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Supporting Information for

Brønsted Acid-Catalyzed Chemodivergent Reactions of *ortho*-Mercaptobenzyl Alcohols with 3-Alkyl-2-vinylindoles and Styrenes: [5+2] Cyclization *versus* Hydroxysulfenylation

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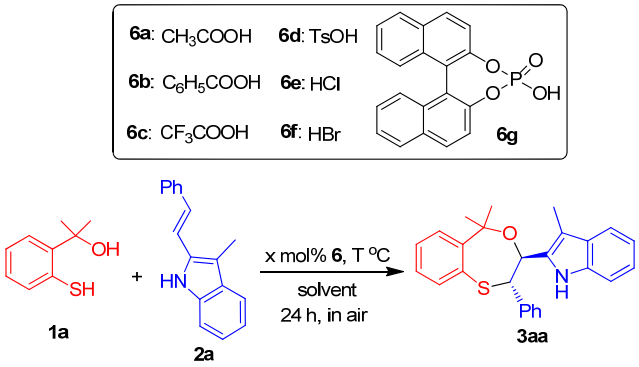
1. General information

^{1}H and ^{13}C NMR spectra were measured respectively at 400 and 100 MHz, respectively. The solvents used for NMR spectroscopy were $CDCl_3$ and acetone-d_6, using tetramethylsilane as the internal reference. HRMS (ESI) was determined by a HRMS/MS instrument. Analytical grade solvents for the column chromatography were used after distillation. All starting materials commercially available were used directly. Substrates **1** and **2** were synthesized according to the literature method.[1]

2. Screening of Catalysts and optimization of reaction conditions

Table 1. Screening of Catalysts and optimization of reaction conditions for [5+2] cyclization[a]



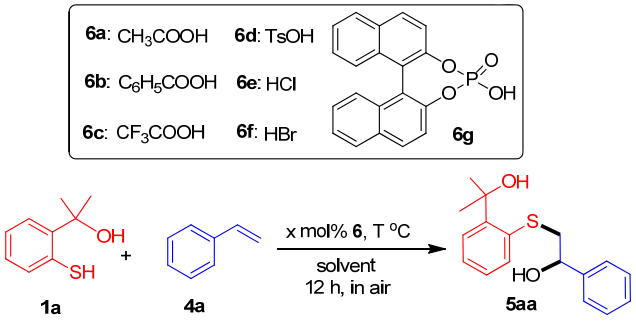
entry	**6** (x mol%)	solvent (v mL)	T (^{o}C)	**1a**:**2a**	dr[b]	yield (%)[c]
1	**6a** (10 mol%)	CH_2ClCH_2Cl (1mL)	25	2:1	>95:5	trace
2	**6b** (10 mol%)	CH_2ClCH_2Cl (1mL)	25	2:1	>95:5	34
3	**6c** (10 mol%)	CH_2ClCH_2Cl (1mL)	25	2:1	>95:5	trace
4	**6d** (10 mol%)	CH_2ClCH_2Cl (1mL)	25	2:1	>95:5	trace
5	**6e** (10 mol%)	CH_2ClCH_2Cl (1mL)	25	2:1	>95:5	trace
6	**6f** (10 mol%)	CH_2ClCH_2Cl (1mL)	25	2:1	>95:5	trace
7	**6g** (10 mol%)	CH_2ClCH_2Cl (1mL)	25	2:1	>95:5	42
8	**6g** (10 mol%)	toluene (1mL)	25	2:1	>95:5	56
9	**6g** (10 mol%)	1,4-dioxane (1mL)	25	2:1	>95:5	19
10	**6g** (10 mol%)	EtOAc (1mL)	25	2:1	>95:5	28
11	**6g** (10 mol%)	CH_3CN (1mL)	25	2:1	>95:5	37
12	**6g** (10 mol%)	ethanol (1mL)	25	2:1	>95:5	trace
13	**6g** (10 mol%)	toluene (1mL)	50	2:1	>95:5	34
14	**6g** (10 mol%)	toluene (1mL)	80	2:1	>95:5	trace
15	**6g** (10 mol%)	toluene (1mL)	25	1:1	>95:5	38

1. a) S. Kamila, O. Khan, H. Zhang, E. Biehl, *Synth. Commun.* **2006**, *36*, 1419; b) W. Tan, X. Li, Y.-X. Gong, M.-D. Ge, F. Shi, *Chem. Commun.* **2014**, *50*, 15901.

16	**6g** (10 mol%)	toluene (1mL)	25	4:1	>95:5	25
17	**6g** (10 mol%)	toluene (1mL)	25	6:1	>95:5	21
18	**6g** (10 mol%)	toluene (1mL)	25	1:2	>95:5	12
19	**6g** (10 mol%)	toluene (1mL)	25	1:3	>95:5	15
20	**6g** (10 mol%)	toluene (1mL)	25	1:4	>95:5	14
21	**6g** (10 mol%)	toluene (2mL)	25	2:1	>95:5	35
22	**6g** (10 mol%)	toluene (4mL)	25	2:1	>95:5	32
23	**6g** (10 mol%)	toluene (6mL)	25	2:1	>95:5	29
24	**6g** (20 mol%)	toluene (1mL)	25	2:1	>95:5	50
25	**6g** (50 mol%)	toluene (1mL)	25	2:1	>95:5	51
26	**6g** (100 mol%)	toluene (1mL)	25	2:1	>95:5	50
27	**6g** (200 mol%)	toluene (1mL)	25	2:1	>95:5	48

[a]Unless indicated otherwise, the reaction was carried out in 0.1 mmol scale catalyzed by x mol% **6** in solvent (v mL) at T ^{o}C for 24 h. [b]The *dr* value was determined by ^{1}H NMR. [c]Isolated yield.

Table 2. Screening of Catalysts and optimization of reaction conditions for hydroxysulfenylation[a]



entry	**6** (x mol%)	solvent	T (^{o}C)	**1a**:**4a**	yield (%)[b]
1	**6a** (100 mol%)	toluene (1mL)	35	2:1	41
2	**6b** (100 mol%)	toluene (1mL)	35	2:1	63
3	**6c** (100 mol%)	toluene (1mL)	35	2:1	trace
4	**6d** (100 mol%)	toluene (1mL)	35	2:1	N.R
5	**6e** (100 mol%)	toluene (1mL)	35	2:1	N.R
6	**6f** (100 mol%)	toluene (1mL)	35	2:1	N.R
7	**6g** (100 mol%)	toluene (1mL)	35	2:1	74
8	**6g** (100 mol%)	$CHCl_3$ (1mL)	35	2:1	84
9	**6g** (100 mol%)	1,4-dioxane (1mL)	35	2:1	66
10	**6g** (100 mol%)	EtOAc (1mL)	35	2:1	44
11	**6g** (100 mol%)	CH_3CN (1mL)	35	2:1	37
12	**6g** (100 mol%)	ethanol (1mL)	35	2:1	47
13	**6g** (100 mol%)	acetone (1mL)	35	2:1	54
14	**6g** (100 mol%)	CH_2ClCH_2Cl (1mL)	35	2:1	63
15	**6g** (100 mol%)	CH_2Cl_2 (1mL)	35	2:1	61
16	**6g** (100 mol%)	$CHCl_3$ (1mL)	35	1:1	49
17	**6g** (100 mol%)	$CHCl_3$ (1mL)	35	3:1	61
18	**6g** (100 mol%)	$CHCl_3$ (1mL)	35	4:1	65
19	**6g** (100 mol%)	$CHCl_3$ (1mL)	35	1:2	47

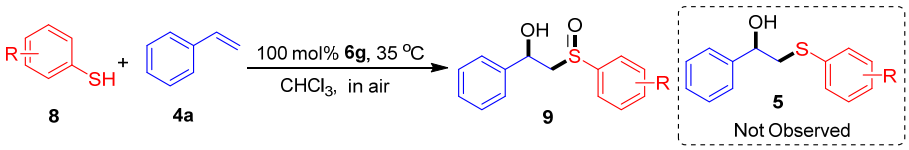
20	**6g** (100 mol%)	$CHCl_3$ (1mL)	35	1:4	50
21	**6g** (100 mol%)	$CHCl_3$ (1mL)	0	2:1	56
22	**6g** (100 mol%)	$CHCl_3$ (1mL)	50	2:1	63
23	**6g** (100 mol%)	$CHCl_3$ (1mL)	80	2:1	trace
24	**6g** (100 mol%)	$CHCl_3$ (0.5mL)	35	2:1	72
25	**6g** (100 mol%)	$CHCl_3$ (2mL)	35	2:1	73
26	**6g** (100 mol%)	$CHCl_3$ (4mL)	35	2:1	64
27	**6g** (10 mol%)	$CHCl_3$ (1mL)	35	2:1	54
28	**6g** (50 mol%)	$CHCl_3$ (1mL)	35	2:1	64
29	**6g** (200 mol%)	$CHCl_3$ (1mL)	35	2:1	61

[a]Unless indicated otherwise, the reaction was carried out in 0.1 mmol scale promoted by x mol% **6** in solvent (v mL) at T°C for 12 h. [b]Isolated yield.

3. Investigation on using thiophenols 8 as substrates

In order to explore the use of thiophenols as a more general class of substrates, several thiophenols **8** were subjected to the reactions with styrene **4a** under the optimal reaction conditions (Table 3). Very interestingly, instead of the expected β-hydroxy sulfides **5**, these reactions afforded the β-hydroxy sulfoxides **9** in generally good yields albeit with low diastereoselectivities. These results indicated that the OH group at the *ortho*-benzylic position of substrates **1** played an important role in directing the reactions with styrenes **4** toward the formation of the β-hydroxy sulfide products **5**.

Table 3. Using thiophenols **8** as substrates under standard conditions[a]

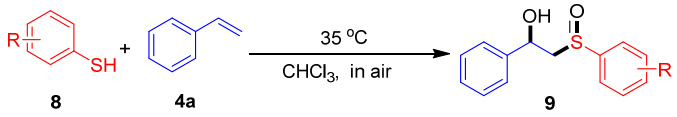


Entry	**9**	R (**8**)	dr[c]	yield (%)[b]
1	**9aa**	H(**8a**)	56:44	78
2	**9ba**	*o*-Me(**8b**)	53:47	63
3	**9ca**	*o*-F(**8c**)	56:44	66
4	**9da**	*m*-Me (**8d**)	56:44	70
5	**9ea**	*p*-Me (**8e**)	56:44	77
6	**9fa**	*p*-F (**8f**)	50:50	87

[a]Unless indicated otherwise, the reaction was carried out in 0.1 mmol scale promoted by 100 mol% **6g** in chloroform (1 mL) at 35°C for 12 h, and the mole ratio of **8**:**4a** was 2:1. [b]Isolated total yield of two diastereomers. [c]The diastereomeric ratio (dr) was determined by ^{1}H NMR.

Besides, the same reactions in Table 3 were also performed in the absence of catalyst **6g** (neutral conditions), which could still generate the products **9** albeit with lower yields (Table 4).

Table 4. Using thiophenols **8** as substrates under neutral conditions[a]



8 **4a** **9**

Entry	**9**	R (**8**)	dr[c]	yield (%)[b]
1	**9aa**	H(**8a**)	53:47	28
2	**9ba**	*o*-Me(**8b**)	50:50	21
3	**9ca**	*o*-F(**8c**)	53:47	17
4	**9da**	*m*-Me (**8d**)	53:47	23
5	**9ea**	*p*-Me (**8e**)	53:47	30
6	**9fa**	*p*-F (**8f**)	50:50	40

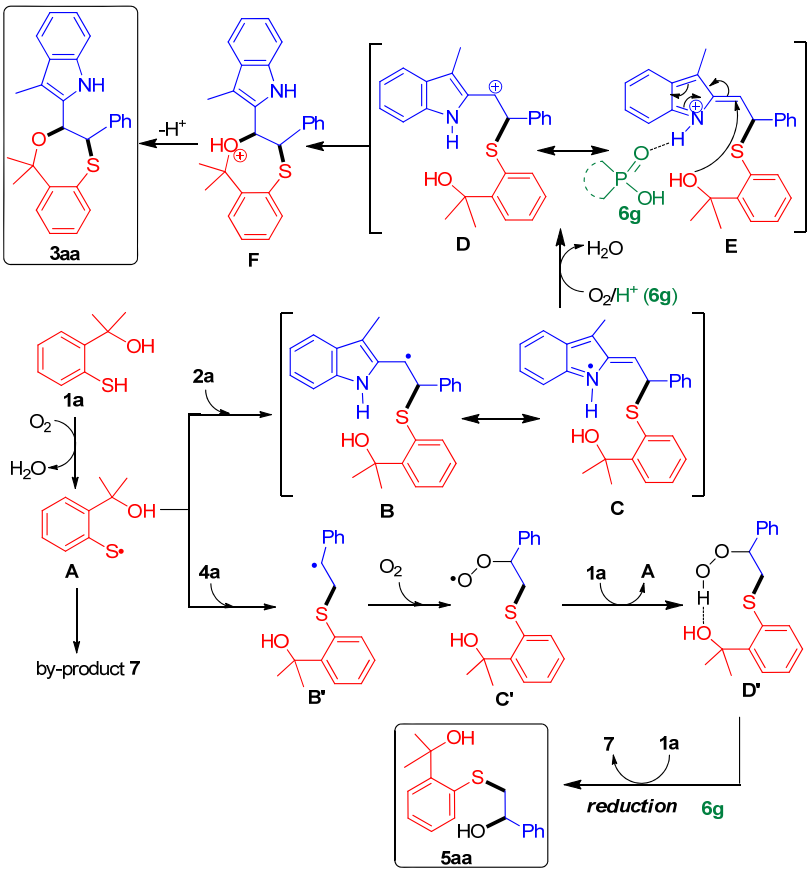
[a]Unless indicated otherwise, the reaction was carried out in 0.1 mmol scale in chloroform (1 mL) at 35°C for 12 h, and the mole ratio of **8**:**4a** was 2:1. [b]Isolated total yield of two diastereomers. [c]The diastereomeric ratio (dr) was determined by ^{1}H NMR.

4. Discussion on the reaction mechanisms

Based on the control experiments and previous reports on hydroxysulfenylation of olefins,[2] we suggested possible reaction mechanisms to explain the formation of products **3aa** and **5aa** (Scheme 1). At the outset, the autoxidation of *ortho*-mercaptobenzyl alcohol **1** generated the arenethiyl radical **A**, which performed an addition to 3-methyl-2-vinylindole **2a** or styrene **4a** to produce carbon-centered radical **B** or **B'**. Then, the two reactions underwent different mechanistic pathways. In the case of 2-vinylindole **2a**, the radical **B** could resonate to radical **C** by the delocalisation of the radical onto the indole ring, thus receiving higher stabilisation. In the presence of oxygen (air) and acid **6g**, the resonant radicals **B** and **C** would be oxidised to give resonant carbocation **D** and vinyliminium **E**, which would be finally trapped by the hydroxyl group at the *ortho*-benzylic position to give the [5+2] cyclization product **3aa** via the deprotonation of oxonium **F**. There might be a hydrogen-bonding interaction between the N-H

[2] a) S.-F. Zhou, X. Pan, Z.-H. Zhou, A. Shoberu, J.-P. Zou, *J. Org. Chem.* **2015**, *80*, 3682; b) H. Wang, Q. Lu, C. Qian, C. Liu, W. Liu, K. Chen, A. Lei, *Angew. Chem. Int. Ed.* **2016**, *55*, 1094.

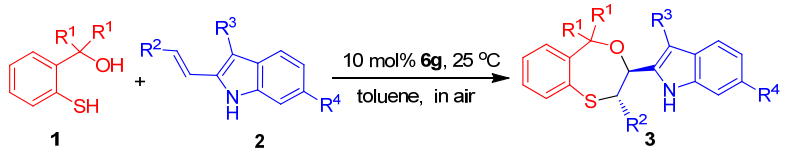
group of vinyliminium **E** and the P=O group of phosphoric acid **6g**,[3] which would facilitate the intramolecular nucleophilic addition of the OH group to vinyliminium **E**. However, in the case of styrene **4a**, the radical **B'** would react with oxygen (air) to generate peroxy radical **C'**, which abstracted the hydrogen from substrate **1a** and became hydroperoxide **D'**. Subsequently, a reduction of hydroperoxides **D'** occurred, which involved a number of single-electron transfer (SET) steps, leading to the oxidation of excess thiol **1a** into disulfide by-product **7** and the generation of hydroxysulfenylation product **5aa**. The role of phosphoric acid **6g** in this transformation was tentatively suggested to act as both a Brønsted acid and an electron shuttle facilitating the SET reactions. Besides, it is suggested that there might be an intramolecular hydrogen bond between the OOH group and the benzylic OH group of hydroperoxy sulphide **D'**. This interaction would act just like a "solvent-bonding" effect[2b] to assist an intermolecular redox process and the production of β-hydroxy sulphides **5**, thus avoiding a self-redox process and the formation of β-hydroxy sulfoxides **9**.



Scheme 1. Suggested reaction mechanisms.

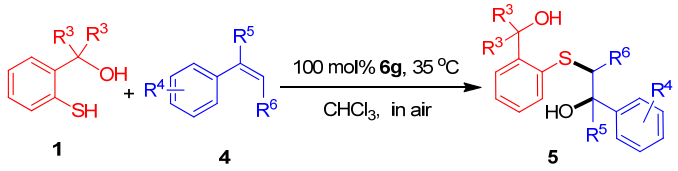
[3] For a review: Y. Chen, L. Wang, J. Xiao, *Asian J. Org. Chem.* **2014**, *3*, 1036.

5. General procedure for the synthesis of products 3, 5 and 9



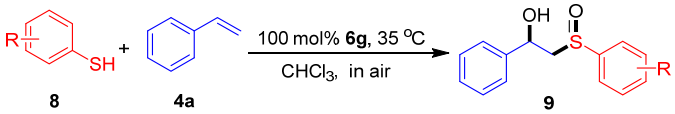
1 2 3

To the mixture of *ortho*-mercaptobenzyl alcohols **1** (0.2 mmol), 3-alkyl-2-vinylindoles **2** (0.1 mmol) and the catalyst **6g** (0.01 mmol), was added toluene (1 mL). After being stirred at 25 °C for 24 h, the reaction mixture was directly purified through flash column chromatography on silica gel to afford pure products **3**.



1 4 5

To the mixture of *ortho*-mercaptobenzyl alcohols **1** (0.2 mmol), styrenes **4** (0.1 mmol) and the catalyst **6g** (0.1 mmol), was added chloroform (1 mL). After being stirred at 35 °C for 12 h, the reaction mixture was directly purified through flash column chromatography or preparative thin layer chromatography on silica gel to afford pure products **5**.



8 4a 9

To the mixture of thiophenols **8** (0.2 mmol), styrene **4a** (0.1 mmol) and the catalyst **6g** (0.1 mmol), was added chloroform (1 mL). After being stirred at 35 °C for 12 h, the reaction mixture was directly purified through preparative thin layer chromatography on silica gel to afford pure products **9**.

6. Characterization data of compounds 3, 5, 7 and 9

2-(5,5-dimethyl-2-phenyl-3,5-dihydro-2*H*-benzo[e][1,4]oxathiepin-3-yl)-3-methyl-1*H*-indole (3aa): Flash column chromatography eluent, petroleum ether/ methylene dichloride = 4/1; Reaction time = 24 h; yield: 56% (22.3 mg); >95:5 dr; white solid; m.p. 143–144 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (s, 1H), 7.67 (dd, *J* = 7.6, 1.3 Hz, 1H), 7.49 – 7.43 (m, 1H), 7.42 – 7.33 (m, 4H), 7.23 – 7.06 (m, 5H), 6.93 – 6.87 (m, 2H), 4.99 (d, *J* = 10.4 Hz, 1H), 4.41 (d, *J* = 10.4 Hz, 1H), 1.76 (s, 3H), 1.68 (s, 3H), 1.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.2, 141.5, 136.7, 136.0, 132.8, 129.3, 129.0, 128.7, 128.4, 128.3, 127.9, 127.6, 127.4, 121.9, 118.8, 118.7, 110.8, 108.2, 83.4, 72.0, 57.7, 31.4, 27.7, 7.6; IR (KBr): 3324, 3059, 2967, 2921, 1873, 1583, 1492, 1454,

1428, 1383, 1308, 1236, 1161, 1057, 754, 735 cm^{-1}; ESI FTMS exact mass calcd for $(C_{26}H_{25}NOS+Na)^+$ requires m/z 422.1549, found m/z 422.1538.

2-(5,5-dimethyl-2-(o-tolyl)-3,5-dihydro-2*H*-benzo[e][1,4]oxathiepin-3-yl)-3-methyl-1*H*-indole (3ab): Flash column chromatography eluent, petroleum ether/ methylene dichloride = 4/1; Reaction time = 24 h; yield: 54% (22.5 mg); >95:5 dr; pale yellow solid; m.p. 148–149 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 8.36 (s, 1H), 7.60 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.45 – 7.40 (m, 1H), 7.38 – 7.29 (m, 4H), 7.19 – 7.12 (m, 2H), 7.08 – 7.00 (m, 3H), 6.91 – 6.83 (m, 1H), 4.99 (d, *J* = 10.4 Hz, 1H), 4.77 (d, *J* = 10.4 Hz, 1H), 1.73 (s, 3H), 1.65 (s, 3H), 1.61 (s, 3H), 1.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.2, 140.0, 136.6, 135.9, 135.8, 132.6, 130.1, 129.2, 128.8, 128.3, 127.5, 127.1, 126.0, 121.8, 118.9, 118.6, 110.8, 107.9, 83.2, 72.1, 52.2, 31.3, 27.6, 18.9, 7.4; IR (KBr): 3454, 2974, 2925, 1718, 1685, 1542, 1459, 1429, 1380, 1299, 1170, 1067, 943, 732 cm^{-1}; ESI FTMS exact mass calcd for $(C_{27}H_{27}NOS+Na)^+$ requires m/z 436.1706, found m/z 436.1700.

2-(2-(2-fluorophenyl)-5,5-dimethyl-3,5-dihydro-2*H*-benzo[e][1,4]oxathiepin-3-yl)-3-methyl-1*H*-indole (3ac): Flash column chromatography eluent, petroleum ether/ methylene dichloride = 4/1; Reaction time = 24 h; yield: 46% (19.1 mg); >95:5 dr; pale yellow solid; m.p. 160–161 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 8.32 (s, 1H), 7.56 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.46 – 7.40 (m, 1H), 7.38 – 7.28 (m, 4H), 7.18 – 7.07 (m, 2H), 7.06 – 6.99 (m, 2H), 6.96 – 6.90 (m, 1H), 6.82 – 6.74 (m, 1H), 5.03 (d, *J* = 10.5 Hz, 1H), 4.83 (d, *J* = 10.5 Hz, 1H), 1.71 (s, 3H), 1.65 (s, 3H), 1.52 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.8 (*J* = 245.7 Hz), 148.1, 136.7, 136.1, 132.5, 129.3, 128.8 (*J* = 8.4 Hz), 128.6, 128.4, 127.5, 124.0, 123.9, 121.9, 118.8 (*J* = 22.4 Hz), 115.5, 110.8, 107.8, 83.3, 70.6, 49.0, 31.2, 27.7, 7.9; IR (KBr): 3338, 3058, 2978, 2919, 1718, 1585, 1490, 1456, 1301, 1244, 1161, 1058, 935, 748, 733 cm^{-1}; ESI FTMS exact mass calcd for $(C_{26}H_{24}FNOS+Na)^+$ requires m/z 440.1455, found m/z 440.1448.

2-(5,5-dimethyl-2-(m-tolyl)-3,5-dihydro-2*H*-benzo[e][1,4]oxathiepin-3-yl)-3-methyl-1*H*-indole (3ad): Flash column chromatography eluent, petroleum ether/ methylene dichloride = 4/1; Reaction time = 24 h; yield: 50% (20.7 mg); >95:5 dr; white solid; m.p. 145–146 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 8.33 (s, 1H), 7.59 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.45 – 7.40 (m, 1H), 7.38 – 7.29 (m, 4H), 7.19 – 7.13 (m, 1H), 7.07 – 6.93 (m, 3H), 6.63 (d, *J* = 9.0 Hz, 2H), 4.95 (d, *J* = 10.4 Hz, 1H), 4.30 (d, *J* = 10.4 Hz, 1H), 2.14 (s, 3H), 1.72 (s, 3H), 1.65 (s, 3H), 1.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.1, 141.2, 137.8, 136.8, 135.9, 132.9, 129.2, 128.9, 128.7, 128.5, 128.2,

127.4, 124.7, 121.7, 118.8, 118.6, 110.7, 108.0, 83.2, 71.8, 57.6, 31.3, 27.6, 21.3, 7.7; IR (KBr): 3369, 3058, 2970, 2922, 1456, 1383, 1299, 1235, 1170, 1056, 943, 775, 733 cm^{-1}; ESI FTMS exact mass calcd for $(C_{27}H_{27}NOS+Na)^+$ requires m/z 436.1706, found m/z 436.1704.

2-(2-(3-fluorophenyl)-5,5-dimethyl-3,5-dihydro-2*H*-benzo[e][1,4]oxathiepin-3-yl)-3-methyl-1*H*-indole (3ae): Flash column chromatography eluent, petroleum ether/ methylene dichloride = 4/1; Reaction time = 24 h; yield: 42% (17.7 mg); >95:5 dr; white solid; m.p. 158–159 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 8.33 (s, 1H), 7.61 (dd, *J* = 7.5, 1.3 Hz, 1H), 7.47 – 7.41 (m, 1H), 7.40 – 7.31 (m, 4H), 7.21 – 7.15 (m, 1H), 7.09 – 6.99 (m, 2H), 6.89 – 6.80 (m, 1H), 6.69 – 6.61 (m, 1H), 6.55 (d, *J* = 7.7 Hz, 1H), 4.89 (d, *J* = 10.3 Hz, 1H), 4.33 (d, *J* = 10.3 Hz, 1H), 1.71 (s, 3H), 1.63 (s, 3H), 1.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.5 (*J* = 244.4 Hz), 148.1, 144.0, 143.9, 136.7, 136.0, 132.5, 129.7 (*J* = 8.3 Hz), 129.5, 128.6, 128.4, 127.6, 123.7, 121.9, 119.0 (*J* = 24.5 Hz), 114.6, 114.3 (*J* = 21.3 Hz), 110.8, 108.1, 83.4, 71.7, 57.0, 31.2, 27.7, 7.7; IR (KBr): 3337, 3062, 2968, 2921, 2855, 1718, 1611, 1588, 1444, 1305, 1258, 1160, 1056, 961, 779, 736,692 cm^{-1}; ESI FTMS exact mass calcd for $(C_{26}H_{24}FNOS+Na)^+$ requires m/z 440.1455, found m/z 440.1450.

2-(5,5-dimethyl-2-(p-tolyl)-3,5-dihydro-2*H*-benzo[e][1,4]oxathiepin-3-yl)-3-methyl-1*H*-indole (3af): Flash column chromatography eluent, petroleum ether/ methylene dichloride = 4/1; Reaction time = 24 h; yield: 50% (20.6 mg); >95:5 dr; pale yellow solid; m.p. 161–162 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 8.32 (s, 1H), 7.60 (dd, *J* = 7.6, 1.3 Hz, 1H), 7.45 – 7.39 (m, 1H), 7.37 – 7.29 (m, 4H), 7.19 – 7.13 (m, 1H), 7.07 – 7.01 (m, 1H), 6.90 (d, *J* = 7.9 Hz, 2H), 6.73 (d, *J* = 8.1 Hz, 2H), 4.93 (d, *J* = 10.4 Hz, 1H), 4.32 (d, *J* = 10.4 Hz, 1H), 2.24 (s, 3H), 1.71 (s, 3H), 1.64 (s, 3H), 1.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.1, 138.4, 137.0, 136.6, 135.9, 132.9, 129.2, 129.0, 128.9, 128.7, 128.2, 127.6, 127.4, 121.7, 118.8, 118.7, 110.7, 108.0, 83.2, 71.8, 57.4, 31.3, 27.6, 21.1, 7.7; IR (KBr): 3337, 2966, 2919, 2815, 1653, 1513, 1457, 1427, 1384, 1303, 1237, 1172, 1058, 822, 755, 730 cm^{-1}; ESI FTMS exact mass calcd for $(C_{27}H_{27}NOS+Na)^+$ requires m/z 436.1706, found m/z 436.1698.

2-(2-(4-fluorophenyl)-5,5-dimethyl-3,5-dihydro-2*H*-benzo[e][1,4]oxathiepin-3-yl)-3-methyl-1*H*-indole (3ag): Flash column chromatography eluent, petroleum ether/ methylene dichloride = 4/1; Reaction time = 24 h; yield: 49% (20.6 mg); >95:5 dr; white solid; m.p. 130–131 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 8.32 (s, 1H), 7.61 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.46 – 7.40 (m, 1H), 7.38

– 7.30 (m, 4H), 7.21 – 7.14 (m, 1H), 7.08 – 7.03 (m, 1H), 6.86 – 6.73 (m, 4H), 4.87 (d, *J* = 10.4 Hz, 1H), 4.34 (d, *J* = 10.4 Hz, 1H), 1.70 (s, 3H), 1.63 (s, 3H), 1.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.0 (*J* = 244.6 Hz), 148.1, 137.4, 137.3, 136.5, 136.0, 132.5, 129.4 (*J* = 7.9 Hz), 128.6, 128.5, 128.3, 127.6, 121.9, 119.0, 118.8, 115.1 (*J* = 21.3 Hz), 110.7, 108.1, 83.3, 71.9, 56.9, 31.2, 27.6, 7.7; IR (KBr): 3367, 2923, 1718, 1654, 1605, 1509, 1458, 1226, 1055, 841, 758, 739 cm^{-1}; ESI FTMS exact mass calcd for $(C_{26}H_{24}FNOS+Na)^+$ requires m/z 440.1455, found m/z 440.1465.

2-(2-(4-chlorophenyl)-5,5-dimethyl-3,5-dihydro-2*H*-benzo[e][1,4]oxathiepin-3-yl)-3-methyl-1*H*-indole (3ah): Flash column chromatography eluent, petroleum ether/ methylene dichloride = 4/1; Reaction time = 24 h; yield: 51% (22.2 mg); >95:5 dr; pale yellow solid; m.p. 163–164 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (s, 1H), 7.60 (dd, *J* = 7.5, 1.3 Hz, 1H), 7.48 – 7.41 (m, 1H), 7.40 – 7.30 (m, 4H), 7.20 – 7.11 (m, 2H), 7.09 – 6.98 (m, 2H), 6.91 (t, *J* = 1.8 Hz, 1H), 6.64 (d, *J* = 7.8 Hz, 1H), 4.89 (d, *J* = 10.3 Hz, 1H), 4.30 (d, *J* = 10.3 Hz, 1H), 1.71 (s, 3H), 1.63 (s, 3H), 1.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.0, 143.5, 136.7, 136.0, 133.9, 132.4, 129.6, 129.5, 128.7, 128.5, 128.3, 127.8, 127.7, 127.5, 126.1, 121.9, 119.1, 118.8, 110.8, 108.0, 83.4, 71.6, 56.9, 31.2, 27.7, 7.7.; IR (KBr): 3360, 3061, 2971, 2922, 1594, 1573, 1455, 1427, 1382, 1306, 1235, 1189, 1158, 1055, 936, 906, 751, 736. 697 cm^{-1}; ESI FTMS exact mass calcd for $(C_{26}H_{24}ClNOS+Na)^+$ requires m/z 456.1159, found m/z 456.1150.

