Electronic Supplementary Information for

Electrochemical deoxygenative homo-couplings of aromatic aldehydes

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1. General information

Reagents were purchased at the highest commercial quality grade and used without further purification, unless otherwise stated. Yields refer to chromatographically and spectroscopically (^{1}H NMR) homogeneous material, unless otherwise stated. Reactions were monitored by preparative thin-layer chromatography (TLC) carried out on 0.25 mm E. Merck silica plates (60F-254), using UV light (254 nm) and TLC stain with 2,4-dinitrophenylhydrazine-sulfuric acid for visualization. Flash chromatography columns were packed with 200-300 mesh silica gel in petroleum (bp. 60-90 ℃). ^{1}H, ^{13}C and ^{19}F NMR data were recorded with Bruker (400 MHz) or Jeol (400 MHz) spectrometers with tetramethylsilane as an internal standard. All chemical shifts (δ) are reported in ppm and coupling constants (*J*) in Hz. All chemical shifts were reported relative to tetramethylsilane (0 ppm for ^{1}H), $CDCl_3$ (77.0 ppm for ^{13}C).

2. Electrode materials and dimensions

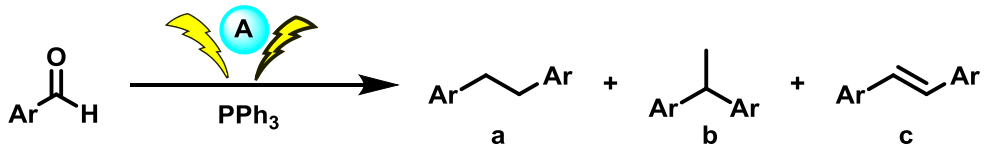
The instrument for undivided electrolysis is IKA® ElectraSyn 2.0 with carousel. The electrodes used in IKA® ElectraSyn 2.0 were purchased from IKA Company. The anodic electrode was the carbon electrode (3.0 cm × 0.8 cm × 0.2 cm) (3.0 cm is the height of the electrode immersed in the solution) and the cathodic electrode was the nickel plate (3.0 cm × 0.8 cm × 0.2 cm).

IKA ElectraSyn 2.0

IKA Carousel complete

3. General procedure for the electrochemical deoxygenative homo-couplings of aromatic aldehydes

General procedure A



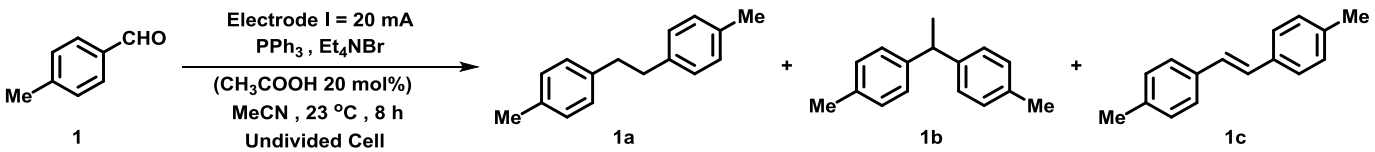
The electrolysis was carried out in the electrolysis cell of IKA® ElectraSyn 2.0. The anodic electrode was the carbon electrode (3.0 cm × 0.8 cm × 0.2 cm) and the cathodic electrode was the nickel plate (3.0 cm × 0.8 cm × 0.2 cm). Aromatic aldehyde (1.0 mmol), Et_4NBr (210.0 mg, 1.0 mmol), PPh_3 (787.0 mg, 3.0 mmol), MeCN (4 mL) were added to an oven-dried undivided cell (6 mL) equipped with a stirring bar (the order of the addition did not affect the result). Then the reaction mixture was stirred and electrolyzed at a constant current of 20 mA at room temperature for 8 h. When the reaction was finished, the solvent was evaporated under vacuum and the crude material was purified by column chromatography on silica gel or preparative thin-layer chromatography (TLC) to furnish the desired product.

General procedure B

The electrolysis was carried out in the electrolysis cell of IKA® ElectraSyn 2.0. The anodic electrode was the carbon electrode (3.0 cm × 0.8 cm × 0.2 cm) and the cathodic electrode was the nickel plate (3.0 cm × 0.8 cm × 0.2 cm). Aromatic aldehyde (1.0 mmol), Et_4NBr (210.0 mg, 1.0 mmol), PPh_3 (787.0 mg, 3.0 mmol), DCM (4 mL) were added to an oven-dried undivided cell (6 mL) equipped with a stirring bar (the order of the addition did not affect the result). Then the reaction mixture was stirred and electrolyzed at a constant current of 20 mA at room temperature for 8 h. When the reaction was finished, the solvent was evaporated under vacuum and the crude material was purified by column chromatography on silica gel or preparative thin-layer chromatography (TLC) to furnish the desired product.

4. Optimization of the reaction conditions

Table S1. Optimization of the electrode

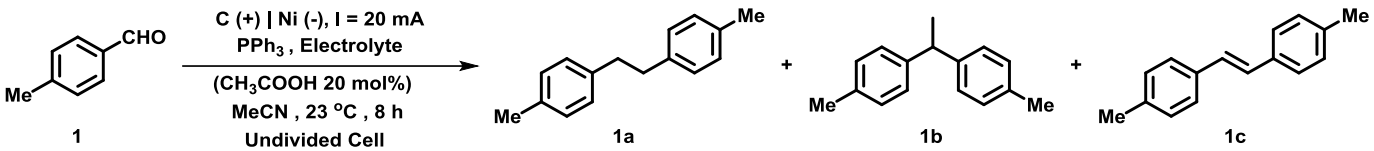


Entry	Electrode	Yield[a]	1a : 1b : 1c[b]
1	**C (+)|Ni (-)**	**76%**	**3.7: 1 : 0**
2	C (+)|C (-)	66%	14.3: 3.6 : 1
3	C (+)|Pt (-)	50%	11: 1 : 3.3

4	C (+)|SST (-)	52%	6.7: 1 : 2.4

[a] The total isolated yields of **1a**, **1b** and **1c** were reported after chromatography. [b] The ratios were determined by ^{1}H NMR analysis.

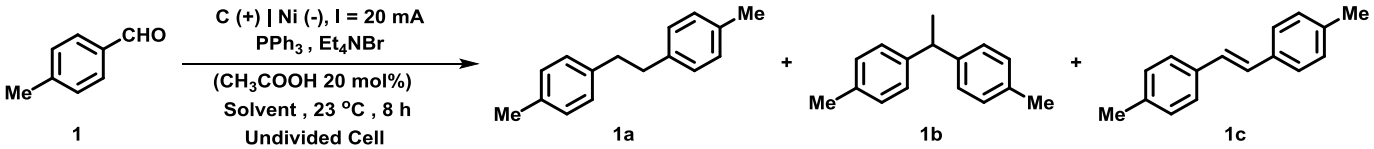
Table S2. Optimization of the electrolyte.



Entry	Electrolyte	Yield[a]	1a : 1b : 1c[b]
1	**Et_4NBr**	**76%**	**3.7: 1 : 0**
2	Et_4NI	67%	14: 2.6 : 1
3	Et_4NBF_4	18%	1.3: 1 : 0
4	$^nBu_4NBr$	66%	10: 1 : 0

[a] The total isolated yields of **1a**, **1b** and **1c** were reported after chromatography. [b] The ratios were determined by ^{1}H NMR analysis.

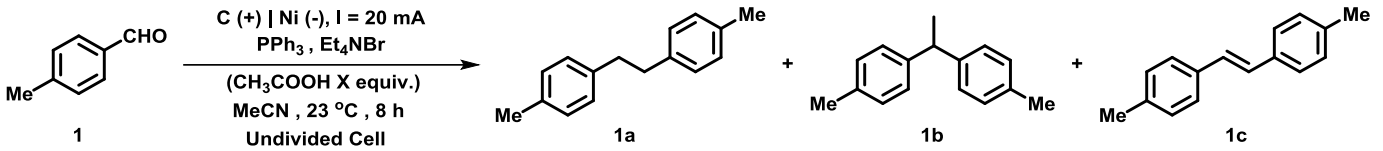
Table S3. Optimization of the solvent



Entry	Solvent	Yield[a]	1a : 1b : 1c[b]
1	**MeCN**	**76%**	**3.7: 1 : 0**
2	DCM	39%	0: 0 : 1
3	DMF	42%	8.3: 1.6 : 1
4	NMP	38%	6.3: 1.8 : 1
5	DCE	25%	0: 0 : 1
6	DMSO	trace	

[a] The total isolated yields of **1a**, **1b** and **1c** were reported after chromatography. [b] The ratios were determined by ^{1}H NMR analysis.

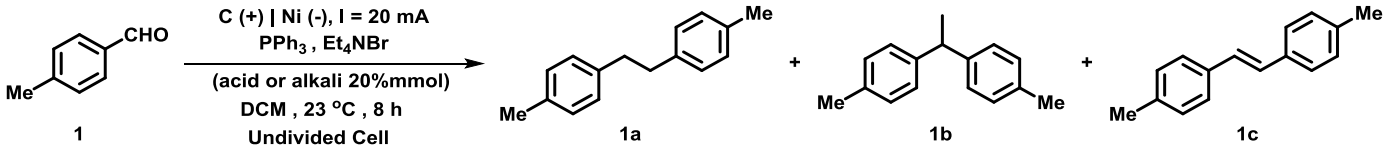
Table S4. Optimization of the CH_3COOH content.



Entry	CH_3COOH (equiv.)	Yield[a]	1a : 1b : 1c[b]
1	**0.2**	**76%**	**3.7: 1 : 0**
2	—	62%	5 : 1 : 0
3	0.4	52%	3.3 : 1 : 0
4	1.0	20%	11: 1 : 0
5	2.0	trace	

[a] The total isolated yields of **1a**, **1b** and **1c** were reported after chromatography. [b] The ratios were determined by ^{1}H NMR analysis.

Table S5. Optimization of the acid or alkali in condition B



Entry	acid or alkali	Yield[a]	1a : 1b : 1c[b]
1	**CH3COOH**	**39%**	**0: 0 : 1**
2	2,6-Lutidine	37%	0 : 0 : 1
3	HCOOH	38%	0 : 0 : 1
4	TfOH	30%	0: 0 : 1
5	DIPEA	30%	

[a] The total isolated yields of **1a**, **1b** and **1c** were reported after chromatography. [b] The ratios were determined by ^{1}H NMR analysis.

5. Procedure for gram-scale synthesis

The electrolysis was carried out in the electrolysis cell of IKA® ElectraSyn 2.0. The anodic electrode was the carbon electrode (3.0 cm × 0.8 cm × 0.2 cm) and the cathodic electrode was the nickel plate (3.0 cm × 0.8 cm × 0.2 cm). According to General Procedure A, starting 4-(methylthio)benzaldehyde (0.9 mL, 7.0 mmol) and PPh_3 (5.5 g, 21 mmol) were added to an oven-dried undivided cell with MeCN (8 mL) equipped

with a stirring bar. The reaction mixture was stirred and electrolyzed at a constant current of 20 mA at room temperature for 30 h. Solvent was evaporated under vacuum and the crude material was purified by column chromatography (petroleum ether) to afford the title compound as a white solid in 38% yield (0.36 g).

6. Procedure for cyclic voltammetry (CV)

Cyclic voltammetry was performed in a three-electrode cell under air at room temperature. A steady glassy carbon disk electrode (3 mm in diameter) was used as the working electrode; a platinum plate was used as the counter electrode; the reference was an $Ag/AgNO_3$ electrode with (0.01 M) $AgNO_3$ in acetonitrile. 8 mL acetonitrile solvent containing (0.1 M) Et_4NBr was used as the blank. The spectrums were recorded with the scan rate of 100 mV s^{-1} (starting from 0 V). The CV of Background, PPh_3 and *p*-Tolualdehyde were conducted respectively.

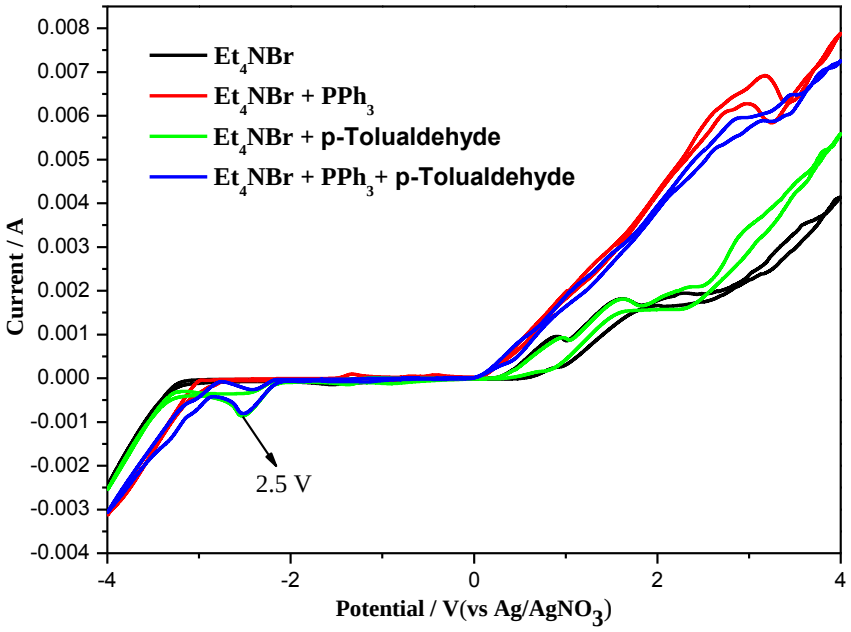
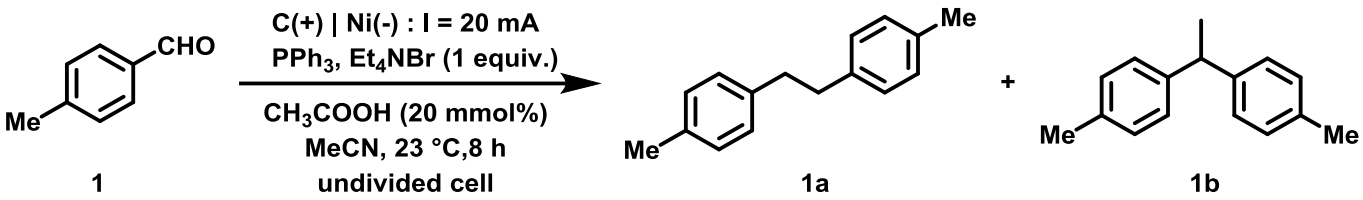


Fig 1. Cyclic voltammograms recorded in (0.1 M) Et_4NBr-MeCN solution: scan rate: 100 mV s^{-1}; starting potential: 0 V; glass carbon (3 mm diameter, Working Electrode); platinum plate (Counter Electrode); $Ag/AgNO_3$ (0.01 M) $AgNO_3$ in MeCN (Reference Electrode); Concentrations: PPh_3 (0.8 mmol / 8 ml MeCN), *p*-Tolualdehyde (0.8 mmol / 8 ml MeCN), PPh_3 + *p*-Tolualdehyde (0.8 mmol PPh_3 + 0.8 mmol *p*-Tolualdehyde / 8 ml MeCN).

7. Detail descriptions for products of condition A

1,2-di-*p*-tolylethane (1a) and 4,4'-(ethane-1,1-diyl)bis(methylbenzene) (1b)



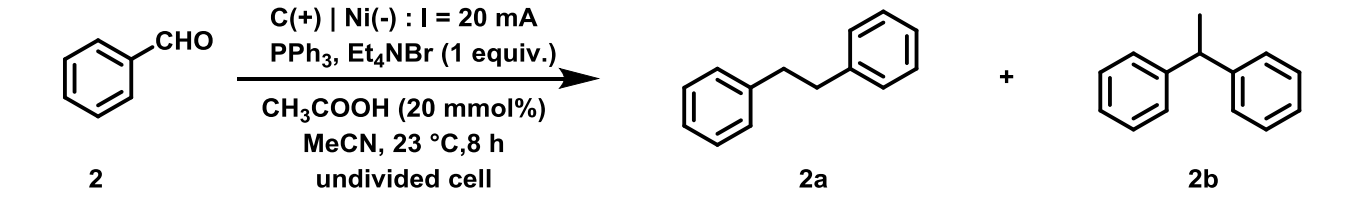
1 1a 1b

The starting *p*-Tolualdehyde (118 μL, 1.0 mmol) was reacted with PPh_3 (787.0 mg, 3.0 mmol) according to general procedure A. The crude product was purified by column chromatography on silica gel (petroleum ether) to afford the title compound as a white solid in 76% yield (79.8 mg). **1a** : **1b** = 3.7 : 1 (The proportion was determined by ^{1}H NMR).

The reported NMR spectra were obtained with the sample purified by preparative thin-layer chromatography (TLC) on silica gel. **1a** : **1b** = 3.2 : 1; Rf (petroleum ether): 0.5; **1a ^{1}H NMR** (400 MHz, Chloroform-d) δ 7.18 (s, 8H), 2.94 (s, 4H), 2.41 (s, 6H); **1b ^{1}H NMR** (400 MHz, Chloroform-d) δ 7.18 (s, 8H), 4.16 (q, *J* = 7.2 Hz, 1H), 2.39 (s, 6H), 1.69 (d, *J* = 7.3 Hz, 3H); **1a + 1b ^{13}C NMR** (101 MHz, Chloroform-d) δ 143.73, 138.96, 135.38, 129.11, 128.40, 127.52, 44.04, 37.78, 22.12, 21.15.

Spectroscopic data were in good agreement with literature.[1, 2]

1,2-diphenylethane (2a) and ethane-1,1-diyldibenzene (2b)



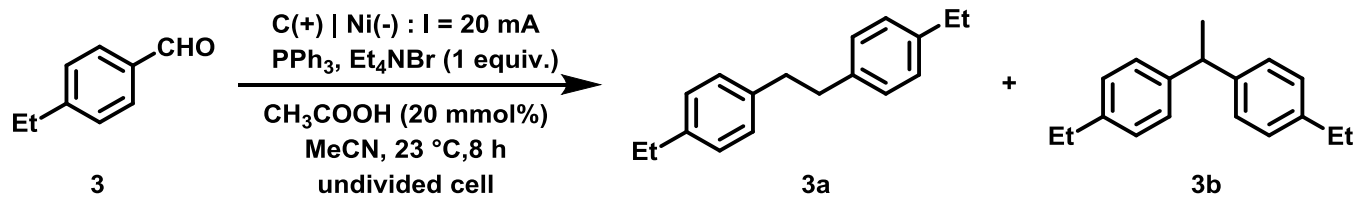
2 2a 2b

The starting benzaldehyde (102.0 μL, 1.0 mmol) was reacted with PPh_3 (787.0 mg, 3.0 mmol) according to general procedure A. The crude product was purified by column chromatography on silica gel (petroleum ether) to afford the title compound as a white solid in 52% yield (47.3 mg). **2a** : **2b** = 5.6 : 1 (The proportion was determined by ^{1}H NMR).

The reported NMR spectra were obtained with the sample purified by preparative thin-layer chromatography (TLC) on silica gel. Rf (petroleum ether): 0.5; **1a ^{1}H NMR** (400 MHz, Chloroform-d) δ 7.39 – 7.34 (m, 4H), 7.28 (m, 6H), 3.00 (s, 4H). **^{13}C NMR** (101 MHz, Chloroform-d) δ 141.85, 128.52, 128.41, 125.99, 38.05.

Spectroscopic data were in good agreement with literature.[1, 2]

1,2-bis(4-ethylphenyl)ethane (3a) and 4,4'-(ethane-1,1-diyl)bis(ethylbenzene) (3b)



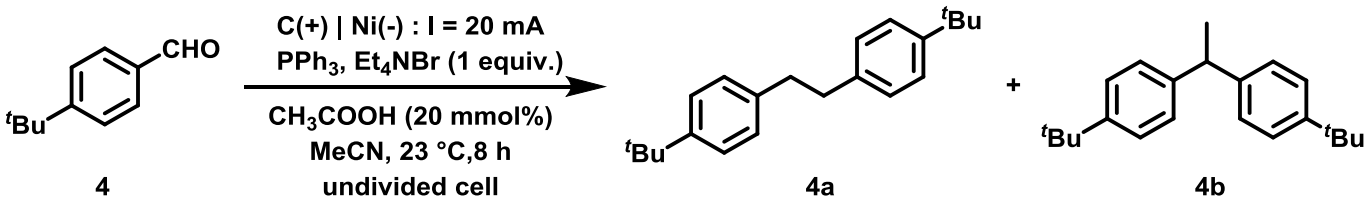
3 3a 3b

The starting 4-ethylbenzaldehyde (137.0 μL, 1.0 mmol) was reacted with PPh_3 (787.0 mg, 3.0 mmol) according to general procedure A. The crude product was purified by column chromatography on silica gel (petroleum ether) to afford the title compound as a white solid in 62% yield (74.0 mg). **3a** : **3b** = 7.7 : 1 (The proportion was determined by ^{1}H NMR).

The reported NMR spectra were obtained with the sample purified by preparative thin-layer chromatography (TLC) on silica gel. **3a** : **3b** = 6.7 : 1; Rf (petroleum ether): 0.5; **3a ^{1}H NMR** (400 MHz, Chloroform-d) δ 7.20 (s, 8H), 2.95 (s, 4H), 2.70 (q, *J* = 7.6 Hz, 4H), 1.30 (t, *J* = 7.6 Hz, 6H); **3b ^{1}H NMR** (400 MHz, Chloroform-d) δ 7.20 (s, 8H), 4.16 (q, *J* = 7.2 Hz, 1H), 2.70 (q, *J* = 7.6 Hz, 4H), 1.68 (d, *J* = 7.2 Hz, 3H), 1.30 (t, *J* = 7.6 Hz, 6H); **3a ^{13}C NMR** (101 MHz, Chloroform-d) δ 141.83, 139.27, 128.41, 127.91, 37.76, 28.56, 15.81.

Spectroscopic data were in good agreement with literature.[3]

1,2-bis(4-(*tert*-butyl)phenyl)ethane (4a) and 4,4'-(ethane-1,1-diyl)bis(*tert*-butylbenzene) (4b)



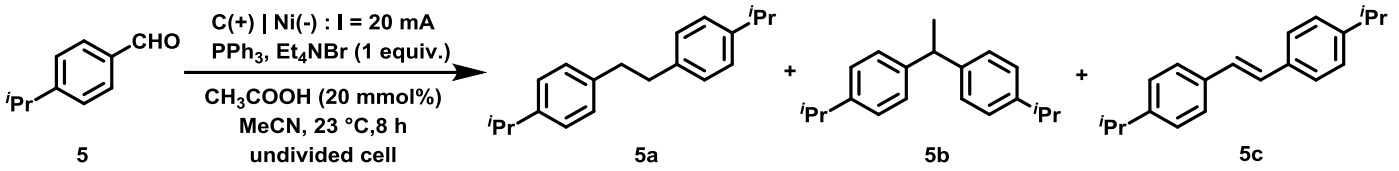
4 4a 4b

The starting 4-(*tert*-butyl)benzaldehyde (167.0 μL, 1.0 mmol) was reacted with PPh_3 (787.0 mg, 3.0 mmol) according to general procedure A. The crude product was purified by column chromatography on silica gel (petroleum ether) to afford the title compound as a white solid in 53% yield (77.7 mg). **4a** : **4b** = 10 : 1 (The proportion was determined by ^{1}H NMR).

The reported NMR spectra were obtained with the sample purified by preparative thin-layer chromatography (TLC) on silica gel. **4a** : **4b** = 8.3 : 1; Rf (petroleum ether): 0.5; **4a ^{1}H NMR** (400 MHz, Chloroform-d) δ 7.46 – 7.40 (m, 4H), 7.31 – 7.25 (m, 4H), 3.00 (s, 4H), 1.43 (s, 18H); **4b ^{1}H NMR** (400 MHz, Chloroform-d) δ 7.46 – 7.40 (m, 4H), 7.31 – 7.25 (m, 4H), 4.20 (q, J = 7.3 Hz, 1H), 3.00 (s, 4H), 1.73 (d, J = 7.2 Hz, 3H), 1.41 (s, 18H); **4a+4b ^{13}C NMR** (101 MHz, Chloroform-d) δ 148.75, 148.64, 143.53, 139.13, 128.06, 127.23, 125.33, 125.25, 43.94, 37.50, 34.45, 34.40, 31.51, 31.48, 22.07.

Spectroscopic data were in good agreement with literature.[1, 4]

1,2-bis(4-isopropylphenyl)ethane (5a), 4,4'-(ethane-1,1-diyl)bis(isopropylbenzene) (5b) and (*E*)-1,2-bis(4-isopropylphenyl)ethene (5c)

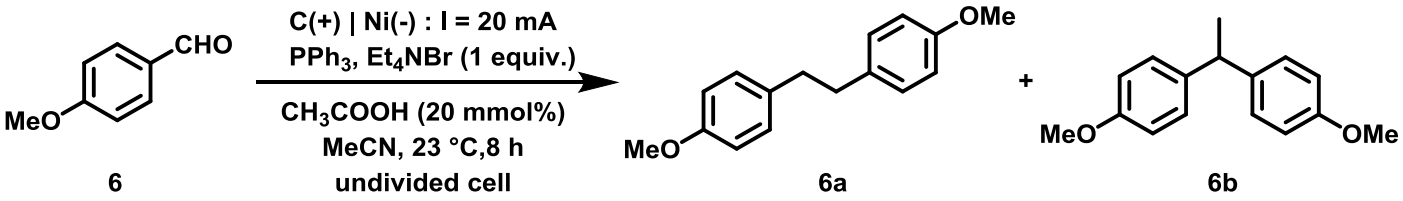


The starting cuminaldehyde (152.0 μL, 1.0 mmol) was reacted with PPh_3 (787.0 mg, 3.0 mmol) according to general procedure A. The crude product was purified by column chromatography on silica gel (petroleum ether) to afford the title compound as a white solid in 56% yield (74.1 mg). **5a** : **5b** : **5c** = 3.7 : 1 : 1.5 (The proportion was determined by ^{1}H NMR).

The reported NMR spectra were obtained with the sample purified by preparative thin-layer chromatography (TLC) on silica gel. **5a** : **5c** = 1.1 : 1; Rf (petroleum ether): 0.5; **5a ^{1}H NMR** (400 MHz, Chloroform-d) δ 7.19 (s, 8H), 2.96 – 2.89 (m, 6H), 1.30 – 1.27 (m, 12H); **5c ^{1}H NMR** (400 MHz, Chloroform-d) δ 7.51 – 7.47 (m, 4H), 7.29 – 7.25 (m, 4H), 7.11 (s, 2H), 2.99 – 2.93 (m, 2H), 1.31 (d, *J* = 6.9 Hz, 12H); **5a + 5c ^{13}C NMR** (101 MHz, Chloroform-d) δ 148.43, 146.45, 139.43, 135.21, 128.29, 127.77, 126.75, 126.43, 126.41, 37.63, 33.93, 33.75, 24.12, 23.99.

Spectroscopic data were in good agreement with literature.[5]

1,2-bis(4-methoxyphenyl)ethane (6a) and 4,4'-(ethane-1,1-diyl)bis(methoxybenzene) (6b)

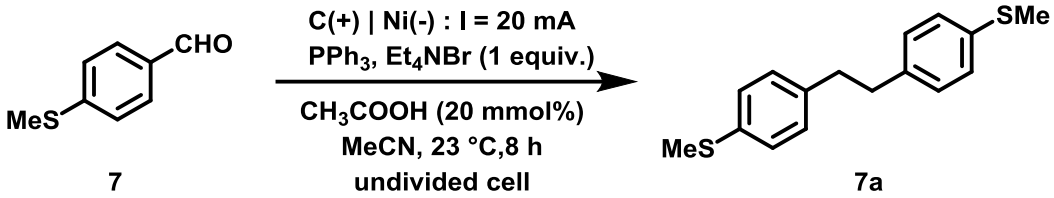


The starting *p*-anisaldehyde (121.0 μL, 1.0 mmol) was reacted with PPh_3 (787.0 mg, 3.0 mmol) according to general procedure A. The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 100:1) to afford the title compound as a white solid in 68% yield (82.3 mg). **6a** : **6b** = 1.8 : 1 (The proportion was determined by ^{1}H NMR).

The reported NMR spectra were obtained with the sample purified by preparative thin-layer chromatography (TLC) on silica gel. **6a** : **6b** = 5 : 1; Rf (petroleum ether/ethyl acetate = 10:1): 0.6; **6a ^{1}H NMR** (400 MHz, Chloroform-d) δ 7.12 (d, *J* = 8.6 Hz, 4H), 6.86 (d, *J* = 8.6 Hz, 4H), 3.82 (s, 6H), 2.87 (s, 4H); **6b ^{1}H NMR** (400 MHz, Chloroform-d) δ 7.16 (d, *J* = 8.6 Hz, 4H), 6.86 (d, J = 8.6 Hz, 4H), 4.10 (q, *J* = 7.2 Hz, 1H), 3.81 (s, 6H), 1.63 (d, *J* = 7.3 Hz, 3H); **6a + 6b ^{13}C NMR** (101 MHz, Chloroform-d) δ 157.82, 138.99, 134.00, 129.43, 128.46, 113.73, 55.28, 43.13, 37.35, 22.33.

Spectroscopic data were in good agreement with literature.[3, 6]

1,2-bis(4-(methylthio)phenyl)ethane (7a)



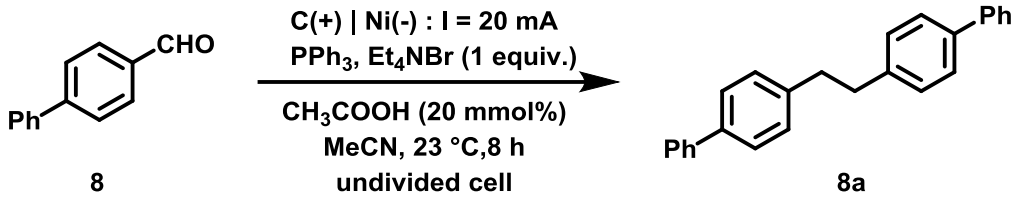
7 7a

The starting 4-(methylthio)benzaldehyde (133.0 μL, 1.0 mmol) was reacted with PPh_3 (787.0 mg, 3.0 mmol) according to general procedure A. The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 100:1) to afford the title compound as a slight yellow solid in 45% yield (61.0 mg).

Rf (petroleum ether/ethyl acetate = 10:1): 0.5; **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.19 (d, *J* = 8.3 Hz, 4H), 7.09 (d, *J* = 8.3 Hz, 4H), 2.86 (s, 4H), 2.48 (s, 6H); **^{13}C NMR** (101 MHz, Chloroform-d) δ 138.66, 135.48, 129.06, 126.99, 37.34, 16.28.

Spectroscopic data were in good agreement with literature.[3]

1,2-di([1,1'-biphenyl]-4-yl)ethane (8a)



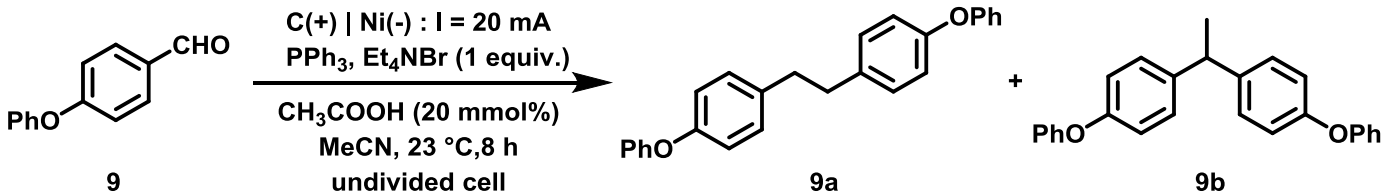
8 8a

The starting 4-biphenylcarboxaldehyde (182.2 mg, 1.0 mmol) was reacted with PPh_3 (787.0 mg, 3.0 mmol) according to general procedure A. The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 100:1) to afford the title compound as a white solid in 45% yield (75.1 mg).

Rf (petroleum ether): 0.2; **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.63 – 7.59 (m, 4H), 7.55 (d, *J* = 8.2 Hz, 4H), 7.45 (t, *J* = 7.6 Hz, 4H), 7.37 – 7.33 (m, 2H), 7.30 (d, *J* = 8.2 Hz, 4H), 3.02 (s, 4H); **^{13}C NMR** (101 MHz, Chloroform-d) δ 141.12, 140.95, 139.00, 128.99, 128.83, 127.20, 127.16, 127.10, 37.63.

Spectroscopic data were in good agreement with literature.[3]

1,2-bis(4-phenoxyphenyl)ethane (9a) and 4,4'-(ethane-1,1-diyl)bis(phenoxybenzene) (9b)



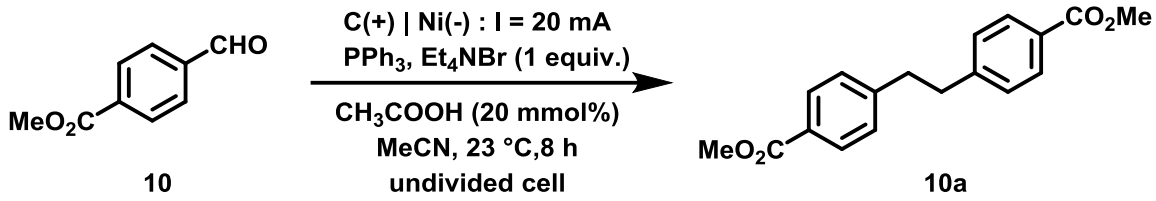
9 9a 9b

The starting 4-phenoxybenzaldehyde (175.0 μL, 1.0 mmol) was reacted with PPh_3 (787.0 mg, 3.0 mmol) according to general procedure A. The crude product was purified by column chromatography on silica gel

(petroleum ether/ethyl acetate = 100:1) to afford the title compound as a white solid in 57% yield (103.5 mg). **9a** : **9b** = 16.7 : 1 (The proportion was determined by ^{1}H NMR).

The reported NMR spectra were obtained with the sample purified by preparative thin-layer chromatography (TLC) on silica gel. **9a** : **9b** = 2.8 : 1; Rf (petroleum ether/ethyl acetate = 50:1): 0.3; **9a ^{1}H NMR** (400 MHz, Chloroform-d) δ 7.38 – 7.33 (m, 4H), 7.19 – 7.15 (m, 4H), 7.14 – 7.10 (m, 2H), 7.05 – 7.01 (m, 4H), 6.99 – 6.96 (m, 4H), 2.93 (s, 4H); **9b ^{1}H NMR** (400 MHz, Chloroform-d) δ 7.38 – 7.33 (m, 4H), 7.23 – 7.20 (m, 4H), 7.14 – 7.10 (m, 2H), 7.05 – 7.01 (m, 4H), 6.99 – 6.96 (m, 4H), 4.16 (q, *J* = 7.2 Hz, 1H), 1.66 (d, *J* = 7.2 Hz, 3H); **9a + 9b ^{13}C NMR** (101 MHz, Chloroform-d) δ 157.63, 155.20, 136.68, 129.71, 128.77, 123.09, 122.96, 119.05, 118.82, 118.74, 118.51, 37.35. **HRMS** m/z (ESI) calcd for $C_{26}H_{23}O_2$ ([M+H]$^+$) 367.1693, found 367.1690.

dimethyl 4,4'-(ethane-1,2-diyl)dibenzoate (10a)



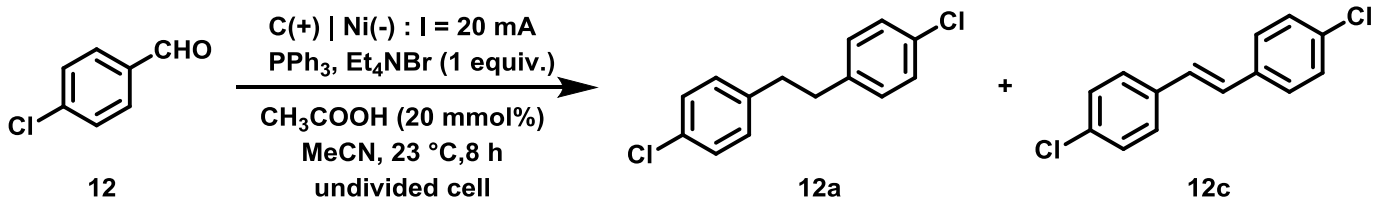
10 10a

The starting methyl 4-formylbenzoate (164.2 mg, 1.0 mmol) was reacted with PPh_3 (787.0 mg, 3.0 mmol) according to general procedure A. The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) to afford the title compound as a white solid in 67% yield (99.8 mg).

Rf (petroleum ether/ethyl acetate = 10:1): 0.3; **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.93 (d, *J* = 8.3 Hz, 4H), 7.19 (d, *J* = 8.3 Hz, 4H), 3.90 (s, 6H), 2.98 (s, 4H); **^{13}C NMR** (101 MHz, Chloroform-d) δ 167.09, 146.52, 129.75, 128.56, 128.08, 52.07, 37.45.

Spectroscopic data were in good agreement with literature.[3]

1,2-bis(4-chlorophenyl)ethane (12a) and (*E*)-1,2-bis(4-chlorophenyl)ethane (12c)

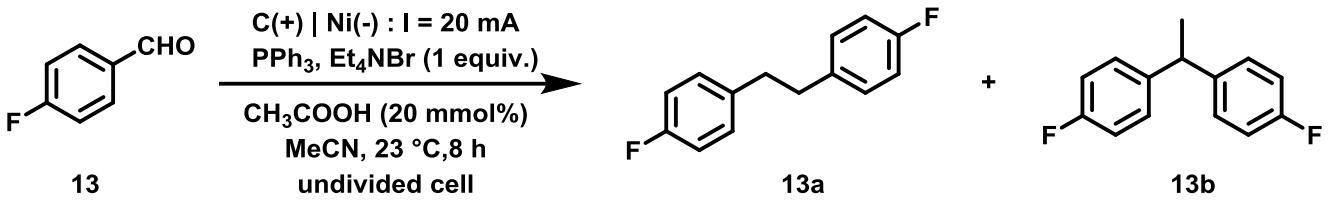


12 12a 12c

The starting 4-chlorobenzaldehyde (140.5 mg, 1.0 mmol) was reacted with PPh_3 (787.0 mg, 3.0 mmol) according to general procedure A. The crude product was purified by column chromatography on silica gel (petroleum ether) to afford the title compound as a white solid in 22% yield (28.0 mg). **12a** : **12c** = 1 : 20 (The proportion was determined by ^{1}H NMR).

The reported NMR spectra were obtained with the sample purified by preparative thin-layer chromatography (TLC) on silica gel. **11c** Rf (petroleum ether): 0.5; NMR spectra see the condition B vide infra.

1,2-bis(4-fluorophenyl)ethane (13a) and 4,4'-(ethane-1,1-diyl)bis(fluorobenzene) (13b)



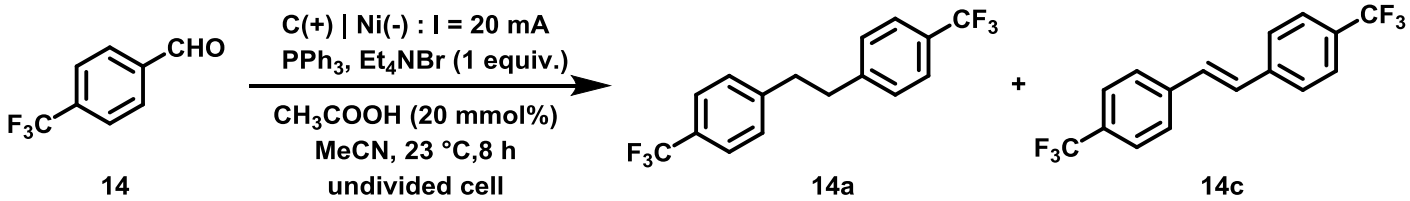
13 13a 13b

The starting 4-fluorobenzaldehyde (107 μL, 1.0 mmol) was reacted with PPh_3 (787.0 mg, 3.0 mmol) according to general procedure A. The crude product was purified by column chromatography on silica gel (petroleum ether) to afford the title compound as a white solid in 50% yield (55.5 mg). **13a** : **13b** = 33.3 : 1 (The proportion was determined by ^{1}H NMR).

The reported NMR spectra were obtained with the sample purified by preparative thin-layer chromatography (TLC) on silica gel. Rf (petroleum ether): 0.5; **13a ^{1}H NMR** (400 MHz, Chloroform-d) δ 7.10 – 7.06 (m, 4H), 6.99 – 6.93 (m, 4H), 2.87 (s, 4H); **^{13}C NMR** (101 MHz, Chloroform-d) δ 161.33 (d, *J* = 243.5 Hz), 136.96 (d, *J* = 3.3 Hz), 129.85 (d, *J* = 7.8 Hz), 115.08 (d, *J* = 21.1 Hz), 37.19; **^{19}F NMR** (376 MHz, Chloroform-d) δ -117.45.

Spectroscopic data were in good agreement with literature.[7]

1,2-bis(4-(trifluoromethyl)phenyl)ethane (14a) and (*E*)-1,2-bis(4-(trifluoromethyl)phenyl)ethane (14c)



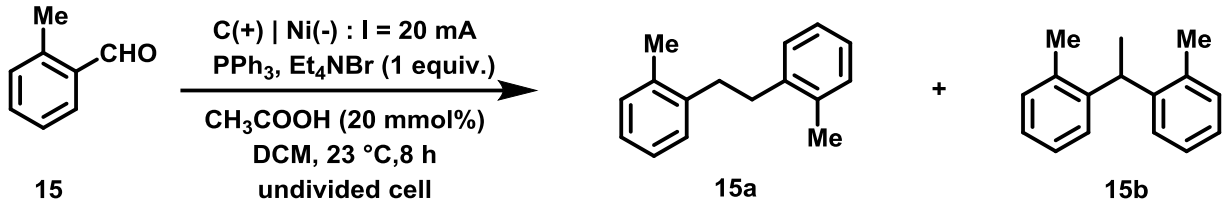
14 14a 14c

The starting 4-(trifluoromethyl)benzaldehyde (137.0 μL, 1.0 mmol) was reacted with PPh_3 (787.0 mg, 3.0 mmol) according to general procedure B. The crude product was purified by column chromatography on silica gel (petroleum ether) to afford the title compound as a white solid in 46% yield (73.4 mg). **14a** : **14c** = 1 : 2.5 (The proportion was determined by ^{1}H NMR).

