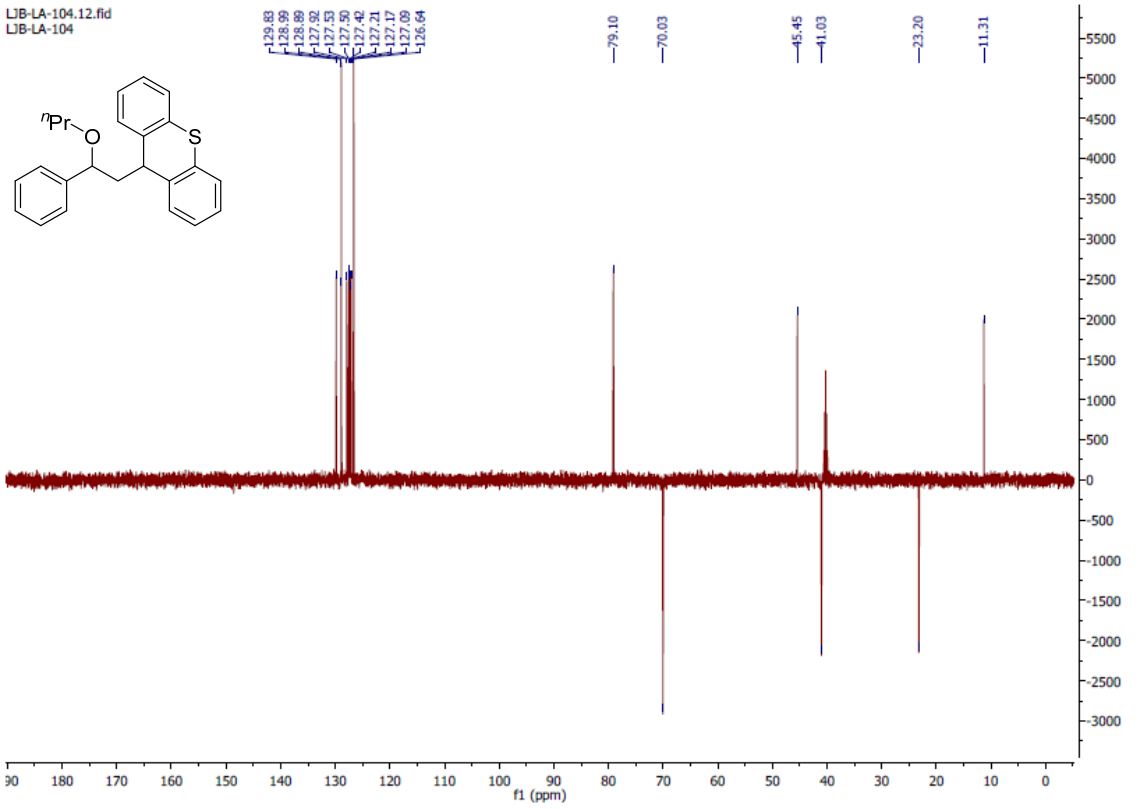

LJB-LA-093.13.fid
LJB-LA-093
129.90
129.01
128.94
128.08
127.51
127.50
127.44
127.20
127.12
126.80
80.67
56.16
45.29
40.80
Me
O
S
f1 (ppm)

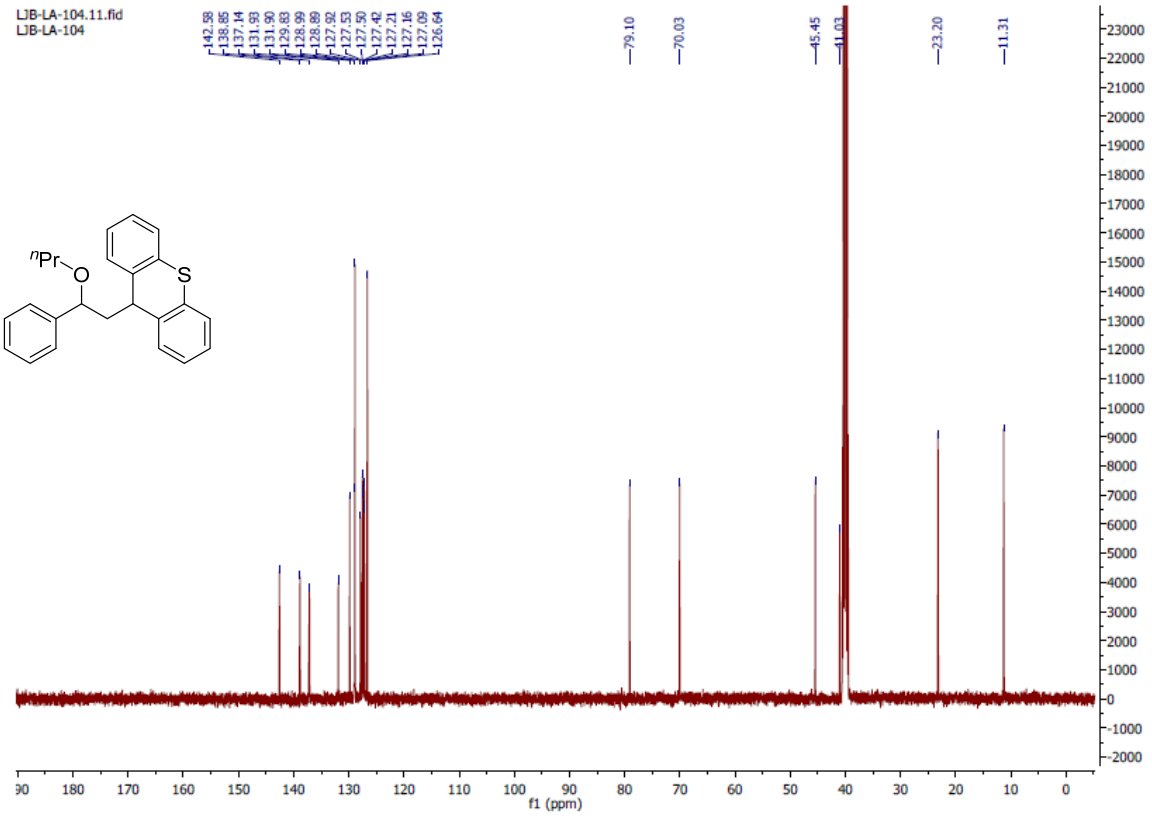

LJB-LA-098.10.fid
LJB-LA-098
f1 (ppm)
Et
O
S

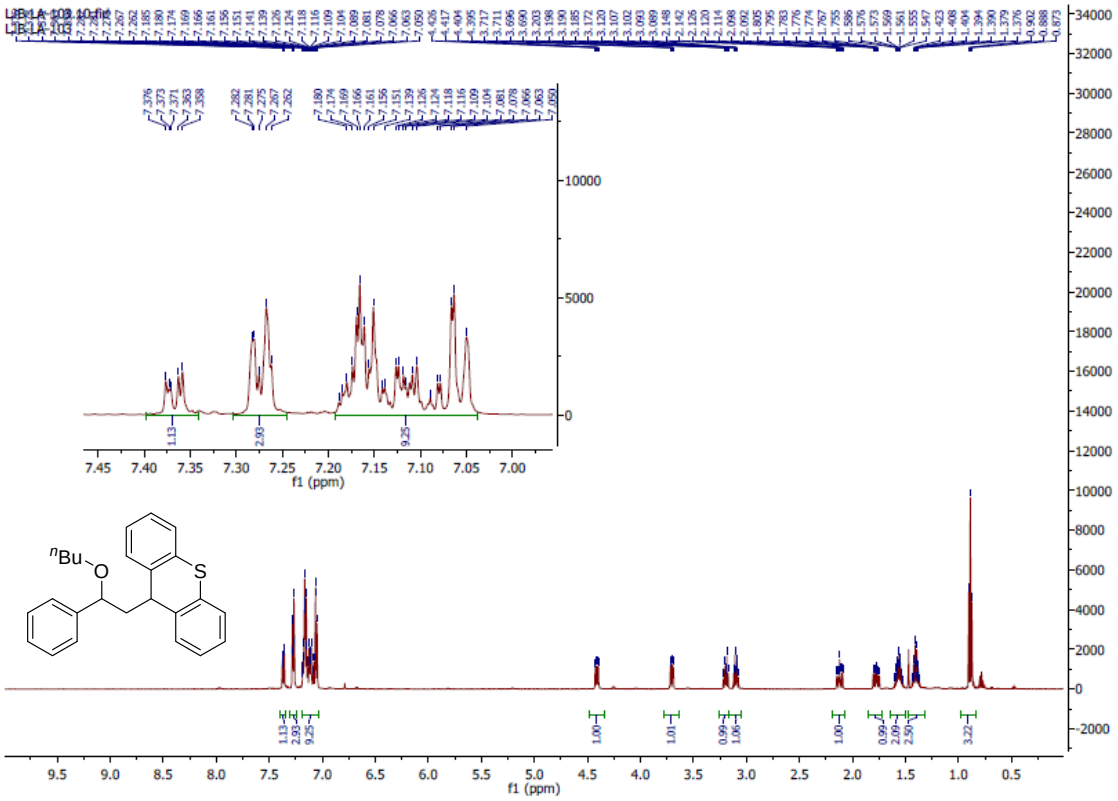

LJB-LA-098.11.fid
LJB-LA-098
f1 (ppm)
Et
O
S

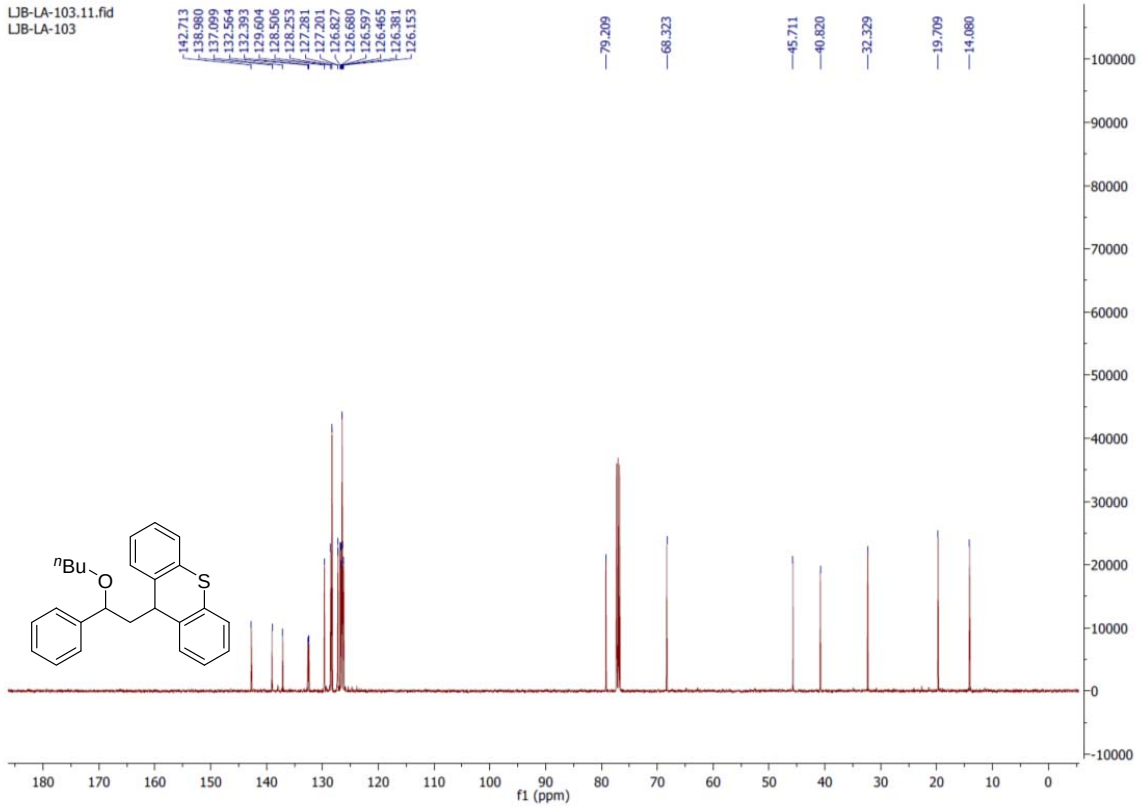

LJB-LA-098.12.fid
LJB-LA-098
129.87
128.99
128.89
127.91
127.50
127.47
127.40
127.30
127.14
127.07
126.61
79.01
63.73
45.44
40.91
15.79
Et
O
S
f1 (ppm)

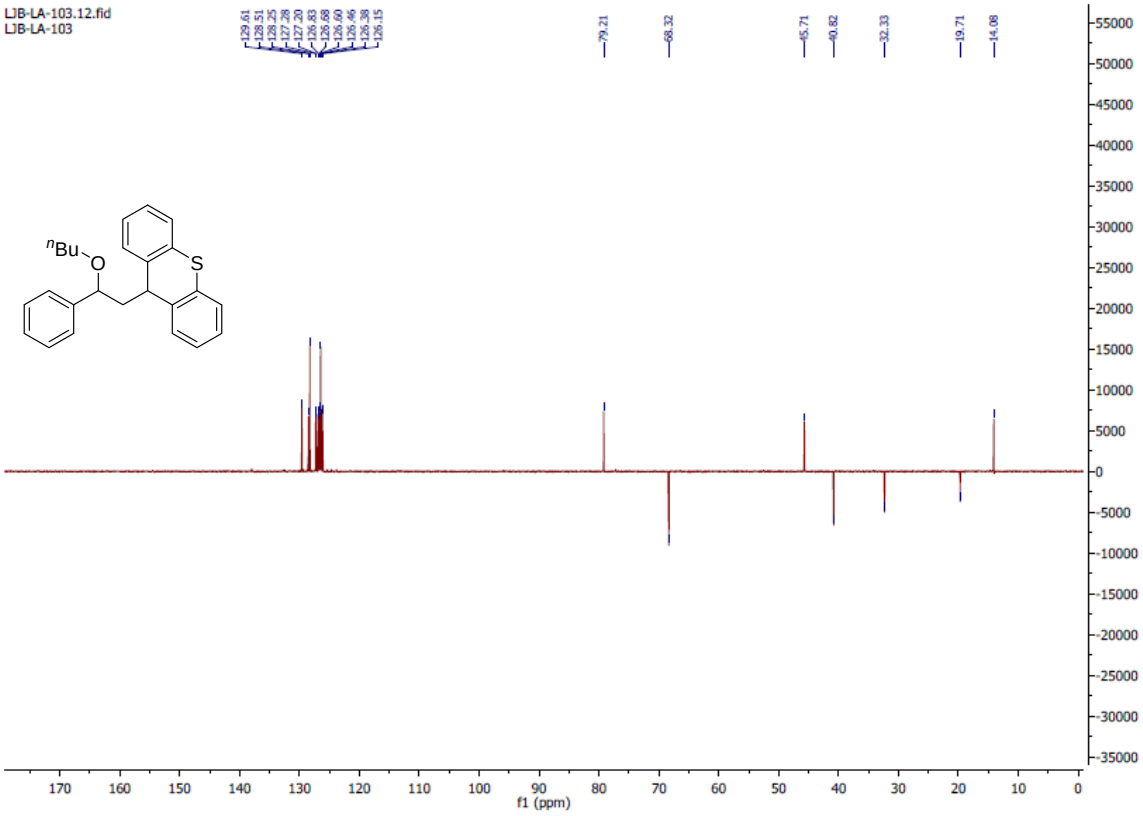

f1 (ppm)
nPr
O
S
f1 (ppm)

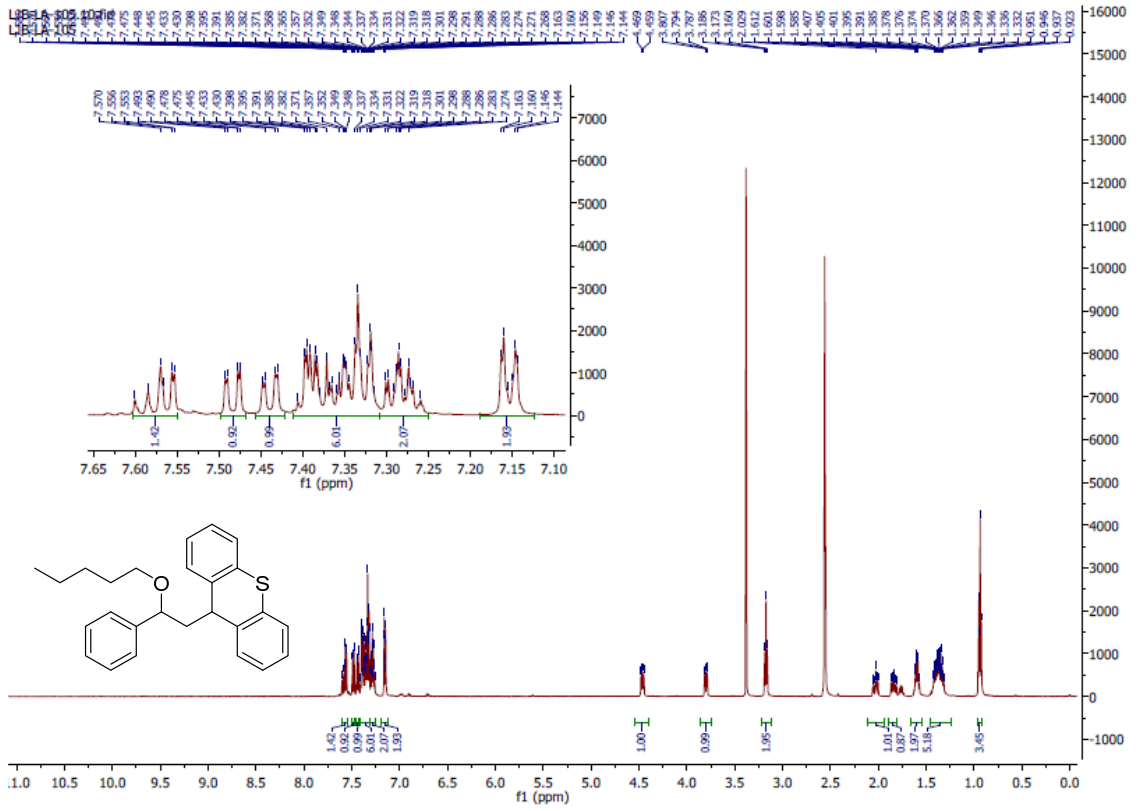

LJB-LA-104.12.fid
LJB-LA-104
129.83
128.99
128.89
127.92
127.53
127.50
127.42
127.21
127.17
127.09
126.64
79.10
70.03
45.45
41.03
23.20
11.31
nPr
O
S
f1 (ppm)

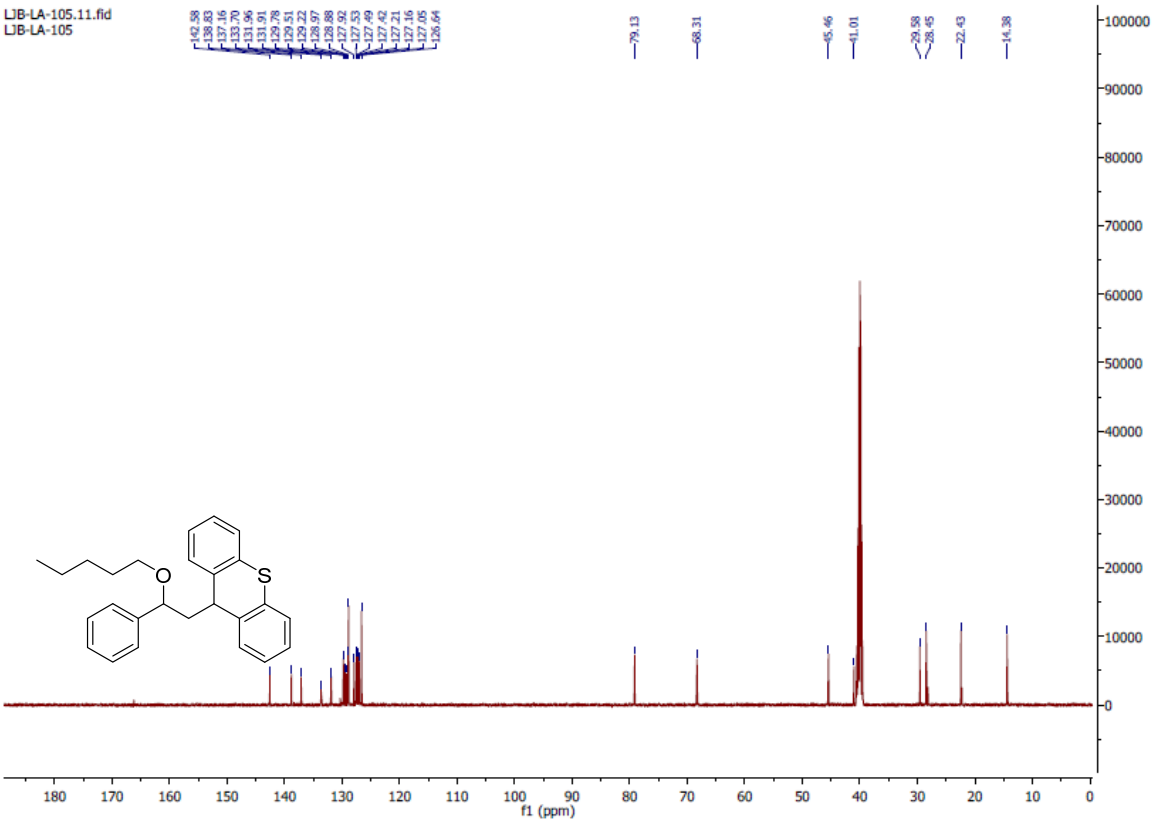

LJB-LA-104.11.fid
LJB-LA-104
142.58
138.85
137.14
131.93
131.90
129.83
128.99
128.89
127.92
127.53
127.50
127.42
127.21
127.16
127.09
126.64
79.10
70.03
45.45
41.03
23.20
11.31
nPr
O
S
f1 (ppm)

