Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

A copper-catalyzed direct C(sp^2)-H alkylsulfonylation of alkenes, alkylsilyl peroxides and DABCO·$(SO_2)_2$

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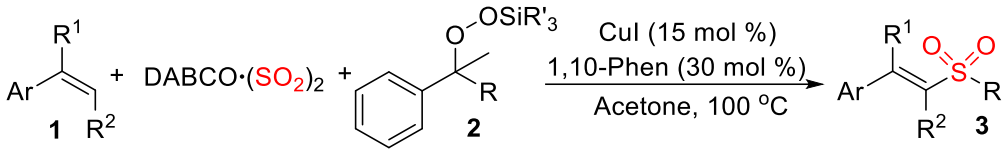
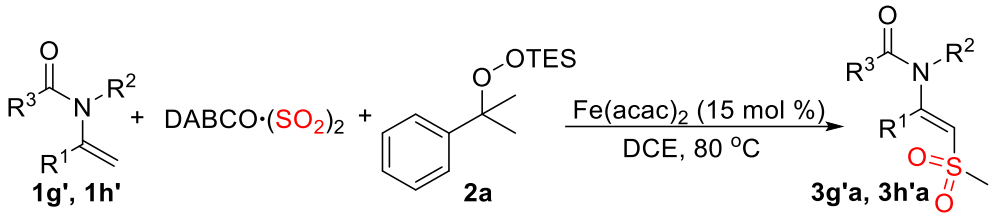
General Information

All reactions were carried out in oven dried Schlenk tubes under nitrogen atmosphere. Alkylsilyl peroxides **2** were prepared as reported.[1] Copper iodide (CuI) was purchased from Adamas-beta, DABCO·$(SO_2)_2$ and 1,10-phenanthroline were purchased from Bidepharm.com. ^{1}H, ^{13}C, ^{19}F NMR spectra were recorded in $CDCl_3$ on Bruker Avance 400 MHz spectrometers. High resolution mass spectra (HRMS) were obtained using a commercial apparatus (ESI Source). Electrospray–ionisation HRMS data were acquired on a Q–Tof mass spectrometer (Waters SYNAPT G2-Si) LC-MS TOF. NMR spectra were taken using TMS (^{1}H, δ = 0), $CDCl_3$(^{1}H, δ = 7.26) and $CDCl_3$(^{13}C, CPD δ = 77.0) as the internal standards, respectively. Column chromatography was generally performed on silica gel (300-400 mesh) and reactions were monitored by thin layer chromatography (TLC) using UV light to visualize the course of the reactions.

General procedures for the synthesis of (E)-vinyl sulfone derivatives

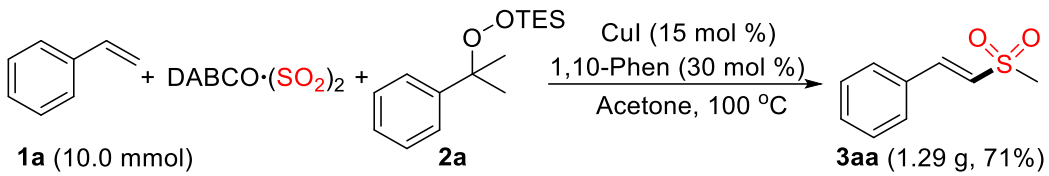


Alkene **1** (0.2 mmol), DABCO·$(SO_2)_2$ (0.3 mmol, 1.5 equiv), CuI (0.03 mmol, 15 mol %) and 1,10-phenanthroline (0.06 mmol, 30 mol %) were added sequentially into Schlenk tube under nitrogen. Then, alkylsilyl peroxide **2** (0.6 mmol, 3.0 equiv) and actone (1 mL) were added rapidly by syringe. The resulting mixture was allowed to stir at 100 °C in the oil bath for 3 hours. Upon completion, the solvent was removed under vacuum and the residue was purified by flash column chromatography to afford product **3**.



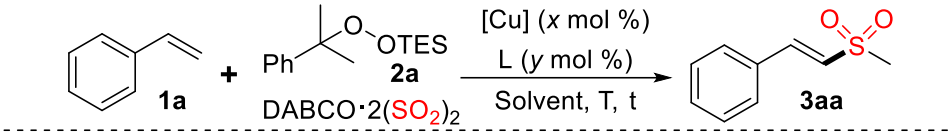
Enamide **1g'** or **1g'** (0.2 mmol), DABCO·$(SO_2)_2$ (0.3 mmol, 1.5 equiv), $Fe(acac)_2$ (0.03 mmol, 15 mol %) were added sequentially into Schlenk tube under nitrogen. Then, triethyl((2-phenylpropan-2-yl)peroxy)silane **2a** (0.6 mmol, 3.0 equiv)and 1,2-dichloroethane (1 mL) were added rapidly by syringe. The resulting mixture was allowed to stir at 80 °C in the oil bath for 12 hours. Upon completion, the solvent was removed under vacuum and the residue was purified by flash column chromatography to afford product **3g'a** or **3h'a**.

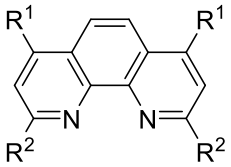
***Gram-scale and gram-scale synthesis of* 3aa**



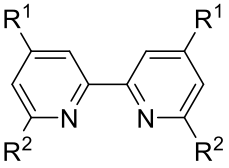
$DABCO·(SO_2)_2$ (15.0 mmol, 1.5 equiv), CuI (1.5 mmol, 15 mol %) and 1,10-phenanthroline (3.0 mmol, 30 mol %) were added sequentially into Schlenk tube under nitrogen. Then, styrene **1a** (10.0 mmol), triethyl((2-phenylpropan-2-yl)peroxy)silane **2a** (30.0 mmol, 3.0 equiv) and actone (50 mL) were added rapidly by syringe. The resulting mixture was allowed to stir at 100 °C in the oil bath for 3 hours. Upon completion, the solvent was removed under vacuum and the residue was purified by flash column chromatography to afford product **3aa** (1.29 g, 71%).

Optimization of reaction conditions[a]

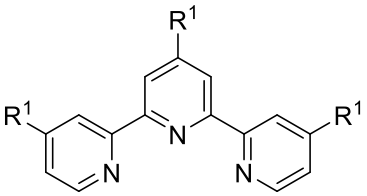




L1, R^1 = H, R^2 = H
L2, R^1 = Ph, R^2 = H
L3, R^1 = H, R^2 = Me
L4, R^1 = Ph, R^2 = Me



L5, R^1 = H, R^2 = H
L6, R^1 = H, R^2 = Me
L7, R^1 = Me, R^2 = H
L8, R^1 = Bu^t, R^2 = H
L9, R^1 = OMe, R^2 = H



L10, R^1 = H
L11, R^1 = Bu^t

Entry	[Cu] (mol %)	L (mol %)	Solvent	T (°C)	t (h)	Yield (%)[b]
1	CuCl (10)	**L1** (15)	MeCN	80	12	10
2	CuBr (10)	**L1** (15)	MeCN	80	12	17
3	CuI (10)	**L1** (15)	MeCN	80	12	25
4	CuOAc (10)	**L1** (15)	MeCN	80	12	9
5	CuTc (10)	**L1** (15)	MeCN	80	12	Trace
6	CuCN (10)	**L1** (15)	MeCN	80	12	Trace
7	CuOTf (10)	**L1** (15)	MeCN	80	12	Trace
8	$Cu(MeCN)_4BF_4$ (10)	**L1** (15)	MeCN	80	12	8
9	$Cu(MeCN)_4PF_6$ (10)	**L1** (15)	MeCN	80	12	9
10	$CuCl_2$ (10)	**L1** (15)	MeCN	80	12	13
11	$CuBr_2$ (10)	**L1** (15)	MeCN	80	12	18
12	$Cu(acac)_2$ (10)	**L1** (15)	MeCN	80	12	Trace
13	CuI (10)	**L2** (15)	MeCN	80	12	23
14	CuI (10)	**L3** (15)	MeCN	80	12	18
15	CuI (10)	**L4** (15)	MeCN	80	12	15
16	CuI (10)	**L5** (15)	MeCN	80	12	22
17	CuI (10)	**L6** (15)	MeCN	80	12	12
18	CuI (10)	**L7** (15)	MeCN	80	12	20
19	CuI (10)	**L8** (15)	MeCN	80	12	19
20	CuI (10)	**L9** (15)	MeCN	80	12	23
21	CuI (10)	**L10** (15)	MeCN	80	12	23
22	CuI (10)	**L11** (15)	MeCN	80	12	23
23	CuI (10)	**L1** (15)	EA	80	12	8
24	CuI (10)	**L1** (15)	Acetone	80	12	31
25	CuI (10)	**L1** (15)	DMSO	80	12	13
26	CuI (10)	**L1** (15)	DMF	80	12	N.D.
27	CuI (10)	**L1** (15)	DCE	80	12	17
28	CuI (10)	**L1** (15)	Toluene	80	12	14
29	CuI (10)	**L1** (15)	1.4-dioxane	80	12	N.D.
30	CuI (10)	**L1** (15)	Acetone	80	6	33
31	CuI (10)	**L1** (15)	Acetone	80	3	32
32	CuI (10)	**L1** (15)	Acetone	80	1	20
33	CuI (10)	**L1** (15)	Acetone	60	3	8
34	CuI (10)	**L1** (15)	Acetone	100	3	36
35	CuI (10)	**L1** (15)	Acetone	120	3	34
36[c]	CuI (10)	**L1** (15)	Acetone	100	3	30

37[d]	CuI (10)	**L1** (15)	Acetone	100	3	51
38[e]	CuI (10)	**L1** (15)	Acetone	100	3	58
39[e,f]	CuI (10)	**L1** (15)	Acetone	100	3	36
40[e,g]	CuI (10)	**L1** (15)	Acetone	100	3	46
41[e]	CuI (5)	**L1** (7.5)	Acetone	100	3	37
42[e]	CuI (15)	**L1** (22.5)	Acetone	100	3	78
43[e]	CuI (20)	**L1** (30)	Acetone	100	3	76
44[e]	CuI (15)	**L1** (15)	Acetone	100	3	26
45[e]	CuI (15)	**L1** (18)	Acetone	100	3	58
46[e]	**CuI (15)**	**L1 (30)**	**Acetone**	**100**	**3**	**81**

[a] Reaction conditions: styrene **1a** (0.2 mmol), alkylsilyl peroxide **2a**, DABCO·$(SO_2)_2$, Cu-catalyst, ligand, solvent (1.0 mL), N_2, in oil bath. [b] GC yield using dodecane as internal standard. [b] GC yield using dodecane as internal standard. [c] 1.2 equiv of **2a** was used. [d] 2.0 equiv of **2a** was used. [e] 3.0 equiv of **2a** was used. [f] 1.2 equiv of DABCO·$(SO_2)_2$ was used. [g] 2.0 equiv of DABCO·$(SO_2)_2$ was used.

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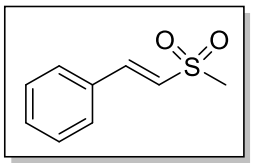
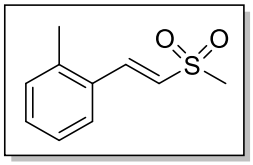
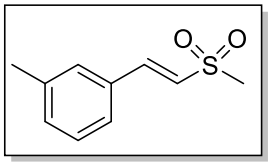
Characterization data for compounds



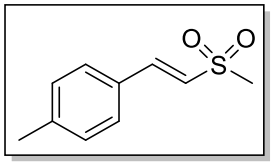
(*E*)-(2-(methylsulfonyl)vinyl)benzene **(3aa)**[2]: 28.1 mg, 77%, white solid, m.p.: 75.2 – 77.5 °C. *n*-hexane/ethyl acetate = 3/1 – 2/1 as an eluent. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.63 (d, *J* = 15.5 Hz, 1H), 7.50 – 7.55 (m, 2H), 7.49 – 7.39 (m, 3H), 6.94 (d, *J* = 15.5 Hz, 1H), 3.05 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 143.9, 131.9, 131.3, 129.1, 128.5, 126.0, 43.19.



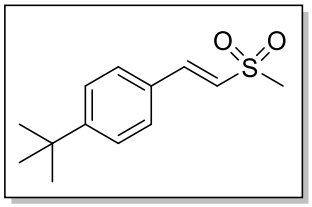
(*E*)-1-methyl-2-(2-(methylsulfonyl)vinyl)benzene **(3ba)**[3]: 29.3 mg, 75%, light yellow solid, m.p.: 78.0 – 80.7 °C. *n*-hexane/ethyl acetate = 3/1 – 2/1 as an eluent. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.91 (d, *J* = 15.4 Hz, 1H), 7.54 – 7.49 (m, 1H), 7.37 – 7.31 (m, 1H), 7.28 – 7.20 (m, 2H), 6.86 (d, *J* = 15.4 Hz, 1H), 3.05 (s, 3H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 141.5, 138.2, 131.1, 131.0, 130.8, 126.9, 126.8, 126.5, 43.2, 19.7.



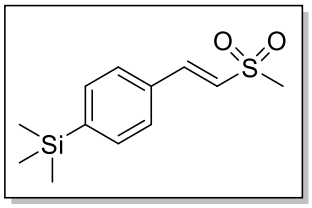
(*E*)-1-methyl-3-(2-(methylsulfonyl)vinyl)benzene **(3ca)**[3]: 29.6 mg, 75%, light yellow oil, *n*-hexane/ethyl acetate = 3/1 – 2/1 as an eluent. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.59 (d, *J* = 15.4 Hz, 1H), 7.36 – 7.22 (m, 4H), 6.93 (d, *J* = 15.4 Hz, 1H), 3.04 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 144.0, 138.8, 132.1, 131.9, 129.1, 128.9, 125.75, 125.68, 43.2, 21.2.



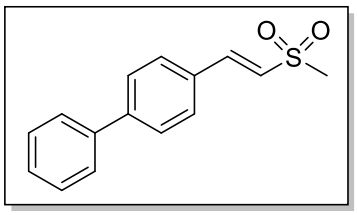
(*E*)-1-methyl-4-(2-(methylsulfonyl)vinyl)benzene **(3da)**[2]: 32.6 mg, 83%, white solid, m.p.: 105.1 – 107.7 °C. *n*-hexane/ethyl acetate = 3/1 – 2/1 as an eluent. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.59 (d, *J* = 15.4 Hz, 1H), 7.41 (d, *J* = 7.9 Hz, 2H), 7.23 (d, *J* = 7.8 Hz, 2H), 6.88 (d, *J* = 15.4 Hz, 1H), 3.03 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 143.9, 142.0, 129.8, 129.2, 128.5, 124.8, 43.3, 21.5.



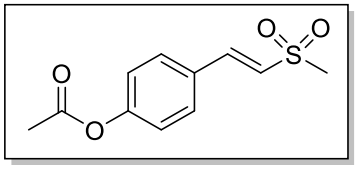
(*E*)-1-(*tert*-butyl)-4-(2-(methylsulfonyl)vinyl)benzene **(3ea)**[2]: 32.1 mg, 67%, light yellow solid, m.p.: 87.3 – 90.1 °C. *n*-hexane/ethyl acetate = 3/1 as an eluent. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.61 (d, *J* = 15.4 Hz, 1H), 7.49 – 7.41 (m, 4H), 6.91 (d, *J* = 15.5 Hz, 1H), 3.03 (s, 3H), 1.33 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 155.0, 143.8, 129.2, 128.4, 126.1, 125.0, 43.3 34.9, 31.0.



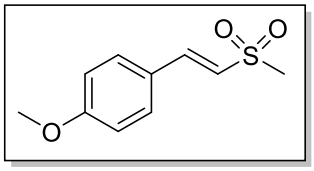
(*E*)-trimethyl(4-(2-(methylsulfonyl)vinyl)phenyl)silane **(3fa)**: 36.6 mg, 72%, white solid, m.p.: 89.1 – 91.1 °C. *n*-hexane/ethyl acetate = 3/1 as an eluent. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.63 (d, *J* = 15.5 Hz, 1H), 7.58 (d, *J* = 8.0 Hz, 2H), 7.49 (d, *J* = 7.9 Hz, 2H), 6.96 (d, *J* = 15.4 Hz, 1H), 3.04 (s, 3H), 0.28 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 145.2, 144.0, 134.0, 132.0, 127.6, 126.1, 43.2, -1.4; HRMS (ESI) *m/z*: $[M+Na]^+$ calcd for $C_{12}H_{18}NaO_2SSi^+$ 277.0689, found 277.0691.



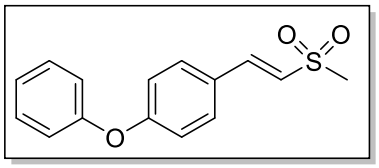
(*E*)-4-(2-(methylsulfonyl)vinyl)-1,1'-biphenyl **(3ga)**: 33.9 mg, 66%, white solid, m.p.: 181.8 – 183.7 °C. *n*-hexane/ethyl acetate = 3/1 – 2/1 as an eluent. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.70 – 7.63 (m, 3H), 7.63 – 7.56 (m, 4H), 7.47 (t, *J* = 7.5 Hz, 2H), 7.39 (t, *J* = 7.3 Hz, 1H), 6.96 (d, *J* = 15.4 Hz, 1H), 3.06 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 144.1, 143.5, 139.7, 130.9, 129.0, 128.9, 128.1, 127.7, 127.0, 125.8, 43.3; HRMS (ESI) *m/z*: $[M+Na]^+$ calcd for $C_{15}H_{14}NaO_2S^+$ 281.0607, found 281.0615.



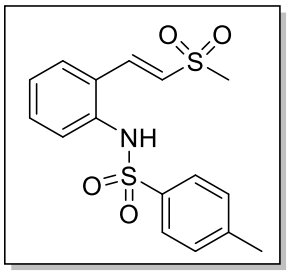
(*E*)-4-(2-(methylsulfonyl)vinyl)phenyl acetate **(3ha)**: 31.4 mg, 65%, white solid, m.p.: 92.6 – 95.4 °C. *n*-hexane/ethyl acetate = 3/1 – 2/1 as an eluent. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.60 (d, *J* = 15.5 Hz, 1H), 7.54 (d, *J* = 8.6 Hz, 2H), 7.17 (d, *J* = 8.6 Hz, 2H), 6.90 (d, *J* = 15.4 Hz, 1H), 3.04 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 168.9, 152.8, 142.8, 129.7, 129.6, 126.2, 122.4, 43.2, 21.1; HRMS (ESI) *m/z*: $[M+Na]^+$ calcd for $C_{11}H_{12}NaO_4S^+$ 263.0349, found 263.0361.



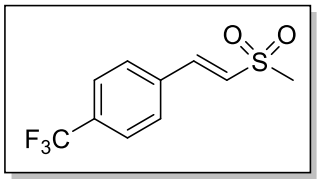
(*E*)-1-methoxy-4-(2-(methylsulfonyl)vinyl)benzene **(3ia)**[3]: 19.2 mg, 45%, white solid, m.p.: 130.5 – 133.1 °C. *n*-hexane/ethyl acetate = 3/1 – 2/1 as an eluent. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.57 (d, *J* = 15.4 Hz, 1H), 7.47 (d, *J* = 8.8 Hz, 2H), 6.93 (d, *J* = 8.8 Hz, 2H), 6.78 (d, *J* = 15.4 Hz, 1H), 3.85 (s, 3H), 3.03 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 162.1, 143.2, 130.3, 124.6, 123.2, 114.5, 55.4, 43.4.



(*E*)-1-(2-(methylsulfonyl)vinyl)-4-phenoxybenzene **(3ja)**: 32.7 mg, 60%, light yellow solid, m.p.: 98.8 – 101.2 °C. *n*-hexane/ethyl acetate = 3/1 as an eluent. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.59 (d, *J* = 15.4 Hz, 1H), 7.48 (d, *J* = 8.7 Hz, 2H), 7.39 (t, *J* = 7.9 Hz, 2H), 7.23 – 7.15 (m, 1H), 7.06 (d, *J* = 7.7 Hz, 2H), 7.02 – 6.97 (m, 2H), 6.83 (d, *J* = 15.4 Hz, 1H), 3.03 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 160.5, 155.5, 143.2, 130.3, 130.0, 126.4, 124.44, 124.41, 119.9, 118.2, 43.3; HRMS (ESI) *m/z*: $[M+Na]^+$ calcd for $C_{15}H_{14}NaO_3S^+$ 297.0556, found 297.0567.

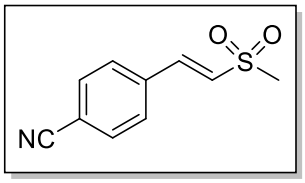


(*E*)-4-methyl-*N*-(2-(2-(methylsulfonyl)vinyl)phenyl)benzenesulfonamide **(3ka)**: 21.7 mg, 31%, white solid, m.p.: 132.4 – 134.2 °C. *n*-hexane/ethyl acetate = 2/1 as an eluent. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.67 (d, *J* = 15.4 Hz, 1H), 7.57 (d, *J* = 8.0 Hz, 2H), 7.50 (d, *J* = 7.7 Hz, 1H), 7.36 (t, *J* = 7.6 Hz, 1H), 7.31 – 7.19 (m, 5H), 6.82 (d, *J* = 15.4 Hz, 1H), 3.03 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 144.2, 139.3, 135.7, 135.2, 131.9, 129.8, 128.7, 128.2, 127.59, 127.57, 127.5, 127.2, 43.1, 21.6; HRMS (ESI) *m/z*: $[M+Na]^+$ calcd for $C_{16}H_{17}NNaO_4S_2^+$ 374.0491, found 374.0501.

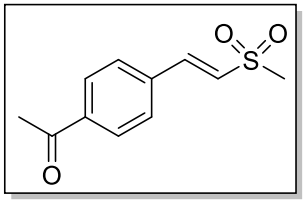


(*E*)-1-(2-(methylsulfonyl)vinyl)-4-(trifluoromethyl)benzene **(3la)**[2]: 40.7 mg, 81%, light yellow solid, m.p.: 137.8 – 140.6 °C. *n*-hexane/ethyl acetate = 3/1 as an eluent. ^{1}H

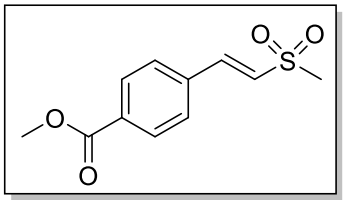
NMR (400 MHz, $CDCl_3$) δ ppm 7.77 – 7.60 (m, 5H), 7.06 (d, J = 15.5 Hz, 1H), 3.08 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 142.0, 135.4, 137 (q, J = 32.7 Hz), 128.7, 126.1 (q, J = 3.7 Hz), 123.5 (q, J = 270.7 Hz), 43.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ ppm -62.96 (s).



(*E*)-4-(2-(methylsulfonyl)vinyl)benzonitrile **(3ma)**[3]: 22.7 mg, 55%, light yellow solid, m.p.: 162.0 – 164.6 °C. *n*-hexane/ethyl acetate = 3/1 as an eluent. ^1H NMR (400 MHz, $CDCl_3$) δ ppm 7.74 (d, J = 8.3 Hz, 2H), 7.68 – 7.61 (m, 3H), 7.06 (d, J = 15.5 Hz, 1H), 3.08 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 141.5, 136.2, 132.8, 129.7, 128.9, 117.9, 114.5, 43.0.

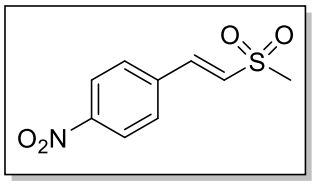


(*E*)-1-(4-(2-(methylsulfonyl)vinyl)phenyl)ethan-1-one **(3na)**[4]: 22.6 mg, 50%, white solid, m.p.: 140.2 – 141.6 °C. *n*-hexane/ethyl acetate = 2/1 as an eluent. ^1H NMR (400 MHz, $CDCl_3$) δ ppm 8.01 (d, J = 8.1 Hz, 2H), 7.71 – 7.59 (m, 3H), 7.06 (d, J = 15.4 Hz, 1H), 3.08 (s, 3H), 2.64 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 197.1, 142.3, 138.7, 136.2, 128.9, 128.6, 128.5, 43.1, 26.7.

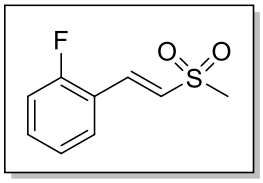


methyl (*E*)-4-(2-(methylsulfonyl)vinyl)benzoate **(3oa)**[3]: 28.4 mg, 59%, white solid, m.p.: 120.0 – 122.2 °C. *n*-hexane/ethyl acetate = 2/1 as an eluent. ^1H NMR (400 MHz,

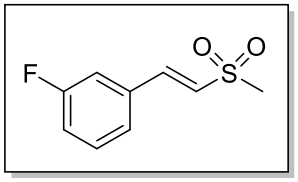
$CDCl_3$) δ ppm 8.09 (d, J = 8.3 Hz, 2H), 7.66 (d, J = 15.5 Hz, 1H), 7.59 (d, J = 8.2 Hz, 2H), 7.04 (d, J = 15.5 Hz, 1H), 3.95 (s, 3H), 3.07 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 166.1, 142.5, 136.1, 132.3, 130.2, 128.43, 128.41, 52.4, 43.1.



(*E*)-1-(2-(methylsulfonyl)vinyl)-4-nitrobenzene **(3pa)**[3]: 24.9 mg, 55%, light yellow solid, m.p.: 185.0 – 188.0 °C. *n*-hexane/ethyl acetate = 2/1 as an eluent. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 8.31 (d, J = 8.8 Hz, 2H), 7.76 – 7.65 (m, 3H), 7.09 (d, J = 15.5 Hz, 1H), 3.09 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 149.1, 141.1, 138.0, 130.3, 129.3, 124.4, 43.0.

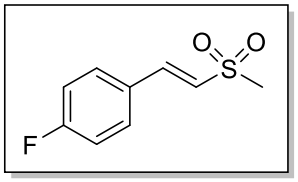


(*E*)-1-fluoro-2-(2-(methylsulfonyl)vinyl)benzene **(3qa)**[5]: 28.2 mg, 70%, light yellow oil, *n*-hexane/ethyl acetate = 3/1 as an eluent. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.70 (d, J = 15.6 Hz, 1H), 7.54 – 7.41 (m, 2H), 7.22 (t, J = 7.6 Hz, 1H), 7.18 – 7.08 (m, 2H), 3.06 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 161.5 (d, J = 254.0 Hz), 137.0 (d, J = 2.0 Hz), 132.9 (d, J = 9.0 Hz), 130.4 (d, J = 3.0 Hz), 129.0 (d, J = 9.0 Hz), 124.7 (d, J = 4.0 Hz), 120.1 (d, J = 12.0 Hz), 116.4 (d, J = 21.0 Hz), 43.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ ppm -112.23 (dt, J = 12.0, 6.1 Hz).

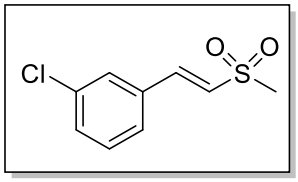


(*E*)-1-fluoro-3-(2-(methylsulfonyl)vinyl)benzene **(3ra)**[5]: 26.0 mg, 65%, light yellow solid, m.p.: 82.2 – 84.6 °C. *n*-hexane/ethyl acetate = 3/1 as an eluent. ^{1}H NMR (400

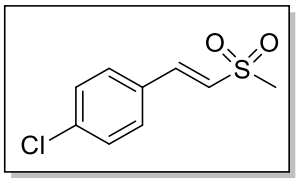
MHz, $CDCl_3$) δ ppm 7.60 (d, J = 15.4 Hz, 1H), 7.42 (td, J = 8.0, 5.7 Hz, 1H), 7.31 (dt, J = 7.7, 1.3 Hz, 1H), 7.23 (dt, J = 9.4, 1.7 Hz, 1H), 7.16 (tdd, J = 8.3, 2.6, 1.1 Hz, 1H), 6.95 (d, J = 15.4 Hz, 1H), 3.06 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 162.9 (d, J = 246.0 Hz), 142.5 (d, J = 2.0 Hz), 134.1 (d, J = 8.0 Hz), 130.8 (d, J = 8.0 Hz), 127.5, 124.6 (d, J = 3.0 Hz), 118.3 (d, J = 21.0 Hz), 114.8 (d, J = 22.0 Hz), 43.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ ppm -111.62 (td, J = 8.8, 5.9 Hz).



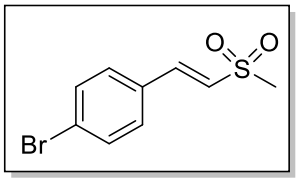
(*E*)-1-fluoro-4-(2-(methylsulfonyl)vinyl)benzene **(3sa)**[2]: 28.8 mg, 72%, white solid, m.p.: 122.5 – 124.6 °C. *n*-hexane/ethyl acetate = 3/1 as an eluent. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.60 (d, J = 15.5 Hz, 1H), 7.56 – 7.50 (m, 2H), 7.18 – 7.08 (m, 2H), 6.88 (d, J = 15.5 Hz, 1H), 3.05 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 164.4 (d, J = 252.0 Hz), 142.6, 130.6 (d, J = 8.0 Hz), 128.2 (d, J = 3.0 Hz), 125.8 (d, J = 3.0 Hz), 116.3 (d, J = 21.0 Hz), 43.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ ppm -107.42 (tt, J = 9.1, 5.5 Hz).



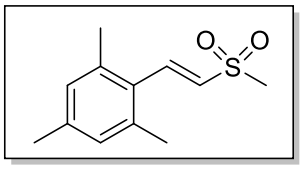
(*E*)-1-chloro-3-(2-(methylsulfonyl)vinyl)benzene **(3ta)**: 32.5 mg, 75%, white solid, m.p.: 69.7 – 70.2 °C. *n*-hexane/ethyl acetate = 3/1 as an eluent. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.57 (d, J = 15.5 Hz, 1H), 7.51 (t, J = 1.8 Hz, 1H), 7.45 – 7.34 (m, 3H), 6.97 (d, J = 15.5 Hz, 1H), 3.06 (s, 3H).; ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 142.2, 135.0, 133.7, 131.1, 130.3, 128.1, 127.6, 126.8, 43.1; HRMS (ESI) *m/z*: $[M+Na]^+$ calcd for $C_9H_9{}^{35}ClNaO_2S^+$ 238.9904, found 238.9907; calcd for $C_9H_9{}^{37}ClNaO_2S^+$ 240.9874, found 240.9879.



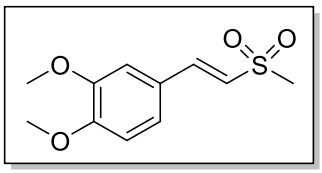
(*E*)-1-chloro-4-(2-(methylsulfonyl)vinyl)benzene **(3ua)**[2]: 33.9 mg, 78%, white solid, m.p.: 119.4 – 121.5 °C. *n*-hexane/ethyl acetate = 3/1 as an eluent. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.58 (d, *J* = 15.4 Hz, 1H), 7.50 – 7.44 (m, 2H), 7.43 – 7.37 (m, 2H), 6.93 (d, *J* = 15.5 Hz, 1H), 3.05 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 142.5, 137.4, 130.5, 129.7, 129.4, 126.6, 43.2.



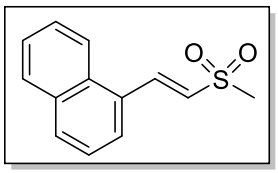
(*E*)-1-bromo-4-(2-(methylsulfonyl)vinyl)benzene **(3va)**[2]: 35.8 mg, 69%, white solid, m.p.: 120.3 – 122.5 °C. *n*-hexane/ethyl acetate = 3/1 as an eluent. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.63 – 7.50 (m, 3H), 7.39 (d, *J* = 8.5 Hz, 2H), 6.96 (d, *J* = 15.5 Hz, 1H), 3.05 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 142.5, 132.3, 130.9, 129.8, 126.7, 125.7, 43.1.



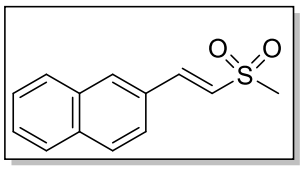
(*E*)-1,3,5-trimethyl-2-(2-(methylsulfonyl)vinyl)benzene **(3wa)**[4]: 18.0 mg, 40%, white solid, m.p.: 103.8 – 105.6 °C. *n*-hexane/ethyl acetate = 3/1 as an eluent. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.81 (d, *J* = 15.8 Hz, 1H), 6.92 (s, 2H), 6.62 (d, *J* = 15.8 Hz, 1H), 3.04 (s, 3H), 2.35 (s, 6H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 142.0, 139.6, 137.1, 130.4, 129.5, 128.1, 43.2, 21.1, 21.0.



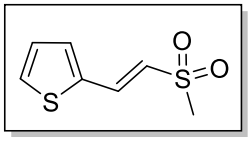
(*E*)-1,2-dimethoxy-4-(2-(methylsulfonyl)vinyl)benzene **(3xa)**[6]: 22.9 mg, 47%, white solid, m.p.: 116.5 – 118.7 °C. *n*-hexane/ethyl acetate = 2/1 – 1/1 as an eluent. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.55 (d, *J* = 15.4 Hz, 1H), 7.12 (dd, *J* = 8.3, 1.9 Hz, 1H), 7.02 (d, *J* = 2.0 Hz, 1H), 6.90 (d, *J* = 8.3 Hz, 1H), 6.81 (d, *J* = 15.3 Hz, 1H), 3.93 (d, *J* = 3.8 Hz, 6H), 3.04 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 151.8, 149.2, 143.9, 124.8, 123.4, 123.4, 111.0, 109.8, 55.94, 55.87, 43.4.



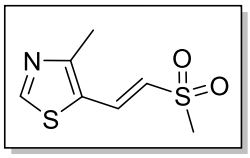
(*E*)-1-(2-(methylsulfonyl)vinyl)naphthalene **(3ya)**[4]: 20.0 mg, 43%, light yellow solid, m.p.: 114.2 – 116.3 °C. *n*-hexane/ethyl acetate = 3/1 as an eluent. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 8.47 (d, *J* = 15.1 Hz, 1H), 8.14 (d, *J* = 8.3 Hz, 1H), 7.95 (d, *J* = 8.2 Hz, 1H), 7.90 (d, *J* = 8.0 Hz, 1H), 7.73 (d, *J* = 7.2 Hz, 1H), 7.63 – 7.47 (m, 3H), 7.03 (d, *J* = 15.2 Hz, 1H), 3.10 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 141.0, 133.6, 131.6, 131.2, 129.1, 128.8, 128.4, 127.3, 126.5, 125.7, 125.3, 122.9, 43.2.



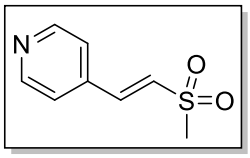
(*E*)-2-(2-(methylsulfonyl)vinyl)naphthalene **(3za)**[3]: 36.6 mg, 79%, light yellow solid, m.p.: 141.6 – 143.8 °C. *n*-hexane/ethyl acetate = 3/1 as an eluent. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.94 – 7.81 (m, 4H), 7.77 (d, *J* = 15.4 Hz, 1H), 7.63 – 7.50 (m, 3H), 7.04 (d, *J* = 15.4 Hz, 1H), 3.07 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 143.9, 134.4, 133.0, 131.0, 129.4, 129.0, 128.6, 127.8, 127.7, 126.9, 126.0, 123.2, 43.3.



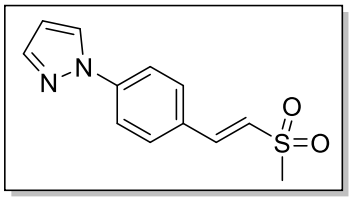
(*E*)-2-(2-(methylsulfonyl)vinyl)thiophene **(3a'a)**[2]: 19.9 mg, 53%, brown oil, *n*-hexane/ethyl acetate = 3/1 – 2/1 as an eluent. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.74 (d, *J* = 15.2 Hz, 1H), 7.49 (d, *J* = 5.1 Hz, 1H), 7.34 (d, *J* = 3.6 Hz, 1H), 7.10 (dd, *J* = 5.0, 3.7 Hz, 1H), 6.71 (d, *J* = 15.1 Hz, 1H), 3.04 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 136.5, 136.5, 132.7, 130.1, 128.4, 124.1, 43.4.



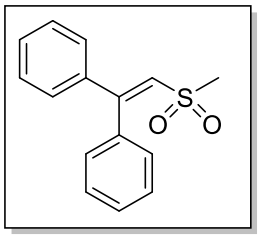
(*E*)-4-methyl-5-(2-(methylsulfonyl)vinyl)thiazole **(3b'a)**[3]: 10.2 mg, 25%, brown solid, m.p.: 115.2 – 117.8 °C. *n*-hexane/ethyl acetate = 3/1 – 2/1 as an eluent. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 8.80 (s, 1H), 7.77 (d, *J* = 15.0 Hz, 1H), 6.67 (d, *J* = 15.0 Hz, 1H), 3.06 (s, 3H), 2.60 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 157.7, 154.0, 133.2, 126.8, 125.7, 43.3, 15.7.



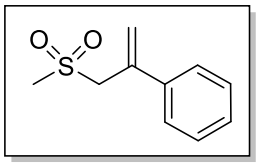
(*E*)-4-(2-(methylsulfonyl)vinyl)pyridine **(3c'a)**: 11.0 mg, 30%, brown solid, m.p.: 121.9 – 122.5 °C. *n*-hexane/ethyl acetate = 1/1 as an eluent. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 8.77 (br, 2H), 7.59 (d, *J* = 15.5 Hz, 1H), 7.41 (br, 2H), 7.15 (d, *J* = 15.5 Hz, 1H), 3.08 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 150.7, 141.1, 139.2, 130.9, 122.2, 42.9; HRMS (ESI) *m/z*: $[M+Na]^+$ calcd for $C_8H_{10}NO_2S^+$ 184.0427, found 184.0434.



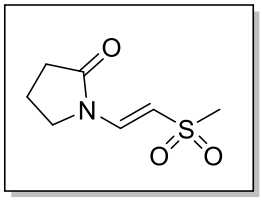
(*E*)-1-(4-(2-(methylsulfonyl)vinyl)phenyl)-1*H*-pyrazole **(3d'a)**: 20.8 mg, 42%, light yellow solid, m.p.: 150.3 – 151.6 °C. *n*-hexane/ethyl acetate = 3/1 as an eluent. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 8.00 (s, 1H), 7.84 – 7.74 (m, 3H), 7.68 – 7.58 (m, 3H), 6.93 (d, *J* = 15.5 Hz, 1H), 6.52 (s, 1H), 3.06 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 142.8, 142.0, 141.9, 129.9, 129.8, 126.7, 125.9, 119.1, 108.5, 43.3; HRMS (ESI) *m/z*: $[M+Na]^+$ calcd for $C_{12}H_{12}N_2NaO_2S^+$ 271.0512, found 271.0525.



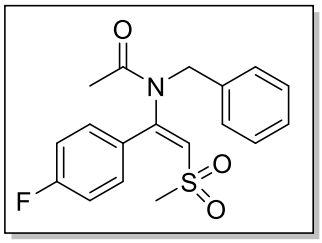
(2-(methylsulfonyl)ethene-1,1-diyl)dibenzene **(3e'a)**[3]: 12.4 mg, 24%, white solid, m.p.: 101.5 – 103.7 °C. *n*-hexane/ethyl acetate = 3/1 as an eluent. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.52 – 7.23 (m, 10H), 6.87 (s, 1H), 2.68 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 154.8, 139.0, 135.6, 130.4, 129.8, 129.5, 128.7, 128.31, 128.29, 128.0, 43.2.



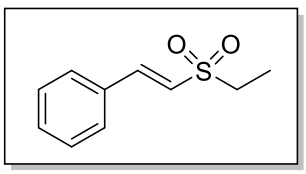
(3-(methylsulfonyl)prop-1-en-2-yl)benzene **(3f'a)**[3]: 12.6 mg, 32%, light yellow oil, *n*-hexane/ethyl acetate = 3/1 as an eluent. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.50 – 7.44 (m, 2H), 7.42 – 7.31 (m, 3H), 5.77 (s, 1H), 5.57 (s, 1H), 4.20 (s, 2H), 2.72 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 138.6, 136.6, 128.8, 128.5, 126.2, 122.1, 60.7, 40.2.



(*E*)-1-(2-(methylsulfonyl)vinyl)pyrrolidin-2-one **(3g'a)**[8]: 22.4 mg, 59%, light yellow solid, m.p.: 100.1 – 102.9 °C. *n*-hexane/ethyl acetate = 3/1 as an eluent. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 8.01 (d, *J* = 13.7 Hz, 1H), 5.79 (d, *J* = 13.7 Hz, 1H), 3.58 (t, *J* = 7.2 Hz, 2H), 3.00 (s, 3H), 2.58 (t, *J* = 8.2 Hz, 2H), 2.29 – 2.17 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 174.3, 137.1, 108.8, 45.1, 44.4, 30.6, 17.4.

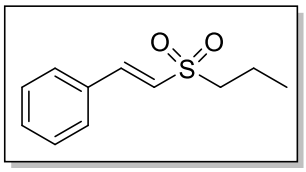


(*E*)-*N*-benzyl-*N*-(1-(4-fluorophenyl)-2-(methylsulfonyl)vinyl)acetamide **(3h'a)**: 20.2 mg, 29%, white solid, m.p.: 113.9 – 116.7 °C. *n*-hexane/ethyl acetate = 3/1 -2/1 as an eluent. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.51 – 7.45 (m, 2H), 7.36 – 7.28 (m, 3H), 7.19 – 7.11 (m, 4H), 6.20 (s, 1H), 4.62 (s, 2H), 2.73 (s, 3H), 2.20 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 170.1, 164.5 (d, *J* = 253.0 Hz), 150.9, 136.1, 132.1 (d, *J* = 9.0 Hz), 128.8, 128.3, 128.1 (d, *J* = 4.0 Hz), 128.0, 127.1, 116.0 (d, *J* = 22.0 Hz), 50.6, 43.3, 23.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ ppm -106.72 (tt, *J* = 8.8, 5.2 Hz); HRMS (ESI) *m/z*: $[M+Na]^+$ calcd for $C_{18}H_{18}FNNaO_3S^+$ 370.0884, found 370.0883.

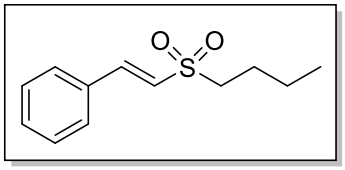


(*E*)-(2-(ethylsulfonyl)vinyl)benzene **(3ab)**[9]: 18.2 mg, 46%, light yellow solid, m.p.: 60.1 – 62.5 °C. *n*-hexane/ethyl acetate = 3/1 – 2/1 as an eluent. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.61 (d, *J* = 15.5 Hz, 1H), 7.56 – 7.50 (m, 2H), 7.48 – 7.40 (m, 3H), 6.83 (d, *J* = 15.5 Hz, 1H), 3.10 (q, *J* = 7.5 Hz, 2H), 1.39 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$)

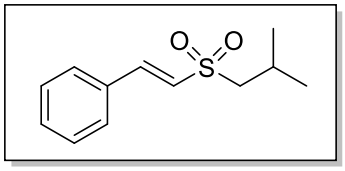
δ ppm 145.2, 132.2, 131.3, 129.1, 128.5, 123.9, 49.4, 7.2.



(*E*)-(2-(propylsulfonyl)vinyl)benzene **(3ac)**[7]: 18.0 mg, 43%, colorless oil, *n*-hexane/ethyl acetate = 3/1 as an eluent. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.60 (d, *J* = 15.5 Hz, 1H), 7.55 – 7.49 (m, 2H), 7.48 – 7.39 (m, 3H), 6.84 (d, *J* = 15.5 Hz, 1H), 3.12 – 2.99 (m, 2H), 1.94 – 1.81 (m, 2H), 1.07 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 144.7, 132.2, 131.3, 129.1, 128.5, 124.7, 56.8, 16.3, 13.0.

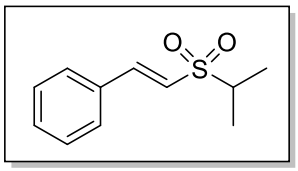


(*E*)-(2-(propylsulfonyl)vinyl)benzene **(3ad)**[10]: 18.0 mg, 40%, light yellow oil, *n*-hexane/ethyl acetate = 3/1 as an eluent. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.60 (d, *J* = 15.5 Hz, 1H), 7.55 – 7.50 (m, 2H), 7.46 – 7.39 (m, 3H), 6.85 (d, *J* = 15.5 Hz, 1H), 3.12 – 3.03 (m, 2H), 1.85 – 1.76 (m, 2H), 1.52 – 1.41 (m, 2H), 0.95 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 144.6, 132.1, 131.2, 129.0, 128.5, 124.6, 54.8, 24.4, 21.5, 13.5.

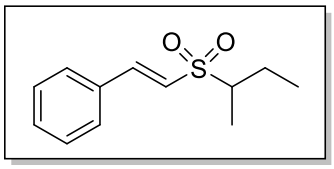


(*E*)-(2-(isobutylsulfonyl)vinyl)benzene **(3ae)**[11]: 16.3 mg, 36%, colorless oil, *n*-hexane/ethyl acetate = 3/1 as an eluent. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.60 (d, *J* = 15.5 Hz, 1H), 7.55 – 7.49 (m, 2H), 7.46 – 7.39 (m, 3H), 6.85 (d, *J* = 15.5 Hz, 1H), 2.98 (d, *J* = 6.5 Hz, 2H), 2.41 – 2.29 (m, 1H), 1.13 (d, *J* = 6.7 Hz, 6H); ^{13}C NMR (100 MHz,

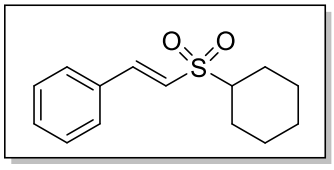
$CDCl_3$) δ ppm 144.2, 132.2, 131.2, 129.1, 128.5, 125.6, 62.8, 24.0, 22.8.



(*E*)-(2-(isopropylsulfonyl)vinyl)benzene **(3af)**[12]: 23.1 mg, 55%, light yellow solid, m.p.: 44.1 – 46.9 °C. *n*-hexane/ethyl acetate = 3/1 as an eluent. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.59 (d, *J* = 15.6 Hz, 1H), 7.56 – 7.50 (m, 2H), 7.48 – 7.40 (m, 3H), 6.81 (d, *J* = 15.5 Hz, 1H), 3.20 – 3.11 (m, 1H), 1.40 (d, *J* = 6.9 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 145.7, 132.2, 131.2, 129.0, 128.4, 122.2, 54.6, 15.5.

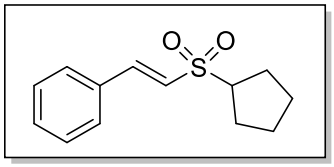


(*E*)-(2-(*sec*-butylsulfonyl)vinyl)benzene **(3ag)**: 18.5 mg, 41%, colorless oil, *n*-hexane/ethyl acetate = 3/1 as an eluent. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.63 – 7.49 (m, 3H), 7.48 – 7.38 (m, 3H), 6.79 (d, *J* = 15.5 Hz, 1H), 2.96 – 2.86 (m, 1H), 2.19 – 2.07 (m, 1H), 1.61 – 1.48 (m, 1H), 1.39 (d, *J* = 6.9 Hz, 3H), 1.05 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 145.5, 132.3, 131.2, 129.0, 128.5, 122.6, 60.6, 22.5, 12.4, 11.2; HRMS (ESI) *m/z*: $[M+Na]^+$ calcd for $C_{12}H_{16}NaO_2S^+$ 247.0763, found 247.0770.

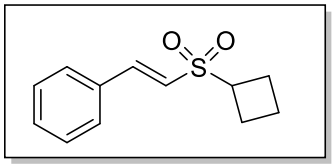


(*E*)-(2-(cyclohexylsulfonyl)vinyl)benzene **(3ah)**[13]: 22.5 mg, 45%, colorless oil, *n*-hexane/ethyl acetate = 3/1 as an eluent. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.59 – 7.50 (m, 3H), 7.48 – 7.38 (m, 3H), 6.80 (d, J = 15.5 Hz, 1H), 2.88 (tt, J = 12.2, 3.5 Hz, 1H), 2.30 – 2.18 (m, 2H), 1.91 (dt, J = 13.1, 3.2 Hz, 2H), 1.71 (dt, J = 12.3, 3.1 Hz, 1H), 1.50

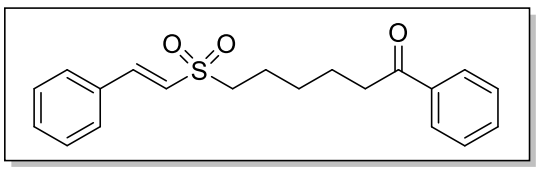
(qd, J = 12.5, 3.5 Hz, 2H), 1.37 – 1.13 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 145.4, 132.2, 131.1, 129.0, 128.4, 122.7, 62.4, 25.3, 24.98, 24.96.