2-(2-ethyl-5,5-dimethyl-3,5-dihydro-2*H*-benzo[e][1,4]oxathiepin-3-yl)-3-methyl-1*H*-indole (3ai): Flash column chromatography eluent, petroleum ether/ methylene dichloride = 4/1; Reaction time = 24 h; yield: 52% (18.2 mg); >95:5 dr; white solid; m.p. 156–157 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (s, 1H), 7.58 – 7.49 (m, 2H), 7.36 (dd, *J* = 11.7, 4.8 Hz, 2H), 7.30 – 7.27 (m, 1H), 7.25 – 7.17 (m, 2H), 7.14 – 7.08 (m, 1H), 4.42 (d, *J* = 10.2 Hz, 1H), 3.23 – 3.14 (m, 1H), 2.17 (s, 3H), 1.64 (s, 3H), 1.59 (s, 3H), 1.49 – 1.40 (m, 1H), 1.26 – 1.18 (m, 1H), 0.97 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.7, 137.4, 136.0, 134.0, 129.1, 128.6, 127.8, 127.5, 127.3, 122.1, 119.2, 118.7, 110.9, 107.9, 83.0, 70.1, 57.1, 31.0, 27.7, 24.6, 12.2, 9.0; IR (KBr): 3708, 3339, 2927, 2921, 1651, 1456, 1381, 1304, 1237, 1172, 1055, 812, 759, 736 cm^{-1}; ESI FTMS exact mass calcd for $(C_{22}H_{25}NOS+Na)^+$ requires m/z 374.1549, found m/z 374.1553.

2-(5,5-dimethyl-2-phenyl-3,5-dihydro-2*H*-benzo[e][1,4]oxathiepin-3-yl)-3-ethyl-1*H*-indole (3aj): Flash column chromatography eluent, petroleum ether/ methylene dichloride = 4/1; Reaction time = 24 h; yield: 44% (18.1 mg); >95:5 dr; white solid; m.p. 142–143 ^{o}C; ^{1}H NMR

(400 MHz, $CDCl_3$) δ 8.28 (s, 1H), 7.60 (dd, *J* = 7.6, 1.3 Hz, 1H), 7.45 – 7.29 (m, 5H), 7.19 – 7.01 (m, 5H), 6.87 – 6.81 (m, 2H), 4.94 (d, *J* = 10.4 Hz, 1H), 4.41 (d, *J* = 10.4 Hz, 1H), 2.03 – 1.92 (m, 2H), 1.69 (s, 3H), 1.63 (s, 3H), 0.55 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.2, 141.5, 136.7, 136.4, 132.3, 129.4, 128.8, 128.3, 127.8, 127.5, 127.4, 121.8, 119.2, 118.8, 114.8, 110.9, 83.3, 71.6, 57.7, 31.3, 27.7, 16.9, 14.4; IR (KBr): 3365, 2924, 1686, 1560, 1542, 1458, 1437, 1388, 1336, 1299, 1057, 742, 699 cm^{-1}; ESI FTMS exact mass calcd for $(C_{27}H_{27}NOS+Na)^+$ requires m/z 436.1706, found m/z 436.1715.

6-chloro-2-(5,5-dimethyl-2-phenyl-3,5-dihydro-2*H*-benzo[e][1,4]oxathiepin-3-yl)-3-methyl-1*H*-indole (3ak): Flash column chromatography eluent, petroleum ether/ methylene dichloride = 4/1; Reaction time = 24 h; yield: 41% (17.8 mg); >95:5 dr; pale yellow solid; m.p. 161–162 ^oC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (s, 1H), 7.62 (dd, *J* = 7.5, 1.3 Hz, 1H), 7.45 – 7.39 (m, 1H), 7.37 – 7.29 (m, 3H), 7.20 (d, *J* = 8.4 Hz, 1H), 7.17 – 7.06 (m, 3H), 7.02 – 6.97 (m, 1H), 6.87 – 6.80 (m, 2H), 4.90 (d, *J* = 10.4 Hz, 1H), 4.30 (d, *J* = 10.4 Hz, 1H), 1.71 (s, 3H), 1.63 (s, 3H), 1.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.0, 141.2, 136.6, 136.2, 133.4, 129.2, 128.9, 128.4, 128.3, 127.7, 127.5, 127.2, 119.6, 110.7, 108.2, 83.3, 71.9, 57.6, 31.2, 27.6, 7.4; IR (KBr): 3310, 2967, 2922, 1718, 1617, 1458, 1426, 1383, 1240, 1173, 1058, 916, 839, 794, 698 cm^{-1}; ESI FTMS exact mass calcd for $(C_{26}H_{24}ClNOS+Na)^+$ requires m/z 456.1159, found m/z 456.1145.

2-(5,5-diethyl-2-phenyl-3,5-dihydro-2*H*-benzo[e][1,4]oxathiepin-3-yl)-3-methyl-1*H*-indole (3ba): Flash column chromatography eluent, petroleum ether/ methylene dichloride = 4/1; Reaction time = 24 h; yield: 45% (19.1 mg); >95:5 dr; white solid; m.p. 163–164 ^oC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (s, 1H), 7.67 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.45 – 7.40 (m, 1H), 7.38 – 7.27 (m, 4H), 7.19 – 7.10 (m, 2H), 7.10 – 7.02 (m, 3H), 6.85 – 6.78 (m, 2H), 4.90 (d, *J* = 10.4 Hz, 1H), 4.34 (d, *J* = 10.3 Hz, 1H), 2.39 – 2.28 (m, 1H), 2.12 – 2.03 (m, 1H), 1.99 – 1.88 (m, 2H), 1.30 (s, 3H), 0.78 (t, *J* = 7.6 Hz, 3H), 0.68 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.7, 141.7, 137.0, 136.0, 132.7, 130.0, 128.8, 128.6, 128.2, 127.8, 127.2, 121.7, 118.7, 110.7, 108.4, 88.4, 71.9, 57.7, 32.0, 28.7, 8.9, 7.6; IR (KBr): 3382, 2967, 1654, 1542, 1490, 1458, 1300, 1074, 754, 731, 669 cm^{-1}; ESI FTMS exact mass calcd for $(C_{28}H_{29}NOS+Na)^+$ requires m/z 450.1862, found m/z 450.1855.

3-methyl-2-(2-phenyl-3,5-dihydro-2*H*-benzo[e][1,4]oxathiepin-3-yl)-1*H*-indole (3ca): Flash column chromatography eluent, petroleum ether/ methylene dichloride = 4/1; Reaction time = 24

h; yield: 51% (18.9 mg); >95:5 dr; yellow sticky oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (s, 1H), 7.69 (dd, *J* = 7.3, 1.3 Hz, 1H), 7.43 – 7.29 (m, 4H), 7.19 (d, *J* = 8.1 Hz, 1H), 7.16 – 7.04 (m, 6H), 7.02 – 6.96 (m, 1H), 5.35 – 5.28 (m, 2H), 5.02 (d, *J* = 13.0 Hz, 1H), 4.16 (d, *J* = 9.5 Hz, 1H), 1.70 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.9, 137.7, 136.5, 135.7, 132.9, 132.6, 129.2, 128.6, 128.3, 127.8, 121.9, 118.8, 110.6, 109.1, 82.6, 75.0, 56.8, 8.2; IR (KBr): 3586, 3420, 3056, 2917, 2850, 1716, 1669, 1607, 1457, 1303, 1209, 1075, 1007, 736, 697 cm^{-1}; ESI FTMS exact mass calcd for $(C_{24}H_{21}NOS+Na)^+$ requires m/z 394.1237, found m/z 394.1243.

2-(2-((2-hydroxy-2-phenylethyl)thio)phenyl)propan-2-ol (5aa): Preparative thin layer chromatography, methylbenzene/ ethyl acetate = 2/1; Reaction time = 12 h; yield: 84% (24.2 mg); white solid; m.p. 74–75 °C; ^{1}H NMR (400 MHz, Acetone-d_6) δ 7.67 – 7.61 (m, 1H), 7.56 – 7.51 (m, 1H), 7.46 – 7.38 (m, 2H), 7.36 – 7.30 (m, 2H), 7.28 – 7.13 (m, 3H), 4.92 – 4.81 (m, 1H), 4.74 (d, *J* = 4.2 Hz, 1H), 4.50 (s, 1H), 3.32 (dd, *J* = 13.0, 4.6 Hz, 1H), 3.24 (dd, *J* = 13.0, 8.2 Hz, 1H), 1.68 (s, 3H), 1.67 (s, 3H); ^{13}C NMR (100 MHz, Acetone-d_6) δ 149.0, 144.2, 134.0, 132.2, 128.1, 127.3, 127.2, 126.1, 126.0, 125.9, 72.5, 71.8, 45.4; IR (KBr): 3356, 3045, 2983, 2934, 1686, 1562, 1432, 1366, 1241, 1165, 1057, 968, 867, 758, 746 cm^{-1}; ESI FTMS exact mass calcd for $(C_{17}H_{20}O_2S+Na)^+$ requires m/z 311.1076, found m/z 311.1070.

2-(2-((2-hydroxy-2-(o-tolyl)ethyl)thio)phenyl)propan-2-ol (5ab): Preparative thin layer chromatography, methylbenzene/ ethyl acetate = 2/1; Reaction time = 12 h; yield: 79% (24.0 mg); white sticky oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.53 (m, 1H), 7.51 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.47 – 7.42 (m, 1H), 7.28 – 7.23 (m, 2H), 7.22 – 7.13 (m, 2H), 7.07 (d, *J* = 7.1 Hz, 1H), 5.11 (s, 1H), 4.88 (dd, *J* = 10.0, 2.1 Hz, 1H), 3.41 (s, 1H), 3.23 (dd, *J* = 13.8, 2.5 Hz, 1H), 3.02 (dd, *J* = 13.8, 10.0 Hz, 1H), 2.08 (s, 3H), 1.69 (s, 3H), 1.68 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.3, 140.7, 135.4, 134.1, 131.9, 130.4, 127.8, 127.7, 127.6, 126.4, 126.2, 125.3, 73.9, 68.1, 45.6, 32.0, 30.6, 18.7; IR (KBr): 3387, 3055, 2973, 2924, 1586, 1462, 1431, 1365, 1231, 1164, 1047, 948, 857, 759, 736 cm^{-1}; ESI FTMS exact mass calcd for $(C_{18}H_{22}O_2S+Na)^+$ requires m/z 325.1233, found m/z 325.1228.

2-(2-((2-(2-chlorophenyl)-2-hydroxyethyl)thio)phenyl)propan-2-ol (5ac): Preparative thin layer chromatography, methylbenzene/ ethyl acetate = 2/1; Reaction time = 12 h; yield: 75% (24.3 mg); white solid; m.p. 78–79 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 – 7.56 (m, 2H), 7.46 – 7.40 (m, 1H), 7.30 – 7.23 (m, 4H), 7.21 – 7.15 (m, 1H), 5.05 (dd, *J* = 9.9, 2.2 Hz, 1H), 3.46 (dd, *J* = 13.7,

2.4 Hz, 1H), 2.91 (dd, *J* = 13.7, 9.9 Hz, 1H), 1.71 (s, 3H), 1.70 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.0, 140.0, 135.6, 131.4, 129.3, 128.8, 127.8, 127.7, 127.2, 127.1, 126.1, 74.1, 68.2, 44.7, 32.0, 30.7; IR (KBr): 3383, 3298, 2985, 2916, 2850, 1468, 1433, 1364, 1332, 1275, 1161, 1123, 1072, 1046, 1030, 942, 763, 749 cm^{-1}; ESI FTMS exact mass calcd for $(C_{17}H_{19}ClO_2S+Na)^+$ requires m/z 345.0686, found m/z 345.0678.

2-(2-((2-hydroxy-2-(m-tolyl)ethyl)thio)phenyl)propan-2-ol (5ad): Preparative thin layer chromatography, methylbenzene/ ethyl acetate = 2/1; Reaction time = 12 h; yield: 70% (21.1 mg); white sticky oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.51 (m, 1H), 7.47 – 7.43 (m, 1H), 7.26 – 7.19 (m, 3H), 7.16 – 7.05 (m, 3H), 4.89 (s, 1H), 4.70 (dd, *J* = 9.7, 2.8 Hz, 1H), 3.31 (dd, *J* = 13.6, 3.1 Hz, 1H), 3.16 (dd, *J* = 13.6, 9.8 Hz, 2H), 2.33 (s, 3H), 1.71 (s, 3H), 1.70 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.1, 142.4, 138.3, 134.9, 132.1, 128.7, 128.5, 127.8, 127.6, 126.4, 126.2, 122.8, 73.9, 71.8, 46.6, 31.7, 30.8, 21.4; IR (KBr): 3348, 2974, 2921, 1655, 1607, 1588, 1431, 1364, 1163, 1047, 950, 758, 698 cm^{-1}; ESI FTMS exact mass calcd for $(C_{18}H_{22}O_2S+Na)^+$ requires m/z 325.1233, found m/z 325.1228.

2-(2-((2-(3-chlorophenyl)-2-hydroxyethyl)thio)phenyl)propan-2-ol (5ae): Preparative thin layer chromatography, methylbenzene/ ethyl acetate = 2/1; Reaction time = 12 h; yield: 79% (25.3 mg); white solid; m.p. 79–80 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.50 (m, 1H), 7.45 – 7.41 (m, 1H), 7.31 – 7.22 (m, 5H), 7.17 – 7.13 (m, 1H), 4.66 (dd, *J* = 9.8, 2.8 Hz, 1H), 3.28 (dd, *J* = 13.7, 2.9 Hz, 1H), 3.08 (dd, *J* = 13.7, 9.8 Hz, 1H), 1.68 (s, 3H), 1.67 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.1, 144.7, 135.1, 134.4, 131.8, 129.8, 128.0, 127.9, 127.8, 126.2, 125.9, 123.9, 74.1, 71.1, 46.7, 31.8, 30.8; IR (KBr): 3412, 3064, 2965, 2918, 2880, 1572, 1467, 1430, 1384, 1342, 1271, 1155, 1053, 950, 790, 753. 691 cm^{-1}; ESI FTMS exact mass calcd for $(C_{17}H_{19}ClO_2S+Na)^+$ requires m/z 345.0686, found m/z 345.0686.

2-(2-((2-hydroxy-2-(p-tolyl)ethyl)thio)phenyl)propan-2-ol (5af): Preparative thin layer chromatography, methylbenzene/ ethyl acetate = 2/1; Reaction time = 12 h; yield: 71% (21.3 mg); white sticky oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.50 (m, 1H), 7.46 – 7.42 (m, 1H), 7.26 – 7.22 (m, 2H), 7.20 (d, *J* = 8.1 Hz, 2H), 7.13 (d, *J* = 8.0 Hz, 2H), 4.70 (dd, *J* = 9.6, 3.1 Hz, 1H), 3.30 (dd, *J* = 13.6, 3.2 Hz, 1H), 3.15 (dd, *J* = 13.6, 9.6 Hz, 1H), 2.33 (s, 3H), 1.69 (s, 3H), 1.68 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.0, 139.6, 137.7, 134.9, 132.2, 129.2, 127.8, 127.6, 126.2, 125.7, 73.9, 71.7, 46.6, 31.7, 30.8, 21.2; IR (KBr): 3385, 3053, 2975, 2922, 1905, 1718, 1586,

1513, 1465, 1431, 1365, 1169, 1047, 951, 819, 758 cm^{-1}; ESI FTMS exact mass calcd for $(C_{18}H_{22}O_2S+Na)^+$ requires m/z 325.1233, found m/z 325.1238.

2-(2-((2-(4-fluorophenyl)-2-hydroxyethyl)thio)phenyl)propan-2-ol (5ag): Preparative thin layer chromatography, methylbenzene/ ethyl acetate = 2/1; Reaction time = 12 h; yield: 75% (23.1 mg); white sticky oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.49 (m, 1H), 7.45 – 7.41 (m, 1H), 7.29 – 7.23 (m, 4H), 7.00 (t, *J* = 8.7 Hz, 2H), 4.69 (dd, *J* = 9.6, 2.9 Hz, 1H), 3.28 (dd, *J* = 13.7, 3.0 Hz, 1H), 3.11 (dd, *J* = 13.6, 9.7 Hz, 1H), 1.69 (s, 3H), 1.68 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.3 (*J* = 244.4 Hz), 149.1, 138.4 (*J* = 3.1 Hz), 135.0, 131.9, 127.9, 127.8, 127.7, 127.5 (*J* = 8.1 Hz), 126.2, 115.4 (*J* = 21.3 Hz), 74.0, 71.1, 46.8, 31.8, 30.8; IR (KBr): 3385, 2975, 2925, 1603, 1509, 1431, 1221, 1157, 1047, 951, 838, 758 cm^{-1}; ESI FTMS exact mass calcd for $(C_{17}H_{19}FO_2S+Na)^+$ requires m/z 329.0982, found m/z 329.0976.

2-(2-((2-(4-chlorophenyl)-2-hydroxyethyl)thio)phenyl)propan-2-ol (5ah): Preparative thin layer chromatography, methylbenzene/ ethyl acetate = 2/1; Reaction time = 12 h; yield: 79% (25.4 mg); white sticky oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.48 (m, 1H), 7.45 – 7.40 (m, 1H), 7.28 – 7.26 (m, 2H), 7.25 – 7.18 (m, 4H), 4.66 (dd, *J* = 9.6, 2.7 Hz, 1H), 3.26 (dd, *J* = 13.7, 2.9 Hz, 1H), 3.07 (dd, *J* = 13.7, 9.7 Hz, 1H), 1.66 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.1, 141.1, 135.0, 133.5, 131.9, 128.7, 127.9, 127.8, 127.2, 126.2, 74.0, 71.0, 46.7, 31.8, 30.8; IR (KBr): 3312, 2974, 2923, 1718, 1658, 1588, 1490, 1364, 1163, 1047, 944, 834, 757 cm^{-1}; ESI FTMS exact mass calcd for $(C_{17}H_{19}ClO_2S+Na)^+$ requires m/z 345.0686, found m/z 345.0692.

2-(2-((2-hydroxy-2-(naphthalen-2-yl)ethyl)thio)phenyl)propan-2-ol (5ai): Preparative thin layer chromatography, methylbenzene/ ethyl acetate = 2/1; Reaction time = 12 h; yield: 69% (23.2 mg); pale yellow solid; m.p. 59–60 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.72 (m, 4H), 7.58 – 7.53 (m, 1H), 7.51 – 7.42 (m, 3H), 7.39 (dd, *J* = 8.5, 1.7 Hz, 1H), 7.26 – 7.23 (m, 2H), 4.87 (dd, *J* = 9.7, 3.0 Hz, 1H), 3.38 (dd, *J* = 13.7, 3.1 Hz, 1H), 3.21 (dd, *J* = 13.7, 9.7 Hz, 1H), 1.68 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.1, 140.0, 135.0, 133.2, 133.1, 132.2, 128.4, 128.0, 127.9, 127.7, 126.2, 125.9, 124.6, 123.7, 73.9, 71.8, 46.6, 31.8, 30.7; IR (KBr): 3306, 2968, 1769, 1681, 1505, 1433, 1360, 1266, 1164, 1047, 949, 857, 819, 752 cm^{-1}; ESI FTMS exact mass calcd for $(C_{21}H_{22}O_2S+Na)^+$ requires m/z 361.1233, found m/z 361.1245.

1-((2-(2-hydroxypropan-2-yl)phenyl)thio)-2-phenylpropan-2-ol (5aj): Preparative thin layer chromatography, methylbenzene/ ethyl acetate = 2/1; Reaction time = 12 h; yield: 78% (23.5 mg);

white sticky oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.45 (m, 3H), 7.42 – 7.34 (m, 3H), 7.31 – 7.27 (m, 1H), 7.23 – 7.17 (m, 2H), 4.53 (s, 1H), 3.61 (d, *J* = 13.0 Hz, 1H), 3.39 (d, *J* = 13.0 Hz, 1H), 3.15 (s, 1H), 1.66 (s, 3H), 1.63 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.6, 146.2, 135.5, 133.6, 128.4, 127.9, 127.6, 127.2, 125.9, 124.8, 74.4, 73.9, 52.8, 31.4, 30.9, 29.8; IR (KBr): 3305, 3057, 2974, 2925, 1953, 1493, 1446, 1431, 1367, 1229, 1169, 1047, 945, 857, 758, 699 cm^{-1}; ESI FTMS exact mass calcd for $(C_{18}H_{22}O_2S+Na)^+$ requires m/z 325.1233, found m/z 325.1245.

3-(2-((2-hydroxy-2-phenylethyl)thio)phenyl)pentan-3-ol (5ba): Preparative thin layer chromatography, methylbenzene/ ethyl acetate = 2/1; Reaction time = 12 h; yield: 89% (28.0 mg); white solid; m.p. 128–129 ^{o}C; ^{1}H NMR (400 MHz, Acetone-d_6) δ 7.73 – 7.68 (m, 1H), 7.53 – 7.49 (m, 1H), 7.45 – 7.39 (m, 2H), 7.36 – 7.31 (m, 2H), 7.29 – 7.24 (m, 1H), 7.22 – 7.15 (m, 2H), 4.92 – 4.85 (m, 1H), 4.68 (d, *J* = 4.2 Hz, 1H), 3.91 (s, 1H), 3.28 (d, *J* = 6.4 Hz, 2H), 2.50 – 2.34 (m, 2H), 1.88 – 1.74 (m, 2H), 0.72 – 0.65 (m, 6H); ^{13}C NMR (100 MHz, Acetone-d_6) δ 145.5, 144.2, 133.4, 131.9, 128.5, 128.1, 127.3, 126.9, 126.0, 125.7, 77.9, 72.1, 45.4, 33.1, 32.9, 7.7; IR (KBr): 3395, 3058, 2968, 2876, 1586, 1493, 1456, 1429, 1376, 1294, 1155, 1056, 957, 892, 755, 698 cm^{-1}; ESI FTMS exact mass calcd for $(C_{19}H_{24}O_2S+Na)^+$ requires m/z 339.1389, found m/z 339.1380.

2-((2-(hydroxymethyl)phenyl)thio)-1-phenylethanol (5ca): Preparative thin layer chromatography, methylbenzene/ ethyl acetate = 4/1; Reaction time = 12 h; yield: 58% (15.2 mg); white solid; m.p. 118–119 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 7.0 Hz, 1H), 7.42 – 7.27 (m, 8H), 4.91 (d, *J* = 12.4 Hz, 1H), 4.72 (d, *J* = 12.5 Hz, 1H), 4.64 (dd, *J* = 9.6, 2.7 Hz, 1H), 3.32 (dd, *J* = 13.8, 2.9 Hz, 1H), 3.13 – 2.78 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.3, 141.9, 133.8, 132.5, 129.3, 128.8, 128.6, 128.0, 127.7, 125.8, 71.7, 64.1, 44.8; IR (KBr): 3586, 3298, 3157, 2915, 2888, 1464, 1430, 1191, 1047, 993, 750, 696 cm^{-1}; ESI FTMS exact mass calcd for $(C_{15}H_{16}O_2S+Na)^+$ requires m/z 283.0764, found m/z 283.0779.

2-((2-(2-hydroxypropan-2-yl)phenyl)thio)-2,3-dihydro-1*H*-inden-1-ol (5ak): Preparative thin layer chromatography, methylbenzene/ ethyl acetate = 2/1; Reaction time = 12 h; yield: 63% (19.0 mg); 85:15 dr (inseparable diastereomers); pale orange solid; m.p. 59–60 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.61 (m, 1H), 7.47 – 7.44 (m, 1H), 7.36 – 7.31 (m, 1H), 7.26 – 7.14 (m, 5H), 5.08 (d, *J* = 6.5 Hz, 1H), 3.80 – 3.72 (m, 1H), 3.41 (dd, *J* = 16.0, 7.7 Hz, 1H), 2.96 (dd, *J* = 16.0, 8.2 Hz, 1H), 1.68 (s, 3H), 1.67 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.3, 142.8, 139.8, 136.1, 131.3, 128.5, 128.0, 127.7, 127.3, 126.3, 124.5, 124.2, 80.4, 74.3, 57.9, 37.3, 31.5, 31.3; IR (KBr): 3306,

2968, 1769, 1681, 1600, 1505, 1433, 1360, 1164, 1047, 949, 857, 819, 752 cm^{-1}; ESI FTMS exact mass calcd for $(C_{18}H_{20}O_2S+Na)^+$ requires m/z 323.1076, found m/z 323.1083.

2,2'-(disulfanediylbis(2,1-phenylene))bis(propan-2-ol) (byproduct 7) [4] : Flash column chromatography eluent, petroleum ether/ ethyl acetate = 5/1; white solid; ^1H NMR (400 MHz, $CDCl_3$) δ 7.74 (dd, *J* = 6.0, 3.2 Hz, 2H), 7.37 (dd, *J* = 5.7, 3.5 Hz, 2H), 7.20 – 7.14 (m, 4H), 2.39 (s, 2H), 1.75 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.9, 135.5, 128.6, 127.9, 126.4, 125.6, 74.3, 30.5.

1-phenyl-2-(phenylsulfinyl)ethanol (9aa): Preparative thin layer chromatography, methylbenzene/ ethyl acetate = 4/1; Reaction time = 12 h; yield: 78% (19.2 mg); 56:44 dr (inseperable diastereomers); white solid; m.p. 89–90 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 7.72 – 7.61 (m, 4H), 7.58 – 7.46 (m, 5H), 7.41 – 7.20 (m, 9H), 5.37 (d, *J* = 9.3 Hz, 0.8H), 5.27 (d, *J* = 10.5 Hz, 1H), 4.43 (d, *J* = 2.6 Hz, 1H), 4.38 (s, 0.8H), 3.30 – 3.17 (m, 1.8H), 2.96 (dd, *J* = 13.2, 2.8 Hz, 0.8H), 2.87 (dd, *J* = 13.5, 1.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.5, 142.7, 142.0, 141.9, 131.5, 131.2, 129.5, 128.7, 128.2, 128.0, 125.8, 125.6, 123.9, 123.8, 71.2, 68.7, 64.3, 63.9; IR (KBr): 3566, 3258, 3082, 3024, 2923, 2852, 1653, 1490, 1442, 1315, 1261, 1087, 1061, 998, 771, 690 cm^{-1}; ESI FTMS exact mass calcd for $(C_{14}H_{14}O_2S+Na)^+$ requires m/z 269.0608, found m/z 269.0600.

1-phenyl-2-(o-tolylsulfinyl)ethan-1-ol (9ba): Preparative thin layer chromatography, methylbenzene/ ethyl acetate = 4/1; Reaction time = 12 h; yield: 63% (16.5 mg); 53:47 dr (inseperable diastereomers); white sticky oil; ^1H NMR (400 MHz, $CDCl_3$) δ 8.04 – 7.90 (m, 2H), 7.49 – 7.16 (m, 16H), 5.40 (dd, *J* = 9.3, 2.2 Hz, 1H), 5.32 (d, *J* = 10.5 Hz, 1H), 4.63 – 4.46 (m, 2H), 3.22 (dd, *J* = 13.5, 10.4 Hz, 1H), 3.10 (dd, *J* = 13.3, 9.5 Hz, 1H), 3.00 (dd, *J* = 13.3, 3.1 Hz, 1H), 2.79 (dd, *J* = 13.5, 1.8 Hz, 1H), 2.35 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.2, 142.0, 141.9, 140.8, 134.3, 134.1, 131.2, 130.9, 130.7, 128.7, 128.6, 128.2, 127.9, 127.6, 127.3, 125.9, 125.7, 123.9, 123.5, 71.4, 68.6, 62.1, 61.7, 18.2; IR (KBr): 3648, 3334, 3060, 3029, 2921, 2853, 1653, 1600, 1471, 1384, 1197, 1061, 915, 756, 703 cm^{-1}; ESI FTMS exact mass calcd for $(C_{15}H_{16}O_2S+Na)^+$ requires m/z 283.0764, found m/z 283.0758.

2-((2-fluorophenyl)sulfinyl)-1-phenylethan-1-ol (9ca): Preparative thin layer chromatography,

[4] R. Sanz, R. Aguado, M. R. Pedrosa, F. J. Arnaiz, *Synthesis* **2002**, 856.

methylbenzene/ ethyl ether = 1/1; Reaction time = 12 h; yield: 66% (17.5 mg); 56:44 dr.

One diastereomer of **9ca**: white solid; m.p. 129–130 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 – 7.90 (m, 1H), 7.58 – 7.50 (m, 1H), 7.48 – 7.41 (m, 1H), 7.36 – 7.26 (m, 5H), 7.19 – 7.12 (m, 1H), 5.24 (d, *J* = 10.4 Hz, 1H), 4.10 (d, *J* = 2.7 Hz, 1H), 3.55 – 3.40 (m, 1H), 2.98 (d, *J* = 12.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.4 (*J* = 245.7 Hz), 141.7, 133.1, 133.0, 129.8, 129.6, 128.7, 128.1, 126.4, 125.6, 125.5, 125.4, 115.8 (*J* = 20.5 Hz), 69.2, 60.2; IR (KBr): 3607, 3335, 3085, 2921, 2850, 1653, 1469, 1256, 1212, 1028, 985, 817, 766, 704 cm^{-1}; ESI FTMS exact mass calcd for $(C_{14}H_{13}FO_2S+Na)^+$ requires m/z 287.0513, found m/z 287.0523.

Another diastereomer of **9ca**: white solid; m.p. 129–130 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 – 7.85 (m, 1H), 7.55 – 7.46 (m, 1H), 7.45 – 7.28 (m, 6H), 7.15 – 7.07 (m, 1H), 5.50 (d, *J* = 9.4 Hz, 1H), 4.04 (d, *J* = 1.7 Hz, 1H), 3.32 – 3.14 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.4 (*J* = 245.7 Hz), 141.8, 133.1, 133.0, 130.8, 128.7, 128.2, 125.8, 125.6 , 125.4, 115.8 (*J* = 19.9 Hz), 71.0, 61.6; IR (KBr): 3607, 3335, 3085, 2921, 2850, 1653, 1469, 1256, 1212, 1028, 985, 817, 766, 704 cm^{-1}; ESI FTMS exact mass calcd for $(C_{14}H_{13}FO_2S+Na)^+$ requires m/z 287.0513, found m/z 287.0523.