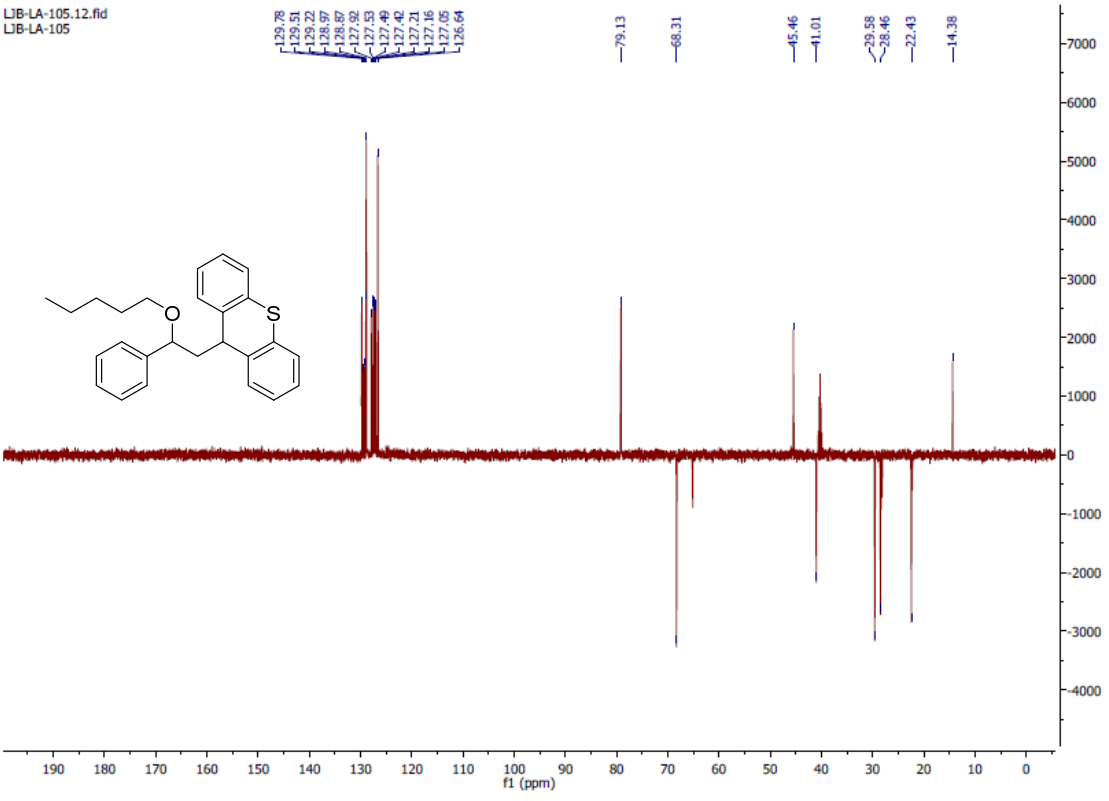

LJB-LA-103.10.fid
LJB-LA-103
f1 (ppm)
nBu
O
S

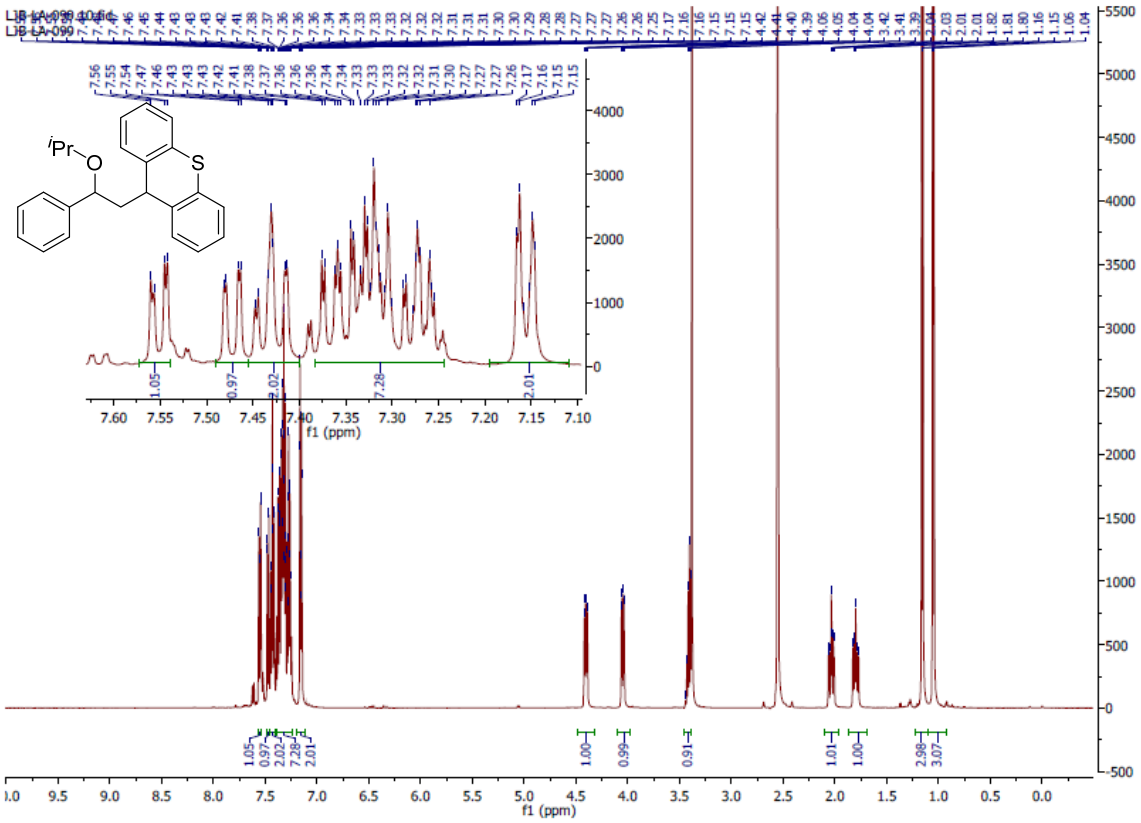

LJB-LA-103.11.fid
LJB-LA-103
142.713
138.980
137.099
132.564
132.393
129.604
128.506
128.253
127.281
127.201
126.827
126.680
126.597
126.465
126.381
126.153
79.209
68.323
45.711
40.820
32.329
19.709
14.080
f1 (ppm)
nBu
O
S

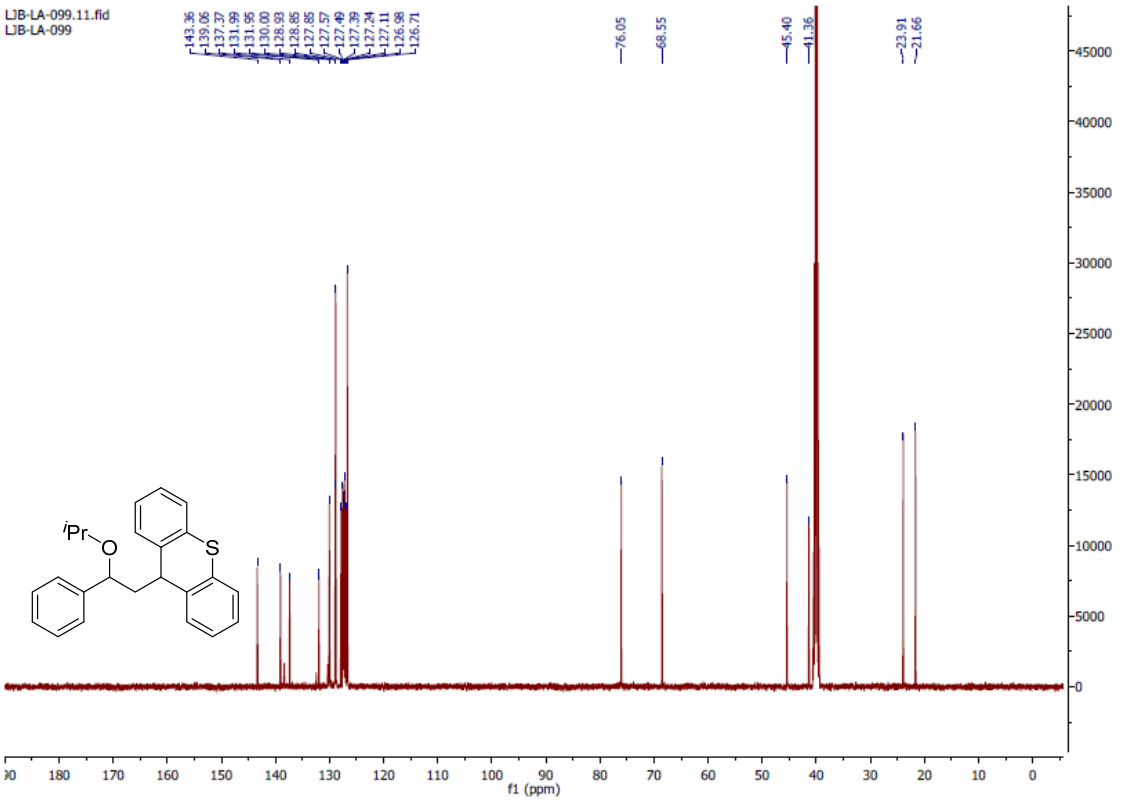

LJB-LA-103.12.fid
LJB-LA-103
129.61
128.51
128.25
127.28
127.20
126.63
126.60
126.46
126.38
126.15
79.21
68.32
45.71
40.82
32.33
19.71
14.08
nBu
O
S
f1 (ppm)

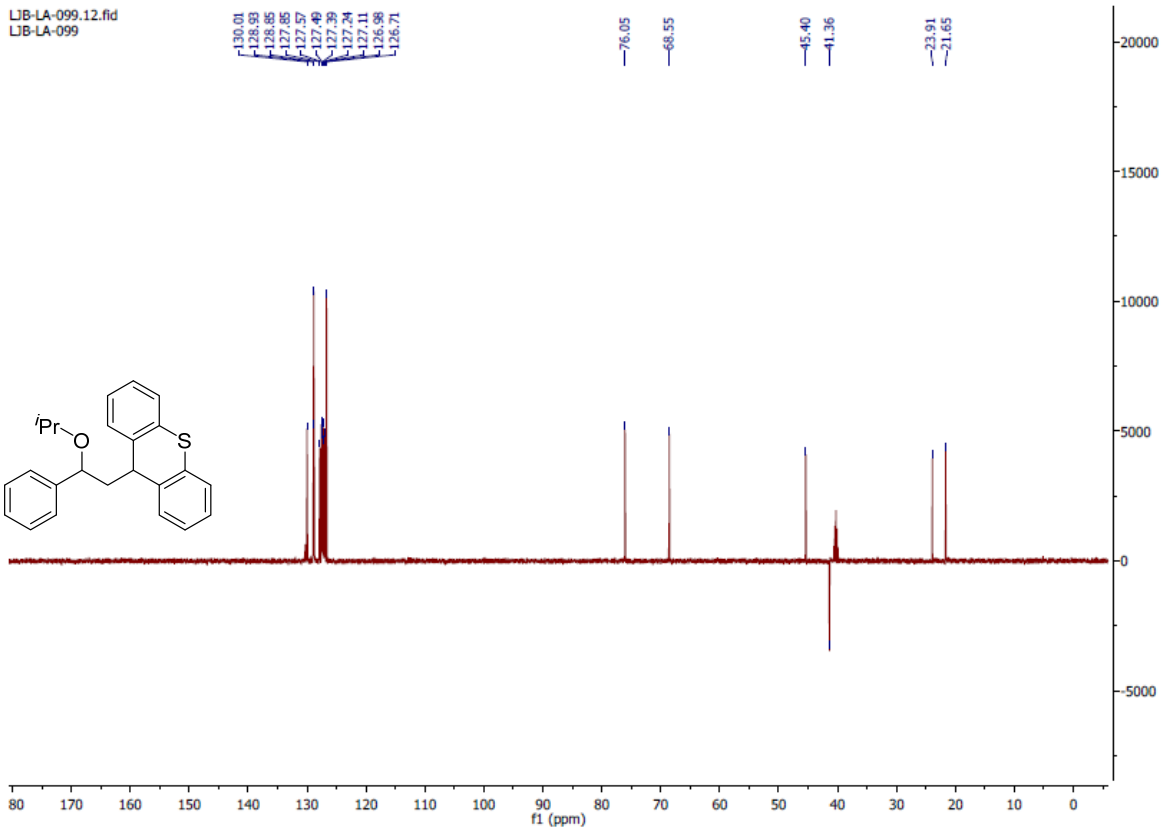

f1 (ppm)
O
S

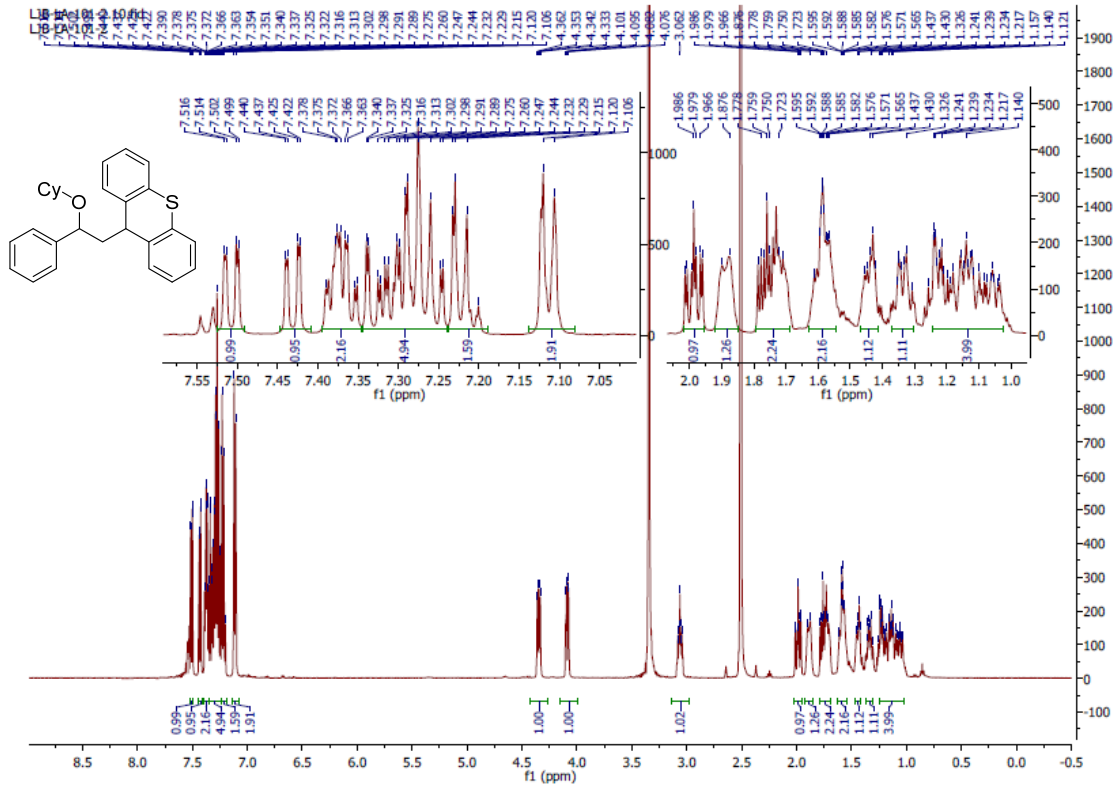

LJB-LA-105.11.fid
LJB-LA-105
142.58
138.83
137.16
133.70
131.96
131.91
129.78
129.51
129.22
128.97
128.88
127.92
127.53
127.49
127.42
127.21
127.16
127.05
126.64
79.13
68.31
45.46
41.01
29.58
28.45
22.43
14.38
O
S
f1 (ppm)

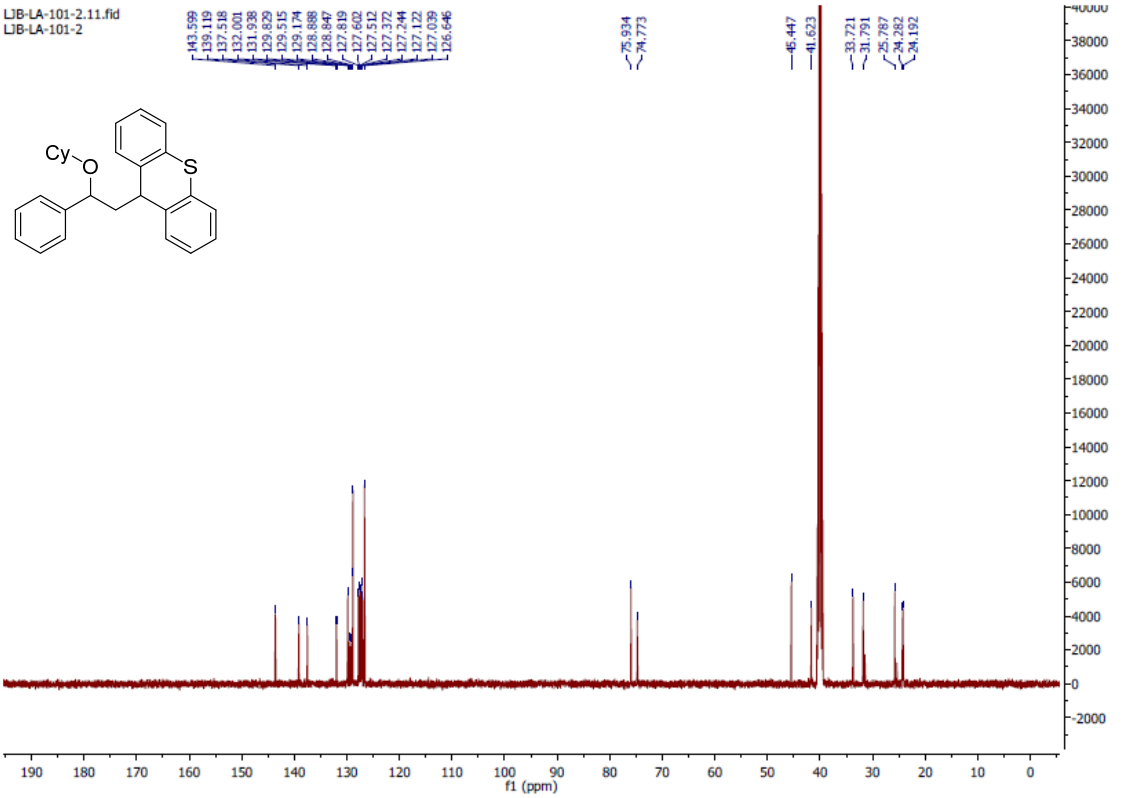

LJB-LA-105.12.fid
LJB-LA-105
129.78
129.51
129.22
128.97
128.87
127.92
127.53
127.49
127.42
127.21
127.16
127.05
126.64
79.13
68.31
45.46
41.01
29.58
28.46
22.43
14.38
O
S
f1 (ppm)

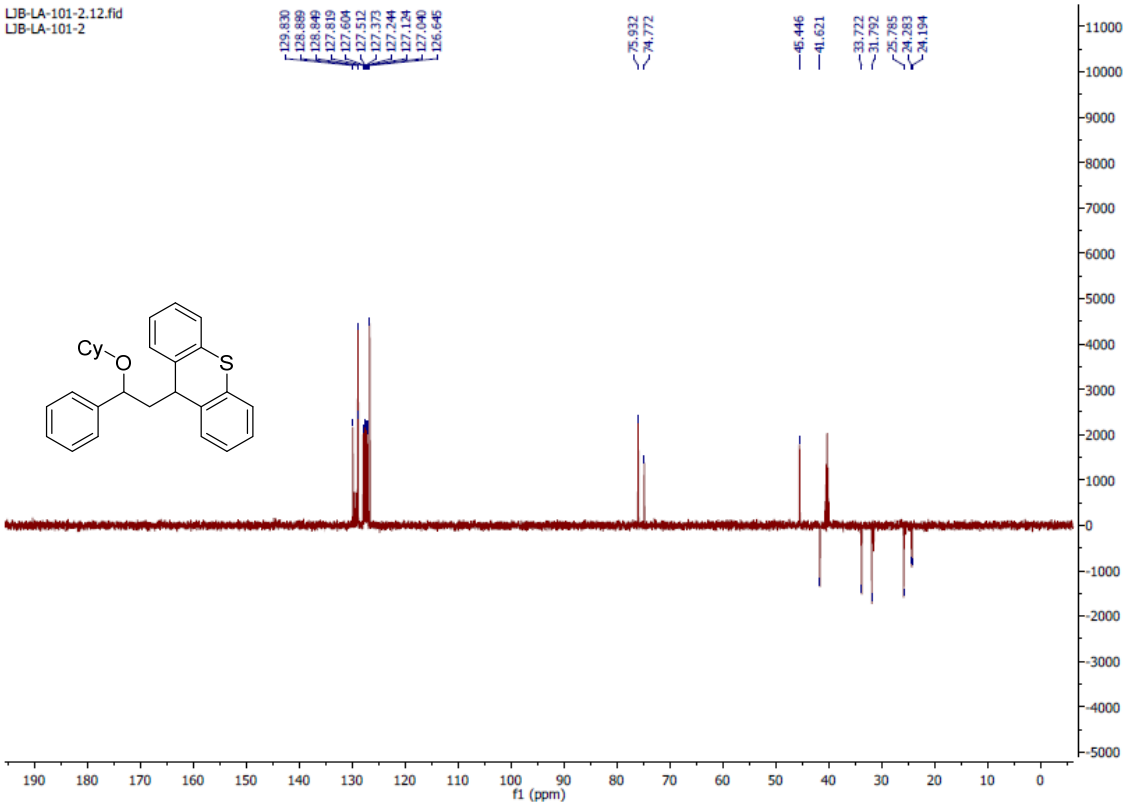

LJB-LA-099.10.fid
LJB-LA-099
iPr
O
S
f1 (ppm)

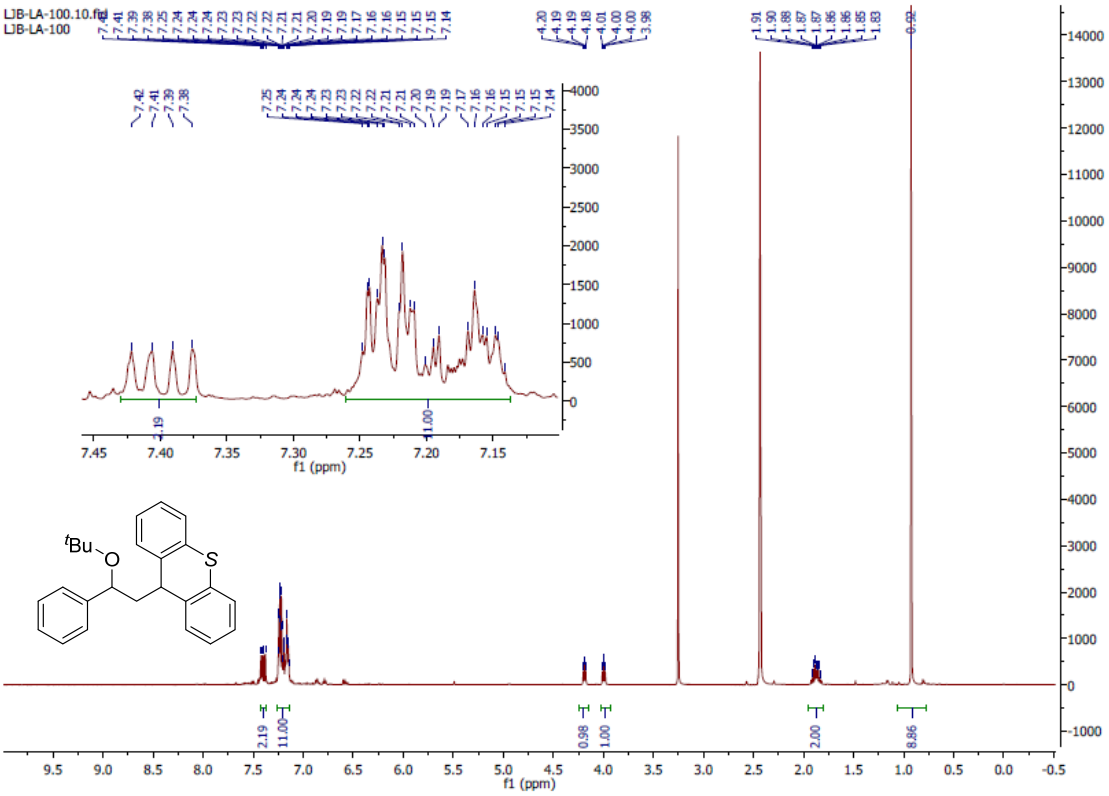

LJB-LA-099.11.fid
LJB-LA-099
iPr
O
S
f1 (ppm)

