

Supporting Information

Rhodium-Catalyzed 1,4-Hydroxyl Migration of Alkenyl Alcohols

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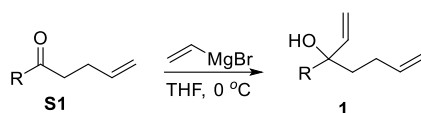
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I General information

^1H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance 600 MHz and 400 MHz instruments. Chemical shifts were reported in parts per million (ppm), and the residual solvent peak was used as an internal reference: proton (chloroform δ 7.26), carbon (chloroform δ 77.0) or tetramethylsilane (TMS δ 0.00) was used as a reference. Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublet), bs (broad singlet). Coupling constants were reported in Hertz (Hz). All high resolution mass spectra (**HRMS**) were obtained on a Bruker Apex-2. For thin layer chromatography (**TLC**), Qingdao Haiyang Chemical was used, and compounds were visualized with a UV light at 254 nm. Further visualization was achieved by staining with iodine, or potassium permanganate solution followed by heating using a heat gun. Flash chromatography separations were performed on Qingdao Haiyang Chemical 200-300 mesh silica gel. All reactions were carried out under a nitrogen atmosphere. All commercially available reagents were used as received for the reactions without any purification. All solvents were dried on alumina columns using a solvent dispensing system.

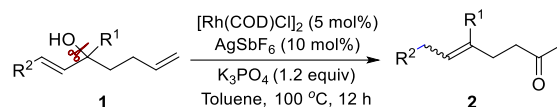
II General procedure

General procedure for preparation of alkenyl alcohols **1**



Allylic alcohols were prepared by vinyl-magnesium bromide added to **S1**. To a solution of ketones¹ **S1** (1 mmol) in dry THF was added vinyl-magnesium bromide (1 M in THF, 1.2 equiv.) under nitrogen by a syringe over 5 min at 0 °C. Then, the reaction mixture was allowed to warm to room temperature and stirred for 3 h. The reaction was quenched *via* the addition of saturated aqueous NH₄Cl at 0 °C, and the mixture was extracted with ethyl acetate. The organic layer was washed with brine and dried over Na₂SO₄, filtered, and concentrated in vacuo. The crude product was purified by flash column chromatography on silica gel using EtOAc in hexanes to afford the alkenyl alcohols **1**.

General procedure for 1,4-migration of hydroxyl groups within the alkenyl alcohols *via* rhodium-catalyzed

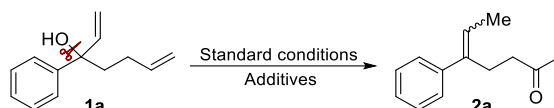


To a vial equipped with a dried stir bar was added alkenyl alcohols **1** (0.1 mmol), $[\text{Rh}(\text{COD})\text{Cl}]_2$ (5 mol%), AgSbF_6 (10 mol%), K_3PO_4 (1.2 equiv), toluene (0.5 mL) in the glovebox. The reaction mixture was taken outside the glovebox and allowed to stir at 100 °C (oil bath) for 12 h. After cooling to room temperature, the reaction mixture was added to water (10 mL), extracted with EtOAc (3×5 mL). The organic layer was washed with aqueous NaHCO_3 and brine and dried over Na_2SO_4 , filtered, and concentrated in vacuo. And the residue was purified by column chromatography with silica gel to give pure products **2**.

III Mechanism Studies

General Procedure for Scheme 4

Radical experiments

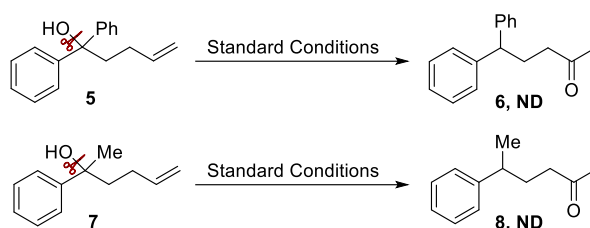


Entry	Additives	Yield
1	-	78%
2	TEMPO	70%
3	BHT	77%

Reaction conditions: **1a** (0.1 mmol), $[\text{Rh}(\text{COD})\text{Cl}]_2$ (5 mol%), AgSbF_6 (10 mol%), K_3PO_4 (1.2 equiv.), additives (1.0 equiv.) Toluene (0.5 mL) at 100 °C for 12 h. The yields are isolated yields.

In a nitrogen glove box, an oven-dried 10 mL reaction tube equipped with a magnetic stirring bar was charged with **1a** (0.1 mmol), $[\text{Rh}(\text{COD})\text{Cl}]_2$ (5 mol%), AgSbF_6 (10 mol%), K_3PO_4 (1.2 equiv.), additives (1.0 equiv.) and Toluene (0.5 mL). The reaction mixture was sealed with a screw cap, taken out of the glove box and placed in oil-bath at 100 °C and stirred for 12 h. After cooling to room temperature, the reaction mixture was exposed to air, concentrated and further purified by flash column chromatography

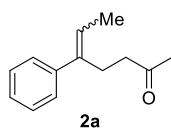
over silica (petroleum/ethyl acetate) to give desired product **2a**. The transformation was not suppressed in the presence of 1.0 equiv. of 2,2,6,6-tetramyl-1-piperidoxo (TEMPO) or butylated hydroxytoluene (BHT) under the standard condition, and the target product was obtained with 70% and 77% yield respectively. These radical experiments indicated that the radical process might not involve in this reaction.



In a nitrogen glove box, an oven-dried 10 mL reaction tube equipped with a magnetic stirring bar was charged with **5** (**7**) (0.1 mmol), [Rh(COD)Cl]₂ (5 mol%), AgSbF₆ (10 mol%), K₃PO₄ (1.2 equiv.), additives (1.0 equiv.) and Toluene (0.5 mL). The reaction mixture was sealed with a screw cap, taken out of the glove box and placed in oil-bath at 100 °C and stirred for 12 h. After cooling to room temperature, the reaction mixture was exposed to air and no 1,4-hydroxyl migration product was detected.

IV The analytical and spectral characterization data

5-Phenylhept-5-en-2-one (2a)²

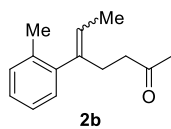


The title compound was prepared according to the general procedure as described, silica gel flash column chromatography was performed using hexanes and ethyl acetate (30:1) ($R_f = 0.40$ in hexane:ethyl acetate = 15:1) resulting in 14.6 mg of yellow liquid in 78% yield, *E/Z* 60:40.

¹H NMR (400 MHz, CDCl₃) (*E*) δ 7.36-7.30 (m, 3H), 7.25-7.20 (m, 1H), 7.15-7.13 (m, 1H), 5.76 (q, $J = 6.8$ Hz, 1H), 2.78 (t, $J = 7.6$ Hz, 2H), 2.46-2.43 (m, 2H), 2.07 (s, 3H), 1.80 (d, $J = 7.2$ Hz, 3H). (*Z*) δ 7.36-7.30 (m, 3H), 7.25-7.20 (m, 1H), 7.15-7.13 (m, 1H), 5.58 (q, $J = 6.8$ Hz, 1H), 2.62 (t, $J = 7.2$ Hz, 2H), 2.42-2.39 (m, 2H), 2.06 (s, 3H), 1.80 (d, $J = 6.8$ Hz, 3H).

¹³C NMR (151 MHz, CDCl₃) (*E*) δ 208.7, 142.6, 139.5, 128.5, 126.9, 126.8, 122.2, 42.3, 30.1, 23.6, 14.2. (*Z*) δ 208.6, 140.3, 140.2, 128.7, 128.3, 126.4, 124.0, 42.7, 33.4, 30.1, 14.8.

5-(*o*-Tolyl)hept-5-en-2-one (2b)



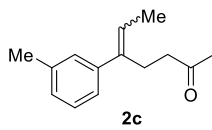
The title compound was prepared according to the general procedure as described, silica gel flash column chromatography was performed using hexanes and ethyl acetate (30:1) ($R_f = 0.40$ in hexane:ethyl acetate = 10:1) resulting in 13.4 mg of yellow liquid in 66% yield, *E/Z* 45:55.

¹H NMR (600 MHz, CDCl₃) (*E*) δ 7.20-7.10 (m, 3H), 6.96 (d, $J = 7.8$ Hz, 1H), 5.57 (q, $J = 6.6$ Hz, 1H), 2.63 (t, $J = 7.8$ Hz, 2H), 2.55-2.44 (m, 2H), 2.19 (s, 3H), 2.08 (s, 3H), 1.35 (d, $J = 7.2$ Hz, 3H). (*Z*) δ 7.20-7.10 (m, 3H), 6.99 (d, $J = 7.2$ Hz, 1H), 5.36 (q, $J = 6.6$ Hz, 1H), 2.55-2.44 (m, 2H), 2.36 (t, $J = 7.8$ Hz, 2H), 2.24 (s, 3H), 2.04 (s, 3H), 1.78 (d, $J = 6.6$ Hz, 3H).

¹³C NMR (151 MHz, CDCl₃) (*E*) δ 208.6, 143.5, 139.7, 135.7, 130.1, 129.0, 126.9, 125.7, 122.3, 42.2, 30.0, 25.4, 19.3, 14.6. (*Z*) δ 208.5, 140.1, 139.7, 135.6, 130.2, 129.2, 126.8, 125.5, 124.7, 41.7, 33.0, 25.4, 20.0, 13.7.

HRMS(ESI): m/z Calcd. for C₁₄H₁₈NaO [M+Na]⁺:225.1250; Found:225.1247.

5-(*m*-Tolyl)hept-5-en-2-one (2c)



The title compound was prepared according to the general procedure as described, silica gel flash column chromatography was performed using hexanes and ethyl acetate (30:1) ($R_f = 0.40$ in hexane:ethyl

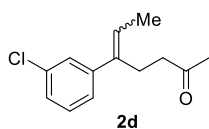
acetate = 15:1) resulting in 13.0 mg of yellow liquid in 64% yield, *E/Z* 60:40.

$^1\text{H NMR}$ (600 MHz, CDCl_3) (*E*) δ 7.19 (t, $J = 7.8$ Hz, 1H), 7.09 (t, $J = 7.8$ Hz, 2H), 7.05 (t, $J = 8.4$ Hz, 1H), 5.74 (q, $J = 6.6$ Hz, 1H), 2.77 (t, $J = 7.8$ Hz, 2H), 2.45-2.40 (m, 2H), 2.34 (s, 3H), 2.08 (s, 3H), 1.79 (d, $J = 6.6$ Hz, 3H). (*Z*) δ 7.22 (t, $J = 7.8$ Hz, 1H), 7.05 (t, $J = 8.4$ Hz, 1H), 6.93 (t, $J = 7.8$ Hz, 2H), 5.55 (q, $J = 6.6$ Hz, 1H), 2.60 (t, $J = 7.8$ Hz, 2H), 2.45-2.40 (m, 2H), 2.35 (s, 3H), 2.07 (s, 3H), 1.54 (d, $J = 7.2$ Hz, 3H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) (*E*) δ 208.7, 142.6, 139.6, 138.0, 128.4, 127.6, 127.2, 123.7, 123.5, 42.4, 30.1, 23.6, 21.6, 14.2. (*Z*) δ 208.7, 140.3, 140.3, 137.9, 129.3, 128.2, 127.5, 125.8, 122.0, 42.7, 33.4, 30.1, 21.6, 14.8.

HRMS(ESI): m/z Calcd. for $\text{C}_{14}\text{H}_{18}\text{NaO}$ [$\text{M}+\text{Na}$] $^+$:225.1250; Found:225.1249.

5-(3-Chlorophenyl)hept-5-en-2-one (2d)



The title compound was prepared according to the general procedure as described, silica gel flash column chromatography was performed using hexanes and ethyl acetate (30:1) ($R_f = 0.40$ in hexane:ethyl

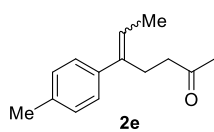
acetate = 15:1) resulting in 17.1 mg of yellow liquid in 71% yield, *E/Z* 60:40.

$^1\text{H NMR}$ (600 MHz, CDCl_3) (*E*) δ 7.29-7.27 (m, 1H), 7.24-7.23 (m, 1H), 7.21-7.19 (m, 1H), 7.17-7.15 (d, $J = 7.2$ Hz, 1H), 5.77 (q, $J = 6.6$ Hz, 1H), 2.75 (t, $J = 7.8$ Hz, 2H), 2.44-2.40 (m, 2H), 2.09 (s, 3H), 1.80 (d, $J = 6.6$ Hz, 3H). (*Z*) δ 7.29-7.27 (m, 1H), 7.24-7.23 (m, 1H), 7.13-7.12 (m, 1H), 7.02 (d, $J = 7.2$ Hz, 1H), 5.60 (q, $J = 7.2$ Hz, 1H), 2.59 (t, $J = 7.8$ Hz, 2H), 2.44-2.40 (m, 2H), 2.08 (s, 3H), 1.54 (d, $J = 7.2$ Hz, 3H).

$^{13}\text{C NMR}$ (151 MHz, CDCl_3) (*E*) δ 208.3, 144.5, 138.4, 134.4, 129.7, 128.7, 126.9, 125.3, 124.5, 42.2, 30.1, 23.4, 14.3. (*Z*) δ 208.4, 142.3, 139.0, 134.2, 129.7, 127.0, 126.9, 126.6, 123.2, 42.5, 33.0, 30.1, 14.8.

HRMS(ESI): m/z Calcd. for $\text{C}_{13}\text{H}_{15}\text{ClNaO}$ [$\text{M}+\text{Na}$] $^+$:245.0704; Found:245.0704.

5-(*p*-Tolyl)hept-5-en-2-one (2e)



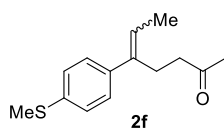
The title compound was prepared according to the general procedure as described, silica gel flash column chromatography was performed using hexanes and ethyl acetate (30:1) ($R_f = 0.40$ in hexane:ethyl acetate = 15:1) resulting in 11.8 mg of yellow liquid in 54% yield, *E/Z* 60:40.

$^1\text{H NMR}$ (400 MHz, CDCl_3) (*E*) δ 7.20-7.16 (m, 3H), 7.04-7.02 (m, 1H), 5.73 (q, $J = 6.8$ Hz, 1H), 2.78-2.74 (m, 2H), 2.45-2.42 (m, 2H), 2.33 (s, 3H), 2.07 (s, 3H), 1.79 (d, $J = 6.8$ Hz, 3H). (*Z*) δ 7.14-7.10 (m, 3H), 7.04-7.02 (m, 1H), 5.73 (q, $J = 6.8$ Hz, 1H), 2.62-2.58 (m, 2H), 2.41-2.38 (m, 2H), 2.35 (s, 3H), 2.06 (s, 3H), 1.55 (d, $J = 6.8$ Hz, 3H).

$^{13}\text{C NMR}$ (151 MHz, CDCl_3) (*E*) δ 208.7, 139.6, 139.2, 136.5, 129.2, 126.2, 123.2, 42.4, 30.1, 23.5, 21.2, 14.2. (*Z*) δ 208.8, 140.1, 137.2, 136.4, 129.0, 128.6, 121.9, 42.7, 33.4, 30.1, 21.3, 14.8.

HRMS(ESI): m/z Calcd. for $\text{C}_{14}\text{H}_{18}\text{NaO}$ [$\text{M}+\text{Na}$] $^+$:225.1250; Found:225.1249.

5-(4-(Methylthio)phenyl)hept-5-en-2-one (2f)



The title compound was prepared according to the general procedure as described, silica gel flash column chromatography was performed using hexanes and ethyl acetate (30:1) ($R_f = 0.40$ in hexane:ethyl acetate = 10:1) resulting in 11.5 mg of yellow liquid in 49% yield, *E/Z* 60:40.

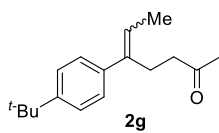
$^1\text{H NMR}$ (600 MHz, CDCl_3) (*E*) δ 7.24-7.19 (m, 3H), 7.07 (d, $J = 8.4$ Hz, 1H), 5.75 (q, $J = 6.6$ Hz, 1H), 2.76 (t, $J = 7.8$ Hz, 2H), 2.48 (s, 3H), 2.45-2.39 (m, 2H), 2.08 (s, 3H), 1.79 (d, $J = 7.2$ Hz, 3H). (*Z*) δ 7.24-7.19 (m, 4H), 5.57 (q, $J = 7.2$ Hz, 1H), 2.60 (t, $J = 7.2$ Hz, 2H), 2.50 (s, 3H), 2.45-2.39 (m, 2H), 2.06 (s, 3H), 1.56 (d, $J = 6.6$ Hz, 3H).

$^{13}\text{C NMR}$ (151 MHz, CDCl_3) (*E*) δ 208.4, 139.3, 136.6, 129.0, 126.7, 126.4, 123.5, 42.2, 30.0, 23.2, 16.0, 14.1. (*Z*) δ 208.5, 139.4, 138.6, 136.6, 126.7, 126.5, 122.3, 42.5, 33.1,

29.9, 15.9, 14.7.

HRMS(ESI): m/z Calcd. for $C_{14}H_{18}NaOS$ $[M+Na]^+$:257.0971; Found:257.0971.

5-(4-(Tert-butyl)phenyl)hept-5-en-2-one (2g)



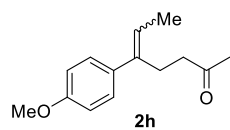
The title compound was prepared according to the general procedure as described, silica gel flash column chromatography was performed using hexanes and ethyl acetate (30:1) ($R_f = 0.40$ in hexane:ethyl acetate = 15:1) resulting in 13.8 mg of yellow liquid in 58% yield, *E/Z* 70:30.

1H NMR (600 MHz, $CDCl_3$) (*E*) δ 7.32 (d, $J = 8.4$ Hz, 2H), 7.24-7.23 (m, 2H), 5.76 (q, $J = 6.6$ Hz, 1H), 2.77 (t, $J = 7.8$ Hz, 2H), 2.47-2.41 (m, 2H), 2.08 (s, 3H), 1.79 (d, $J = 7.2$ Hz, 3H), 1.32 (s, 9H). (*Z*) δ 7.34 (d, $J = 7.8$ Hz, 2H), 7.07-7.02 (m, 2H), 5.55 (q, $J = 7.2$ Hz, 1H), 2.61 (t, $J = 7.8$ Hz, 2H), 2.47-2.41 (m, 2H), 2.06 (s, 3H), 1.57 (d, $J = 6.6$ Hz, 3H), 1.33 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$) (*E*) δ 208.8, 149.8, 139.4, 128.3, 125.9, 125.1, 123.2, 42.5, 34.6, 31.5, 30.1, 23.5, 14.2. (*Z*) δ 209.0, 149.5, 139.0, 127.9, 125.4, 125.2, 121.9, 42.8, 34.6, 33.4, 31.5, 30.1, 14.9.

HRMS(ESI): m/z Calcd. for $C_{17}H_{24}NaO$ $[M+Na]^+$:267.1719; Found:267.1720.

5-(4-Methoxyphenyl)hept-5-en-2-one (2h)³



The title compound was prepared according to the general procedure as described, silica gel flash column chromatography was performed using hexanes and ethyl acetate (30:1) ($R_f = 0.40$ in hexane:ethyl acetate = 15:1) resulting in 13.8 mg of yellow liquid in 58% yield, *E/Z* 70:30.

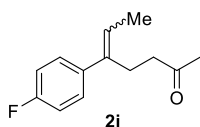
1H NMR (600 MHz, $CDCl_3$) (*E*) δ 7.24-7.22 (m, 2H), 6.85-6.83 (m, 2H), 5.69 (q, $J = 7.2$ Hz, 1H), 3.80 (s, 3H), 2.75 (t, $J = 7.8$ Hz, 2H), 2.45-2.42 (m, 2H), 2.07 (s, 3H), 1.78 (d, $J = 6.6$ Hz, 3H). (*Z*) δ 7.08-7.06 (m, 2H), 6.89-6.87 (m, 2H), 5.54 (q, $J = 7.2$ Hz, 1H), 3.82 (s, 3H), 2.59 (t, $J = 7.8$ Hz, 2H), 2.42-2.39 (m, 2H), 2.06 (s, 3H), 1.78 (d, $J =$

7.2 Hz, 3H).

^{13}C NMR (151 MHz, CDCl_3) (*E*) δ 208.7, 158.7, 138.8, 132.4, 127.4, 113.8, 113.7, 55.4, 42.4, 30.1, 23.6, 14.2. (*Z*) δ 208.7, 158.4, 139.7, 135.0, 129.8, 122.5, 121.9, 55.4, 42.8, 33.5, 30.1, 14.8.

HRMS(ESI): m/z Calcd. for $\text{C}_{14}\text{H}_{19}\text{O}_2$ $[\text{M}+\text{H}]^+$:219.1380; Found:219.1380.

5-(4-Fluorophenyl)hept-5-en-2-one (2i)



The title compound was prepared according to the general procedure as described, silica gel flash column chromatography was performed using hexanes and ethyl acetate (30:1) ($R_f = 0.40$ in hexane:ethyl acetate = 15:1) resulting in 11.7 mg of yellow liquid in 57% yield, *E/Z* 60:40.

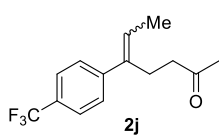
^1H NMR (600 MHz, CDCl_3) (*E*) δ 7.26-7.23 (m, 2H), 7.00-6.96 (m, 2H), 5.70 (q, $J = 7.2$ Hz, 1H), 2.75 (t, $J = 7.8$ Hz, 2H), 2.43-2.42 (m, 2H), 2.08 (s, 3H), 1.79 (d, $J = 7.2$ Hz, 3H). (*Z*) δ 7.11-7.09 (m, 2H), 7.04-7.01 (m, 2H), 5.58 (q, $J = 6.6$ Hz, 1H), 2.59 (t, $J = 7.8$ Hz, 2H), 2.41-2.39 (m, 2H), 2.07 (s, 3H), 1.53 (d, $J = 7.2$ Hz, 3H).

^{13}C NMR (151 MHz, CDCl_3) (*E*) δ 208.4, 162.0 (d, $J = 246.1$ Hz), 138.6 (d, $J = 4.5$ Hz), 138.5, 127.9 (d, $J = 7.6$ Hz), 124.0, 115.3 (d, $J = 21.1$ Hz), 42.2, 30.1, 23.7, 14.2. (*Z*) δ 208.5, 161.8 (d, $J = 246.1$ Hz), 139.2, 138.6 (d, $J = 4.5$ Hz), 130.2 (d, $J = 7.6$ Hz), 122.6, 115.2 (d, $J = 21.1$ Hz), 42.5, 33.3, 30.1, 14.7.

^{19}F NMR (565 MHz, CDCl_3) (*E*) δ -116.30. (*Z*) δ -115.94.

HRMS(ESI): m/z Calcd. for $\text{C}_{13}\text{H}_{15}\text{FNaO}$ $[\text{M}+\text{Na}]^+$:229.0999; Found:229.1000.

5-(4-(Trifluoromethyl)phenyl)hept-5-en-2-one (2j)



The title compound was prepared according to the general procedure as described, silica gel flash column chromatography was performed using hexanes and ethyl acetate (30:1) ($R_f = 0.40$ in hexane:ethyl acetate = 15:1) resulting in 16.1 mg of yellow liquid in 63% yield, *E/Z*

60:40.

^1H NMR (600 MHz, CDCl_3) (*E*) δ 7.55 (d, $J = 7.8$ Hz, 2H), 7.39 (d, $J = 7.8$ Hz, 2H),

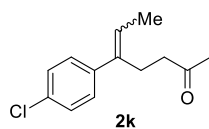
5.84 (q, $J = 7.2$ Hz, 1H), 2.80 (t, $J = 7.8$ Hz, 2H), 2.44-2.43 (m, 2H), 2.08 (s, 3H), 1.83 (d, $J = 7.2$ Hz, 3H). (*Z*) δ 7.60 (d, $J = 8.4$ Hz, 2H), 7.39 (d, $J = 7.8$ Hz, 2H), 5.64 (q, $J = 7.2$ Hz, 1H), 2.63 (t, $J = 7.8$ Hz, 2H), 2.42-2.40 (m, 2H), 2.08 (s, 3H), 1.54 (d, $J = 7.2$ Hz, 3H).

^{13}C NMR (151 MHz, CDCl_3) (*E*) δ 208.1, 146.2, 138.5, 128.9 (q, $J = 31.9$ Hz), 126.6, 126.1, 125.5 (q, $J = 3.6$ Hz), 124.4 (q, $J = 275.4$ Hz), 42.1, 30.1, 23.3, 14.3. (*Z*) δ 208.2, 144.3, 139.1, 129.1 (q, $J = 32.5$ Hz), 126.6, 126.1, 125.3 (q, $J = 3.8$ Hz), 124.4 (q, $J = 275.4$ Hz), 42.4, 32.9, 30.1, 14.8.

^{19}F NMR (565 MHz, CDCl_3) (*E*) δ -62.39. (*Z*) δ -62.44.

HRMS(ESI): m/z Calcd. for $\text{C}_{14}\text{H}_{15}\text{F}_3\text{NaO}$ $[\text{M}+\text{Na}]^+$:279.0967; Found:279.0968.

5-(4-Chlorophenyl)hept-5-en-2-one (2k)



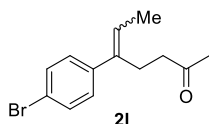
The title compound was prepared according to the general procedure as described, silica gel flash column chromatography was performed using hexanes and ethyl acetate (30:1) ($R_f = 0.40$ in hexane:ethyl acetate = 15:1) resulting in 14.4 mg of yellow liquid in 65% yield, *E/Z* 60:40.

^1H NMR (600 MHz, CDCl_3) (*E*) δ 7.32-7.30 (m, 1H), 7.22-7.21 (m, 2H), 7.08-7.07 (m, 1H), 5.75 (q, $J = 7.2$ Hz, 1H), 2.75 (t, $J = 7.8$ Hz, 2H), 2.43-2.41 (m, 2H), 2.08 (s, 3H), 1.80 (d, $J = 7.2$ Hz, 3H). (*Z*) δ 7.27-7.26 (m, 1H), 7.22-7.21 (m, 2H), 7.08-7.07 (m, 1H), 5.59 (q, $J = 6.6$ Hz, 1H), 2.59 (t, $J = 7.8$ Hz, 2H), 2.41-2.39 (m, 2H), 2.07 (s, 3H), 1.53 (d, $J = 7.2$ Hz, 3H).

^{13}C NMR (151 MHz, CDCl_3) (*E*) δ 208.3, 141.0, 138.4, 130.1, 128.6, 127.7, 124.6, 42.2, 30.1, 23.4, 14.2. (*Z*) δ 208.4, 139.1, 138.7, 132.6, 128.6, 127.7, 122.9, 42.5, 33.1, 30.1, 14.8.

HRMS(ESI): m/z Calcd. for $\text{C}_{13}\text{H}_{15}\text{ClNaO}$ $[\text{M}+\text{Na}]^+$:245.0704; Found:245.0703.

5-(4-Bromophenyl)hept-5-en-2-one (2l)³



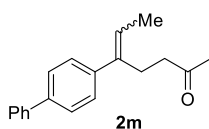
The title compound was prepared according to the general procedure as described, silica gel flash column chromatography was performed

using hexanes and ethyl acetate (30:1) ($R_f = 0.40$ in hexane:ethyl acetate = 15:1) resulting in 11.4 mg of yellow liquid in 43% yield, *E/Z* 70:30.

^1H NMR (600 MHz, CDCl_3) (*E*) δ 7.43-7.41 (m, 2H), 7.17-7.15 (m, 2H), 5.75 (q, $J = 7.2$ Hz, 1H), 2.75 (t, $J = 7.8$ Hz, 2H), 2.43-2.39 (m, 2H), 2.08 (s, 3H), 1.79 (d, $J = 7.2$ Hz, 3H). (*Z*) δ 7.47-7.46 (m, 2H), 7.02-7.01 (m, 2H), 5.59 (q, $J = 6.6$ Hz, 1H), 2.59 (t, $J = 7.8$ Hz, 2H), 2.43-2.39 (m, 2H), 2.07 (s, 3H), 1.53 (d, $J = 6.6$ Hz, 3H).

^{13}C NMR (151 MHz, CDCl_3) (*E*) δ 208.3, 141.5, 138.5, 131.5, 128.1, 124.7, 120.7, 42.2, 30.1, 23.4, 14.3. (*Z*) δ 208.3, 139.2, 139.1, 131.6, 130.4, 122.9, 120.7, 42.5, 33.1, 29.8, 14.8.

5-([1,1'-Biphenyl]-4-yl)hept-5-en-2-one (2m)



The title compound was prepared according to the general procedure as described, silica gel flash column chromatography was performed using hexanes and ethyl acetate (30:1) ($R_f = 0.40$ in hexane:ethyl

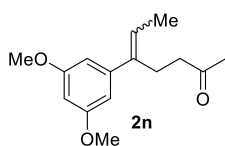
acetate = 15:1) resulting in 20.3 mg of yellow liquid in 77% yield, *E/Z* 60:40.

^1H NMR (600 MHz, CDCl_3) (*E*) δ 7.62-7.57 (m, 5H), 7.54 (d, $J = 8.4$ Hz, 2H), 7.35-7.34 (m, 1H), 7.22 (d, $J = 7.2$ Hz, 1H), 5.84 (q, $J = 6.6$ Hz, 1H), 2.82 (t, $J = 7.8$ Hz, 2H), 2.50-2.47 (m, 2H), 2.09 (s, 3H), 1.83 (d, $J = 6.6$ Hz, 3H). (*Z*) δ 7.45-7.42 (m, 5H), 7.38 (d, $J = 7.8$ Hz, 2H), 7.34-7.33 (m, 1H), 7.22 (d, $J = 7.2$ Hz, 1H), 5.61 (q, $J = 7.2$ Hz, 1H), 2.66 (t, $J = 7.8$ Hz, 2H), 2.47-2.44 (m, 2H), 2.08 (s, 3H), 1.61 (d, $J = 7.2$ Hz, 3H).

^{13}C NMR (151 MHz, CDCl_3) (*E*) δ 208.6, 141.4, 140.9, 139.8, 139.0, 128.9, 127.3, 127.2, 127.1, 126.7, 124.0, 42.4, 30.2, 23.4, 14.9. (*Z*) δ 208.7, 141.0, 139.7, 139.6, 139.3, 129.1, 127.4, 127.1, 127.0, 126.7, 122.5, 42.7, 33.3, 30.1, 14.3.

HRMS(ESI): m/z Calcd. for $\text{C}_{19}\text{H}_{20}\text{NaO}$ $[\text{M}+\text{Na}]^+$:287.1406; Found:287.1402.

5-(3,5-dimethoxyphenyl)hept-5-en-2-one (2n)



The title compound was prepared according to the general procedure as described, silica gel flash column chromatography was performed using hexanes and ethyl acetate (30:1) ($R_f = 0.40$ in

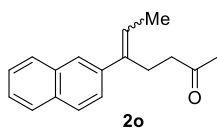
hexane:ethyl acetate = 15:1) resulting in 16.1 mg of yellow liquid in 65% yield, *E/Z* 60:40.

¹H NMR (600 MHz, CDCl₃) (*E*) δ 6.45-6.44 (m, 2H), 6.37-6.36 (m, 1H), 5.77 (q, *J* = 7.2 Hz, 1H), 3.79 (s, 6H), 2.74 (t, *J* = 7.8 Hz, 2H), 2.46-2.42 (m, 2H), 2.08 (s, 3H), 1.79 (d, *J* = 6.6 Hz, 3H). (*Z*) δ 6.37-6.36 (m, 1H), 6.29-6.28 (m, 2H), 5.54 (q, *J* = 7.2 Hz, 1H), 3.79 (s, 6H), 2.58 (t, *J* = 7.8 Hz, 2H), 2.46-2.42 (m, 2H), 2.07 (s, 3H), 1.56 (d, *J* = 6.6 Hz, 3H).

¹³C NMR (151 MHz, CDCl₃) (*E*) δ 208.6, 160.8, 145.0, 139.5, 124.1, 104.8, 98.8, 55.4, 42.3, 30.1, 23.6, 14.1. (*Z*) δ 208.7, 160.7, 142.5, 140.2, 122.3, 106.8, 98.7, 55.4, 42.6, 33.2, 30.1, 14.8.

HRMS(ESI): *m/z* Calcd. for C₁₅H₂₀NaO₃ [M+Na]⁺:271.1305; Found:271.1304.

5-(Naphthalen-2-yl)hept-5-en-2-one (2o)



The title compound was prepared according to the general procedure as described, silica gel flash column chromatography was performed using hexanes and ethyl acetate (30:1) (*R_f* = 0.40 in

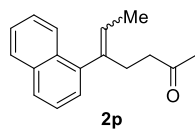
hexane:ethyl acetate = 15:1) resulting in 16.5 mg of yellow liquid in 69% yield, *E/Z* 60:40.

¹H NMR (600 MHz, CDCl₃) (*E*) δ 7.85-7.80 (m, 3H), 7.71 (s, 1H), 7.49-7.46 (m, 2H), 7.29-7.28 (m, 1H), 5.92 (q, *J* = 6.6 Hz, 1H), 2.89 (t, *J* = 7.8 Hz, 2H), 2.12 (t, *J* = 7.8 Hz, 2H), 2.06 (s, 3H), 1.86 (d, *J* = 6.6 Hz, 3H). (*Z*) δ 7.79-7.77 (m, 3H), 7.59 (s, 1H), 7.45-7.43 (m, 2H), 7.29-7.28 (m, 1H), 5.67 (q, *J* = 7.2 Hz, 1H), 2.71 (t, *J* = 7.8 Hz, 2H), 2.43 (t, *J* = 7.8 Hz, 2H), 2.04 (s, 3H), 1.60 (d, *J* = 7.2 Hz, 3H).

¹³C NMR (151 MHz, CDCl₃) (*E*) δ 208.6, 139.8, 139.4, 133.6, 132.6, 128.1, 127.9, 127.6, 127.1, 126.3, 125.7, 125.1, 124.6, 42.4, 30.1, 23.5, 14.4. (*Z*) δ 208.6, 140.1, 137.8, 133.5, 132.4, 128.0, 127.9, 127.8, 127.3, 126.2, 125.8, 124.6, 122.7, 42.7, 33.3, 30.1, 14.9.

HRMS(ESI): *m/z* Calcd. for C₁₇H₁₈NaO [M+Na]⁺:261.1250; Found:261.1250.

