Supporting Information

Gold-Catalyzed Ring Enlargement and Cycloisomerization of Alkynylamide Tethered Alkylidenecyclopropanes

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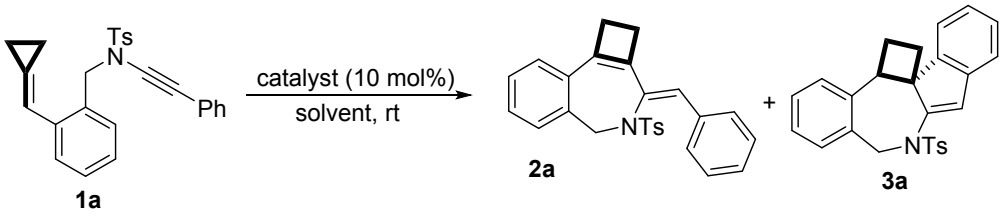
CONTENTS

1. General remarks.

^{1}H NMR spectra were recorded on a Varian Mercury-300 and 400 spectrometer for solution in $CDCl_3$ with tetramethylsilane (TMS) as an internal standard; coupling constants J are given in Hz. ^{13}C NMR spectra were recorded on a Varian Mercury-300 and 400 spectrophotometers (75 or 100 MHz) with complete proton decoupling spectrophotometers ($CDCl_3$: 77.0 ppm). Mass and HRMS spectra were recorded by EI or ESI method. Organic solvents used were dried by standard methods when necessary. Infrared spectra were recorded on a Perkin-Elmer PE-983 spectrometer with absorption in cm^{-1}. Melting points were determined on a digital melting point apparatus and temperatures were uncorrected. Fluorescence spectra for emission and excitation were obtained on a Hitachi F-2700 FL Spectrophotometer. Commercially obtained reagents were used without further purification. All these reactions were monitored by TLC with silica gel coated plates. Flash column chromatography was carried out using silica gel at increased pressure.

2. Optimization of reaction conditions.

Table S1: Optimization of reaction condition for the products **2a** and **3a**.

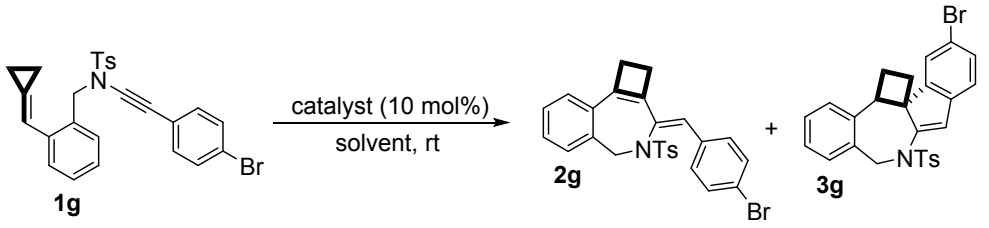


1a **2a** **3a**

entry	catalyst	solvent	temp/^{o}C	yield/%[a]	
				2a	**3a**
1	$Ph_3PAuSbF_6$	DCE	rt	22	51
2	IPrAuSbF$_6$	DCE	rt	37	14
3	^{t}-BuXPhosAuSbF$_6$	DCE	rt	28	53
4	$(ArO)_3PAuSbF_6$	DCE	rt	-	-
5	$Me_2PhPAuCl/AgSbF_6$	DCE	rt	34	13
6	$Ph_3PAuCl/AgSbF_6$	DCE	rt	31	39
7	$Ph_3PAuCl/AgBF_4$	DCE	rt	53	7
8	**Ph_3PAuCl/AgOTf**	**DCE**	**rt**	**77**	**-**
9	AgOTf	DCE	rt	54	-
10	Ph_3PAuCl/AgOTf	THF	rt	55	-
11	Ph_3PAuCl/AgOTf	toluene	rt	68	-
12	Ph_3PAuCl/AgOTf	MeCN	rt	63	-
13	Ph_3PAuCl/AgOTf	1,4-dioxane	rt	35	27
14	Ph_3PAuCl/NaBARF	DCE	rt	15	55
15	^{t}-BuXPhosAuCl/NaBARF	DCE	rt	15	22
16	BrettPhosAuCl/NaBARF	DCE	rt	15	14
17	$(p\text{-}FC_6H_4)_3PAuCl$/NaBARF	DCE	rt	25	36
18	$(p\text{-}F_3CC_6H_4)_3PAuCl$/NaBARF	DCE	rt	11	44
19	JackiephosAuCl/NaBARF	DCE	rt	21	40
20	^{t}-$Bu_2CyPAuCl$/NaBARF	DCE	rt	10	33
21	IPrAuCl/NaBARF	DCE	rt	-	21
22	**JohnphosAuCl/NaBARF**	**DCE**	**rt**	**-**	**76**
23	JohnphosAuNTf$_2$	DCE	rt	33	45
24	JohnphosAuOTf	DCE	rt	51	30
25	JohnphosAuSbF$_6$	DCE	rt	44	27
26	JohnphosAuOAc	DCE	rt	-	-
27	JohnphosAuCl/NaBARF	toluene	rt	-	65
28	JohnphosAuCl/NaBARF	THF	rt	13	23
29	JohnphosAuCl/NaBARF	MeCN	rt	14	24
30	JohnphosAuCl/NaBARF	1,4-dioxane	rt	14	26
31	JohnphosAuCl/NaBARF	DCM	rt	-	52
32	JohnphosAuCl/NaBARF	chlorobenzene	rt	-	55
33	JohnphosAuCl/NaBARF	DCE	60	13	29
34	JohnphosAuCl/NaBARF	DCE	80	12	22
35	JohnphosAuCl/NaBARF	DCE	110	20	25

[a] Yields are determined by ^{1}H NMR using 1,3,5-trimethoxybenzene as an internal standard.

Table S2: Optimization of reaction condition for the products **2g** and **3g**.

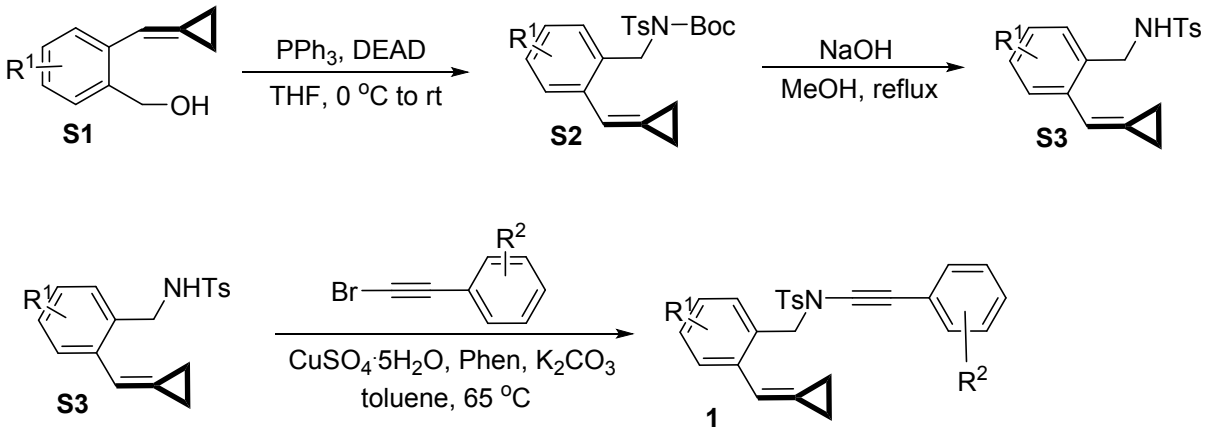


entry	catalyst	solvent	temp/^{o}C	yield/%[a]	
				2g	**3g**
1	**$Ph_3PAuCl/AgOTf$**	**DCE**	**rt**	**73**	**<10**
2	JohnphosAuCl/NaBARF	DCE	rt	49	28
3	IPrAuCl/NaBARF	DCE	rt	50	<10
4	^{t}BuBrettphosAuCl/NaBARF	DCE	rt	52	<10
5	$PEt_3AuCl/NaBARF$	DCE	rt	21	30
6	$PPh_3AuCl/NaBARF$	DCE	rt	16	53
7	$(p\text{-}FC_6H_4)_3PAuCl/NaBARF$	DCE	rt	9	38
8	$[2,3\text{-}(CF_3)_2C_6H_4]_3PAuCl/NaBARF$	DCE	rt	12	58
9	$(p\text{-}MeOC_6H_4)_3PAuCl/NaBARF$	DCE	rt	22	48
10	**$(p\text{-}CF_3C_6H_4)_3PAuCl/NaBARF$**	**DCE**	**rt**	**11**	**70**
11	$(p\text{-}CF_3C_6H_4)_3PAuCl/NaBARF$	DCM	rt	9	32
12	$(p\text{-}CF_3C_6H_4)_3PAuCl/NaBARF$	toluene	rt	8	51
13	$(p\text{-}CF_3C_6H_4)_3PAuCl/NaBARF$	THF	rt	35	32
14	$(p\text{-}CF_3C_6H_4)_3PAuCl/NaBARF$	CH_3CN	rt	23	40

[a] Yields are determined by ^{1}H NMR using 1,3,5-trimethoxybenzene as an internal standard.

3. General procedures.

General procedure for the preparation of substrates **1**:

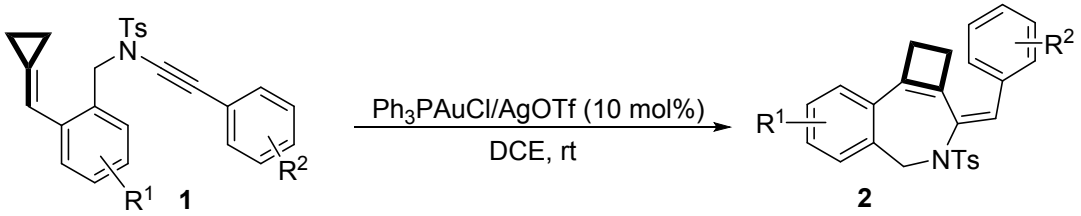


S1, **S2** and **S3** were prepared according to the previous literaure.[1]

To a solution of (bromoethynyl)benzene (1.2 equiv.) in 10 mL of freshly distilled anhydrous toluene in a reaction vial were added **S3** (1.0 mmol, 1.0 equiv.), K_2CO_3 (3.0 equiv.), $CuSO_4 \cdot 5H_2O$ (0.1 equiv.), and 1,10-phenanthroline (0.2 equiv.). The reaction mixture was capped under argon atmosphere and heated in an oil bath at 60-65 °C. After the reaction completion monitored by TLC analysis, the solid was filtered from the solution via a celite, and the filtrate was evaporated under reduced pressure. The residue was purified by a silica-gel column chromatography using ethyl acetate/hexane (1:100) as an eluent to obtain the product **1** in good yield.

[1] K. Chen, J.-X. Liu, X.-Y. Tang, and M. Shi. *Chem. Eur. J.* **2016**, 22, 11549-11553.

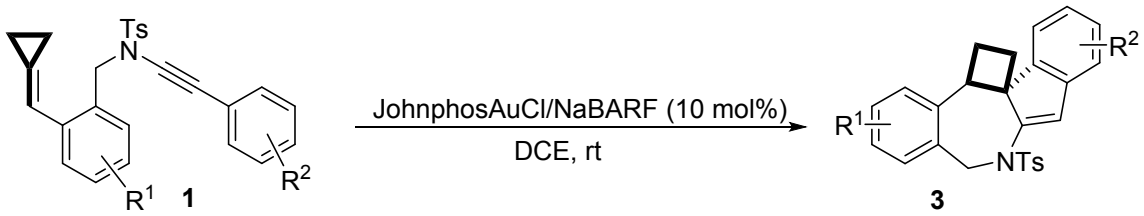
General procedure for the synthesis of products **2**:



A solution of substrates **1** (0.2 mmol, 1.0 equiv.), Ph_3PAuCl (0.02mmol, 10.0 mol%) and AgOTf (0.02mmol, 10.0 mol%) in dry DCE (2.0 mL) was stirred at room temperature under argon atmosphere. After the reaction completion monitored by TLC analysis, the solvent was removed

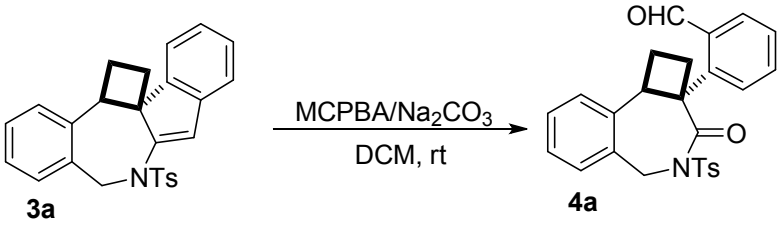
under reduced pressure. The reaction mixture was purified by a silica-gel column chromatography using ethyl acetate/hexane (1:100) as an eluent to give the desired product **2**.

General procedure for the synthesis of products **3**:



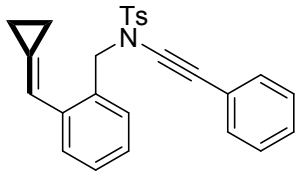
A solution of substrate **1** (0.2 mmol, 1.0 equiv.), JohnphosAuCl (0.02 mmol, 10.0 mol%) and NaBARF (0.02 mmol, 10.0 mol%) in dry DCE (2.0 mL) was stirred at room temperature under argon atmosphere. After the reaction completion monitored by TLC analysis, the solvent was removed under reduced pressure. The residue was purified by a silica-gel column chromatography using ethyl acetate/hexane (1:100) as an eluent to give the desired product **3**.

General procedure for the synthesis of product **4a**:

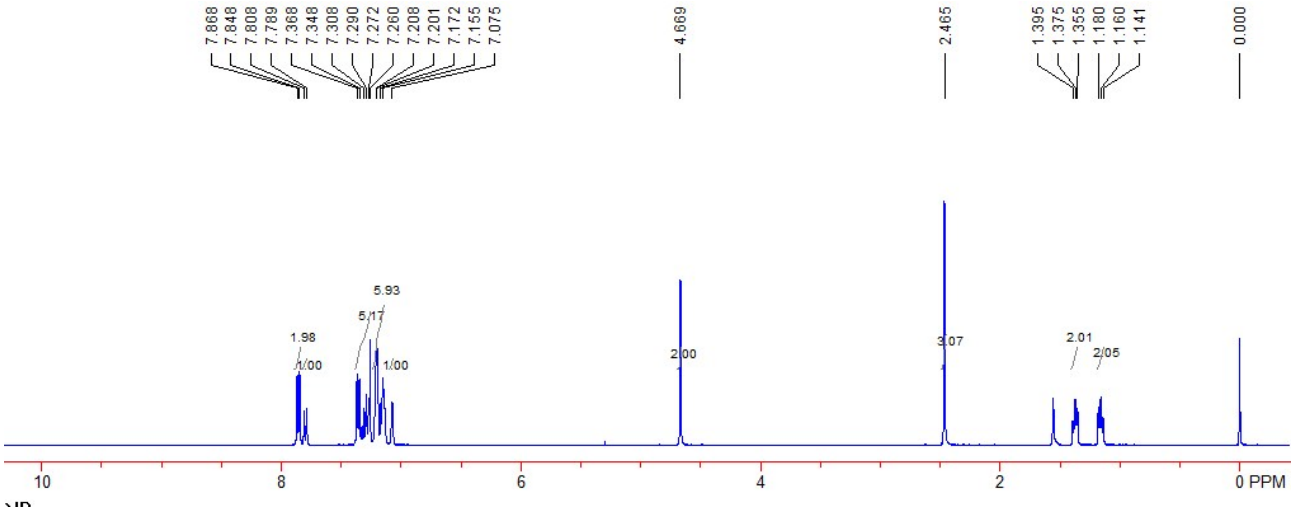


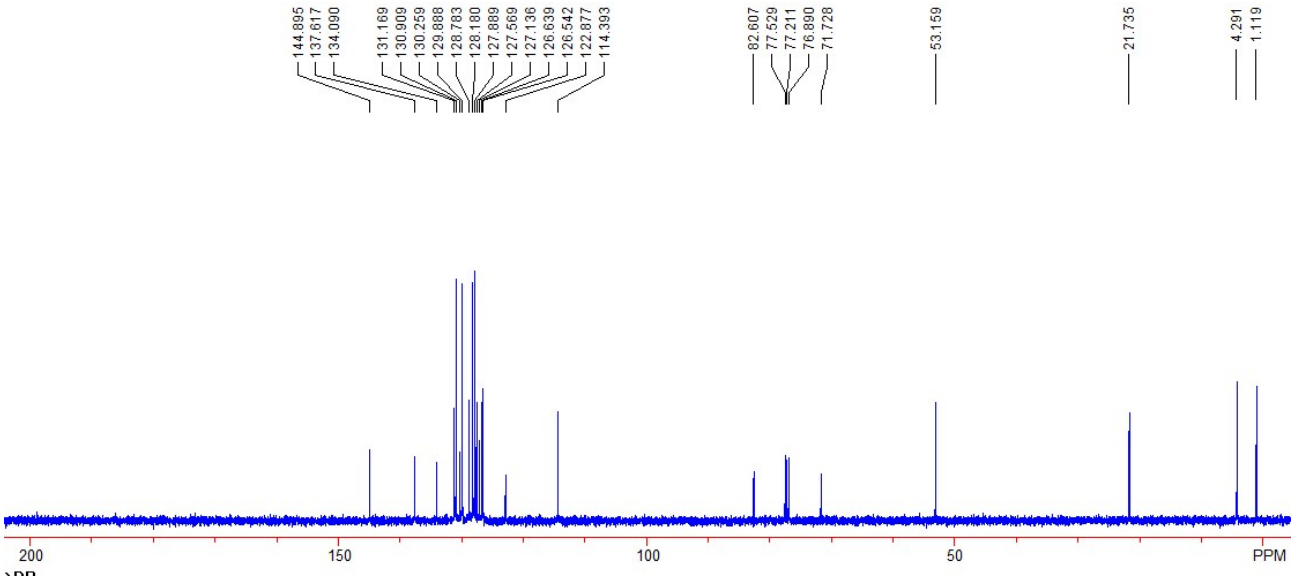
A solution of substrate **3a** (0.20 mmol, 1.0 equiv.), MCPBA (0.22 mmol, 1.1 equiv.) and Na_2CO_3 (0.24 mmol, 1.2 equiv.) in DCM (5.0 mL) was stirred at room temperature. After the reaction completion monitored by TLC analysis, the solvent was removed under reduced pressure. Then, the residue was purified by a silica-gel column chromatography using ethyl acetate/hexane (1:10) as an eluent to give the desired product **4a**.

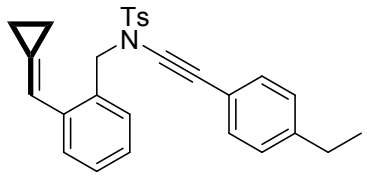
4. Characterization and spectra charts.



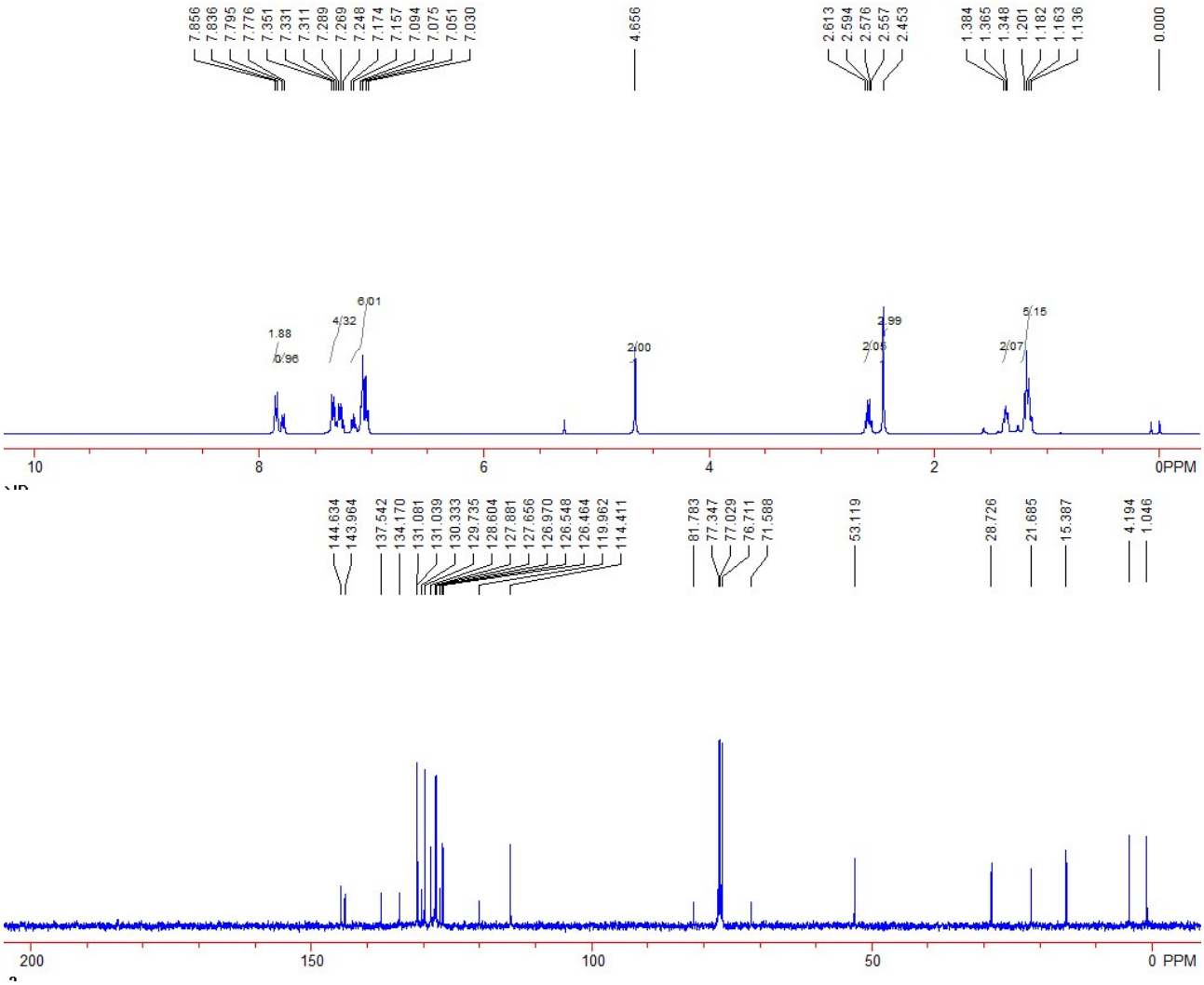
Compound 1a: A white solid. 272 mg, 66% yield. m.p. 105-110 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.13-1.19 (m, 2H), 1.35-1.40 (m, 2H), 2.47 (s, 3H), 4.67 (s, 2H), 7.08 (s, 1H), 7.15-7.22 (m, 5H), 7.25-7.37 (m, 5H), 7.80 (d, *J* = 7.6 Hz, 1H), 7.86 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 1.1, 4.3, 21.7, 53.2, 71.7, 82.6, 114.4, 122.9, 126.5, 126.6, 127.1, 127.6, 127.9, 128.2, 128.8, 129.9, 130.3, 130.9, 131.2, 134.1, 137.6, 144.9. IR (neat) ν 2967, 2919, 2849, 2229, 1602, 1491, 1439, 1363, 1168, 1089, 751, 687 cm^{-1}. HRMS (EI) Calcd. for $[C_{26}H_{24}NO_2S]$ $[M+H]^+$ requires 414.1522 , found 414.1519.

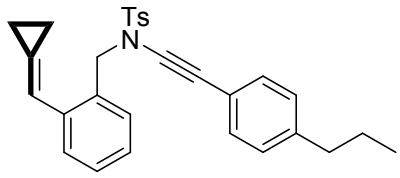




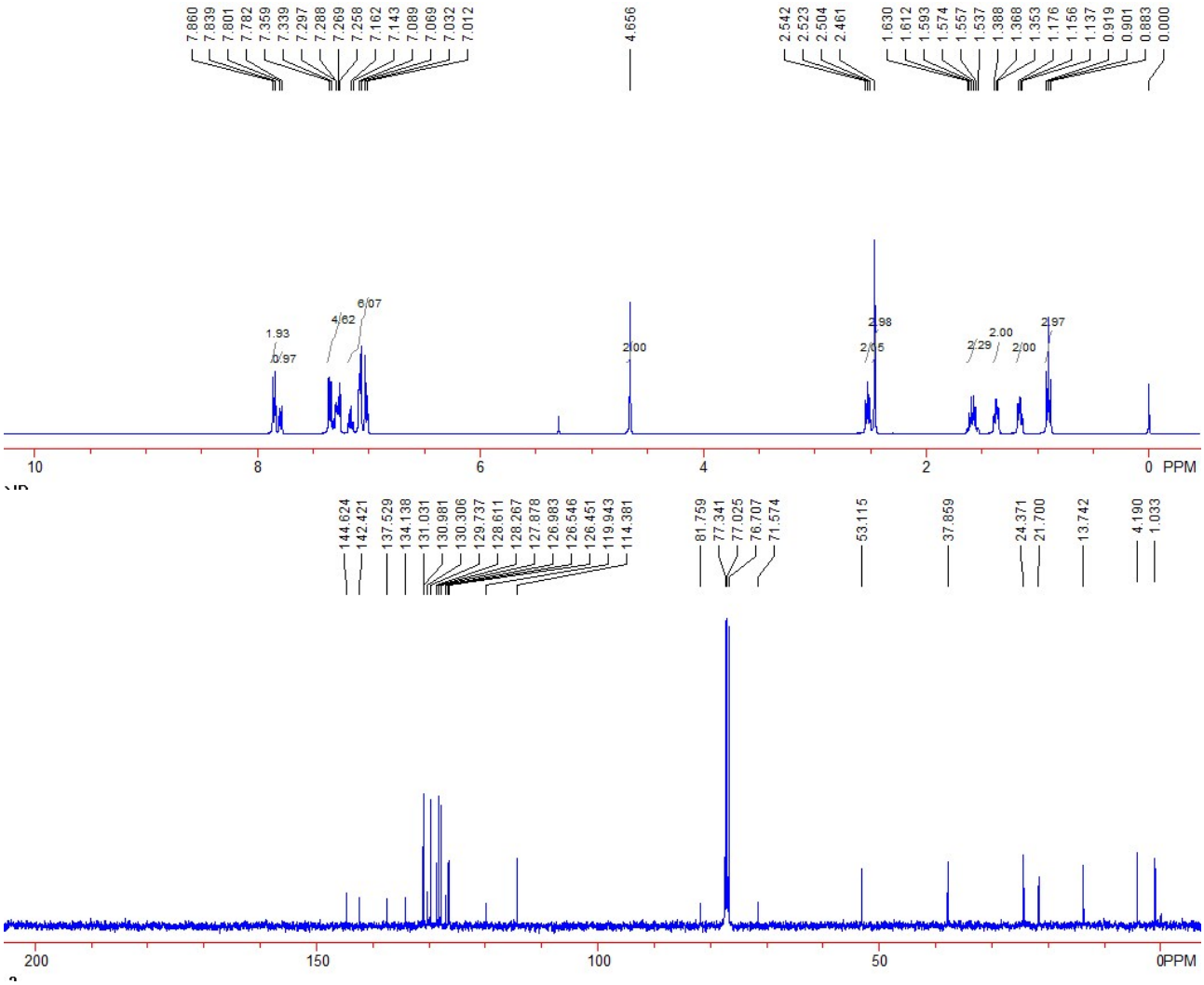


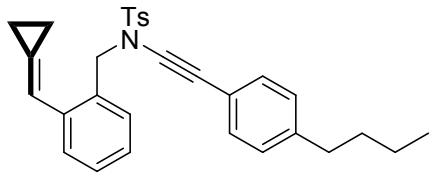
Compound 1b: A white solid. 216 mg, 49% yield. m.p. 144-150 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.13-1.21 (m, 2H), 1.18 (t, *J* = 7.6 Hz, 3H), 1.34-1.39 (m, 2H), 2.45 (s, 3H), 2.58 (q, *J* = 7.2 Hz, 2H), 4.66 (s, 2H), 7.00-7.18 (m, 6H), 7.24-7.36 (m, 4H), 7.78 (d, *J* = 7.6 Hz, 1H), 7.85 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 1.0, 4.2, 15.4, 21.7, 28.7, 53.1, 71.6, 81.8, 114.4, 120.0, 126.5, 126.6, 127.0, 127.7, 127.9, 128.6, 129.7, 130.3, 131.0, 131.3, 134.2, 137.5, 144.0, 144.6. IR (neat) ν 2978, 2924, 2842, 2234, 1711, 1597, 1448, 1361, 1186, 1168, 752, 724 cm^{-1}. HRMS (EI) Calcd. for $[C_{28}H_{28}NO_2S]$ $[M+H]^+$ requires 442.1835, found 442.1835.



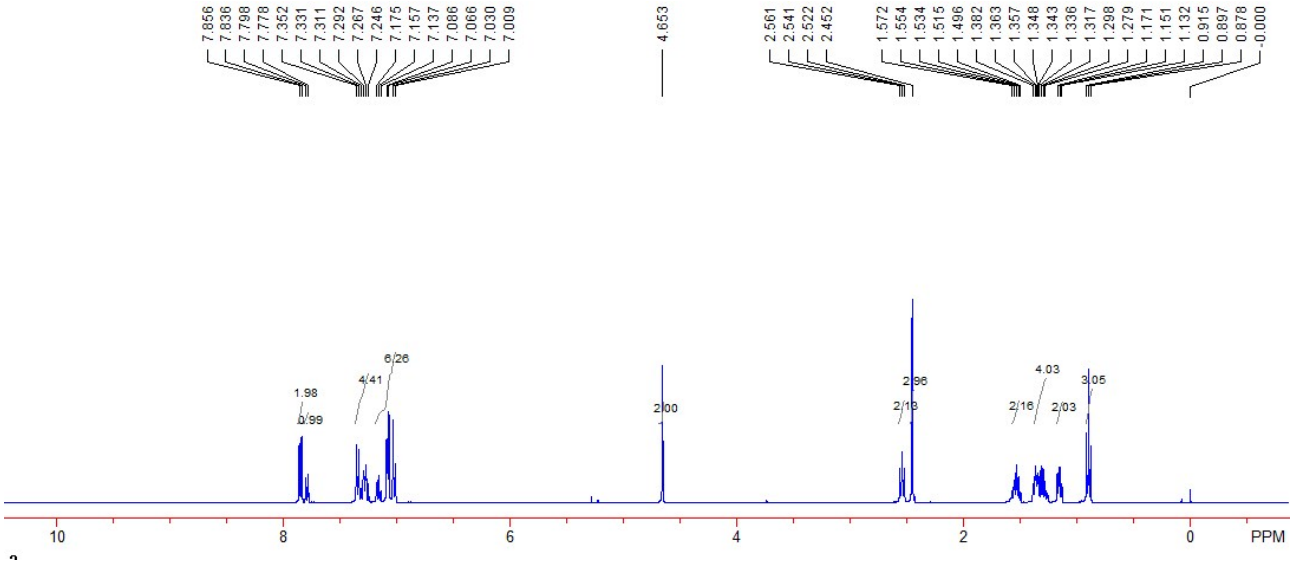


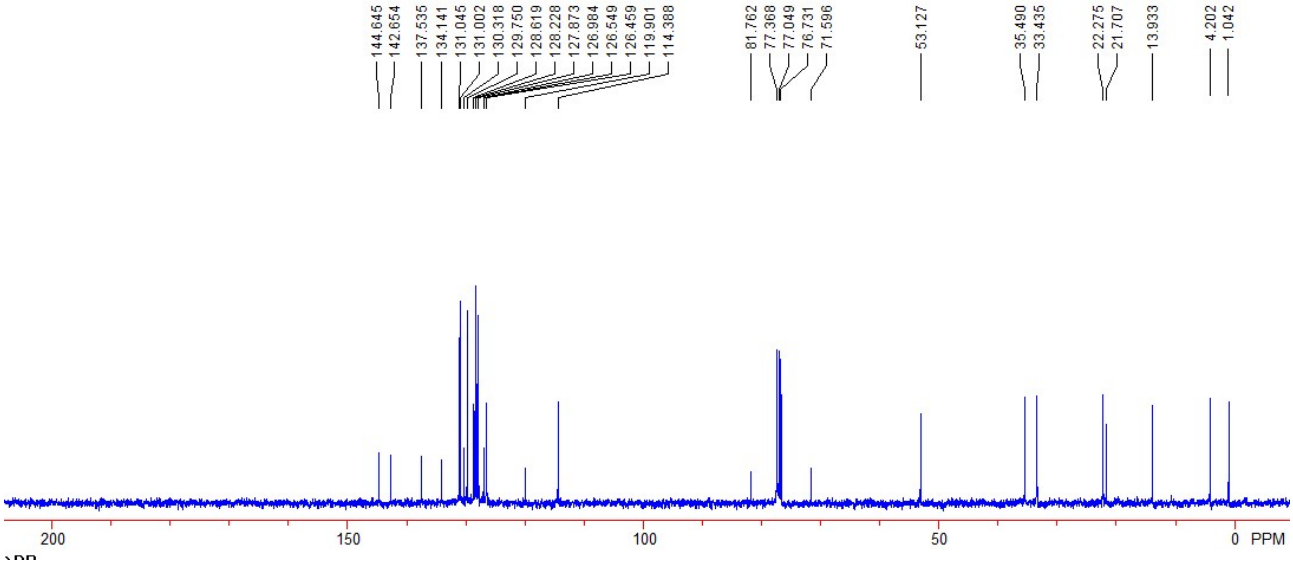
Compound 1c: A white solid. 227 mg, 50% yield. m.p. 110-112 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 0.90 (t, *J* = 7.2 Hz, 3H), 1.13-1.19 (m, 2H), 1.34-1.40 (m, 2H), 1.53-1.64 (m, 2H), 2.46 (s, 3H), 2.52 (t, *J* = 7.6 Hz, 2H), 4.66 (s, 2H), 7.00-7.19 (m, 6H), 7.25-7.37 (m, 4H), 7.79 (d, *J* = 7.6 Hz, 1H), 7.85 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 1.0, 4.2, 13.7, 21.7, 24.4, 37.9, 53.1, 71.6, 81.8, 114.4, 119.9, 126.5, 126.6, 127.0, 127.9, 128.3, 128.6, 129.7, 130.3, 131.0, 131.1, 134.1, 137.5, 142.4, 144.6. IR (neat) ν 2963, 2927, 2866, 2236, 1593, 1458, 1357, 1169, 1088, 999, 923, 810, 663 cm^{-1}. HRMS (EI) Calcd. for $[C_{29}H_{30}NO_2S]$ $[M+H]^+$ requires 456.1992, found 456.1988.

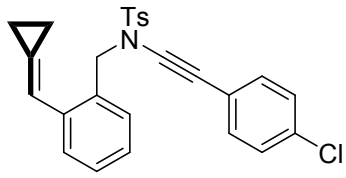




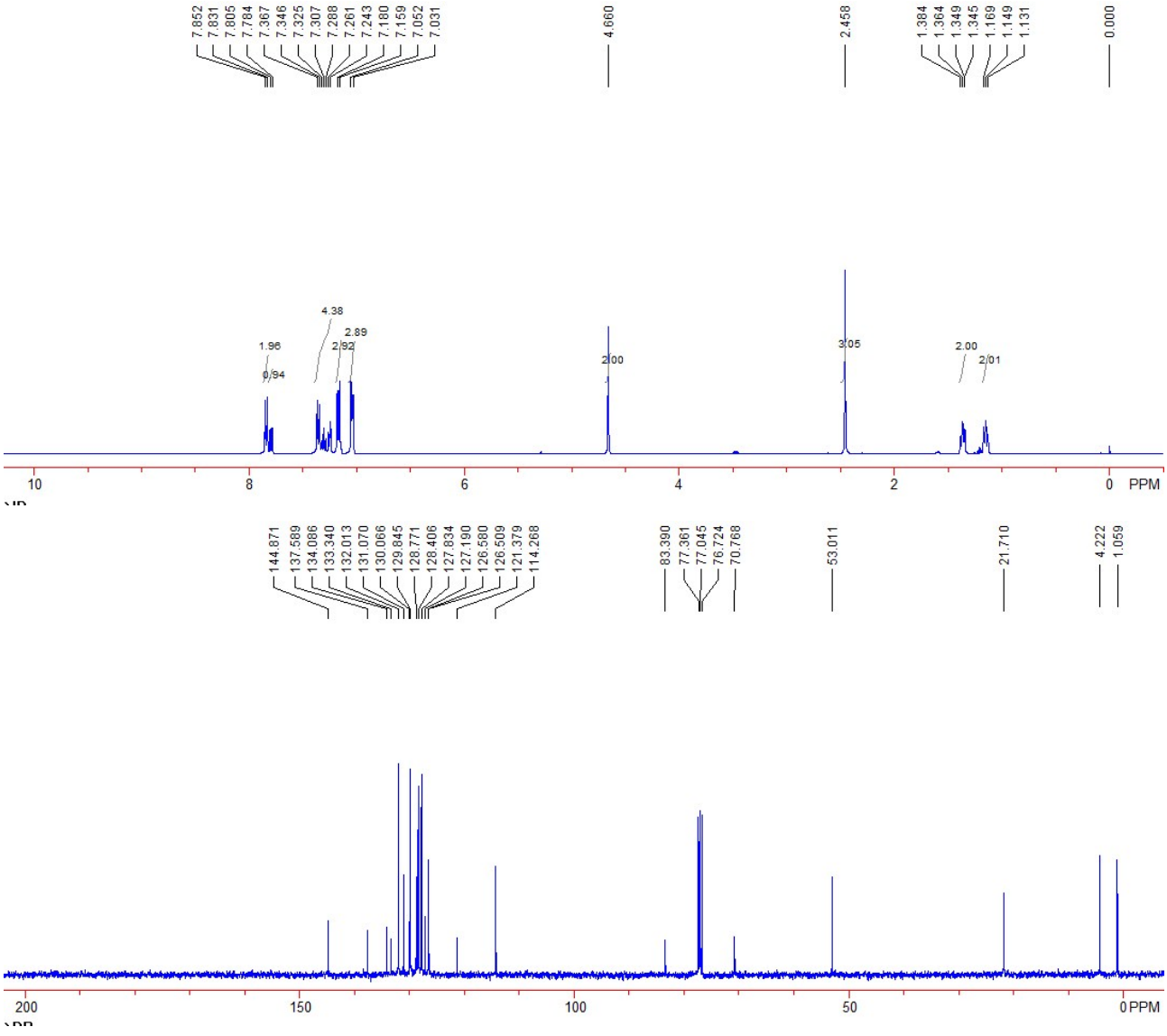
Compound 1d: A white solid. 203 mg, 43% yield. m.p. 60-65 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 0.90 (t, *J* = 7.2 Hz, 3H), 1.13-1.18 (m, 2H), 1.25-1.35 (m, 2H), 1.30-1.39 (m, 2H), 1.49-1.58 (m, 2H), 2.45 (s, 3H), 2.54 (t, *J* = 8.0 Hz, 2H), 4.65 (s, 2H), 7.00-7.18 (m, 6H), 7.24-7.36 (m, 4H), 7.79 (d, *J* = 8.0 Hz, 1H), 7.85 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 1.0, 4.2, 13.9, 21.7, 22.3, 33.4, 35.5, 53.1, 71.6, 81.8, 114.4, 119.9, 126.5, 126.6, 127.0, 127.9, 128.2, 128.6, 129.8, 130.3, 131.0, 131.1, 134.1, 137.5, 142.7, 144.6. IR (neat) ν 2956, 2928, 2858, 2237, 1712, 1597, 1448, 1364, 1186, 1168, 1088, 927, 813, 663 cm^{-1}. HRMS (EI) Calcd. for $[C_{30}H_{32}NO_2S]$ $[M+H]^+$ requires 470.2148, found 470.2148.

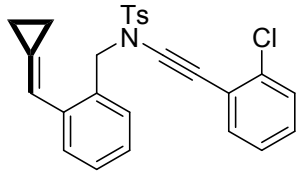




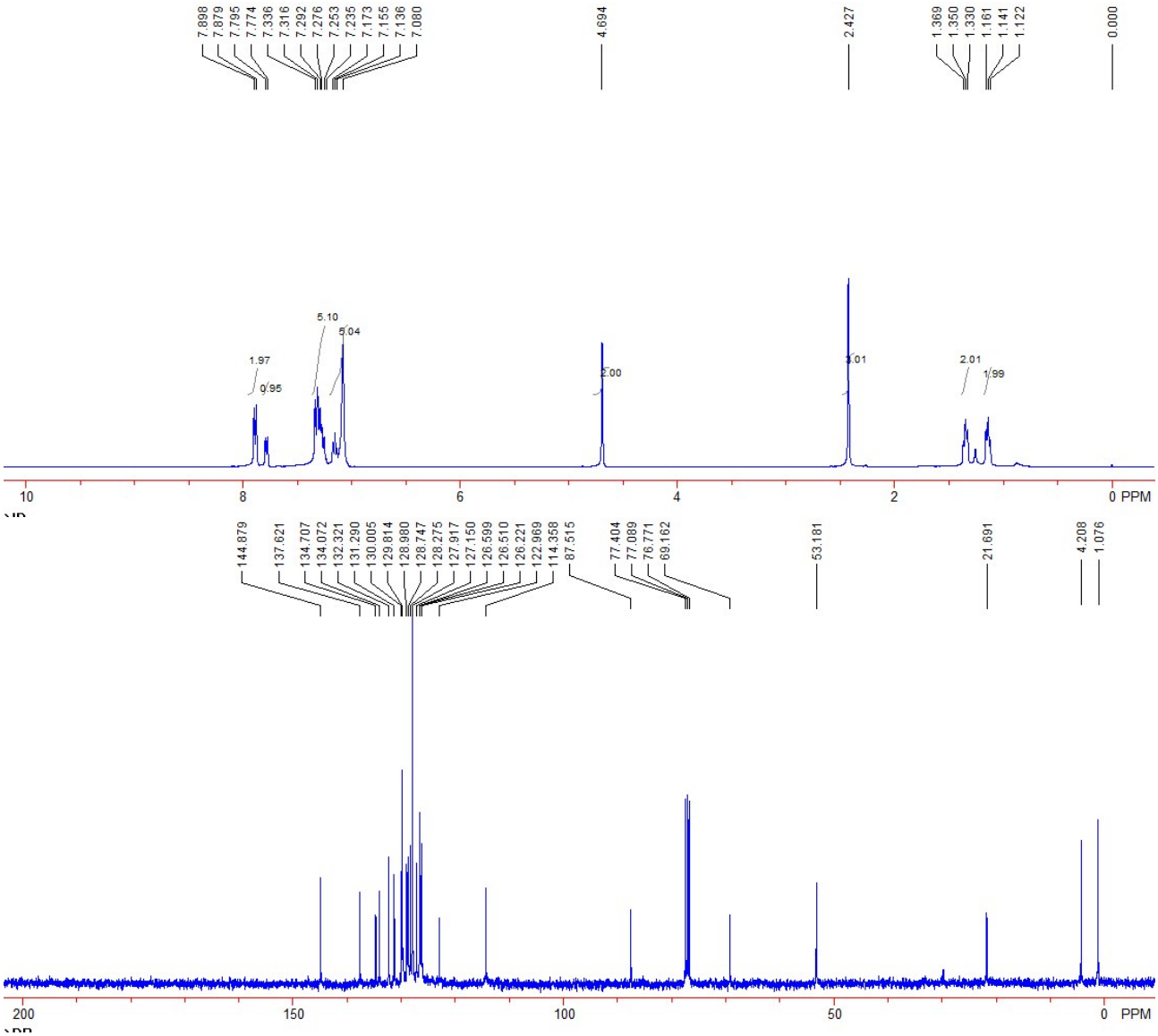


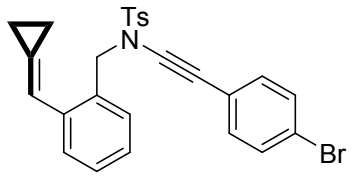
Compound 1e: A white solid. 149 mg, 33% yield. m.p. 134-136 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.12-1.18 (m, 2H), 1.34-1.40 (m, 2H), 2.46 (s, 3H), 4.66 (s, 2H), 7.00-7.06 (m, 3H), 7.15-7.19 (m, 3H), 7.24-7.38 (m, 4H), 7.79 (d, *J* = 8.4 Hz, 1H), 7.84 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 1.1, 4.2, 21.7, 53.0, 70.8, 83.4, 114.3, 121.4, 126.5, 126.6, 127.2, 127.8, 128.4, 128.8, 129.8, 130.1, 131.1, 132.0, 133.3, 134.1, 137.6, 144.9. IR (neat) ν 2974, 2918, 2840, 2237, 1711, 1596, 1491, 1362, 1186, 1169, 1089, 813, 757, 707 cm^{-1}. HRMS (EI) Calcd. for $[C_{26}H_{23}ClNO_2S]$ $[M+H]^+$ requires 448.1133, found 448.1130.



