Electronic Supplementary Information

Phosphine-Catalyzed [4 + 3] and [4 + 4] Annulations of β'-Acetoxy Allenoates with N,N-Dinucleophiles: Access to 1,3-Diazepine and 1,4-Diazocine Derivatives

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1. General Information

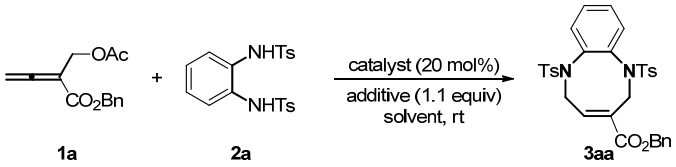
Unless otherwise noted, all reagents were obtained commercially and used without further purification.

NMR spectrum: ^{1}H and ^{13}C spectra are recorded on the Bruker AVANCE spectrometer, operating at 400 MHz for ^{1}H NMR and 100 MHz for ^{13}C NMR. Chemical shifts are reported in parts per million (ppm). Chemical shifts are reported downfield from $CDCl_3$ (δ: 7.26 ppm) for ^{1}H NMR. Chemical shifts of ^{13}C NMR are reported in the scale relative to the solvent of $CDCl_3$ (δ: 77.0 ppm) used as an internal reference. Multiplicities are recorded as follows: s (singlet), d (doublet), t (triplet), dd (doublet of doublet), m (multiplet). Coupling constants are reported in Hertz (Hz).

Mass spectroscopy: Mass spectra were in general recorded on Waters Micromass Q-TOF Premier Mass Spectrometer.

Chromatography: Column chromatography was performed with silica gel (200-300 mesh ASTM).

2. Optimization of the Reaction Conditions[a]

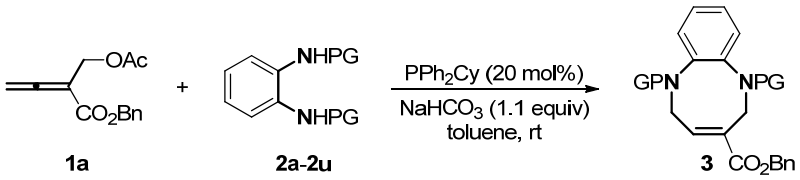


1a 2a 3aa

Entry	Catalyst	Solvent	Additive	Yield(%)[b]
1	PPh_3	toluene	K_2CO_3	69
2	DABCO	toluene	K_2CO_3	ND[c]
3	DMAP	toluene	K_2CO_3	ND[c]
4	$(4\text{-}MeC_6H_4)_3P$	toluene	K_2CO_3	73
5	$(4\text{-}MeOC_6H_4)_3P$	toluene	K_2CO_3	75
6	P^nBu_3	toluene	K_2CO_3	43
7	Ph_2PMe	toluene	K_2CO_3	78
8	Ph_2PCy	toluene	K_2CO_3	84
9	$(4\text{-}FC_6H_4)_3P$	toluene	K_2CO_3	61
10	$(4\text{-}CF_3C_6H_4)_3P$	toluene	K_2CO_3	ND[c]
11	Ph_2PCy	toluene	Na_2CO_3	87
12	Ph_2PCy	toluene	Cs_2CO_3	81
13	Ph_2PCy	toluene	$NaHCO_3$	93
14	Ph_2PCy	toluene	DIPEA	49
15	Ph_2PCy	toluene	Et_3N	67
16	Ph_2PCy	toluene	NaOAc	86
17	Ph_2PCy	CH_2Cl_2	$NaHCO_3$	58
18	Ph_2PCy	1,4-dioxane	$NaHCO_3$	19
19	Ph_2PCy	EtOAc	$NaHCO_3$	54
20	Ph_2PCy	THF	$NaHCO_3$	88
21	Ph_2PCy	$CHCl_3$	$NaHCO_3$	80
22	Ph_2PCy	CH_3CN	$NaHCO_3$	52
23	Ph_2PCy	acetone	$NaHCO_3$	37
24	Ph_2PCy	DME	$NaHCO_3$	44
25	Ph_2PCy	DMF	$NaHCO_3$	23
26	Ph_2PCy	$ClCH_2CH_2Cl$	$NaHCO_3$	62

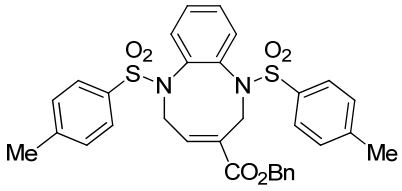
[a]The reaction was carried out with **1a** (0.12 mmol), **2a** (0.1 mmol), catalyst (20 mol%), and additive (0.11 mmol) in solvent (2.0 mL) at room temperature. [b]The isolated yield was reported. [c]ND = Not detected.

3. The Synthesis and Data for Products 3



To a 10 mL Schlenk tube was added **2** (0.1 mmol, 1.0 equiv), PPh_2Cy (0.02 mmol, 0.2 equiv), $NaHCO_3$ (0.11 mmol, 1.1 equiv), and toluene (1 mL). The mixture was stirred at room temperature. Then, the solution of allenoate **1a** (0.12 mmol, 1.2 equiv) in toluene (1 mL) was slowly added to the mixture over 1 h. After the completion of the reaction (monitored by TLC), the solvent was removed and the residue was directly subjected to silica gel column chromatography (petroleum ether/ethyl acetate as eluent) to give the products **3**.

(E)-Benzyl 1,6-ditosyl-1,2,5,6-tetrahydrobenzo[b][1,4]diazocine-3-carboxylate (3aa)



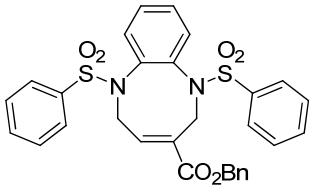
93% yield, 56.1 mg, slight yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (d, *J* = 8.4 Hz, 2H), 7.59 (d, *J* = 8.4 Hz, 2H), 7.38-7.26 (m, 9H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.20-7.16 (m, 2H), 6.89 (t, *J* = 5.6 Hz, 1H), 5.14 (s, 2H), 4.50 (s, 2H), 4.30 (d, *J* = 5.6 Hz, 2H), 2.41 (s, 3H), 2.39 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 165.0, 144.2, 143.9, 139.4, 136.4, 136.1, 135.5, 135.5, 134.9, 131.3, 129.7, 129.7, 128.5, 128.3, 128.3, 128.3, 128.0, 128.0, 127.9, 127.9, 127.4, 66.9, 48.1, 46.2, 21.5.

HRMS (ESI) Calcd for $C_{32}H_{31}N_2O_6S_2$ $[M+H]^+$ 603.1618, found 603.1616.

(E)-Benzyl 1,6-bis(phenylsulfonyl)-1,2,5,6-tetrahydrobenzo[b][1,4]diazocine-3-carboxylate (3ab)



94% yield, 54.0 mg, slight yellow oil.

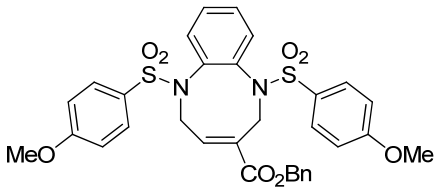
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86-7.83 (m, 2H), 7.74-7.71 (m, 2H), 7.61-7.54 (m, 2H), 7.53-7.43 (m, 4H), 7.38-7.26 (m, 6H), 7.25-7.16 (m, 3H), 6.89 (t, *J* = 5.6 Hz, 1H), 5.13 (s, 2H), 4.56 (s, 2H), 4.35 (d, *J* = 6.0 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 164.9, 139.3, 139.3, 138.5, 136.2, 135.5, 134.9, 133.3, 133.1, 131.3, 129.1, 129.1, 128.5, 128.5, 128.4, 128.3, 128.3, 128.0, 127.9, 127.7,

66.9, 48.1, 46.2.

HRMS (ESI) Calcd for $C_{30}H_{27}N_2O_6S_2$ $[M+H]^+$ 575.1305, found 575.1314.

(E)-Benzyl 1,6-bis((4-methoxyphenyl)sulfonyl)-1,2,5,6-tetrahydrobenzo[b][1,4]diazocine-3-carboxylate (3ac)



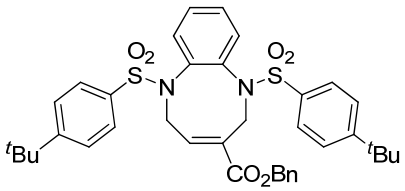
91% yield, 57.8 mg, colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80-7.75 (m, 2H), 7.67-7.63 (m, 2H), 7.38-7.28 (m, 7H), 7.21-7.16 (m, 2H), 6.96-6.92 (m, 2H), 6.91-6.87 (m, 3H), 5.13 (s, 2H), 4.50 (s, 2H), 4.31 (d, J = 5.6 Hz, 2H), 3.84 (s, 3H), 3.82 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 165.0, 163.3, 163.1, 139.4, 136.2, 135.5, 135.0, 131.3, 131.0, 130.1, 130.0, 128.5, 128.3, 128.3, 128.2, 128.0, 127.9, 127.4, 114.2, 114.2, 66.9, 55.6, 55.6, 48.0, 46.2.

HRMS (ESI) Calcd for $C_{32}H_{31}N_2O_8S_2$ $[M+H]^+$ 635.1516, found 635.1522.

(E)-Benzyl 1,6-bis((4-(tert-butyl)phenyl)sulfonyl)-1,2,5,6-tetrahydrobenzo[b][1,4]diazocine-3-carboxylate (3ad)



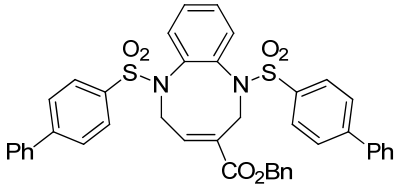
89% yield, 61.1 mg, colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77-7.72 (m, 2H), 7.62-7.58 (m, 2H), 7.51-7.47 (m, 2H), 7.44-7.40 (m, 2H), 7.37-7.30 (m, 7H), 7.23-7.18 (m, 2H), 6.89 (t, J = 5.6 Hz, 1H), 5.14 (s, 2H), 4.48 (s, 2H), 4.32 (d, J = 5.6 Hz, 2H), 1.32 (s, 9H), 1.30 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 165.0, 157.1, 156.8, 139.2, 136.3, 136.1, 135.5, 135.5, 135.0, 131.4, 128.5, 128.5, 128.3, 128.0, 128.0, 127.7, 127.5, 126.1, 66.9, 48.0, 46.3, 35.1, 31.0, 31.0.

HRMS (ESI) Calcd for $C_{38}H_{43}N_2O_6S_2$ $[M+H]^+$ 687.2557, found 687.2559.

(E)-Benzyl 1,6-bis([1,1'-biphenyl]-4-ylsulfonyl)-1,2,5,6-tetrahydrobenzo[b][1,4]diazocine-3-carboxylate (3ae)



88% yield, 63.9 mg, slight yellow oil.

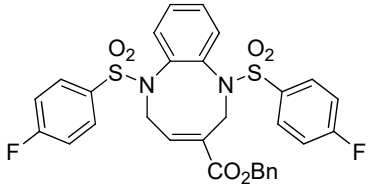
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95-7.91 (m, 2H), 7.81-7.78 (m, 2H), 7.73-7.69 (m,

2H), 7.67-7.63 (m, 2H), 7.62-7.56 (m, 4H), 7.50-7.39 (m, 6H), 7.37-7.29 (m, 7H), 7.25-7.19 (m, 2H), 6.95 (t, *J* = 5.6 Hz, 1H), 5.15 (s, 2H), 4.62 (s, 2H), 4.42 (d, *J* = 5.6 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 164.9, 146.1, 145.9, 139.4, 139.2, 139.0, 137.9, 137.0, 136.3, 135.4, 134.9, 131.3, 129.0, 128.5, 128.5, 128.4, 128.4, 128.4, 128.3, 128.0, 127.7, 127.7, 127.3, 127.3, 66.9, 48.2, 46.3.

HRMS (ESI) Calcd for $C_{42}H_{35}N_2O_6S_2$ $[M+H]^+$ 727.1931, found 727.1933.

(E)-Benzyl 1,6-bis((4-fluorophenyl)sulfonyl)-1,2,5,6-tetrahydrobenzo[b][1,4]diazocine-3-carboxylate (3af)



90% yield, 55.0 mg, slight yellow oil.

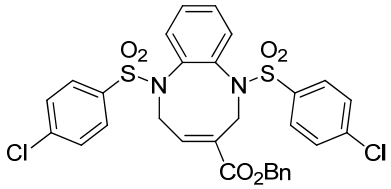
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91-7.85 (m, 2H), 7.81-7.75 (m, 2H), 7.38-7.27 (m, 5H), 7.23-7.12 (m, 8H), 6.89 (t, *J* = 6.8 Hz, 1H), 5.12 (s, 2H), 4.65 (s, 2H), 4.40 (d, *J* = 5.6 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 165.4 (d, *J* = 254.5 Hz), 165.3 (d, *J* = 253.8 Hz), 164.8, 139.4, 136.3, 135.3, 135.2 (d, *J* = 3.1 Hz), 134.8, 134.4 (d, *J* = 3.0 Hz), 131.2, 130.7 (d, *J* = 9.4 Hz), 130.7 (d, *J* = 9.3 Hz), 128.7, 128.6, 128.5, 128.5, 128.4, 128.0, 127.9, 116.5 (d, *J* = 22.6 Hz), 116.3 (d, *J* = 22.5 Hz), 67.0, 48.2, 46.1.

^{19}F NMR (376 MHz, $CDCl_3$): δ -103.8--103.9 (m), -104.3--104.5 (m).

HRMS (ESI) Calcd for $C_{30}H_{24}F_2N_2NaO_6S_2$ $[M+Na]^+$ 633.0936, found 633.0943.

(E)-Benzyl 1,6-bis((4-chlorophenyl)sulfonyl)-1,2,5,6-tetrahydrobenzo[b][1,4]diazocine-3-carboxylate (3ag)



92% yield, 59.2 mg, slight yellow oil.

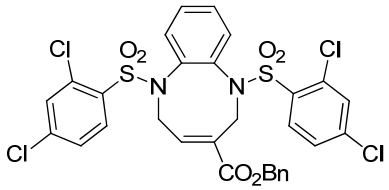
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83-7.78 (m, 2H), 7.72-7.68 (m, 2H), 7.48-7.44 (m, 4H), 7.38-7.27 (m, 5H), 7.23-7.17 (m, 3H), 7.14-7.10 (m, 1H), 6.89 (t, *J* = 5.6 Hz, 1H), 5.12 (s, 2H), 4.65 (s, 2H), 4.39 (d, *J* = 5.6 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 164.7, 139.9, 139.6, 139.5, 137.7, 136.8, 136.3, 135.3, 134.6, 131.1, 129.5, 129.4, 129.3, 128.8, 128.5, 128.5, 128.4, 128.0, 67.0, 48.3, 46.1.

HRMS (ESI) Calcd for $C_{30}H_{25}Cl_2N_2O_6S_2$ $[M+H]^+$ 643.0526, found 643.0527.

(E)-Benzyl 1,6-bis((2,4-dichlorophenyl)sulfonyl)-1,2,5,6-tetrahydrobenzo[b][1,4]diazocine-3-

carboxylate (3ah)



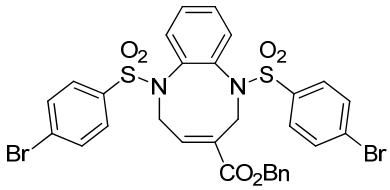
89% yield, 63.4 mg, slight yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (d, *J* = 8.4 Hz, 1H), 7.80 (d, *J* = 8.8 Hz, 1H), 7.56 (dd, *J* = 10.8, 2.0 Hz, 2H), 7.38-7.25 (m, 7H), 7.16-7.04 (m, 3H), 7.02 (t, *J* = 5.2 Hz, 1H), 6.86 (dd, *J* = 8.0, 1.2 Hz, 1H), 5.16 (s, 2H), 5.05 (s, 2H), 4.85 (d, *J* = 5.2 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 165.1, 140.4, 140.0, 139.5, 137.0, 136.4, 136.3, 135.4, 134.3, 133.4, 133.4, 132.9, 132.4, 131.9, 131.9, 130.9, 128.8, 128.7, 128.7, 128.5, 128.3, 128.0, 127.9, 127.6, 127.3, 67.0, 49.8, 46.7.

HRMS (ESI) Calcd for $C_{30}H_{23}Cl_4N_2O_6S_2$ $[M+H]^+$ 710.9746, found 710.9735.

(E)-Benzyl 1,6-bis((4-bromophenyl)sulfonyl)-1,2,5,6-tetrahydrobenzo[b][1,4]diazocine-3-carboxylate (3ai)



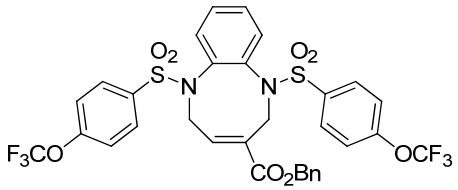
92% yield, 67.3 mg, slight yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75-7.71 (m, 2H), 7.65-7.60 (m, 6H), 7.38-7.26 (m, 5H), 7.23-7.17 (m, 3H), 7.14-7.10 (m, 1H), 6.89 (t, *J* = 5.6 Hz, 1H), 5.12 (s, 2H), 4.65 (s, 2H), 4.39 (d, *J* = 5.6 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 164.7, 139.5, 138.3, 137.3, 136.3, 135.3, 134.6, 132.5, 132.4, 131.1, 129.4, 129.4, 128.8, 128.6, 128.5, 128.5, 128.4, 128.1, 128.0, 67.0, 48.3, 46.1.

HRMS (ESI) Calcd for $C_{30}H_{24}Br_2N_2NaO_6S_2$ $[M+Na]^+$ 752.9335, found 752.9331.

(E)-Benzyl 1,6-bis((4-(trifluoromethoxy)phenyl)sulfonyl)-1,2,5,6-tetrahydrobenzo[b][1,4]diazocine-3-carboxylate (3aj)



92% yield, 68.3 mg, colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93-7.88 (m, 2H), 7.83-7.79 (m, 2H), 7.37-7.18 (m, 12H), 7.13-7.09 (m, 1H), 6.89 (t, *J* = 5.6 Hz, 1H), 5.12 (s, 2H), 4.69 (s, 2H), 4.42 (d, *J* = 5.6 Hz, 2H).

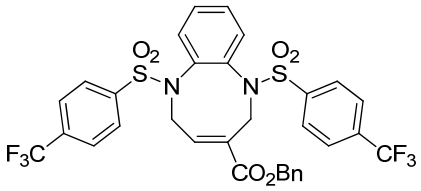
^{13}C NMR (100 MHz, $CDCl_3$): δ 164.7, 152.6 (d, *J* = 1.7 Hz), 152.4 (d, *J* = 1.8 Hz),

139.5, 137.5, 136.6, 136.4, 135.3, 134.7, 131.2, 130.1, 130.1, 128.9, 128.6, 128.6, 128.6, 128.4, 128.1, 128.0, 121.0, 120.9, 120.2 (q, J = 257.8 Hz), 120.1 (d, J = 252.8 Hz), 67.1, 48.3, 48.1.

^{19}F NMR (376 MHz, $CDCl_3$): δ -57.6, -57.6.

HRMS (ESI) Calcd for $C_{32}H_{25}F_6N_2O_8S_2$ $[M+H]^+$ 743.0951, found 743.0947.

(E)-Benzyl 1,6-bis((4-(trifluoromethyl)phenyl)sulfonyl)-1,2,5,6-tetrahydrobenzo[b][1,4]diazocine-3-carboxylate (3ak)



84% yield, 59.7 mg, colorless oil.

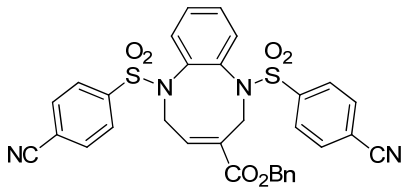
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01 (d, J = 8.4 Hz, 2H), 7.92 (d, J = 8.0 Hz, 2H), 7.77 (dd, J = 8.0, 6.0 Hz, 4H), 7.39-7.32 (m, 3H), 7.31-7.20 (m, 4H), 7.18 (dd, J = 7.6, 2.4 Hz, 1H), 7.08 (dd, J = 7.2, 1.6 Hz, 1H), 6.91 (t, J = 6.0 Hz, 1H), 5.13 (s, 2H), 4.74 (s, 2H), 4.46 (d, J = 5.6 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 164.7, 142.7, 141.8, 139.5, 136.4, 135.2, 134.9 (d, J = 33.1 Hz), 134.6 (d, J = 32.9 Hz), 134.5, 134.5, 131.1, 129.2, 128.6, 128.6, 128.5, 128.4, 128.4, 128.3, 128.0, 126.4 (q, J = 3.4 Hz), 126.3 (q, J = 3.6 Hz), 123.2 (d, J = 271.5 Hz), 123.1 (d, J = 271.5 Hz), 67.1, 48.4, 46.1.

^{19}F NMR (376 MHz, $CDCl_3$): δ -63.1, -63.1.

HRMS (ESI) Calcd for $C_{32}H_{25}F_6N_2O_6S_2$ $[M+H]^+$ 711.1053, found 711.1053.

(E)-Benzyl 1,6-bis((4-cyanophenyl)sulfonyl)-1,2,5,6-tetrahydrobenzo[b][1,4]diazocine-3-carboxylate (3al)



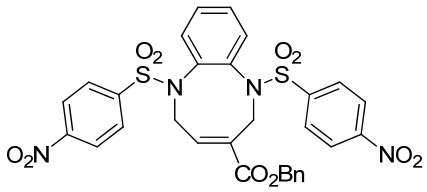
81% yield, 50.6 mg, white foam.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00-7.96 (m, 2H), 7.91-7.88 (m, 2H), 7.83-7.78 (m, 4H), 7.40-7.34 (m, 3H), 7.32-7.22 (m, 4H), 7.17 (dd, J = 7.6, 2.0 Hz, 1H), 7.03 (dd, J = 7.6, 1.6 Hz, 1H), 6.91 (t, J = 5.6 Hz, 1H), 5.14 (s, 2H), 4.76 (s, 2H), 4.48 (d, J = 5.2 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 164.5, 143.1, 142.2, 139.4, 136.3, 135.1, 134.3, 133.1, 132.9, 131.0, 129.4, 128.7, 128.6, 128.6, 128.5, 128.5, 128.4, 128.0, 117.3, 117.2, 117.0, 116.7, 67.2, 48.4, 46.0.

HRMS (ESI) Calcd for $C_{32}H_{25}N_4O_6S_2$ $[M+H]^+$ 625.1210, found 625.1216.

(E)-Benzyl 1,6-bis((4-nitrophenyl)sulfonyl)-1,2,5,6-tetrahydrobenzo[b][1,4]diazocine-3-carboxylate (3am)



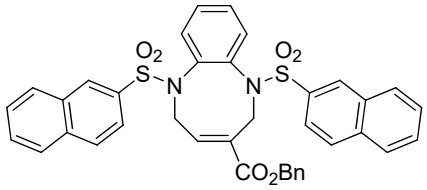
80% yield, 53.1 mg, slight yellow foam.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.39-8.31 (m, 4H), 8.07-8.03 (m, 2H), 7.99-7.95 (m, 2H), 7.39-7.32 (m, 3H), 7.31-7.24 (m, 4H), 7.18 (dd, *J* = 7.6, 2.0 Hz, 1H), 7.05 (dd, *J* = 7.6, 2.0 Hz, 1H), 6.93 (t, *J* = 5.6 Hz, 1H), 5.14 (s, 2H), 4.81 (s, 2H), 4.52 (d, *J* = 5.2 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 164.5, 150.4, 150.2, 144.6, 143.7, 139.5, 136.3, 135.1, 134.3, 131.0, 129.6, 129.2, 129.1, 128.8, 128.7, 128.6, 128.6, 128.5, 128.0, 124.5, 124.4, 67.2, 48.5, 46.1.

HRMS (ESI) Calcd for $C_{30}H_{25}N_4O_{10}S_2$ $[M+H]^+$ 665.1007, found 665.1009.

(E)-Benzyl 1,6-bis(naphthalen-2-ylsulfonyl)-1,2,5,6-tetrahydrobenzo[b][1,4]diazocine-3-carboxylate (3an)



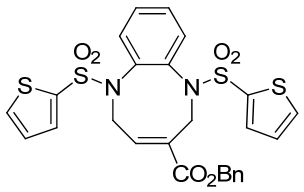
89% yield, 60.0 mg, slight yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.47 (d, *J* = 1.6 Hz, 1H), 8.36 (d, *J* = 1.2 Hz, 1H), 7.94-7.81 (m, 7H), 7.68-7.55 (m, 5H), 7.35-7.29 (m, 4H), 7.26-7.14 (m, 5H), 6.89 (t, *J* = 5.6 Hz, 1H), 5.06 (s, 2H), 4.83 (s, 2H), 4.39 (d, *J* = 6.4 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 164.9, 139.6, 136.4, 136.4, 135.4, 135.0, 134.9, 134.8, 132.1, 132.0, 131.1, 129.6, 129.4, 129.4, 129.3, 129.0, 128.9, 128.5, 128.5, 128.4, 128.3, 128.2, 127.9, 127.9, 127.6, 127.6, 127.4, 123.0, 122.8, 66.9, 48.4, 46.2.

HRMS (ESI) Calcd for $C_{38}H_{31}N_2O_6S_2$ $[M+H]^+$ 675.1618, found 675.1627.

(E)-Benzyl 1,6-bis(thiophen-2-ylsulfonyl)-1,2,5,6-tetrahydrobenzo[b][1,4]diazocine-3-carboxylate (3ao)



87% yield, 51.1 mg, slight yellow oil.

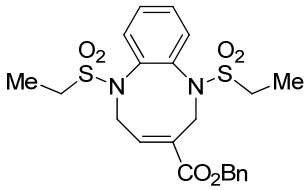
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64 (dd, *J* = 4.0, 1.6 Hz, 1H), 7.62 (dd, *J* = 5.2, 1.6 Hz, 2H), 7.42-7.23 (m, 9H), 7.13-7.09 (m, 2H), 6.95 (t, *J* = 5.6 Hz, 1H), 5.16 (s, 2H),

4.75 (s, 2H), 4.49 (d, J = 5.6 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 164.8, 139.3, 139.3, 138.8, 136.1, 135.4, 134.8, 133.5, 133.4, 132.8, 132.5, 131.3, 128.7, 128.7, 128.5, 128.3, 128.2, 128.0, 127.7, 127.6, 67.0, 48.2, 46.1.

HRMS (ESI) Calcd for $C_{26}H_{22}N_2NaO_6S_4$ $[M+Na]^+$ 609.0253, found 609.0253.

(E)-Benzyl 1,6-bis(ethylsulfonyl)-1,2,5,6-tetrahydrobenzo[b][1,4]diazocine-3-carboxylate (3ap)



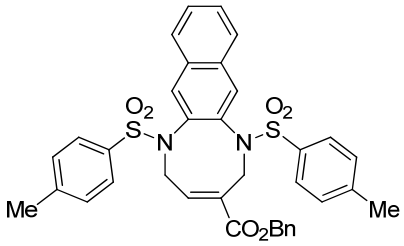
95% yield, 45.5 mg, white foam.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 (dd, J = 5.6 Hz, 1H), 7.38-7.27 (m, 8H), 6.93 (t, J = 5.6 Hz, 1H), 5.13 (s, 2H), 4.86 (s, 2H), 4.63 (d, J = 5.6 Hz, 2H), 3.28 (q, J = 7.2 Hz, 2H), 3.23 (q, J = 7.6 Hz, 2H), 1.46-1.40 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 164.9, 140.6, 136.9, 135.2, 134.5, 130.4, 129.7, 129.2, 128.8, 128.6, 128.4, 128.1, 128.1, 67.1, 48.2, 47.2, 46.7, 45.6, 7.9, 7.6.