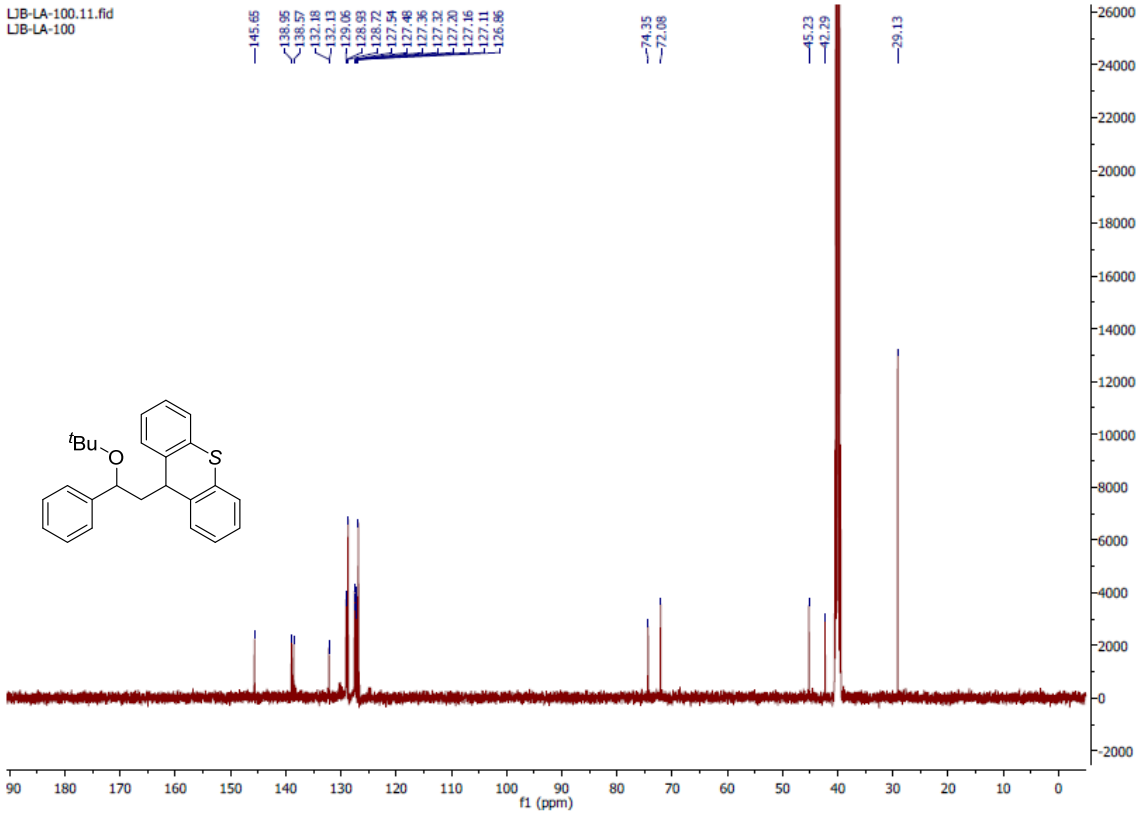

LJB-LA-099.12.fid
LJB-LA-099
130.01
128.93
128.85
127.85
127.57
127.49
127.39
127.24
127.11
126.98
126.71
76.05
68.55
45.40
41.36
23.91
21.65
iPr
O
S
f1 (ppm)

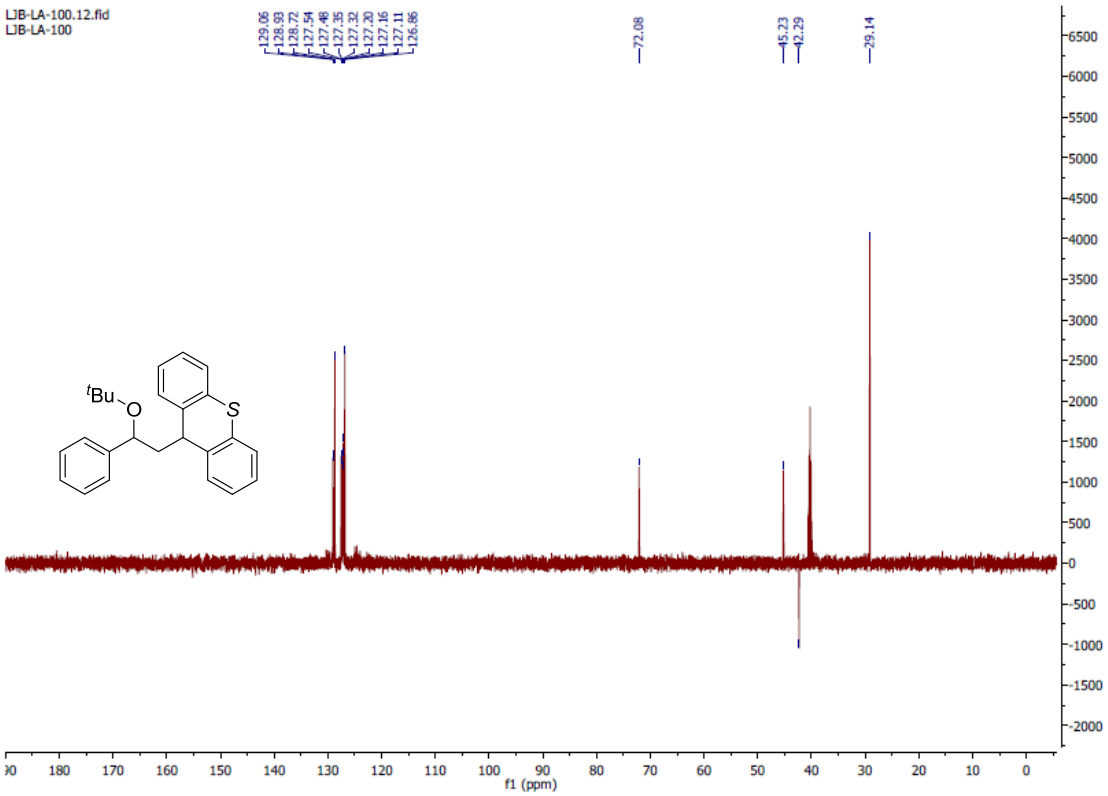

Cy
O
S
f1 (ppm)

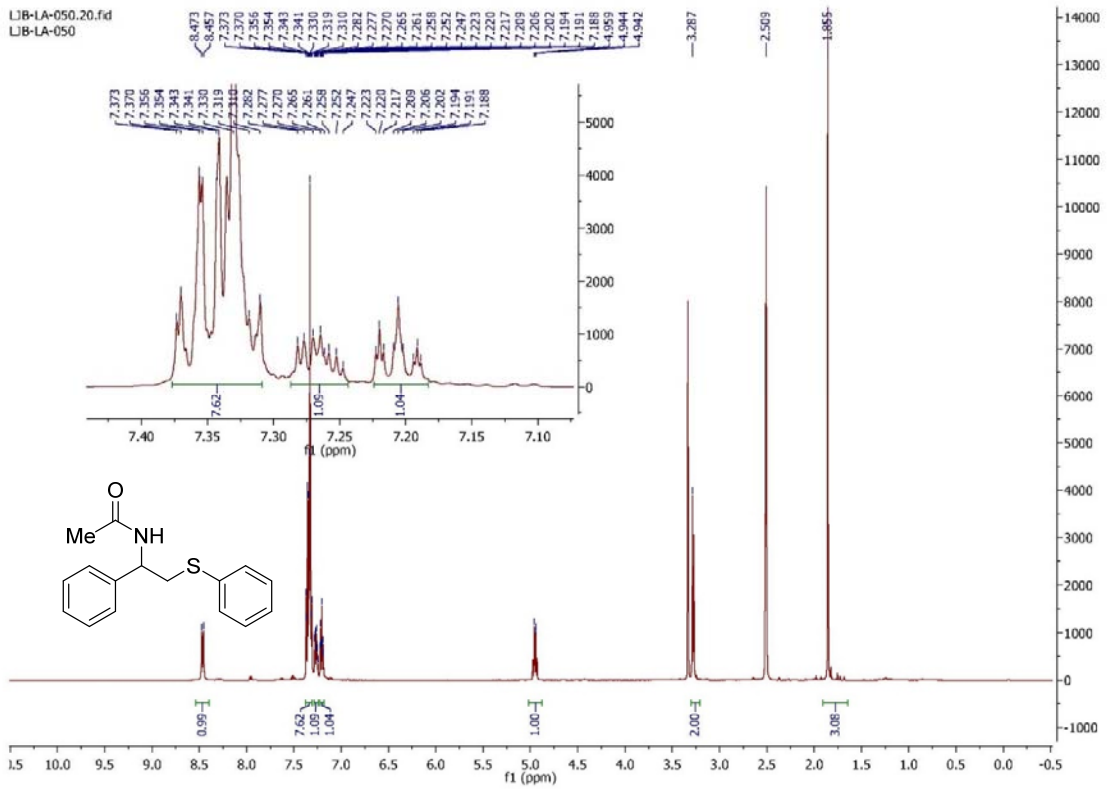

LJB-LA-101-2.11.fid
LJB-LA-101-2
143.599
139.119
137.518
132.001
131.938
129.829
129.515
129.174
128.888
128.847
127.819
127.602
127.512
127.372
127.244
127.122
127.039
126.646
75.934
74.773
45.447
41.623
33.721
31.791
25.787
24.282
24.192
Cy
O
S
f1 (ppm)

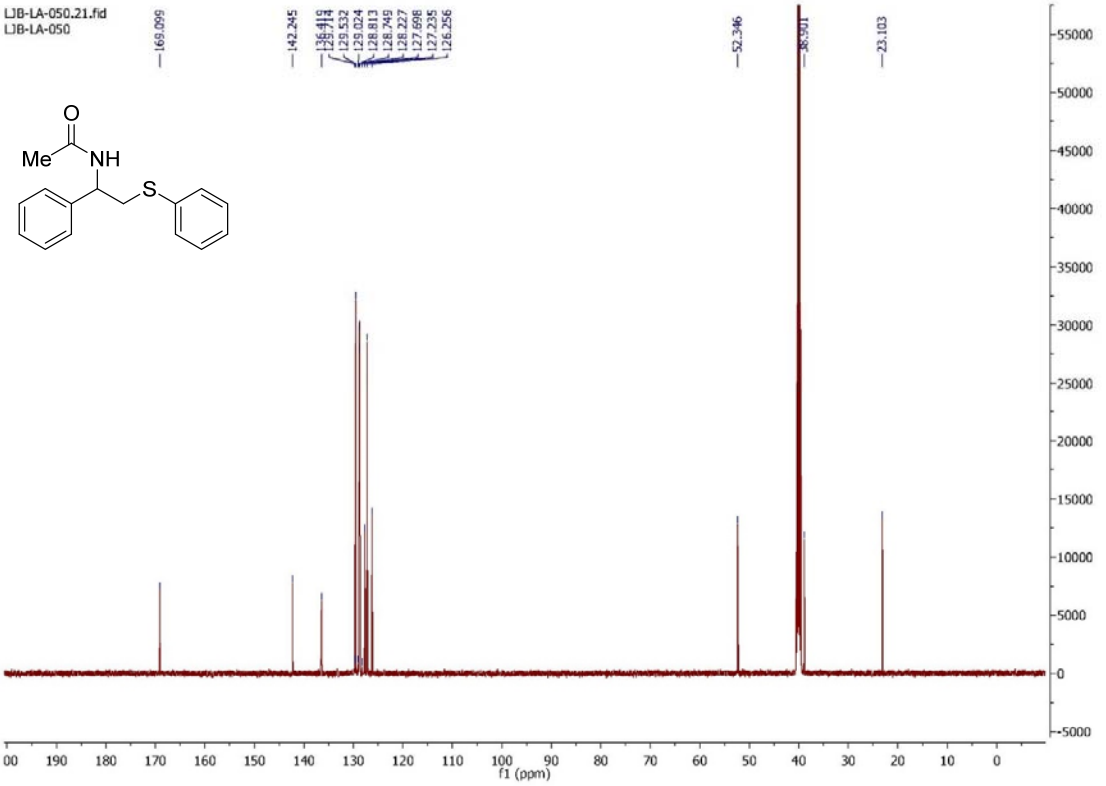

LJB-LA-101-2.12.fid
LJB-LA-101-2
129.830
128.889
128.849
127.819
127.604
127.512
127.373
127.244
127.124
127.040
126.646
75.932
74.772
45.446
41.621
33.722
31.792
25.785
24.283
24.194
Cy
O
S
f1 (ppm)

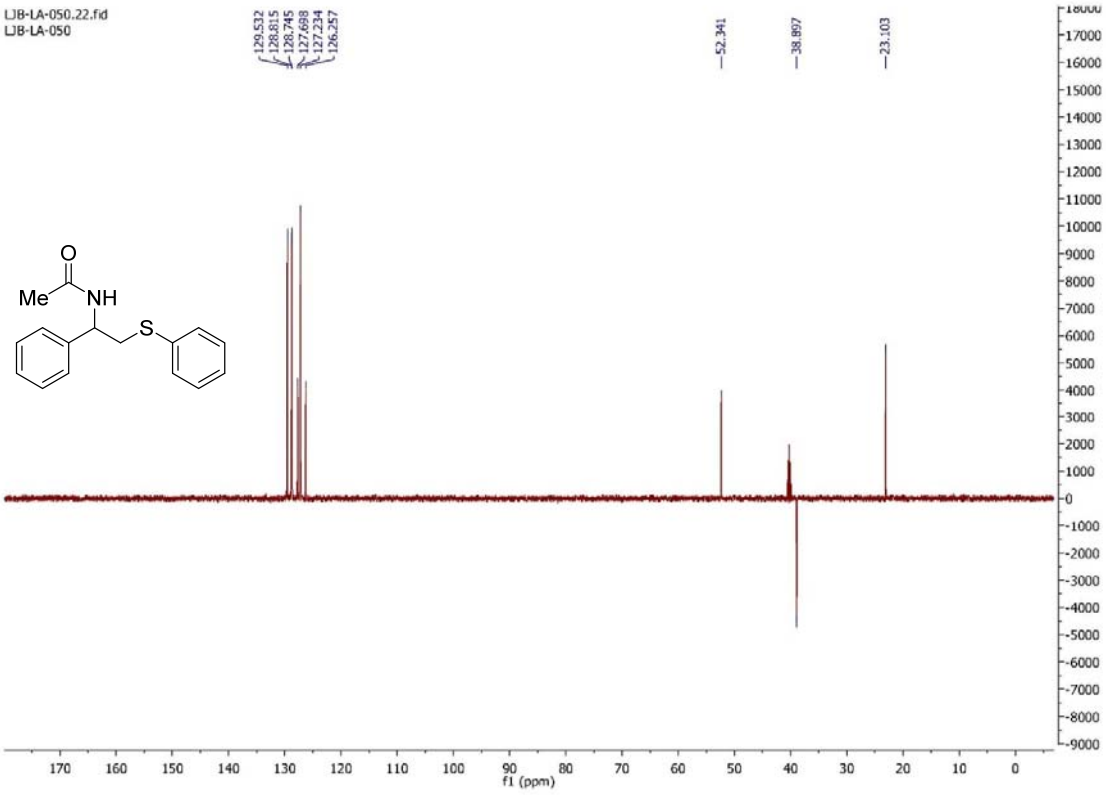

LJB-LA-100.10.fid
LJB-LA-100
f1 (ppm)

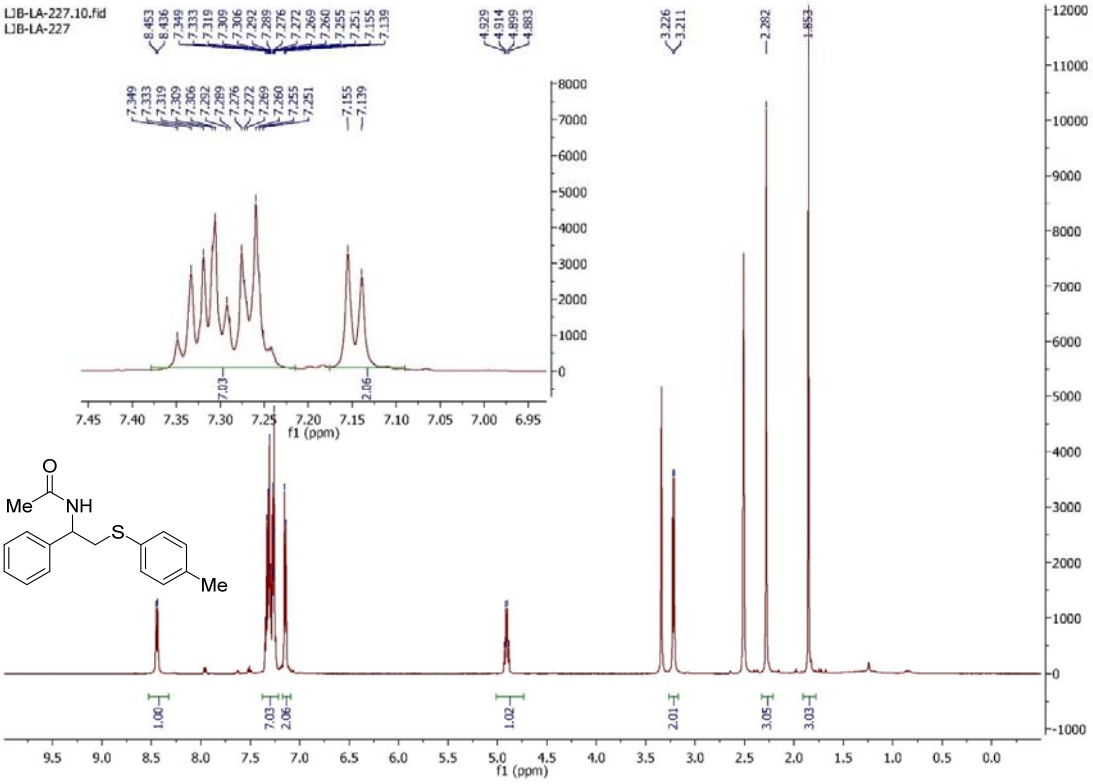

LJB-LA-100.11.fid
LJB-LA-100
f1 (ppm)

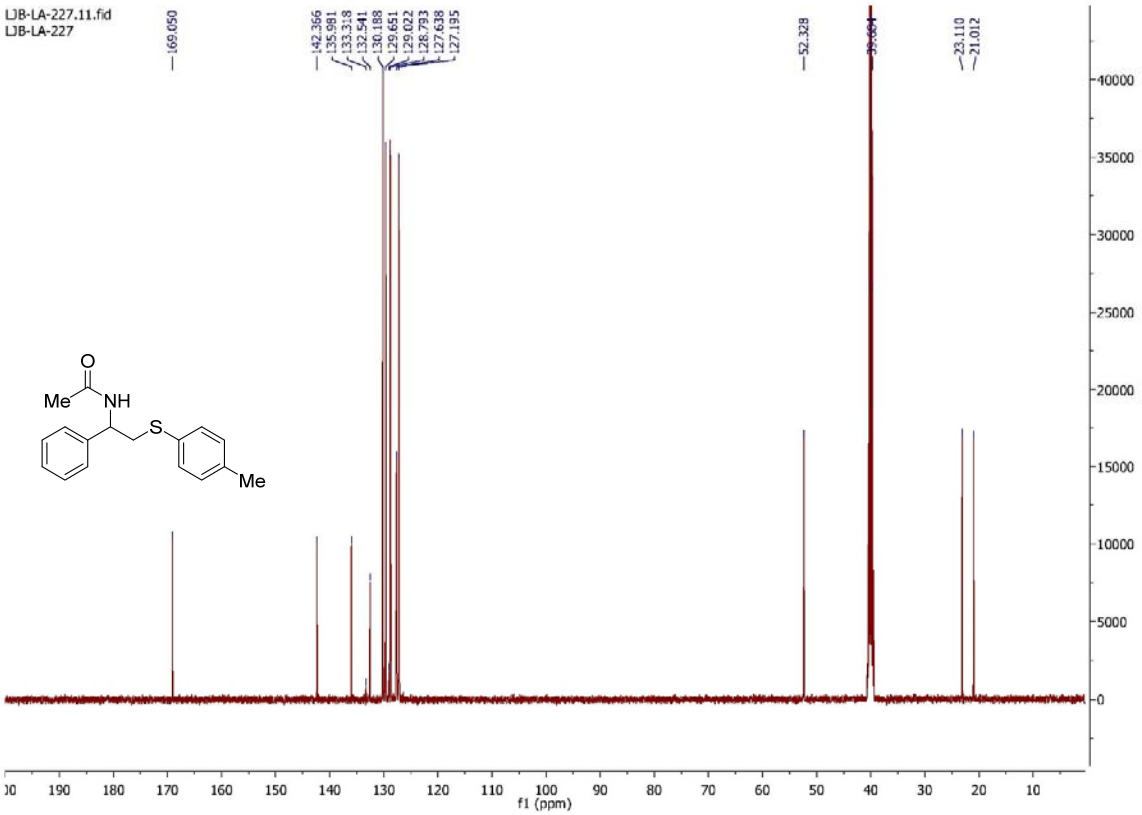

LJB-LA-100.12.fid
LJB-LA-100
129.06
128.93
128.72
127.54
127.48
127.35
127.32
127.20
127.16
127.11
126.86
72.08
45.23
42.29
29.14
tBu
O
S
f1 (ppm)