The reported NMR spectra were obtained with the sample purified by preparative thin-layer chromatography (TLC) on silica gel. **14a** : **14c** = 20 : 1; Rf (petroleum ether): 0.5; **14a ^{1}H NMR** (400 MHz, Chloroform-d) δ 7.54 (d, *J* = 8.0 Hz, 4H), 7.26 (d, *J* = 8.0 Hz, 4H), 3.00 (s, 4H); **14c ^{1}H NMR** (400 MHz, Chloroform-d) δ 7.63 (s, 8H), 7.20 (s, 2H); **14a ^{13}C NMR** (101 MHz, Chloroform-d) δ 145.02, 128.78, 128.25 (q, *J* = 32.2 Hz), 125.37 (q, *J* = 3.8 Hz), 124.28 (q, *J* = 271.7 Hz), 37.26; **^{19}F NMR** (376 MHz, Chloroform-d) δ -62.37.

Spectroscopic data were in good agreement with literature.[3]

1,2-di-*o*-tolylethane (15a) and 2,2'-(ethane-1,1-diyl)bis(methylbenzene) (15b)



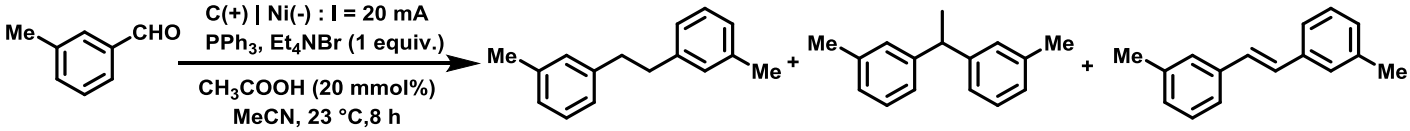
15 15a 15b

The starting 2-methylbenzaldehyde (116.0 μL, 1.0 mmol) was reacted with PPh_3 (787.0 mg, 3.0 mmol) according to general procedure A. The crude product was purified by column chromatography on silica gel (petroleum ether) to afford the title compound as a white solid in 56% yield (58.3 mg). **15a** : **15b** = 3 : 1 (The proportion was determined by ^{1}H NMR).

The reported NMR spectra were obtained with the sample purified by preparative thin-layer chromatography (TLC) on silica gel. Rf (petroleum ether): 0.5; **15a ^{1}H NMR** (400 MHz, Chloroform-d) δ 7.30 – 7.27 (m, 7H), 2.98 (s, 4H), 2.44 (s, 6H); **^{13}C NMR** (101 MHz, Chloroform-d) δ 140.27, 136.01, 130.31, 128.96, 126.23, 126.17, 34.26, 19.41.

Spectroscopic data were in good agreement with literature.[8]

1,2-di-*m*-tolylethane (16a), 3,3'-(ethane-1,1-diyl)bis(methylbenzene) (16b) and (*E*)-1,2-di-*m*-tolylethene (16c)



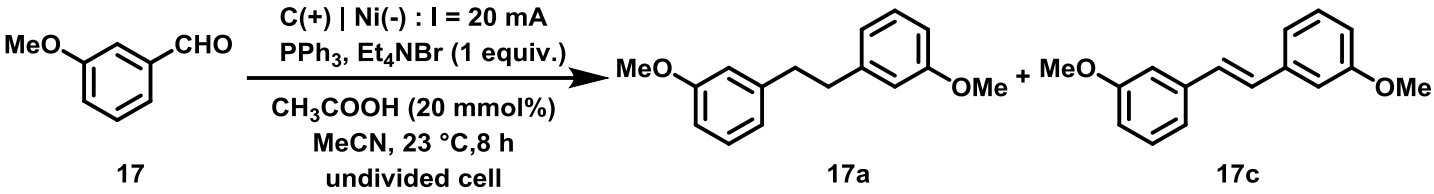
16 16a 16b 16c

The starting 3-methylbenzaldehyde (118.0 μL, 1.0 mmol) was reacted with PPh_3 (787.0 mg, 3.0 mmol) according to general procedure. The crude product was purified by column chromatography on silica gel (petroleum ether) to afford the title compound as a white solid in 55% yield (57.6 mg). **16a** : **16b** : **16c**= 8.3 : 1.8 : 1 (The proportion was determined by ^{1}H NMR).

The reported NMR spectra were obtained with the sample purified by preparative thin-layer chromatography (TLC) on silica gel. **16a** :**16b** = 2 : 1; Rf (petroleum ether): 0.3; **16a ^{1}H NMR** (400 MHz, Chloroform-d) δ 7.23 – 7.17 (m, 2H), 7.06 – 7.02 (m, 6H), 2.89 (s, 4H), 2.36 (s, 6H); **16b ^{1}H NMR** (400 MHz, Chloroform-d) δ 7.23 – 7.17 (m, 2H), 7.06 – 7.02 (m, 6H), 4.09 (q, *J* = 7.2 Hz, 1H), 2.33 (s, 6H), 1.63 (d, *J* = 7.3 Hz, 3H); **16a + 16b ^{13}C NMR** (101 MHz, Chloroform-d) δ 146.43, 141.95, 137.93, 129.27, 128.44, 128.28, 126.77, 126.66, 125.42, 124.61, 44.71, 38.07, 21.55, 21.46.

Spectroscopic data were in good agreement with literature.[9]

1,2-bis(3-methoxyphenyl)ethane (17a) and (*E*)-1,2-bis(3-methoxyphenyl)ethane (17c)



17 17a 17c

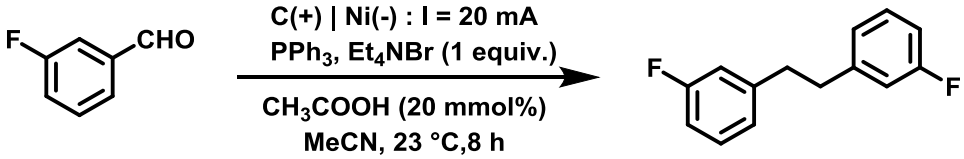
The starting 3-methoxybenzaldehyde (122.0 μL, 1.0 mmol) was reacted with PPh_3 (787.0 mg, 3.0 mmol) according to general procedure A. The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 100:1) to afford the title compound as a colorless oil in 61% yield (73.9 mg).

17a : **17c**= 6 : 1 (The proportion was determined by ^{1}H NMR).

The reported NMR spectra were obtained with the sample purified by preparative thin-layer chromatography (TLC) on silica gel. Rf (petroleum ether/ethyl acetate = 50:1): 0.3; **17a ^{1}H NMR** (400 MHz, Chloroform-d) δ 7.30 – 7.23 (m, 2H), 6.86 – 6.84 (m, 2H), 6.82 – 6.78 (m, 4H), 3.83 (s, 6H), 2.95 (s, 4H); **^{13}C NMR** (101 MHz, Chloroform-d) δ 159.62, 143.42, 129.35, 120.89, 114.20, 111.30, 55.18, 37.92.

Spectroscopic data were in good agreement with literature.[3]

1,2-bis(3-fluorophenyl)ethane (18a)



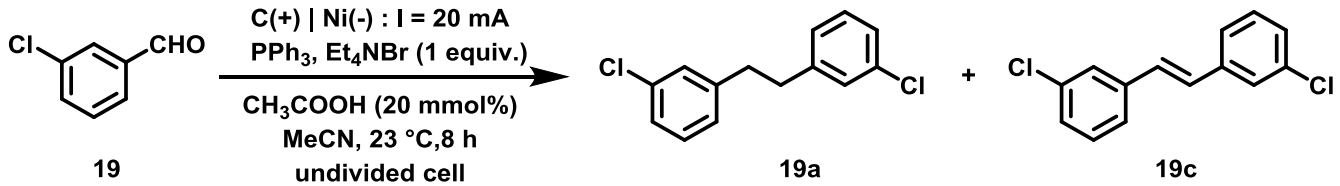
18 18a

The starting 3-fluorobenzaldehyde (106.0 μL, 1.0 mmol) was reacted with PPh_3 (787.0 mg, 3.0 mmol) according to general procedure A. The crude product was purified by column chromatography on silica gel (petroleum ether) to afford the title compound as a white solid in 63% yield (67.5 mg).

Rf (petroleum ether): 0.5; **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.31 – 7.25 (m, 2H), 7.00 – 6.89 (m, 6H), 2.96 (s, 4H); **^{13}C NMR** (101 MHz, Chloroform-d) δ 162.92 (d, J = 245.4 Hz), 143.81 (d, *J* = 7.1 Hz), 129.84 (d, *J* = 8.3 Hz), 124.16 (d, *J* = 2.8 Hz), 115.32 (d, *J* = 20.9 Hz), 113.00 (d, *J* = 21.1 Hz), 37.27 (d, *J* = 1.7 Hz); **^{19}F NMR** (376 MHz, Chloroform-d) δ -113.58.

Spectroscopic data were in good agreement with literature.[10]

1,2-bis(3-chlorophenyl)ethane (19a) and (*E*)-1,2-bis(3-chlorophenyl)ethane (19c)



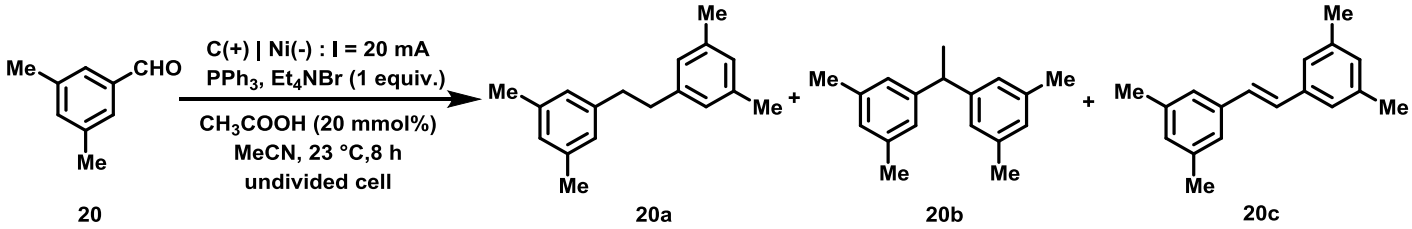
19 19a 19c

The starting 3-Chlorobenzaldehyde (113.0 μL, 1.0 mmol) was reacted with PPh_3 (787.0 mg, 3.0 mmol) according to general procedure A. The crude product was purified by column chromatography on silica gel (petroleum ether) to afford the title compound as a white solid in 40% yield (49.0 mg). **19a** : **19c**= 1 : 1.8 (The proportion was determined by ^{1}H NMR).

The reported NMR spectra were obtained with the sample purified by preparative thin-layer chromatography (TLC) on silica gel. **19a** : **19c**= 3.8 : 1; Rf (petroleum ether): 0.5; **19a ^{1}H NMR** (400 MHz, Chloroform-d) δ, 7.22 – 7.16 (m, 6H), 7.04 – 7.00 (m, 2H), 2.88 (s, 4H); **19c ^{1}H NMR** (400 MHz, Chloroform-d) δ 7.53 – 7.52 (m, 2H), 7.40 – 7.38 (m, 2H), 7.35 – 7.26 (m, 4H), 7.05 (s, 2H); **19a + 19c ^{13}C NMR** (101 MHz, Chloroform-d) δ 143.18, 134.73, 134.14, 129.98, 129.66, 128.57, 127.93, 126.67, 126.43, 126.32, 124.92, 37.27.

Spectroscopic data were in good agreement with literature.[10]

1,2-bis(3,5-dimethylphenyl)ethane (20a), 5,5'-(ethane-1,1-diyl)bis(1,3-dimethylbenzene) (20b) and (*E*)-1,2-bis(3,5-dimethylphenyl)ethane (20c)



20 20a 20b 20c

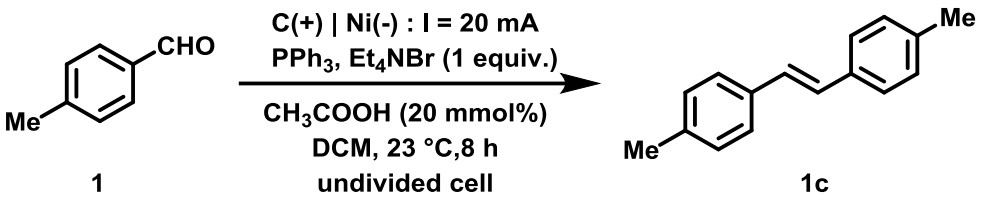
The starting 3,5-dimethylbenzaldehyde (134.0 μL, 1.0 mmol) was reacted with PPh_3 (787.0 mg, 3.0 mmol) according to general procedure A. The crude product was purified by column chromatography on silica gel (petroleum ether) to afford the title compound as a white solid in 54% yield (64.5 mg). **20a** : **20b** : **20c** = 16.7 : 3 : 1 (The proportion was determined by ^{1}H NMR).

The reported NMR spectra were obtained with the sample purified by preparative thin-layer chromatography (TLC) on silica gel. **20a** : **20b** = 4 : 1; Rf (petroleum ether): 0.5; **20a ^{1}H NMR** (400 MHz, Chloroform-d) δ 6.92 – 6.88 (m, 6H), 2.87 (s, 4H), 2.37 (s, 12H); **20b ^{1}H NMR** (400 MHz, Chloroform-d) δ 6.92 – 6.88 (m, 6H), 4.05 (q, *J* = 7.2 Hz, 1H), 2.34 (s, 12H), 1.64 (d, *J* = 7.2 Hz, 3H); **20a + 20b ^{13}C NMR** (101 MHz, Chloroform-d) δ 146.51, 142.12, 137.89, 137.74, 127.69, 127.56, 126.25, 125.44, 44.64, 38.20, 22.02, 21.46, 21.35.

Spectroscopic data were in good agreement with literature.[1]

8. Detail descriptions for products of condition B

(*E*)-1,2-di-*p*-tolylethene (1c)



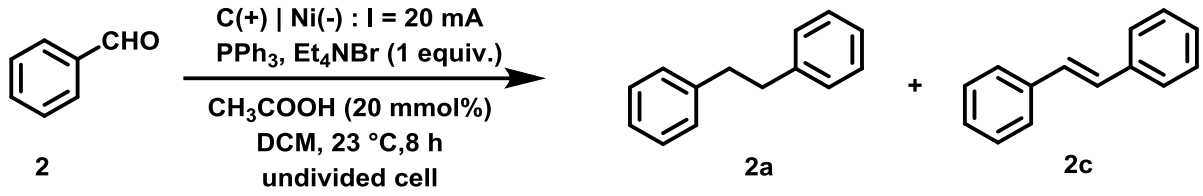
1 1c

The starting *p*-Tolualdehyde (118 μL, 1.0 mmol) was reacted with PPh_3 (787.0 mg, 3.0 mmol) according to general procedure B. The crude product was purified by column chromatography on silica gel (petroleum ether) to afford the title compound as a white solid in 39% yield (40.5 mg).

Rf (petroleum ether): 0.5; **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.44 (d, *J* = 8.1 Hz, 4H), 7.19 (d, *J* = 7.5 Hz, 4H), 7.07 (s, 2H), 2.39 (s, 6H); **^{13}C NMR** (101 MHz, Chloroform-d) δ 137.27, 134.75, 129.37, 127.65, 126.31, 21.25.

Spectroscopic data were in good agreement with literature.[11]

1,2-diphenylethane (2a) and (*E*)-1,2-diphenylethene (2c)



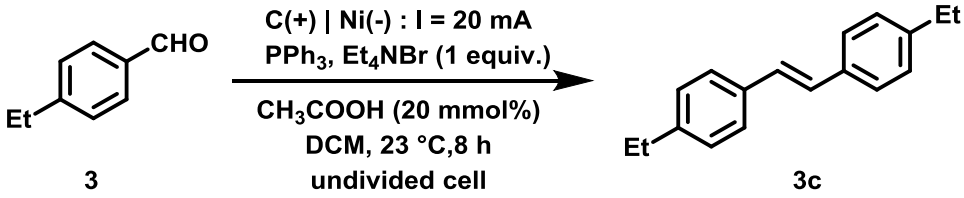
2 2a 2c

The starting benzaldehyde (102.0 μL, 1.0 mmol) was reacted with PPh_3 (787.0 mg, 3.0 mmol) according to general procedure B. The crude product was purified by column chromatography on silica gel (petroleum ether) to afford the title compound as a white solid in 48% yield (43.3 mg). **2a** : **2c** = 1 : 33.3 (The proportion was determined by ^{1}H NMR).

The reported NMR spectra were obtained with the sample purified by preparative thin-layer chromatography (TLC) on silica gel. Rf (petroleum ether): 0.5; **2c ^{1}H NMR** (400 MHz, Chloroform-d) δ 7.59 – 7.52 (m, 4H), 7.42 – 7.38 (m, 4H), 7.33 – 7.27 (m, 2H), 7.15 (s, 2H); **^{13}C NMR** (101 MHz, Chloroform-d) δ 137.36, 128.77, 128.73, 127.71, 126.59.

Spectroscopic data were in good agreement with literature.[12]

(*E*)-1,2-bis(4-ethylphenyl)ethene (3c)



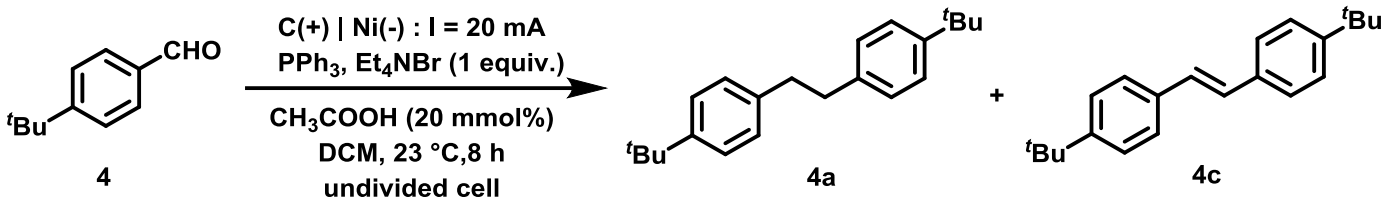
3 3c

The starting 4-ethylbenzaldehyde (137.0 μL, 1.0 mmol) was reacted with PPh_3 (787.0 mg, 3.0 mmol) according to general procedure B. The crude product was purified by column chromatography on silica gel (petroleum ether) to afford the title compound as a white solid in 29% yield (34.2 mg).

Rf (petroleum ether): 0.5; **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.48 (d, *J* = 8.2 Hz, 4H), 7.24 (d, *J* = 8.1 Hz, 4H), 7.10 (s, 2H), 2.70 (q, *J* = 7.6 Hz, 4H), 1.29 (t, *J* = 7.6 Hz, 6H); **^{13}C NMR** (101 MHz, Chloroform-d) δ 143.73, 135.02, 128.22, 127.72, 126.43, 28.69, 15.64.

Spectroscopic data were in good agreement with literature.[13]

1,2-bis(4-(*tert*-butyl)phenyl)ethane (4a) and (*E*)-1,2-bis(4-(*tert*-butyl)phenyl)ethene (4c)

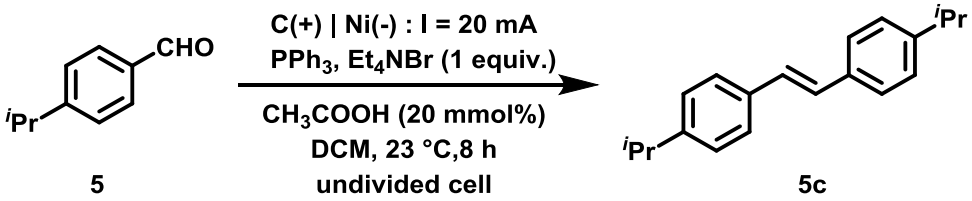


The starting 4-(*tert*-butyl)benzaldehyde (167.0 μL, 1.0 mmol) was reacted with PPh_3 (787.0 mg, 3.0 mmol) according to general procedure B. The crude product was purified by column chromatography on silica gel (petroleum ether) to afford the title compound as a white solid in 34% yield (49.1 mg). **4a** : **4c** = 1 : 33.3 (The proportion was determined by ^{1}H NMR).

The reported NMR spectra were obtained with the sample purified by preparative thin-layer chromatography (TLC) on silica gel. Rf (petroleum ether): 0.5; **4c ^{1}H NMR** (400 MHz, Chloroform-d) δ 7.49 – 7.46 (m, 4H), 7.42 – 7.39 (m, 4H), 7.09 (s, 2H), 1.36 (s, 18H); **^{13}C NMR** (101 MHz, Chloroform-d) δ 150.59, 134.79, 127.73, 126.18, 125.63, 34.66, 31.36.

Spectroscopic data were in good agreement with literature.[14]

(*E*)-1,2-bis(4-isopropylphenyl)ethene (5c)

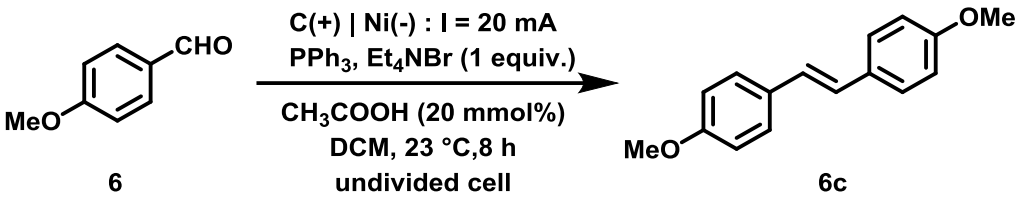


The starting cuminaldehyde (152.0 μL, 1.0 mmol) was reacted with PPh_3 (787.0 mg, 3.0 mmol) according to general procedure B. The crude product was purified by column chromatography on silica gel (petroleum ether) to afford the title compound as a white solid in 33% yield (43.6 mg).

Rf (petroleum ether): 0.5; **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.51 – 7.47 (m, 4H), 7.29 – 7.25 (m, 4H), 7.11 (s, 2H), 2.99 – 2.93 (m, 2H), 1.31 (d, *J* = 6.9 Hz, 12H); **^{13}C NMR** (101 MHz, Chloroform-d) δ 148.35, 135.20, 127.75, 126.77, 126.43, 33.94, 24.01.

Spectroscopic data were in good agreement with literature.[14]

(*E*)-1,2-bis(4-methoxyphenyl)ethene (6c)



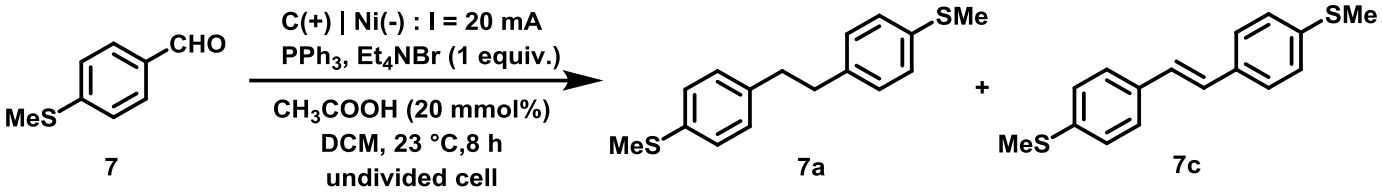
6 6c

The starting *p*-anisaldehyde (121.0 μL, 1.0 mmol) was reacted with PPh_3 (787.0 mg, 3.0 mmol) according to general procedure B. The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 100:1) to afford the title compound as a white solid in 53% yield (63.5 mg).

Rf (petroleum ether/ethyl acetate = 10:1): 0.6; **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.48 – 7.43 (m, 4H), 6.96 (s, 2H), 6.94 – 6.90 (m, 4H), 3.85 (s, 6H); **^{13}C NMR** (101 MHz, Chloroform-d) δ 159.00, 130.47, 127.42, 126.17, 114.11, 55.35.

Spectroscopic data were in good agreement with literature.[15]

1,2-bis(4-(methylthio)phenyl)ethane (7a) and (*E*)-1,2-bis(4-(methylthio)phenyl)ethene (7c)

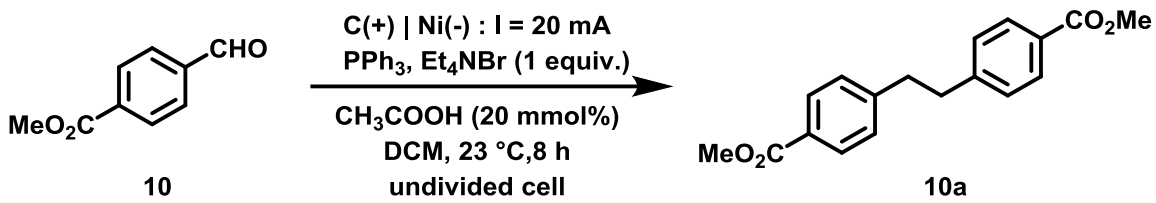


7 7a 7c

The starting 4-(methylthio)benzaldehyde (133.0 μL, 1.0 mmol) was reacted with PPh_3 (787.0 mg, 3.0 mmol) according to general procedure B. The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 100:1) to afford the title compound as a slight yellow solid in 18% yield (24.5 mg). **7a** : **7c** = 1.57 : 1 (The proportion was determined by ^{1}H NMR).

The reported NMR spectra were obtained with the sample purified by preparative thin-layer chromatography (TLC) on silica gel. **7a** Rf (petroleum ether/ethyl acetate = 10:1): 0.5; NMR spectra see the condition A in the above.

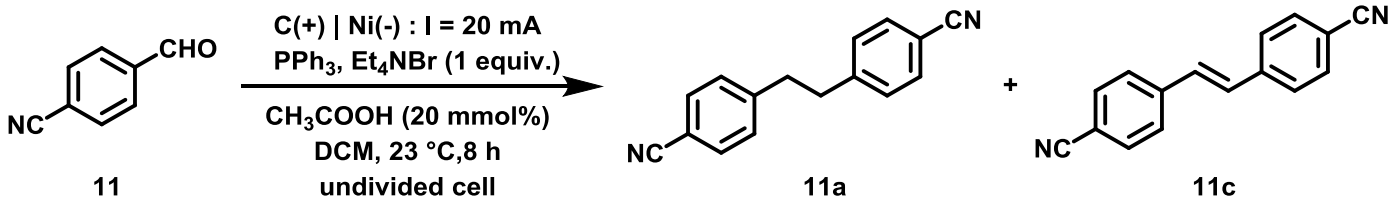
dimethyl 4,4'-(ethane-1,2-diyl)dibenzoate (10a)



10 10a

The starting methyl 4-formylbenzoate (164.2 mg, 1.0 mmol) was reacted with PPh_3 (787.0 mg, 3.0 mmol) according to general procedure B. The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) to afford the title compound as a white solid in 50% yield (74.3 mg). NMR spectra see the condition A in the above.

4,4'-(ethane-1,2-diyl)dibenzonitrile (11a) and (*E*)-4,4'-(ethene-1,2-diyl)dibenzonitrile (11c)



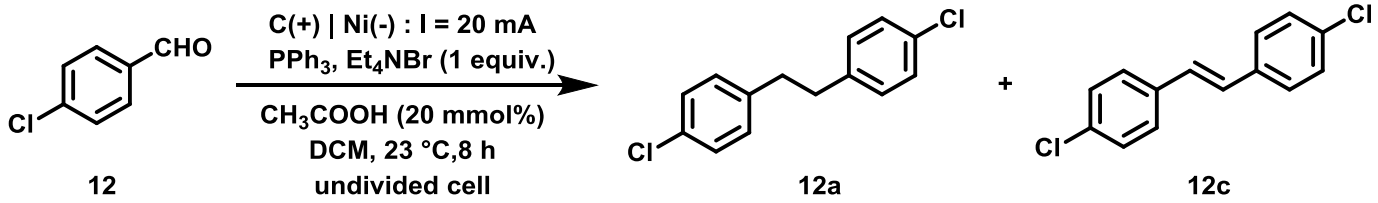
11 11a 11c

The starting methyl 4-formylbenzonitrile (131. mg, 1.0 mmol) was reacted with PPh_3 (787.0 mg, 3.0 mmol) according to general procedure B. The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) to afford the title compound as a white solid in 46% yield (52.5 mg). **11a** : **11c** = 8.5 : 1 (The proportion was determined by ^{1}H NMR).

Rf (petroleum ether/ethyl acetate = 5:1): 0.3; **11a ^{1}H NMR** (400 MHz, Chloroform-d) δ 7.56 (d, J = 8.3 Hz, 4H), 7.21 (d, J = 8.2 Hz, 4H), 2.99 (s, 4H); **11c ^{1}H NMR** (400 MHz, Chloroform-d) δ 7.67 (d, J = 8.6 Hz, 4H), 7.61 (d, J = 8.4 Hz, 4H), 7.21 (d, J = 8.2 Hz, 2H); **11a + 11c ^{13}C NMR** (101 MHz, Chloroform-d) δ 146.08, 132.64, 132.32, 129.26, 127.30, 118.85, 110.31, 37.23.

Spectroscopic data were in good agreement with literature.[16, 17]

1,2-bis(4-chlorophenyl)ethane (12a) and (*E*)-1,2-bis(4-chlorophenyl)ethane (12c)



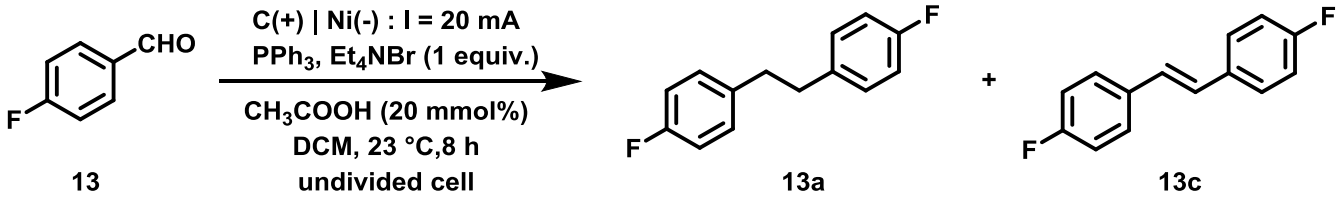
12 12a 12c

The starting 4-chlorobenzaldehyde (140.5 mg, 1.0 mmol) was reacted with PPh_3 (787.0 mg, 3.0 mmol) according to general procedure B. The crude product was purified by column chromatography on silica gel (petroleum ether) to afford the title compound as a white solid in 37% yield (45.8 mg). **12a** : **12c** = 1 : 50 (The proportion was determined by ^{1}H NMR).

The reported NMR spectra were obtained with the sample purified by preparative thin-layer chromatography (TLC) on silica gel. Rf (petroleum ether): 0.5; **12c** **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.44 – 7.41 (m, 4H), 7.35 – 7.31 (m, 4H), 7.02 (s, 2H); **^{13}C NMR** (101 MHz, Chloroform-d) δ 135.49, 133.45, 128.92, 127.97, 127.70.

Spectroscopic data were in good agreement with literature.[15]

1,2-bis(4-fluorophenyl)ethane (13a) and (*E*)-1,2-bis(4-fluorophenyl)ethane (13c)

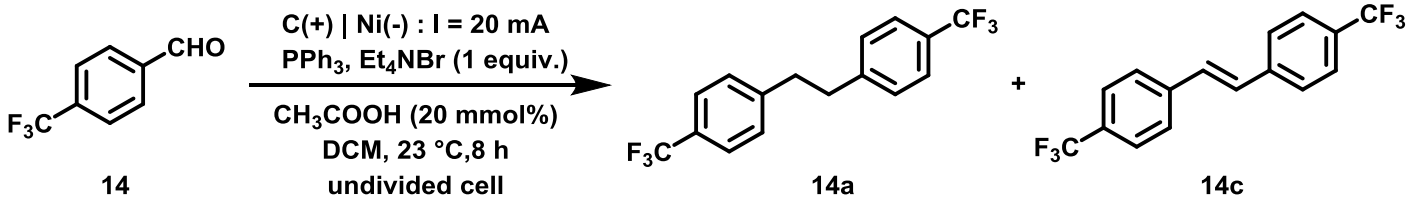


The starting 4-fluorobenzaldehyde (107 μL, 1.0 mmol) was reacted with PPh_3 (787.0 mg, 3.0 mmol) according to general procedure B. The crude product was purified by column chromatography on silica gel (petroleum ether) to afford the title compound as a white solid in 40% yield (43.2 mg). **13a** : **13c** = 1 : 20 (The proportion was determined by ^{1}H NMR).

The reported NMR spectra were obtained with the sample purified by preparative thin-layer chromatography (TLC) on silica gel. Rf (petroleum ether): 0.5; **13c** **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.49 – 7.44 (m, 4H), 7.09 – 7.02 (m, 4H), 6.98 (s, 2H); **^{13}C NMR** (101 MHz, Chloroform-d) δ 162.34 (d, *J* = 247.2 Hz), 133.34 (d, *J* = 3.2 Hz), 127.94 (d, *J* = 8.1 Hz), 127.26, 115.68 (d, *J* = 21.7 Hz); **^{19}F NMR** (376 MHz, Chloroform-d) δ -114.11.

Spectroscopic data were in good agreement with literature.[15]

1,2-bis(4-(trifluoromethyl)phenyl)ethane (14a) and (*E*)-1,2-bis(4-(trifluoromethyl)phenyl)ethane (14c)



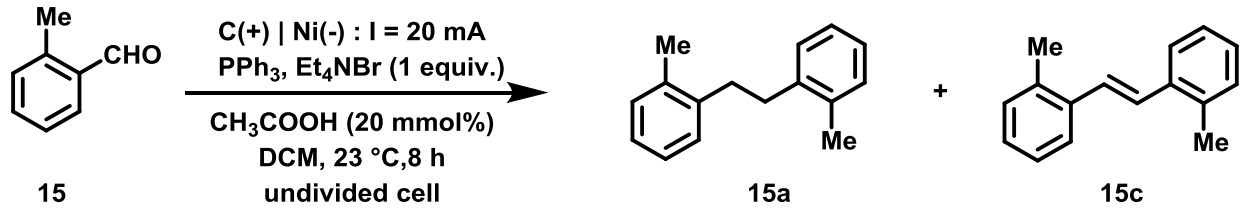
The starting 4-(trifluoromethyl)benzaldehyde (137.0 μL, 1.0 mmol) was reacted with PPh_3 (787.0 mg, 3.0 mmol) according to general procedure B. The crude product was purified by column chromatography on silica gel (petroleum ether) to afford the title compound as a white solid in 46% yield (73.4 mg). **14a** : **14c** = 1 : 2.5 (The proportion was determined by ^{1}H NMR).

The reported NMR spectra were obtained with the sample purified by preparative thin-layer chromatography (TLC) on silica gel. Rf (petroleum ether): 0.5; **14c** **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.63 (s, 8H), 7.20

(s, 2H); **^{13}C NMR** (101 MHz, Chloroform-d) δ 140.06, 129.90 (q, *J* = 32.6 Hz), 129.59, 126.87, 125.75 (q, *J* = 3.9 Hz), 124.12 (q, *J* = 271.8 Hz); **^{19}F NMR** (376 MHz, Chloroform-d) δ -62.54.

Spectroscopic data were in good agreement with literature.[11]

1,2-di-*o*-tolylethane (15a) and (*E*)-1,2-di-*o*-tolylethene (15c)



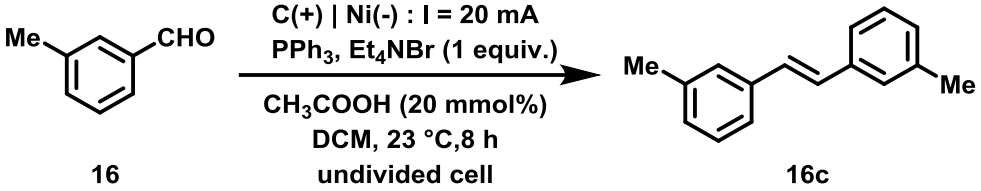
15 15a 15c

The starting 2-methylbenzaldehyde (116.0 μL, 1.0 mmol) was reacted with PPh_3 (787.0 mg, 3.0 mmol) according to general procedure B. The crude product was purified by column chromatography on silica gel (petroleum ether) to afford the title compound as a white solid in 61% yield (64.0 mg). **15a** : **15c** = 1 : 33.3 (The proportion was determined by ^{1}H NMR).

The reported NMR spectra were obtained with the sample purified by preparative thin-layer chromatography (TLC) on silica gel. Rf (petroleum ether): 0.5; **15c ^{1}H NMR** (400 MHz, Chloroform-d) δ 7.65 (d, *J* = 6.8 Hz, 2H), 7.31 – 7.23 (m, 8H), 2.48 (s, 6H); **^{13}C NMR** (101 MHz, Chloroform-d) δ 136.85, 135.87, 130.42, 128.06, 127.56, 126.23, 125.60, 19.99.

Spectroscopic data were in good agreement with literature.[15]

(*E*)-1,2-di-*m*-tolylethene (16c)



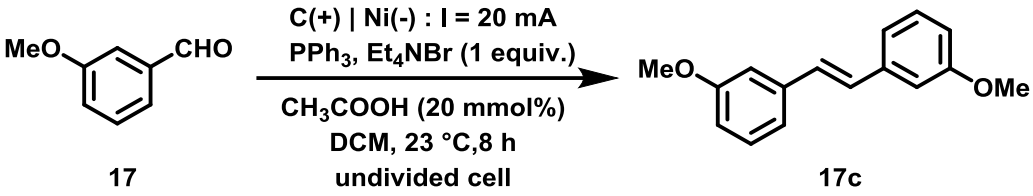
16 16c

The starting 3-methylbenzaldehyde (118.0 μL, 1.0 mmol) was reacted with PPh_3 (787.0 mg, 3.0 mmol) according to general procedure. The crude product was purified by column chromatography on silica gel (petroleum ether) to afford the title compound as a white solid in 38% yield (40.0 mg).

Rf (petroleum ether): 0.3; **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.38 – 7.32 (m, 4H), 7.29 – 7.25 (m, 2H), 7.11 – 7.09 (m, 4H), 2.40 (s, 6H); **^{13}C NMR** (101 MHz, Chloroform-d) δ 138.23, 137.37, 128.60, 128.41, 127.21, 123.71, 21.51.

Spectroscopic data were in good agreement with literature.[15]

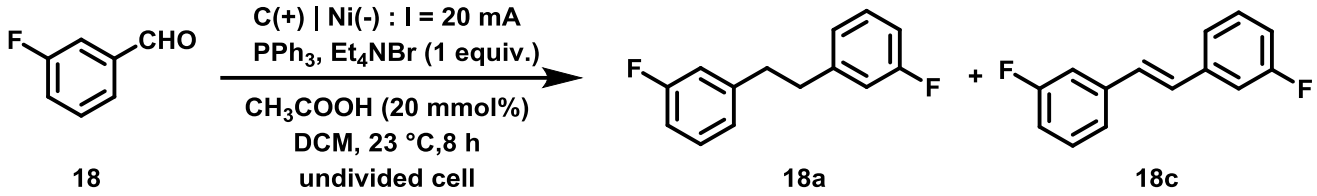
(*E*)-1,2-bis(3-methoxyphenyl)ethene (17c)



The starting 3-methoxybenzaldehyde (122.0 μL, 1.0 mmol) was reacted with PPh_3 (787.0 mg, 3.0 mmol) according to general procedure B. The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 100:1) to afford the title compound as a white solid in 49% yield (58.2 mg). Rf (petroleum ether/ethyl acetate = 50:1): 0.3; **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.30 (t, *J* = 7.9 Hz, 2H), 7.13 (d, *J* = 8.0 Hz, 2H), 7.09 (s, 2H), 7.08 – 7.07 (m, 2H), 6.86 – 6.83 (m, 2H), 3.86 (s, 6H); **^{13}C NMR** (101 MHz, Chloroform-d) δ 160.18, 138.98, 129.96, 129.20, 119.59, 113.68, 112.06, 55.57.

Spectroscopic data were in good agreement with literature.[18]

1,2-bis(3-fluorophenyl)ethane (18a) and (*E*)-1,2-bis(3-fluorophenyl)ethene (18c)

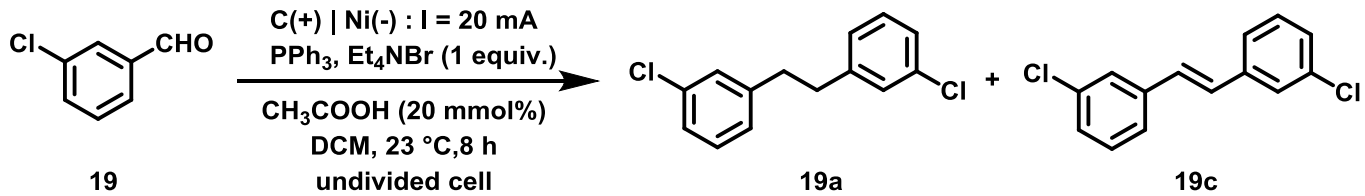


The starting 3-fluorobenzaldehyde (106.0 μL, 1.0 mmol) was reacted with PPh_3 (787.0 mg, 3.0 mmol) according to general procedure B. The crude product was purified by column chromatography on silica gel (petroleum ether) to afford the title compound as a white solid in 56% yield (60.9 mg). **18a** : **18c** = 1 : 13 (The proportion was determined by ^{1}H NMR).

