Ruthenium-and Palladium-Catalyzed Consecutive Coupling and Cyclization of Aromatic Sulfoximines with Phenylboronic Acids: an efficient Route to Dibenzothiazines

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Electronic Supplementary Information (ESI)

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Experimental Section

Procedure A: General procedure for the coupling of sulfoximine 1 with aromaticboronic acids 2 catalyzed by ruthenium complex.

A 15-mL pressure tube equipped with a magnetic stirrer and septum containing sulfoximine (**1**) (100 mg, if it is solid), [{$RuCl_2$(*p*-cymene)}$_2$] (10 mol %), Ag_2O (1.5 equiv) and boronic acid (**2a)** (3.0 equiv) was evacuated and purged with nitrogen gas three times. Then, to the tube was then added $AgSbF_6$ (40 mol %) inside the glove box ($AgSbF_6$ was moisture sensitive, thus, it was added inside the glove box). Later, sulfoximine (**1a**) (100 mg, if it is liquid along with solvent via syringes) and dry THF (3.0 mL) were added via syringes. Then, the pressure tube was covered with a screw cap and the reaction mixture was allowed to stir at 100 °C for 16 h. After cooling to ambient temperature, the reaction mixture was diluted with CH_2Cl_2, filtered through Celite and silica gel, and the filtrate was concentrated. The crude residue was purified through a silica gel column using hexanes and ethyl acetate as eluent to give pure **5**.

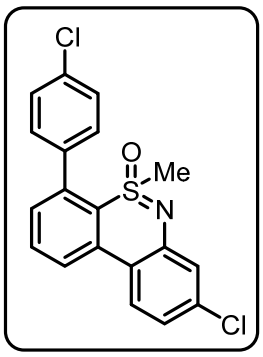
Note: Dry THF solvent is crucial for the reaction. If the solvent is not dry, the yield of product is decreased. This reaction requires inert condition (N_2 gas).

Procedure B. General procedure for the synthesis of dibenzothiazines catalysed by palladium catalyst.

A Schlenk tube (25 mL) equipped with a stir bar was loaded with *ortho*-aryl sulfoximine **(5)** (100 mg), $Pd(OAc)_2$ (10 mol %) and $PhI(OAc)_2$ (2.0 equiv). Then, dry toluene (2.0 mL) was added, and the mixture was allowed to stir at 120 °C for 10 h. After cooling to room temperature, the mixture was filtered through a short celite pad and washed with dichloromethane (3 × 20 mL). The filtrate was concentrated, and the product was purified by column chromatography using silica gel as stationary phase and a mixture of hexane and ethyl acetate as eluent to give pure **6**.

X-ray Analysis

8-Chloro-4-(4-Chlorophenyl)-5-methyldibenzo[c,e][1,2]thiazine 5-oxide (6f).



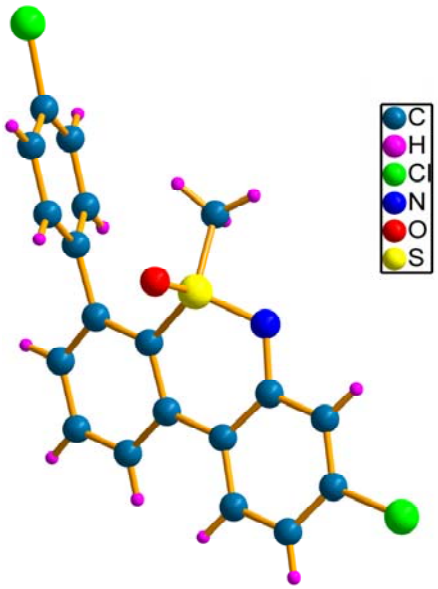
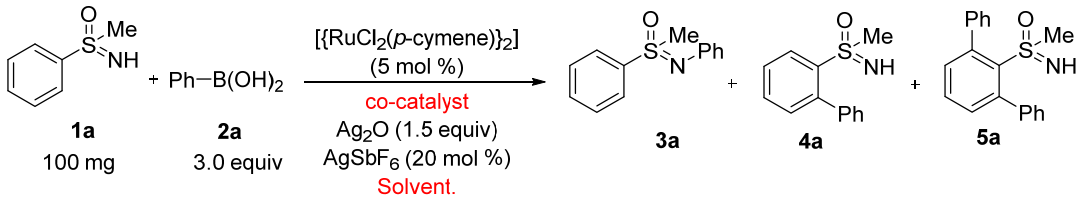


Table 1. Crystal data and structure refinement for (6f).

Identification code	RK-855	
Empirical formula	C19 H13 Cl2 N O S	
Formula weight	374.26	
Temperature	298(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 7.960(2) Å	□= 89.003(6)°.
	b = 9.715(3) Å	□= 75.173(7)°.
	c = 11.230(3) Å	□ = 82.452(6)°.
Volume	832.1(4) $Å^3$	
Z	2	
Density (calculated)	1.494 Mg/m^3	
Absorption coefficient	0.521 mm^{-1}	
F(000)	384	
Crystal size	0.400 x 0.350 x 0.250 mm^3	
Theta range for data collection	1.876 to 28.575°.	
Index ranges	-10<=h<=8, -12<=k<=13, -13<=l<=15	
Reflections collected	14798	
Independent reflections	4149 [R(int) = 0.0426]	

Completeness to theta = 25.242°	99.5 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.878 and 0.812
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4149 / 0 / 218
Goodness-of-fit on F^2	0.898
Final R indices [I>2sigma(I)]	R1 = 0.0460, wR2 = 0.1373
R indices (all data)	R1 = 0.0512, wR2 = 0.1493
Extinction coefficient	n/a
Largest diff. peak and hole	0.633 and -0.600 e.$Å^{-3}$

Optimization studies



1a 100 mg | **2a** 3.0 equiv | **3a** | **4a** | **5a**

S NO	Solvent	Co-catalyst	**3a**	**4a**	**5a**
1	THF	$Cu(OTf)_2$	32%	0%	15%
2	THF	Ag(OTf)	3%	5%	20%
3	THF	AgOAc	0%	7%	19%
4	THF	$Zn(OTf)_2$	0%	0%	0%
5	MeOH	--	0%	8%	26%
6	1,4-Dioxane	--	0%	6%	33%
7	DMF	--	0%	5%	24%
8	Tolune	--	0%	5%	10%

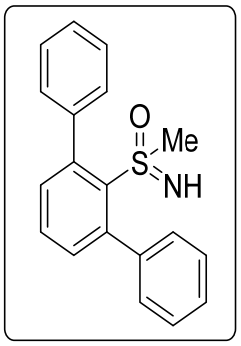
All reactions (entry 1-7) were carried out using **1a** (100 mg) with **2b** (3.0 equiv), [{$RuCl_2$(*p*-cymene)}$_2$] (10 mol %), $AgSbF_6$ (40 mol %) , Ag_2O (1.5 equiv), co-catalyst (50 mol%) in Solvent (3.0 mL) at 100 °C for 16 h. All reactions (entry 1-8) isolated yields.

Furthermore, the coupling reaction was examined with solvents such as toluene, MeOH, 1,4-dioxane and DMF apart from THF. However, in all these solvents, a mixture of **4a** and **5a** was observed in moderate yields. THF solvent was effective solvent for the reaction. Furthermore, the reaction was tested with other additives such as AgOTf, $AgBF_4$ and KPF_6 apart from $AgSbF_6$. $AgBF_4$ and AgOTf were partially active, providing product **5a** in 55% and 40% yields, respectively. KPF_6 was not active for the reaction. The optimization studies clearly revealed that [{$RuCl_2$(*p*-cymene)}$_2$] (10 mol %), AgSbF6 (40 mol %) and Ag_2O (1.5 equiv.) in THF at 100 °C for 16 h is the best condition for the reaction. It is important to note that the C–H bond activation of both *ortho* carbons of phenyl sulfoximines were very facile and cannot be controlled. Due to the facile bis arylation, an excess amount of catalyst is required.

Spectral Data of Compounds.

2'-(*S*-Methylsulfonimidoyl)-1,1':3',1''-terphenyl (5aa).

The representative general procedure **A** was followed using **1a** (100 mg) and phenylboronic acid (**2a**) (3.0 equiv). Product **5aa** was isolated in 135.0 mg and yield is 68%.



Colorless solid; mp 130-133 °C; eluent (40% ethyl acetate in hexanes).

IR (ATR) ṽ (cm^{-1}): 3564, 3524, 3065, 2876, 2354, 2367, 1743, 1698, 1648, 1540, 1518, 1424, 1218, 1017.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.63 (bs, 4 H), 7.59 (t, *J* = 8.0, Hz, 2 H), 7.52 – 7.49 (m, 6 H), 7.40 (d, *J* = 8.0, Hz, 2 H), 2.56 (s, 3 H).

^{13}C NMR ($CDCl_3$, 100 MHz):δ 141.9, 141.4, 140.2, 132.3, 130.6, 129.8, 129.1, 128.8, 46.3.

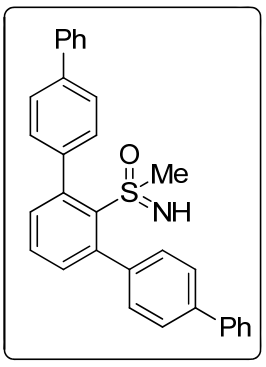
Elemental Analysis: C (72.7%), H (6.0%), N (4.2%), S (9.3%).

HRMS (ESI): calc. for [($C_{19}H_{17}NOS$)H] (M+H) 308.1109, measured 308.1106.

MALDI-TOF-MS: calc. for [($C_{19}H_{17}NOS$)K] (M+K) 346.06, measured 346.02.

2''-(*S*-Methylsulfonimidoyl)-1,1':4',1'':3'',1''':4''',1''''-quinquephenyl (5ab).

The representative general procedure **A** was followed using **1a** (100 mg) and boronic acid **2b** (3.0 equiv). Product **5ab** was isolated in 213 mg and yield is 72%.



Colorless solid; mp 213-216 °C; (35% ethyl acetate in hexanes).

IR (ATR) ṽ (cm^{-1}): 3563, 3524, 3095, 2962, 2362, 2317, 1743, 1699, 1649, 1540, 1517, 1459, 1424, 1221, 1018.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.76 (bm, 8 H), 7.69 (d, *J* = 8.0 Hz, 4 H), 7.58 (t, *J* = 8.0 Hz, 1 H), 7.50 (t, *J* = 8.0 Hz, 4 H), 7.43 (s, 1 H), 7.42 – 7.38 (m, 3 H), 2.59 (s, 3 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 143.5, 141.3, 140.7, 140.1, 139.5, 132.1, 130.2, 130.0, 128.9, 127.7, 127.3, 127.1, 46.7.

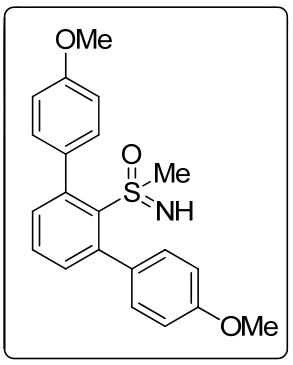
Elemental Analysis: C (83.5%), H (6.3%), N (3.4%), S (7.1%).

HRMS (ESI): calc. for [($C_{31}H_{25}NOS$)H] (M+H) 460.1735, measured 460.1731.

MALDI-TOF-MS: calc. for [($C_{31}H_{25}NOS$)K] (M+K) 498.12, measured 498.08.

4,4''-Dimethoxy-2'-(*S*-methylsulfonimidoyl)-1,1':3',1''-terphenyl (**5ac**).

The representative general procedure **A** was followed using **1a** (100 mg) and boronic acid **2c** (3.0 equiv). Product **5ac** was isolated in 156 mg and yield is 66%.



Colorless solid; mp 120-123 °C; eluent (50% ethyl acetate in hexanes).

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 3562, 3525, 3000, 2936, 2360, 2317, 1743, 1699, 1648, 1540, 1513, 1457, 1248, 1029.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.55 (t, *J* = 8.0 Hz 1 H), 7.54 (bs, 4 H), 7.35 (d, *J* = 8.0 Hz, 2 H), 7.04 (d, *J* = 8.0 Hz, 4 H), 3.88 (s, 6 H), 2.60 (s, 3 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 160.2, 141.2, 132.0, 131.1, 130.9, 129.4, 123.5, 114.4, 55.4, 46.0.

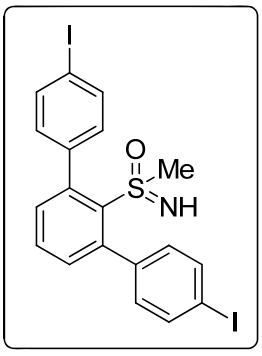
Elemental Analysis: C (70.2%), H (7.1%), N (3.6%), S (7.2%).

HRMS (ESI): calc. for [($C_{21}H_{21}NO_3S$)H] (M+H) 368.1320, measured 368.1314.

MALDI-TOF-MS: calc. for [($C_{21}H_{21}NO_3S$)K] (M+K) 406.08, measured 406.12.

4,4''-Iodo-2'-(*S*-methylsulfonimidoyl)-1,1':3',1''-terphenyl (**5ad**).

The representative general procedure **A** was followed using **1a** (100 mg) and boronic acid **2d** (3.0 equiv). Product **5ad** was isolated in 234 mg and yield is 65%.



Colorless solid; mp 225-227 °C; eluent (35% ethyl acetate in hexanes).

IR (ATR) ṽ (cm^{-1}): 3565, 3523, 3054, 2927, 2367, 2314, 1741, 1693, 1646, 1540, 1515, 1484, 1424, 1264, 1217, 1004.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.83 (d, *J* = 8.0 Hz, 4 H), 7.53 (t, *J* = 8.0 Hz, 1 H), 7.34 (d, *J* = 8.0 Hz, 4 H), 7.31 (d, *J* = 8.0 Hz, 2 H), 2.55 (s, 3 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 142.8, 140.3, 140.0, 137.7, 132.2, 131.5, 130.3, 94.6, 46.9.

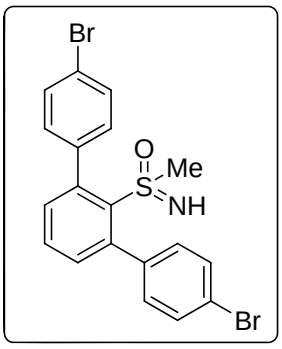
Elemental Analysis: C (40.8%), H (2.5%), N (2.5%), S (5.8%).

HRMS (ESI): calc. for [($C_{19}H_{15}I_2NOS$)H] (M+H) 559.9042, measured 559.9059.

MALDI-TOF-MS: calc. for [($C_{19}H_{15}I_2NOS$)K] (M+K) 597.86, measured 597.82.

4,4''-Bromo-2'-(*S*-methylsulfonimidoyl)-1,1':3',1''-terphenyl (**5ae**).

The representative general procedure **A** was followed using **1a** (100 mg) and boronic acid **2e** (3.0 equiv). Product **5ae** was isolated in 185 mg and yield is 62%.



Colorless solid; mp 145-148 °C; eluent (40% ethyl acetate in hexanes).

IR (ATR) ṽ (cm^{-1}): 3564, 3525, 3056, 2925, 2367, 2315, 1741, 1700, 1648, 1540, 1518, 1418, 1220, 1009.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.63 (d, *J* = 8.0 Hz, 4 H), 7.54 (t, *J* = 8.0 Hz, 1 H), 7.48 (d, *J* = 8.0 Hz, 4 H), 7.32 (d, *J* = 8.0 Hz, 2 H), 2.55 (s, 3 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 143.0, 140.2, 139.4, 132.3, 131.8, 131.3, 130.3, 122.9, 46.7.

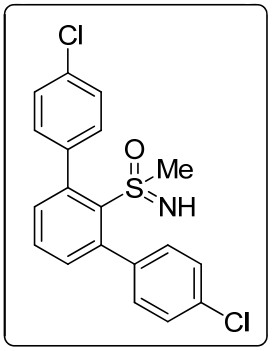
Elemental Analysis: C (47.2%), H (3.4%), N (3.1%), S (6.3%).

HRMS (ESI): calc. for [($C_{19}H_{15}Br_2NOS$)H] (M+H) 463.9319, measured 463.9321.

MALDI-TOF-MS: calc. for [($C_{19}H_{15}Br_2NOS$)K] (M+K) 501.88, measured 501.85.

4,4''-Dichloro-2'-(*S*-methylsulfonimidoyl)-1,1':3',1''-terphenyl (**5af**).

The representative general procedure **A** was followed using **1a** (100 mg) and boronic acid **2f** (3.0 equiv). Product **5af** was isolated in 154 mg and yield is 64%.



Colorless solid; mp 125-128 °C; eluent (40% ethyl acetate in hexanes).

IR (ATR) ṽ (cm^{-1}): 3565, 2962, 2962, 2367, 1723, 1647, 1493, 1452, 1279, 1125, 1077, 1013.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.55 (d, *J* = 8.0 Hz, 4 H), 7.54 (t, *J* = 8.0 Hz, 1 H), 7.47 (d, *J* = 8.0 Hz, 4 H), 7.32 (d, *J* = 8.0 Hz, 2 H), 2.55 (s, 3 H).

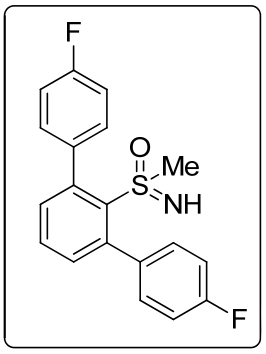
^{13}C NMR ($CDCl_3$, 100 MHz): δ 143.1, 140.1, 138.9, 134.8, 132.4, 131.0, 130.3, 128.8, 46.8.

HRMS (ESI): calc. for [($C_{19}H_{15}Cl_2NOS$)H] (M+H) 376.0330, measured 376.0331.

MALDI-TOF-MS: calc. for [($C_{19}H_{15}Cl_2NOS$)K] (M+K) 413.98, measured 413.94.

4,4''-Difluoro-2'-(*S*-methylsulfonimidoyl)-1,1':3',1''-terphenyl (**5ag**).

The representative general procedure **A** was followed using **1a** (100 mg) and boronic acid **2g** (3.0 equiv). Product **5ag** was isolated in 132 mg and yield is 60%.



Colorless solid; mp 150-153 °C; eluent (40% ethyl acetate in hexanes).

IR (ATR) ṽ (cm^{-1}): 3565, 3523, 3059, 2927, 2365, 1740, 1693, 1647, 1510, 1451, 1416, 1221, 1044.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.59 (bs, 4 H), 7.53 (t, *J* = 8.0, Hz 1 H), 7.33 (d, *J* = 8.0 Hz, 2 H), 7.20 (t, *J* = 8.0 Hz, 4 H), 2.52 (s, 3 H).

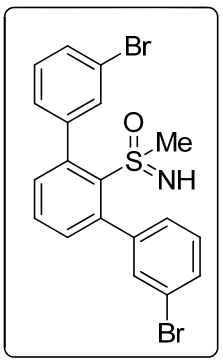
^{13}C NMR ($CDCl_3$, 100 MHz): δ 164.1, 161.6 (F-coupling), 143.3, 140.1, 136.45 and 136.42 (F-coupling), 132.4, 131.5 and 131.4 (F-coupling), 130.1, 115.8 and 115.6 (F-coupling), 46.7.

HRMS (ESI): calc. for [($C_{19}H_{15}F_2NOS$)H] (M+H) 344.0921, measured 344.0927.

MALDI-TOF-MS: calc. for [($C_{19}H_{15}F_2NOS$)K] (M+K) 382.04, measured 382.01.

3,3''-Dibromo-2'-(S-methylsulfonimidoyl)-1,1':3',1''-terphenyl (**5ah**).

The representative general procedure **A** was followed using **1a** (100 mg) and boronic acid **2h** (3.0 equiv). Product **5ah** was isolated in 56 mg and yield is 19%.



Colorless solid; mp 146-149 °C; eluent (40% ethyl acetate in hexanes).

IR (ATR) ṽ (cm^{-1}): 3563, 3525, 3060, 2922, 2361, 2317, 1741, 1699, 1648, 1553, 1518, 1456, 1218, 1042.

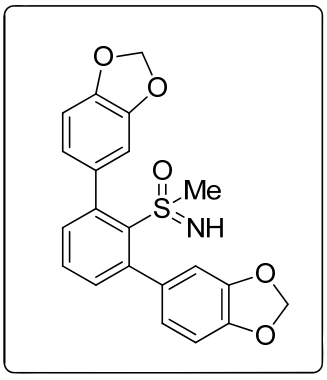
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.73 (bs, 1 H), 7.61 – 7.53 (m, 6 H), 7.38 – 7.33 (m, 4 H), 2.59 (s, 3 H).

HRMS (ESI): calc. for [($C_{19}H_{15}Br_2NOS$)H] (M+H) 463.9319, measured 463.9321.

MALDI-TOF-MS: calc. for [($C_{19}H_{15}Br_2NOS$)K] (M+K) 501.88, measured 501.84.

5,5'-(2-(*S*-Methylsulfonimidoyl)-1,3-phenylene)bis(benzo[*d*][1,3]dioxole) (**5ai**).

The representative general procedure **A** was followed using **1a** (100 mg) and boronic acid **2i** (3.0 equiv). Product **5ai** was isolated in 155 mg and yield is 61%.



Colorless solid; mp 165-168 °C; eluent (50% ethyl acetate in hexanes).

IR (ATR) ṽ (cm^{-1}): 3564, 3524, 3059, 2923, 2363, 2321, 1742, 1700, 1649, 1540, 1516, 1459, 1264, 1037.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.59 (t, *J* = 8.0 Hz, 1 H), 7.37 (d, *J* = 8.0, 4.0 Hz, 2 H), 7.08 (bs, 4 H), 6.95 (d, *J* = 8.0 Hz, 2 H), 6.09 (s, 4 H), 2.68 (s, 3 H).

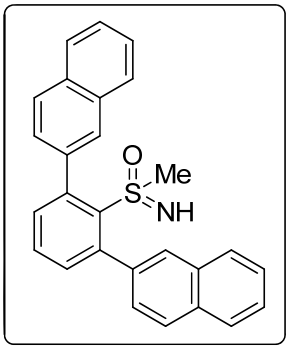
^{13}C NMR ($CDCl_3$, 100 MHz): δ 148.6, 148.2, 145.3, 141.4, 132.9, 132.3, 131.1, 129.4, 123.5, 108.7, 101.7, 43.8.

HRMS (ESI): calc. for [($C_{21}H_{17}NO_5S$)H] (M+H) 396.0906, measured 396.0903.

MALDI-TOF-MS: calc. for [($C_{21}H_{17}NO_5S$)K] (M+K) 434.04, measured 434.06.

2,2'-(2-(*S*-Methylsulfonimidoyl)-1,3-phenylene)dinaphthalene (**5aj**).

The representative general procedure **A** was followed using **1a** (100 mg) and boronic acid **2j** (3.0 equiv). Product **5aj** was isolated in 168 mg and yield is 64%.



Colorless solid; mp 85-88 °C; eluent (30% ethyl acetate in hexanes).

IR (ATR) ṽ (cm^{-1}): 3563, 3527, 3060, 2925, 2358, 2321, 1742, 1699, 1648, 1540, 1516, 1459, 1216, 1043.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.13 (bs, 2 H), 8.01 – 7.91 (m, 6 H), 7.79 (bs, 2 H), 7.61 – 7.55 (m, 5 H), 7.47 (d, *J* = 8.0 Hz, 2 H), 2.48 (s, 3 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 143.6, 141.2, 138.1, 137.8, 132.9, 132.9, 132.5, 129.8, 128.98, 128.9, 128.3, 127.8, 127.6, 126.8, 46.7.

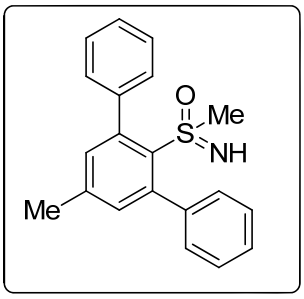
Elemental Analysis: C (80.2%), H (5.8%), N (3.2%), S (6.5%).

HRMS (ESI): calc. for [($C_{27}H_{21}NOS$)H] (M+H) 408.1422, measured 408.1419.

MALDI-TOF-MS: calc. for [($C_{27}H_{21}NOS$)K] (M+K) 446.09, measured 446.06.

5'-Methyl-2'-(*S*-methylsulfonimidoyl)-1,1':3',1''-terphenyl (**5ba**).

The representative general procedure **A** was followed using **1b** (100 mg) and phenyl boronic acid (**2a)** (3.0 equiv). Product **5ba** was isolated in 135 mg and yield is 65%.



Colorless solid; mp 156-159 °C; eluent (40% ethyl acetate in hexanes).

IR (ATR) ṽ (cm^{-1}): 3564, 3523, 3062, 2923, 2364, 1741, 1706, 1646, 1547, 1516, 1462, 1221, 1049.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.61 (bs, 4 H), 7.51 – 7.43 (m, 6 H), 7.16 (s, 2 H), 2.46 (s, 3 H), 2.43 (s, 3 H).

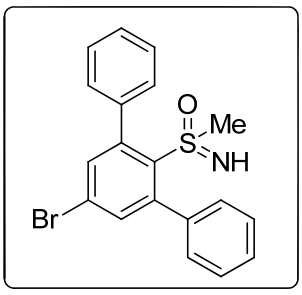
^{13}C NMR ($CDCl_3$, 100 MHz): δ 141.0, 140.7, 140.3, 132.7, 129.7, 128.7, 128.5, 128.3, 46.6, 20.9.

HRMS (ESI): calc. for [($C_{20}H_{19}NOS$)H] (M+H) 322.1266, measured 322.1269.

MALDI-TOF-MS: calc. for [($C_{20}H_{19}NOS$)K] (M+K) 360.08, measured 360.05.

5'-Bromo-2'-(*S*-methylsulfonimidoyl)-1,1':3',1''-terphenyl (**5ca**).

The representative general procedure **A** was followed using **1c** (100 mg) and phenyl boronic acid (**2a)** (3.0 equiv). Product **5ca** was isolated in 104 mg and yield is 63%.



Colorless solid; mp 162-165 °C; eluent (40% ethyl acetate in hexanes).

IR (ATR) ṽ (cm^{-1}): 3564, 3526, 3056, 2928, 2356, 2325, 1741, 1701, 1647, 1542, 1515, 1455, 1218, 1045.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.61 (bs, 4 H), 7.53 – 7.48 (m, 8 H), 2.45 (s, 3 H).

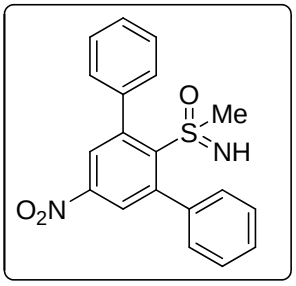
^{13}C NMR ($CDCl_3$, 100 MHz): δ 142.8, 142.6, 139.3, 134.5, 129.7, 129.0, 128.8, 124.0, 46.5.

HRMS (ESI): calc. for [($C_{19}H_{16}BrNOS$)H] (M+H) 386.0214, measured 386.0218.

MALDI-TOF-MS: calc. for [($C_{19}H_{16}BrNOS$)K] (M+K) 423.97, measured 423.95.

2'-(*S*-Methylsulfonimidoyl)-5'-nitro-1,1':3',1''-terphenyl (**5da**).

The representative general procedure **A** was followed using **1d** (100 mg) and phenyl boronic acid (**2a)** (3.0 equiv). Product **5da** was isolated in 95 mg and yield is 54%.



Yellow solid; mp 173-176 °C; eluent (40% ethyl acetate in hexanes).

IR (ATR) ṽ (cm^{-1}): 3565, 3525, 3065, 2924, 2356, 2320, 1744, 1697, 1647, 1543, 1515, 1459, 1217, 1040.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.20 (s, 2 H), 7.66 (bs, 4 H), 7.58 – 7.55 (m, 6 H), 2.48 (s, 3 H).

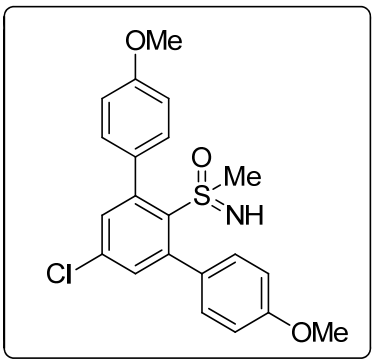
^{13}C NMR ($CDCl_3$, 100 MHz): δ 148.9, 146.9, 142.9, 138.7, 129.7, 129.6, 129.1, 126.2, 46.3.

HRMS (ESI): calc. for [($C_{19}H_{16}N_2O_3S$)H] (M+H) 353.0960, measured 353.0974.

MALDI-TOF-MS: calc. for [($C_{19}H_{16}N_2O_3S$)K] (M+K) 391.05, measured 391.03.

5'-Chloro-4,4''-dimethoxy-2'-(S-methylsulfonimidoyl)-1,1':3',1''-terphenyl (**5ec**).

The representative general procedure **A** was followed using **1e** (100 mg) and boronic acid **2c** (3.0 equiv). Product **5ec** was isolated in 127 mg and yield is 60%.



Colorless solid; 153-156 °C; eluent (50% ethyl acetate in hexanes).

IR (ATR) ṽ (cm^{-1}): 3565, 3523, 3055, 2938, 2364, 1741, 1706, 1646, 1548, 1512, 1462, 1217, 1030.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.54 (bs, 4 H), 7.31 (s, 2 H), 7.03 (d, *J* = 8.0 Hz, 4 H), 3.88 (s, 6 H), 2.48 (s, 3 H).

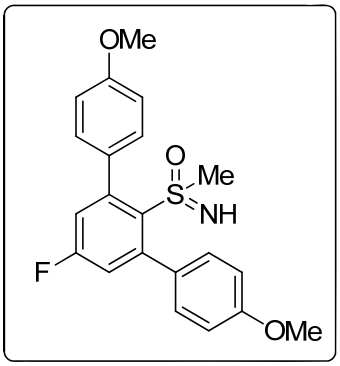
^{13}C NMR ($CDCl_3$, 100 MHz):δ 160.2, 142.5, 142.3, 135.5, 131.6, 131.3, 130.9, 114.3, 55.4, 46.5.

HRMS (ESI): calc. for [($C_{21}H_{20}ClNO_3S$)H] (M+H) 402.0931, measured 402.0930.

MALDI-TOF-MS: calc. for [($C_{21}H_{20}ClNO_3S$)K] (M+K) 440.04, measured 440.01.

5'-Fluoro-4,4''-dimethoxy-2'-(*S*-methylsulfonimidoyl)-1,1':3',1''-terphenyl (**5fc**).

The representative general procedure **A** was followed using **1f** (100 mg) and boronic acid **2c** (3.0 equiv). Product **5fc** was isolated in 140 mg and yield is 63%.



Colorless solid; 133-136 °C; eluent (50% ethyl acetate in hexanes).

IR (ATR) ṽ (cm^{-1}): 3564, 3525, 3062, 2939, 2360, 2321, 1743, 1699, 1648, 1540, 1513, 1460, 1215, 1078.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.55 (bd, *J* = 8.0 Hz, 4 H), 7.04 (d, *J* = 8.0 Hz, 4 H), 7.03 (d, *J* = 8.0 Hz, 2 H), 7.88 (s, 6 H), 2.51 (s, 3 H).

^{13}C NMR ($CDCl_3$, 100 MHz):δ 163.0, 160.5 and 160.3 (C-F coupling), 144.0, 143.9 (C-F coupling), 139.6, 131.7, 130.8, 118.5 and 118.2 (C-F coupling), 114.3, 55.4, 46.6.

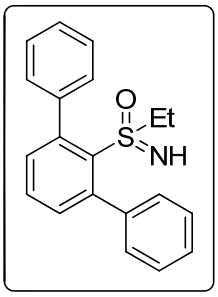
Elemental Analysis: C (66.3%), H (5.5%), N (3.2%), S (7.7%).

HRMS (ESI): calc. for [($C_{21}H_{20}FNO_3S$)H] (M+H) 386.1226, measured 386.1227.

MALDI-TOF-MS: calc. for [($C_{21}H_{20}FNO_3S$)K] (M+K) 424.07, measured 424.02.

2'-(Ethylsulfonimidoyl)-1,1':3',1''-terphenyl (**5ga**).

The representative general procedure **A** was followed using **1g** (100 mg) and phenyl boronic acid (**2a)** (3.0 equiv). Product **5ga** was isolated in 135 mg and yield is 71%.



Colorless solid; 152-155 °C; (40% ethyl acetate in hexanes).

IR (ATR) ṽ (cm^{-1}): 3565, 3523, 3057, 2925, 2362, 2322, 1740, 1693, 1646, 1546, 1516, 1452, 1208, 1052.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.61 (bs, 4 H), 7.55 – 7.43 (m, 7 H), 7.34 (d, *J* = 8.0 Hz, 2 H), 2.55 – 2.48 (m, 1 H), 2.45 – 2.38 (m, 1 H), 0.93 (d, *J* = 8.0 Hz, 3 H).

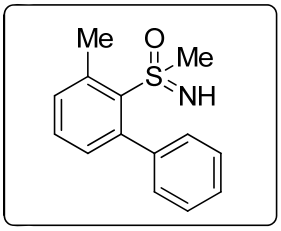
^{13}C NMR ($CDCl_3$, 100 MHz): δ 141.9, 140.6, 132.3, 130.0, 129.7, 129.6, 128.4, 128.3, 50.5, 8.5.

HRMS (ESI): calc. for [($C_{20}H_{19}NOS$)H] (M+H) 322.1266, measured 322.1269.

MALDI-TOF-MS: calc. for [($C_{20}H_{19}NOS$)K] (M+K) 360.08, measured 360.03.

3-Methyl-2-(S-methylsulfonimidoyl)-1,1'-biphenyl (5ha).

The representative general procedure **A** was followed using **1h** (100 mg) and phenyl boronic acid (**2a)** (3.0 equiv). Product **5ha** was isolated in 133 mg and yield is 70%.



Colorless solid; 91-94 °C; (50% ethyl acetate in hexanes).

IR (ATR) ṽ (cm^{-1}): 3565, 3524, 3056, 2932, 2363, 2323, 1741, 1706, 1646, 1546, 1515, 1453, 1217, 1047.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.42 – 7.38 (m, 5 H), 7.35 (d, *J* = 8.0 Hz, 2 H), 7.13 (d, *J* = 8.0 Hz, 1 H), 2.94 (s, 3 H), 2.87 (s, 3 H).

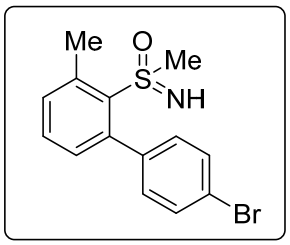
^{13}C NMR ($CDCl_3$, 100 MHz): δ 141.8, 141.1, 138.2, 132.8, 131.0, 130.6, 129.1, 128.6, 128.2, 127.7, 46.7, 22.9.

HRMS (ESI): calc. for [($C_{14}H_{15}NOS$)H] (M+H) 246.0952, measured 246.0950.

MALDI-TOF-MS: calc. for [($C_{14}H_{15}NOS$)K] (M+K) 284.05, measured 284.02.

4'-Chloro-3-methyl-2-(*S*-methylsulfonimidoyl)-1,1'-biphenyl (5he).

The representative general procedure **A** was followed using **1h** (100 mg) and boronic acid **2e** (3.0 equiv). Product **5he** was isolated in 138 mg and yield is 62%.



Colorless solid; 122-125 °C; (50% ethyl acetate in hexanes).

IR (ATR) ṽ (cm^{-1}): 3567, 3523, 3054, 2931, 2363, 2323, 1743, 1709, 1649, 1548, 1517, 1455, 1219, 1046.

^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.54 (t, *J* = 8.0 Hz, 2 H), 7.43 (t, *J* = 8.0 Hz, 1 H), 7.36 (d, *J* = 8.0 Hz, 1 H), 7.24 – 7.19 (m, 2 H), 7.10 (d, *J* = 8.0 Hz, 1 H), 3.03 (s, 3 H), 2.86 (s, 3 H).