(*E*)-(2-(cyclopentylsulfonyl)vinyl)benzene **(3ai)**: 23.8 mg, 50%, colorless oil, *n*-hexane/ethyl acetate = 3/1 as an eluent. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.60 (d, *J* = 15.5 Hz, 1H), 7.56 – 7.49 (m, 2H), 7.48 – 7.38 (m, 3H), 6.83 (d, *J* = 15.5 Hz, 1H), 3.45 (tt, *J* = 9.0, 6.9 Hz, 1H), 2.16 – 1.97 (m, 4H), 1.87 – 1.77 (m, 2H), 1.67 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 144.7, 132.3, 131.2, 129.1, 128.4, 123.8, 62.9, 27.0, 26.0; HRMS (ESI) *m/z*: $[M+Na]^+$ calcd for $C_{13}H_{16}NaO_2S^+$ 259.0763, found 259.0771.

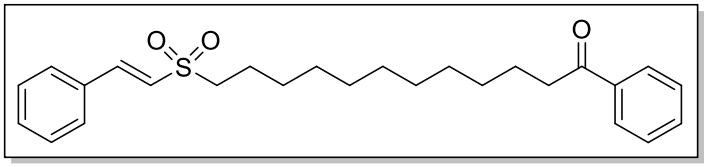


(*E*)-(2-(cyclobutylsulfonyl)vinyl)benzene **(3aj)**[13]: 24.7 mg, 56%, light yellow solid, m.p.: 76.8 – 79.7 °C. *n*-hexane/ethyl acetate = 3/1 as an eluent. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.59 (d, *J* = 15.5 Hz, 1H), 7.55 – 7.49 (m, 2H), 7.47 – 7.39 (m, 3H), 6.78 (d, *J* = 15.5 Hz, 1H), 3.80 (quint, *J* = 8.2 Hz, 1H), 2.64 – 2.50 (m, 2H), 2.37 – 2.26 (m, 2H), 2.12 – 2.00 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 145.0, 132.3, 131.2, 129.0, 128.4, 122.8, 55.6, 22.4, 17.0.

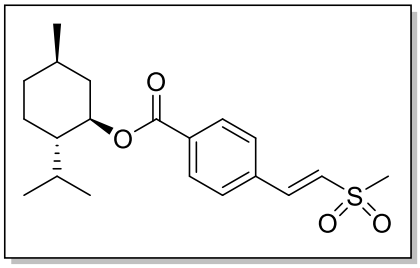


(*E*)-1-phenyl-6-(styrylsulfonyl)hexan-1-one **(3al)**: 17.4 mg, 25%, white solid, m.p.: 58.7 – 60.1 °C. *n*-hexane/ethyl acetate = 3/1 – 2/1 as an eluent. ^{1}H NMR (400 MHz,

$CDCl_3$) δ ppm 7.96 – 7.91 (m, 2H), 7.60 (d, J = 15.6 Hz, 1H), 7.57 – 7.51 (m, 3H), 7.45 (td, J = 7.5, 4.9 Hz, 5H), 6.84 (d, J = 15.5 Hz, 1H), 3.13 – 3.07 (m, 2H), 2.99 (t, J = 7.1 Hz, 2H), 1.94 – 1.84 (m, 2H), 1.83 – 1.73 (m, 2H), 1.59 – 1.48 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 199.7, 144.9, 136.7, 133.0, 132.1, 131.3, 129.1, 128.6, 128.5, 127.9, 124.5, 54.9, 37.9, 28.0, 23.4, 22.5; HRMS (ESI) *m/z*: $[M+Na]^+$ calcd for $C_{20}H_{22}NaO_3S^+$ 365.1182, found 365.1188.

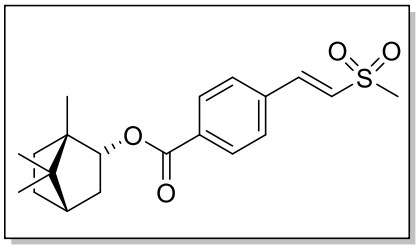


(*E*)-1-phenyl-12-(styrylsulfonyl)dodecan-1-one **(3am)**: 22.8 mg, 27%, white solid, m.p.: 76.3 – 78.7 °C. *n*-hexane/ethyl acetate = 3/1 – 2/1 as an eluent. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.99 – 7.93 (m, 2H), 7.63 – 7.55 (m, 2H), 7.54 – 7.50 (m, 2H), 7.49 – 7.40 (m, 5H), 6.83 (d, J = 15.5 Hz, 1H), 3.10 – 3.02 (m, 2H), 2.96 (t, J = 7.4 Hz, 2H), 1.87 – 1.77 (m, 2H), 1.76 – 1.68 (m, 2H), 1.48 – 1.22 (m, 14H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 200.6, 144.7, 137.0, 132.8, 132.2, 131.3, 129.1, 128.53, 128.51, 128.0, 124.6, 55.2, 38.6, 29.39, 29.37, 29.34, 29.29, 29.2, 29.0, 28.3, 24.3, 22.5; HRMS (ESI) *m/z*: $[M+Na]^+$ calcd for $C_{26}H_{34}NaO_3S^+$ 449.2121, found 449.2115.

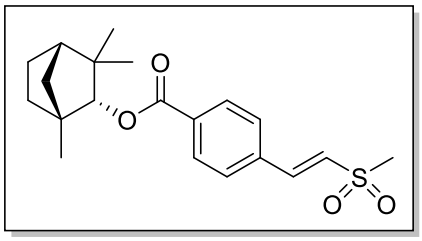


(1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl 4-((*E*)-2-(methylsulfonyl)vinyl)benzoate **(3n'a)**: 40.8 mg, 56%, colorless oil, *n*-hexane/ethyl acetate = 3/1 -2/1 as an eluent. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 8.09 (d, J = 8.1 Hz, 2H), 7.67 (d, J = 15.5 Hz, 1H), 7.59 (d, J = 8.2 Hz, 2H), 7.04 (d, J = 15.5 Hz, 1H), 4.95 (td, J = 10.9, 4.4 Hz, 1H), 3.07 (s, 3H), 2.17 – 2.09 (m, 1H), 2.01 – 1.88 (m, 1H), 1.79 – 1.70 (m, 2H), 1.64 – 1.50 (m, 2H), 1.20

– 1.05 (m, 2H), 0.93 (dd, *J* = 6.8, 4.4 Hz, 7H), 0.80 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 165.1, 142.6, 135.9, 133.1, 130.2, 128.4, 128.2, 75.3, 47.1, 43.1, 40.8, 34.2, 31.4, 26.5, 23.5, 22.0, 20.7, 16.4; HRMS (ESI) *m/z*: $[M+Na]^+$ calcd for $C_{20}H_{28}NaO_4S^+$ 387.1601, found 387.1598.

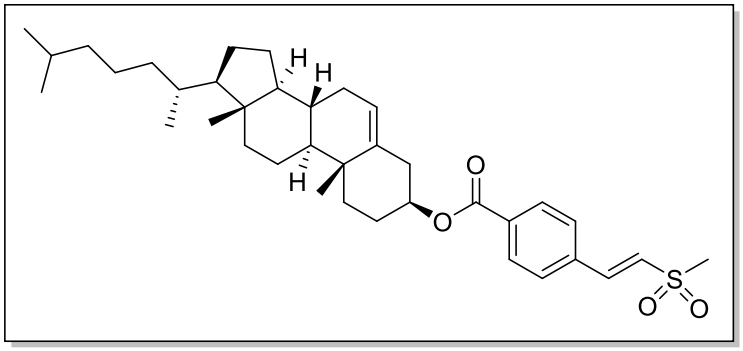


(1*S*,2*R*,4*S*)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl 4-((*E*)-2-(methylsulfonyl)vinyl) benzoate **(3o'a)**: 44.5 mg, 61%, white solid, m.p.: 100.8 – 103.2 °C. *n*-hexane/ethyl acetate = 3/1 -2/1 as an eluent. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 8.11 (d, *J* = 8.2 Hz, 2H), 7.68 (d, *J* = 15.5 Hz, 1H), 7.61 (d, *J* = 8.1 Hz, 2H), 7.04 (d, *J* = 15.4 Hz, 1H), 5.17 – 5.09 (m, 1H), 3.08 (s, 3H), 2.54 – 2.44 (m, 1H), 2.17 – 2.07 (m, 1H), 1.88 – 1.72 (m, 2H), 1.50 – 1.38 (m, 1H), 1.37 – 1.27 (m, 1H), 1.13 (dd, *J* = 13.8, 3.5 Hz, 1H), 0.97 (s, 3H), 0.92 (d, *J* = 1.9 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 165.8, 142.6, 135.9, 133.1, 130.1, 128.4, 128.3, 81.0, 49.0, 47.8, 44.8, 43.1, 36.8, 28.0, 27.3, 19.6, 18.8, 13.6; HRMS (ESI) *m/z*: $[M+Na]^+$ calcd for $C_{20}H_{26}NaO_4S^+$ 385.1444, found 385.1446.

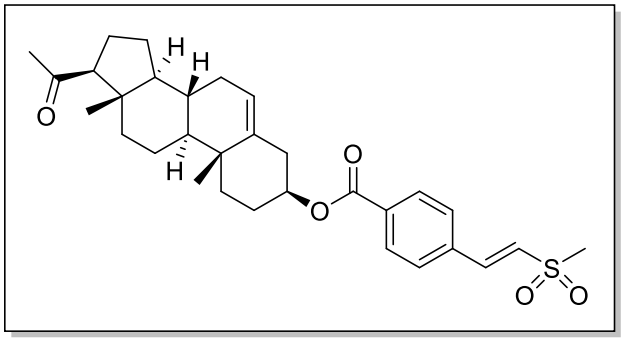


(1*R*,2*R*,4*S*)-1,3,3-trimethylbicyclo[2.2.1]heptan-2-yl 4-((*E*)-2-(methylsulfonyl)vinyl) benzoate **(3p'a)**: 40.7 mg, 56%, colorless oil, *n*-hexane/ethyl acetate = 3/1 -2/1 as an eluent. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 8.11 (d, *J* = 8.3 Hz, 2H), 7.68 (d, *J* = 15.5 Hz, 1H), 7.61 (d, *J* = 8.3 Hz, 2H), 7.03 (d, *J* = 15.5 Hz, 1H), 4.63 (d, *J* = 1.8 Hz, 1H), 3.08 (s, 3H), 1.98 – 1.87 (m, 1H), 1.83 – 1.75 (m, 2H), 1.70 – 1.65 (m, 1H), 1.60 – 1.48 (m, 1H), 1.30 – 1.21 (m, 2H), 1.19 (s, 3H), 1.12 (s, 3H), 0.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$)

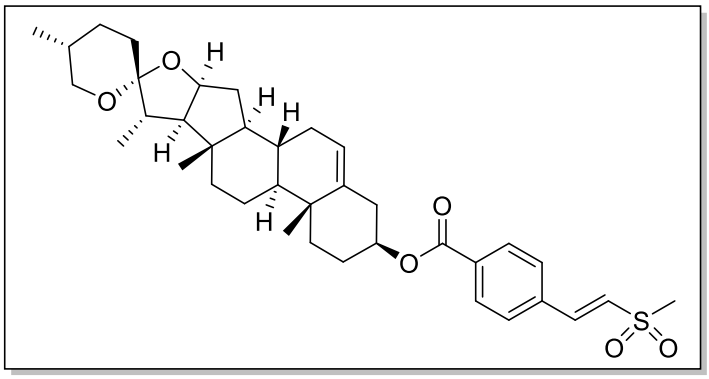
δ ppm 165.9, 142.6, 136.0, 132.9, 130.2, 128.4, 128.3, 87.2, 48.6, 48.3, 43.1, 41.4, 39.8, 29.7, 26.8, 25.8, 20.2, 19.4; HRMS (ESI) *m/z*: $[M+Na]^+$ calcd for $C_{20}H_{26}NaO_4S^+$ 385.1444, found 385.1457.



(3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl 4-((*E*)-2-(methylsulfonyl)vinyl)benzoate **(3q'a)**: 48.1 mg, 40%, white solid, m.p.: 184.5 – 186.5 °C. *n*-hexane/ethyl acetate = 3/1 -2/1 as an eluent. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 8.09 (d, *J* = 8.1 Hz, 2H), 7.66 (d, *J* = 15.5 Hz, 1H), 7.58 (d, *J* = 8.2 Hz, 2H), 7.02 (d, *J* = 15.5 Hz, 1H), 5.43 (d, *J* = 3.9 Hz, 1H), 4.95 – 4.81 (m, 1H), 3.06 (s, 3H), 2.47 (d, *J* = 8.1 Hz, 2H), 2.08 – 1.90 (m, 4H), 1.64 – 1.44 (m, 6H), 1.43 – 0.96 (m, 19H), 0.92 (d, *J* = 6.5 Hz, 3H), 0.87 (dd, *J* = 6.6, 1.8 Hz, 6H), 0.69 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 165.0, 142.7, 139.4, 135.9, 133.1, 130.2, 128.3, 128.2, 122.9, 75.1, 56.6, 56.1, 50.0, 43.1, 42.3, 39.7, 39.5, 38.1, 36.9, 36.6, 36.1, 35.7, 31.9, 31.8, 28.2, 28.0, 27.8, 24.2, 23.8, 22.8, 22.5, 21.0, 19.3, 18.7, 11.8; HRMS (ESI) *m/z*: $[M+Na]^+$ calcd for $C_{37}H_{54}NaO_4S^+$ 617.3635, found 617.3651.

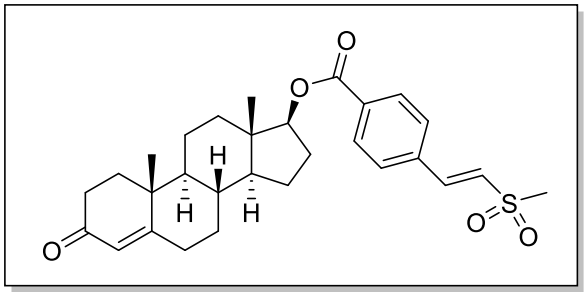


(3*S*,8*S*,9*S*,10*R*,13*S*,14*S*,17*S*)-17-acetyl-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[a]phenanthren-3-yl 4-((*E*)-2-(methylsulfonyl)vinyl)benzoate **(3r'a)**: 58.1 mg, 55%, yellow solid, m.p.: 176.5 – 179.4 °C. *n*-hexane/ethyl acetate = 3/1 -2/1 as an eluent. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 8.09 (d, *J* = 8.1 Hz, 2H), 7.66 (d, *J* = 15.5 Hz, 1H), 7.59 (d, *J* = 8.1 Hz, 2H), 7.03 (d, *J* = 15.5 Hz, 1H), 5.43 (d, *J* = 3.0 Hz, 1H), 4.94 – 4.82 (m, 1H), 3.07 (s, 3H), 2.56 (t, *J* = 8.9 Hz, 1H), 2.48 (d, *J* = 7.8 Hz, 2H), 2.25 – 2.11 (m, 4H), 2.10 – 1.99 (m, 3H), 1.94 (dt, *J* = 13.4, 3.6 Hz, 1H), 1.82 – 1.42 (m, 9H), 1.31 – 1.15 (m, 3H), 1.08 (s, 3H), 0.65 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 209.6, 165.0, 142.6, 139.4, 135.9, 133.0, 130.2, 128.34, 128.29, 122.6, 74.9, 63.6, 56.8, 49.8, 43.9, 43.1, 38.7, 38.0, 36.9, 36.6, 31.8, 31.7, 31.5, 27.7, 24.4, 22.8, 21.0, 19.3, 13.2; HRMS (ESI) *m/z*: $[M+Na]^+$ calcd for $C_{31}H_{40}NaO_5S^+$ 547.2489, found 547.2493.

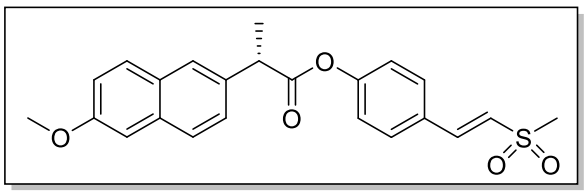


(4*S*,5'*R*,6a*R*,6b*S*,8a*S*,8b*R*,9*S*,10*R*,11a*S*,12a*S*,12b*S*)-5',6a,8a,9-tetramethyl-1,3,3',4,4',5,5',6,6a,6b,6',7,8,8a,8b,9,11a,12,12a,12b-icosahydrospiro[naphtho[2',1':4,5]indeno[2,1-*b*]furan-10,2'-pyran]-4-yl 4-((*E*)-2-(methylsulfonyl)vinyl)benzoate **(3s'a)**: 32.4 mg, 26%, light yellow solid, m.p.: 237.1 – 240.0 °C. *n*-hexane/ethyl acetate = 3/1 -2/1 as an eluent. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 8.09 (d, *J* = 8.1 Hz, 2H), 7.66 (d, *J* = 15.5 Hz, 1H), 7.58 (d, *J* = 8.1 Hz, 2H), 7.02 (d, *J* = 15.5 Hz, 1H), 5.43 (d, *J* = 4.1 Hz, 1H), 4.92 – 4.82 (m, 1H), 4.42 (q, *J* = 7.4 Hz, 1H), 3.48 (dd, *J* = 10.4, 3.1 Hz, 1H), 3.38 (t, *J* = 10.9 Hz, 1H), 3.07 (s, 3H), 2.48 (d, *J* = 8.1 Hz, 2H), 2.08 – 1.41 (m, 18H), 1.35 – 1.12 (m, 4H), 1.09 (s, 3H), 0.98 (d, *J* = 6.9 Hz, 3H), 0.79 (d, *J* = 7.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 165.0, 142.7, 139.4, 135.9, 133.1, 130.2, 128.35, 128.26, 122.6, 109.2, 80.7,

75.0, 66.8, 62.0, 56.4, 49.9, 43.1, 41.6, 40.2, 39.7, 38.1, 36.9, 36.7, 32.0, 31.8, 31.4, 31.3, 30.2, 28.7, 27.8, 20.8, 19.3, 17.1, 16.3, 14.5; HRMS (ESI) *m/z*: $[M+Na]^+$ calcd for $C_{37}H_{50}NaO_6S^+$ 645.3220, found 645.3228.

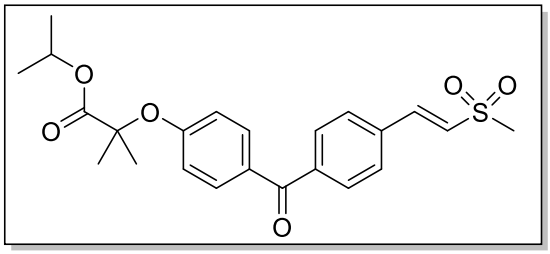


(8*R*,9*S*,10*R*,13*S*,14*S*,17*S)*-10,13-dimethyl-3-oxo-2,3,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[a]phenanthren-17-yl 4-((*E*)-2-(methylsulfonyl)vinyl) benzoate **(3t'a)**: 37.5 mg, 38%, white solid, m.p.: 189.3 – 191.7 °C. *n*-hexane/ethyl acetate = 3/1 -2/1 as an eluent. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 8.09 (d, *J* = 8.1 Hz, 2H), 7.67 (d, *J* = 15.5 Hz, 1H), 7.60 (d, *J* = 8.1 Hz, 2H), 7.03 (d, *J* = 15.5 Hz, 1H), 5.75 (d, *J* = 1.6 Hz, 1H), 4.87 (t, *J* = 8.4 Hz, 1H), 3.07 (s, 3H), 2.50 – 2.26 (m, 5H), 2.09 – 1.99 (m, 1H), 1.94 – 1.84 (m, 2H), 1.81 – 1.57 (m, 6H), 1.51 – 1.38 (m, 2H), 1.33 – 1.14 (m, 6H), 0.99 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 199.5, 170.9, 165.5, 142.6, 136.0, 132.9, 130.2, 128.4, 128.3, 123.9, 83.4, 53.6, 50.2, 43.1, 42.9, 38.6, 36.7, 35.6, 35.4, 33.9, 32.9, 31.4, 27.6, 23.6, 20.5, 17.4, 12.3; HRMS (ESI) *m/z*: $[M+Na]^+$ calcd for $C_{29}H_{36}NaO_5S^+$ 519.2176, found 519.2178.



(*E*)-4-(2-(methylsulfonyl)vinyl)phenyl (*S*)-2-(6-methoxynaphthalen-2-yl)propanoate **(3u'a)**: 36.4 mg, 44%, white solid, m.p.: 160.8 – 164.1 °C. *n*-hexane/ethyl acetate = 2/1 as an eluent. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.79 – 7.71 (m, 3H), 7.57 (d, *J* = 15.5 Hz, 1H), 7.51 – 7.44 (m, 3H), 7.20 – 7.13 (m, 2H), 7.06 (d, *J* = 8.6 Hz, 2H), 6.84 (d, *J* = 15.4 Hz, 1H), 4.10 (q, *J* = 7.1 Hz, 1H), 3.92 (s, 3H), 3.01 (s, 3H), 1.69 (d, *J* = 7.1 Hz,

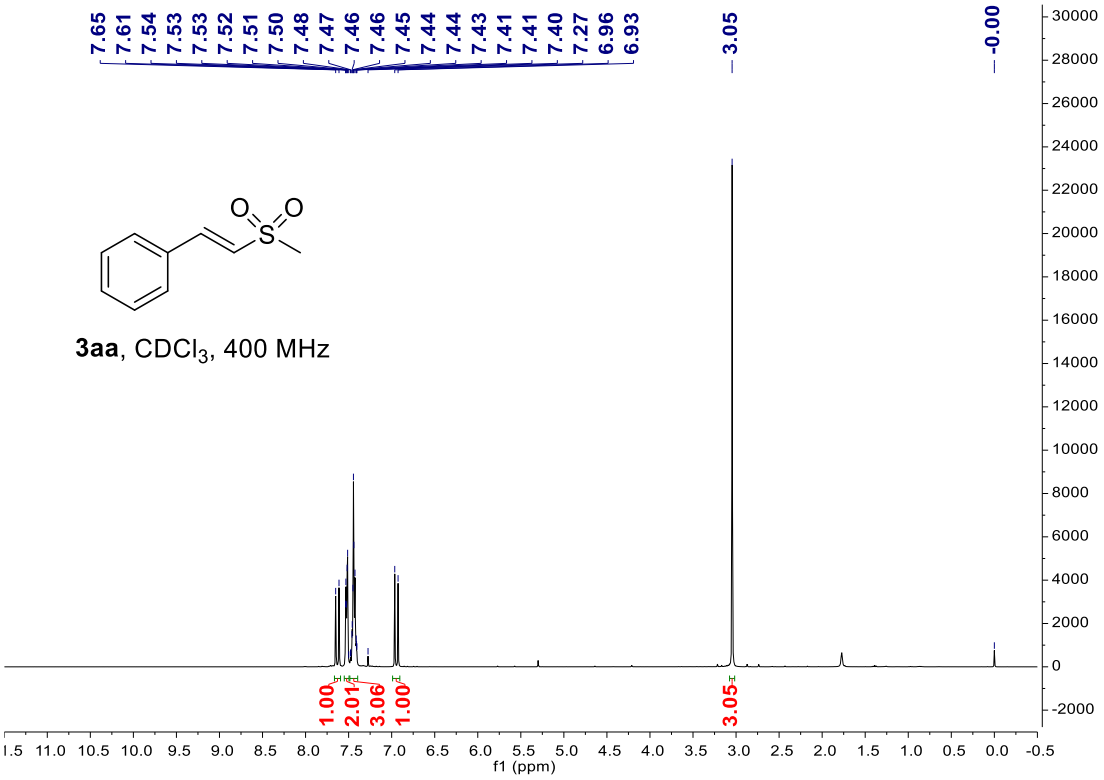
3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 172.7, 157.8, 153.1, 142.9, 134.7, 133.8, 129.7, 129.6, 129.3, 128.9, 127.4, 126.14, 126.09, 125.9, 122.3, 119.2, 105.5, 55.3, 45.5, 43.2, 18.4; HRMS (ESI) *m/z*: $[M+Na]^+$ calcd for $C_{23}H_{22}NaO_5S^+$ 433.1080, found 433.1092.



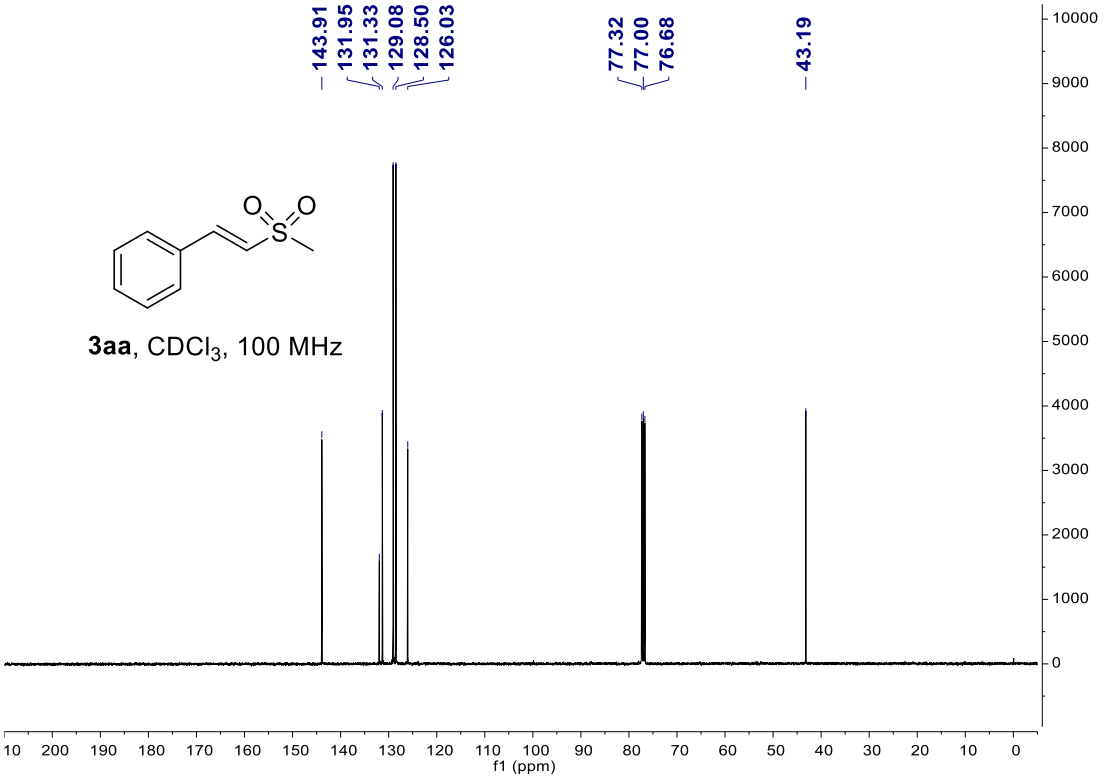
isopropyl (*E*)-2-methyl-2-(4-(4-(2-(methylsulfonyl)vinyl)benzoyl)phenoxy)propanoate **(3v'a)**: 40.2 mg, 47%, white solid, m.p.: 109.6 – 112.1 °C. *n*-hexane/ethyl acetate = 2/1 as an eluent. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.82 – 7.73 (m, 4H), 7.69 (d, *J* = 15.5 Hz, 1H), 7.63 (d, *J* = 8.2 Hz, 2H), 7.06 (d, *J* = 15.5 Hz, 1H), 6.88 (d, *J* = 8.9 Hz, 2H), 5.16 – 5.04 (m, 1H), 3.08 (s, 3H), 1.67 (s, 6H), 1.21 (d, *J* = 6.3 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 194.3, 172.9, 159.8, 142.6, 140.3, 135.1, 131.9, 130.3, 129.8, 128.3, 128.1, 117.1, 79.3, 69.3, 43.1, 25.3, 21.4; HRMS (ESI) *m/z*: $[M+Na]^+$ calcd for $C_{23}H_{26}NaO_6S^+$ 453.1342, found 453.1335.

