Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

$Cu(OTf)_2$-Mediated $C(sp^2)$−H Arylsulfonylation of Enamides *via* the Insertion of Sulfur Dioxide

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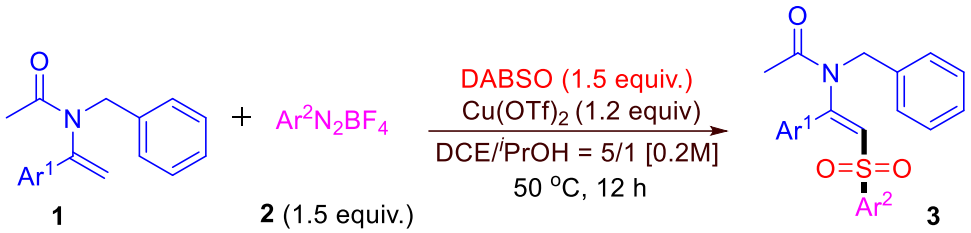
Supporting Information

Table of Contents

General information.

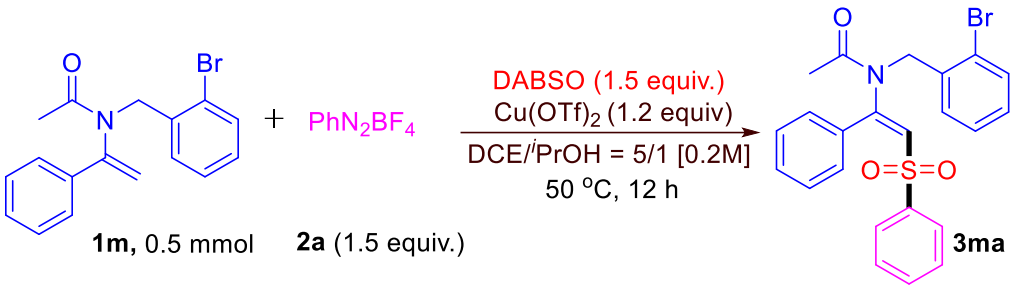
All reactions were carried out in oven dried Schlenk tubes under nitrogen atmosphere. All of Enamides were prepared as reported in the reference.[1] DABSO was prepared according to the reported method.[2] And diazonium salts were freshly prepared according to the literature.[3] $Cu(OTf)_2$ and dry 1,2-dichloroethane(DCE) were purchased from Energy Chemical. Isopropanol was purchased from Greagent. All reactions were using undistilled solvent, without the need of precautions to exclude air and moisture. All the temperatures are referred to the bath temperature. Melting points were recorded on an Electrothermal digital melting point apparatus. ^{1}H, ^{19}F, ^{13}C 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). 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 3



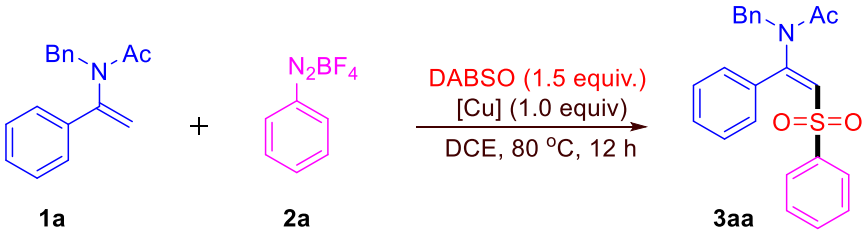
Enamides **1** (0.3 mmol), diazonium salts **2** (0.45 mmol, 1.5 equiv.), DABSO (0.45 mmol, 1.5 equiv.), and $Cu(OTf)_2$ (0.36 mmol, 1.2 equiv.) were added sequentially into Schlenk tube under nitrogen. Then mixed solvent (DCE/^{i}PrOH = 5/1, 1.5 mL) was added rapidly by syringe. The resulting mixture was allowed to stir at 50 ^{o}C in the oil bath for 12 hours as monitored by TLC. Upon completion, solvent was removed under vacuum and the residue was purified by flash silica gel column chromatography using petroleum ether/ethyl acetate as eluent to afford pure products **3**.

General procedures for the synthesis of (*E*)-vinyl sulfone derivatives 3ma



Enamide **1m** (0.5 mmol), diazonium salt **2a** (0.75 mmol, 1.5 equiv.), DABSO (0.75 mmol, 1.5 equiv.), and $Cu(OTf)_2$ (0.60 mmol, 1.2 equiv.) were added sequentially into Schlenk tube under nitrogen. Then mixed solvent (DCE/^{i}PrOH = 5/1, 2.5 mL) was added rapidly by syringe. The resulting mixture was allowed to stir at 50 °C in the oil bath for 12 hours as monitored by TLC. Upon completion, solvent was removed under vacuum and the residue was purified by flash silica gel column chromatography using petroleum ether/ethyl acetate as eluent to afford pure products **3ma**.

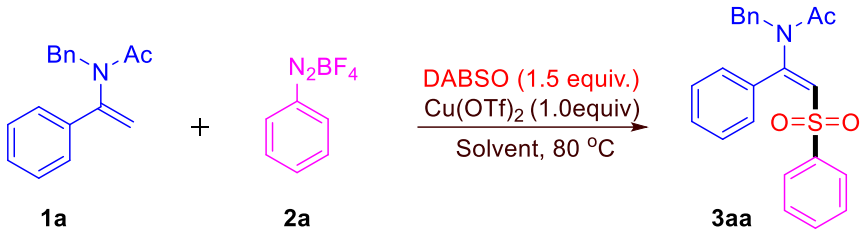
Table S1. Optimization of Cu(II)-sources[a]



Entry	[Cu]	NMR yield of **3aa**[b] (%)	Recovery of **1a**[b](%)
1	----	16	60
2	**$Cu(OTf)_2$**	**49**	**36**
3	$Cu(OAc)_2$	32	42
4	$Cu(acac)_2$	18	50
5	$CuBr_2$	16	51
6	$CuCl_2$	10	67
7	CuF_2	21	64
8	CuO	13	68

[a] Reaction conditions: enamide **1a** (0.2 mmol), diazonium salt **2a** (0.3 mmol, 1.5 equiv.), DABSO (0.3 mmol, 1.5 equiv.), and Cu(II)-sources (0.2 mmol, 1.0 equiv.) in DCE (1.0 mL) at 80 °C for 12 h under nitrogen. [b] Determined by NMR analysis of the crude reaction mixture by using mesitylene as an internal standard.

Table S2. Effect of solvents[a]

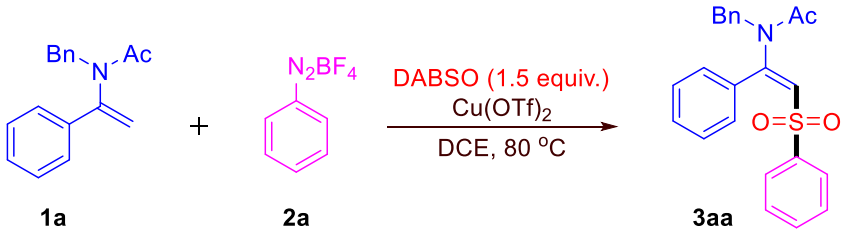


1a 2a 3aa

Entry	Solvent	NMR yield of **3aa**[b](%)	Recovery of **1a**[b](%)
1	**DCE**	**49**	**36**
2	MeCN	12	66
3	1,4-dioxane	46	46
4	Toluene	48	10
5	DMSO[c]	trace	62
6	DMF[d]	28	44
7	EtOH	36	0
8	MeOH	46	0
9	$CHCl_3$	15	46

[a] Reaction conditions: enamide **1a** (0.2 mmol), diazonium salt **2a** (0.3 mmol, 1.5 equiv.), DABSO (0.3 mmol, 1.5 equiv.), and $Cu(OTf)_2$ (0.2 mmol, 1.0 equiv.) in solvent (1.0 mL) at 80 °C for 12 h under nitrogen. [b] Determined by NMR analysis of the crude reaction mixture by using mesitylene as an internal standard. [c] DMSO = dimethyl sulfoxide. [d] DMF = N,N-dimethylformamide.

Table S3. Effect of the loading of Cu(II)-sources[a]

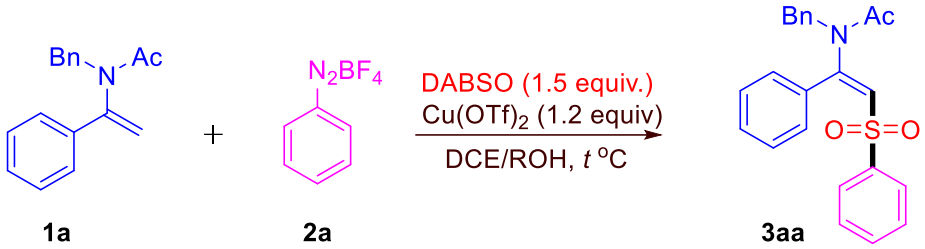


1a 2a 3aa

Entry	$Cu(OTf)_2$ (equiv)	NMR yield of **3aa**[b] (%)	Recovery of **1a**[b] (%)
1	0.5	41	37
2	1.0	49	36
3	**1.2**	**54**	**25**
4	1.5	35	23

[a] Reaction conditions: enamide **1a** (0.2 mmol), diazonium salt **2a** (0.3 mmol, 1.5 equiv.), DABSO (0.3 mmol, 1.5 equiv.), and $Cu(OTf)_2$ in DCE (1.0 mL) at 80 °C for 12 h under nitrogen. [b] Determined by NMR analysis of the crude reaction mixture by using mesitylene as an internal standard.

Table S4. Optimization of mixed solvents and temperature[a]



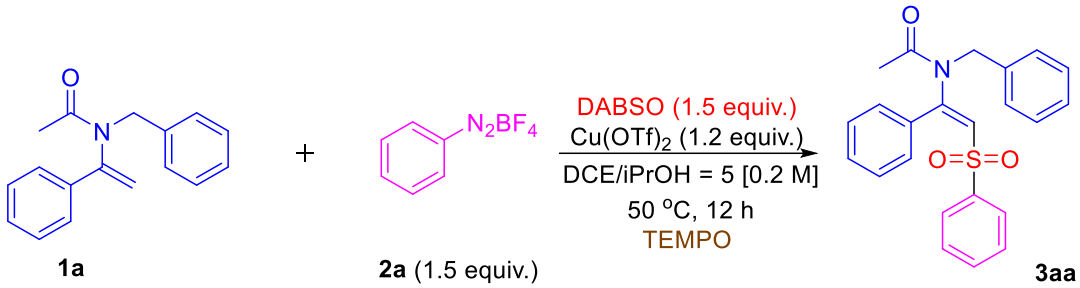
1a **2a** **3aa**

Entry	DCE/ROH	*t* (°C)	NMR yield of **3aa**[b] (%)	Recovery of **1a**[b] (%)
1	DCE/MeOH = 3/1	80	31	0
2	DCE/EtOH = 3/1	80	48	0
3	DCE/^{i}PrOH = 3/1	80	67	0
4	DCE/^{t}BuOH = 3/1	80	57	4
5	DCE/^{i}PrOH = 5/1	80	72	0
6	DCE/^{i}PrOH = 5/1	100	51	0
7	DCE/^{i}PrOH = 5/1	70	74	0
8	DCE/^{i}PrOH = 5/1	60	80	0
9	**DCE/^{i}PrOH = 5/1**	**50**	**90**	**0**
10	DCE/^{i}PrOH = 5/1	40	71	9

[a] Reaction conditions: enamide **1a** (0.2 mmol), diazonium salt **2a** (0.3 mmol, 1.5 equiv.), DABSO (0.3 mmol, 1.5 equiv.), and $Cu(OTf)_2$ (0.24 mmol, 1.2 equiv.) in a mixed solvent (1.0 mL) for 12 h under nitrogen. [b] Determined by NMR analysis of the crude reaction mixture by using mesitylene as an internal standard.

Mechanistic studies

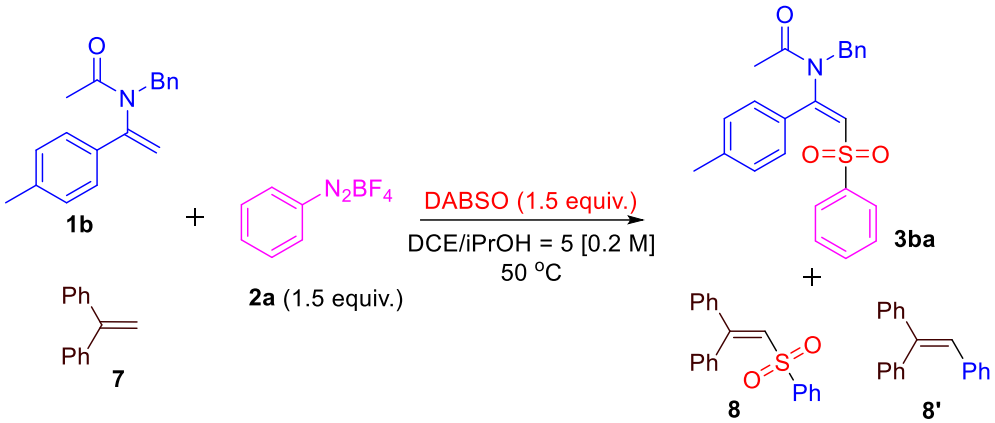
1) Trapping experiment with 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO) [a]



Entry	Additive (equiv.)	NMR yield of **3aa**[b] (%)
1	----	90
2	TEMPO (2.0)	45
3	TEMPO (3.0)	Trace

[a] Reaction conditions: enamide **1a** (0.2 mmol), diazonium salt **2a** (0.3 mmol, 1.5 equiv.), DABSO (0.3 mmol, 1.5 equiv.), $Cu(OTf)_2$ (0.24 mmol, 1.2 equiv.), and TEMPO in a mixed solvent (DCE/^{i}PrOH = 5/1, 1.0 mL) at 50 °C for 12 h under nitrogen. [b] Determined by NMR analysis of the crude reaction mixture by using mesitylene as an internal standard.

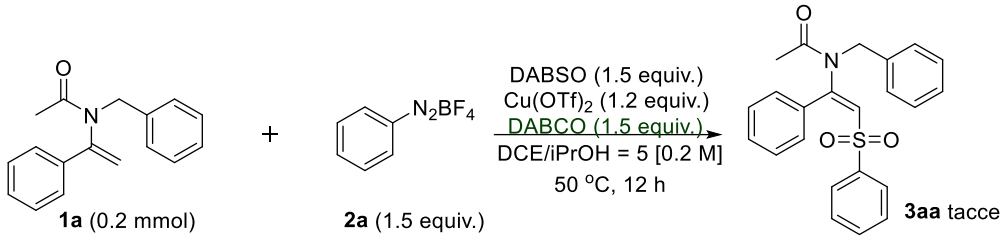
2) Trapping experiment with ethene-1,1-diyldibenzene (7) [a]



Entry	$Cu(OTf)_2$ (equiv.)	NMR yield of **3ba**[b] (%)	NMR yield of **8**[b] (%)	NMR yield of **8'**[b] (%)
1	1.2	48	69	9
2	0	trace	trace	9

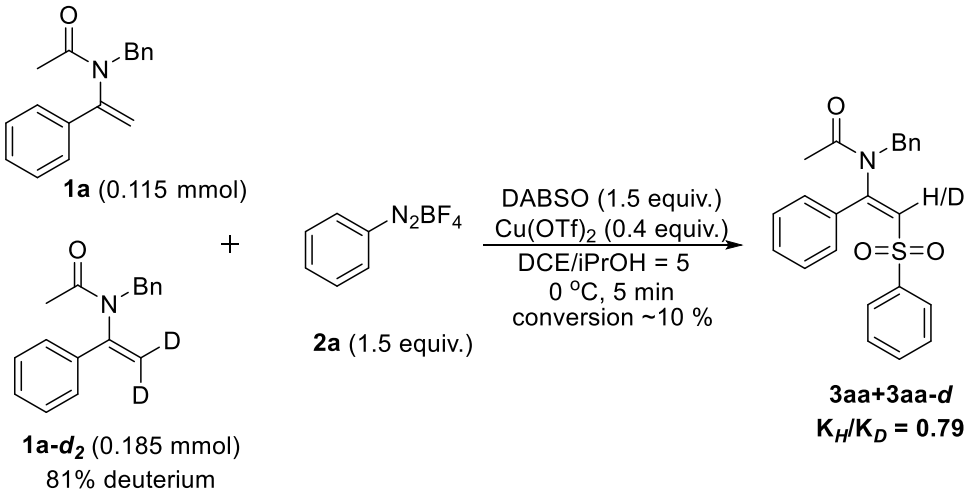
[a] Reaction conditions: enamide **1b** (0.2 mmol), ethene-1,1-diyldibenzene **7** (0.2 mmol), diazonium salt **2a** (0.3 mmol, 1.5 equiv.), DABSO (0.3 mmol, 1.5 equiv.), $Cu(OTf)_2$ in a mixed solvent (DCE/^{i}PrOH = 5/1, 1.0 mL) at 50 °C for 12 h under nitrogen. [b] Determined by NMR analysis of the crude reaction mixture by using mesitylene as an internal standard.

3) Poison reaction of catalyst with 1,4-Diaza[2.2.2]bicyclooctane (DABCO)[a]



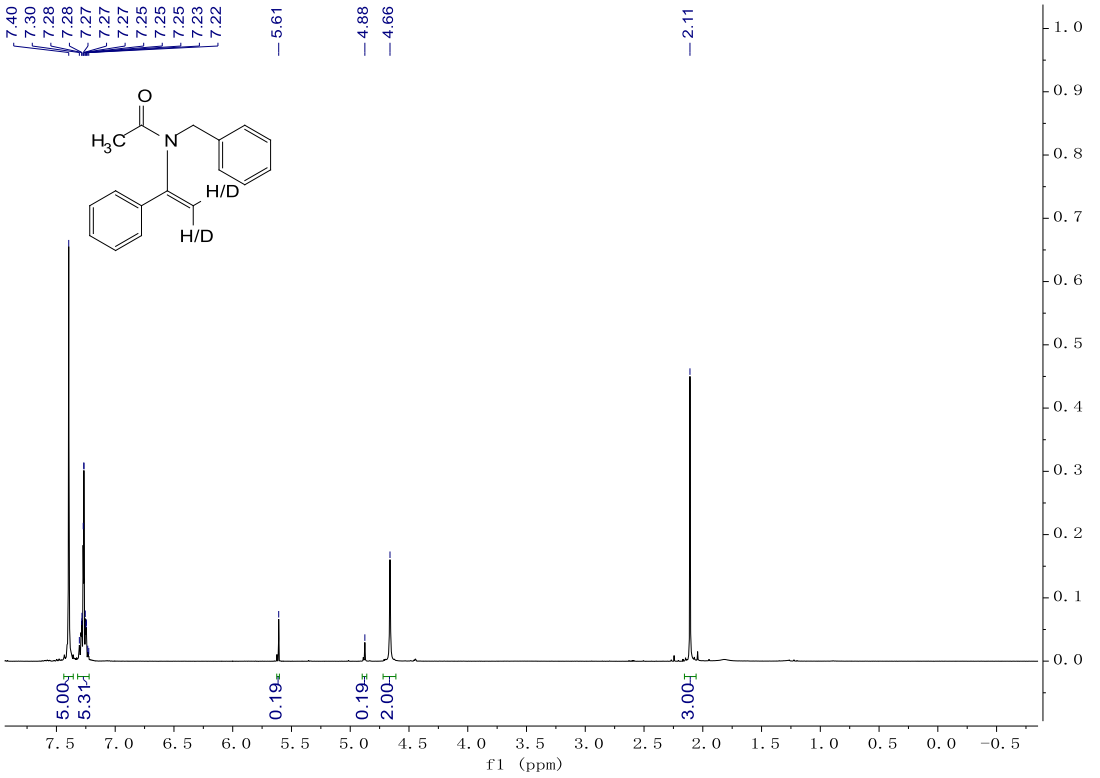
Enamide **1a** (0.2 mmol), diazonium salts **2a** (0.3 mmol, 1.5 equiv.), DABSO (0.3 mmol, 1.5 equiv.), $Cu(OTf)_2$ (0.24 mmol, 1.2 equiv.) and DABCO (0.3 mmol, 1.5 equiv.) were added sequentially into Schlenk tube under nitrogen. Then mixed solvent (DCE/^{i}PrOH = 5/1, 1.5 mL) was added rapidly by syringe. Then, the resulting mixture was allowed to stir at 50 ^{o}C in the oil bath for 12 hours. Then, the resulting mixture was filtered through a short column of silica gel eluted with ethyl acetate and concentrated. Subsequently, determined by NMR analysis of the crude reaction mixture by using mesitylene as an internal standard.

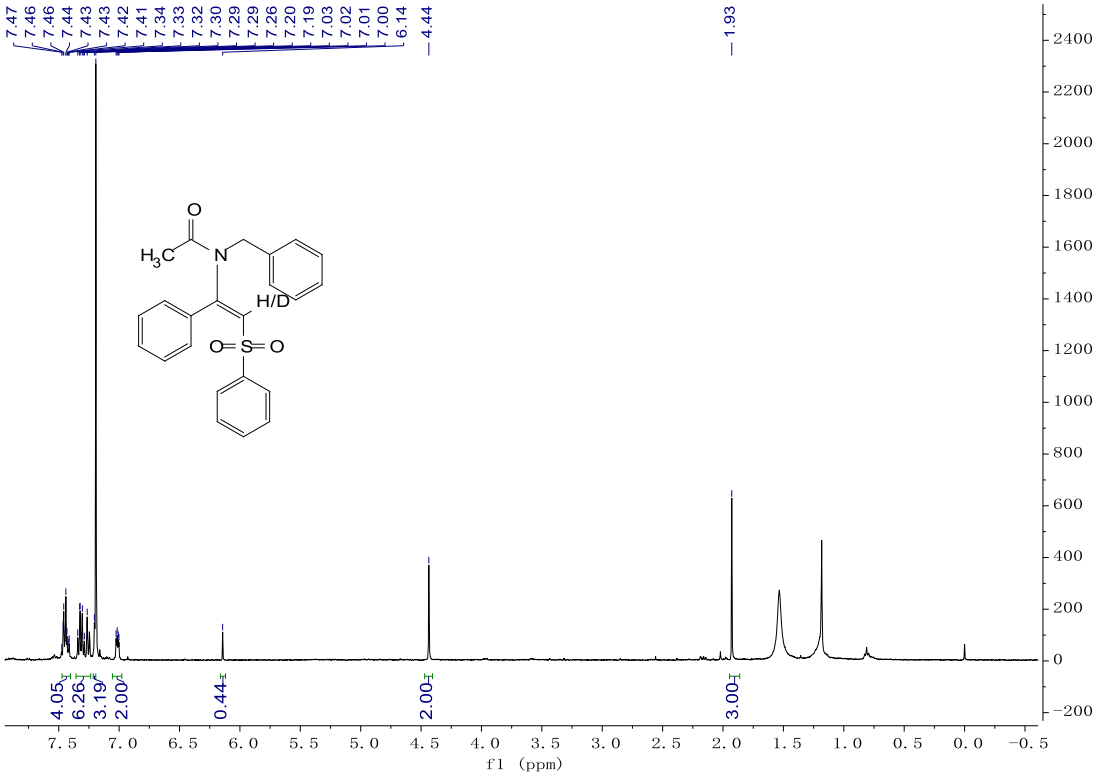
4) Intermolecular kinetic isotopic effect (KIE) study



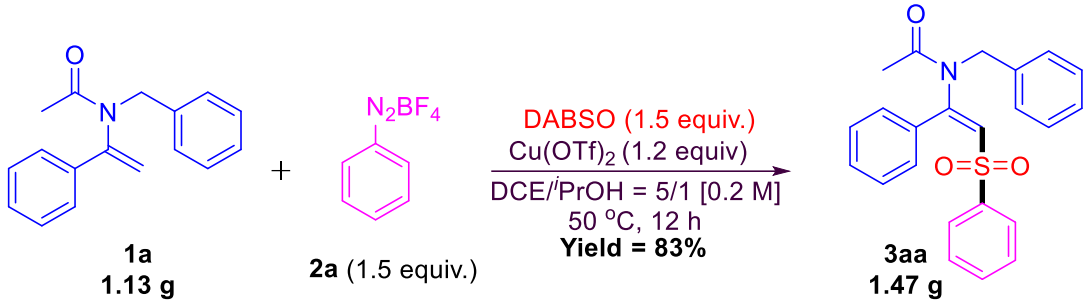
Enamide **1a-*d*$_2$** was prepared according to the literatures[1,4] as a light yellow oil with 81% deuterium.

Enamide **1a** (0.115 mmol), **1a-*d*$_2$**[1] (0.185 mmol), diazonium salt **2a** (0.45 mmol, 1.5 equiv.), DABSO (0.45 mmol, 1.5 equiv.), and $Cu(OTf)_2$ (0.12 mmol, 0.4 equiv.) were added sequentially into Schlenk tube under nitrogen. Then mixed solvent(DCE/^{i}PrOH = 5/1, 1.5 mL) was added rapidly by syringe. The resulting mixture was allowed to stir at 0 ^{o}C for 5 minutes. The product was isolated through thin-layer chromatography(petroleum ether/ethyl acetate = 2/1 as developing solvent) to afford crude mixture (Yield ~ 4%) as white solid. The KIE value (K_H/K_D = 0.79) was determined from the ^{1}H-NMR.


7.40
7.30
7.28
7.28
7.27
7.27
7.27
7.25
7.25
7.25
7.23
7.22
5.61
4.88
4.66
2.11
O
H3C
N
H/D
H/D
5.00
5.31
0.19
0.19
2.00
3.00
f1 (ppm)


7.47
7.46
7.46
7.44
7.43
7.43
7.42
7.41
7.34
7.33
7.32
7.30
7.29
7.29
7.26
7.20
7.19
7.03
7.02
7.01
7.00
6.14
4.44
1.93
O
H3C
N
H/D
O=S=O
4.05
6.26
3.19
2.00
0.44
2.00
3.00
f1 (ppm)

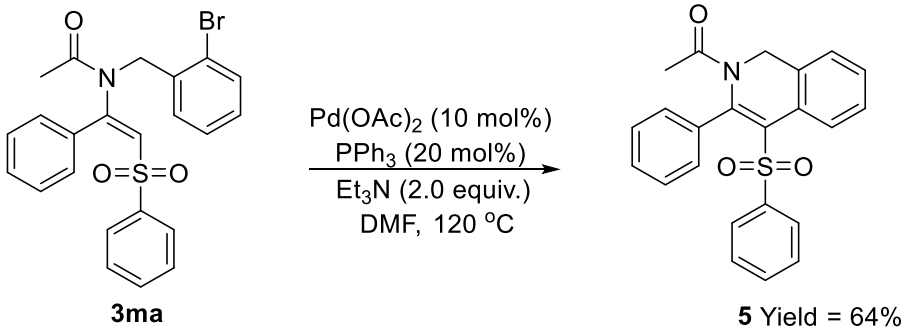
Gram-scale experiment



Enamide **1a** (1.13 g, 4.5 mmol), diazonium salt **2a** (6.75 mmol, 1.5 equiv.), DABSO (6.75 mmol, 1.5 equiv.), and $Cu(OTf)_2$ (5.4 mmol, 1.2 equiv.) were added sequentially into Schlenk tube under nitrogen. Then mixed solvent (DCE/^{i}PrOH = 5/1, 22.5 mL) was added rapidly by syringe. The resulting mixture was allowed to stir at 50 °C in the oil bath for 12 hours as monitored by TLC. Upon completion, solvent was removed under vacuum and the residue was purified by flash silica gel column chromatography using petroleum ether/ethyl acetate as eluent to afford pure products **3aa** (1.47 g , Yield = 83%).

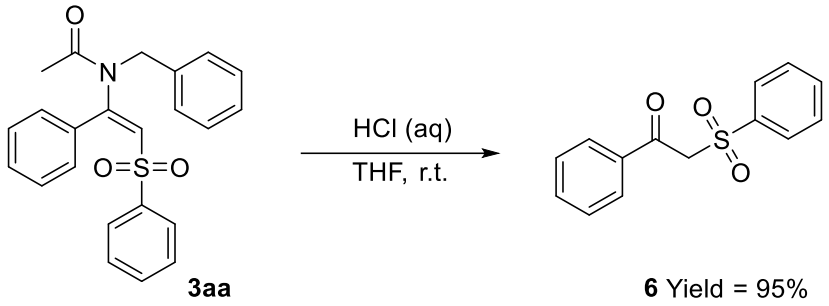
Derivatization reactions

The palladium-catalyzed coupling reaction[5]



(*E*)-*N*-(2-bromobenzyl)-*N*-(1-phenyl-2-(phenylsulfonyl)vinyl)acetamide **3ma** (0.2 mmol), $Pd(OAc)_2$ (0.02 mmol), PPh_3 (0.04 mmol) were added sequentially into a flask Schlenk tube under nitrogen. Then triethylamine (0.4 mmol) and DMF were added by syringe. Then, the resulting mixture was allowed to stir at 120 °C in the oil bath for 24 hours as monitored by TLC. Upon completion, solvent was removed under vacuum and the residue was purified by flash silica gel column chromatography using petroleum ether/ethyl acetate as eluent to afford pure products **5**.

Hydrolyzation of 3aa



3aa **6** Yield = 95%

(*E*)-*N*-benzyl-*N*-(1-phenyl-2-(phenylsulfonyl)vinyl)acetamide **3aa** (0.3 mmol) was added into a tube. Then THF (1 mL) and concentrated hydrochloric acid (1 mL) were added sequentially by syringe. The resulting mixture was stirred at room temperature for 12 hours as monitored by TLC. Upon completion, solvent was removed under vacuum and the residue was purified by flash silica gel column chromatography using petroleum ether/ethyl acetate as eluent to afford pure products **6**.

References

1. (a) M.van den Berg, R. M. Haak, A. J. Minnaard, A. H. M. de Vries, J. G. de Vries, B. L. Feringa, *Adv. Synth. Catal.* **2002**, *344*, 1003; (b) S. Pankajakshan, Y.-H. Xu, J.-K. Cheng, M.-T. Low, T.-P. Loh, *Angew. Chem. Int. Ed*. **2012**, *51*, 5701.

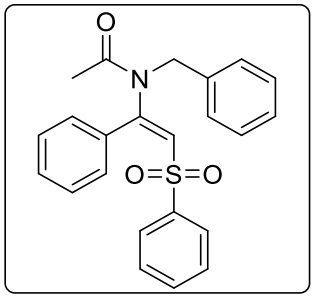
2. S. V. Mileghem, W. M. De Borggraeve, *Org. Process Res. Dev*. **2017**, *21*, 785.

3. N. Zhang, Z.-J. Quan, Z. Zhang, Y.-X. Da, X.-C. Wang, *Chem. Commun*. **2016**, *52*, 14234.

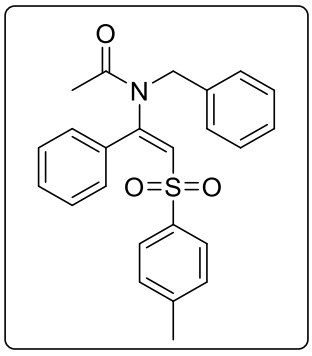
4. W.-L. Yu, J. Chen, Z.-X. Liu, Y.-H. Zhang, *Org. Lett*. **2014**, *16*, 4870.

5. M. Wang, X. Zhang, Y.-X. Zhuang, Y.-H. Xu, T.-P. Loh, *J. Am. Chem. Soc.* **2015**, *137*, 1341.

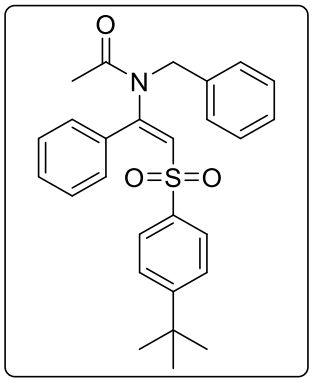
Characterization data for products



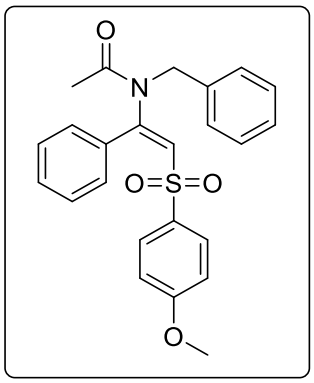
(*E*)-*N*-benzyl-*N*-(1-phenyl-2-(phenylsulfonyl)vinyl)acetamide (3aa): Yield = 87%. White solid. m.p. = 116.2 – 117.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.46 (m, 4H, ArH), 7.43 – 7.30 (m, 6H, ArH), 7.29 – 7.24 (m, 3H, ArH), 7.13 – 7.05 (m, 2H, ArH), 6.22 (s, 1H, C=CH), 4.50 (s, 2H, CH_2), 2.00 (s, 3H,CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.0, 151.7, 140.7, 136.2, 133.3, 131.9, 131.3, 130.0, 128.9, 128.6, 128.5, 128.4, 128.3, 127.7, 127.2, 50.1, 23.0 ppm. HRMS m/z: calcd for $C_{23}H_{22}NO_3S^+$ $[M+H]^+$ 392.1315, found: 392.1335.