The reported NMR spectra were obtained with the sample purified by preparative thin-layer chromatography (TLC) on silica gel. Rf (petroleum ether): 0.5; **18c ^{1}H NMR** (400 MHz, Chloroform-d) δ 7.39 – 7.22 (m, 6H), 7.09 (s, 2H), 7.04 – 6.99 (m, 2H); **^{13}C NMR** (101 MHz, Chloroform-d) δ 163.18 (d, *J* = 245.4 Hz), 139.18 (d, *J* = 7.9 Hz), 130.21 (d, *J* = 8.5 Hz), 128.78 (d, *J* = 2.8 Hz), 122.66 (d, *J* = 2.7 Hz), 114.82 (d, *J* = 21.5 Hz), 112.93 (d, *J* = 21.9 Hz); **^{19}F NMR** (376 MHz, Chloroform-d) δ -113.18.

Spectroscopic data were in good agreement with literature.[19]

1,2-bis(3-chlorophenyl)ethane (19a) and (*E*)-1,2-bis(3-chlorophenyl)ethane (19c)

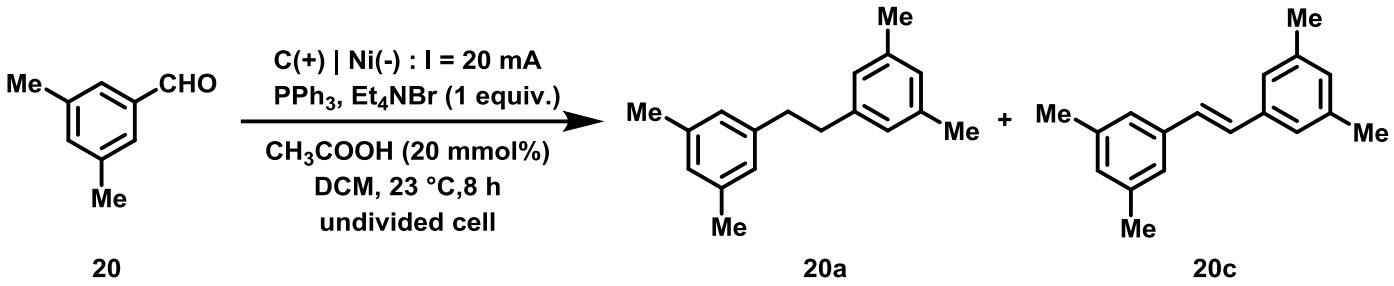


The starting 3-Chlorobenzaldehyde (113.0 μL, 1.0 mmol) was reacted with PPh_3 (787.0 mg, 3.0 mmol) according to general procedure B. The crude product was purified by column chromatography on silica gel (petroleum ether) to afford the title compound as a white solid in 56% yield (70.7 mg). **19a** : **19c**= 1 : 16.7 (The proportion was determined by ^{1}H NMR).

Rf (petroleum ether): 0.5; **19a ^{1}H NMR** (400 MHz, Chloroform-d) δ, 7.22 – 7.16 (m, 6H), 7.04 – 7.00 (m, 2H), 2.88 (s, 4H); **19c ^{1}H NMR** (400 MHz, Chloroform-d) δ 7.53 – 7.52 (m, 2H), 7.40 – 7.38 (m, 2H), 7.35 – 7.26 (m, 4H), 7.05 (s, 2H); **19c ^{13}C NMR** (101 MHz, Chloroform-d) δ 138.68, 134.73, 129.98, 128.61, 127.93, 126.44, 124.93.

Spectroscopic data were in good agreement with literature.[19]

1,2-bis(3,5-dimethylphenyl)ethane (20a) and (*E*)-1,2-bis(3,5-dimethylphenyl)ethane (20c)



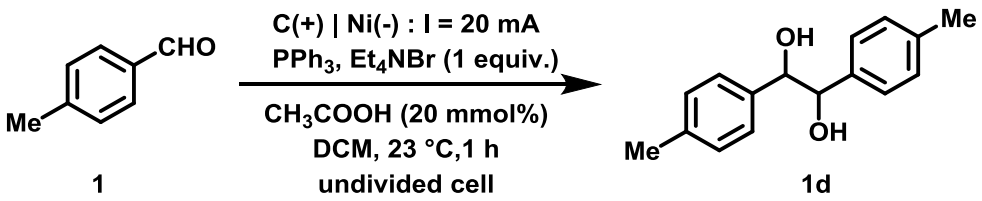
The starting 3,5-dimethylbenzaldehyde (134.0 μL, 1.0 mmol) was reacted with PPh_3 (787.0 mg, 3.0 mmol) according to general procedure B. The crude product was purified by column chromatography on silica gel (petroleum ether) to afford the title compound as a white solid in 36% yield (42.0 mg). **20a** : **20c** = 1 : 25 (The proportion was determined by ^{1}H NMR).

The reported NMR spectra were obtained with the sample purified by preparative thin-layer chromatography (TLC) on silica gel. Rf (petroleum ether): 0.5; **20c ^{1}H NMR** (400 MHz, Chloroform-d) δ 7.15 (s, 4H), 7.05 (s, 2H), 6.92 (s, 2H), 2.36 (s, 12H); **^{13}C NMR** (101 MHz, Chloroform-d) δ 138.12, 137.41, 129.31, 128.47, 124.39, 21.38.

Spectroscopic data were in good agreement with literature.[11]

9. Procedure for control experiment

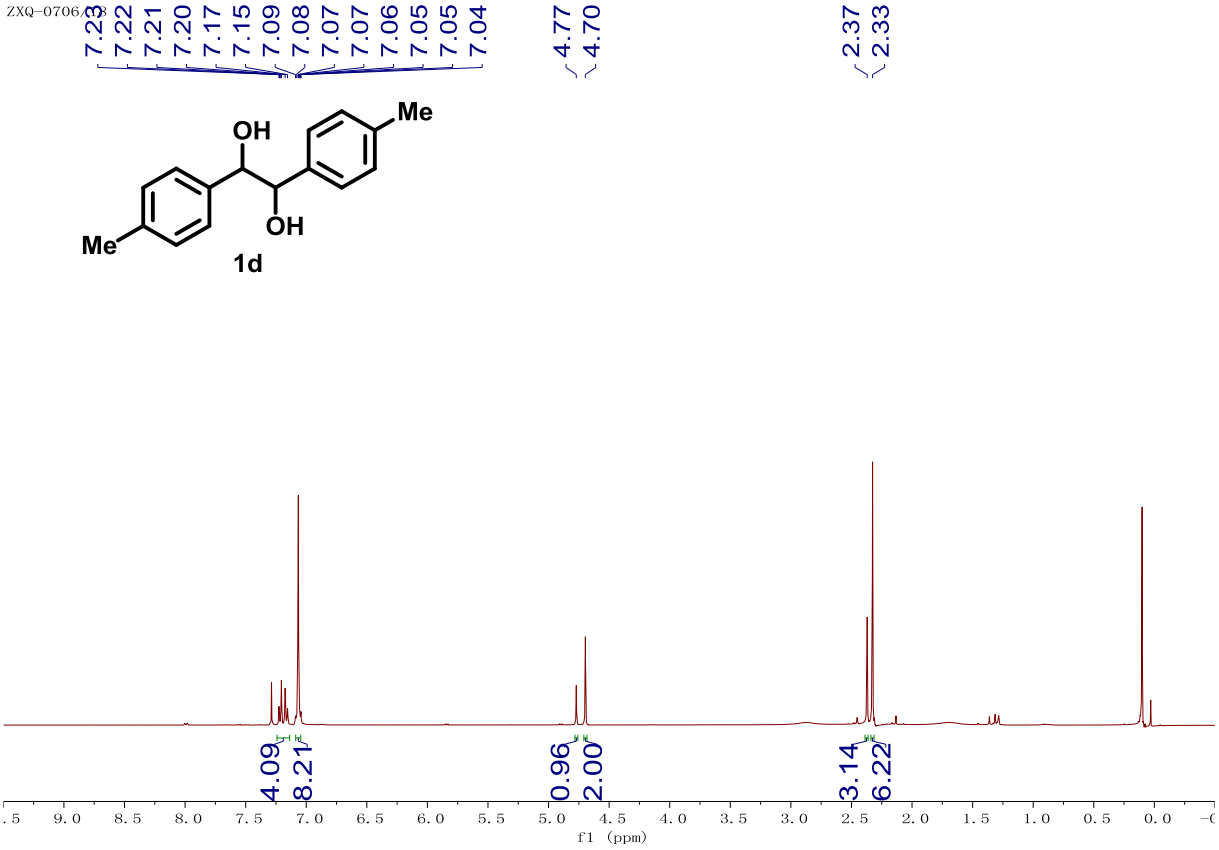
1,2-Bis(4-methylphenyl)-1,2-ethanediol (*dl* and *meso*) (1d)



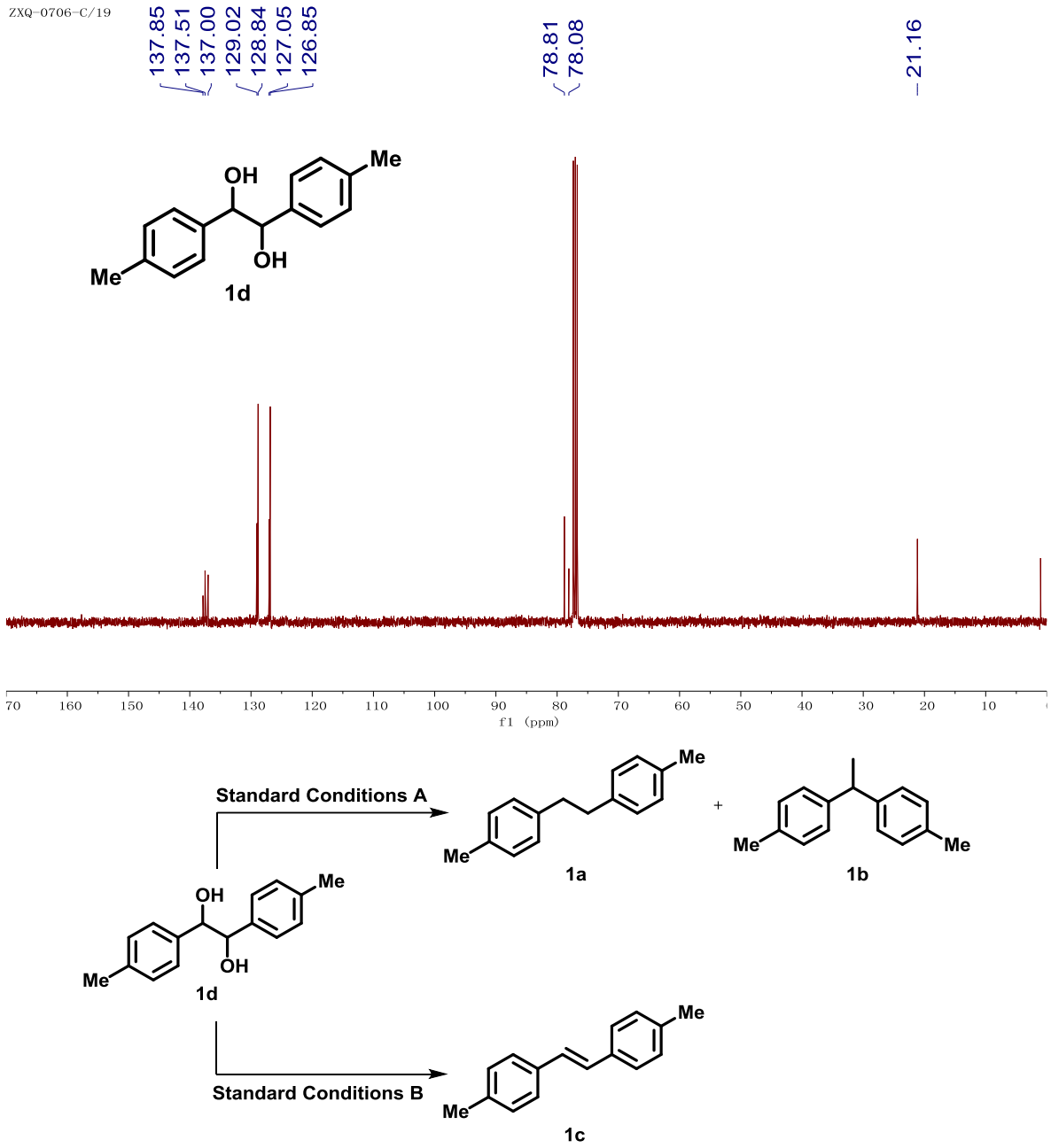
The starting p-Tolualdehyde (118.0 μL, 1.0 mmol), PPh_3 (787.0mg, 3.0mmol), CH_3COOH (0.2 mmol) and Et_4NBr (210.0 mg, 1.0 mmol) were added to an oven-dried undividedcell with DCM (4 mL) equipped with a stirring bar. The reaction mixture wasstirred and electrolyzed at a constant current of 20 mA at room temperature for 1h. The crude product was purified by column chromatography on silica gel (petroleumether/ethyl acetate = 5:1) to afford the reaction intermediate **1d** as a white solid.

Rf (petroleum ether/ethyl acetate = 3:1): 0.3; ***dl* : *meso* = 2: 1**; ***dl* ^{1}H NMR** (400 MHz, Chloroform-d) δ 7.08 – 7.05 (m, 8H), 4.70 (s, 2H), 2.33 (s, 6H); ***meso* ^{1}H NMR** (400 MHz, Chloroform-d) δ 7.24 – 7.14 (m, 8H), 4.77 (s, 2H), 2.37 (s, 6H); **^{13}C NMR** (101 MHz, Chloroform-d) δ 137.85, 137.51, 137.00, 129.02, 128.84, 127.05, 126.85, 78.81, 78.08, 21.16.

^{1}H NMR for **1d**



^{13}C NMR for **1d**



Then the electrolysis was carried out in the electrolysis cell of IKA® ElectraSyn 2.0. The anodic electrode was the carbon electrode (3.0 cm × 0.8 cm × 0.2 cm) and the cathodic electrode was the nickel plate (3.0 cm × 0.8 cm × 0.2 cm). 1,2-di-*p*-tolylethane-1,2-diol (**1d**) (0.5 mmol), Et_4NBr (105.0 mg, 0.5 mmol), PPh_3 (393.0 mg, 1.5 mmol), MeCN (4 mL) (or DCM (4 mL) in condition B) were added to an oven-dried undivided cell (6 mL) equipped with a stirring bar (the order of the addition did not affect the result). Then the reaction mixture was stirred and electrolyzed at a constant current of 20 mA at room temperature for 4 h. When the reaction was finished, the solution was treated by the standard procedure. It got the **1a** and **1b** product in condition A with 33% yield, **1a** : **1b** = 6 : 1 and **1c** product in condition B with 38% yield.

10. Reference

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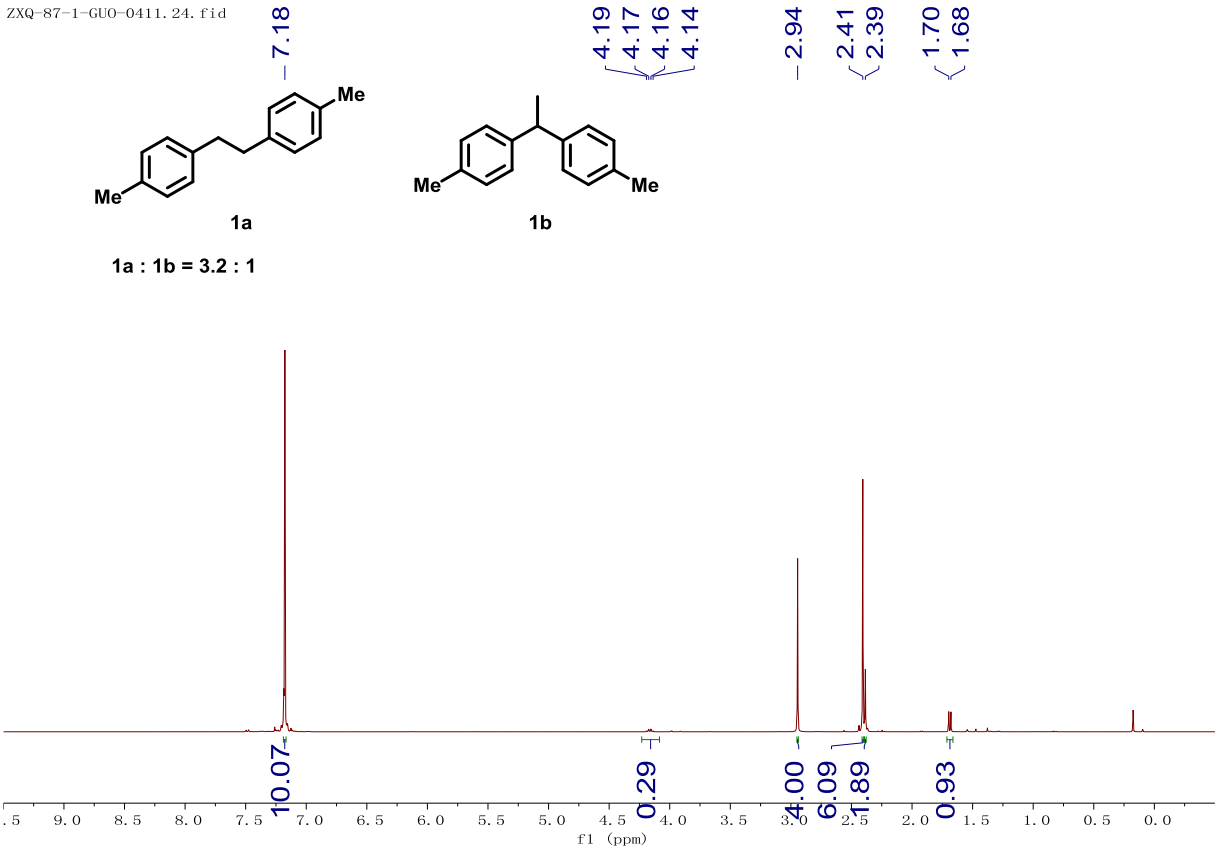
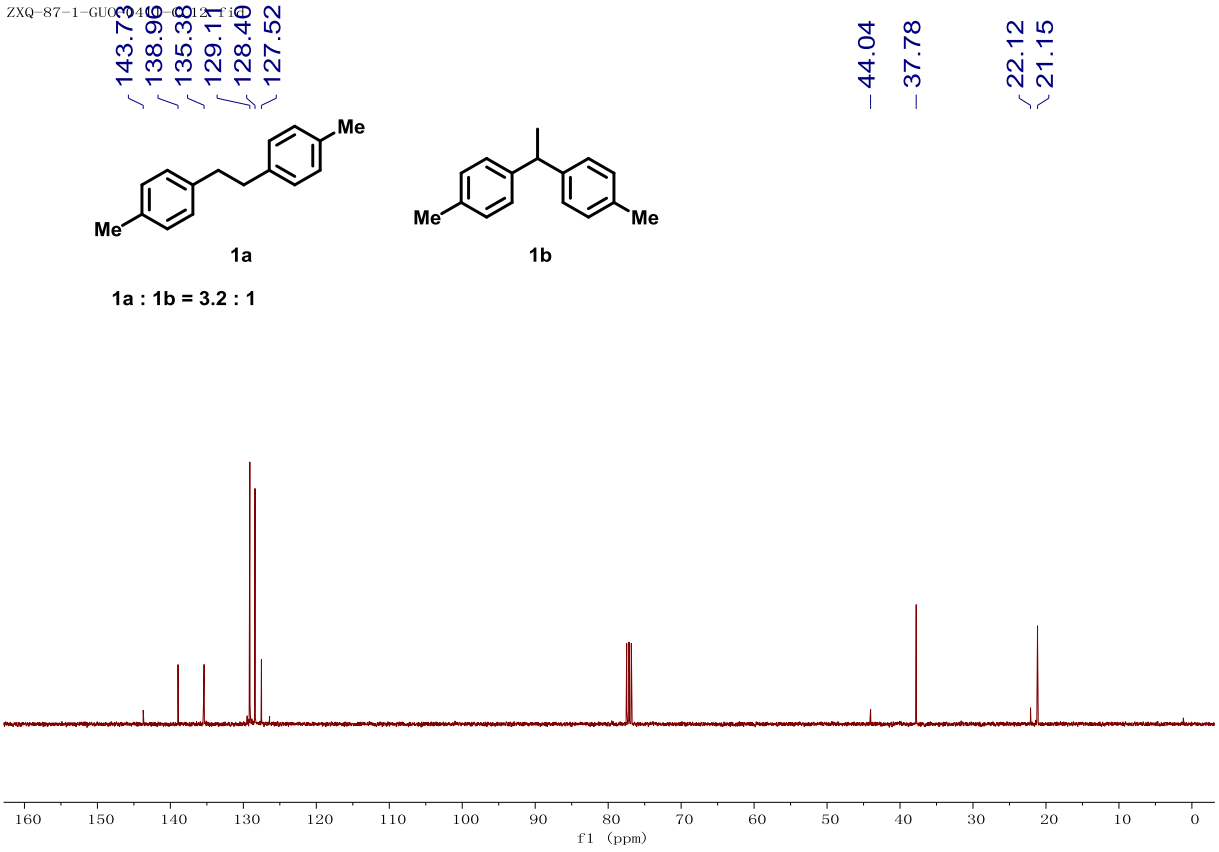
11. ^{1}H, ^{13}C and ^{19}F NMR spectra

