Electronic Supplementary Information

Neutrally Photoinduced $MgCl_2$-catalyzed Alkenylation and Imidoylation of Alkanes

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Materials: THF was distilled from Na/benzophenone before use. Acetone was distilled from $CaSO_4$ under N_2. $MeNO_2$ distilled from $CaCl_2$ and $CaSO_4$ before use. MeCN and DCM were purified by a Vigor solvent purification system. Anhydrous $MgCl_2$ was purchased from Damas-beta. Anhydrous $MgCl_2$ was stored and weighed in the glovebox. Other commercially available chemicals were purchased and used without additional purification unless noted otherwise. The heating source used is a shot (metal pellets) bath. Infrared spectra were recorded on a Nicolet iS5 using neat thin film technique. High-resolution mass spectra (HRSM) were obtained on a Waters I-Class VION IMS QTof and are reported as m/z (relative intensity). Accurate masses are reported for the molecular ion $[M+Na]^+$ or $[M+H]^+$. ^1H NMR spectra were recorded on a JEOL-400 MHz spectrometer, ^{13}C NMR spectra were recorded at 101 MHz, and ^{19}F NMR spectra were recorded at 376 MHz. Unless otherwise noted, all spectra were acquired in $CDCl_3$. Chemical shifts are reported in parts per million (ppm, δ), downfield from tetramethylsilane (TMS, δ = 0.00 ppm) and are referenced to residual solvent ($CDCl_3$, δ = 7.26 ppm (^1H) and 77.00 ppm (^{13}C)). Coupling constants were reported in Hertz (Hz). Data for NMR spectra were reported as follows: s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, dd = doublet of doublets, td = triplet of doublets, ddd = doublet of doublet of doublets, tt = triplet of triplets, m = multiplet, coupling constant (Hz), and integration.

The vinyl sulfones including **1a**, **1e**, **1f**, **1g**, and **1h** were known and were prepared according to the known literature.[1-2] The oxime ethers including **4a**, **4d**, **4e**, **4g**, **4h, 4i**, and **4j** were known and were prepared according to the known literature.[3]

The LED light (100 W, emitting area: 30 × 30 mm) was assembled using the 390-395 nm chips purchased from GuangHong Chips. The emission spectrum of the LED light is shown below (Figure S1) and wavelength of peak intensity is 390-395 nm. The material of the reaction vessels is regular borosilicate glass. The distance from the light source to the reaction vessel is 5 cm (Figure S2).

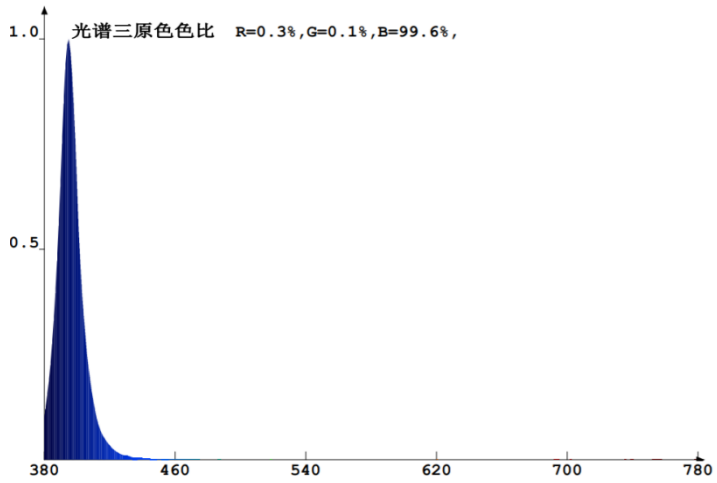
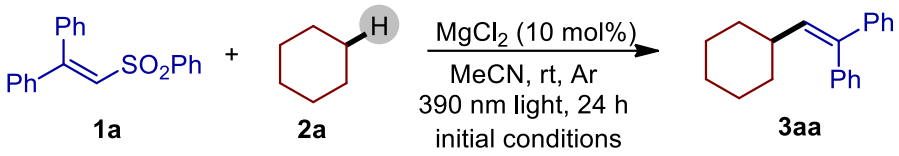


Figure S1: The emission spectrum of the LED light.

Figure S2: The setting-up reactions.

Table S1 Optimization of the Reaction Condition[a]



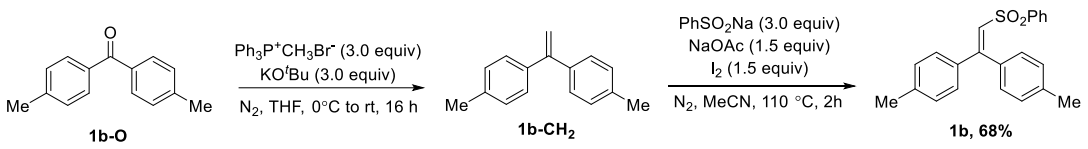
1a 2a 3aa

Entry	Change from initial conditions[a]	Yield[b]	
		1a	**3aa**
1	None	33%	54%
2	No LED	97%	0
3	No $MgCl_2$	98%	0
4	$FeCl_3$ was used instead of $MgCl_2$	69%	30%
5	LiCl was used instead of $MgCl_2$	69%	28%
6	TBACl was used instead of $MgCl_2$	78%	20%
7	CH_3NO_2 was used as solvent	94%	0
8	DCM was used as solvent	42%	25%
9	Acetone was used as solvent	51%	43%
10	The reaction time was 48 h	18%	60%
11	The reaction time was 72 h	8%	70%[c]
12	20 mol% of $MgCl_2$, 24 h	17%	67%
13	20 mol% of $MgCl_2$, 72 h	0%	79%(78%[c])
14	20 mol% of $MgCl_2$, 2.0 equiv of **2a**	63%	22%
15	20 mol% of $MgCl_2$, 5.0 equiv of **2a**	50%	48%

[a] The initial reaction was conducted with **1a** (0.2 mmol), **2a** (2.0 mmol, 10 equiv), MgCl2 (0.02 mmol), and MeCN (0.5 mL) in a 4 mL vial with 390 nm LED photo-irradiation at rt for 24 h. [b] All yields were determined by 1H NMR with mesitylene as the internal standard. [c] The yield in the parentheses was based on isolation.

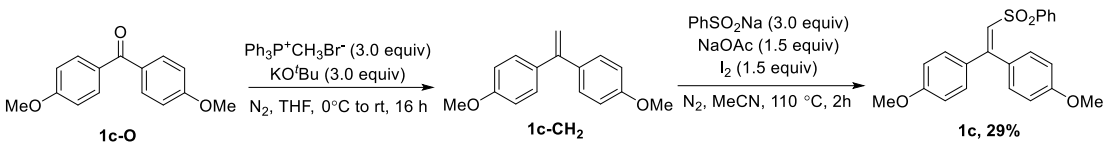
We began our exploration in the chlorine radical catalyzed C(sp^3)─H alkenylation of alkanes by exposing an acetonitrile solution of diphenyl-substituted vinyl sulfone **1a**, 10 mol% of $MgCl_2$, and 10 equiv of cyclohexane **2a** to the irradiation of 390 nm LED under argon atmosphere for 24 hours (Table S1). Gladly, although about 33% of starting material was recovered, the desired alkenylation product **3aa** was able to obtain successfully in 54% yield even in the absence of strong acid, oxidant, and photocatalyst (entry 1). This result was truly encouraging because it proved that the chlorine radical could be generated from chloride ion under such a neutral condition. The controlled experiments were then conducted to prove the critical roles of the light and magnesium catalyst since that the reaction did not occur in the absence of light or magnesium chloride (entries 2-3). Other metal chlorides with different cations, such as $FeCl_3$ and LiCl, could also proceed the transformation successfully, but the yields were lower than $MgCl_2$ (entries 4-5 vs entry 1). When the tetrabutylammonium chloride TBACl was used, 20% of the desired product **3aa** was obtained, confirming that reaction was catalyzed by the chloride ion instead of the metal cation (entry 6). Solvent effect was also explored. Other solvents, such as DCM, acetone, and CH_3NO_2, resulted in the yield decreasing dramatically (entries 7-9). We tried to achieve a higher conversion by extending the reaction time to 48 h and 72 h, and the reaction yields were indeed increased to 60% and 70%, respectively (entries 10-11). When the catalyst loading was increasing to 20 mol%, the corresponding yield also increased to 67% (entry 12). Finally, the yield of **3aa** was able to increase to 78% by additional extending the reaction time to 72 h (entry 13). Reducing the amount of **2a** to 5 or 2 equiv., the corresponding yields decreased to only 49% and 22%, respectively (entries 14-15).

Preparation of Starting Materials



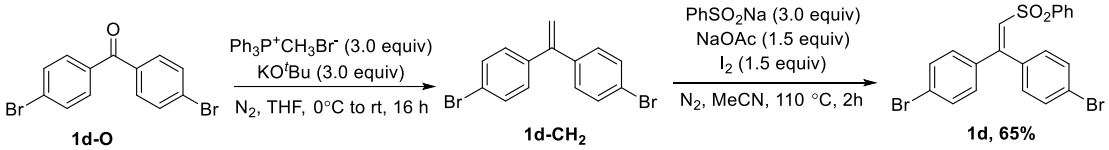
Typical Procedure 1: According to the reported literature,[4] to an oven-dried 50 mL round-bottom flask were added methyltriphenylphosphonium bromide (3.5392 g, 9.91 mmol), THF (15 mL), and KO^{t}Bu (1.1088 g, 9.90 mmol) under a nitrogen atmosphere at 0 ℃. A bright yellow color was observed. After stirring at 0 °C for 30 min, **1b-O** (0.6931 g, 3.30 mmol) was then added and the resulting mixture was stirred for additional 15 h. The temperature was allowed to increase to rt. The reaction was quenched with H_2O (10 mL) and extracted with ethyl acetate (10 mL × 3). The combined organic layer was dried over anhydrous Na_2SO_4. Evaporation and flash chromatography on silica gel (eluent: PE) afforded **1b-CH$_2$** (0.5930 g) as a white solid, which was used for next step directly.

Typical Procedure 2: To an oven-dried 50 mL round-bottom flask were added $PhSO_2Na$ (1.3854 g, 8.56 mmol), NaOAc (0.3504 g, 4.27 mmol), MeCN (12 mL), **1b-CH$_2$** (0.5912 g, 2.84 mmol), and I_2 (1.0855 g, 4.27 mmol) under a nitrogen atmosphere. The resulting mixture was heated at 110 °C for 2 h and then cooled to rt. The reaction was quenched with saturated $Na_2S_2O_3$ solution (20 mL) and extracted with ethyl acetate (10 mL× 3). The combined organic layer was dried over anhydrous Na_2SO_4. Evaporation and flash chromatography on silica gel afforded **1b** (0.7787 g, 68% for two steps) (eluent: PE/EA = 10/1): white solid. mp. 100.9-101.9 ℃ (DCM/Hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63-7.57 (m, 2 H, Ar-H), 7.52-7.44 (m, 1 H, Ar-H), 7.35 (t, *J* = 7.8 Hz, 2 H, Ar-H), 7.11-7.06 (m, 6 H, Ar-H), 6.97 (d, *J* = 8.1 Hz, 2 H, Ar-H), 6.94 (s, 1 H, CH=), 2.38 (s, 3 H, CH_3), 2.34 (s, 3 H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.4, 141.7, 140.7, 138.8, 136.5, 132.7, 129.7, 129.2, 128.5, 128.4, 128.2, 127.5, 127.3, 21.3, 21.2. IR (neat, cm^{-1}) 3027, 2919, 1586, 1304, 1149, 1083. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{22}H_{20}O_2SNa$ 371.1076; found 371.1077.



Following the typical procedure 1, the reaction of methyltriphenylphosphonium bromide (5.3558 g, 15.0 mmol), KO^{t}Bu (1.6810 g, 15.0 mmol), and **1c-O** (1.2113 g, 5.01 mmol) in THF (25 mL) afforded **1c-CH$_2$** (0.3823 g) as a white solid, which was used for next step directly.

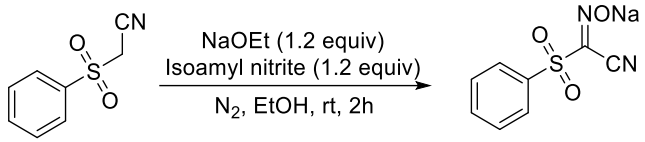
Following the typical procedure 2, the reaction of PhSO$_2$Na (0.7745 g, 4.78 mmol), NaOAc (0.1960 g, 2.39 mmol), **1c-CH$_2$** (0.3823 g, 1.59 mmol), and I_2 (0.6072 g, 2.39 mmol) in MeCN (6.4 mL) afforded **1c** (0.5439 g, 29% for two steps): (eluent: petroleum ether/ethyl acetate = 5/1): colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65-7.56 (m, 2 H, Ar-H), 7.51-7.43 (m, 1 H, Ar-H), 7.35 (t, *J* = 7.8 Hz, 2 H, Ar-H), 7.18-7.12 (m, 2 H, Ar-H), 7.07-6.98 (m, 2 H, Ar-H), 6.87 (s, 1 H, CH=), 6.83-6.76 (m, 4 H, Ar-H), 3.85 (s, 3 H, CH_3), 3.80 (s, 3 H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.4, 160.2, 154.9, 132.6, 131.5, 130.0, 128.5, 127.5, 125.9, 113.9, 113.2, 55.4, 55.3. IR (neat, cm^{-1}) 2956, 2837, 1605, 1537, 1253, 1174. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{22}H_{21}O_4S$ 381.1155; found 381.1153.



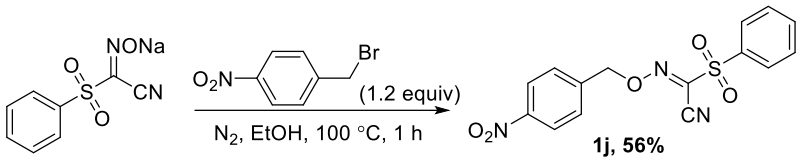
Following the typical procedure 1, the reaction of methyltriphenylphosphonium bromide (10.7104 g, 30.0 mmol), KO^{t}Bu (3.3610 g, 30.0 mmol), and **1d-O** (3.4051 g, 10.0 mmol) in THF (50 mL) afforded **1d-CH$_2$** (3.0686 g) as a colorless oil, which was used for next step directly.

Following the typical procedure 2, the reaction of PhSO$_2$Na (4.4390 g, 27.4 mmol), NaOAc (1.1231 g, 13.7 mmol), **1d-CH$_2$** (3.0686 g, 9.13 mmol), and I_2 (3.4799 g, 13.7 mmol) in MeCN (36 mL) afforded **1d** (3.0855 g, 65% for two steps) (eluent: petroleum ether/ethyl acetate = 10/1): white solid. mp. 163.6-164.0 °C (DCM/Hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64-7.59 (m, 2 H, Ar-H), 7.58-7.51 (m, 1 H, Ar-H), 7.48-7.38 (m, 6 H, Ar-H), 7.07-7.03 (m, 2 H, Ar-H), 6.99 (s, 1 H, CH=), 6.98-6.94 (m, 2 H, Ar-

H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.5, 141.0, 137.4, 133.8, 133.2, 131.9, 131.3, 131.2, 129.6, 129.4, 128.9, 127.6, 125.2, 123.7. IR (neat, cm^{-1}) 2954, 2922, 1488, 1305, 1150, 1010. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{15}Br_2O_2S$ 476.9154; found 476.9153.

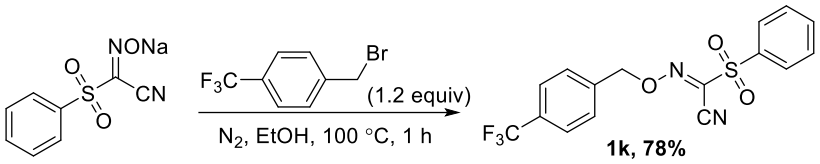


To the solution of (phenylsulfonyl)acetonitrile (5.2911 g, 29.23 mmol) in EtOH (7 mL) was added a freshly prepared solution of NaOEt in EtOH [790 mg of Na (34.35 mmol) dissolved in 20 mL EtOH] and then isoamyl nitrite (4.8 mL, d = 0.872 g/mL, 34.33 mmol, 95% purity) at rt. The resulting mixture was stirred at rt for 14 h, and a yellow solid precipitated. The precipitate was filtered and washed with cold EtOH (20 mL) and Et_2O (20 mL). Evaporation afforded the sodium salt of *N*-hydroxy-1-(phenylsulfonyl)methanimidoyl cyanide (3.5716 g, 54%) as a yellow powder, which was used for next step directly.

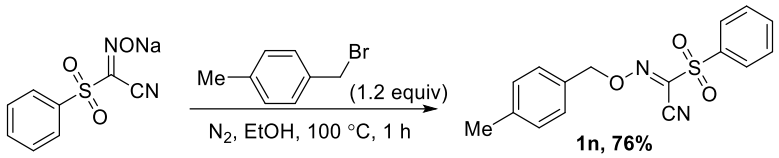


Typical Procedure 3: To the suspension of the sodium salt of *N*-hydroxy-1-(phenylsulfonyl)methanimidoyl cyanide (0.1955 g, 0.86 mmol) in EtOH (2 mL) was added 1-(bromomethyl)-4-nitrobenzene (0.2201 g, 1.03 mmol) under a nitrogen atmosphere. The mixture was heated to 100 ℃ for 1 h and then concentrated under reduced pressure. The mixture was extracted with ethyl acetate (5 mL × 3). The combined organic layer was washed with sat. NH_4Cl (5 mL) and water (5 mL) and dried over anhydrous Na_2SO_4. Evaporation and flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 2.5/1) afforded **1j** (0.1634 g, 56%): yellow solid. mp. 83.3-84.3 ℃ (DCM/Hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27-8.18 (m, 2 H, Ar-H), 8.00-7.95 (m, 2 H, Ar-H), 7.84-7.75 (m, 1 H, Ar-H), 7.69-7.60 (m, 2 H, Ar-H), 7.53-7.46 (m, 2 H, Ar-H), 5.53 (s, 2 H, CH_2). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.3, 140.6, 136.1, 135.8, 130.0, 129.4, 129.3, 124.0, 105.4, 79.3. IR (neat, cm^{-1}) 2953, 2918, 2950,

2228, 1607, 1520, 1448, 1346. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{12}N_3O_5S$ 346.0492; found 346.0497.

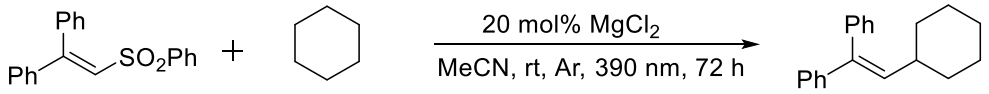


Following the typical procedure 3, the reaction of sodium salt of *N*-hydroxy-1-(phenylsulfonyl)methanimidoyl cyanide (0.2324 g, 1.00 mmol) and 1-(bromomethyl)-4-(trifluoromethyl)benzene (0.2870 g, 1.20 mmol) in EtOH (2.3 mL) afforded **1k** (0.2868 g, 78%) (eluent: petroleum ether/ethyl acetate = 10/1 to 8/1): yellow solid. mp. 67.6-68.0 ℃ (DCM/Hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00-7.93 (m, 2 H, Ar-H), 7.80-7.73 (m, 1 H, Ar-H), 7.66-7.57 (m, 4 H, Ar-H), 7.43 (d, *J* = 8.0 Hz, 2 H, Ar-H), 5.48 (s, 2 H, CH_2). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.6, 136.2, 135.7, 135.4, 131.4 (q, C-F, $^2J_{C\text{-}F}$ = 32.8 Hz), 129.9, 129.5, 129.4, 129.19, 129.16, 128.7, 125.8 (q, C-F, $^3J_{C\text{-}F}$ = 3.8 Hz), 123.7 (q, C-F, $^1J_{C\text{-}F}$ = 272.4 Hz), 105.5, 80.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.7. IR (neat, cm^{-1}) 3066, 2955, 2917, 2227, 1449, 1357, 1326, 1171, 1015. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{16}H_{11}F_3N_2O_3SNa$ 391.0335; found 391.0333.



Following the typical procedure 3, the reaction of sodium salt of *N*-hydroxy-1-(phenylsulfonyl)methanimidoyl cyanide (0.2319 g, 1.00 mmol) and 1-(bromomethyl)-4-methylbenzene (0.2221 g, 1.20 mmol) in EtOH (2.3 mL) afforded **1n** (0.2381 g, 76%) (eluent: petroleum ether/ethyl acetate = 8/1 to 7/1): white solid. mp. 77.8-78.4 ℃ (DCM/Hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03-7.92 (m, 2 H, Ar-H), 7.83-7.71 (m, 1 H, Ar-H), 7.67-7.55 (t, *J* = 7.9 Hz, 2 H, Ar-H), 7.21 (d, *J* = 8.2 Hz, 2 H, Ar-H), 7.17 (d, *J* = 8.1 Hz, 2 H, Ar-H), 5.40 (s, 2 H, CH_2), 2.37 (s, 3 H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.5, 136.5, 135.4, 134.5, 130.6, 129.8, 129.5, 129.3, 129.2, 105.7, 81.6, 21.3. IR (neat, cm^{-1}) 3062, 2954, 2921, 2228, 1448, 1355, 1171, 1016. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{15}N_2O_3S$ 315.0798; found 315.0792.

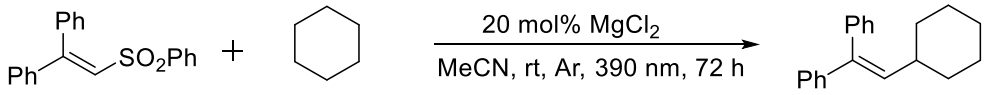
C(sp^3)─H Alkenylation and Imidoylation of Alkanes



1a 0.2 mmol　　**2a** 2.0 mmol　　**3aa, 78%**

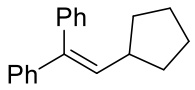
Typical Procedure 4: To a 4 mL vial were added **1a** (64.1 mg, 0.20 mmol), $MgCl_2$ (4.0 mg, 0.04 mmol), **2a** (216 μL, *d* = 0.779 g/mL, 168.0 mg), and MeCN (0.5 mL) in an Ar glovebox. The vial was sealed and then transferred out of glovebox. Under irradiation at 390 nm LEDs, the resulting mixture was stirred for 72 hours at rt. Evaporation and flash chromatography on silica gel afforded **3aa** (40.8 mg, 78%) (eluent: PE): colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.14 (m, 10 H, Ar-H), 5.90 (d, *J* = 10.1 Hz, 1 H, CH=), 2.21-2.05 (m, 1 H, CH), 1.75-1.56 (m, 5 H), 1.23-1.08 (m, 5 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.9, 142.5, 139.5, 136.0, 129.8, 128.1, 128.0, 127.2, 126.7, 126.7, 38.3, 33.3, 26.0, 25.6. IR (neat, cm^{-1}) 3055, 3020, 2921, 2849, 1597, 1445, 1073. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{23}$ 263.1794; found 263.1800.

Gram scale reaction:



1a 3.13 mmol　　**2a** 31.3 mmol　　**3aa, 66%**

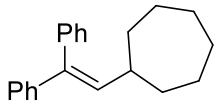
Following Typical Procedure 4, the reaction of $MgCl_2$ (59.8 mg, 0.63 mmol), **1a** (1.0006 g, 3.13 mmol), and **2a** (3.4 mL, *d* = 0.779 g/mL, 2.6250 g) in MeCN (7.8 mL) afforded **3aa** (0.5410 g, 66%) (eluent: PE): colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.14 (m, 10 H, Ar-H), 5.90 (d, *J* = 10.1 Hz, 1 H, CH=), 2.21-2.05 (m, 1 H, CH), 1.75-1.56 (m, 5 H), 1.23-1.08 (m, 5 H).



3ab

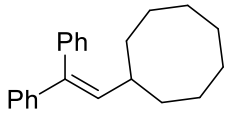
Following Typical Procedure 4, the reaction of $MgCl_2$ (3.8 mg, 0.04 mmol), **1a** (63.9 mg, 0.20 mmol), and **2b** (187 μL, *d* = 0.75 g/mL, 140 mg) in MeCN (0.5 mL) afforded **3ab** (36.2 mg, 73%) (eluent: PE): colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.18 (m, 10 H, Ar-H), 5.97 (d, *J* = 10.1 Hz, 1 H, CH=), 2.59-2.43 (m, 1 H, CH),

1.84-1.72 (m, 2 H), 1.71-1.63 (m, 2 H), 1.54-1.46 (m, 2 H), 1.45-1.33 (m, 2 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.9, 140.6, 139.9, 135.5, 130.0, 128.1, 128.0, 127.2, 126.8, 126.7, 40.4, 34.2, 25.6. IR (neat, cm^{-1}) 3054, 3021, 2951, 2865, 1492, 1444, 1264, 1073. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{19}H_{21}$ 249.1638; found 249.1637.



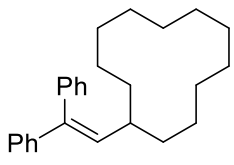
3ac

Following Typical Procedure 4, the reaction of $MgCl_2$ (3.9 mg, 0.04 mmol), **1a** (64.1 mg, 0.20 mmol), and **2c** (242 μL, *d* = 0.811 g/mL, 196 mg) in MeCN (0.5 mL) afforded **3ac** (39.7 mg, 72%) (eluent: PE): colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.14 (m, 10 H, Ar-H), 6.01 (d, *J* = 10.3 Hz, 1 H, CH=), 2.40-2.25 (m, 1 H, CH), 1.78-1.70 (m, 2 H), 1.68-1.60 (m, 2 H), 1.54-1.33 (m, 8 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.0, 140.5, 138.1, 136.6, 129.8, 128.1, 128.0, 127.2, 126.7, 126.6, 39.5, 35.0, 28.6, 26.1. IR (neat, cm^{-1}) 2923, 2850, 1559, 1490, 1457, 1443. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{21}H_{25}$ 277.1951; found 277.1950.



3ad

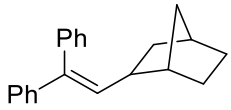
Following Typical Procedure 4, the reaction of $MgCl_2$ (3.9 mg, 0.04 mmol), **1a** (64.5 mg, 0.20 mmol), and **2d** (269 μL, *d* = 0.834 g/mL, 224 mg) in MeCN (0.5 mL) afforded **3ad** (44.5 mg, 77%) (eluent: PE): colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.15 (m, 10 H, Ar-H), 6.03 (d, *J* = 10.3 Hz, 1 H, CH=), 2.45-2.31 (m, 1 H, CH), 1.75-1.58 (m, 4 H), 1.53-1.32 (m, 10 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.9, 140.6, 138.2, 136.7, 129.8, 128.1, 128.0, 127.2, 126.7, 126.6, 37.4, 32.5, 27.2, 26.3, 25.0. IR (neat, cm^{-1}) 3054, 3020, 2917, 2850, 1597, 1494, 1471, 1444. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{22}H_{26}Na$ 313.1927; found 313.1929.



3ae

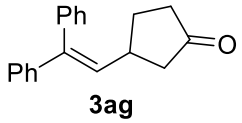
Following Typical Procedure 4, the reaction of $MgCl_2$ (3.9 mg, 0.04 mmol), **1a**

(64.1 mg, 0.20 mmol), and **2e** (335.9 mg, 2.0 mmol) in MeCN (1.0 mL) afforded **3ae** (49.6 mg, 71%) (eluent: PE): white solid. mp. 85.8-86.9 ℃ (DCM/Hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.15 (m, 10 H, Ar-H), 5.92 (d, *J* = 10.2 Hz, 1 H, CH=), 2.44-2.28 (m, 1 H, CH), 1.59-1.44 (m, 2 H), 1.40-0.88 (m, 20 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.5, 140.64, 140.55, 136.0, 129.8, 128.1, 128.0, 127.0, 126.7, 33.5, 30.8, 23.9, 23.73, 23.68, 23.1, 22.5. IR (neat, cm^{-1}) 2928, 2847, 1559, 1507, 1468, 1457, 1443. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{26}H_{34}Na$ 369.2553; found 369.2552.



3af

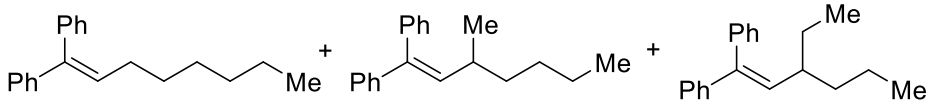
Following Typical Procedure 4, the reaction of $MgCl_2$ (3.8 mg, 0.04 mmol), **1a** (64.1 mg, 0.20 mmol), and **2f** (192.1 mg, 2.0 mmol) in MeCN (1.0 mL) afforded **3af** (39.0 mg, 71%) (eluent: PE): colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.15 (m, 10 H, Ar-H), 5.92 (d, *J* = 10.3 Hz, 1 H, CH=), 2.26 (s, 1 H), 2.23-2.15 (m, 1 H), 2.10 (s, 1 H), 1.58-1.52 (m, 1 H), 1.52-1.42 (m, 3 H), 1.39-1.31 (m, 1 H), 1.29-1.16 (m, 1 H), 1.13-1.04 (m, 2 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.2, 140.5, 138.9, 136.0, 130.2, 128.02, 127.96, 127.4, 126.8, 126.7, 43.4, 41.9, 39.7, 36.6, 36.2, 29.5, 28.8. IR (neat, cm^{-1}) 2947, 2867, 1559, 1457, 1443, 1132, 1075. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{21}H_{23}$ 275.1794; found 275.1791.



3ag

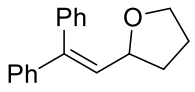
Following Typical Procedure 4, the reaction of $MgCl_2$ (3.9 mg, 0.04 mmol), **1a** (64.1 mg, 0.20 mmol), and **2g** (0.5 mL) in MeCN (0.5 mL) afforded **3ag** (21.2 mg, 40%) (eluent: PE/EA = 30/1 to 15/1): colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43-7.31 (m, 3 H, Ar-H), 7.31-7.26 (m, 2 H, Ar-H), 7.26-7.16 (m, 5 H, Ar-H), 5.98 (d, *J* = 9.6 Hz, 1 H, CH=), 3.01-2.85 (m, 1 H), 2.43-2.26 (m, 2 H), 2.21-2.01 (m, 3 H), 1.88-1.72 (m, 1 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 218.7, 142.6, 141.9, 139.8, 131.5, 129.6, 128.4, 128.2, 127.3, 127.2, 45.7, 38.3, 37.5, 30.6. IR (neat, cm^{-1}) 2956, 2924, 2853, 1740, 1491,

1456, 1444, 1153. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{19}H_{18}ONa$ 285.1250; found 281.1254.



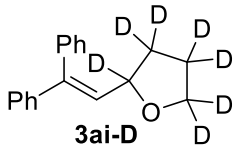
3ah-1 **3ah-2** **3ha-3**

Following Typical Procedure 4, the reaction of $MgCl_2$ (3.9 mg, 0.04 mmol), **1a** (64.2 mg, 0.20 mmol), and **2h** (261 μL, *d* = 0.659 g/mL, 172 mg) in MeCN (0.5 mL) afforded **3ah** (32.3 mg, 61%) (eluent: PE): colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.33 (m, 2 H, Ar-H), 7.32-7.27 (m, 1 H, Ar-H), 7.25-7.15 (m, 7 H, Ar-H), 6.09 (t, *J* = 7.5 Hz, 0.29 H, CH= of **3ah-1**), 5.86 (d, *J* = 10.3 Hz, 0.47 H, CH= of **3ah-2**), and 5.83 (d, *J* = 10.5 Hz, 0.28 H, CH= of **3ah-3**), 2.32-2.22 (m, 0.46 H), 2.11 (q, *J* = 7.4 Hz, 1 H), 1.48-1.39 (m, 1 H), 1.36-1.20 (m, 6 H), 1.00 (d, *J* = 6.7 Hz, 1.58 H), 0.89-0.83 (m, 3 H). All ratios were determined by ^{1}H NMR with mesitylene as the internal standard. The spectra are matching with the literature.[5,6,7]



3ai

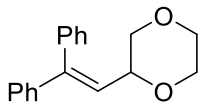
Following Typical Procedure 4, the reaction of $MgCl_2$ (3.7 mg, 0.04 mmol), **1a** (64.1 mg, 0.20 mmol), and **2i** (0.5 mL) in MeCN (0.5 mL) afforded **3ai** (26.3 mg, 53%) (eluent: PE/EA = 50/1 to 30/1): white solid. mp. 51.2-51.8 ℃ (DCM/Hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.19 (m, 10 H, Ar-H), 6.06 (d, *J* = 9.0 Hz, 1 H, CH=), 4.38-4.19 (m, 1 H, CH), 3.98-3.89 (m, 1 H), 3.76-3.69 (m, 1 H), 2.10-1.92 (m, 2 H), 1.91-1.79 (m, 1 H), 1.78-1.67 (m, 1 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.7, 142.0, 139.4, 129.9, 129.7, 128.1, 127.6, 127.4, 127.3, 76.6, 68.1, 33.1, 26.4. IR (neat, cm^{-1}) 2923, 2853, 1049. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{19}O$ 251.1430; found 251.1436.



3ai-D

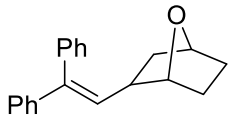
Following Typical Procedure 4, the reaction of $MgCl_2$ (3.9 mg, 0.04 mmol), **1a** (64.2 mg, 0.20 mmol), and **2i-D** (0.5 mL) in MeCN (0.5 mL) afforded **3ai-D** (27.8 mg,

54%) (eluent: PE/EA = 100/1 to 50/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.31 (m, 3 H, Ar-H), 7.27-7.19 (m, 7 H, Ar-H), 6.06 (d, *J* = 9.0 Hz, 1 H, CH=). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.7, 142.0, 139.4, 129.9, 129.7, 128.1, 127.6, 127.4, 127.3, 76.4-75.9 (m), 67.7-66.8 (quin), 32.5-31.7 (quin), 25.8-25.0 (quin). IR (neat, cm^{-1}) 2924, 1443, 1384, 1043. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{12}D_7O$ 258.1870; found 258.1860.



3aj

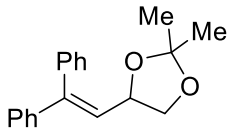
Following Typical Procedure 4, the reaction of $MgCl_2$ (3.7 mg, 0.04 mmol), **1a** (63.9 mg, 0.20 mmol), and **2j** (170 μL, *d* = 1.034 g/mL, 176 mg) in MeCN (0.5 mL) afforded **3aj** (27.9 mg, 52%) (eluent: PE/EA = 100/1 to 50/1): white solid. mp. 90.0-90.9 °C (DCM/Hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.10 (m, 10 H, Ar-H), 5.86 (d, *J* = 8.9 Hz, 1 H, CH=), 4.22-3.95 (td, J_1 = 9.2 Hz, J_2 = 2.8 Hz, 1 H, CH), 3.74-3.53 (m, 5 H), 3.41 (dd, J_1 = 11.6 Hz, J_2 = 9.9 Hz, 1 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.8, 141.4, 139.0, 129.5, 128.3, 128.2, 127.9, 127.7, 127.5, 124.1, 73.7, 70.3, 66.12, 66.08. IR (neat, cm^{-1}) 2955, 2917, 2849, 1445, 1117. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{18}H_{19}O_2$ 289.1199; found 289.1195.



3ak

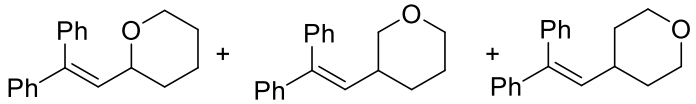
Following Typical Procedure 4, the reaction of $MgCl_2$ (3.9 mg, 0.04 mmol), **1a** (64.1 mg, 0.20 mmol), and **2k** (202 μL, *d* = 0.968 g/mL, 196 mg) in MeCN (0.5 mL) afforded **3ak** (36.6 mg, 66%) (eluent: PE/EA = 50/1 to 30/1 to 20/1): white solid. mp. 112.7-113.7 °C (DCM/Hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.12 (m, 10 H, Ar-H), 6.05 (d, *J* = 10.4 Hz, 1 H, CH=), 4.63 (t, *J* = 5.1 Hz, 1 H), 4.38-4.34 (m, 1 H), 2.46 (ddd, J_1 = 10.3 Hz, J_2 = 8.4 Hz, J_3 = 4.2 Hz, 1 H, CH), 1.81-1.59 (m, 4 H), 1.42-1.31 (m, 2 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.3, 140.1, 139.6, 133.6, 130.1, 128.1, 128.0, 127.3, 126.9, 126.9, 81.7, 76.5, 43.6, 39.9, 29.7, 29.4. IR (neat, cm^{-1}) 2923, 2868, 1495, 1464, 1457, 1444. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{21}O$ 277.1587; found

277.1573.



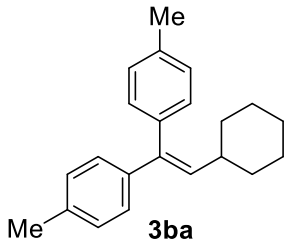
3al

Following Typical Procedure 4, the reaction of $MgCl_2$ (3.8 mg, 0.04 mmol), **1a** (64.2 mg, 0.20 mmol), and **2l** (220 μL, *d* = 0.926 g/mL, 204 mg) in MeCN (0.5 mL) afforded **3al** (27.6 mg, 49%) (eluent: PE/EA = 50/1 to 40/1): colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05-7.78 (m, 10 H, Ar-H), 6.67 (d, J = 9.0 Hz, 1 H, CH=), 5.18 (ddd, J_1 = 8.8 Hz, J_2 = 7.8 Hz, J_3 = 6.0 Hz, 1 H, CH), 4.68 (dd, J_1 = 8.1 Hz, J_2 = 6.1 Hz, 1 H, CH), 4.35 (t, J = 7.9 Hz, 1 H, CH), 2.10 (s, 3 H, CH_3), 1.96 (s, 3 H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.2, 141.5, 138.9, 129.8, 128.20, 128.16, 127.8, 127.70, 127.65, 126.1, 109.3, 74.0, 69.7, 26.8, 25.9. IR (neat, cm^{-1}) 3056, 3024, 2923, 2853, 1457, 1378, 1215, 1155, 1059. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{19}H_{21}O_2$ 281.1536; found 281.1550.