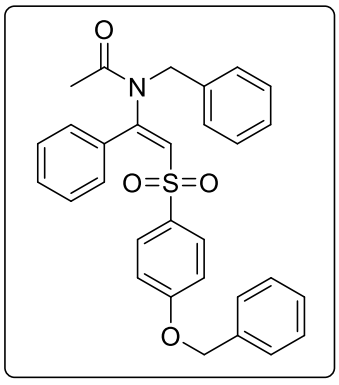
(*E*)-*N*-benzyl-*N*-(1-phenyl-2-tosylvinyl)acetamide (3ab): Yield = 88%. White solid. m.p. = 125.5 – 126.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (t, J = 7.3 Hz, 1H, ArH), 7.44 – 7.31 (m, 6H, ArH), 7.29 – 7.24 (m, 3H, ArH), 7.17 (d, J = 8.1 Hz, 2H, ArH), 7.12 – 7.05 (m, 2H, ArH), 6.19 (s, 1H, C=CH), 4.49 (s, 2H, CH_2), 2.39 (s, 3H, CH_3), 2.00 (s, 3H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.0, 151.3, 144.3, 137.8, 136.3, 131.9, 131.3, 130.1, 129.5, 128.9, 128.6, 128.4, 128.3, 127.7, 127.3, 50.0, 23.0, 21.5 ppm. HRMS m/z: calcd for $C_{24}H_{24}NO_3S^+$ $[M+H]^+$ 406.1471, found: 406.1479.



(*E*)-*N*-benzyl-*N*-(2-((4-(*tert*-butyl)phenyl)sulfonyl)-1-phenylvinyl)acetamide (3ac): Yield = 85%. Faint yellow solid. m.p. = 112.0 – 113.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.43 (m, 3H, ArH), 7.42 – 7.30 (m, 6H, ArH), 7.29 – 7.21 (m, 3H, ArH), 7.16 – 7.02 (m, 2H, ArH), 6.20 (s, 1H, C=CH), 4.50 (s, 2H, CH_2), 2.02 (s, 3H, CH_2), 1.30 (s, 9H, $C(CH_3)_3$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.0, 157.2, 151.1, 137.5, 136.3, 132.1, 131.2, 130.0, 129.0, 128.6, 128.5, 128.3, 127.7, 127.2, 125.9, 50.2, 35.1, 30.9, 23.0 ppm. HRMS m/z: calcd for $C_{27}H_{30}NO_3S^+$ $[M+H]^+$ 448.1941, found: 448.1948.

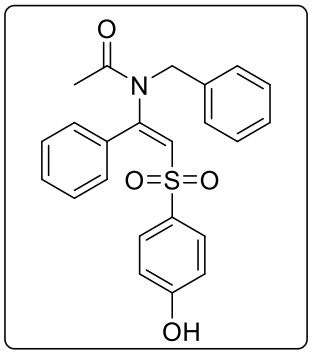


(*E*)-*N*-benzyl-*N*-(2-((4-methoxyphenyl)sulfonyl)-1-phenylvinyl)acetamide (3ad): Yield = 88%. White solid. m.p. = 144.8 – 145.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.47 (m, 1H, ArH), 7.47 – 7.32 (m, 6H, ArH), 7.28 – 7.24 (m, 3H, ArH), 7.12 – 7.06 (m, 2H, ArH), 6.85 – 6.80 (m, 2H, ArH), 6.21 (s, 1H, C=CH), 4.49 (s, 2H, CH_2), 3.83 (s, 3H, OCH_3), 2.01 (s, 3H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.0, 163.4, 150.9, 136.3, 132.3, 132.0, 131.3, 130.1, 129.5, 129.4, 128.6, 128.5, 128.3, 127.7, 114.1, 55.6, 50.0, 23.0 ppm. HRMS m/z: calcd for $C_{24}H_{24}NO_4S^+$ $[M+H]^+$ 422.1421, found: 422.1431.

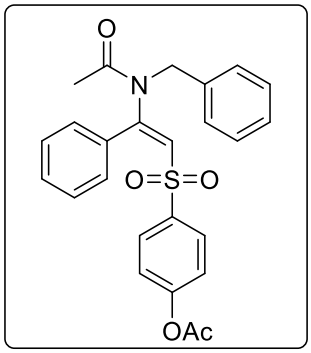


(*E*)-*N*-benzyl-*N*-(2-((4-(benzyloxy)phenyl)sulfonyl)-1-phenylvinyl)acetamide (3ae): Yield = 88%. White solid. m.p. = 115.9 – 117.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.29 (m, 12H, ArH), 7.28 – 7.22 (m, 3H, ArH), 7.13 – 7.05 (m, 2H, ArH), 6.88 (d, J = 8.9 Hz, 2H, ArH), 6.20 (s, 1H, C=CH), 5.09 (s, 2H, OCH_2), 4.49 (s, 2H, CH_2), 2.00 (s, 3H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.0, 162.4, 150.9, 136.3, 135.6, 132.5, 132.0, 131.2, 130.1, 129.5, 129.4, 128.7, 128.6, 128.5, 128.4,

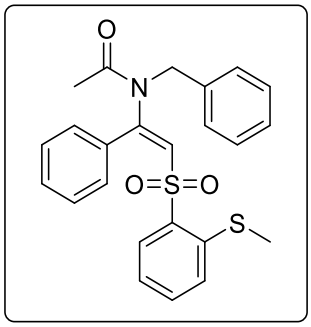
128.3, 127.7, 127.4, 115.0, 70.3, 50.1, 23.0 ppm. HRMS m/z: calcd for $C_{30}H_{28}NO_4S^+$ $[M+H]^+$ 498.1734, found: 498.1755.



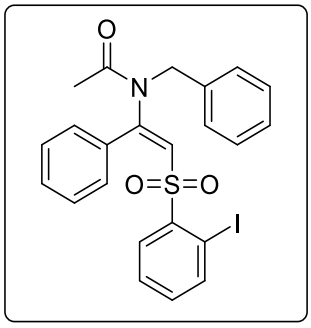
(*E*)-*N*-benzyl-*N*-(2-((4-hydroxyphenyl)sulfonyl)-1-phenylvinyl)acetamide (3af): Yield = 50%. White solid. m.p. = 159.8 – 161.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.45 (m, 2H, ArH+OH), 7.43 – 7.33 (m, 6H, ArH), 7.31 – 7.23 (m, 3H, ArH), 7.14 -7.05 (m, 2H, ArH), 6.75 (d, J = 8.7 Hz, 2H, ArH), 6.19 (s, 1H, C=CH), 4.49 (s, 2H, CH_2), 2.00 (s, 3H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.9, 161.2, 150.4, 135.8, 131.6, 131.5, 131.1, 130.1, 129.9, 129.7, 128.7, 128.4, 127.9, 115.9, 50.3, 22.8 ppm. HRMS m/z: calcd for $C_{23}H_{22}NO_4S^+$ $[M+H]^+$ 408.1264, found: 408.1236.



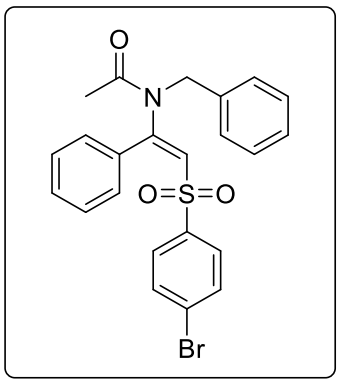
(*E*)-4-((2-(*N*-benzylacetamido)-2-phenylvinyl)sulfonyl)phenyl acetate (3ag): Yield = 54%. Faint yellow solid. m.p. = 110.4 – 112.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.46 (m, 3H, ArH), 7.39 (t, J = 8.0 Hz, 2H, ArH), 7.33 – 7.24 (m, 5H, ArH), 7.13 – 7.05 (m, 4H, ArH), 6.23 (s, 1H, C=CH), 4.53 (s, 2H, CH_2), 2.32 (s, 3H,CH_3), 2.02 (s, 3H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.1, 168.3, 154.3, 151.9, 137.9, 136.2, 132.0, 131.4, 130.0, 128.9, 128.7, 128.43, 128.38, 128.3, 127.8, 122.2, 50.3, 23.2, 21.1 ppm. HRMS m/z: calcd for $C_{25}H_{24}NO_5S^+$ $[M+H]^+$ 450.1370, found: 450.1351.



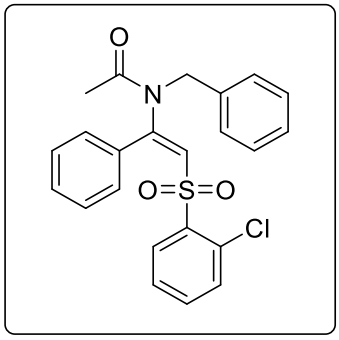
(*E*)-*N*-benzyl-*N*-(2-((2-methylthiophenyl)sulfonyl)-1-phenylvinyl)acetamide (3ah): Yield = 70%, (*E/Z* = 88:12). Yellow viscous liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 [d, *J* = 8.0 Hz, 0.13H, ArH of *(Z)*-isomer],7.61 – 7.53 [m, 1H, ArH + 0.13H of *(Z)*-isomer], 7.48 – 7.42 (m, 2H, ArH), 7.39 – 7.29 [m, 4H, ArH + 0.65H ArH of *(Z)*-isomer], 7.28 – 7.22 (m, 4H, ArH), 7.16 – 7.06 [m, 3H, ArH + 1.04H ArH and C=CH of *(Z)*-isomer], 6.49 (s, 1H, C=CH), 5.05 [d, *J* = 16.0 Hz, 0.13H one of proton of CH_2 of *(Z)*-isomer], 4.60 (s, 2H, CH_2), 4.36 [d, *J* = 16.0 Hz, 0.13H one of proton of CH_2 of *(Z)*-isomer], 2.65 [s, 0.39H, SCH_3 of *(Z)*-isomer], 2.45 (s, 3H, SCH_3), 2.07 (s, 3H, CH_3), 1.78 [s, 0.39H, CH_3 of *(Z)*-isomer] ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 152.5, 139.5, 137.6, 136.6, 133.4, 132.4, 131.1, 129.9, 128.5, 128.23, 128.19, 127.5, 126.8, 126.2, 124.6, 50.7, 23.1, 16.1 ppm. HRMS m/z: calcd for $C_{24}H_{24}NO_3S_2^+$ $[M+H]^+$ 438.1192, found: 438.1198.



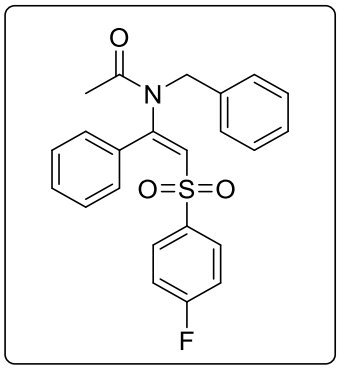
(*E*)-*N*-benzyl-*N*-(2-((2-iodophenyl)sulfonyl)-1-phenylvinyl)acetamide (3ai): Yield = 48%. Light yellow solid. m.p. = 90.3 – 92.1 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.8 Hz, 1H, ArH), 7.69 (d, *J* = 7.9 Hz, 1H, ArH), 7.42 (t, *J* = 7.2 Hz, 1H, ArH), 7.38 – 7.22 (m, 8H, ArH), 7.20 – 7.09 (m, 3H, ArH), 6.56 (s, 1H, C=CH), 4.72 (s, 2H, CH_2), 2.10 (s, 3H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 153.3, 143.4, 142.2, 136.6, 133.9, 132.5, 131.1, 130.7, 129.8, 128.8, 128.3, 128.2, 127.8, 127.7, 124.9, 92.6, 51.1, 23.8 ppm. HRMS m/z: calcd for $C_{23}H_{21}INO_3S^+$ $[M+H]^+$ 518.0281, found: 518.0307.



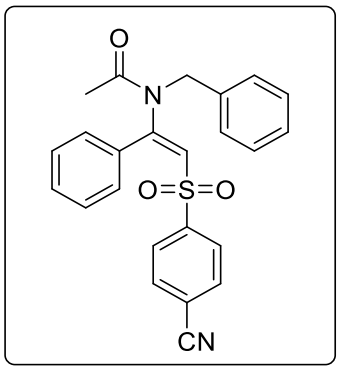
(*E*)-*N*-benzyl-*N*-(2-((4-bromophenyl)sulfonyl)-1-phenylvinyl)acetamide (3aj): Yield = 92%. Light yellow solid. m.p. = 128.6 – 129.1 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.45 (m, 3H, ArH), 7.39 (t, J = 7.6 Hz, 2H, ArH), 7.34 – 7.24 (m, 7H, ArH), 7.14 – 7.05 (m, 2H, ArH), 6.23 (s, 1H, C=CH), 4.54 (s, 2H, CH_2), 2.02 (s, 3H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.1, 152.3, 139.8, 136.2, 132.1, 132.0, 131.4, 130.0, 128.8, 128.7, 128.5, 128.4, 128.3, 127.8, 127.8, 50.4, 23.2 ppm. HRMS m/z: calcd for $C_{23}H_{21}{}^{79}BrNO_3S^+$ $[M+H]^+$ 470.0420, found: 470.0422, $C_{23}H_{21}{}^{81}BrNO_3S^+$ $[M+H]^+$472.0400, found: 472.0403.



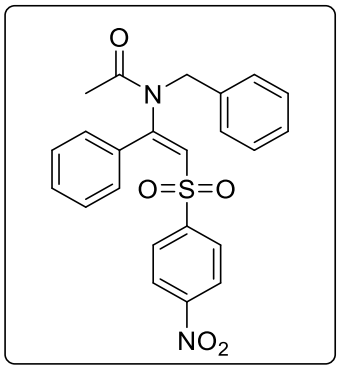
(*E*)-*N*-benzyl-*N*-(2-((2-chlorophenyl)sulfonyl)-1-phenylvinyl)acetamide (3ak): Yield = 72%. Light yellow solid. m.p. = 107.5 – 108.0 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, J = 7.5 Hz, 1H, ArH), 7.48 – 7.40 (m, 3H, ArH), 7.36 – 7.20 (m, 8H, ArH), 7.15 – 7.06 (m, 2H, ArH), 6.47 (s, 1H, C=CH), 4.64 (s, 2H, CH_2), 2.12 (s, 3H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 153.4, 138.5, 136.4, 134.3, 132.3, 132.2, 131.5, 131.1, 130.7, 129.7, 128.6, 128.2, 127.9, 127.7, 127.0, 126.1, 51.0, 23.4 ppm. HRMS m/z: calcd for $C_{23}H_{21}{}^{35}ClNO_3S^+$ $[M+H]^+$ 426.0925, found: 426.0927, $C_{23}H_{21}{}^{37}ClNO_3S^+$ $[M+H]^+$ 428.0896, found: 428.0898.



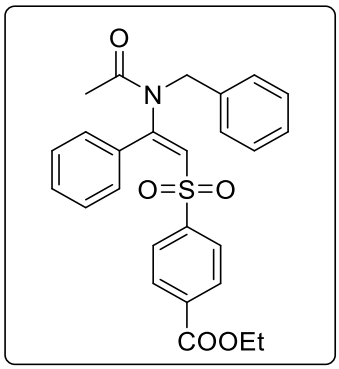
(*E*)-*N*-benzyl-*N*-(2-((4-fluorophenyl)sulfonyl)-1-phenylvinyl)acetamide (3al): Yield = 85%. Light yellow solid. m.p. = 96.4 – 97.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.44 (m, 3H, ArH), 7.39 (t, J = 8.0 Hz, 2H, ArH), 7.34 – 7.24 (m, 5H, ArH), 7.14 – 7.07 (m, 2H, ArH), 7.01 (t, J = 8.5 Hz, 2H, ArH), 6.25 (s, 1H, C=CH), 4.53 (s, 2H, CH_2), 2.02 (s, 3H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.0, 165.30 (d, J = -256.4 Hz), 151.9, 136.77 (d, J = 3.0 Hz), 136.2, 132.0, 131.4, 130.12 (d, J = 9.6 Hz), 130.0, 128.6, 128.40, 128.36, 128.3, 127.8, 116.10 (d, J = 22.6 Hz), 50.3, 23.2 ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ -103.59 ppm. HRMS m/z: calcd for $C_{23}H_{21}FNO_3S^+$ $[M+H]^+$ 410.1221, found: 410.1225.



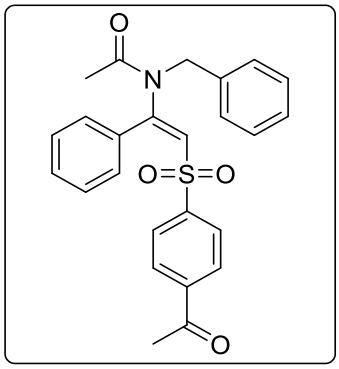
(*E*)-*N*-benzyl-*N*-(2-((4-cyanophenyl)sulfonyl)-1-phenylvinyl)acetamide (3am): Yield = 70%. m.p. = 150.2 – 152.0 °C. Light yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, J = 8.2 Hz, 2H, ArH), 7.53 – 7.45 (m, 3H, ArH), 7.42 – 7.28 (m, 5H, ArH), 7.23 (d, J = 7.8 Hz, 2H, ArH), 7.14 – 7.05 (m, 2H, ArH), 6.31 (s, 1H, C=CH), 4.59 (s, 2H, CH_2), 2.00 (s, 3H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 153.3, 144.9, 136.0, 132.4, 132.0, 131.5, 130.0, 128.7, 128.5, 128.2, 127.9, 127.8, 126.4, 117.0, 116.6, 50.6, 23.5 ppm. HRMS m/z: calcd for $C_{24}H_{21}N_2O_3S^+$ $[M+H]^+$ 417.1267, found: 417.1245.



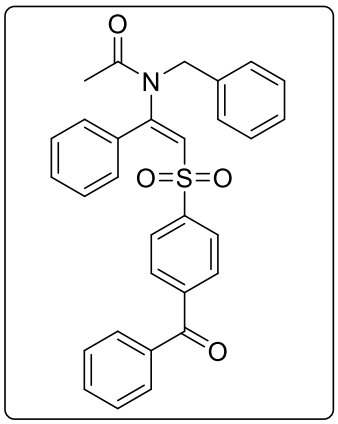
(*E*)-*N*-benzyl-*N*-(2-((4-nitrophenyl)sulfonyl)-1-phenylvinyl)acetamide (3an): Yield = 46% Yellow solid. m.p. = 125.9 – 127.0 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, J = 8.8 Hz, 2H, ArH), 7.61 – 7.47 (m, 3H, ArH), 7.41 – 7.28 (m, 5H, ArH), 7.27 – 7.19 (m, 2H, ArH), 7.15 – 7.08 (m, 2H, ArH), 6.34 (s, 1H, C=CH), 4.60 (s, 2H, CH_2), 2.01 (s, 3H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 153.6, 150.0, 146.4, 136.0, 132.0, 131.6, 130.0, 128.8, 128.6, 128.5, 128.1, 127.9, 126.2, 123.8, 50.7, 23.6 ppm. HRMS m/z: calcd for $C_{23}H_{21}N_2O_5S^+$ $[M+H]^+$ 437.1166, found: 437.1169.



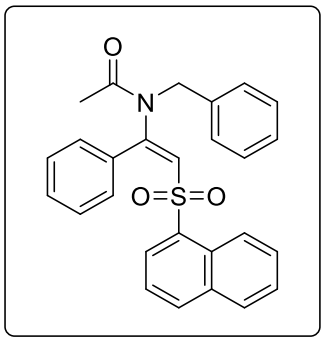
ethyl (*E*)-4-((2-(*N*-benzylacetamido)-2-phenylvinyl)sulfonyl)benzoate (3ao): Yield = 58%. Light yellow solid. m.p. = 78.6 – 80.1 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, J = 8.4 Hz, 2H, ArH), 7.57 – 7.48 (m, 3H, ArH), 7.39 (t, J = 7.7 Hz, 2H, ArH), 7.33 – 7.24 (m, 5H, ArH), 7.13 – 7.05 (m, 2H, ArH), 6.25 (s, 1H, C=CH), 4.53 (s, 2H, CH_2), 4.41 (q, J = 7.1 Hz, 2H, CH_2), 2.00 (s, 3H, CH_3), 1.41 (t, J = 7.1 Hz, 3H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.1, 164.9, 152.8, 144.5, 136.1, 134.6, 131.9, 131.5, 130.0, 129.9, 128.7, 128.4, 128.3, 127.8, 127.4, 127.3, 61.8, 50.3, 23.2, 14.2. HRMS m/z: calcd for $C_{26}H_{26}NO_5S^+$ $[M+H]^+$ 464.1526, found: 464.1533.



(*E*)-*N*-(2-((4-acetylphenyl)sulfonyl)-1-phenylvinyl)-*N*-benzylacetamide (3ap): Yield = 61%. Light yellow solid. m.p. = 125.1 – 126.5 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, J = 8.5 Hz, 2H, ArH), 7.56 (d, J = 8.4 Hz, 2H, ArH), 7.51 (t, J = 7.4 Hz, 1H, ArH), 7.38 (t, J = 7.7 Hz, 2H, ArH), 7.33 – 7.25 (m, 5H, ArH), 7.13 – 7.05 (m, 2H, ArH), 6.26 (s, 1H, C=CH), 4.53 (s, 2H, CH_2), 2.62 (s, 3H, CH_3), 2.01 (s, 3H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.6, 170.1, 152.8, 144.6, 140.2, 136.1, 131.9, 131.5, 130.1, 128.7, 128.6, 128.4, 128.3, 127.8, 127.6, 127.3, 50.4, 26.9, 23.2 ppm. HRMS m/z: calcd for $C_{25}H_{24}NO_4S^+$ $[M+H]^+$ 434.1421, found: 434.1434.

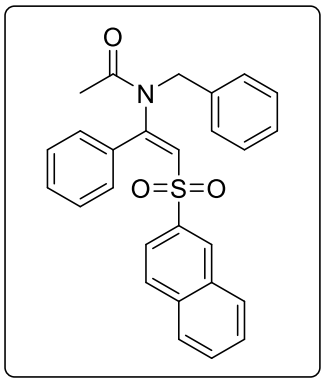


(*E*)-*N*-(2-((4-benzoylphenyl)sulfonyl)-1-phenylvinyl)-*N*-benzylacetamide (3aq): Yield = 80%. Yellow solid. m.p. = 133.4 -134.2 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 – 7.68 (m, 4H, ArH), 7.65 (t, J = 7.4 Hz, 1H, ArH), 7.57 (d, J = 8.3 Hz, 2H,ArH), 7.55 – 7.47 (m, 3H, ArH), 7.39 (t, J = 7.7 Hz, 2H, ArH), 7.34 – 7.26 (m, 5H, ArH), 7.16 – 7.08 (m, 2H, ArH), 6.31 (s, 1H, C=CH), 4.56 (s, 2H, CH_2), 2.04 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.0, 170.2, 152.7, 143.7, 141.6, 136.3, 136.2, 133.3, 132.1, 131.5, 130.1, 130.03, 129.97, 128.7, 128.5, 128.4, 128.3, 127.8, 127.5, 127.2, 50.5, 23.1 ppm. HRMS m/z: calcd for $C_{30}H_{26}NO_4S^+$ $[M+H]^+$ 496.1577, found: 496.1599.

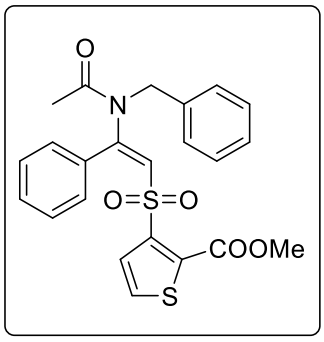


(*E*)-*N*-benzyl-*N*-(2-(naphthalen-1-ylsulfonyl)-1-phenylvinyl)acetamide (3ar): Yield = 73%. Light yellow solid. m.p. = 121.1 – 121.7 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 – 8.36 (m, 1H, ArH), 8.02 (d, J = 8.2 Hz, 1H, ArH), 7.96 – 7.88 (m, 2H, ArH), 7.63 - 7.55 (m, 2H, ArH), 7.48 (t, J = 7.2 Hz, 1H, ArH), 7.41 – 7.30 (m, 5H, ArH), 7.23 – 7.14 (m, 3H, ArH), 7.02 – 6.94 (m, 2H, ArH), 6.33 (s, 1H, C=CH), 4.48 (s, 2H,

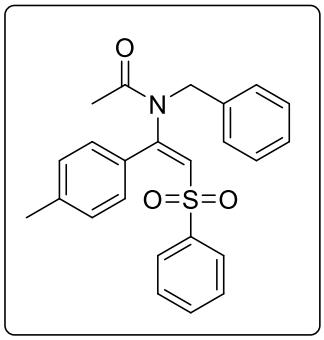
CH_2), 1.83 (s, 3H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.0, 152.0, 136.3, 135.4, 134.8, 133.9, 132.1, 131.3, 130.0, 129.7, 129.1, 128.5, 128.41, 128.39, 128.23, 128.16, 127.6, 126.9, 124.24 124.18, 50.6, 23.0 ppm. HRMS m/z: calcd for $C_{27}H_{24}NO_3S^+$ $[M+H]^+$ 442.1471, found: 442.1486.



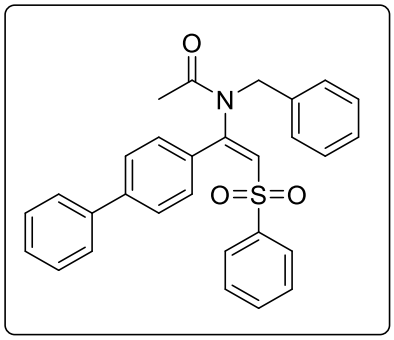
(*E*)-*N*-benzyl-*N*-(2-(naphthalen-2-ylsulfonyl)-1-phenylvinyl)acetamide (3as): Yield = 69%. Light yellow solid. m.p. = 130.3 – 131.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (s, 1H, ArH), 7.89 – 7.82 (m, 2H, ArH), 7.78 (d, J = 8.1 Hz, 1H, ArH), 7.67 – 7.62 (m, 1H, ArH), 7.61 – 7.56 (m, 1H, ArH), 7.53 (dd, J = 8.7, 1.8 Hz, 1H, ArH), 7.50 – 7.42 (m, 1H, ArH), 7.37 – 7.29 (m, 4H, ArH), 7.25 – 7.21 (m, 3H, ArH), 7.11 – 7.04 (m, 2H, ArH), 6.30 (s, 1H, C=CH), 4.50 (s, 2H, CH_2), 1.99 (s, 3H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.1, 151.9, 137.3, 136.3, 134.9, 132.0, 131.8, 131.4, 130.1, 129.3, 129.25, 129.22, 128.60, 128.57, 128.4, 128.3, 127.8, 127.7, 127.6, 122.0, 50.3, 23.1 ppm. HRMS m/z: calcd for $C_{27}H_{24}NO_3S^+$ $[M+H]^+$ 442.1471, found: 442.1470.



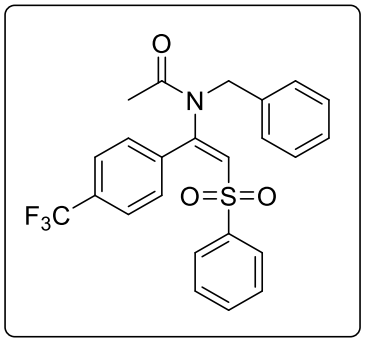
methyl (*E*)-3-((2-(*N*-benzylacetamido)-2-phenylvinyl)sulfonyl)thiophene-2-carboxylate (3at): Yield = 26%. Light brown solid. m.p. = 91.6 – 92.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (t, J = 7.1 Hz, 1H, ArH), 7.42 – 7.32 (m, 3H, ArH), 7.31 – 7.17 (m, 6H, ArH), 7.15 – 7.07 (m, 2H, ArH), 6.82 (s, 1H, C=CH), 4.63 (s, 2H, CH_2), 3.88 (s, 3H, CH_3), 2.12 (s, 3H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 159.6, 152.8, 145.3, 136.6, 133.8, 132.7, 131.1, 130.5, 129.8, 129.6, 128.5, 128.24, 128.18, 127.5, 127.3, 53.0, 50.7, 23.3. HRMS m/z: calcd for $C_{23}H_{22}NO_5S_2^+$ $[M+H]^+$ 456.0934, found: 456.0929.



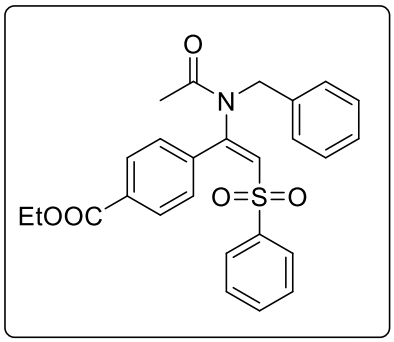
(*E*)-*N*-benzyl-*N*-(2-(phenylsulfonyl)-1-(*p*-tolyl)vinyl)acetamide (3ba): Yield = 90%. White Solid. m.p. = 130.7 – 132.3 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.50 (m, 3H, ArH), 7.39 (t, J = 7.7 Hz, 2H, ArH), 7.30 – 7.18 (m, 7H, ArH), 7.12 – 7.06 (m, 2H, ArH), 6.12 (s, 1H, C=CH), 4.50 (s, 2H, CH_2), 2.42 (s, 3H, CH_3), 1.97 (s, 3H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.0, 151.8, 142.0, 140.9, 136.3, 133.2, 130.1, 129.1, 129.0, 128.9, 128.55, 128.48, 127.71, 127.67, 127.2, 50.2, 23.0, 21.5 ppm. HRMS m/z: calcd for $C_{24}H_{24}NO_3S^+$ $[M+H]^+$ 406.1471, found: 406.1486.



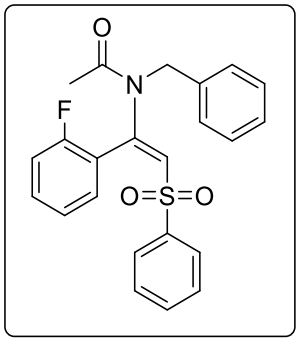
(*E*)-*N*-(1-([1,1'-biphenyl]-4-yl)-2-(phenylsulfonyl)vinyl)-*N*-benzylacetamide (3ca): Yield = 93%. Yellow viscous oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 – 7.47 (m, 10H, ArH), 7.40 (quint, J = 8.0 Hz, 5H, ArH), 7.30 – 7.25 (m, 2H, ArH), 7.14 – 7.08 (m, 2H, ArH), 6.22 (s, 1H, C=CH), 4.56 (s, 2H, CH_2), 2.03 (s, 3H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.1, 151.4, 144.2, 140.7, 139.6, 136.3, 133.3, 130.7, 130.6, 128.94, 128.92, 128.6, 128.5, 128.4, 128.1, 127.8, 127.3, 127.1, 126.9, 50.3, 23.1 ppm. HRMS m/z: calcd for $C_{29}H_{26}NO_3S^+$ $[M+H]^+$ 468.1628, found: 468.1637.



(*E*)-*N*-benzyl-*N*-(2-(phenylsulfonyl)-1-(4-(trifluoromethyl)phenyl)vinyl)acetamide (3da): Yield = 87%. White solid. m.p. = 136.2 – 136.7 ºC.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, J = 8.0 Hz, 2H, ArH), 7.59 – 7.50 (m, 3H, ArH), 7.46 – 7.36 (m, 4H, ArH), 7.32 – 7.25 (m, 3H, ArH), 7.11 – 7.02 (m, 2H, ArH), 6.32 (s, 1H, C=CH), 4.52 (s, 2H, CH_2), 2.03 (s, 3H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.9, 149.9, 140.4, 135.9, 135.7, 133.6, 132.8 (q, J = 33.0 Hz), 130.4, 129.7, 129.1, 128.7, 128.3, 127.9, 127.2, 125.2 (q, J = 4.0 Hz), 123.5 (q, J = 271.0 Hz), 50.3, 23.0 ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.93 ppm. HRMS m/z: calcd for $C_{24}H_{21}F_3NO_3S^+$ $[M+H]^+$ 460.1189, found: 460.1180.

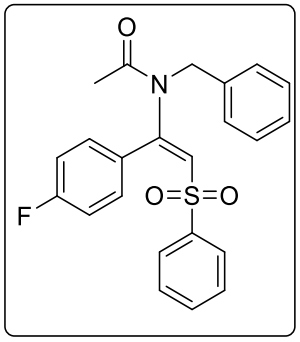


ethyl (*E*)-4-(1-(*N*-benzylacetamido)-2-(phenylsulfonyl)vinyl)benzoate (3ea): Yield = 92%. Light yellow solid. M. P. = 91.5 – 93.2 ºC.^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, J = 8.3 Hz, 2H, ArH), 7.60 – 7.52 (m, 3H, ArH), 7.44 – 7.36 (m, 4H, ArH), 7.31 – 7.22 (m, 3H, ArH), 7.09 – 7.02 (m, 2H, ArH), 6.27 (s, 1H, C=CH), 4.50 (s, 2H, CH_2), 4.43 (q, J = 7.1 Hz, 2H, CH_2), 2.01 (s, 3H, CH_3), 1.43 (t, J = 7.2 Hz, 3H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.9, 165.6, 150.5, 140.6, 136.2, 136.0, 133.5, 132.8, 130.0, 129.4, 129.3, 129.1, 128.7, 128.3, 127.9, 127.3, 61.4, 50.2, 23.0, 14.3 ppm. HRMS m/z: calcd for $C_{26}H_{26}NO_5S^+$ $[M+H]^+$ 464.1526, found: 464.1515.