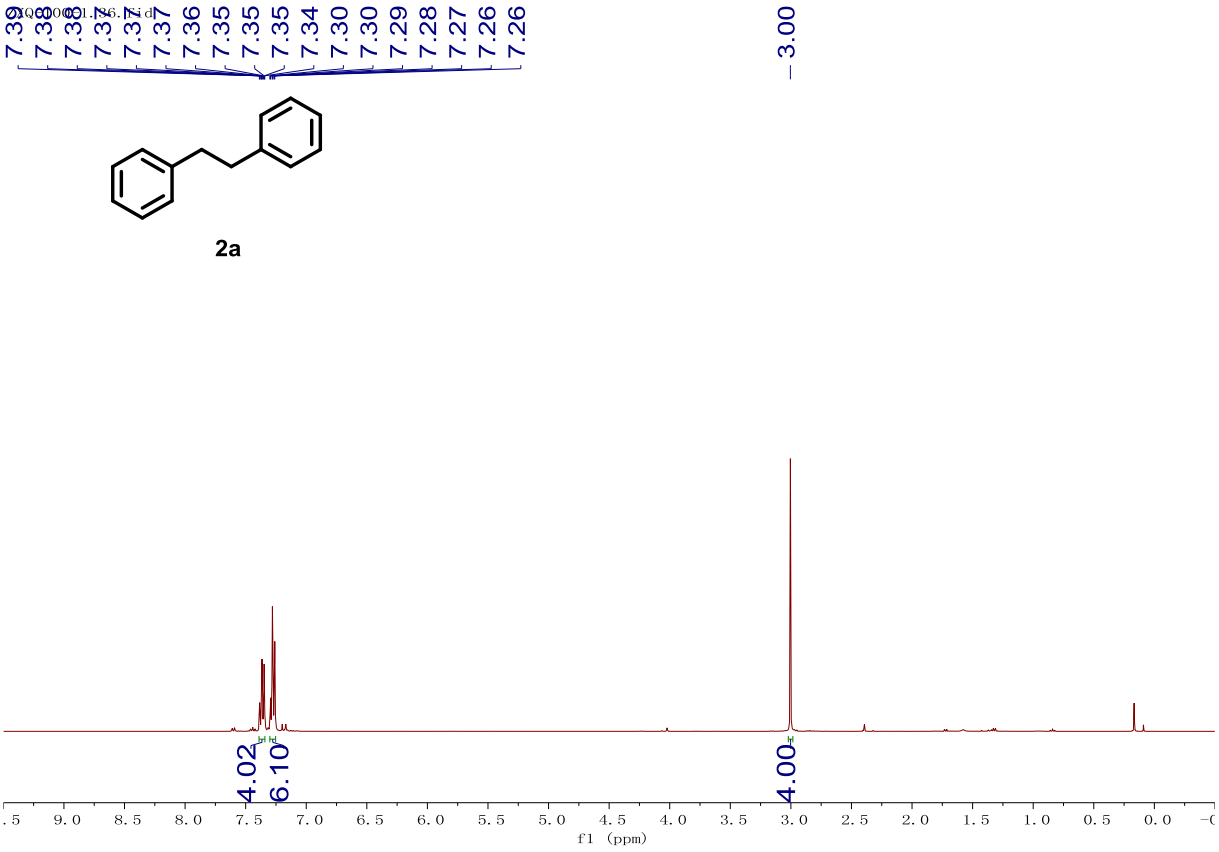
^{1}H NMR for **1a** and **1b**



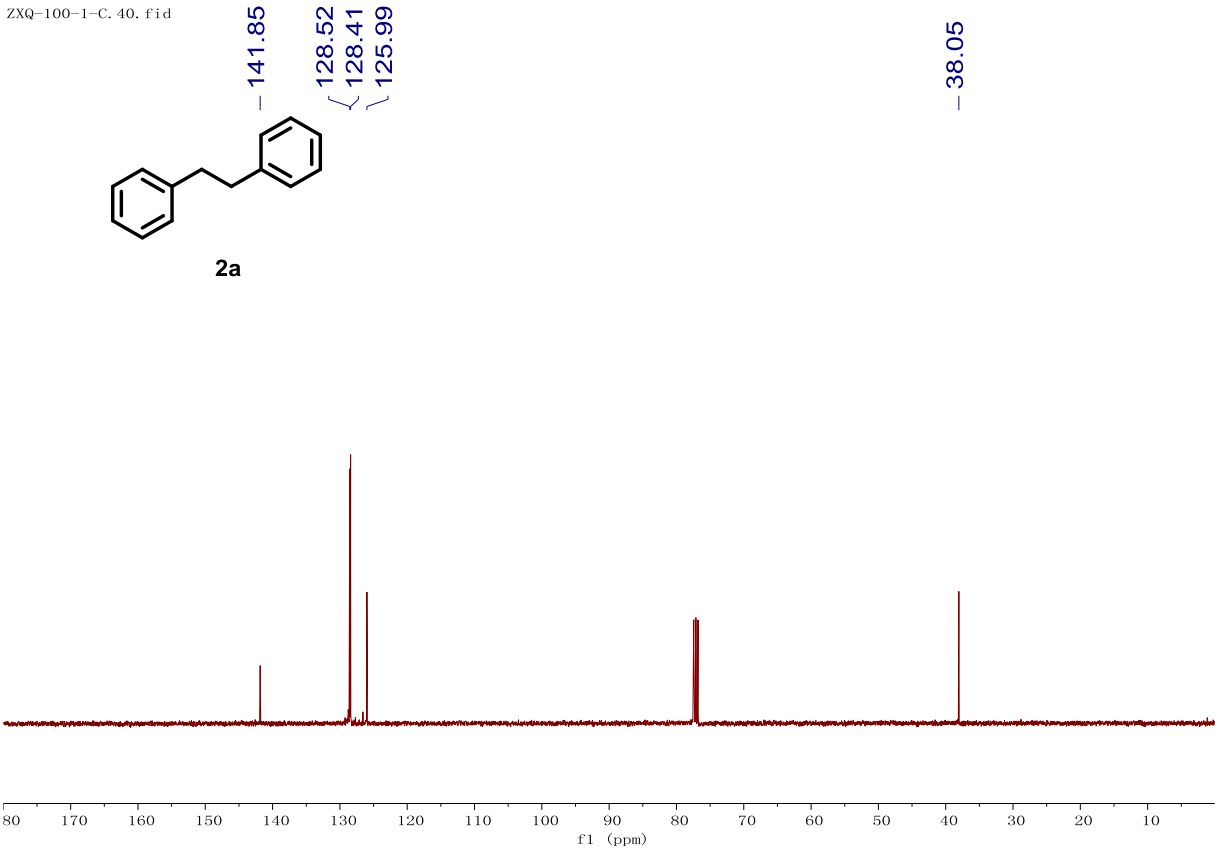
^{13}C NMR for **1a** and **1b**



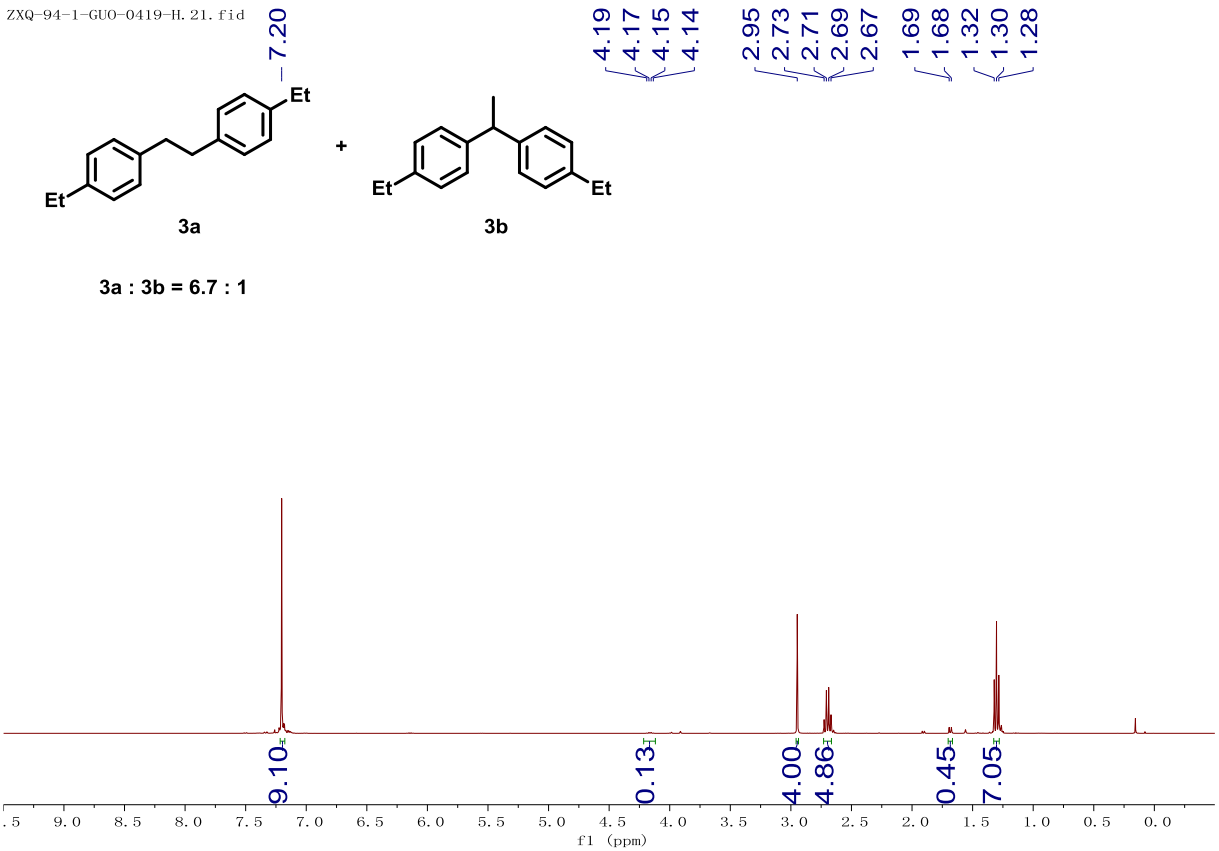
^{1}H NMR for **2a**



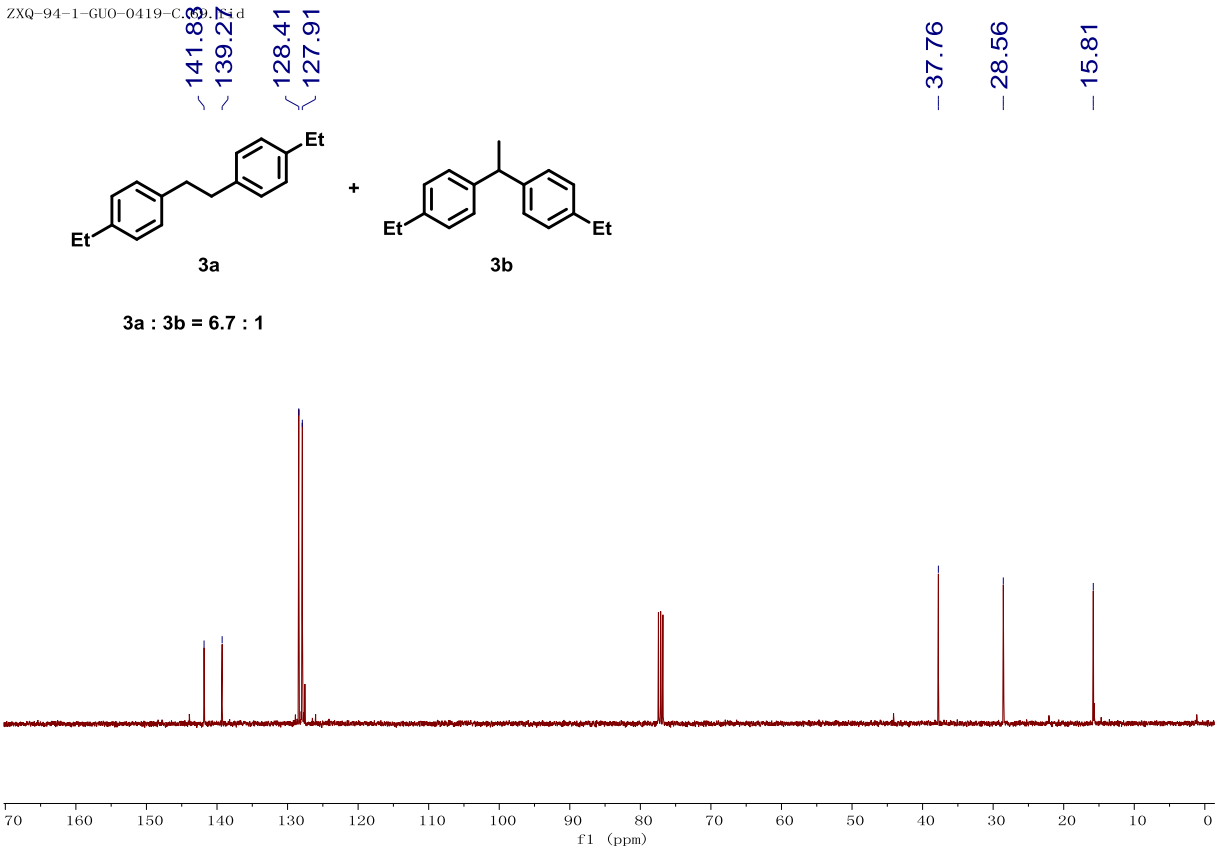
^{13}C NMR for **2a**



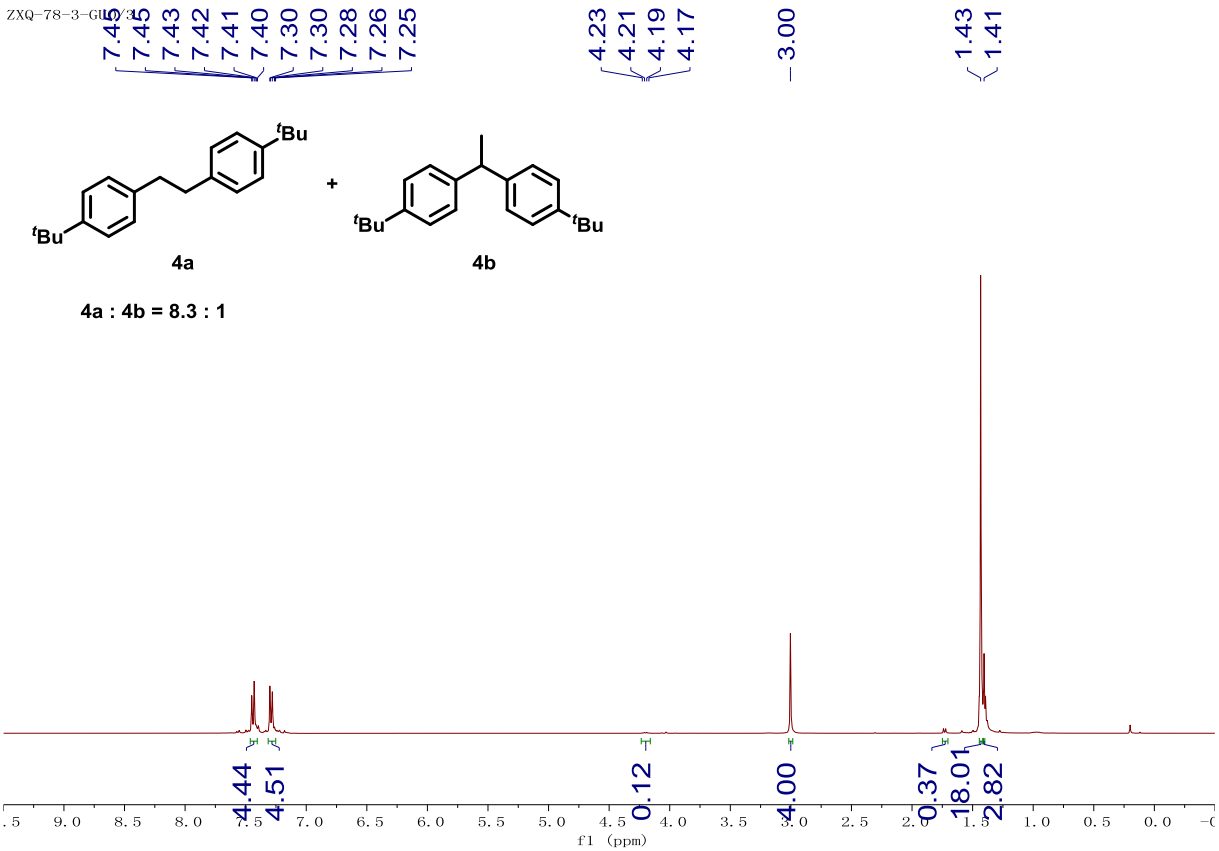
^{1}H NMR for **3a** and **3b**



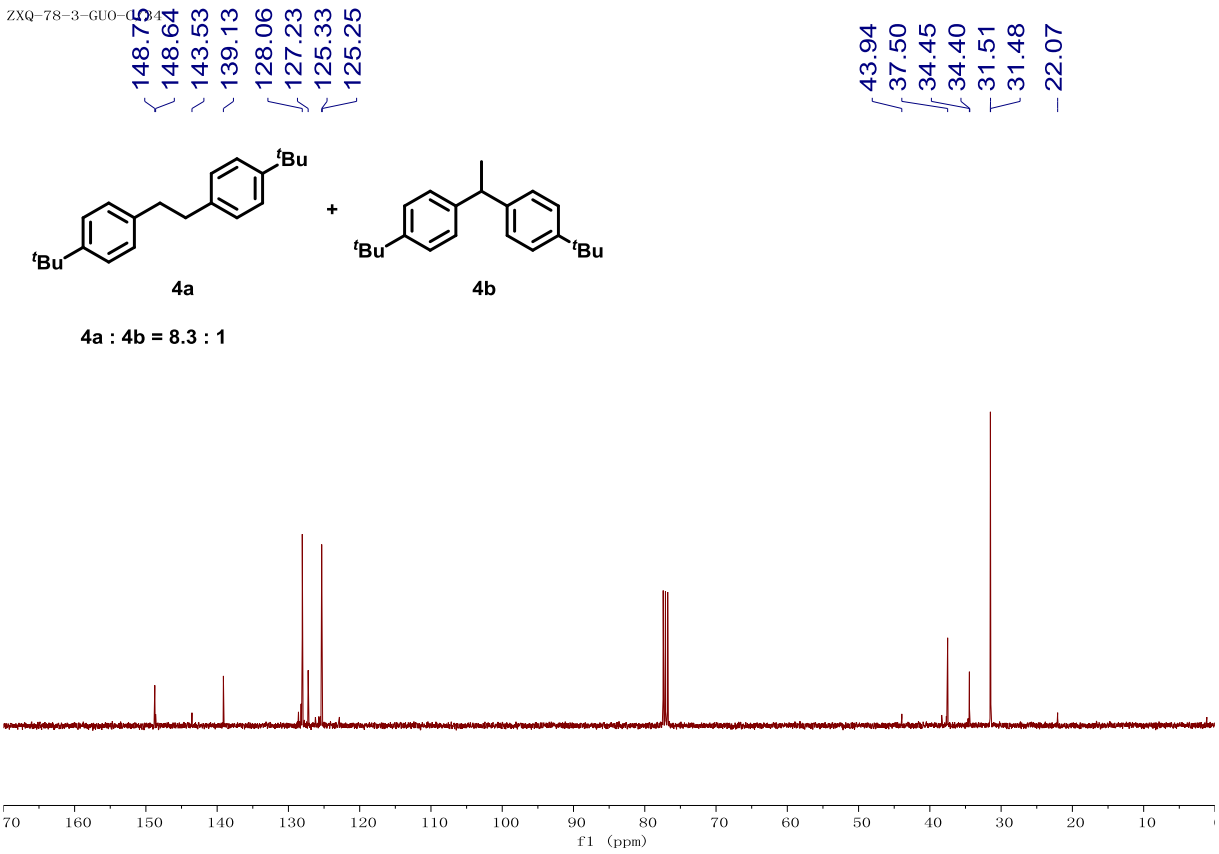
^{13}C NMR for **3a** and **3b**



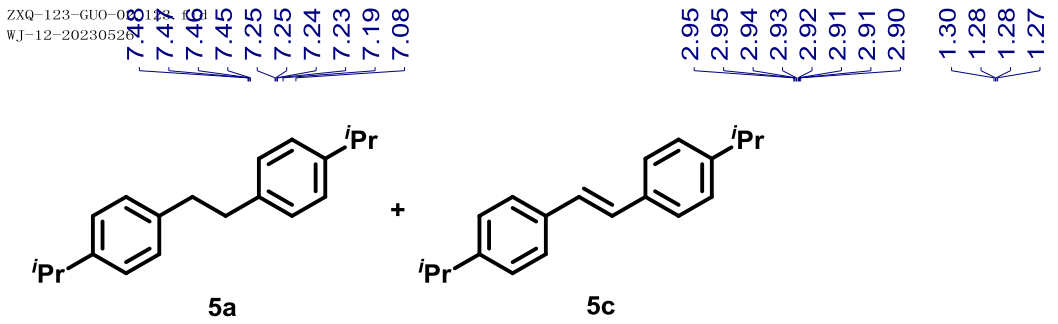
^{1}H NMR for **4a** and **4b**



^{13}C NMR for **4a** and **4b**

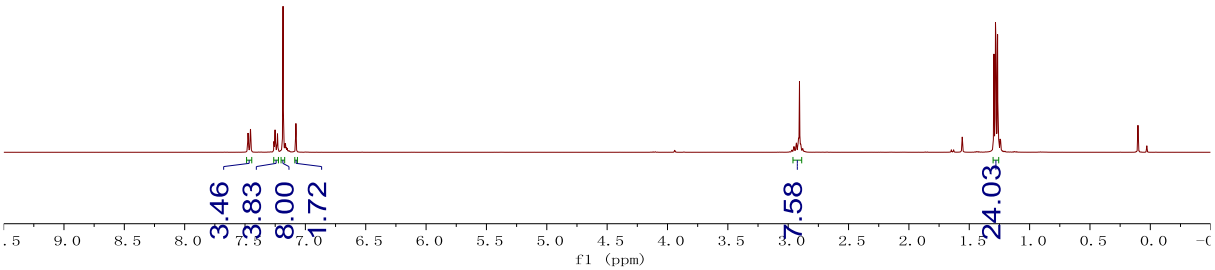


^{1}H NMR for **5a** and **5c**

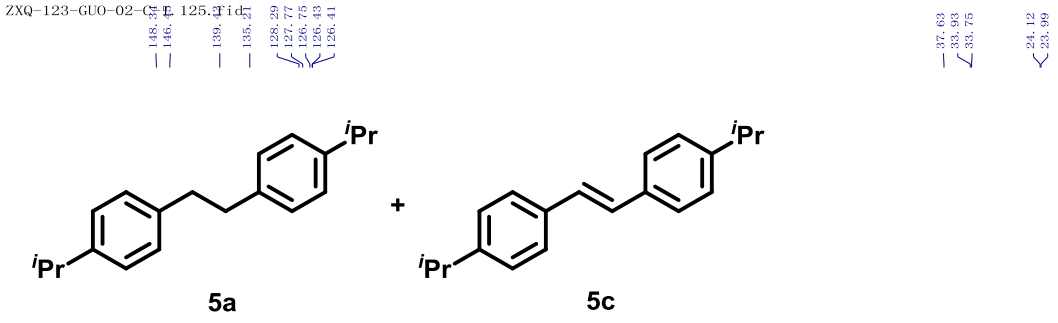


5a **5c**

5a : 5c = 1.1 : 1

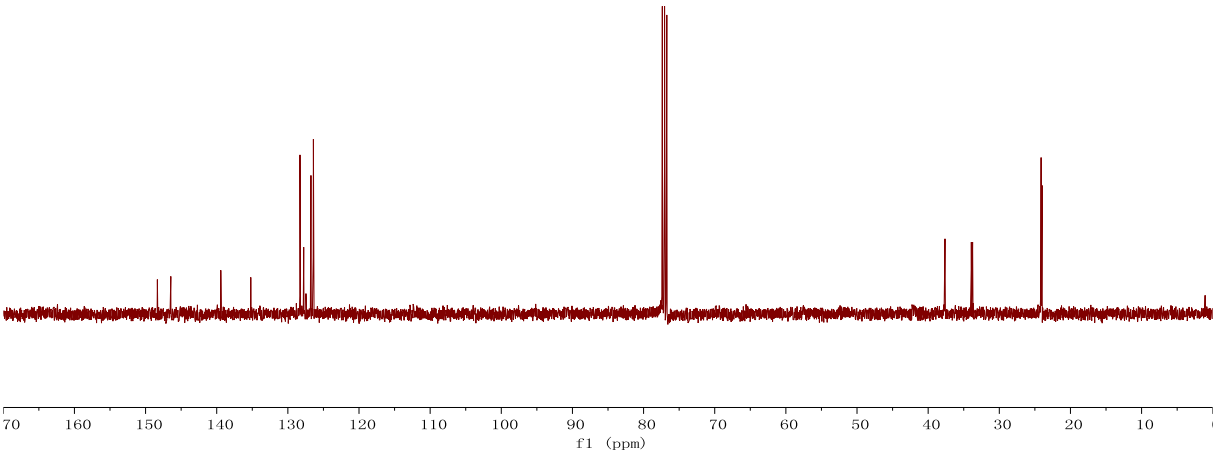


^{13}C NMR for **5a** and **5c**

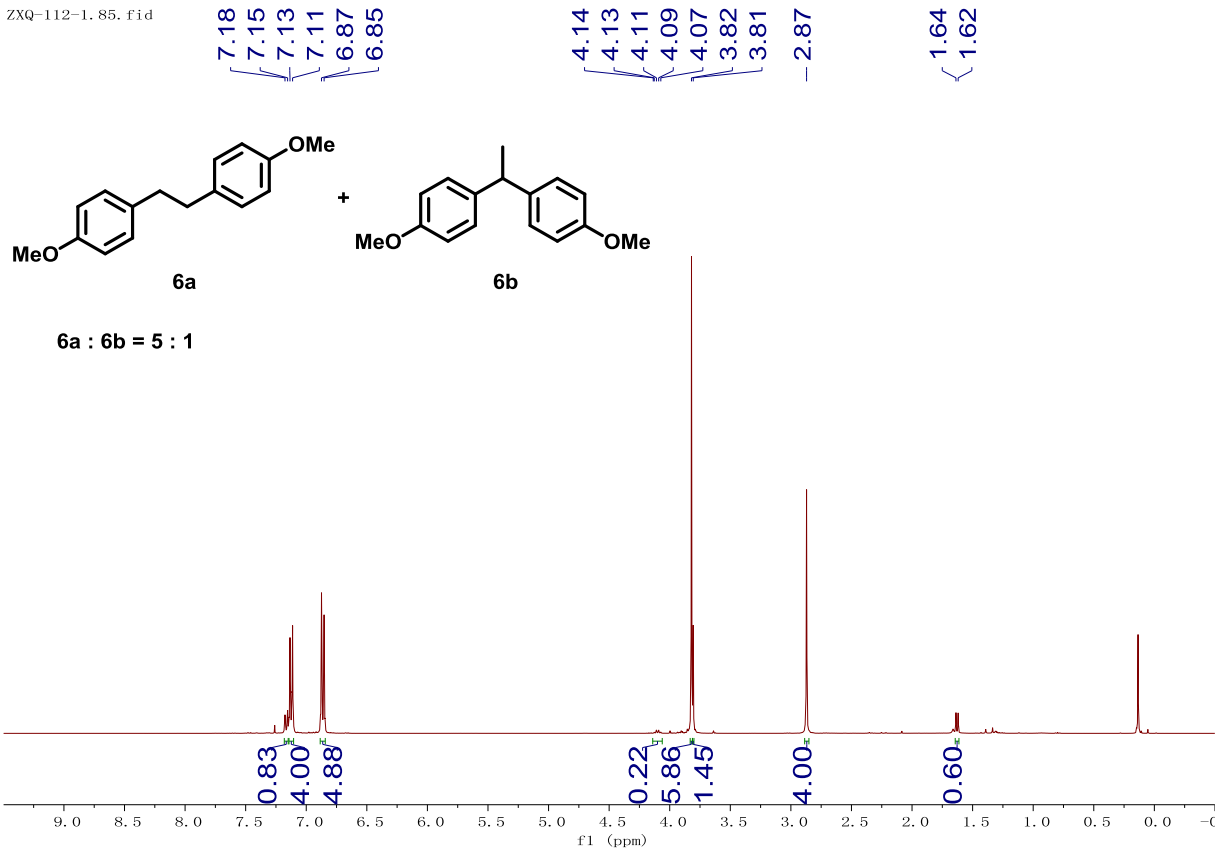


5a **5c**

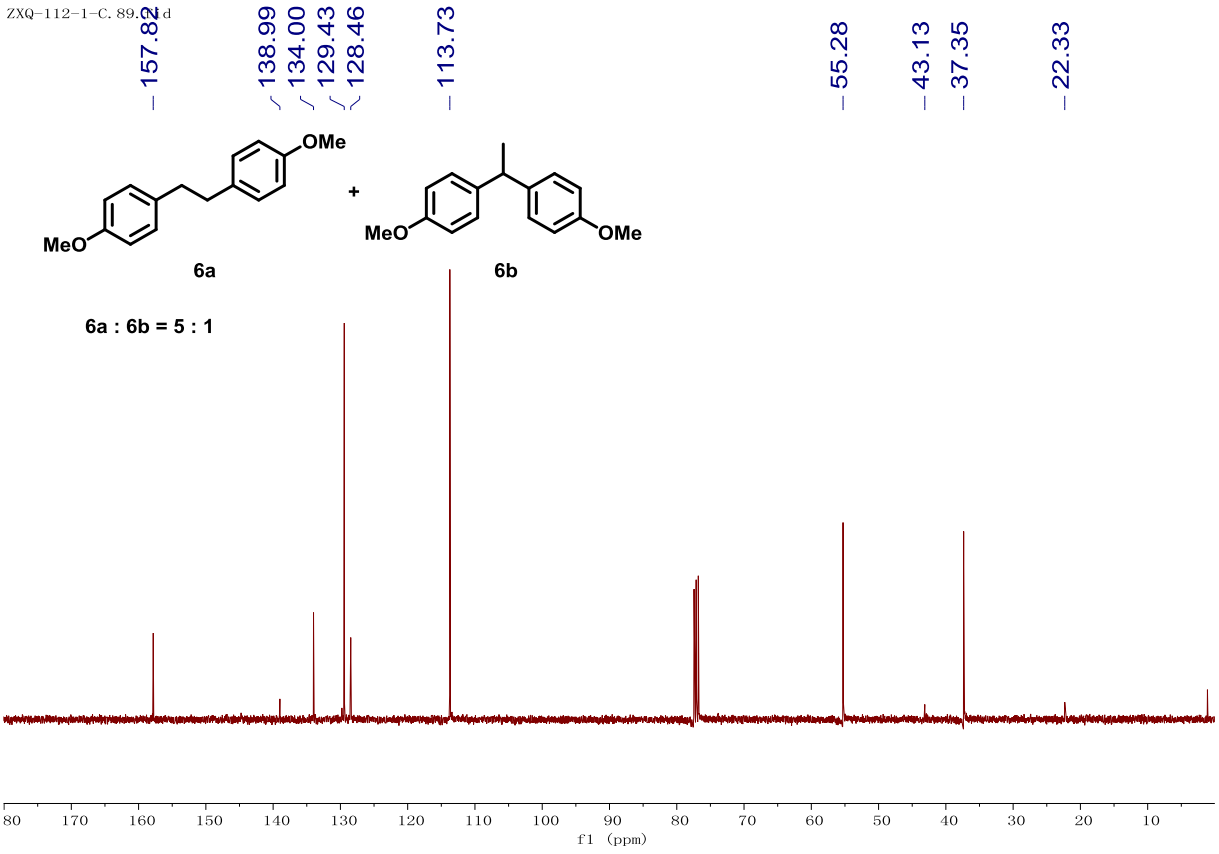
5a : 5c = 1.1 : 1



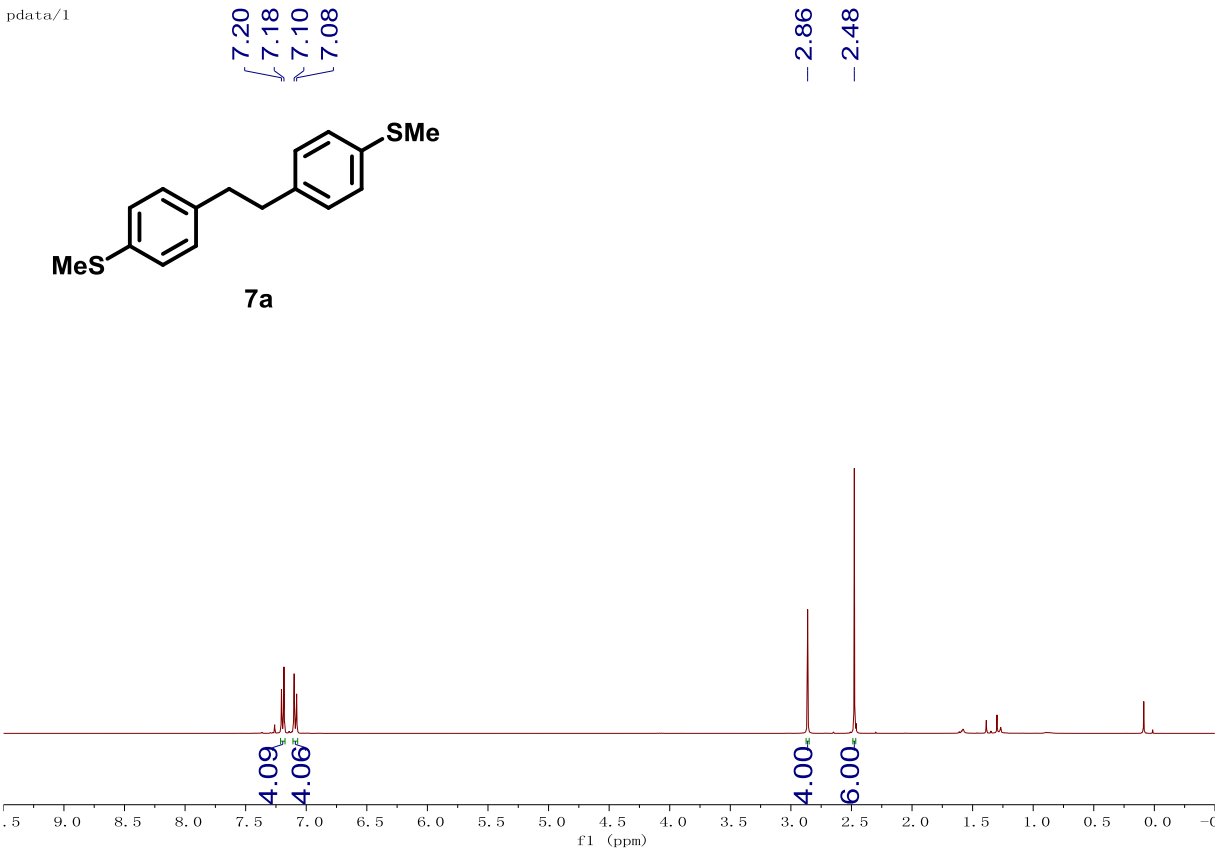
^{1}H NMR for **6a** and **6b**



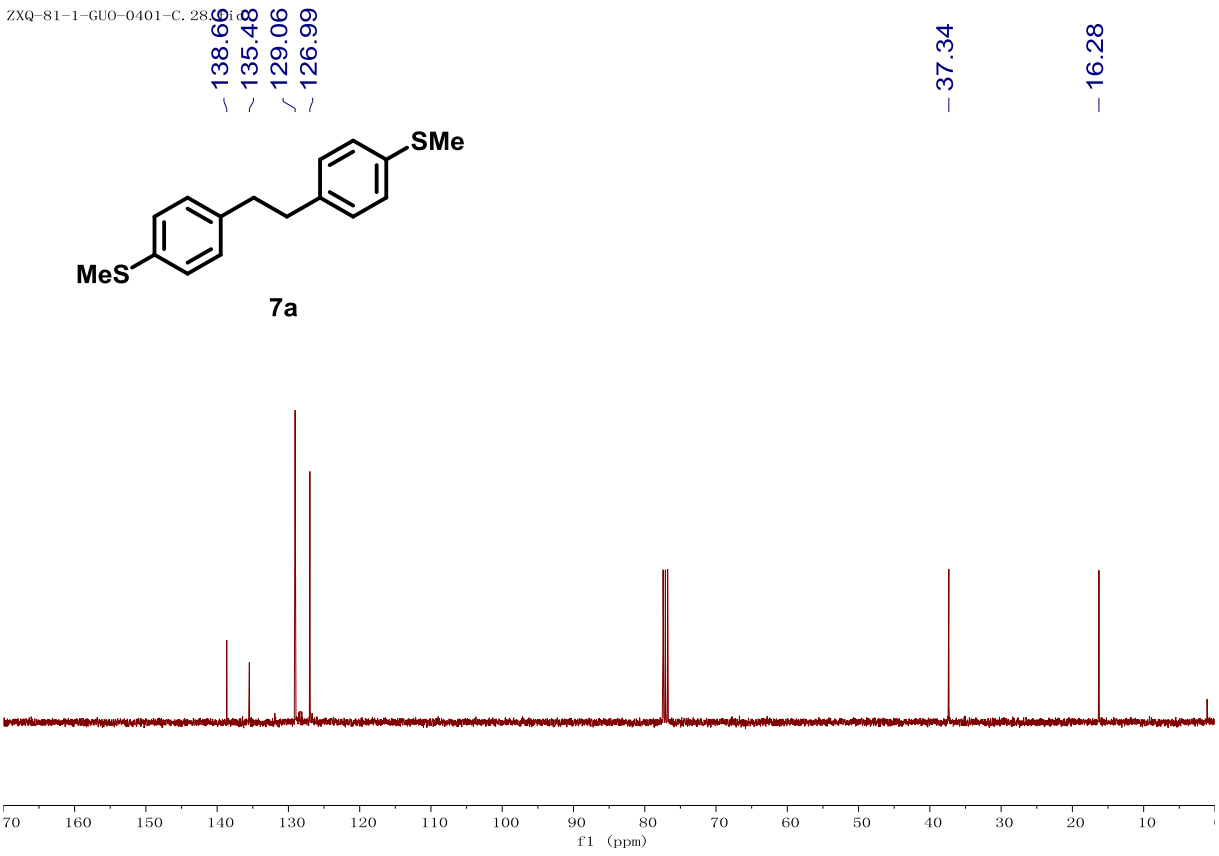
^{13}C NMR for **6a** and **6b**



