Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Photoredox-Enabled Ring-Opening of Cyclobutanes via The Formation of Carbon Radical

Chunhang Zhao,[a] WenJing Ma,[a] Kairui Liu,[a] Ruoyang Xu,[a] Xiuya Ma,[a] and Yan Zhang*[a]

[a] Key Laboratory of the Ministry of Education for Advanced Catalysis Materials, and Drug Discovery & Innovation Center, Department of Chemistry, ZheJiang Normal University, 688 Yingbin Road, 321004 Jinhua P. R. China

*zhangyan001@zjnu.edu.cn

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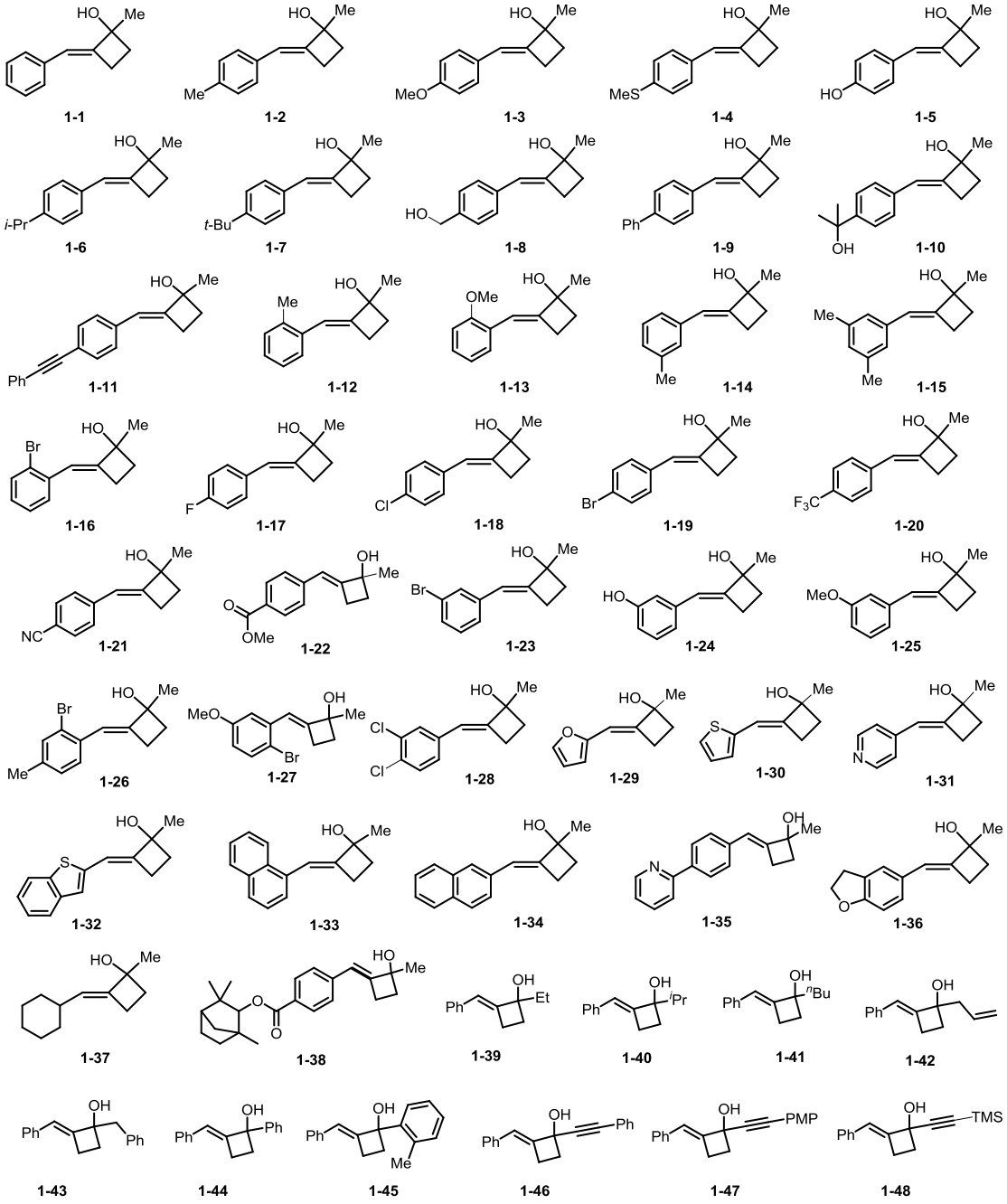
1. General Remarks

NMR spectra were recorded on BRUKER AVANCE III 400 or BRUKER AVANCE III 600. $CDCl_3$ was used as the solvent. Chemical shifts were referenced relative to residual solvent signal ($CDCl_3$: ^{1}H NMR: δ 7.26 ppm, ^{13}C NMR: δ 77.16 ppm). The following abbreviations are used to describe peak patterns where appropriate: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Coupling constants (*J*) are reported in Hertz (Hz). Electrospray-ionization (ESI) mass spectra were obtained on AB Sciex LC 30A-Triple TOF 4600 apparatus. All photochemical reactions were performed with a 30 W blue light blud (λ = 460 nm) at a distance of 3-5 cm away from the reaction flask. All systems are equipped with time-of-flight (TOF) analyzers. Melting points were measured with micro melting point apparatus. Catalytic reactions were performed in sealed tubes under a N_2 atmosphere, which was evacuated and backfilled with N_2 for three times. The reaction temperature was measured by the thermometer, which was in the range of 30 to 35 °C. Unless otherwise noted, some materials (or alternatively chemicals) obtained from commercial suppliers were used directly without further purification. 2-methylenecyclobutan-1-ol **1** were prepared according to the literatures.[1,2]

Table S–1. Scopes of 2-methylenecyclobutan-1-ol **1** and sulfonyl chlorides **2**. (PMP = *para*-methoxyphenyl)



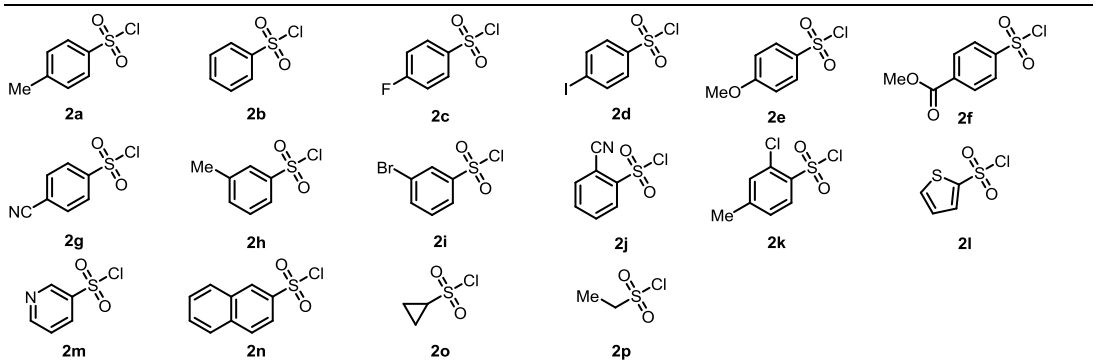
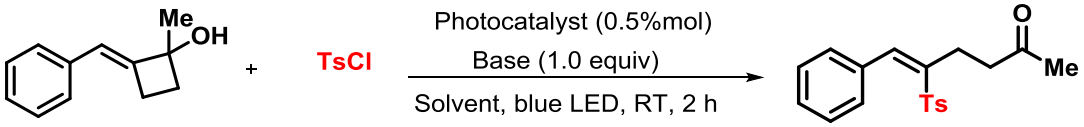


Table S–2. Optimization of the cascade ring-opening/remote carbonylation.[a]

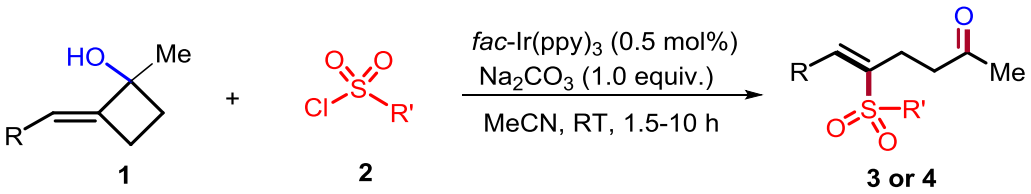


1 **2a** **3**

Entry	Solvent	Photocatalyst	Base	Yield/%
1	MeCN	*fac*-Ir(ppy)$_3$	Na_2CO_3	89
2	DMF	*fac*-Ir(ppy)$_3$	Na_2CO_3	30
3	EA	*fac*-Ir(ppy)$_3$	Na_2CO_3	38
4	THF	*fac*-Ir(ppy)$_3$	Na_2CO_3	26
5	DCE	*fac*-Ir(ppy)$_3$	Na_2CO_3	46
6	MeCN/H_2O (20/1)	*fac*-Ir(ppy)$_3$	Na_2CO_3	60
7	MeCN/H_2O (10/1)	*fac*-Ir(ppy)$_3$	Na_2CO_3	56
8	MeCN	*fac*-Ir(ppy)$_3$	-	NR
9	MeCN	*fac*-Ir(ppy)$_3$	K_2CO_3	88
10	MeCN	*fac*-Ir(ppy)$_3$	NaOAc	60
11	MeCN	*fac*-Ir(ppy)$_3$	Et_3N	49
12[b]	MeCN	*fac*-Ir(ppy)$_3$	Na_2CO_3	90
13	MeCN	[Ru(bpy)$_3$]Cl_2	Na_2CO_3	NR
14	MeCN	Eosin Y	Na_2CO_3	15
15	MeCN	-	Na_2CO_3	NR
16[c]	MeCN	*fac*-Ir(ppy)$_3$	Na_2CO_3	NR
17[d]	MeCN	*fac*-Ir(ppy)$_3$	Na_2CO_3	35
18[e]	MeCN	*fac*-Ir(ppy)$_3$	Na_2CO_3	NR

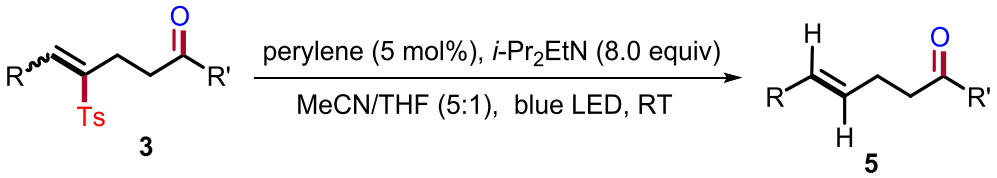
[a] 1 (0.20 mmol), 2a (0.20 mmol, 1.0 equiv), Na_2CO_3 (0.20 mmol, 1.0 equiv), solvent (2 mL), N_2, photocatalyst (0.5 mol%), 2 h, r.t. Yield of isolated products. [b] *fac*-Ir(ppy)$_3$ (1 mol%). [c] Without light. [d] 5 W Blue LED, [e] air instead of N_2.

2. (A) General Procedure for the Cascade Ring-opening/Remote Formylation.

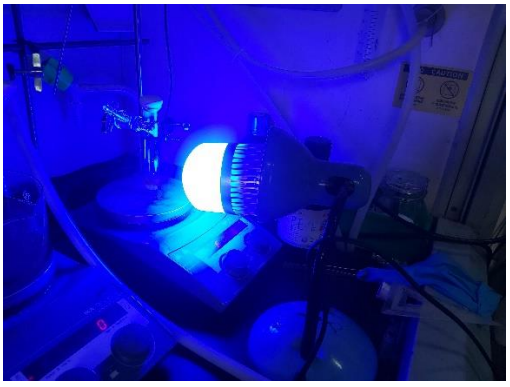


Methyenecyclobutanols **1** (0.2 mmol, 1.0 equiv), sulfonyl chlorides **2** (0.22 mmol, 1.1 equiv), *fac*-Ir(ppy)$_3$ (1.5 mg, 0.5 mol%) and Na_2CO_3 (22 mg, 0.2 mmol, 1.0 equiv) were placed in a 15 mL Schlenk tube. The tube was evacuated and purged with N_2 three times. Acetonitrile (3.0 mL) was then added and the mixture was stirred under blue light irradiation (30 W LEDs, temperature was maintained between 30 °C and 35 °C). After 1.5-10 h, the crude reaction solution was transferred to the round bottom flask. Silica was added to the flask and all volatiles were evaporated under vacuum. Purification of the residue by colum chromatography (SiO_2, petroleum ether/EtOAc) yielded the corresponding product **3** or **4** ((In some cases, we get the mixture of (*E*)-or (*Z*)-product. As TLC shows that the polarities of the two different configurations are very similar, we then can only provide the mixed ^{1}H NMR spectra for several products).

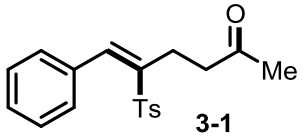
(B) General Procedure for Desulfonylation.



Compound **3** (0.2 mmol) was placed into a Schlenk tube, perylene (2.5 mg, 0.05 mmol) was added and the flask was evaculated and back filled with N_2 for three times. Then, *i*-Pr$_2$EtN (8.0 eq.) and a solvent mixture of MeCN/THF (5:1, 2.4 mL) were added. The solution was kept stirring under irradiation of 30 W blue LEDs at room temperature for 10 h. Afterwards, the solution was diluted with CH_2Cl_2 and transferred to a round bottom flask. Silica was added to the flask and volatiles were evaporated under vacuum. The purification was performed by flash column chromatography on silica gel (petroleum ether/EtOAc = 10:1) to obtain product **5**.



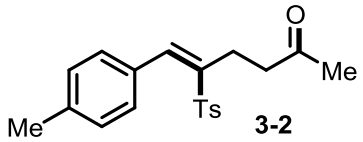
3. Characterization Data of All the Synthesized Products (3, 4 and 5)



3-1

(*Z*)-6-Phenyl-5-tosylhex-5-en-2-one (3-1)

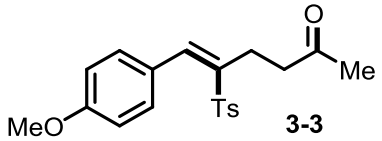
The general procedure (A) was followed using **1-1** (34.8 mg, 0.20 mmol) and **2a** (41.8 mg, 0.22 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc = 5:1) yielded **3-1** (58.4 mg, 89%) as a yellow oil. For **3-1**: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.83 (s, 1H), 7.81 (s, 1H), 7.78 (s, 1H), 7.42–7.38 (m, 4H), 7.37–7.36 (m, 2H), 7.34 (s, 1H), 2.84–2.80 (m, 2H), 2.73–2.69 (m, 2H), 2.45 (s, 3H), 2.13 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 207.0, 144.6, 140.5, 138.5, 136.1, 133.4, 130.1, 129.8, 129.4, 129.1, 128.3, 42.1, 29.9, 21.7, 21.1. **HR–MS** (ESI) m/z calc. for $C_{19}H_{21}O_3S^+$. $[M+H]^+$: 329.1206, found: 329.1207.



3-2

(*Z*)-6-(P-tolyl)-5-tosylhex-5-en-2-one (3-2)

The general procedure (A) was followed using **1-2** (37.6 mg, 0.20 mmol) and **2a** (41.8 mg, 0.22 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc = 5:1) yielded **3-2** (54.7 mg, 80%) as a yellow oil. For **3-2**: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.80 (d, J = 8.6 Hz, 3H), 7.35 (d, J = 8.4 Hz, 2H), 7.23 (d, J = 8.4 Hz, 2H), 2.84–2.82 (m, 2H), 2.72–2.70 (m, 2H), 2.45 (s, 3H), 2.39 (s, 3H), 2.14 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 207.2, 144.4, 140.3, 139.2, 138.4, 136.3, 130.5, 130.0, 129.9, 129.5, 128.3, 42.1, 30.0, 21.7, 21.5, 21.1. **HR–MS** (ESI) m/z calc. for $C_{20}H_{23}O_3S^+$. $[M+H]^+$: 343.1363, found: 343.1366.

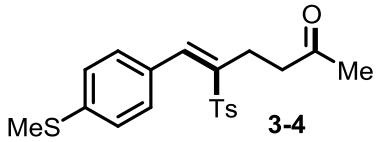


3-3

(*Z*)-6-(4-Methoxyphenyl)-5-tosylhex-5-en-2-one (3-3)

The general procedure (A) was followed using **1-3** (40.8 mg, 0.20 mmol) and **2a** (41.8 mg, 0.22 mmol). Purification by column chromatography on silica gel (petroleum

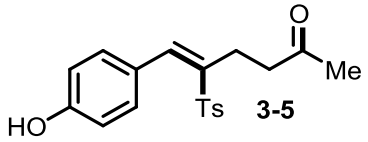
ether/EtOAc = 5:1) yielded **3-3** (43.0 mg, 60%) as a yellow oil. For **3-3**: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.78 (d, J = 8.3 Hz, 2H), 7.76 (s, 1H), 7.37 (d, J = 8.8 Hz, 2H), 7.34 (d, J = 8.1 Hz, 2H), 6.94 (d, J = 8.8 Hz, 2H), 3.84 (s, 3H), 2.84–2.81 (m, 2H), 2.73–2.71 (m, 2H), 2.44 (s, 3H), 2.15 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 207.3, 160.9, 144.3, 138.0, 137.5, 136.5, 131.5, 130.0, 128.2, 125.8, 114.6, 55.5, 41.9, 30.0, 21.7, 21.2. **HR-MS** (ESI) m/z calc. for $C_{20}H_{23}O_4S^+$. $[M+H]^+$: 359.1312, found: 359.1294.



3-4

(*Z*)-6-(4-(Methylthio)phenyl)-5-tosylhex-5-en-2-one (3-4)

The general procedure (A) was followed using **1-4** (44.0 mg, 0.20 mmol) and **2a** (41.8 mg, 0.22 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc = 5:1) yielded **3-4** (41.9 mg, 56%) as a yellow solid. **M.p.**: 68–70 °C. For **3-4**: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.79 (d, J = 8.3 Hz, 2H), 7.76 (s, 1H), 7.36 (s, 1H), 7.34 (d, J = 2.6 Hz, 2H), 7.32 (s, 1H), 7.26 (d, J = 8.5 Hz, 2H), 2.85–2.81 (m, 2H), 2.73–2.69 (m, 2H), 2.52 (s, 3H), 2.46 (s, 3H), 2.15 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 207.2, 144.5, 141.8, 139.3, 137.8, 136.2, 130.1, 130.0, 129.6, 128.3, 126.1, 42.0, 30.0, 21.8, 21.2, 15.2. **HR-MS** (ESI) m/z calc. for $C_{20}H_{23}O_3S_2^+$. $[M+H]^+$: 375.1083, found: 375.1081.

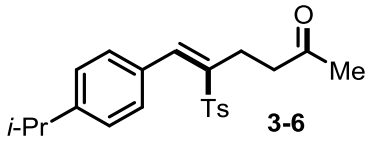


3-5

(*Z*)-6-(4-Hydroxyphenyl)-5-tosylhex-5-en-2-one (3-5)

The general procedure (A) was followed using **1-5** (38.2 mg, 0.20 mmol) and **2a** (41.8 mg, 0.22 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc = 3:1) yielded **3-5** (27.5 mg, 40%) as a yellow oil. For **3-5**: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.55 (d, J = 7.8 Hz, 2H), 7.43 (d, J = 8.4 Hz, 2H), 7.30–7.29 (m, 2H), 7.18 (d, J = 7.8 Hz, 2H), 7.08 (s, 1H), 2.95 (t, J = 7.2 Hz, 2H), 2.79 (t, J = 8.4 Hz, 2H), 2.40 (s, 3H), 2.22 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 206.7, 145.2, 144.8, 139.0,

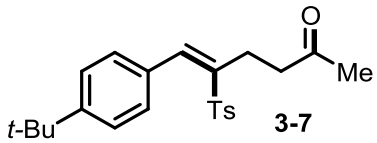
137.3, 131.5, 129.7, 129.6, 127.8, 118.7, 111.9, 42.8, 30.3, 28.3, 21.7. **HR-MS** (ESI) m/z calc. for $C_{19}H_{21}O_4S^+$. $[M+H]^+$: 345.1155, found: 345.1157.



3-6

(*Z*)-6-(4-Isopropylphenyl)-5-tosylhex-5-en-2-one (3-6)

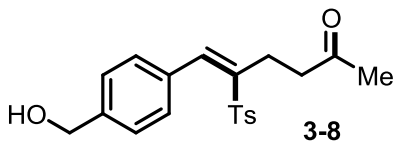
The general procedure (A) was followed using **1-6** (43.2 mg, 0.20 mmol) and **2a** (41.8 mg, 0.22 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc = 5:1) yielded **3-6** (51.8 mg, 56%) as a yellow oil. For **3-6**: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.80 (s, 1H), 7.78 (d, J = 8.4 Hz, 2H), 7.35–7.33 (m, 4H), 7.29 (d, J = 8.4 Hz, 2H), 2.96–2.91 (m, 1H), 2.87–2.84 (m, 2H), 2.73–2.71 (m, 2H), 2.44 (s, 3H), 2.15 (s, 3H), 1.27 (s, 3H), 1.25 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 207.2, 151.2, 144.4, 139.1, 138.4, 136.3, 130.8, 130.0, 129.7, 128.2, 127.3, 42.1, 34.1, 30.0, 23.8, 21.7, 21.2. **HR-MS** (ESI) m/z calc. for $C_{22}H_{27}O_3S^+$. $[M+H]^+$: 371.1676, found: 371.1676.



3-7

(*Z*)-6-(4-(Tert-butyl)phenyl)-5-tosylhex-5-en-2-one (3-7)

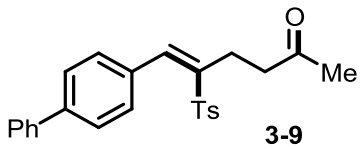
The general procedure (A) was followed using **1-7** (46.0 mg, 0.20 mmol) and **2a** (41.8 mg, 0.22 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc = 5:1) yielded **3-7** (46.8 mg, 61%) as a yellow oil. For **3-7**: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.81 (s, 1H), 7.78 (d, J = 8.4 Hz, 2H), 7.45 (d, J = 9.0 Hz, 2H), 7.37–7.34 (m, 4H), 2.88–2.85 (m, 2H), 2.74–2.71 (m, 2H), 2.45 (s, 3H), 2.16 (s, 3H), 1.33 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 207.2, 153.5, 144.4, 139.3, 138.3, 136.3, 130.5, 130.0 129.5, 128.2, 126.1, 42.1, 35.0, 31.2, 30.0, 21.7, 21.2. **HR-MS** (ESI) m/z calc. for $C_{23}H_{29}O_3S^+$. $[M+H]^+$: 385.1832, found: 385.1839.



3-8

(*Z*)-6-(4-(Hydroxymethyl)phenyl)-5-tosylhex-5-en-2-one (3-8)

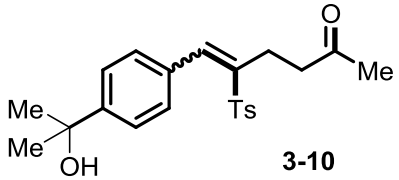
The general procedure (A) was followed using **1-8** (40.8 mg, 0.20 mmol) and **2a** (41.8 mg, 0.22 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc = 5:1) yielded **3-8** (46.5 mg, 65%) as a yellow oil. For **3-8**: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81 (s, 1H), 7.78 (d, J = 8.4 Hz, 2H), 7.41–7.38 (m, 4H), 7.35 (d, J = 8.0 Hz, 2H), 5.12 (s, 2H), 2.83–2.79 (m, 2H), 2.71–2.67 (m, 2H), 2.44 (s, 3H), 2.13 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 206.9, 144.6, 140.9, 137.8, 137.7, 136.0, 133.2, 130.0, 129.6, 128.6, 128.3, 65.6, 42.0, 29.9, 21.7, 21.0. **HR-MS** (ESI) m/z calc. for $C_{21}H_{23}O_4S^+$. $[M+H]^+$: 359.1312, found: 359.1312.



3-9

(*Z*)-6-([1,1'-Biphenyl]-4-yl)-5-tosylhex-5-en-2-one (3-9)

The general procedure (A) was followed using **1-9** (50.0 mg, 0.20 mmol) and **2a** (41.8 mg, 0.22 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc = 5:1) yielded **3-9** (40.4 mg, 50%) as a yellow oil. For **3-9**: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.60 (d, J = 1.6 Hz, 1H), 7.58 (d, J = 1.2 Hz, 1H), 7.50–7.45 (m, 6H), 7.40 (d, J = 7.6 Hz, 1H), 7.27 (d, J = 9.2 Hz, 2H), 7.13 (s, 1H), 7.11 (s, 1H), 7.09 (s, 1H), 2.99 (t, J = 7.6 Hz, 2H), 2.85 (t, J = 7.2 Hz, 2H), 2.35 (s, 3H), 2.24 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 207.0, 143.9, 143.0, 141.1, 140.5, 139.3, 137.5, 132.8, 129.6, 129.2, 128.9, 127.7, 127.6, 127.0, 126.3, 43.2, 30.2, 28.6, 21.6. **HR-MS** (ESI) m/z calc. for $C_{25}H_{25}O_3S^+$. $[M+H]^+$: 405.1519, found: 405.1522.

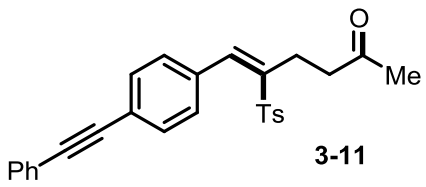


3-10

6-(4-(2-Hydroxypropan-2-yl)phenyl)-5-tosylhex-5-en-2-one (3-10)

The general procedure (A) was followed using **1-10** (46.4 mg, 0.20 mmol) and **2a** (41.8 mg, 0.22 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc = 3:1) yielded **3-10** (34.7 mg, 45%) as a yellow oil. For **3-10**: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.81 (s, 1H), 7.79 (s, 1H), 7.78 (s, 1H), 7.56 (s, 1H), 7.54 (s, 1H),

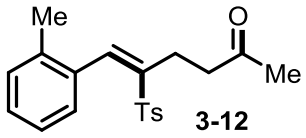
7.38–7.36 (m, 3H), 7.09 (d, *J* = 5.1 Hz, 1H), 2.85–2.82 (m, 2H), 2.73–2.70 (m, 2H), 2.45 (s, 3H), 2.15 (s, 3H), 1.59 (s, 6H). **^{13}C NMR** (151 MHz, $CDCl_3$) *δ* 207.1, 151.1, 144.5, 138.2, 131.7, 130.1, 129.5, 128.3, 127.8, 125.3, 123.8, 72.5, 42.2, 31.8, 30.0, 21.8, 21.2. **HR-MS** (ESI) m/z calc. for $C_{22}H_{27}O_4S^+$. $[M+H]^+$: 387.1625, found: 345. 387.1625.



3-11

(*Z*)-6-(4-(Phenylethynyl)phenyl)-5-tosylhex-5-en-2-one (3-11)

The general procedure (A) was followed using **1-11** (54.8 mg, 0.20 mmol) and **2a** (41.8 mg, 0.22 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc = 3:1) yielded **3-11** (40.2 mg, 47%) as a yellow solid. **M.p.**: 132–135 °C. For **3-11**: **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* 7.57–7.56 (m, 1H), 7.55 (d, *J* = 2.0 Hz, 1H), 7.44 (d, *J* = 8.4 Hz, 2H), 7.41–7.37 (m, 5H), 7.19 (d, *J* = 7.6 Hz, 2H), 7.15 (d, *J* = 7.6 Hz, 2H), 7.07 (s, 1H), 2.97 (t, *J* = 6.4 Hz, 2H), 2.82 (t, *J* = 6.4 Hz, 2H), 2.38 (s, 3H), 2.22 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) *δ* 207.0, 144.3, 143.5, 139.0, 137.4, 133.8, 131.7, 130.9, 129.4, 129.3, 128.6, 128.5, 127.8, 123.3, 123.2, 90.5, 89.2, 43.2, 30.3, 28.7, 21.7. **HR-MS** (ESI) m/z calc. for $C_{27}H_{25}O_3S^+$. $[M+H]^+$: 429.1519, found: 429.1517.

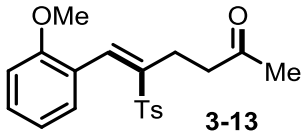


3-12

(*Z*)-6-(O-tolyl)-5-tosylhex-5-en-2-one (3-12)

The general procedure (A) was followed using **1-12** (37.6 mg, 0.20 mmol) and **2a** (41.8 mg, 0.22 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc = 5:1) yielded **3-12** (53.4 mg, 78%) as a yellow solid. **M.p.**: 85–87 °C. For **3-12**: **^{1}H NMR** (600 MHz, $CDCl_3$) *δ* 7.93 (s, 1H), 7.81 (d, *J* = 8.4 Hz, 2H), 7.7 (dd, *J* = 9.0, 1.2 Hz, 2H), 7.27–7.23 (m, 2H), 7.19 (td, *J* = 7.2, 1.2 Hz, 1H), 7.10 (dd, *J* = 7.8, 1.2 Hz, 1H), 2.75–2.72 (m, 2H), 2.54–2.51 (m, 2H), 2.46 (s, 3H), 2.29 (s, 3H), 2.06 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) *δ* 206.8, 144.6, 141.8, 138.9, 136.8, 136.2, 132.8,

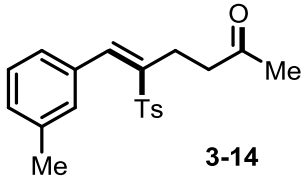
130.5, 130.1, 129.2, 128.3, 127.5, 126.2, 42.4, 29.8, 21.7, 20.7, 20.0. **HR-MS** (ESI) m/z calc. for $C_{20}H_{23}O_3S^+$. $[M+H]^+$: 343.1363, found: 343.1366.



3-13

(*Z*)-6-(2-Methoxyphenyl)-5-tosylhex-5-en-2-one (3-13)

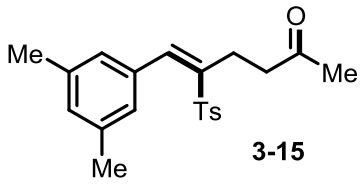
The general procedure (A) was followed using **1-13** (40.8 mg, 0.20 mmol) and **2a** (41.8 mg, 0.22 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc = 3:1) yielded **3-13** (39.4 mg, 45%) as a yellow oil. For **3-13**: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.06 (s, 1H), 7.81 (d, J = 8.4 Hz, 2H), 7.37–7.34 (m, 3H), 7.20 (dd, J = 7.2, 1.2 Hz, 1H), 6.96–6.93 (m, 2H), 3.87 (s, 3H), 2.81 (t, J = 7.8 Hz, 2H), 2.61 (t, J = 7.8 Hz, 2H), 2.45 (s, 3H), 2.10 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 207.1, 157.8, 144.3, 140.2, 136.5, 135.3, 131.1, 129.9, 128.7, 128.2, 122.4, 120.6, 111.0, 55.7, 42.4, 29.9, 21.7, 21.1. **HR-MS** (ESI) m/z calc. for $C_{20}H_{23}O_4S^+$. $[M+H]^+$: 359.1312, found: 359.1294.



3-14

(*Z*)-6-(M-tolyl)-5-tosylhex-5-en-2-one (3-14)

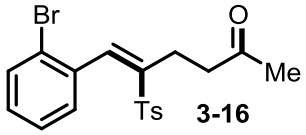
The general procedure (A) was followed using **1-14** (37.6 mg, 0.20 mmol) and **2a** (41.8 mg, 0.22 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc = 5:1) yielded **3-14** (49.9 mg, 73%) as a yellow solid. **M.p.**: 84–86 °C. For **3-14**: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81–7.78 (m, 3H), 7.35 (d, J = 8.0 Hz, 2H), 7.32–7.29 (m, 1H), 7.21–7.17 (m, 3H), 2.84–2.79 (m, 2H), 2.74–2.69 (m, 2H), 2.45 (s, 3H), 2.37 (s, 3H), 2.13 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 207.1, 144.5, 140.2, 138.8, 138.7, 136.1, 133.3, 130.6, 130.3, 130.0, 129.0, 128.3, 126.1, 42.1, 29.9, 21.7, 21.5, 21.1. **HR-MS** (ESI) m/z calc. for $C_{20}H_{23}O_3S^+$. $[M+H]^+$: 343.1363, found: 343.1364.



3-15

(*Z*)-6-(3,5-Dimethylphenyl)-5-tosylhex-5-en-2-one (3-15)

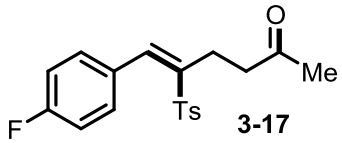
The general procedure (A) was followed using **1-15** (40.4 mg, 0.20 mmol) and **2a** (41.8 mg, 0.22 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc = 5:1) yielded **3-15** (46.3 mg, 65%) as a yellow oil. For **3-15**: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.79 (d, J = 8.4 Hz, 2H), 7.77 (s, 1H), 7.36 (d, J = 1.2 Hz, 1H), 7.34 (d, J = 1.2 Hz, 1H), 7.03 (s, 1H), 7.00 (s, 2H), 2.83–2.81 (m, 2H), 2.72–2.70 (m, 2H), 2.45 (s, 3H), 2.33 (s, 6H), 2.14 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 207.1, 144.5, 140.0, 138.9, 138.7, 136.3, 133.3, 131.5, 130.0, 128.3, 127.2, 42.2, 30.0, 21.7, 21.4, 21.1. **HR-MS** (ESI) m/z calc. for $C_{21}H_{25}O_3S^+$. $[M+H]^+$: 357.1519, found: 357.1525.



3-16

(*Z*)-6-(2-Bromophenyl)-5-tosylhex-5-en-2-one (3-16)

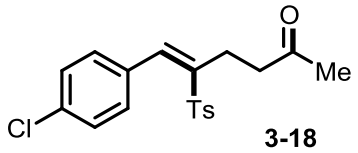
The general procedure (A) was followed using **1-16** (50.4 mg, 0.20 mmol) and **2a** (41.8 mg, 0.22 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc = 3:1) yielded **3-16** (40.7 mg, 50%) as a yellow oil. For **3-16**: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.41 (d, J = 8.4 Hz, 2H), 7.36 (d, J = 8.4 Hz, 2H), 7.15 (d, J = 7.8 Hz, 2H), 7.05 (d, J = 7.8 Hz, 2H), 7.00 (s, 1H), 2.95 (t, J = 7.2 Hz, 2H), 2.80 (t, J = 6.6 Hz, 2H), 2.39 (s, 3H), 2.22 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 207.0, 144.4, 143.9, 138.4, 137.3, 132.8, 130.9, 130.8, 129.4, 127.8, 122.7, 43.1, 29.8, 28.5, 21.7. **HR-MS** (ESI) *m/z* calc. for $C_{19}H_{20}BrO_3S^+$. $[M+H]^+$: 407.0311, found: 407.0313.



3-17

(*Z*)-6-(4-Fluorophenyl)-5-tosylhex-5-en-2-one (3-17)

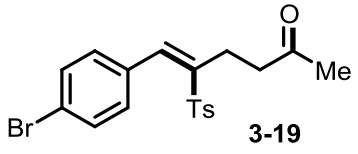
The general procedure (A) was followed using **1-17** (38.4 mg, 0.20 mmol) and **2a** (41.8 mg, 0.22 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc = 3:1) yielded **3-17** (30.5 mg, 44%) as a yellow oil. For **3-17**: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.41 (d, J = 8.3 Hz, 2H), 7.19–7.17 (m, 2H), 7.14 (d, J = 8.4 Hz, 2H), 7.04 (s, 1H), 6.94–6.91 (m, 2H), 2.96 (t, J = 7.2 Hz, 2H), 2.81 (t, J = 7.2 Hz, 2H), 2.37 (s, 3H), 2.22 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 207.1, 162.7 (d, J = 249.2 Hz), 144.2, 143.3, 138.8, 137.5, 131.2(d, J = 7.6 Hz), 129.8 (d, J = 3.0 Hz) ,129.4, 127.7, 114.8 (d, J = 30.2 Hz), 43.2, 30.3, 28.7, 21.7. **^{19}F NMR** (565 MHz, $CDCl_3$) δ –112.7. **HR-MS** (ESI) *m/z* calc. for $C_{19}H_{20}FO_3S^+$. $[M+H]^+$: 347.1112, found: 347.1117.



3-18

(*Z*)-6-(4-Chlorophenyl)-5-tosylhex-5-en-2-one (3-18)

The general procedure (A) was followed using **1-18** (41.6 mg, 0.20 mmol) and **2a** (41.8 mg, 0.22 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc = 3:1) yielded **3-18** (36.3 mg, 50%) as a yellow oil. For **3-18**: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.41 (d, J = 8.4 Hz, 2H), 7.20 (d, J = 8.4 Hz, 2H), 7.15 (d, J = 7.8 Hz, 2H), 7.11 (d, J = 8.4 Hz, 2H), 7.03 (s, 1H), 2.95 (t, J = 7.2 Hz, 2H), 2.79 (t, J = 7.2 Hz, 2H), 2.38 (s, 3H), 2.21 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 207.0, 144.4, 143.8, 138.4, 137.3, 134.4, 132.3, 130.5, 129.4, 127.9, 127.7, 43.1, 30.3, 28.5, 21.7. **HR-MS** (ESI) *m/z* calc. for $C_{19}H_{20}ClO_3S^+$. $[M+H]^+$: 363.0816, found: 363.0817.

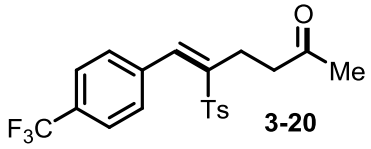


3-19

(*Z*)-6-(4-Bromophenyl)-5-tosylhex-5-en-2-one (3-19)

The general procedure (A) was followed using **1-15** (50.6 mg, 0.20 mmol) and **2a** (41.8 mg, 0.22 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc = 3:1) yielded **3-19** (48.8 mg, 60%) as a yellow solid. **M.p.**: 106–108 °C. For **3-19**: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.41 (d, J = 7.8 Hz, 2H), 7.35 (d, J = 8.4 Hz, 2H), 7.15 (d, J = 7.7 Hz, 2H), 7.04 (d, J = 7.2 Hz, 2H), 7.00 (s, 1H), 2.95 (t, J = 7.2 Hz,

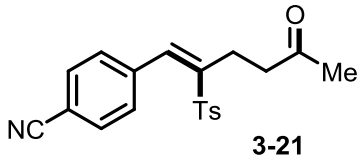
2H), 2.79 (t, *J* = 6.0 Hz, 2H), 2.38 (s, 3H), 2.21 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) *δ* 206.9, 144.4, 143.8, 138.3, 137.3, 132.8, 130.8, 130.7, 129.4, 127.7, 122.6, 43.0, 30.3, 28.5, 21.7. **HR-MS** (ESI) *m/z* calc. for $C_{19}H_{20}BrO_3S^+$. $[M+H]^+$: 407.0311, found: 407.0314.



3-20

(*Z*)-5-Tosyl-6-(4-(Trifluoromethyl)phenyl)hex-5-en-2-one (3-20)

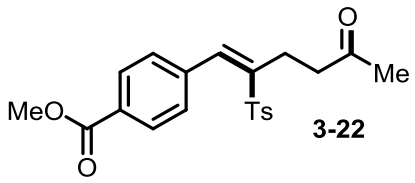
The general procedure (A) was followed using **1-20** (48.4 mg, 0.20 mmol) and **2a** (41.8 mg, 0.22 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc = 2:1) yielded **3-20** (31.7 mg, 40%) as a yellow oil. For **3-20**: **^{1}H NMR** (600 MHz, $CDCl_3$) *δ* 7.46 (d, *J* = 8.1 Hz, 2H), 7.37 (d, *J* = 7.8 Hz, 2H), 7.23 (d, *J* = 8.4 Hz, 2H), 7.10 (d, *J* = 8.4 Hz, 3H), 2.98 (t, *J* = 7.2 Hz, 2H), 2.85 (t, *J* = 7.8 Hz, 2H), 2.36 (s, 3H), 2.23 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) *δ* 206.9, 145.2, 144.5, 137.8, 137.6, 137.1, 130.1 (d, *J* = 32.3 Hz), 129.4, 129.3, 127.8, 124.6 (d, *J* = 4.0 Hz), 124.1 (d, *J* = 272.7 Hz), 42.9, 30.3, 28.3, 21.6. **^{19}F NMR** (377 MHz, $CDCl_3$) *δ* –62.8. **HR-MS** (ESI) *m/z* calc. for $C_{20}H_{20}F_3O_3S^+$. $[M+H]^+$: 397.1080, found: 397.1084.



3-21

(*Z*)-4-(5-Oxo-2-tosylhex-1-en-1-yl)benzonitrile (3-21)

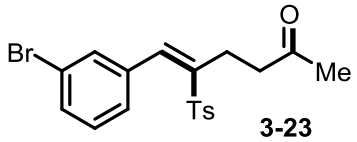
The general procedure (A) was followed using **1-21** (43.2 mg, 0.20 mmol) and **2a** (41.8 mg, 0.22 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc = 2:1) yielded **3-21** (28.1 mg, 38%) as a yellow oil. For **3-21**: **^{1}H NMR** (600 MHz, $CDCl_3$) *δ* 7.54 (d, *J* = 8.0 Hz, 2H), 7.42 (d, *J* = 8.3 Hz, 2H), 7.30 (s, 1H), 7.28 (d, *J* = 1.6 Hz, 1H), 7.18 (d, *J* = 8.0 Hz, 2H), 7.07 (s, 1H), 2.95 (t, *J* = 7.2 Hz, 2H), 2.78 (t, *J* = 7.3 Hz, 2H), 2.40 (s, 3H), 2.21 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) *δ* 206.7, 145.2, 144.8, 139.0, 137.3, 136.9, 131.4, 129.7, 129.6, 127.8, 118.6, 111.9, 42.7, 30.2, 28.2, 21.7. **HR-MS** (ESI) m/z calc. for $C_{20}H_{20}NO_3S^+$. $[M+H]^+$: 354.1159, found: 354.1161.



3-22

(*Z*)-Methyl-4-(5-oxo-2-tosylhex-1-en-1-yl) benzoate (3-22)

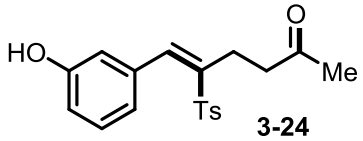
The general procedure (A) was followed using **1-22** (46.4 mg, 0.20 mmol) and **2a** (41.8 mg, 0.22 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc = 2:1) yielded **3-22** (23.2 mg, 30%) as a yellow oil. For **3-22**: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.91 (d, J = 8.4 Hz, 2H), 7.41 (d, J = 8.4 Hz, 2H), 7.24 (d, J = 7. 8 Hz, 2H), 7.13 (d, J = 7.2 Hz, 2H), 7.10 (s, 1H), 3.94 (s, 3H), 2.97 (t, J = 7.2 Hz, 2H), 2.81 (t, J = 7.2 Hz, 2H), 2.37 (s, 3H), 2.22 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 206.9, 166.8, 144.5, 144.4, 138.8, 138.5, 137.2, 129.7, 129.5, 129.0, 129.0, 127.8, 52.4, 43.0, 30.3, 28.4, 21.7. **HR-MS** (ESI) *m/z* calc. for $C_{21}H_{23}O_5S^+$. $[M+H]^+$: 387.1261, found: 387.1260.



3-23

(*Z*)-6-(3-Bromophenyl)-5-tosylhex-5-en-2-one (3-23)

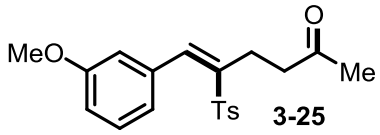
The general procedure (A) was followed using **1-23** (50.4 mg, 0.20 mmol) and **2a** (41.8 mg, 0.22 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc = 3:1) yielded **3-23** (49.6 mg, 61%) as a yellow oil. For **3-23**: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.79 (d, J = 8.4 Hz, 2H), 7.75 (s, 1H), 7.53–7.51 (m, 2H), 7.37 (d, J = 7.2 Hz, 2H), 7.30–7.29 (m, 2H), 2.81 (t, J = 7.2 Hz, 2H), 2.67 (t, J = 8.4 Hz, 2H), 2.46 (s, 3H), 2.14 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 206.7, 144.8, 142.4, 136.9, 135.8, 135.5, 132.6, 132.2, 130.6, 130.2, 128.4, 127.5, 123.1, 42.0, 30.0, 21.8, 21.0. **HR-MS** (ESI) *m/z* calc. for $C_{19}H_{20}BrO_3S^+$. $[M+H]^+$: 407.0311, found: 407.0292.



3-24

(*Z*)-6-(3-Hydroxyphenyl)-5-tosylhex-5-en-2-one (3-24)

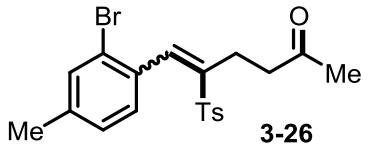
The general procedure (A) was followed using **1-24** (38.0 mg, 0.20 mmol) and **2a** (41.8 mg, 0.22 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc = 3:1) yielded **3-24** (37.8 mg, 55%) as a yellow solid. **M.p.**: 105–107 °C. For **3-24**: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 (d, J = 8.0 Hz, 2H), 7.10 (d, J = 8.0 Hz, 2H), 7.04–7.02 (m, 1H), 6.73 (dd, J = 8.0, 2.4 Hz, 1H), 6.68 (s, 1H), 6.62 (d, J = 7.6 Hz, 1H), 6.38 (s, 1H), 2.96 (t, J = 7.2 Hz, 2H), 2.82 (t, J = 6.8 Hz, 2H), 2.34 (s, 3H), 2.22 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 207.8, 155.4, 144.2, 143.0, 139.5, 137.2, 135.1, 129.3, 129.0, 127.8, 121.0, 116.1, 115.5, 43.2, 30.3, 28.5, 21.6. **HR-MS** (ESI) *m/z* calc. for $C_{19}H_{21}O_4S^+$. $[M+H]^+$: 345.1155, found: 345.1157.



3-25

(*Z*)-6-(3-Methoxyphenyl)-5-tosylhex-5-en-2-one (3-25)

The general procedure (A) was followed using **1-25** (40.8 mg, 0.20 mmol) and **2a** (41.8 mg, 0.22 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc = 3:1) yielded **3-25** (42.2 mg, 59%) as a yellow oil. For **3-25**: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.80 (d, J = 3.6 Hz, 2H), 7.78 (s, 1H), 7.37 (s, 1H), 7.35–7.31 (m, 2H), 6.98–6.91 (m, 3H), 3.81 (s, 3H), 2.84–2.79 (m, 2H), 2.74–2.69 (m, 2H), 2.45 (s, 3H), 2.13 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 207.0, 159.9, 144.6, 140.7, 138.4, 136.0, 134.6, 130.1, 130.1, 128.3, 121.6, 115.5, 114.7, 55.4, 42.1, 29.9, 21.7, 21.1. **HR-MS** (ESI) *m/z* calc. for $C_{20}H_{23}O_4S^+$. $[M+H]^+$: 359.1312, found: 359.1311.

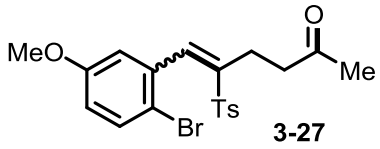


3-26

6-(2-Bromo-4-methylphenyl)-5-tosylhex-5-en-2-one (3-26)

The general procedure (A) was followed using **1-26** (53.4 mg, 0.20 mmol) and **2a** (41.8 mg, 0.22 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc = 3:1) yielded **3-26** (50.5 mg, 60%) as a yellow oil. For **3-26**: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.85 (s, 1H), 7.83 (d, J = 8.4 Hz, 2H), 7.46 (s, 1H), 7.36 (d, J = 7.8 Hz, 2H), 7.13 (dd, J = 7.8, 0.6 Hz, 1H), 7.08 (d, J = 7.8 Hz, 1H), 2.76–2.74 (m, 2H),

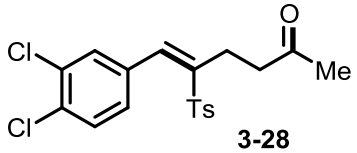
2.52–2.49 (m, 2H), 2.45 (s, 3H), 2.34 (s, 3H), 2.08 (s, 3H). **HR-MS** (ESI) m/z calc. for $C_{20}H_{22}BrO_3S^+$. $[M+H]^+$: 421.0468, found: 421.0468.



3-27

6-(2-Bromo-5-methoxyphenyl)-5-tosylhex-5-en-2-one (3-27)

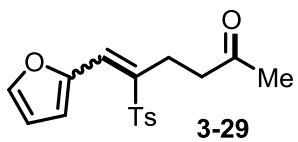
The general procedure (A) was followed using **1-27** (56.6 mg, 0.20 mmol) and **2a** (41.8 mg, 0.22 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc = 3:1) yielded **3-27** (45.4 mg, 52%) as a yellow oil. For **3-27**: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.84 (d, J = 8.4 Hz, 2H), 7.80 (s, 1H), 7.50 (d, J = 8.4 Hz, 1H), 7.37 (d, J = 8.0 Hz, 2H), 7.18–7.11 (m, 1H), 6.77–6.76 (m, 1H), 3.78 (s, 3H), 2.75 (t, J = 7.6 Hz, 2H), 2.52 (t, J = 8.4 Hz, 2H), 2.46 (s, 3H), 2.08 (s, 3H). **HR-MS** (ESI) *m/z* calc. for $C_{20}H_{22}BrO_4S^+$. $[M+H]^+$: 437.0417, found: 437.0417.



3-28

(*Z*)-6-(3,4-Dichlorophenyl)-5-tosylhex-5-en-2-one (3-28)

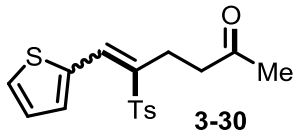
The general procedure (A) was followed using **1-28** (48.4 mg, 0.20 mmol) and **2a** (41.8 mg, 0.22 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc = 3:1) yielded **3-28** (39.7 mg, 50%) as a yellow solid. **M.p.**: 84–86 °C. For **3-28**: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40 (d, J = 8.8 Hz, 2H), 7.30 (d, J = 8.0 Hz, 1H), 7.16 (d, J = 8.8 Hz, 2H), 7.08–7.03 (m, 2H), 6.96 (s, 1H), 2.95 (t, J = 6.4 Hz, 2H), 2.83 (t, J = 7.2 Hz, 2H), 2.39 (s, 3H), 2.22 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 206.8, 145.4, 144.7, 137.1, 136.5, 133.8, 132.4, 131.9, 130.5, 129.7, 129.4, 128.6, 127.8, 42.8, 30.3, 28.3, 21.7. **HR-MS** (ESI) *m/z* calc. for $C_{19}H_{19}Cl_2O_3S^+$. $[M+H]^+$: 397.0427, found: 397.0431.



3-29

6-(Furan-2-yl)-5-tosylhex-5-en-2-one (3-29)

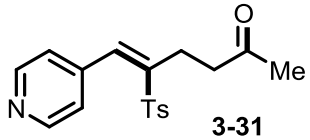
The general procedure (A) was followed using **1-29** (32.8 mg, 0.20 mmol) and **2a** (41.8 mg, 0.22 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc = 5:1) yielded **3-29** (33.1 mg, 52%) as a yellow oil. For **3-29**: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.76 (d, J = 7.8 Hz, 2H), 7.55 (s, 1H), 7.54 (d, J = 1.8 Hz, 1H), 7.33 (d, J = 8.4 Hz, 2H), 6.72 (d, J = 3.6 Hz, 1H), 6.52 (dd, J = 3.6, 1.8 Hz, 1H), 2.79 (s, 4H), 2.44 (s, 3H), 2.15 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 207.5, 149.6, 145.6, 144.5, 136.7, 136.3, 130.0, 128.3, 124.7, 117.3, 112.5, 42.8, 29.9, 21.9, 21.7. **HR-MS** (ESI) *m/z* calc. for $C_{17}H_{19}O_4S^+$. $[M+H]^+$: 319.0999, found: 319.0994.



3-30

6-(Thiophen-2-yl)-5-tosylhex-5-en-2-one (3-30)

The general procedure (A) was followed using **1-30** (36.0 mg, 0.20 mmol) and **2a** (41.8 mg, 0.22 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc = 5:1) yielded **3-30** (43.4 mg, 65%) as a yellow oil. For **3-30**: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.79 (d, J = 2.4 Hz, 2H), 7.77 (s, 1H), 7.56 (d, J = 1.6 Hz, 1H), 7.34 (d, J = 8.0 Hz, 2H), 7.22 (dd, J = 5.2, 1.2 Hz, 1H), 7.17–7.15 (m, 1H), 2.83–2.79 (m, 2H), 2.75–2.70 (m, 2H), 2.45 (s, 3H), 2.16 (s, 3H). **HR-MS** (ESI) *m/z* calc. for $C_{17}H_{19}O_3S_2^+$. $[M+H]^+$: 335.0770, found: 335.0772.

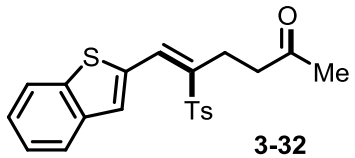


3-31

(*Z*)-6-(Pyridin-4-yl)-5-tosylhex-5-en-2-one (3-31)

The general procedure (A) was followed using **1-31** (35.0 mg, 0.20 mmol) and **2a** (41.8 mg, 0.22 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc = 1:1) yielded **3-31** (23.0 mg, 35%) as a yellow solid. **M.p.**: 90–92 °C. For **3-31**: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.68 (d, J = 4.8 Hz, 2H), 7.79 (d, J = 8.4 Hz, 2H), 7.73 (s, 1H), 7.38 (d, J = 8.0 Hz, 2H), 7.25 (d, J = 6.0 Hz, 2H), 2.80 (t, J = 7.2 Hz, 2H), 2.67 (t, J = 8.8 Hz, 2H), 2.47 (s, 3H), 2.12 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 206.4, 150.4, 149.5, 145.4, 145.2, 141.3, 135.5, 135.3, 130.3, 129.9, 128.5, 123.2,

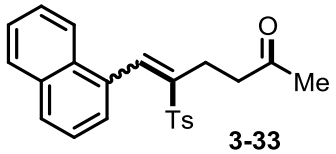
42.0, 29.9, 21.8, 21.0. **HR-MS** (ESI) *m/z* calc. for $C_{18}H_{20}NO_3S^+$. $[M+H]^+$: 330.1159, found: 330.1161.



3-32

(*Z*)-6-(Benzo[b]thiophen-2-yl)-5-tosylhex-5-en-2-one (3-32)

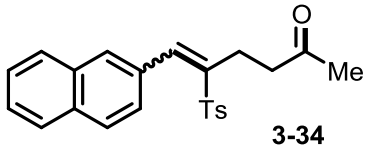
The general procedure (A) was followed using **1-32** (46.0 mg, 0.30 mmol) and **2a** (41.8 mg, 0.22 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc = 3:1) yielded **3-32** (23.8 mg, 31%) as a yellow oil. For **3-32**: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.74–7.73 (m, 2H), 7.30 (s, 1H), 7.29 (d, J = 4.6 Hz, 2H), 7.22–7.20 (m, 2H), 7.07 (d, J = 1.3 Hz, 1H), 6.82 (d, J = 7.7 Hz, 2H), 3.08–3.06 (m, 2H), 3.04–3.01 (m, 2H), 2.27 (s, 3H), 2.08 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 207.1, 146.7, 143.5, 139.0, 137.5, 137.1, 132.2, 129.3, 128.8, 128.5, 127.2, 124.5, 124.1, 122.5, 121.7, 43.1, 30.4, 28.7, 21.3. **HR-MS** (ESI) *m/z* calc. for $C_{21}H_{21}O_3S_2^+$. $[M+H]^+$: 385.0927, found: 385.0930.



3-33

6-(Naphthalen-1-yl)-5-tosylhex-5-en-2-one (3-33)

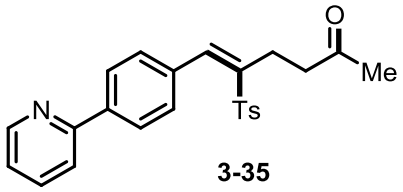
The general procedure (A) was followed using **1-33** (44.8 mg, 0.20 mmol) and **2a** (41.8 mg, 0.22 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc = 3:1) yielded **3-33** (45.4 mg, 60%) as a yellow oil. For **3-33**: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.38 (s, 1H), 7.90 (d, J = 8.3 Hz, 3H), 7.58–7.56 (m, 2H), 7.49–7.45 (m, 2H), 7.41 (d, J = 5.7 Hz, 2H), 7.33 (dt, J = 7.1, 1.2 Hz, 1H), 7.07 (d, J = 8.2 Hz, 1H), 2.72–2.68 (m, 2H), 2.60–2.57 (m, 2H), 2.49 (s, 3H), 1.99 (s, 3H). **HR-MS** (ESI) *m/z* calc. for $C_{23}H_{23}O_3S^+$. $[M+H]^+$: 379.1363, found: 379.1365.



3-34

6-(Naphthalen-2-yl)-5-tosylhex-5-en-2-one (3-34)

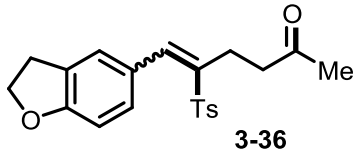
The general procedure (A) was followed using **1-34** (44.8 mg, 0.20 mmol) and **2a** (41.8 mg, 0.22 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc = 5:1) yielded **3-34** (37.8 mg, 50%) as a yellow oil. For (*Z*)-**3-34**: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.00 (s, 1H), 7.90 (s, 1H), 7.88–7.83 (m, 5H), 7.57–7.53 (m, 2H), 7.48 (dd, *J* = 8.5, 1.6 Hz, 1H), 7.37 (d, *J* = 8.0 Hz, 2H), 2.88–2.85 (m, 2H), 2.84–2.81 (m, 2H), 2.46 (s, 3H), 2.14 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 207.1, 144.6, 140.6, 138.5, 136.2, 133.5, 133.2, 130.8, 130.1, 128.9, 128.6, 128.3, 127.8, 127.5, 127.0, 125.8, 42.2, 30.0, 21.7, 21.2. For (*E*)-**3-34**: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.80–7.75 (m, 2H), 7.65 (d, *J* = 9.0 Hz, 2H), 7.51–7.48 (m, 2H), 7.34 (d, *J* = 8.3 Hz, 2H), 7.24 (s, 1H), 7.19 (dd, *J* = 8.4, 1.6 Hz, 1H), 6.90 (d, *J* = 8.2 Hz, 2H), 3.02 (t, *J* = 7.4 Hz, 2H), 2.90 (t, *J* = 7.4 Hz, 2H), 2.25 (s, 3H), 2.22 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 207.1, 143.9, 143.5, 139.5, 137.4, 132.8, 132.5, 131.3, 129.0, 128.8, 128.2, 127.7, 127.6, 127.2, 126.6, 126.4, 126.3, 43.3, 30.3, 28.6, 21.5. **HR-MS** (ESI) *m/z* calc. for $C_{23}H_{23}O_3S^+$. $[M+H]^+$: 379.1363, found: 379.1359.



3-35

(*Z*)-6-(4-(Pyridin-4-yl)phenyl)-5-tosylhex-5-en-2-one (3-35)

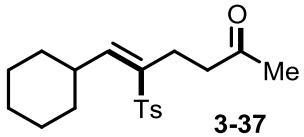
The general procedure (A) was followed using **1-35** (50.2 mg, 0.20 mmol) and **2a** (41.8 mg, 0.22 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc = 1:1) yielded **3-35** (38.9 mg, 48%) as a yellow oil. For **3-35**: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.72 (dd, *J* = 6.0, 1.0 Hz, 1H), 8.07 (d, *J* = 8.4 Hz, 2H), 7.88 (s, 1H), 7.82 (d, *J* = 8.3 Hz, 2H), 7.80–7.76 (m, 2H), 7.51 (d, *J* = 8.3 Hz, 2H), 7.37 (d, *J* = 8.1 Hz, 2H), 7.30–7.29 (m, 1H), 2.86–2.83 (m, 2H), 2.77–2.75 (m, 2H), 2.46 (s, 3H), 2.15 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 207.0, 156.2, 150.0, 144.6, 141.0, 140.6, 137.9, 137.1, 136.1, 133.9, 130.1, 129.9, 128.4, 127.5, 122.8, 120.8, 42.1, 30.0, 21.8, 21.2. **HR-MS** (ESI) *m/z* calc. for $C_{24}H_{24}O_3S^+$. $[M+H]^+$: 406.1472, found: 406.1474.



3-36

6-(2,3-Dihydrobenzofuran-5-yl)-5-tosylhex-5-en-2-one (3-36)

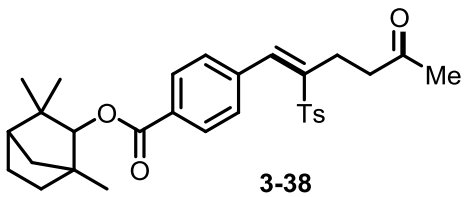
The general procedure (A) was followed using **1-36** (43.2 mg, 0.20 mmol) and **2a** (41.8 mg, 0.22 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc = 3:1) yielded **3-36** (55.5 mg, 75%) as a yellow oil. For **3-36**: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.77 (d, J = 8.3 Hz, 2H), 7.75 (s, 1H), 7.34 (d, J = 8.0 Hz, 2H), 7.28 (s, 1H), 7.15 (s, 1H), 6.82 (d, J = 8.4 Hz, 1H), 4.64 (t, J = 8.8 Hz, 2H), 3.24 (t, J = 8.7 Hz, 2H), 2.83 (dd, J = 9.8, 6.2 Hz, 2H), 2.71 (dd, J = 9.8, 6.2 Hz, 2H), 2.45 (s, 3H), 2.15 (s, 3H). **HR-MS** (ESI) *m/z* calc. for $C_{21}H_{23}O_4S^+$. $[M+H]^+$: 371.1312, found: 371.1316.



3-37

(*Z*)-6-Cyclohexyl-5-tosylhex-5-en-2-one (3-37)

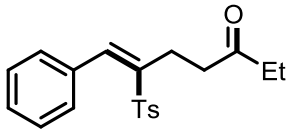
The general procedure (A) was followed using **1-37** (36.0 mg, 0.20 mmol) and **2a** (41.8 mg, 0.22 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc = 3:1) yielded **3-37** (25.4 mg, 38%) as a yellow oil. For **3-37**: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.70 (d, J = 8.2 Hz, 2H), 7.32 (d, J = 8.0 Hz, 2H), 6.76 (d, J = 10.4 Hz, 1H), 2.71 (t, J = 8.2 Hz, 2H), 2.44 (s, 3H), 2.40 (t, J = 8.4 Hz, 2H), 2.13 (s, 3H), 1.76 (d, J = 12.0 Hz, 2H), 1.70 (d, J = 12.0 Hz, 1H), 1.61 (d, J = 12.0 Hz, 2H), 1.32–1.22 (m, 6H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 207.2, 147.4, 144.1, 137.8, 136.5, 129.8, 127.9, 43.1, 37.7, 31.9, 29.9, 25.6, 25.2, 21.6, 20.4. **HR-MS** (ESI) *m/z* calc. for $C_{19}H_{27}O_3S^+$. $[M+H]^+$: 335.1676, found: 335.1679.



3-38

(*Z*)-1,3,3-Trimethylbicyclo[2.2.1]heptan-2-yl-4-(5-oxo-2-tosylhex-1-en-1-yl)benzoate (3-38)

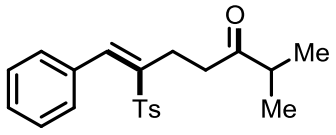
The general procedure (A) was followed using **1-38** (70.8 mg, 0.20 mmol) and **2a** (41.8 mg, 0.22 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc = 5:1) yielded **3-38** (55.9 mg, 55%) as a yellow oil. For **3-38**: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.91 (d, J = 7.8 Hz, 2H), 7.40 (d, J = 8.4 Hz, 2H), 7.21 (d, J = 8.4 Hz, 2H), 7.10 (d, J = 8.4 Hz, 3H), 4.63 (s, 1H), 2.97 (t, J = 7.2 Hz, 2H), 2.82 (t, J = 7.8 Hz, 2H), 2.35 (s, 3H), 2.22 (s, 3H), 1.96–1.91 (m, 1H), 1.81–1.78 (m, 2H), 1.69 (d, J = 10.2 Hz, 1H), 1.58–1.52 (m, 1H), 1.28 (d, J = 10.8 Hz, 1H), 1.24–1.22 (m, 1H), 1.21 (s, 3H), 1.13 (s, 3H), 0.87 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 206.8, 166.5, 144.5, 144.3, 138.6, 138.4, 137.2, 130.2, 129.4, 128.9, 128.8, 127.8, 86.9, 48.7, 48.5, 43.0, 41.6, 40.0, 30.3, 29.9, 28.3, 27.0, 26.0, 21.6, 20.4, 19.6. **HR-MS** (ESI) *m/z* calc. for $C_{30}H_{37}O_5S^+$. $[M+H]^+$: 509.2356, found: 509.2357.