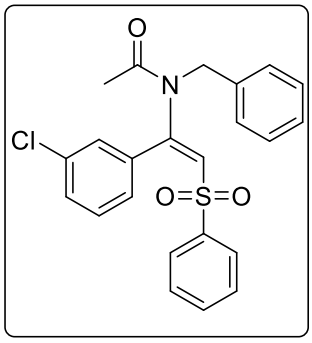


(*E*)-*N*-benzyl-*N*-(1-(2-fluorophenyl)-2-(phenylsulfonyl)vinyl)acetamide (3fa): Yield = 90%. White solid. m.p. = 105.8 – 107.0 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.53 (m, 3H, ArH), 7.52 – 7.38 (m, 3H, ArH), 7.34 – 7.17 (m, 5H, ArH), 7.09 – 6.95 (m, 3H, ArH), 6.33 (s, 1H, C=CH), 4.50 (s, 2H, CH_2), 2.09 (s, 3H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.0, 161.1, 158.7, 146.6, 140.4, 136.2, 133.5, 133.05, 132.96, 129.0, 128.7 (d, J = -224.0 Hz), 128.5, 128.0, 127.3, 123.8 (d, J = 4.0 Hz), 119.7 (d, J = 14.0 Hz), 115.7 (d, J = 21.0 Hz), 49.6, 22.7 ppm. ^{19}F NMR (376

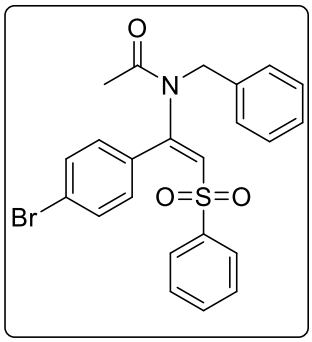
MHz, $CDCl_3$) δ -111.94 ppm. HRMS m/z: calcd for $C_{23}H_{21}FNO_3S^+$ $[M+H]^+$ 410.1221, found: 410.1239.



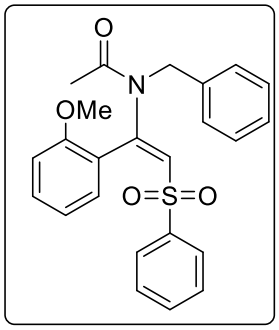
(*E*)-*N*-benzyl-*N*-(1-(4-fluorophenyl)-2-(phenylsulfonyl)vinyl)acetamide (3ga): Yield = 87%. White solid. m.p. = 119.5 – 120.3 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.51 (m, 3H, ArH), 7.42 (t, *J* = 7.7 Hz, 2H, ArH), 7.33 (dd, *J* = 8.5, 5.3 Hz, 2H, ArH), 7.29 – 7.24 (m, 3H, ArH), 7.13 – 7.02 (m, 4H, ArH), 6.20 (s, 1H, C=CH), 4.51 (s, 2H, CH_2), 1.98 (s, 3H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.0, 164.4 (d, *J* = -252.0 Hz), 150.5, 140.6, 136.1, 133.5, 132.3 (d, *J* = 9.0 Hz), 129.0, 128.7, 128.42, 128.39, 128.0 (d, *J* = 4.0 Hz), 127.8, 127.2, 115.6 (d, *J* = 22.0 Hz),50.2, 23.0 ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ -107.25 ppm. HRMS m/z: calcd for $C_{23}H_{21}FNO_3S^+$ $[M+H]^+$ 410.1221, found: 410.1222.



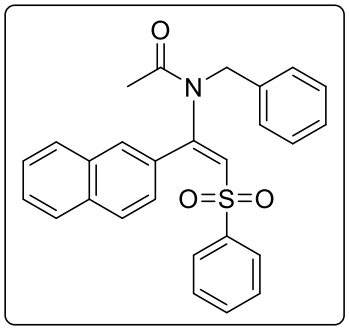
(*E*)-*N*-benzyl-*N*-(1-(3-chlorophenyl)-2-(phenylsulfonyl)vinyl)acetamide (3ha): Yield = 94%, Light yellow solid. m.p. = 137.4 – 137.7 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.52 (m, 3H, ArH), 7.48 – 7.38 (m, 3H, ArH), 7.34 (t, *J* = 7.8 Hz, 1H, ArH), 7.30 – 7.24 (m, 4H, ArH), 7.14 (s, 1H, ArH), 7.10 – 7.04 (m, 2H, ArH), 6.26 (s, 1H, C=CH), 4.51 (s, 2H, CH_2), 2.03 (s, 3H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.9, 150.0, 140.5, 136.0, 134.4, 133.7, 133.5, 131.2, 129.6, 129.4, 129.3, 129.0, 128.7, 128.6, 128.3, 127.9, 127.3, 50.2, 23.0 ppm. HRMS m/z: calcd for $C_{23}H_{21}{}^{35}ClNO_3S^+$ $[M+H]^+$ 426.0925, found:426.0928, $C_{23}H_{21}{}^{37}ClNO_3S^+$ $[M+H]^+$ 428.0896, found: 428.0899.



(*E*)-*N*-benzyl-*N*-(1-(4-bromophenyl)-2-(phenylsulfonyl)vinyl)acetamide (3ia): Yield = 95%, Light yellow solid. m.p. = 144.5 – 144.8 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.51 (m, 5H, ArH), 7.46 – 7.39 (m, 2H, ArH), 7.30 – 7.24 (m, 3H, ArH), 7.22 – 7.17 (m, 2H, ArH), 7.09 – 7.03 (m, 2H, ArH), 6.21 (s, 1H, C=CH), 4.51 (s, 2H, CH_2), 1.98 (s, 3H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.9, 150.4, 140.6, 136.0, 133.5, 131.6, 131.5, 130.9, 129.1, 128.75, 128.68, 128.4, 127.9, 127.2, 126.1, 50.2, 23.0 ppm. HRMS m/z: calcd for $C_{23}H_{21}{}^{79}BrNO_3S^+$ $[M+H]^+$ 470.0420, found: 470.0406, $C_{23}H_{21}{}^{81}BrNO_3S^+$ $[M+H]^+$472.0400, found: 472.0391.

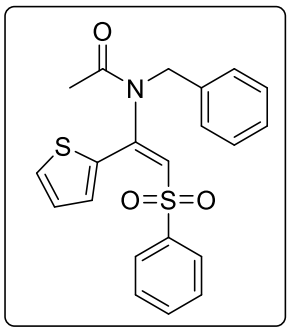


(*E*)-*N*-benzyl-*N*-(1-(2-methoxyphenyl)-2-(phenylsulfonyl)vinyl)acetamide (3ja): Yield = 85%. White solid. m.p. = 129.4 – 129.8 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.43 (m, 3H, ArH), 7.42 – 7.29 (m, 3H, ArH), 7.26 – 7.17 (m, 4H, ArH), 7.09 - 6.94 (m, 3H, ArH), 6.63 (d, J = 8.3 Hz, 1H, ArH), 6.36 (s, 1H, C=CH), 4.45 (s, 2H, CH_2), 3.48 (s, 3H, OCH_3), 2.18 (s, 3H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 157.0, 150.7, 140.7, 136.7, 133.5, 132.8, 132.5, 129.4, 128.5, 128.3, 128.0, 127.35, 127.28, 120.02, 119.96, 110.3, 54.9, 49.2, 22.8 ppm. HRMS m/z: calcd for $C_{24}H_{24}NO_4S^+$ $[M+H]^+$ 422.1421, found: 422.1426.

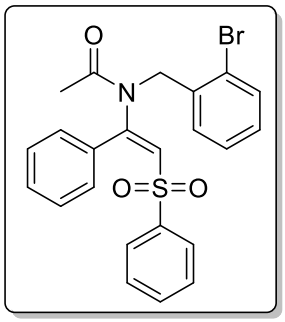


(*E*)-*N*-benzyl-*N*-(1-(naphthalen-2-yl)-2-(phenylsulfonyl)vinyl)acetamide (3ka):

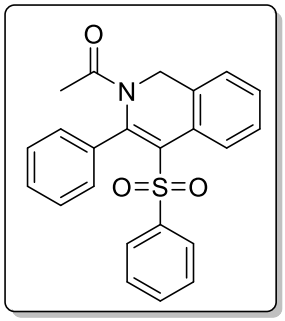
Yield = 93%. Light yellow solid. m.p. = 165.1 – 165.6 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 – 7.76 (m, 4H, ArH), 7.64 – 7.54 (m, 2H, ArH), 7.52 – 7.43 (m, 3H, ArH), 7.32 – 7.23 (m, 6H, ArH), 7.15 – 7.06 (m, 2H, ArH), 6.31 (s, 1H, C=CH), 4.54 (s, 2H, CH_2), 2.06 (s, 3H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.1, 151.8, 140.7, 136.3, 134.3, 133.2, 132.2, 131.4, 129.2, 128.82, 128.79, 128.6, 128.5, 128.2, 128.0, 127.8, 127.7, 127.2, 127.0, 125.5, 50.3, 23.1 ppm. HRMS m/z: calcd for $C_{27}H_{24}NO_3S^+$ $[M+H]^+$ 442.1471, found: 442.1465.



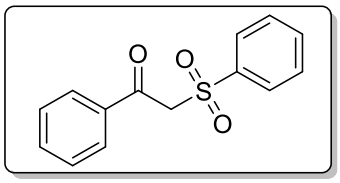
(*E*)-*N*-benzyl-*N*-(2-(phenylsulfonyl)-1-(thiophen-2-yl)vinyl)acetamide (3la): Yield = 81%, (*E/Z* = 84/16). Light yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 [d, *J* = 3.8 Hz, 1H, ArH + 0.19H, ArH of *(Z)*-isomer], 7.70 – 7.53 (m, 4H, ArH + 0.57H ArH of *(Z)*-isomer), 7.41 (t, *J* = 7.8 Hz, 2H, ArH), 7.35 – 7.20 (m, 3H, ArH +1.33H ArH of *(Z)*-isomer), 7.19 – 7.09 (m, 3H, ArH), 6.81 (t, *J* = 6.0 Hz, 0.19H, ArH of *(Z)*-isomer), 6.71 [s, 0.19H, C=CH of (*Z*)-isomer], 6.64 (d, *J* = 4.0 Hz, 0.19H, ArH of *(Z)*-isomer), 6.07 (s, 1H, C=CH), 5.33 [d, *J* = 14.2 Hz, 0.2H, one proton of CH_2 of *(Z)*-isomer], 4.61 (s, 2H), 4.52 [d, *J* = 14.2 Hz, 0.2H, one proton of CH_2 of *(Z)*-isomer], 1.96 (s, 3H, CH_3), 1.71 [s, 0.57H, CH_3 of *(Z)*-isomer]. ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.7, 144.2, 140.4, 136.2, 135.2, 134.5, 133.5, 131.7, 129.0, 128.9, 128.6, 128.3, 127.9, 127.2, 50.7, 22.5 ppm. HRMS m/z: calcd for $C_{21}H_{20}NO_3S_2^+$ $[M+H]^+$ 398.0879, found: 398.0883.



(*E*)-*N*-(2-bromobenzyl)-*N*-(1-phenyl-2-(phenylsulfonyl)vinyl)acetamide (3ma): Yield = 87%. Light yellow solid. m.p. = 90.5 – 91.2 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.20 (m, 12H, ArH), 7.18 – 6.98 (m, 2H, ArH), 6.42 (s, 1H, C=CH), 4.67 (s, 2H, CH_2), 2.04 (s, 3H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.2, 151.9, 140.6, 135.0, 133.3, 132.9, 131.6, 131.3, 130.0, 129.8, 129.2, 128.9, 128.4, 128.3, 127.5, 127.2, 123.2, 50.4, 23.1 ppm. $C_{23}H_{21}{}^{79}BrNO_3S^+$ $[M+H]^+$ 470.0420, found: 470.0421, $C_{23}H_{21}{}^{81}BrNO_3S^+$ $[M+H]^+$472.0400, found: 472.0403.



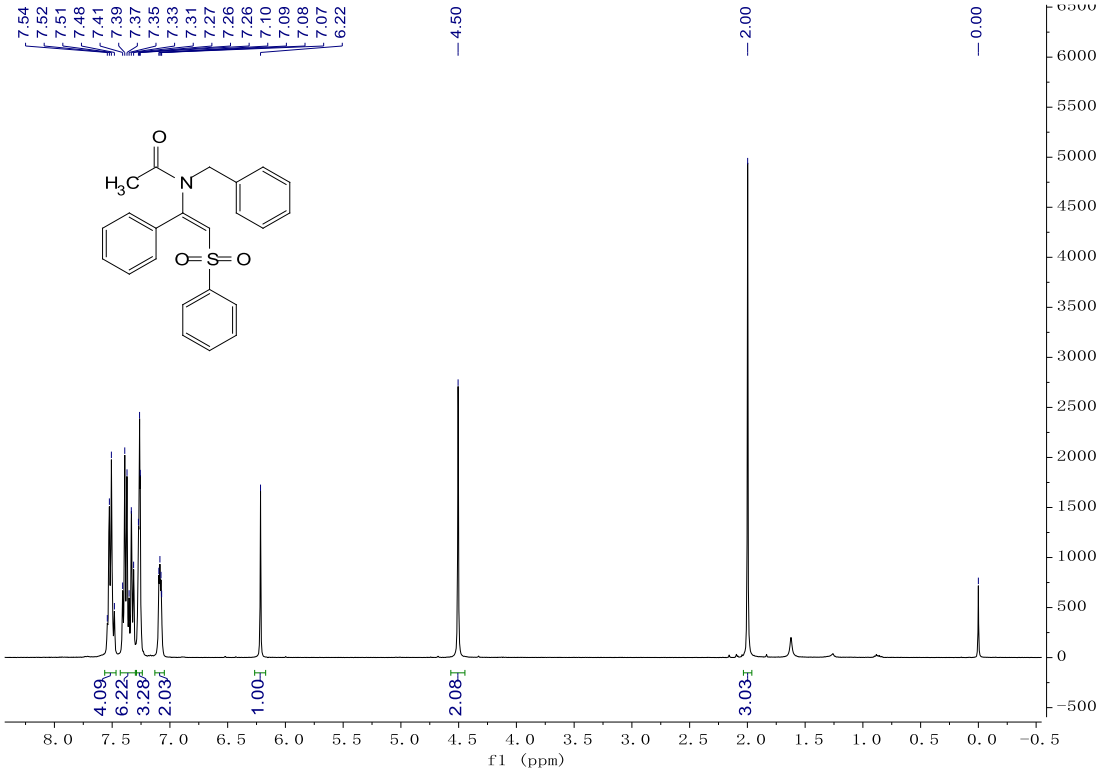
1-(3-phenyl-4-(phenylsulfonyl)isoquinolin-2(1H)-yl)ethan-1-one 5: Yield = 64%. White solid. m.p. = 184.0 – 184.3°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, J = 7.8 Hz, 1H, ArH), 7.58 - 7.45 (m, 5H, ArH), 7.43 – 7.18 (m, 8H, ArH), 4.83 (s, 2H, CH_2), 1.40 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.5, 148.7, 142.0, 134.8, 133.2, 132.4, 131.9, 131.1, 129.1, 128.3, 128.33, 128.30, 128.2, 127.5, 127.0, 126.0, 125.0, 46.9, 24.9. HRMS m/z: calcd for $C_{23}H_{20}NO_3S^+$ $[M+H]^+$ 390.1178, found: 390.1158.

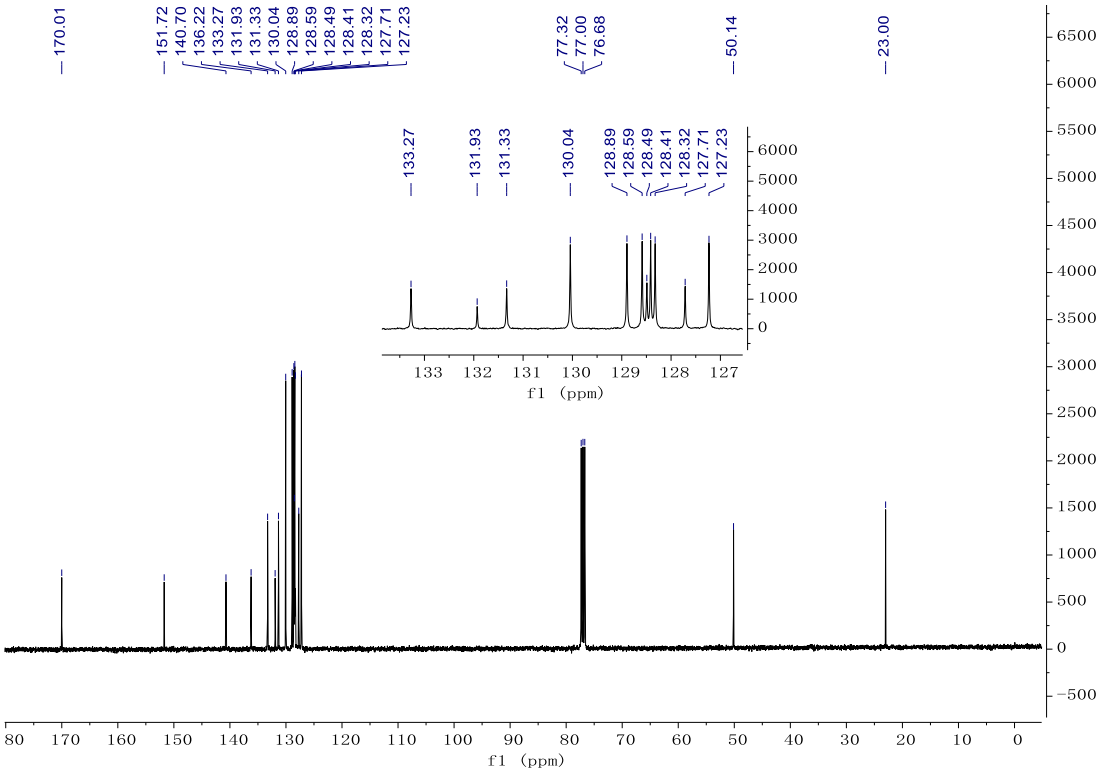


1-phenyl-2-(phenylsulfonyl)ethan-1-one 6: Yield = 95%. White solid. m.p. = 95.0 – 95.4 °C. ^{1}H NMR (401 MHz, $CDCl_3$) δ 7.98 – 7.86 (m, 4H, ArH), 7.69 – 7.58 (m, 2H, ArH), 7.58 – 7.51 (m, 2H, ArH), 7.50 – 7.44 (m, 2H, ArH), 4.74 (s, 2H, CH_2) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.9, 138.6, 135.6, 134.3, 134.2, 129.2, 129.1, 128.8, 128.5, 63.3 ppm. HRMS m/z: calcd for $C_{14}H_{13}O_3S^+$ $[M+H]^+$ 261.0580, found: 261.0584.

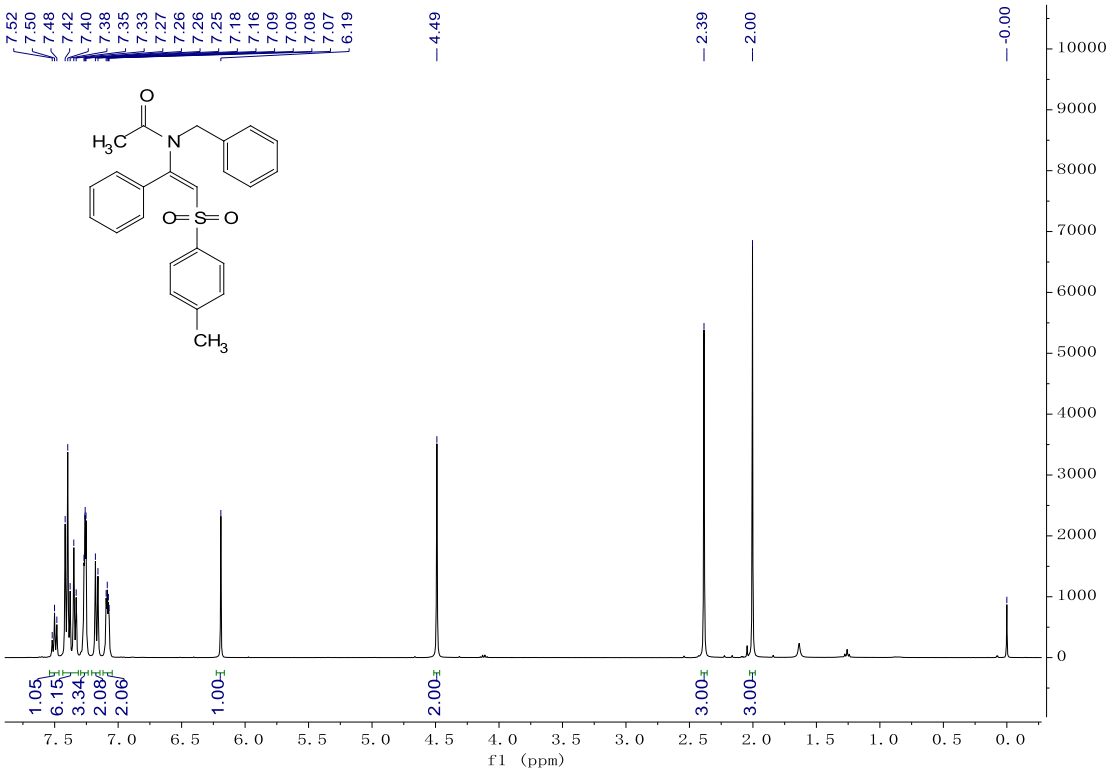
^{1}H, ^{19}F and ^{13}C NMR spectra of products

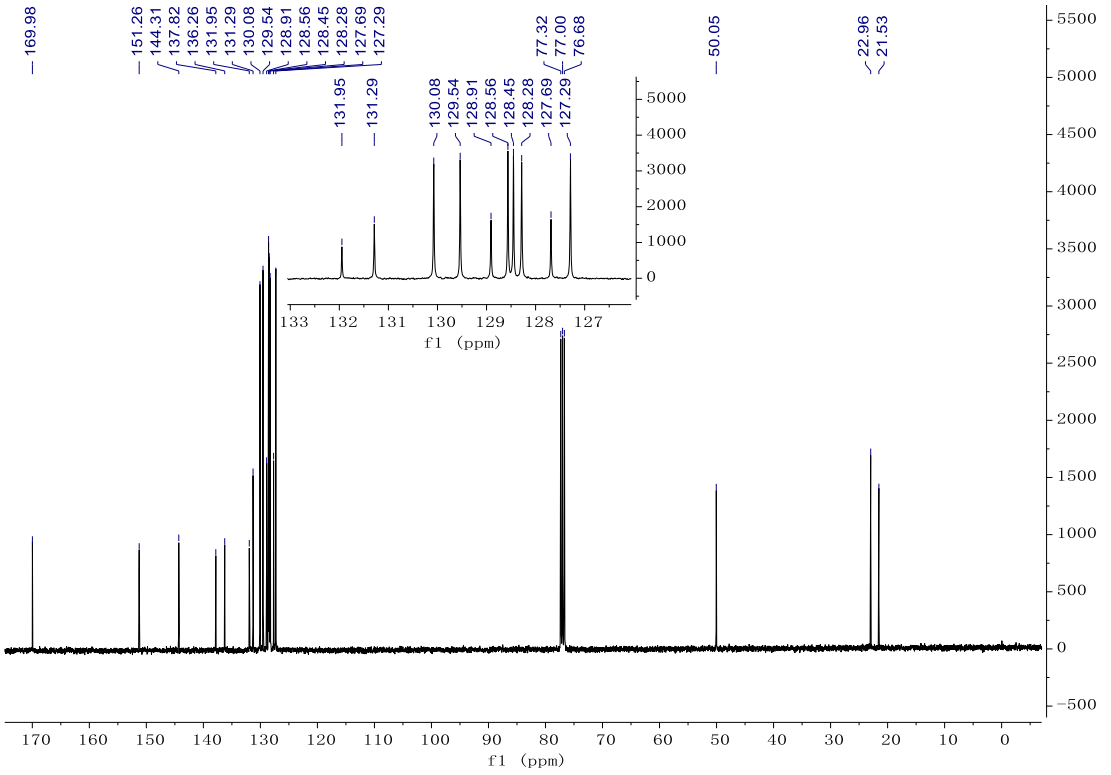
(*E*)-*N*-benzyl-*N*-(1-phenyl-2-(phenylsulfonyl)vinyl)acetamide (3aa)



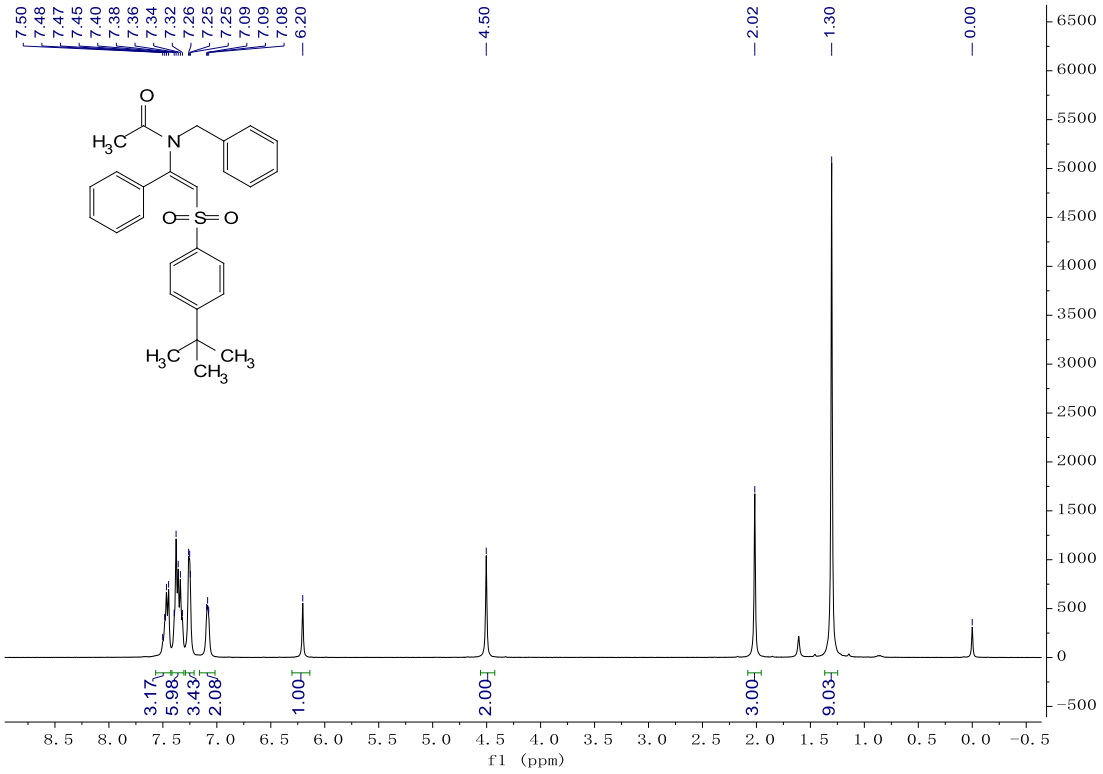


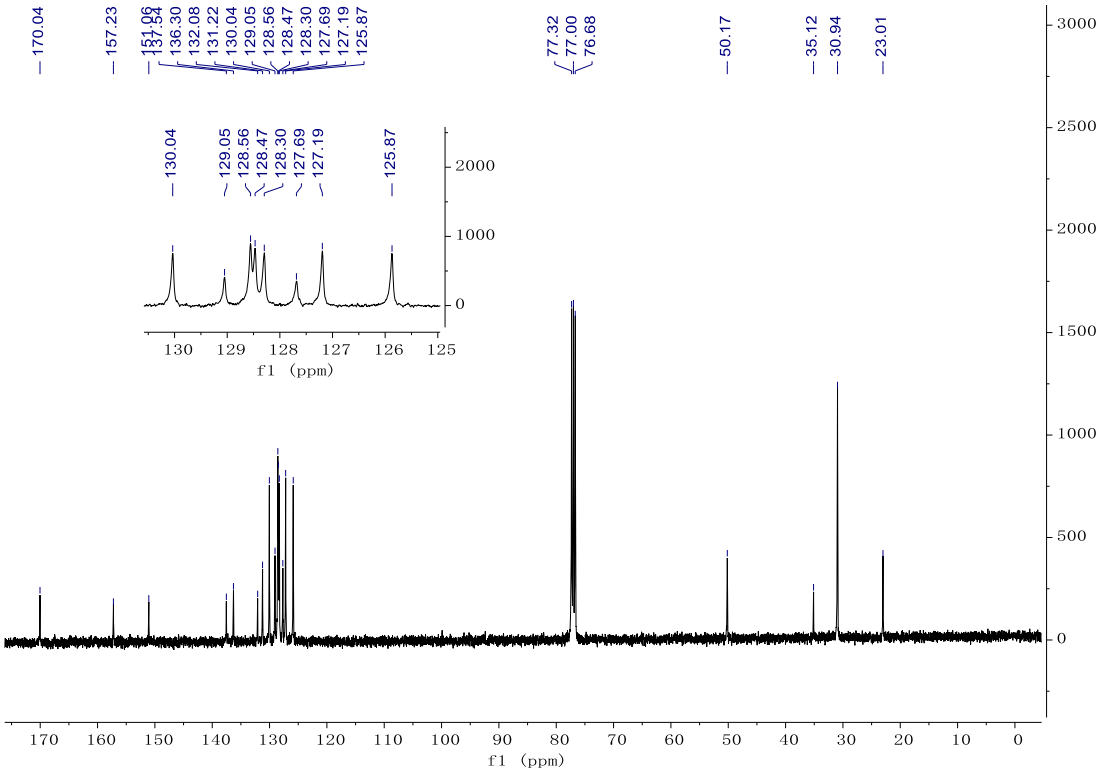
(*E*)-*N*-benzyl-*N*-(1-phenyl-2-tosylvinyl)acetamide (3ab)



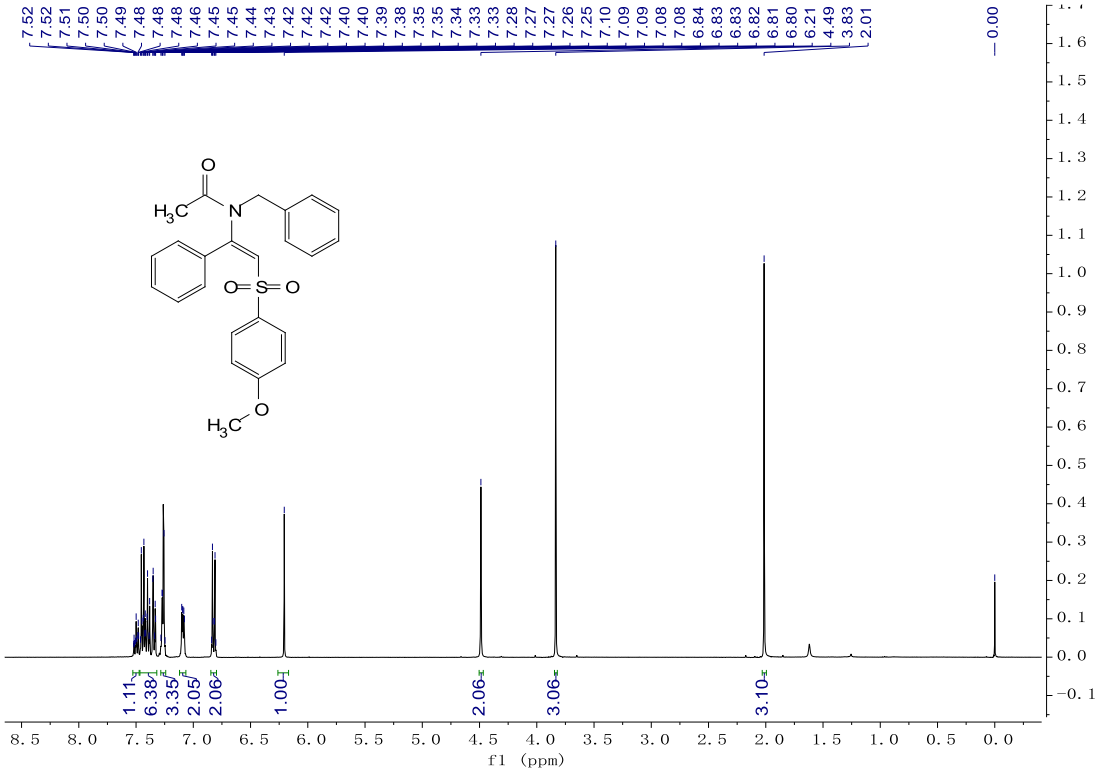


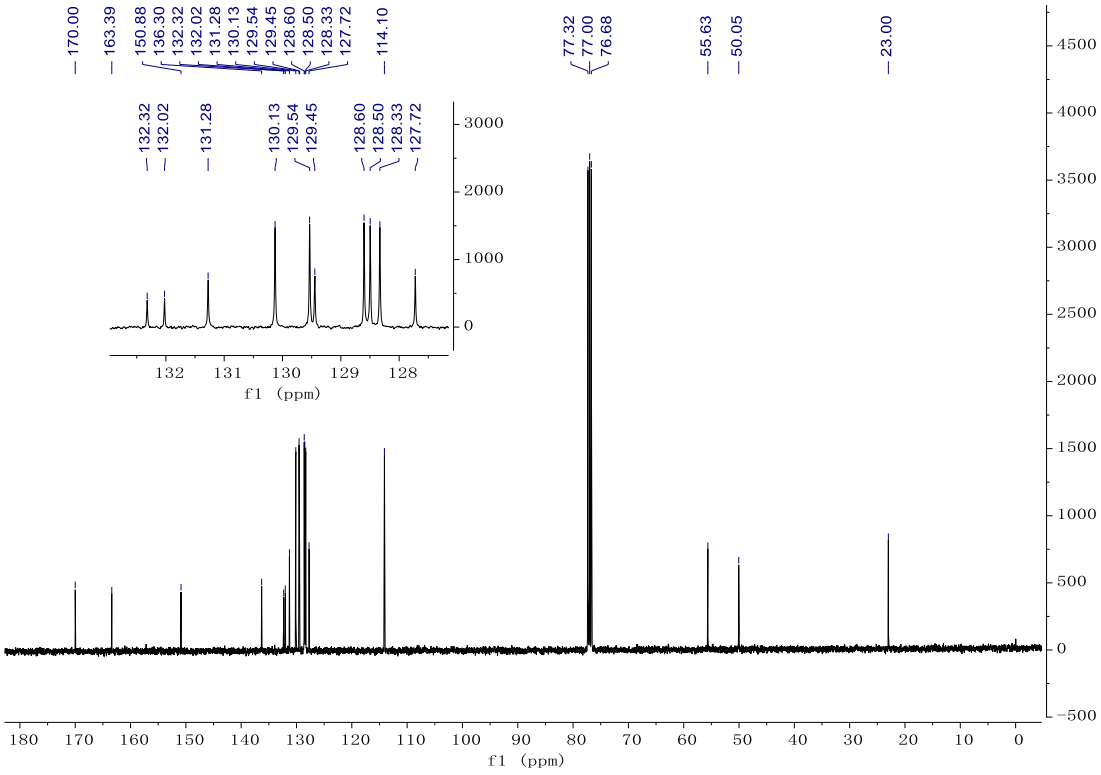
(*E*)-*N*-benzyl-*N*-(2-((4-(*tert*-butyl)phenyl)sulfonyl)-1-phenylvinyl)acetamide (3ac)