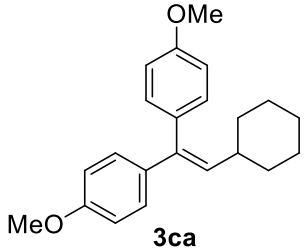
3am-1 **3am-2** **3am-3**

Following Typical Procedure 4, the reaction of $MgCl_2$ (3.8 mg, 0.04 mmol), **1a** (64.1 mg, 0.20 mmol), and **2m** (195 μL, *d* = 0.881 g/mL, 172 mg) in MeCN (0.5 mL) afforded **3am** (31.5 mg, 60%) (eluent: PE/EA = 30:1): colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.32 (m, 3 H, Ar-H), 7.26-7.15 (m, 7 H, Ar-H), 6.04 (d, J = 8.8 Hz, 0.32 H, CH= of **3am-1**), 5.90 (d, J = 9.8 Hz, 0.24 H, CH= of **3am-3**), and 5.83 (d, J = 10.0 Hz, 0.43 H, CH= of **3am-2**), 4.01-3.89 (m, 1 H), 3.89-3.78 (m, 1.24 H), 3.42-3.32 (m, 1 H), 3.31-3.23 (m, 0.88 H), 2.54-2.42 (m, 0.43 H), 2.42-2.32 (m, 0.23 H), 1.89-1.76 (m, 0.83 H), 1.68-1.60 (m, 1 H), 1.58-1.36 (m, 3 H). All ratios were determined by ^{1}H NMR with mesitylene as the internal standard. The spectra are matching with the literature.[8,9]



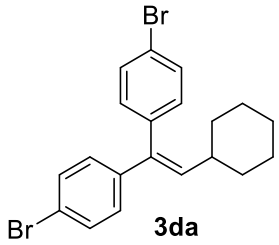
3ba

Following Typical Procedure 4, the reaction of $MgCl_2$ (3.1 mg, 0.032 mmol), **1b** (56.0 mg, 0.16 mmol), and **2a** (173 μL, *d* = 0.779 g/mL, 134.4 mg) in MeCN (0.5 mL) afforded **3ba** (29.8 mg, 64%) (eluent: PE): colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 (d, J = 7.9 Hz, 2 H, Ar-H), 7.12-7.02 (m, 6 H, Ar-H), 5.82 (d, *J* = 10.0 Hz, 1 H, CH=), 2.38 (s, 3 H, CH_3), 2.31 (s, 3 H, CH_3), 2.20-2.07 (m, 1 H, CH), 1.74-1.57 (m, 5 H), 1.24-1.09 (m, 5 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.4, 139.2, 137.7, 136.3, 136.2, 135.1, 129.6, 128.8, 128.7, 127.1, 38.2, 33.4, 26.0, 25.6, 21.2, 21.0. IR (neat, cm^{-1}) 2922, 2849, 1507, 1456, 1447, 1264. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{18}H_{19}O$ 313.1927; found 313.1918.



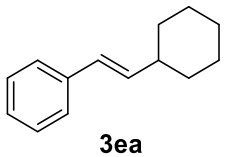
3ca

Following Typical Procedure 4, the reaction of $MgCl_2$ (4.0 mg, 0.04 mmol), **1c** (76.3 mg, 0.20 mmol), and **2a** (216 μL, *d* = 0.779 g/mL, 168.0 mg) in MeCN (0.5 mL) afforded **3ca** (36.5 mg, 57%) (eluent: PE/EA = 100/1 to 50/1): colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16-7.06 (m, 4 H, Ar-H), 6.92-6.87 (m, 2 H, Ar-H), 6.82-6.75 (m, 2 H, Ar-H), 5.75 (d, *J* = 10.0 Hz, 1 H, CH=), 3.84 (s, 3 H, CH_3), 3.78 (s, 3 H, CH_3), 2.20-2.05 (m, 1 H, CH), 1.74-1.57 (m, 5 H), 1.24-1.09 (m, 5 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.5, 158.3, 138.5, 136.0, 134.2, 133.1, 130.8, 128.3, 113.4, 113.3, 55.24, 55.16, 38.2, 33.5, 26.0, 25.7. IR (neat, cm^{-1}) 2922, 2847, 1606, 1508, 1457, 1172, 1036. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{22}H_{26}O_2Na$ 345.1825; found 345.1815.



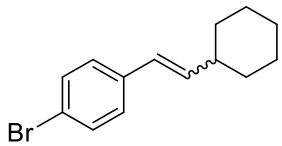
3da

Following Typical Procedure 4, the reaction of $MgCl_2$ (3.9 mg, 0.04 mmol), **1d** (95.1 mg, 0.20 mmol), and **2a** (216 μL, *d* = 0.779 g/mL, 168.0 mg) in MeCN (0.5 mL) afforded **3da** (41.9 mg, 50%) (eluent: PE): colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57-7.45 (m, 2 H, Ar-H), 7.42-7.31 (m, 2 H, Ar-H), 7.09-6.76 (m, 4 H, Ar-H), 5.89 (d, *J* = 10.1 Hz, 1 H, CH=), 2.14-2.00 (m, 1 H, CH), 1.73-1.59 (m, 5 H), 1.24-1.10 (m, 5 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.3, 138.9, 137.5, 137.0, 131.5, 131.4, 131.2, 128.8, 121.1, 120.9, 38.4, 33.1, 25.9, 25.5. IR (neat, cm^{-1}) 2956, 2923, 2853, 1661, 1622, 1586, 1463. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{21}Br_2$ 419.0005; found 419.0009.



3ea

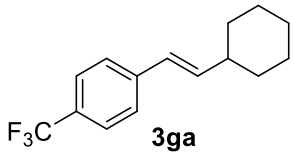
Following Typical Procedure 4, the reaction of $MgCl_2$ (3.9 mg, 0.04 mmol), **1e** (48.7 mg, 0.20 mmol), and **2a** (216 μL, *d* = 0.779 g/mL, 168.0 mg) in MeCN (0.5 mL) afforded **3ea** (18.3 mg, 49%) (eluent: PE): colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.33 (m, 2 H, Ar-H), 7.29 (t, *J* = 7.6 Hz, 2 H, Ar-H), 7.18 (t, *J* = 7.2 Hz, 1 H, Ar-H), 6.35 (d, *J* = 16.0 Hz, 1 H, CH=), 6.18 (dd, J_1 = 16.0 Hz, J_2 = 6.9 Hz, 1 H, CH=), 2.17-2.09 (m, 1 H, CH), 1.87-1.64 (m, 5 H), 1.41-1.09 (m, 5 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.0, 136.9, 128.4, 127.2, 126.7, 125.9, 41.2, 32.9, 26.2, 26.0. IR (neat, cm^{-1}) 2923, 2851, 1558, 1540, 1506, 1456, 1448, 1375. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{14}H_{18}Na$ 209.1301; found 209.1305.



3fa, *E*/*Z* = 46:54

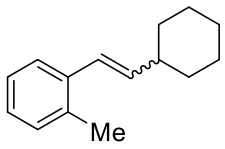
Following Typical Procedure 4, the reaction of $MgCl_2$ (3.9 mg, 0.04 mmol), **1f** (64.4 mg, 0.20 mmol), and **2a** (216 μL, *d* = 0.779 g/mL, 168.0 mg) in MeCN (0.5 mL)

afforded **3fa** (23.6 mg, 45%) (eluent: PE): colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48-7.36 (m, 2 H, Ar-H), 7.23-7.09 (m, 2 H, Ar-H), 6.32-6.20 (m, 1 H, CH=), 6.16 (dd, J_1 = 15.9 Hz, J_2 = 6.8 Hz, 0.45 H, CH=, *E*-isomer) and 5.51 (dd, J_1 = 11.7 Hz, J_2 = 10.2 Hz, 0.54 H, CH=, *Z*-isomer), 2.55-2.40 (m, 0.54 H, Cy, *Z*-isomer) and 2.18-2.03 (m, 0.46 H, Cy, *E*-isomer), 1.86-1.61 (m, 5 H), 1.40-1.09 (m, 5 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.7, 137.7, 137.0, 136.8, 131.5, 131.2, 130.2, 128.5, 127.5, 127.1, 126.1, 125.7, 120.3, 120.2, 41.1, 36.9, 33.1, 32.8, 26.1, 26.0, 25.9, 25.6. IR (neat, cm^{-1}) 2922, 2849, 1559, 1507, 1486, 1457, 1448. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{14}H_{17}BrNa$ 287.0406; found 287.0410.



3ga

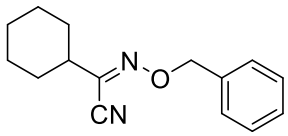
Following Typical Procedure 4, the reaction of $MgCl_2$ (3.8 mg, 0.04 mmol), **1g** (62.5 mg, 0.20 mmol), and **2a** (216 μL, *d* = 0.779 g/mL, 168.0 mg) in MeCN (0.5 mL) afforded **3ga** (24.5 mg, 48%) (eluent: PE): colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.2 Hz, 2 H, Ar-H), 7.42 (d, *J* = 8.2 Hz, 2 H, Ar-H), 6.37 (d, *J* = 16.0 Hz, 1 H, CH=) and 6.27 (dd, J_1 = 16.0 Hz, J_2 = 6.6 Hz, 1 H, CH=), 2.22-2.08 (m, 1 H, CH), 1.96-1.62 (m, 5 H), 1.40-1.10 (m, 5 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.6, 139.6, 128.5 (C-F, q, $^2J_{C\text{-}F}$ = 31.9 Hz), 126.1, 126.0, 125.4 (C-F, q, $^3J_{C\text{-}F}$ = 3.9 Hz), 124.3 (C-F, q, $^1J_{C\text{-}F}$ = 272.8 Hz), 41.2, 32.8, 26.1, 26.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.2. IR (neat, cm^{-1}) 2923, 2852, 1615, 1449, 1324, 1125, 1067. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{18}F_3$ 255.1355; found 255.1371.



3ha, *E*/*Z* = 13:1

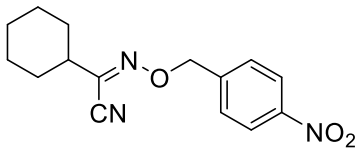
Following Typical Procedure 4, the reaction of $MgCl_2$ (3.9 mg, 0.04 mmol), **1h** (51.6 mg, 0.20 mmol), and **2a** (216 μL, *d* = 0.779 g/mL, 168.0 mg) in MeCN (0.5 mL) afforded **3ha** (10.1 mg, 25%) (eluent: PE): colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (dd, J_1 = 7.2 Hz, J_2 = 1.3 Hz, 1 H, Ar-H), 7.18-7.14 (m, 1 H, Ar-H), 7.13-7.09

(m, 2 H, Ar-H), 6.53 (d, J = 15.9 Hz, 0.95 H, CH=, *E*-isomer) and 6.30 (d, J = 11.6 Hz, 0.08 H, CH=, *Z*-isomer), 6.04 (dd, J_1 = 15.7 Hz, J_2 = 7.1 Hz, 0.95 H, CH=, *E*-isomer) and 5.52 (dd, J_1 = 11.5 Hz, J_2 = 10.2 Hz, 0.07 H, CH=, *Z*-isomer), 2.33 (s, 3 H, CH_3), 2.20-2.09 (m, 1 H, CH), 1.87-1.73 (m, 4 H), 1.72-1.65 (m, 1 H), 1.36-1.27 (m, 2 H), 1.25-1.16 (m, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.7, 138.3, 137.1, 134.9, 130.1, 129.7, 128.8, 126.7, 126.0, 125.4, 125.3, 125.0, 41.5, 36.7, 33.3, 33.1, 26.2, 26.0, 25.6, 19.8. IR (neat, cm^{-1}) 2922, 2851, 1558, 1506, 1457, 1375. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{21}$ 201.1638; found 201.1628.



5aa, *E/Z* = 3.5:1

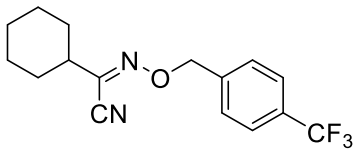
Following Typical Procedure 4, the reaction of $MgCl_2$ (3.9 mg, 0.04 mmol), **4a** (60.1 mg, 0.20 mmol), and **2a** (216 μL, d = 0.779 g/mL, 168.0 mg) in MeCN (0.5 mL) afforded **5aa** (40.7 mg, 84%) (eluent: PE/EA = 30/1 to 20/1): colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43-7.29 (m, 5 H, Ar-H), 5.23 (s, 2 H, CH_2), 3.05 (tt, J_1 = 11.6 Hz, J_2 = 3.5 Hz, 0.75 H, *E*-isomer) and 2.43 (tt, J_1 = 11.6 Hz, J_2 = 3.5 Hz, 0.21 H, *Z*-isomer), 1.90-1.65 (m, 5 H), 1.48-1.15 (m, 5 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.1, 137.6, 136.1, 136.0, 128.6, 128.5, 128.5, 128.4, 128.3, 128.3, 113.6, 109.8, 78.1, 77.6, 40.7, 35.8, 29.8, 28.7, 25.32, 25.29, 25.26, 25.2. IR (neat, cm^{-1}) 2930, 2855, 2226, 1449, 1017. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{19}N_2O$ 243.1492; found 243.1499.



5ba, *E/Z* = 1:7.7

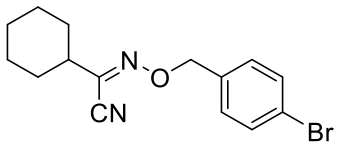
Following Typical Procedure 4, the reaction of $MgCl_2$ (3.8 mg, 0.04 mmol), **4b** (68.9 mg, 0.20 mmol), and **2a** (216 μL, d = 0.779 g/mL, 168.0 mg) in MeCN (0.5 mL) afforded **5ba** (29.9 mg, 52%) (eluent: PE/EA = 30/1 to 15/1): yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35-8.10 (m, 2 H, Ar-H), 7.56-7.45 (m, 2 H, Ar-H), 5.31 (s, 2 H, CH_2), 3.06 (tt, J_1 = 11.8 Hz, J_2 = 3.6 Hz, 0.11 H, *E*-isomer) and 2.43 (tt, J_1 = 11.6 Hz, J_2 = 3.5 Hz, 0.87 H, *Z*-isomer), 1.92-1.62 (m, 5 H), 1.48-1.16 (m, 5 H). ^{13}C NMR (101 MHz,

$CDCl_3$) δ 147.8, 143.5, 138.5, 128.7, 128.6, 123.9, 123.8, 109.5, 75.9, 40.8, 36.0, 29.8, 28.7, 25.3, 25.24, 25.20. IR (neat, cm^{-1}) 2930, 2854, 2228, 1522, 1449, 1346. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{15}H_{17}N_3O_3Na$ 310.1162; found 310.1165.



5ca, *E/Z* = 2.4:1

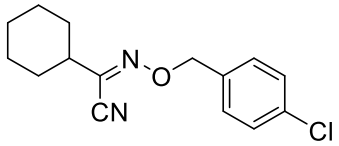
Following Typical Procedure 4, the reaction of $MgCl_2$ (3.9 mg, 0.04 mmol), **4c** (73.8 mg, 0.20 mmol), and **2a** (216 μL, d = 0.779 g/mL, 168.0 mg) in MeCN (0.5 mL) afforded **5ca** (37.3 mg, 60%) (eluent: PE/EA = 80/1 to 65/1): colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (dd, J_1 = 8.1 Hz, J_2 = 6.0 Hz, 2 H, Ar-H), 7.46 (t, J = 8.4 Hz, 2 H, Ar-H), 5.27 (s, 2 H, CH_2), 3.05 (tt, J_1 = 11.7 Hz, J_2 = 3.4 Hz, 0.71 H, *E*-isomer) and 2.43 (tt, J_1 = 11.6 Hz, J_2 = 3.5 Hz, 0.30 H, *Z*-isomer), 1.90-1.73 (m, 4 H), 1.73-1.66 (m, 1 H), 1.47-1.26 (m, 5 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.7, 140.2, 140.0, 138.0, 130.6 (C-F, q, $^2J_{C\text{-}F}$ = 32.1 Hz), 129.3, 128.4, 128.3, 125.6 (q, ^3J = 4.0 Hz), 124.0 (q, ^1J = 271.7 Hz), 113.4, 109.7, 76.5, 40.8, 35.9, 29.8, 29.7, 28.7, 25.29, 25.26, 25.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.48, -62.51. IR (neat, cm^{-1}) 2930, 2856, 2228, 1450, 1418, 1326, 1129. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{18}F_3N_2O$ 311.1366; found 311.1369.



5da, *E/Z* = 2.2:1

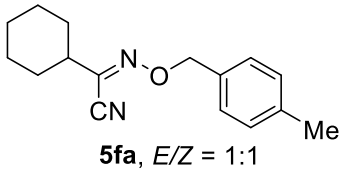
Following Typical Procedure 4, the reaction of $MgCl_2$ (3.9 mg, 0.04 mmol), **4d** (75.9 mg, 0.20 mmol), and **2a** (216 μL, d = 0.779 g/mL, 168.0 mg) in MeCN (0.5 mL) afforded **5da** (43.7 mg, 68%) (eluent: PE/EA = 100/1 to 80/1): yellow solid. mp. 68.4-70.5 °C (DCM/Hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (dd, J_1 = 8.4 Hz, J_2 = 6.2 Hz, 2 H, Ar-H), 7.22 (dd, J_1 = 8.5 Hz, J_2 = 7.1 Hz, 2 H, Ar-H), 5.16 (s, 2 H, CH_2), 3.02 (tt, J_1 = 11.7 Hz, J_2 = 3.5 Hz, 0.67 H, *E*-isomer) and 2.42 (tt, J_1 = 11.6 Hz, J_2 = 3.6 Hz, 0.31 H, *Z*-isomer), 1.91-1.63 (m, 5 H), 1.45-1.23 (m, 5 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.4, 137.7, 135.2, 135.0, 131.8, 131.7, 130.2, 130.0, 122.7, 122.4, 113.5, 109.7,

77.3, 40.8, 35.9, 29.8, 29.7, 28.7, 25.32, 25.25, 25.2. IR (neat, cm^{-1}) 2930, 2854, 2227, 1488, 1449, 1404, 1361, 1009. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{18}BrN_2O$ 321.0597; found 321.0594.



5ea, *E/Z* = 2.9:1

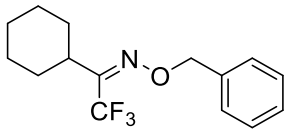
Following Typical Procedure 4, the reaction of $MgCl_2$ (4.0 mg, 0.04 mmol), **4e** (67.0 mg, 0.20 mmol), and **2a** (216 μL, *d* = 0.779 g/mL, 168.0 mg) in MeCN (0.5 mL) afforded **5ea** (40.0 mg, 72%) (eluent: PE/EA = 100/1 to 50/1): colorless oil. ^1H NMR (400 MHz, $CDCl_3$) δ 7.38-7.32 (m, 2 H, Ar-H), 7.31-7.26 (m, 2 H, Ar-H), 5.18 (s, 2 H, CH_2), 3.02 (tt, J_1 = 11.6 Hz, J_2 = 3.5 Hz, 0.75 H, *E*-isomer) and 2.42 (tt, J_1 = 11.6 Hz, J_2 = 3.5 Hz, 0.27 H, *Z*-isomer), 1.89-1.65 (m, 5 H), 1.45-1.15 (m, 5 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.4, 137.6, 134.6, 134.5, 134.4, 134.2, 129.9, 129.7, 128.8, 128.7, 113.5, 109.7, 77.3, 76.6, 40.8, 35.8, 29.8, 28.6, 25.30, 25.26, 25.23, 25.19. IR (neat, cm^{-1}) 2930, 2854, 2228, 1491, 1449, 1264, 1090, 1013. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{15}H_{17}ClN_2ONa$ 299.0922; found 299.0927.



5fa, *E/Z* = 1:1

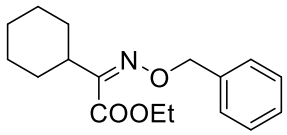
Following Typical Procedure 4, the reaction of $MgCl_2$ (4.0 mg, 0.04 mmol), **4f** (63.5 mg, 0.20 mmol), and **2a** (216 μL, *d* = 0.779 g/mL, 168.0 mg) in MeCN (0.5 mL) afforded **5fa** (29.3 mg, 57%) (eluent: PE/EA = 100/1 to 70/1): colorless oil. ^1H NMR (400 MHz, $CDCl_3$) δ 7.27-7.22 (m, 2 H, Ar-H), 7.18 (dd, J_1 = 8.0 Hz, J_2 = 6.4 Hz, 2 H, Ar-H), 5.18 (s, 2 H, CH_2), 3.03 (tt, J_1 = 11.8 Hz, J_2 = 3.4 Hz, 0.53 H, *E*-isomer) and 2.42 (tt, J_1 = 11.6 Hz, J_2 = 3.6 Hz, 0.53 H, *Z*-isomer), 2.36 (d, *J* = 4.4 Hz, 3 H), 1.92-1.72 (m, 4 H), 1.71-1.65 (m, 1 H), 1.46-1.27 (m, 5 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.9, 138.4, 138.1, 137.1, 133.2, 133.0, 129.3, 129.2, 128.6, 128.5, 113.7, 109.9, 78.1, 77.5, 40.8, 35.8, 29.9, 29.7, 28.7, 25.4, 25.32, 25.30, 25.2, 21.2. IR (neat, cm^{-1}) 2924, 2852, 2227, 1457, 1448, 1264, 1015. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for

$C_{16}H_{20}N_2ONa$ 279.1468; found 279.1455.



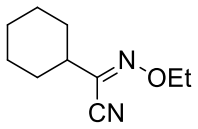
5ga, *E/Z* = 1:3.3

Following Typical Procedure 4, the reaction of $MgCl_2$ (4.0 mg, 0.04 mmol), **4g** (68.4 mg, 0.20 mmol), and **2a** (216 μL, *d* = 0.779 g/mL, 168.0 mg) in MeCN (0.5 mL) afforded **5ga** (34.1 mg, 60%) (eluent: PE): yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43-7.27 (m, 5 H, Ar-H), 5.20 (s, 2 H, CH_2), 3.16-3.05 (m, 0.23 H, *E*-isomer) and 2.91 (tt, J_1 = 12.1 Hz, J_2 = 3.4 Hz, 0.75 H, *Z*-isomer), 1.82-1.56 (m, 6 H), 1.44-1.15 (m, 4 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.0 (C-F, q, $^2J_{C\text{-}F}$ = 29.8Hz), 136.6, 135.1, 131.8, 128.7, 128.5, 128.3, 128.2, 127.9, 126.6, 121.2 (C-F, q, $^1J_{C\text{-}F}$ = 275.6 Hz), 77.5, 46.5, 36.7, 33.3, 27.8, 26.2, 26.0, 25.7, 25.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ -66.5. IR (neat, cm^{-1}) 2930, 2855, 1455, 1302, 1191. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{18}F_3NONa$ 308.1233; found 308.1232.



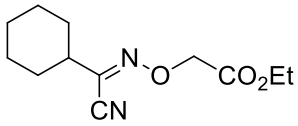
5ha, *E/Z* = 1:1.4

Following Typical Procedure 4, the reaction of $MgCl_2$ (3.9 mg, 0.04 mmol), **4h** (69.3 mg, 0.20 mmol), and **2a** (216 μL, *d* = 0.779 g/mL, 168.0 mg) in MeCN (0.5 mL) afforded **5ha** (32.3 mg, 56%) (eluent: PE/EA = 100/1 to 50/1 to 30/1): colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.27 (m, 5 H, Ar-H), 5.23 (s, 1.1 H, CH_2, *Z*-isomer) and 5.10 (s, 0.8 H, CH_2, *E*-isomer), 4.35-4.23 (m, 2 H), 3.19-3.06 (m, 0.53 H, *Z*-isomer) and 2.45-2.33 (m, 0.39 H, *E*-isomer), 1.89-1.62 (m, 6 H), 1.34 (t, *J* = 7.1 Hz, 2 H), 1.30 (t, *J* = 7.1 Hz, 3 H), 1.27-1.18 (m, 2 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.1, 163.7, 156.7, 156.6, 137.6, 137.0, 128.4, 127.98, 127.96, 128.0, 127.64, 127.57, 77.1, 76.0, 61.4, 61.2, 40.2, 36.8, 29.7, 28.1, 26.1, 25.8, 25.7, 14.2, 14.1. IR (neat, cm^{-1}) 2926, 2853, 1733, 1451, 1368, 1154, 1019. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{24}NO_3$ 290.1751; found 290.1745.



5ia, *E*/*Z* = 1:1.6

Following Typical Procedure 4, the reaction of $MgCl_2$ (3.9 mg, 0.04 mmol), **4i** (47.2 mg, 0.20 mmol), and **2a** (216 μL, *d* = 0.779 g/mL, 168.0 mg) in MeCN (0.5 mL) afforded **5ia** (18.3 mg, 51%) (eluent: PE/EA = 100/1 to 50/1): colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.26 (qd, J_1 = 7.1 Hz, J_2 = 1.9 Hz, 2 H, CH_2), 3.01 (tt, J_1 = 11.8 Hz, J_2 = 3.4 Hz, 0.37 H, *E*-isomer), 2.43 (tt, J_1 = 11.6 Hz, J_2 =3.6 Hz, 0.59 H, *Z*-isomer), 1.97-1.65 (m, 5 H), 1.48-1.34 (m, 2 H, CH_2), 1.34-1.19 (m, 6 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.3, 136.3, 113.9, 110.0, 72.0, 71.5, 40.7, 35.6, 29.9, 28.7, 25.4, 25.3, 14.4, 14.3. IR (neat, cm^{-1}) 2928, 2855, 2224, 1449, 1064. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{10}H_{16}N_2ONa$ 203.1155; found 203.1147.



5ja, *E*/*Z* = 1.3:1

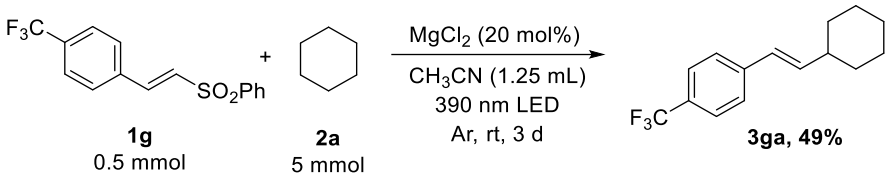
Following Typical Procedure 4, the reaction of $MgCl_2$ (3.9 mg, 0.04 mmol), **4j** (59.0 mg, 0.20 mmol), and **2a** (216 μL, *d* = 0.779 g/mL, 168.0 mg) in MeCN (0.5 mL) afforded **5ja** (25.2 mg, 53%) (eluent: PE/EA = 100/1 to 40/1): colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.73 (d, *J* = 7.6 Hz, 2 H, CH_2), 4.24 (q, *J* = 7.2 Hz, 2 H, CH_2), 3.12 (tt, J_1 = 11.9 Hz, J_2 =3.5 Hz, 0.56 H, *E*-isomer) and 2.46 (tt, J_1 = 11.6 Hz, J_2 =3.6 Hz, 0.42 H, *Z*-isomer), 1.94-1.78 (m, 4 H), 1.76-1.65 (m, 1 H), 1.49-1.32 (m, 3 H), 1.32-1.21 (m, 5 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.5, 168.5, 145.6, 138.7, 113.1, 109.4, 71.7, 71.4, 61.4, 61.2, 40.8, 36.1, 29.7, 28.6, 25.30, 25.25, 25.2, 14.1. IR (neat, cm^{-1}) 2932, 2856, 2229, 1759, 1449, 1266, 1210, 1027. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{12}H_{18}N_2O_3Na$ 261.1210; found 261.1204.

Mechanistic studies

1. The light on/off experiment

The light on/off experiments were conducted by monitoring the product formation using (*E*)-1-(2-(phenylsulfonyl)vinyl)-4-(trifluoromethyl)benzene (**1g**) as a substrate. The reaction was proceeded smoothly under irradiation of blue LED and ceased when the light was turned off, indicating that the light plays a crucial role for the transformation.

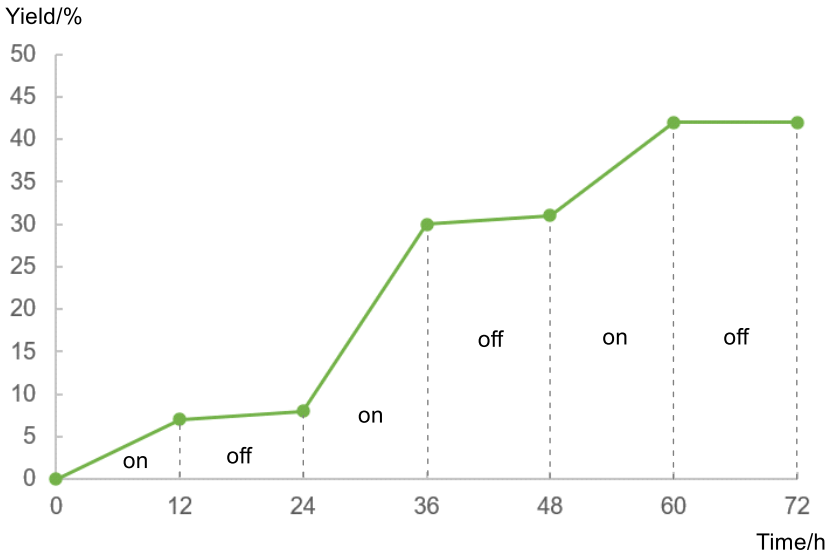
Table S1 The light on/off experiment



1g 0.5 mmol **2a** 5 mmol **3ga, 49%**

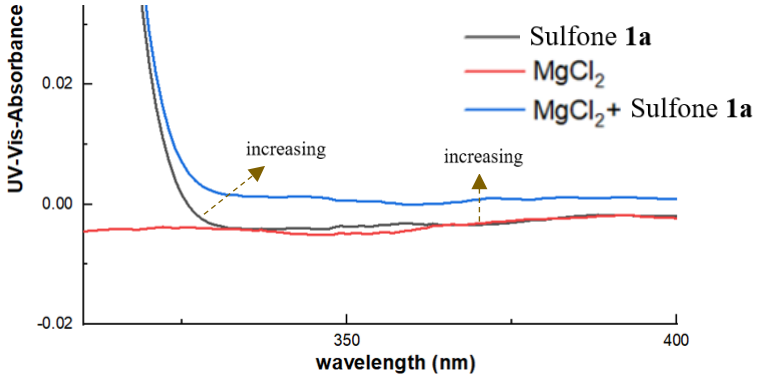
Time scale	Light on/off	Yield[a]/%
0-12 h	On	7
12-24 h	Off	8
24-36 h	On	30
36-48 h	Off	31
48-60 h	On	42
60-72 h	Off	42

[a] All yields were based on crude ^{19}F NMR.



2. The UV/Vis absorption spectra

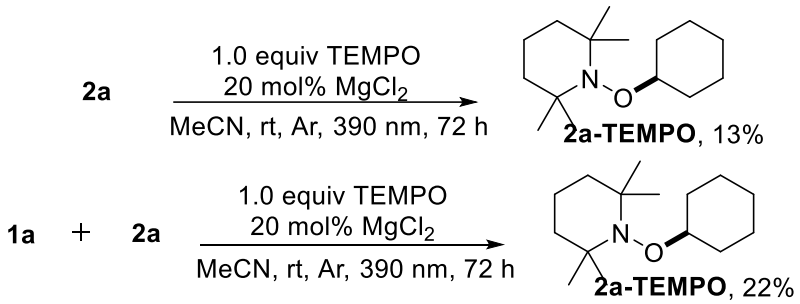
The UV-Vis absorption spectra of $MgCl_2$, the sulfone **1a**, and $MgCl_2$/**1a** in MeCN were tested. While the $MgCl_2$ or **1a** solution barely absorb the light over 330 nm, the mixture of $MgCl_2$ and **1a** presented a weak absorption even the light wavelength reached 400 nm. These results indicated that the weak interaction between the unsaturated compound with chloride ion might be responsible and crucial to the photoinduced transformation. This is also consistent with the absorption of EDA complexes reported in the literature.[10] It is reasonable to propose that the Cl radical was derived from photoinduced electron transfer of the electron donor−acceptor complex of sulfone/Cl^- when the sulfones were used.



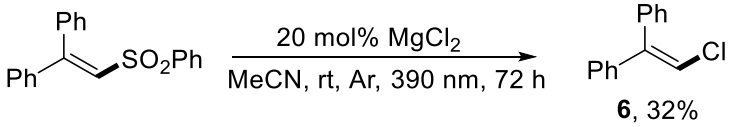
3. Alkyl radical capture experiment

Treating **2a** with TEMPO under N_2, the radical captured product **2a**-TEMPO could be also detected by high resolution mass spectroscopy (HRMS) (ESI^+, m/z: Calcd for $C_{15}H_{30}NO^+$ $[M + H]^+$ 240.2322; found 240.2319.).

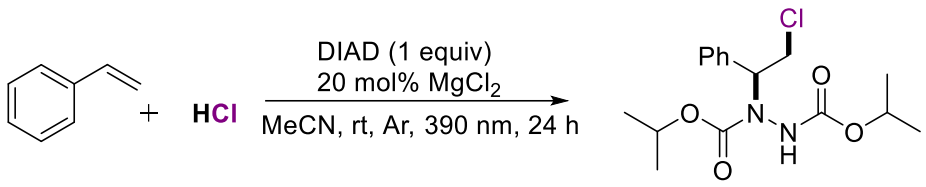
Treating **1a** and **2a** with TEMPO under N_2, the radical captured product **2a**-TEMPO could be also detected by high resolution mass spectroscopy (HRMS) (ESI^+, m/z: Calcd for $C_{15}H_{30}NO^+$ $[M + H]^+$ 240.2322; found 240.2320.), confirming that the cyclohexyl radical was generated via HAT process. The yield was determined by ^1H NMR with 1,3,5-trimethoxybenzene as the internal standard by comparison with standard spectra reported in the literature.[11]



4. Chlorine radical capture experiment



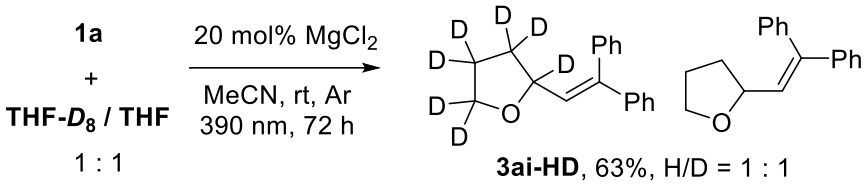
To a 4 mL vial were added $MgCl_2$ (3.9 mg, 0.04 mmol), **1a** (63.9 mg, 0.20 mmol) and MeCN (0.5 mL) in an Ar glovebox. The reaction tube was transferred out of glovebox. Under irradiation at 390 nm LEDs, the resulting mixture was stirred for 72 hours at rt. Evaporation and flash chromatography on silica gel afforded **6** (5.6 mg, 32%) (eluent: PE). ^1H NMR (400 MHz, $CDCl_3$) δ 7.44-7.38 (m, 2 H, Ar-H), 7.38-7.28 (m, 6 H, Ar-H), 7.23-7.19 (m, 2 H, Ar-H), 6.60 (s, 1 H, CH=). NMR spectra are matching with the literature.[12]



7

To a Schlenk tube were added $MgCl_2$ (7.5 mg, 0.08 mmol), A 12 M HCl aqueous (33 μL), diisopropyl azodicarboxylate (DIAD) (79 μL, d = 1.027 g/mL, 81.1 mg, 0.4 mmol) and styrene (69 μL, d = 0.906 g/mL, 62.5 mg, 0.6 mmol) in MeCN (4.0 mL) in an Ar glovebox. The vial was then sealed and transferred out of glovebox. Under irradiation at 390 nm LEDs, the resulting mixture was stirred at rt for 24 hours. Filtered with silica gel, and the filtrate was evaporated to afford the crude product. The structure of compound **7** could be confirmed by HRMS. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{16}H_{23}ClN_2O_4Na$ 365.1236; found 365.1239.

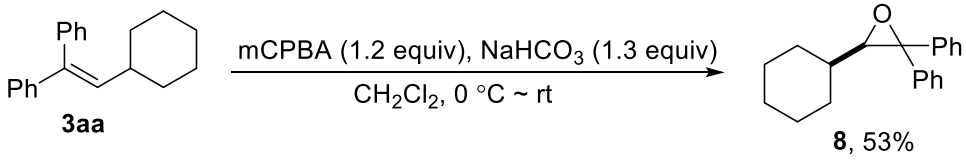
5. KIE experiment



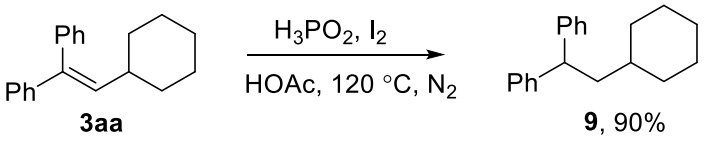
3ai-HD, 63%, H/D = 1 : 1

To a 4 mL reaction tube were added $MgCl_2$ (3.9 mg, 0.04 mmol), **1a** (64.5 mg, 0.20 mmol), MeCN (0.5 mL), **THF** (250 μL) and **THF-*D*8** (250 μL) in an Ar glovebox. The reaction tube was transferred out of glovebox. Under irradiation at 390 nm LEDs, the resulting mixture was stirred for 72 hours at rt. Evaporation and flash chromatography on silica gel afforded **3ai-HD** (32.4 mg, 63%) (eluent: PE). The KIE was determined to be k_H/k_D = 1/1 by the analysis of the ^1H NMR spectrum.

Synthetic potentials

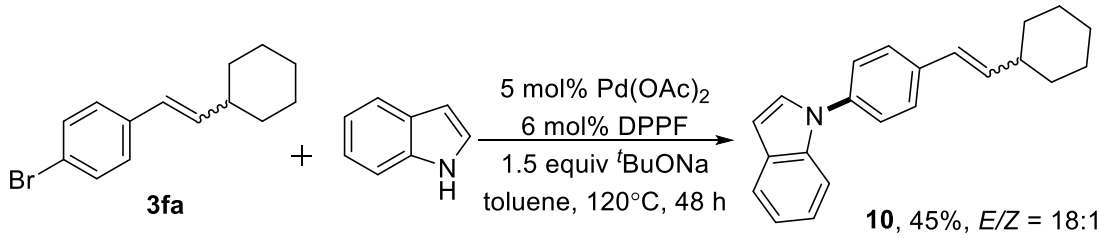


To a dried Schlenk tube were added **3aa** (0.1330 g, 0.51 mmol), $NaHCO_3$ (0.0545 g, 0.65 mmol), and CH_2Cl_2 (3 mL) under N_2. Then a solution of 3-chloroperoxybenzoic acid (0.1219 g, 0.60 mmol, 85% purity) in CH_2Cl_2 (3 mL) was added dropwise over 10 minutes at 0 ºC. The resulting mixture was then stirred for an additional 1 h and warmed to rt for 22 h. The reaction mixture is quenched with aqueous $Na_2S_2O_4$ (5 mL), and the aqueous phase is extracted with CH_2Cl_2 (10 mL × 3). The combined organic layers are dried over Na_2SO_4. Evaporation and flash chromatography on silica gel afforded the product **8** (0.0751 g, 53%) (petroleum ether/ethyl acetate = 20/1 with 1% Et_3N): white solid. mp. 62.2-63.0 ℃ (DCM/Hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44-7.26 (m, 10 H, Ar-H), 3.13 (d, J = 9.2 Hz, 1 H, CH), 2.01-1.84 (m, 1 H), 1.73-1.58 (m, 4 H), 1.30-0.75 (m, 6 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.4, 137.9, 128.9, 128.2, 128.0, 127.72, 127.65, 127.4, 127.1, 70.8, 66.6, 36.9, 30.0, 28.5, 26.2, 25.2. IR (neat, cm^{-1}) 2925 2850, 1661, 1447. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{20}H_{23}O$ 279.1743; found 279.1748.