3-39

(*Z*)-7-Phenyl-6-tosylhept-6-en-3-one (3-39)

The general procedure (A) was followed using **1-1** (37.6 mg, 0.20 mmol) and **2a** (41.8 mg, 0.22 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc = 5:1) yielded **3-39** (61.6 mg, 90%) as a yellow oil. For **3-39**: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.83 (s, 1H), 7.79 (d, J = 8.3 Hz, 2H), 7.43–7.38 (m, 5H), 7.36 (s, 1H), 7.34 (s, 1H), 2.81–2.76 (m, 2H), 2.74–2.71 (m, 2H), 2.44 (s, 3H), 2.40 (q, J = 7.3 Hz, 2H), 1.04 (t, J = 7.3 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 209.8, 144.5, 140.6, 138.4, 136.1, 133.3, 130.0, 129.8, 129.4, 129.1, 128.3, 40.6, 35.8, 21.6, 21.1, 7.8. **HR-MS** (ESI) *m/z* calc. for $C_{20}H_{23}O_3S^+$. $[M+H]^+$: 343.1363, found: 343.1362.

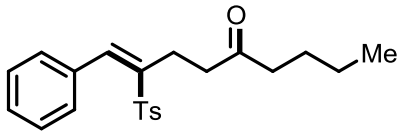


3-40

(Z)-2-Methyl-7-phenyl-6-tosylhept-6-en-3-one (3-40)

The general procedure (A) was followed using **1-40** (40.4 mg, 0.20 mmol) and **2a** (41.8 mg, 0.22 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc = 5:1) yielded **3-40** (49.8 mg, 70%) as a yellow oil. For **3-40**: **^{1}H NMR**

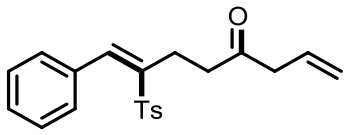
(400 MHz, $CDCl_3$) δ 7.83 (s, 1H), 7.80 (d, J = 8.0 Hz, 2H), 7.41–7.39 (m, 4H), 7.35 (d, J = 7.6 Hz, 2H), 2.81–2.78 (m, 2H), 2.74–2.70 (m, 2H), 2.59–2.52 (m, 1H), 2.45 (s, 3H), 1.08 (s, 3H), 1.06 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 213.1, 144.5, 140.7, 138.2, 136.1, 130.0, 129.8, 129.4, 129.1, 128.3, 40.9, 38.7, 21.7, 21.3, 18.3. **HR-MS** (ESI) *m/z* calc. for $C_{21}H_{25}O_3S^+$. $[M+H]^+$: 357.1519, found: 357.1524.



3-41

(Z)-1-Phenyl-2-tosylnon-1-en-5-one (3-41)

The general procedure (A) was followed using **1-41** (43.2 mg, 0.20 mmol) and **2a** (41.8 mg, 0.22 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc = 5:1) yielded **3-41** (45.9 mg, 62%) as a yellow solid. **M.p.**: 77**–**79 °C. For **3-41**: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.83 (s, 1H), 7.80 (d, J = 7.8 Hz, 2H), 7.43–7.39 (m, 5H), 7.36 (s, 1H), 7.35 (s, 1H), 2.79–2.76 (m, 2H), 2.73–2.70 (m, 2H), 2.45 (s, 3H), 2.37 (t, J = 7.2 Hz, 2H), 1.54 (dt, J = 20.9, 7.5 Hz, 2H), 1.29 (dd, J = 15.0, 7.2 Hz, 2H), 0.90 (t, J = 7.8 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 209.6, 144.5, 140.6, 138.3, 136.1, 133.4, 130.0, 129.8, 129.4, 129.1, 128.3, 42.5, 41.0, 25.9, 22.3, 21.6, 21.0, 13.9. **HR-MS** (ESI) *m/z* calc. for $C_{22}H_{27}O_3S^+$. $[M+H]^+$: 371.1676, found: 371.1678.

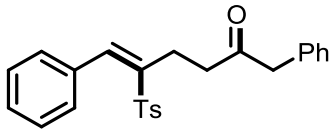


3-42

(Z)-8-Phenyl-7-tosylocta-1,7-dien-4-one (3-42)

The general procedure (A) was followed using **1-42** (40.0 mg, 0.20 mmol) and **2a** (41.8 mg, 0.22 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc = 5:1) yielded **3-42** (31.9 mg, 45%) as a yellow solid. **M.p.**: 63**–**65 °C. For **3-42**: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.84 (s, 1H), 7.80 (d, J = 8.4 Hz, 2H), 7.43–7.38 (m, 5H), 7.36 (s, 1H), 7.35 (s, 1H), 5.92–5.86 (m, 1H), 5.20 (dd, J = 10.2, 1.8 Hz, 1H), 5.14 (dd, J = 17.4, 1.8 Hz, 1H), 3.16 (d, J = 7.0 Hz, 2H), 2.85–2.82 (m, 2H), 2.73–2,71 (m, 2H), 2.45 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 207.0, 144.6, 140.5, 138.5,

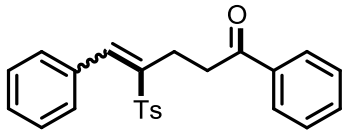
136.1, 133.4, 130.2, 130.1, 129.8, 129.4, 129.1, 128.3, 119.3, 47.7, 40.8, 21.7, 21.1. **HR-MS** (ESI) *m/z* calc. for $C_{21}H_{23}O_3S^+$. $[M+H]^+$: 355.1363, found: 355.1367.



3-43

(Z)-1,6-Diphenyl-5-tosylhex-5-en-2-one (3-43)

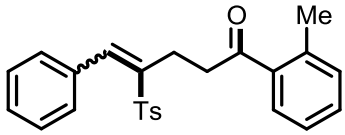
The general procedure (A) was followed using **1-43** (50.0 mg, 0.20 mmol) and **2a** (41.8 mg, 0.22 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc = 3:1) yielded **3-43** (71.1 mg, 88%) as a yellow oil. For **3-43**: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.81 (s, 1H), 7.77 (d, J = 12.6 Hz, 2H), 7.37–7.29 (m, 10H), 7.19 (dd, J = 12.2, 2.4 Hz, 2H), 3.68 (s, 2H), 2.87–2.83 (m, 2H), 2.72–2.68 (m, 2H), 2.45 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 206.7, 144.5, 140.4, 138.5, 136.0, 133.9, 133.3, 130.0, 129.7, 129.4, 129.3, 129.0, 128.9, 128.3, 127.2, 50.0, 40.5, 21.7, 21.2. **HR-MS** (ESI) *m/z* calc. for $C_{25}H_{25}O_3S^+$. $[M+H]^+$: 405.1519, found: 405.1519.



3-44

1,5-Diphenyl-4-tosylpent-4-en-1-one (3-44)

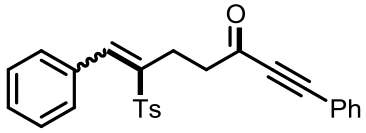
The general procedure (A) was followed using **1-44** (47.2 mg, 0.20 mmol) and **2a** (41.8 mg, 0.22 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc = 3:1) yielded **3-44** (42.9 mg, 55%) as a yellow oil. For **3-44**: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.94 (d, J = 7.8 Hz, 2H), 7.91 (s, 1H), 7.83 (d, J = 7.8 Hz, 2H), 7.59 (t, J = 7.2 Hz, 1H), 7.49–7.46 (m, 3H), 7.45–7.42 (m, 3H), 7.40 (d, J = 1.3 Hz, 1H), 7.36 (d, J = 9.0 Hz, 2H), 3.34 (t, J = 7.8 Hz, 2H), 2.91 (t, J = 8.4 Hz, 2H), 2.44 (s, 3H). **HR-MS** (ESI) *m/z* calc. for $C_{24}H_{23}O_3S^+$. $[M+H]^+$: 391.1363, found: 391.1362.



3-45

5-Phenyl-1-(o-tolyl)-4-tosylpent-4-en-1-one (3-45)

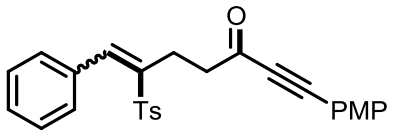
The general procedure (A) was followed using **1-45** (50.0 mg, 0.20 mmol) and **2a** (41.8 mg, 0.22 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc = 3:1) yielded **3-45** (32.3 mg, 40%) as a yellow oil. For **3-45**: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89 (s, 1H), 7.83 (d, *J* = 8.2 Hz, 2H), 7.77 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.61 (dd, *J* = 7.2, 1.6 Hz, 1H), 7.46–7.41 (m, 9H), 7.39–7.32 (m, 4H), 7.27–7.18 (m, 8H), 7.09 (d, *J* = 8.0 Hz, 2H), 3.42 (t, *J* = 7.3 Hz, 2H), 3.28–3.24 (m, 2H), 3.01 (t, *J* = 7.2 Hz, 2H), 2.92–2.88 (m, 2H), 2.53 (s, 3H), 2.51 (s, 3H), 2.45 (s, 3H), 2.36 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 202.5, 202.1, 144.6, 143.9, 143.2, 140.8, 140.1, 138.5, 138.3, 137.7, 137.6, 137.0, 136.3, 134.1, 133.5, 132.2, 132.1, 131.8, 131.7, 130.1, 129.9, 129.5, 129.3, 129.2, 129.1, 129.0, 128.9, 128.4, 128.3, 127.8, 127.7, 126.0, 125.9, 41.2, 40.0, 29.8, 29.3, 21.9, 21.8, 21.7, 21.5. **HR-MS** (ESI) *m/z* calc. for $C_{25}H_{25}O_3S^+$. $[M+H]^+$: 405.1519, found: 405.1517.



3-46

1,7-Diphenyl-6-tosylhept-6-en-1-yn-3-one (3-46)

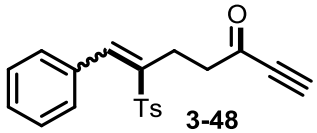
The general procedure (A) was followed using **1-46** (52.0 mg, 0.20 mmol) and **2a** (41.8 mg, 0.22 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc = 3:1) yielded **3-46** (37.3 mg, 45%) as a yellow oil. For **3-46**: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90 (s, 1H), 7.84 (d, *J* = 8.4 Hz, 2H), 7.63 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.58 (dd, *J* = 8.0, 1.2 Hz, 2H), 7.50–7.48 (m, 2H), 7.45–7.41 (m, 11H), 7.36 (d, *J* = 8.4 Hz, 3H), 7.24 (d, *J* = 7.6 Hz, 2H), 7.20–7.16 (m, 3H), 7.09 (d, *J* = 8.0 Hz, 2H), 3.22 (t, *J* = 7.2 Hz, 2H), 3.10–3.06 (m, 2H), 3.00 (t, *J* = 7.2 Hz, 2H), 2.89–2.85 (m, 2H), 2.45 (s, 3H), 2.35 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 185.9, 185.8, 144.7, 144.0, 142.5, 140.1, 139.9, 138.9, 137.5, 136.1, 133.9, 133.3, 133.2, 131.9, 131.1, 131.0, 130.1, 129.9, 129.4, 129.3, 129.2, 129.1, 128.8, 128.6, 128.4, 128.2, 127.8, 127.7, 119.8, 119.8, 91.8, 91.8, 87.7, 87.5, 45.0, 44.0, 29.8, 28.6, 21.7, 21.4. **HR-MS** (ESI) *m/z* calc. for $C_{26}H_{23}O_3S^+$. $[M+H]^+$: 415.1363, found: 415.1360.



3-47

1-(4-Methoxyphenyl)-7-phenyl-6-tosylhept-6-en-1-yn-3-one (3-47)

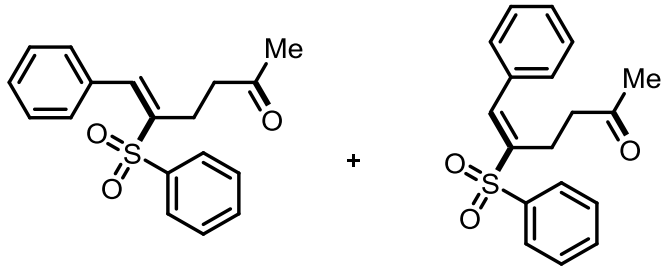
The general procedure (A) was followed using **1-47** (58.0 mg, 0.20 mmol) and **2a** (41.8 mg, 0.22 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc = 5:1) yielded **3-47** (35.5 mg, 40%) as a yellow oil. For **3-47**: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.89 (s, 1H), 7.84 (d, J = 7.8 Hz, 2H), 7.58 (d, J = 9.0 Hz, 1H), 7.53 (d, J = 9.0 Hz, 2H), 7.45–7.42 (m, 5H), 7.42 (s, 1H), 7.36 (d, J = 7.8 Hz, 2H), 7.26–7.24 (m, 1H), 7.23–7.21 (m, 1H), 7.18 (d, J = 7.8 Hz, 1H), 7.15 (s, 1H), 7.09 (d, J = 8.0 Hz, 1H), 6.93 (t, J = 8.4 Hz,, 4H), 3.87 (s, 2H), 3.87 (s, 3H), 3.19 (t, J = 7.8 Hz, 2H), 3.07–3.04 (m, 2H), 2.99 (t, J = 7.2 Hz, 2H), 2.87–2.84 (m, 2H), 2.45 (s, 3H), 2.35 (s, 2H). **HR-MS** (ESI) *m/z* calc. for $C_{27}H_{25}O_4S^+$. $[M+H]^+$: 445.1468, found: 445.1469.



3-48

7-Phenyl-6-tosylhept-6-en-1-yn-3-one (3-48)

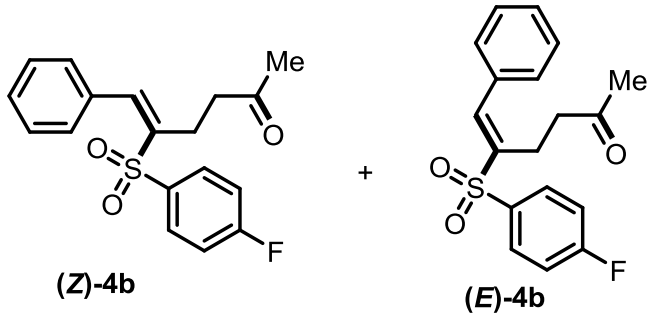
The general procedure (A) was followed using **1-48** (34.8 mg, 0.2 mmol) and **2a** (41.8 mg, 0.22 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc = 5:1) yielded **3-48** (35.2 mg, 52%) as a yellow oil. For **3-48**: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.87 (s, 1H), 7.81 (d, J = 8.4 Hz, 2H), 7.41–7.37 (m, 5H), 7.17 (dd, J = 7.6, 1.6 Hz, 1H), 7.11 (d, J = 4.4 Hz, 2H), 3.27 (s, 1H), 3.01–2.97 (m, 2H), 2.81–2.77 (m, 2H), 2.46 (s, 3H). **HR-MS** (ESI) *m/z* calc. for $C_{20}H_{19}O_3S^+$. $[M+H]^+$: 339.1050, found: 339.1052.



(***Z***)**-4a** (***E***)**-4a**

6-Phenyl-5-(phenylsulfonyl)hex-5-en-2-one (4a)

The general procedure (A) was followed using **1-1** (34.8 mg, 0.2 mmol) and **2b** (38.7 mg, 0.22 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc = 3:1) yielded **4a** (52.8 mg, 84%) as a yellow solid. **M.p.**: 78–80 °C. For (*Z*)-**4a: ^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.93–7.91 (m, 2H), 7.86 (s, 1H), 7.67–7.62 (m, 1H), 7.59–7.55 (m, 2H), 7.45–7.38 (m, 5H), 2.85–2.80 (, 2H), 2.75–2.70 (m, 2H), 2.14 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 207.0, 140.2, 139.2, 139.0, 133.6, 133.3, 129.9, 129.5, 129.2, 128.3, 42.1, 30.0, 21.1. For (*E*)-**4a: ^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.51–7.48 (m, 2H), 7.44 (t, *J* = 7.5 Hz, 1H), 7.28 (t, *J* = 7.8 Hz, 2H), 7.25–7.17 (m, 3H), 7.14 (d, *J* = 7.7 Hz, 3H), 3.00–2.98 (m, 2H), 2.89–2.83 (m, 2H), 2.22 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 207.0, 143.0, 140.5, 140.1, 133.8, 133.0, 129.0, 128.6, 128.3, 127.7, 127.6, 43.2, 30.2, 28.6. **HR-MS** (ESI) *m/z* calc. for $C_{18}H_{19}O_3S^+$. $[M+H]^+$: 315.1050, found: 315.1055.

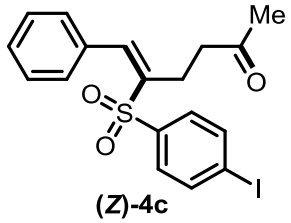


(*Z*)-**4b** (*E*)-**4b**

5-((4-Fluorophenyl)sulfonyl)-6-phenylhex-5-en-2-one (4b)

The general procedure (A) was followed using **1-1** (34.8 mg, 0.2 mmol) and **2c** (42.7 mg, 0.22 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc = 3:1) yielded **4b** (59.8 mg, 90%) as a yellow solid. **M.p.**: 92–94 °C. For (*Z*)-**4b: ^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.96–7.92 (m, 2H), 7.85 (s, 1H), 7.45–7.38 (m, 5H), 7.28–7.23 (m, 2H), 2.87–2.83 (m, 2H), 2.74–2.70 (m, 2H), 2.16 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 206.9, 165.8 (d. *J* = 256.7 Hz), 140.1, 139.2, 135.2, 133.2, 131.1 (d, *J* = 9.5 Hz), 130.1, 129.5, 129.2, 116.8 (d, *J* = 22.7 Hz), 42.1, 30.0, 21.1. **^{19}F NMR** (377 MHz, $CDCl_3$) δ –103.74. For (*E*)-**4b: ^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.48–7.45 (m, 2H), 7.26–7.19 (m, 3H), 7.13–7.09 (m, 3H), 6.95–6.91 (m, 2H), 3.01–2.96 (m, 2H), 2.91–2.86 (m, 2H), 2.24 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 206.9, 165.3 (d, *J* =

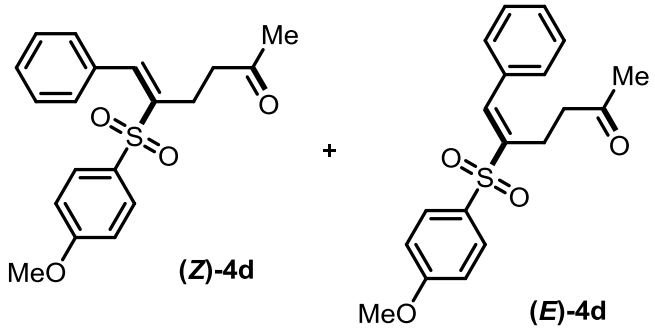
255.2 Hz), 143.4, 140.0, 136.6 (d, J = 3.0 Hz), 133.8, 130.5 (d, J = 9.5 Hz), 129.0, 128.4, 127.9, 115.8 (d, J = 22.7 Hz), 43.1, 30.3, 28.5. **^{19}F NMR** (377 MHz, $CDCl_3$) δ –104.50. **HR-MS** (ESI) *m/z* calc. for $C_{18}H_{18}O_3SF^+$. $[M+H]^+$: 333.0955, found: 333.0965.



(*Z*)-4c

5-((4-Iodophenyl)sulfonyl)-6-phenylhex-5-en-2-one (4c)

The general procedure (A) was followed using **1-1** (60.2 mg, 0.2 mmol) and **2d** (66.4 mg, 0.22 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc = 3:1) yielded **4c** (37.0 mg, 42%) as a yellow solid. **M.p.**: 162–164 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.93 (d, J = 8.6 Hz, 2H), 7.85 (s, 1H), 7.63 (d, J = 8.6 Hz, 2H), 7.45–7.41 (m, 3H), 7.40–7.38 (m, 2H), 2.87–2.83 (m, 2H), 2.73–2.69 (m, 2H), 2.16 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 206.8, 139.8, 139.5, 138.9, 138.7, 133.1, 130.1, 129.6, 129.5, 129.2, 101.5, 42.1, 30.0, 21.1. **HR-MS** (ESI) *m/z* calc. for $C_{18}H_{18}IO_3S^+$. $[M+H]^+$: 441.0016, found: 441.0028.

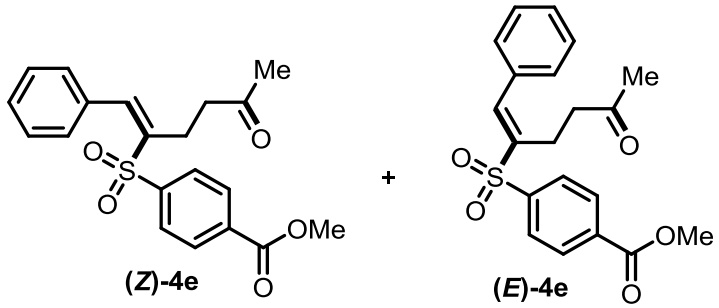


(*Z*)-4d (*E*)-4d

5-((4-Methoxyphenyl)sulfonyl)-6-phenylhex-5-en-2-one (4d)

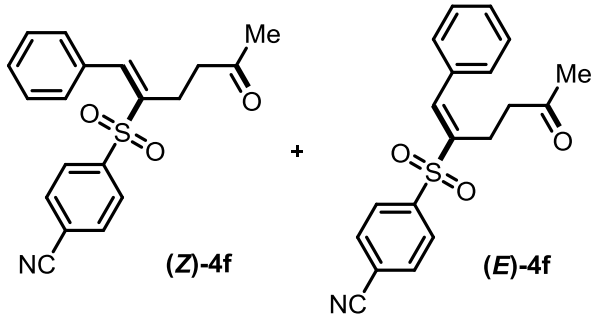
The general procedure (A) was followed using **1-1** (34.8 mg, 0.2 mmol) and **2e** (45.3 mg, 0.22 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc = 5:1) yielded **4d** (46.8 mg, 68%) as a yellow oil. For (*Z*)-**4d: ^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.84 (d, J = 9.0 Hz, 2H), 7.81 (s, 1H), 7.44–7.36 (m, 5H), 7.03 (d, J = 9.0 Hz, 2H), 3.90 (s, 3H), 2.85–2.80 (m, 2H), 2.75–2.70 (m, 2H), 2.14 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 207.1, 163.7, 140.8, 138.1, 133.5, 130.5, 130.5, 129.8, 129.4, 129.1, 114.7, 55.8, 42.2, 30.0, 21.0. For (*E*)-**4d: ^{1}H NMR** (400 MHz, $CDCl_3$) δ

7.45–7.41 (m, 2H), 7.26–7.22 (m, 3H), 7.19–7.15 (m, 2H), 7.08 (s, 1H), 6.78–6.74 (m, 2H), 3.82 (s, 3H), 2.97 (t, *J* = 7.3 Hz, 2H), 2.85–2.81 (m, 2H), 2.23 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 207.1, 163.3, 143.5, 139.4, 134.1, 132.1, 129.9, 129.0, 128.3, 127.8, 113.9, 55.7, 43.3, 30.3, 28.7. **HR-MS** (ESI) *m/z* calc. for $C_{19}H_{21}O_4S^+$. $[M+H]^+$: 345.1155, found: 345.1160.



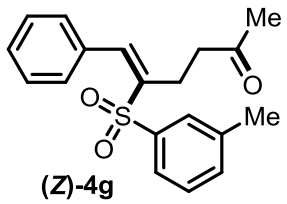
Methyl-4-((5-oxo-1-phenylhex-1-en-2-yl)sulfonyl)benzoate (4e)

The general procedure (A) was followed using **1-1** (34.8 mg, 0.2 mmol) and **2f** (51.5 mg, 0.22 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc = 3:1) yielded **4e** (57.3 mg, 77%) as a yellow solid. **M.p.**: 118–120 °C. For (*Z*)-**4e: ^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.24–8.21 (m, 2H), 8.01–7.98 (m, 2H), 7.89 (s, 1H), 7.45–7.39 (m, 5H), 3.98 (s, 3H), 2.85 (dd, *J* = 9.7, 5.9 Hz, 2H), 2.72 (dd, *J* = 9.8, 6.0 Hz, 2H), 2.15 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 206.8, 165.6, 143.2, 140.0, 139.5, 134.7, 133.1, 130.6, 130.2, 129.5, 129.2, 128.3, 52.9, 42.0, 30.0, 21.1. For (*E*)-**4e: ^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.92–7.89 (m, 2H), 7.54–7.50 (m, 2H), 7.24–7.16 (m, 4H), 7.09 (dd, *J* = 7.0, 0.9 Hz, 2H), 3.94 (s, 3H), 2.99 (dd, *J* = 10.6, 3.8 Hz, 2H), 2.93–2.87 (m, 2H), 2.24 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 206.8, 165.6, 144.5, 142.9, 140.7, 133.9, 133.5, 129.6, 129.0, 128.6, 127.9, 127.6, 52.7, 43.0, 30.3, 28.5. **HR-MS** (ESI) *m/z* calc. for $C_{20}H_{21}O_5S^+$. $[M+H]^+$: 373.1104, found: 373.1113.



4-((5-Oxo-1-phenylhex-1-en-2-yl)sulfonyl)benzonitrile (4f)

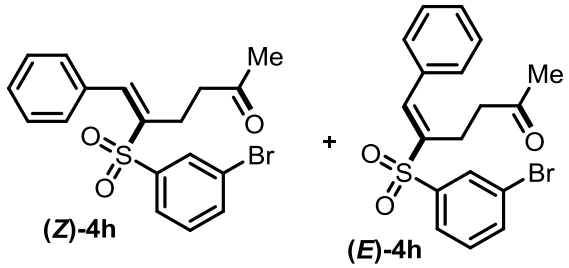
The general procedure (A) was followed using **1-1** (34.8 mg, 0.2 mmol) and **2g** (44.2 mg, 0.22 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc = 3:1) yielded **4f** (49.5 mg, 73%) as a green oil. For (*Z*)-**4f: ^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.05–8.04 (m, 2H), 7.90–7.87 (m, 3H), 7.46–7.44 (m, 3H), 7.42–7.40 (m, 2H), 2.89–2.87 (m, 2H), 2.72–2.69 (m, 2H), 2.17 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 206.6, 143.6, 140.9, 138.9, 133.2, 132.8, 130.5, 129.6, 129.3, 128.9, 117.3, 117.3, 42,0, 29.8, 21.1. For (*E*)-**4f: ^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.54–7.51 (m, 4H), 7.25 (t, *J* = 7.3 Hz, 1H), 7.19 (t, *J* = 7.5 Hz, 3H), 7.05 (d, *J* = 8.0 Hz, 2H), 3.01 (t, *J* = 6.7 Hz, 2H), 2.94 (t, *J* = 6.9 Hz, 2H), 2.26 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 206.6, 144.8, 143.0, 140.9, 133.4, 132.1, 129.0, 128.7, 128.2, 128.0, 117.3, 116.4, 42.8, 29.8, 28.3. **HR-MS** (ESI) *m/z* calc. for $C_{19}H_{18}NO_3S^+$. $[M+H]^+$: 340.1002, found: 340.1008.



(*Z*)-4g

(*Z*)-6-Phenyl-5-(m-tolylsulfonyl)hex-5-en-2-one (4g)

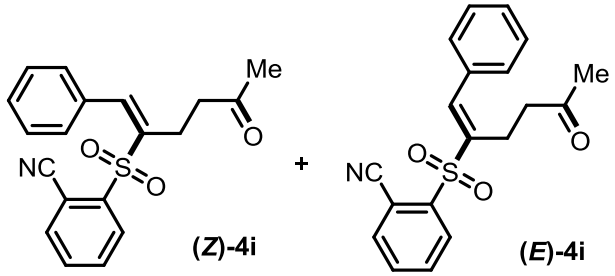
The general procedure (A) was followed using **1-1** (34.8 mg, 0.2 mmol) and **2h** (41.8 mg, 0.22 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc = 3:1) yielded **4g** (29.5 mg, 45%) as a yellow oil. For **4g**: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.85 (s, 1H), 7.73–7.72 (m, 2H), 7.45–7.40 (m, 7H), 2.86–2.81 (m, 2H), 2.76–2.71 (m, 2H), 2.46 (s, 3H), 2.14 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 207.0, 140.3, 139.7, 139.0, 138.8, 134.4, 133.4, 129.9, 129.5, 129.3, 129.2, 128.5, 125.4, 42.1, 30.0, 21.5, 21.1. **HR-MS** (ESI) *m/z* calc. for $C_{19}H_{21}O_3S^+$. $[M+H]^+$: 329.1206, found: 329.1215.



(*Z*)-4h (*E*)-4h

5-((3-Bromophenyl)sulfonyl)-6-phenylhex-5-en-2-one (4h)

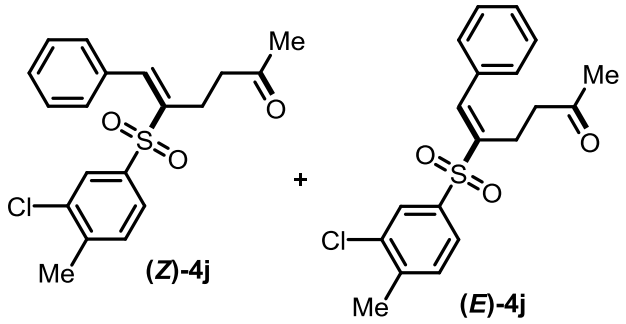
The general procedure (A) was followed using **1-1** (34.8 mg, 0.2 mmol) and **2i** (55.8 mg, 0.22 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc = 3:1) yielded **4h** (66.6 mg, 85%) as a yellow oil. For (*Z*)-**4h**: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.05 (t, *J* = 1.8 Hz, 1H), 7.87–7.85 (m, 2H), 7.77 (ddd, *J* = 8.0, 1.8, 1.0 Hz, 1H), 7.47–7.40 (m, 6H), 2.85 (dd, *J* = 9.7, 5.9 Hz, 2H), 2.76–2.70 (m, 2H), 2.16 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 206.8, 141.2, 139.9, 139.6, 136.7, 133.0, 131.0, 130.9, 130.2, 129.6, 129.2, 126.8, 123.5, 42.0, 30.0, 21.1. For (*E*)-**4h**: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.55–7.50 (m, 2H), 7.42 (ddd, *J* = 7.9, 1.7, 1.0 Hz, 1H), 7.28–7.26 (m, 1H), 7.24–7.20 (m, 2H), 7.18–7.13 (m, 2H), 7.09 (dd, *J* = 6.9, 0.9 Hz, 2H), 3.02–2.98 (m, 2H), 2.94–2.89 (m, 2H), 2.25 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 207.0, 143.3, 142.4, 140.6, 136.0, 133.4, 130.9, 130.0, 128.9, 128.8, 127.9, 126.1, 122.5, 43.0, 30.3, 28.5. **HR-MS** (ESI) *m/z* calc. for $C_{18}H_{18}BrO_3S^+$. $[M+H]^+$: 393.0155, found: 393.0155.



2-((5-Oxo-1-phenylhex-1-en-2-yl)sulfonyl)benzonitrile (4i)

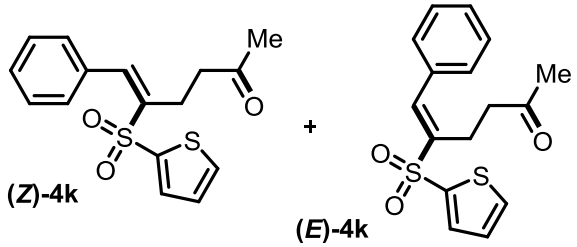
The general procedure (A) was followed using **1-1** (34.8 mg, 0.2 mmol) and **2j** (44.2 mg, 0.22 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc = 3:1) yielded **4i** (47.5 mg, 70%) as a yellow oil. For (*Z*)-**4i**: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.61 (dd, *J* = 7.6, 1.1 Hz, 1H), 7.46–7.40 (m, 2H), 7.28–7.24 (m, 2H), 7.11–6.99 (m, 5H), 3.16 (t, *J* = 7.1 Hz, 2H), 3.05 (t, *J* = 7.3 Hz, 2H), 2.26 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 206.9, 143.3, 142.8, 140.0, 134.4, 133.3, 132.5, 132.0, 129.8, 128.8, 128.4, 127.9, 115.4, 110.3, 42.3, 30.3, 28.3. For (*E*)-**4i**: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.26 (dd, *J* = 7.9, 1.1 Hz, 1H), 8.17 (s, 1H), 7.90–7.82 (m, 2H), 7.76 (td, *J* = 7.6, 1.3 Hz, 1H), 7.47–7.42 (m, 5H), 2.94–2.90 (m, 2H), 2.66–2.62 (m, 2H), 2.18 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 206.8, 143.6, 141.0, 137.0, 135.9, 133.6,

133.2, 132.8, 131.0, 130.3, 129.8, 129.2, 115.7, 111.5, 42.3, 30.0, 20.9. **HR-MS** (ESI) *m/z* calc. for $C_{19}H_{18}NO_3S^+$. $[M+H]^+$: 340.1002, found: 340.1006.



5-((3-Chloro-4-methylphenyl)sulfonyl)-6-phenylhex-5-en-2-one (4j)

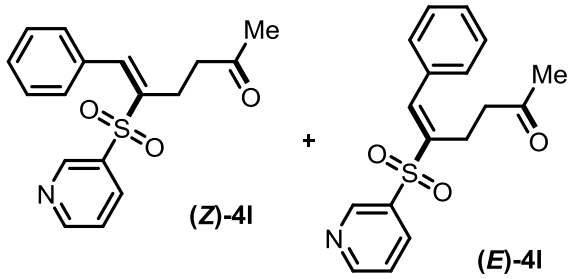
The general procedure (A) was followed using **1-1** (34.8 mg, 0.2 mmol) and **2k** (49.3 mg, 0.22 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc = 3:1) yielded **4j** (34.0 mg, 47%) as a yellow oil. For (*Z*)-**4j**: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.88 (d, *J* = 1.8 Hz, 1H), 7.85 (s, 1H), 7.70 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.45–7.40 (m, 6H), 2.88–2.85 (m, 2H), 2.73–2.71 (m, 2H), 2.48 (s, 3H), 2.16 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 206.9, 142.7, 139.9, 139.4, 138.1, 135.7, 133.2 131.8, 130.1, 129.5, 129.2, 128.7, 126.4, 42.1, 30.0, 21.1, 20.5. For (*E*)-**4j**: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.36 (d, *J* = 1.8 Hz, 1H), 7.28–7.25 (m, 2H), 7.23–7.21 (m, 2H), 7.15–7.13 (m, 2H), 7.11 (dd, *J* = 7.2, 1.2 Hz, 2H), 2.98 (t, *J* = 7.2 Hz, 2H), 2.87 (t, *J* = 6.6 Hz, 2H), 2.35 (s, 3H), 2.24 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 206.9, 143.3, 141.9, 140.3, 139.4, 134.7, 133.6, 130.9, 128.9, 128.6, 128.5, 127.7, 125.7, 43.1, 30.3, 28.5, 20.4. **HR-MS** (ESI) *m/z* calc. for $C_{19}H_{20}ClO_3S^+$. $[M+H]^+$: 363.0816, found: 363.0816.



6-Phenyl-5-(thiophen-2-ylsulfonyl)hex-5-en-2-one (4k)

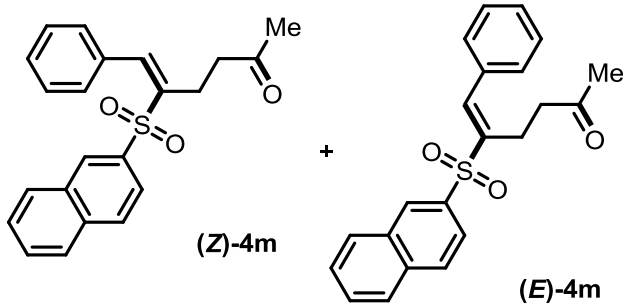
The general procedure (A) was followed using **1-1** (34.8 mg, 0.2 mmol) and **2l** (40.0 mg, 0.22 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc = 3:1) yielded **4k** (60.8 mg, 95%) as a yellow solid. **M.p.**: 97–99 °C. For

(*Z*)-**4k**: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.83 (s, 1H), 7.72–7.71 (m, 2H), 7.43–7.38 (m, 5H), 7.14 (dd, *J* = 6.5, 2.3 Hz, 1H), 2.87–2.83 (m, 4H), 2.15 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 206.8, 140.9, 140.5, 138.6, 134.4, 134.3, 133.1, 129.9, 129.4, 129.1, 128.0, 42.1, 29.9, 21.1. For (*E*)-**4k**: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.55 (dd, *J* = 4.9, 1.3 Hz, 1H), 7.30–7.28 (m, 3H), 7.27–7.25 (m, 2H), 7.22 (dd, *J* = 3.8, 1.3 Hz, 1H), 7.17 (s, 1H), 6.88 (dd, *J* = 4.9, 3.8 Hz, 1H), 2.96 (t, *J* = 7.3 Hz, 2H), 2.87 (dd, *J* = 7.6, 6.9 Hz, 2H), 2.22 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 206.9, 143.0, 141.7, 140.6, 134.3, 133.8, 133.7, 129.0, 128.5, 127.8, 127.2, 43.3, 30.2, 28.6. **HR-MS** (ESI) *m/z* calc. for $C_{16}H_{17}O_3S_2^+$. $[M+H]^+$: 321.0614, found: 321.0617.



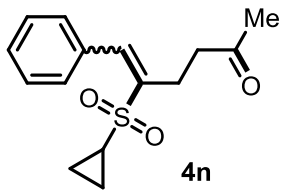
6-Phenyl-5-(pyridin-3-ylsulfonyl)hex-5-en-2-one (4l)

The general procedure (A) was followed using **1-1** (34.8 mg, 0.2 mmol) and **2m** (38.9 mg, 0.22 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc = 3:1) yielded **4l** (58.0 mg, 92%) as a yellow solid. **M.p.**: 107–108 °C. For (*Z*)-**4l**: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.09 (d, *J* = 1.8 Hz, 1H), 8.83 (dd, *J* = 4.8, 1.6 Hz, 1H), 8.20–8.18 (m, 1H), 7.87 (s, 1H), 7.51–7.49 (m, 1H), 7.43–7.37 (m, 5H), 2.85 (dd, *J* = 9.0, 6.8 Hz, 2H), 2.71 (dd, *J* = 9.5, 6.3 Hz, 2H), 2.13 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 206.5, 153.9, 149.1, 140.3, 139.5, 135.9, 135.8, 132.8, 130.2, 129.4, 129.1, 123.9, 41.9, 29.8, 21.0. For (*E*)-**4l**: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.62–8.58 (m, 2H), 7.65–7.63 (m, 1H), 7.23 (t, *J* = 7.1 Hz, 1H), 7.18 (t, *J* = 7.4 Hz, 3H), 7.13 (dd, *J* = 8.0, 4.9 Hz, 1H), 7.06 (d, *J* = 7.7 Hz, 2H), 2.99 (t, *J* = 6.9 Hz, 2H), 2.93 (t, *J* = 7.1 Hz, 2H), 2.23 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 206.6, 153.1, 148.4, 143.4, 140.5, 137.1, 135.0, 133.3, 128.9, 128.7, 128.0, 122.9, 42.9, 30.2, 28.2. **HR-MS** (ESI) *m/z* calc. for $C_{17}H_{18}NO_3S^+$. $[M+H]^+$: 316.1002, found: 316.1005.



5-(Naphthalen-2-ylsulfonyl)-6-phenylhex-5-en-2-one (4m)

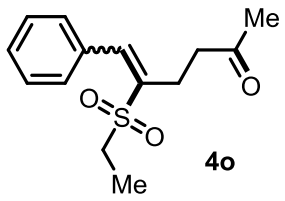
The general procedure (A) was followed using **1-1** (34.8 mg, 0.2 mmol) and **2n** (49.7 mg, 0.22 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc = 3:1) yielded **4m** (32.8mg, 45%) as a brown oil. For (*Z*)-**4m**: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.54 (d, *J* = 1.4 Hz, 1H), 8.02 (t, *J* = 8.9 Hz, 2H), 7.94 (d, *J* = 8.0 Hz, 2H), 7.83 (dd, *J* = 8.6, 1.9 Hz, 1H), 7.72–7.64 (m, 2H), 7.44–7.40 (m, 5H), 2.88–2.84 (m, 2H), 2.79–2.74 (m, 2H), 2.12 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 207.0, 140.2, 139.2, 135.9, 135.3, 133.4, 132.3, 130.1, 130.0, 129.8, 129.6, 129.5, 129.4, 129.2, 128.1, 127.9, 122.9, 42.1, 29.9, 21.2. For (*E*)-**4m**:**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 1.6 Hz, 1H), 7.83 (d, *J* = 8.2 Hz, 1H), 7.80–7.74 (m, 2H), 7.64–7.60 (m, 1H), 7.57–7.53 (m, 1H), 7.52 (dd, *J* = 8.7, 1.9 Hz, 1H), 7.15 (s, 1H), 7.11 (s, 5H), 3.05–3.01 （m, 2H), 2.94–2.90 (m, 2H), 2.25 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 207.1, 143.2, 140.3, 137.1, 134.9, 133.8, 131.8, 129.9, 129.4, 129.1, 129.0, 128.4, 127.8, 127.6, 127.4, 122.3, 43.3, 30.3, 28.7. **HR-MS** (ESI) *m/z* calc. for $C_{22}H_{21}O_3S^+$. $[M+H]^+$: 365.1206, found: 365.1211.



5-(Cyclopropylsulfonyl)-6-phenylhex-5-en-2-one (4n)

The general procedure (A) was followed using **1-1** (34.8 mg, 0.2 mmol) and **2o** (30.8 mg, 0.22 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc = 3:1) yielded **4n** (45.6 mg, 82%) as a yellow oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.57 (s, 1H), 7.47 (d, *J* = 7.2 Hz, 2H), 7.44–7.41 (m, 2H), 7.40–7.39 (m, 1H). 7.38–7.32 (m, 5H), 7.15 (s, 1H), 2.99 (t, *J* = 7.8 Hz, 2H), 2.92–2.88 (m, 4H), 2.83 (t, *J*

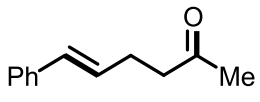
= 6.6 Hz, 2H), 2.51–2.47 (m, 1H), 2.20 (s, 3H), 2.16 (s, 3H), 2.06–2.01 (m, 1H), 1.29–1.25 (m, 2H), 1.10–1.06 (m, 4H), 0.78–0.75 (m, 2H) **^{13}C NMR** (101 MHz, $CDCl_3$) δ 206.9, 142.7, 140.1, 138.6, 138.2, 134.4, 133.3, 129.6, 129.2, 129.2, 129.0, 128.8, 128.2, 43.0, 42.1, 31.2, 30.2, 29.9, 29.8, 28.5, 21.3, 5.6, 5.6. **HR-MS** (ESI) *m/z* calc. for $C_{15}H_{18}O_3S^+$. $[M+H]^+$: 279.1050, found: 279.1055.



4o

5-(Ethylsulfonyl)-6-phenylhex-5-en-2-one (4o)

The general procedure (A) was followed using **1-1** (34.8 mg, 0.2 mmol) and **2p** (28.2 mg, 0.22 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc = 5:1) yielded **4o** (50.5 mg, 95%) as a yellow oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.59 (s, 1H), 7.49–7.48 (m, 2H), 7.43–7.39 (m, 3H), 7.38–7.34 (m, 5H), 7.21 (s, 1H), 3.08 (q, J = 7.4 Hz, 2H), 2.88 (s, 6H), 2.82 (t, J = 7.3 Hz, 2H), 2.64 (q, J = 7.4 Hz, 2H), 2.18 (d, J = 3.8 Hz, 3H), 2.14 (d, J = 3.8 Hz, 3H), 1.34–1.29 (m, 3H), 1.15–1.05 (m, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 206.8, 206.8, 140.7, 140.5, 139.1, 138.0, 133.7, 133.1, 129.8, 129.2, 129.1, 129.1, 129.0, 128.4, 48.0, 46.7, 42.9, 42.0, 30.1, 29.8, 28.8, 21.4, 7.2, 6.9. **HR-MS** (ESI) *m/z* calc. for $C_{14}H_{19}O_3S^+$. $[M+H]^+$: 267.1050, found: 267.1051.

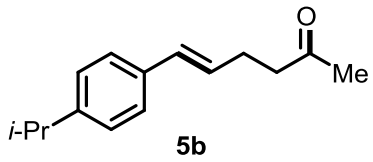


5a

(*E*)-6-Phenylhex-5-en-2-one (5a)

The general procedure (B) was followed using **3-1** (34.8 mg, 0.20 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc = 10:1) yielded **5a** (22.6 mg, 65%) as a yellow oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.36–7.34 (m, 2H), 7.31 (t, J = 7.7 Hz, 2H), 7.23 (t, J = 7.2 Hz, 1H), 6.43 (d, J = 15.8 Hz, 1H), 6.25–6.20 (m, 1H), 2.64 (t, J = 7.3 Hz, 2H), 2.53–2.49 (m, 2H), 2.20 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 208.2, 137.5, 130.9, 128.9, 128.6, 127.2, 126.1, 43.3, 30.2, 27.3. **HR-MS**

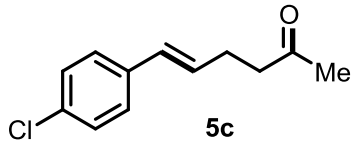
(ESI) *m/z* calc. for $C_{12}H_{15}O^+$. $[M+H]^+$: 175.1118, found: 175.1111.



5b

(*E*)-6-(4-Isopropylphenyl)hex-5-en-2-one (5b)

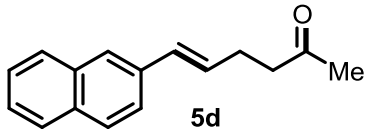
The general procedure (B) was followed using **3-6** (74.0 mg, 0.20 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc = 10:1) yielded 5b (22.5 mg, 52%) as a yellow oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.28 (d, J = 8.2 Hz, 2H), 7.18 (d, J = 8.2 Hz, 2H), 6.41 (d, J = 15.8 Hz, 1H), 6.17 (dt, J = 15.8, 6.9 Hz, 1H), 2.92–2.88 (m, 1H), 2.63 (t, J = 7.3 Hz, 2H), 2.51–2.47 (m, 2H), 2.19 (s, 3H), 1.26 (s, 3H), 1.25 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 208.3, 148.0, 135.1, 130.7, 128.0, 126.7, 126.1, 43.4, 34.0, 30.2, 29.8, 27.3, 24.1. **HR-MS** (ESI) *m/z* calc. for $C_{15}H_{21}O^+$. $[M+H]^+$: 217.1587, found: 217.1565.



5c

(*E*)-6-(4-Chlorophenyl)hex-5-en-2-one (5c)

The general procedure (B) was followed using **3-18** (72.4 mg, 0.20 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc = 10:1) yielded **5c** (25.8 mg, 62%) as a yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.26 (s, 4H), 6.37 (dt, J = 15.8, 1.4 Hz, 1H), 6.19 (dt, J = 15.8, 6.8 Hz, 1H), 2.63 (t, J = 7.2 Hz, 2H), 2.52–2.46 (m, 2H), 2.19 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 208.0, 136.0, 132.7, 129.7, 128.7, 127.3, 43.1, 30.1, 27.1. **HR-MS** (ESI) *m/z* calc. for $C_{12}H_{14}ClO^+$. $[M+H]^+$: 209.0728, found: 209.0731.

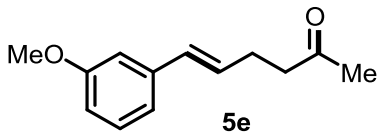


5d

(*E*)-6-(Naphthalen-2-yl)hex-5-en-2-one (5d)

The general procedure (B) was followed using **3-34** (75.6 mg, 0.20 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc = 10:1) yielded **5d**

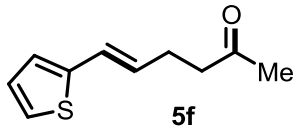
(25.1 mg, 56%) as a yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.80 (dd, J = 12.6, 4.8 Hz, 3H), 7.70 (s, 1H), 7.58 (dd, J = 8.5, 1.6 Hz, 1H), 7.49–7.43 (m, 2H), 6.60 (d, J = 15.8 Hz, 1H), 6.35 (dt, J = 15.7, 6.7 Hz, 1H), 2.68 (t, J = 7.0 Hz, 2H), 2.59–2.54 (m, 2H), 2.21 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 208.2, 135.0, 133.8, 132.9, 131.0, 129.4, 128.2, 128.0, 127.7, 126.3, 125.7, 123.6, 43.3, 30.2, 27.3. **HR-MS** (ESI) *m/z* calc. for $C_{16}H_{17}O_3^+$. $[M+H]^+$: 225.1274, found: 225.1272.



5e

(*E*)-6-(3-Methoxyphenyl)hex-5-en-2-one (5e)

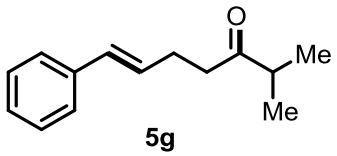
The general procedure (B) was followed using **3-25** (71.6 mg, 0.20 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc = 10:1) yielded **5e** (23.7 mg, 58%) as a yellow oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.23 (t, J = 7.9 Hz, 1H), 6.95 (d, J = 7.6 Hz, 1H), 6.90–6.88 (m, 1H), 6.80–6.77 (m, 1H), 6.40 (d, J = 15.8 Hz, 1H), 6.22 (dt, J = 15.8, 6.9 Hz, 1H), 3.83 (s, 3H), 2.64 (t, J = 7.3 Hz, 2H), 2.52–2.48 (m, 2H), 2.20 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 208.2, 159.9, 139.0, 130.8, 129.6, 129.3, 118.8, 112.9, 111.5, 55.3, 43.3, 29.9, 27.2. **HR-MS** (ESI) *m/z* calc. for $C_{13}H_{17}O_2^+$. $[M+H]^+$: 205.1223, found: 205.1217.



5f

(*E*)-6-(Thiophen-2-yl)hex-5-en-2-one (5f)

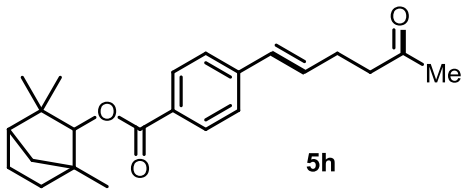
The general procedure (B) was followed using **3-30** (66.8 mg, 0.20 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc = 10:1) yielded **5f** (15.1 mg, 42%) as a yellow oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.27 (dd, J = 5.0, 2.9 Hz, 1H), 7.19 (dd, J = 5.0, 0.9 Hz, 1H), 7.08 (d, J = 2.2 Hz, 1H), 6.44 (d, J = 15.8 Hz, 1H), 6.07 (dt, J = 15.8, 6.9 Hz, 1H), 2.62 (t, J = 7.3 Hz, 2H), 2.49–2.45 (m, 2H), 2.19 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 208.2, 140.1, 128.9, 126.0, 125.2, 125.0, 121.1, 43.3, 30.2, 27.1. **HR-MS** (ESI) *m/z* calc. for $C_{10}H_{13}OS^+$. $[M+H]^+$: 181.0682, found: 181.0683.



5g

(*E*)-2-methyl-7-phenylhept-6-en-3-one (5g)

The general procedure (B) was followed using **3-40** (71.2 mg, 0.20 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc = 10:1) yielded **5g** (22.2 mg, 55%) as a yellow oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.35 (dd, J = 8.4, 1.8 Hz, 2H), 7.31 (t, J = 7.7 Hz, 2H), 7.24–7.21 (m, 1H), 6.43 (d, J = 15.6 Hz, 1H), 6.25–6.20 (m, 1H), 2.65 (t, J = 7.2 Hz, 2H), 2.52–2.49 (m, 2H), 1.14 (s, 3H), 1.13 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 214.0, 137.6, 130.8, 129.3, 128.6, 127.2, 126.1, 41.1, 40.0, 27.3, 18.4. **HR-MS** (ESI) *m/z* calc. for $C_{10}H_{13}OS^+$. $[M+H]^+$: 203.1431, found: 203.1423.

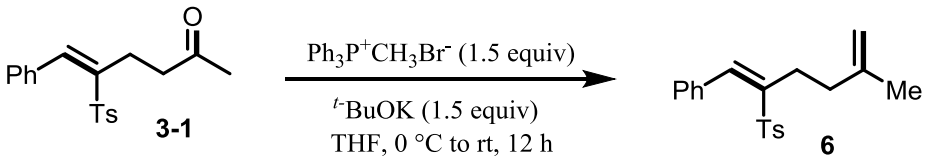


5h

1,3,3-Trimethylbicyclo[2.2.1]heptan-2-yl (*E*)-4-(5-oxohex-1-en-1-yl)benzoate (5h)

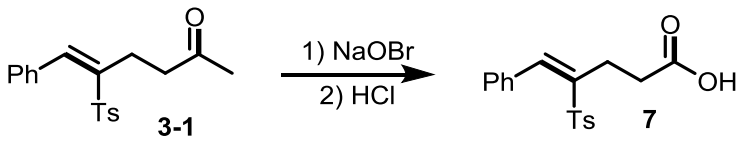
The general procedure (B) was followed using **3-38** (101.6 mg, 0.20 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc = 10:1) yielded **5h** (26.2 mg, 37%) as a yellow oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.00 (d, J = 7.9 Hz, 2H), 7.41 (d, J = 7.9 Hz, 2H), 6.47 (d, J = 16 l.0 Hz, 1H), 6.38–6.31 (m, 1H), 4.63 (s, 1H), 2.66 (t, J = 7.1 Hz, 2H), 2.54 (d, J = 6.9 Hz, 2H), 2.21 (s, 3H), 1.95 (s, 1H), 1.80 (s, 2H), 1.68 (d, J = 9.9 Hz, 1H), 1.62 (s, 1H), 1.56–1.50 (m, 1H), 1.27 (d, J = 9.8 Hz, 1H), 1.20 (s, 3H), 1.13 (s, 3H), 0.85 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 207.9, 166.9, 141.9, 131.8, 130.2, 130.0, 129.3, 126.0, 86.7, 48.8, 48.6, 43.0, 41.6, 40.0, 30.2, 29.9, 27.3, 27.0, 26.1, 20.4, 19.7. **HR-MS** (ESI) *m/z* calc. for $C_{23}H_{31}O_3^+$. $[M+H]^+$: 355.2267, found: 355.2266.

4. Late-stage Transformation from Product 3-1



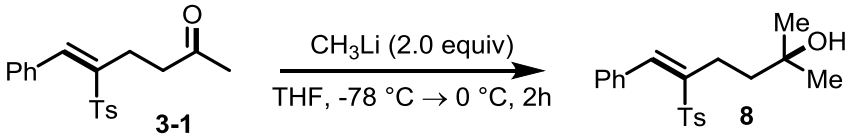
(Z)-1-Methyl-4-((5-methyl-1-phenylhexa-1,5-dien-2-yl)sulfonyl)benzene (6)

To a solution of methyltriphenylphosphoniumbromide (142.8 mg, 0.4 mmol) in THF (5 mL) under Ar atmosphere, potassium tert-butoxide (44.9 mg, 0.4 mmol) was added as a solution in THF (3 mL) at 25 °C. The reaction mixture was stirred for 1 h at room temperature. Then **3-1** (65.6 mg, 0.2 mmol) was added and the reaction was stirred for 6 h at room temperature and quenched with saturated NH_4Cl aqueous solution (10 mL). The solvent was removed in vacuo and the resulting mixture was extracted with diethyl ether (3 × 10 mL). The combined organic layer was washed with brine, and dried over anhydrous sodium sulfate.[3] Evaporation of the solvent followed by purification by flash chromatography on silica gel (n-hexane/EtOAc = 10:1) gave compound **6** (42.4 mg, 65%) as a white solid. **M.p.**: 66–68 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.85–7.83 (m, 3H), 7.45–7.39 (m, 5H), 7.37 (d, J = 8.2 Hz, 2H), 4.73 (s, 1H), 4.63 (s, 1H), 2.65–2.61 (m, 2H), 2.46 (s, 3H), 2.19–2.15 (m, 2H), 1.67 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 144.5, 144.4, 141.6, 137.9, 136.7, 133.7, 130.0, 129.6, 129.6, 129.0, 128.4, 110.6, 36.2, 26.0, 22.4, 21.7. **HR-MS** (ESI) m/z calc. for $C_{20}H_{23}O_2S^+$. $[M+H]^+$: 327.1414, found: 327.1418.

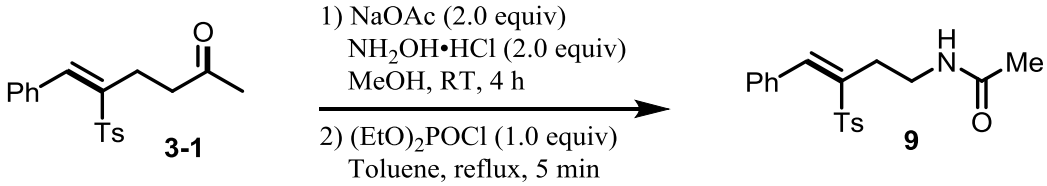


NaOH (304.0 mg, 7.6 mmol) was dissolved in H_2O (5.0 mL) and cooled on ice with stirring before Br_2 (447.5 mg, 2.8 mmol) was added and stirring continued for a further 20 min. This NaOBr solution was then slowly added to a suspension of **3-1** (65.6 mg, 0.2 mmol) in 1,4-dioxane (5 mL). The yellow solution was stirred at 60 °C for 2 hours. After cooling to room temperature, the reaction was quenched by the addition of aq. $NH_2OH{\cdot}HCl$ (0.23 g, 4 mL H_2O) and the 1,4-dioxane removed under vacuum. The resulting suspension was cooled on ice and acidified with 3 M HCl and stirred overnight

at room temperature.[4] Purification by column chromatography on silica gel (petroleum ether/EtOAc = 1:1) yielded **7** (34.3 mg, 52%) as a yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88 (s, 1H), 7.83 (d, J = 8.3 Hz, 2H), 7.47–7.41 (m, 5H), 7.37 (d, J = 8.0 Hz, 2H), 2.83–2.79 (m, 2H), 2.69–2.62 (m., 2H), 2.46 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 144.7, 139.8, 139.2, 136.2, 133.3, 130.2, 130.0, 129.4, 129.2, 128.4, 32.7, 22.4, 21.8. **HR-MS** (ESI) *m/z* calc. for $C_{18}H_{19}O_4S^+$. $[M+H]^+$: 331.0999, found: 331.1005.



Cool a solution of **3-1** (65.6 mg, 0.2 mmol) in anhydrous THF (2 mL) to -78 °C under nitrogaaaen atmosphere. Add Methyllithium (0.4 mmol) to the mixture. Stir the reaction mixture at -78°C for 1 hour. Warm the resulting mixture gradually to 0 °C and keep the stirring for 1 h. Purification by column chromatography on silica gel (petroleum ether/EtOAc = 3:1) yielded **8** (51.6 mg, 75%) as a yellow oil.**^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.84 (s, 1H), 7.82 (d, J = 6.1 Hz, 2H), 7.51–7.50 (m, 2H), 7.43 (t, J = 7.4 Hz, 2H), 7.41–7.39 (m, 1H), 7.36 (d, J = 8.1 Hz, 2H), 2.63–2.60 (m, 2H), 2.46 (s, 3H), 1.75–1.72 (m, 2H), 1.19 (s, 6H). **^{13}C NMR** (151 MHz, CDCl3) δ 144.4, 141.8, 137.9, 136.6, 133.7, 130..0, 129.6, 128.9, 128.4, 70.6, 41.7, 29.1, 22.2, 21.7. HR-MS (ESI) m/z calc. for $C_{20}H_{24}O_3SNa^+$. $[M+Na]^+$: 367.1338, found: 367.1344.

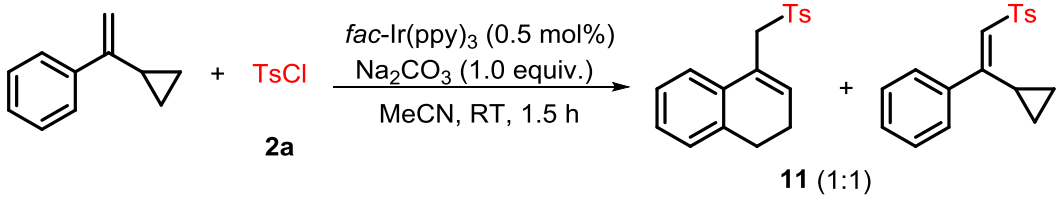


A mixture of **3-1** (65.6 mg, 0.2 mmol), $NH_2OH{\cdot}HCl$ (27.8 mg, 0.4 mmol) and sodium acetate (32.8 mg, 0.4 mmol） in a 15 mL Schlenk tube with 1 mL of MeOH. The resulting solution was stirred at room temperature and monitored by TLC. After reaction completed, the solvent was removed in vacuo, which was used directly for the next step. The oxime and toluene (1 mL) were charged into a 15 mL Schlenk tube, The reaction was heated to reflux and diethyl chlorophosphate (34.5 mg, 0.2 mmol) was

added to the mixture. The reaction was heated for 5 minutes and then cooled to room temperature. The crude mixture was neutralized with 1 ml of an aqueous solution of sodium hydroxide (5%). Purification by column chromatography on silica gel (petroleum ether/EtOAc = 5:1) yielded **9** (34.3 mg, 50%) as a brown oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.90 (s, 1H), 7.81 (d, J = 8.3 Hz, 2H), 7.56 (d, J = 7.4 Hz, 2H), 7.46 (t, J = 7.5 Hz, 2H), 7.41 (dd, J = 5.9, 3.8 Hz, 1H), 7.37 (d, J = 8.0 Hz, 2H), 3.51 (dd, J = 12.8, 6.8 Hz, 2H), 2.75 (t, J = 6.9 Hz, 2H), 2.46 (s, 3H), 1.90 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 170.6, 144.8, 140.3, 138.5, 136.0, 133.0, 130.2, 129.9, 129.2, 128.3, 38.3, 26.9, 23.3, 21.8. **HR-MS** (ESI) *m/z* calc. for $C_{19}H_{21}NO_3SNa^+$. $[M+Na]^+$: 366.1140, found: 366.1138.

5. Mechanistic Studies

5.1 Radical Trapping Experiment (1)

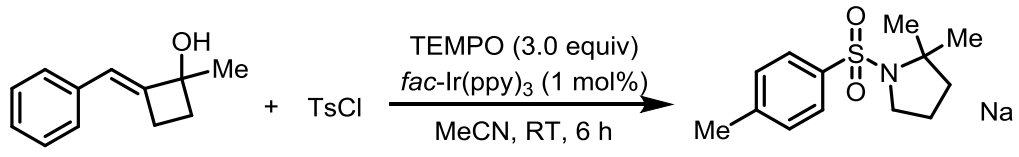


11 (1:1)

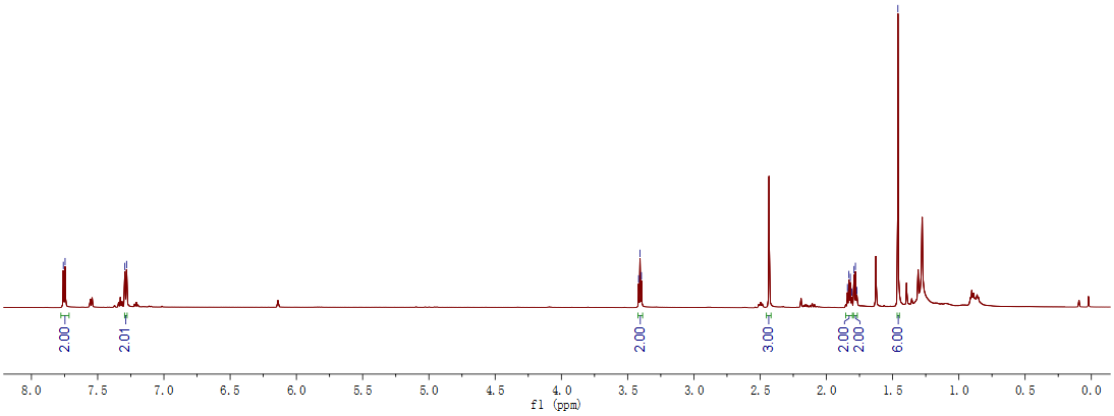
Radical receptor (1-cyclopropylvinyl)benzene (28.8 mg, 0.2 mmol), sulfonyl chlorides **2a** (41.8 mg， 0.22 mmol), *fac*-Ir(ppy)$_3$ (0.7 mg, 0.001 mmol) and Na_2CO_3 (21.2 mg, 0.2 mmol) were placed in a 15 mL Schlenk tube. The tube was evacuated and purged with N_2 three times. Acetonitrile (2.0 mL) was then added and the mixture was stirred under blue light irradiation (30 W LEDs, temperature was maintained between 30 °C and 35 °C). After 1.5 h, the crude reaction solution was transferred to the round bottom flask. Silica was added to the flask and all volatiles were evaporated under vacuum. Purification of the residue by colum chromatography (SiO_2, petroleum ether/EtOAc = 5:1) yielded the corresponding product **8** (26.8 mg, 45%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.64 (d, J = 8.3 Hz, 2H), 7.37 (d, J = 8.3 Hz, 2H), 7.26 (d, J = 14.8 Hz, 3H), 7.20 (d, J = 17.5 Hz, 6H), 7.14 (d, J = 7.9 Hz, 2H), 6.92 (dt, J = 8.4, 1.7 Hz, 2H), 6.54 (s, 1H), 6.06 (t, J = 7.3 Hz, 1H), 4.37 (s, 2H), 3.59 (t, J = 6.6 Hz, 2H), 2.65 (q, J = 6.7 Hz, 2H), 2.40 (s, 3H), 2.38 (s, 3H), 1.68 (d, J = 26.5 Hz, 1H), 0.82 (d, J = 19.6 Hz, 2H), 0.51 (d, J = 16.2 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.3, 144.8, 143.6, 140.6, 139.2, 136.0, 133.8, 133.7, 130.8, 129.7, 129.5, 129.3, 128.8, 128.5, 128.4, 128.4, 128.2, 127.6, 127.6, 127.5, 127.0, 126.6, 123.3, 58.1, 43.8, 32.6, 21.7, 20.0, 7.1. This compound is known and the NMR data match previous reported.[5]

5.2 Radical Trapping Experiment (2)

Trapping experiment for addition product using NMR and HRMS



1-1 **2a** **10:** 25%



^{1}H NMR (600 MHz, $CDCl_3$) δ 7.75 (d, J = 8.1 Hz, 2H), 7.29 (d, J = 7.7 Hz, 2H), 3.41 (t, J = 6.5 Hz, 2H), 2.43 (s, 3H), 1.82 (dd, J = 13.0, 6.5 Hz, 2H), 1.78 (t, J = 6.4 Hz, 2H), 1.46 (s, 6H). **HR-MS** (ESI) *m/z* calc. for $C_{13}H_{19}NNaO_2S^+$. $[M+Na]^+$: 276.1034, found: 276.1026. This compound is known and the NMR data match previous reported.[6]

5.3 Determination Rate Product Formation

The rate of product formation was determined initially according to *(A) General procedure for the cascade ring-opening/ remote formylation*. Following this procedure, Methyenecyclobutanols **1-1** (34.8 mg, 0.2 mmol, 1.0 equiv.) and sulfonyl chlorides **2a** (38 mg, 0.2 mmol, 1.0 equiv) as reactant was used. The reaction was irradiated using Kessil LED (λmax = 456 nm). Monitoring of the product formation was accomplished after 2, 4, 6, 8, 10, 15, 20, 30, 50, 70, 90 min, The yield of compound **3-1** was determined by silica gel (petroleum ether / ethyl acetate = 5:1) column chromatography. A linear regression in the interval 0 to 90 min gave the product formation rate.