1-phenyl-2-(m-tolylsulfinyl)ethan-1-ol (9da): Preparative thin layer chromatography, methylbenzene/ ethyl acetate = 4/1; Reaction time = 12 h; yield: 70% (18.2 mg); 56:44 dr (inseperable diastereomers); white sticky oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.46 (m, 2H), 7.45 – 7.36 (m, 6H), 7.35 – 7.27 (m, 8H), 5.39 (dd, *J* = 9.8, 2.1 Hz, 0.8H), 5.28 (d, *J* = 10.3 Hz, 1H), 4.44 (s, 0.8H), 4.42 (s, 1H), 3.28 – 3.17 (m, 1.8H), 2.95 (dd, *J* = 13.2, 2.7 Hz, 0.8H), 2.87 (dd, *J* = 13.5, 1.9 Hz, 1H), 2.43 (s, 3H), 2.41 (s, 2.5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.4, 142.5, 142.1, 139.9, 139.7, 132.4, 132.0, 129.3, 128.7, 128.2, 127.9, 125.8, 124.3, 124.1, 121.1, 120.9, 71.3, 68.8, 64.2, 63.7, 21.5; IR (KBr): 3648, 3566, 3365, 3060, 2921, 2852, 1733, 1662, 1507, 1081, 1027, 994, 784, 688 cm^{-1}; ESI FTMS exact mass calcd for $(C_{15}H_{16}O_2S+Na)^+$ requires m/z 283.0764, found m/z 283.0768.

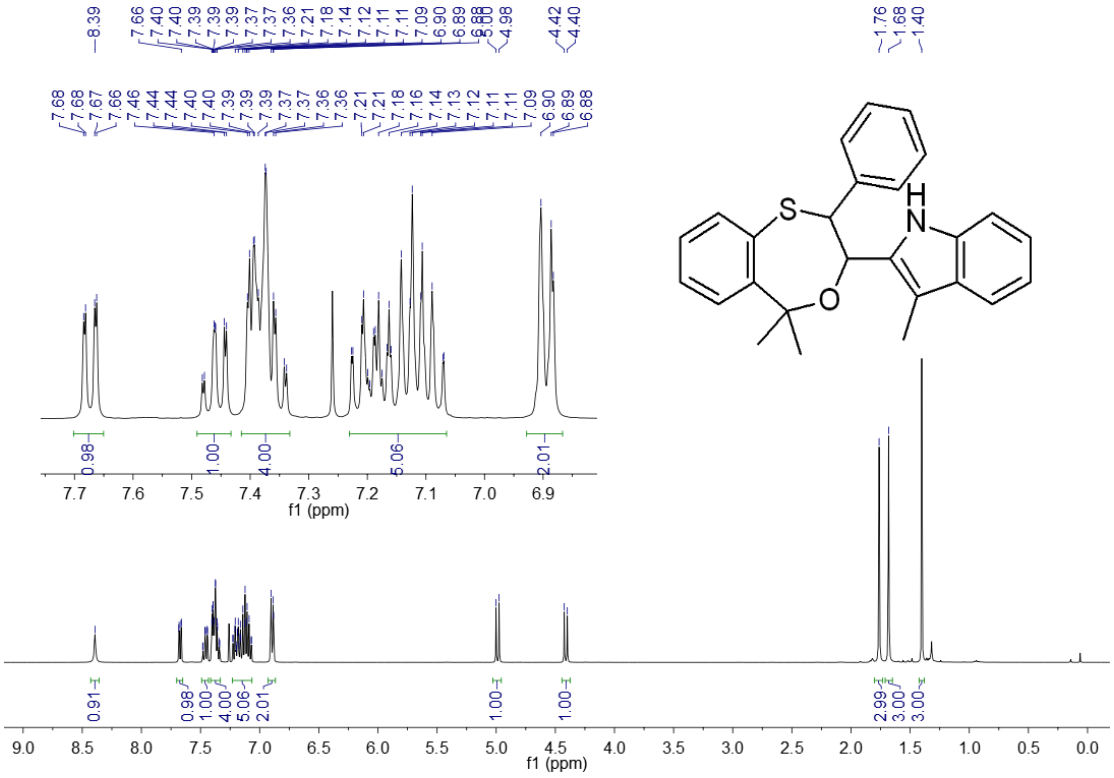
1-phenyl-2-(p-tolylsulfinyl)ethan-1-ol (9ea): Preparative thin layer chromatography, methylbenzene/ ethyl acetate = 4/1; Reaction time = 12 h; yield: 77% (19.9 mg); 56:44 dr (inseperable diastereomers); white solid; m.p. 103–104 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.2 Hz, 3.6H), 7.41 – 7.22 (m, 12.6H), 5.36 (d, *J* = 9.2 Hz, 0.8H), 5.26 (d, *J* = 10.4 Hz, 1H), 4.46 (d, *J* = 2.7 Hz, 1H), 4.41 (s, 0.8H), 3.29 – 3.15 (m, 1.8H), 2.92 (dd, *J* = 13.2, 2.7 Hz, 0.8H),

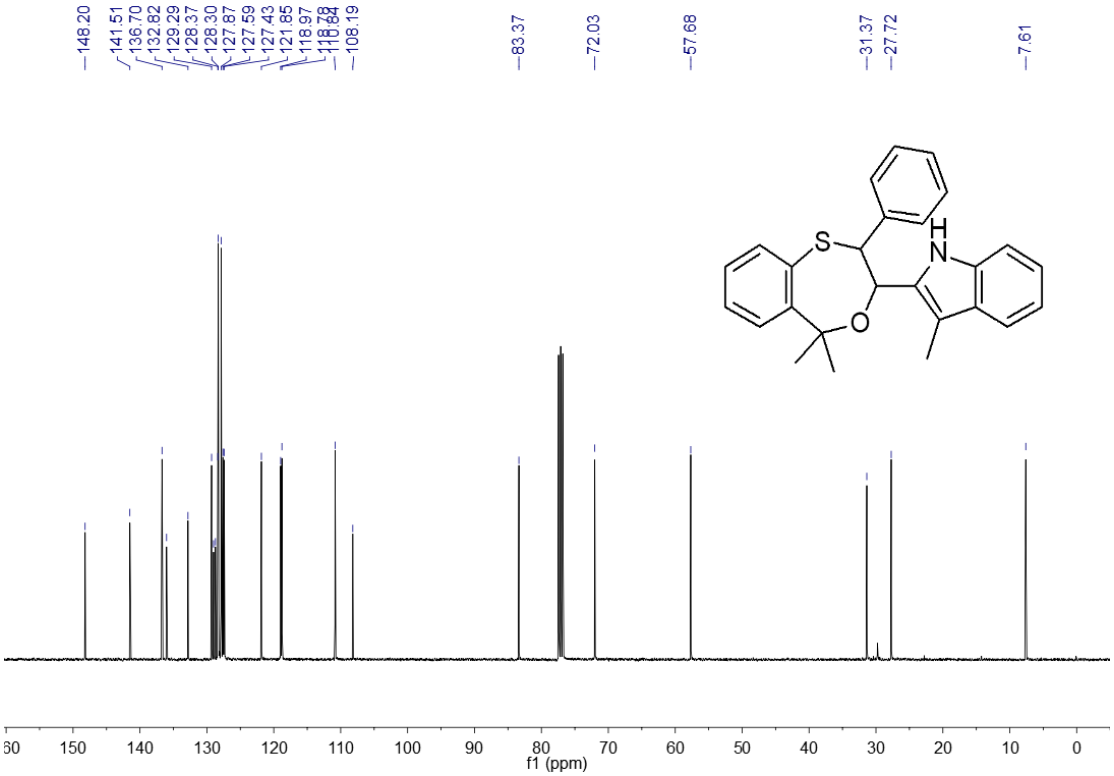
2.84 (dd, *J* = 13.6, 1.9 Hz, 1H), 2.42 (s, 3H), 2.41 (s, 2.4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.2, 142.1, 142.0, 141.7, 140.3, 139.3, 130.2, 128.6, 128.1, 127.9, 125.8, 124.0, 123.9, 71.2, 68.8, 64.3, 63.5, 21.5; IR (KBr): 3618, 3566, 3275, 3024, 2921, 2852, 1653, 1457, 1405, 1386, 1084, 999, 816, 804, 691 cm^{-1}; ESI FTMS exact mass calcd for $(C_{15}H_{16}O_2S+Na)^+$ requires m/z 283.0764, found m/z 283.0771.

2-((4-fluorophenyl)sulfinyl)-1-phenylethan-1-ol (9fa): Preparative thin layer chromatography, methylbenzene/ ethyl acetate = 4/1; Reaction time = 12 h; yield: 87% (23 mg); 50:50 dr (inseperable diastereomers); white sticky oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 – 7.59 (m, 4H), 7.43 – 7.16 (m, 14H), 5.37 – 5.22 (m, 2H), 4.33 (s, 1H), 4.25 (s, 1H), 3.31 – 3.11 (m, 2H), 2.94 (dd, *J* =13.2, 2.8 Hz, 1H), 2.86 (dd, *J* =13.6, 2.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.5 (*J* = 250.8 Hz), 164.4 (*J* = 250.3 Hz), 163.3, 163.1, 141.9, 141.8, 138.9, 138.3, 128.7, 128.3, 128.1, 126.4 (*J* = 8.8 Hz), 126.3 (*J* = 8.8 Hz), 125.8, 125.6, 116.9 (*J* = 22.5 Hz), 71.0, 64.5; IR (KBr): 3648, 3287, 3064, 2921, 2851, 1636, 1587, 1491, 1399, 1260, 1174, 1024, 919, 837, 702 cm^{-1}; ESI FTMS exact mass calcd for $(C_{14}H_{13}FO_2S+Na)^+$ requires m/z 287.0513, found m/z 287.0519.

7. NMR Spectra of compounds 3, 5, 7 and 9

3aa





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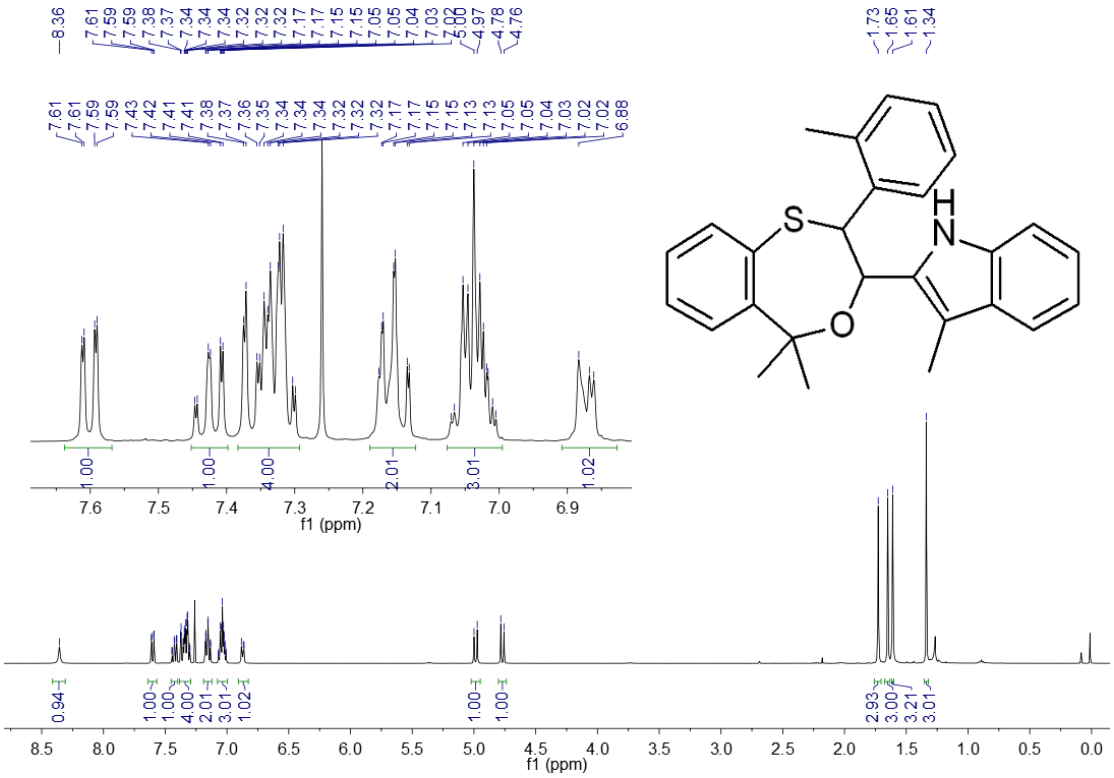
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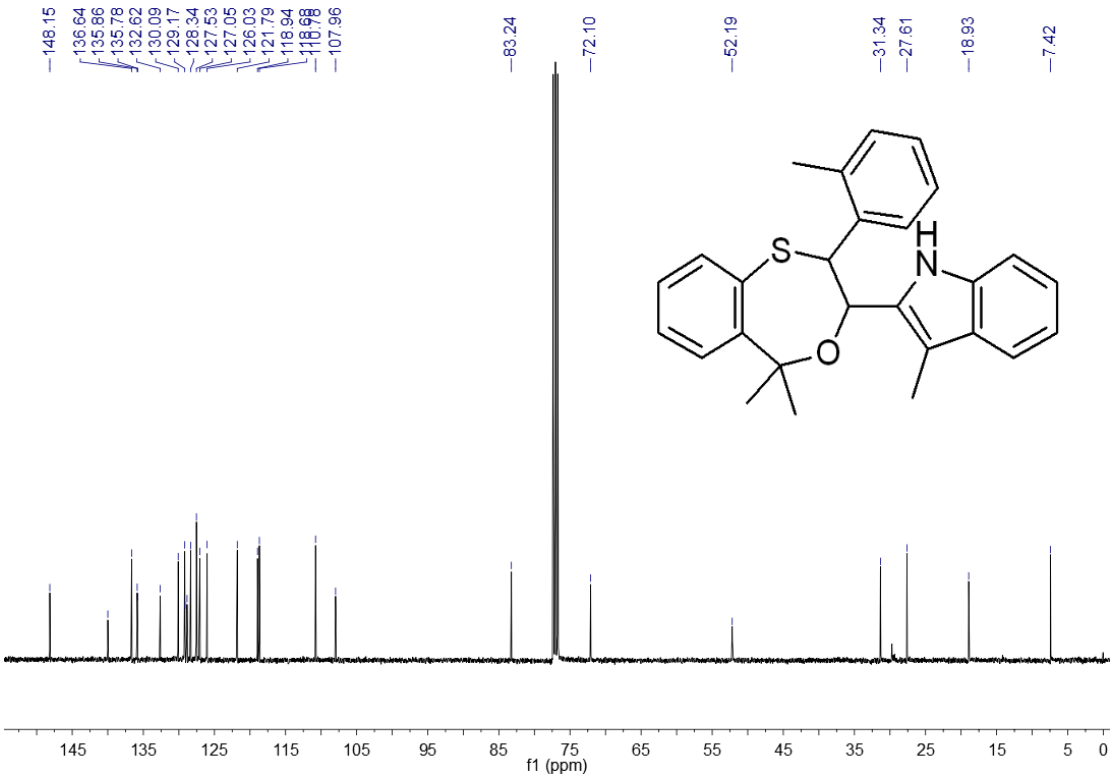
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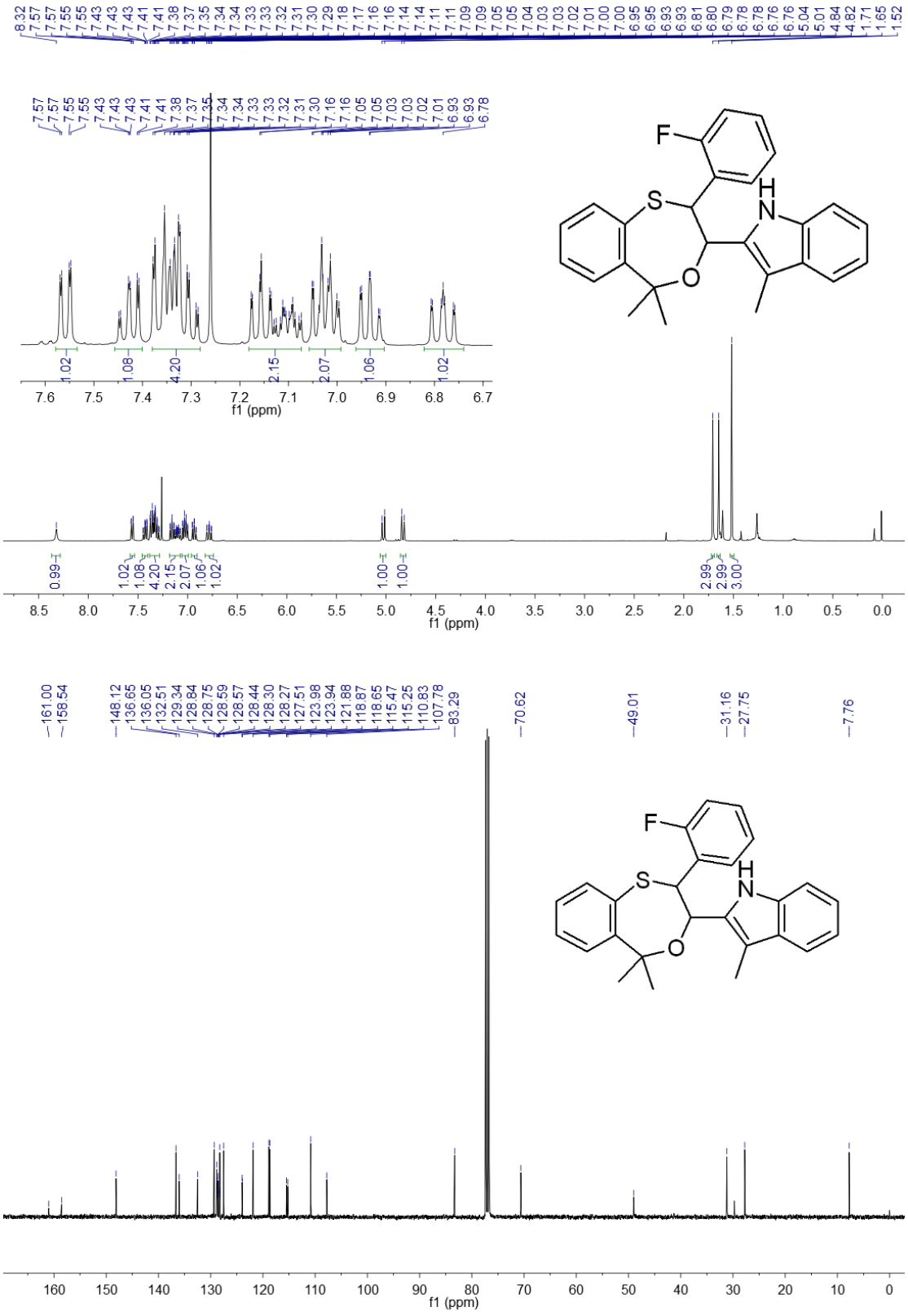

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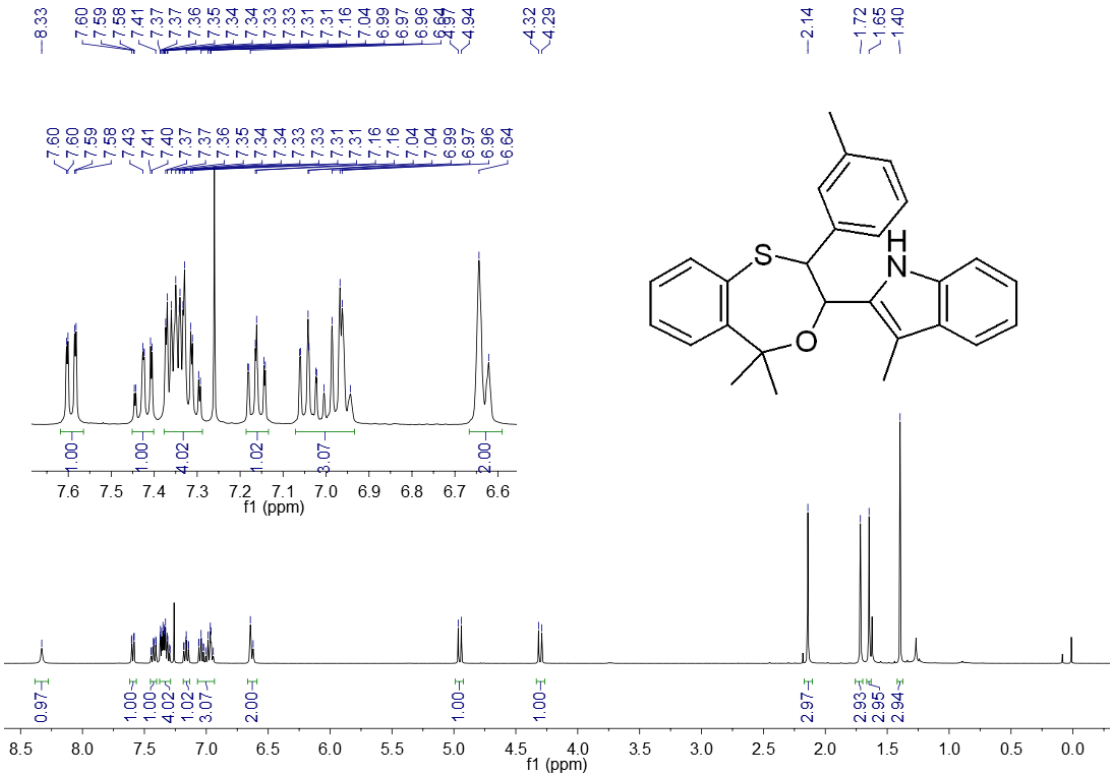
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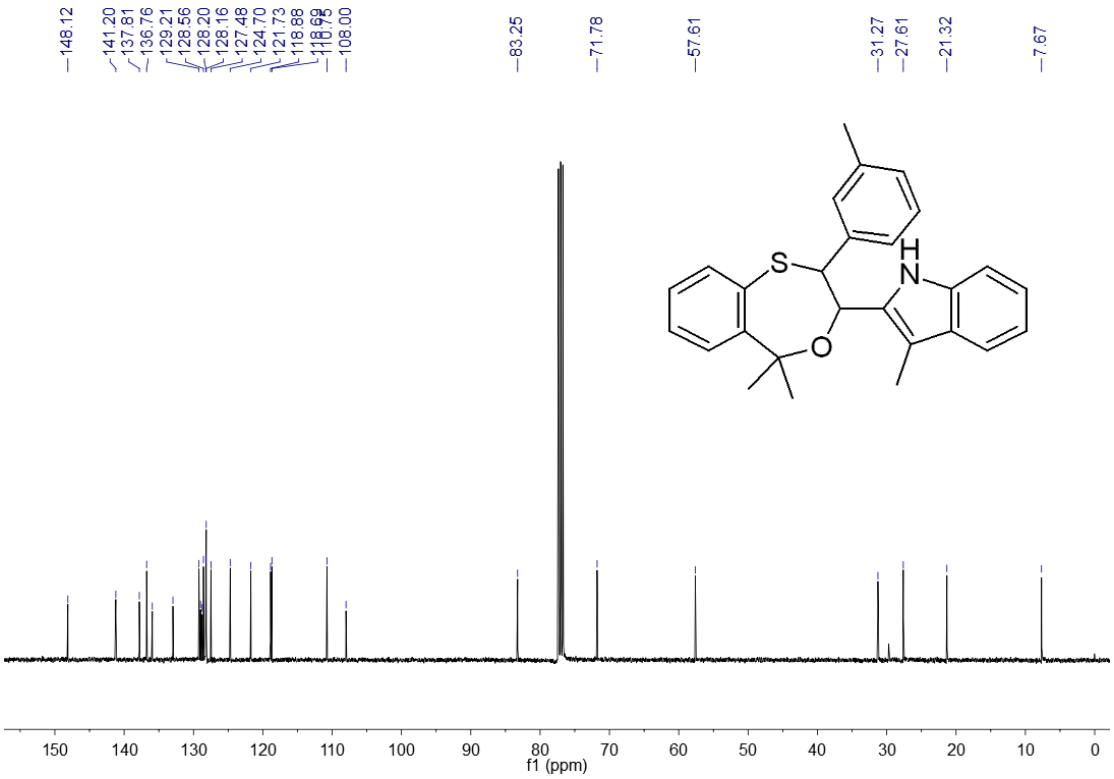
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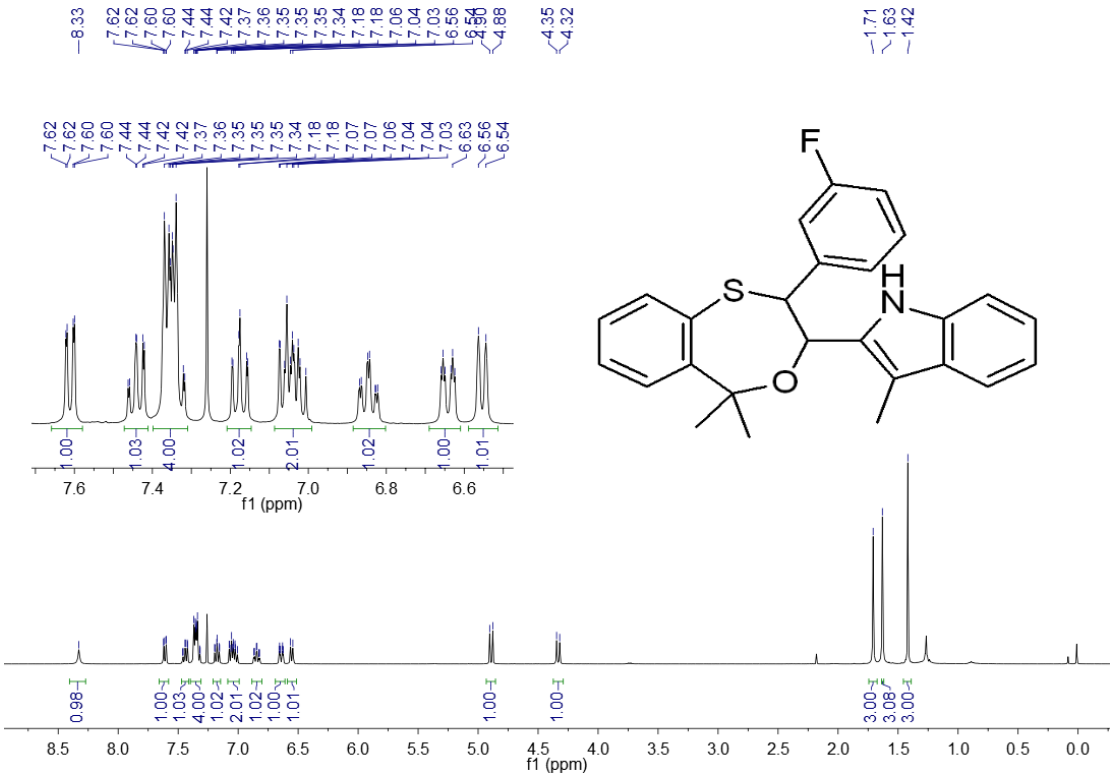
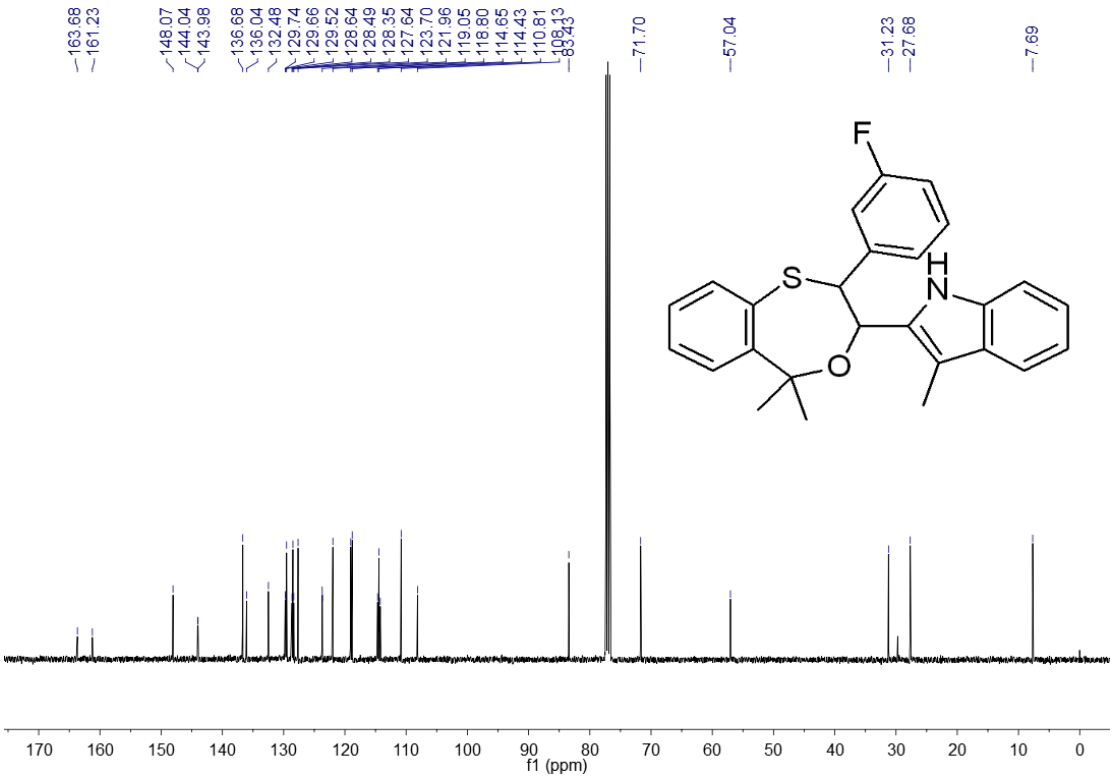
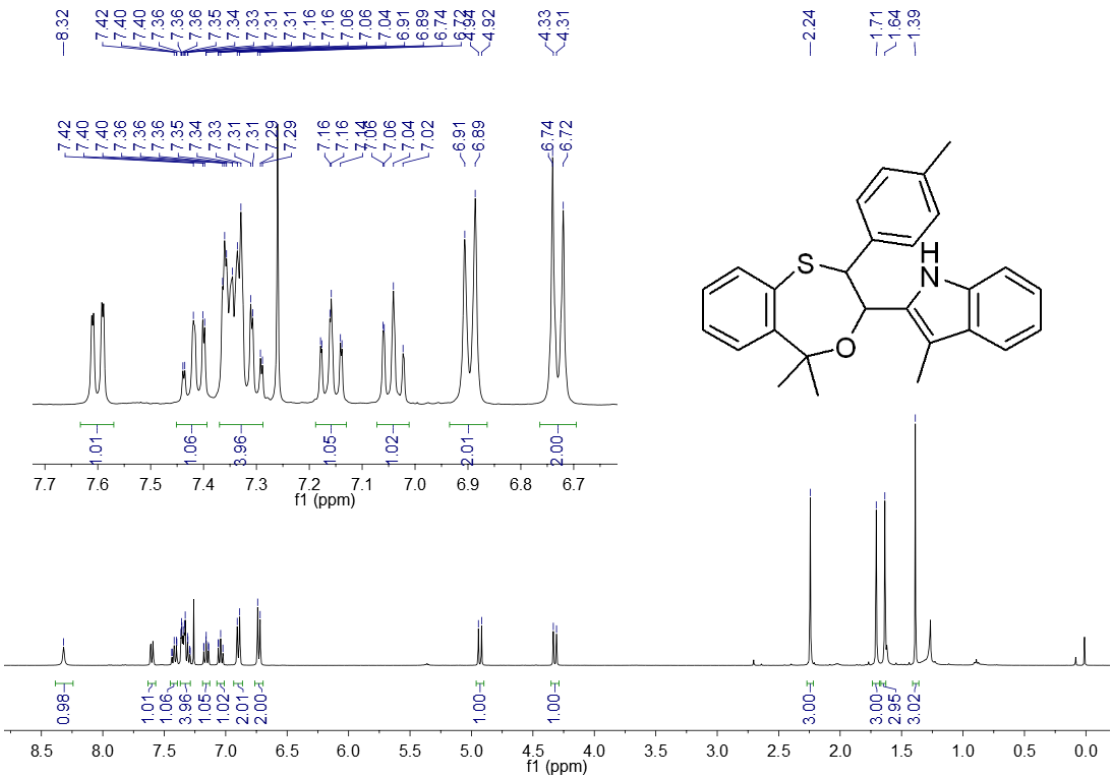
118.88
108.00
83.25
71.78
57.61
31.27
27.61
21.32
7.67
S
H
N
O
f1 (ppm)