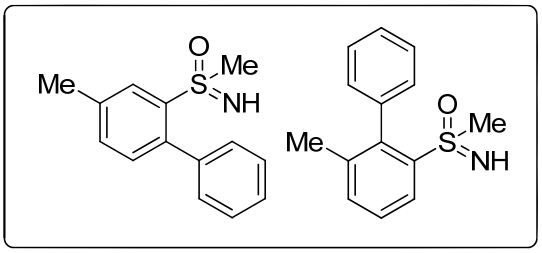
^{13}C NMR (CDCl$_3$, 100 MHz): δ 141.6, 139.1, 138.3, 134.0, 133.6, 131.9, 131.4, 130.2, 128.5, 128.2, 46.4, 22.9.

HRMS (ESI): calc. for [(C$_{14}$H$_{14}$BrNOS)H] (M+H) 324.0058, measured 324.0061.

MALDI-TOF-MS: calc. for [(C$_{14}$H$_{14}$BrNOS)K] (M+K) 361.96, measured 361.92.

4-Methyl-2-(S-methylsulfonimidoyl)-1,1'-biphenyl and 2-Methyl-6-(S -methylsulfonimidoyl)-1,1'-biphenyl (7.3 : 2.7) (**5ia** and **5ia).**

The representative general procedure **A** was followed using **1i** (100 mg) and phenyl boronic acid (**2a)** (3.0 equiv). Product **5ia** and **5ia'** were isolated.in 118 mg and 13 mg yield is 62% and yield is 7%.



Colorless semisolid; (45% ethyl acetate in hexanes).

IR (ATR) ṽ (cm^{-1}): 3563, 3524, 3016, 2922, 2360, 1742, 1699, 1647, 1541, 1517, 1475, 1256, 1018.

^{1}H NMR (CDCl$_3$, 400 MHz): δ 8.07 (d, *J* = 8.0 Hz, 0.76 H), 7.59 (d, *J* = 8.0 Hz, 0.76 H), 7.46 – 7.31 (m, 8 H), 7.46 – 7.31 (m, 1.14 H), 7.20 (d, *J* = 8.0 Hz, 0.38 H), 3.20 (s, 1.21 H), 2.72 (s, 3 H), 2.51 (s, 1.16 H), 2.44 (s, 3 H).

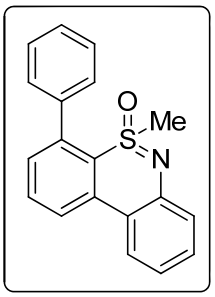
^{13}C NMR (CDCl$_3$, 100 MHz): δ 144.8, 139.9, 139.7, 139.5, 136.7, 136.2, 133.6, 132.6, 132.1, 130.2, 130.2, 129.8, 129.5, 129.2, 129.1, 128.4, 128.0, 127.8, 123.8, 120.6, 43.6, 43.1, 21.4, 21.0.

HRMS (ESI): calc. for [(C$_{14}$H$_{15}$NOS)H] (M+H) 246.0952, measured 246.0951.

MALDI-TOF-MS: calc. for [(C$_{14}$H$_{15}$NOS)K] (M+K) 284.05, measured 284.02.

5-Methyl-4-phenyldibenzo[c,e][1,2]thiazine 5-oxide (6a).

The representative general procedure **B** was followed using **5aa** (100 mg). Product **6a** was isolated in 76 mg and yield is 76%.



Colorless solid; 170-173 °C; eluent (20% ethyl acetate in hexanes).

IR (ATR) ṽ (cm^{-1}): 3058, 2926, 1706, 1647, 1578, 1456, 1313, 1269, 1204, 1010.

^{1}H NMR (CDCl$_3$, 400 MHz): δ 8.24 (d, *J* = 8.0 Hz, 1 H), 8.07 (d, *J* = 8.0 Hz, 1 H), 7.88 (bs, 1 H), 7.76 (d, *J* = 8.0 Hz, 1 H), 7.55 – 7.51 (m, 3 H), 7.45 (d, *J* = 8.0 Hz, 2 H), 7.41 (d, *J* = 8.0 Hz, 1 H), 7.29 (s, 1 H), 7.14 (t, *J* = 8.0 Hz, 1 H), 2.81 (s, 3 H).

^{13}C NMR (CDCl$_3$, 100 MHz): δ 141.9, 139.0, 138.7, 134.3, 131.5, 131.2, 130.6, 129.4, 129.3, 129.0, 128.9, 128.5, 126.6, 124.6, 124.2, 124.1, 121.1, 118.7, 45.3.

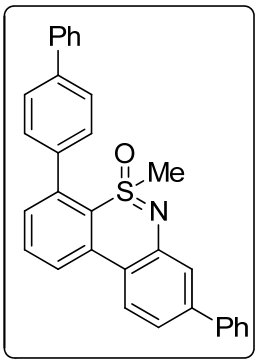
Elemental Analysis: C (72.5%), H (5.1%), N (4.1%), S (9.2%).

HRMS (ESI): calc. for [($C_{19}H_{15}NOS$)H] (M+H) 306.0953, measured 306.0951.

MALDI-TOF-MS: calc. for [($C_{19}H_{15}NOS$)K] (M+K) 344.05, measured 344.00.

4-([1,1'-Biphenyl]-4-yl)-5-methyl-8 phenyldibenzo[c,e][1,2]thiazine 5-oxide (6b).

The representative general procedure **B** was followed using **5ab** (100 mg). Product **6b** was isolated in 84 mg and yield is 85%.



Colorless solid; 172-175 °C; (20% ethyl acetate in hexanes).

IR (ATR) ṽ (cm^{-1}): 3034, 2922, 1707, 1647, 1570, 1452, 1324, 1226, 1195, 1013.

^{1}H NMR (CDCl$_3$, 400 MHz): δ 8.28 (d, *J* = 8.0 Hz, 1 H), 8.14 (d, *J* = 8.0 Hz, 1 H), 7.81 - 7.77 (m, 3 H), 7.73 - 7.70 (m, 5 H), 7.56 (s, 1 H), 7.53 – 7.45 (m, 6 H), 7.42 – 7.36 (m, 3 H), 2.93 (s, 3 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 143.2, 142.3, 141.6, 140.4, 139.9, 138.5, 137.9, 134.2, 131.7, 130.6, 129.8, 128.9, 128.8, 127.9, 127.6, 127.5, 127.4, 127.1, 126.4, 124.7, 124.1, 122.7, 120.1, 117.7, 45.6.

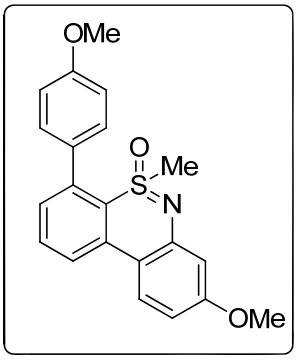
Elemental Analysis: C (80.3%), H (5.0%), N (3.4%), S (6.2%).

HRMS (ESI): calc. for [($C_{31}H_{23}NOS$)H] (M+H) 458.1579, measured 458.1583.

MALDI-TOF-MS: calc. for [($C_{31}H_{23}NOS$)K] (M+K) 496.11, measured 496.06.

8-Methoxy-4-(4-methoxyphenyl)-5-methyldibenzo[c,e][1,2]thiazine 5-oxide (6c).

The representative general procedure **B** was followed using **5ac** (100 mg). Product **6c** was isolated in 64 mg and yield is 65%.



Colorless solid; 273-176 °C; eluent (40% ethyl acetate in hexanes).

IR (ATR) ṽ (cm^{-1}): 3002, 2927, 1741, 1707, 1646, 1578, 1453, 1338, 1251, 1220, 1029.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.10 (d, *J* = 8.0 Hz, 1 H), 7.95 (d, *J* = 8.0 Hz, 1 H), 7.80 (bs, 1 H), 7.69 (t, *J* = 8.0 Hz, 1 H), 7.34 (d, *J* = 8.0 Hz, 2 H), 7.05 (d, *J* = 8.0 Hz, 2 H), 6.77 (s, 1 H), 6.73 (d, *J* = 8.0 Hz 1 H), 3.90 (s, 3 H), 3.87 (s, 3 H), 2.84 (s, 3 H).

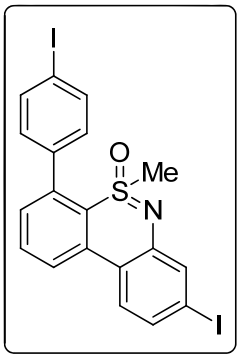
^{13}C NMR ($CDCl_3$, 100 MHz): δ 161.6, 159.9, 143.7, 138.7, 138.6, 134.5, 132.3, 131.6, 131.2, 129.7, 125.5, 125.2, 123.2, 114.8, 112.0, 110.2, 106.7, 55.6, 45.5.

HRMS (ESI): calc. for [($C_{21}H_{19}NO_3S$)H] (M+H) 366.1164, measured 366.1162.

MALDI-TOF-MS: calc. for [($C_{21}H_{19}NO_3S$)K] (M+K) 404.07, measured 404.02.

8-Iodo-4-(4-iodophenyl)-5-methyldibenzo[c,e][1,2]thiazine 5-oxide (6d).

The representative general procedure **B** was followed using **5ad** (100 mg). Product **6d** was isolated in 76 mg and yield is 77%.



Colorless solid; 262-265 °C; eluent (20% ethyl acetate in hexanes).

IR (ATR) ṽ (cm^{-1}): 3057, 2920, 2375, 1741, 1706, 1647, 1579, 1451, 1312, 1264, 1193, 1017.

^{1}H NMR (CDCl$_3$, 400 MHz): δ 8.19 (d, *J* = 8.0 Hz, 1 H), 7.88 (d, *J* = 8.0 Hz, 2 H), 7.78 – 7.74 (m, 2 H), 7.72 (s, 1 H), 7.66 (bs, 1 H), 7.43 (t, *J* = 8.0 Hz, 2 H), 7.20 (s, 1 H), 2.87 (s, 3 H).

^{13}C NMR (CDCl$_3$, 100 MHz): δ 143.0, 138.3, 137.8, 134.0, 133.4, 132.9, 131.9, 131.1, 130.9, 130.1, 130.0, 126.1, 125.5, 125.4, 124.2, 118.0, 96.3, 95.2, 45.7.

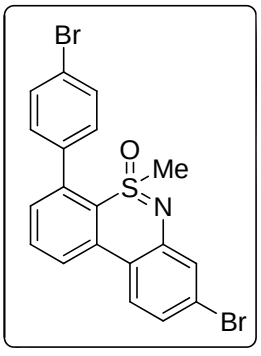
Elemental Analysis: C (42.3%), H (2.1%), N (3.3%), S (6.1%).

HRMS (ESI): calc. for [($C_{19}H_{13}I_2NOS$)H] (M+H) 557.8885, measured 557.8879.

MALDI-TOF-MS: calc. for [($C_{19}H_{13}I_2NOS$)K] (M+K) 595.84, measured 595.80.

8-Bromo-4-(4-bromophenyl)-5-methyldibenzo[c,e][1,2]thiazine 5-oxide (6e).

The representative general procedure **B** was followed using **5ae** (100 mg). Product **6e** was isolated in 84 mg and yield is 85%.



Colorless solid; 239-242 °C; eluent (20% ethyl acetate in hexanes).

IR (ATR) ṽ (cm^{-1}): 3061, 2952, 2375, 1741, 1706, 1646, 1562, 1462, 1316, 1268, 1205, 1017.

^{1}H NMR (CDCl$_3$, 400 MHz): δ 8.18 (d, *J* = 8.0 Hz, 1 H), 7.88 (d, *J* = 8.0 Hz, 1 H), 7.78 – 7.76 (m, *J* = 8.0 Hz, 2 H), 7.68 (d, *J* = 8.0 Hz, 2 H), 7.44 (s, 1 H), 7.42 (d, *J* = 8.0 Hz, 1 H), 7.34 (bs, 1 H), 7.24 (d, *J* = 8.0 Hz, 1 H), 2.87 (s, 3 H).

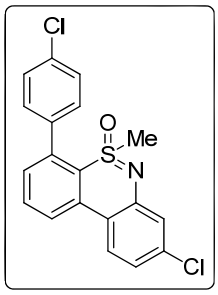
^{13}C NMR (CDCl$_3$, 100 MHz): δ 143.2, 137.7, 137.6, 133.9, 132.9, 132.8, 132.1, 132.3, 131.9, 130.8, 127.2, 126.0, 125.5, 124.34, 124.3, 124.2, 123.5, 117.4, 45.7.

Elemental Analysis: C (48.5%), H (2.8%), N (3.1%), S (7.4%).

HRMS (ESI): calc. for [($C_{19}H_{13}Br_2NOS$)H] (M+H) 461.9163, measured 461.9160.

MALDI-TOF-MS: calc. for [($C_{19}H_{13}Br_2NOS$)K] (M+K) 499.87, measured 499.82.

8-Chloro-4-(4-chlorophenyl)-5-methyldibenzo[c,e][1,2]thiazine 5-oxide (6f).



The representative general procedure **B** was followed using **5af** (100 mg). Product **6f** was isolated in 78 mg and yield is 79%.

Colorless solid; 252-255 °C; eluent (20% ethyl acetate in hexanes).

IR (ATR) ṽ (cm^{-1}): 3062, 2949, 2375, 1742, 1699, 1649, 1541, 1457, 1315, 1272, 1206, 1021.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.17 (d, *J* = 8.0 Hz, 1 H), 7.81 (bs, 1 H), 7.76 (t, *J* = 8.0 Hz, 2 H), 7.52 (d, *J* = 8.0 Hz, 2 H), 7.41 (d, *J* = 8.0 Hz, 2 H), 7.27 (s, 1 H), 7.08 (d, *J* = 8.0 Hz, 1 H), 2.86 (s, 3 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 143.1, 137.7, 137.2, 136.1, 135.3, 133.9, 132.6, 131.9, 130.8, 130.6, 129.3, 128.8, 126.0, 125.3, 124.3, 124.2, 121.5, 117.0, 45.6.

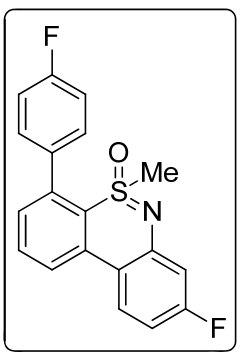
Elemental Analysis: C (59.5%), H (3.5%), N (3.6%), S (8.6%).

HRMS (ESI): calc. for [($C_{19}H_{13}Cl_2NOS$)H] (M+H) 374.0173, measured 374.0168.

MALDI-TOF-MS: calc. for [($C_{19}H_{13}Cl_2NOS$)K] (M+K) 411.97, measured 411.92.

8-Fluoro-4-(4-fluorophenyl)-5-methyldibenzo[c,e][1,2]thiazine 5-oxide (6g).

The representative general procedure **B** was followed using **5ag** (100 mg). Product **6g** was isolated in 80 mg and yield is 81%.



Colorless solid; 115-118 °C; eluent (20% ethyl acetate in hexanes)

IR (ATR) ṽ (cm^{-1}): 3070, 2370, 1743, 1699, 1648, 1513, 1458, 1338, 1223, 1161, 1020.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.15 (d, *J* = 8.0 Hz 1 H), 8.01 (dd, *J* = 8.0, 4.0 Hz 1 H), 7.84 (bs, 1 H), 7.75 (t, *J* = 8.0 Hz 1 H), 7.44 (d, *J* = 8.0 Hz 1 H), 7.40 (d, *J* = 8.0 Hz 1 H), 7.23 (d, *J* = 8.0 Hz 2 H), 6.95 (d, *J* = 8.0 Hz 1 H), 6.85 (d, *J* = 8.0 Hz 1 H), 2.86 (s, 3 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 165.4, 164.3, 162.9, 161.8, 144.0 and 143.9 (C-F coupling), 137.9, 134.8 and 134.1 (C-F coupling), 133.1, 131.8, 131.1, 130.6, 126.0 and 125.9 (C-F coupling), 125.8, 124.0, 115.7, 115.1, 110.5 and 110.3 (C-F coupling), 109.3 and 109.0 (C-F coupling), 45.5.

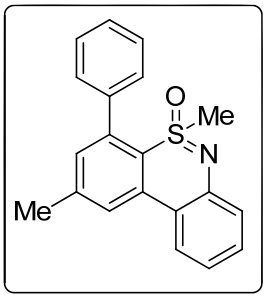
Elemental Analysis: C (67.4%), H (4.5%), N (4.3%), S (10.6%).

HRMS (ESI): calc. for [($C_{19}H_{13}F_2NOS$)H] (M+H) 342.0764, measured 342.0765.

MALDI-TOF-MS: calc. for [($C_{19}H_{13}F_2NOS$)K] (M+K) 380.03, measured 380.00.

2,5-Dimethyl-4-phenyldibenzo[c,e][1,2]thiazine 5-oxide (6h).

The representative general procedure **B** was followed using **5ba** (100 mg) Product **6h** was isolated in 79 mg and yield is 80%.



Colorless solid; 185-188 °C; eluent (20% ethyl acetate in hexanes).

IR (ATR) ṽ (cm^{-1}): 3061, 2926, 2372, 1742, 1700, 1649, 1542, 1460, 1317, 1277, 1161, 1057.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.06 (d, *J* = 8.0 Hz 1 H), 8.03 (s, 1 H), 7.86 (bs, 1 H), 7.54 – 7.49 (m, 3 H), 7.43 – 7.38 (m, 2 H), 7.28 – 7.25 (m, 2 H), 7.12 (t, *J* = 8.0 Hz 1 H), 2.79 (s, 3 H), 2.56 (s, 3 H).

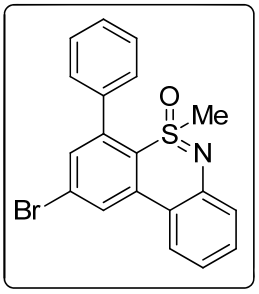
^{13}C NMR ($CDCl_3$, 100 MHz): δ 142.1, 142.0, 139.1, 138.7, 134.4, 131.9, 131.6, 131.2, 130.4, 129.3, 128.7, 128.4, 128.1, 124.5, 124.2, 124.1, 120.9, 118.7, 45.4, 21.8.

HRMS (ESI): calc. for [($C_{20}H_{17}NOS$)H] (M+H) 320.1109, measured 320.1108.

MALDI-TOF-MS: calc. for [($C_{20}H_{17}NOS$)K] (M+K) 358.06, measured 358.02.

2-Bromo-5-methyl-4-phenyldibenzo[c,e][1,2]thiazine 5-oxide (6i).

The representative general procedure **B** was followed using **5ca** (100 mg). Product **6i** was isolated in 83 mg and yield is 84%.



Colorless solid; 166-169 °C; eluent (20% ethyl acetate in hexanes).

IR (ATR) ṽ (cm^{-1}): 3060, 2926, 2373, 1742, 1700, 1648, 1555, 1459, 1316, 1268, 1208, 1008.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.36 (s, 1 H), 8.00 (d, *J* = 8.0 Hz 1 H), 7.85 (bs, 1 H), 7.59 (s, 1 H), 7.54 – 7.53 (m, 3 H), 7.44 (t, *J* = 8.0 Hz, 2 H), 7.27 (d, *J* = 8.0 Hz, 1 H), 7.14 (d, *J* = 8.0 Hz, 1 H), 2.78 (s, 3 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 142.2, 140.2, 137.7, 136.1, 133.1, 131.2, 131.1, 129.3, 129.1, 128.6, 126.9, 126.3, 125.3, 124.7, 124.3, 121.3, 117.7, 45.3.

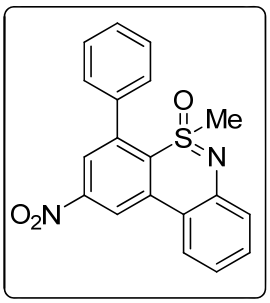
Elemental Analysis: C (58.6%), H (4.3%), N (3.7%), S (8.0%).

HRMS (ESI): calc. for [($C_{19}H_{14}BrNOS$)H] (M+H) 384.0058, measured 384.0060.

MALDI-TOF-MS: calc. for [($C_{19}H_{14}BrNOS$)K] (M+K) 421.96, measured 421.90.

5-Methyl-2-nitro-4-phenyldibenzo[c,e][1,2]thiazine 5-oxide (6j).

The representative general procedure **B** was followed using **5da** (100 mg). Product **6j** was isolated in 78 mg and yield is 79%.



Yellow color solid; 156-159 °C; eluent (20% ethyl acetate in hexanes).

IR (ATR) ṽ (cm^{-1}): 3068, 2925, 2315, 1742, 1700, 1648, 1529, 1459, 1317, 1269, 1211, 1014.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.07 (s, 1 H), 8.25 (s, 1 H), 8.14 (d, *J* = 8.0 Hz 1 H), 7.87 (bs, 1 H), 7.59 (s, 3 H), 7.51 (d, *J* = 8.0 Hz, 2 H), 7.32 (d, *J* = 8.0 Hz, 1 H), 7.23 (d, *J* = 8.0 Hz, 1 H), 2.83 (s, 3 H).

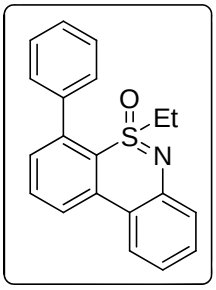
^{13}C NMR ($CDCl_3$, 100 MHz): δ 148.5, 142.1, 140.8, 137.2, 136.2, 131.97, 130.9, 130.0, 129.8, 129.5, 129.1, 128.9, 124.9, 124.5, 124.0, 121.9, 119.2, 118.0, 45.1.

HRMS (ESI): calc. for [($C_{19}H_{14}N_2O_3S$)H] (M+H) 351.0803, measured 351.0804.

MALDI-TOF-MS: calc. for [($C_{19}H_{14}N_2O_3S$)K] (M+K) 389.03, measured 389.01.

5-Ethyl-4-phenyldibenzo[c,e][1,2]thiazine 5-oxide (**6k**).

The representative general procedure **B** was followed using **5ga** (100 mg). Product **6k** was isolated in 82 mg and yield is 83%.



Colorless solid; 183-186 °C; eluent (20% ethyl acetate in hexanes).

IR (ATR) ṽ (cm^{-1}): 3059, 2927, 2312, 1742, 1700, 1648, 1573, 1458, 1319, 1274, 1195, 1015.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.27 (d, *J* = 8.0 Hz, 1 H), 8.07 (d, *J* = 8.0 Hz, 1 H), 7.90 (bs, 1 H), 7.76 (t, *J* = 8.0 Hz, 1 H), 7.53 – 7.50 (m, 1 H), 7.45 – 7.40 (m, 3 H), 7.29 (d, *J* = 8.0 Hz 3 H), 7.12 (t, *J* = 8.0 Hz, 1 H), 7.15 – 7.06 (m, 1 H), 7.49 – 7.40 (m, 1 H), 7.12 (t, *J* = 8.0 Hz, 3 H),

^{13}C NMR ($CDCl_3$, 100 MHz): δ 142.6, 139.2, 138.8, 135.6, 131.7, 131.5, 130.7, 130.5, 128.8, 128.7, 128.2, 124.6, 124.1, 122.3, 120.7, 117.9, 49.7, 9.9.

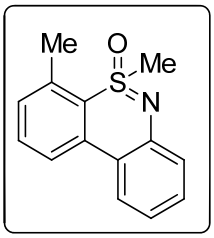
Elemental Analysis: C (73.0%), H (5.2%), N (4.0%), S (9.4%).

HRMS (ESI): calc. for [($C_{20}H_{17}NOS$)H] (M+H) 320.1109, measured 320.1107.

MALDI-TOF-MS: calc. for [($C_{20}H_{17}NOS$)K] (M+K) 358.06, measured 358.01.

4,5-Dimethyldibenzo[c,e][1,2]thiazine 5-oxide (6l).

The representative general procedure **B** was followed using **5ha** (100 mg). Product **6l** was isolated in 40 mg and yield is 41%.



Colorless solid; 174-177 °C; eluent (35% ethyl acetate in hexanes).

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 3064, 2927, 2366, 1742, 1699, 1648, 1541, 1460, 1321, 1261, 1202, 1015.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.08 (d, *J* = 8.0 Hz, 1 H), 7.96 (dd, *J* = 8.0, 4.0 Hz, 1 H), 7.63 (t, *J* = 8.0 Hz, 1 H), 7.37 (d, *J* = 8.0 Hz, 1 H), 7.37 (t, *J* = 8.0 Hz, 1 H), 7.23 (d, *J* = 8.0 Hz, 1 H), 7.06 (t, *J* = 8.0 Hz, 1 H), 3.51 (s, 3 H), 2.85 (s, 3 H).

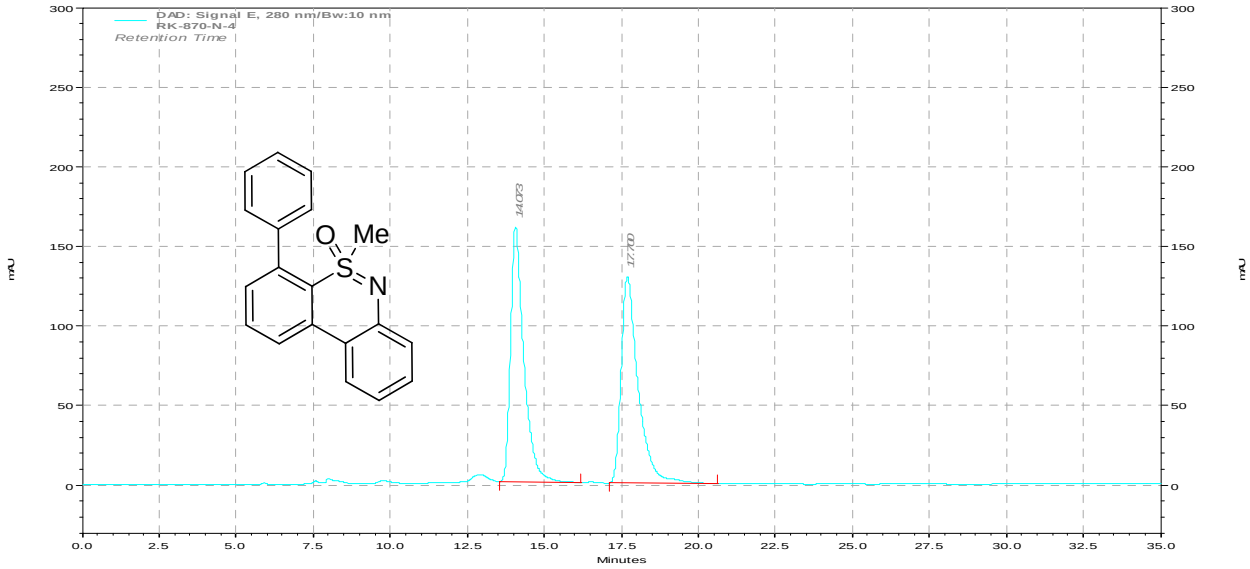
^{13}C NMR ($CDCl_3$, 100 MHz): δ 142.2, 135.5, 135.2, 132.6, 131.2, 130.5, 124.6, 124.2, 123.9, 121.9, 120.6, 117.5, 47.8, 21.0.

HRMS (ESI): calc. for [($C_{14}H_{13}NOS$)H] (M+H) 244.0796, measured 244.0799.

MALDI-TOF-MS: calc. for [($C_{14}H_{13}NOS$)K] (M+K) 282.03, measured 282.01.

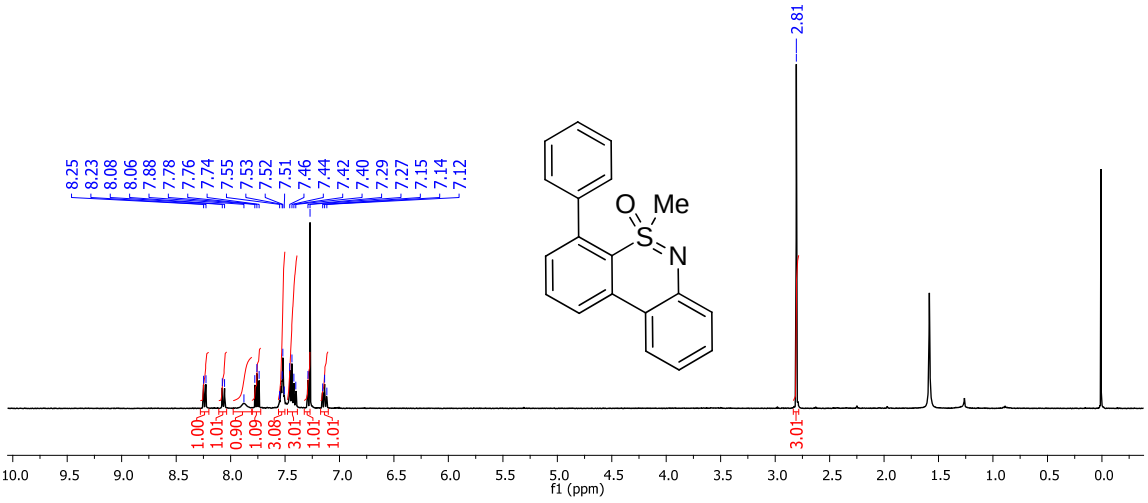
5-Methyl-4-phenyldibenzo[c,e][1,2]thiazine 5-oxide (6a).

HPLC analysis of **6a**: Chiralpak IA 7:3 *n*-Hexane : Ethyl acetate, 0.5 mL/min; t_R = 14.07 min (*S*), t_R = 17.70 min (*R*).



DAD: Signal E, 280 nm/Bw:10 nm Results

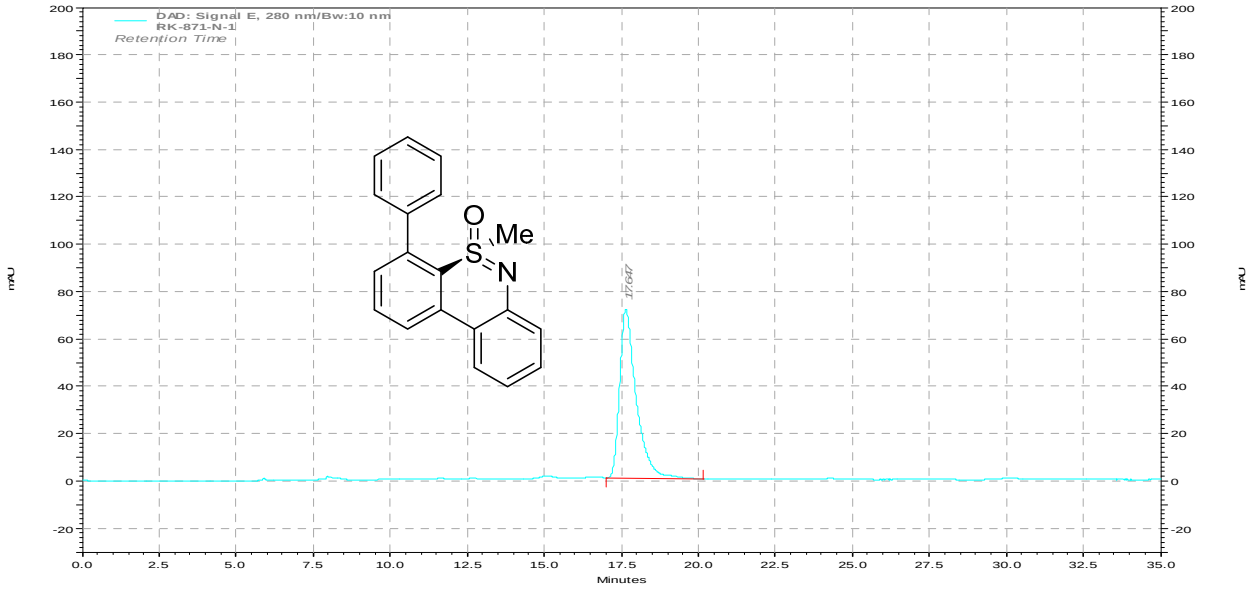
Retention Time	Area	Area %	Height	Height %
14.073	10116408	49.22	335880	55.26
17.700	10436761	50.78	271969	44.74
Totals	20553169	100.00	607849	100.00



(*R*)-(-)-5-Methyl-4-phenyldibenzo[c,e][1,2]thiazine 5-oxide (8a).

100 mg of **7aa** was taken and 74.4 mg of product **8a** was isolated (yield 74%).

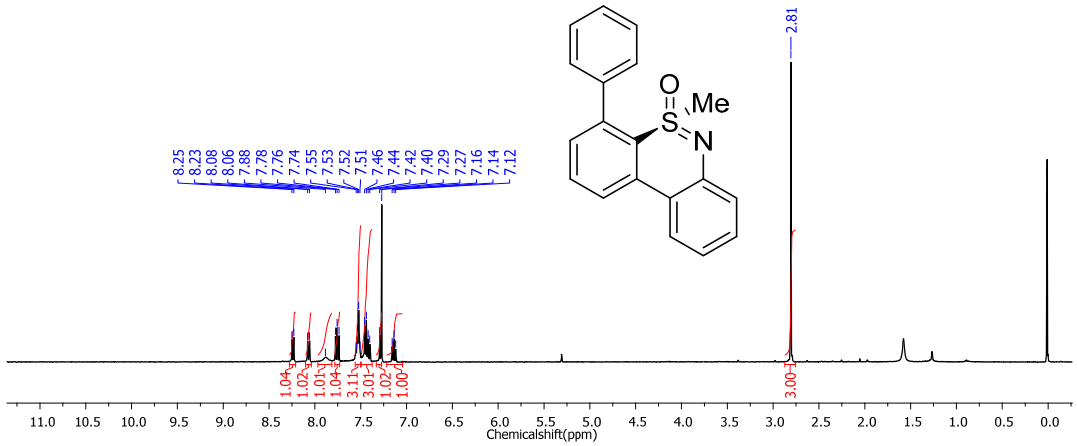
HPLC analysis of **8a**: Chiralpak IA 7:3 *n*-Hexane : Ethyl acetate, 0.5 mL/min; t_R = 17.64 min (*R*).



DAD: Signal E, 280 nm/Bw:10 nm Results

Retention Time	Area	Area %	Height	Height %
17.647	5610162	100.00	149265	100.00

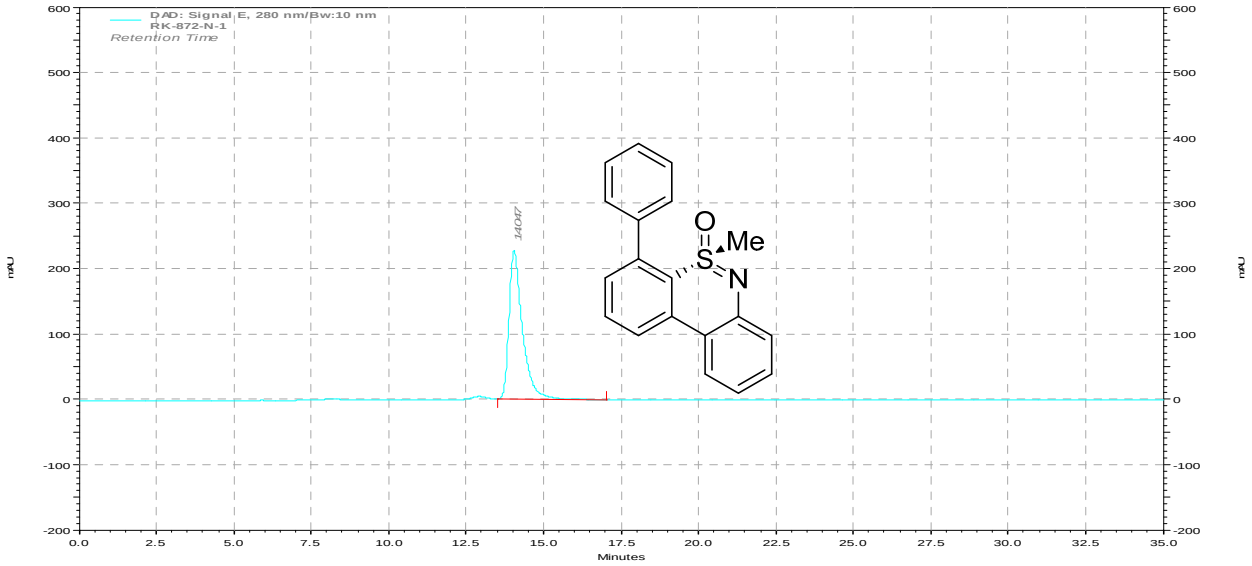
Totals				
	5610162	100.00	149265	100.00



(*S*)-(+)-5-Methyl-4-phenyldibenzo[c,e][1,2]thiazine 5-oxide (8e).