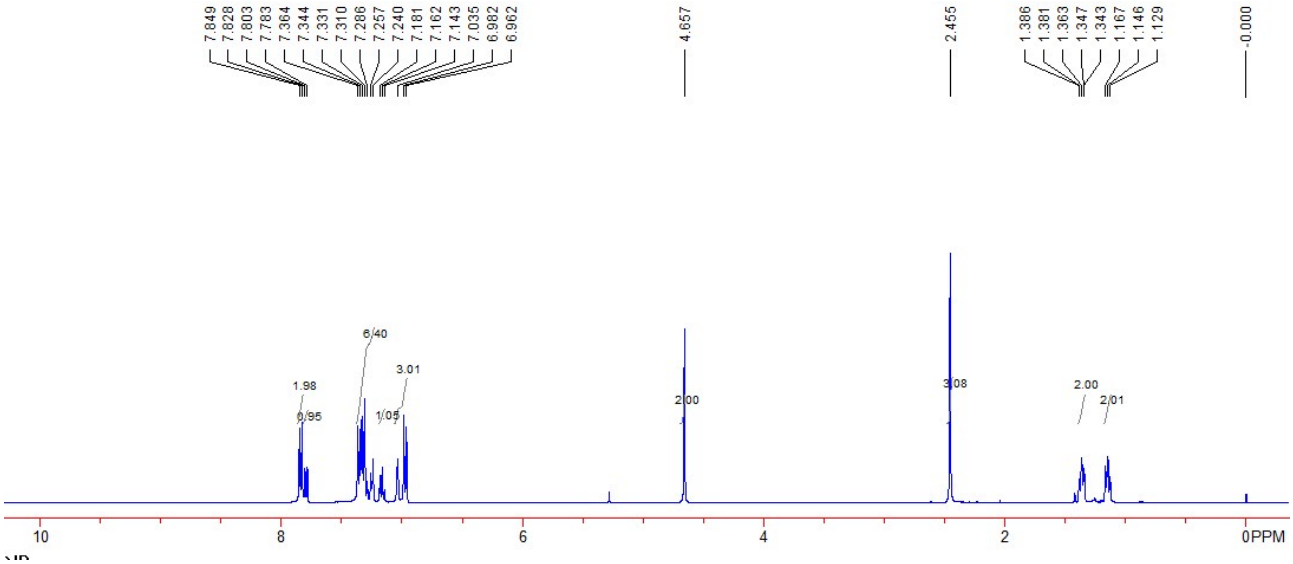


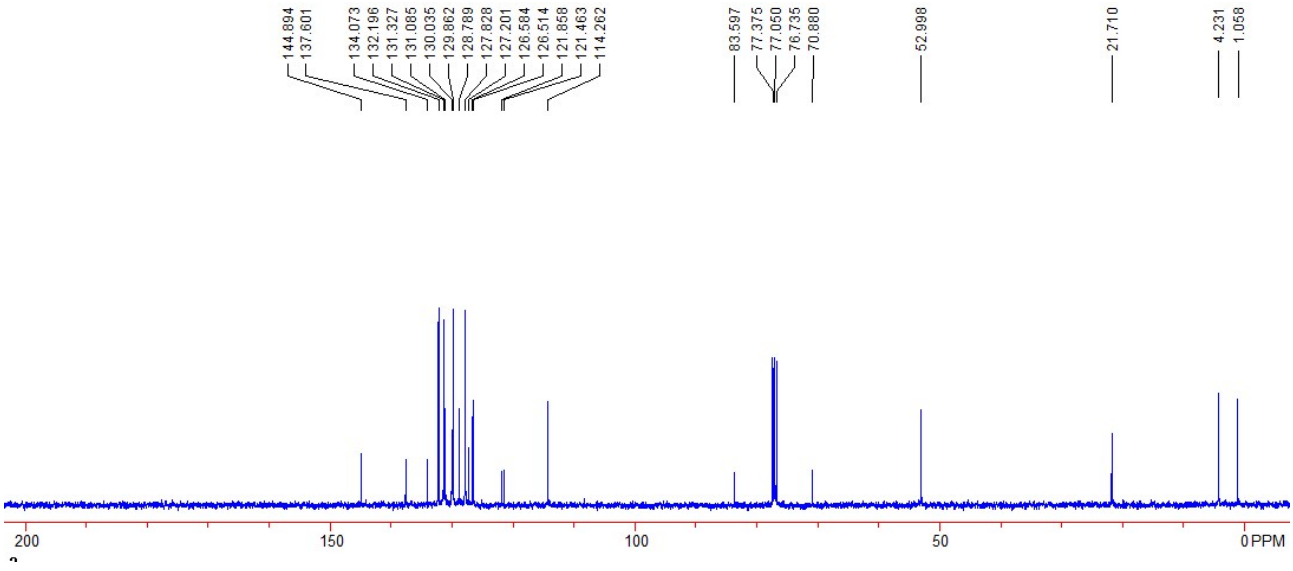
Compound 1f: A white solid. 224 mg, 50% yield. m.p. 110-112 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.11-1.17 (m, 2H), 1.32-1.38 (m, 2H), 2.43 (s, 3H), 4.69 (s, 2H), 7.00-7.18 (m, 5H), 7.22-7.35 (m, 5H), 7.78 (d, *J* = 8.4 Hz, 1H), 7.89 (d, *J* = 7.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 1.1, 4.2, 21.7, 53.2, 69.2, 87.5, 114.4, 123.0, 126.2, 126.5, 126.6, 127.2, 127.9, 128.3, 128.7, 129.0, 129.8, 130.0, 131.3, 132.3, 134.1, 134.7, 137.6, 144.9. IR (neat) ν 2977, 2924, 2853, 2236, 1709, 1597, 1436, 1363, 1220, 1166, 928, 753, 706 cm^{-1}. HRMS (EI) Calcd. for [$C_{26}H_{23}ClNO_2S$] $[M+H]^+$ requires 448.1133, found 448.1129.

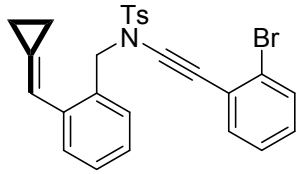




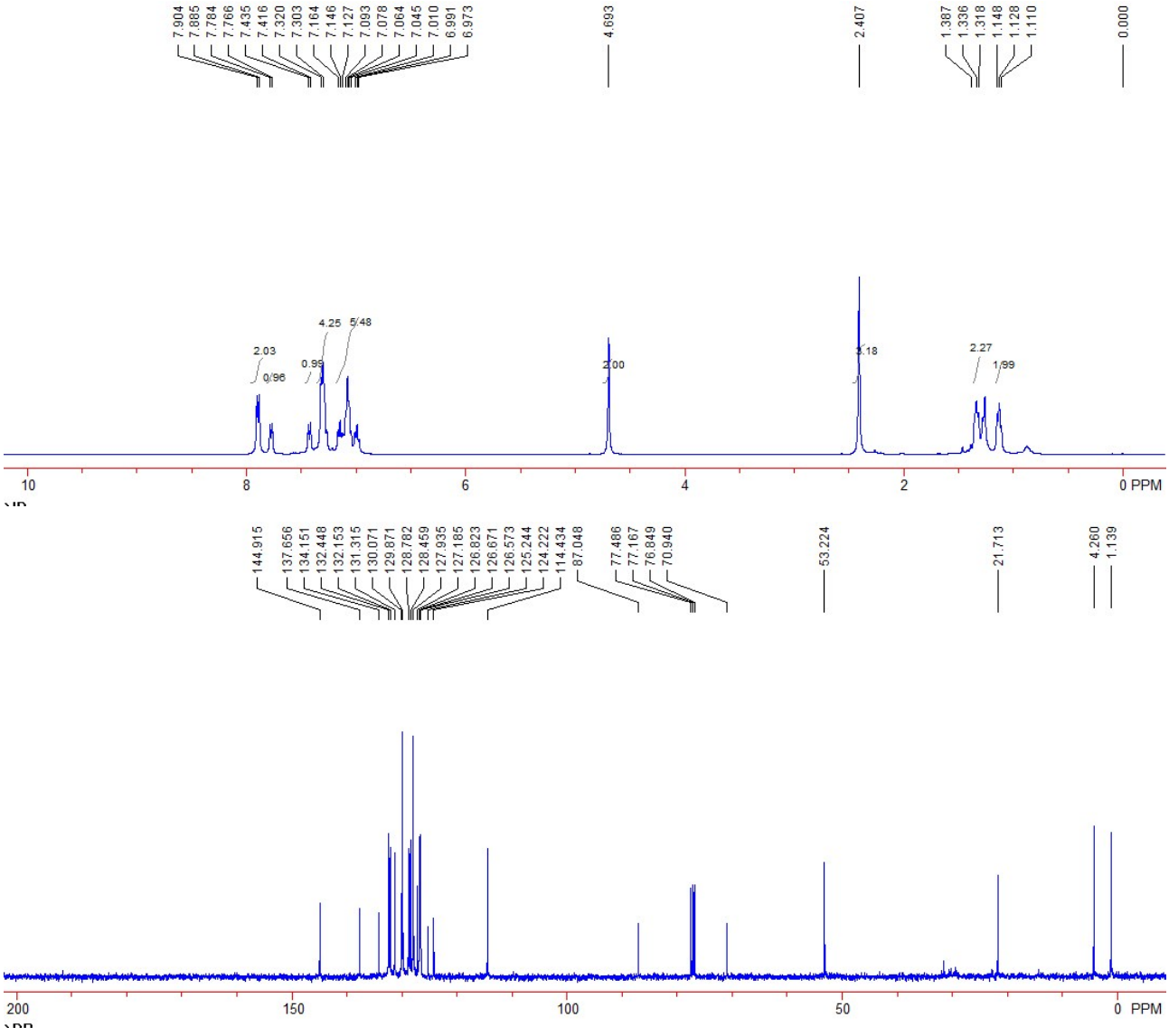
Compound 1g: A white solid. 200 mg, 41% yield. m.p. 139-142 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.12-1.18 (m, 2H), 1.34-1.39 (m, 2H), 2.46 (s, 3H), 4.66 (s, 2H), 6.96-7.04 (m, 3H), 7.14-7.19 (m, 1H), 7.23-7.37 (m, 6H), 7.79 (d, *J* = 8.0 Hz, 1H), 7.84 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 1.1, 4.2, 21.7, 53.0, 70.9, 83.6, 114.3, 121.5, 121.9, 126.5, 126.6, 127.2, 127.8, 128.9, 129.9, 130.0, 131.1, 131.3, 132.2, 134.1, 137.6, 144.9. IR (neat) ν 2956, 2924, 2845, 2237, 1700, 1595, 1488, 1359, 1169, 1089, 811, 696 cm^{-1}. HRMS (EI) Calcd. for [$C_{26}H_{23}BrNO_2S$] [M+H]$^{+}$ requires 492.0627, found 492.0626.

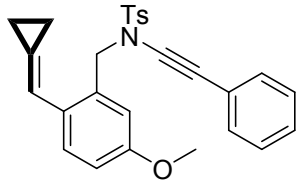




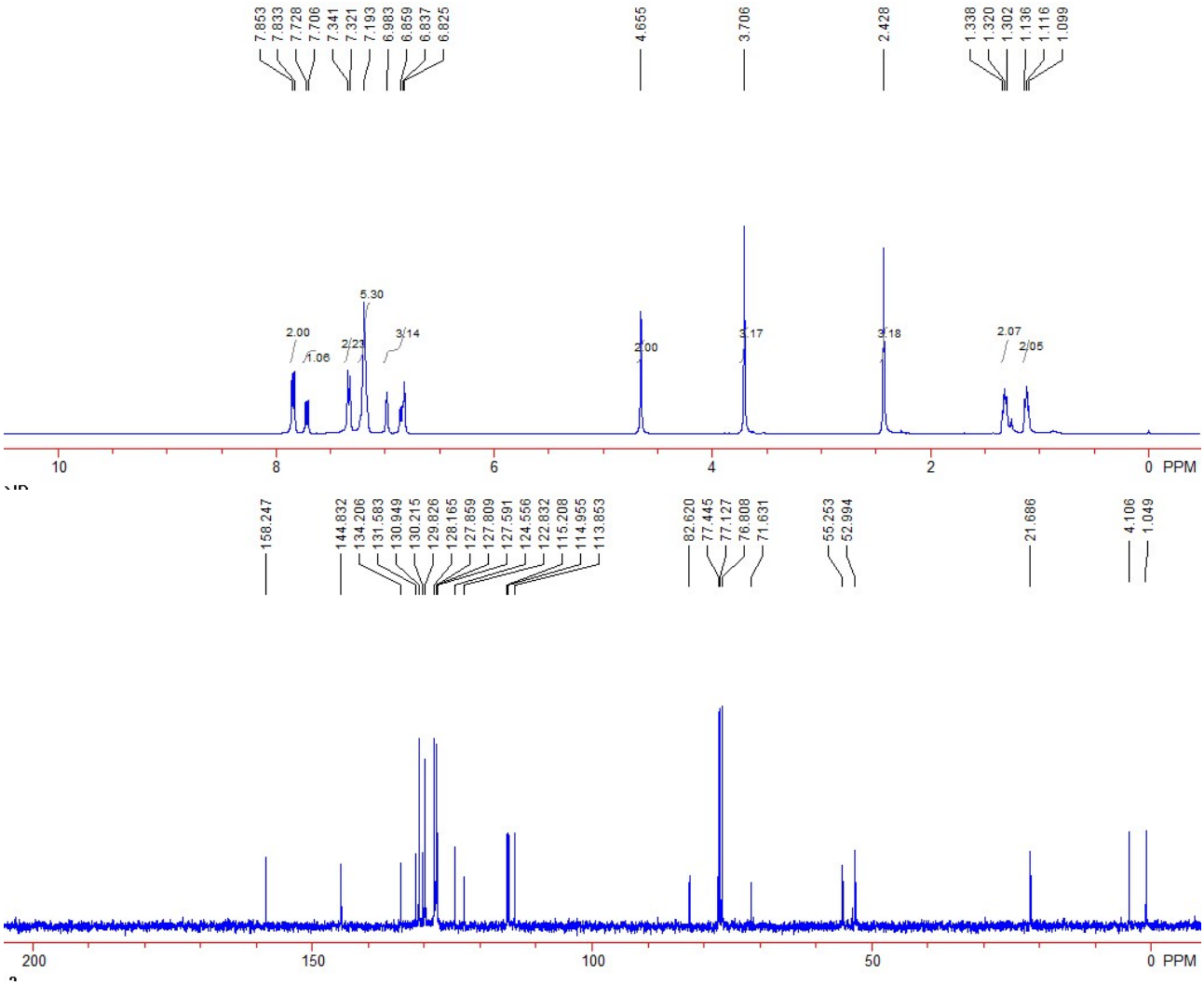


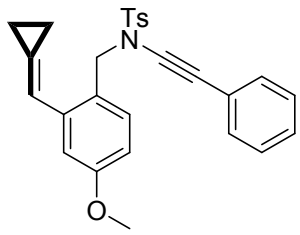
Compound 1h: A white solid. 202 mg, 41% yield. m.p. 112-114 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.10-1.16 (m, 2H), 1.30-1.39 (m, 2H), 2.41 (s, 3H), 4.69 (s, 2H), 6.96-7.17 (m, 5H), 7.25-7.33 (m, 4H), 7.42 (d, *J* = 7.6 Hz, 1H), 7.77 (d, *J* = 7.2 Hz, 1H), 7.89 (d, *J* = 7.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 1.1, 4.3, 21.7, 53.2, 70.9, 87.0, 114.4, 124.2, 125.2, 126.6, 126.7, 126.8, 127.2, 127.9, 128.5, 128.8, 129.9, 130.1, 131.3, 132.2, 132.4, 134.2, 137.7, 144.9. IR (neat) ν 2972, 2924, 2858, 2237, 1711, 1596, 1462, 1362, 1186, 1168, 931, 751, 658 cm^{-1}. HRMS (EI) Calcd. for $[C_{26}H_{23}BrNO_2S]$ $[M+H]^+$ requires 492.0627, found 492.0640.



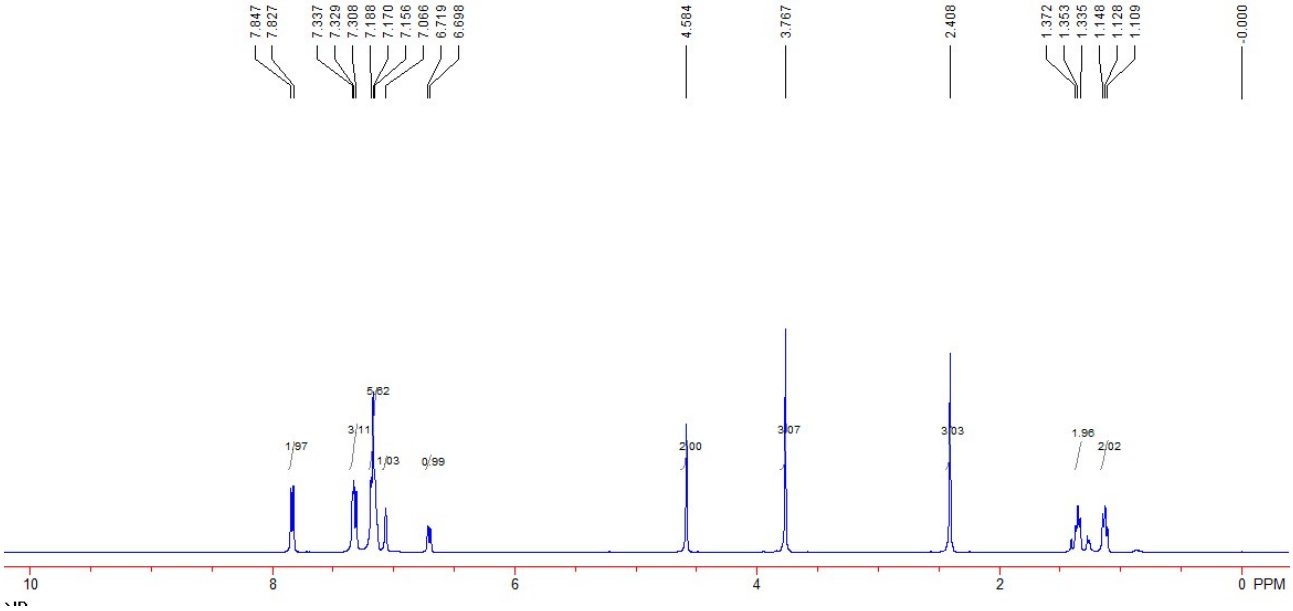


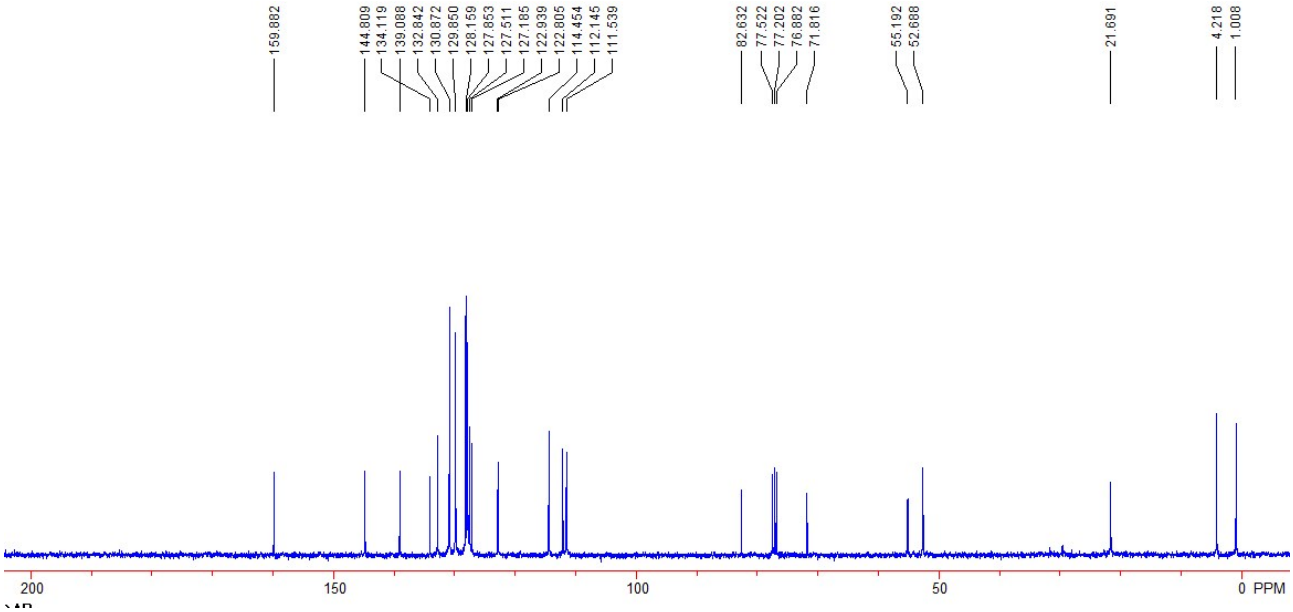
Compound 1i: A white solid. 200 mg, 45% yield. m.p. 94-97 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.09-1.15 (m, 2H), 1.29-1.35 (m, 2H), 2.43 (s, 3H), 3.71 (s, 3H), 4.66 (s, 2H), 6.82-6.87 (m, 2H), 6.98 (s, 1H), 7.18-7.20 (m, 5H), 7.33 (d, J = 8.0 Hz, 2H), 7.72 (d, J = 8.8 Hz, 1H), 7.84 (d, J = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 1.0, 4.1, 21.7, 53.0, 55.3, 71.6, 82.6, 113.8, 115.0, 115.2, 122.8, 124.6, 127.6, 127.8, 127.9, 128.2, 129.8, 130.2, 131.0, 131.6, 134.2, 144.8, 158.2. IR (neat) ν 2967, 2923, 2856, 2236, 1607, 1500, 1446, 1364, 1263, 1168, 1089, 1018, 755, 659 cm^{-1}. HRMS (EI) Calcd. for $[C_{27}H_{26}NO_3S]$ $[M+H]^+$ requires 444.1628, found 444.1630.

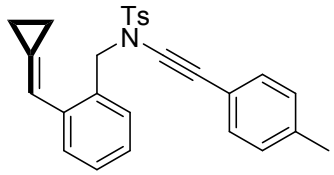




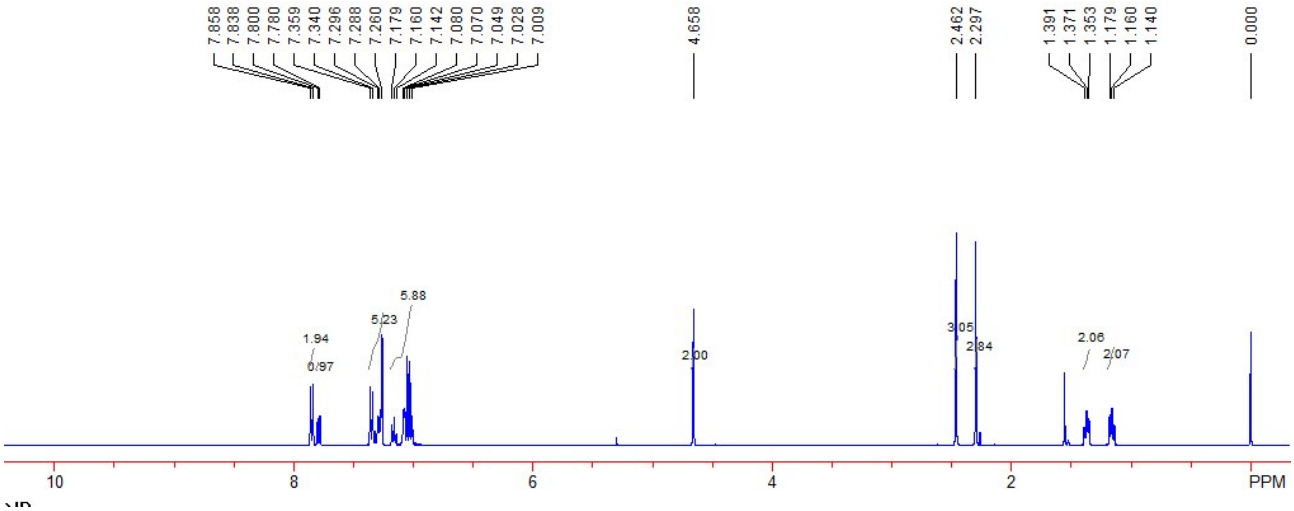
Compound 1j: A white solid. 235 mg, 53% yield. m.p. 99-101 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.10-1.16 (m, 2H), 1.33-1.38 (m, 2H), 2.41 (s, 3H), 3.77 (s, 3H), 4.59 (s, 2H), 6.71 (d, J = 8.4 Hz, 1H), 7.07 (s, 1H), 7.15-7.20 (m, 5H), 7.30-7.35 (m, 3H), 7.84 (d, J = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 1.0, 4.2, 21.7, 52.7, 55.2, 71.8, 82.6, 111.5, 112.1, 114.5, 122.8, 122.9, 127.2, 127.5, 127.9, 128.2, 129.9, 130.9, 132.8, 134.1, 139.1, 144.8, 159.9. IR (neat) ν 2974, 2930, 2834, 2237, 1604, 1558, 1457, 1363, 1287, 1186, 1167, 1089, 755, 683 cm^{-1}. HRMS (EI) Calcd. for $[C_{27}H_{26}NO_3S]$ $[M+H]^+$ requires 444.1628, found 444.1629.

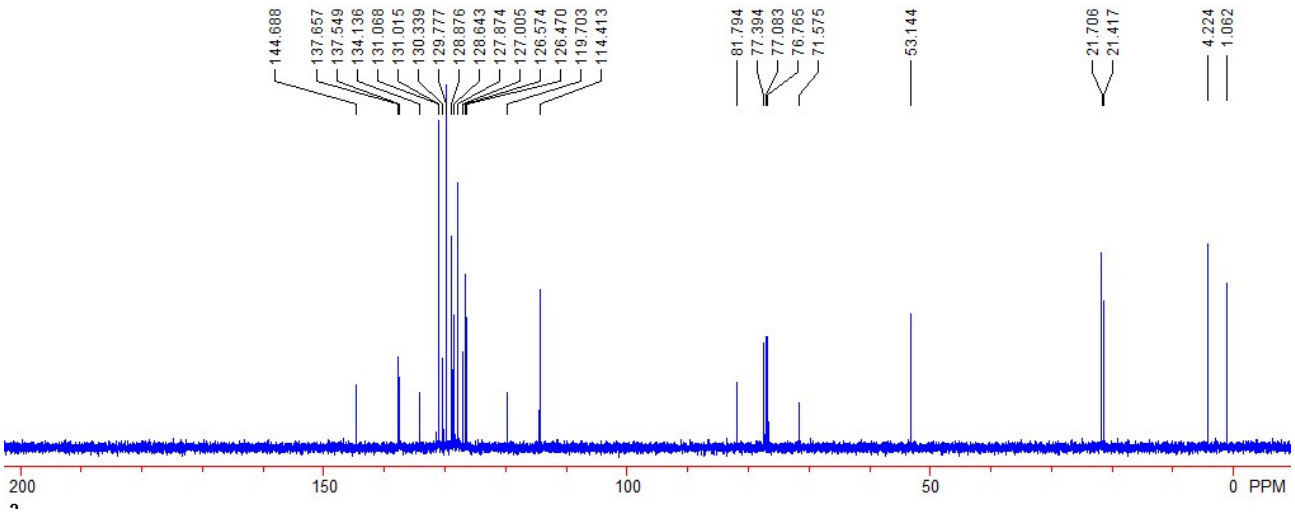


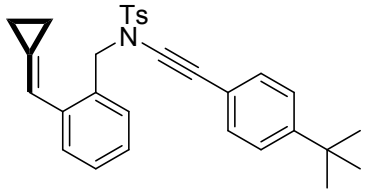




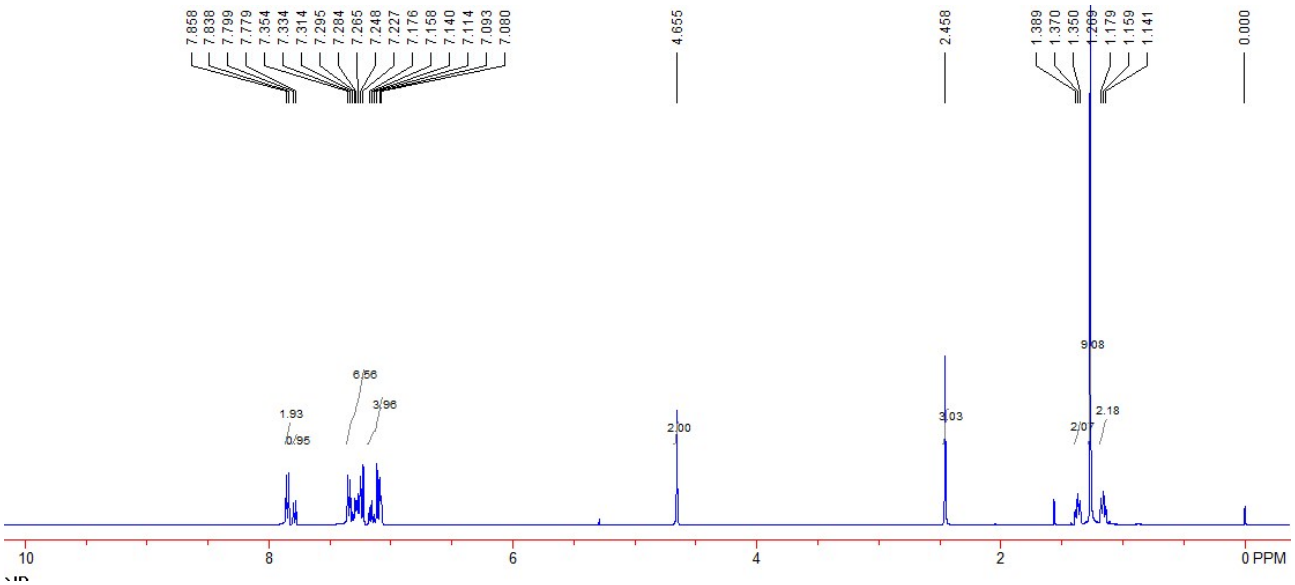
Compound 1k: A white solid. 230 mg, 54% yield. m.p. 120-130 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.13-1.19 (m, 2H), 1.35-1.40 (m, 2H), 2.30 (s, 3H), 2.46 (s, 3H), 4.66 (s, 2H), 7.00-7.19 (m, 5H), 7.25-7.37 (m, 5H), 7.79 (d, *J* = 8.0 Hz, 1H), 7.84 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 1.1, 4.2, 21.4, 21.7, 53.1, 71.6, 81.8, 114.4, 119.7, 126.5, 126.6, 127.0, 127.9, 128.6, 128.9, 129.8, 130.3, 131.0, 131.1, 134.1, 137.5, 137.6, 144.7. IR (neat) ν 2963, 2923, 2852, 2235, 1711, 1597, 1488, 1363, 1140 1088, 951, 811, 719, 662 cm^{-1}. HRMS (EI) Calcd. for $[C_{27}H_{26}NO_2S]$ $[M+H]^+$ requires 428.1679, found 428.1674.

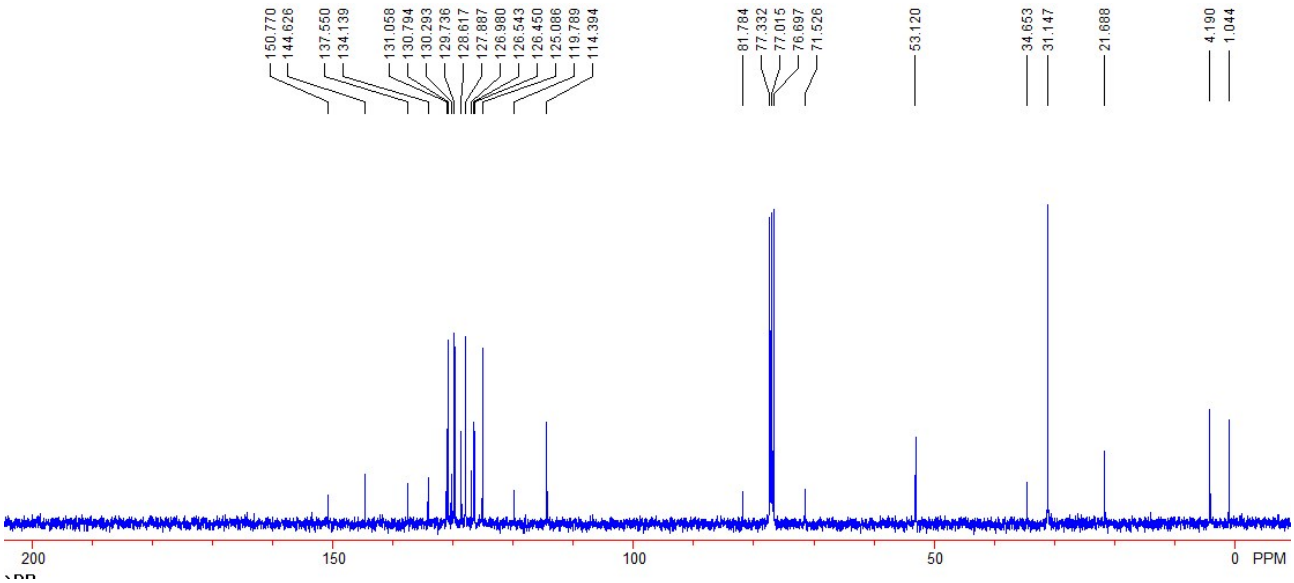


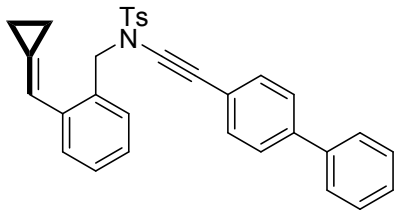




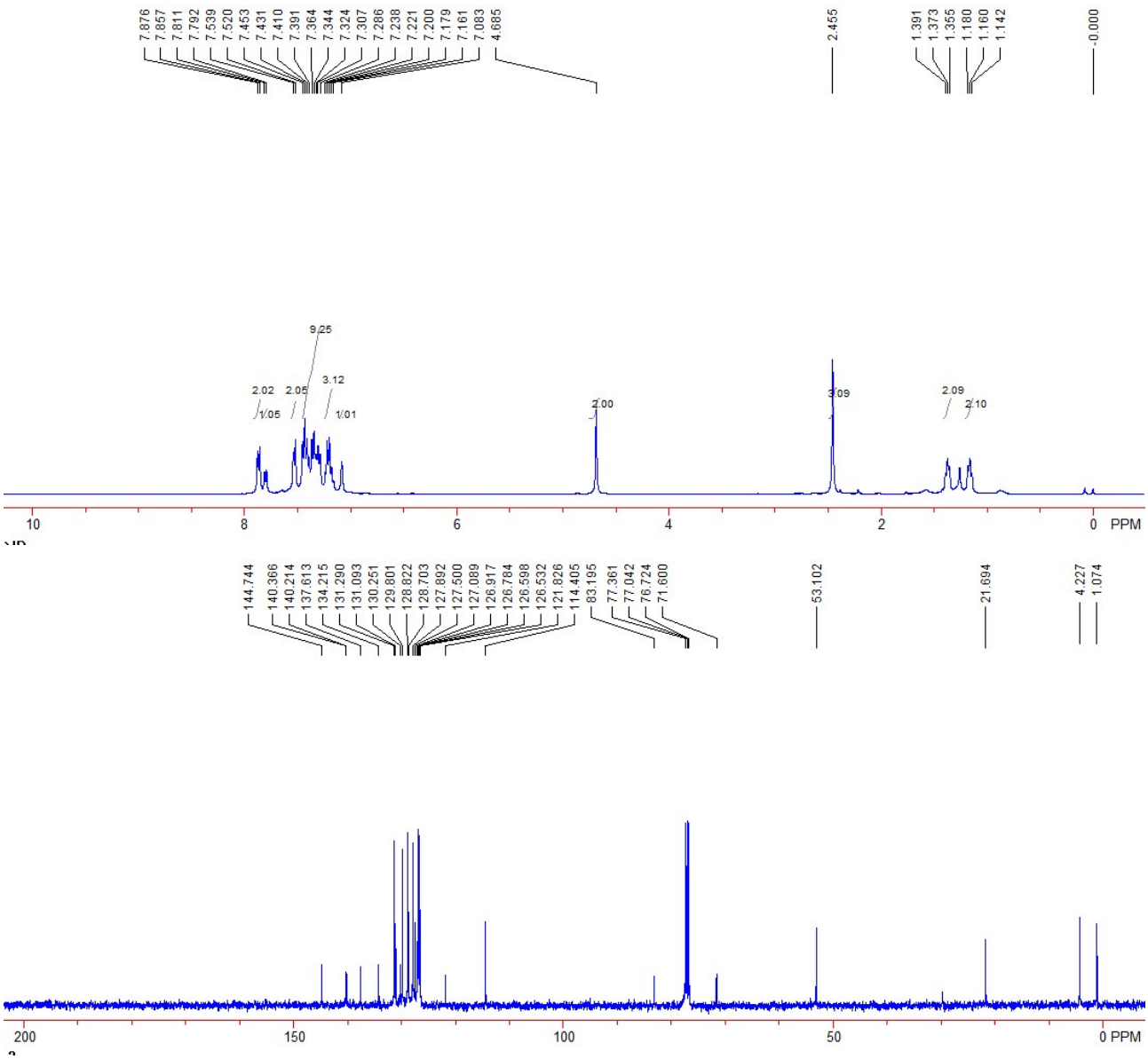
Compound 1l: A white solid. 265 mg, 56% yield. m.p. 110-113 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.13-1.19 (m, 2H), 1.27 (s, 9H), 1.34-1.40 (m, 2H), 2.46 (s, 3H), 4.66 (s, 2H), 7.00-7.18 (m, 4H), 7.22-7.36 (m, 6H), 7.79 (d, *J* = 8.0 Hz, 1H), 7.85 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 1.0, 4.2, 21.7, 31.2, 34.7, 53.1, 71.5, 81.8, 114.4, 119.8, 125.1, 126.5, 126.6, 127.0, 127.9, 128.6, 129.7, 130.3, 130.8, 131.1, 134.1, 137.6, 144.6, 150.8. IR (neat) ν 2962, 2918, 2866, 2236, 1712, 1597, 1488, 1362, 1186, 1168, 813, 708, 658 cm^{-1}. HRMS (EI) Calcd. for $[C_{30}H_{32}NO_2S]$ $[M+H]^+$ requires 470.2148, found 470.2148.

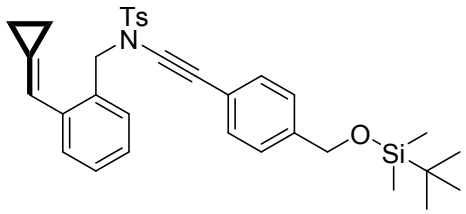






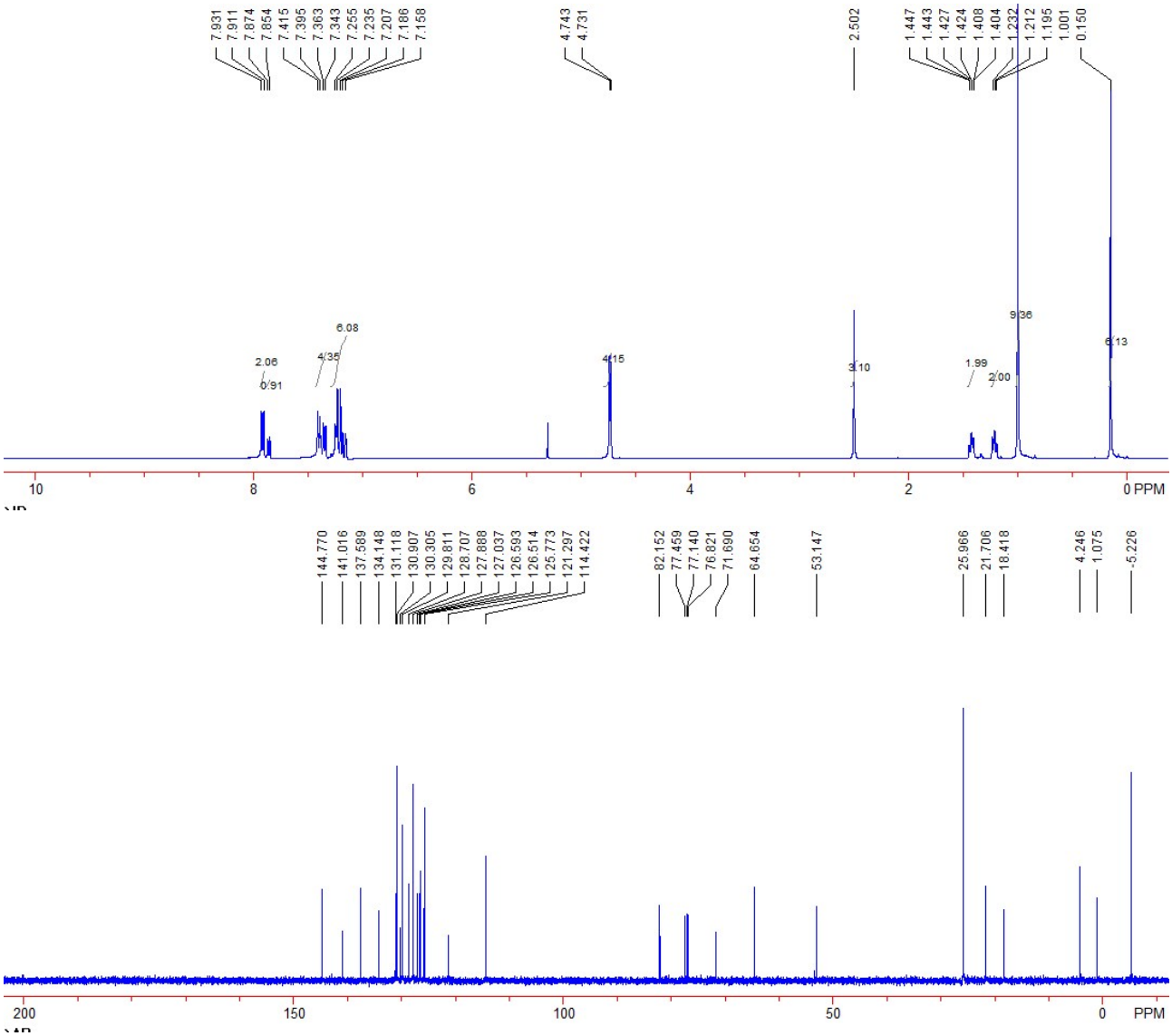
Compound 1m: A white solid. 195 mg, 40% yield. m.p. 114-117 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.14-1.19 (m, 2H), 1.35-1.40 (m, 2H), 2.46 (s, 3H), 4.69 (s, 2H), 7.09 (s, 1H), 7.15-7.25 (m, 3H), 7.28-7.46 (m, 9H), 7.53 (d, *J* = 7.6 Hz, 5H), 7.80 (d, *J* = 7.6 Hz, 1H), 7.87 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 1.1, 4.2, 21.7, 53.1, 71.6, 82.2, 114.4, 121.8, 126.5, 126.6, 126.8, 126.9, 127.1, 127.5, 127.9, 128.7, 128.8, 129.8, 130.3, 131.1, 131.3, 134.2, 137.6, 140.2, 140.4, 144.7. IR (neat) ν 2978, 2924, 2851, 2235, 1778, 1710, 1597, 1487, 1362, 1186, 1167, 763, 667 cm^{-1}. HRMS (EI) Calcd. for $[C_{32}H_{28}NO_2S]$ $[M+H]^+$ requires 490.1835, found 490.1834.