^{1}H, ^{19}F and ^{13}C NMR spectra of products

(*E*)-(2-(methylsulfonyl)vinyl)benzene **(3aa)**

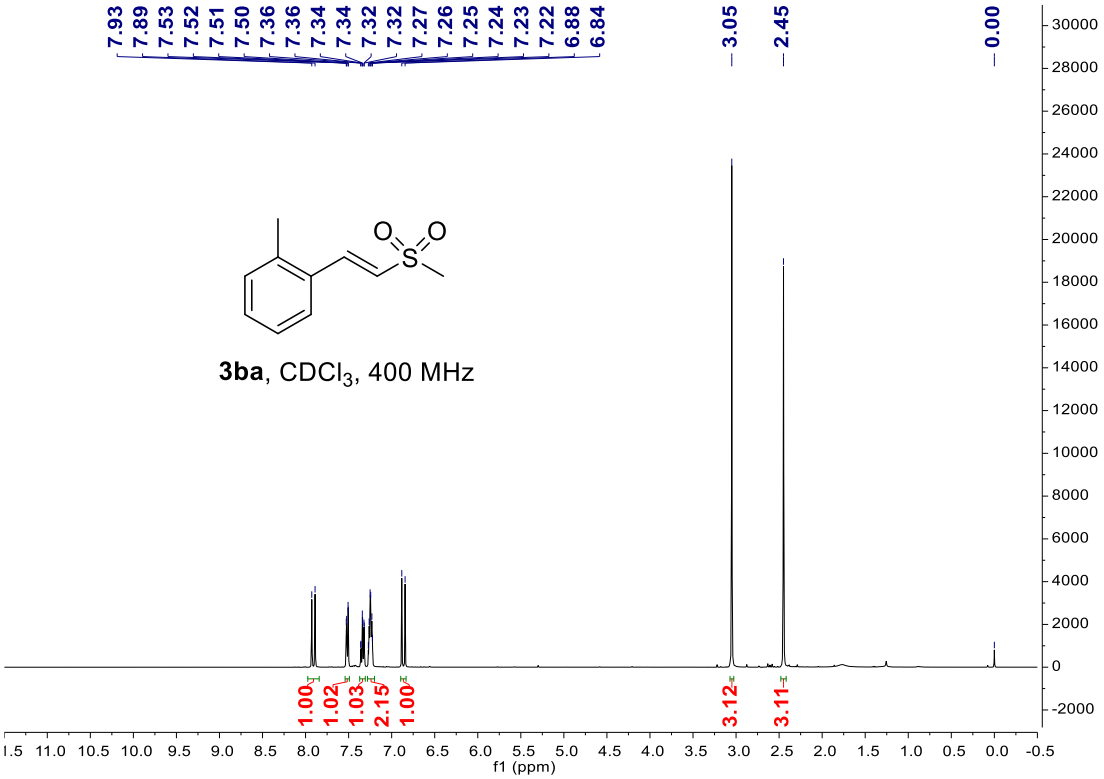


3aa, $CDCl_3$, 400 MHz

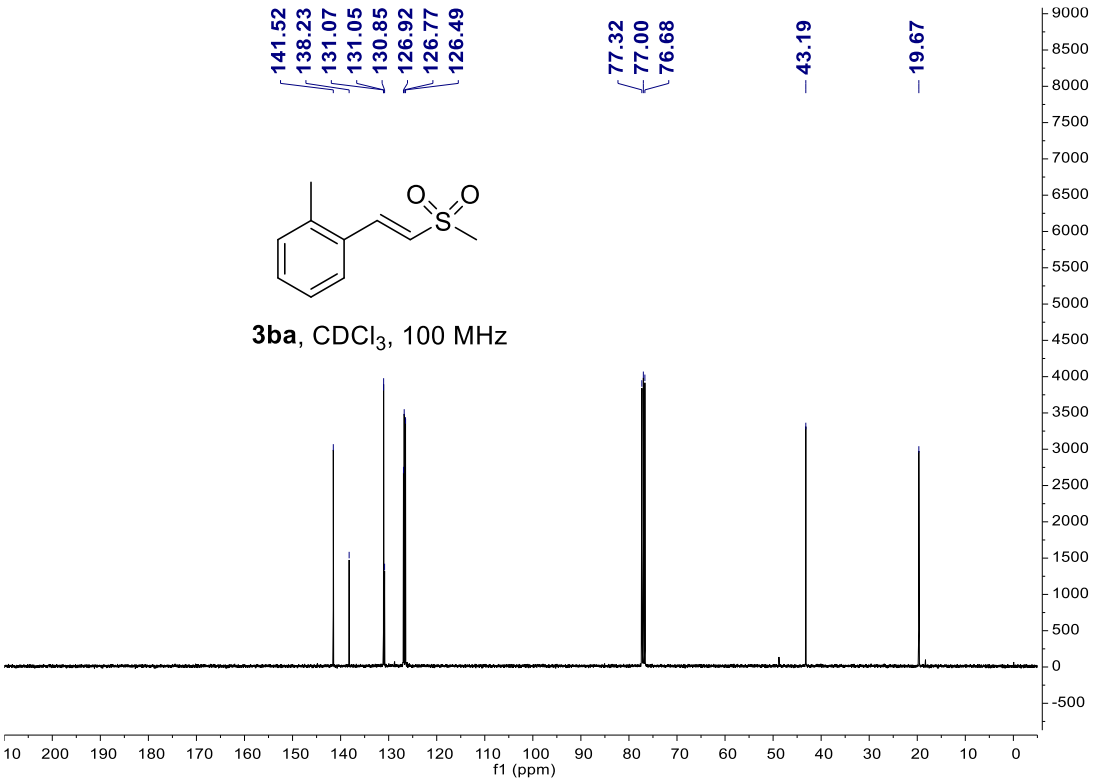


3aa, $CDCl_3$, 100 MHz

(*E*)-1-methyl-2-(2-(methylsulfonyl)vinyl)benzene **(3ba)**

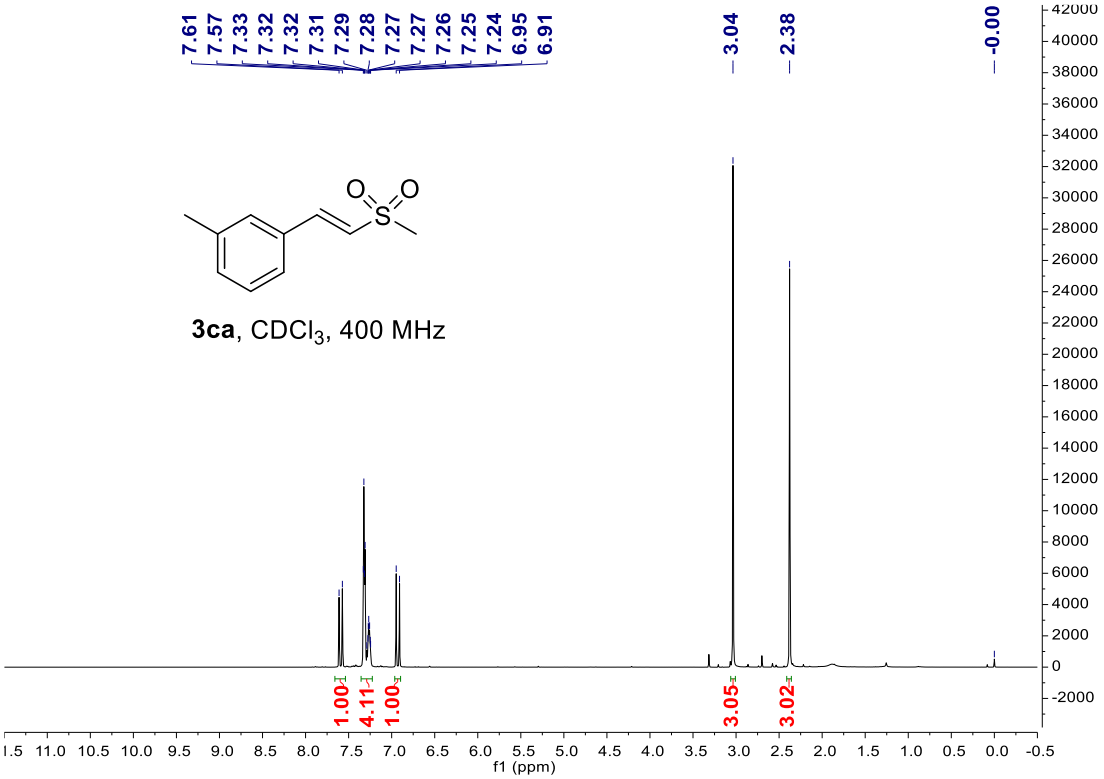


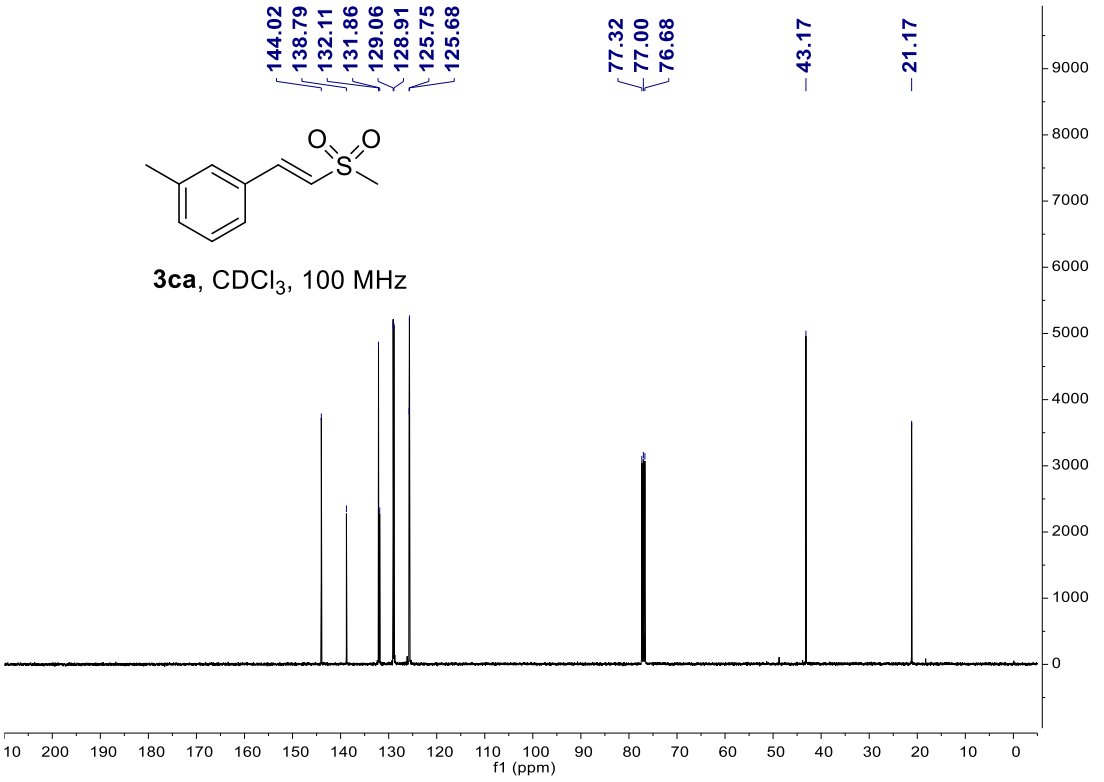
3ba, $CDCl_3$, 400 MHz



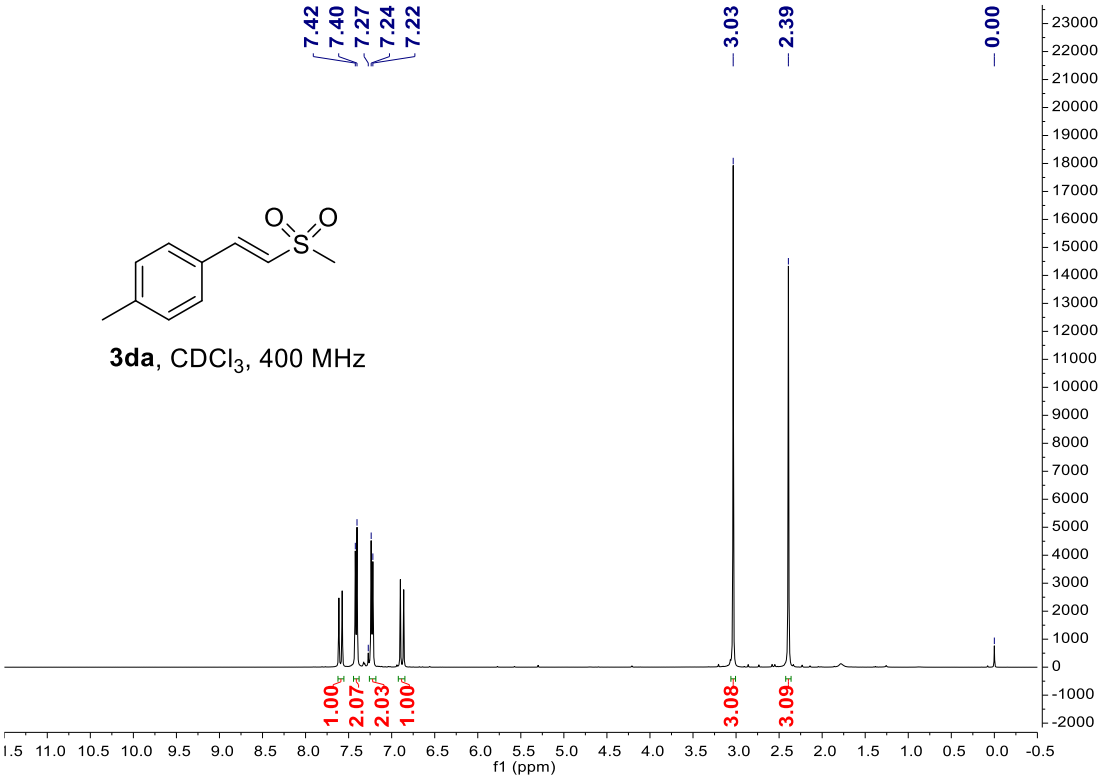
3ba, $CDCl_3$, 100 MHz

(*E*)-1-methyl-3-(2-(methylsulfonyl)vinyl)benzene **(3ca)**

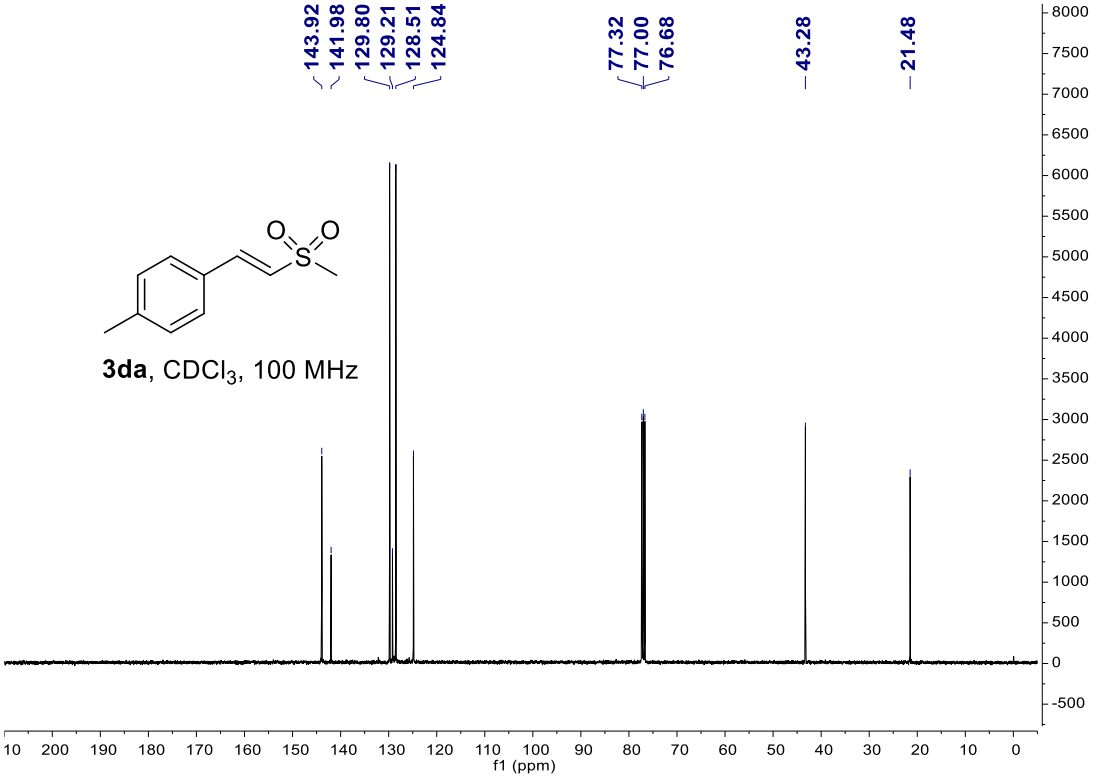




(*E*)-1-methyl-4-(2-(methylsulfonyl)vinyl)benzene **(3da)**

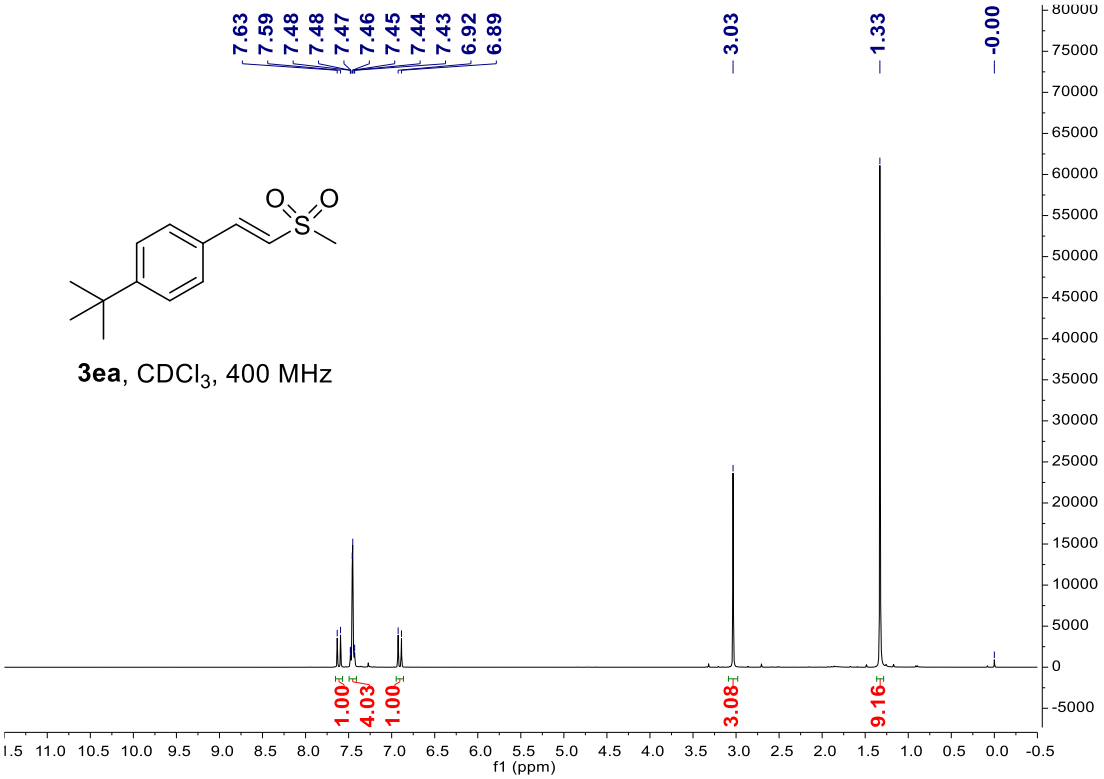


3da, $CDCl_3$, 400 MHz

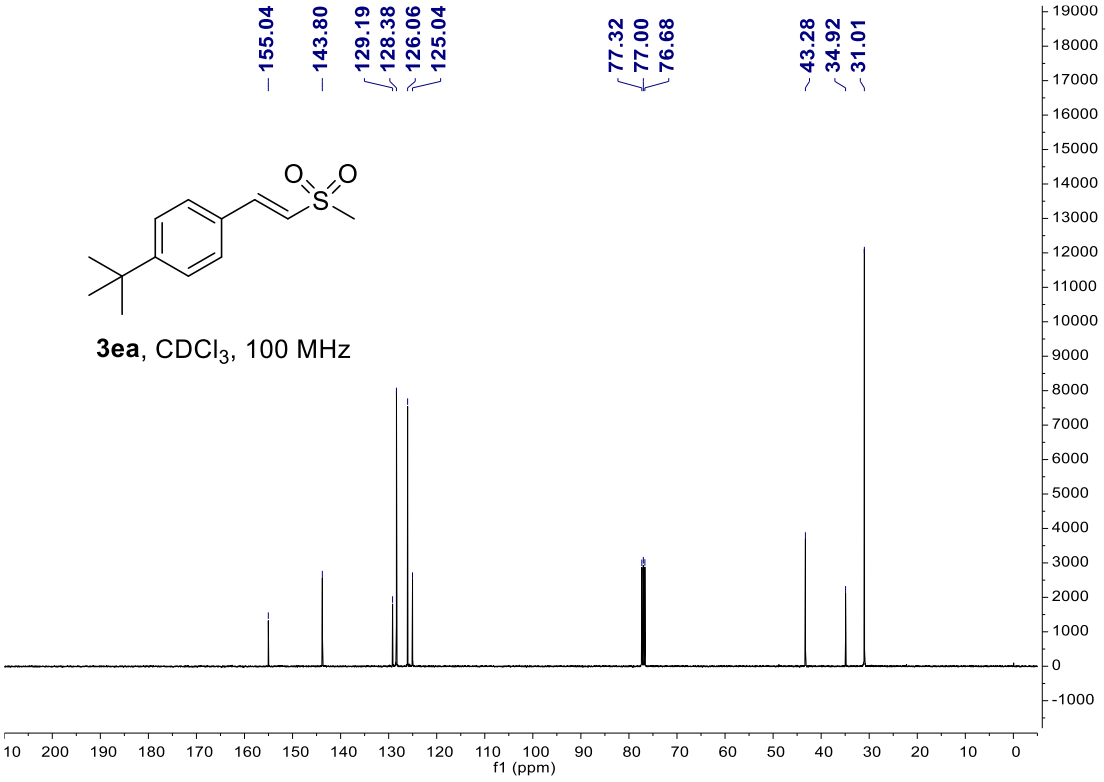


3da, $CDCl_3$, 100 MHz

(*E*)-1-(*tert*-butyl)-4-(2-(methylsulfonyl)vinyl)benzene **(3ea)**

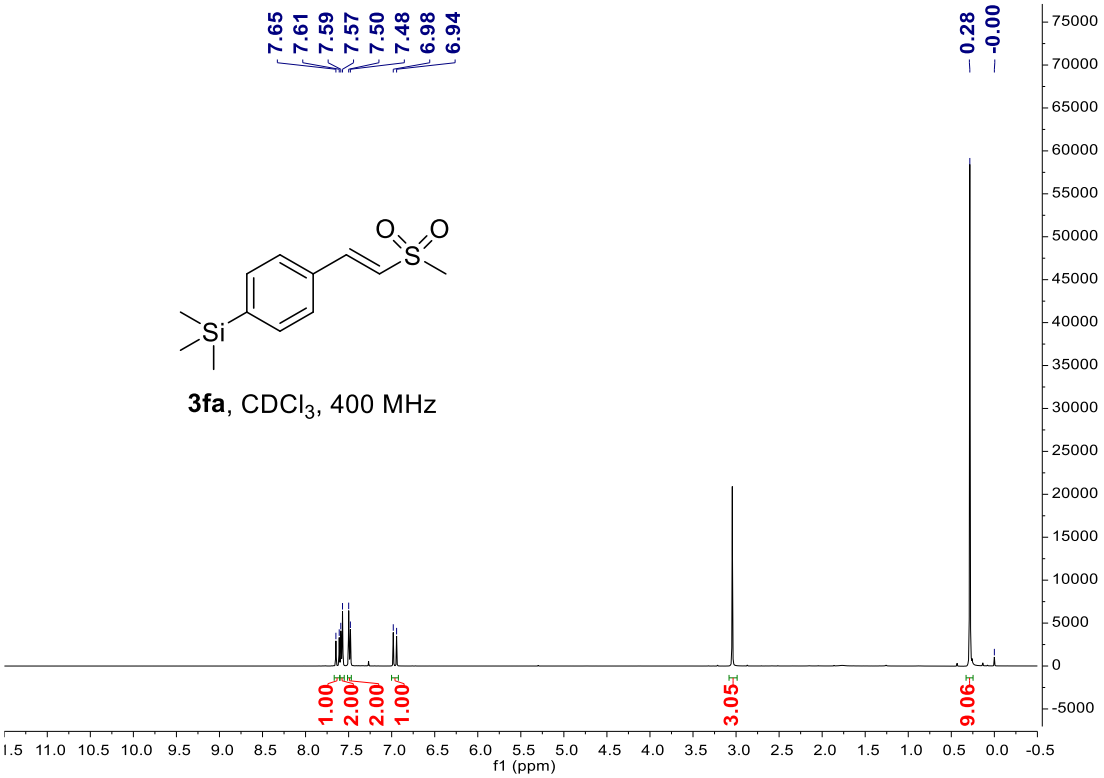


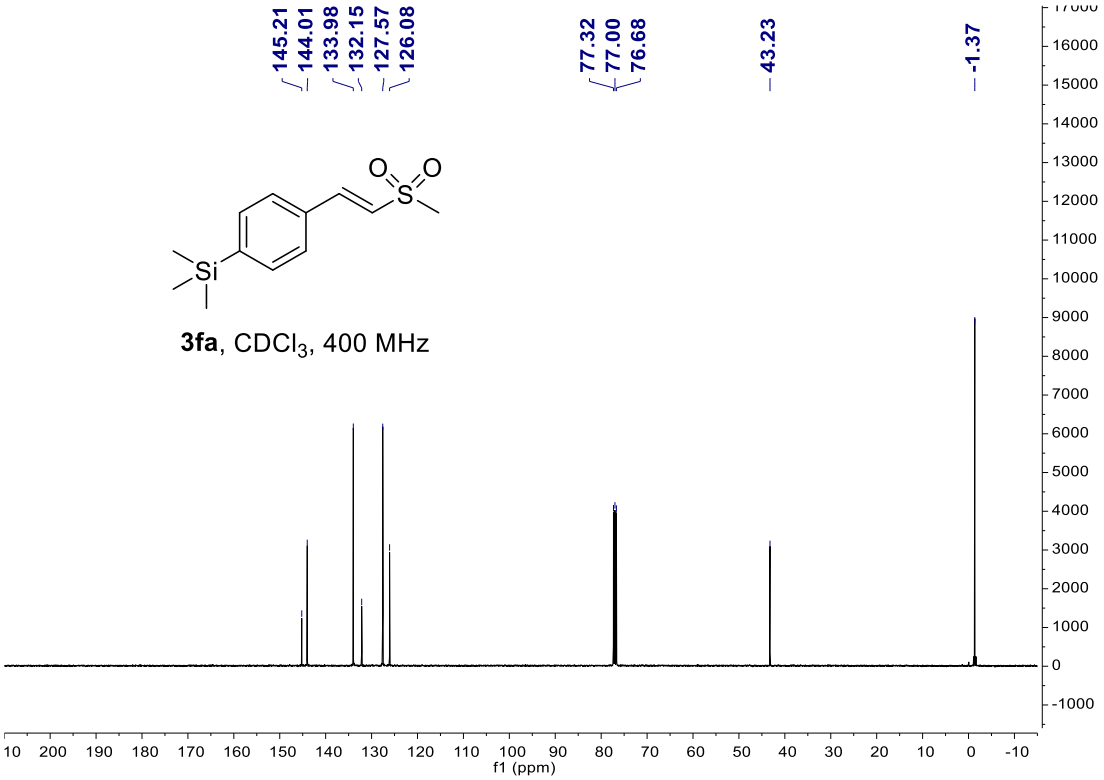
3ea, $CDCl_3$, 400 MHz



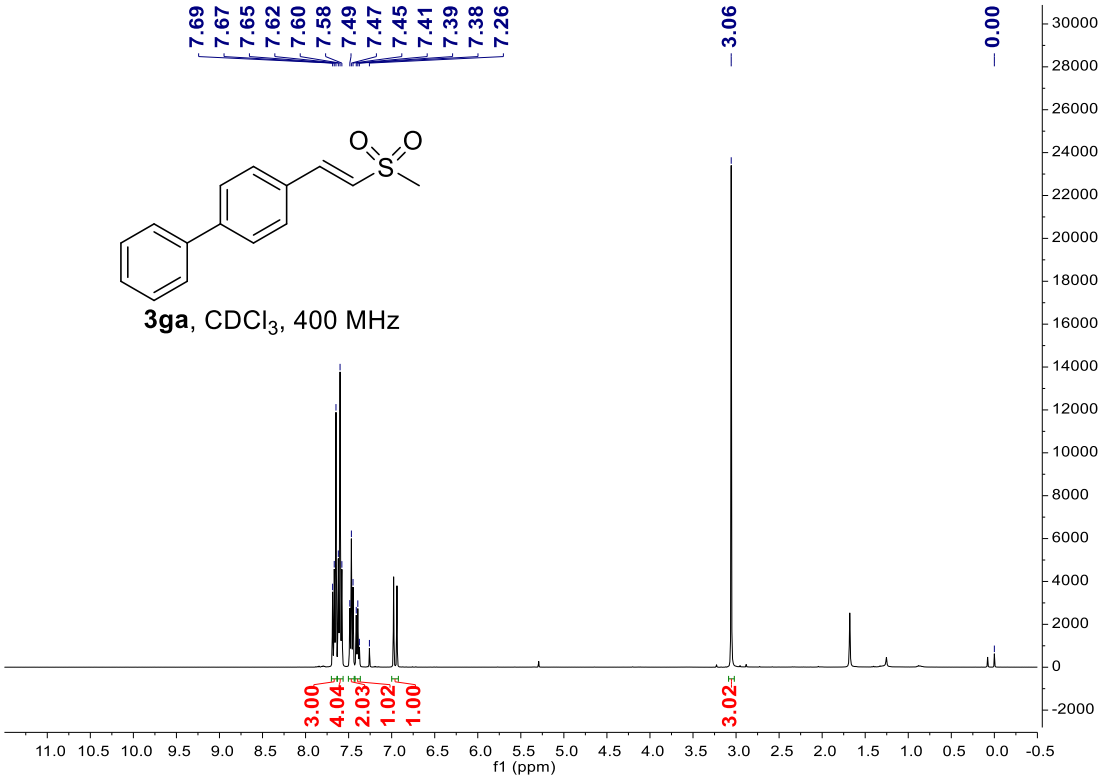
3ea, $CDCl_3$, 100 MHz

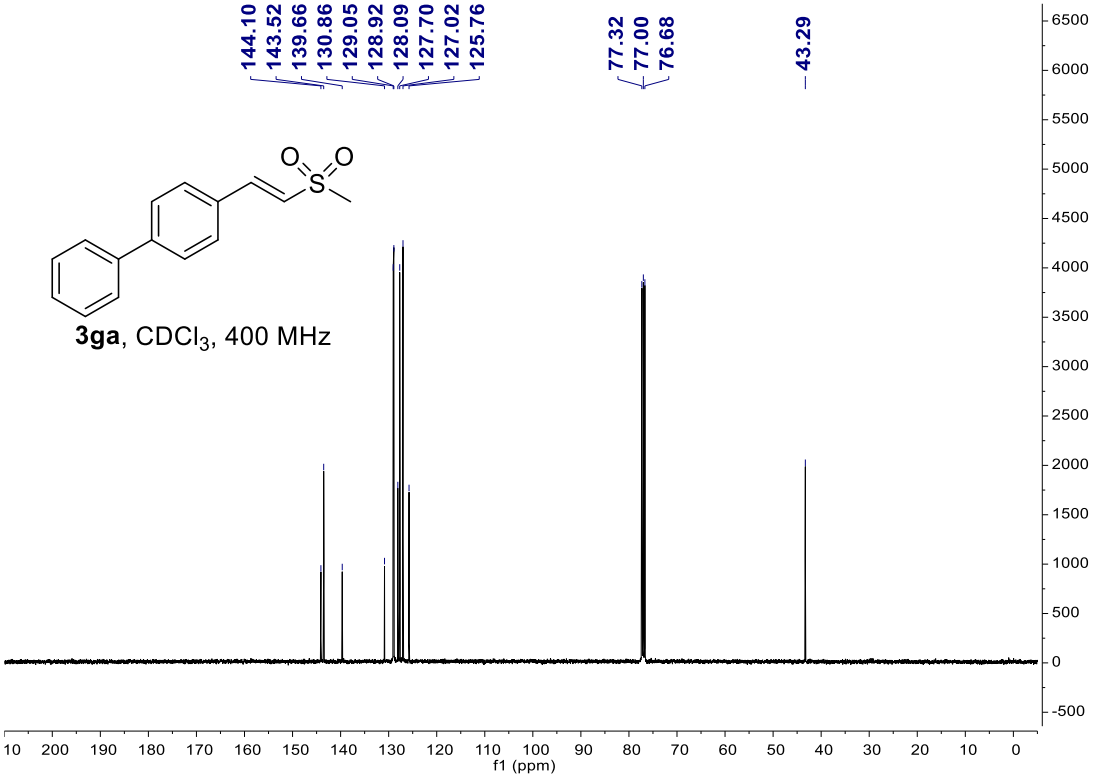
(*E*)-trimethyl(4-(2-(methylsulfonyl)vinyl)phenyl)silane **(3fa)**



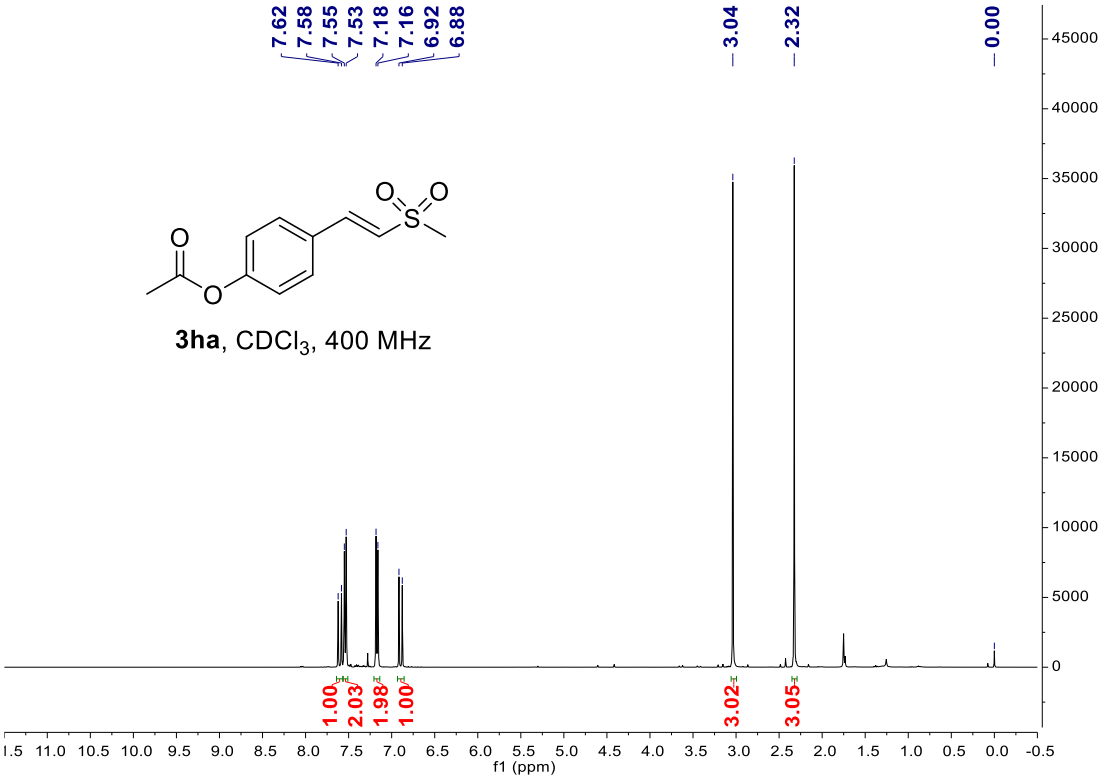


(*E*)-4-(2-(methylsulfonyl)vinyl)-1,1'-biphenyl **(3ga)**

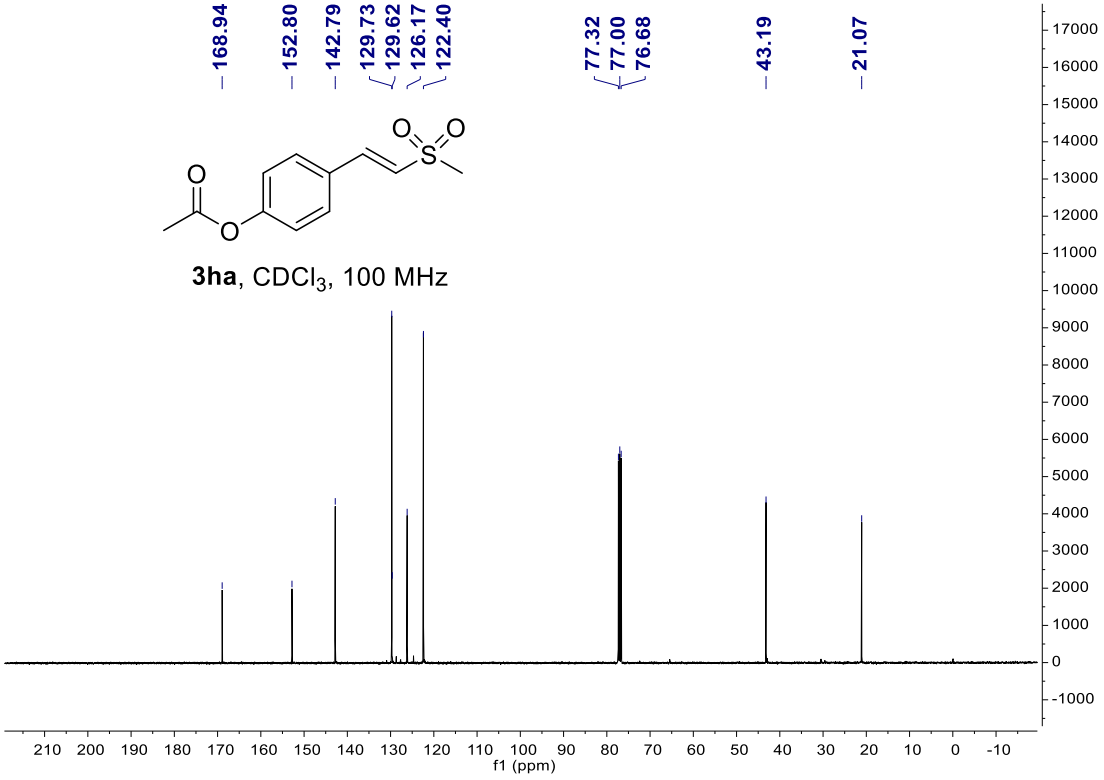




(*E*)-4-(2-(methylsulfonyl)vinyl)phenyl acetate **(3ha)**

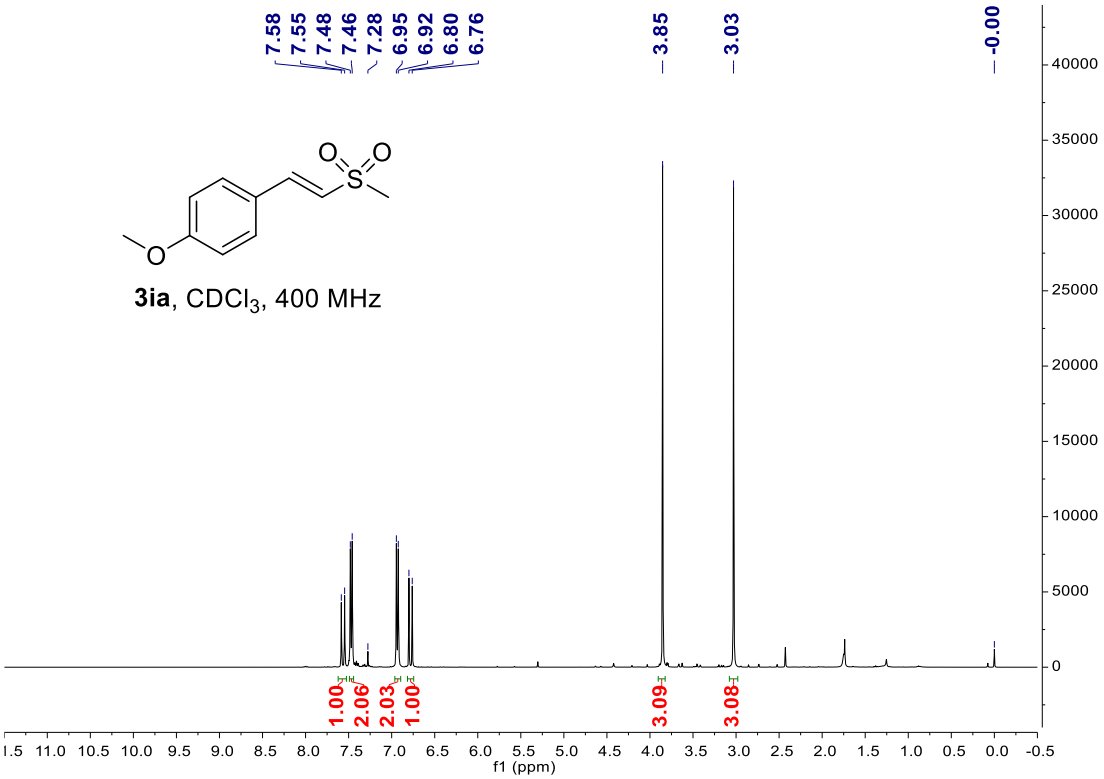


3ha, $CDCl_3$, 400 MHz

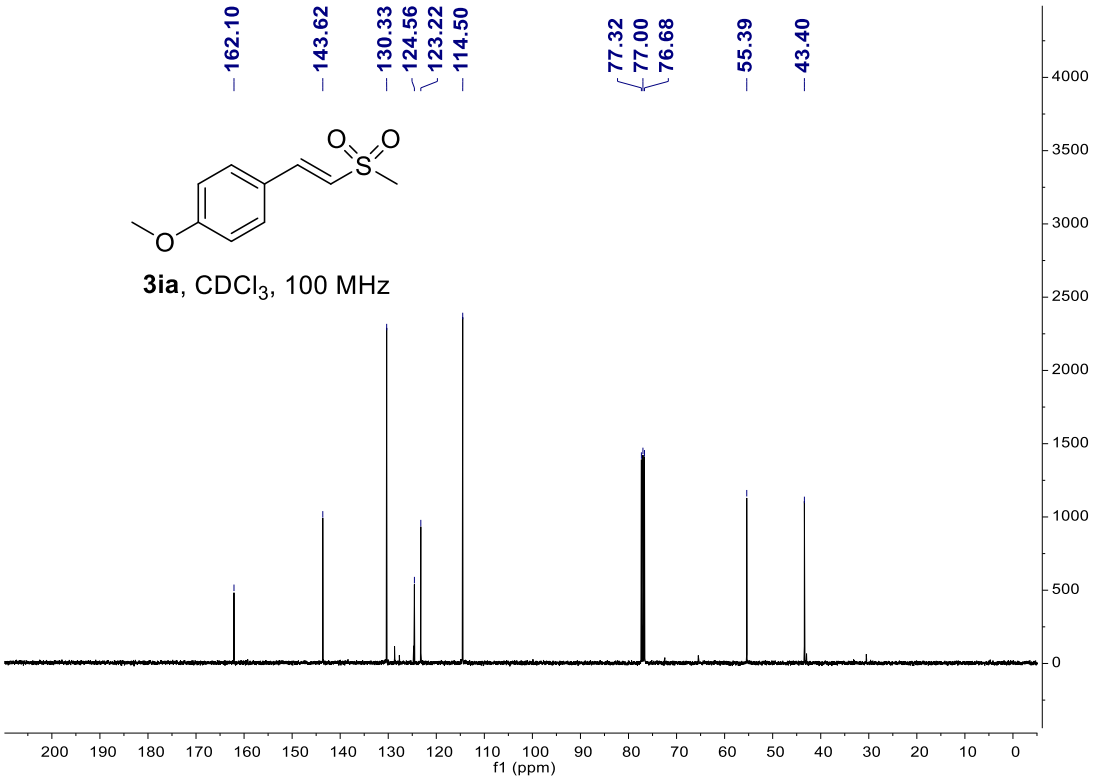


3ha, $CDCl_3$, 100 MHz

(*E*)-1-methoxy-4-(2-(methylsulfonyl)vinyl)benzene **(3ia)**

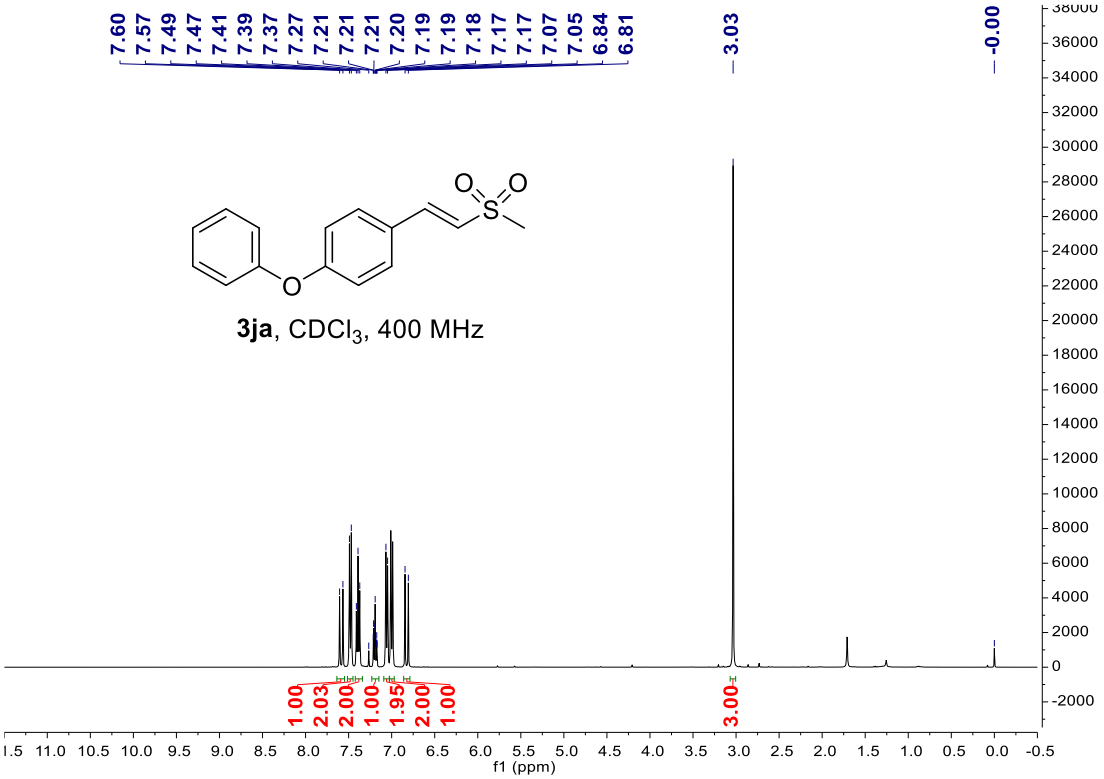


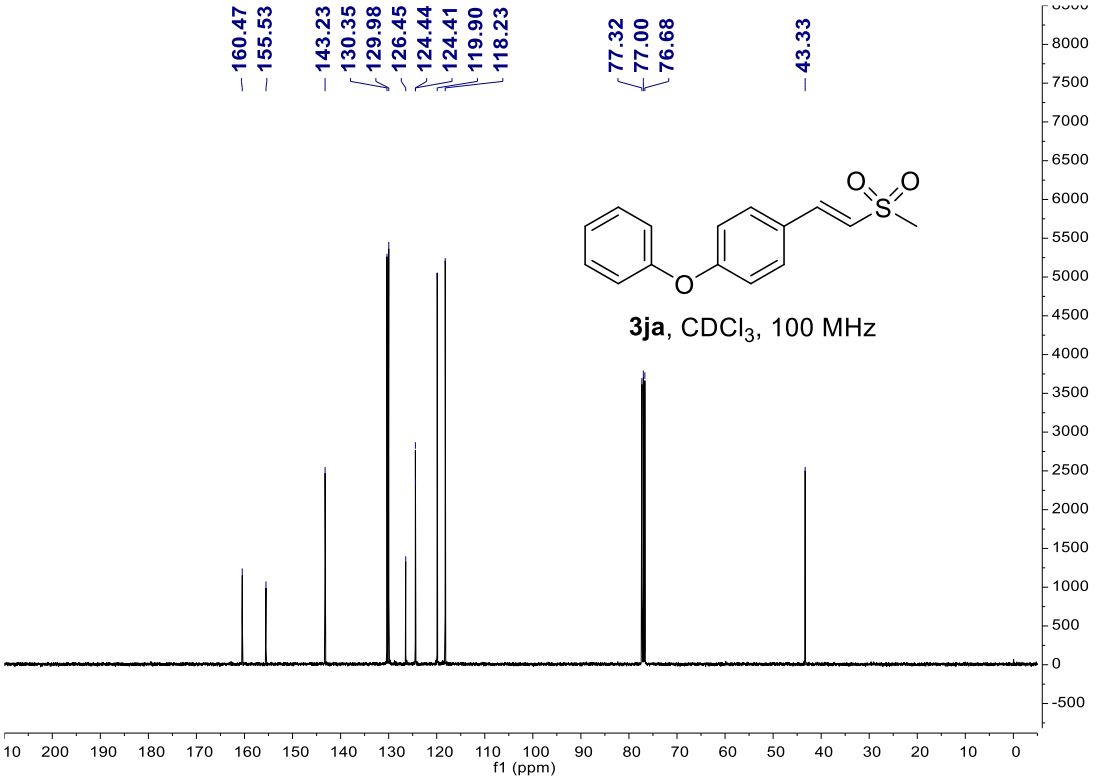
3ia, $CDCl_3$, 400 MHz



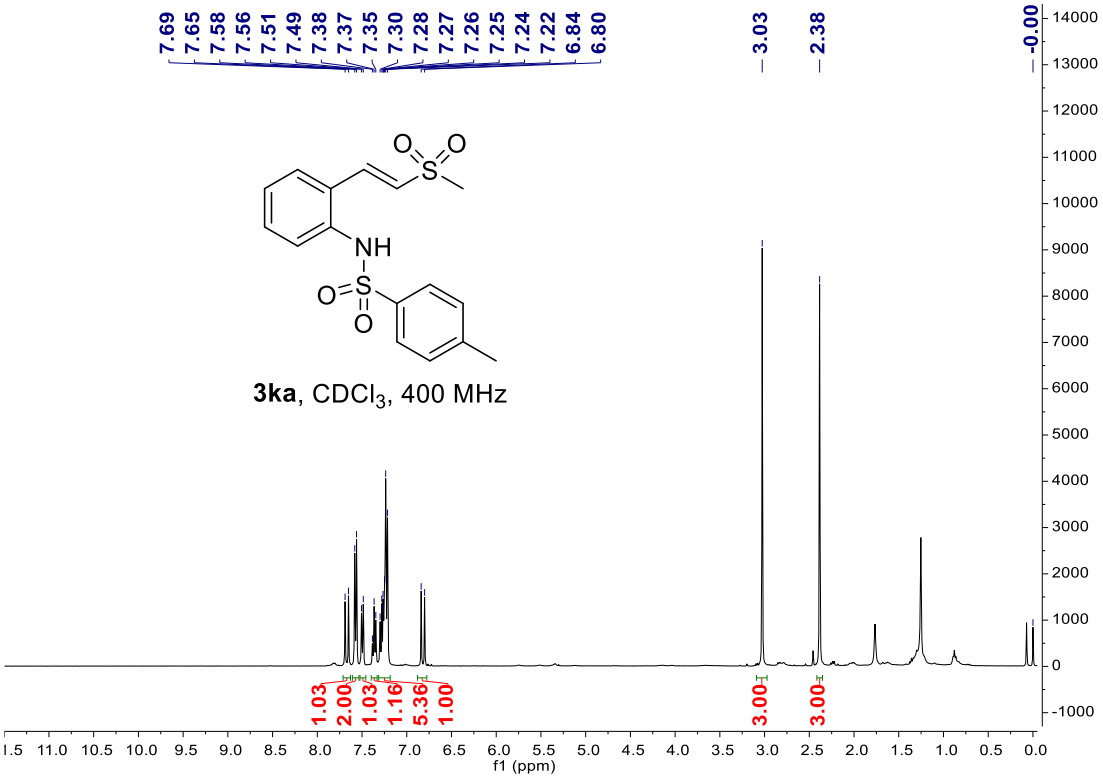
3ia, $CDCl_3$, 100 MHz

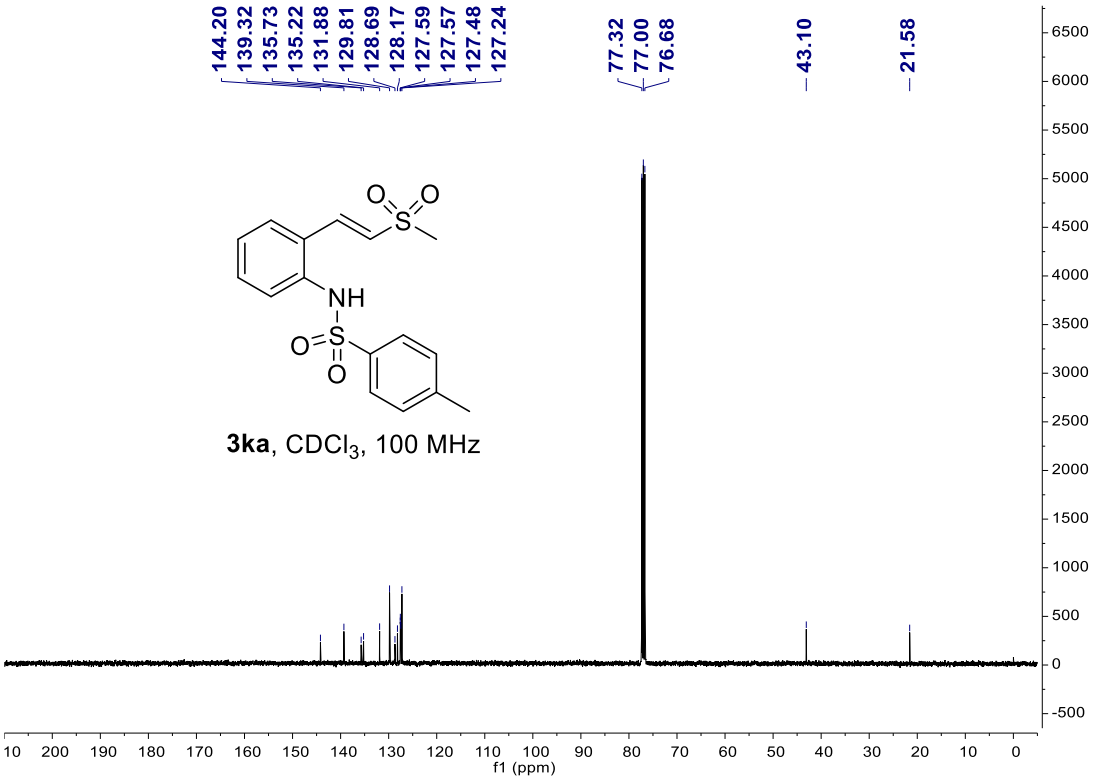
(*E*)-1-(2-(methylsulfonyl)vinyl)-4-phenoxybenzene **(3ja)**



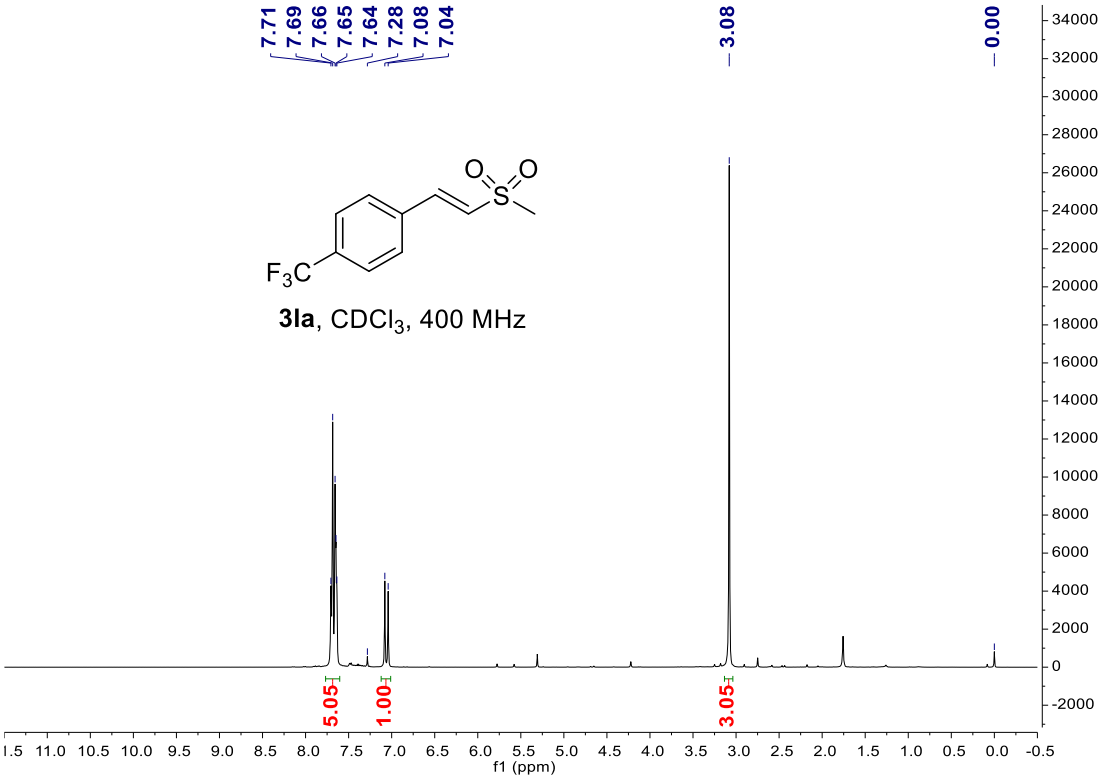


(*E*)-4-methyl-*N*-(2-(2-(methylsulfonyl)vinyl)phenyl)benzenesulfonamide **(3ka)**

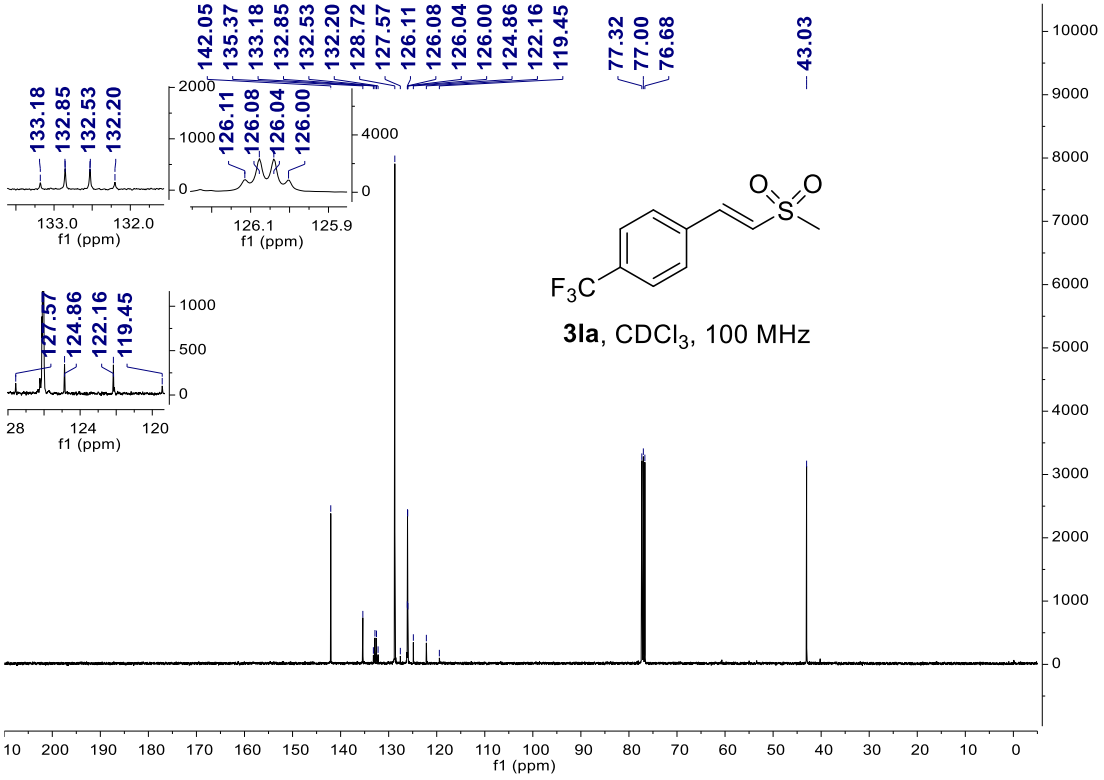




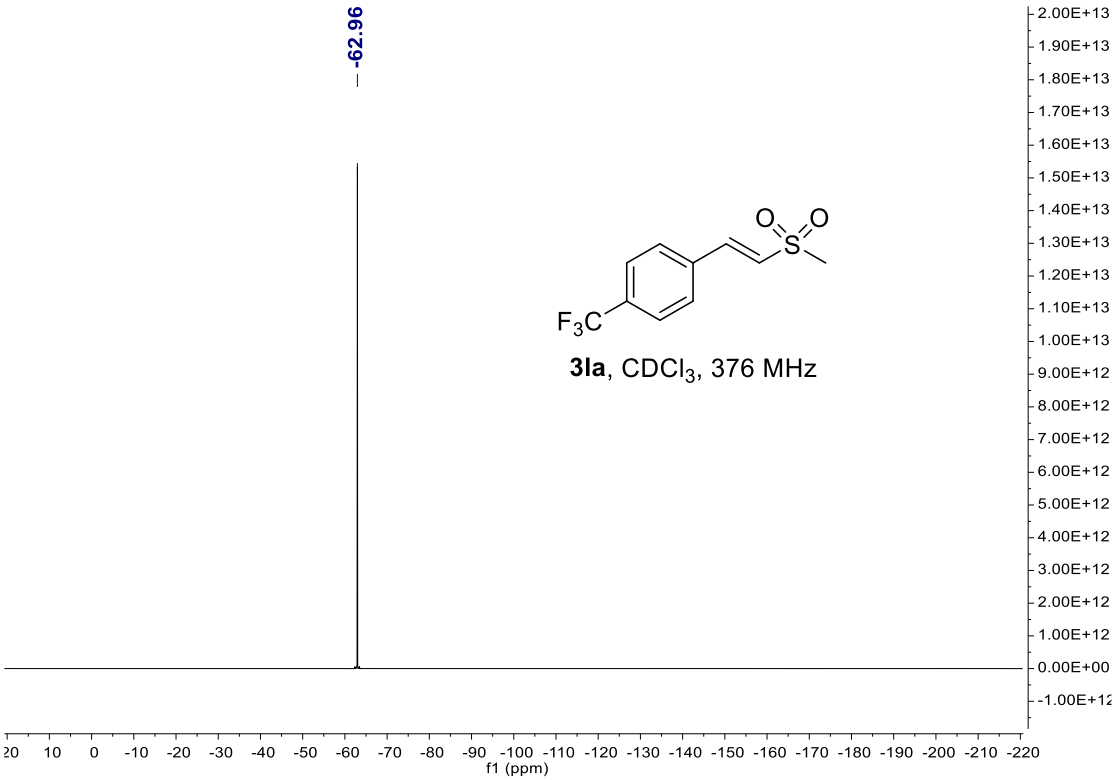
(*E*)-1-(2-(methylsulfonyl)vinyl)-4-(trifluoromethyl)benzene **(3la)**



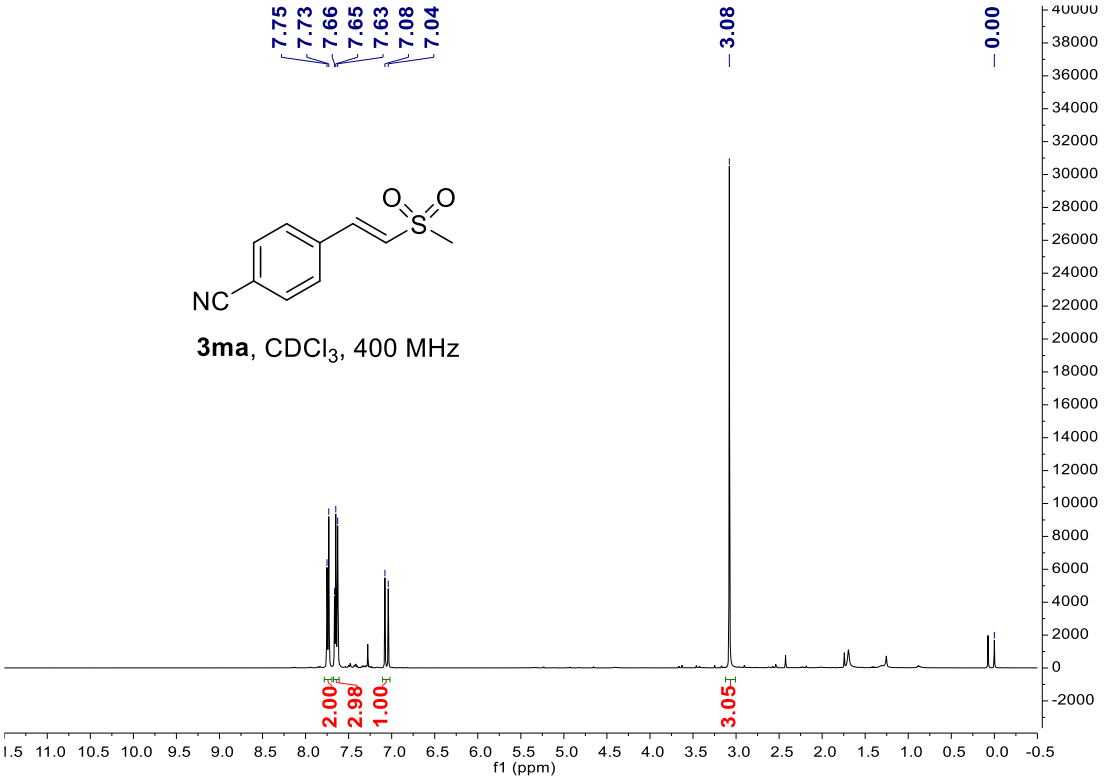
3la, $CDCl_3$, 400 MHz

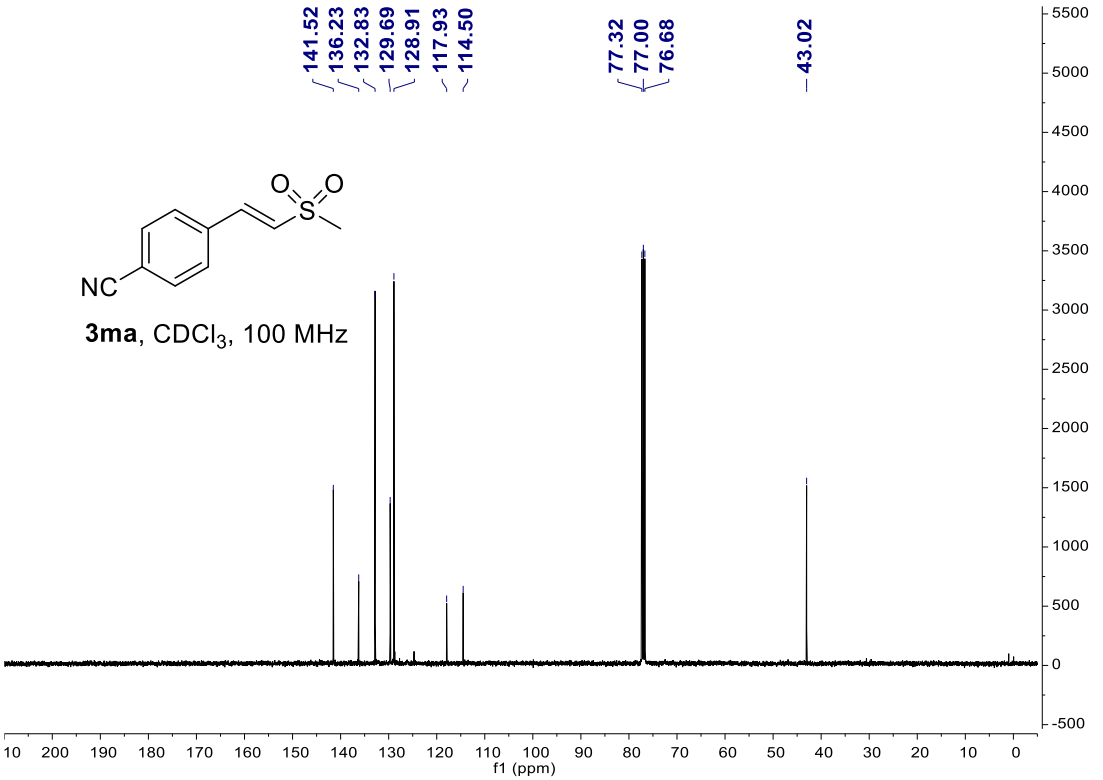


3la, $CDCl_3$, 100 MHz

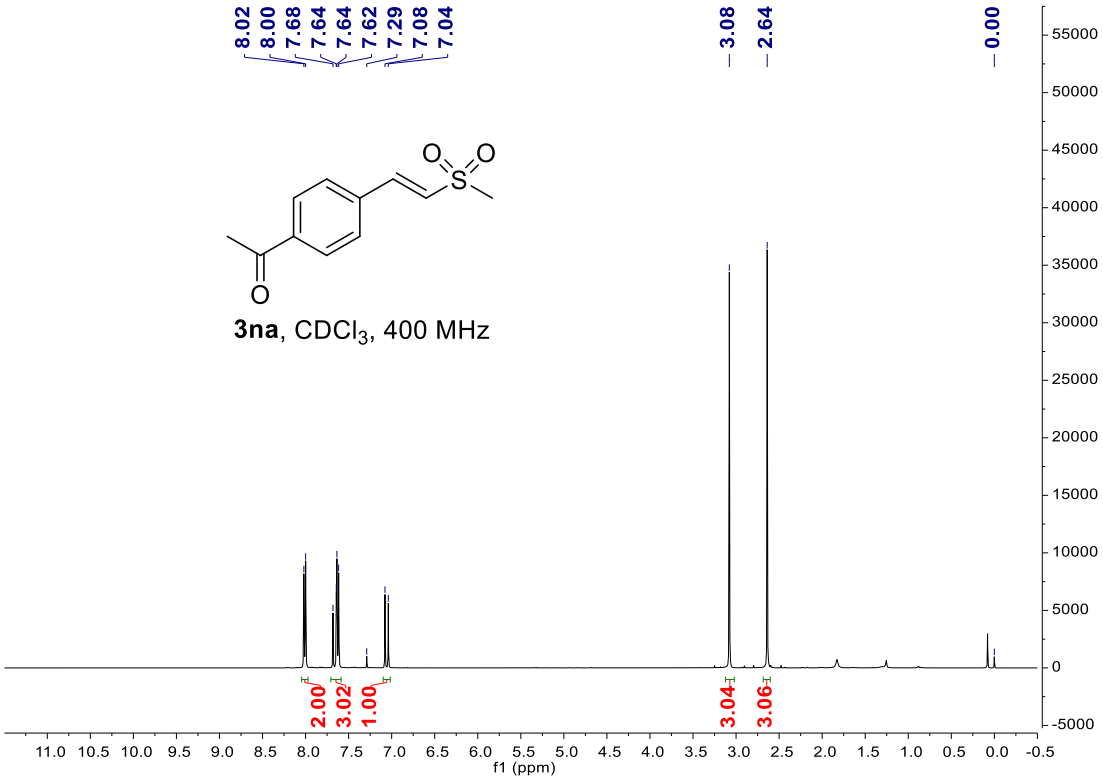


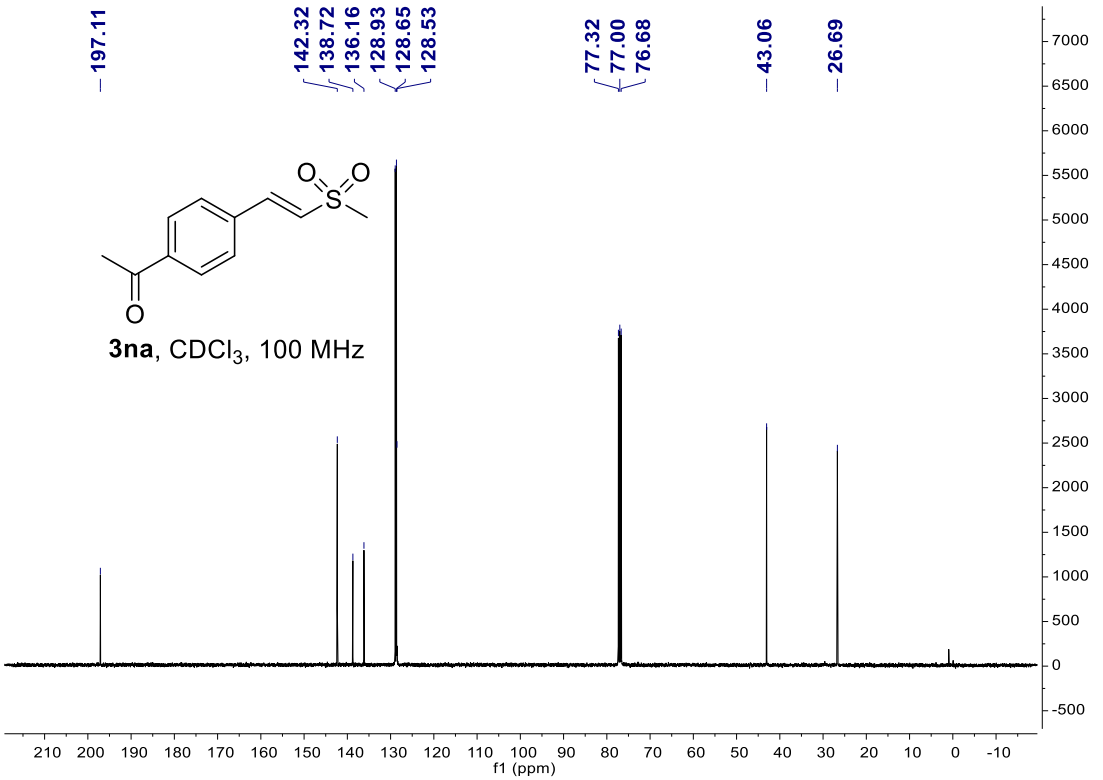
(*E*)-4-(2-(methylsulfonyl)vinyl)benzonitrile **(3ma)**