100 mg of **7ba** was taken and 72.4 mg of product **8e** was isolated (yield 72%).

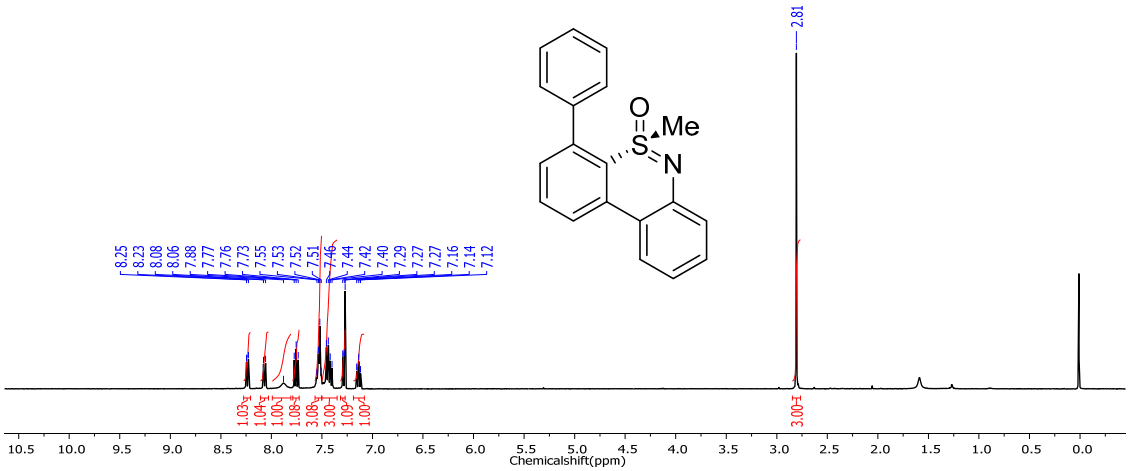
HPLC analysis of **8e**: Chiralpak IA 7:3 *n*-Hexane : Ethyl acetate, 0.5 mL/min; t_R = 14.04 min (*S*)**.**



DAD: Signal E, 280 nm/Bw:10 nm Results

Retention Time	Area	Area %	Height	Height %
14.047	14447782	100.00	477825	100.00

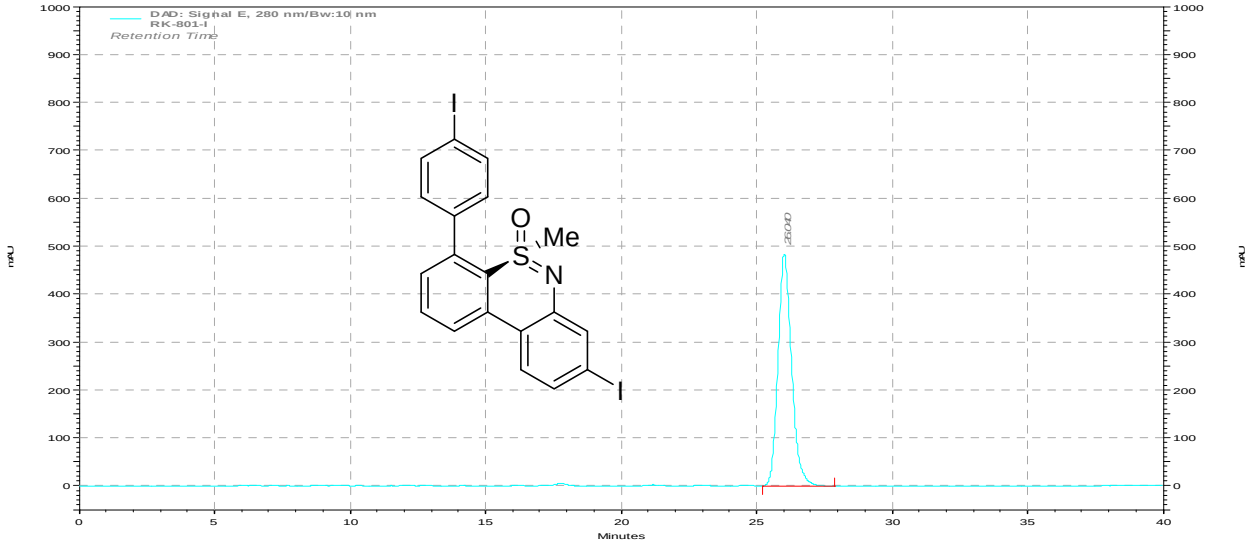
Totals				
	14447782	100.00	477825	100.00



(*R*)-(-)-8-Iodo-4-(4-iodophenyl)-5-methyldibenzo[c,e][1,2]thiazine 5-oxide (8b).

100 mg of **7ad** was taken and 72.7 mg of product **8b** was isolated (yield 73%).

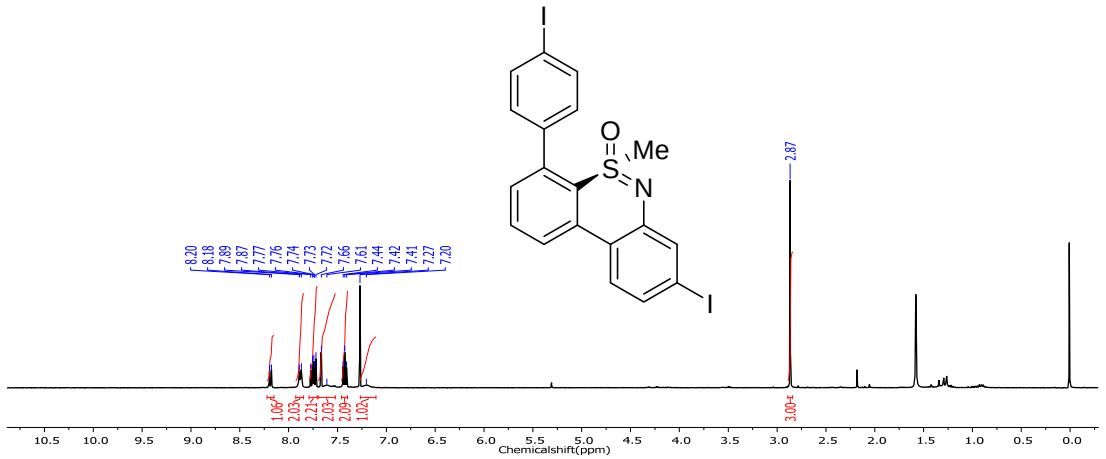
HPLC analysis of **8b**: Chiralpak IA 7:3 *n*-Hexane : Ethyl acetate, 0.5 mL/min; t_R = 26.04 min (*R*).



DAD: Signal E, 280 nm/Bw:10 nm Results

Retention Time	Area	Area %	Height	Height %
26.040	35556658	100.00	1015144	100.00

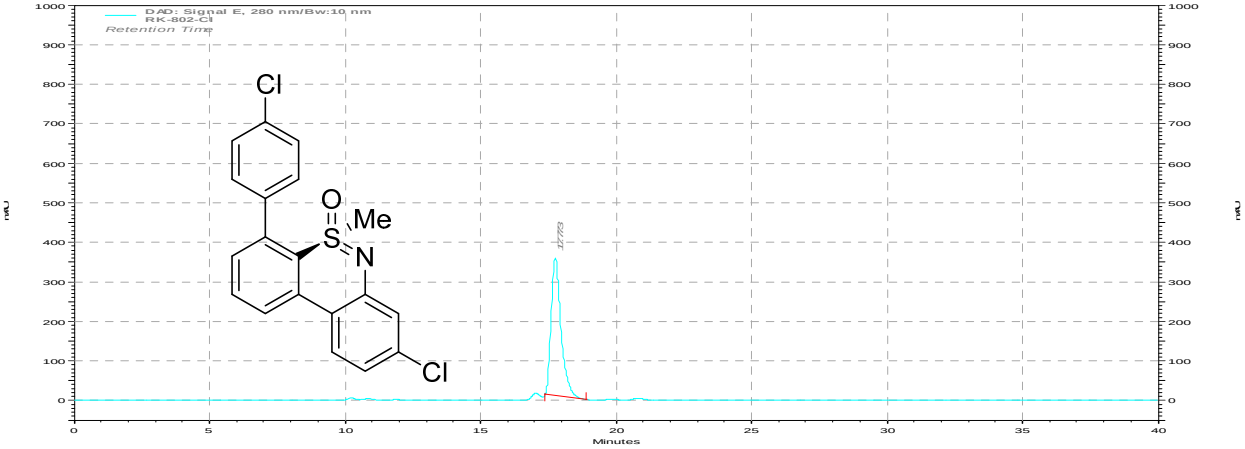
Totals				
	35556658	100.00	1015144	100.00



(*R*)-(-)-8-Chloro-4-(4-chlorophenyl)-5-methyldibenzo[c,e][1,2]thiazine 5-oxide (8c).

100 mg of **7af** was taken and 74.5 mg of product **8c** was isolated (yield 75%).

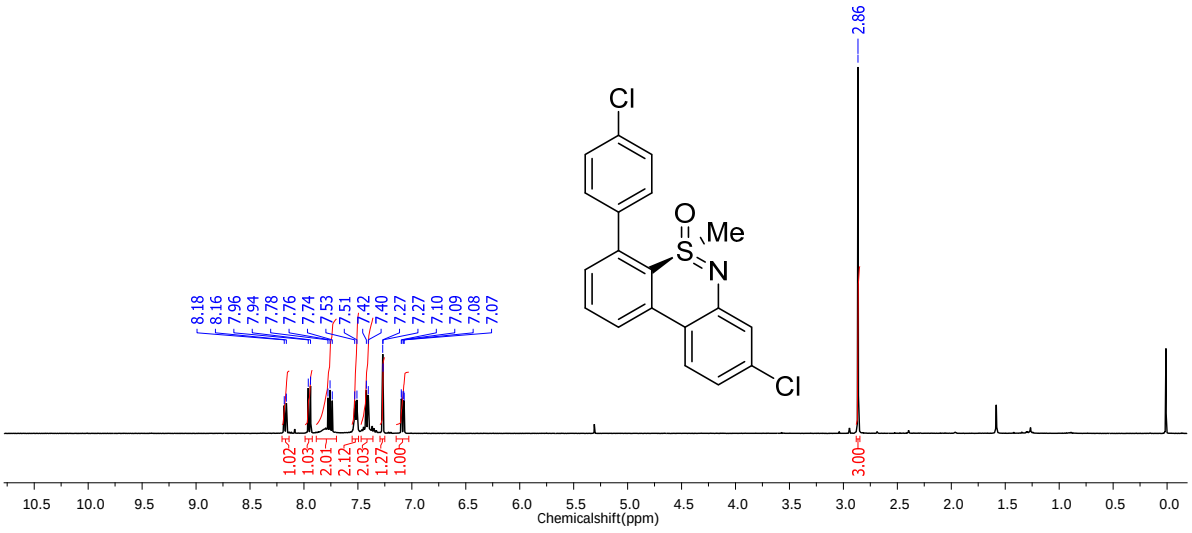
HPLC analysis of **8c**: Chiralpak IA 7:3 *n*-Hexane : Ethyl acetate, 0.5 mL/min; t_R = 17.77 min (*R*).



DAD: Signal E, 280 nm/Bw:10 nm Results

Retention Time	Area	Area %	Height	Height %
17.773	18630870	100.00	730877	100.00

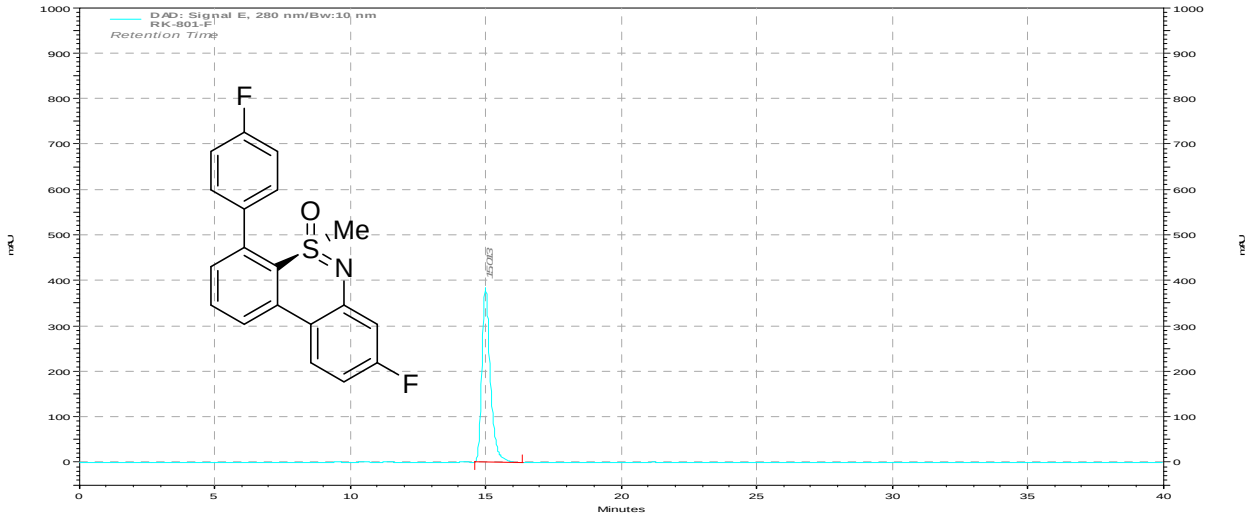
Totals				
	18630870	100.00	730877	100.00



(*R*)-(-)-8-Fluoro-4-(4-fluorophenyl)-5-methyldibenzo[c,e][1,2]thiazine 5-oxide (8d).

100 mg of **7ag** was taken and 78.5 mg of product **8d** was isolated (yield 79%).

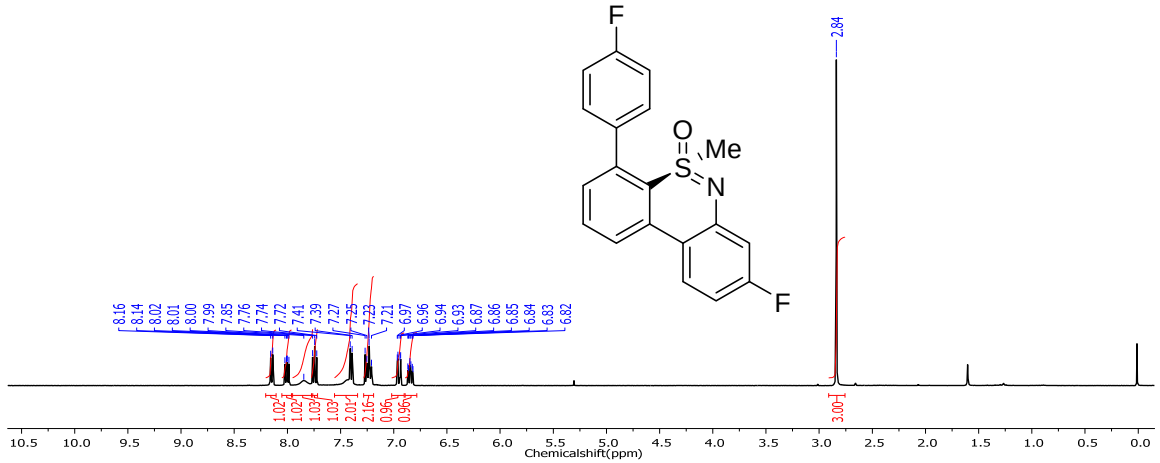
HPLC analysis of **8d**: Chiralpak IA 7:3 *n*-Hexane : Ethyl acetate, 0.5 mL/min; t_R = 15.01 min (*R*).



DAD: Signal E, 280 nm/Bw:10 nm Results

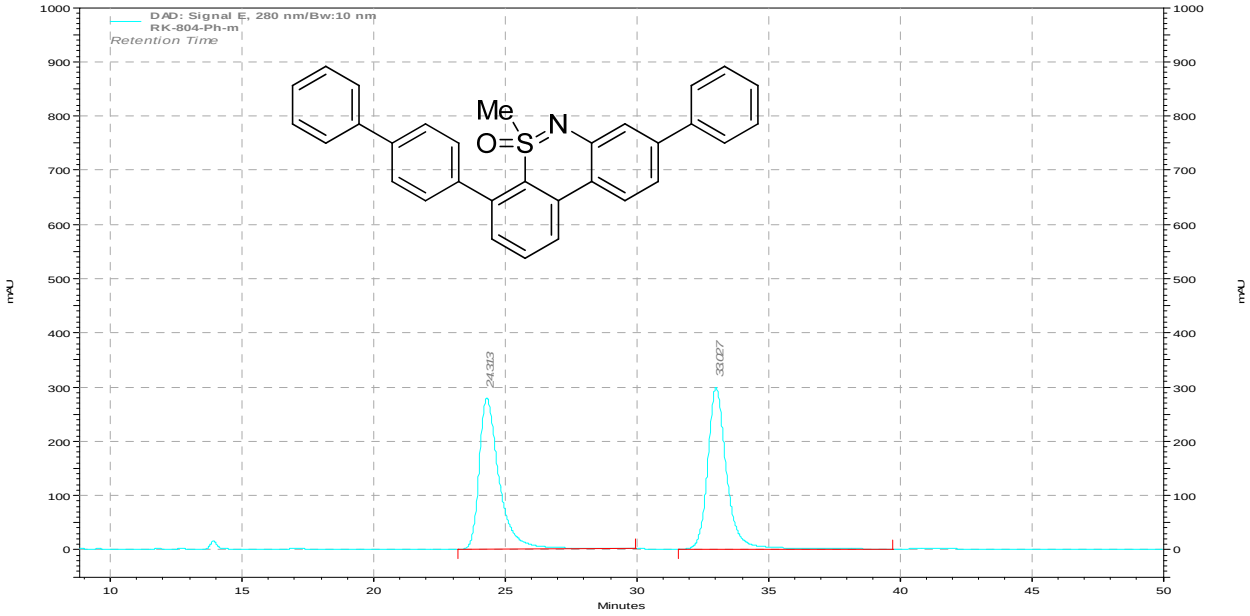
Retention Time	Area	Area %	Height	Height %
15.013	17692346	100.00	804860	100.00

Totals				
	17692346	100.00	804860	100.00



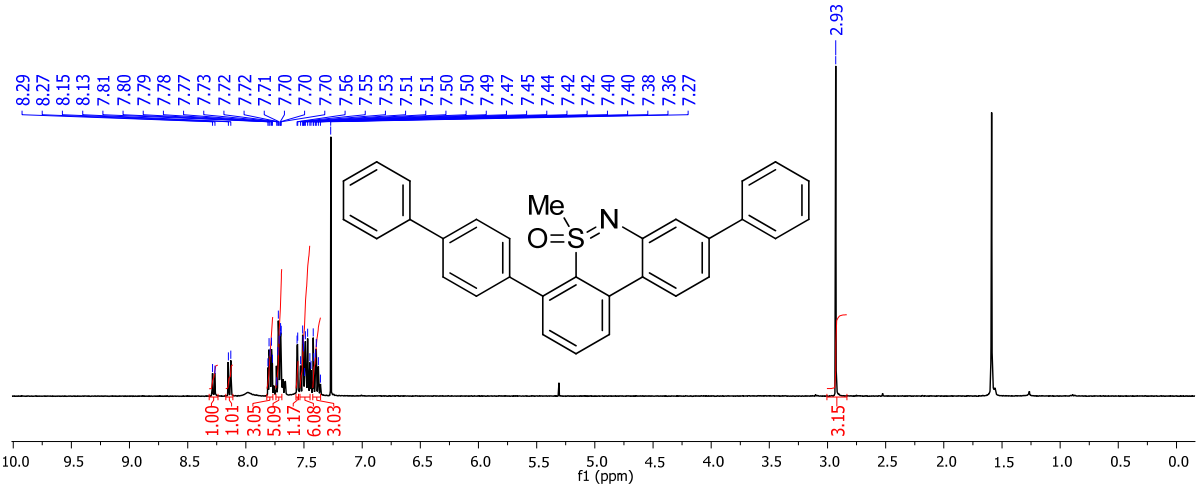
4-([1,1'-Biphenyl]-4-yl)-5-methyl-8 phenyldibenzo[c,e][1,2]thiazine 5-oxide (6b).

HPLC analysis of **6b**: Chiralpak IA 7:3 *n*-Hexane : Ethyl acetate, 0.5 mL/min; t_R = 24.31 min (*S*), t_R = 33.02 min (*R*).



DAD: Signal E, 280 nm/Bw:10 nm Results

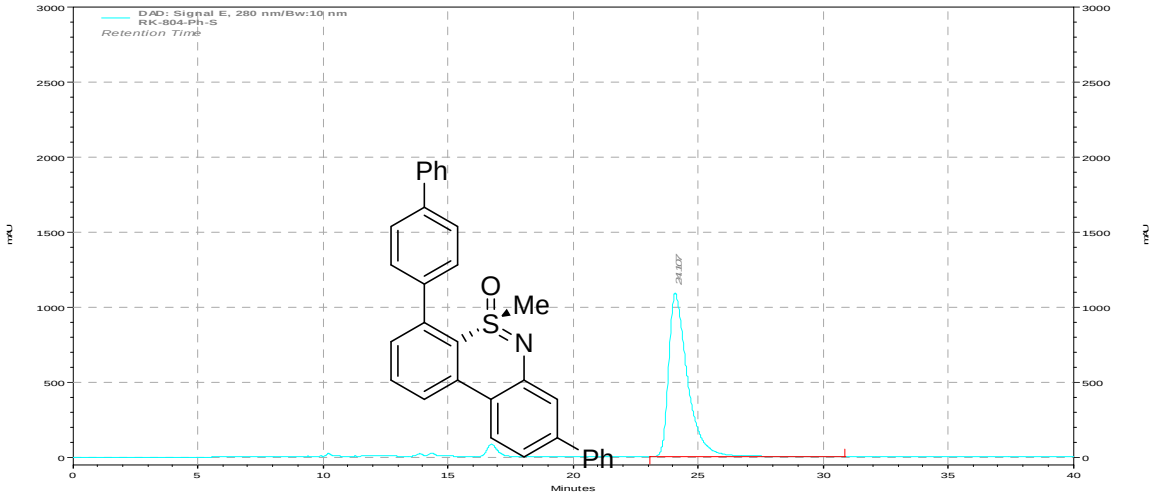
Retention Time	Area	Area %	Height	Height %
24.313	31140080	49.79	584240	48.29
33.027	31402759	50.21	625676	51.71
Totals	62542839	100.00	1209916	100.00



(*S*)-(+)-4-([1,1'-Biphenyl]-4-yl)-5-methyl-8-phenyldibenzo[c,e][1,2]thiazine 5-oxide (8f).

100 mg of **7bb** was taken and 81.6 mg of product **8f** was isolated (yield 82%).

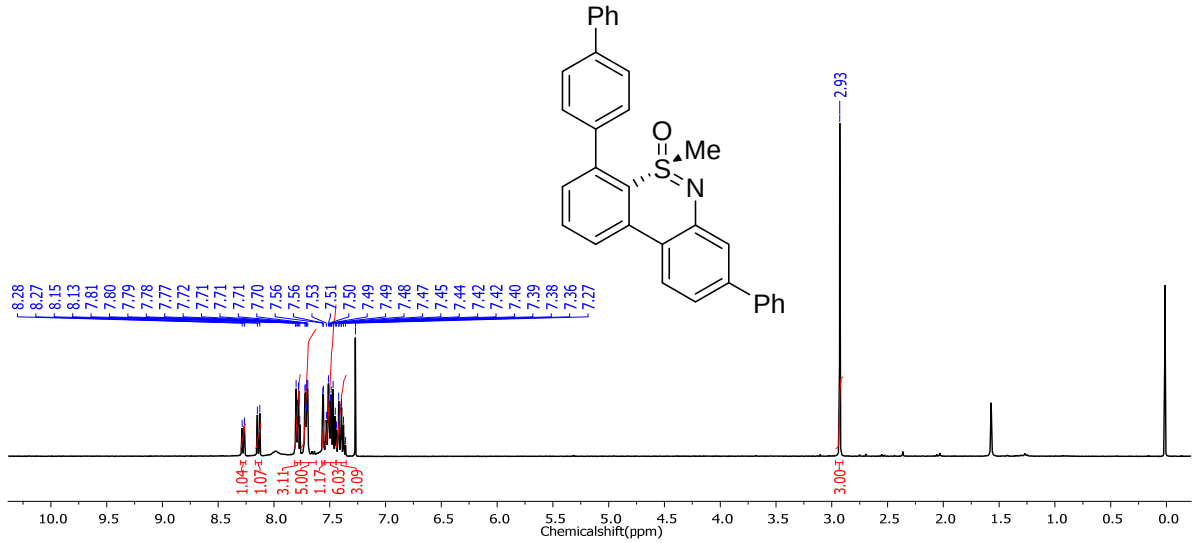
HPLC analysis of **8f**: Chiralpak IA 7:3 *n*-Hexane : Ethyl acetate, 0.5 mL/min; t_R = 24.31 min (*S*).



DAD: Signal E, 280 nm/Bw:10 nm Results

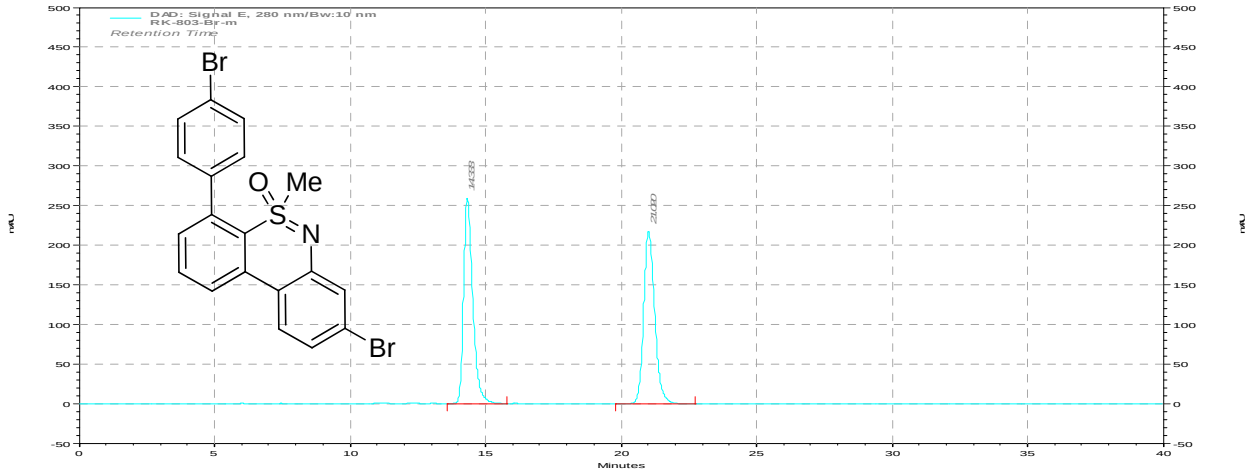
Retention Time	Area	Area %	Height	Height %
24.107	120311701	100.00	2286249	100.00

Totals	120311701	100.00	2286249	100.00



8-Bromo-4-(4-bromophenyl)-5-methyldibenzo[c,e][1,2]thiazine 5-oxide (6e).

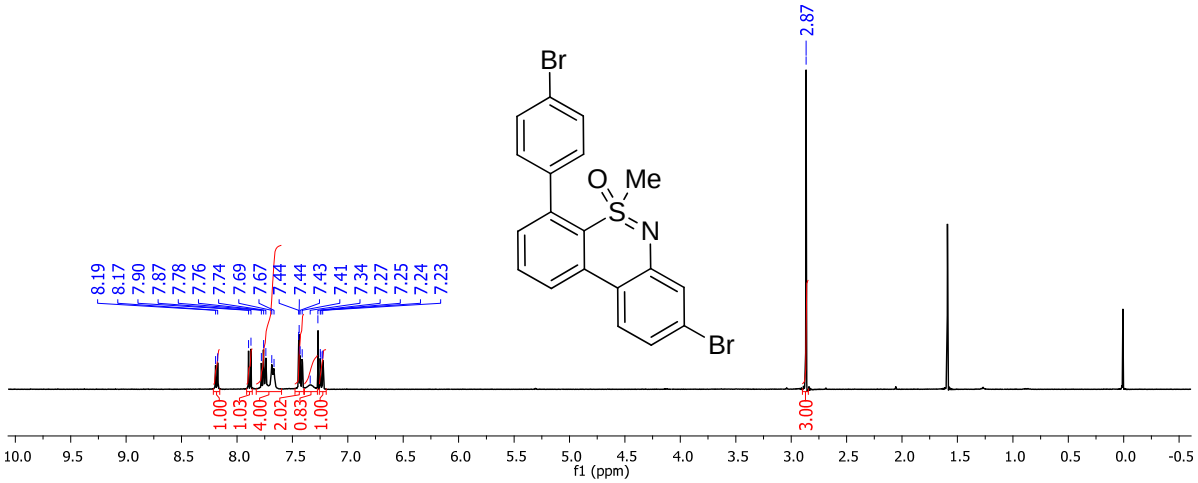
HPLC analysis of **6e**: Chiralpak IA 7:3 *n*-Hexane : Ethyl acetate, 0.5 mL/min; t_R = 14.33 min (*S*), t_R = 21.02 min (*R*).



DAD: Signal E, 280 nm/Bw:10 nm Results

Retention Time	Area	Area %	Height	Height %
14.333	12784527	49.62	542993	54.34
21.020	12981589	50.38	456238	45.66

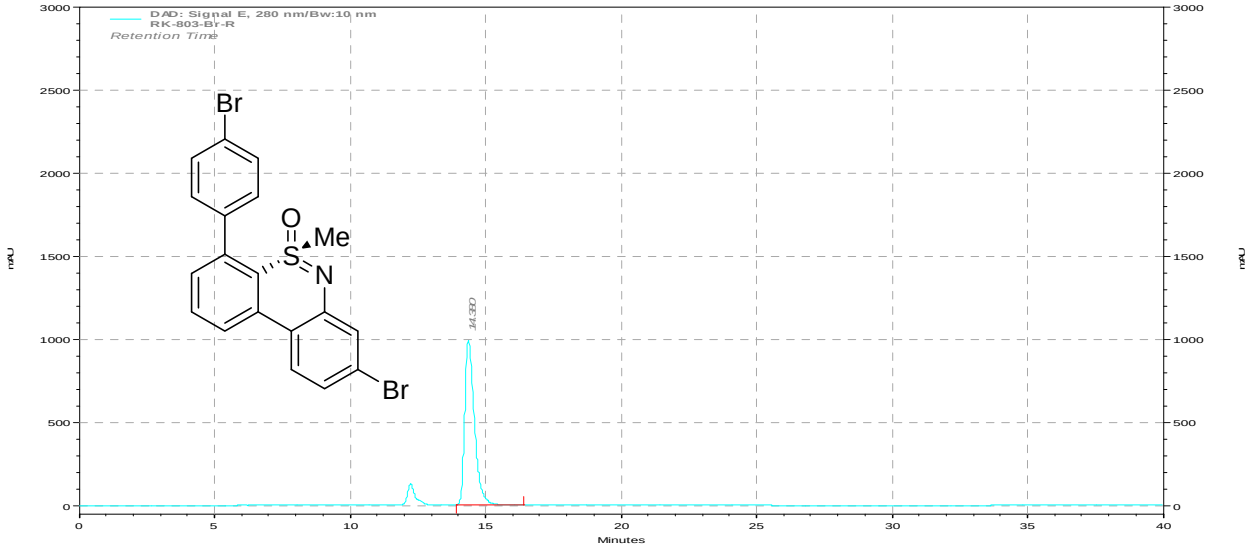
Totals	25766116	100.00	999231	100.00



(*S*)-(+)-8-Bromo-4-(4-bromophenyl)-5-methyldibenzo[c,e][1,2]thiazine 5-oxide (8g).

100 mg of **7be** was taken and 82.0 mg of product **8g** was isolated (yield 83%).

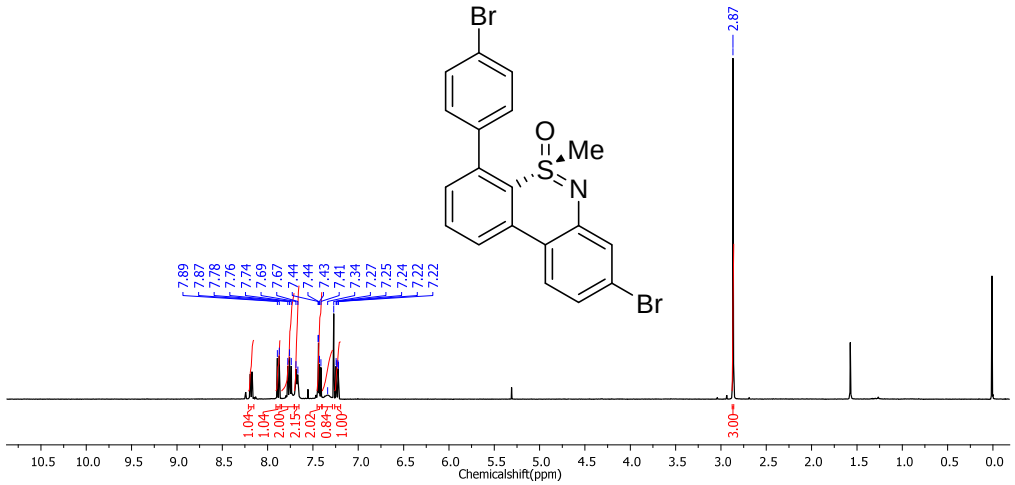
HPLC analysis of **8g**: Chiralpak IA 7:3 *n*-Hexane : Ethyl acetate, 0.5 mL/min; t_R = 14.38 min (*S*).



DAD: Signal E, 280 nm/Bw:10 nm Results

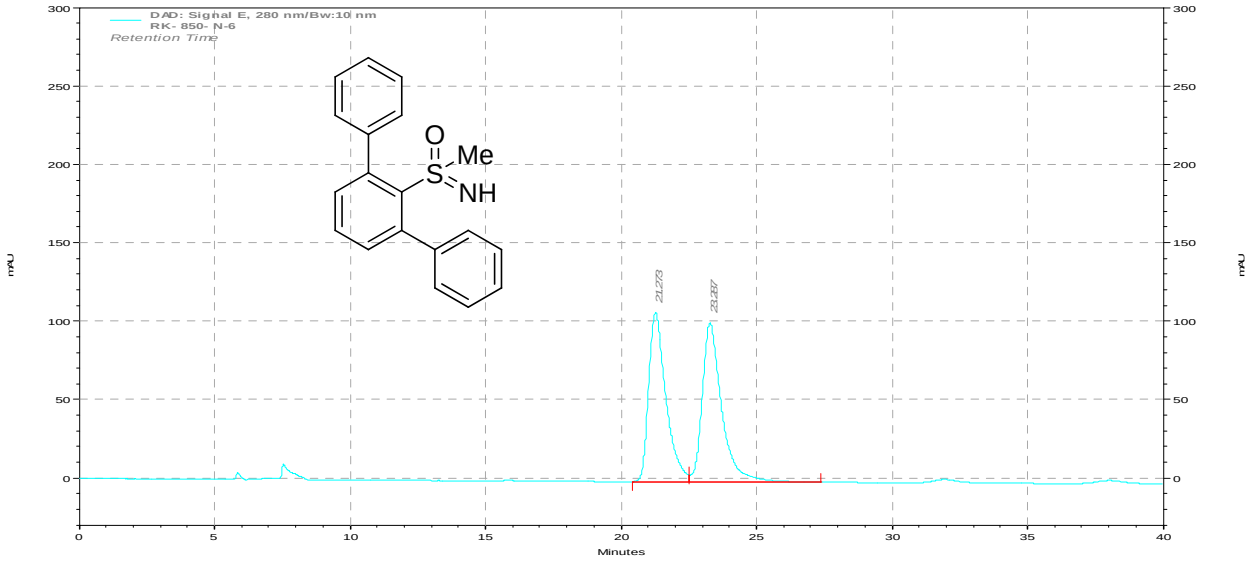
Retention Time	Area	Area %	Height	Height %
14.380	51349286	100.00	2076540	100.00

Totals	51349286	100.00	2076540	100.00



2'-(*S*-Methylsulfonimidoyl)-1,1':3',1''-terphenyl (5a).