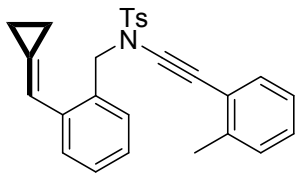




Compound 1n: A white solid. 278 mg, 50% yield. m.p. 75-78 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 0.15 (s, 6H), 1.00 (s, 9H), 1.19-1.23 (m, 2H), 1.40-1.46 (m, 2H), 2.50 (s, 3H), 4.73 (s, 2H), 4.74 (s, 2H), 7.15-7.26 (m, 6H), 7.34-7.42 (m, 4H), 7.86 (d, J = 8.0 Hz, 1H), 7.92 (d, J = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ -5.2, 1.1, 4.2, 18.4, 21.7, 26.0, 53.1, 64.7, 71.7, 82.2, 114.4, 121.3, 125.8, 126.5, 126.6, 127.0, 127.9, 128.7, 129.8, 130.3, 130.9, 131.1, 134.1, 137.6, 141.0, 144.8. IR (neat) ν 2954, 2928, 2856, 2236, 1598, 1461, 1368, 1170, 1089, 838, 776, 666 cm-

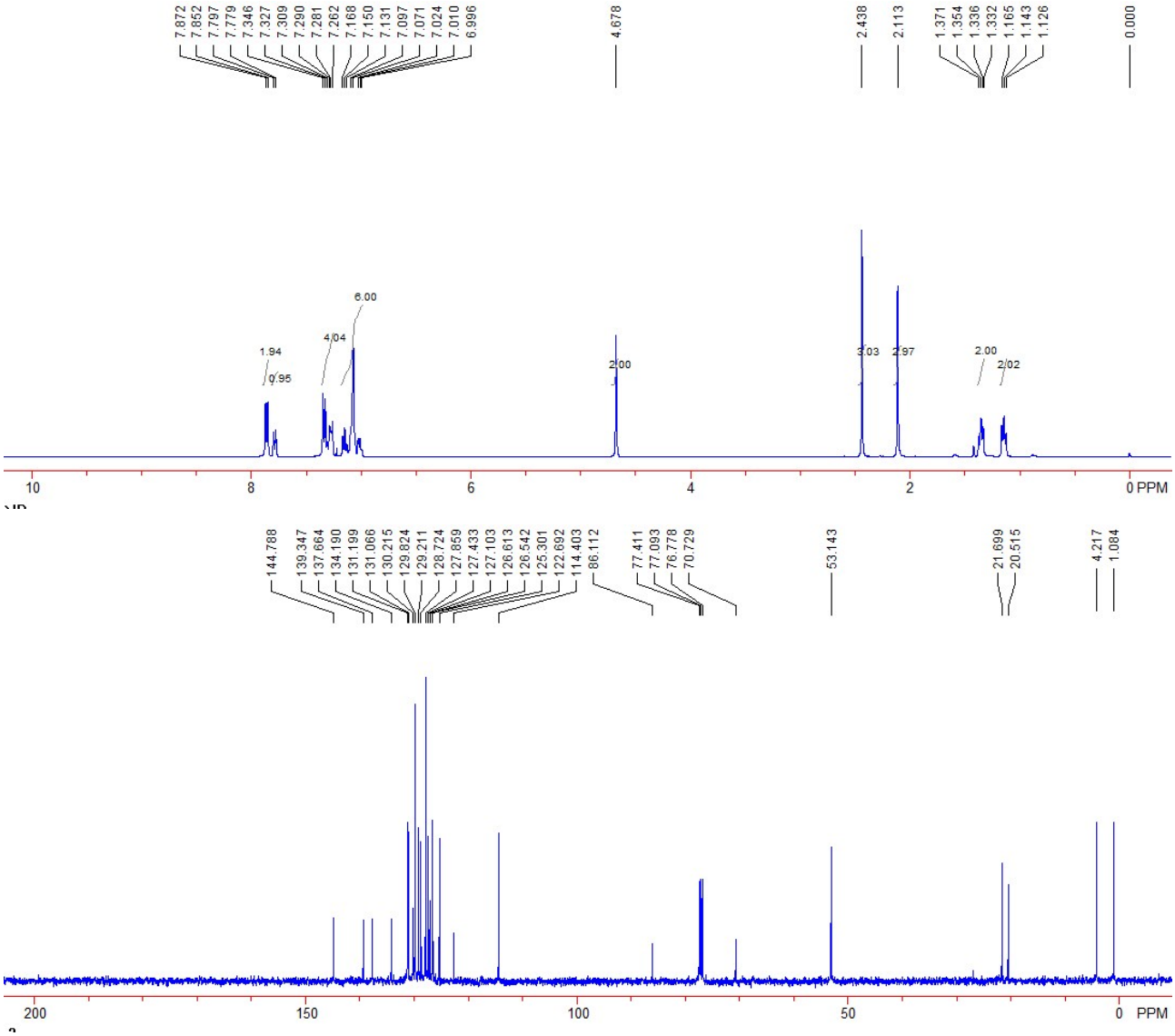
[1]. HRMS (EI) Calcd. for $[C_{33}H_{40}NO_3SSi]$ $[M+H]^+$ requires 558.2493, found 558.2495.

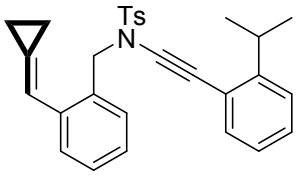




Compound 1o: A white solid. 196 mg, 46% yield. m.p. 1102-105 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.12-1.17 (m, 2H), 1.33-1.37 (m, 2H), 2.11 (s, 3H), 2.44 (s, 3H), 4.68 (s, 2H), 6.99-7.18 (m, 6H), 7.26-7.36 (m, 4H), 7.79 (d, J = 7.2 Hz, 1H), 7.86 (d, J = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 1.1, 4.2, 20.5, 21.7, 53.1, 70.7, 86.1, 114.4, 122.7, 125.3, 126.5, 126.6, 127.1, 127.4, 127.9, 128.7, 129.2, 129.8, 130.2, 131.1, 131.2, 134.2, 137.7, 139.4, 144.8. IR (neat) ν 2958, 2924, 2848, 2230, 1713, 1588, 1436, 1348, 1144, 1108, 852, 724 cm^{-1}. HRMS (EI) Calcd. for

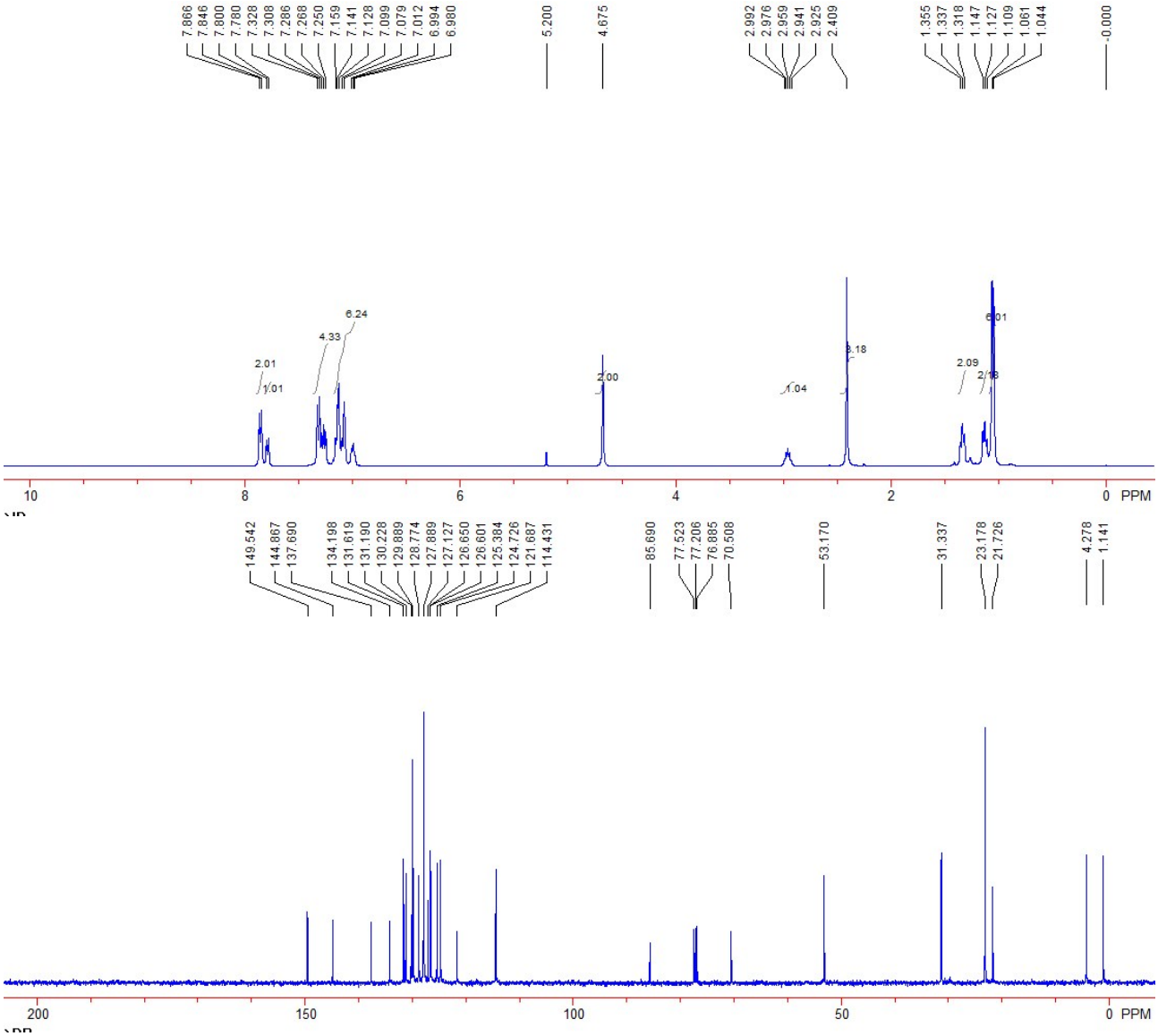
$[C_{27}H_{26}NO_2S]$ $[M+H]^+$ requires 428.1679, found 428.1675.

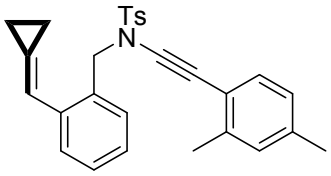




Compound 1p: A white solid. 214 mg, 47% yield. m.p. 60-63 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.05 (d, *J* = 6.8 Hz, 6H), 1.10-1.16 (m, 2H), 1.31-1.36 (m, 2H), 2.41 (s, 3H), 2.92-3.00 (m, 1H), 4.68 (s, 2H), 6.96-7.17 (m, 6H), 7.24-7.34 (m, 4H), 7.79 (d, *J* = 8.0 Hz, 1H), 7.86 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 1.1, 4.3, 21.7, 23.2, 31.3, 53.2, 70.5, 85.7, 114.4, 121.7, 124.7, 125.4, 126.6, 126.7, 127.1, 127.8, 127.9, 128.8, 129.9, 130.2, 131.2, 131.6, 134.2, 137.7, 144.9, 149.5. IR (neat) ν 2960, 2916, 2862, 2234, 1712, 1597, 1487, 1363, 1186, 1168, 1088,

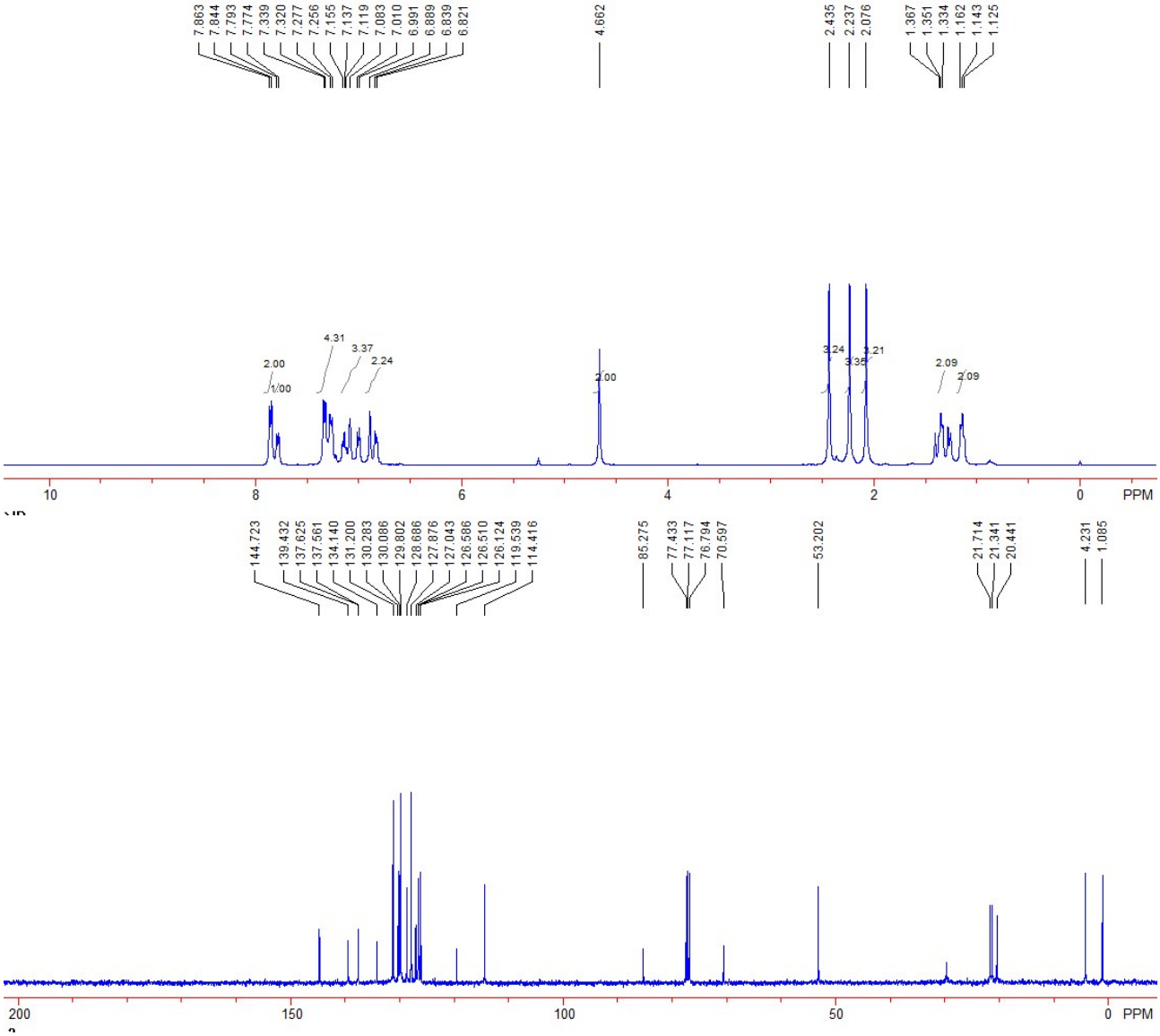
1019, 927, 756, 677 cm^{-1}. HRMS (EI) Calcd. for $[C_{29}H_{30}NO_2S]$ $[M+H]^+$ requires 456.1992, found 456.1986.

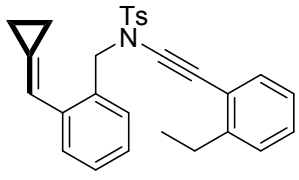




Compound 1q: A white solid. 238 mg, 54% yield. m.p. 160-163 ^oC (It is a highly viscous oily compound containing trace of petroleum ether). ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 1.11-1.17 (m, 2H), 1.32-1.38 (m, 2H), 2.08 (s, 3H), 2.24 (s, 3H), 2.44 (s, 3H), 4.66 (s, 2H), 6.81-6.90 (m, 2H), 6.98-7.16 (m, 3H), 7.25-7.35 (m, 4H), 7.78 (d, J = 7.6 Hz, 1H), 7.85 (d, J = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 1.1, 4.2, 20.4, 21.3, 21.7, 53.2, 70.6, 85.3, 114.4, 119.5, 126.1, 126.5,

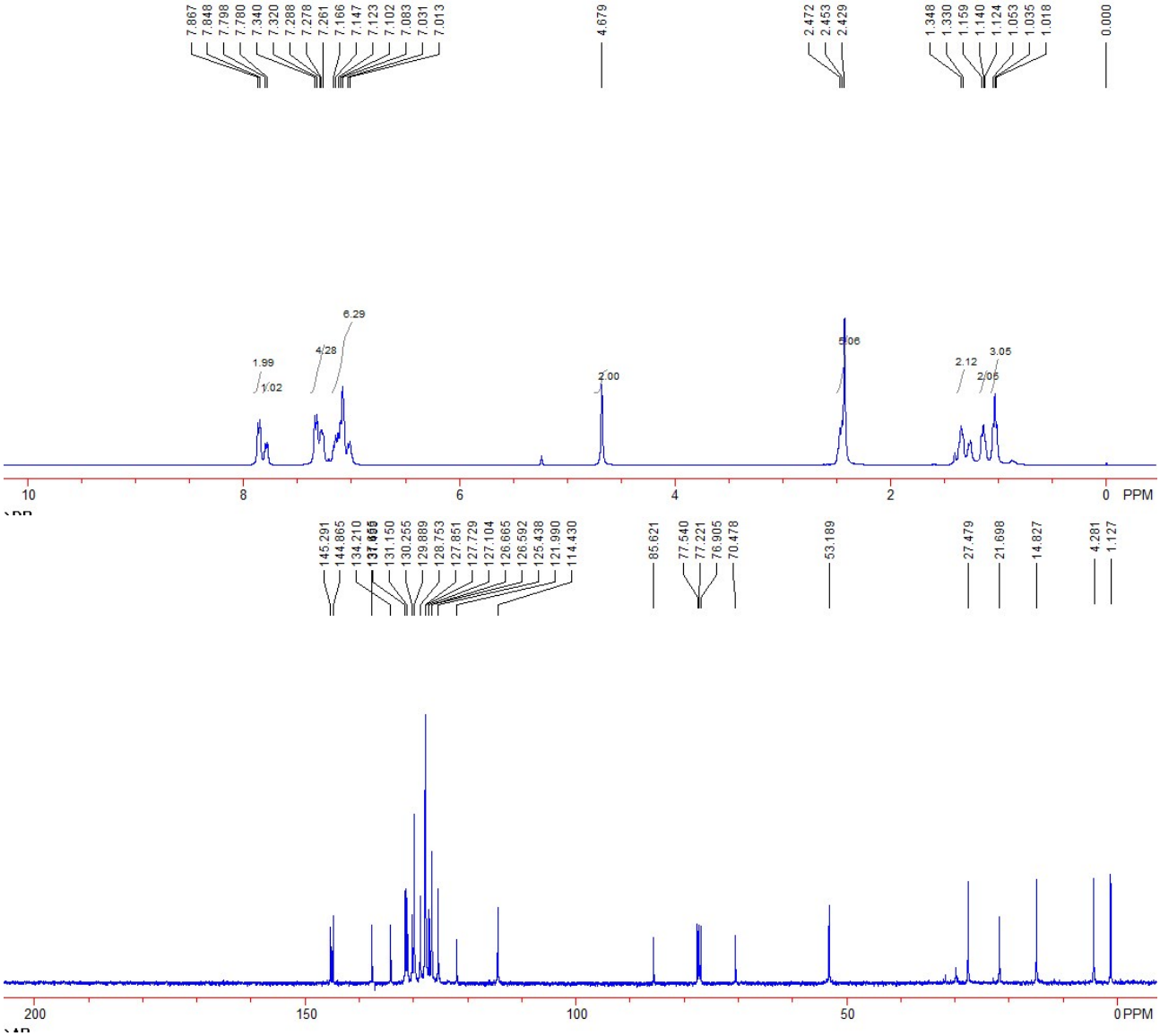
126.6, 127.0, 127.9, 128.7, 129.8, 130.1, 130.3, 131.2, 134.1, 137.5, 137.6, 139.4, 144.9. IR (neat) ν 2974, 2922, 2853, 2235, 1597, 1488, 1364, 1169, 1088, 1007, 813, 748, 663 cm^{-1}. HRMS (EI) Calcd. for $[C_{28}H_{28}NO_2S]$ $[M+H]^+$ requires 442.1835, found 442.1831.

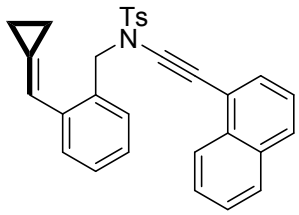




Compound 1r: A white solid. 225 mg, 51% yield. m.p. 56-58 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.04 (t, *J* = 7.2 Hz, 3H), 1.12-1.17 (m, 2H), 1.30-1.40 (m, 2H), 2.43 (s, 3H), 2.40-2.50 (m, 2H), 4.68 (s, 2H), 7.00-7.18 (m, 6H), 7.25-7.35 (m, 4H), 7.79 (d, *J* = 7.2 Hz, 1H), 7.86 (d, *J* = 7.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 1.1, 4.3, 14.8, 21.7, 27.5, 53.2, 70.5, 85.6, 114.4,

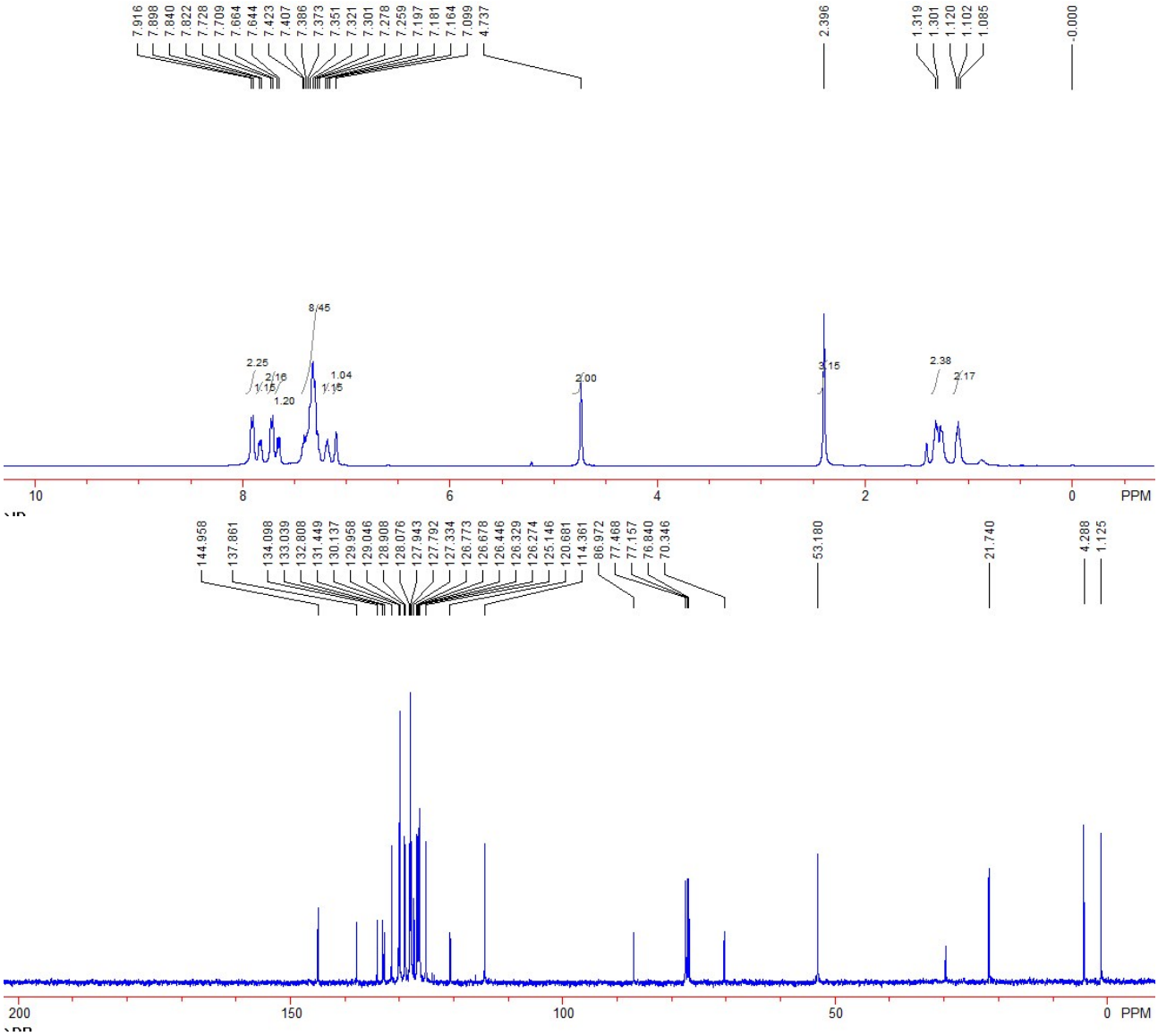
122.0, 125.4, 126.6, 126.7, 127.1, 127.7, 127.8, 127.9, 128.8, 129.9, 130.3, 131.2, 131.5, 134.2, 137.7, 144.9, 145.3. IR (neat) ν 2964, 2926, 2844, 2234, 1597, 1487, 1364, 1186, 1168, 1089, 813, 752, 676 cm^{-1}. HRMS (EI) Calcd. for $[C_{28}H_{28}NO_2S]$ $[M+H]^+$ requires 442.1835, found 442.1833.

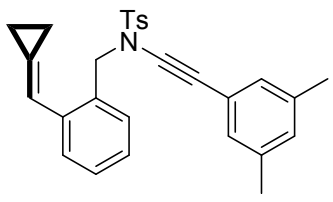




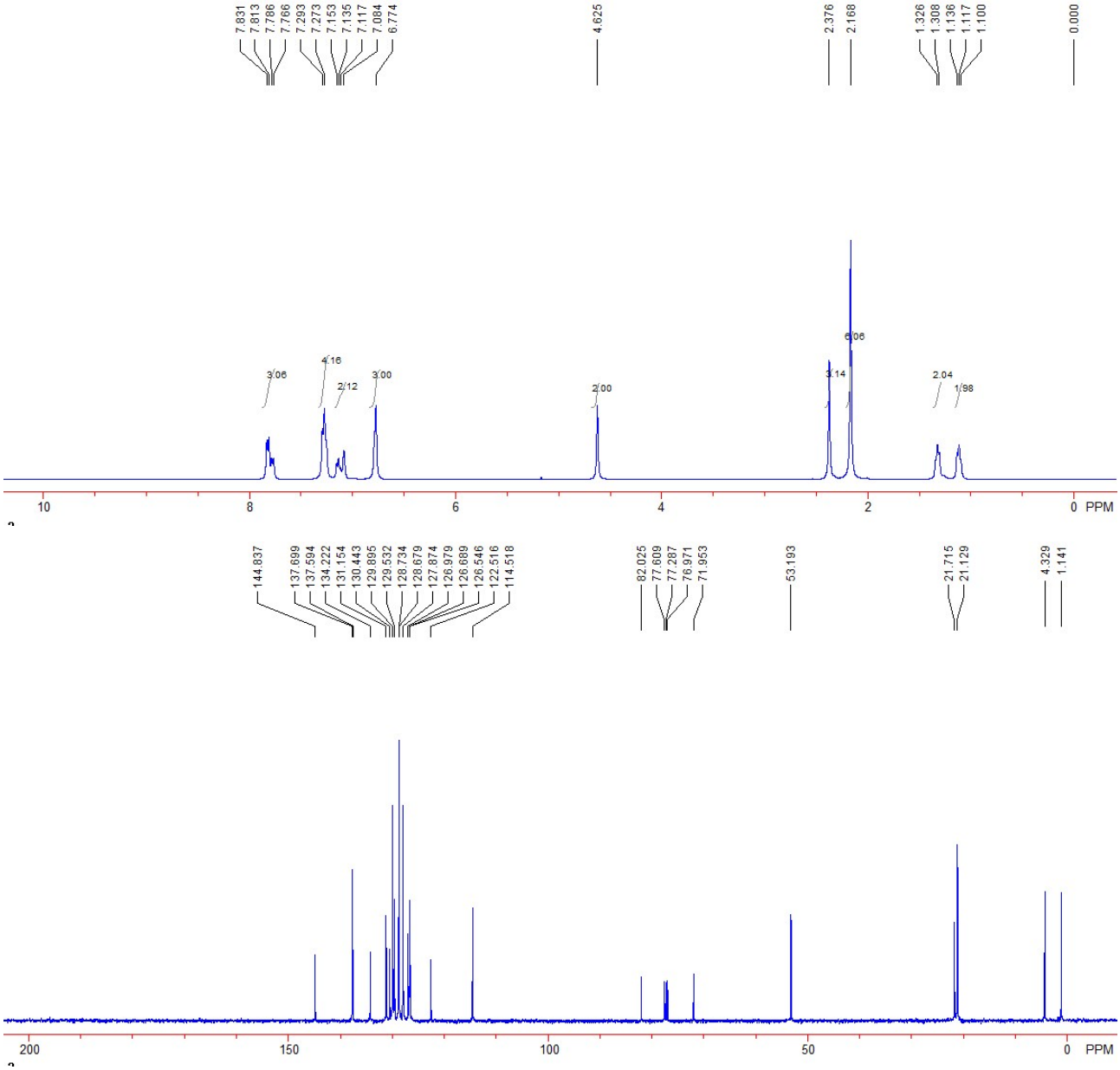
Compound 1s: A white solid. 148 mg, 32% yield. m.p. 132-135 ^oC (It is a highly viscous oily compound containing trace of petroleum ether). ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 1.07-1.13 (m, 2H), 1.28-1.35 (m, 2H), 2.40 (s, 3H), 4.74 (s, 2H), 7.10 (s, 1H), 7.15-7.22 (m, 1H), 7.25-7.42 (m,

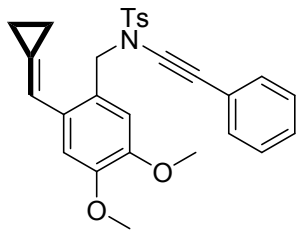
8H), 7.65 (d, J = 8.0 Hz, 1H), 7.72 (d, J = 7.6 Hz, 2H), 7.83 (d, J = 7.2 Hz, 1H), 7.91 (d, J = 7.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 1.1, 4.3, 21.7, 53.2, 70.3, 87.0, 114.4, 120.7, 125.1, 126.2, 126.3, 126.4, 126.7, 126.8, 127.3, 127.8, 127.9, 128.0, 128.1, 128.9, 129.0, 130.0, 130.1, 131.5, 132.8, 133.0, 134.1, 137.9, 145.0. IR (neat) ν 2952, 2924, 2856, 2232, 1698, 1596, 1483, 1365, 1186, 1169, 1089, 799, 773, 670 cm^{-1}. HRMS (EI) Calcd. for $[C_{30}H_{26}NO_2S]$ $[M+H]^+$ requires 464.1679, found 464.1677.



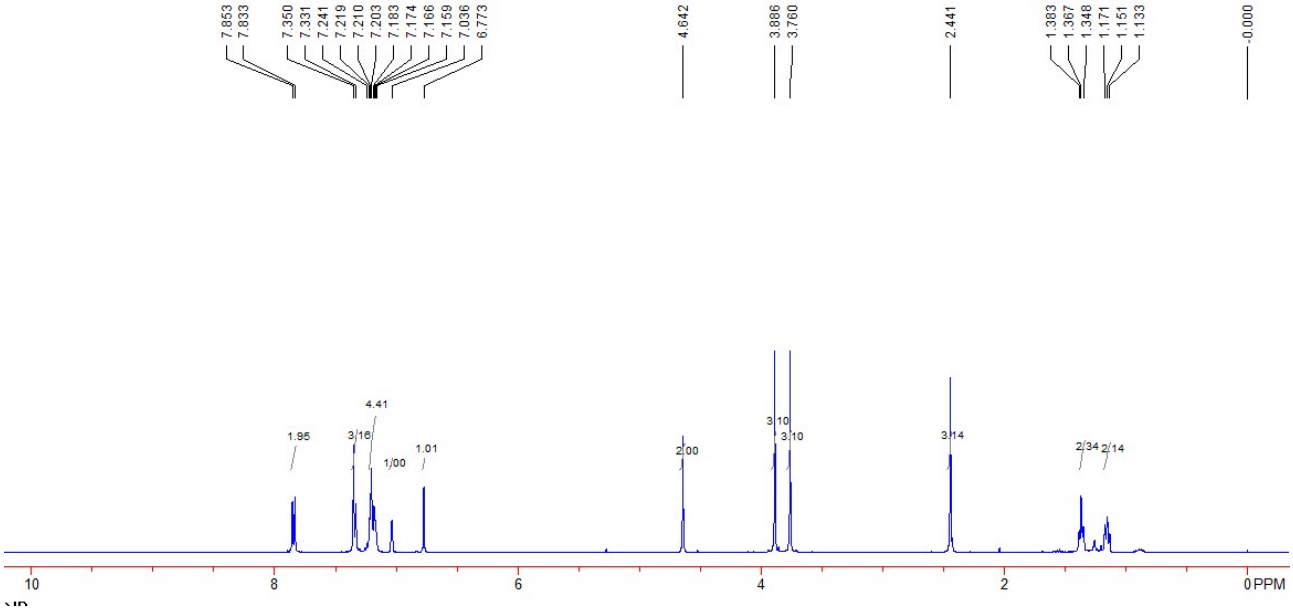


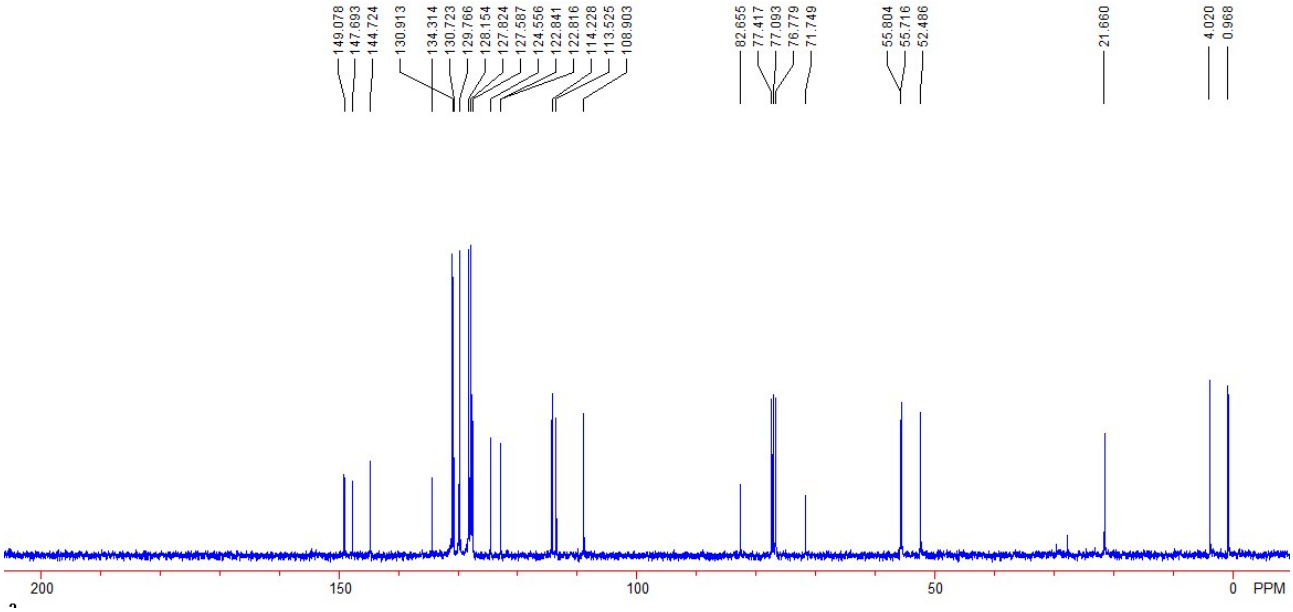
Compound 1t: A white solid. 336 mg, 76% yield. m.p. 135-138 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.09-1.15 (m, 2H), 1.30-1.35 (m, 2H), 2.17 (s, 6H), 2.38 (s, 3H), 4.63 (s, 2H), 6.75-6.80 (m, 3H), 7.07-7.17 (m, 2H), 7.25-7.30 (m, 4H), 7.76-7.84 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 1.1, 4.3, 21.7, 53.2, 72.0, 82.0, 114.5, 122.5, 126.5, 126.7, 127.0, 127.9, 128.6, 128.7, 129.5, 129.9, 130.4, 131.2, 134.2, 137.6, 137.7, 144.8. IR (neat) ν 2959, 2922, 2856, 2236, 1597, 1454, 1365, 1170, 1089, 1015, 847, 709, 657 cm^{-1}. HRMS (EI) Calcd. for $[C_{28}H_{28}NO_2S]$ $[M+H]^+$ requires 442.1835, found 442.1833.

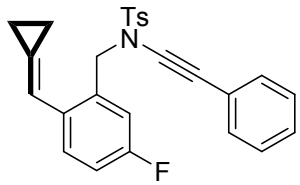




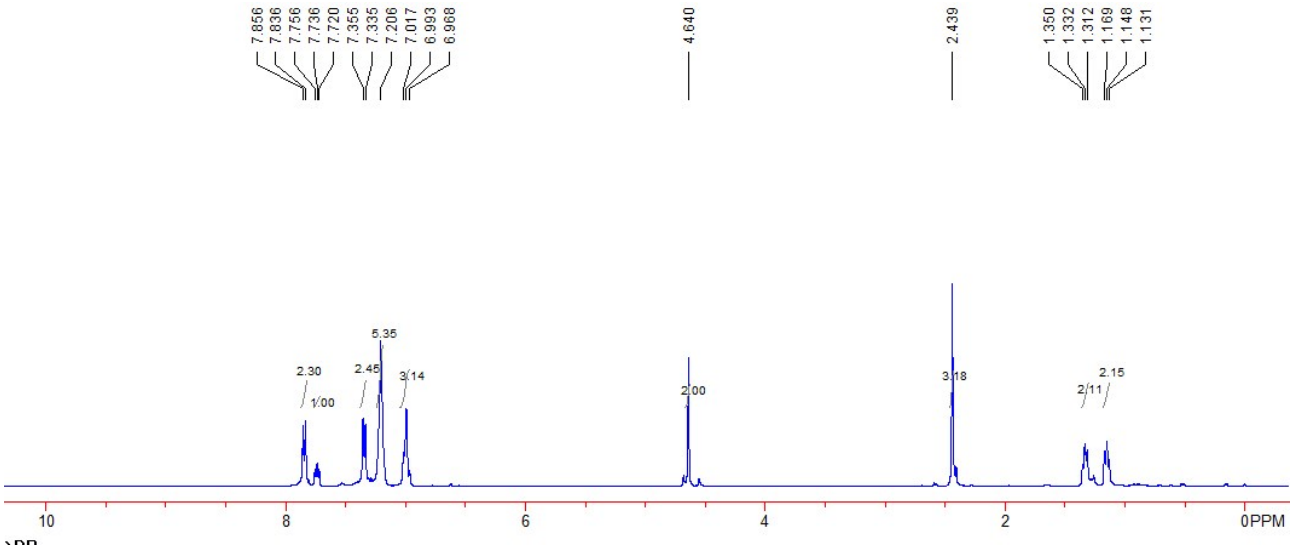
Compound 1u: A white solid. 166 mg, 35% yield. m.p. 59-73 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.12-1.18 (m, 2H), 1.34-1.39 (m, 2H), 2.44 (s, 3H), 3.76 (s, 3H), 3.89 (s, 3H), 4.64 (s, 2H), 6.77 (s, 1H), 7.02-7.04 (m, 1H), 7.15-7.23 (m, 4H), 7.32-7.36 (m, 3H), 7.84 (d, J = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 1.0, 4.0, 21.7, 52.5, 55.7, 55.8, 71.8, 82.7, 108.9, 113.5, 114.2, 122.8, 122.9, 124.6, 127.6, 127.8, 128.2, 129.8, 130.7, 130.9, 134.3, 144.7, 147.7, 149.1. IR (neat) ν 2963, 2925, 2853, 2240, 1605, 1516, 1461, 1363, 1269, 1168, 1114, 755, 664 cm^{-1}. HRMS (EI) Calcd. for $[C_{28}H_{28}NO_4S]$ $[M+H]^+$ requires 474.1734, found 474.1726.