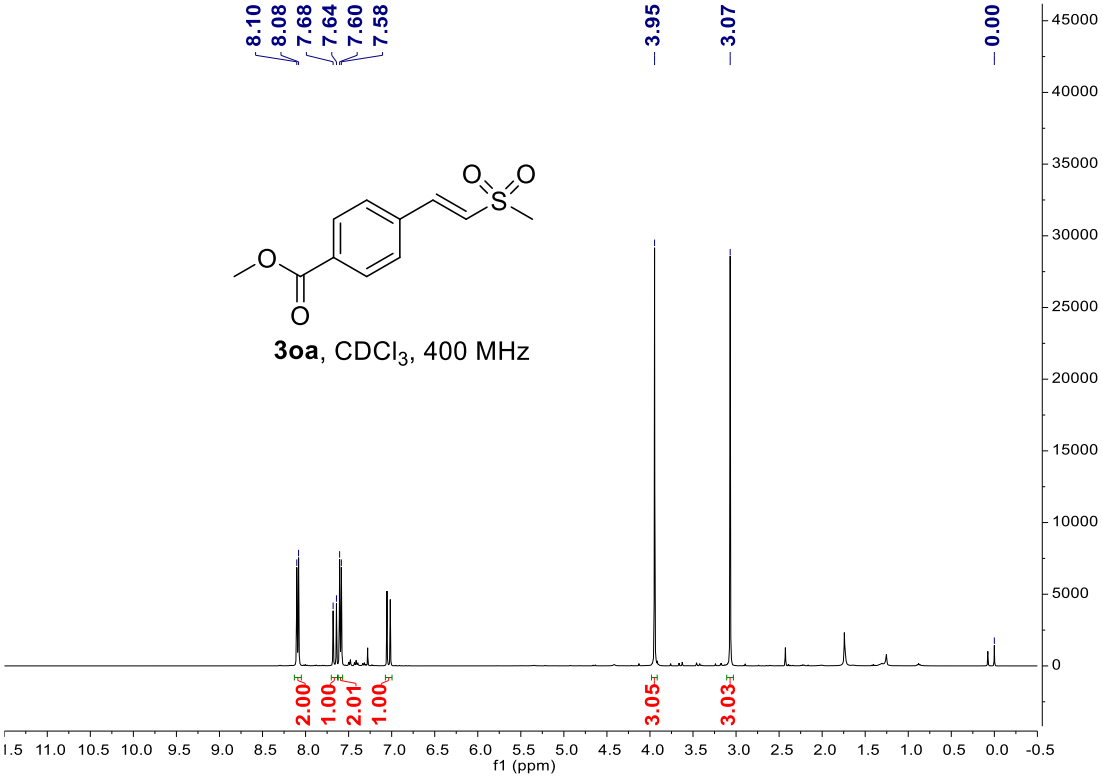


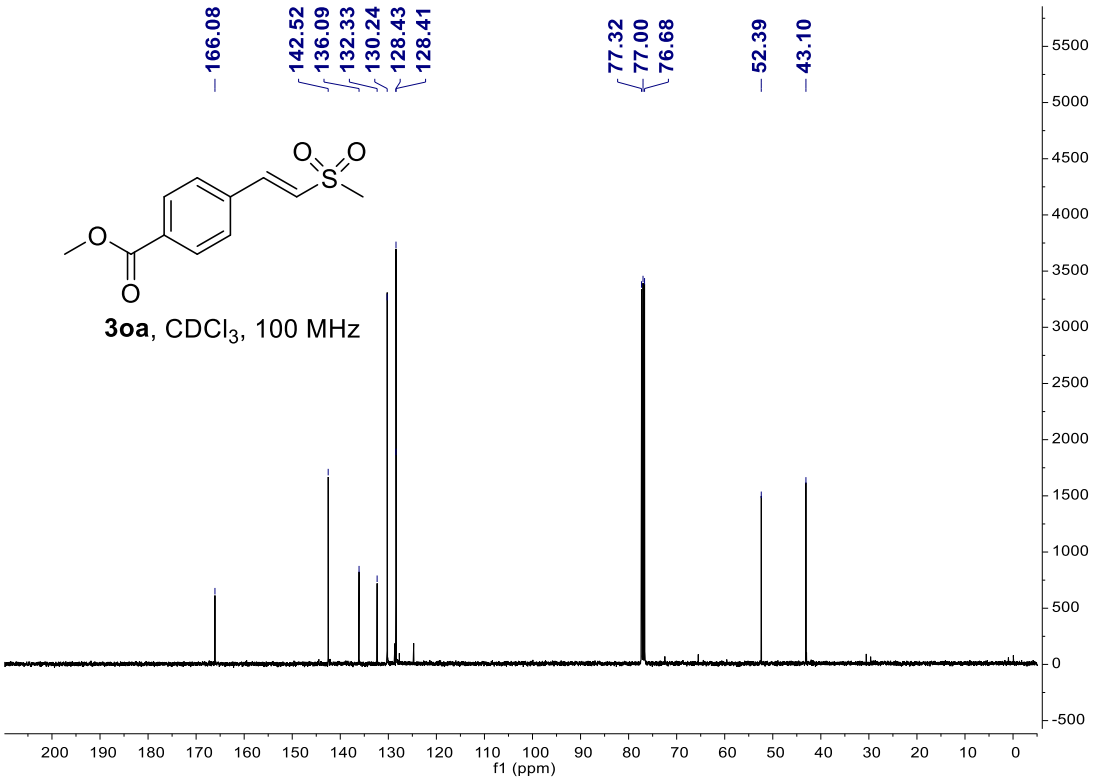
(*E*)-1-(4-(2-(methylsulfonyl)vinyl)phenyl)ethan-1-one **(3na)**



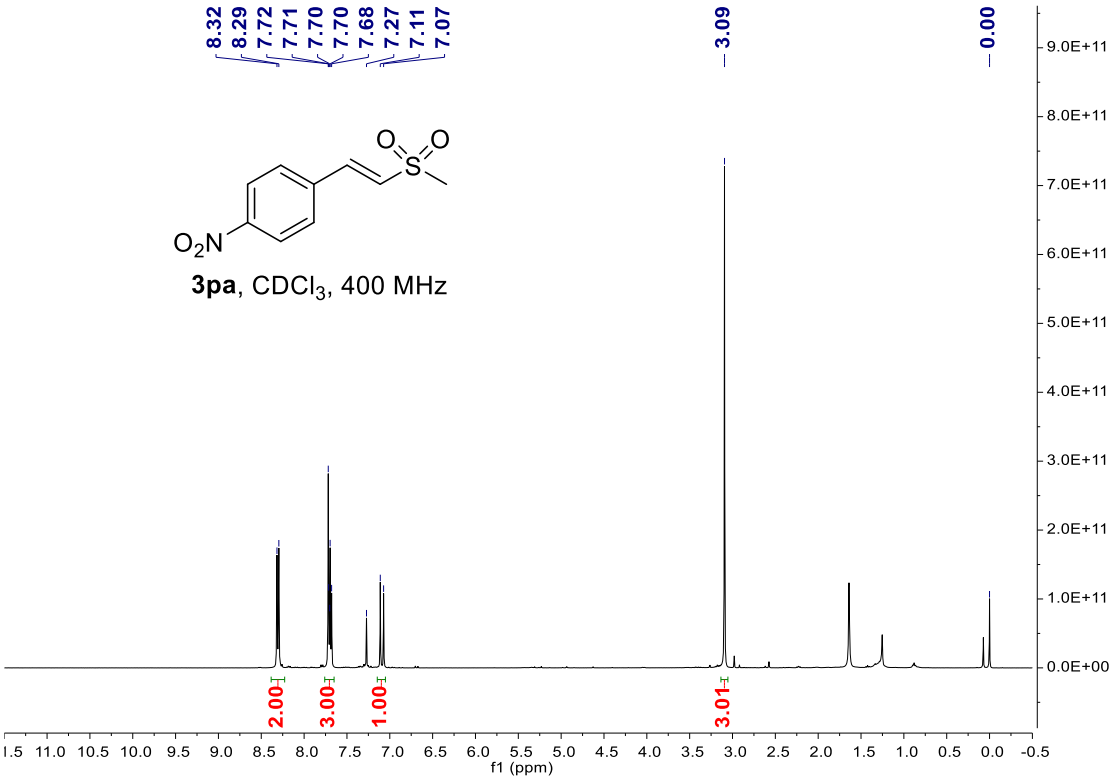


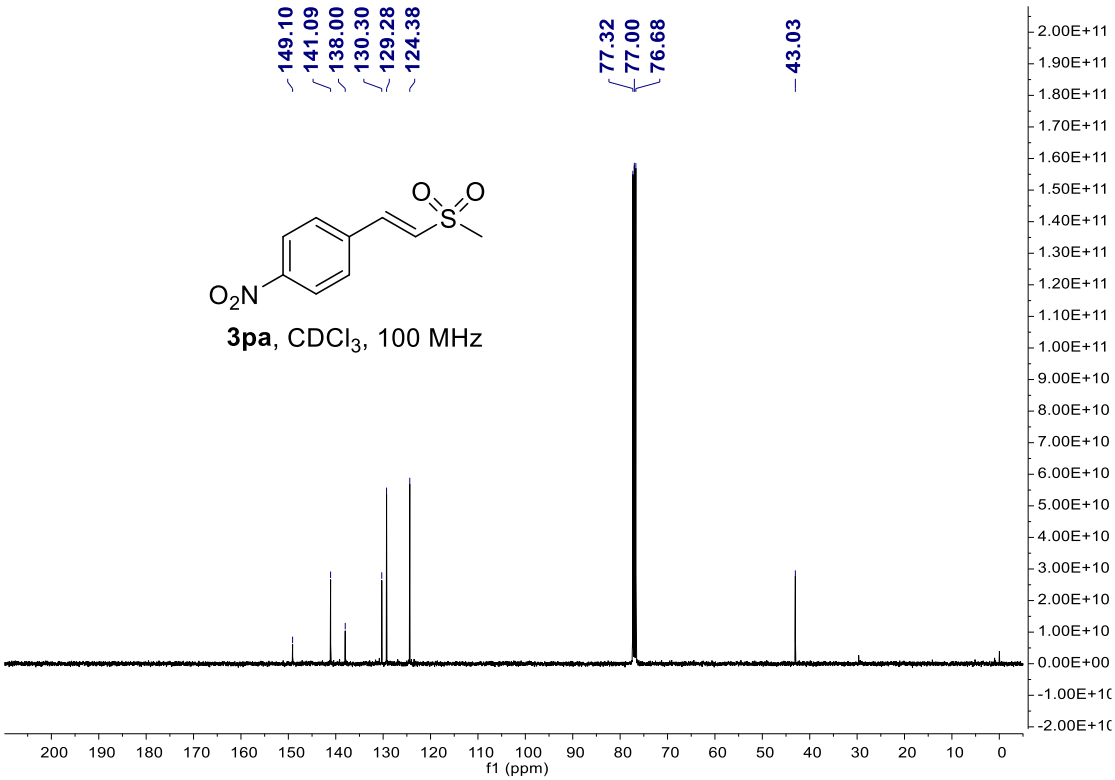
methyl (*E*)-4-(2-(methylsulfonyl)vinyl)benzoate **(3oa)**



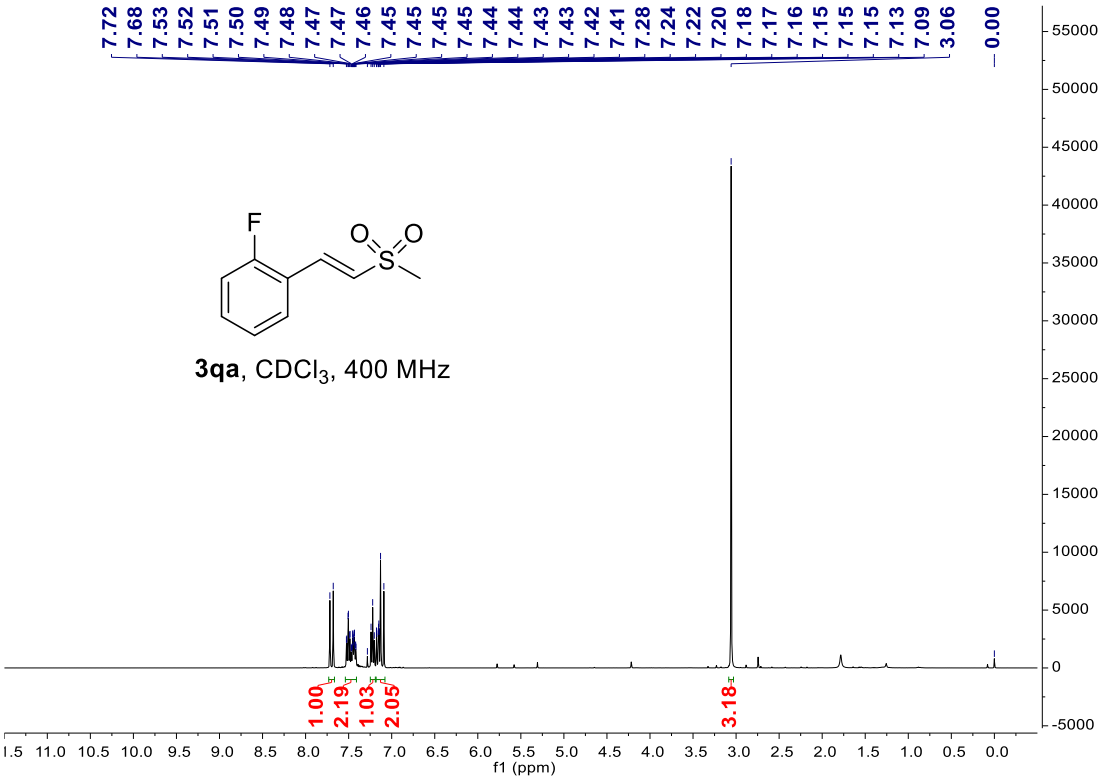


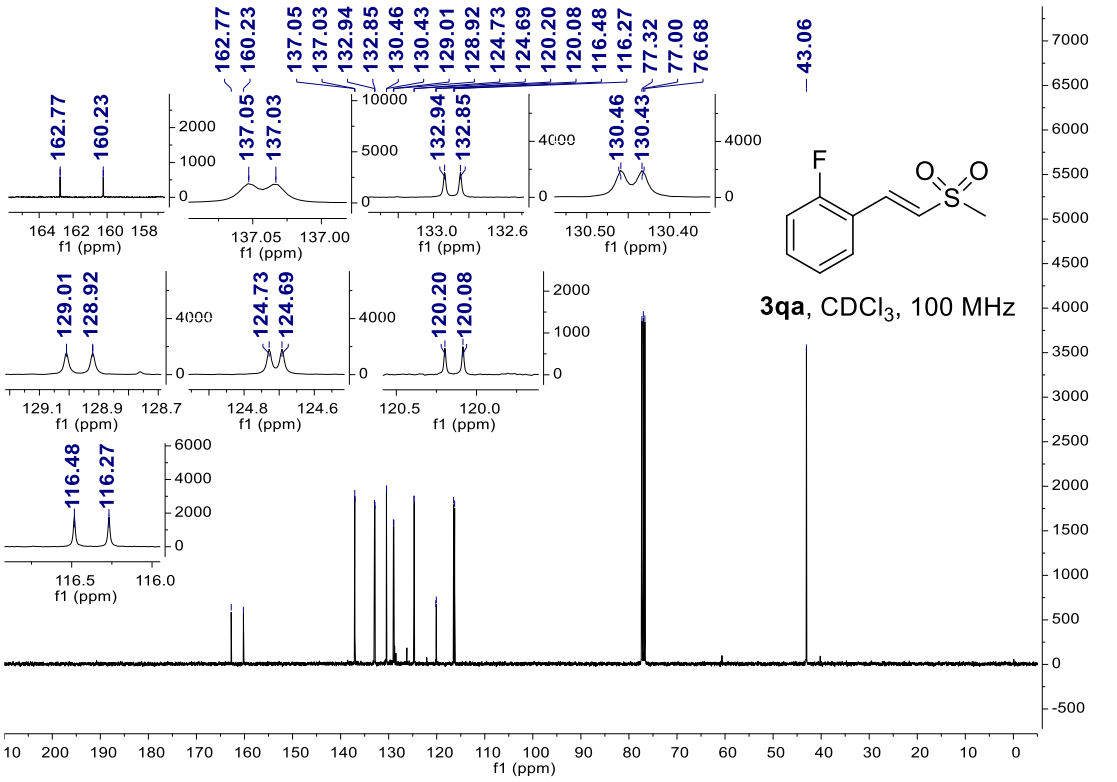
(*E*)-1-(2-(methylsulfonyl)vinyl)-4-nitrobenzene **(3pa)**

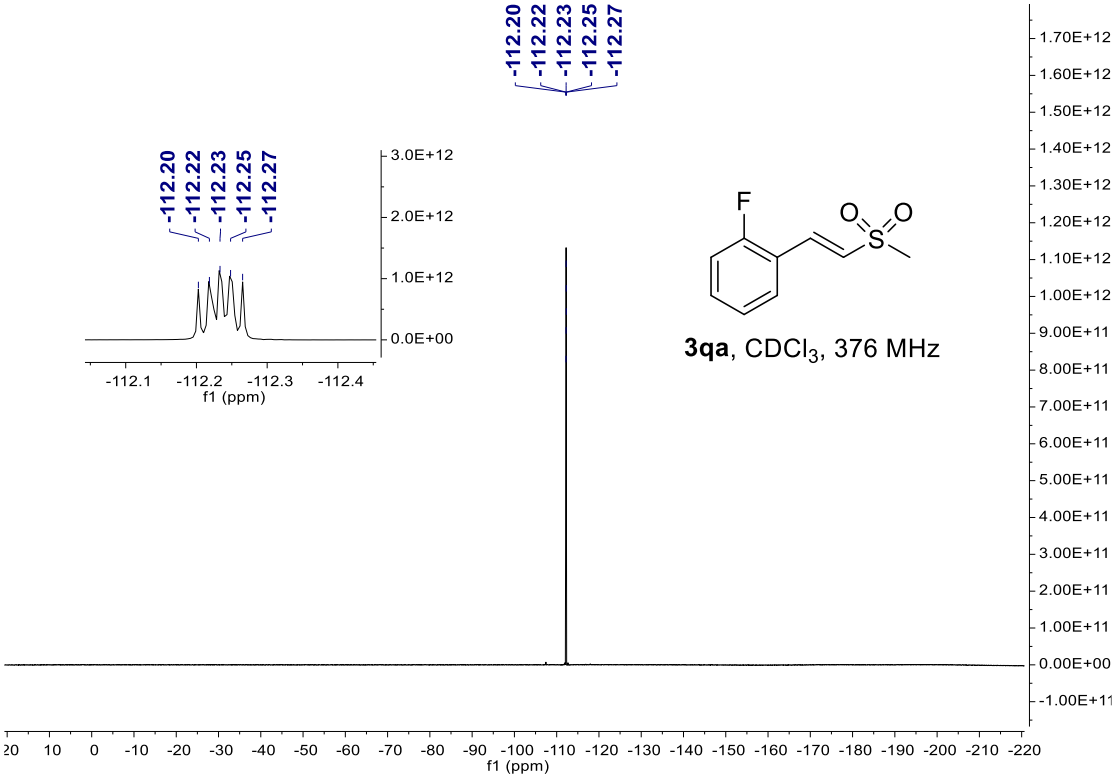




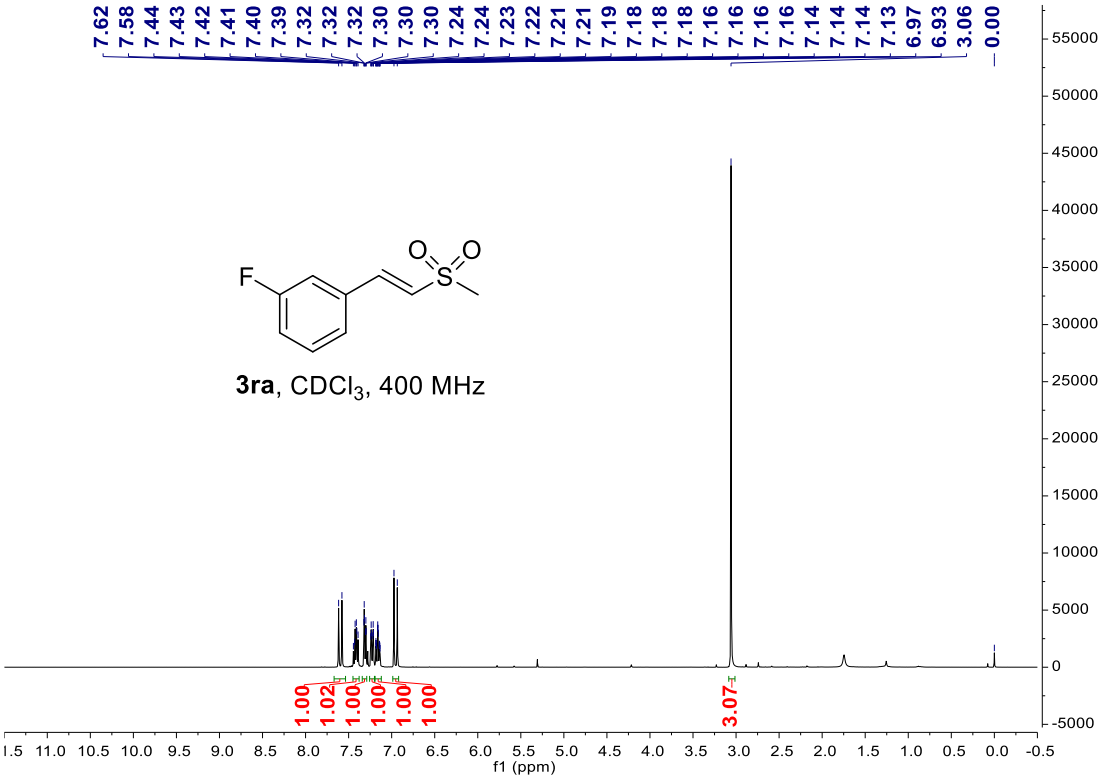
(*E*)-1-fluoro-2-(2-(methylsulfonyl)vinyl)benzene **(3qa)**

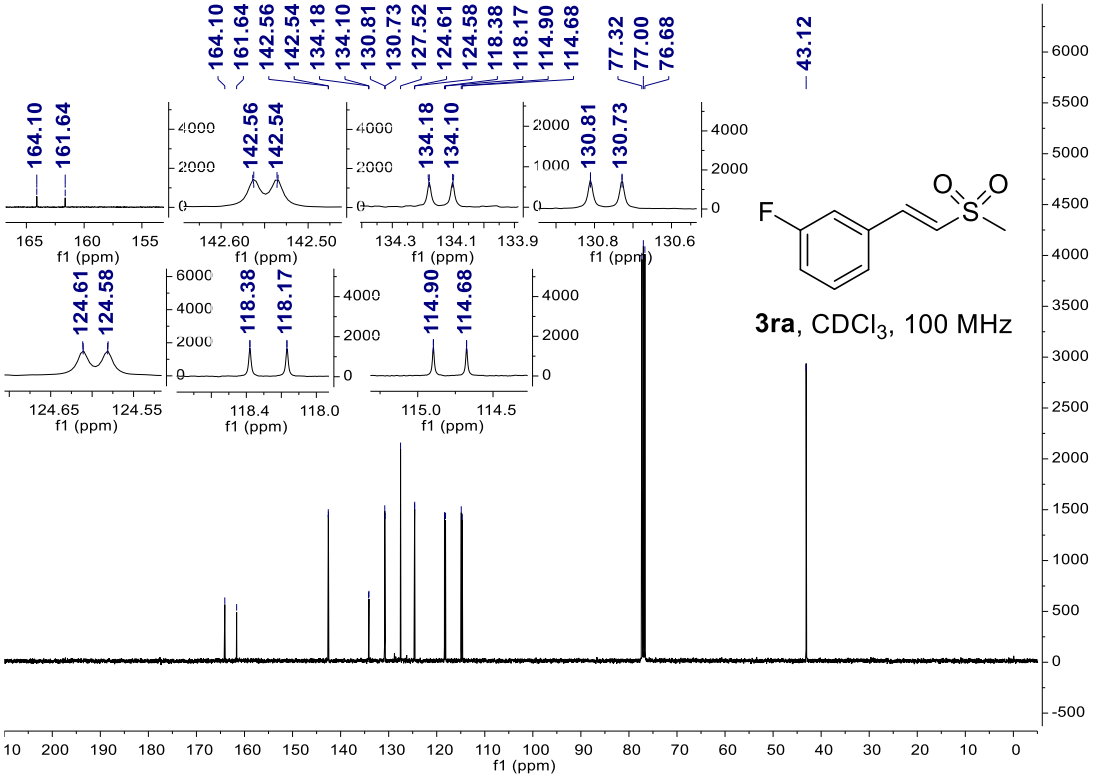


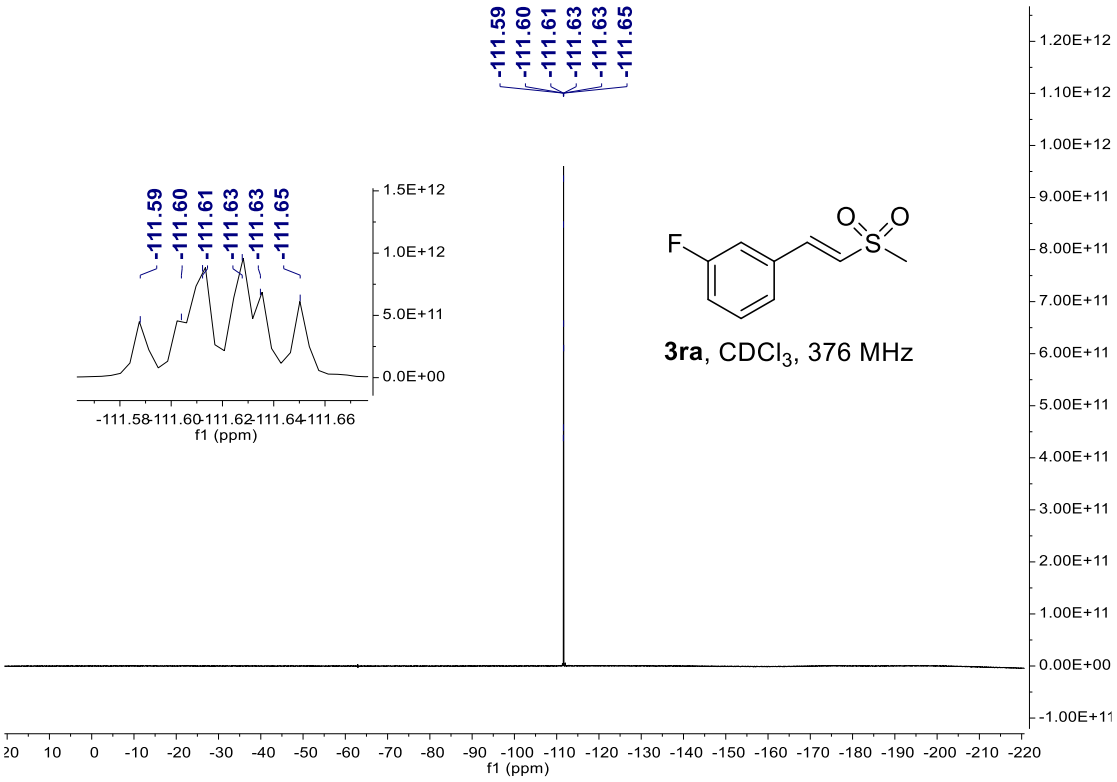

162.77
160.23
137.05
137.03
132.94
132.85
130.46
130.43
129.01
128.92
124.73
124.69
120.20
120.08
116.48
116.27
77.32
77.00
76.68
43.06
F
O
O
S
3qa, CDCl3, 100 MHz
f1 (ppm)


-112.20
-112.22
-112.23
-112.25
-112.27
F
O
O
S
3qa, CDCl3, 376 MHz
f1 (ppm)

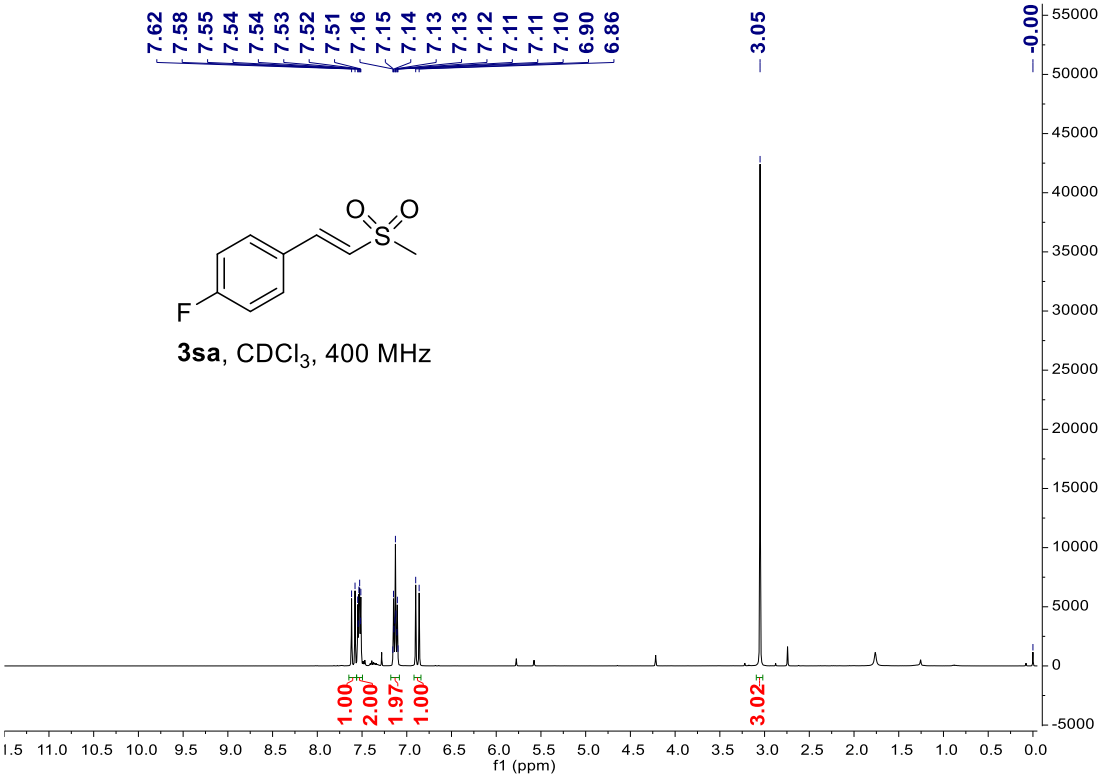
(*E*)-1-fluoro-3-(2-(methylsulfonyl)vinyl)benzene **(3ra)**

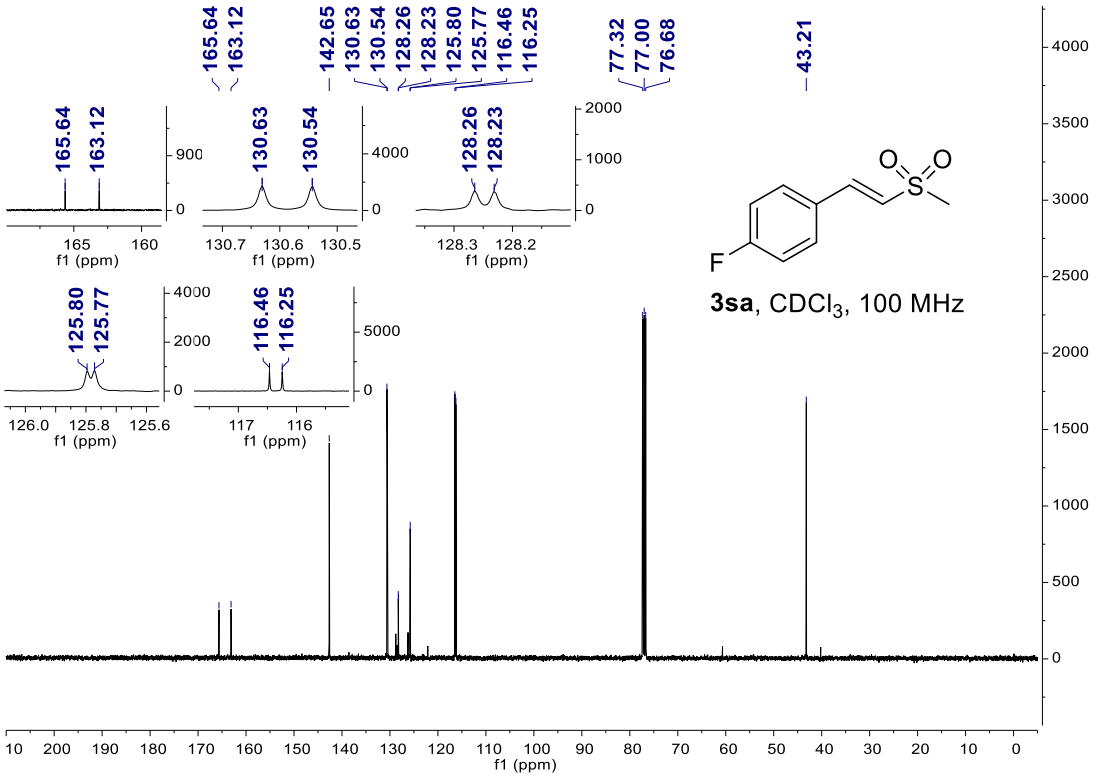


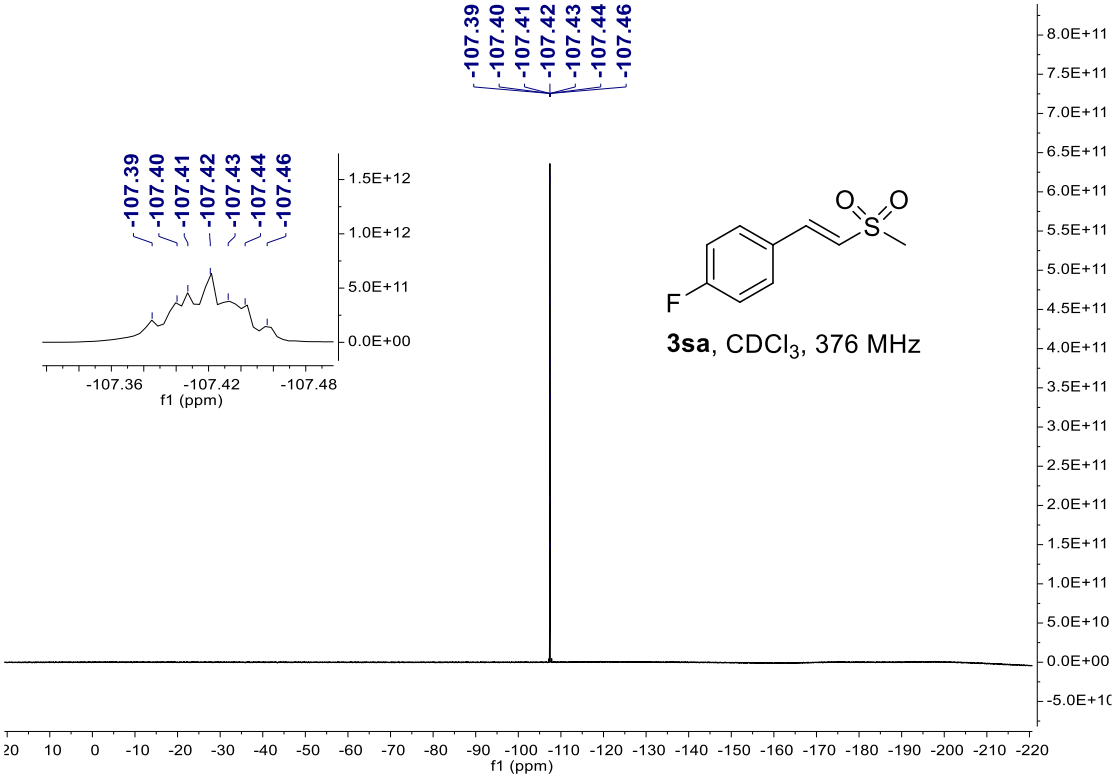




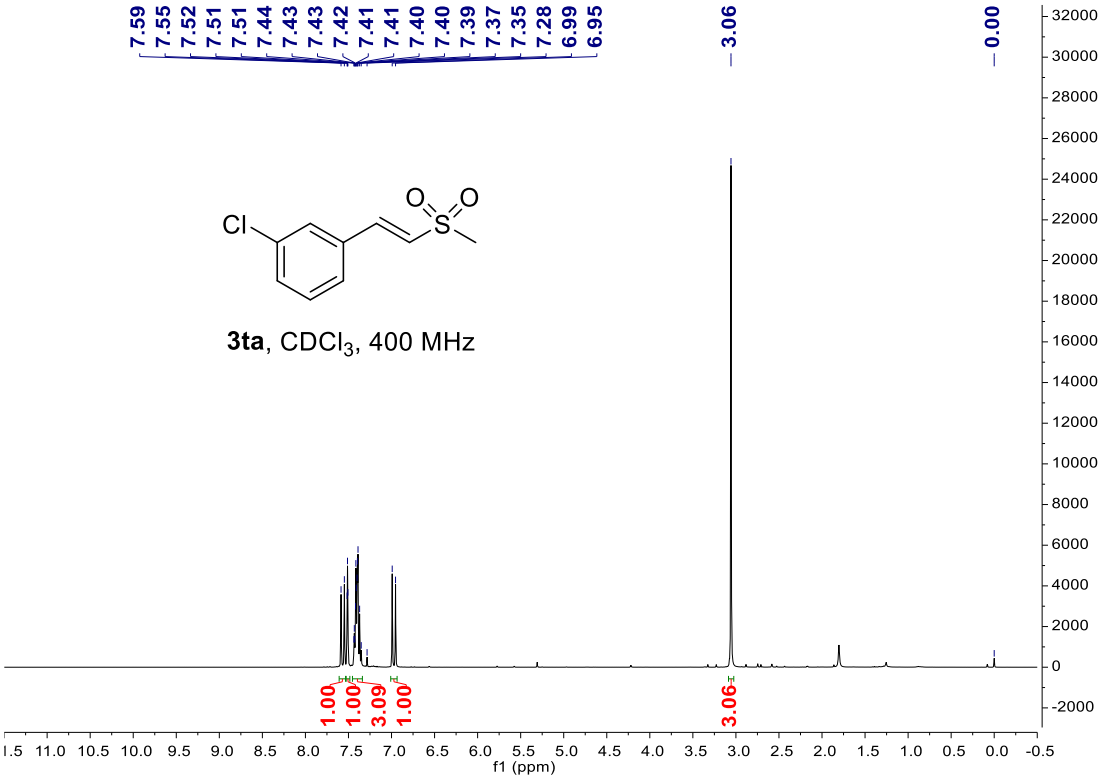
(*E*)-1-fluoro-4-(2-(methylsulfonyl)vinyl)benzene **(3sa)**

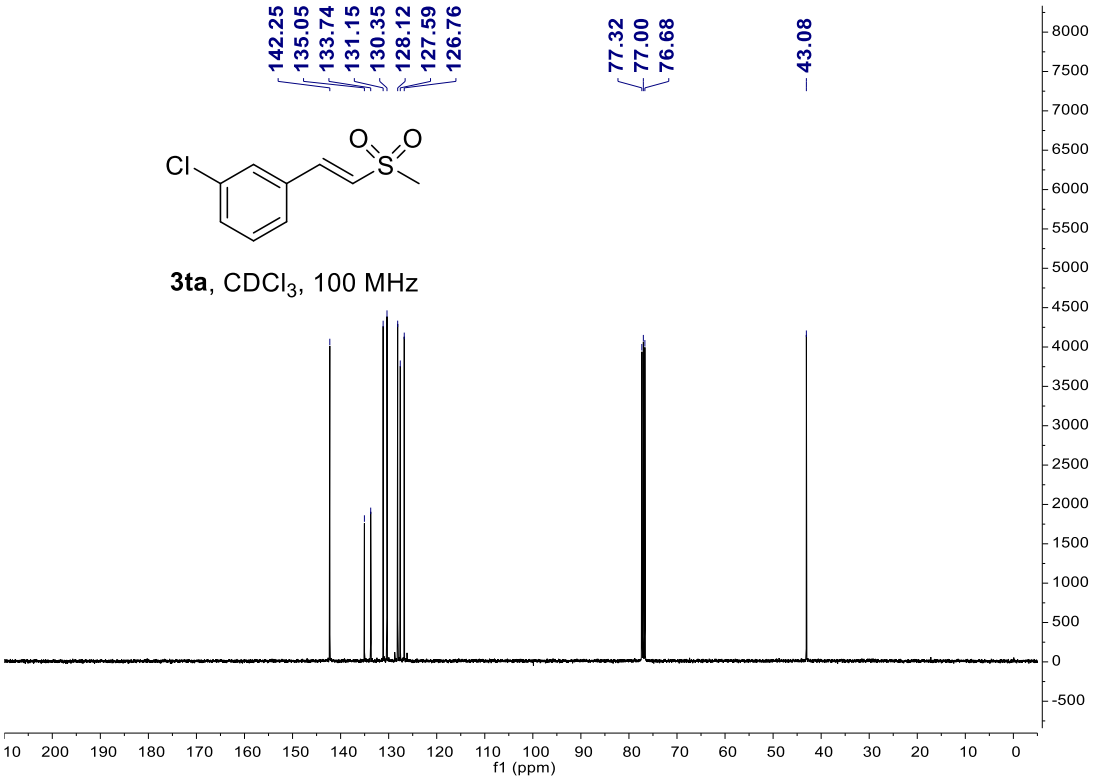



165.64
163.12
142.65
130.63
130.54
128.26
128.23
125.80
125.77
116.46
116.25
77.32
77.00
76.68
43.21
f1 (ppm)
O
O
S
F
3sa, CDCl3, 100 MHz

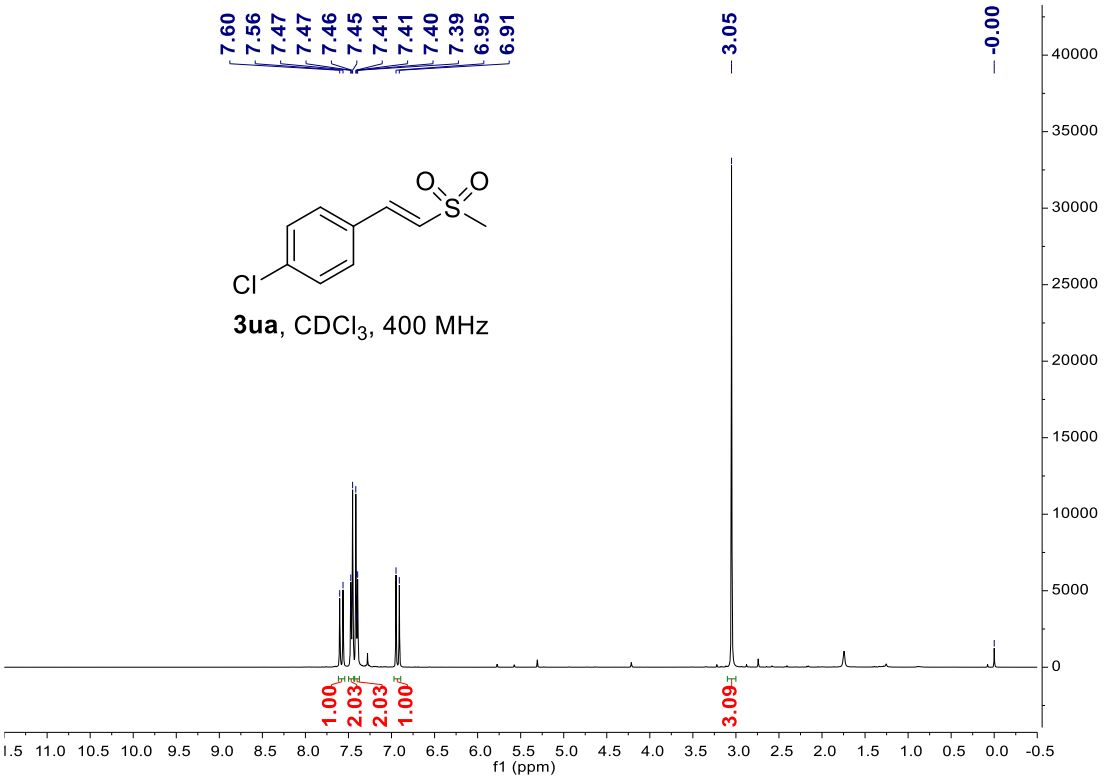

-107.39
-107.40
-107.41
-107.42
-107.43
-107.44
-107.46
f1 (ppm)
O
O
S
F
3sa, CDCl3, 376 MHz