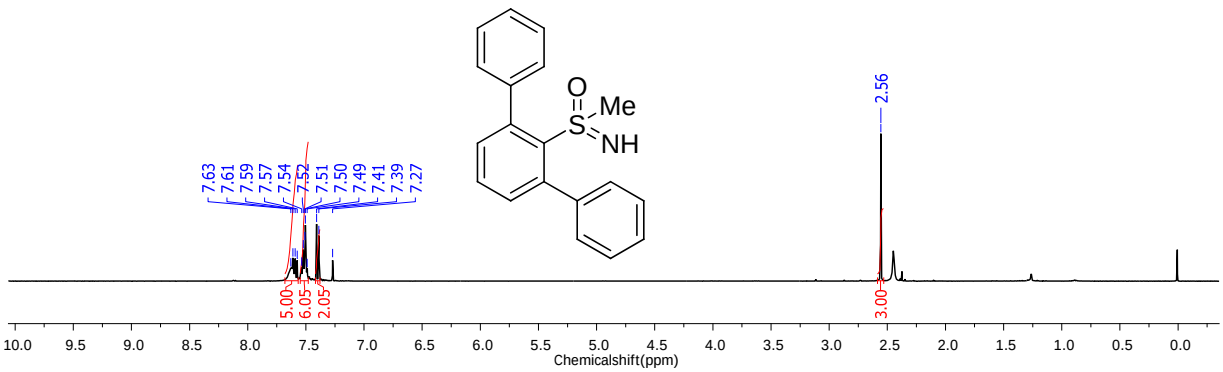
HPLC analysis of 5a: Chiralpak IA 6:4 *n*-Hexane : Ethyl acetate, 0.5 mL/min; t_R = 21.27 min (*S*), t_R = 23.28 min (*R*).



DAD: Signal E, 280 nm/Bw:10 nm Results

Retention Time	Area	Area %	Height	Height %
21.273	10002524	48.58	226528	51.63
23.287	10588614	51.42	212195	48.37

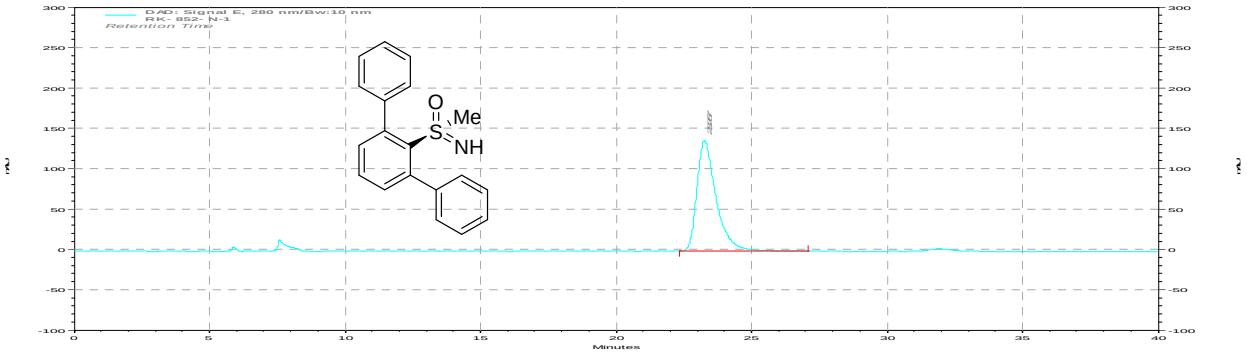
Totals	20591138	100.00	438723	100.00



(*R*)-(-)-[1,1':3',1''-Terphenyl]-2'-yl(imino)(methyl)sulfanone (7aa).

100 mg of **7a** was taken and 128.7 mg of product **7aa** was isolated (yield 65%). 3.0 equiv of boronic acid (**2a**) was taken.

HPLC analysis of **7aa**: Chiralpak IA 6:4 *n*-Hexane : Ethyl acetate, 0.5 mL/min; t_R = 23.26 min (*R*).



DAD: Signal E, 280 nm/Bw:10 nm Results

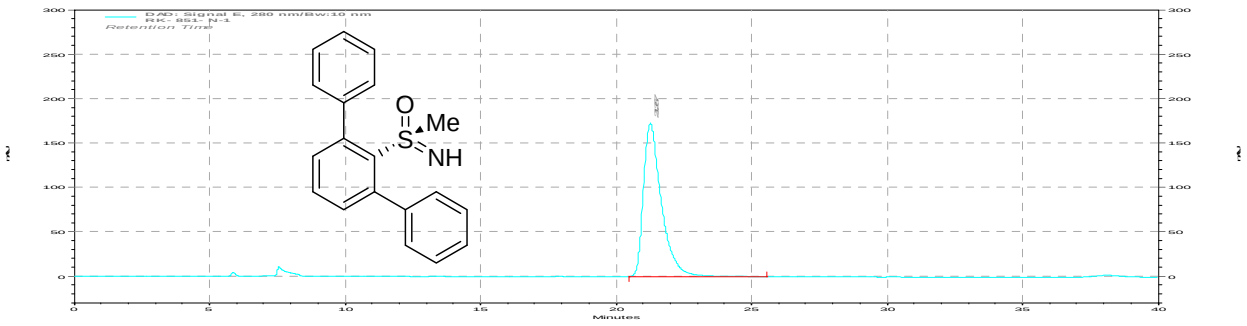
Retention Time	Area	Area %	Height	Height %
23.267	14140439	100.00	287085	100.00

Totals	14140439	100.00	287085	100.00

(*S*)-(+)-[1,1':3',1''-Terphenyl]-2'-yl(imino)(methyl)sulfanone (7ba).

100 mg of **7b** was taken and 133.0 mg of product **7ba** was isolated (yield 67%). 3.0 equiv of boronic acid (**2a**) was taken.

HPLC analysis of **7ba**: Chiralpak IA 6:4 *n*-Hexane : Ethyl acetate, 0.5 mL/min; t_R = 21.26 min (*S*).



DAD: Signal E, 280 nm/Bw:10

nm Results

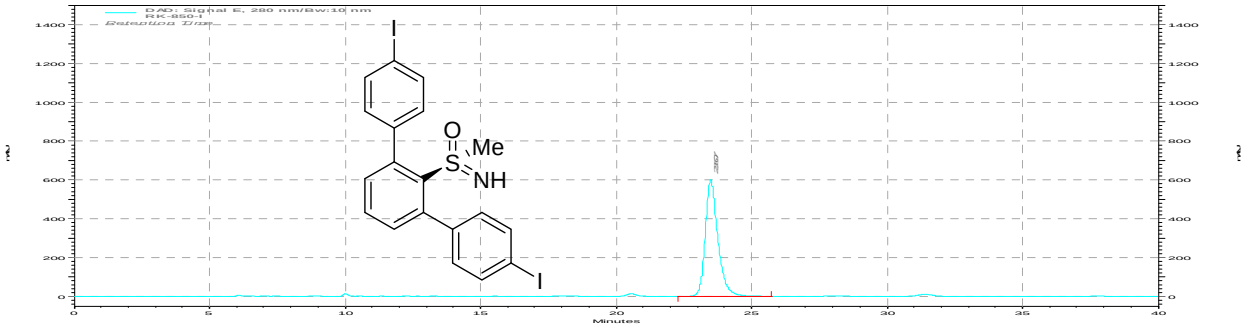
Retention Time	Area	Area %	Height	Height %
21.267	16713945	100.00	362213	100.00

Totals	16713945	100.00	362213	100.00

(*R*)-(-)-(4,4''-Diiodo-[1,1':3',1''-terphenyl]-2'-yl)(imino)(methyl)sulfanone (7ad).

100 mg of **7a** was taken and 227 mg of product **7ad** was isolated (yield 63%). 3.0 equiv of boronic acid (**2d**) was taken.

HPLC analysis of **7ad**: Chiralpak IA 6:4 *n*-Hexane : Ethyl acetate, 0.5 mL/min; t_R = 23.50 min (*R*).



DAD: Signal E, 280 nm/Bw:10 nm Results

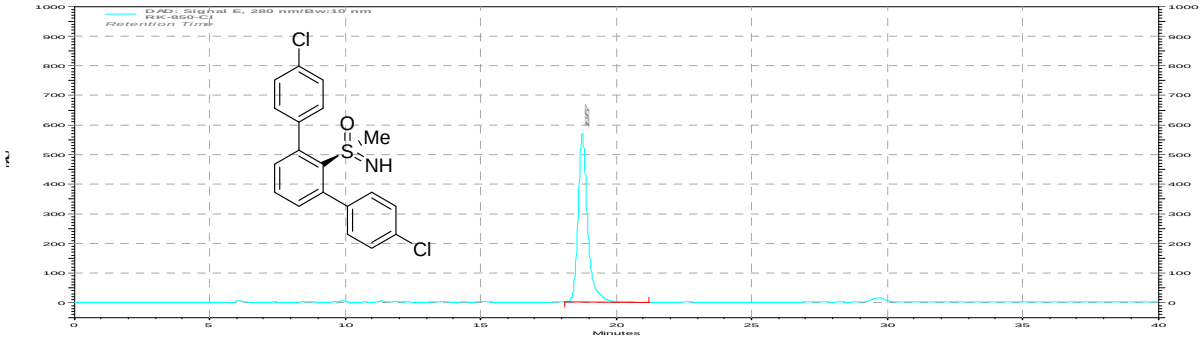
Retention Time	Area	Area %	Height	Height %
23.507	40833180	100.00	1262191	100.00

Totals	40833180	100.00	1262191	100.00

(*R*)-(-)-(4,4''-Dichloro-[1,1':3',1''-terphenyl]-2'-yl)(imino)(methyl)sulfanone (7af).

100 mg of **7a** was taken and 144.6 mg of product **7af** was isolated (yield 60%). 3.0 equiv of boronic acid (**2f**) was taken.

HPLC analysis of **7af**: Chiralpak IA 6:4 *n*-Hexane : Ethyl acetate, 0.5 mL/min; t_R = 18.76 min (*R*).



DAD: Signal E, 280 nm/Bw:10 nm Results

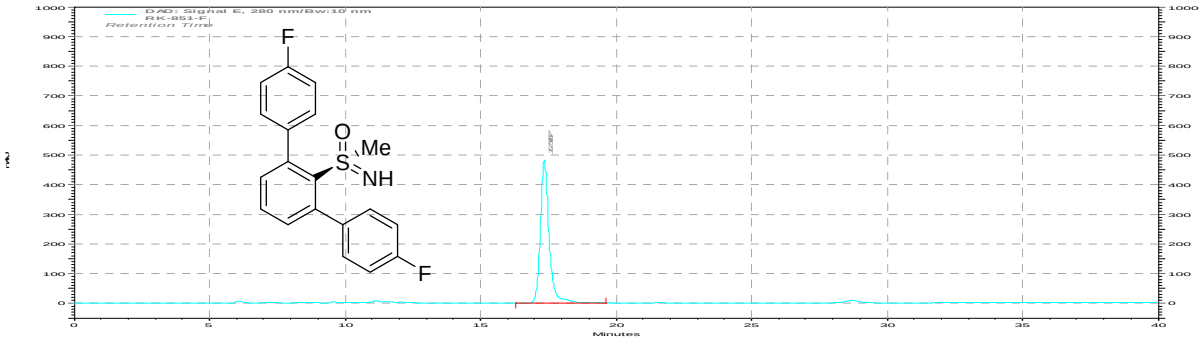
Retention Time	Area	Area %	Height	Height %
18.767	29470445	100.00	1190787	100.00

Totals	29470445	100.00	1190787	100.00

(*R*)-(-)-(4,4''-Difluoro-[1,1':3',1''-terphenyl]-2'-yl)(imino)(methyl)sulfanone (7ag).

100 mg of **7a** was taken and 137 mg of product **7ag** was isolated (yield 62%). 3.0 equiv of boronic acid (**2g**) was taken.

HPLC analysis of **7ag**: Chiralpak IA 6:4 *n*-Hexane : Ethyl acetate, 0.5 mL/min; t_R = 17.36 min (*R*).



DAD: Signal E, 280 nm/Bw:10 nm Results

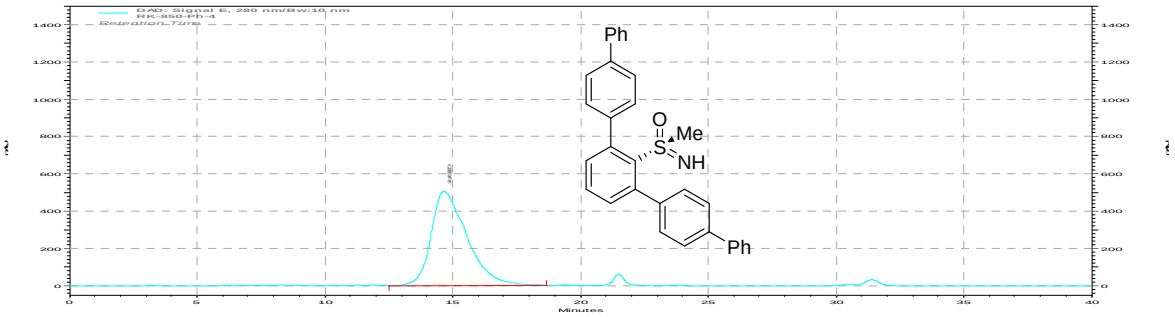
Retention Time	Area	Area %	Height	Height %
17.367	22660941	100.00	1009735	100.00

Totals	22660941	100.00	1009735	100.00

(*S*)-(+)-[1,1':4',1'':3'',1''':4''',1''''-Quinquephenyl]-2''-yl(imino)(methyl)sulfanone (7bb).

100 mg of **7b** was taken and 192.4 mg of product **7bb** was isolated (yield 65%). 3.0 equiv of boronic acid (**2b**) was taken.

HPLC analysis of **7bb**: Chiralpak IA 6:4 *n*-Hexane : Ethyl acetate, 0.5 mL/min; t_R = 21.26 min (*S*).



DAD: Signal E, 280 nm/Bw:10 nm Results

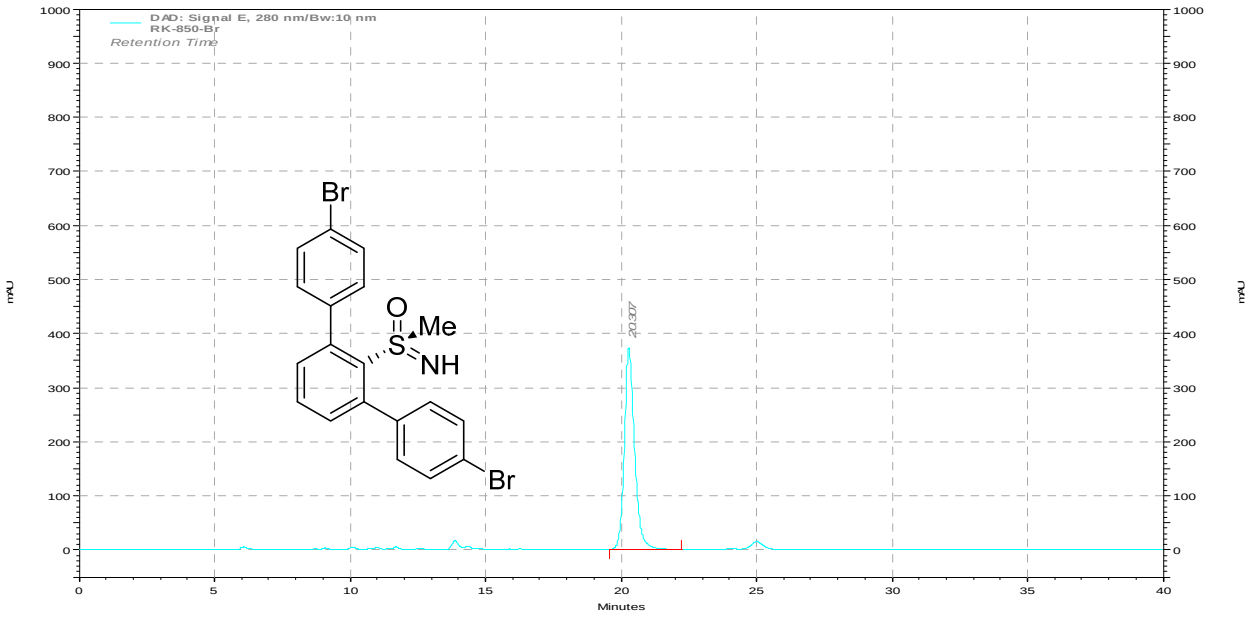
Retention Time	Area	Area %	Height	Height %
14.680	102546930	100.00	1055789	100.00

Totals	102546930	100.00	1055789	100.00

(*S*)-(+)-(4,4''-Dibromo-[1,1':3',1''-terphenyl]-2'-yl)(imino)(methyl)sulfanone (7bc).

100 mg of **7b** was taken and 181.7 mg of product **7be** was isolated (yield 61%). 3.0 equiv of boronic acid (**2c**) was taken.

HPLC analysis of **7bc**: Chiralpak IA 6:4 *n*-Hexane : Ethyl acetate, 0.5 mL/min; t_R = 23.30 min (*S*).

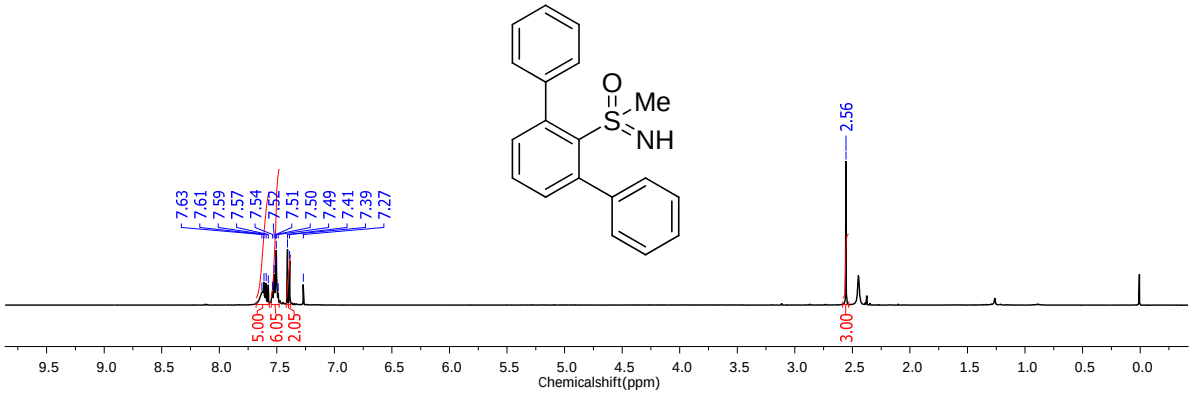


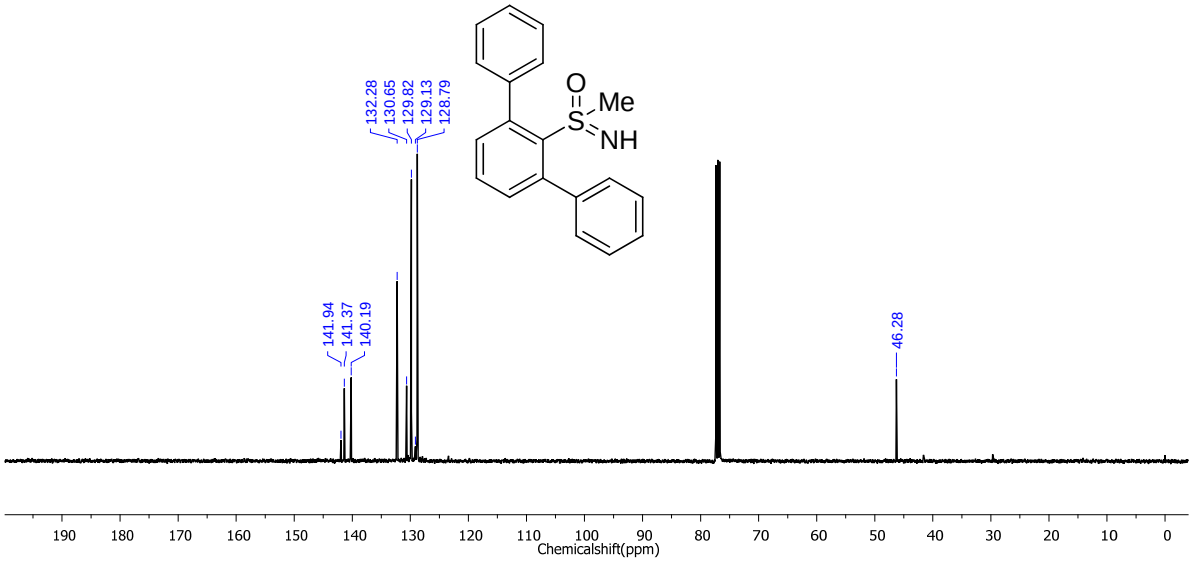
DAD: Signal E, 280 nm/Bw:10 nm Results

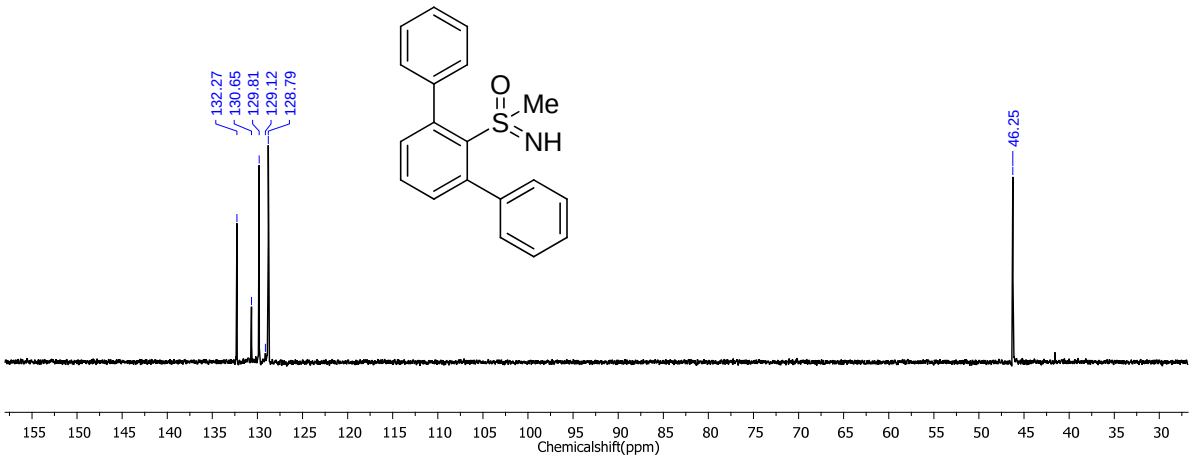
Retention Time	Area	Area %	Height	Height %
20.307	20584097	100.00	781762	100.00

Totals	20584097	100.00	781762	100.00

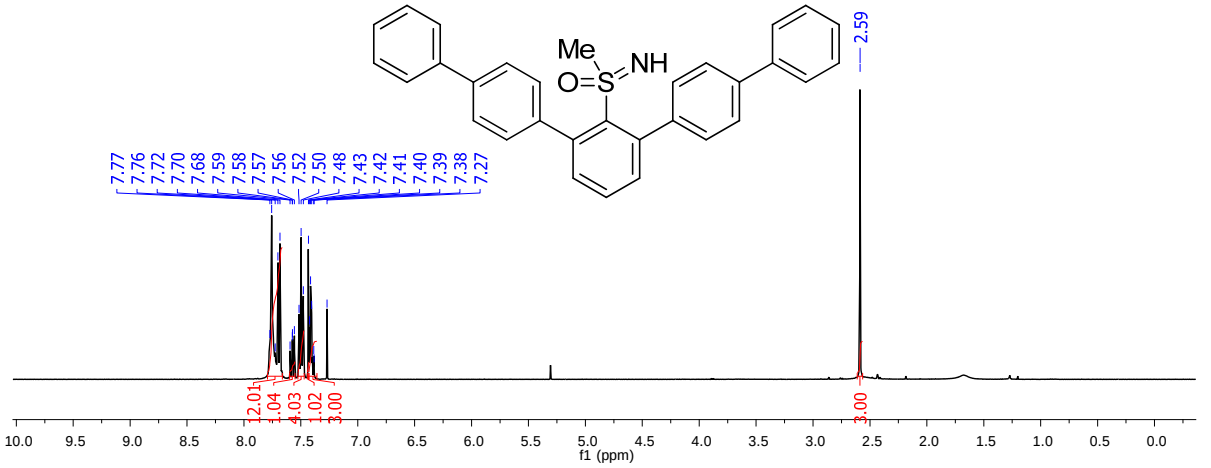
2'-(*S*-Methylsulfonimidoyl)-1,1':3',1''-terphenyl (5aa).

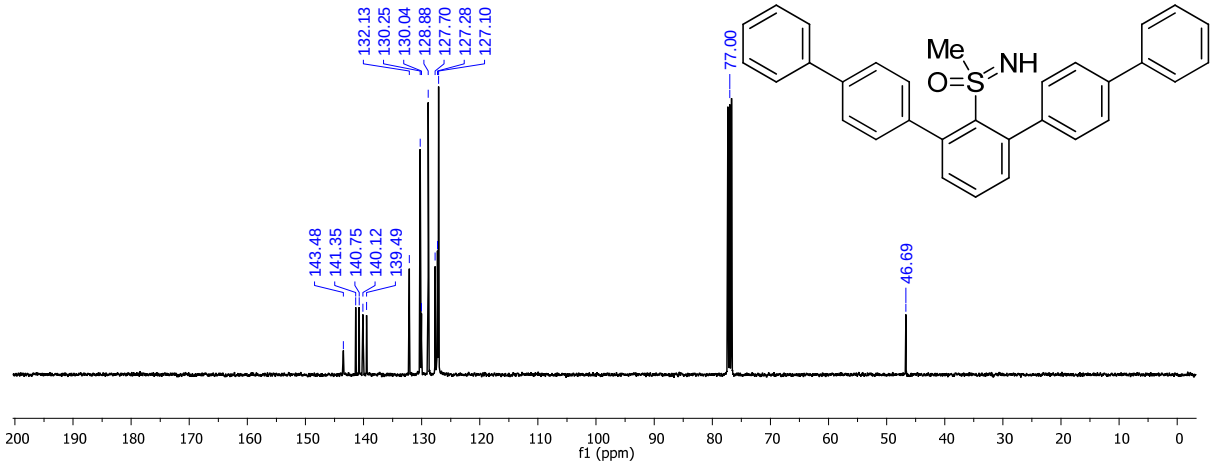


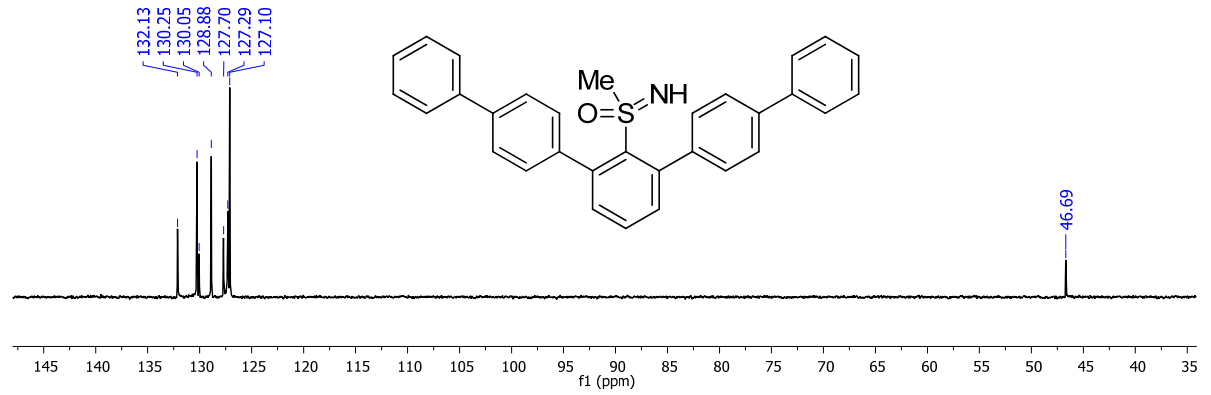




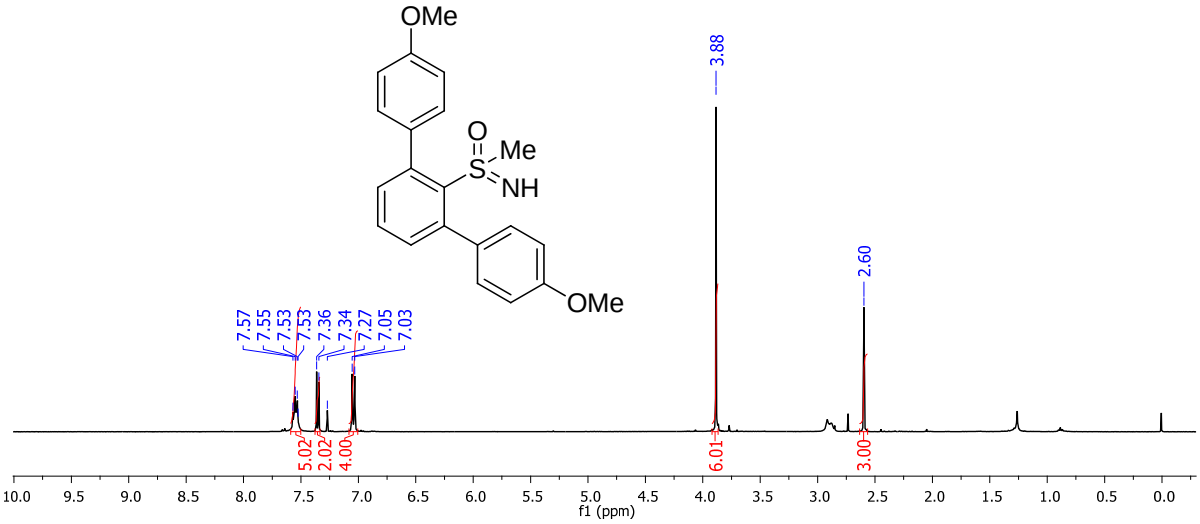
2''-(*S*-Methylsulfonimidoyl)-1,1':4',1'':3'',1''':4''',1''''-quinquephenyl (5ab).

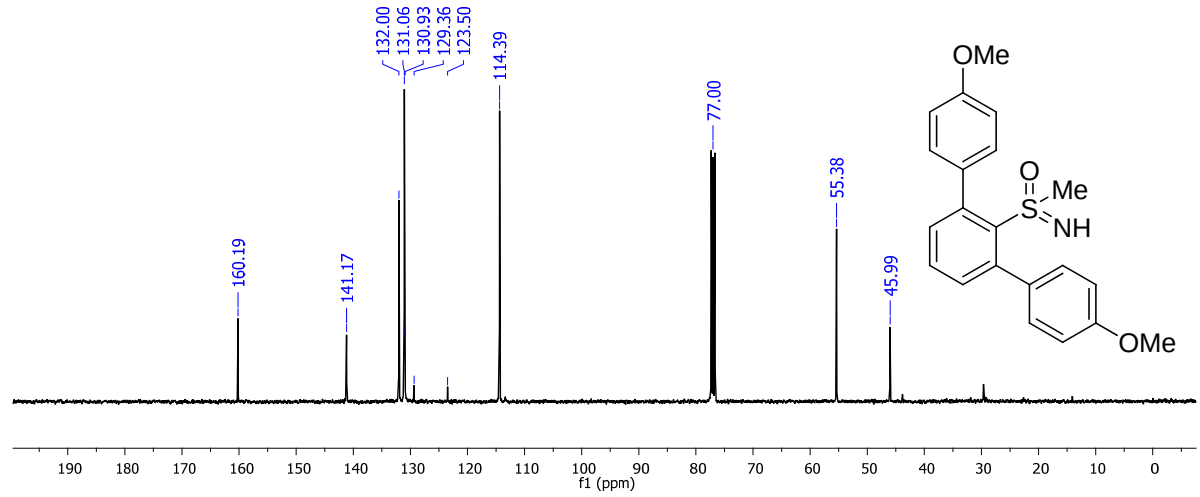


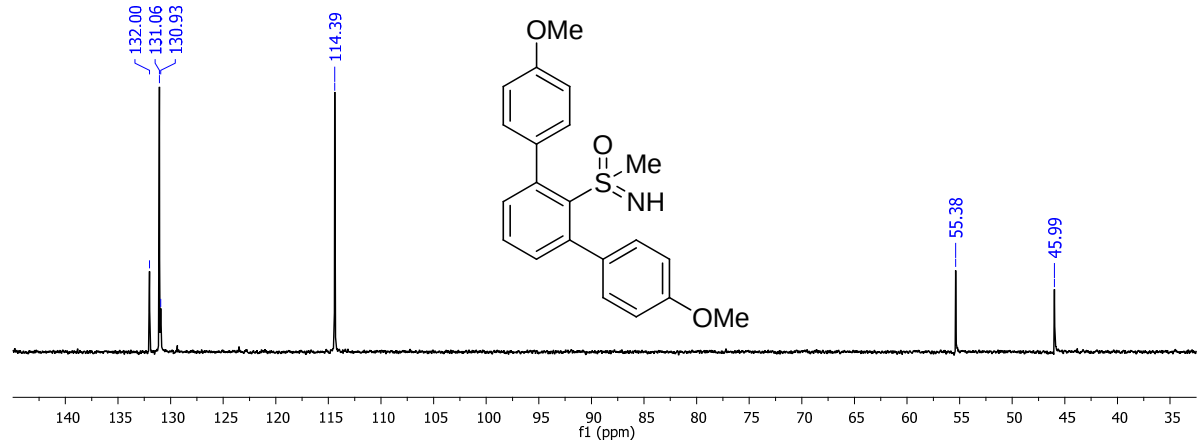




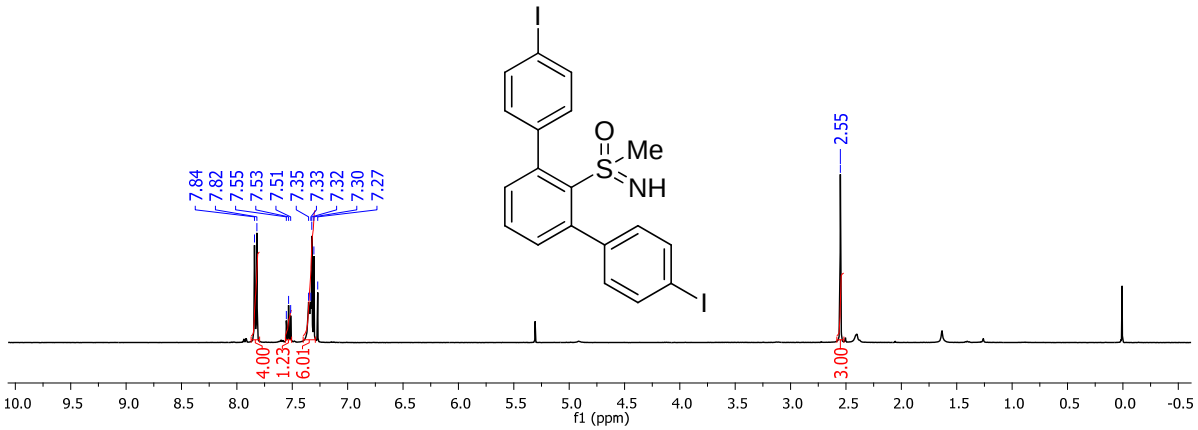
4,4''-Dimethoxy-2'-(*S*-methylsulfonimidoyl)-1,1':3',1''-terphenyl (5ac).