Compound 1v: A white solid. 194 mg, 45% yield. m.p. 71-74 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.12-1.18 (m, 2H), 1.30-136 (m, 2H), 2.44 (s, 3H), 4.64 (s, 2H), 6.96-7.01 (m, 3H), 7.18-7.22 (m, 5H), 7.34 (d, *J* = 7.6 Hz, 2H), 7.74 (t, *J* = 8.0 Hz, 1H), 7.84 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 1.2, 4.1, 21.7, 52.6, 71.7, 82.3, 113.5, 115.6 (d, *J* = 21.0 Hz), 117.0 (d, *J* = 22.1 Hz), 122.6, 126.8, 127.7, 127.8, 128.2, 128.3, 129.9, 131.0, 132.4 (d, *J* = 8.3 Hz), 133.5 (d, *J* = 4.0 Hz), 134.0, 145.0, 161.3 (d, *J* = 245.2 Hz). ^{19}F NMR ($CDCl_3$, 376 MHz, $CFCl_3$) δ -115.53 ~ -115.46 (m). IR (neat) ν 2959, 2922, 2863, 2236, 1595, 1489, 1365, 1169, 1089, 937, 814, 754, 690, 657 cm^{-1}. HRMS (EI) Calcd. for $[C_{26}H_{23}FNO_2S]$ $[M+H]^+$ requires 432.1428, found 432.1427.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7.756
7.736
7.720
7.355
7.335
7.206
7.017
6.993
6.968
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2.439
1.350
1.332
1.312
1.169
1.148
1.131
5.35
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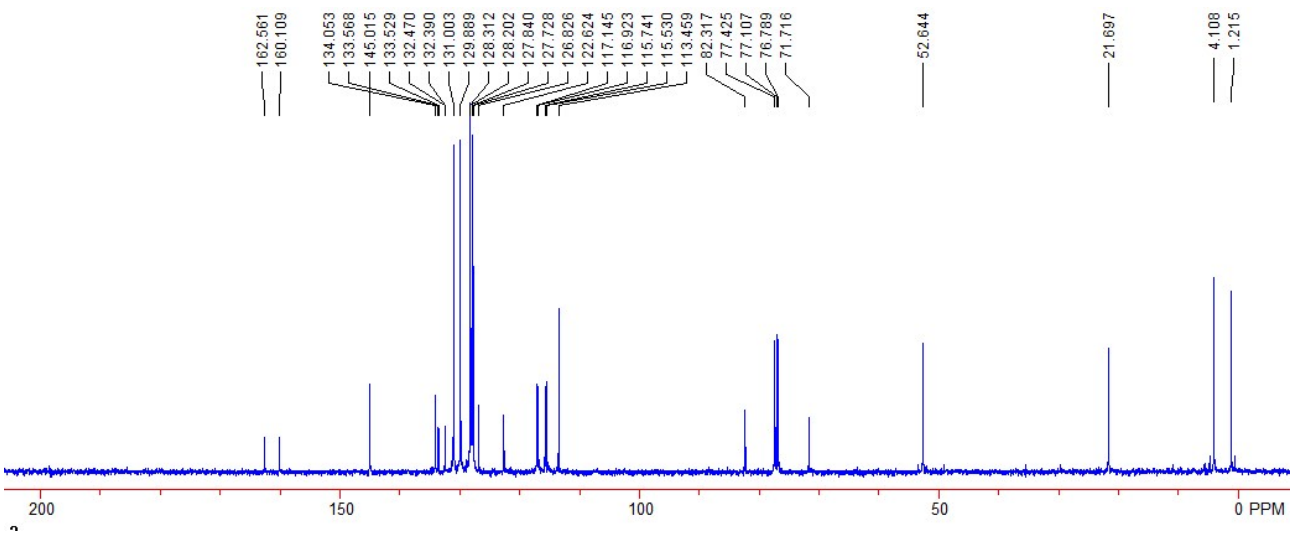
2.15
2.11
10
8
6
4
2
0PPM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134.053
133.568
145.015
133.529
132.470
132.390
131.003
129.889
128.312
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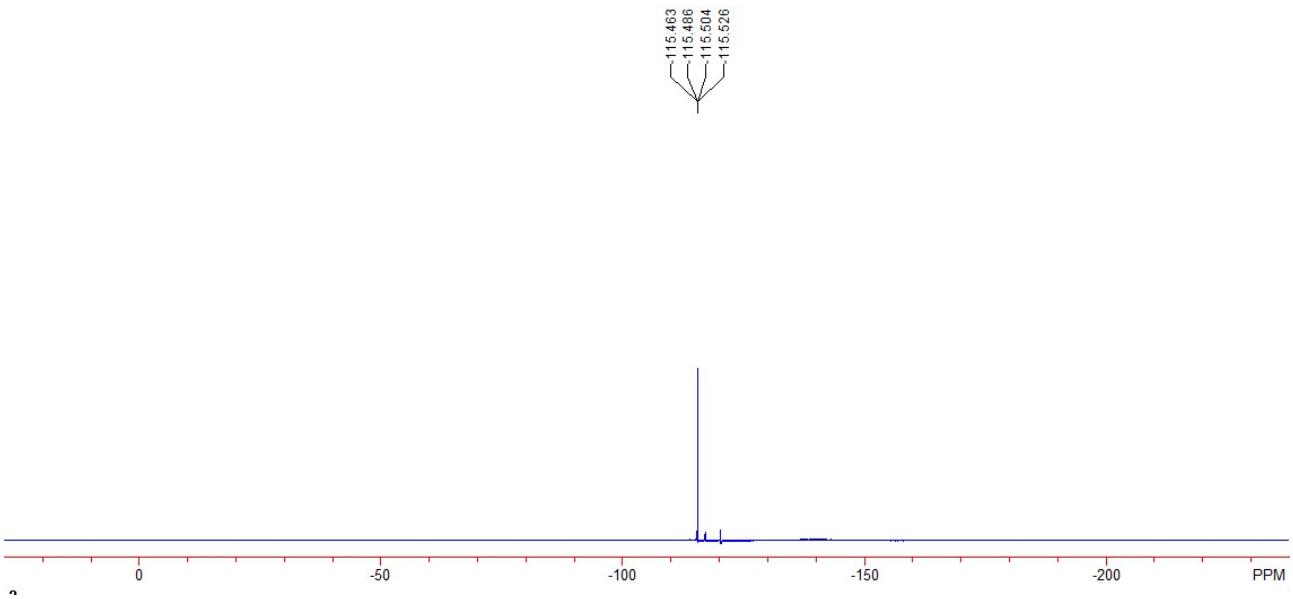
1.215
200
150
100
50
0 PPM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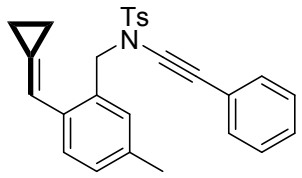
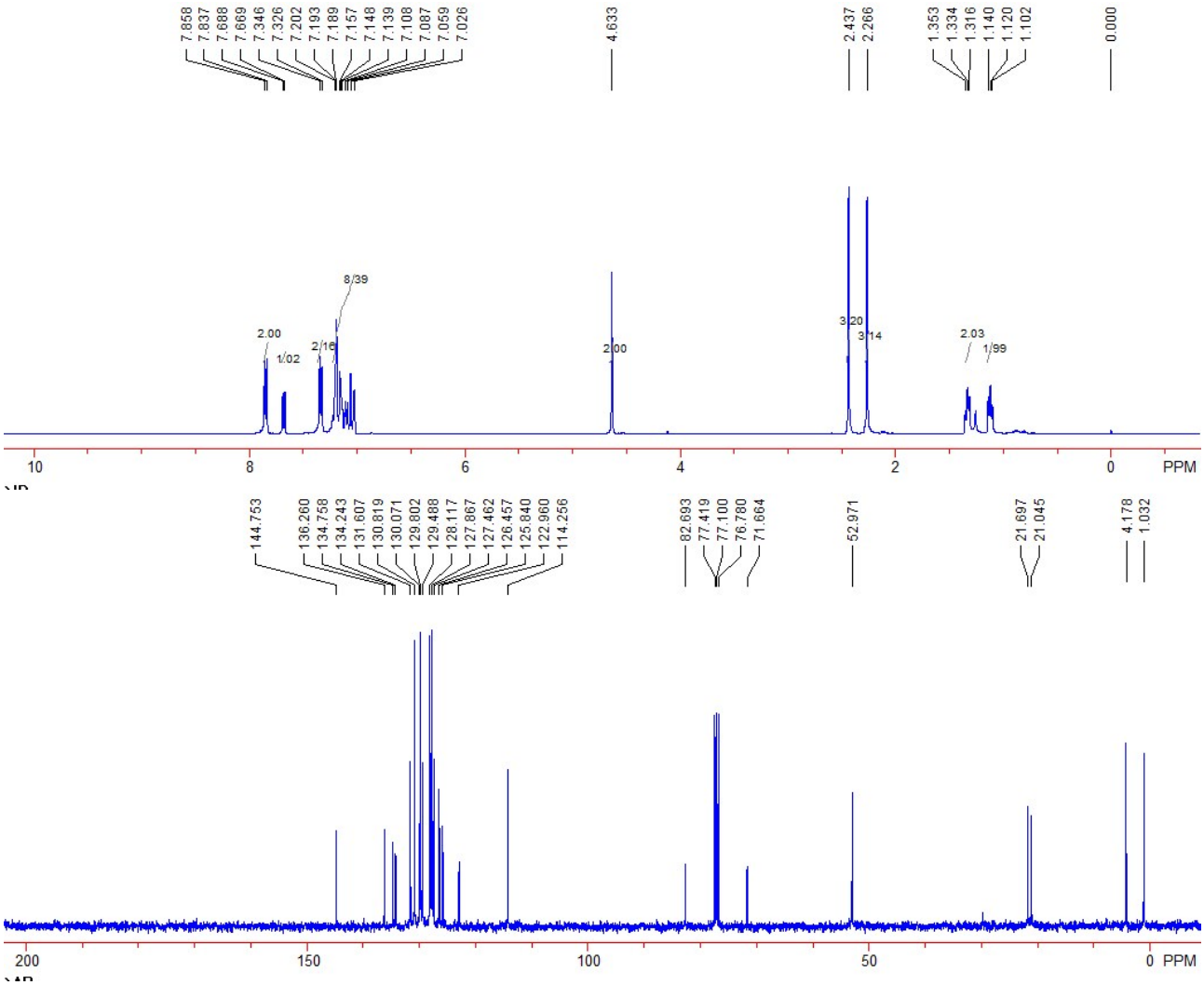
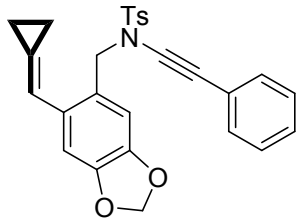
-100
-150
-200
PPM

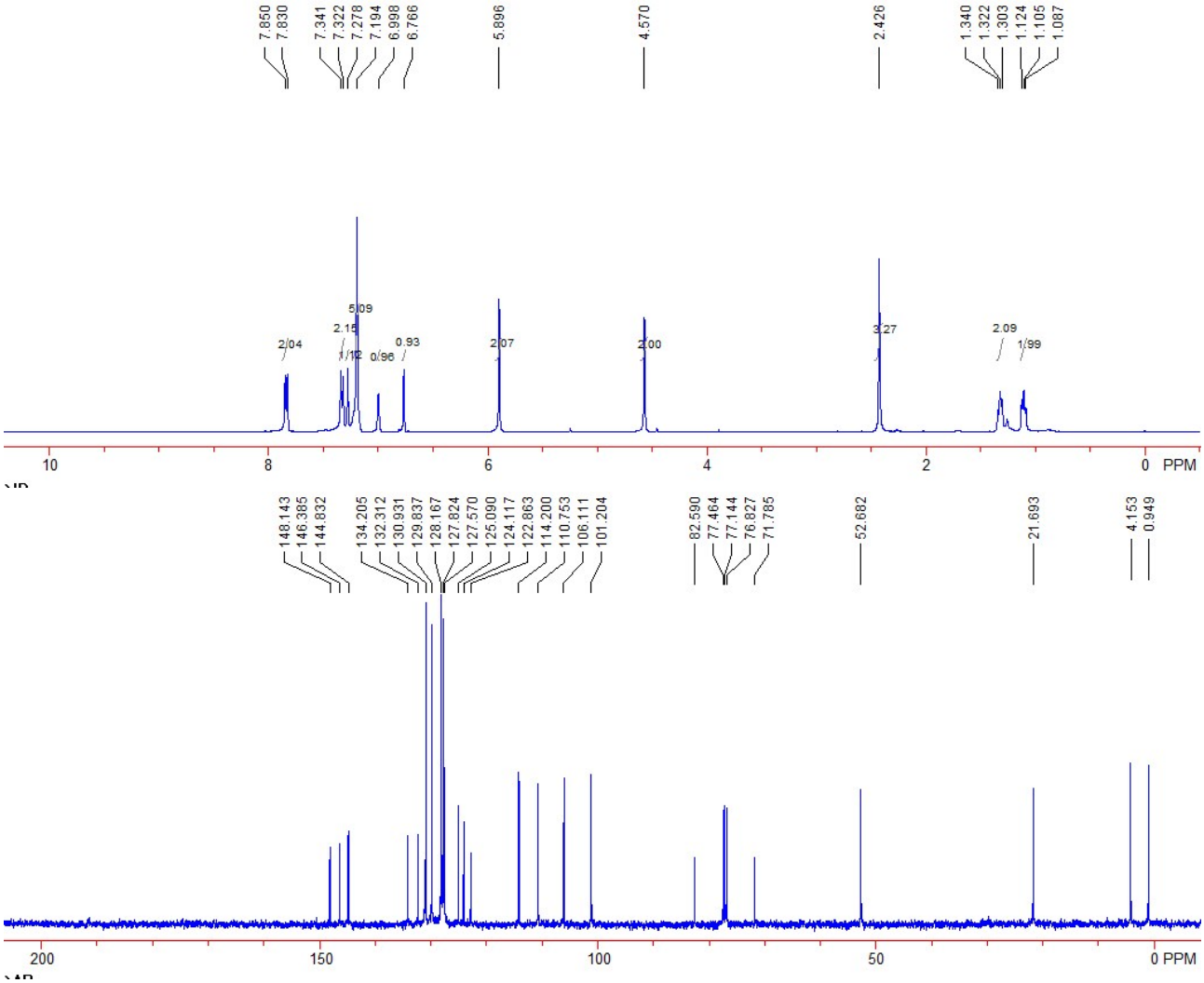


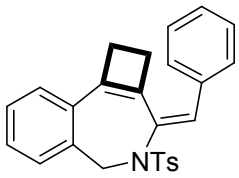
Compound 1w: A white solid. 162 mg, 38% yield. m.p. 108-111°C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.09-1.15 (m, 2H), 1.30-1.36 (m, 2H), 2.27 (s, 3H), 2.44 (s, 3H), 4.63 (s, 2H), 7.02-7.23 (m, 8H), 7.34 (d, *J* = 8.4 Hz, 2H), 7.68 (d, *J* = 7.6 Hz, 1H), 7.85 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 1.0, 4.2, 21.1, 21.7, 53.0, 71.7, 82.7, 114.3, 123.0, 125.8, 126.5, 127.5, 127.9, 128.1, 129.5, 129.8, 130.1, 130.8, 131.6, 134.2, 134.8, 136.3, 144.8. IR (neat) ν 2957, 2923, 2854, 2235, 1597, 1494, 1463, 1365, 1169, 1089, 813, 755, 689 cm^{-1}. HRMS (EI) Calcd. for $[C_{27}H_{26}NO_2S]$ $[M+H]^+$ requires 428.1679, found 428.1674.



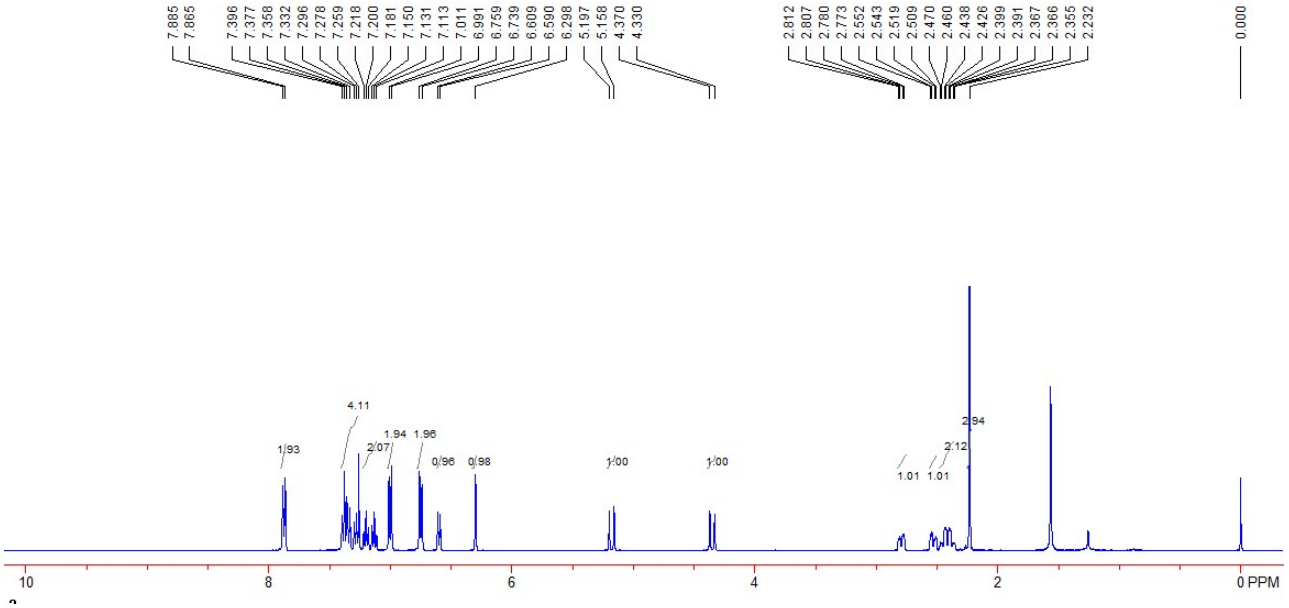


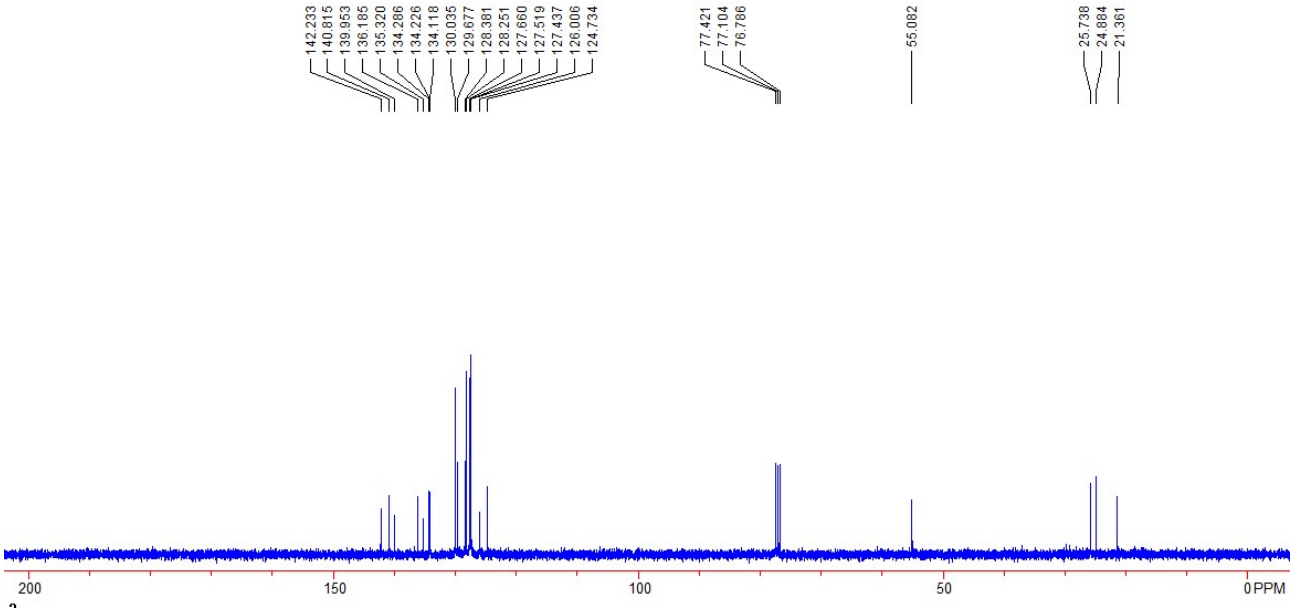
Compound 1x: A white solid. 238 mg, 52% yield. m.p. 76-78 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.07-1.14 (m, 2H), 1.29-1.35 (m, 2H), 2.43 (s, 3H), 4.57 (s, 2H), 5.90 (s, 2H), 6.77 (s, 1H), 7.00 (s, 1H), 7.18-7.20 (m, 5H), 7.28 (s, 1H), 7.33 (d, J = 7.6 Hz, 2H), 7.84 (d, J = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 1.0, 4.2, 21.7, 52.7, 71.8, 82.6, 101.2, 106.1, 110.8, 114.2, 122.9, 124.1, 125.1, 127.6, 127.8, 128.2, 129.8, 130.9, 132.3, 134.2, 144.8, 146.4, 148.1. IR (neat) ν 2959, 2923, 2852, 2234, 1712, 1596, 1503, 1483, 1363, 1186, 1167, 1089, 1038, 813, 755, 668 cm^{-1}. HRMS (EI) Calcd. for $[C_{27}H_{24}NO_4S]$ $[M+H]^+$ requires 458.1421, found 458.1424.

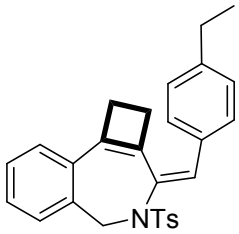




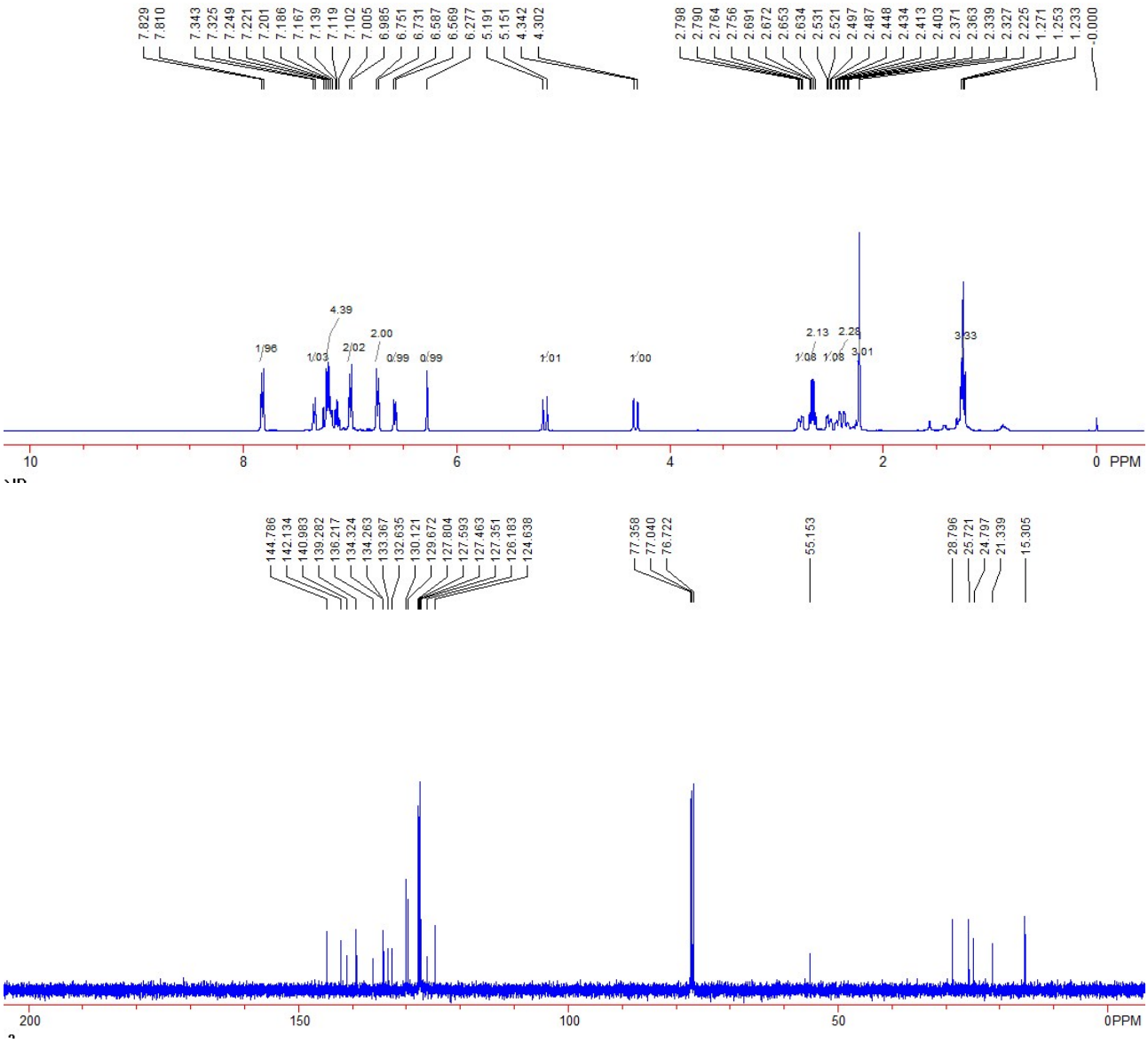
Compound 2a: A white solid. 59 mg, 70% yield. m.p. 160-162 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 2.23 (s, 3H), 2.35-2.48 (m, 2H), 2.50-2.56 (m, 1H), 2.76-2.82 (m, 1H), 4.35 (d, *J* = 16.0 Hz, 1H), 5.18 (d, *J* = 16.0 Hz, 1H), 6.30 (s, 1H), 6.60 (d, *J* = 7.6 Hz, 1H), 6.75 (d, *J* = 8.0 Hz, 2H), 7.00 (d, *J* = 8.0 Hz, 2H), 7.11-7.22 (m, 2H), 7.25-7.40 (m, 4H), 7.88 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 21.4, 24.9, 25.7, 55.1, 124.7, 126.0, 127.4, 127.5, 127.7, 128.3, 128.4, 129.7, 130.0, 134.1, 134.2, 134.3, 135.3, 136.2, 140.0, 140.8, 142.2. IR (neat) ν 2952, 2915, 2852, 1705, 1597, 1488, 1355, 1161, 1088, 1059, 928, 837, 757, 677 cm^{-1}. HRMS (EI) Calcd. for $[C_{26}H_{24}NO_2S]$ $[M+H]^+$ requires 414.1522 , found 414.1519.

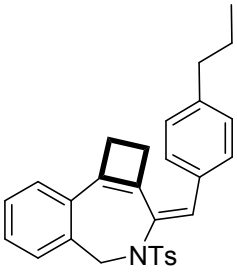






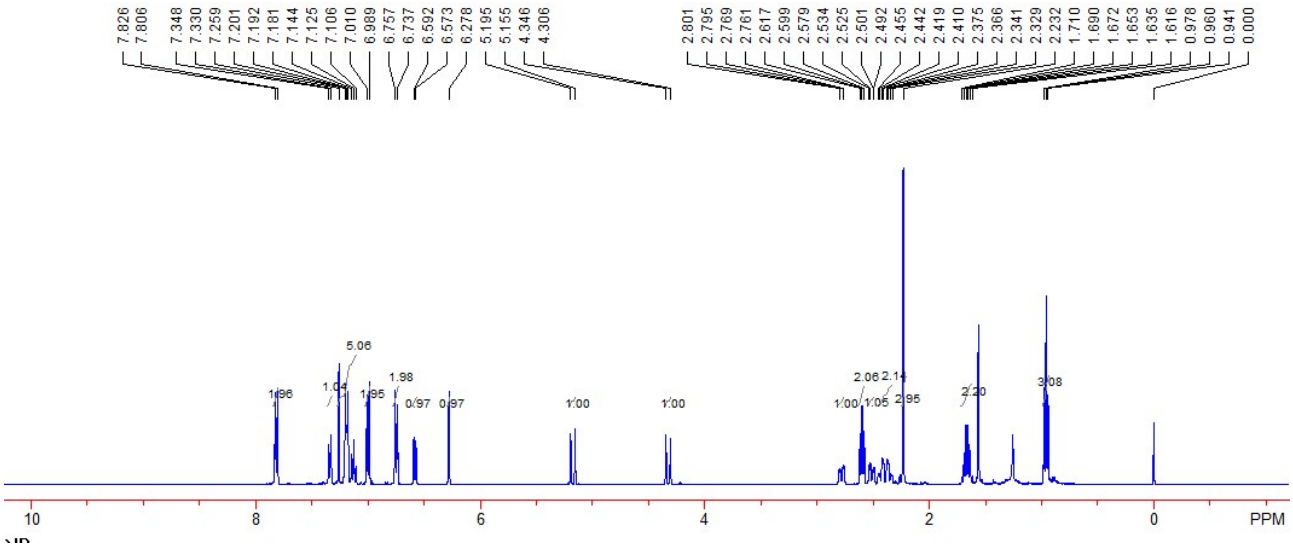
Compound 2b: A white solid. 53 mg, 60% yield. m.p. 152-155 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.25 (t, J = 7.6 Hz, 3H), 2.23 (s, 3H), 2.32-2.46 (m, 2H), 2.48-2.54 (m, 1H), 2.66 (q, J = 7.6 Hz, 2H), 2.75-2.80 (m, 1H), 4.32 (d, J = 16.0 Hz, 1H), 5.17 (d, J = 16.0 Hz, 1H), 6.28 (s, 1H), 6.58 (d, J = 7.2 Hz, 1H), 6.74 (d, J = 8.0 Hz, 2H), 7.00 (d, J = 8.0 Hz, 2H), 7.09-7.26 (m, 4H), 7.33 (d, J = 7.2 Hz, 1H), 7.82 (d, J = 7.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 15.3, 21.3, 24.8, 25.7, 28.8, 55.2, 124.6, 126.2, 127.4, 127.5, 127.6, 127.8, 129.7, 130.1, 132.6, 133.4, 134.2, 134.3, 136.2, 139.3, 141.0, 142.1, 144.8. IR (neat) ν 2961, 2916, 2863, 1598, 1491, 1446, 1354, 1161, 1088, 811, 757, 664 cm^{-1}. HRMS (EI) Calcd. for $[C_{28}H_{28}NO_2S]$ $[M+H]^+$ requires 442.1835, found 442.1837.

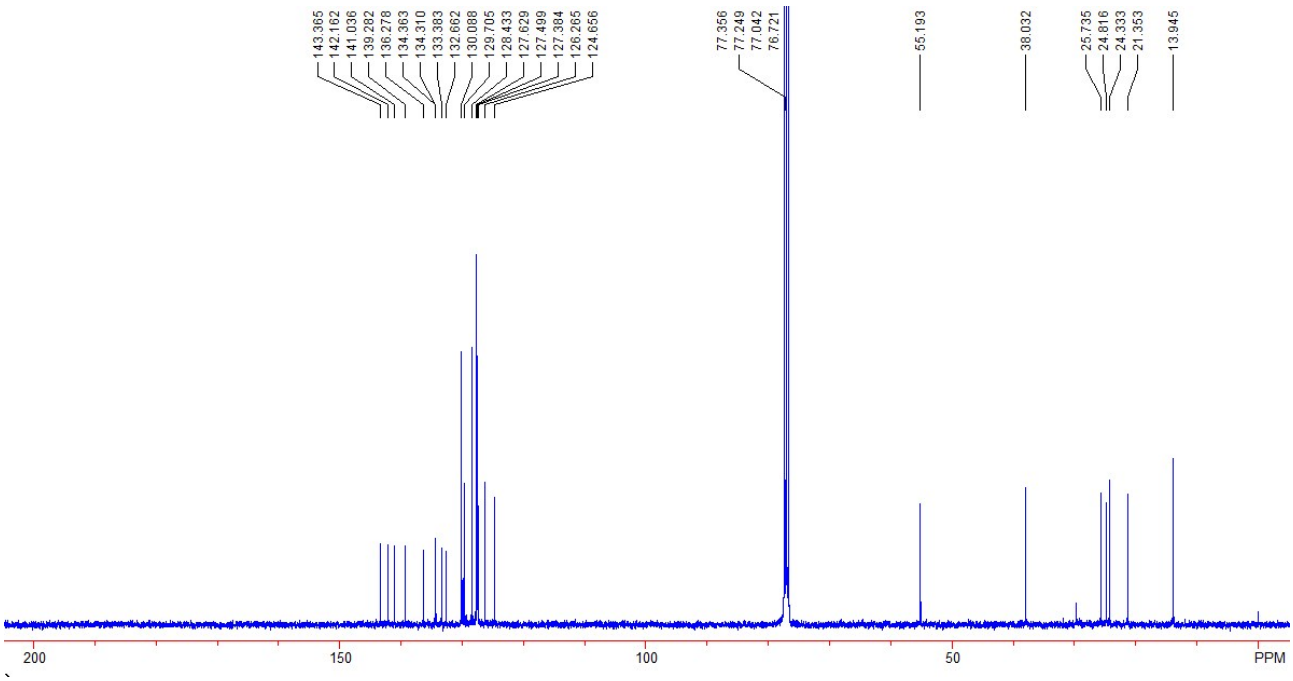


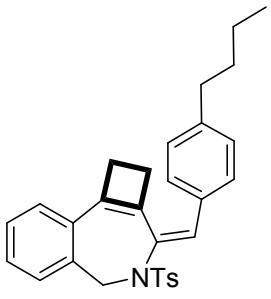


Compound 2c: A white solid. 57 mg, 61% yield. m.p. 147-150 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 0.96 (t, *J* = 7.2 Hz, 3H), 1.61-1.72 (m, 2H), 2.23 (s, 3H), 2.32-2.46 (m, 2H), 2.48-2.54 (m, 1H), 2.60 (t, *J* = 7.2 Hz, 2H), 2.75-2.81 (m, 1H), 4.33 (d, *J* = 16.0 Hz, 1H), 5.18 (d, *J* = 16.0 Hz, 1H), 6.28 (s, 1H), 6.58 (d, *J* = 7.6 Hz, 1H), 6.75 (d, *J* = 8.0 Hz, 2H), 7.00 (d, *J* = 7.6 Hz, 2H), 7.10-7.27 (m, 5H), 7.34 (d, *J* = 7.2 Hz, 1H), 7.82 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS)

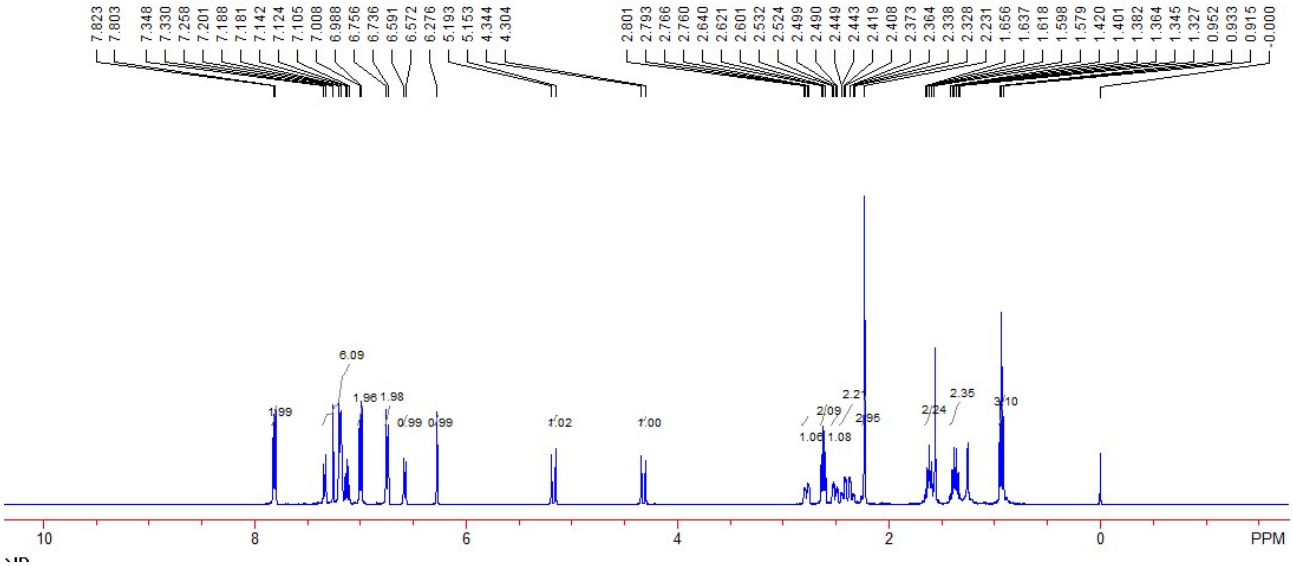
δ 13.9, 21.4, 24.3, 24.8, 25.7, 38.0, 55.2, 124.7, 126.3, 127.4, 127.5, 127.6, 128.4, 129.7, 130.1, 132.7, 133.4, 134.3, 134.4, 136.3, 139.3, 141.0, 142.2, 143.4. IR (neat) ν 2972, 2922, 2856, 2234, 1711, 1597, 1488, 1363, 1186, 1168, 749, 723 cm^{-1}. HRMS (EI) Calcd. for $[C_{29}H_{33}N_2O_2S]$ $[M+NH_4]^+$ requires 473.2257, found 473.2249.

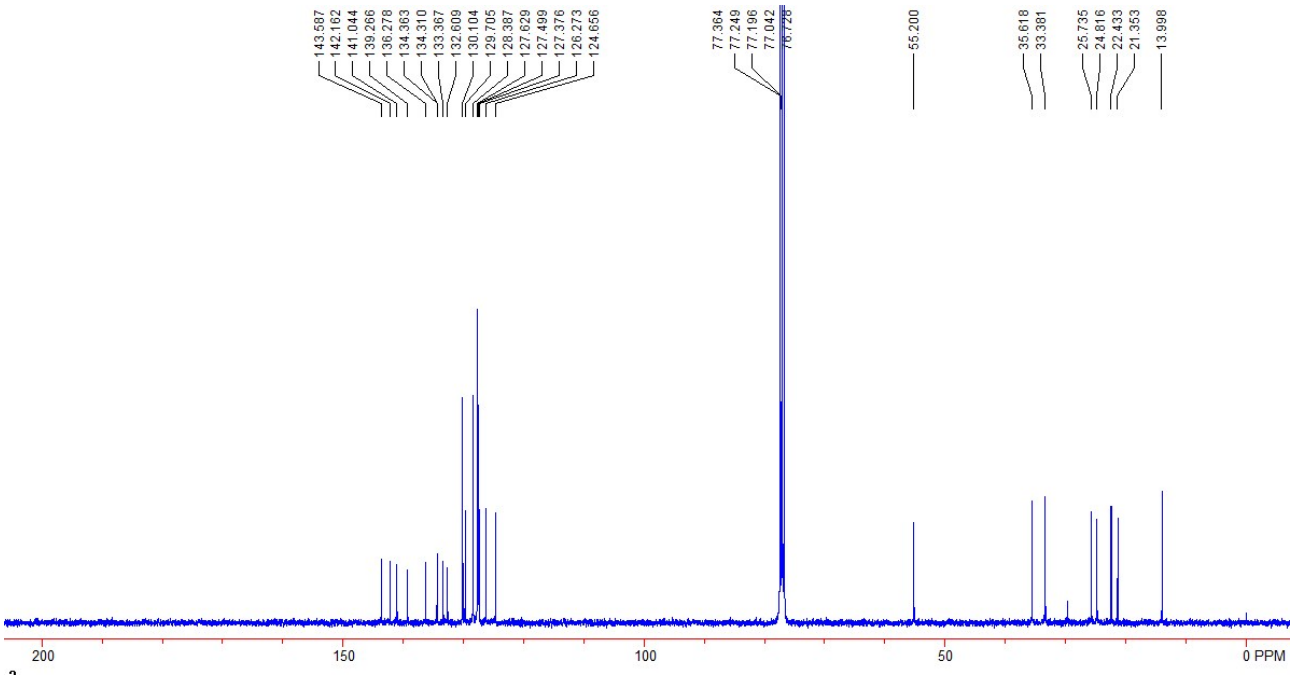


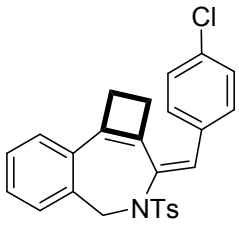




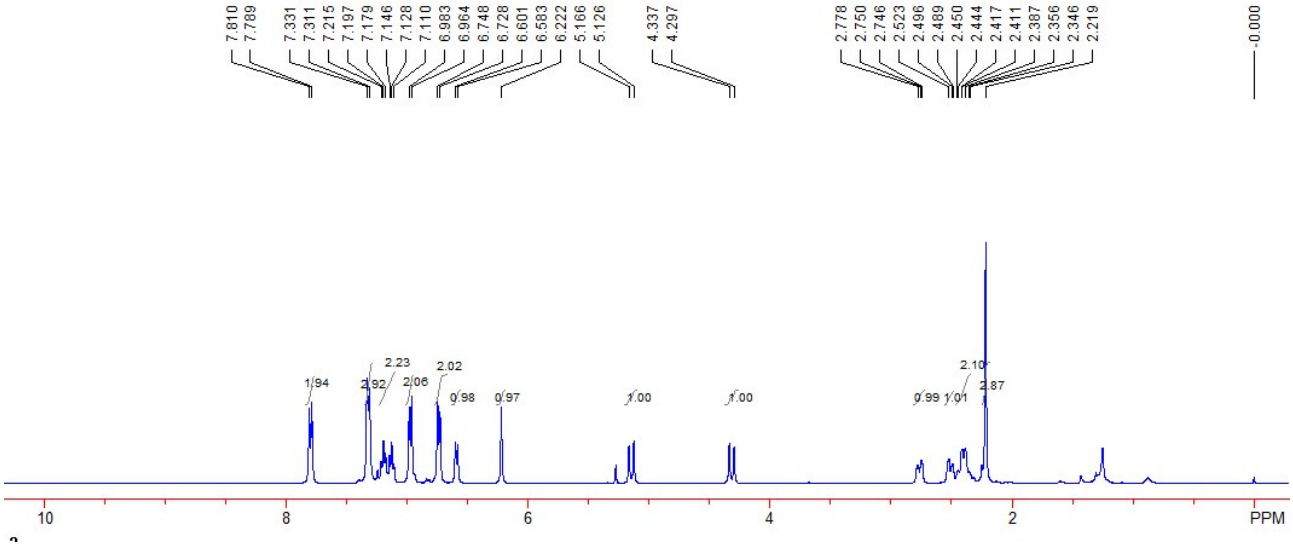
Compound 2d: A white solid. 58 mg, 60% yield. m.p. 148-151 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 0.93 (t, *J* = 7.6 Hz, 3H), 1.32-1.43 (m, 2H), 1.57-1.67 (m, 2H), 2.23 (s, 3H), 2.32-2.46 (m, 2H), 2.48-2.54 (m, 1H), 2.62 (t, *J* = 7.6 Hz, 2H), 2.75-2.81(m, 1H), 4.32 (d, *J* = 16.0 Hz, 1H), 5.17 (d, *J* = 16.0 Hz, 1H), 6.28 (s, 1H), 6.58 (d, *J* = 7.6 Hz, 1H), 6.75 (d, *J* = 8.0 Hz, 2H), 7.00 (d, *J* = 8.0 Hz, 2H), 7.10-7.27 (m, 5H), 7.34 (d, *J* = 7.2 Hz, 1H), 7.81 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 14.0, 21.4, 22.4, 24.8, 25.7, 33.4, 35.6, 55.2, 124.7, 126.3, 127.4, 127.5, 127.6, 128.4, 129.7, 130.1, 132.6, 133.4, 134.3, 134.4, 136.3, 139.3, 141.0, 142.2, 143.6. IR (neat) ν 2972, 2922, 2856, 2234, 1711, 1597, 1488, 1363, 1186, 1168, 749, 723 cm^{-1}. HRMS (EI) Calcd. for $[C_{30}H_{35}N_2O_2S]$ $[M+NH_4]^+$ requires 487.2414, found 487.2406.