Table 1. Yield *vs*. time profile for the product formation of **3-1**.

Entry	***t* / min**	**Yield (3-1) / mmol**	**Yield (3-1) / %**
1	0	0	0
2	2	0.0092	4.55
3	4	0.0152	7.60
4	6	0.0274	13.70
5	8	0.0427	21.35
6	10	0.0518	25.90
7	15	0.0762	38.10
8	20	0.1006	50.30
9	30	0.1311	65.55
10	50	0.1600	80.00
11	70	0.1640	82.00
12	90	0.1660	83.00

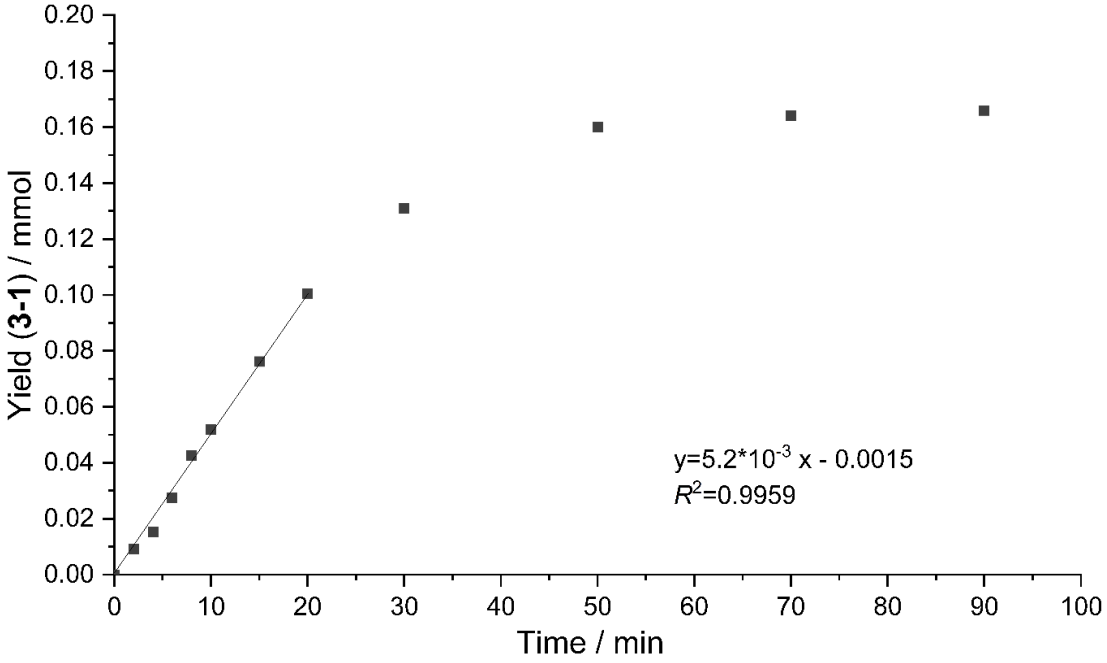


Figure 1. Graphical representation for the yield *vs.* time profile for the product formation of **3-1** with a linear regression in the interval 0 to 90 min.

5.4. Determination of Quantum Yield

One Kessil LED (λ_{max} = 456 nm) was used for measurement of quantum yield. According to the procedure of Yoon[7] the photon flux of the LED (λ max = 456 nm) was determined by standard ferrioxalate actinometry. A 0.15 M solution of ferrioxalate was prepared by dissolving potassium ferrioxalate hydrate (0.737 g) in H_2SO_4 (10 mL of a 0.05 M solution). A buffered solution of 1,10-phenanthroline was prepared by dissolving 1,10-phenanthroline (10.0 mg) and sodium acetate (2.25 g) in H_2SO_4 (10.0 mL of a 0.5 M solution). Both solutions were stored in the dark. To determine the photon flux of the spectrophotometer, 2.0 mL of the ferrioxalate solution was placed in a cuvette and irradiated for 10.0 seconds at 456 nm. After irradiation, the 1,10-phenanthroline solution (0.35 mL) was added to the cuvette. The solution was then allowed to rest for 1 h to allow the ferrous ions to completely coordinate to the phenanthroline. The absorbance of the solution was measured at 510 nm. A non-irradiated sample was also prepared and the absorbance at 510 nm was measured (Figure 2). Conversion was calculated using eq 1.

	Nonn-irrad	Irrad 01	Irrad 02	Irrad 03
$A_{510\ nm}$	0.0775	1.0775	1.0791	1.0711
		Average $A_{510\ nm}$ of Irradiation samples		0.9984

$$\text{mol of } Fe^{2+} = \frac{V \cdot \Delta A}{l \cdot \varepsilon} = \frac{(0.00235\ \text{L}) \cdot (0.9984)}{(1.00\ \text{cm}) \cdot (11{,}100\ \text{L} \cdot \text{mol}^{-1} \cdot \text{cm})} = 2.1137 \times 10^{-7}\ \text{mol} \quad (1)$$

Where V is the total volume (0.00235 L) of the solution after addition of phenanthroline, ΔA is the difference in absorbance at 510 nm between the irradiated and non-irradiated solutions, l is the path length (1.00 cm), and ε is the molar absorptivity of the ferrioxalate actinometer at 510 nm (11,100 L mol^{-1} cm^{-1}).[8] The photon flux can be calculated using eq 2.

$$\text{photon flux} = \frac{\text{mol of } Fe^{2+}}{\emptyset \cdot t \cdot f} = \frac{2.1137 \times 10^{-7}\ \text{mol}}{(0.84) \cdot (90\text{s}) \cdot (0.915)} = 3.0556 \times 10^{-9}\ \text{einstein/ s} \quad (2)$$

Where Φ is the quantum yield for the ferrioxalate actinometer (0.84 for a 0.15 M solution at λ = 456 nm),[9] t is the irradiation time (90 s), and f is the fraction of light absorbed at 456 nm by the ferrioxalate actinometer. This value is calculated using eq 3 where $A_{456\ nm}$ is the absorbance of the ferrioxalate solution at 456 nm. An absorption spectrum gave an $A_{456\ nm}$ value of 1.073, indicating that the fraction of absorbed light (f) is 0.915.

$$f = 1 - 10^{-A_{510\ nm}} \quad (3)$$

The photon flux was thus calculated (average of three experiments) to be 3.0556×10^{-9} einsteins s^{-1}.

The reaction quantum yield (Φ) was determined using eq 4 where the photon flux is 3.0556×10^{-9} einsteins s^{-1} (determined by actinometry as described above) and f is the fraction of incident light absorbed by the catalyst, determined using eq 3. An absorption spectrum of the catalyst (0.05 M in MeCN) gave an absorbance value of 0.4751 at 456 nm (Figure 3), indicating that the fraction of light absorbed by the photocatalyst (f) is 0.6651.

$$\Phi = \frac{\text{product formation rate}}{\text{flux} \cdot \text{f}} \quad (4)$$

$$\Phi = \frac{8.67 \times 10^{-8}\ \text{mol s}^{-1}}{3.0556 \times 10^{-9}\ \text{einsteins s}^{-1} \cdot 0.6651} = 42.7$$

The reaction quantum yield () was calculated to be 42.7.

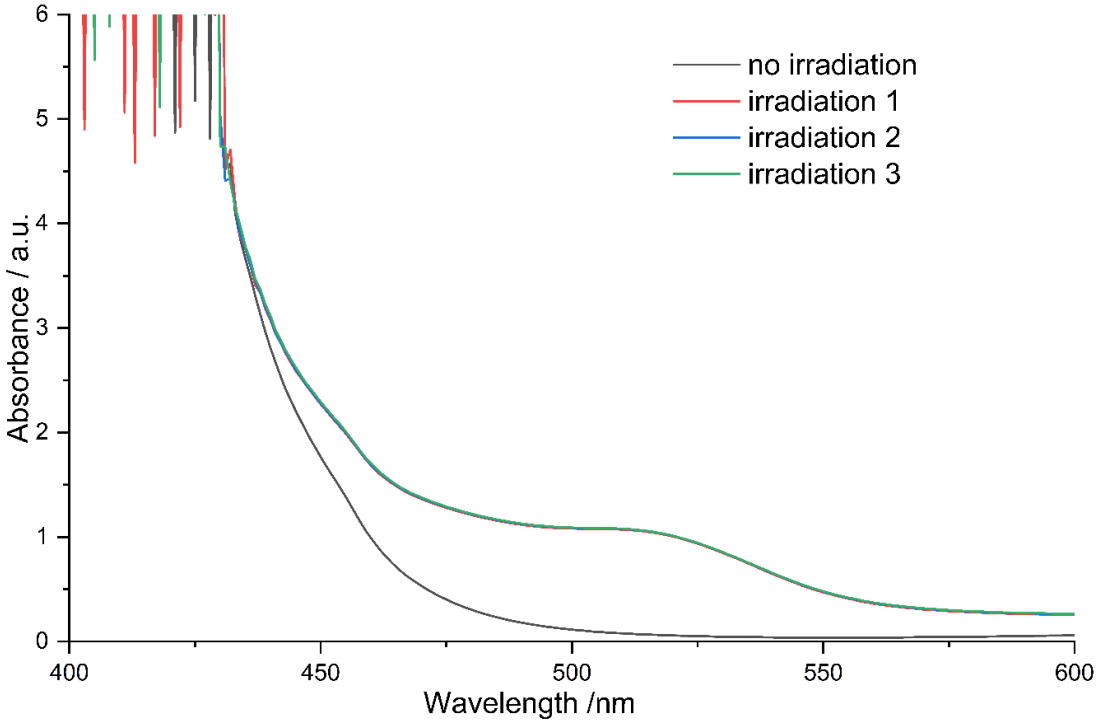


Figure 2. Absorption spectra of three irradiated ferrioxalate solutions and one non-irradiated sample.

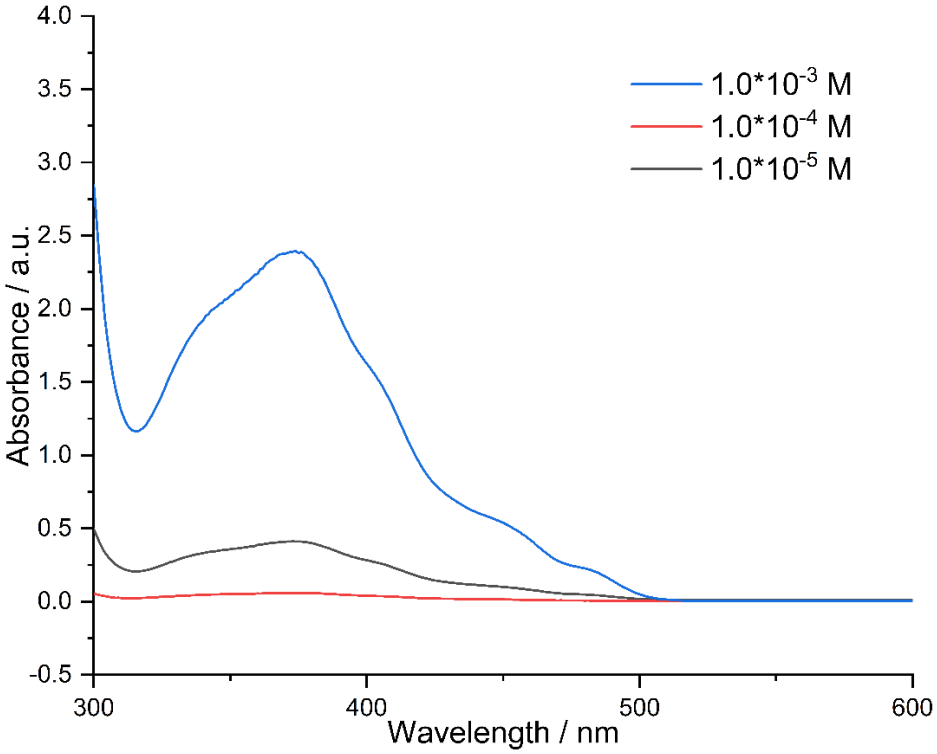
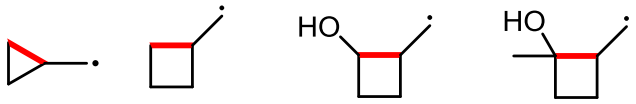


Figure 3. Absorption spectrum of *fac*-[Ir(ppy)$_3$] in MeCN.

6. Density Functional Theory (DFT) Computations

Computational details: All density functional theory (DFT) calculations were performed using Gaussian 16.[10] Geometry optimizations and frequencies were calculated at the M06-2X/def2-SVP-SMD(DMSO) level of theory.[11,12] Frequency calculations confirmed that optimized structures are minima (no imaginary frequency) or transition structures (one imaginary frequency). To obtain more accurate electronic energies, single-point energy calculations were performed at the M06-2X-D3/def2-TZVP-SMD(DMSO) level of theory with the optimized structures.

Table S1. Calculated barriers for ring opening of various cyclic compounds.



1 **2** **3** **4**

Substrate	TS for cleavage of the red bond	DG‡ (kcal/mol)
1	**TS1**	8.5
2	**TS2**	14.6
3	**TS3**	12.8
4	**TS4**	10.0

The calculated Cartesian coordinates and energies of structures

1

C 0.8953 0.75087 -0.15485
C -0.23847 0.00064 0.48843
C 0.89539 -0.75108 -0.15234
H 0.68203 1.25229 -1.10218
H 1.60605 1.26716 0.49318
H -0.22843 0.00291 1.58708
H 1.60639 -1.26502 0.49727
H 0.68227 -1.25563 -1.09806
C -1.57158 -0.00032 -0.14626
H -2.11328 -0.9373 -0.29854
H -2.11889 0.93495 -0.28863

M06-2X-D3/def2TZVP-SMD(DMSO): E = -156.519453348 hartree

Thermal correction to Gibbs Free Energy = 0.067400 hartree

2

C -1.54737 -0.00001 -0.04182
C -0.44399 1.07572 -0.09167
C 0.5602 0.00008 0.39302
C -0.44393 -1.07572 -0.09113
H -2.05669 0.00022 0.93279
H -2.30265 -0.00023 -0.83954
H -0.56762 1.98107 0.51903
H -0.21663 1.3665 -1.12883
H 0.56622 0.00049 1.50099
H -0.56756 -1.98078 0.51999
H -0.21656 -1.36699 -1.12815
C 1.93769 -0.00002 -0.14916
H 2.49386 0.93619 -0.24364
H 2.49207 -0.93683 -0.24804

M06-2X-D3/def2TZVP-SMD(DMSO): E = -195.825165543 hartree

Thermal correction to Gibbs Free Energy = 0.094965 hartree

3

C 0.91756 1.19933 0.06323
C -0.60465 1.38297 -0.08337
C -0.73494 -0.13667 -0.3666
C 0.63987 -0.28064 0.36712
H 1.41808 1.29152 -0.91386
H 1.45945 1.79475 0.81033
H -0.9729 2.07222 -0.8543
H -1.07393 1.63292 0.87987
H -0.54586 -0.3239 -1.43725
H 0.45503 -0.42198 1.44362
C -1.90762 -0.8884 0.11415
H -2.31984 -0.67089 1.10298
H -2.29119 -1.75844 -0.42116
O 1.53564 -1.26749 -0.02648
H 1.72461 -1.1359 -0.96568

M06-2X-D3/def2TZVP-SMD(DMSO): E = -271.062978882 hartree

Thermal correction to Gibbs Free Energy = 0.098223 hartree

4

C 0.56281 1.43347 0.1492
C -0.97388 1.33693 0.1892
C -0.88853 -0.03237 -0.52453
C 0.61589 -0.09758 -0.04174
H 0.90555 1.94068 -0.7659
H 1.08902 1.85343 1.01875
H -1.54741 2.1255 -0.31527
H -1.35186 1.22042 1.21555
H -0.84599 0.12381 -1.61603
C -1.82907 -1.11336 -0.18153
H -2.24895 -1.17994 0.82464
H -2.0183 -1.93904 -0.86993
O 1.54851 -0.61522 -0.94568
H 1.46655 -0.11993 -1.77162
C 0.78787 -0.85408 1.25852
H 0.61204 -1.92804 1.09598
H 1.81445 -0.71702 1.62987
H 0.08619 -0.49624 2.02472

M06-2X-D3/def2TZVP-SMD(DMSO): E = -310.377251357 hartree

Thermal correction to Gibbs Free Energy = 0.125008 hartree

TS1

C	-1.21824	-0.68568	-0.10416
C	0.44029	0.16053	0.48253
C	-0.78708	0.726	-0.15382
H	-1.02362	-1.34605	-0.94905
H	-1.76485	-1.07631	0.75453
H	0.40207	0.03071	1.56745
H	-1.3546	1.41924	0.47644
H	-0.61631	1.12784	-1.1593
C	1.60153	-0.13422	-0.18476
H	1.69467	0.04431	-1.25966
H	2.4436	-0.59953	0.33087

M06-2X-D3/def2TZVP-SMD(DMSO): E = -156.504835194 hartree

Thermal correction to Gibbs Free Energy = 0.066366 hartree

TS2

C	1.52315	-0.16235	0.01933
C	0.29239	-1.06406	-0.10372
C	-0.74631	-0.09043	0.43474
C	0.79761	1.15078	-0.14859
H	1.95383	-0.23593	1.02855
H	2.32421	-0.35451	-0.71144
H	0.33589	-2.01932	0.44301
H	0.07124	-1.27983	-1.1605
H	-0.63755	0.15256	1.49886
H	0.53144	1.44091	-1.17012
C	-1.97195	0.13092	-0.14453
H	-2.18717	-0.22574	-1.15603
H	-2.72884	0.74795	0.34512
H	0.96761	1.98469	0.53916

M06-2X-D3/def2TZVP-SMD(DMSO): E = -195.800611194 hartree

Thermal correction to Gibbs Free Energy = 0.093726 hartree

TS3

C	0.79849	1.18856	0.01603
C	-0.72842	1.25997	-0.02905
C	-0.99642	-0.18598	-0.41854
C	0.87595	-0.25992	0.42281
H	1.21068	1.29808	-1.00116
H	1.31423	1.90302	0.67723
H	-1.14881	2.00455	-0.72166
H	-1.14103	1.4512	0.97361
H	-0.62444	-0.46103	-1.41521
H	0.64323	-0.49359	1.46811
C	-2.00657	-0.95595	0.11747
H	-2.52162	-0.64747	1.03197
H	-2.24779	-1.94069	-0.28941
O	1.84322	-1.07817	-0.0553
H	2.11152	-0.76877	-0.93339

M06-2X-D3/def2TZVP-SMD(DMSO): E = -271.042267724 hartree

Thermal correction to Gibbs Free Energy = 0.097915 hartree

TS4

C	0.51727	1.37764	0.24713
C	-1.00565	1.24336	0.32876
C	-1.15757	0.01488	-0.5562
C	0.8096	-0.0857	-0.01658
H	0.8028	1.97072	-0.63671
H	1.02481	1.80349	1.12836
H	-1.57248	2.12233	-0.01351
H	-1.33211	1.00551	1.35255
H	-0.91649	0.18533	-1.6143
C	-1.97365	-1.0563	-0.25541
H	-2.38271	-1.18574	0.75083
H	-2.15413	-1.85478	-0.97906
O	1.69187	-0.4196	-0.9976
H	1.69285	0.27571	-1.67124
C	0.89789	-1.02224	1.14263
H	0.75487	-2.06079	0.80717
H	1.88959	-0.94644	1.62193
H	0.1306	-0.7884	1.89278

M06-2X-D3/def2TZVP-SMD(DMSO): E = -310.360284309 hartree

Thermal correction to Gibbs Free Energy = 0.123898 hartree

7. References

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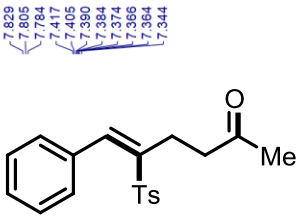
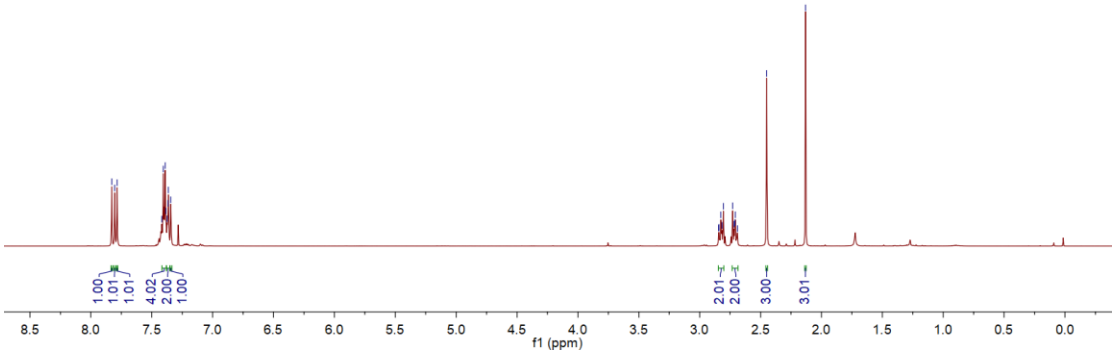
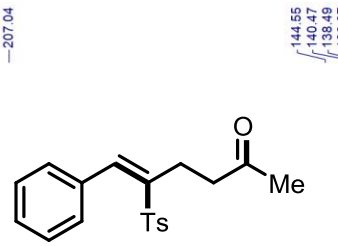
8. NMR Spectra



3-1

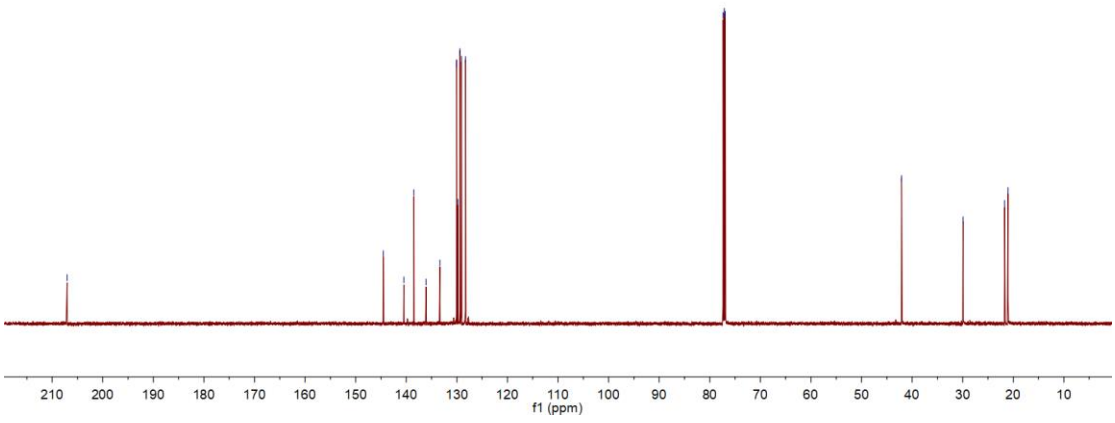
^{1}H NMR (400 MHz, $CDCl_3$)

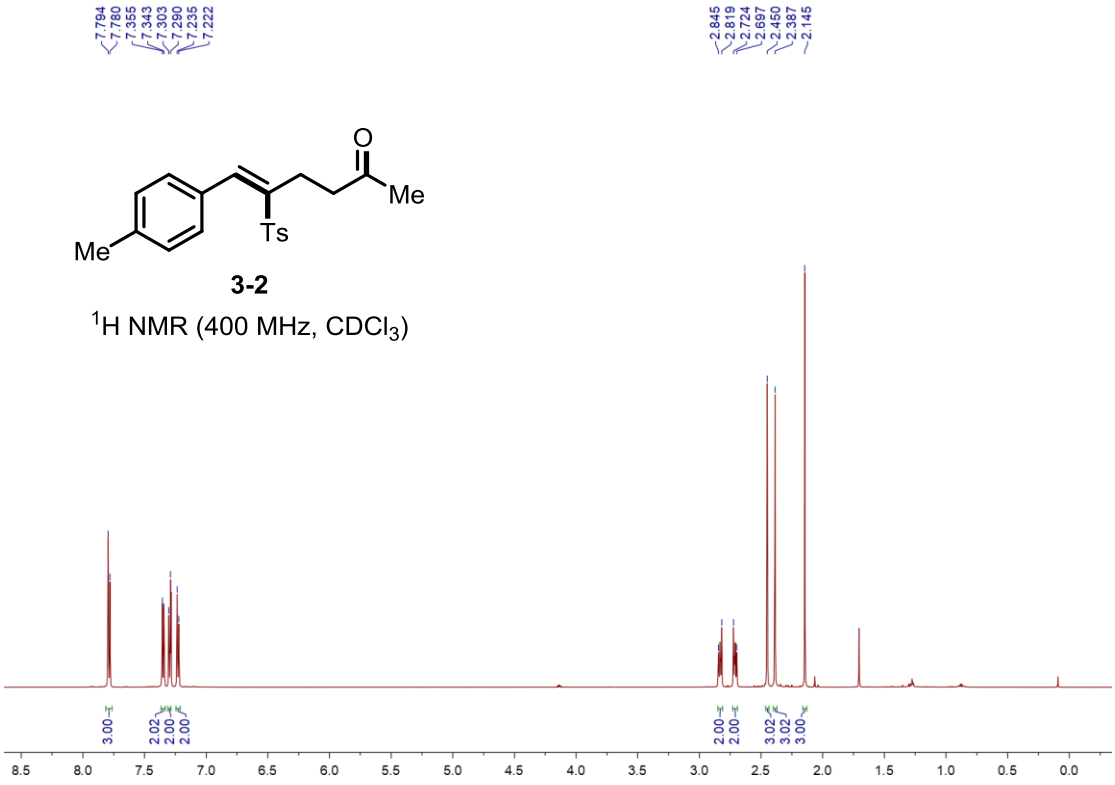




3-1

^{13}C NMR (101 MHz, $CDCl_3$)





3-2

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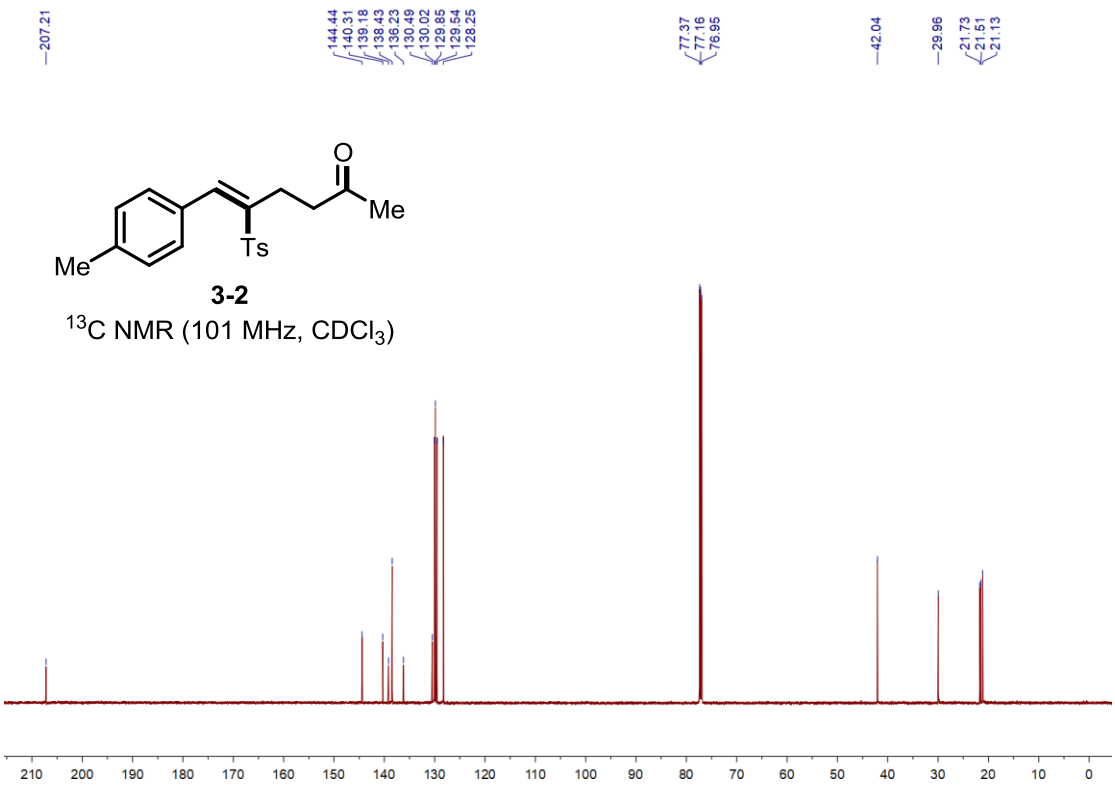
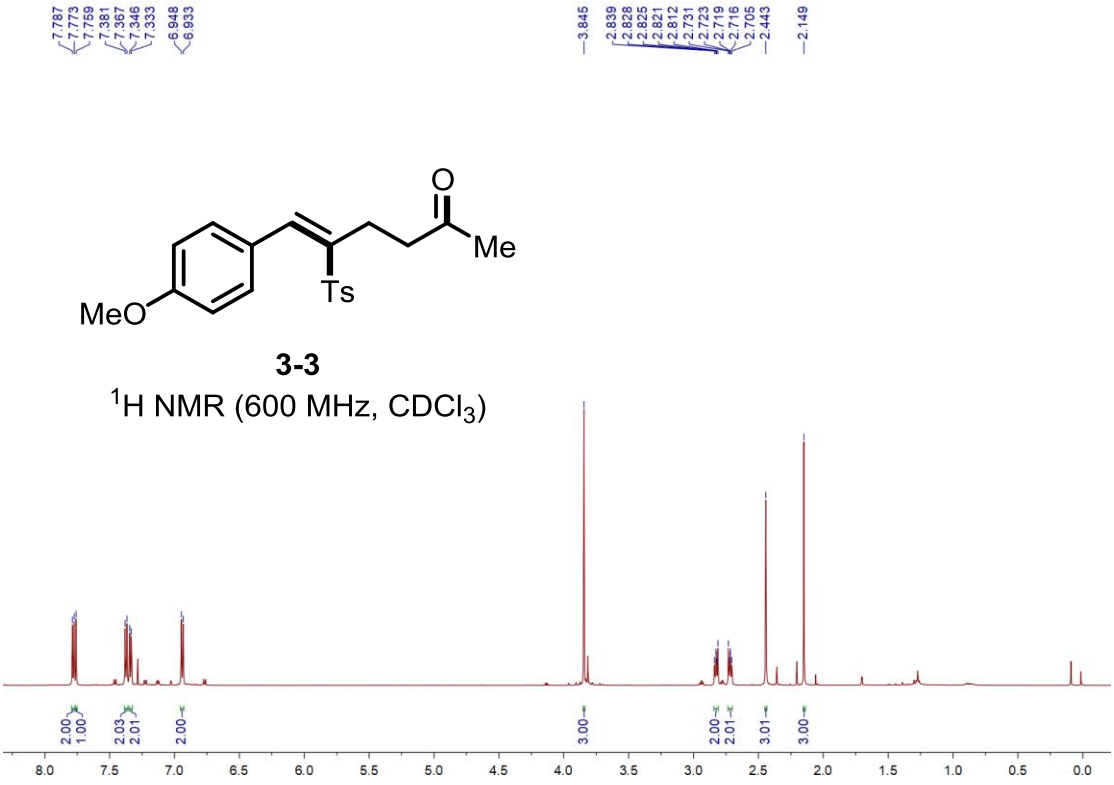


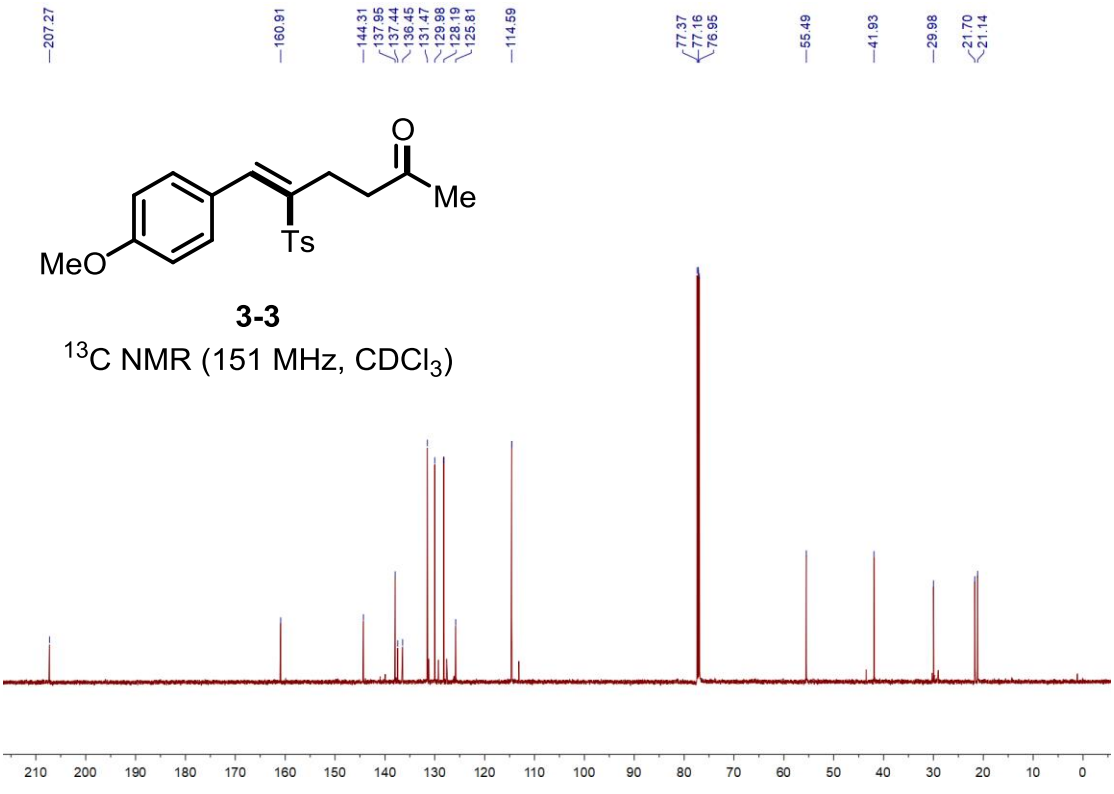
3-2

^{13}C NMR (101 MHz, $CDCl_3$)



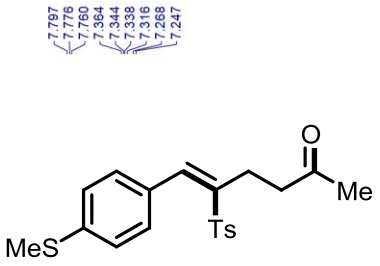
3-3

^{1}H NMR (600 MHz, $CDCl_3$)



3-3

^{13}C NMR (151 MHz, $CDCl_3$)



3-4

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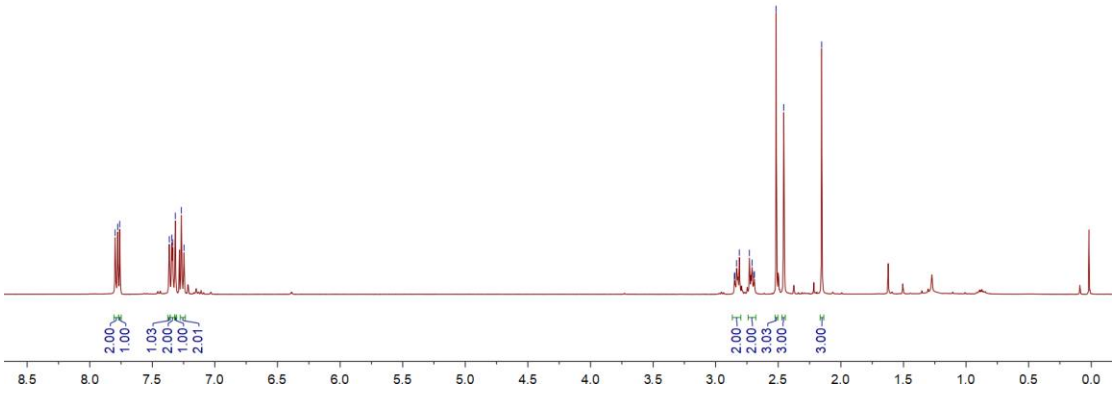
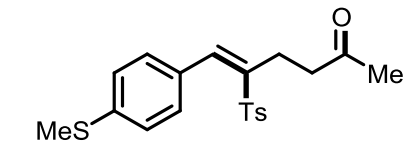
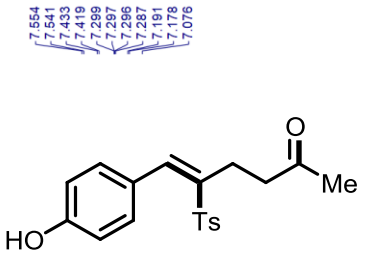




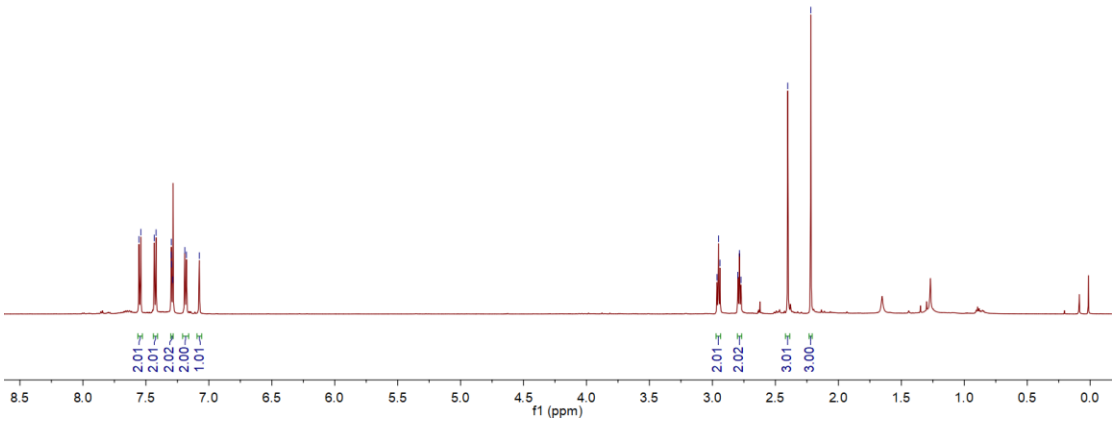
3-4

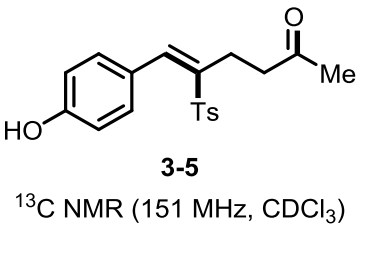
^{13}C NMR (151 MHz, $CDCl_3$)



3-5

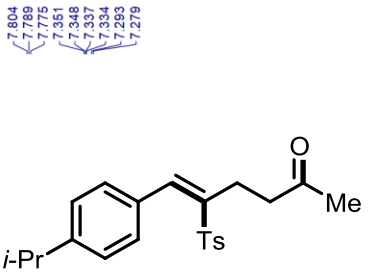
^{1}H NMR (600 MHz, $CDCl_3$)





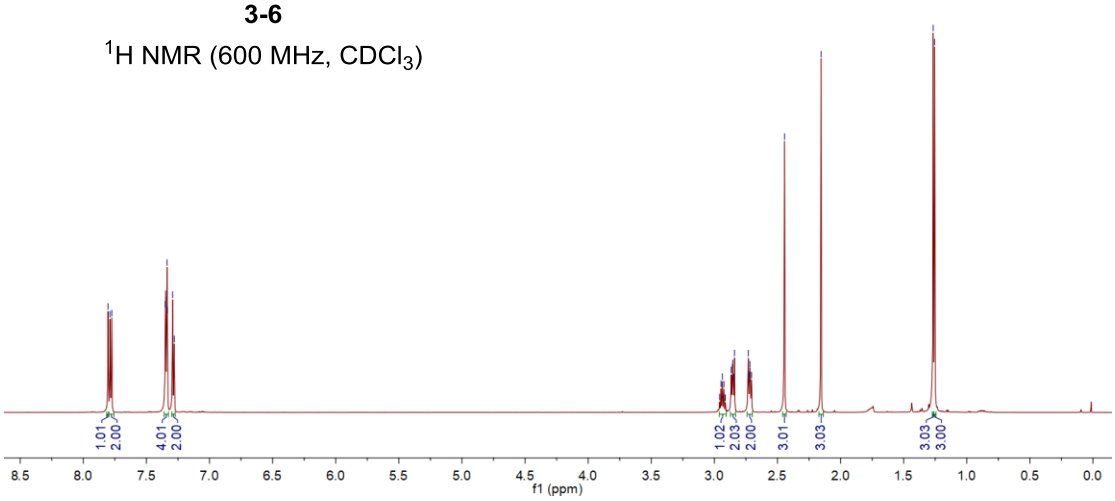
3-5

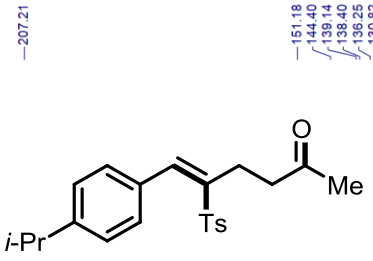
^{13}C NMR (151 MHz, $CDCl_3$)



3-6

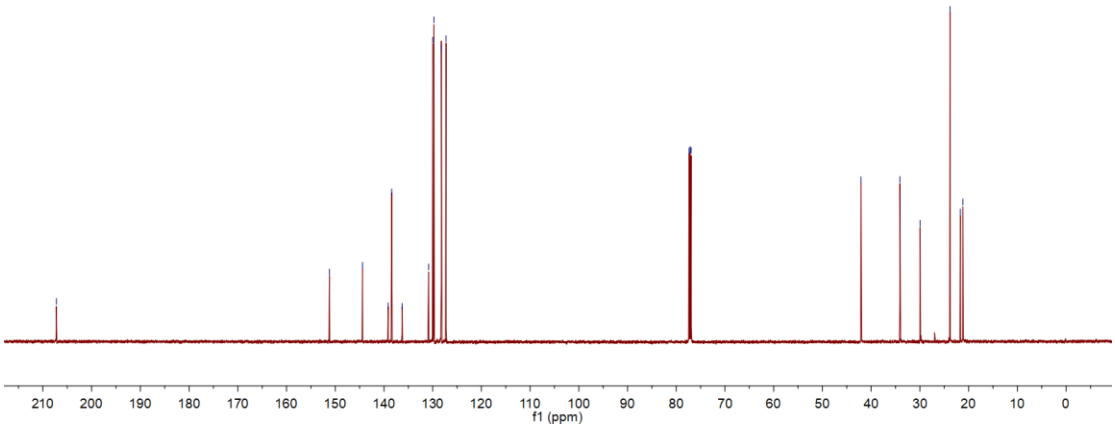
^{1}H NMR (600 MHz, $CDCl_3$)

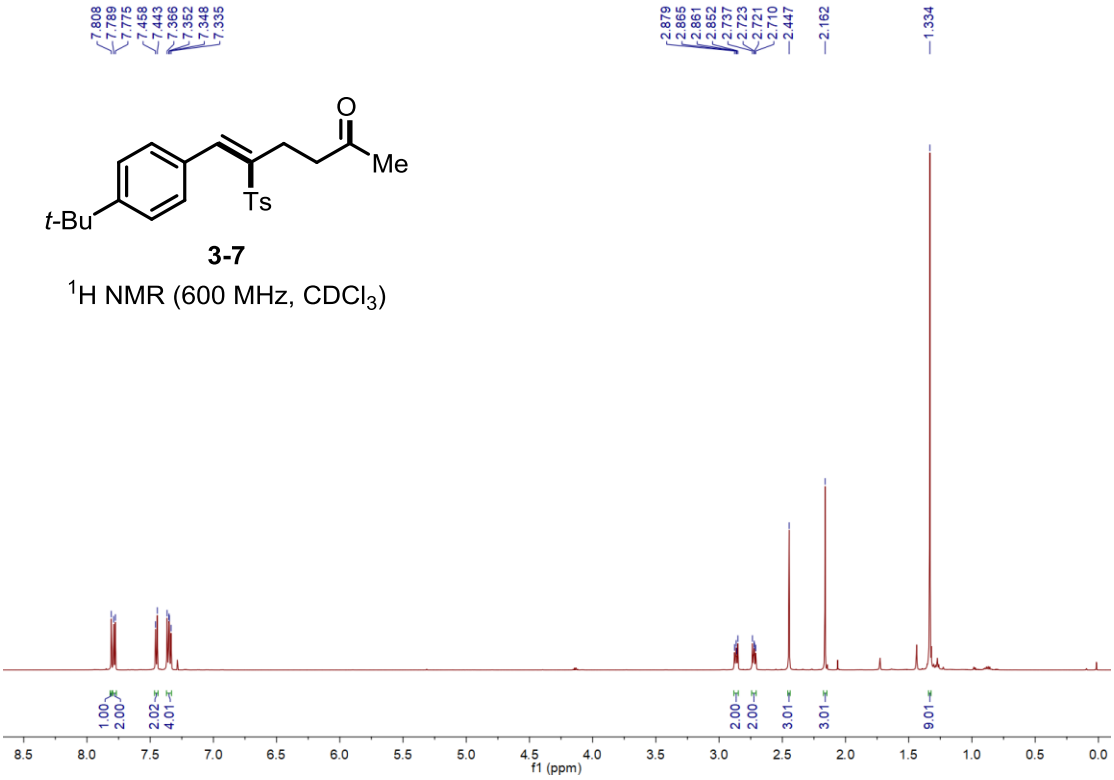




3-6

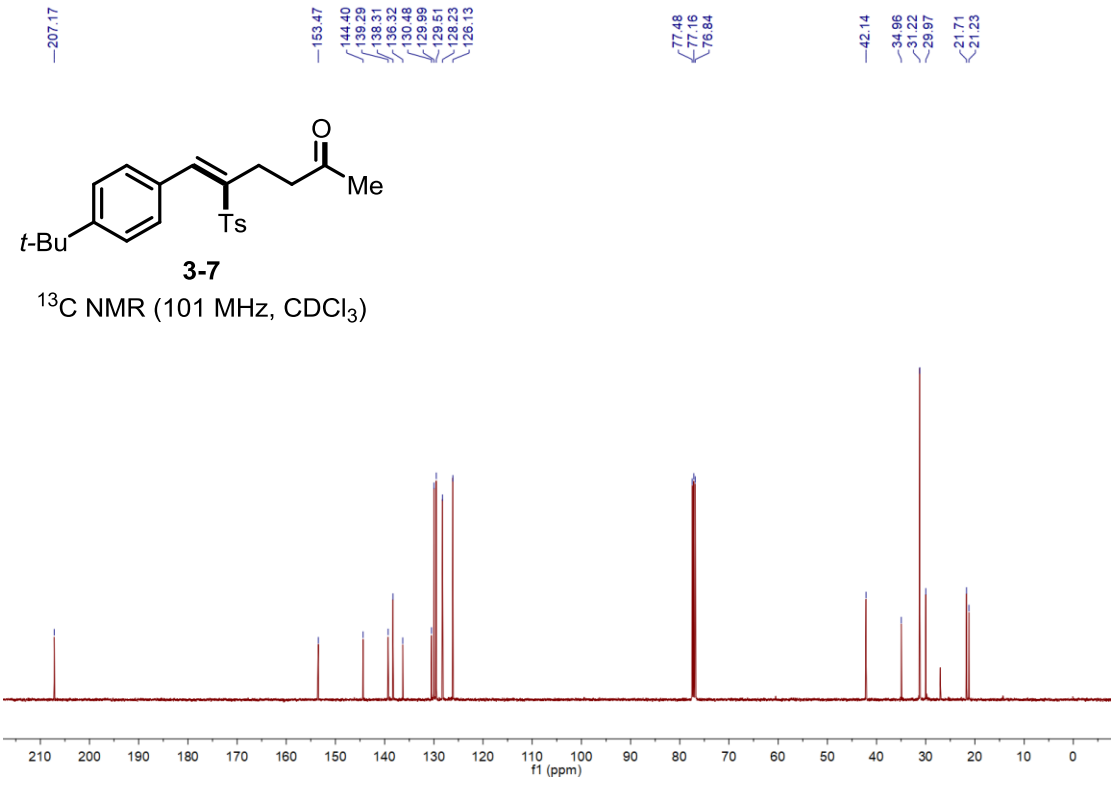
^{13}C NMR (151 MHz, $CDCl_3$)





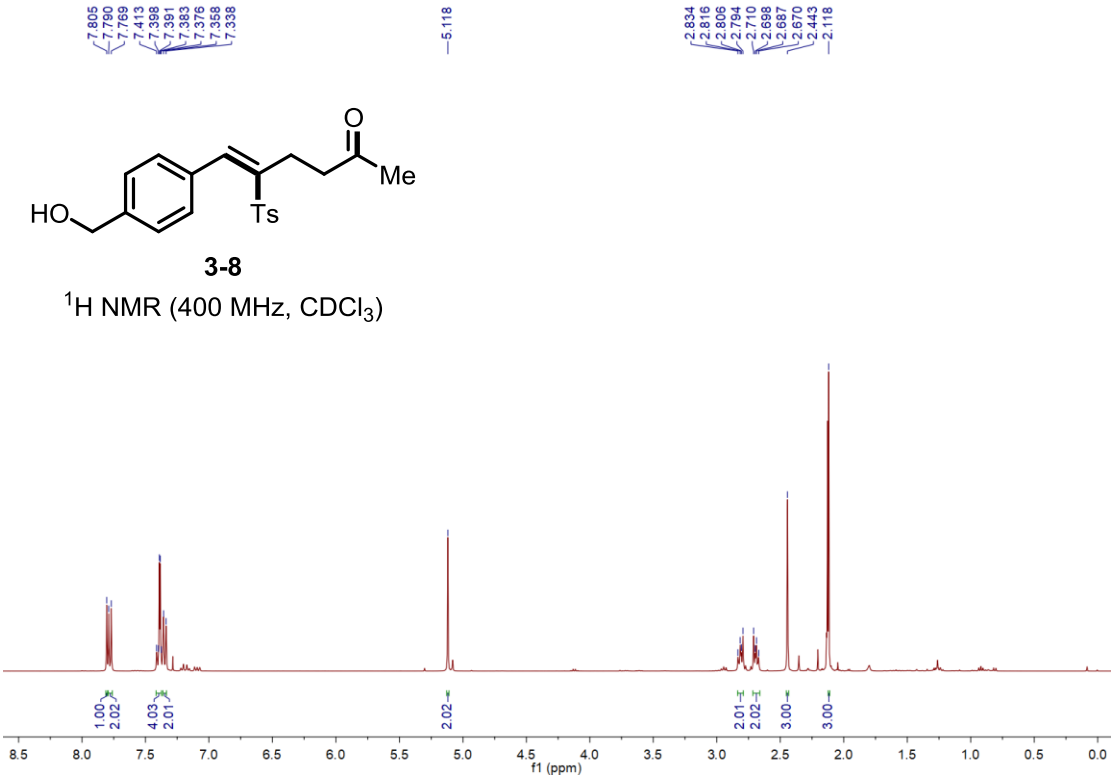
3-7

^{1}H NMR (600 MHz, $CDCl_3$)



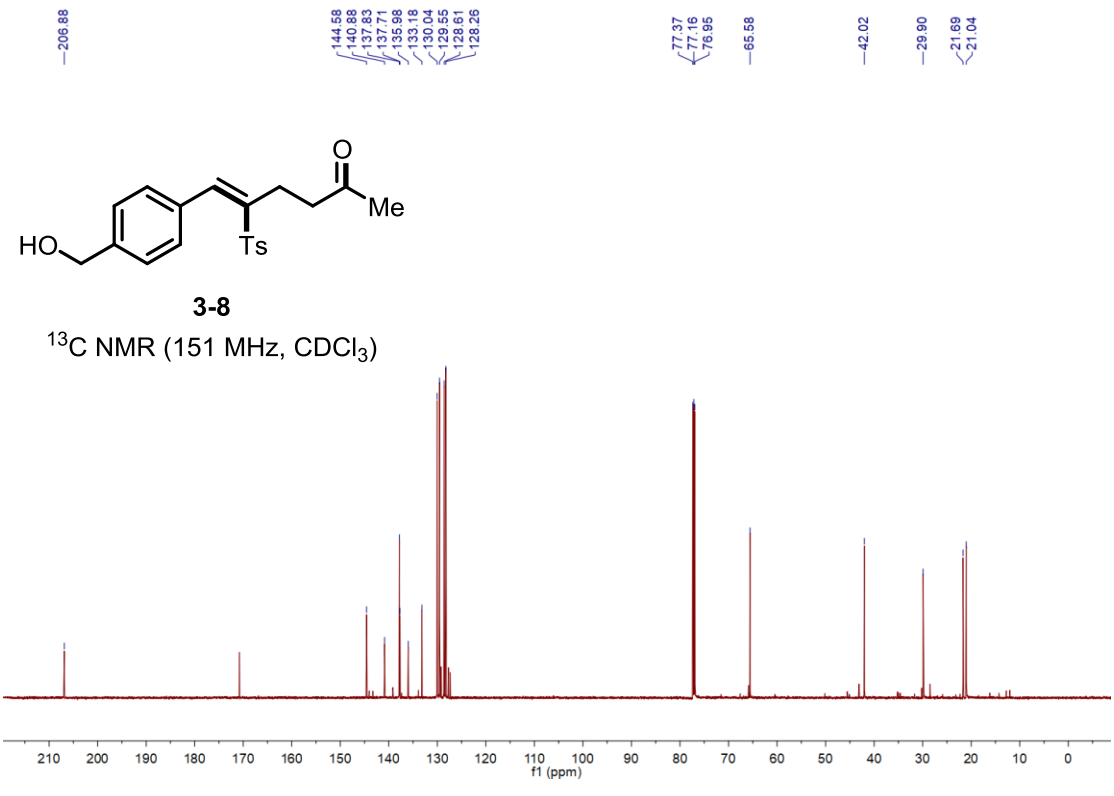
3-7

^{13}C NMR (101 MHz, $CDCl_3$)



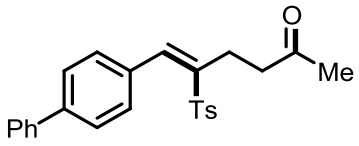
3-8

^{1}H NMR (400 MHz, $CDCl_3$)



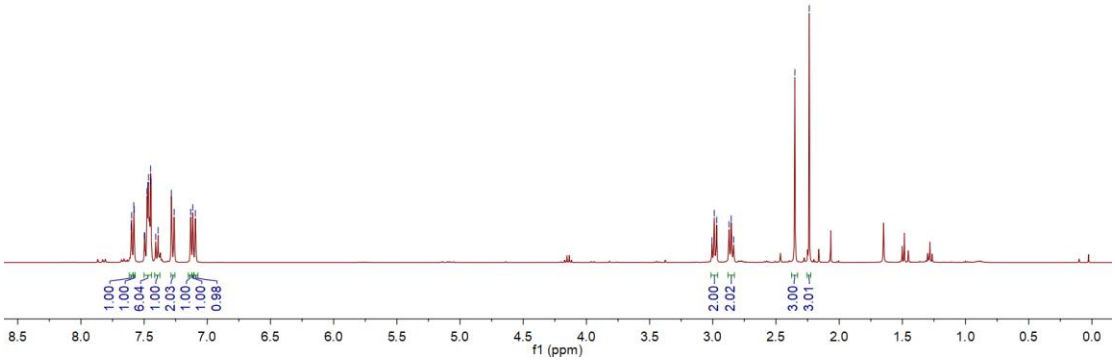
3-8

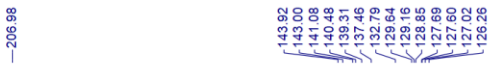
^{13}C NMR (151 MHz, $CDCl_3$)

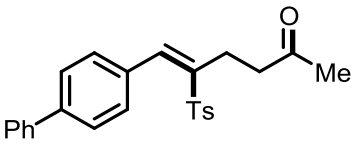


3-9

^{1}H NMR (400 MHz, $CDCl_3$)

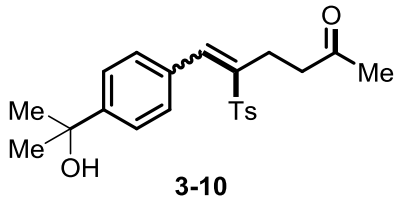






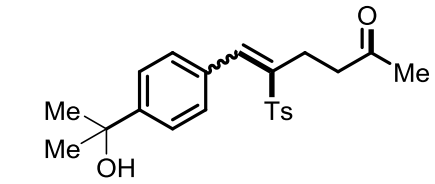
3-9

^{13}C NMR (151 MHz, $CDCl_3$)



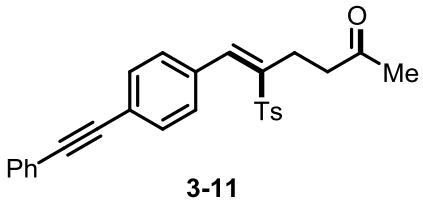
3-10

^{1}H NMR (600 MHz, $CDCl_3$)



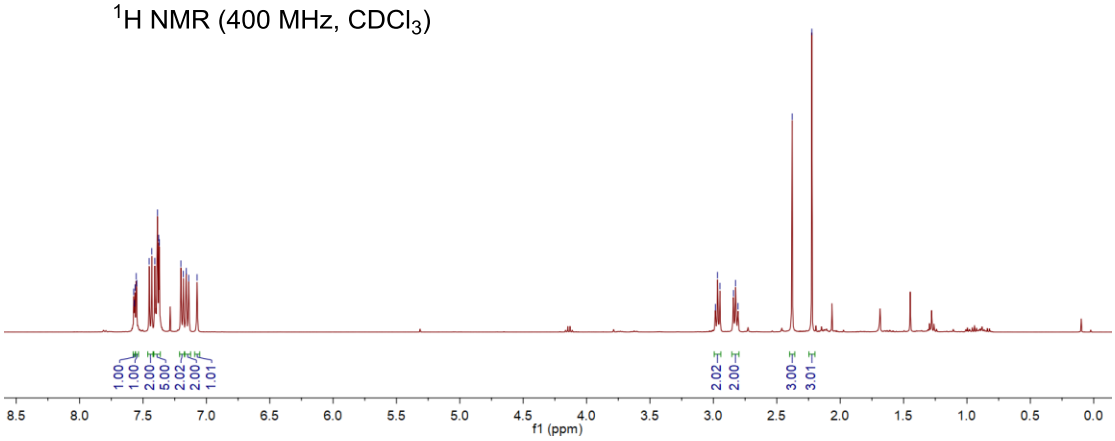
3-10

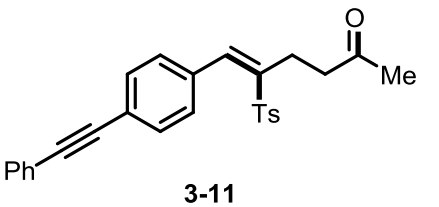
^{13}C NMR (151 MHz, $CDCl_3$)



3-11

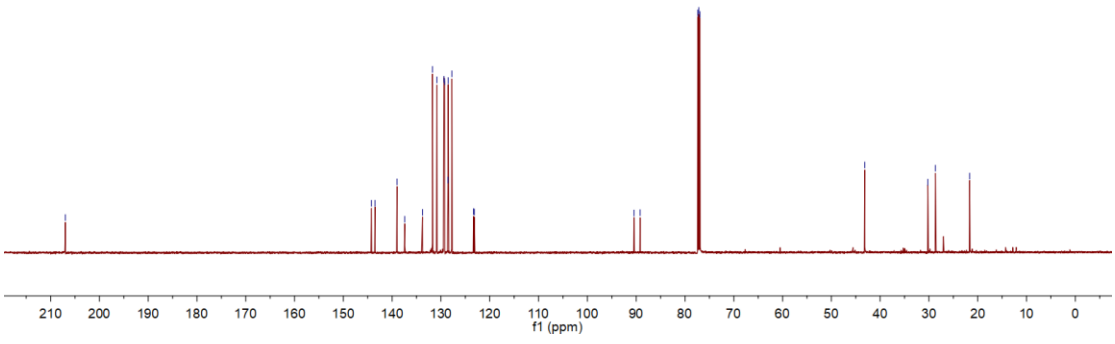
^{1}H NMR (400 MHz, $CDCl_3$)

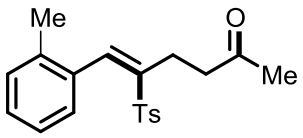




3-11

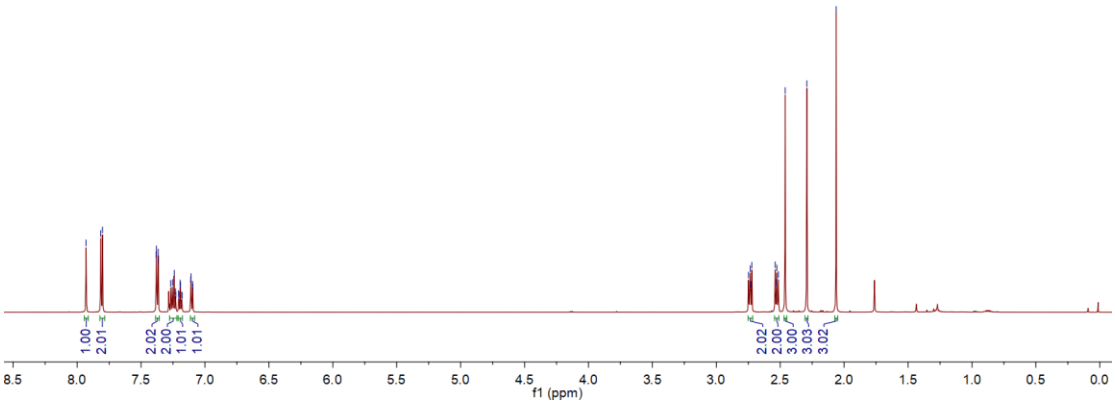
^{13}C NMR (151 MHz, $CDCl_3$)

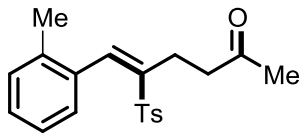




3-12

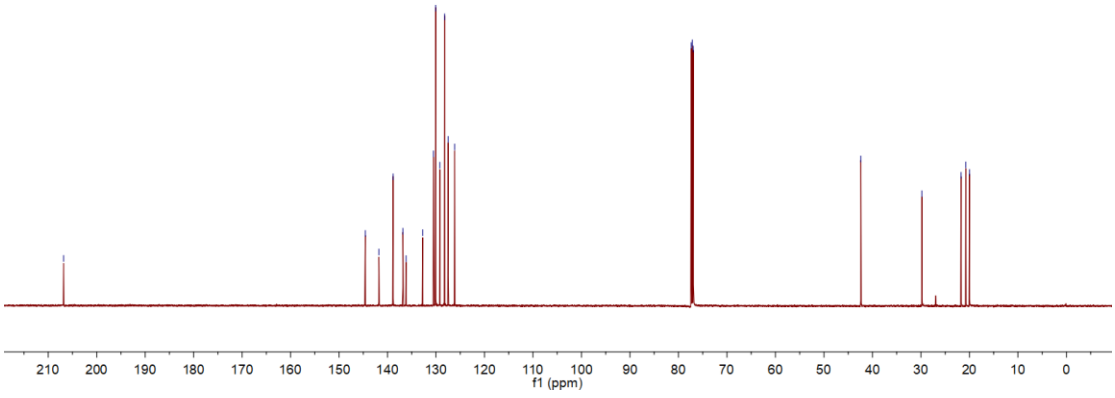
^{1}H NMR (600 MHz, $CDCl_3$)