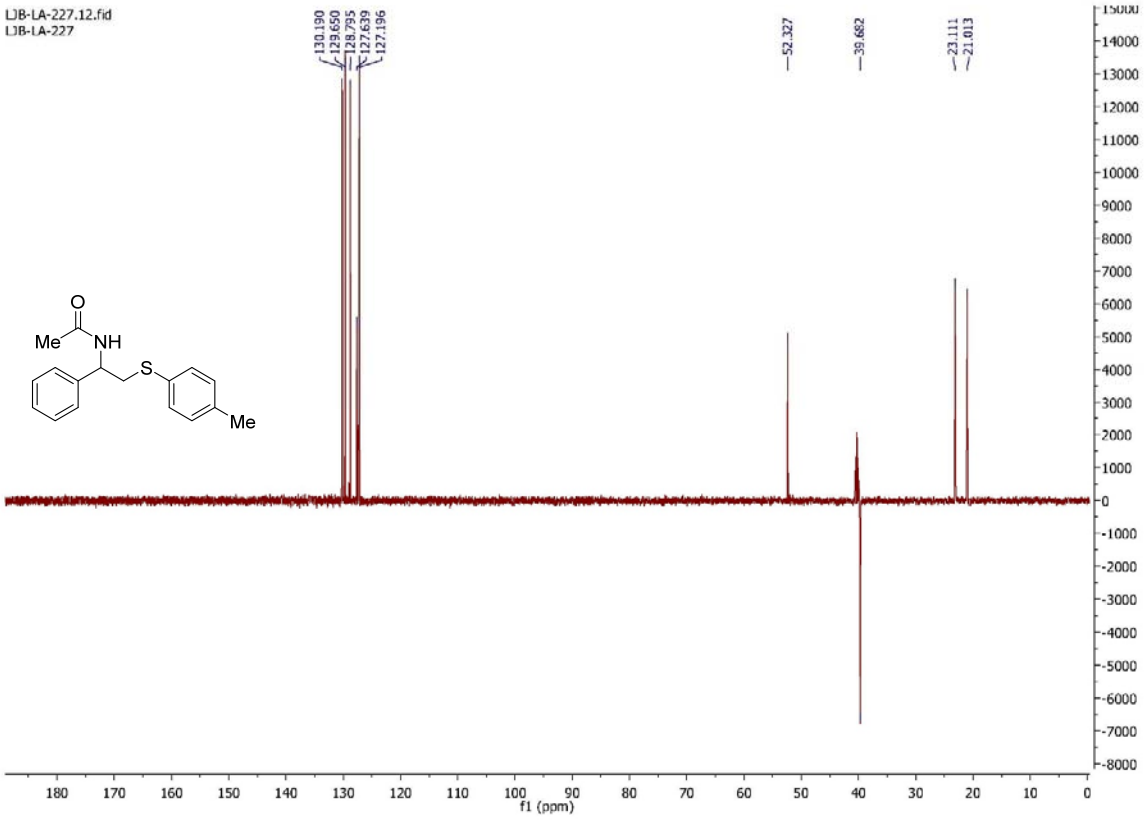

LJB-LA-050.20.fid
LJB-LA-050
8.473
8.457
7.373
7.370
7.356
7.354
7.343
7.341
7.330
7.319
7.310
7.282
7.277
7.270
7.265
7.261
7.258
7.252
7.247
7.223
7.220
7.217
7.209
7.206
7.202
7.194
7.191
7.188
4.959
4.944
4.942
3.287
2.569
1.855
7.62
1.09
1.04
Me
NH
S
0.99
7.62
1.09
1.04
1.00
2.00
3.08
f1 (ppm)

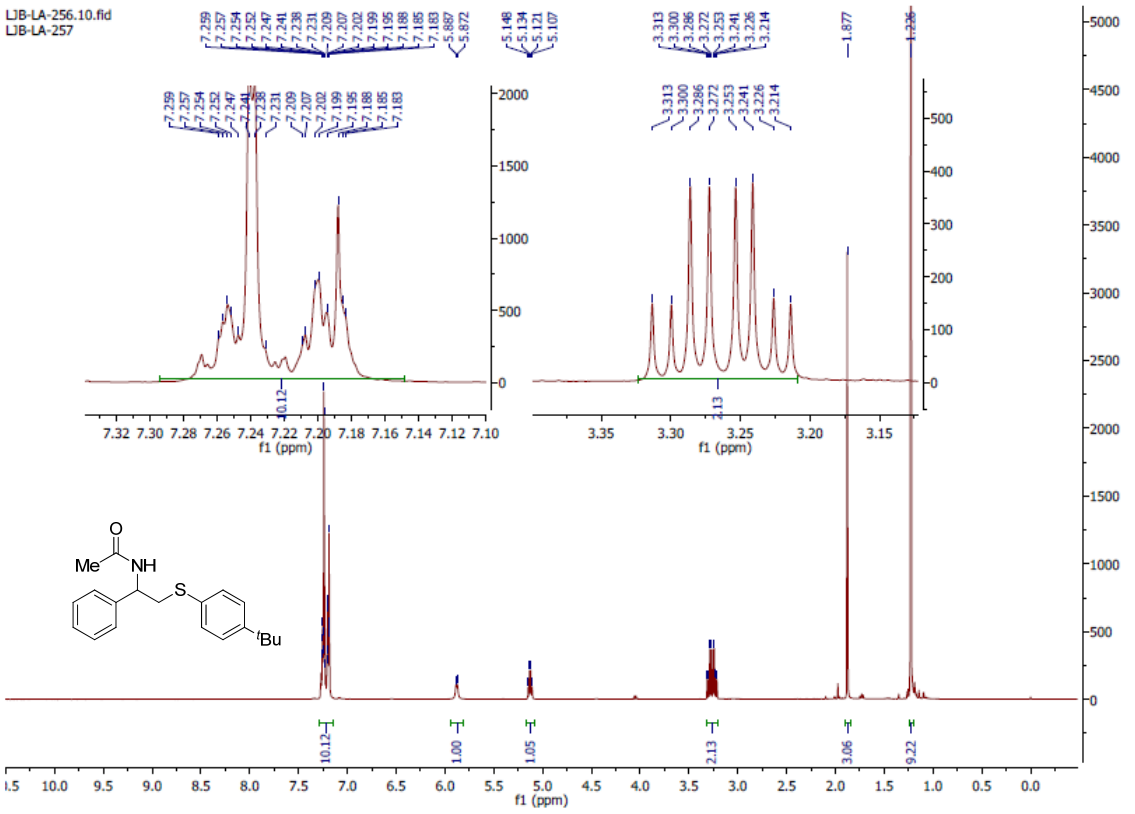

LJB-LA-050.21.fid
LJB-LA-050
169.099
142.245
136.414
129.532
129.024
128.813
128.749
128.227
127.698
127.235
126.256
52.346
38.591
23.103
O
Me
NH
S
f1 (ppm)

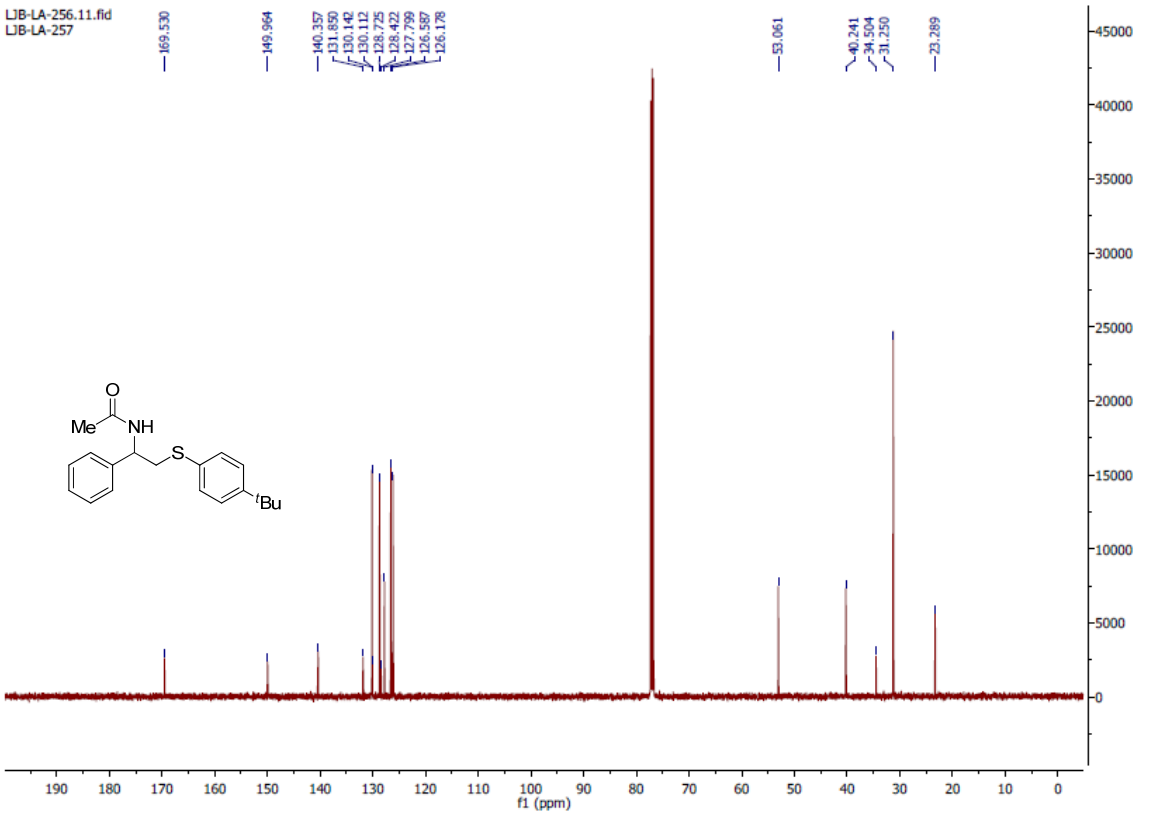

LJB-LA-050.22.fid
LJB-LA-050
129.532
128.815
128.745
127.698
127.234
126.257
52.341
38.897
23.103
O
Me
NH
S
f1 (ppm)

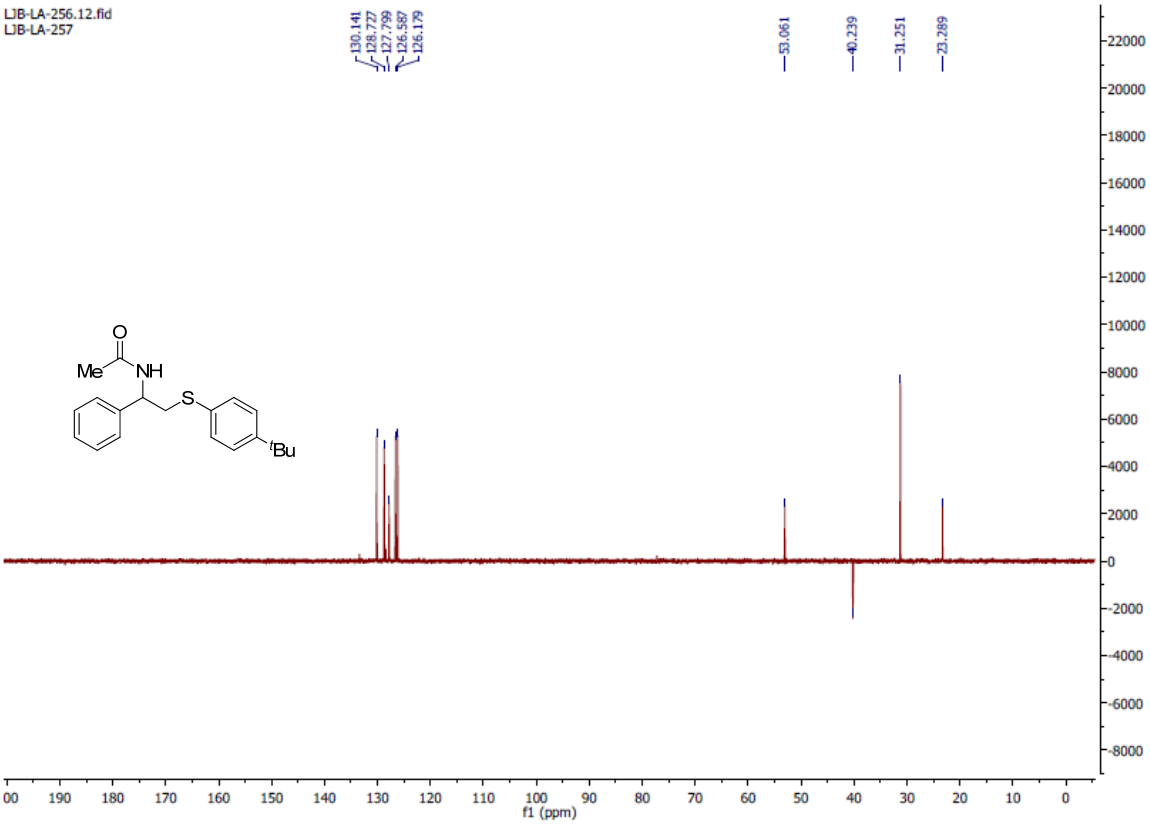

LJB-LA-227.10.fid
LJB-LA-227
f1 (ppm)

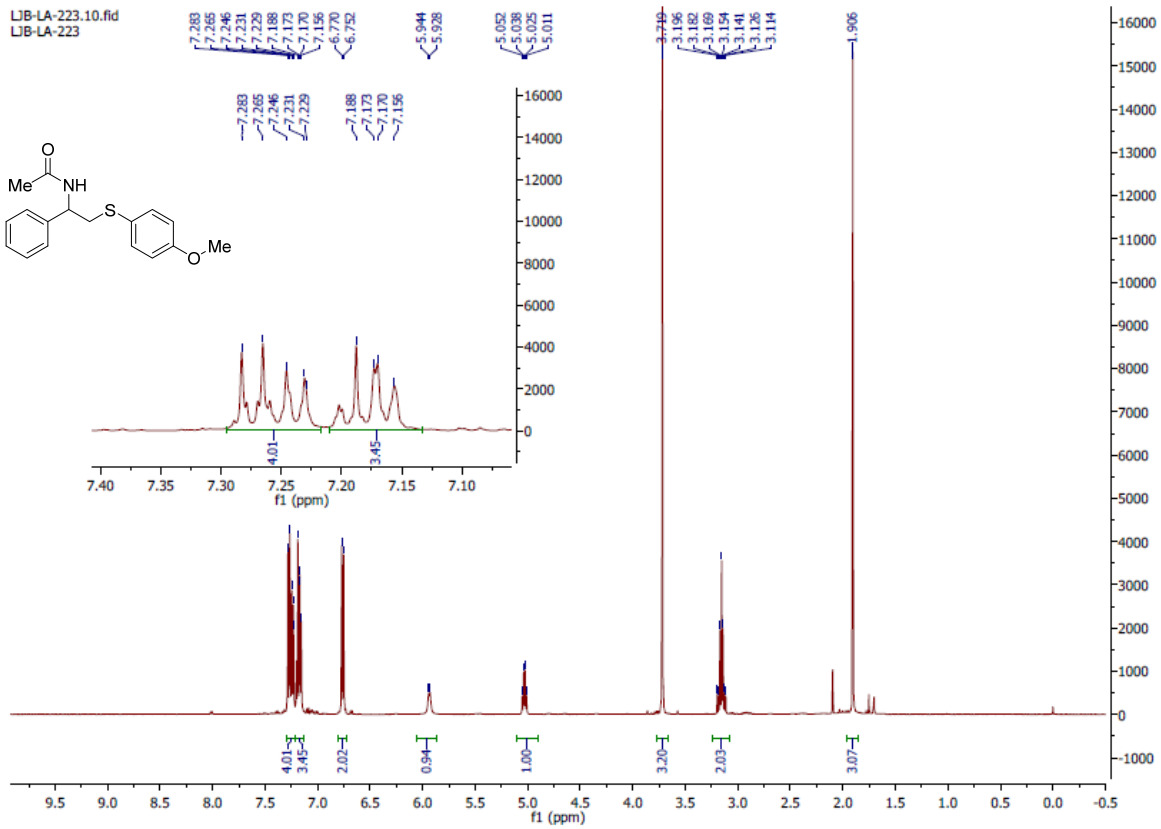

LJB-LA-227.11.fid
LJB-LA-227
f1 (ppm)

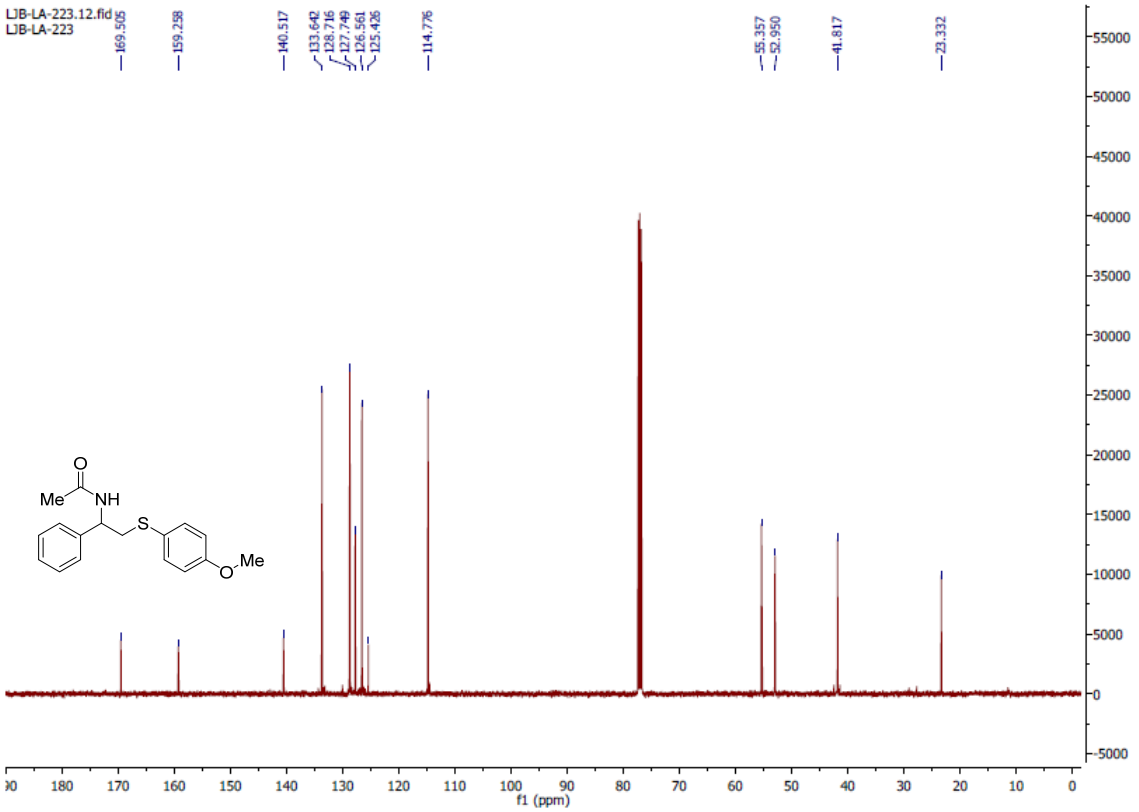

LJB-LA-227.12.fid
LJB-LA-227
130.190
129.650
128.795
127.639
127.196
52.327
39.682
23.111
21.013
Me
NH
S
Me
f1 (ppm)

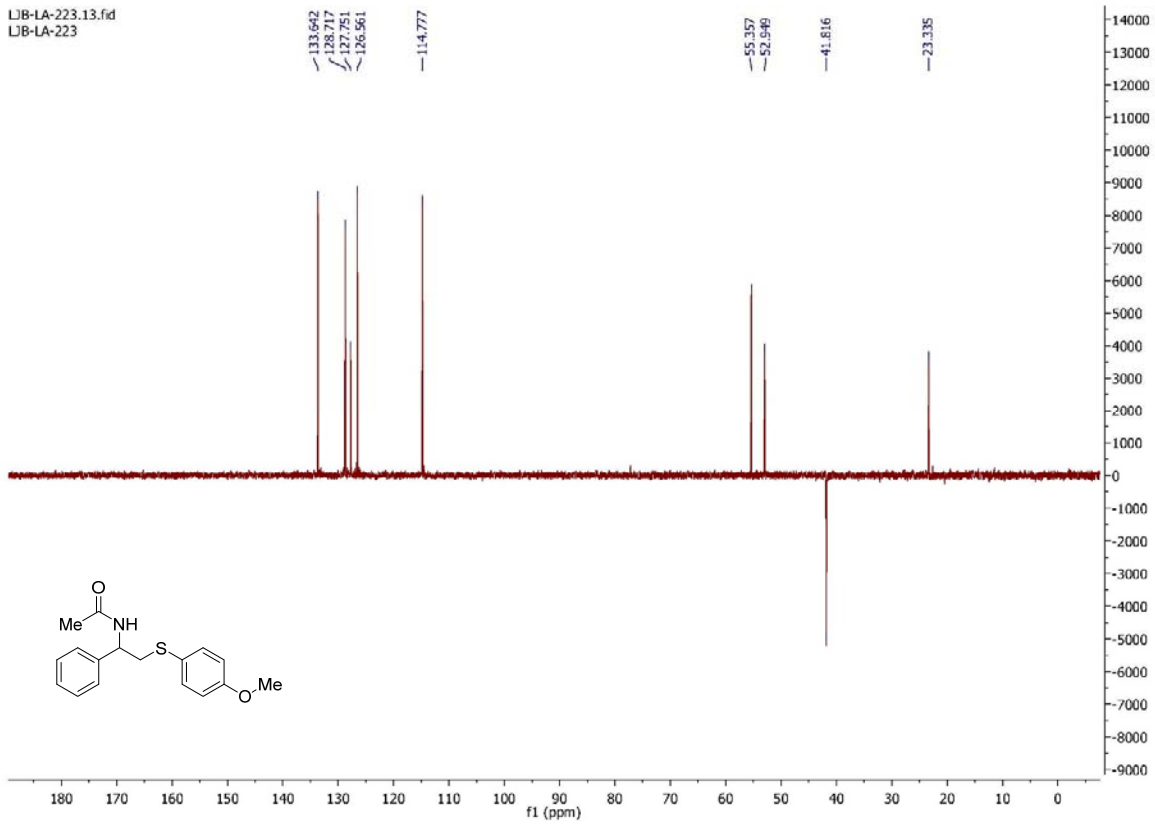

LJB-LA-256.10.fid
LJB-LA-257
7.259
7.257
7.254
7.252
7.247
7.241
7.238
7.231
7.209
7.207
7.202
7.199
7.195
7.188
7.185
7.183
5.867
5.872
5.148
5.134
5.121
5.107
3.313
3.300
3.286
3.272
3.253
3.241
3.226
3.214
1.877
1.226
10.12
2.13
f1 (ppm)
Me
NH
S
tBu
10.12
1.00
1.05
2.13
3.06
9.22
f1 (ppm)