5-(Naphthalen-1-yl)hept-5-en-2-one (2p)



The title compound was prepared according to the general procedure as described, silica gel flash column chromatography was performed using hexanes and ethyl acetate (30:1) ($R_f = 0.40$ in hexane:ethyl

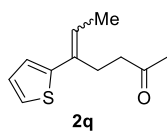
acetate = 15:1) resulting in 13.3 mg of yellow liquid in 56% yield, *E/Z* 45:55.

$^1\text{H NMR}$ (600 MHz, CDCl_3) (*E*) δ 7.93-7.92 (m, 1H), 7.87-7.85 (m, 1H), 7.78-7.74 (m, 1H), 7.48-7.45 (m, 2H), 7.41 (t, $J = 7.8$ Hz, 1H), 7.21-7.19 (m, 1H), 5.84 (q, $J = 6.6$ Hz, 1H), 2.74-2.65 (m, 2H), 2.50-2.42 (m, 2H), 2.02 (s, 3H), 1.33 (d, $J = 6.6$ Hz, 3H). (*Z*) δ 7.85-7.82 (m, 2H), 7.78-7.74 (m, 1H), 7.48-7.45 (m, 2H), 7.41 (t, $J = 7.8$ Hz, 1H), 7.21-7.19 (m, 1H), 5.58 (q, $J = 6.6$ Hz, 1H), 2.82 (t, $J = 7.8$ Hz, 2H), 2.37 (t, $J = 7.8$ Hz, 2H), 1.98 (s, 3H), 1.90 (d, $J = 6.6$ Hz, 3H).

$^{13}\text{C NMR}$ (151 MHz, CDCl_3) (*E*) δ 208.5, 141.9, 138.5, 133.9, 132.0, 128.4, 127.2, 126.3, 125.9, 125.9, 125.8, 125.6, 125.4, 42.4, 30.0, 26.3, 14.9. (*Z*) δ 208.5, 141.9, 138.6, 133.8, 131.5, 128.5, 127.2, 126.1, 126.0, 125.9, 125.9, 125.7, 124.2, 42.0, 33.8, 30.0, 13.9.

HRMS(ESI): m/z Calcd. for $\text{C}_{17}\text{H}_{18}\text{NaO}$ [$\text{M}+\text{Na}$] $^+$:261.1250; Found:261.1250.

5-(Thiophen-2-yl)hept-5-en-2-one (2q)



The title compound was prepared according to the general procedure as described, silica gel flash column chromatography was performed using hexanes and ethyl acetate (30:1) ($R_f = 0.40$ in hexane:ethyl acetate =

15:1) resulting in 8.1 mg of yellow liquid in 42% yield, *E/Z* 55:45.

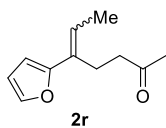
$^1\text{H NMR}$ (600 MHz, CDCl_3) (*E*) δ 7.10-7.09 (m, 1H), 6.96-6.94 (m, 1H), 6.91-6.90 (m, 1H), 5.98 (q, $J = 7.2$ Hz, 1H), 2.75 (t, $J = 7.8$ Hz, 2H), 2.59 (t, $J = 7.8$ Hz, 2H), 2.13 (s, 3H), 1.80-1.78 (m, 3H). (*Z*) δ 7.28-7.27 (m, 1H), 7.04-7.02 (m, 1H), 6.93-6.92 (m, 1H), 5.67 (q, $J = 7.2$ Hz, 1H), 2.67 (t, $J = 7.2$ Hz, 2H), 2.55 (t, $J = 7.2$ Hz, 2H), 2.10 (s, 3H), 1.80-1.78 (m, 3H).

$^{13}\text{C NMR}$ (151 MHz, CDCl_3) (*E*) δ 208.4, 146.5, 133.3, 127.4, 124.5, 123.3, 122.1, 42.6, 30.2, 24.1, 14.0. (*Z*) δ 208.5, 141.8, 132.8, 126.9, 125.9, 124.6, 123.1, 43.1, 33.9, 30.2,

15.4.

HRMS(ESI): m/z Calcd. for $C_{11}H_{14}NaOS$ $[M+Na]^+$:217.0658; Found:217.0657.

5-(furan-2-yl)hept-5-en-2-one (2r)



The title compound was prepared according to the general procedure as described, silica gel flash column chromatography was performed using hexanes and ethyl acetate (30:1) (R_f = 0.40 in hexane:ethyl acetate =

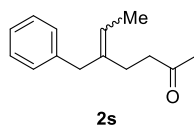
15:1) resulting in 8.2 mg of yellow liquid in 46% yield, E/Z 60:40.

1H NMR (600 MHz, $CDCl_3$) (E) δ 7.31 (s, 1H), 6.36-6.35 (m, 1H), 6.17-6.16 (m, 1H), 6.13 (q, J = 7.2 Hz, 1H), 2.66-2.58 (m, 4H), 2.14 (s, 3H), 1.79 (d, J = 7.2 Hz, 3H). (Z) δ 7.40 (s, 1H), 6.42-6.41 (m, 1H), 6.29-6.28 (m, 1H), 5.59 (q, J = 7.2 Hz, 1H), 2.66-2.58 (m, 4H), 2.12 (s, 3H), 1.89 (d, J = 7.2 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) (E) δ 208.5, 155.2, 141.4, 129.3, 121.2, 111.1, 104.3, 43.0, 30.2, 21.9, 15.4. (Z) δ 208.7, 153.6, 141.2, 129.1, 123.8, 110.9, 108.7, 43.7, 30.1, 21.9, 13.4.

HRMS(ESI): m/z Calcd. for $C_{11}H_{14}NaO_2$ $[M+Na]^+$:201.0886; Found:201.0887.

5-Benzylhept-5-en-2-one (2s)



The title compound was prepared according to the general procedure as described, silica gel flash column chromatography was performed using hexanes and ethyl acetate (30:1) (R_f = 0.40 in hexane:ethyl

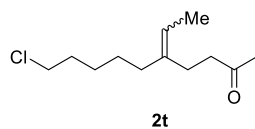
acetate = 15:1) resulting in 17.2 mg of yellow liquid in 85% yield, E/Z 50:50.

1H NMR (400 MHz, $CDCl_3$) (E) δ 7.29-7.14 (m, 5H), 5.42 (q, J = 6.8 Hz, 1H), 3.40 (s, 2H), 2.48-2.44 (m, 2H), 2.27-2.19 (m, 2H), 2.05 (s, 3H), 1.72 (d, J = 6.8 Hz, 3H). (Z) δ 7.29-7.14 (m, 5H), 5.32 (q, J = 6.8 Hz, 1H), 3.29 (s, 2H), 2.41-2.37 (m, 2H), 2.27-2.19 (m, 2H), 2.07 (s, 3H), 1.63 (d, J = 6.8 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) (E) δ 208.8, 140.0, 137.2, 128.6, 128.5, 126.1, 121.0, 43.9, 42.4, 30.9, 24.0, 13.8. (Z) δ 208.7, 140.2, 138.0, 129.1, 128.4, 126.2, 122.4, 43.9, 42.2, 36.1, 29.9, 13.5.

HRMS(ESI): m/z Calcd. for $C_{14}H_{18}NaO$ $[M+Na]^+$:225.1250; Found:225.1249.

10-Chloro-5-ethylidenedecan-2-one (2t)



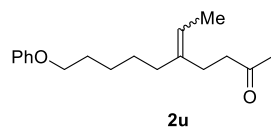
The title compound was prepared according to the general procedure as described, silica gel flash column chromatography was performed using hexanes and ethyl acetate (30:1) (R_f = 0.40 in hexane:ethyl acetate = 15:1) resulting in 15.6 mg of yellow liquid in 72% yield, E/Z 50:50.

1H NMR (600 MHz, $CDCl_3$) (E) δ 5.24 (q, J = 6.6 Hz, 1H), 3.56-3.53 (m, 2H), 2.52 (t, J = 7.8 Hz, 2H), 2.30-2.27 (m, 2H), 2.15 (s, 3H), 2.03 (t, J = 7.8 Hz, 2H), 1.81-1.74 (m, 5H), 1.60-1.57 (m, 2H), 1.46-1.43 (m, 2H). (Z) δ 5.20 (q, J = 6.6 Hz, 1H), 3.53-3.52 (m, 2H), 2.47 (t, J = 7.8 Hz, 2H), 2.26-2.23 (m, 2H), 2.14 (s, 3H), 1.97 (t, J = 7.2 Hz, 2H), 1.81-1.74 (m, 5H), 1.60-1.57 (m, 2H), 1.39-1.36 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) (E) δ 208.9, 138.5, 120.0, 45.2, 42.4, 36.7, 32.7, 30.0, 29.9, 27.5, 24.0, 13.3. (Z) δ 209.0, 138.3, 119.4, 45.2, 42.6, 36.7, 32.7, 30.8, 30.0, 27.0, 26.7, 13.4.

HRMS(ESI): m/z Calcd. for $C_{12}H_{21}ClNaO$ $[M+Na]^+$:239.1173; Found:239.1172.

5-Ethylidene-10-phenoxydecane-2-one (2u)



The title compound was prepared according to the general procedure as described, silica gel flash column chromatography was performed using hexanes and ethyl acetate (30:1) (R_f = 0.40 in hexane:ethyl acetate = 15:1) resulting in 17.7 mg of yellow liquid in 65% yield, E/Z 50:50.

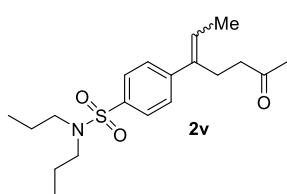
1H NMR (600 MHz, $CDCl_3$) (E) δ 7.28 (d, J = 7.8 Hz, 2H), 6.93 (t, J = 7.2 Hz, 1H), 6.90-6.88 (m, 2H), 5.24 (q, J = 7.2 Hz, 1H), 3.96-3.94 (m, 2H), 2.51 (t, J = 7.2 Hz, 2H), 2.30-2.24 (m, 2H), 2.15 (s, 3H), 2.06-2.03 (m, 2H), 1.82-1.76 (m, 5H), 1.59-1.57 (m, 2H), 1.49-1.46 (m, 2H). (Z) δ 7.28 (d, J = 7.8 Hz, 2H), 6.93 (t, J = 7.2 Hz, 1H), 6.90-6.88 (m, 2H), 5.20 (q, J = 6.6 Hz, 1H), 3.96-3.94 (m, 2H), 2.47 (t, J = 7.8 Hz, 2H), 2.30-

2.24 (m, 2H), 2.14 (s, 3H), 1.99-1.97 (m, 2H), 1.82-1.76 (m, 5H), 1.59-1.57 (m, 2H), 1.45-1.42 (m, 2H).

^{13}C NMR (151 MHz, CDCl_3) (*E*) δ 209.0, 159.2, 138.7, 129.5, 120.6, 119.3, 114.6, 67.9, 42.7, 36.8, 30.9, 30.0, 29.4, 28.0, 24.0, 13.3. (*Z*) δ 208.9, 159.2, 138.5, 129.5, 120.6, 119.9, 114.6, 67.9, 42.4, 36.8, 30.0, 29.8, 29.3, 26.3, 26.0, 13.4.

HRMS(ESI): m/z Calcd. for $\text{C}_{18}\text{H}_{26}\text{NaO}_2$ $[\text{M}+\text{Na}]^+$:297.1825; Found:197.1823.

4-(6-Oxohept-2-en-3-yl)-N,N-dipropylbenzenesulfonamide (2v)



The title compound was prepared according to the general procedure as described, silica gel flash column chromatography was performed using hexanes and ethyl acetate (30:1) (R_f = 0.40 in hexane:ethyl acetate = 15:1)

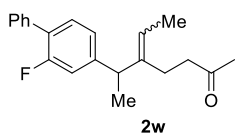
resulting in 16.5 mg of yellow liquid in 47% yield, *E/Z* 70:30.

^1H NMR (600 MHz, CDCl_3) (*E*) δ 7.73 (d, J = 8.4 Hz, 2H), 7.40 (d, J = 8.4 Hz, 2H), 5.88 (q, J = 7.2 Hz, 1H), 3.12-3.07 (m, 4H), 2.80 (t, J = 7.8 Hz, 2H), 2.44-2.40 (m, 2H), 2.09 (s, 3H), 1.84 (d, J = 7.2 Hz, 3H), 1.60-1.53 (m, 4H), 0.88 (t, J = 7.2 Hz, 6H). (*Z*) δ 7.73 (d, J = 8.4 Hz, 2H), 7.27-7.25 (m, 2H), 5.65 (q, J = 6.6 Hz, 1H), 3.12-3.07 (m, 4H), 2.62 (t, J = 7.8 Hz, 2H), 2.44-2.40 (m, 2H), 2.08 (s, 3H), 1.60-1.53 (m, 7H), 0.88 (t, J = 7.2 Hz, 6H).

^{13}C NMR (151 MHz, CDCl_3) (*E*) δ 207.8, 146.4, 138.8, 138.2, 129.1, 127.2, 126.6, 50.1, 41.9, 30.0, 23.1, 22.1, 14.3, 11.2. (*Z*) δ 207.9, 144.7, 138.5, 138.2, 127.1, 126.5, 123.6, 50.0, 42.2, 32.7, 29.9, 22.1, 14.7, 11.2.

HRMS(ESI): m/z Calcd. for $\text{C}_{19}\text{H}_{29}\text{NNaO}_3\text{S}$ $[\text{M}+\text{Na}]^+$:374.1760; Found:374.1753.

5-(1-(2-Fluoro-[1,1'-biphenyl]-4-yl)ethyl)hept-5-en-2-one (2w)



The title compound was prepared according to the general procedure as described, silica gel flash column chromatography was performed using hexanes and ethyl acetate (30:1) (R_f = 0.40

in hexane:ethyl acetate = 15:1) resulting in 9.5 mg of yellow liquid in 31% yield, *E/Z*

70:30.

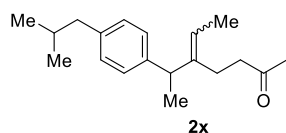
^1H NMR (600 MHz, CDCl_3) (*E*) δ 7.55-7.53 (m, 2H), 7.43 (t, $J = 7.8$ Hz, 2H), 7.36-7.34 (m, 2H), 7.08-7.03 (m, 2H), 5.49 (q, $J = 6.6$ Hz, 1H), 3.43 (q, $J = 7.2$ Hz, 1H), 2.37-2.32 (m, 2H), 2.24-2.16 (m, 2H), 2.06 (s, 3H), 1.68 (d, $J = 6.6$ Hz, 3H), 1.36 (d, $J = 7.2$ Hz, 3H). (*Z*) δ 7.55-7.53 (m, 2H), 7.43 (t, $J = 7.8$ Hz, 2H), 7.36-7.34 (m, 2H), 7.01-6.96 (m, 2H), 5.30 (q, $J = 7.2$ Hz, 1H), 4.13 (q, $J = 7.2$ Hz, 1H), 2.37-2.32 (m, 2H), 2.13-2.09 (m, 2H), 2.05 (s, 3H), 1.76 (d, $J = 6.6$ Hz, 3H), 1.42 (d, $J = 7.2$ Hz, 3H).

^{13}C NMR (151 MHz, CDCl_3) (*E*) δ 208.6, 159.9 (d, $J = 247.9$ Hz), 147.6, 141.8, 136.0, 130.6 (d, $J = 3.9$ Hz), 129.1 (d, $J = 3.0$ Hz), 128.5, 127.6, 123.8, 120.4, 119.3, 115.2 (d, $J = 23.1$ Hz), 45.5, 42.8, 29.9, 24.0, 20.5, 13.5. (*Z*) δ 208.7, 159.9 (d, $J = 247.9$ Hz), 147.6, 141.7, 136.0, 130.4 (d, $J = 4.4$ Hz), 129.1 (d, $J = 3.0$ Hz), 128.5, 127.6, 123.4, 120.4, 119.3, 115.1 (d, $J = 23.2$ Hz), 45.5, 42.9, 29.9, 25.6, 20.5, 17.2.

^{19}F NMR (565 MHz, CDCl_3) (*E*) δ -118.4. (*Z*) δ -118.5.

HRMS(ESI): m/z Calcd. for $\text{C}_{21}\text{H}_{23}\text{FNaO}$ $[\text{M}+\text{Na}]^+$:333.1625; Found:333.1628.

5-(1-(4-Isobutylphenyl)ethyl)hept-5-en-2-one (2x)



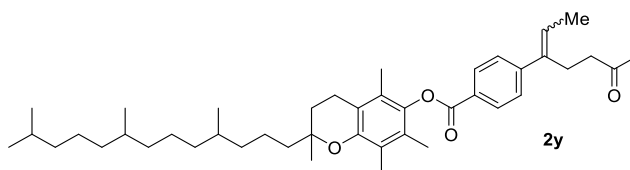
The title compound was prepared according to the general procedure as described, silica gel flash column chromatography was performed using hexanes and ethyl acetate (30:1) ($R_f = 0.40$ in hexane:ethyl acetate = 15:1) resulting in 9.9 mg of yellow liquid in 36% yield, *E/Z* 50:50.

^1H NMR (600 MHz, CDCl_3) (*E*) δ 7.13-7.03 (m, 4H), 5.44 (q, $J = 7.2$ Hz, 1H), 3.36 (q, $J = 7.2$ Hz, 1H), 2.44-2.42 (m, 2H), 2.36-2.24 (m, 2H), 2.21-2.16 (m, 2H), 1.98 (s, 3H), 1.85-1.81 (m, 1H), 1.64 (d, $J = 6.6$ Hz, 3H), 1.32 (d, $J = 6.6$ Hz, 3H), 0.89 (d, $J = 6.6$ Hz, 6H). (*Z*) δ 7.13-7.03 (m, 4H), 5.24 (q, $J = 6.6$ Hz, 1H), 4.10 (q, $J = 7.2$ Hz, 1H), 2.44-2.42 (m, 2H), 2.21-2.16 (m, 2H), 2.14-2.07 (m, 2H), 1.96 (s, 3H), 1.85-1.81 (m, 1H), 1.75 (d, $J = 6.6$ Hz, 3H), 1.37 (d, $J = 7.2$ Hz, 3H), 0.89 (d, $J = 6.6$ Hz, 6H).

^{13}C NMR (151 MHz, CDCl_3) (*E*) δ 208.7, 142.8, 139.6, 139.4, 129.1, 127.5, 119.4, 45.9, 45.2, 42.9, 30.4, 29.7, 24.0, 22.5, 20.5, 13.5. (*Z*) δ 208.8, 141.7, 139.6, 139.4, 129.1, 127.2, 118.7, 45.9, 45.2, 43.4, 38.2, 29.7, 26.0, 22.5, 17.3, 13.4.

HRMS(ESI): m/z Calcd. for $\text{C}_{19}\text{H}_{28}\text{NaO}$ $[\text{M}+\text{Na}]^+$:295.2032; Found:295.2031.

2,5,7,8-Tetramethyl-2-(4,8,12-trimethyltridecyl)chroman-6-yl-4-(6-oxohept-2-en-3-yl)benzoate (2y)



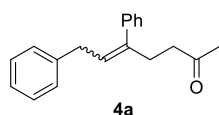
The title compound was prepared according to the general procedure as described, silica gel flash column chromatography was performed using hexanes and ethyl acetate (30:1) ($R_f = 0.40$ in hexane:ethyl acetate = 15:1) resulting in 35.5 mg of yellow liquid in 55% yield, *E/Z* 60:40.

^1H NMR (400 MHz, CDCl_3) (*E*) δ 8.18 (d, $J = 8.4$ Hz, 2H), 7.44 (d, $J = 7.8$ Hz, 2H), 5.92 (q, $J = 7.2$ Hz, 1H), 2.84 (t, $J = 7.8$ Hz, 2H), 2.63-2.61 (m, 2H), 2.49-2.43 (m, 2H), 2.13-2.02 (m, 14H), 1.86 (d, $J = 7.2$ Hz, 3H), 1.60-1.37 (m, 12H), 1.16-1.03 (m, 8H), 0.89-0.83 (m, 16H). (*Z*) δ 8.22 (d, $J = 7.8$ Hz, 2H), 7.29 (d, $J = 8.4$ Hz, 2H), 5.67 (q, $J = 7.2$ Hz, 1H), 2.67 (t, $J = 7.8$ Hz, 2H), 2.63-2.61 (m, 2H), 2.49-2.43 (m, 2H), 2.13-2.02 (m, 14H), 1.86 (d, $J = 7.2$ Hz, 3H), 1.60-1.37 (m, 12H), 1.16-1.03 (m, 8H), 0.89-0.83 (m, 16H).

^{13}C NMR (151 MHz, CDCl_3) (*E*) δ 208.0, 165.0, 147.6, 140.7, 138.7, 130.3, 128.8, 127.9, 126.9, 126.3, 125.1, 123.1, 117.5, 75.1, 42.1, 39.8, 39.4, 37.6, 37.5, 37.4, 37.3, 32.9, 32.8, 31.2, 30.0, 29.7, 28.0, 24.8, 24.5, 23.7, 23.1, 22.6, 20.7, 19.7, 19.7, 19.6, 14.3, 13.1, 12.2, 11.9. (*Z*) δ 208.0, 165.0, 149.5, 145.8, 139.3, 130.1, 128.8, 128.1, 126.9, 126.2, 123.4, 123.1, 117.5, 75.1, 42.4, 40.5, 39.4, 37.6, 37.5, 37.4, 37.3, 32.8, 32.7, 31.1, 30.0, 29.7, 28.0, 24.8, 24.5, 24.2, 23.1, 22.7, 21.1, 19.8, 19.7, 19.6, 14.7, 13.1, 12.2, 11.9.

HRMS(ESI): m/z Calcd. for $C_{43}H_{64}NaO_4$ $[M+Na]^+$:667.4697; Found:667.4696.

5,7-Diphenylhept-5-en-2-one (4a)



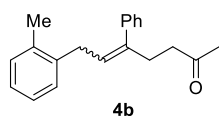
The title compound was prepared according to the general procedure as described, silica gel flash column chromatography was performed using hexanes and ethyl acetate (30:1) ($R_f = 0.40$ in hexane:ethyl acetate = 15:1) resulting in 14.5 mg of yellow liquid in 55% yield, *E/Z* 40:60.

1H NMR (400 MHz, $CDCl_3$) (*E*) δ 7.30-7.37 (m, 5H), 7.24-7.22 (m, 3H), 7.11 (d, $J = 7.6$ Hz, 2H), 5.87 (t, $J = 7.6$ Hz, 1H), 3.58 (d, $J = 7.2$ Hz, 2H), 2.88 (t, $J = 7.6$ Hz, 2H), 2.48-2.44 (m, 2H), 2.06 (s, 3H). (*Z*) δ 7.37-7.32 (m, 5H), 7.20-7.17 (m, 3H), 7.11 (d, $J = 7.6$ Hz, 2H), 5.67 (t, $J = 7.2$ Hz, 1H), 3.27 (d, $J = 7.6$ Hz, 2H), 2.67 (t, $J = 7.6$ Hz, 2H), 2.48-2.44 (m, 2H), 2.06 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) (*E*) δ 208.4, 142.3, 140.7, 140.2, 128.6, 128.5, 128.4, 127.1, 126.6, 126.2, 126.0, 42.5, 35.2, 33.4, 30.1. (*Z*) δ 208.3, 142.2, 141.0, 139.6, 128.7, 128.5, 128.2, 127.2, 126.7, 126.2, 125.6, 42.5, 34.8, 30.1, 23.9.

HRMS(ESI): m/z Calcd. for $C_{19}H_{20}NaO$ $[M+Na]^+$:287.1406 Found:287.1406.

5-Phenyl-7-(*o*-tolyl)hept-5-en-2-one (4b)



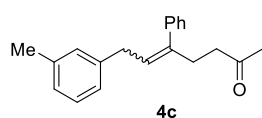
The title compound was prepared according to the general procedure as described, silica gel flash column chromatography was performed using hexanes and ethyl acetate (30:1) ($R_f = 0.40$ in hexane:ethyl acetate = 15:1) resulting in 17.3 mg of yellow liquid in 62% yield, *E/Z* 50:50.

1H NMR (600 MHz, $CDCl_3$) (*E*) δ 7.36-7.28 (m, 4H), 7.18 (d, $J = 7.8$ Hz, 3H), 7.15-7.12 (m, 2H), 5.79 (t, $J = 7.2$ Hz, 1H), 3.53 (d, $J = 7.2$ Hz, 2H), 2.89 (t, $J = 7.8$ Hz, 2H), 2.46 (t, $J = 7.8$ Hz, 2H), 2.33 (s, 3H), 2.06 (s, 3H). (*Z*) δ 7.36-7.28 (m, 4H), 7.15-7.12 (m, 2H), 7.10-7.07 (m, 3H), 5.61 (t, $J = 7.2$ Hz, 1H), 3.24 (d, $J = 7.2$ Hz, 2H), 2.67 (t, $J = 7.8$ Hz, 2H), 2.46 (t, $J = 7.8$ Hz, 2H), 2.13 (s, 3H), 2.06 (s, 3H).

^{13}C NMR (151 MHz, CDCl_3) (*E*) δ 208.4, 142.2, 140.2, 139.2, 136.4, 130.3, 128.7, 128.5, 127.7, 127.2, 126.4, 126.2, 125.7, 42.4, 32.6, 30.2, 23.9, 19.8. (*Z*) δ 208.5, 140.7, 139.6, 139.5, 136.3, 130.2, 128.5, 128.4, 127.7, 127.1, 126.5, 126.2, 126.1, 42.5, 33.4, 32.9, 30.1, 19.5.

HRMS(ESI): m/z Calcd. for $\text{C}_{20}\text{H}_{22}\text{NaO}$ $[\text{M}+\text{Na}]^+$:301.1563; Found:301.1562.

5-Phenyl-7-(*m*-tolyl)hept-5-en-2-one (4c)



The title compound was prepared according to the general procedure as described, silica gel flash column chromatography was performed using hexanes and ethyl acetate (30:1) ($R_f = 0.40$

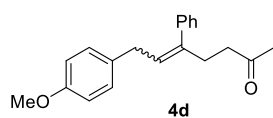
in hexane:ethyl acetate = 15:1) resulting in 8.4 mg of yellow liquid in 30% yield, *E/Z* 40:60.

^1H NMR (600 MHz, CDCl_3) (*E*) δ 7.37-7.31 (m, 3H), 7.20-7.18 (m, 3H), 7.04-7.02 (m, 1H), 6.92-6.91 (m, 2H), 5.87 (t, $J = 7.8$ Hz, 1H), 3.54 (d, $J = 7.2$ Hz, 2H), 2.88 (t, $J = 7.8$ Hz, 2H), 2.46 (t, $J = 7.8$ Hz, 2H), 2.34-2.32 (m, 3H), 2.07 (s, 3H). (*Z*) δ 7.37-7.31 (m, 3H), 7.20-7.18 (m, 3H), 7.04-7.02 (m, 1H), 6.92-6.91 (m, 2H), 5.66 (t, $J = 7.8$ Hz, 1H), 3.24 (d, $J = 7.2$ Hz, 2H), 2.67 (t, $J = 7.8$ Hz, 2H), 2.46 (t, $J = 7.8$ Hz, 2H), 2.34-2.32 (m, 3H), 2.07 (s, 3H).

^{13}C NMR (151 MHz, CDCl_3) (*E*) δ 208.2, 142.3, 140.9, 139.5, 138.3, 129.4, 128.6, 128.5, 127.4, 126.9, 126.4, 125.6, 125.5, 46.2, 34.8, 30.1, 23.2, 22.8. (*Z*) δ 208.3, 141.3, 140.6, 140.3, 138.1, 129.2, 128.6, 128.5, 127.1, 126.8, 126.6, 125.7, 125.4, 42.5, 35.2, 33.5, 24.0, 21.5.

HRMS(ESI): m/z Calcd. for $\text{C}_{20}\text{H}_{22}\text{NaO}$ $[\text{M}+\text{Na}]^+$:301.1563; Found:301.1560.

7-(4-Methoxyphenyl)-5-phenylhept-5-en-2-one (4d)



The title compound was prepared according to the general procedure as described, silica gel flash column chromatography was performed using hexanes and ethyl acetate (20:1) ($R_f =$

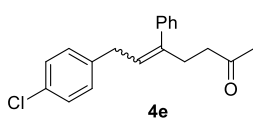
0.40 in hexane:ethyl acetate = 10:1) resulting in 18.8 mg of yellow liquid in 65% yield, *E/Z* 40:60.

¹H NMR (600 MHz, CDCl₃) (*E*) δ 7.32-7.27 (m, 3H), 7.15-7.12 (m, 2H), 6.84 (d, *J* = 8.4 Hz, 2H), 6.81 (d, *J* = 8.4 Hz, 2H), 5.85 (t, *J* = 7.2 Hz, 1H), 3.79 (s, 3H), 3.51 (d, *J* = 7.2 Hz, 2H), 2.88 (t, *J* = 7.8 Hz, 2H), 2.47-2.44 (m, 2H), 2.06 (s, 3H). (*Z*) δ 7.36-7.32 (m, 3H), 7.19-7.17 (m, 2H), 7.03 (d, *J* = 8.4 Hz, 2H), 6.81 (d, *J* = 8.4 Hz, 2H), 5.64 (t, *J* = 7.2 Hz, 1H), 3.78 (s, 3H), 3.21 (d, *J* = 7.2 Hz, 2H), 2.66 (t, *J* = 7.8 Hz, 2H), 2.47-2.44 (m, 2H), 2.06 (s, 3H).

¹³C NMR (151 MHz, CDCl₃) (*E*) δ 208.4, 158.1, 142.2, 139.2, 133.0, 129.4, 128.6, 128.5, 127.1, 126.6, 114.1, 55.4, 42.5, 34.3, 30.2, 23.8. (*Z*) δ 208.5, 157.9, 140.3, 140.2, 133.4, 129.3, 128.6, 128.4, 127.1, 126.6, 114.0, 55.4, 42.5, 33.9, 33.4, 30.1.

HRMS(ESI): *m/z* Calcd. for C₂₀H₂₂NaO₂ [M+Na]⁺:317.1512; Found:317.1511.

7-(4-Chlorophenyl)-5-phenylhept-5-en-2-one (4e)



The title compound was prepared according to the general procedure as described, silica gel flash column chromatography was performed using hexanes and ethyl acetate (30:1) (*R_f* = 0.40

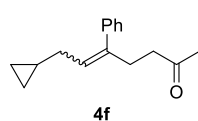
in hexane:ethyl acetate = 15:1) resulting in 17.9 mg of yellow liquid in 60% yield, *E/Z* 30:70.

¹H NMR (600 MHz, CDCl₃) (*E*) δ 7.35 (t, *J* = 7.2 Hz, 1H), 7.32-7.28 (m, 2H), 7.22 (d, *J* = 7.8 Hz, 2H), 7.16-7.15 (m, 2H), 7.03 (d, *J* = 8.4 Hz, 2H), 5.81 (t, *J* = 7.2 Hz, 1H), 3.54 (d, *J* = 7.8 Hz, 2H), 2.86 (t, *J* = 7.8 Hz, 2H), 2.47-2.44 (m, 2H), 2.06 (s, 3H). (*Z*) δ 7.35 (t, *J* = 7.2 Hz, 1H), 7.32-7.28 (m, 2H), 7.22 (d, *J* = 7.8 Hz, 2H), 7.16-7.15 (m, 2H), 7.03 (d, *J* = 8.4 Hz, 2H), 5.62 (t, *J* = 7.2 Hz, 1H), 3.23 (d, *J* = 7.2 Hz, 2H), 2.66 (t, *J* = 7.8 Hz, 2H), 2.47-2.44 (m, 2H), 2.06 (s, 3H).

¹³C NMR (151 MHz, CDCl₃) (*E*) δ 208.2, 145.5, 135.6, 133.2, 129.9, 129.4, 128.8, 128.6, 127.1, 126.7, 125.1, 42.4, 34.5, 34.1, 13.3. (*Z*) δ 208.3, 145.5, 136.3, 131.9, 129.8, 129.7, 128.5, 128.5, 127.9, 126.6, 125.6, 46.1, 40.0, 33.4, 18.3.

HRMS(ESI): *m/z* Calcd. for C₁₉H₁₉ClNaO [M+Na]⁺:321.1017; Found:321.1019.

7-Cyclopropyl-5-phenylhept-5-en-2-one (4f)



The title compound was prepared according to the general procedure as described, silica gel flash column chromatography was performed using hexanes and ethyl acetate (30:1) ($R_f = 0.40$ in hexane:ethyl

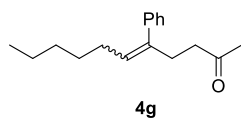
acetate = 15:1) resulting in 17.1 mg of yellow liquid in 75% yield, *E/Z* 70:30.

^1H NMR (600 MHz, CDCl_3) (*E*) δ 7.38-7.34 (m, 2H), 7.33-7.32 (m, 1H), 7.27-7.25 (m, 1H), 7.14 (d, $J = 7.8$ Hz, 1H), 5.80 (t, $J = 7.2$ Hz, 1H), 2.79 (t, $J = 7.8$ Hz, 2H), 2.47-2.44 (m, 2H), 2.15 (t, $J = 7.2$ Hz, 2H), 2.09 (s, 3H), 0.84-0.81 (m, 1H), 0.48 (d, $J = 7.8$ Hz, 2H), 0.15-0.14 (m, 2H). (*Z*) δ 7.38-7.34 (m, 2H), 7.33-7.32 (m, 1H), 7.27-7.25 (m, 1H), 7.14 (d, $J = 7.8$ Hz, 1H), 5.60 (t, $J = 7.2$ Hz, 1H), 2.65 (t, $J = 7.8$ Hz, 2H), 2.47-2.44 (m, 2H), 2.09 (s, 3H), 1.85 (t, $J = 7.2$ Hz, 2H), 0.69-0.67 (m, 1H), 0.40 (d, $J = 7.8$ Hz, 2H), 0.025-0.007 (m, 2H).

^{13}C NMR (151 MHz, CDCl_3) (*E*) δ 208.5, 142.5, 138.6, 128.6, 128.5, 127.0, 126.5, 42.7, 33.5, 33.3, 23.9, 11.1, 4.4. (*Z*) δ 208.7, 140.6, 139.6, 129.1, 128.3, 127.3, 126.8, 42.7, 33.7, 30.1, 30.1, 11.2, 4.2.