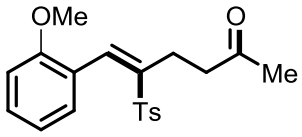




3-12

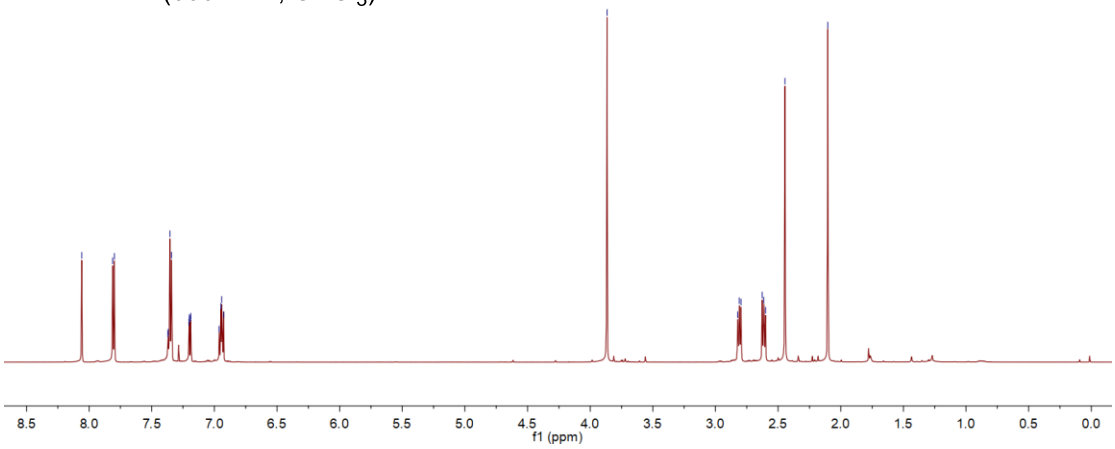
^{13}C NMR (151 MHz, $CDCl_3$)

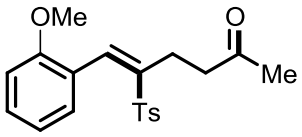




3-13

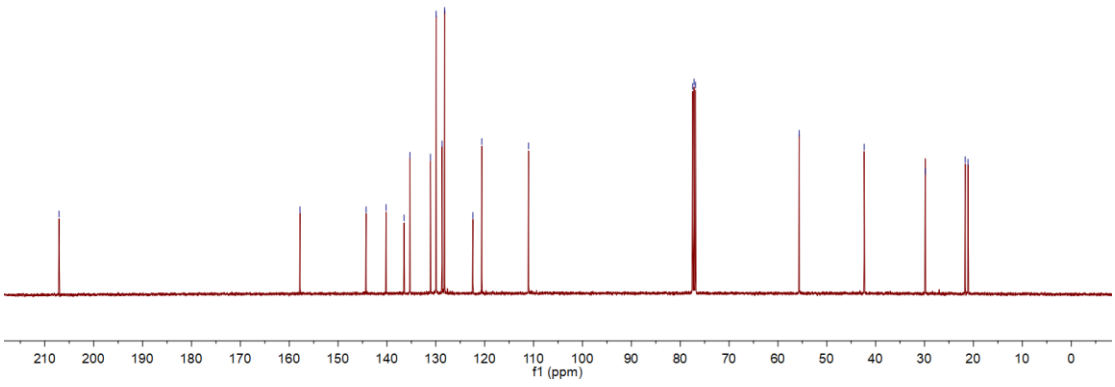
^{1}H NMR (600 MHz, $CDCl_3$)

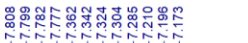


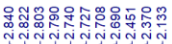


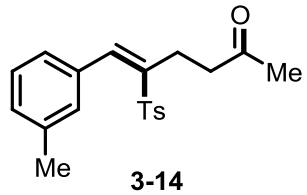
3-13

^{13}C NMR (101 MHz, $CDCl_3$)



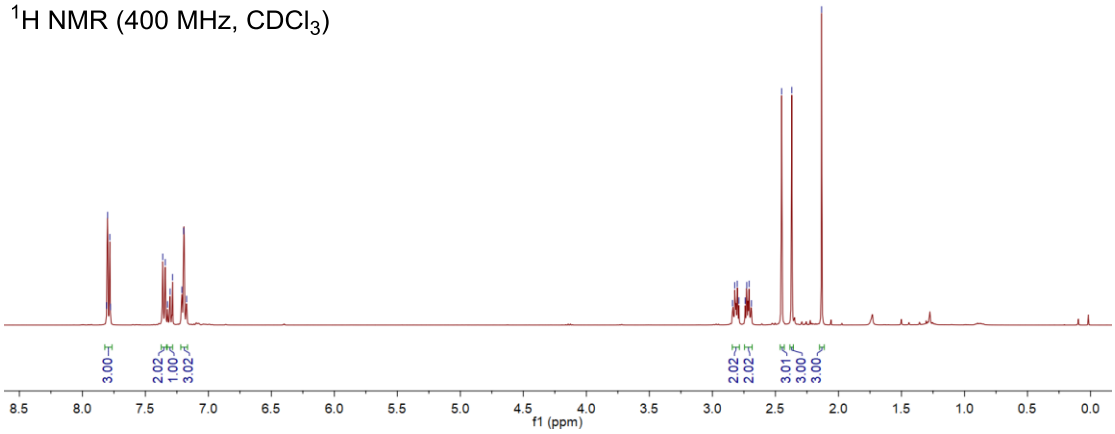


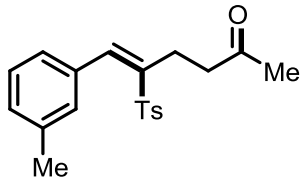




3-14

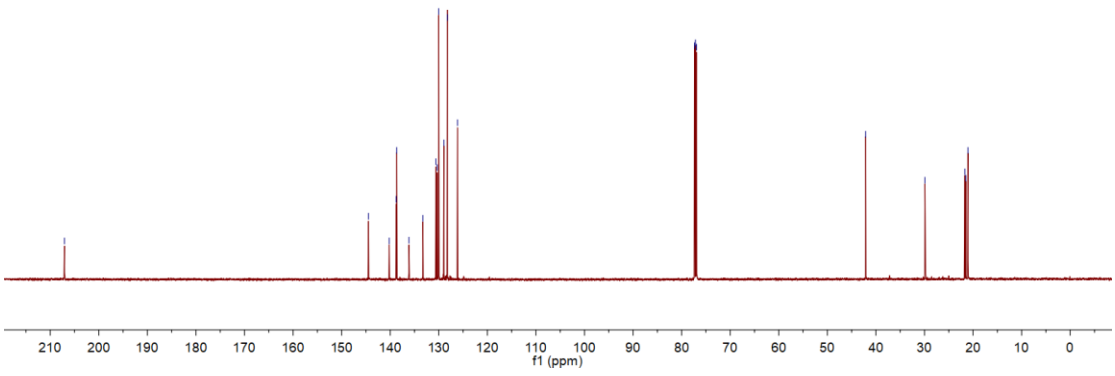
^{1}H NMR (400 MHz, $CDCl_3$)

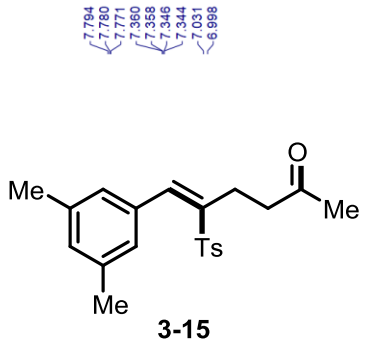




3-14

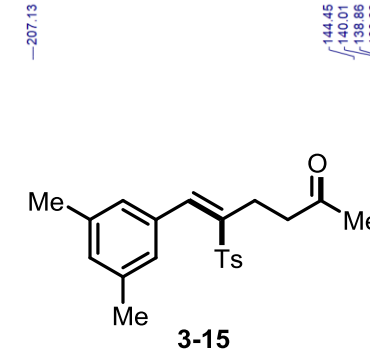
^{13}C NMR (151 MHz, $CDCl_3$)





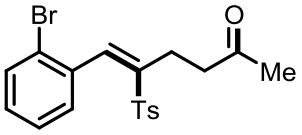
3-15

^{1}H NMR (600 MHz, $CDCl_3$)



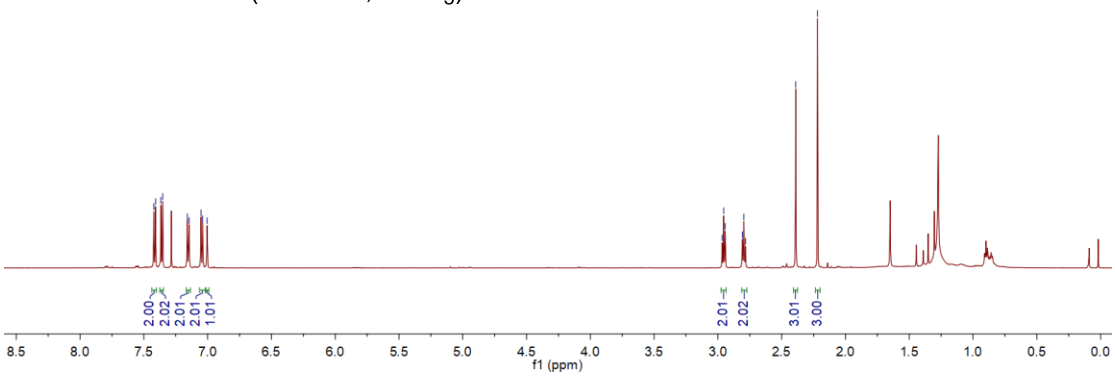
3-15

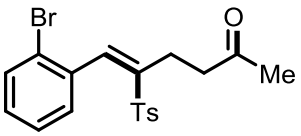
^{13}C NMR (151 MHz, $CDCl_3$)



3-16

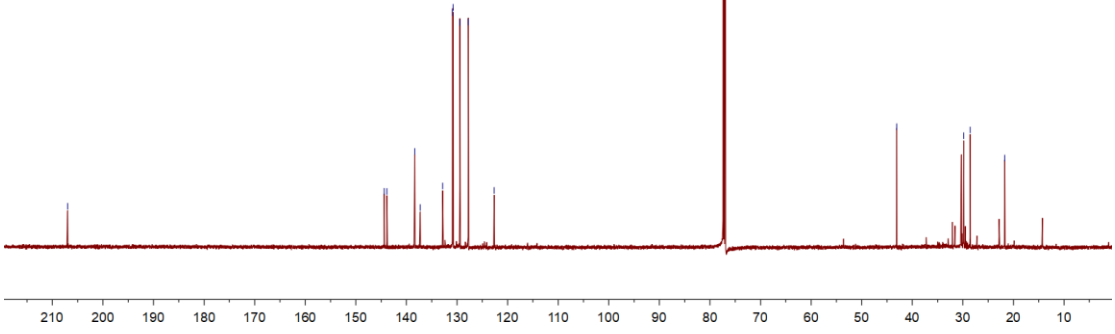
^{1}H NMR (600 MHz, $CDCl_3$)

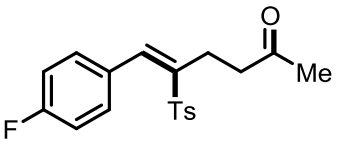




3-16

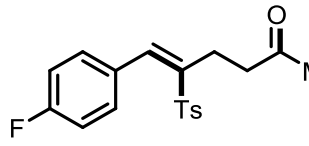
^{13}C NMR (151 MHz, $CDCl_3$)





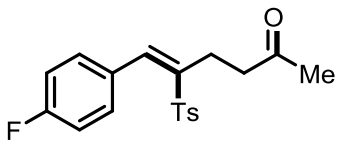
3-17

^{1}H NMR (600 MHz, $CDCl_3$)



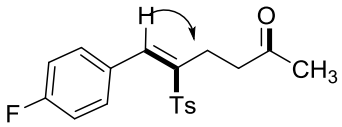
3-17

^{13}C NMR (151 MHz, $CDCl_3$)



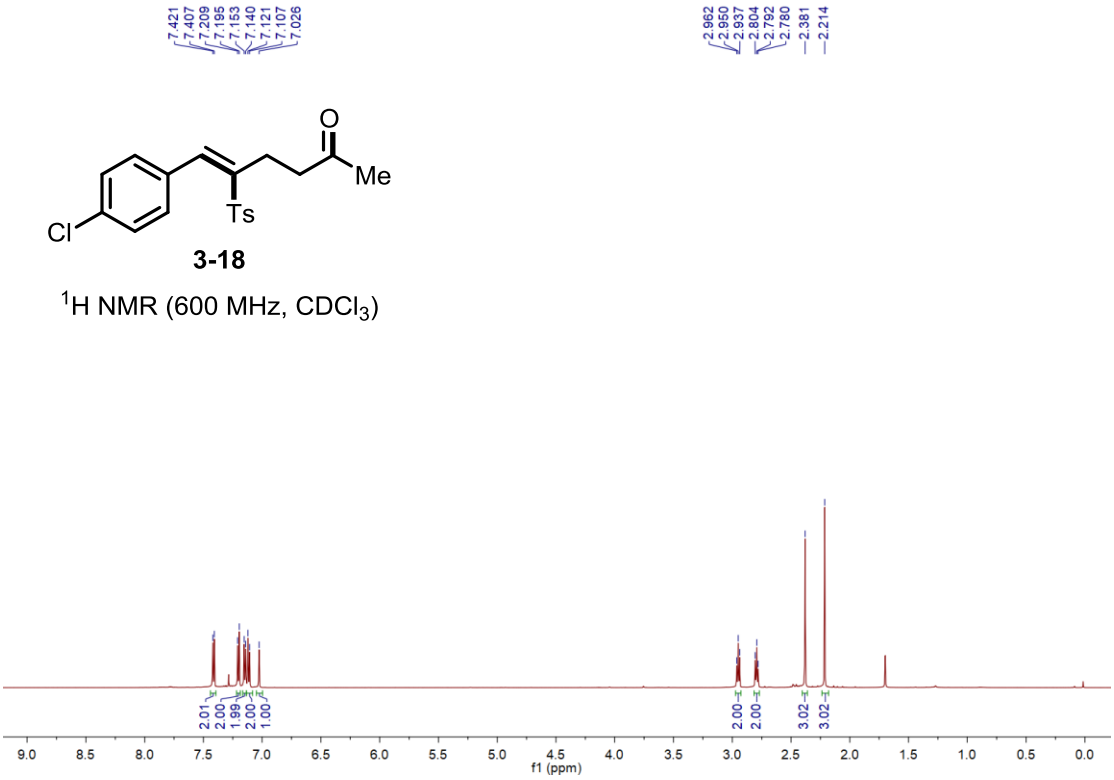
3-17

^{19}F NMR (565 MHz, $CDCl_3$)



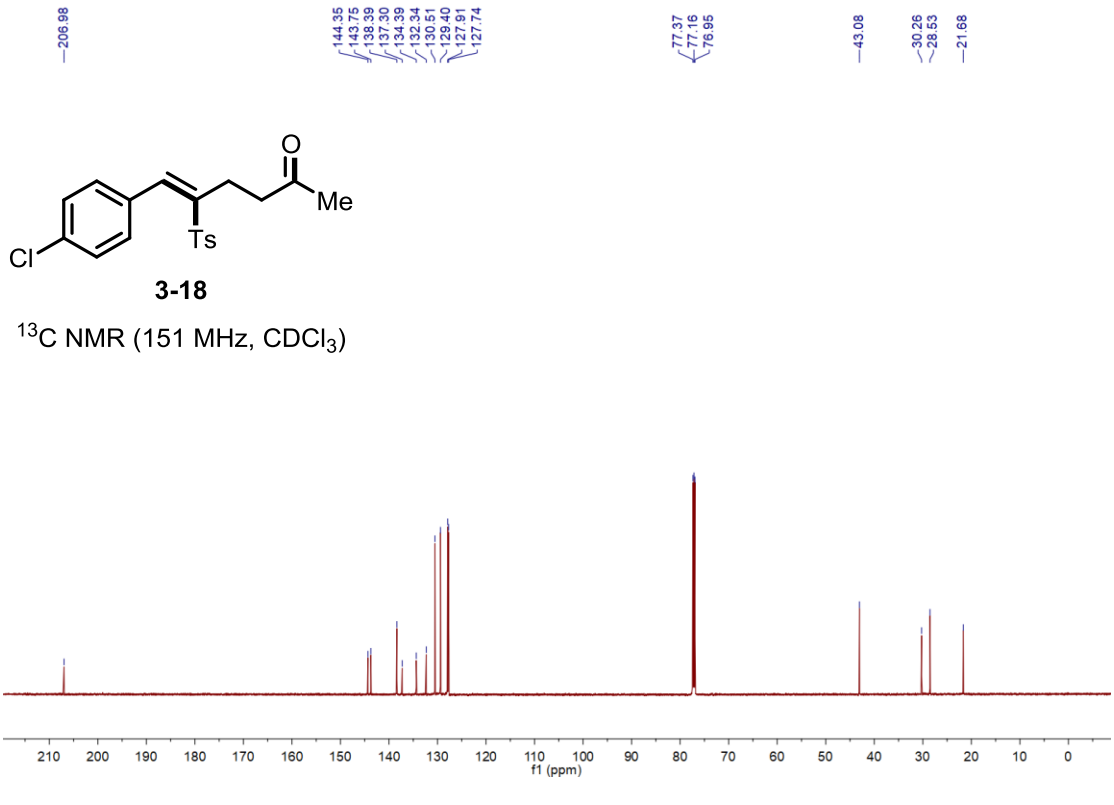
3-17

^{1}H NMR (600 MHz, $CDCl_3$,[1] H-^{1}H NOESY)



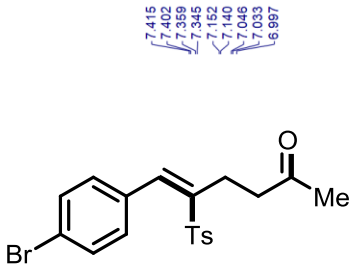
3-18

^{1}H NMR (600 MHz, $CDCl_3$)



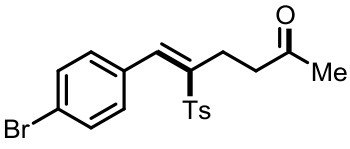
3-18

^{13}C NMR (151 MHz, $CDCl_3$)



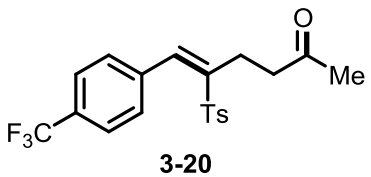
3-19

^{1}H NMR (600 MHz, $CDCl_3$)



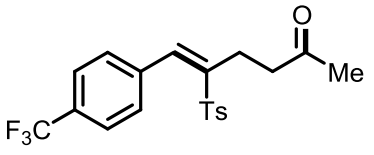
3-19

^{13}C NMR (151 MHz, $CDCl_3$)



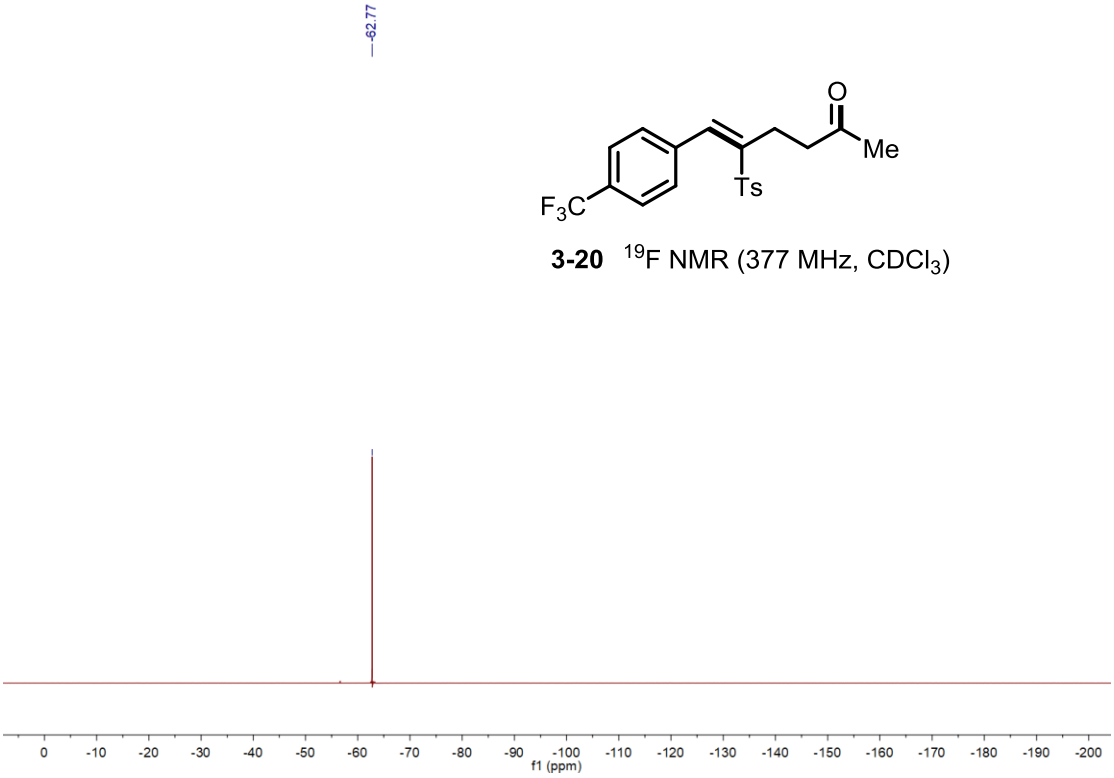
3-20

^{1}H NMR (600 MHz, $CDCl_3$)

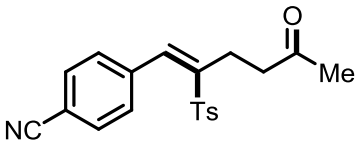


3-20

^{13}C NMR (101 MHz, $CDCl_3$)

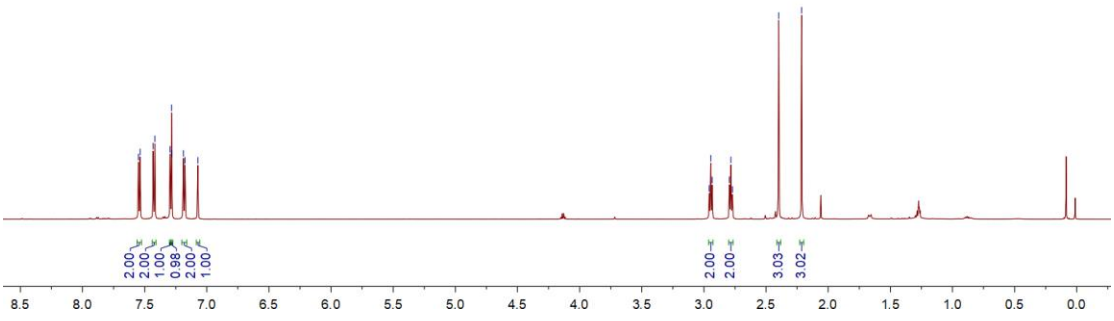


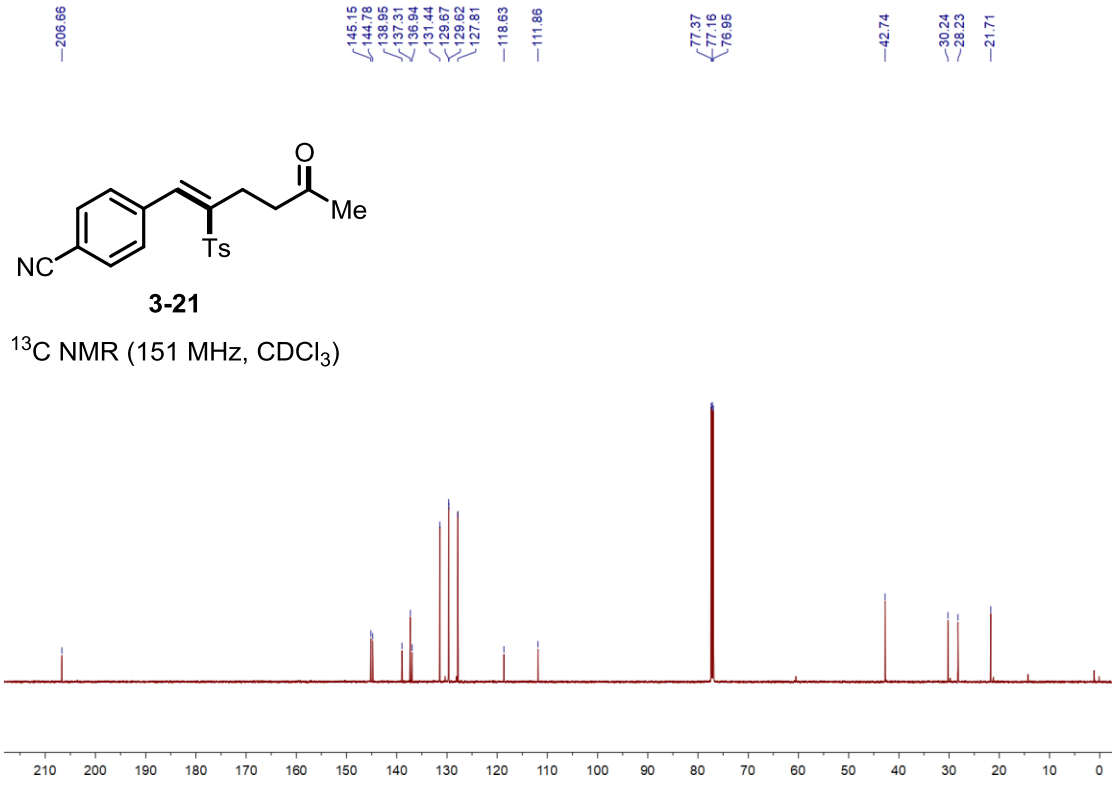
3-20 ^{19}F NMR (377 MHz, $CDCl_3$)



3-21

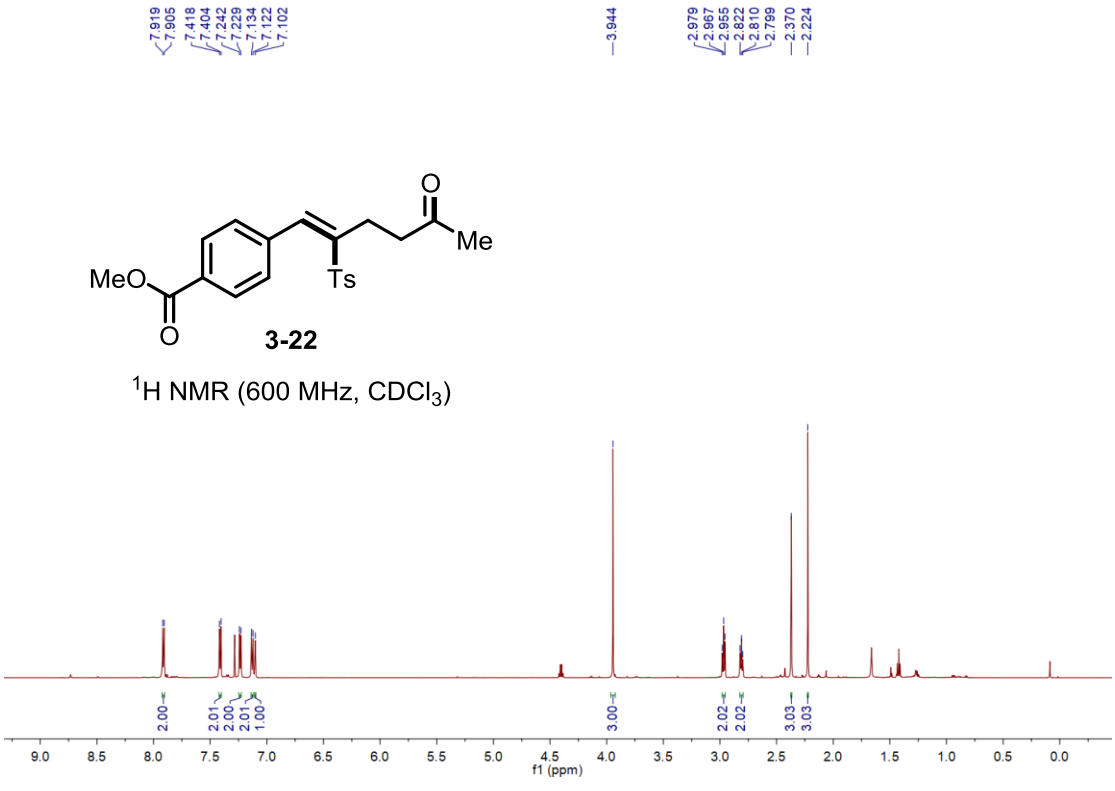
^{1}H NMR (600 MHz, $CDCl_3$)





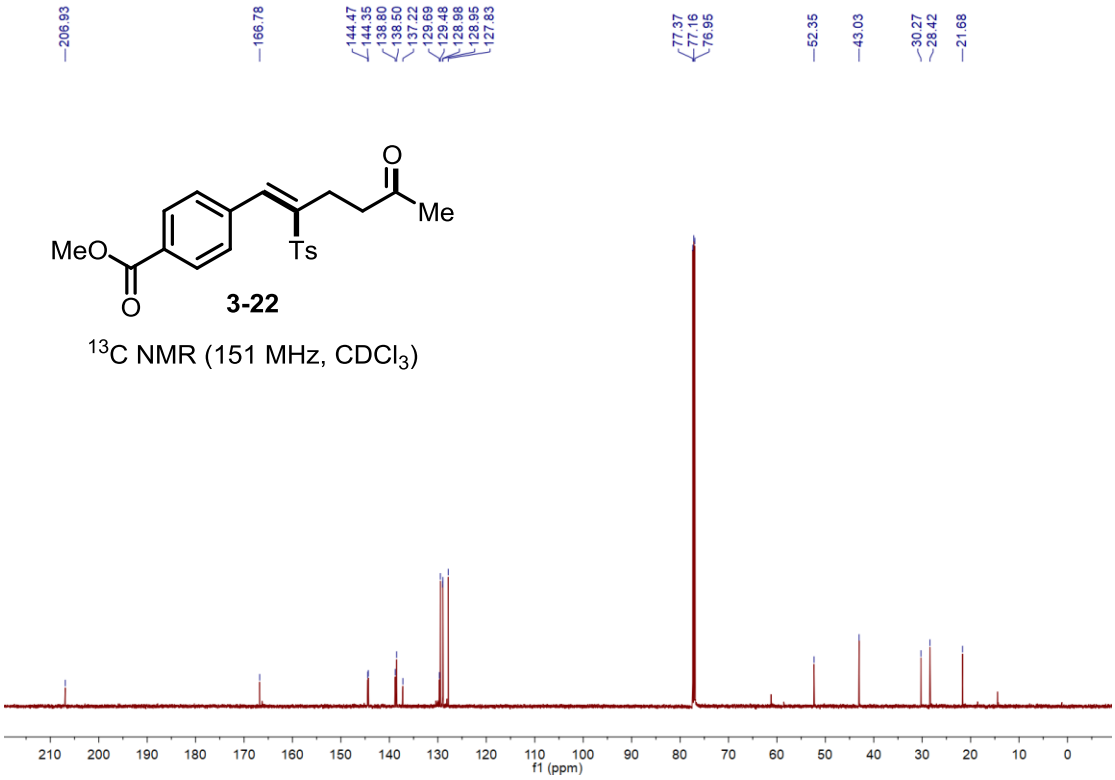
3-21

^{13}C NMR (151 MHz, $CDCl_3$)



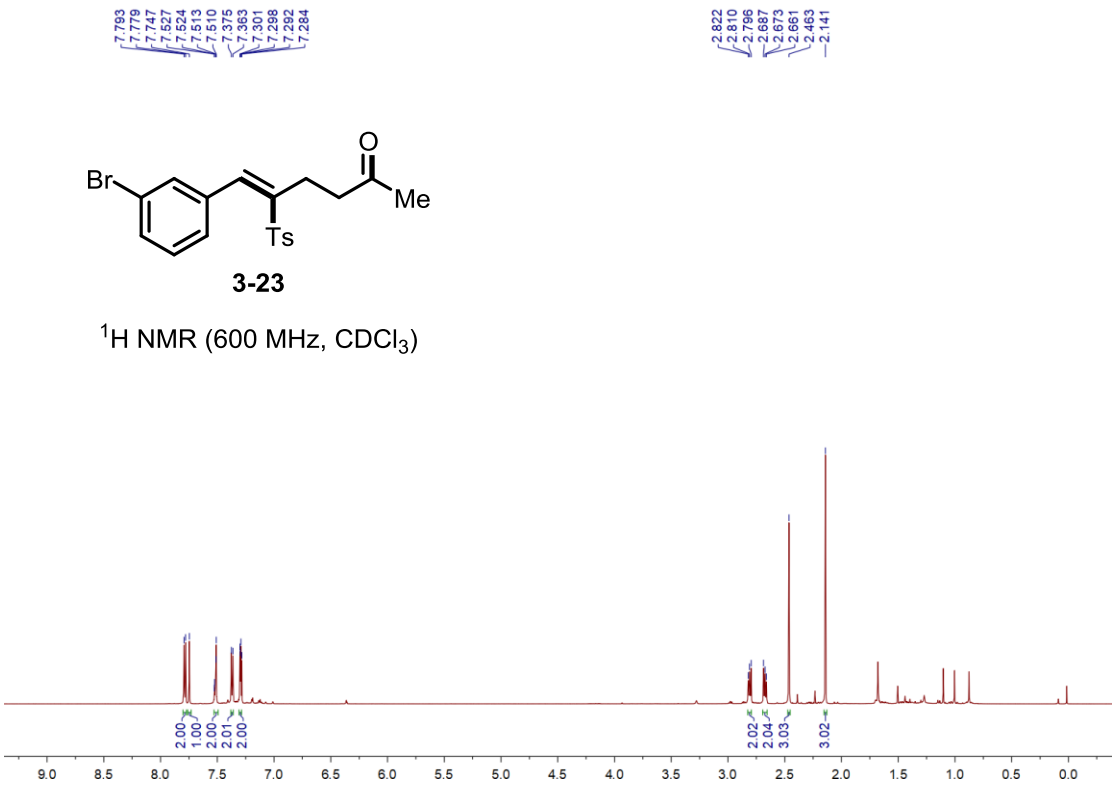
3-22

^{1}H NMR (600 MHz, $CDCl_3$)



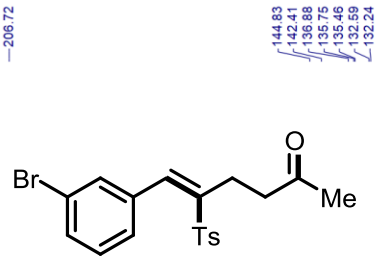
3-22

^{13}C NMR (151 MHz, $CDCl_3$)



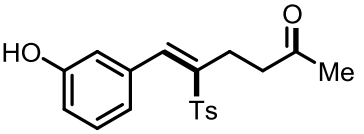
3-23

^{1}H NMR (600 MHz, $CDCl_3$)



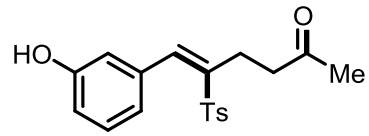
3-23

^{13}C NMR (151 MHz, $CDCl_3$)



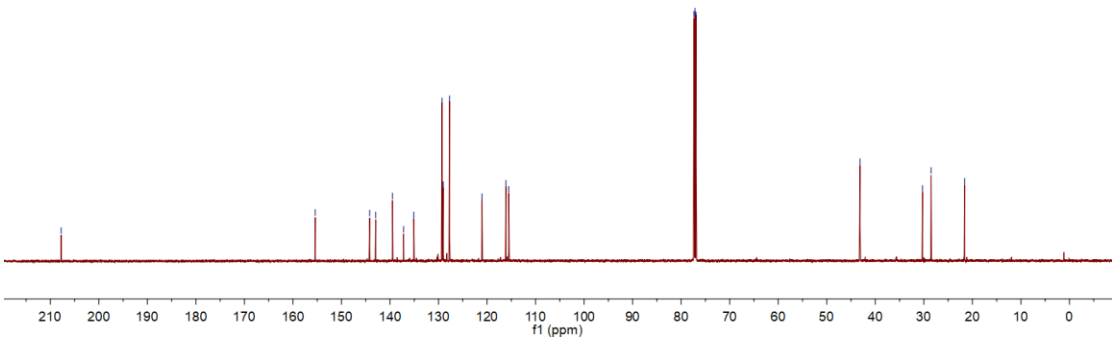
3-24

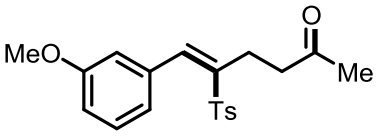
^{1}H NMR (400 MHz, $CDCl_3$)



3-24

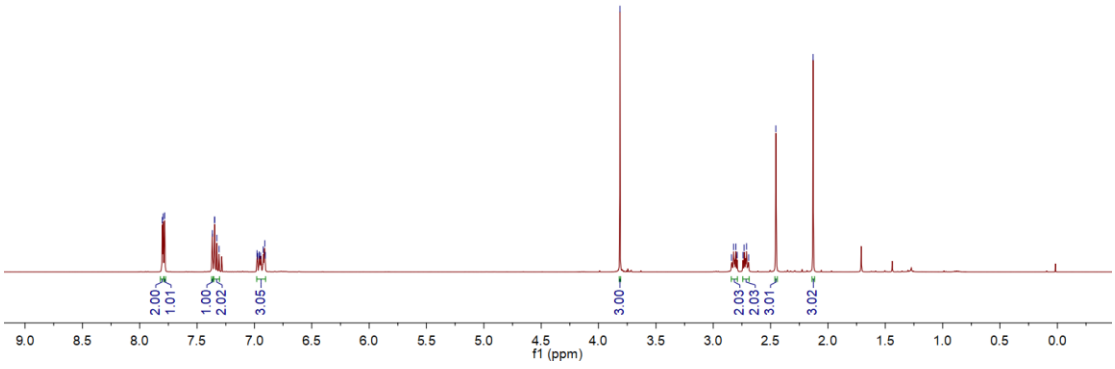
^{13}C NMR (151 MHz, $CDCl_3$)

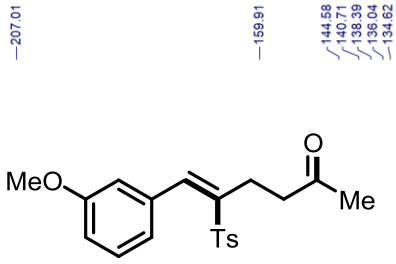




3-25

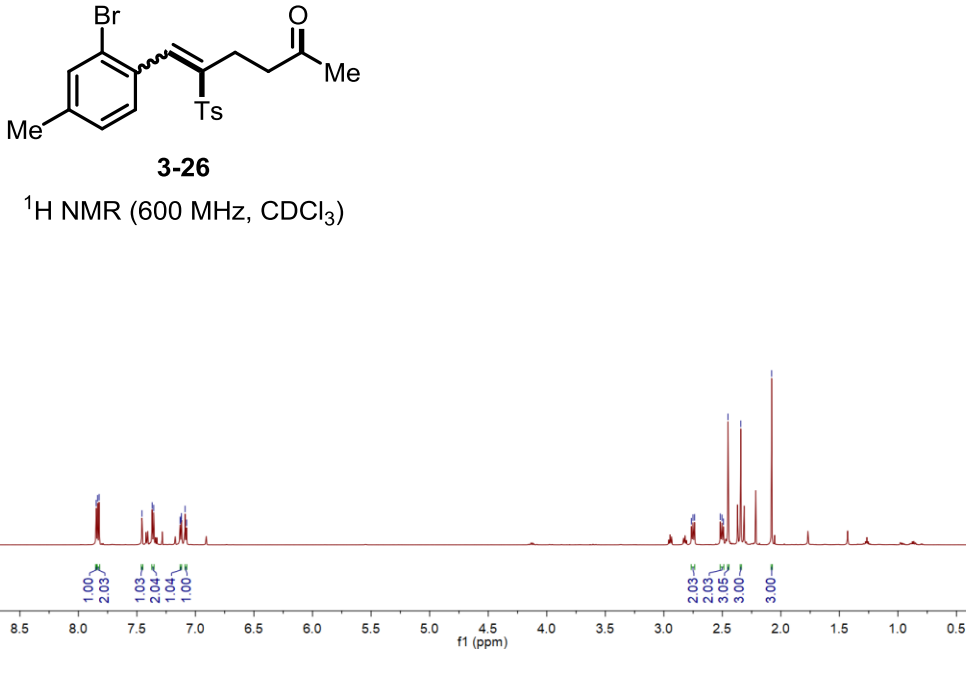
^{1}H NMR (400 MHz, $CDCl_3$)





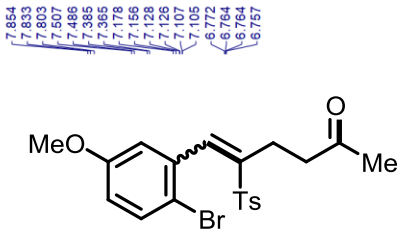
3-25

^{13}C NMR (151 MHz, $CDCl_3$)



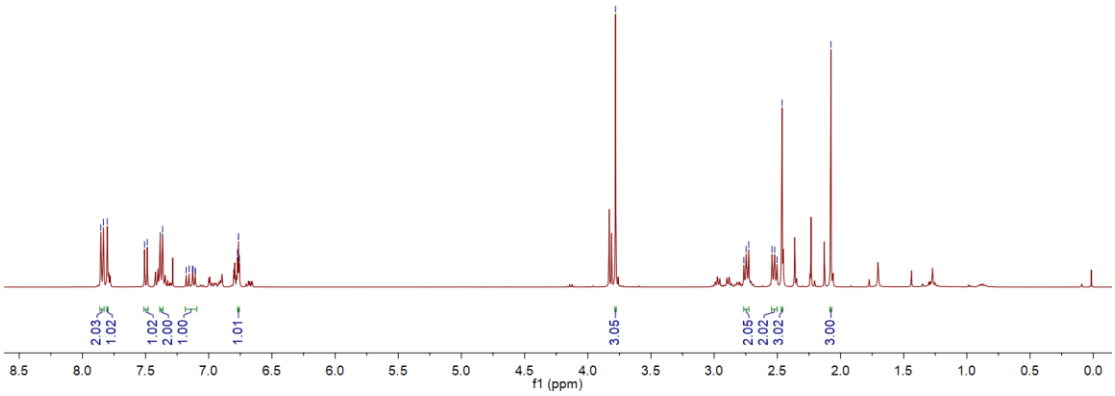
3-26

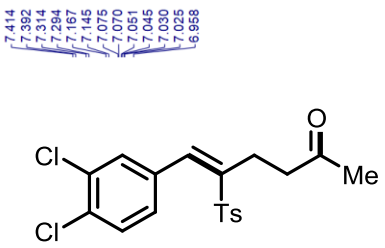
^{1}H NMR (600 MHz, $CDCl_3$)



3-27

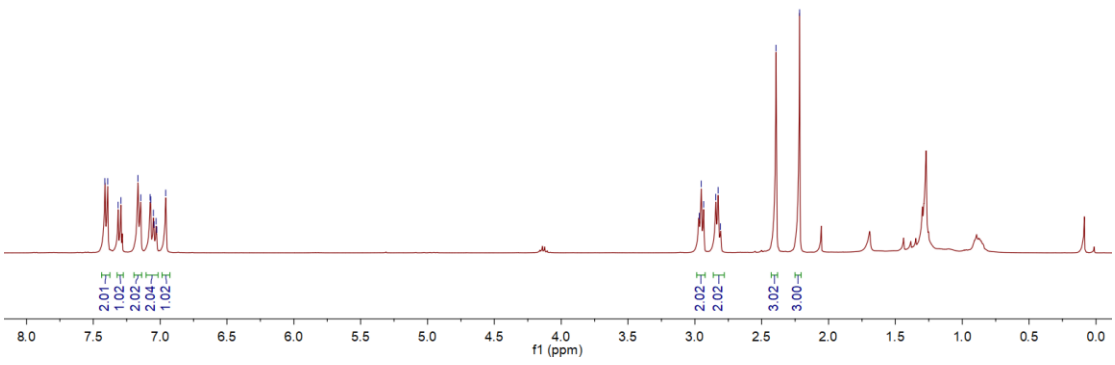
^{1}H NMR (400 MHz, $CDCl_3$)

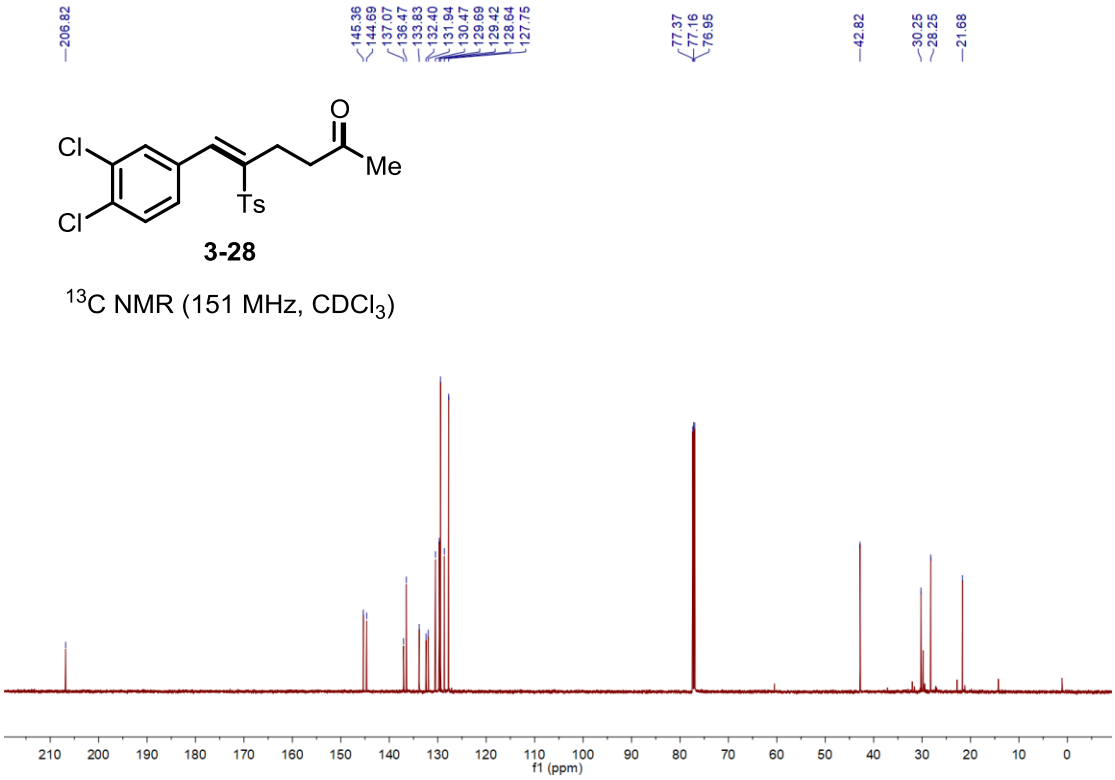




3-28

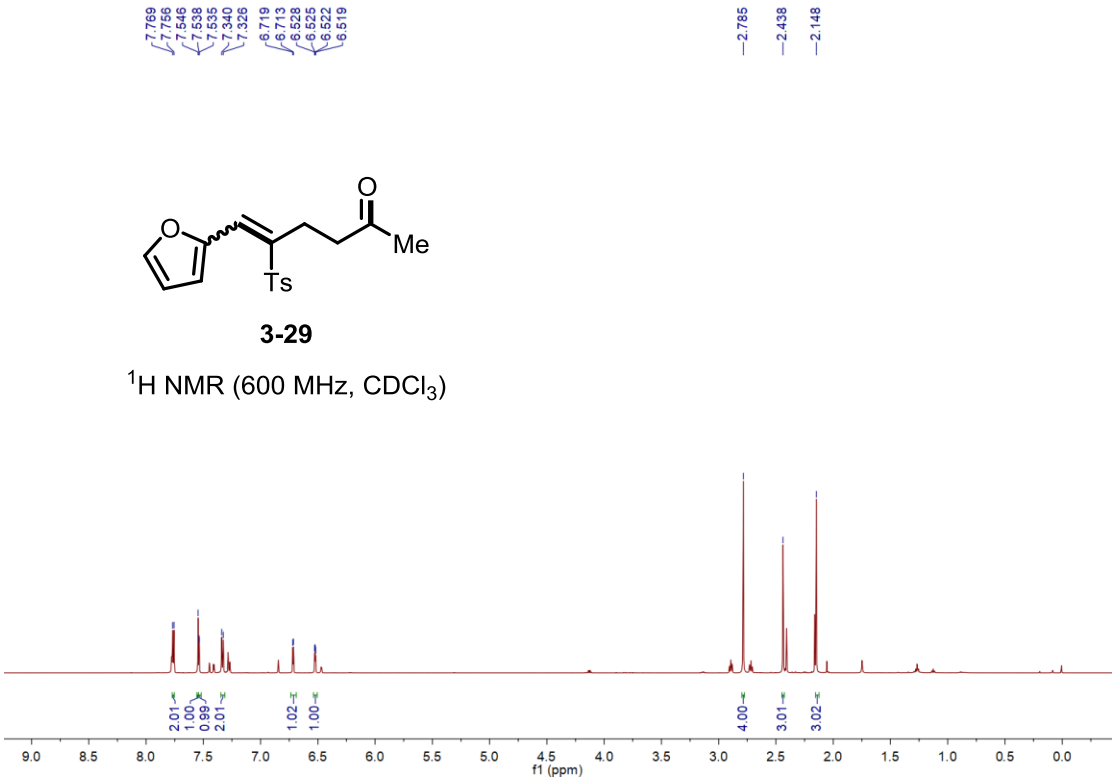
^{1}H NMR (400 MHz, $CDCl_3$)





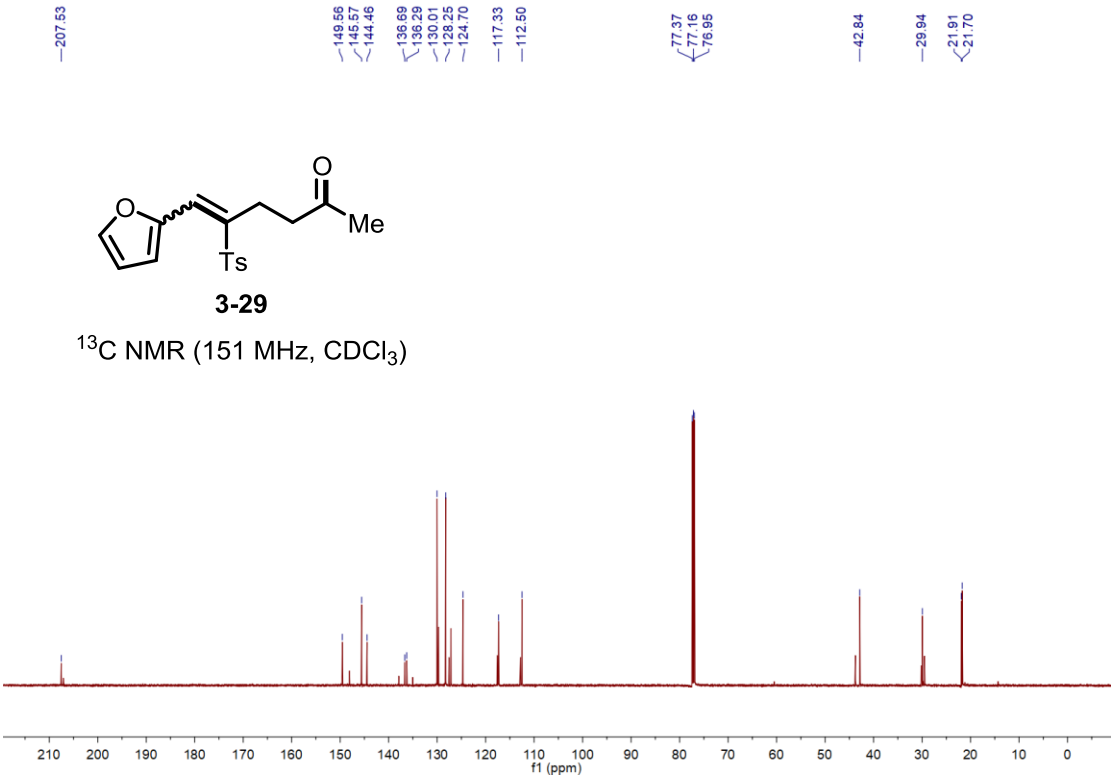
3-28

^{13}C NMR (151 MHz, $CDCl_3$)



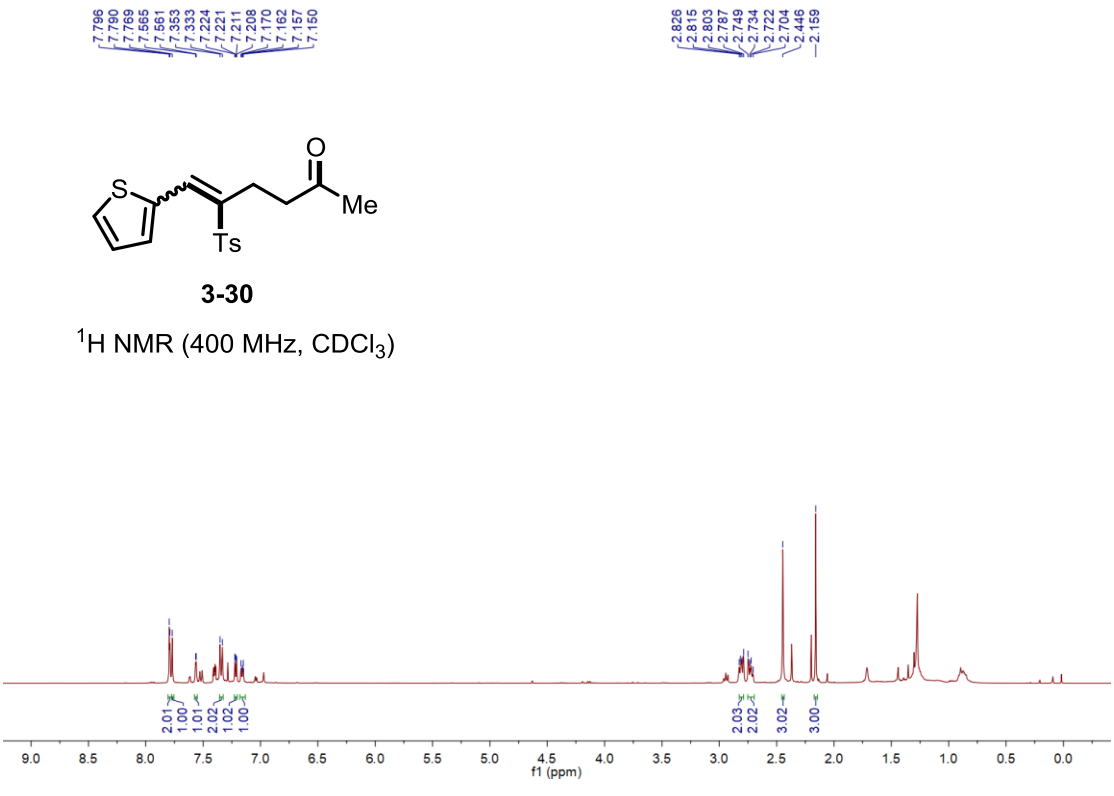
3-29

^{1}H NMR (600 MHz, $CDCl_3$)



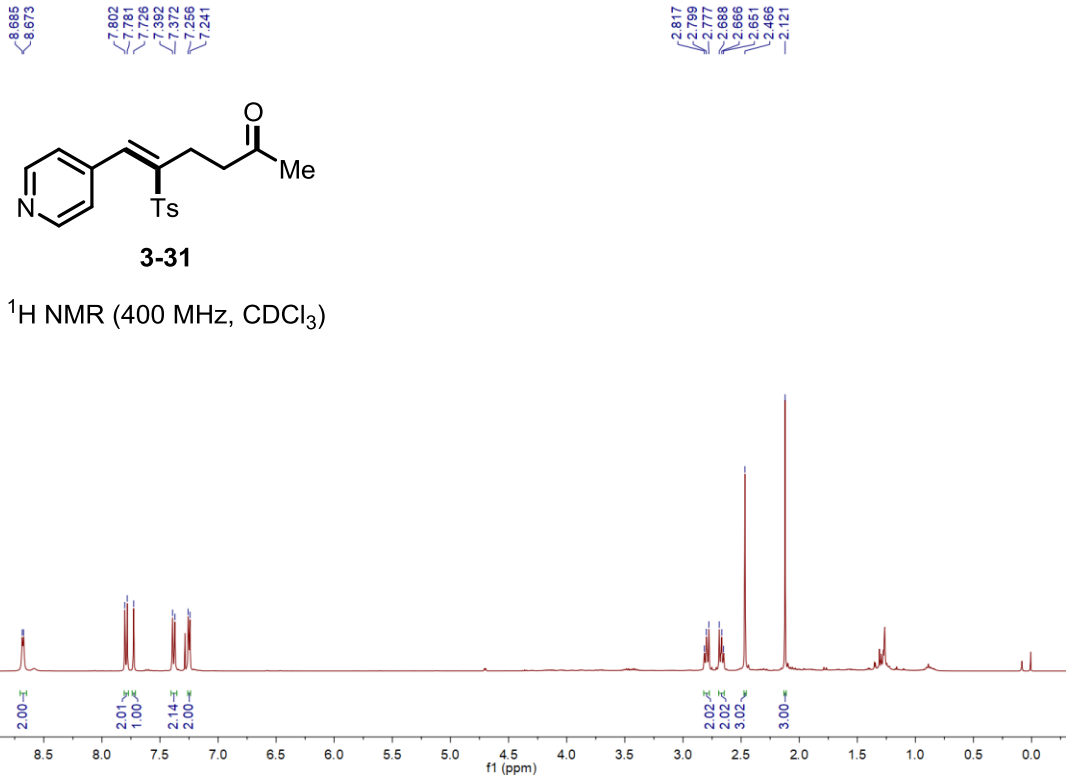
3-29

^{13}C NMR (151 MHz, $CDCl_3$)



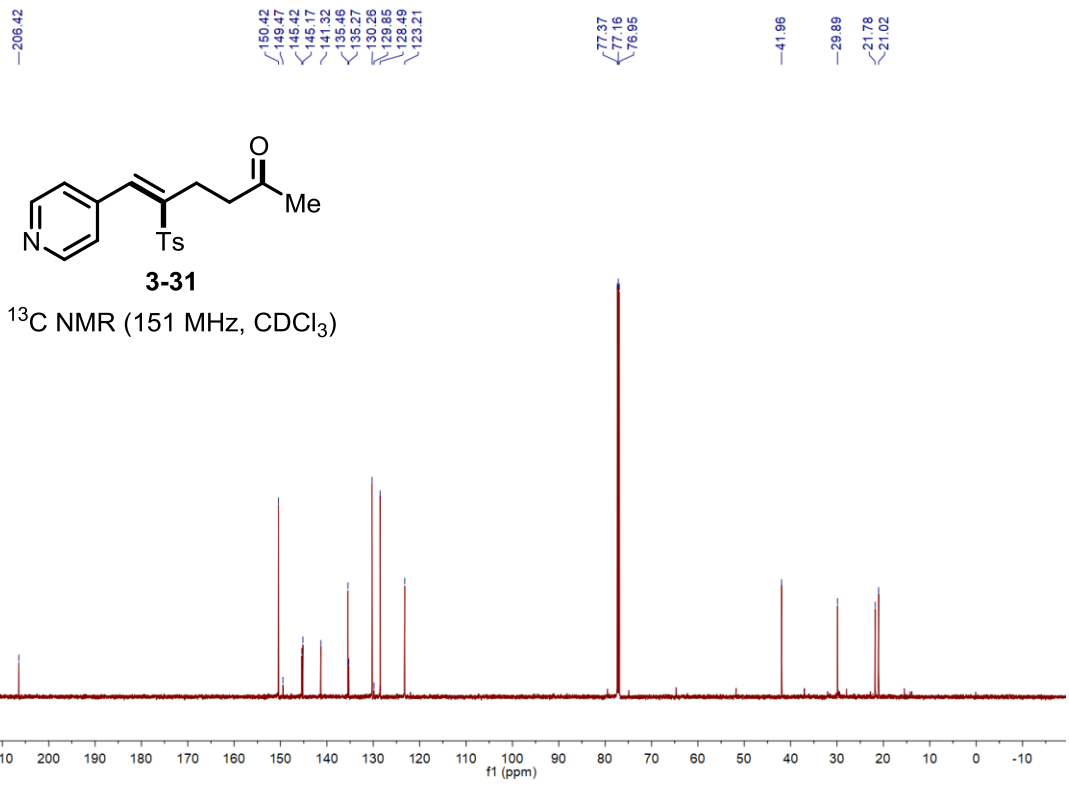
3-30

^{1}H NMR (400 MHz, $CDCl_3$)



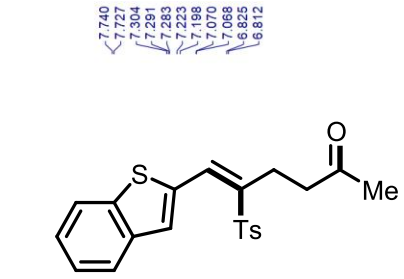
3-31

^{1}H NMR (400 MHz, $CDCl_3$)



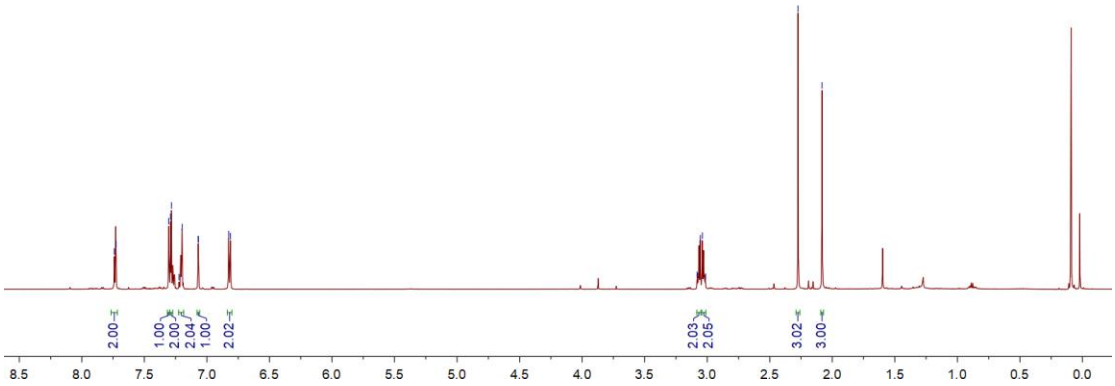
3-31

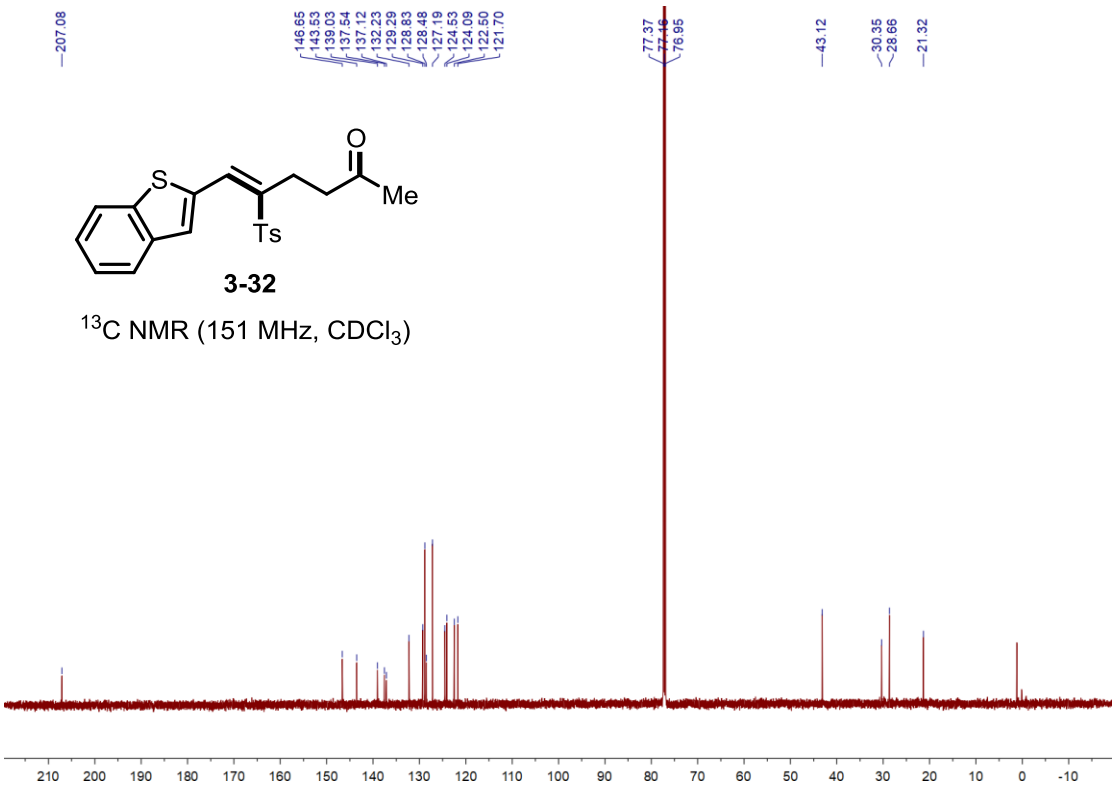
^{13}C NMR (151 MHz, $CDCl_3$)