HRMS (ESI) Calcd for $C_{22}H_{27}N_2O_6S_2$ $[M+H]^+$ 479.1305, found 479.1309.

(E)-Benzyl 1,6-ditosyl-1,2,5,6-tetrahydronaphtho[2,3-b][1,4]diazocine-3-carboxylate (3aq)



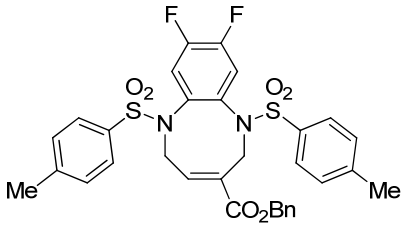
73% yield, 47.7 mg, slight yellow foam.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 (d, J = 10.4 Hz, 2H), 7.74 (d, J = 4.8 Hz, 2H), 7.72-7.66 (m, 2H), 7.63 (d, J = 8.4 Hz, 2H), 7.50-7.44 (m, 2H), 7.34-7.27 (m, 7H), 7.23 (d, J = 8.4 Hz, 2H), 6.91 (t, J = 6.0 Hz, 1H), 5.13 (s, 2H), 4.57 (s, 2H), 4.39 (d, J = 5.6 Hz, 2H), 2.43 (s, 3H), 2.40 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 164.9, 144.3, 144.0, 139.5, 136.5, 135.6, 135.5, 133.8, 133.4, 132.1, 131.8, 131.8, 129.7, 129.7, 128.5, 128.3, 128.0, 128.0, 128.0, 127.6, 127.5, 127.2, 126.9, 126.7, 66.9, 48.3, 46.5, 21.6.

HRMS (ESI) Calcd for $C_{36}H_{33}N_2O_6S_2$ $[M+H]^+$ 653.1775, found 653.1770.

(E)-Benzyl 8,9-difluoro-1,6-ditosyl-1,2,5,6-tetrahydrobenzo[b][1,4]diazocine-3-carboxylate (3ar)



90% yield, 57.5 mg, slight yellow oil.

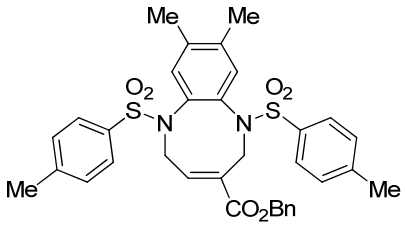
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69 (d, *J* = 8.4 Hz, 2H), 7.56 (d, *J* = 8.4 Hz, 2H), 7.38-7.29 (m, 7H), 7.24 (d, *J* = 8.0 Hz, 2H), 7.20-7.12 (m, 2H), 6.89 (t, *J* = 5.6 Hz, 1H), 5.15 (s, 2H), 4.45 (s, 2H), 4.24 (d, *J* = 5.6 Hz, 2H), 2.42 (s, 3H), 2.40 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 164.7, 148.7 (dd, *J* = 249.8, 12.8 Hz), 148.3 (dd, *J* = 249.7, 13.0 Hz), 144.7, 144.4, 139.0, 135.6, 135.4, 134.8, 132.8 (dd, *J* = 7.8, 3.4 Hz), 131.3, 131.2 (dd, *J* = 7.3, 3.2 Hz), 129.9, 129.8, 128.6, 128.4, 128.1, 127.9, 116.9 (d, *J* = 19.4 Hz), 116.8 (d, *J* = 19.5 Hz), 67.0, 47.9, 46.1, 21.6.

^{19}F NMR (376 MHz, $CDCl_3$): δ -134.4--134.6 (m), -135.3--135.5 (m).

HRMS (ESI) Calcd for $C_{32}H_{29}F_2N_2O_6S_2$ $[M+H]^+$ 639.1430, found 639.1431.

(E)-Benzyl 8,9-dimethyl-1,6-ditosyl-1,2,5,6-tetrahydrobenzo[b][1,4]diazocine-3-carboxylate (3as)



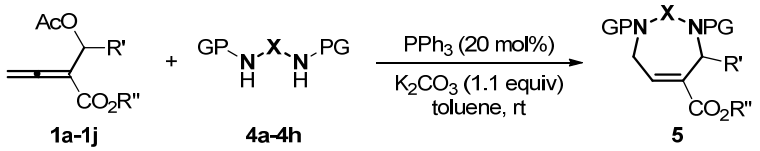
84% yield, 52.9 mg, slight yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (d, *J* = 8.4 Hz, 2H), 7.60 (d, *J* = 8.0 Hz, 2H), 7.36-7.27 (m, 7H), 7.24 (d, *J* = 8.0 Hz, 2H), 7.01 (d, *J* = 17.6 Hz, 2H), 6.86 (t, *J* = 5.6 Hz, 1H), 5.13 (s, 2H), 4.49 (s, 2H), 4.25 (d, *J* = 5.6 Hz, 2H), 2.41 (s, 3H), 2.40 (s, 3H), 2.15 (s, 3H), 2.14 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 165.0, 144.1, 143.7, 139.6, 137.0, 136.5, 136.4, 135.5, 135.5, 133.4, 132.1, 131.2, 129.6, 129.6, 129.2, 129.0, 128.5, 128.2, 128.0, 128.0, 127.9, 66.8, 48.2, 46.0, 21.5, 19.5, 19.3.

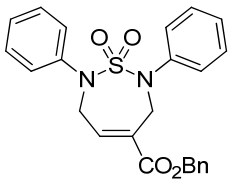
HRMS (ESI) Calcd for $C_{34}H_{35}N_2O_6S_2$ $[M+H]^+$ 631.1931, found 631.1939.

4. The Synthesis and Data for Products 5



To a 10 mL Schlenk tube was added **4** (0.1 mmol, 1.0 equiv), PPh_3 (0.02 mmol, 0.2 equiv), K_2CO_3 (0.11 mmol, 1.1 equiv), and toluene (1 mL). The mixture was stirred at room temperature. Then, the solution of allenoate **1** (0.12 mmol, 1.2 equiv) in toluene (1 mL) was slowly added to the mixture over 1 h. After the completion of the reaction (monitored by TLC), the solvent was removed and the residue was directly subjected to silica gel column chromatography (petroleum ether/ethyl acetate as eluent) to give the products **5**.

Benzyl 2,7-diphenyl-2,3,6,7-tetrahydro-1,2,7-thiadiazepine-4-carboxylate 1,1-dioxide (5aa)



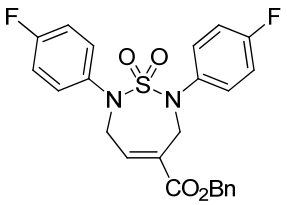
94% yield, 40.8 mg, slight yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38-7.26 (m, 13H), 7.26-7.20 (m, 3H), 5.21 (s, 2H), 4.74 (d, *J* = 1.2 Hz, 2H), 4.53-4.51 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 165.1, 141.6, 141.5, 139.1, 135.3, 132.2, 129.3, 129.2, 128.6, 128.5, 128.2, 127.3, 127.2, 125.9, 125.8, 67.2, 49.9, 48.8.

HRMS (ESI) Calcd for $C_{24}H_{23}N_2O_4S$ $[M+H]^+$ 435.1373, found 435.1372.

Benzyl 2,7-bis(4-fluorophenyl)-2,3,6,7-tetrahydro-1,2,7-thiadiazepine-4-carboxylate 1,1-dioxide (5ab)



71% yield, 33.4 mg, red oil.

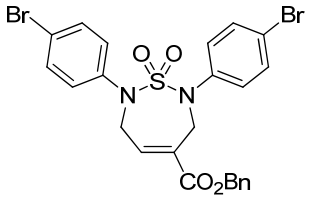
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43-7.35 (m, 5H), 7.33-7.27 (m, 5H), 7.09-7.01 (m, 4H), 5.25 (s, 2H), 4.74 (d, *J* = 1.2 Hz, 2H), 4.54-4.52 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 165.0, 161.6 (d, *J* = 246.5 Hz), 138.9, 137.4 (d, *J* = 3.1 Hz), 137.3 (d, *J* = 3.3 Hz), 135.2, 132.4, 128.7, 128.6, 128.3 (d, *J* = 8.6 Hz), 128.3 (d, *J* = 7.9 Hz), 116.2 (d, *J* = 22.7 Hz), 116.2 (d, *J* = 22.6 Hz), 67.4, 50.1, 49.1.

^{19}F NMR (376 MHz, $CDCl_3$): δ -113.3--113.5 (m), -113.4--113.6 (m).

HRMS (ESI) Calcd for $C_{24}H_{21}F_2N_2O_4S$ $[M+H]^+$ 471.1185, found 471.1189.

Benzyl 2,7-bis(4-bromophenyl)-2,3,6,7-tetrahydro-1,2,7-thiadiazepine-4-carboxylate 1,1-dioxide (5ac)



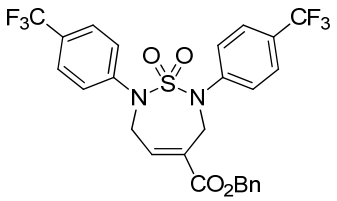
87% yield, 51.5 mg, slight yellow foam.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48-7.33 (m, 9H), 7.26-7.23 (m, 1H), 7.18-7.11 (m, 4H), 5.23 (s, 2H), 4.70 (s, 2H), 4.49 (d, *J* = 4.4 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 164.9, 140.4, 140.3, 138.8, 135.1, 132.4, 132.4, 128.7, 128.6, 128.3, 127.4, 127.4, 121.1, 121.0, 67.4, 49.7, 48.7.

HRMS (ESI) Calcd for $C_{24}H_{21}Br_2N_2O_4S$ $[M+H]^+$ 590.9583, found 590.9580.

Benzyl 2,7-bis(4-(trifluoromethyl)phenyl)-2,3,6,7-tetrahydro-1,2,7-thiadiazepine-4-carboxylate 1,1-dioxide (5ad)



73% yield, 41.6 mg, slight yellow foam.

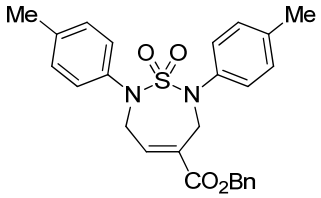
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 (d, *J* = 8.4 Hz, 2H), 7.57 (d, *J* = 8.4 Hz, 2H), 7.42-7.35 (m, 9H), 7.32 (t, *J* = 4.4 Hz, 1H), 5.27 (s, 2H), 4.77 (s, 2H), 4.56 (d, *J* = 4.4 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 164.7, 144.3, 138.7, 135.0, 132.5, 129.1 (d, *J* = 32.8 Hz), 128.8 (d, *J* = 32.9 Hz), 128.7, 128.4, 126.5 (d, *J* = 3.6 Hz), 126.4 (d, *J* = 3.7 Hz), 125.2, 124.8, 123.7 (d, *J* = 270.5 Hz), 123.6 (d, *J* = 270.5 Hz), 67.6, 49.5, 48.3.

^{19}F NMR (376 MHz, $CDCl_3$): δ -62.6, -62.6.

HRMS (ESI) Calcd for $C_{26}H_{21}F_6N_2O_4S$ $[M+H]^+$ 571.1121, found 571.1125.

Benzyl 2,7-di-p-tolyl-2,3,6,7-tetrahydro-1,2,7-thiadiazepine-4-carboxylate 1,1-dioxide (5ae)



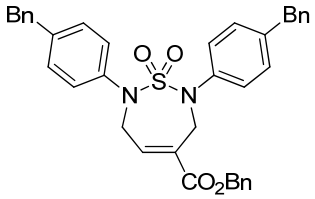
91% yield, 42.1 mg, slight yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44-7.38 (m, 5H), 7.31-7.23 (m, 5H), 7.20-7.16 (m, 4H), 5.27 (s, 2H), 4.78 (s, 2H), 4.58-4.55 (m, 2H), 2.38 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 165.2, 139.1, 139.1, 139.0, 137.3, 137.2, 135.3, 132.2, 129.9, 128.6, 128.5, 128.2, 126.1, 126.0, 67.1, 50.0, 48.9, 21.0.

HRMS (ESI) Calcd for $C_{26}H_{27}N_2O_4S$ $[M+H]^+$ 463.1686, found 463.1686.

Benzyl 2,7-bis(4-benzylphenyl)-2,3,6,7-tetrahydro-1,2,7-thiadiazepine-4-carboxylate 1,1-dioxide (5af)



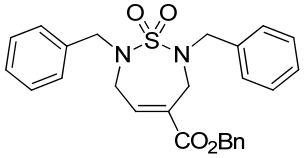
87% yield, 53.5 mg, brown oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40-7.29 (m, 9H), 7.26-7.13 (m, 15H), 5.23 (s, 2H), 4.75 (s, 2H), 4.53-4.51 (m, 2H), 3.97 (s, 4H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 165.1, 140.4, 140.4, 140.2, 139.6, 139.6, 139.0, 135.3, 132.2, 129.7, 129.6, 128.9, 128.9, 128.6, 128.5, 128.5, 128.2, 126.2, 126.2, 126.1, 126.0, 67.2, 49.9, 48.9, 41.3.

HRMS (ESI) Calcd for $C_{38}H_{35}N_2O_4S$ $[M+H]^+$ 615.2312, found 615.2314.

Benzyl 2,7-dibenzyl-2,3,6,7-tetrahydro-1,2,7-thiadiazepine-4-carboxylate 1,1-dioxide (5ag)



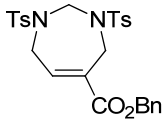
73% yield, 33.8 mg, slight yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39-7.32 (m, 8H), 7.31-7.27 (m, 7H), 6.97 (t, J = 5.2 Hz, 1H), 5.15 (s, 2H), 4.44 (s, 2H), 4.42 (s, 2H), 4.14 (s, 2H), 3.85 (d, J = 5.2 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 165.2, 139.4, 135.9, 135.7, 135.3, 132.9, 128.8, 128.6, 128.5, 128.3, 128.2, 128.1, 127.9, 67.1, 52.8, 52.5, 43.5, 42.8.

HRMS (ESI) Calcd for $C_{26}H_{27}N_2O_4S$ $[M+H]^+$ 463.1686, found 463.1686.

Benzyl 1,3-ditosyl-2,3,4,7-tetrahydro-1H-1,3-diazepine-5-carboxylate (5ah)



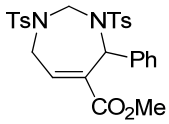
93% yield, 50.2 mg, slight yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 (d, J = 8.4 Hz, 4H), 7.43-7.35 (m, 5H), 7.22 (d, J = 8.0 Hz, 4H), 6.79 (t, J = 4.8 Hz, 1H), 5.16 (s, 2H), 4.86 (s, 2H), 4.15 (s, 2H), 4.05 (d, J = 4.8 Hz, 2H), 2.40 (s, 3H), 2.37 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 164.7, 144.1, 144.0, 138.6, 136.6, 136.3, 135.6, 131.9, 129.8, 129.8, 128.6, 128.4, 128.2, 126.8, 126.8, 66.8, 62.7, 44.9, 44.2, 21.5, 21.5.

HRMS (ESI) Calcd for $C_{27}H_{29}N_2O_6S_2$ $[M+H]^+$ 541.1462, found 541.1466.

Methyl (R)-4-phenyl-1,3-ditosyl-2,3,4,7-tetrahydro-1H-1,3-diazepine-5-carboxylate (5bh)



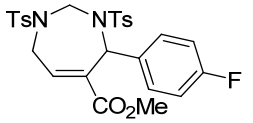
64% yield, 34.6 mg, white foam.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (d, *J* = 8.0 Hz, 2H), 7.54 (d, *J* = 8.4 Hz, 2H), 7.33-7.26 (m, 7H), 7.13 (dd, *J* = 6.4, 3.6 Hz, 1H), 7.07-7.03 (m, 2H), 6.34 (s, 1H), 4.98 (d, *J* = 11.2 Hz, 1H), 4.23 (d, *J* = 11.6 Hz, 1H), 4.08 (dd, *J* = 18.0, 6.8 Hz, 1H), 3.69-3.64 (m, 4H), 2.46 (s, 3H), 2.43 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 165.6, 144.1, 143.9, 139.2, 137.1, 135.3, 134.6, 134.3, 130.0, 129.8, 128.7, 128.4, 128.2, 127.1, 126.8, 59.2, 58.9, 52.3, 44.0, 21.6, 21.5.

HRMS (ESI) Calcd for $C_{27}H_{29}N_2O_6S_2$ $[M+H]^+$ 541.1462, found 541.1463.

Methyl (R)-4-(4-fluorophenyl)-1,3-ditosyl-2,3,4,7-tetrahydro-1H-1,3-diazepine-5-carboxylate (5ch)



79% yield, 44.1 mg, white foam.

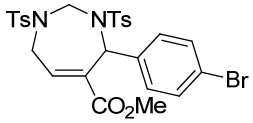
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69 (d, *J* = 8.4 Hz, 2H), 7.54 (d, *J* = 8.4 Hz, 2H), 7.33-7.28 (m, 4H), 7.12 (dd, *J* = 6.8, 3.2 Hz, 1H), 7.05-7.00 (m, 2H), 6.97-6.91 (m, 2H), 6.29 (s, 1H), 4.91 (d, *J* = 11.6 Hz, 1H), 4.24 (d, *J* = 12.0 Hz, 1H), 4.13 (dd, *J* = 18.0, 6.8 Hz, 1H), 3.69 (s, 3H), 3.61 (dd, *J* = 19.2, 4.0 Hz, 1H), 2.45 (s, 3H), 2.43 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 165.5, 162.5 (d, *J* = 246.3 Hz), 144.2, 144.0, 139.5, 137.1, 135.2, 134.1, 130.3 (d, *J* = 3.0 Hz), 130.1 (d, *J* = 8.4 Hz),, 130.0, 129.9, 127.0, 126.7, 115.7 (d, *J* = 21.5 Hz), 58.9, 58.6, 52.4, 43.9, 21.6, 21.5.

^{19}F NMR (376 MHz, $CDCl_3$): δ -113.1--113.3 (m).

HRMS (ESI) Calcd for $C_{27}H_{27}FN_2NaO_6S_2$ $[M+Na]^+$ 581.1187, found 581.1188.

Methyl (R)-4-(4-bromophenyl)-1,3-ditosyl-2,3,4,7-tetrahydro-1H-1,3-diazepine-5-carboxylate (5dh)



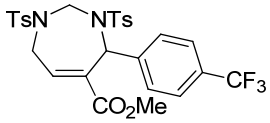
83% yield, 51.4 mg, slight yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69 (d, *J* = 8.4 Hz, 2H), 7.53 (d, *J* = 8.4 Hz, 2H), 7.38-7.34 (m, 2H), 7.32-7.28 (m, 4H), 7.12 (dd, *J* = 6.8, 3.6 Hz, 1H), 6.90 (d, *J* = 8.0 Hz, 2H), 6.26 (s, 1H), 4.94 (d, *J* = 11.6 Hz, 1H), 4.23 (d, *J* = 11.6 Hz, 1H), 4.12 (dd, *J* = 18.0, 6.8 Hz, 1H), 3.69 (s, 3H), 3.61 (dd, *J* = 18.0, 3.2 Hz, 1H), 2.45 (s, 3H), 2.43 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 165.4, 144.3, 144.1, 139.7, 137.0, 135.1, 133.7, 133.7, 131.9, 130.0, 129.9, 127.0, 126.7, 122.5, 58.9, 58.6, 52.4, 43.9, 21.6, 21.5.

HRMS (ESI) Calcd for $C_{27}H_{28}BrN_2O_6S_2$ $[M+H]^+$ 619.0567, found 619.0573.

Methyl (R)-1,3-ditosyl-4-(4-(trifluoromethyl)phenyl)-2,3,4,7-tetrahydro-1H-1,3-diazepine-5-carboxylate (5eh)



74% yield, 45.1 mg, slight yellow oil.

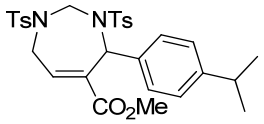
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71 (d, *J* = 8.4 Hz, 2H), 7.51 (dd, *J* = 8.0, 2.8 Hz, 4H), 7.33 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 8.4 Hz, 2H), 7.18-7.14 (m, 3H), 6.37 (s, 1H), 4.92 (d, *J* = 11.6 Hz, 1H), 4.24 (d, *J* = 11.6 Hz, 1H), 4.15 (dd, J = 18.4, 6.8 Hz, 1H), 3.70 (s, 3H), 3.61 (dd, *J* = 18.0, 2.8 Hz, 1H), 2.46 (s, 3H), 2.42 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 165.4, 144.4, 144.1, 140.1, 138.9, 136.9, 135.2, 133.4, 130.4 (d, *J* = 32.4 Hz), 130.0, 129.9, 128.5, 127.0, 126.7, 125.7 (q, *J* = 3.5 Hz), 123.8 (d, *J* = 270.8 Hz), 59.0, 58.6, 52.5, 44.1, 21.6, 21.5.

^{19}F NMR (376 MHz, $CDCl_3$): δ -62.6.

HRMS (ESI) Calcd for $C_{28}H_{28}F_3N_2O_6S_2$ $[M+H]^+$ 609.1335, found 609.1336.

Methyl (R)-4-(4-isopropylphenyl)-1,3-ditosyl-2,3,4,7-tetrahydro-1H-1,3-diazepine-5-carboxylate (5fh)



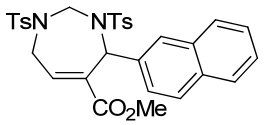
61% yield, 35.5 mg, slight yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (d, *J* = 8.0 Hz, 2H), 7.56 (d, *J* = 8.4 Hz, 2H), 7.32-7.28 (m, 4H), 7.12-7.08 (m, 3H), 6.93 (d, *J* = 8.0 Hz, 2H), 6.29 (s, 1H), 5.04 (d, *J* = 11.6 Hz, 1H), 4.21 (d, *J* = 11.6 Hz, 1H), 4.05 (dd, *J* = 17.6, 6.8 Hz, 1H), 3.72 (dd, *J* = 17.6, 3.6 Hz, 1H), 3.68 (s, 3H), 2.89-2.81 (m, 1H), 2.45 (s, 3H), 2.43 (s, 3H), 1.20 (d, *J* = 6.8 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 165.7, 149.0, 144.0, 143.8, 138.8, 137.2, 135.4, 134.6, 131.7, 129.9, 129.8, 128.1, 127.2, 126.9, 126.8, 59.2, 58.8, 52.3, 43.8, 33.6, 23.8, 23.8, 21.6, 21.5.

HRMS (ESI) Calcd for $C_{30}H_{35}N_2O_6S_2$ $[M+H]^+$ 583.1931, found 583.1931.

Methyl (R)-4-(naphthalen-2-yl)-1,3-ditosyl-2,3,4,7-tetrahydro-1H-1,3-diazepine-5-carboxylate (5gh)



76% yield, 44.9 mg, slight yellow oil.

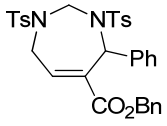
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80-7.69 (m, 5H), 7.50-7.45 (m, 5H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.22-7.15 (m, 4H), 6.51 (s, 1H), 5.10 (d, *J* = 11.6 Hz, 1H), 4.17 (d, *J* = 12.0

Hz, 1H), 4.05 (dd, *J* = 17.6, 6.4 Hz, 1H), 3.75 (dd, *J* = 18.0, 4.0 Hz, 1H), 3.69 (s, 3H), 2.48 (s, 3H), 2.38 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 165.7, 144.2, 143.9, 139.4, 137.1, 135.2, 134.3, 133.0, 133.0, 131.9, 129.9, 129.8, 128.8, 128.2, 127.8, 127.5, 127.3, 126.8, 126.5, 126.3, 125.6, 59.4, 59.2, 52.4, 44.1, 21.6, 21.5.

HRMS (ESI) Calcd for $C_{31}H_{31}N_2O_6S_2$ $[M+H]^+$ 591.1618, found 591.1619.

Benzyl (R)-4-phenyl-1,3-ditosyl-2,3,4,7-tetrahydro-1H-1,3-diazepine-5-carboxylate (5hh)



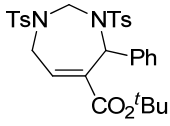
76% yield, 46.9 mg, colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 (d, *J* = 8.0 Hz, 2H), 7.54 (d, *J* = 8.0 Hz, 2H), 7.33-7.26 (m, 8H), 7.22 (d, *J* = 8.4 Hz, 2H), 7.21-7.15 (m, 2H), 7.14 (dd, *J* = 6.8, 3.6 Hz, 1H), 7.09-7.06 (m, 2H), 6.40 (s, 1H), 5.17 (d, *J* = 12.4 Hz, 1H), 5.08 (d, *J* = 12.4 Hz, 1H), 5.01 (d, *J* = 11.6 Hz, 1H), 4.24 (d, *J* = 11.2 Hz, 1H), 4.05 (dd, *J* = 17.6, 6.4 Hz, 1H), 3.66 (dd, *J* = 18.0, 3.6 Hz, 1H), 2.42 (s, 3H), 2.42 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 164.9, 144.0, 143.9, 139.3, 137.1, 135.5, 135.2, 134.6, 134.3, 130.0, 129.7, 128.7, 128.5, 128.4, 128.3, 128.2, 127.9, 127.1, 126.8, 66.9, 59.3, 59.0, 44.0, 21.5, 21.5.

HRMS (ESI) Calcd for $C_{33}H_{33}N_2O_6S_2$ $[M+H]^+$ 617.1775, found 617.1776.

Tert-butyl (R)-4-phenyl-1,3-ditosyl-2,3,4,7-tetrahydro-1H-1,3-diazepine-5-carboxylate (5ih)



80% yield, 46.6mg, slight yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (d, *J* = 8.4 Hz, 2H), 7.54 (d, *J* = 8.4 Hz, 2H), 7.30-7.24 (m, 7H), 7.07-7.04 (m, 2H), 6.98 (dd, *J* = 6.4, 4.0 Hz, 1H), 6.30 (s, 1H), 5.01 (d, *J* = 11.6 Hz, 1H), 4.20 (d, *J* = 11.6 Hz, 1H), 3.99 (dd, *J* = 17.6, 6.8 Hz, 1H), 3.63 (dd, *J* = 17.6, 3.6 Hz, 1H), 2.43 (s, 3H), 2.41 (s, 3H), 1.34 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 164.2, 144.0, 143.9, 137.5, 137.2, 135.8, 135.3, 135.1, 130.0, 129.7, 128.6, 128.2, 128.1, 127.2, 126.8, 81.5, 59.3, 59.0, 43.9, 27.8, 21.6, 21.5.

HRMS (ESI) Calcd for $C_{30}H_{35}N_2O_6S_2$ $[M+H]^+$ 583.1931, found 583.1938.

5. Possible Mechanism

A possible mechanism for these phosphine-catalyzed annulations is depicted in Figure S1. β-Addition of the nucleophilic phosphine to the β'-acetoxy allenoate and departure of the OAc group generates activated buta-1,3-diene intermediate **A**. Next, the N,N-dinucleophile can add to the olefin moiety containing β-carbon, furnishing **B**. Finally, intramolecular addition of another N-nucleophile to the other olefin affords intermediate **C**, which then undergoes elimination to provide the cycloaddition product and regenerate the phosphine catalyst.