3ae





3af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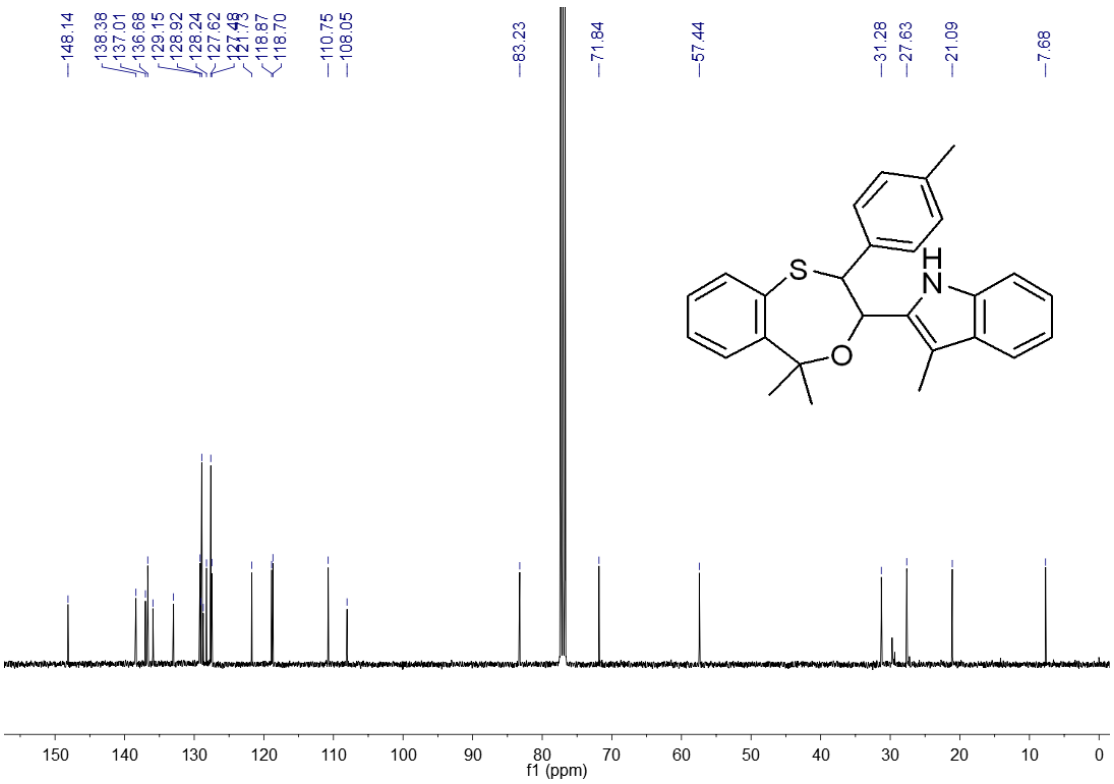
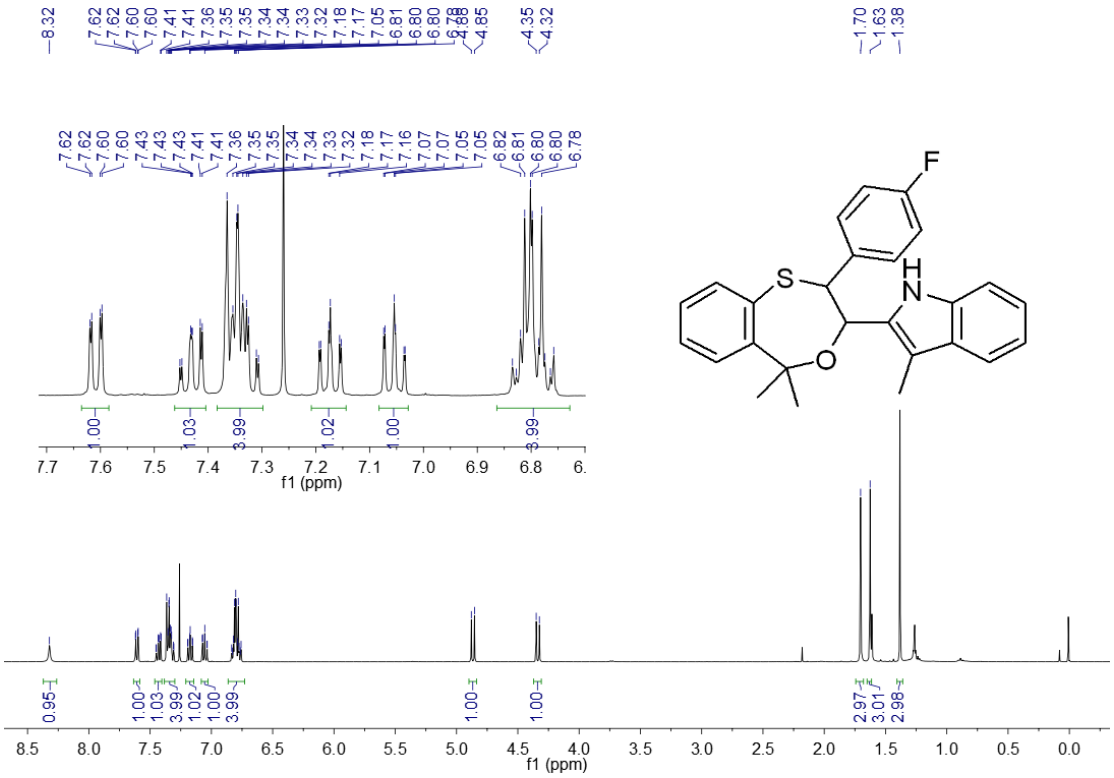
7.42
7.40
7.40
7.36
7.36
7.36
7.35
7.34
7.33
7.31
7.31
7.16
7.16
7.06
7.06
7.04
6.91
6.89
6.74
6.72
4.94
4.92
4.33
4.31
2.24
1.71
1.64
1.39
S
H
N
O
1.01
1.06
3.96
1.05
1.02
2.01
2.00
f1 (ppm)
0.98
1.00
1.00
3.00
3.00
2.95
3.02
f1 (ppm)


148.14
138.38
137.01
136.68
129.15
128.92
128.24
127.62
121.73
118.87
118.70
110.75
108.05
83.23
71.84
57.44
31.28
27.63
21.09
7.68
S
H
N
O
f1 (ppm)

3ag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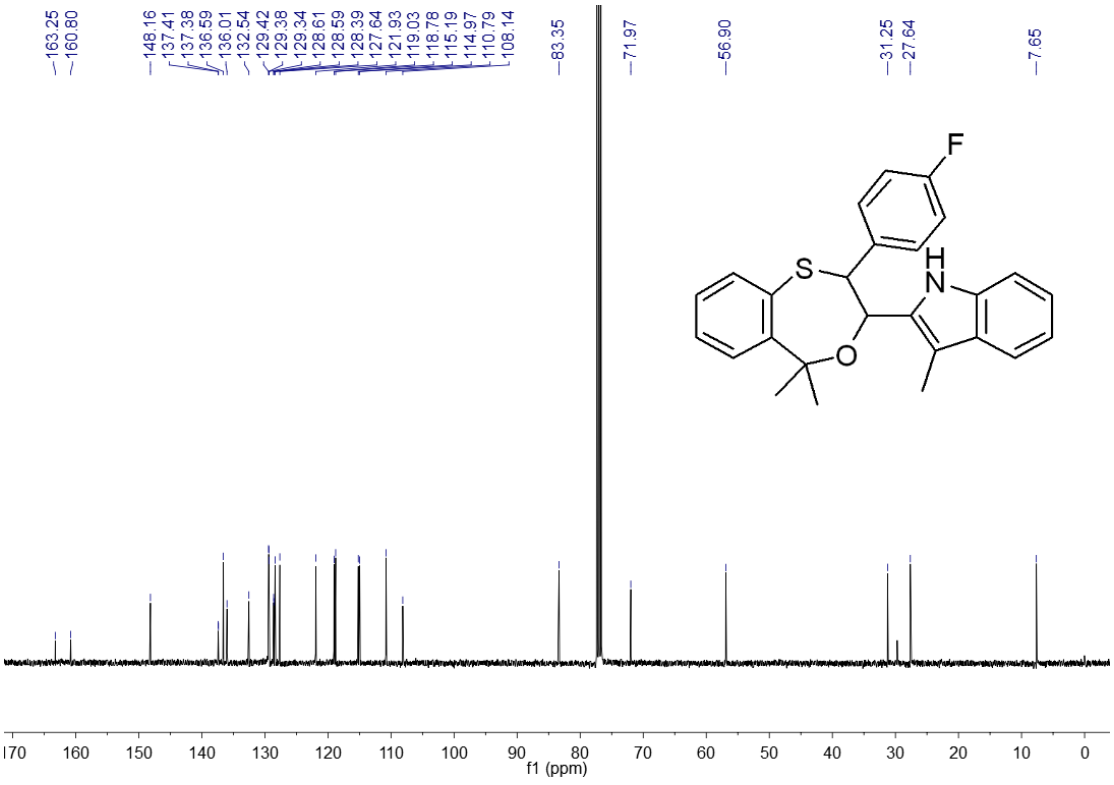
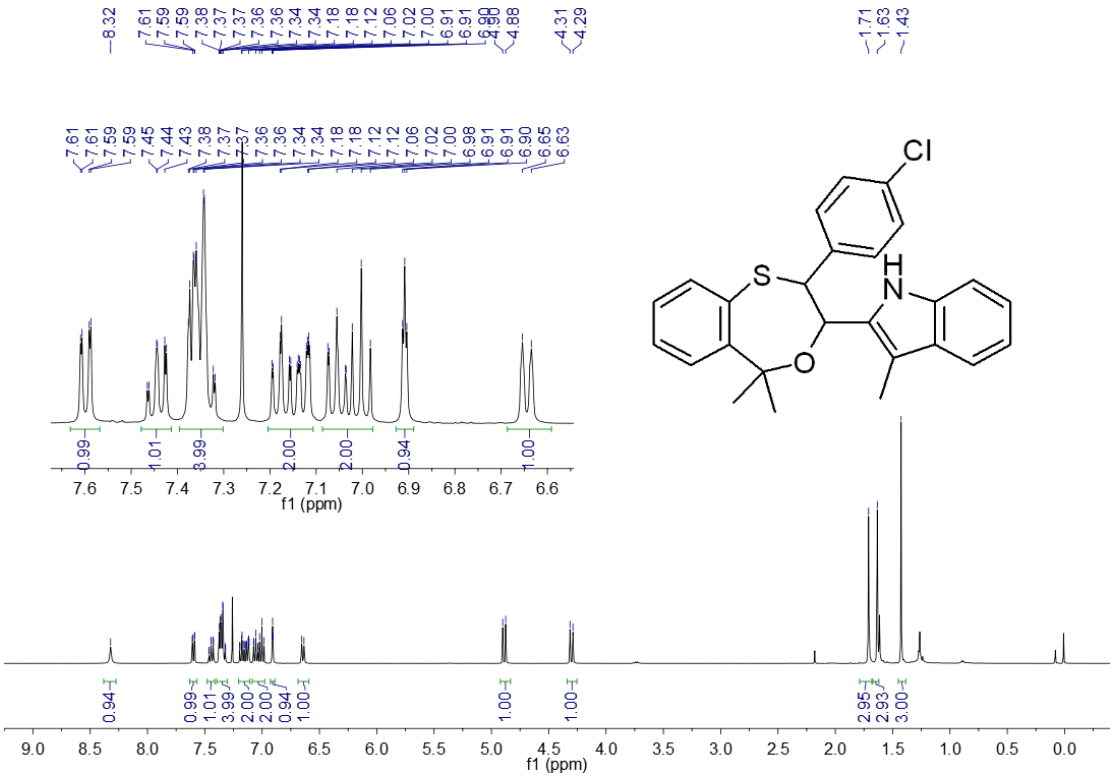
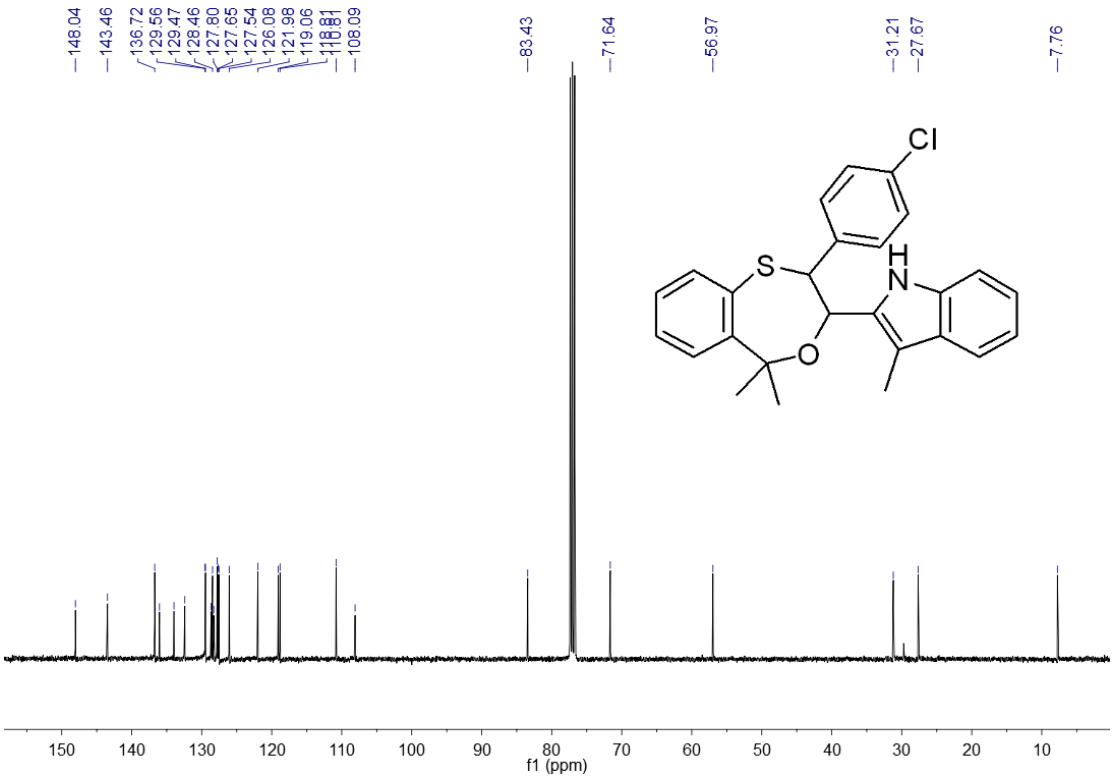
7.62
7.62
7.60
7.60
7.41
7.41
7.36
7.35
7.35
7.34
7.34
7.33
7.32
7.18
7.17
7.05
6.81
6.80
6.80
4.85
4.35
4.32
1.70
1.63
1.38
F
S
H
N
O
f1 (ppm)


163.25
160.80
148.16
137.41
137.38
136.59
136.01
132.54
129.42
129.38
129.34
128.61
128.59
128.39
127.64
121.93
119.03
118.78
115.19
114.97
110.79
108.14
83.35
71.97
56.90
31.25
27.64
7.65
F
S
H
N
O
f1 (ppm)

3ah


8.32
7.61
7.59
7.59
7.38
7.37
7.37
7.36
7.36
7.34
7.34
7.18
7.12
7.06
7.02
7.00
6.91
6.90
4.88
4.31
4.29
1.71
1.63
1.43
Cl
S
H
N
O
f1 (ppm)


148.04
143.46
136.72
129.56
129.47
128.46
127.80
127.65
127.54
126.08
121.98
119.06
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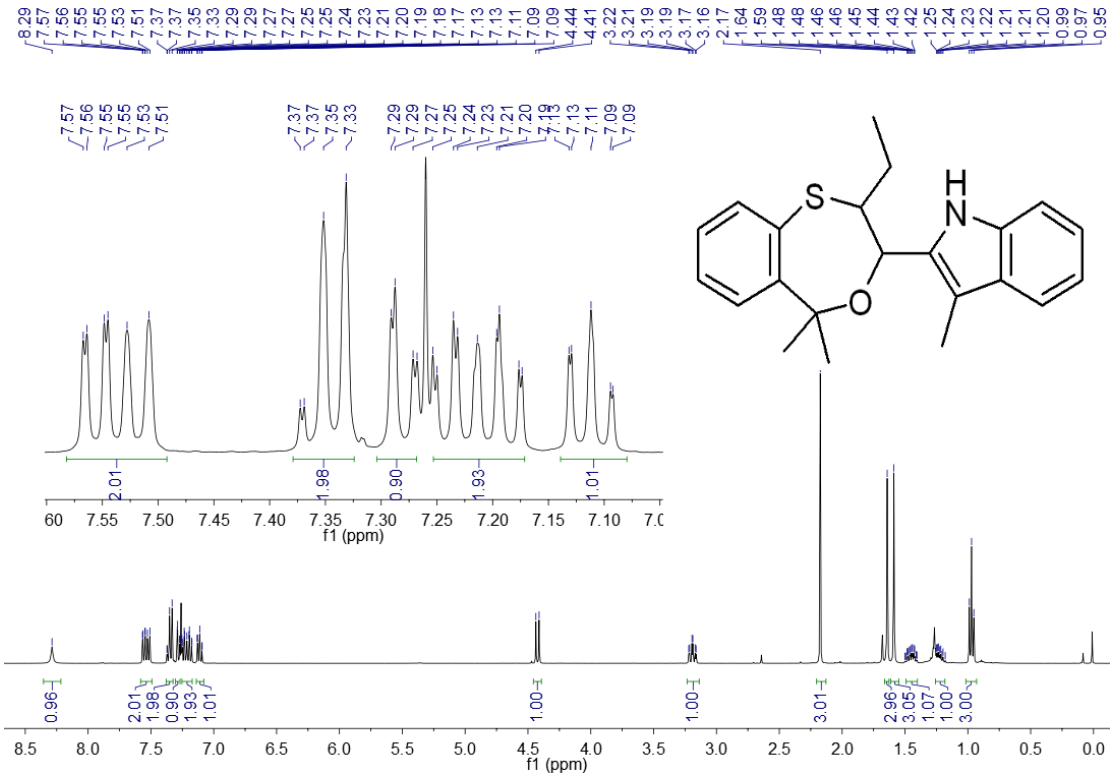
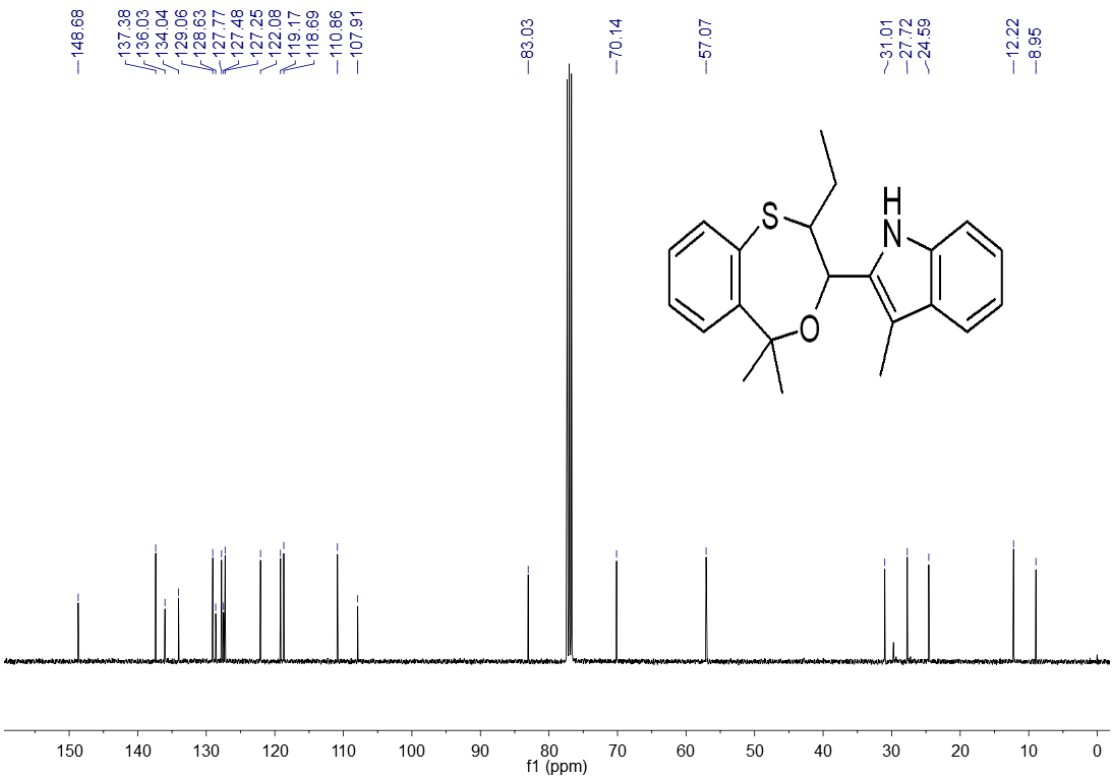
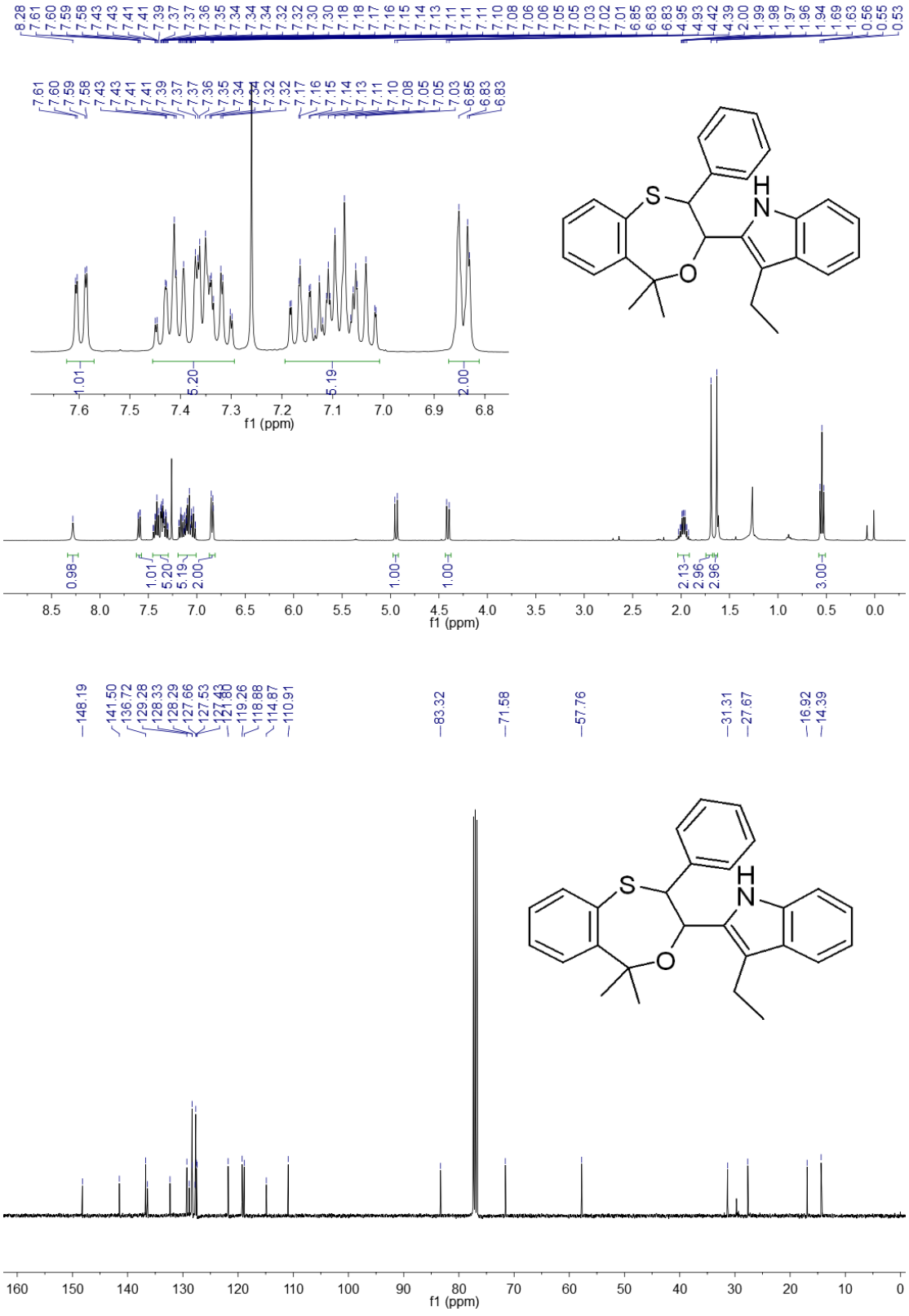
83.43
71.64
56.97
31.21
27.67
7.76
Cl
S
H
N
O
f1 (ppm)