HRMS(ESI): m/z Calcd. for $\text{C}_{16}\text{H}_{20}\text{NaO}$ [$\text{M}+\text{Na}$] $^+$:251.1406; Found:251.1407.

5-Phenylundec-5-en-2-one (4g)



The title compound was prepared according to the general procedure as described, silica gel flash column chromatography was performed using hexanes and ethyl acetate (30:1) ($R_f = 0.40$

in hexane:ethyl acetate = 15:1) resulting in 20.0 mg of yellow liquid in 82% yield, *E/Z* 70:30.

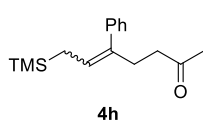
^1H NMR (600 MHz, CDCl_3) (*E*) δ 7.31-7.30 (m, 4H), 7.26-7.21 (m, 1H), 5.68 (t, $J = 7.2$ Hz, 1H), 2.77 (t, $J = 7.8$ Hz, 2H), 2.44-2.40 (m, 2H), 2.18 (q, $J = 7.2$ Hz, 2H), 2.07 (s, 3H), 1.46-1.41 (m, 2H), 1.34-1.29 (m, 2H), 1.23-1.17 (m, 2H), 0.91-0.89 (m, 3H). (*Z*) δ 7.31-7.30 (m, 4H), 7.13-7.11 (m, 1H), 5.47 (t, $J = 7.8$ Hz, 1H), 2.61 (t, $J = 7.8$ Hz,

2H), 2.44-2.40 (m, 2H), 2.07 (s, 3H), 1.90 (q, $J = 7.8$ Hz, 2H), 1.34-1.29 (m, 6H), 0.84 (t, $J = 7.8$ Hz, 3H).

^{13}C NMR (151 MHz, CDCl_3) (*E*) δ 208.7, 142.6, 138.4, 130.4, 128.5, 126.9, 126.5, 42.7, 31.7, 30.1, 29.8, 28.6, 23.8, 22.7, 14.2. (*Z*) δ 208.7, 140.7, 139.2, 128.6, 128.5, 128.3, 126.7, 42.7, 33.5, 31.5, 30.1, 29.8, 28.9, 22.6, 14.2.

HRMS(ESI): m/z Calcd. for $\text{C}_{17}\text{H}_{24}\text{NaO}$ [$\text{M}+\text{Na}$] $^+$:267.1719; Found:267.1721.

5-Phenyl-7-(trimethylsilyl)hept-5-en-2-one (4h)



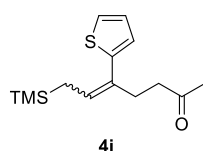
The title compound was prepared according to the general procedure as described, silica gel flash column chromatography was performed using hexanes and ethyl acetate (30:1) ($R_f = 0.40$ in hexane:ethyl acetate = 15:1) resulting in 19.0 mg of yellow liquid in 73% yield, *E/Z* 70:30.

^1H NMR (600 MHz, CDCl_3) (*E*) δ 7.40-7.35 (m, 2H), 7.33-7.26 (m, 2H), 7.17 (d, $J = 7.2$ Hz, 1H), 5.80 (t, $J = 8.4$ Hz, 1H), 2.80 (t, $J = 7.8$ Hz, 2H), 2.50-2.45 (m, 2H), 2.13 (s, 3H), 1.72 (d, $J = 9.0$ Hz, 2H), 0.11 (s, 9H). (*Z*) δ 7.40-7.35 (m, 2H), 7.33-7.26 (m, 2H), 7.17 (d, $J = 7.2$ Hz, 1H), 5.57 (t, $J = 8.4$ Hz, 1H), 2.67 (t, $J = 7.8$ Hz, 2H), 2.50-2.45 (m, 2H), 2.13 (s, 3H), 1.43 (d, $J = 8.4$ Hz, 2H), 0.11 (s, 9H).

^{13}C NMR (151 MHz, CDCl_3) (*E*) δ 211.3, 145.7, 138.8, 131.1, 131.0, 129.2, 129.0, 45.2, 32.7, 26.0, 22.9, 1.2. (*Z*) δ 211.3, 143.6, 140.1, 131.6, 129.2, 129.0, 126.7, 45.6, 36.6, 32.6, 22.1, 1.1.

HRMS(ESI): m/z Calcd. for $\text{C}_{16}\text{H}_{24}\text{NaOSi}$ [$\text{M}+\text{Na}$] $^+$:283.1489; Found:283.1489.

5-(Thiophen-2-yl)-7-(trimethylsilyl)hept-5-en-2-one (4i)



The title compound was prepared according to the general procedure as described, silica gel flash column chromatography was performed using hexanes and ethyl acetate (30:1) ($R_f = 0.40$ in hexane:ethyl acetate = 15:1) resulting in 12.0 mg of yellow liquid in 45% yield, *E/Z* 60:40.

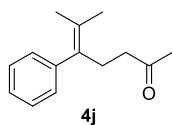
^1H NMR (600 MHz, CDCl_3) (*E*) δ 7.06 (dd, $J = 4.8$ Hz, 0.6 Hz, 1H), 6.95-6.93 (m, 1H), 6.84 (dd, $J = 3.6$ Hz, 1.2 Hz, 1H), 5.96 (t, $J = 8.4$ Hz, 1H), 2.69-2.65 (m, 2H), 2.58 (t,

$J = 8.4$ Hz, 2H), 2.13 (s, 3H), 1.62 (d, $J = 9.0$ Hz, 2H), 0.04 (s, 9H). (Z) δ 7.23 (dd, $J = 5.4$ Hz, 1.2 Hz, 1H), 7.01-7.00 (m, 1H), 6.87 (dd, $J = 3.6$ Hz, 1.2 Hz, 1H), 5.62 (t, $J = 9.0$ Hz, 1H), 2.69-2.65 (m, 2H), 2.52 (t, $J = 7.8$ Hz, 2H), 2.09 (s, 3H), 1.70 (d, $J = 9.0$ Hz, 2H), 0.04 (s, 9H).

^{13}C NMR (101 MHz, CDCl_3) (*E*) δ 211.0, 149.6, 132.4, 129.8, 128.2, 127.9, 125.0, 45.2, 32.6, 26.4, 22.5, 1.0. (*Z*) δ 211.0, 144.6, 131.9, 129.7, 129.2, 126.6, 123.9, 45.8, 36.9, 32.3, 22.9, 1.0.

HRMS(ESI): m/z Calcd. for $\text{C}_{14}\text{H}_{23}\text{OSSi}$ [$\text{M}+\text{Na}$] $^+$:267.1233; Found:267.1234.

6-methyl-5-phenylhept-5-en-2-one (4j)



The title compound was prepared according to the general procedure as described, silica gel flash column chromatography was performed using hexanes and ethyl acetate (30:1) ($R_f = 0.40$ in hexane:ethyl acetate =

15:1) resulting in 6.8 mg of yellow liquid in 34% yield.

^1H NMR (600 MHz, CDCl_3) δ 7.31 (t, $J = 7.2$ Hz, 2H), 7.21 (t, $J = 7.2$ Hz, 1H), 7.07 (d, $J = 7.8$ Hz, 2H), 2.63 (t, $J = 8.4$ Hz, 2H), 2.35 (t, $J = 8.4$ Hz, 2H), 2.04 (s, 3H), 1.82 (s, 3H), 1.53 (s, 3H).

^{13}C NMR (151 MHz, CDCl_3) δ 209.0, 143.2, 133.5, 129.2, 128.6, 128.2, 126.2, 42.3, 30.0, 28.5, 22.4, 20.3.

HRMS(ESI): m/z Calcd. for $\text{C}_{14}\text{H}_{18}\text{NaO}$ [$\text{M}+\text{Na}$] $^+$:225.1250; Found:225.1250.

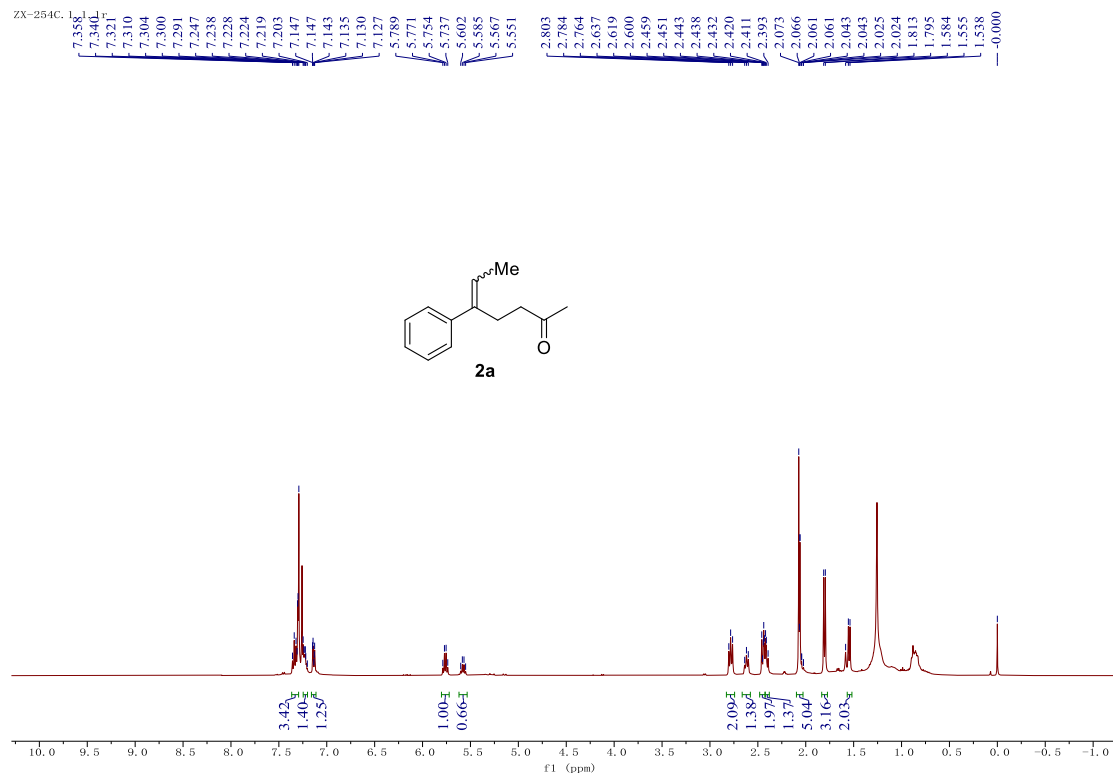
V References

1. S. Scaringi and C. Mazet, Kinetically Controlled Stereoselective Access to Branched 1,3-Dienes by Ru-Catalyzed Remote Conjugative Isomerization. *ACS Catal.* 2021, **11**, 7970-7977.
2. H. Faustino, I. Alonso, J. L. Mascareñas and F. López, Gold(I)-Catalyzed Cascade Cycloadditions between Allenamides and Carbonyl-Tethered Alkenes: An Enantioselective Approach to Oxa-Bridged Medium-Sized Carbocycles. *Angew. Chem. Int. Ed.* 2013, **52**, 6526-6530.
3. H. Chen, L. Huang, W. Fu, X. Liu and H. Jiang, Carbon–Carbon Bond Formation: Palladium-Catalyzed Oxidative Cross-Coupling of N-Tosylhydrazones with Allylic Alcohols. *Chem. Eur. J.* 2012, **18**, 10497-10500.

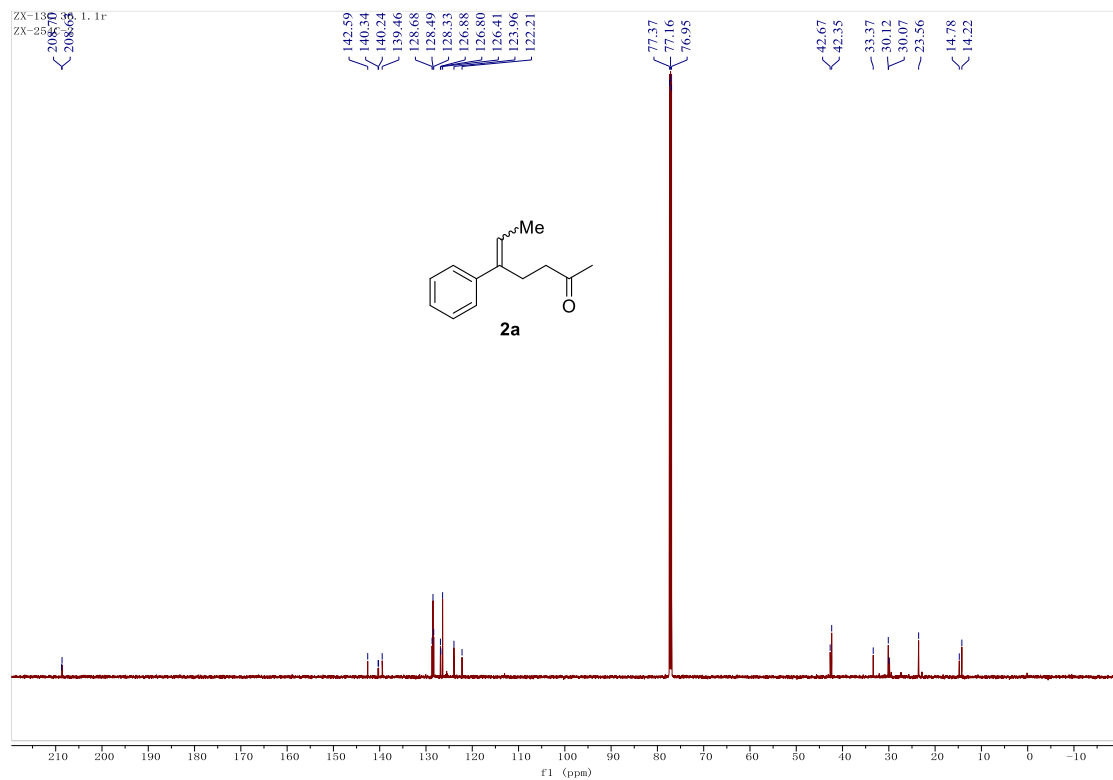
VI NMR spectra

The products 2:

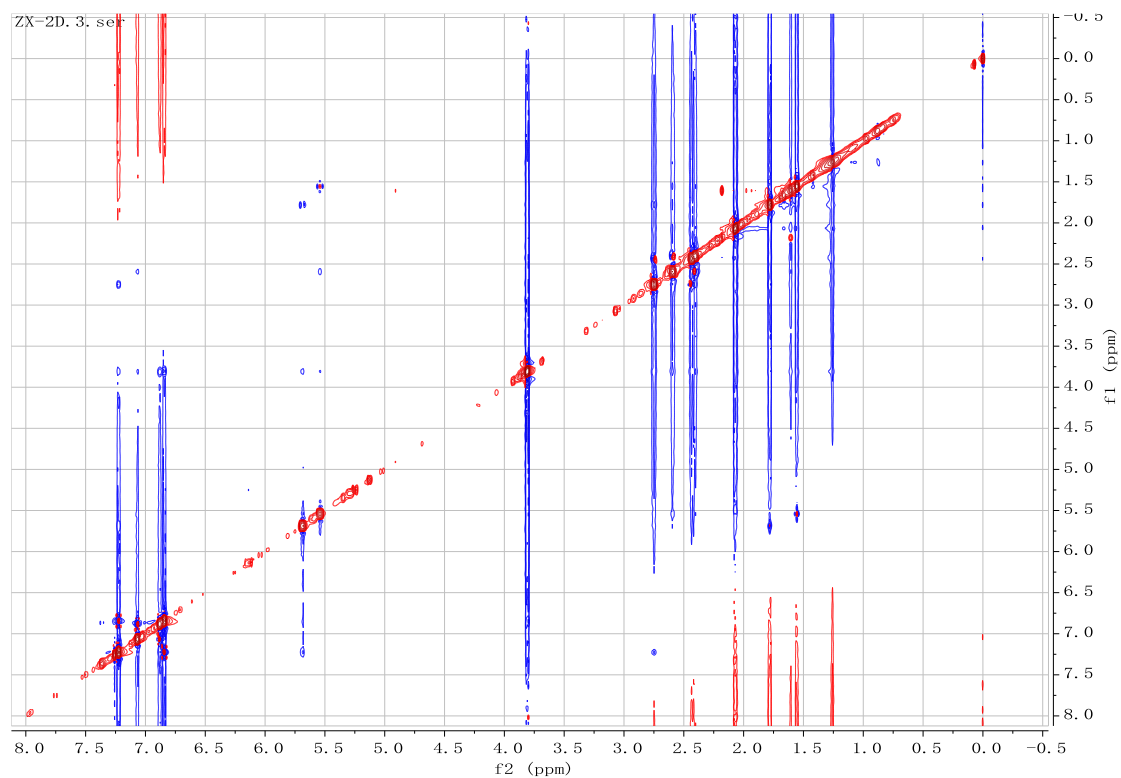
¹H NMR (400 MHz, CDCl₃) for **2a**



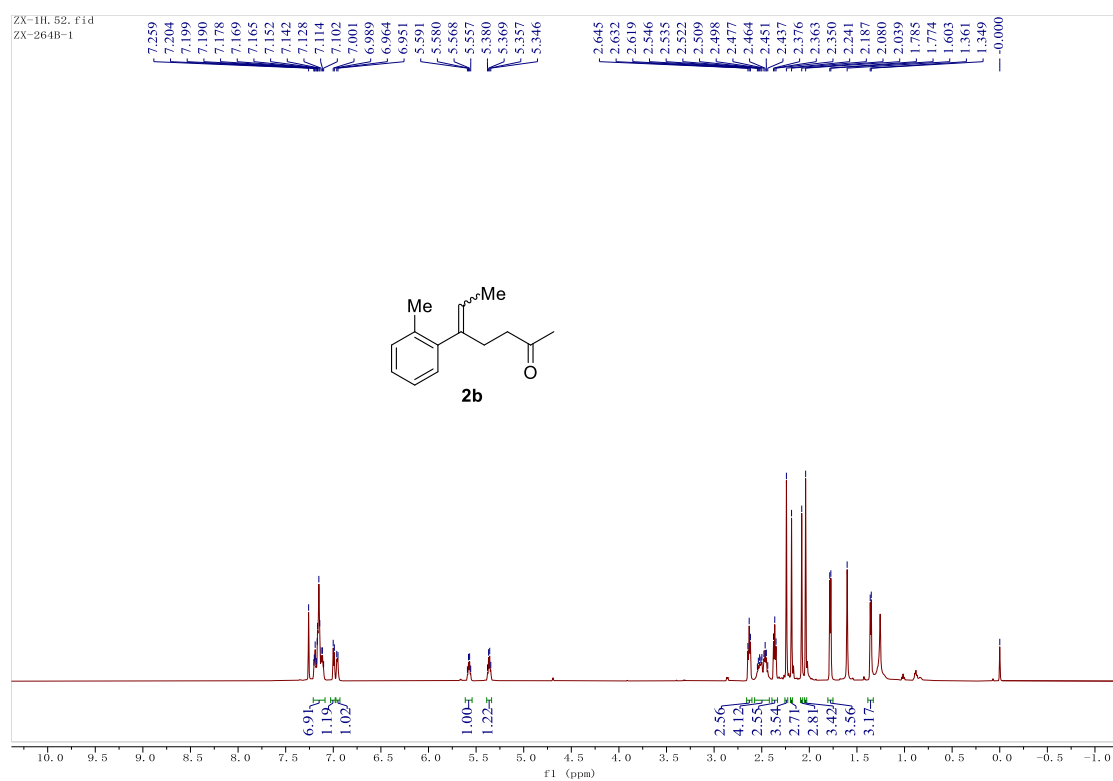
¹³C NMR (151 MHz, CDCl₃) for **2a**



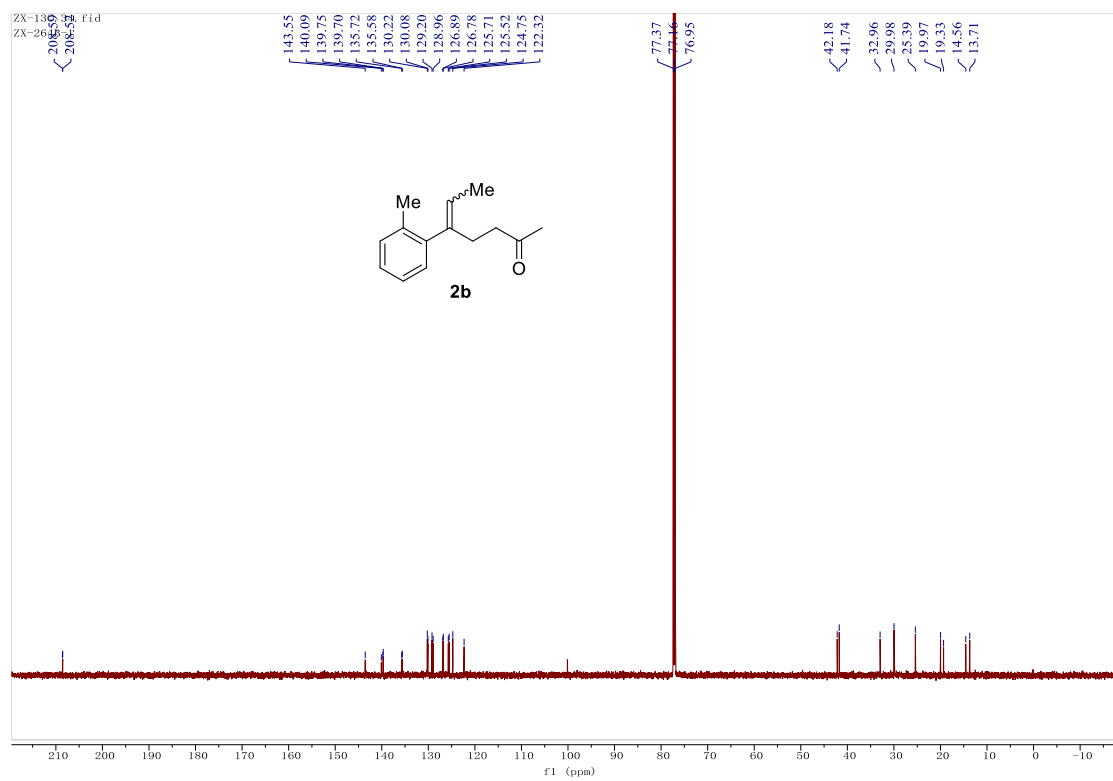
The *Z/E* configuration of **2a** was determined by 2D (^1H - ^1H) NMR measurement as shown below.