3-32

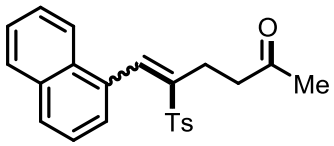
^{1}H NMR (600 MHz, $CDCl_3$)





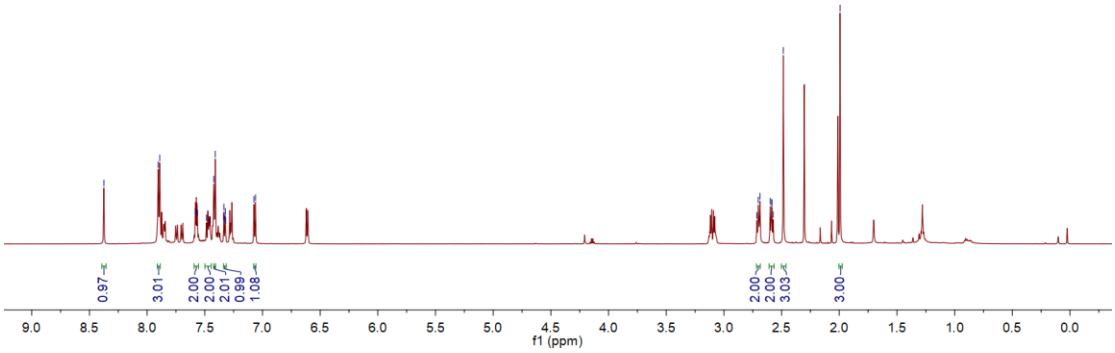
3-32

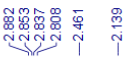
^{13}C NMR (151 MHz, $CDCl_3$)

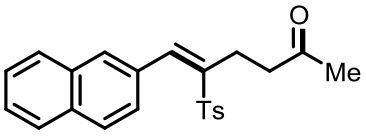


3-33

^{1}H NMR (600 MHz, $CDCl_3$)

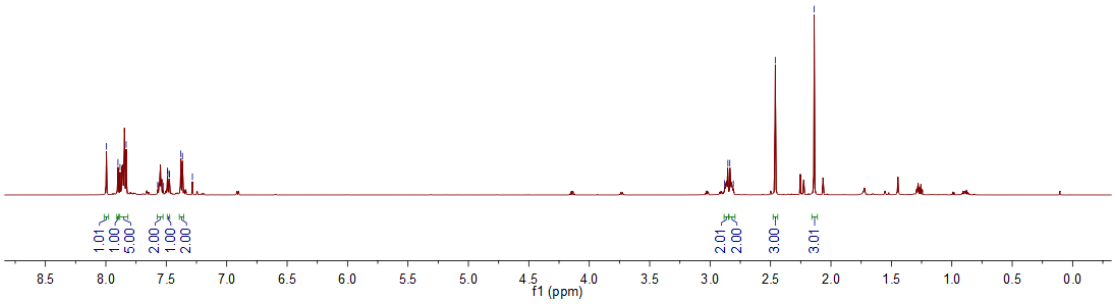


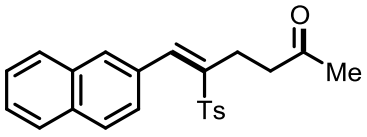




(*Z*)-3-34

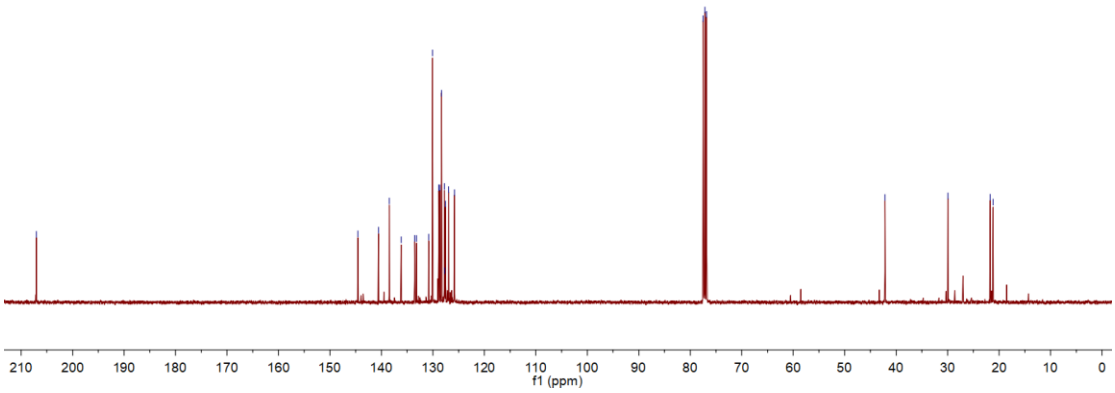
^{1}H NMR (600 MHz, $CDCl_3$)

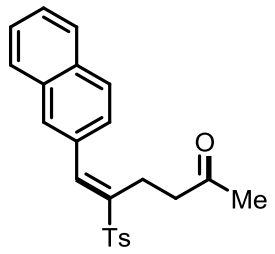




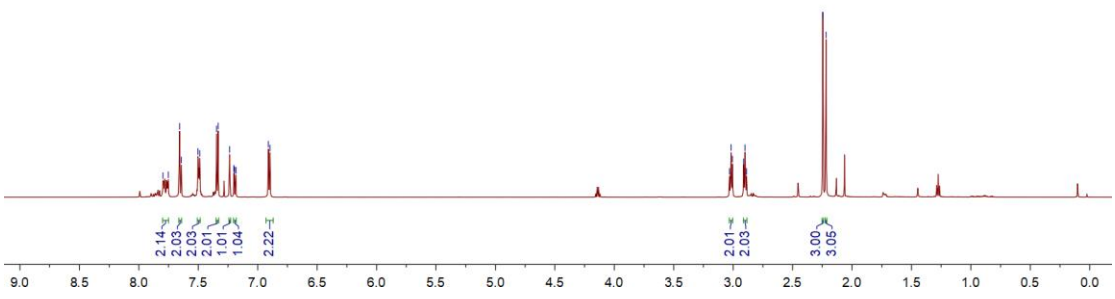
(*Z*)-3-34

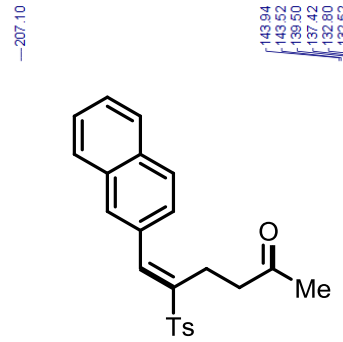
^{13}C NMR (101 MHz, $CDCl_3$)



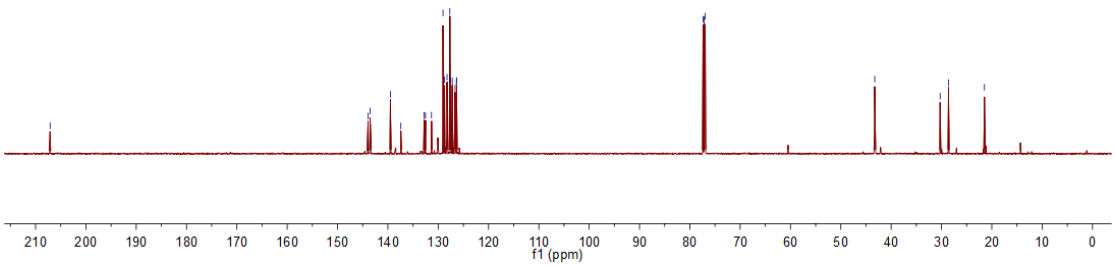


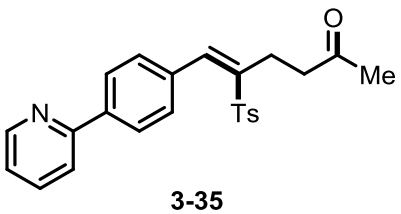
(*E*)-3-34 ^{1}H NMR (600 MHz, $CDCl_3$)





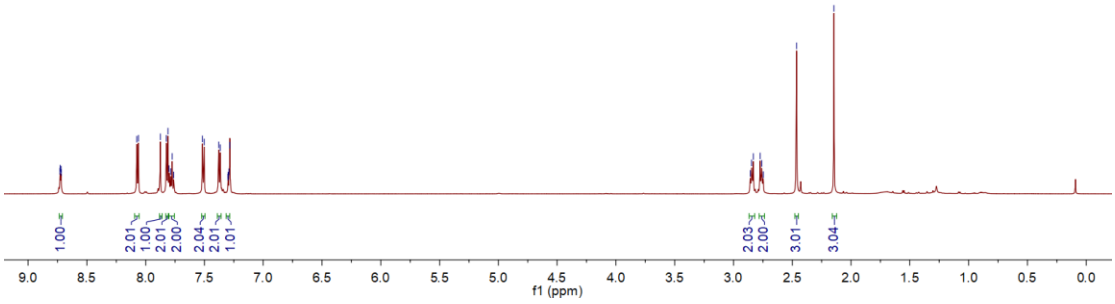
(*E*)-3-34 ^{13}C NMR (151 MHz, $CDCl_3$)

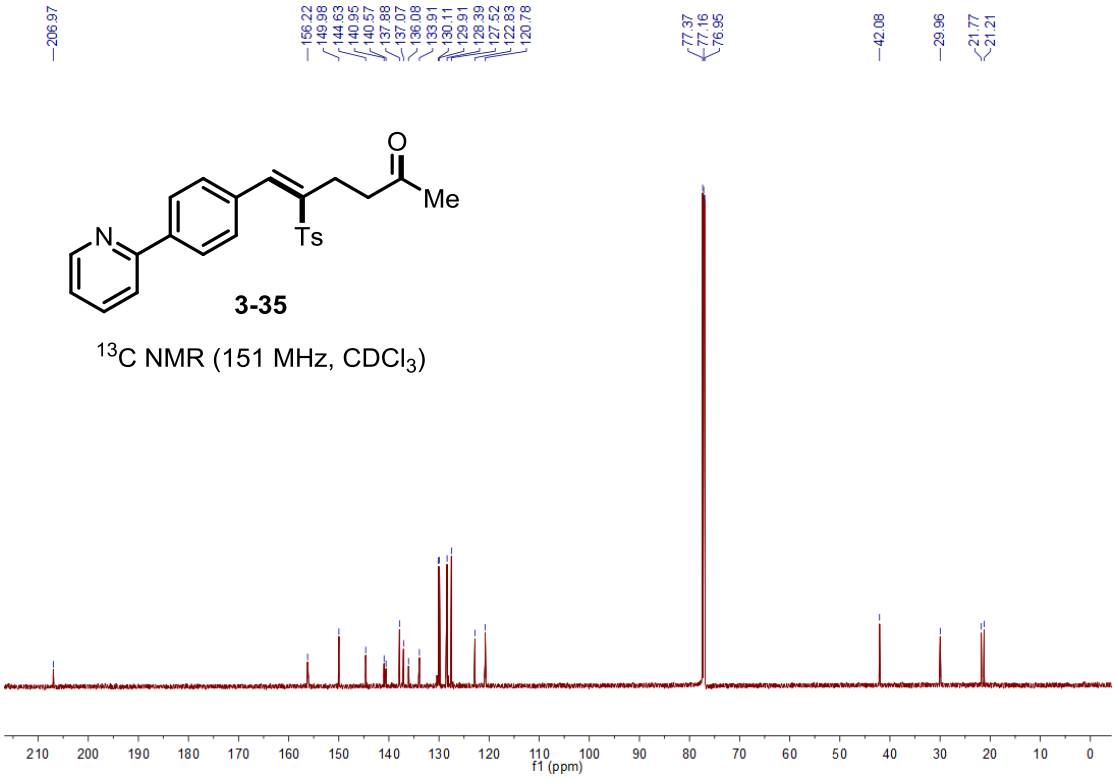




3-35

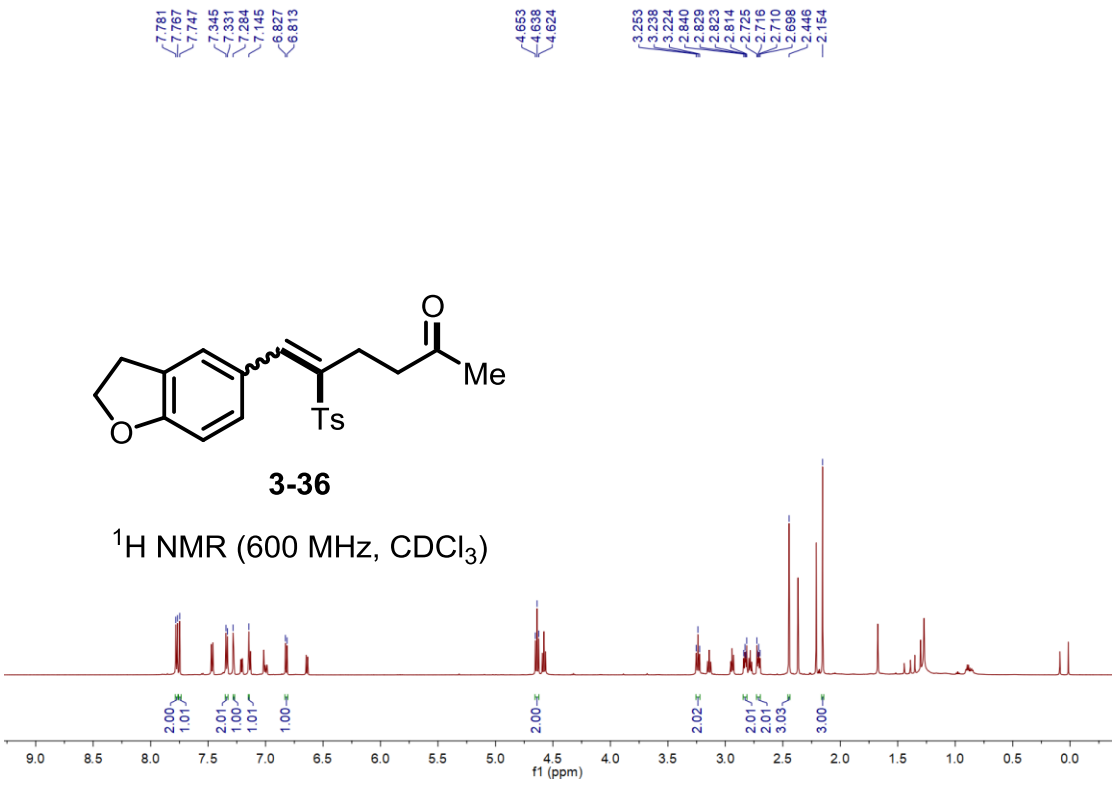
^{1}H NMR (600 MHz, $CDCl_3$)





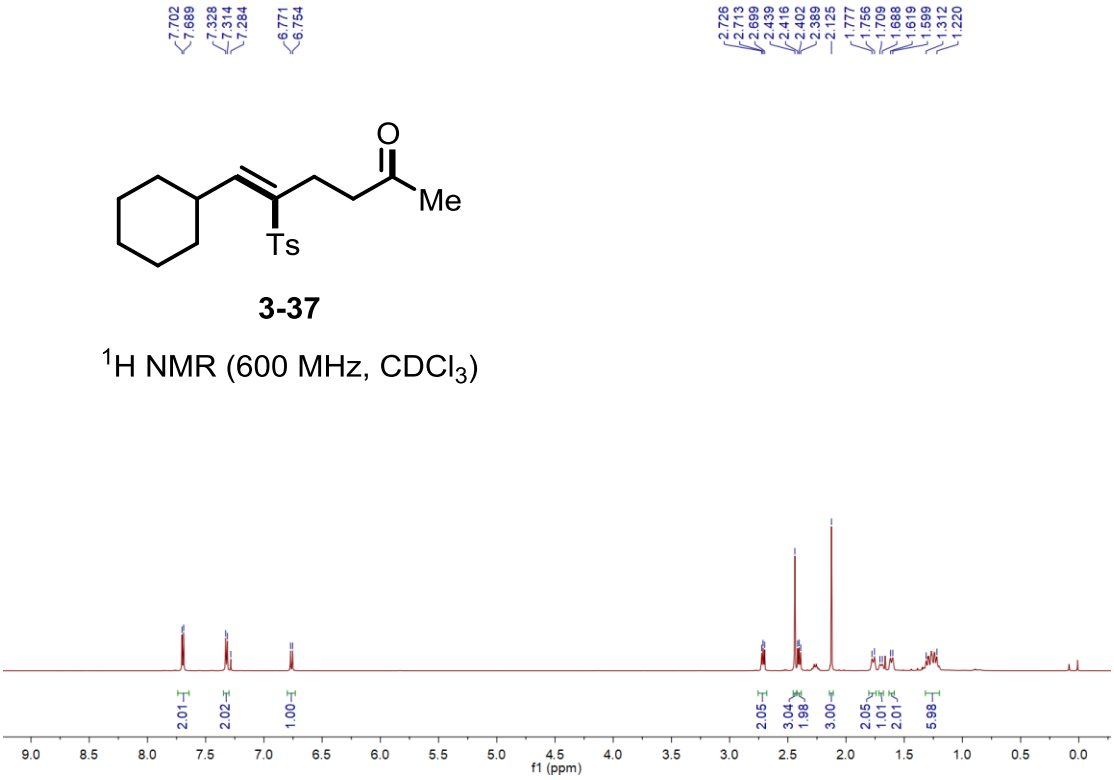
3-35

^{13}C NMR (151 MHz, $CDCl_3$)



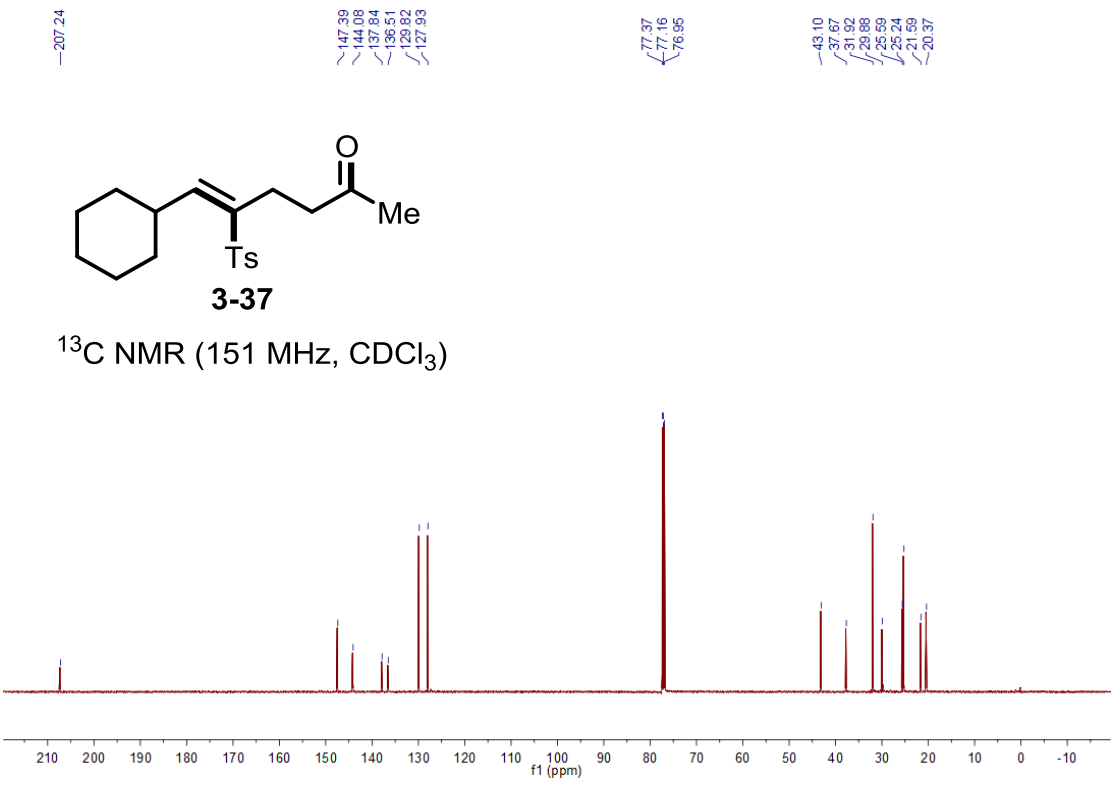
3-36

^{1}H NMR (600 MHz, $CDCl_3$)



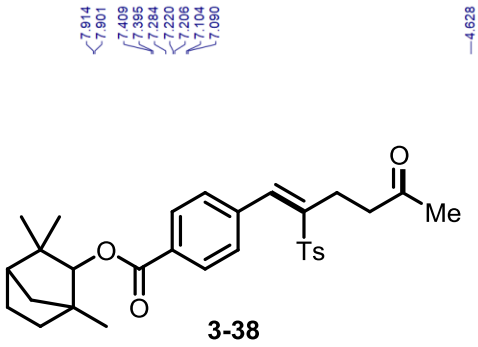
3-37

^{1}H NMR (600 MHz, $CDCl_3$)



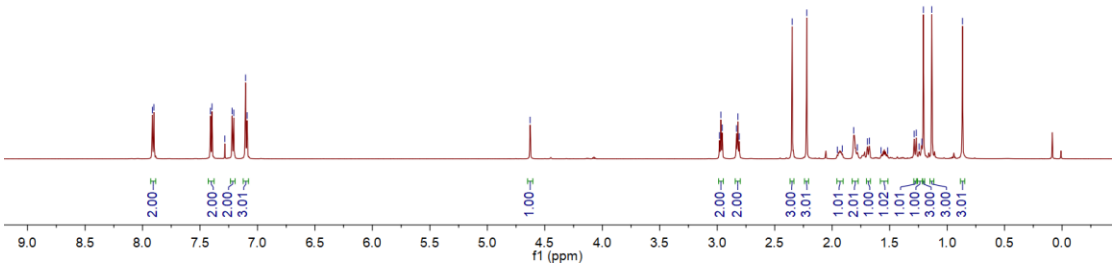
3-37

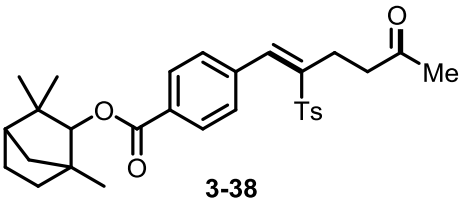
^{13}C NMR (151 MHz, $CDCl_3$)



3-38

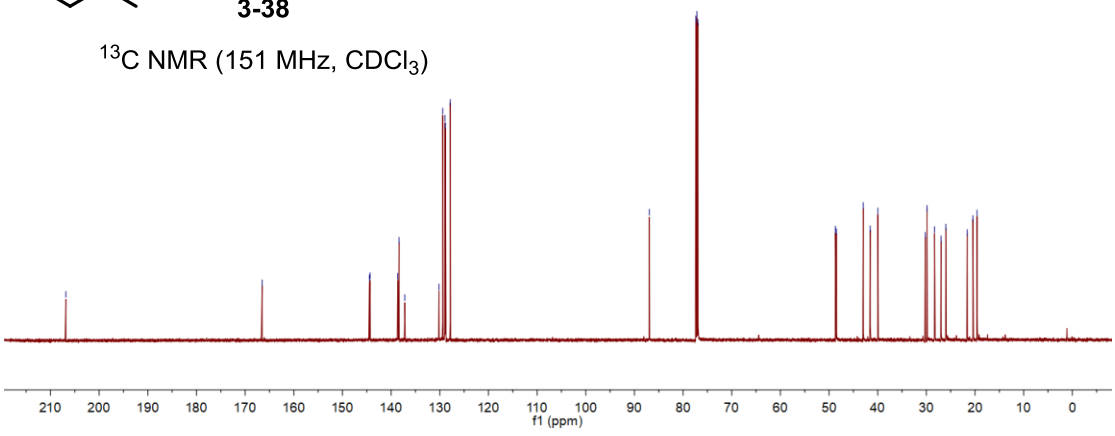
^{1}H NMR (600 MHz, $CDCl_3$)

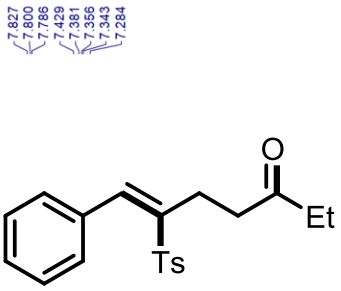




3-38

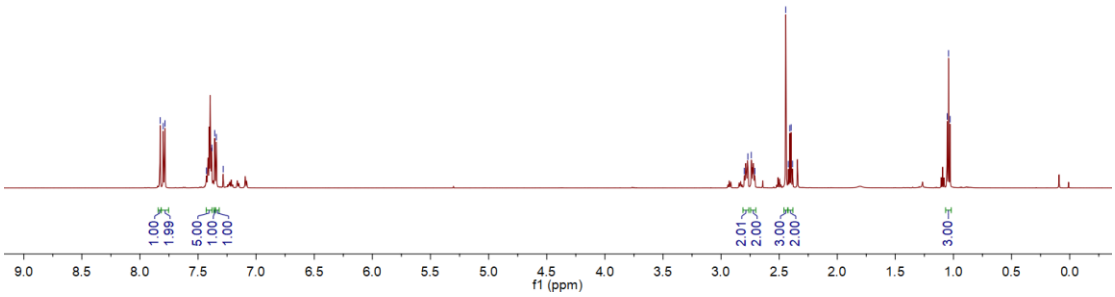
^{13}C NMR (151 MHz, $CDCl_3$)

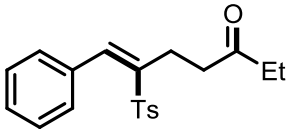




3-39

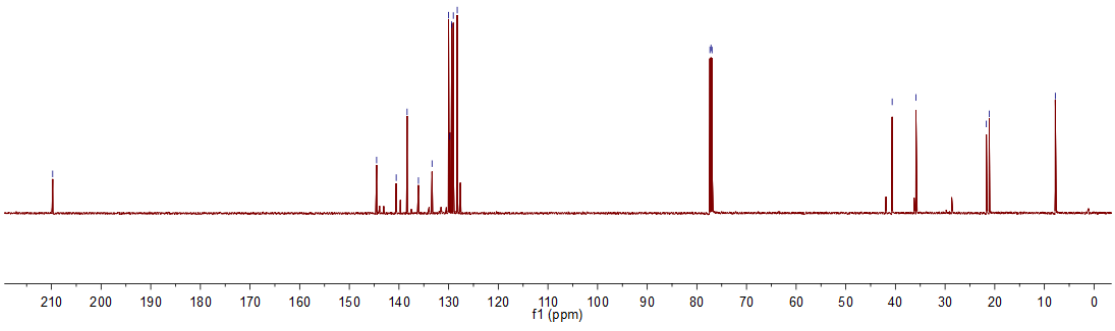
^{1}H NMR (400 MHz, $CDCl_3$)

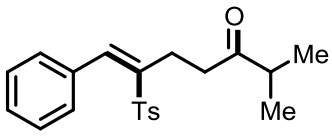




3-39

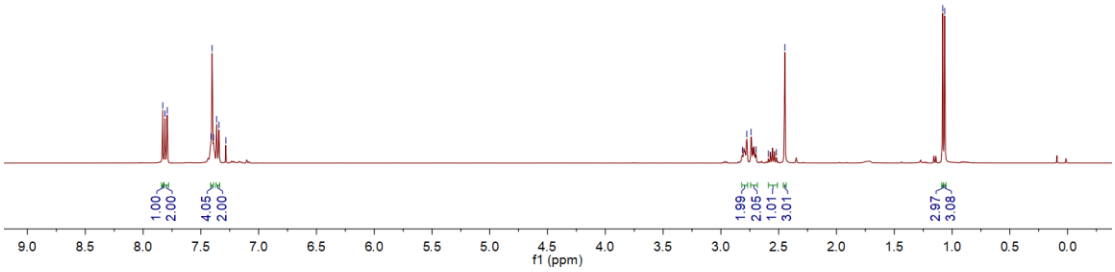
^{13}C NMR (151 MHz, $CDCl_3$)

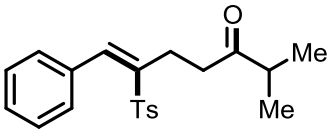




3-40

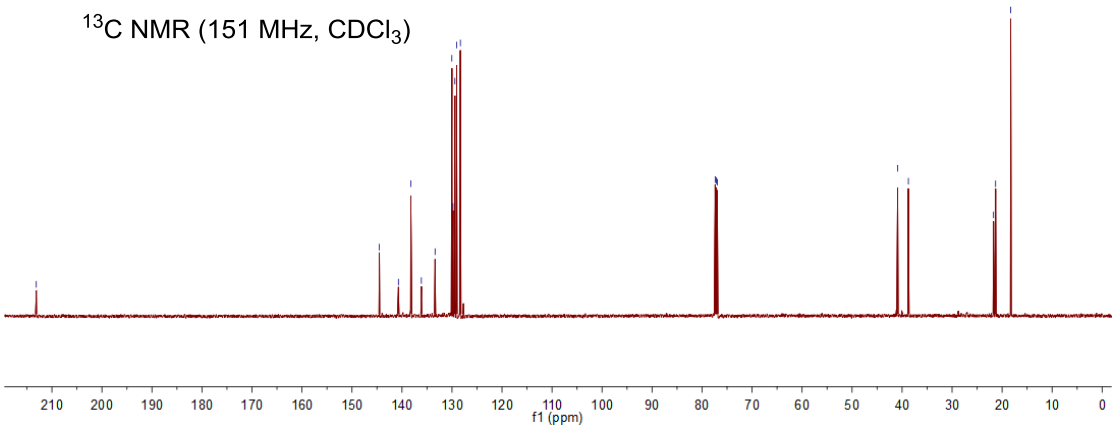
^{1}H NMR (400 MHz, $CDCl_3$)

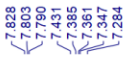


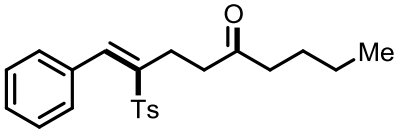


3-40

^{13}C NMR (151 MHz, $CDCl_3$)

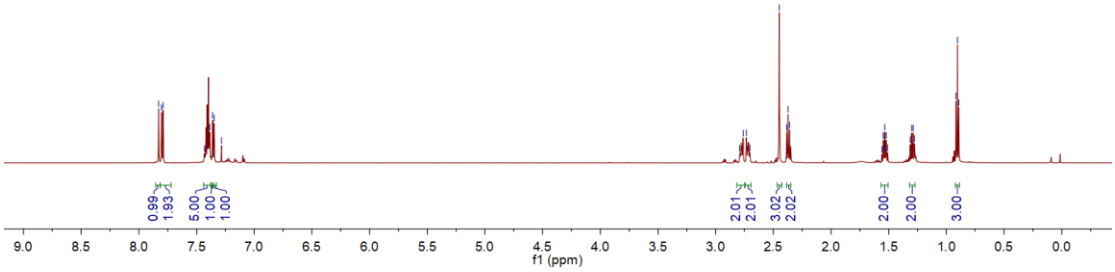


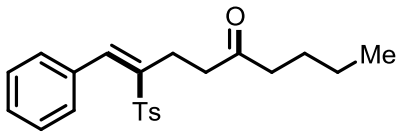




3-41

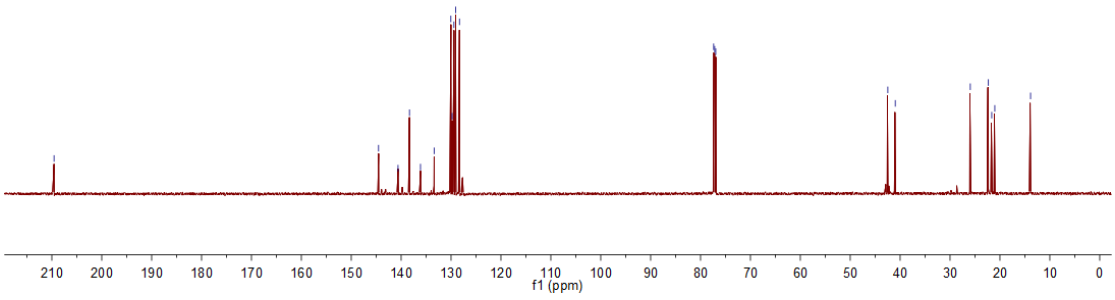
^{1}H NMR (600 MHz, $CDCl_3$)

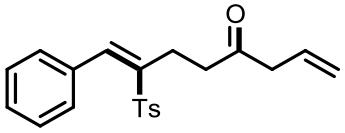




3-41

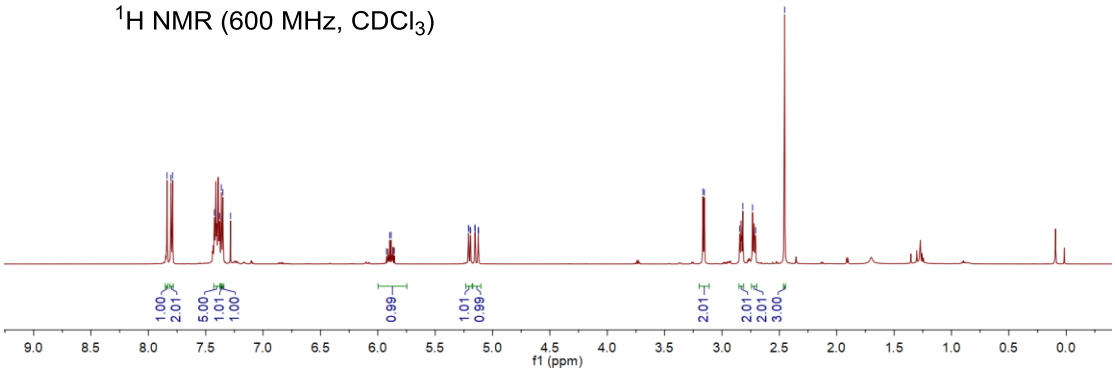
^{13}C NMR (151 MHz, $CDCl_3$)

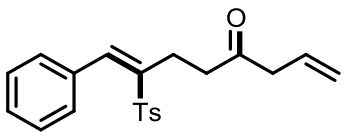




3-42

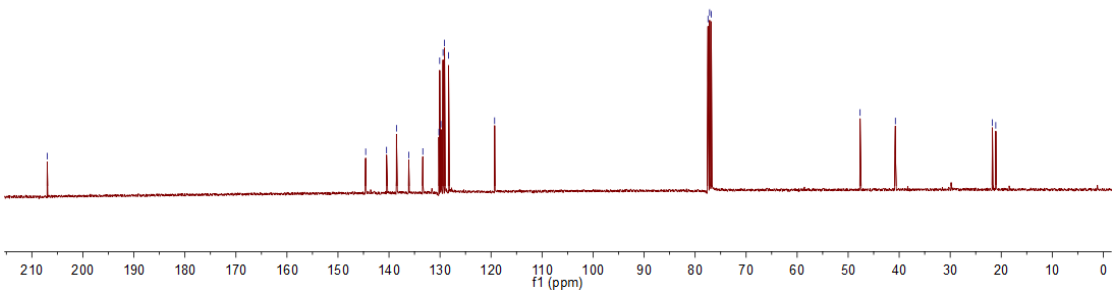
^{1}H NMR (600 MHz, $CDCl_3$)

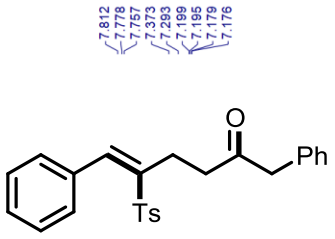




3-42

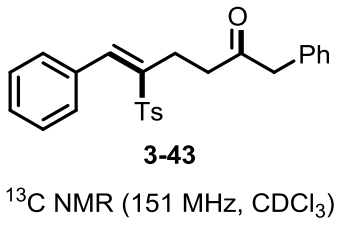
^{13}C NMR (101 MHz, $CDCl_3$)





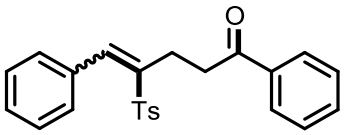
3-43

^{1}H NMR (600 MHz, $CDCl_3$)



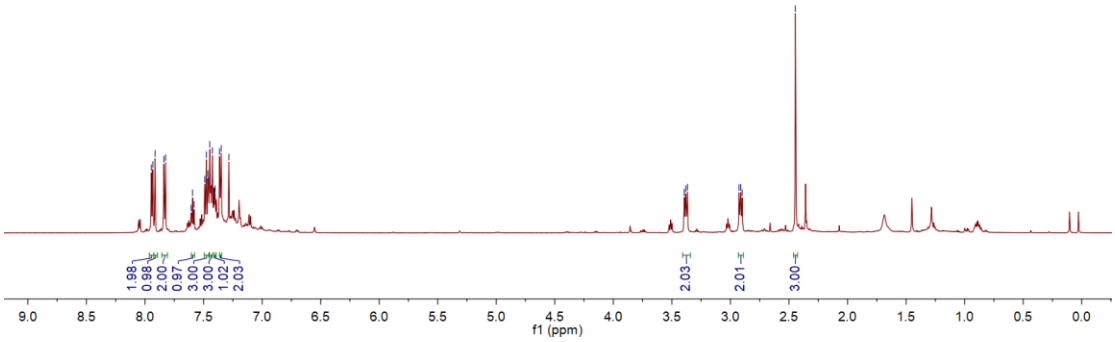
3-43

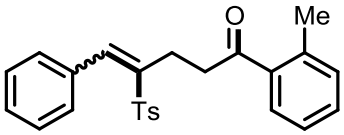
^{13}C NMR (151 MHz, $CDCl_3$)



3-44

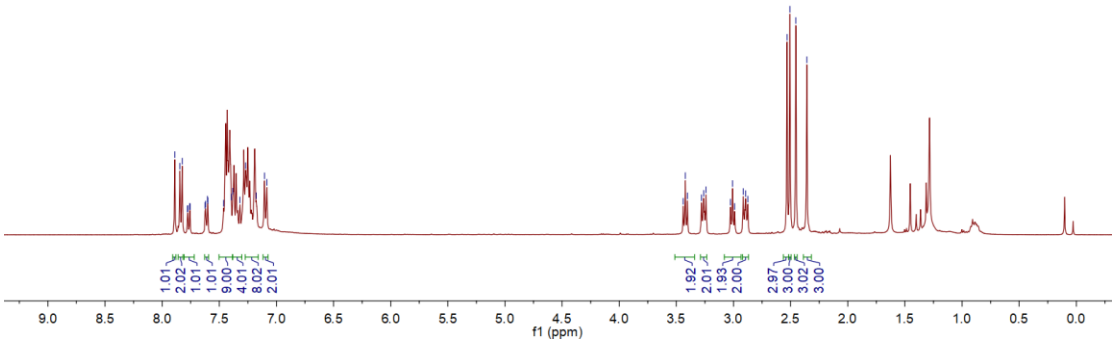
^{1}H NMR (600 MHz, $CDCl_3$)

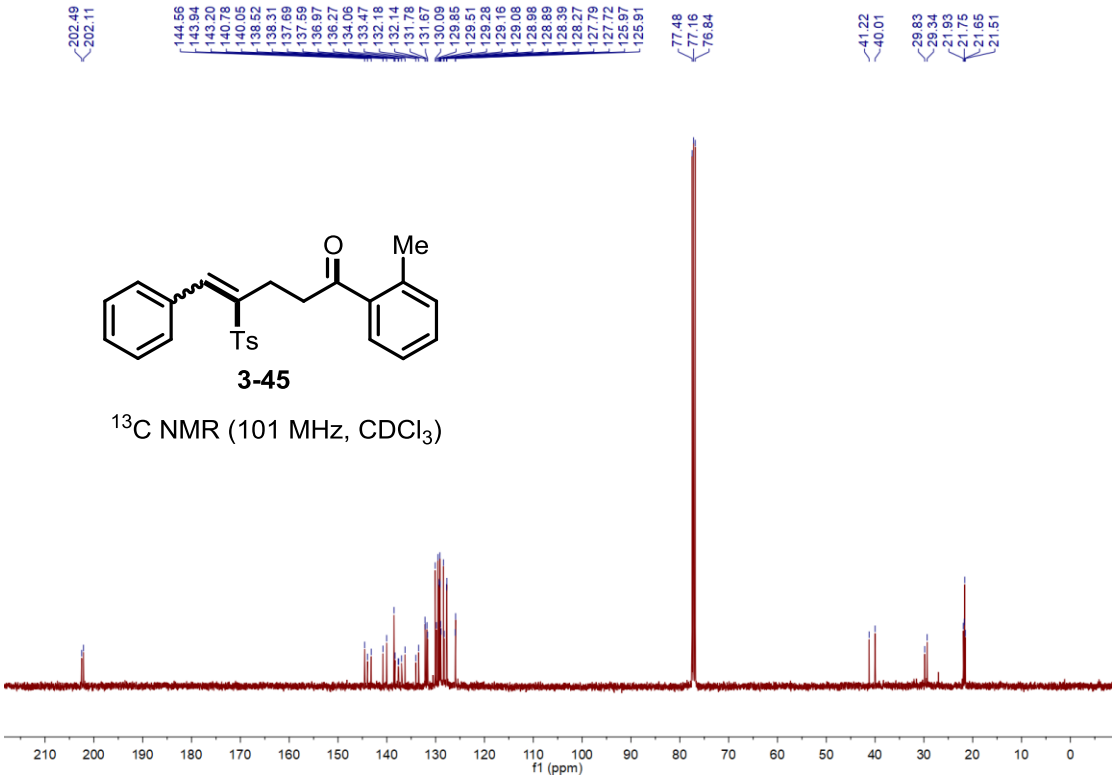




3-45

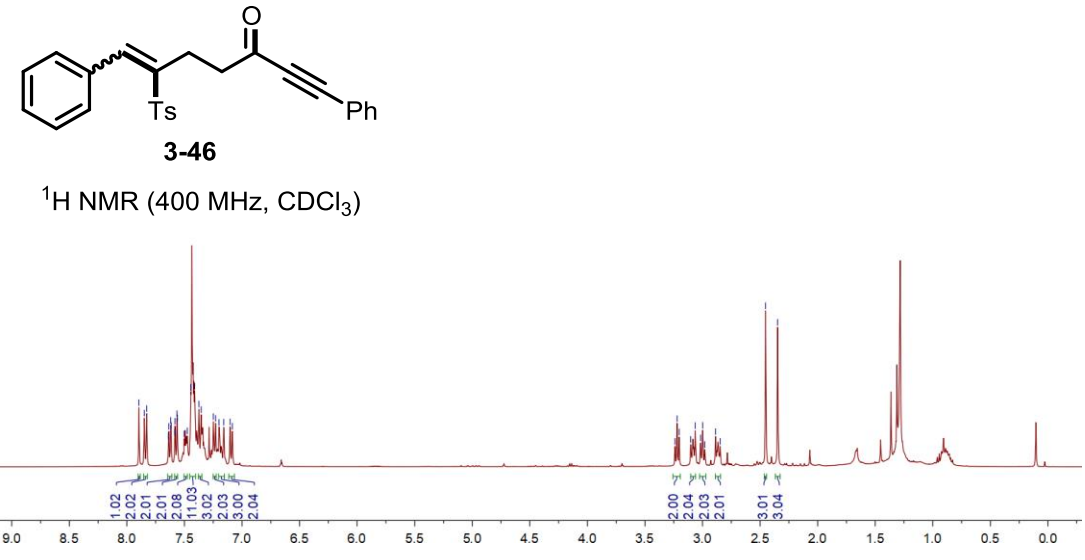
^{1}H NMR (400 MHz, $CDCl_3$)





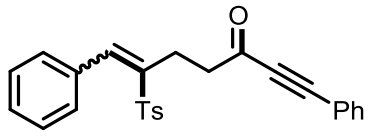
3-45

^{13}C NMR (101 MHz, $CDCl_3$)



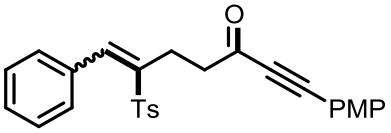
3-46

^{1}H NMR (400 MHz, $CDCl_3$)



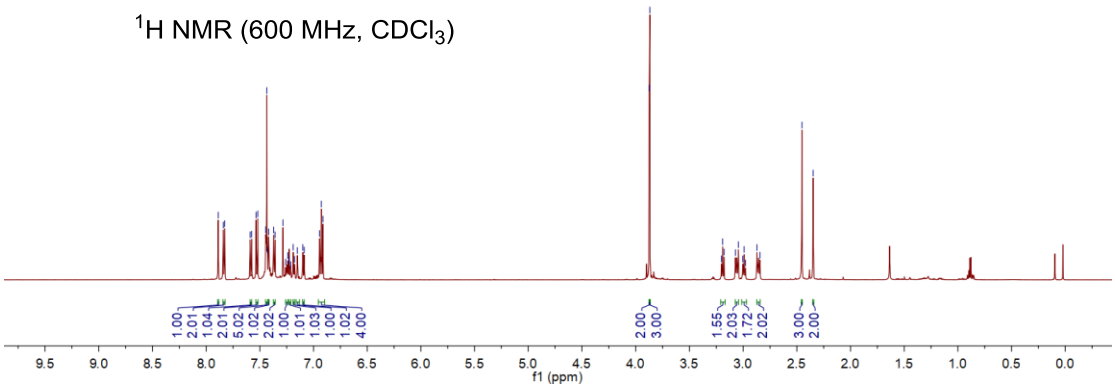
3-46

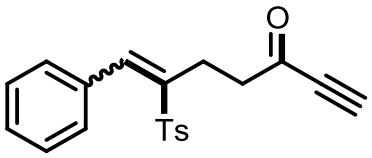
^{13}C NMR (101 MHz, $CDCl_3$)



3-47

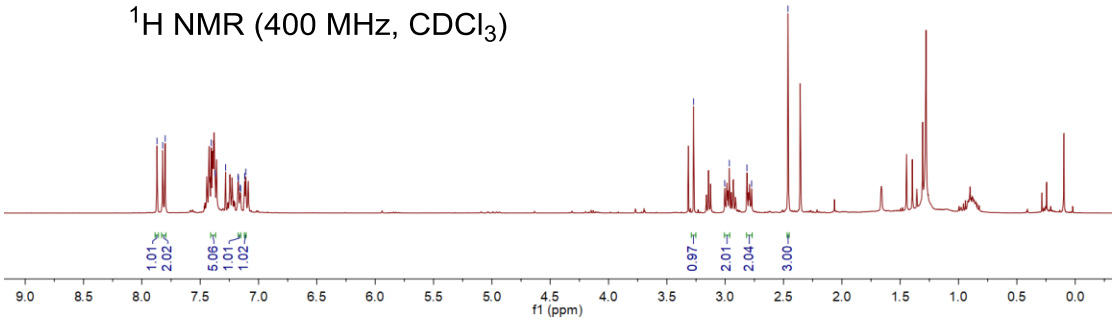
^{1}H NMR (600 MHz, $CDCl_3$)

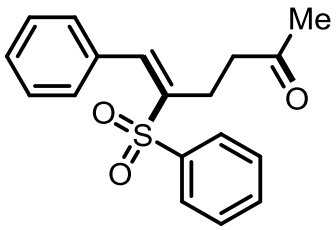




3-48

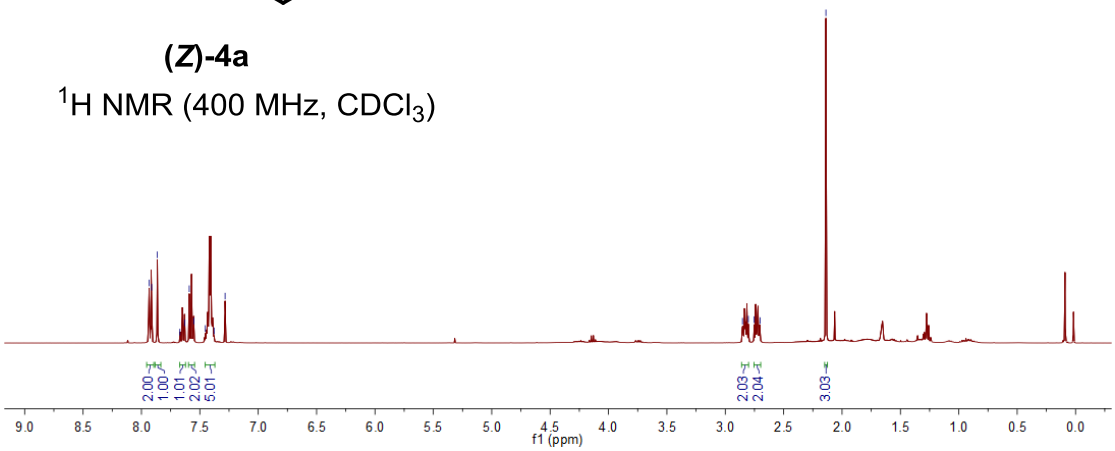
^{1}H NMR (400 MHz, $CDCl_3$)

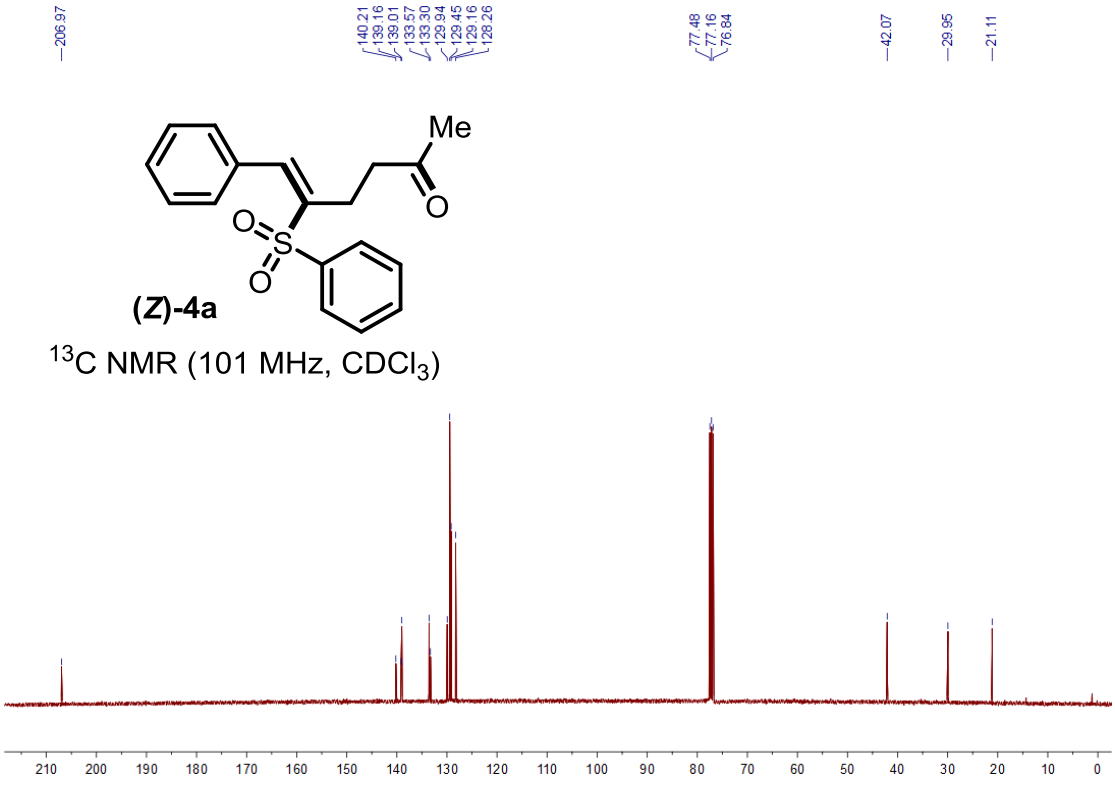


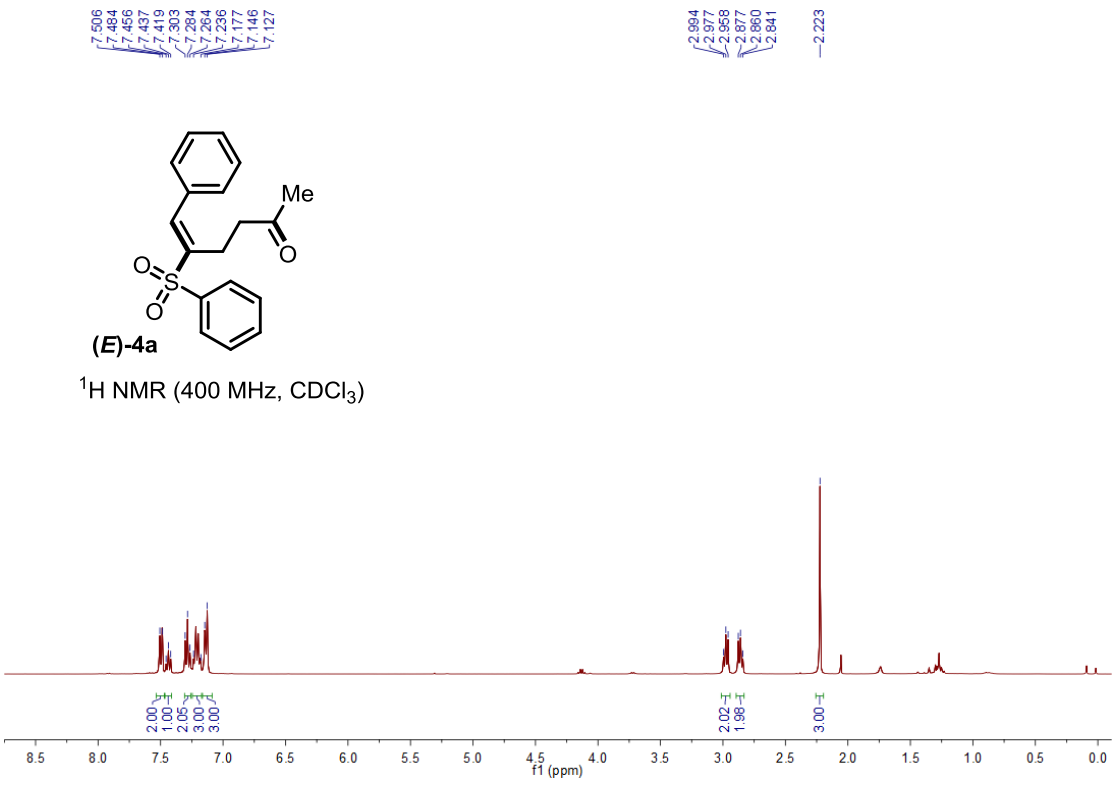


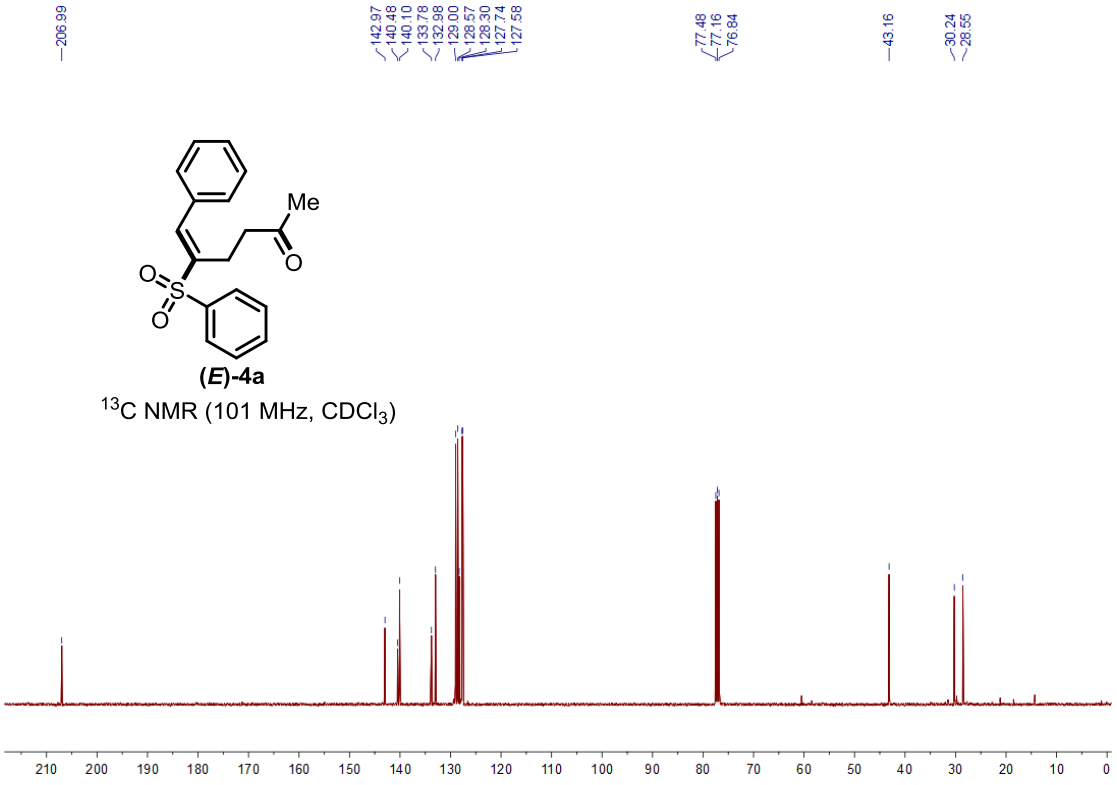
(*Z*)-4a

^{1}H NMR (400 MHz, $CDCl_3$)



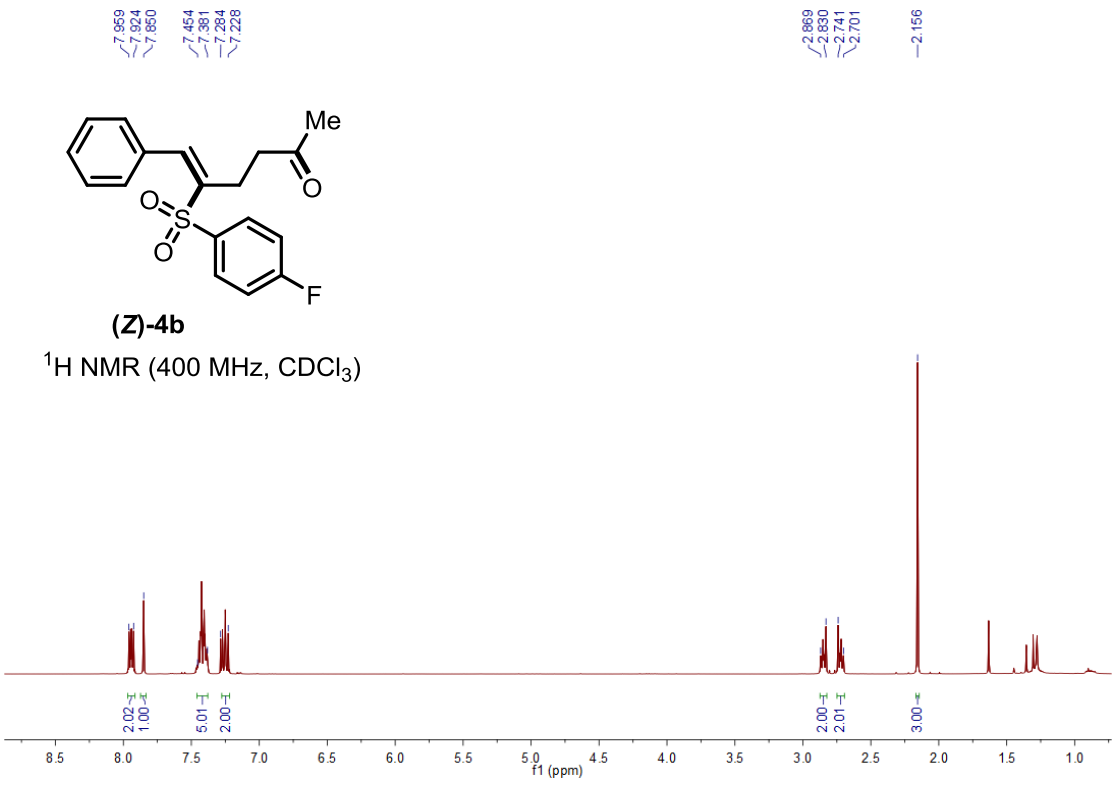

206.97
140.21
139.16
139.01
133.57
133.30
129.94
129.45
129.16
128.26
77.48
77.16
76.84
42.07
29.95
21.11
Me
O
O
S
O
(Z)-4a
13C NMR (101 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


7.506
7.484
7.456
7.437
7.419
7.303
7.284
7.264
7.236
7.177
7.146
7.127
2.994
2.977
2.958
2.877
2.860
2.841
2.223
Me
O
O
S
O
(E)-4a
1H NMR (400 MHz, CDCl3)
2.00
1.00
2.05
3.00
3.00
2.02
1.98
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



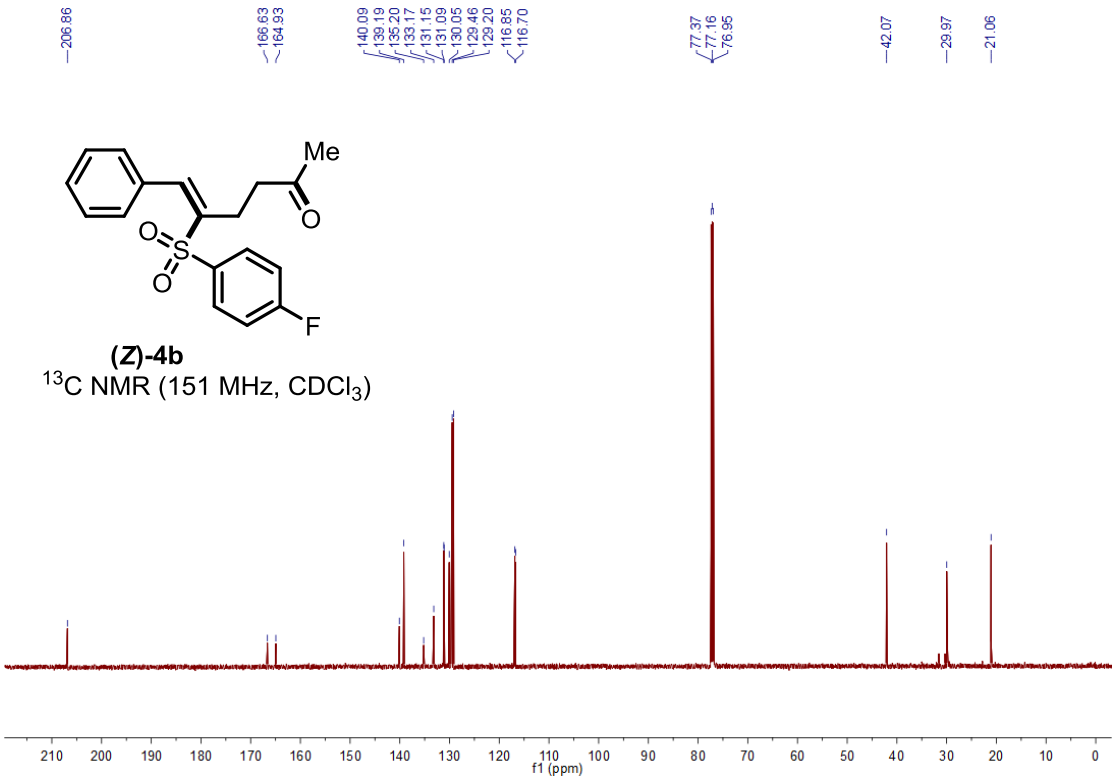
(*E*)-4a

^{13}C NMR (101 MHz, $CDCl_3$)



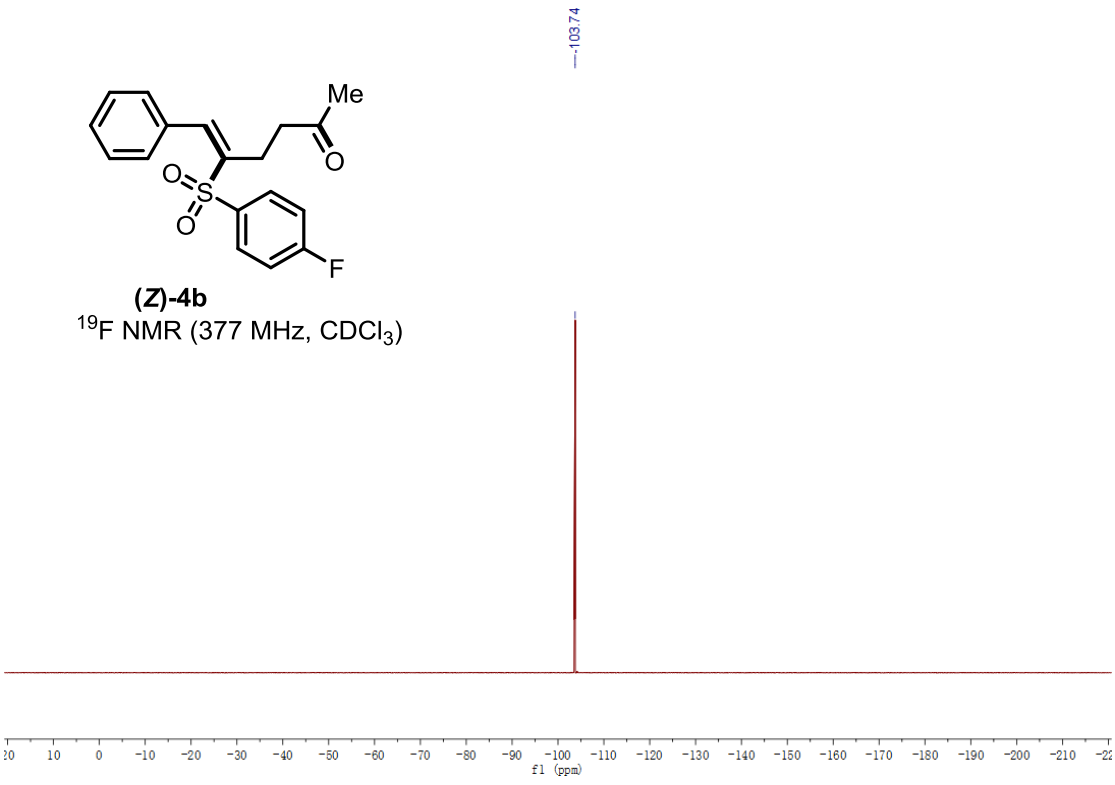
(*Z*)-4b

^{1}H NMR (400 MHz, $CDCl_3$)