3ai

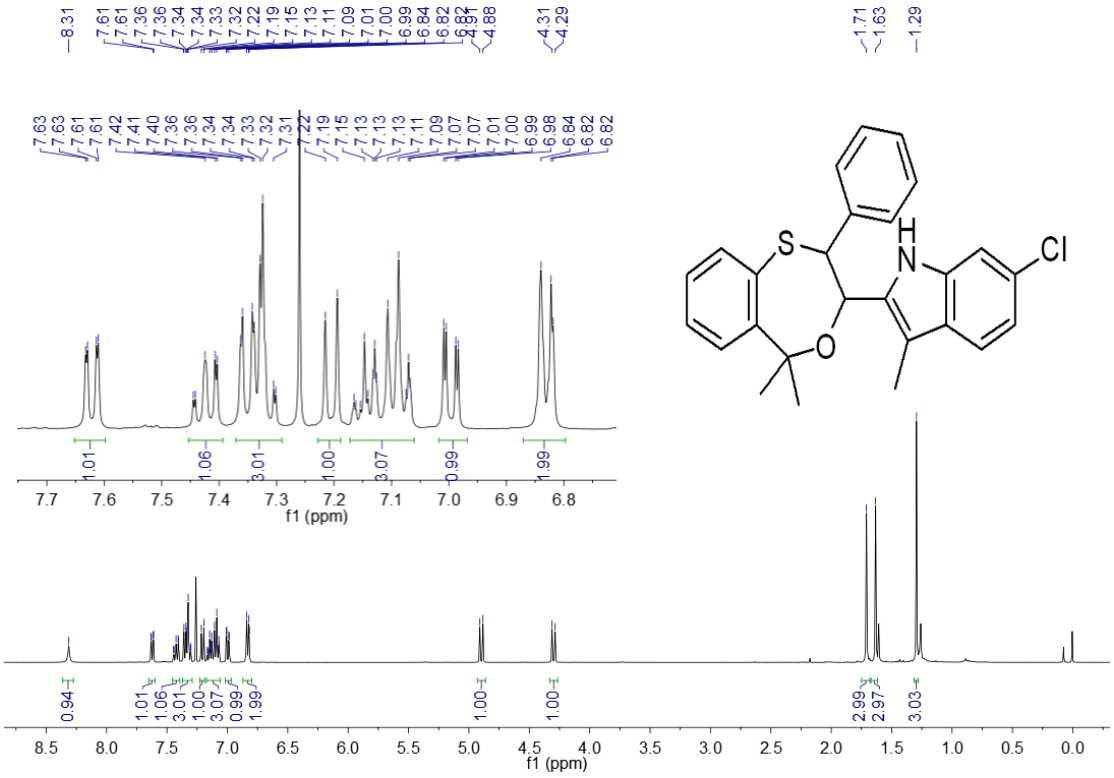


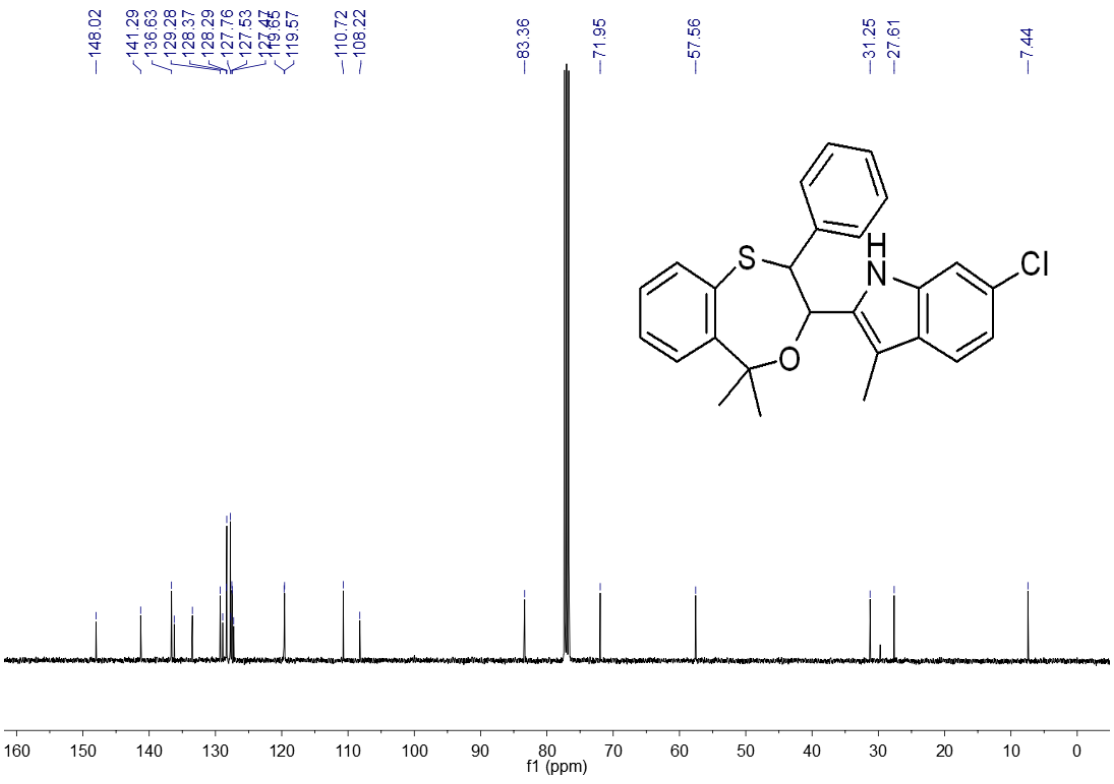


3aj

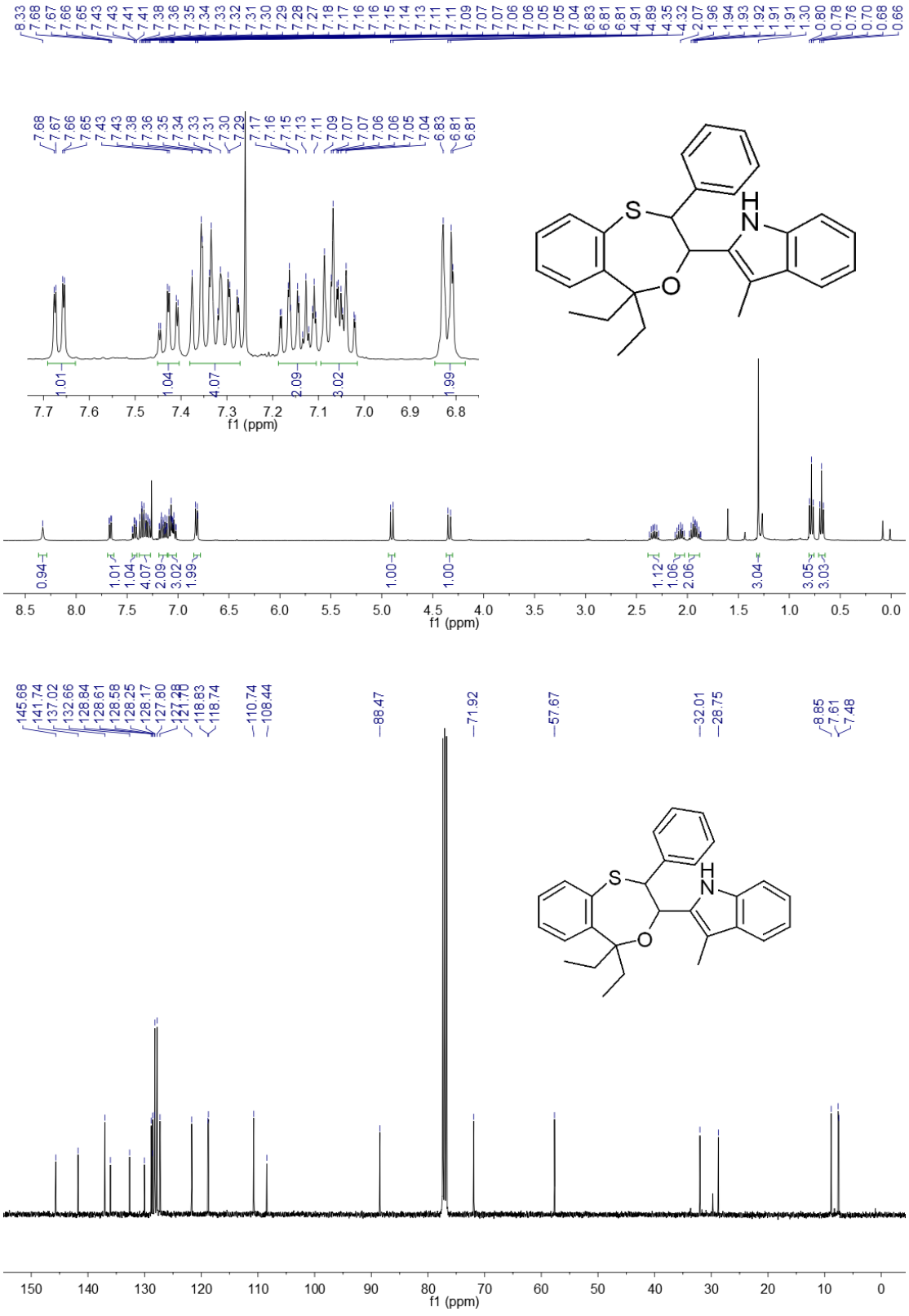


3ak

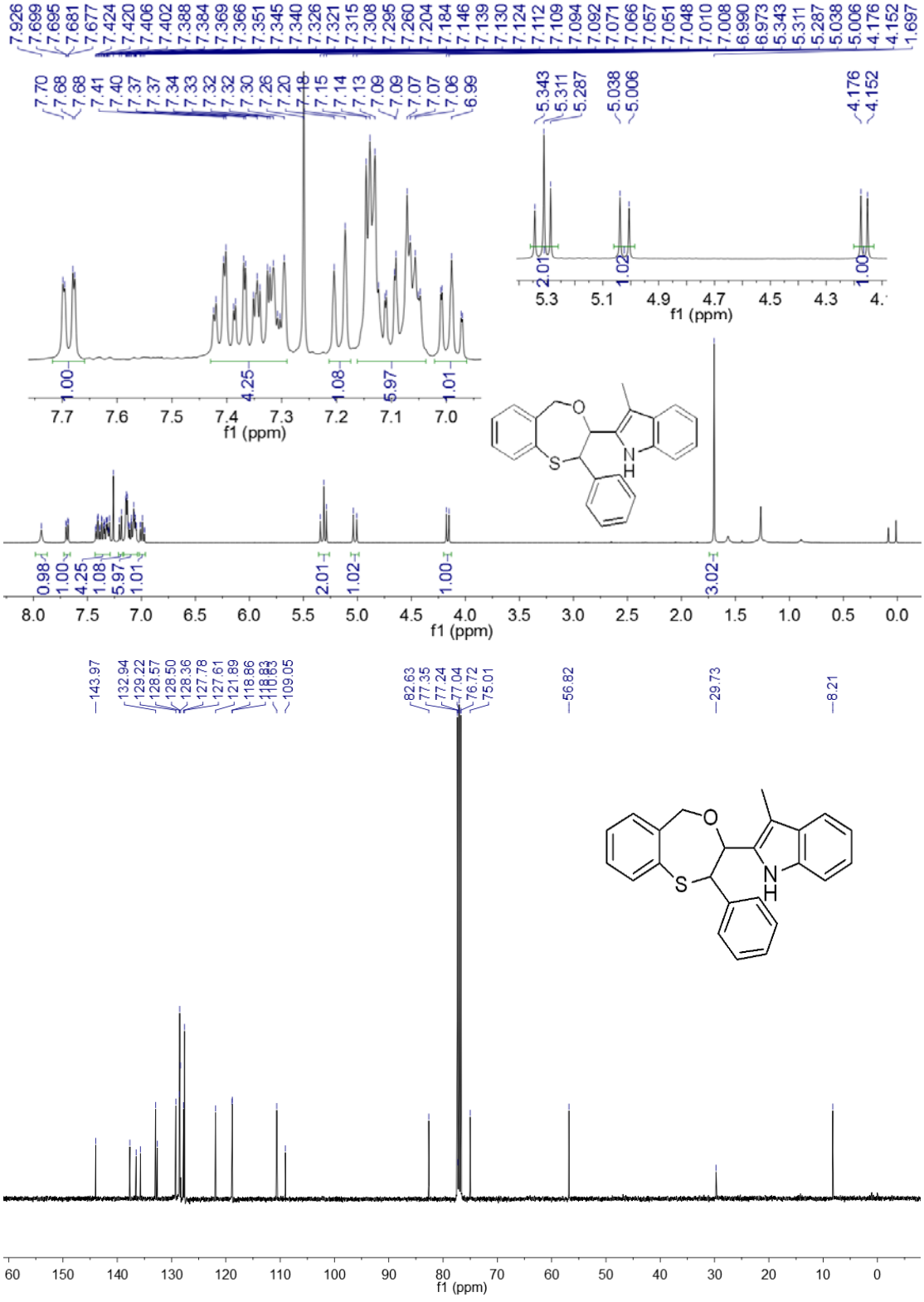

8.31
7.61
7.61
7.36
7.36
7.34
7.34
7.33
7.32
7.22
7.19
7.15
7.13
7.11
7.09
7.01
7.00
6.99
6.84
6.82
6.82
4.91
4.88
4.31
4.29
1.71
1.63
1.29
7.63
7.63
7.61
7.61
7.42
7.41
7.40
7.36
7.36
7.34
7.34
7.33
7.32
7.31
7.22
7.19
7.15
7.13
7.13
7.11
7.09
7.07
7.07
7.01
7.00
6.99
6.98
6.84
6.82
6.82
1.01
1.06
3.01
1.00
3.07
0.99
1.99
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.9
6.8
f1 (ppm)
S
H
N
Cl
O
0.94
1.01
1.06
3.01
1.00
3.07
0.99
1.99
1.00
1.00
2.99
2.97
3.03
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


148.02
141.29
136.63
129.28
128.37
128.29
127.76
127.53
119.57
110.72
108.22
83.36
71.95
57.56
31.25
27.61
7.44
S
H
N
Cl
O
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

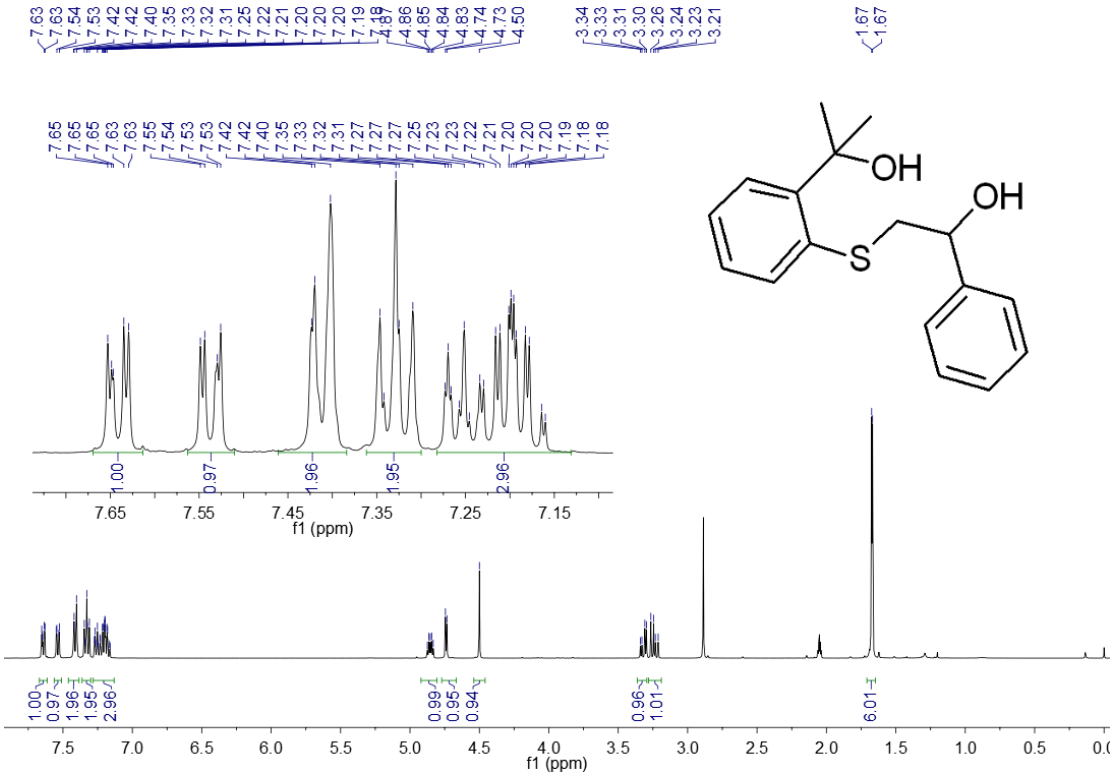
3ba

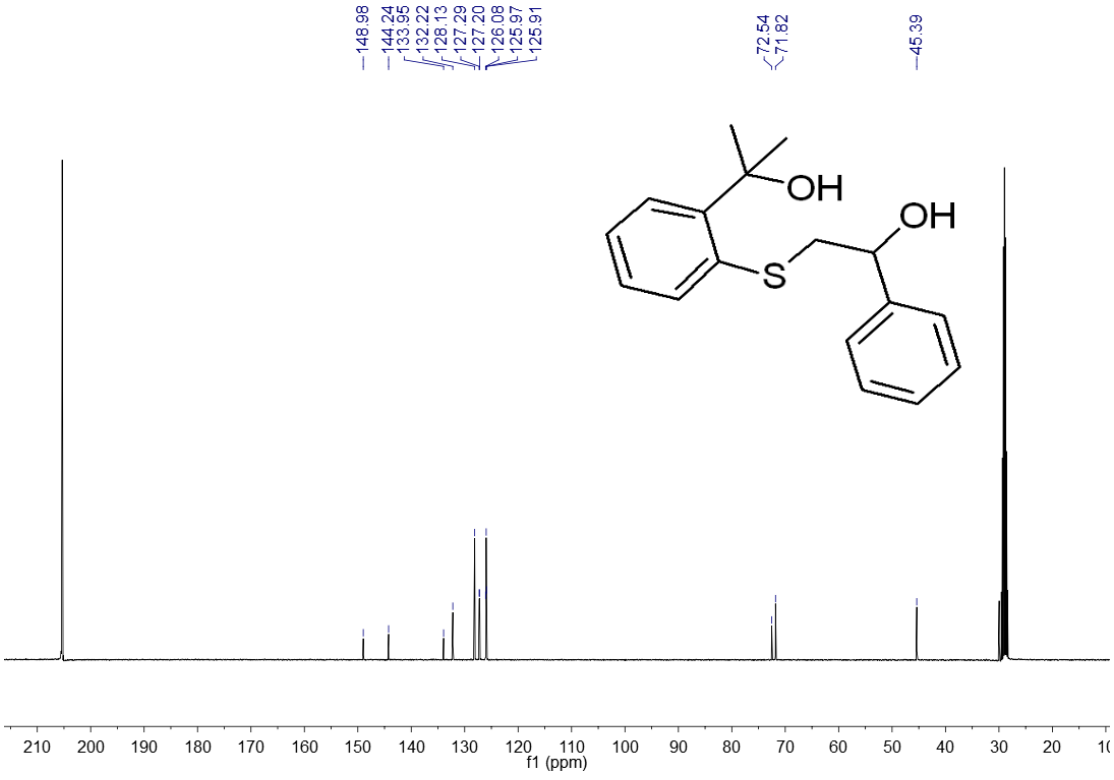

8.33 7.68 7.67 7.66 7.65 7.43 7.43 7.41 7.41 7.38 7.36 7.35 7.34 7.33 7.32 7.31 7.30 7.29 7.28 7.27 7.18 7.17 7.16 7.16 7.15 7.14 7.13 7.11 7.11 7.09 7.07 7.07 7.06 7.06 7.05 7.05 7.04 6.83 6.81 6.81 4.91 4.89 4.35 4.32 2.07 1.96 1.94 1.93 1.92 1.91 1.91 1.30 0.80 0.78 0.76 0.70 0.68 0.66
7.68 7.67 7.66 7.65 7.43 7.43 7.38 7.36 7.35 7.34 7.33 7.31 7.30 7.29 7.17 7.16 7.15 7.13 7.11 7.09 7.07 7.07 7.06 7.06 7.05 7.04 6.83 6.81 6.81
1.01 1.04 4.07 2.09 3.02 1.99
7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8
f1 (ppm)
S
H
N
O
0.94 1.01 1.04 4.07 2.09 3.02 1.99 1.00 1.00 1.12 1.06 2.06 3.04 3.05 3.03
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
145.68 141.74 137.02 132.66 128.84 128.61 128.58 128.25 128.17 127.80 121.28 121.10 118.83 118.74 110.74 108.44 88.47 71.92 57.67 32.01 28.75 8.85 7.61 7.48
S
H
N
O
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

3ca

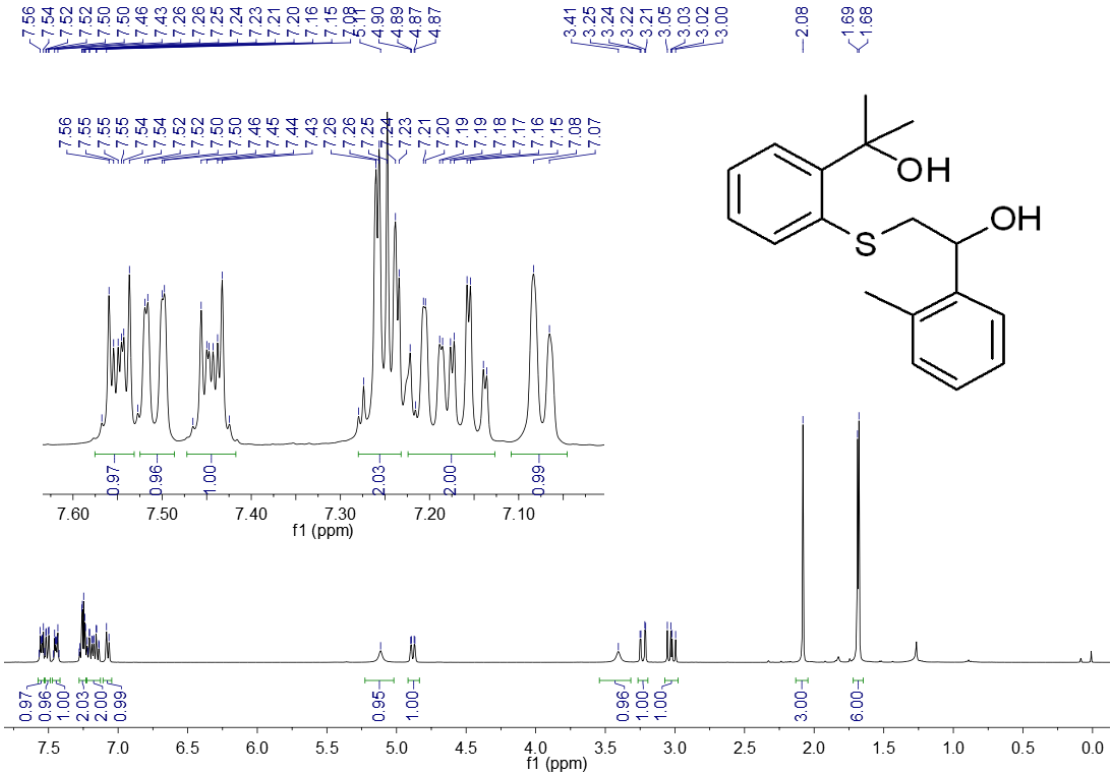


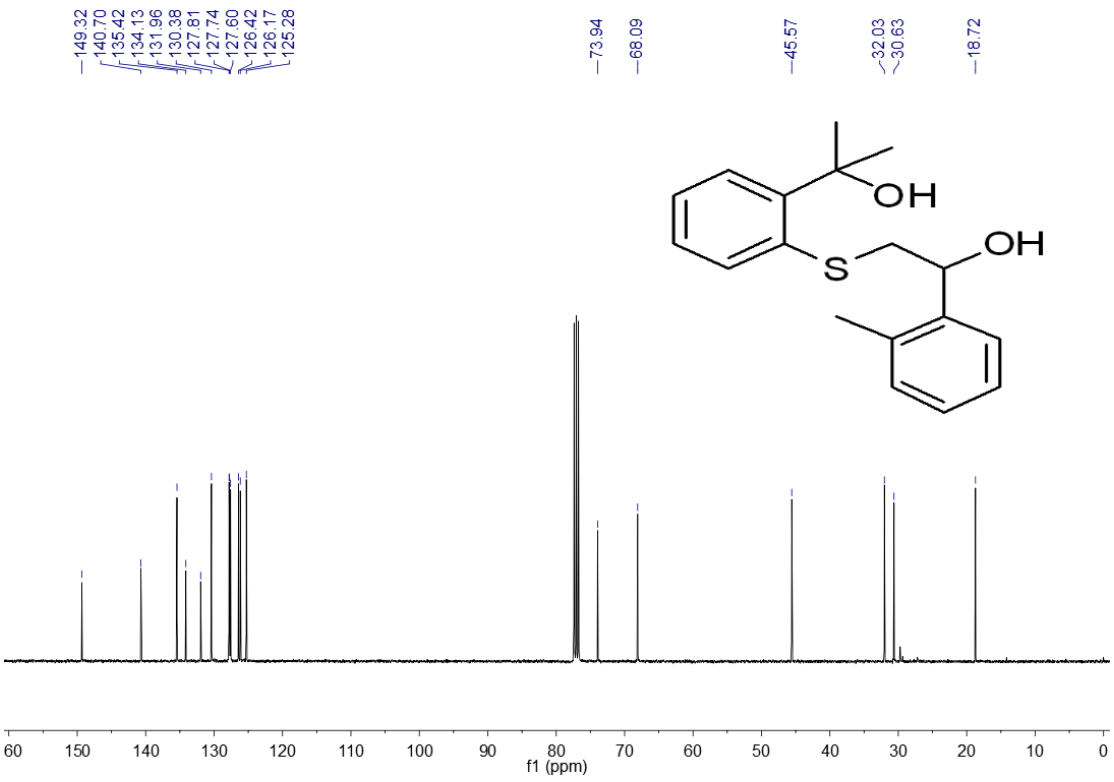
5aa


7.63 7.63 7.54 7.53 7.42 7.42 7.40 7.35 7.33 7.32 7.31 7.25 7.22 7.21 7.20 7.20 7.20 7.19 7.18 4.87 4.86 4.85 4.84 4.83 4.74 4.73 4.50
3.34 3.33 3.31 3.30 3.26 3.24 3.23 3.21
1.67 1.67
OH
OH
S
1.00 0.97 1.96 1.95 2.96
0.99 0.95 0.94
0.96 1.01
6.01
f1 (ppm)

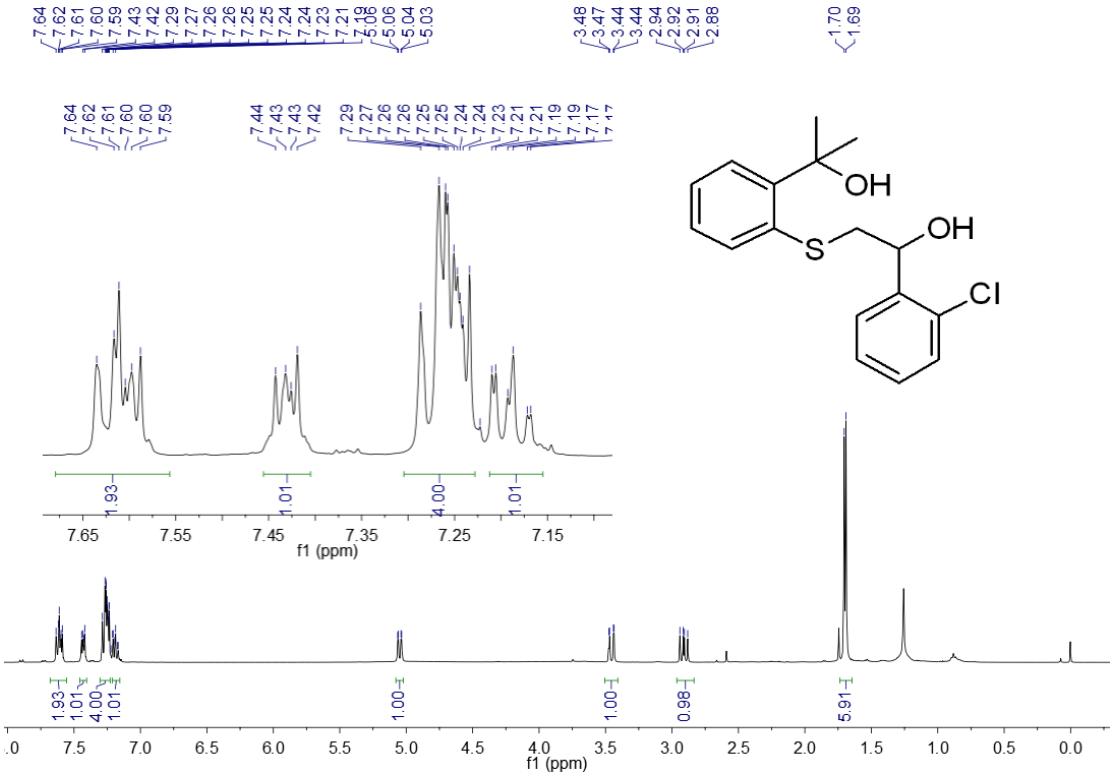

148.98 144.24 133.95 132.22 128.13 127.29 127.20 126.08 125.97 125.91
72.54 71.82
45.39
OH
OH
S
f1 (ppm)

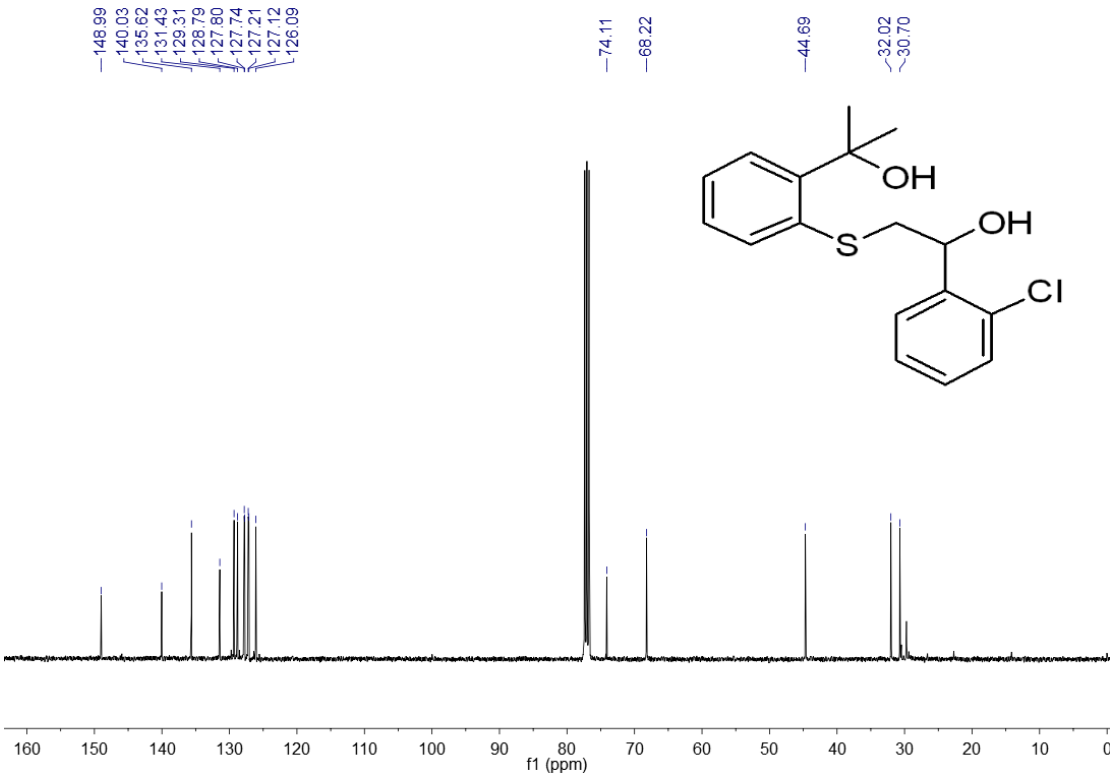
5ab


7.56 7.54 7.52 7.52 7.50 7.50 7.46 7.43 7.26 7.26 7.25 7.24 7.23 7.21 7.20 7.16 7.15 7.08 5.11 4.90 4.89 4.87 4.87
3.41 3.25 3.24 3.22 3.21 3.05 3.03 3.02 3.00
2.08
1.69 1.68
OH
OH
S
0.97 0.96 1.00 2.03 2.00 0.99
0.95 1.00
0.96 1.00 1.00
3.00
6.00
f1 (ppm)

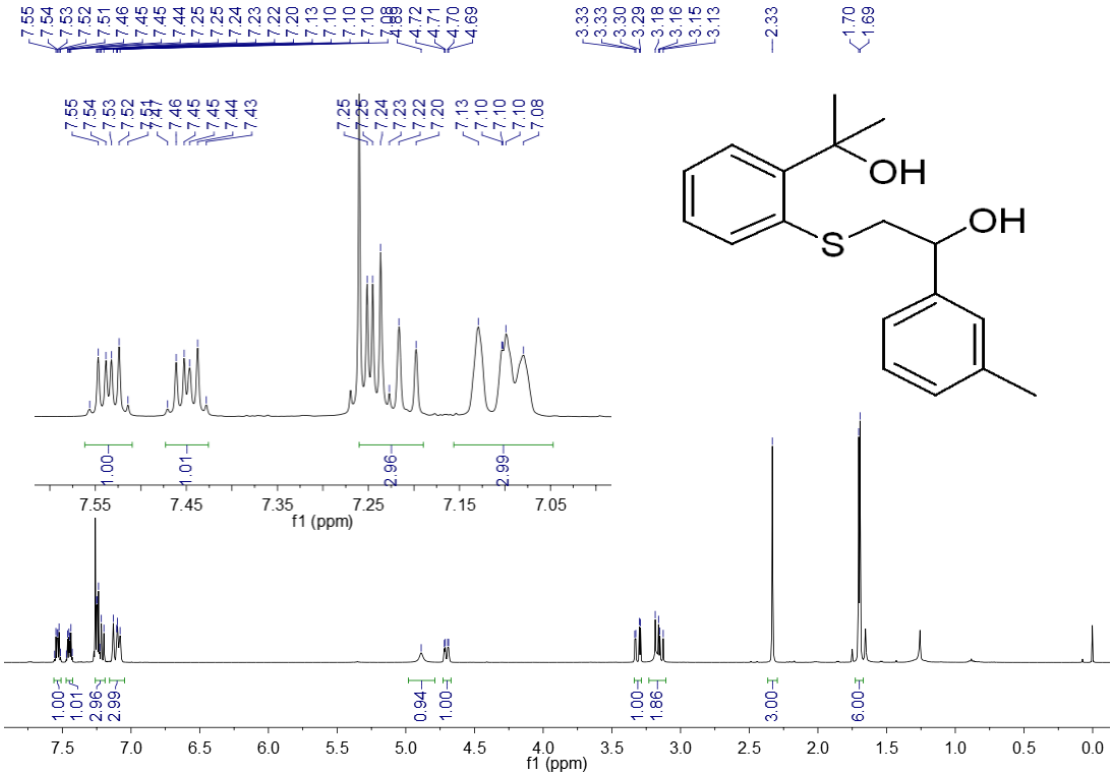

149.32 140.70 135.42 134.13 131.96 130.38 127.81 127.74 127.60 126.42 126.17 125.28
73.94 68.09
45.57
32.03 30.63
18.72
OH
OH
S
f1 (ppm)