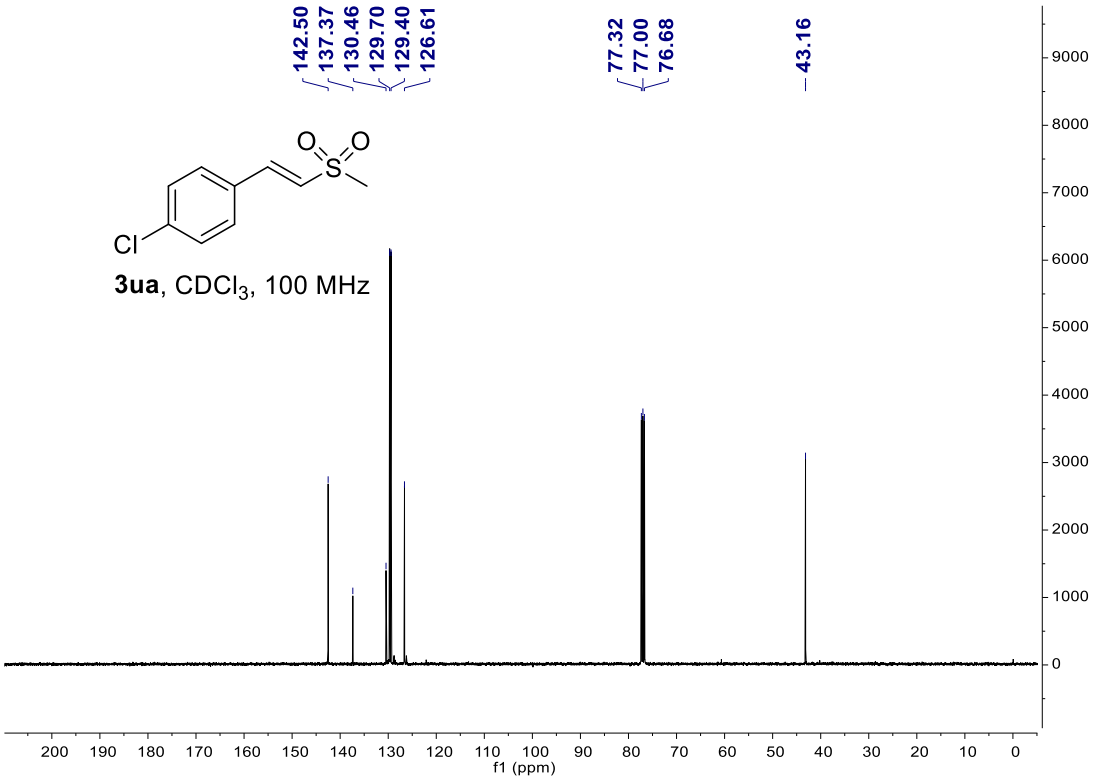
(*E*)-1-chloro-3-(2-(methylsulfonyl)vinyl)benzene **(3ta)**



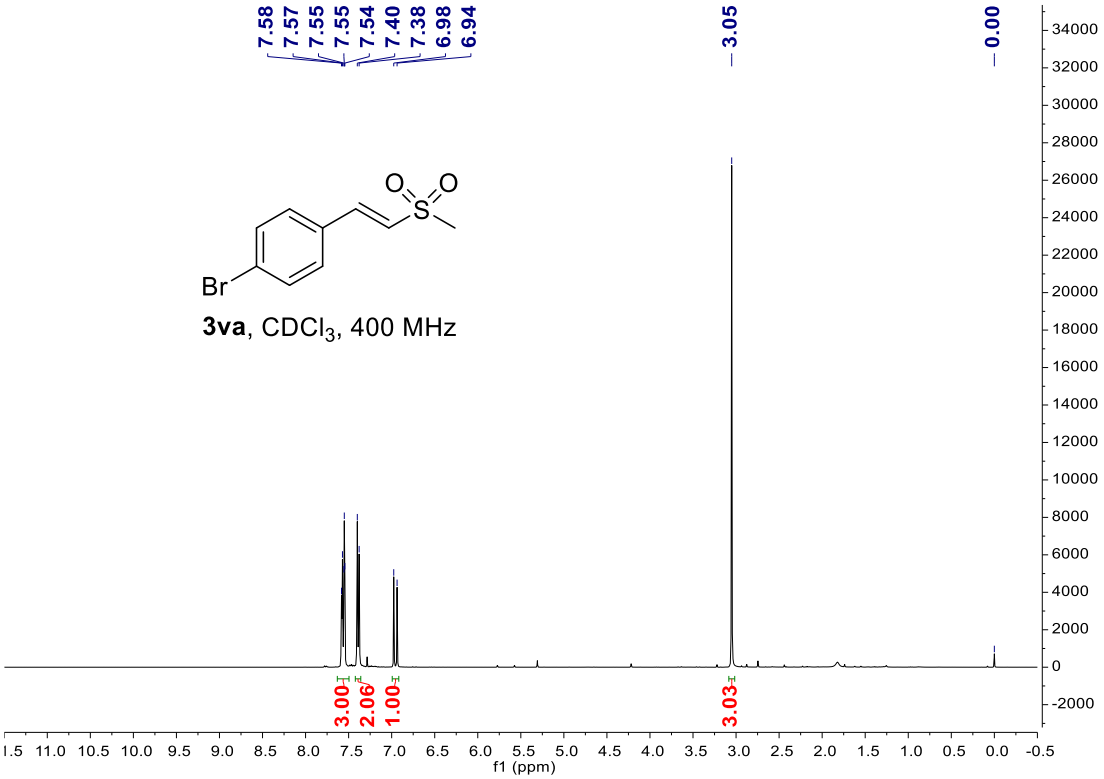


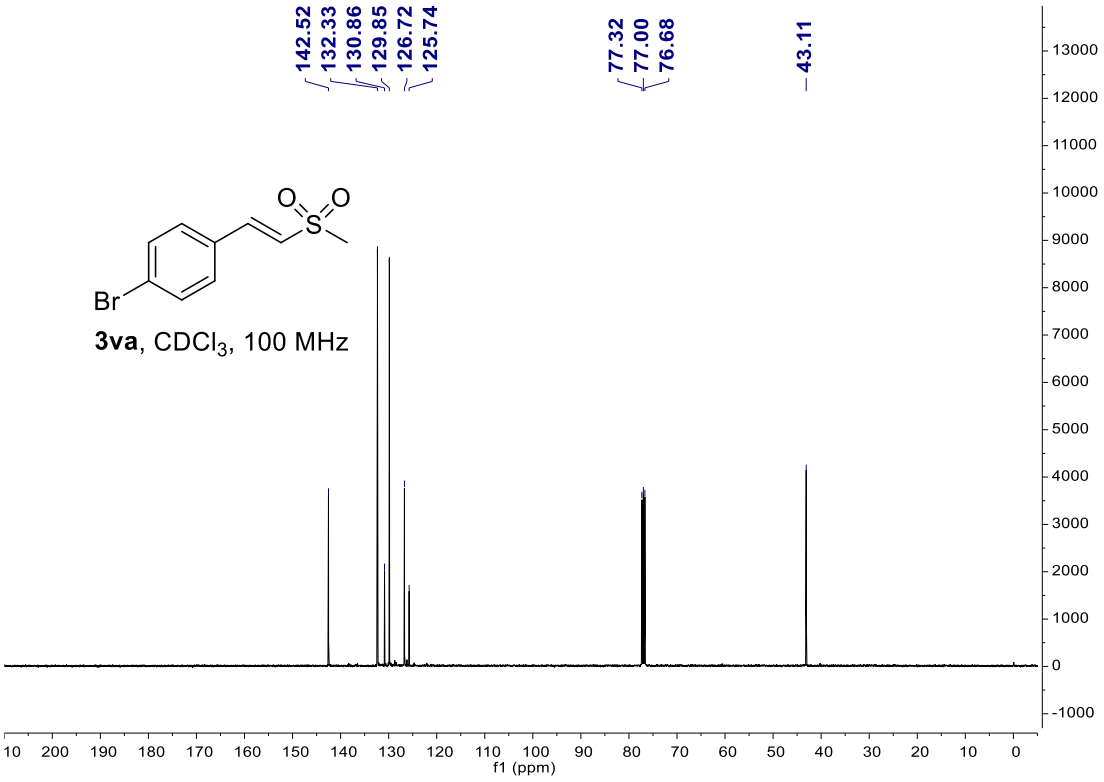
(*E*)-1-chloro-4-(2-(methylsulfonyl)vinyl)benzene **(3ua)**



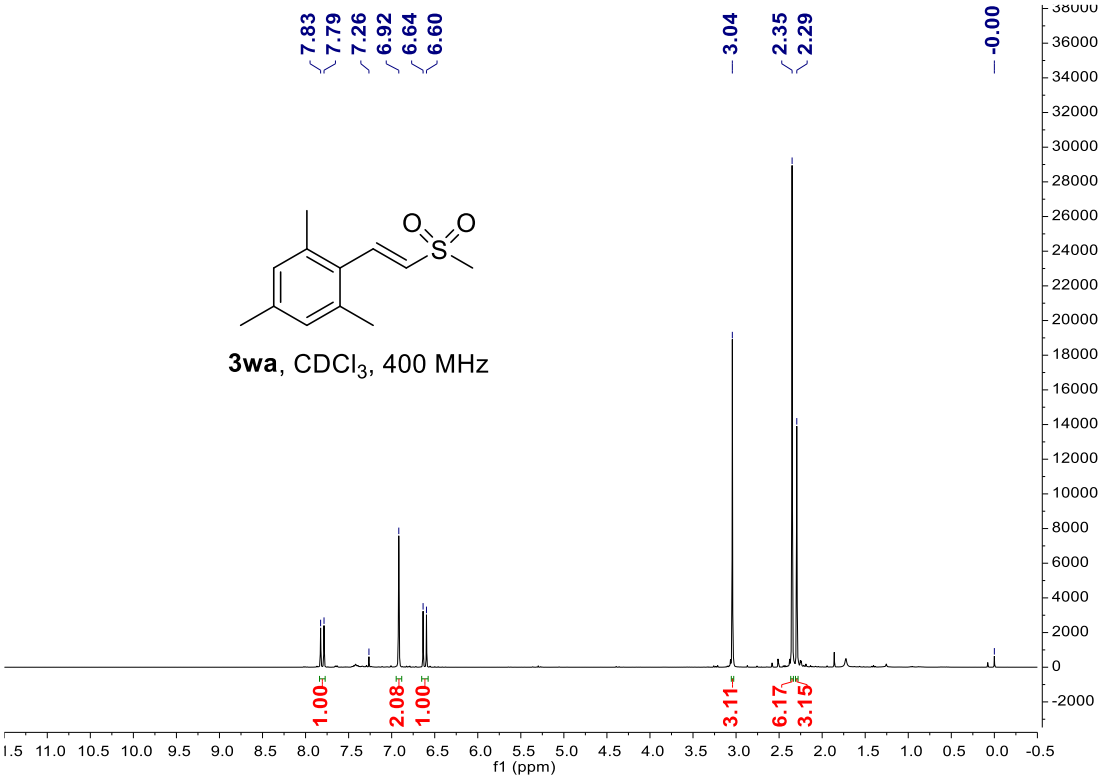


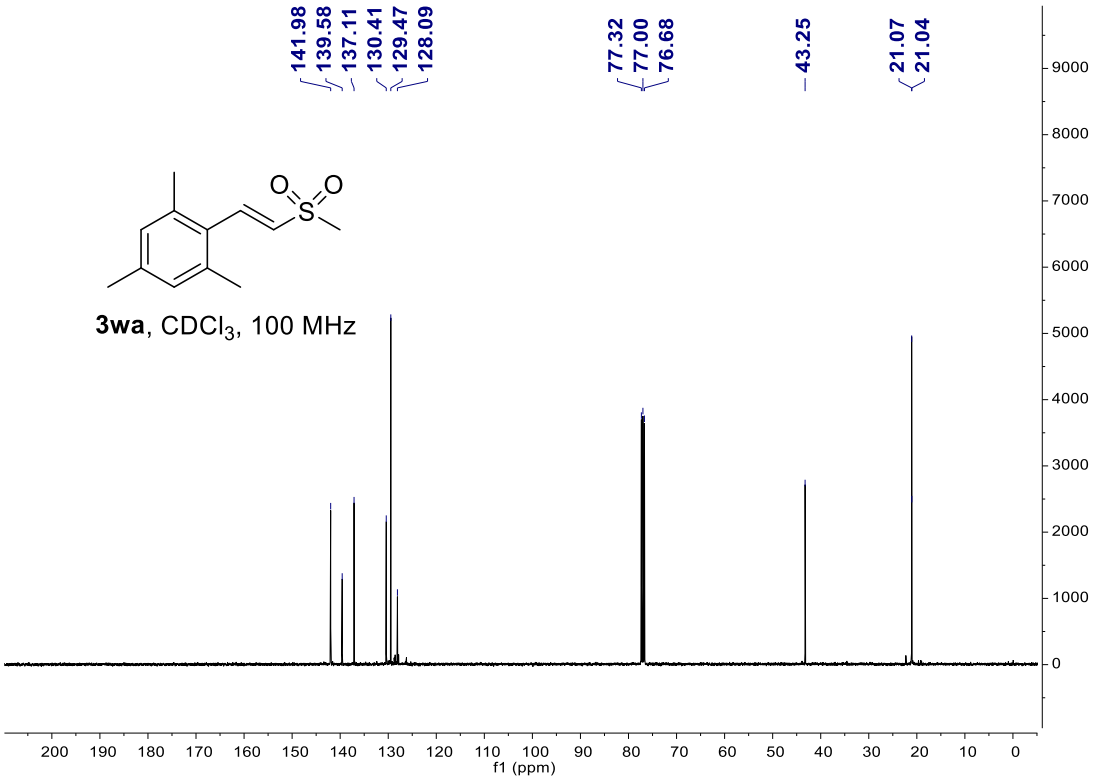
(*E*)-1-bromo-4-(2-(methylsulfonyl)vinyl)benzene **(3va)**



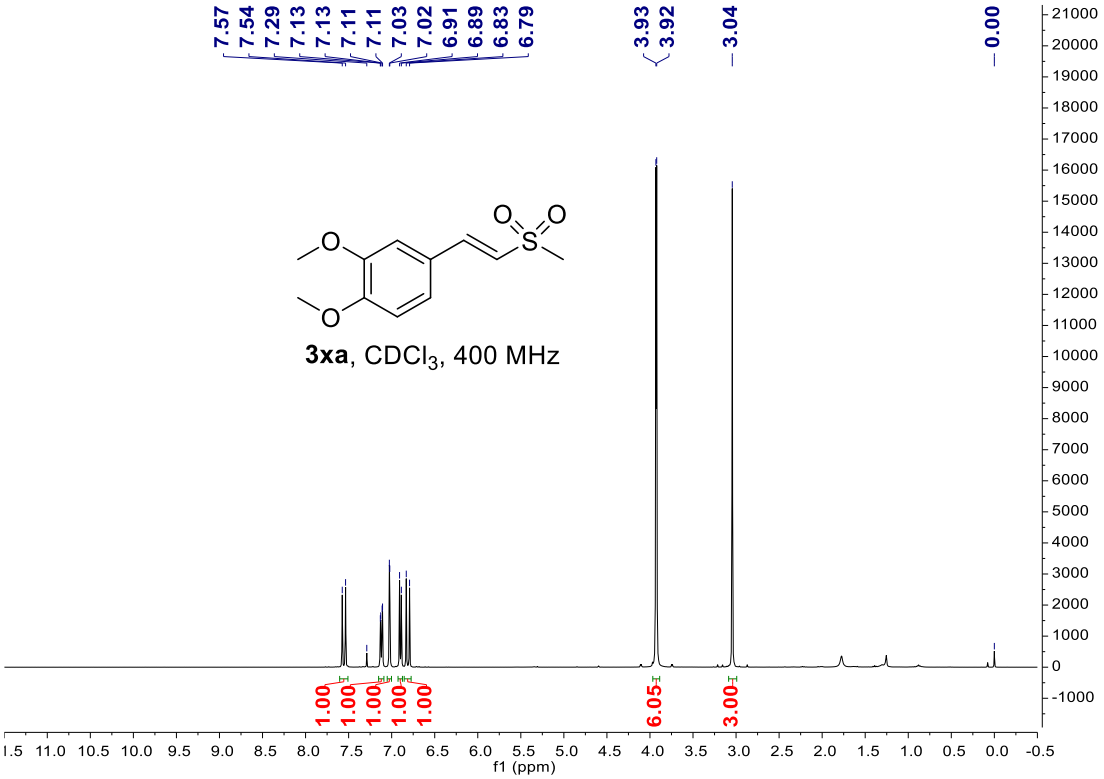


(*E*)-1,3,5-trimethyl-2-(2-(methylsulfonyl)vinyl)benzene **(3wa)**

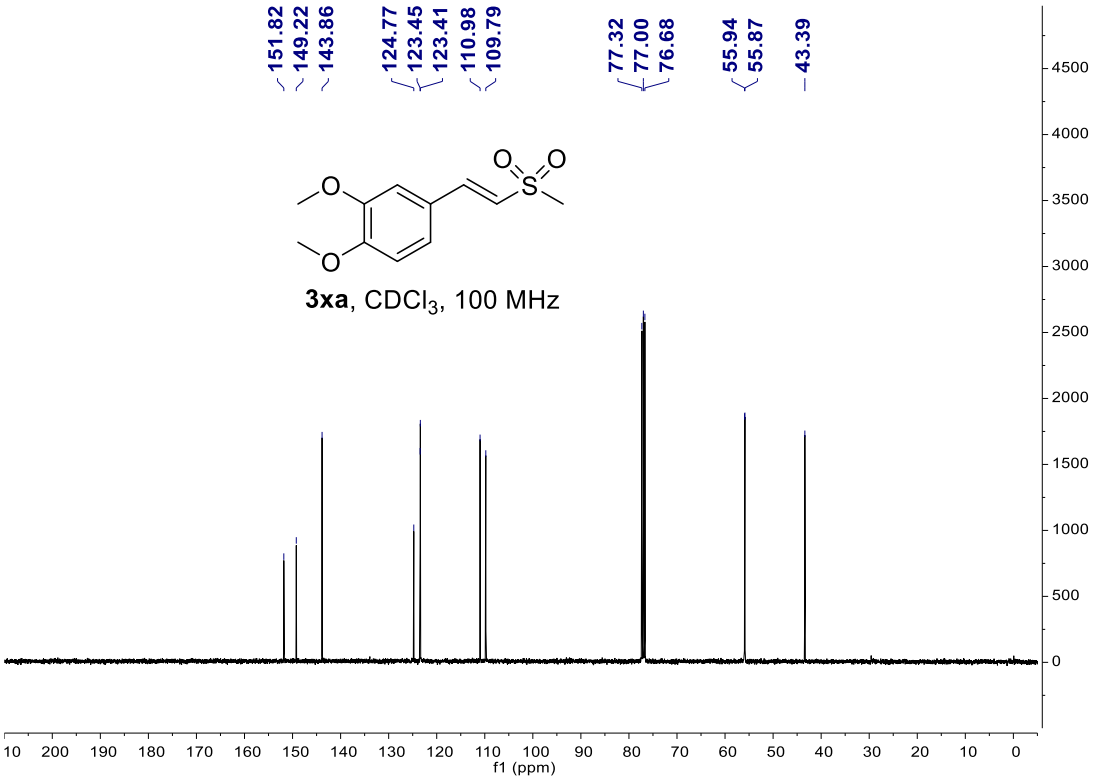




(*E*)-1,2-dimethoxy-4-(2-(methylsulfonyl)vinyl)benzene **(3xa)**

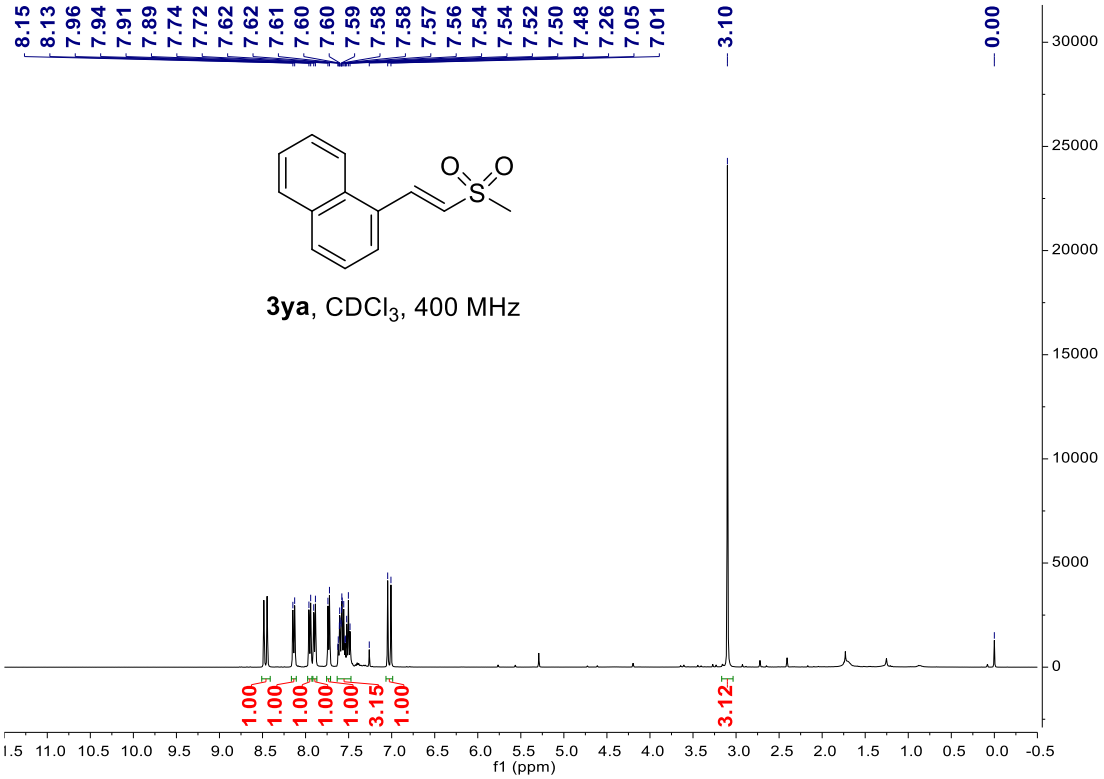


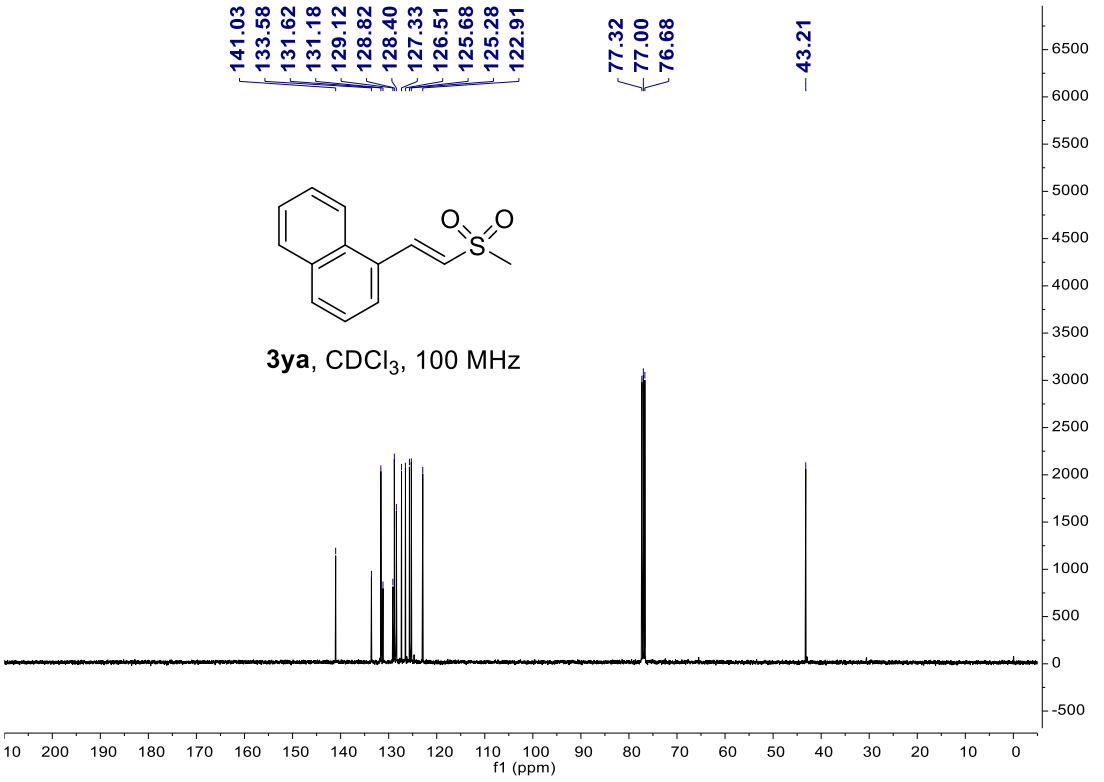
3xa, $CDCl_3$, 400 MHz



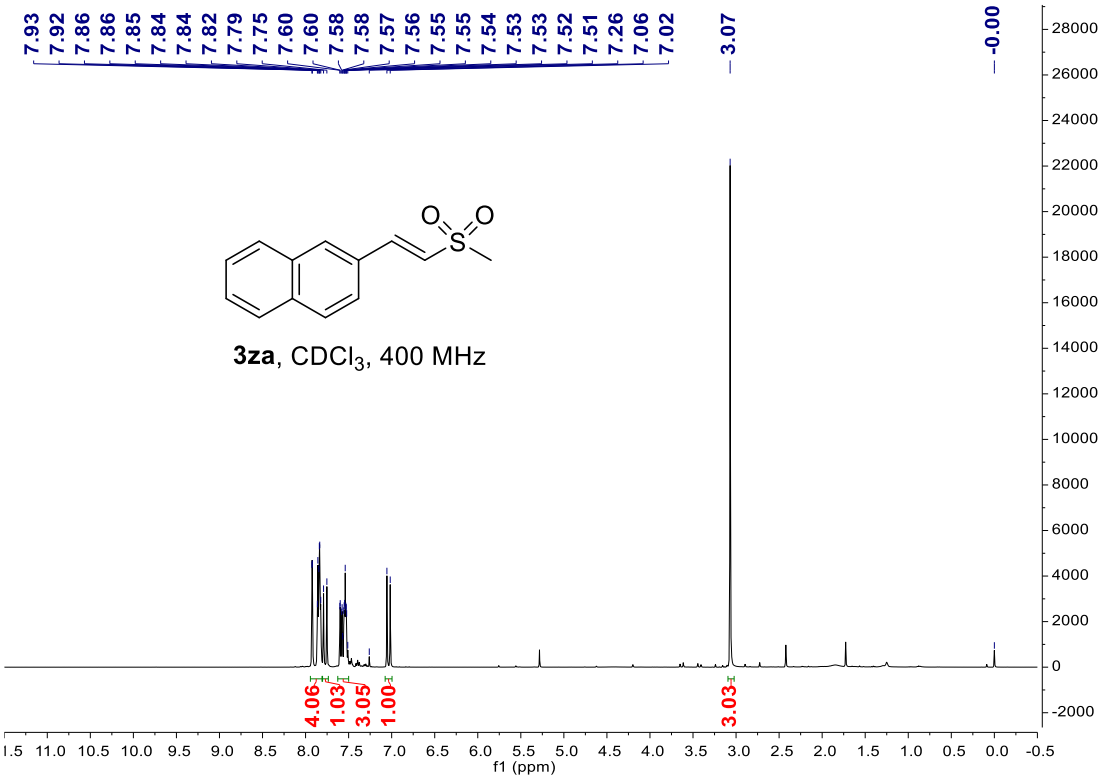
3xa, $CDCl_3$, 100 MHz

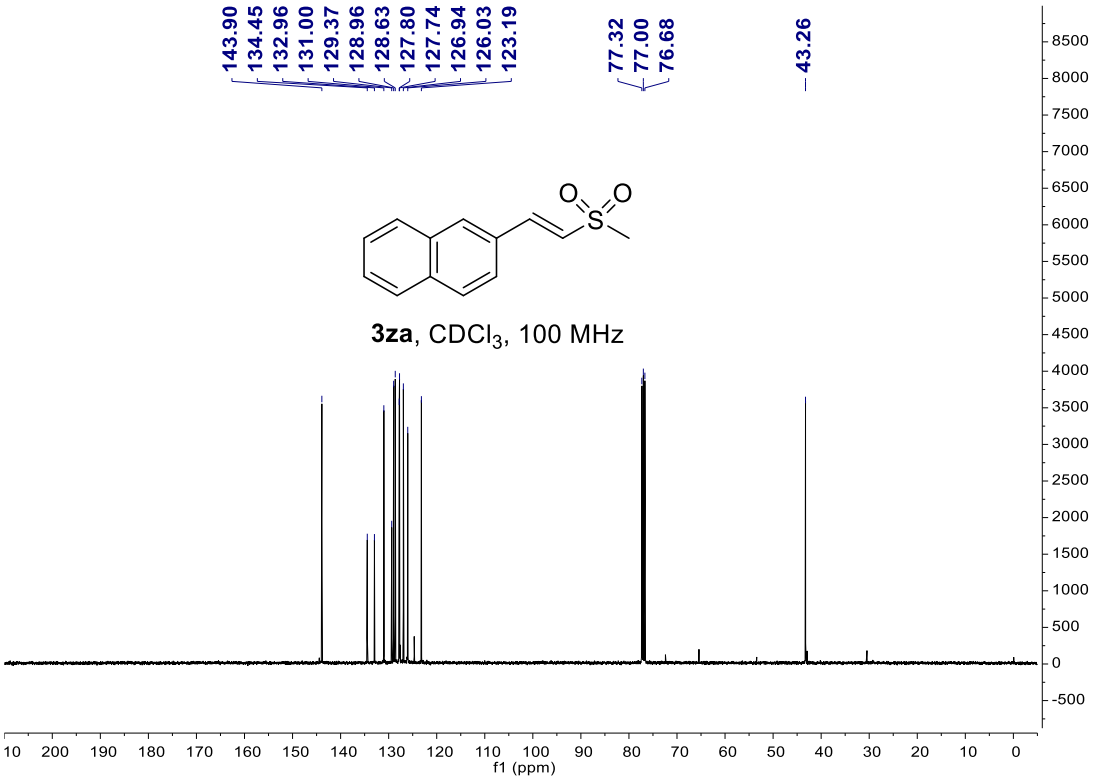
(*E*)-1-(2-(methylsulfonyl)vinyl)naphthalene **(3ya)**