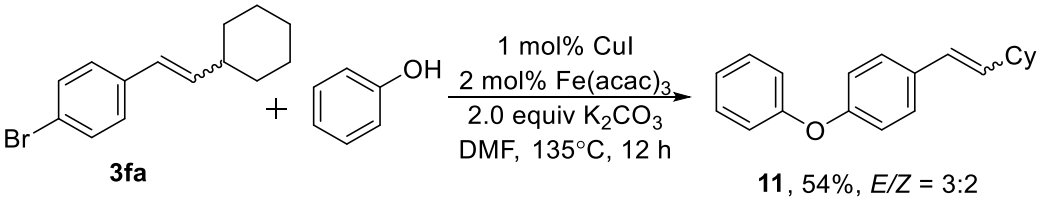


To a dried Schlenk tube were added **3aa** (0.2905 g, 1.11 mmol), HOAc (5 mL), Iodine (0.2033 g, 0.8 mmol), and hypophosphorous acid (50% aq., 0.4 mL, 3.86 mmol) under N_2. The resulting mixture was heated at 120 °C for 24 h and then cooled to rt. The reaction mixture is quenched with H_2O (5 mL), and the aqueous phase is extracted with CH_2Cl_2 (5 mL × 3). The combined organic layers are dried over Na_2SO_4. Evaporation and flash chromatography on silica gel afforded the product **9** (0.2639 g, 90%) (petroleum ether): colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31-7.14 (m, 10 H, Ar-H), 4.08 (t, J = 8.0 Hz, 1 H, CH), 1.93 (dd, J_1 = 8.0, J_2 = 6.8 Hz, 2 H, CH_2), 1.83-

1.73 (m, 2 H), 1.71-1.57 (m, 3 H), 1.24-1.09 (m, 4 H), 1.07-0.90 (m, 2 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.4, 128.3, 127.9, 125.9, 47.9, 43.6, 34.8, 33.4, 26.6, 26.1. IR (neat, cm^{-1}) 2920, 2849, 1599, 1493, 1448. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{20}H_{25}$ 265.1951; found 265.1943.



To a 4 mL vial were added **3fa** (0.0394 g, 0.15 mmol), indole (0.0117 g, 0.10 mmol), ^{t}BuONa (0.0147 g, 0.15 mmol), $Pd(OAc)_2$ (0.0013 g, 0.005 mmol), DPPF (0.0034 g, 0.006 mmol), and toluene (0.5 mL) under N_2. The resulting mixture was heated at 120 °C for 48 h and then cooled to rt. Evaporation and flash chromatography on silica gel afforded the product **10** (0.0202 g, 45%, *E/Z* = 18:1) (petroleum ether): white solid. mp: 86.0-87.1 °C (DCM/Hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 7.4 Hz, 1 H, Ar-H), 7.56 (d, *J* = 8.4 Hz, 1 H, CH of indole), 7.51-7.41 (m, 4 H, Ar-H), 7.33 (d, *J* = 3.3 Hz, 1 H, Ar-H), 7.25-7.14 (m, 2 H, Ar-H), 6.68 (d, *J* = 3.2 Hz, 1 H, CH of indole), 6.41 (d, *J* = 16.1 Hz, 1 H, CH=), 6.24 (dd, J_1 = 16.0 Hz, J_2 = 6.9 Hz, 0.90 H, CH=, *E*-isomer) and 5.57 (dd, J_1 = 11.6 Hz, J_2 = 10.3 Hz, 0.04 H, CH=, *Z*-isomer), 2.71-2.59 (m, 0.05 H, *Z*-isomer) and 2.25-2.11 (m, 0.92 H, *E*-isomer), 1.89-1.61 (m, 5 H), 1.44-1.12 (m, 5 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.2, 137.5, 136.4, 135.8, 129.7, 129.2, 127.9, 127.0, 126.3, 125.9, 124.3, 123.9, 122.3, 121.1, 120.3, 110.5, 103.4, 41.2, 32.9, 26.1, 26.0. IR (neat, cm^{-1}) 2921, 2848, 1604, 1518, 1474, 1456, 1333, 1233. The spectra are matching with the literature.[13]



To a 4 mL vial were added CuI (0.0009 g, 0.004 mmol), $Fe(acac)_3$ (0.0024 g, 0.008 mmol), K_2CO_3 (0.1112 g, 0.81 mmol), phenol (0.0374 g, 0.40 mmol), **3fa** (0.1587 g, 0.60 mmol), and DMF (0.8 mL) under N_2. The resulting mixture was heated at 135 °C

for 12 h and then cooled to rt. The resulting suspension was directly filtered through a pad of celite and filtrate was washed with DCM (10 mL) saturated NaCl (5 mL × 3) and dried over Na_2SO_4. Evaporation and flash chromatography on silica gel afforded the product **11** (0.0605 g, 54%, *E/Z* = 3/2) (petroleum ether): colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.29 (m, 3 H, Ar-H), 7.23 (d, *J* = 8.6 Hz, 1 H, Ar-H), 7.14-6.91 (m, 5 H, Ar-H), 6.32 (d, *J* = 15.9 Hz, 0.6 H, CH=, *E*-isomer) and 6.27 (d, *J* = 11.7 Hz, 0.4 H, CH=, *Z*-isomer), 6.10 (dd, J_1 = 16.0 Hz, J_2 = 6.9 Hz, 0.6 H, CH=, *E*-isomer) and 5.45 (dd, J_1 = 11.7 Hz, J_2 = 10.1 Hz, 0.4 H, CH=, *Z*-isomer), 2.67-2.48 (m, 0.4 H, Cy, *Z*-isomer) and 2.19-2.05 (m, 0.6 H, Cy, *E*-isomer), 1.87-1.62 (m, 5 H), 1.39-1.12 (m, 5 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.4, 157.1, 155.9, 155.8, 138.4, 136.1, 133.4, 133.0, 129.9, 129.7, 129.6, 127.2, 126.3, 126.0, 123.2, 123.0, 119.1, 118.9, 118.54, 118.46, 41.1, 36.9, 33.2, 33.0, 26.1, 26.02, 25.99, 25.7. IR (neat, cm^{-1}) 2923, 2851, 1487, 1447, 1307, 1240, 1147. The spectra are matching with the literature.[13]

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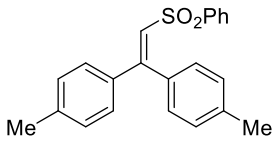
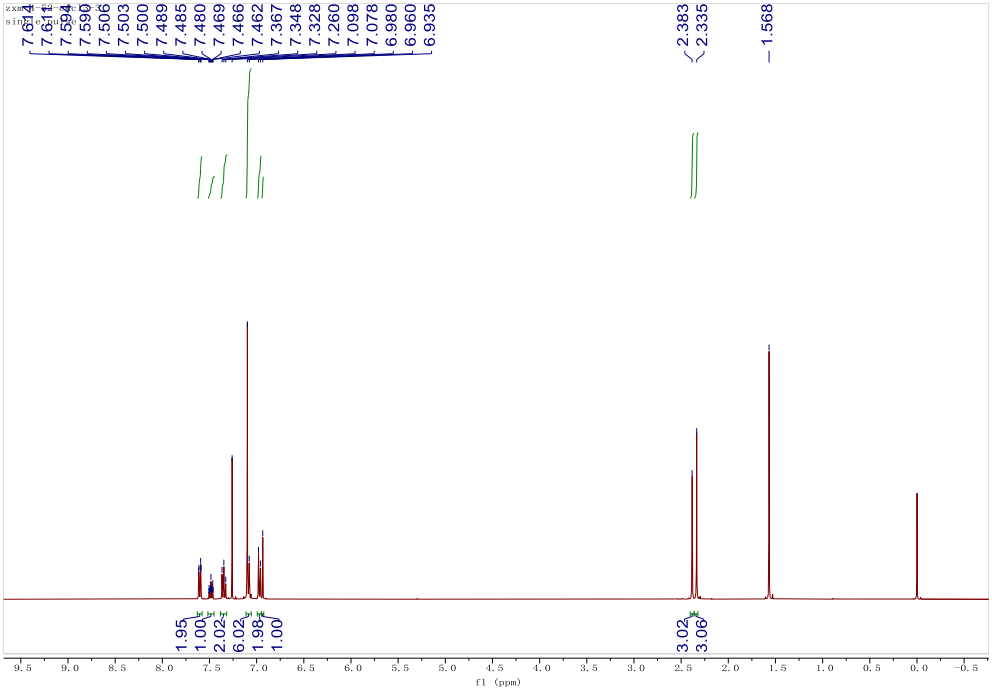
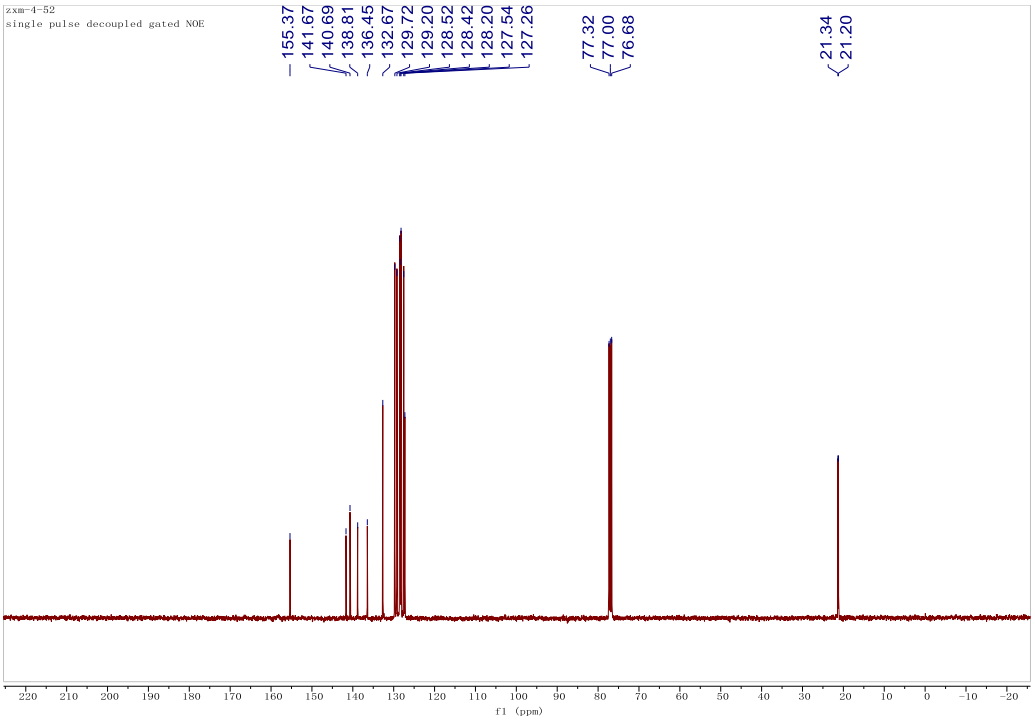


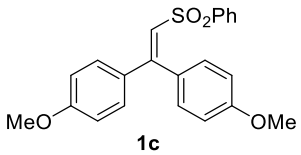
1b

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



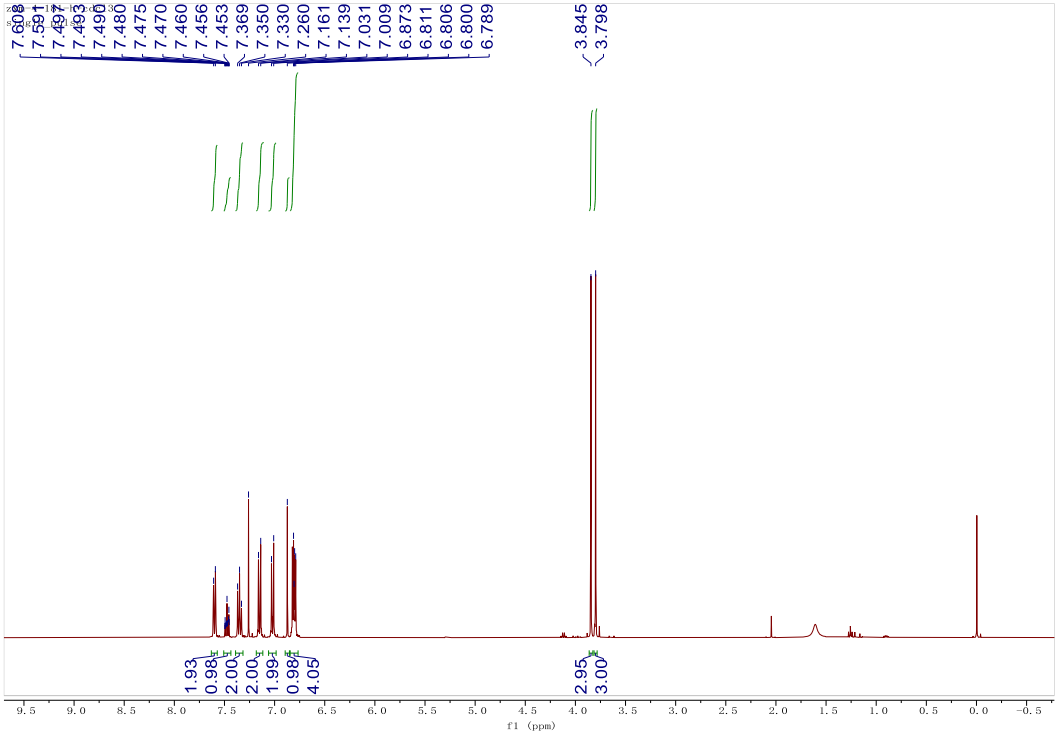
^{13}C NMR (101 MHz, $CDCl_3$) of **1b**



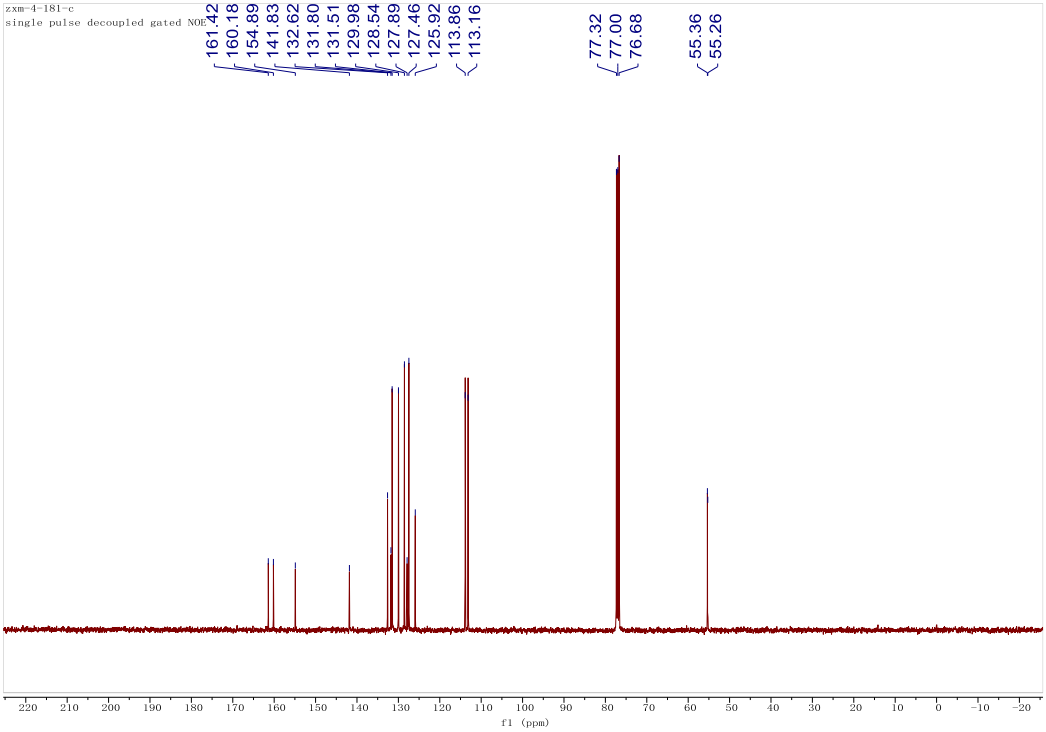


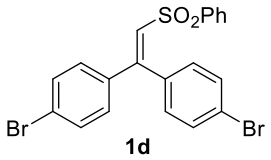
1c

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



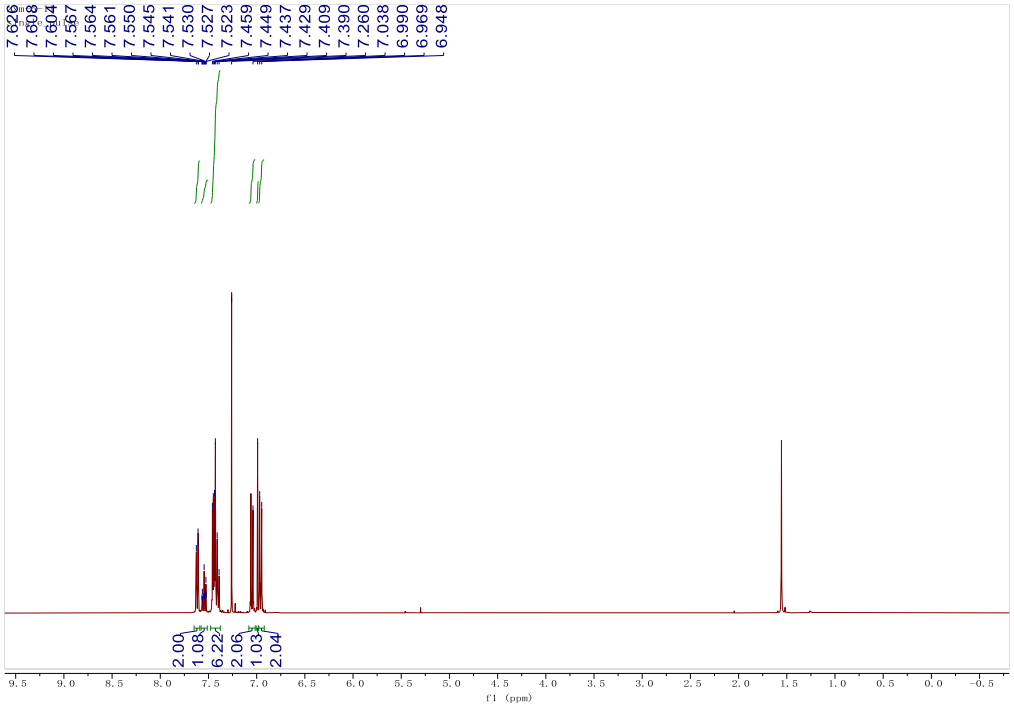
^{13}C NMR (101 MHz, $CDCl_3$) of **1c**



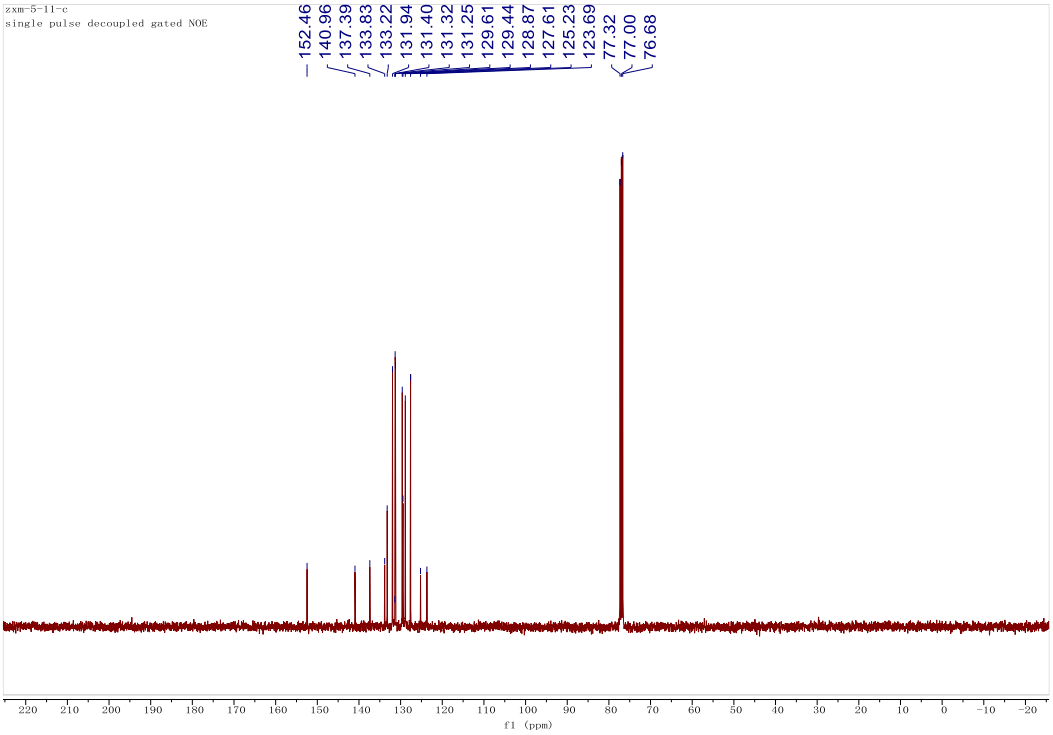


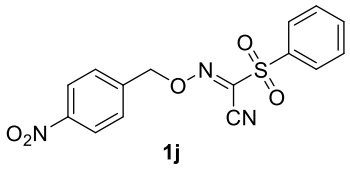
1d

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



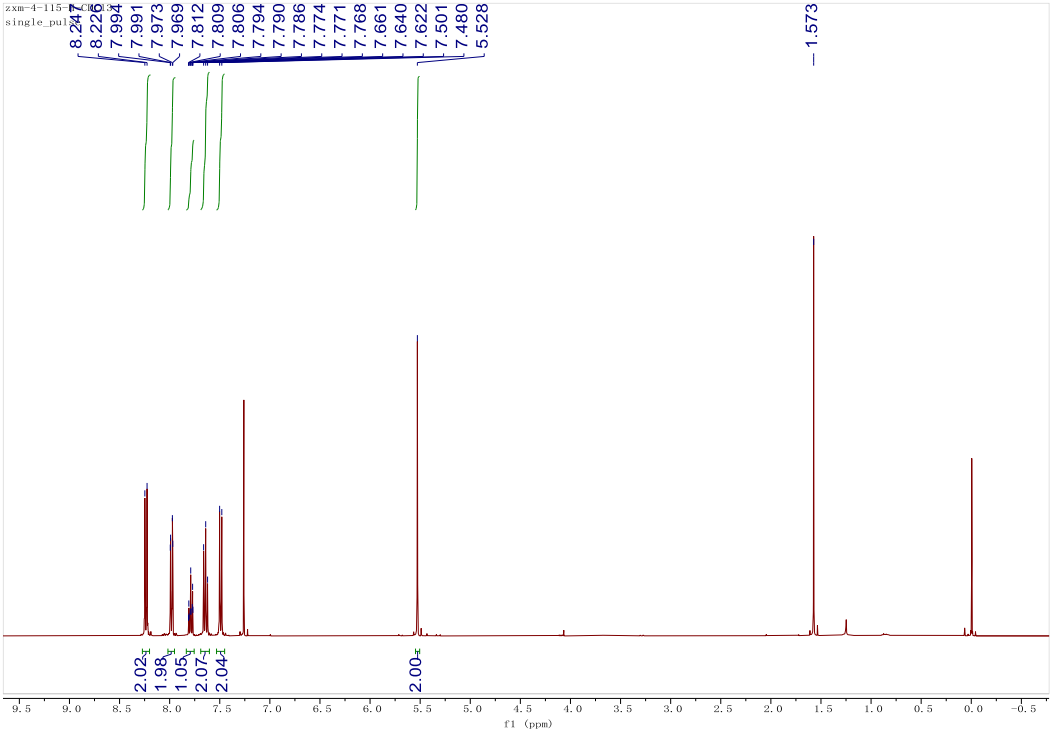
^{13}C NMR (101 MHz, $CDCl_3$) of **1d**



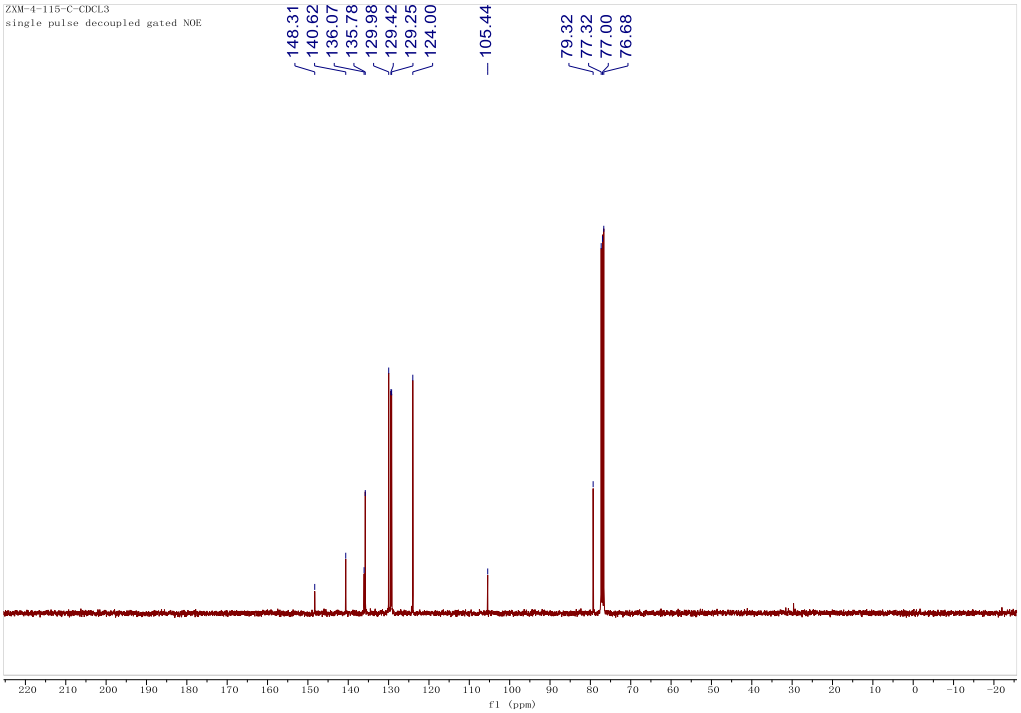


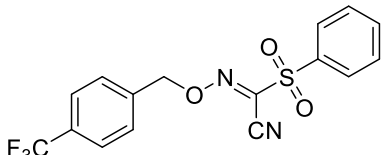
1j

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



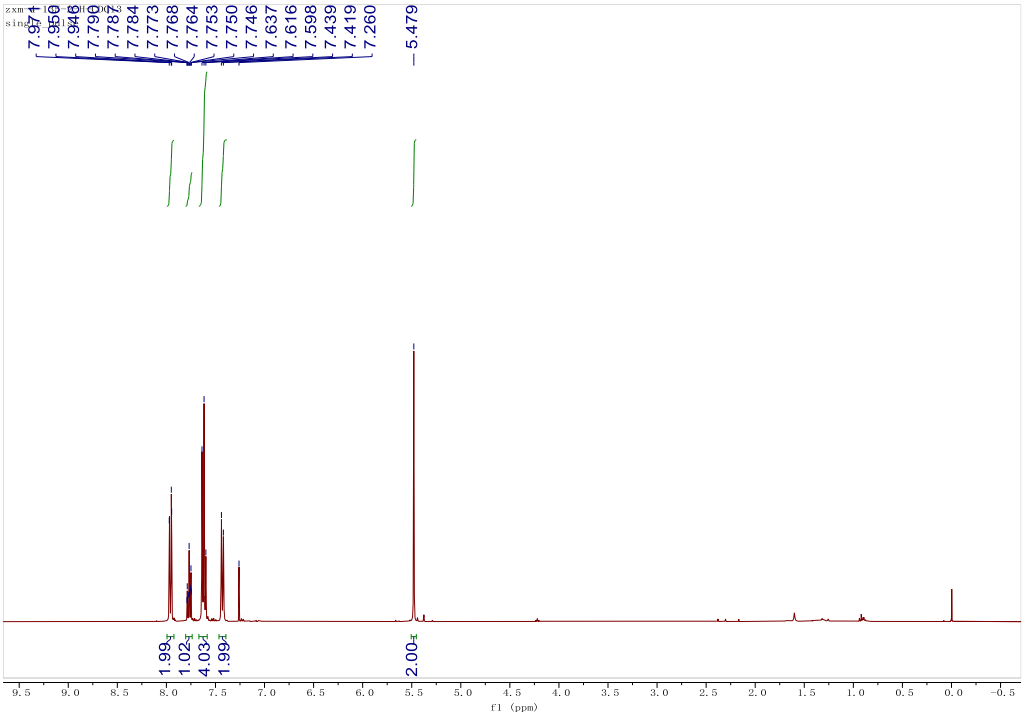
^{13}C NMR (101 MHz, $CDCl_3$) of **1j**



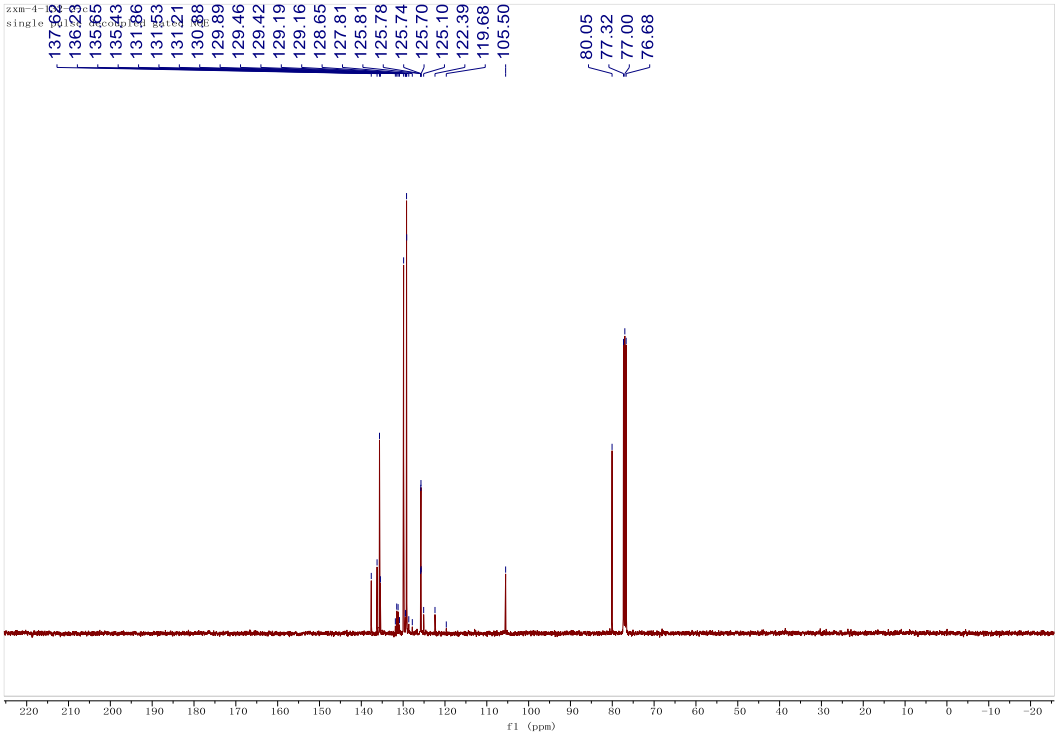


1k

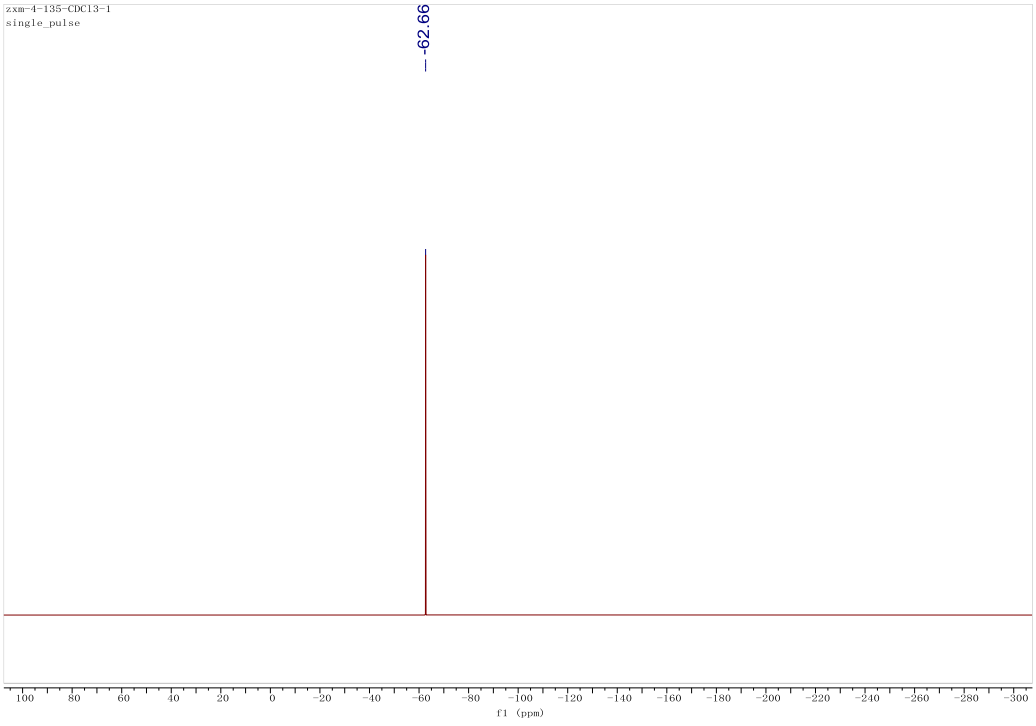
^{1}H NMR (400 MHz, $CDCl_3$) of **1k**

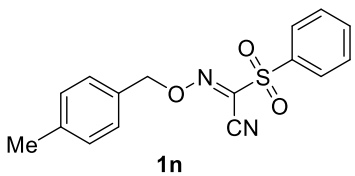


^{13}C NMR (101 MHz, $CDCl_3$) of **1k**



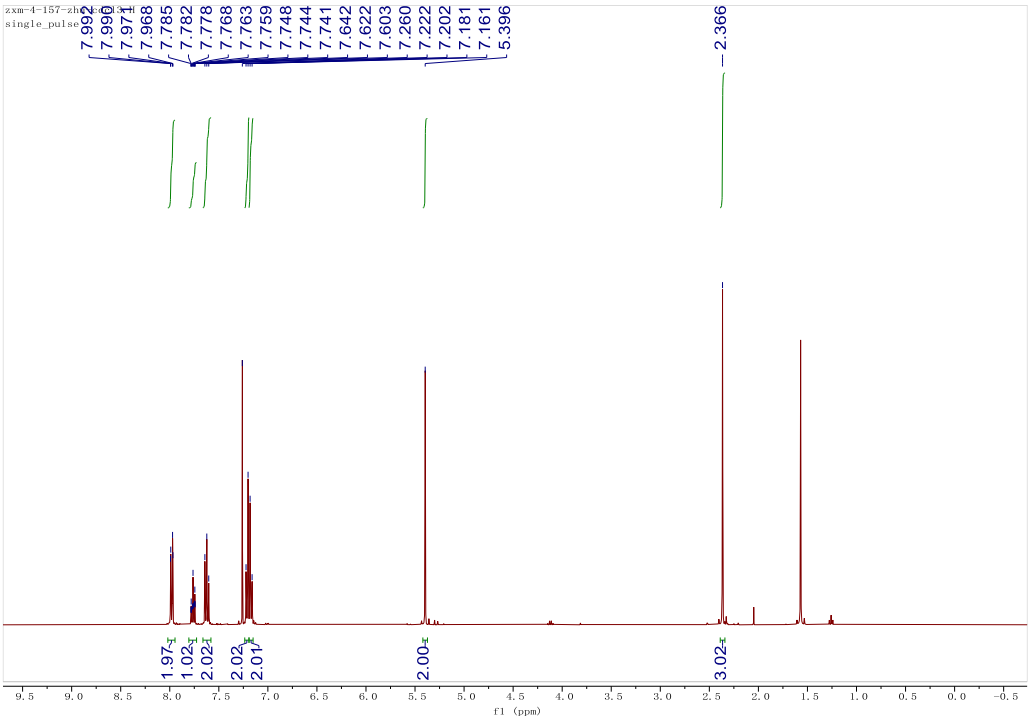
^{19}F NMR (376 MHz, $CDCl_3$) of **1k**