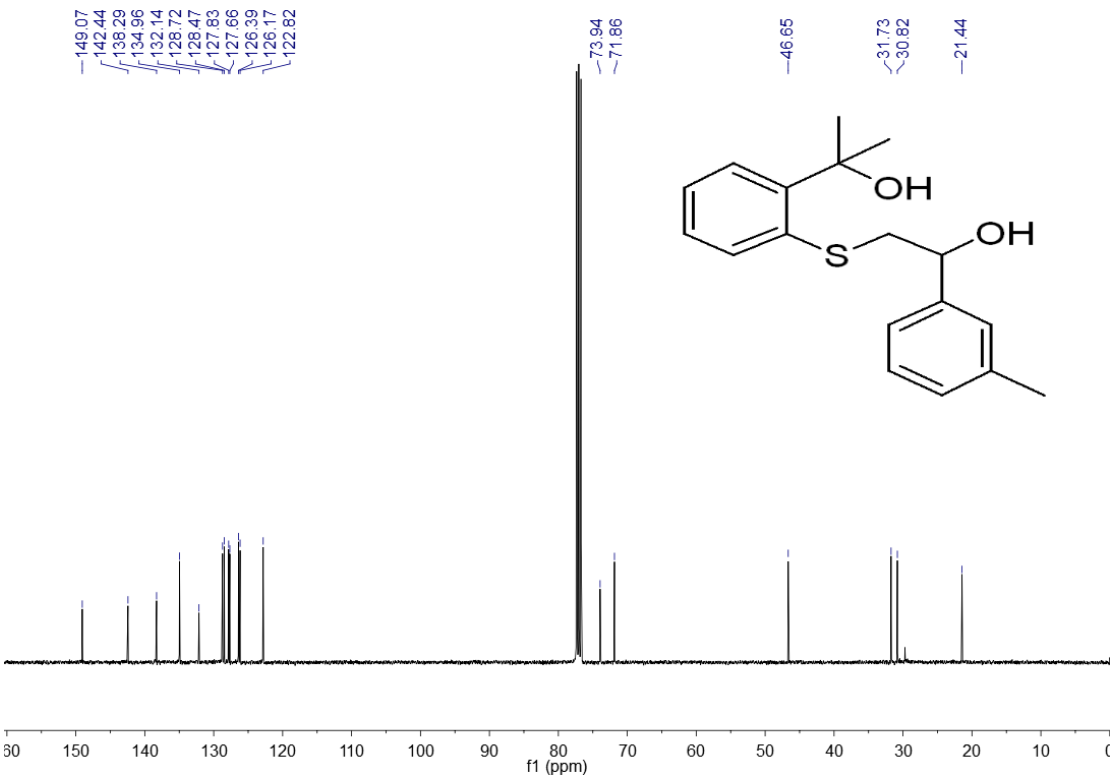
5ac


7.64
7.62
7.61
7.60
7.59
7.43
7.42
7.29
7.27
7.26
7.26
7.25
7.25
7.24
7.24
7.23
7.21
7.19
5.06
5.04
5.03
3.48
3.47
3.44
3.44
2.94
2.92
2.91
2.88
1.70
1.69
OH
OH
S
Cl
1.93
1.01
4.00
1.01
1.00
1.00
0.98
5.91
f1 (ppm)

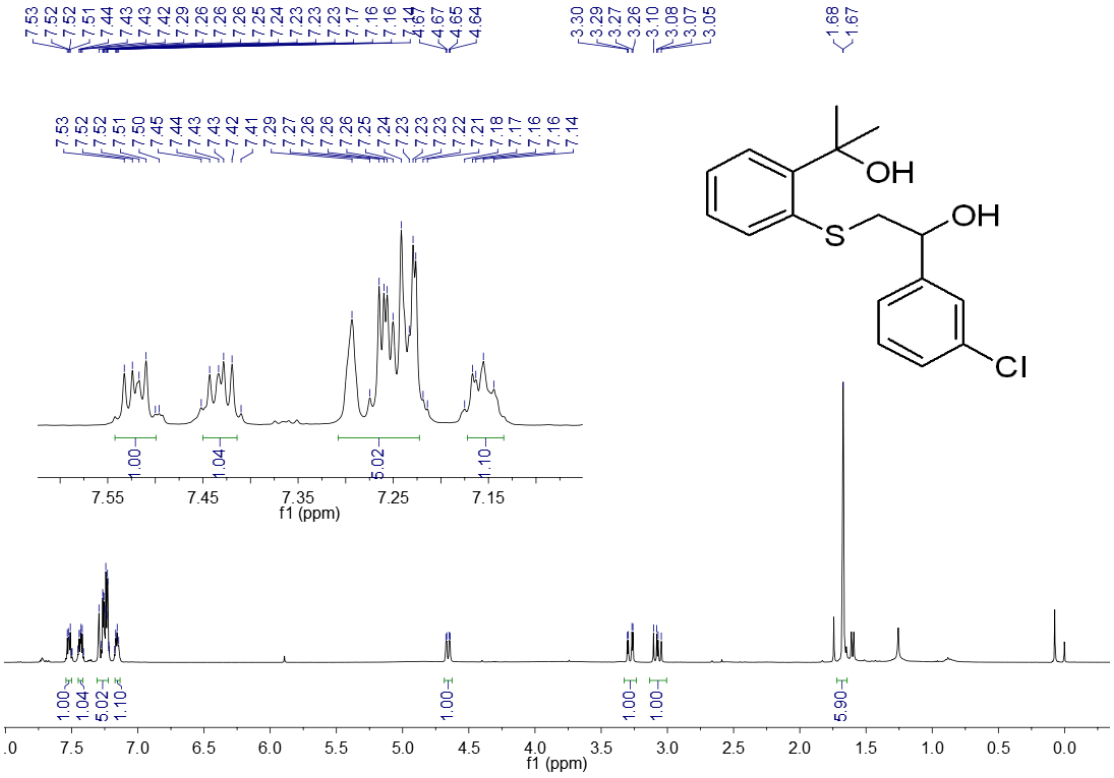

148.99
140.03
135.62
131.43
129.31
128.79
127.80
127.74
127.21
127.12
126.09
74.11
68.22
44.69
32.02
30.70
OH
OH
S
Cl
f1 (ppm)

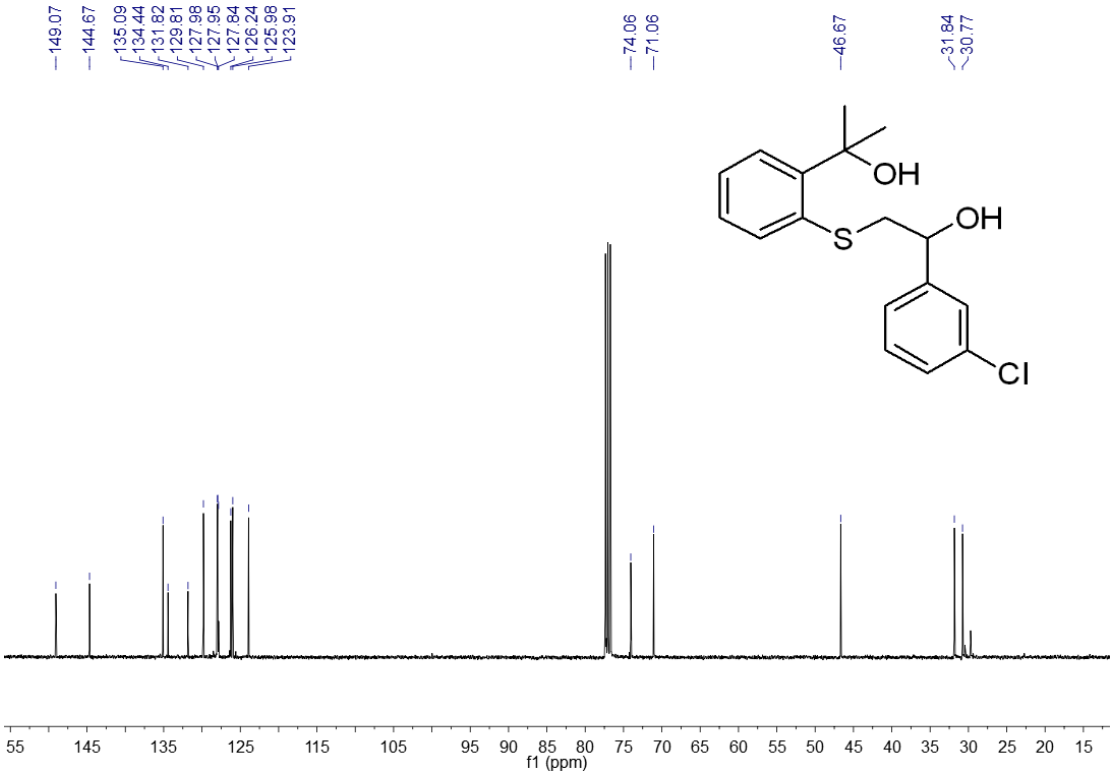
5ad



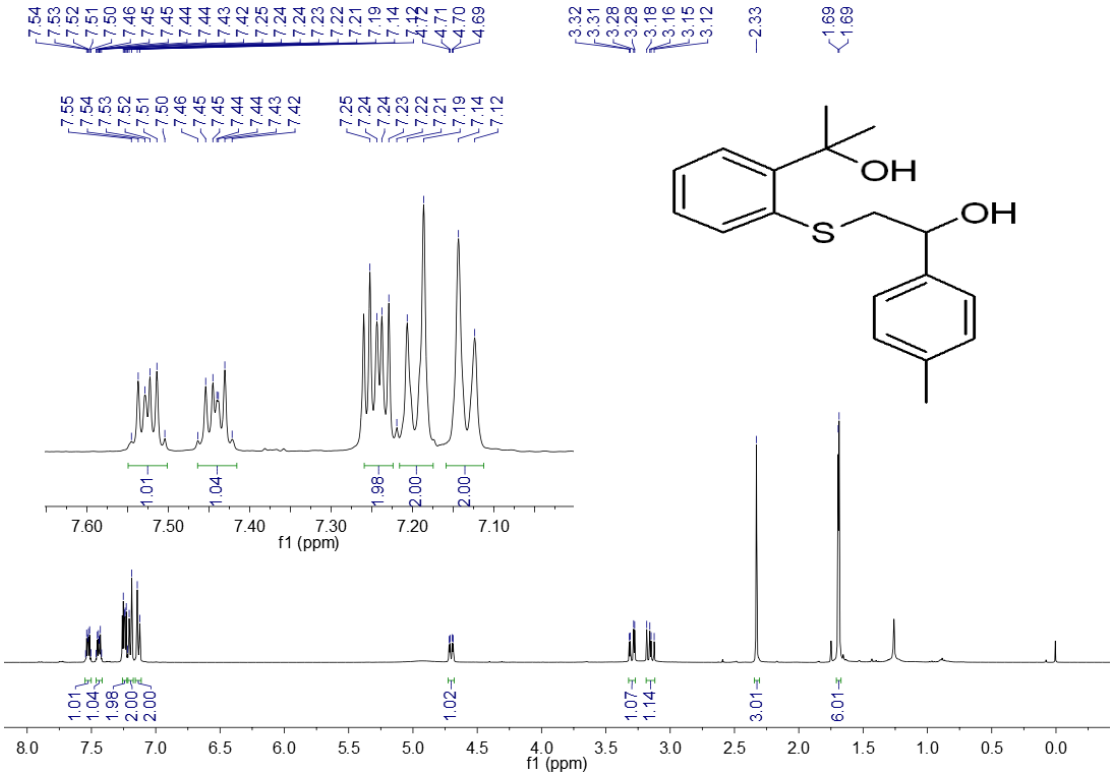


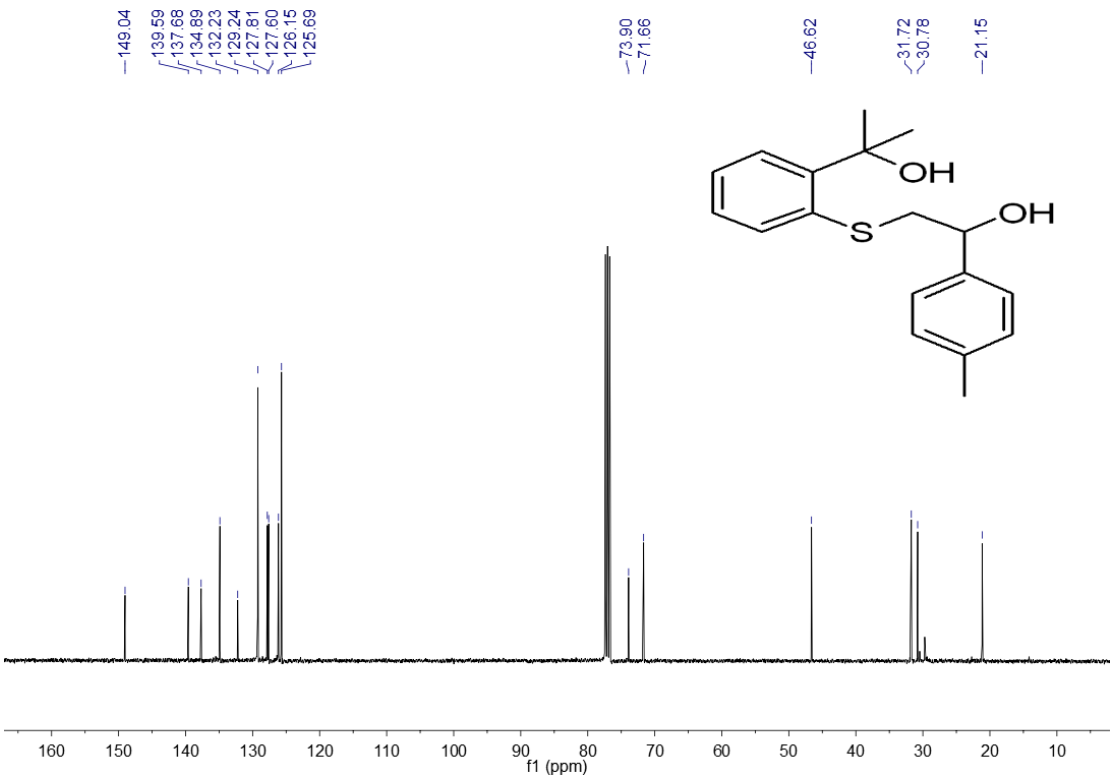
5ae


7.53 7.52 7.52 7.51 7.44 7.43 7.43 7.42 7.29 7.26 7.26 7.25 7.24 7.23 7.23 7.17 7.16 7.16 7.14 4.67 4.65 4.64
3.30 3.29 3.27 3.26 3.10 3.08 3.07 3.05
1.68 1.67
OH
OH
S
Cl
1.00 1.04 5.02 1.10
7.55 7.45 7.35 7.25 7.15
f1 (ppm)
1.00 1.04 5.02 1.10 1.00 1.00 1.00 5.90
f1 (ppm)

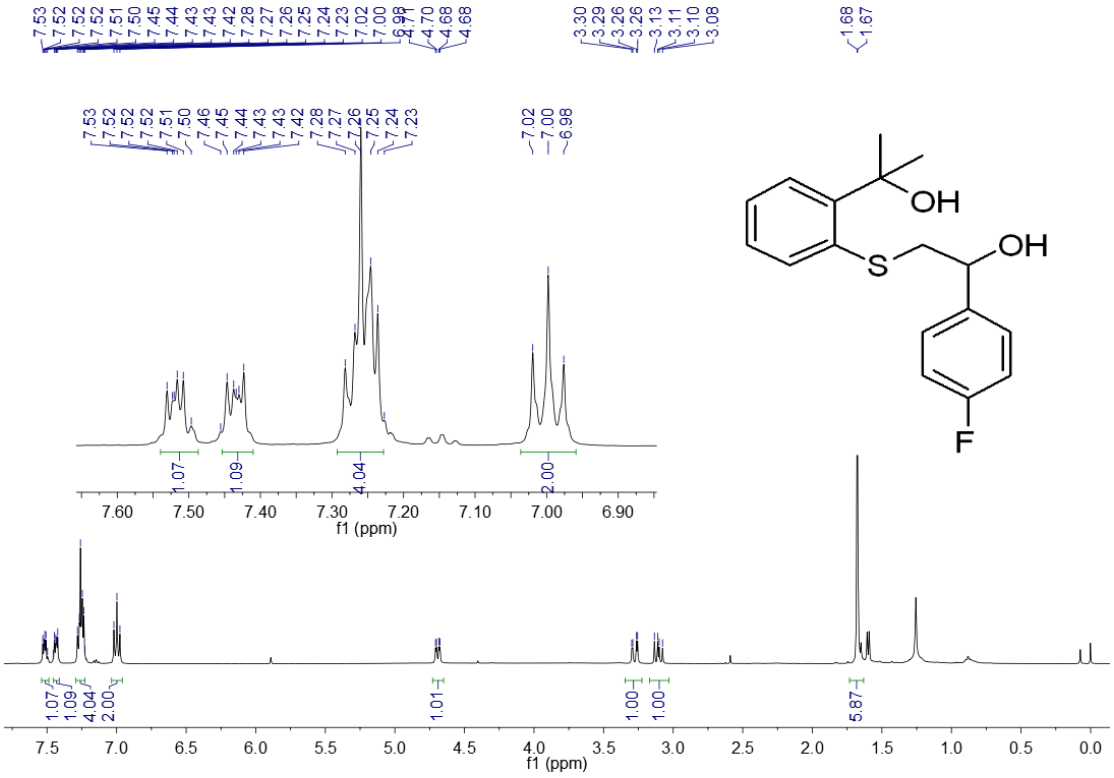

149.07 144.67 135.09 134.44 131.82 129.81 127.98 127.95 127.84 126.24 125.98 123.91
74.06 71.06
46.67
31.84 30.77
OH
OH
S
Cl
f1 (ppm)

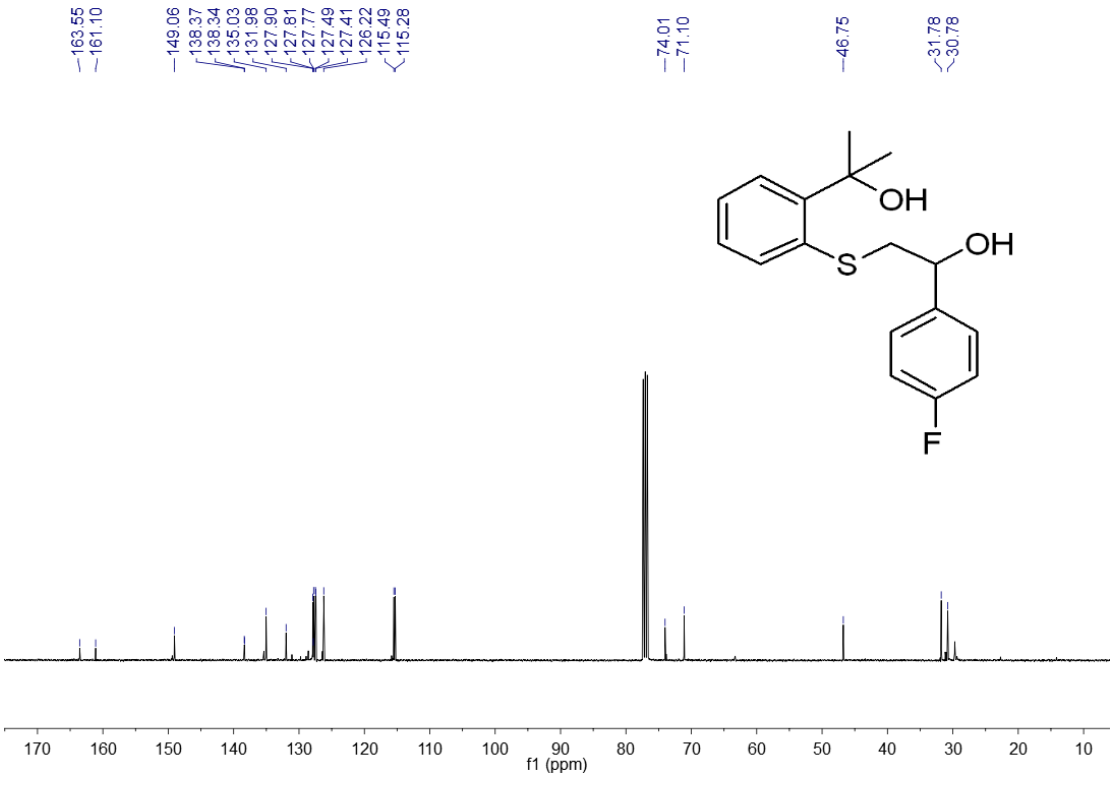
5af


7.54 7.53 7.52 7.51 7.50 7.46 7.45 7.45 7.44 7.44 7.43 7.42 7.25 7.24 7.24 7.23 7.22 7.21 7.19 7.14 7.12 4.71 4.70 4.69
3.32 3.31 3.28 3.28 3.18 3.16 3.15 3.12 2.33 1.69 1.69
OH
OH
S
1.01 1.04 1.98 2.00 2.00
7.60 7.50 7.40 7.30 7.20 7.10
f1 (ppm)
1.01 1.04 1.98 2.00 2.00 1.02 1.07 1.14 3.01 6.01
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

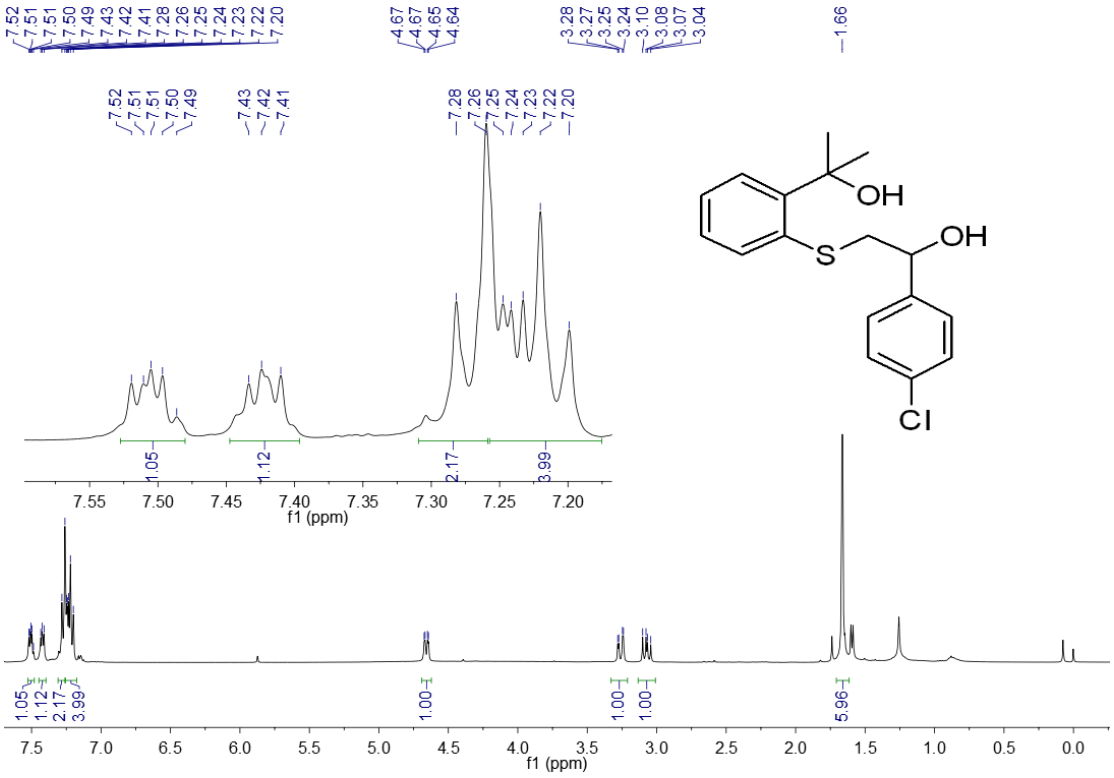

149.04 139.59 137.68 134.89 132.23 129.24 127.81 127.60 126.15 125.69
73.90 71.66 46.62 31.72 30.78 21.15
OH
OH
S
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

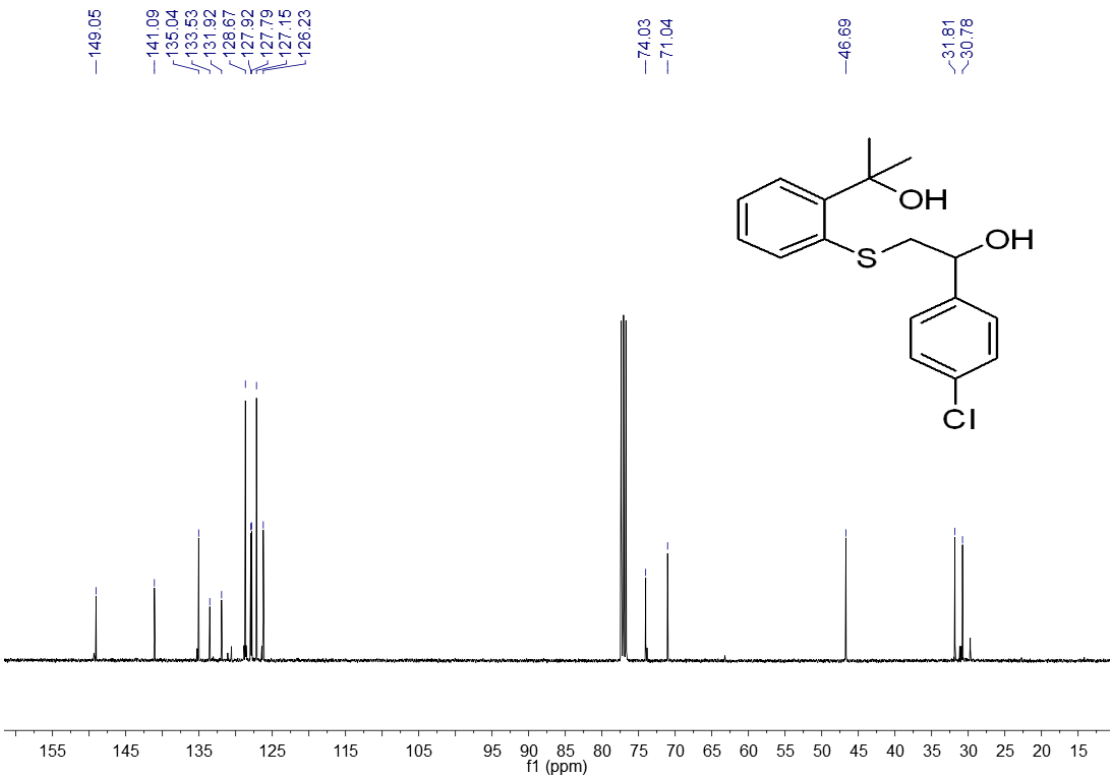
5ag


7.53
7.52
7.52
7.52
7.51
7.50
7.45
7.44
7.43
7.43
7.42
7.28
7.27
7.26
7.25
7.24
7.23
7.02
7.00
6.98
4.70
4.68
4.68
3.30
3.29
3.26
3.26
3.13
3.11
3.10
3.08
1.68
1.67
OH
OH
S
F
1.07
1.09
4.04
2.00
1.01
1.00
1.00
5.87
f1 (ppm)

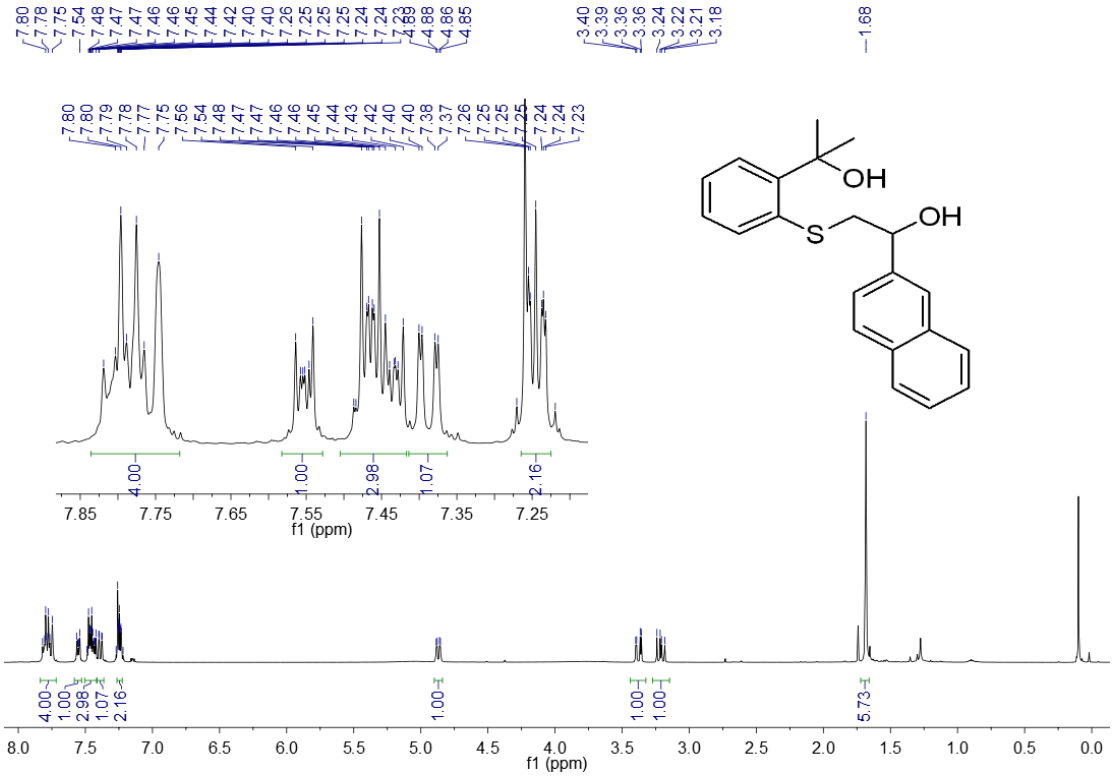

163.55
161.10
149.06
138.37
138.34
135.03
131.98
127.90
127.81
127.77
127.49
127.41
126.22
115.49
115.28
74.01
71.10
46.75
31.78
30.78
OH
OH
S
F
f1 (ppm)