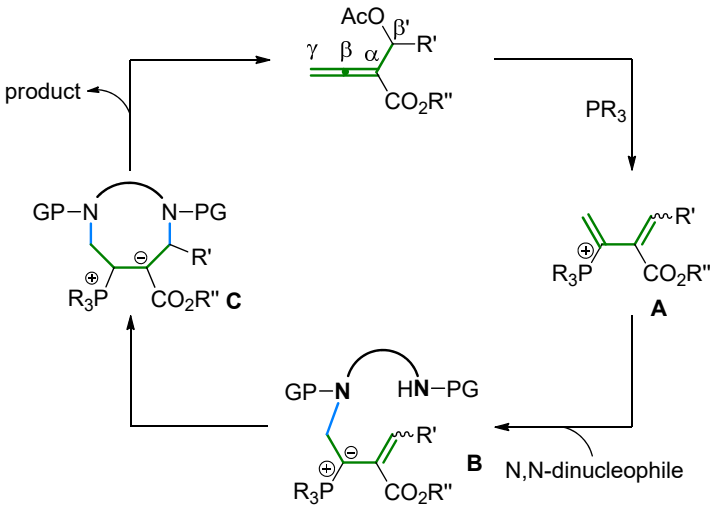
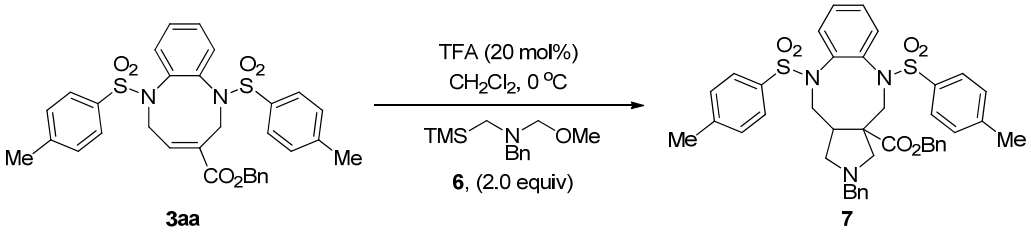


Figure S1. Possible Mechanism

6. Synthetic Transformation



3aa **7**

The product **3aa** (60.2 mg, 0.1 mmol; 1.0 equiv) was added to a dried 10 mL reaction tube, which was filled with nitrogen. Then CH_2Cl_2 (1.0 mL) and the compound **6** (52μL, 0.2 mmol; 2.0 equiv) were added. The resulting mixture was cooled to 0 °C, and then trifluoroacetic acid (1.5 μL, 0.02 mmol; 0.2 equiv) was added to the stirred mixture. After the mixture was stirred at 0 °C for 3 h, the reaction mixture was diluted with CH_2Cl_2 (3 mL) and quenched by the addition of saturated aqueous $NaHCO_3$ (2.0 mL). The organic phase was separated and aqueous phase was extracted with CH_2Cl_2 (3×20 mL). Combined the organic layers, which was dried over anhydrous Na_2SO_4 and concentrated under reduce pressure. The residue was purified by silica gel column chromatography (petroleum ether / ethyl acetate) to afford colorless oil **7** (45.6 mg, 62% yield).

Benzyl 2-benzyl-5,10-ditosyl-2,3,3a,4,5,10,11,11a-octahydro-1H-benzo[b]pyrrolo[3,4-f][1,4]diazocine-3a-carboxylate (7)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (d, *J* = 8.4 Hz, 2H), 7.78 (d, *J* = 8.0 Hz, 2H), 7.45-7.26 (m, 15H), 7.22-7.19 (m, 2H), 7.09-7.04 (m, 1H), 5.11 (d, *J* = 12.4 Hz, 1H), 4.90 (d, *J* = 12.0 Hz, 1H), 4.41 (d, *J* = 12.0 Hz, 1H), 4.23 (d, *J* = 11.6 Hz, 1H), 3.99-3.84 (m, 1H), 3.53 (s, 2H), 3.34-3.21 (m, 1H), 3.07-2.92 (m, 2H), 2.75-2.64 (m, 1H), 2.53-2.40 (m, 7H), 2.13-2.01 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 172.6, 143.8, 143.7, 137.3, 135.7, 135.5, 135.4, 134.6, 131.5, 129.7, 129.6, 128.9, 128.4, 128.3, 128.3, 128.2, 128.1, 128.0, 127.8, 127.1, 67.0, 61.7, 59.0, 57.6, 54.6, 50.6, 50.2, 37.1, 21.5.

HRMS (ESI) Calcd for $C_{41}H_{42}N_3O_6S_2$ $[M+H]^+$ 736.2510, found 736.2516.

7. Screening of Biological Activity

Cell lines and cell culture

HCT116（human colorectal cancer cell line）、A549（human non-small cell lung cancer cell line）and HepG2 (human hepatocellular carcinoma cell line) cells were purchased from the Shanghai Cell Bank, Chinese Academy of Sciences (Shanghai, China). HCT116, A549 and HepG2 cells were respectively cultured in McCoy's 5A, RPMI-1640 and DMEM medium, supplemented with 10% fetal bovine serum (FBS) and 1% penicillin-streptomycin, and were incubated at 37℃ in a humidified atmosphere containing 5% CO_2.

Cell viability assay

Cell viability was assessed by Cell counting kit-8 (CCK-8) assay (PROTRINBIO, Nanjing, China). Cancer cells (HCT116, A549 and HepG2) were respectively seeded in 96-well plates with 5000 cells per well, and placed in a 37°C, 5% CO_2 cell incubator. After 8h, different concentrations of test compounds were added to the plates and the plates were incubated at 37°C for 48h. After incubation, the old solution was removed, 100μL 10% CCK-8 reagent was added to each well, and then the plates were incubated for another 2h. The optical density (OD) value was measured at 450 nm using a microplate reader. The cytotoxic activity was expressed as the IC_{50} values.

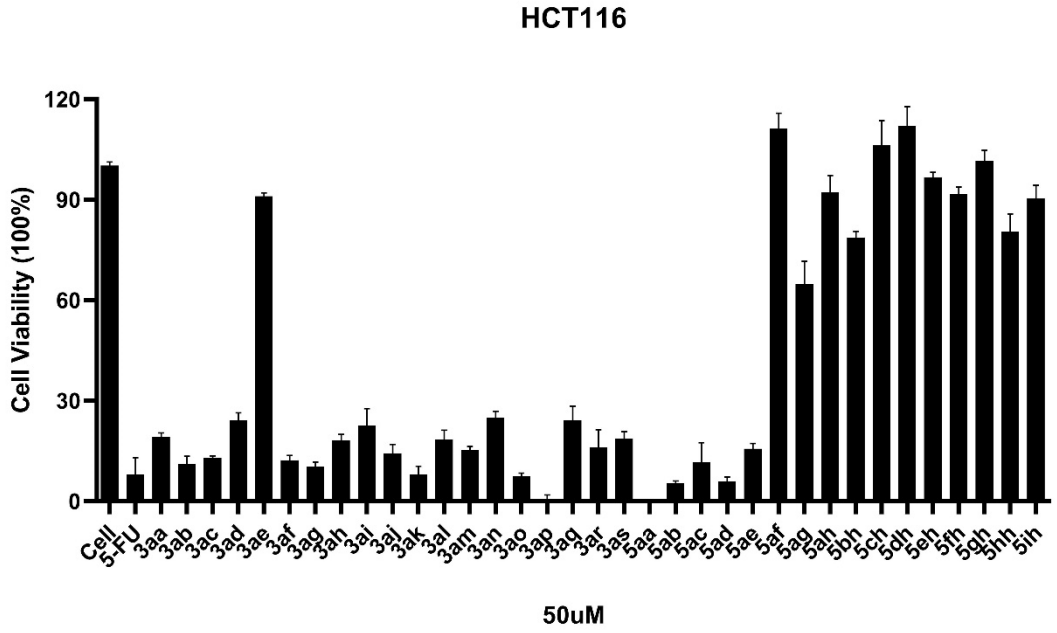


Figure S2. Mean ± standard error of the mean (SEM) of relative cell viability of HCT116 cells after treatment with 5-FU and different doses of obtained products

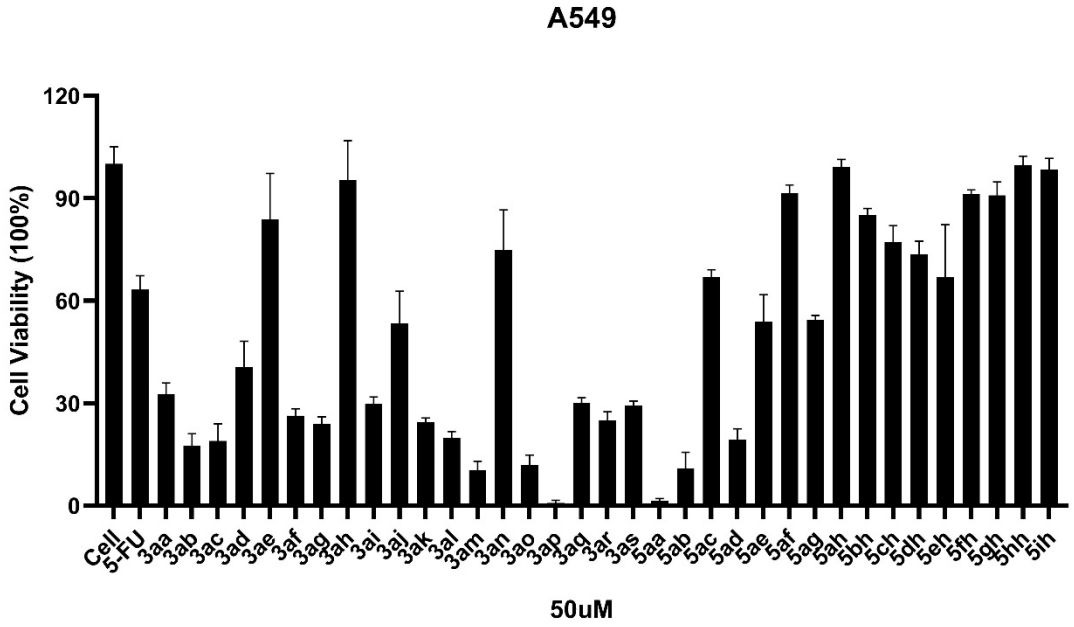


Figure S3. Mean ± standard error of the mean (SEM) of relative cell viability of A549 cells after treatment with 5-FU and different doses of obtained products

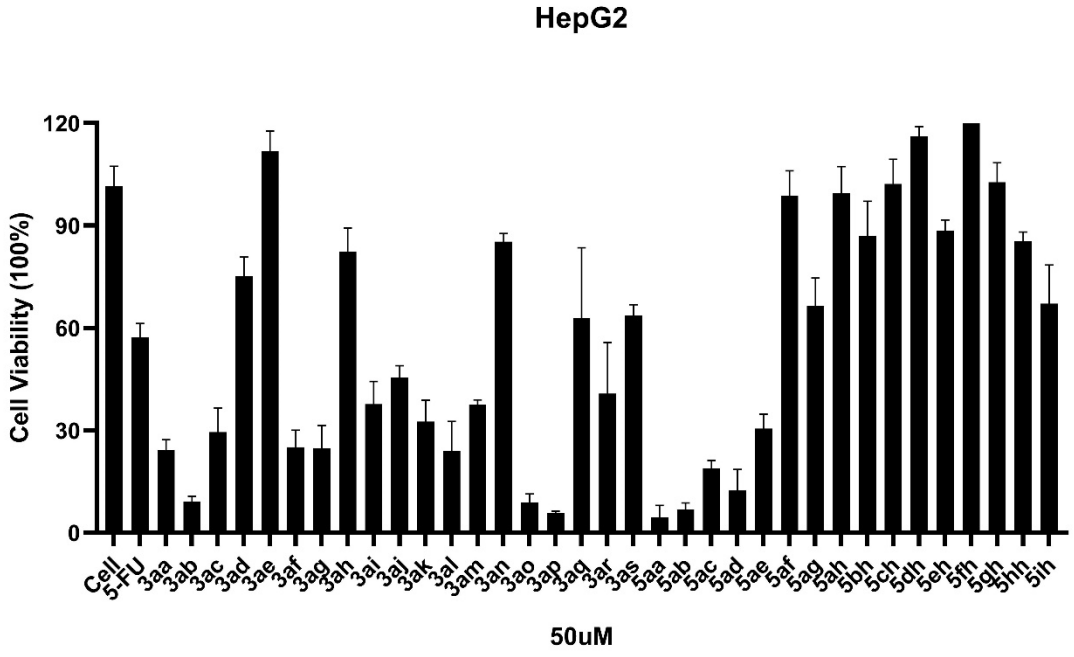
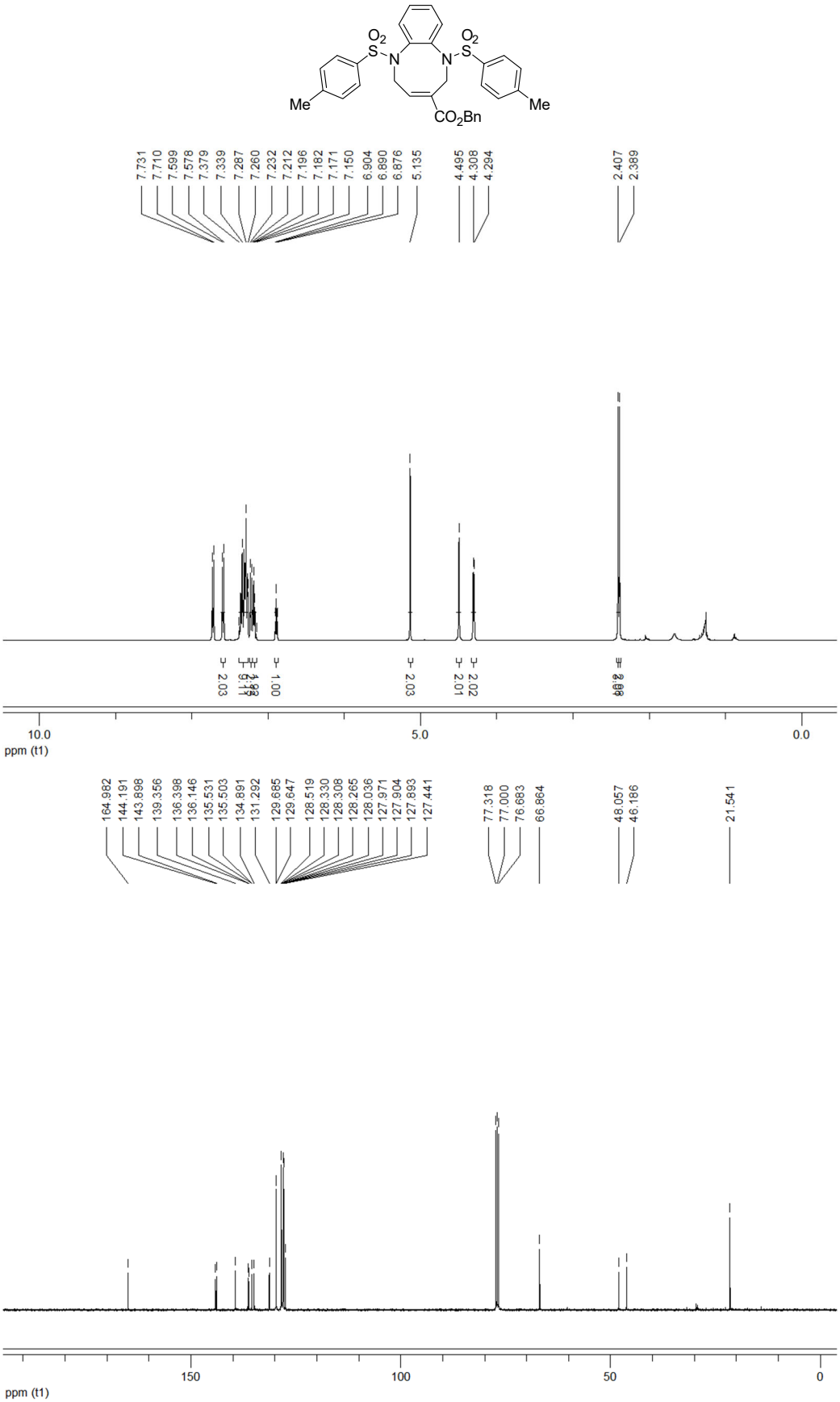


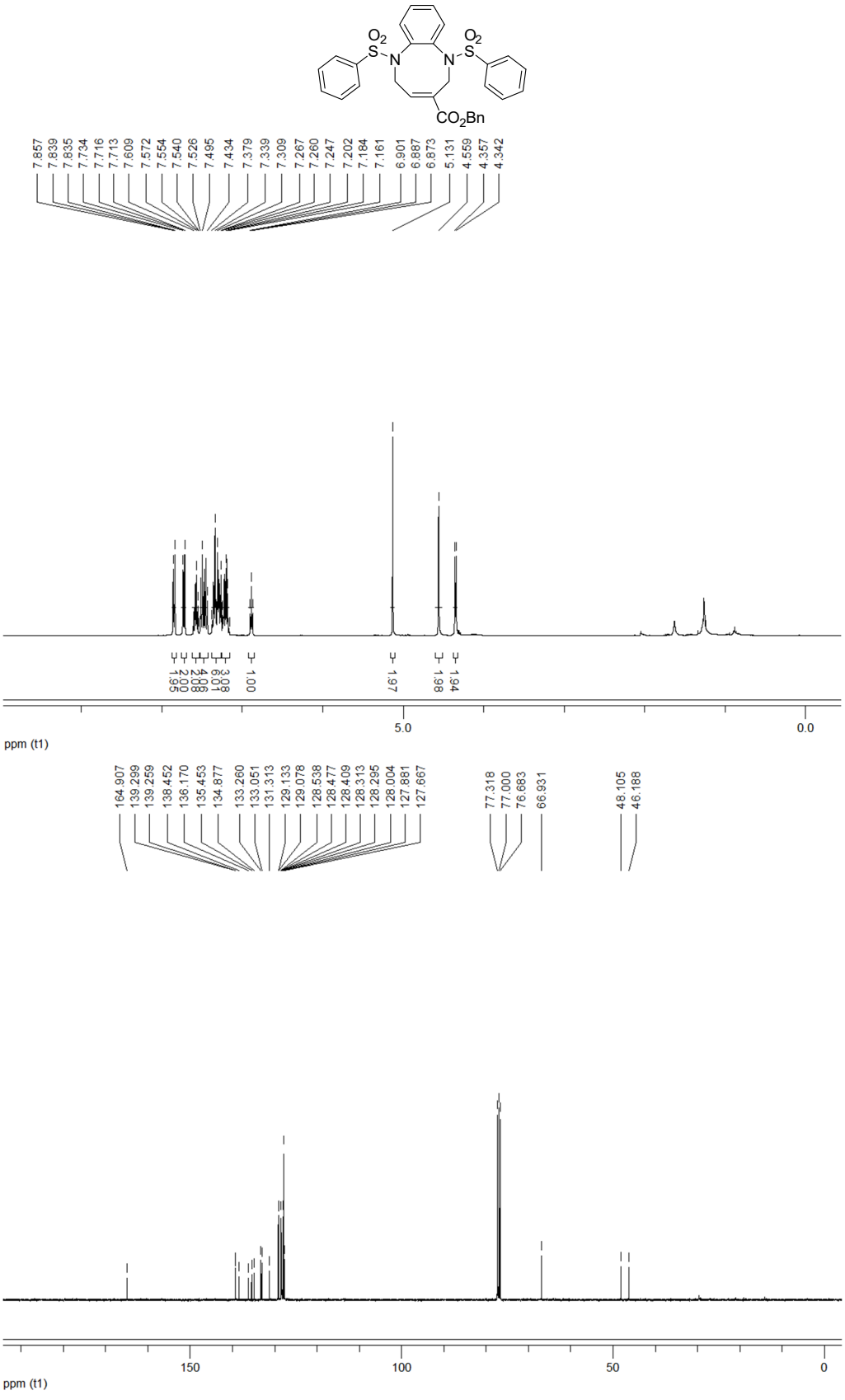
Figure S4. Mean ± standard error of the mean (SEM) of relative cell viability of HepG2 cells after treatment with 5-FU and different doses of obtained products

8. NMR Spectra

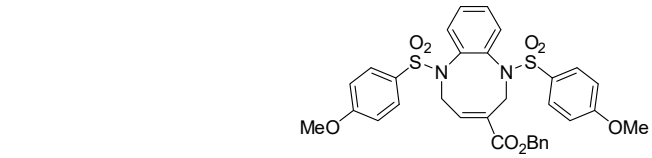
^{1}H NMR (400 MHz, $CDCl_3$), and ^{13}C NMR (100MHz, $CDCl_3$) of 3aa

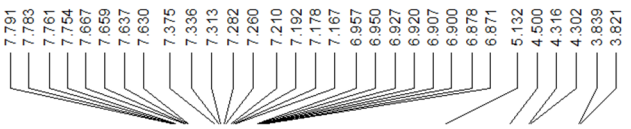


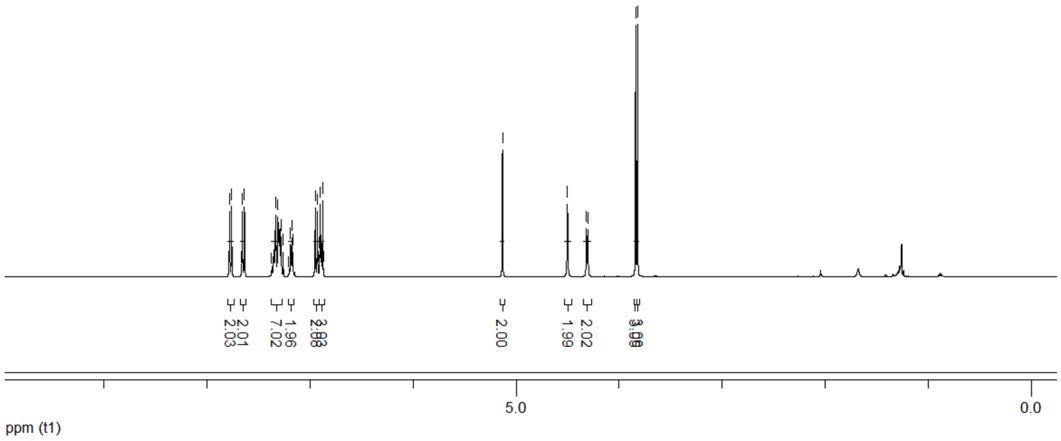
^{1}H NMR (400 MHz, $CDCl_3$), and ^{13}C NMR (100MHz, $CDCl_3$) of 3ab

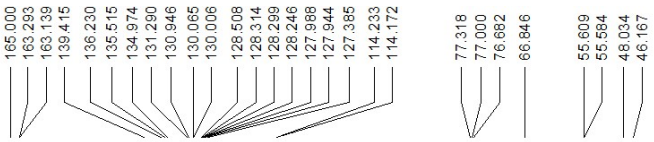


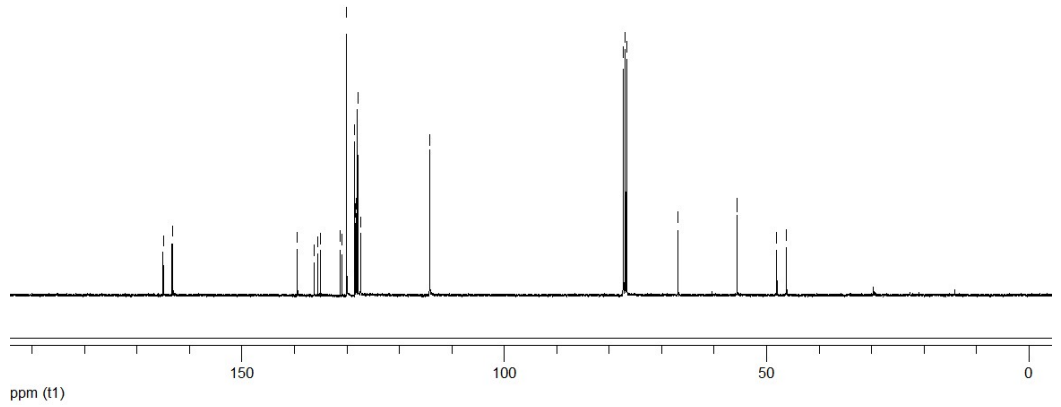
^{1}H NMR (400 MHz, $CDCl_3$), and ^{13}C NMR (100MHz, $CDCl_3$) of 3ac



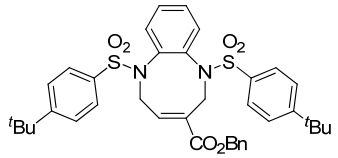


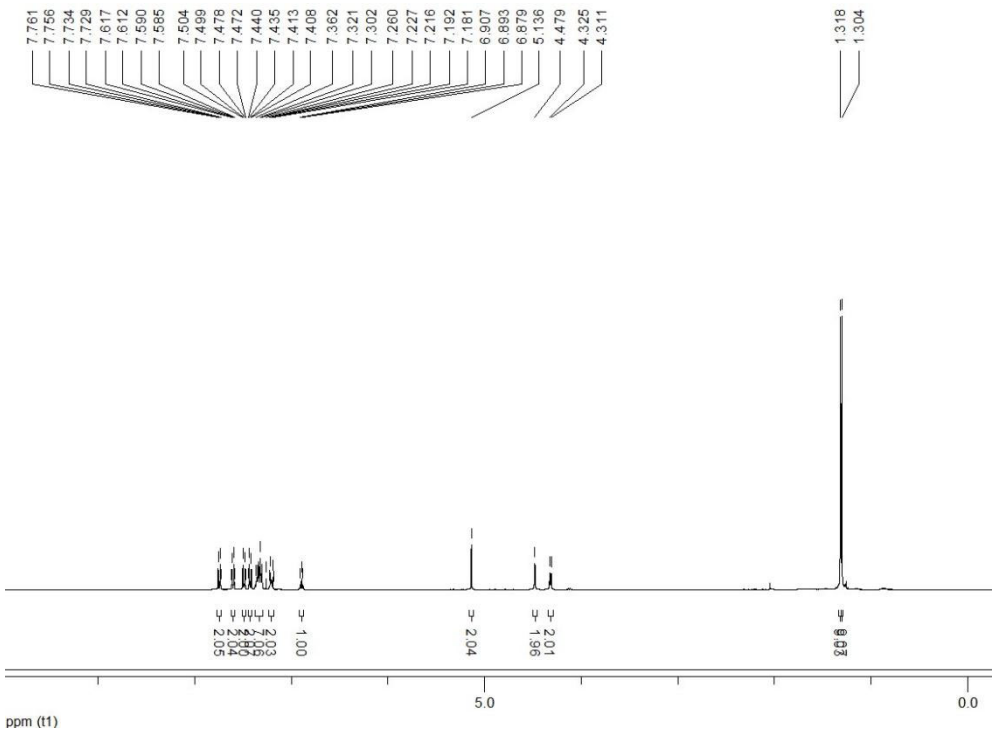


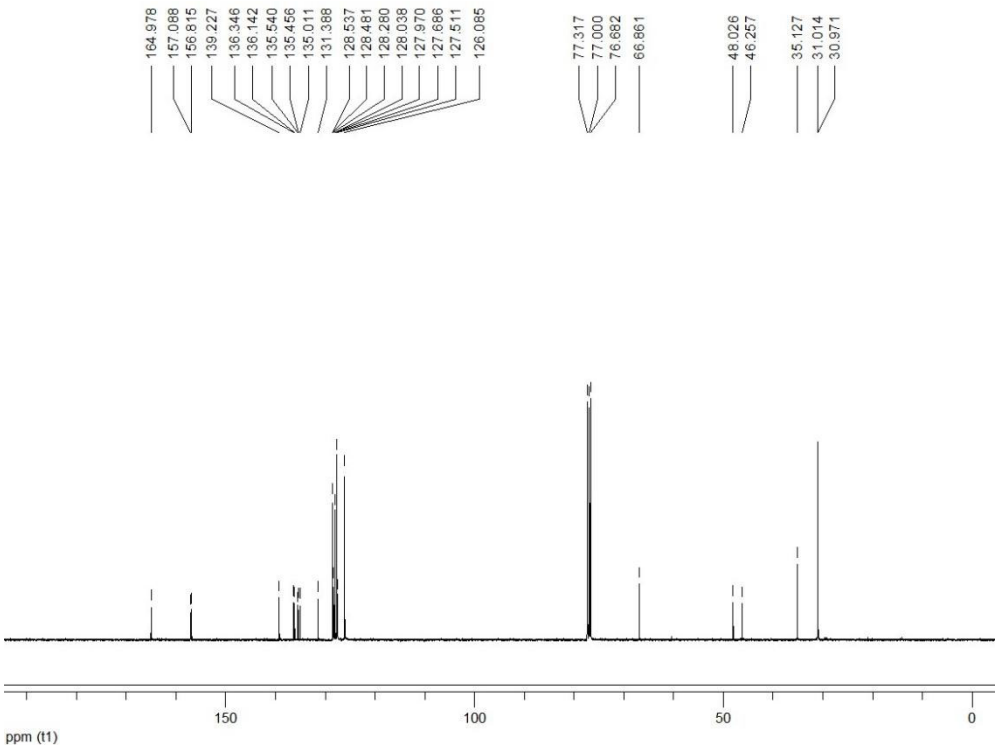




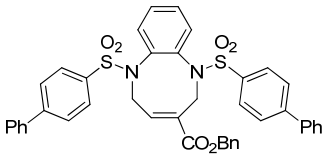
^{1}H NMR (400 MHz, $CDCl_3$), and ^{13}C NMR (100MHz, $CDCl_3$) of 3ad