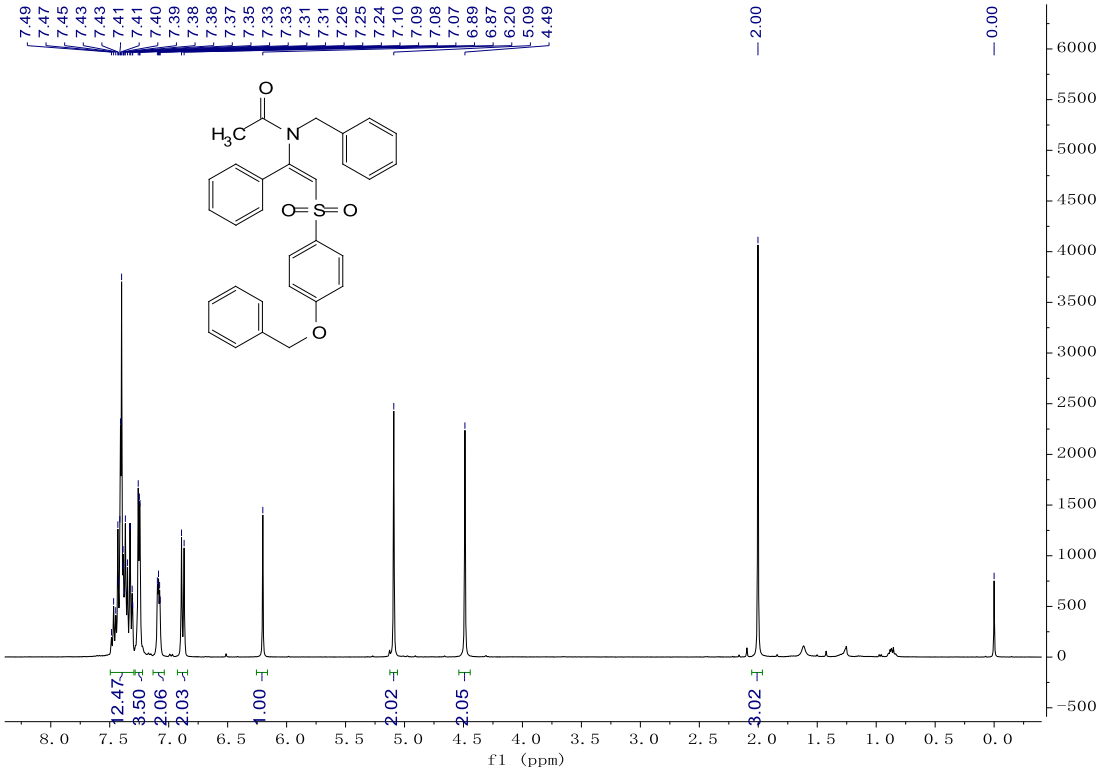


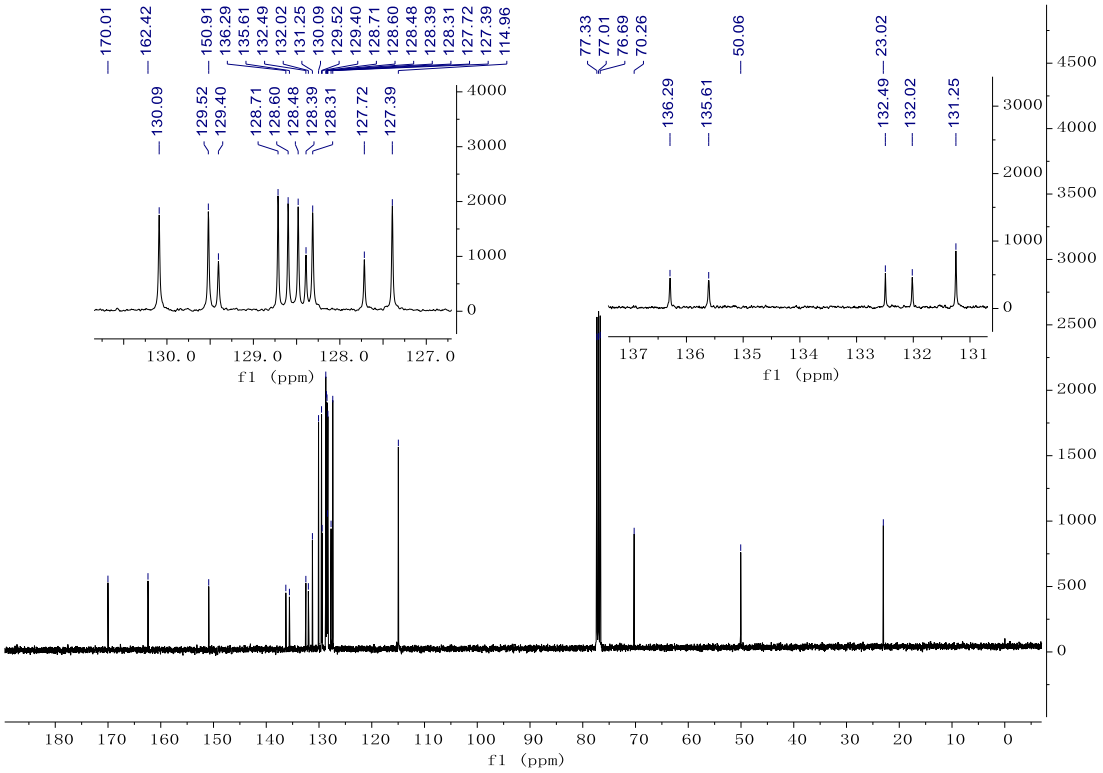
(*E*)-*N*-benzyl-*N*-(2-((4-methoxyphenyl)sulfonyl)-1-phenylvinyl)acetamide (3ad)



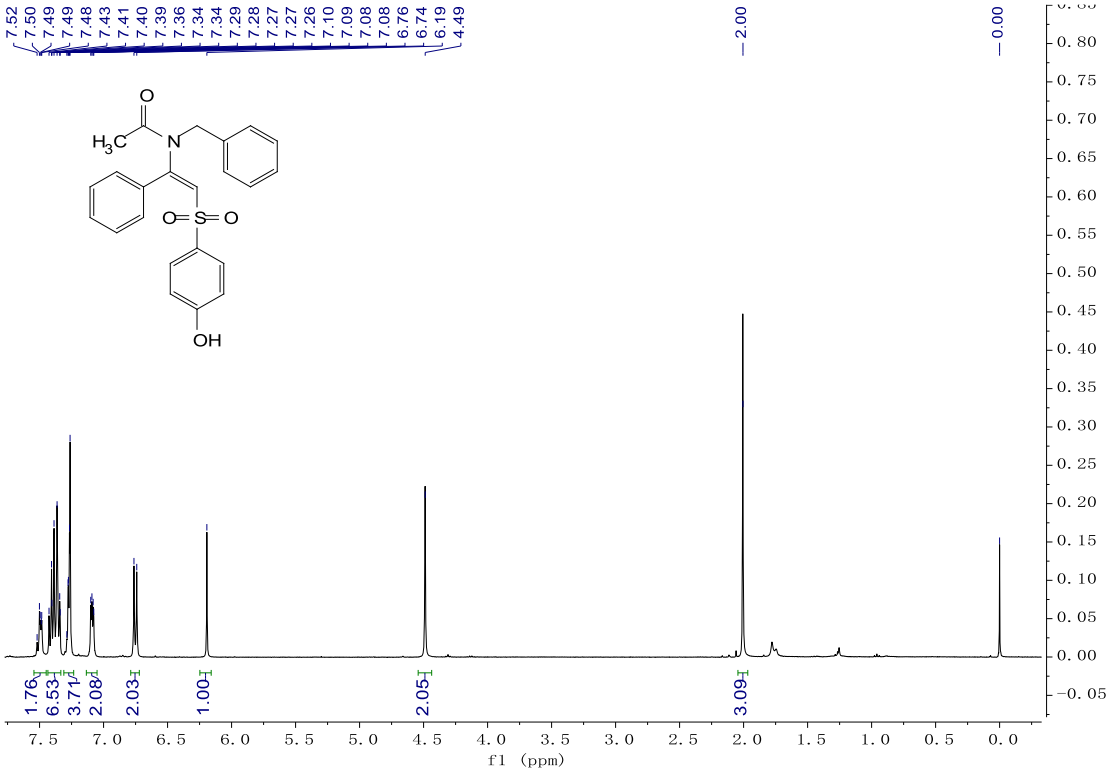


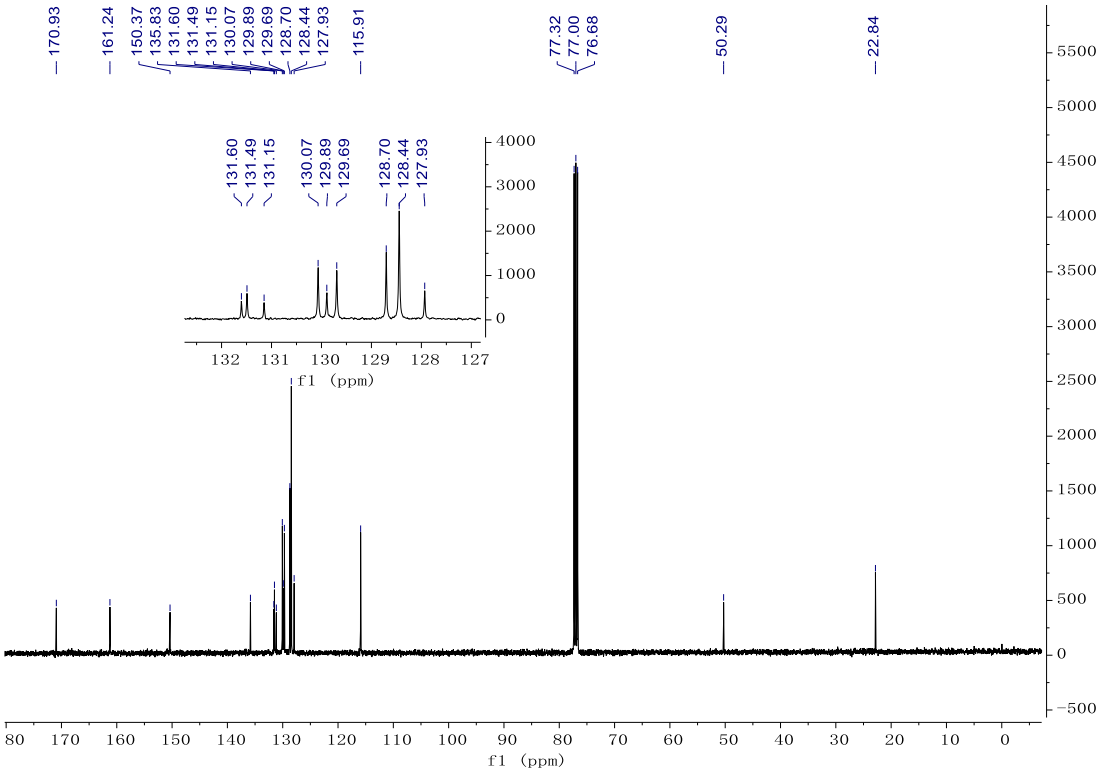
(*E*)-*N*-benzyl-*N*-(2-((4-(benzyloxy)phenyl)sulfonyl)-1-phenylvinyl)acetamide (3ae)



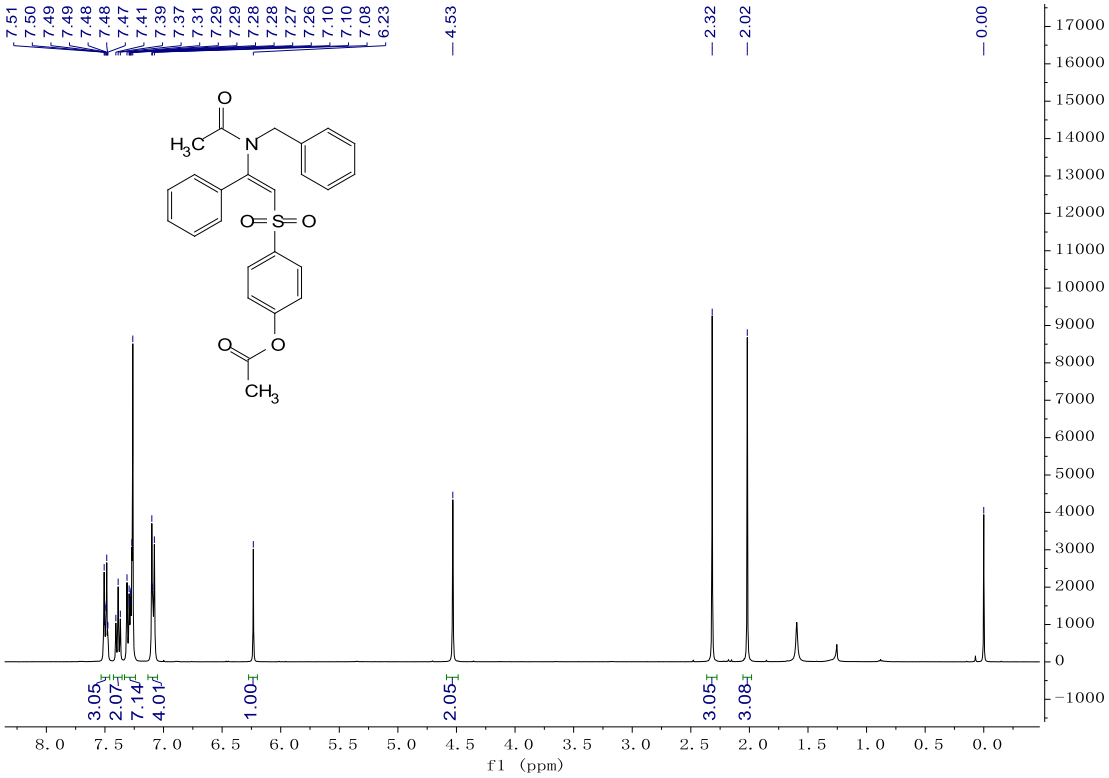


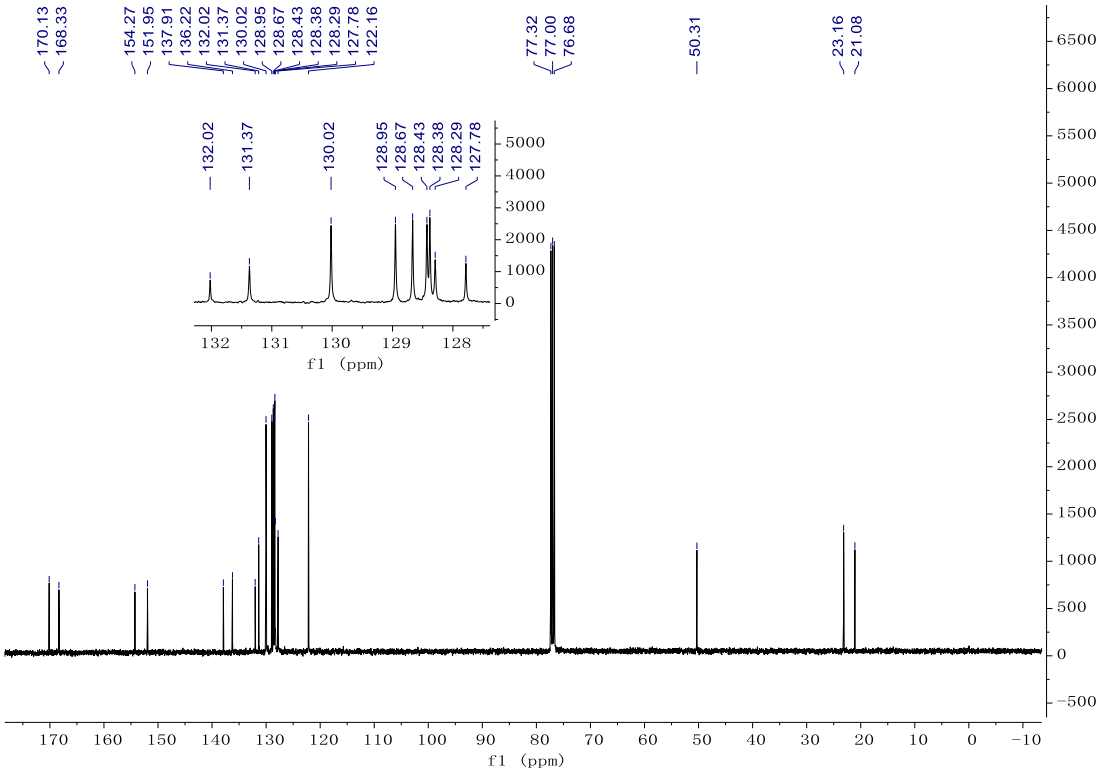
(*E*)-*N*-benzyl-*N*-(2-((4-hydroxyphenyl)sulfonyl)-1-phenylvinyl)acetamide (3af)



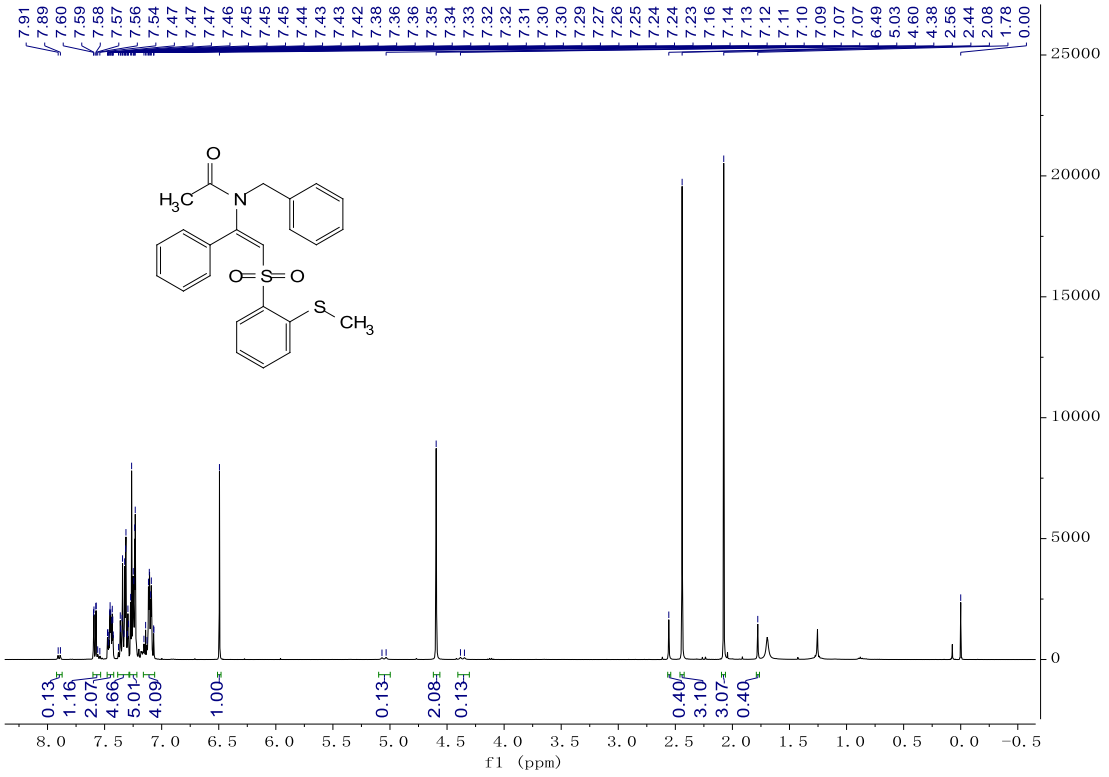


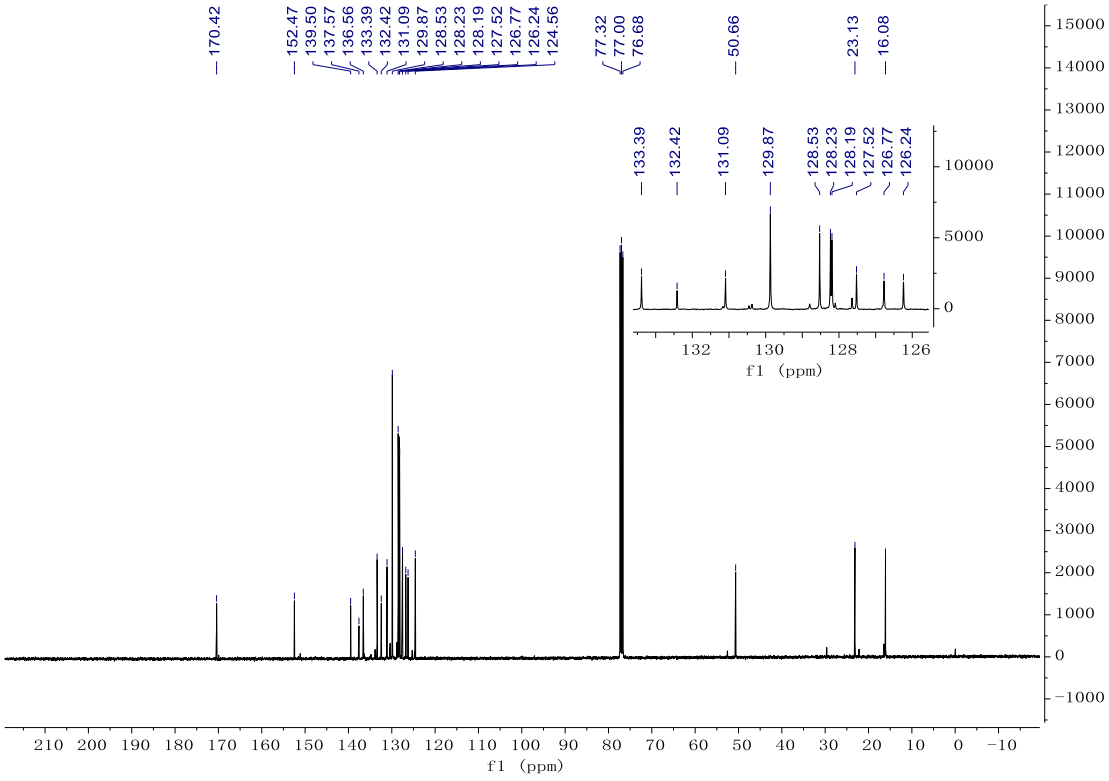
(*E*)-4-((2-(*N*-benzylacetamido)-2-phenylvinyl)sulfonyl)phenyl acetate (3ag)



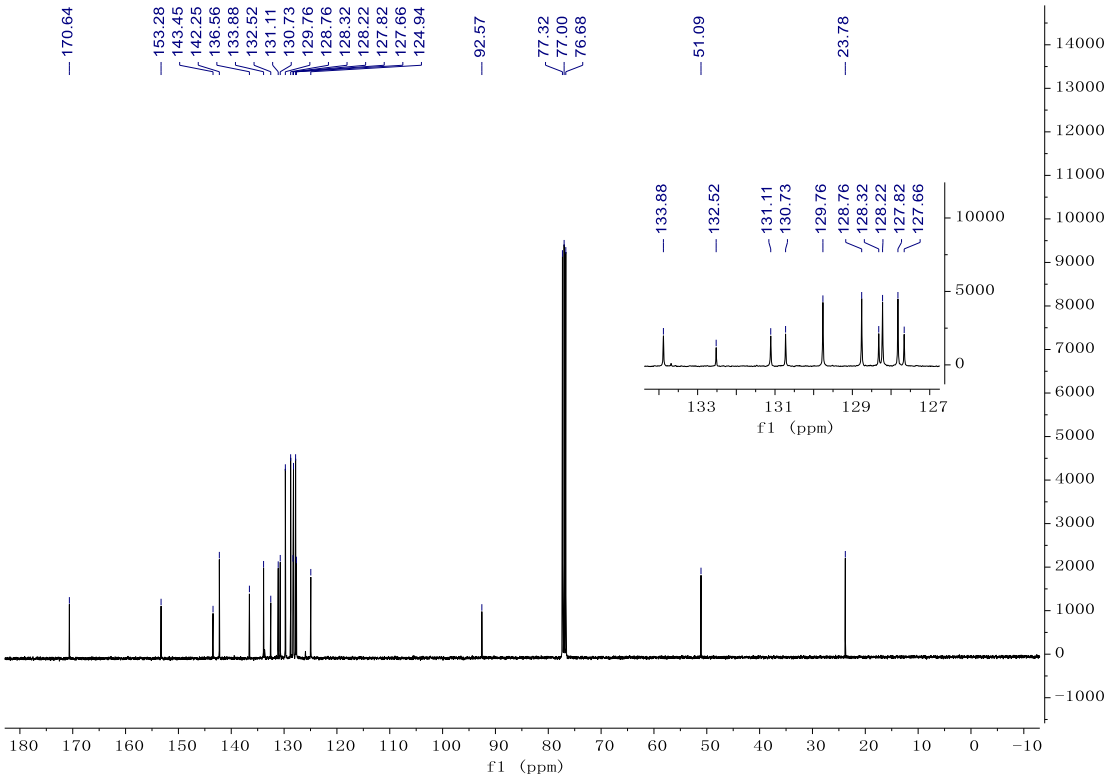


(*E*)-*N*-benzyl-*N*-(2-((2-methylthiophenyl)sulfonyl)-1-phenylvinyl)acetamide (3ah)

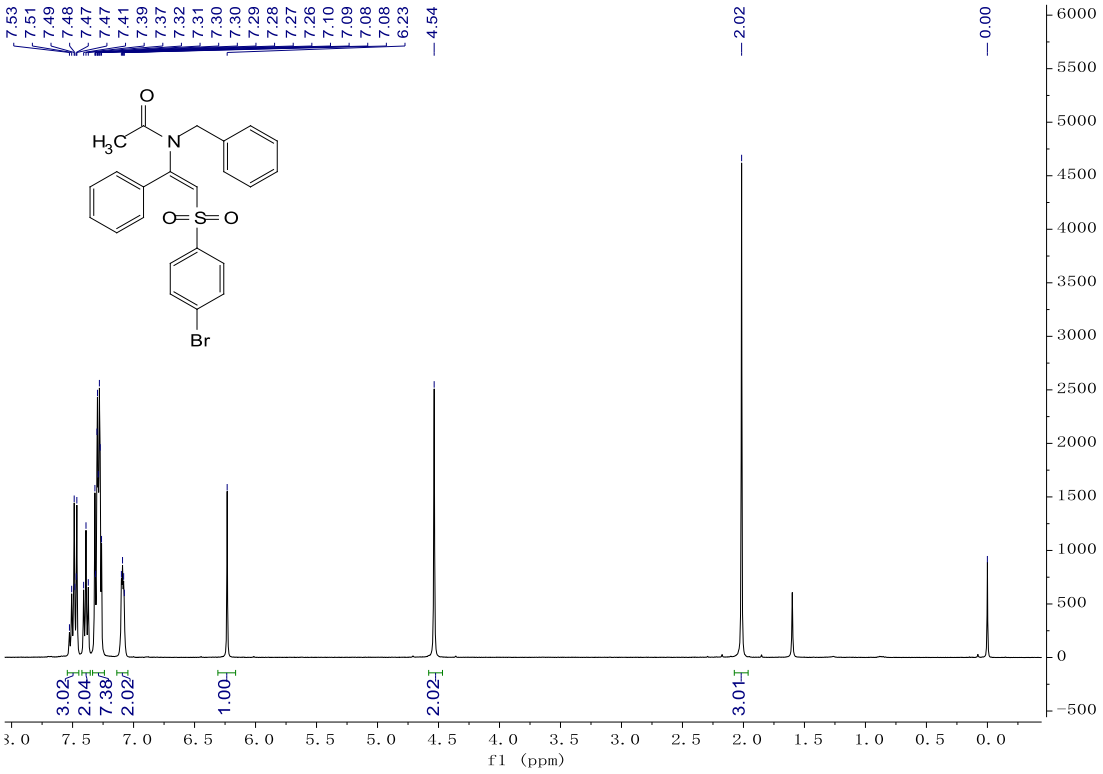


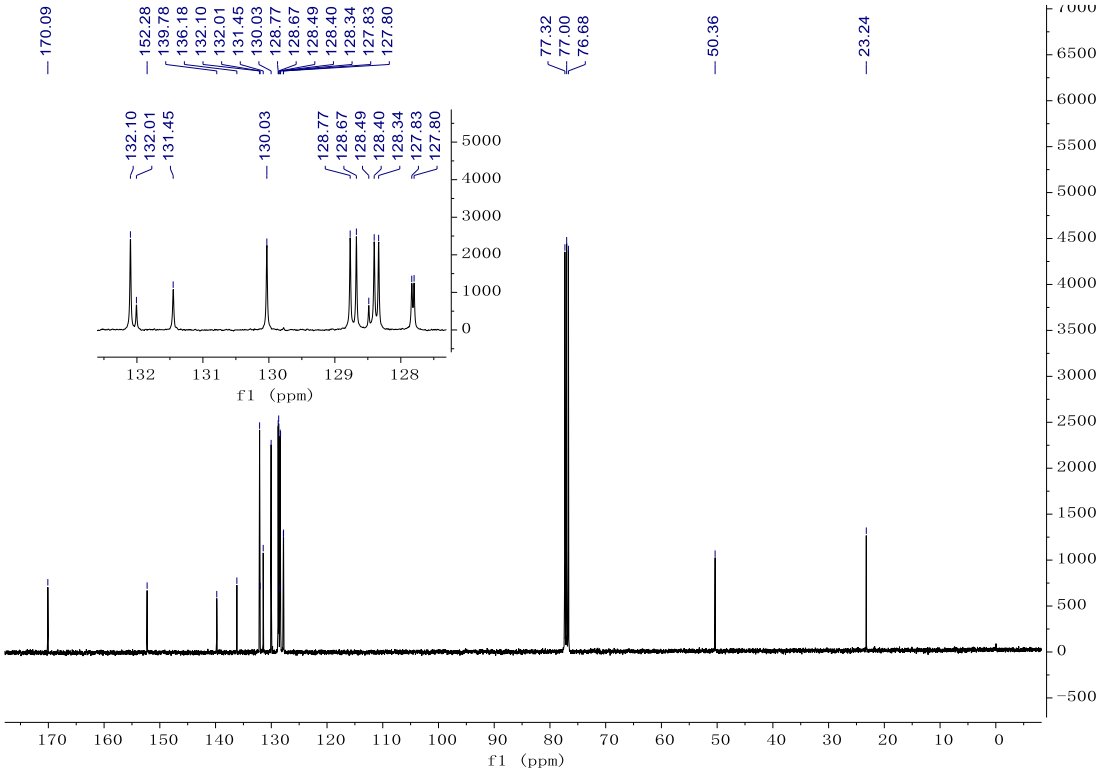


(*E*)-*N*-benzyl-*N*-(2-((2-iodophenyl)sulfonyl)-1-phenylvinyl)acetamide (3ai)