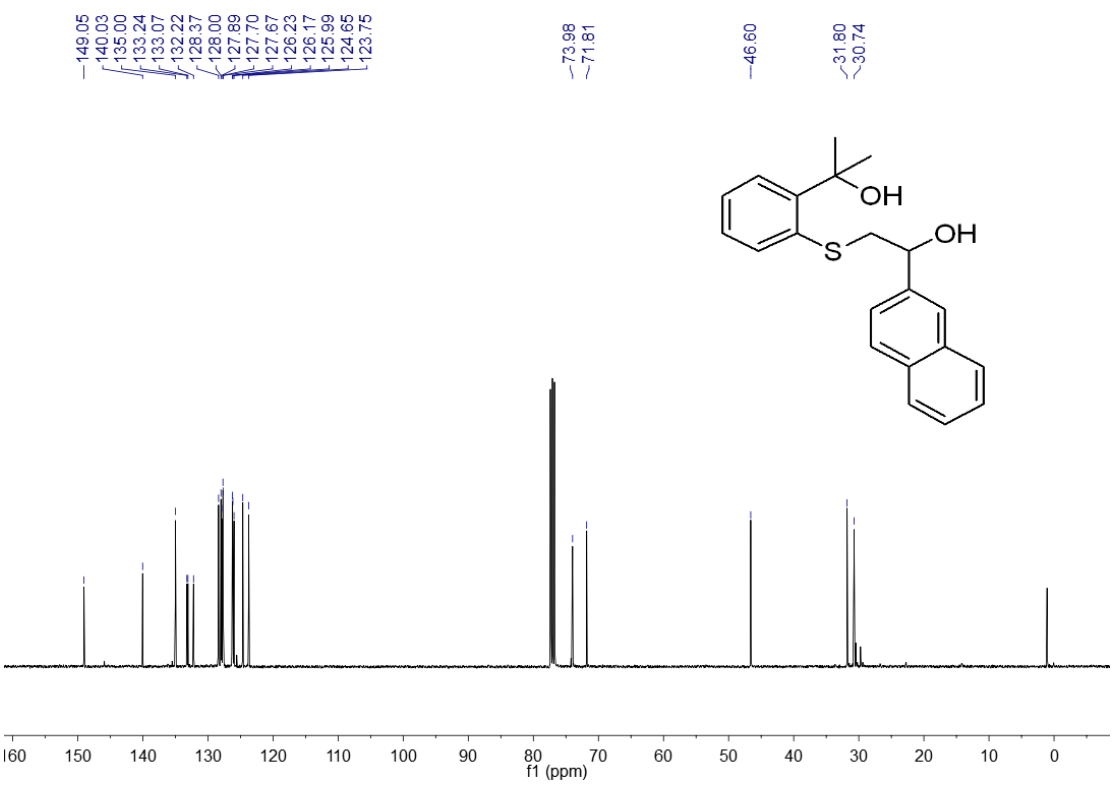
5ah


7.52
7.51
7.51
7.50
7.49
7.43
7.42
7.41
7.28
7.26
7.25
7.24
7.23
7.22
7.20
4.67
4.67
4.65
4.64
3.28
3.27
3.25
3.24
3.10
3.08
3.07
3.04
1.66
1.05
1.12
2.17
3.99
1.00
1.00
1.00
5.96
f1 (ppm)
OH
OH
S
Cl

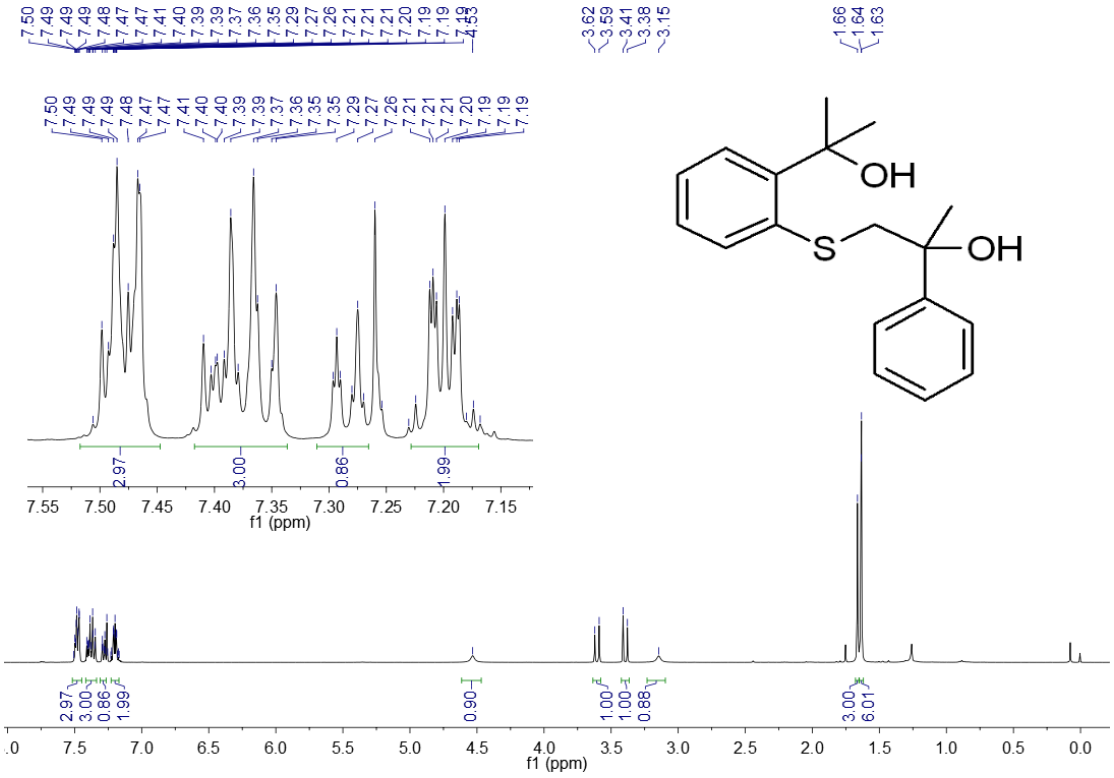

149.05
141.09
135.04
133.53
131.92
128.67
127.92
127.79
127.15
126.23
74.03
71.04
46.69
31.81
30.78
f1 (ppm)
OH
OH
S
Cl

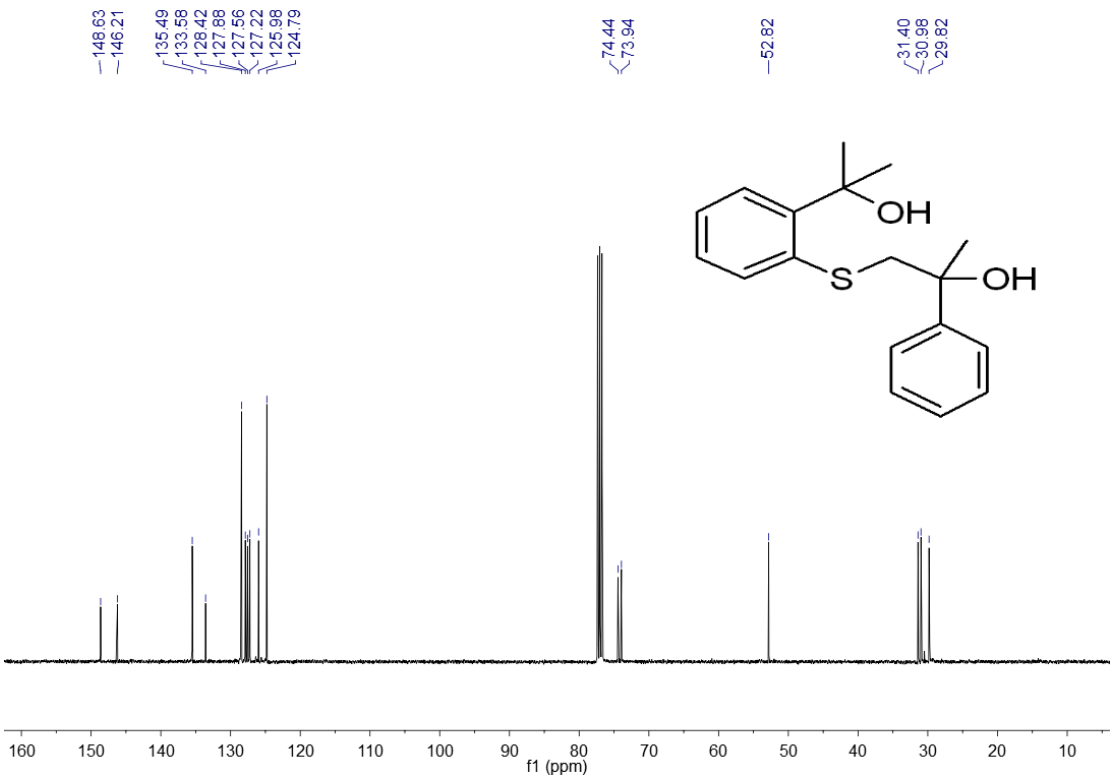
5ai



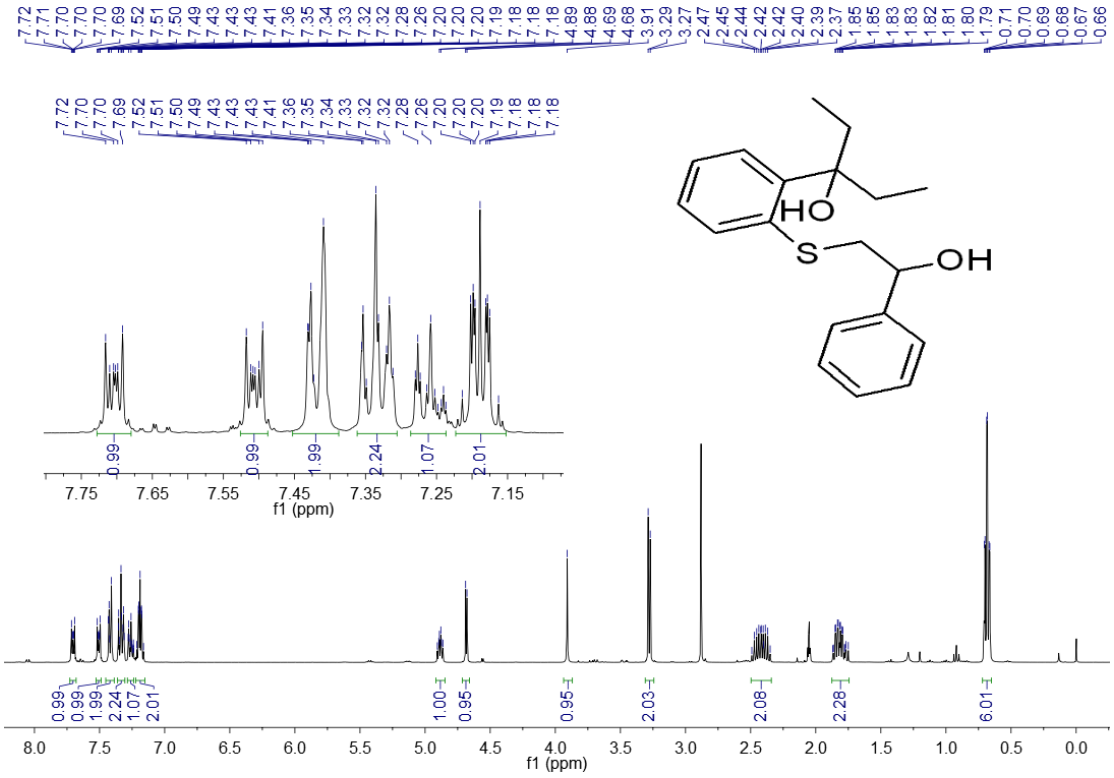


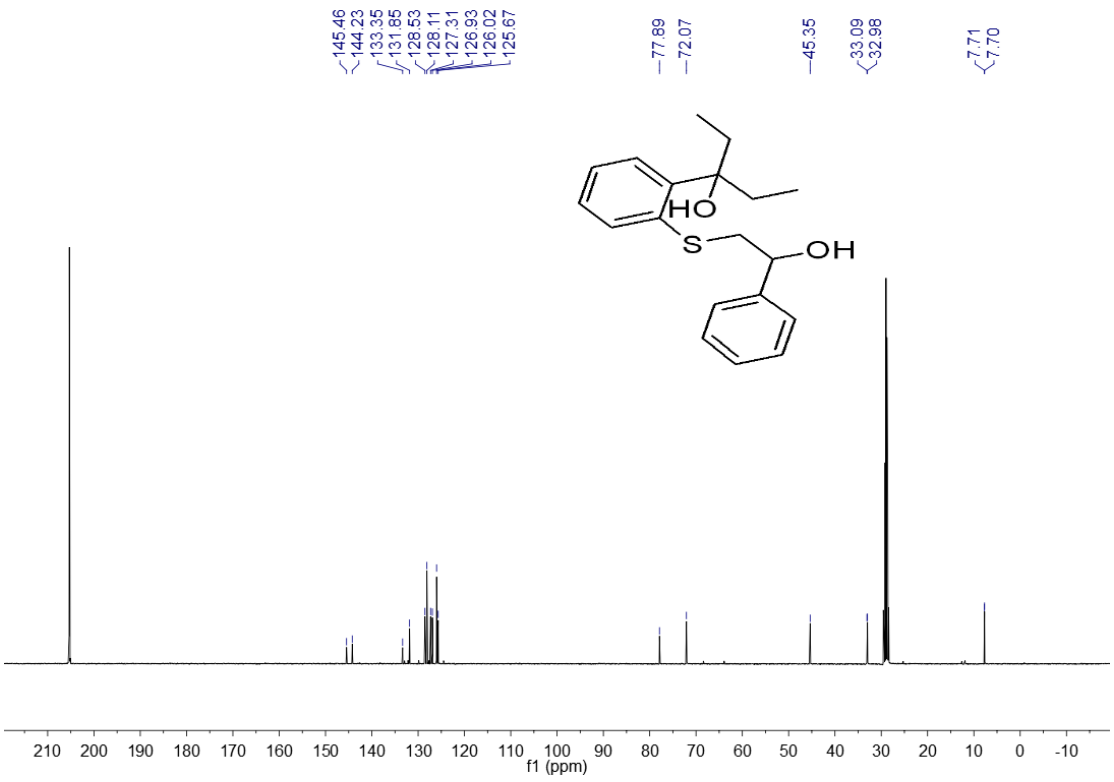
5aj



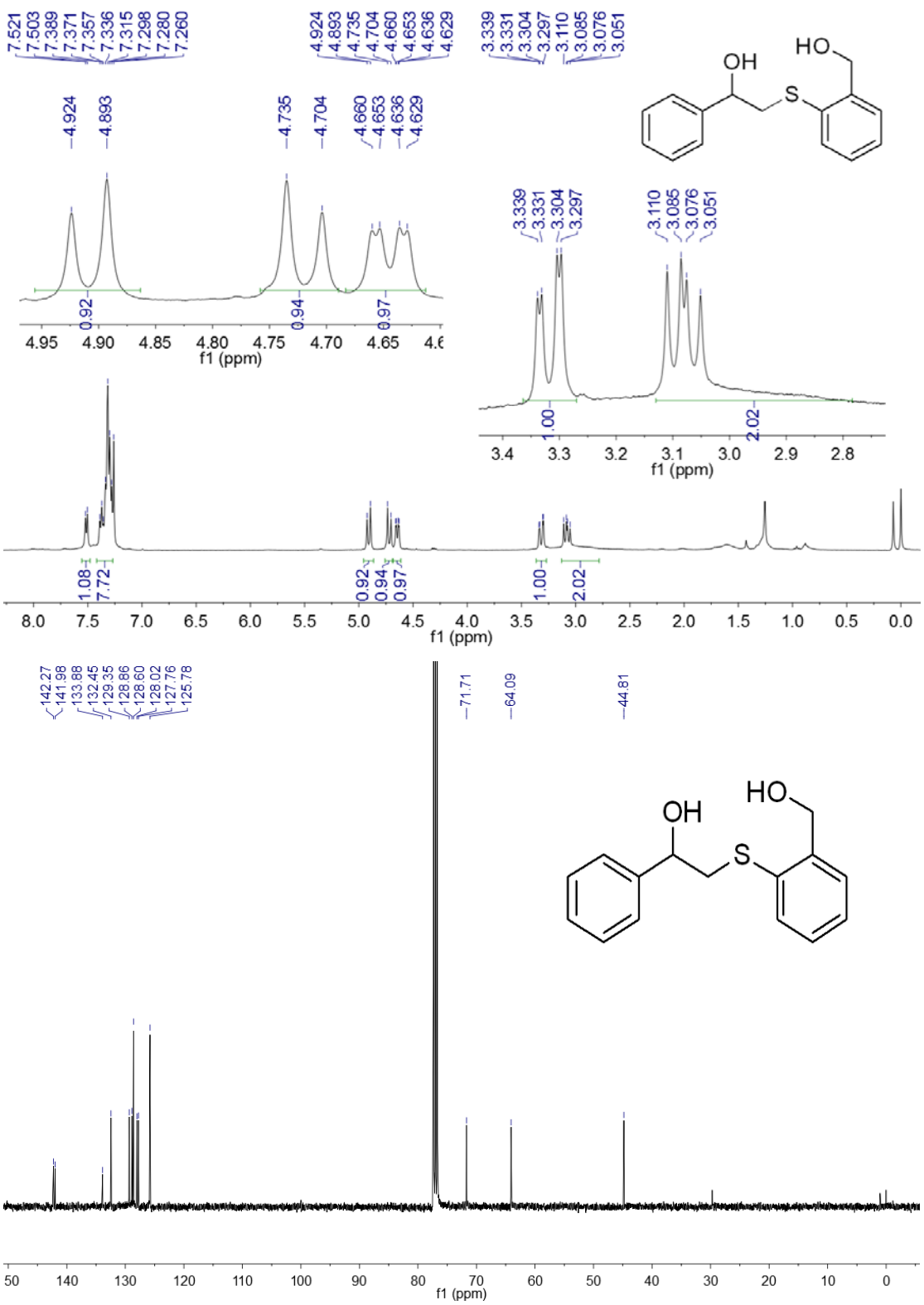


5ba

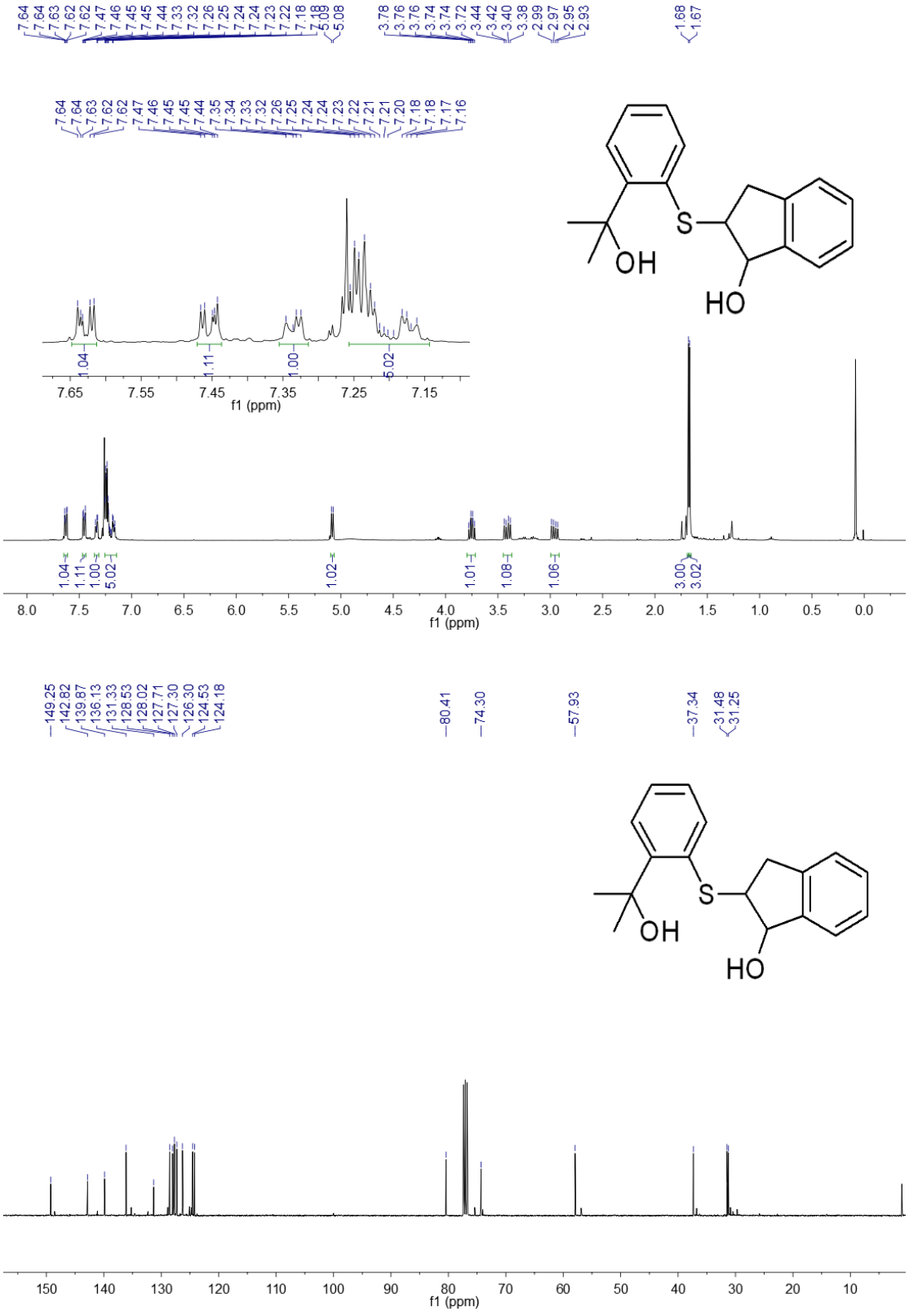




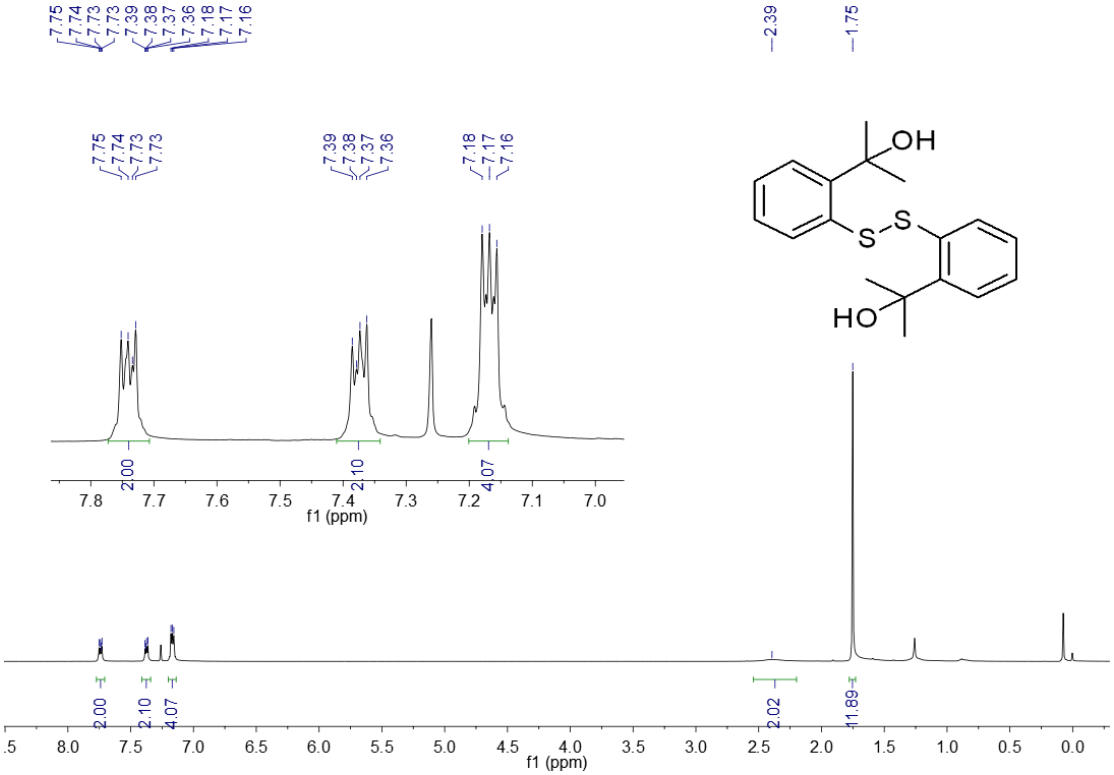
5ca

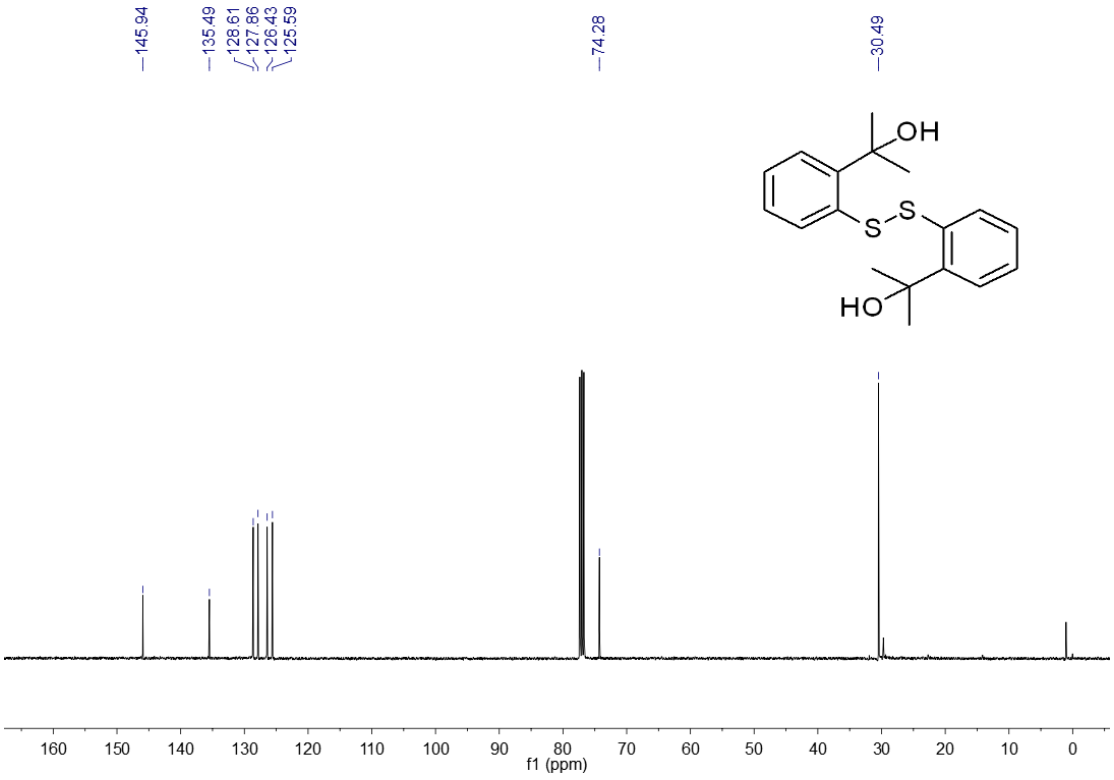

7.521
7.503
7.389
7.371
7.357
7.336
7.315
7.298
7.280
7.260
4.924
4.893
4.735
4.704
4.660
4.653
4.636
4.629
3.339
3.331
3.304
3.297
3.110
3.085
3.076
3.051
OH
HO
S
0.92
0.94
0.97
1.00
2.02
1.08
7.72
f1 (ppm)
142.27
141.98
133.88
132.45
129.35
128.86
128.60
128.02
127.76
125.78
71.71
64.09
44.81

5ak (inseparable diastereomers with 85:15 dr)

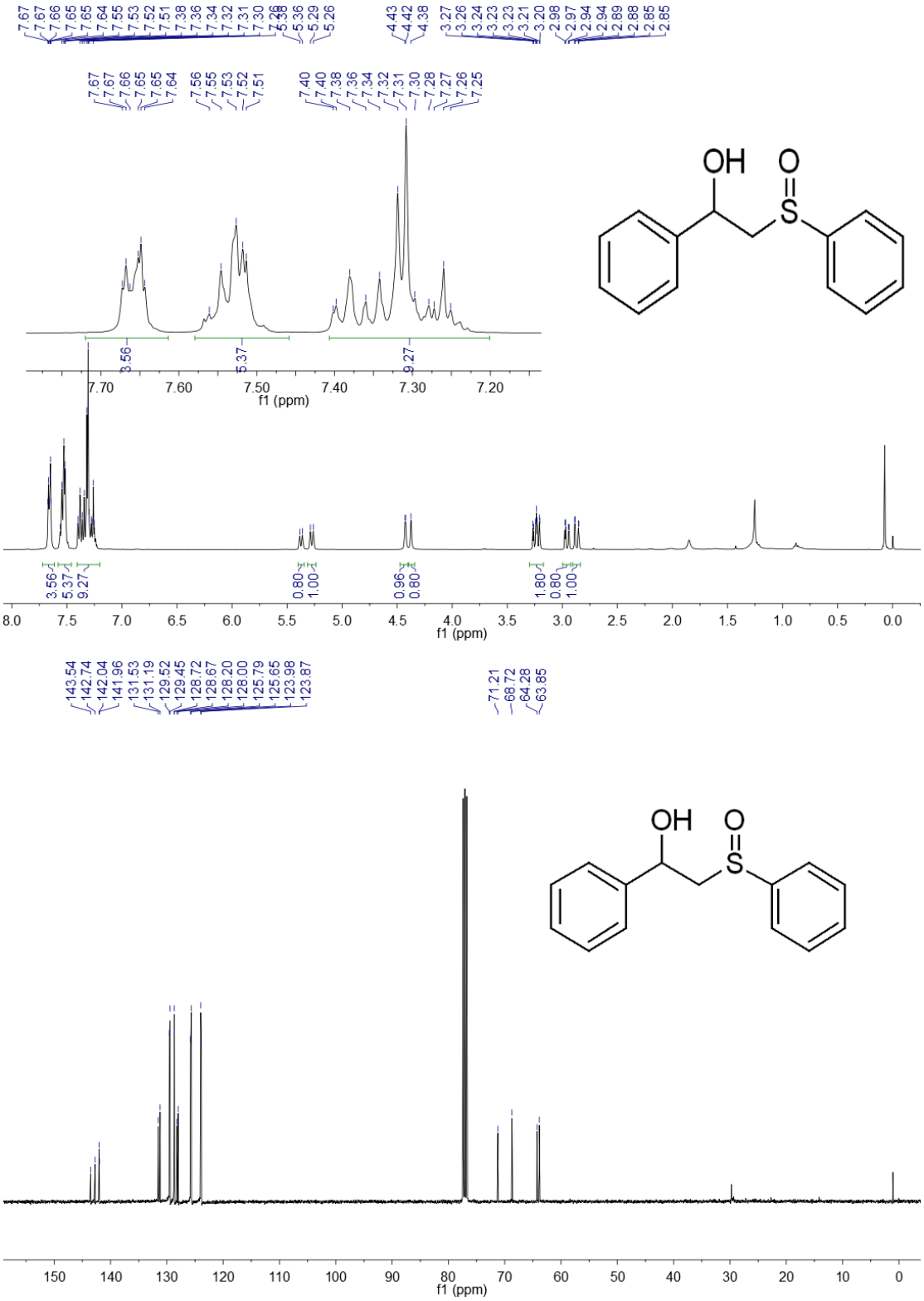


Byproduct 7

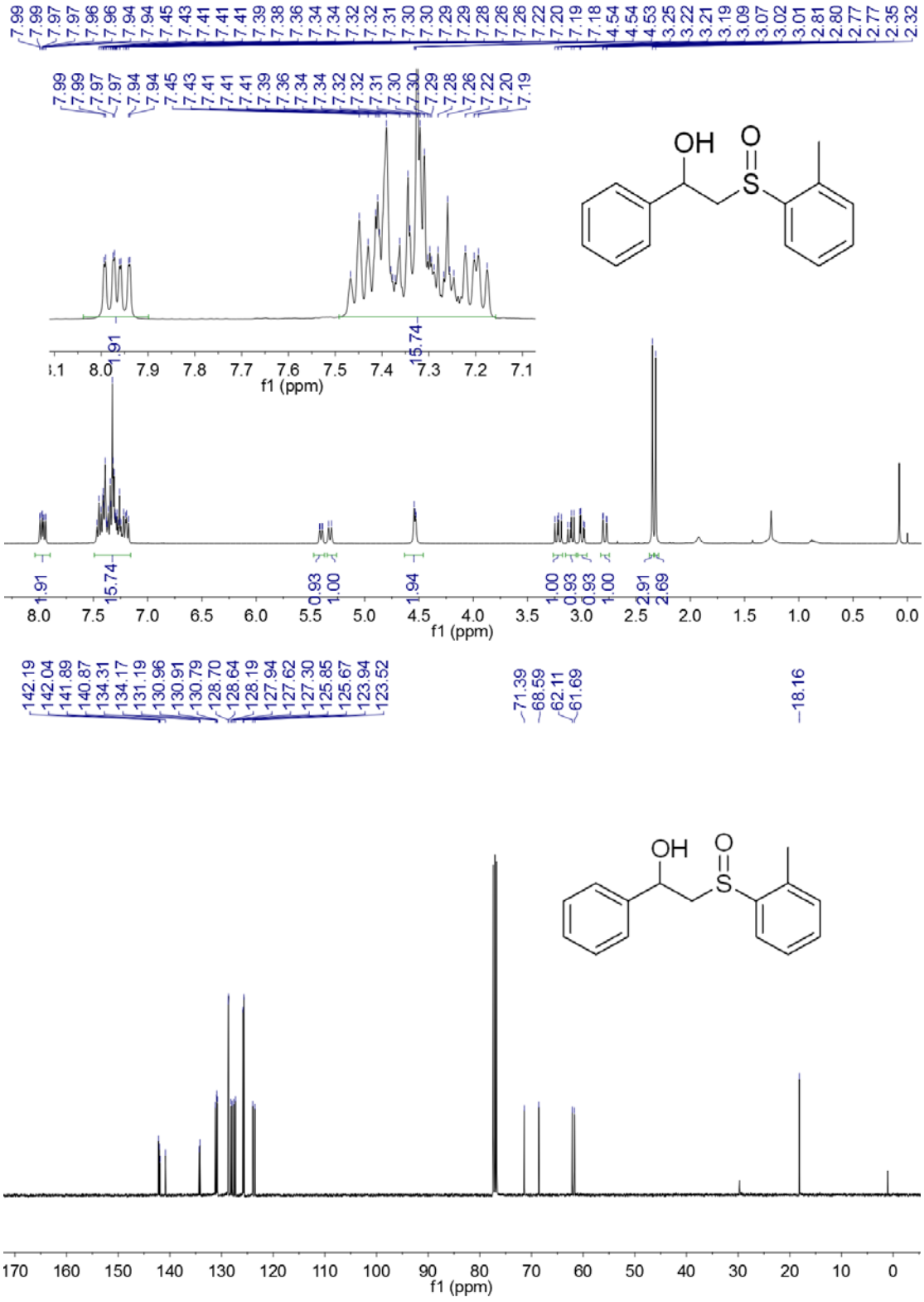

7.75
7.74
7.73
7.73
7.39
7.38
7.37
7.36
7.18
7.17
7.16
2.39
1.75
OH
S
S
HO
2.00
2.10
4.07
2.02
11.89
f1 (ppm)