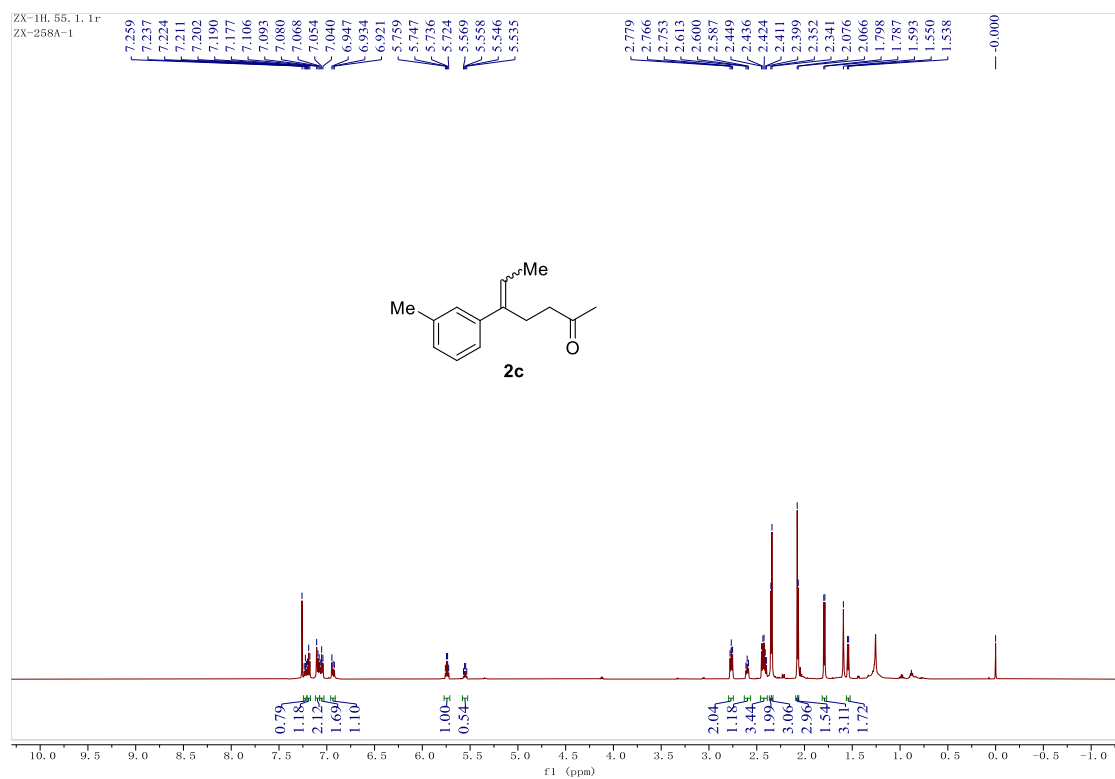
¹H NMR (600 MHz, CDCl₃) for **2b**



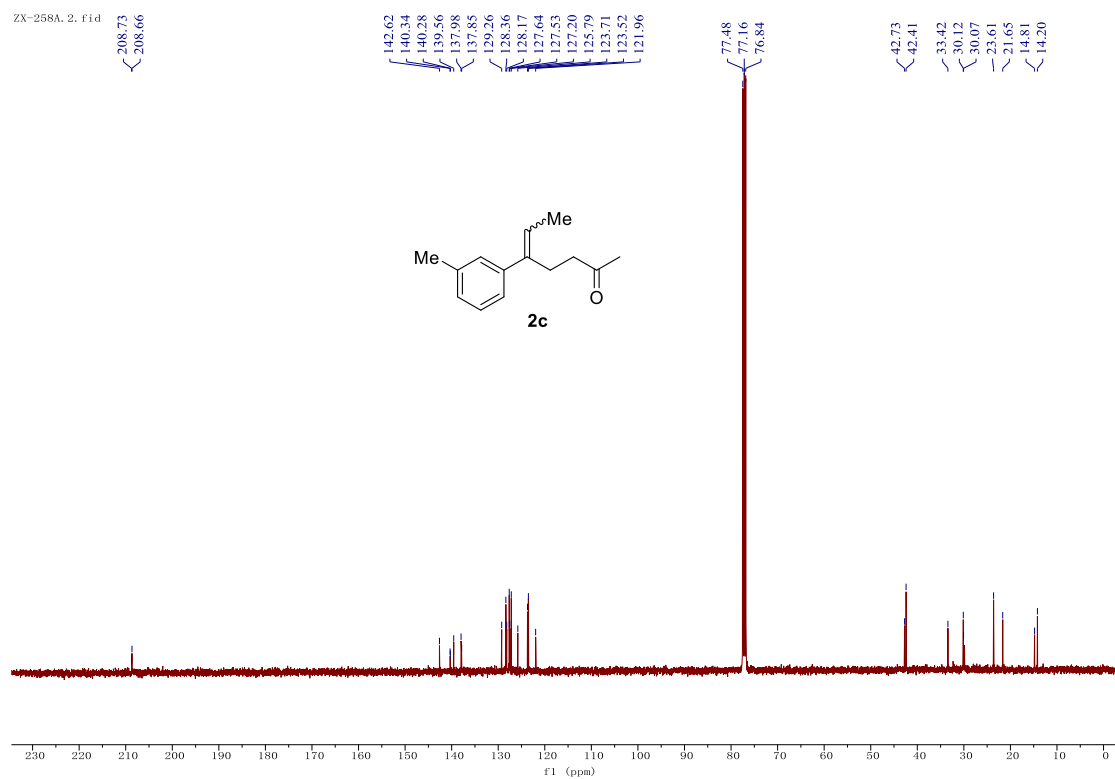
¹³C NMR (151 MHz, CDCl₃) for **2b**



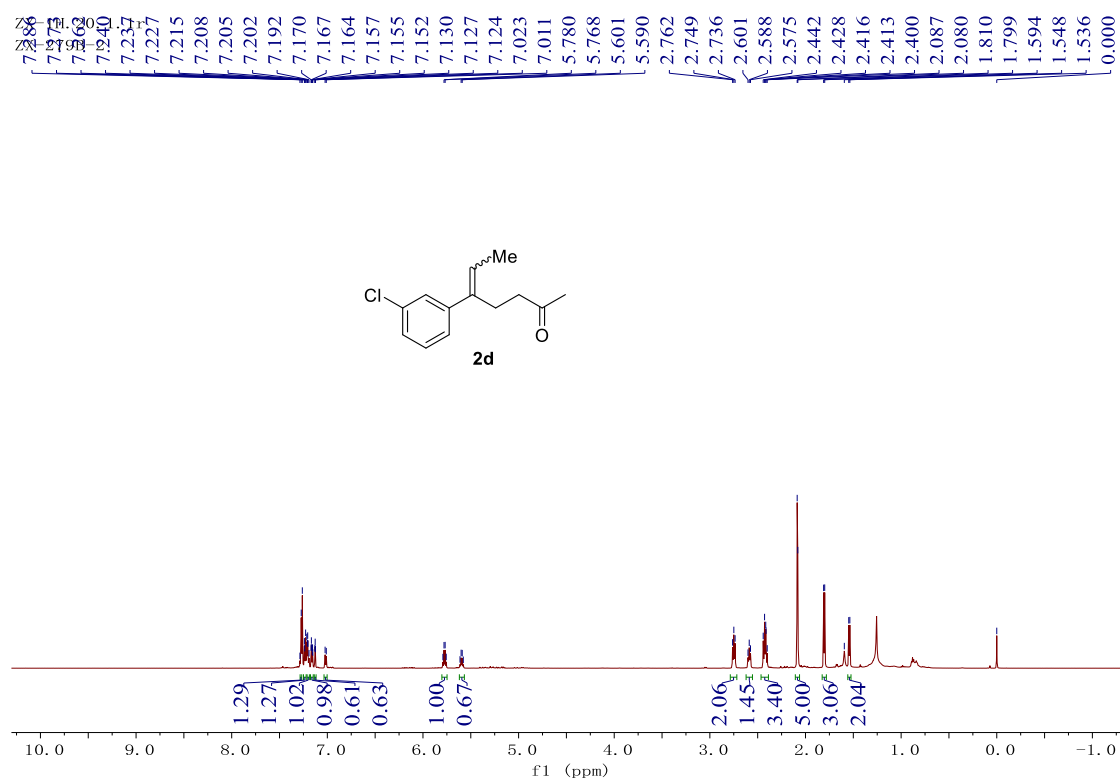
¹H NMR (600 MHz, CDCl₃) for **2c**



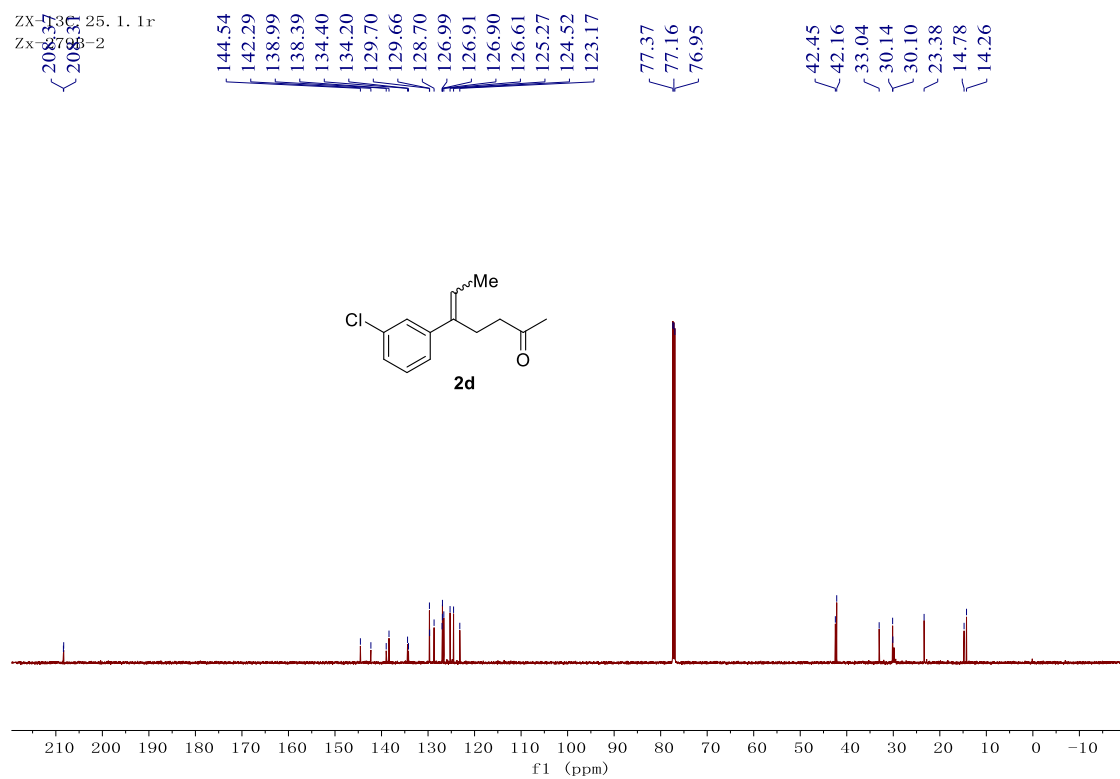
¹³C NMR (101 MHz, CDCl₃) for **2c**



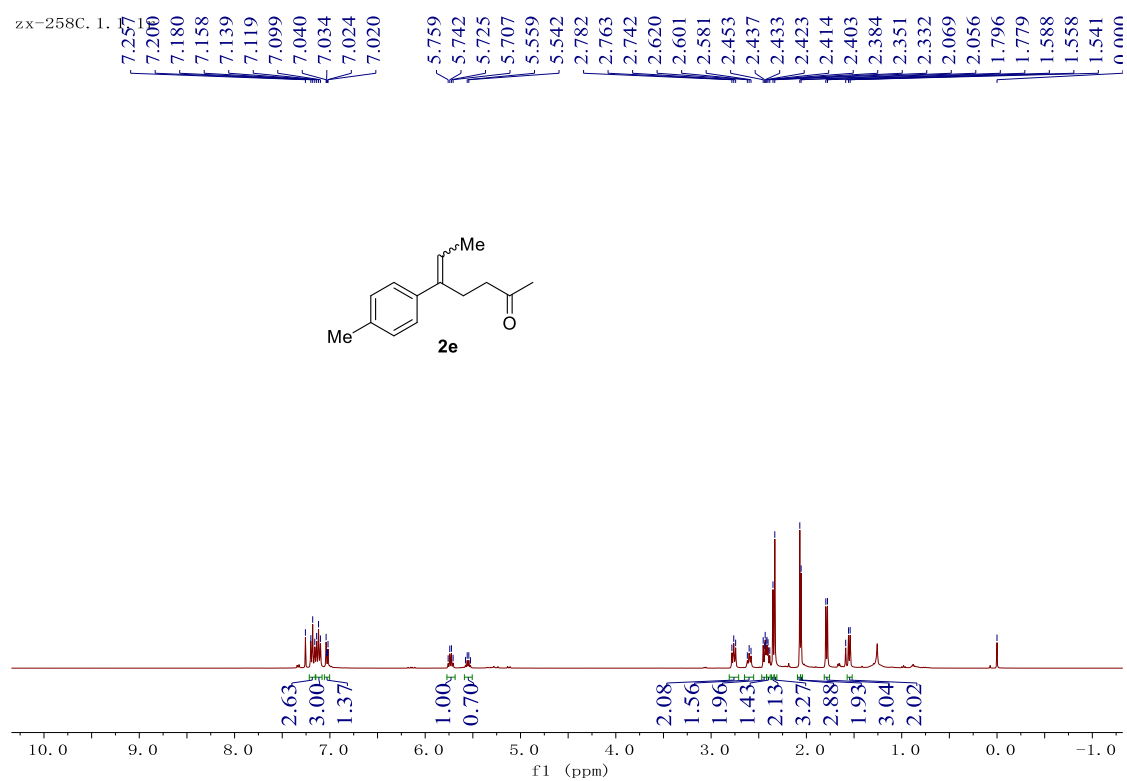
¹H NMR (600 MHz, CDCl₃) for **2d**



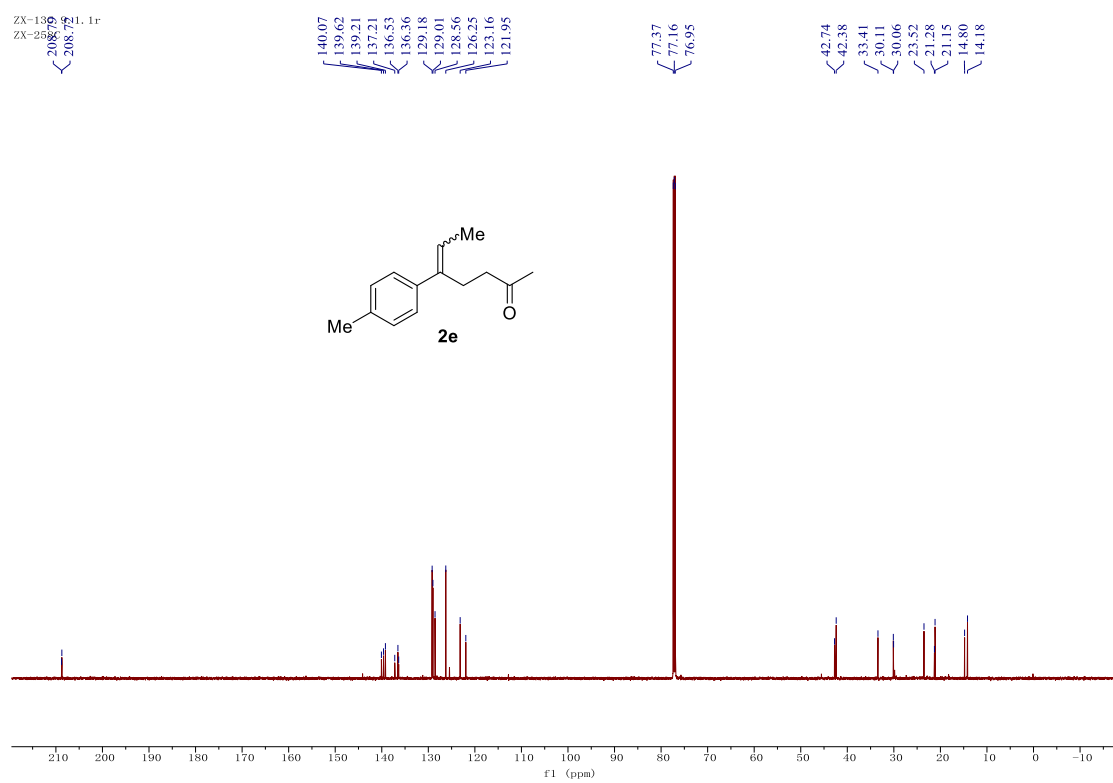
¹³C NMR (151 MHz, CDCl₃) for **2d**



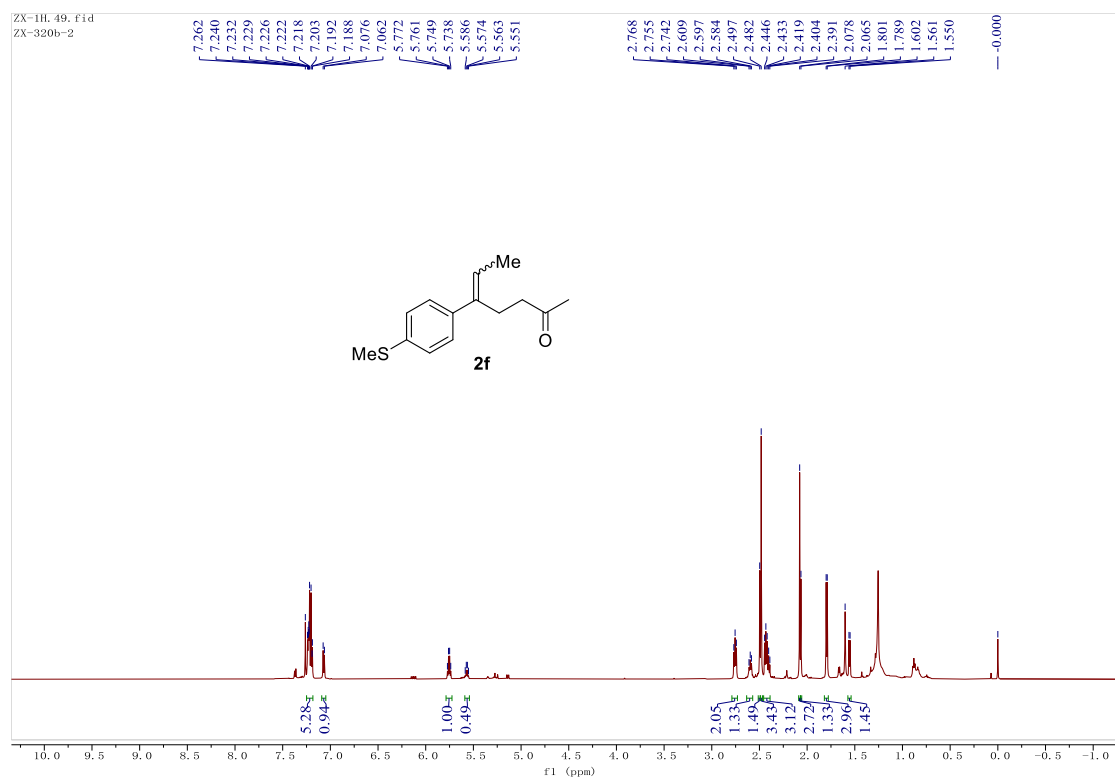
¹H NMR (400 MHz, CDCl₃) for **2e**



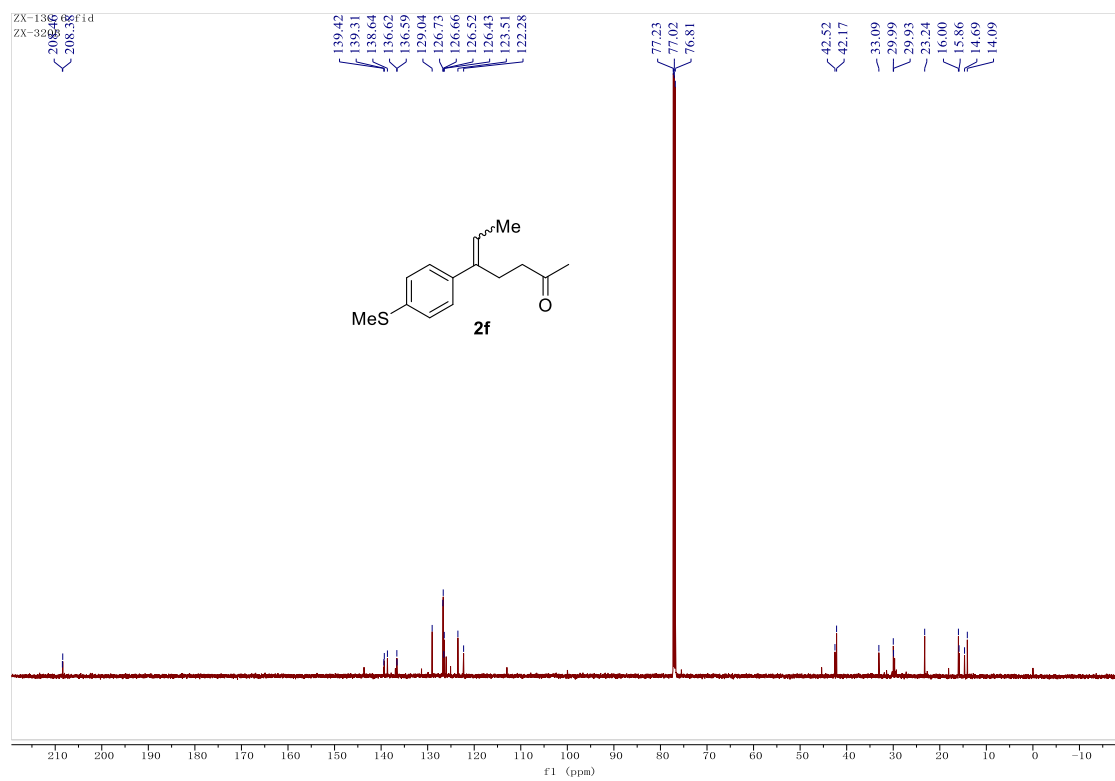
¹³C NMR (151 MHz, CDCl₃) for **2e**



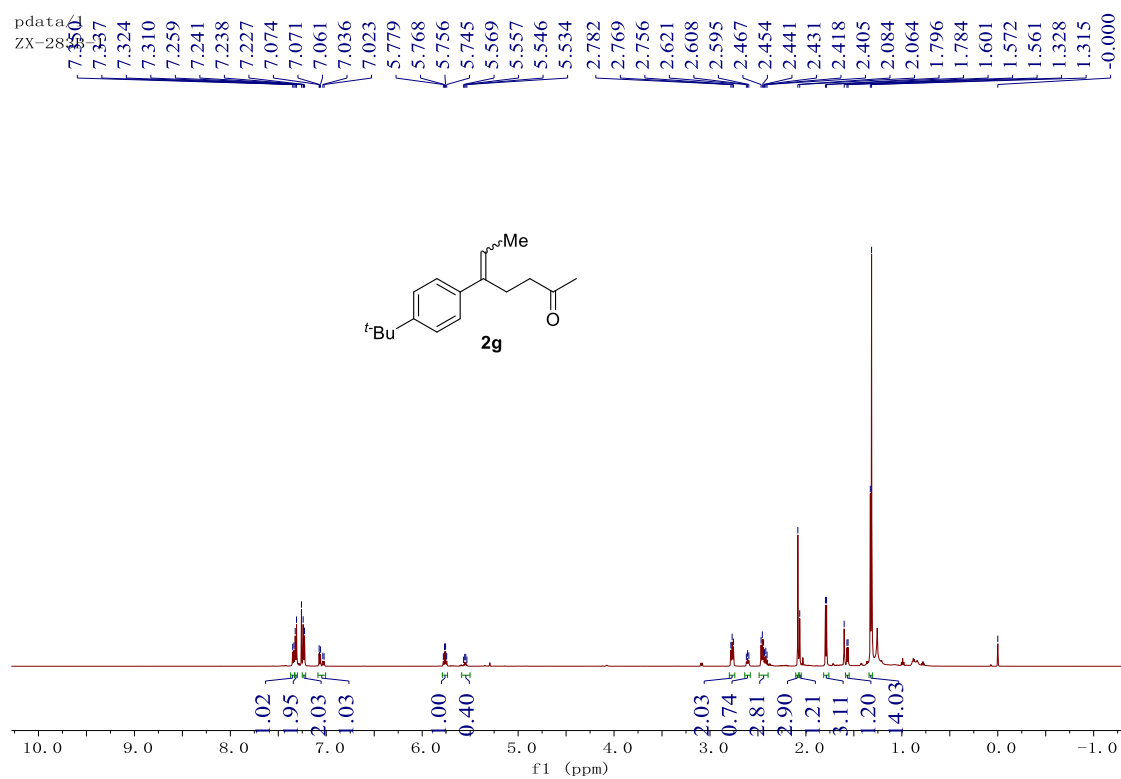
¹H NMR (600 MHz, CDCl₃) for **2f**



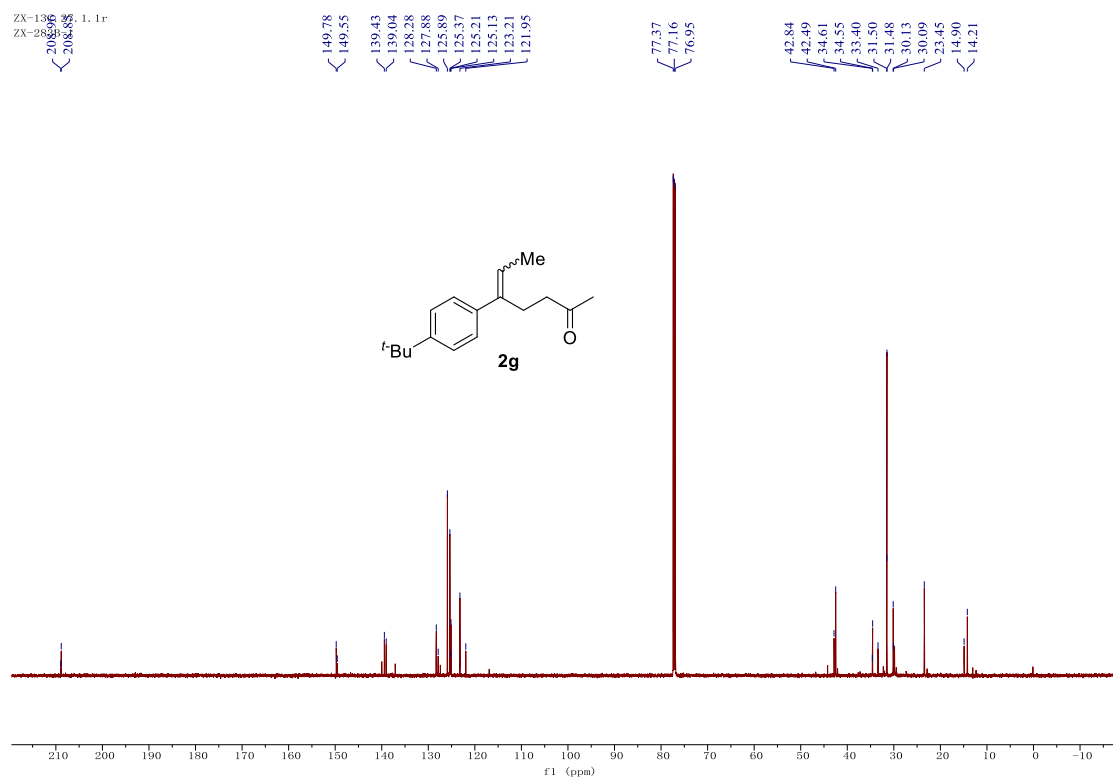
¹³C NMR (151 MHz, CDCl₃) for **2f**



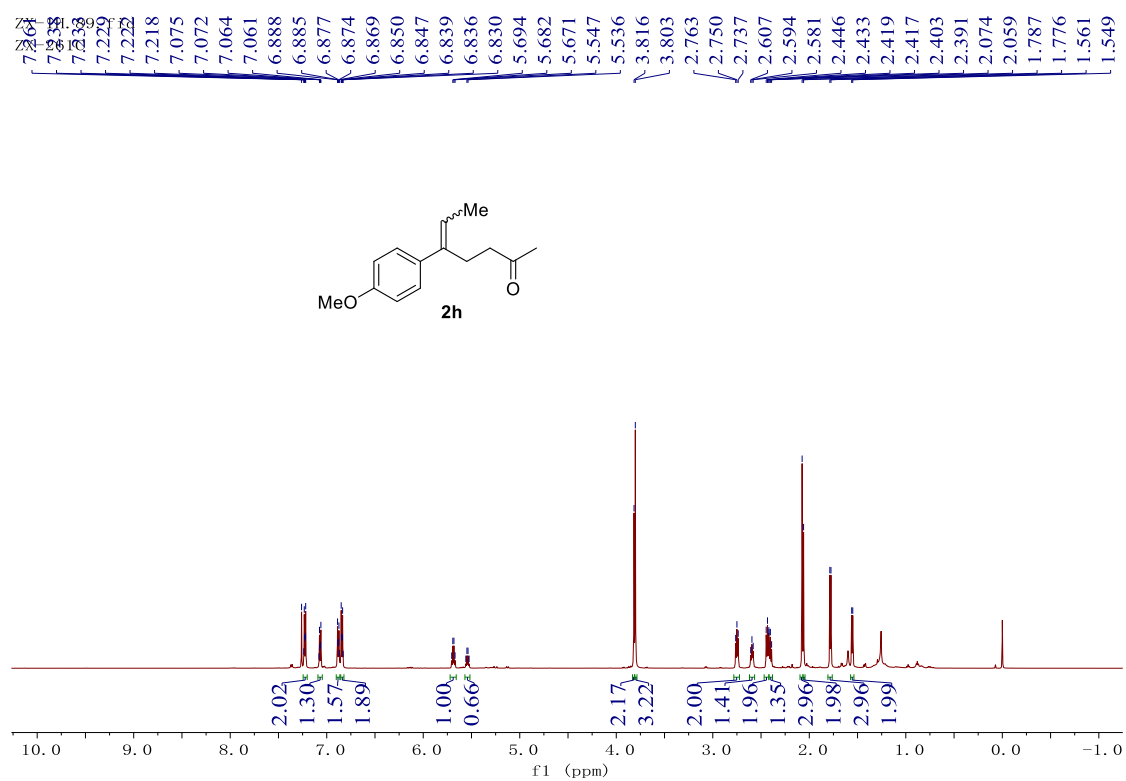
¹H NMR (600 MHz, CDCl₃) for **2g**



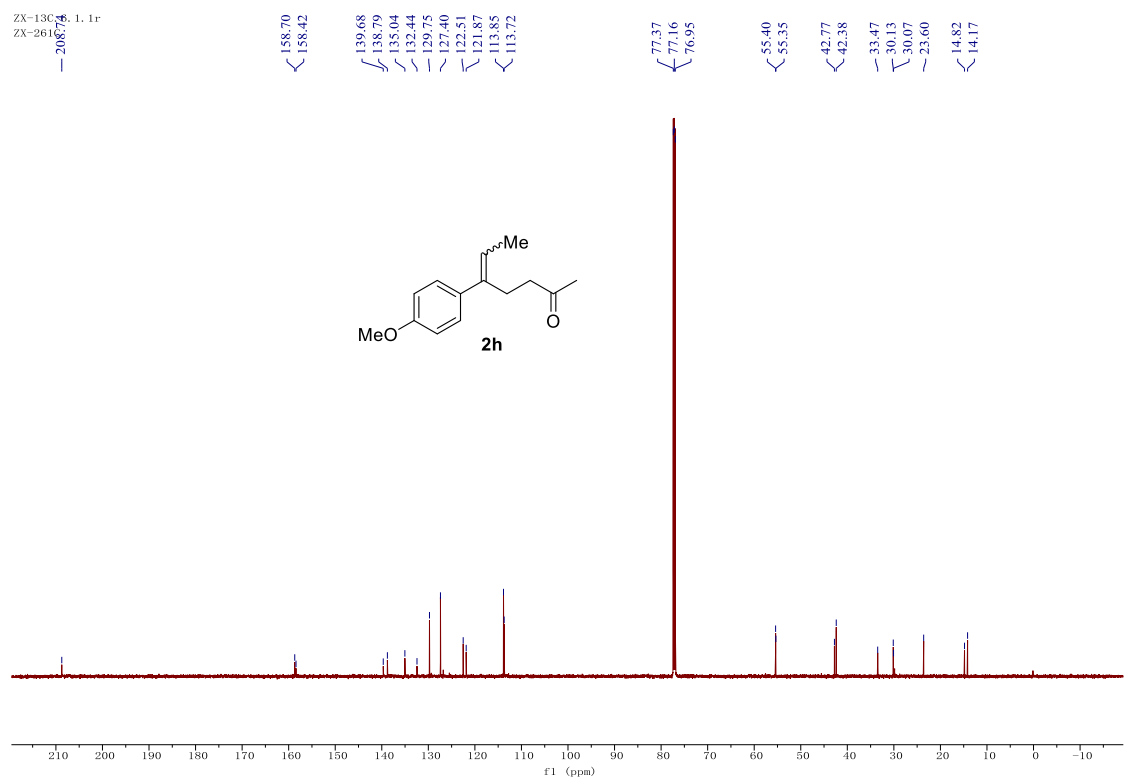
¹³C NMR (151 MHz, CDCl₃) for **2g**



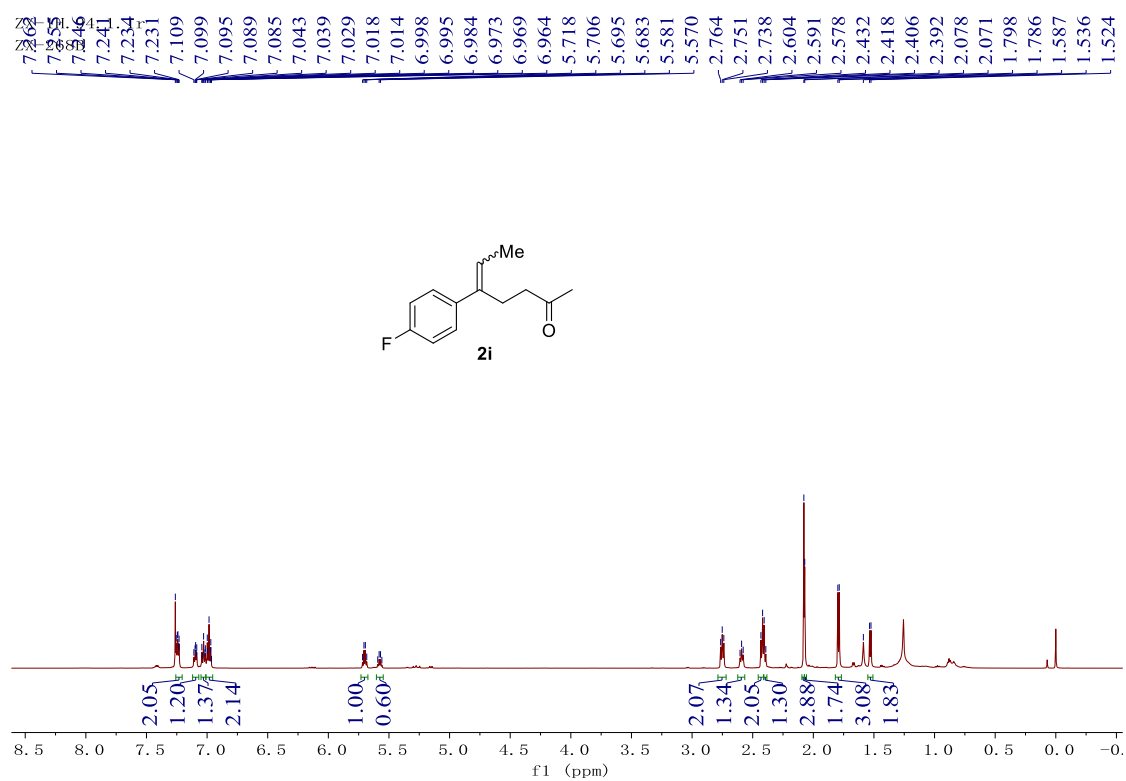
¹H NMR (600 MHz, CDCl₃) for **2h**



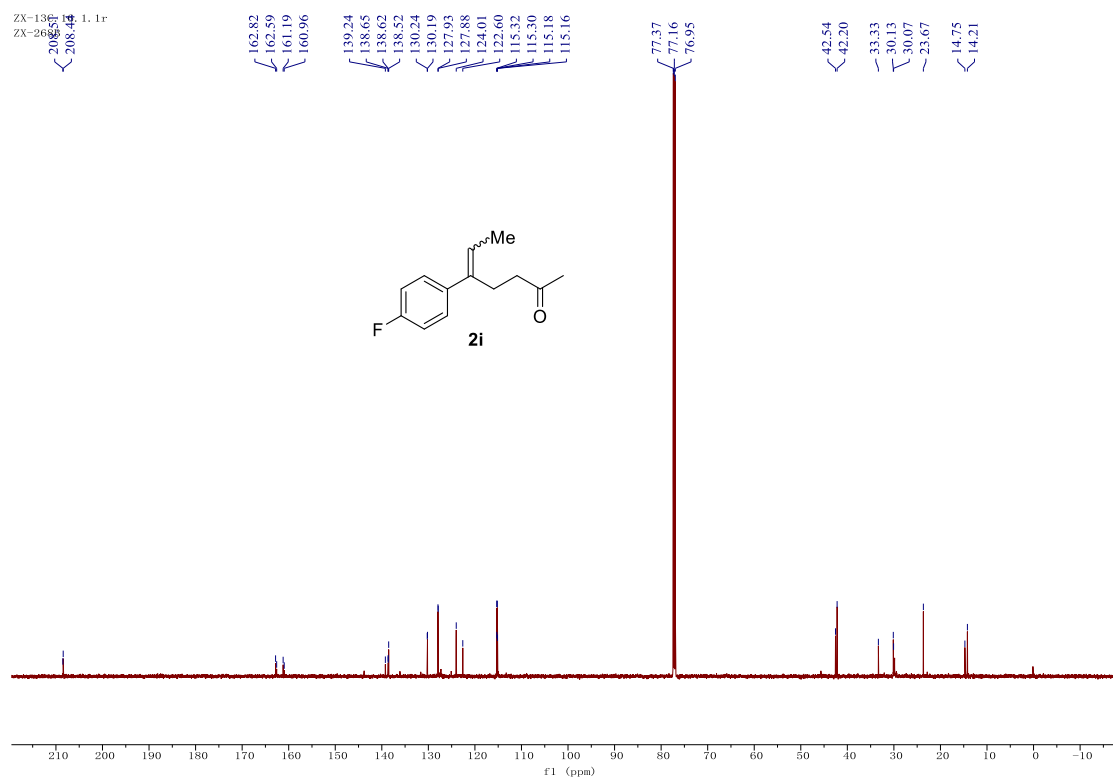
¹³C NMR (151 MHz, CDCl₃) for **2h**



¹H NMR (600 MHz, CDCl₃) for **2i**

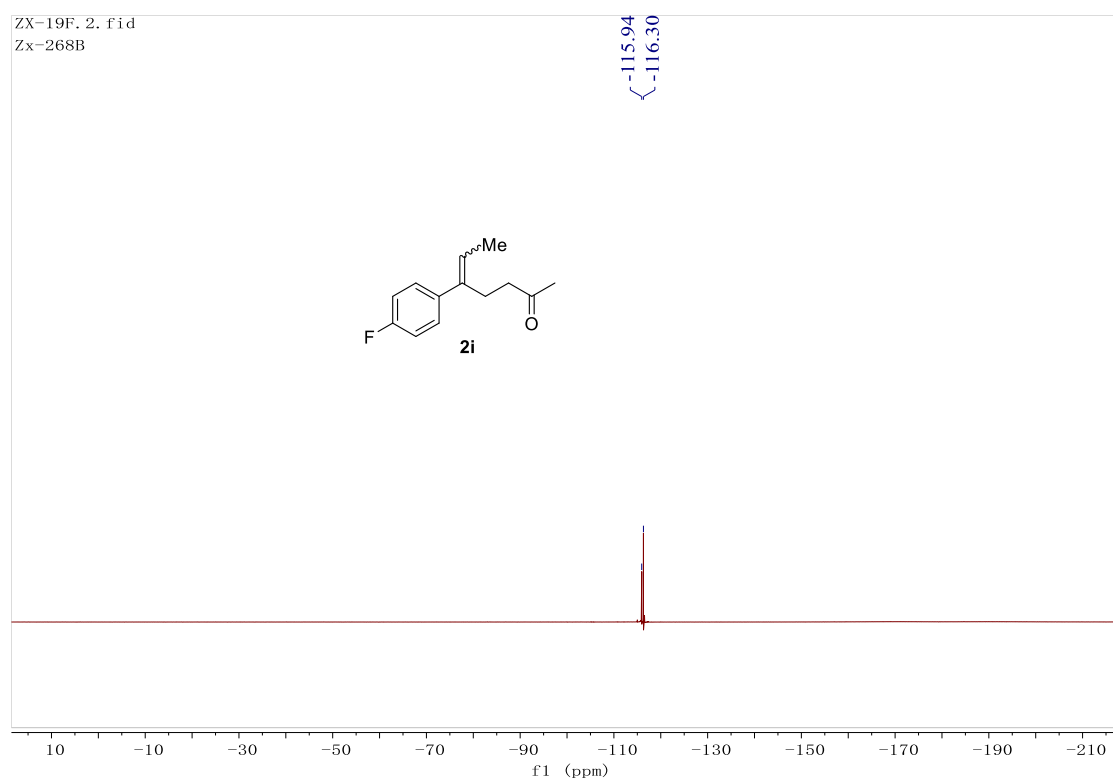


¹³C NMR (151 MHz, CDCl₃) for **2i**



¹⁹F NMR (565 MHz, CDCl₃) for **2i**

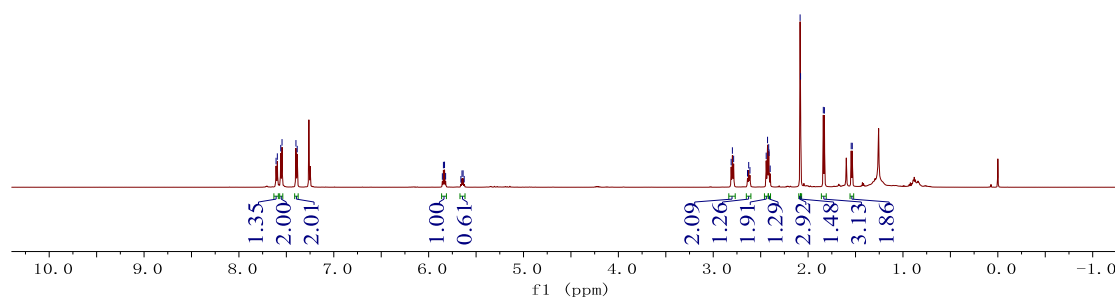
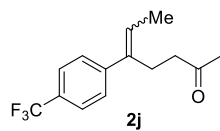
ZX-19F. 2. fid
Zx-268B



¹H NMR (600 MHz, CDCl₃) for **2j**

ZX-1H. 5. 1. 1r
ZX-273C

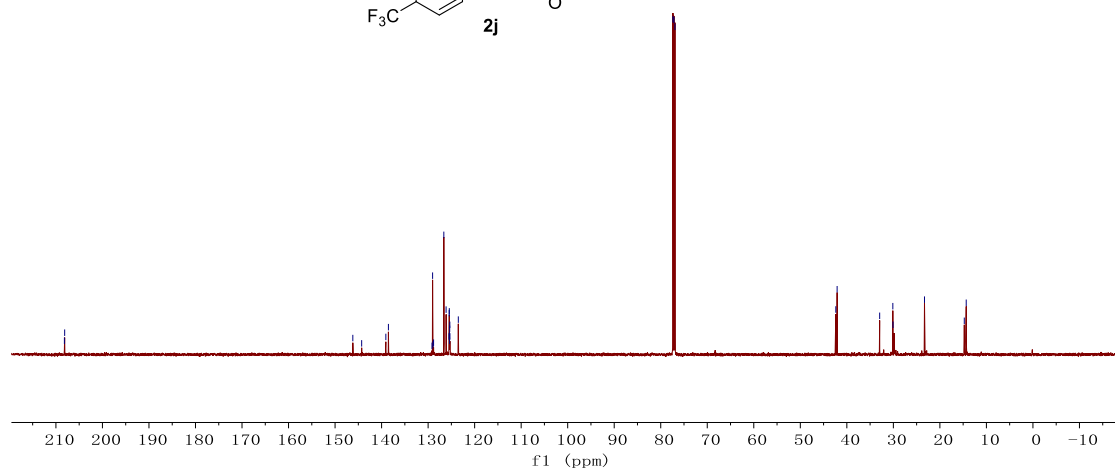
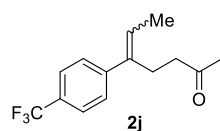
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5.844
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5.821
5.660
5.649
5.637
5.625
2.811
2.798
2.785
2.639
2.626
2.613
2.442
2.427
2.415
2.412
2.400
2.084
2.080
1.840
1.828
1.546
1.534