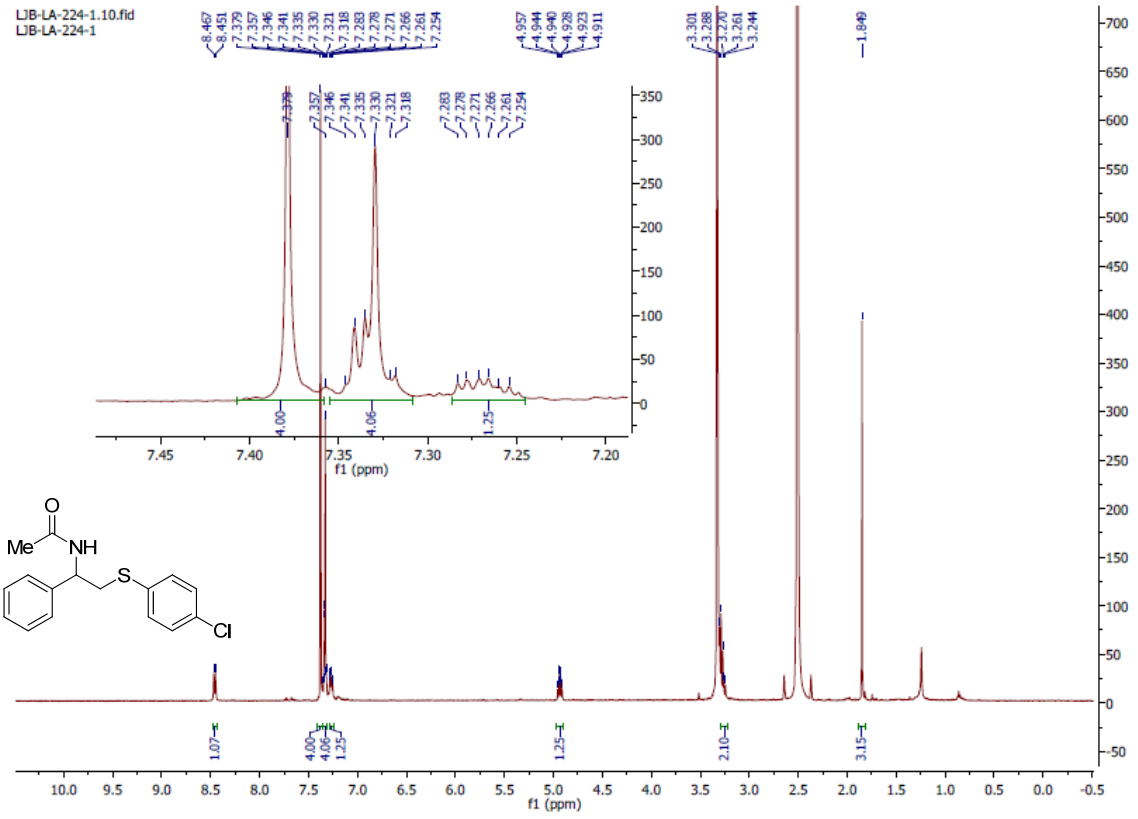

LJB-LA-256.11.fid
LJB-LA-257
169.530
149.964
140.357
131.850
130.142
130.112
128.725
128.422
127.799
126.587
126.178
53.061
40.241
34.504
31.250
23.289
Me
NH
S
tBu
f1 (ppm)

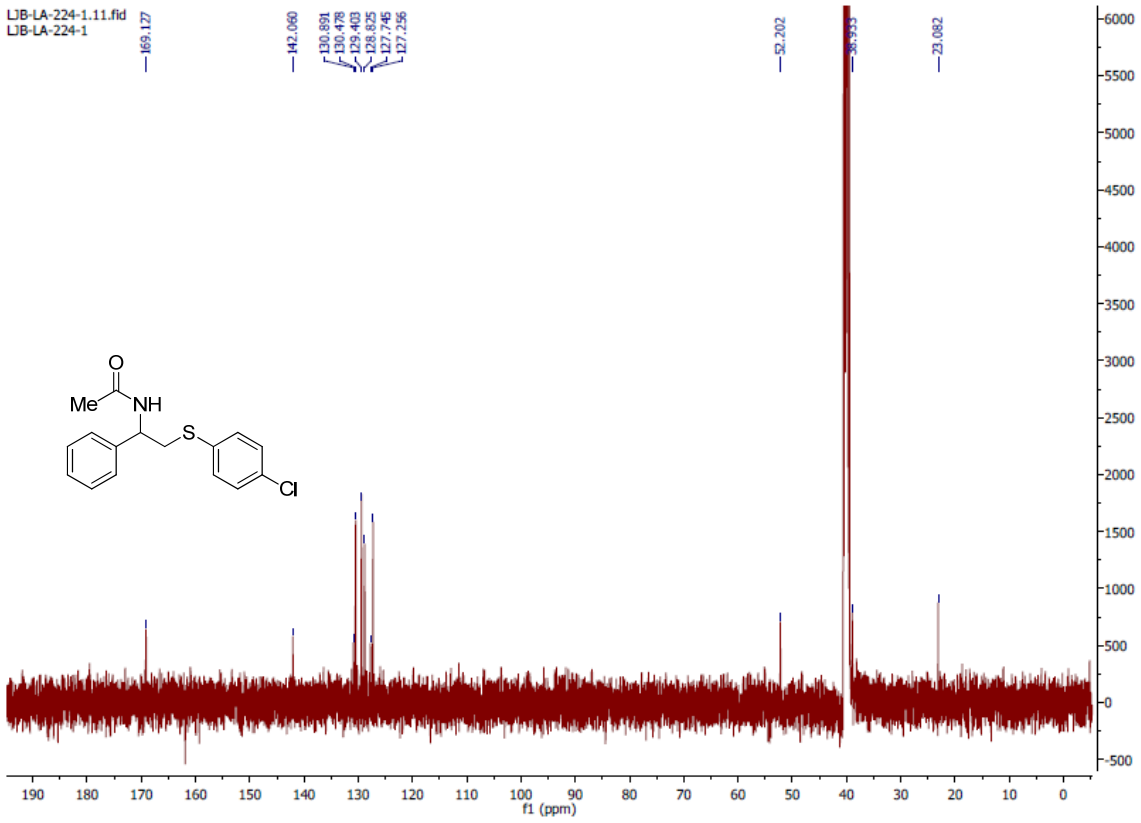

LJB-LA-256.12.fid
LJB-LA-257
130.141
128.727
127.799
126.587
126.179
53.061
40.239
31.251
23.289
Me
NH
S
tBu
f1 (ppm)

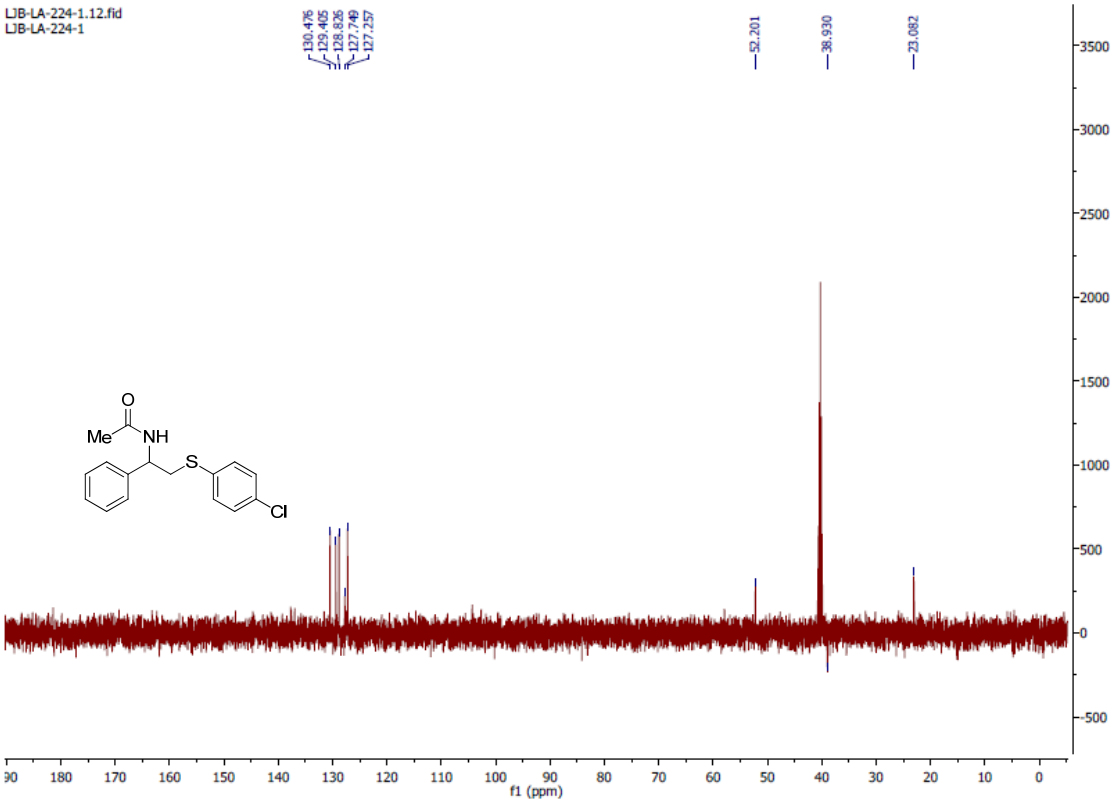

LJB-LA-223.10.fid
LJB-LA-223
f1 (ppm)

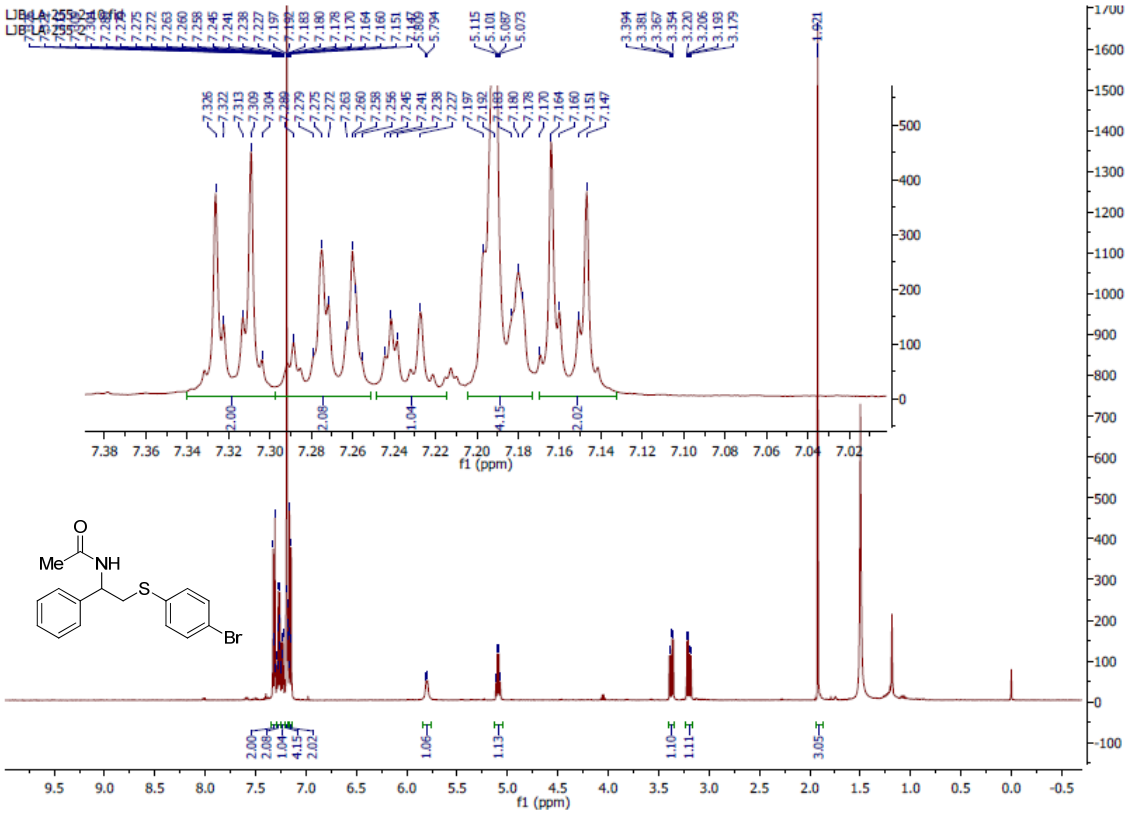

LJB-LA-223.12.fid
LJB-LA-223
f1 (ppm)

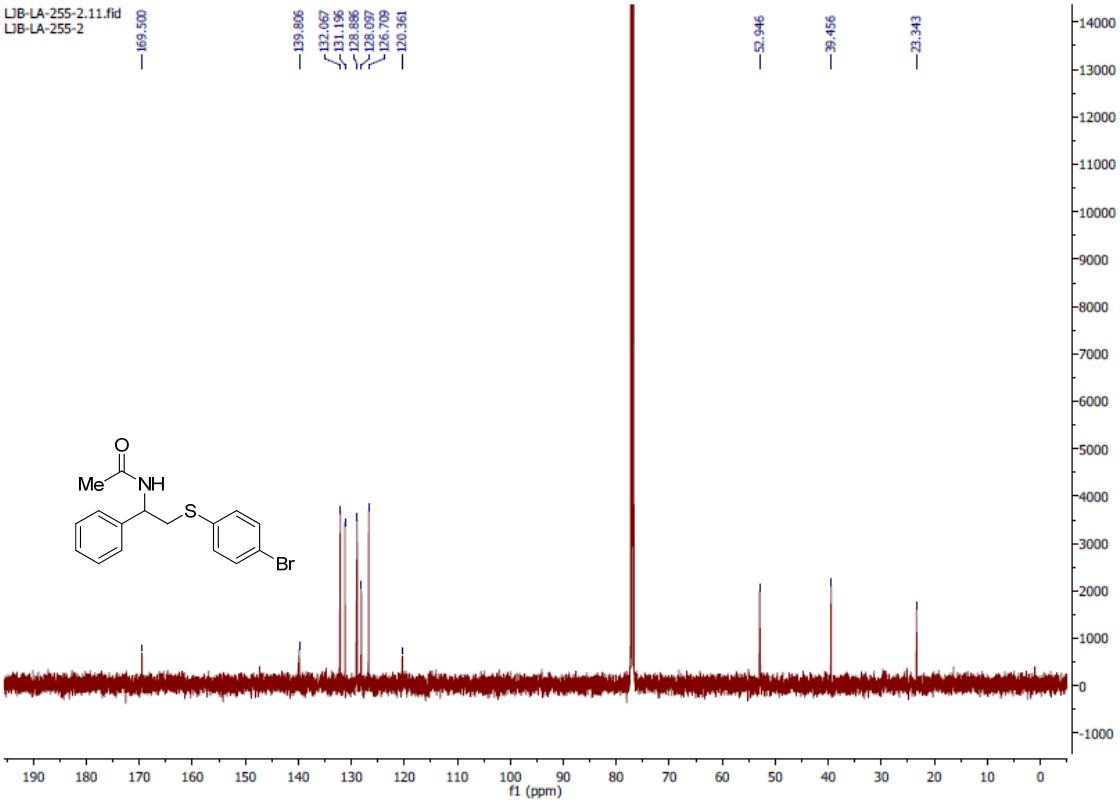

LJB-LA-223.13.fid
LJB-LA-223
133.642
128.717
127.751
126.561
114.777
55.357
52.949
41.816
23.335
Me
NH
S
O
Me
f1 (ppm)

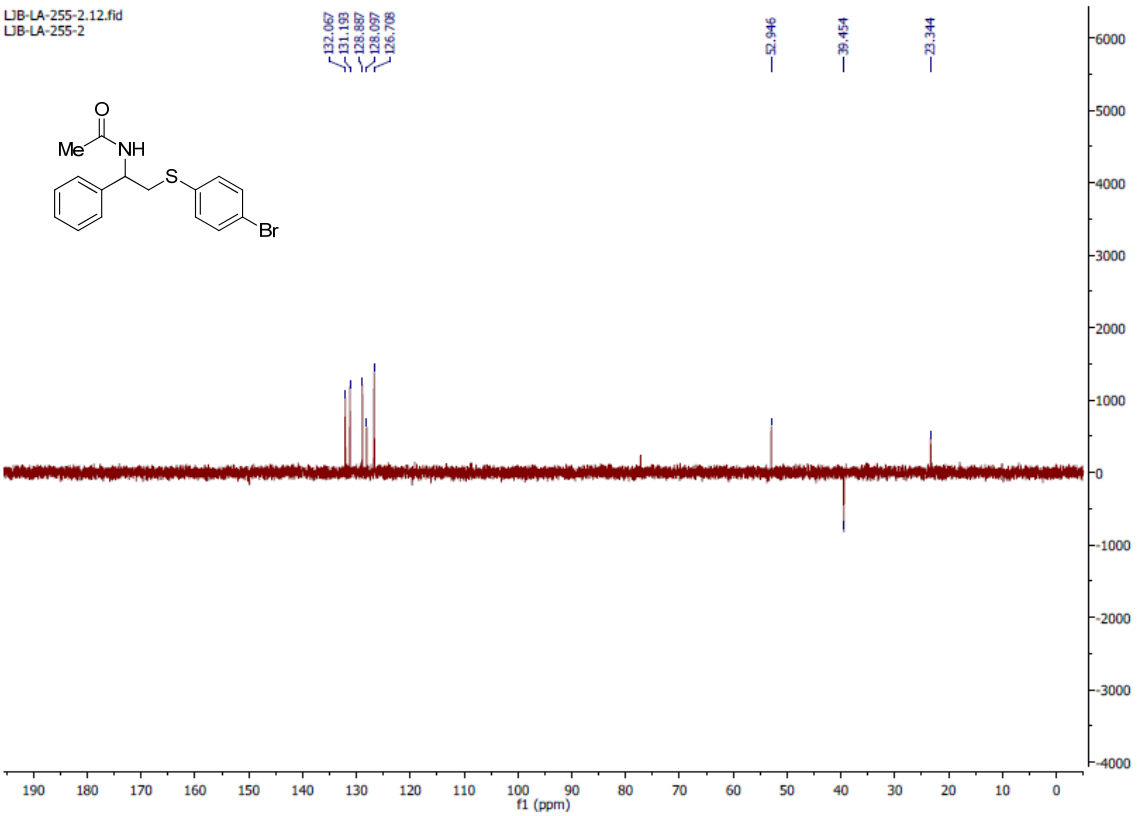

LJB-LA-224-1.10.fid
LJB-LA-224-1
8.467
8.451
7.379
7.357
7.346
7.341
7.335
7.330
7.321
7.318
7.283
7.278
7.271
7.266
7.261
7.254
4.957
4.944
4.940
4.928
4.923
4.911
3.301
3.288
3.270
3.261
3.244
1.849
4.00
4.06
1.25
1.07
2.10
3.15
Me
NH
S
Cl
f1 (ppm)

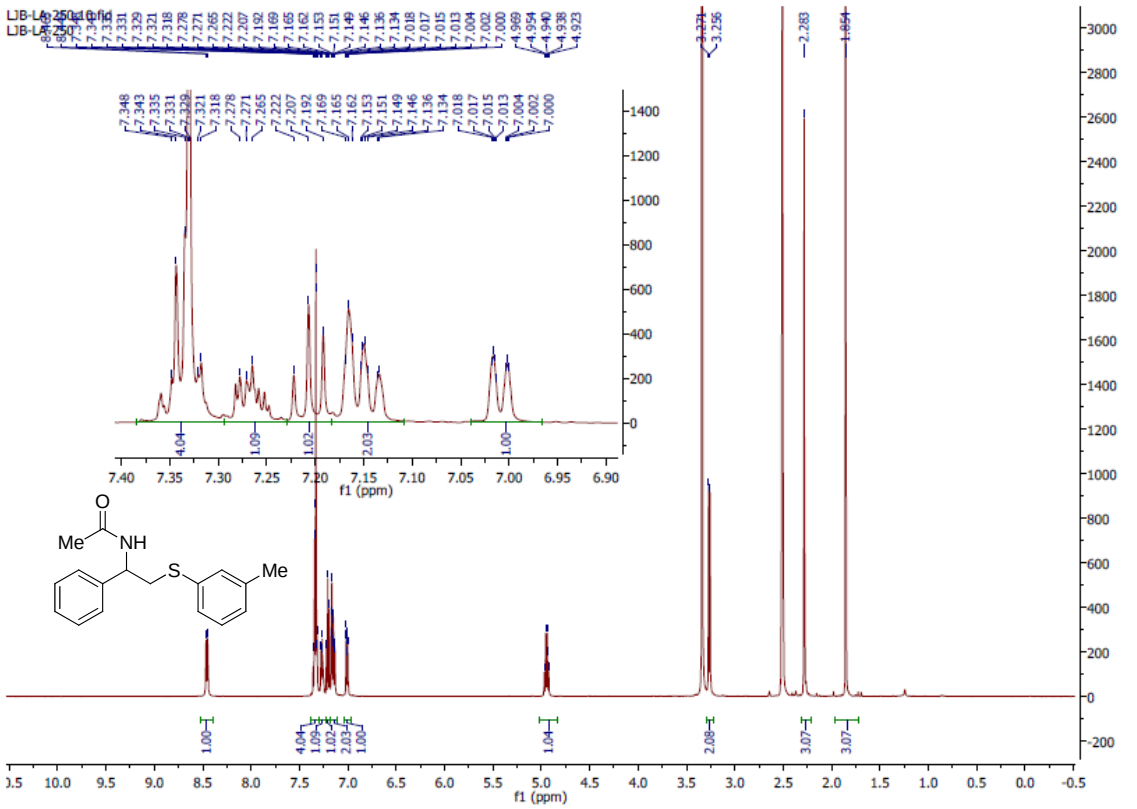

LJB-LA-224-1.11.fid
LJB-LA-224-1
169.127
142.060
130.891
130.478
129.403
128.825
127.745
127.256
52.202
38.933
23.082
O
Me
NH
S
Cl
f1 (ppm)