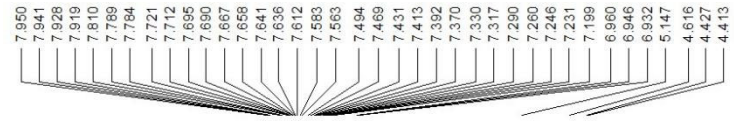


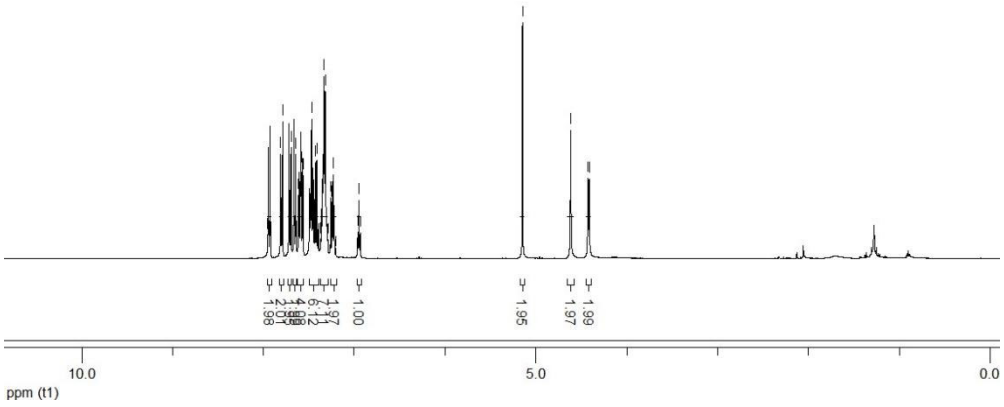


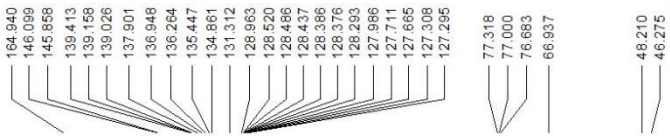


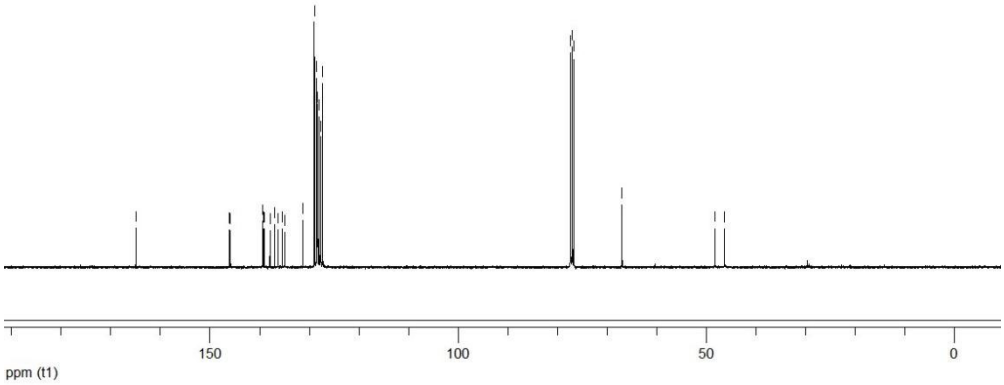
^{1}H NMR (400 MHz, $CDCl_3$), and ^{13}C NMR (100MHz, $CDCl_3$) of 3ae



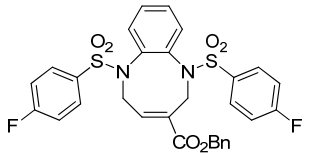


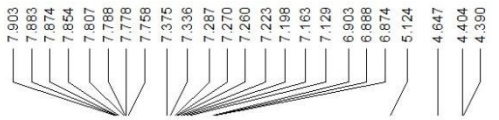


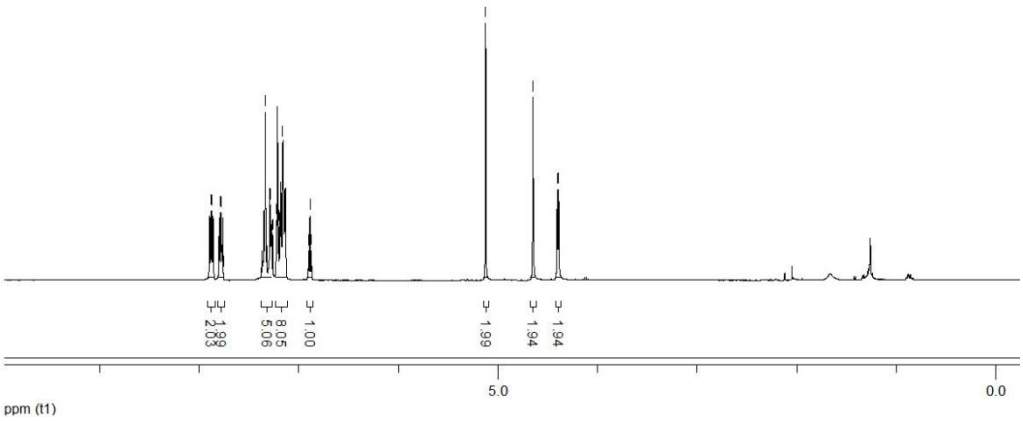


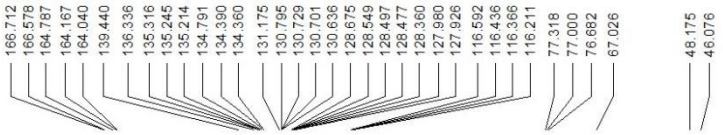


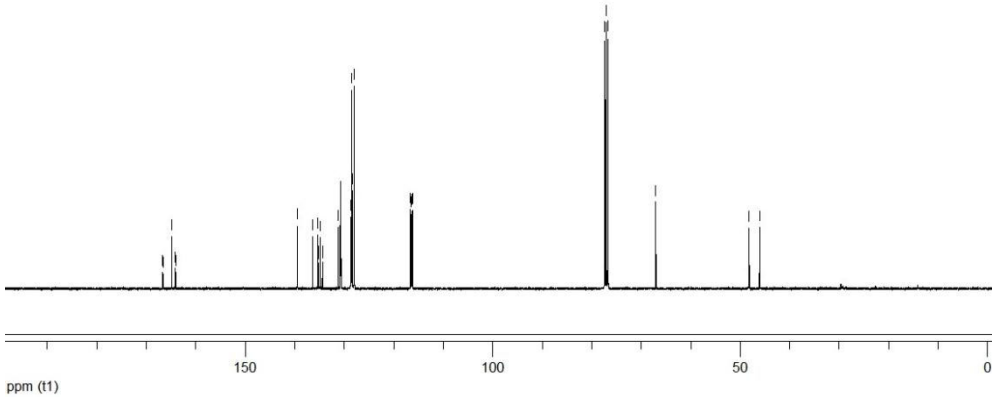
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100MHz, $CDCl_3$), and ^{19}F NMR (376 MHz, $CDCl_3$) of 3af

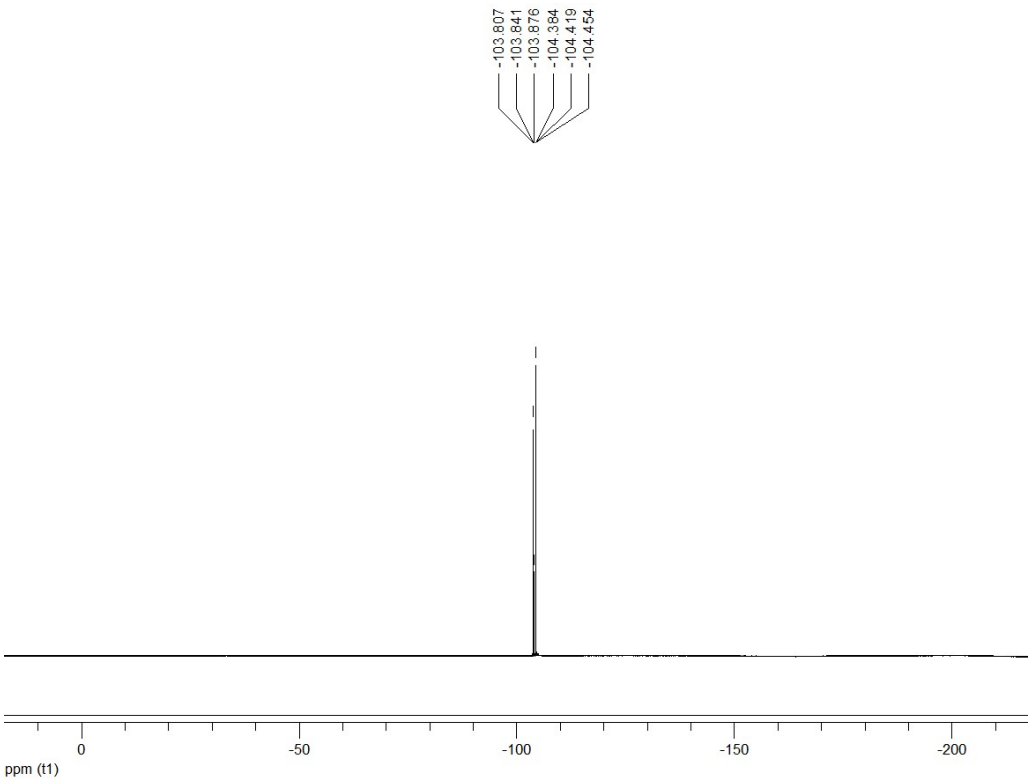




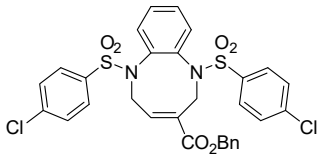


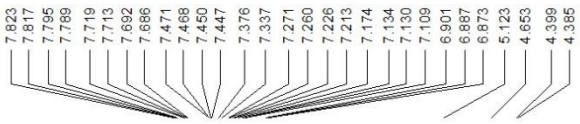


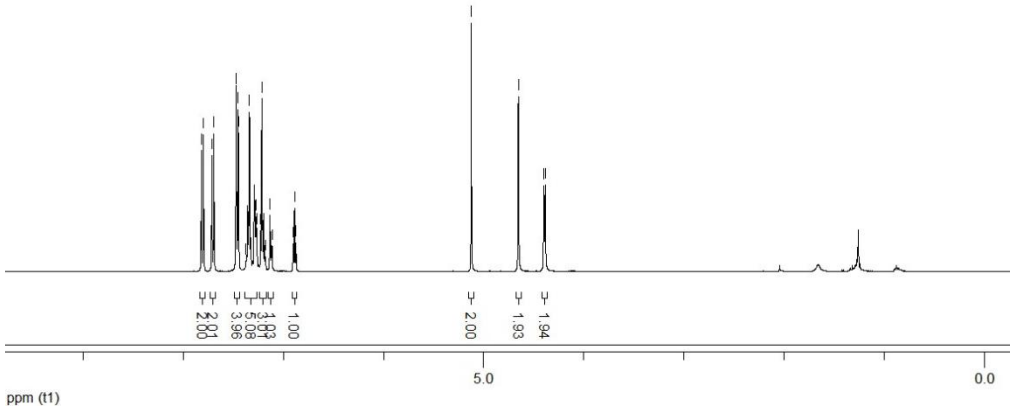


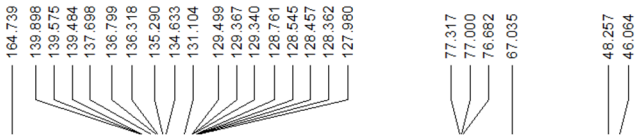

-103.807
-103.841
-103.876
-104.384
-104.419
-104.454
0
-50
-100
-150
-200
ppm (t1)

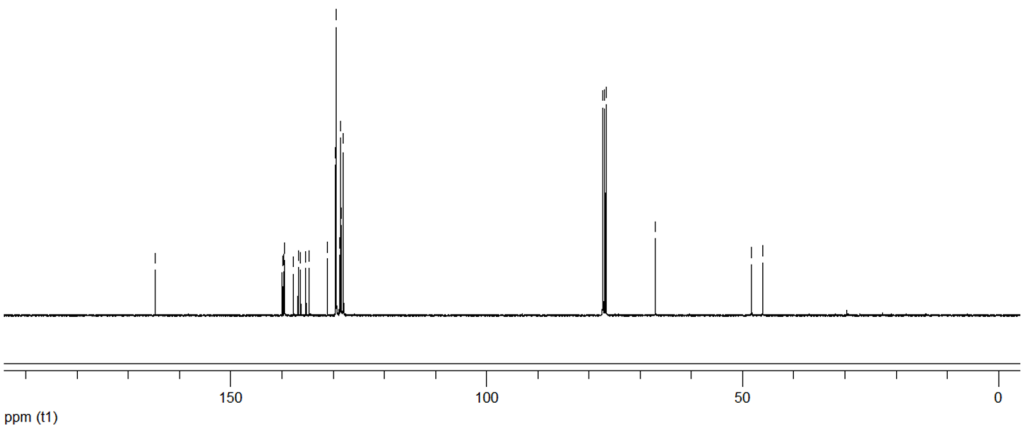
^{1}H NMR (400 MHz, $CDCl_3$), and ^{13}C NMR (100MHz, $CDCl_3$) of 3ag



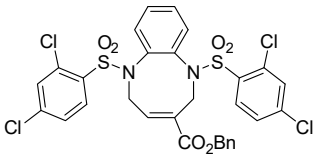


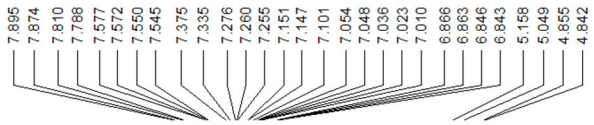


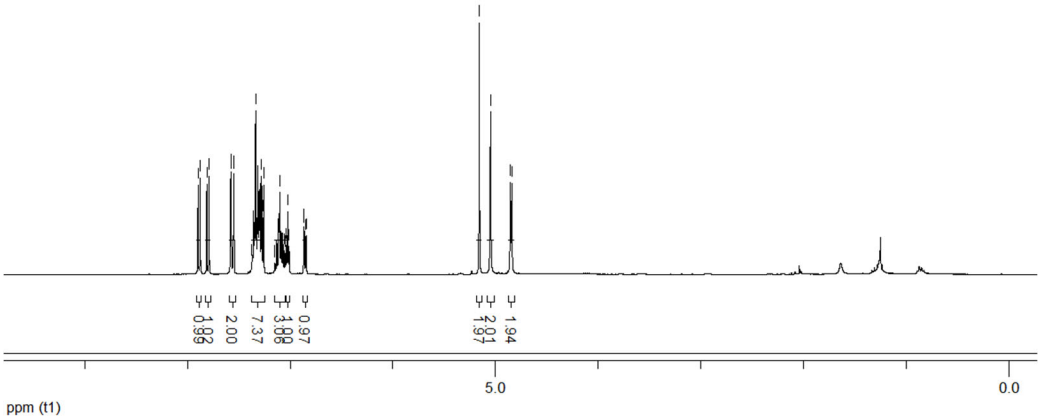


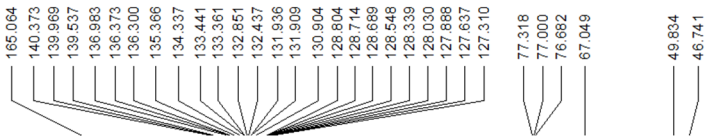


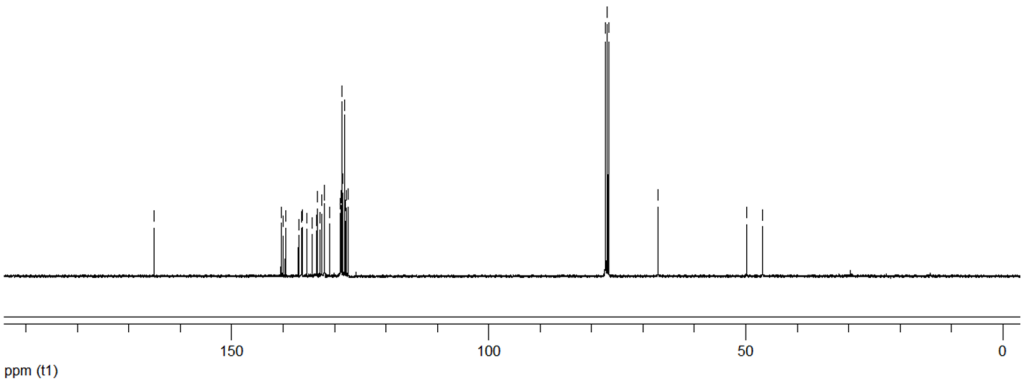
^{1}H NMR (400 MHz, $CDCl_3$), and ^{13}C NMR (100MHz, $CDCl_3$) of 3ah



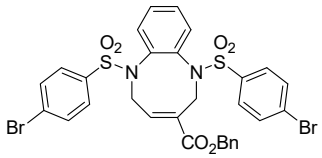


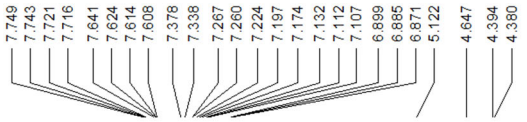


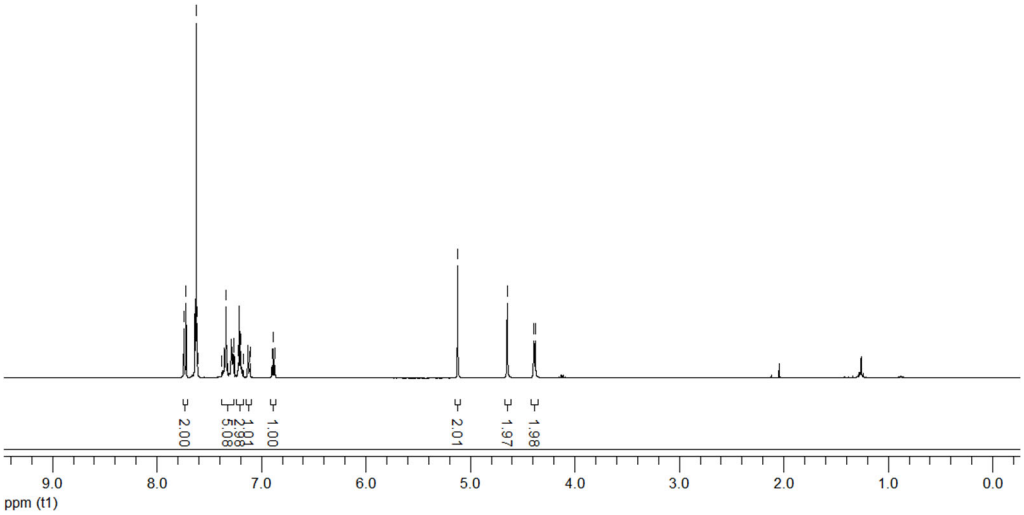


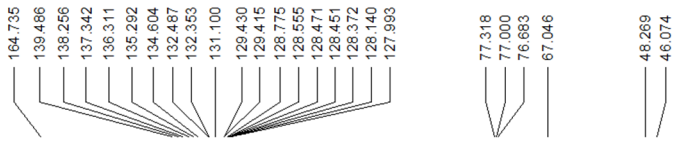


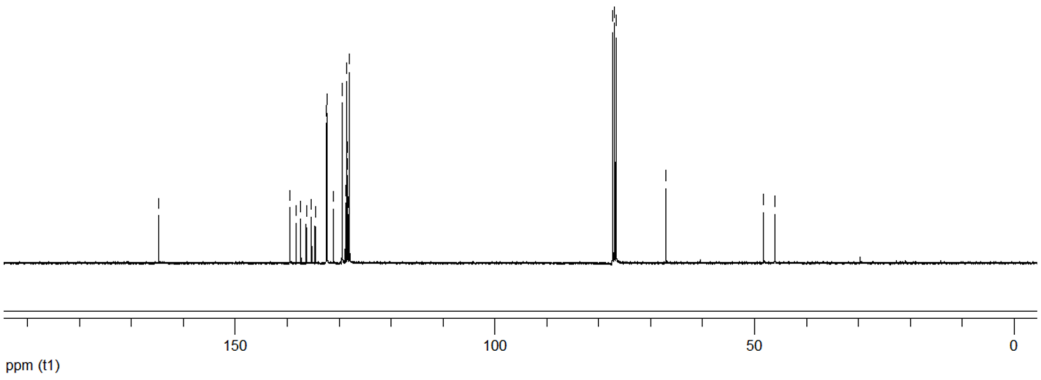
^{1}H NMR (400 MHz, $CDCl_3$), and ^{13}C NMR (100MHz, $CDCl_3$) of 3ai



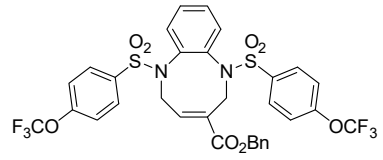


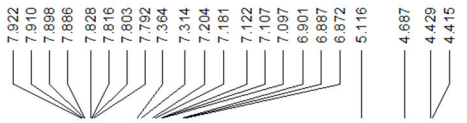


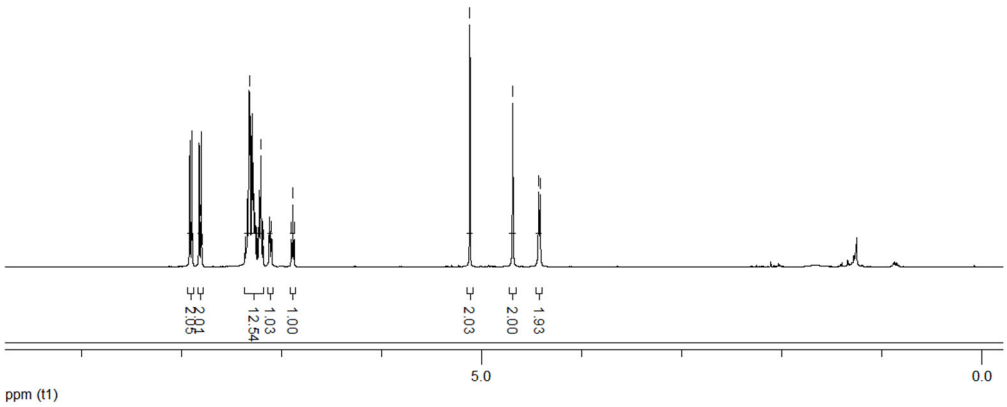


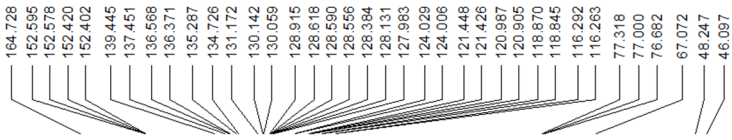


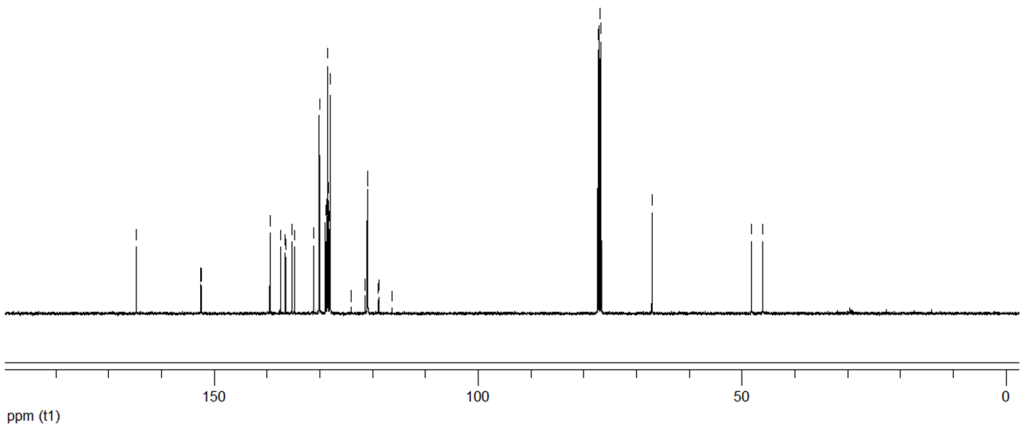
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100MHz, $CDCl_3$), and ^{19}F NMR (376 MHz, $CDCl_3$) of 3aj