¹³C NMR (151 MHz, CDCl₃) for **2j**

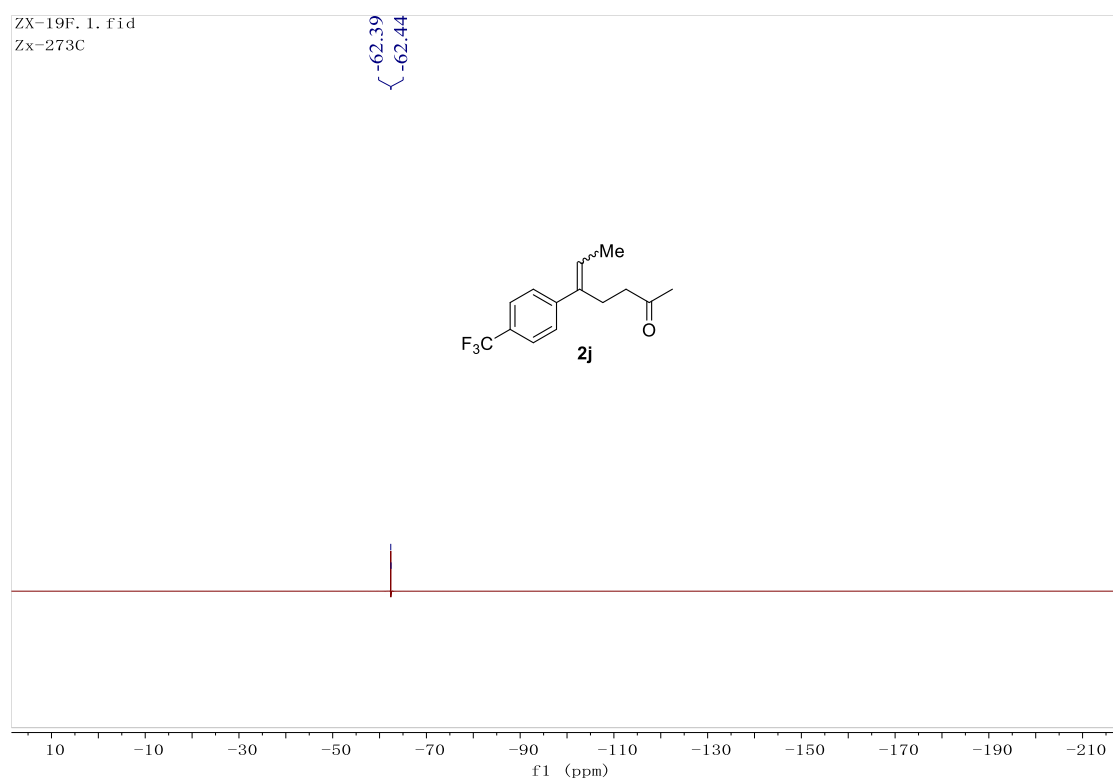
ZX-13C. 18. 1. 1r
ZX-273C

208.18
207.36
146.18
144.28
139.09
138.53
129.16
129.04
128.94
128.83
126.62
126.13
125.49
125.47
125.44
125.42
125.39
125.36
125.33
125.31
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77.16
76.95
42.37
42.09
32.94
30.11
30.07
23.31
14.76
14.34

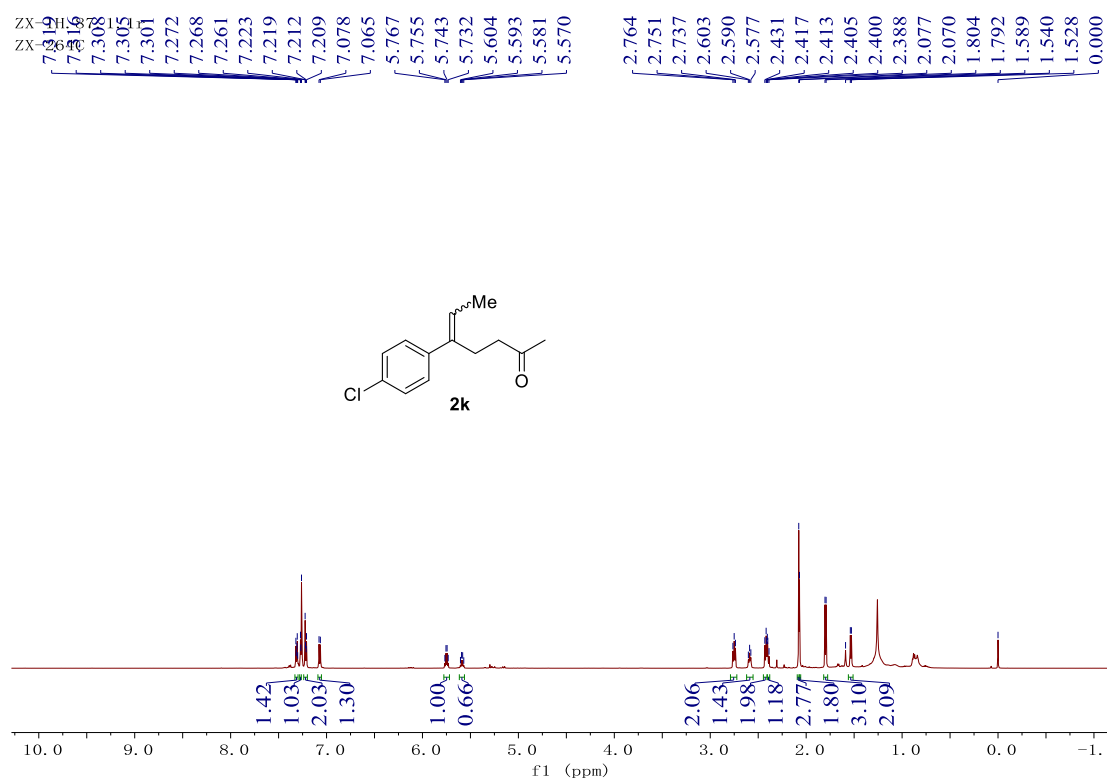


¹⁹F NMR (565 MHz, CDCl₃) for **2i**

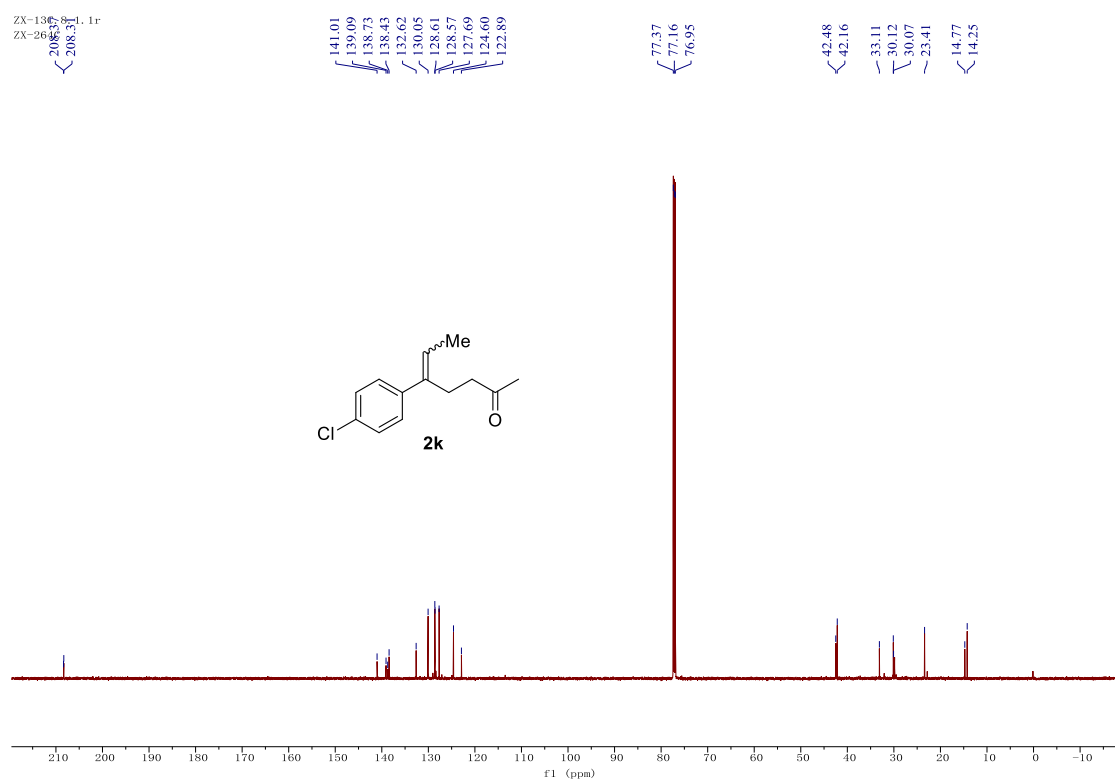
ZX-19F. 1. fid
Zx-273C



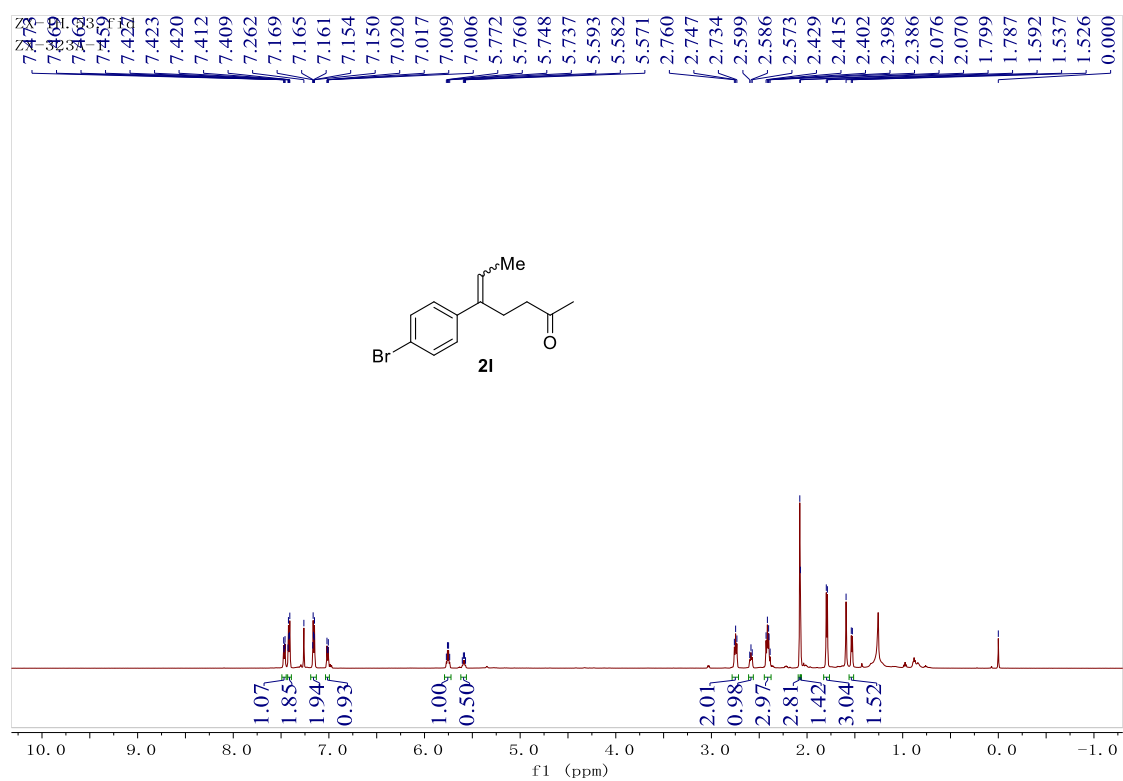
¹H NMR (600 MHz, CDCl₃) for **2k**



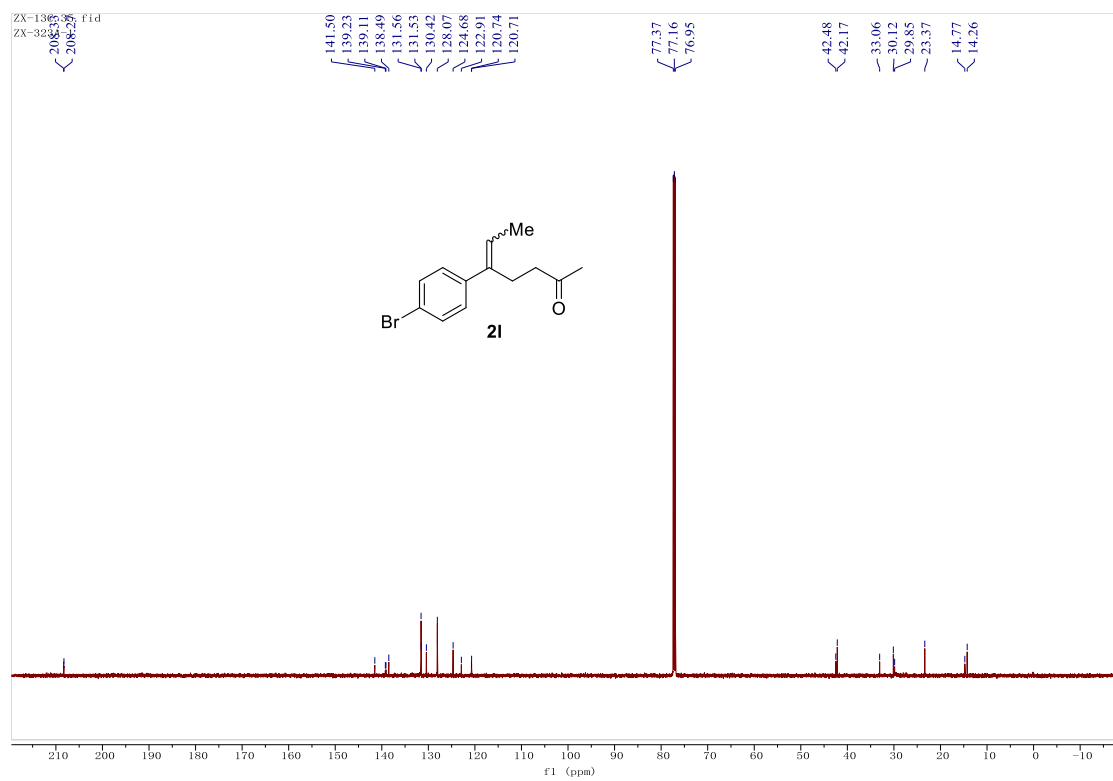
¹³C NMR (151 MHz, CDCl₃) for **2k**



¹H NMR (600 MHz, CDCl₃) for **21**

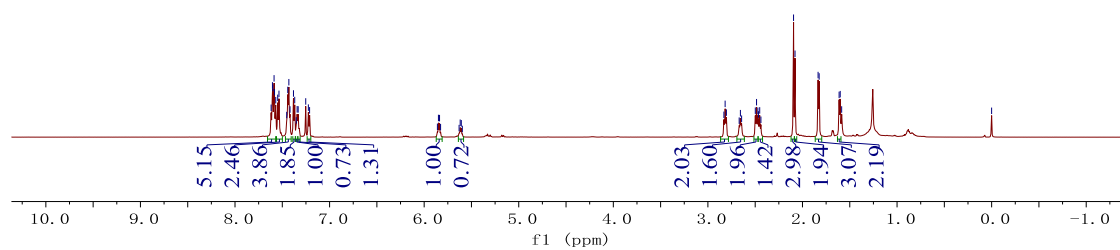
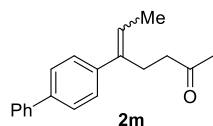


¹³C NMR (151 MHz, CDCl₃) for **21**



¹H NMR (600 MHz, CDCl₃) for **2m**

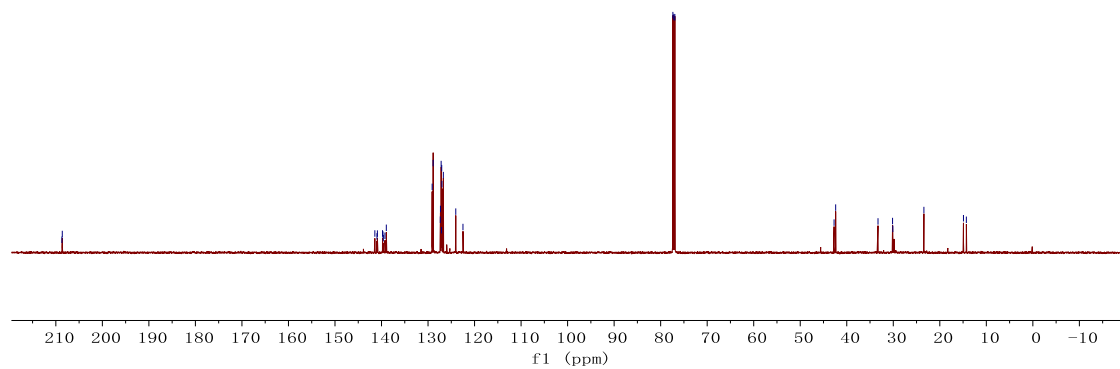
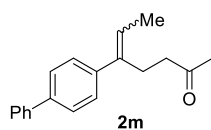
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7.382
7.369
7.352
7.343
7.332
7.252
7.224
7.212
5.860
5.849
5.838
5.619
5.607
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2.818
2.804
2.669
2.656
2.644
2.499
2.486
2.472
2.466
2.452
2.439
2.094
2.079
1.835
1.824
1.613
1.601
1.586
0.000



¹³C NMR (151 MHz, CDCl₃) for **2m**

ZX 208.74
ZX 208.68
14.1, 1r

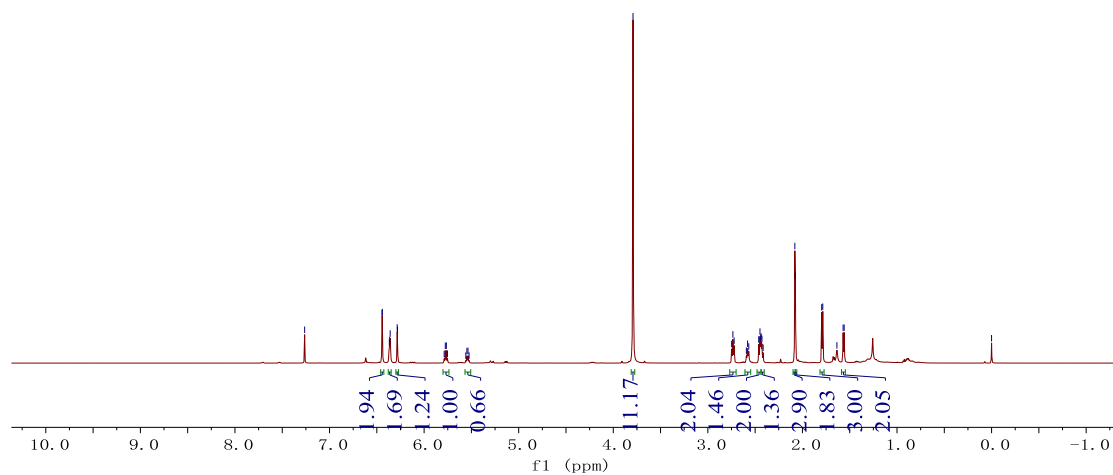
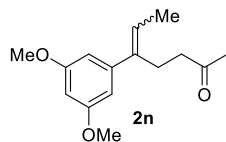
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139.26
138.97
129.11
128.90
127.36
127.33
127.18
127.12
127.06
127.01
126.71
124.04
122.49
77.37
77.16
76.95
42.73
42.38
33.28
30.15
30.10
23.42
14.91
14.29



¹H NMR (600 MHz, CDCl₃) for **2n**

ZX-1H. 1. 1. 1r
ZX-271C

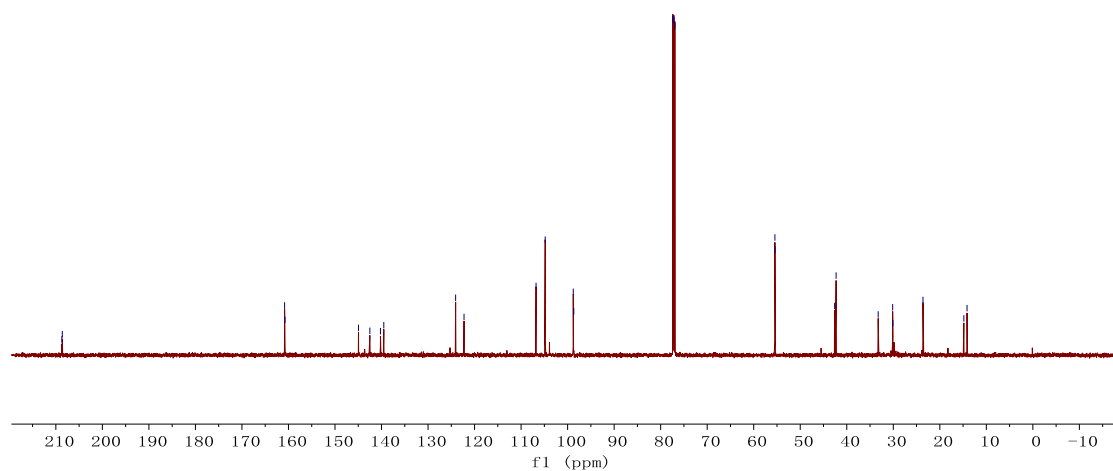
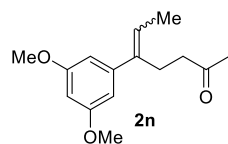
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6.368
6.364
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6.285
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5.765
5.753
5.559
5.548
5.536
5.525
3.791
2.748
2.735
2.722
2.580
2.567
2.462
2.449
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1.785
1.635
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1.559
0.000



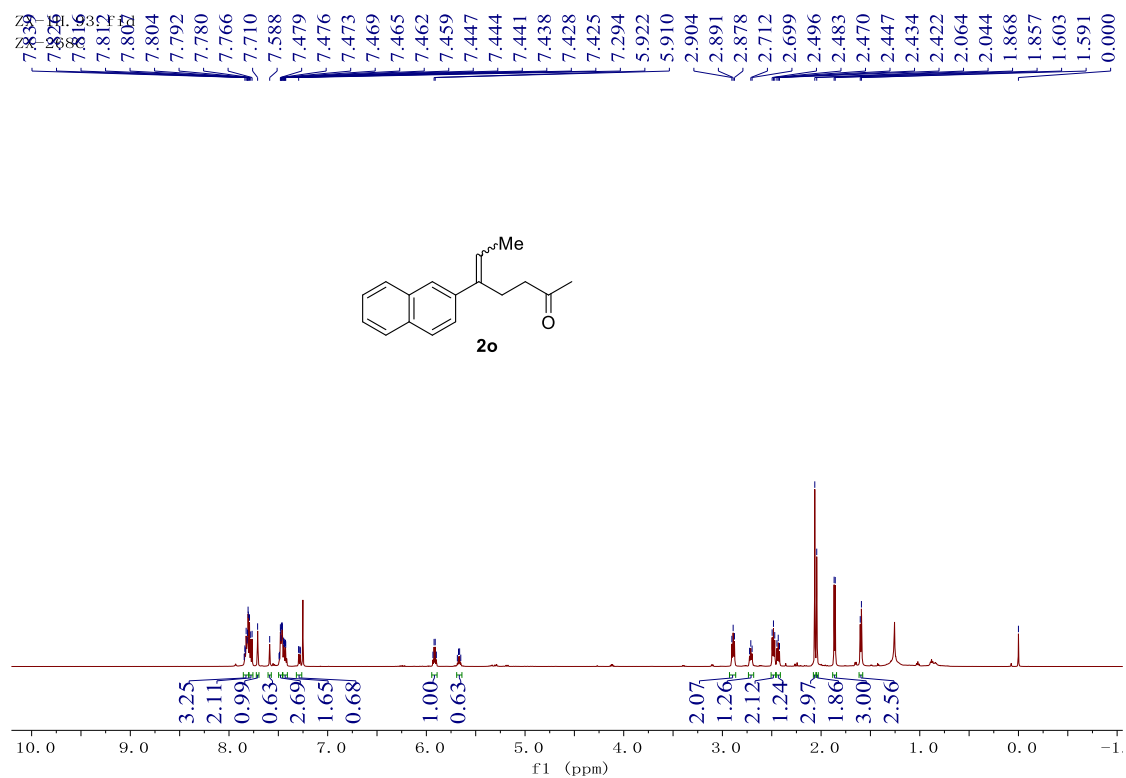
¹³C NMR (151 MHz, CDCl₃) for **2n**

ZX-13C. 17. 1. 1r
ZX-208661

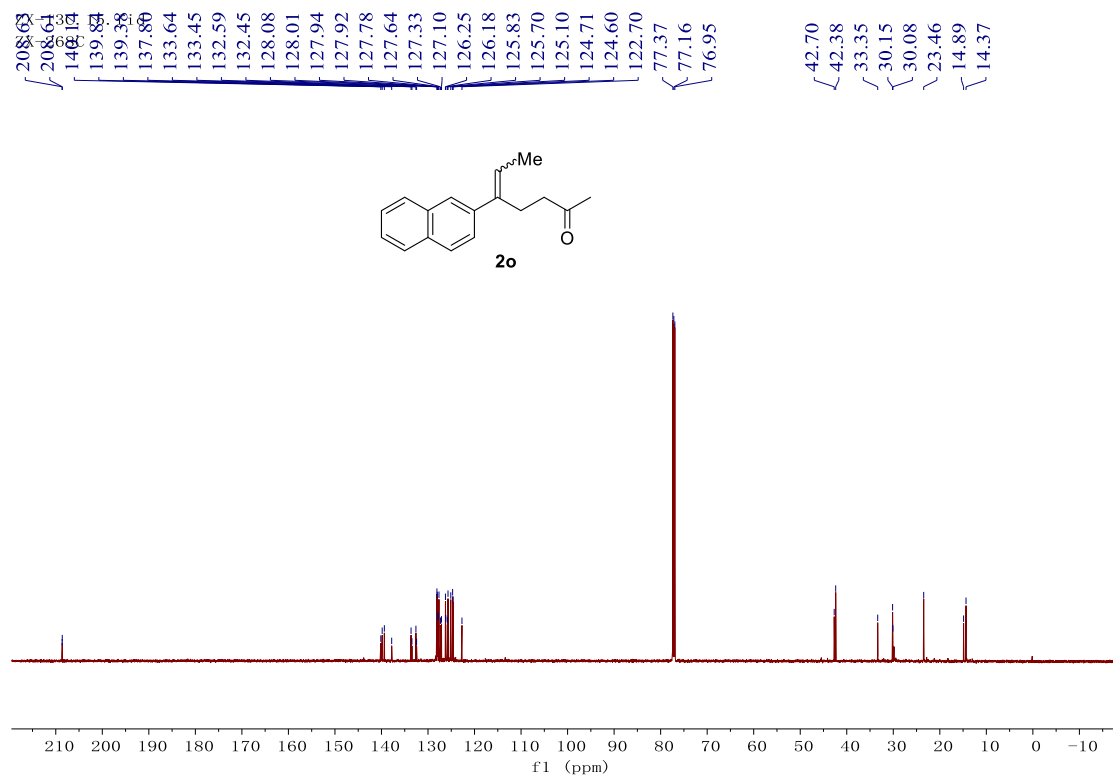
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140.23
139.51
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122.26
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104.82
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98.67
77.37
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42.29
33.25
30.13
30.09
23.62
14.83
14.15



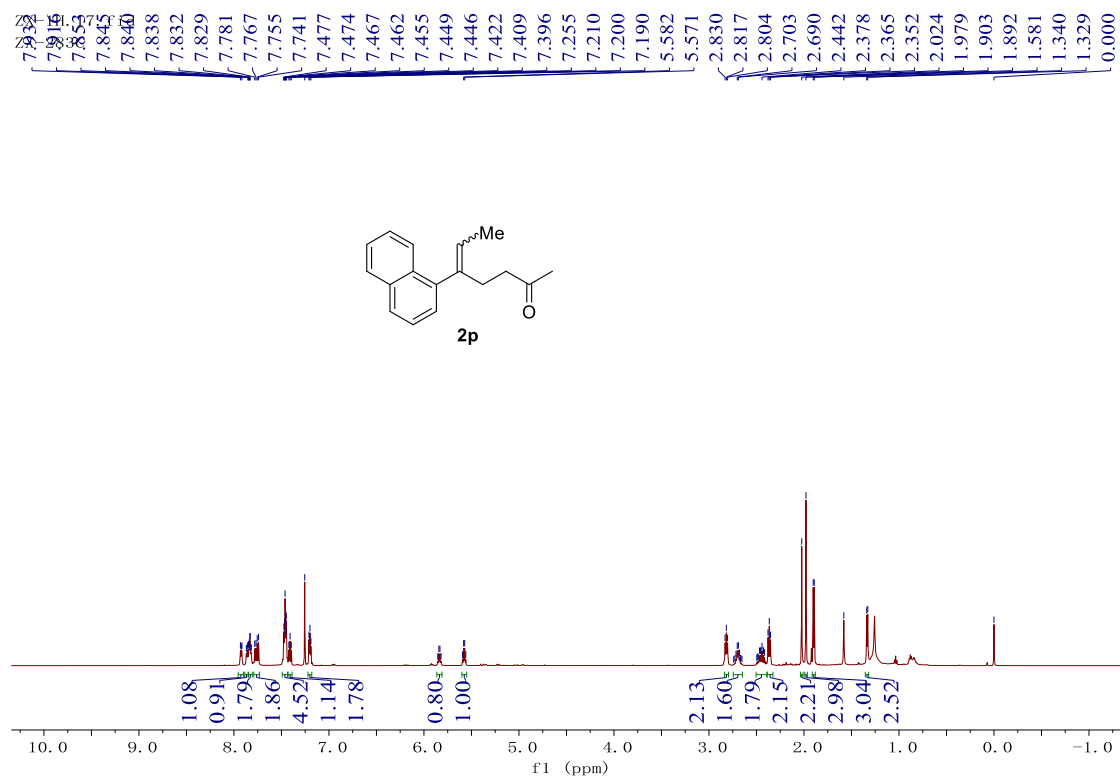
¹H NMR (600 MHz, CDCl₃) for **2o**



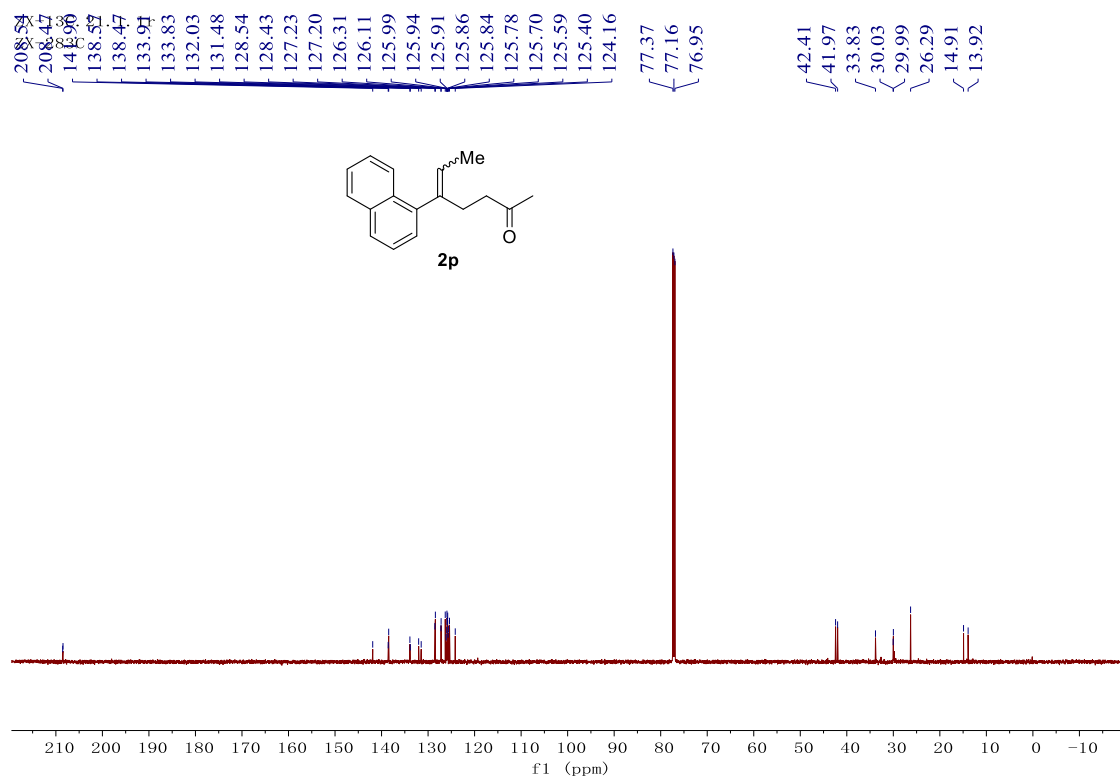
¹³C NMR (151 MHz, CDCl₃) for **2o**



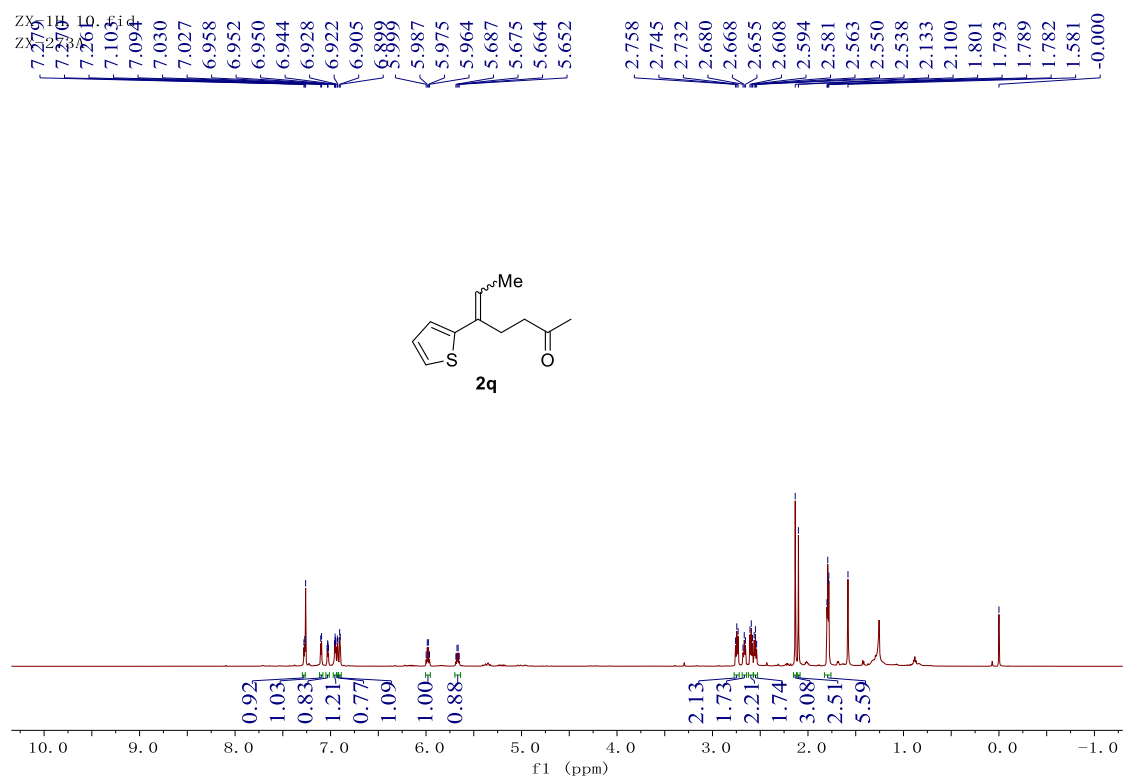
¹H NMR (600 MHz, CDCl₃) for **2p**



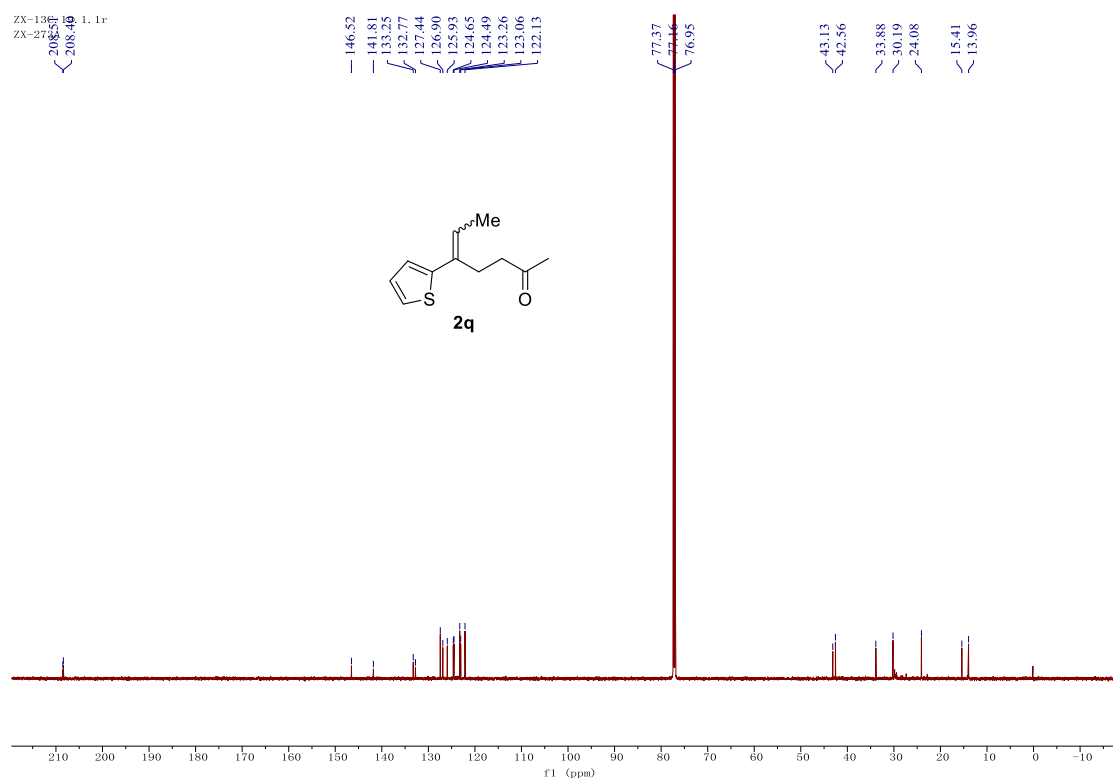
¹³C NMR (151 MHz, CDCl₃) for **2p**



¹H NMR (600 MHz, CDCl₃) for **2q**

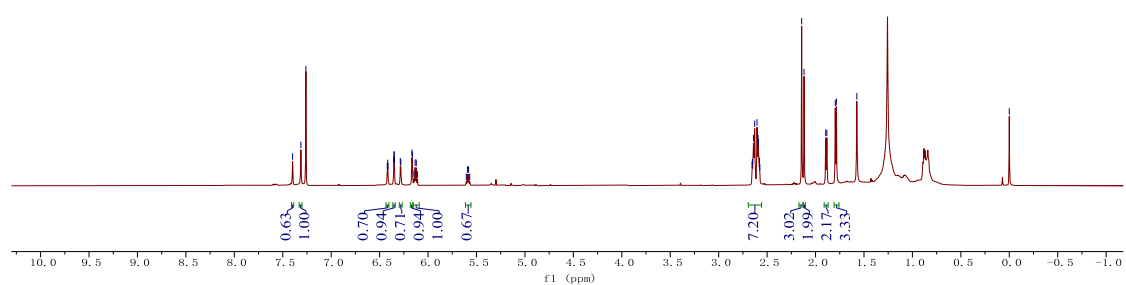
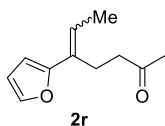