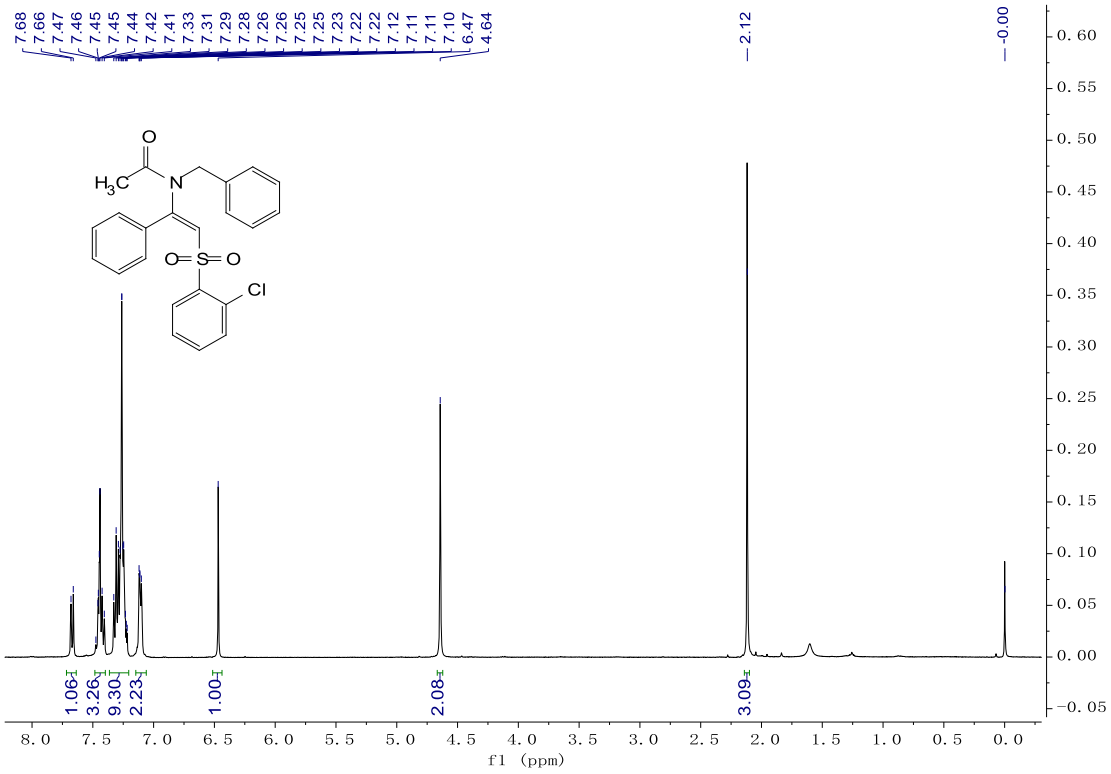


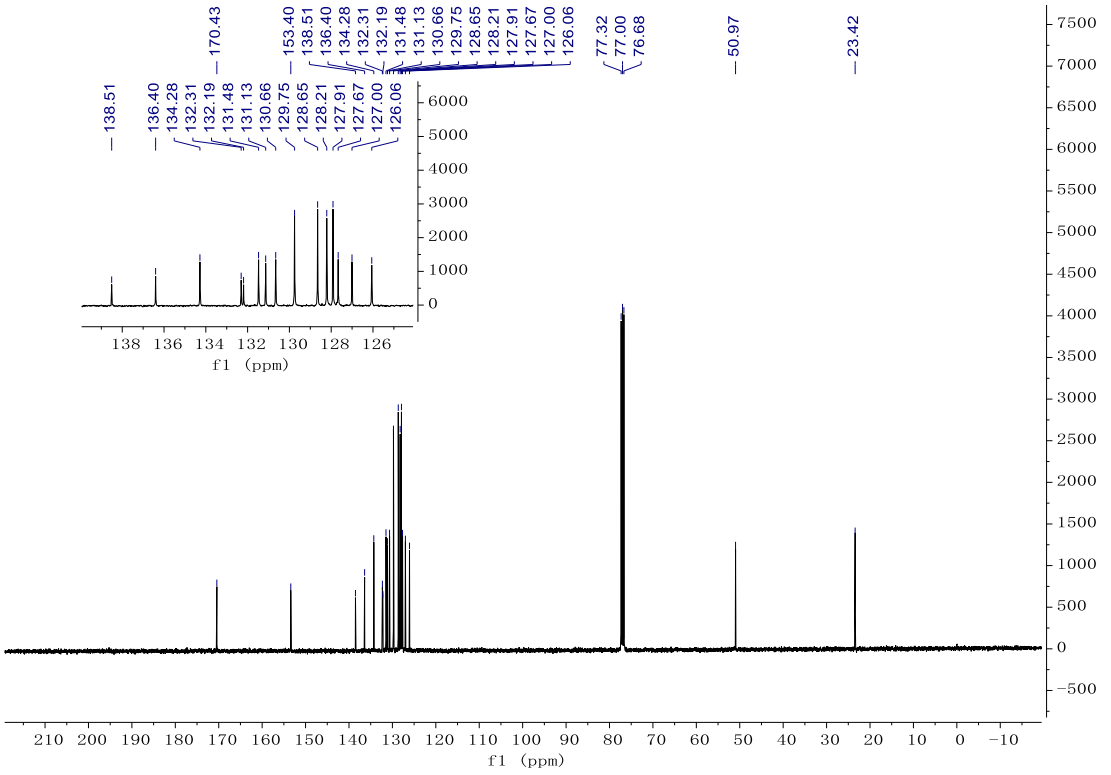
(*E*)-*N*-benzyl-*N*-(2-((4-bromophenyl)sulfonyl)-1-phenylvinyl)acetamide (3aj)



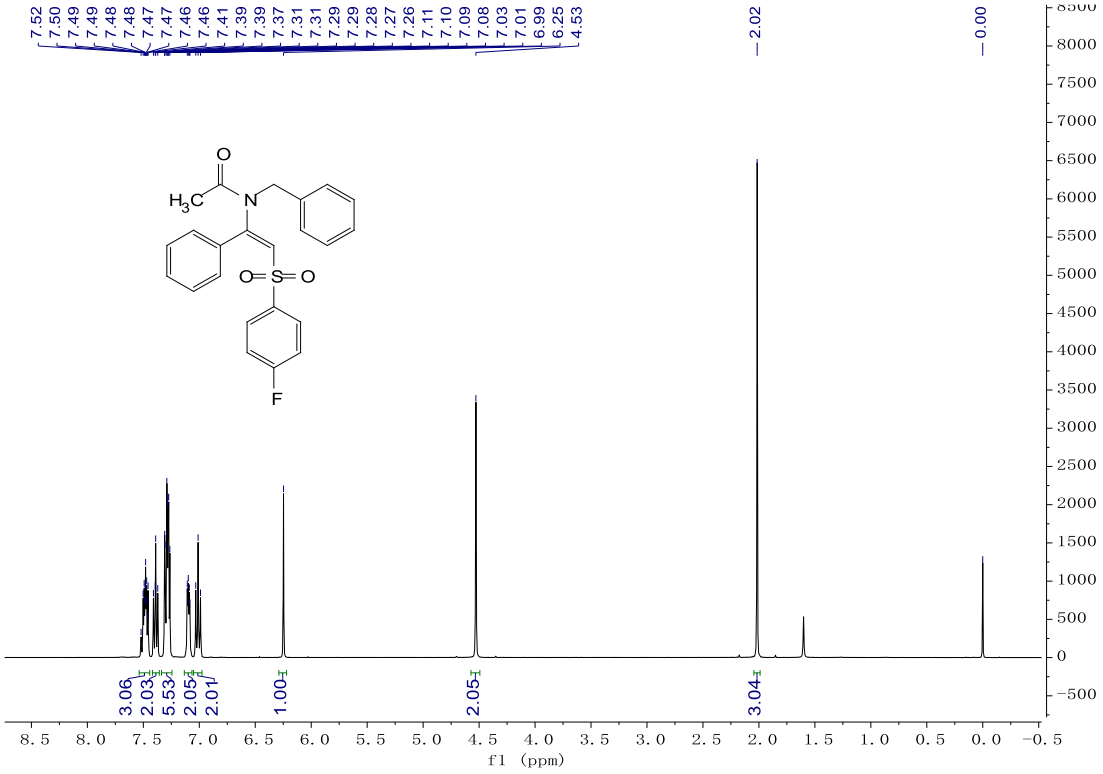


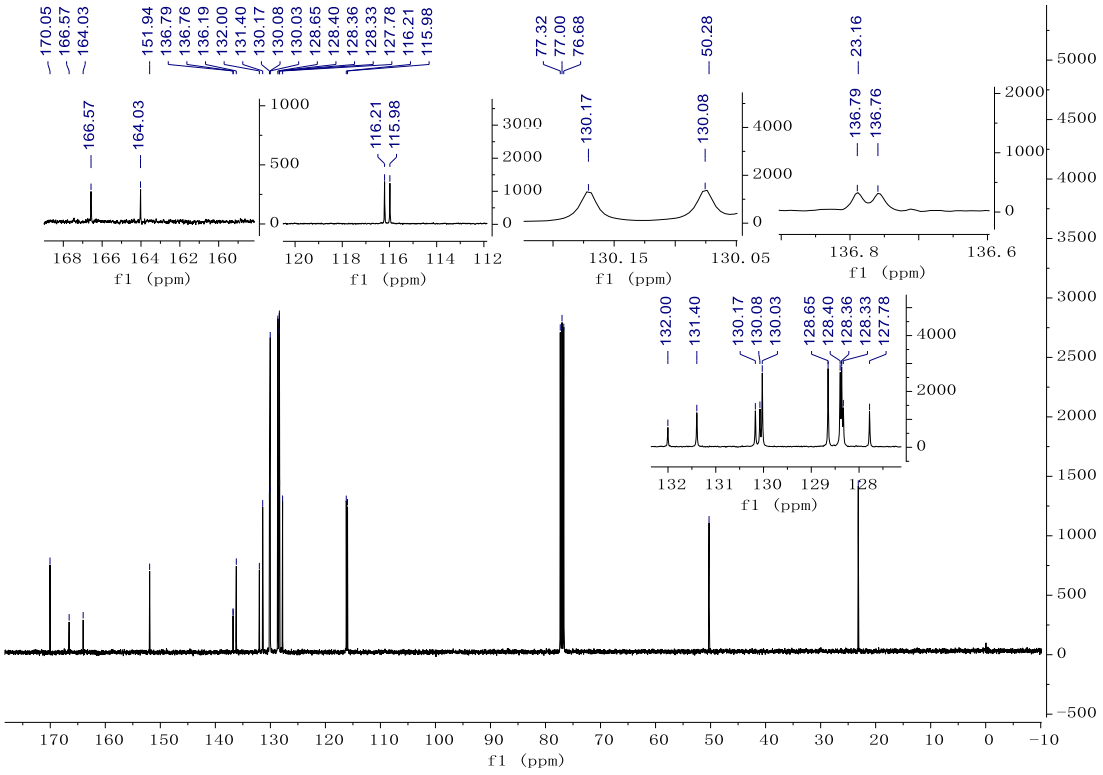
(*E*)-*N*-benzyl-*N*-(2-((2-chlorophenyl)sulfonyl)-1-phenylvinyl)acetamide (3ak)

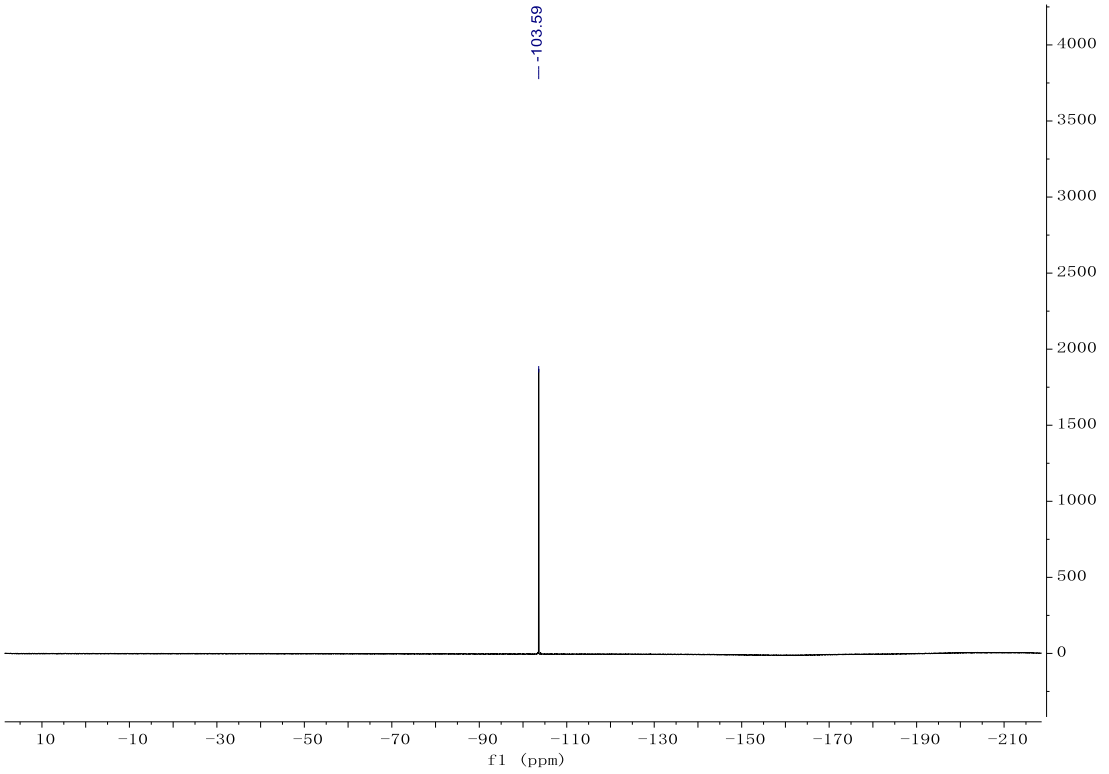




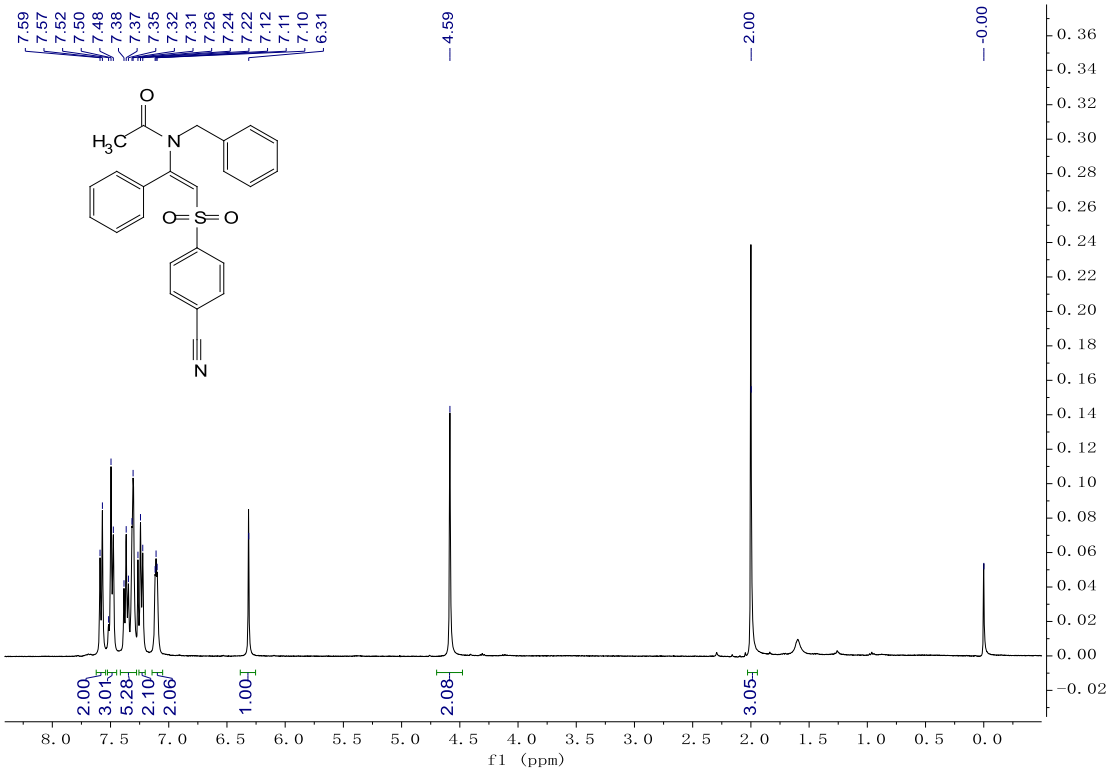
(*E*)-*N*-benzyl-*N*-(2-((4-fluorophenyl)sulfonyl)-1-phenylvinyl)acetamide (3al)

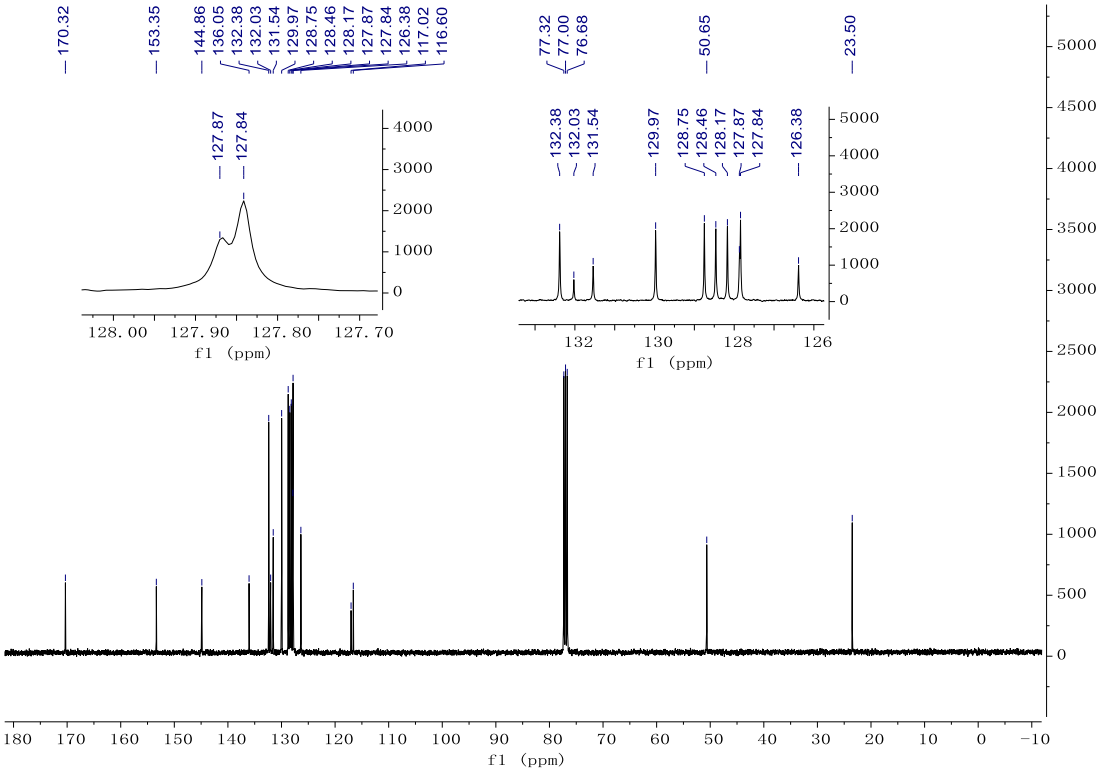




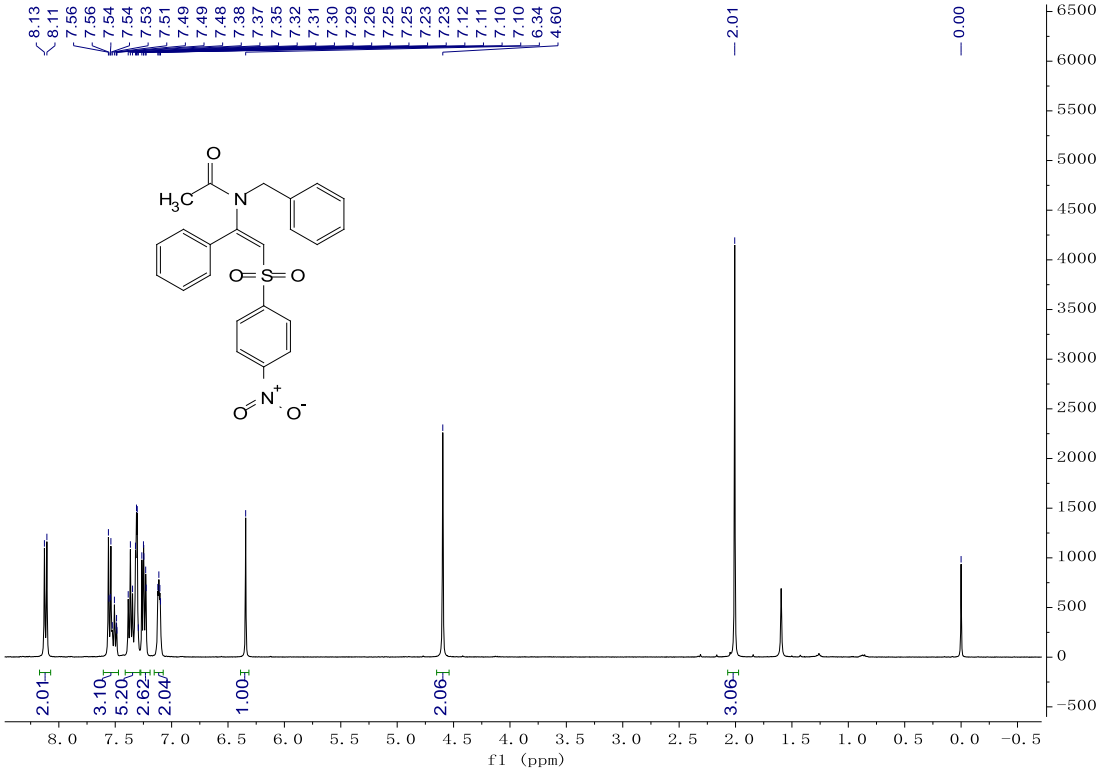


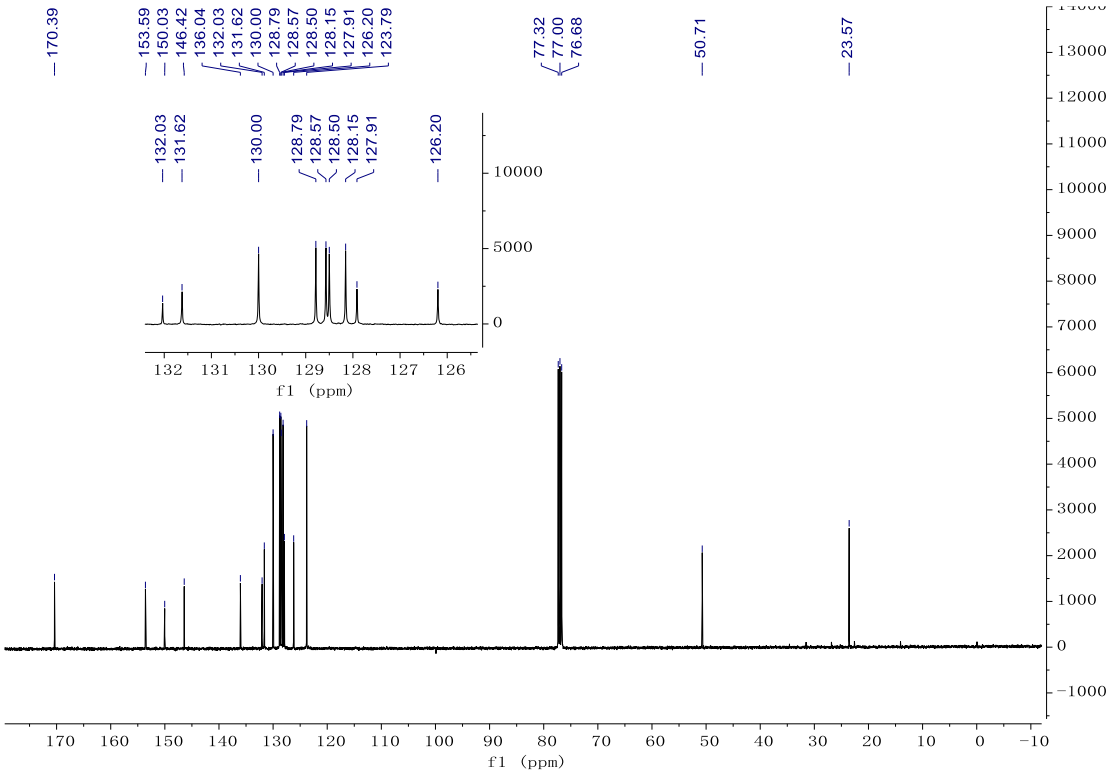
(*E*)-*N*-benzyl-*N*-(2-((4-cyanophenyl)sulfonyl)-1-phenylvinyl)acetamide (3am)



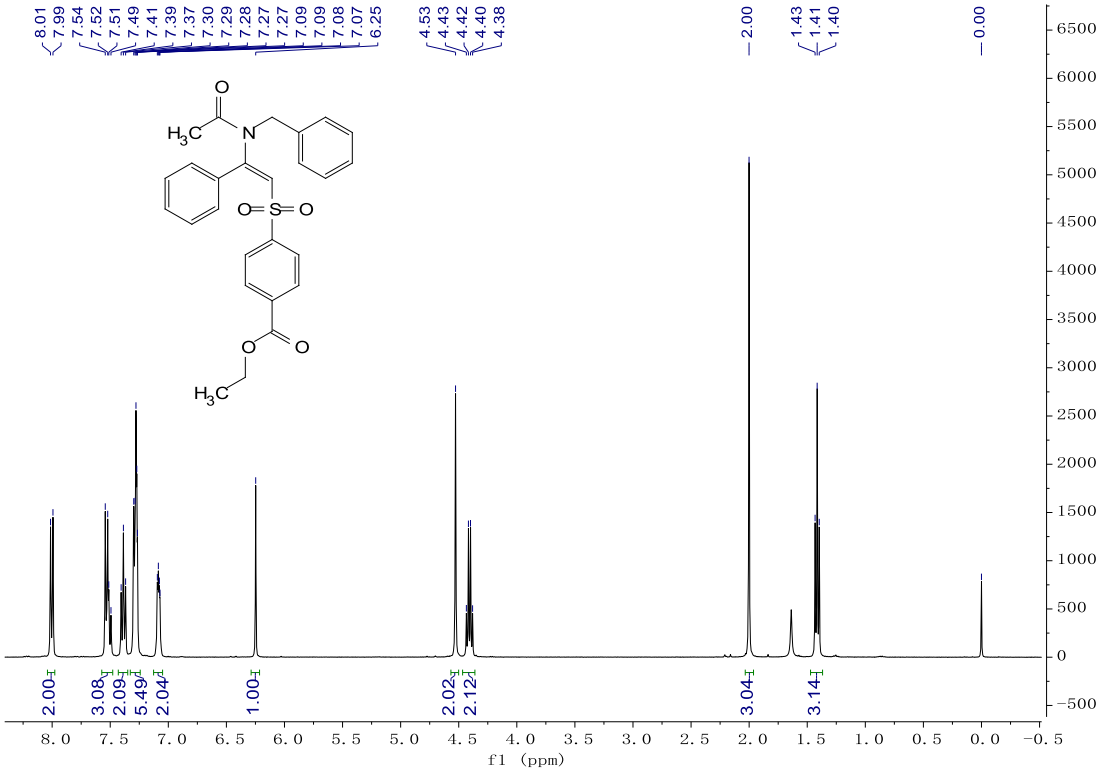


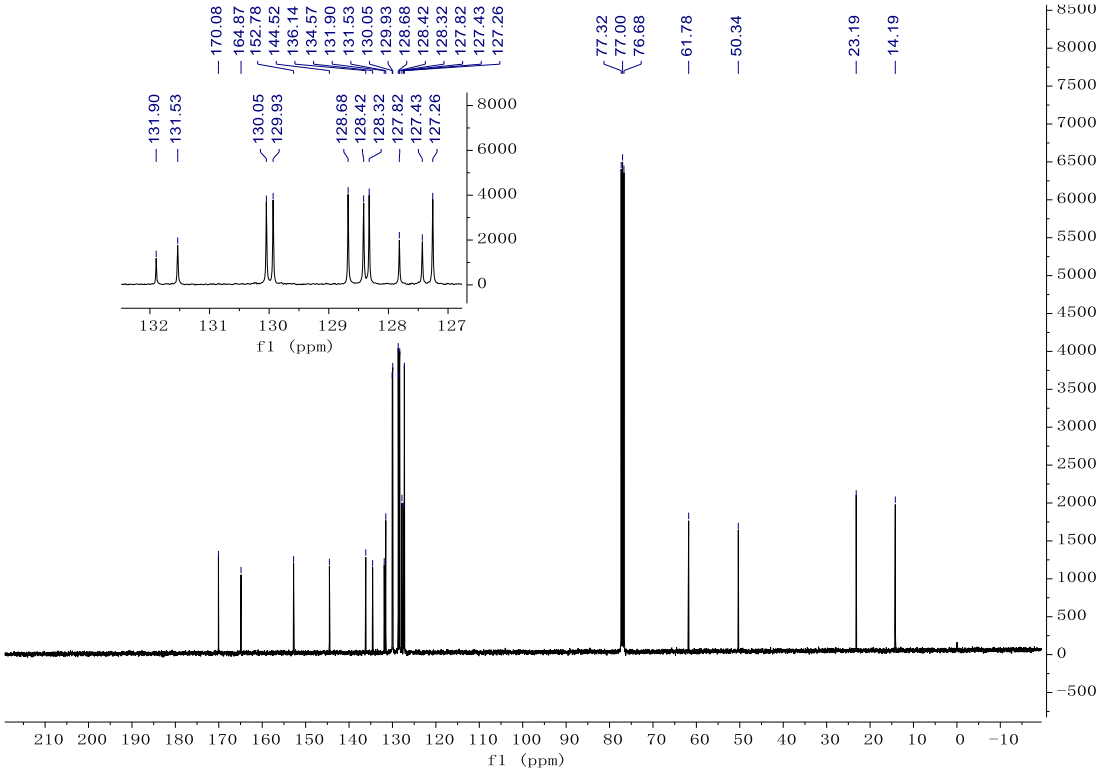
(*E*)-*N*-benzyl-*N*-(2-((4-nitrophenyl)sulfonyl)-1-phenylvinyl)acetamide (3an):



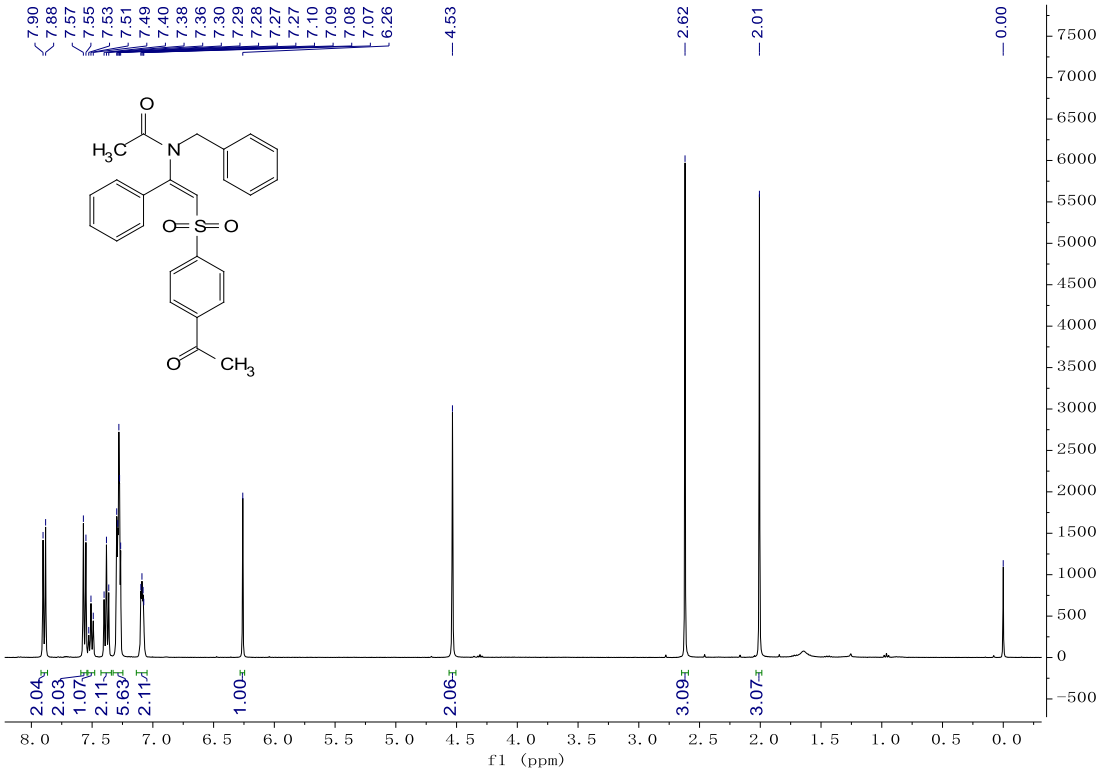


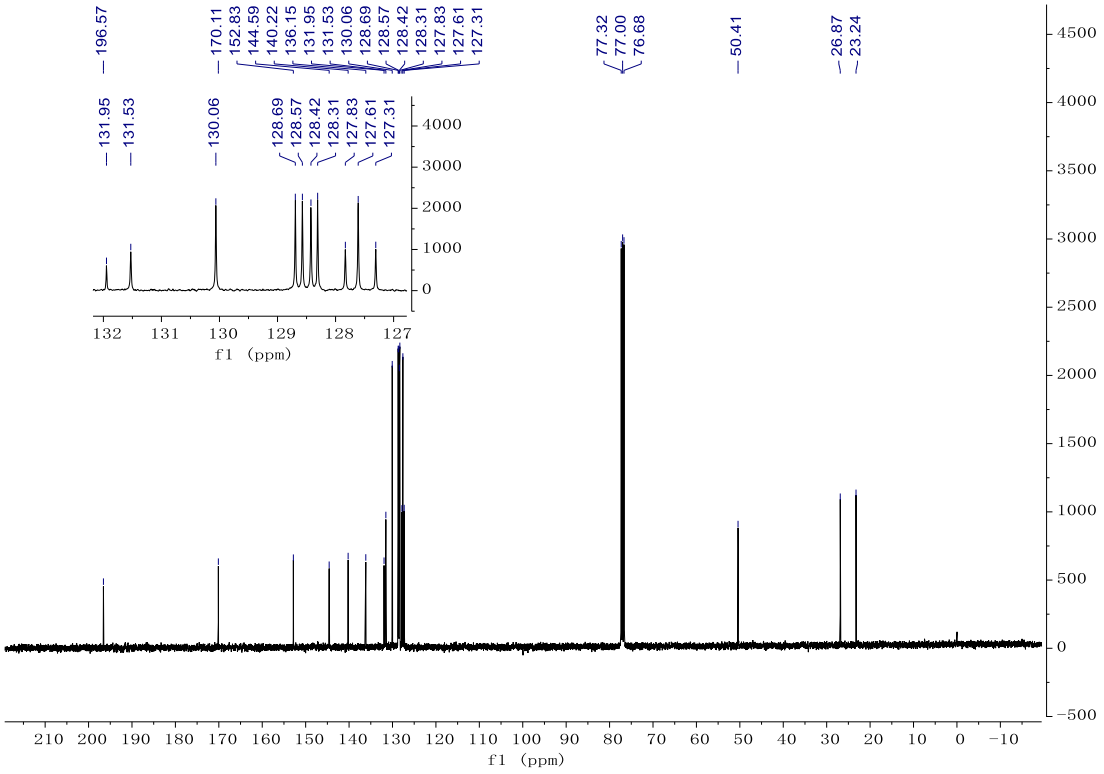
ethyl (*E*)-4-((2-(*N*-benzylacetamido)-2-phenylvinyl)sulfonyl)benzoate (3ao)