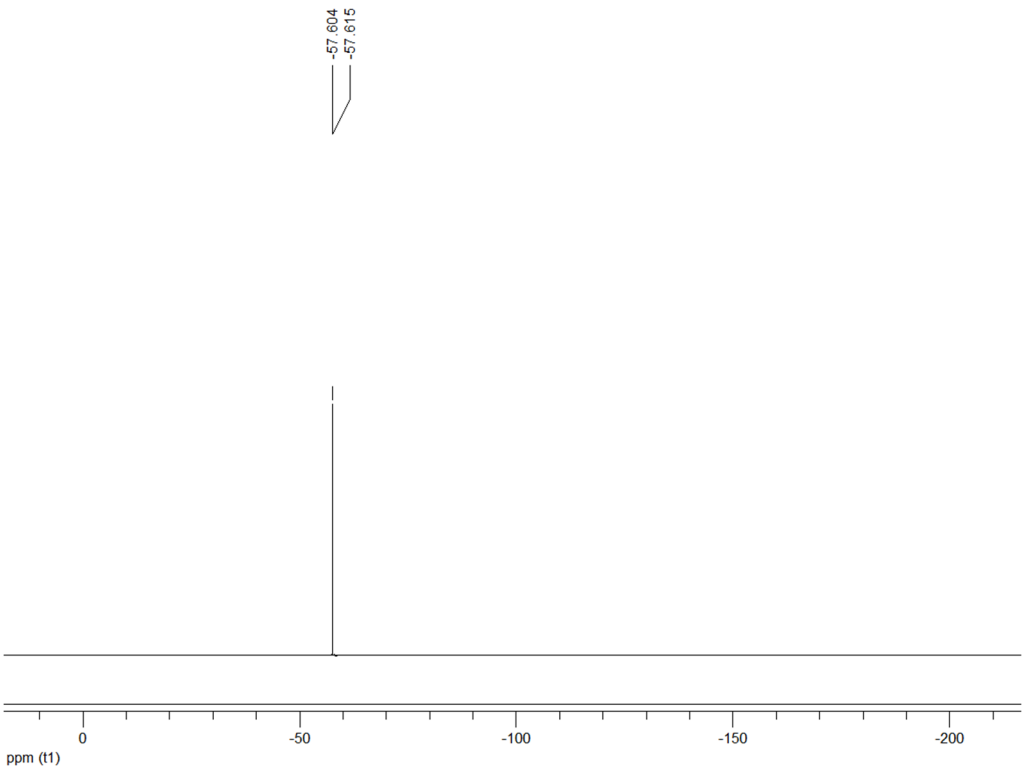




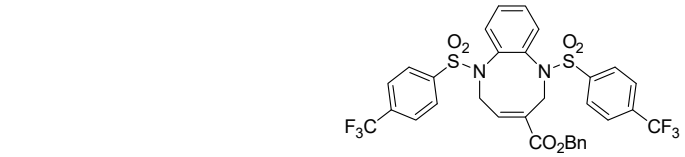


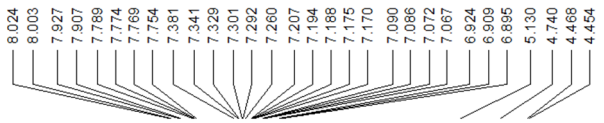


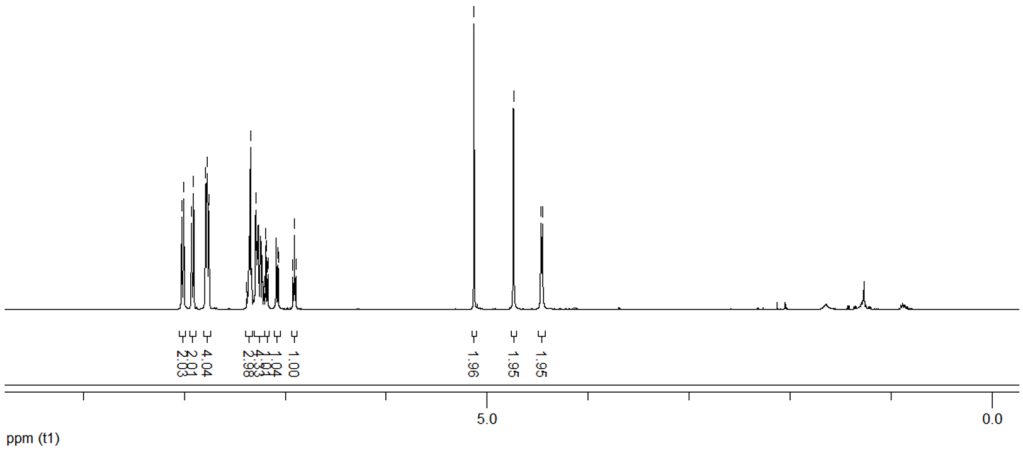


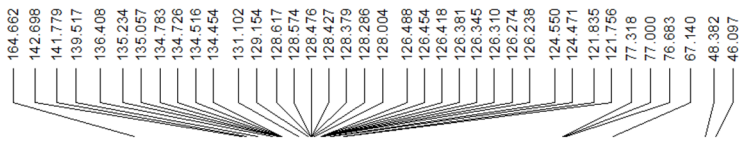

-57.604
-57.615
0
-50
-100
-150
-200
ppm (t1)

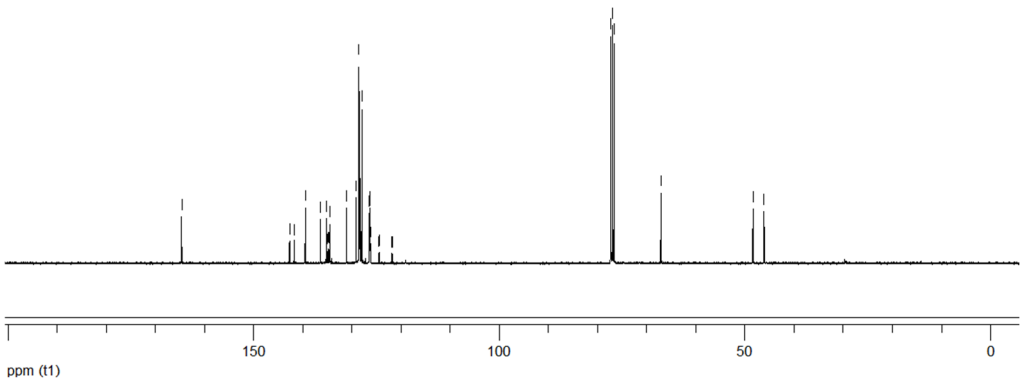
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100MHz, $CDCl_3$), and ^{19}F NMR (376 MHz, $CDCl_3$) of 3ak

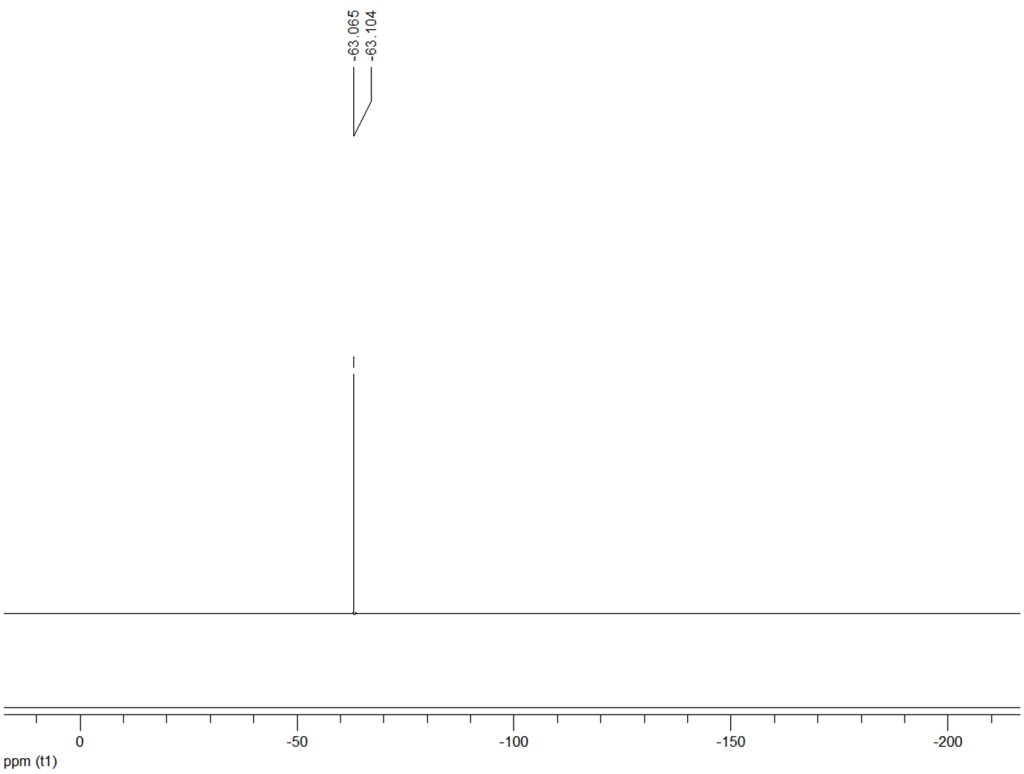




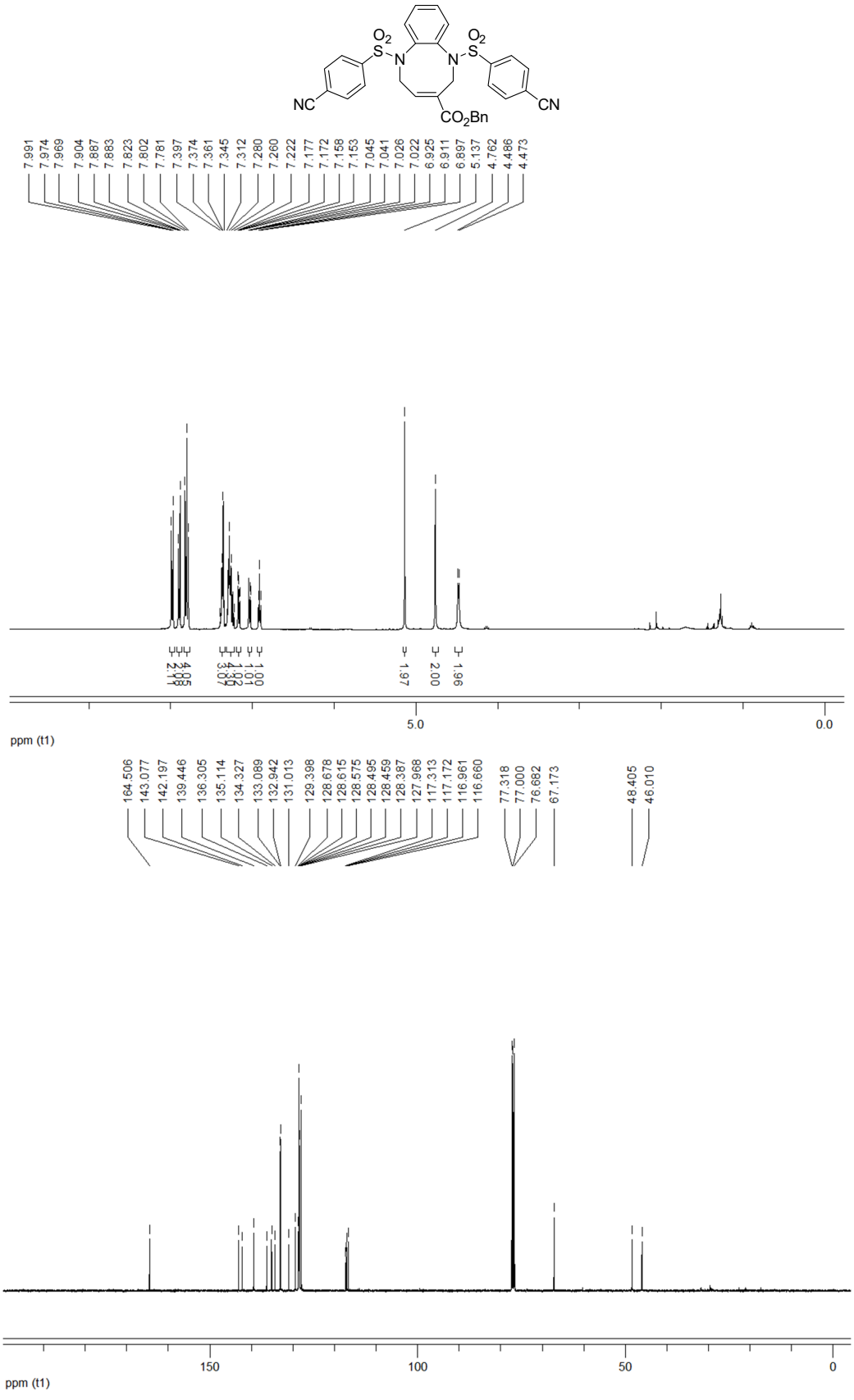




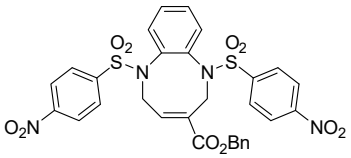


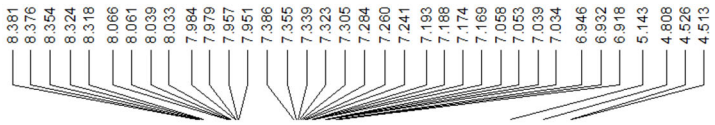

-63.065
-63.104
0
-50
-100
-150
-200
ppm (t1)

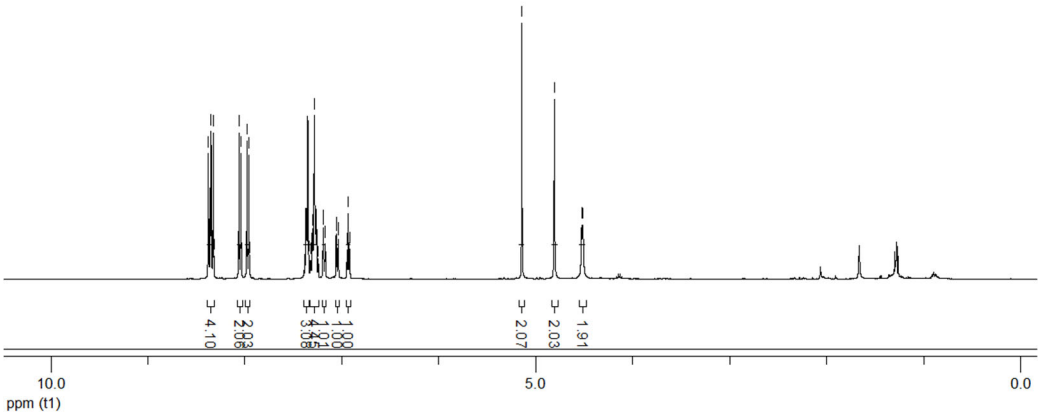
^{1}H NMR (400 MHz, $CDCl_3$), and ^{13}C NMR (100MHz, $CDCl_3$) of 3al

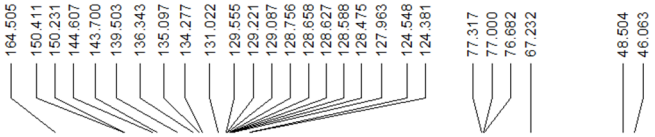


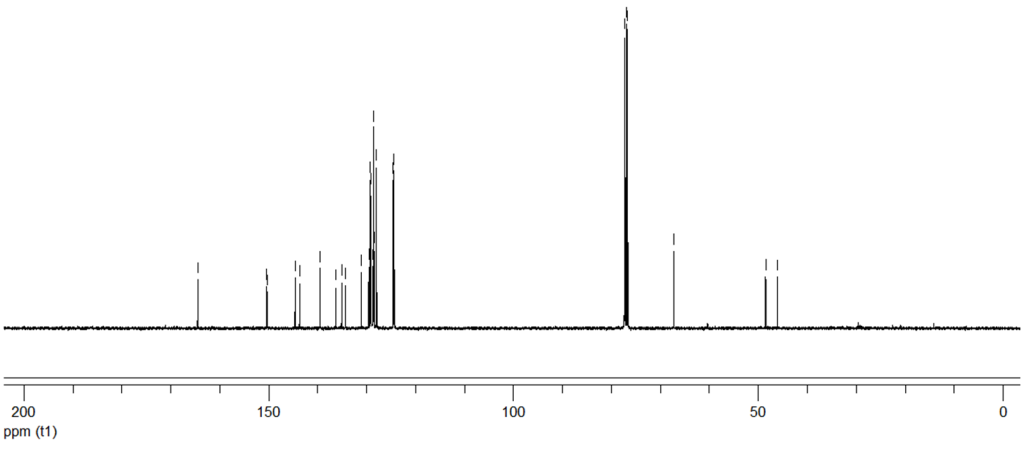
^{1}H NMR (400 MHz, $CDCl_3$), and ^{13}C NMR (100MHz, $CDCl_3$) of 3am



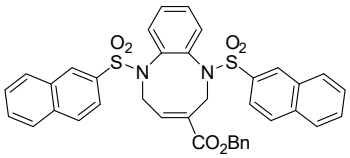


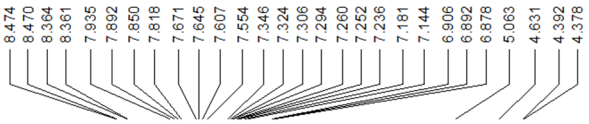


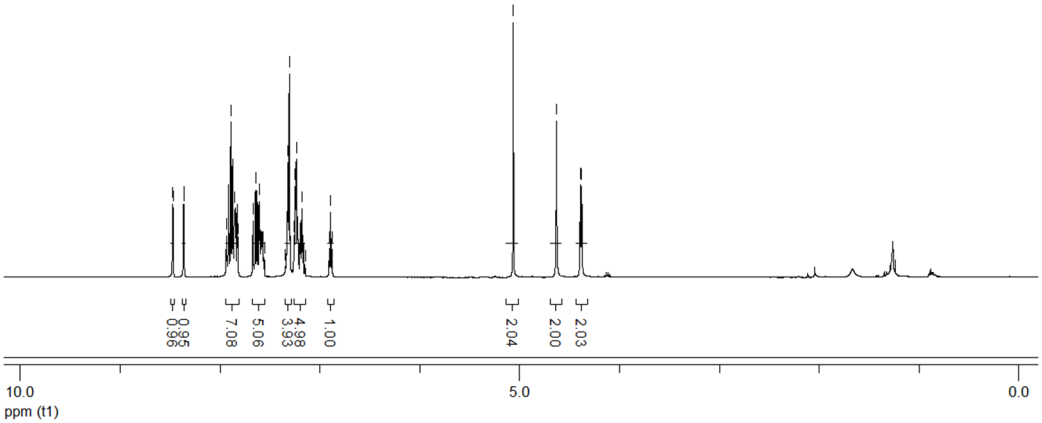


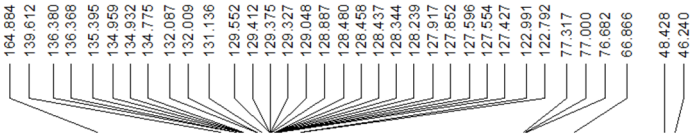


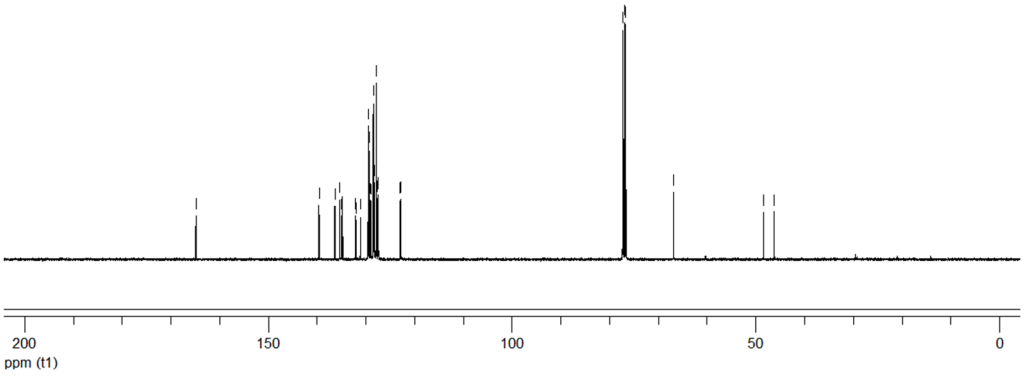
^{1}H NMR (400 MHz, $CDCl_3$), and ^{13}C NMR (100MHz, $CDCl_3$) of 3an



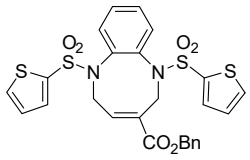


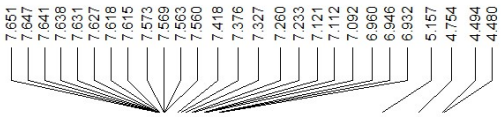


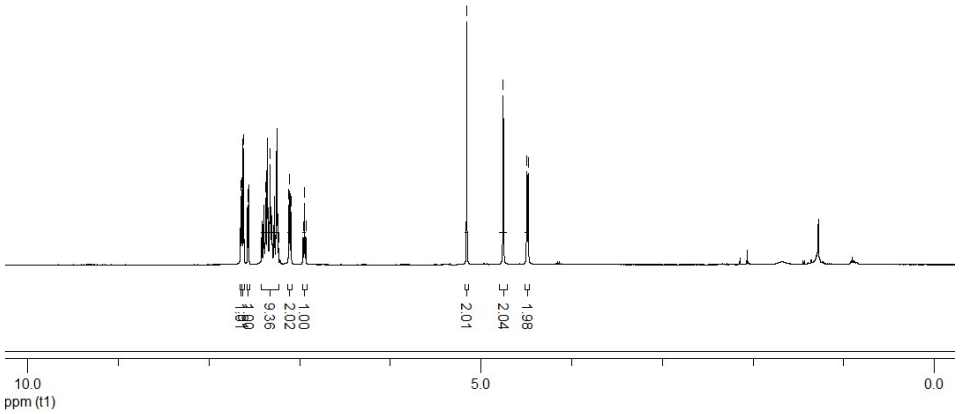


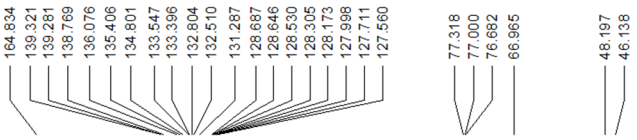


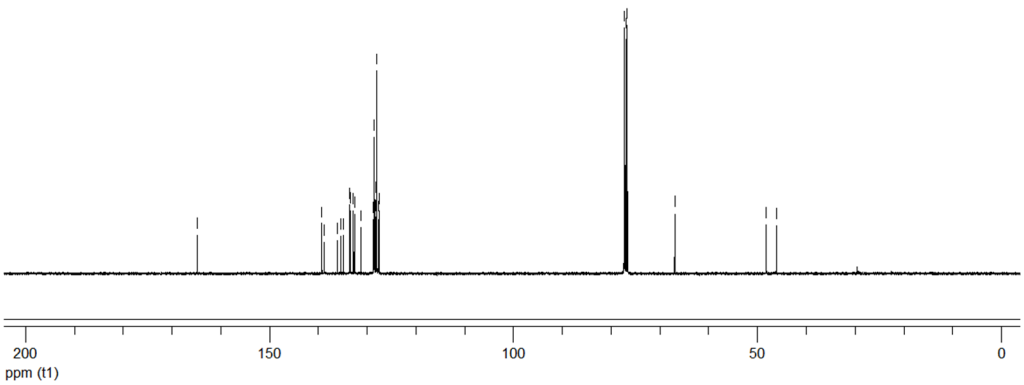
^{1}H NMR (400 MHz, $CDCl_3$), and ^{13}C NMR (100MHz, $CDCl_3$) of 3ao



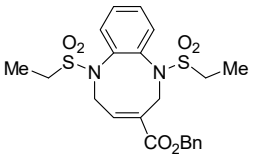


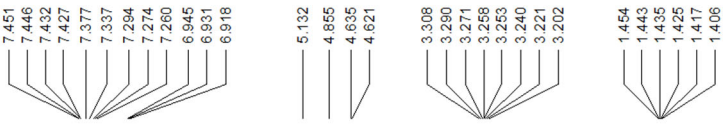


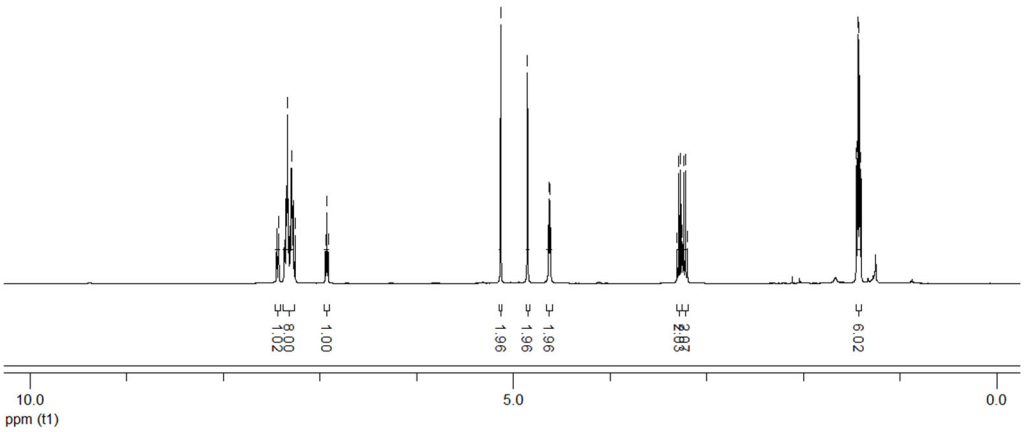


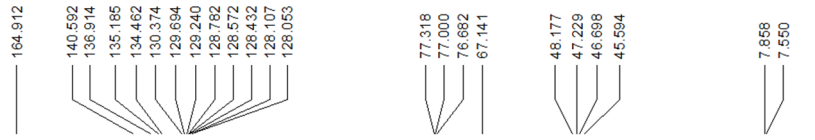


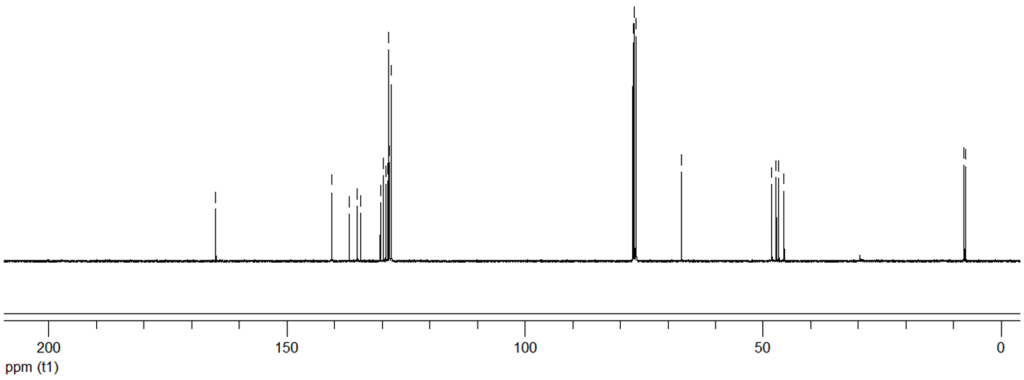
^{1}H NMR (400 MHz, $CDCl_3$), and ^{13}C NMR (100MHz, $CDCl_3$) of 3ap