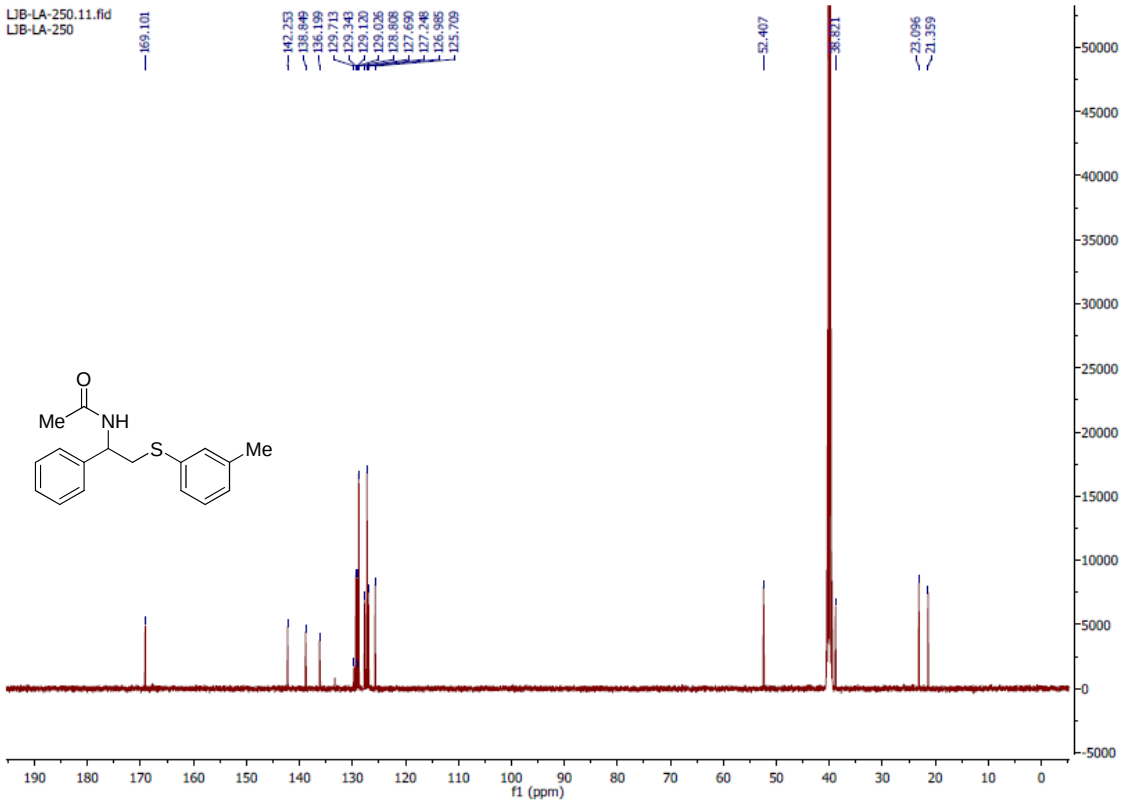

LJB-LA-224-1.12.fid
LJB-LA-224-1
130.476
129.405
128.826
127.749
127.257
52.201
38.930
23.082
O
Me
NH
S
Cl
f1 (ppm)

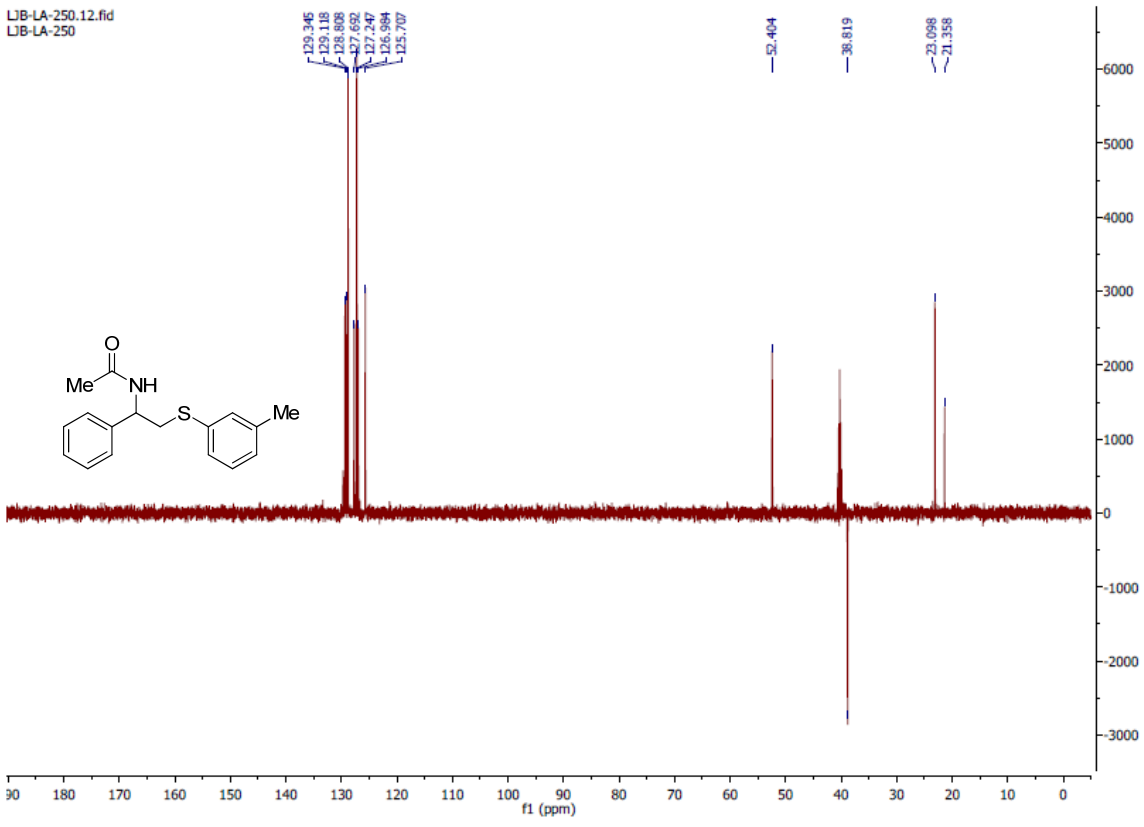

LJB-LA-255-2.11.fid
LJB-LA-255-2
Me
NH
S
Br
f1 (ppm)

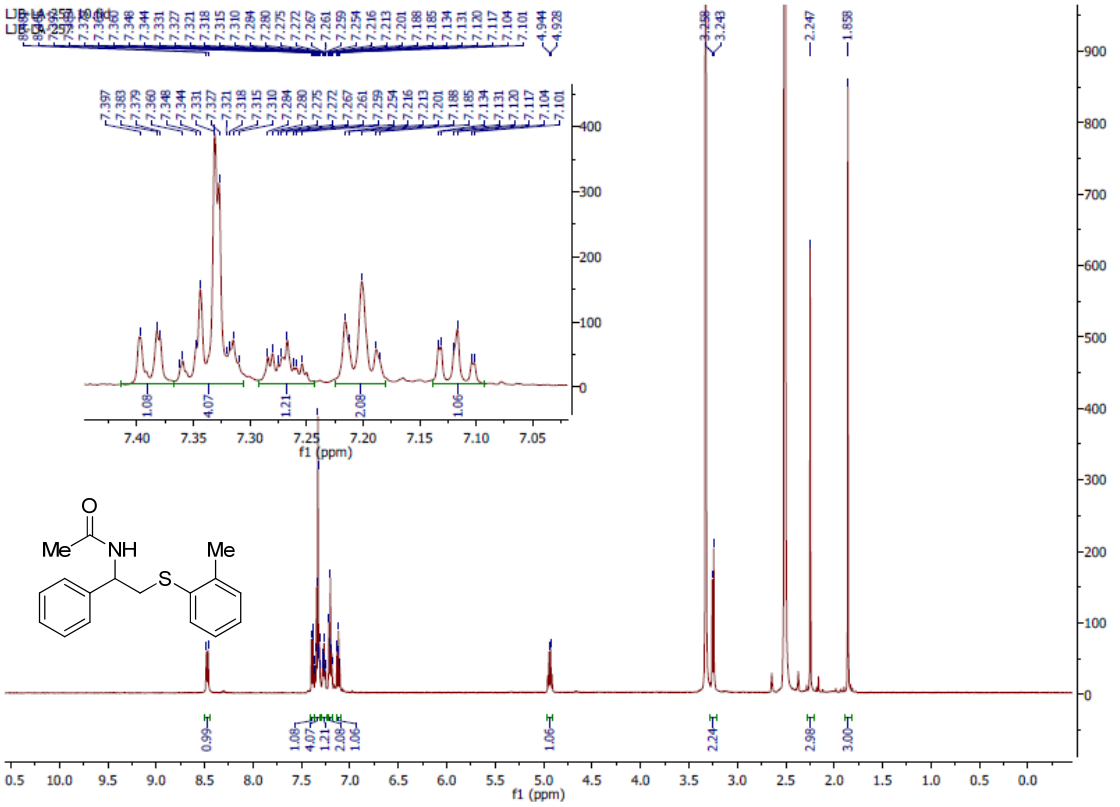

LJB-LA-255-2.11.fid
LJB-LA-255-2
169.500
139.806
132.067
131.196
128.886
128.097
126.709
120.361
52.946
39.456
23.343
Me
NH
S
Br
f1 (ppm)

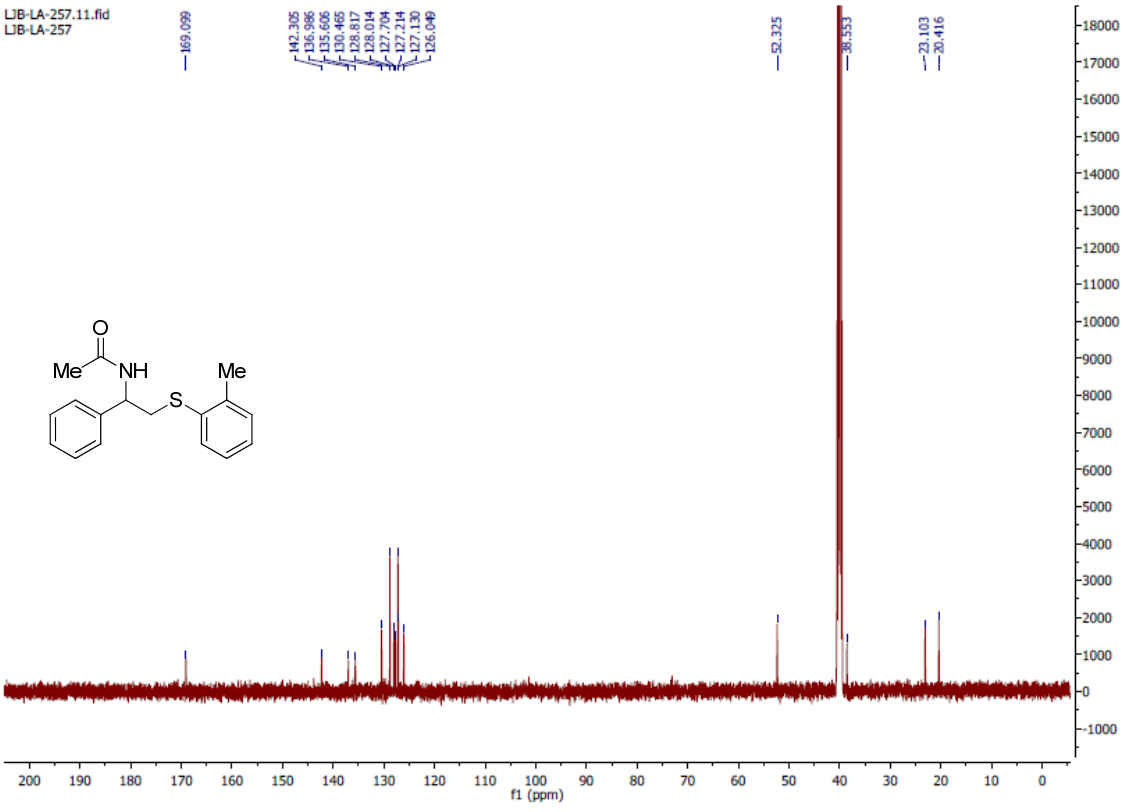

LJB-LA-255-2.12.fid
LJB-LA-255-2
132.067
131.193
128.887
128.097
126.708
52.946
39.454
23.344
Me
NH
S
Br
f1 (ppm)

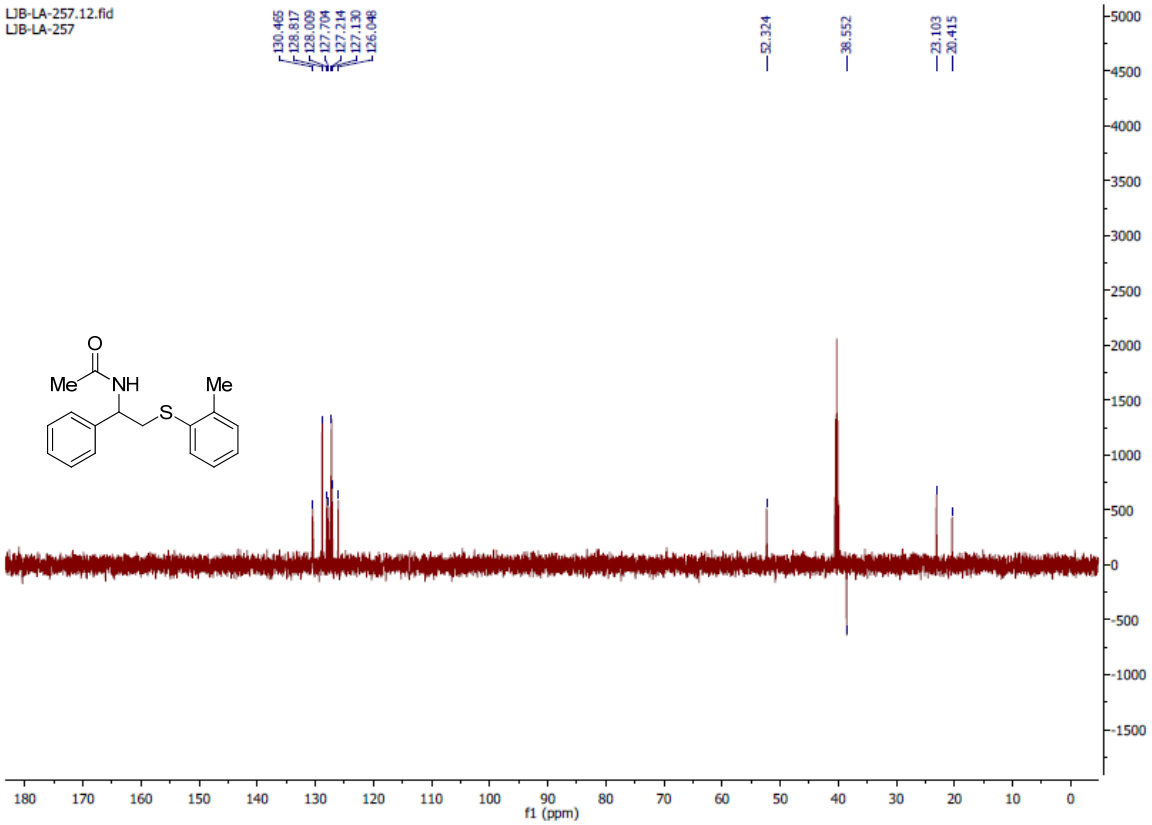

LJB-LA-255-10.fid
LJB-LA-255-10
3.331
3.256
2.283
1.854
Me
NH
S
Me
f1 (ppm)

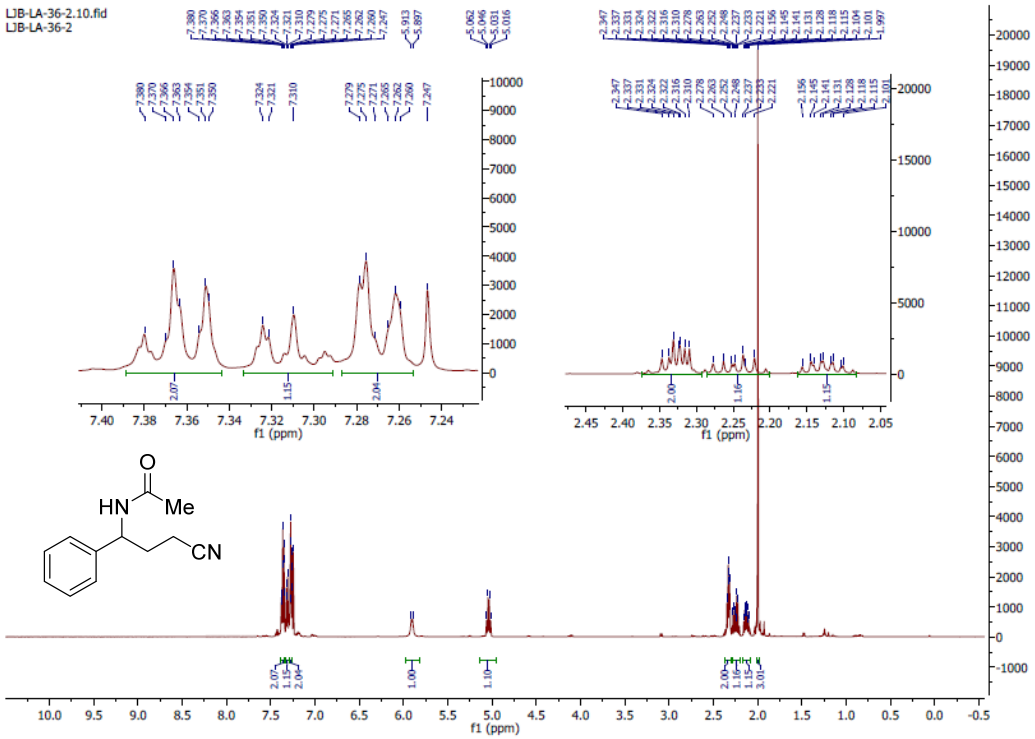

LJB-LA-250.11.fid
LJB-LA-250
169.101
142.253
138.849
136.199
129.713
129.343
129.120
129.026
128.808
127.690
127.248
126.985
125.709
52.407
38.821
23.096
21.359
O
Me
NH
S
Me
f1 (ppm)

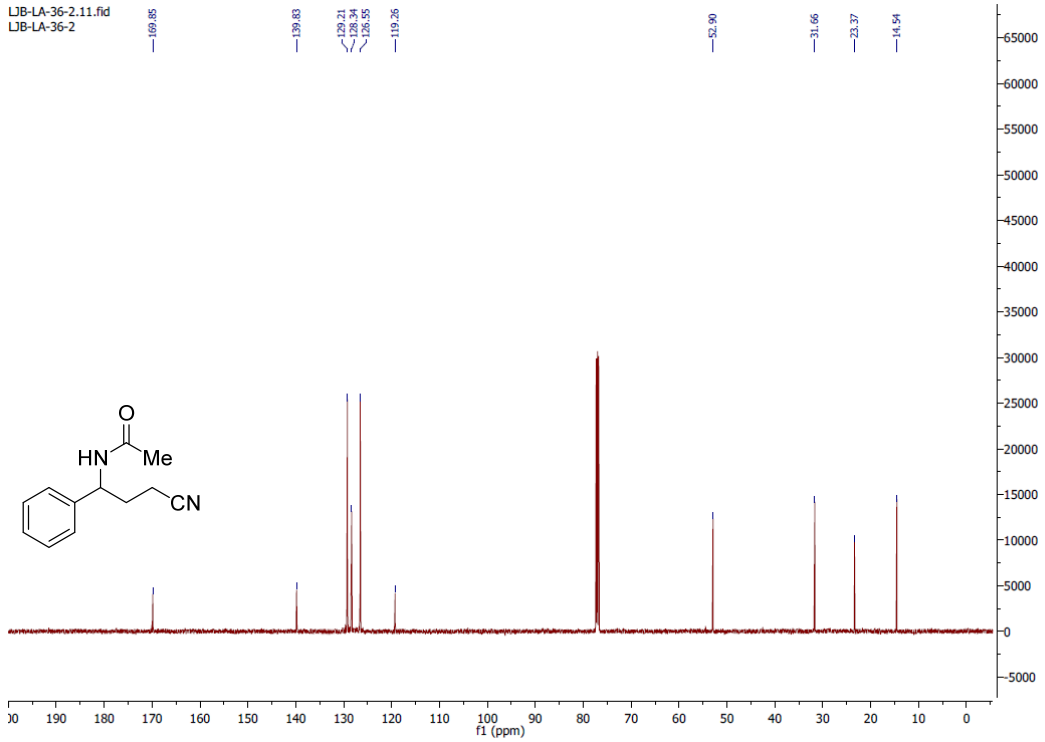

LJB-LA-250.12.fid
LJB-LA-250
129.345
129.118
128.808
127.692
127.247
126.984
125.707
52.404
38.819
23.098
21.358
O
Me
NH
S
Me
f1 (ppm)

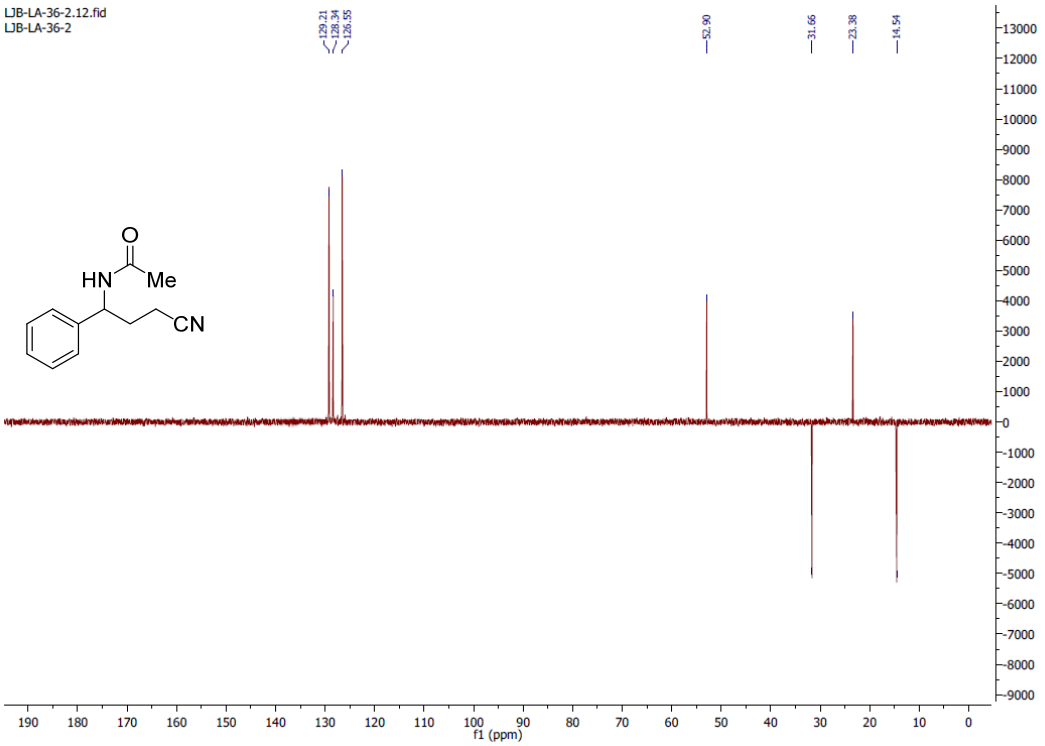

O
Me
NH
S
Me
f1 (ppm)