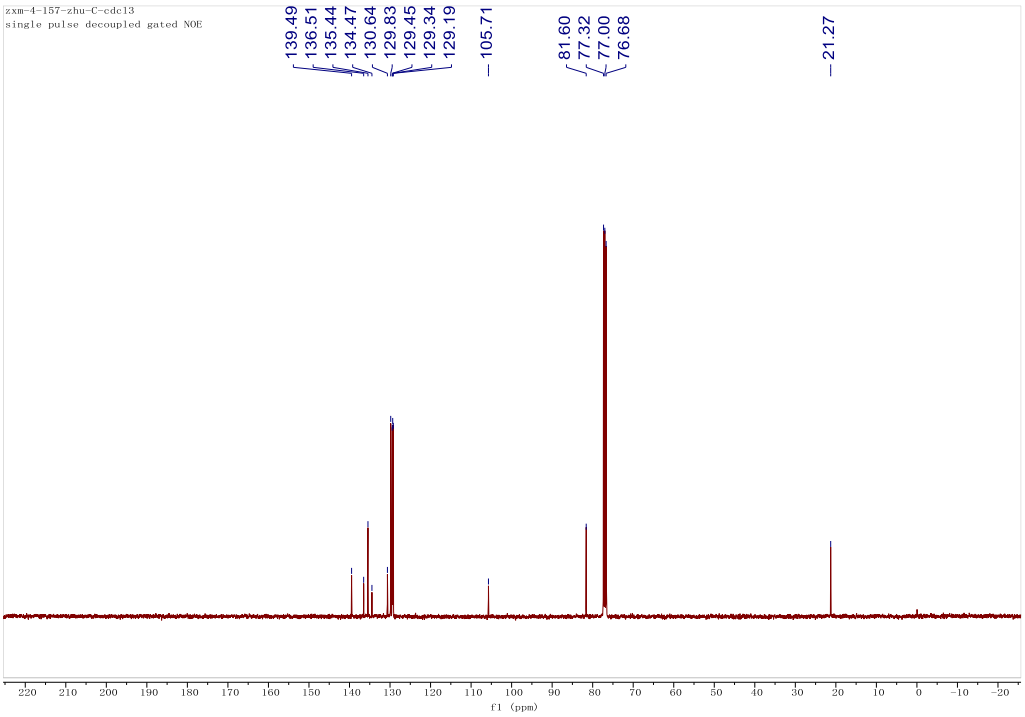


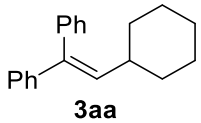
1n

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



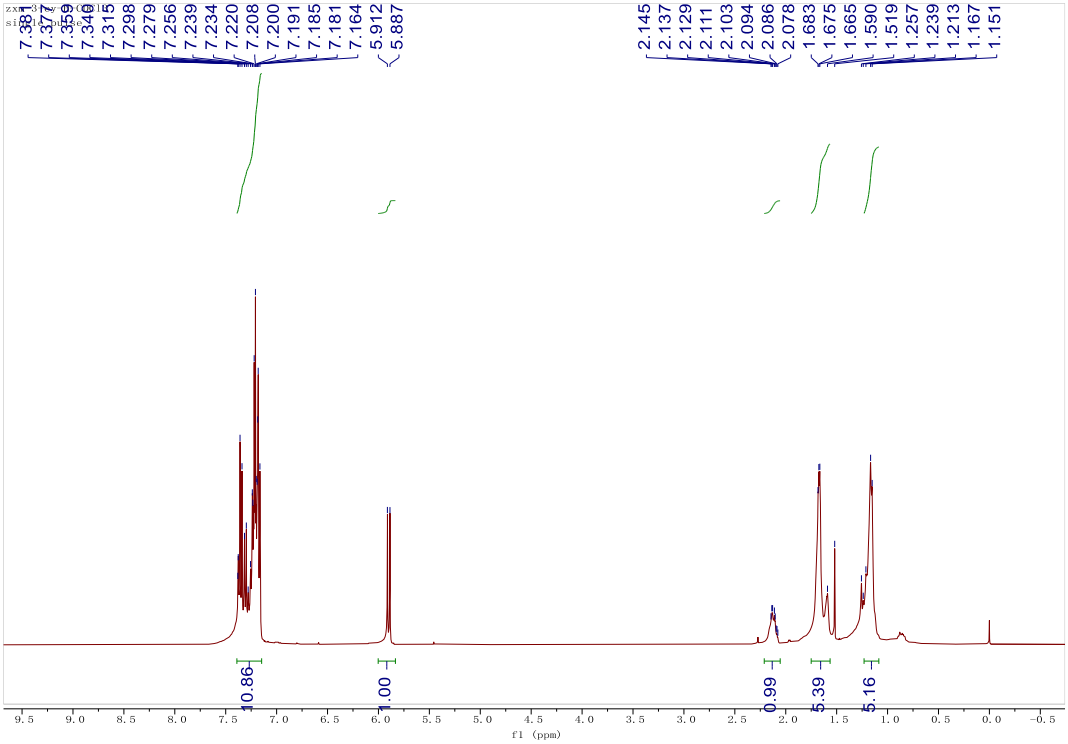
^{13}C NMR (101 MHz, $CDCl_3$) of **1n**



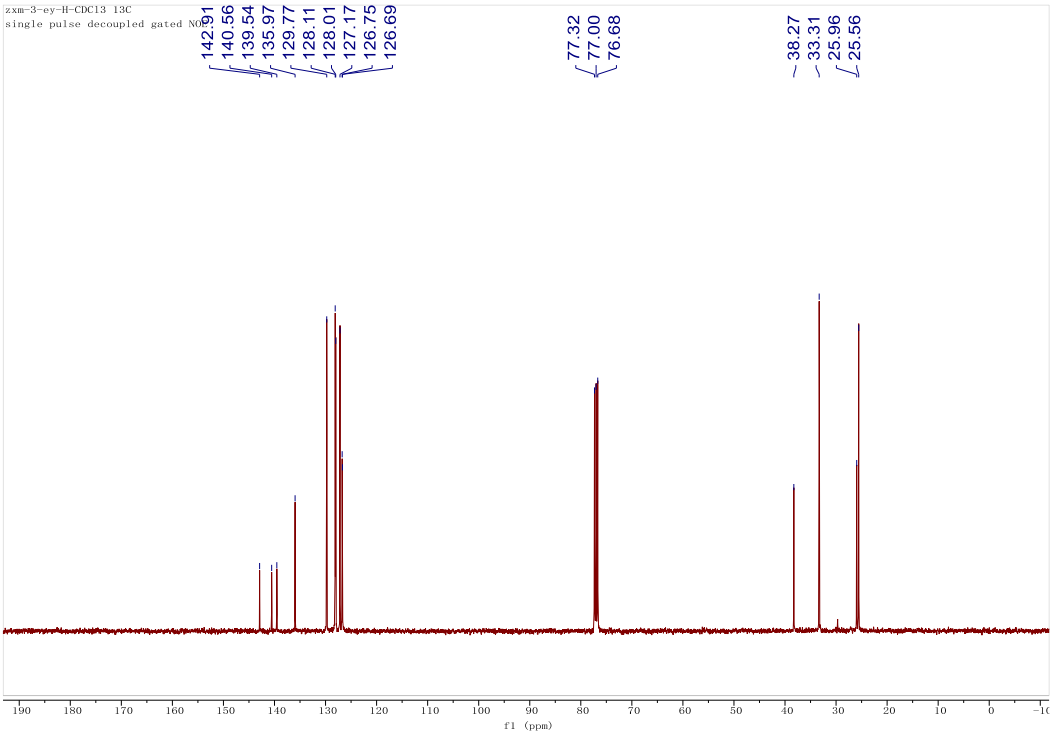


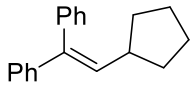
3aa

^{1}H NMR (400 MHz, $CDCl_3$) of **3aa**



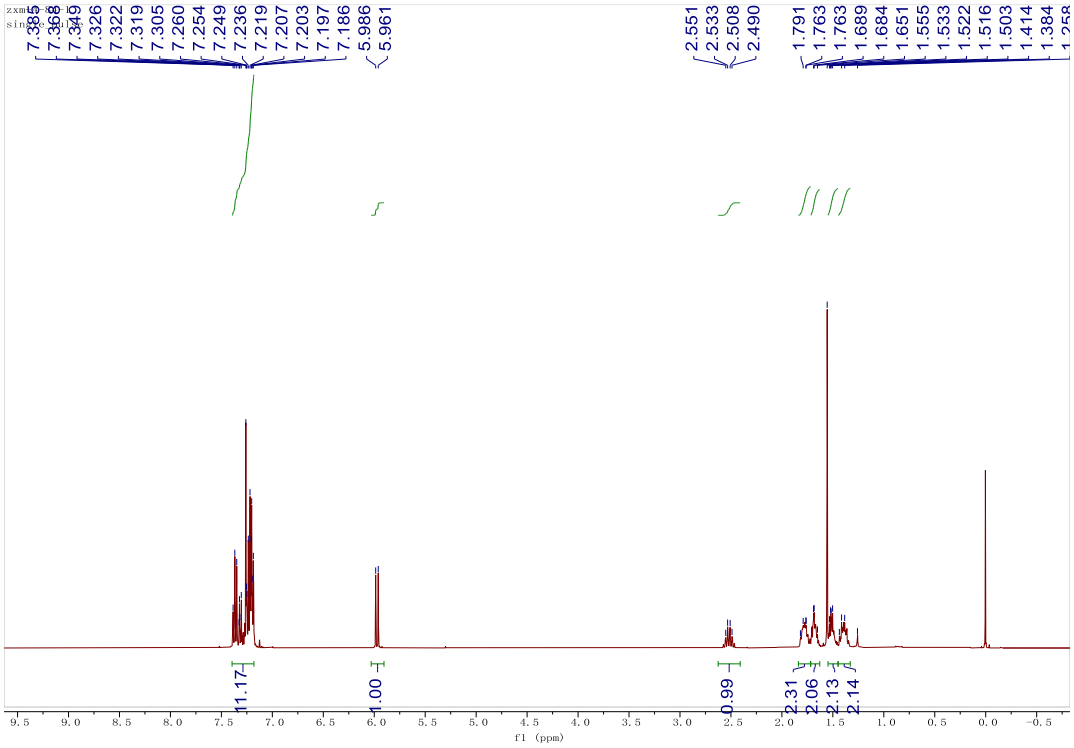
^{13}C NMR (101 MHz, $CDCl_3$) of **3aa**



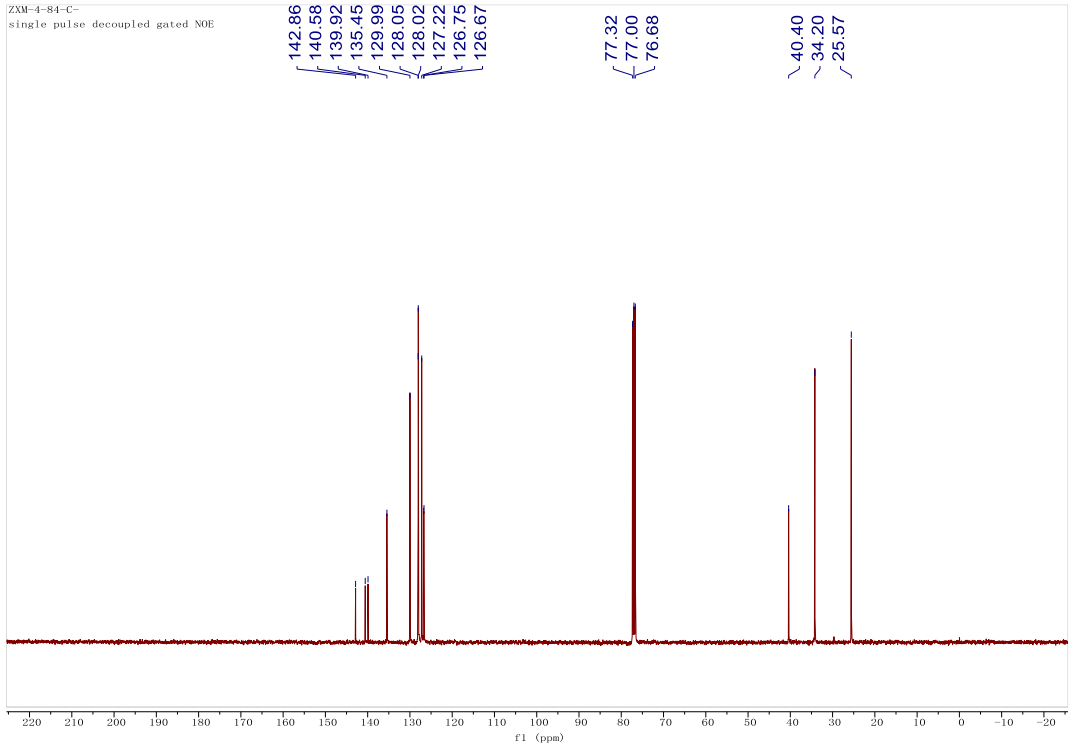


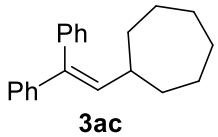
3ab

^{1}H NMR (400 MHz, $CDCl_3$) of **3ab**



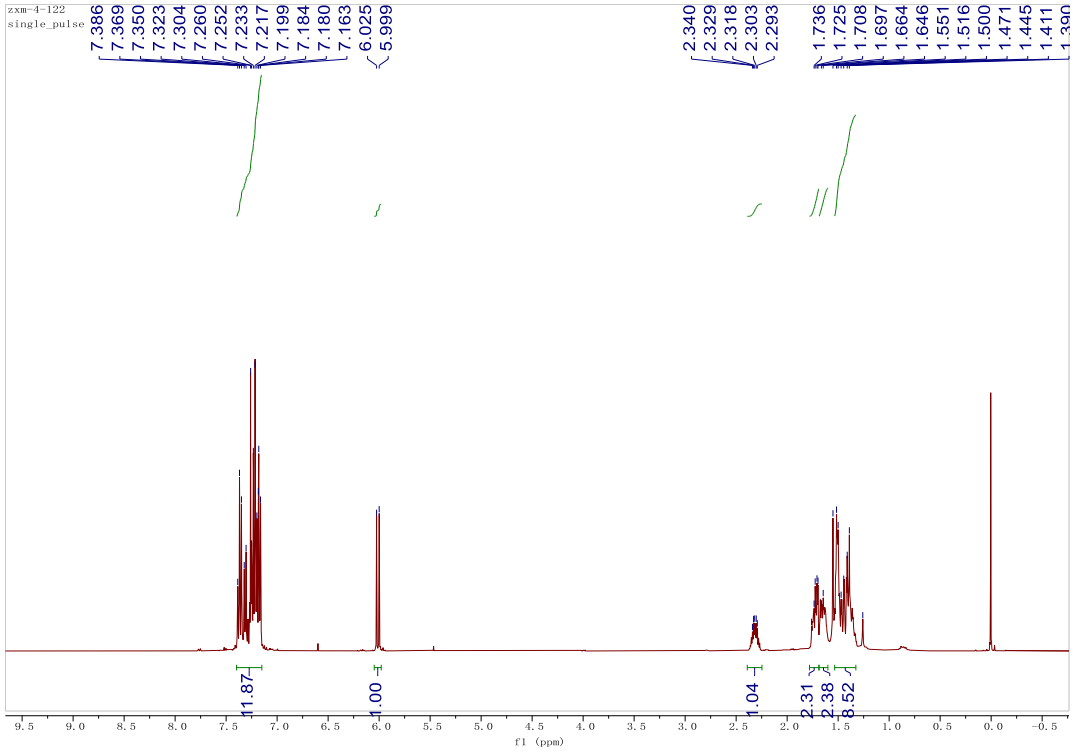
^{13}C NMR (101 MHz, $CDCl_3$) of **3ab**



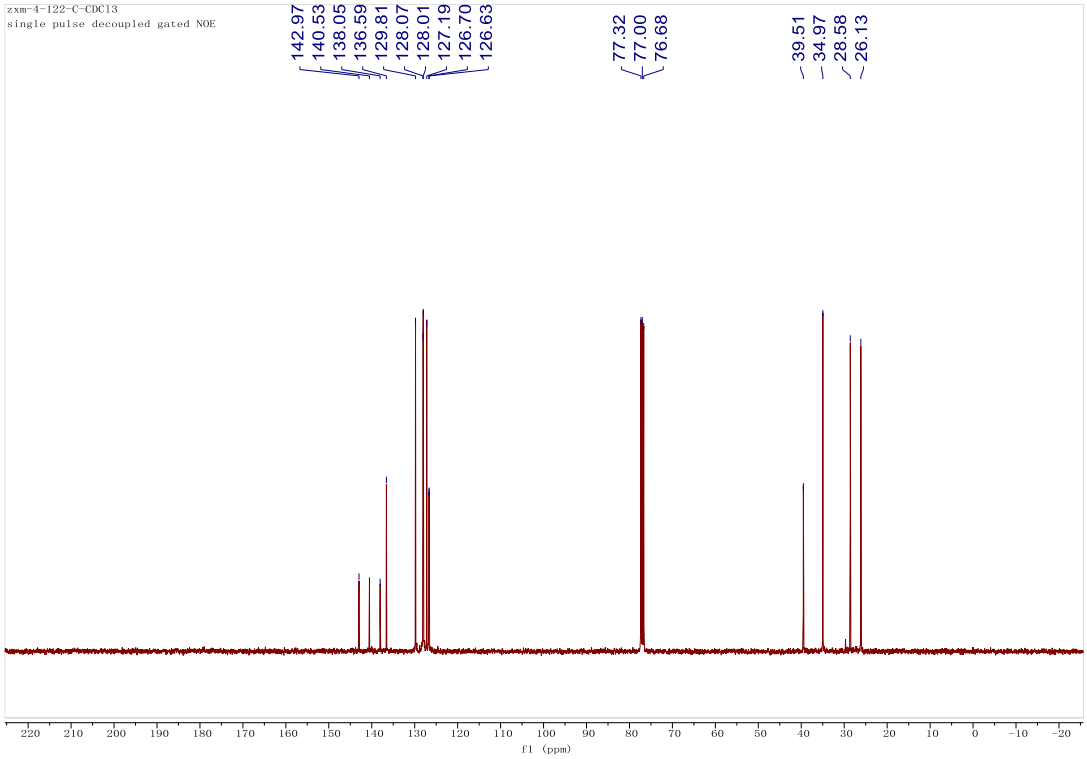


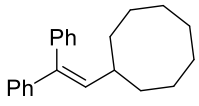
3ac

^{1}H NMR (400 MHz, $CDCl_3$) of **3ac**



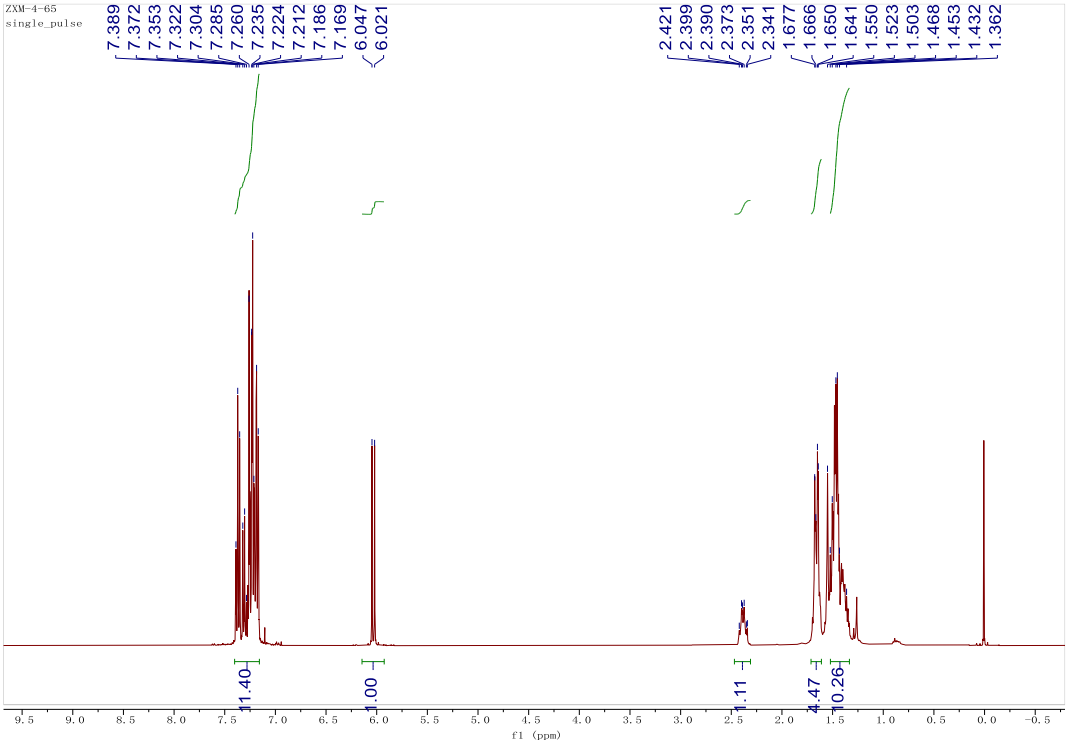
^{13}C NMR (101 MHz, $CDCl_3$) of **3ac**



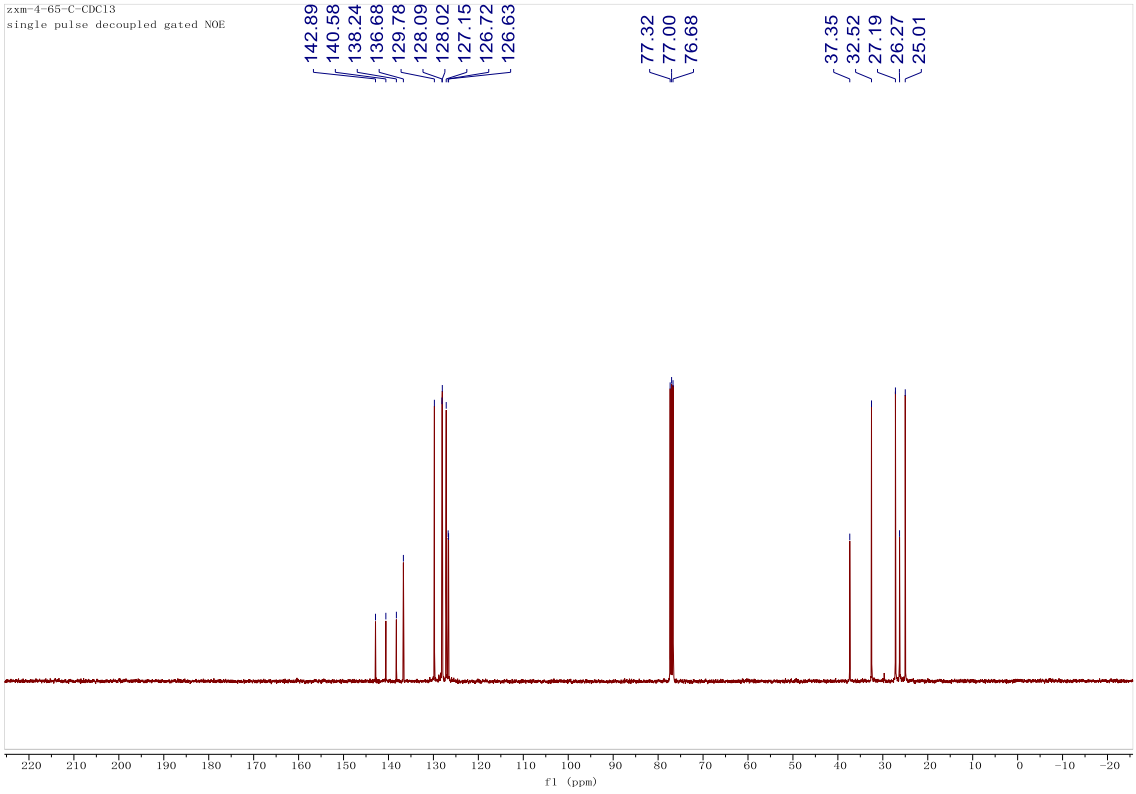


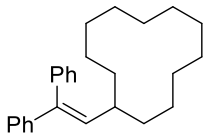
3ad

^{1}H NMR (400 MHz, $CDCl_3$) of **3ad**



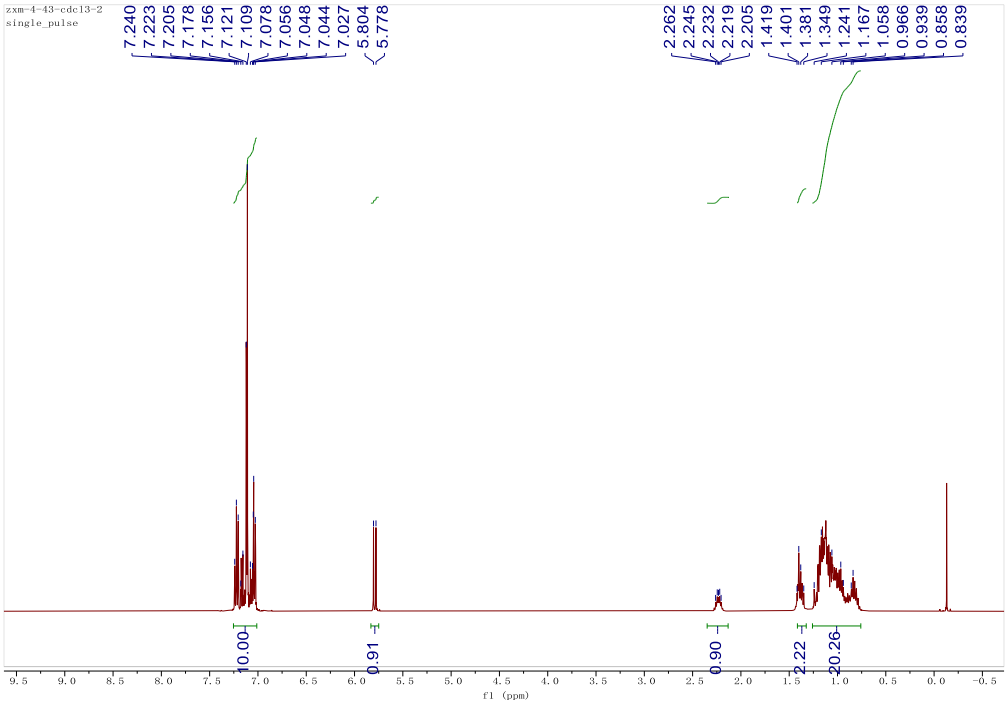
^{13}C NMR (101 MHz, $CDCl_3$) of **3ad**



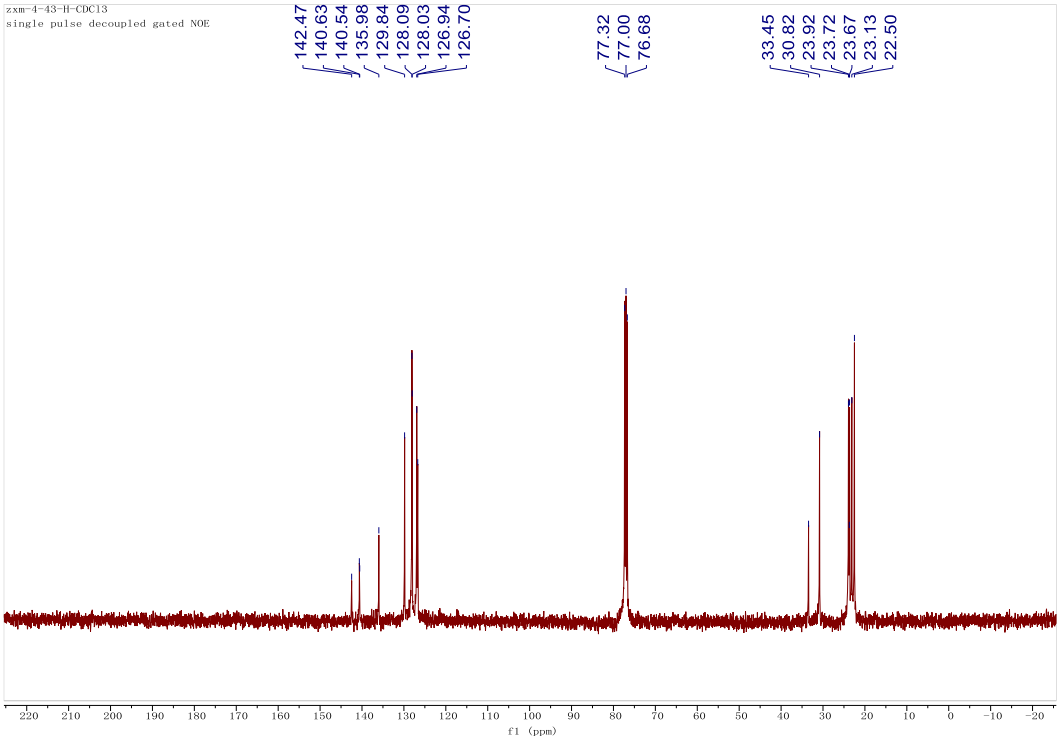


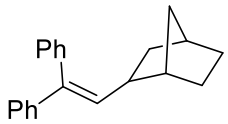
3ae

^{1}H NMR (400 MHz, $CDCl_3$) of **3ae**



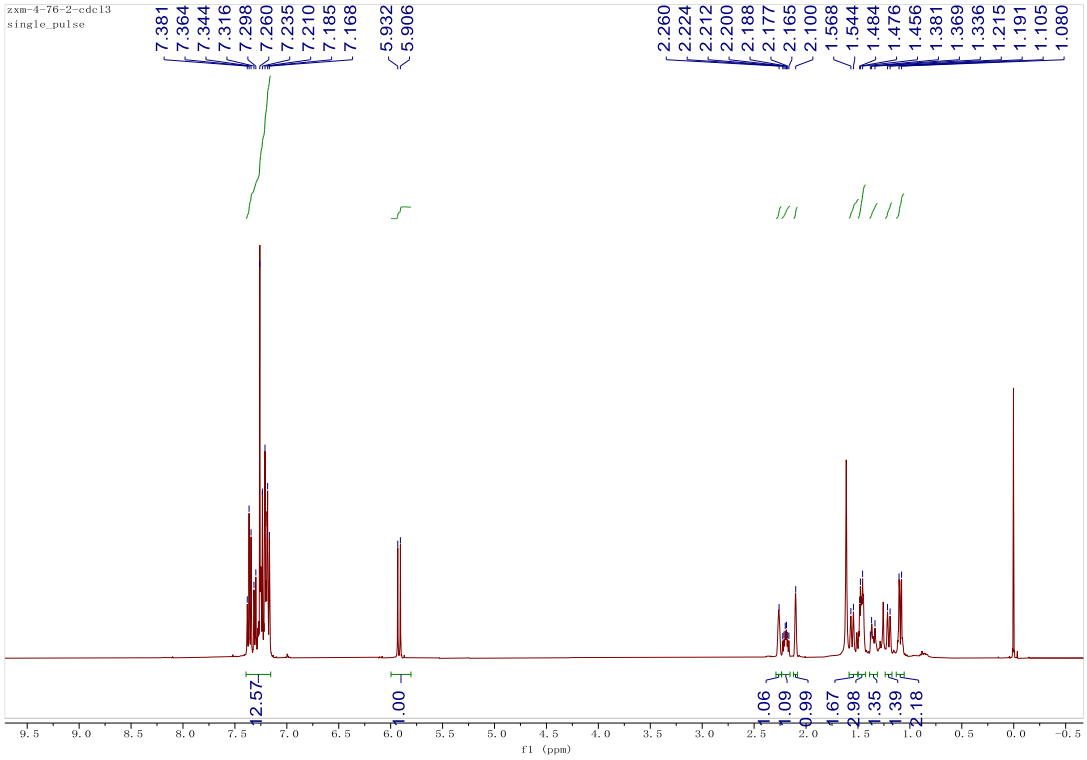
^{13}C NMR (101 MHz, $CDCl_3$) of **3ae**



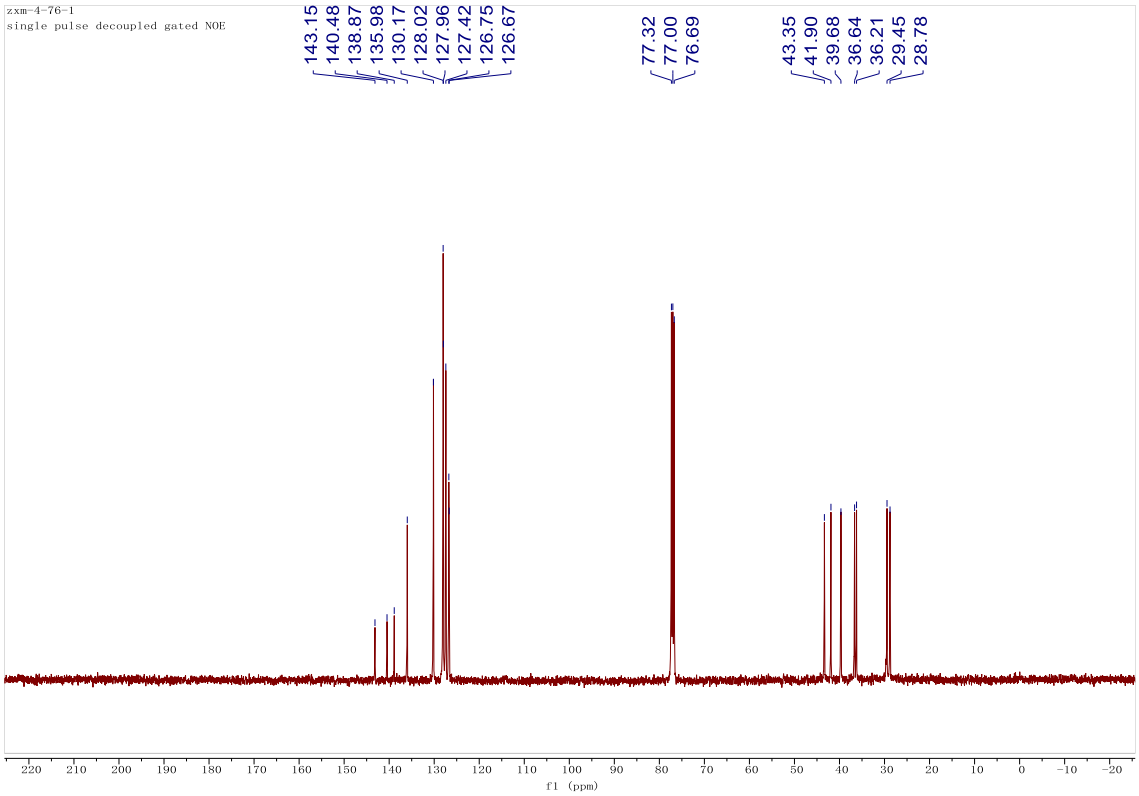


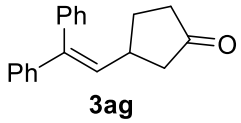
3af

^{1}H NMR (400 MHz, $CDCl_3$) of **3af**



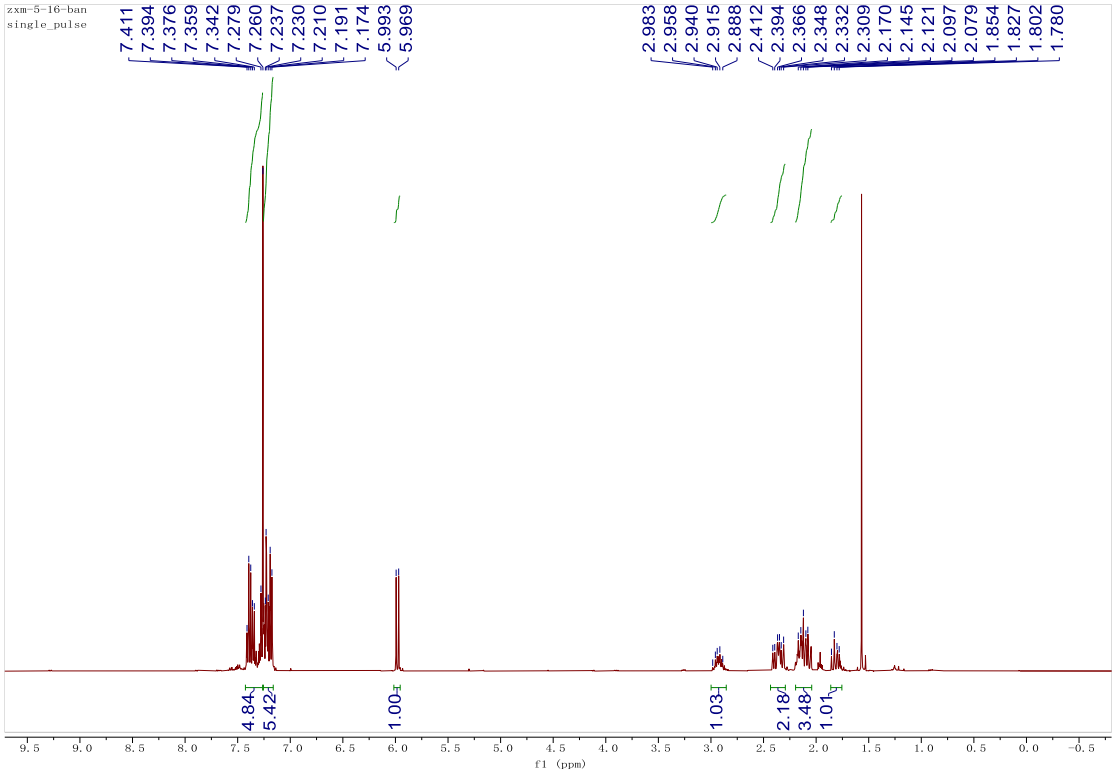
^{13}C NMR (101 MHz, $CDCl_3$) of **3af**



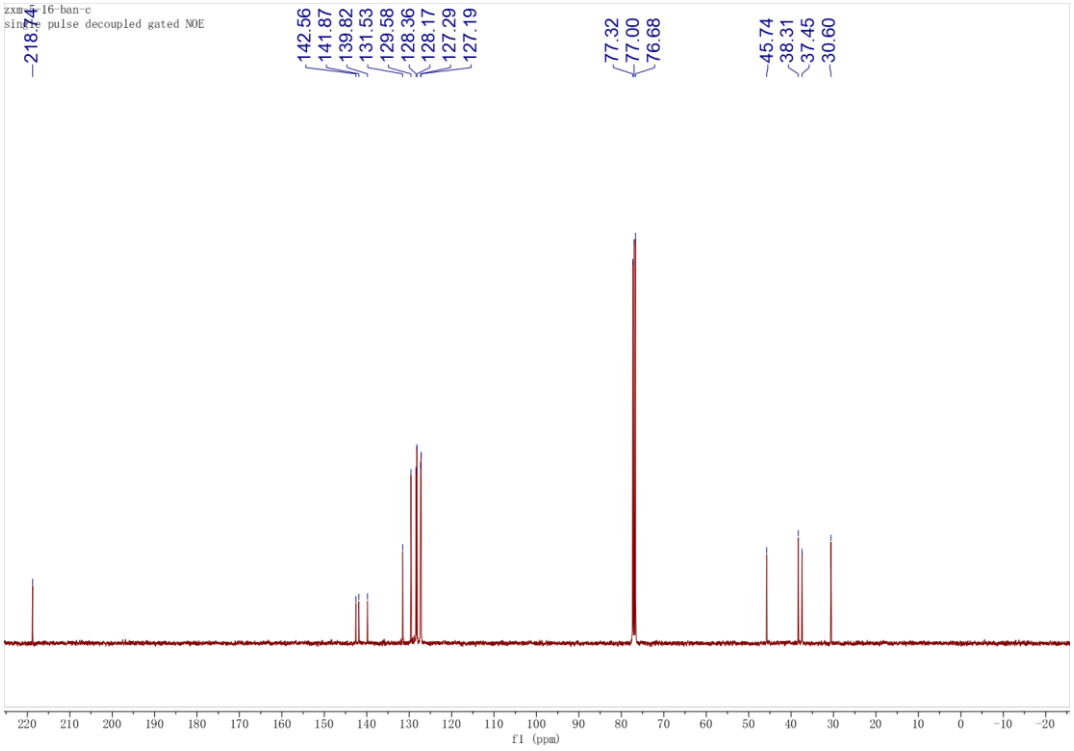


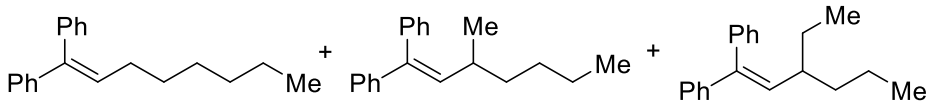
3ag

^{1}H NMR (400 MHz, $CDCl_3$) of **3ag**



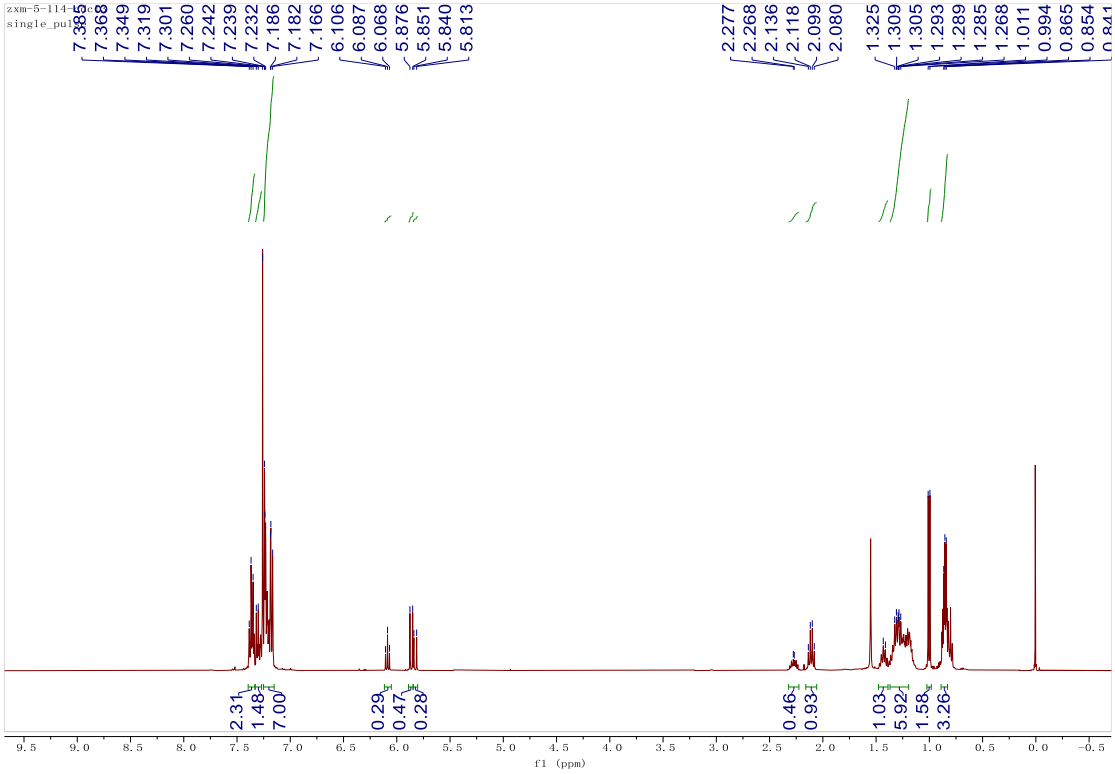
^{13}C NMR (101 MHz, $CDCl_3$) of **3ag**