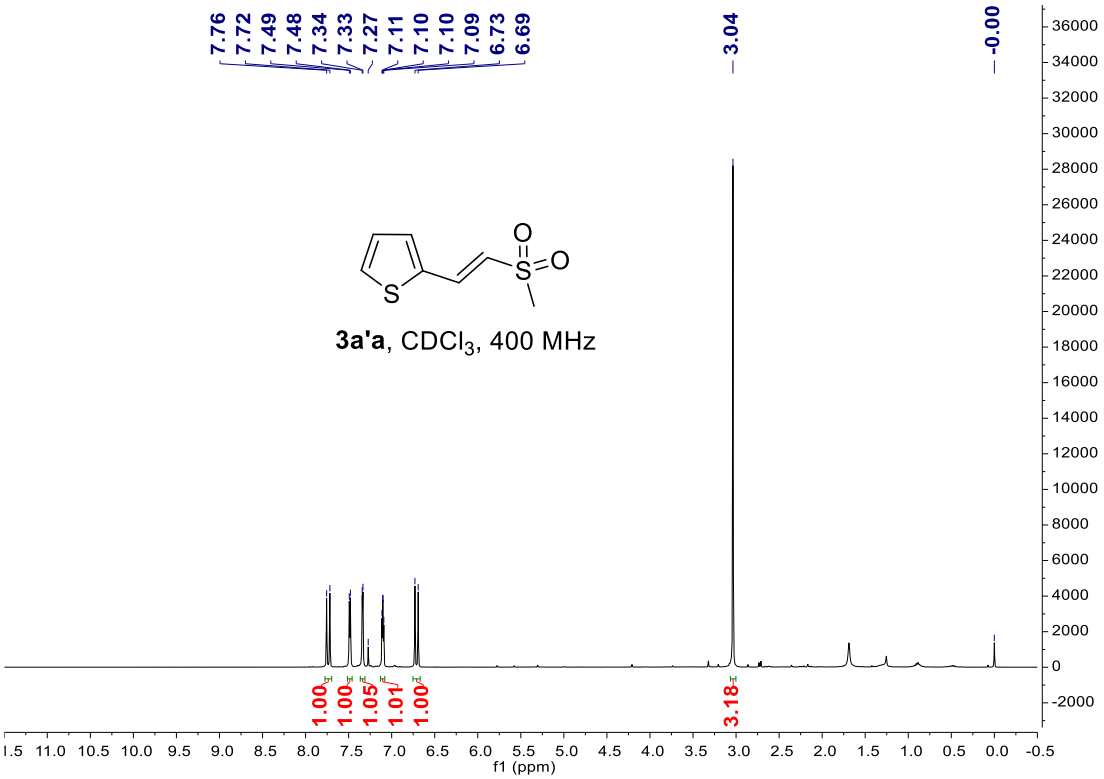


(*E*)-2-(2-(methylsulfonyl)vinyl)naphthalene **(3za)**

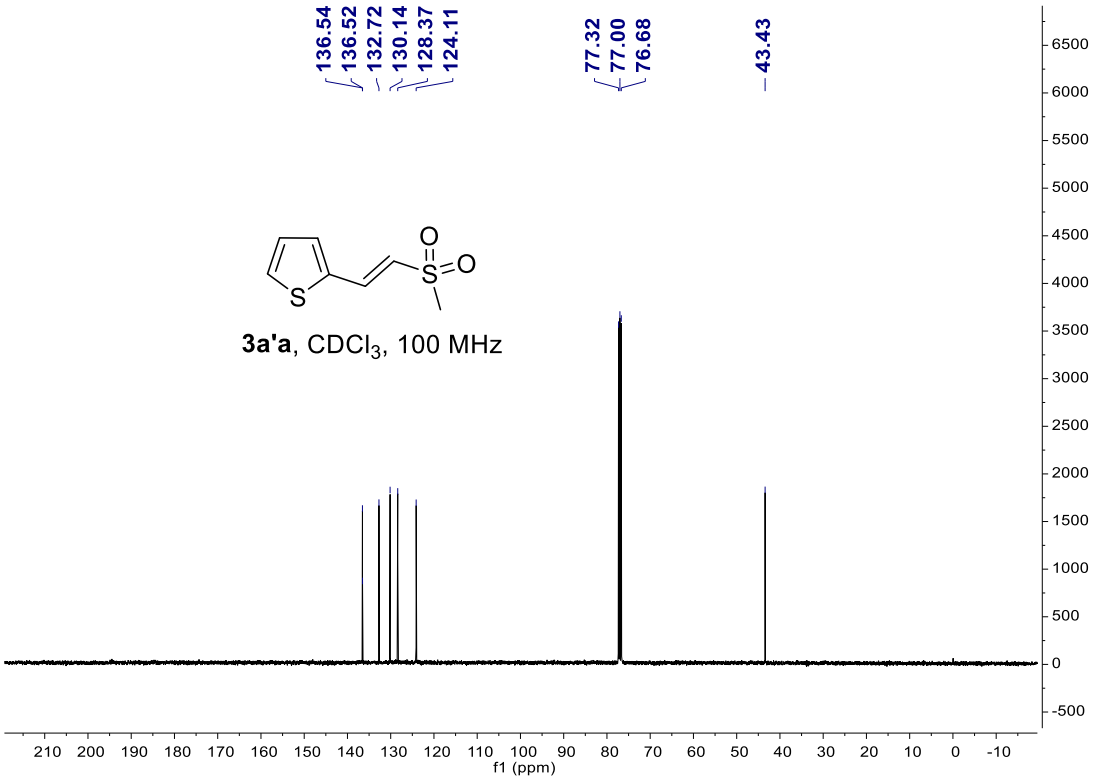




(*E*)-2-(2-(methylsulfonyl)vinyl)thiophene **(3a'a)**

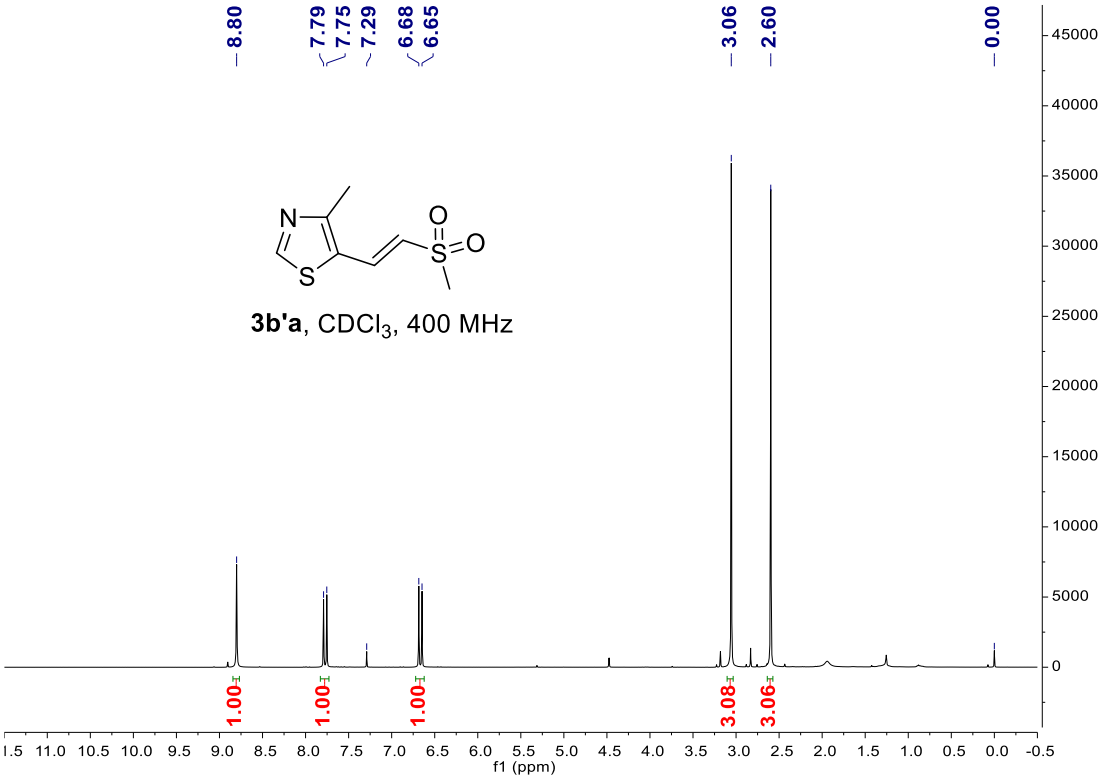


3a'a, $CDCl_3$, 400 MHz

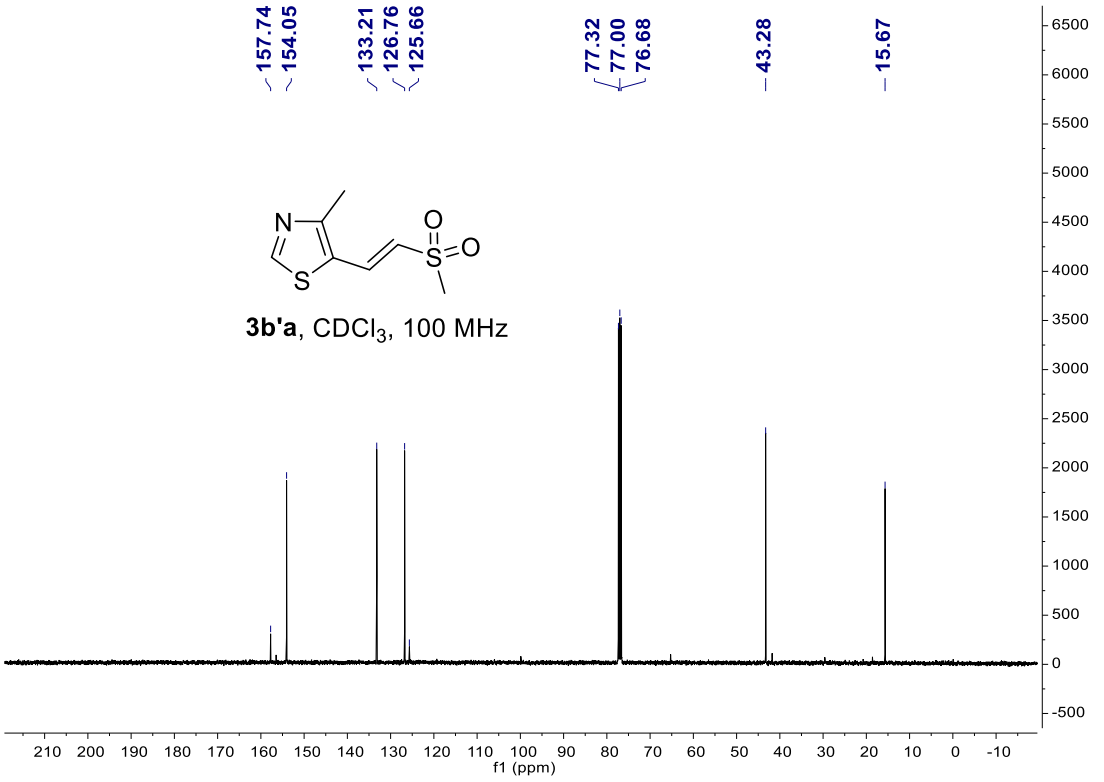


3a'a, $CDCl_3$, 100 MHz

(*E*)-4-methyl-5-(2-(methylsulfonyl)vinyl)thiazole **(3b'a)**

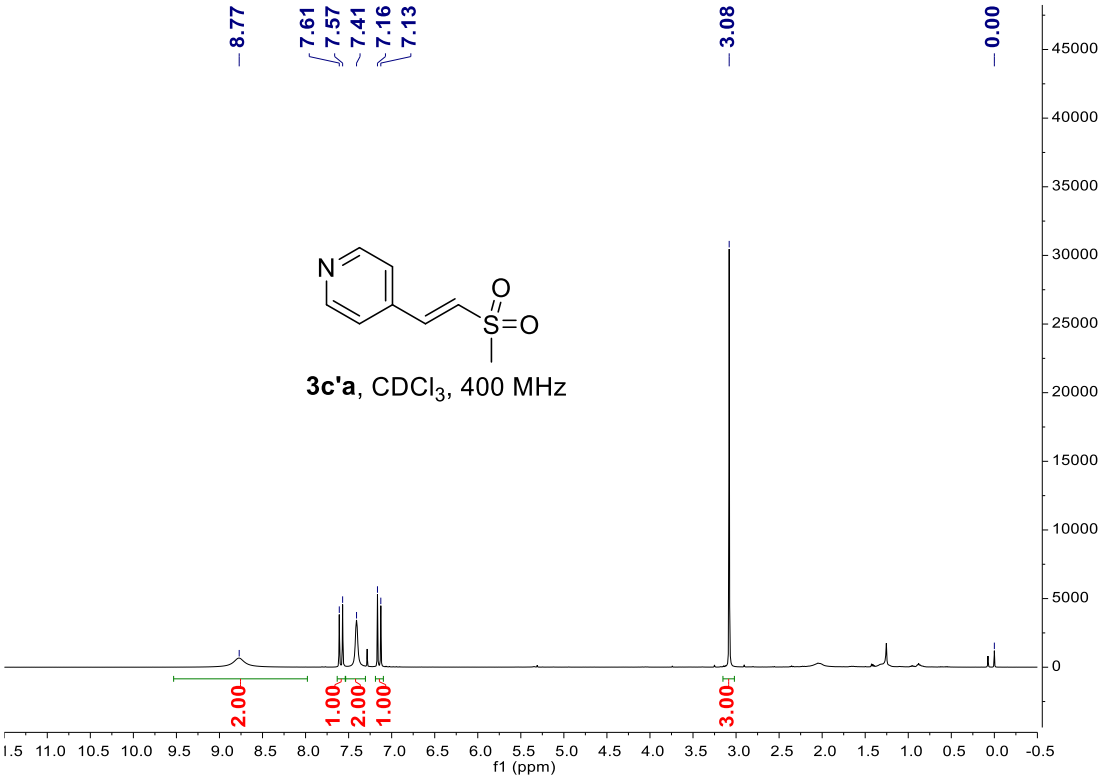


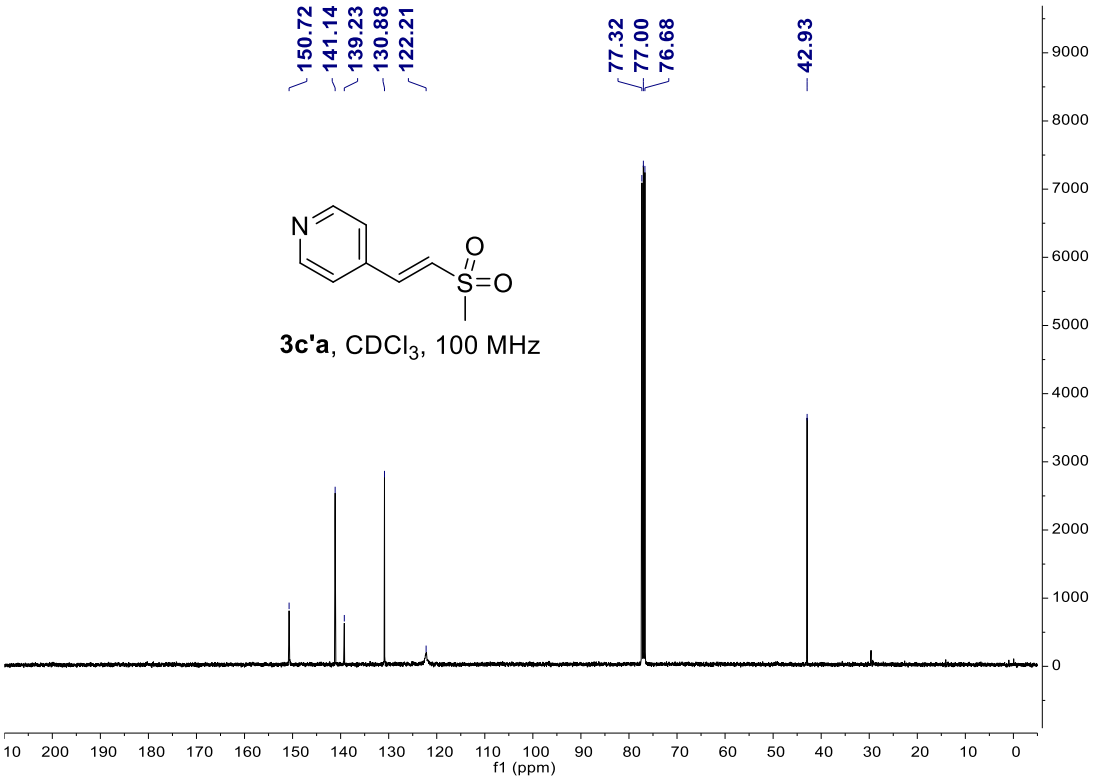
3b'a, $CDCl_3$, 400 MHz



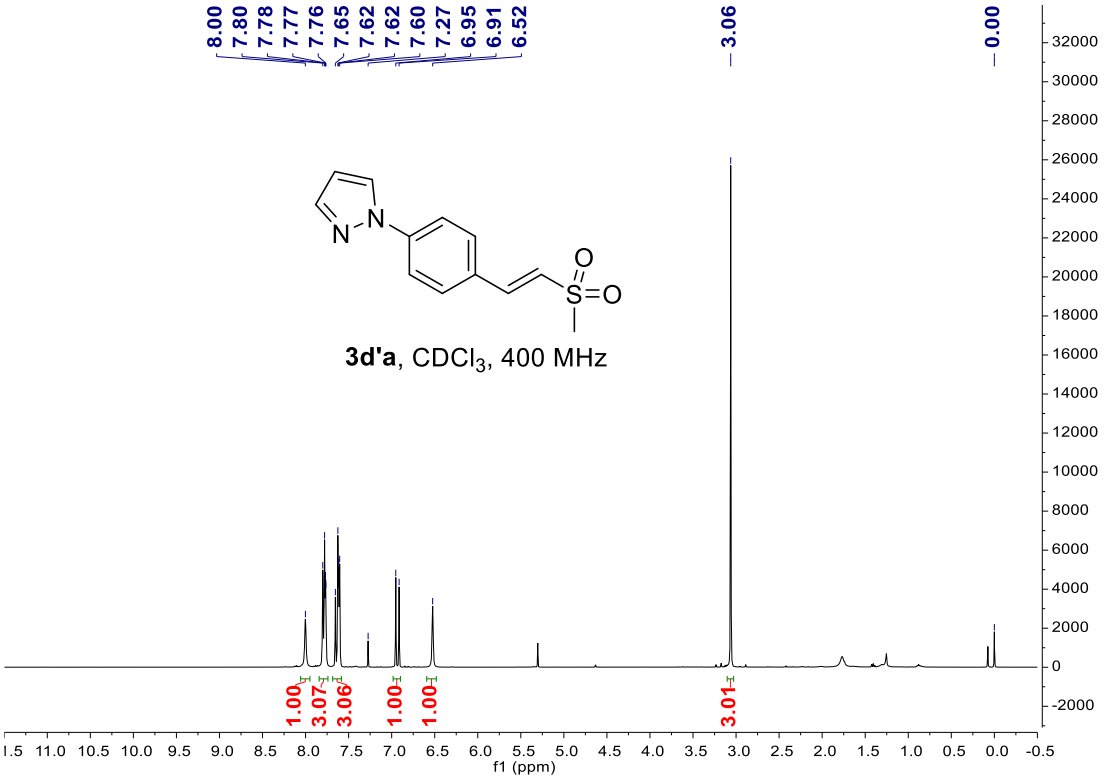
3b'a, $CDCl_3$, 100 MHz

(*E*)-4-(2-(methylsulfonyl)vinyl)pyridine **(3c'a)**

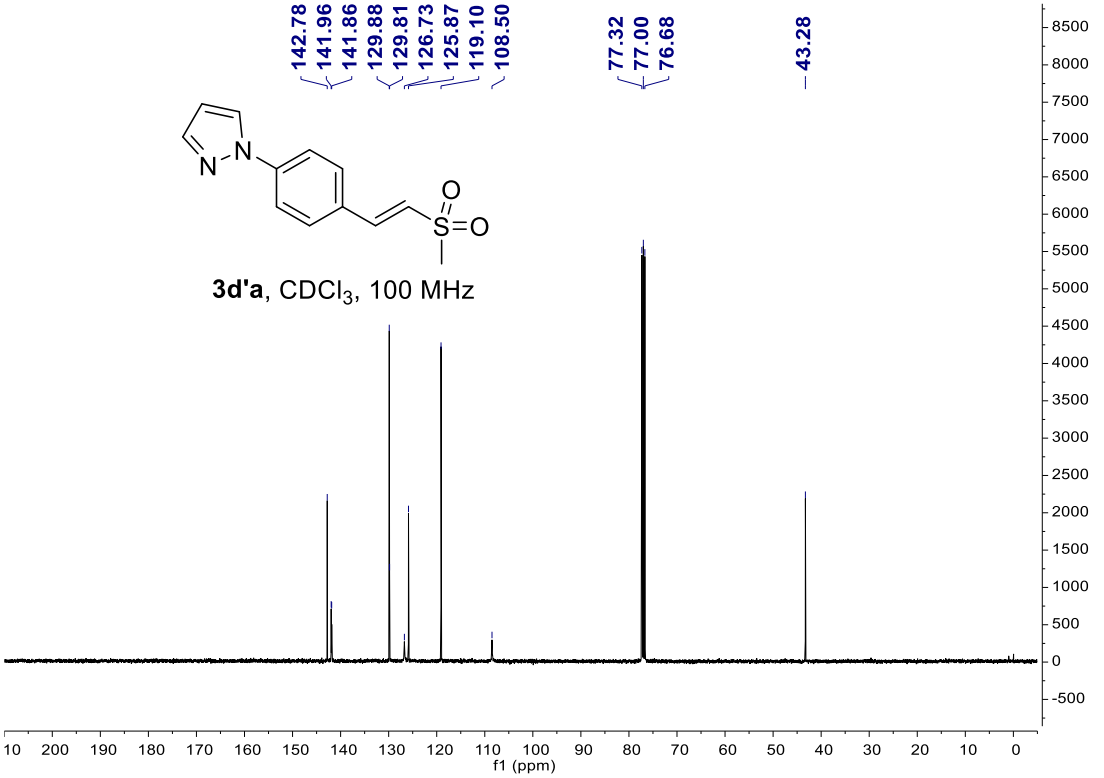




(*E*)-1-(4-(2-(methylsulfonyl)vinyl)phenyl)-1*H*-pyrazole **(3d'a)**

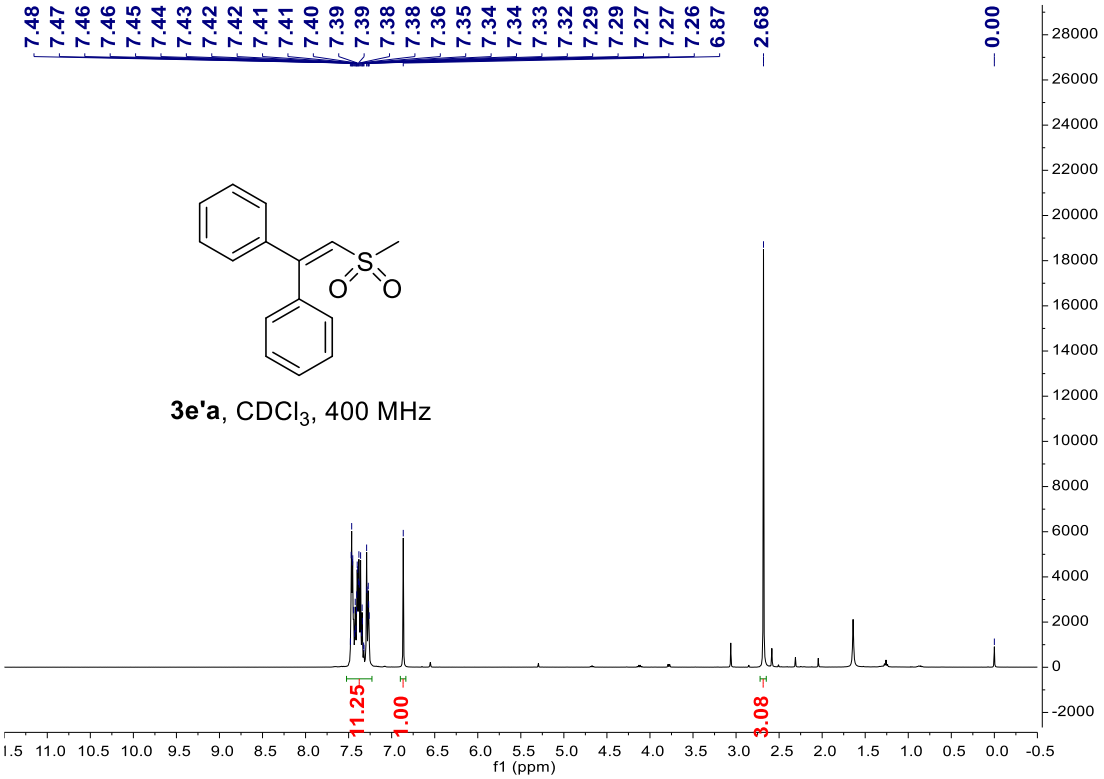


3d'a, $CDCl_3$, 400 MHz

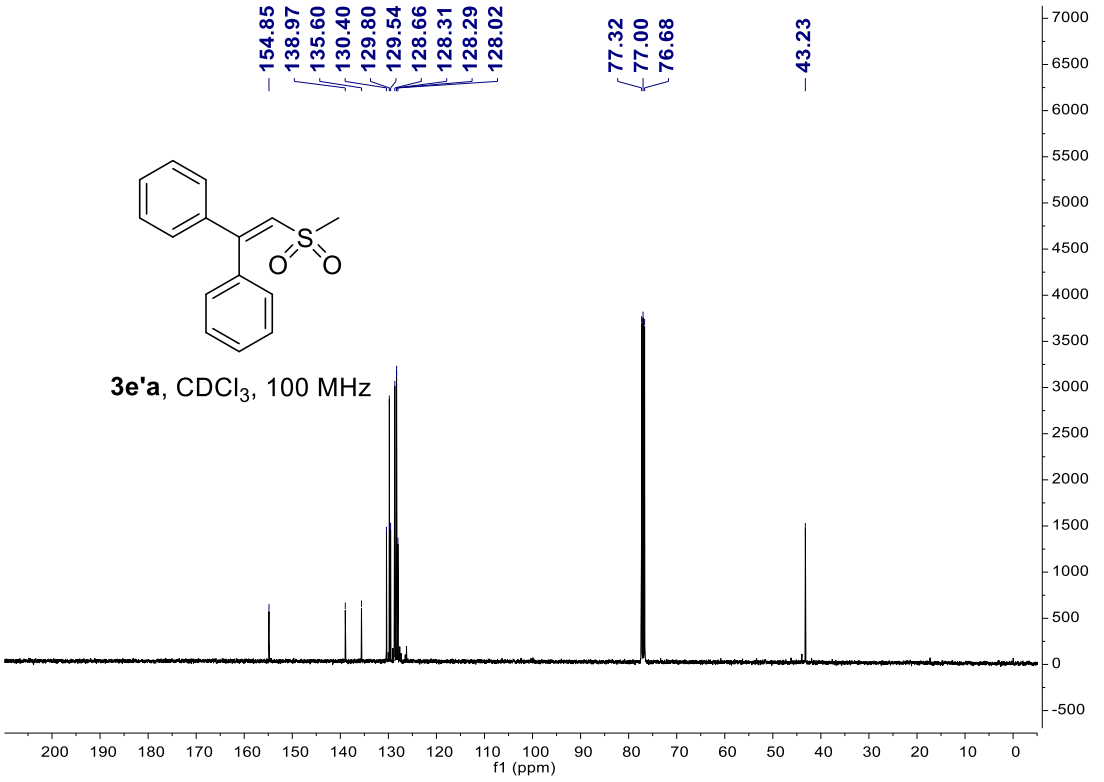


3d'a, $CDCl_3$, 100 MHz

(2-(methylsulfonyl)ethene-1,1-diyl)dibenzene **(3e'a)**

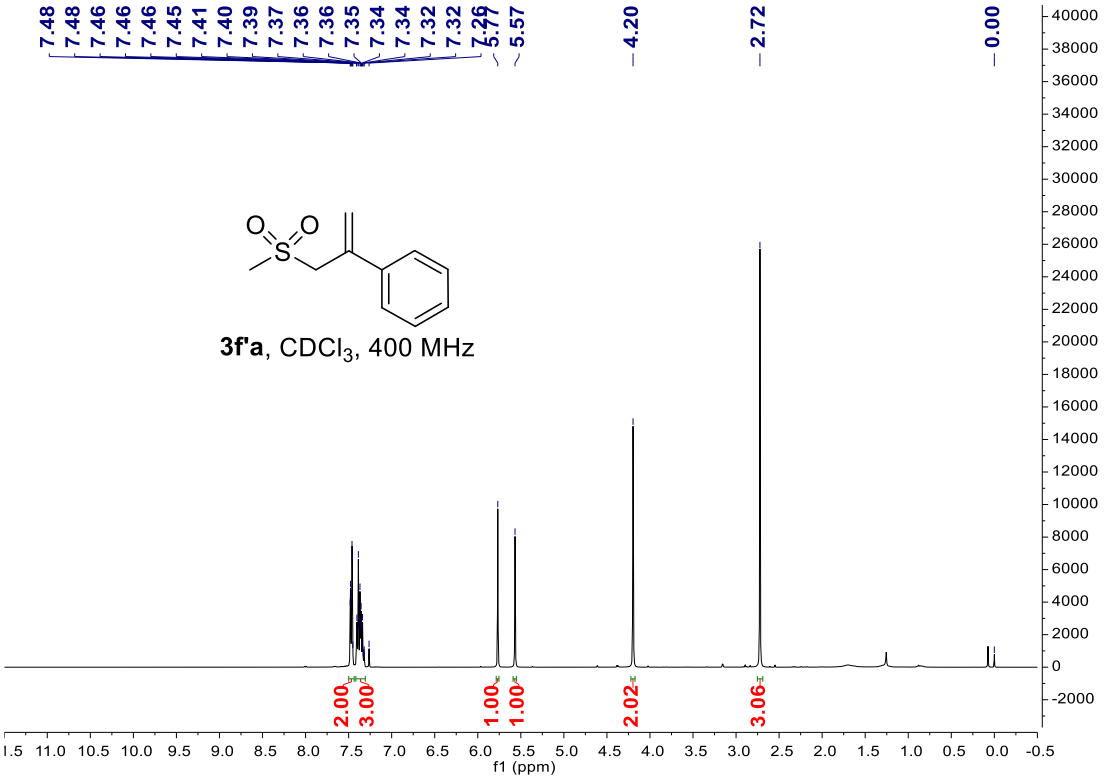


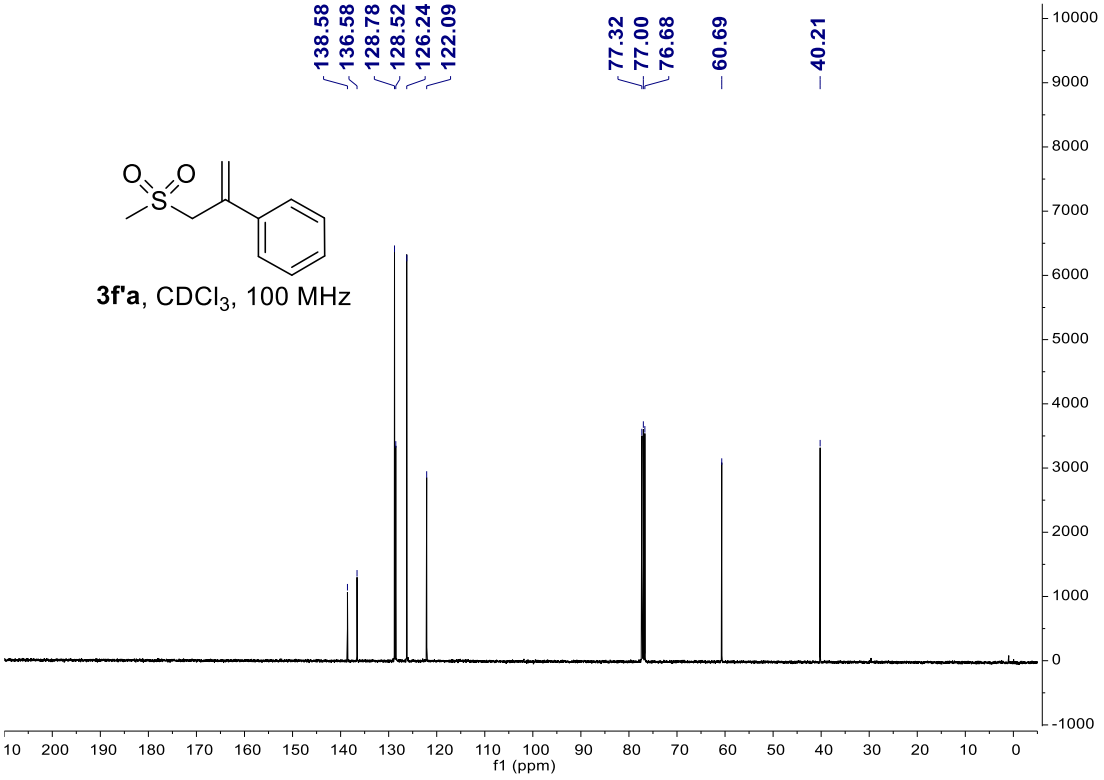
3e'a, $CDCl_3$, 400 MHz



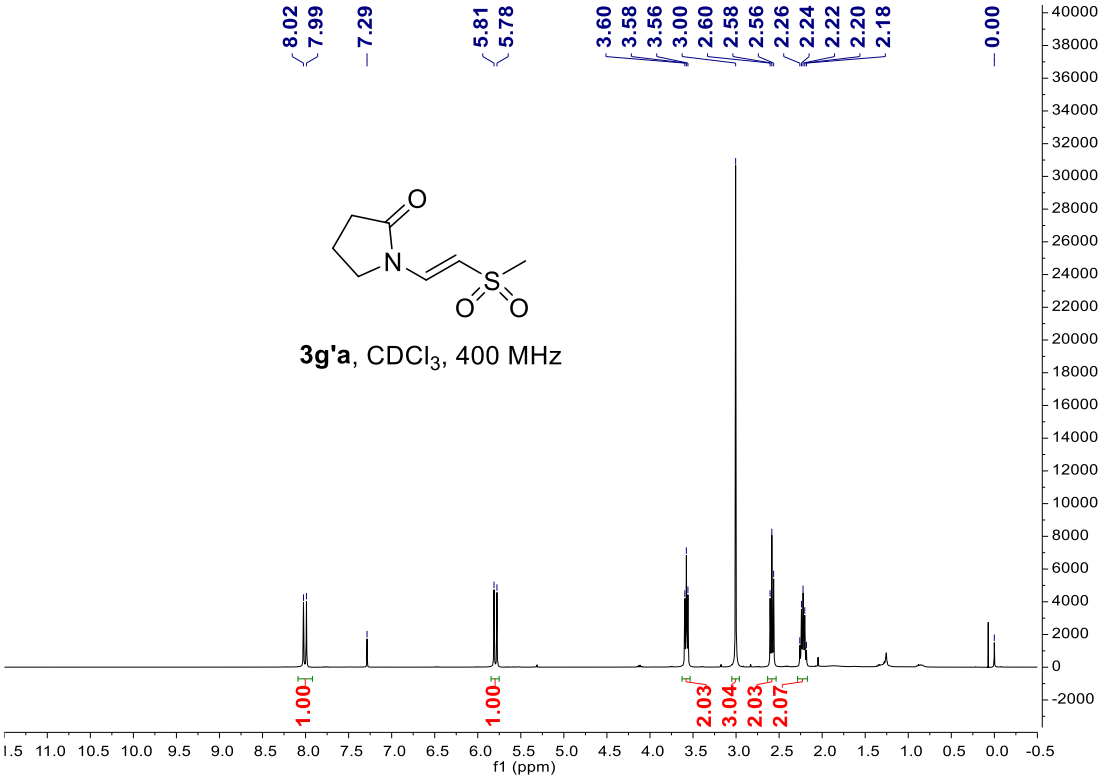
3e'a, $CDCl_3$, 100 MHz

(3-(methylsulfonyl)prop-1-en-2-yl)benzene **(3f'a)**

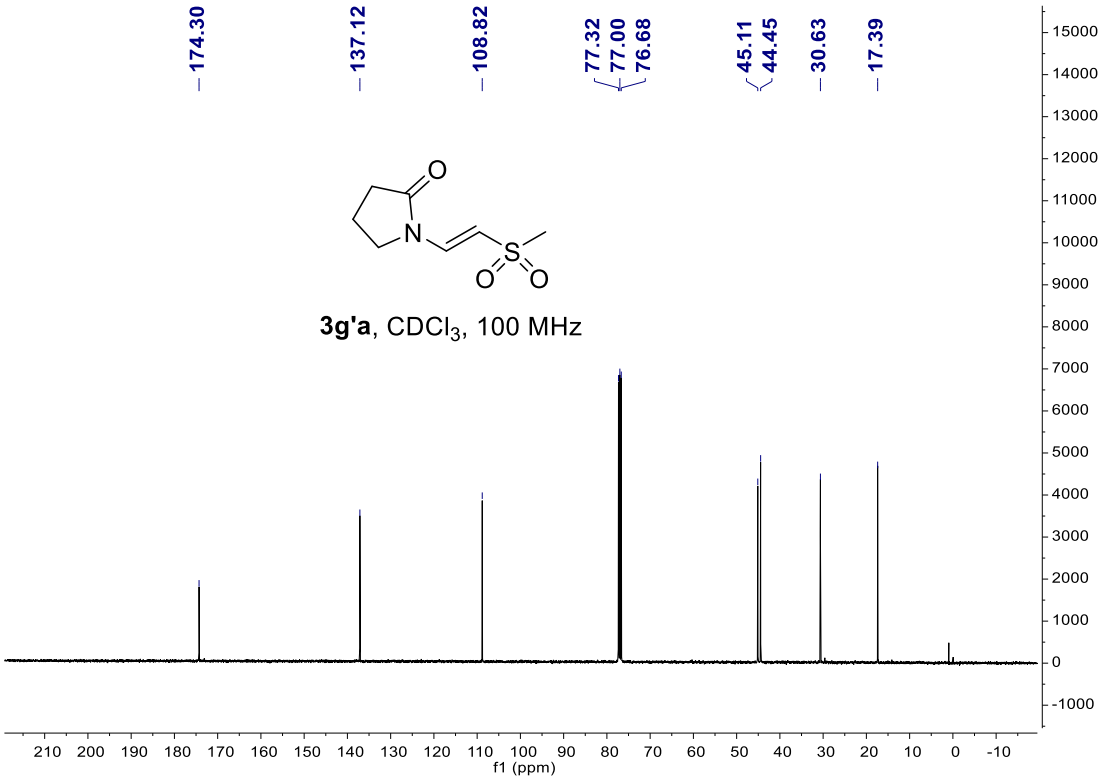




(*E*)-1-(2-(methylsulfonyl)vinyl)pyrrolidin-2-one **(3g'a)**

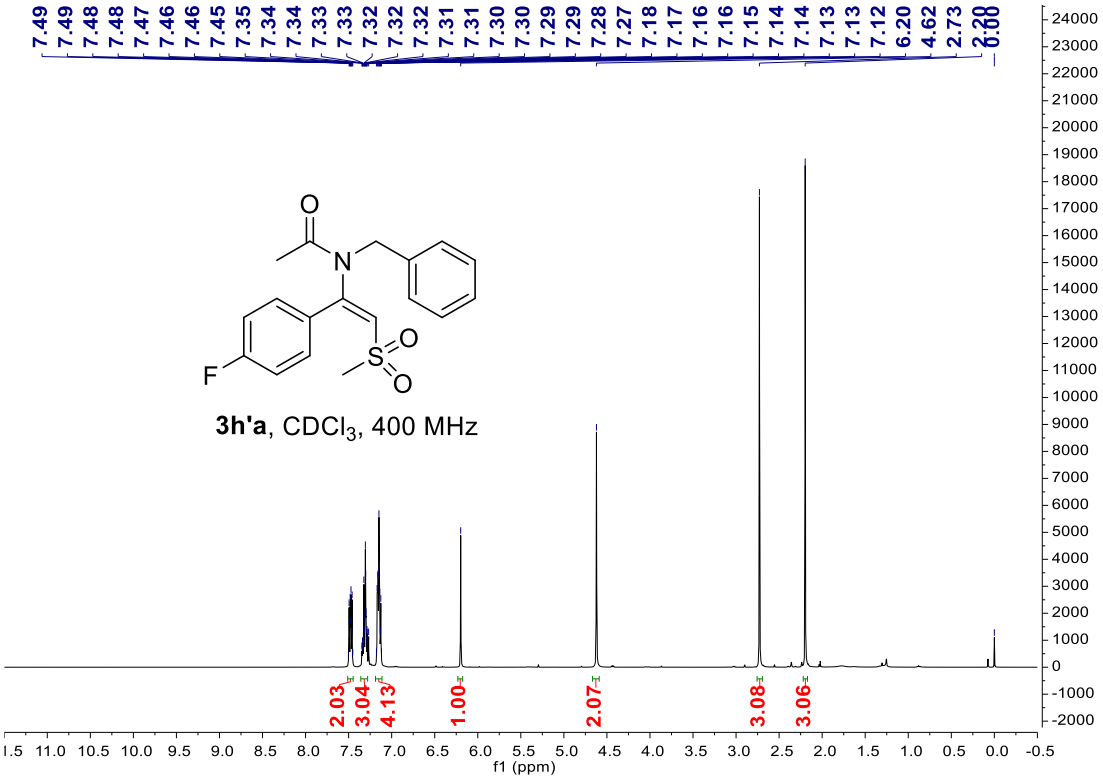


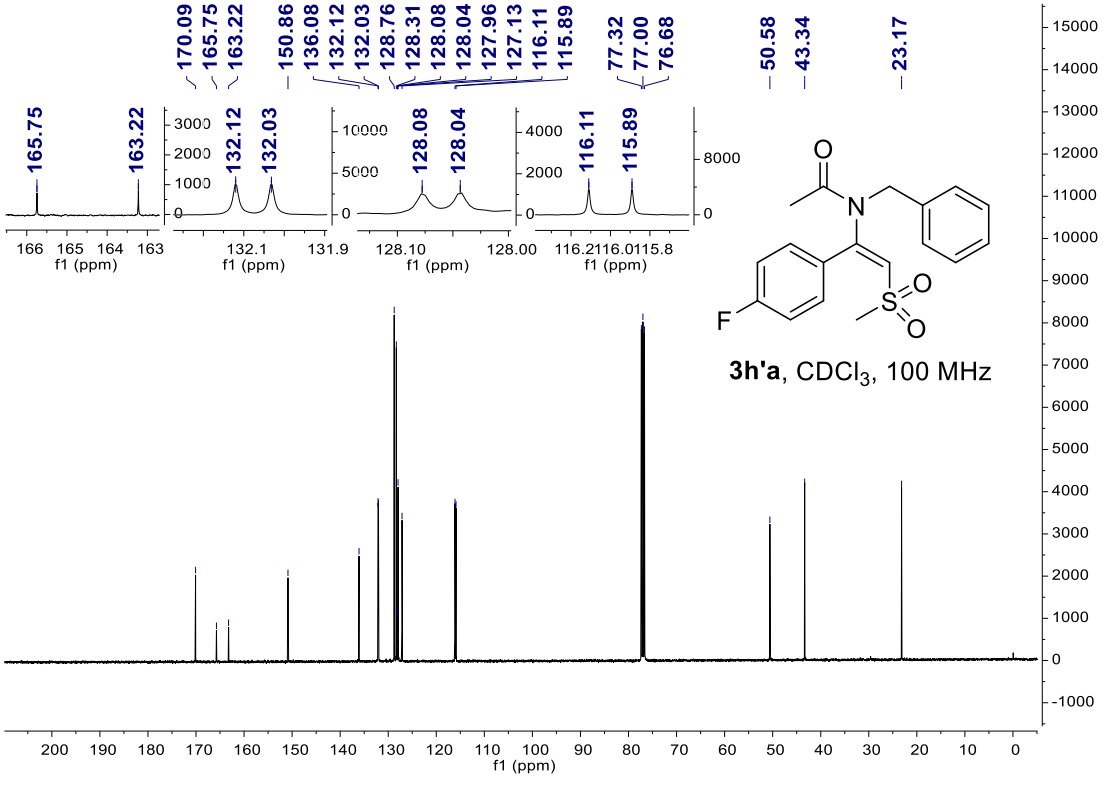
3g'a, $CDCl_3$, 400 MHz

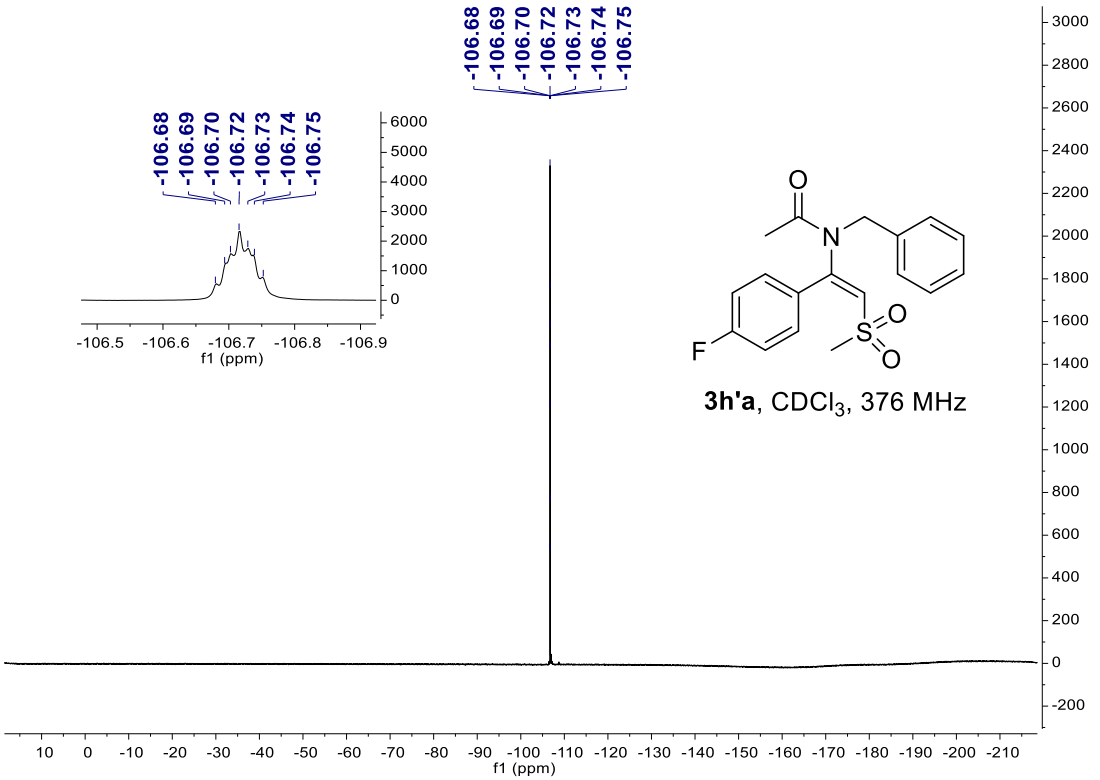


3g'a, $CDCl_3$, 100 MHz

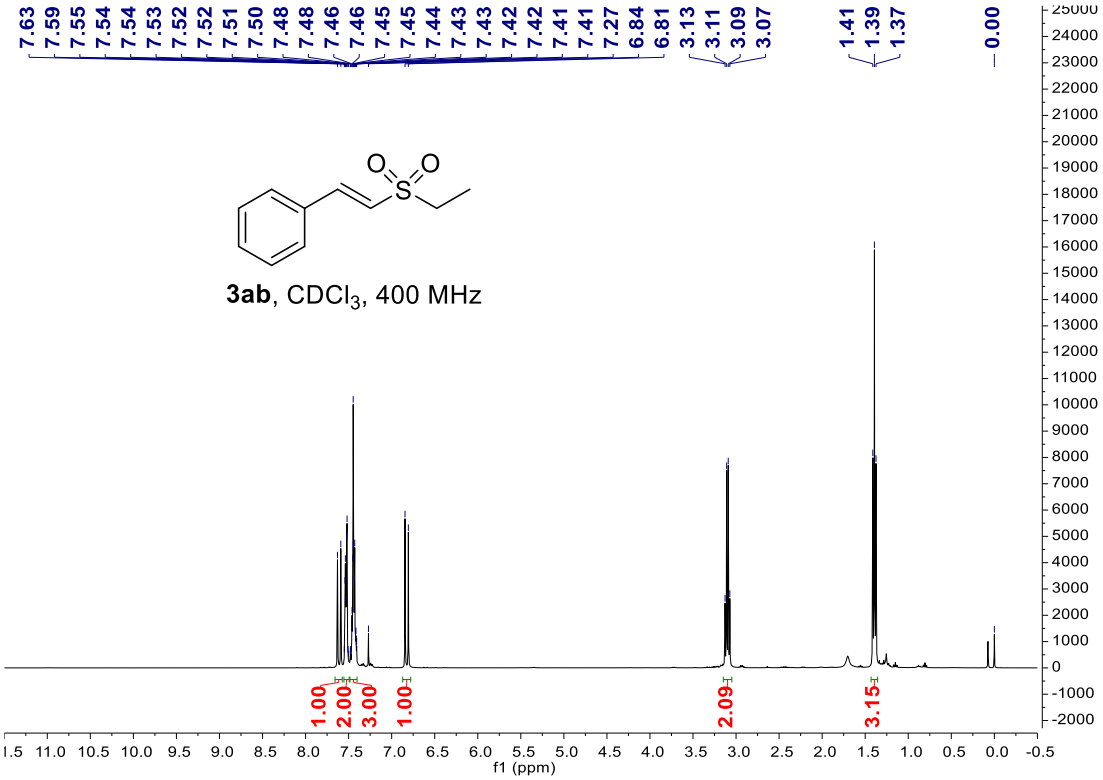
(*E*)-*N*-benzyl-*N*-(1-(4-fluorophenyl)-2-(methylsulfonyl)vinyl)acetamide **(3h'a)**

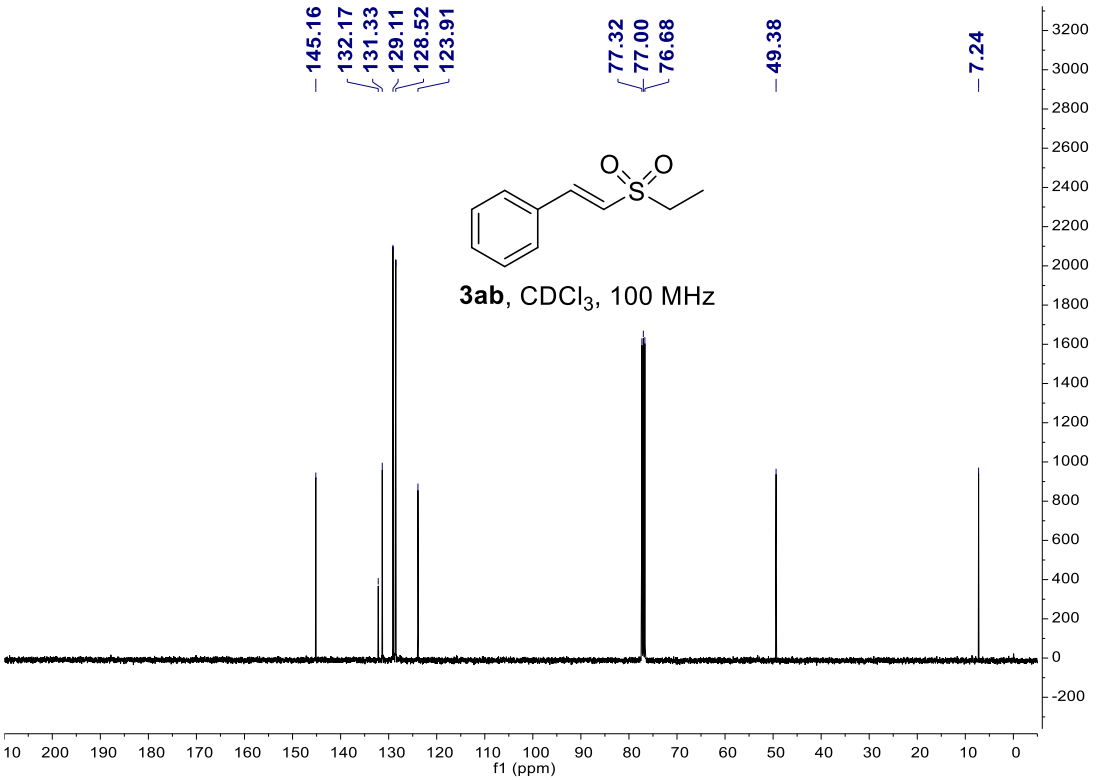




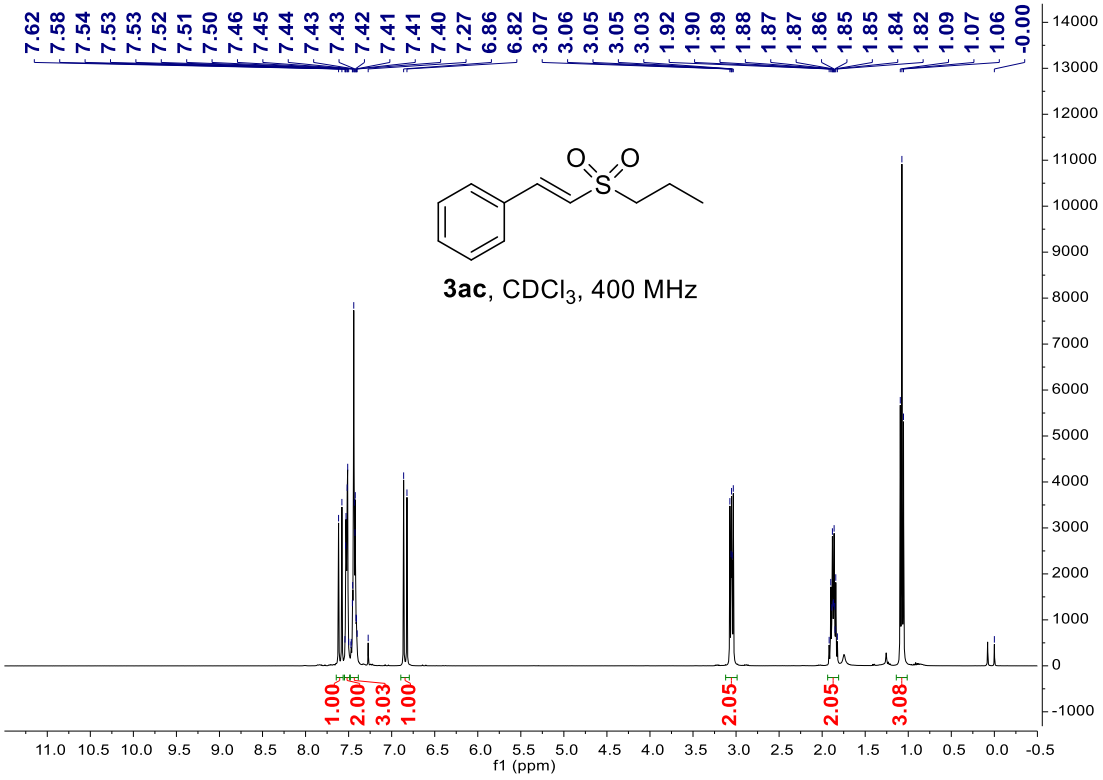


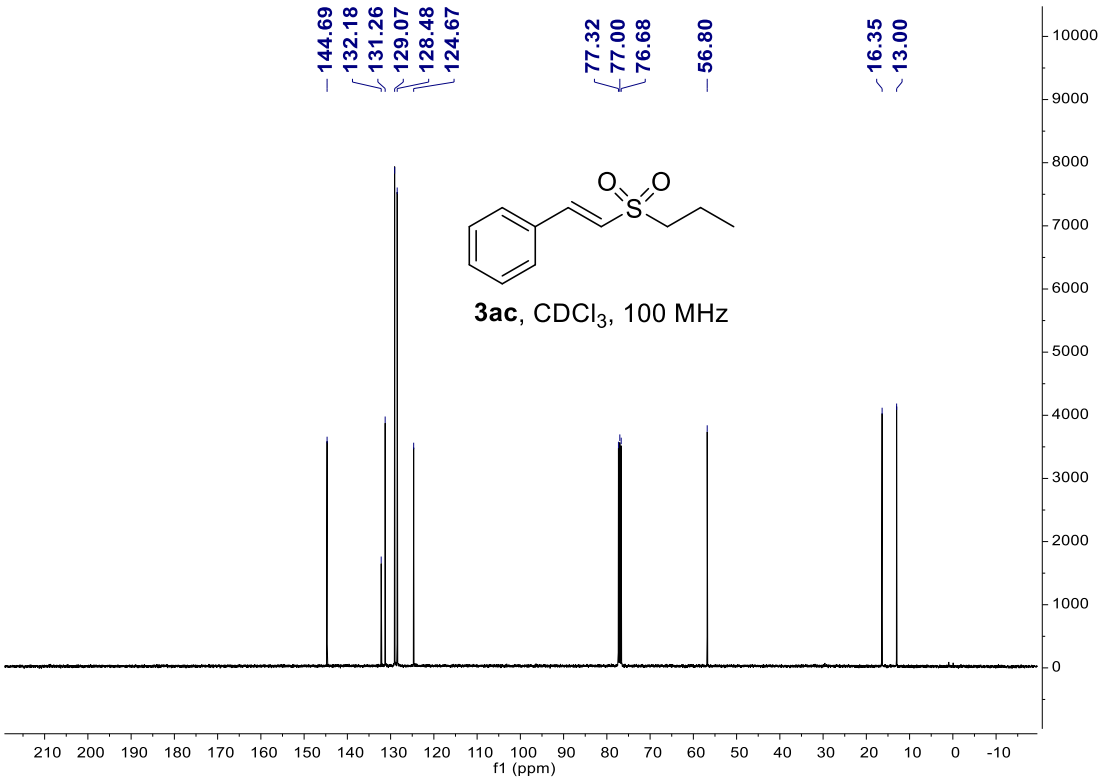
(*E*)-(2-(ethylsulfonyl)vinyl)benzene **(3ab)**



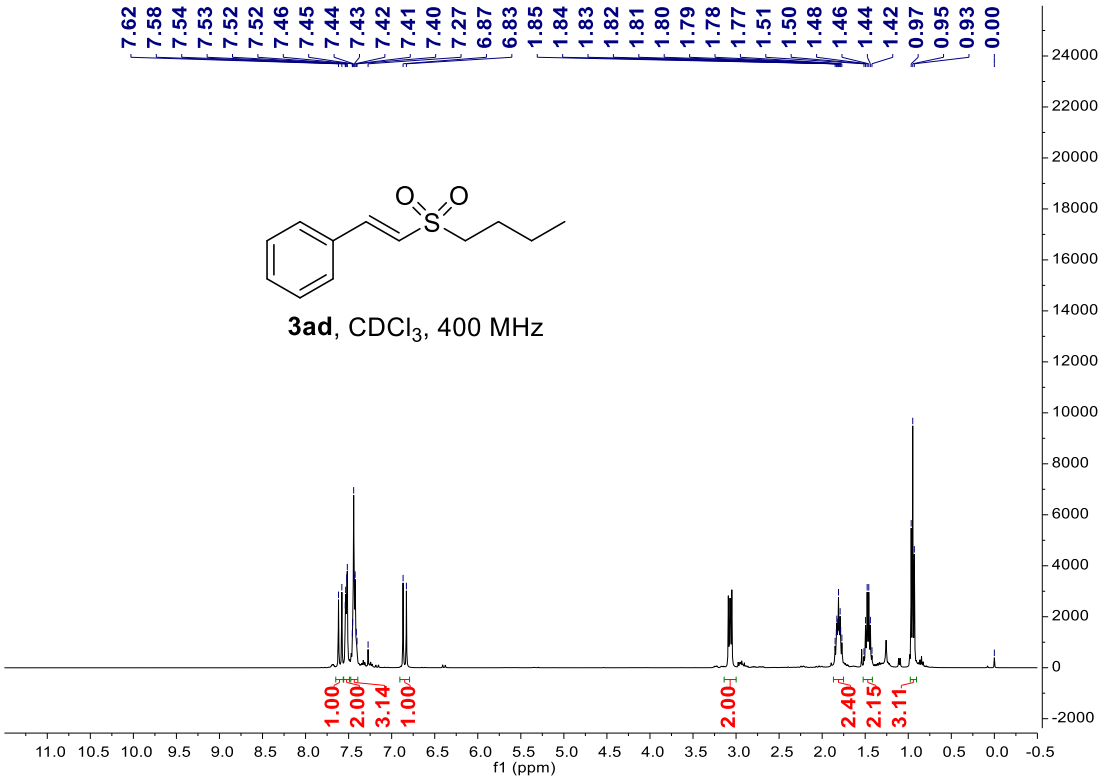


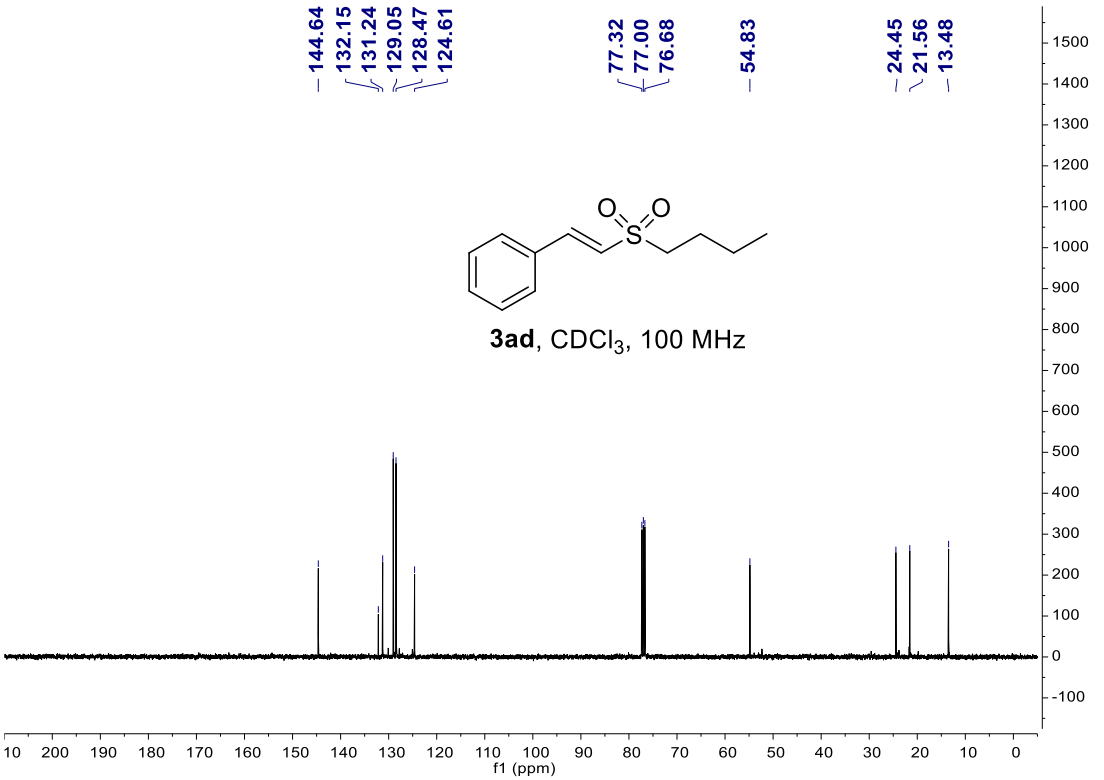
(*E*)-(2-(propylsulfonyl)vinyl)benzene **(3ac)**



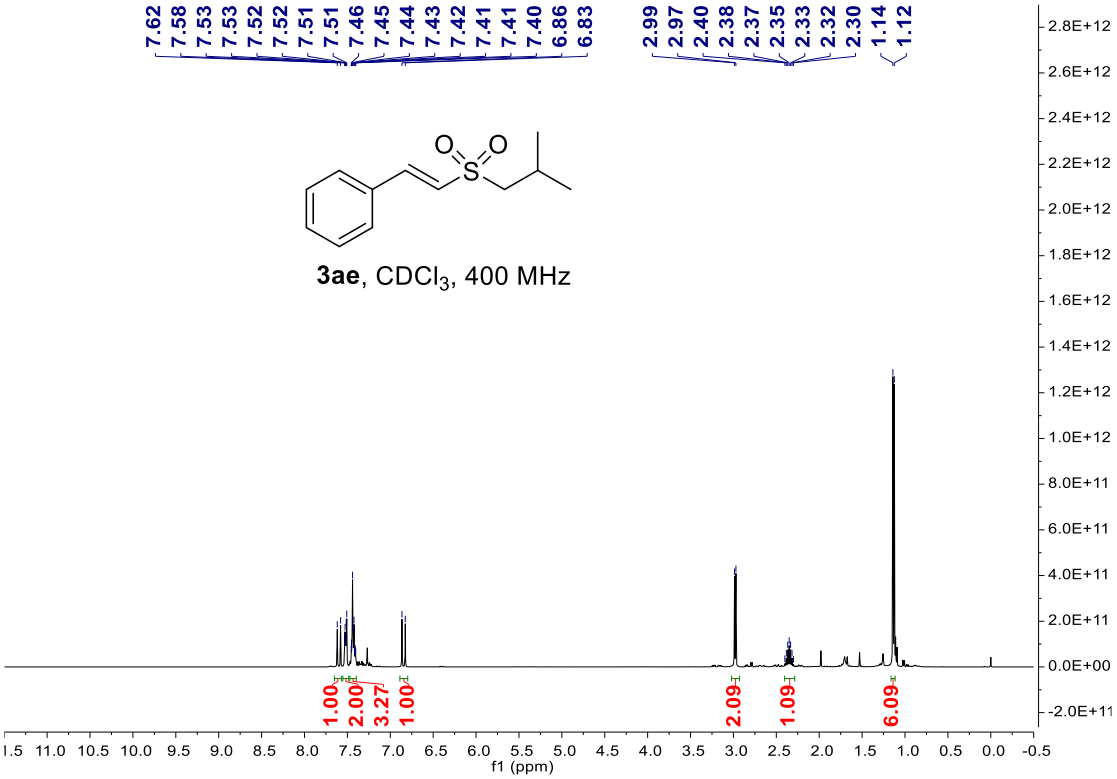


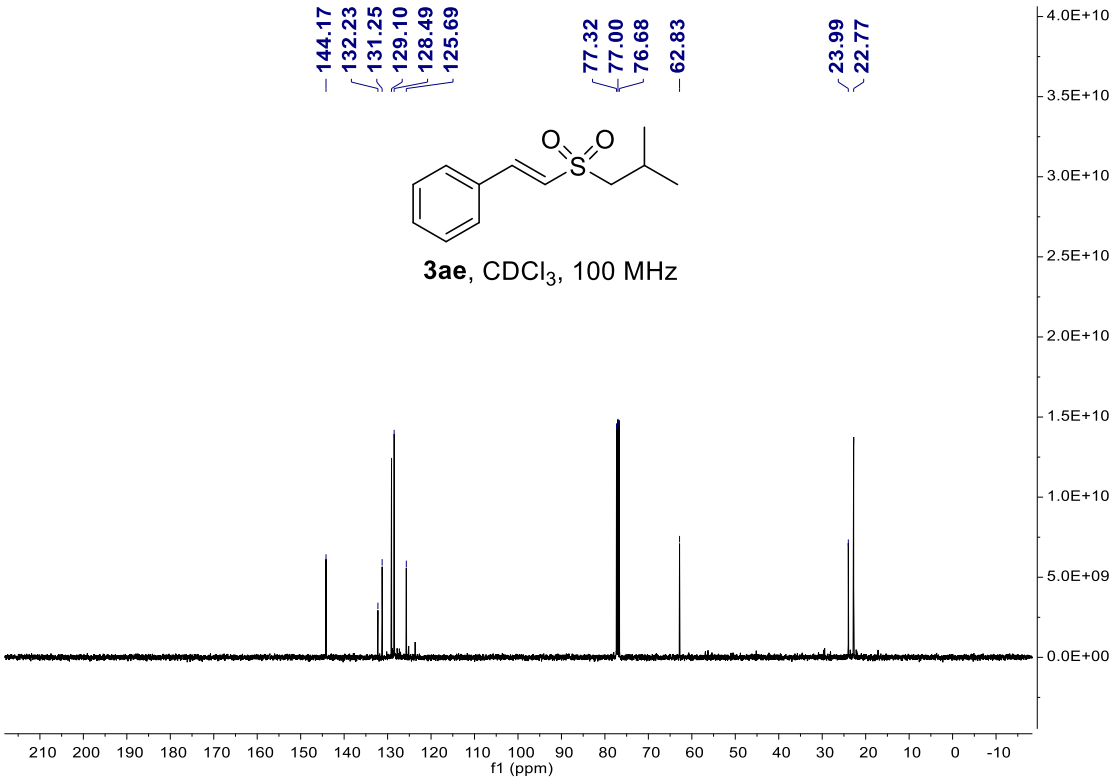
(*E*)-(2-(propylsulfonyl)vinyl)benzene **(3ad)**