¹³C NMR (151 MHz, CDCl₃) for **2q**



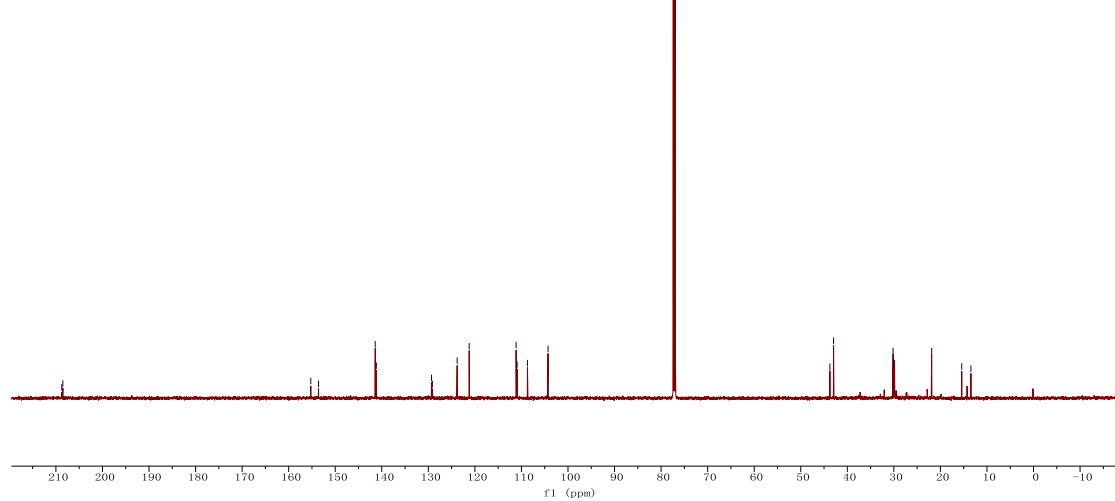
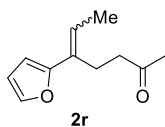
¹H NMR (600 MHz, CDCl₃) for **2r**