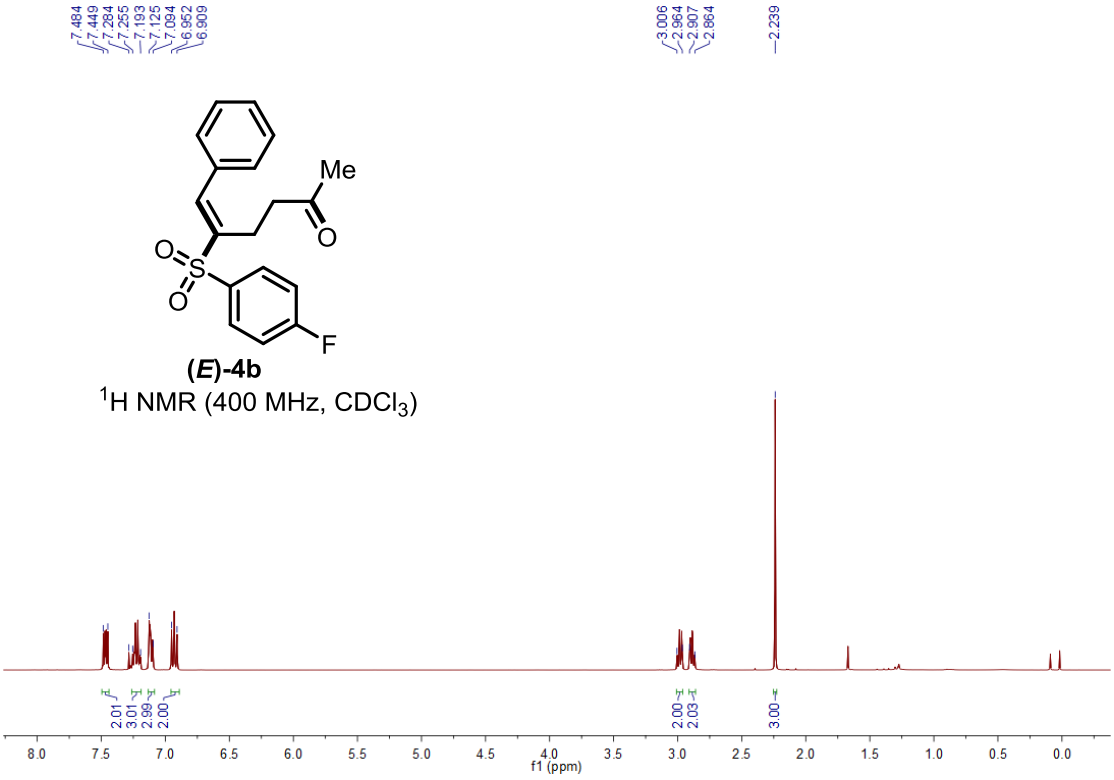
(*Z*)-4b

^{13}C NMR (151 MHz, $CDCl_3$)



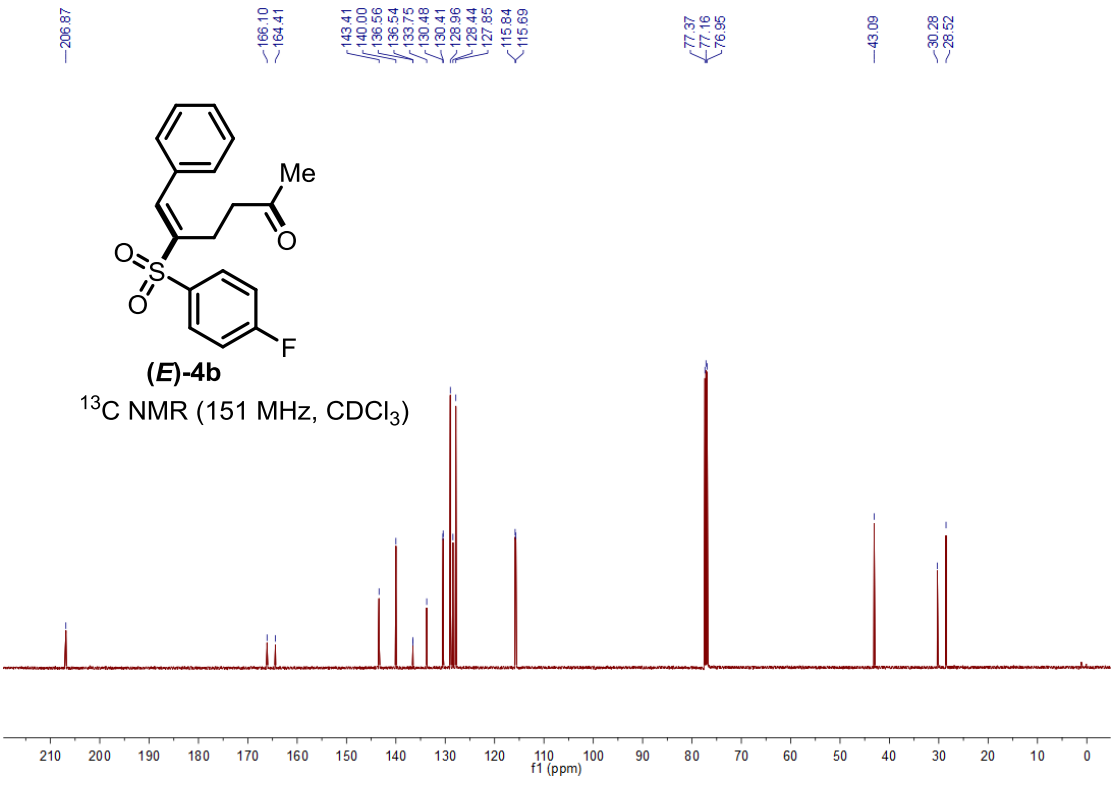
(*Z*)-4b

^{19}F NMR (377 MHz, $CDCl_3$)



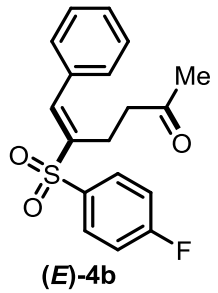
(*E*)-4b

^{1}H NMR (400 MHz, $CDCl_3$)



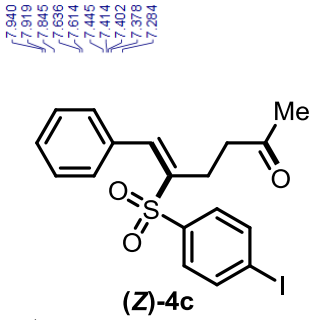
(*E*)-4b

^{13}C NMR (151 MHz, $CDCl_3$)



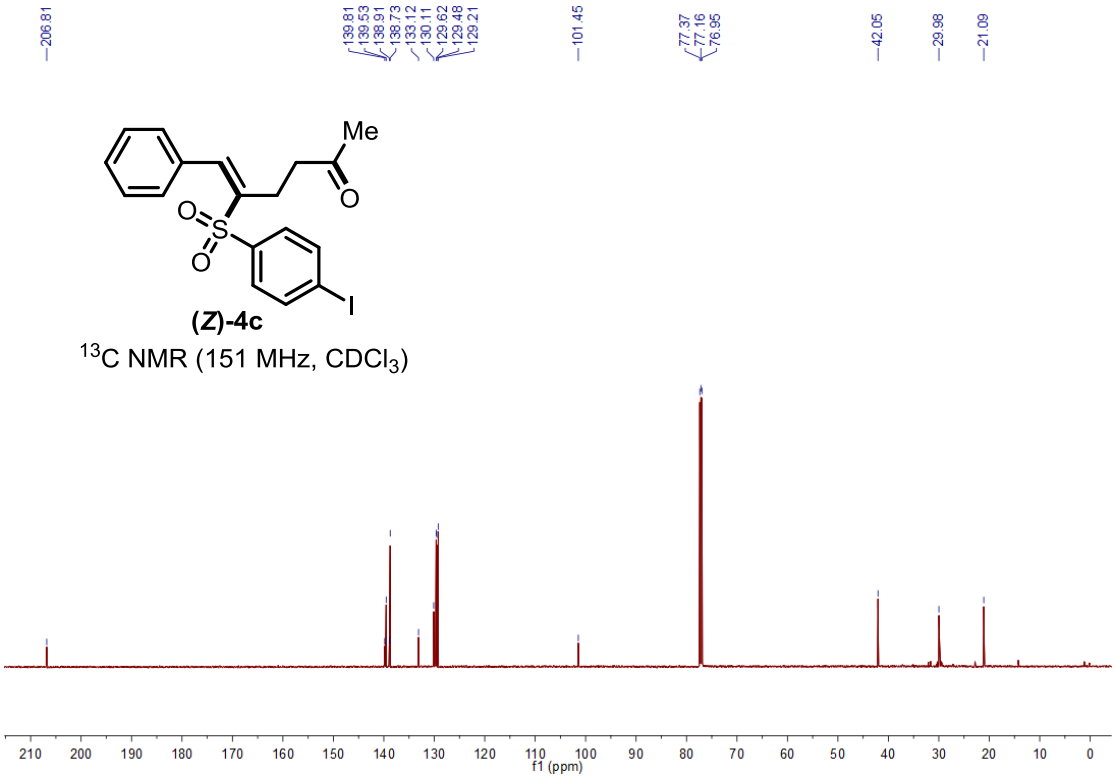
(*E*)-4b

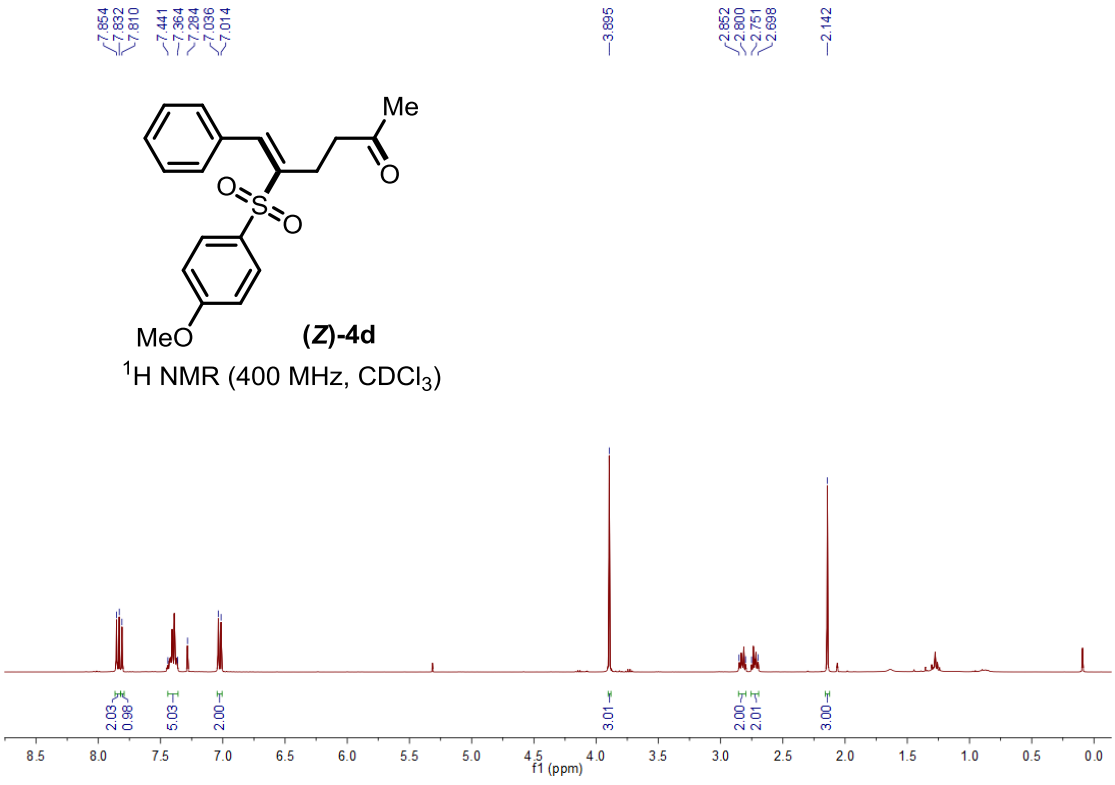
^{19}F NMR (377 MHz, $CDCl_3$)

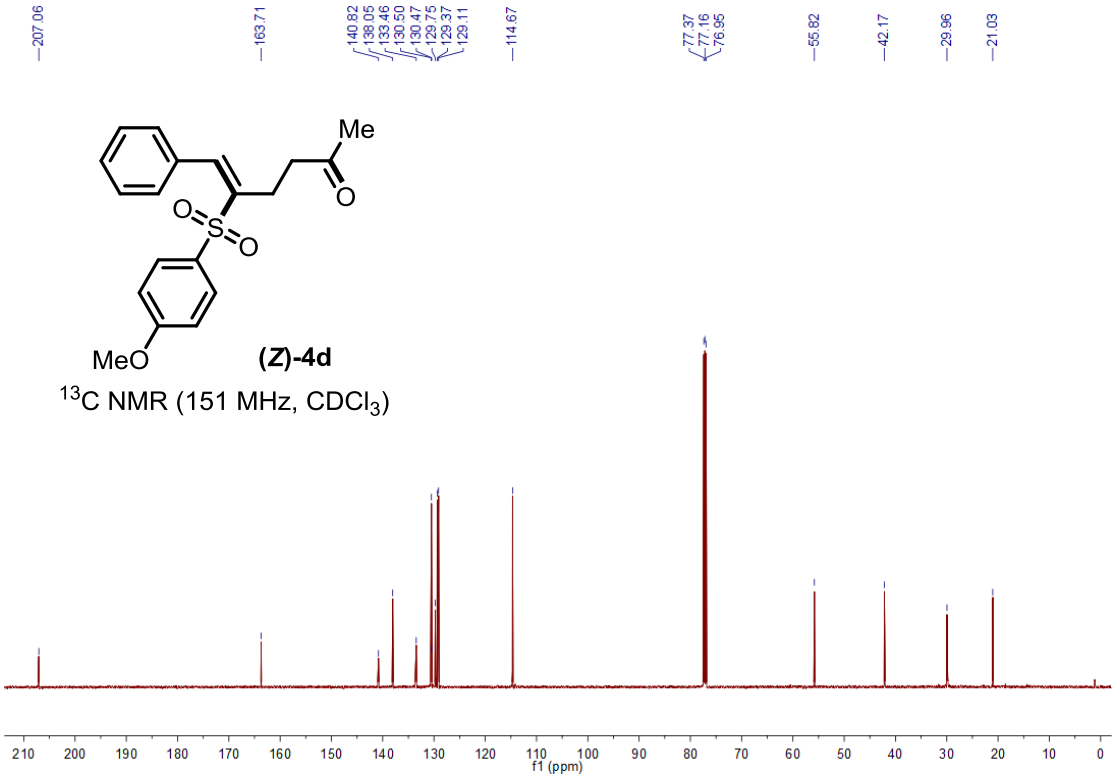


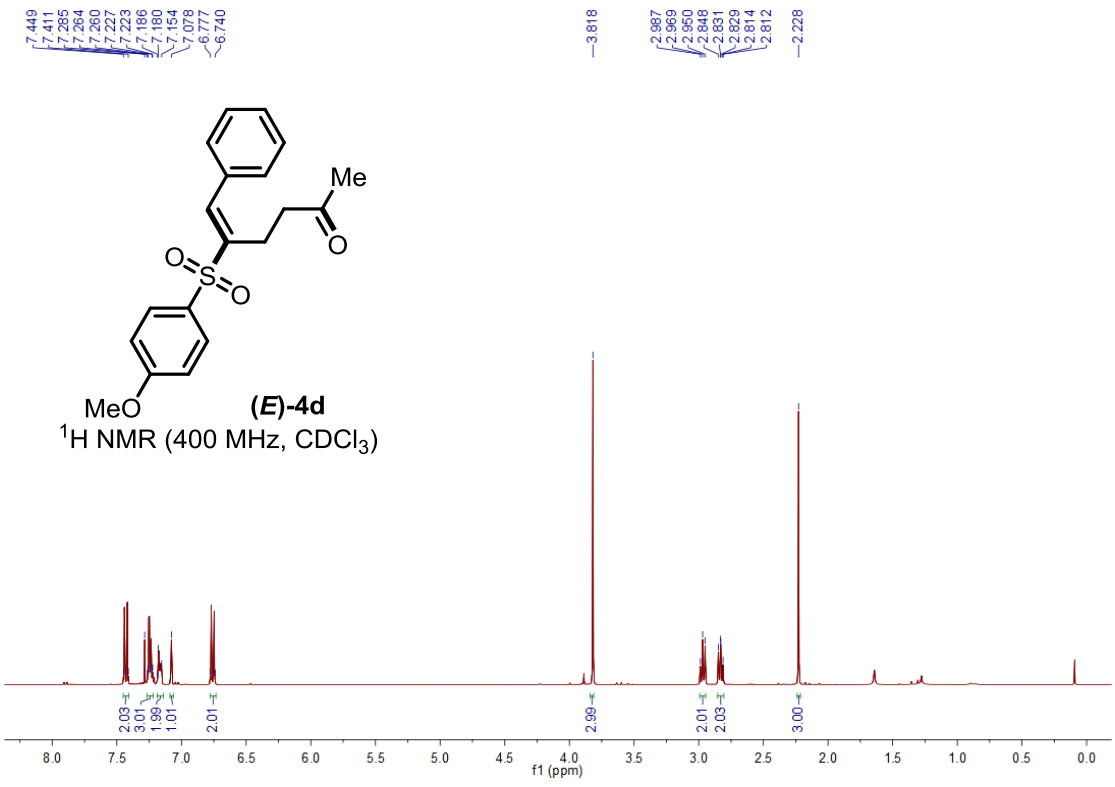
(*Z*)-4c

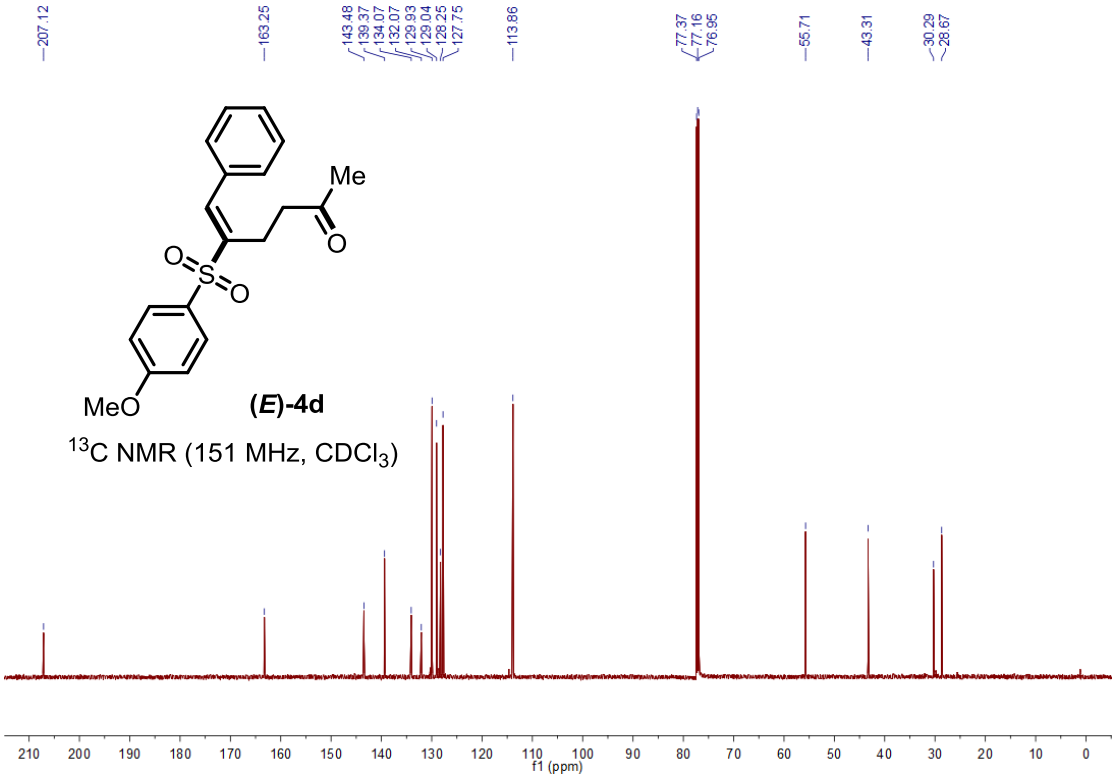
^{1}H NMR (400 MHz, $CDCl_3$)

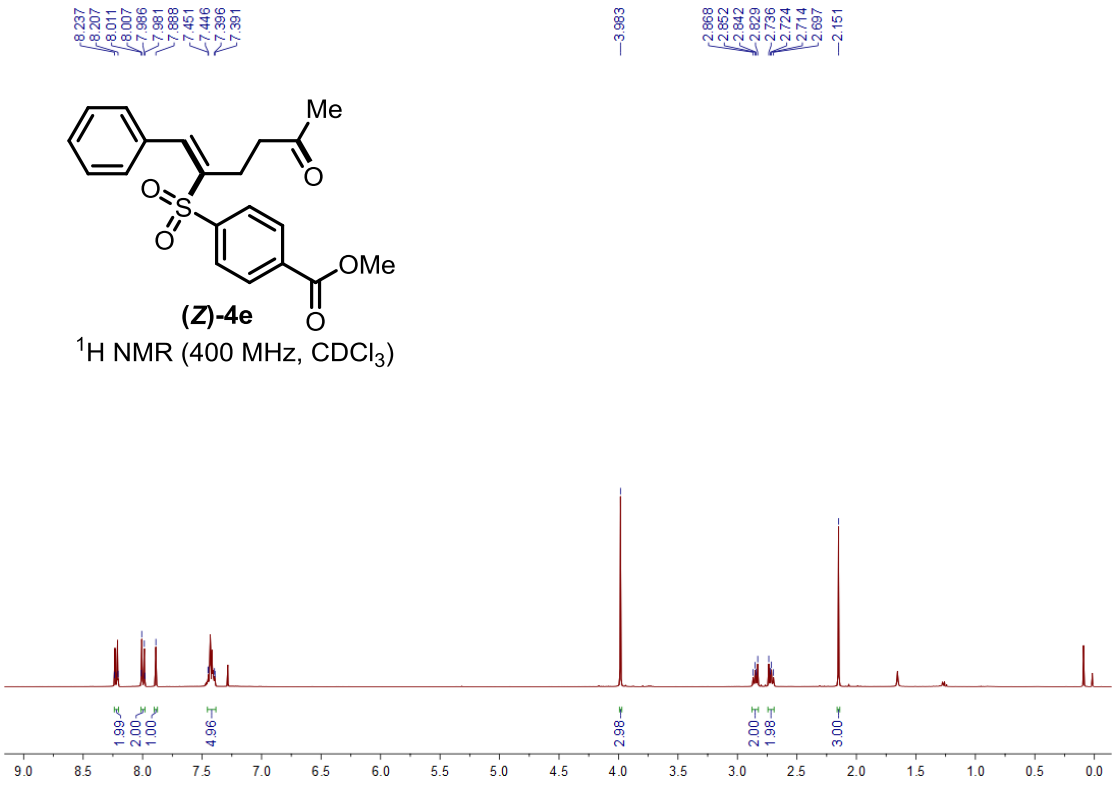

206.81
139.81
139.53
138.91
138.73
133.12
130.11
129.62
129.48
129.21
101.45
77.37
77.16
76.95
42.05
29.98
21.09
Me
O
O
S
O
I
(Z)-4c
13C NMR (151 MHz, CDCl3)
f1 (ppm)

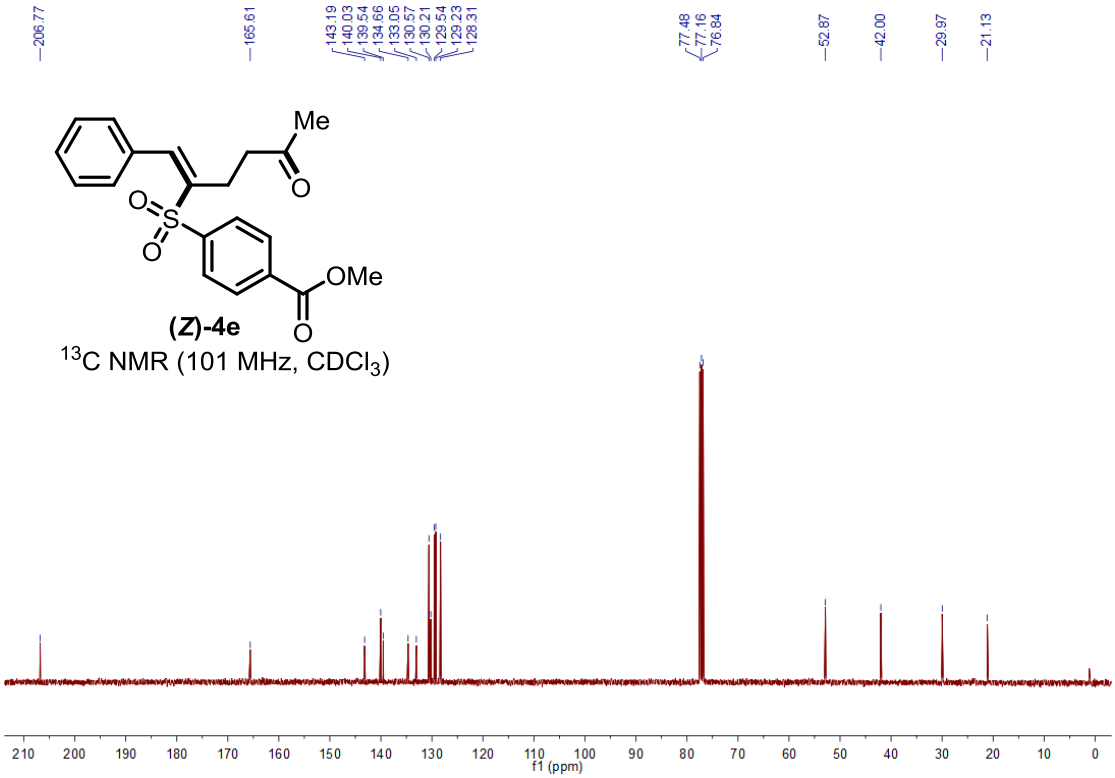

7.854
7.832
7.810
7.441
7.364
7.284
7.036
7.014
3.895
2.852
2.800
2.751
2.698
2.142
Me
O
O
S
O
MeO
(Z)-4d
1H NMR (400 MHz, CDCl3)
2.03
0.98
5.03
2.00
3.01
2.00
2.01
3.00
f1 (ppm)


207.06
163.71
140.82
138.05
133.46
130.50
130.47
129.75
129.37
129.11
114.67
77.37
77.16
76.95
55.82
42.17
29.96
21.03
Me
O
O
S
O
MeO
(Z)-4d
13C NMR (151 MHz, CDCl3)
f1 (ppm)


7.449
7.411
7.285
7.264
7.260
7.227
7.223
7.186
7.180
7.154
7.078
6.777
6.740
3.818
2.987
2.969
2.950
2.848
2.831
2.829
2.814
2.812
2.228
Me
O
O
S
O
MeO
(E)-4d
1H NMR (400 MHz, CDCl3)
2.03
3.01
1.99
1.01
2.01
2.99
2.01
2.03
3.00
f1 (ppm)

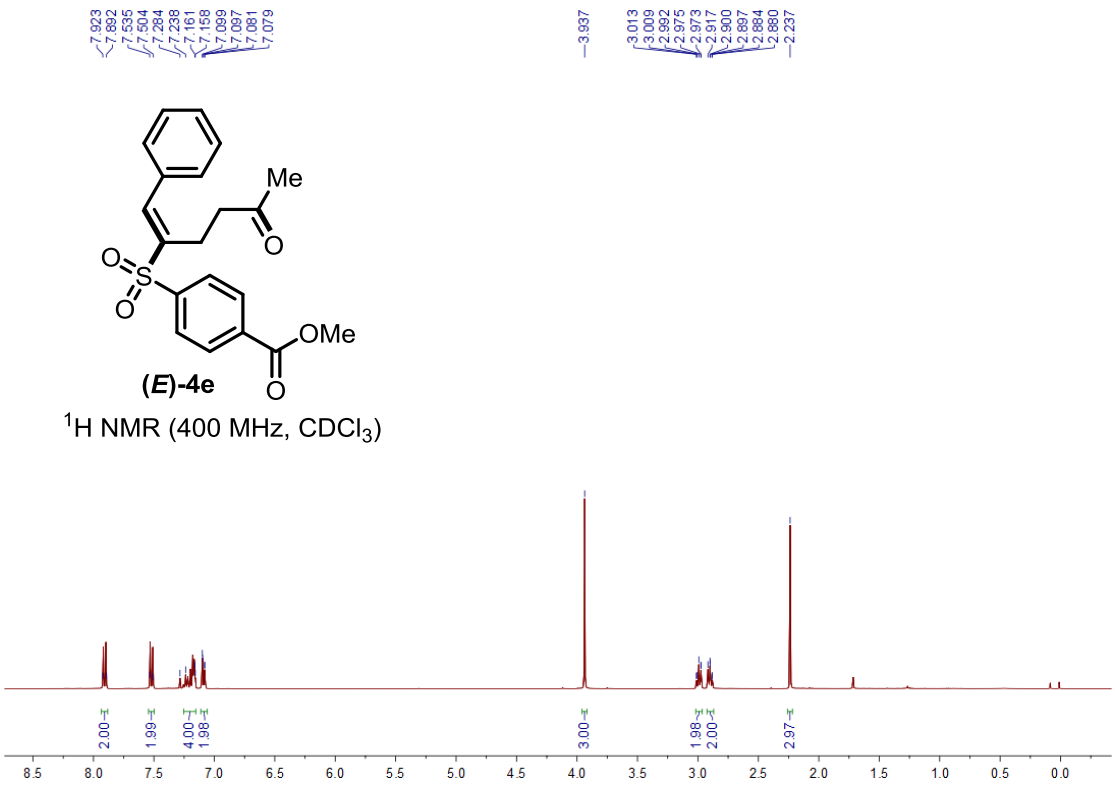

207.12
163.25
143.48
139.37
134.07
132.07
129.93
129.04
128.25
127.75
113.86
77.37
77.16
76.95
55.71
43.31
30.29
28.67
Me
O
O
S
O
MeO
(E)-4d
13C NMR (151 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.237
8.207
8.011
8.007
7.986
7.981
7.888
7.451
7.446
7.396
7.391
3.983
2.868
2.852
2.842
2.829
2.736
2.724
2.714
2.697
2.151
Me
O
O
S
O
OMe
O
(Z)-4e
1H NMR (400 MHz, CDCl3)
1.99
2.00
1.00
4.96
2.98
2.00
1.98
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0



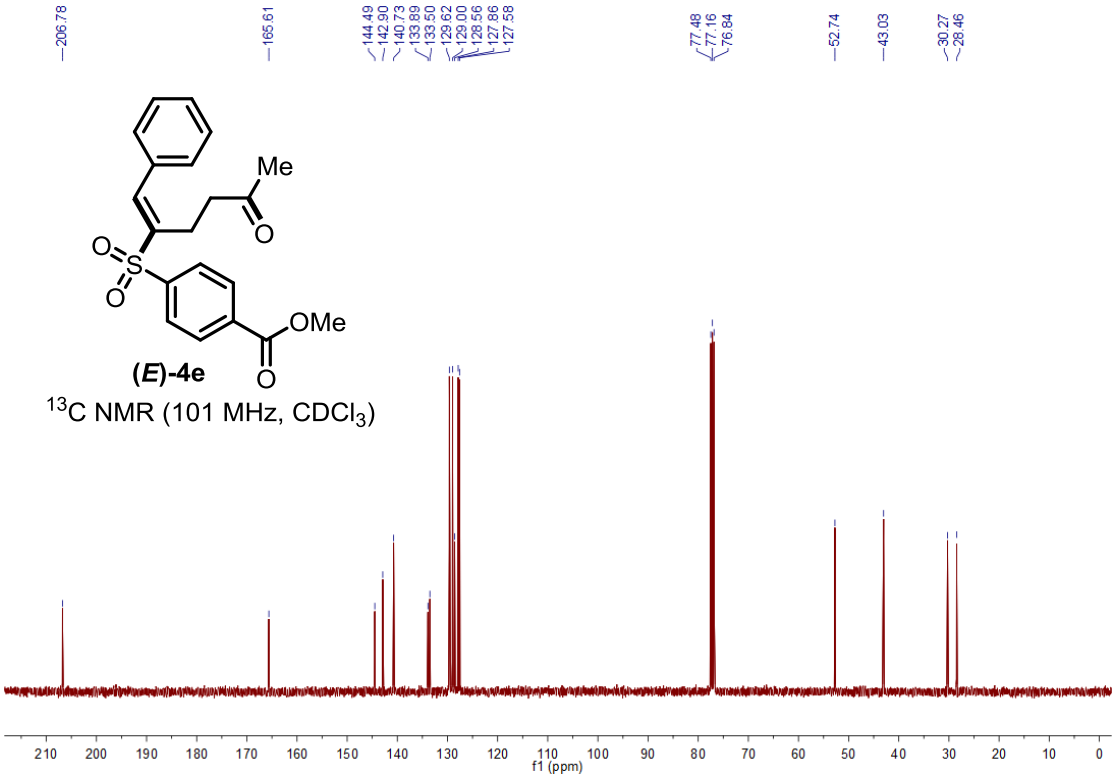
(*Z*)-4e

^{13}C NMR (101 MHz, $CDCl_3$)



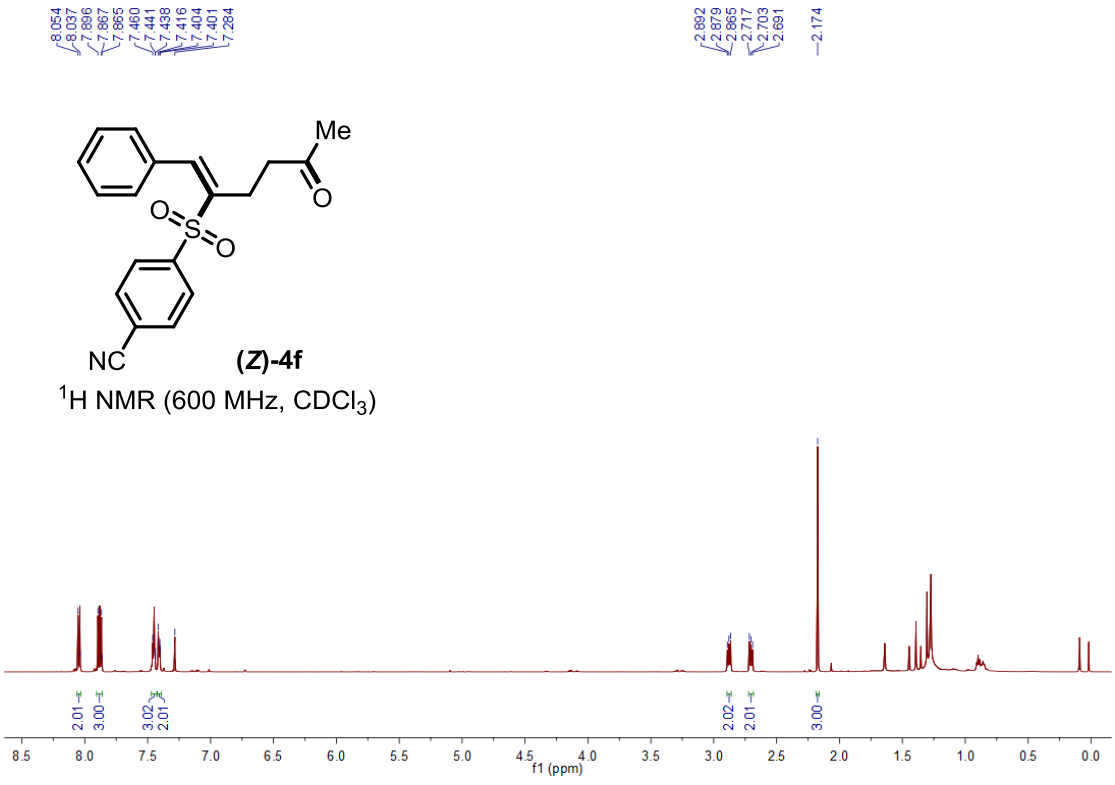
(*E*)-4e

^{1}H NMR (400 MHz, $CDCl_3$)



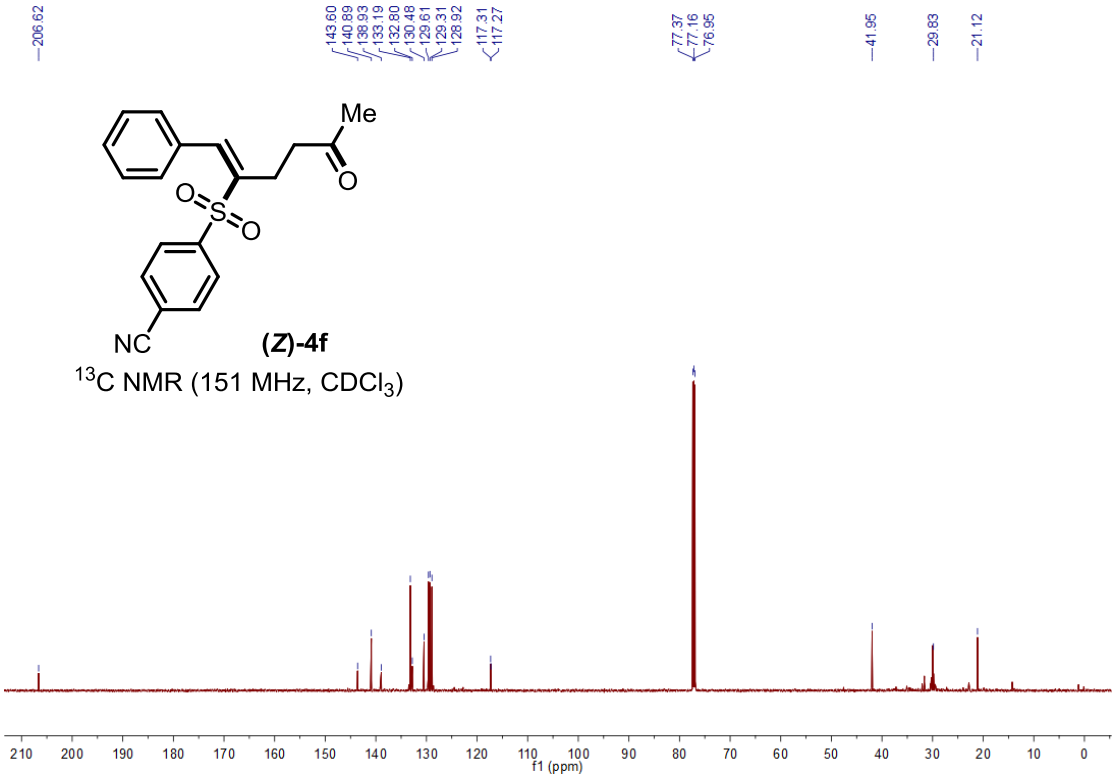
(*E*)-4e

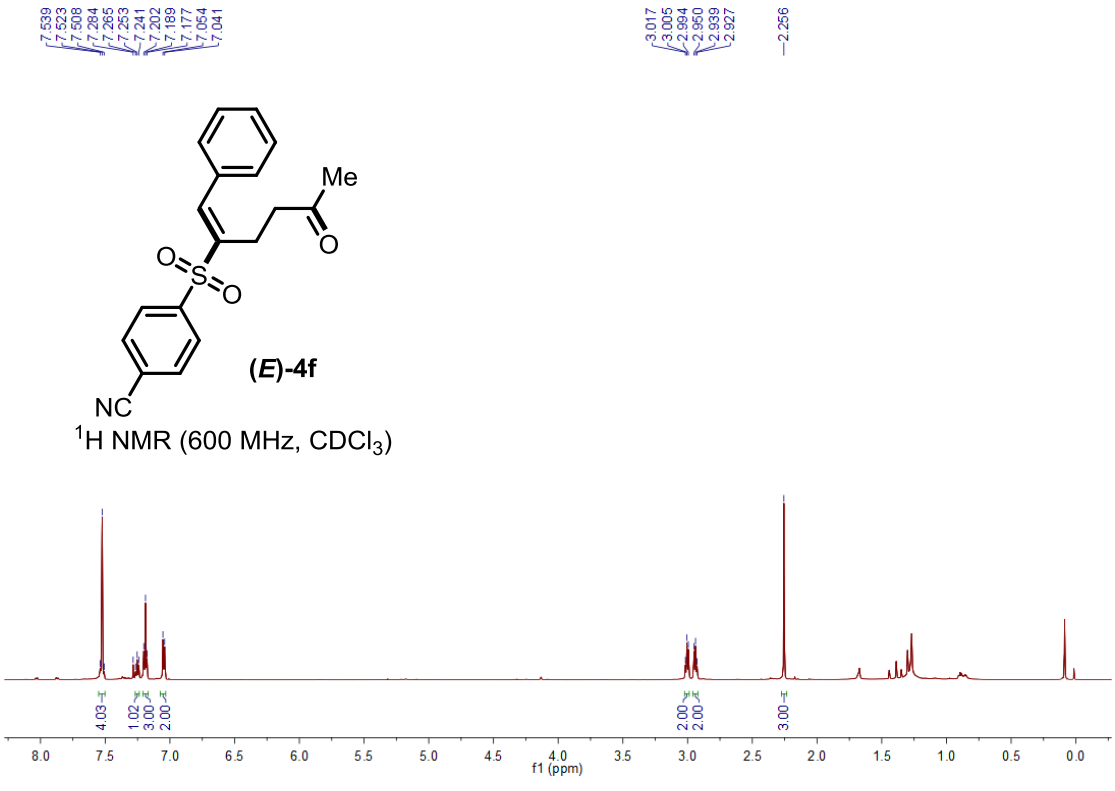
^{13}C NMR (101 MHz, $CDCl_3$)

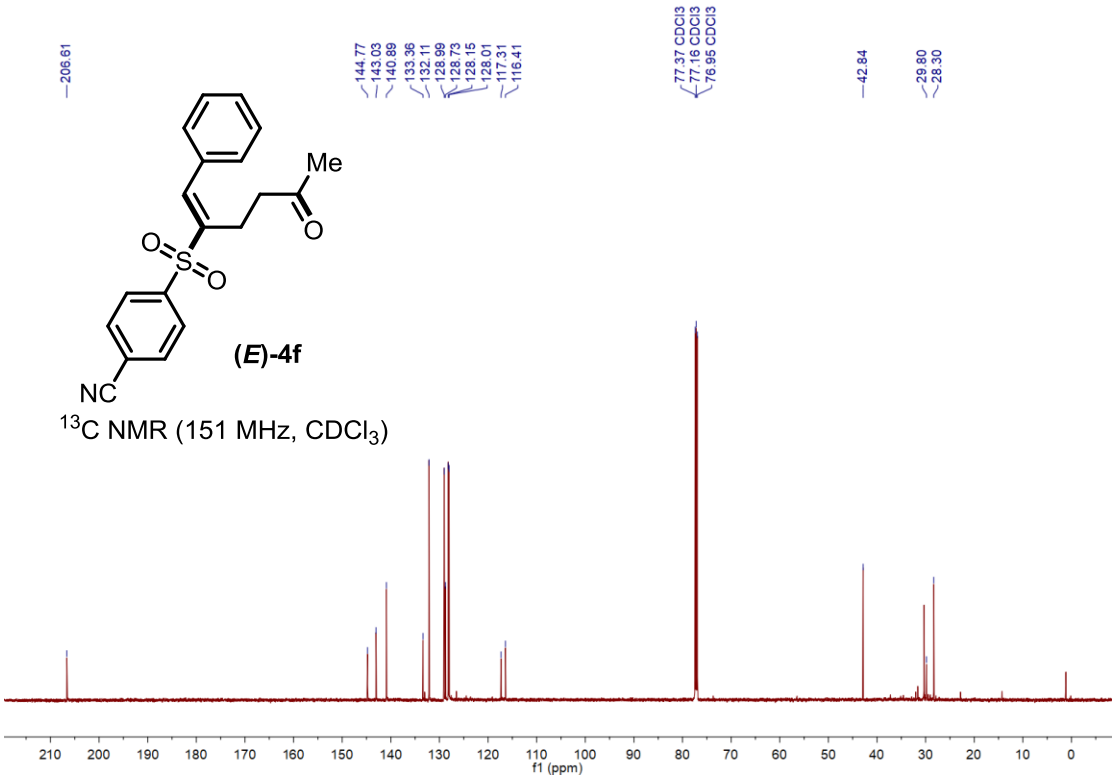


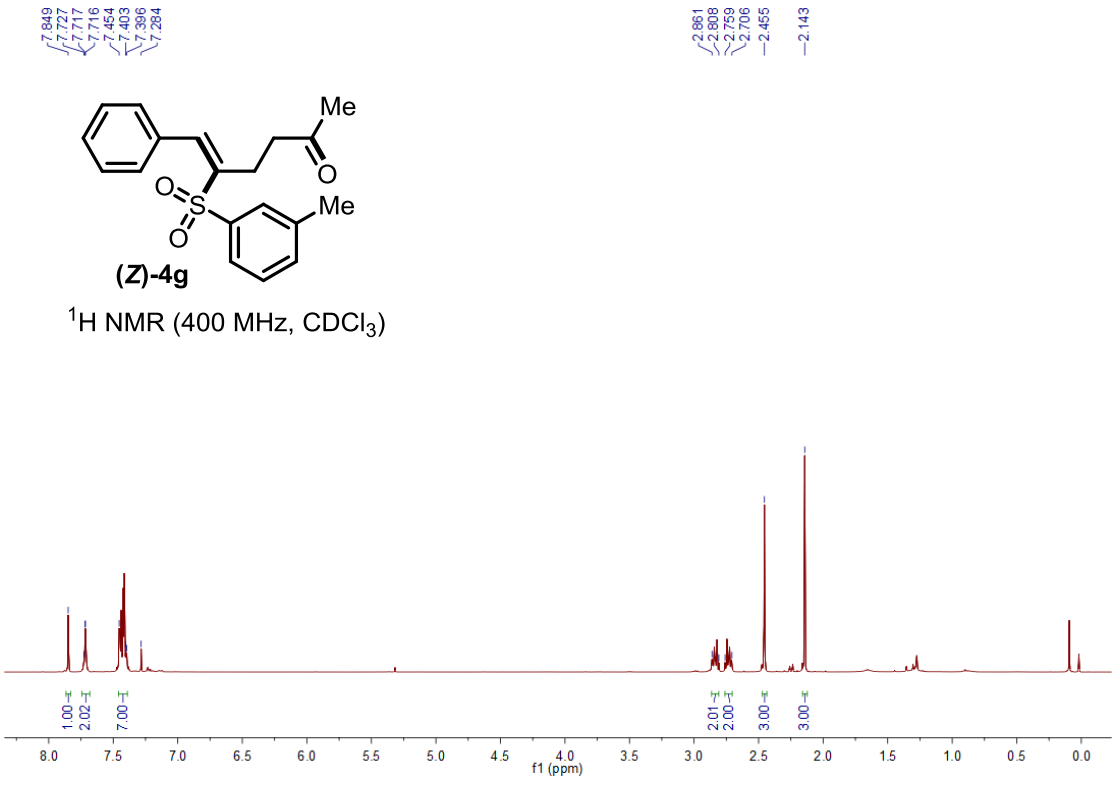
(*Z*)-4f

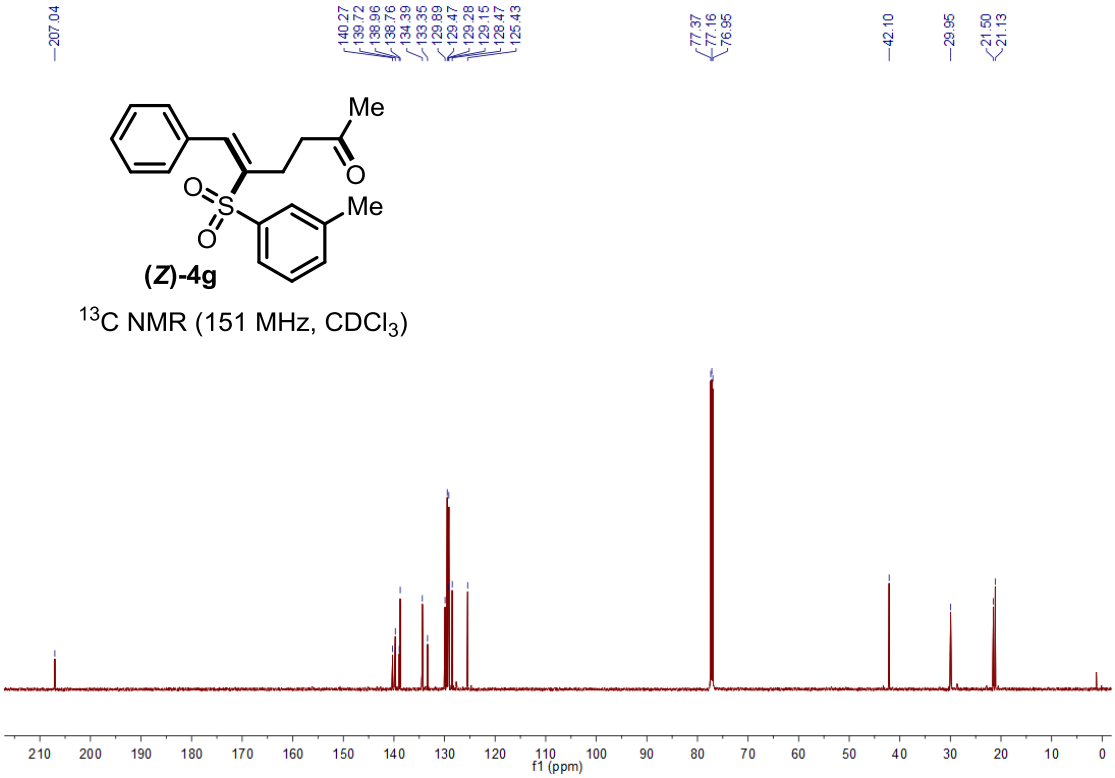
^{1}H NMR (600 MHz, $CDCl_3$)


206.62
143.60
140.89
138.93
133.19
132.80
130.48
129.61
129.31
128.92
117.31
117.27
77.37
77.16
76.95
41.95
29.83
21.12
Me
O
O
S
O
NC
(Z)-4f
13C NMR (151 MHz, CDCl3)
f1 (ppm)


7.539
7.523
7.508
7.284
7.265
7.253
7.241
7.202
7.189
7.177
7.054
7.041
3.017
3.005
2.994
2.950
2.939
2.927
2.256
Me
O
O
S
O
NC
(E)-4f
1H NMR (600 MHz, CDCl3)
4.03
1.02
3.00
2.00
2.00
2.00
3.00
f1 (ppm)

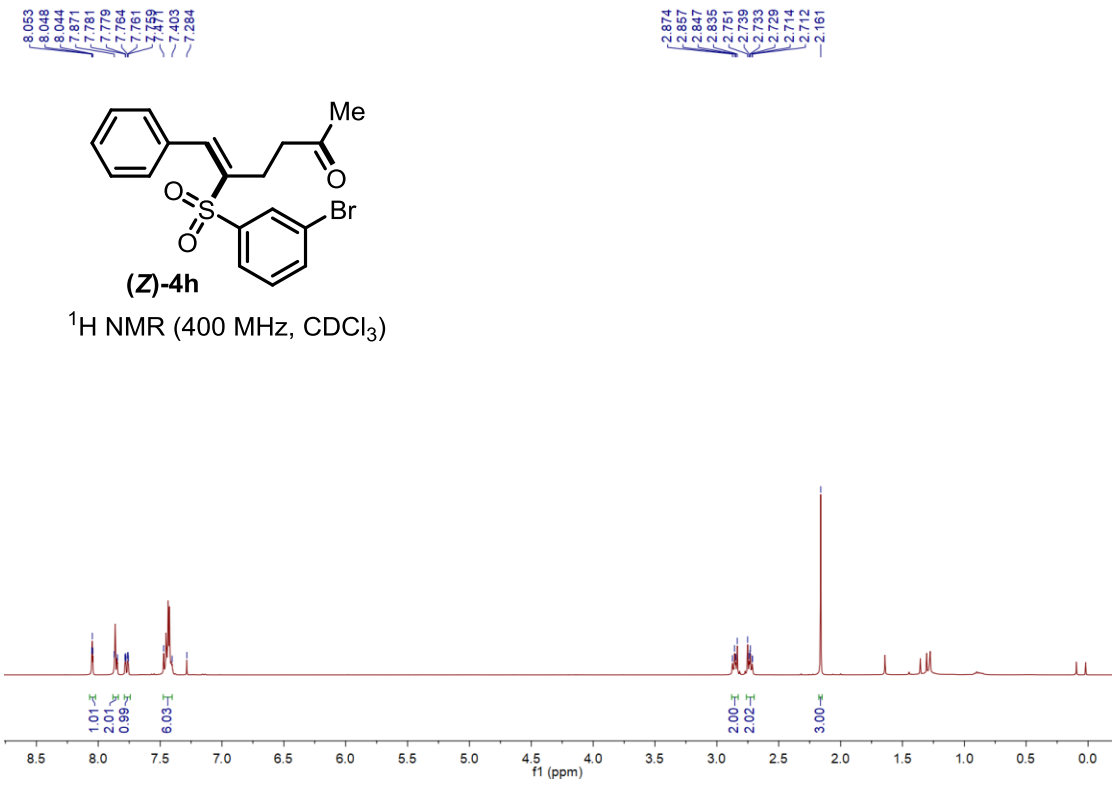

206.61
144.77
143.03
140.89
133.36
132.11
128.99
128.73
128.15
128.01
117.31
116.41
77.37 CDCl3
77.16 CDCl3
76.95 CDCl3
42.84
29.80
28.30
Me
O
O
S
O
NC
(E)-4f
13C NMR (151 MHz, CDCl3)
f1 (ppm)


7.849
7.727
7.717
7.716
7.454
7.403
7.396
7.284
2.861
2.808
2.759
2.706
2.455
2.143
Me
O
O
S
O
Me
(Z)-4g
1H NMR (400 MHz, CDCl3)
1.00
2.02
7.00
2.01
2.00
3.00
3.00
f1 (ppm)



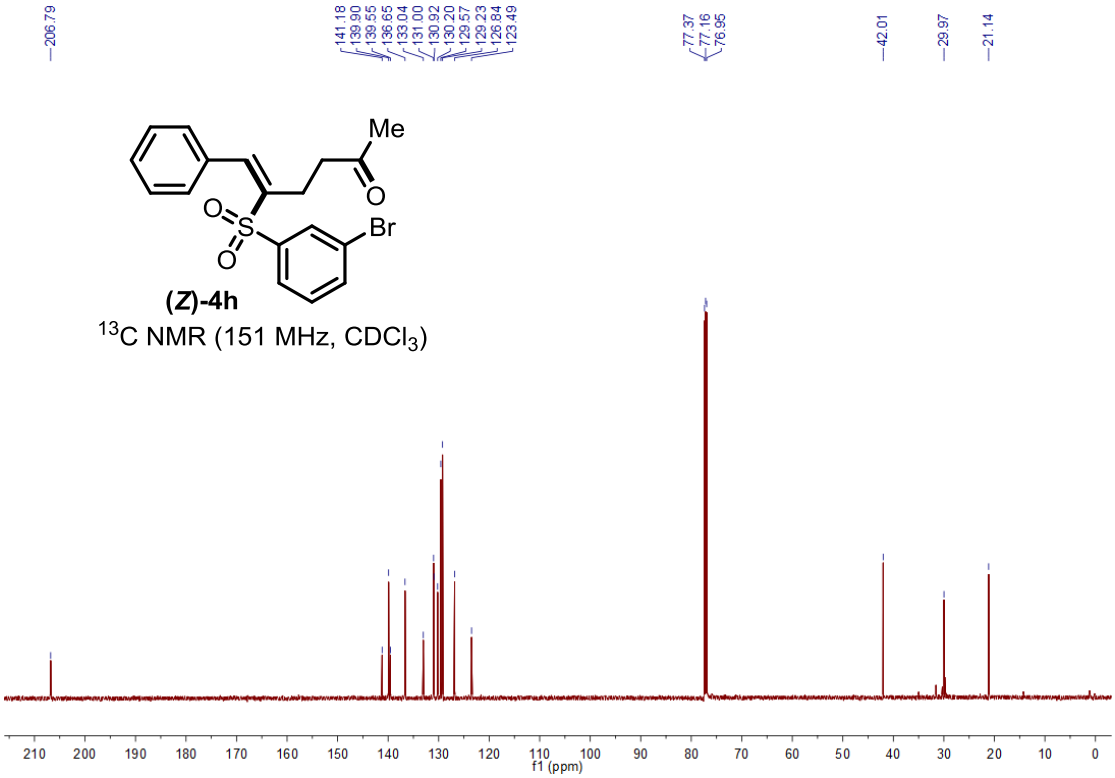
(*Z*)-4g

^{13}C NMR (151 MHz, $CDCl_3$)



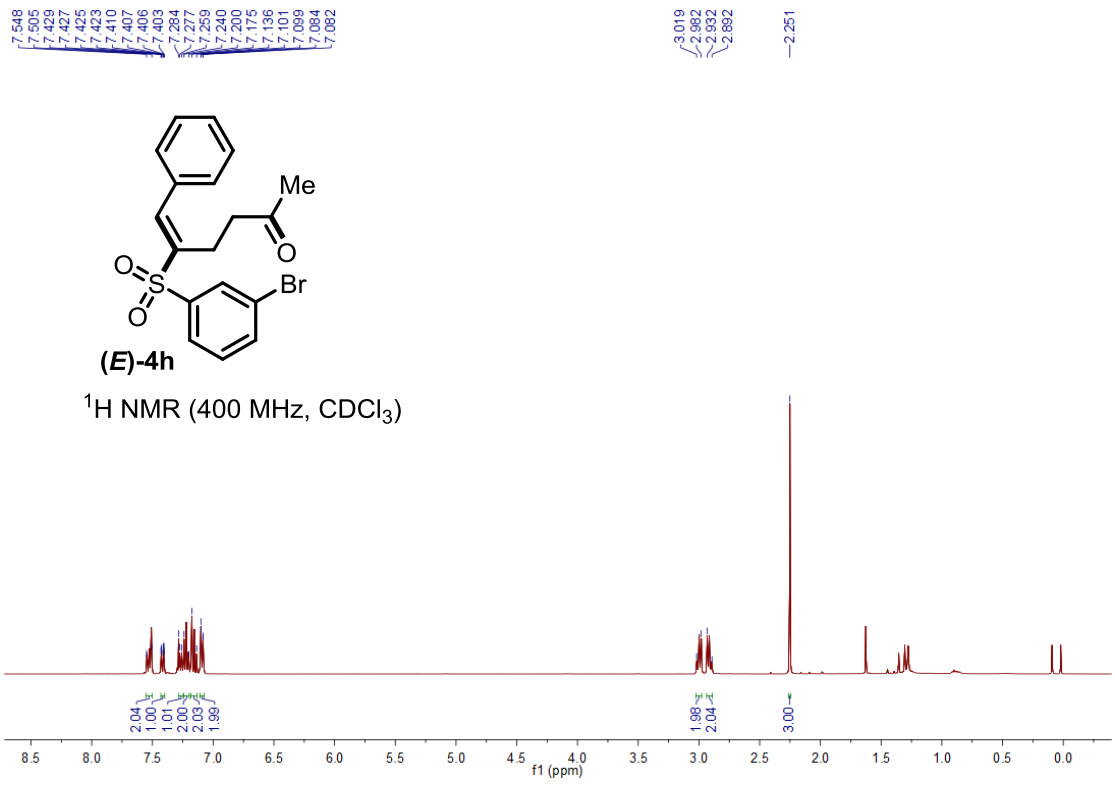
(*Z*)-4h

^{1}H NMR (400 MHz, $CDCl_3$)



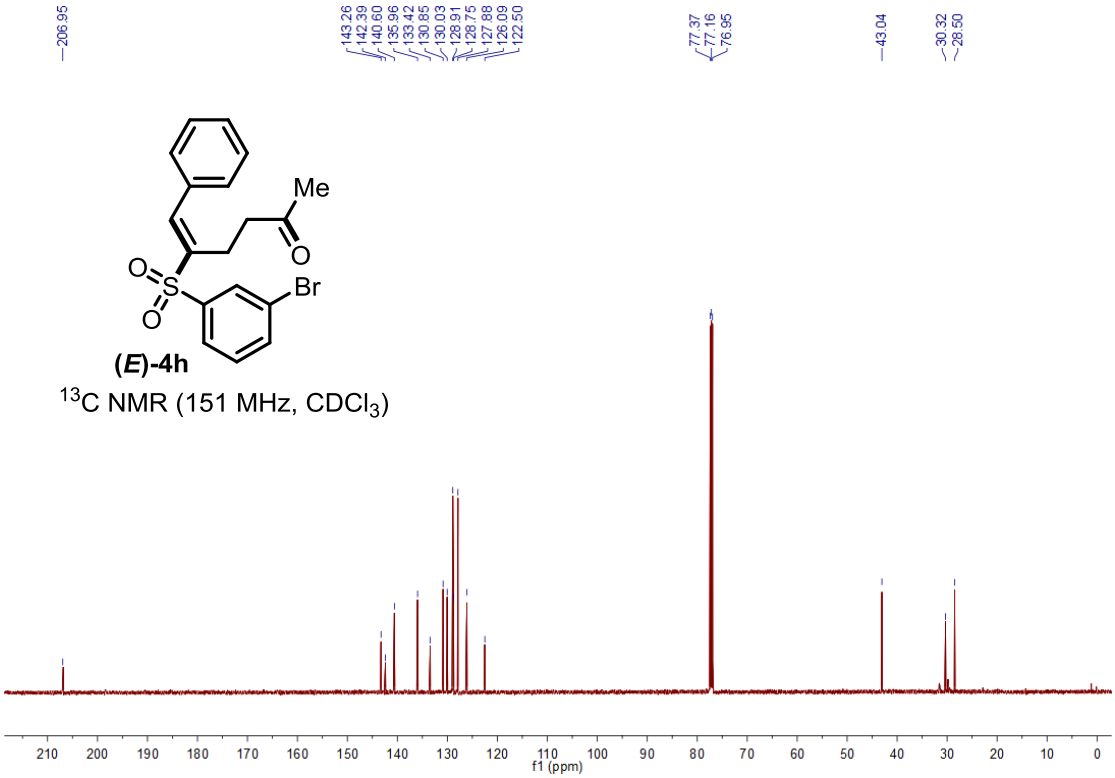
(*Z*)-4h

^{13}C NMR (151 MHz, $CDCl_3$)



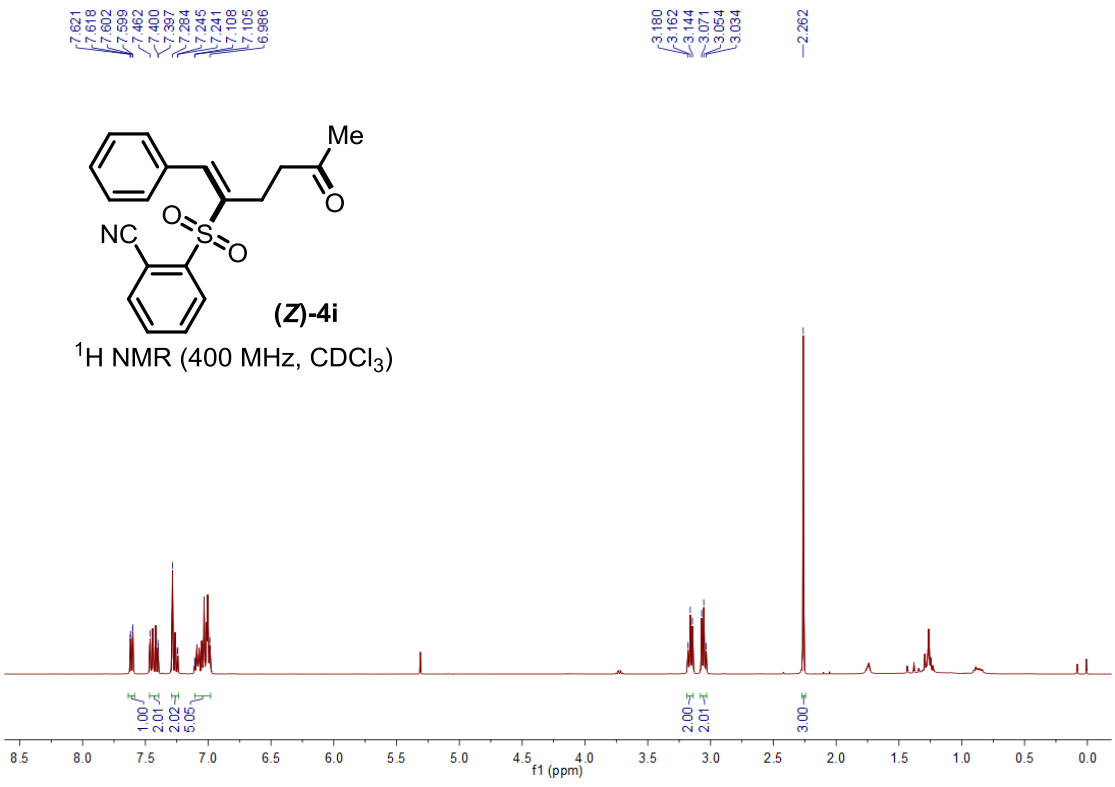
(*E*)-4h

^{1}H NMR (400 MHz, $CDCl_3$)