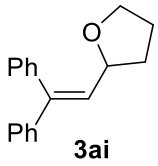




3ah

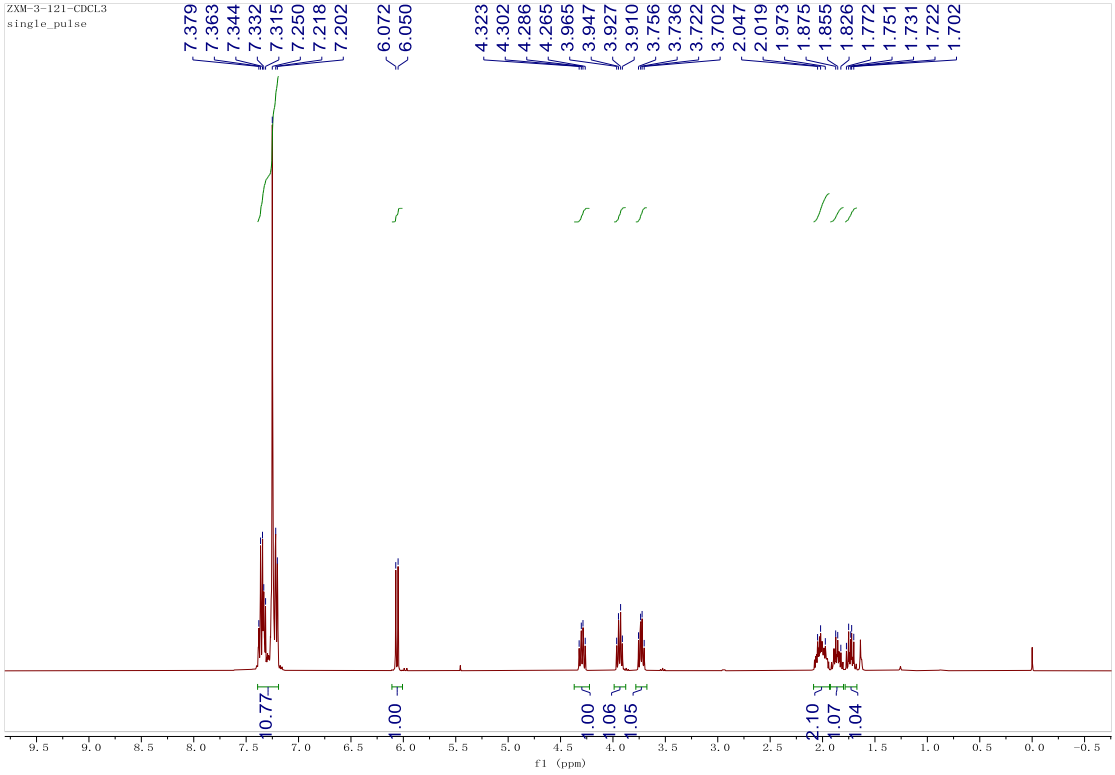
^{1}H NMR (400 MHz, $CDCl_3$) of **3ah**



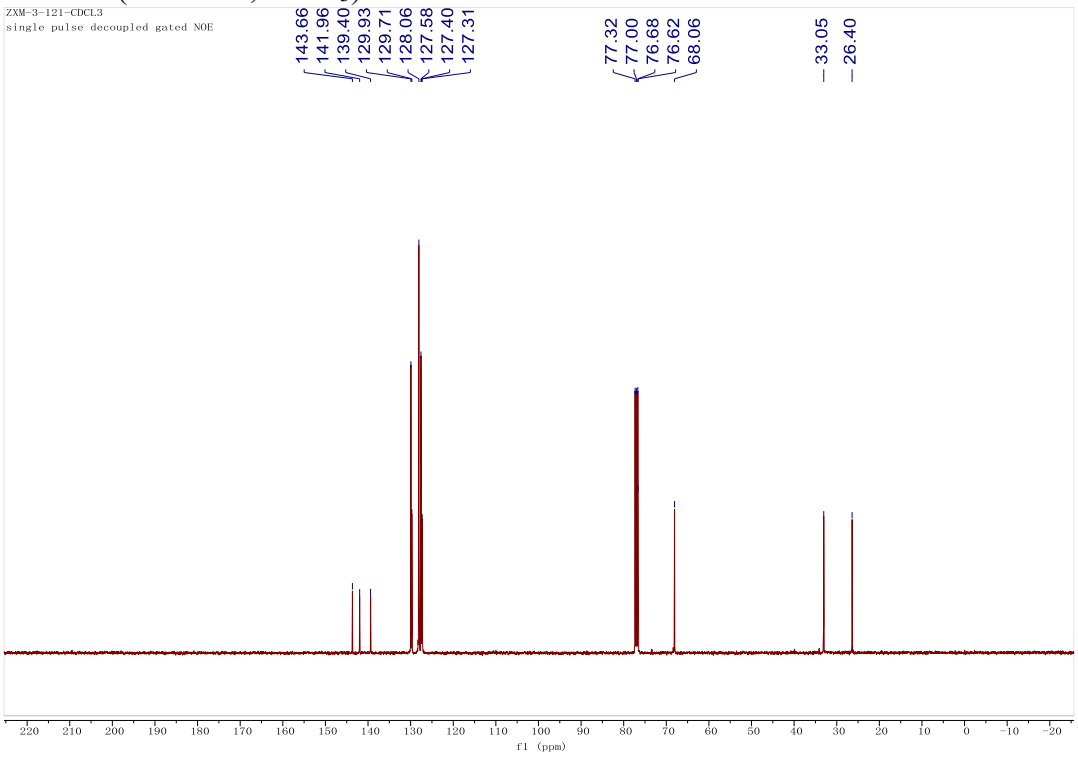


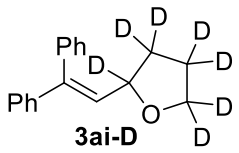
3ai

^{1}H NMR (400 MHz, $CDCl_3$) of **3ai**



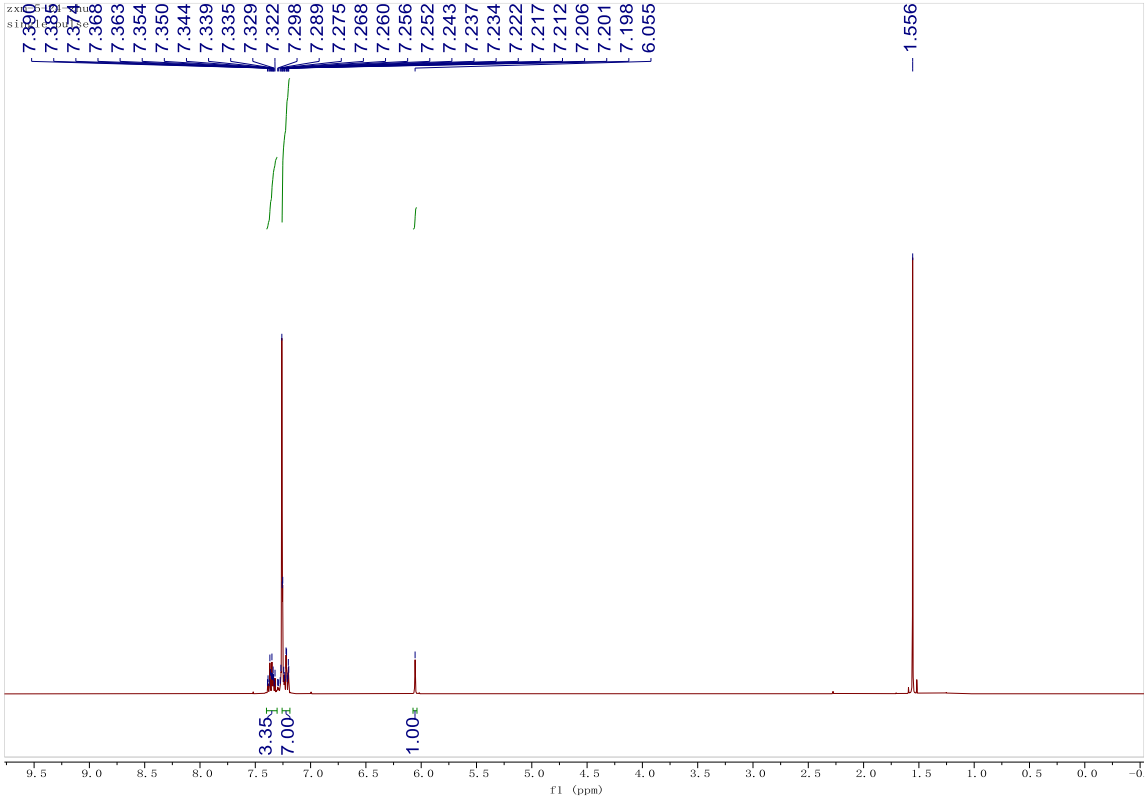
^{13}C NMR (101 MHz, $CDCl_3$) of **3ai**



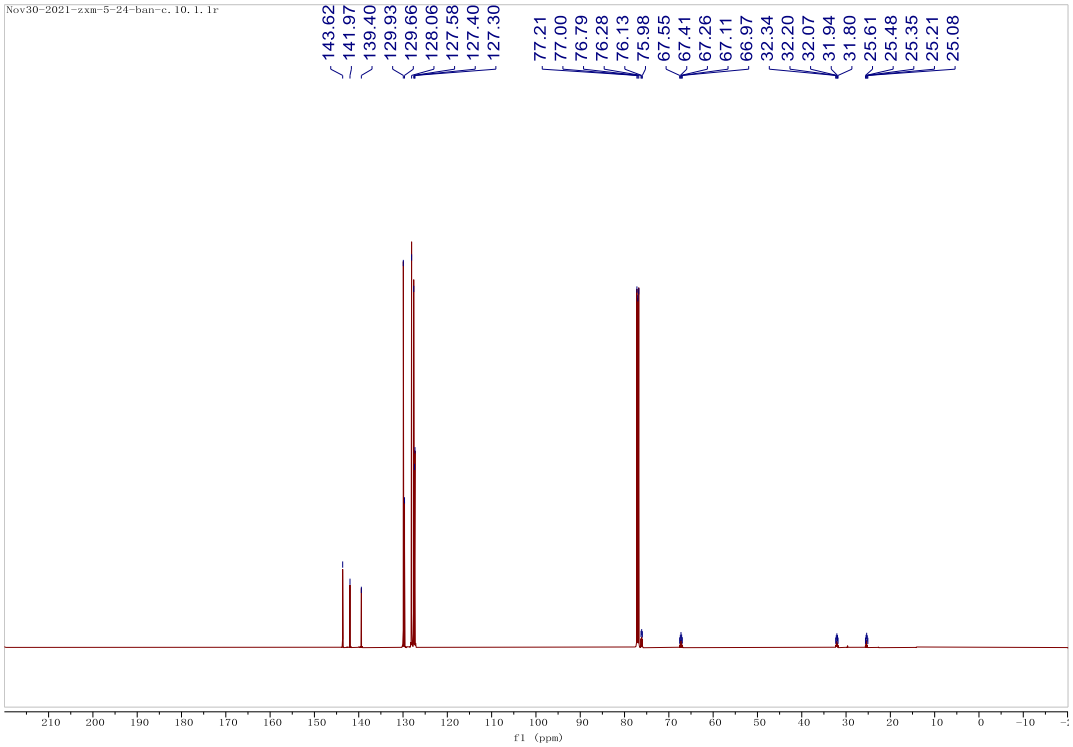


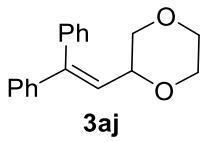
3ai-D

^{1}H NMR (400 MHz, $CDCl_3$) of **3ai-D**



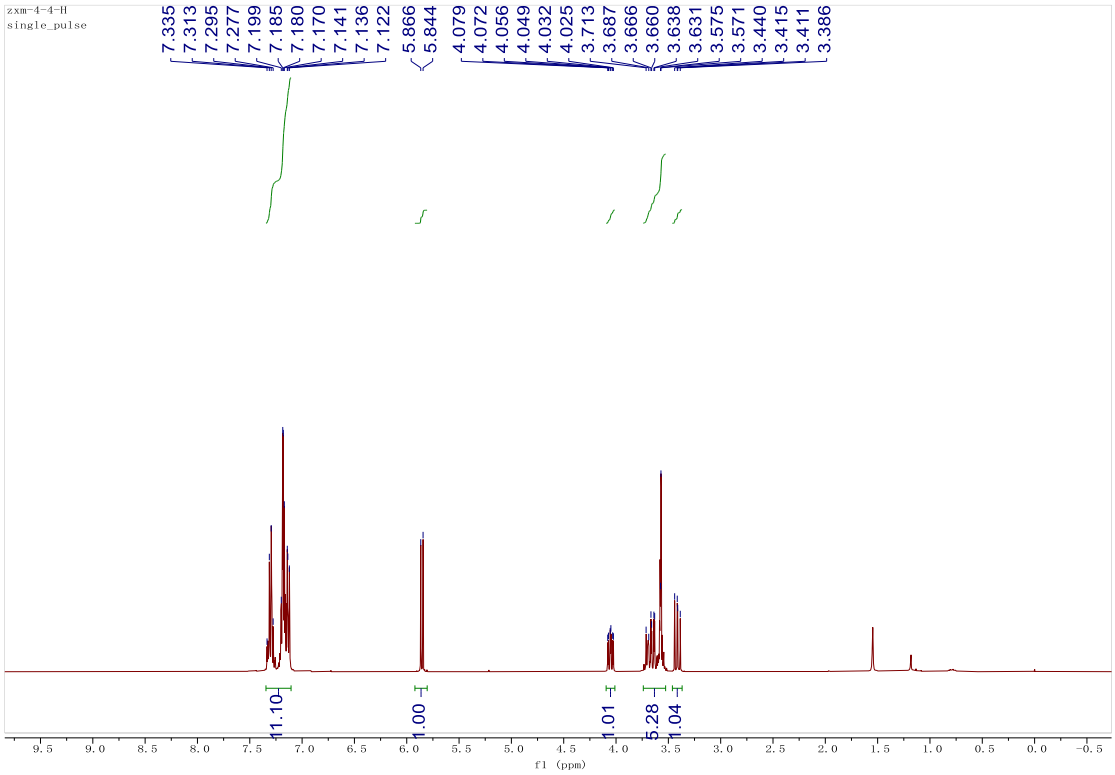
^{13}C NMR (101 MHz, $CDCl_3$) of **3ai-D**



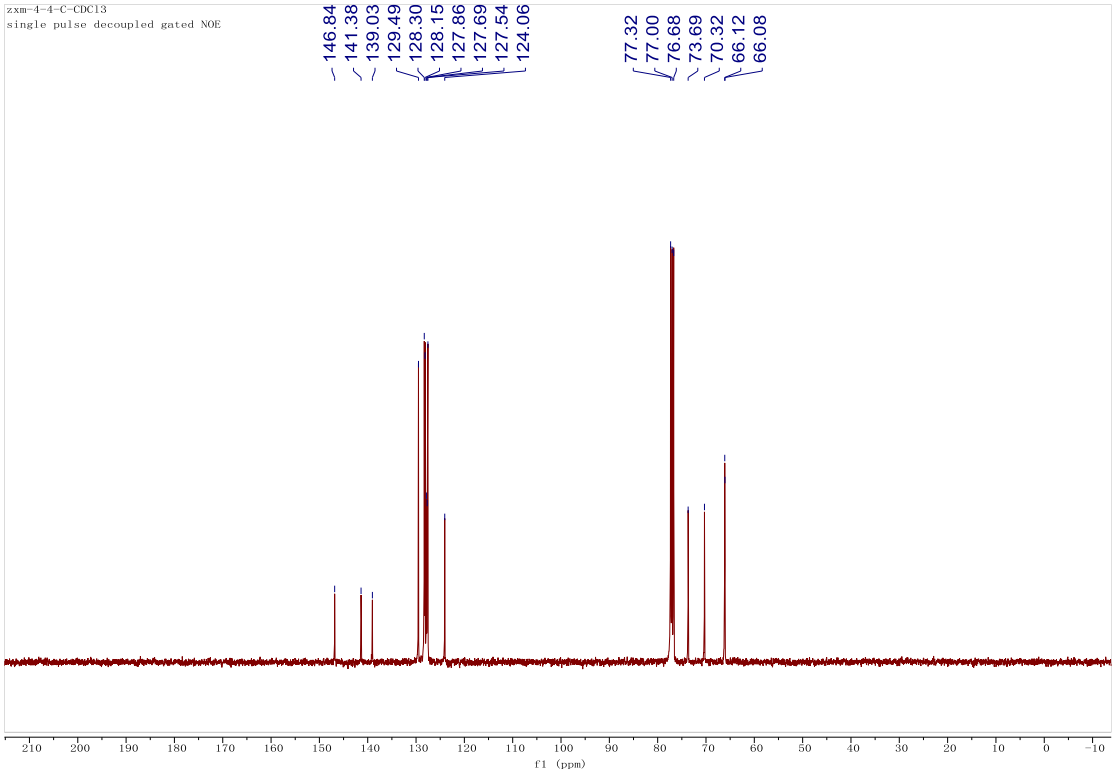


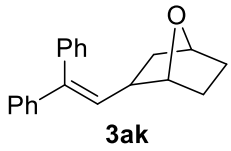
3aj

^{1}H NMR (400 MHz, $CDCl_3$) of **3aj**



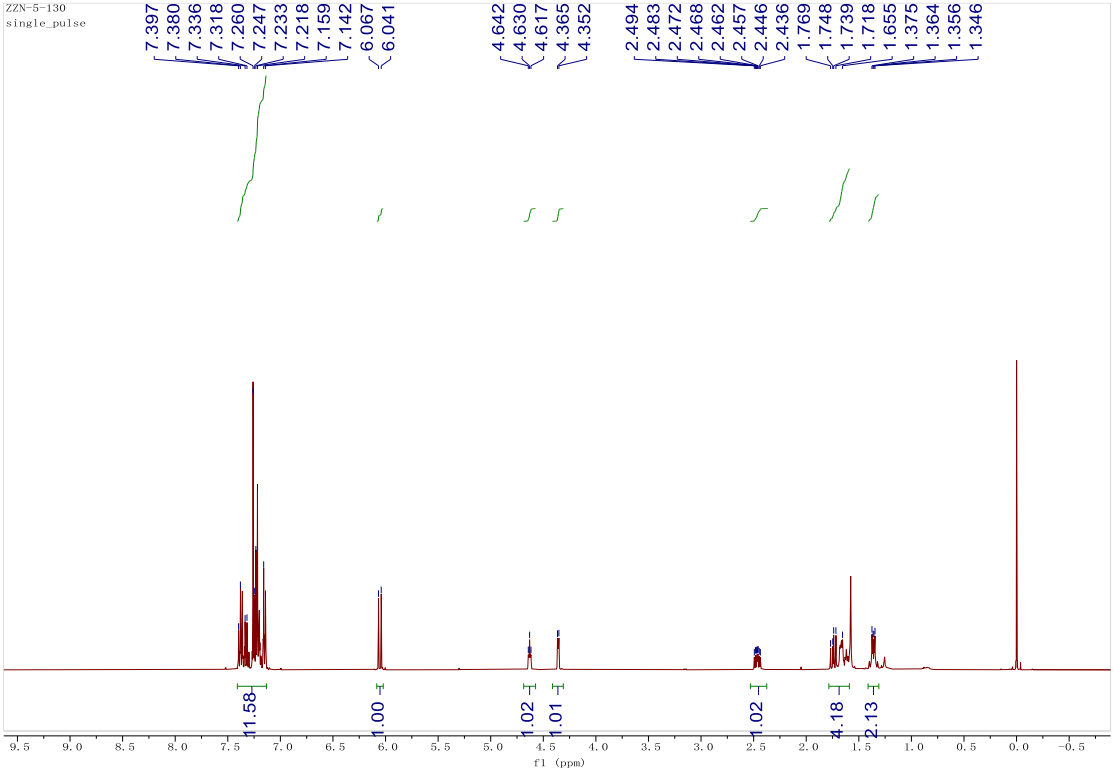
^{13}C NMR (101 MHz, $CDCl_3$) of **3aj**



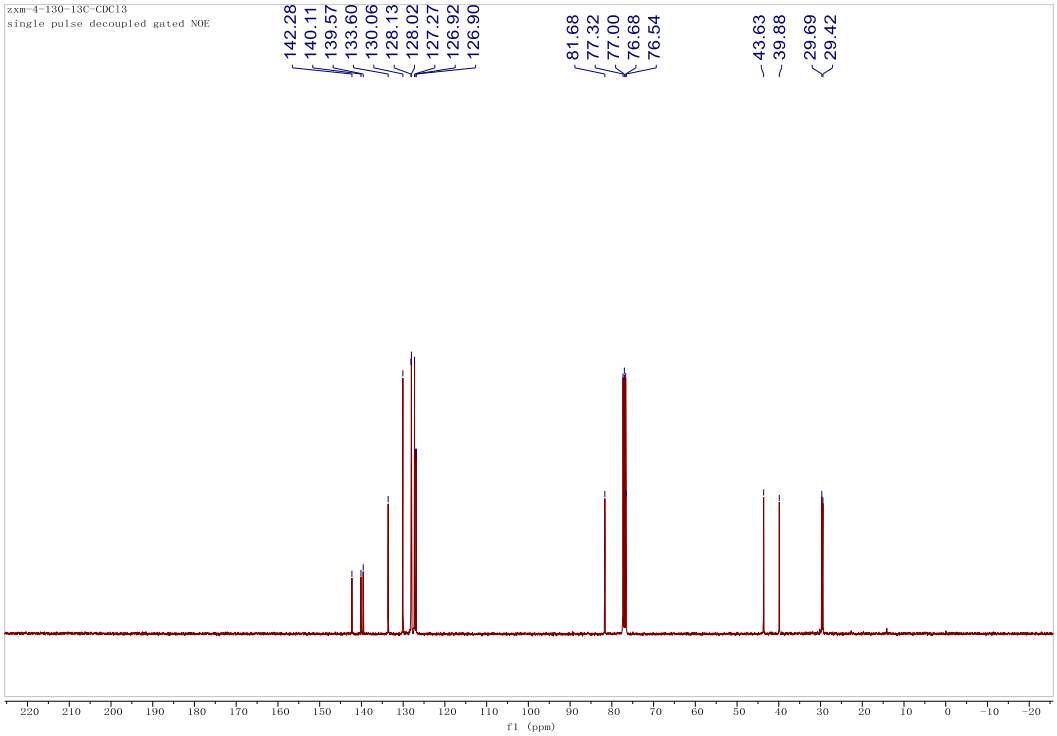


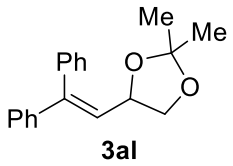
3ak

^{1}H NMR (400 MHz, $CDCl_3$) of **3ak**



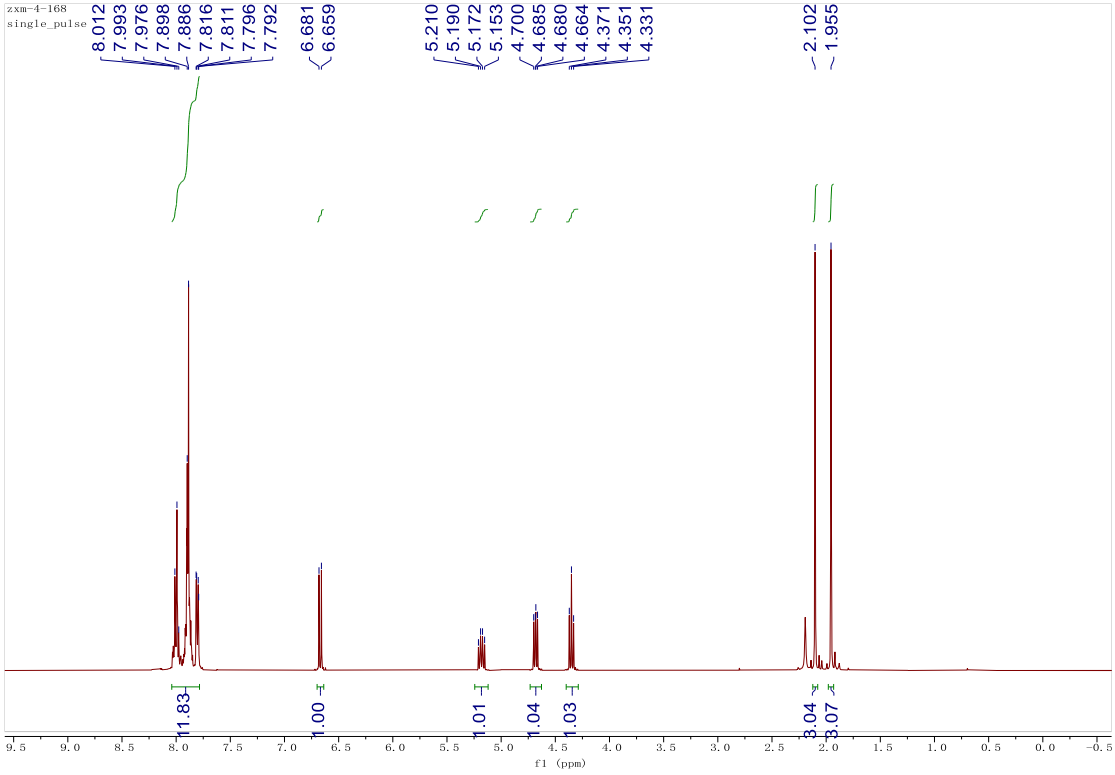
^{13}C NMR (101 MHz, $CDCl_3$) of **3ak**



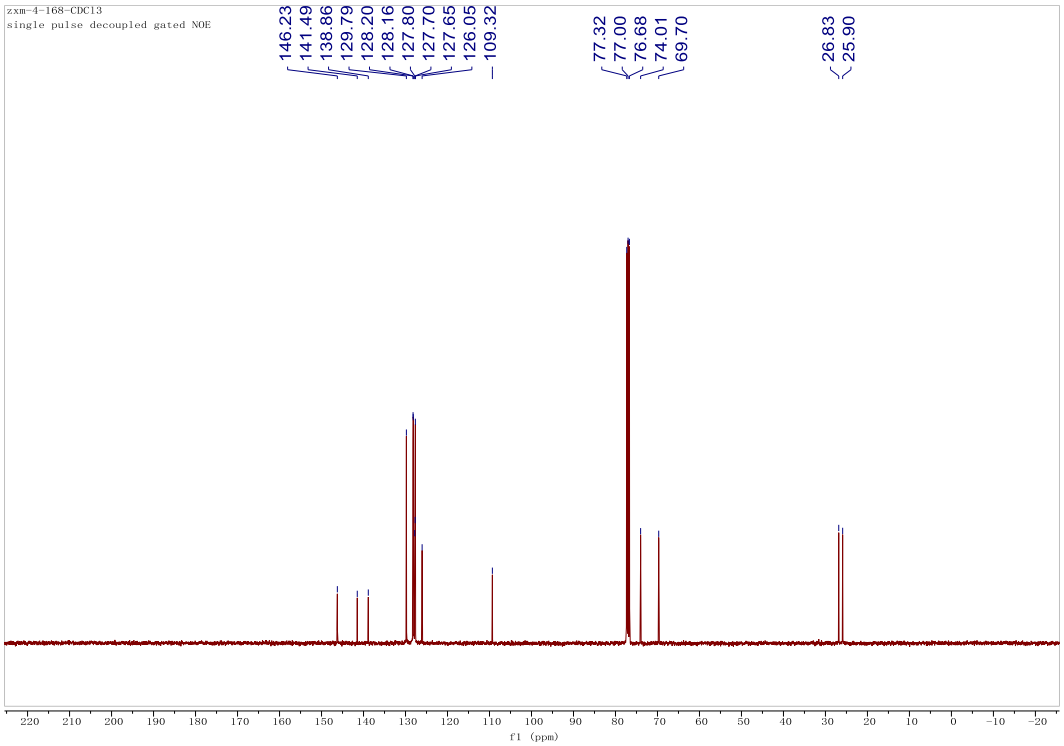


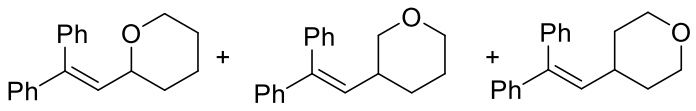
3al

^{1}H NMR (400 MHz, $CDCl_3$) of **3al**



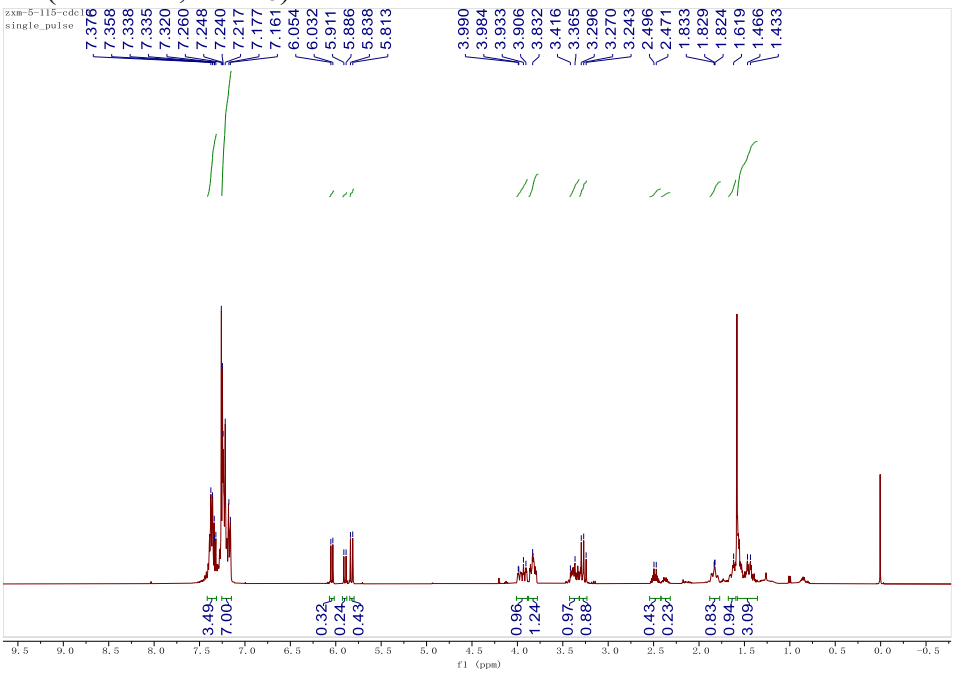
^{13}C NMR (101 MHz, $CDCl_3$) of **3al**

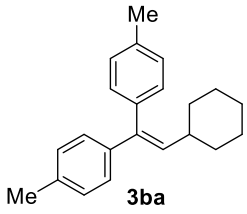




3am

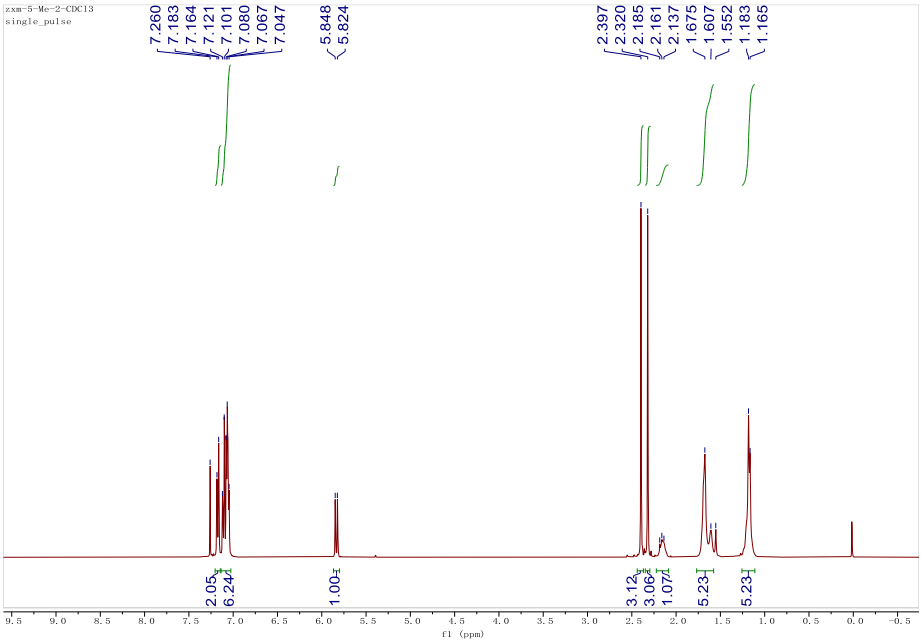
^{1}H NMR (400 MHz, $CDCl_3$) of **3am**



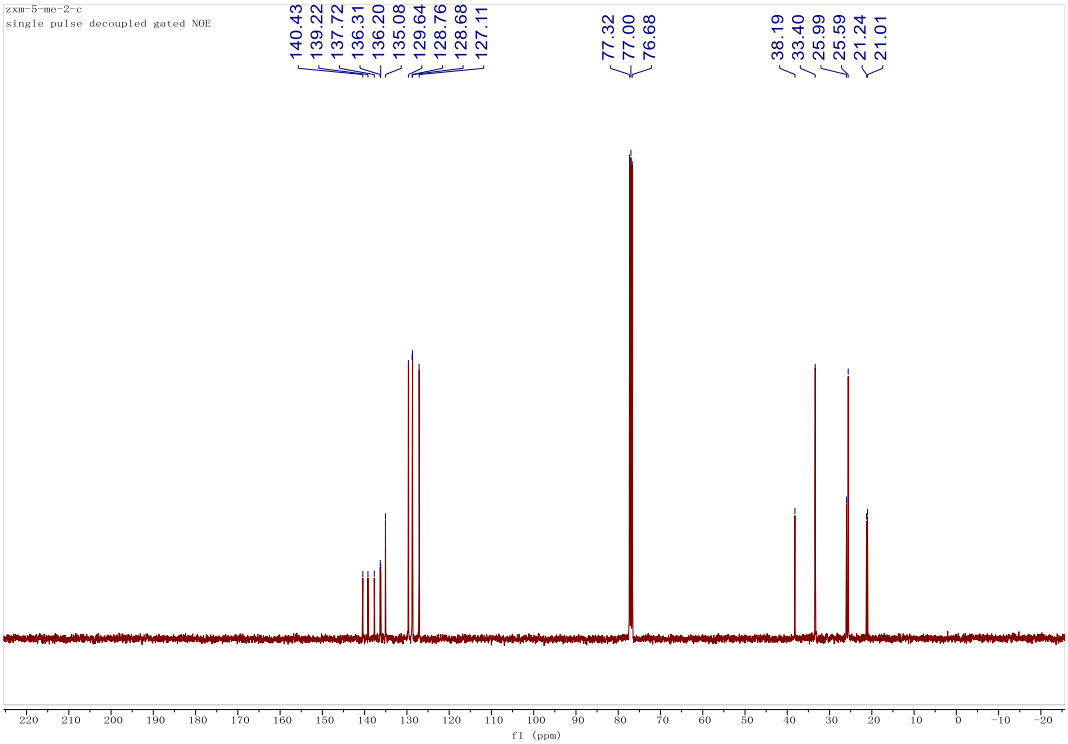


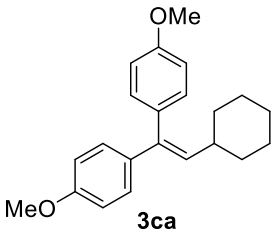
3ba

^{1}H NMR (400 MHz, $CDCl_3$) of **3ba**



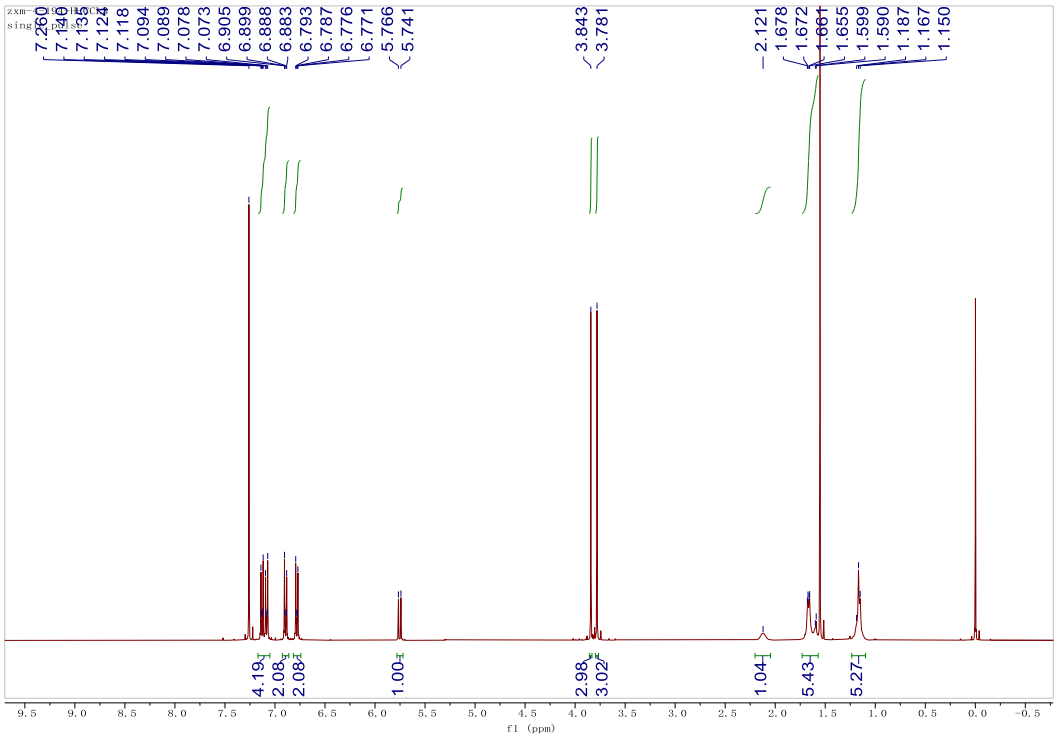
^{13}C NMR (101 MHz, $CDCl_3$) of **3ba**