ZX-1H_13_1_1r
ZX-273B-3

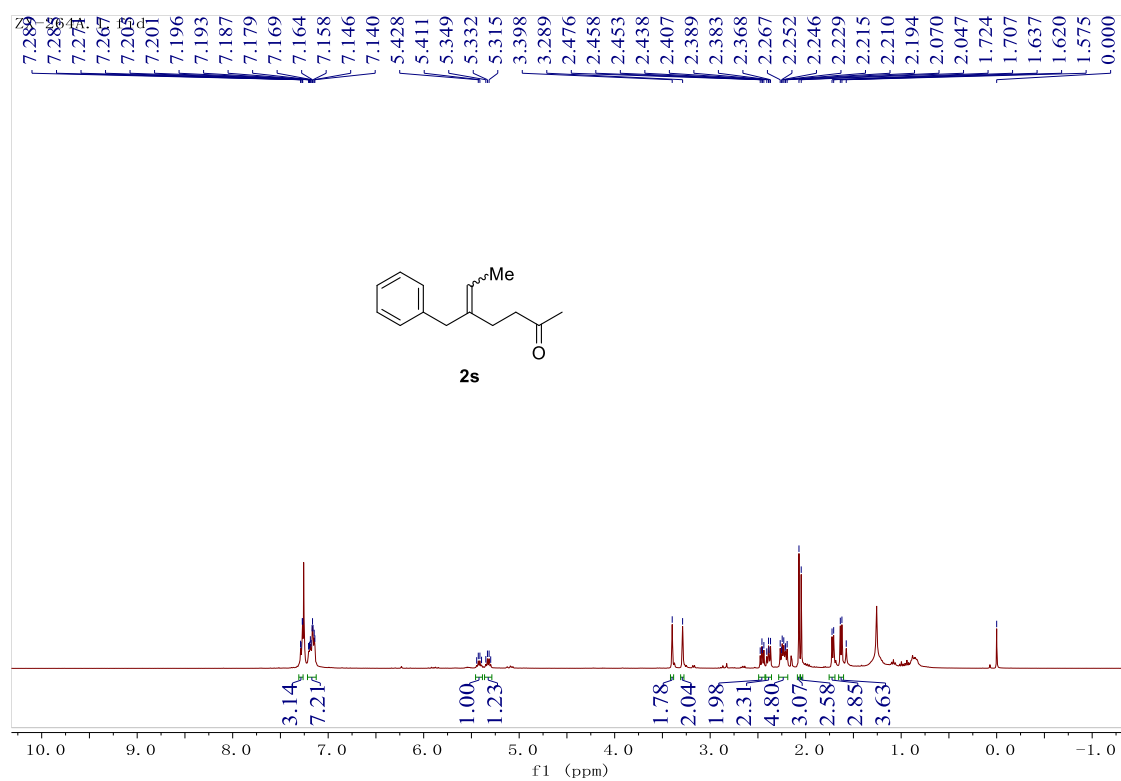


¹³C NMR (151 MHz, CDCl₃) for **2r**

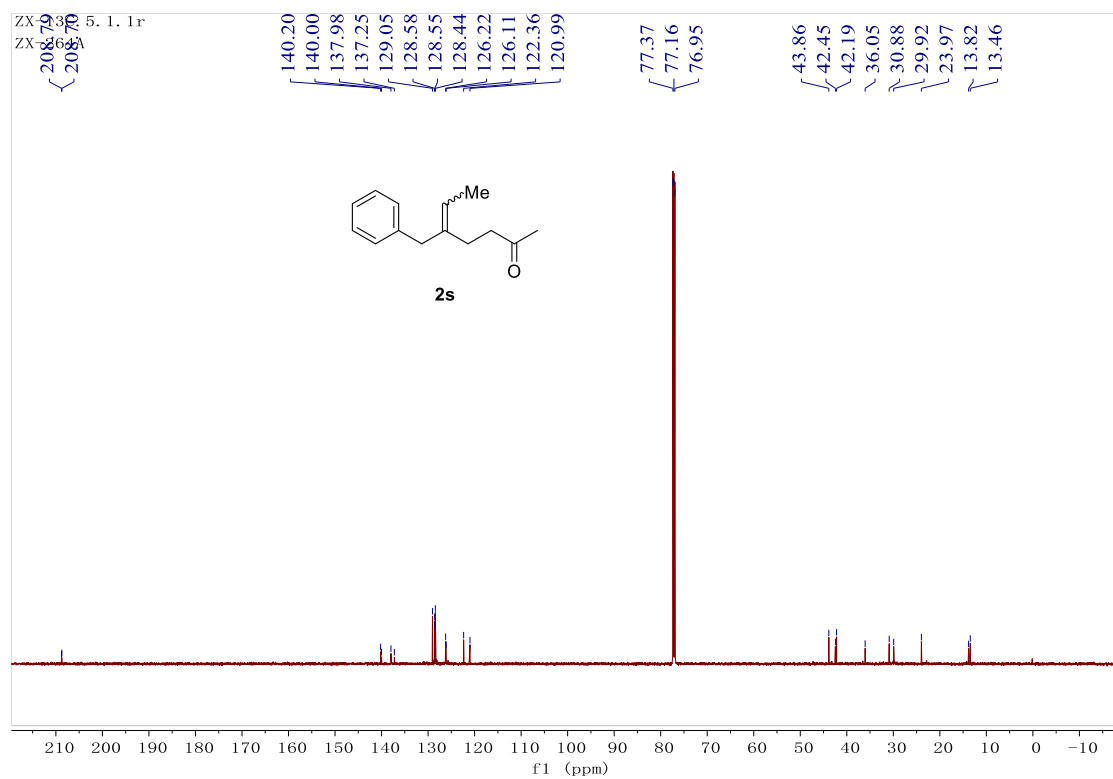
ZX-13C_24_1_1r
ZX-208B-3



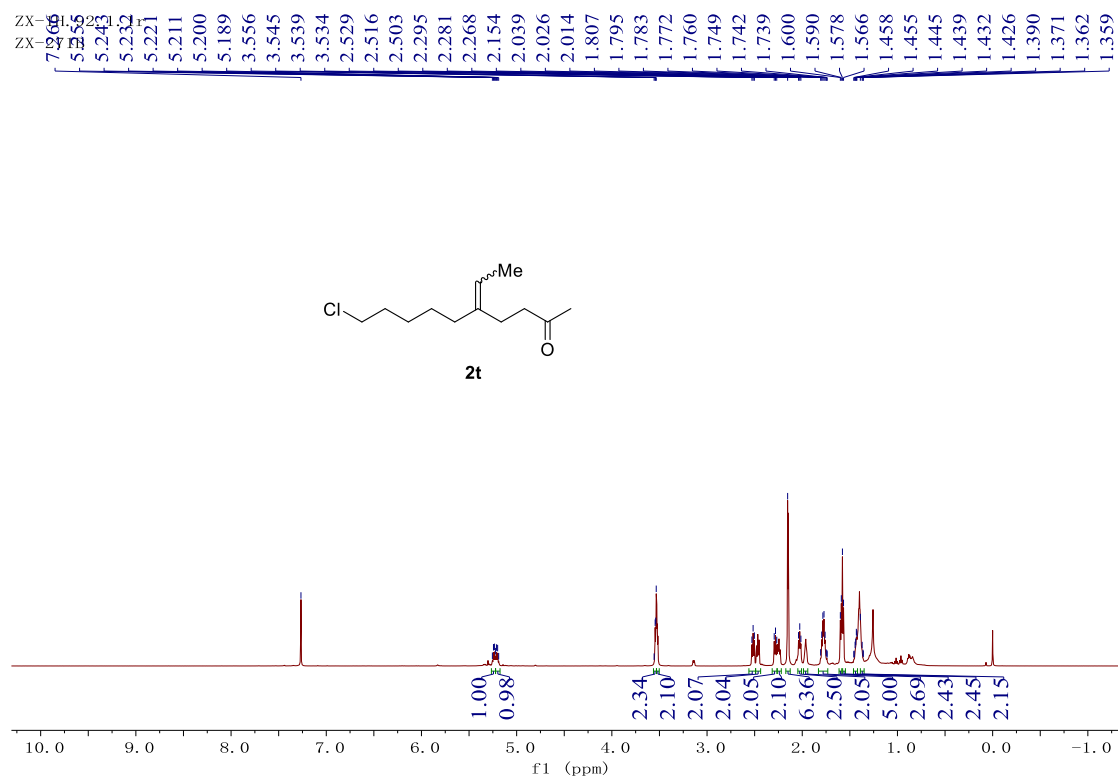
¹H NMR (400 MHz, CDCl₃) for **2s**



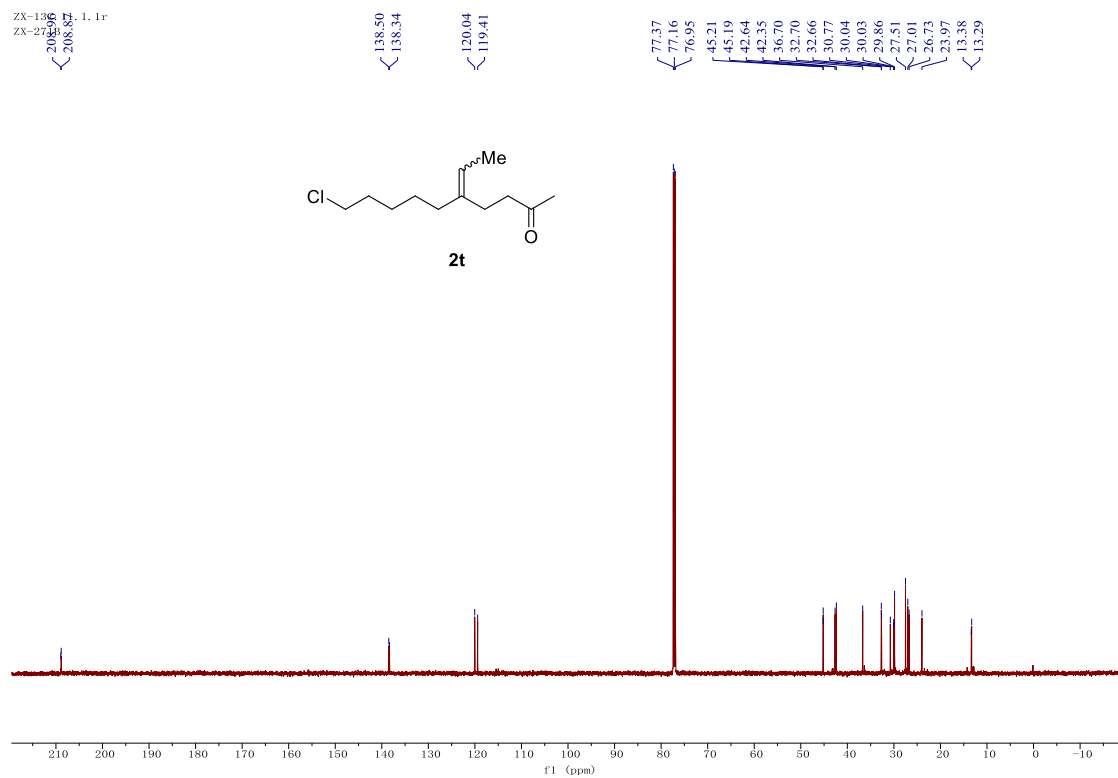
¹³C NMR (151 MHz, CDCl₃) for **2s**



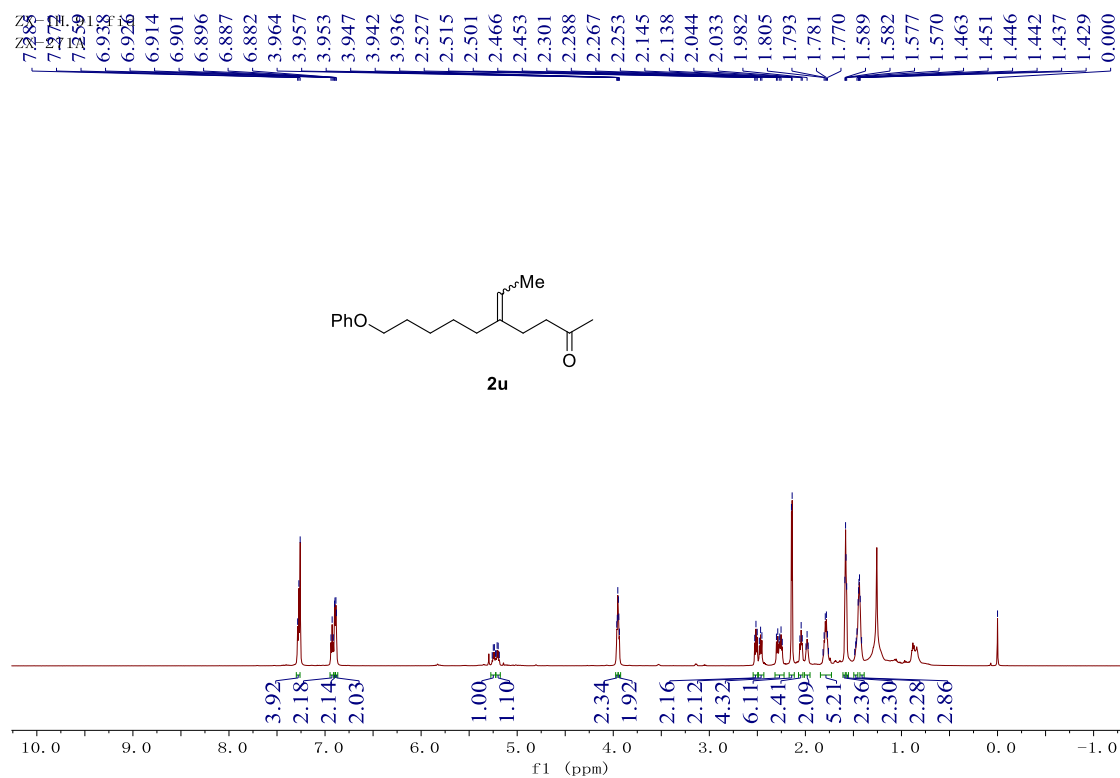
¹H NMR (600 MHz, CDCl₃) for **2t**



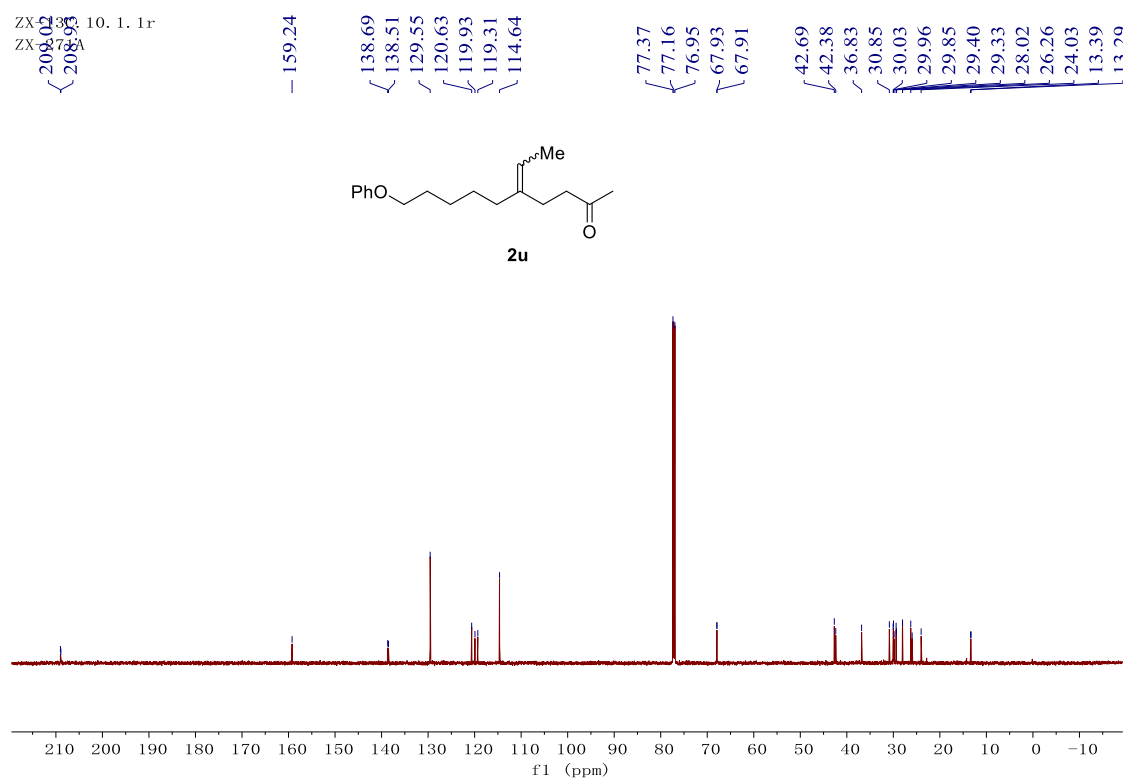
¹³C NMR (151 MHz, CDCl₃) for **2t**



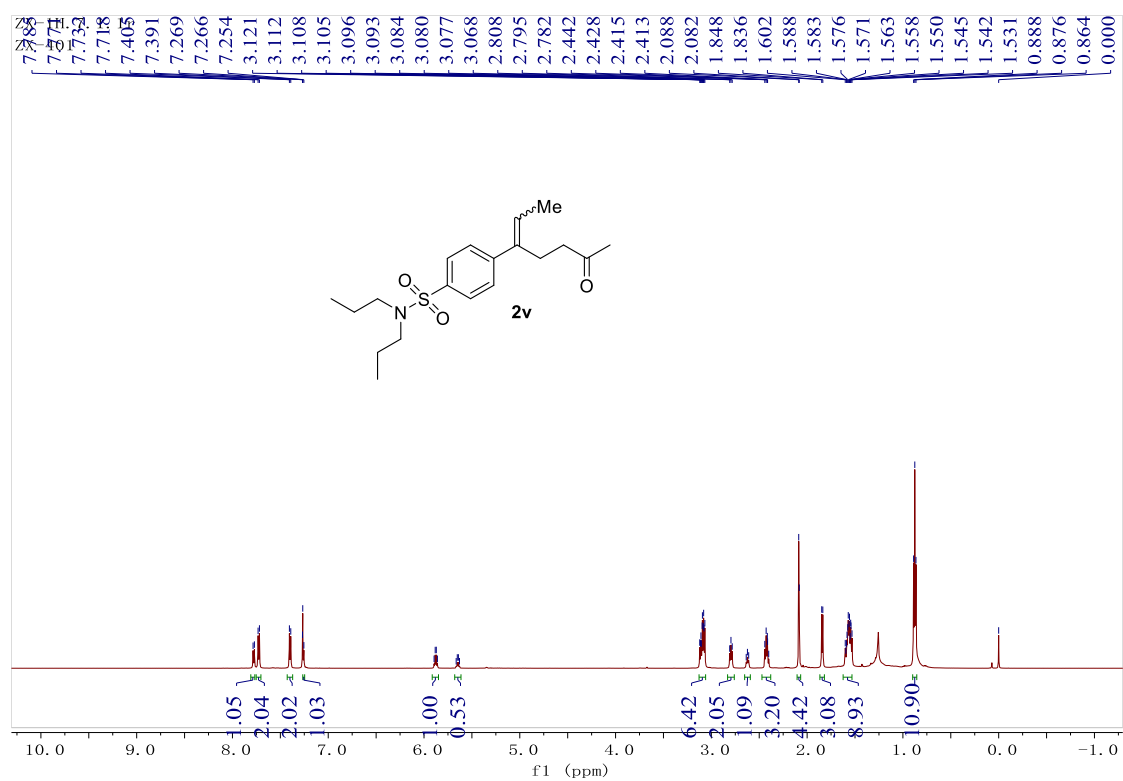
¹H NMR (600 MHz, CDCl₃) for **2u**



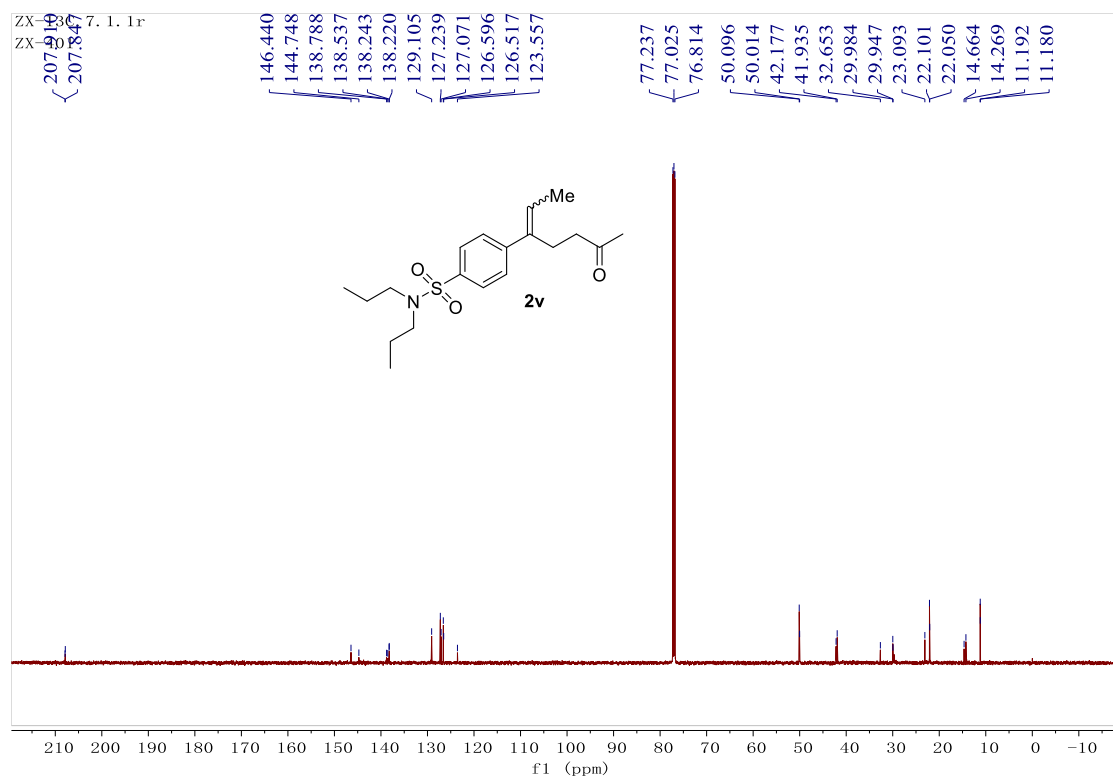
¹³C NMR (151 MHz, CDCl₃) for **2u**



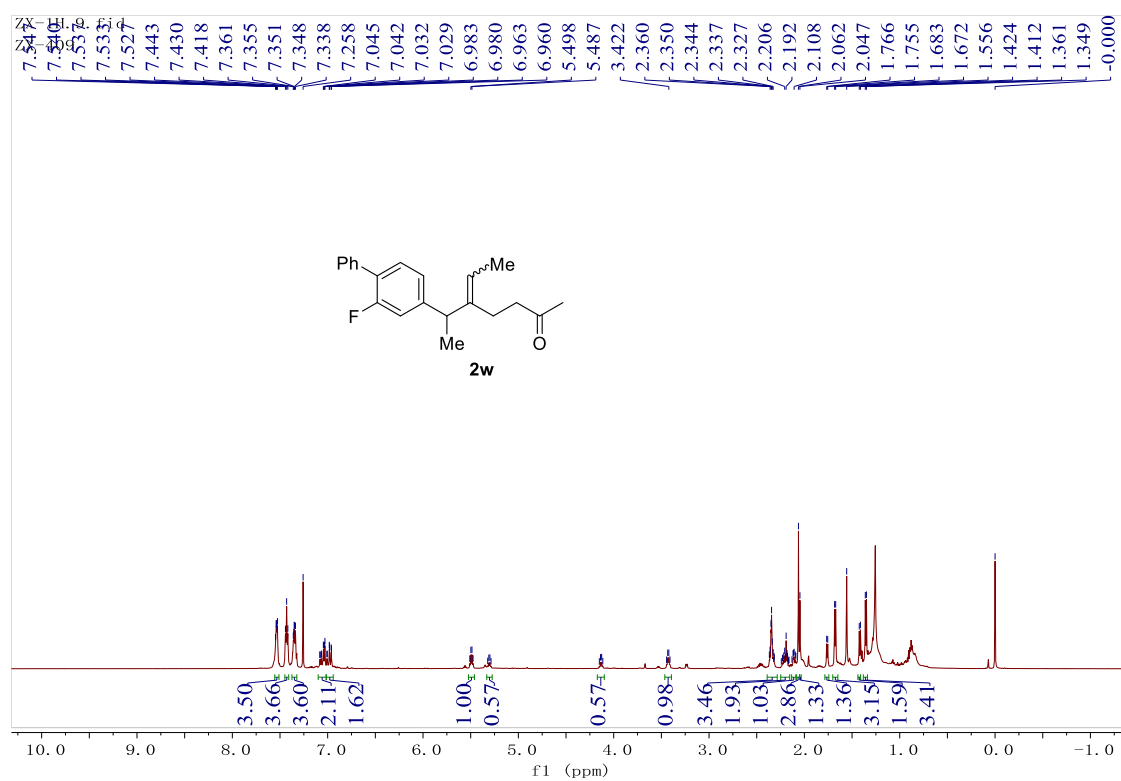
¹H NMR (600 MHz, CDCl₃) for **2v**



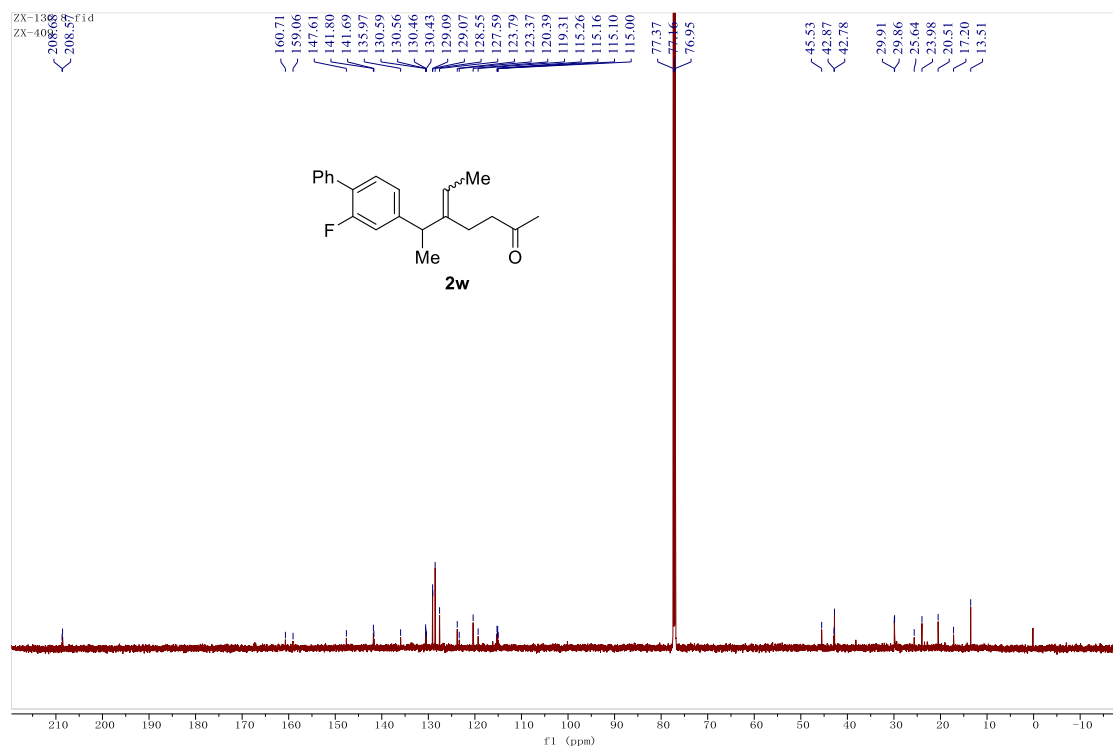
¹³C NMR (151 MHz, CDCl₃) for **2v**



¹H NMR (600 MHz, CDCl₃) for **2w**

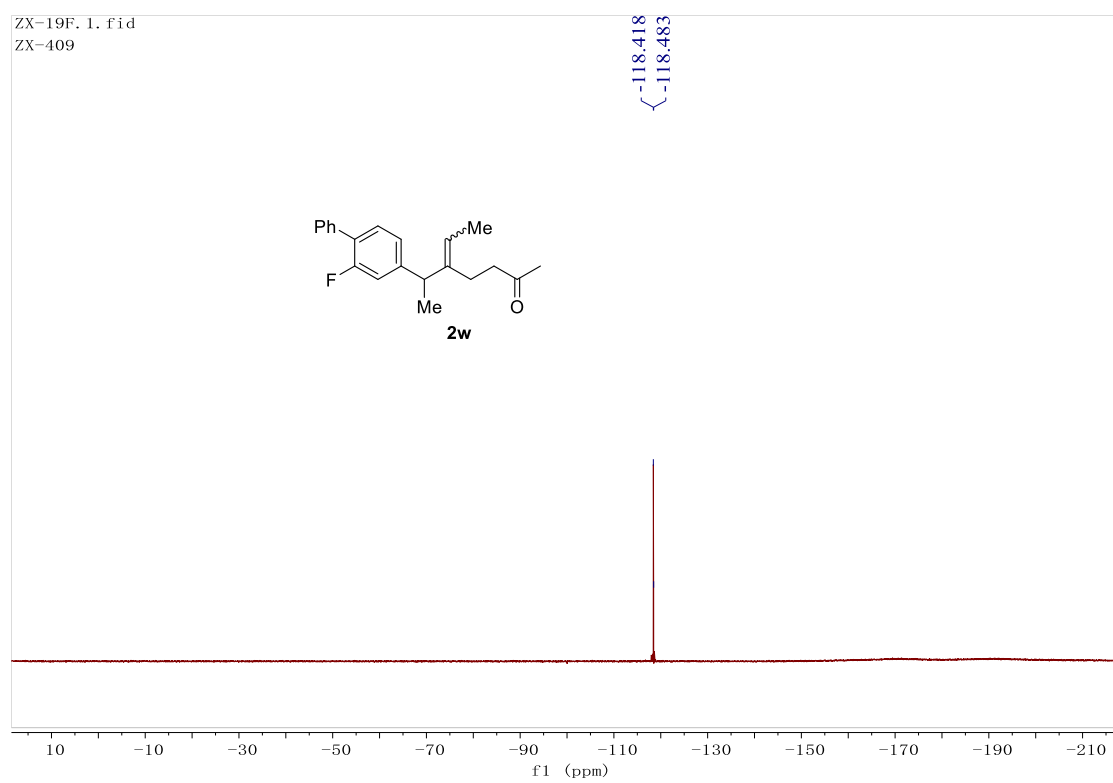


¹³C NMR (151 MHz, CDCl₃) for **2w**

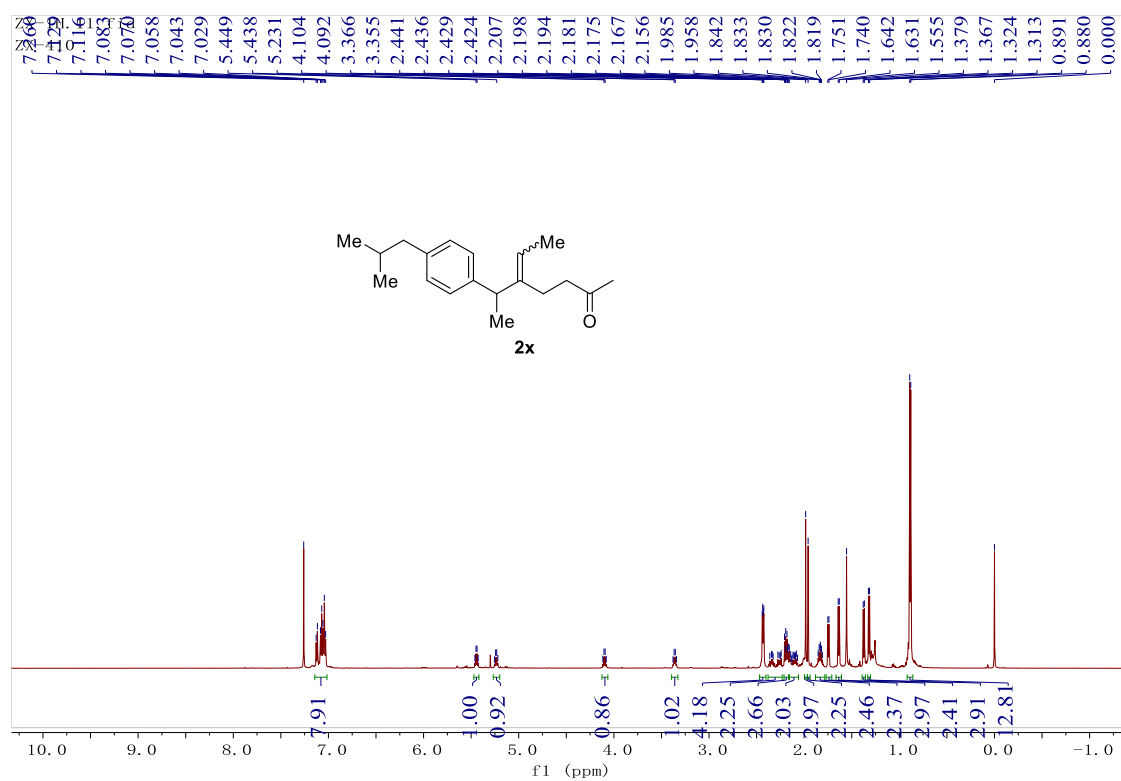


¹⁹F NMR (565 MHz, CDCl₃) for **2w**

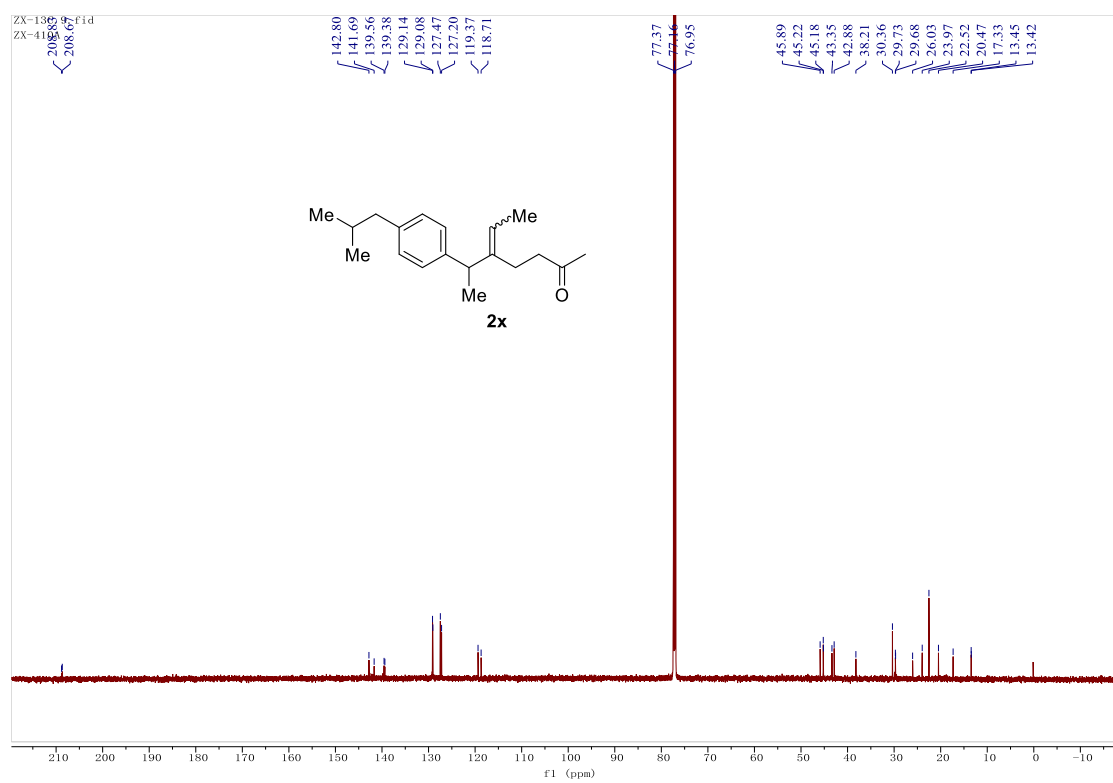
ZX-19F. 1. fid
ZX-409



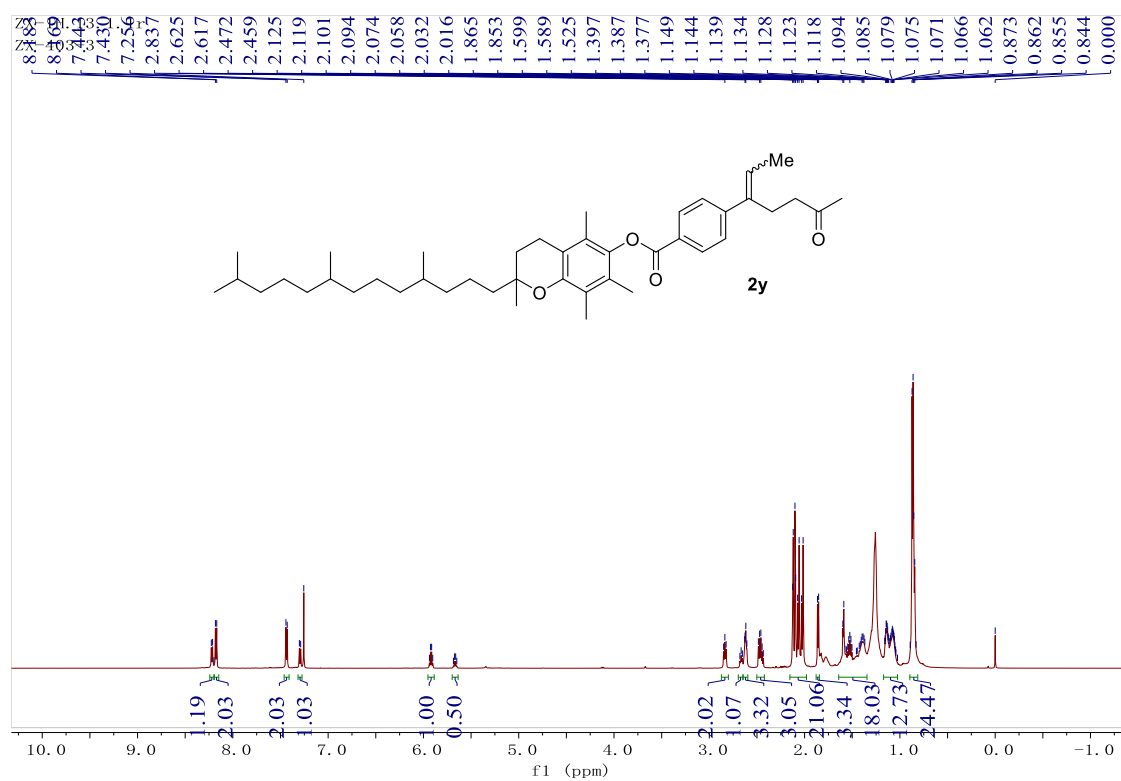
¹H NMR (600 MHz, CDCl₃) for **2x**



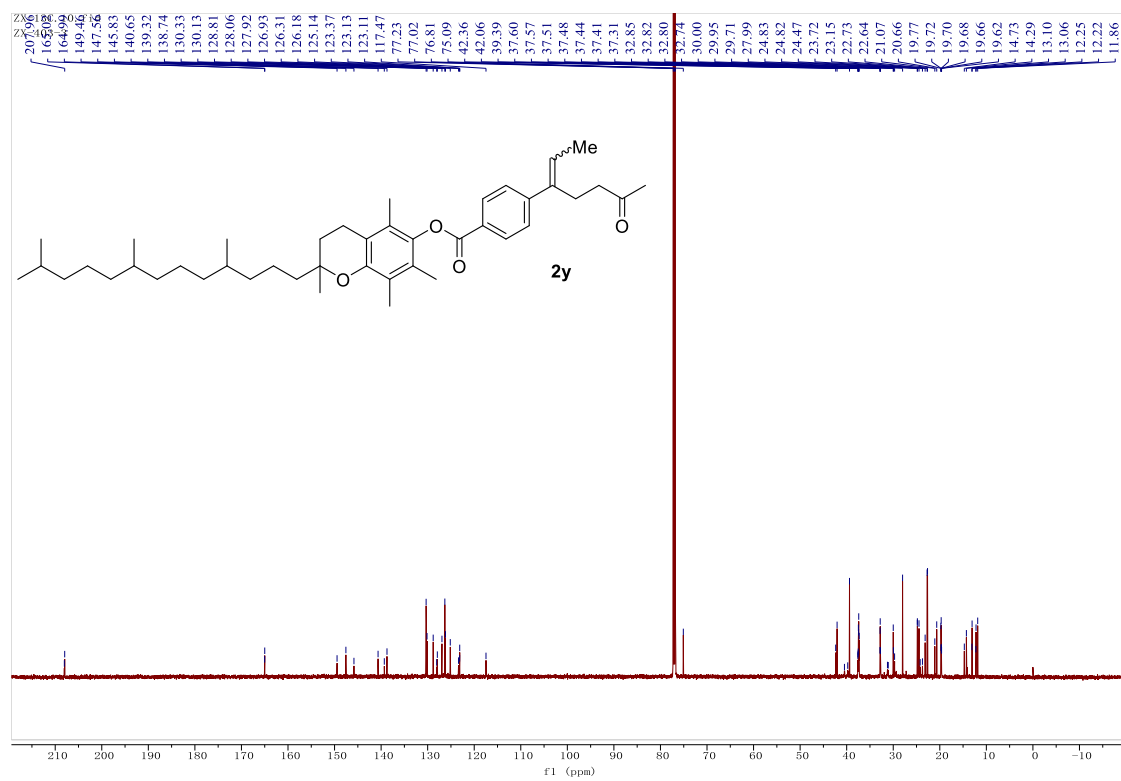
¹³C NMR (151 MHz, CDCl₃) for **2x**



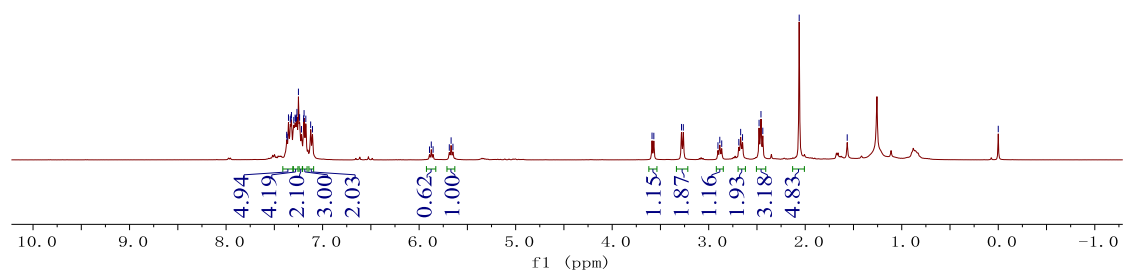
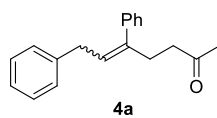
¹H NMR (600 MHz, CDCl₃) for **2y**



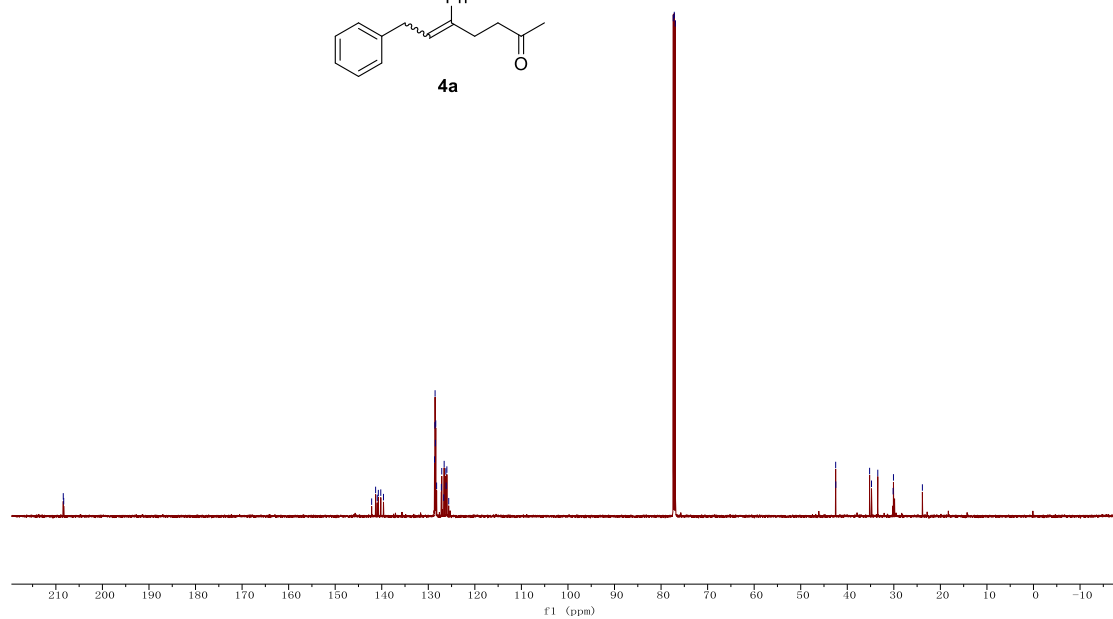
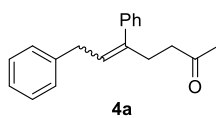
¹³C NMR (151 MHz, CDCl₃) for **2y**



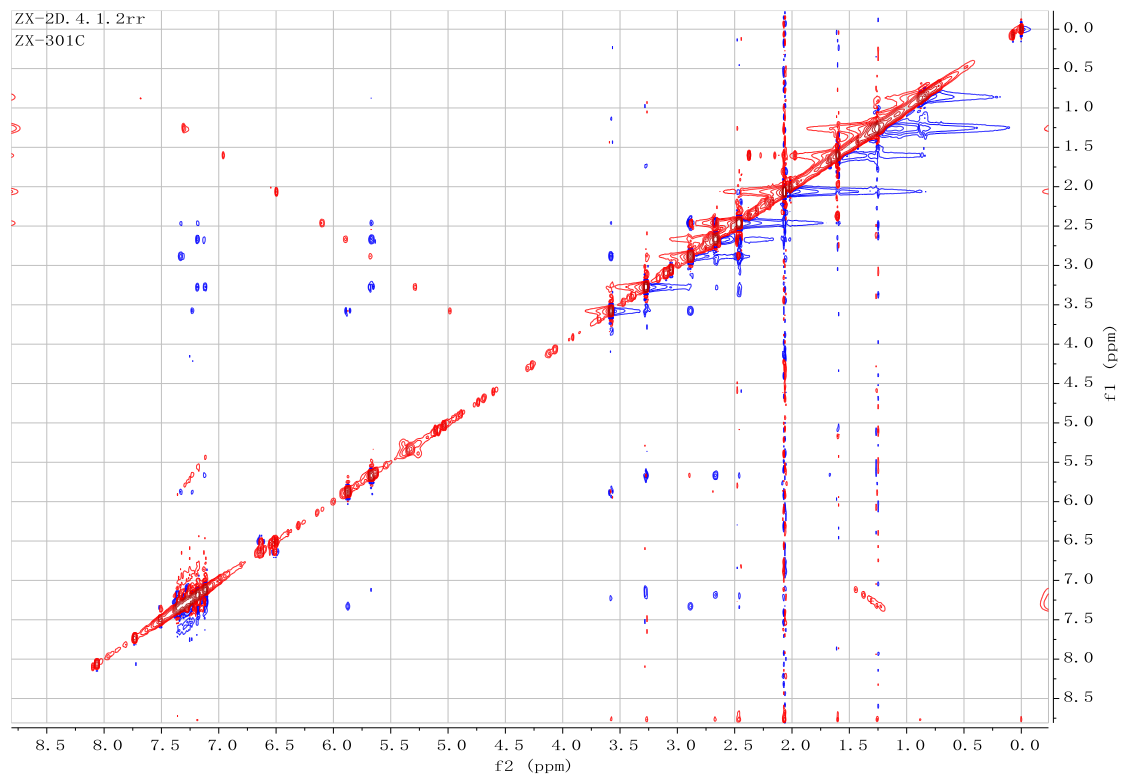
¹H NMR (400 MHz, CDCl₃) for **4a**



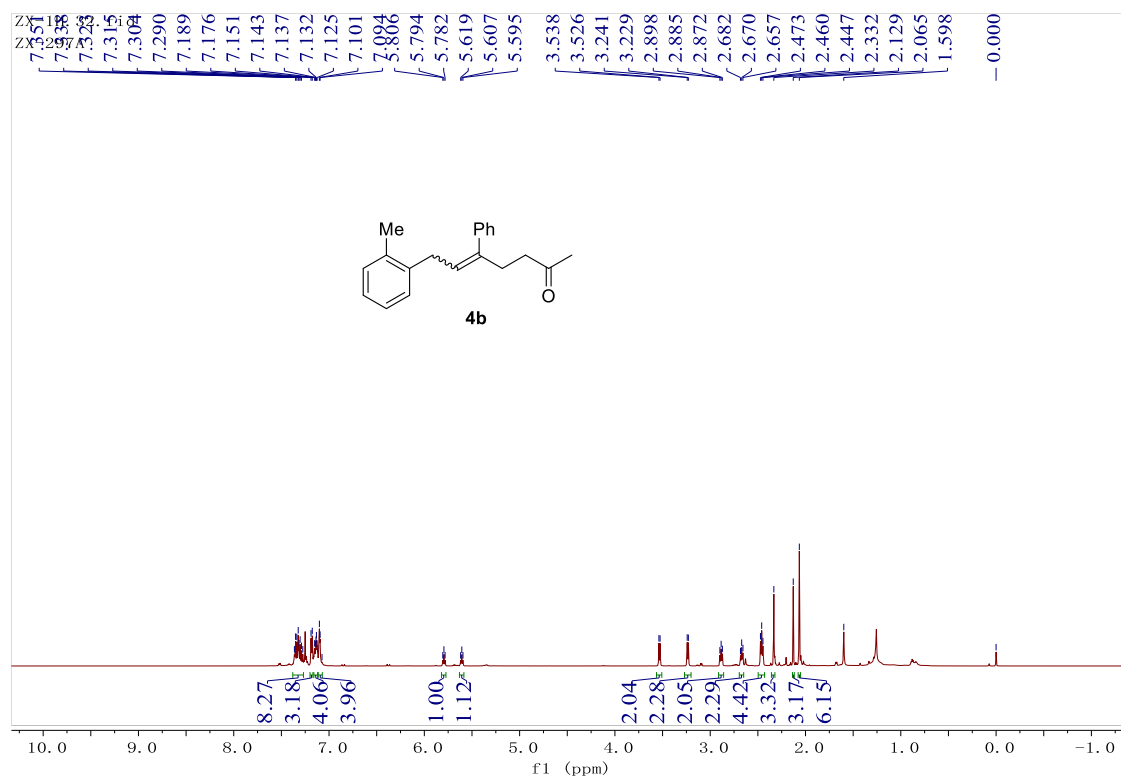
¹³C NMR (151 MHz, CDCl₃) for **4a**



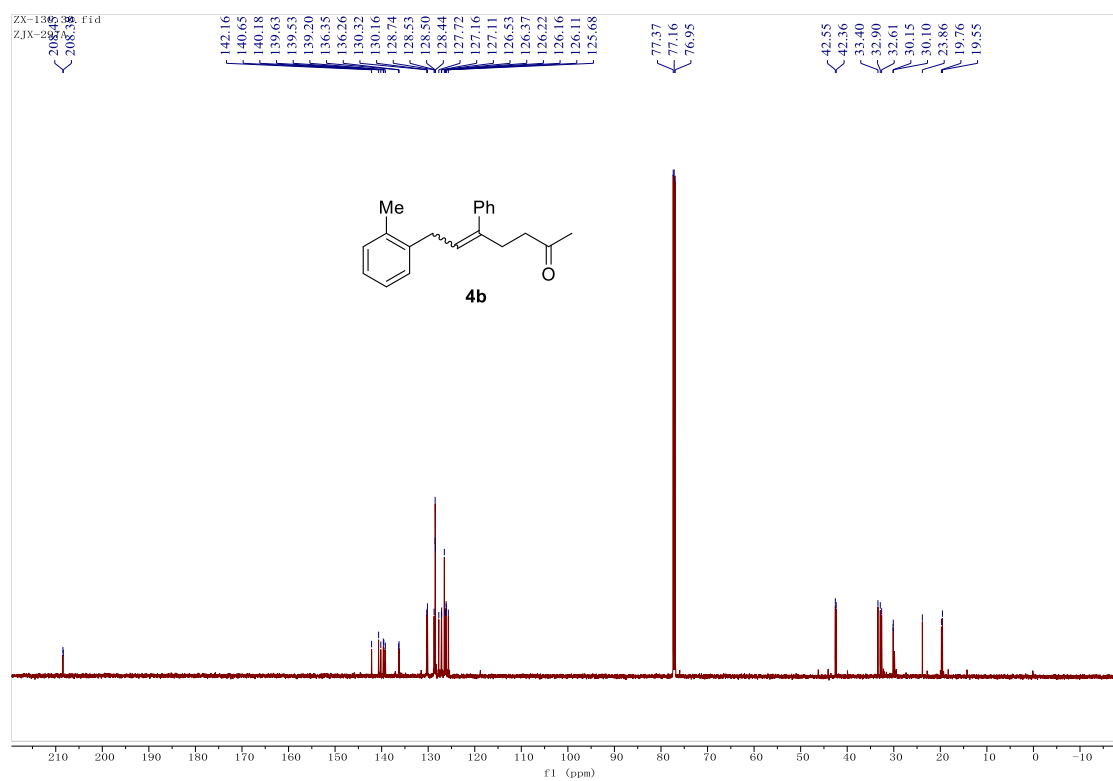
The *Z/E* configuration of **4a** was determined by 2D (^1H - ^1H) NMR measurement as shown below.