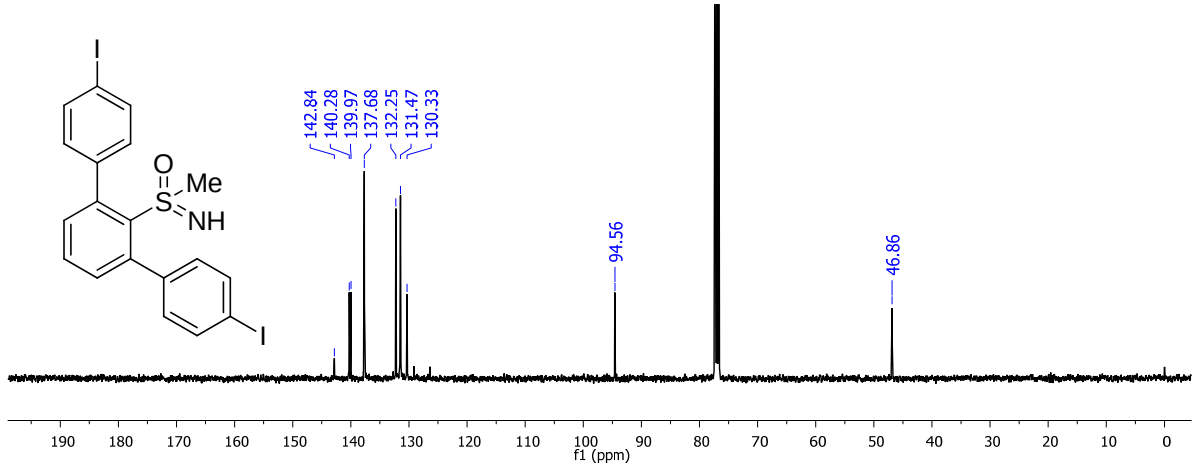


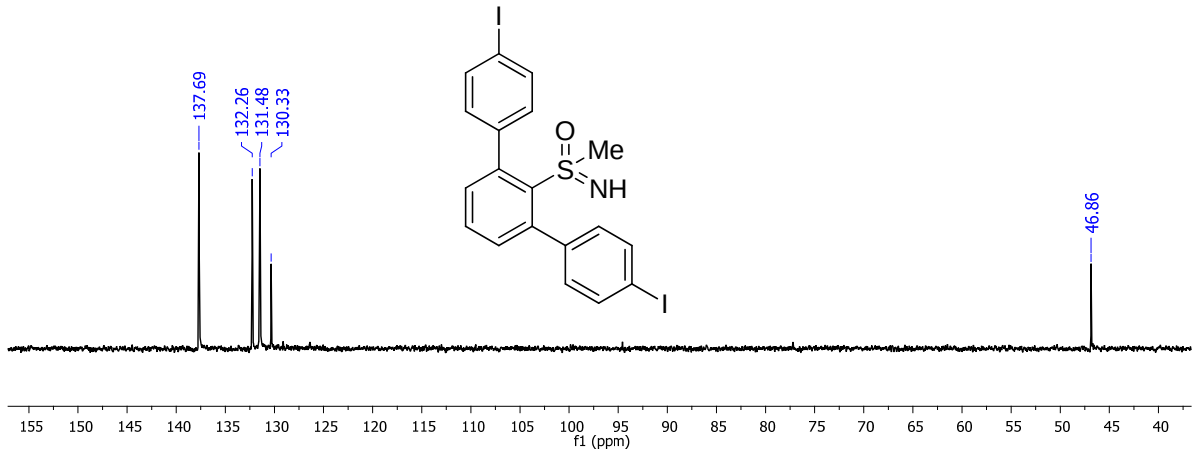




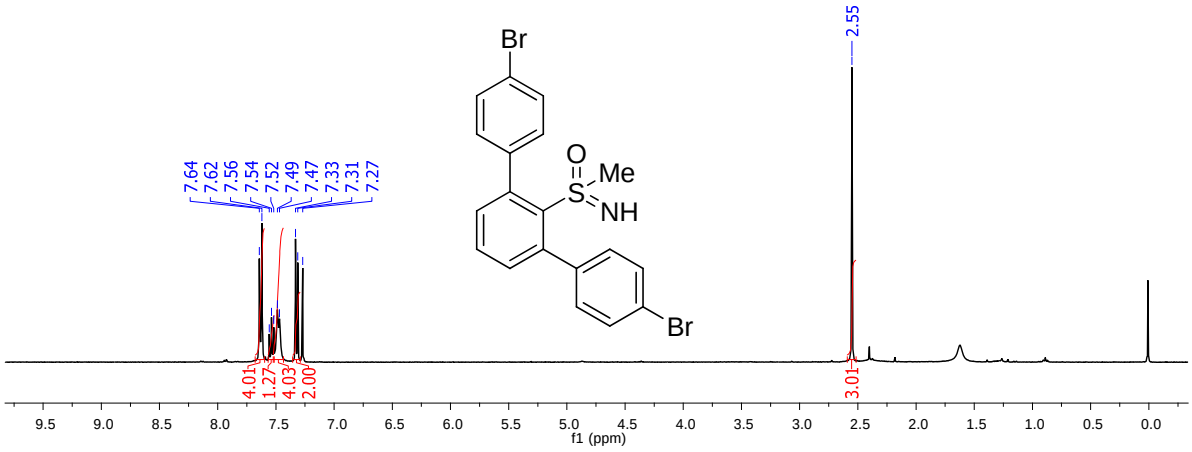
4,4''-Iodo-2'-(*S*-methylsulfonimidoyl)-1,1':3',1''-terphenyl (5ad).

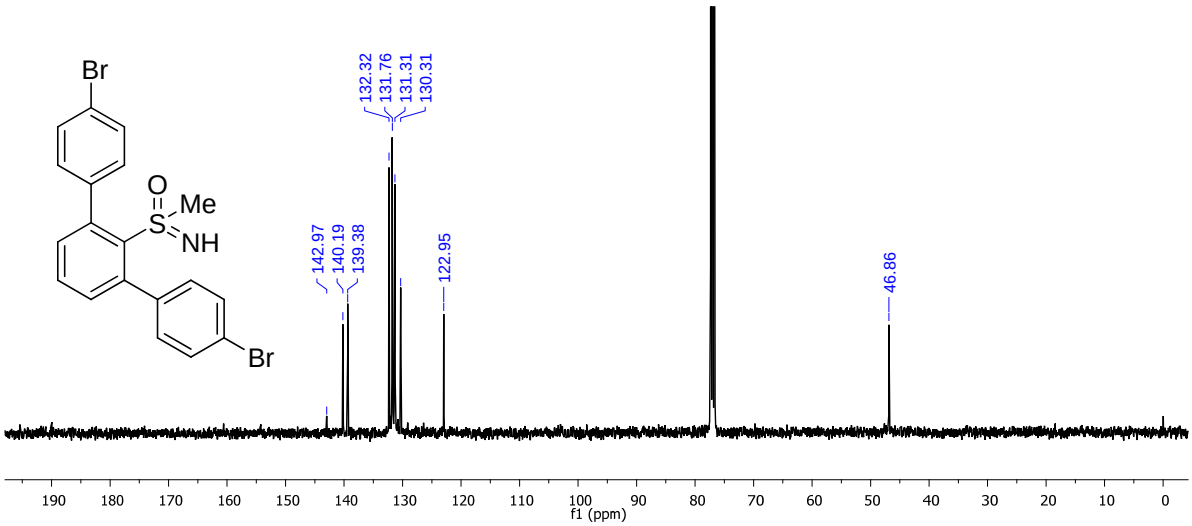


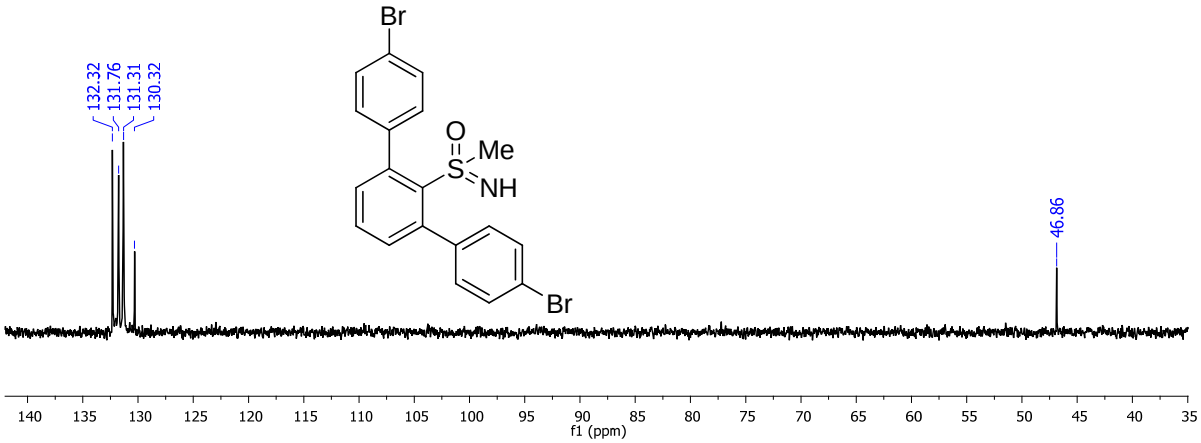




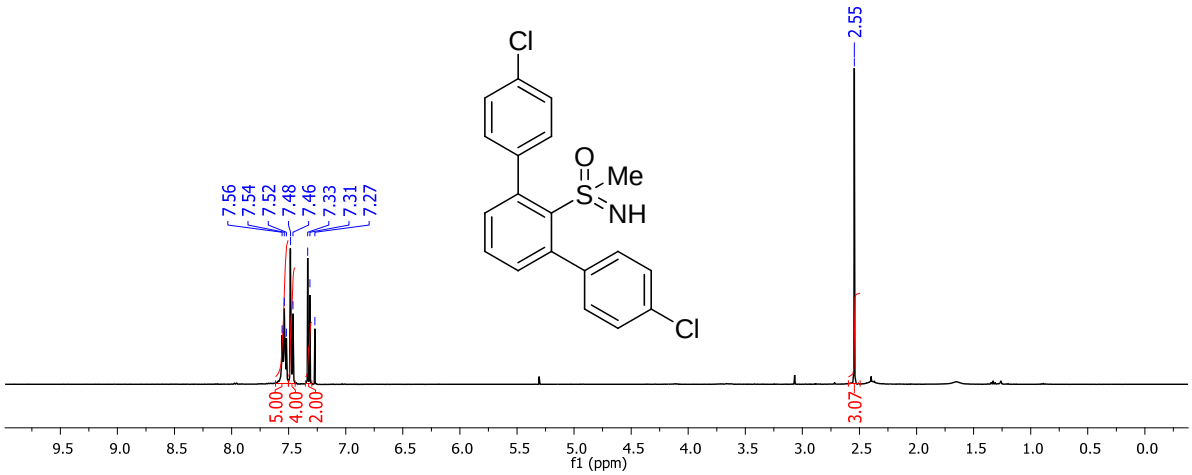
4,4''-Bromo-2'-(*S*-methylsulfonimidoyl)-1,1':3',1''-terphenyl (5ae).

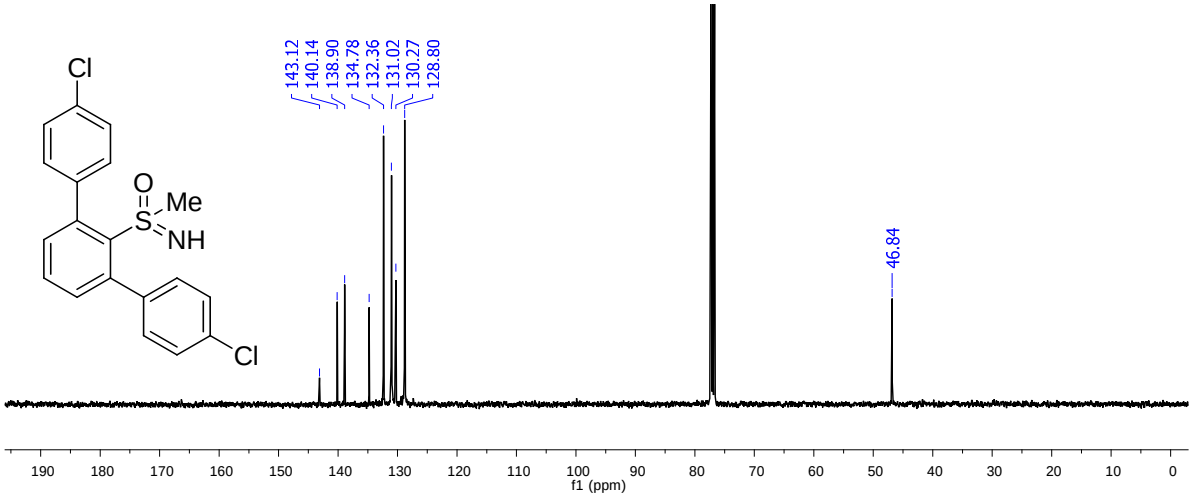


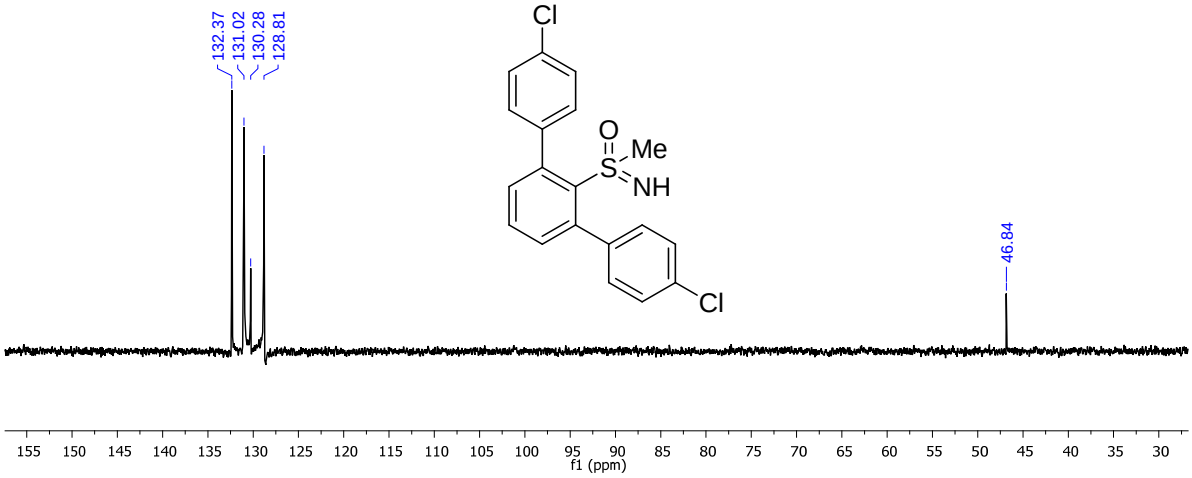




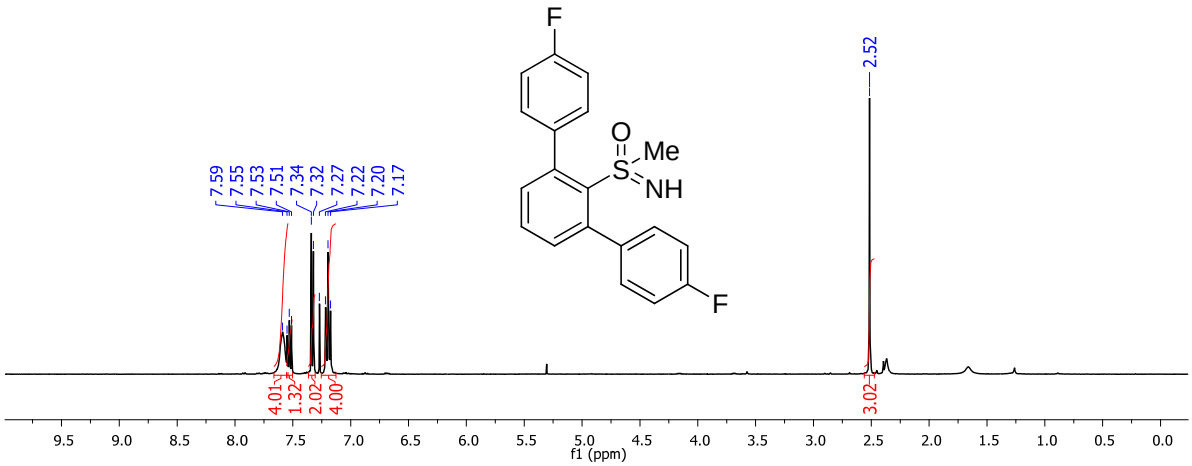
4,4''-Dichloro-2'-(*S*-methylsulfonimidoyl)-1,1':3',1''-terphenyl (5af).

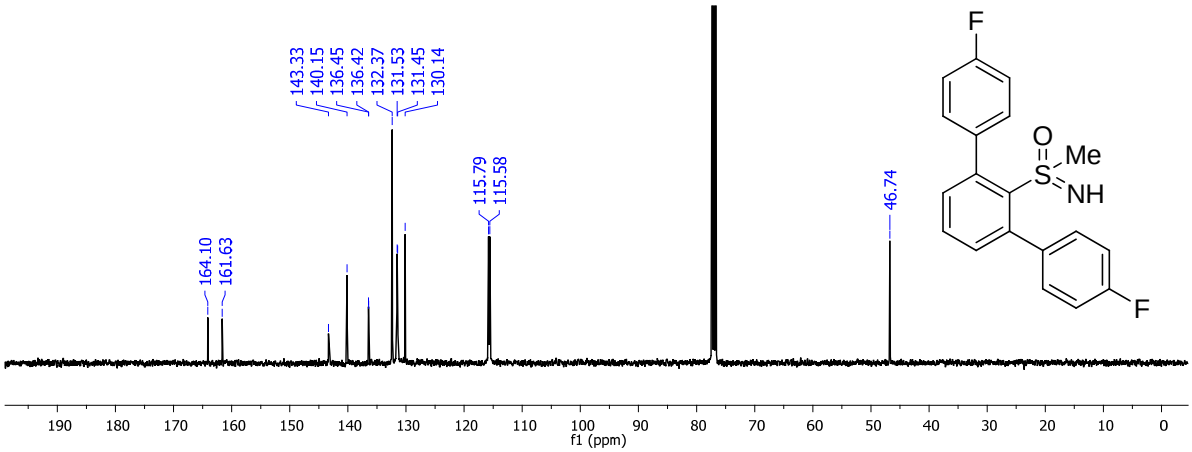


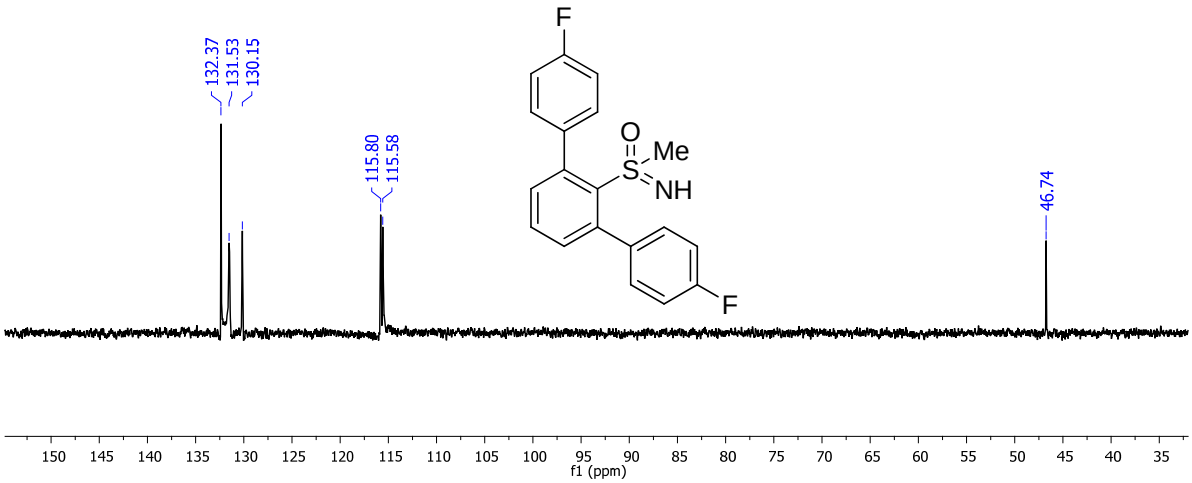




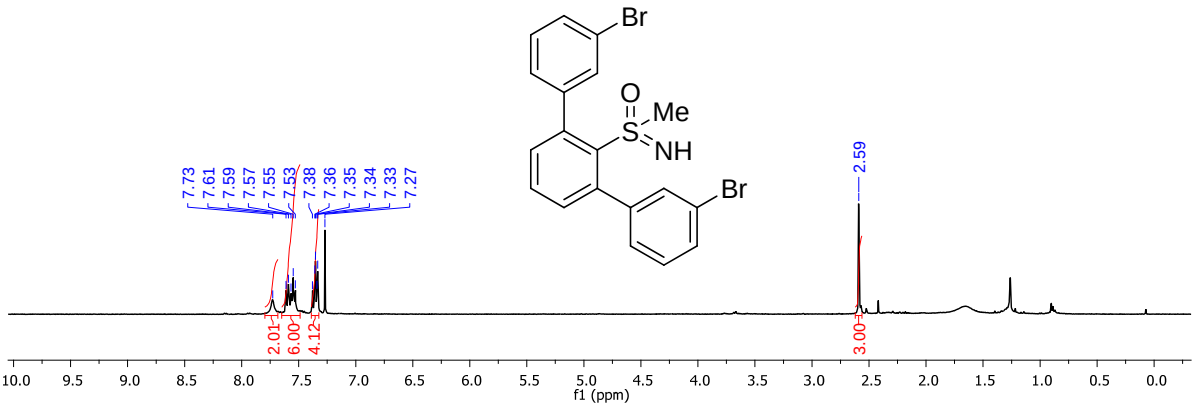
4,4''-Difluoro-2'-(*S*-methylsulfonimidoyl)-1,1':3',1''-terphenyl (5ag).



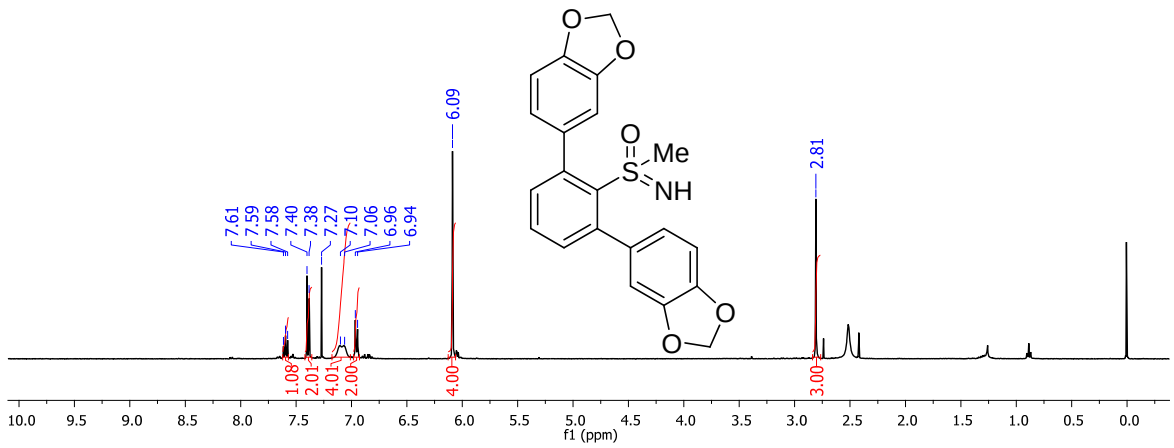


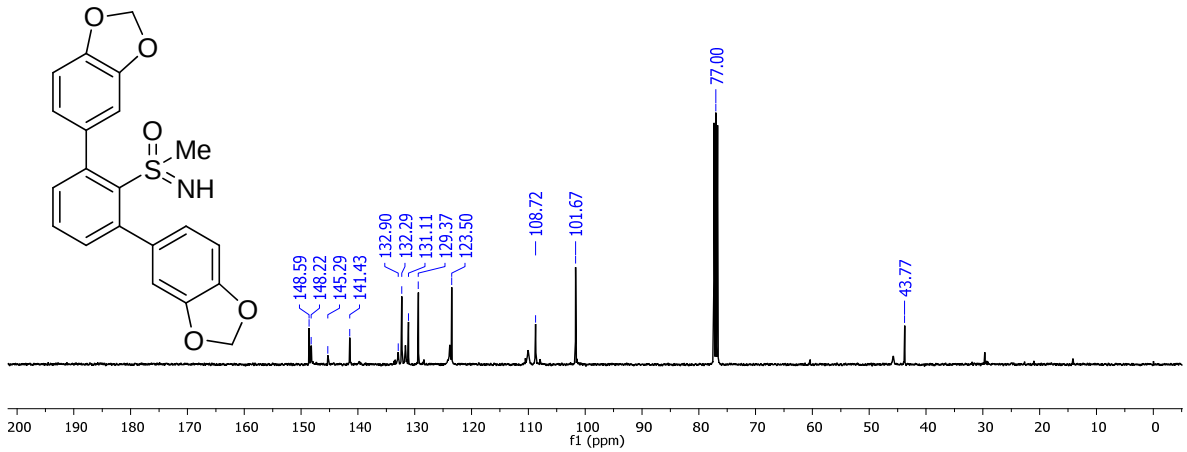


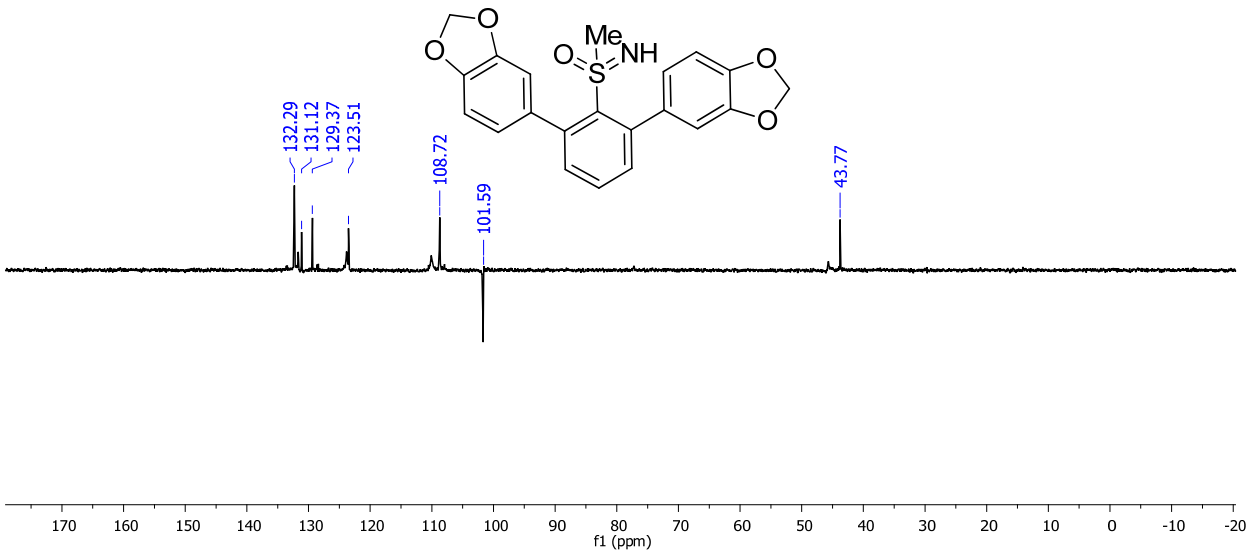
3,3''-Dibromo-2'-(S-methylsulfonimidoyl)-1,1':3',1''-terphenyl (5ah).



5,5'-(2-(*S*-Methylsulfonimidoyl)-1,3 phenylene) Bis(benzo[*d*][1,3]dioxole) (5ai).

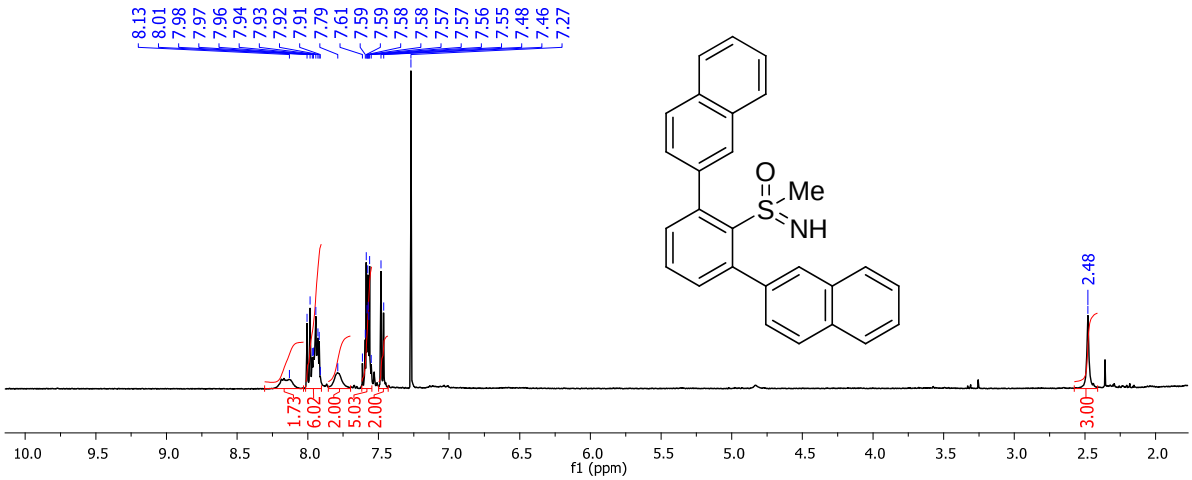


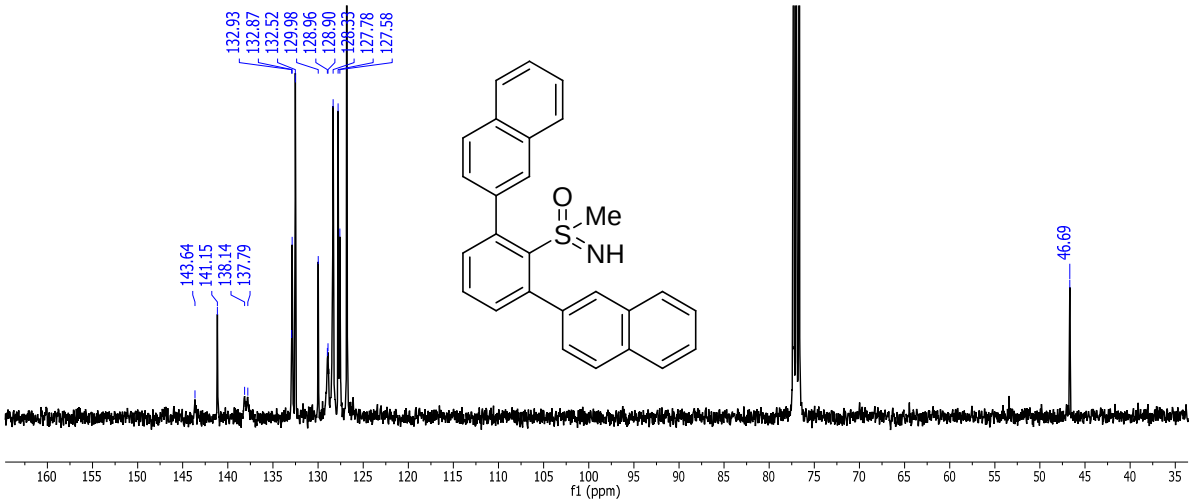


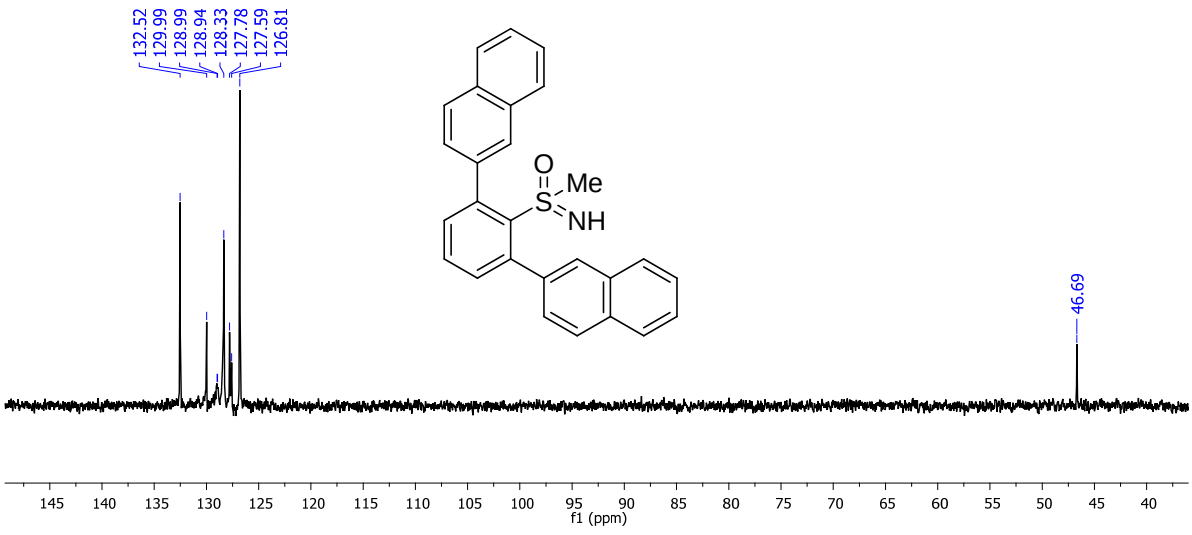

O
O
Me
O
S
NH
O
O
132.29
131.12
129.37
123.51
108.72
101.59
43.77

170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)

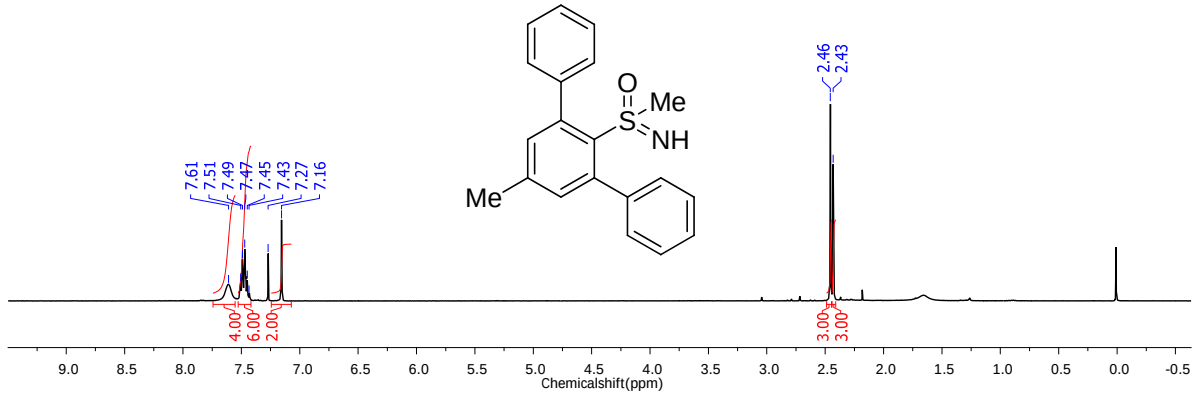
2,2'-(2-(S-methylsulfonimidoyl)-1,3-phenylene)dinaphthalene (5aj).