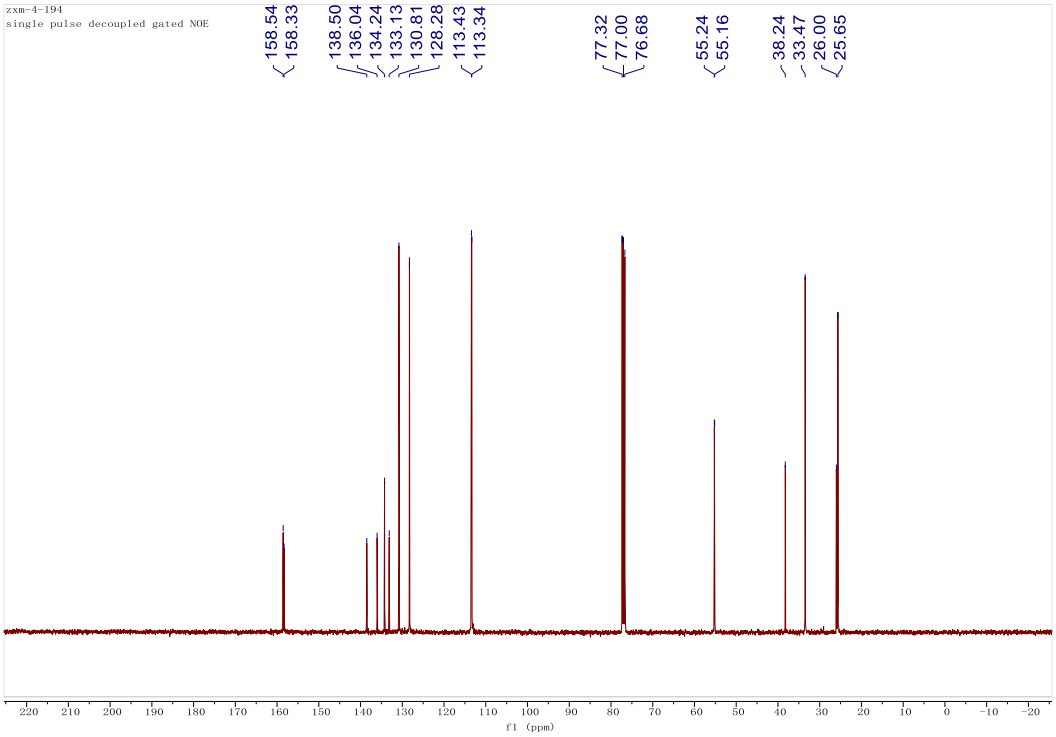


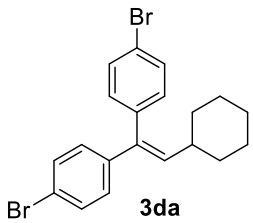
3ca

^{1}H NMR (400 MHz, $CDCl_3$) of **3ca**



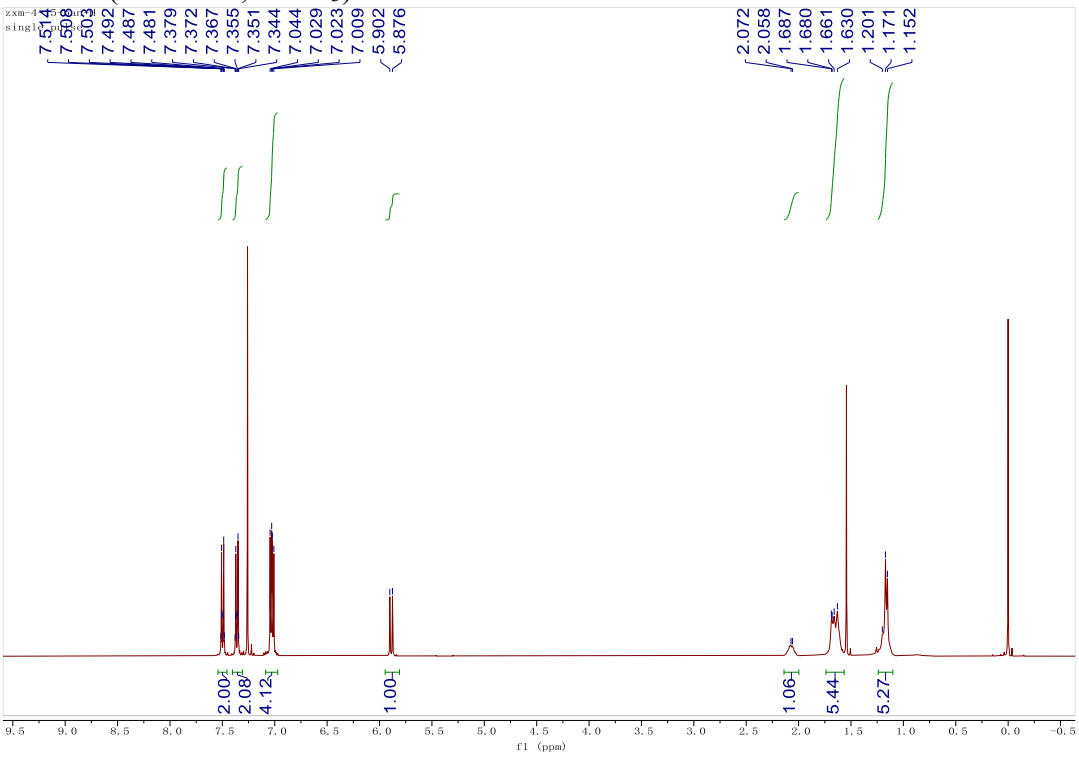
^{13}C NMR (101 MHz, $CDCl_3$) of **3ca**



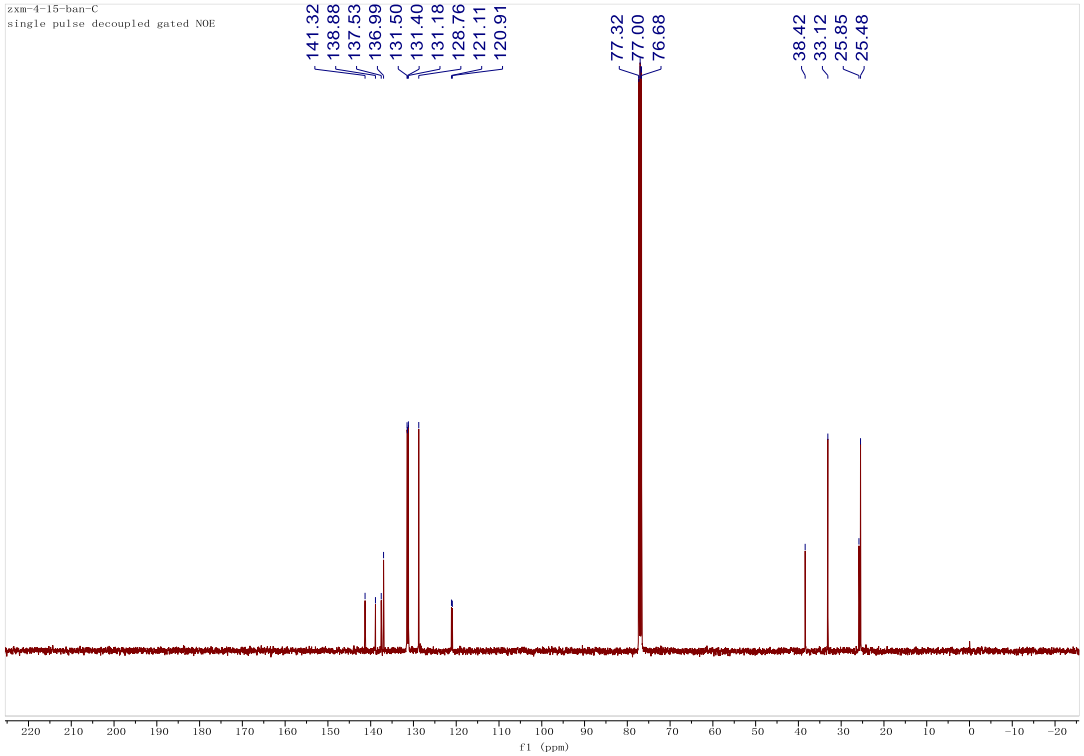


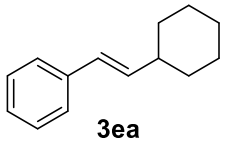
3da

^{1}H NMR (400 MHz, $CDCl_3$) of **3da**



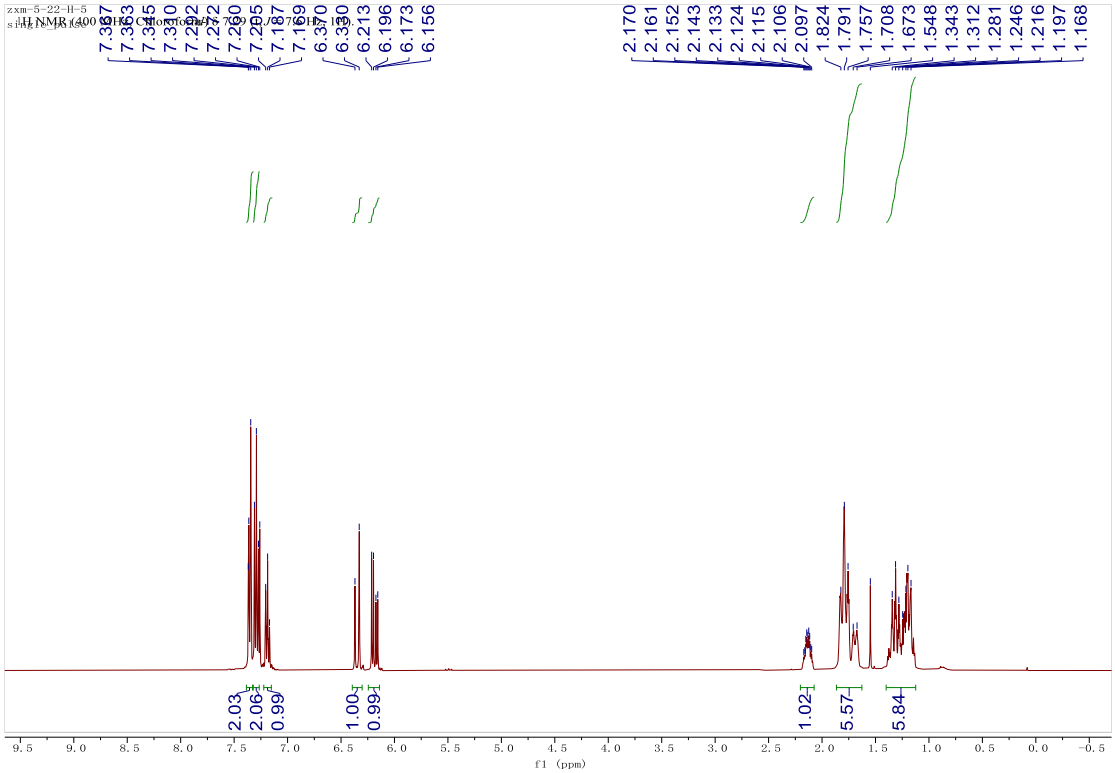
^{13}C NMR (101 MHz, $CDCl_3$) of **3da**



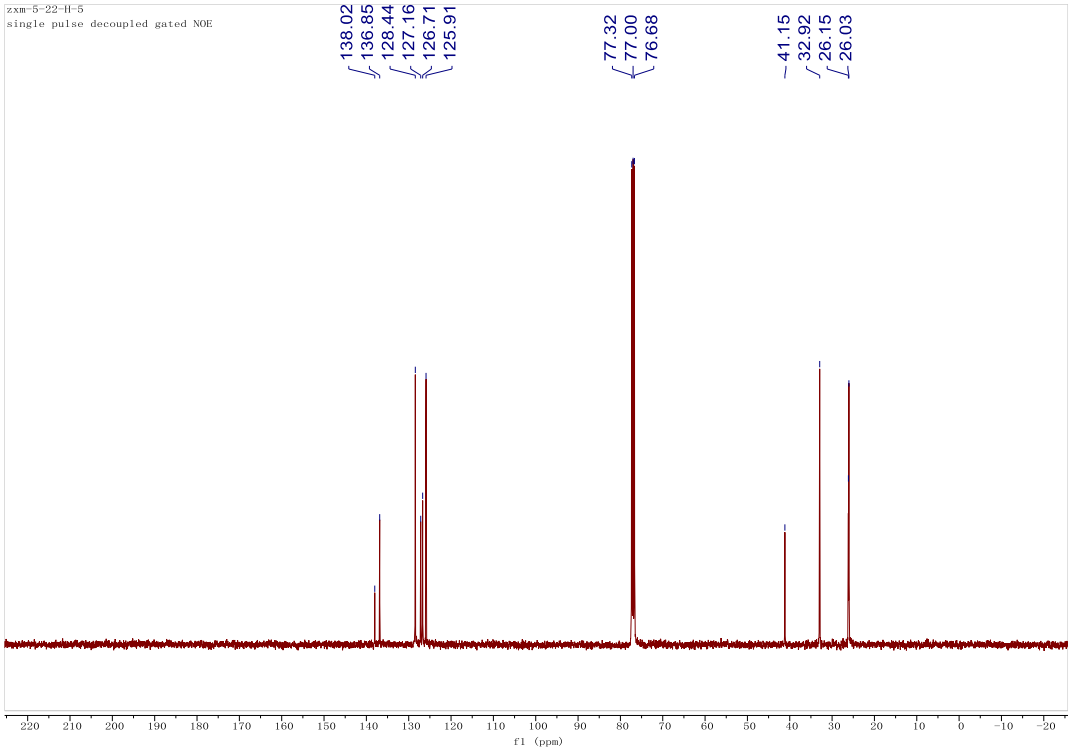


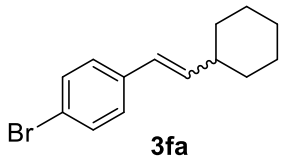
3ea

^{1}H NMR (400 MHz, $CDCl_3$) of **3ea**



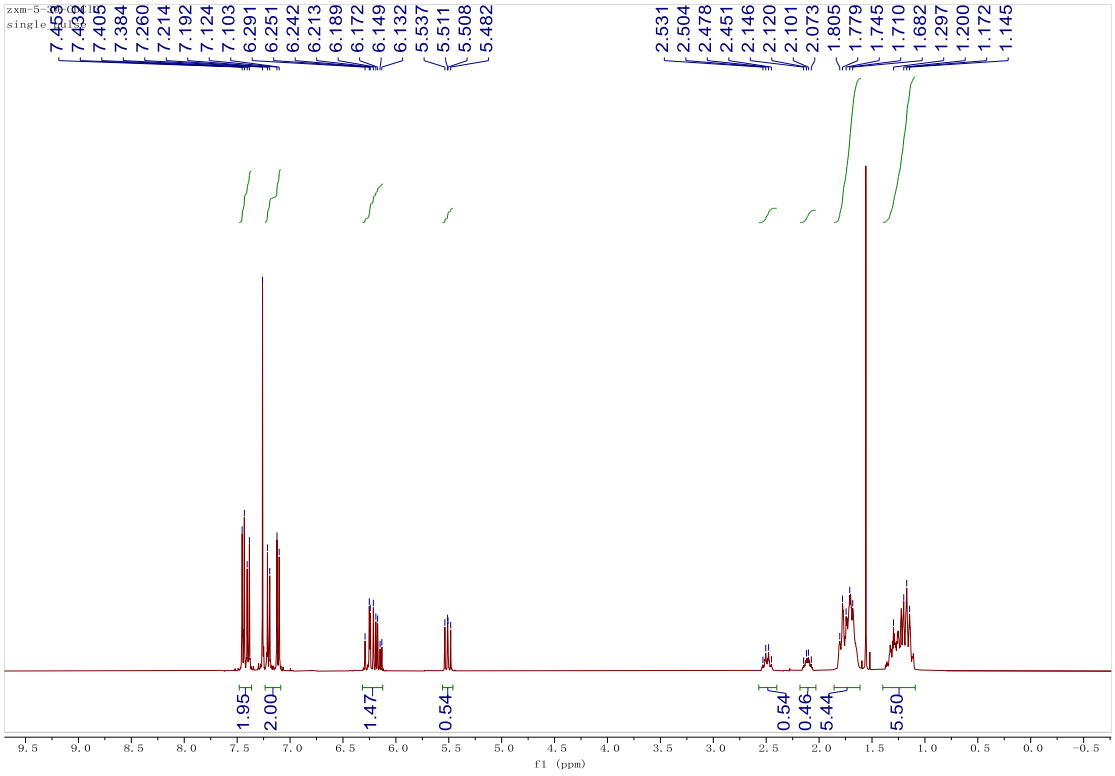
^{13}C NMR (101 MHz, $CDCl_3$) of **3ea**



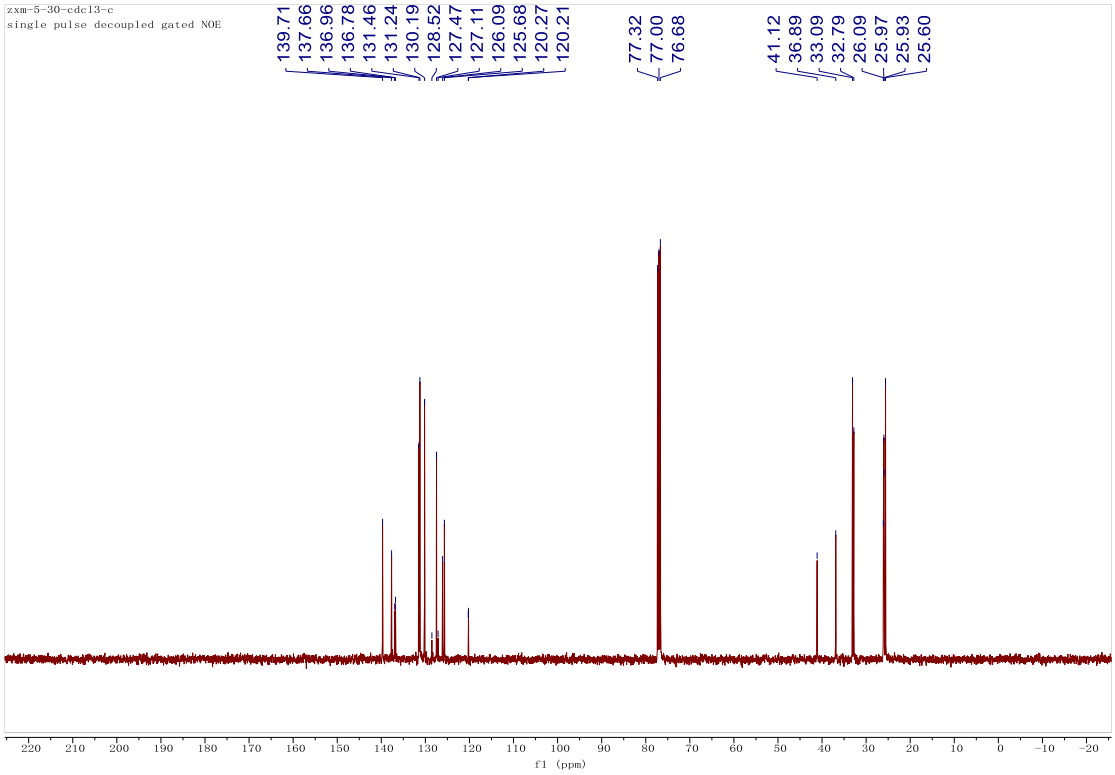


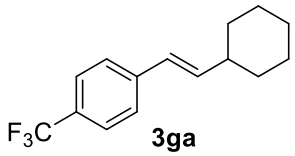
3fa

^{1}H NMR (400 MHz, $CDCl_3$) of **3fa**



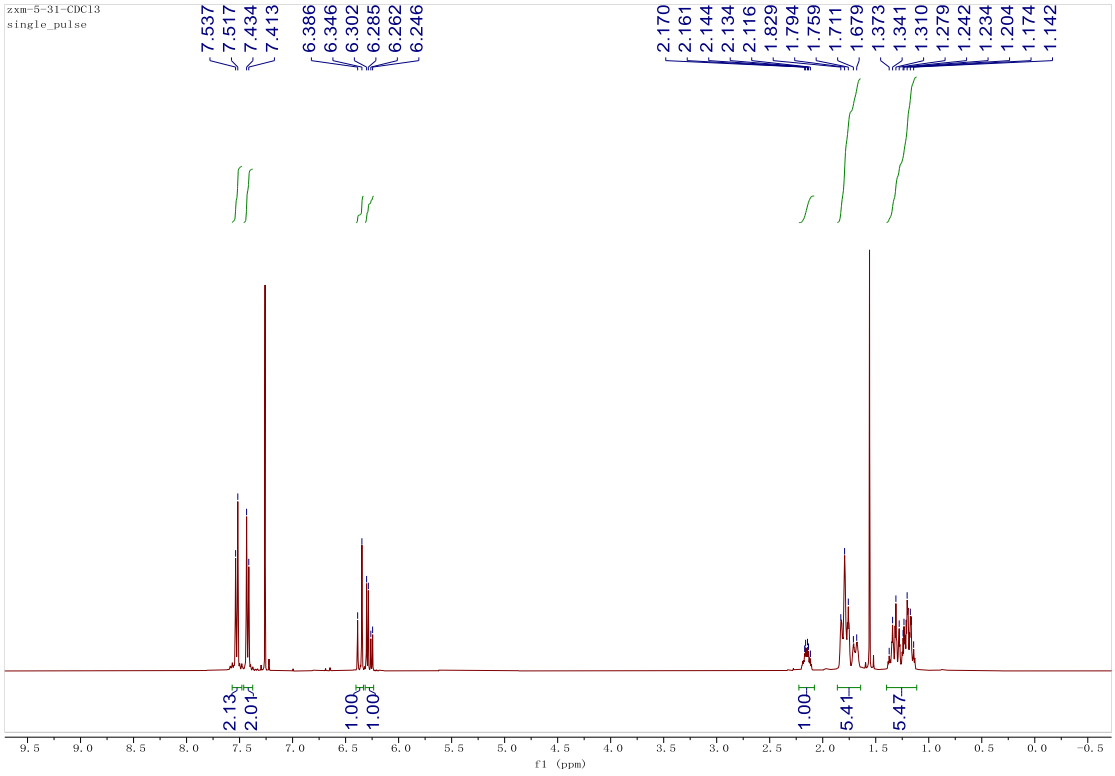
^{13}C NMR (101 MHz, $CDCl_3$) of **3fa**



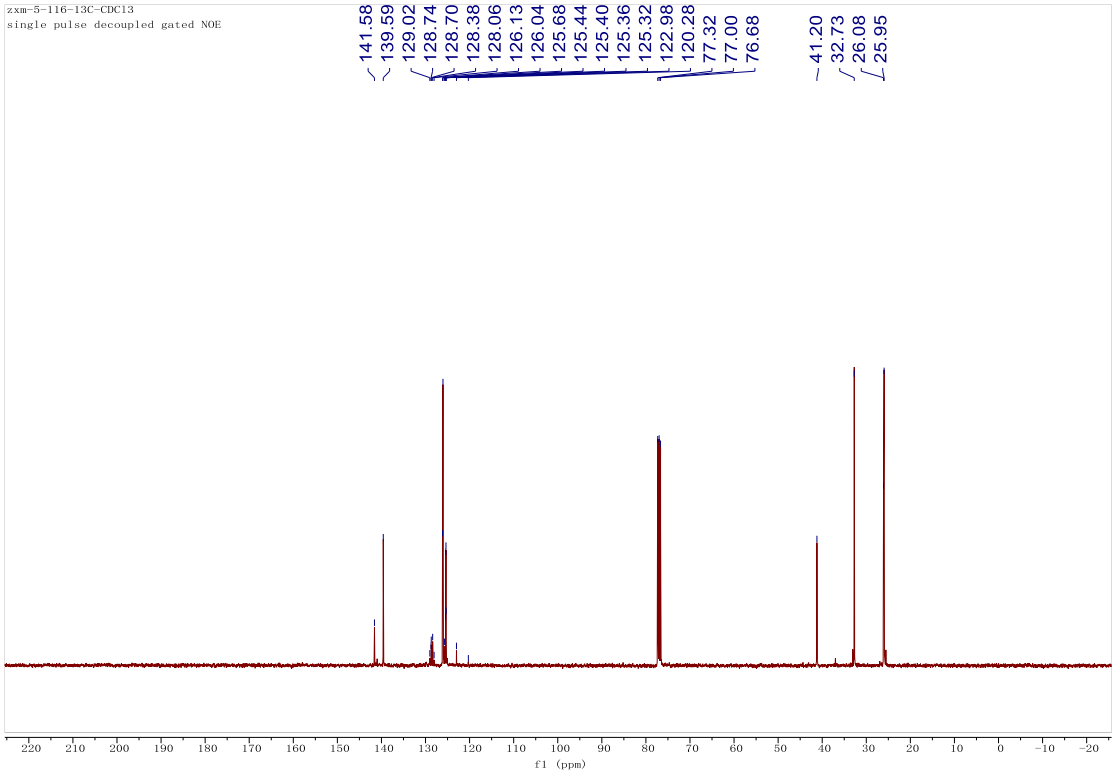


3ga

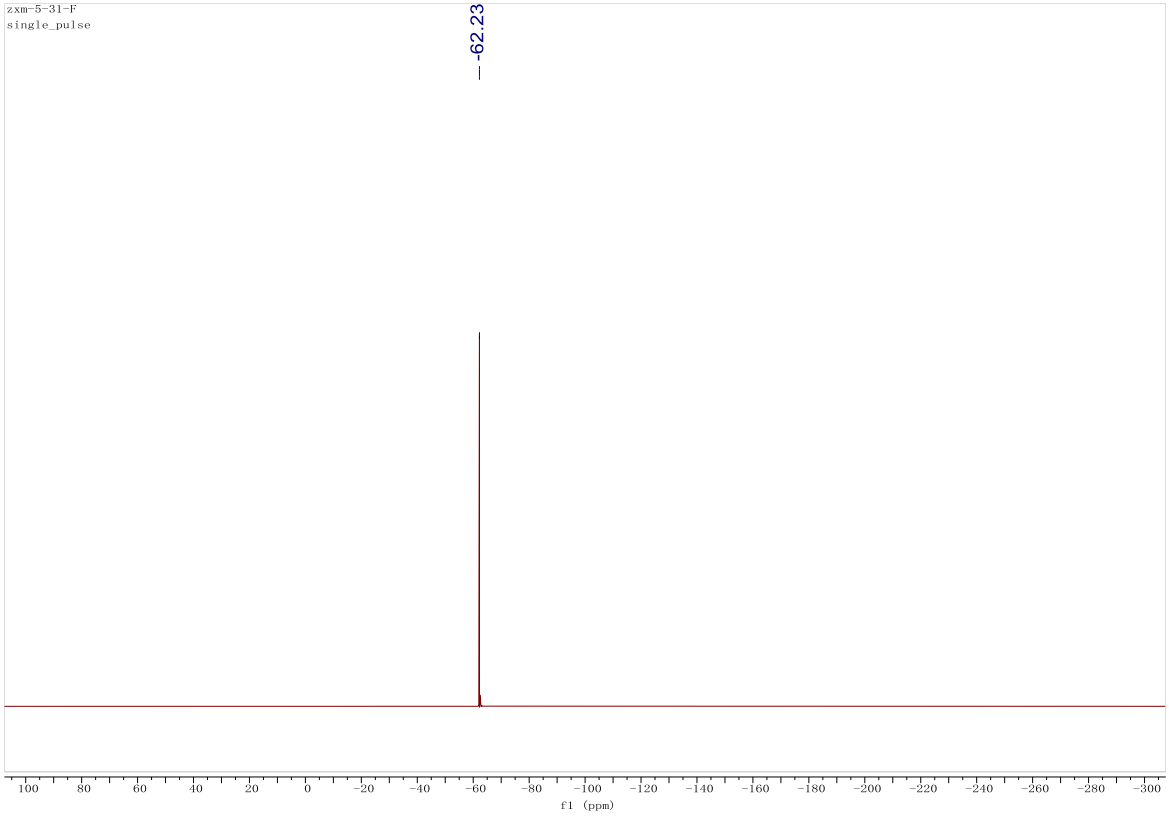
^{1}H NMR (400 MHz, $CDCl_3$) of **3ga**

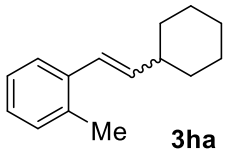


^{13}C NMR (101 MHz, $CDCl_3$) of **3ga**



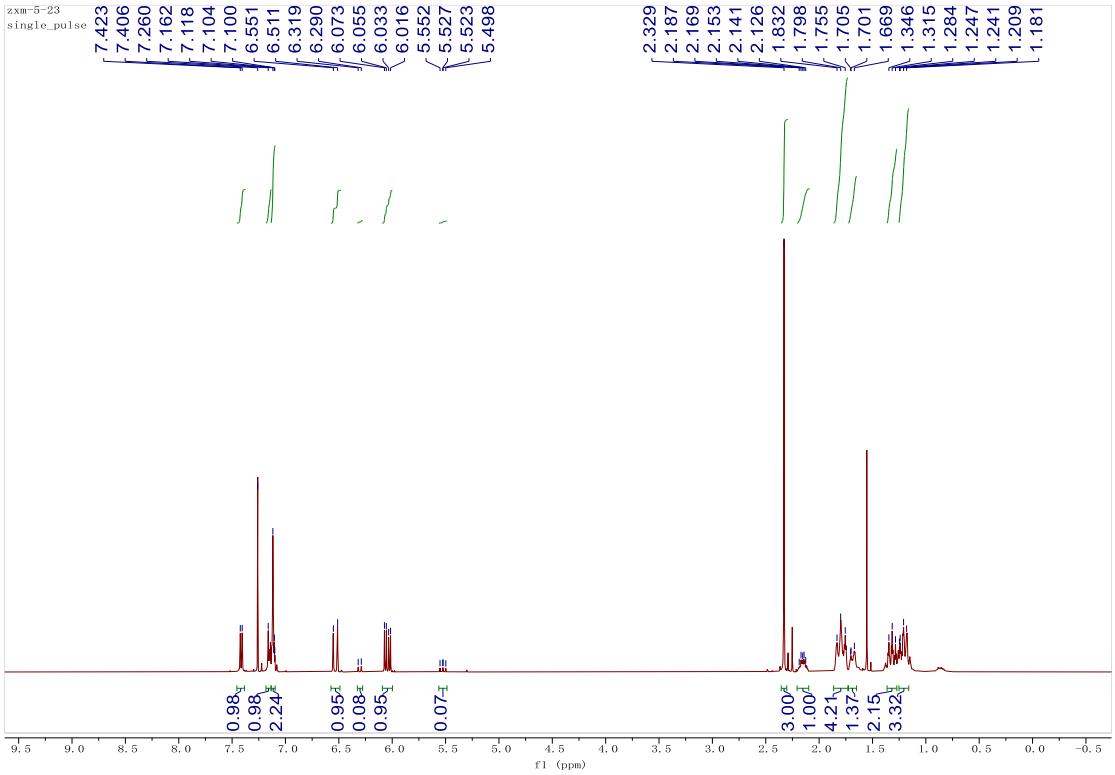
^{19}F NMR (376 MHz, $CDCl_3$) of **3ga**



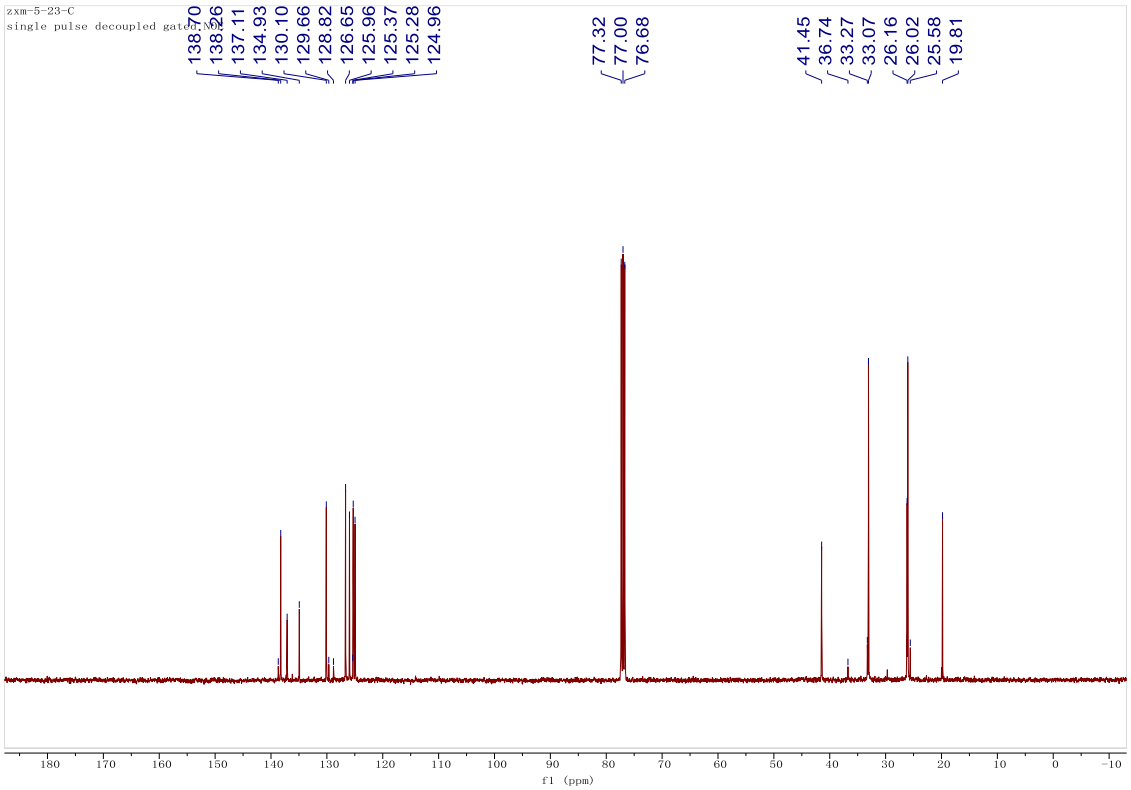


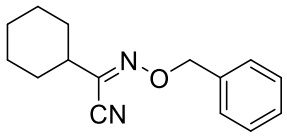
3ha

^{1}H NMR (400 MHz, $CDCl_3$) of **3ha**



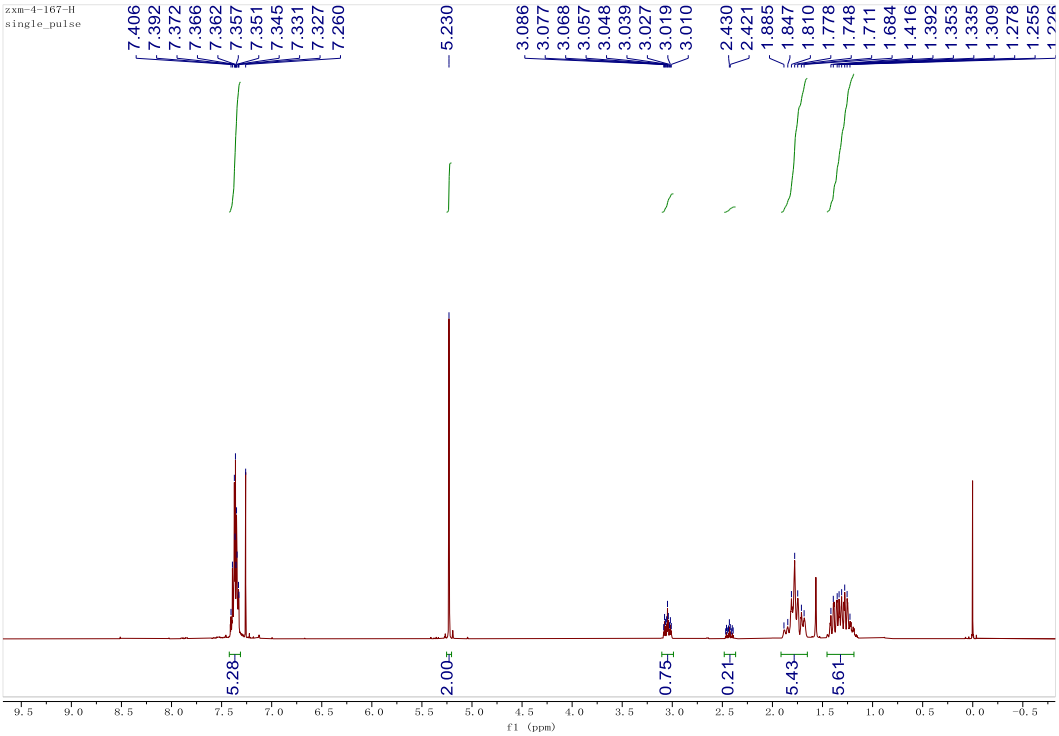
^{13}C NMR (101 MHz, $CDCl_3$) of **3ha**