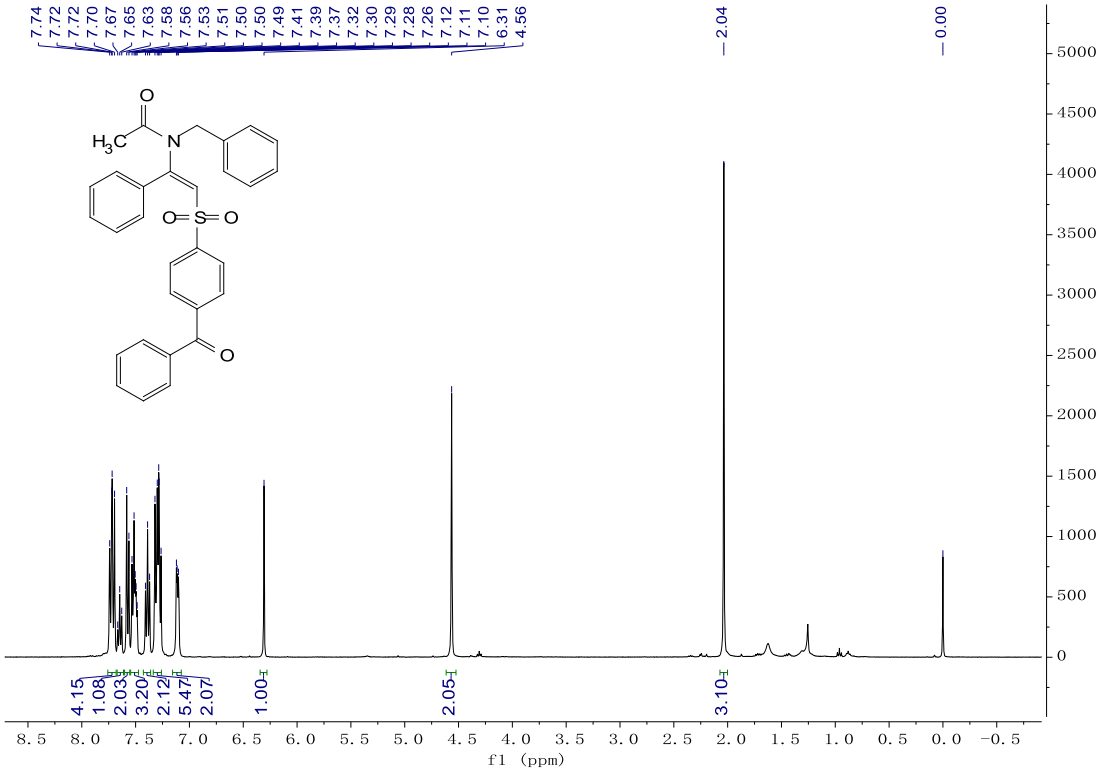


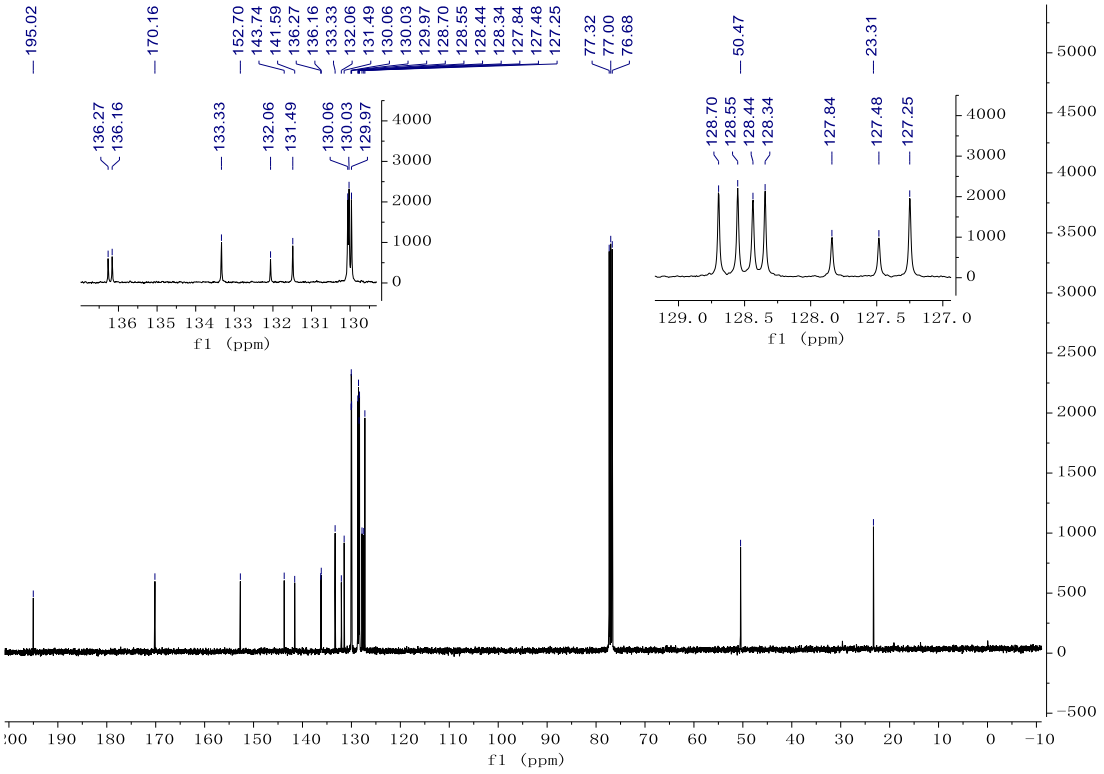
(*E*)-*N*-(2-((4-acetylphenyl)sulfonyl)-1-phenylvinyl)-*N*-benzylacetamide (3ap)



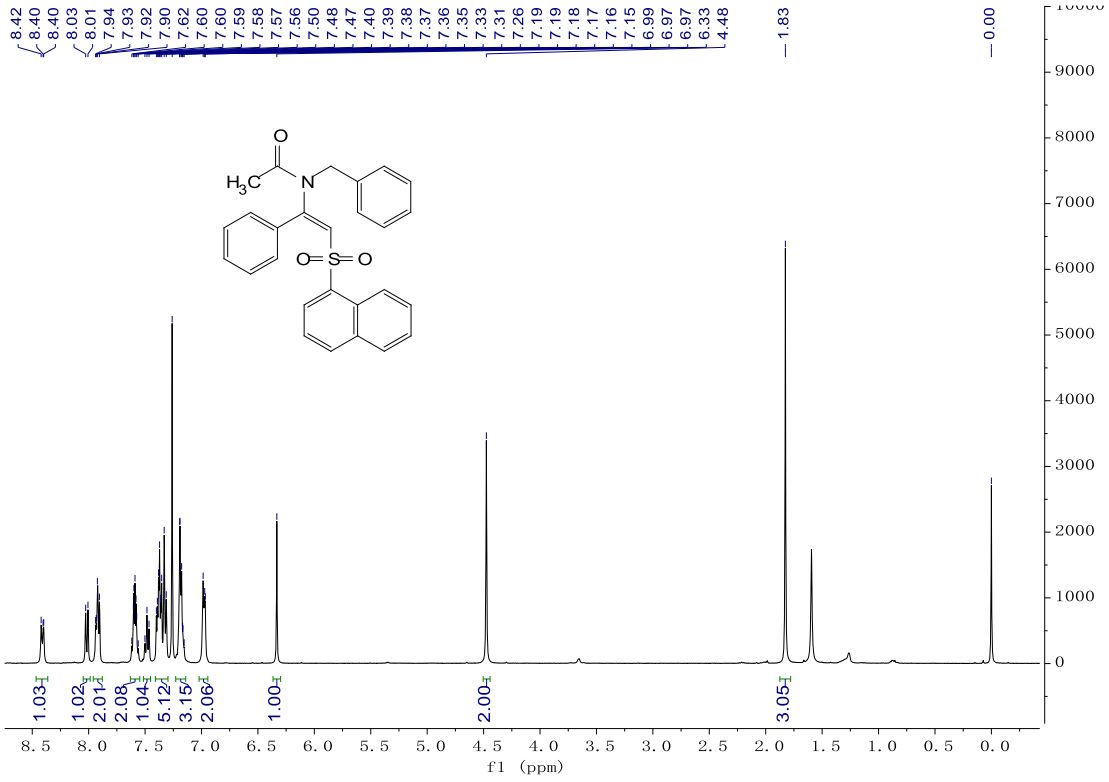


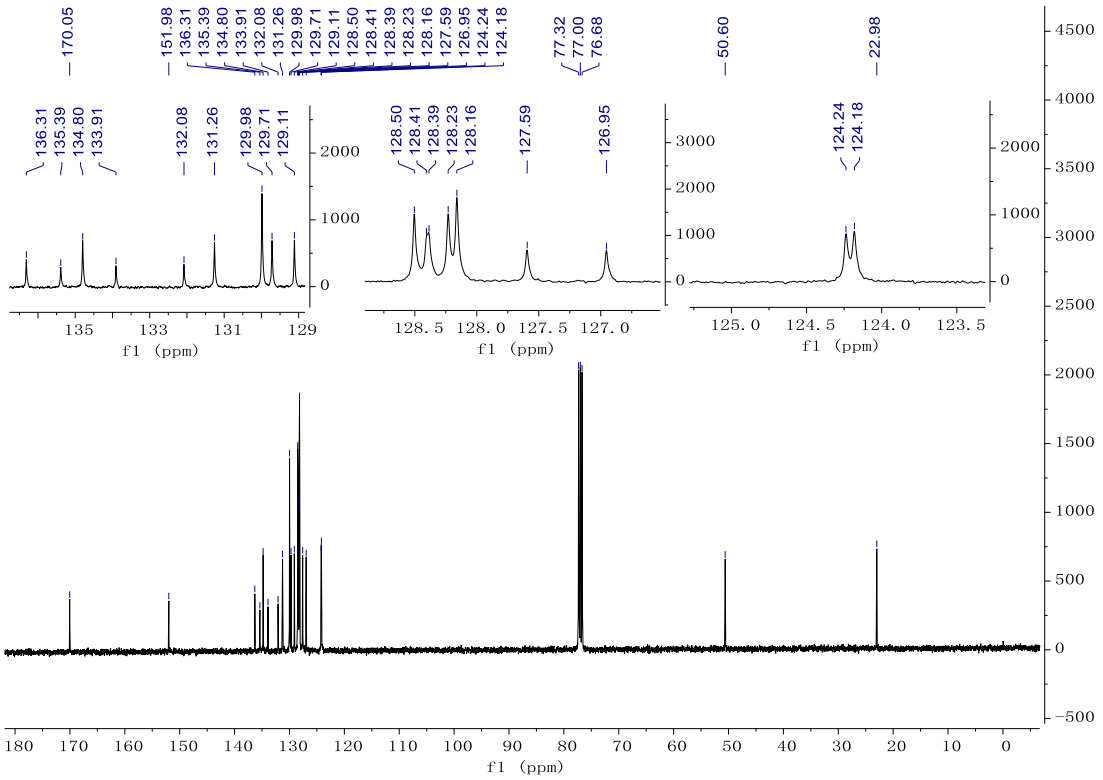
(*E*)-*N*-(2-((4-benzoylphenyl)sulfonyl)-1-phenylvinyl)-*N*-benzylacetamide (3aq)



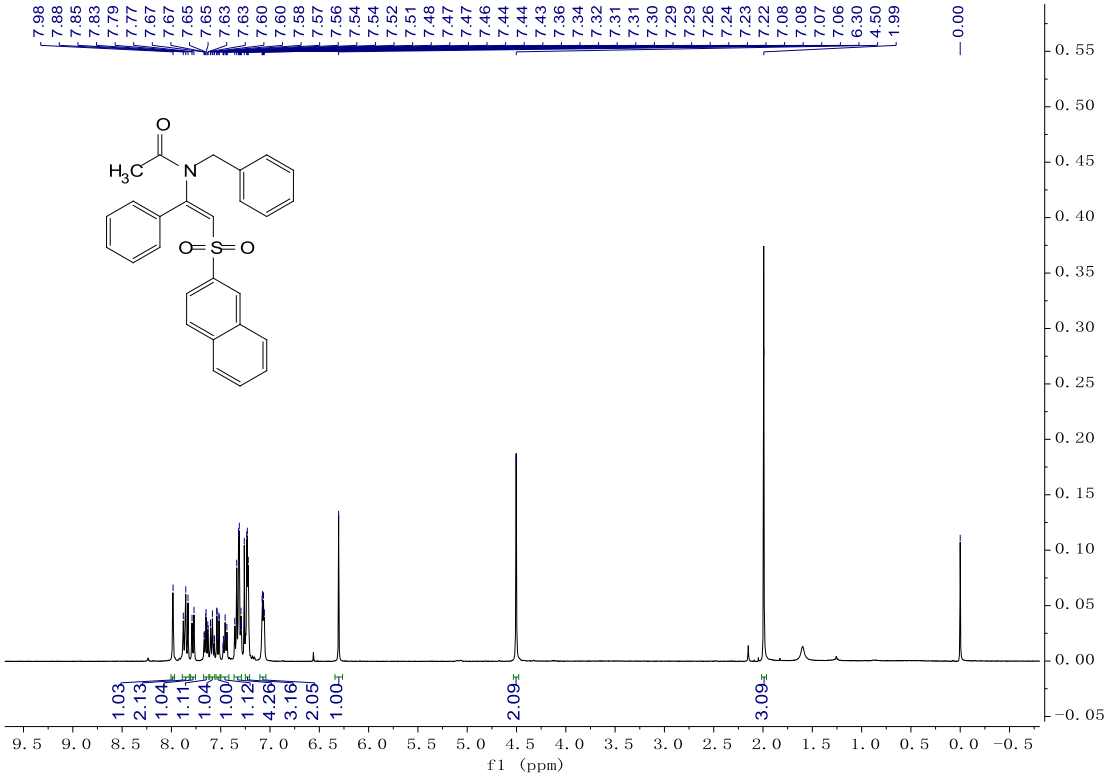


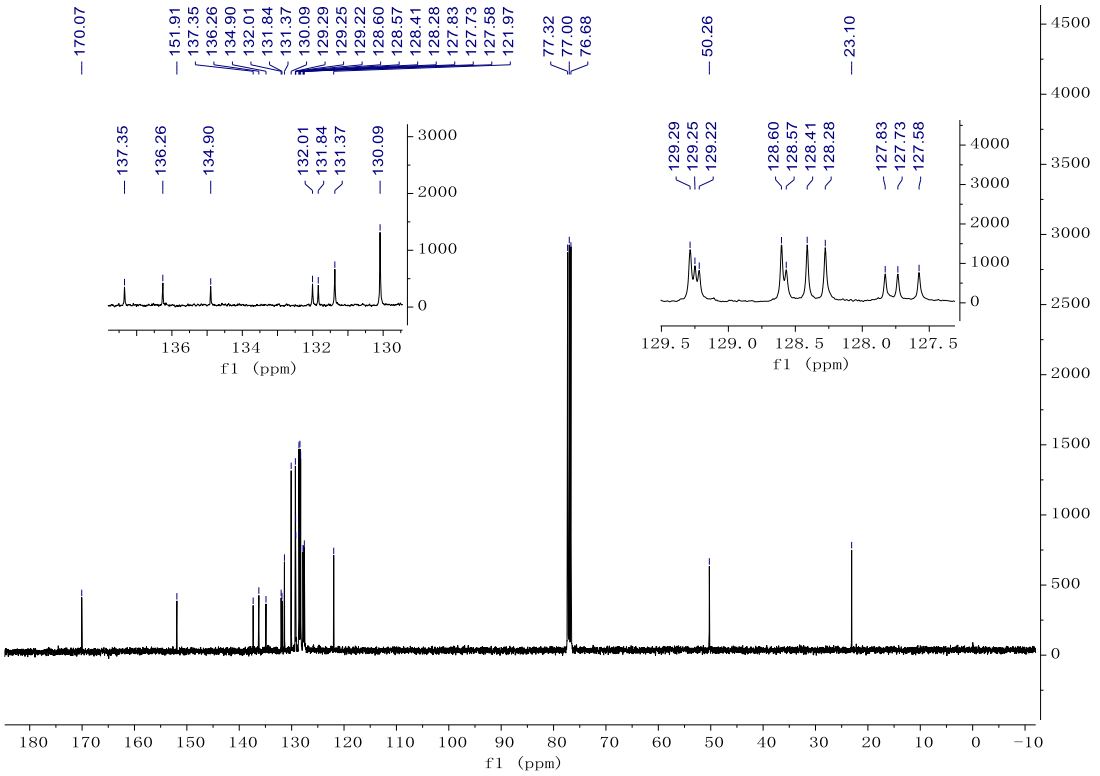
(*E*)-*N*-benzyl-*N*-(2-(naphthalen-1-ylsulfonyl)-1-phenylvinyl)acetamide (3ar)



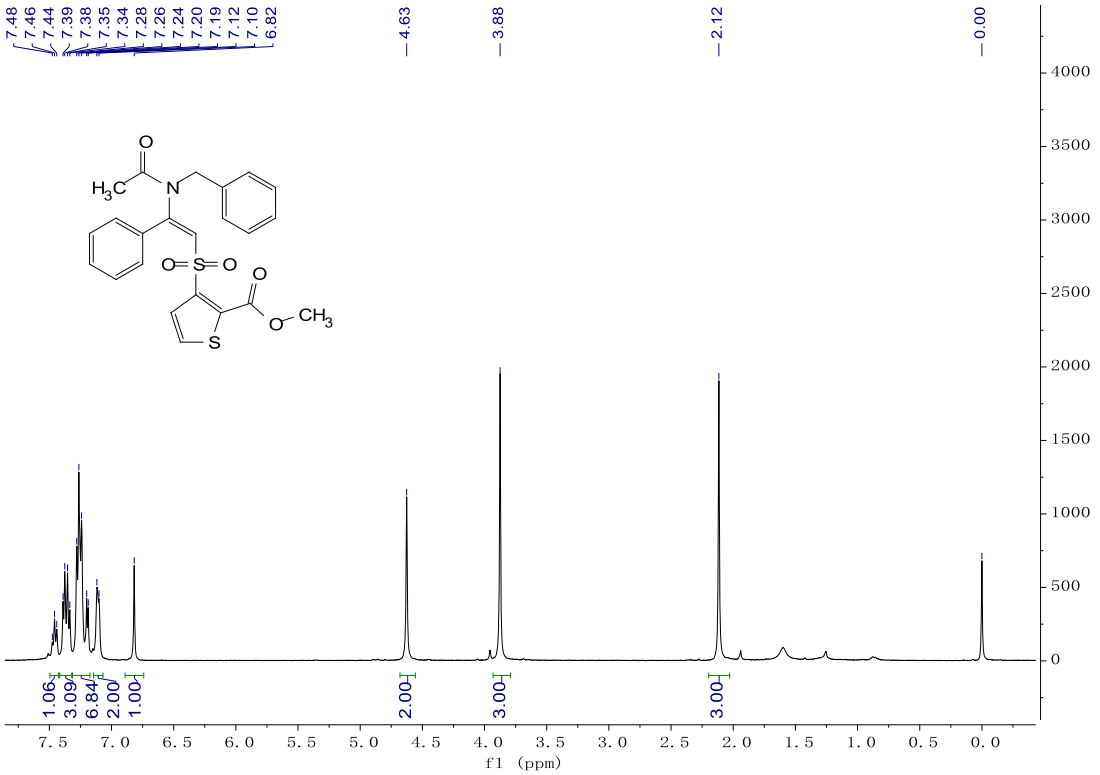


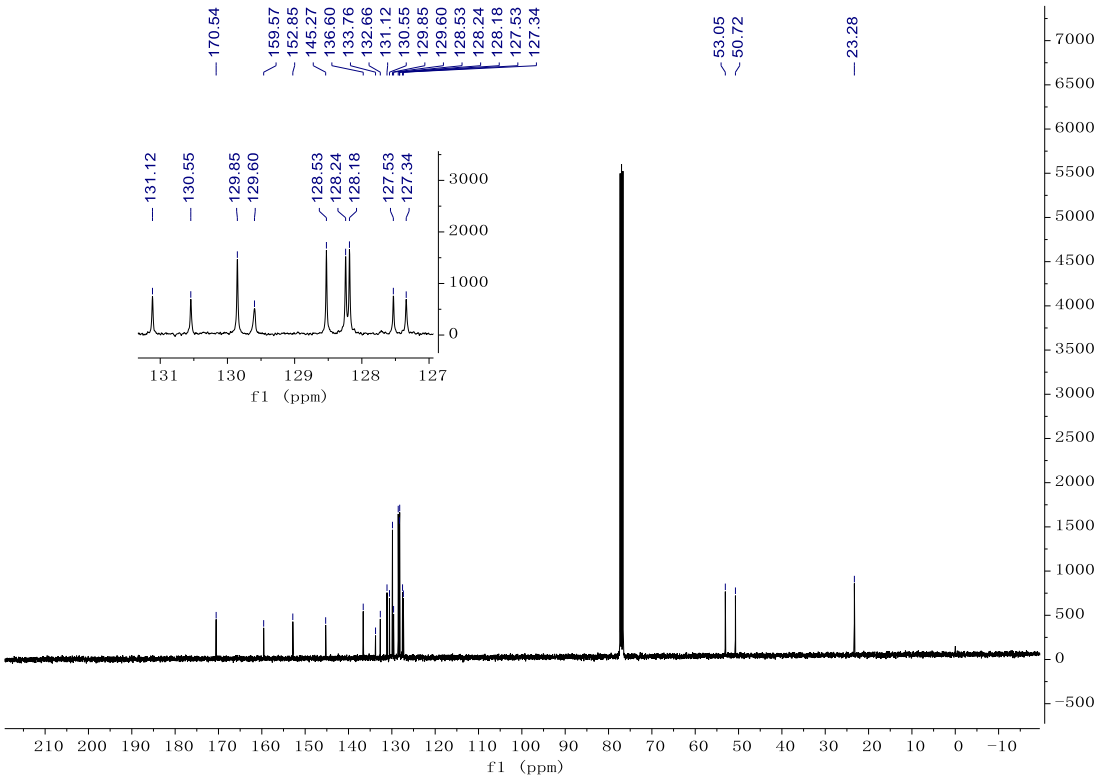
(*E*)-*N*-benzyl-*N*-(2-(naphthalen-2-ylsulfonyl)-1-phenylvinyl)acetamide (3as)



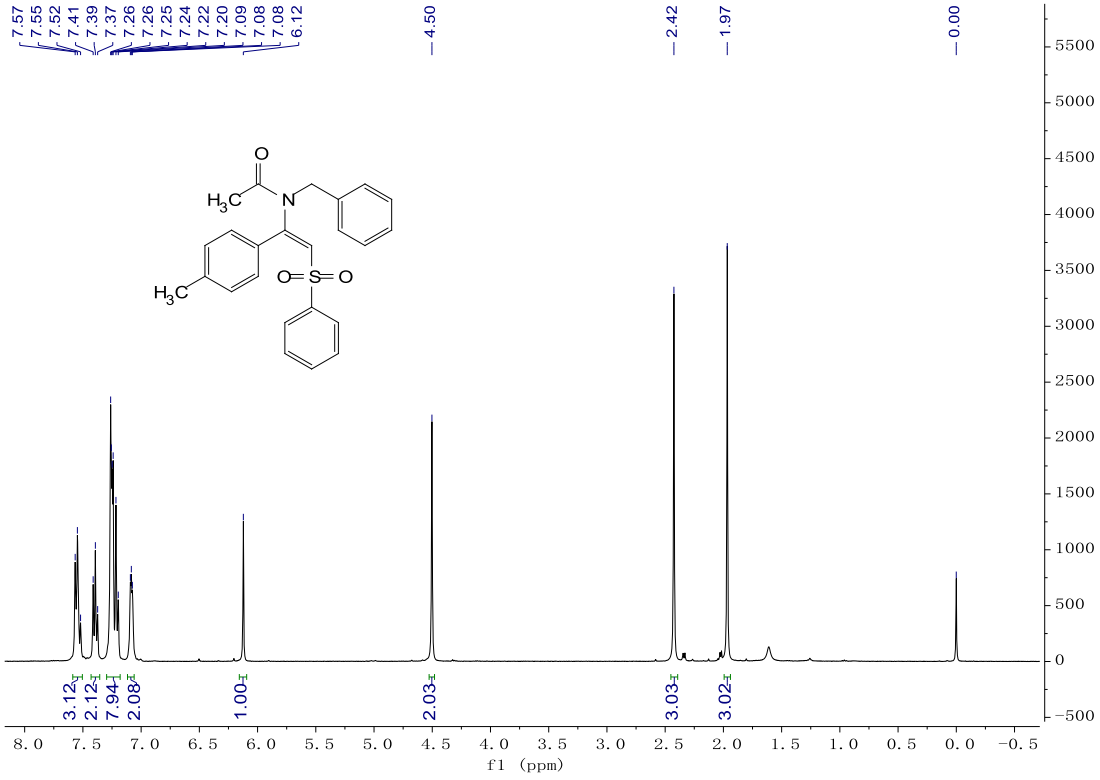


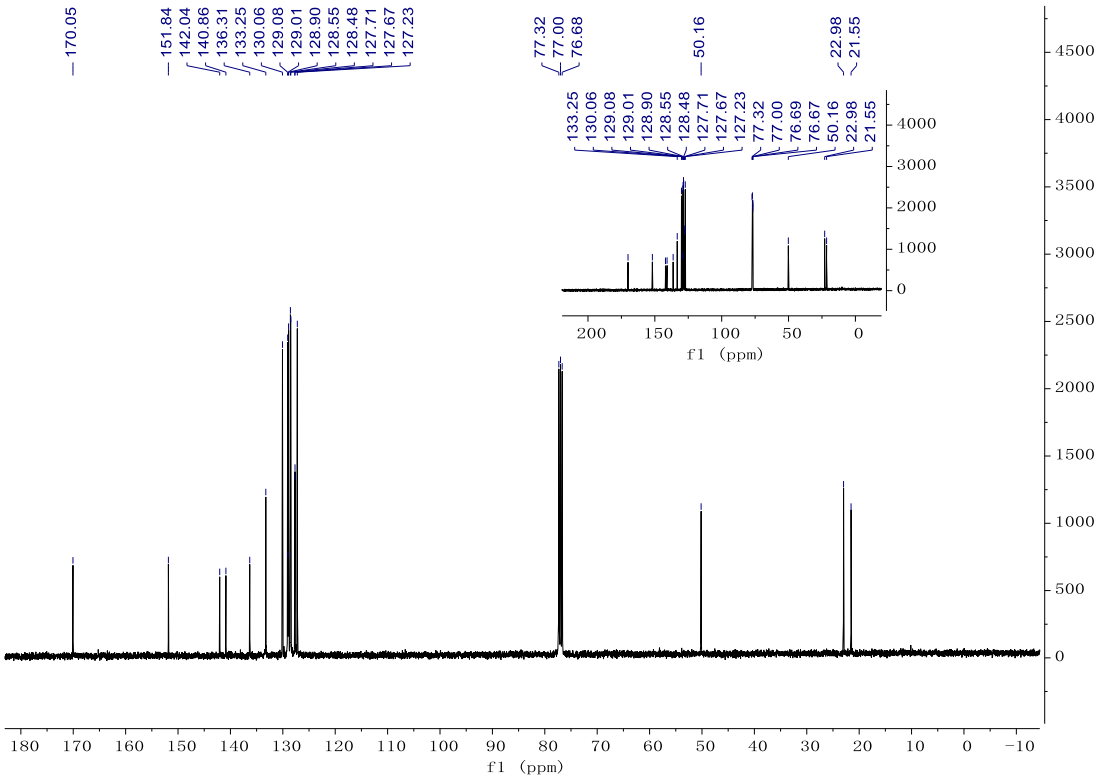
Methyl-(*E*)-3-((2-(*N*-benzylacetamido)-2-phenylvinyl)sulfonyl)thiophene-2-carboxylate (3at)



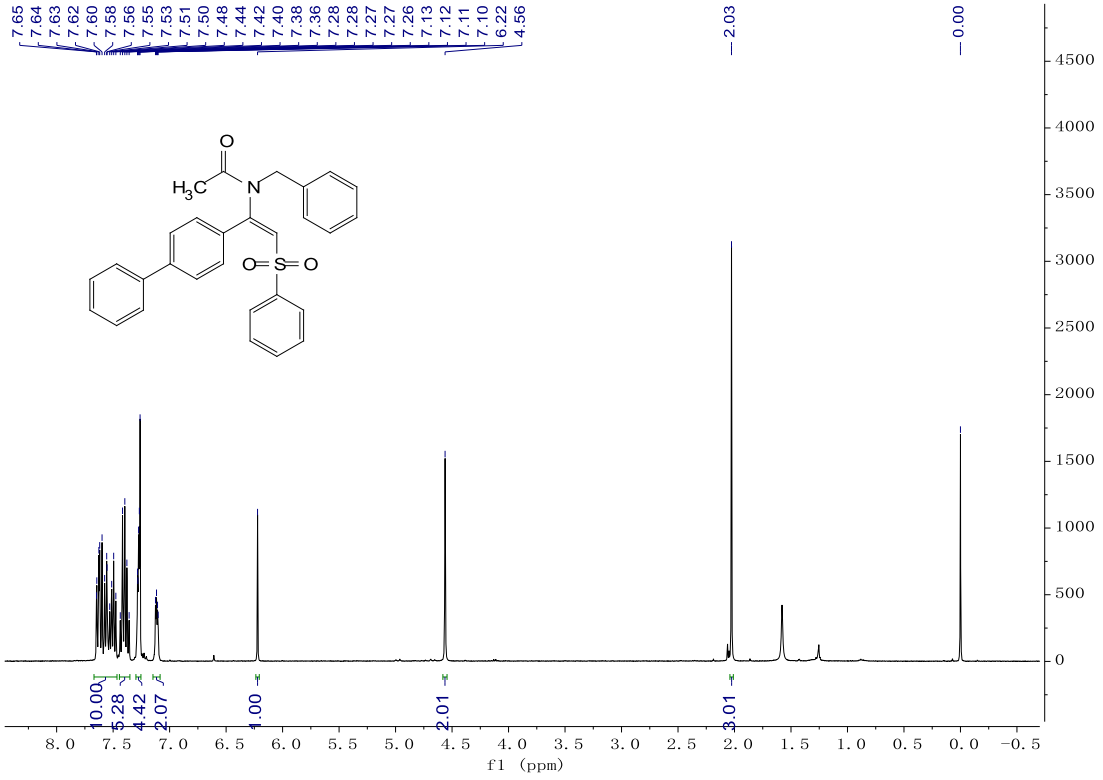


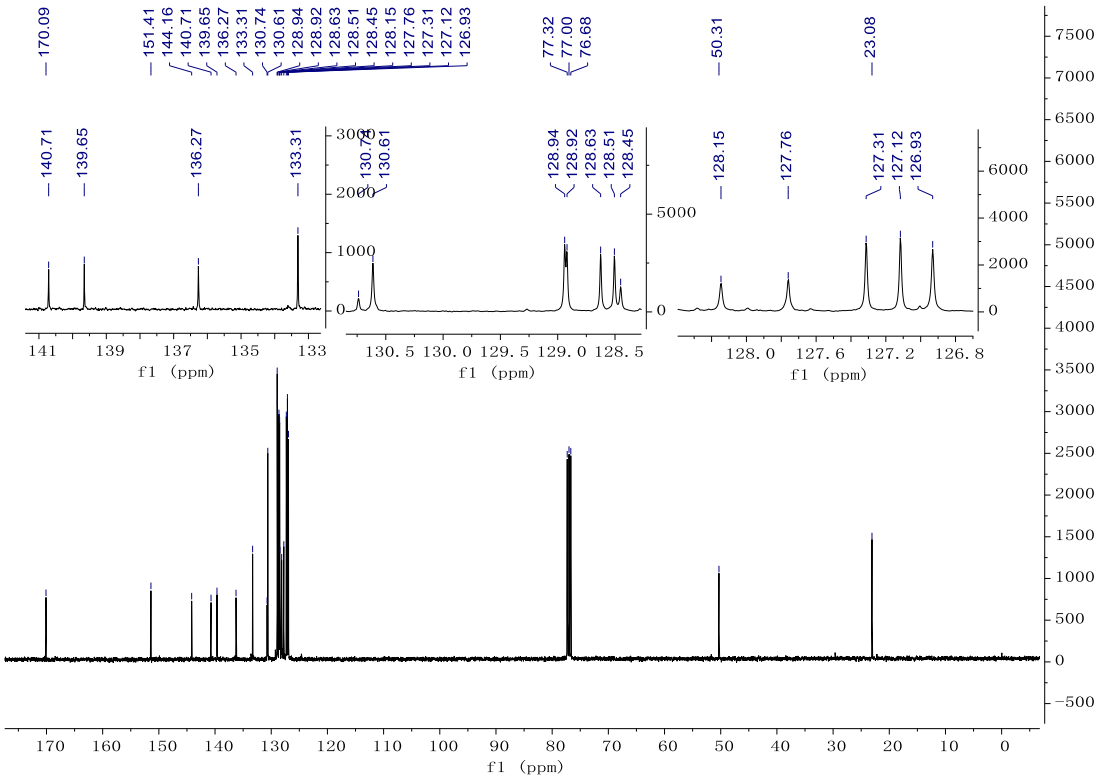
(*E*)-*N*-benzyl-*N*-(2-(phenylsulfonyl)-1-(*p*-tolyl)vinyl)acetamide (3ba)