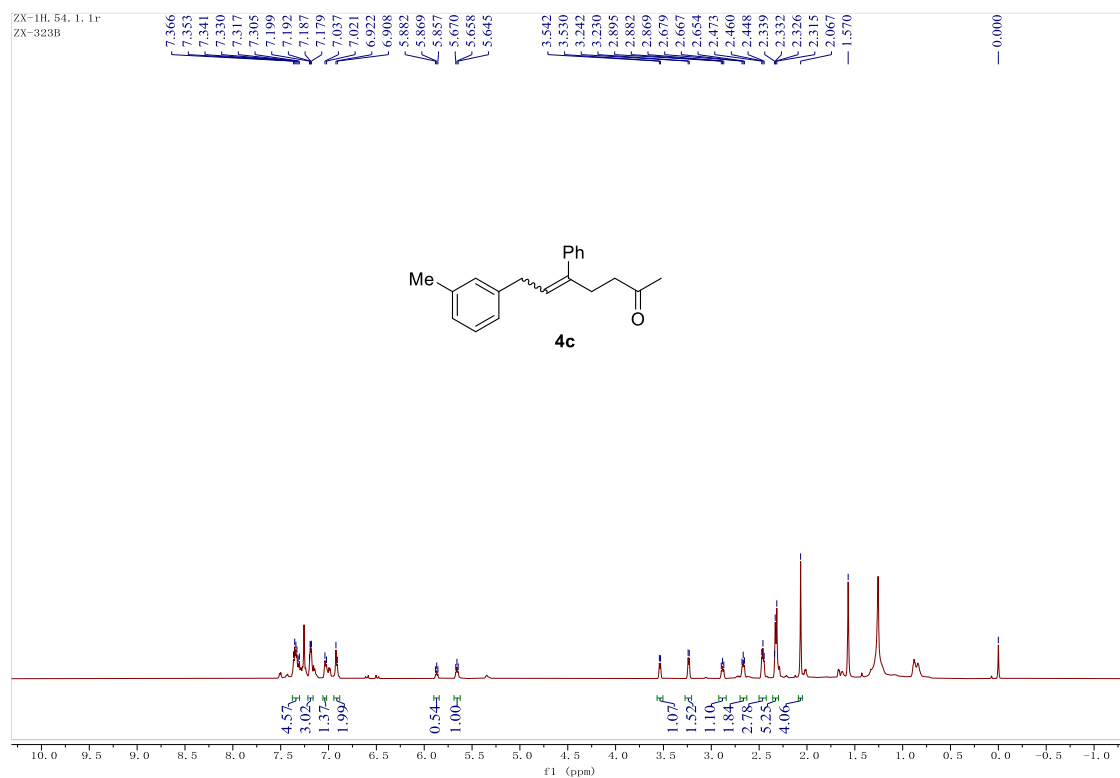
¹H NMR (600 MHz, CDCl₃) for **4b**



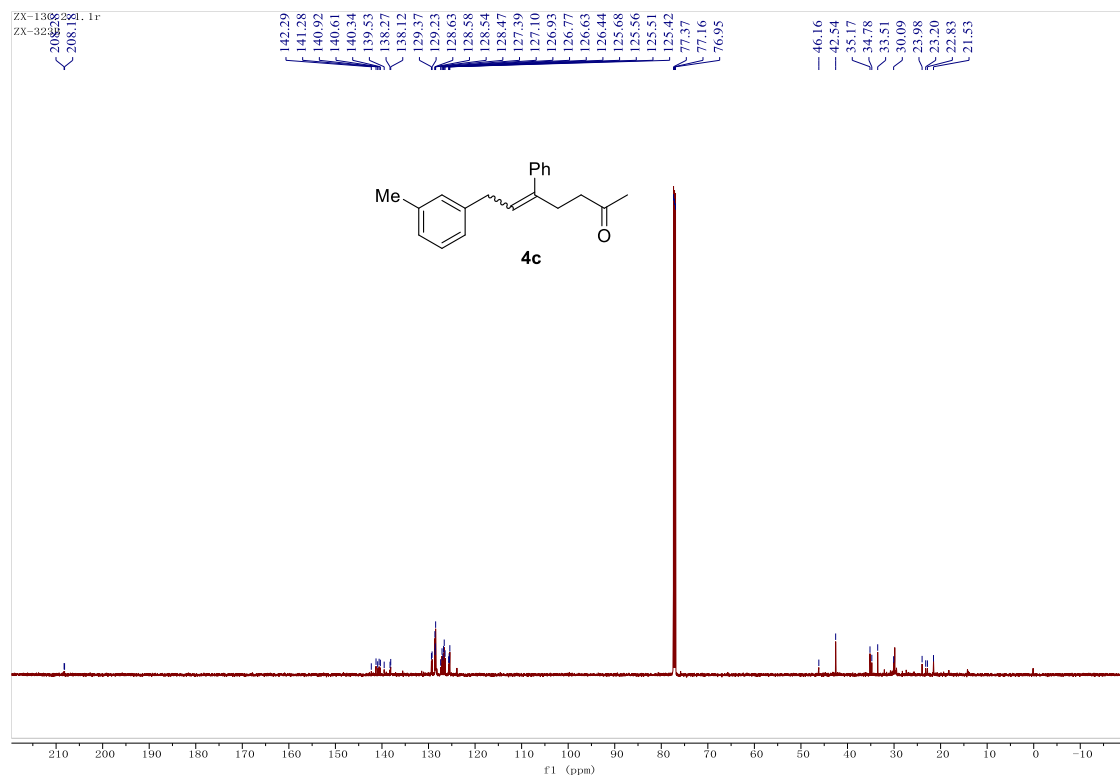
¹³C NMR (151 MHz, CDCl₃) for **4b**



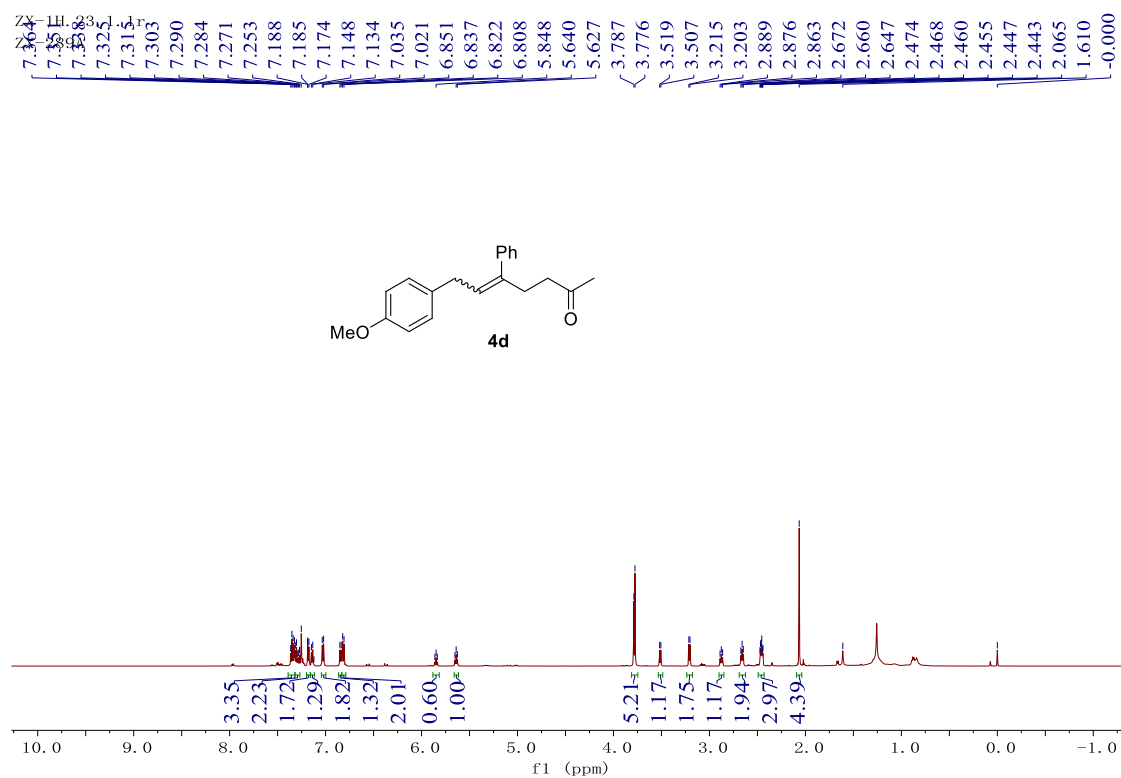
¹H NMR (600 MHz, CDCl₃) for **4c**



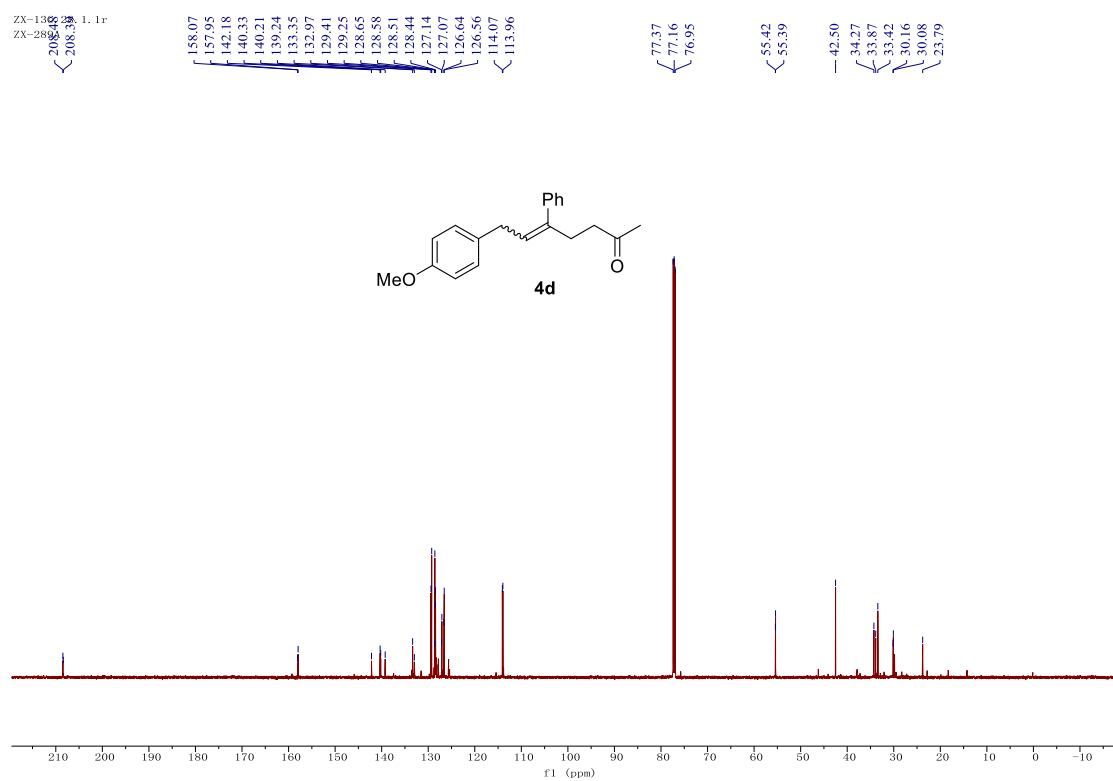
¹³C NMR (151 MHz, CDCl₃) for **4c**



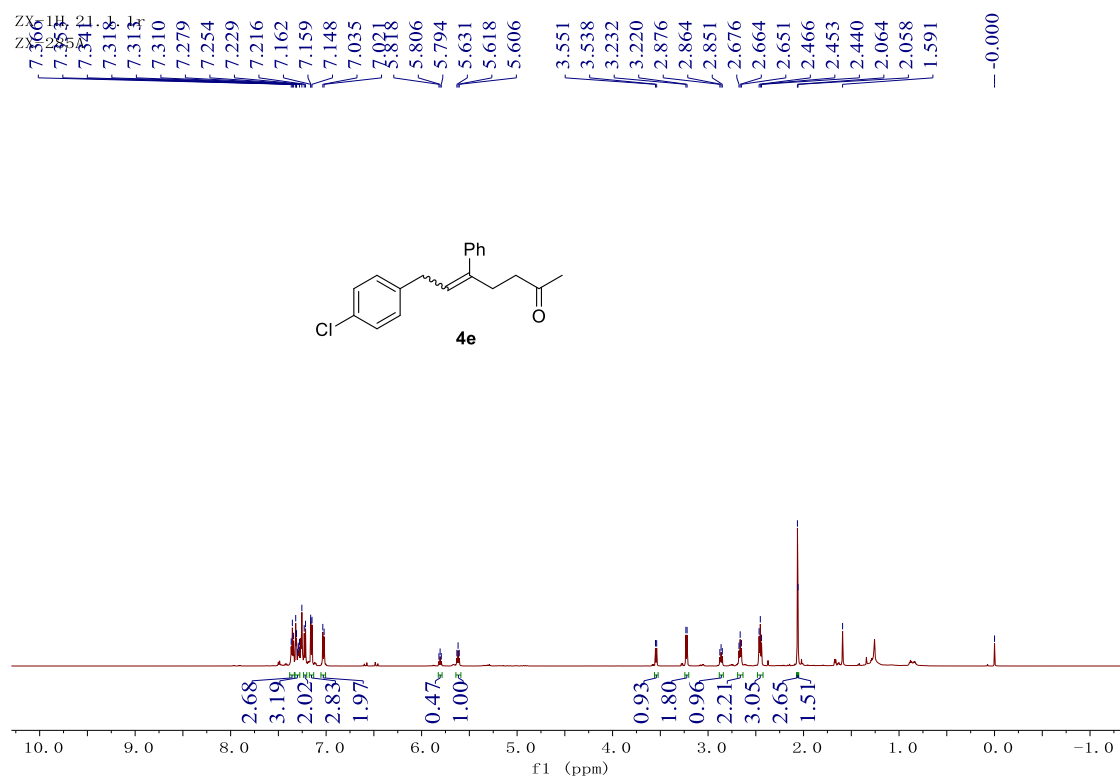
¹H NMR (600 MHz, CDCl₃) for **4d**



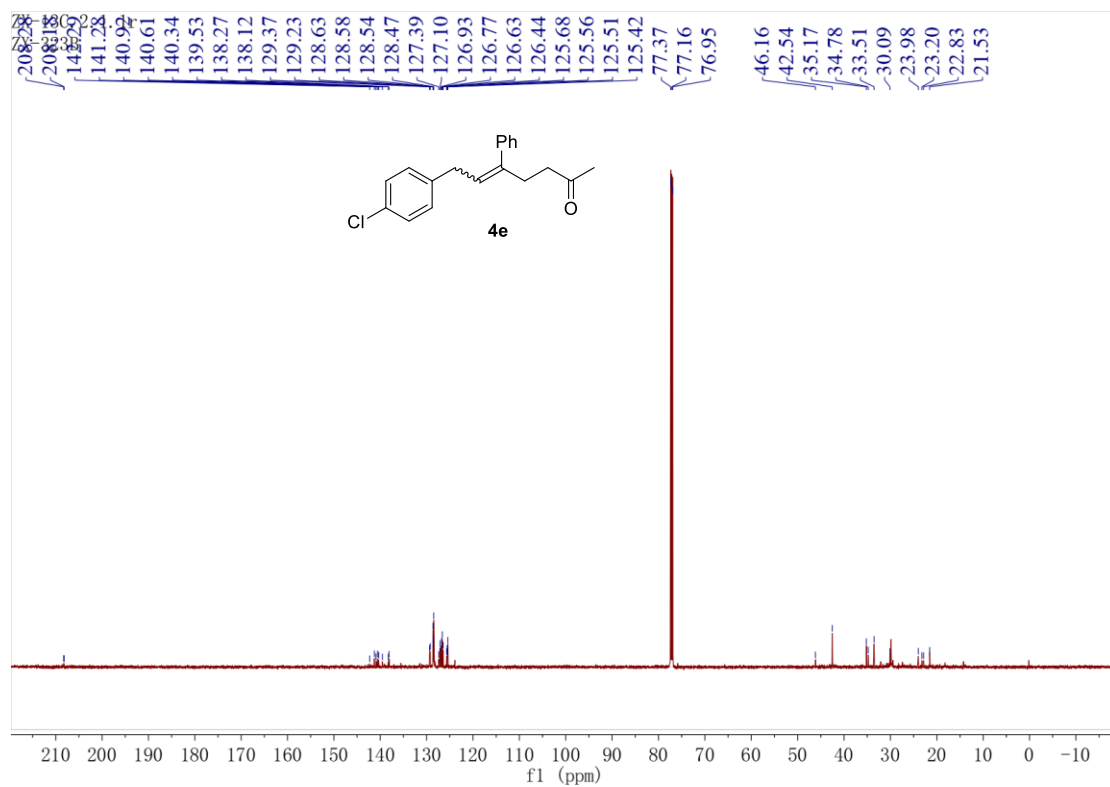
¹³C NMR (151 MHz, CDCl₃) for **4d**



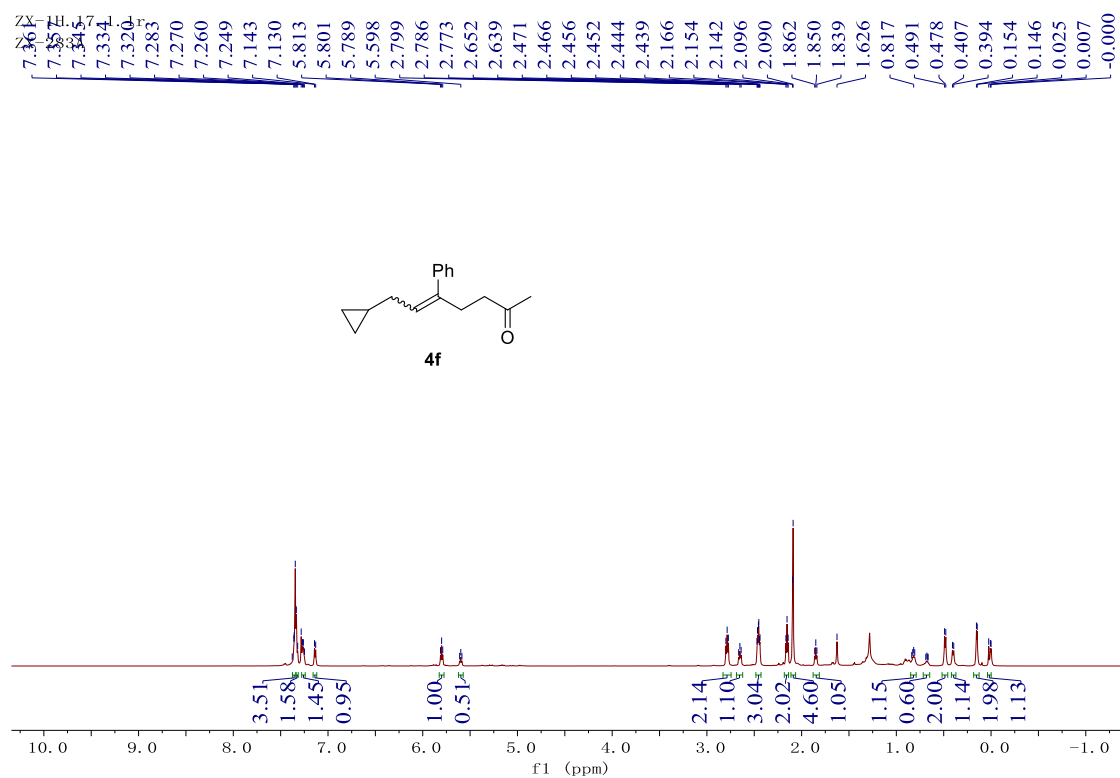
¹H NMR (600 MHz, CDCl₃) for **4e**



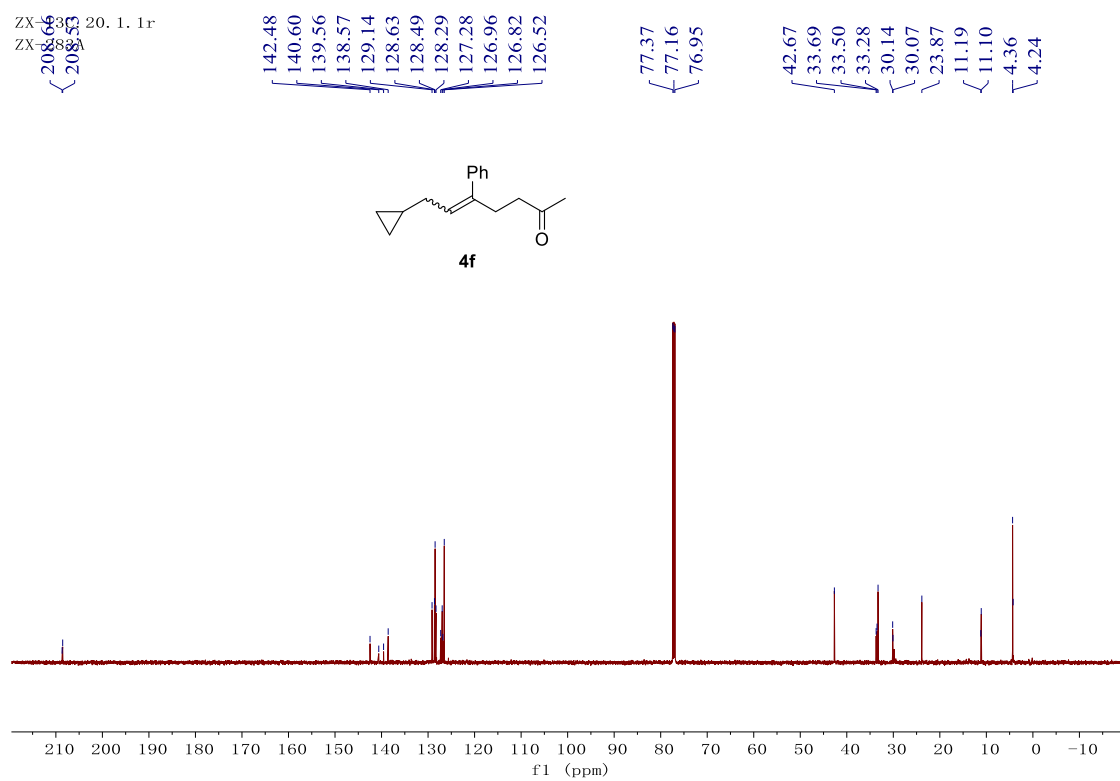
¹³C NMR (151 MHz, CDCl₃) for **4e**



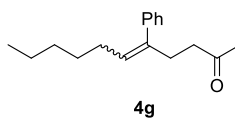
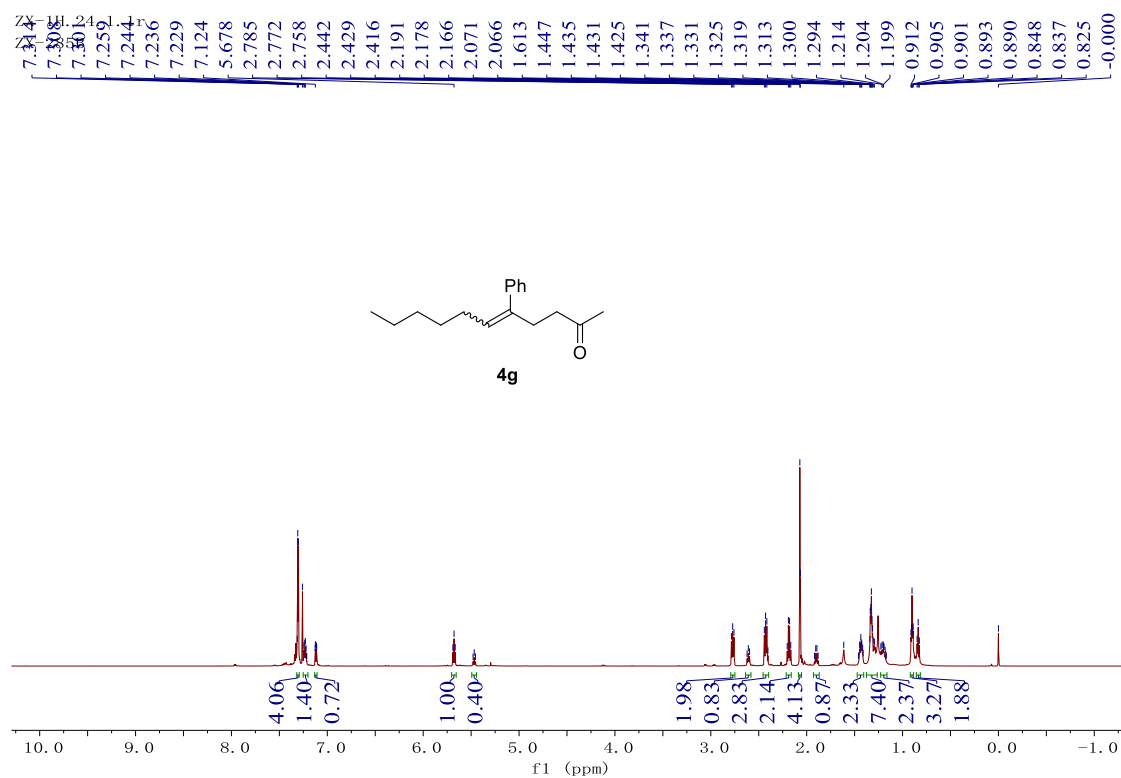
¹H NMR (600 MHz, CDCl₃) for **4f**



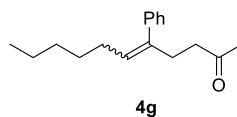
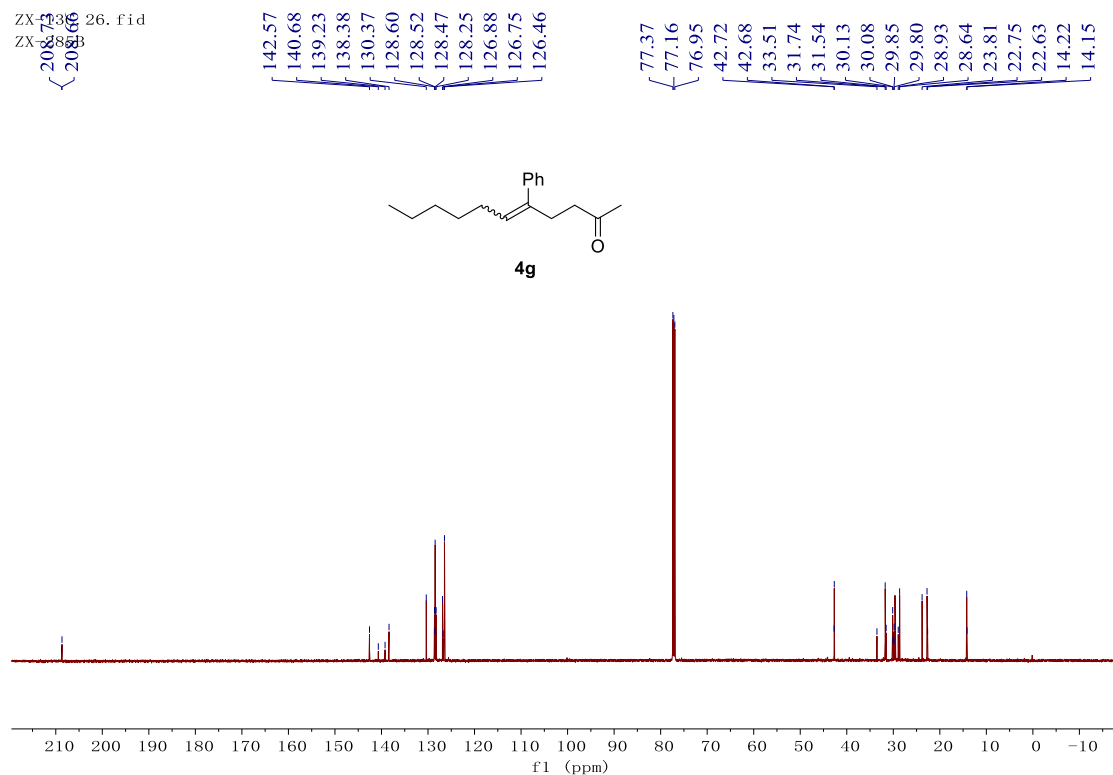
¹³C NMR (151 MHz, CDCl₃) for **4f**



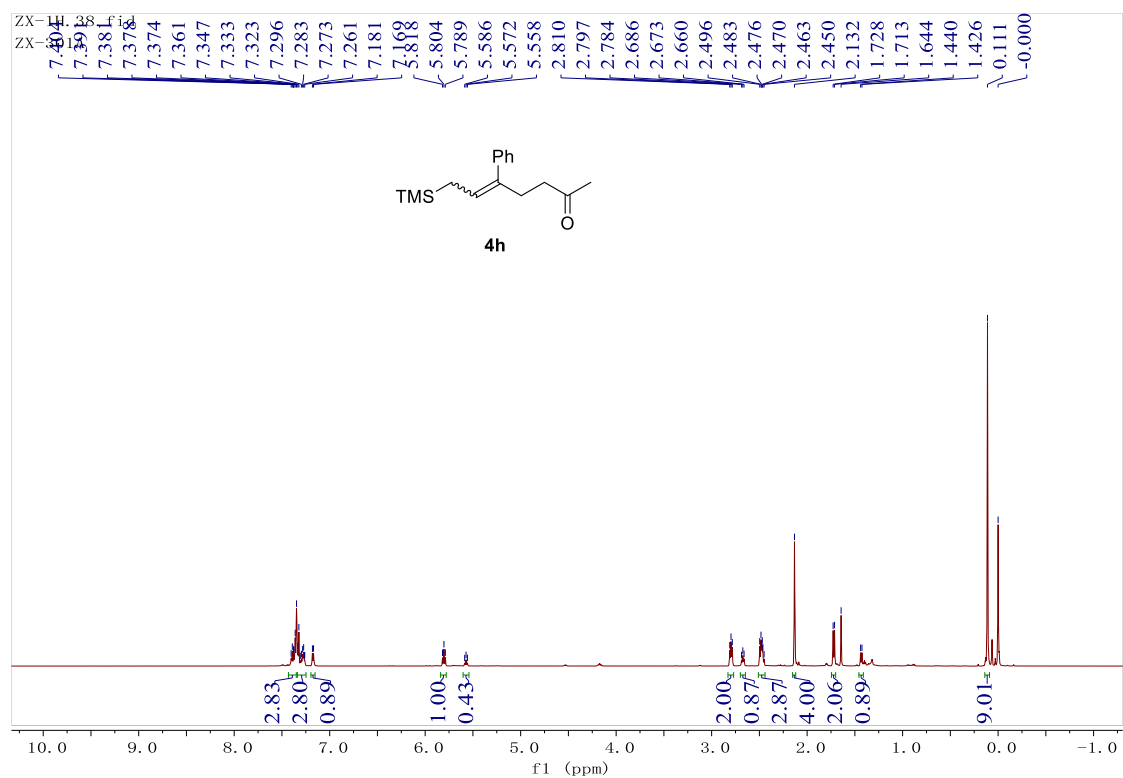
¹H NMR (600 MHz, CDCl₃) for **4g**



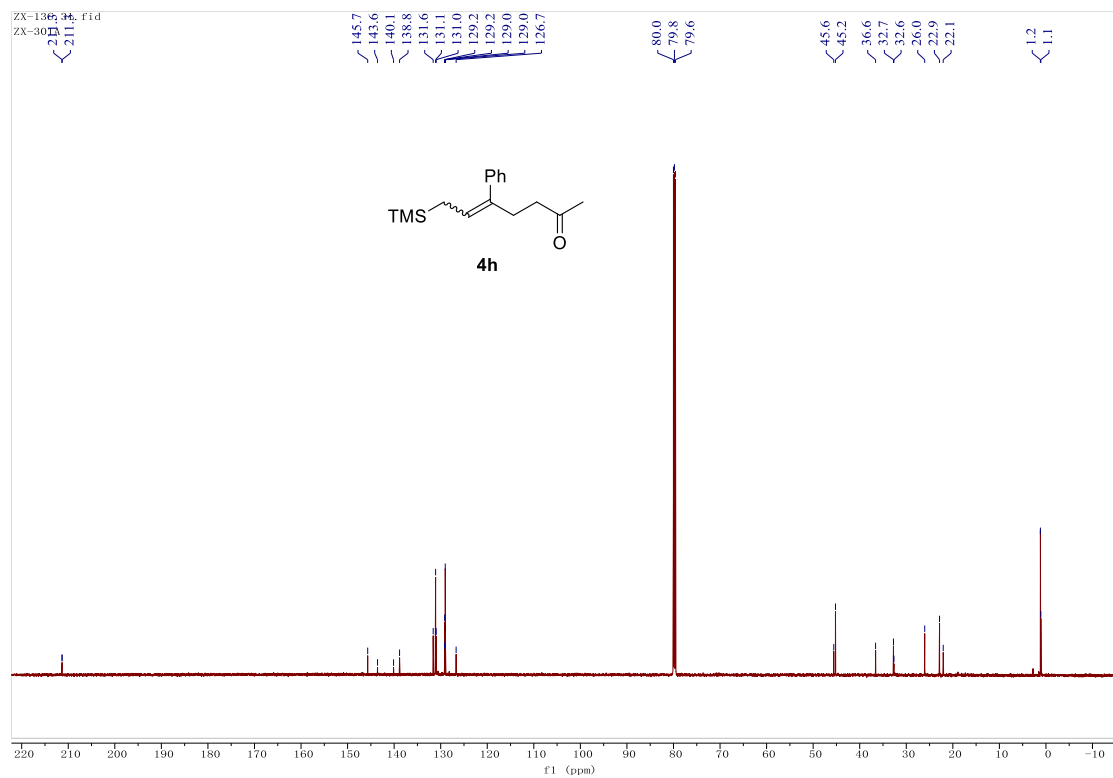
¹³C NMR (151 MHz, CDCl₃) for **4g**



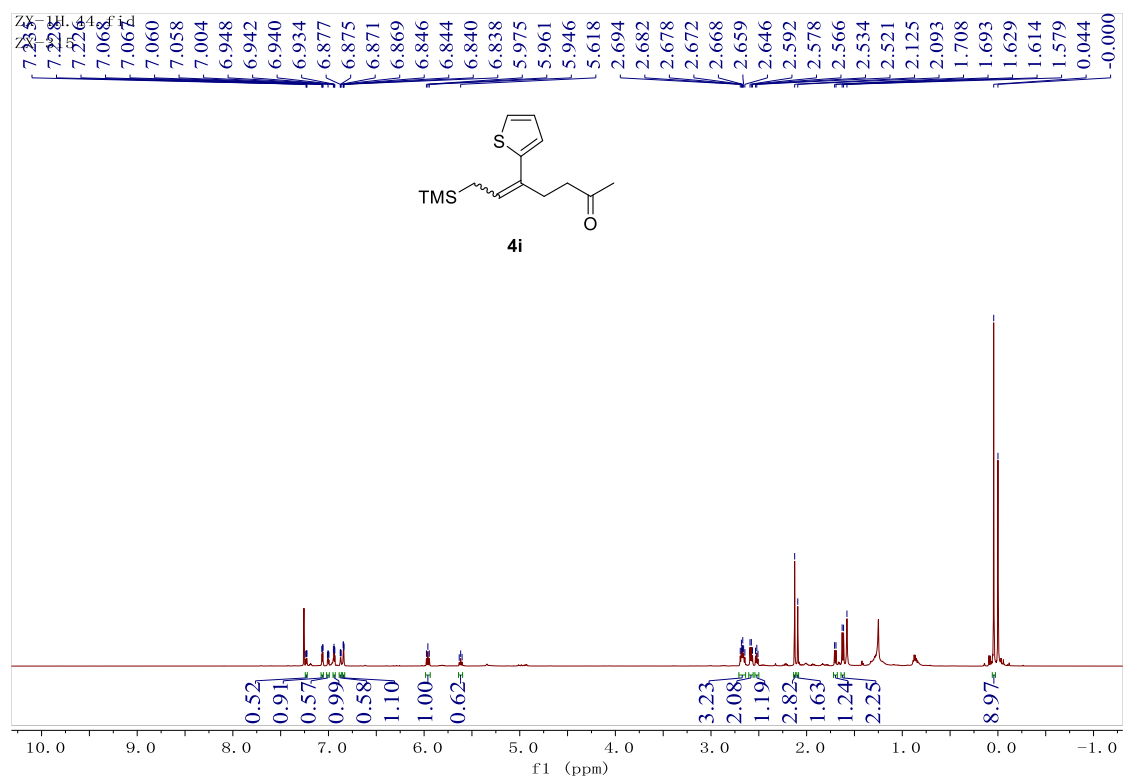
¹H NMR (600 MHz, CDCl₃) for **4h**



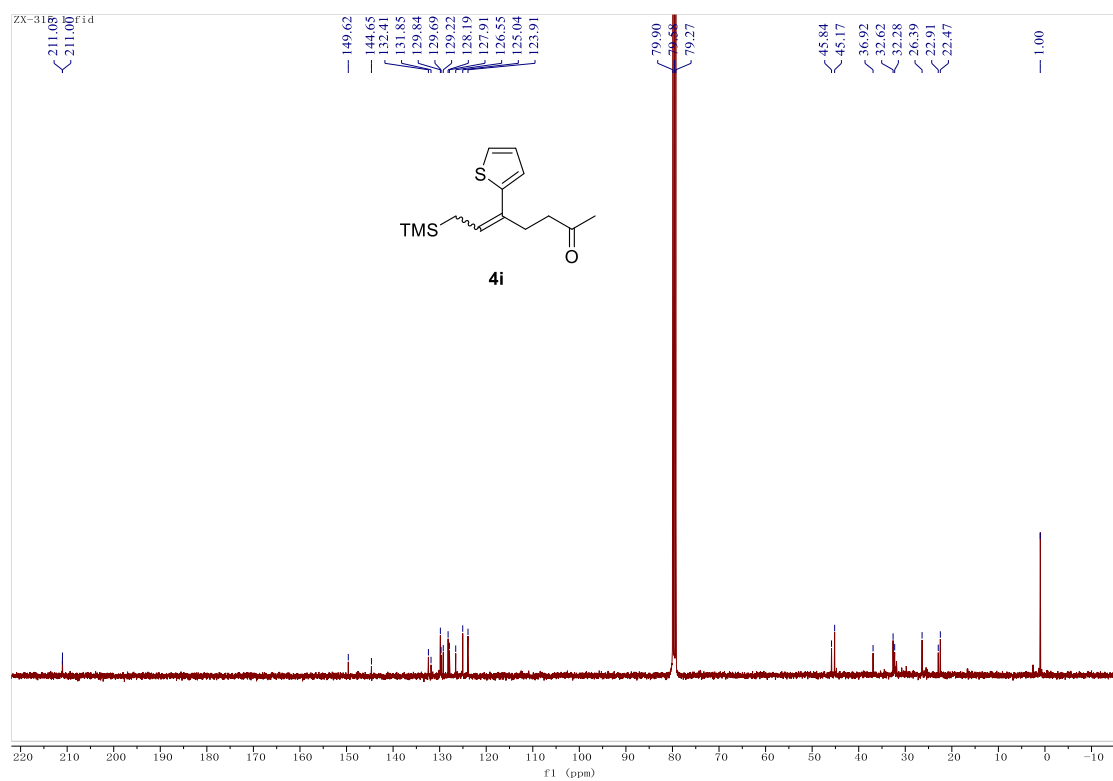
¹³C NMR (151 MHz, CDCl₃) for **4h**



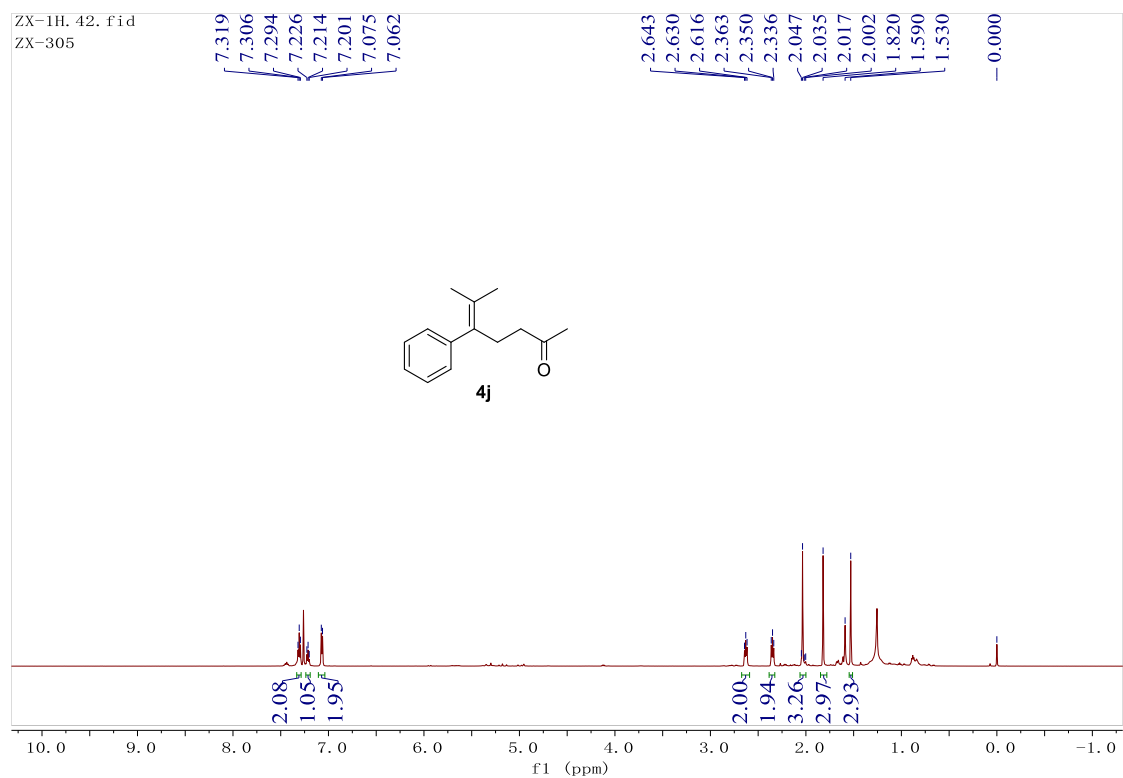
¹H NMR (600 MHz, CDCl₃) for **4i**



¹³C NMR (101 MHz, CDCl₃) for **4i**



¹H NMR (600 MHz, CDCl₃) for **4j**



¹³C NMR (151 MHz, CDCl₃) for **4j**