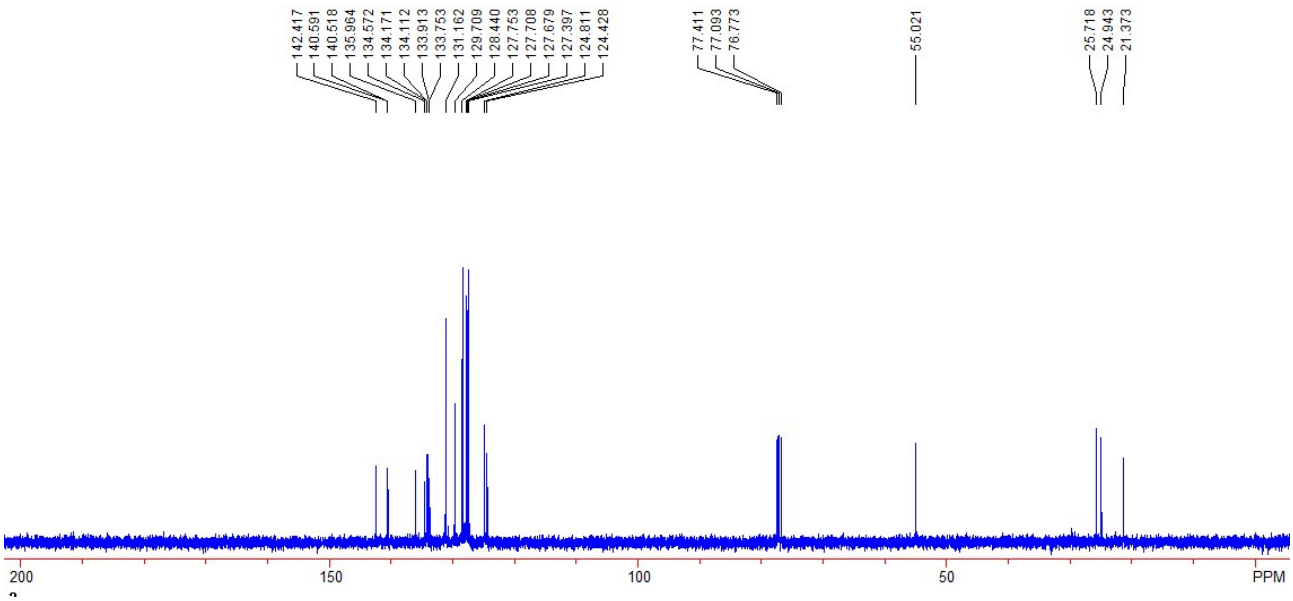


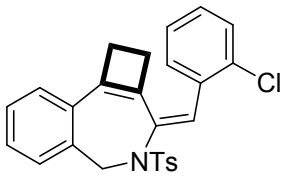




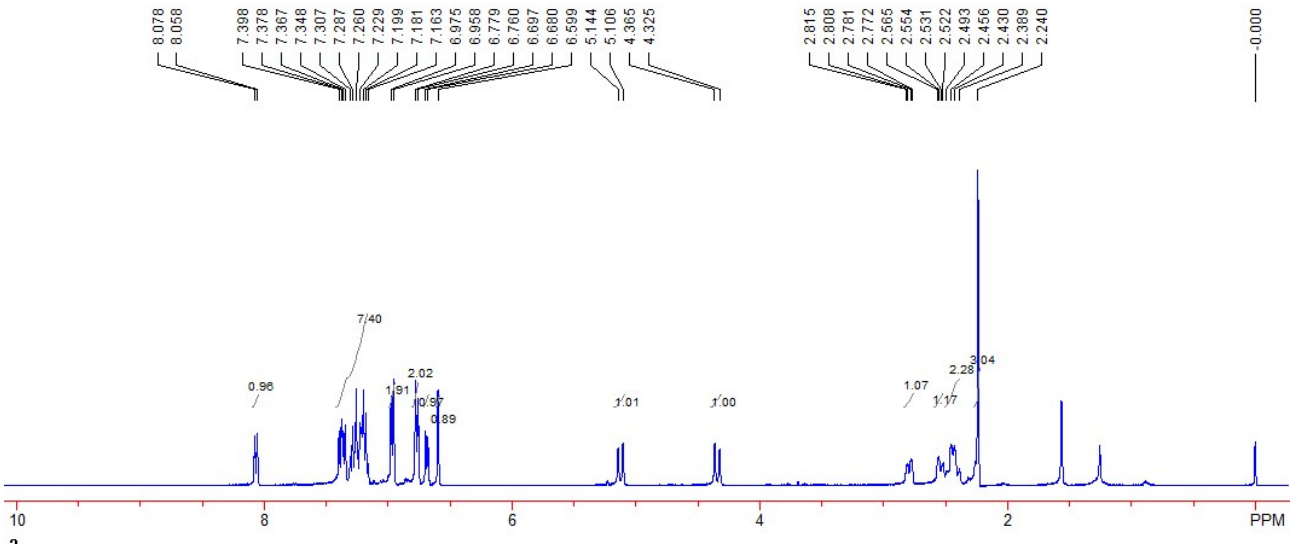
Compound 2e: A white solid. 70 mg, 76% yield. m.p. 172-182 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 2.22 (s, 3H), 2.34-2.46 (m, 2H), 2.48-2.53 (m, 1H), 2.74-2.79 (m, 1H), 4.32 (d, *J* = 16.0 Hz, 1H), 5.15 (d, *J* = 16.0 Hz, 1H), 6.22 (s, 1H), 6.59 (d, *J* = 7.2 Hz, 1H), 6.74 (d, *J* = 8.0 Hz, 2H), 6.97 (d, *J* = 7.6 Hz, 2H), 7.10-7.22 (m, 2H), 7.32 (d, *J* = 8.0 Hz, 3H), 7.80 (d, *J* = 7.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 21.4, 24.9, 25.7, 55.0, 124.4, 124.8, 127.4, 127.6, 127.7, 127.8, 128.4, 129.7, 131.2, 133.8, 133.9, 134.1, 134.2, 134.6, 136.0, 140.5, 140.6, 142.4. IR (neat) ν 2972, 2922, 2856, 2234, 1711, 1597, 1488, 1363, 1186, 1168, 749, 723 cm^{-1}. HRMS (EI) Calcd. for $[C_{26}H_{26}ClN_2O_2S]$ $[M+NH_4]^+$ requires 465.1398, found 465.1395.

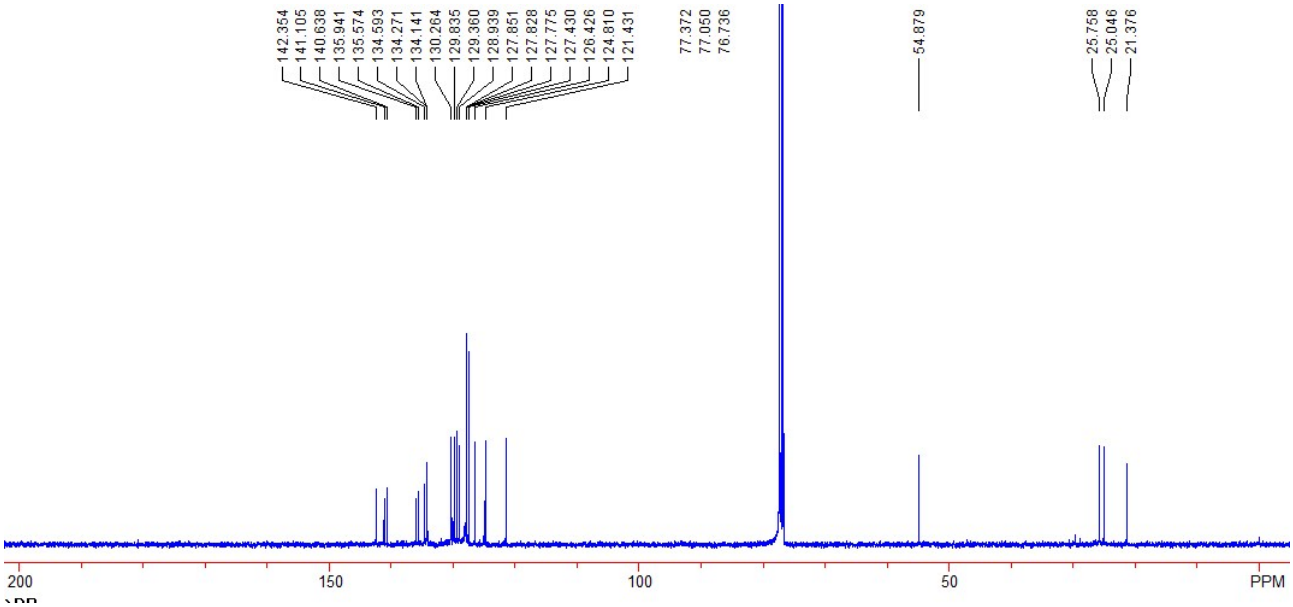


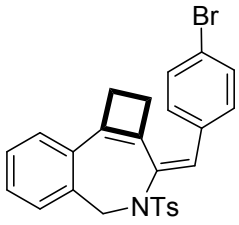




Compound 2f: A white solid. 58 mg, 63% yield. m.p. 190-195 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 2.24 (s, 3H), 2.38-2.50 (m, 2H), 2.51-2.57 (m, 1H), 2.76-2.82 (m, 1H), 4.34 (d, J = 16.0 Hz, 1H), 5.13 (d, J = 15.2 Hz, 1H), 6.60 (s, 1H), 6.69 (d, J = 6.8 Hz, 1H), 6.77 (d, J = 7.6 Hz, 2H), 6.97 (d, J = 6.8 Hz, 2H), 7.15-7.41 (m, 7H), 8.07 (d, J = 8.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 21.4, 25.0, 25.8, 54.9, 121.4, 124.8, 126.4, 127.4, 127.7, 127.8, 127.9, 128.9, 129.4, 129.8, 130.3, 134.1, 134.3, 134.6, 135.6, 135.9, 140.6, 141.1, 142.4. IR (neat) ν 2972, 2922, 2856, 2234, 1711, 1597, 1488, 1363, 1186, 1168, 749, 723 cm^{-1}. HRMS (EI) Calcd. for $[C_{26}H_{26}ClN_2O_2S]$ $[M+NH_4]^+$ requires 465.1398, found 465.1393.

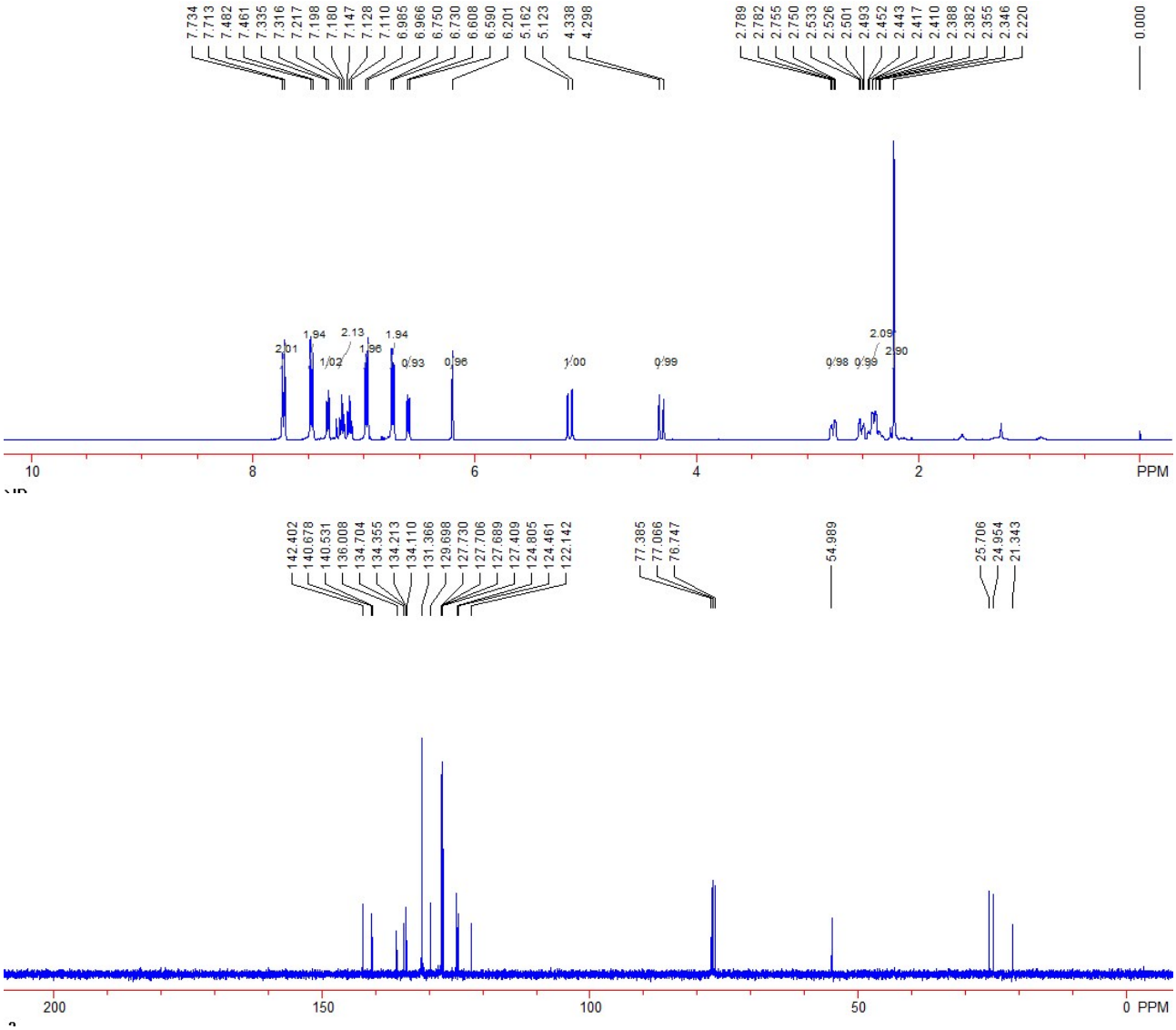


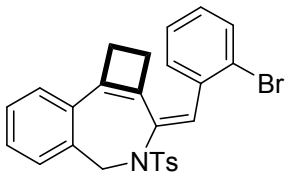




Compound 2g: A white solid. 71 mg, 70% yield. m.p. 181-185 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 2.22 (s, 3H), 2.34-2.46 (m, 2H), 2.48-2.54 (m, 1H), 2.74-2.80 (m, 1H), 4.32 (d, *J* = 16.0 Hz, 1H), 5.14 (d, *J* = 16.0 Hz, 1H), 6.20 (s, 1H), 6.60 (d, *J* = 7.2 Hz, 1H), 6.74 (d, *J* = 8.0 Hz, 2H), 6.98 (d, *J* = 7.6 Hz, 2H), 7.10-7.22 (m, 2H), 7.33 (d, *J* = 7.6 Hz, 1H) , 7.47 (d, *J* = 8.4 Hz, 2H), 7.72 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 21.3, 25.0, 25.7, 55.0, 122.1, 124.5, 124.8, 127.4, 127.6, 127.7, 127.8, 129.7, 131.4, 134.1, 134.2, 134.4, 134.7, 136.0, 140.5, 140.7,

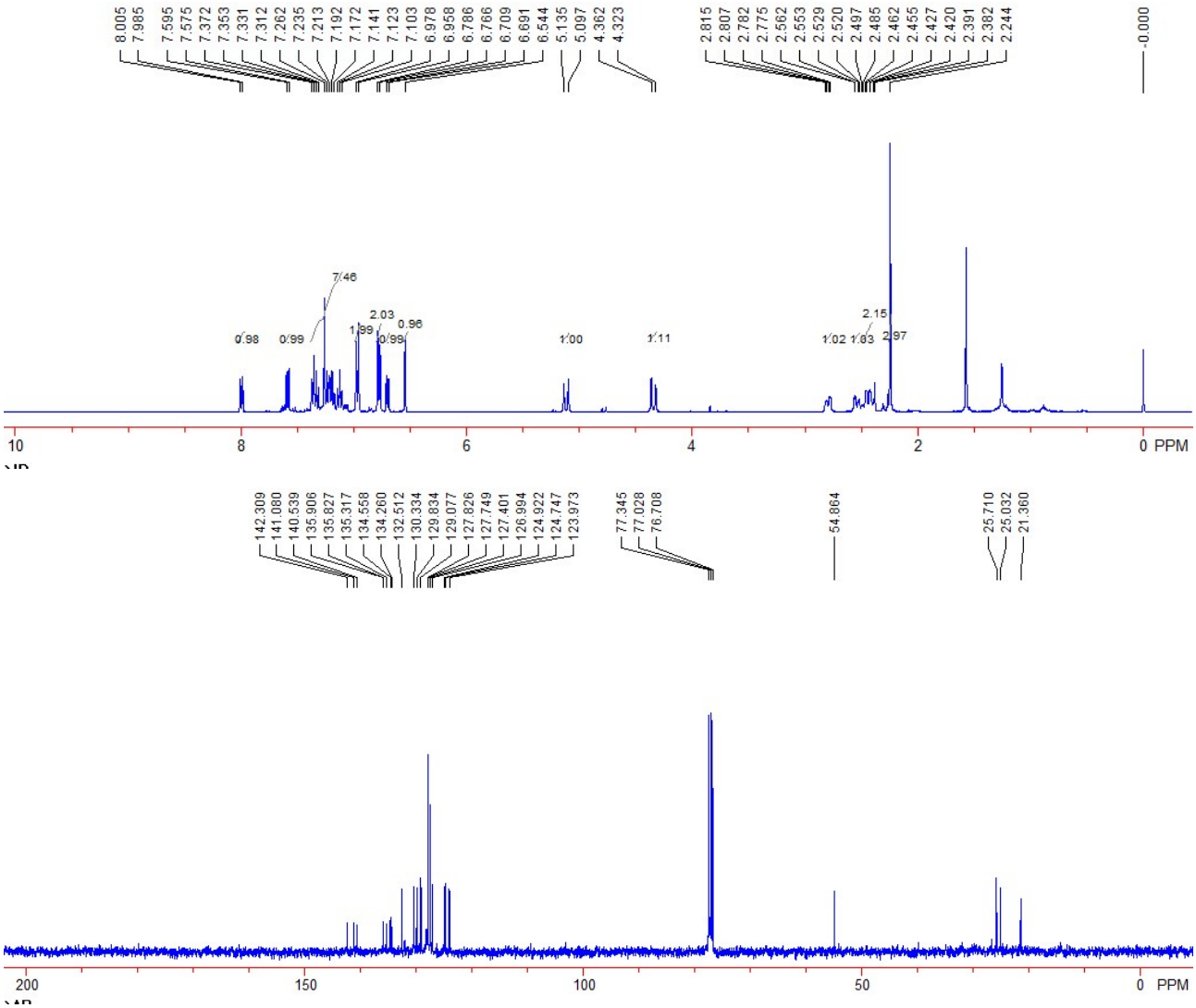
142.4. IR (neat) ν 2972, 2922, 2856, 2234, 1711, 1597, 1488, 1363, 1186, 1168, 749, 723 cm^{-1}. HRMS (EI) Calcd. for $[C_{26}H_{26}BrN_2O_2S]$ $[M+NH_4]^+$ requires 509.0893, found 509.0893.

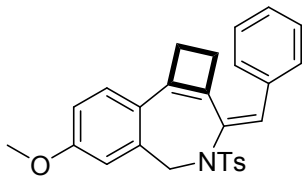




Compound 2h: A white solid. 61 mg, 62% yield. m.p. 189-193 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 2.24 (s, 3H), 2.37-2.50 (m, 2H), 2.51-2.57 (m, 1H), 2.77-2.82 (m, 1H), 4.34 (d, *J* = 15.6 Hz, 1H), 5.12 (d, *J* = 15.2 Hz, 1H), 6.54 (s, 1H), 6.70 (d, *J* = 7.2 Hz, 1H), 6.78 (d, *J* = 8.0 Hz, 2H), 6.97 (d, *J* = 8.0 Hz, 2H), 7.09-7.38 (m, 7H), 7.59 (d, *J* = 8.0 Hz, 1H), 7.99 (d, *J* = 8.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 21.3, 25.0, 25.7, 54.9, 124.0, 124.7, 124.9, 127.0, 127.4, 127.7,

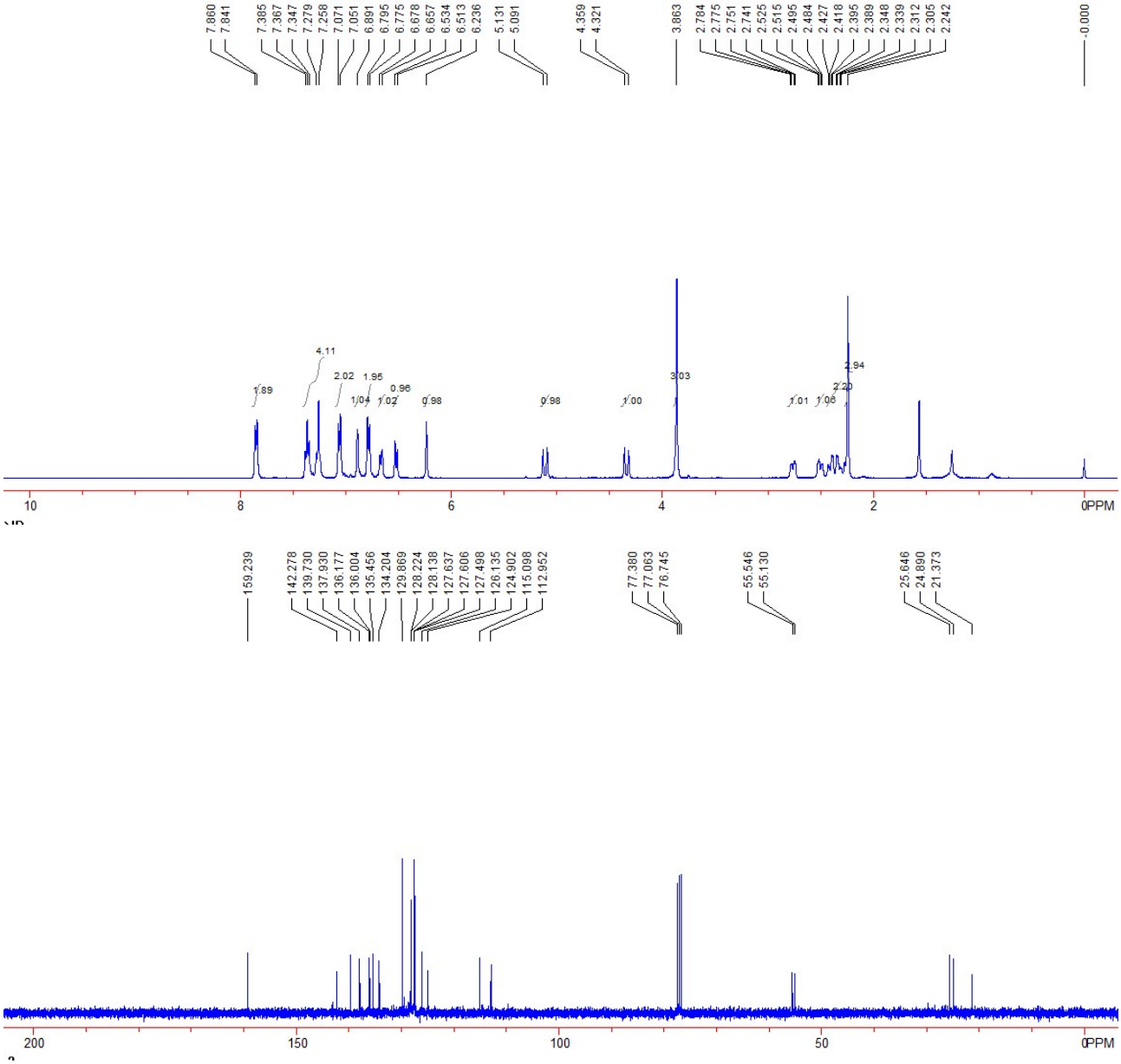
127.8, 129.1, 129.8, 130.3, 132.5, 134.2, 134.6, 135.3, 135.8, 135.9, 140.5, 141.1, 142.3. IR (neat) ν 2972, 2922, 2856, 2234, 1711, 1597, 1488, 1363, 1186, 1168, 749, 723 cm^{-1}. HRMS (EI) Calcd. for $[C_{26}H_{23}BrNO_2S]$ $[M+H]^+$ requires 492.0627, found 492.0626.

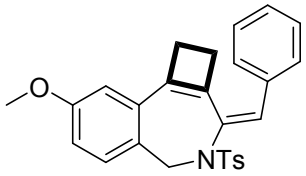




Compound 2i: A white solid. 51 mg, 56% yield. m.p. 180-183 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 2.24 (s, 3H), 2.29-2.44 (m, 2H), 2.47-2.54 (m, 1H), 2.73-2.79 (m, 1H), 3.86 (s, 3H), 4.34 (d, *J* = 15.6 Hz, 1H), 5.11 (d, *J* = 16.0 Hz, 1H), 6.24 (s, 1H), 6.52 (d, *J* = 8.0 Hz, 1H), 6.67 (d, *J* = 8.4 Hz, 2H), 6.78 (d, *J* = 7.6 Hz, 2H), 6.89 (s, 1H), 7.06 (d, *J* = 8.0 Hz, 2H), 7.24-7.39 (m, 4H), 7.85 (d, *J* = 7.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 21.4, 24.9, 25.6, 55.1, 55.5, 113.0, 115.1,

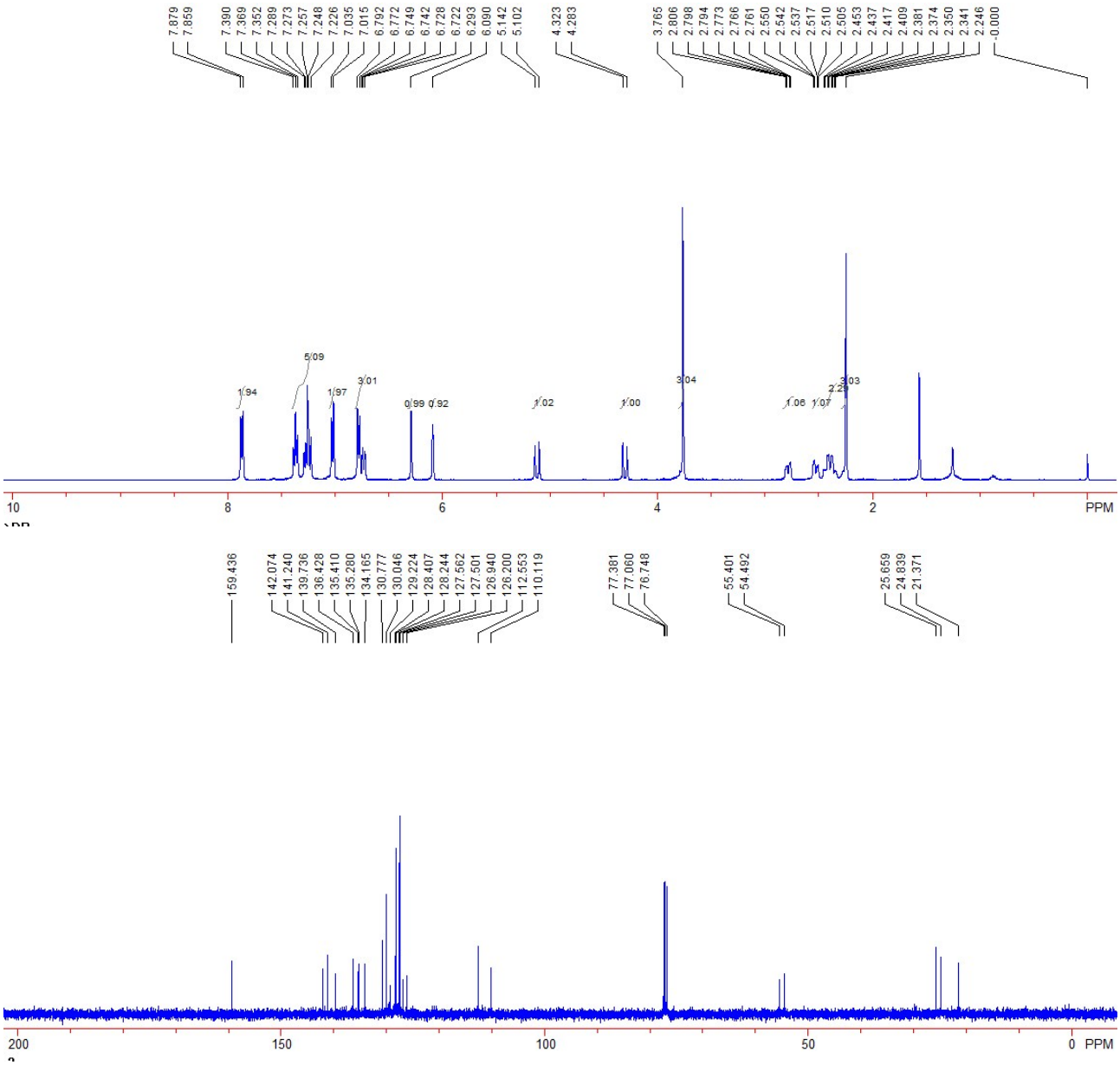
124.9, 126.1, 127.5, 127.6, 127.7, 128.1, 128.2, 129.9, 134.2, 135.5, 136.0, 136.2, 137.9, 139.7, 142.3, 159.2. IR (neat) ν 2972, 2922, 2856, 2234, 1711, 1597, 1488, 1363, 1186, 1168, 749, 723 cm^{-1}. HRMS (EI) Calcd. for $[C_{27}H_{29}N_2O_3S]$ $[M+NH_4]^+$ requires 461.1893, found 461.1888.

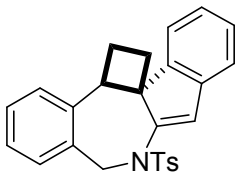




Compound 2j: A white solid. 64 mg, 70% yield. m.p. 179-182 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 2.25 (s, 3H), 2.33-2.46 (m, 2H), 2.50-2.56 (m, 1H), 2.75-2.81 (m, 1H), 3.76 (s, 3H), 4.30 (d, *J* = 15.6 Hz, 1H), 5.12 (d, *J* = 15.6 Hz, 1H), 6.09 (s, 1H), 6.30 (s, 1H), 6.72-6.80 (m, 3H), 7.02

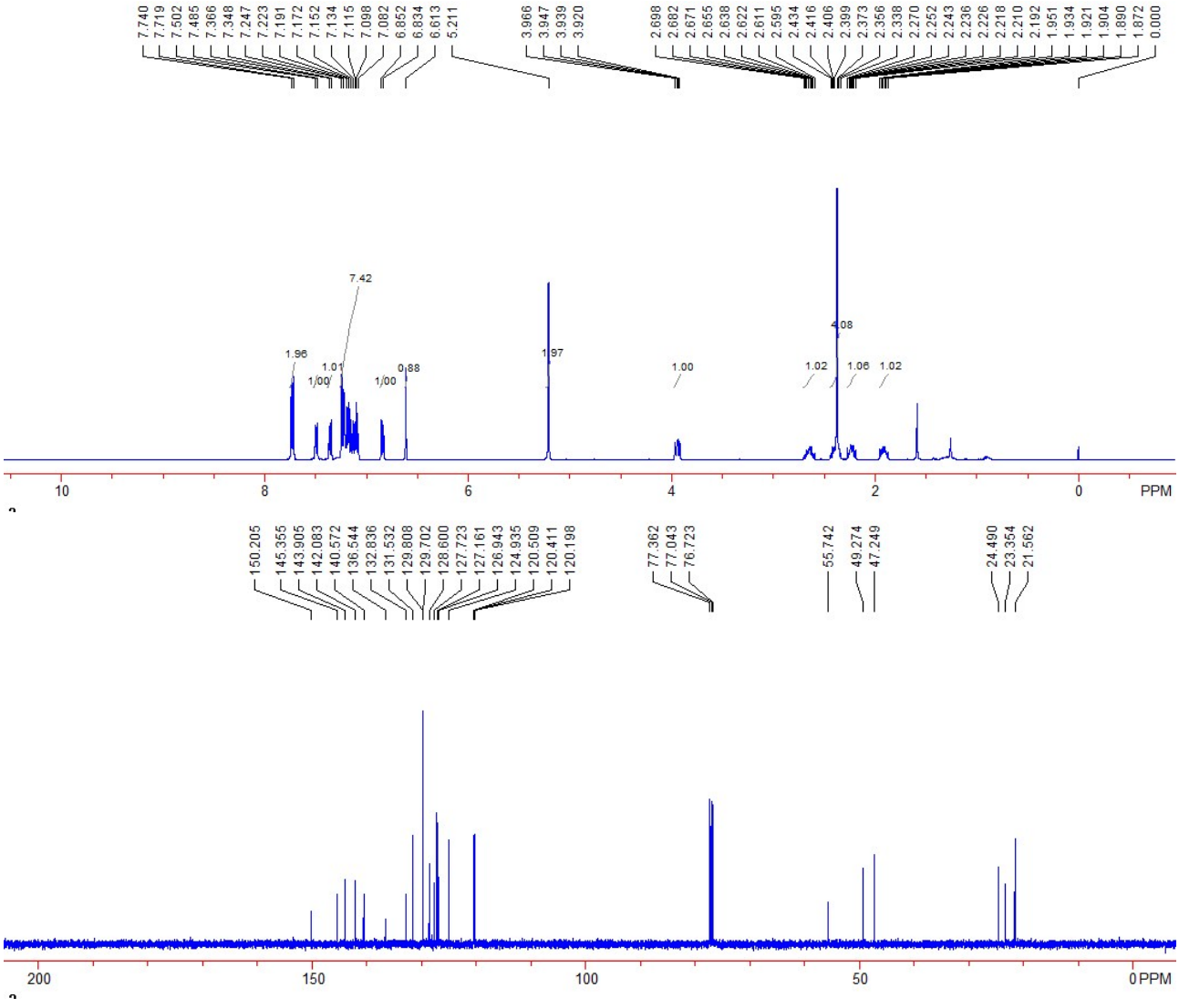
(d, J = 8.4 Hz, 2H), 7.22-7.40 (m, 5H), 7.87 (d, J = 7.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 21.4, 24.8, 25.7, 54.5, 55.4, 110.1, 112.6, 126.2, 126.9, 127.5, 127.6, 128.2, 128.4, 130.0, 130.8, 134.2, 135.3, 135.4, 136.4, 139.7, 141.2, 142.1, 159.4. IR (neat) ν 2972, 2922, 2856, 2234, 1711, 1597, 1488, 1363, 1186, 1168, 749, 723 cm^{-1}. HRMS (EI) Calcd. for [$C_{27}H_{29}N_2O_3S$] [M+NH_4]$^+$ requires 461.1893, found 461.1887.

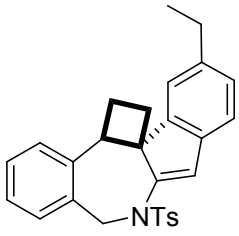




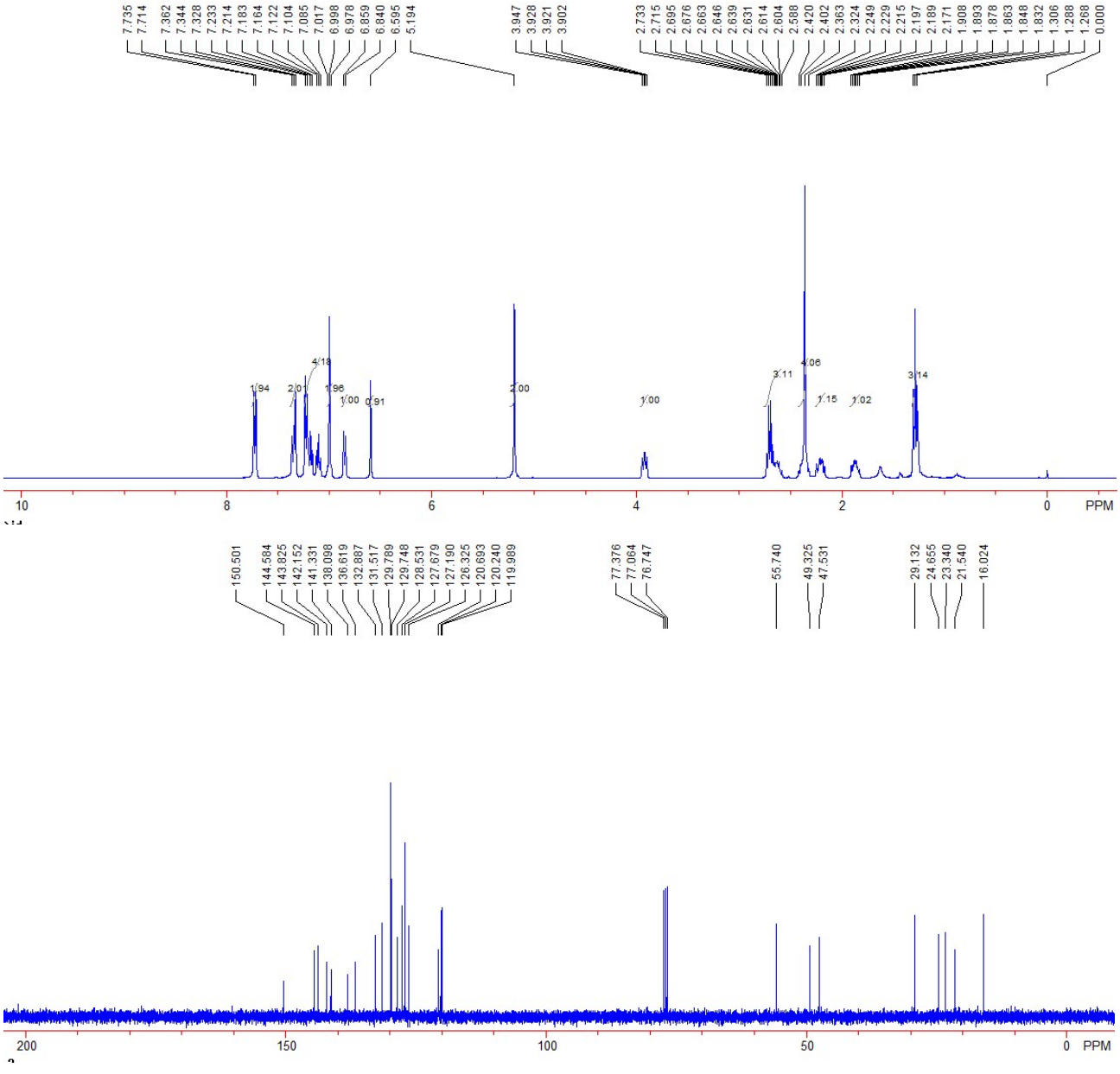
Compound 3a: A white solid. 60 mg, 73% yield. m.p. 179-182 °C. ^{1}H NMR (400 MHz, $CDCl_3$,

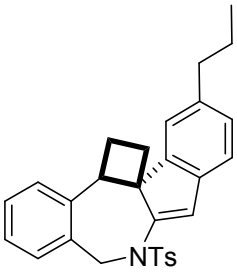
TMS) δ 1.86-1.95 (m, 1H), 2.18-2.28 (m, 1H), 2.37 (s, 3H), 2.33-2.44 (m, 1H), 2.59-2.71 (m, 1H), 3.94 (dd, *J* = 7.2 Hz, *J* = 10.8 Hz, 1H), 5.21 (s, 2H), 6.62 (s, 1H), 6.84 (d, *J* = 7.2 Hz, 1H), 7.08-7.25 (m, 7H), 7.36 (d, *J* = 7.6 Hz, 1H), 7.49 (d, *J* = 7.2 Hz, 1H), 7.73 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 21.6, 23.4, 24.5, 47.3, 49.3, 55.7, 120.2, 120.4, 120.5, 124.9, 126.9, 127.2, 127.7, 128.6, 129.7, 129.8, 131.5, 132.8, 136.6, 140.6, 142.1, 143.9, 145.4, 150.2. IR (neat) ν 2952, 2923, 2845, 1712, 1595, 1568, 1466, 1352, 1163, 1089, 1040, 754, 667 cm^{-1}. HRMS (EI) Calcd. for $[C_{26}H_{24}NO_2S]$ $[M+H]^+$ requires 414.1522 , found 414.1519.



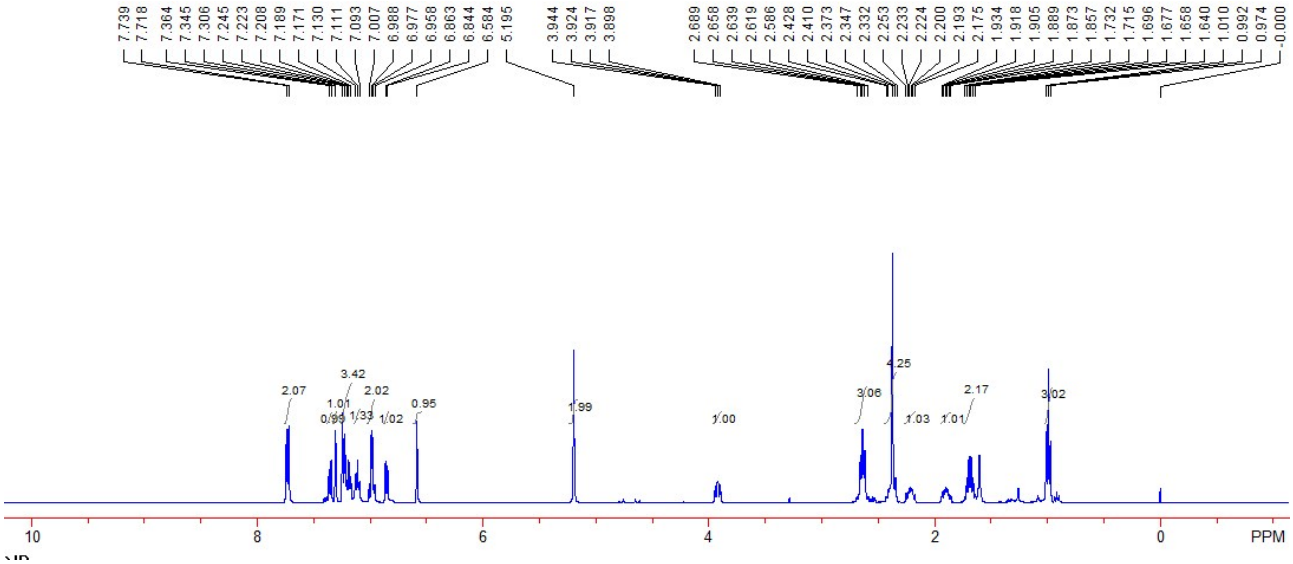


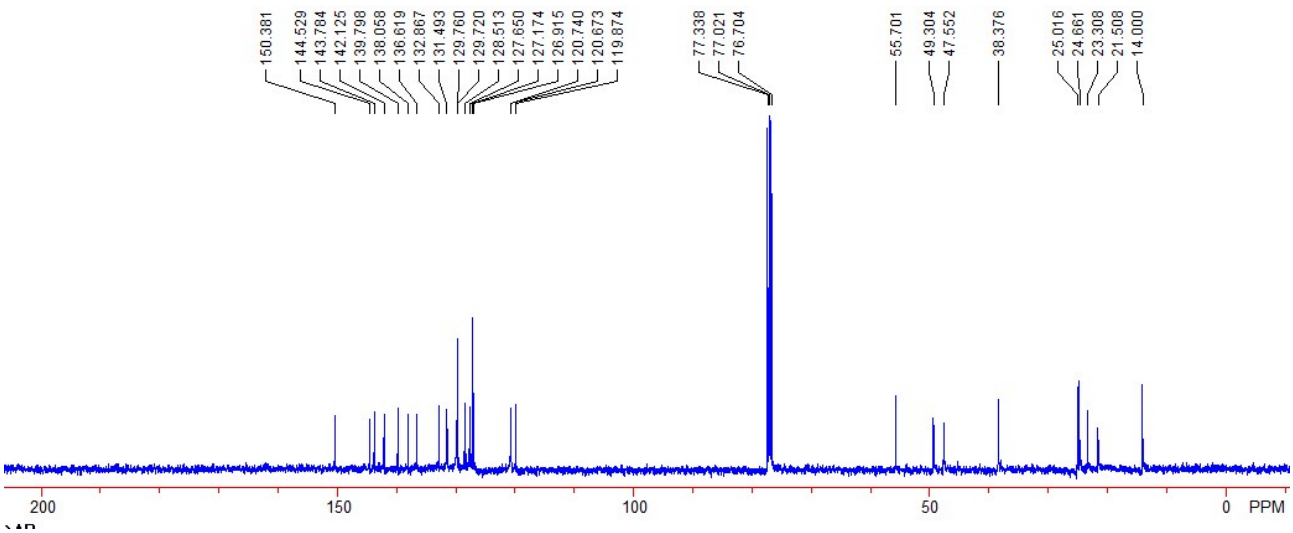
Compound 3b: A white solid. 64 mg, 73% yield. m.p. 132-136 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.29 (t, *J* = 7.6 Hz, 3H), 1.82-1.91 (m, 1H), 2.16-2.25 (m, 1H), 2.37 (s, 3H), 2.32-2.43 (m, 1H), 2.57-2.65 (m, 1H), 2.71 (q, *J* = 7.6 Hz, 2H), 3.93 (dd, *J* = 7.2 Hz, *J* = 10.8 Hz, 1H), 5.19 (s, 2H), 6.60 (s, 1H), 6.85 (d, *J* = 7.2 Hz, 1H), 6.97-7.03 (m, 2H), 7.08-7.24 (m, 4H), 7.32-7.37 (m, 2H), 7.73 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 16.0, 21.5, 23.3, 24.6, 29.1, 47.5, 49.3, 55.7, 120.0, 120.2, 120.7, 126.3, 127.2, 127.7, 127.8, 128.5, 129.7, 129.8, 131.5, 132.9, 136.6, 138.1, 141.3, 142.1, 143.8, 150.5. IR (neat) ν 2961, 2927, 2867, 1705, 1595, 1475, 1352, 1164, 1189, 1040, 884, 758, 669 cm^{-1}. HRMS (EI) Calcd. for $[C_{28}H_{28}NO_2S]$ $[M+H]^+$ requires 442.1835, found 442.1833.