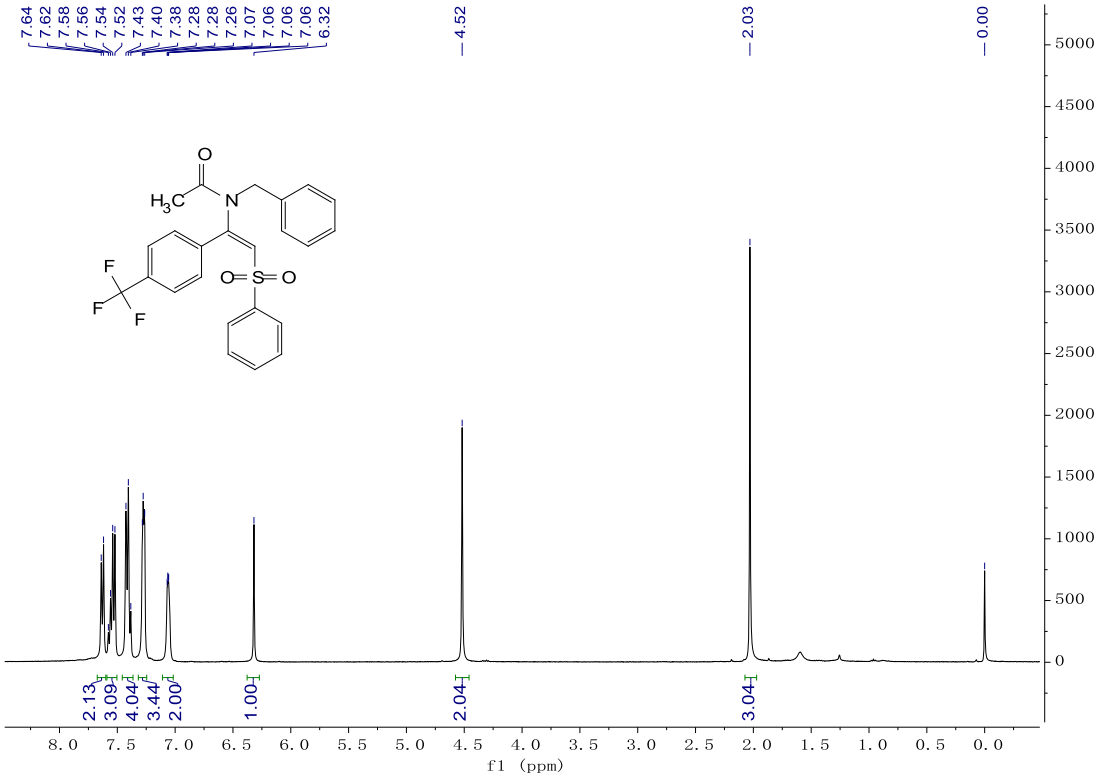


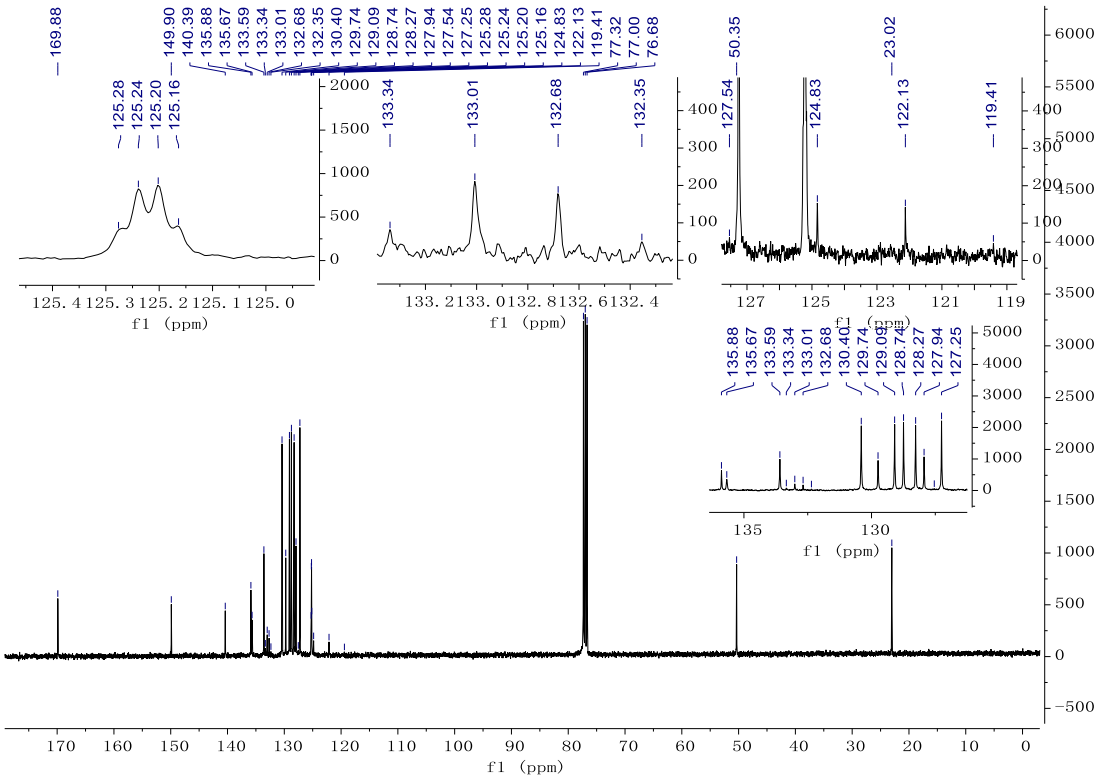
(*E*)-*N*-(1-([1,1'-biphenyl]-4-yl)-2-(phenylsulfonyl)vinyl)-*N*-benzylacetamide (3ca)





(*E*)-*N*-benzyl-*N*-(2-(phenylsulfonyl)-1-(4-(trifluoromethyl)phenyl)vinyl)acetamide (3da)

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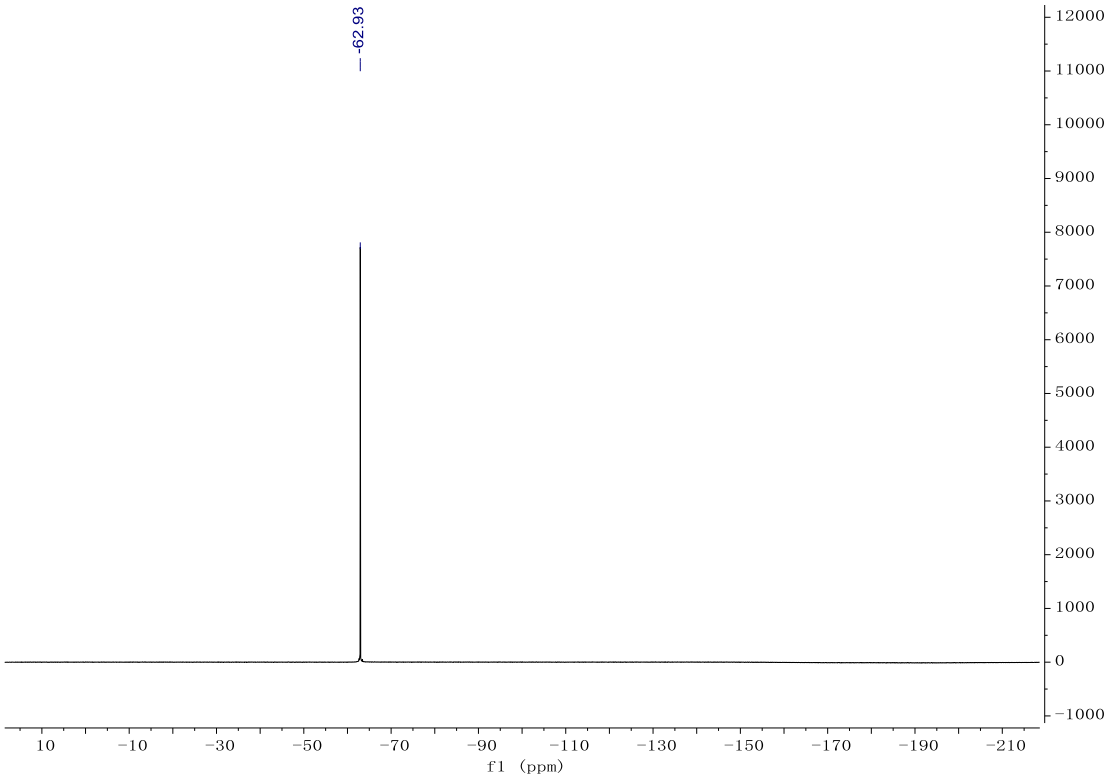
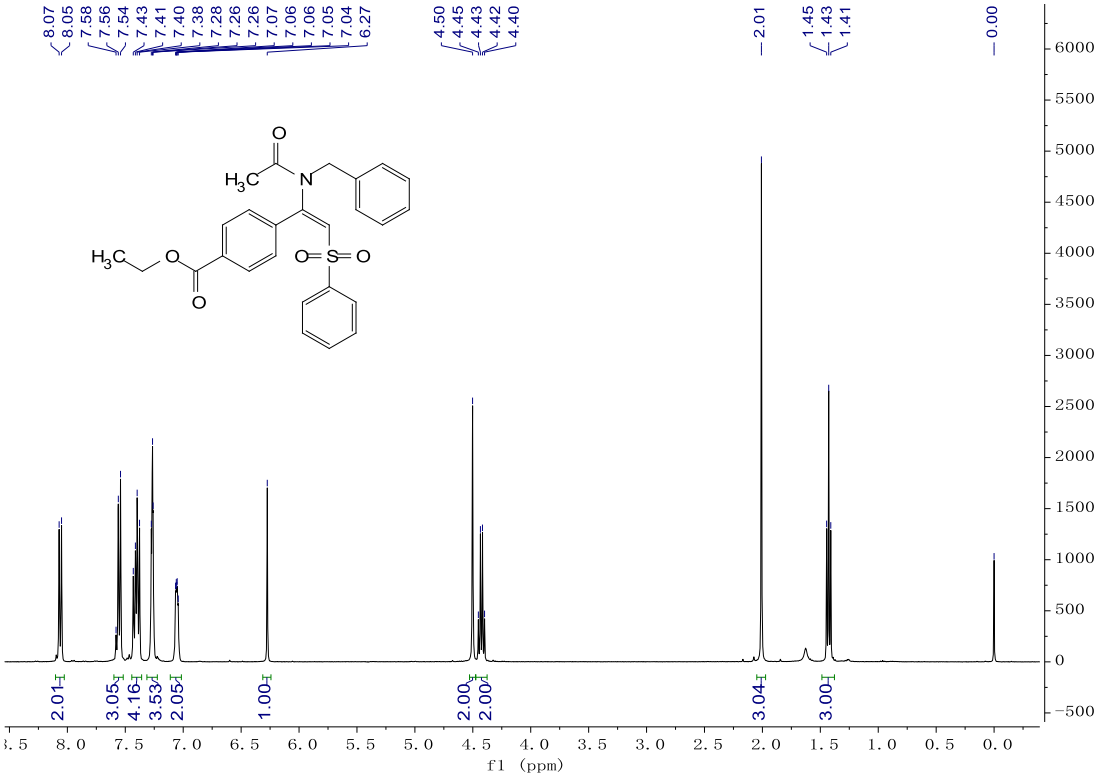
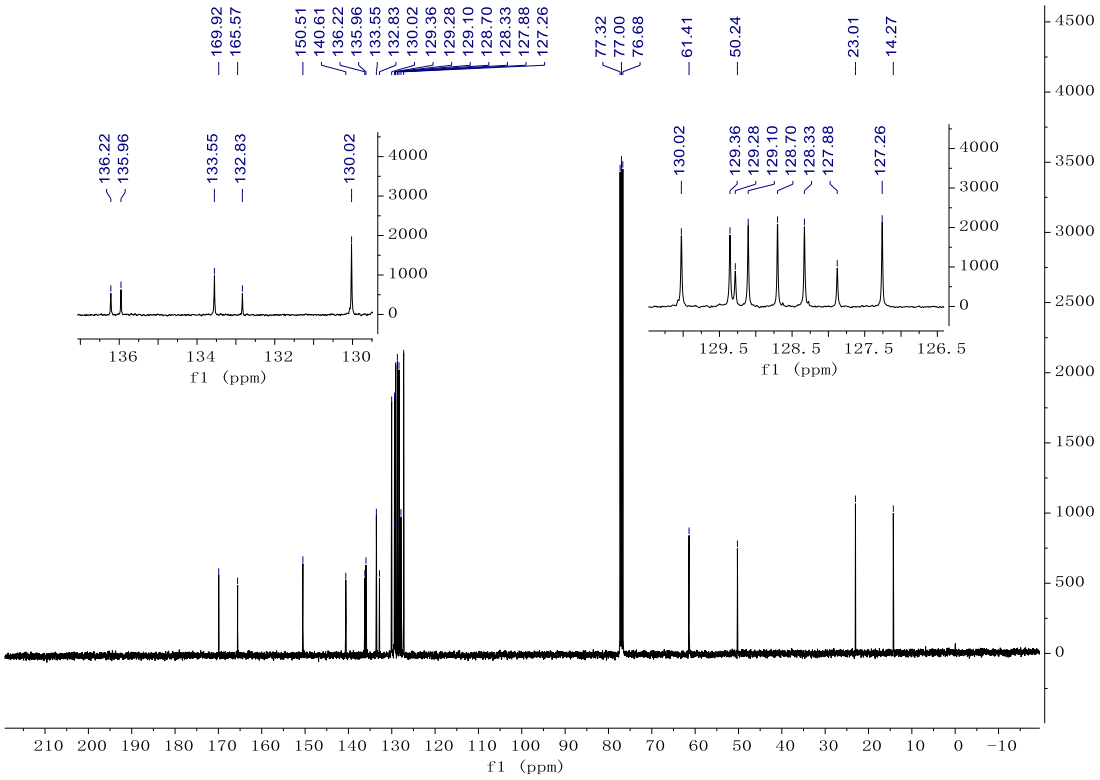
125.20
125.16
50.35
23.02
f1 (ppm)

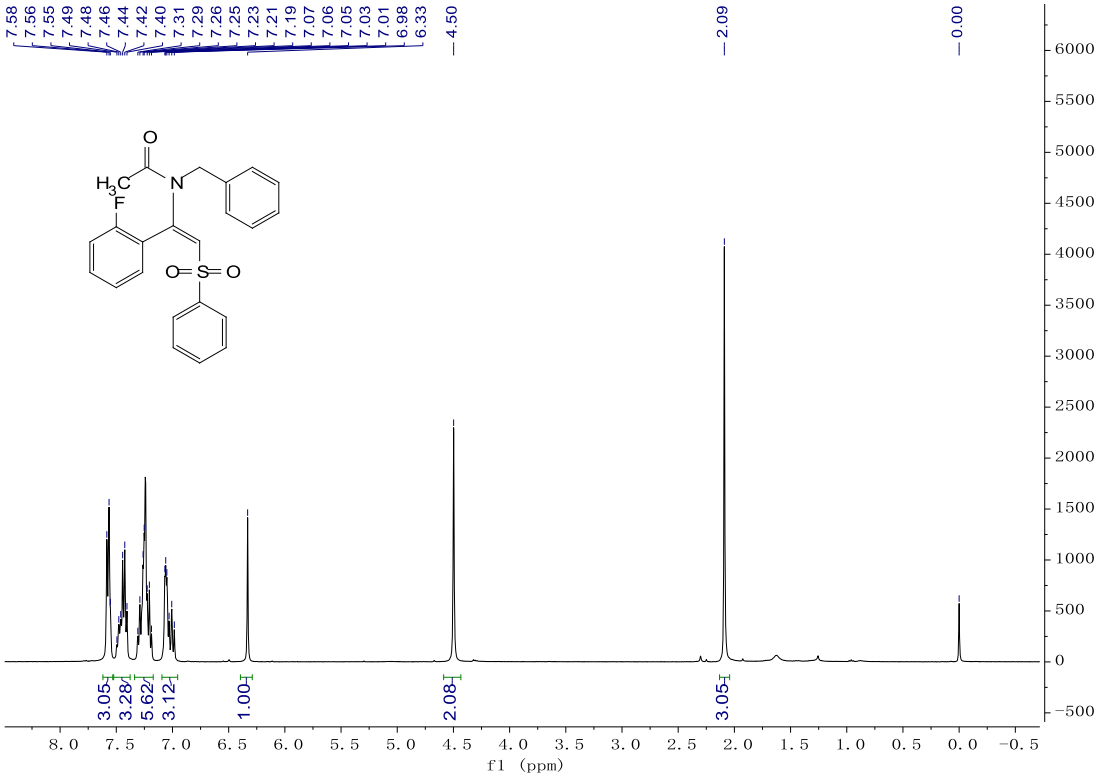

-62.93
f1 (ppm)

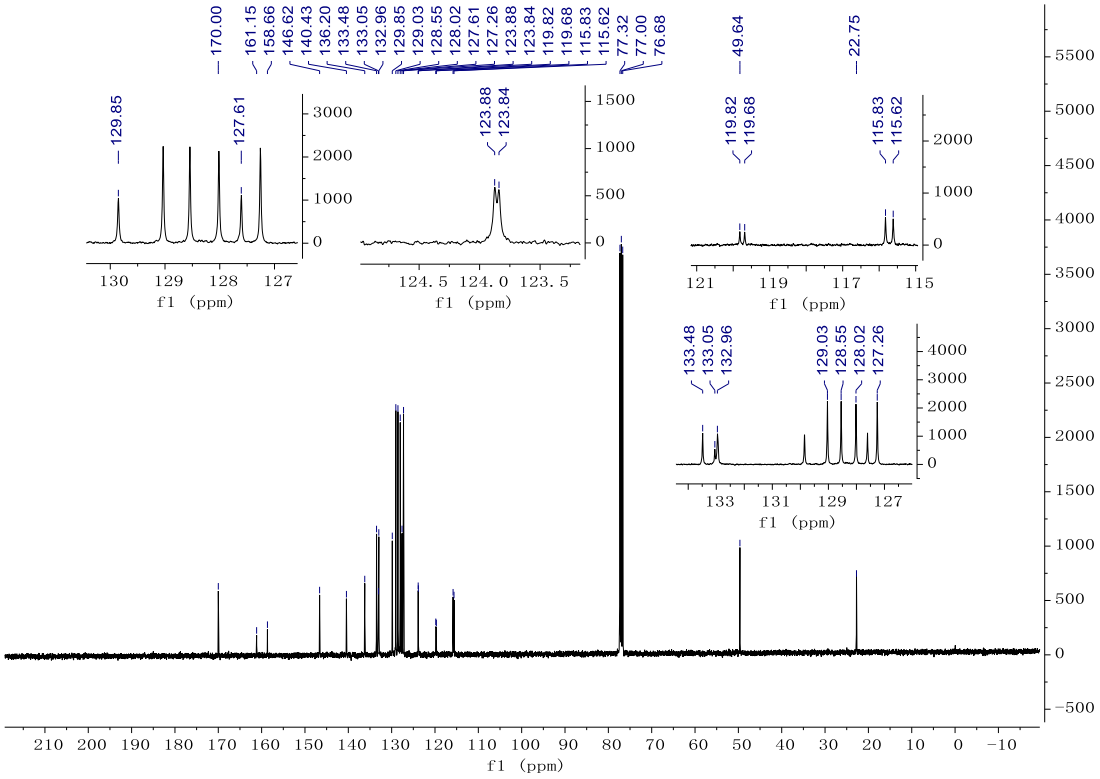
ethyl (*E*)-4-(1-(*N*-benzylacetamido)-2-(phenylsulfonyl)vinyl)benzoate (3ea)

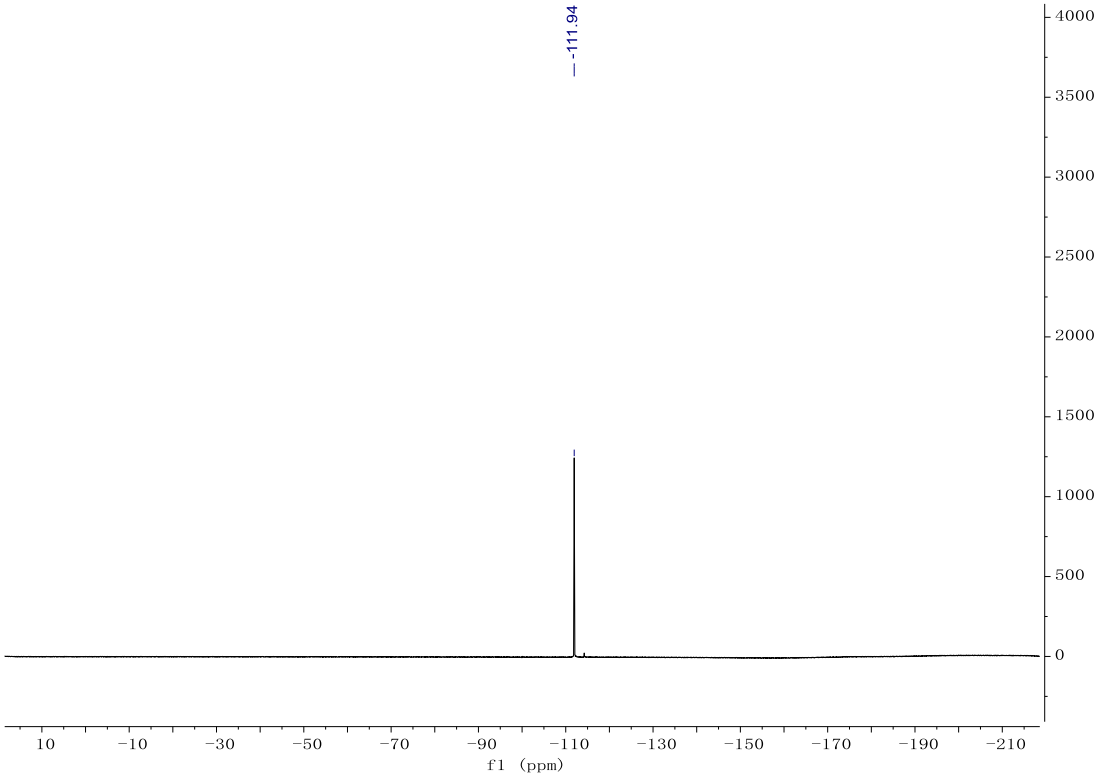




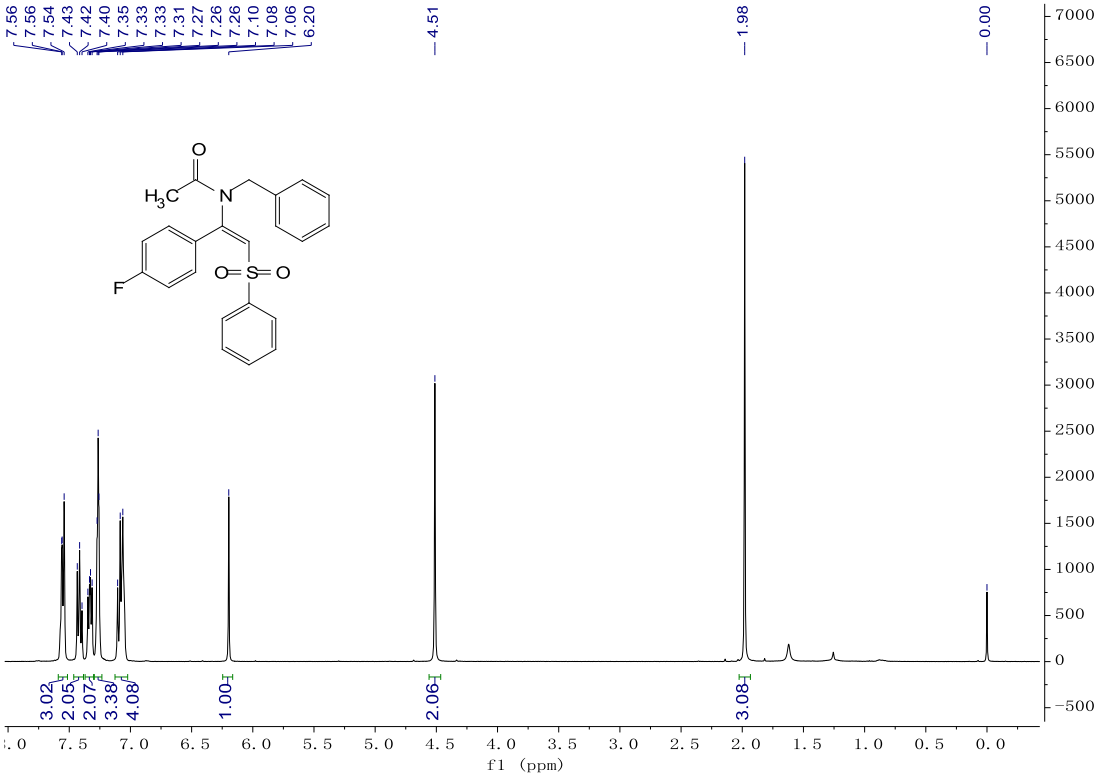
(*E*)-*N*-benzyl-*N*-(1-(2-fluorophenyl)-2-(phenylsulfonyl)vinyl)acetamide (3fa)

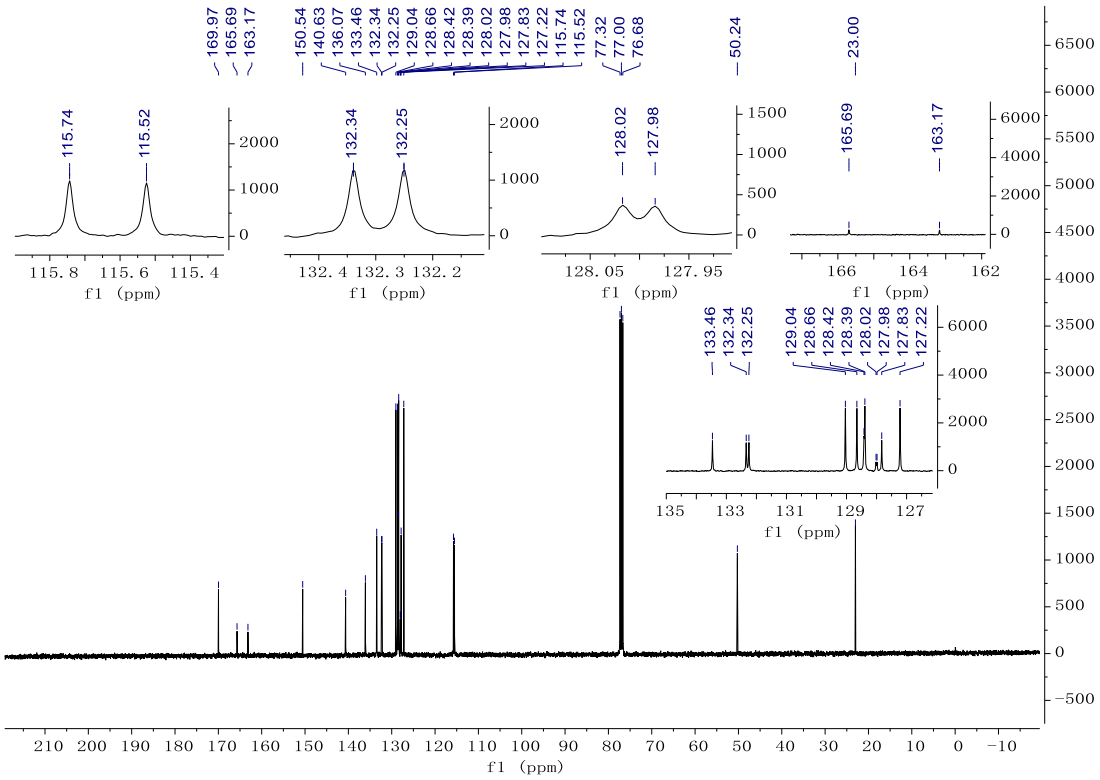






(*E*)-*N*-benzyl-*N*-(1-(4-fluorophenyl)-2-(phenylsulfonyl)vinyl)acetamide (3ga)

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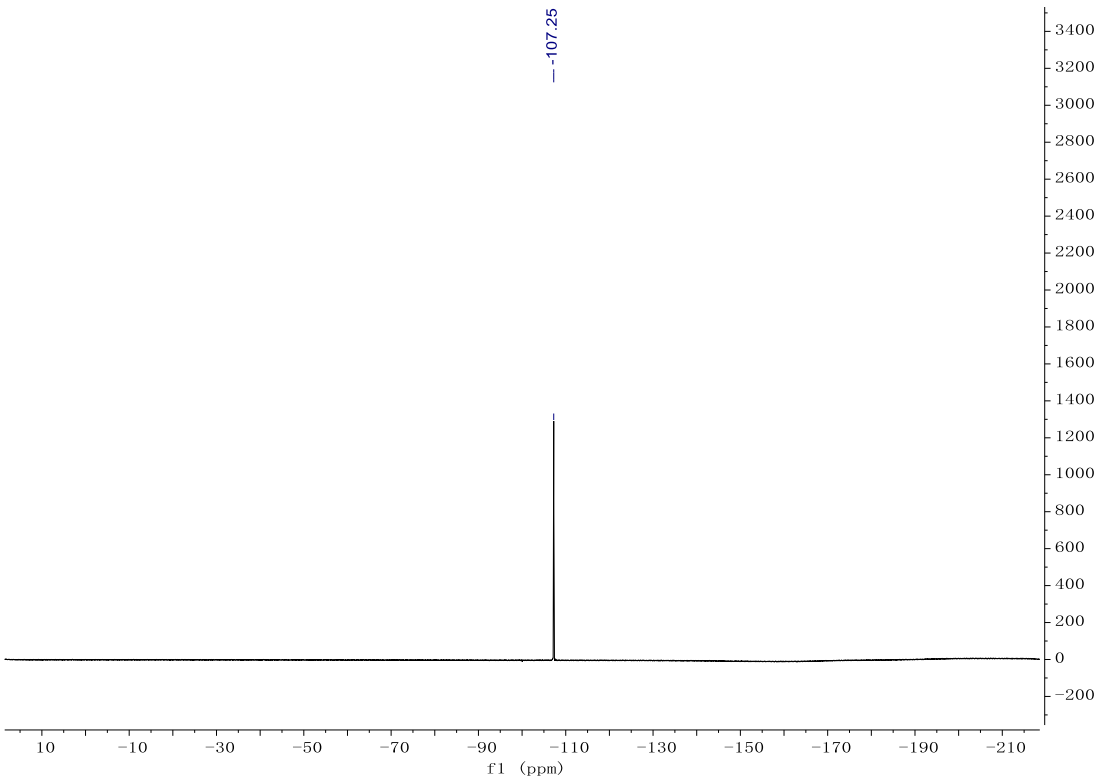
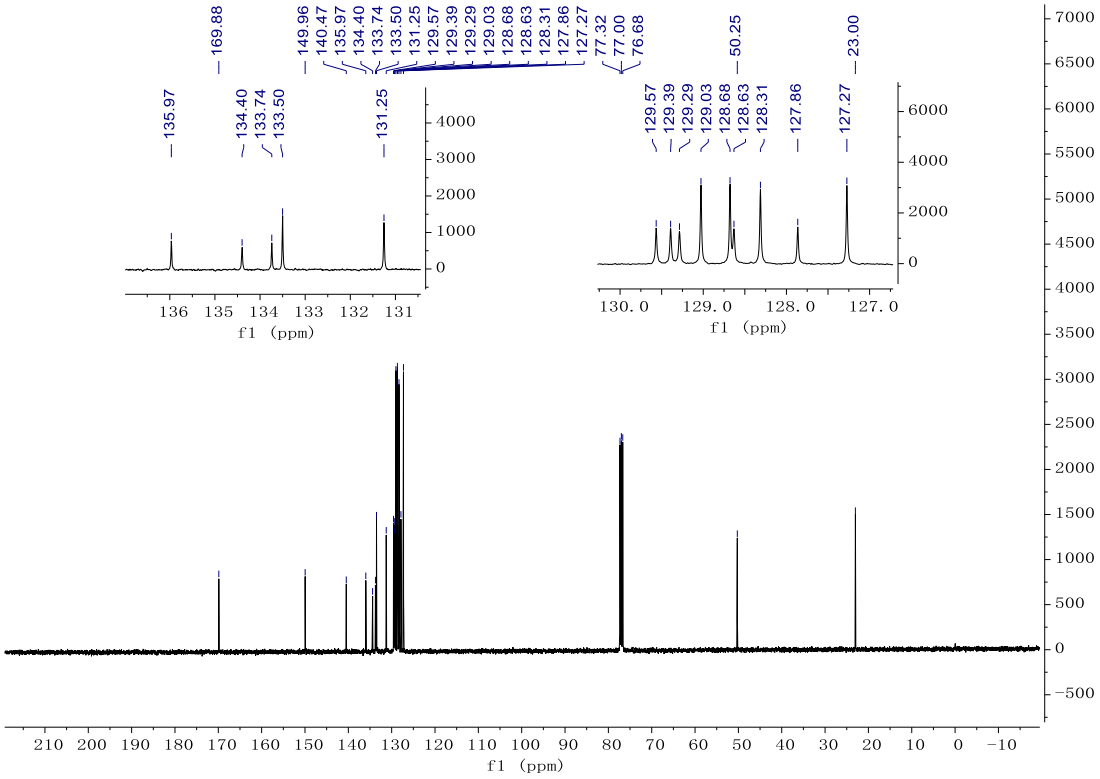
76.68
50.24
23.00
115.74
115.52
132.34
132.25
128.02
127.98
165.69
163.17
f1 (ppm)