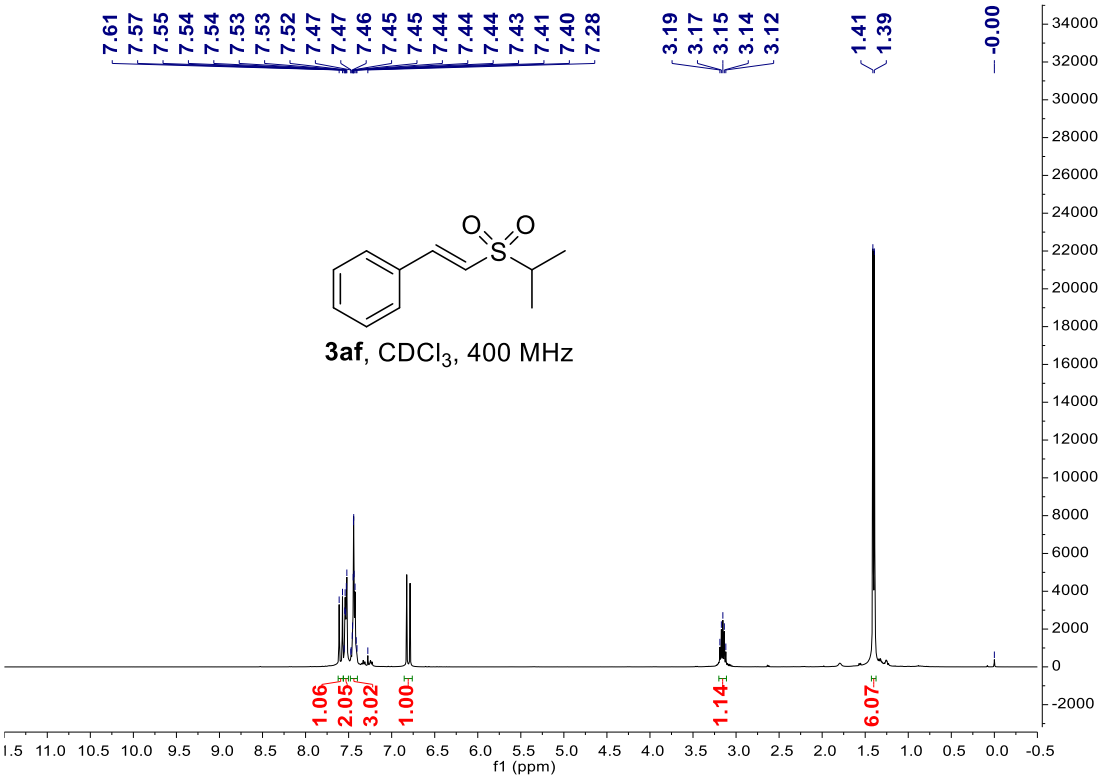


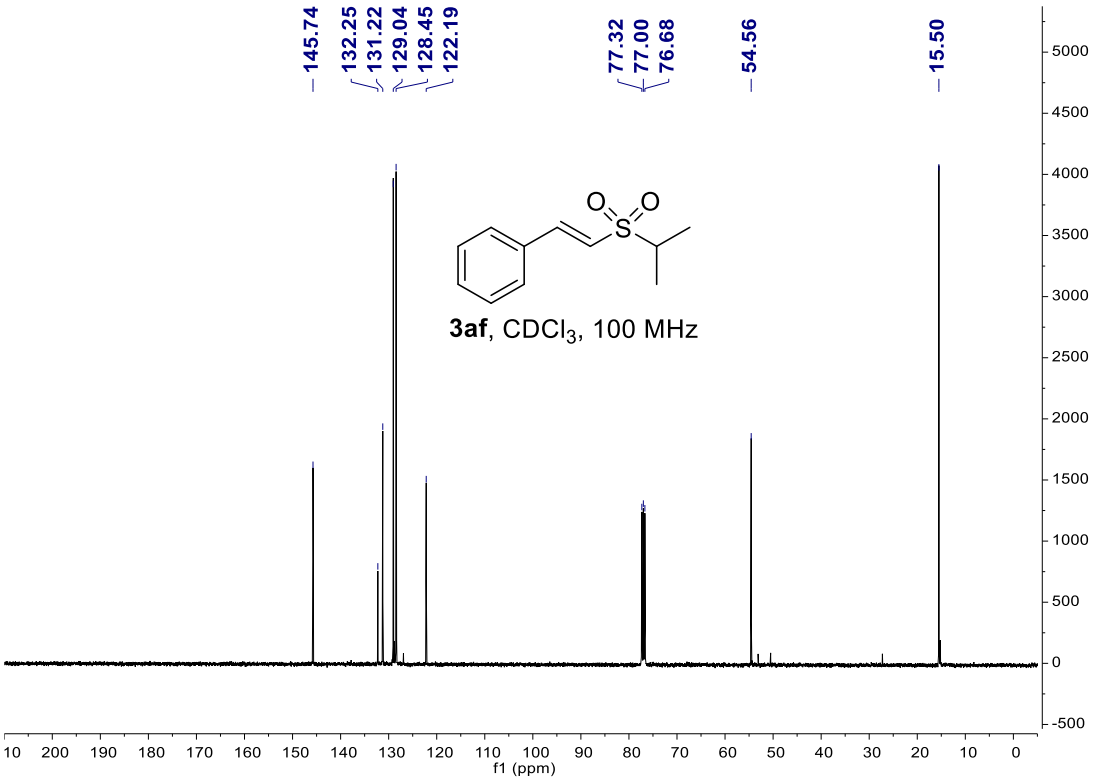
(*E*)-(2-(isobutylsulfonyl)vinyl)benzene **(3ae)**



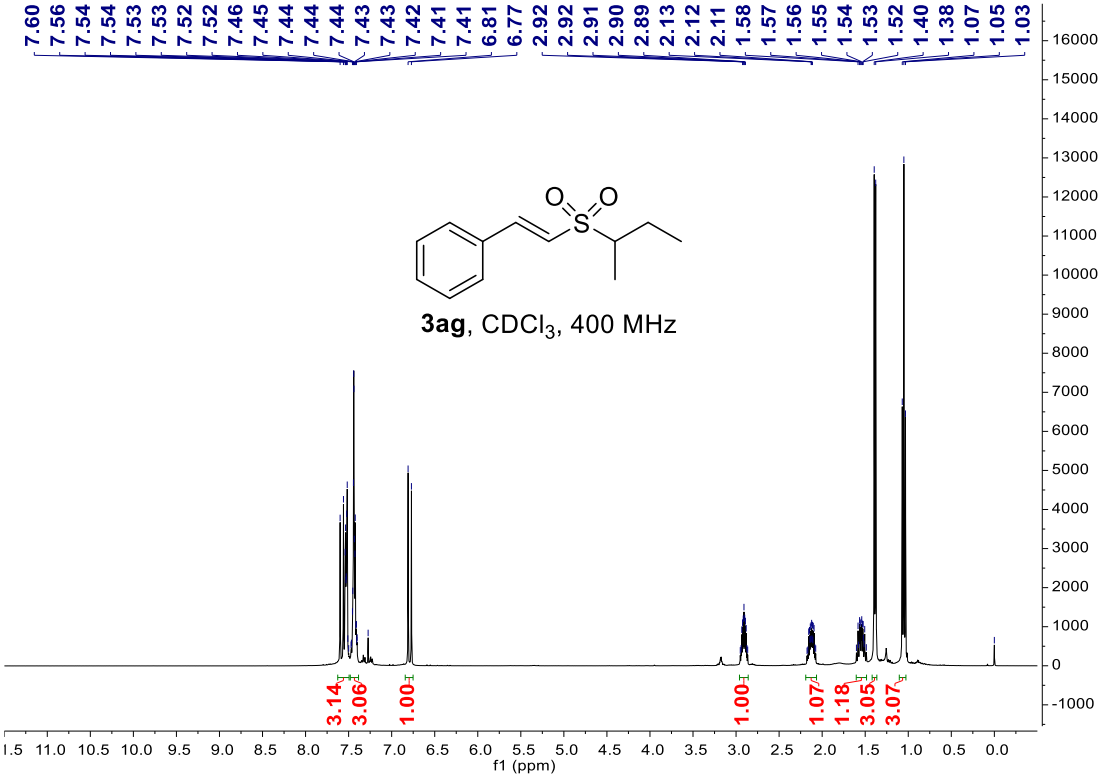


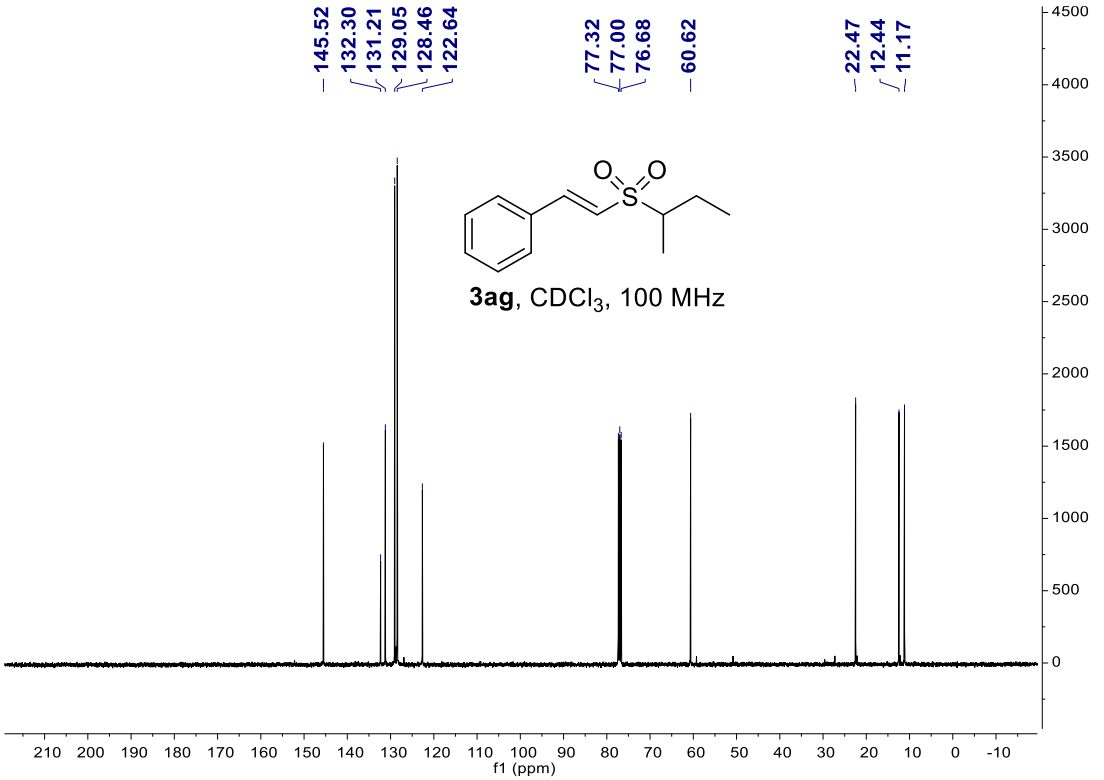
(*E*)-(2-(isopropylsulfonyl)vinyl)benzene **(3af)**



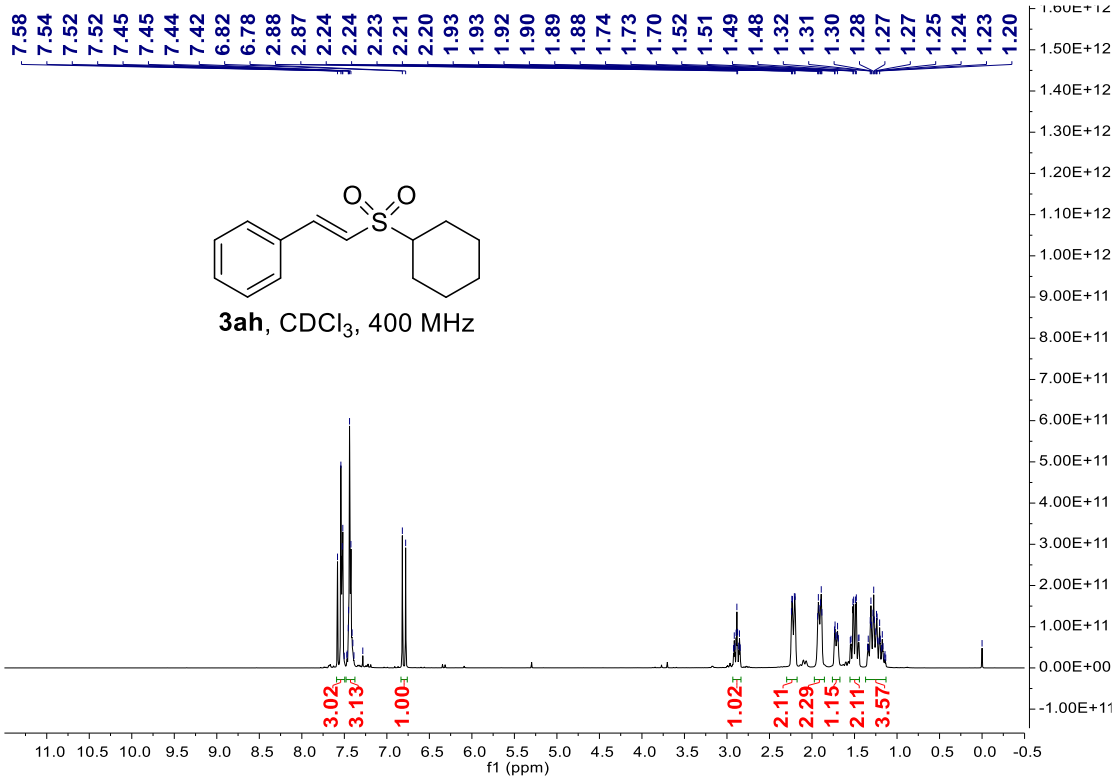


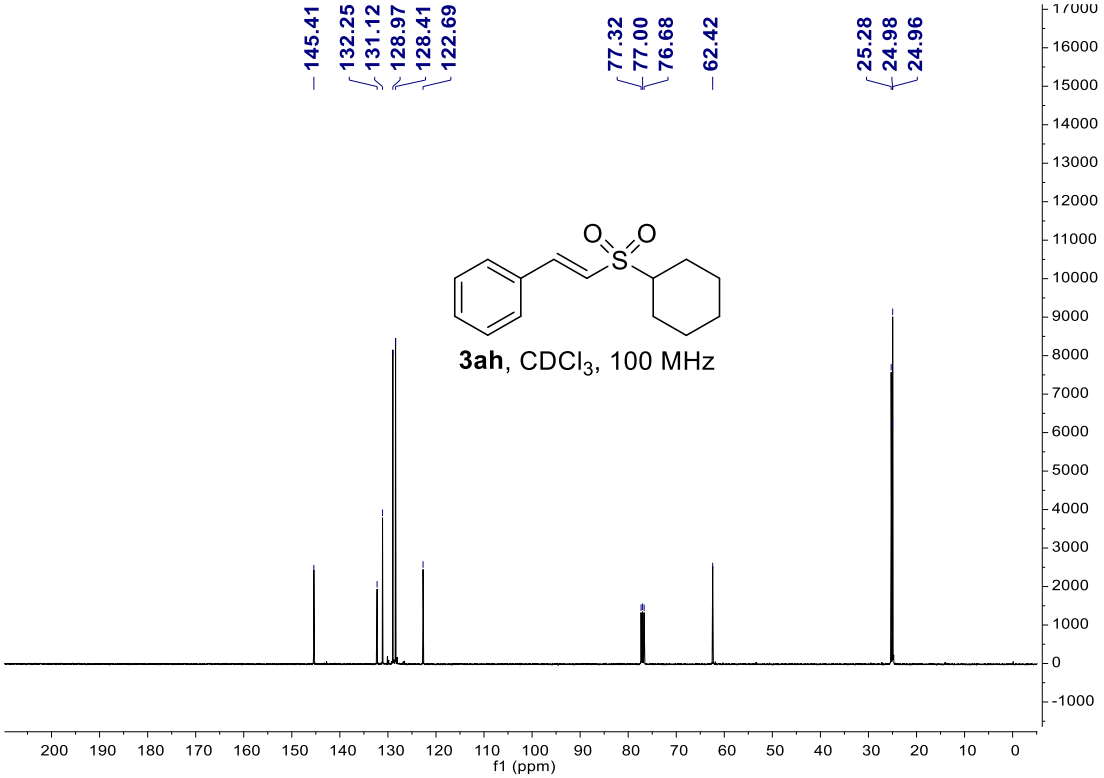
(*E*)-(2-(*sec*-butylsulfonyl)vinyl)benzene **(3ag)**



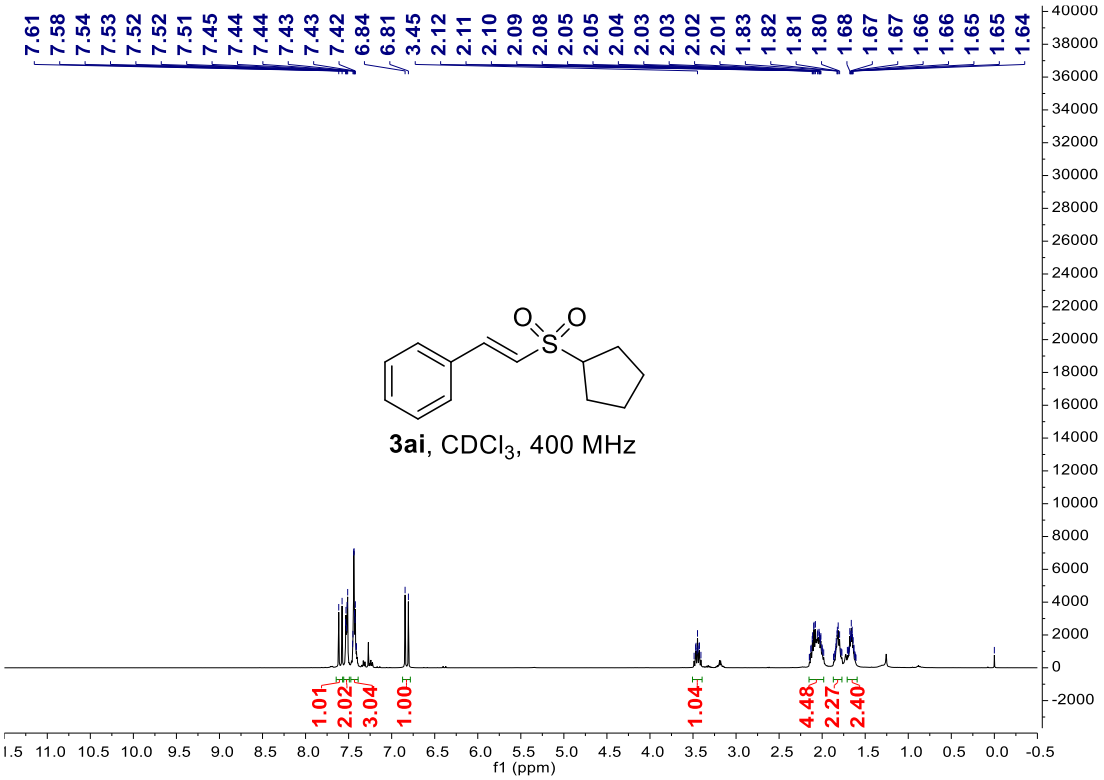


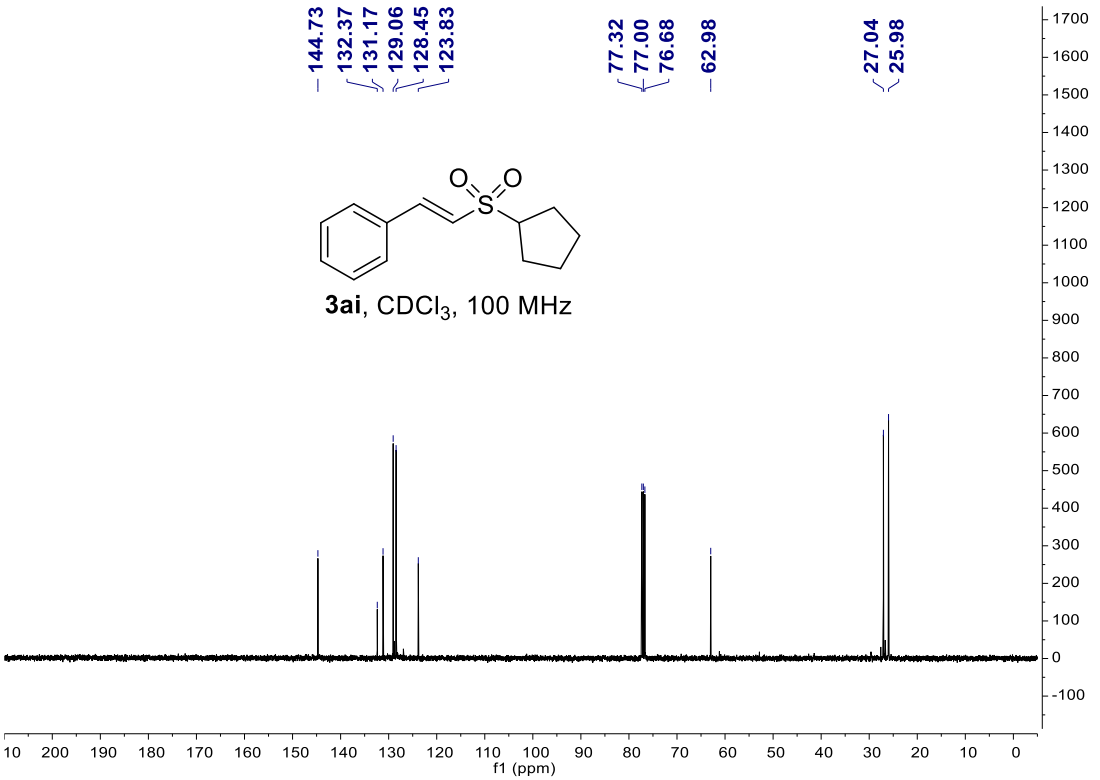
(*E*)-(2-(cyclohexylsulfonyl)vinyl)benzene **(3ah)**



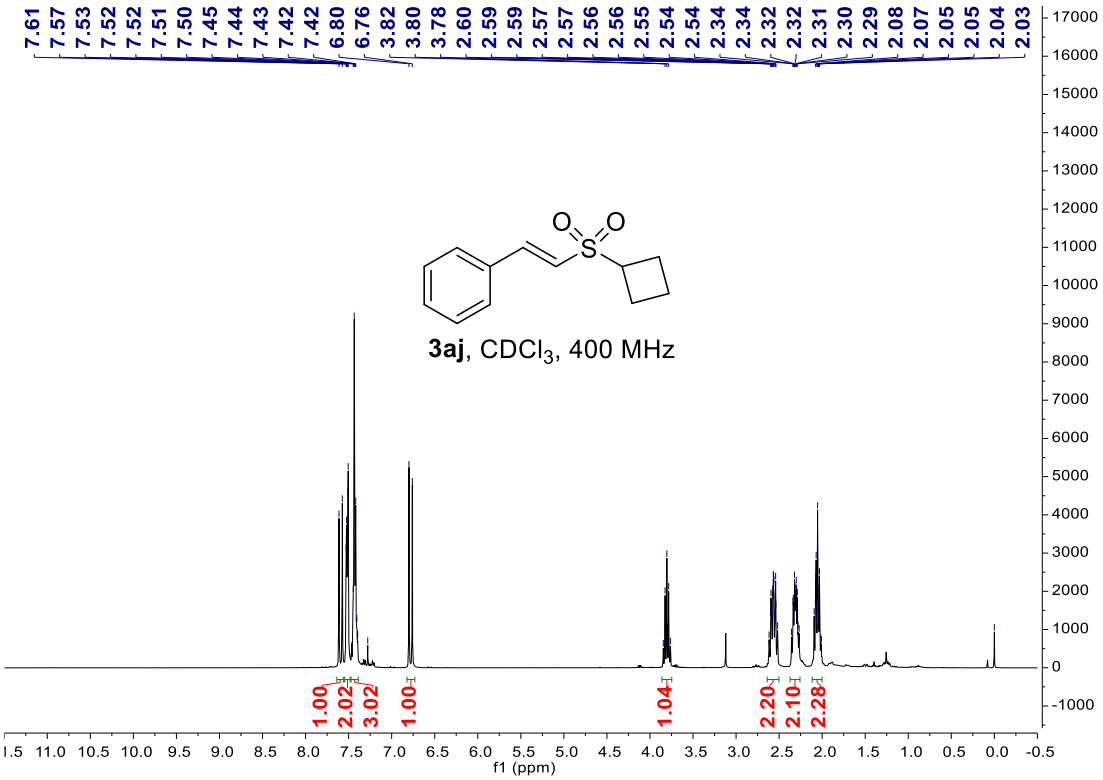


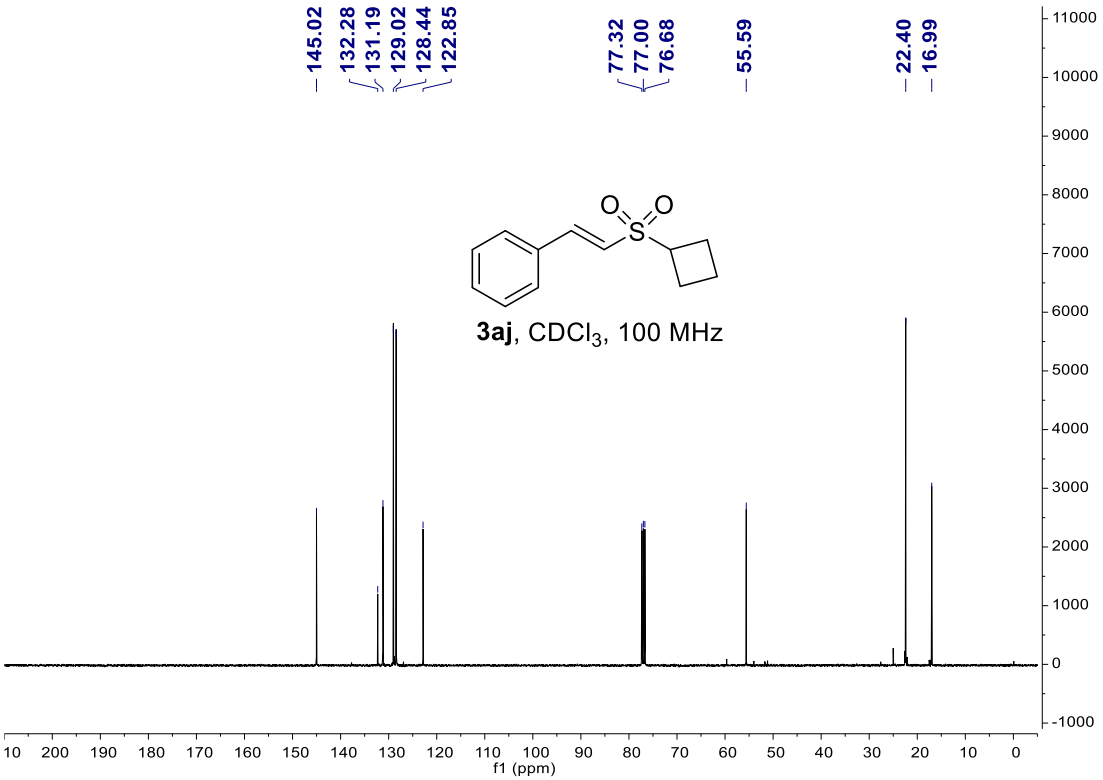
(*E*)-(2-(cyclopentylsulfonyl)vinyl)benzene **(3ai)**



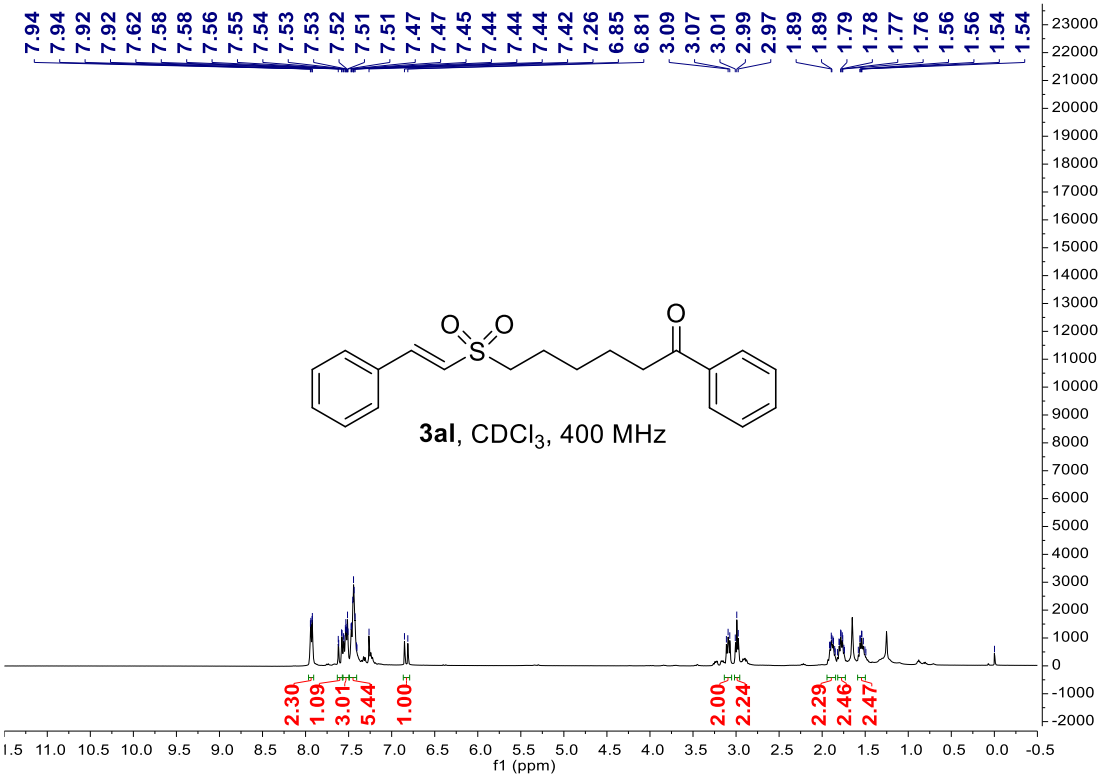


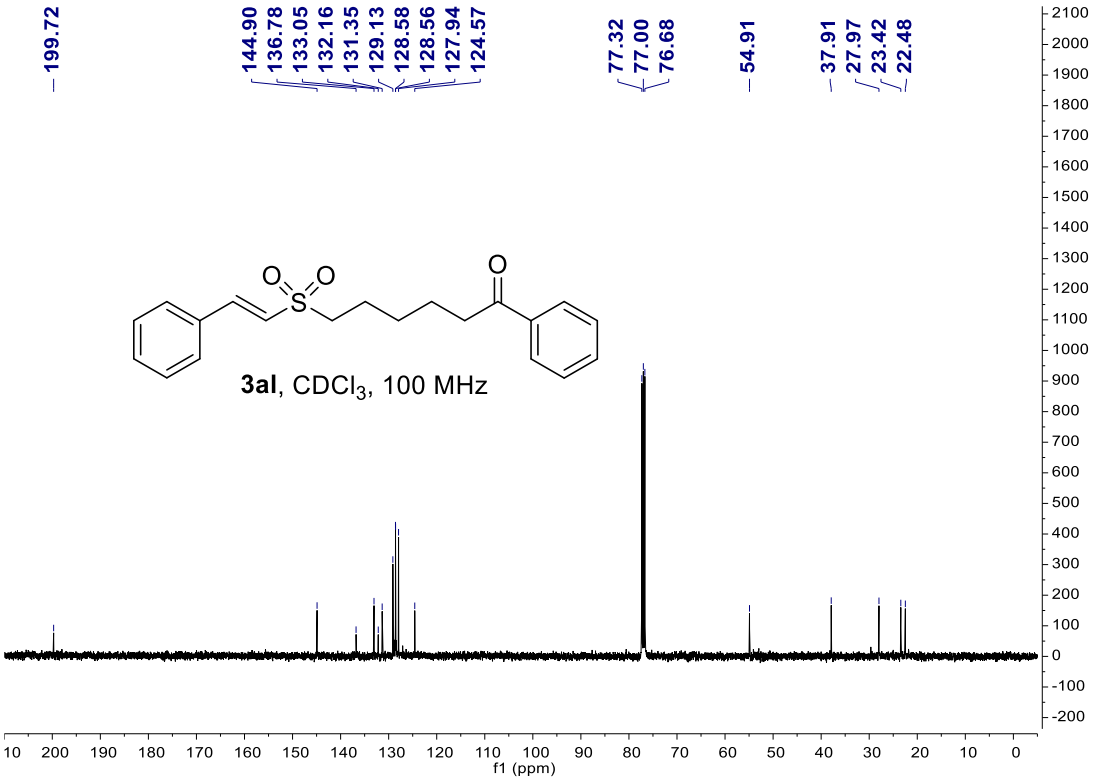
(*E*)-(2-(cyclobutylsulfonyl)vinyl)benzene **(3aj)**



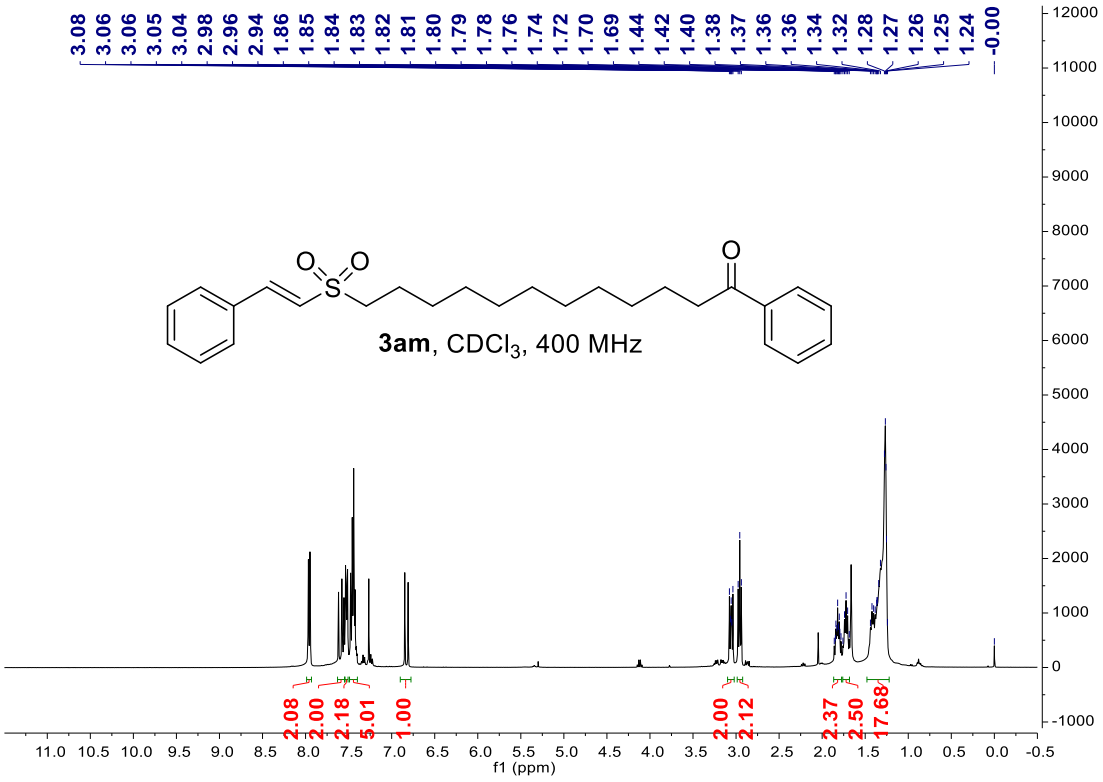


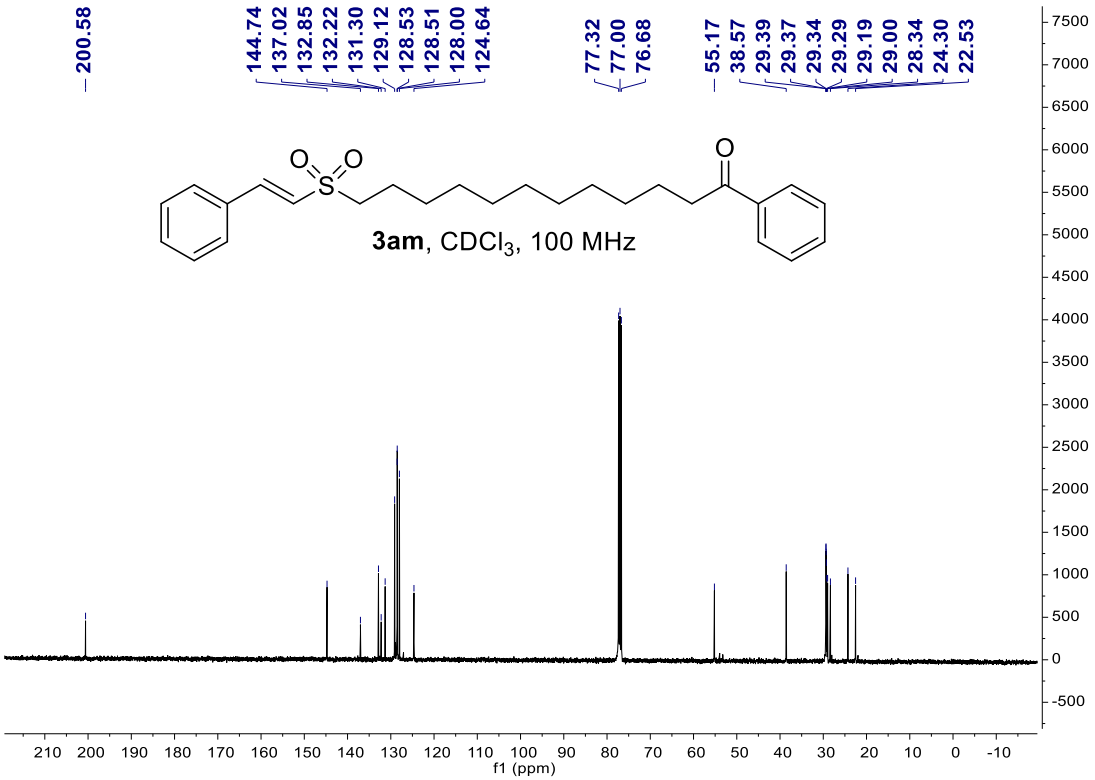
(*E*)-1-phenyl-6-(styrylsulfonyl)hexan-1-one **(3al)**



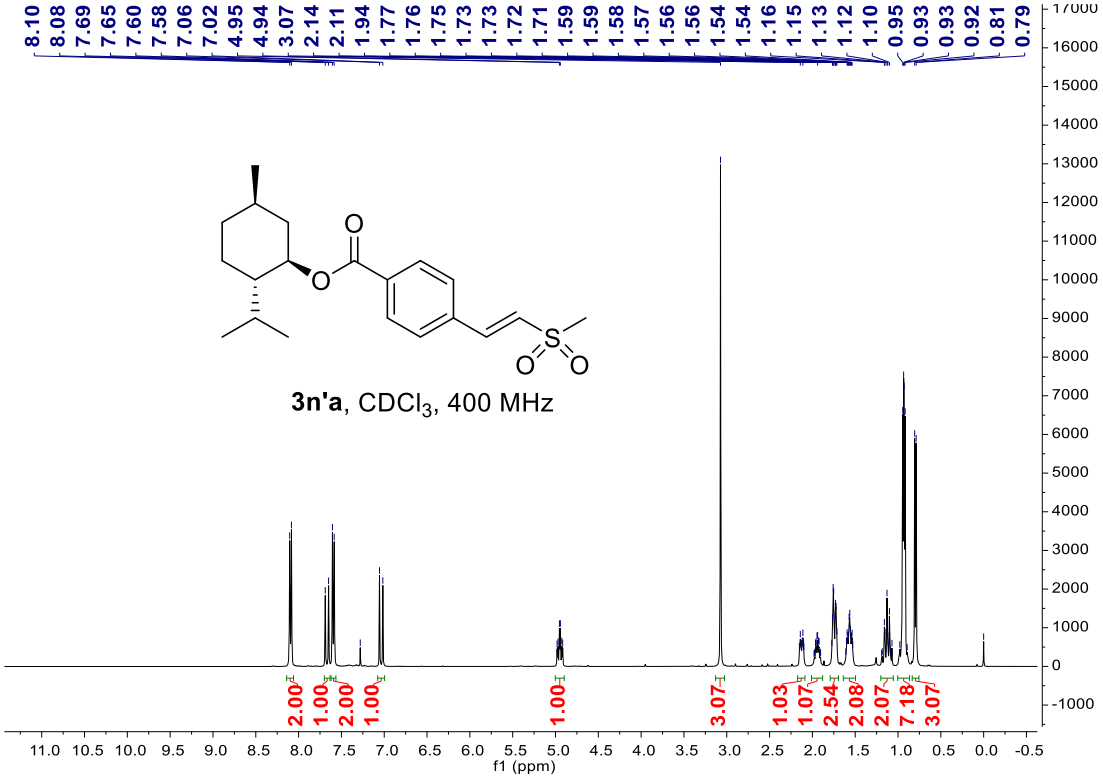


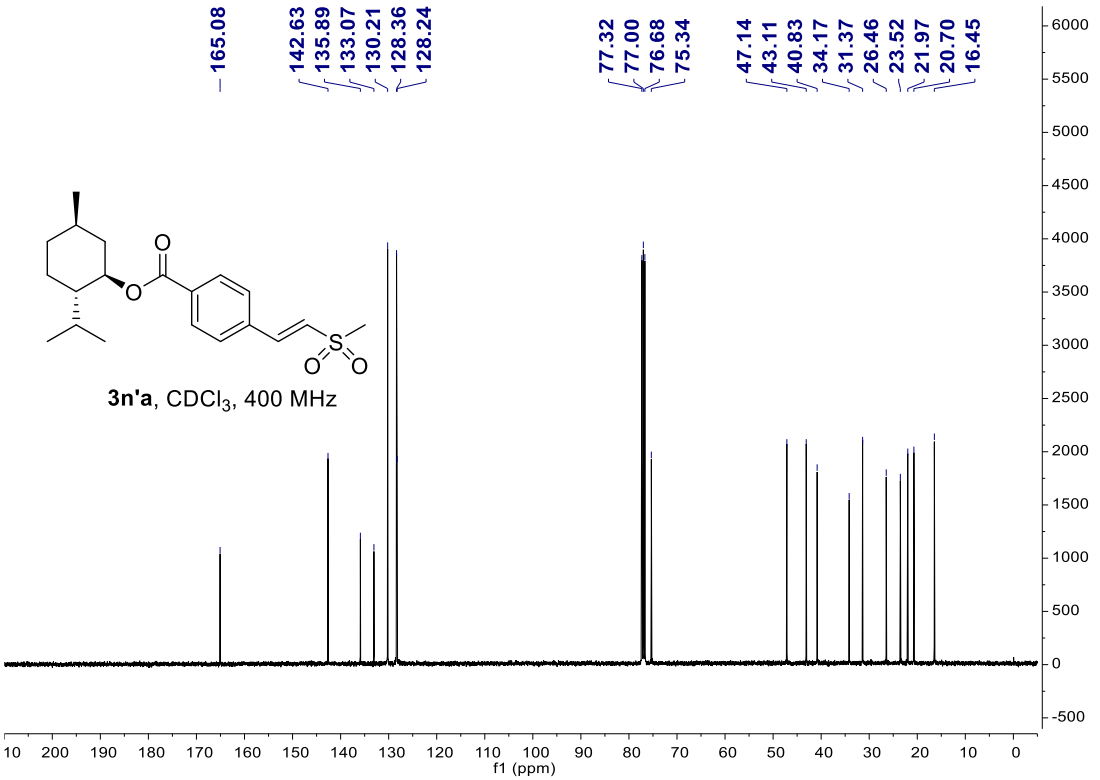
(*E*)-1-phenyl-12-(styrylsulfonyl)dodecan-1-one **(3am)**