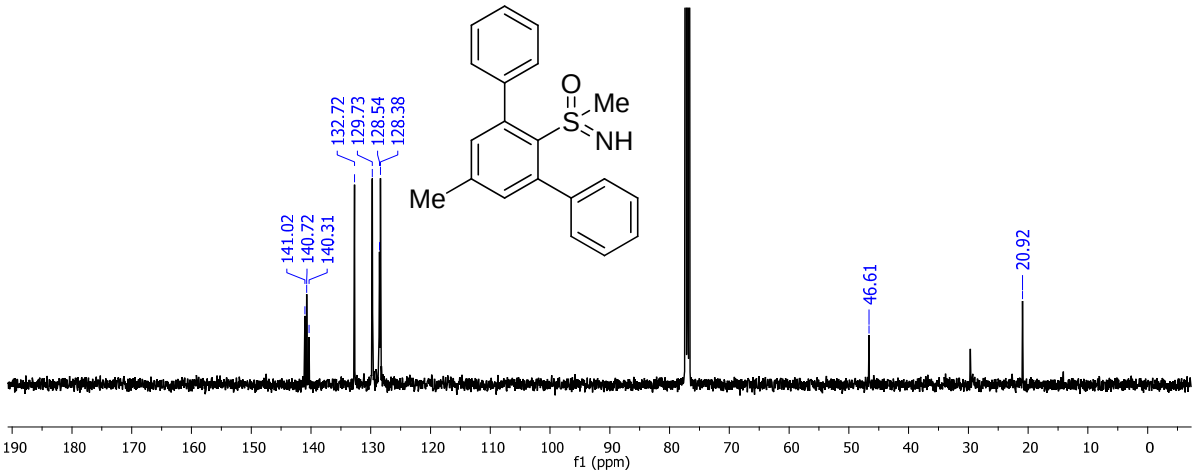


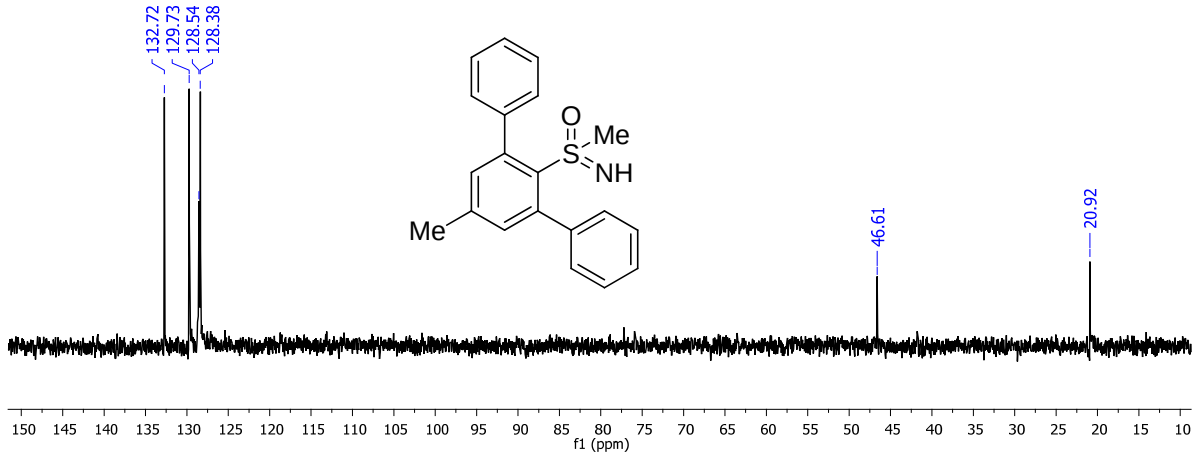




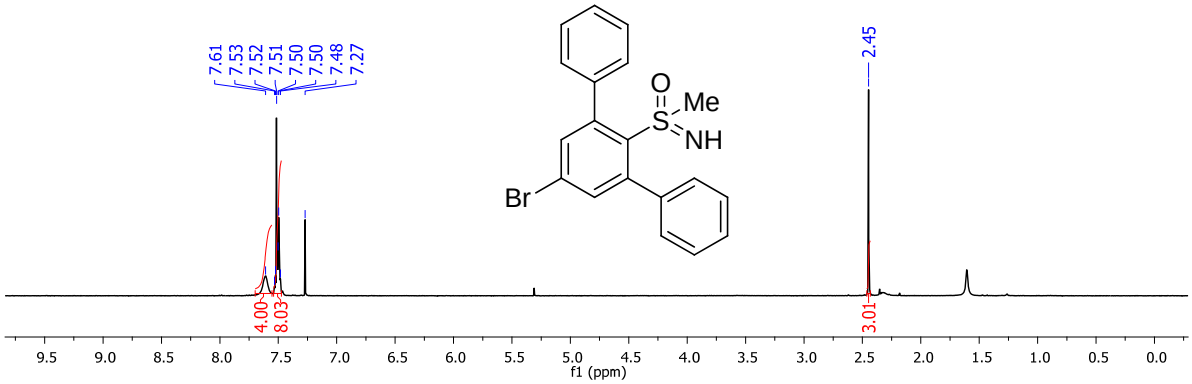
5'-Methyl-2'-(S-methylsulfonimidoyl)-1,1':3',1''-terphenyl (5ba).

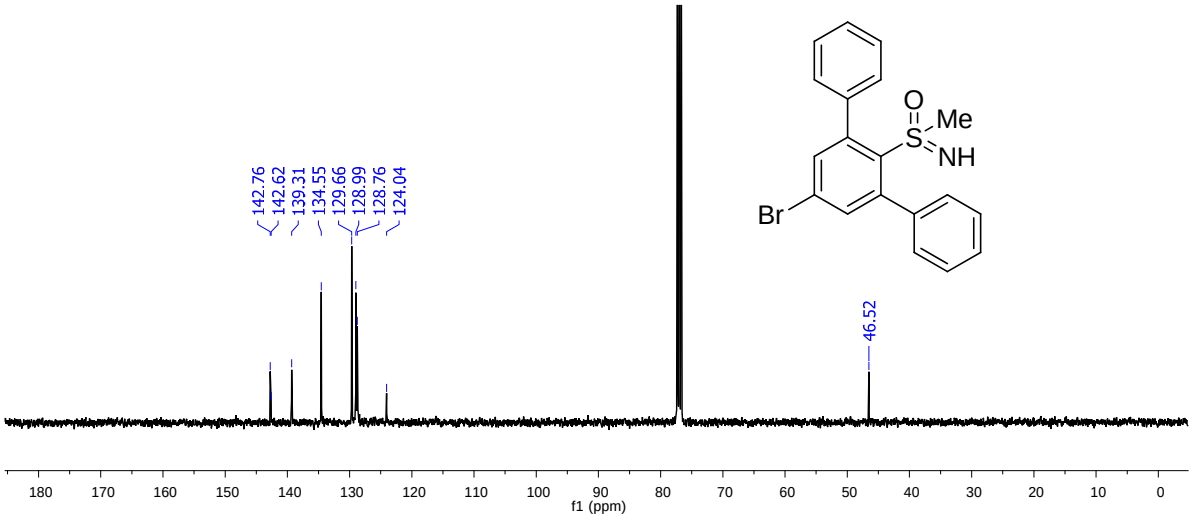


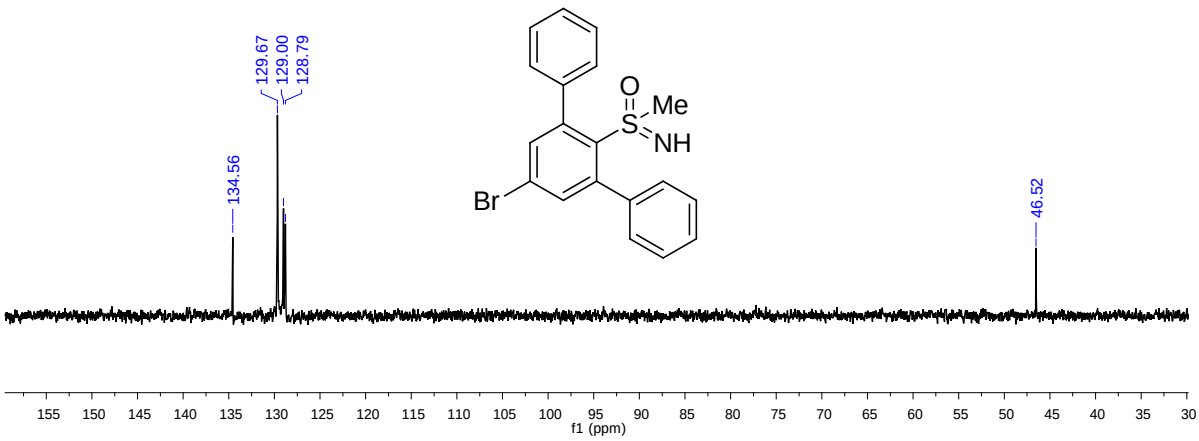




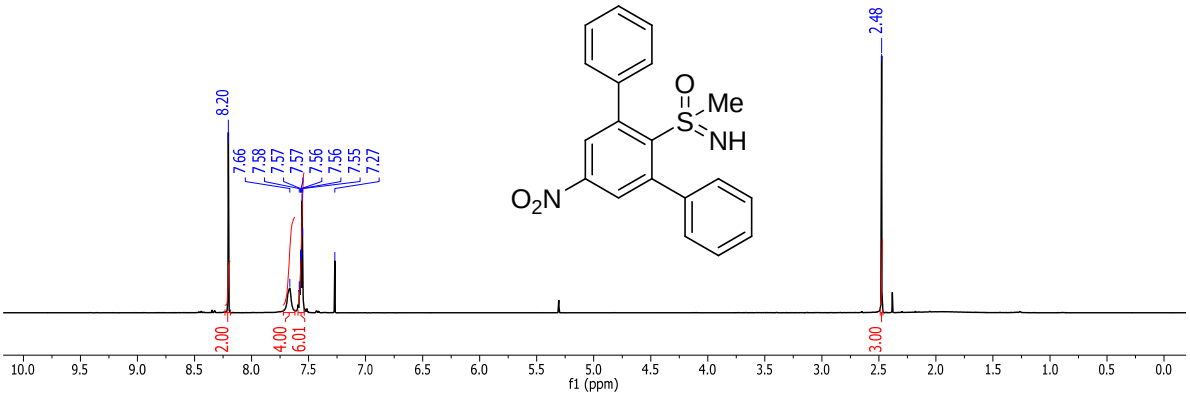
5'-Bromo-2'-(S-methylsulfonimidoyl)-1,1':3',1''-terphenyl (5ca).

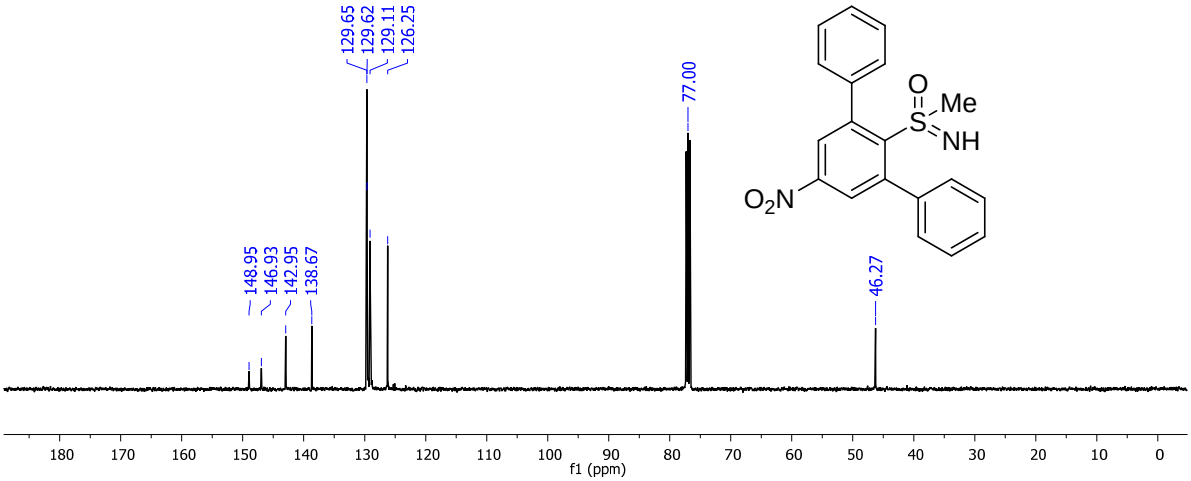


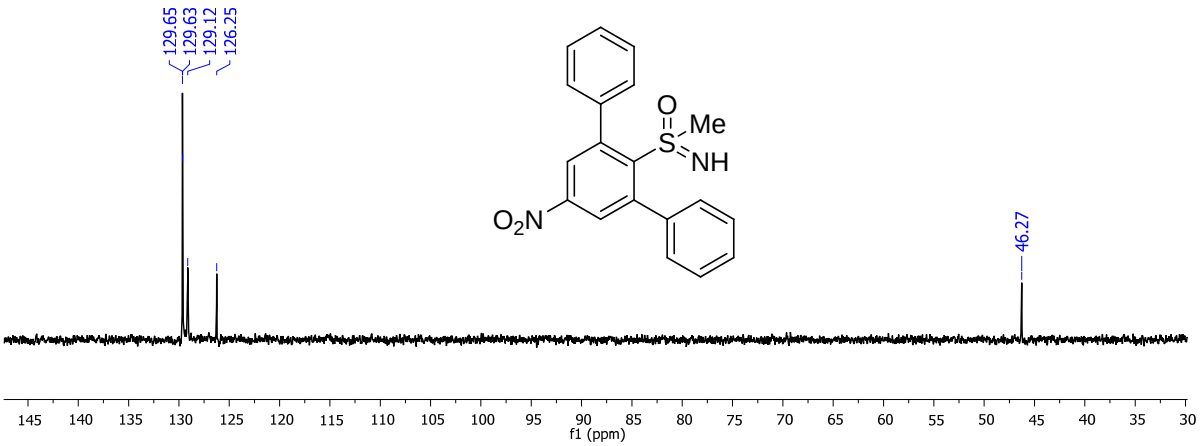




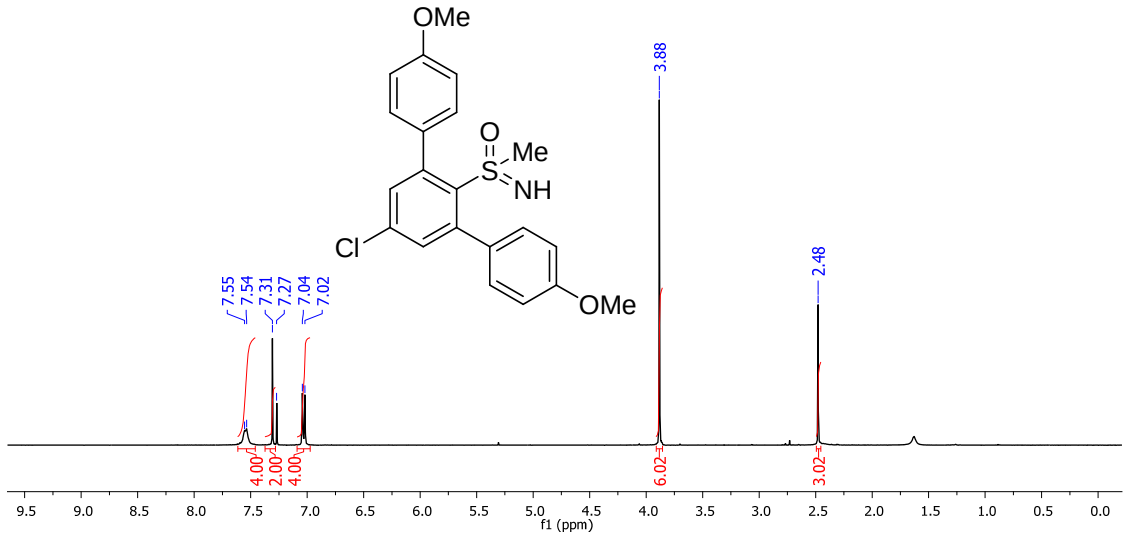
2'-(S-Methylsulfonimidoyl)-5'-nitro-1,1':3',1''-terphenyl (5da).

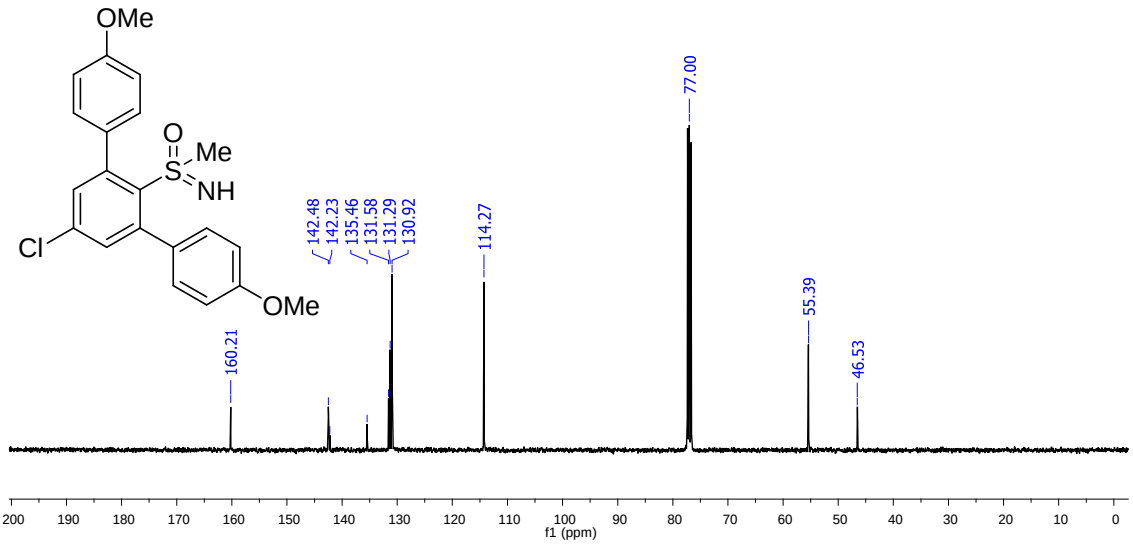


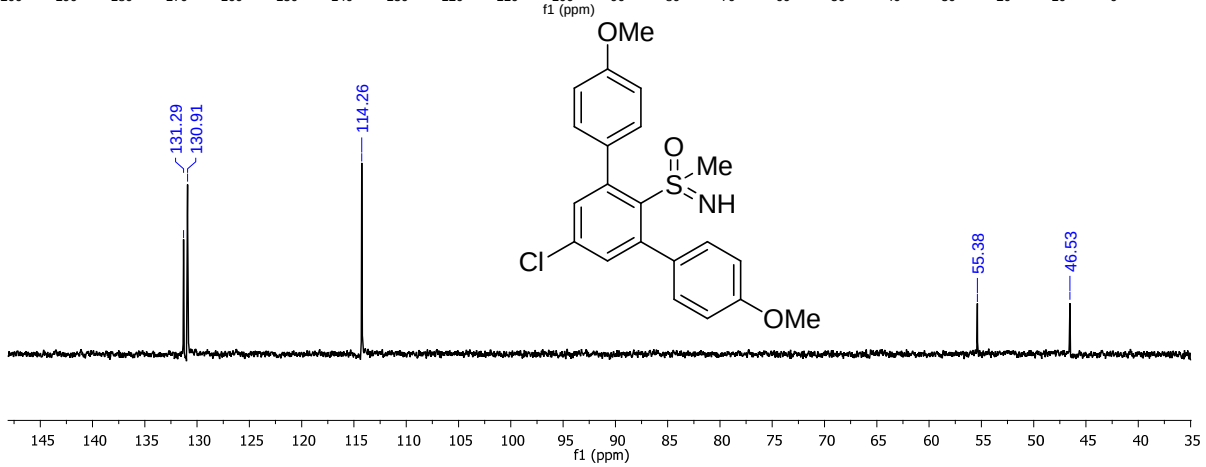




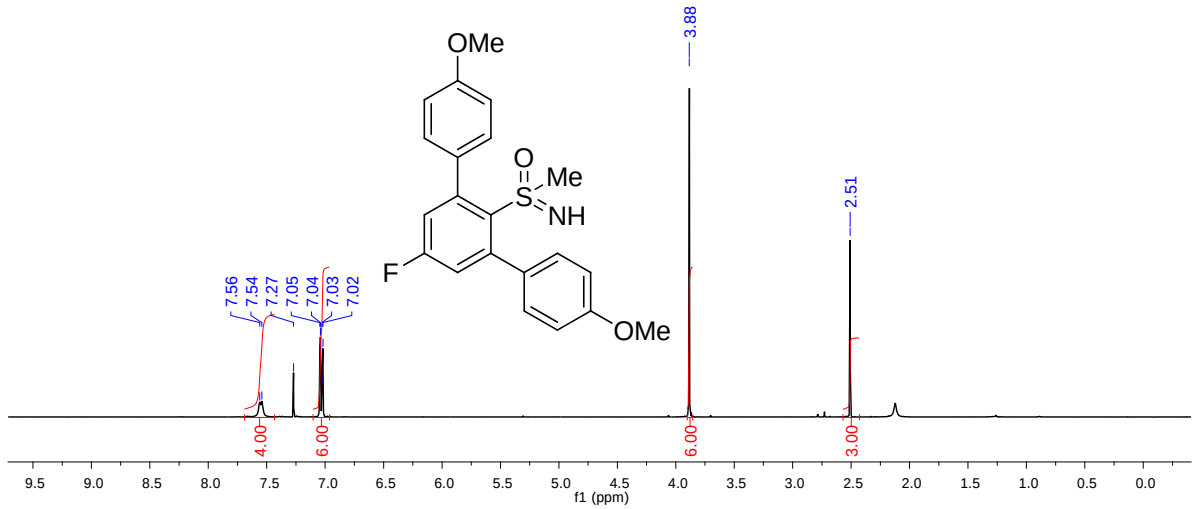
5'-chloro-4,4''-dimethoxy-2'-(S-methylsulfonimidoyl)-1,1':3',1''-terphenyl (5ec).

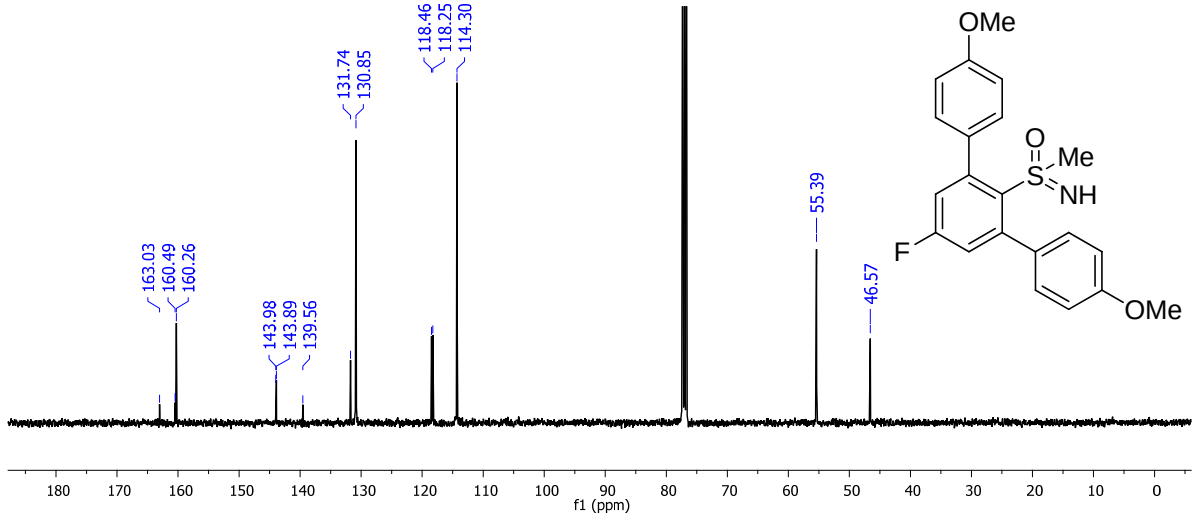


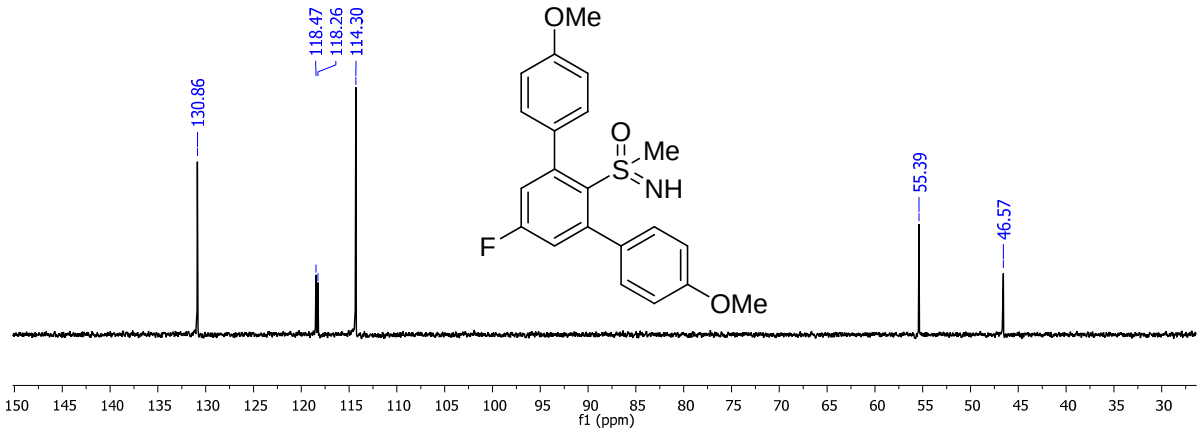




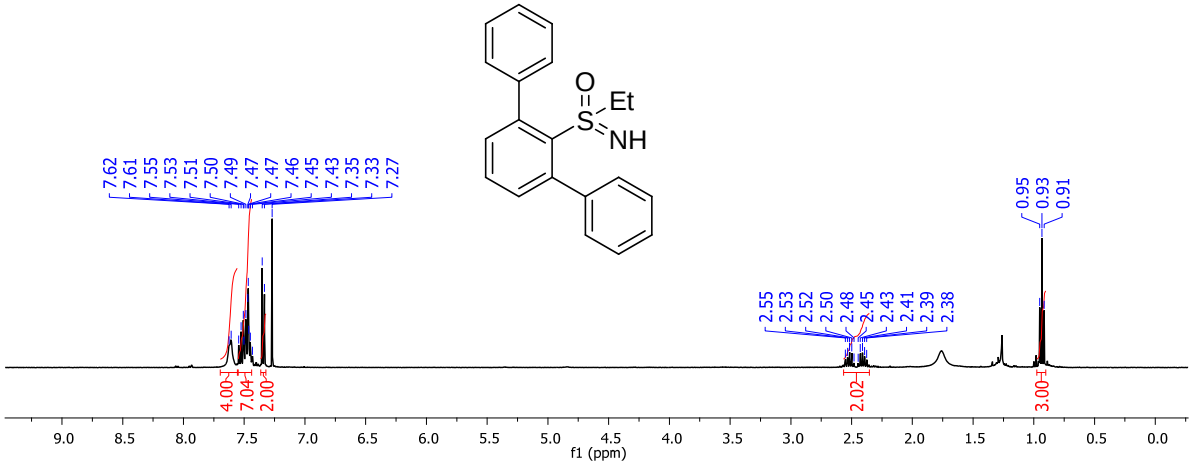
5'-Fluoro-4,4''-dimethoxy-2'-(S-methylsulfonimidoyl)-1,1':3',1''-terphenyl (5fc).

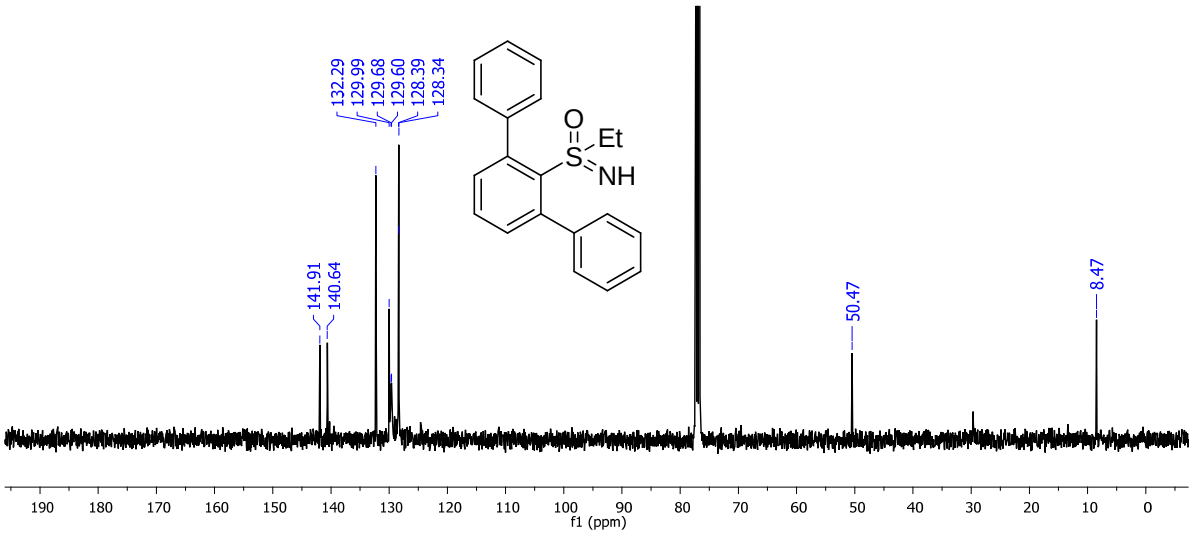


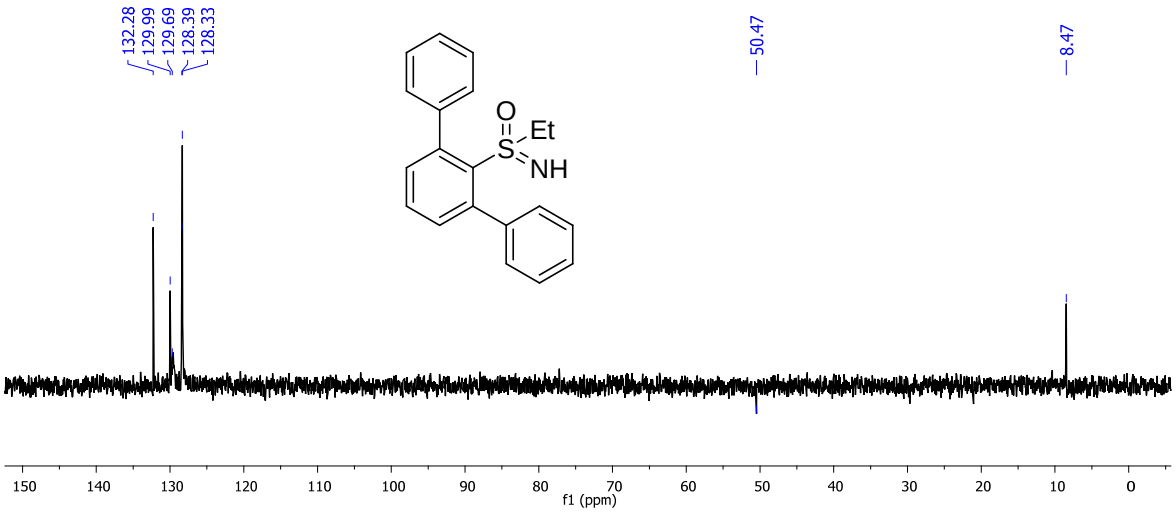




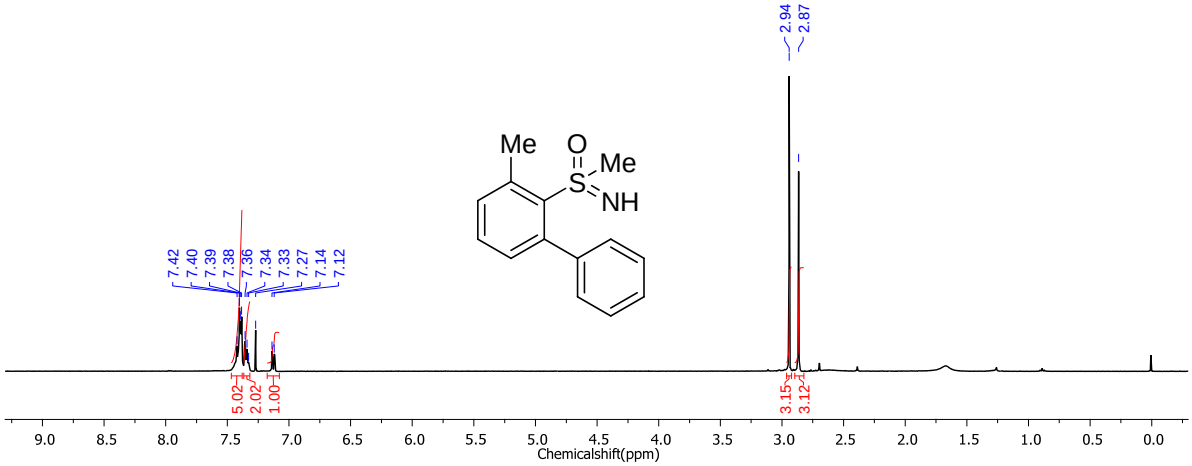
2'-(Ethylsulfonimidoyl)-1,1':3',1''-terphenyl (5ga).

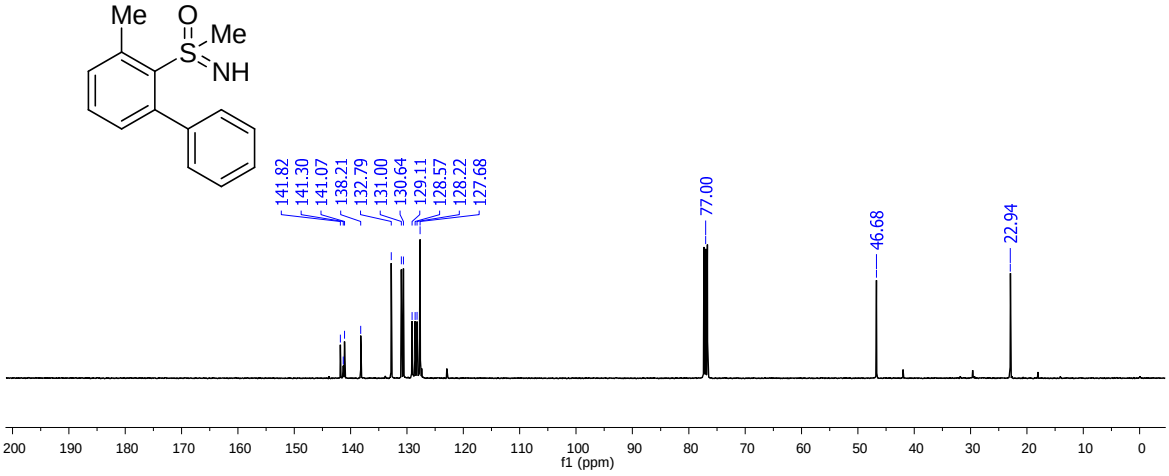


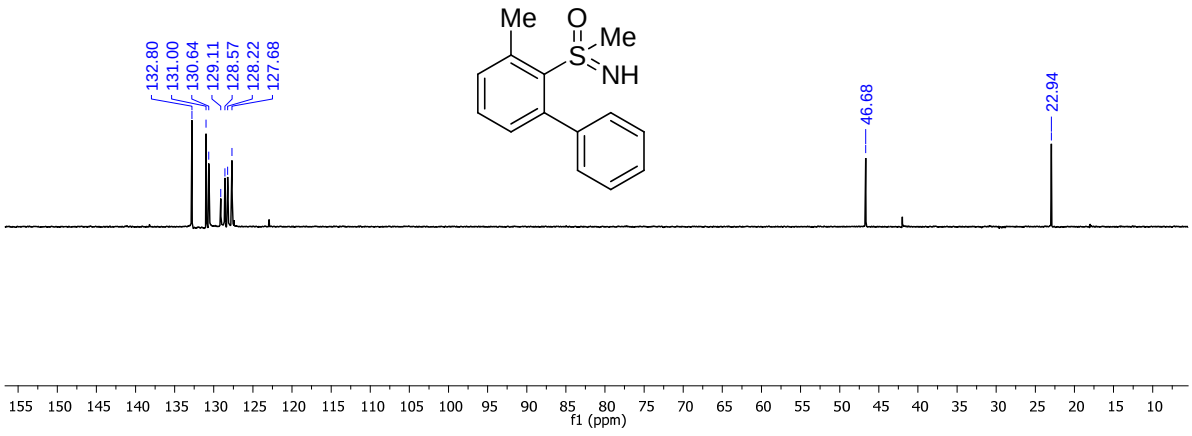




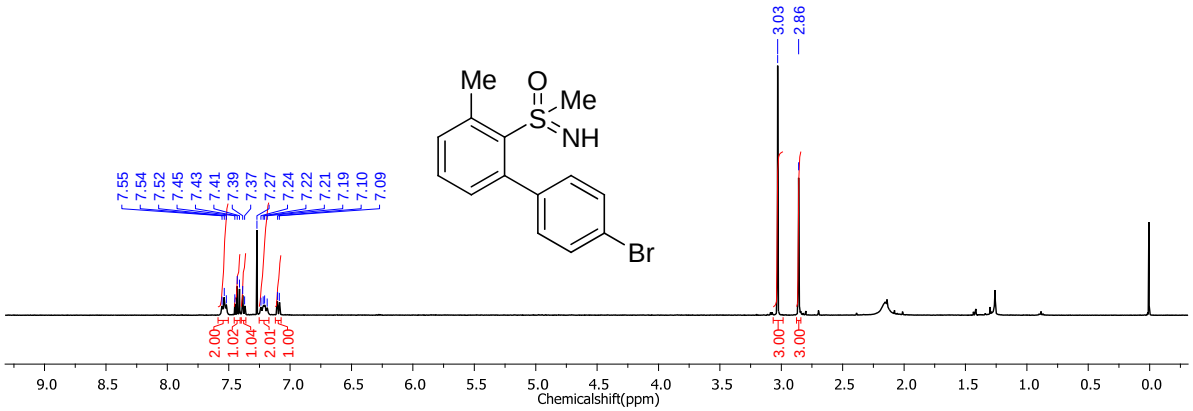
3-Methyl-2-(S-methylsulfonimidoyl)-1,1'-biphenyl (5ha).