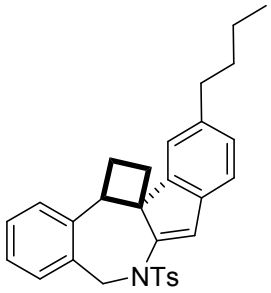




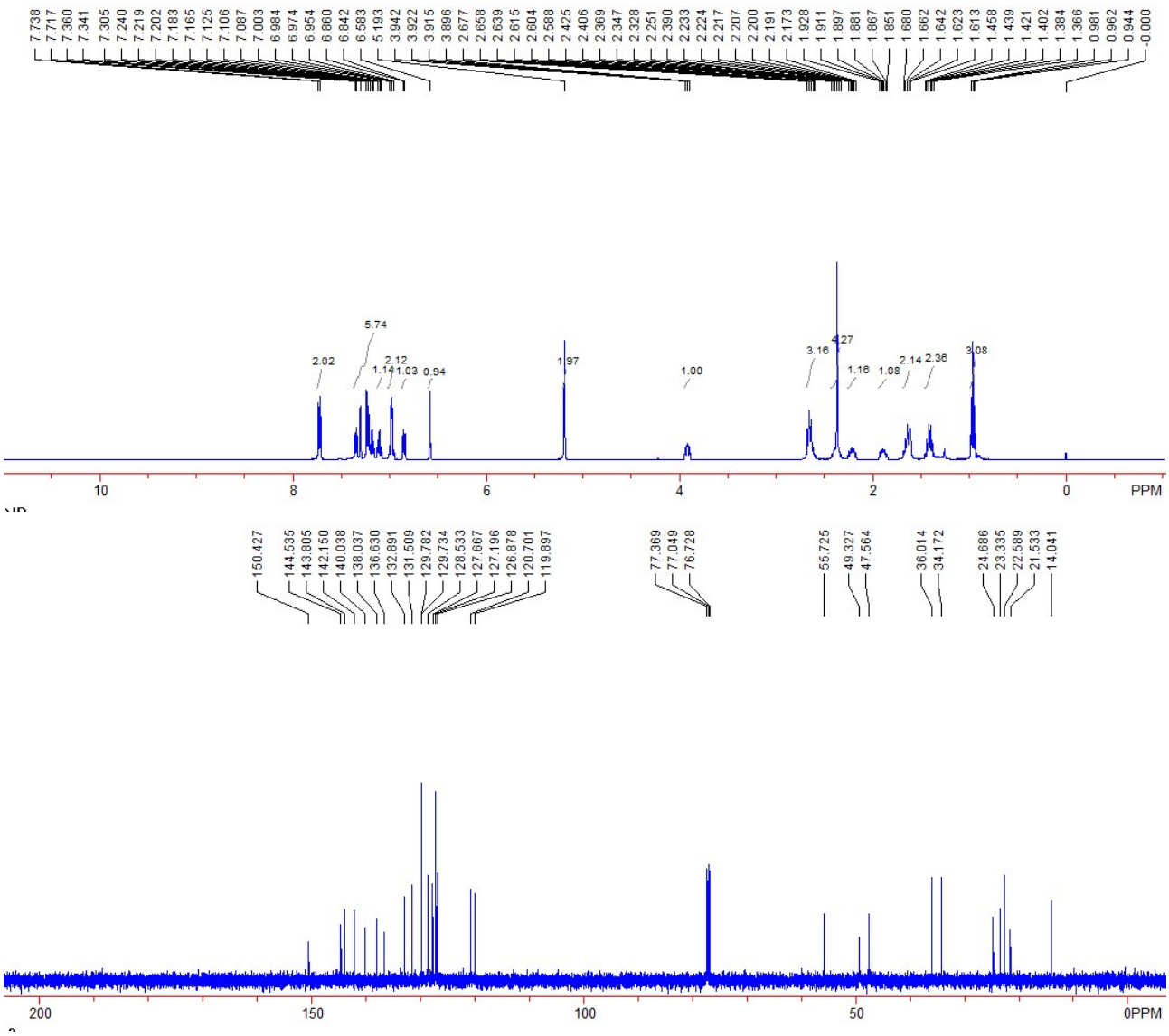
Compound 3c: A white solid. 67 mg, 74% yield. m.p. 92-97 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 0.99 (t, *J* = 7.2 Hz, 3H), 1.63-1.74 (m, 2H), 1.85-1.94 (m, 1H), 2.17-2.26 (m, 1H), 2.37 (s, 3H), 2.32-2.44 (m, 1H), 2.58-2.70 (m, 1H), 2.64 (t, *J* = 7.6 Hz, 2H), 3.92 (dd, *J* = 8.0 Hz, *J* = 10.8 Hz, 1H), 5.20 (s, 2H), 6.58 (s, 1H), 6.85 (d, *J* = 7.6 Hz, 1H), 7.95-7.01 (m, 2H), 7.08-7.14 (m, 1H), 7.16-7.26 (m, 3H), 7.31 (s, 1H), 7.36 (d, *J* = 7.6 Hz, 1H), 7.73 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 14.0, 21.5, 23.3, 24.7, 25.0, 38.4, 47.6, 49.3, 55.7, 119.9, 120.6, 120.7, 126.9, 127.2, 127.7, 128.5, 129.7, 129.8, 131.5, 132.9, 136.6, 138.1, 139.8, 142.1, 143.8, 144.5, 150.4. IR (neat) ν 2958, 2928, 2870, 1711, 1595, 1474, 1354, 1220, 1163, 1089, 1039, 758, 668 cm^{-1}. HRMS (EI) Calcd. for $[C_{29}H_{30}NO_2S]$ $[M+H]^+$ requires 456.1992, found 456.1987.

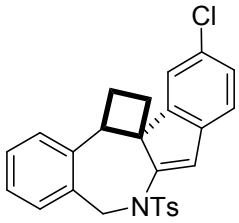






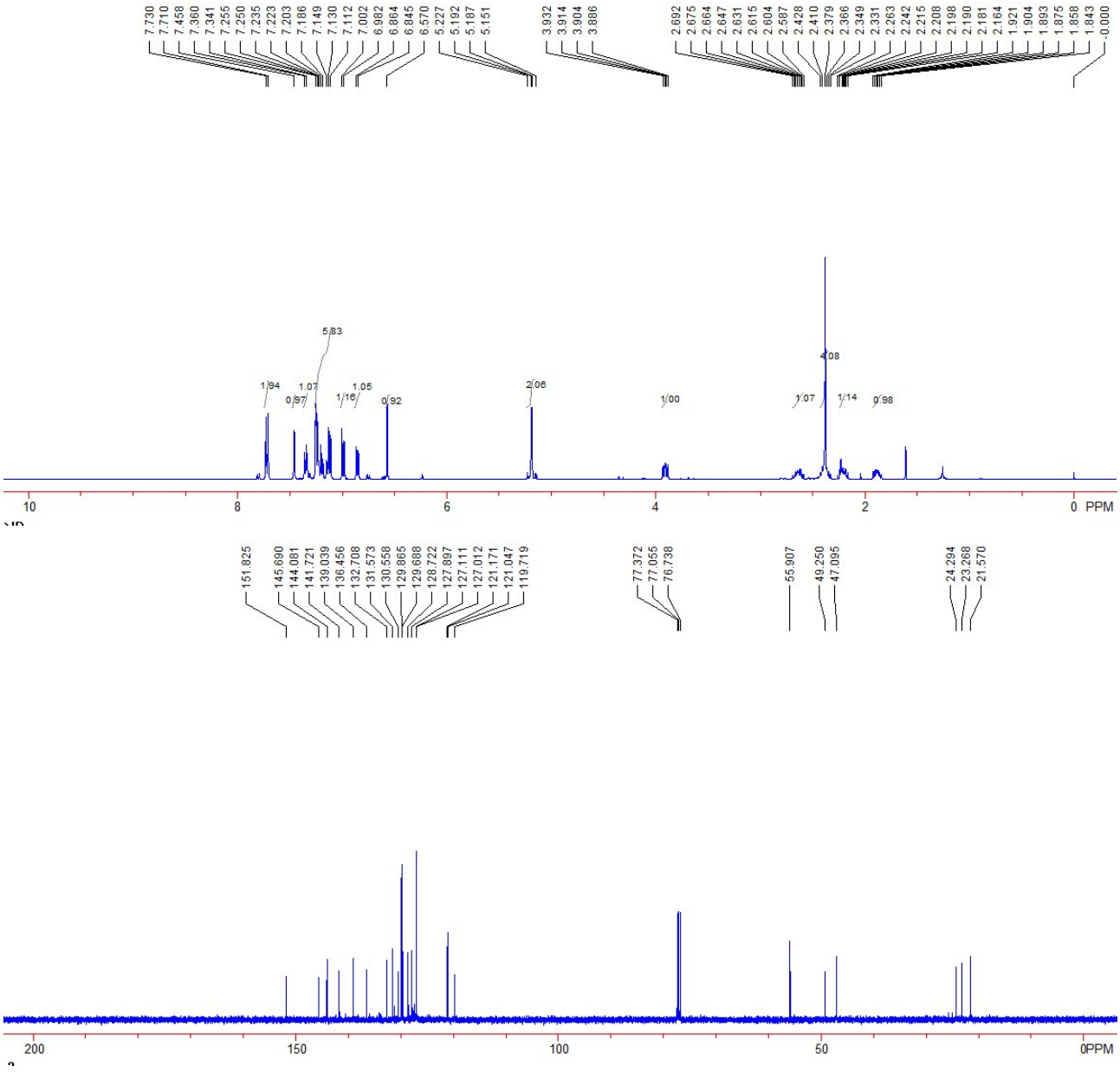
Compound 3d: A white solid. 66 mg, 70% yield. m.p. 77-81 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 0.96 (t, *J* = 7.2 Hz, 3H), 1.36-1.47 (m, 2H), 1.59-1.69 (m, 2H), 1.83-1.93 (m, 1H), 2.16-2.27 (m, 1H), 2.38 (s, 3H), 2.32-2.44 (m, 1H), 2.68 (t, *J* = 6.6 Hz, 2H), 2.60-2.70 (m, 1H), 3.92 (dd, *J* = 7.2 Hz, *J* = 10.8 Hz, 1H), 5.19 (s, 2H), 6.59 (s, 1H), 6.85 (d, *J* = 7.2 Hz, 1H), 6.94-7.01 (m, 2H), 7.08-7.13 (m, 1H), 7.16-7.37 (m, 5H), 7.73 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 14.0, 21.5, 22.6, 23.3, 24.7, 34.2, 36.0, 47.6, 49.3, 55.7, 119.9, 120.7, 126.9, 127.2, 127.7, 128.5, 129.7, 129.8, 131.5, 132.9, 136.6, 138.0, 140.0, 142.2, 143.8, 144.5, 150.4. IR (neat) ν 2954, 2927, 2856, 1712, 1596, 1563, 1474, 1352, 1184, 1163, 1039, 813, 757, 665 cm^{-1}. HRMS (EI) Calcd. for $[C_{30}H_{32}NO_2S]$ $[M+H]^+$ requires 470.2148, found 470.2142.

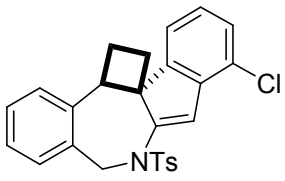




Compound 3e: A white solid. 53 mg, 59% yield. m.p. 179-181 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.84-1.93 (m, 1H), 2.16-2.27 (m, 1H), 2.38 (s, 3H), 2.32-2.44 (m, 1H), 2.58-2.70 (m, 1H), 3.91 (dd, *J* = 7.2 Hz, *J* = 11.2 Hz, 1H), 5.17 (d, *J* = 14.0 Hz, 1H), 5.21 (d, *J* = 14.0 Hz, 1H), 6.57 (s, 1H), 6.85 (d, *J* = 7.6 Hz, 1H), 6.99 (d, *J* = 8.0 Hz, 1H), 7.10-7.26 (m, 5H), 7.35 (d, *J* = 7.6 Hz, 1H), 7.46 (s, 1H), 7.72 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 21.6, 23.3, 24.2, 47.0, 49.2, 55.9, 118.4, 119.7, 121.5, 124.0, 127.1, 127.9, 128.7, 129.7, 129.8, 129.9, 131.6, 132.7, 136.4, 139.5, 141.7, 144.1, 145.7, 152.1. IR (neat) ν 2954, 2924, 2853, 1587, 1562, 1462, 1354, 1341,

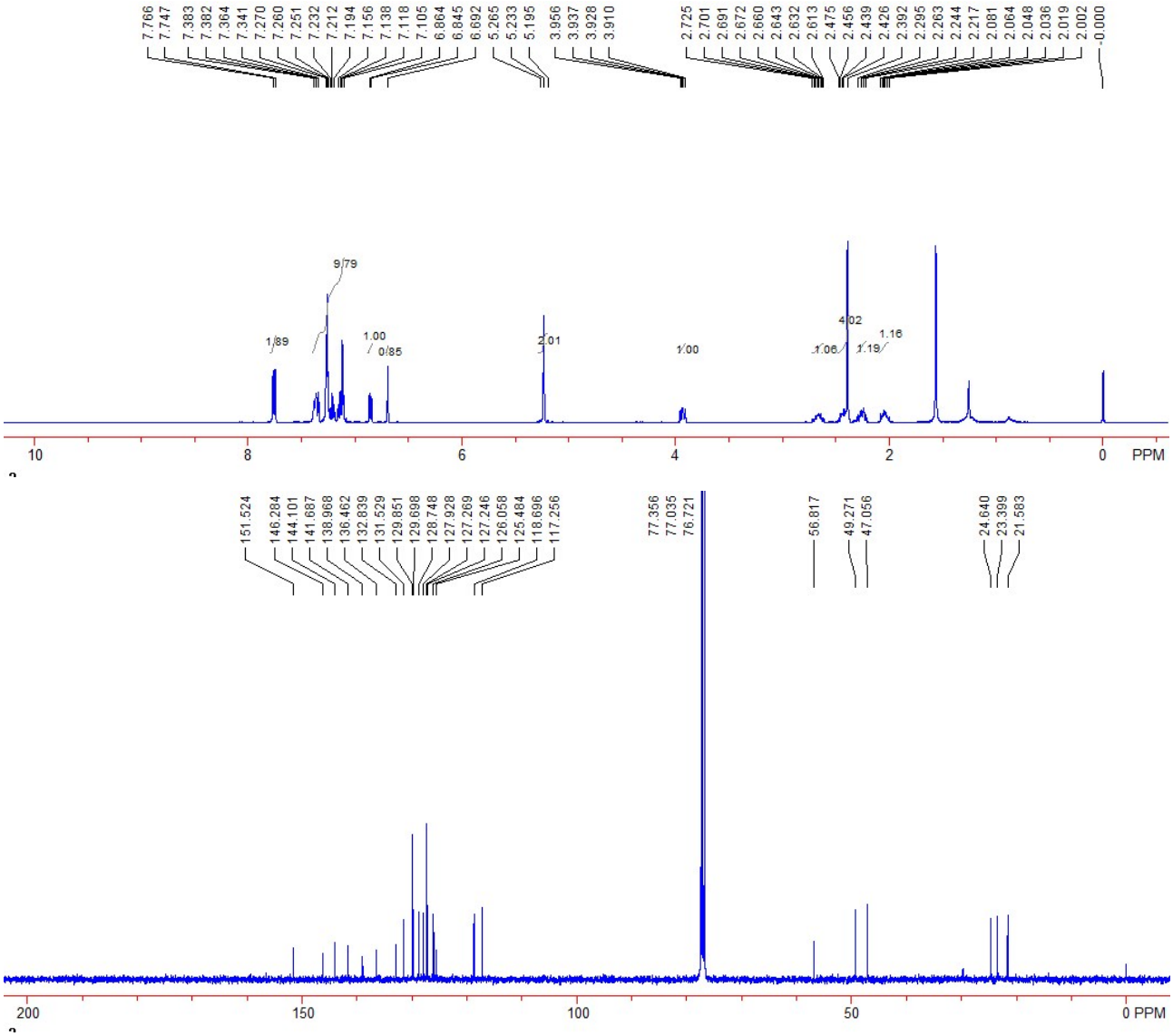
1161, 1089, 1039, 892, 737, 666 cm^{-1}. HRMS (EI) Calcd. for $[C_{26}H_{23}ClNO_2S]$ $[M+H]^+$ requires 448.1133, found 448.1142.

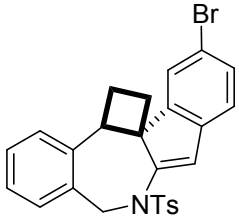




Compound 3f: A white solid. 53 mg, 59% yield. m.p. 191-194 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.99-2.09 (m, 1H), 2.21-2.30 (m, 1H), 2.39 (s, 3H), 2.38-2.48 (m, 1H), 2.61-2.73 (m, 1H), 3.93 (dd, *J* = 7.6 Hz, *J* = 11.2 Hz, 1H), 5.21 (d, *J* = 12.8 Hz, 1H), 5.25 (d, *J* = 12.8 Hz, 1H), 6.69 (s, 1H), 6.85 (d, *J* = 7.6 Hz, 1H), 7.10-7.39 (m, 9H), 7.76 (d, *J* = 7.6 Hz, 2H). ^{13}C NMR (100 MHz,

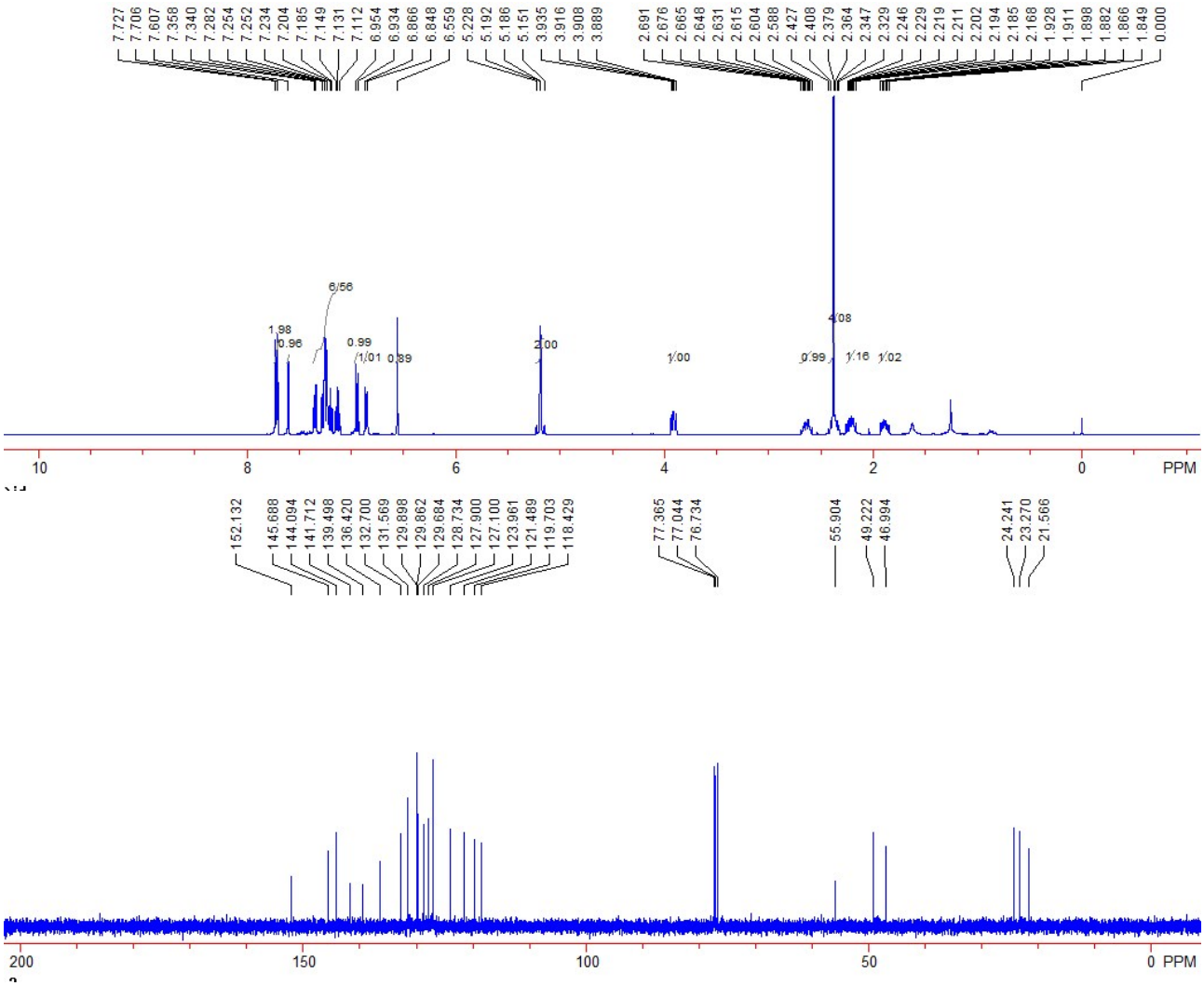
$CDCl_3$, TMS) δ 21.6, 23.4, 24.6, 47.1, 49.3, 56.8, 117.3, 118.7, 125.5, 126.1, 127.2, 127.3, 127.9, 128.7, 129.7, 129.7, 129.9, 131.5, 132.8, 136.5, 139.0, 141.7, 144.1, 146.3, 151.5. IR (neat) ν 2956, 2925, 2860, 1705, 1560, 1455, 1353, 1307, 1163, 1039, 760, 710, 656 cm^{-1}. HRMS (EI) Calcd. for $[C_{26}H_{23}ClNO_2S]$ $[M+H]^+$ requires 448.1133, found 448.1131.

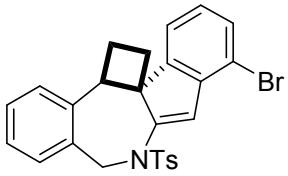




Compound 3g: A white solid. 64 mg, 65% yield. m.p. 176-178 °C. ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 1.84-1.94 (m, 1H), 2.16-2.26 (m, 1H), 2.38 (s, 3H), 2.32-2.44 (m, 1H), 2.58-2.71 (m, 1H),

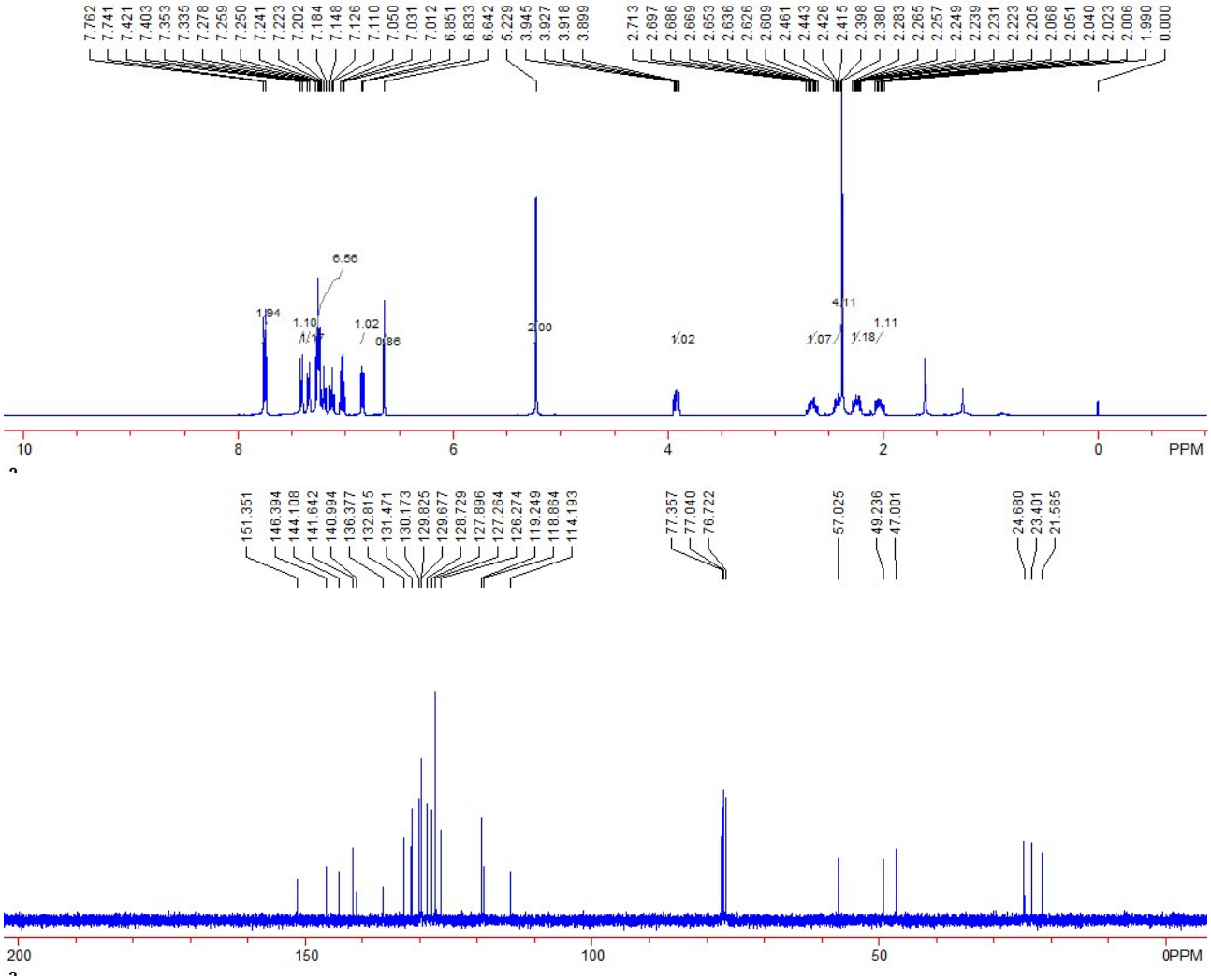
3.91 (dd, J = 7.6 Hz, J = 10.8 Hz, 1H), 5.17 (d, J = 14.0 Hz, 1H), 5.21 (d, J = 14.0 Hz, 1H), 6.56 (s, 1H), 6.86 (d, J = 7.2 Hz, 1H), 6.94 (d, J = 8.0 Hz, 1H), 7.10-7.37 (m, 6H), 7.61 (s, 1H), 7.72 (d, J = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 21.6, 23.3, 24.2, 47.0, 49.2, 55.9, 118.4, 119.7, 121.5, 124.0, 127.1, 127.9, 128.7, 129.7, 129.8, 129.9, 131.6, 132.7, 136.4, 139.5, 141.7, 144.1, 145.7, 152.1. IR (neat) ν 2963, 2930, 2871, 1712, 1585, 1460, 1353, 1161, 1089, 1039, 887, 758, 665 cm^{-1}. HRMS (EI) Calcd. for $[C_{26}H_{23}BrNO_2S]$ $[M+H]^+$ requires 492.0627, found 492.0646.

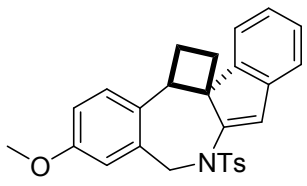




Compound 3h: A white solid. 59 mg, 60% yield. m.p. 193-196 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.98-2.08 (m, 1H), 2.20-2.29 (m, 1H), 2.38 (s, 3H), 2.37-2.47 (m, 1H), 2.60-2.72 (m, 1H), 3.92 (dd, J = 7.2 Hz, J = 10.8 Hz, 1H), 5.23 (s, 2H), 6.64 (s, 1H), 6.84 (d, J = 7.2 Hz, 1H), 7.00-

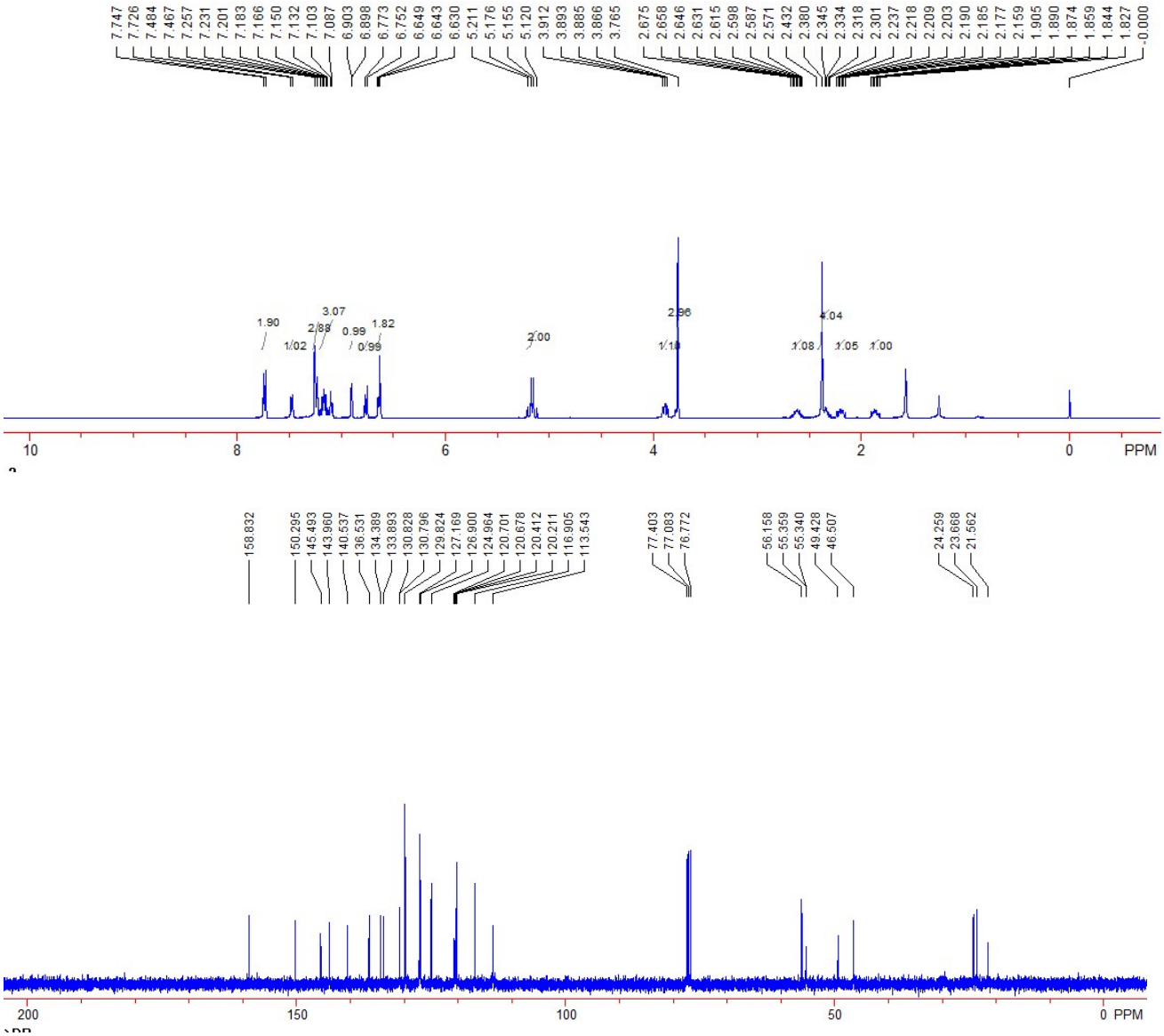
7.29 (m, 6H), 7.34 (d, J = 7.2 Hz, 1H), 7.41 (d, J = 7.2 Hz, 1H), 7.75 (d, J = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 21.6, 23.4, 24.7, 47.0, 49.2, 57.0, 114.2, 118.9, 119.2, 126.3, 127.3, 127.9, 128.7, 129.7, 129.8, 130.2, 131.5, 132.8, 136.4, 141.0, 141.6, 144.1, 146.4, 151.4. IR (neat) ν 2956, 2923, 2849, 1712, 1576, 1491, 1353, 1296, 1163, 886, 758, 685 cm^{-1}. HRMS (EI) Calcd. for $[C_{26}H_{23}BrNO_2S]$ $[M+H]^+$ requires 492.0627, found 492.0633.

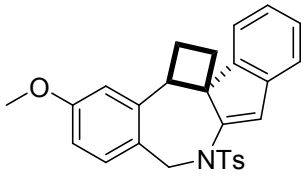




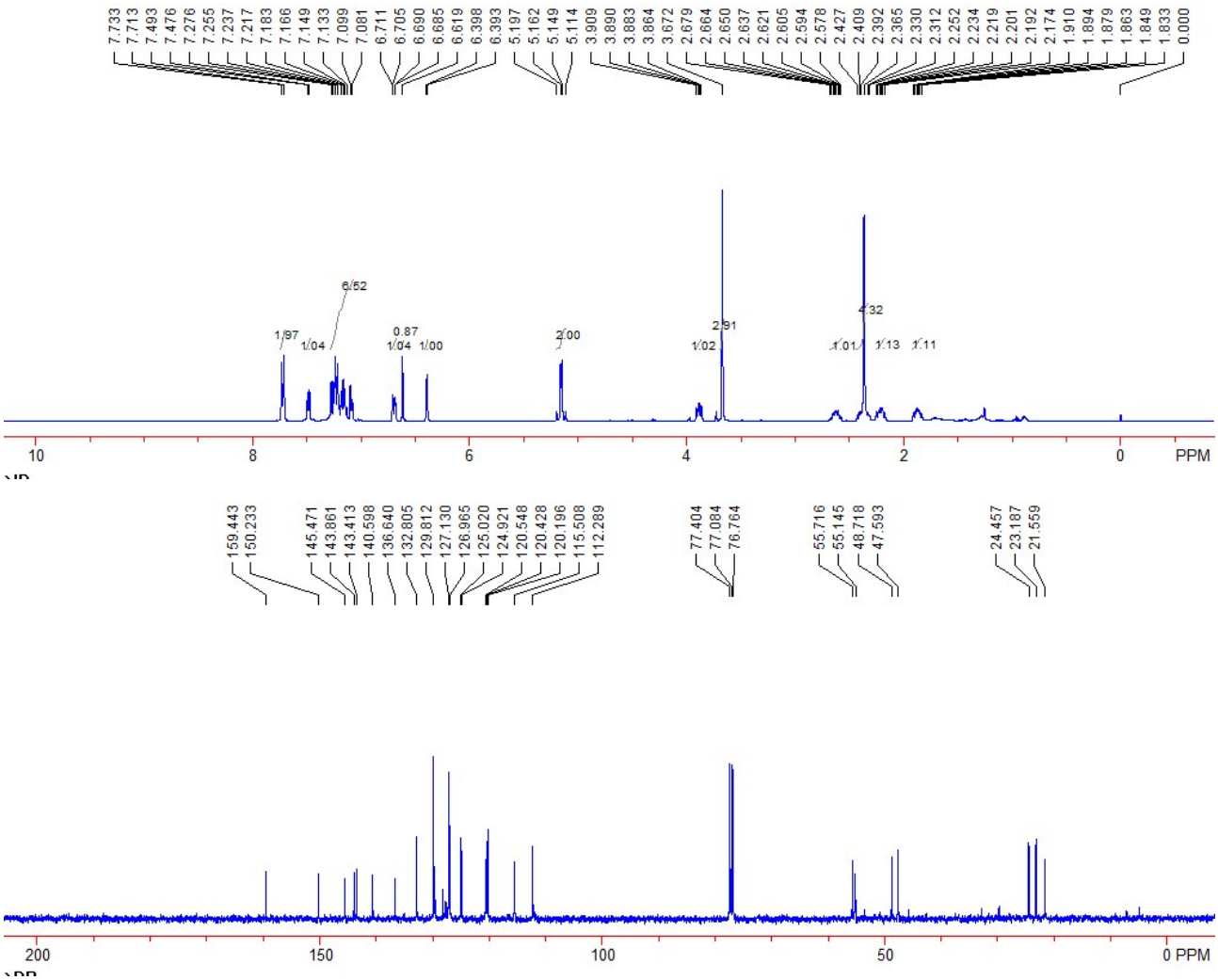
Compound 3i: A white solid. 68 mg, 77% yield. m.p. 209-212 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.83-1.91 (m, 1H), 2.15-2.24 (m, 1H), 2.38 (s, 3H), 2.29-2.44 (m, 1H), 2.56-2.68 (m, 1H), 3.77 (s, 3H), 3.89 (dd, J = 7.6 Hz, J = 10.8 Hz, 1H), 5.14 (d, J = 14.0 Hz, 1H), 5.20 (d, J = 14.0 Hz,

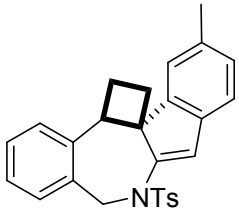
1H), 6.62-6.65 (m, 1H), 6.76 (d, J = 8.4 Hz, 1H), 6.89-6.91 (m, 1H), 7.08-7.21 (m, 3H), 7.22-7.26 (m, 2H), 7.47 (d, J = 6.8 Hz, 1H), 7.73 (d, J = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 21.7, 23.7, 24.3, 46.5, 49.4, 55.3, 55.4, 56.2, 113.5, 116.9, 120.2, 120.4, 120.6, 120.7, 125.0, 126.9, 127.2, 129.8, 130.8, 133.9, 134.4, 136.5, 140.5, 144.0, 145.5, 150.3, 158.8. IR (neat) ν 2955, 2925, 2852, 1607, 1503, 1466, 1350, 1162, 1089, 1037, 814, 749, 665 cm^{-1}. HRMS (EI) Calcd. for $[C_{27}H_{26}NO_3S]$ $[M+H]^+$ requires 444.1628, found 444.1627.



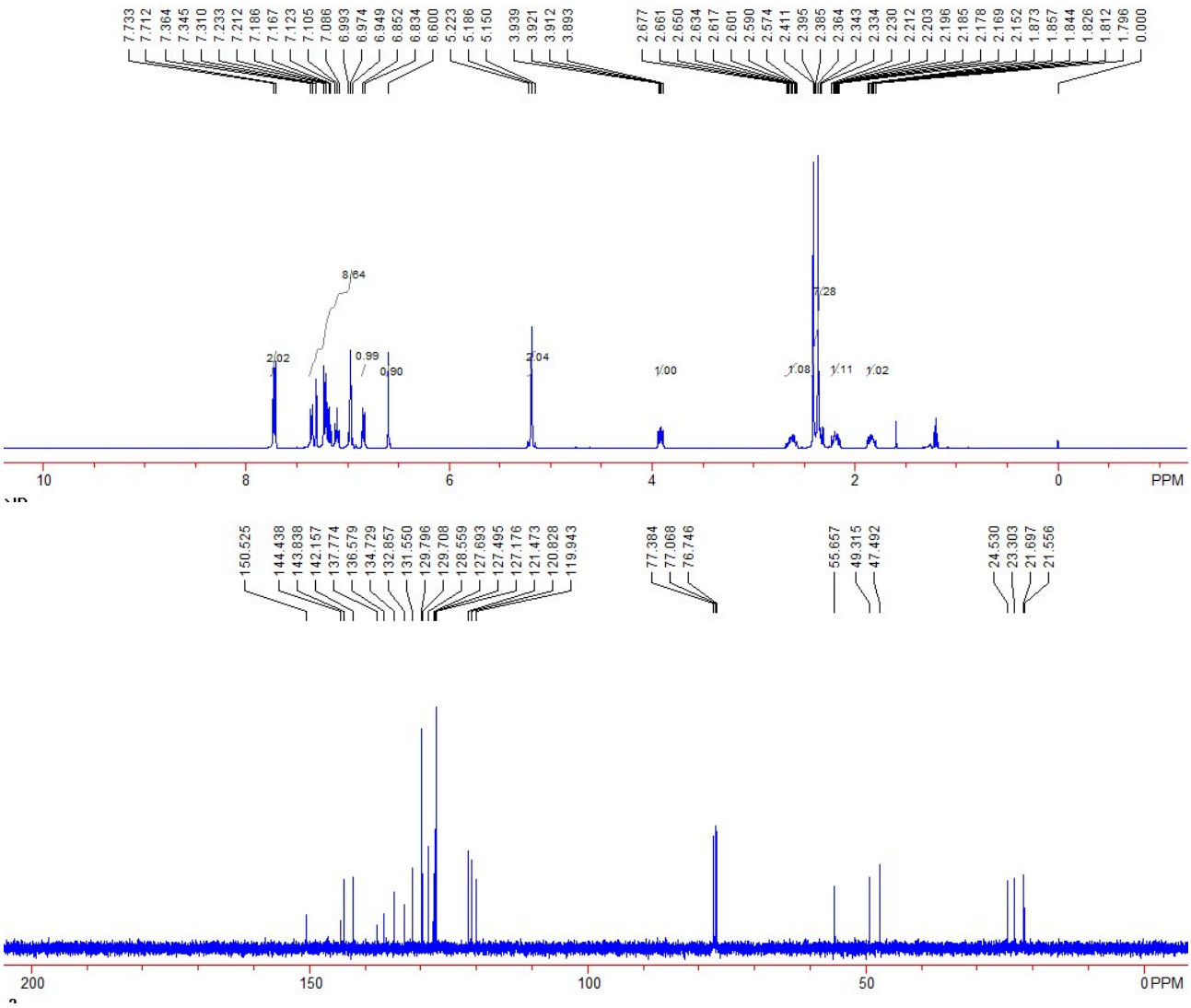


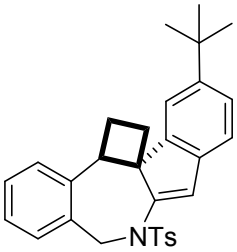
Compound 3j: A white solid. 68 mg, 77% yield. m.p. 210-213 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.82-1.91 (m, 1H), 2.16-2.26 (m, 1H), 2.37 (s, 3H), 2.32-2.43 (m, 1H), 2.57-2.69 (m, 1H), 3.89 (dd, *J* = 7.2 Hz, *J* = 10.0 Hz, 1H), 5.13 (d, *J* = 14.0 Hz, 1H), 5.18 (d, *J* = 14.0 Hz, 1H), 6.38-6.40 (m, 1H), 6.62 (s, 1H), 6.67-6.72 (m, 1H), 7.07-7.28 (m, 6H), 7.48 (d, *J* = 6.8 Hz, 1H), 7.72 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 21.6, 23.2, 24.4, 47.6, 48.7, 55.1, 55.7, 112.3, 115.5, 120.2, 120.4, 124.9, 125.0, 127.0, 127.1, 129.8, 132.8, 136.6, 140.6, 143.4, 143.9, 145.5, 150.2, 159.4. IR (neat) ν 2959, 2937, 2863, 1712, 1568, 1466, 1348, 1269, 1163, 1089, 1037, 881, 750, 670 cm^{-1}. HRMS (EI) Calcd. for $[C_{27}H_{26}NO_3S]$ $[M+H]^+$ requires 444.1628, found 444.1626.