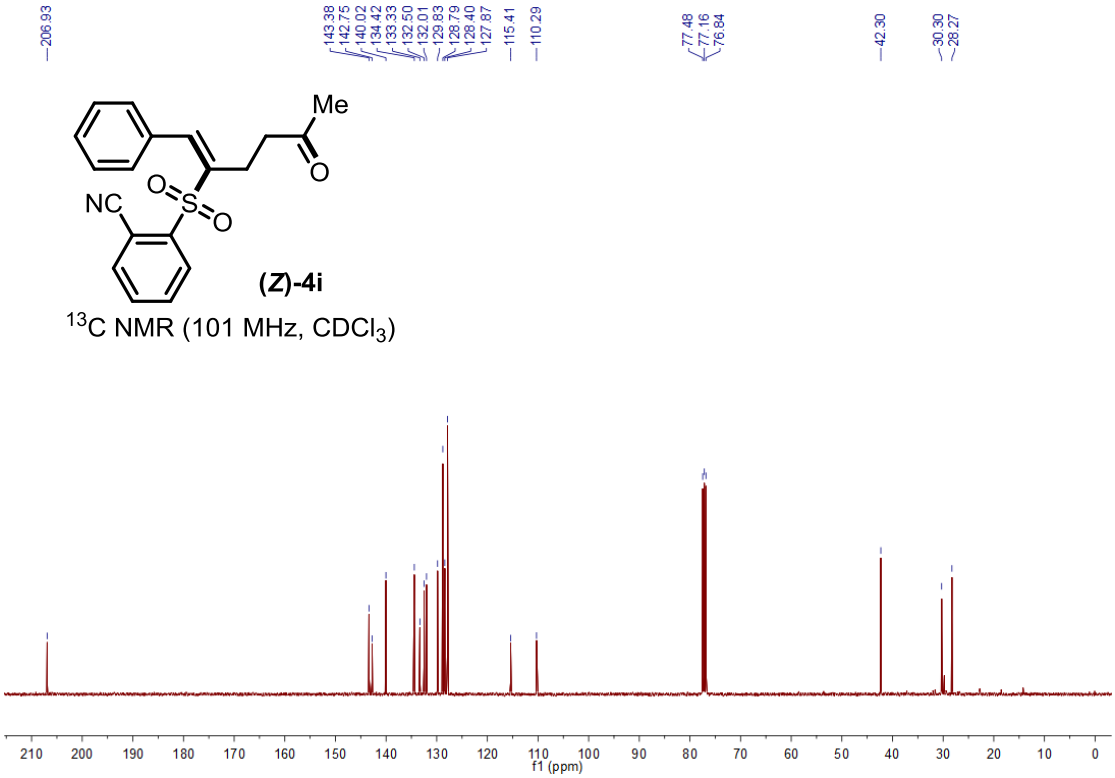
(*E*)-4h

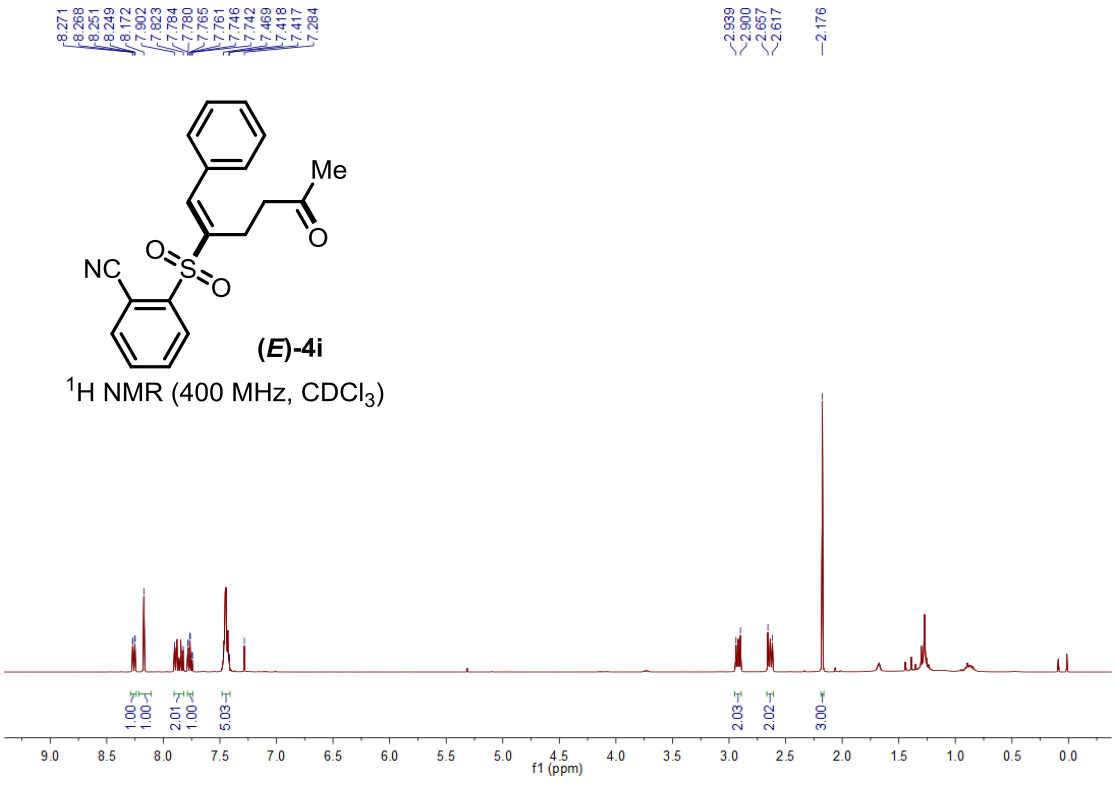
^{13}C NMR (151 MHz, $CDCl_3$)

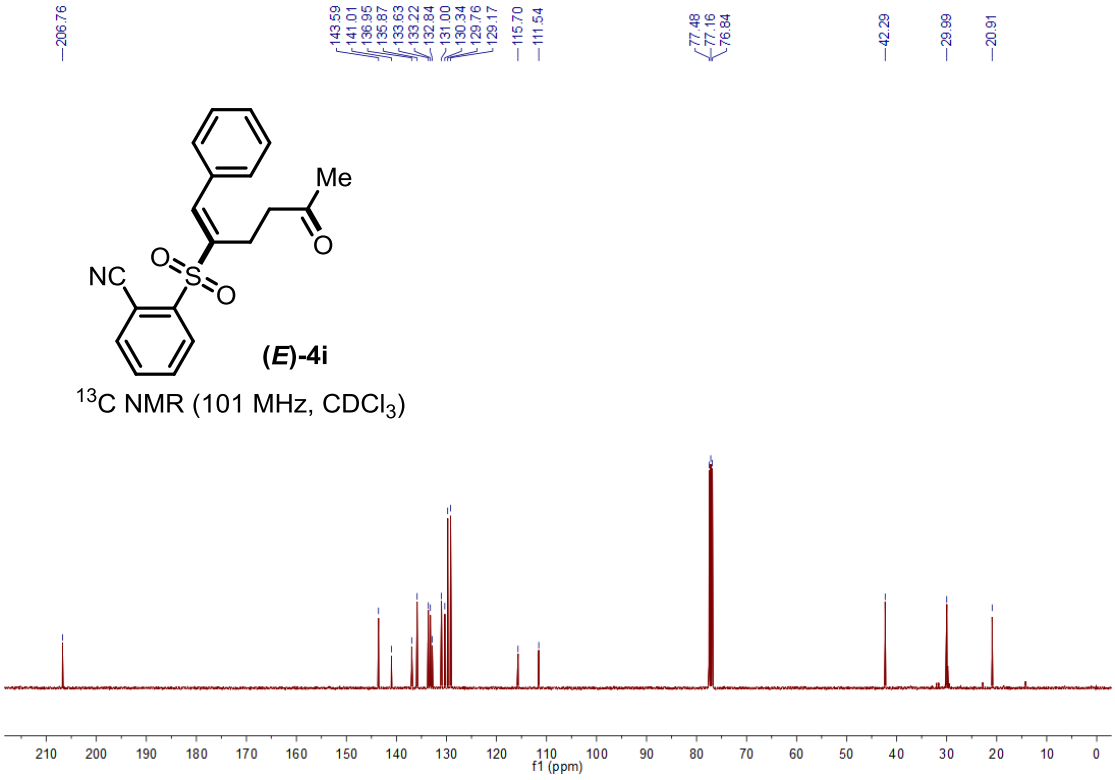


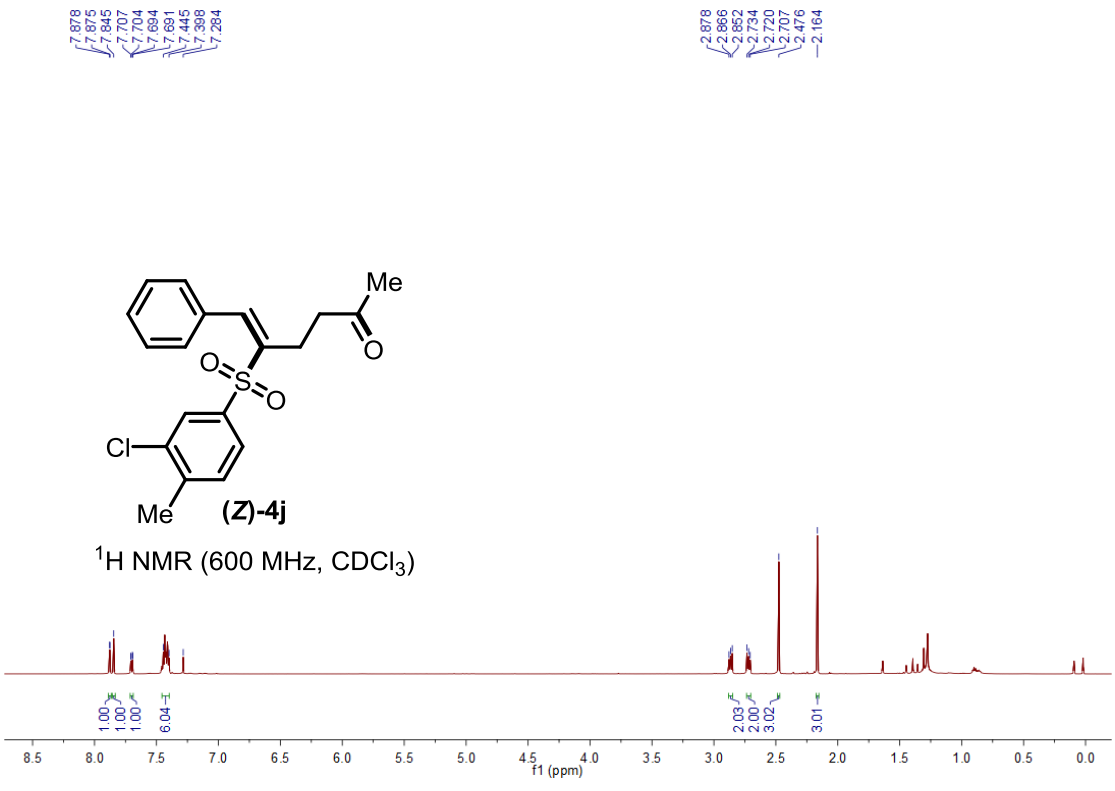
(*Z*)-4i

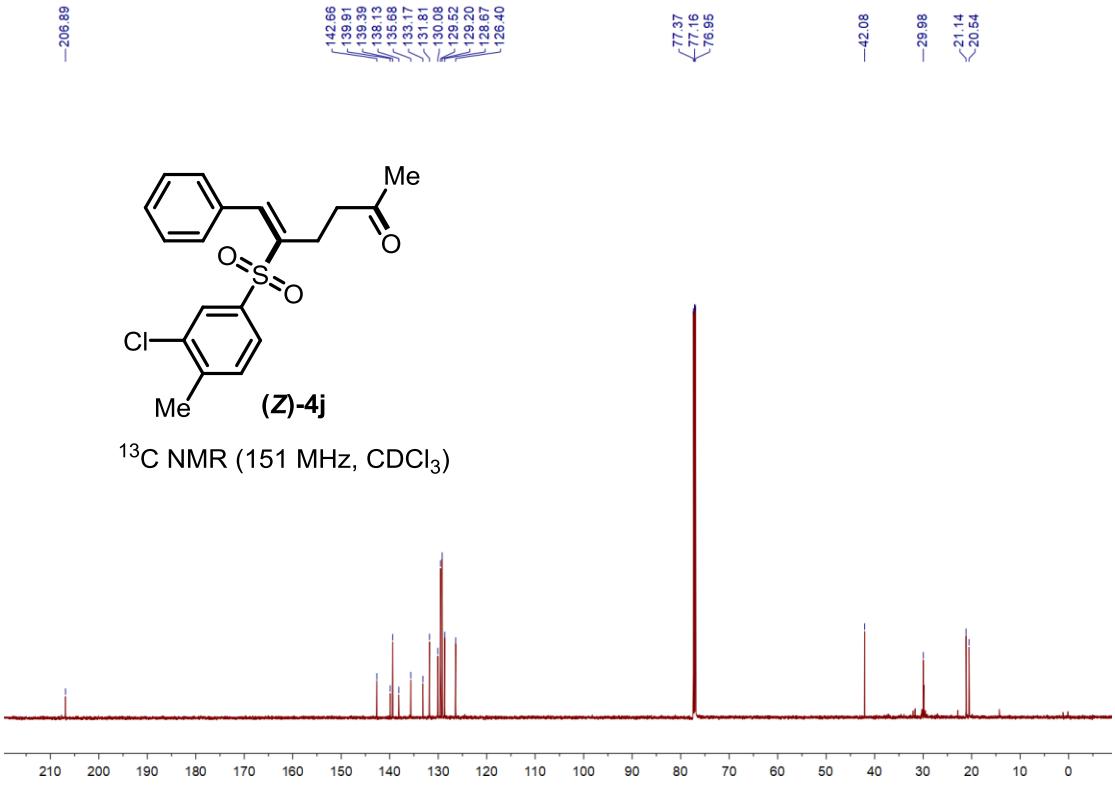
^{1}H NMR (400 MHz, $CDCl_3$)

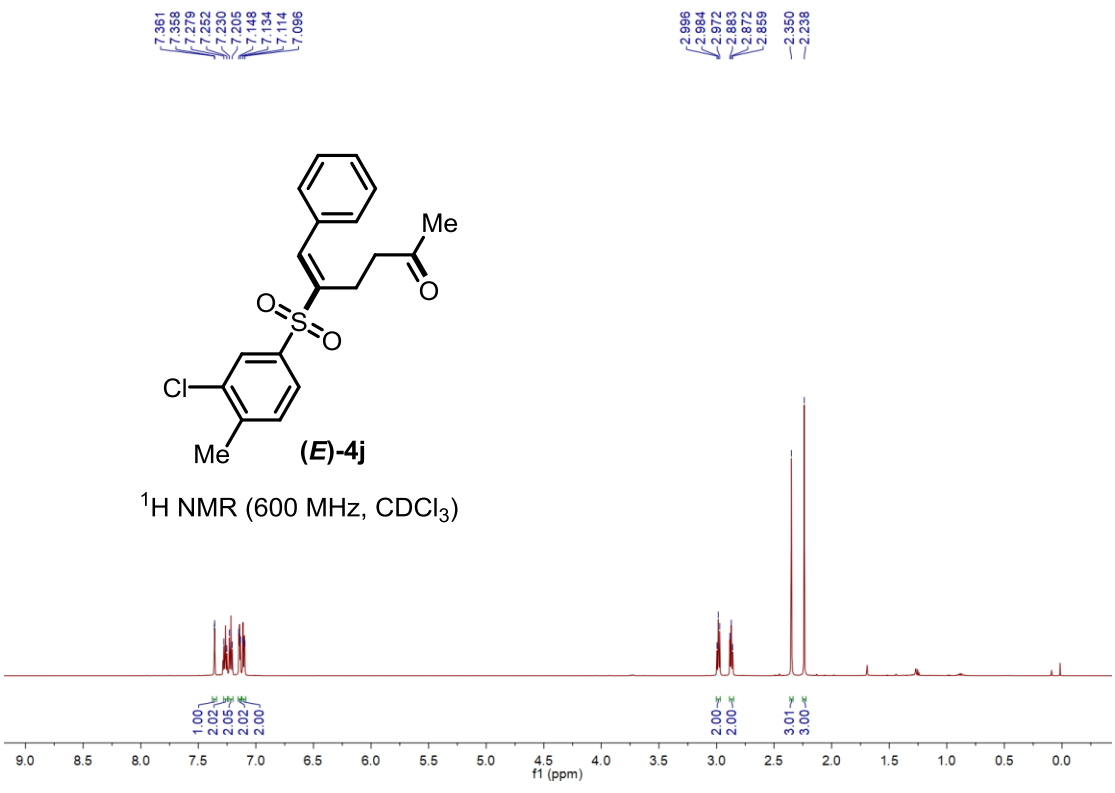

206.93
143.38
142.75
140.02
134.42
133.33
132.50
132.01
129.83
128.79
128.40
127.87
115.41
110.29
77.48
77.16
76.84
42.30
30.30
28.27
Me
O
O
O
S
NC
(Z)-4i
13C NMR (101 MHz, CDCl3)
f1 (ppm)

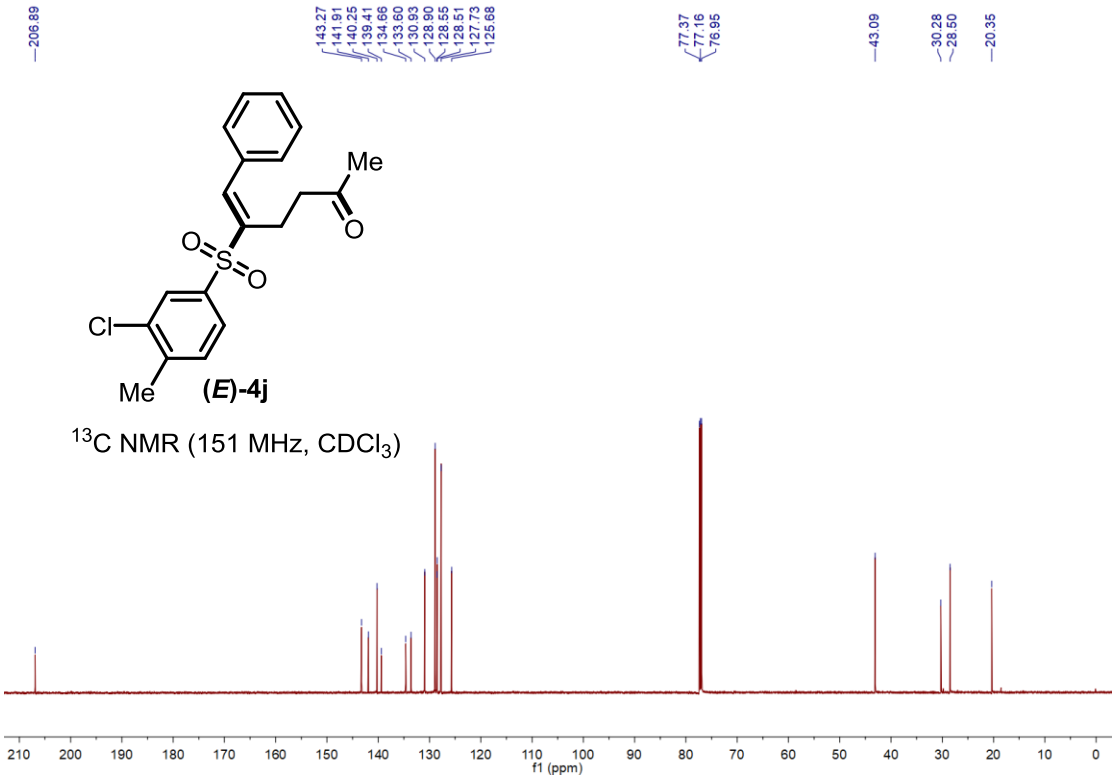

8.271
8.268
8.251
8.249
8.172
7.902
7.823
7.784
7.780
7.765
7.761
7.746
7.742
7.469
7.418
7.417
7.284
2.939
2.900
2.657
2.617
2.176
Me
O
O
O
S
NC
(E)-4i
1H NMR (400 MHz, CDCl3)
1.00
1.00
2.01
1.00
5.03
2.03
2.02
3.00
f1 (ppm)

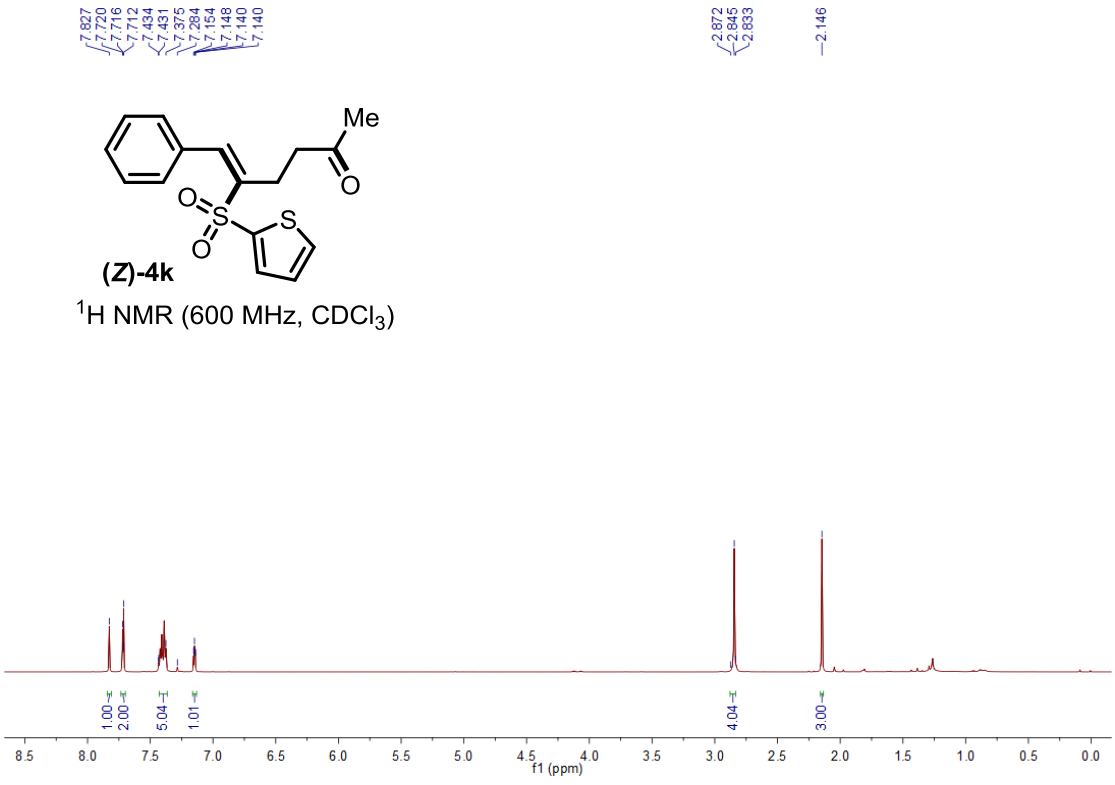

206.76
143.59
141.01
136.95
135.87
133.63
133.22
132.84
131.00
130.34
129.76
129.17
115.70
111.54
77.48
77.16
76.84
42.29
29.99
20.91
Me
O
NC
O
S
O
(E)-4i
13C NMR (101 MHz, CDCl3)
f1 (ppm)

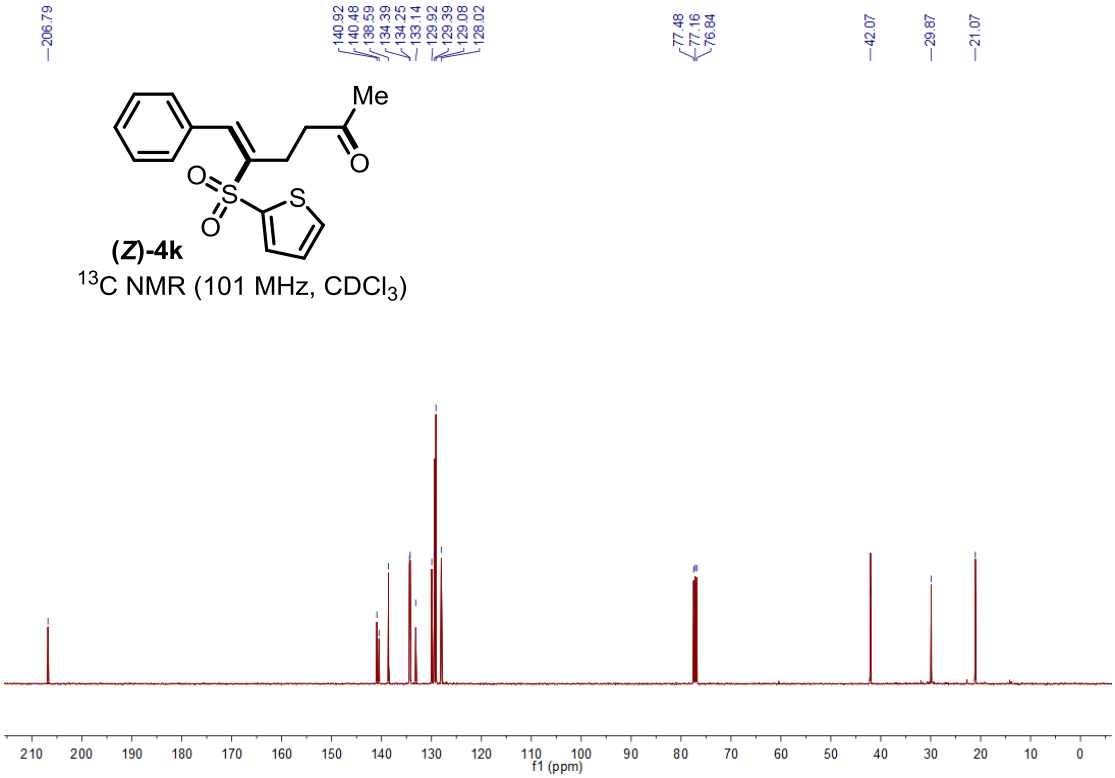

7.878
7.875
7.845
7.707
7.704
7.694
7.691
7.445
7.398
7.284
2.878
2.866
2.852
2.734
2.720
2.707
2.476
2.164
Me
O
O
S
O
Cl
Me
(Z)-4j
1H NMR (600 MHz, CDCl3)
1.00
1.00
1.00
6.04
2.03
2.00
3.02
3.01
f1 (ppm)

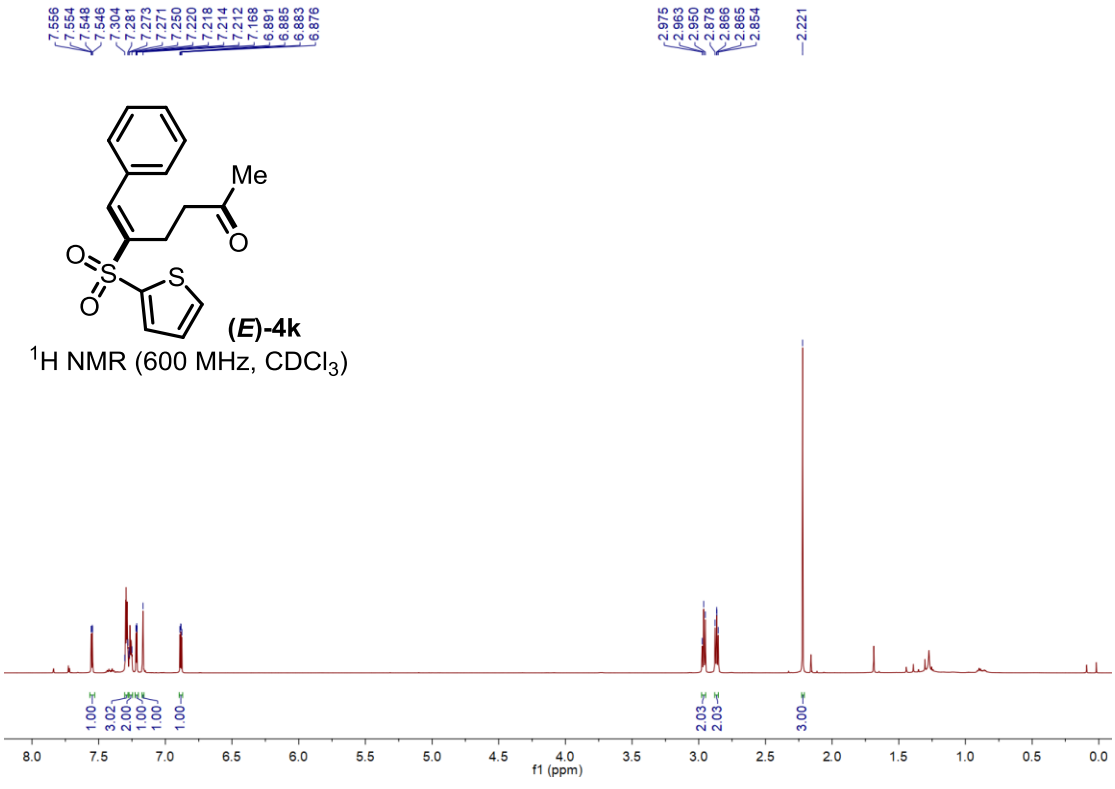

206.89
142.66
139.91
139.39
138.13
135.68
133.17
131.81
130.08
129.52
129.20
128.67
126.40
77.37
77.16
76.95
42.08
29.98
21.14
20.54
Me
O
O
S
O
Cl
Me
(Z)-4j
13C NMR (151 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

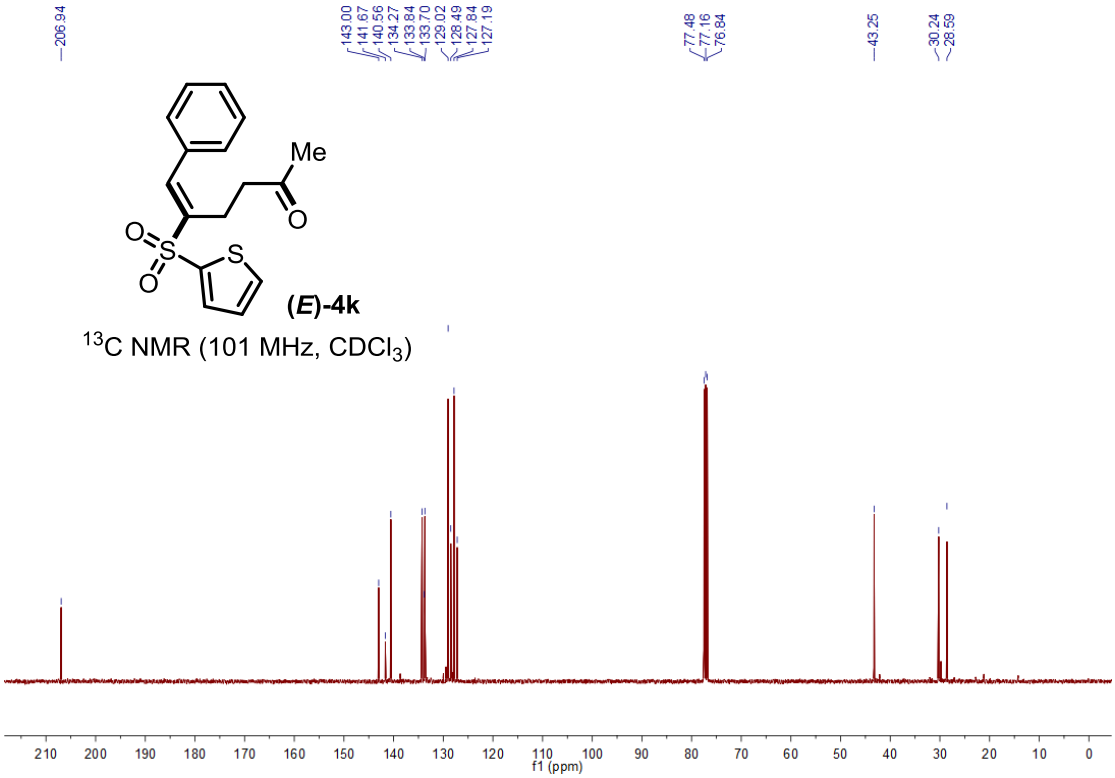

7.361
7.358
7.279
7.252
7.230
7.205
7.148
7.134
7.114
7.096
2.996
2.984
2.972
2.883
2.872
2.859
2.350
2.238
Me
O
O
S
O
Cl
Me
(E)-4j
1H NMR (600 MHz, CDCl3)
1.00
2.02
2.05
2.02
2.00
2.00
2.00
3.01
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

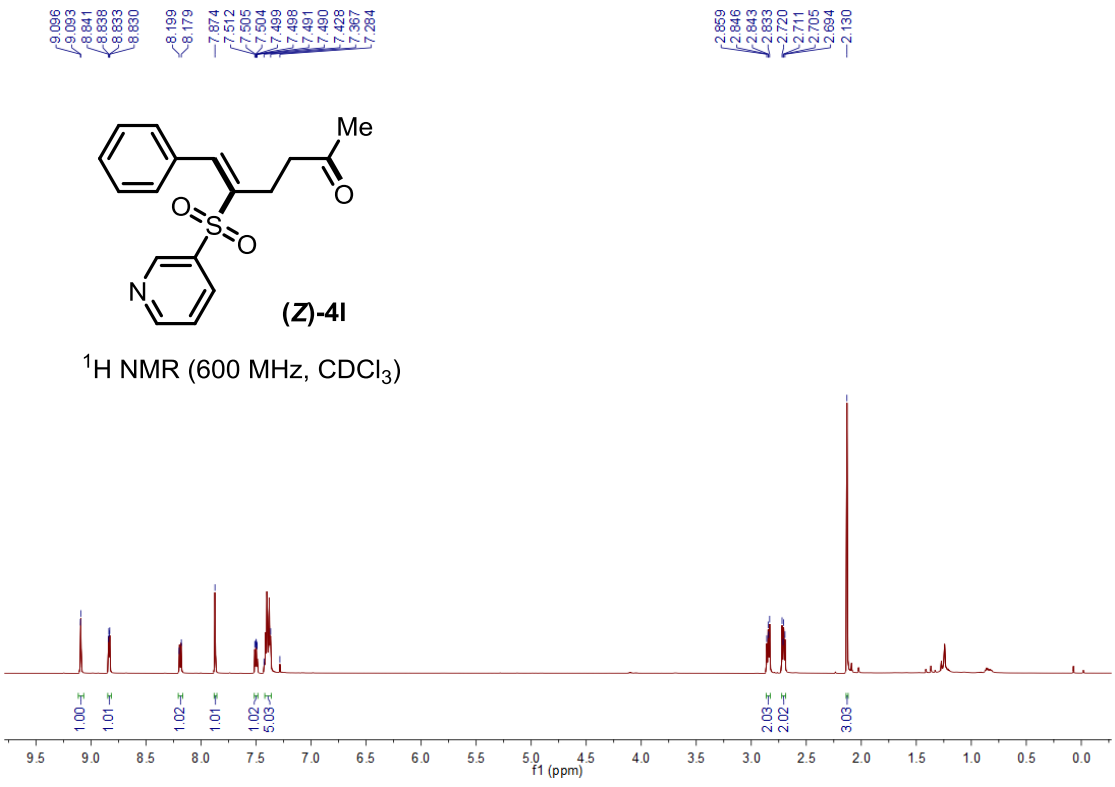

206.89
143.27
141.91
140.25
139.41
134.66
133.60
130.93
128.90
128.55
128.51
127.73
125.68
77.37
77.16
76.95
43.09
30.28
28.50
20.35
Me
O
O
S
O
Cl
Me
(E)-4j
13C NMR (151 MHz, CDCl3)
f1 (ppm)

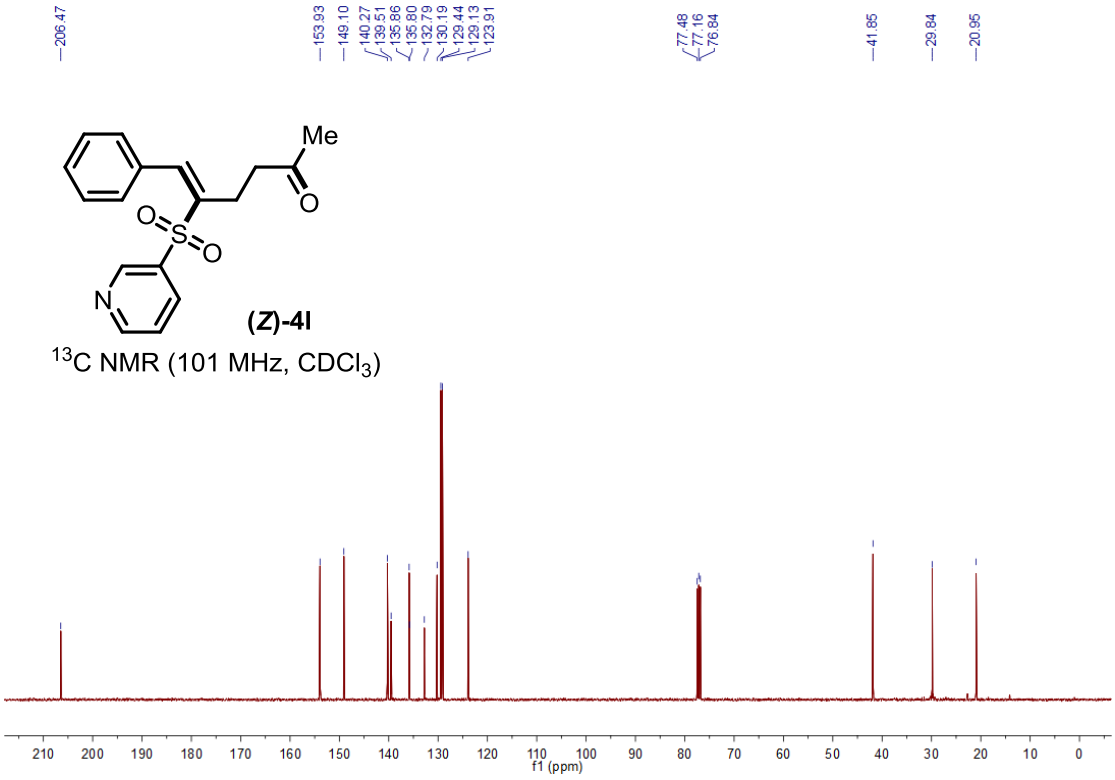

7.827
7.720
7.716
7.712
7.434
7.431
7.375
7.284
7.154
7.148
7.140
7.140
2.872
2.845
2.833
2.146
Me
O
O
S
O
S
(Z)-4k
1H NMR (600 MHz, CDCl3)
1.00
2.00
5.04
1.01
4.04
3.00
f1 (ppm)

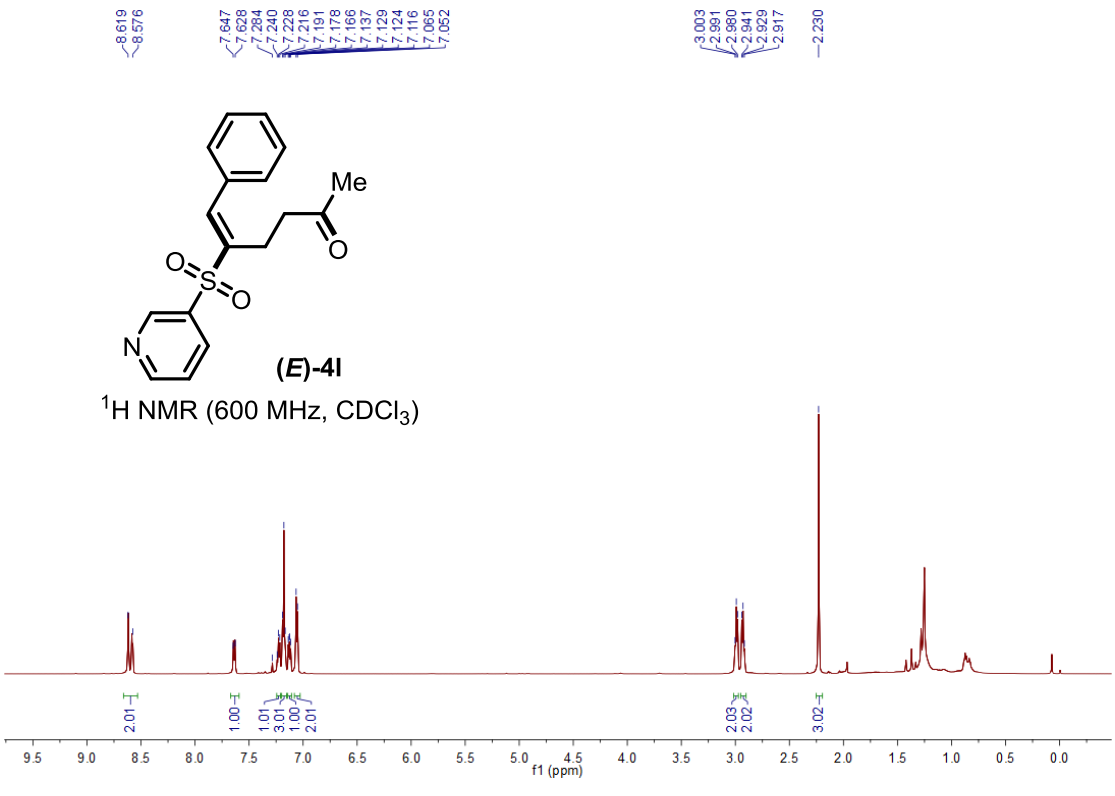

206.79
140.92
140.48
138.59
134.39
134.25
133.14
129.92
129.39
129.08
128.02
77.48
77.16
76.84
42.07
29.87
21.07
Me
O
O
S
O
S
(Z)-4k
13C NMR (101 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

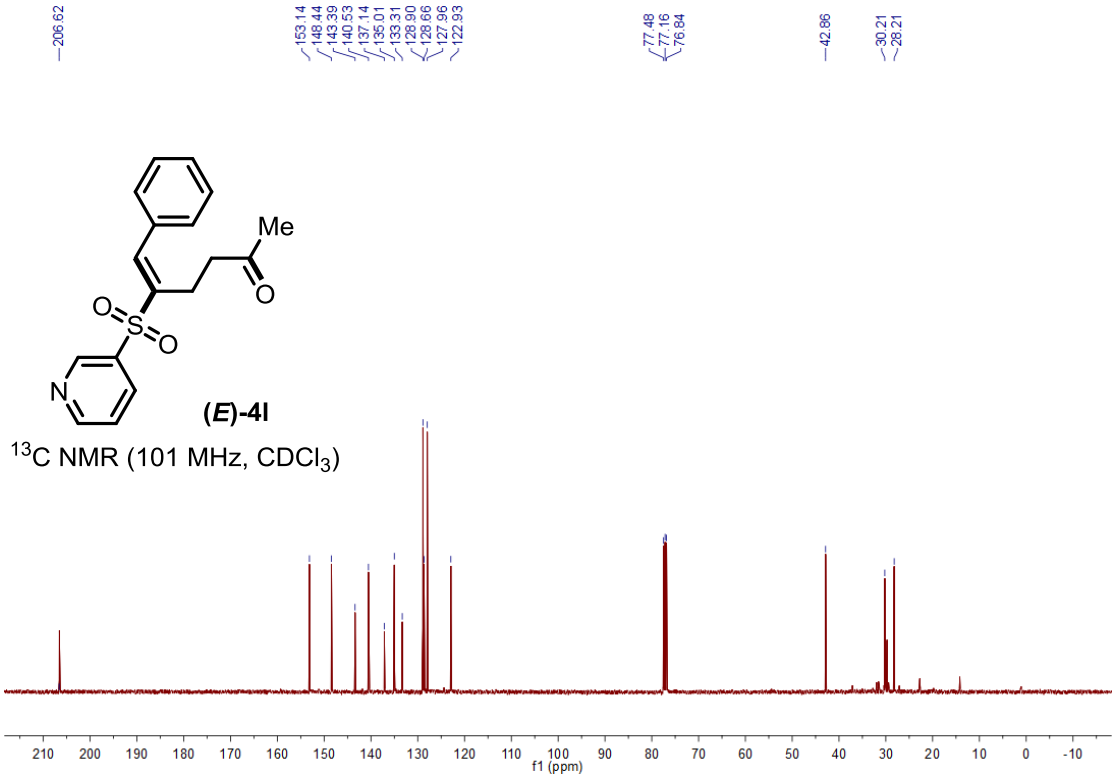

7.556
7.554
7.548
7.546
7.304
7.281
7.273
7.271
7.250
7.220
7.218
7.214
7.212
7.168
6.891
6.885
6.883
6.876
2.975
2.963
2.950
2.878
2.866
2.865
2.854
2.221
Me
O
O
S
O
S
(E)-4k
1H NMR (600 MHz, CDCl3)
1.00
3.02
2.00
1.00
1.00
2.03
2.03
3.00
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

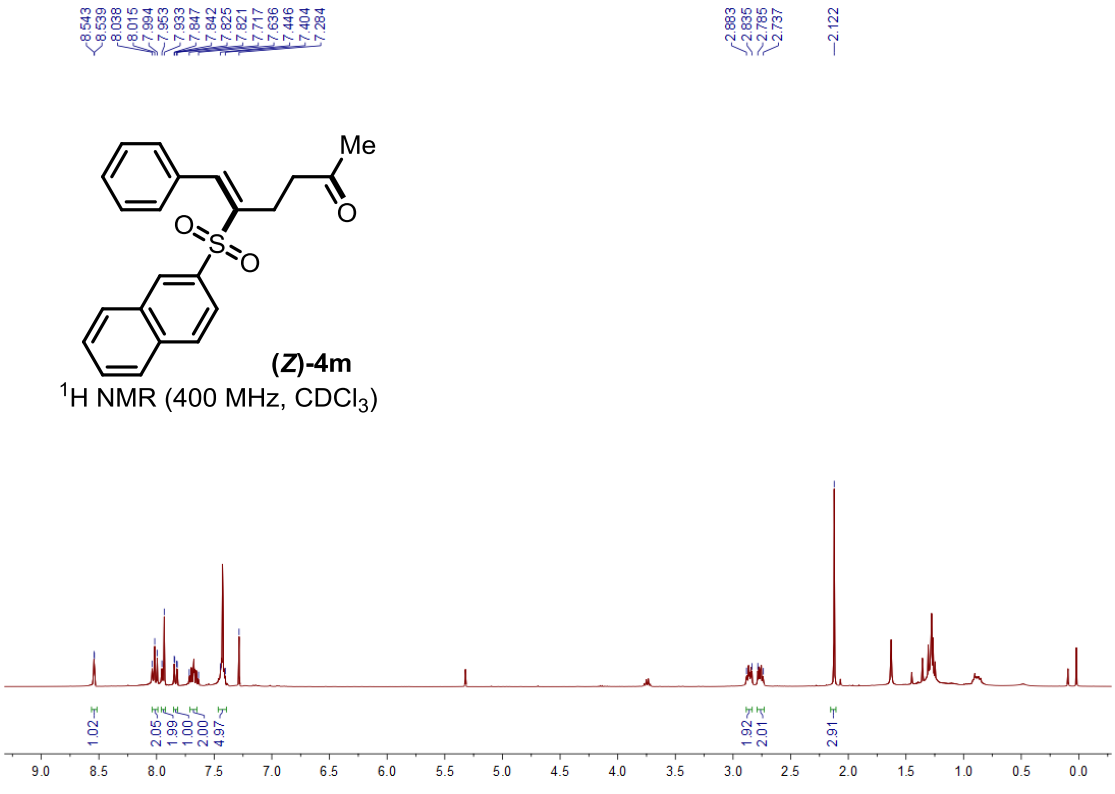

206.94
143.00
141.67
140.56
134.27
133.84
133.70
129.02
128.49
127.84
127.19
77.48
77.16
76.84
43.25
30.24
28.59
Me
O
O
S
O
S
(E)-4k
13C NMR (101 MHz, CDCl3)
f1 (ppm)

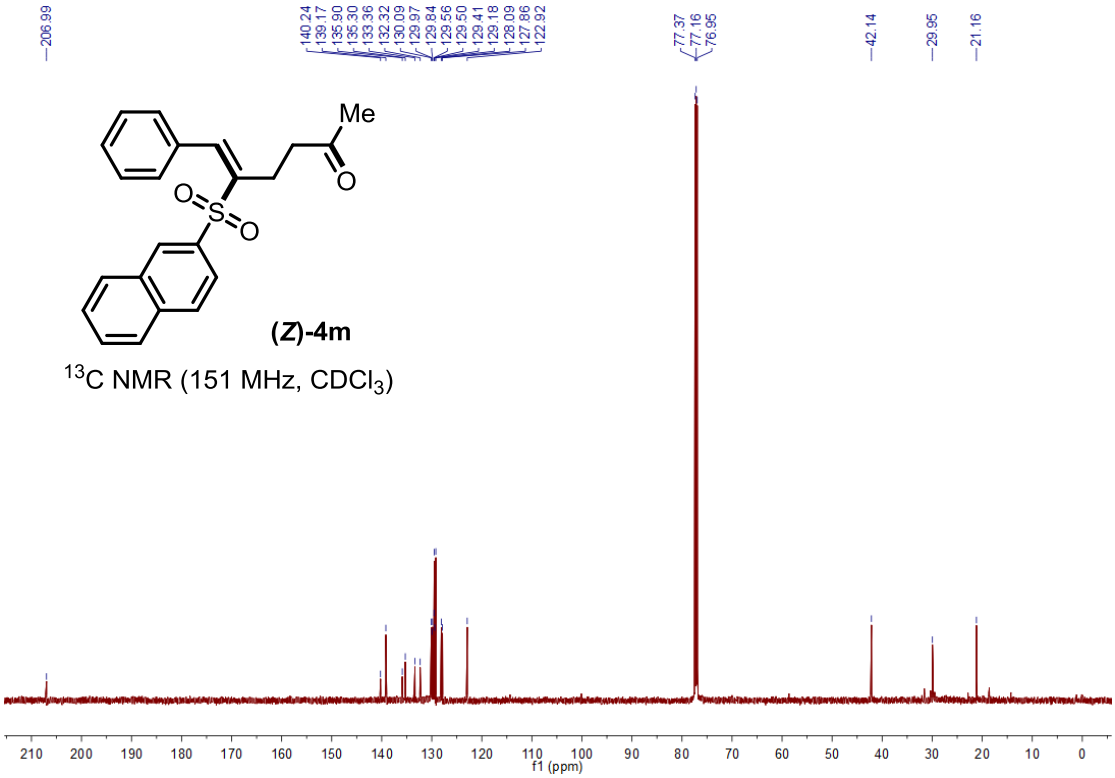

9.096
9.093
8.841
8.838
8.833
8.830
8.199
8.179
7.874
7.512
7.505
7.504
7.499
7.498
7.491
7.490
7.428
7.367
7.284
2.859
2.846
2.843
2.833
2.720
2.711
2.705
2.694
2.130
Me
O
O
S
O
N
(Z)-4l
1H NMR (600 MHz, CDCl3)
1.00
1.01
1.02
1.01
1.02
5.03
2.03
2.02
3.03
f1 (ppm)


206.47
153.93
149.10
140.27
139.51
135.86
135.80
132.79
130.19
129.44
129.13
123.91
77.48
77.16
76.84
41.85
29.84
20.95
Me
O
O
S
O
N
(Z)-4l
13C NMR (101 MHz, CDCl3)
f1 (ppm)


8.619
8.576
7.647
7.628
7.284
7.240
7.228
7.216
7.191
7.178
7.166
7.137
7.129
7.124
7.116
7.065
7.052
3.003
2.991
2.980
2.941
2.929
2.917
2.230
Me
O
O
S
O
N
(E)-4l
1H NMR (600 MHz, CDCl3)
2.01
1.00
1.01
3.01
1.00
2.01
2.03
2.02
3.02
f1 (ppm)

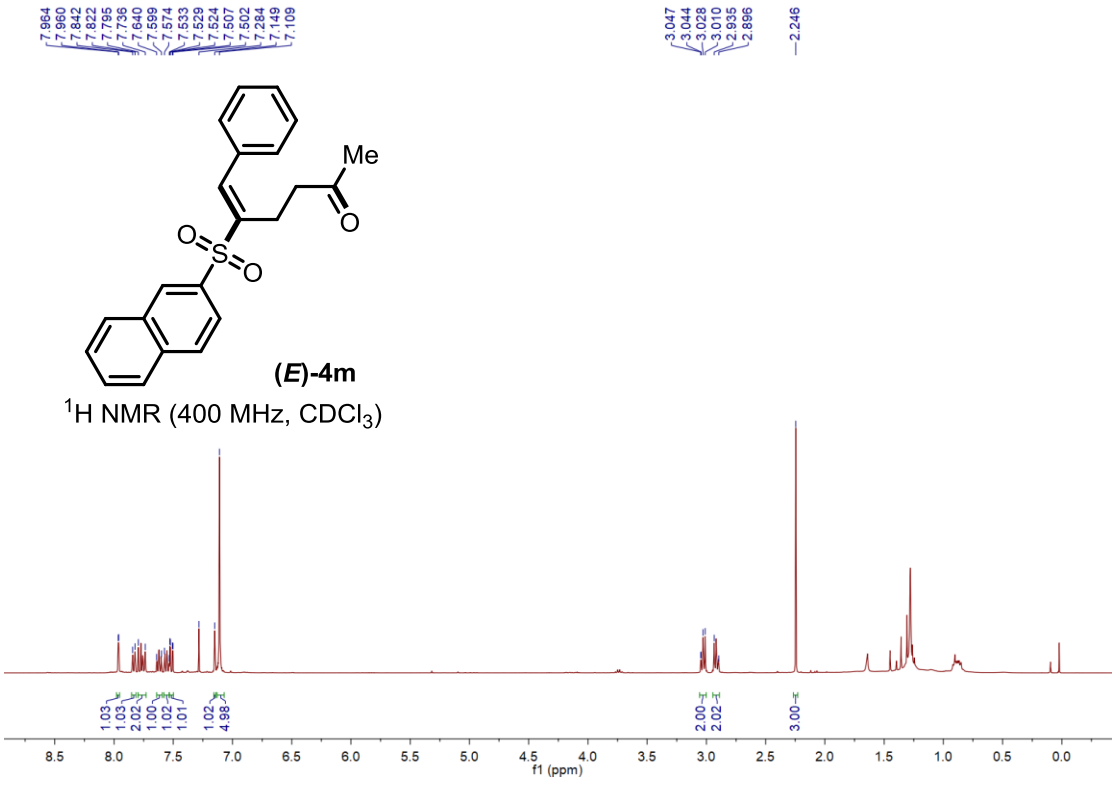

206.62
153.14
148.44
143.39
140.53
137.14
135.01
133.31
128.90
128.66
127.96
122.93
77.48
77.16
76.84
42.86
30.21
28.21
Me
O
O
S
O
N
(E)-4l
13C NMR (101 MHz, CDCl3)
f1 (ppm)


8.543
8.539
8.038
8.015
7.994
7.953
7.933
7.847
7.842
7.825
7.821
7.717
7.636
7.446
7.404
7.284
2.883
2.835
2.785
2.737
2.122
Me
O
O
S
O
(Z)-4m
1H NMR (400 MHz, CDCl3)
1.02
2.05
1.99
1.00
2.00
4.97
1.92
2.01
2.91



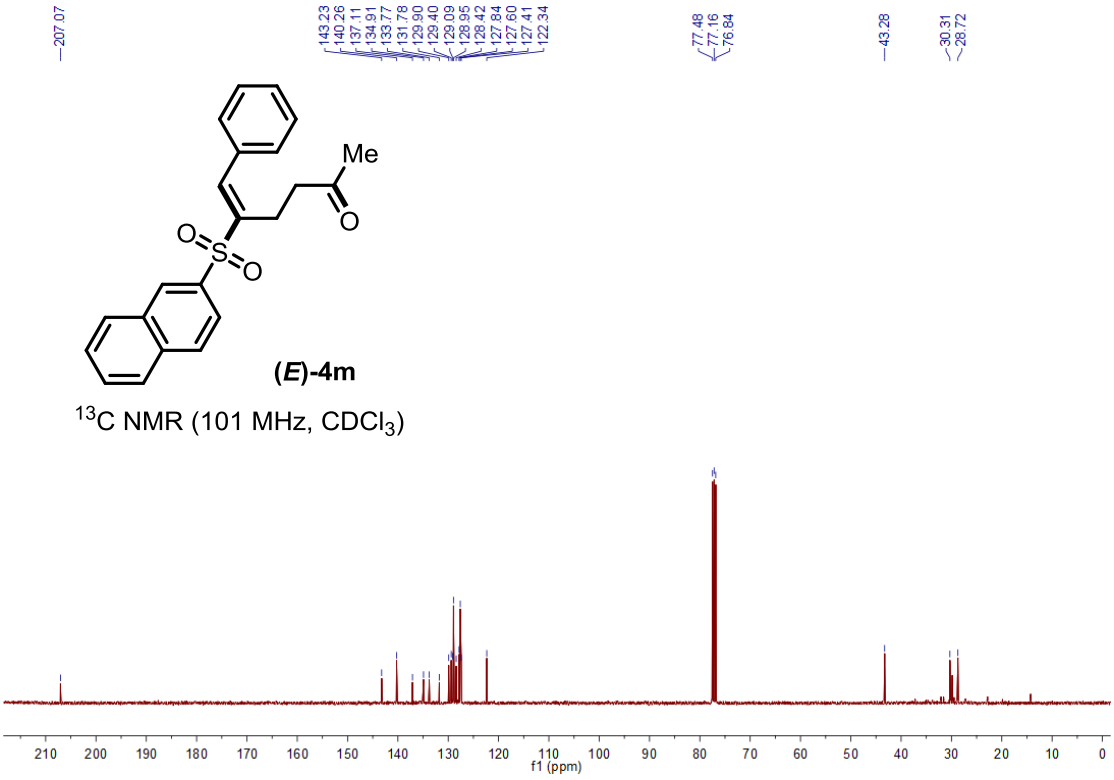
(*Z*)-4m

^{13}C NMR (151 MHz, $CDCl_3$)



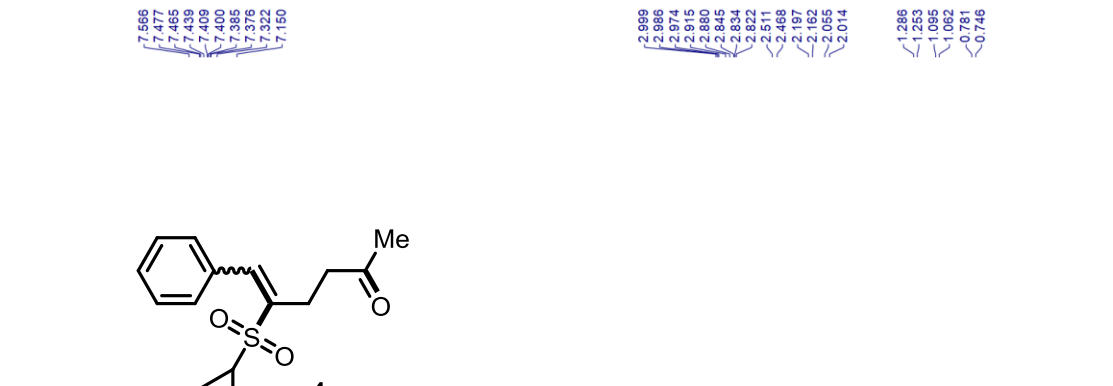
(*E*)-4m

^{1}H NMR (400 MHz, $CDCl_3$)



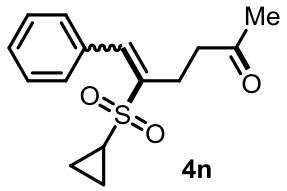
(*E*)-4m

^{13}C NMR (101 MHz, $CDCl_3$)



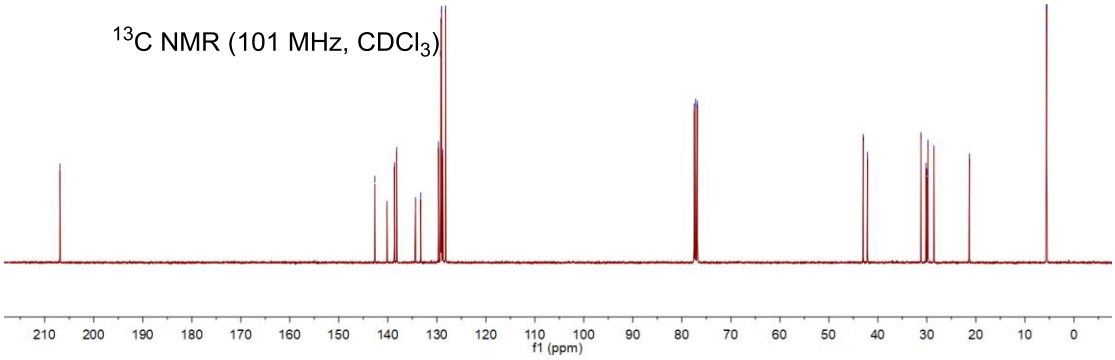
4n

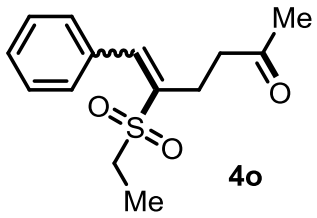
^{1}H NMR (600 MHz, $CDCl_3$)



4n

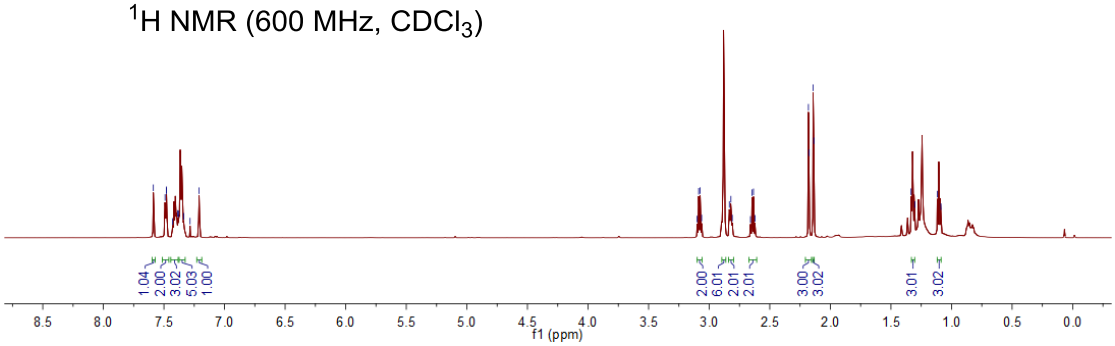
^{13}C NMR (101 MHz, $CDCl_3$)

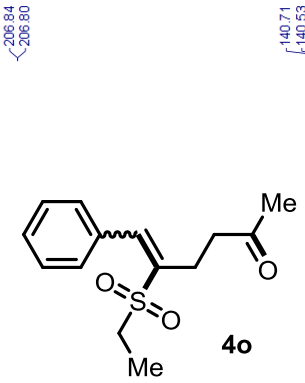




4o

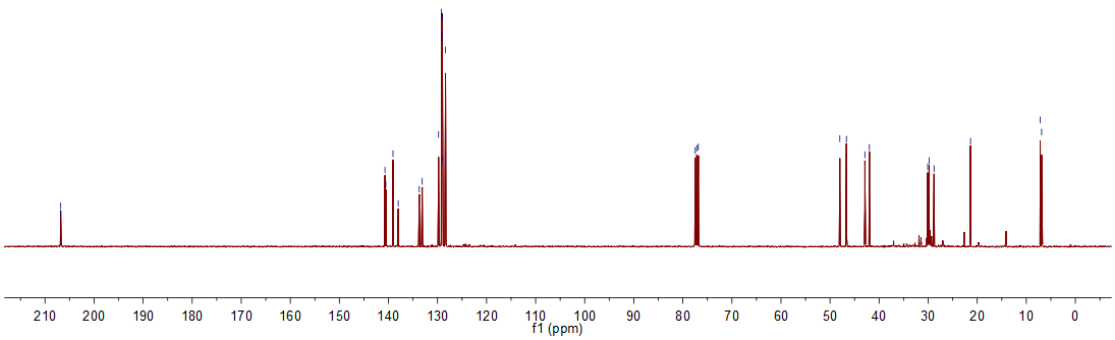
^{1}H NMR (600 MHz, $CDCl_3$)