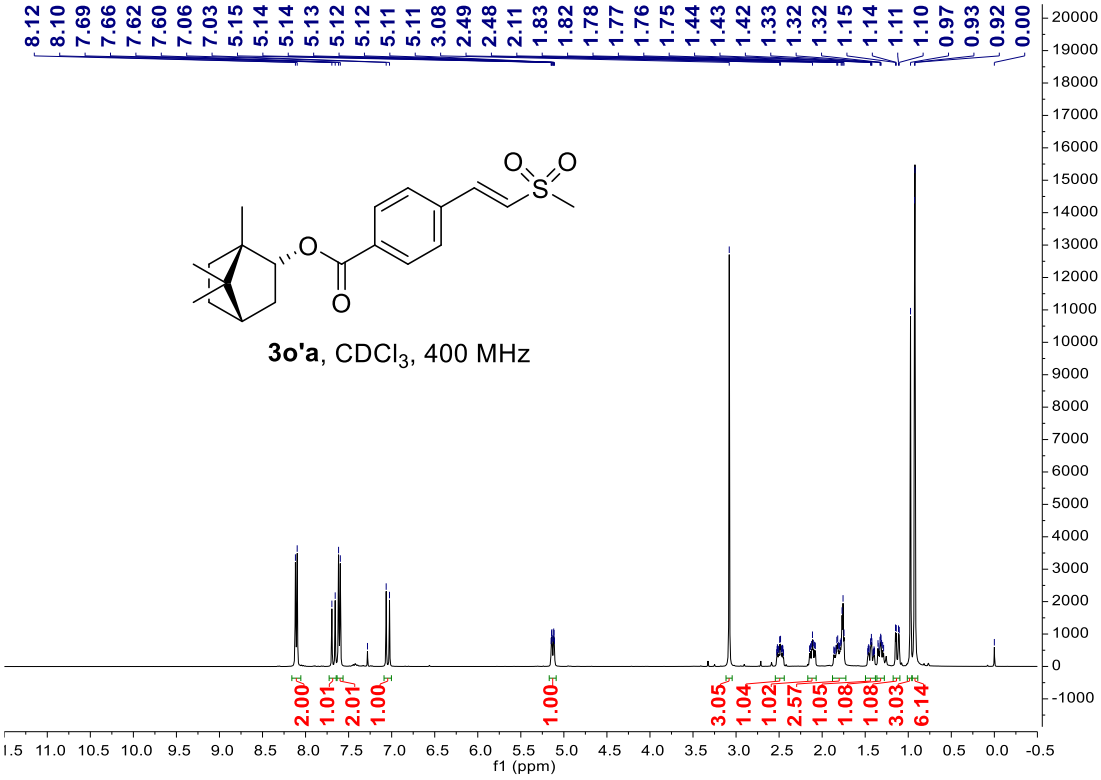


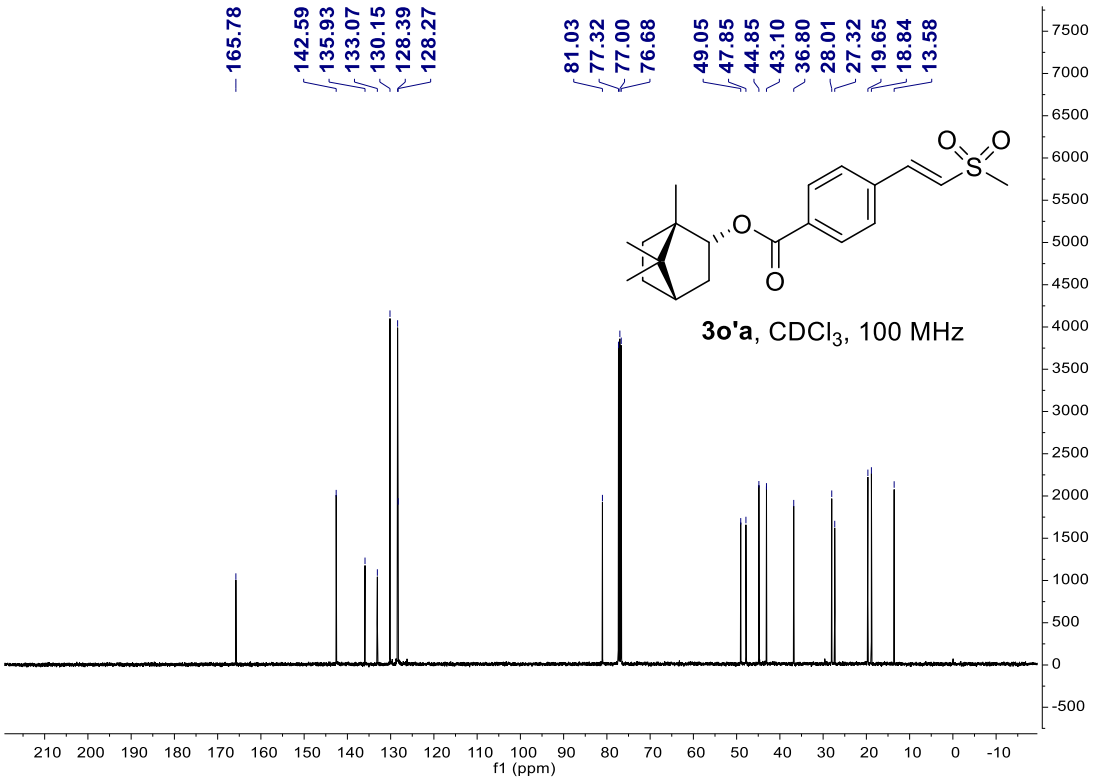
(1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl 4-((*E*)-2-(methylsulfonyl)vinyl)benzoate **(3n'a)**



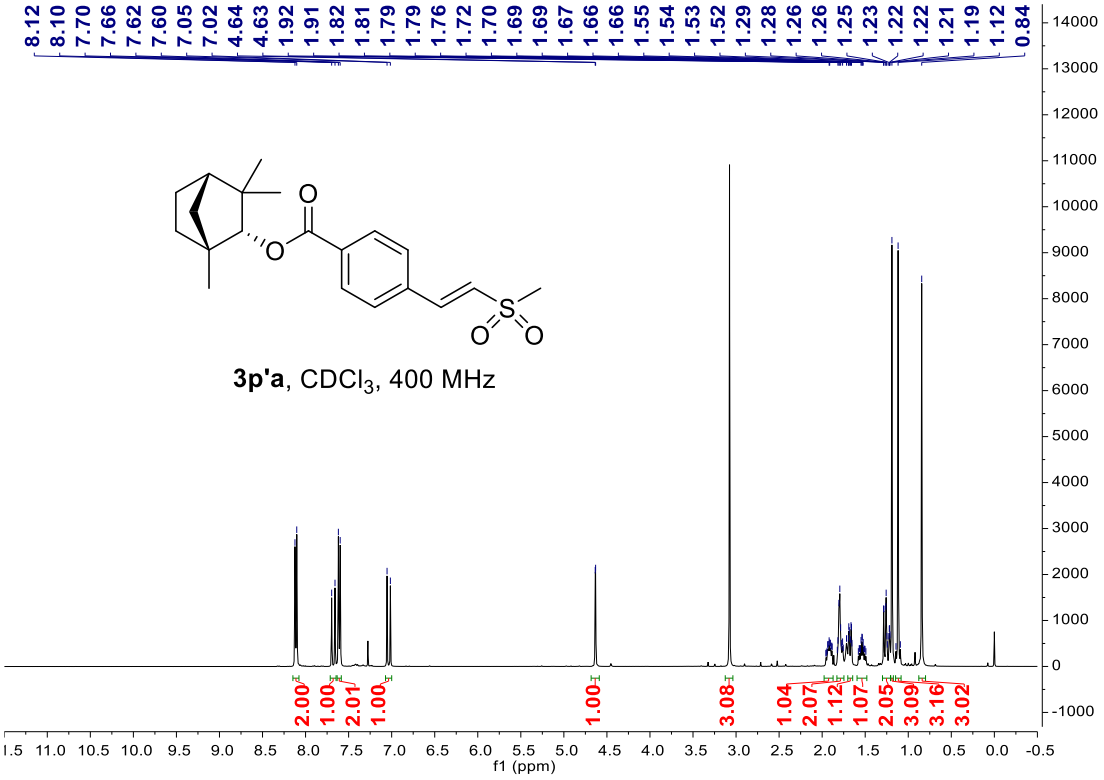


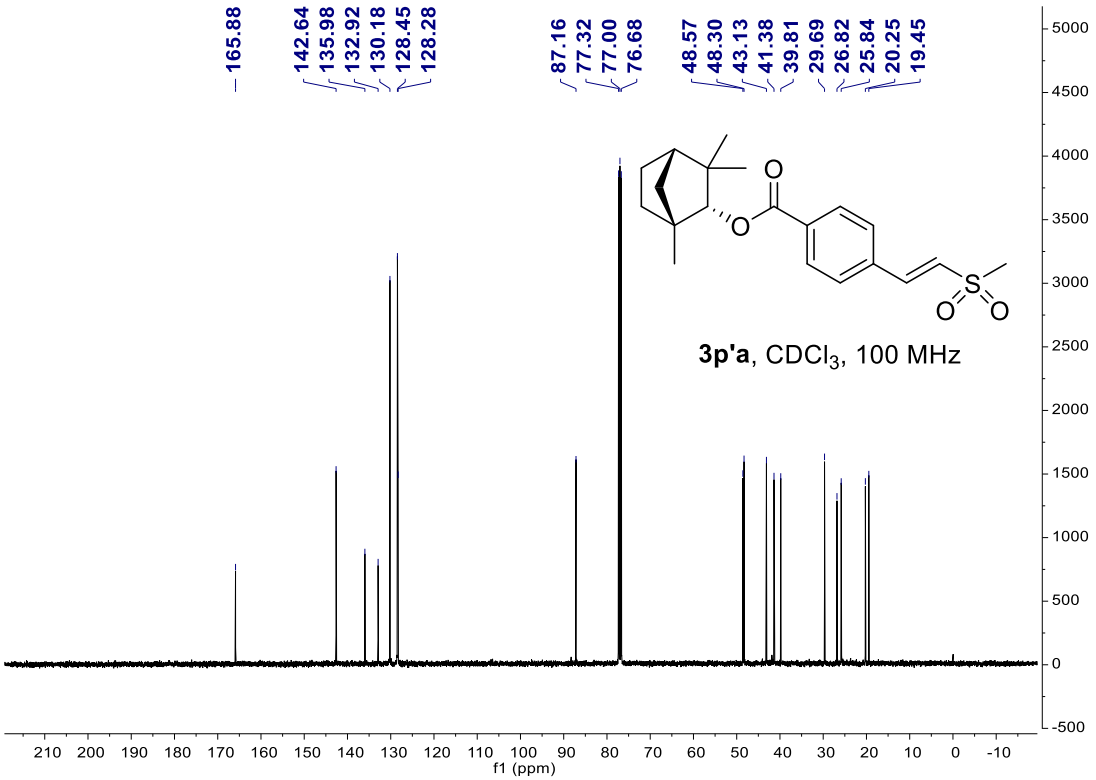
(1*S*,2*R*,4*S*)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl 4-((*E*)-2-(methylsulfonyl)vinyl) benzoate **(3o'a)**



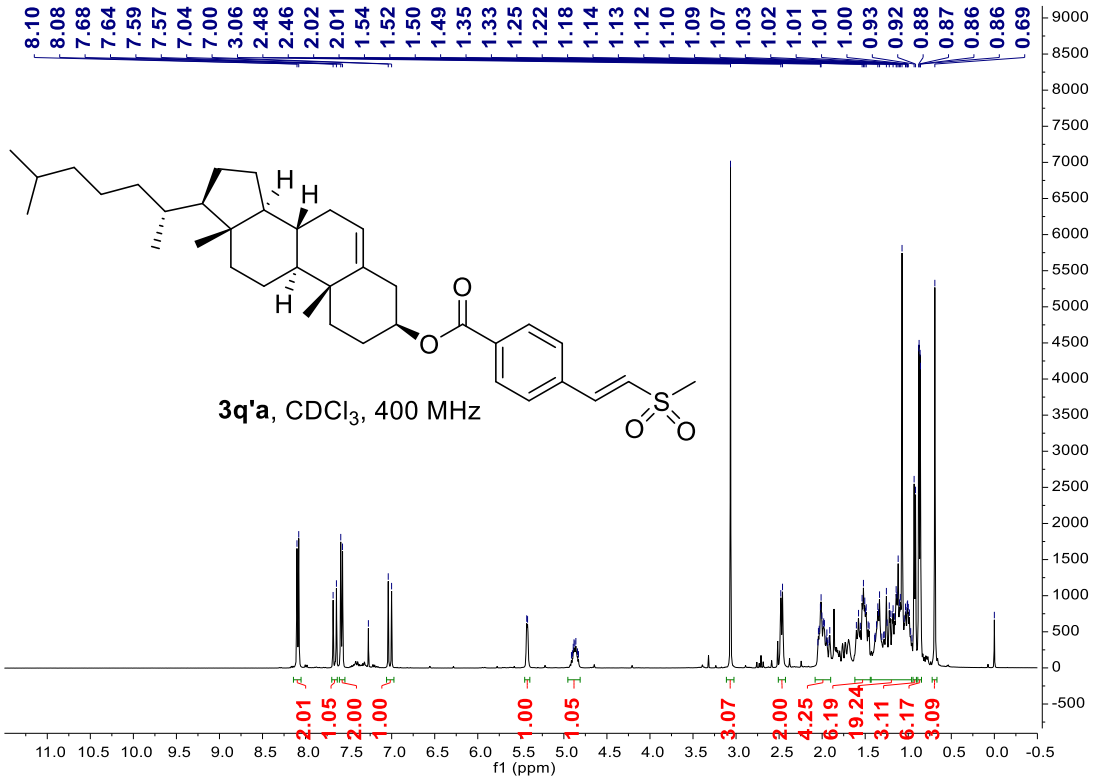


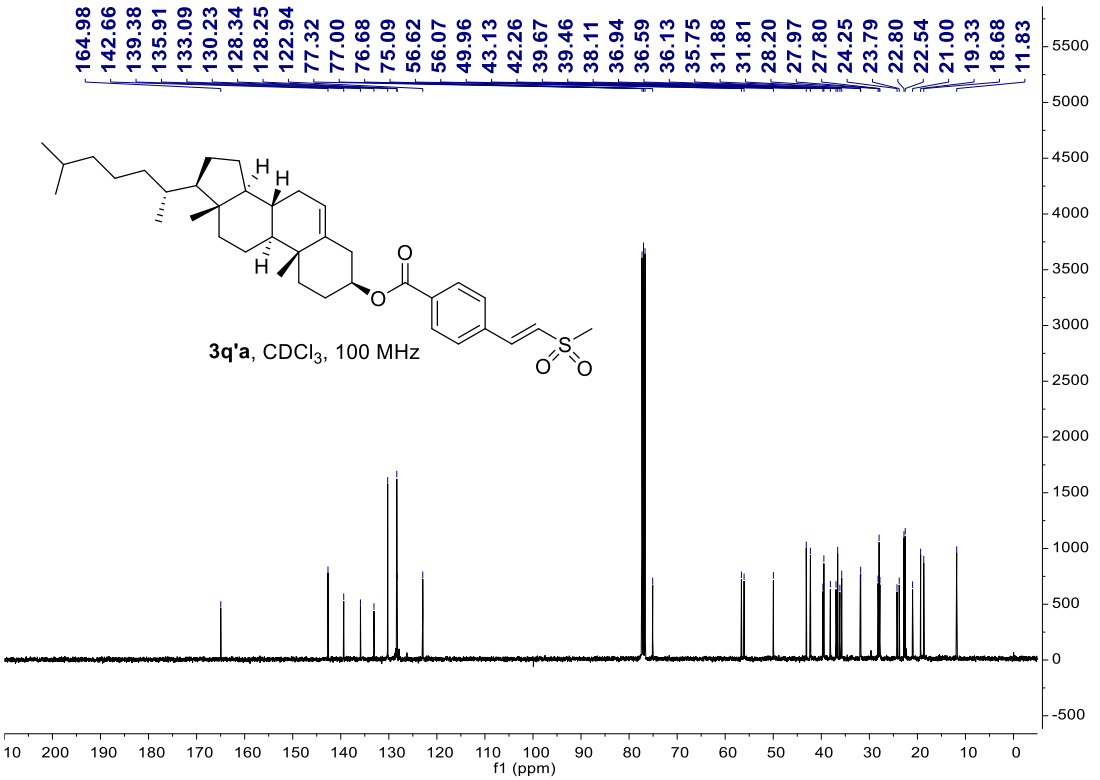
(1*R*,2*R*,4*S*)-1,3,3-trimethylbicyclo[2.2.1]heptan-2-yl 4-((*E*)-2-(methylsulfonyl)vinyl) benzoate **(3p'a)**



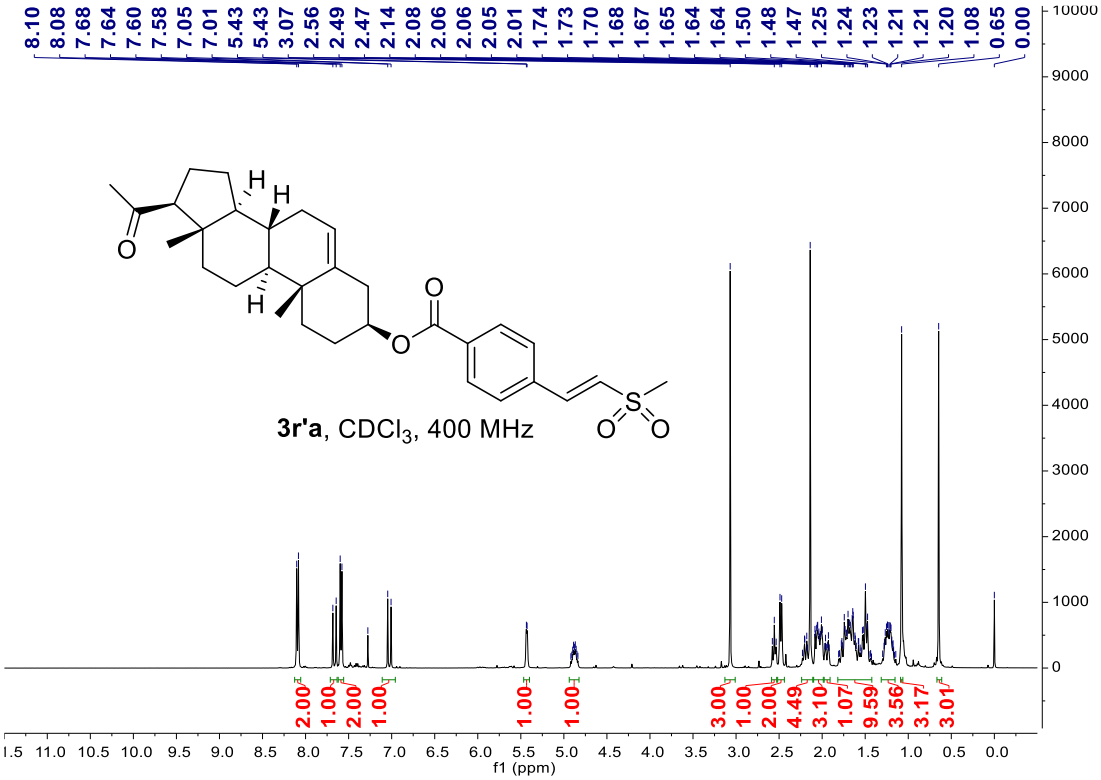


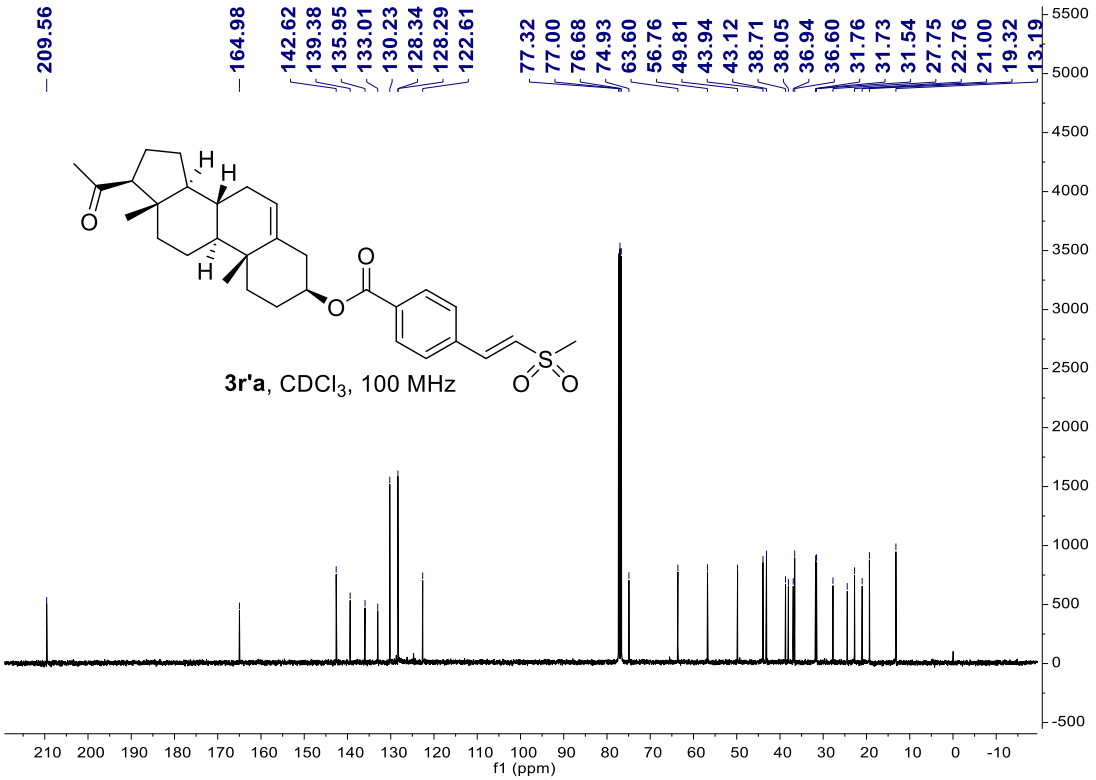
(3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl 4-((*E*)-2-(methylsulfonyl)vinyl)benzoate **(3q'a)**



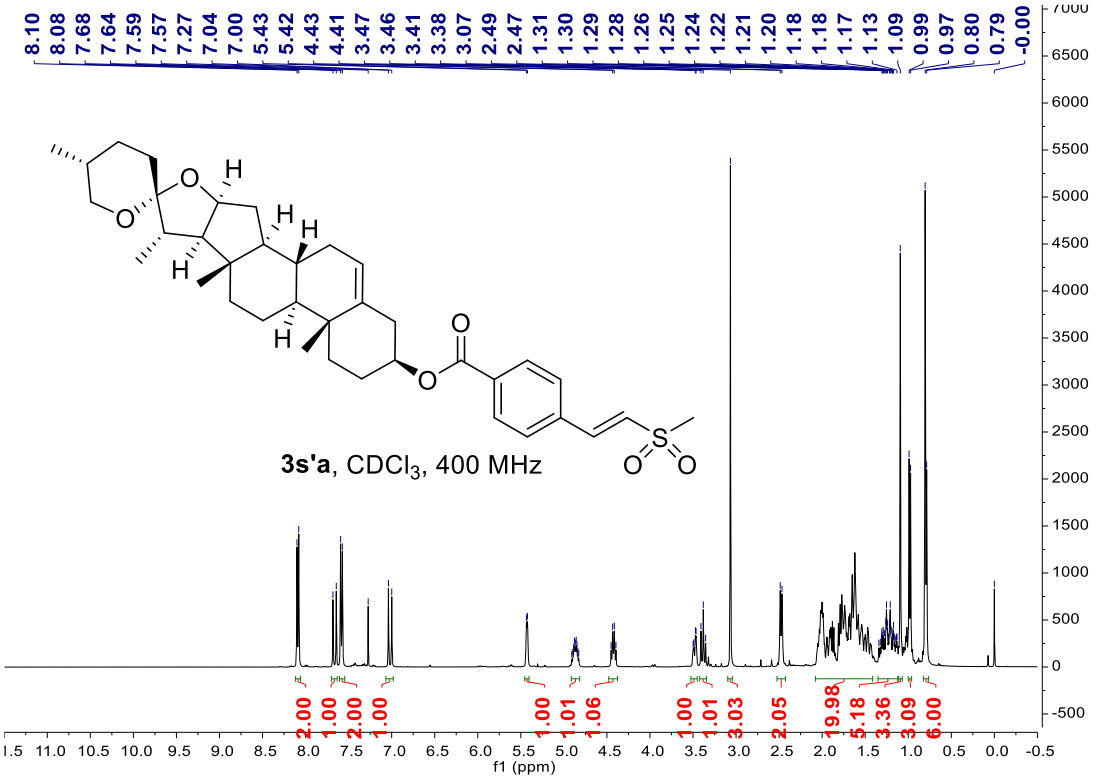


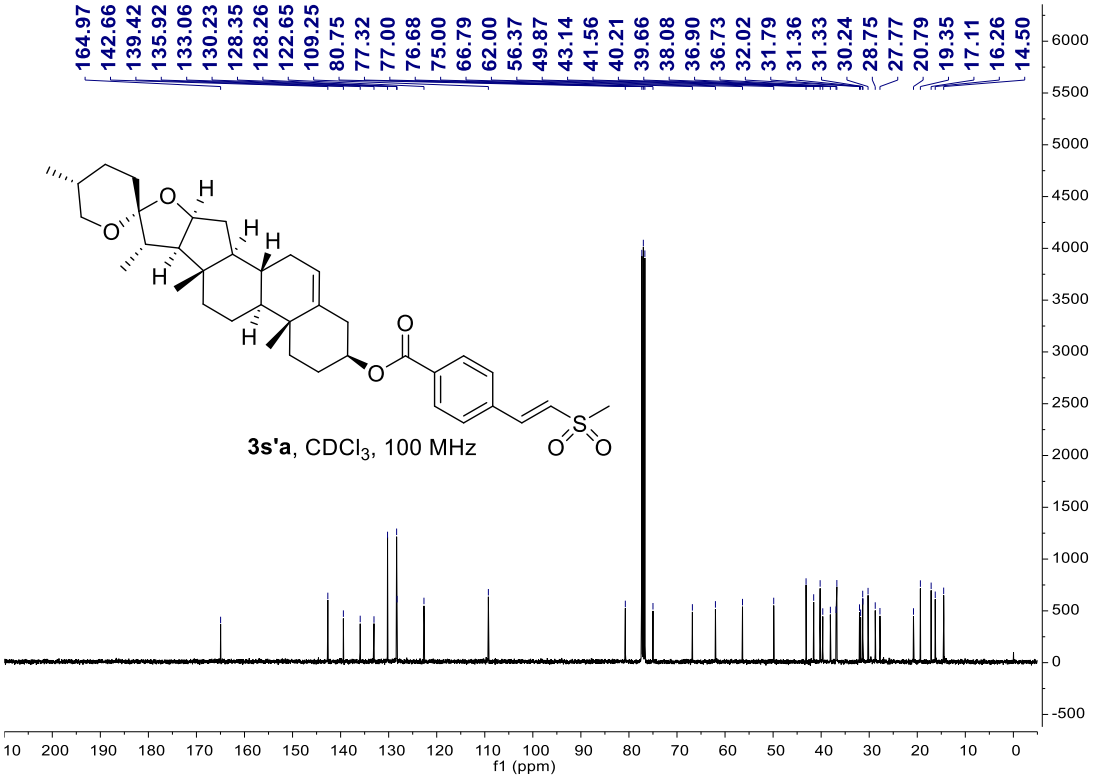
(3*S*,8*S*,9*S*,10*R*,13*S*,14*S*,17*S*)-17-acetyl-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[a]phenanthren-3-yl 4-((*E*)-2-(methylsulfonyl)vinyl)benzoate **(3r'a)**



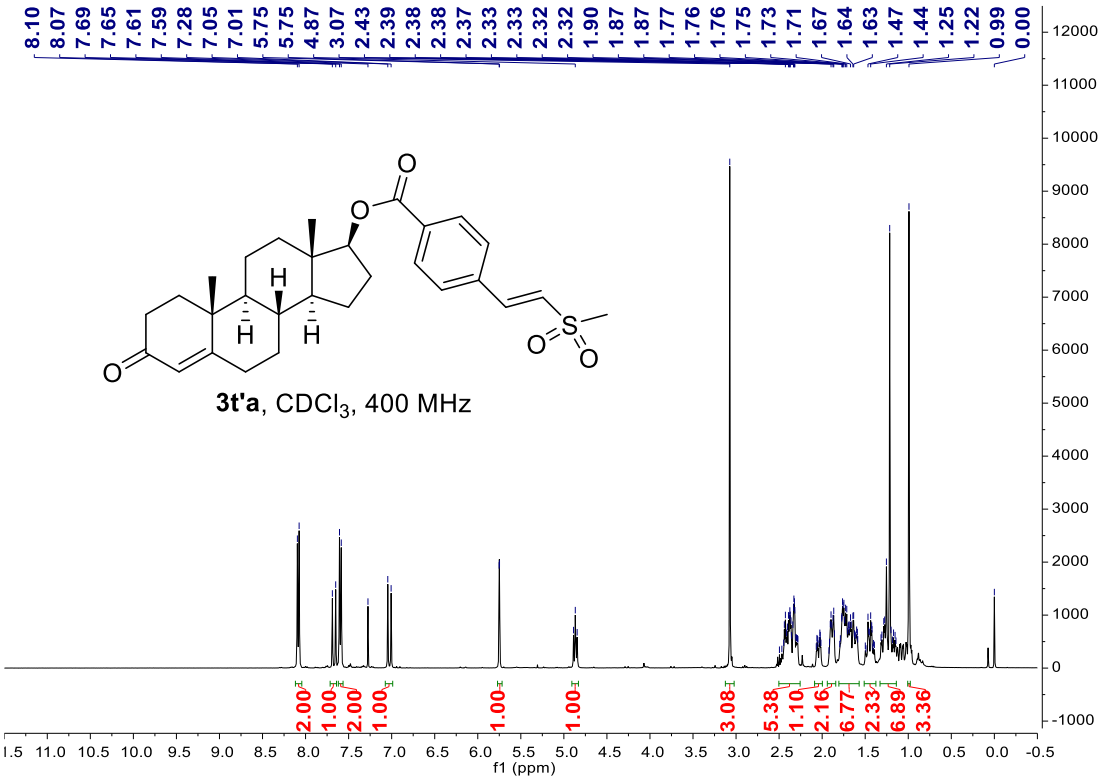


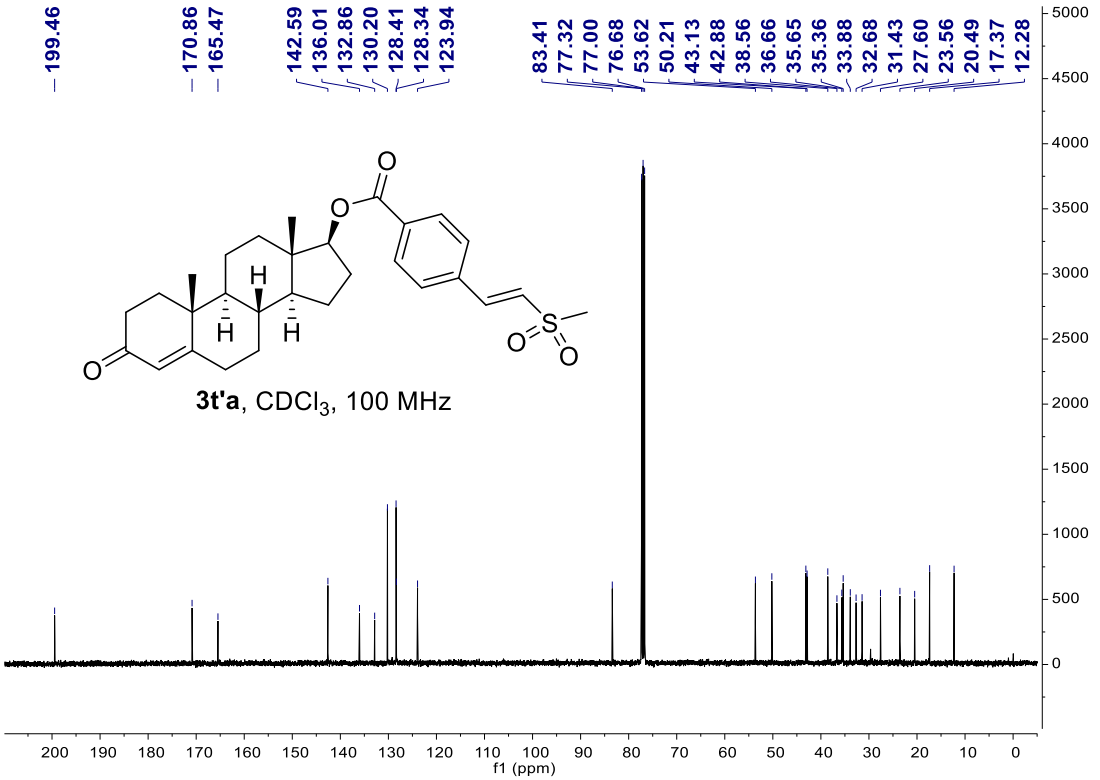
(4*S*,5'*R*,6a*R*,6b*S*,8a*S*,8b*R*,9*S*,10*R*,11a*S*,12a*S*,12b*S*)-5',6a,8a,9-tetramethyl-1,3,3',4,4',5,5',6,6a,6b,6',7,8,8a,8b,9,11a,12,12a,12b-icosahydrospiro[naphtho[2',1':4,5]indeno[2,1-*b*]furan-10,2'-pyran]-4-yl 4-((*E*)-2-(methylsulfonyl)vinyl)benzoate **(3s'a)**



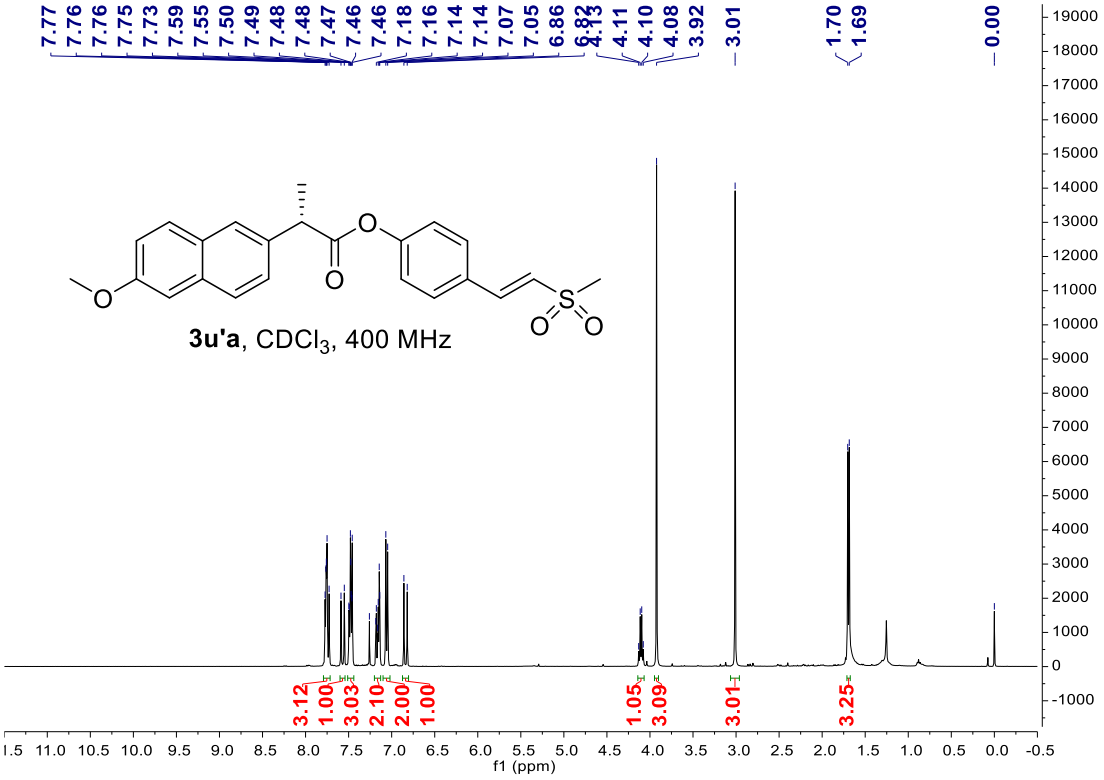


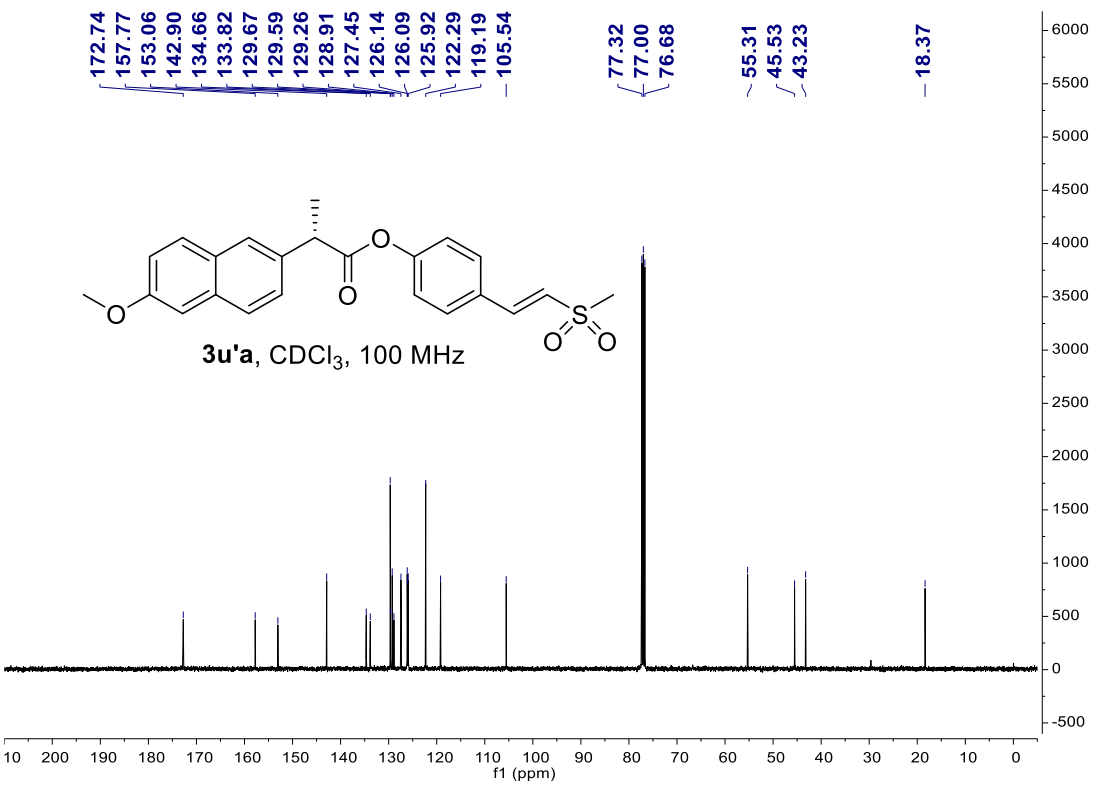
(8*R*,9*S*,10*R*,13*S*,14*S*,17*S)*-10,13-dimethyl-3-oxo-2,3,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[a]phenanthren-17-yl 4-((*E*)-2-(methylsulfonyl)vinyl) benzoate **(3t'a)**



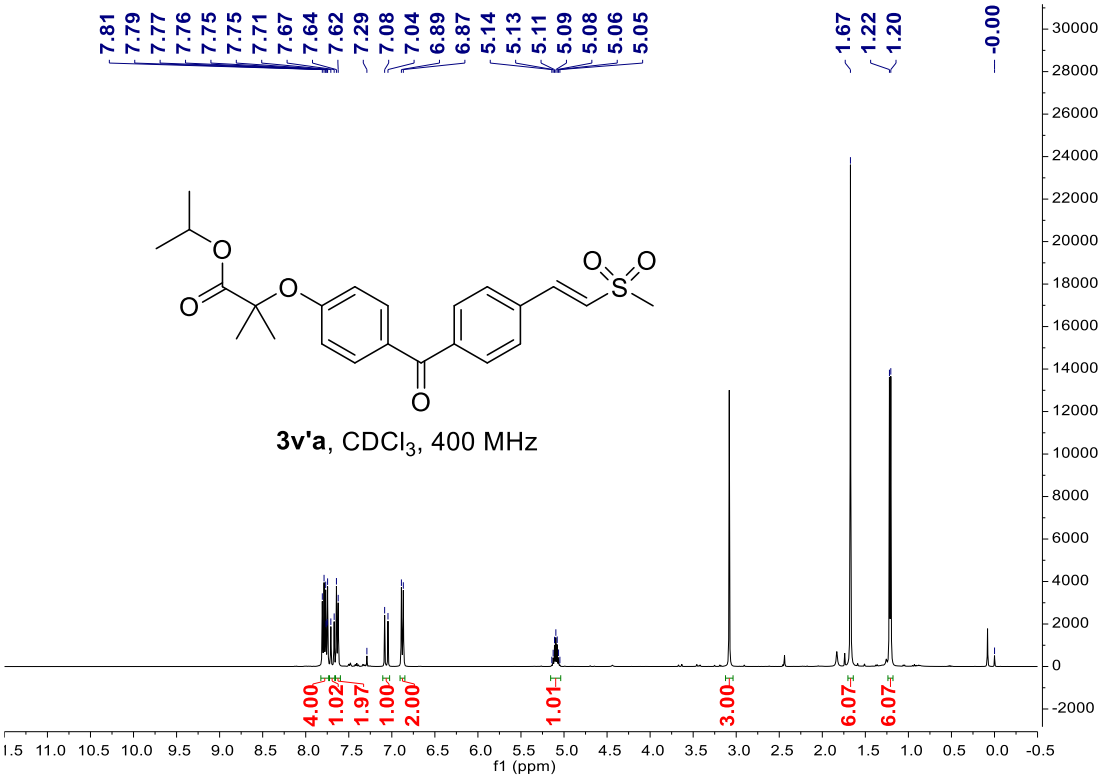


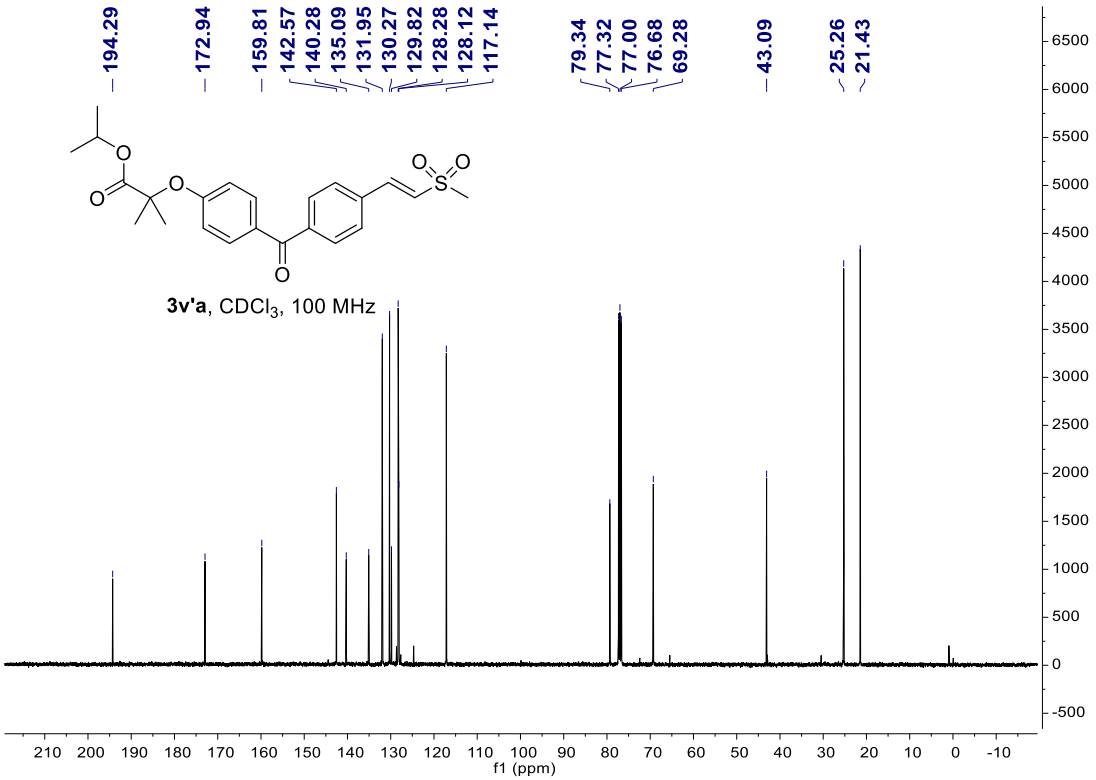
(*E*)-4-(2-(methylsulfonyl)vinyl)phenyl (*S*)-2-(6-methoxynaphthalen-2-yl)propanoate **(3u'a)**



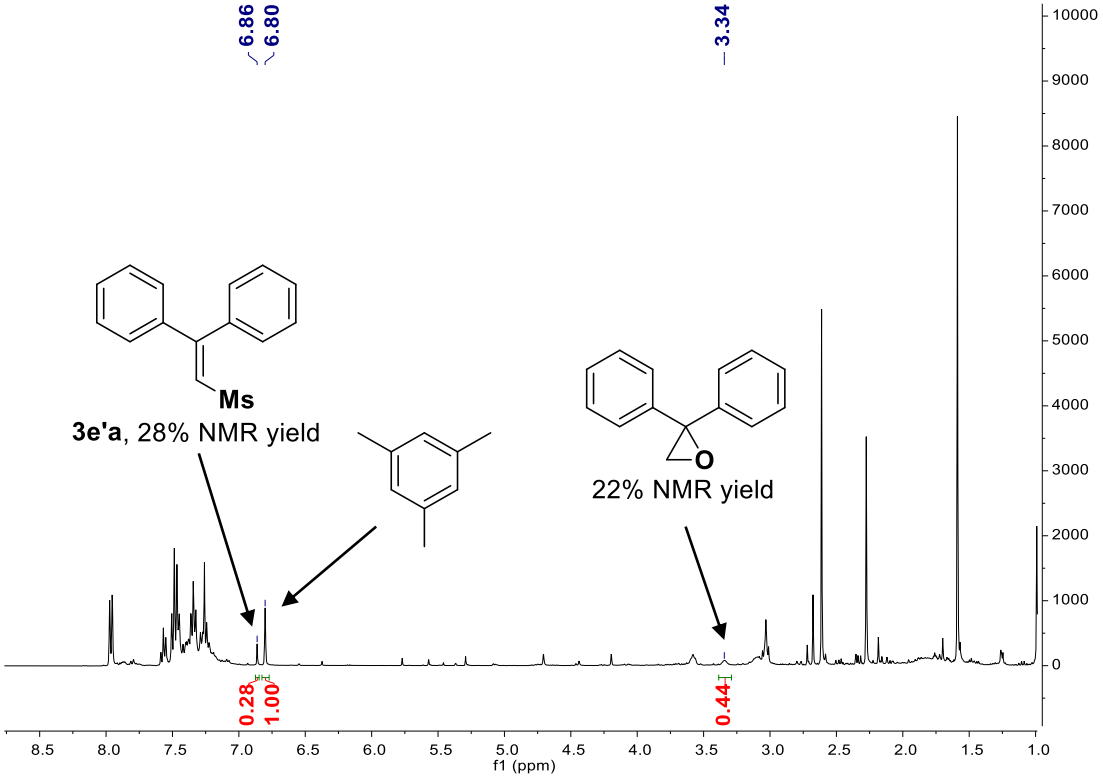


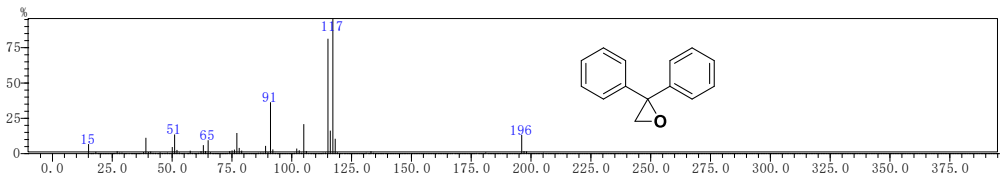
isopropyl (*E*)-2-methyl-2-(4-(4-(2-(methylsulfonyl)vinyl)benzoyl)phenoxy)propanoate **(3v'a)**



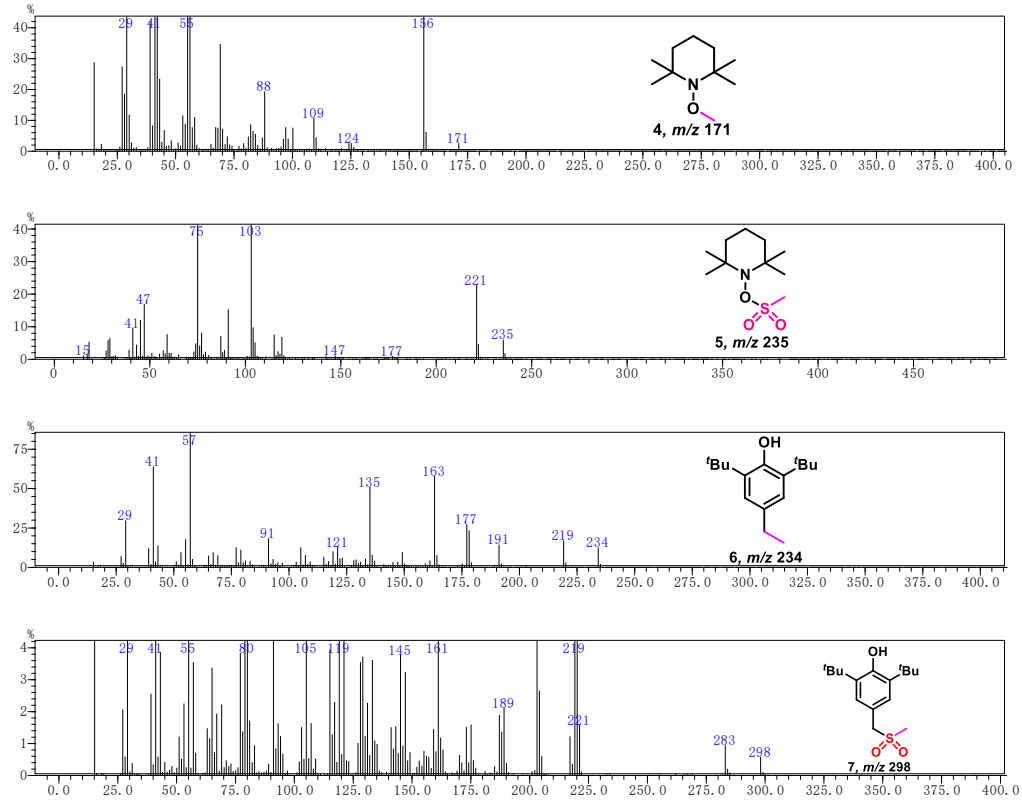


The NMR spectra of the reaction system of **1e'**, **2a** and DABCO·$(SO_2)_2$





The GC-MS spectra of the adducts **4**, **5**, **6** and **7**



The GC-MS spectra of PhCOMe