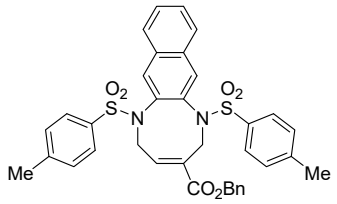


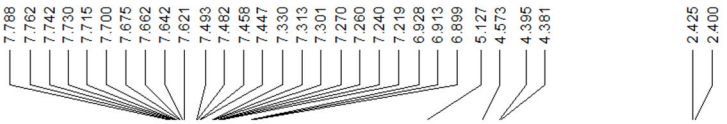


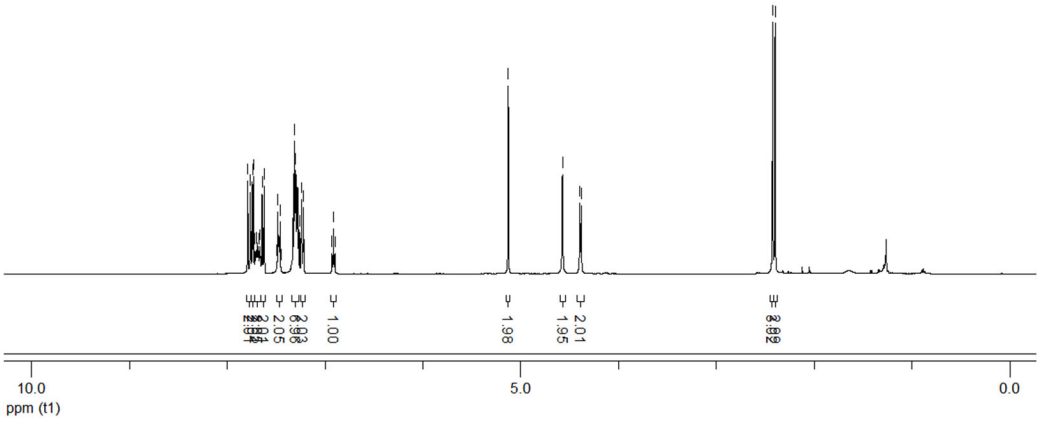


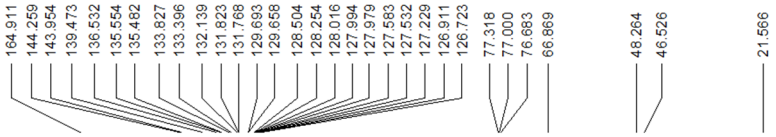


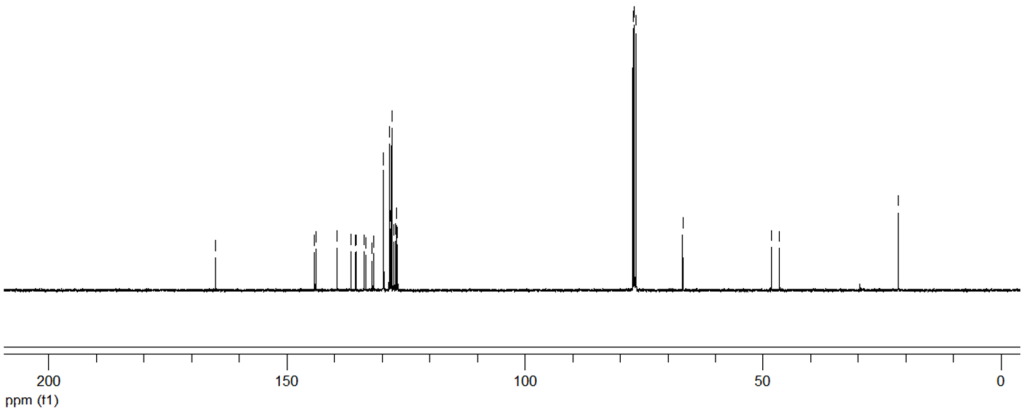
^{1}H NMR (400 MHz, $CDCl_3$), and ^{13}C NMR (100MHz, $CDCl_3$) of 3aq



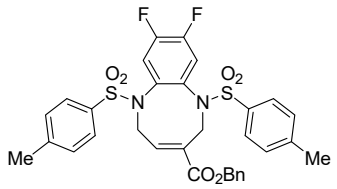


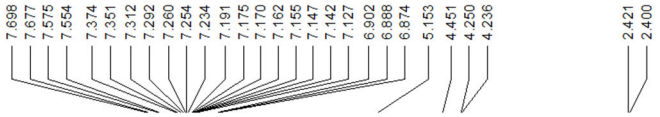


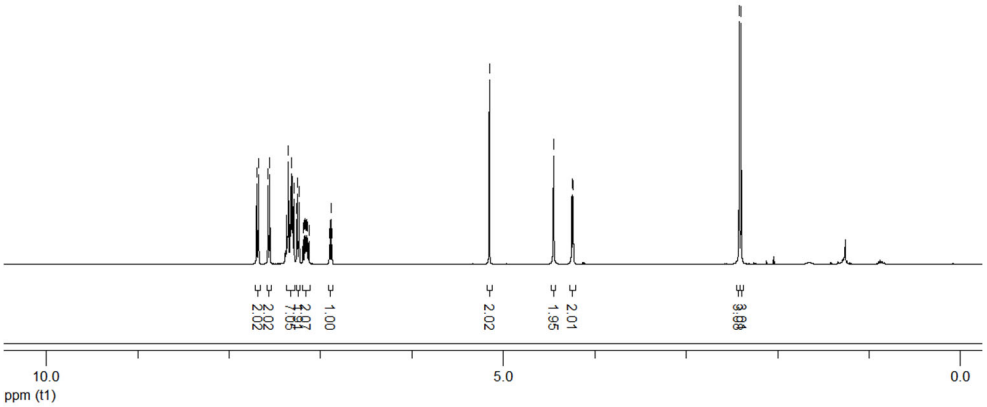


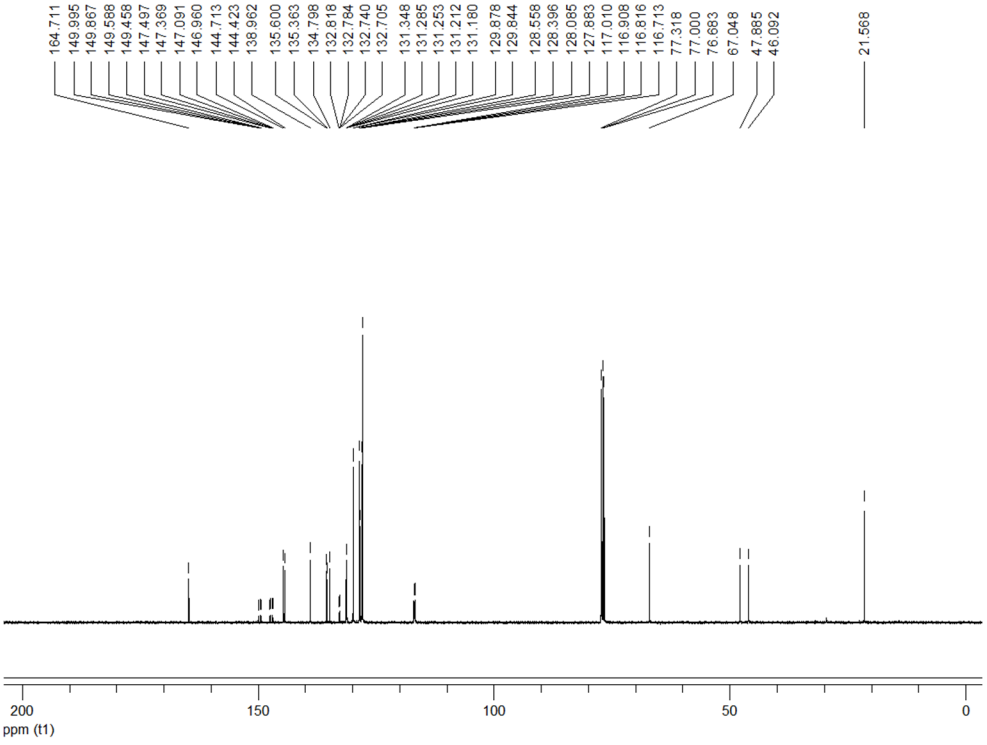


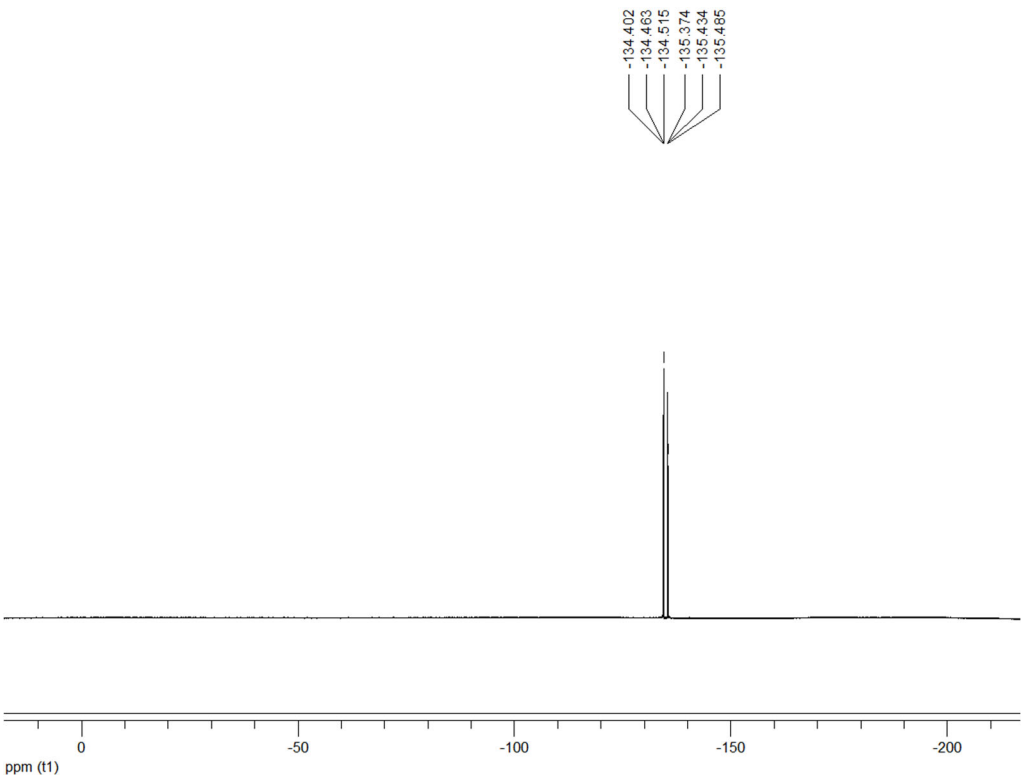
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100MHz, $CDCl_3$), and ^{19}F NMR (376 MHz, $CDCl_3$) of 3ar



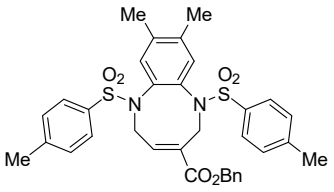


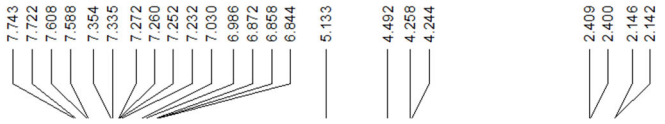


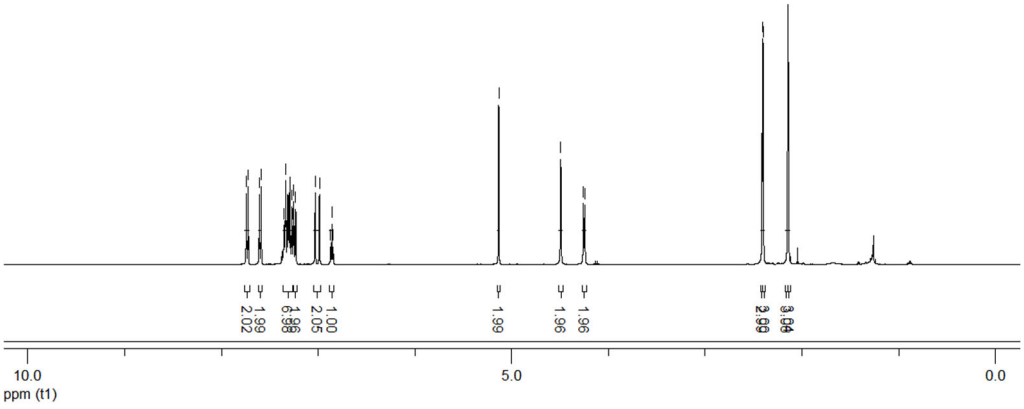


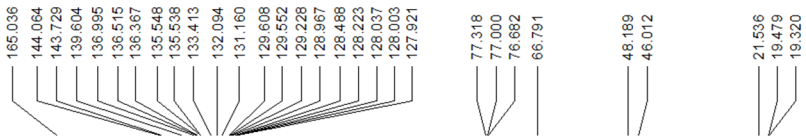

-134.402
-134.463
-134.515
-135.374
-135.434
-135.485
0
-50
-100
-150
-200
ppm (t1)

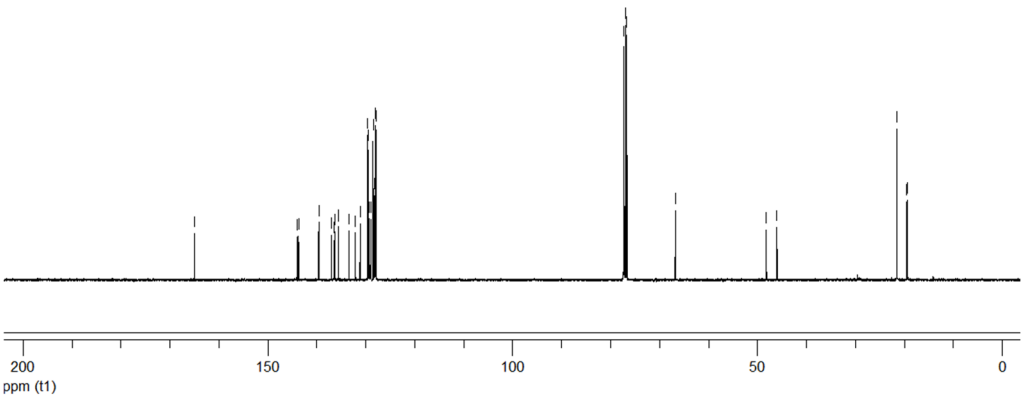
^{1}H NMR (400 MHz, $CDCl_3$), and ^{13}C NMR (100MHz, $CDCl_3$) of 3as



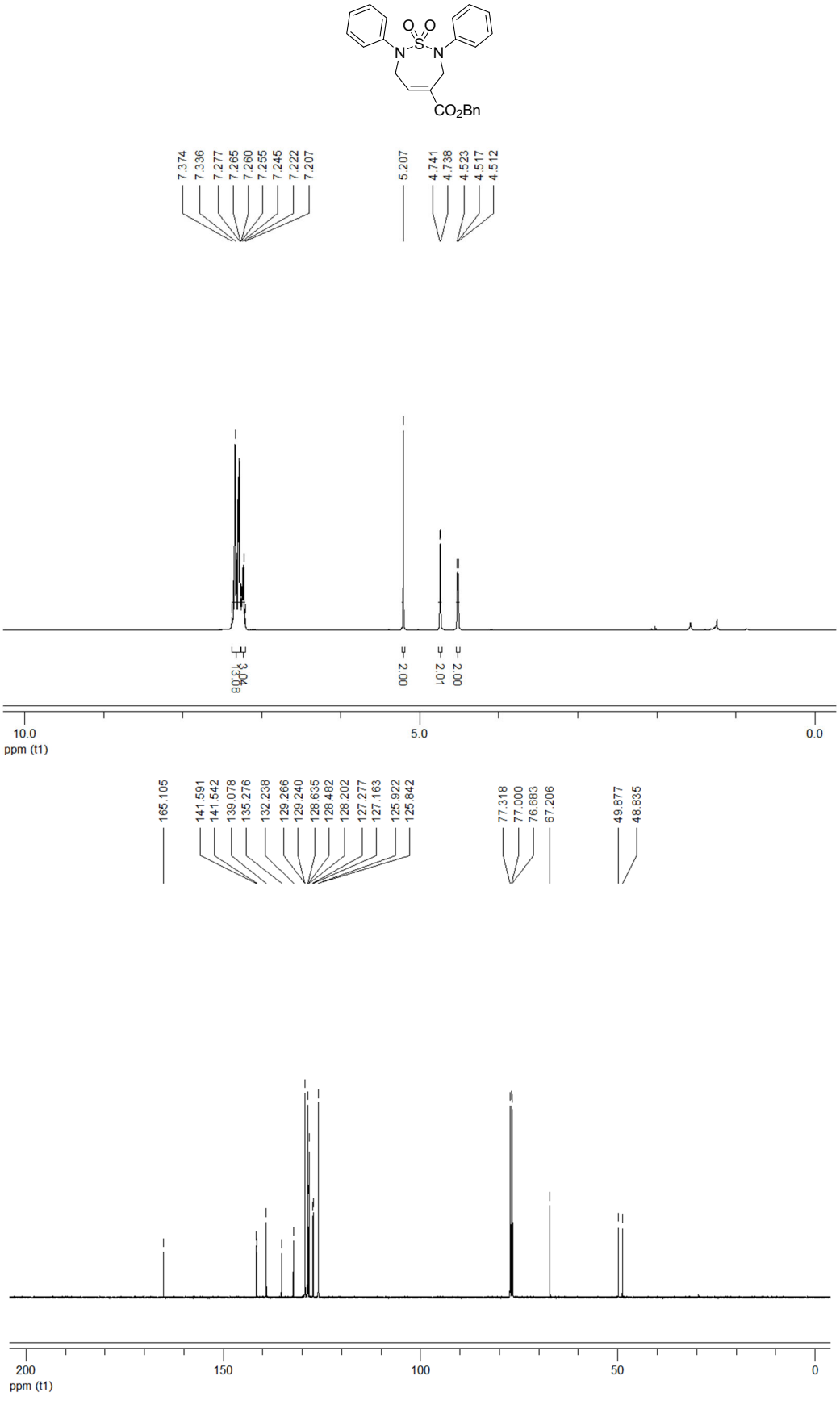




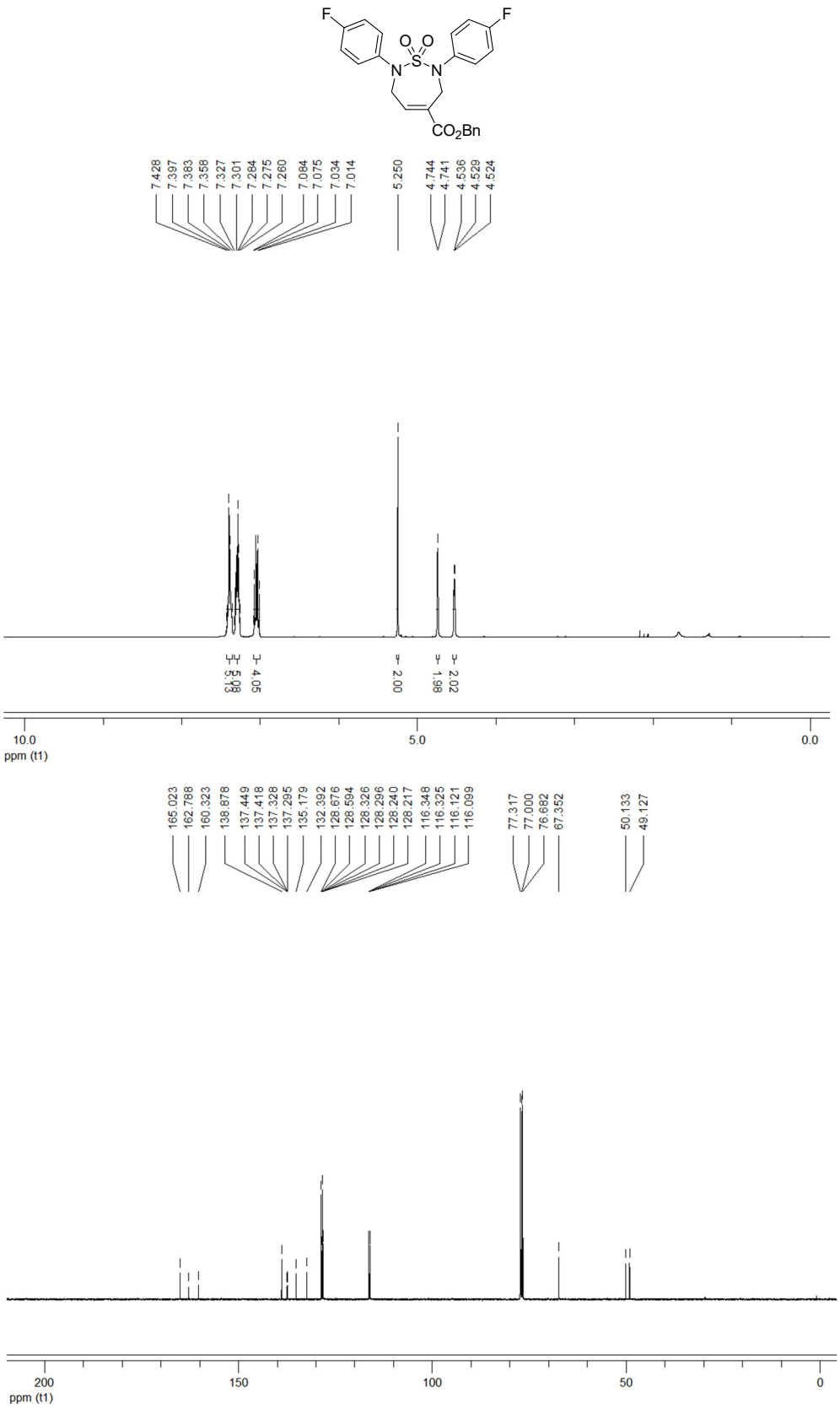


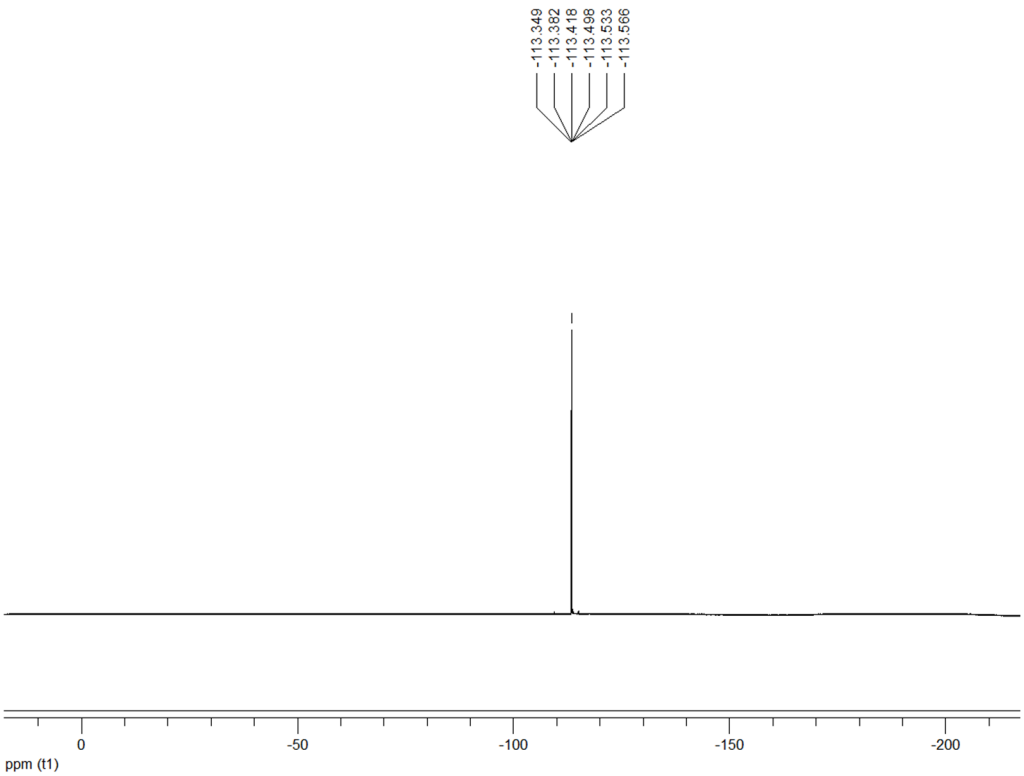


^{1}H NMR (400 MHz, $CDCl_3$), and ^{13}C NMR (100MHz, $CDCl_3$) of 5aa

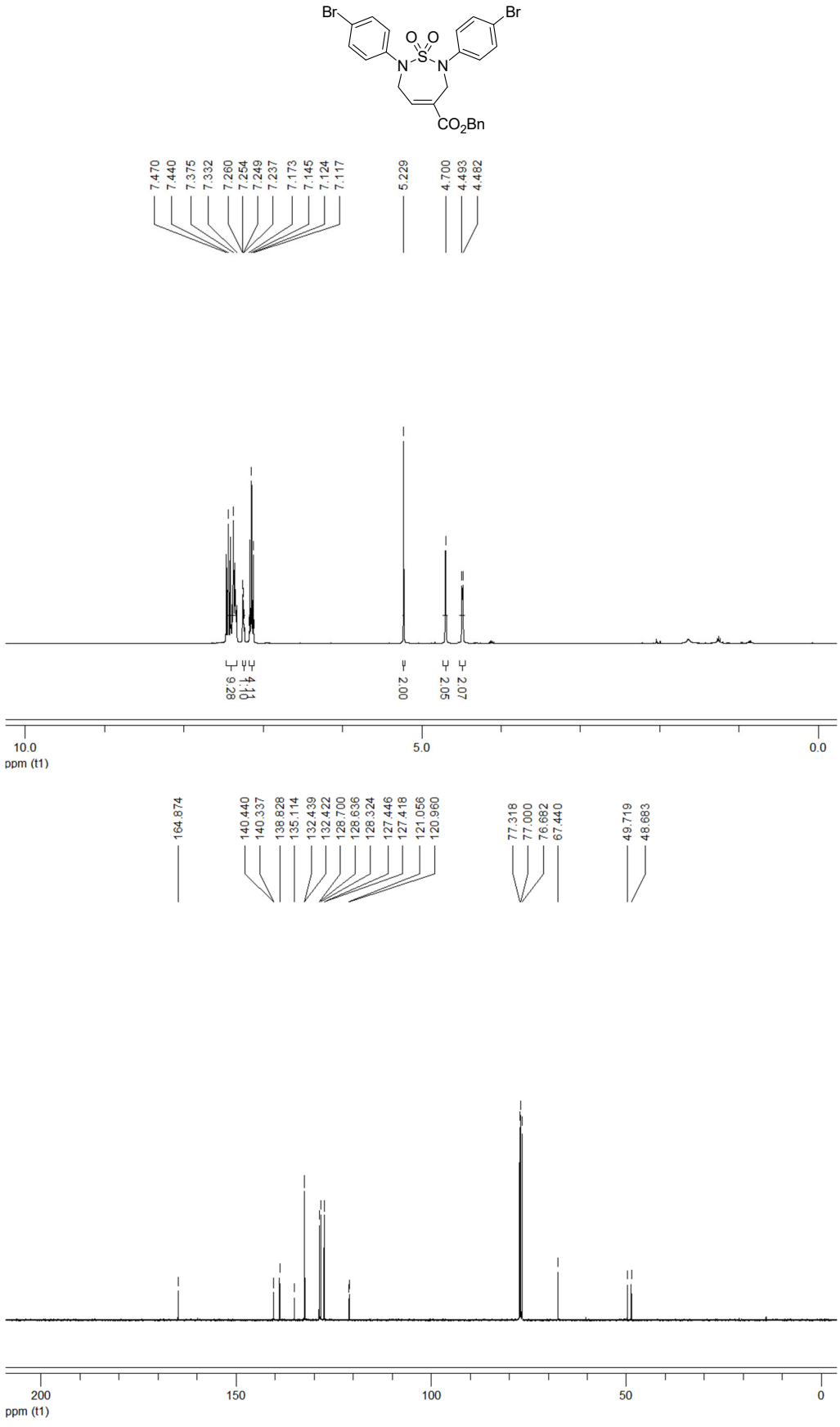


^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100MHz, $CDCl_3$), and ^{19}F NMR (376 MHz, $CDCl_3$) of 5ab