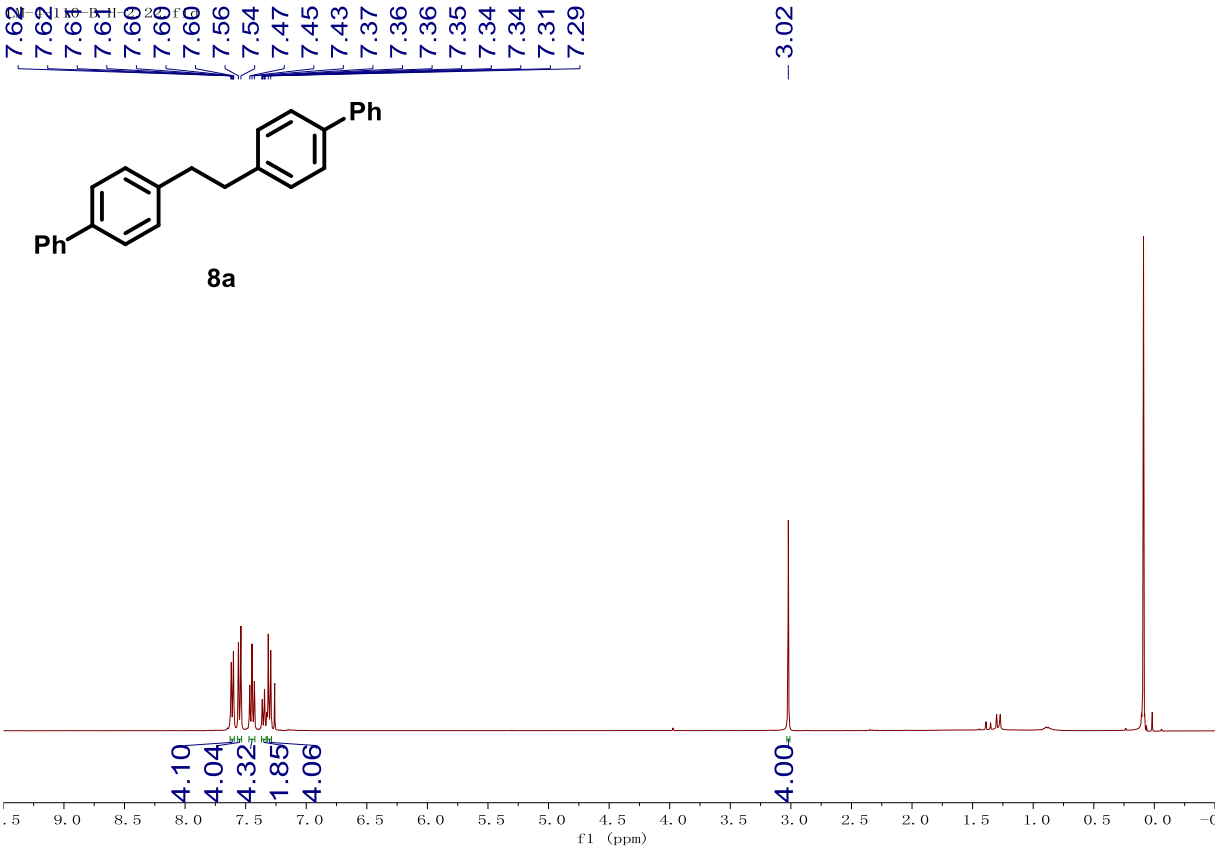
^{1}H NMR for 7**a**



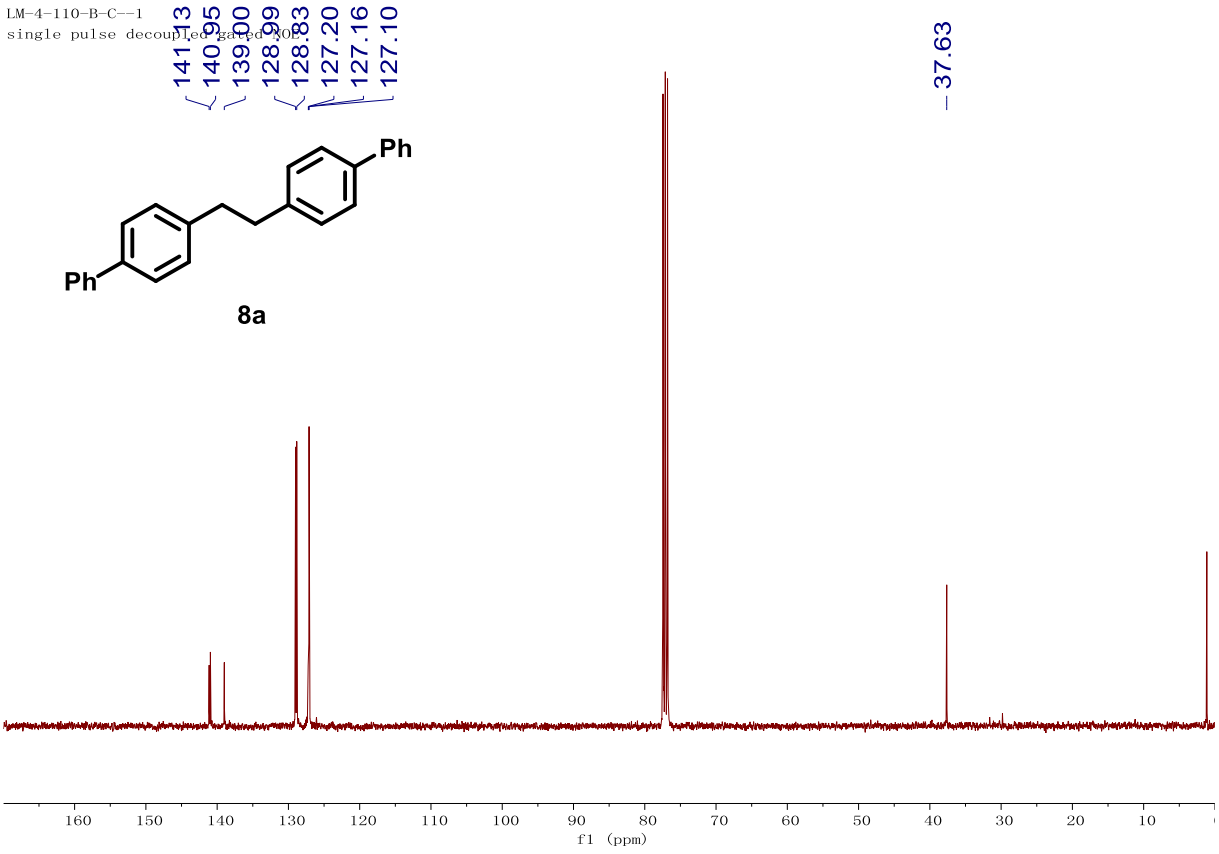
^{13}C NMR for 7**a**



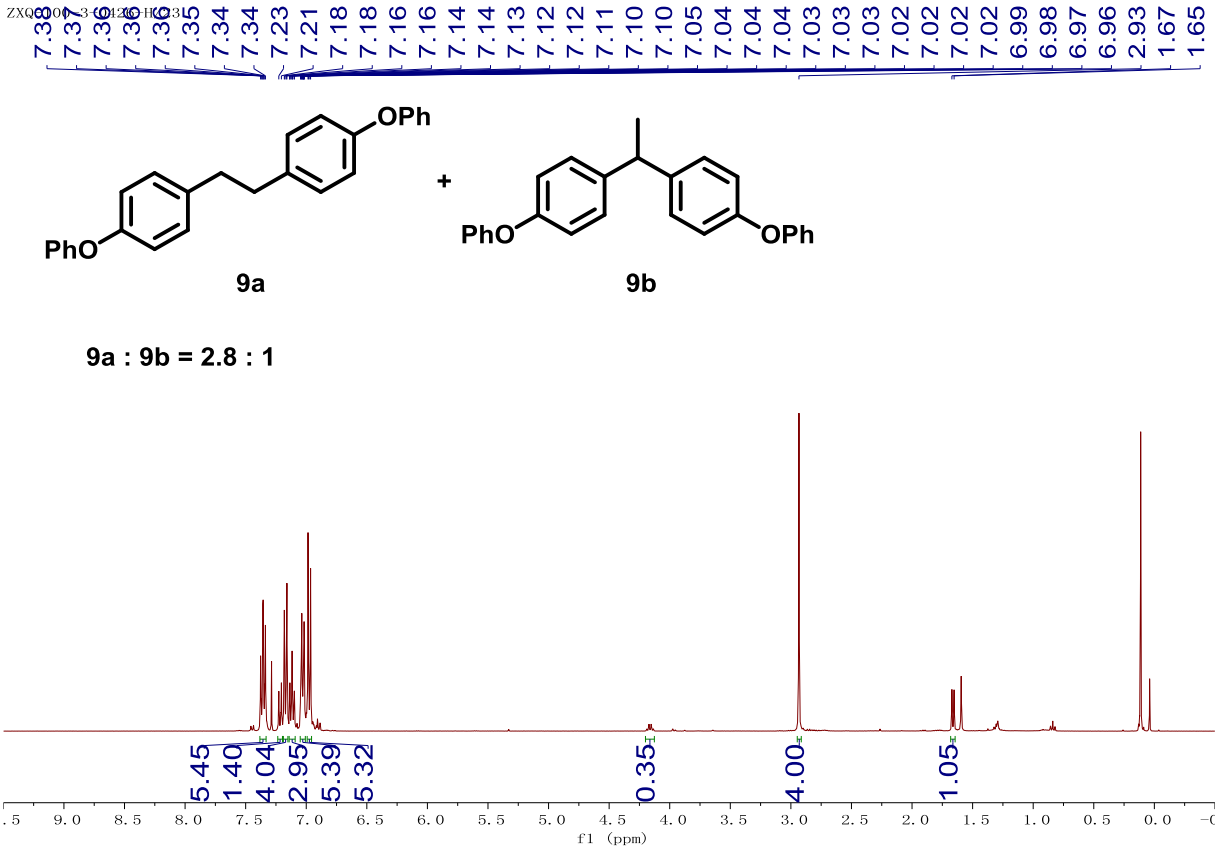
^{1}H NMR for **8a**



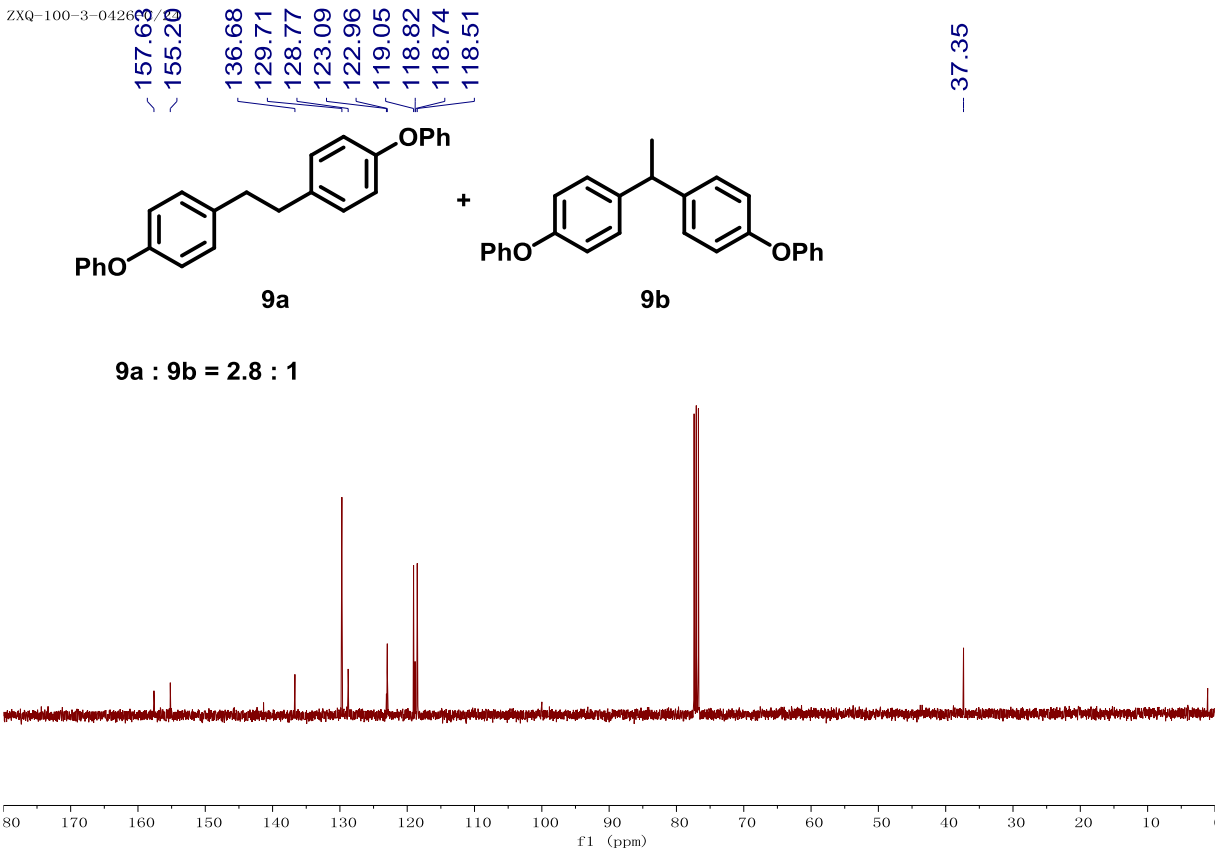
^{13}C NMR for **8a**



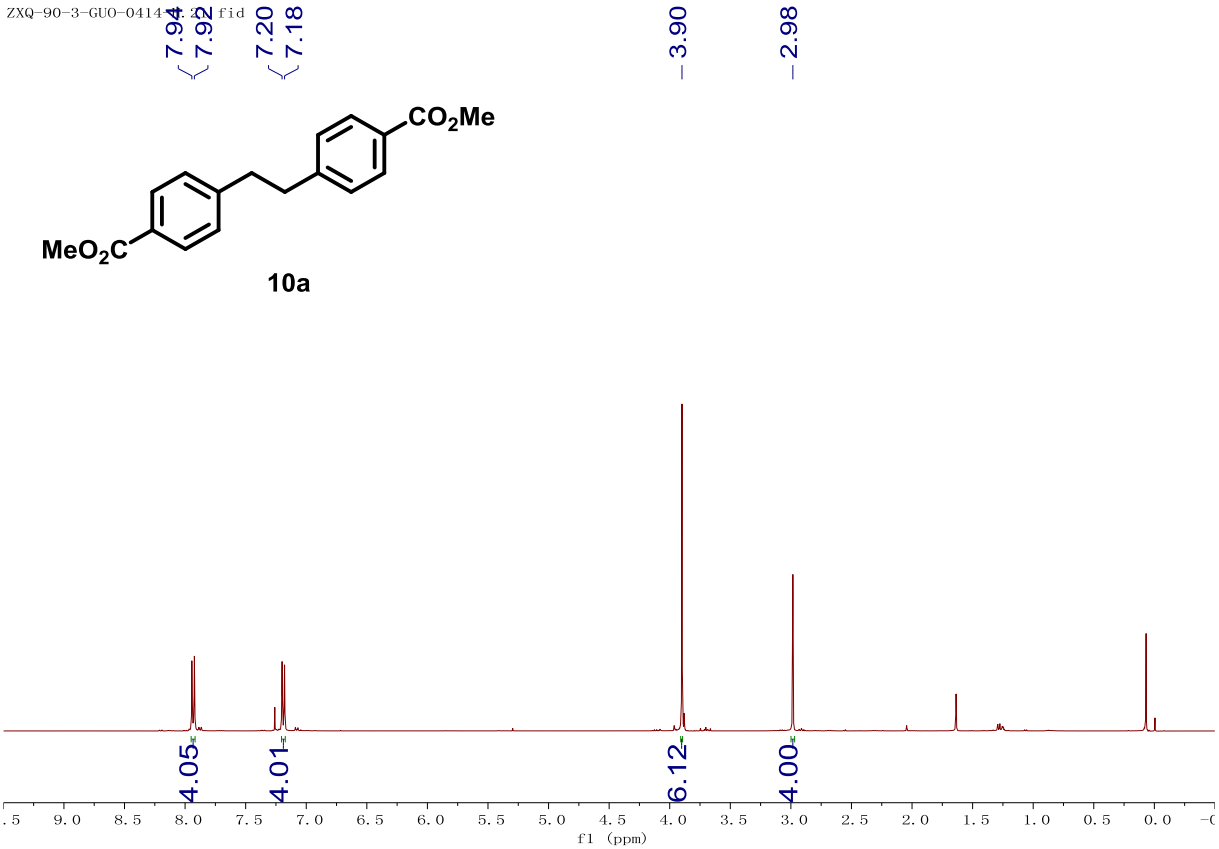
^{1}H NMR for **9a** and **9b**



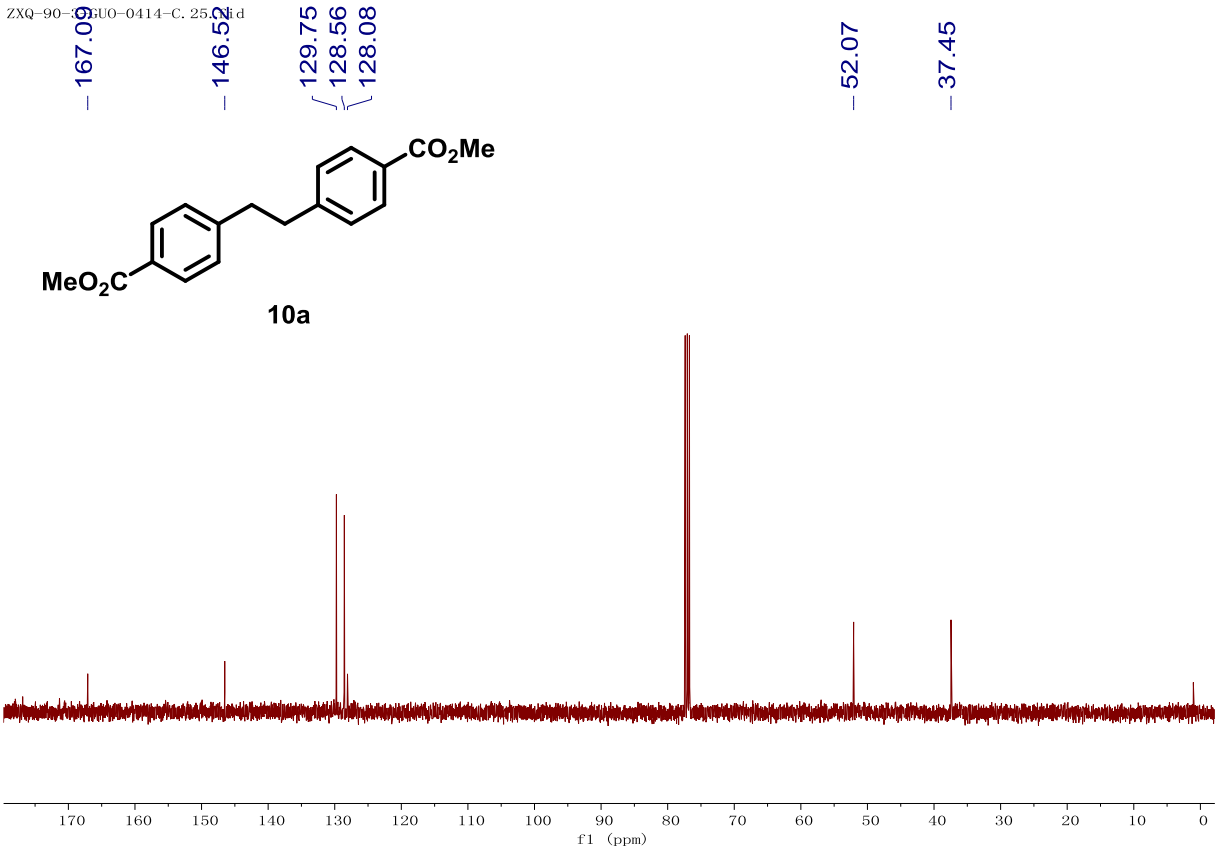
^{13}C NMR for **9a** and **9b**



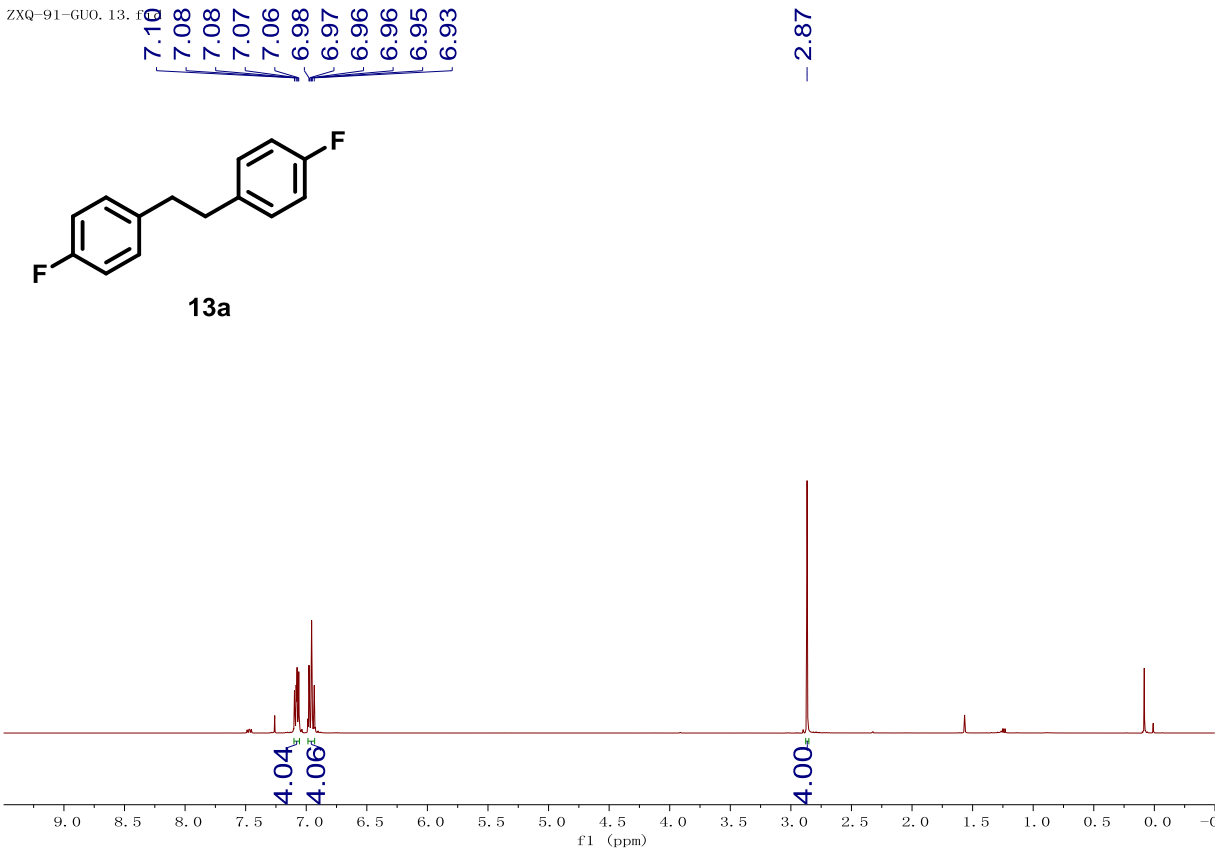
^{1}H NMR for **10a**



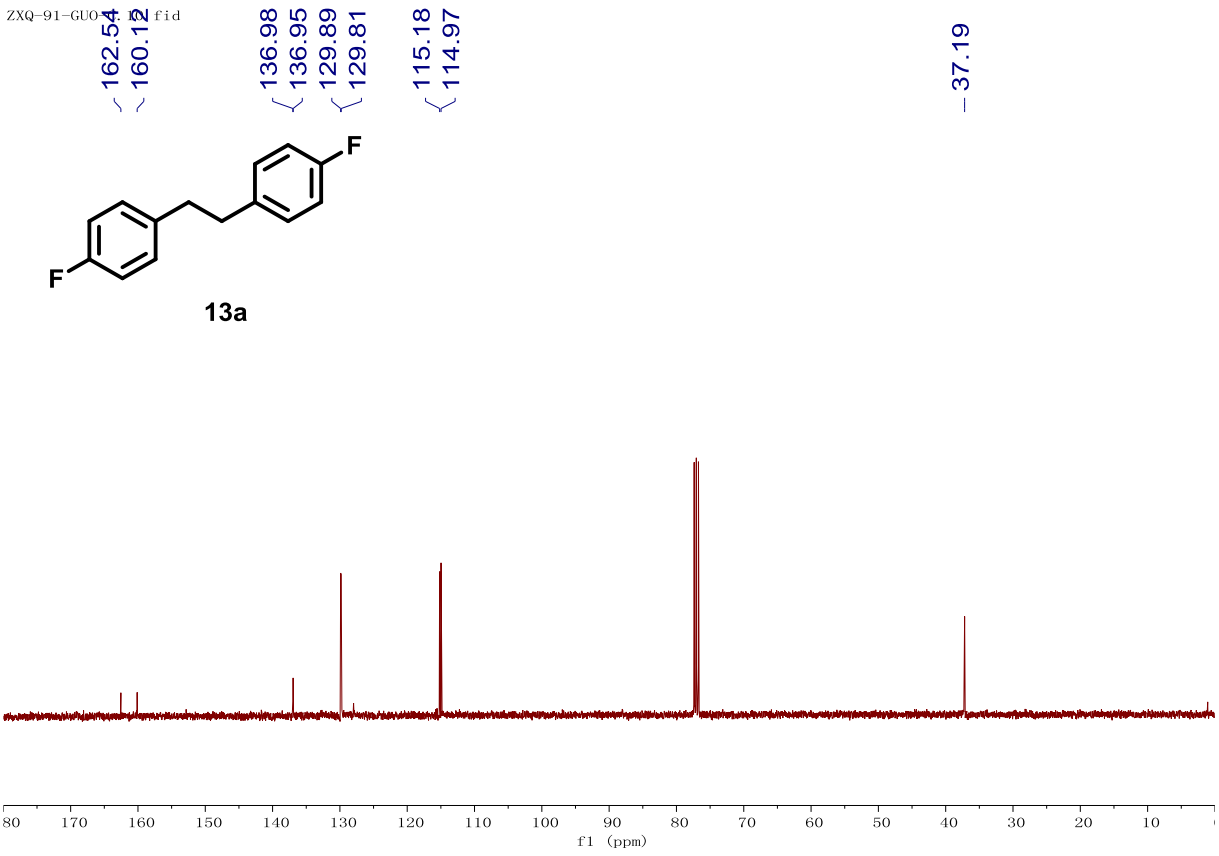
^{13}C NMR for **10a**



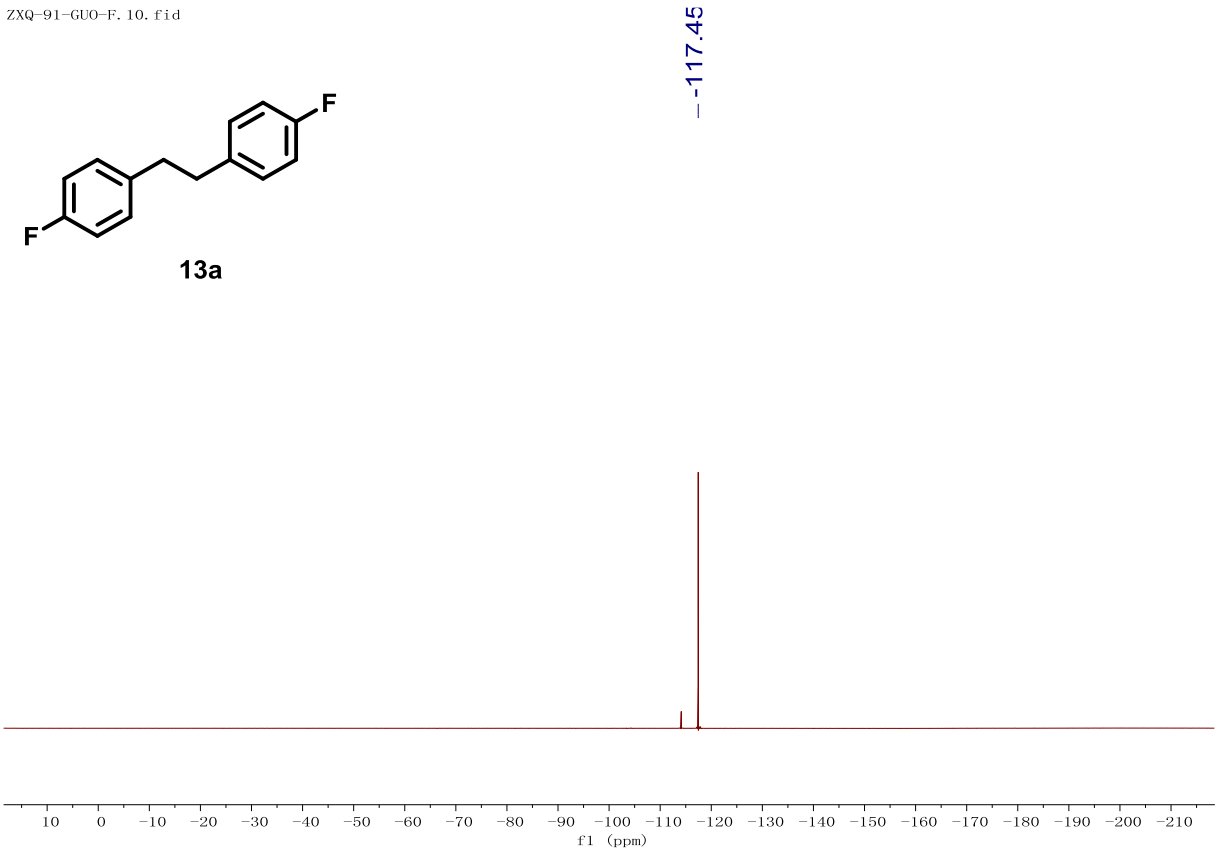
^{1}H NMR for **13a**



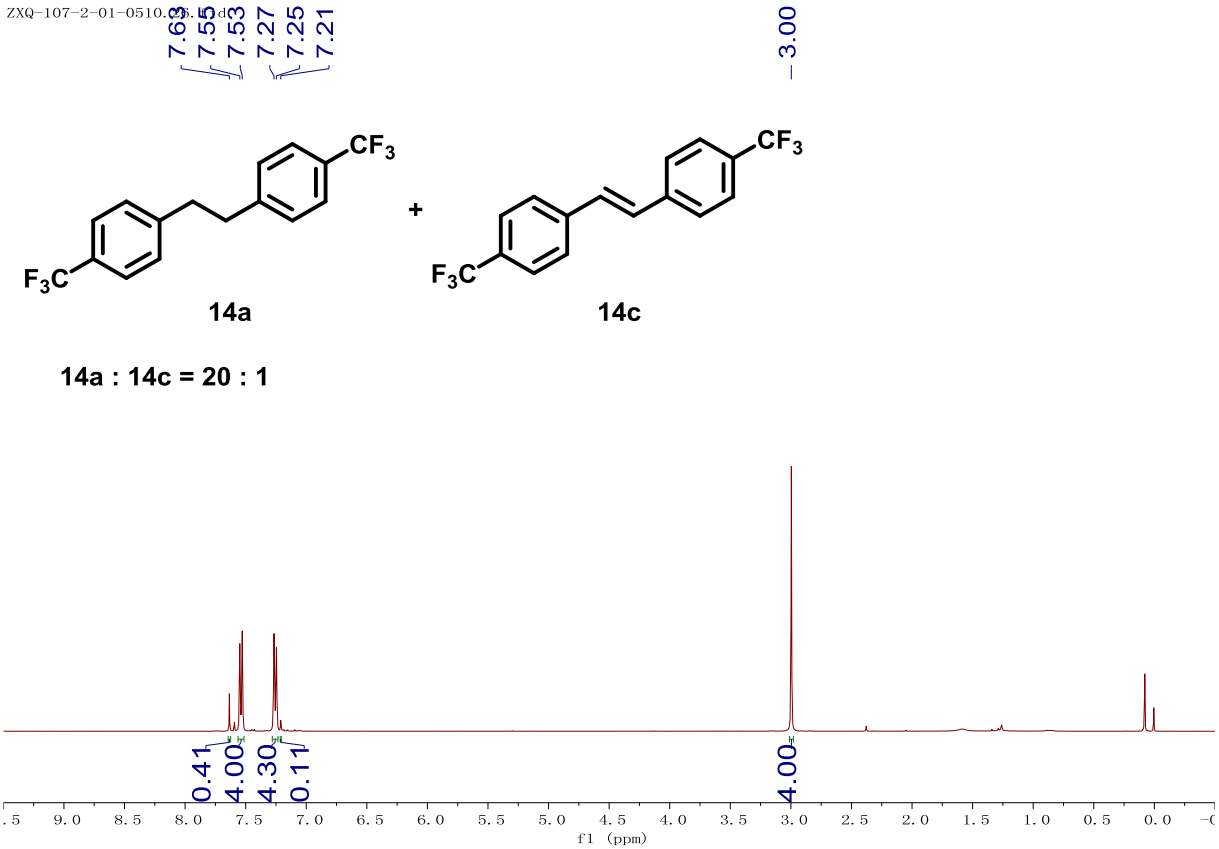
^{13}C NMR for **13a**



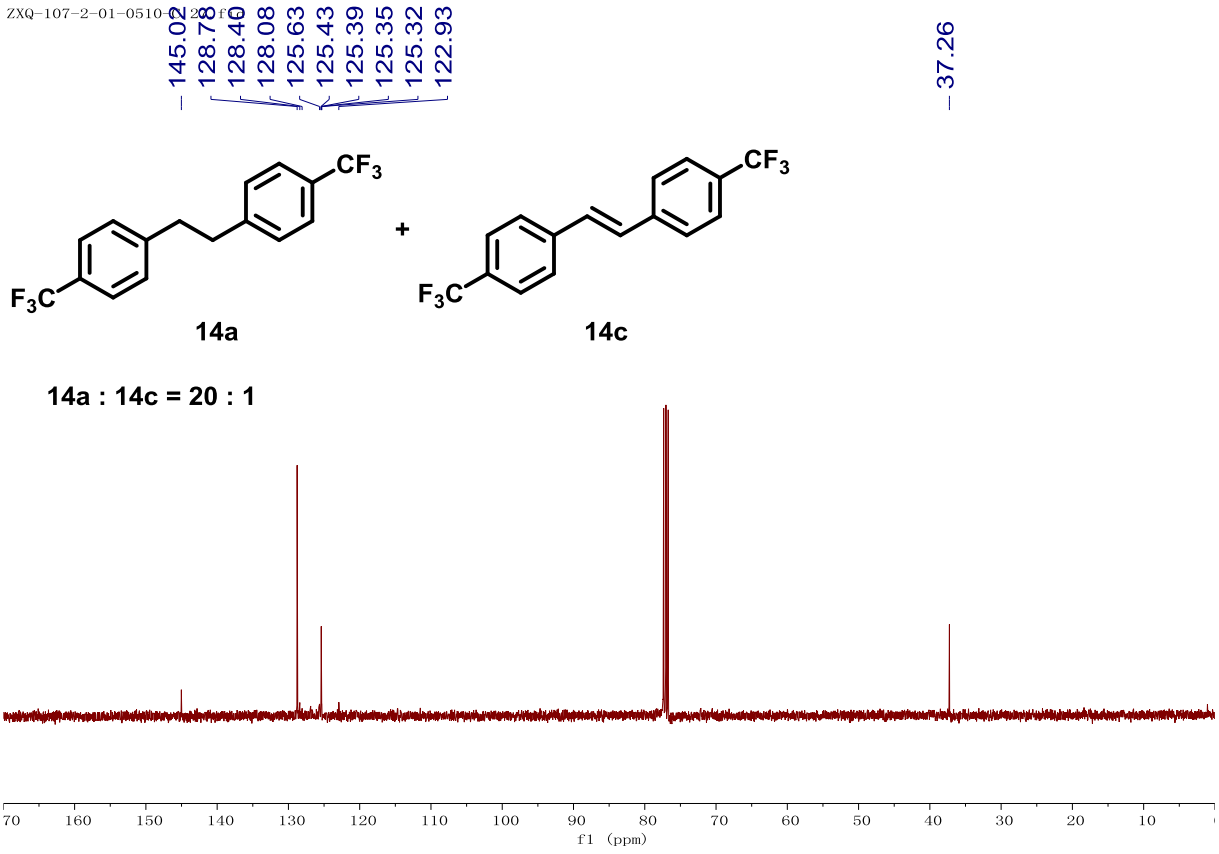
^{19}F NMR for **13a**



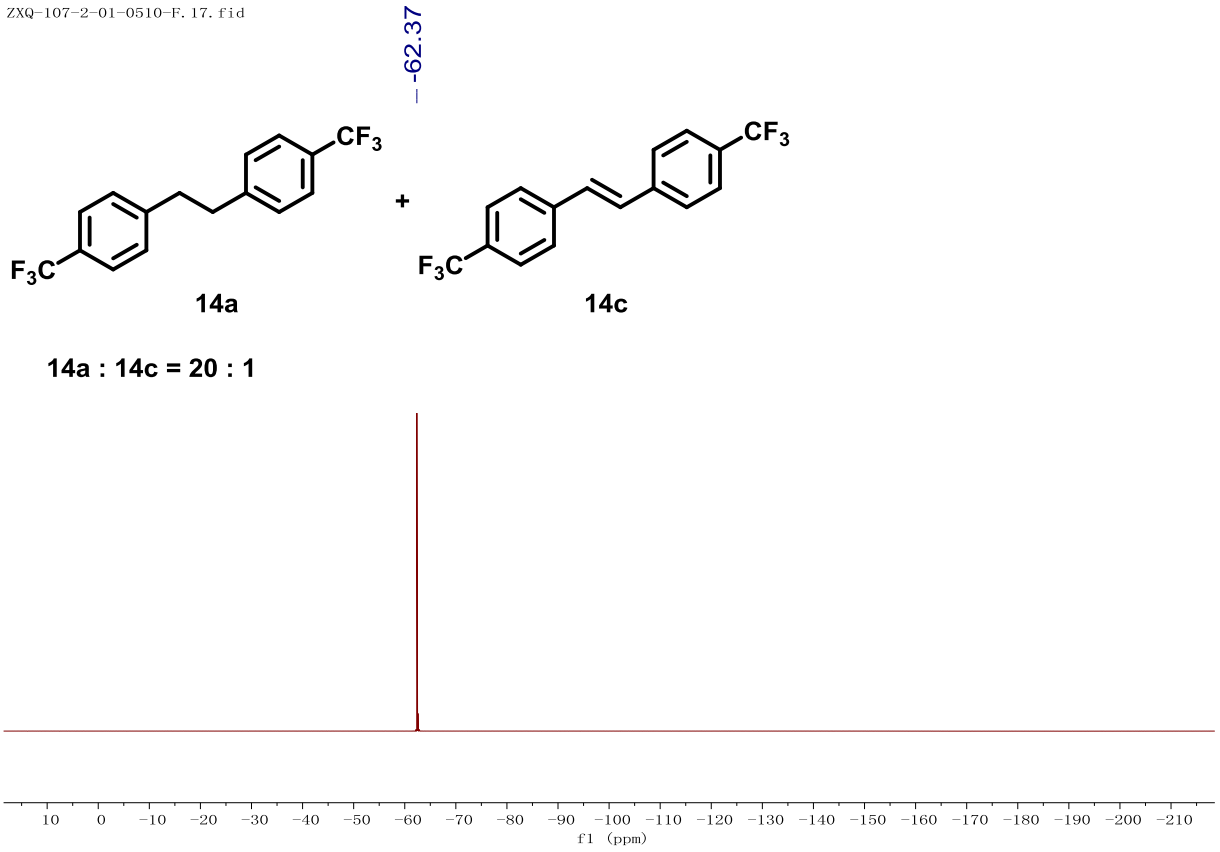
^{1}H NMR for **14a** and **14c**



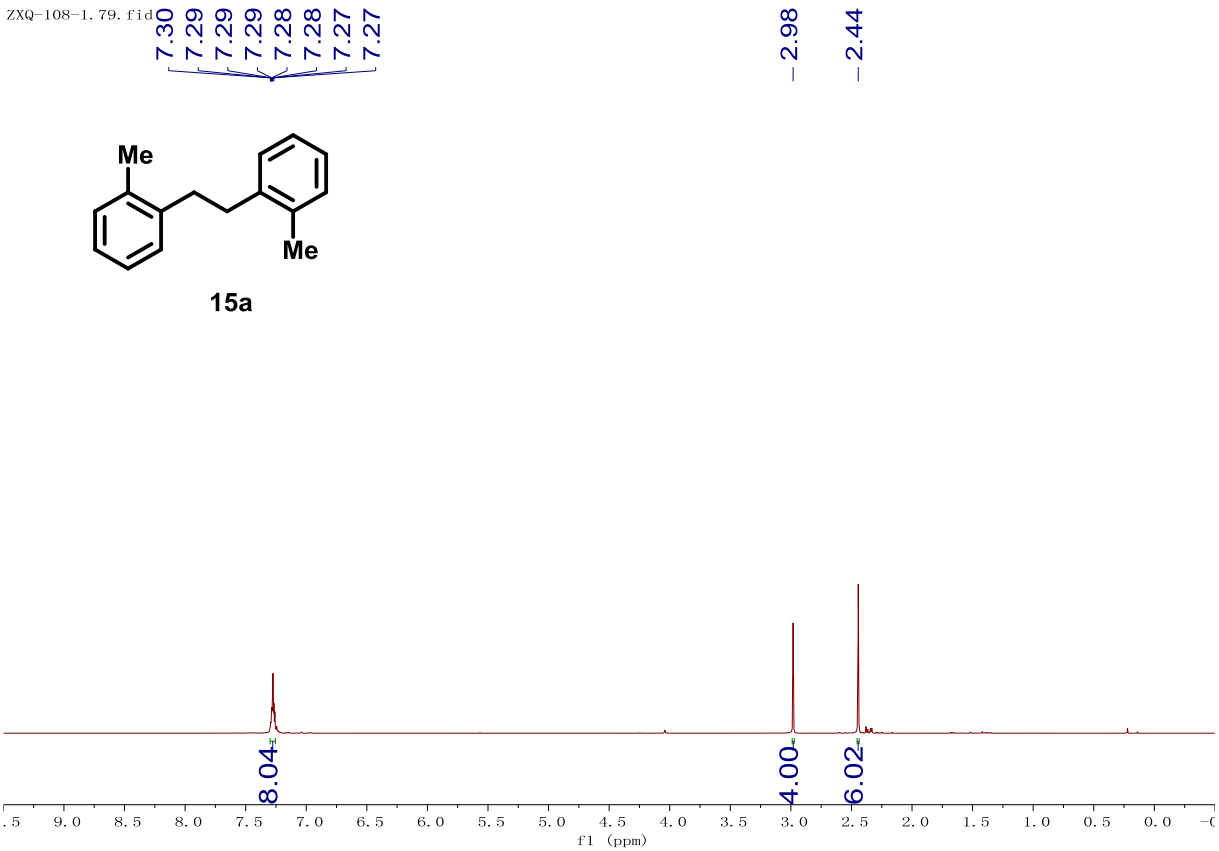
^{13}C NMR for **14a** and **14c**



^{19}F NMR for **14a** and **14c**

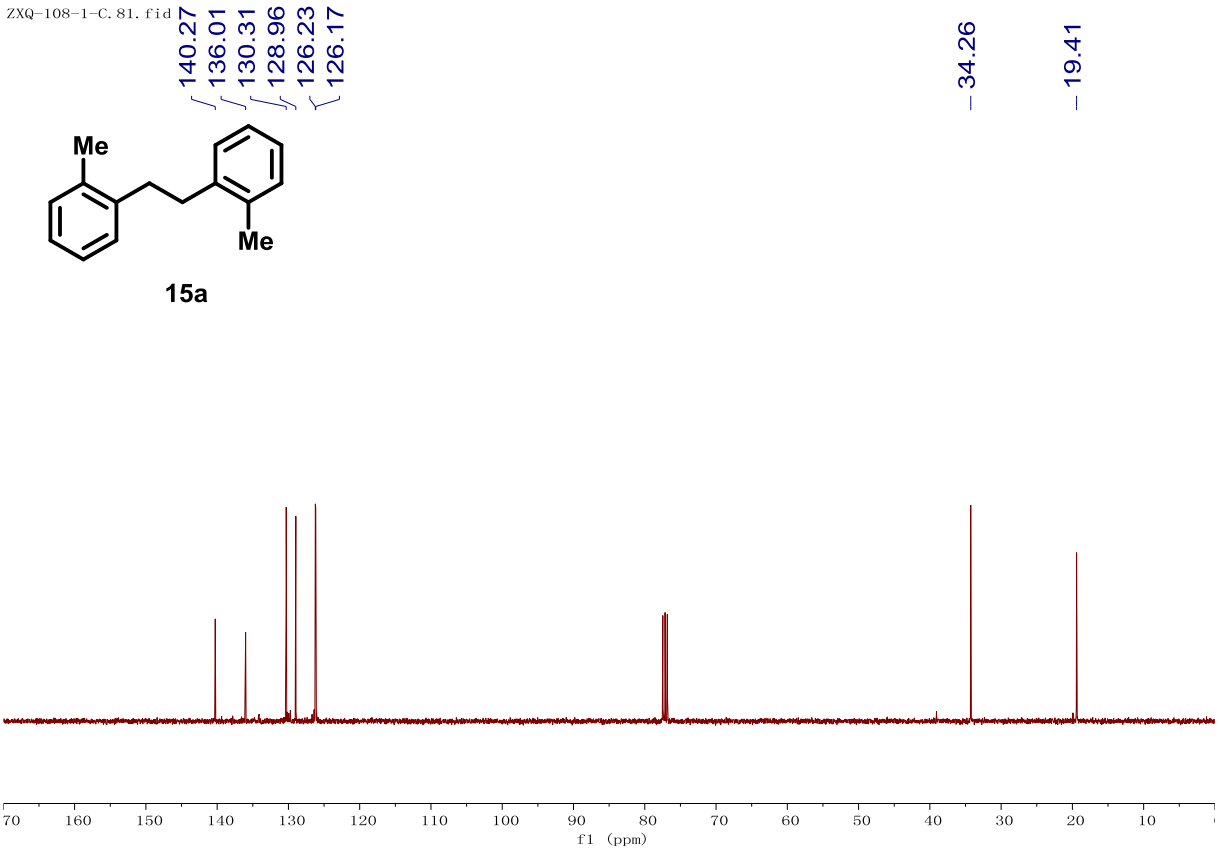


^{1}H NMR for **15a**



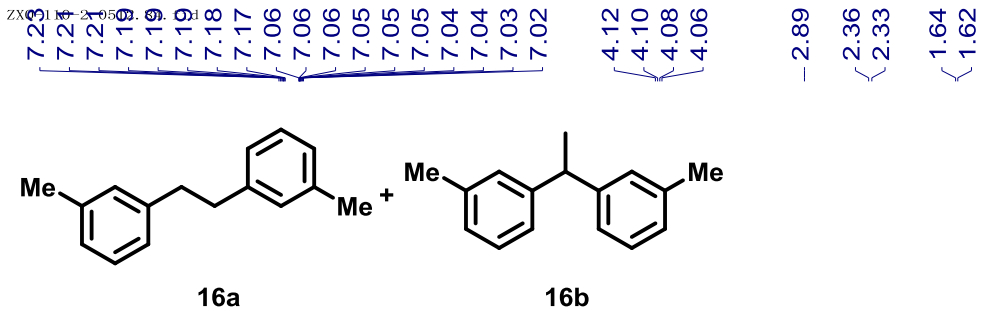