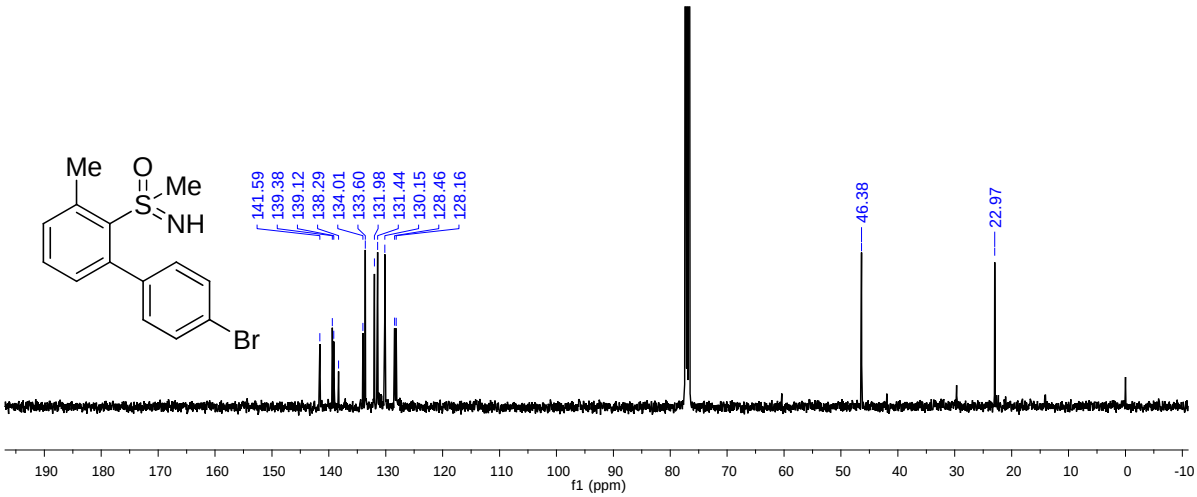


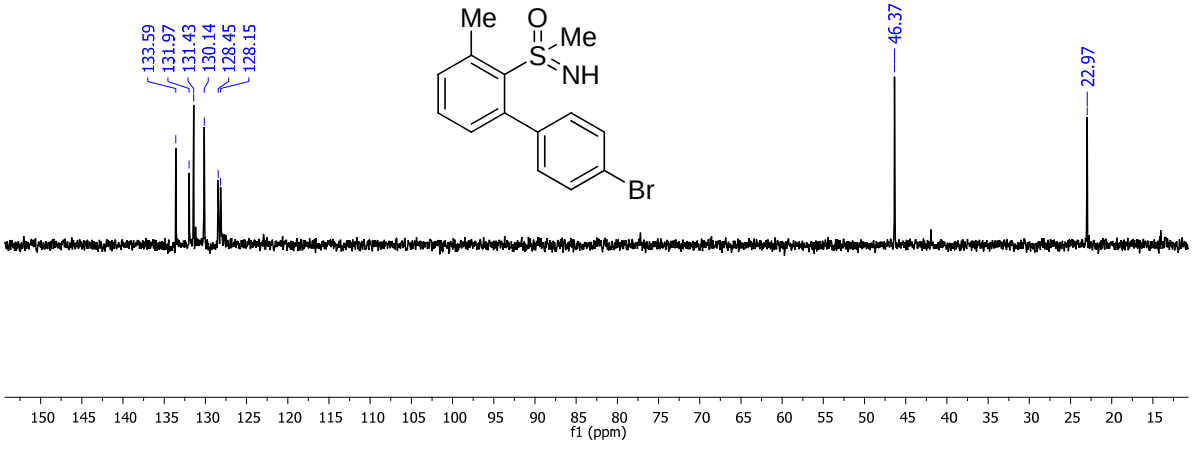




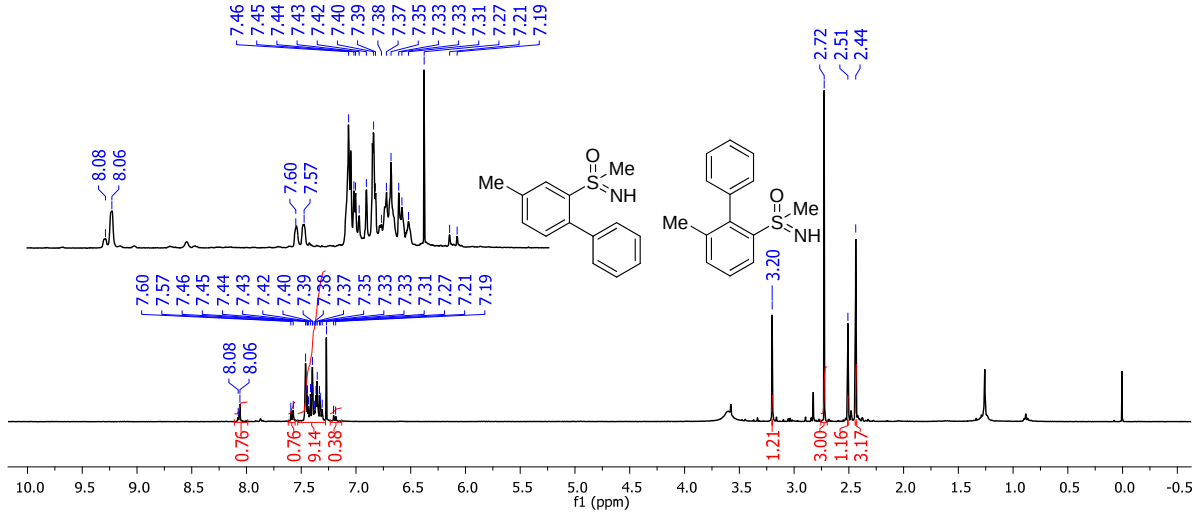
4'-Bromo-3-methyl-2-(S-methylsulfonimidoyl)-1,1'-biphenyl (5he).

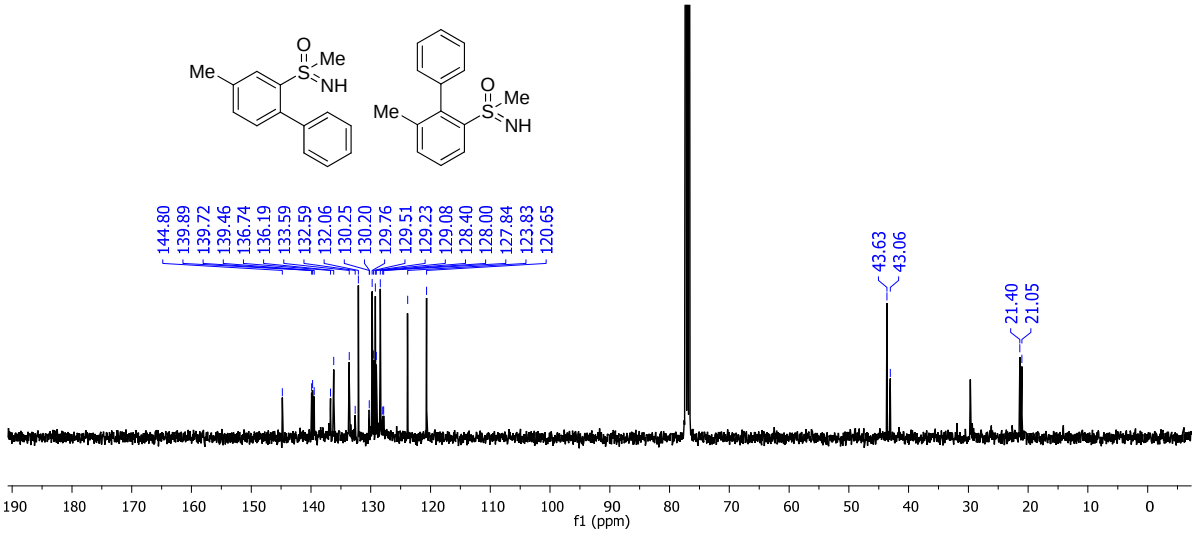


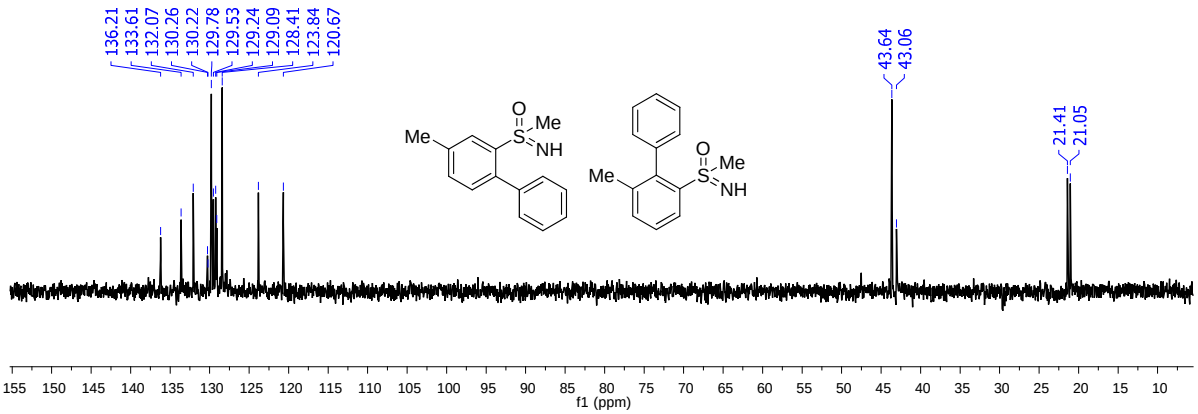




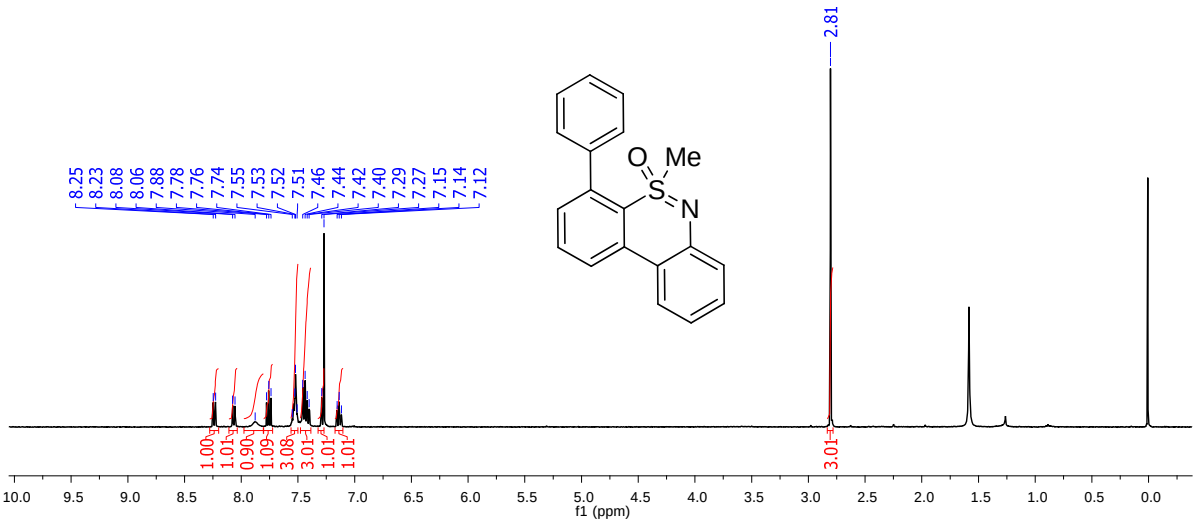
4-Methyl-2-(S-methylsulfonimidoyl)-1,1'-biphenyl (and)2-Methyl-6-(S-methylsulfonimidoyl)-1,1'-biphenyl (5ia and 5ia).

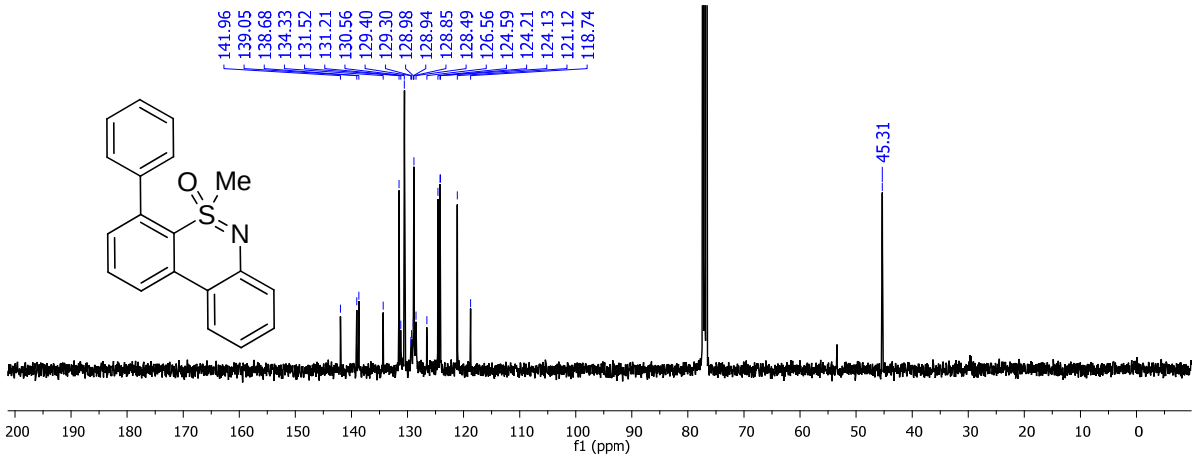


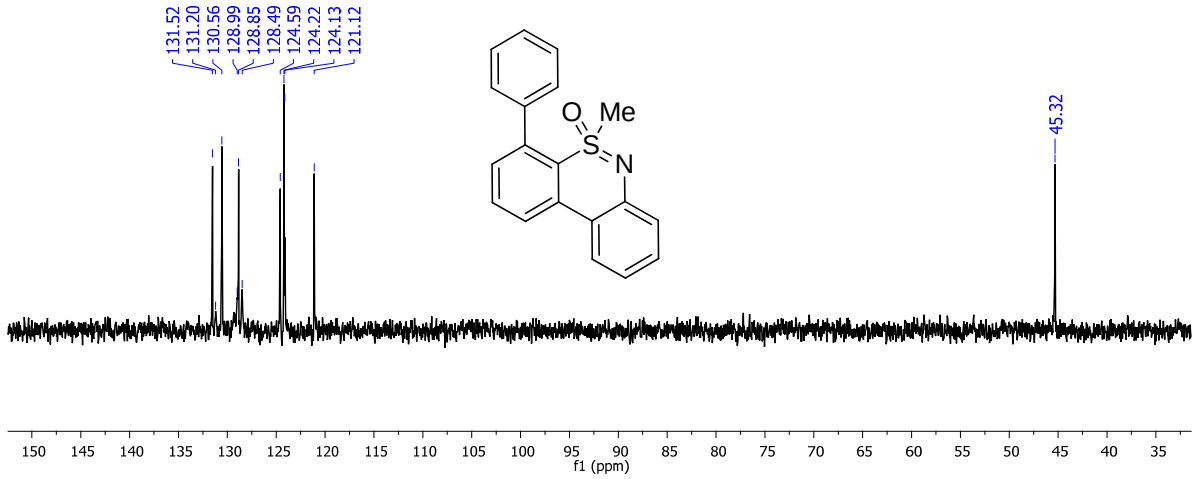




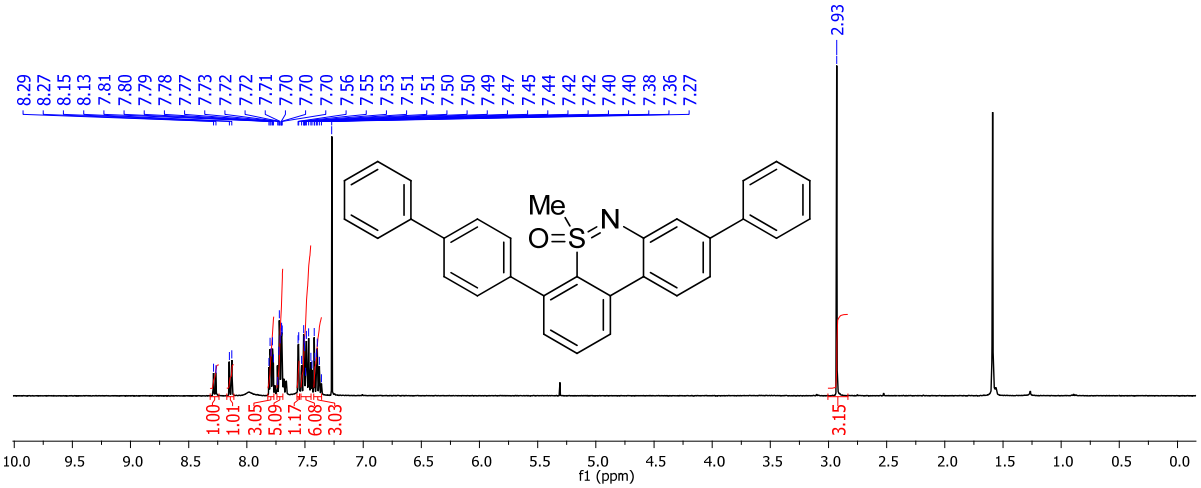
5-Methyl-4-phenyldibenzo[c,e][1,2]thiazine 5-oxide (6a).

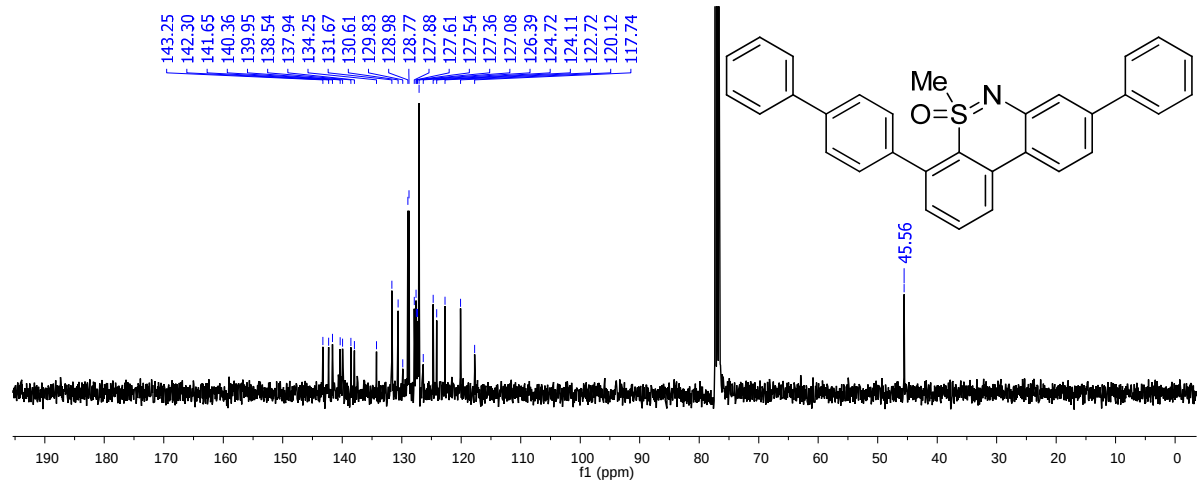


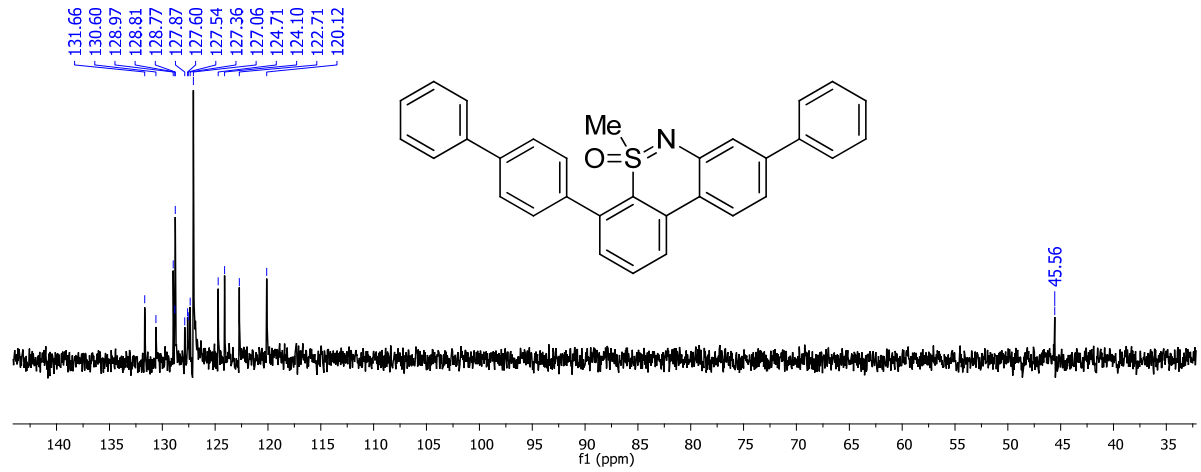




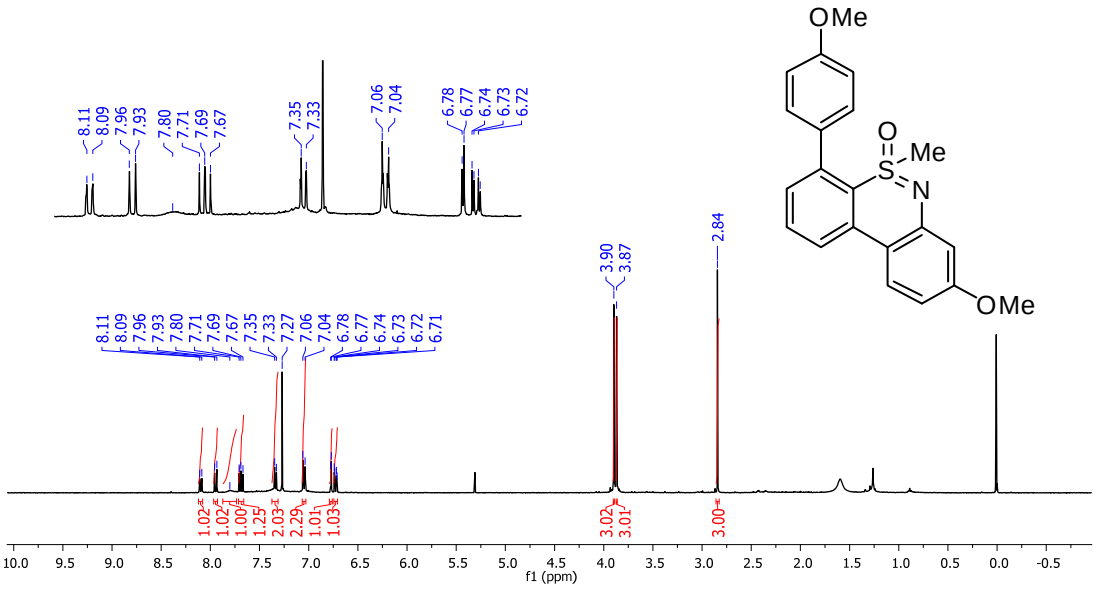
4-([1,1'-biphenyl]-4-yl)-5-methyl-8 phenyldibenzo[c,e][1,2]thiazine 5-oxide (6b).

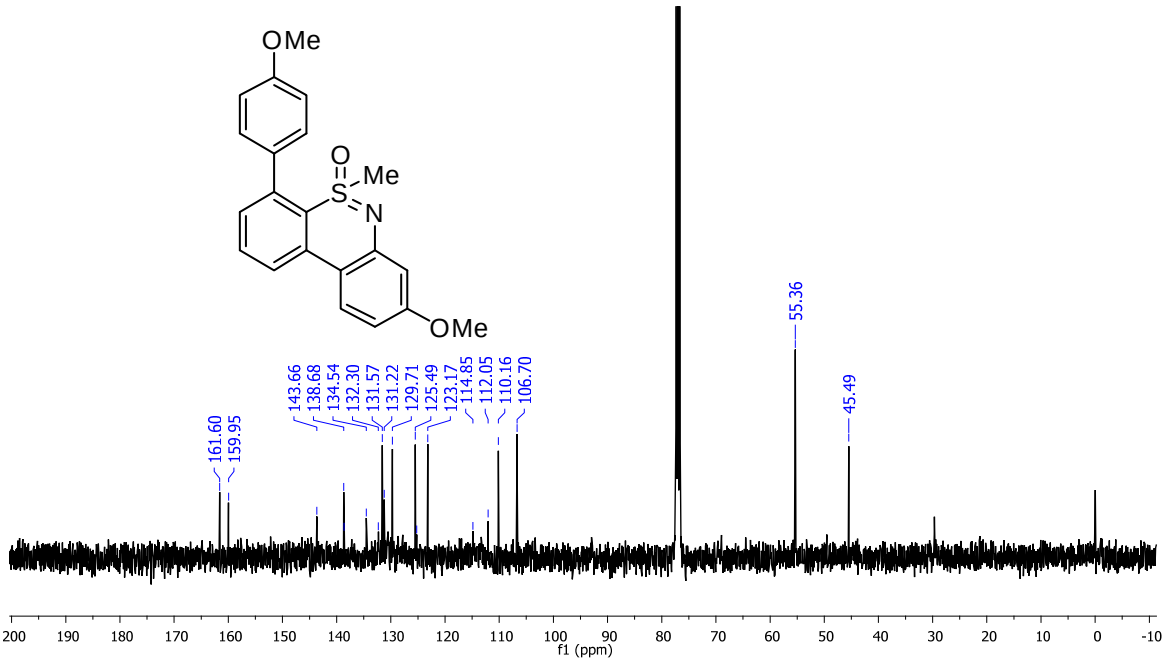




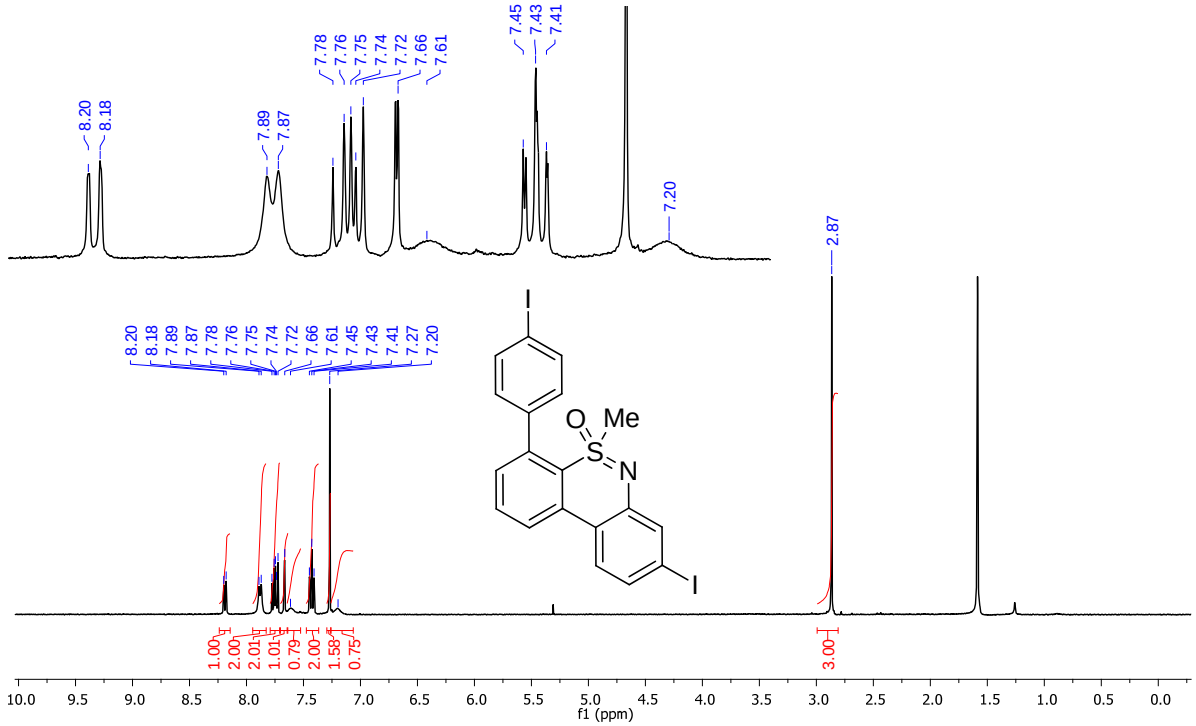


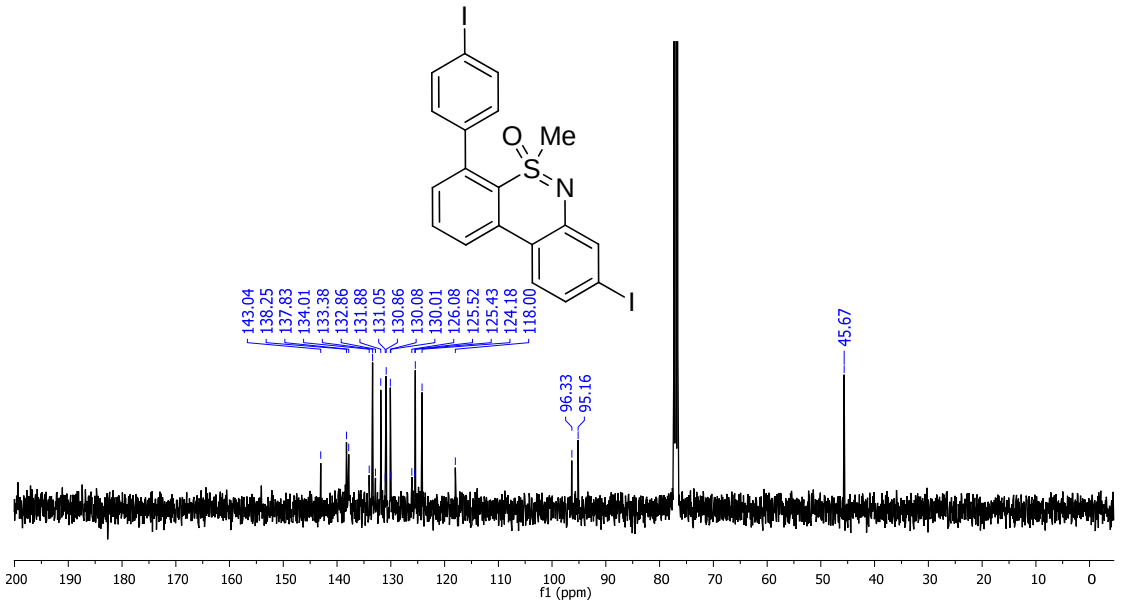
8-Methoxy-4-(4-methoxyphenyl)-5-methyldibenzo[c,e][1,2]thiazine 5-oxide (6c).



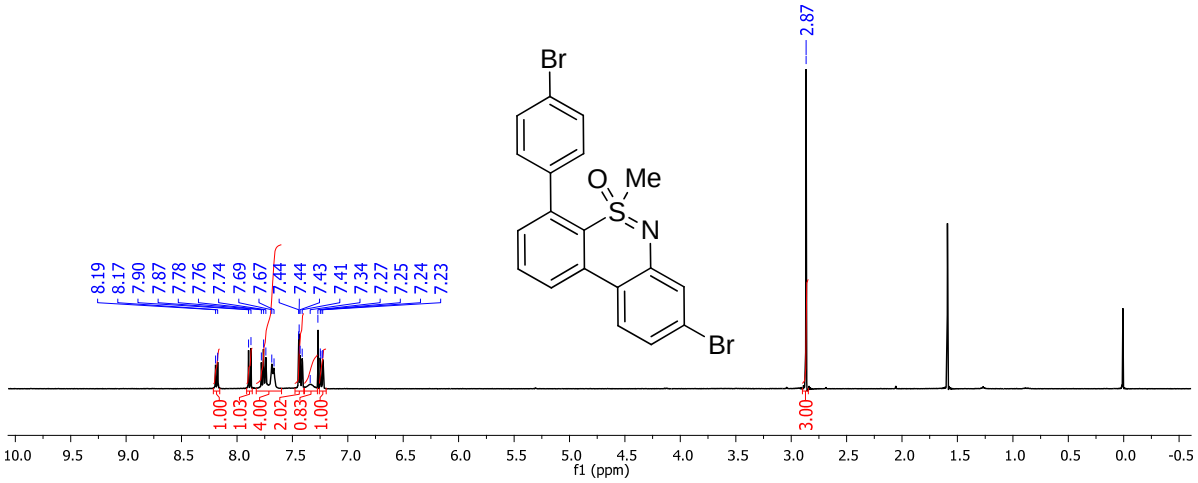


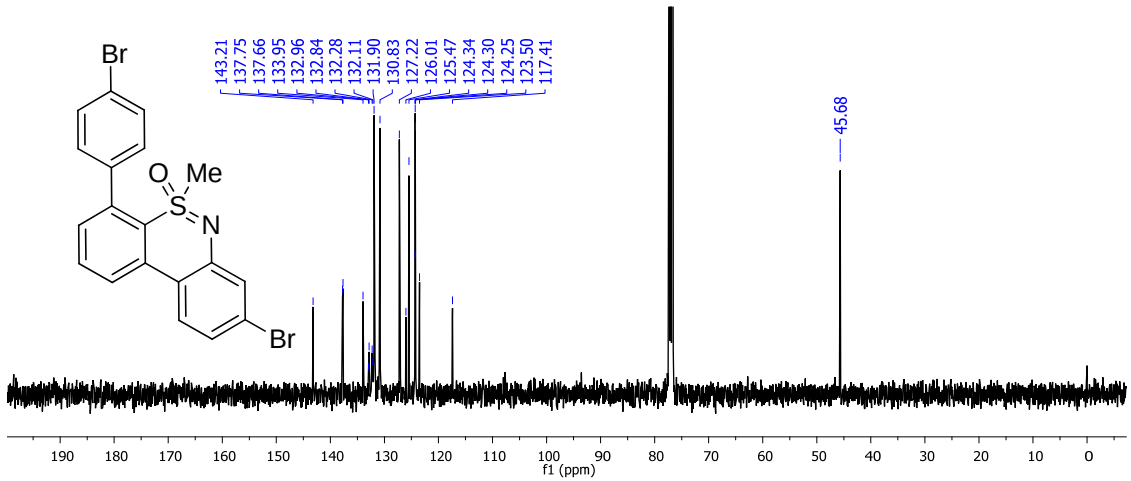
8-Iodo-4-(4-iodophenyl)-5-methyldibenzo[c,e][1,2]thiazine 5-oxide (6d).