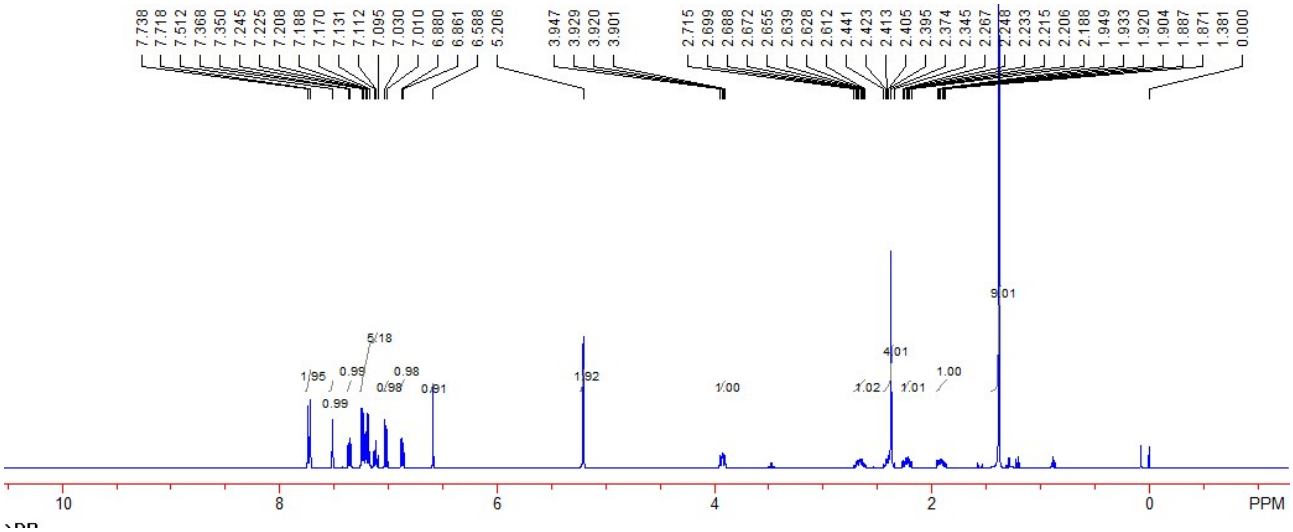


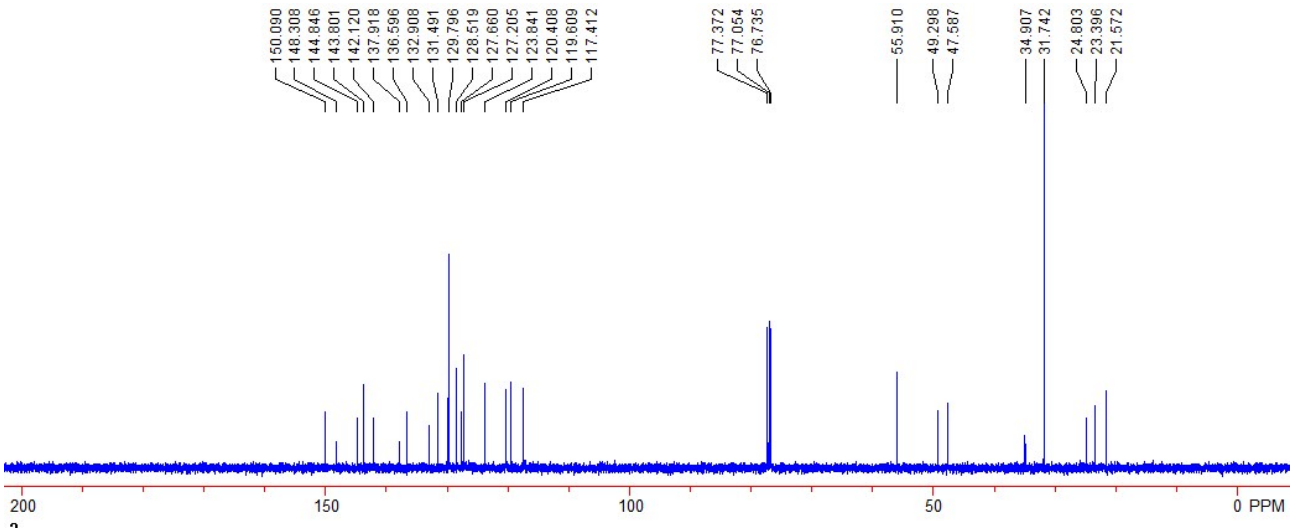
Compound 3k: A white solid. 61 mg, 71% yield. m.p. 184-187 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.80-1.88 (m, 1H), 2.14-2.24 (m, 1H), 2.36 (s, 3H), 2.41 (s, 3H), 2.33-2.42 (m, 1H), 2.57-2.68 (m, 1H), 3.92 (dd, *J* = 7.2 Hz, *J* = 10.8 Hz, 1H), 5.17 (d, *J* = 14.4 Hz, 1H), 5.21 (d, *J* = 14.4 Hz, 1H), 6.60 (s, 1H), 6.84 (d, *J* = 7.2 Hz, 1H), 6.94-7.37 (m, 8H), 7.72 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 21.6, 21.7, 23.3, 24.5, 47.5, 49.3, 55.7, 119.9, 120.8, 121.5, 127.2, 127.5, 127.7, 128.6, 129.7, 129.8, 131.6, 132.9, 134.7, 136.6, 137.7, 142.2, 143.8, 144.4, 150.5. IR (neat) ν 2972, 2923, 2853, 1711, 1597, 1474, 1339, 1160, 1089, 1037, 756, 730, 667 cm^{-1}. HRMS (EI) Calcd. for $[C_{27}H_{26}NO_2S]$ $[M+H]^+$ requires 428.1679, found 428.1675.

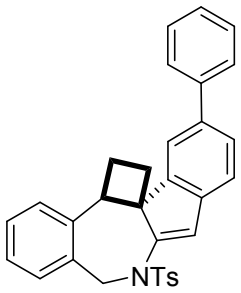




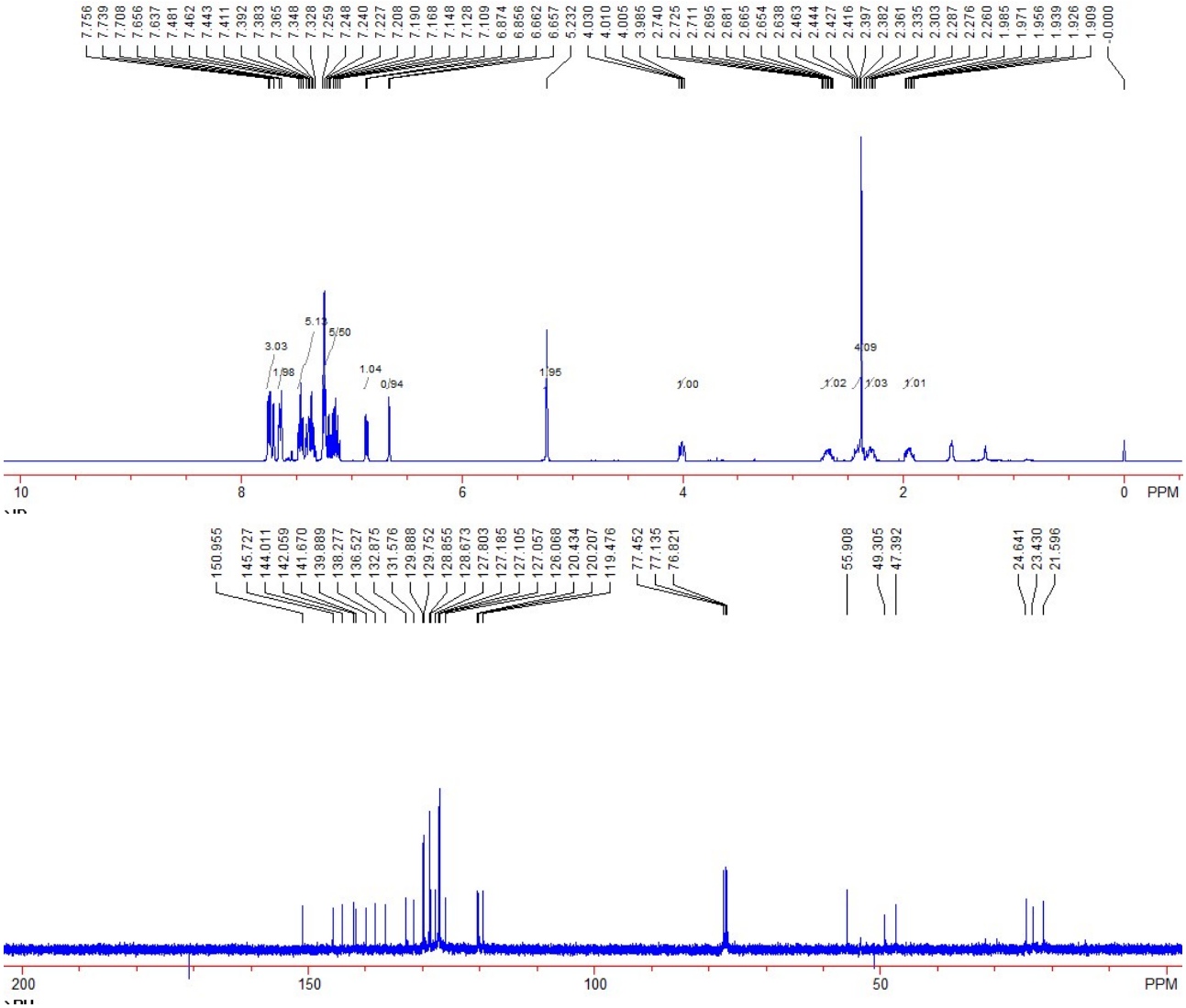
Compound 3l: A white solid. 70 mg, 75% yield. m.p. 99-103 ^{o}C (this is a highly viscous oily product and it contains trace of petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.38 (s, 9H), 1.86-1.96 (m, 1H), 2.18-2.28 (m, 1H), 2.37 (s, 3H), 2.34-2.45 (m, 1H), 2.60-2.72 (m, 1H), 3.92 (dd, *J* = 7.2 Hz, *J* = 10.8 Hz, 1H), 5.21 (s, 2H), 6.59 (s, 1H), 6.87 (d, *J* = 7.6 Hz, 1H), 7.02 (d, *J* = 8.0 Hz, 1H), 7.08-7.25 (m, 5H), 7.36 (d, *J* = 7.2 Hz, 1H), 7.51 (s, 1H), 7.73 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 21.6, 23.4, 24.8, 31.7, 34.9, 47.6, 49.3, 55.9, 117.4, 119.6, 120.4, 123.8, 127.2, 127.7, 128.5, 129.8, 131.5, 132.9, 136.6, 137.9, 142.1, 143.8, 144.8 148.3, 150.1. IR (neat) ν 2961, 2925, 2866, 1710, 1596, 1480, 1354, 1184, 1162, 1089, 1039, 814, 742, 667 cm^{-1}. HRMS (EI) Calcd. for $[C_{30}H_{32}NO_2S]$ $[M+H]^+$ requires 470.2148, found 470.2142.

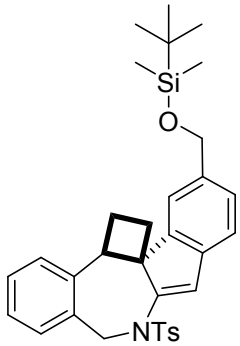






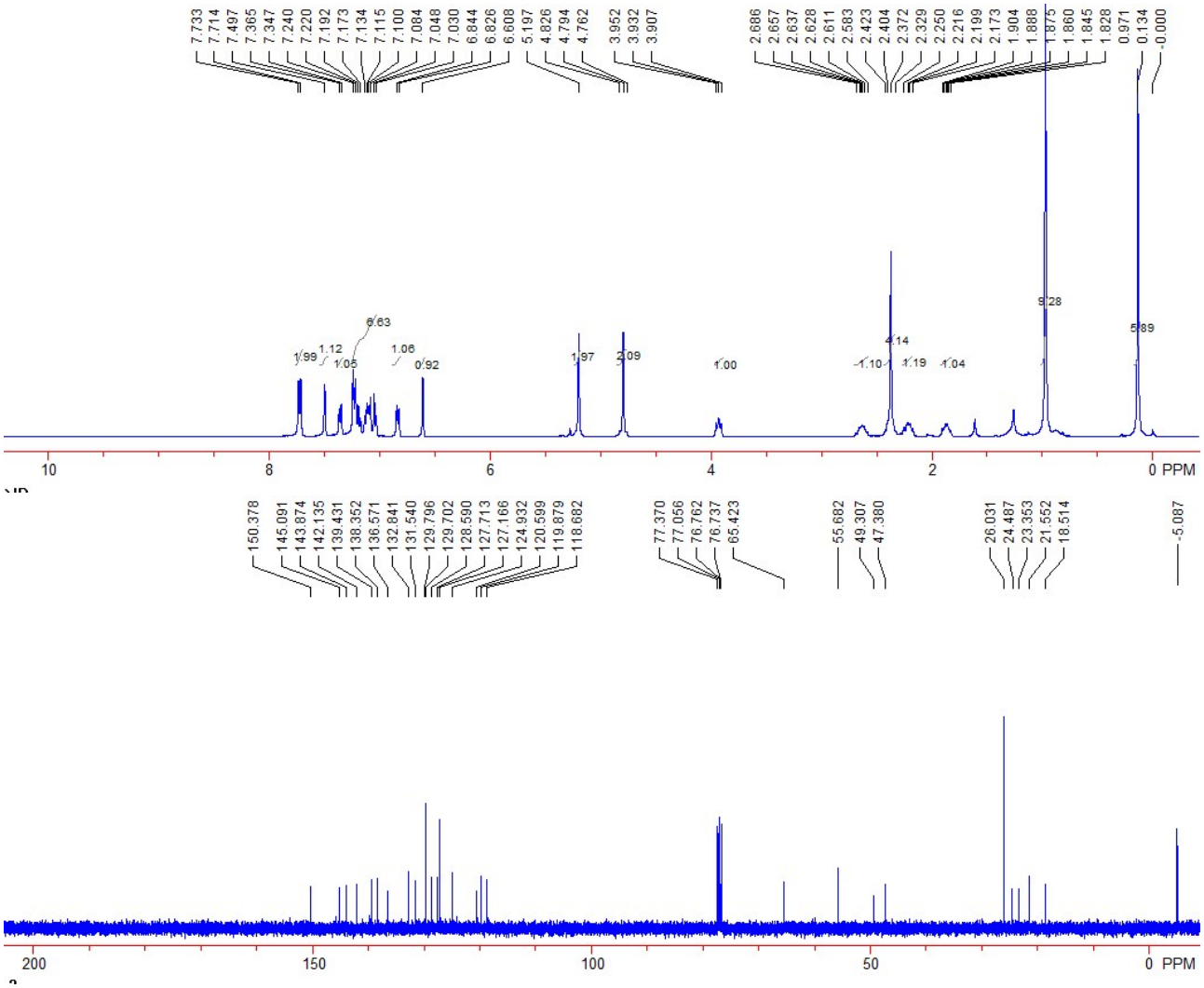
Compound 3m: A white solid. 67 mg, 69% yield. m.p. 116-120 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.90-1.99 (m, 1H), 2.25-2.37 (m, 1H), 2.40 (s, 3H), 2.38-2.47 (m, 1H), 2.63-2.75 (m, 1H), 4.01 (dd, *J* = 8.0 Hz, *J* = 10.0 Hz, 1H), 5.23 (s, 2H), 6.65-6.67 (m, 1H), 6.87 (d, *J* = 7.2 Hz, 1H), 7.10-7.27 (m, 5H), 7.32-7.49 (m, 5H), 7.65 (d, *J* = 7.6 Hz, 2H), 7.70-7.76 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 21.6, 23.4, 24.6, 47.4, 49.3, 55.9, 119.5, 120.2, 120.4, 126.1, 127.0, 127.1, 127.2, 127.8, 128.7, 128.9, 129.8, 129.9, 131.6, 132.9, 136.5, 138.3, 139.9, 141.7, 142.1, 144.0, 145.7, 151.0. IR (neat) ν 2956, 2926, 2853, 1712, 1594, 1470, 1355, 1162, 1089, 1039, 759, 669 cm^{-1}. HRMS (EI) Calcd. for $[C_{32}H_{28}NO_2S]$ $[M+H]^+$ requires 490.1835, found 490.1835.

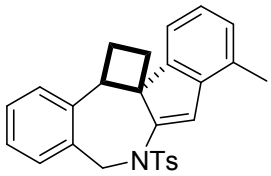




Compound 3n: A white solid. 83 mg, 75% yield. m.p. 133-137 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 0.13 (s, 6H), 0.97 (s, 9H), 1.82-1.91 (m, 1H), 2.16-2.26 (m, 1H), 2.37 (s, 3H), 2.32-2.43 (m, 1H), 2.57-2.69 (m, 1H), 3.94 (t, *J* = 8.0 Hz, 1H), 4.79 (t, *J* = 13.2 Hz, 2H), 5.20 (s, 2H), 6.61 (s, 1H), 6.83 (d, *J* = 7.2 Hz, 1H), 7.02-7.25 (m, 6H), 7.36 (d, *J* = 7.6 Hz, 1H), 7.50 (s, 1H), 7.72 (d, *J* = 7.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ -5.1, 18.5, 21.6, 23.4, 24.5, 26.0, 47.4, 49.3,

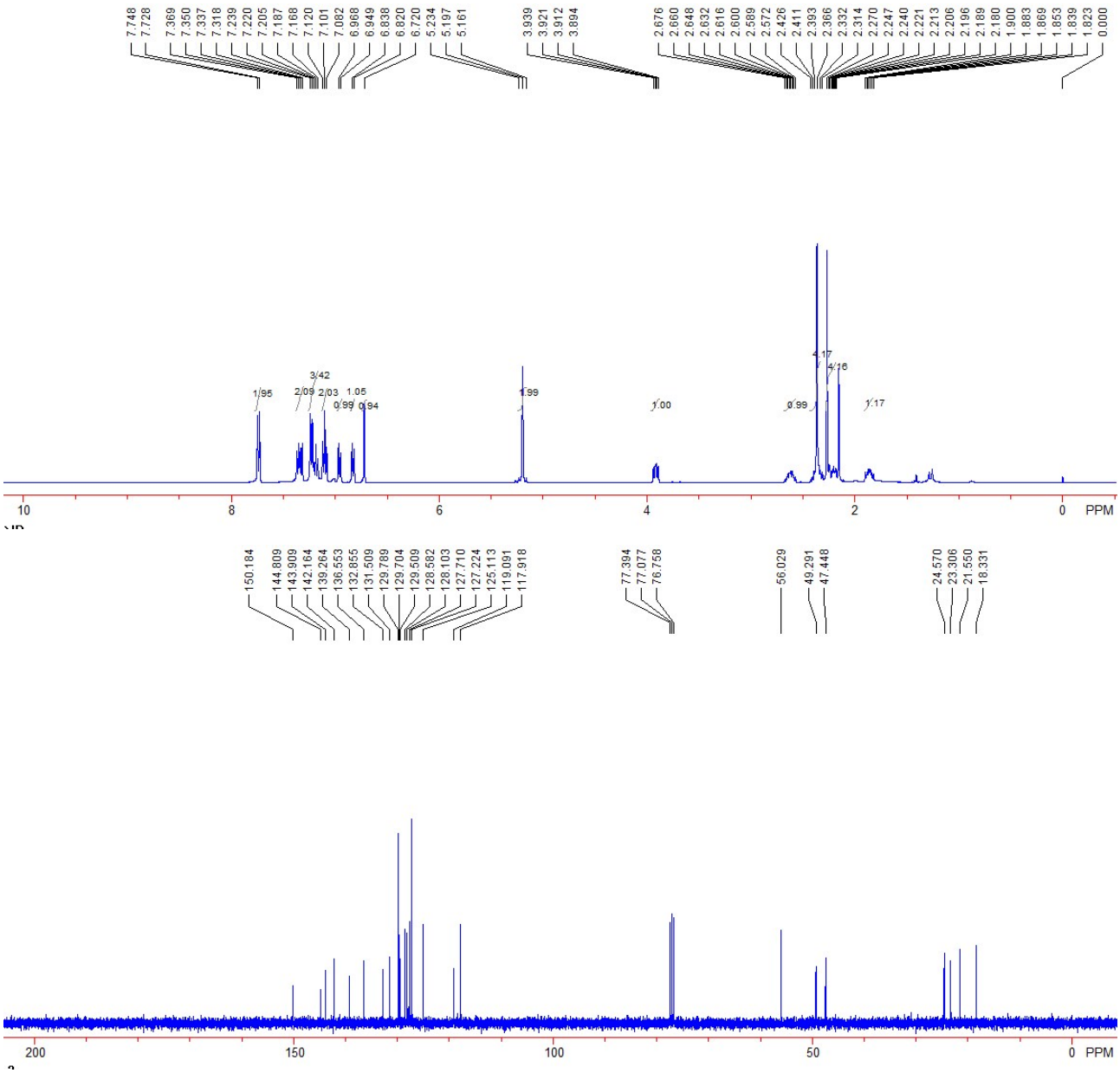
55.7, 65.4, 118.7, 119.9, 120.6, 124.9, 127.2, 127.7, 128.6, 129.7, 129.8, 131.5, 132.8, 136.6, 138.4, 139.4, 142.1, 143.9, 145.1, 150.4. IR (neat) ν 2952, 2927, 2855, 1708, 1594, 1471, 1354, 1254, 1164, 1088, 837, 757, 668 cm^{-1}. HRMS (EI) Calcd. for $[C_{33}H_{40}NO_3SSi]$ $[M+H]^+$ requires 558.2493, found 558.2495.

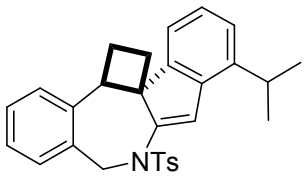




Compound 3o: A white solid. 59 mg, 69% yield. m.p. 184-187 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.81-1.91 (m, 1H), 2.17-2.28 (m, 1H), 2.27 (s, 3H), 2.37 (s, 3H), 2.31-2.43 (m, 1H), 2.56-2.68 (m, 1H), 3.92 (dd, *J* = 7.2 Hz, *J* = 10.8 Hz, 1H), 5.18 (d, *J* = 14.4 Hz, 1H), 5.22 (d, *J* = 14.4 Hz, 1H), 6.72 (s, 1H), 6.83 (d, *J* = 7.2 Hz, 1H), 6.96 (d, *J* = 7.6 Hz, 1H), 7.07-7.38 (m, 7H), 7.74 (d,

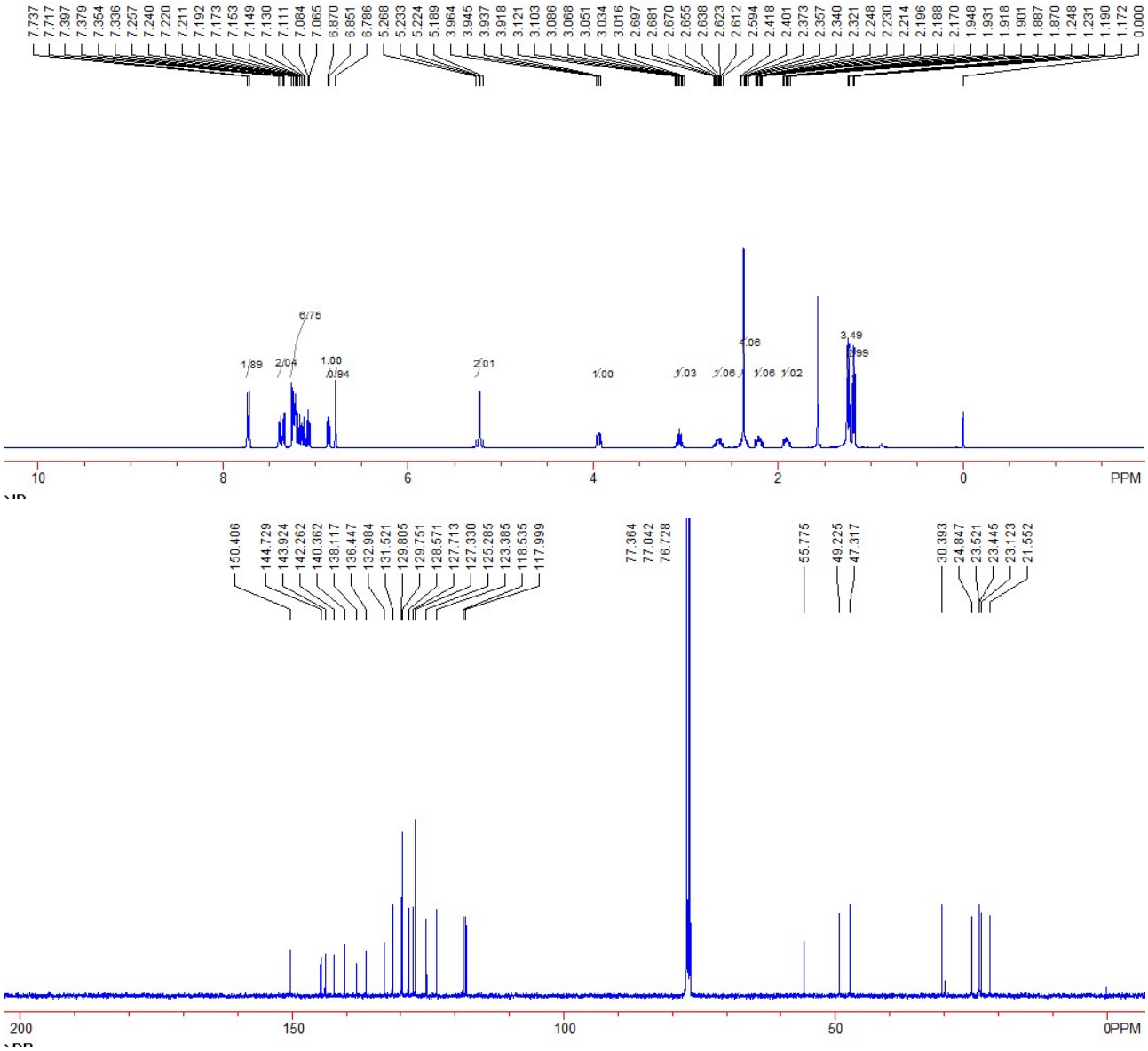
J = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 18.3, 21.6, 23.3, 24.6, 47.4, 49.3, 56.0, 117.9, 119.1, 125.1, 127.2, 127.7, 128.1, 128.6, 129.5, 129.7, 129.8, 131.5, 132.9, 136.6, 139.3, 142.2, 143.9, 144.8, 150.2. IR (neat) ν 2962, 2924, 2853, 1702, 1596, 1454, 1353, 1278, 1163, 1089, 1038, 757,659 cm^{-1}. HRMS (EI) Calcd. for $[C_{27}H_{26}NO_2S]$ $[M+H]^+$ requires 428.1679, found 428.1674.

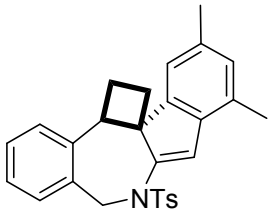




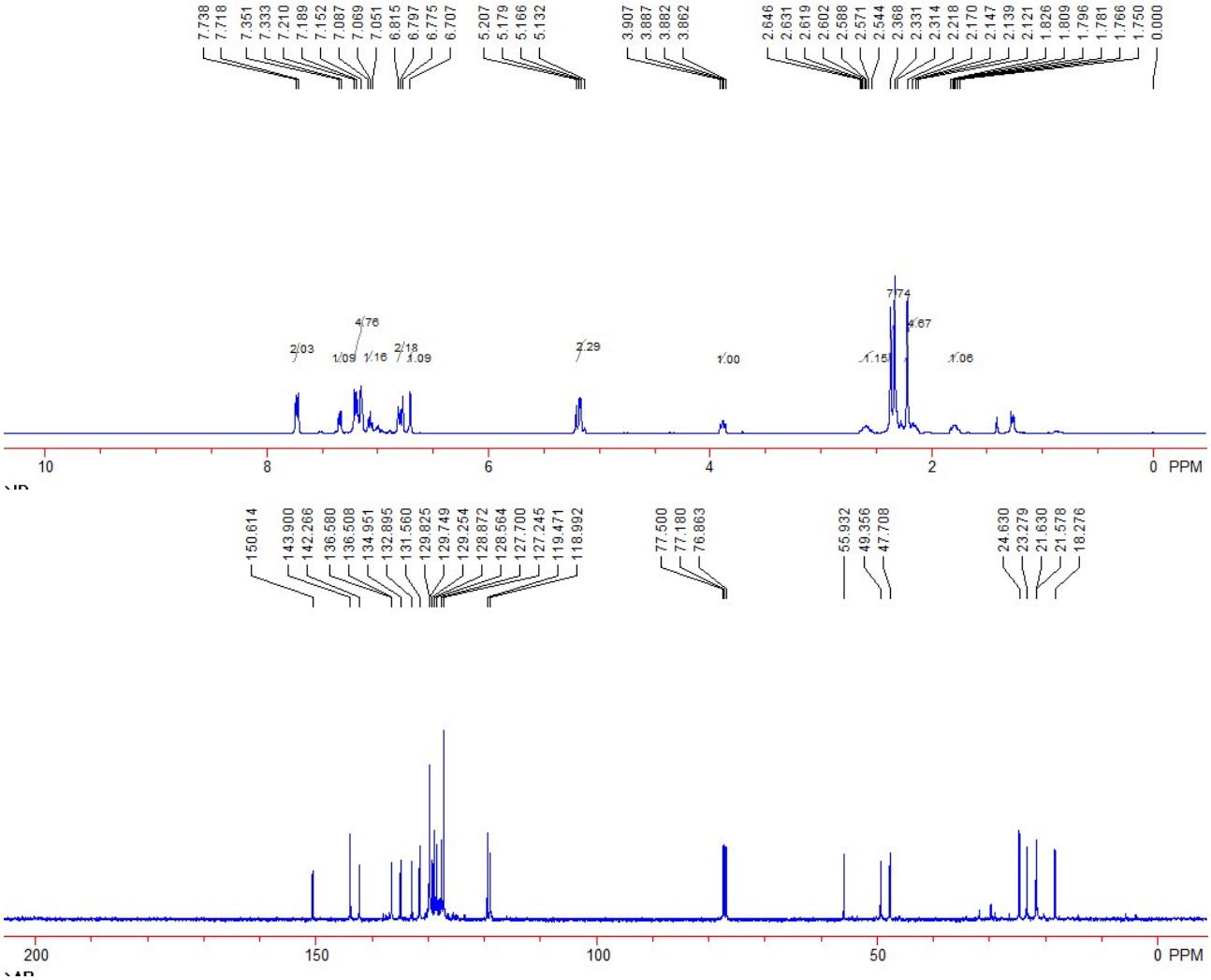
Compound 3p: A white solid. 64 mg, 70% yield. m.p. 195-199 °C. ^{1}H NMR (400 MHz, $CDCl_3$,

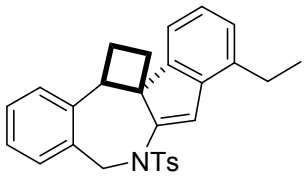
TMS) δ 1.18 (d, *J* = 7.6 Hz, 3H), 1.24 (d, *J* = 6.8 Hz, 3H), 1.88-1.96 (m, 1H), 2.16-2.26 (m, 1H), 2.37 (s, 3H), 2.31-2.43 (m, 1H), 2.58-2.71 (m, 1H), 3.01-3.13 (m, 1H), 3.95 (dd, *J* = 7.6 Hz, *J* = 10.8 Hz, 1H), 5.21 (d, *J* = 14.0 Hz, 1H), 5.25 (d, *J* = 14.0 Hz, 1H), 6.79 (s, 1H), 6.86 (d, *J* = 7.6 Hz, 1H), 7.06-7.27 (m, 6H), 7.34 (d, *J* = 7.2 Hz, 1H), 7.39 (d, *J* = 7.2 Hz, 1H), 7.73 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 21.6, 23.1, 23.4, 23.5, 24.8, 30.4, 47.3, 49.2, 55.8, 118.0, 118.5, 123.4, 125.3, 127.3, 127.7, 128.6, 129.7, 129.8, 131.5, 133.0, 136.4, 138.1, 140.4, 142.3, 143.9, 144.7, 150.4. IR (neat) ν 2959, 2926, 2864, 1716, 1598, 1436, 1352, 1163, 1089, 1039, 757, 713 cm^{-1}. HRMS (EI) Calcd. for $[C_{29}H_{30}NO_2S]$ $[M+H]^+$ requires 456.1992, found 456.1987.



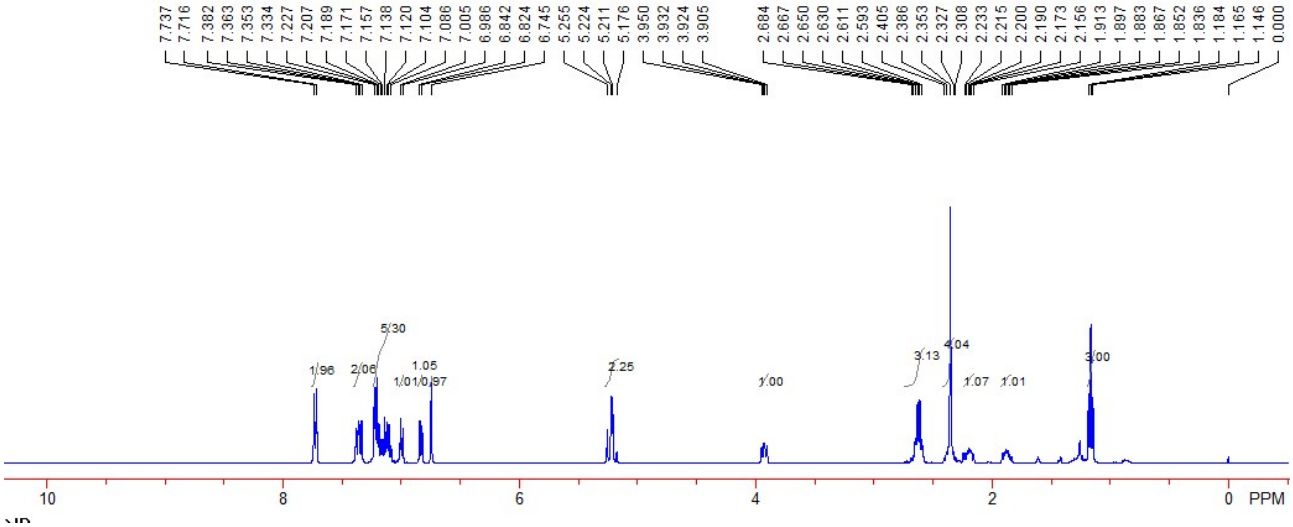


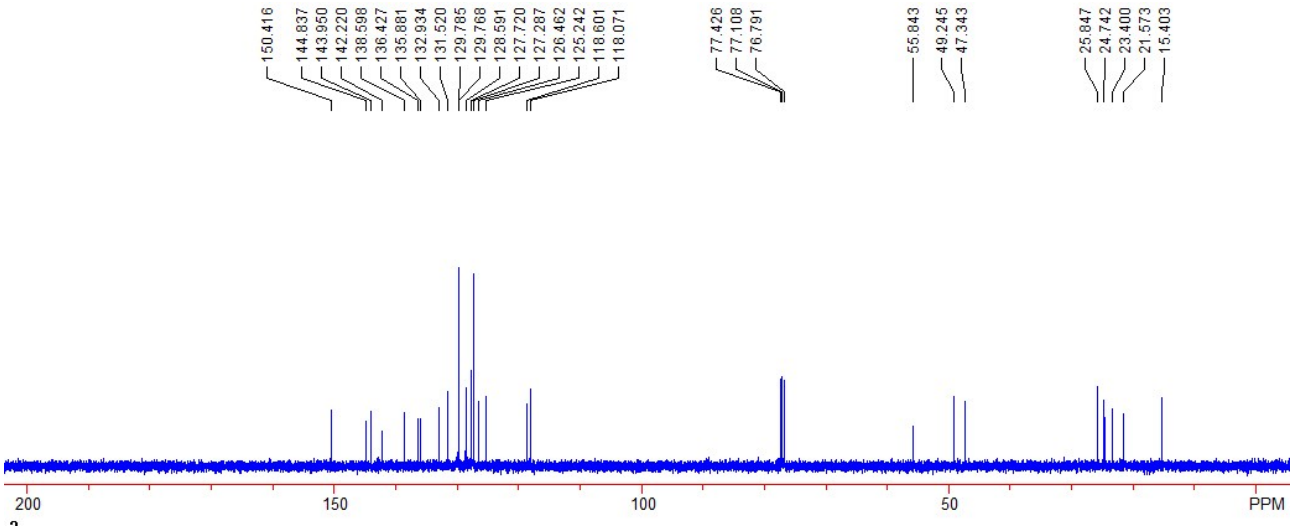
Compound 3q: A white solid. 63 mg, 72% yield. m.p. 106-109 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.74-1.84 (m, 1H), 2.11-2.24 (m, 1H), 2.22 (s, 3H), 2.33 (s, 3H), 2.37 (s, 3H), 2.28-2.38 (m, 1H), 2.53-2.66 (m, 1H), 3.88 (dd, *J* = 8.0 Hz, *J* = 10.0 Hz, 1H), 5.15 (d, *J* = 12.4 Hz, 1H), 5.19 (d, *J* = 12.4 Hz, 1H), 6.71 (s, 1H), 6.77-6.82 (m, 2H), 7.04-7.22 (m, 5H), 7.34 (d, *J* = 7.2 Hz, 1H), 7.73 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 18.3, 21.5, 21.6, 23.3, 24.6, 47.7, 49.4, 55.9, 119.0, 119.5, 127.2, 127.7, 128.6, 129.3, 129.7, 129.8, 131.6, 132.9, 134.9, 136.5, 136.6, 142.3, 143.9, 150.6. IR (neat) ν 2956, 2924, 2849, 1705, 1597, 1470, 1352, 1036, 814, 758, 710, 658 cm^{-1}. HRMS (EI) Calcd. for $[C_{28}H_{28}NO_2S]$ $[M+H]^+$ requires 442.1835, found 442.1834.

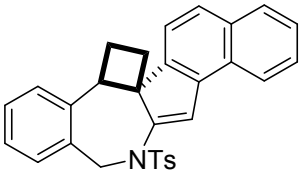




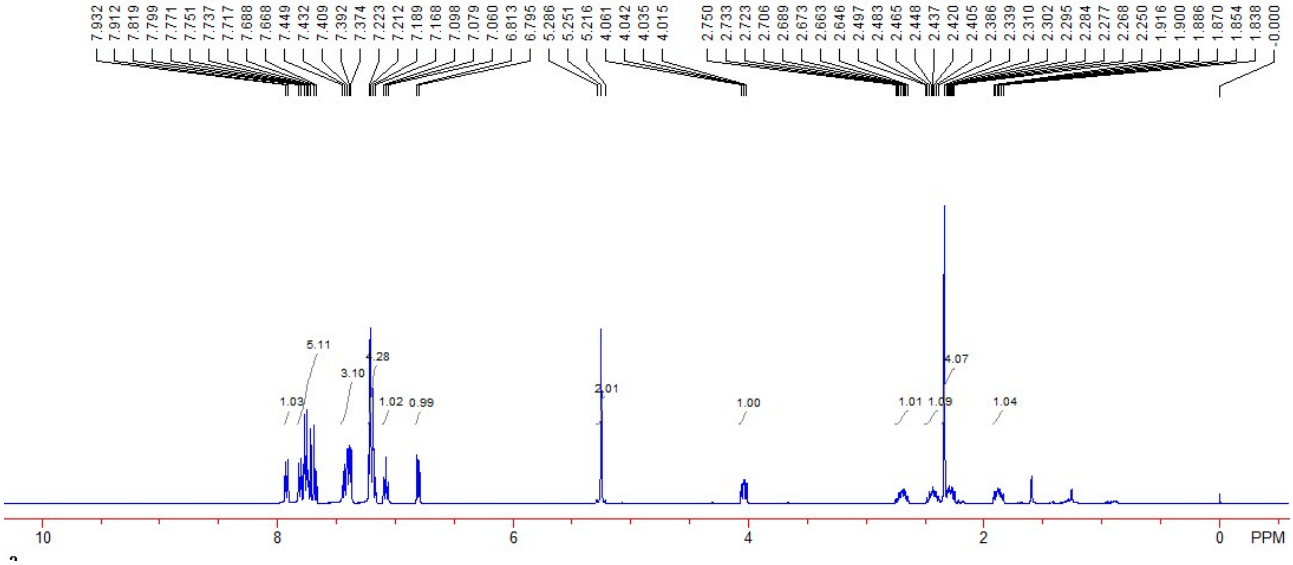
Compound 3r: A white solid. 63 mg, 72% yield. m.p. 194-197 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.17 (d, *J* = 7.2 Hz, 3H), 1.82-1.92 (m, 1H), 2.15-2.26 (m, 1H), 2.36 (s, 3H), 2.30-2.41 (m, 1H), 2.62 (q, *J* = 7.6 Hz, 2H), 2.59-2.70 (m, 1H), 3.93 (dd , *J* = 8.4 Hz, *J* = 9.6 Hz, 1H), 5.19 (d , *J* = 13.2 Hz, 1H), 5.24 (d , *J* = 13.2 Hz, 1H), 6.75 (s, 1H), 6.83 (d, *J* = 6.8 Hz, 1H), 7.00 (d, *J* = 7.6 Hz, 1H), 7.08-7.24 (m, 5H), 7.37 (t, *J* = 7.6 Hz, 2H), 7.73 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 15.4, 21.6, 23.4, 24.7, 25.8, 47.3, 49.2, 55.8, 118.1, 118.6, 125.2, 126.5, 127.3, 127.7, 128.6, 129.7, 129.8, 131.5, 132.9, 136.4, 138.6, 142.2, 144.0, 144.8, 150.4. IR (neat) ν 2962, 2928, 2867, 1712, 1567, 1439, 1352, 1162, 1089, 1039, 813, 757, 713 cm^{-1}. HRMS (EI) Calcd. for $[C_{28}H_{28}NO_2S]$ $[M+H]^+$ requires 442.1835, found 442.1832.