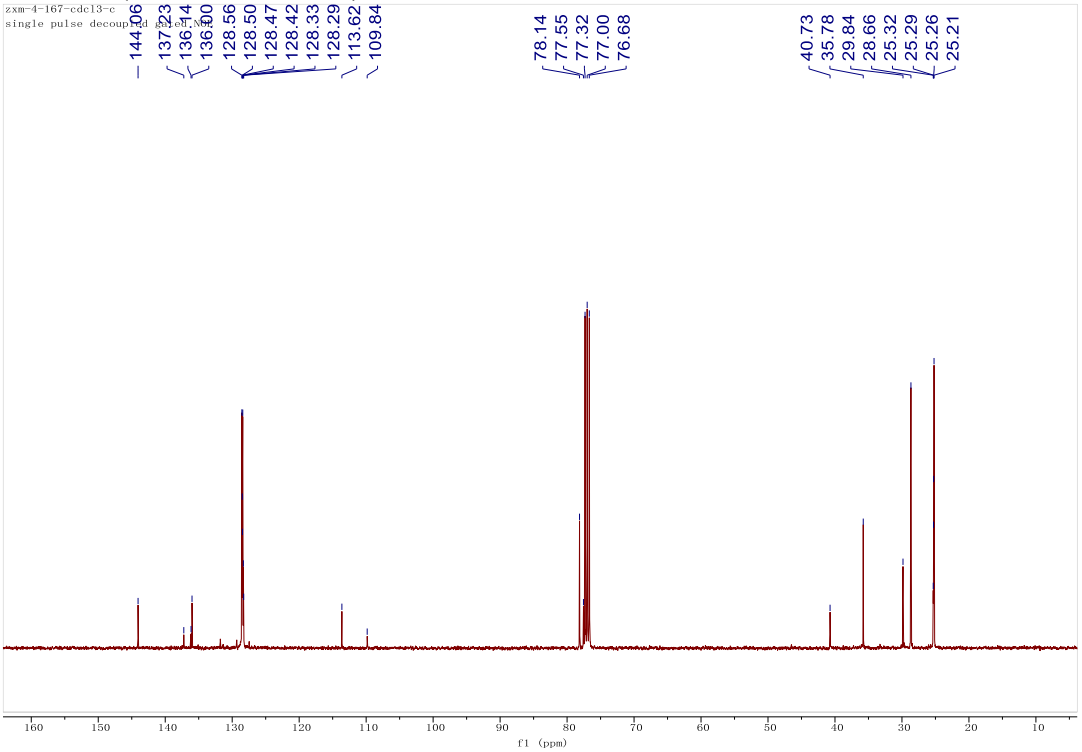


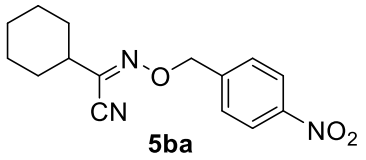
5aa

^{1}H NMR (400 MHz, $CDCl_3$) of **5aa**



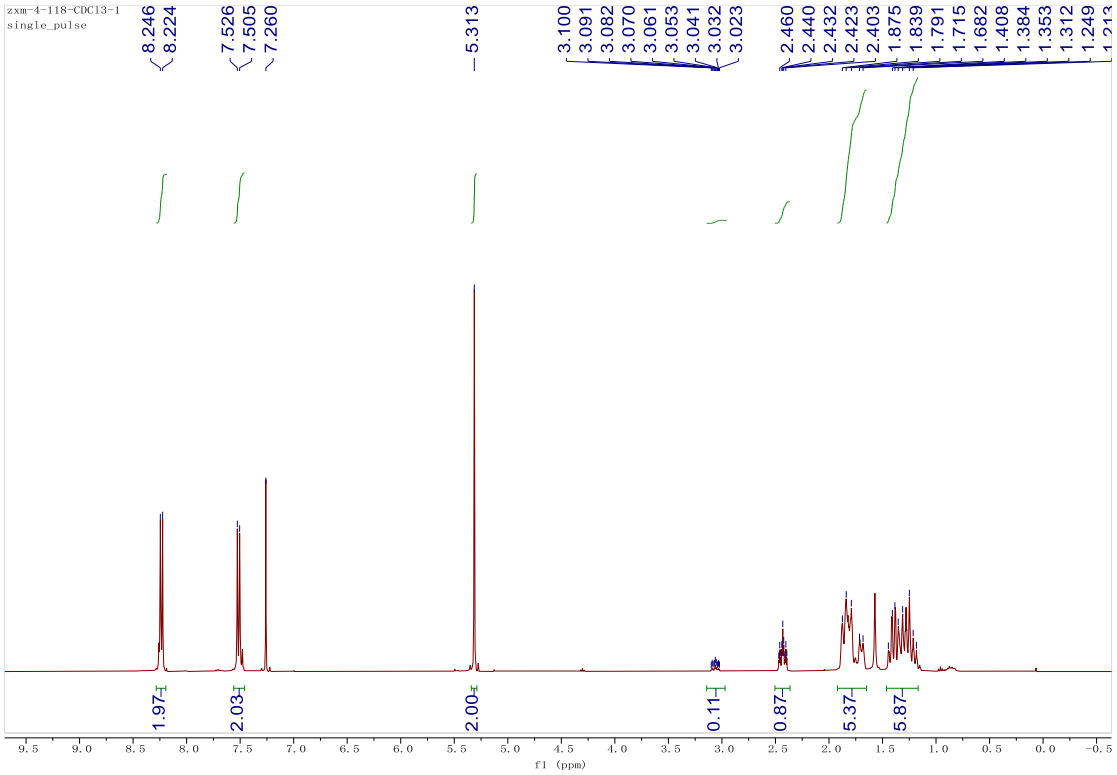
^{13}C NMR (101 MHz, $CDCl_3$) of **5aa**



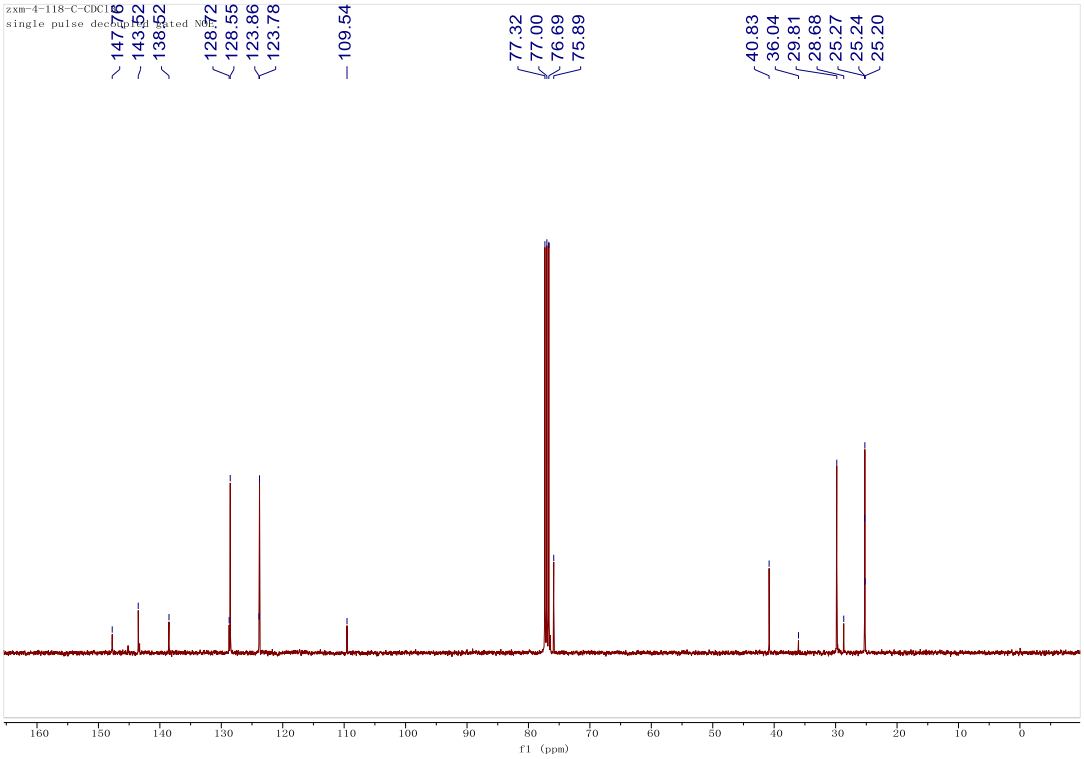


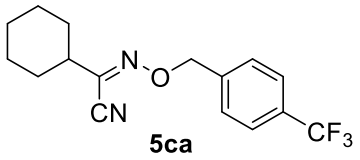
5ba

^{1}H NMR (400 MHz, $CDCl_3$) of **5ba**



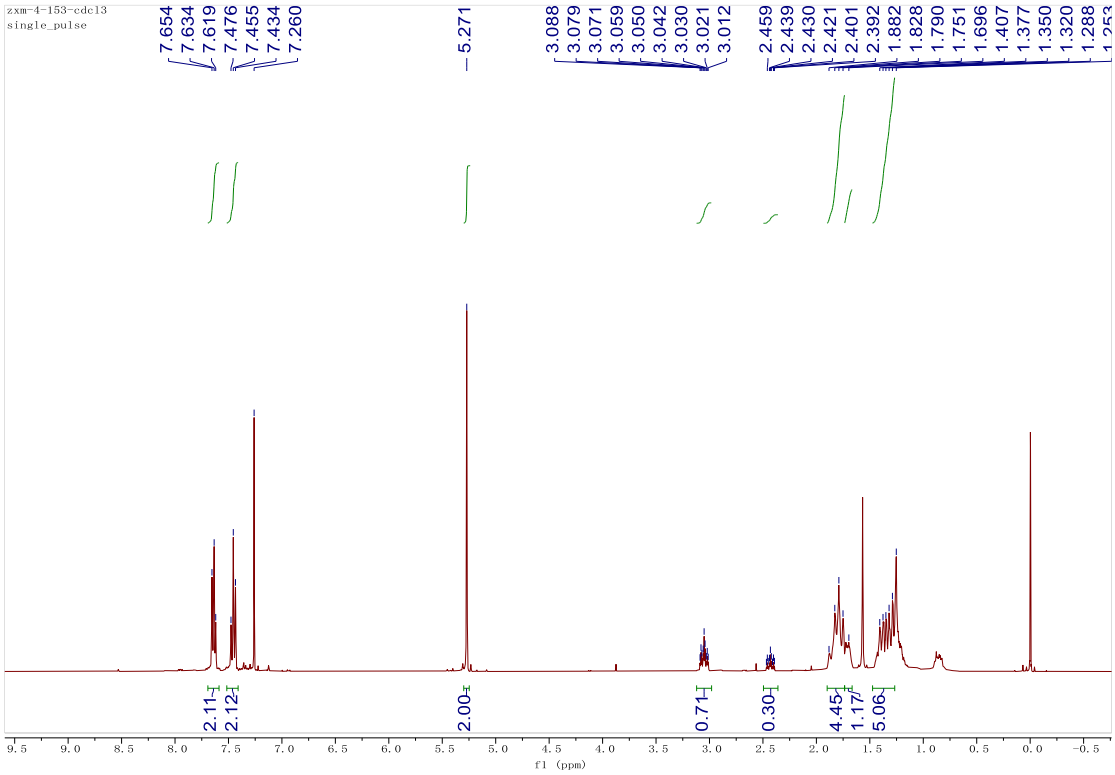
^{13}C NMR (101 MHz, $CDCl_3$) of **5ba**



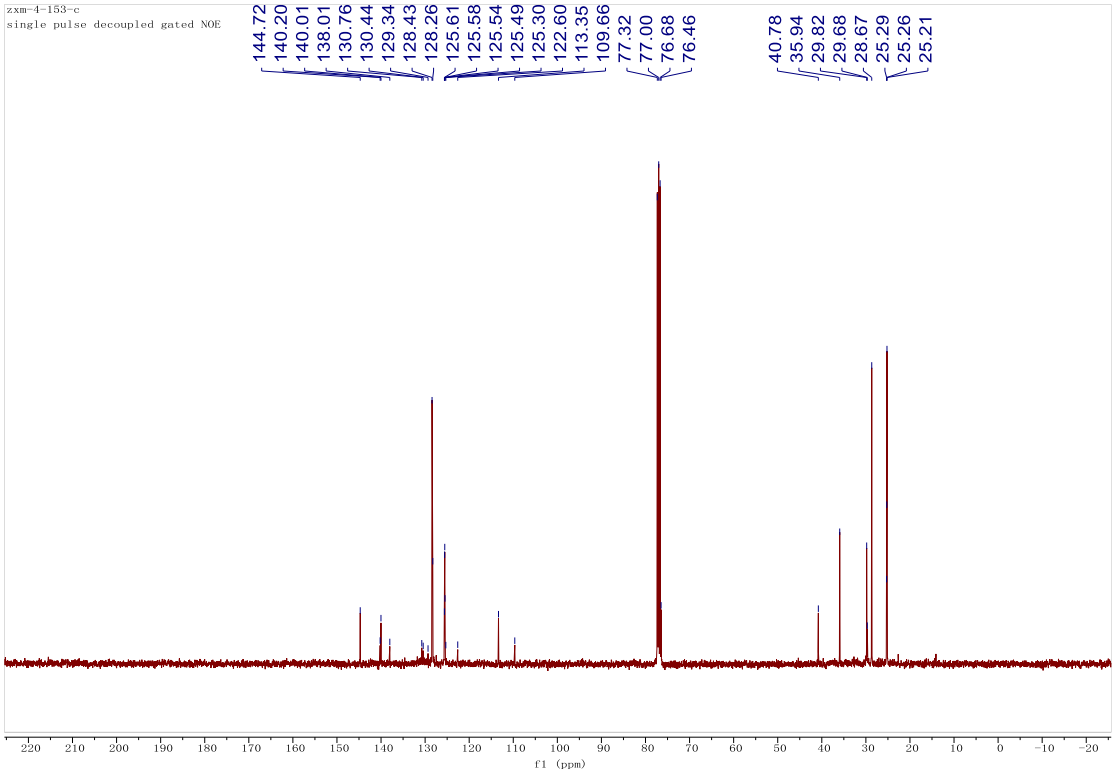


5ca

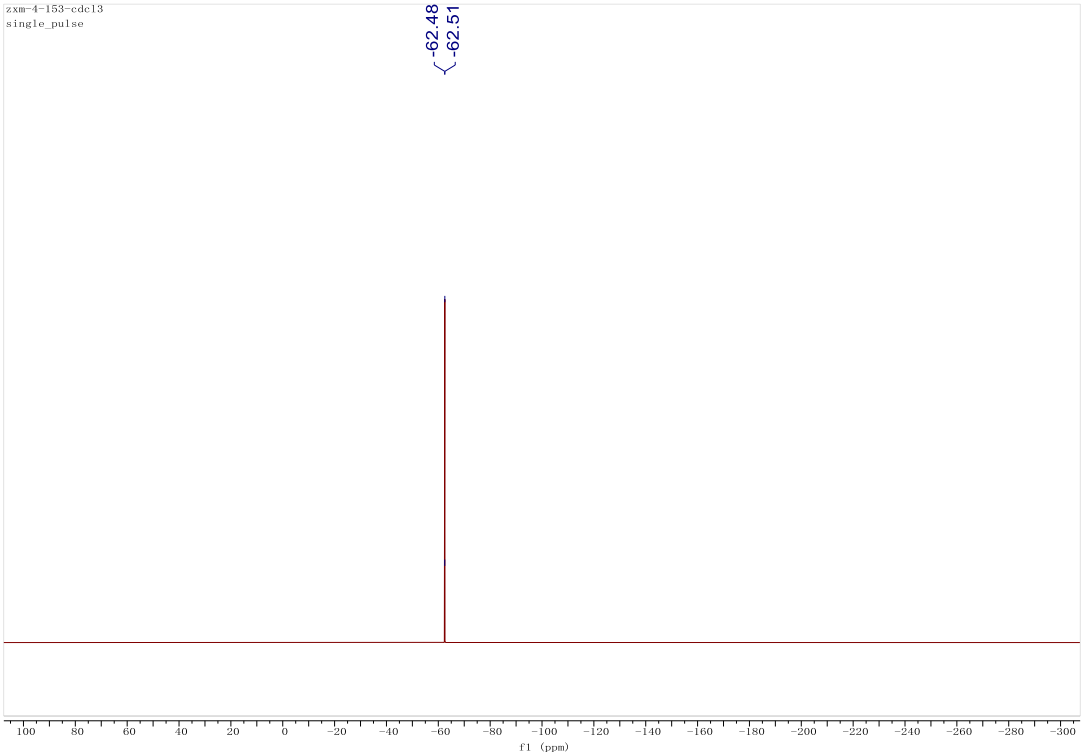
^{1}H NMR (400 MHz, $CDCl_3$) of **5ca**

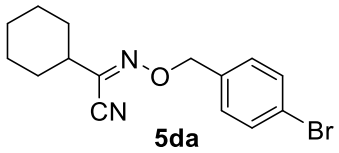


^{13}C NMR (101 MHz, $CDCl_3$) of **5ca**



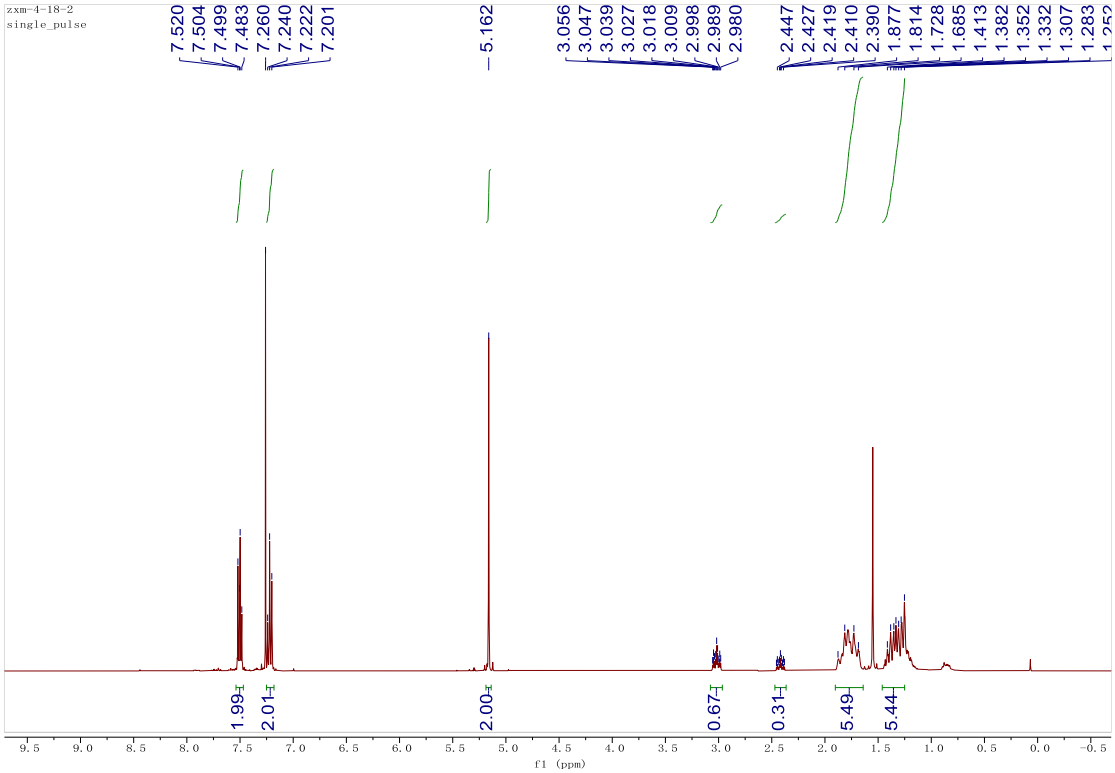
^{19}F NMR (376 MHz, $CDCl_3$) of **5ca**



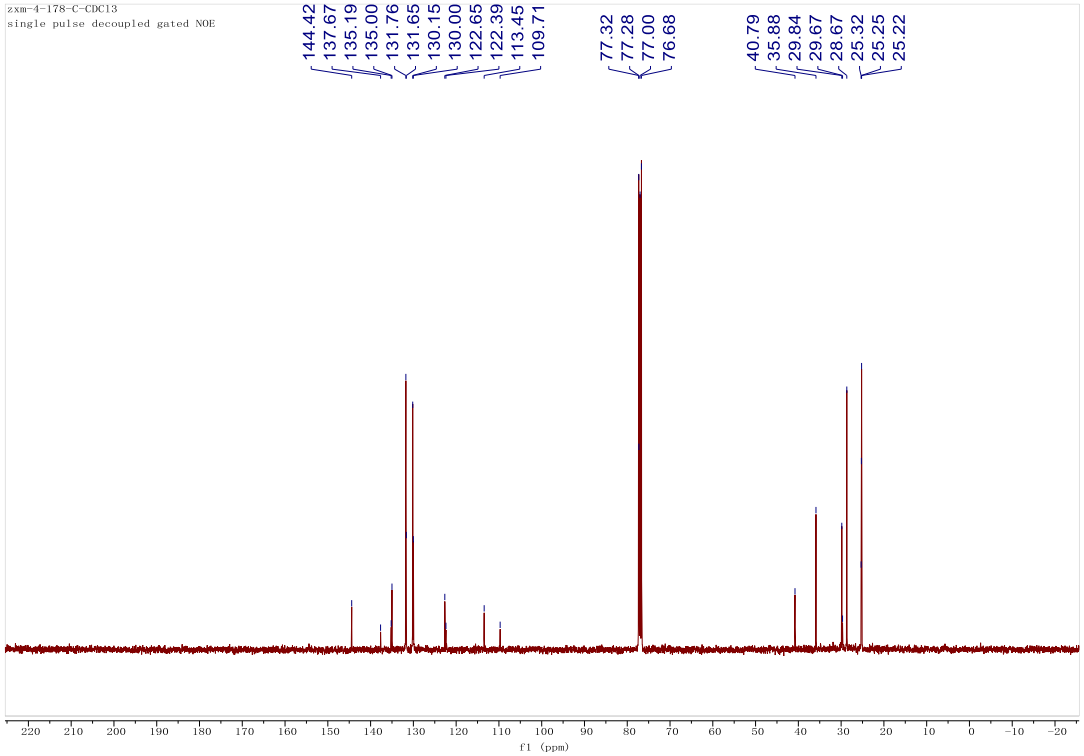


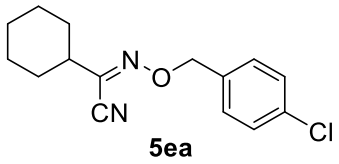
5da

^{1}H NMR (400 MHz, $CDCl_3$) of **5da**



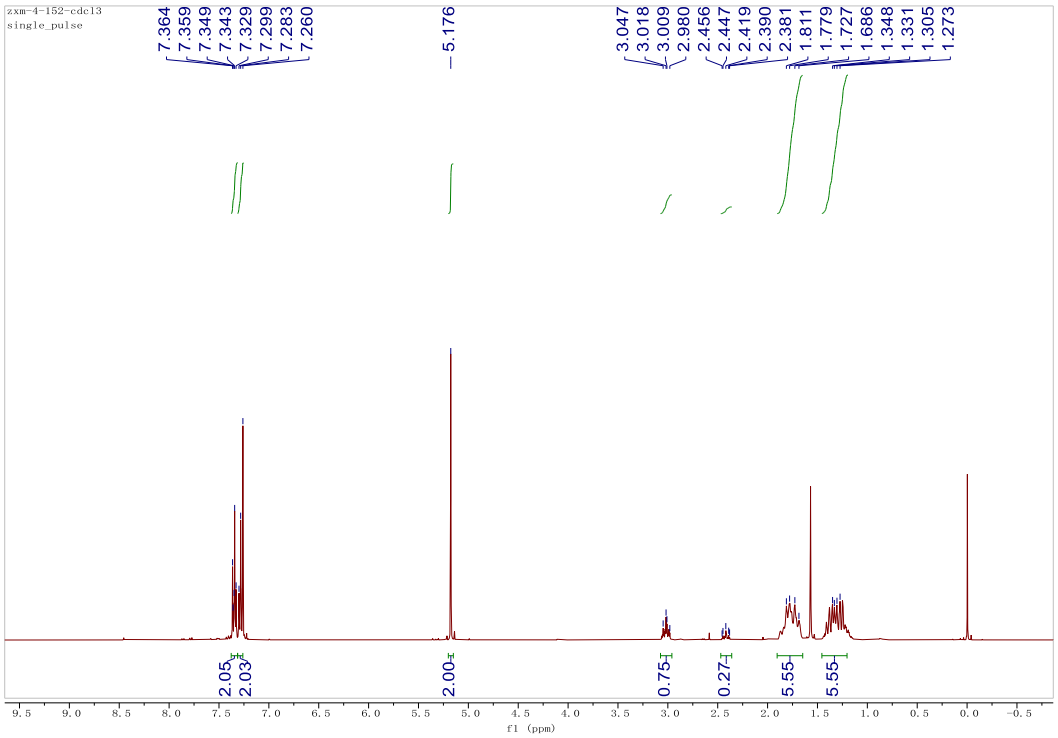
^{13}C NMR (101 MHz, $CDCl_3$) of **5da**



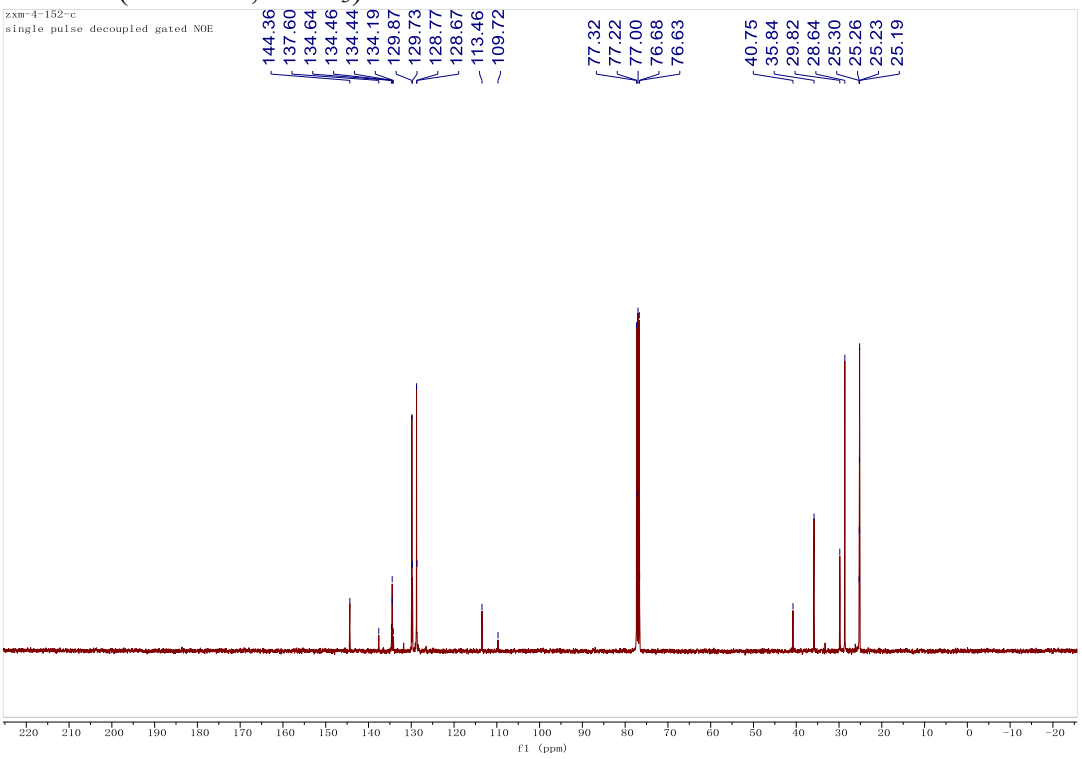


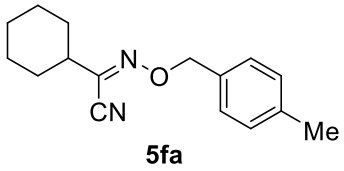
5ea

^{1}H NMR (400 MHz, $CDCl_3$) of **5ea**



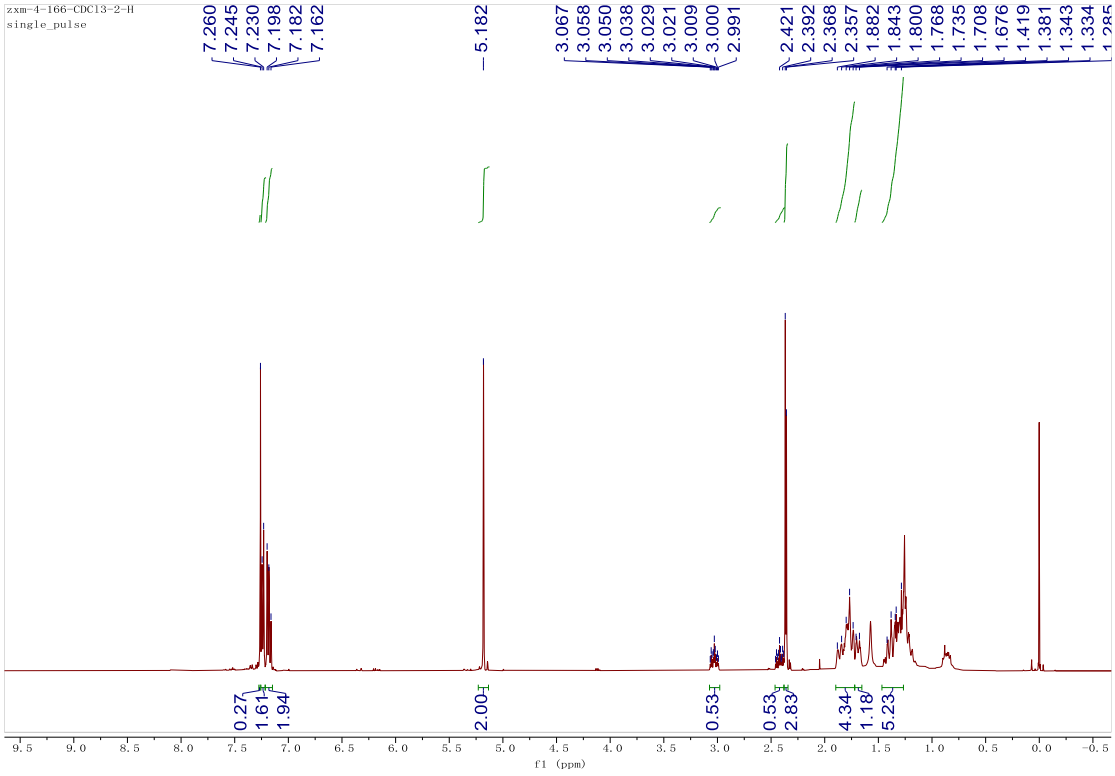
^{13}C NMR (101 MHz, $CDCl_3$) of **5ea**



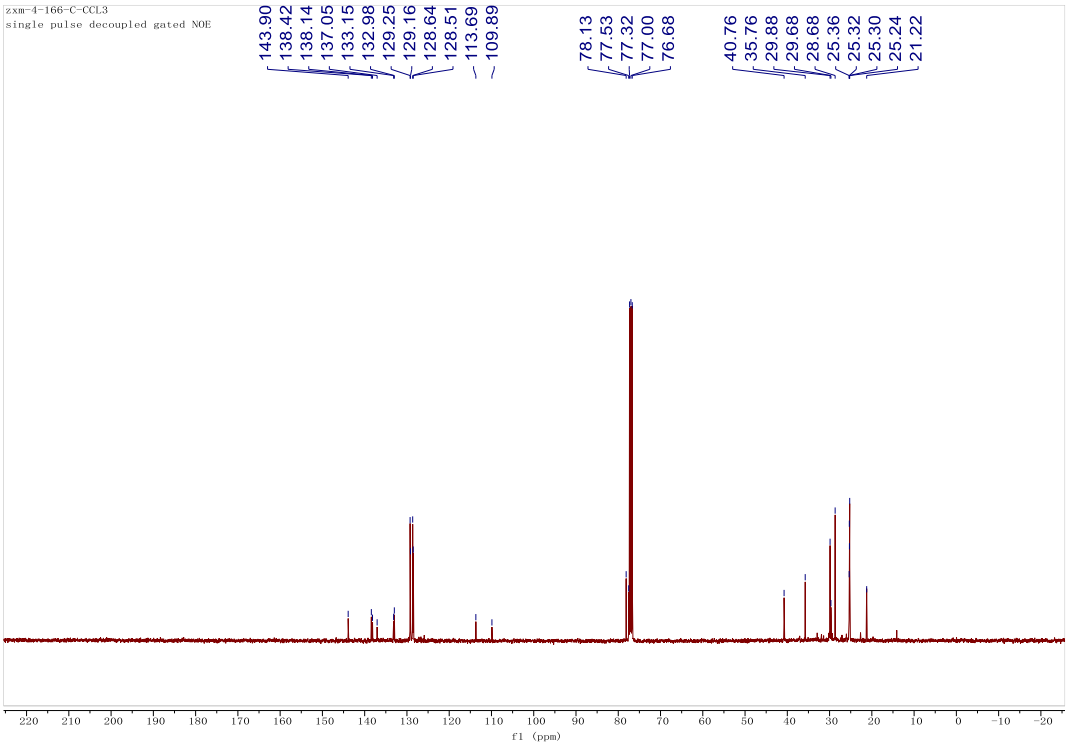


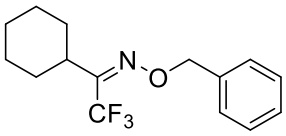
5fa

^{1}H NMR (400 MHz, $CDCl_3$) of **5fa**



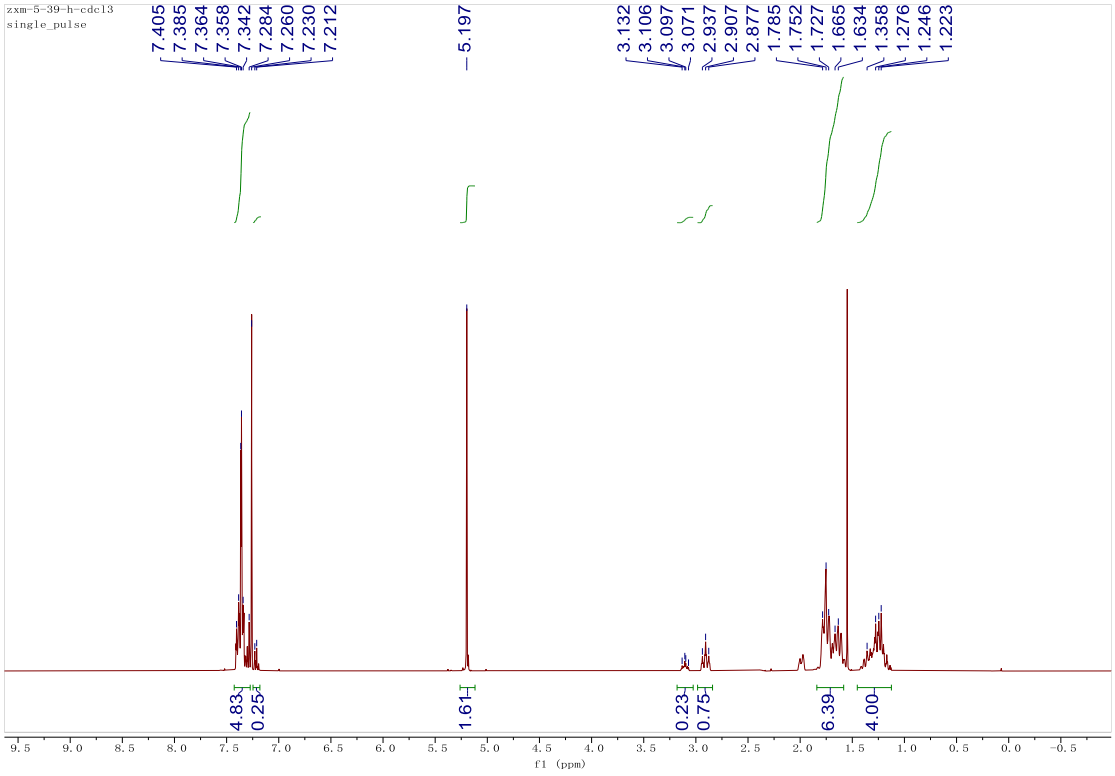
^{13}C NMR (101 MHz, $CDCl_3$) of **5fa**



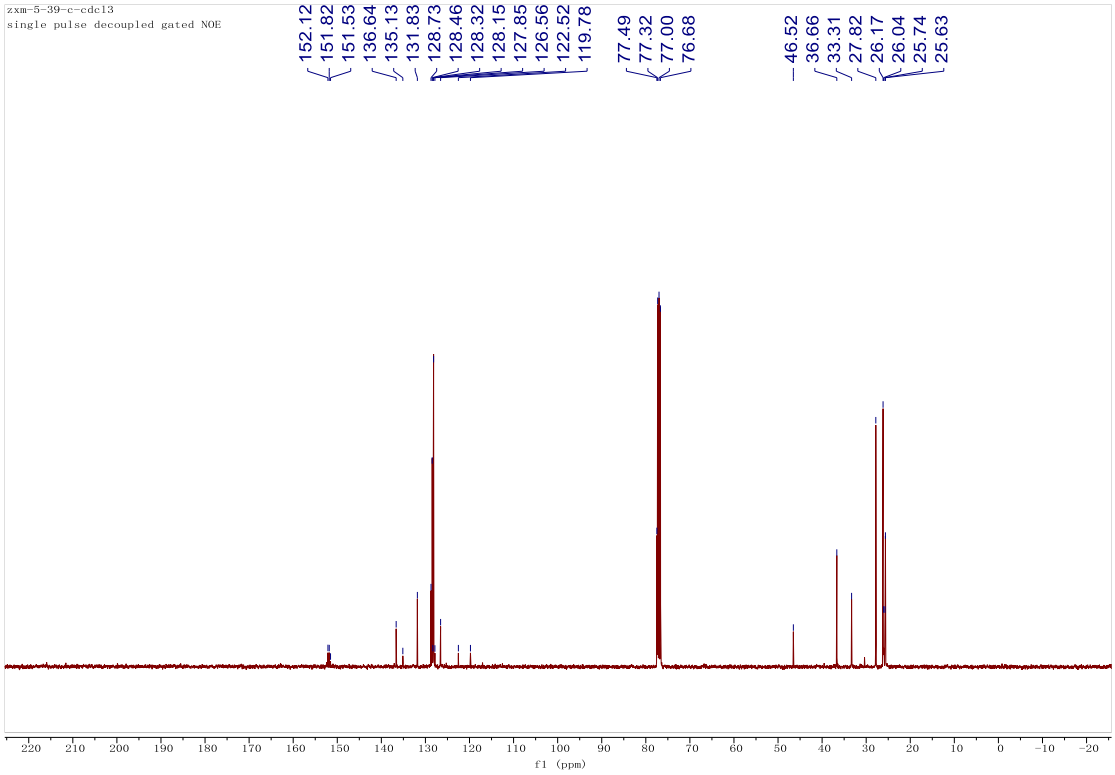


5ga

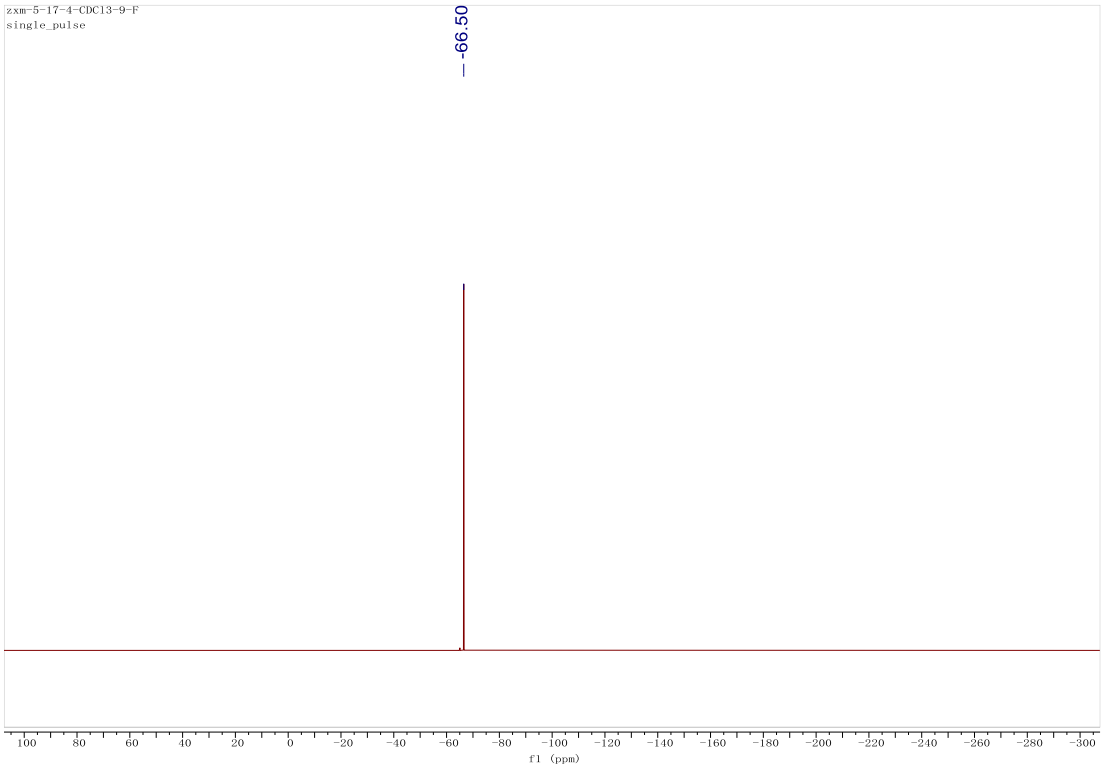
^{1}H NMR (400 MHz, $CDCl_3$) of **5ga**