145.94
135.49
128.61
127.86
126.43
125.59
74.28
30.49
OH
S
S
HO
f1 (ppm)

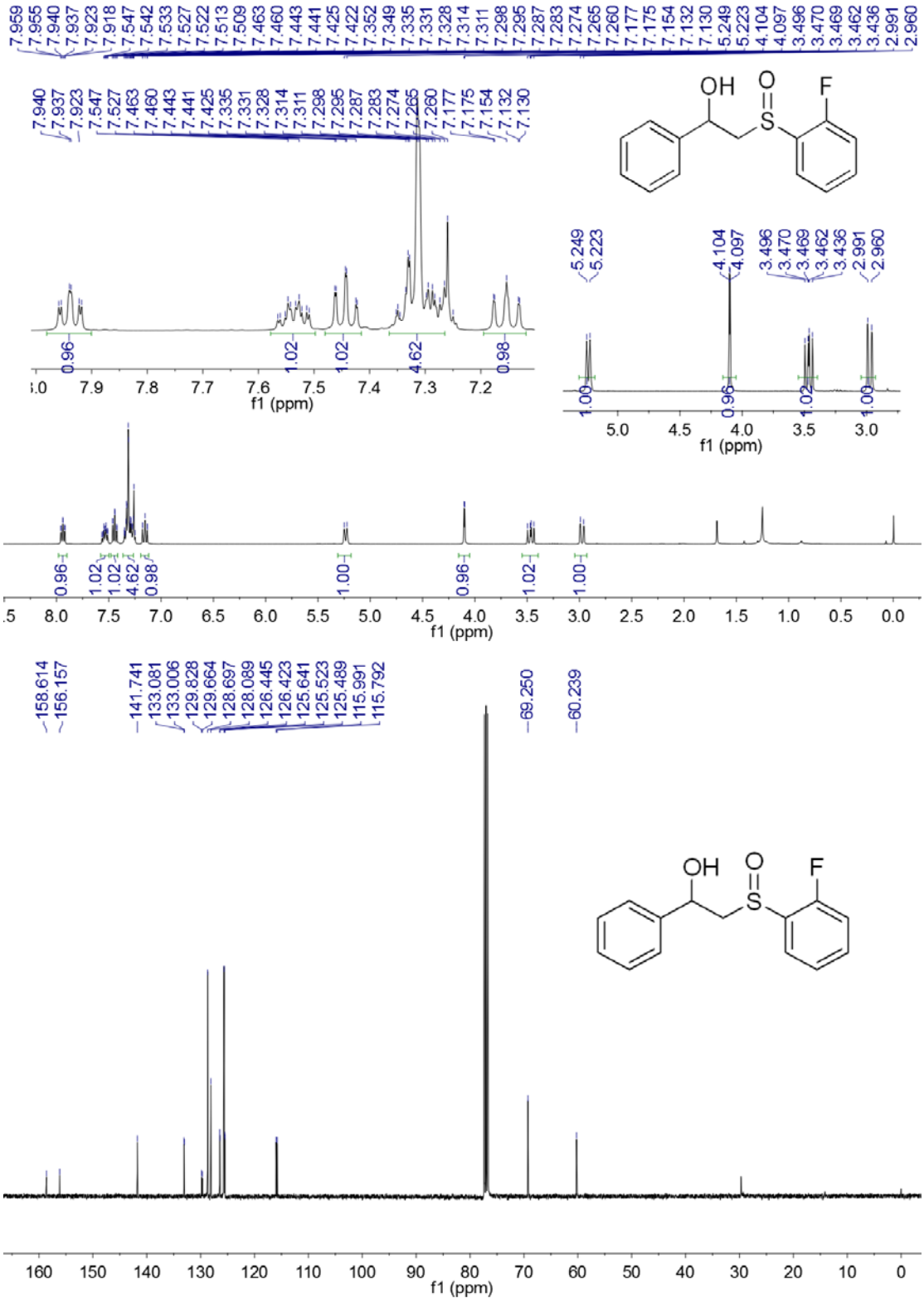
9aa (inseparable diastereomers with 56:44 dr)



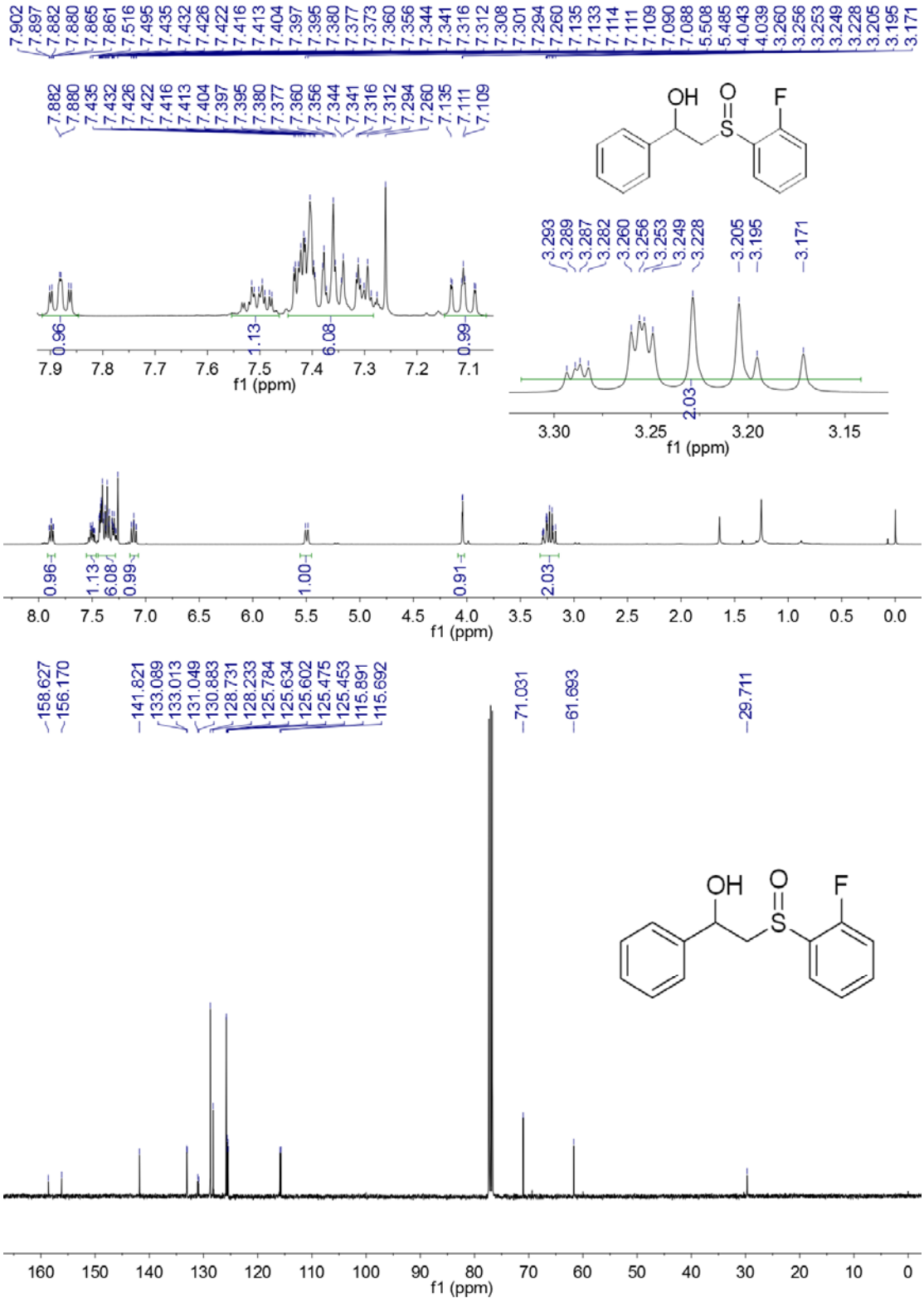
9ba (inseparable diastereomers with 53:47 dr)



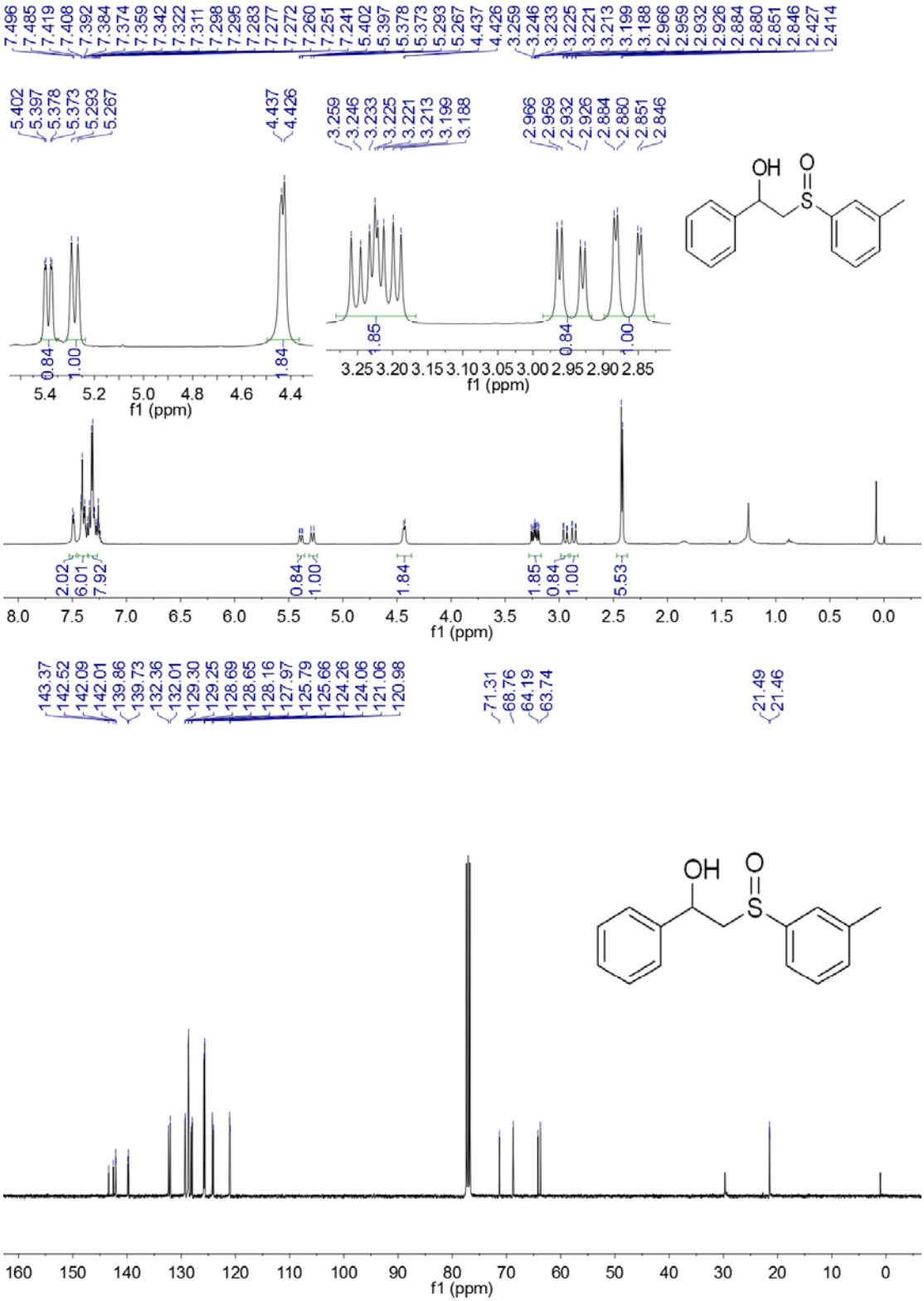
9ca (One diastereomer)



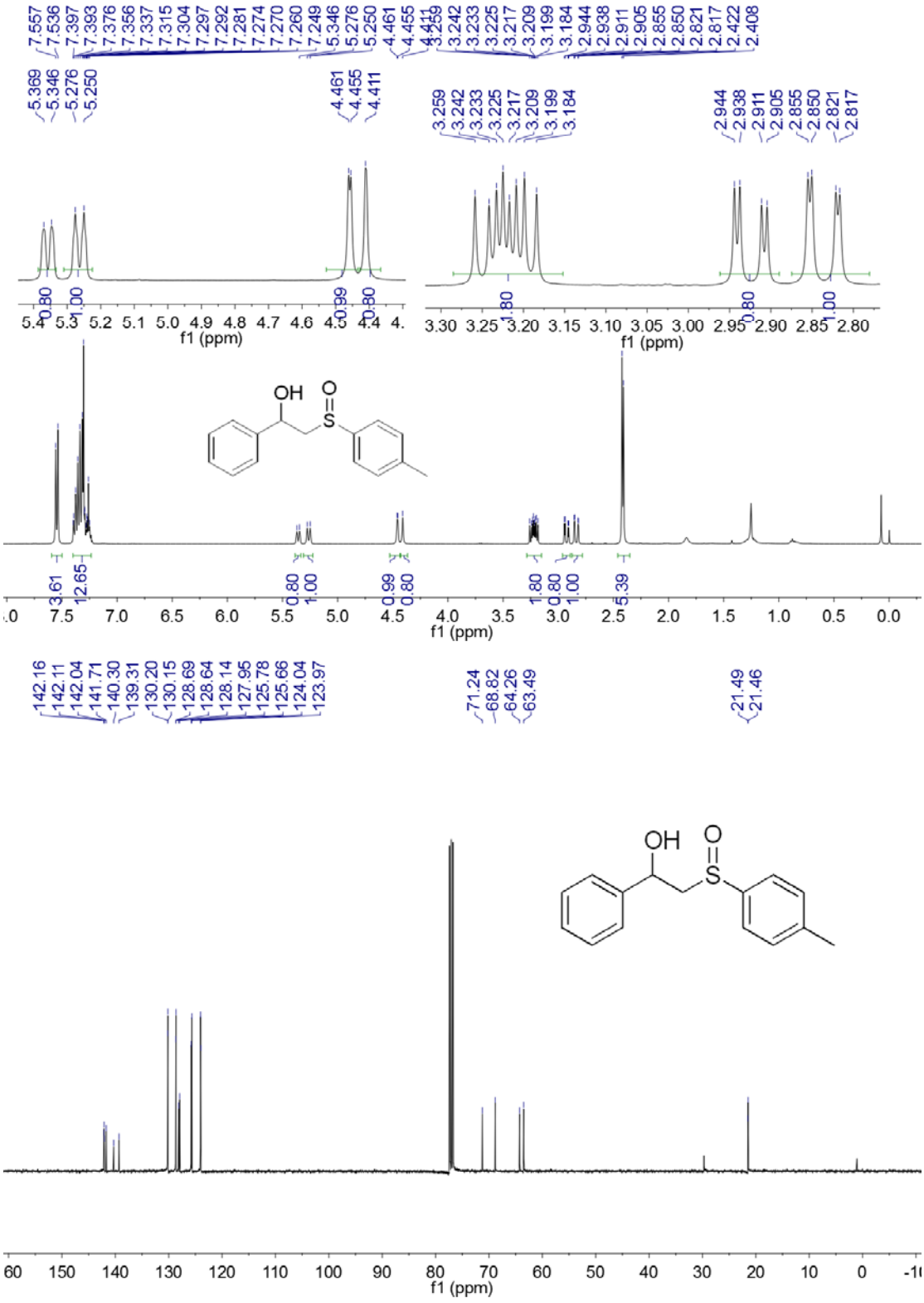
9ca (Another diastereomer)



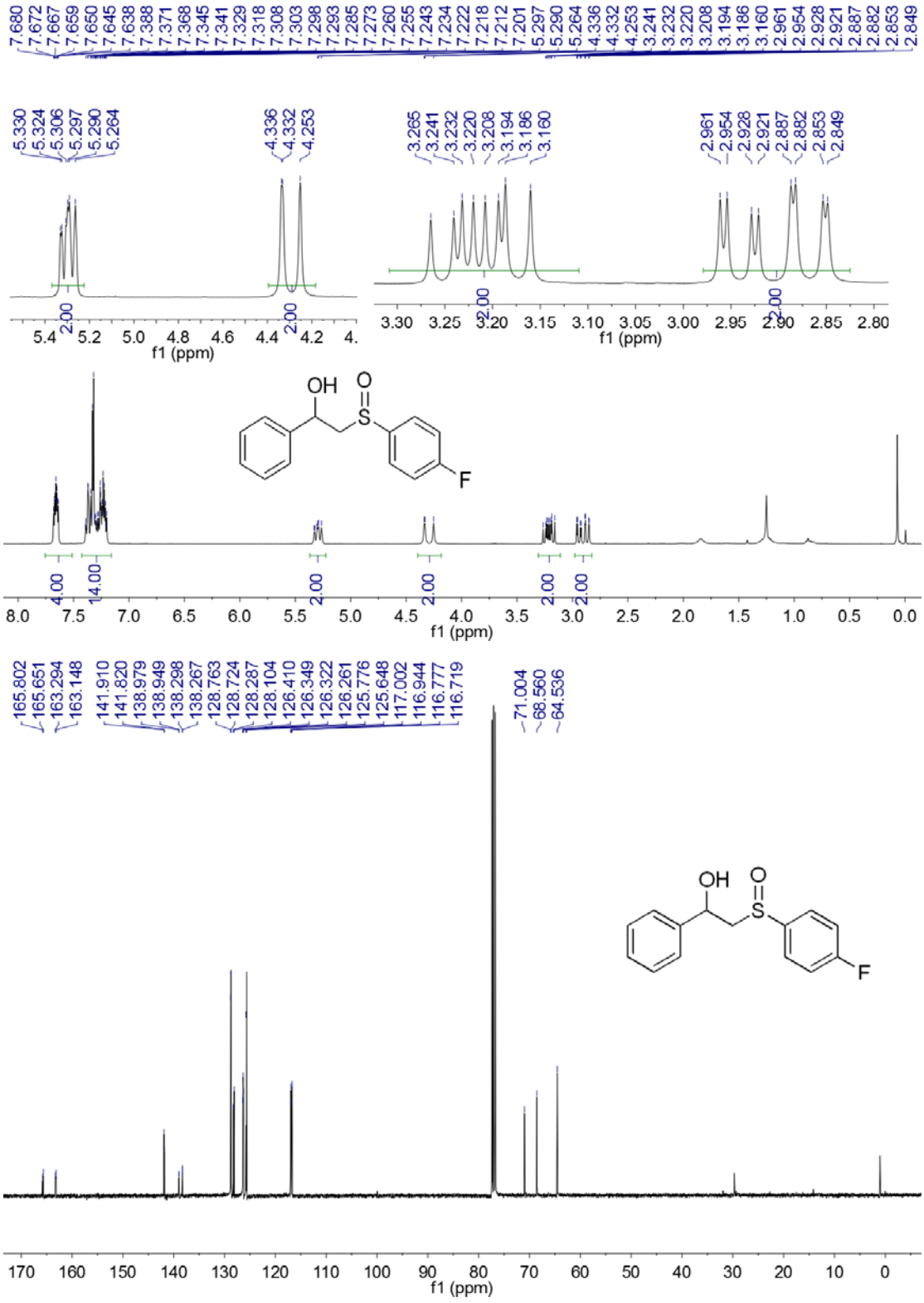
9da (inseparable diastereomers with 56:44 dr)



9ea (inseparable diastereomers with 56:44 dr)

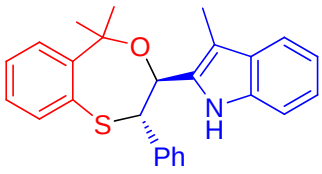


9fa (inseparable diastereomers with 50:50 dr)

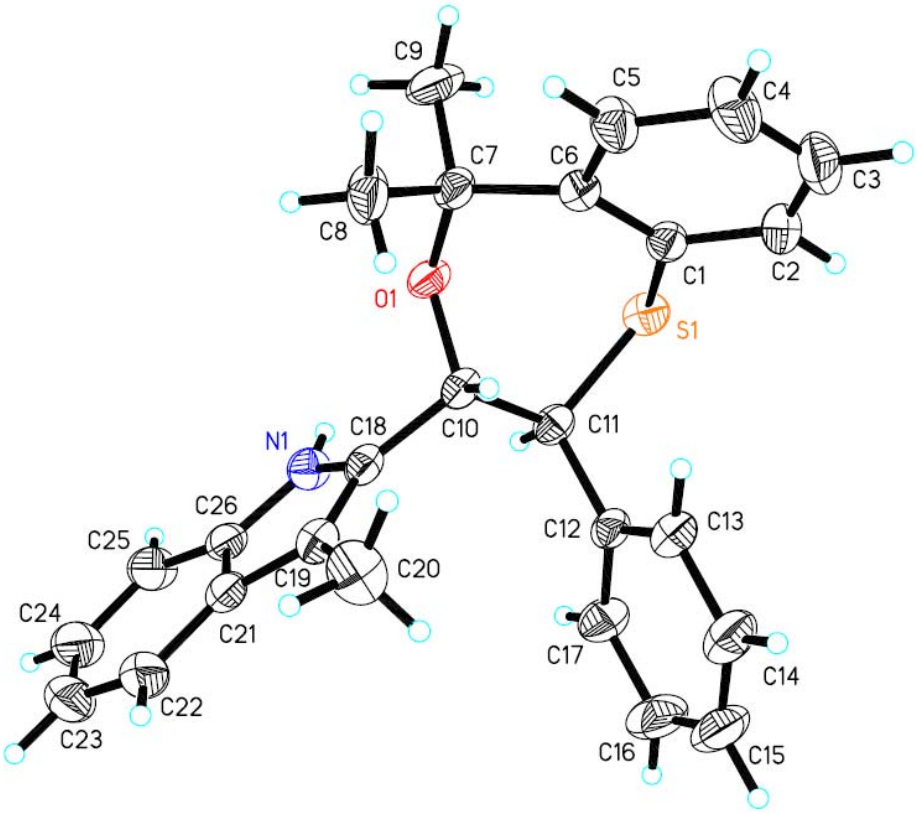


8. X-ray single crystal data for compounds 3aa, 5aa and 7

Compound 3aa:



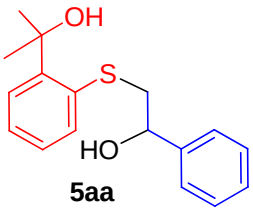
3aa



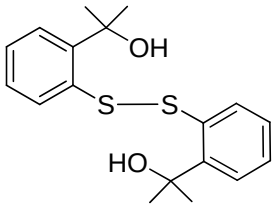
The thermal ellipsoid was drawn at the 30% probability level.

Empirical formula	C26 H25 N O S	
Formula weight	399.53	
Temperature	296.15 K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 8.280(7) Å	α= 64.811(14)°.
	b = 11.804(10) Å	β= 88.065(15)°.
	c = 12.324(10) Å	γ = 80.753(17)°.
Volume	1075.0(15) $Å^3$	
Z	2	
Density (calculated)	1.234 Mg/m^3	
Absorption coefficient	0.167 mm^{-1}	
F(000)	424	
Crystal size	0.2 x 0.12 x 0.08 mm^3	
Theta range for data collection	1.827 to 30.700°.	
Index ranges	-11<=h<=11, -16<=k<=14, -17<=l<=14	
Reflections collected	10942	
Independent reflections	6542 [R(int) = 0.0325]	
Completeness to theta = 26.000°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7461 and 0.6457	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6542 / 0 / 265	
Goodness-of-fit on F^2	0.973	
Final R indices [I>2sigma(I)]	R1 = 0.0534, wR2 = 0.1197	
R indices (all data)	R1 = 0.1149, wR2 = 0.1454	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.215 and -0.325 $e.Å^{-3}$	

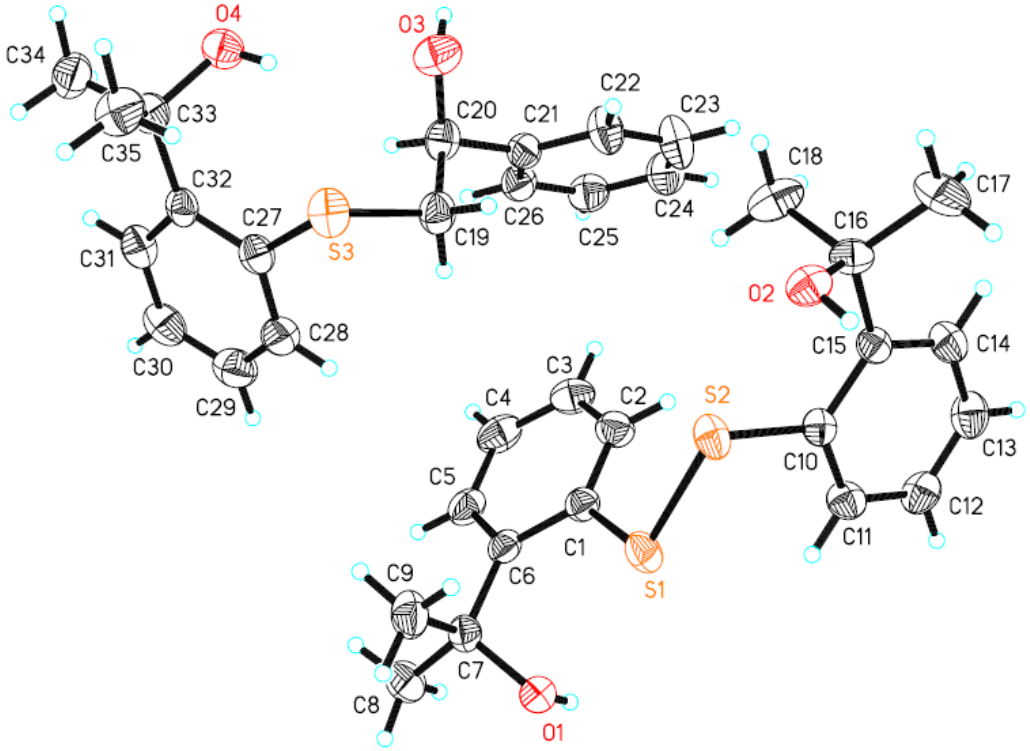
Compounds 5aa and 7:



5aa



7



The thermal ellipsoid was drawn at the 30% probability level.

Empirical formula	C35 H42 O4 S3	
Formula weight	622.86	
Temperature	296 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C 1 c 1	
Unit cell dimensions	a = 8.5603(3) Å	α= 90°.
	b = 22.8130(7) Å	β= 94.2688(17)°.
	c = 17.3998(6) Å	γ = 90°.
Volume	3388.5(2) $Å^3$	
Z	4	
Density (calculated)	1.221 Mg/m^3	
Absorption coefficient	0.254 mm^{-1}	
F(000)	1328	
Crystal size	0.39 x 0.32 x 0.3 mm^3	
Theta range for data collection	2.137 to 27.527°.	
Index ranges	-11<=h<=10, -28<=k<=29, -13<=l<=22	
Reflections collected	14890	
Independent reflections	5699 [R(int) = 0.0239]	
Completeness to theta = 26.000°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.6206	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5699 / 2 / 389	
Goodness-of-fit on F^2	1.022	
Final R indices [I>2sigma(I)]	R1 = 0.0308, wR2 = 0.0660	
R indices (all data)	R1 = 0.0417, wR2 = 0.0712	
Absolute structure parameter	0.05(2)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.145 and -0.146 $e.Å^{-3}$	