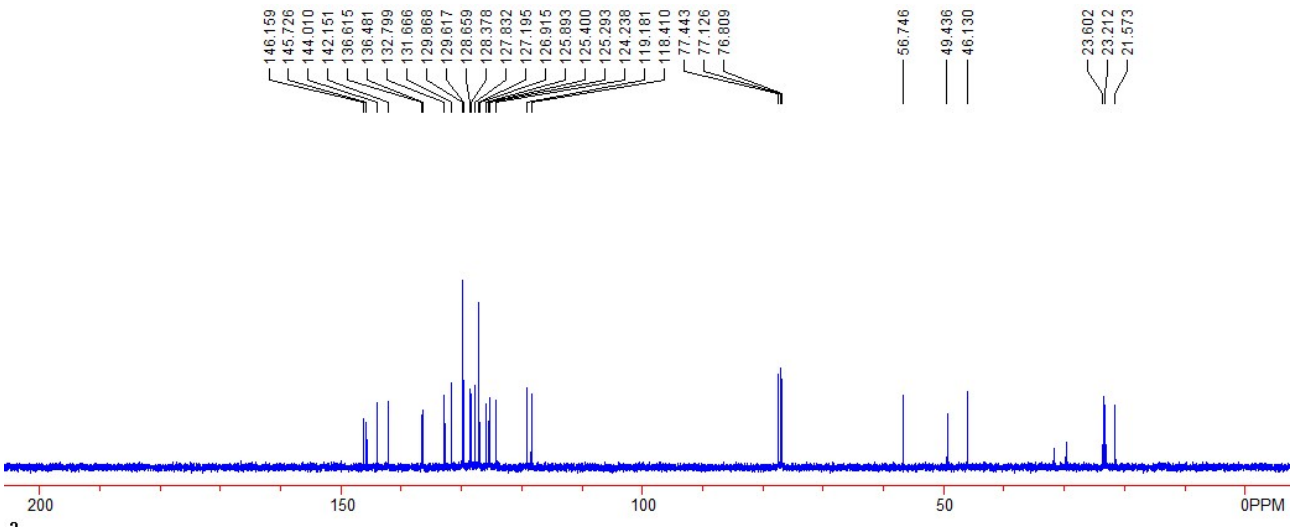


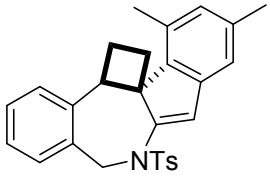




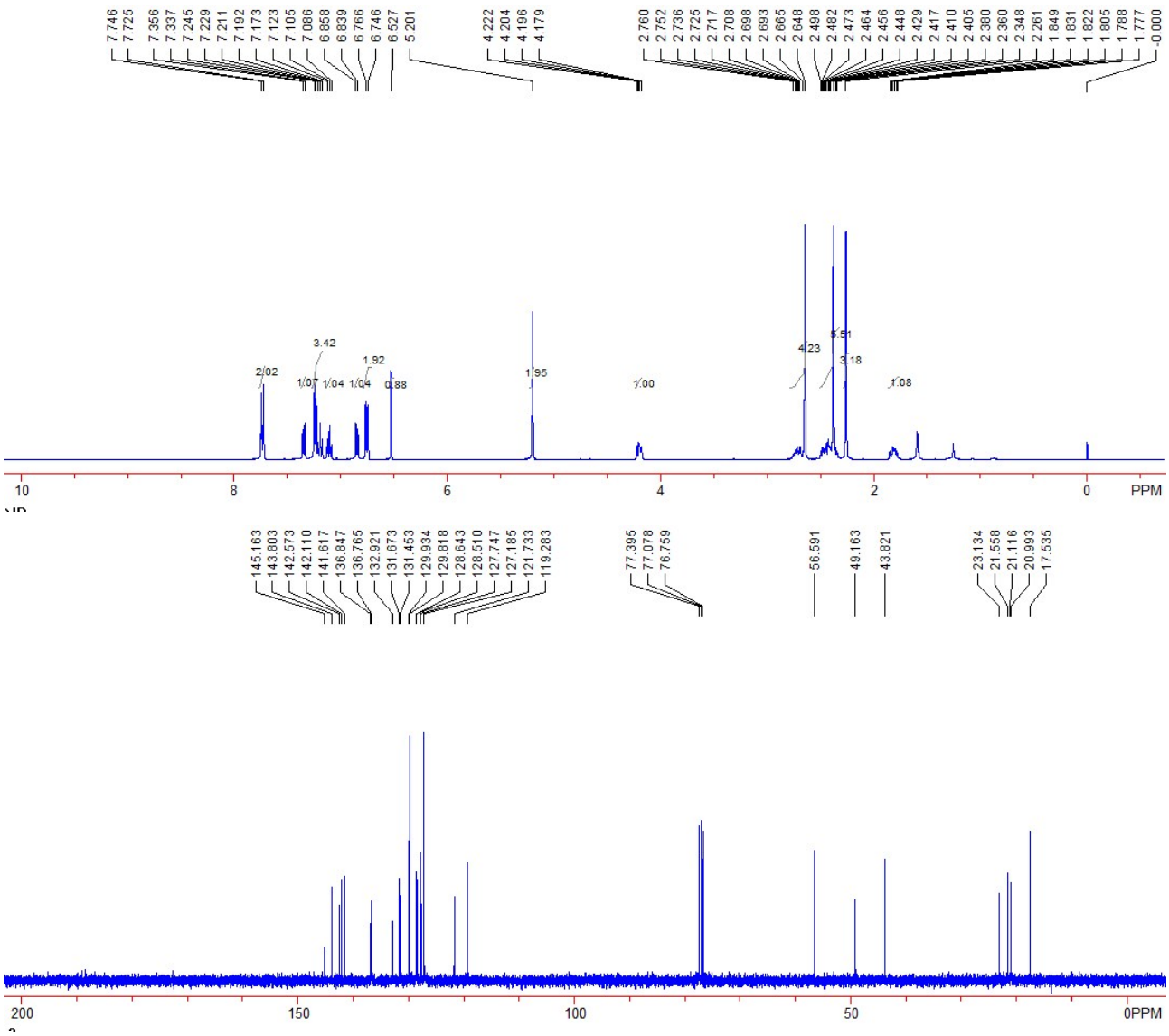
Compound 3s: A white solid. 83 mg, 92% yield. m.p. 121-124 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.83-1.92 (m, 1H), 2.24-2.35 (m, 1H), 2.39 (s, 3H), 2.40-2.50 (m, 1H), 2.64-2.76 (m, 1H), 4.04 (dd, *J* = 7.6 Hz, *J* = 10.4 Hz, 1H), 5.23 (d, *J* = 14.0 Hz, 1H), 5.27 (d, *J* = 14.0 Hz, 1H), 6.80 (s, *J* = 7.6 Hz, 1H), 7.08 (t, *J* = 7.6 Hz, 1H), 7.16-7.23 (m, 4H), 7.37-7.45 (m, 3H), 7.66-7.82 (m, 5H), 7.92 (d, *J* = 8.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 21.6, 23.2, 23.6, 46.1, 49.4, 56.7, 118.4, 119.2, 124.2, 125.3, 125.4, 125.9, 126.9, 127.2, 127.8, 128.4, 128.7, 129.6, 129.9, 131.7, 132.8, 132.9, 136.5, 136.6, 142.2, 144.0, 145.7, 146.2. IR (neat) ν 2956, 2925, 2864, 1711, 1554, 1450, 1352, 1164, 1089, 1039, 812, 755, 717 cm^{-1}. HRMS (EI) Calcd. for $[C_{30}H_{26}NO_2S]$ $[M+H]^+$ requires 464.1679, found 464.1676.

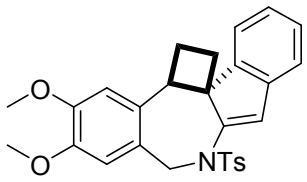






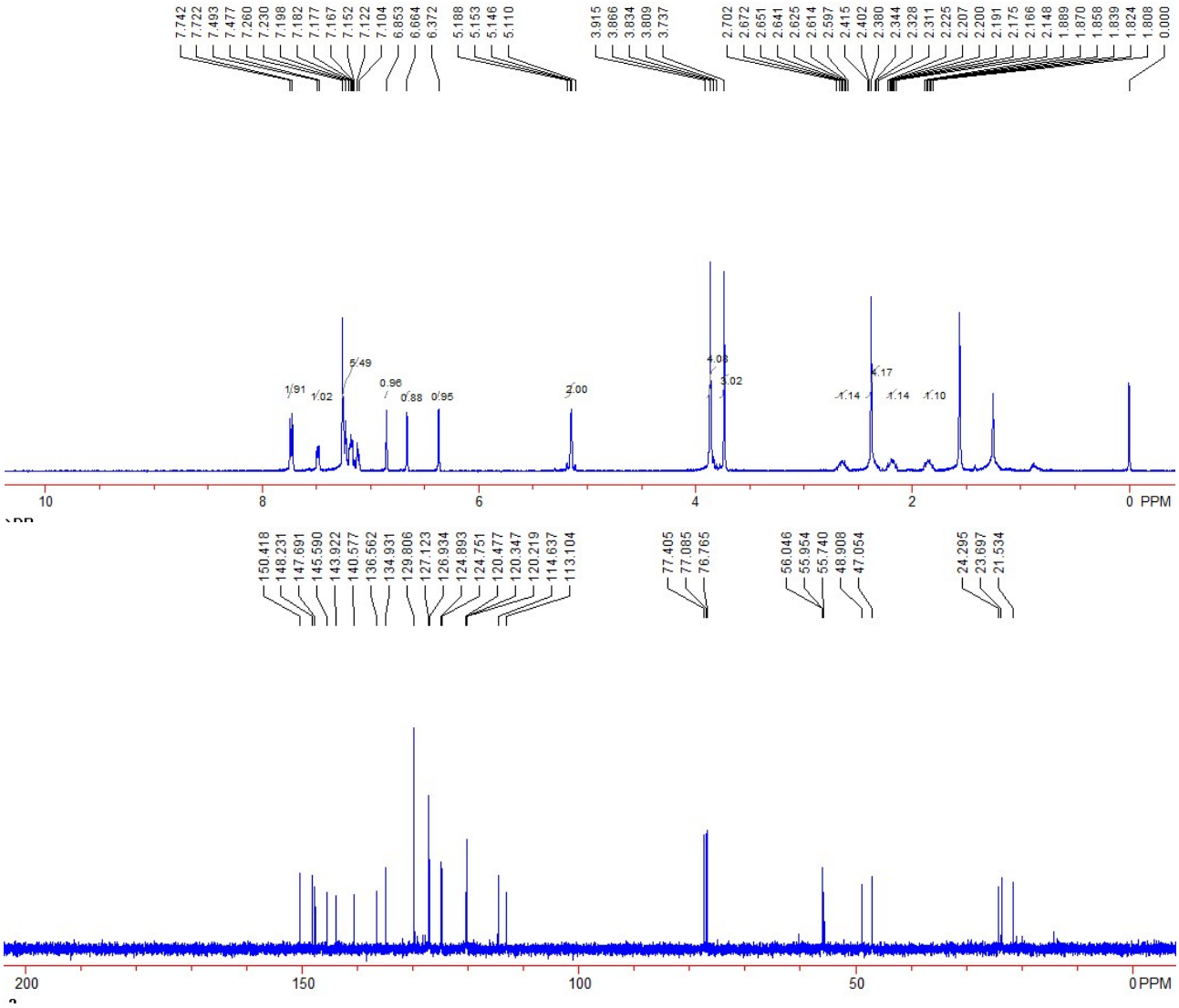
Compound 3t: A white solid. 79 mg, 90% yield. m.p. 116-119 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.75-1.86 (m, 1H), 2.26 (s, 3H), 2.34-2.48 (m, 1H), 2.38 (s, 3H), 2.37-2.51 (m, 1H), 2.65 (s, 3H), 2.64-2.77 (m, 1H), 4.20 (dd, *J* = 7.2 Hz, *J* = 10.4 Hz, 1H), 5.20 (s, 2H), 6.53 (s, 1H), 6.76 (d, *J* = 8.0 Hz, 2H), 6.85 (d, *J* = 7.6 Hz, 1H), 7.08-7.25 (m, 4H), 7.35 (d, *J* = 7.6 Hz, 1H), 7.74 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 17.5, 21.0, 21.1, 21.6, 23.1, 43.8, 49.2, 56.6, 119.3, 121.7, 127.2, 127.7, 128.5, 128.6, 129.8, 129.9, 131.5, 131.7, 132.9, 136.7, 136.8, 141.6, 142.1, 142.6, 143.9, 145.2. IR (neat) ν 2952, 2923, 2860, 1708, 1594, 1465, 1351, 1295, 1163, 1089, 1039, 882, 759, 669 cm^{-1}. HRMS (EI) Calcd. for $[C_{28}H_{28}NO_2S]$ $[M+H]^+$ requires 442.1835, found 442.1832.

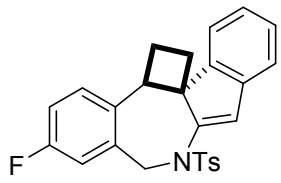




Compound 3u: A white solid. 63 mg, 67% yield. m.p. 92-96 ^{o}C (this is a highly viscous oily product and it contains trace of petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.80-1.90 (m, 1H), 2.14-2.23 (m, 1H), 2.38 (s, 3H), 2.30-2.42 (m, 1H), 2.59-2.71 (m, 1H), 3.74 (s, 3H), 3.87 (s, 3H), 3.80-3.92 (m, 1H), 5.13 (d, J = 14.0 Hz, 1H), 5.17 (d, J = 14.0 Hz, 1H), 6.37 (s, 1H), 6.66 (s, 1H), 6.85 (s, 1H), 7.10-7.27 (m, 5H), 7.49 (d, J = 6.4 Hz, 1H), 7.73 (d, J = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 21.5, 23.7, 24.3, 47.1, 48.9, 55.7, 56.0, 56.1, 113.1, 114.6, 120.2, 120.3, 120.5, 124.8, 124.9, 126.9, 127.1, 129.8, 134.9, 136.6, 140.6, 143.9, 145.6, 147.7, 148.2,

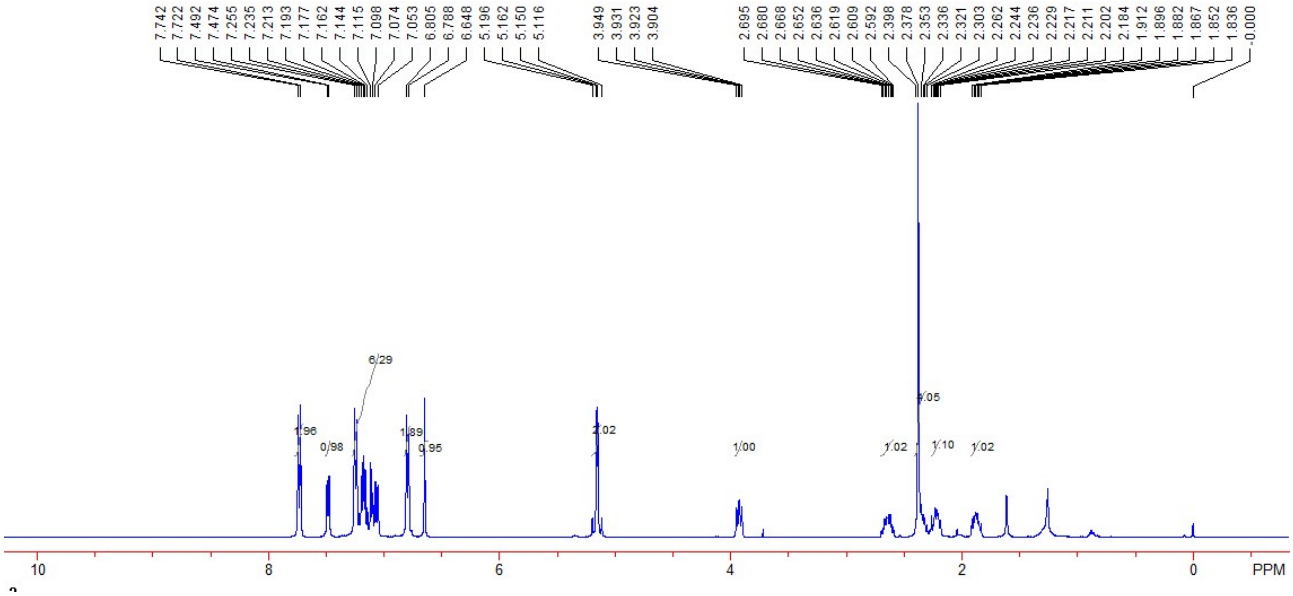
150.4. IR (neat) ν 2972, 2853, 1711, 1597, 1568, 1517, 1465, 1346, 1186, 1161, 1039, 856, 750, 660 cm^{-1}. HRMS (EI) Calcd. for $[C_{28}H_{28}NO_4S]$ $[M+H]^+$ requires 474.1734, found 474.1727.

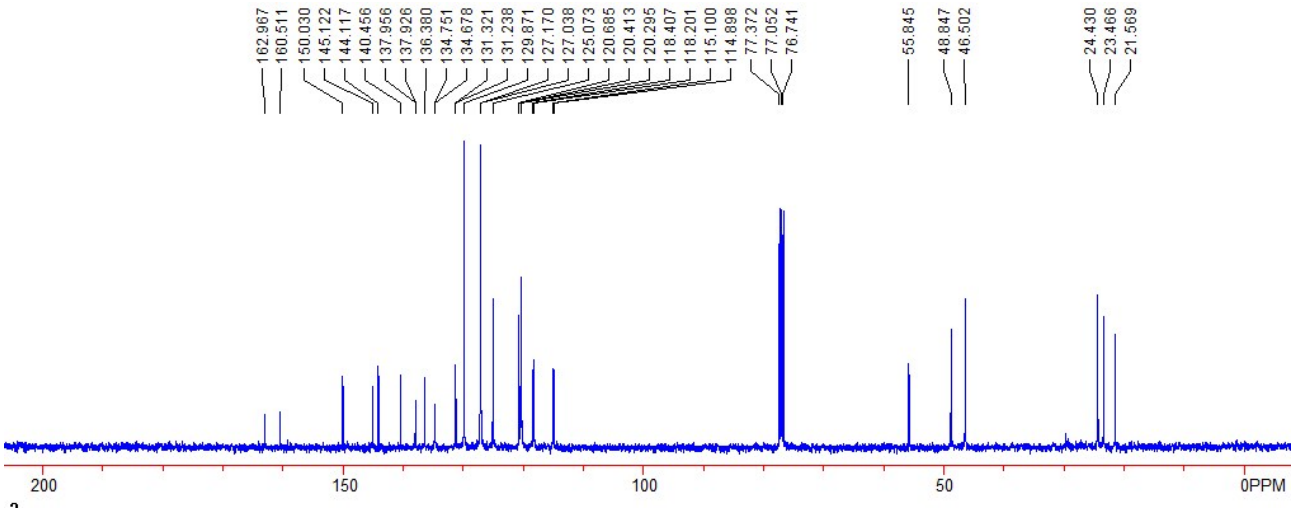


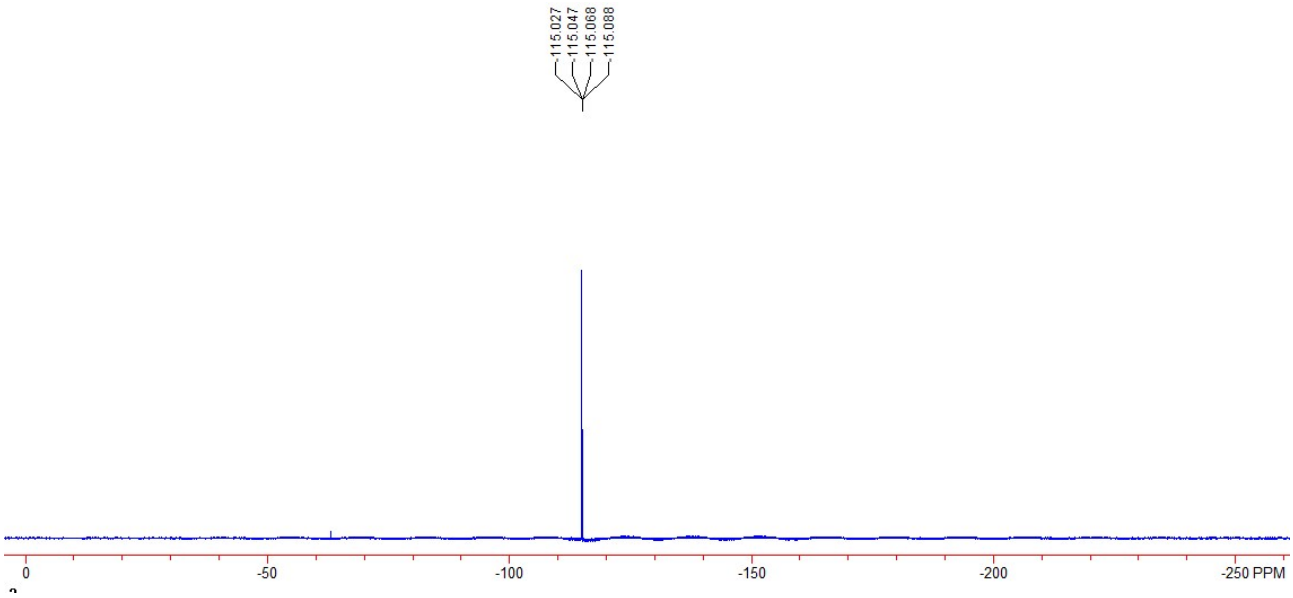


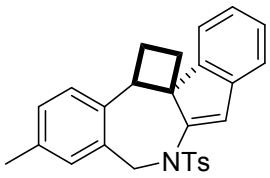
Compound 3v: A white solid. 61 mg, 71% yield. m.p. 206-209 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.83-1.92 (m, 1H), 2.17-2.27 (m, 1H), 2.38 (s, 3H), 2.29-2.41 (m, 1H), 2.58-2.70 (m, 1H), 3.93 (dd, *J* = 7.2 Hz, *J* = 10.4 Hz, 1H), 5.13 (d, *J* = 13.6 Hz, 1H), 5.18 (d, *J* = 13.6 Hz, 1H), 6.65 (s, 1H), 6.80 (d, *J* = 6.8 Hz, 2H), 7.04-7.26 (m, 6H), 7.48 (d, *J* = 7.2 Hz, 1H), 7.73 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 21.6, 23.5, 24.4, 46.5, 48.8, 55.8, 115.0 (d, *J* = 20.3 Hz), 118.3 (d, *J* = 21.5 Hz), 120.3, 120.4, 120.7, 125.1, 127.0, 127.2, 129.9, 131.3 (d, *J* = 8.7 Hz), 134.7

(d, J = 7.7 Hz), 136.4, 137.9 (d, J = 3.7 Hz), 140.5, 144.1, 145.1, 150.0, 161.7 (d, J = 246.0 Hz). ^{19}F NMR ($CDCl_3$, 376 MHz, $CFCl_3$) δ -115.09 ~ -115.03 (m). IR (neat) ν 2955, 2930, 2848, 1712, 1595, 1565, 1498, 1349, 1162, 1089, 1042, 885, 742, 668. 664 cm^{-1}. HRMS (EI) Calcd. for $[C_{26}H_{23}FNO_2S]$ $[M+H]^+$ requires 432.1428 , found 432.1427 .

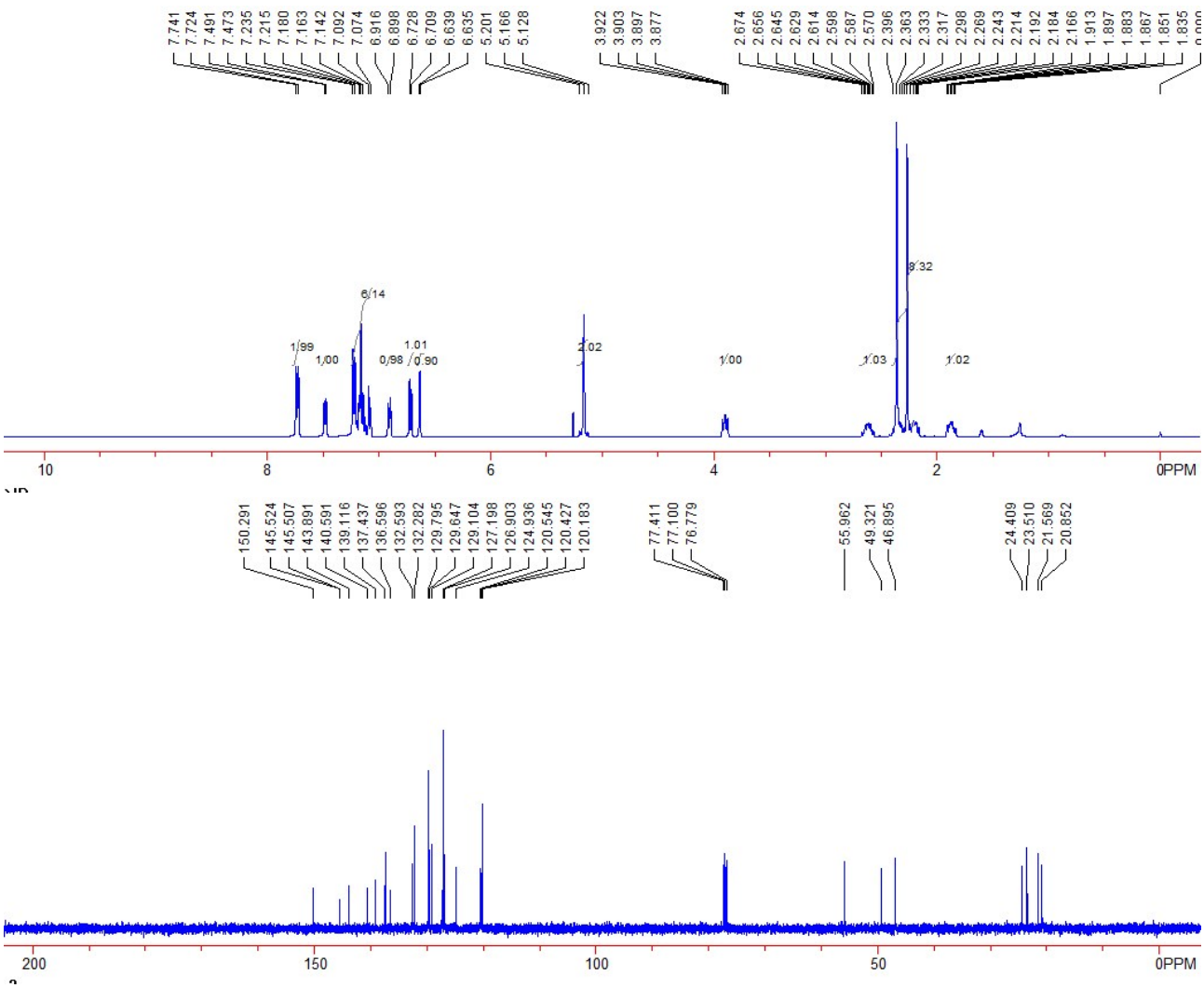


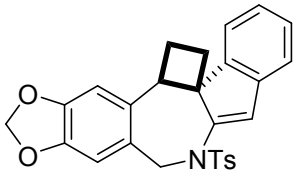






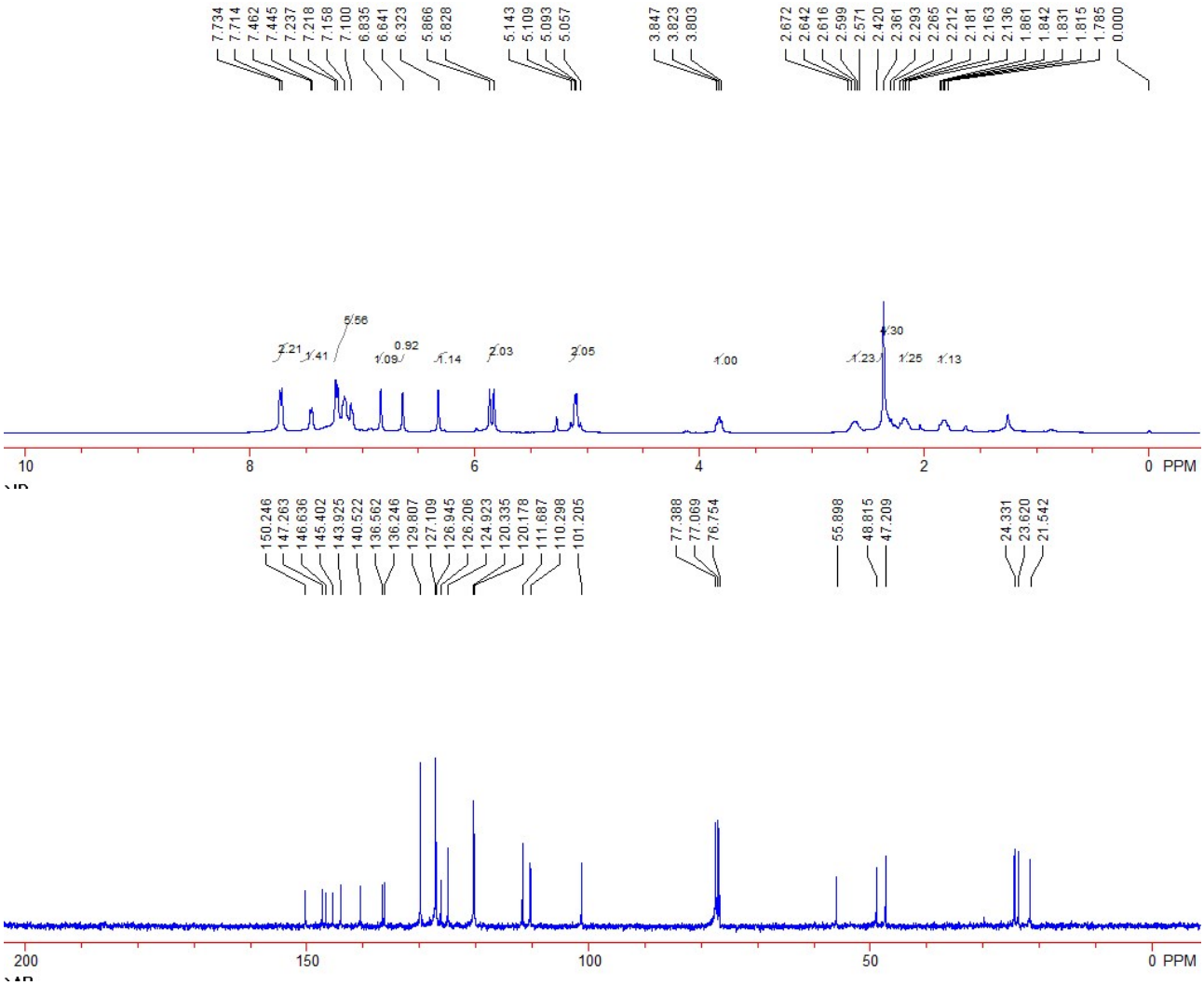
Compound 3w: A white solid. 67 mg, 78% yield. m.p. 188-191 ^{o}C (containing trace of DCM). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.83-1.92 (m, 1H), 2.16-2.30 (m, 1H), 2.27 (s, 3H), 2.36 (s, 3H), 2.26-2.41 (m, 1H), 2.56-2.68 (m, 1H), 3.90 (dd, *J* = 7.6 Hz, *J* = 10.0 Hz, 1H), 5.15 (d, *J* = 14.0 Hz, 1H), 5.18 (d, *J* = 14.0 Hz, 1H), 6.62 (s, 1H), 6.63-6.65 (m, 1H), 6.72 (d, *J* = 7.6 Hz, 1H), 6.91 (d, *J* = 7.2 Hz, 1H), 7.06-7.25 (m, 6H), 7.48 (d, *J* = 7.2 Hz, 1H), 7.73 (d, *J* = 6.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 20.9, 21.6, 23.5, 24.4, 46.9, 49.3, 56.0, 120.2, 120.4, 120.5, 124.9, 126.9, 127.2, 129.1, 129.6, 129.8, 132.3, 132.6, 136.6, 137.4, 139.1, 140.6, 143.9, 145.5, 150.3. IR (neat) ν 2954, 2924, 2852, 1595, 1567, 1466, 1350, 1163, 1089, 1040, 815, 745, 664 cm^{-1}. HRMS (EI) Calcd. for $[C_{27}H_{26}NO_2S]$ $[M+H]^+$ requires 428.1679, found 428.1673.

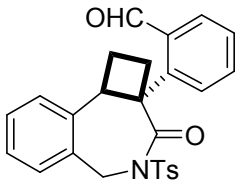




Compound 3x: A white solid. 69 mg, 76% yield. m.p. 230-233 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.77-1.87 (m, 1H), 2.13-2.22 (m, 1H), 2.36 (s, 3H), 2.30-2.37 (m, 1H), 2.56-2.68 (m, 1H), 3.82 (t, *J* = 9.6 Hz, 1H), 5.07 (d, *J* = 14.0 Hz, 1H), 5.13 (d, *J* = 14.0 Hz, 1H), 5.83 (s, 1H), 5.87 (s, 1H), 6.32 (s, 1H), 6.64 (s, 1H), 6.84 (s, 1H), 7.08-7.25 (m, 5H), 7.45 (d, *J* = 6.8 Hz, 1H), 7.72 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 21.5, 23.6, 24.3, 47.2, 48.8, 55.9, 101.2, 110.3, 111.7, 120.2, 120.3, 124.9, 126.2, 126.9, 127.1, 129.8, 136.2, 136.6, 140.5, 142.1, 143.9, 145.4, 146.6, 147.3, 150.2. IR (neat) ν 2952, 2924, 2848, 1712, 1594, 1561, 1487, 1347, 1230, 1161, 1089, 1038, 813, 750, 667 cm^{-1}. HRMS (EI) Calcd. for $[C_{27}H_{24}NO_4S]$ $[M+H]^+$ requires 458.1421, found

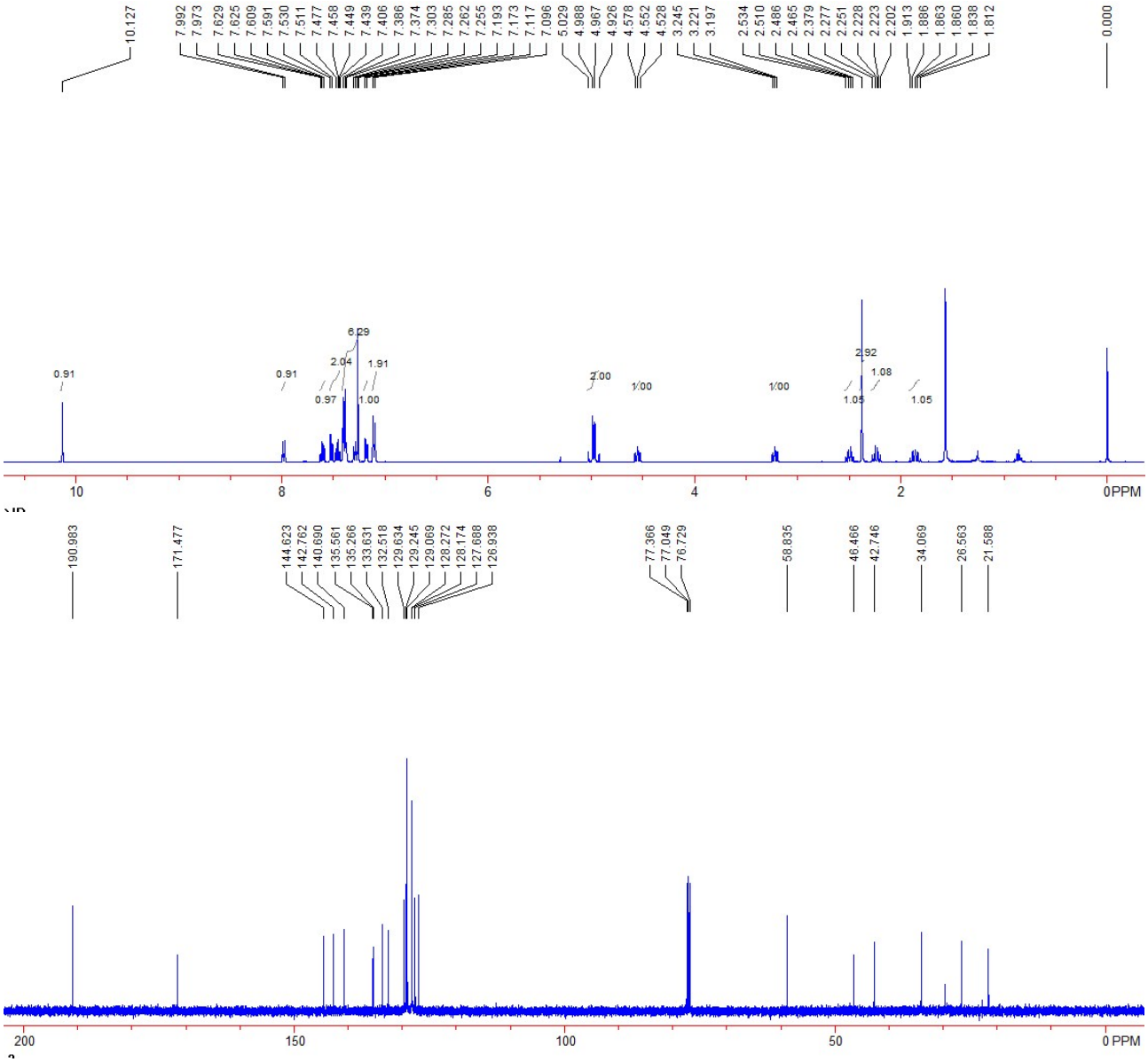
458.1420.



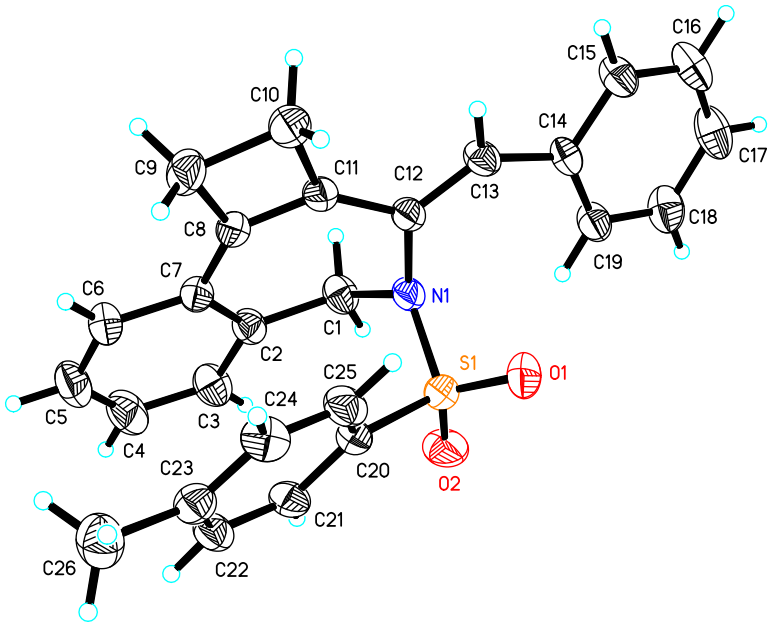


Compound 4a: A white solid. 60 mg, 66% yield. m.p. 108-112 ^{o}C (containing trace of petroleum ether and H_2O). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.80-1.92 (m, 1H), 2.19-2.28 (m, 1H), 2.38 (s, 3H), 2.45-2.54 (m, 1H), 3.22 (t, *J* = 9.6 Hz, 1H), 4.55 (t, *J* = 10.0 Hz, 1H), 4.98 (d, *J* = 16.4 Hz, 1H), 5.01 (d, *J* = 16.4 Hz, 1H), 7.11 (d, *J* = 8.4 Hz, 2H), 7.18 (d, *J* = 8.0 Hz, 1H), 7.25-7.41 (m, 6H), 7.43-7.54 (m, 2H), 7.58-7.64 (m, 1H), 7.98 (d, *J* = 7.6 Hz, 1H), 10.1 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 21.6, 26.6, 34.1, 42.7, 46.5, 58.8, 126.9, 127.7, 128.2, 128.3, 129.1, 129.2, 129.6, 132.5, 133.6, 135.3, 135.6, 140.7, 142.8, 144.6, 171.5, 191.0. IR (neat) ν 3059, 2952, 2919,

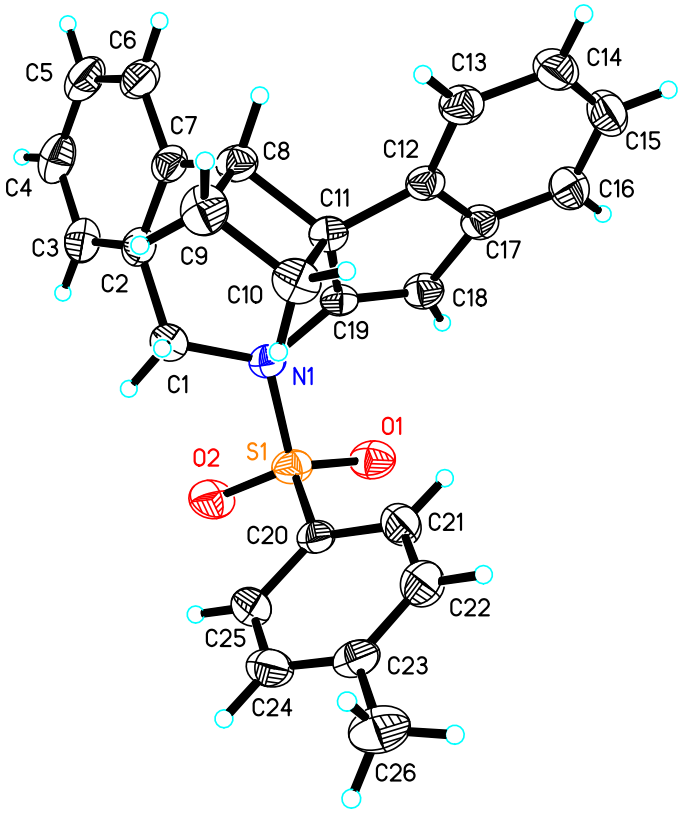
2848, 1686, 1595, 1494, 1454, 1353, 1277, 1167, 1086, 1071, 812, 749, 713 cm^{-1}. HRMS (EI) Calcd. for $[C_{26}H_{27}N_2O_4S]$ $[M+NH_4]^+$ requires 463.1686, found 463.1681.



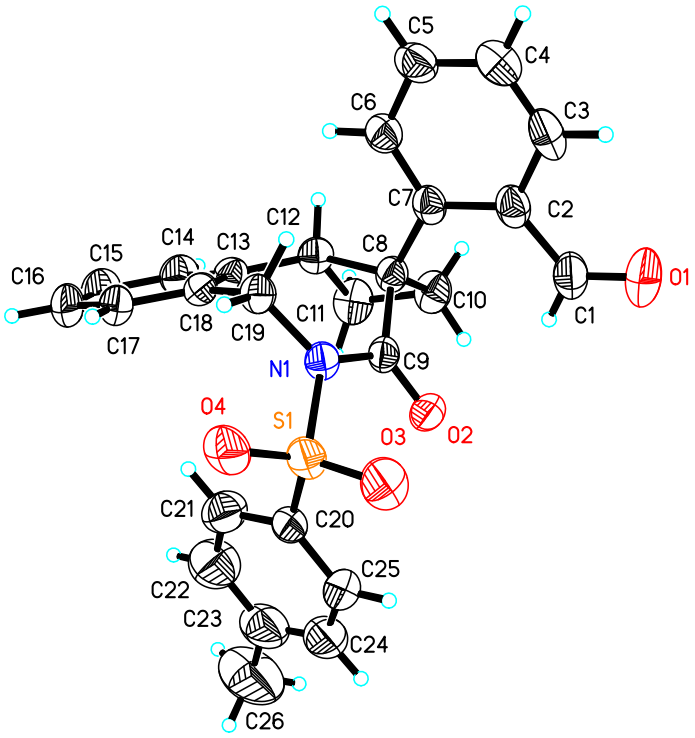
5. X-ray crystal data of 2a, 3a and 4a.



The crystal data of **2a** have been deposited in CCDC with number 1498705. Empirical Formula: $C_{26}H_{23}NO_2S$; Formula Weight: 413.51; Crystal Color, Habit: colorless; Crystal Dimensions: 0.220 x 0.170 x 0.120 mm^3; Crystal System: Monoclinic; Lattice Parameters: a = 12.1152(14) Å, alpha = 90 deg. b = 14.1577(18) Å, beta = 93.519(2) deg. c = 24.768(3) Å, gamma = 90 deg.; V = 4240.2(9) $Å^3$; Space group: C c; Z = 8; D_{calc} = 1.296 g/cm^3; F_{000} = 1744; Diffractometer: Rigaku AFC7R; Residuals: R; R_w: 0.0373, 0.0883.



The crystal data of **3a** have been deposited in CCDC with number 1498706. Empirical Formula: $C_{26}H_{23}NO_2S$; Formula Weight: 413.51; Crystal Color, Habit: colorless; Crystal Dimensions: 0.200 x 0.170 x 0.130 mm^3; Crystal System: Monoclinic; Lattice Parameters: a = 10.875(12) Å, alpha = 90 deg. b = 11.830(14) Å, beta = 98.80(2) deg. c = 16.54(2) Å, gamma = 90 deg.; V = 2103(4) $Å^3$; Space group: P 21/n; Z = 4; D_{calc} = 1.306 g/cm^3; F_{000} = 872; Diffractometer: Rigaku AFC7R; Residuals: R; R_w: 0.0430, 0.1015.



The crystal data of **4a** have been deposited in CCDC with number 1857759. Empirical Formula: $C_{26}H_{23}NO_4S$; Formula Weight: 445.51; Crystal Color, Habit: colorless; Crystal Dimensions: 0.200 x 0.170 x 0.130 mm^3; Crystal System: Monoclinic; Lattice Parameters: a = 20.5631(7) Å, alpha = 90 deg. b = 27.2351(11) Å, beta = 92.0880(10) deg. c = 9.3277(3) Å, gamma = 90 deg.; V = 5220.4(3) $Å^3$; Space group: C 2/c; Z = 8; D_{calc} = 1.134 g/cm^3; F_{000} = 1872; Diffractometer: Rigaku AFC7R; Residuals: R; R_w: 0.0673, 0.2068.