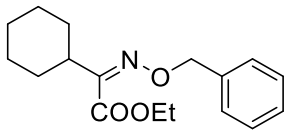


^{13}C NMR (101 MHz, $CDCl_3$) of **5ga**



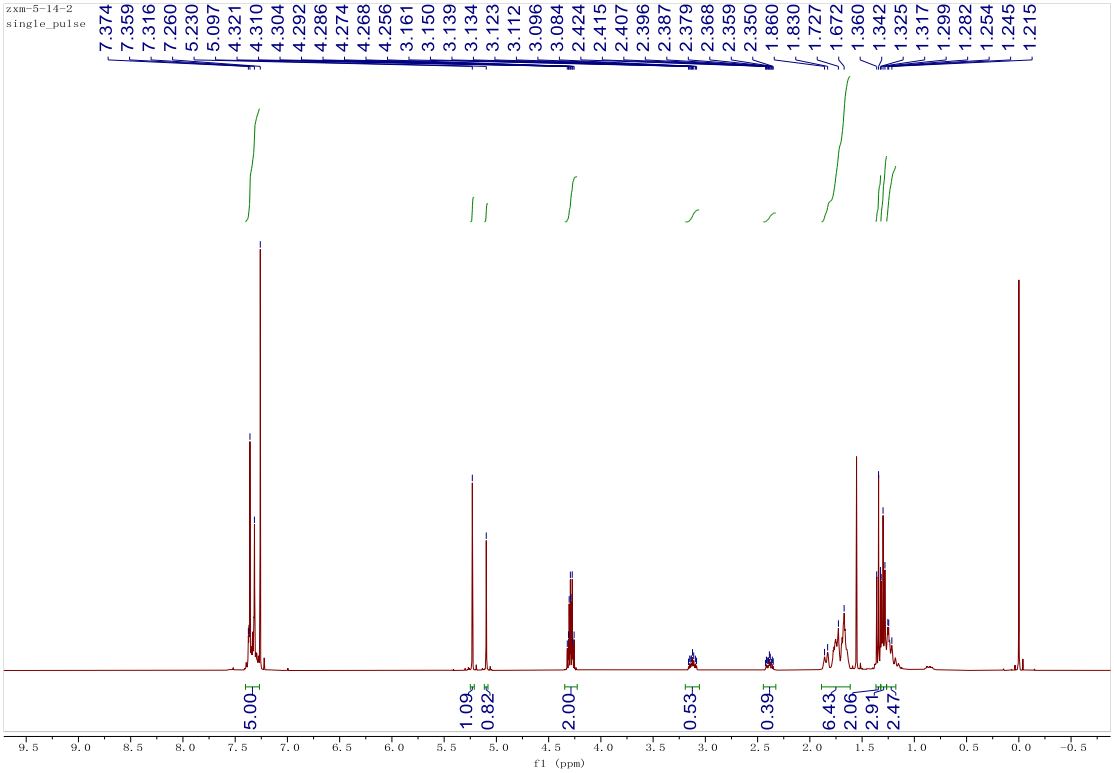
^{19}F NMR (376 MHz, $CDCl_3$) of **5ga**



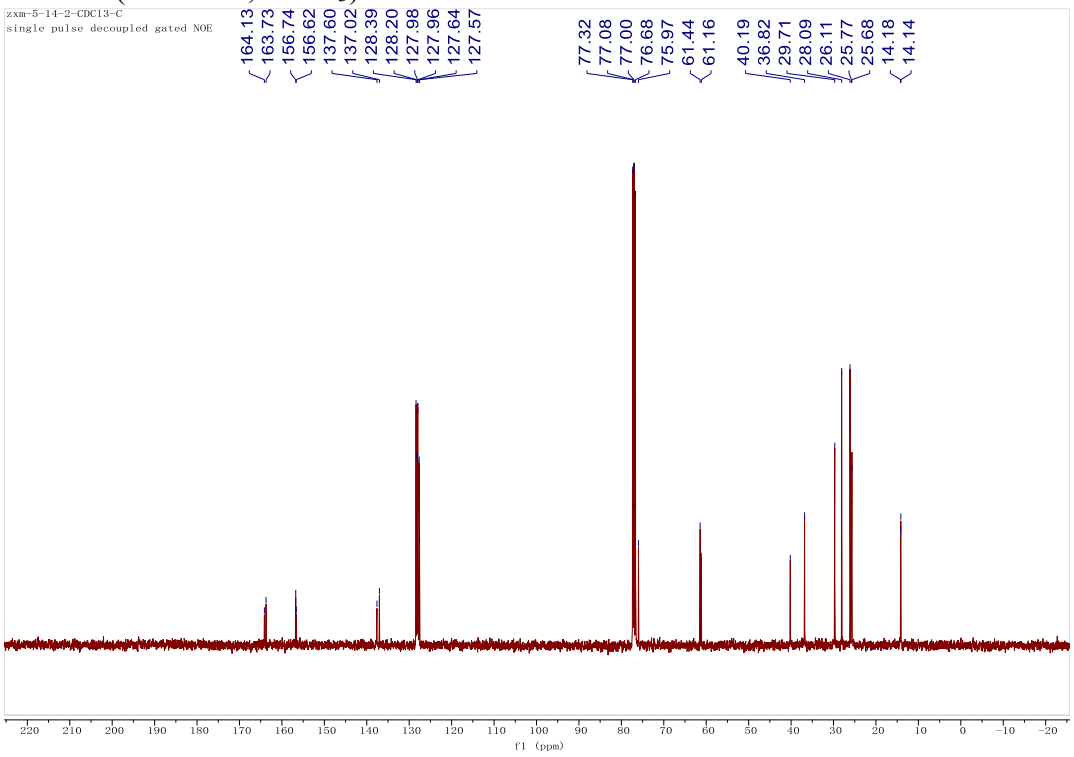


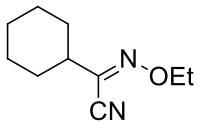
5ha

^{1}H NMR (400 MHz, $CDCl_3$) of **5ha**



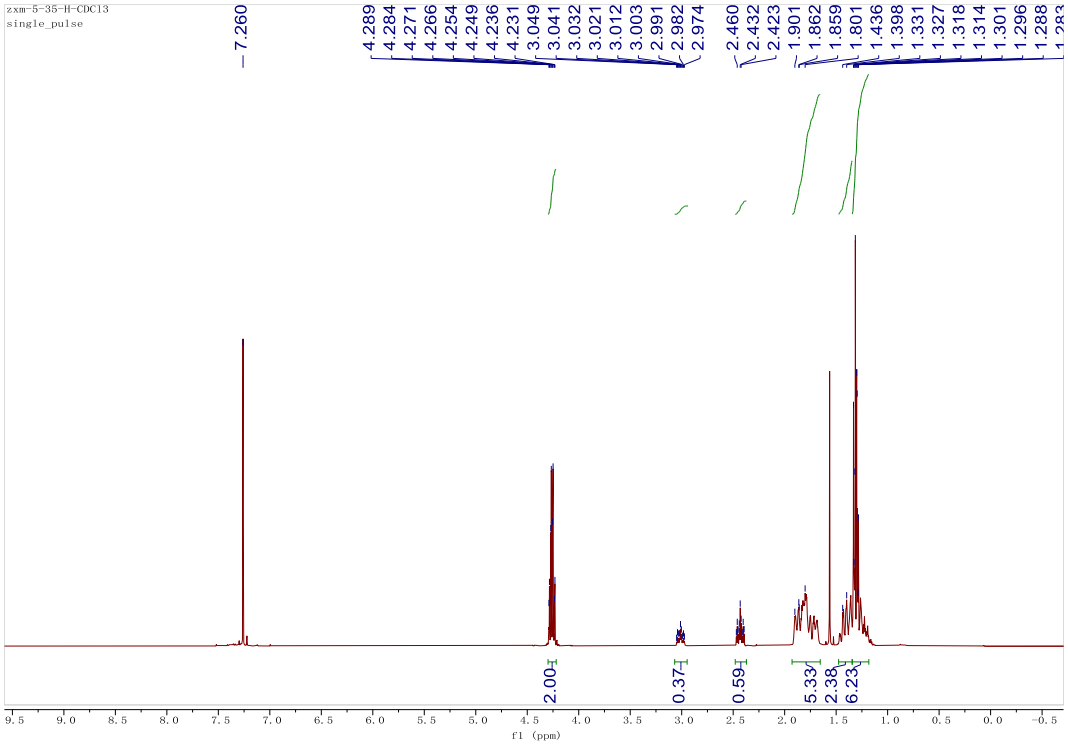
^{13}C NMR (101 MHz, $CDCl_3$) of **5ha**



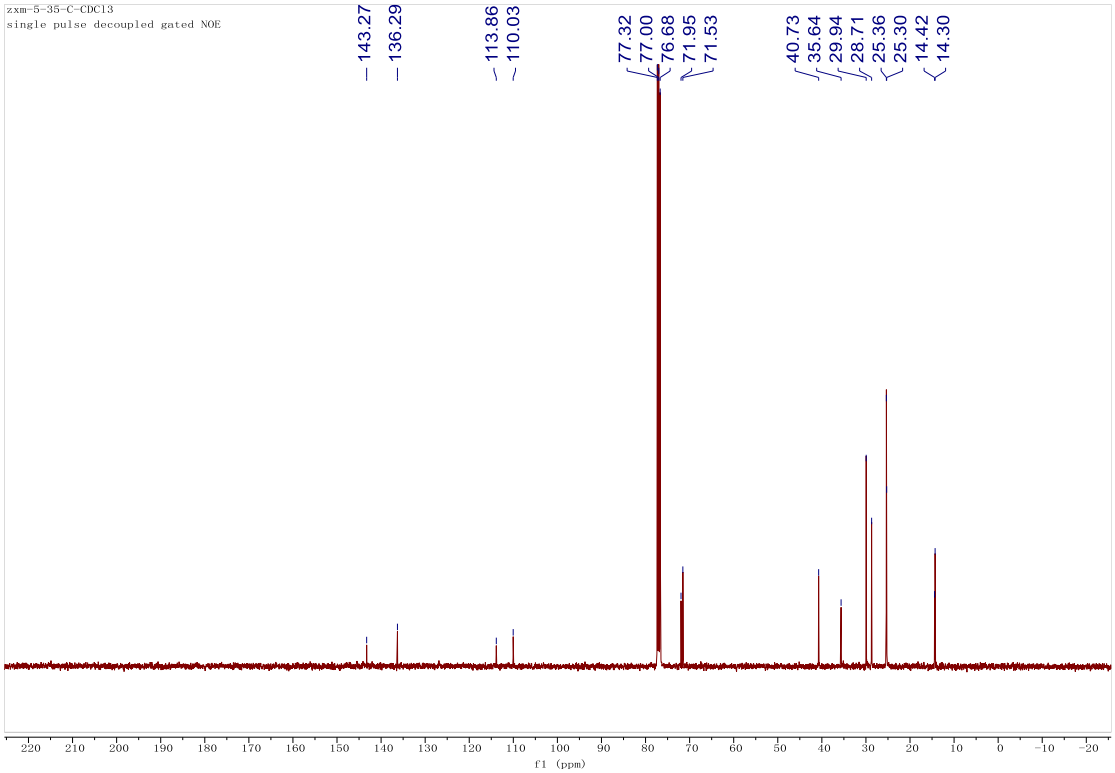


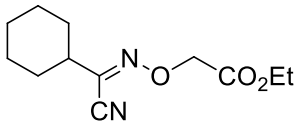
5ia

^{1}H NMR (400 MHz, $CDCl_3$) of **5ia**



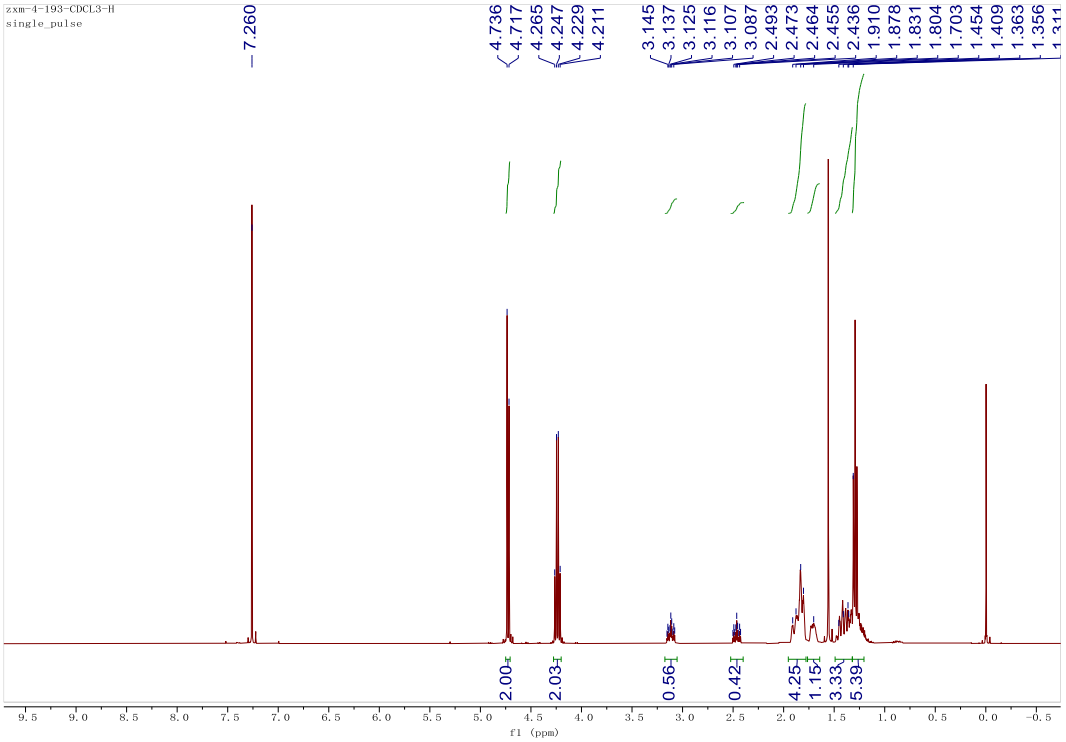
^{13}C NMR (101 MHz, $CDCl_3$) of **5ia**



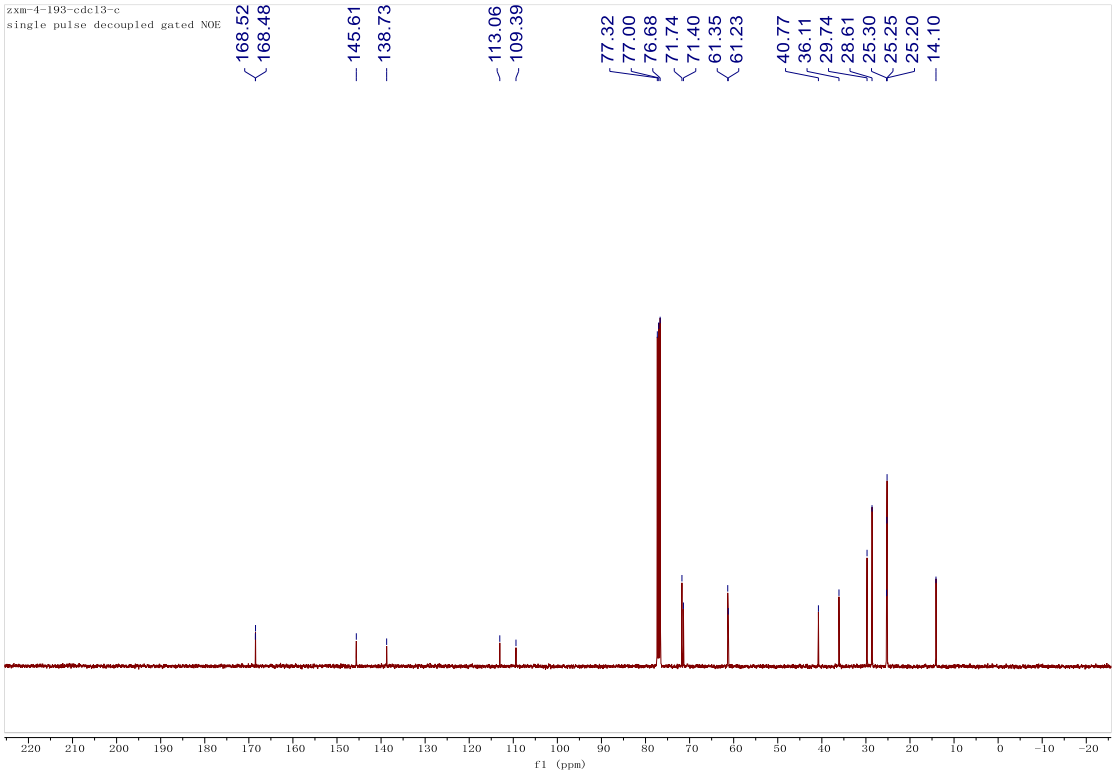


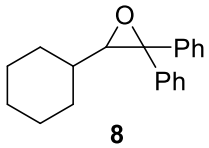
5ja

^{1}H NMR (400 MHz, $CDCl_3$) of **5ja**



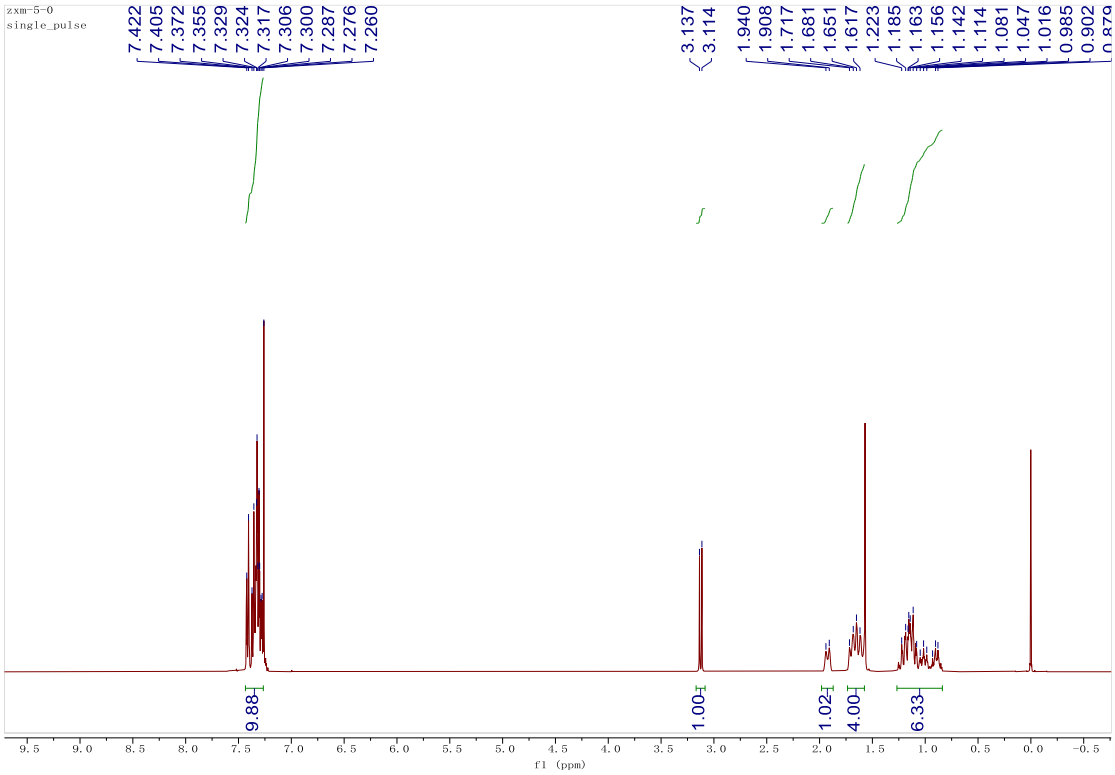
^{13}C NMR (101 MHz, $CDCl_3$) of **5ja**



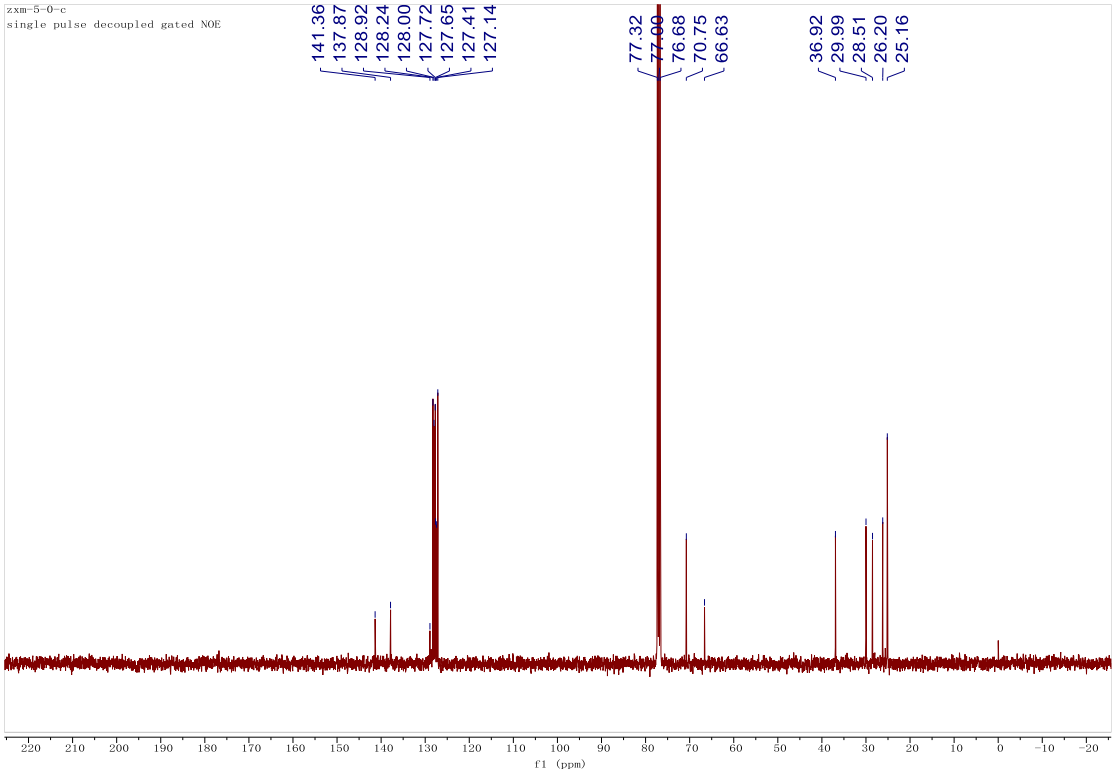


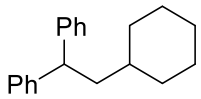
8

^{1}H NMR (400 MHz, $CDCl_3$) of **8**



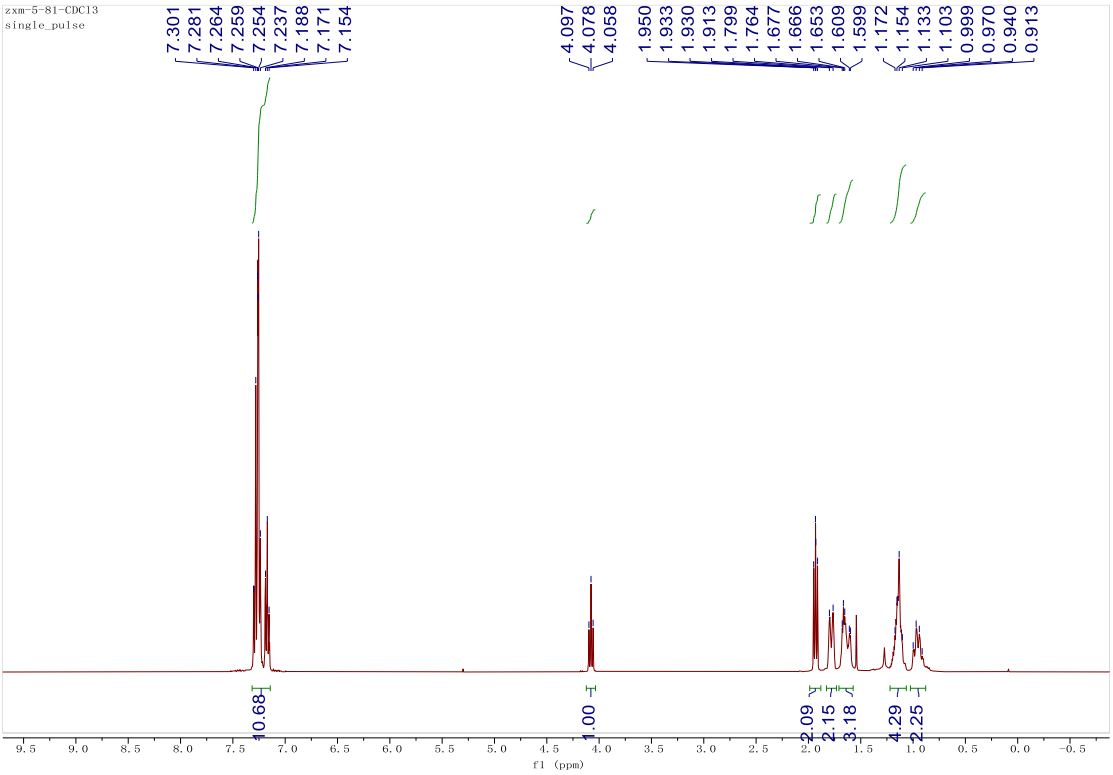
^{13}C NMR (101 MHz, $CDCl_3$) of **8**



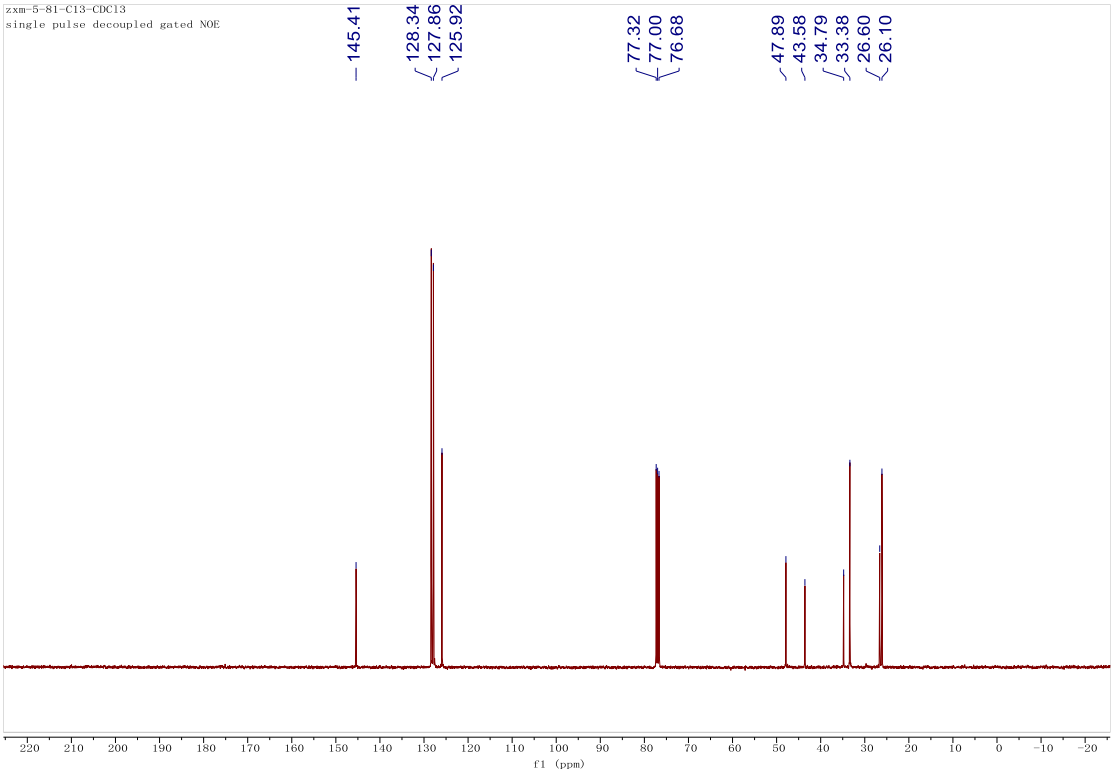


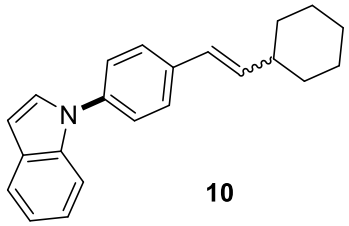
9

^{1}H NMR (400 MHz, $CDCl_3$) of **9**



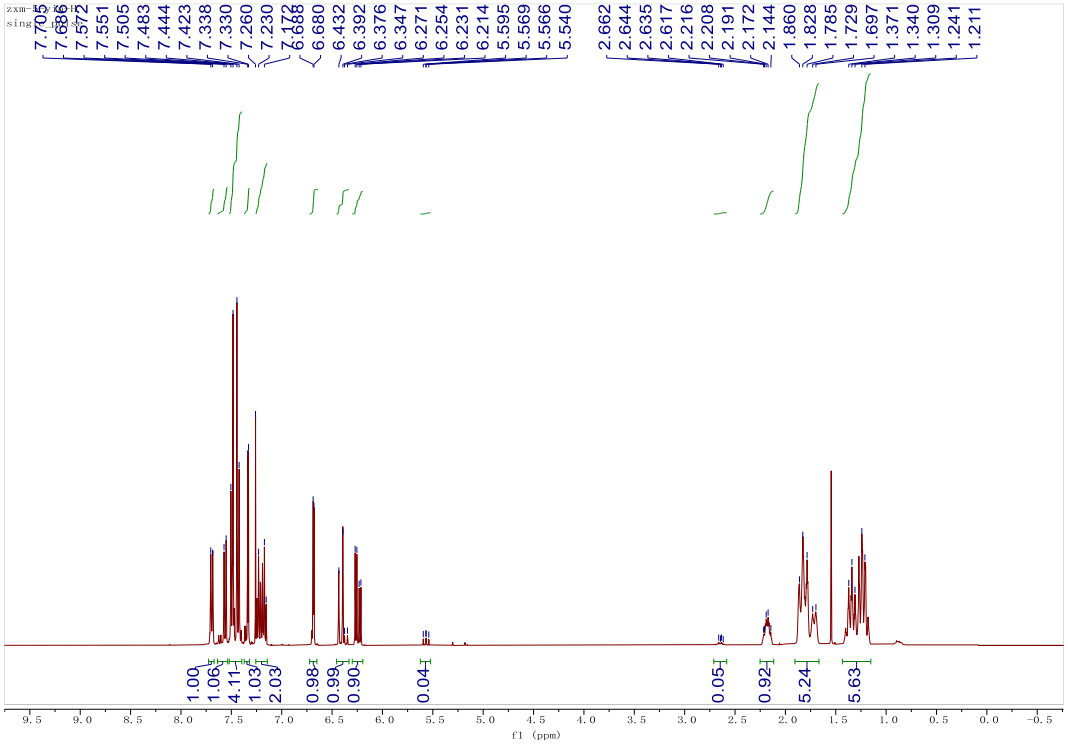
^{13}C NMR (101 MHz, $CDCl_3$) of **9**



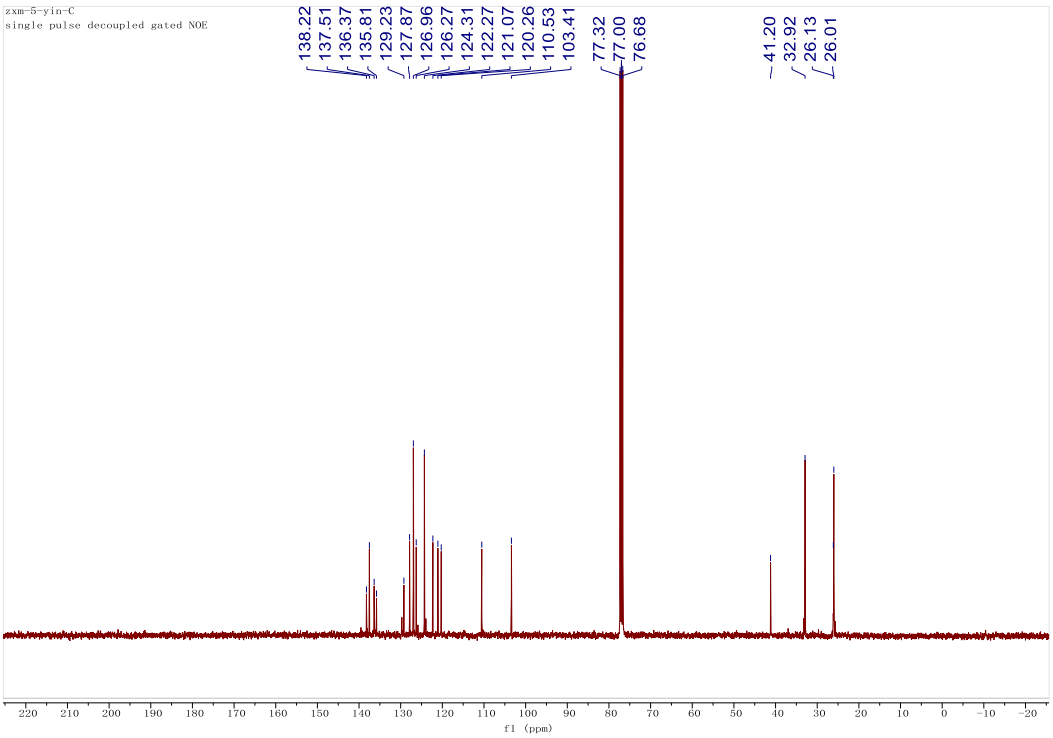


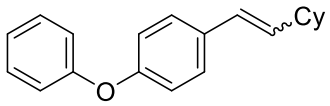
10

^{1}H NMR (400 MHz, $CDCl_3$) of **10**



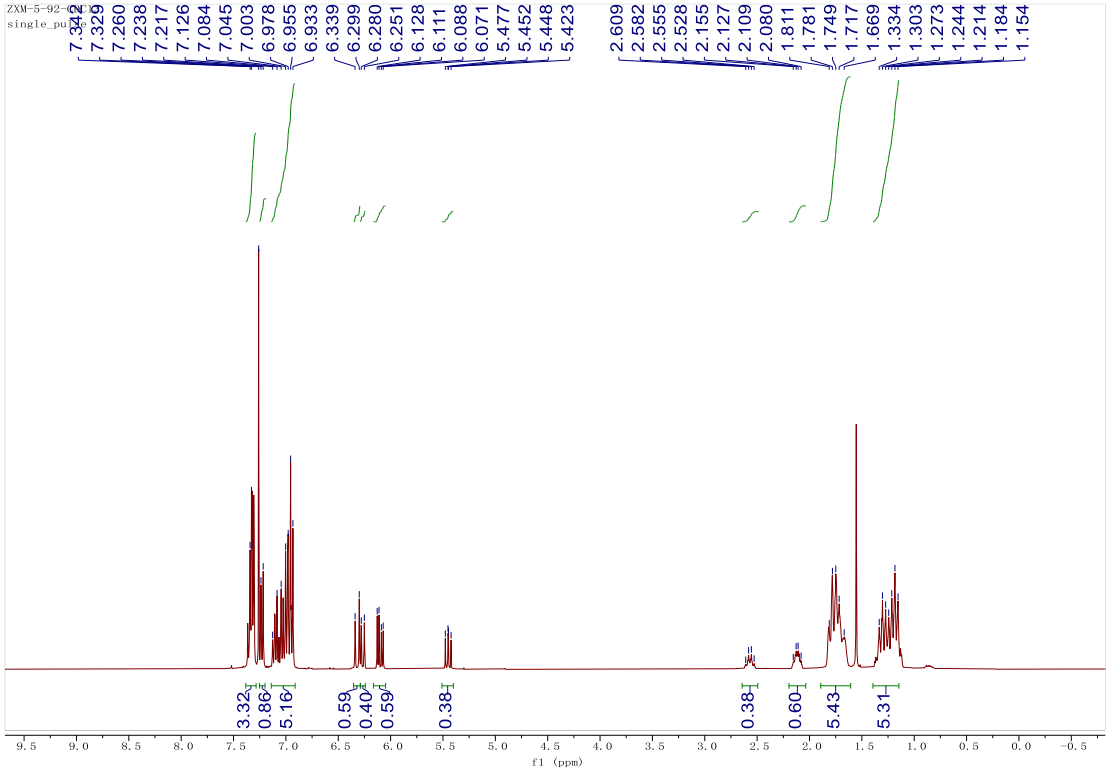
^{13}C NMR (101 MHz, $CDCl_3$) of **10**





11

^{1}H NMR (400 MHz, $CDCl_3$) of **11**



^{13}C NMR (101 MHz, $CDCl_3$) of **11**