LJB-LA-257.11.fid
LJB-LA-257
O
Me
NH
S
Me
f1 (ppm)

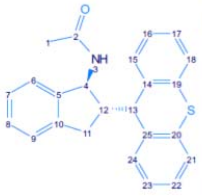

LJB-LA-257.12.fid
LJB-LA-257
130.465
128.817
128.009
127.704
127.214
127.130
126.048
52.324
38.552
23.103
20.415
Me
NH
S
Me
f1 (ppm)


LJB-LA-36-2.10.fid
LJB-LA-36-2
HN
Me
CN
f1 (ppm)


LJB-LA-36-2.11.fid
LJB-LA-36-2
169.85
139.83
129.21
128.34
126.55
119.26
52.90
31.66
23.37
14.54
O
HN
Me
CN
f1 (ppm)


LJB-LA-36-2.12.fid
LJB-LA-36-2
129.21
128.34
126.55
52.90
31.66
23.38
14.54
O
HN
Me
CN
f1 (ppm)

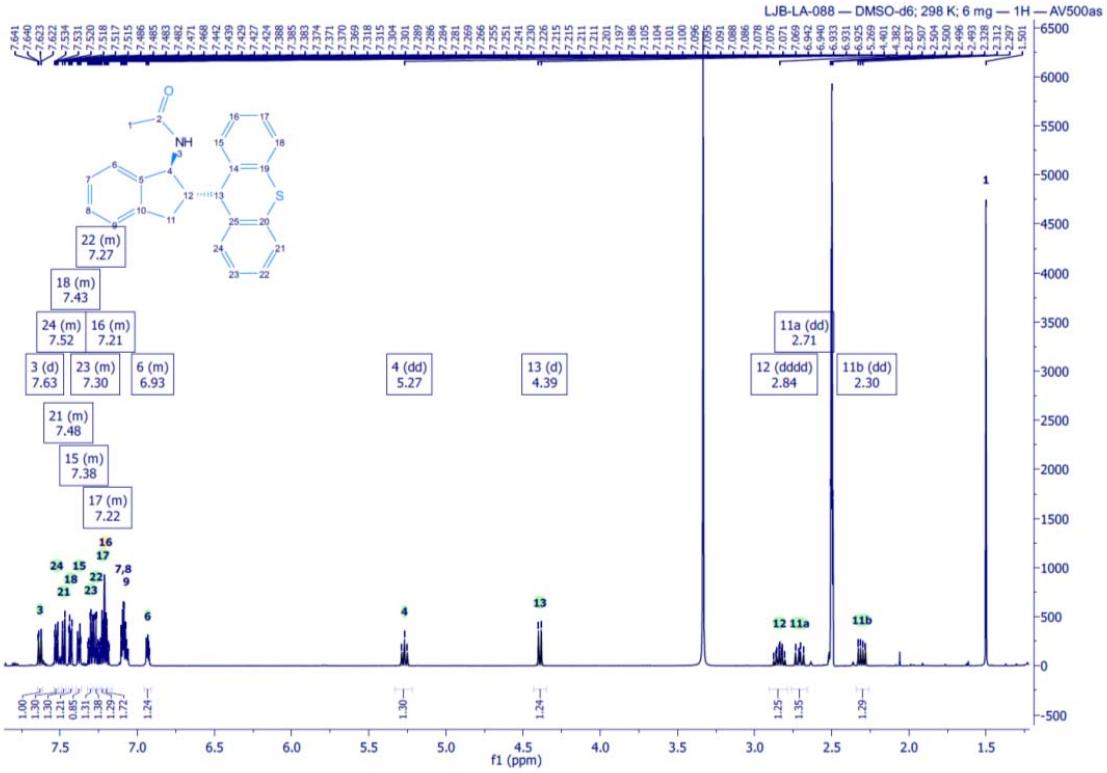
Configuration of *trans*-3p and *trans*-3r:

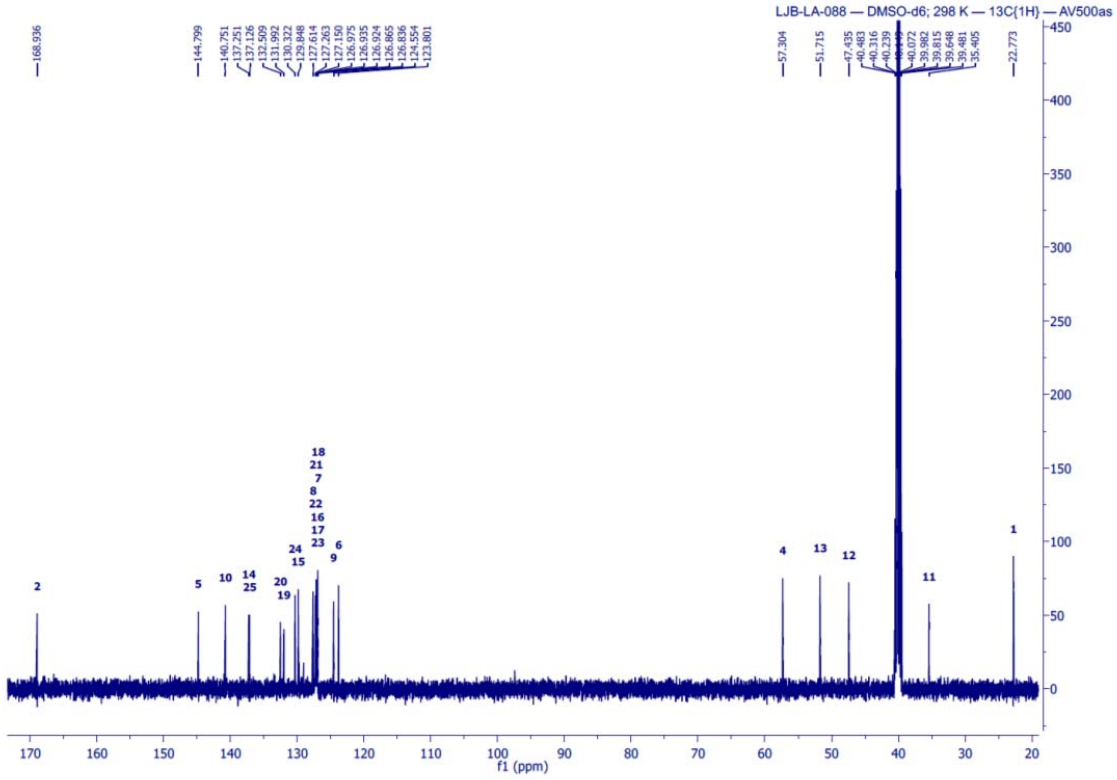


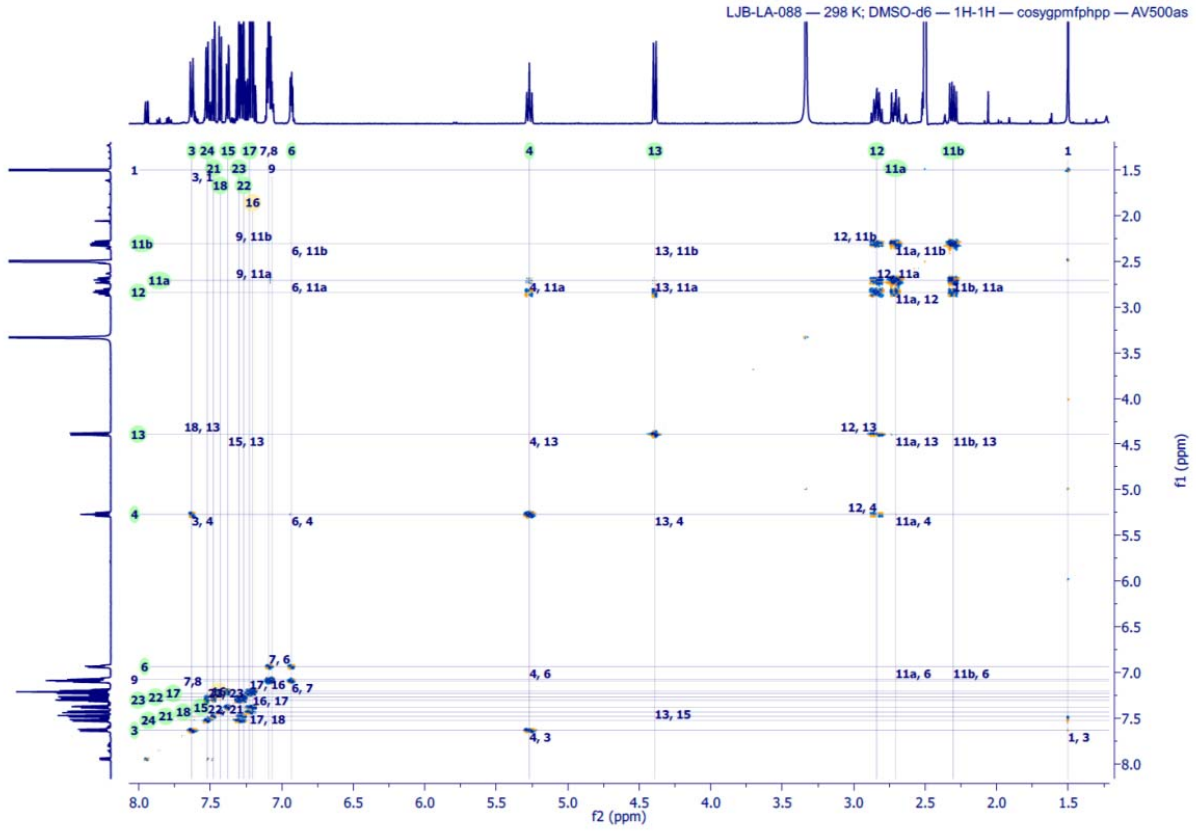
LJB-LA-088
AV500as; 298 K; 6 mg; DMSO-d6

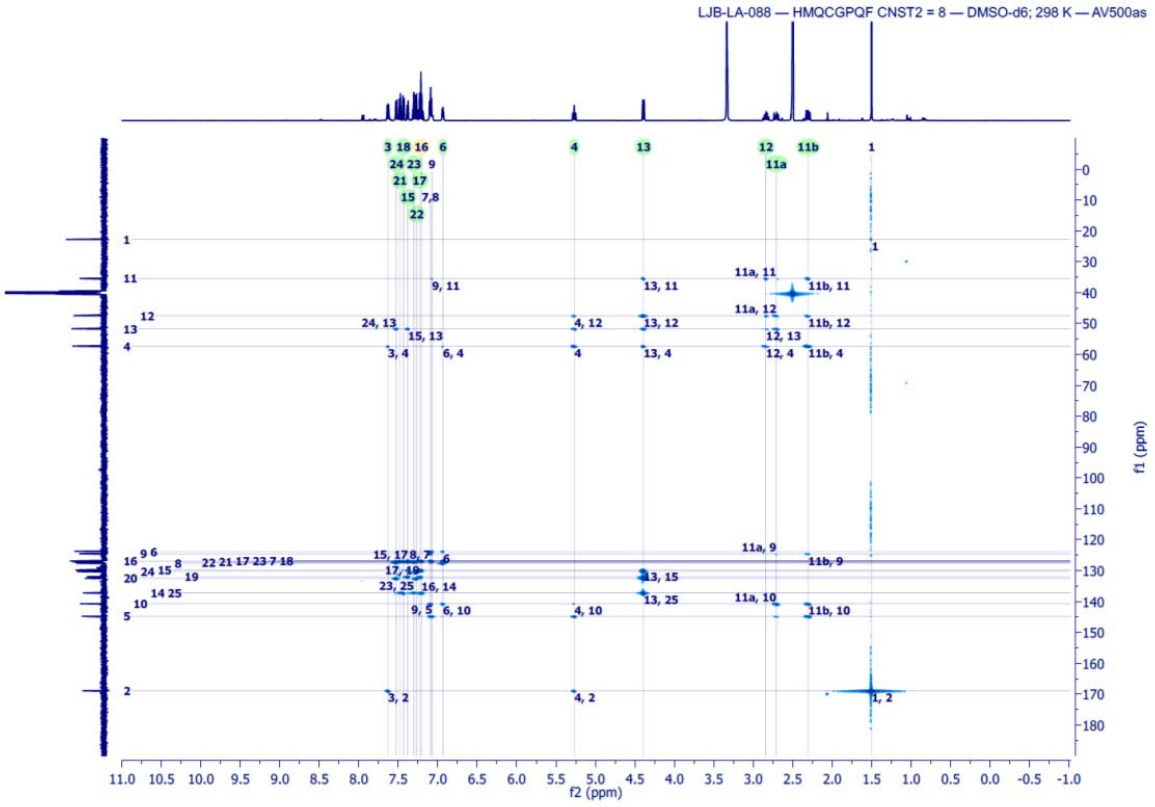
The NOESY cross peaks are in good agreement with a relative *trans* configuration.

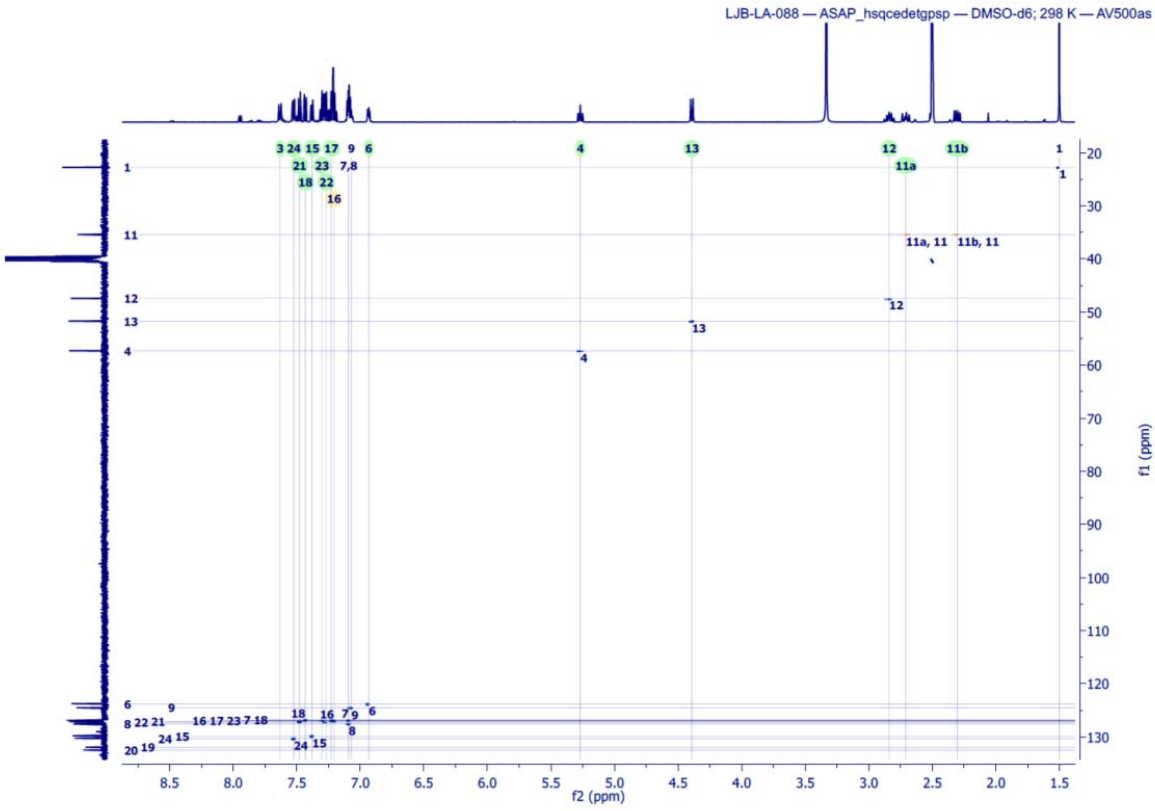
Atom	δ	J	COSY	HSQC	HMQC(MB)	NOESY
C1	22.77			1	1	
H1	1.50	s	3	1	1, 2	3, 4, 6, 15, 16, 17, 18
C2	168.94				1, 3, 4	
N3						
H3	7.63	d 8.9(4)	1, 4		2, 4	1, 4, 6, 12
C4	57.30			4	3, 4, 6, 11b, 12, 13	
H4	5.27	d 9.3(12), d 8.9(3)	3, 6, 11a, 12, 13	4	2, 4, 5, 10, 12, 13	1, 3, 6, 11a, 12, 13, 15, 24
C5	144.80				4, 7, 9, 11a, 11b	
C6	123.80			6	6	
H6	6.93	m	4, 7, 11a, 11b	6	4, 6, 7, 8, 10	1, 3, 4
C7	126.87			7	6, 8	
H7	7.09	m	6	7	5	
C8	127.61			8	6	
H8	7.09	m		8	7, 10	
C9	124.55			9	11a, 11b	
H9	7.07	m	11a, 11b	9	5, 11	11b
C10	140.75				4, 6, 8, 11a, 11b	
C11	35.41			11a, 11b	9, 11a, 11b, 12, 13	
H11a	2.71	d 15.6(11b), d 10.3(12)	4, 6, 9, 11b, 12, 13	11	5, 9, 10, 11, 12, 13	4, 11b, 13, 24
H11b	2.31	d 7.8(12), d 15.6(11a)	6, 9, 11a, 12, 13	11	4, 5, 9, 10, 11, 12	9, 11a, 12
C12	47.44			12	4, 11a, 11b, 12, 13	
H12	2.84	d 7.8(11b), d 9.3(4), d 9.1(13), d 10.3(11a)	4, 11a, 11b, 13	12	4, 11, 12, 13, 25	3, 4, 11b, 13, 15
C13	51.72			13	4, 11a, 12, 13, 15, 24	
H13	4.39	d 9.1(12)	4, 11a, 11b, 12, 15, 18, 21, 24	13	4, 11, 12, 13, 14, 15, 19, 20, 24, 25	4, 11a, 12, 15, 24
C14	137.25				13, 16, 18	
C15	129.85			15	13, 15, 17	
H15	7.38	m	13, 16	15	13, 15, 17, 19	1, 4, 12, 13
C16	126.97			16	18	
H16	7.21	m	15, 17	16	14, 18	1
C17	126.94			17	15	
H17	7.23	m	16, 18	17	15, 19	1
C18	126.84			18	16	
H18	7.43	m	13, 17	18	14, 16	1
C19	131.99				13, 15, 17	
C20	132.51				13, 22, 24	
C21	127.15			21	23	
H21	7.48	m	13, 22	21	23, 25	
C22	127.26			22	24	
H22	7.27	m	21, 23	22	20, 24	
C23	126.92			23	21	
H23	7.30	m	22, 24	23	21, 24, 25	
C24	130.32			24	13, 22, 23	
H24	7.52	m	13, 23	24	13, 20, 22	4, 11a, 13
C25	137.13				12, 13, 21, 23	

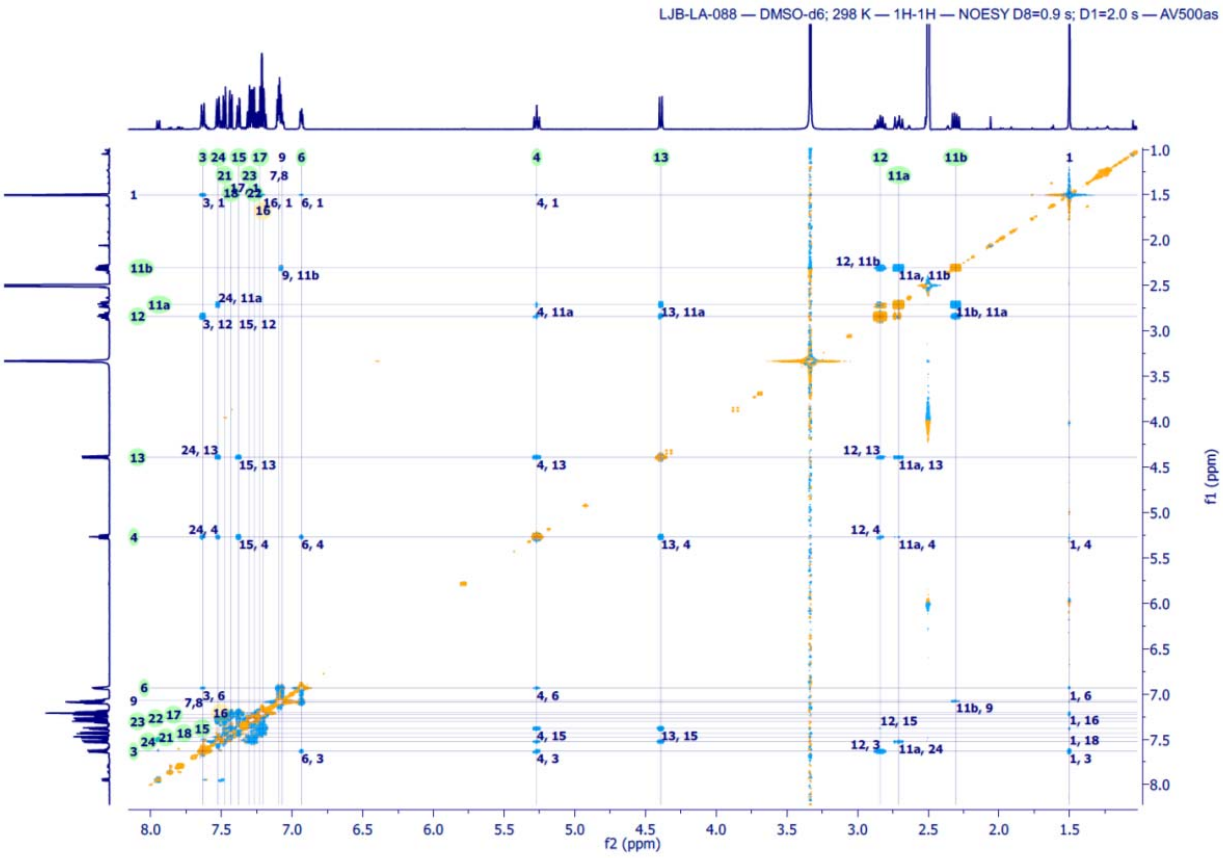



LJB-LA-088 — DMSO-d6; 298 K — 13C{1H} — AV500as
f1 (ppm)


LJB-LA-088 — 298 K; DMSO-d6 — 1H-1H — cosygpmfphpp — AV500as
f2 (ppm)
f1 (ppm)