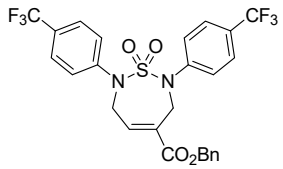


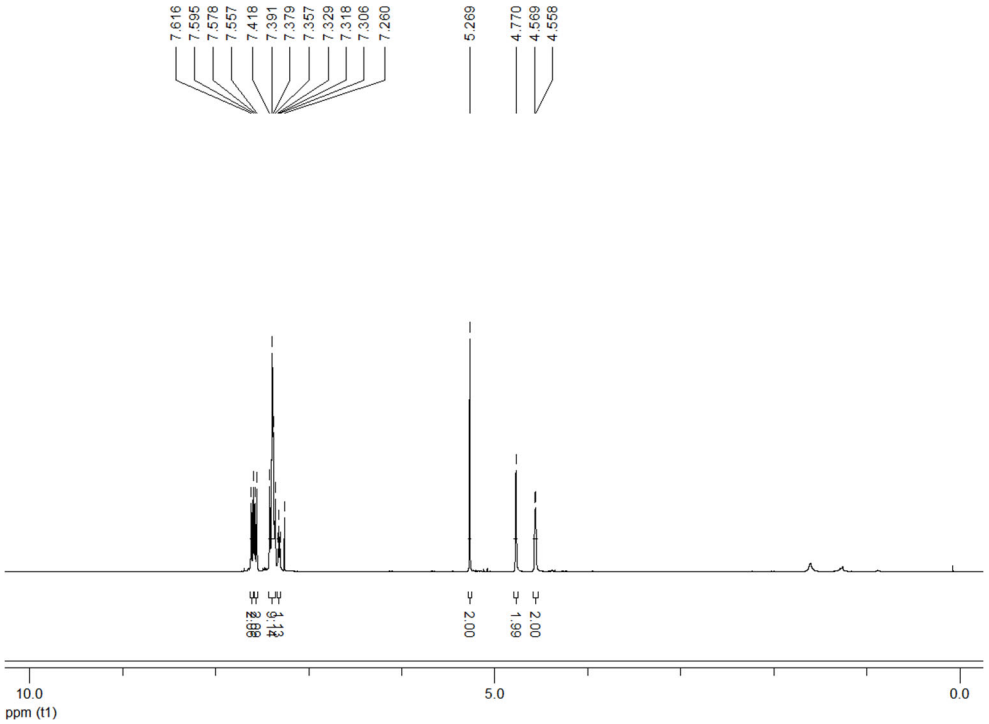

-113.349
-113.382
-113.418
-113.498
-113.533
-113.566
0
-50
-100
-150
-200
ppm (t1)

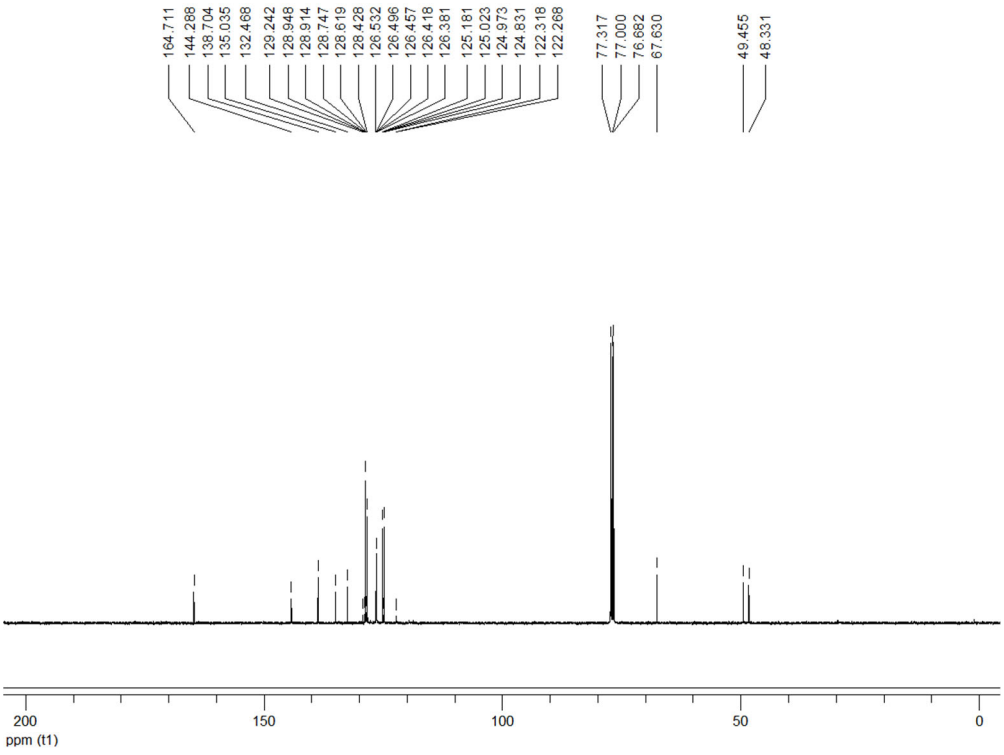
^{1}H NMR (400 MHz, $CDCl_3$), and ^{13}C NMR (100MHz, $CDCl_3$) of 5ac

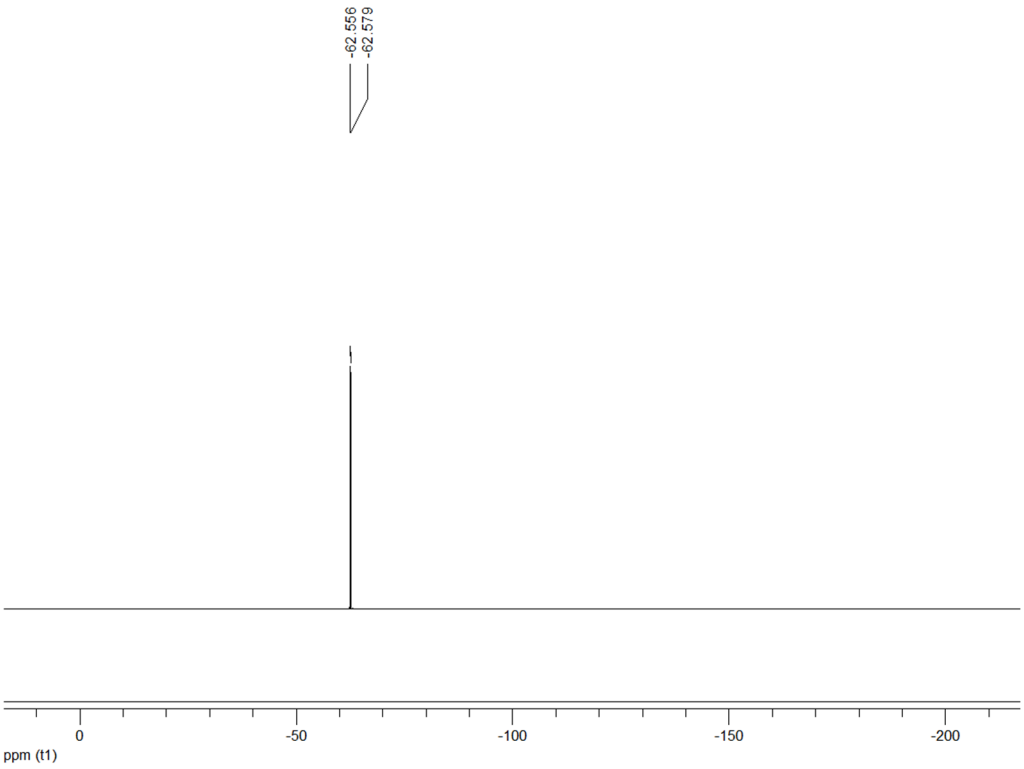


^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100MHz, $CDCl_3$), and ^{19}F NMR (376 MHz, $CDCl_3$) of 5ad

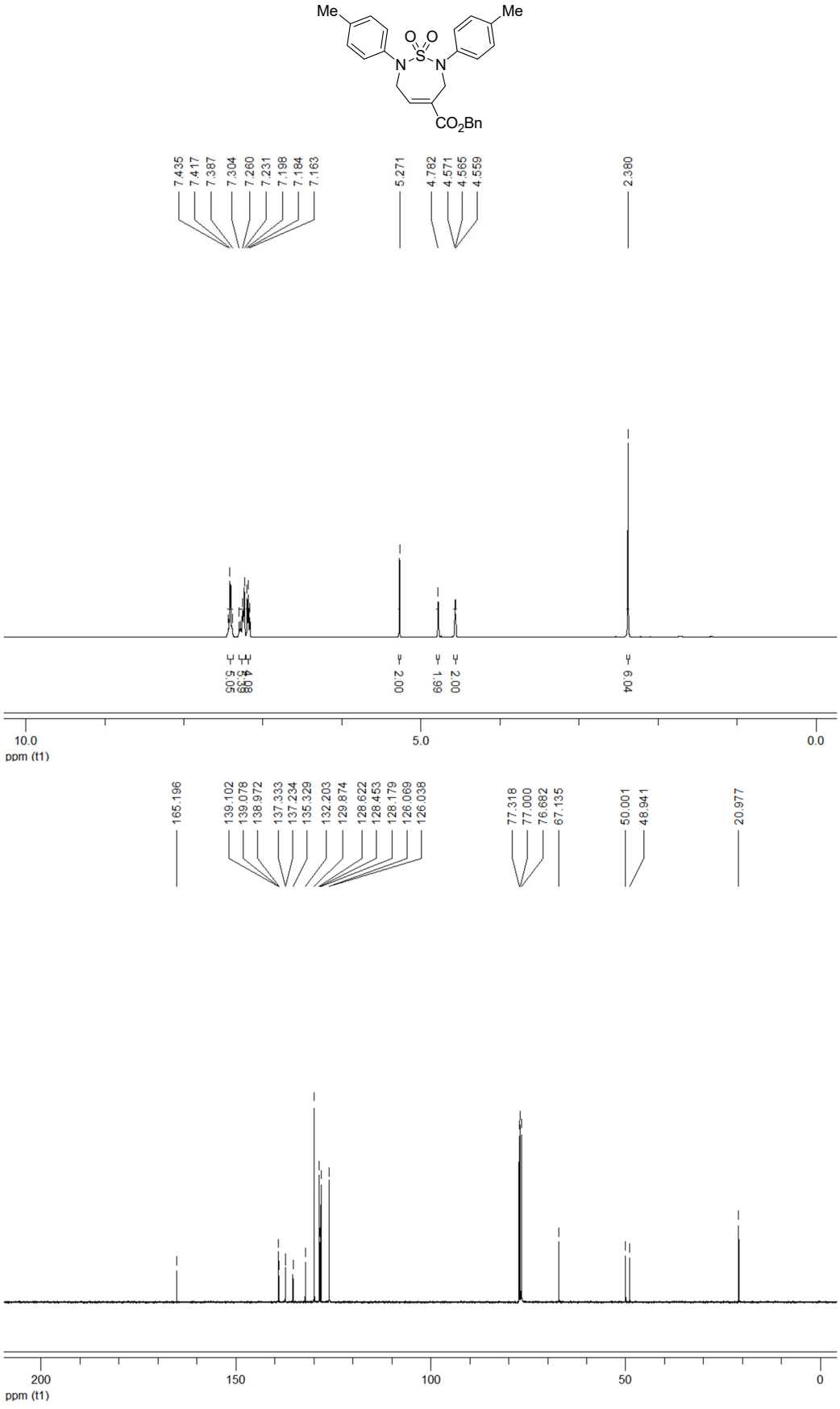




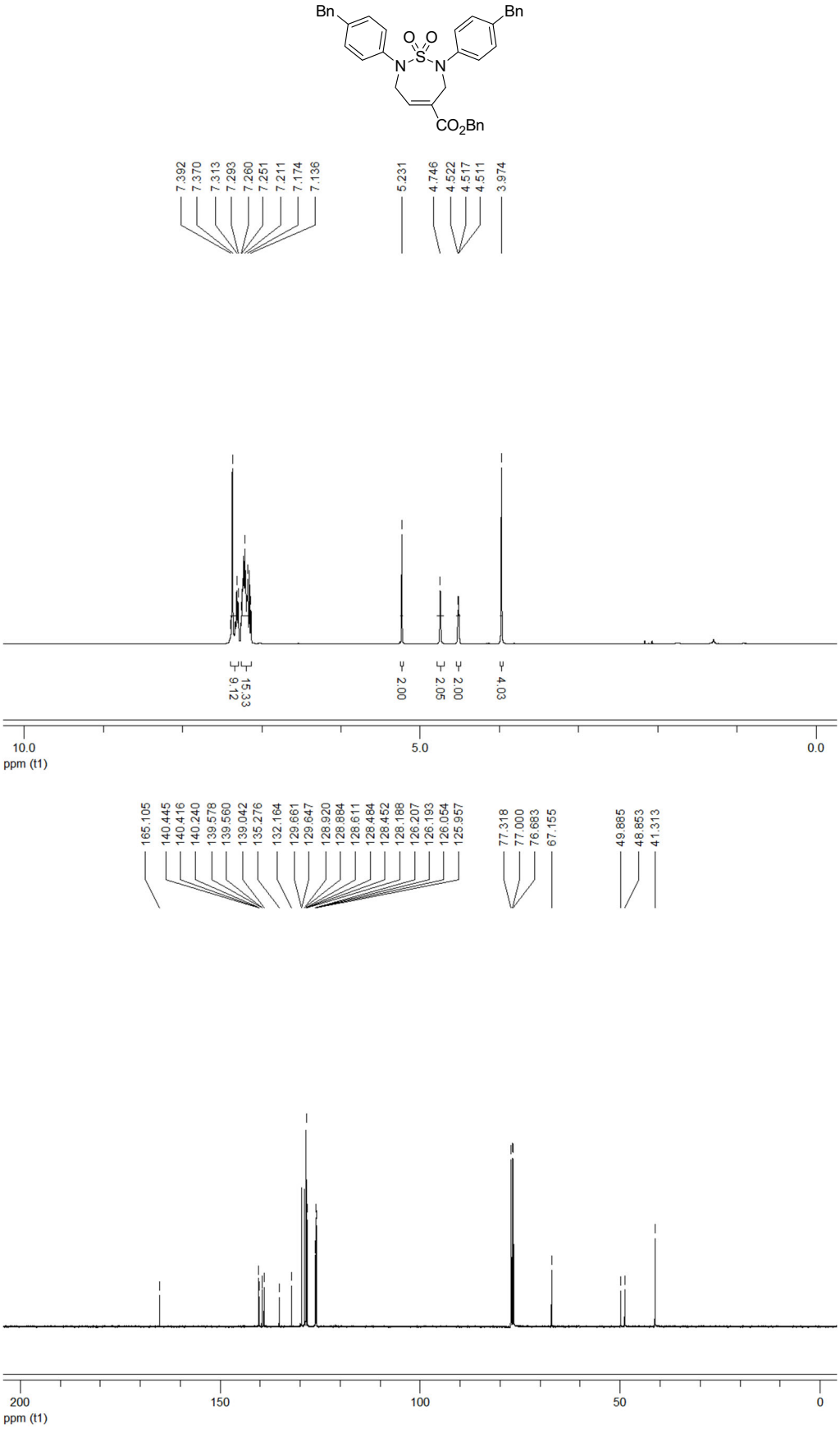



-62.556
-62.579
0
-50
-100
-150
-200
ppm (t1)

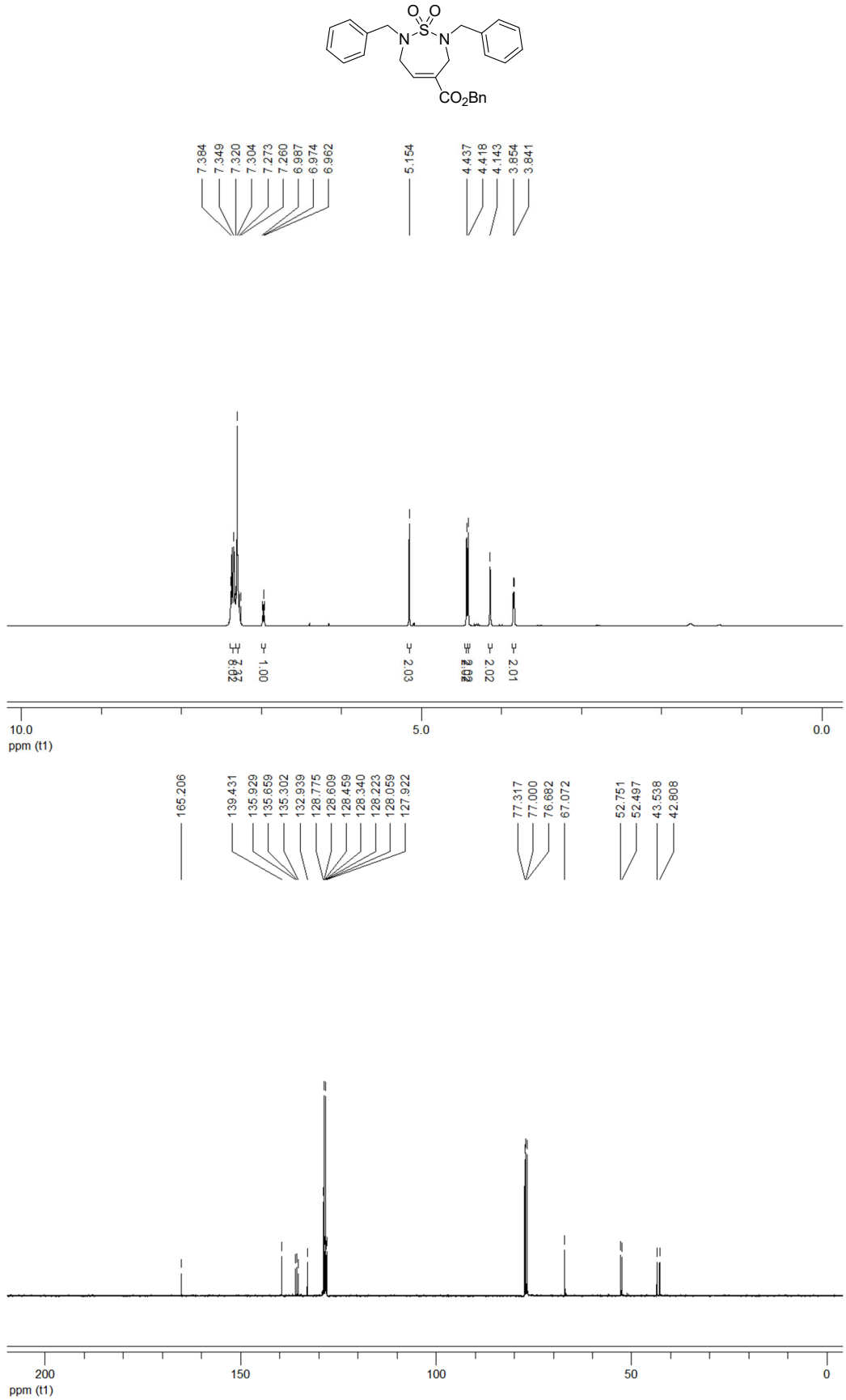
^{1}H NMR (400 MHz, $CDCl_3$), and ^{13}C NMR (100MHz, $CDCl_3$) of 5ae



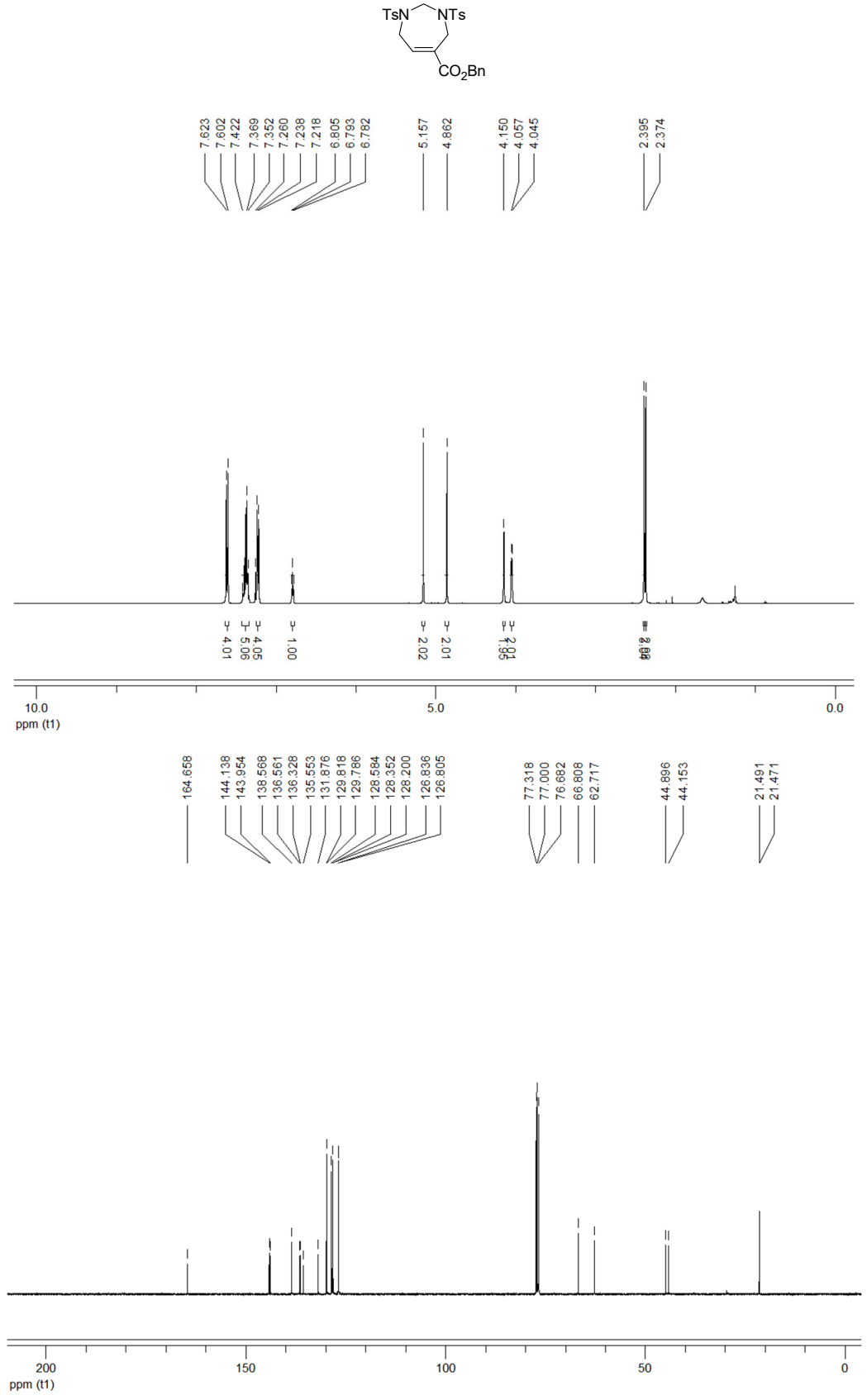
^{1}H NMR (400 MHz, $CDCl_3$), and ^{13}C NMR (100MHz, $CDCl_3$) of 5af



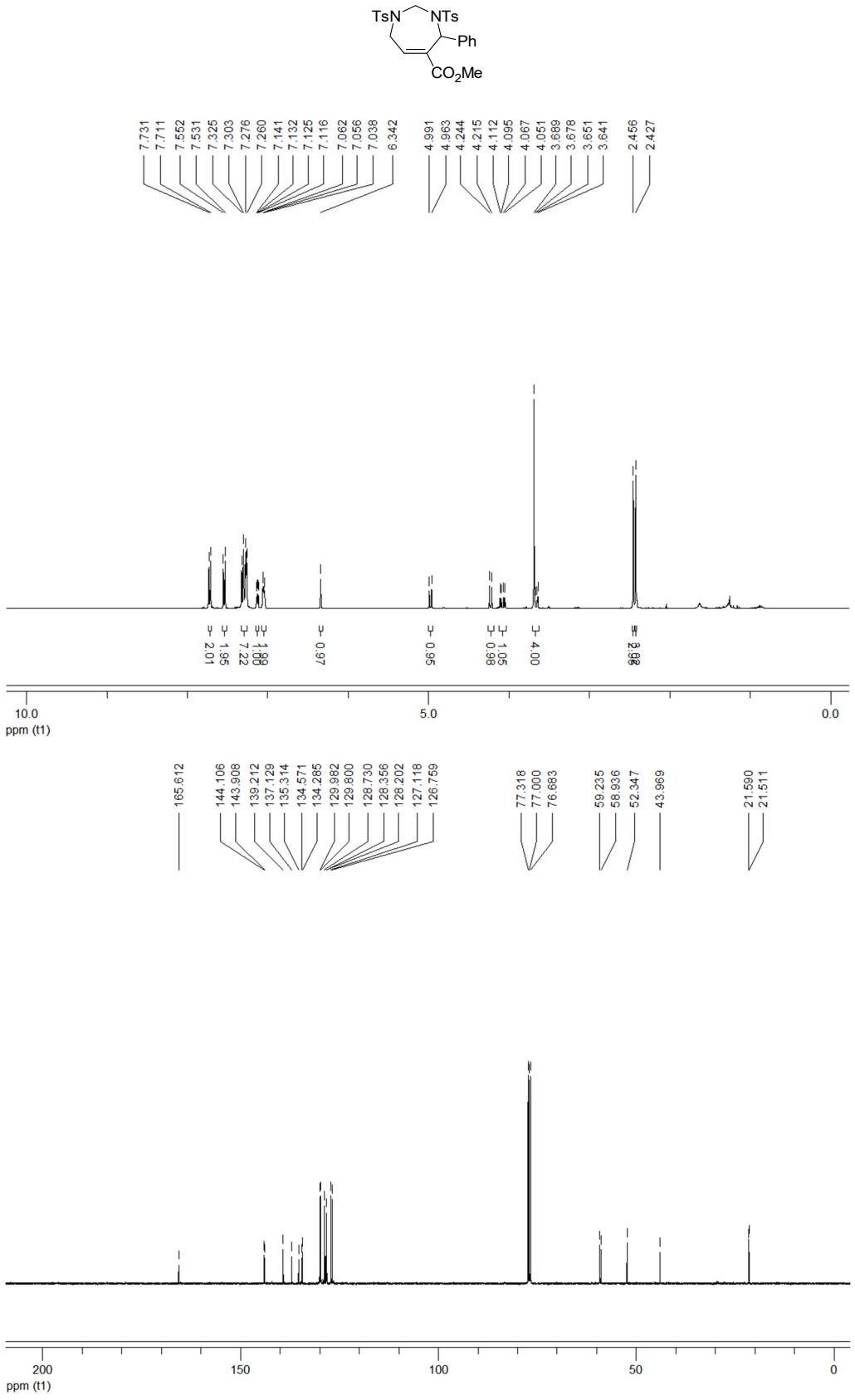
^{1}H NMR (400 MHz, $CDCl_3$), and ^{13}C NMR (100MHz, $CDCl_3$) of 5ag