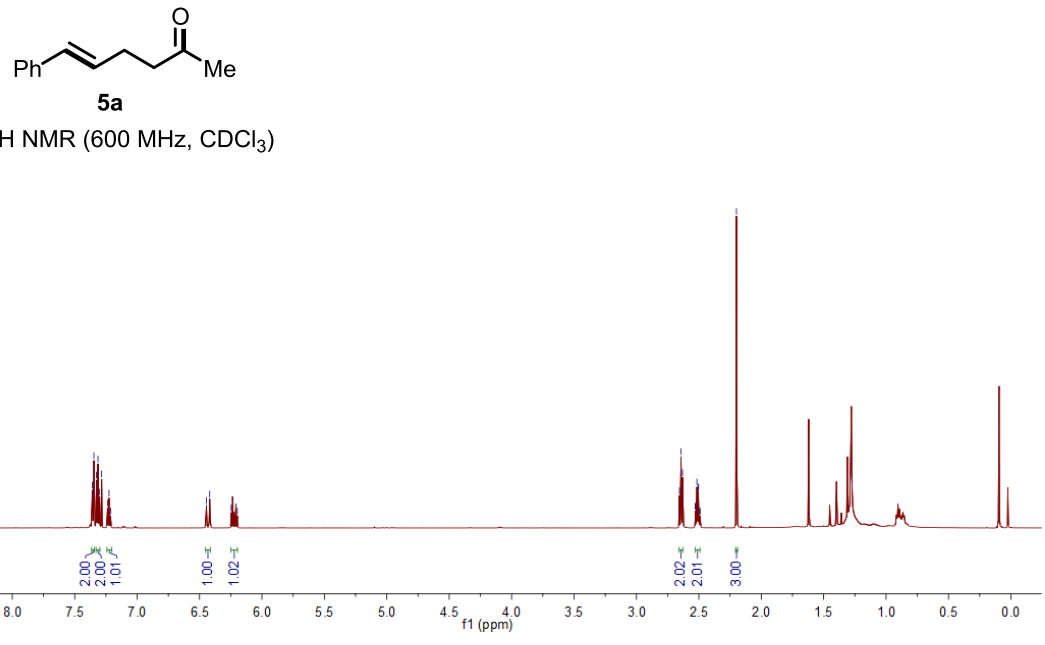




4o

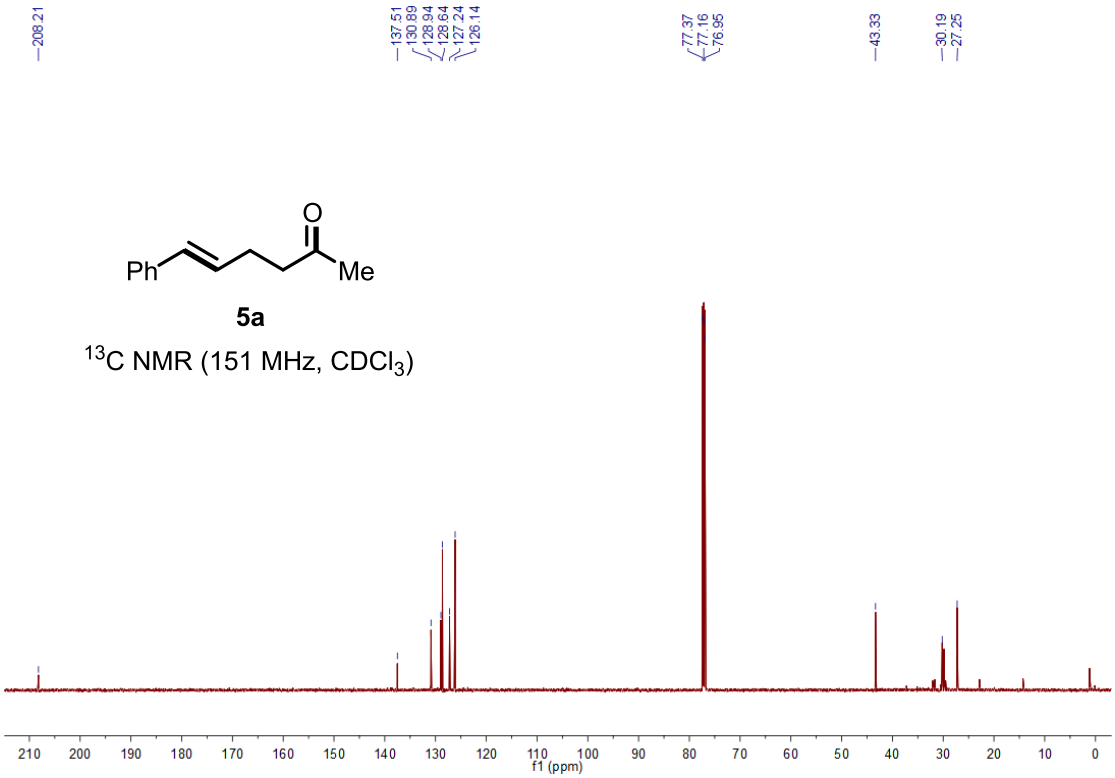
^{13}C NMR (101 MHz, $CDCl_3$)





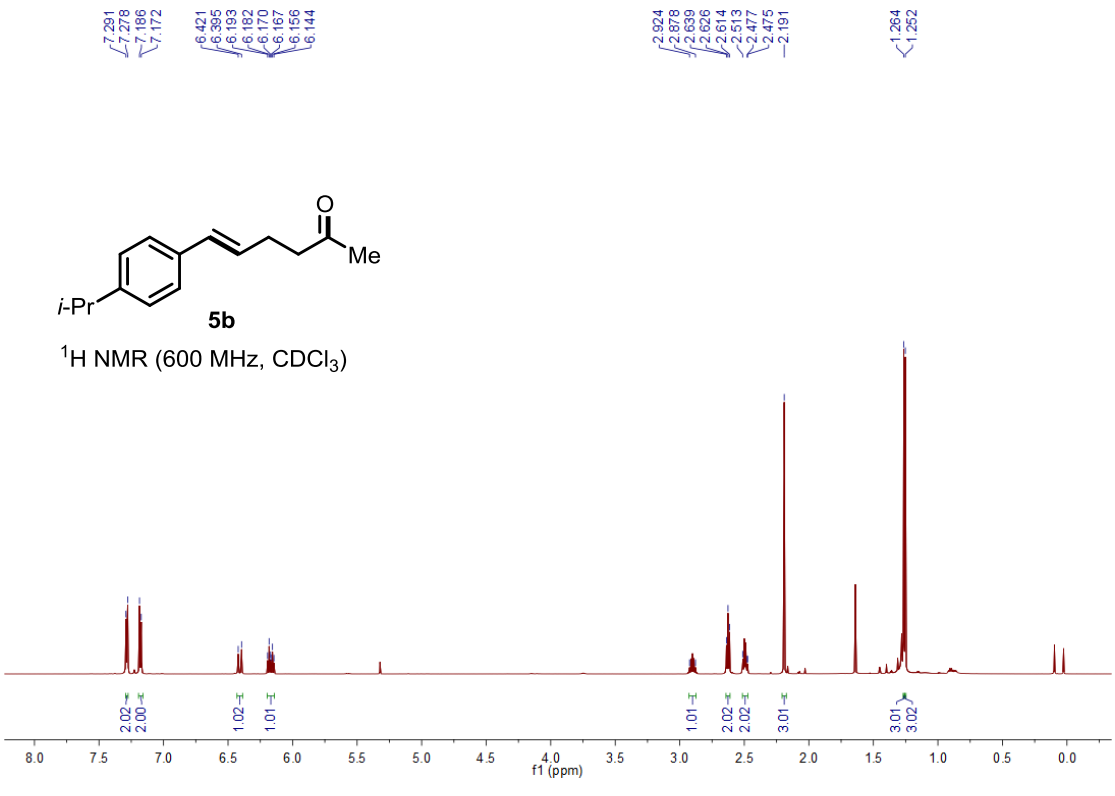
5a

^{1}H NMR (600 MHz, $CDCl_3$)



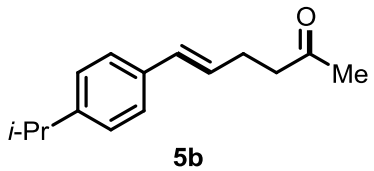
5a

^{13}C NMR (151 MHz, $CDCl_3$)



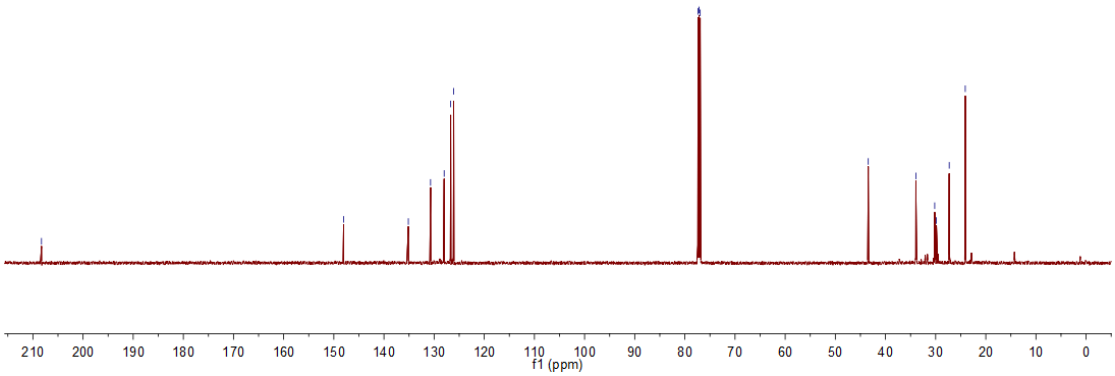
5b

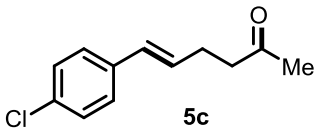
^{1}H NMR (600 MHz, $CDCl_3$)



5b

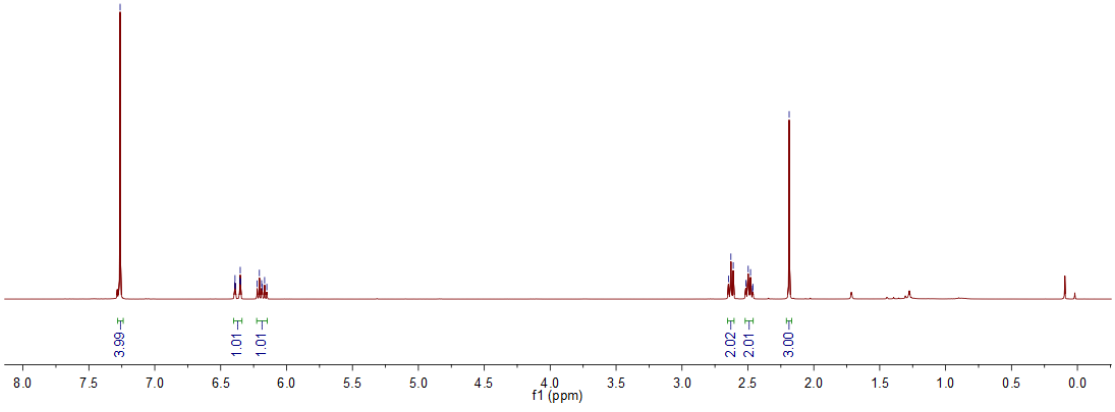
^{13}C NMR (151 MHz, $CDCl_3$)

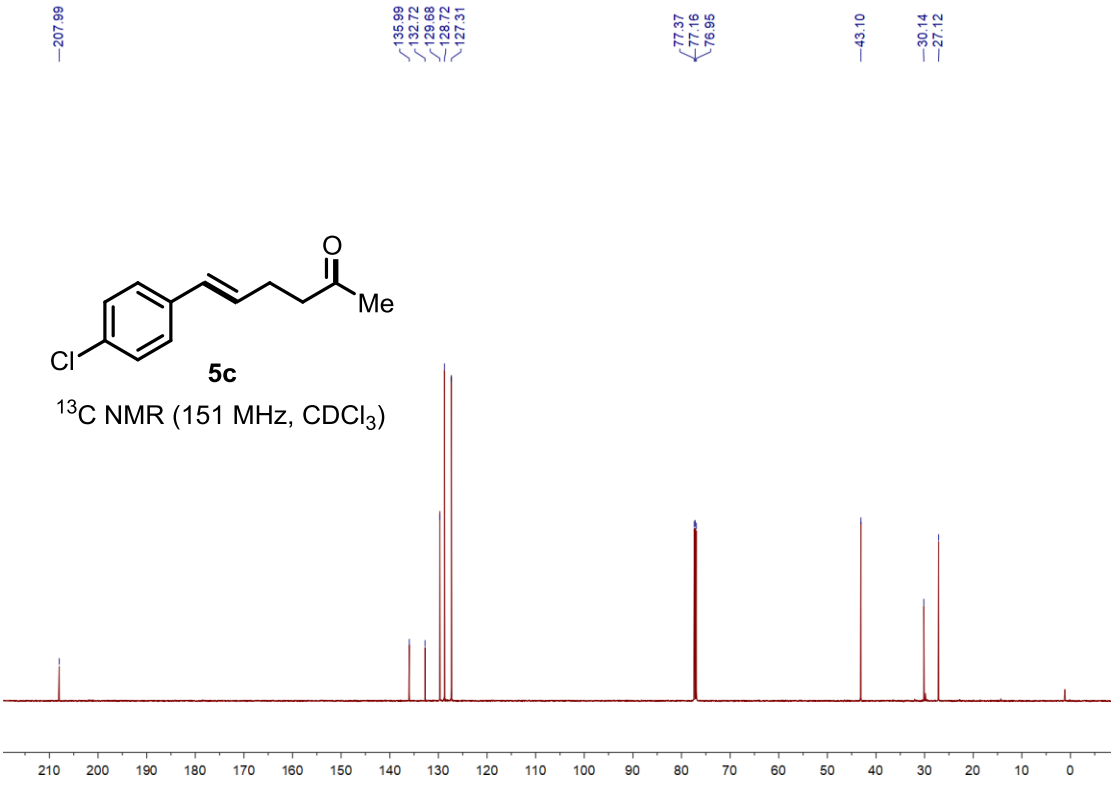


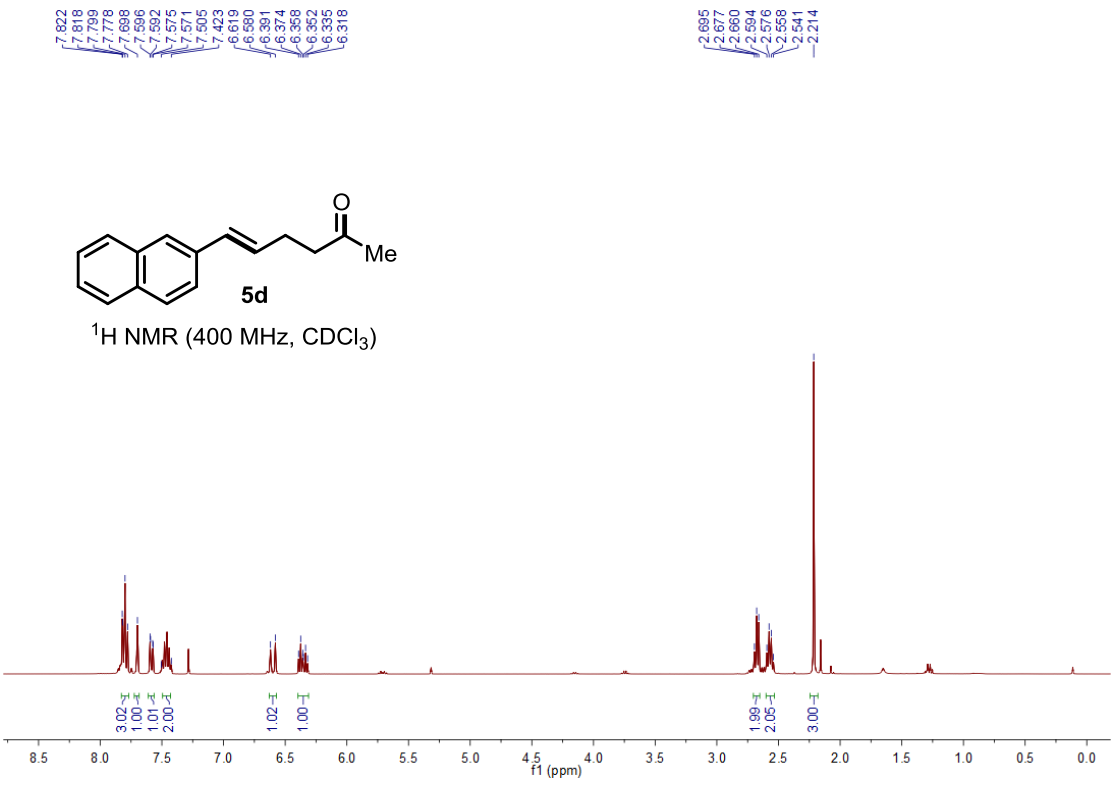


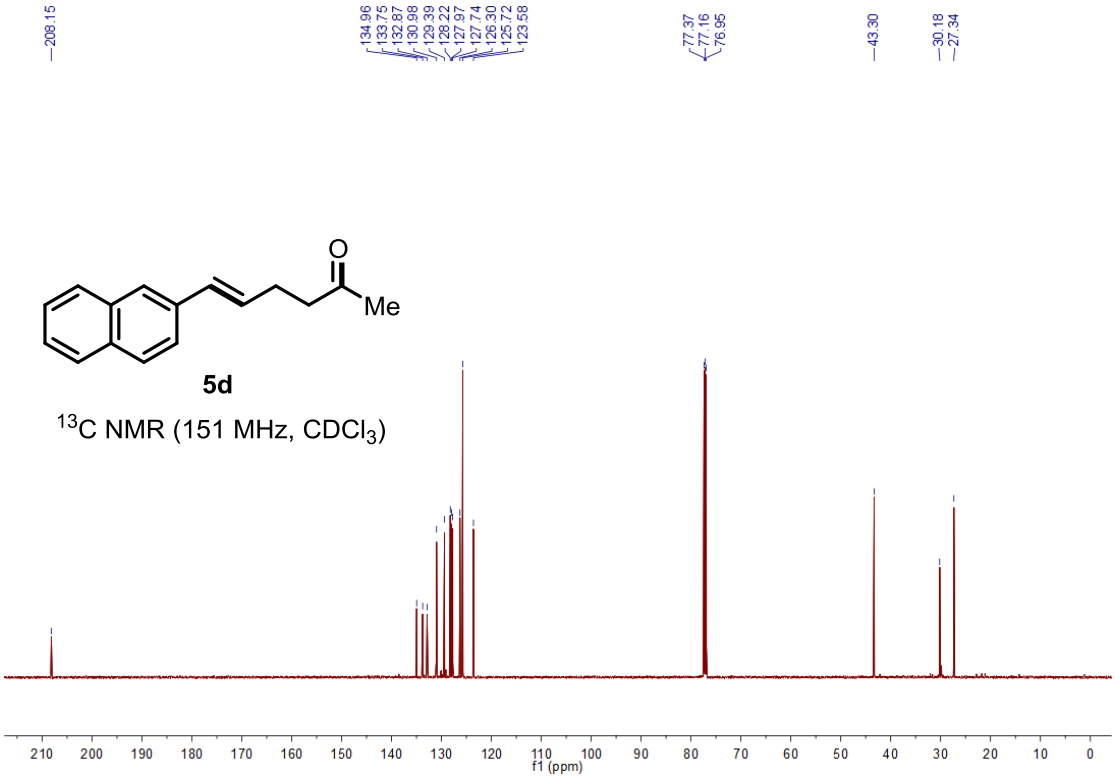
5c

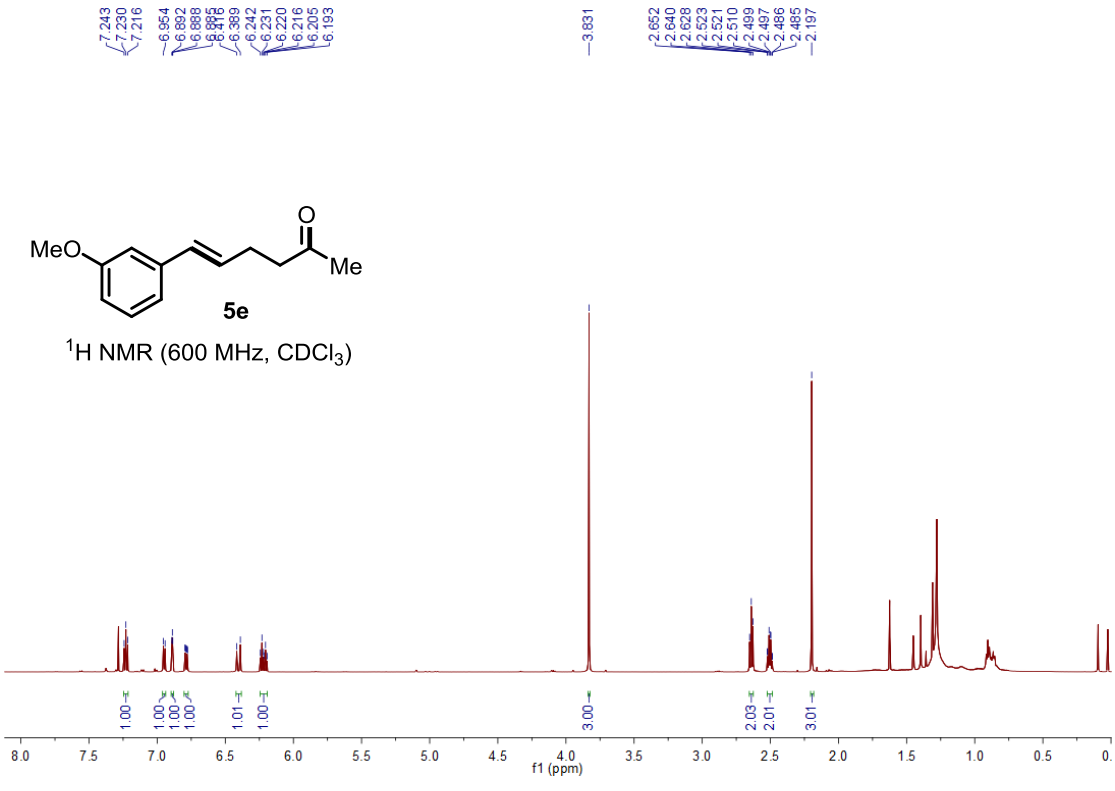
^{1}H NMR (400 MHz, $CDCl_3$)

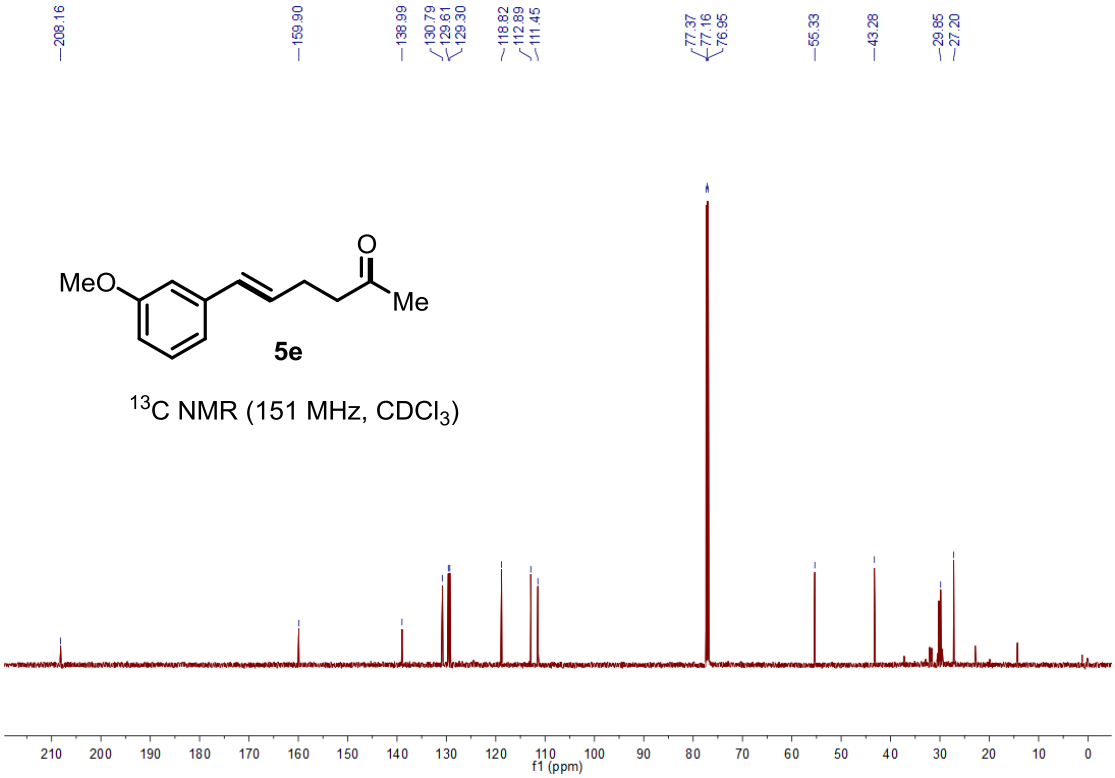



207.99
135.99
132.72
129.68
128.72
127.31
77.37
77.16
76.95
43.10
30.14
27.12
O
Me
Cl
5c
13C NMR (151 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

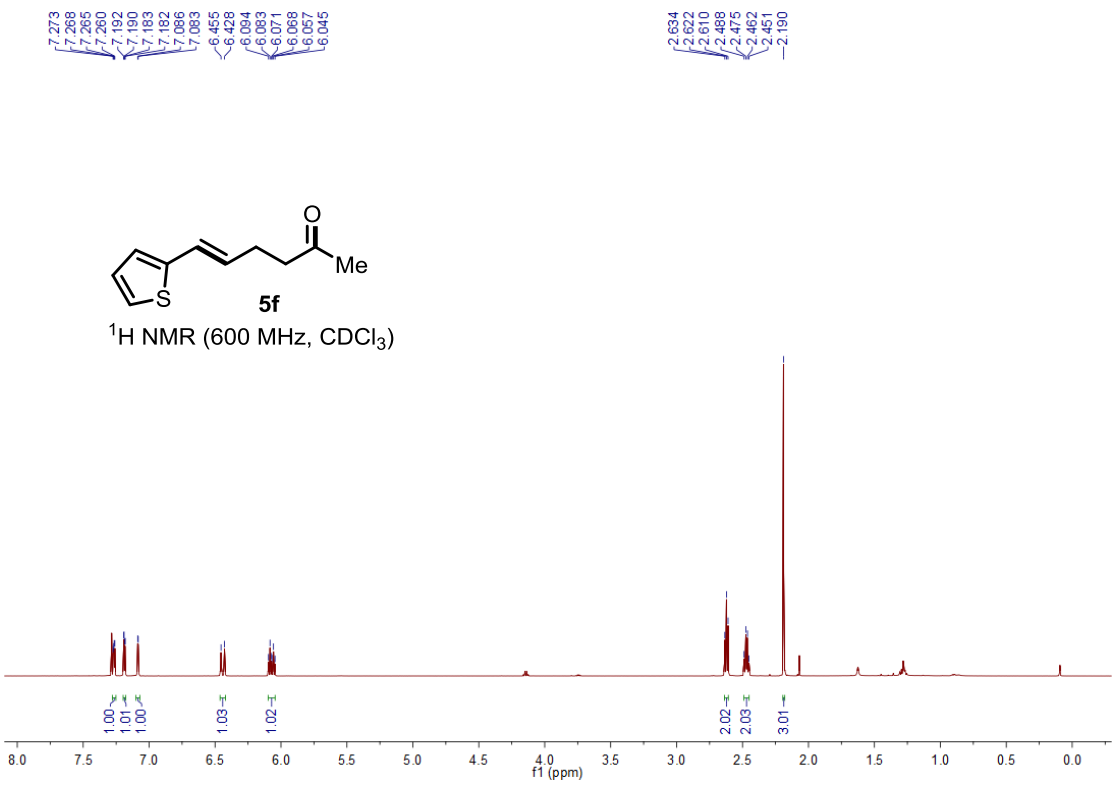

7.822
7.818
7.799
7.778
7.698
7.596
7.592
7.575
7.571
7.505
7.423
6.619
6.580
6.391
6.374
6.358
6.352
6.335
6.318
2.695
2.677
2.660
2.594
2.576
2.558
2.541
2.214
O
Me
5d
1H NMR (400 MHz, CDCl3)
3.02
1.00
1.01
2.00
1.02
1.00
1.99
2.05
3.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


208.15
134.96
133.75
132.87
130.98
129.39
128.22
127.97
127.74
126.30
125.72
123.58
77.37
77.16
76.95
43.30
30.18
27.34
O
Me
5d
13C NMR (151 MHz, CDCl3)
f1 (ppm)

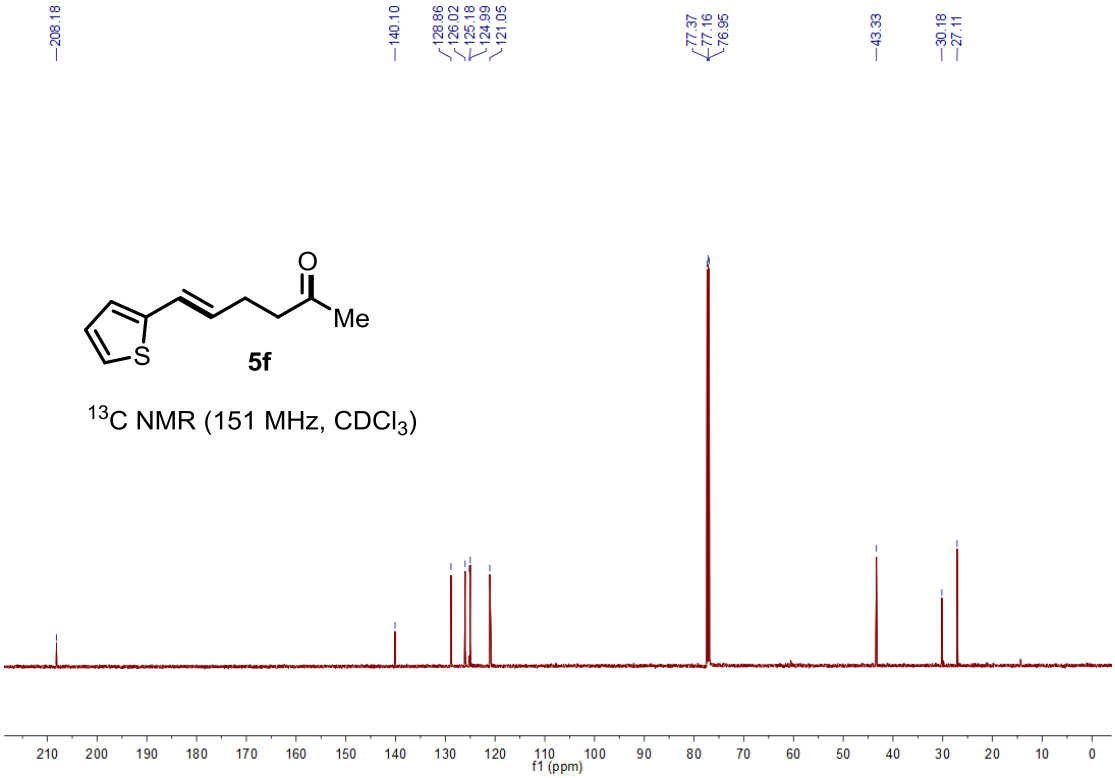

7.243
7.230
7.216
6.954
6.892
6.888
6.885
6.389
6.242
6.231
6.220
6.216
6.205
6.193
3.831
2.652
2.640
2.628
2.523
2.521
2.510
2.499
2.497
2.486
2.485
2.197
MeO
O
Me
5e
1H NMR (600 MHz, CDCl3)
1.00
1.00
1.00
1.00
1.01
1.00
3.00
2.03
2.01
3.01
f1 (ppm)



^{13}C NMR (151 MHz, $CDCl_3$)

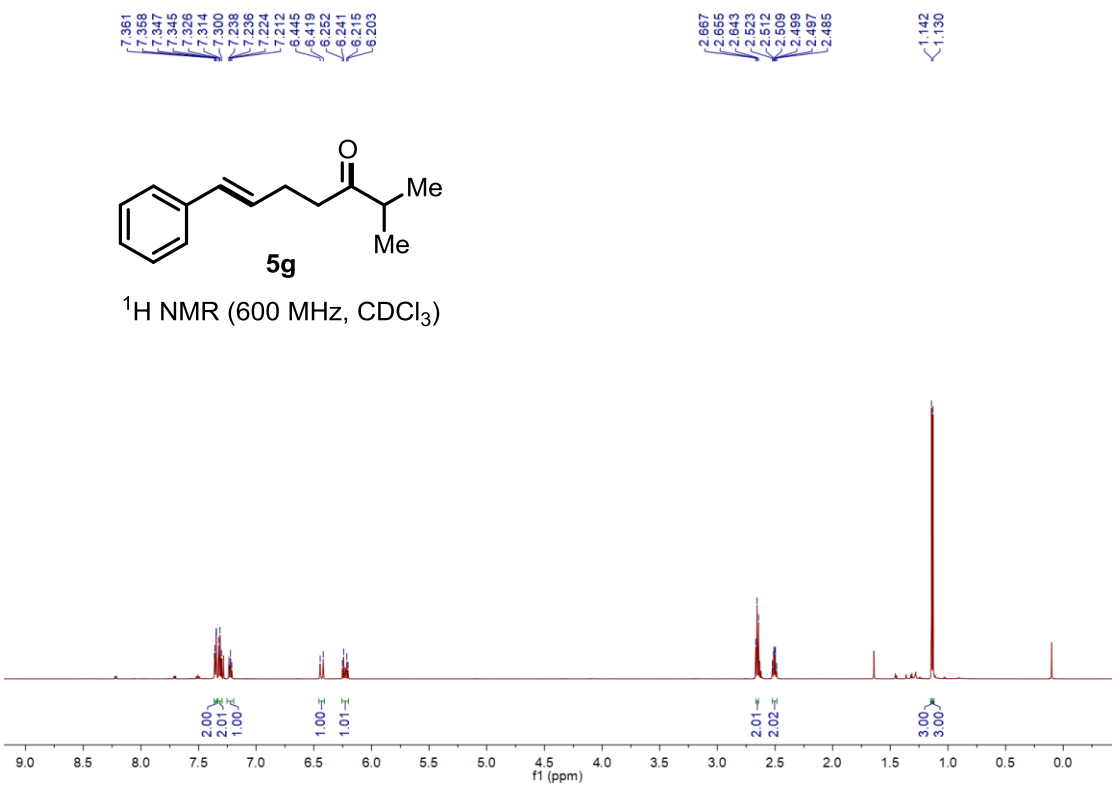


^{1}H NMR (600 MHz, $CDCl_3$)



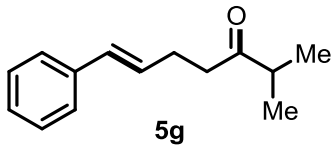
5f

^{13}C NMR (151 MHz, $CDCl_3$)



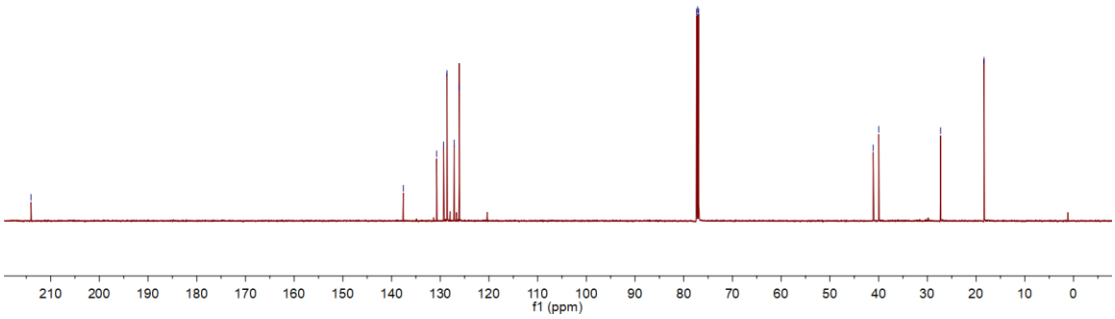
5g

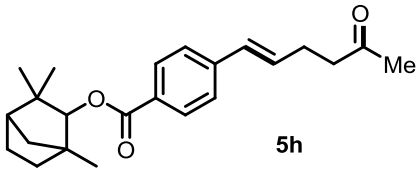
^{1}H NMR (600 MHz, $CDCl_3$)



5g

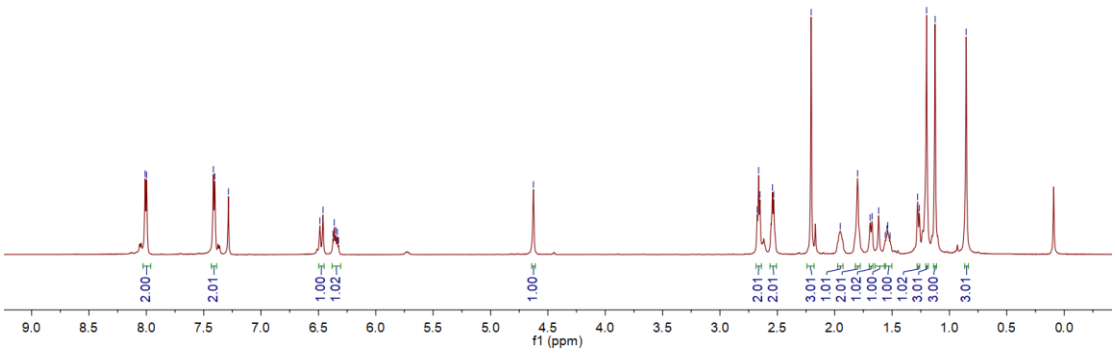
^{13}C NMR (151 MHz, $CDCl_3$)

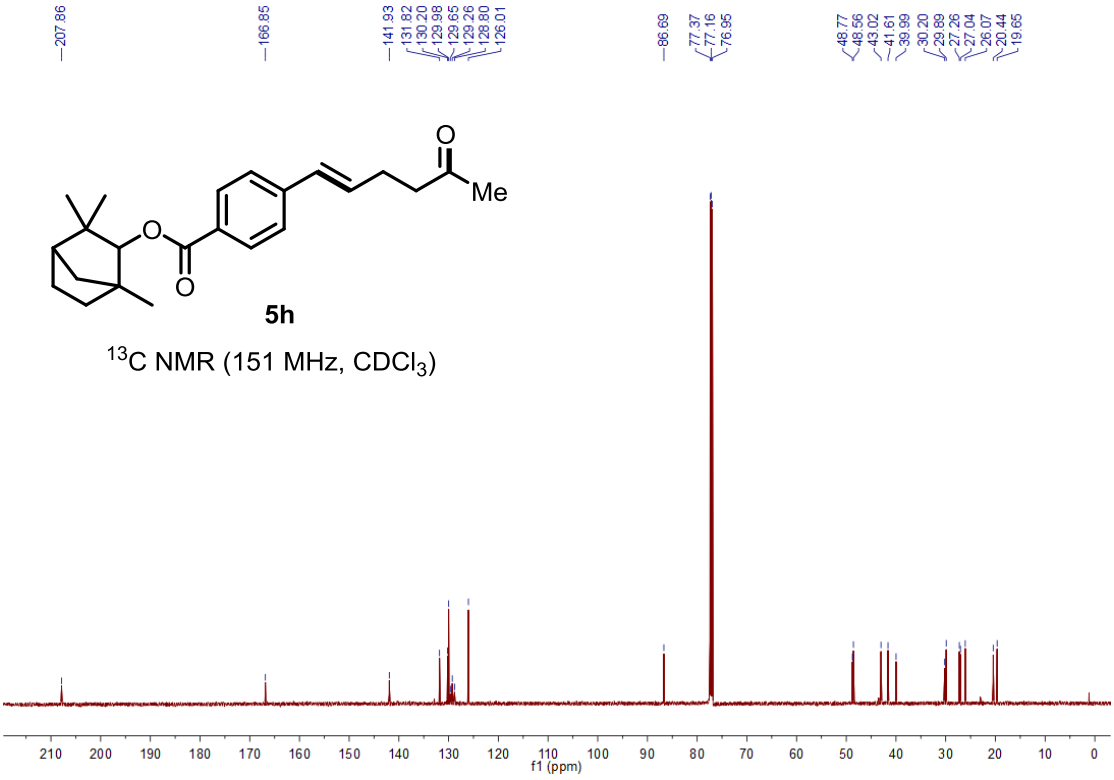




5h

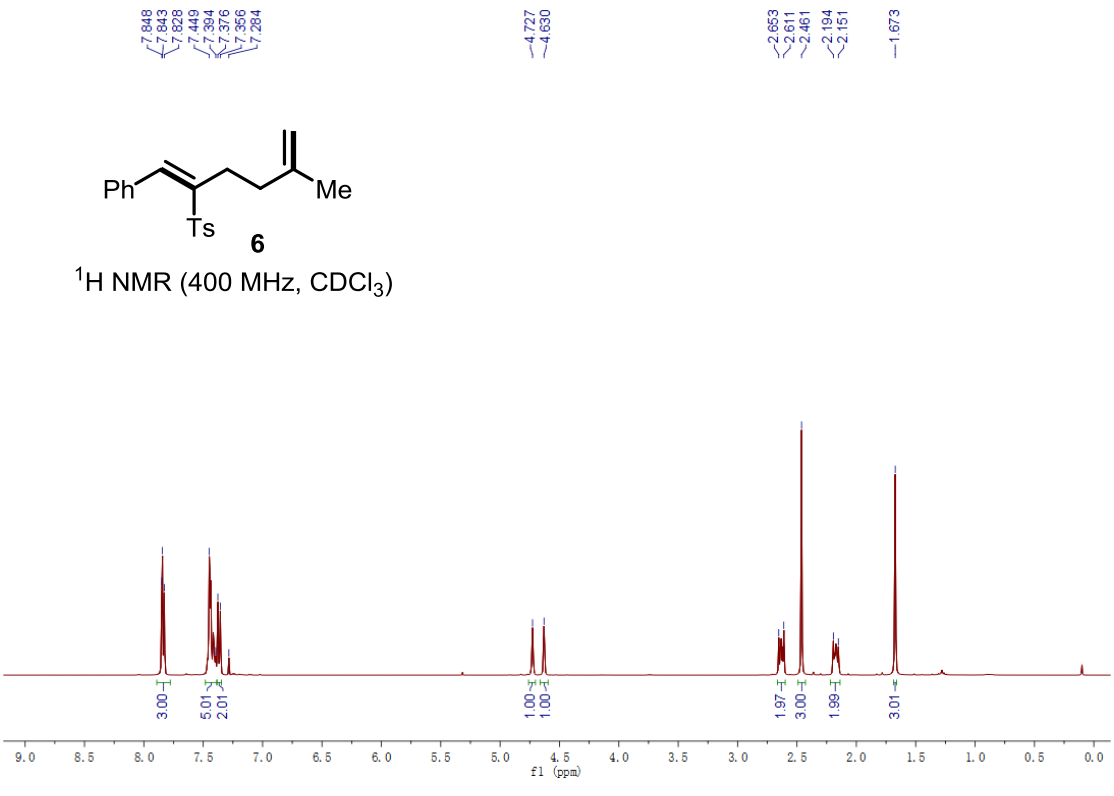
^{1}H NMR (600 MHz, $CDCl_3$)





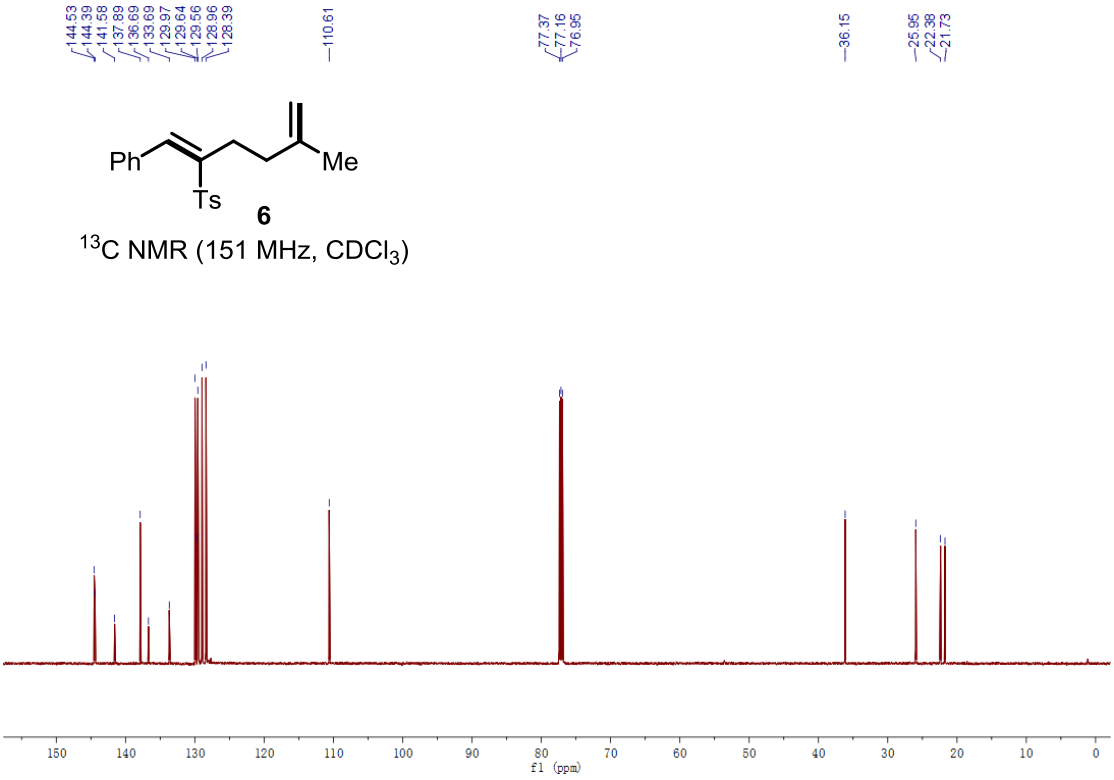
5h

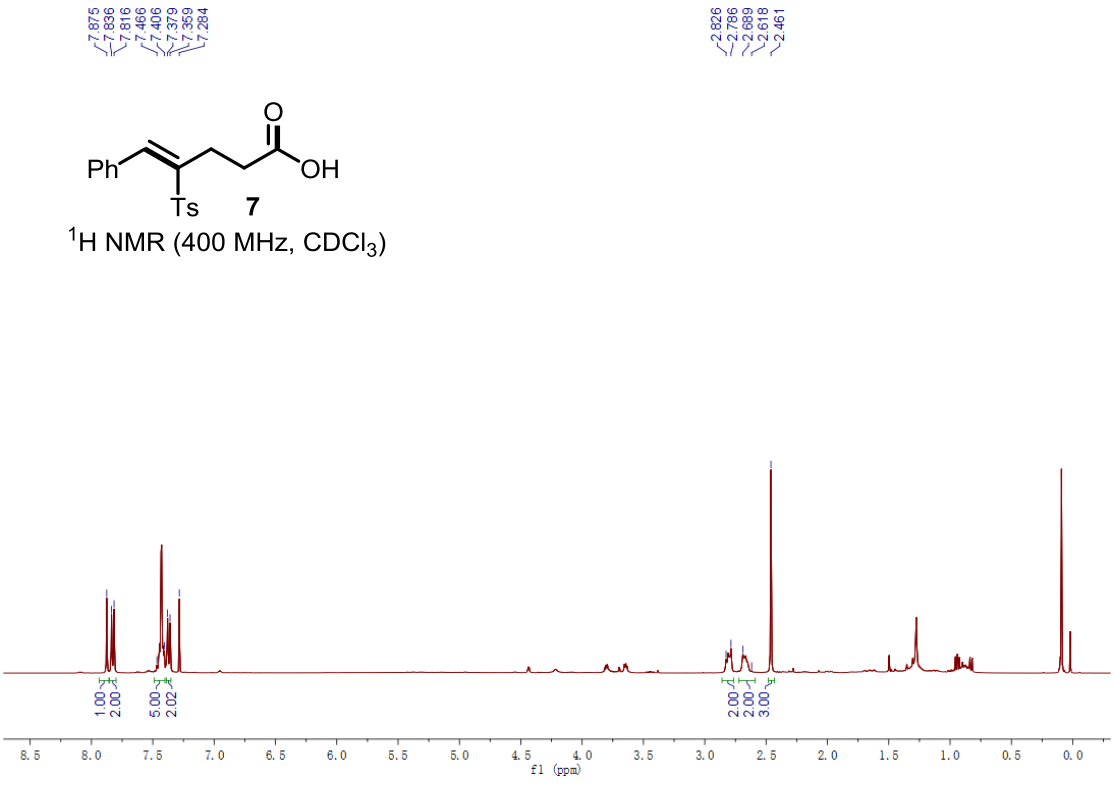
^{13}C NMR (151 MHz, $CDCl_3$)

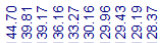


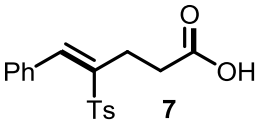
6

^{1}H NMR (400 MHz, $CDCl_3$)


144.53
144.39
141.58
137.89
136.69
133.69
129.97
129.64
129.56
128.96
128.39
110.61
77.37
77.16
76.95
36.15
25.95
22.38
21.73
Ph
Ts
Me
6
13C NMR (151 MHz, CDCl3)
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

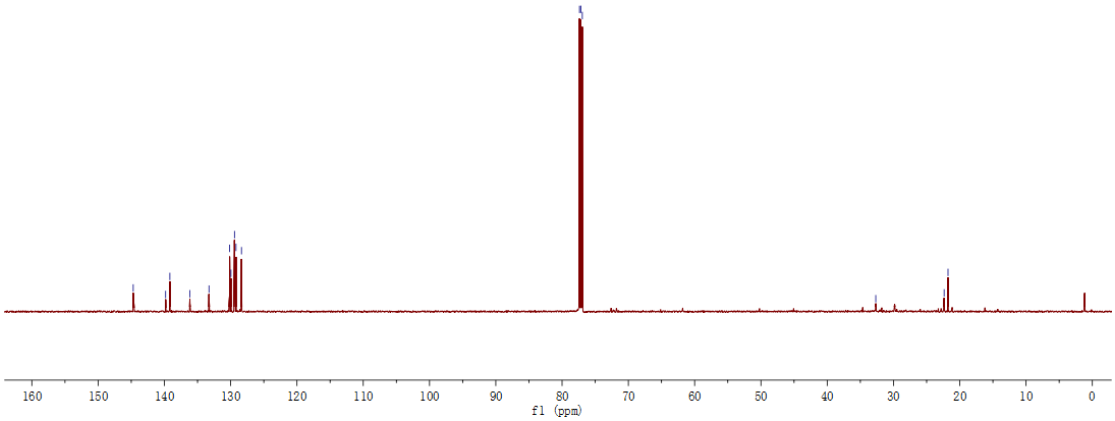

7.875
7.836
7.816
7.466
7.406
7.379
7.359
7.284
2.826
2.786
2.689
2.618
2.461
Ph
Ts
O
OH
7
1H NMR (400 MHz, CDCl3)
1.00
2.00
5.00
2.02
2.00
2.00
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

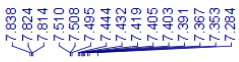


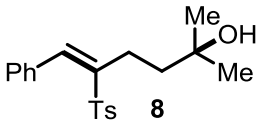


7

^{13}C NMR (151 MHz, $CDCl_3$)

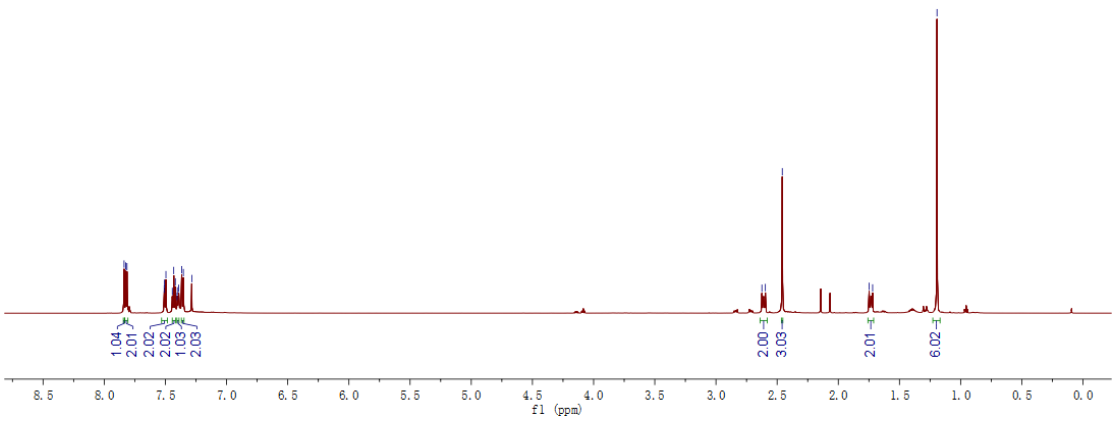


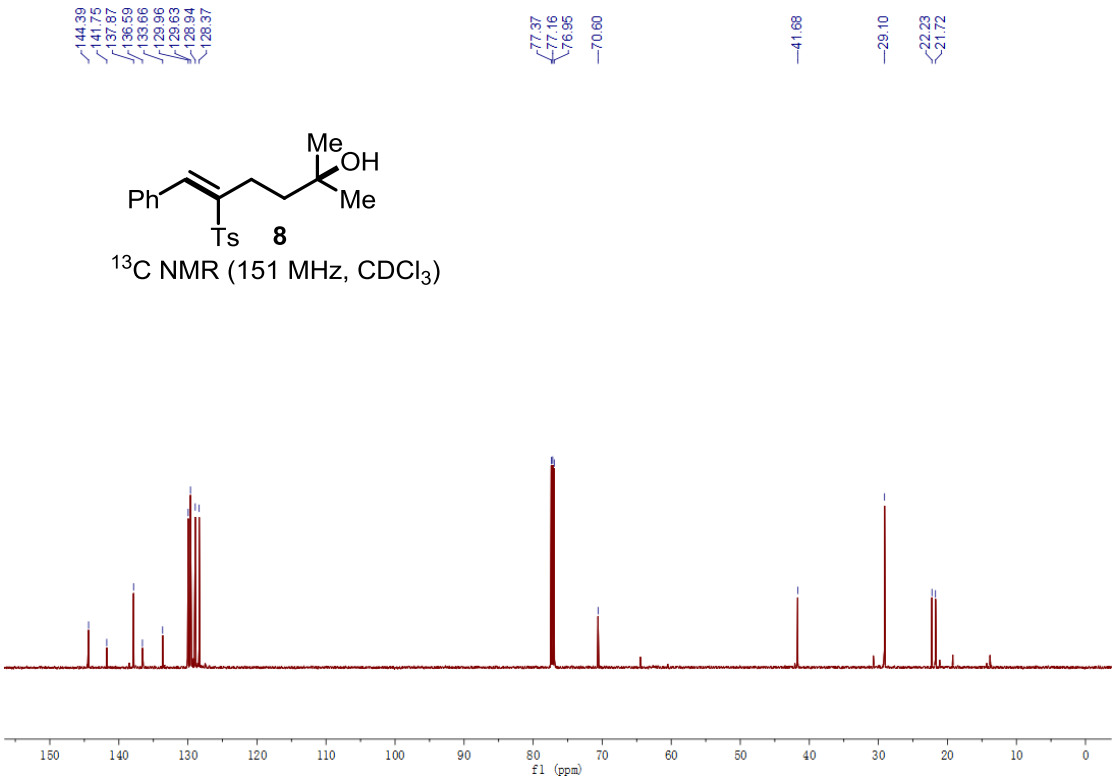




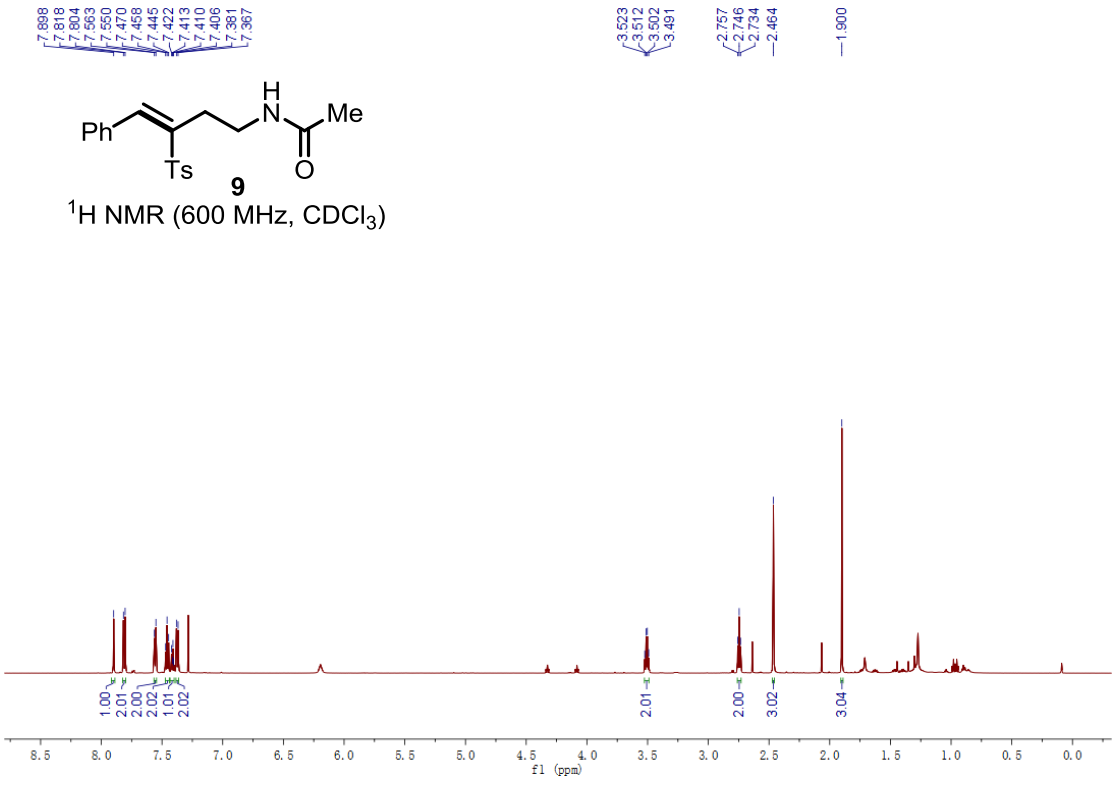
8

^{1}H NMR (600 MHz, $CDCl_3$)

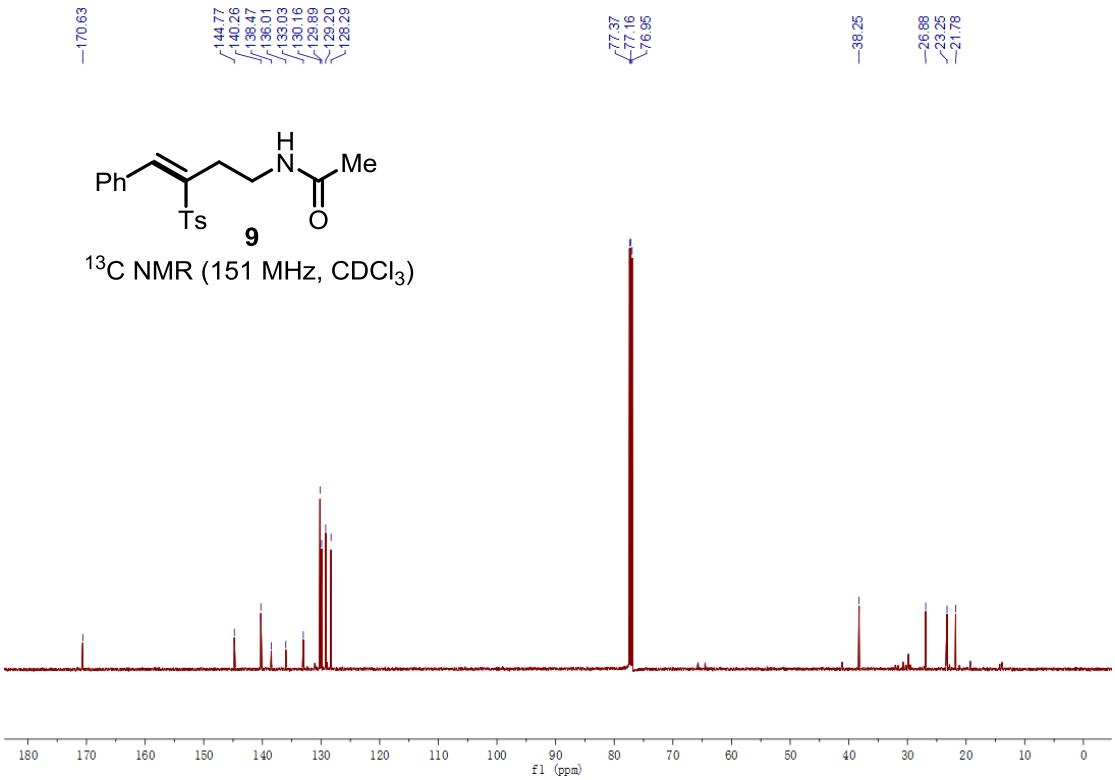




^{13}C NMR (151 MHz, $CDCl_3$)

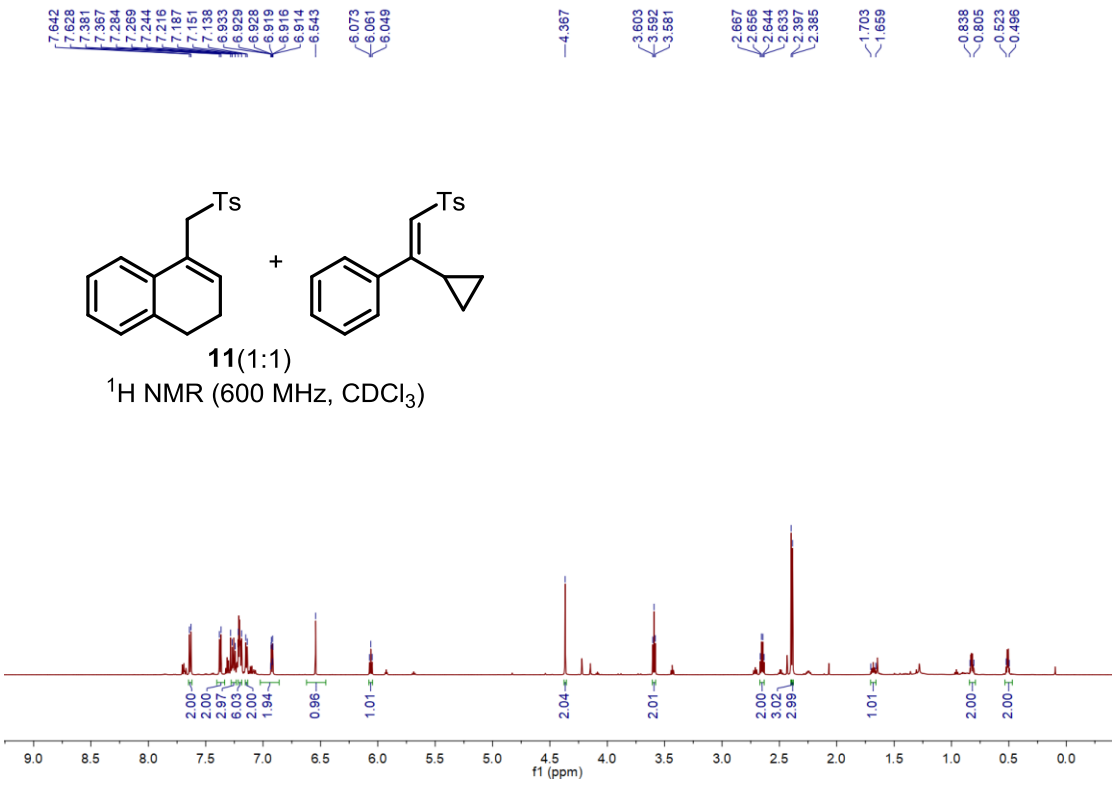


^{1}H NMR (600 MHz, $CDCl_3$)



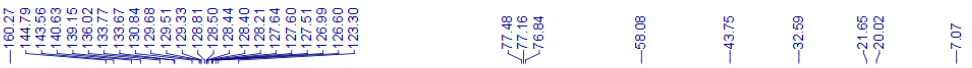
9

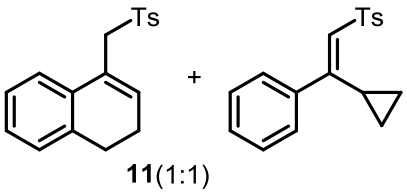
^{13}C NMR (151 MHz, $CDCl_3$)



11(1:1)

^{1}H NMR (600 MHz, $CDCl_3$)





11(1:1)

^{13}C NMR (101 MHz, $CDCl_3$)