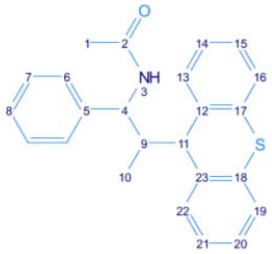

LJB-LA-088 — HMQCGPQF CNST2 = 8 — DMSO-d6; 298 K — AV500as
f2 (ppm)
f1 (ppm)


LJB-LA-088 — ASAP_hsqcedetgpsp — DMSO-d6; 298 K — AV500as
f2 (ppm)
f1 (ppm)

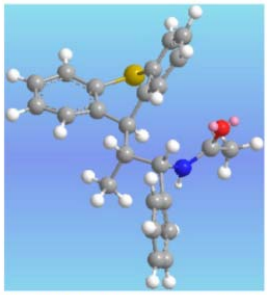

LJB-LA-088 — DMSO-d6; 298 K — 1H-1H — NOESY D8=0.9 s; D1=2.0 s — AV500as
f2 (ppm)
f1 (ppm)

LJB-LA-077

AV500as; 6 mg; 298 K; DMSO-d_6

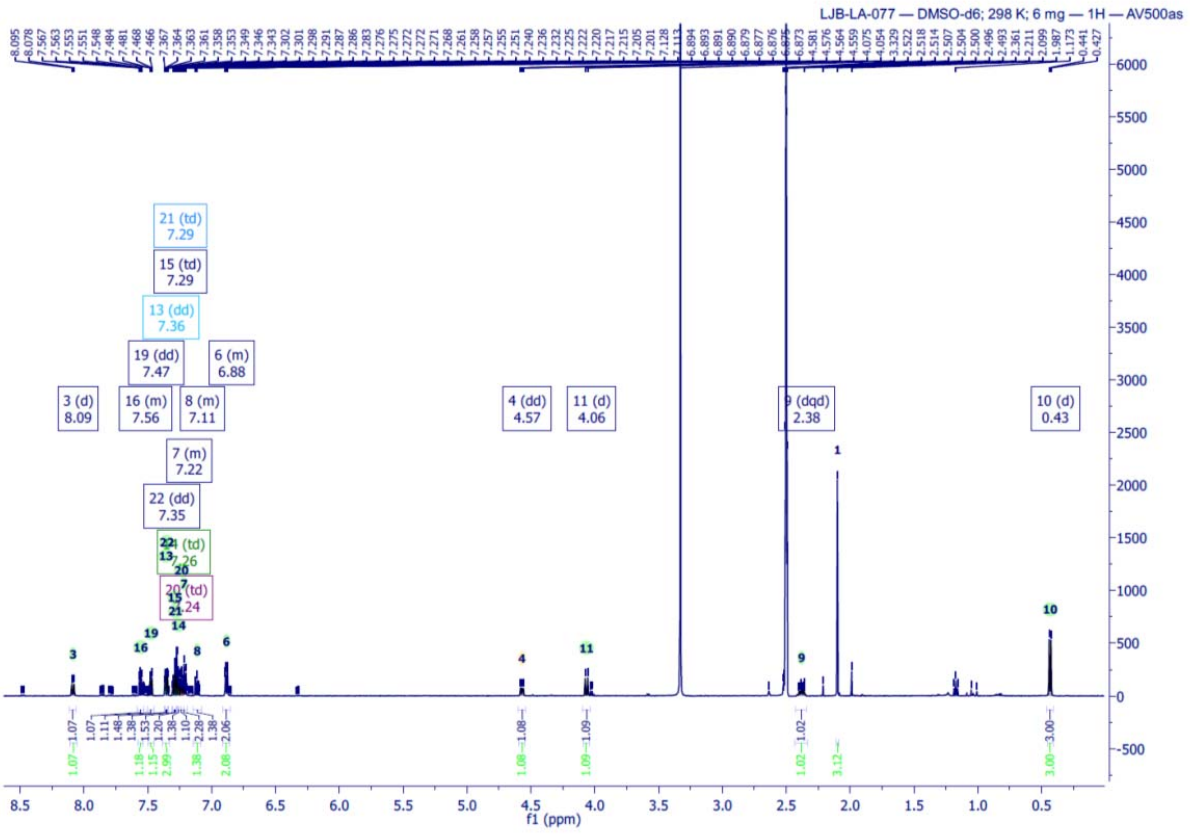


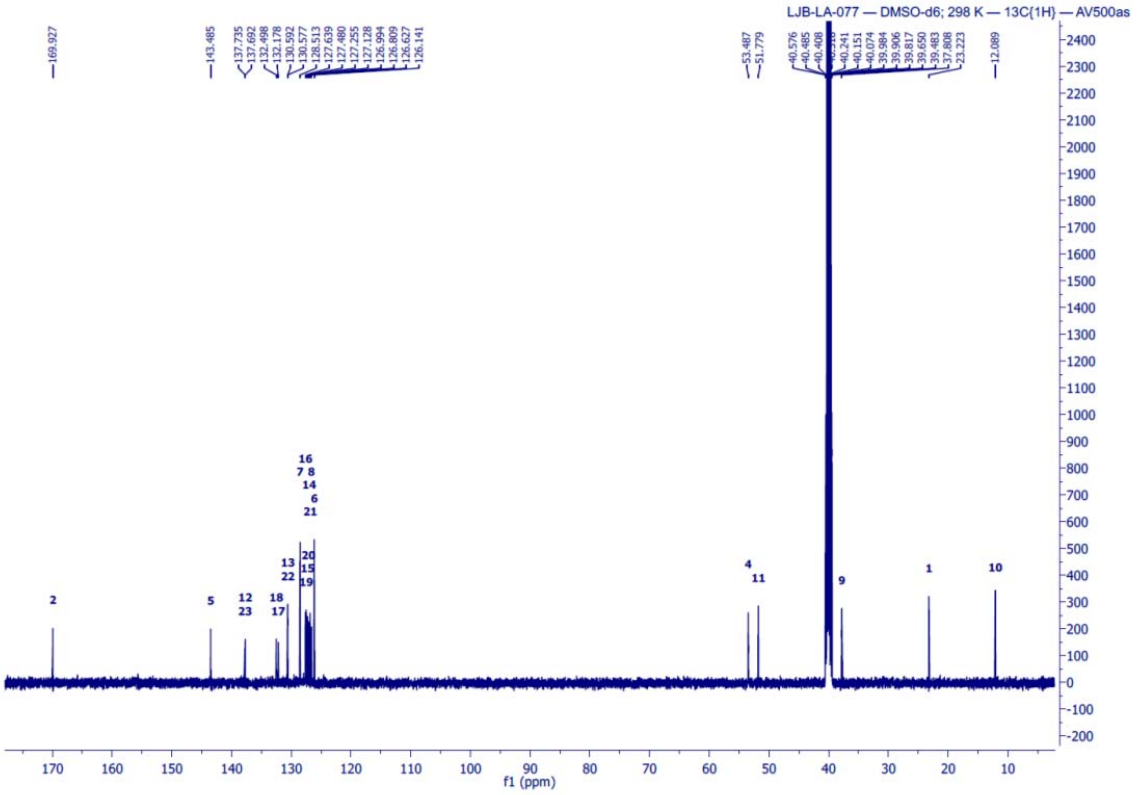
The NOESY correlations support the relative stereochemistry SR/RS rather than RR/SS. For stereocenters in open-chain positions, such observations must not be regarded as conclusive evidence though.

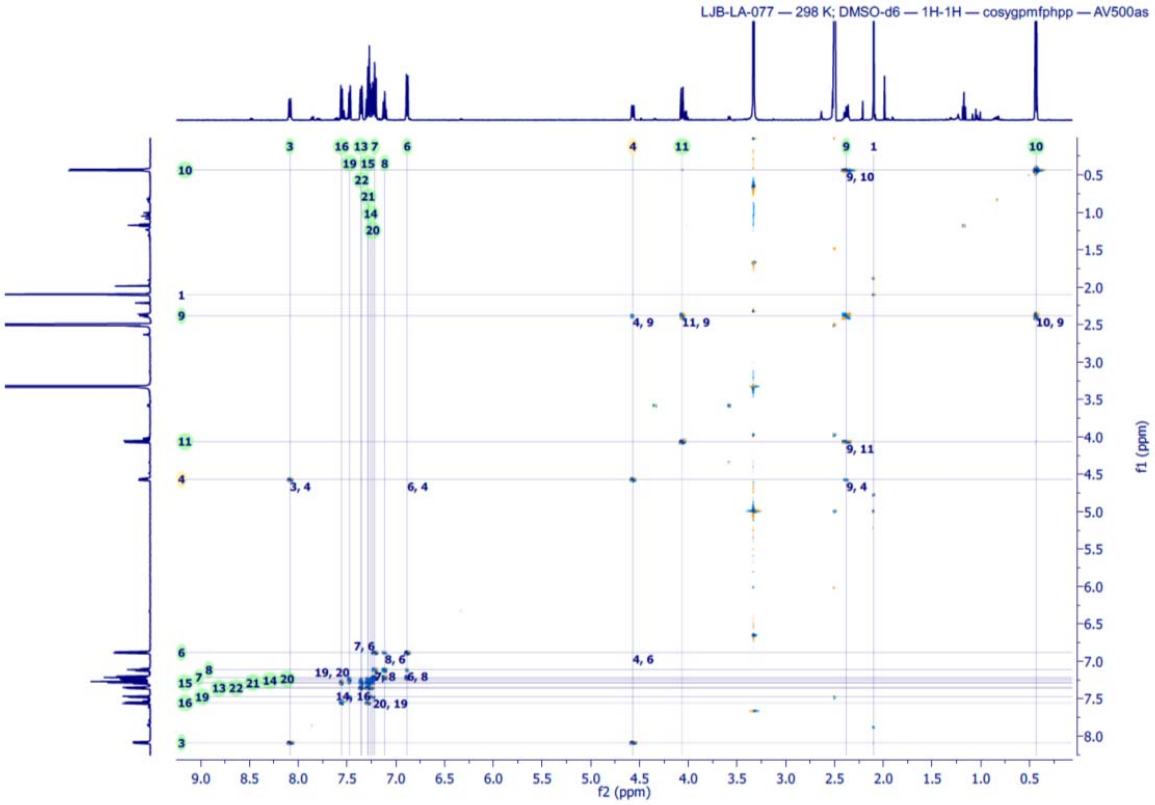


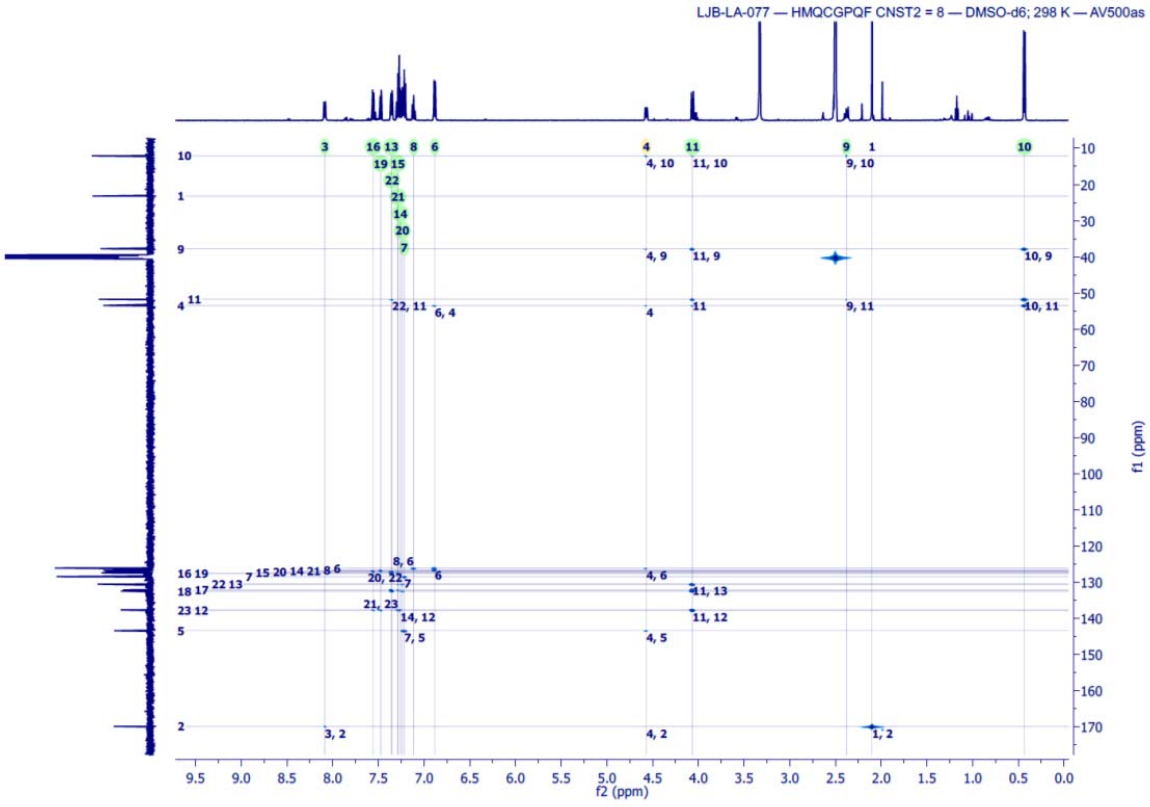
The structure model above shows one possible conformation.

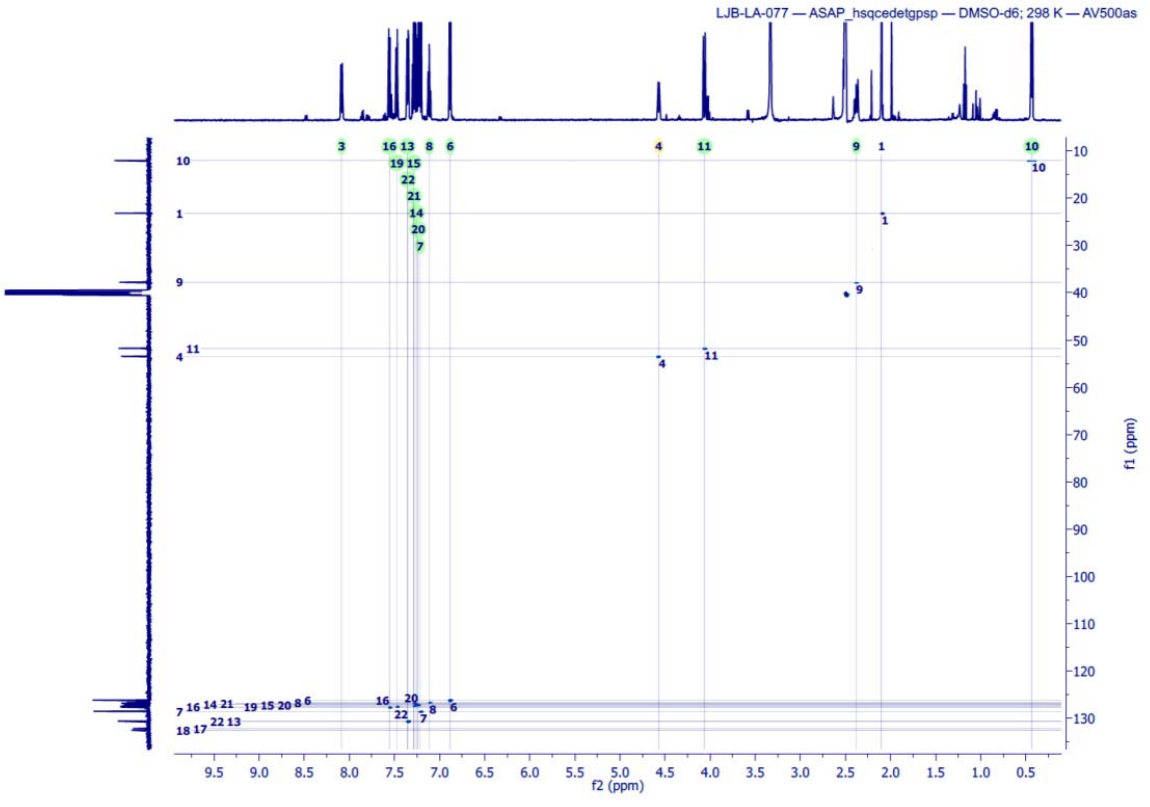
C1	23.22			1		
H1	2.099	s		1	2	3, 4, 6, 11, 13
C2	169.93				1, 3, 4	
N3	n.d.					
H3	8.086	d 8.5(4)	4		2	1, 4, 6, 10, 11
C4	53.49			4	4, 6, 10, 11	
H4	4.570	d 8.5(3), d 2.9(9)	3, 6, 9	4	2, 4, 5, 6, 9, 10	1, 3, 6, 9, 10, 11, 1
C5	143.49				4, 7	
C6	126.14			6	4, 6, 8	
H6	6.884	m	4, 7, 8	6	4, 6, 8	1, 3, 4, 9, 10
C7	128.51			7	7	
H7	7.217	m	6, 8	7	5, 7	
C8	126.63			8	6	
H8	7.113	m	6, 7	8	6	
C9	37.81			9	4, 10, 11	
H9	2.381	d 10.3(11), q 7.1(10), d 2.9(4)	4, 10, 11	9	10, 11	4, 6, 10, 11
C10	12.09			10	4, 9, 11	
H10	0.434	d 7.1(9)	9	10	4, 9, 11	3, 4, 6, 9, 11, 22
C11	51.78			11	9, 10, 11, 13, 22	
H11	4.065	d 10.3(9)	9	11	4, 9, 10, 11, 12, 13, 17, 18, 22, 23	1, 3, 4, 9, 10, 13, 2
C12	137.69				11, 14, 16	
C13	130.58			13	11, 15	
H13	7.358	d 2.1(15), d 7.1(14)	16	13	11, 15, 17	1, 4, 11
C14	126.99			14	16	
H14	7.259	d 1.6(16), d 7.4(15), d 7.1(13)	16	14	12, 16	
C15	127.26			15	13	
H15	7.288	d 7.4(16), d 7.4(14), d 2.1(13)	16	15	13, 17	
C16	127.64			16	14	
H16	7.556	m	13, 14, 15	16	12, 14	
C17	132.18				11, 13, 15	
C18	132.50				11, 20, 22	
C19	127.48			19	21	
H19	7.475	d 1.9(21), d 7.6(20)	20, 21, 22	19	21, 23	
C20	127.13			20	22	
H20	7.238	d 1.6(22), d 7.4(21), d 7.6(19)	19	20	18, 22	
C21	126.81			21	19	
H21	7.285	d 7.5(22), d 7.4(20), d 1.9(19)	19	21	19, 23	
C22	130.59			22	11, 20	
H22	7.352	d 1.6(20), d 7.5(21)	19	22	11, 18, 20	10, 11

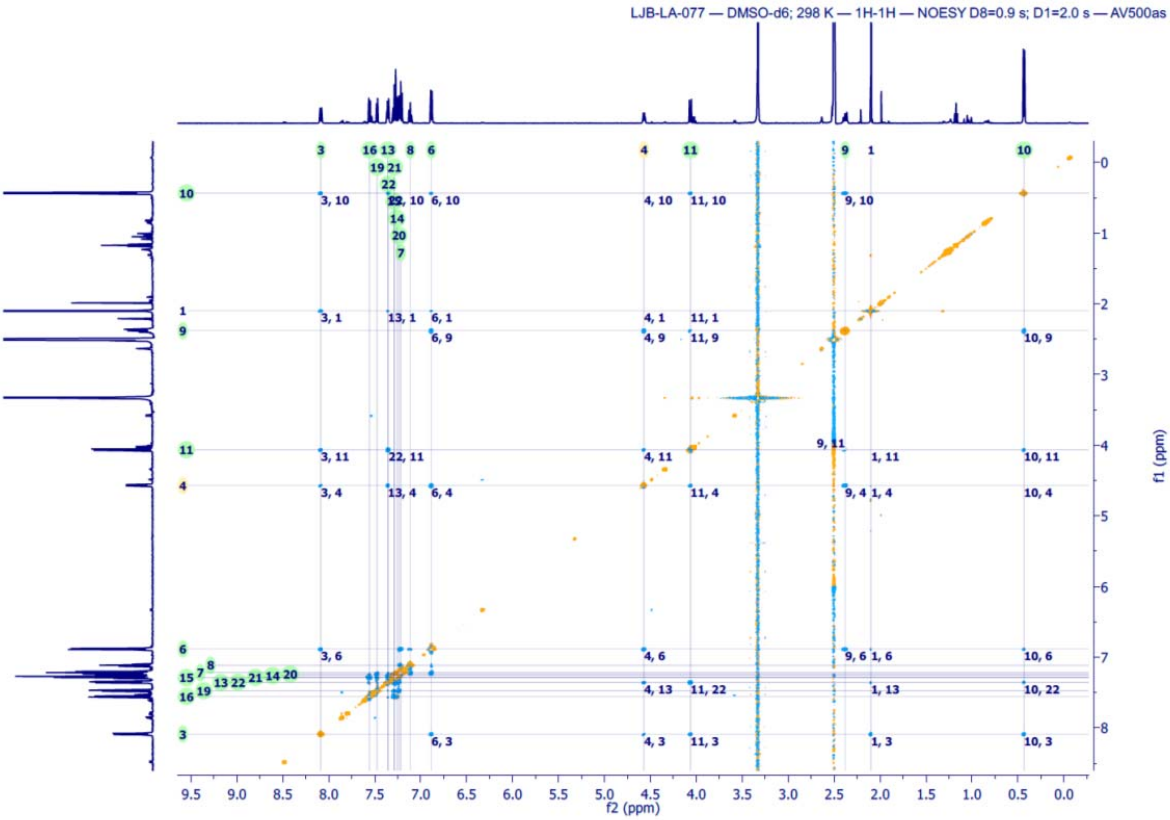



LJB-LA-077 — DMSO-d6; 298 K — 13C{1H} — AV500as
f1 (ppm)


LJB-LA-077 — 298 K; DMSO-d6 — 1H-1H — cosygpmfphpp — AV500as
f2 (ppm)
f1 (ppm)


LJB-LA-077 — HMQCGPQF CNST2 = 8 — DMSO-d6; 298 K — AV500as
f2 (ppm)
f1 (ppm)


LJB-LA-077 — ASAP_hsqcedetgpsp — DMSO-d6; 298 K — AV500as
f2 (ppm)
f1 (ppm)


LJB-LA-077 — DMSO-d6; 298 K — 1H-1H — NOESY D8=0.9 s; D1=2.0 s — AV500as
f2 (ppm)
f1 (ppm)

Reference:

[1] G. R. Fulmer, A. J. M. Miller, N. H. Sherden, H. E. Gottlieb, A. Nudelman, B. M. Stoltz, J. E. Bercaw, K. I. Goldberg, *Organometallics* **2010**, *29*, 2176.