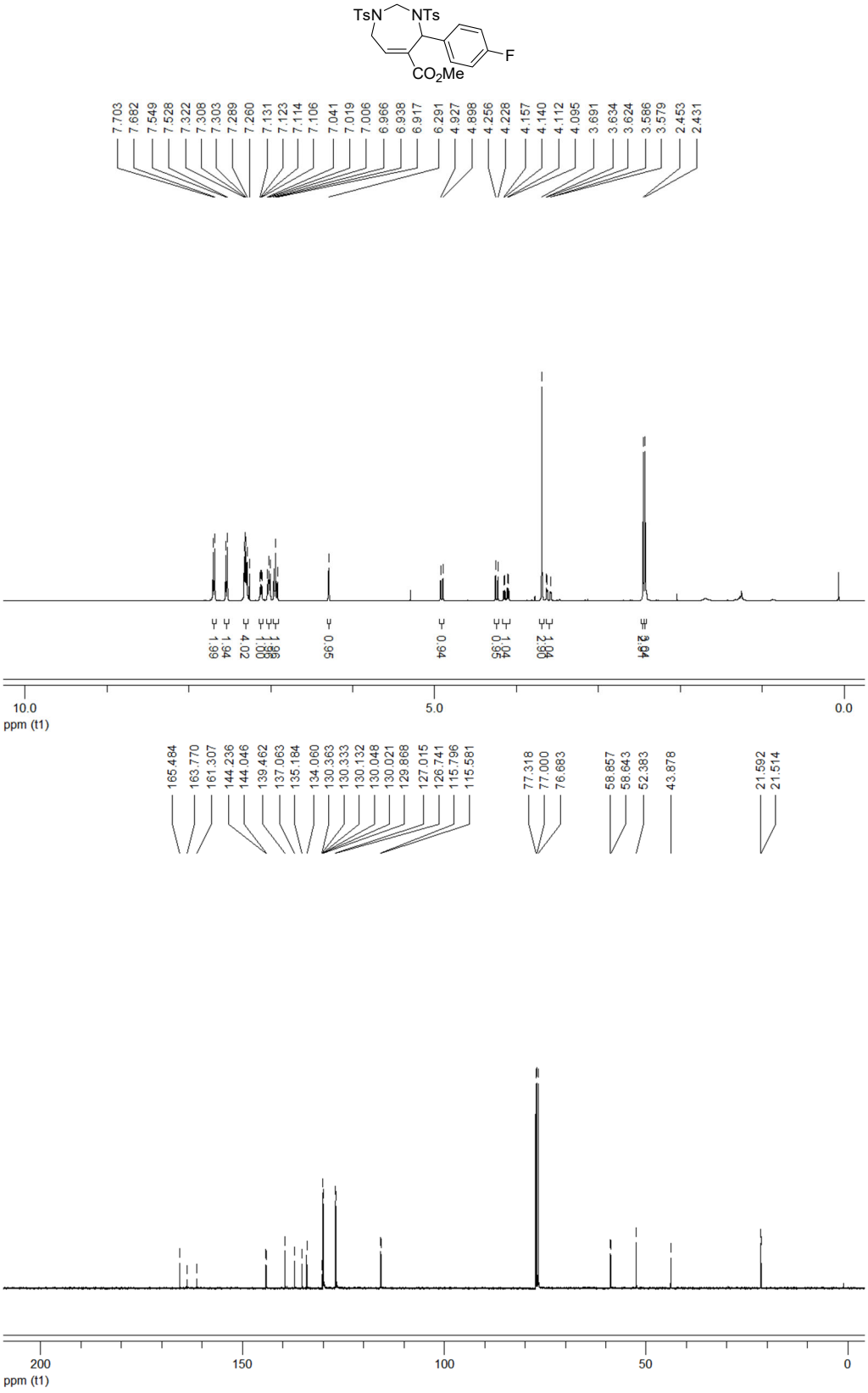
^{1}H NMR (400 MHz, $CDCl_3$), and ^{13}C NMR (100MHz, $CDCl_3$) of 5ah

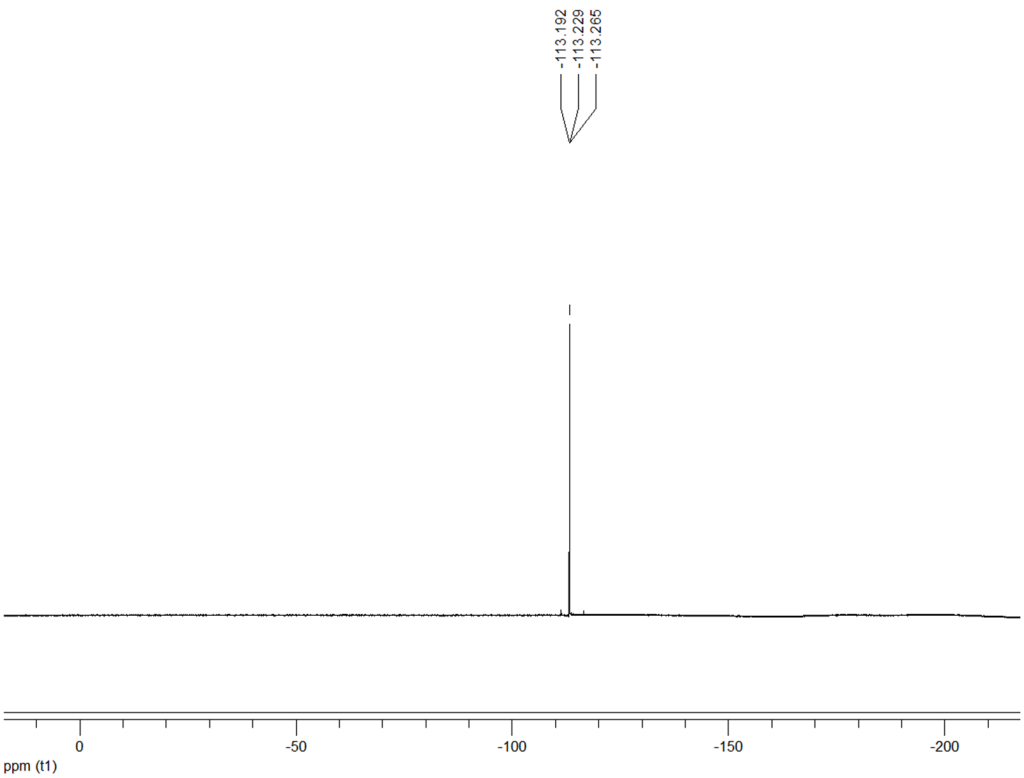


^{1}H NMR (400 MHz, $CDCl_3$), and ^{13}C NMR (100MHz, $CDCl_3$) of 5bh

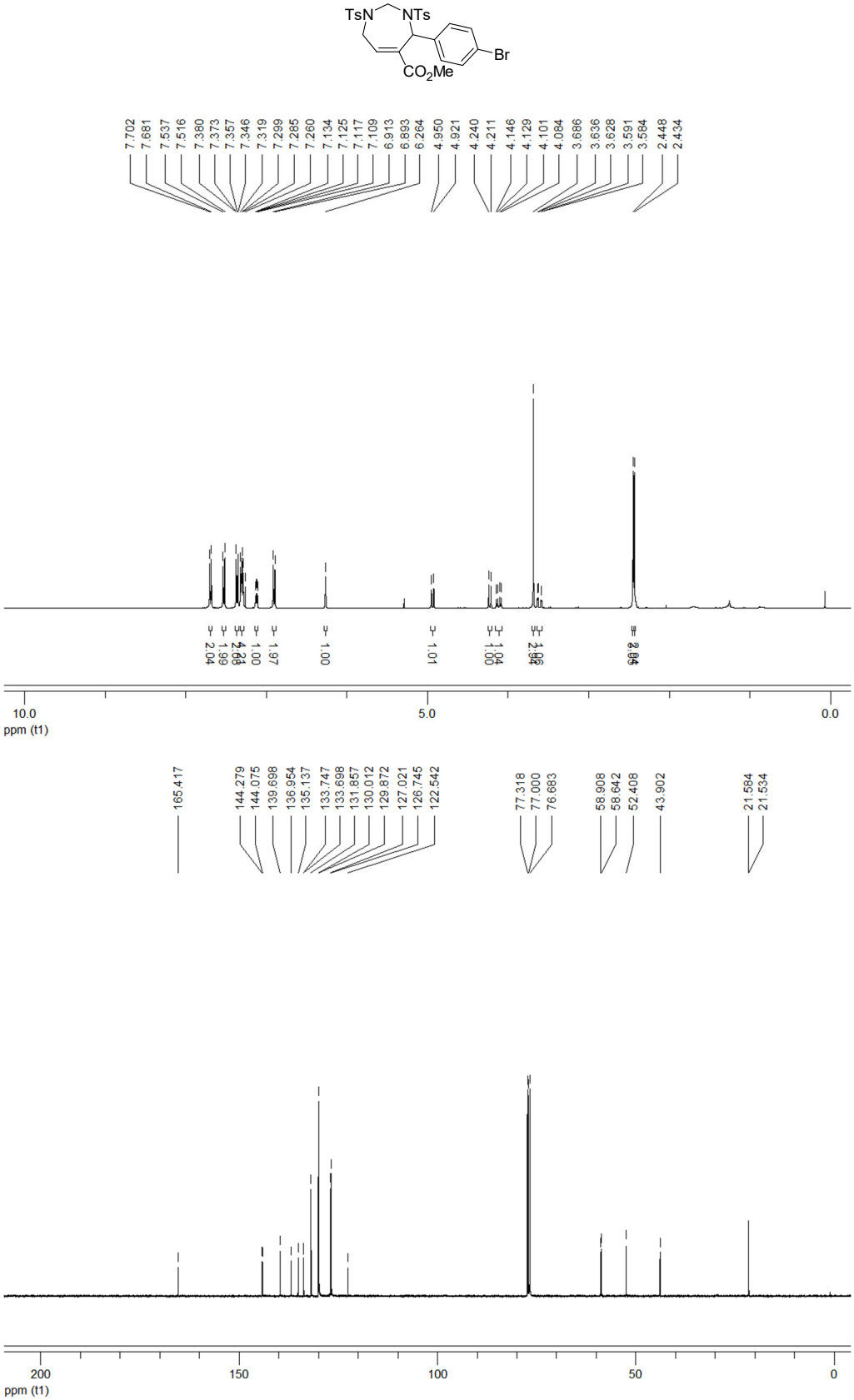


^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100MHz, $CDCl_3$), and ^{19}F NMR (376 MHz, $CDCl_3$) of 5ch

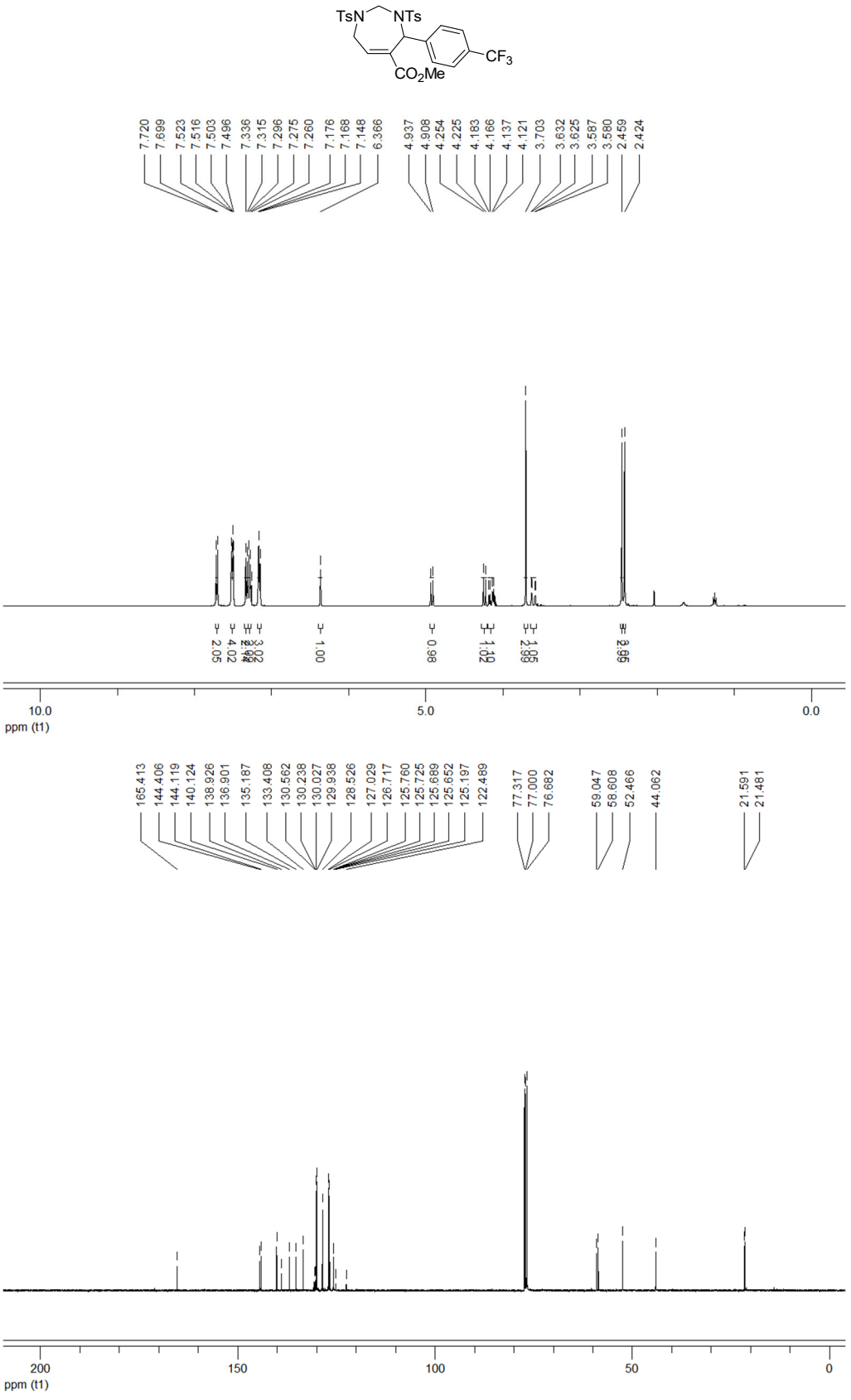


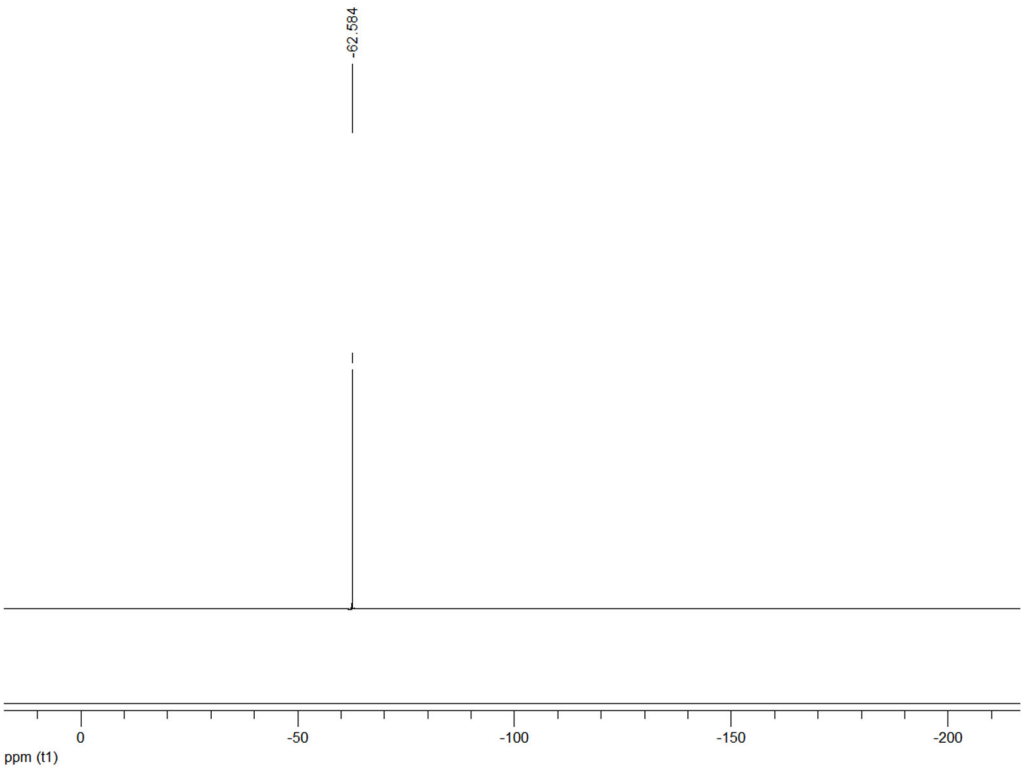

-113.192
-113.229
-113.265
0
-50
-100
-150
-200
ppm (t1)

^{1}H NMR (400 MHz, $CDCl_3$), and ^{13}C NMR (100MHz, $CDCl_3$) of 5dh

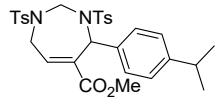


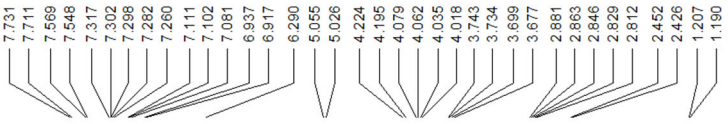
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100MHz, $CDCl_3$), and ^{19}F NMR (376 MHz, $CDCl_3$) of 5eh

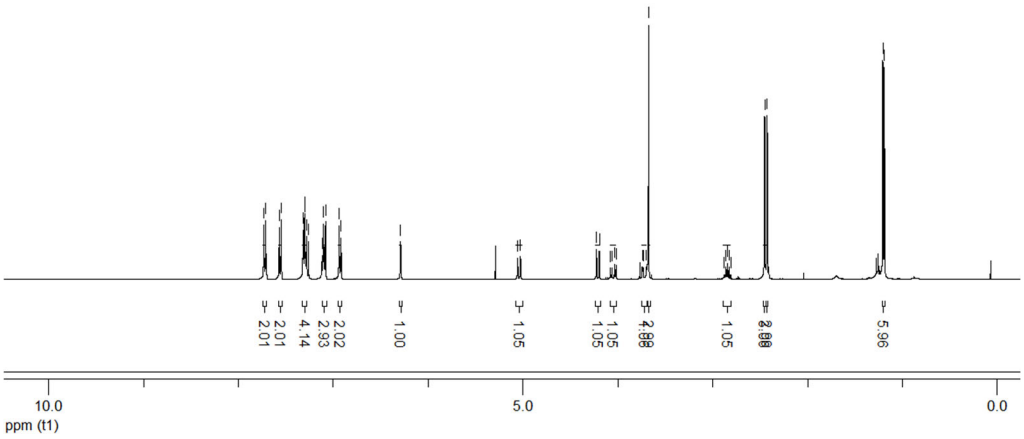


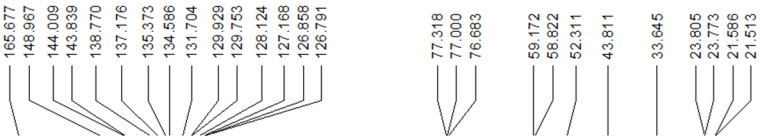

-62.584
0
-50
-100
-150
-200
ppm (t1)

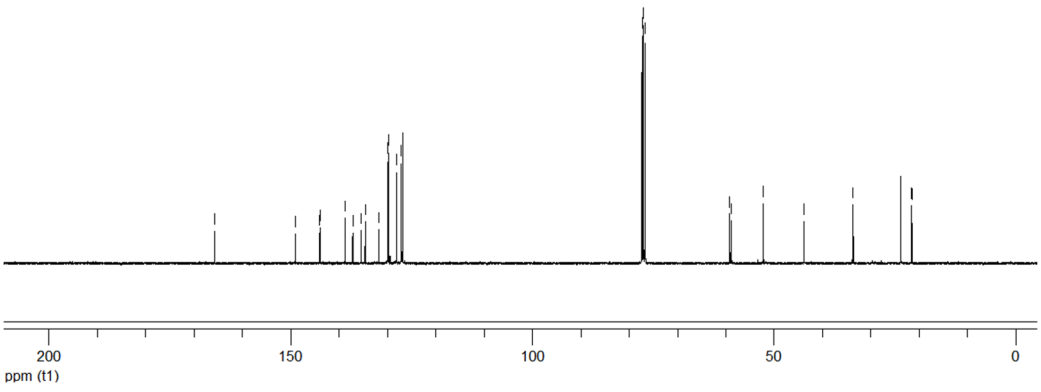
^{1}H NMR (400 MHz, $CDCl_3$), and ^{13}C NMR (100MHz, $CDCl_3$) of 5fh



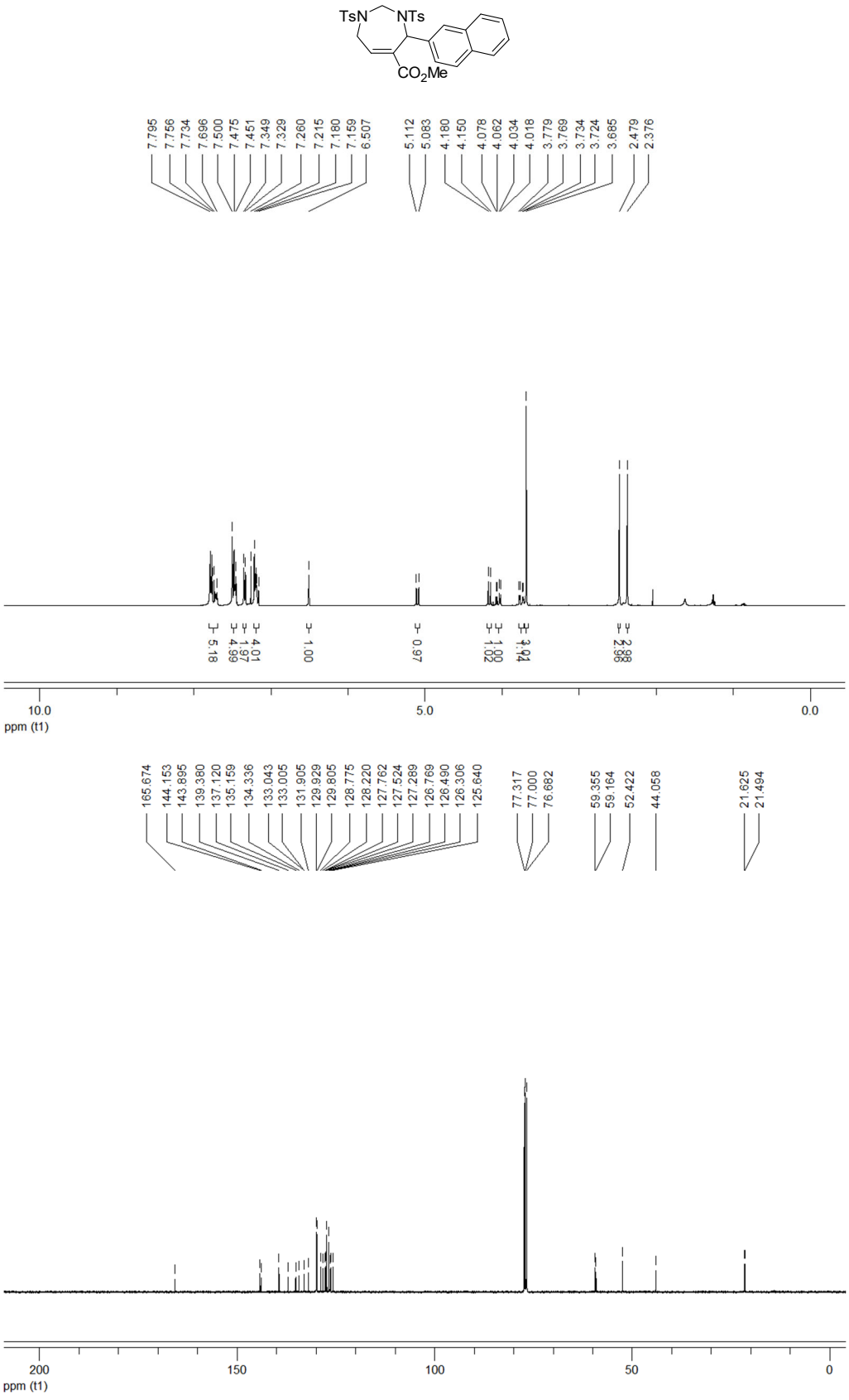




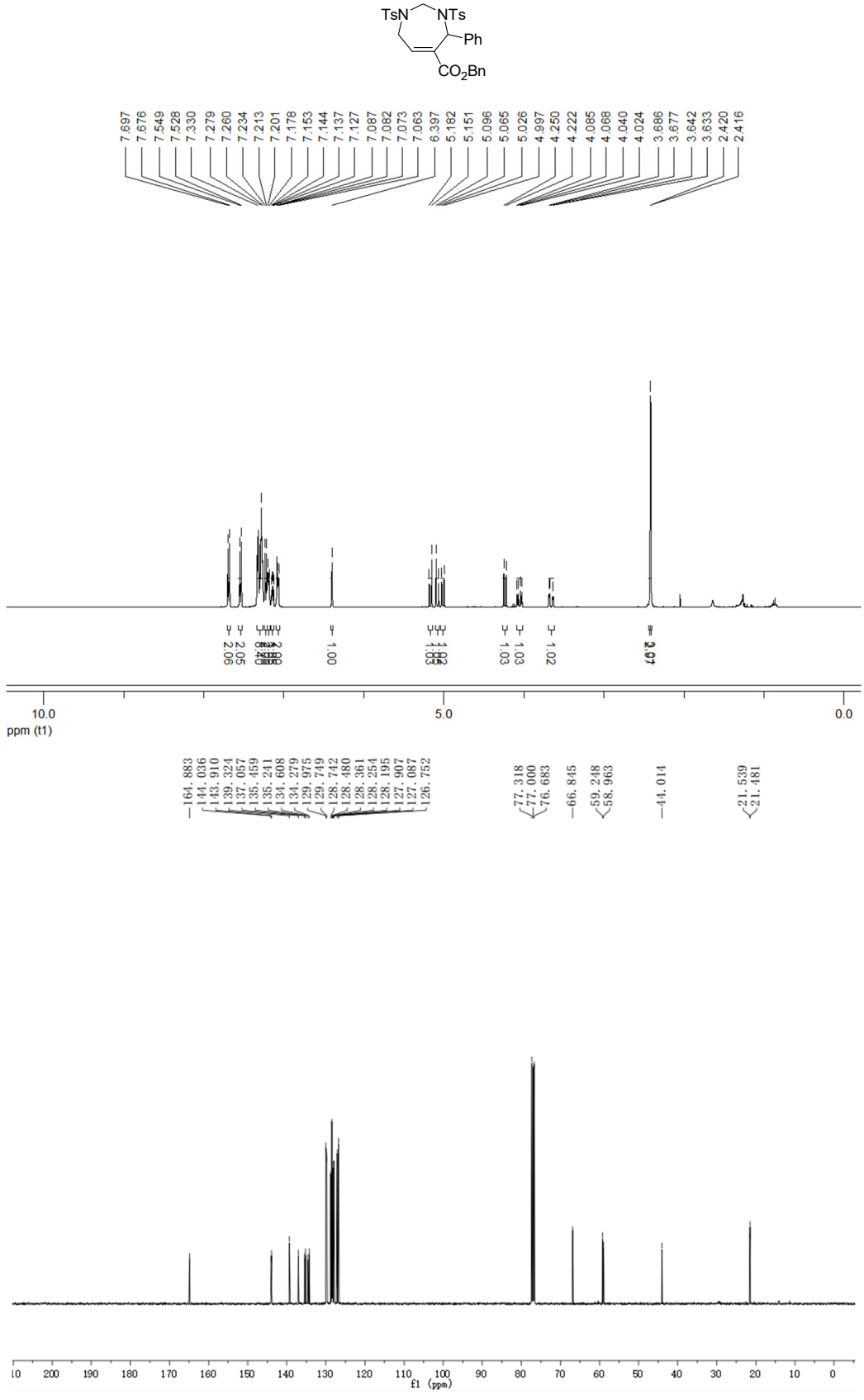




^{1}H NMR (400 MHz, $CDCl_3$), and ^{13}C NMR (100MHz, $CDCl_3$) of 5gh



^{1}H NMR (400 MHz, $CDCl_3$), and ^{13}C NMR (100MHz, $CDCl_3$) of 5hh



^{1}H NMR (400 MHz, $CDCl_3$), and ^{13}C NMR (100MHz, $CDCl_3$) of 5ih