133.46
132.34
132.25
129.04
128.66
128.42
128.39
128.02
127.98
127.83
127.22
f1 (ppm)

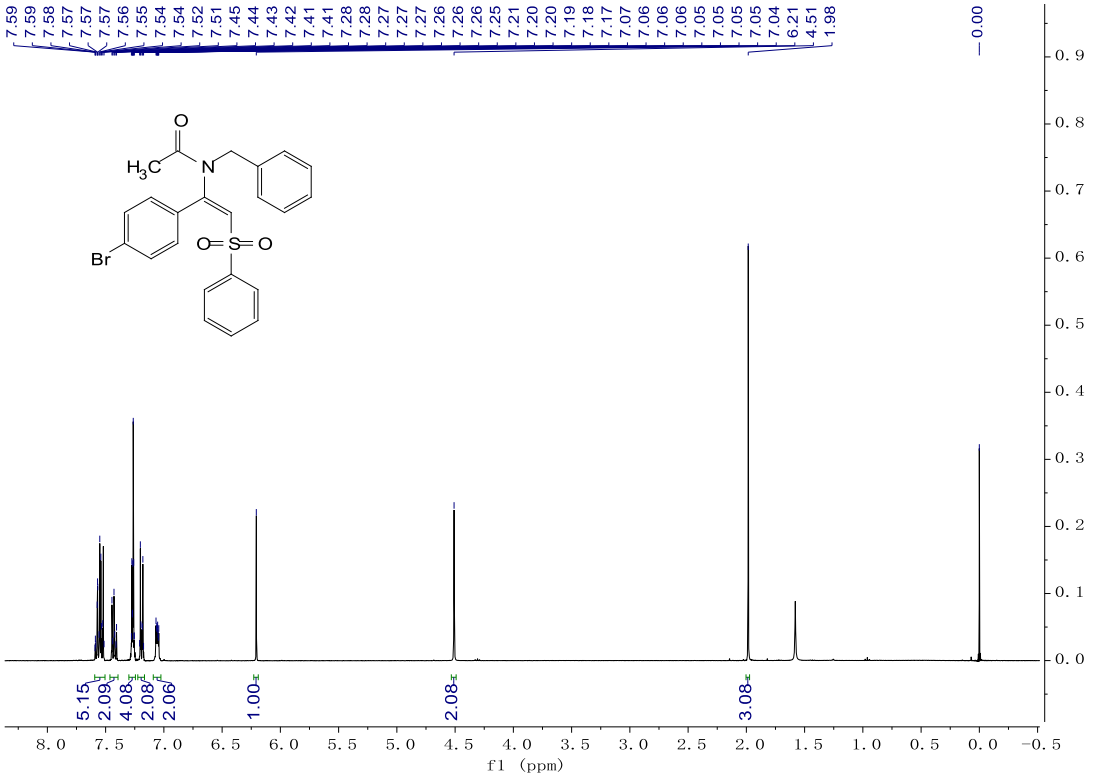
f1 (ppm)

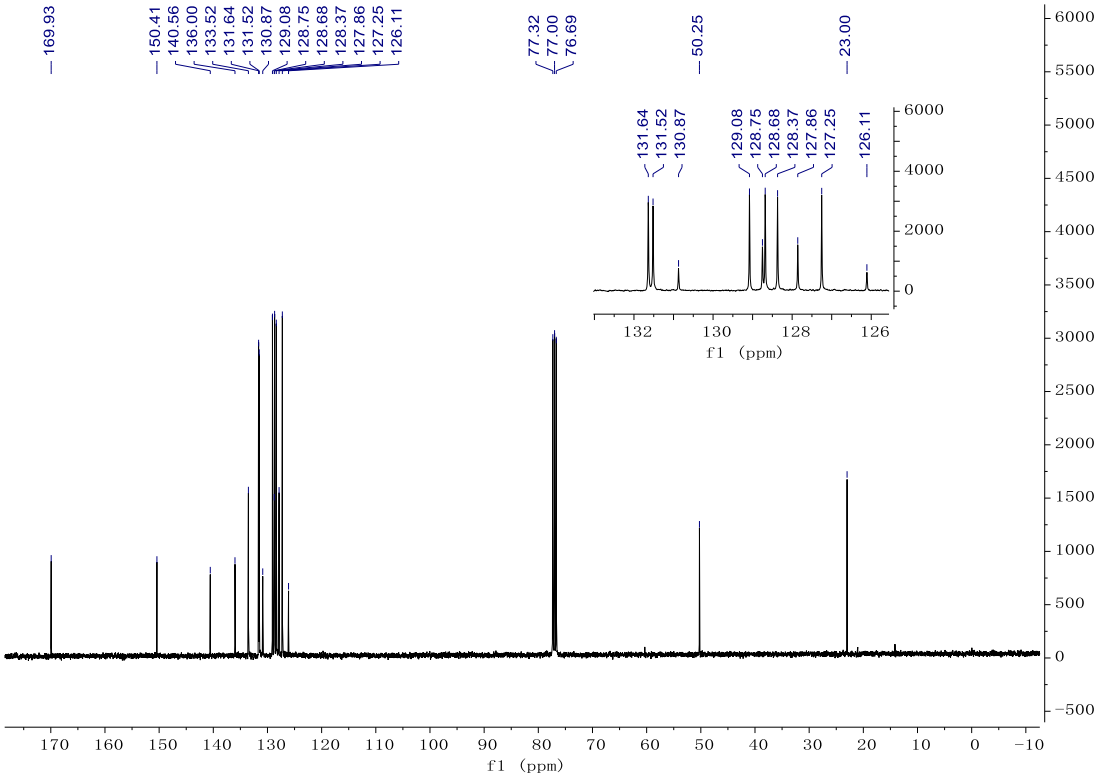
-107.25
f1 (ppm)

(*E*)-*N*-benzyl-*N*-(1-(3-chlorophenyl)-2-(phenylsulfonyl)vinyl)acetamide (3ha)

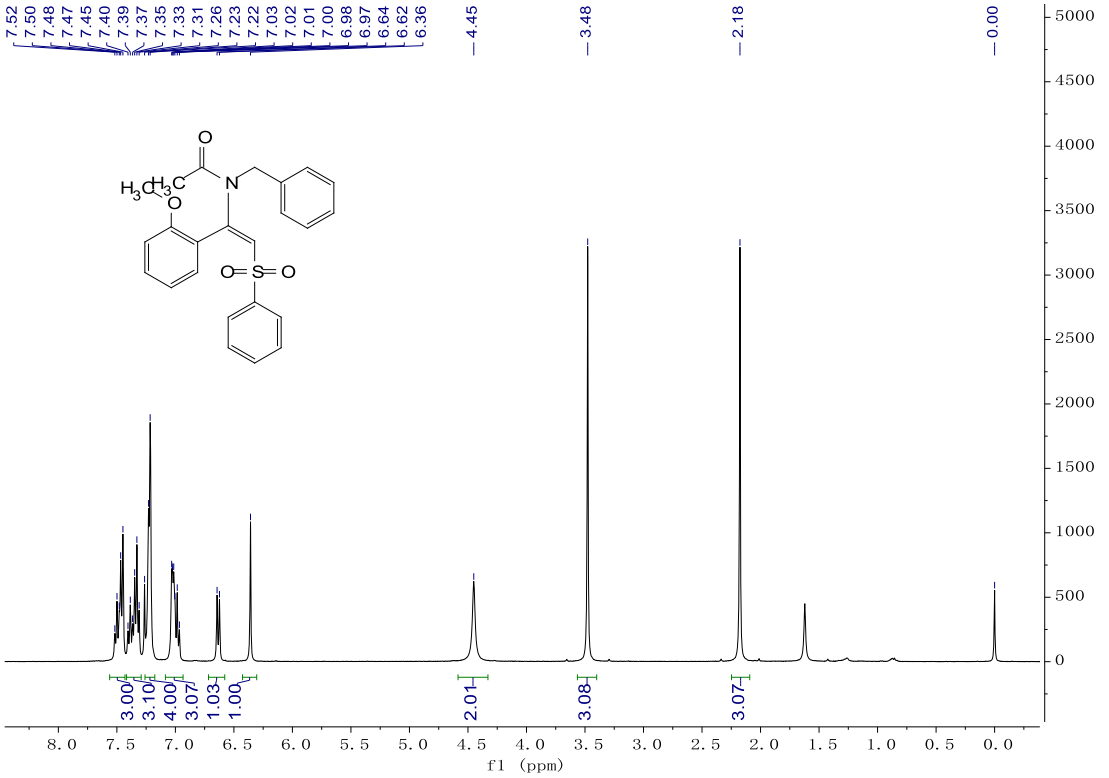


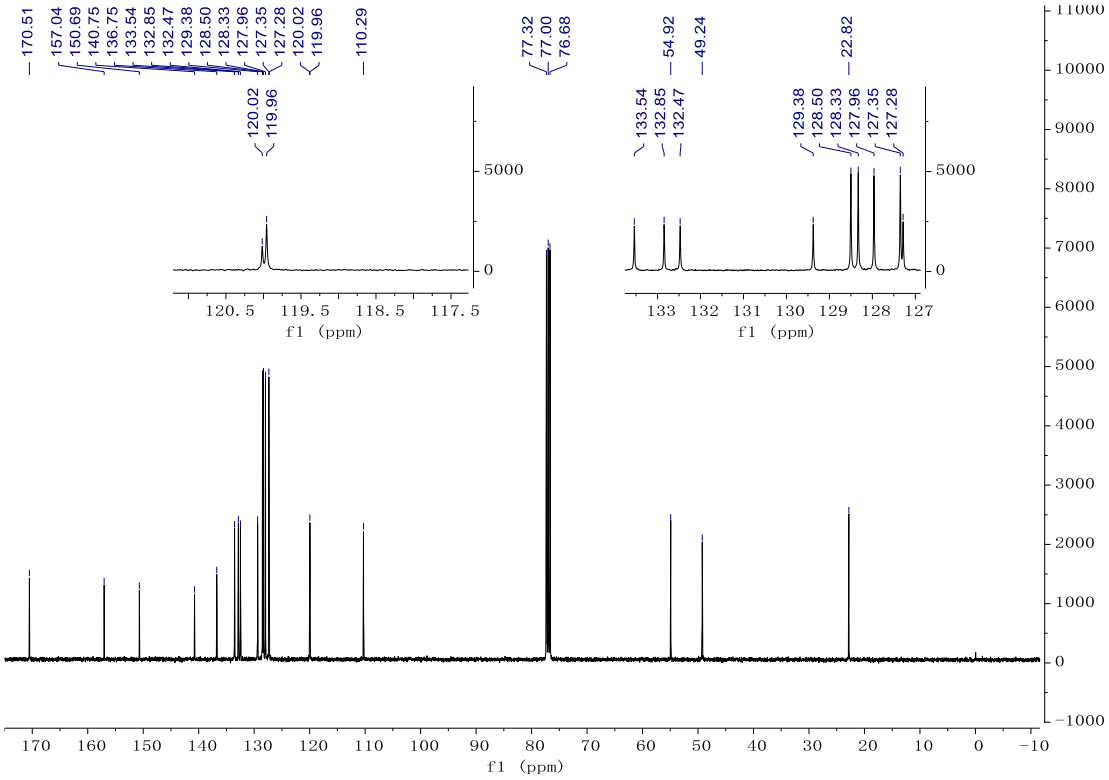
(*E*)-*N*-benzyl-*N*-(1-(4-bromophenyl)-2-(phenylsulfonyl)vinyl)acetamide (3ia)



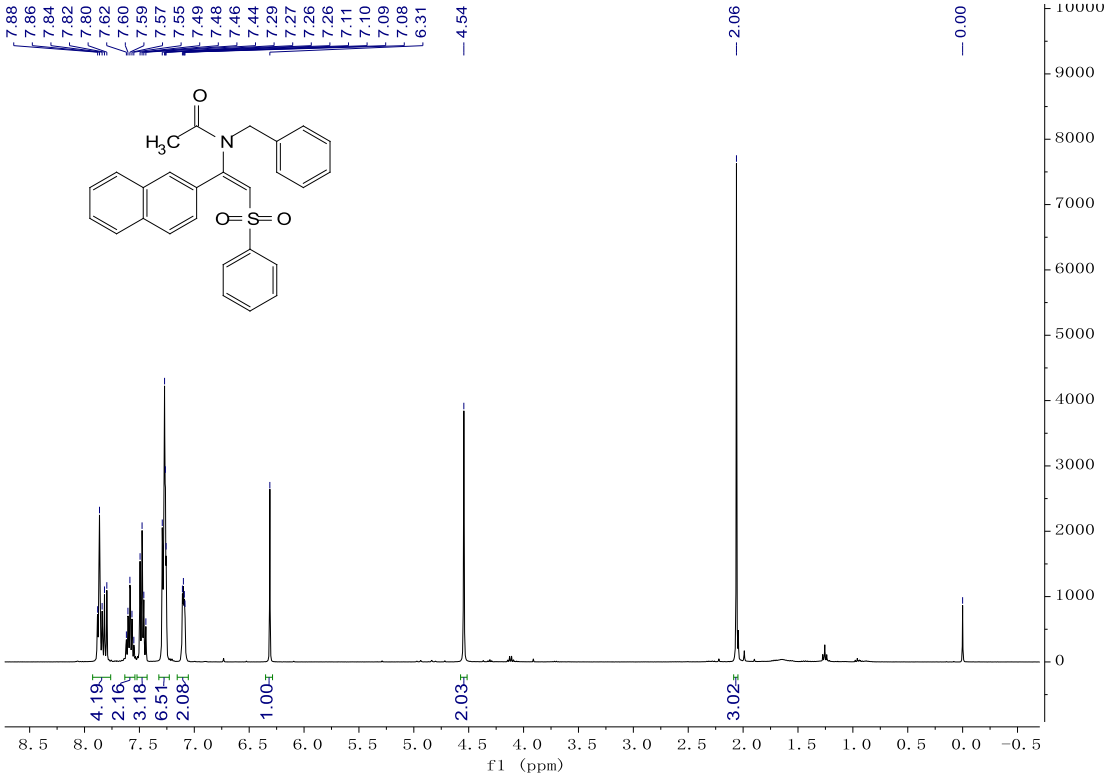


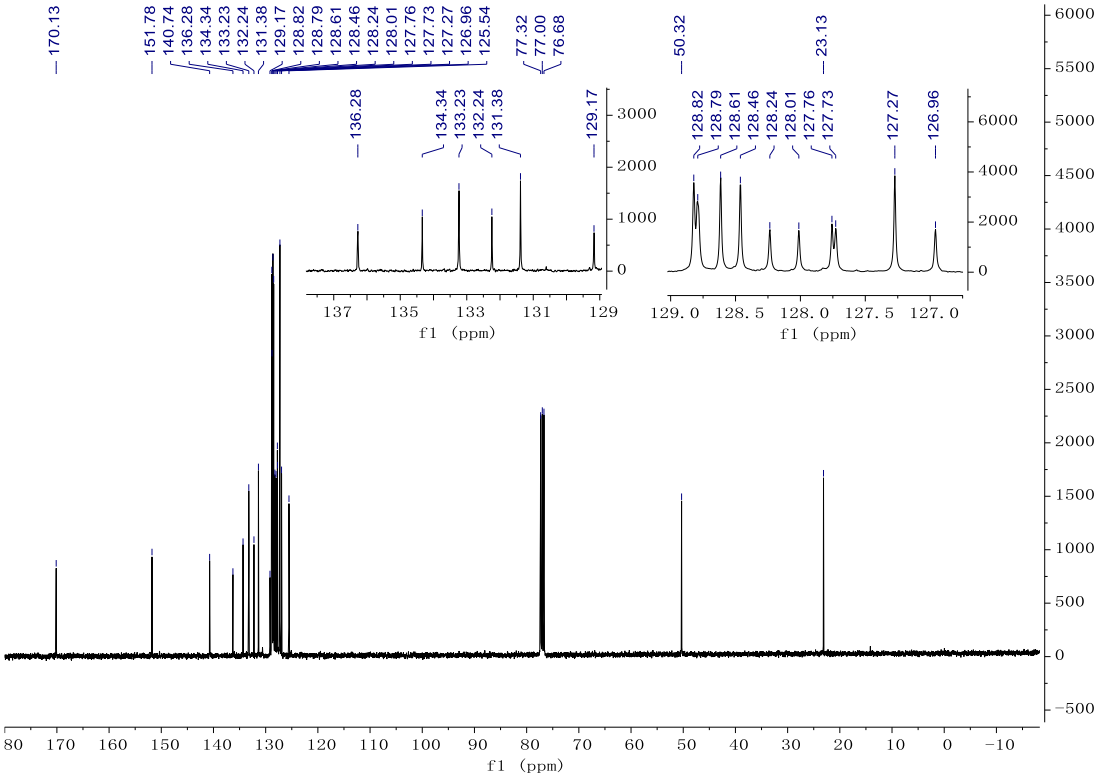
(*E*)-*N*-benzyl-*N*-(1-(2-methoxyphenyl)-2-(phenylsulfonyl)vinyl)acetamide (3ja)



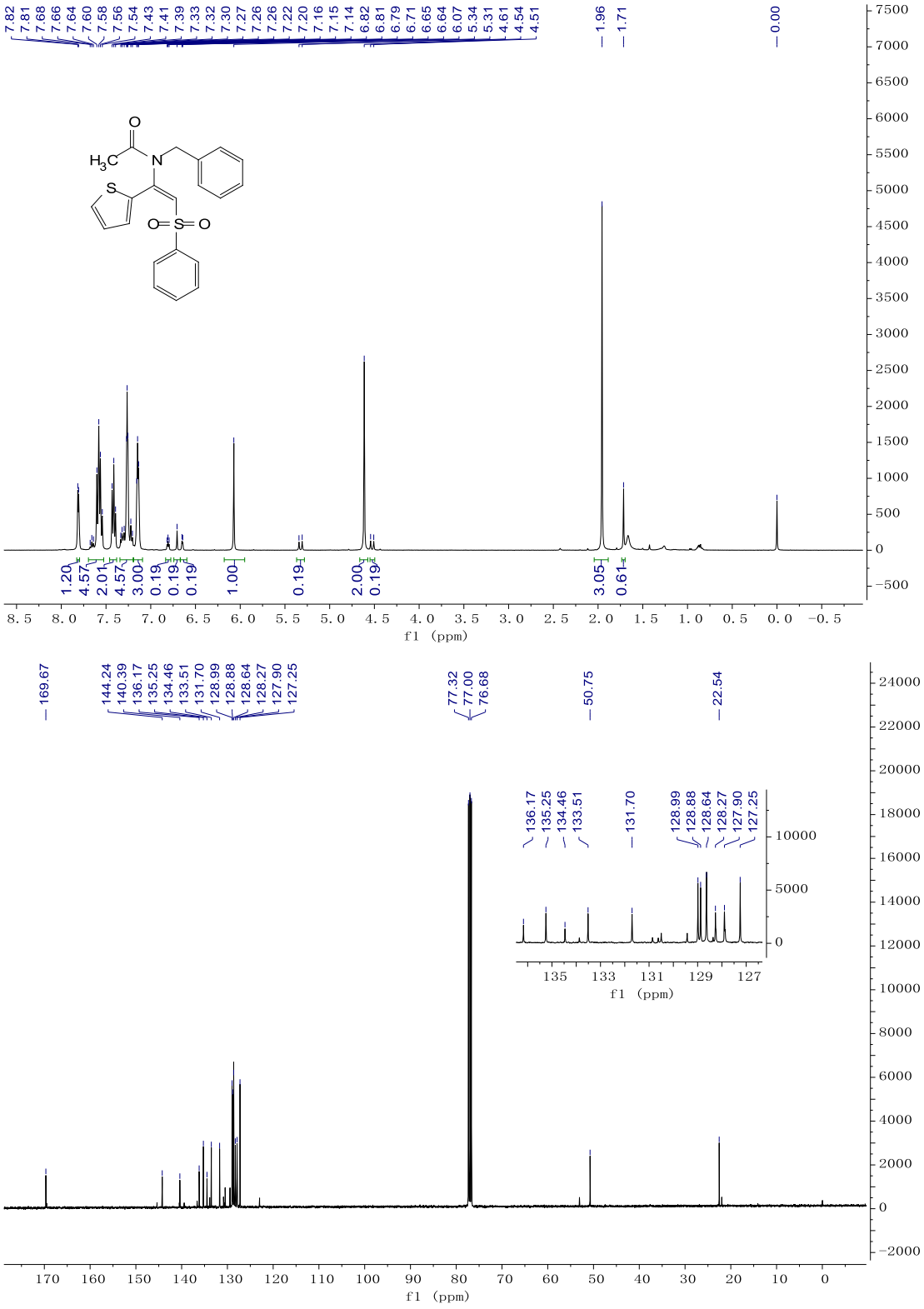


(*E*)-*N*-benzyl-*N*-(1-(naphthalen-2-yl)-2-(phenylsulfonyl)vinyl)acetamide (3ka)

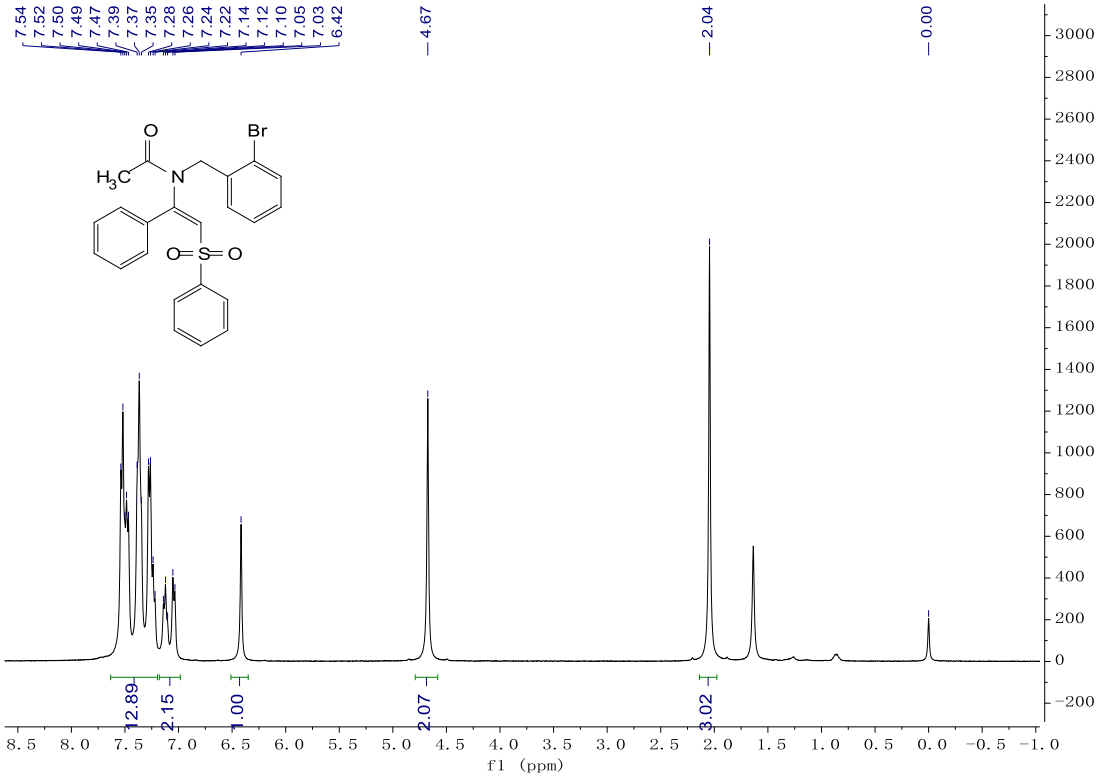


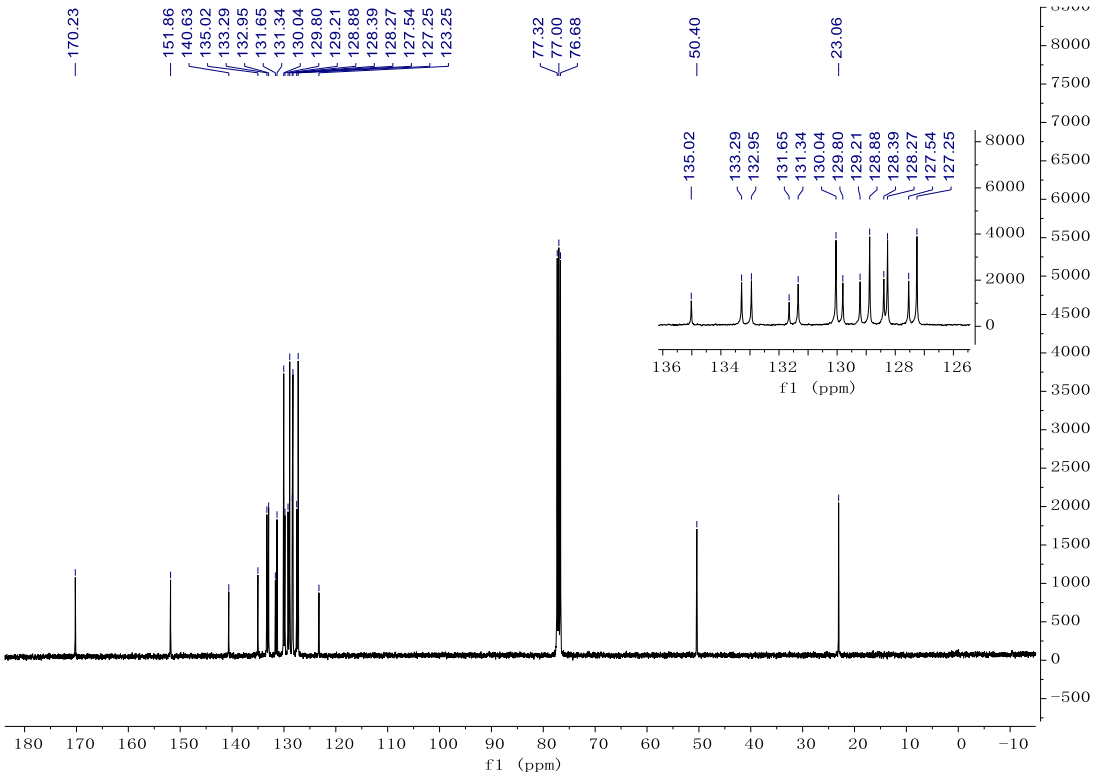


(*E*)-*N*-benzyl-*N*-(2-(phenylsulfonyl)-1-(thiophen-2-yl)vinyl)acetamide (3la)

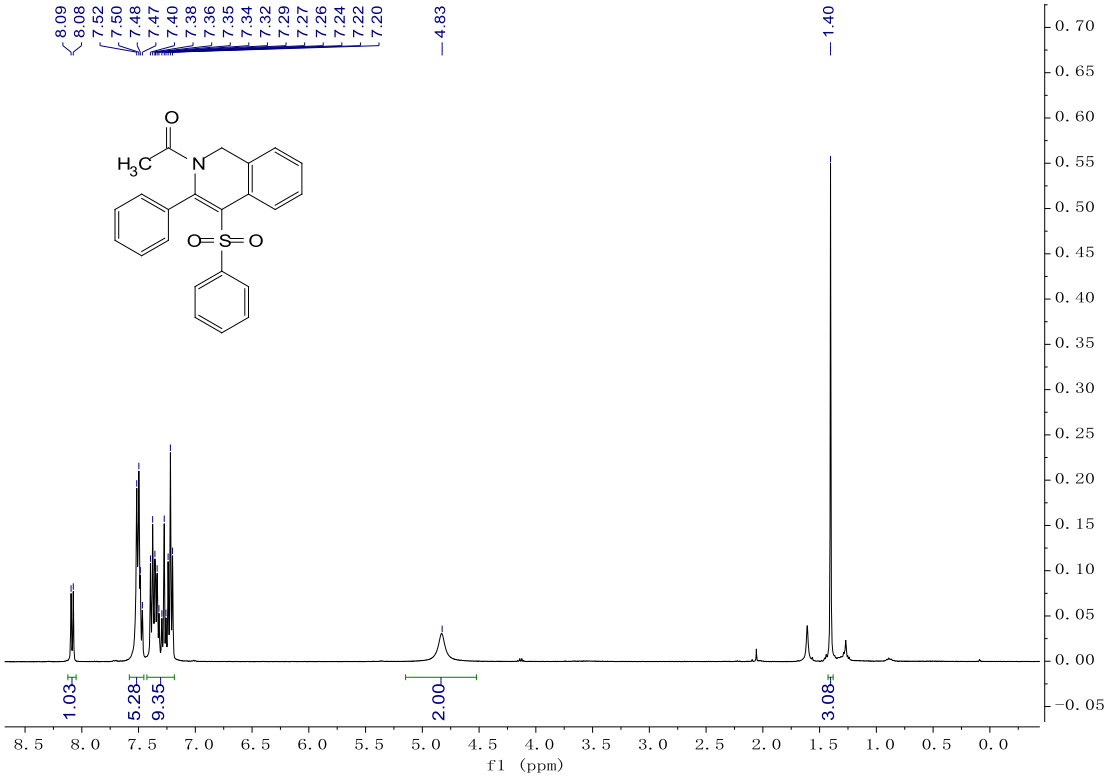


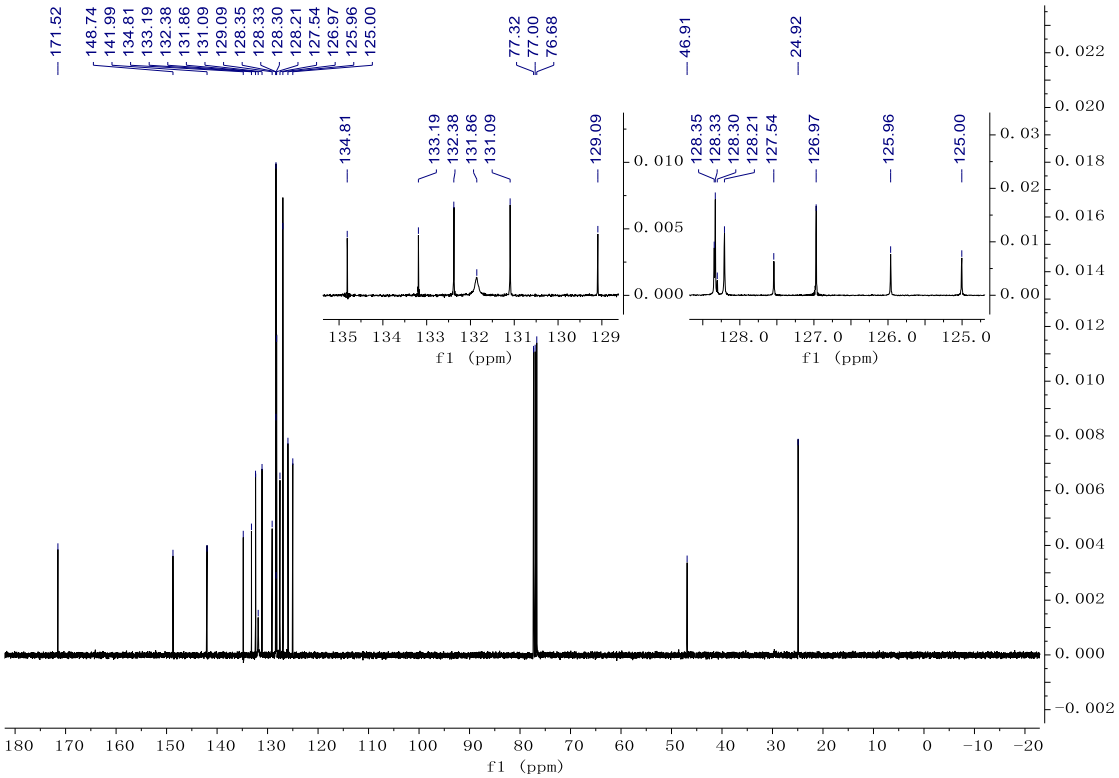
(*E*)-*N*-(2-bromobenzyl)-*N*-(1-phenyl-2-(phenylsulfonyl)vinyl)acetamide (3ma)





1-(3-phenyl-4-(phenylsulfonyl)isoquinolin-2(*1H*)-yl)ethan-1-one 5





1-phenyl-2-(phenylsulfonyl)ethan-1-one 6