15a

^{13}C NMR for **15a**



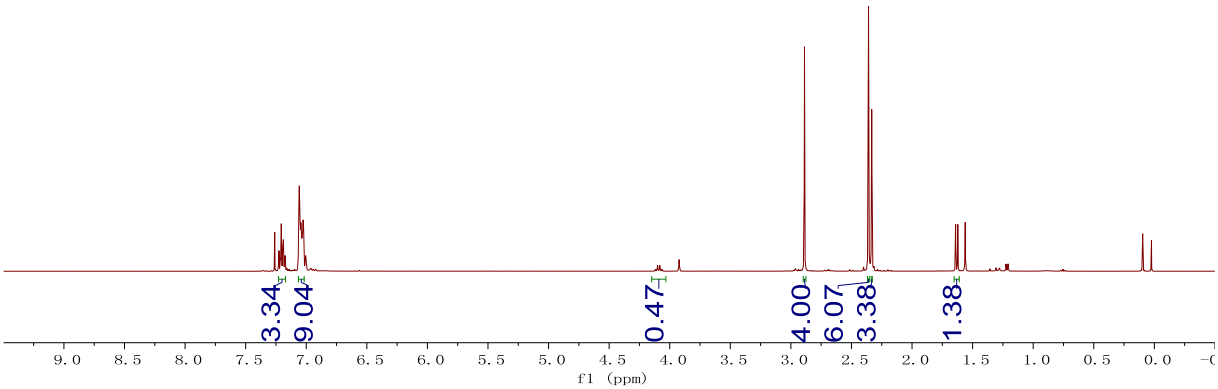
15a

^{1}H NMR for **16a** and **16b**

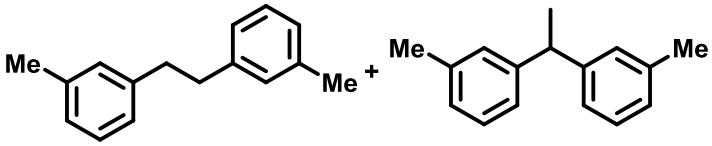


16a **16b**

16a : 16b = 2 : 1

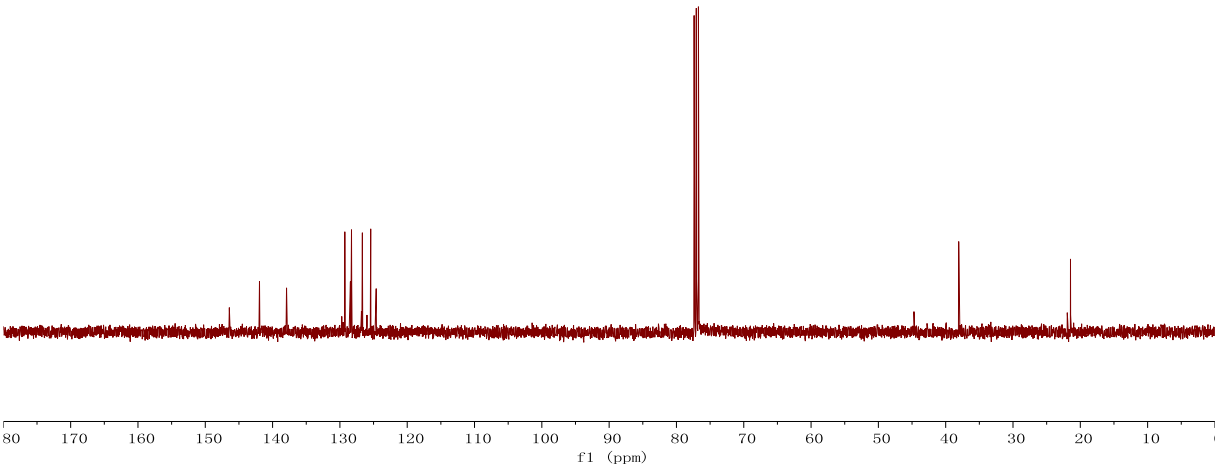


^{13}C NMR for **16a** and **16b**

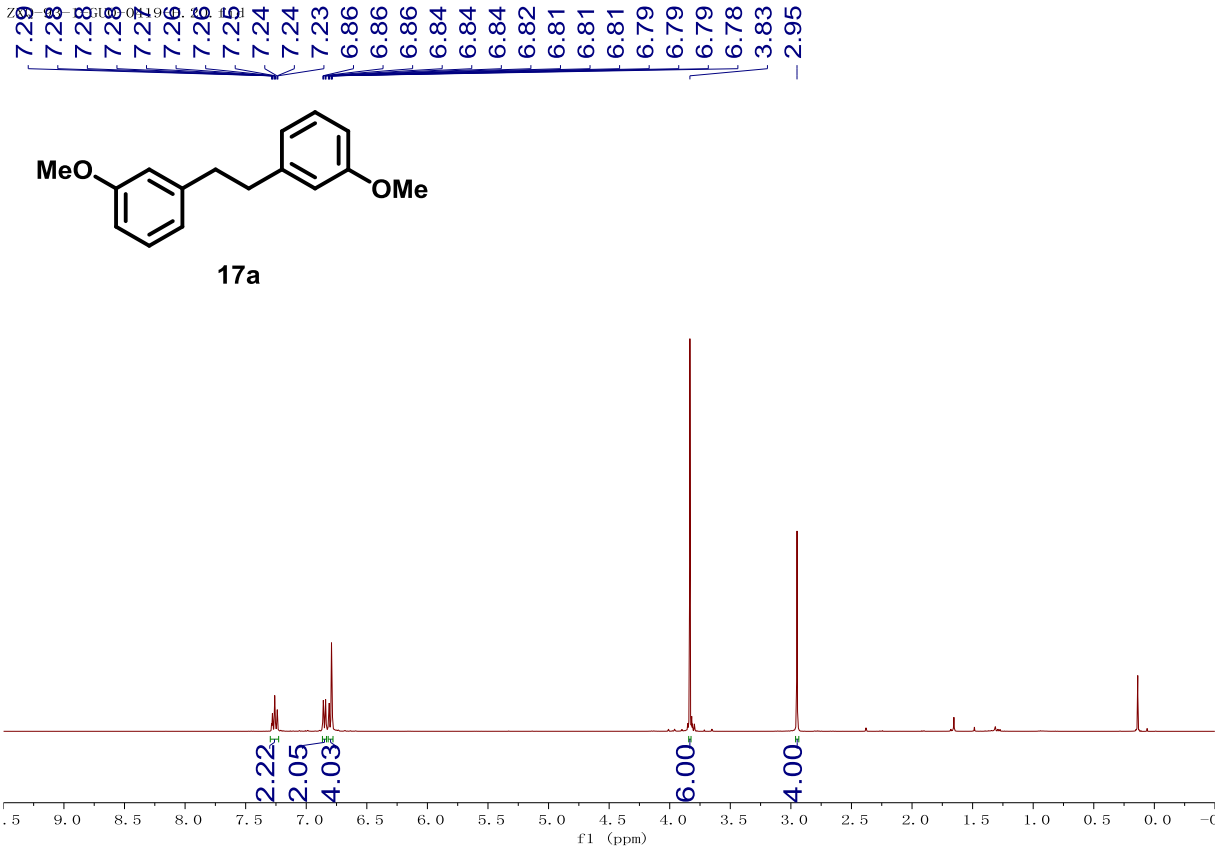


16a **16b**

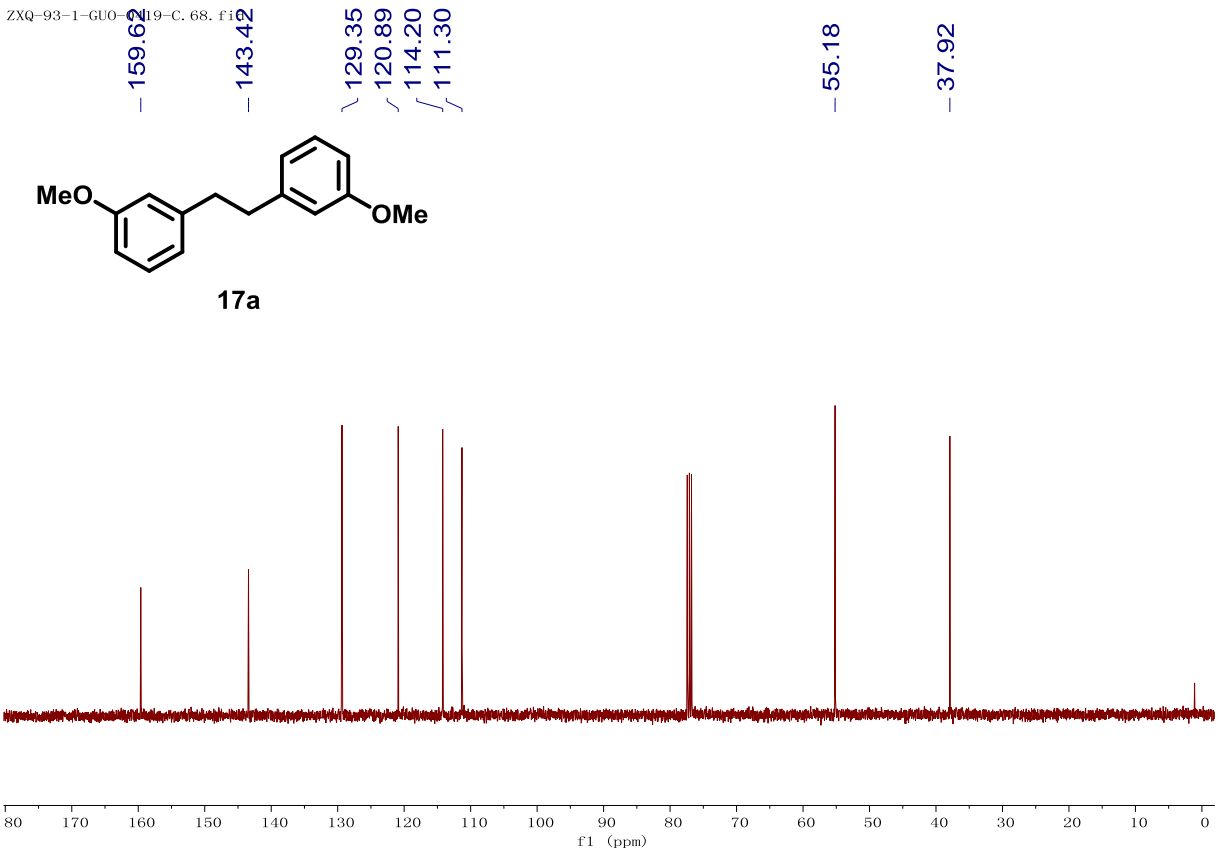
16a : 16b = 2 : 1



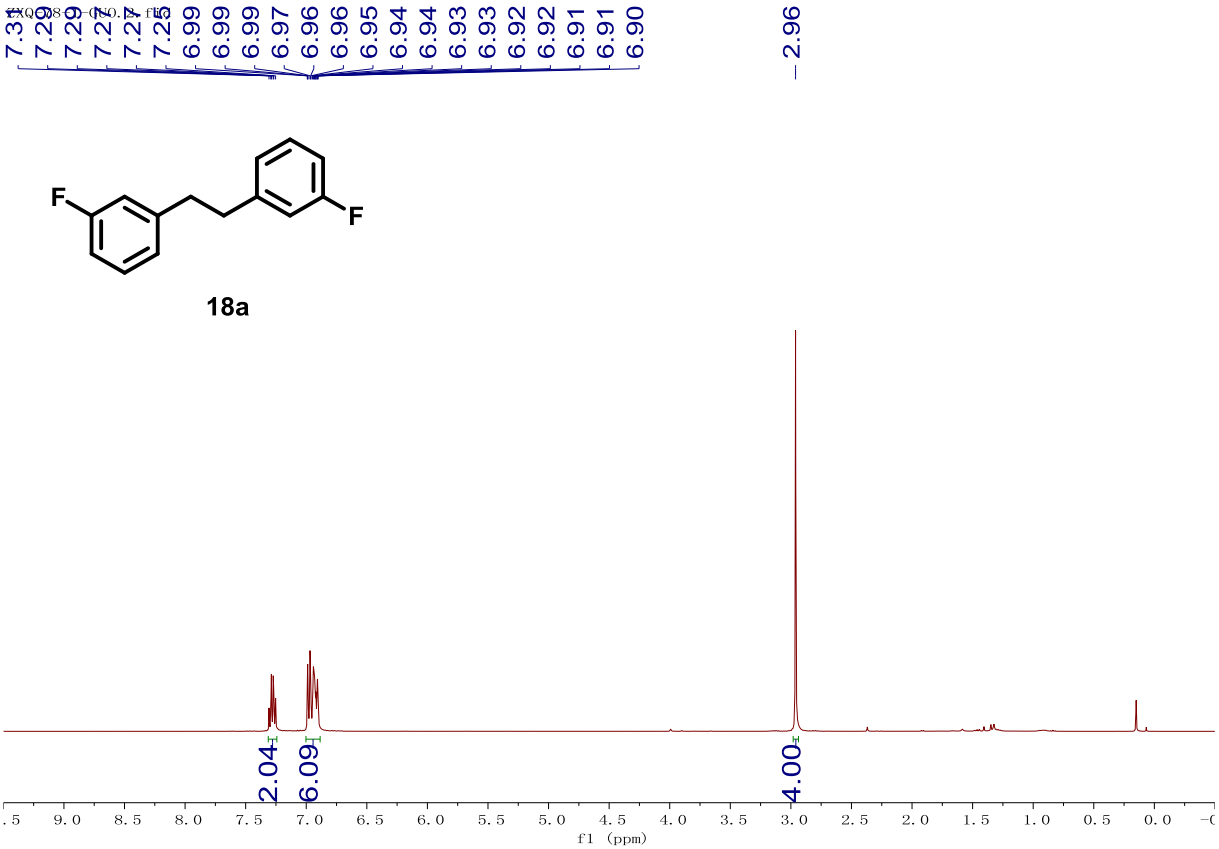
^{1}H NMR for **17a**



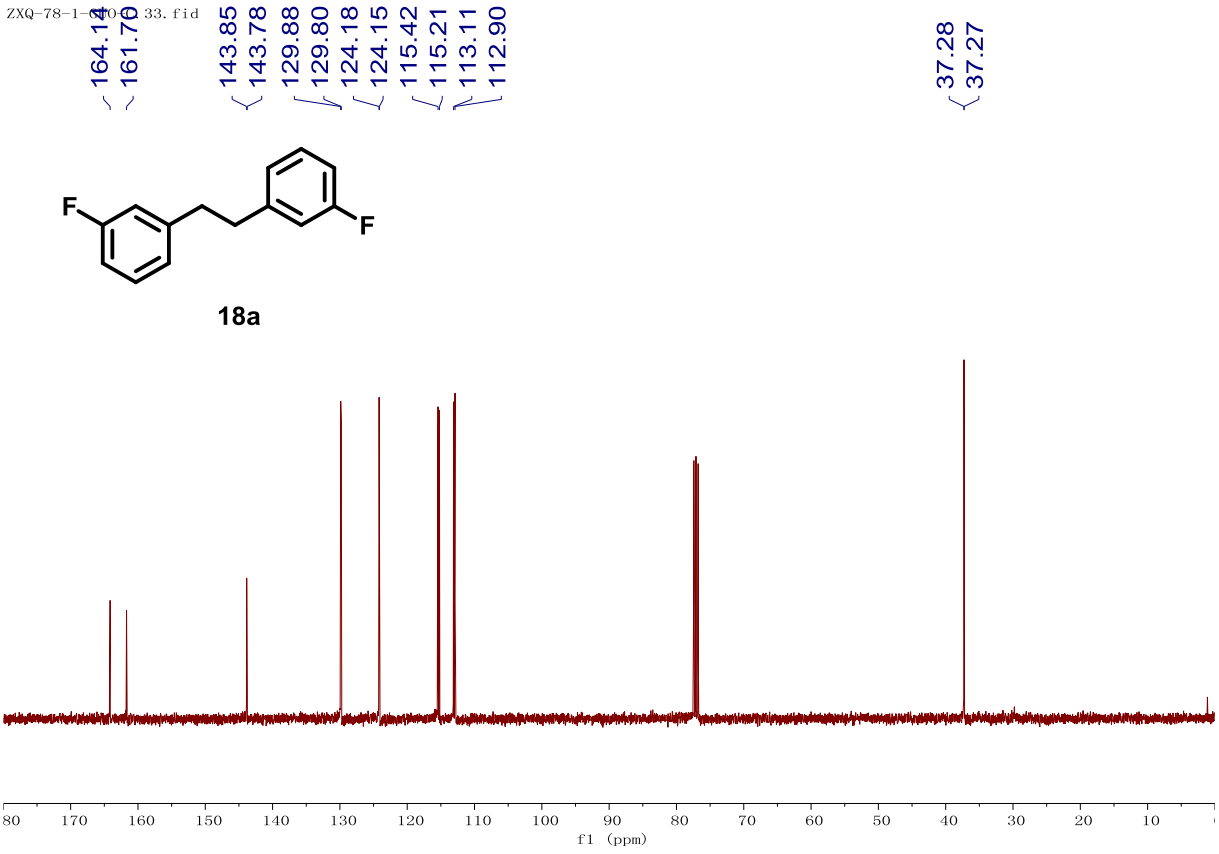
^{13}C NMR for **17a**



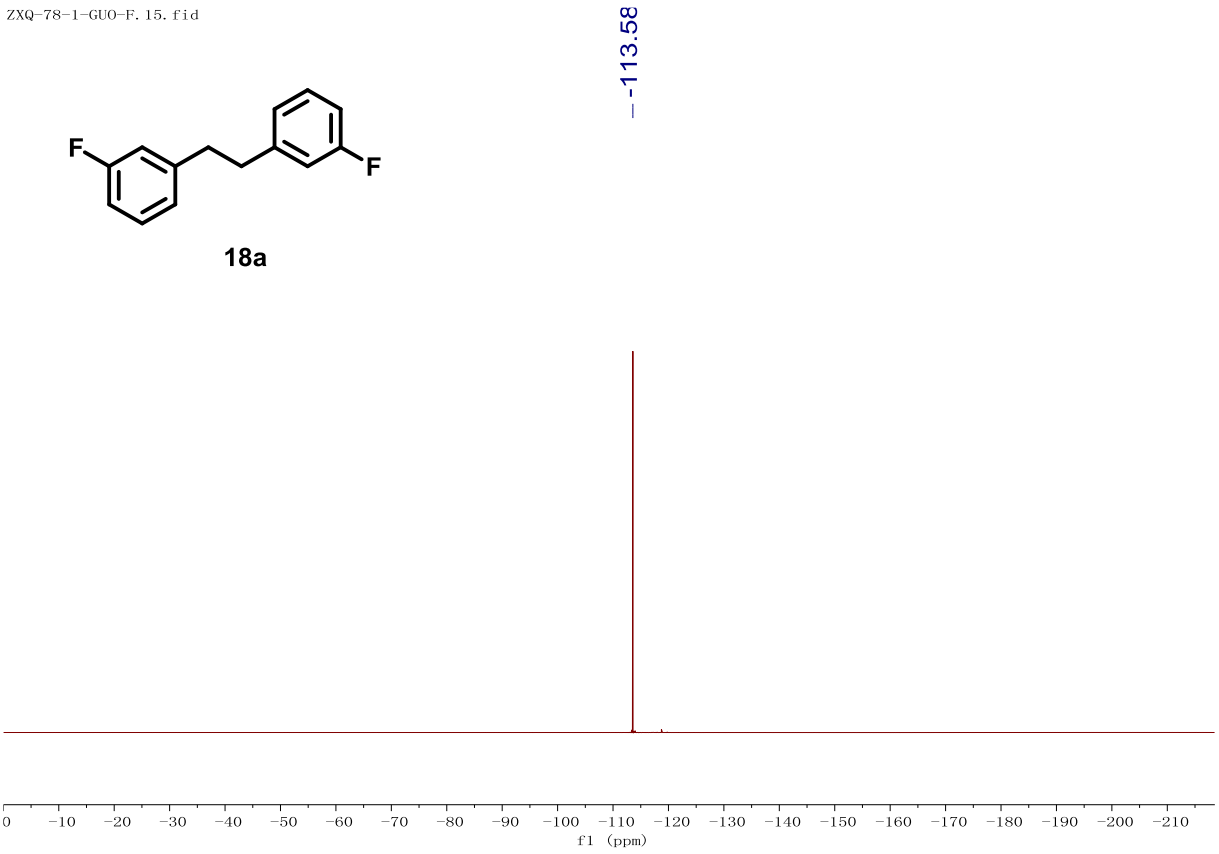
^{1}H NMR for **18a**



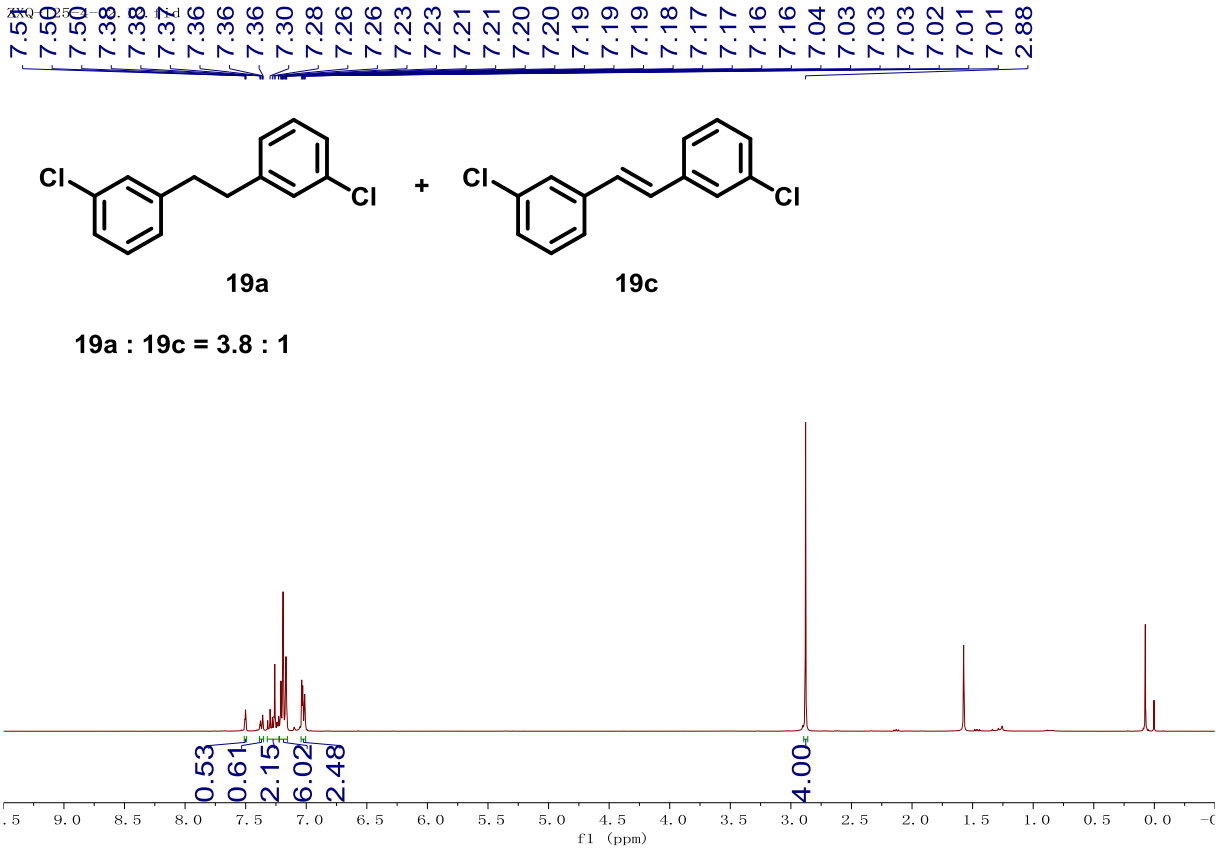
^{13}C NMR for **18a**



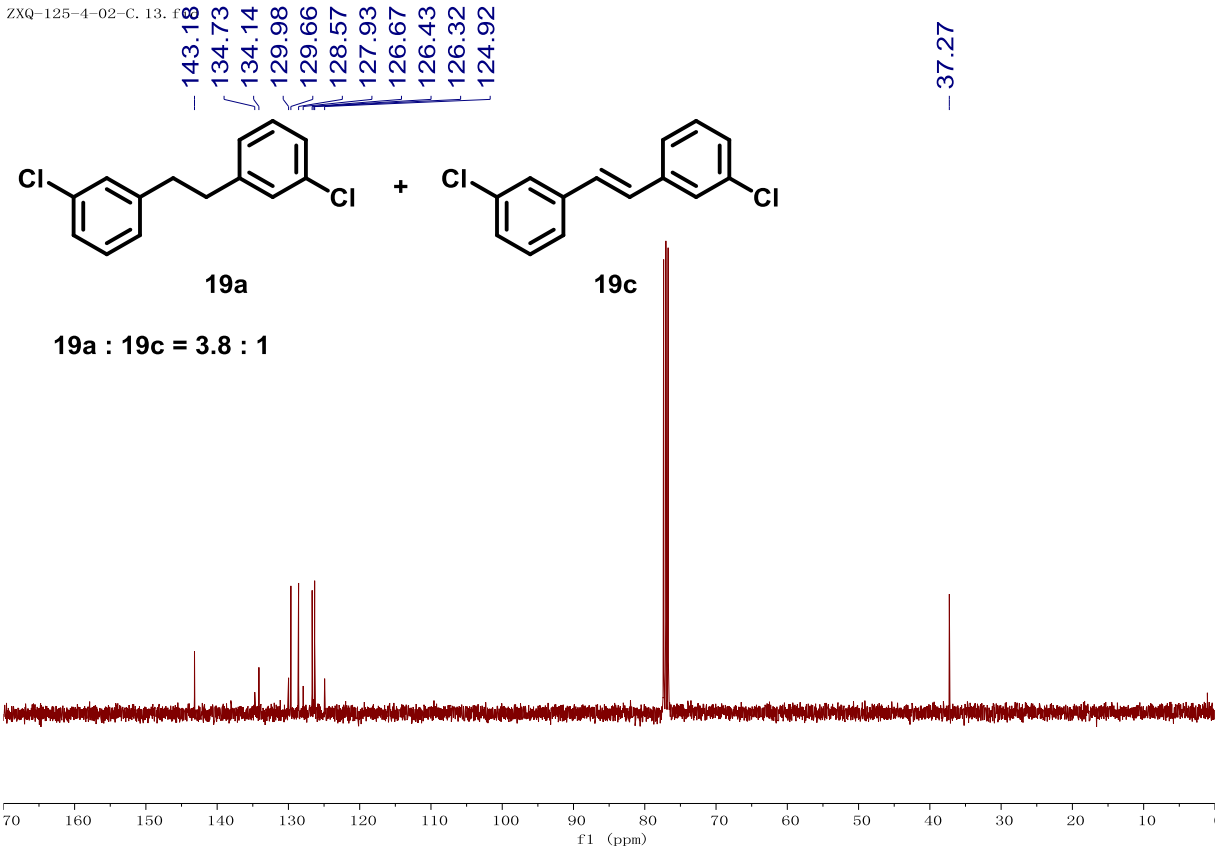
^{19}F NMR for **18a**



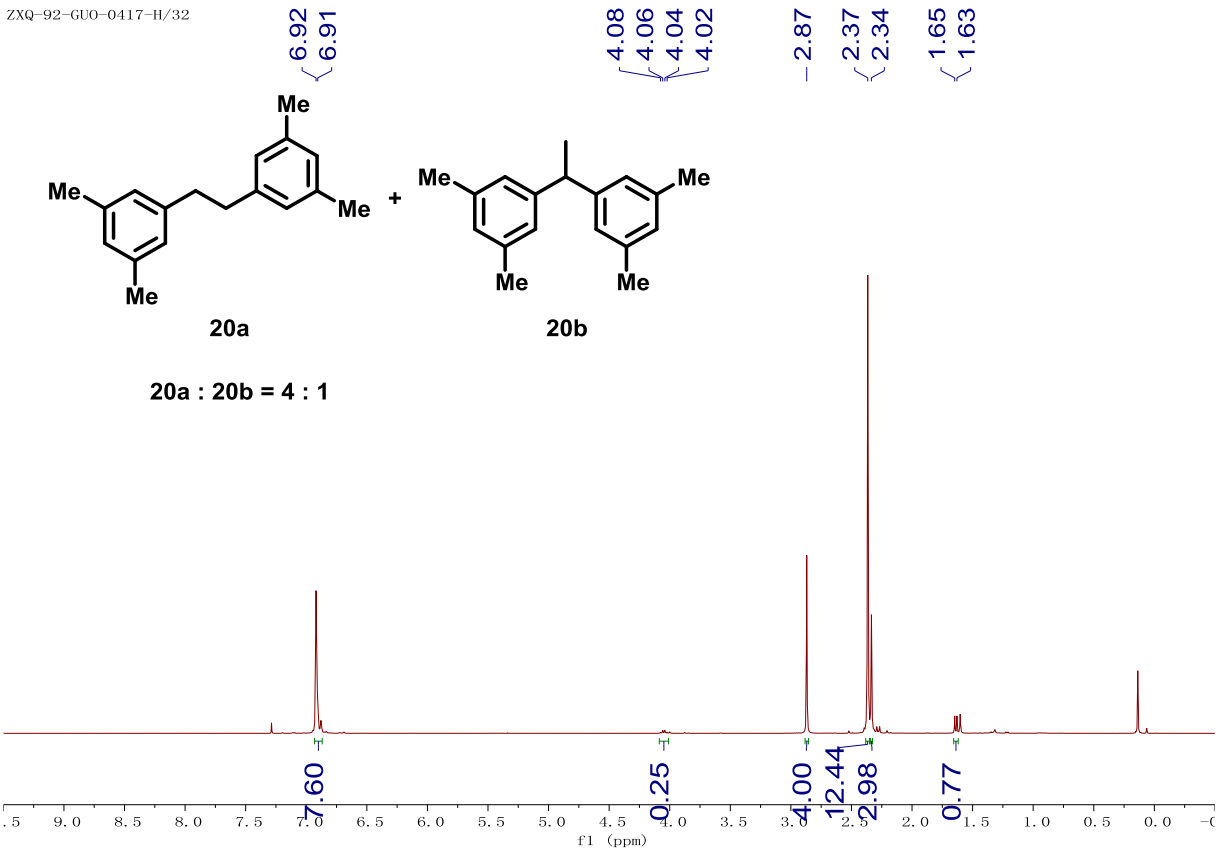
^{1}H NMR for **19a** and **19c**



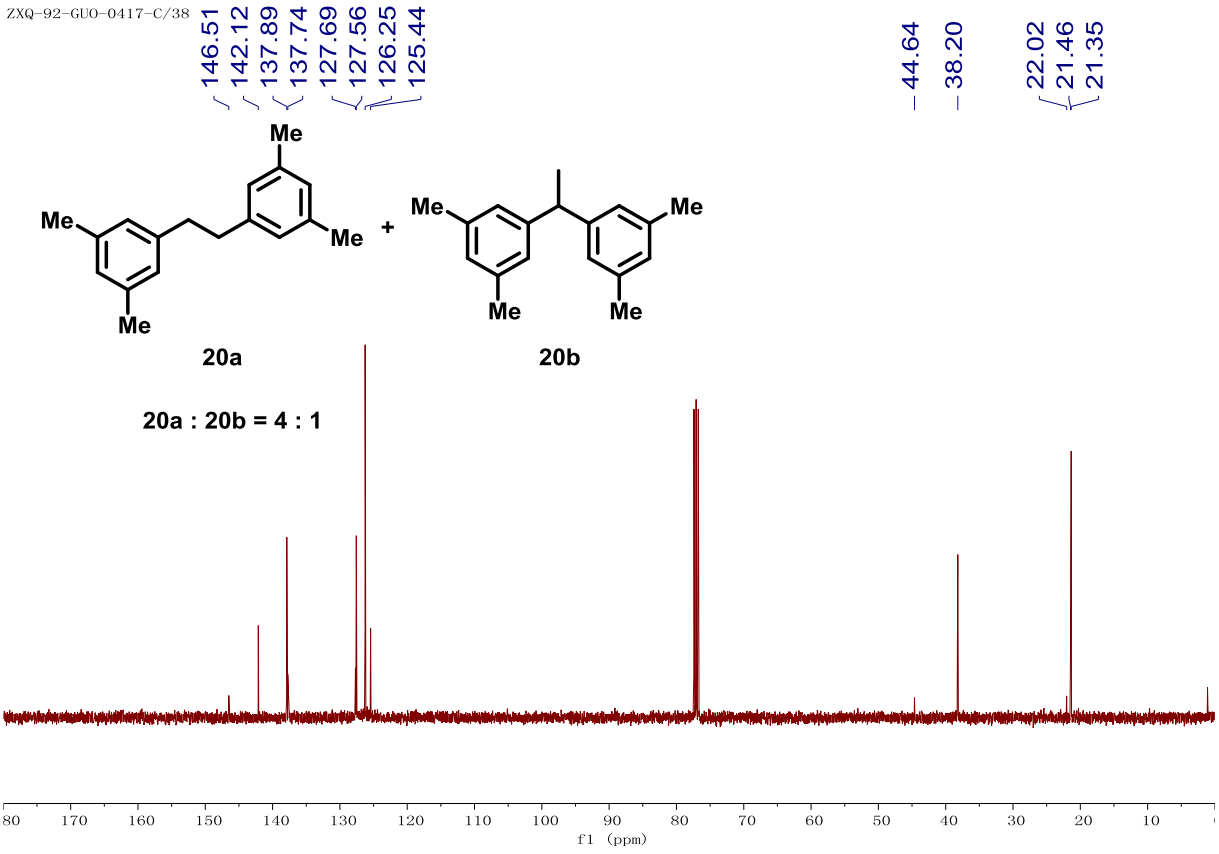
^{13}C NMR for **19a** and **19c**



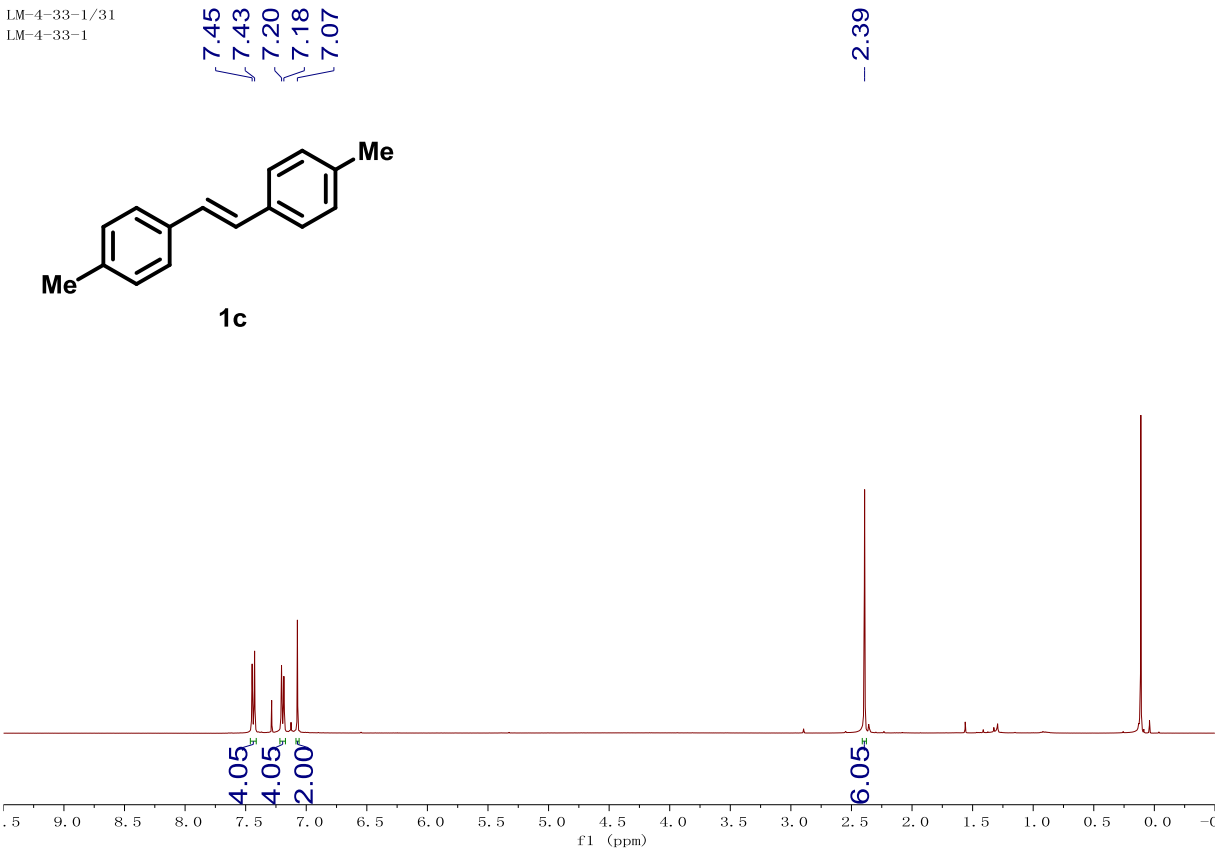
^{1}H NMR for **20a** and **20b**



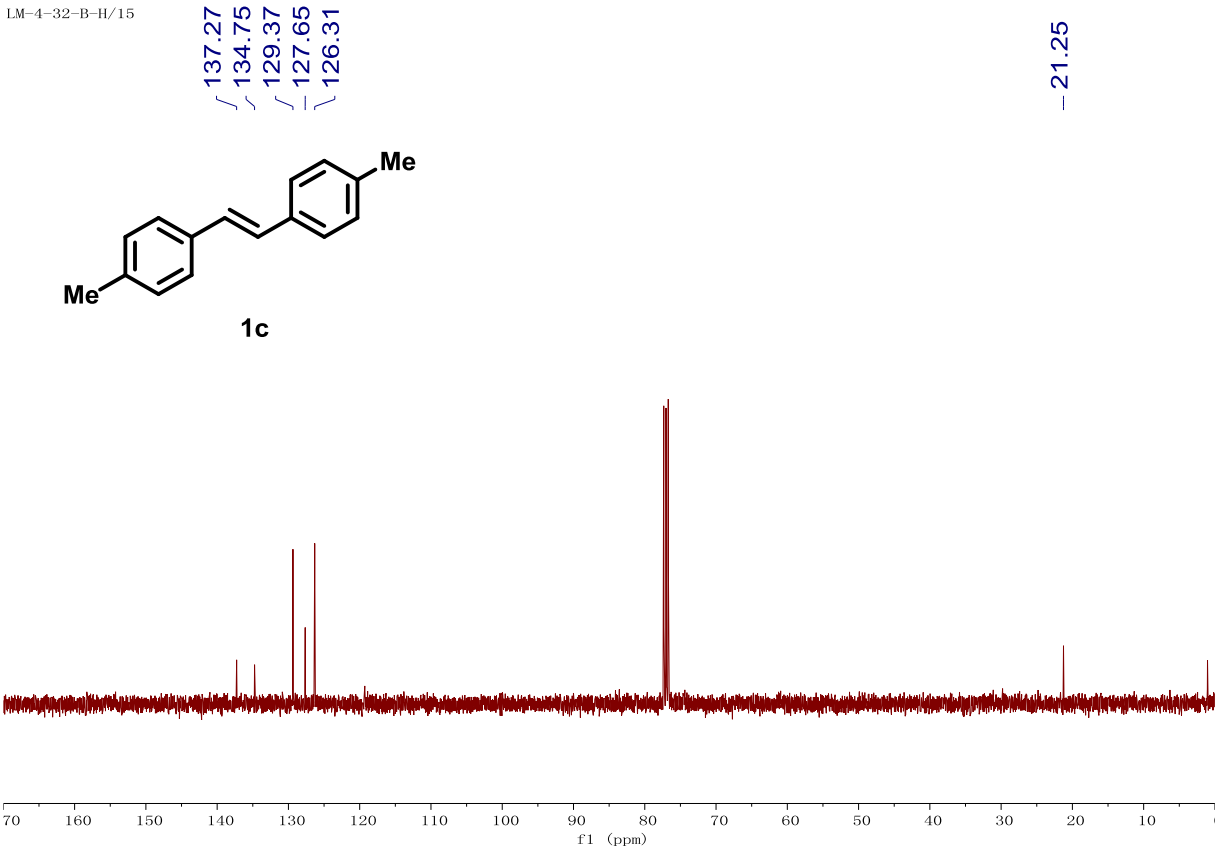
^{13}C NMR for **20a** and **20b**