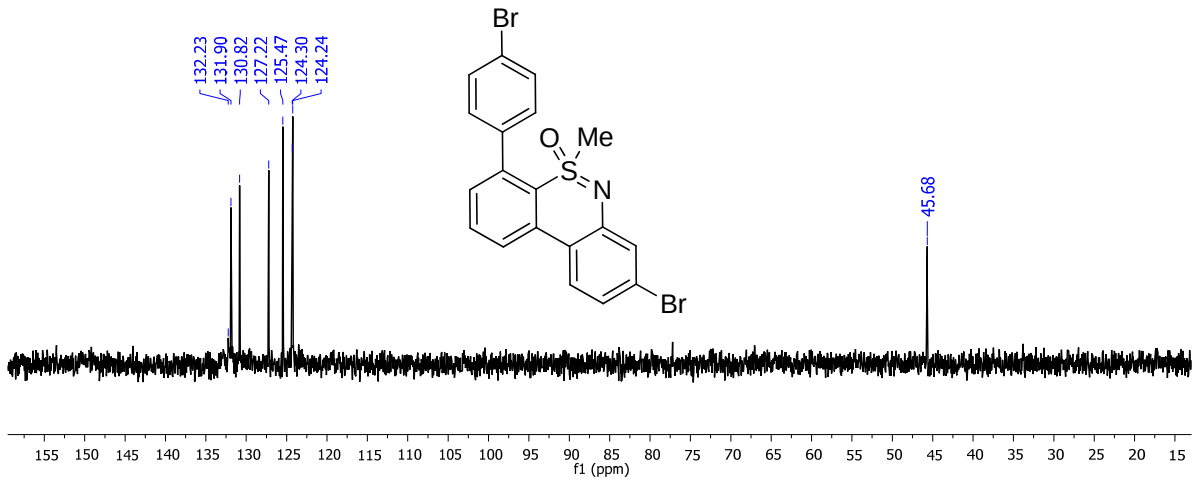




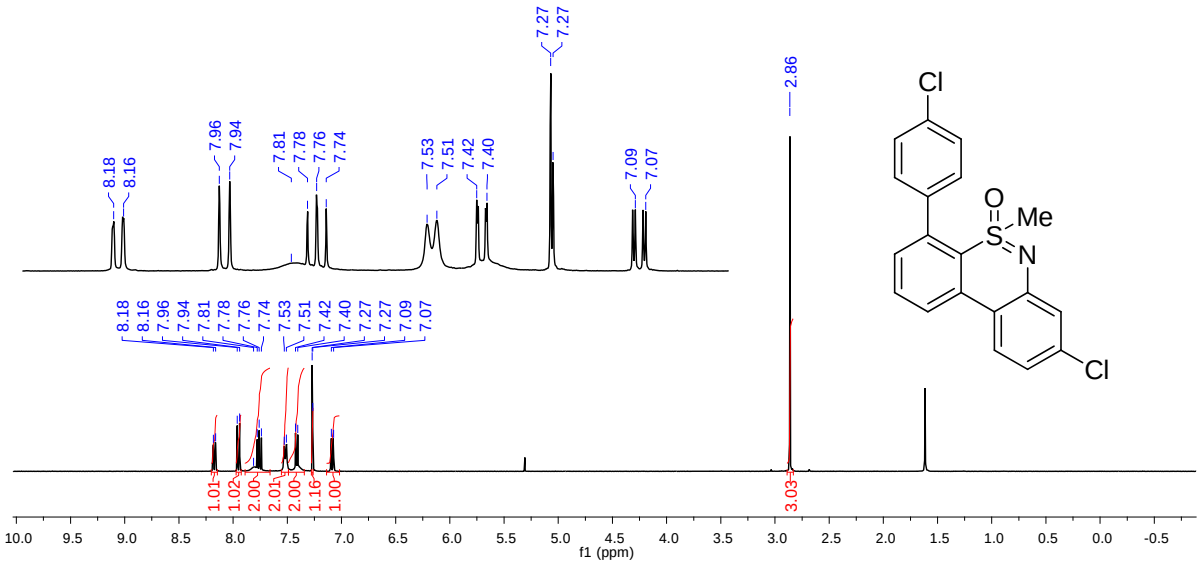
8-Bromo-4-(4-bromophenyl)-5-methyldibenzo[c,e][1,2]thiazine 5-oxide (6e).

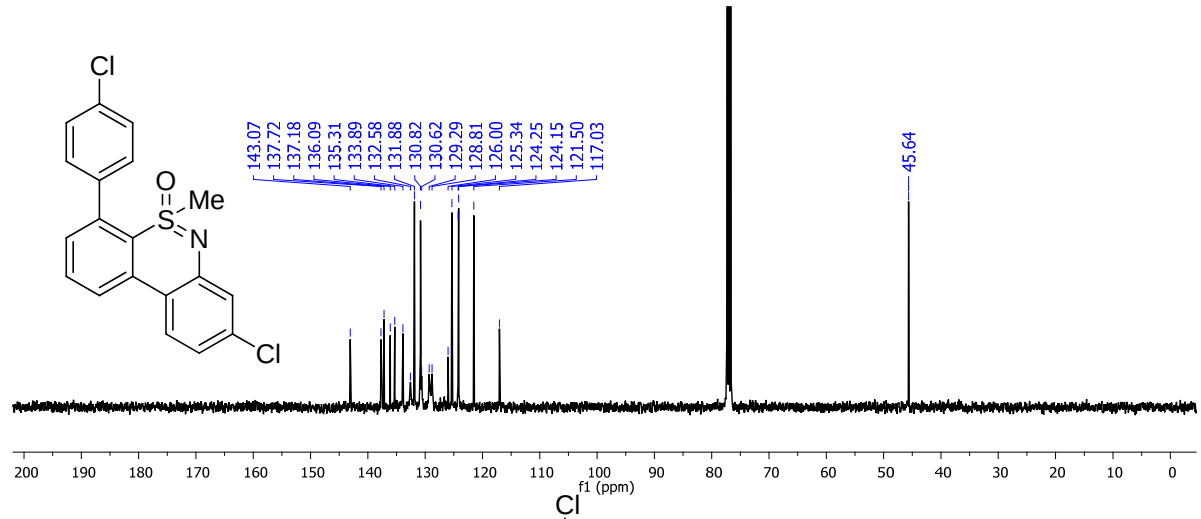


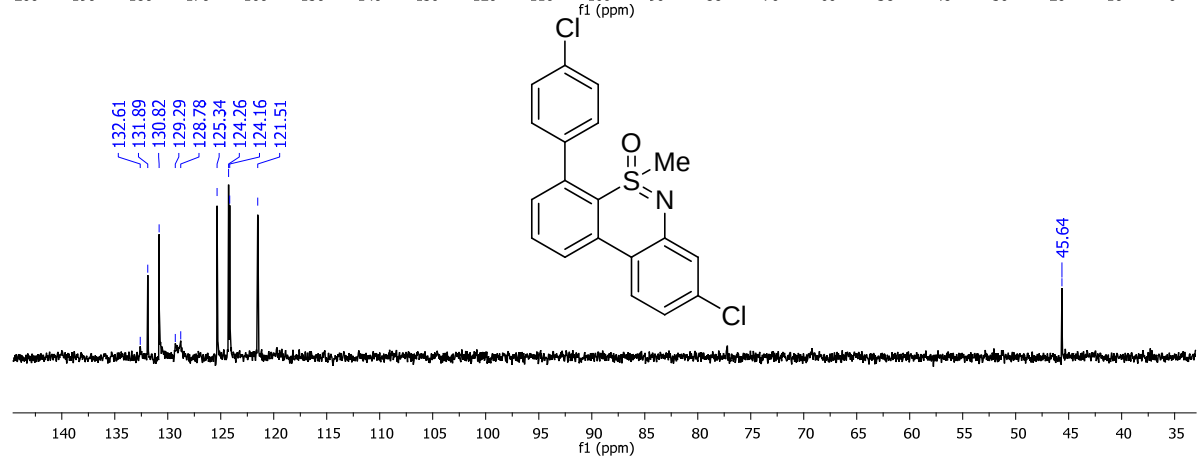




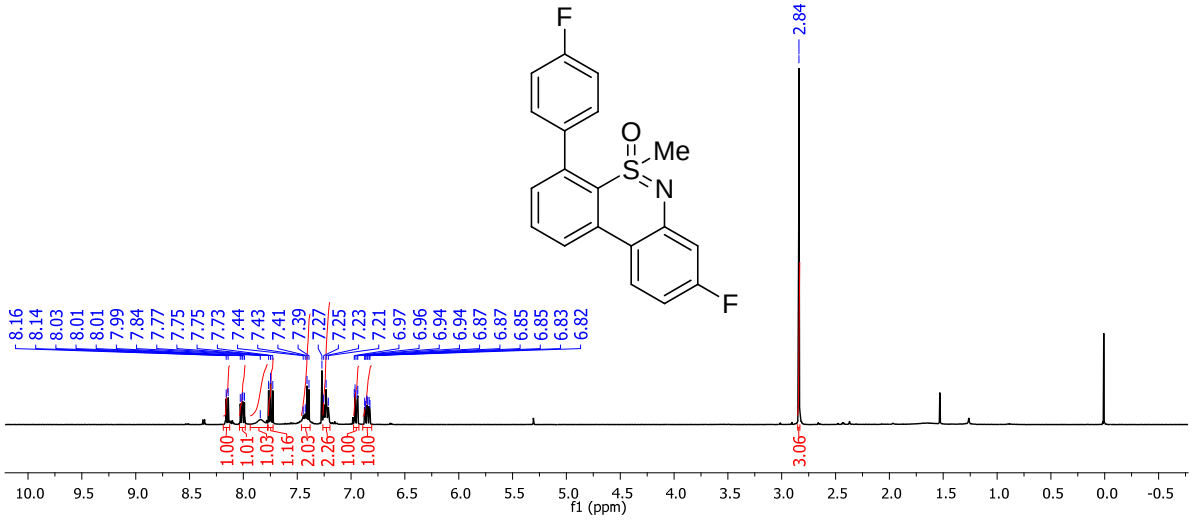
8-Chloro-4-(4-chlorophenyl)-5-methyldibenzo[c,e][1,2]thiazine 5-oxide (6f).

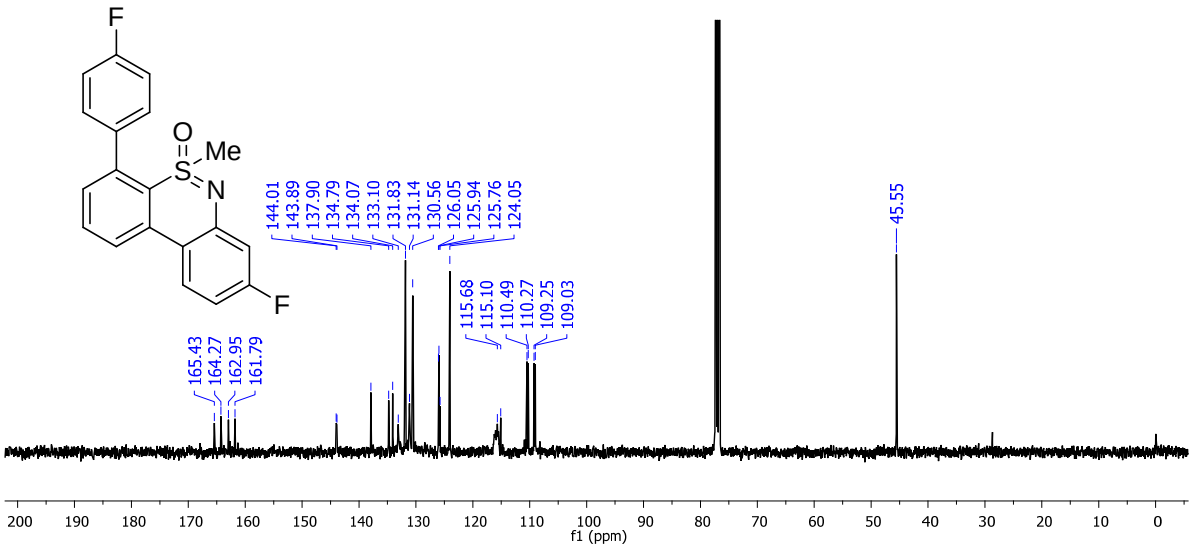


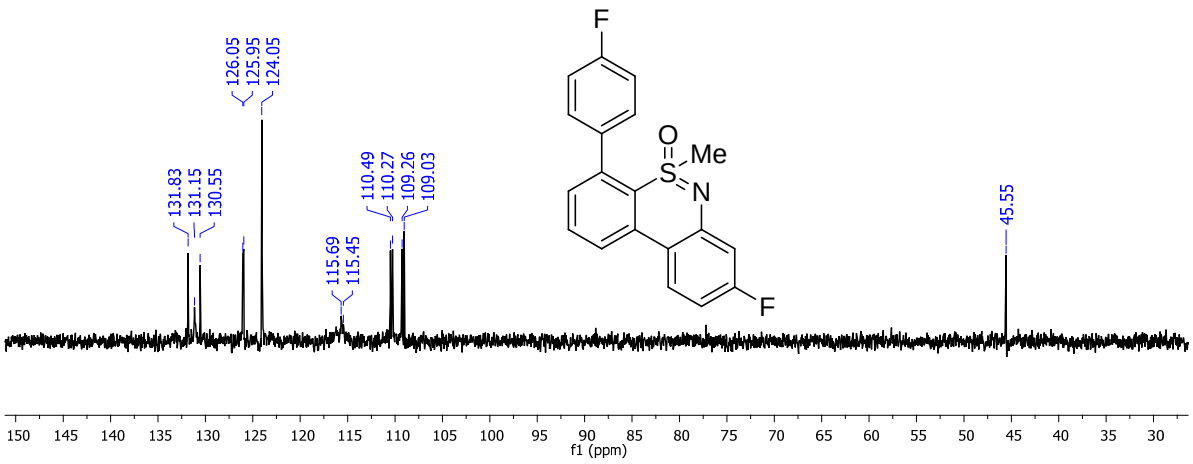




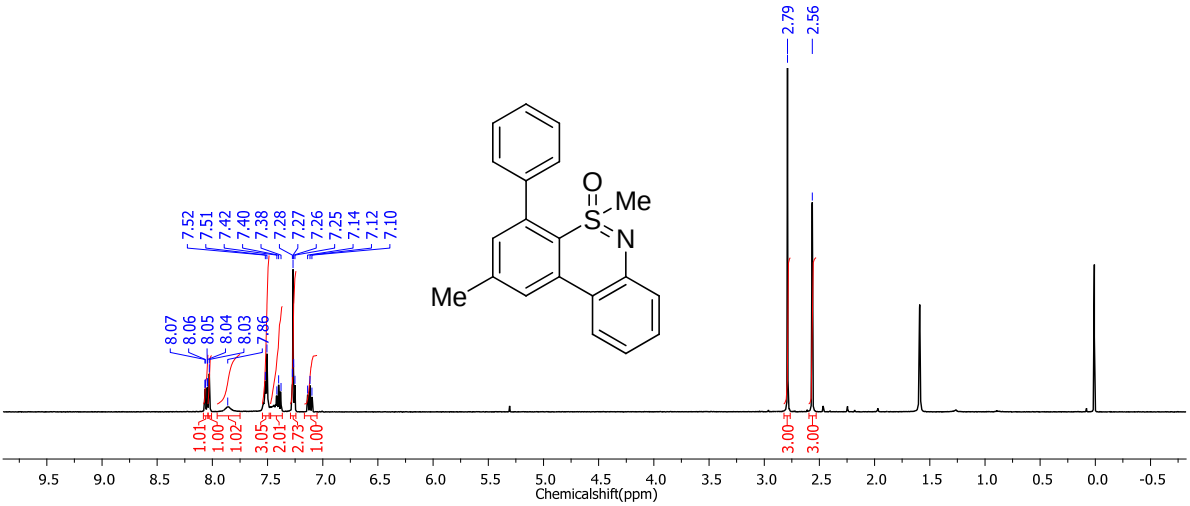
8-Fluoro-4-(4-fluorophenyl)-5-methyldibenzo[c,e][1,2]thiazine 5-oxide (6g).

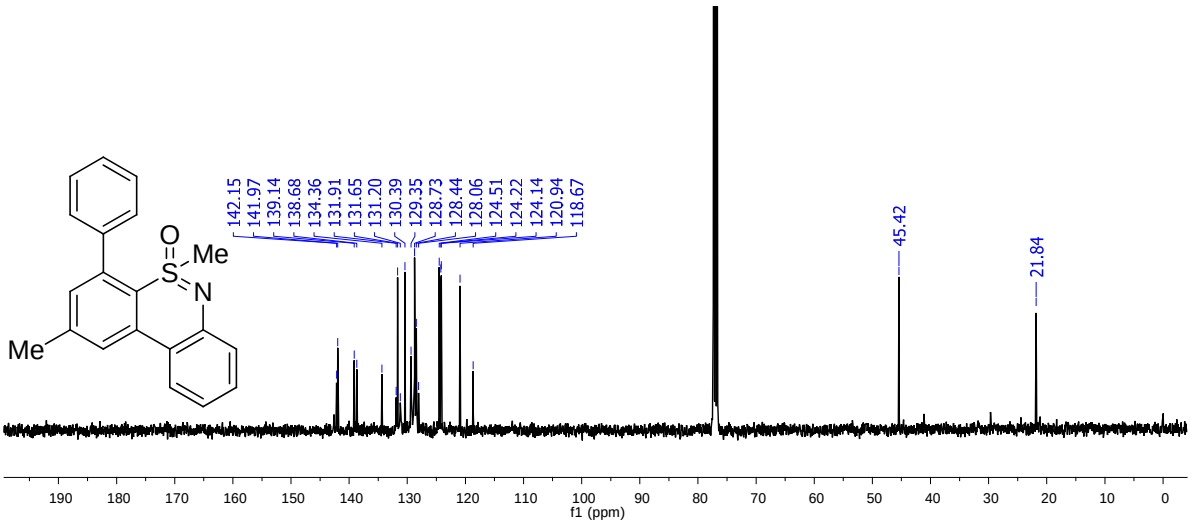


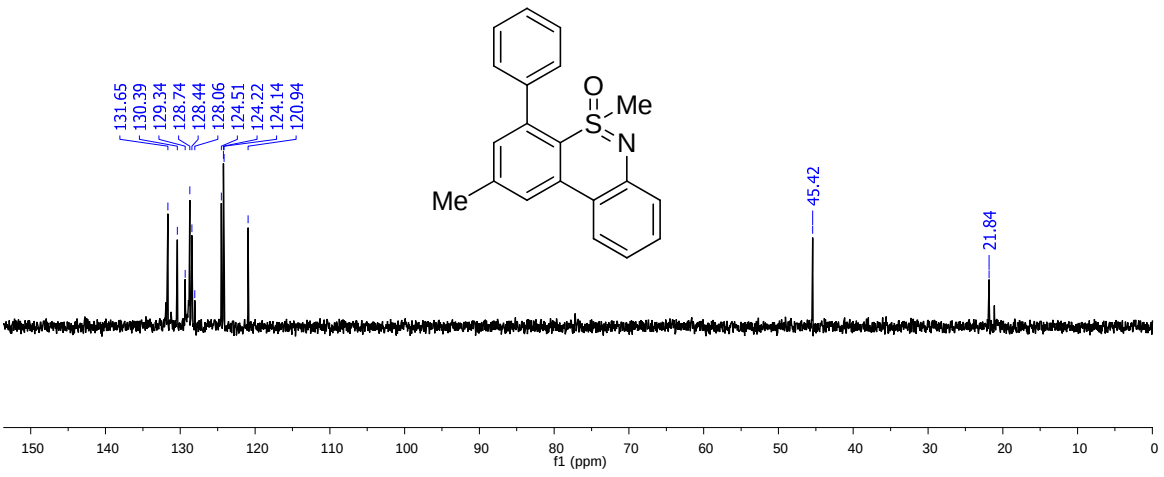




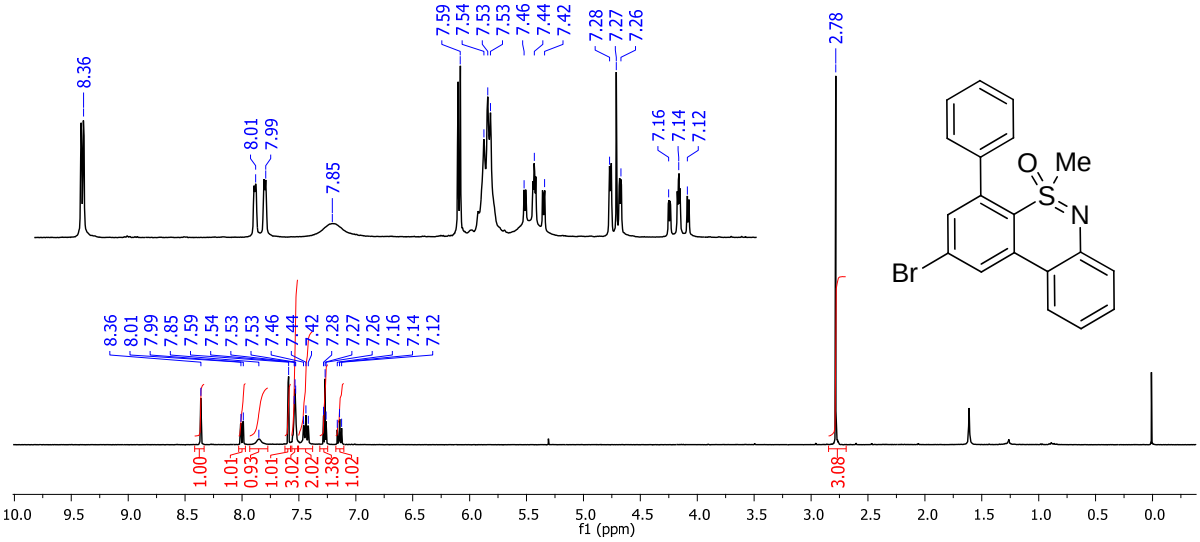
2,5-Dimethyl-4-phenyldibenzo[c,e][1,2]thiazine 5-oxide (6h).

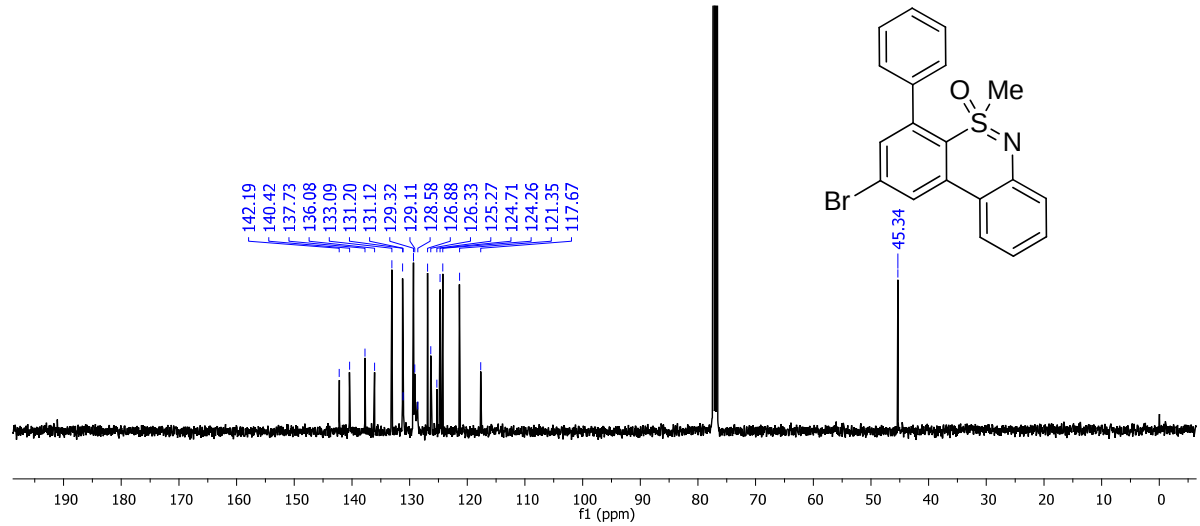


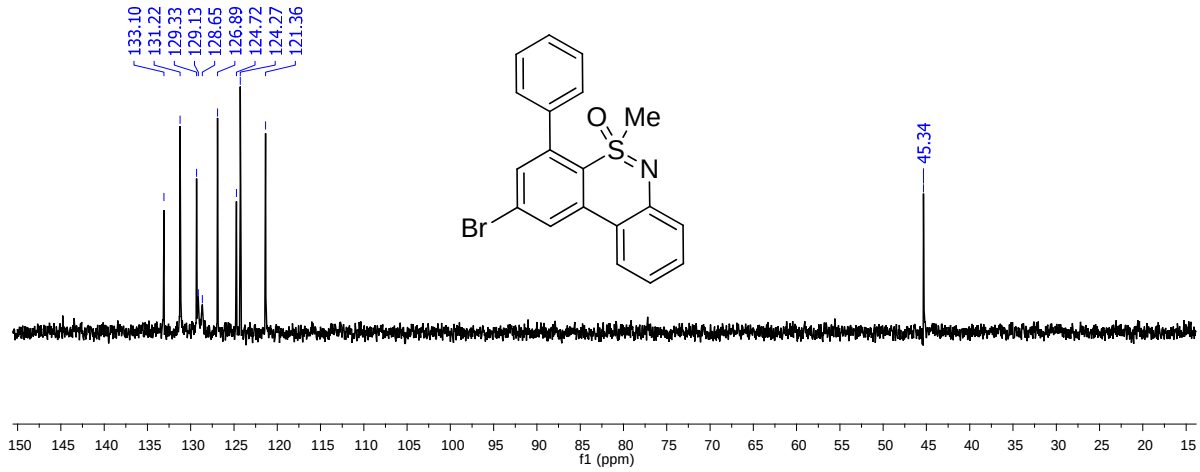




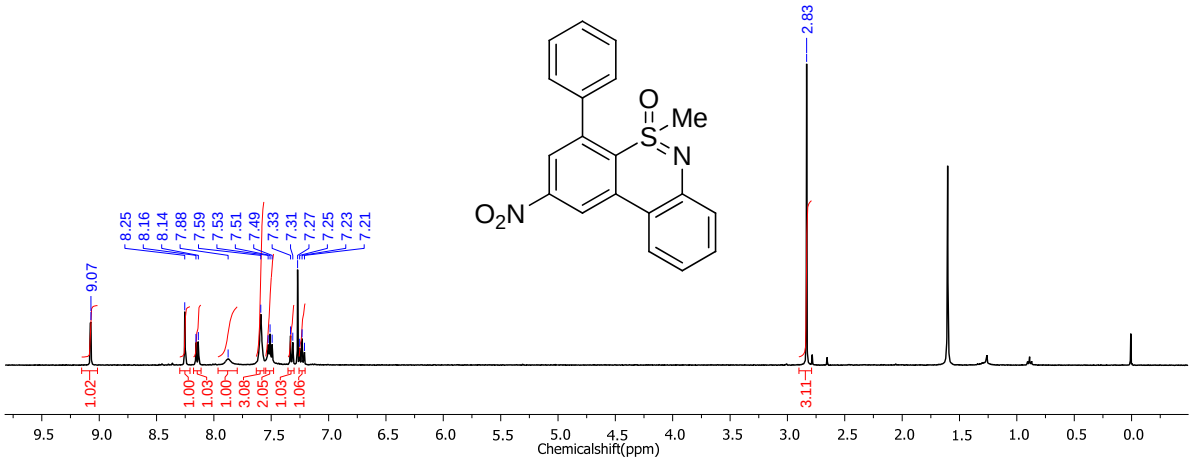
2-Bromo-5-methyl-4-phenyldibenzo[c,e][1,2]thiazine 5-oxide (6i).

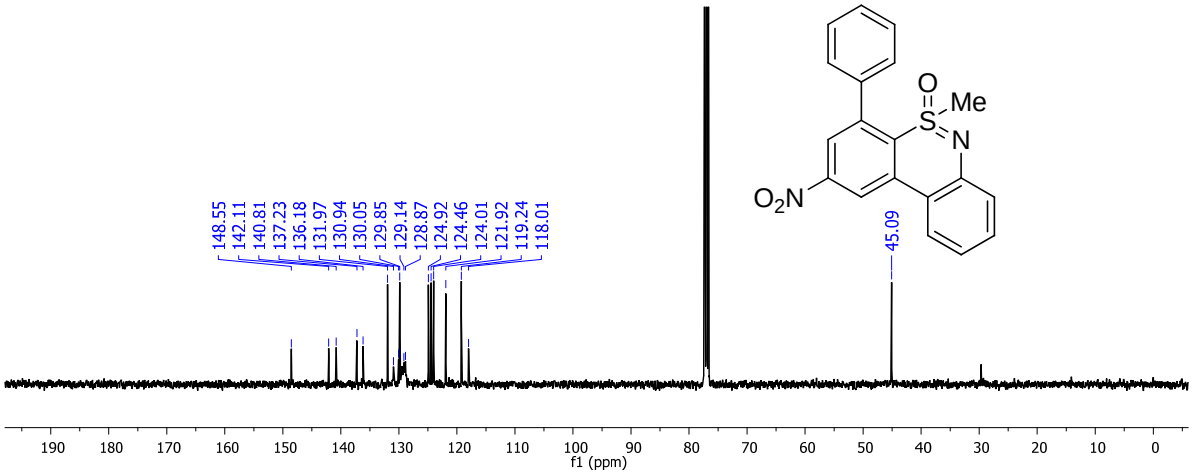


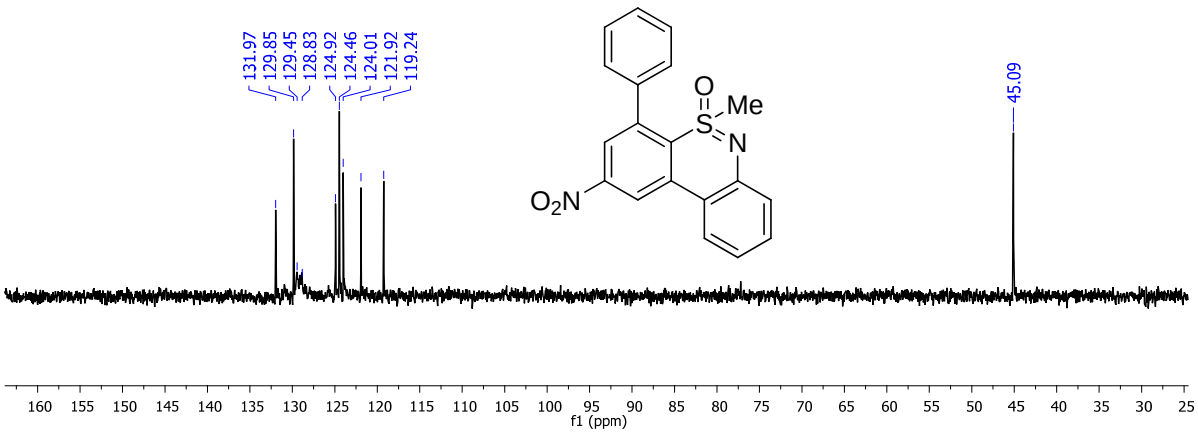




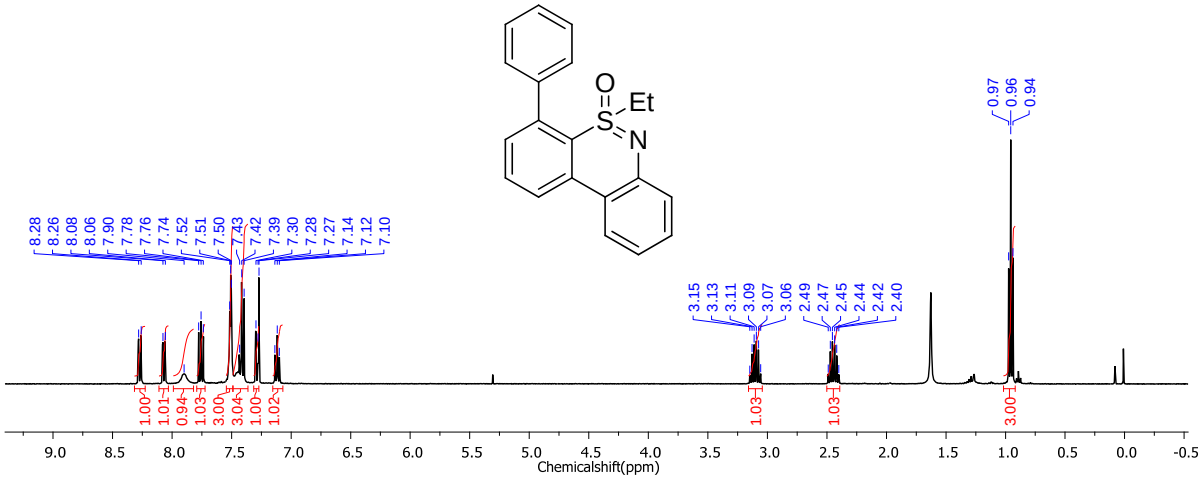
5-Methyl-2-nitro-4-phenyldibenzo[c,e][1,2]thiazine 5-oxide (6j).

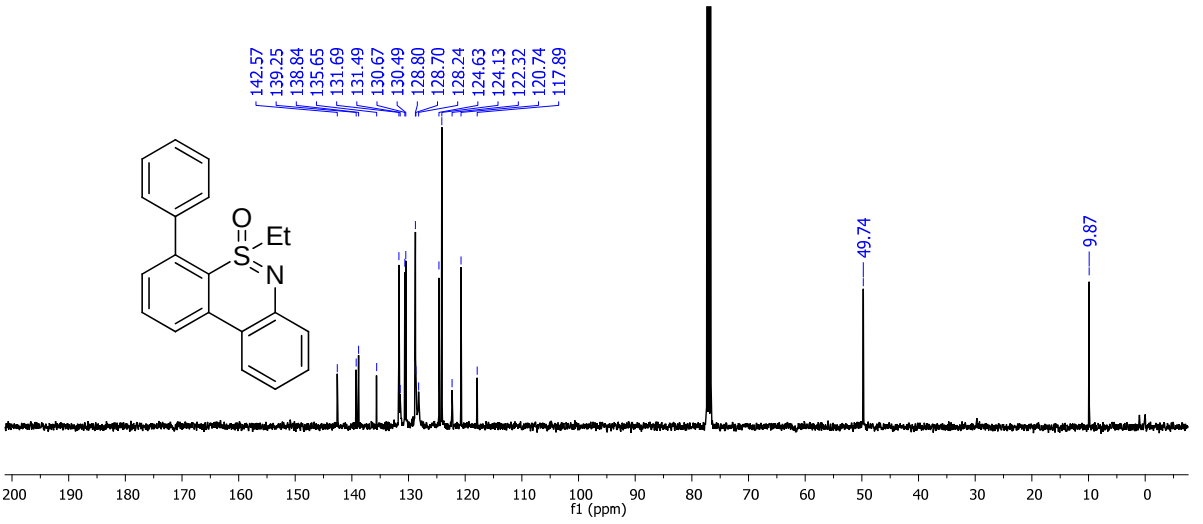


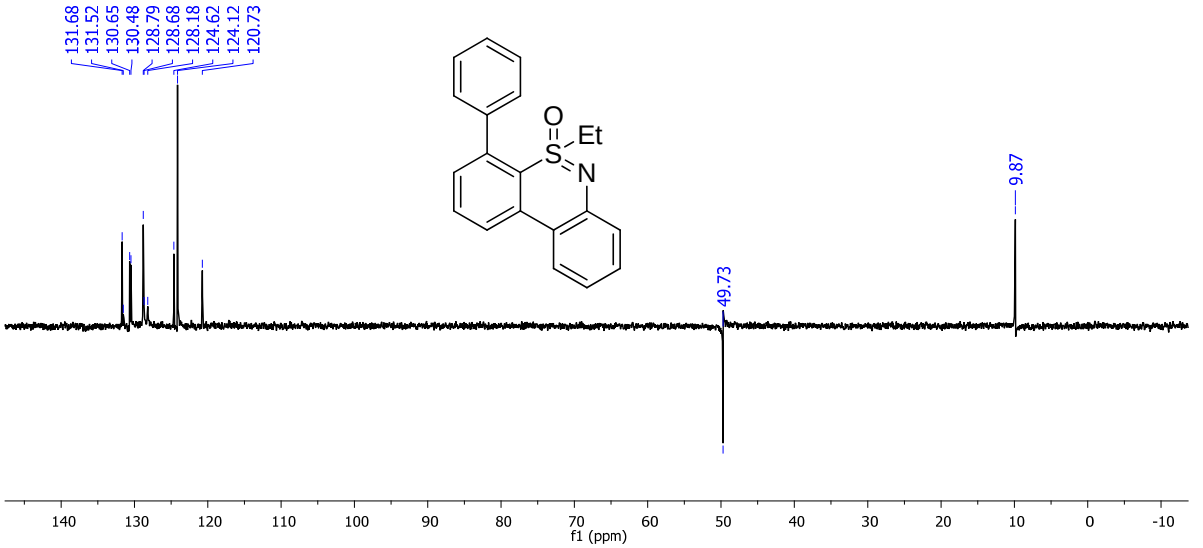




5-Ethyl-4-phenyldibenzo[c,e][1,2]thiazine 5-oxide (6k).







4,5-Dimethyldibenzo[c,e][1,2]thiazine 5-oxide (6l).