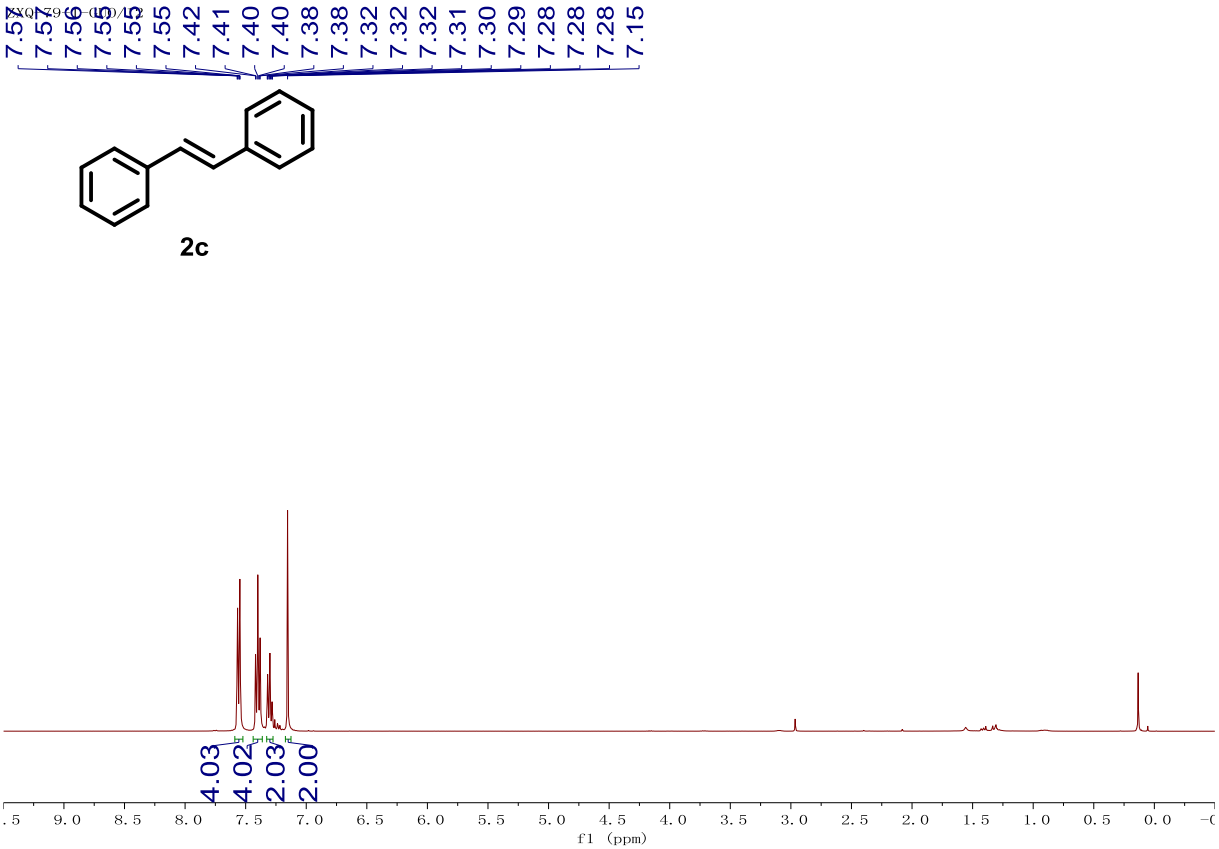
^{1}H NMR for **1c**



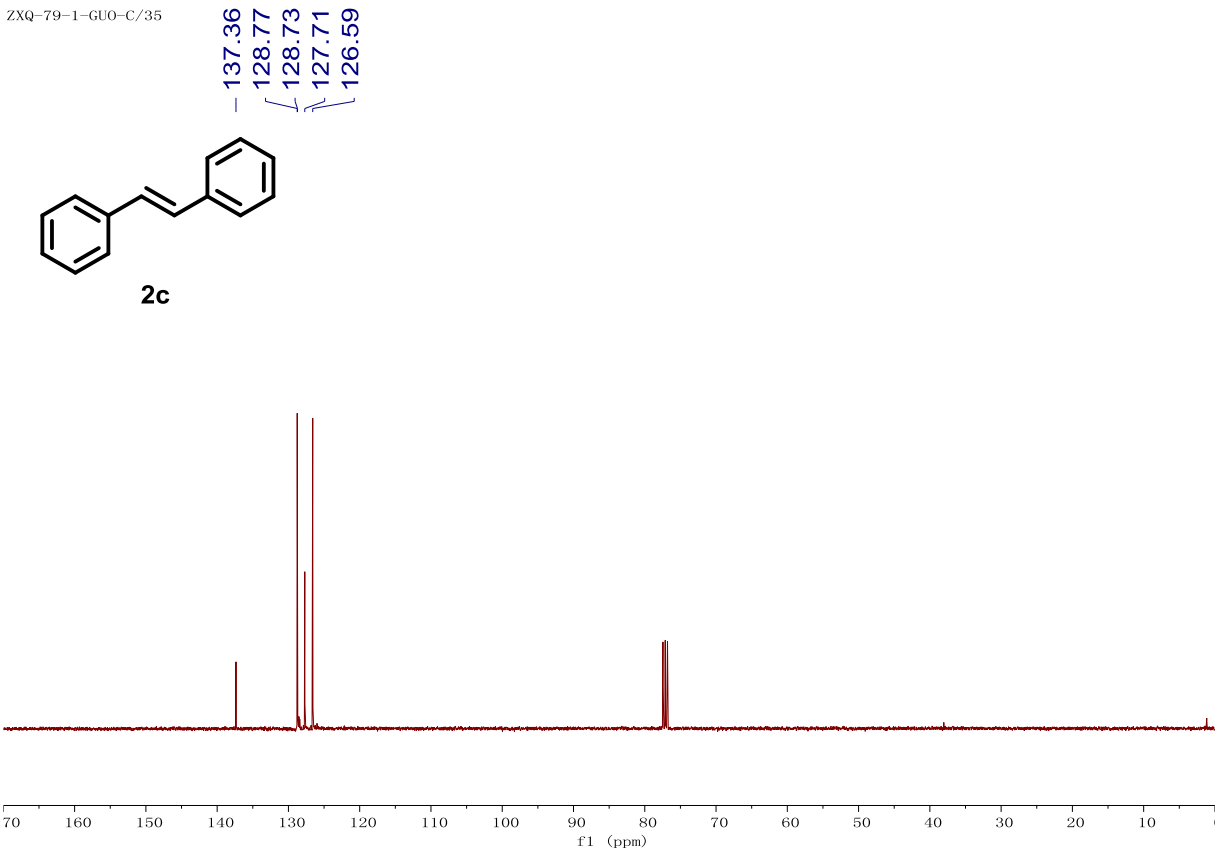
^{13}C NMR for **1c**



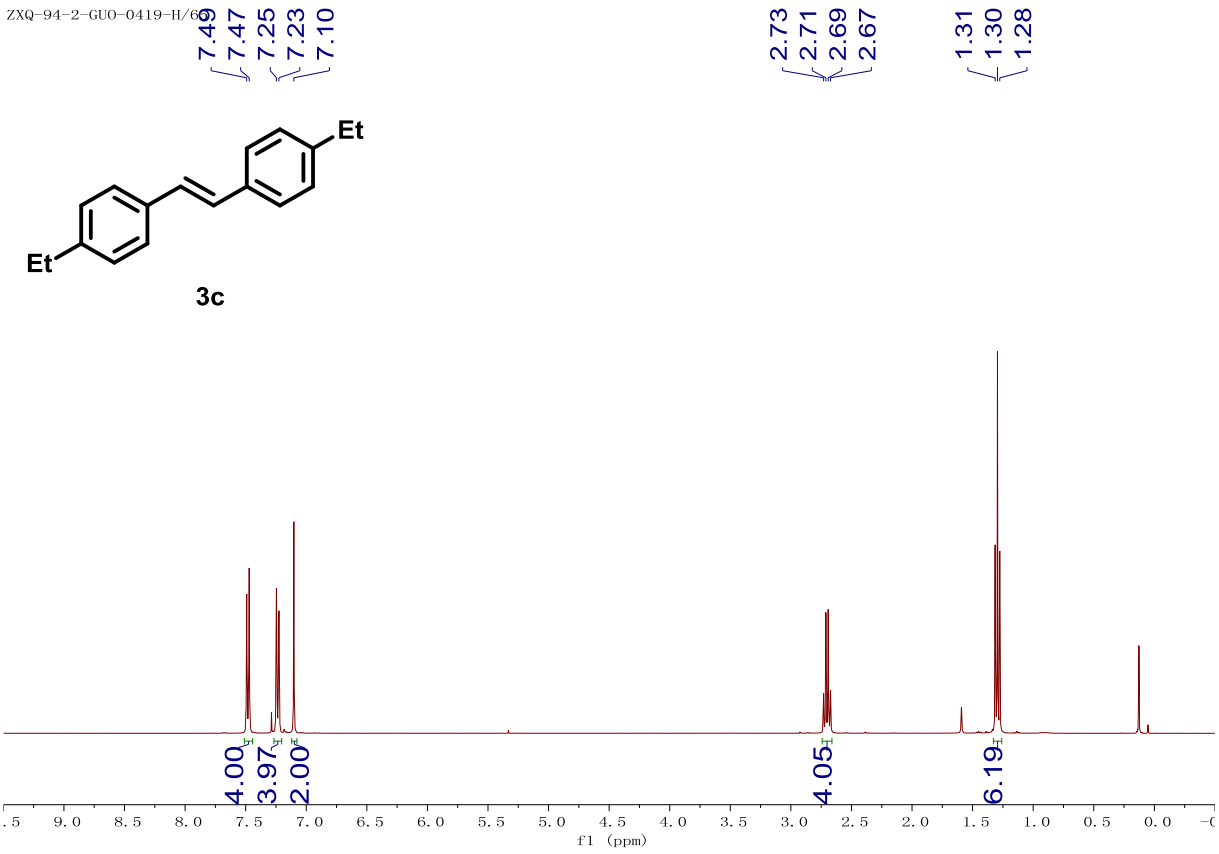
^{1}H NMR for **2c**



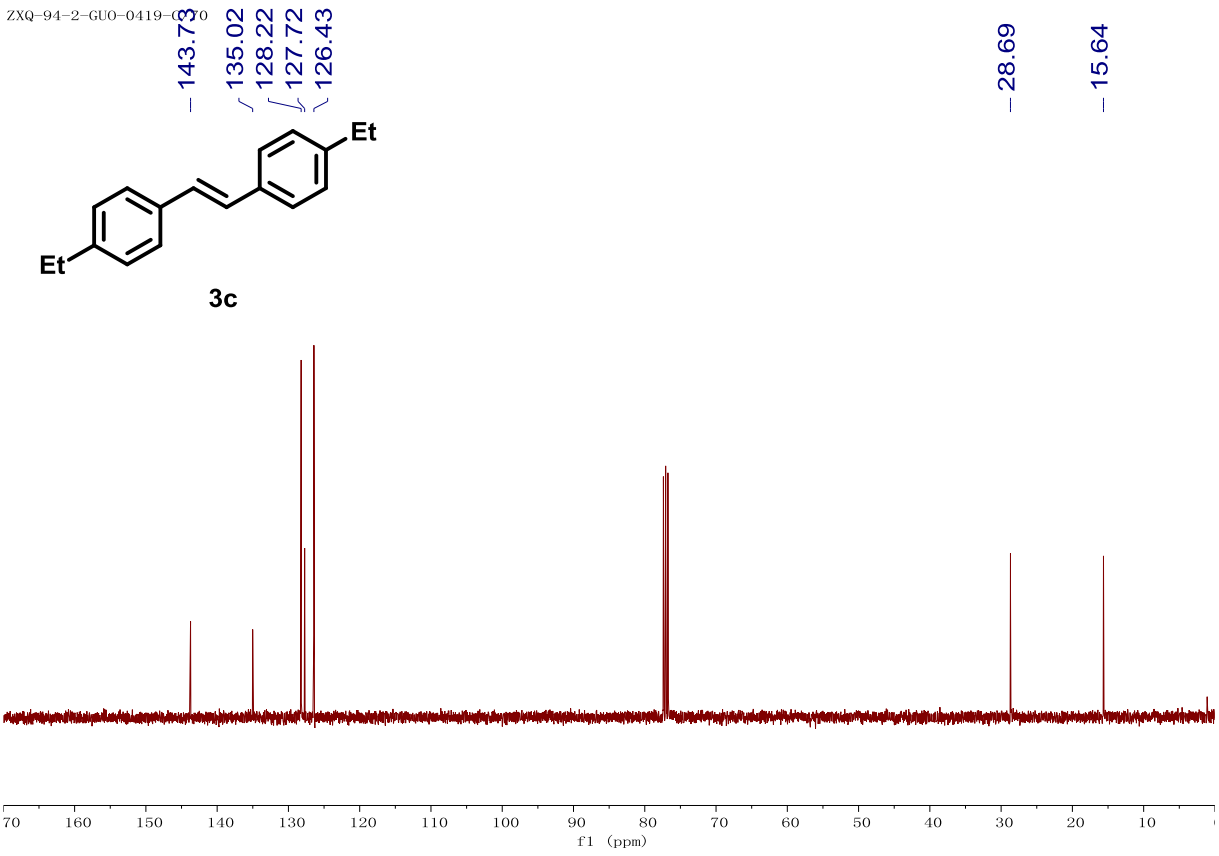
^{13}C NMR for **2c**



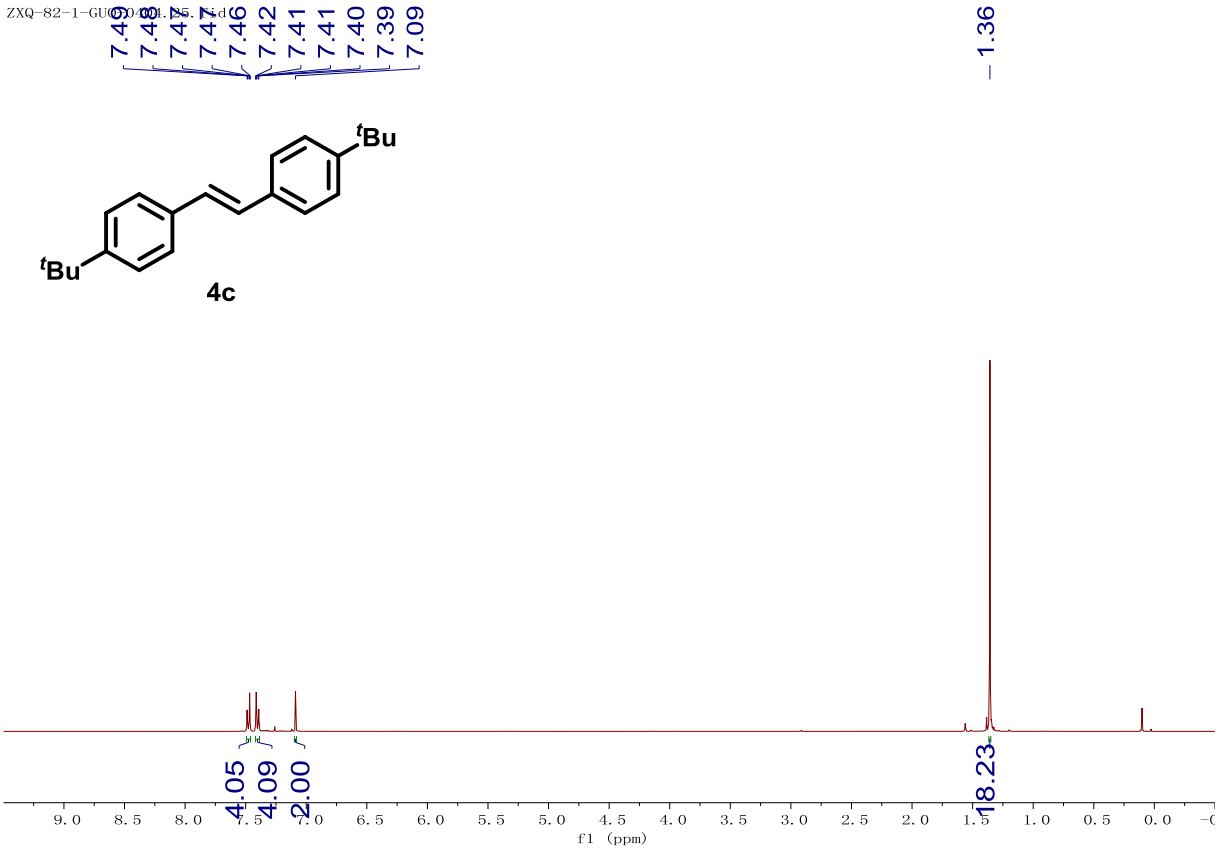
^{1}H NMR for **3c**



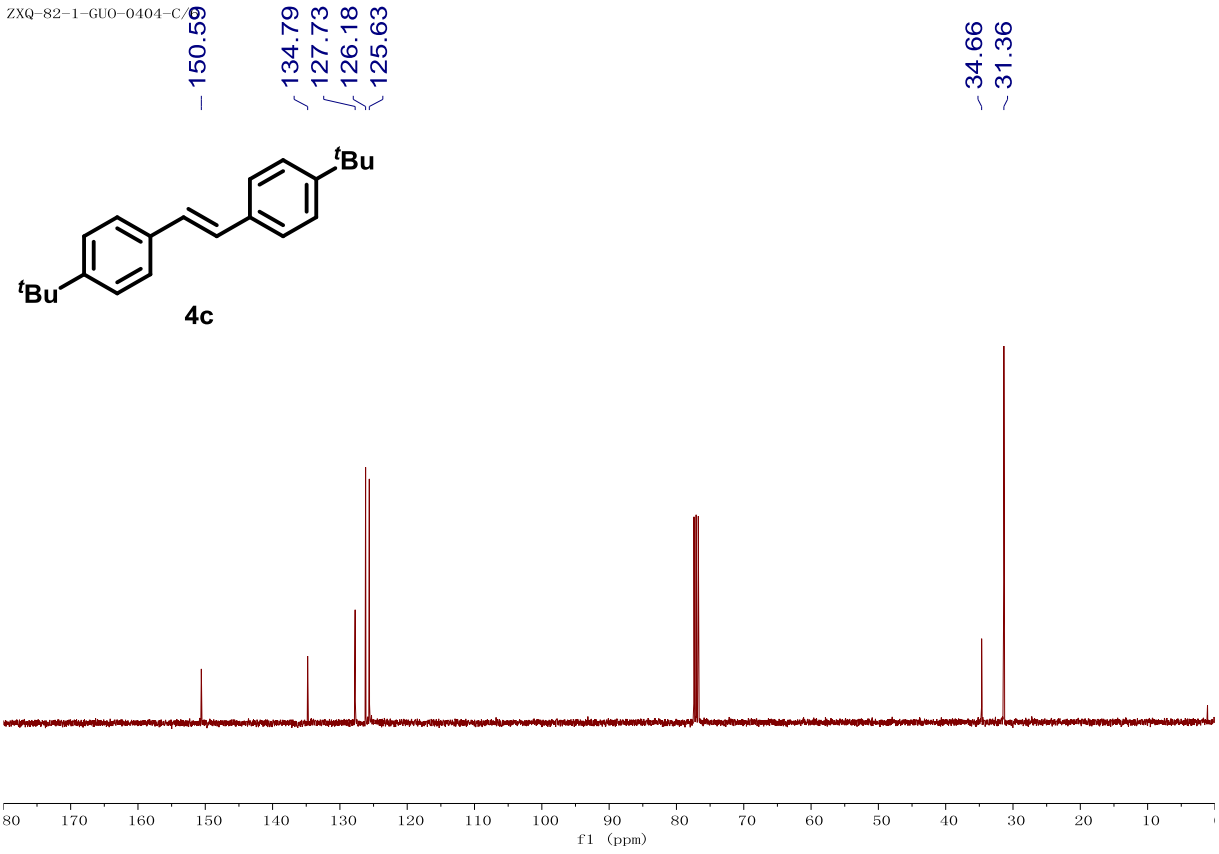
^{13}C NMR for **3c**



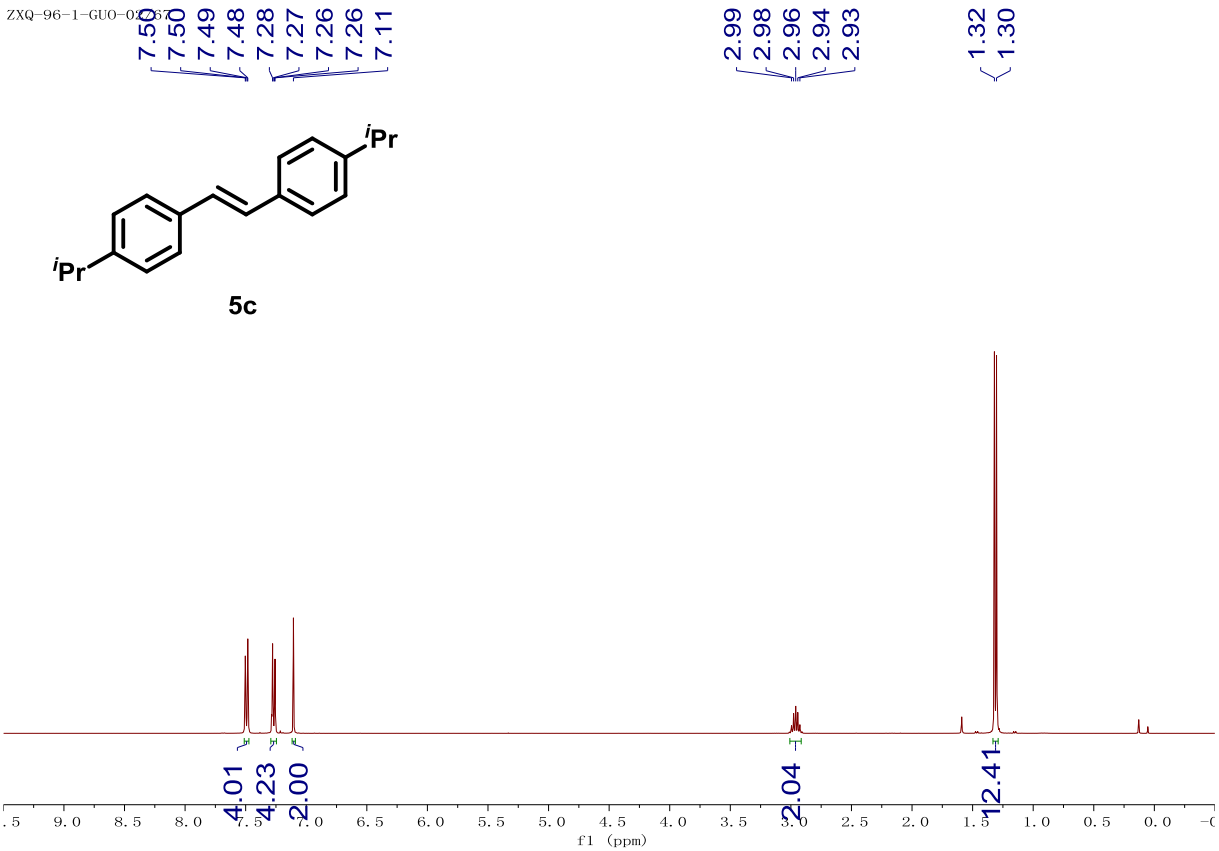
^{1}H NMR for **4c**



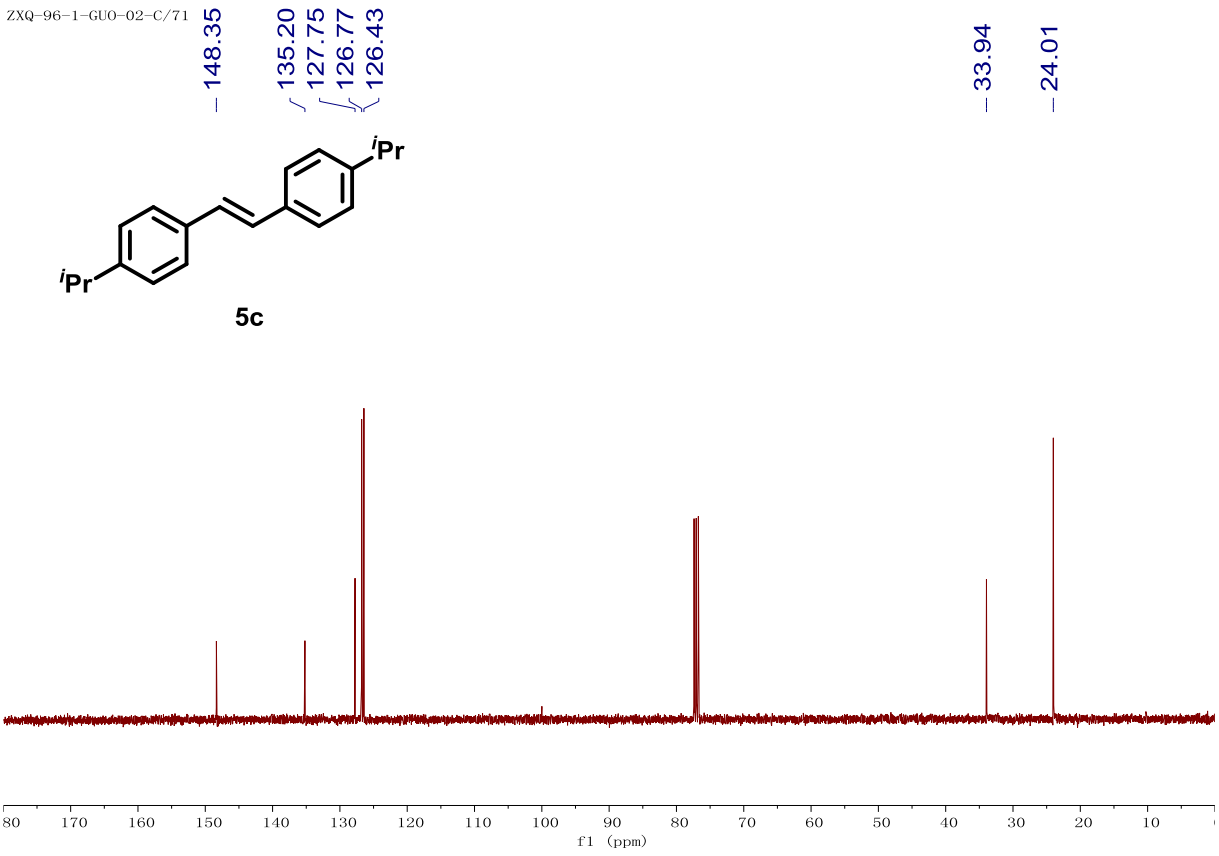
^{13}C NMR for **4c**



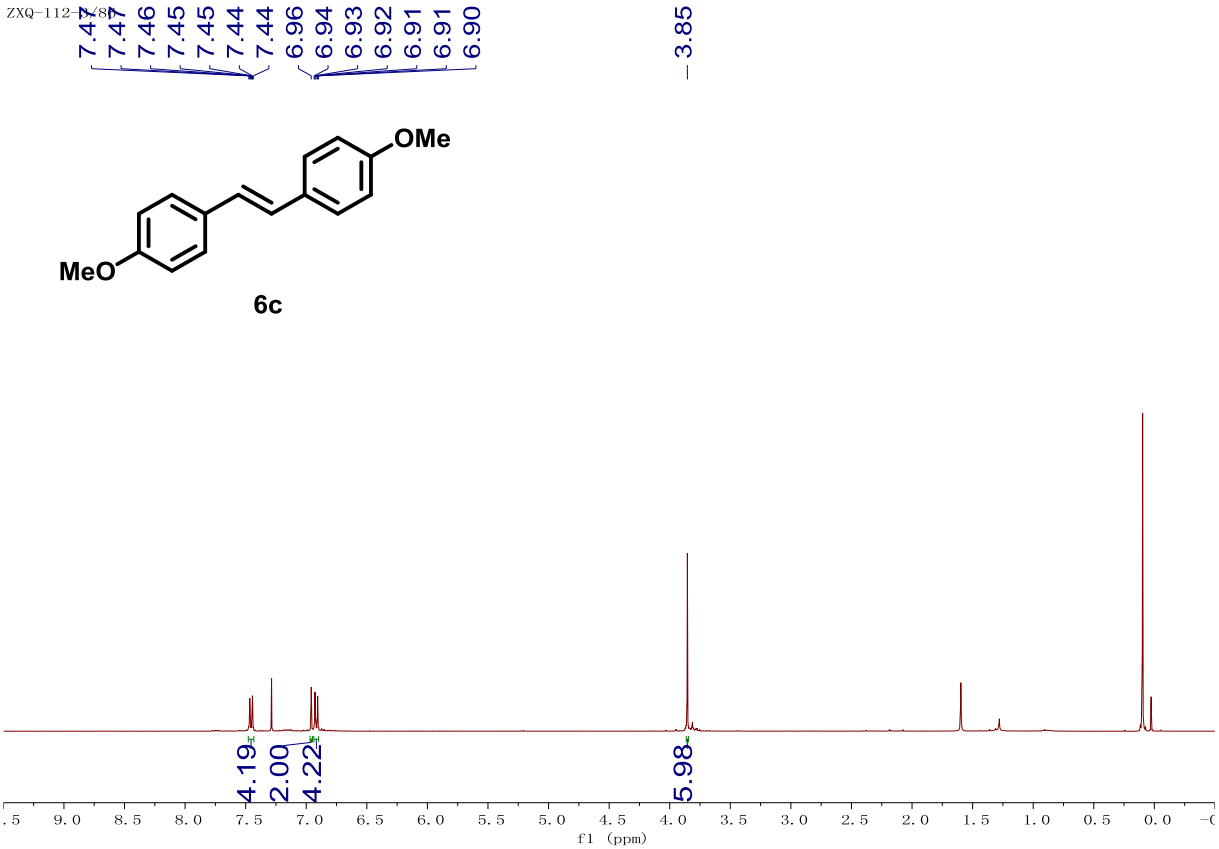
^{1}H NMR for **5c**



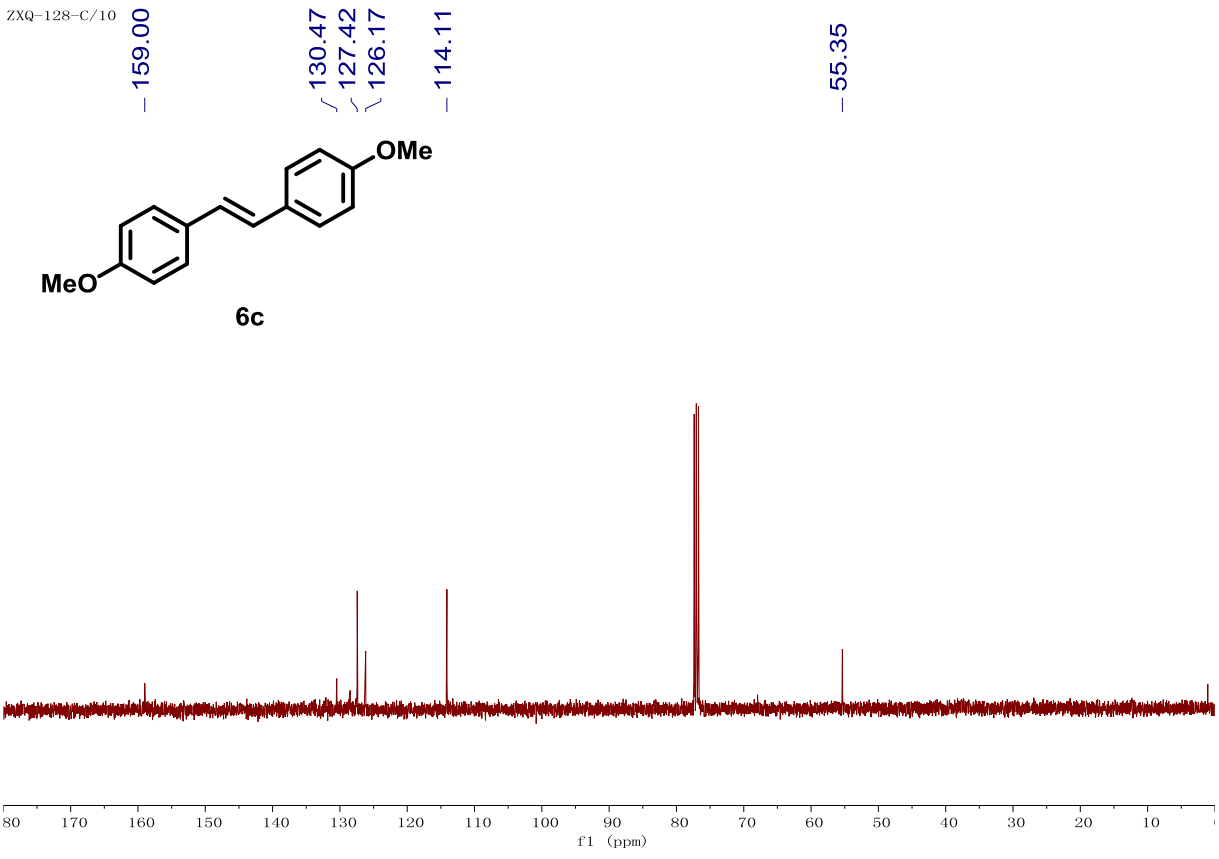
^{13}C NMR for **5c**



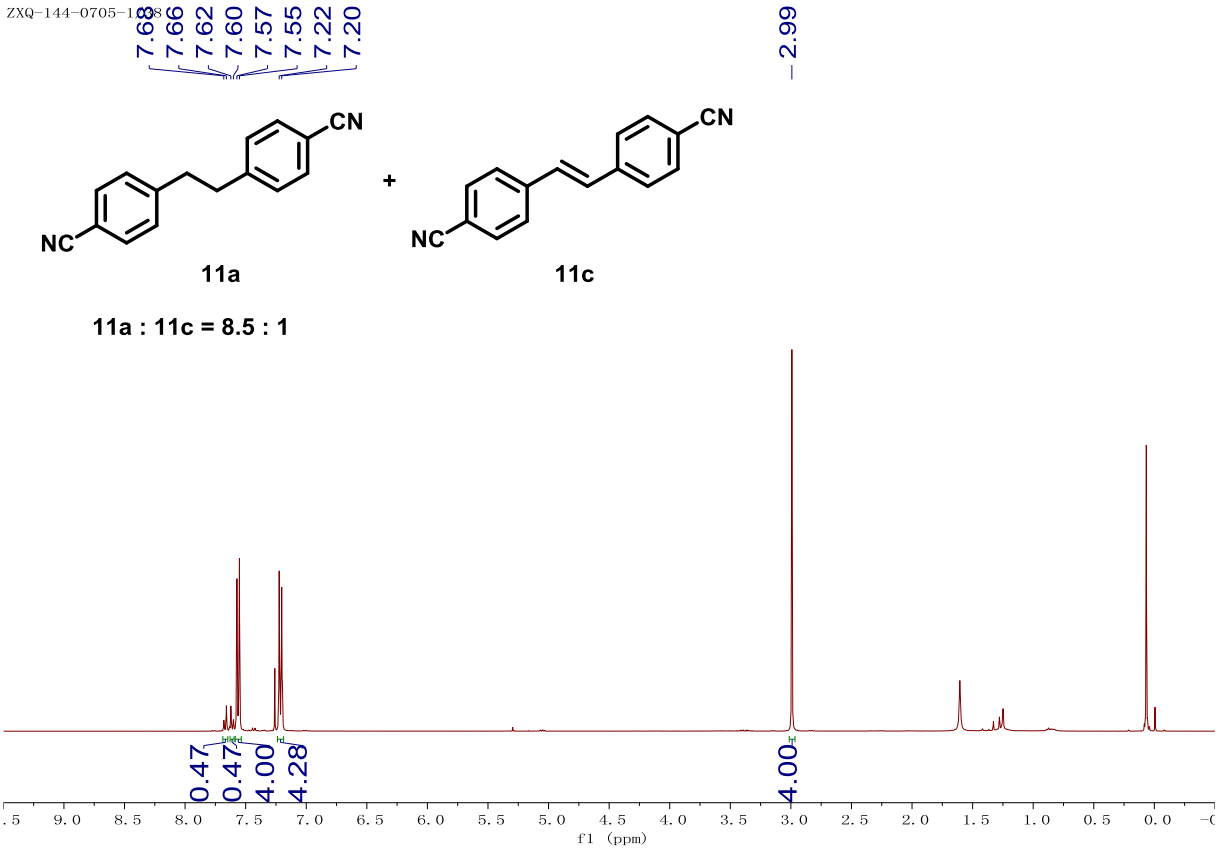
^{1}H NMR for **6c**



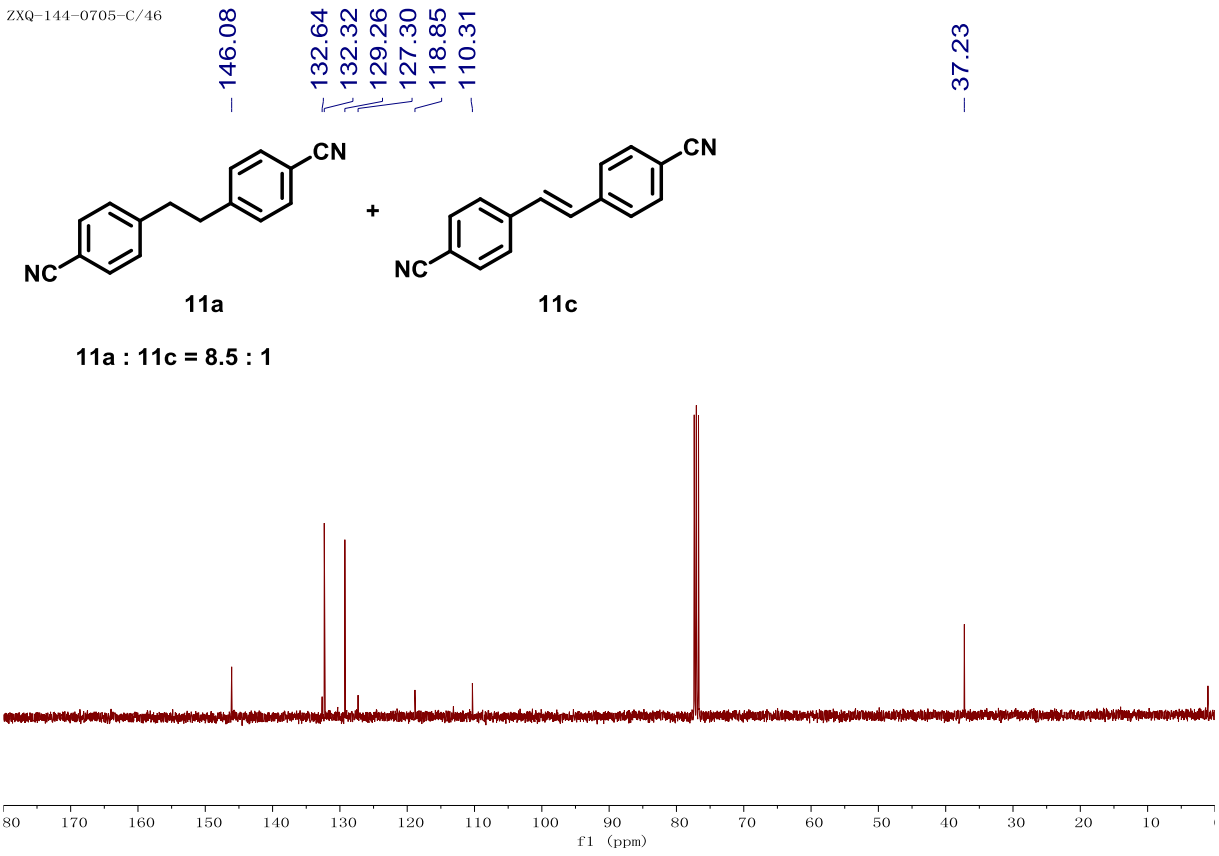
^{13}C NMR for **6c**



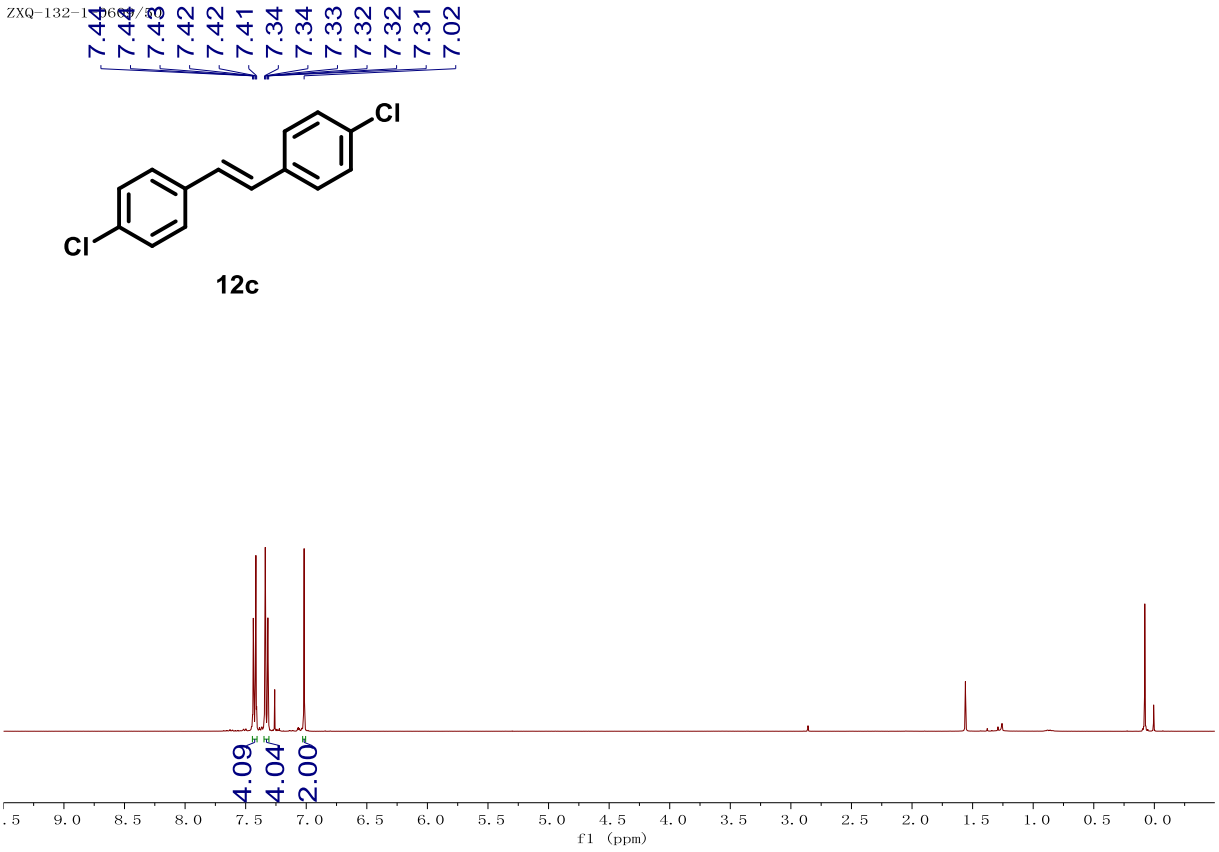
^{1}H NMR for **11a** and **11c**



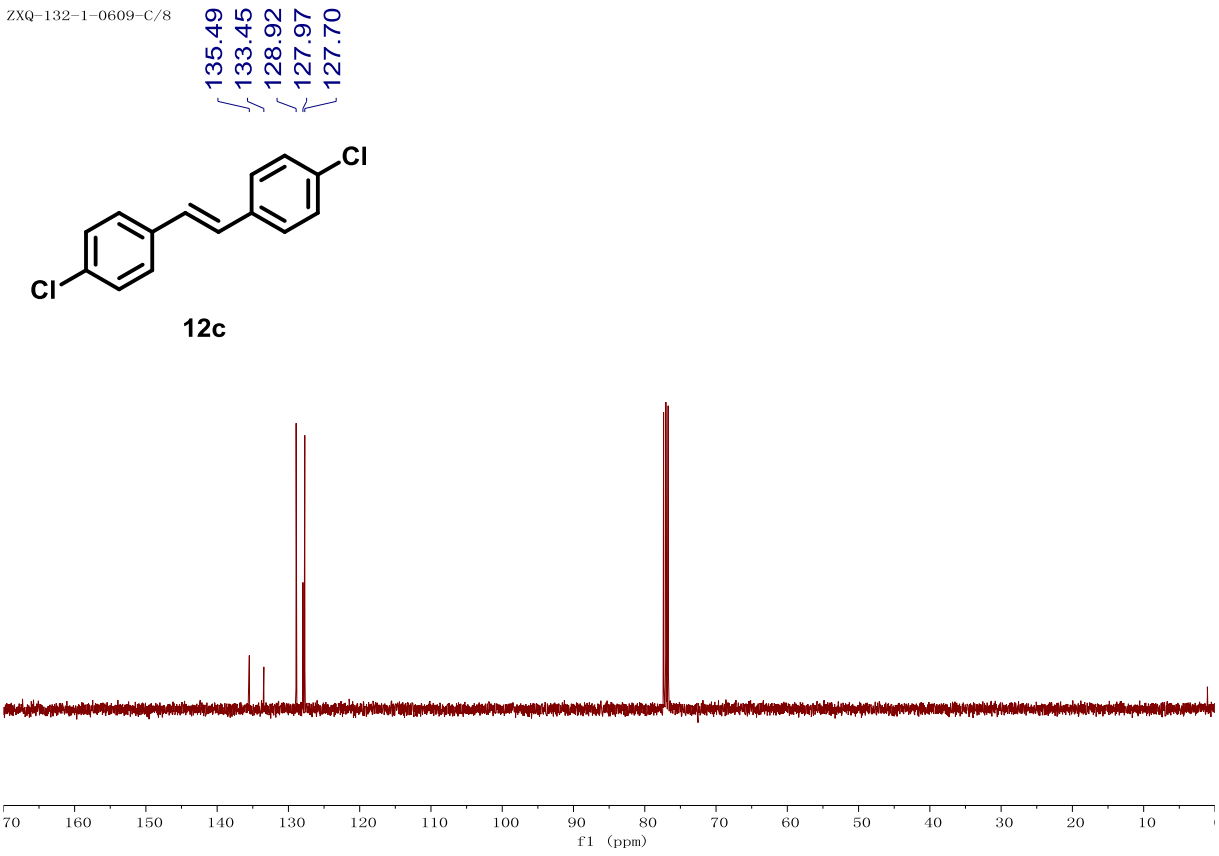
^{13}C NMR for **11a** and **11c**



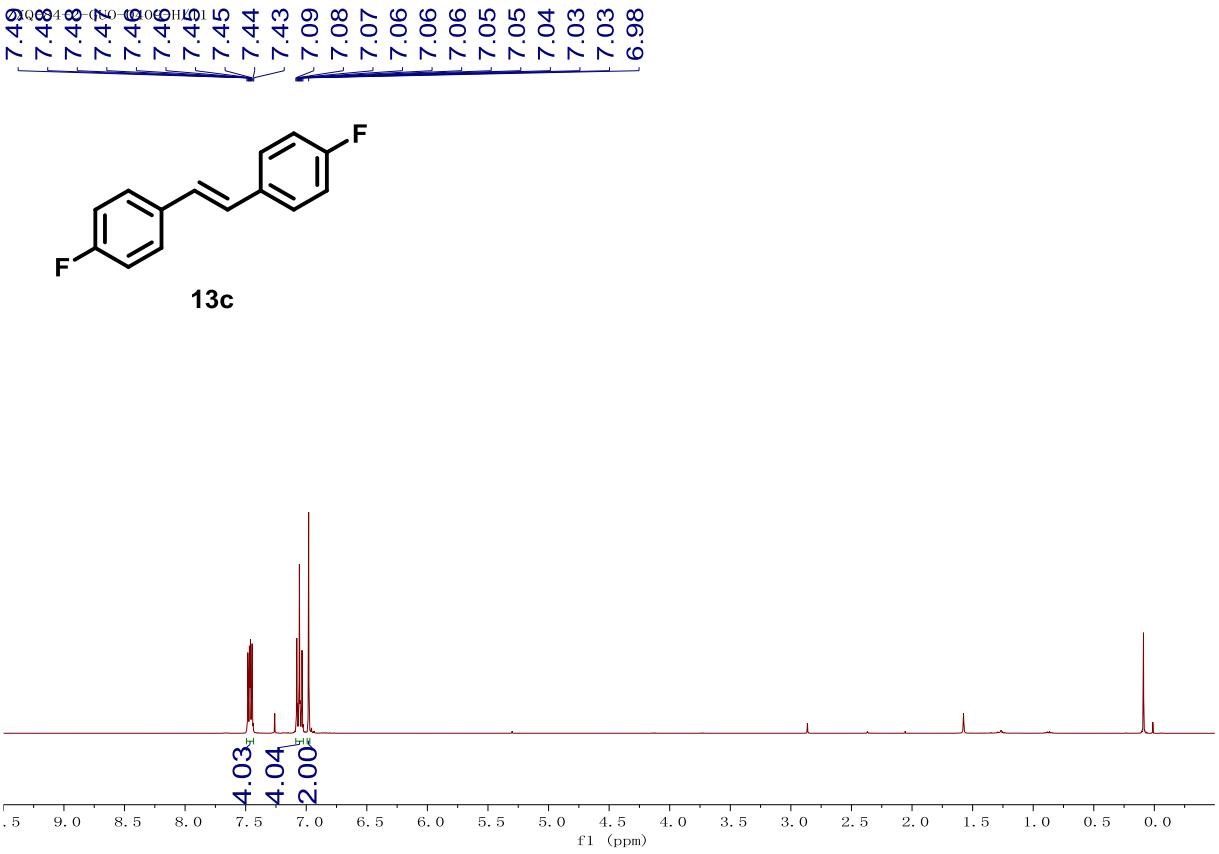
^{1}H NMR for **12c**



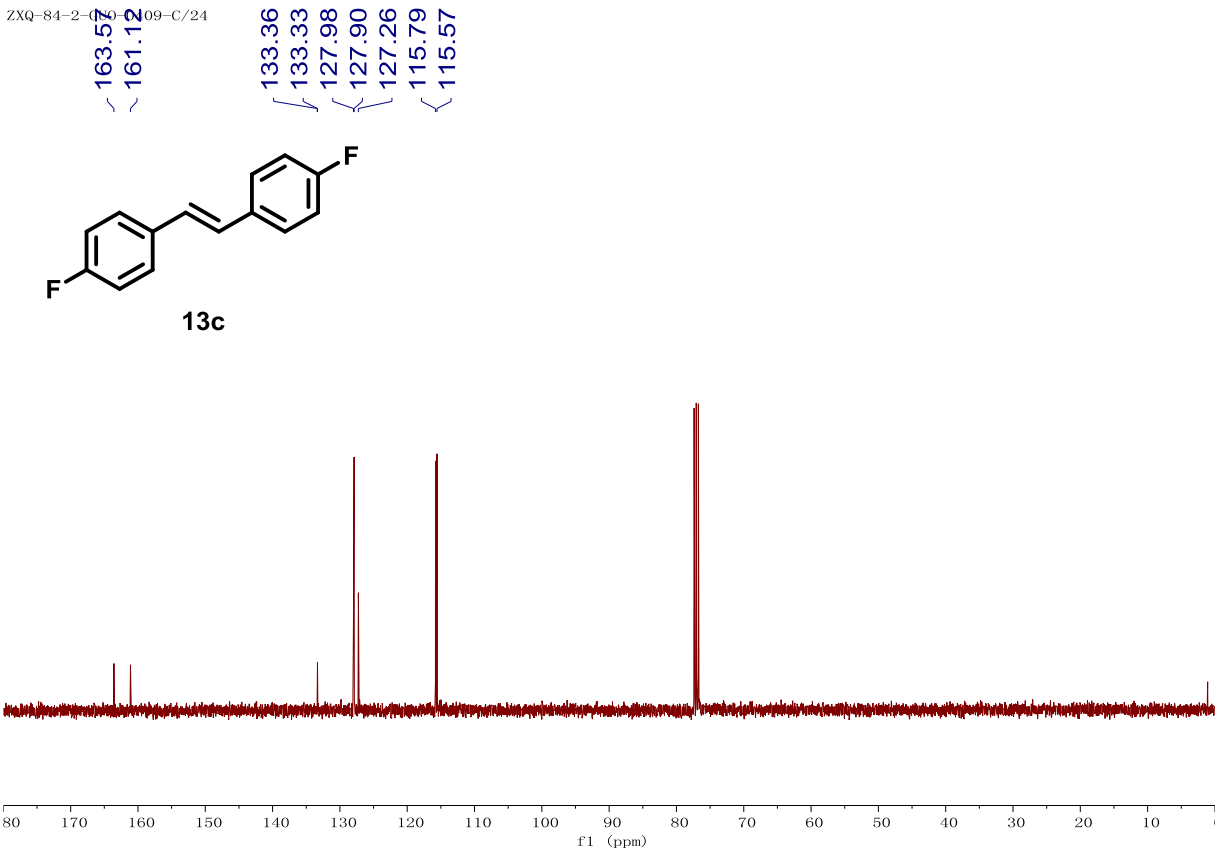
^{13}C NMR for **12c**



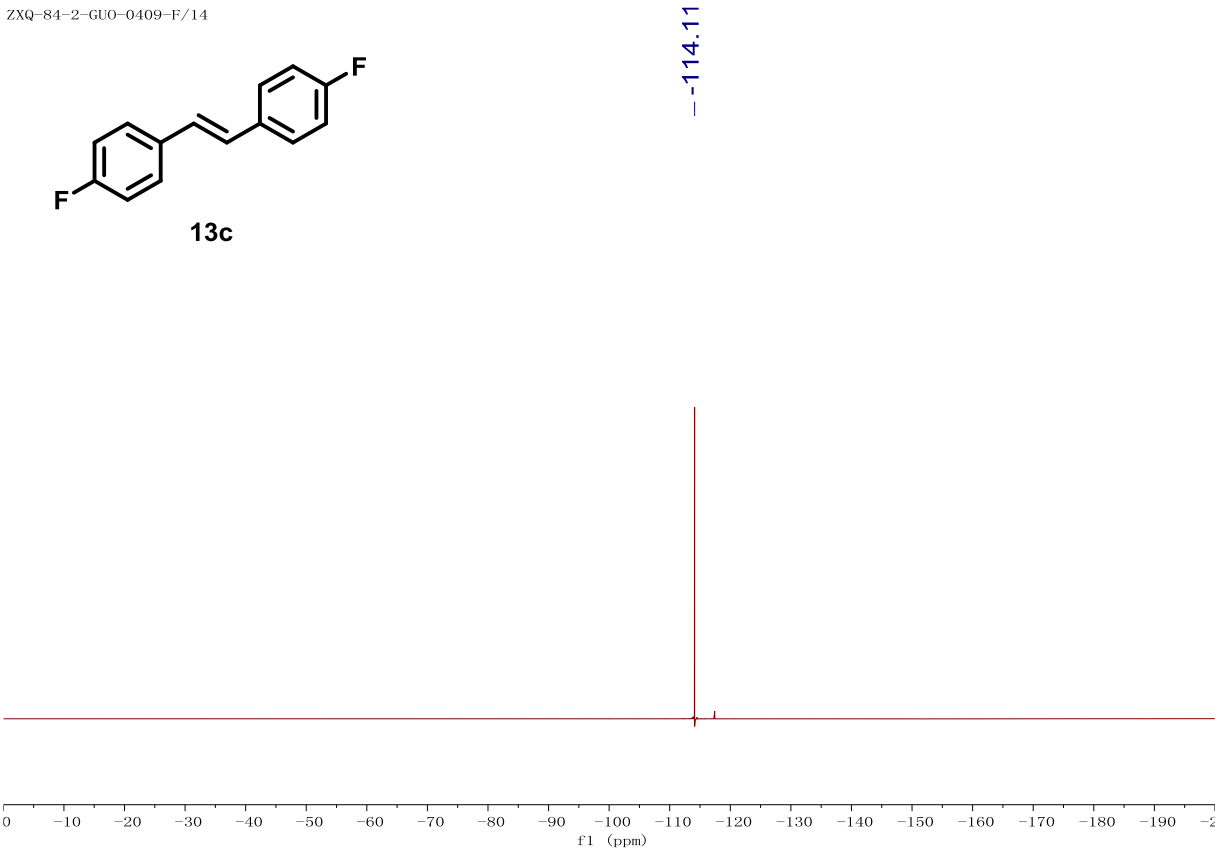
^{1}H NMR for **13c**



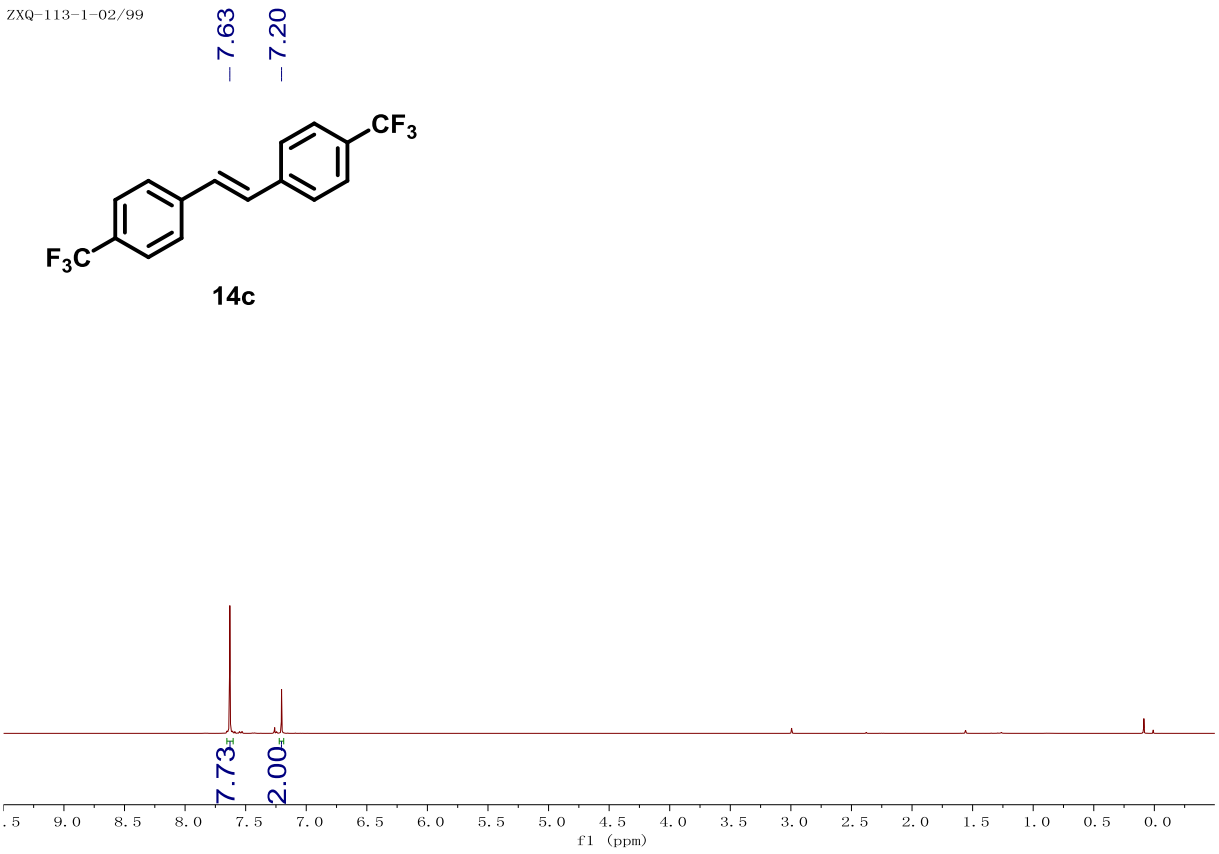
^{13}C NMR for **13c**



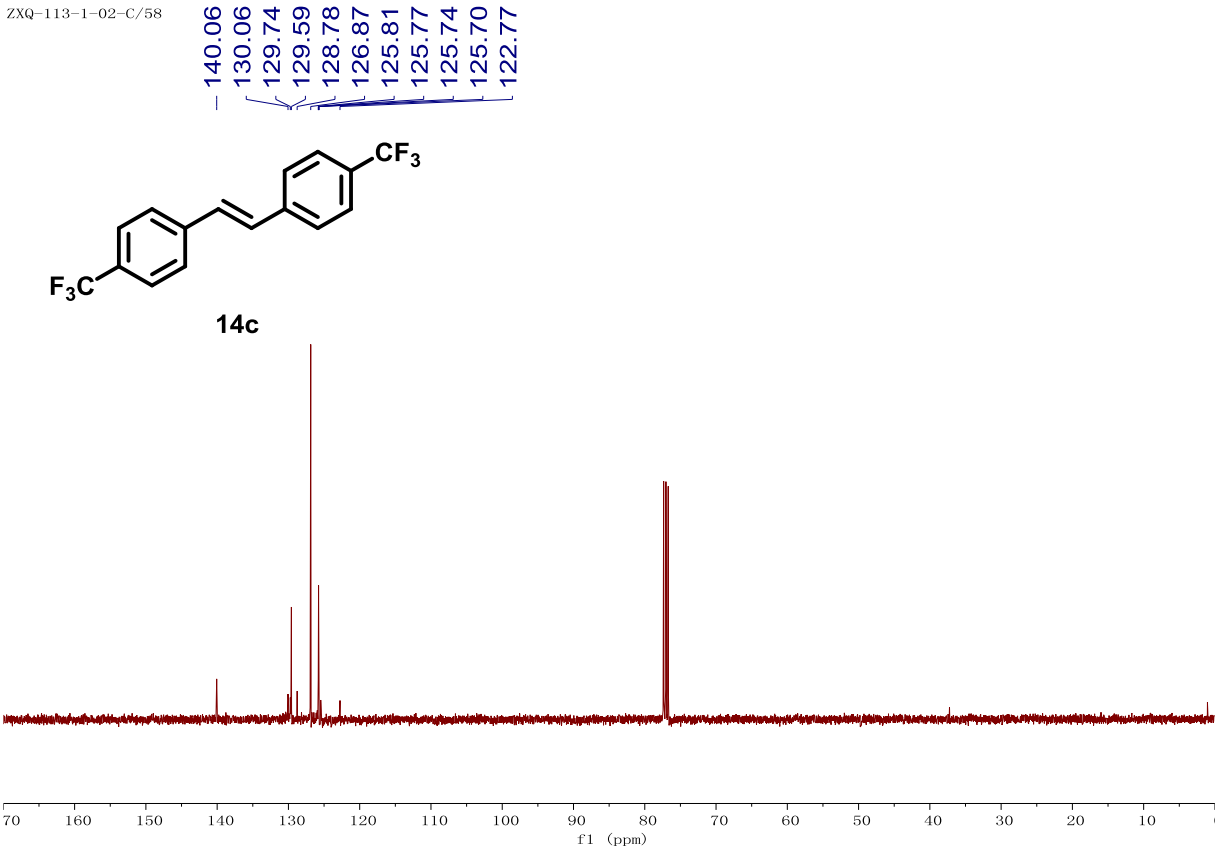
^{19}F NMR for **13c**



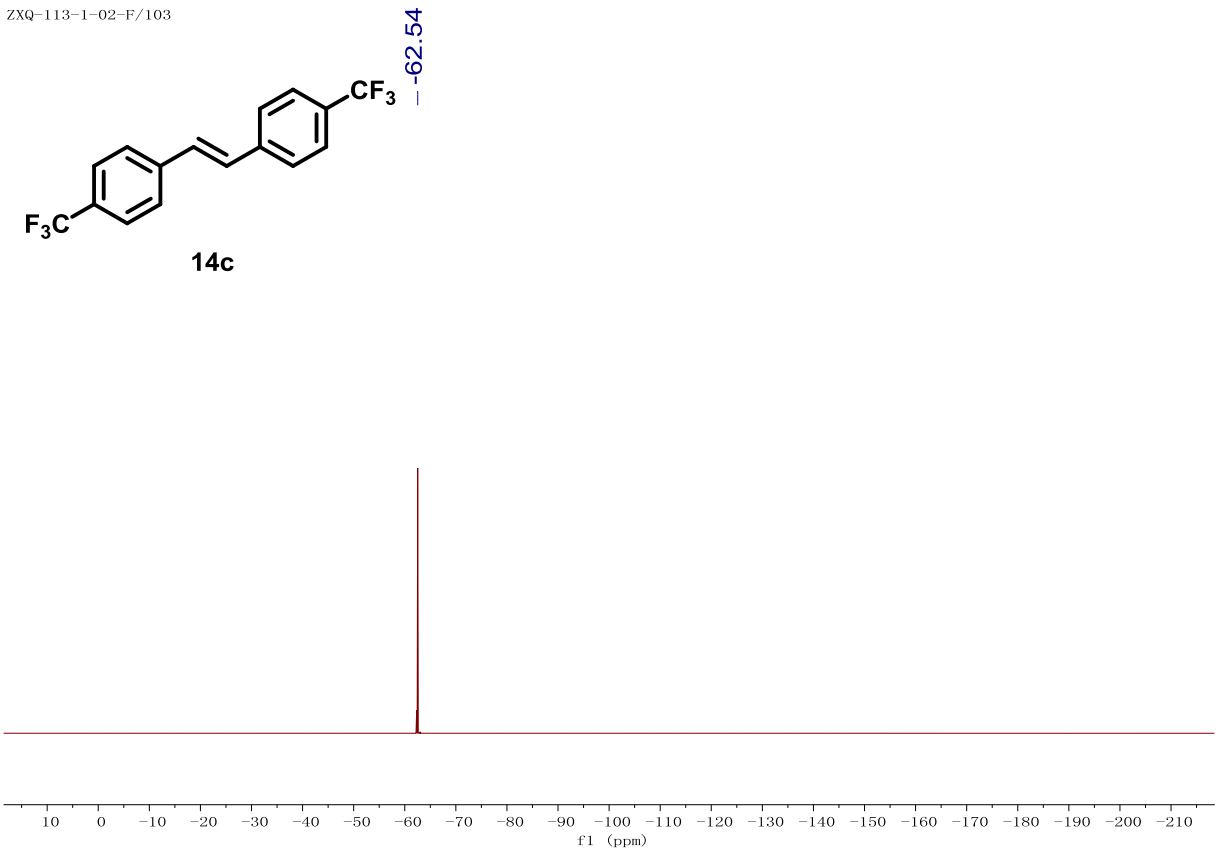
^{1}H NMR for **14c**



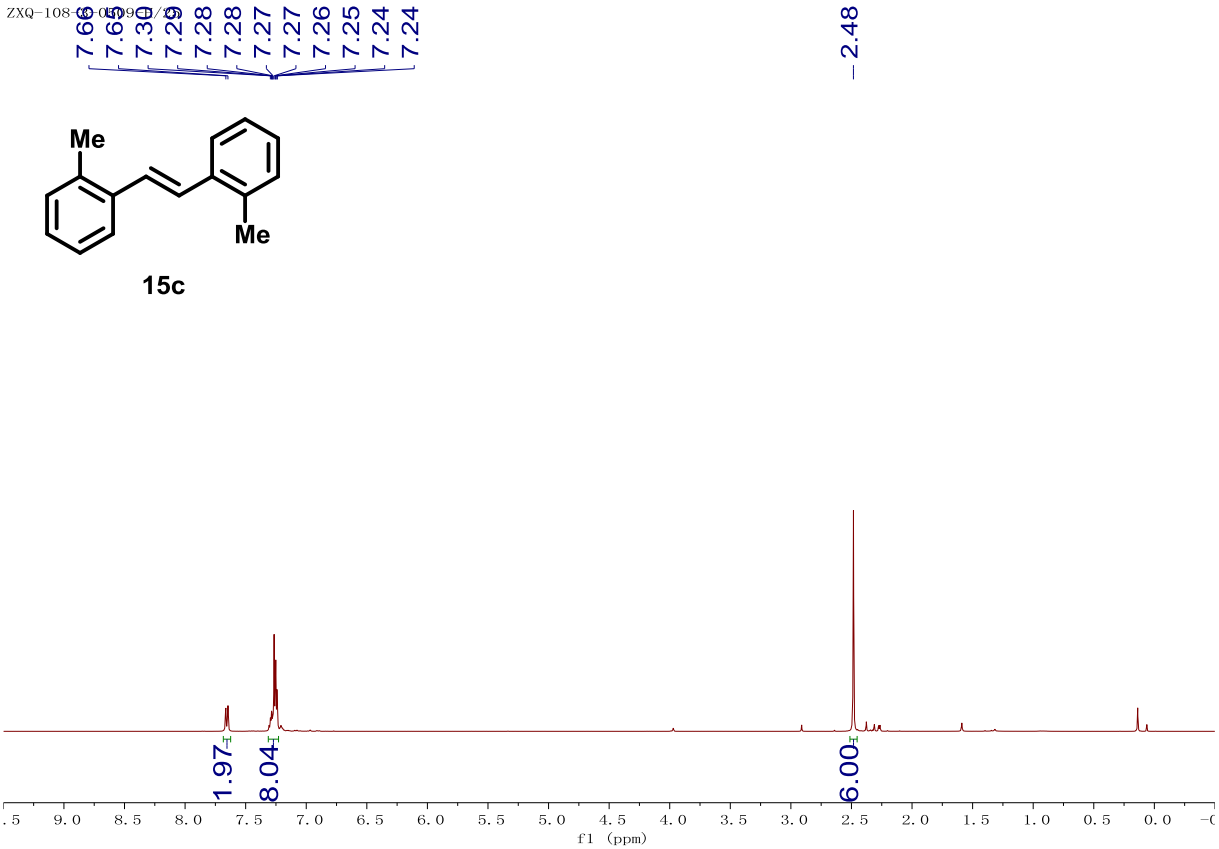
^{13}C NMR for **14c**



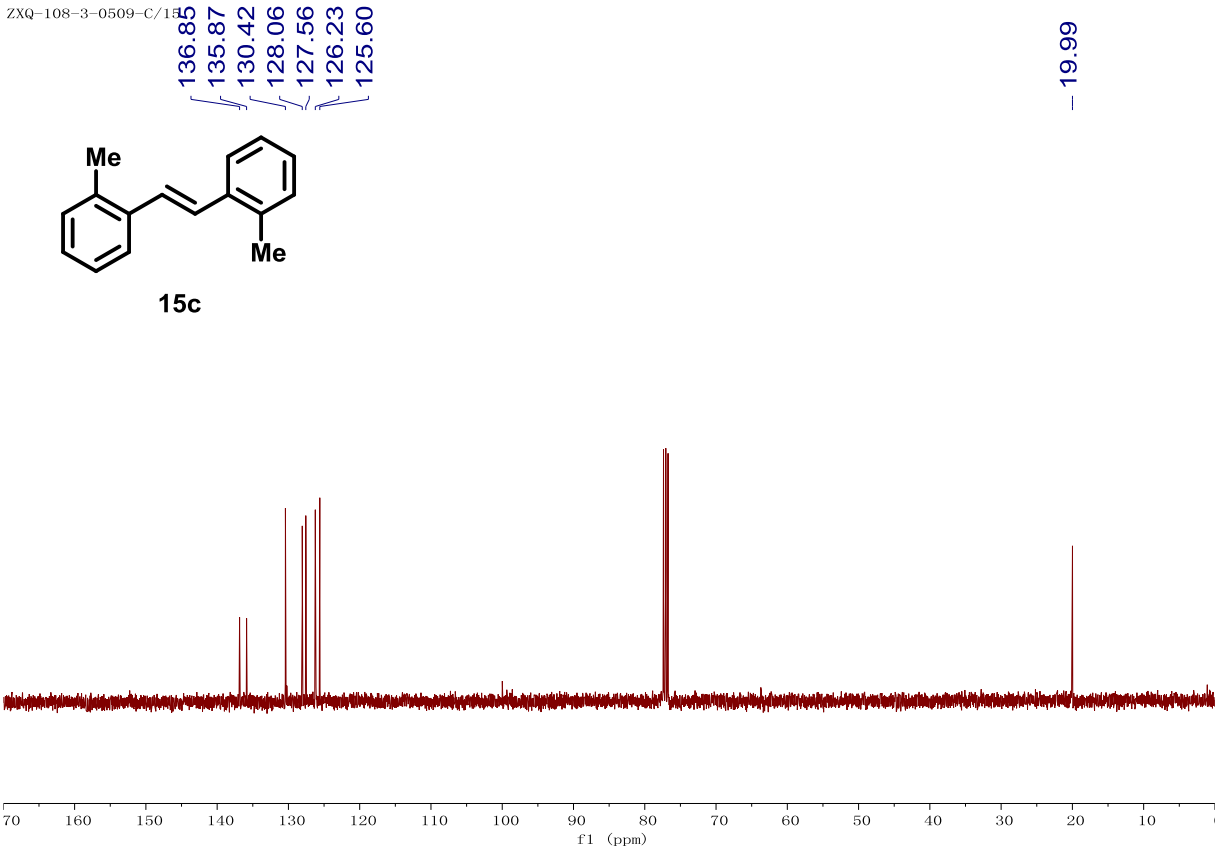
^{19}F NMR for **14c**



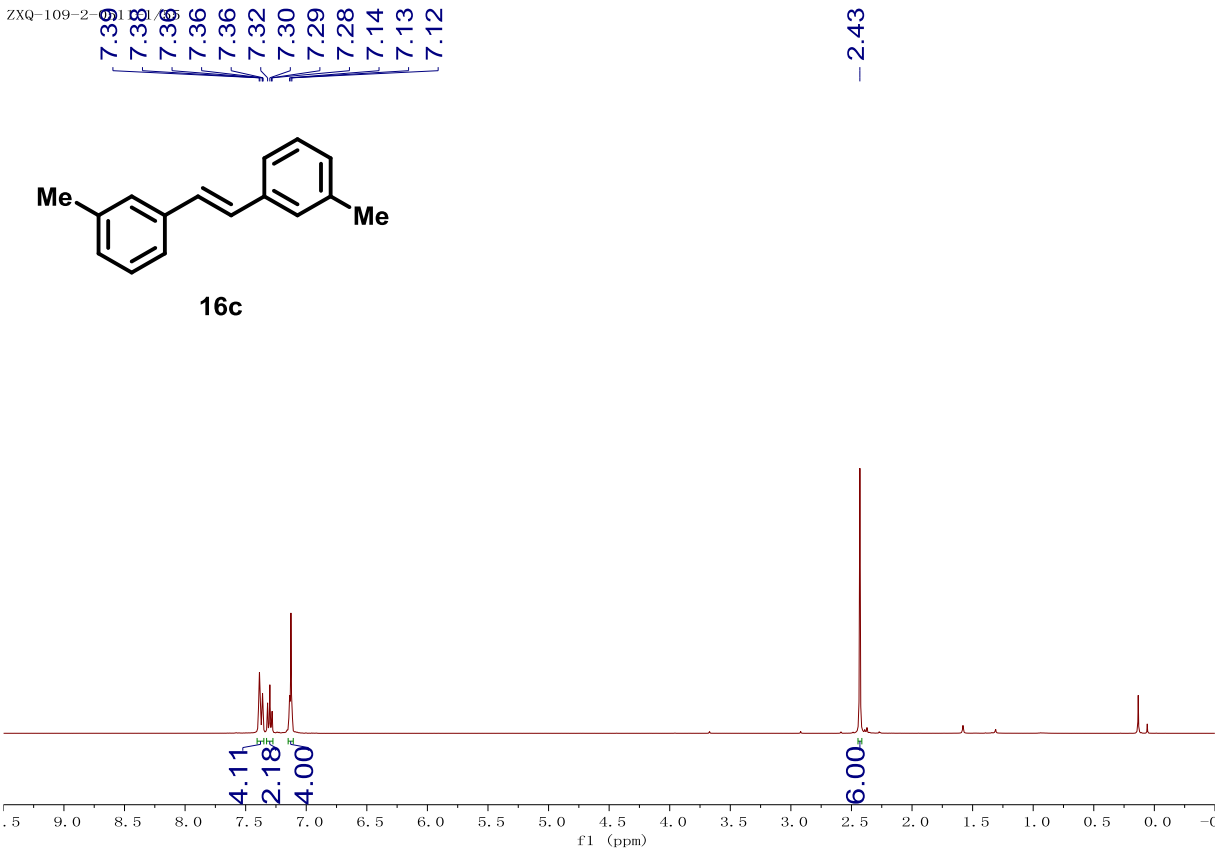
^{1}H NMR for **15c**



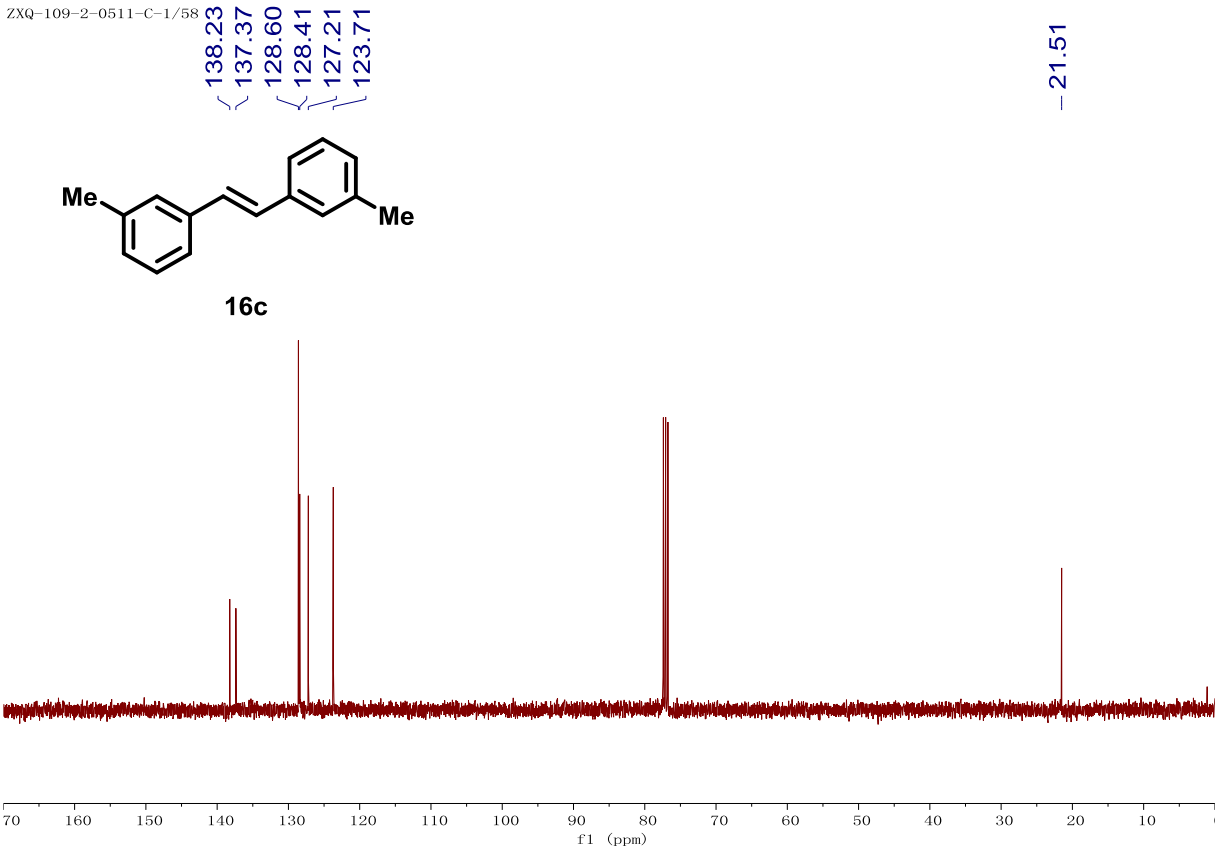
^{13}C NMR for **15c**



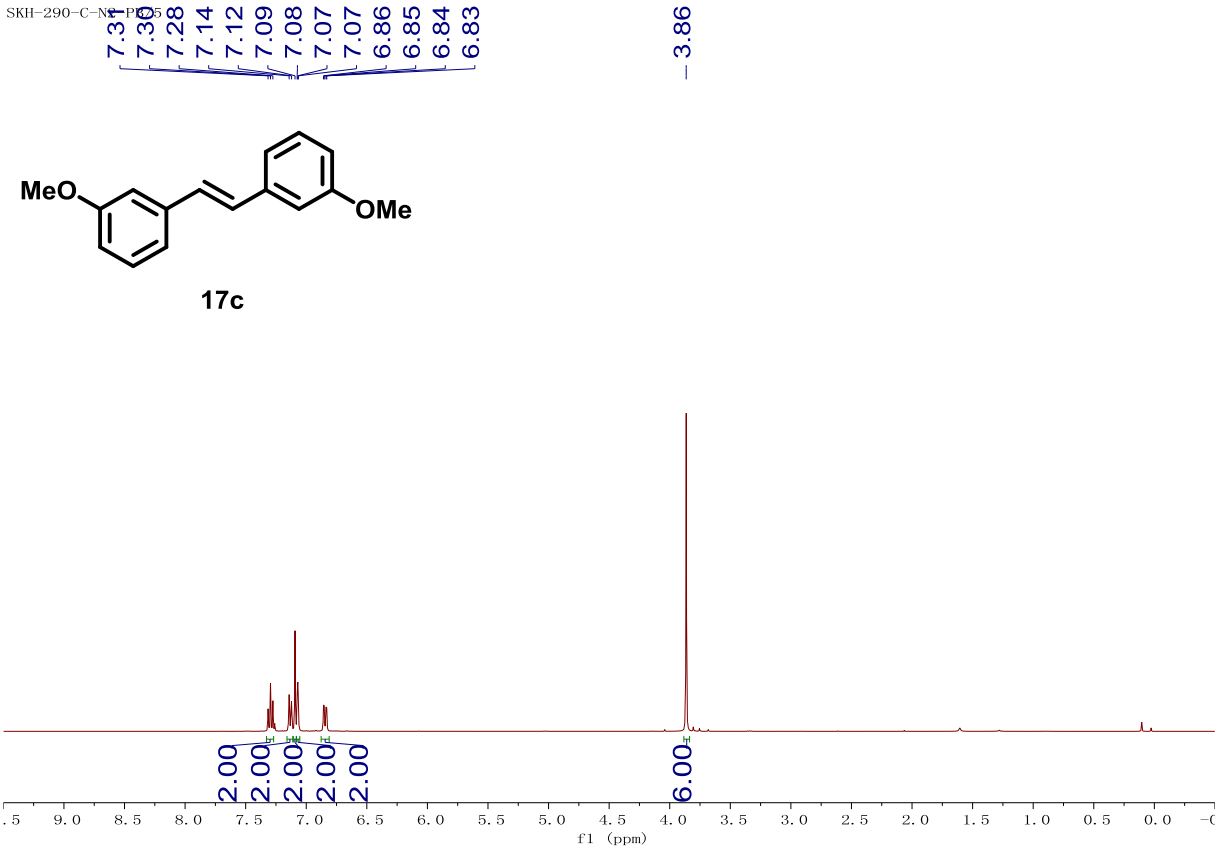
^{1}H NMR for **16c**



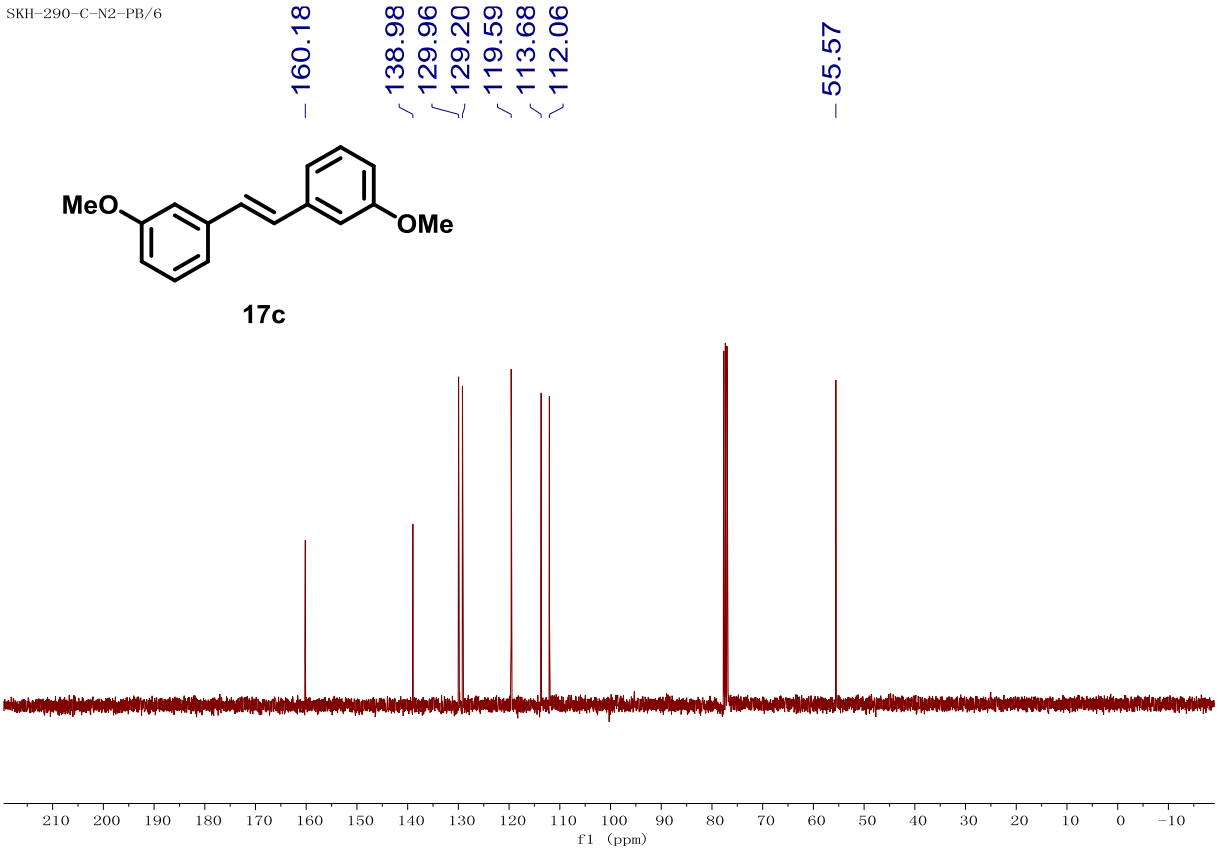
^{13}C NMR for **16c**



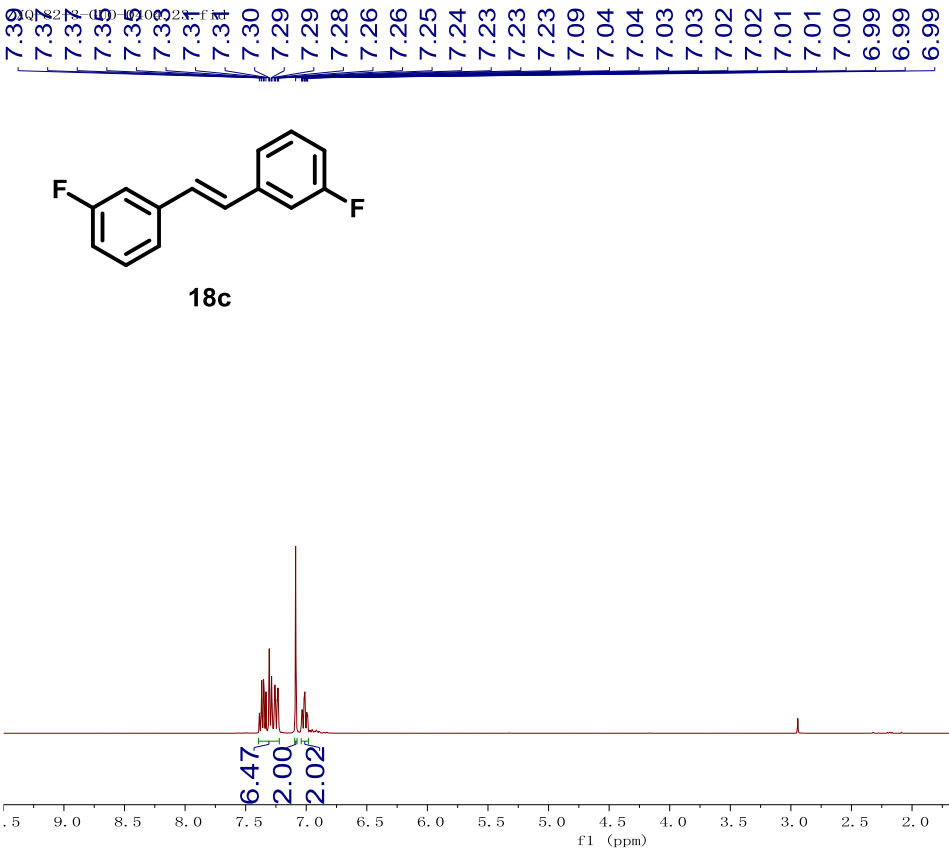
^{1}H NMR for **17c**



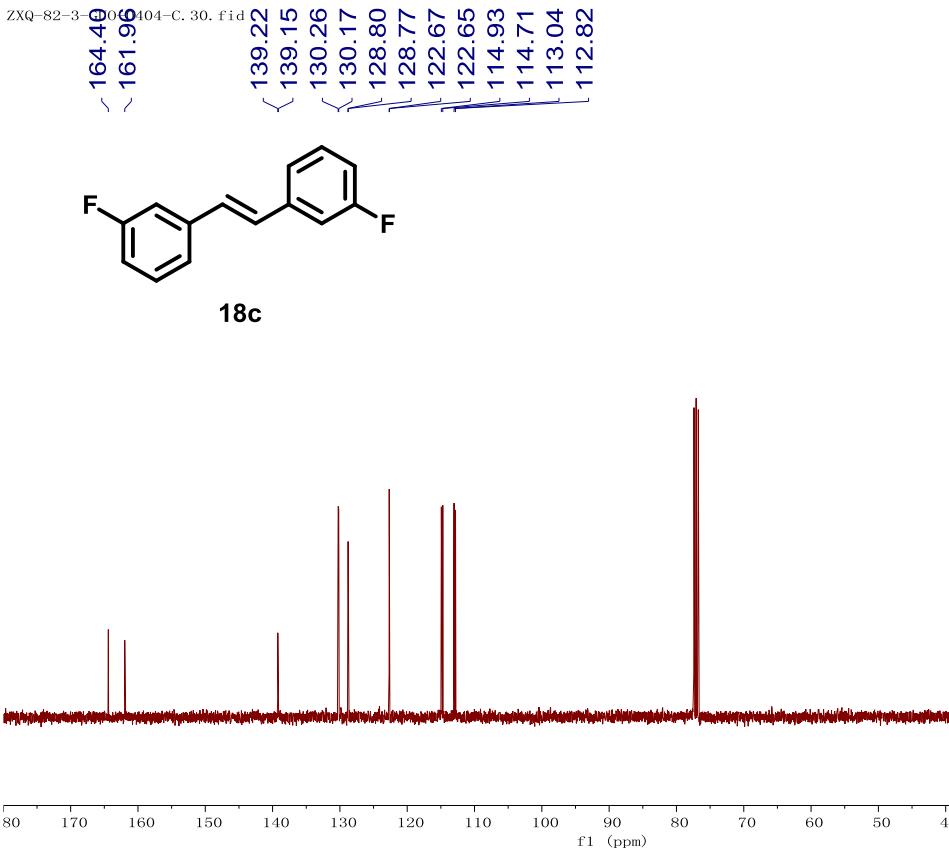
^{13}C NMR for **17c**



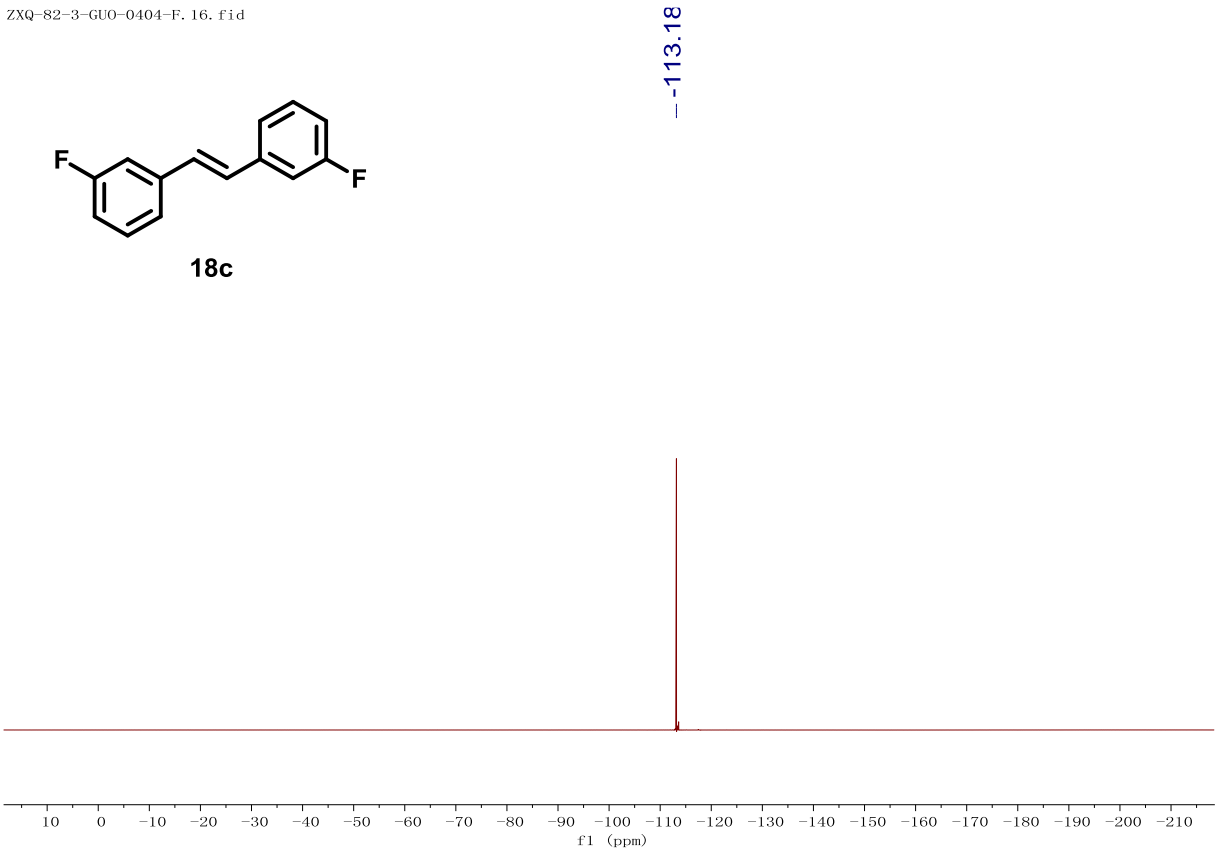
^{1}H NMR for **18c**



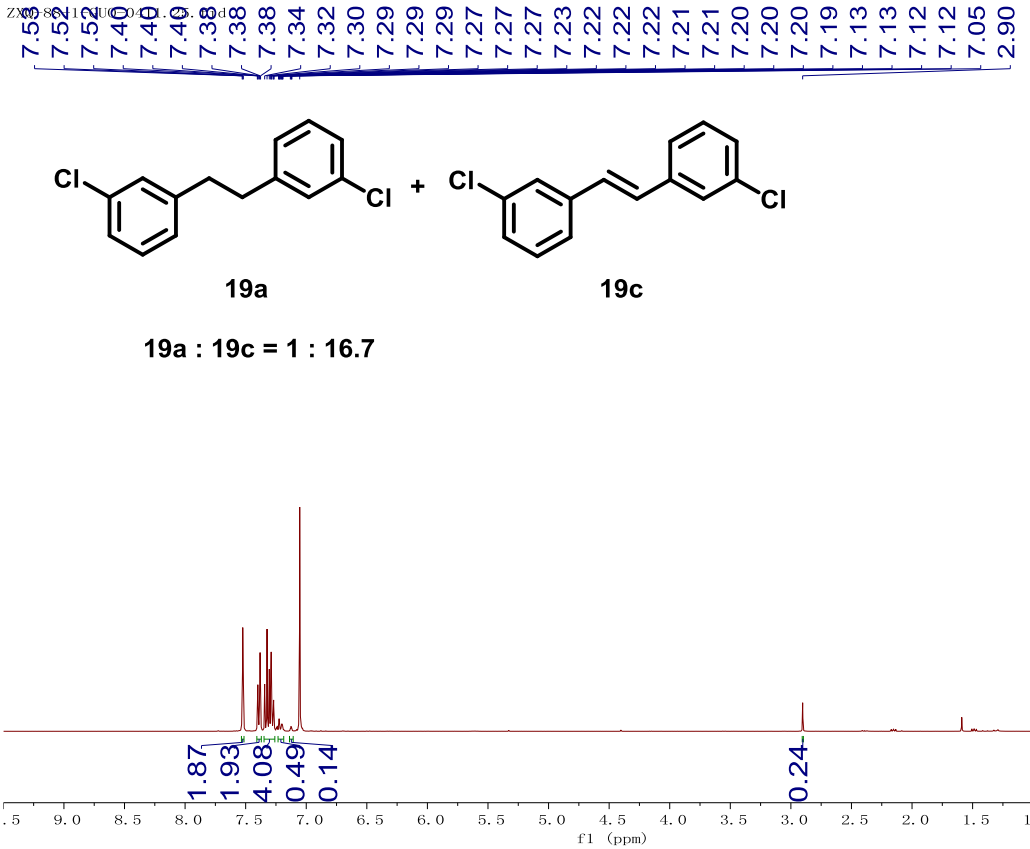
^{13}C NMR for **18c**



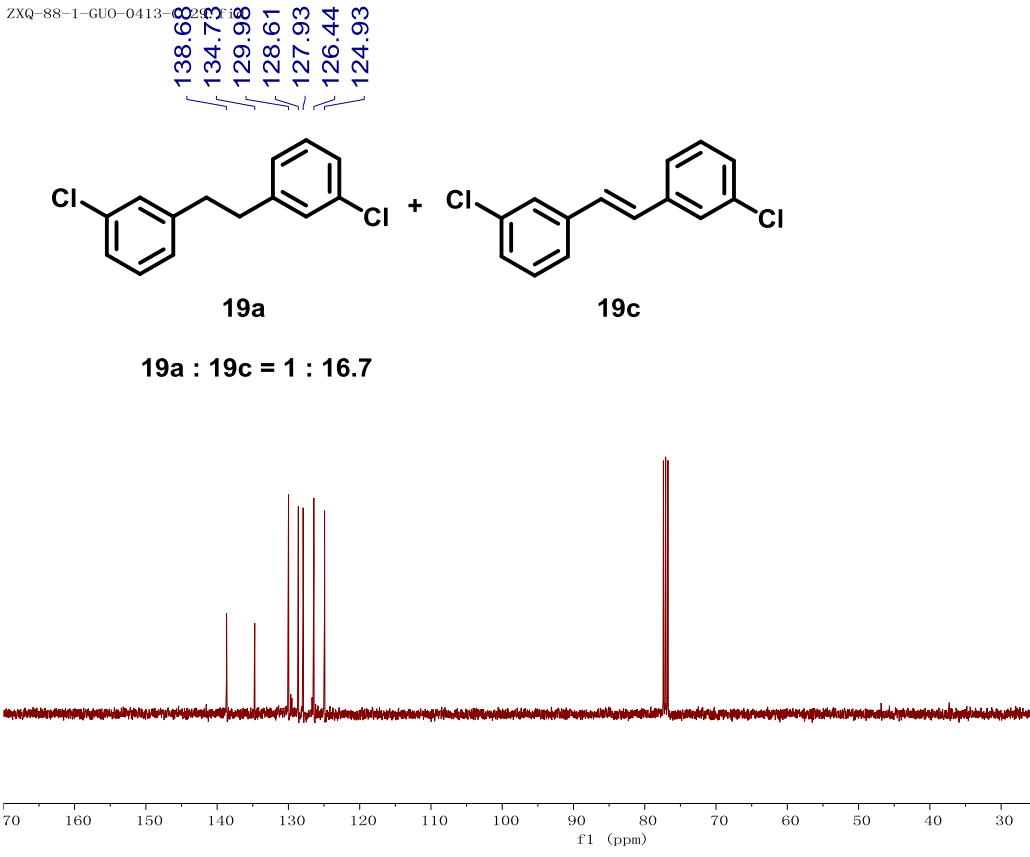
^{19}F NMR for **18c**



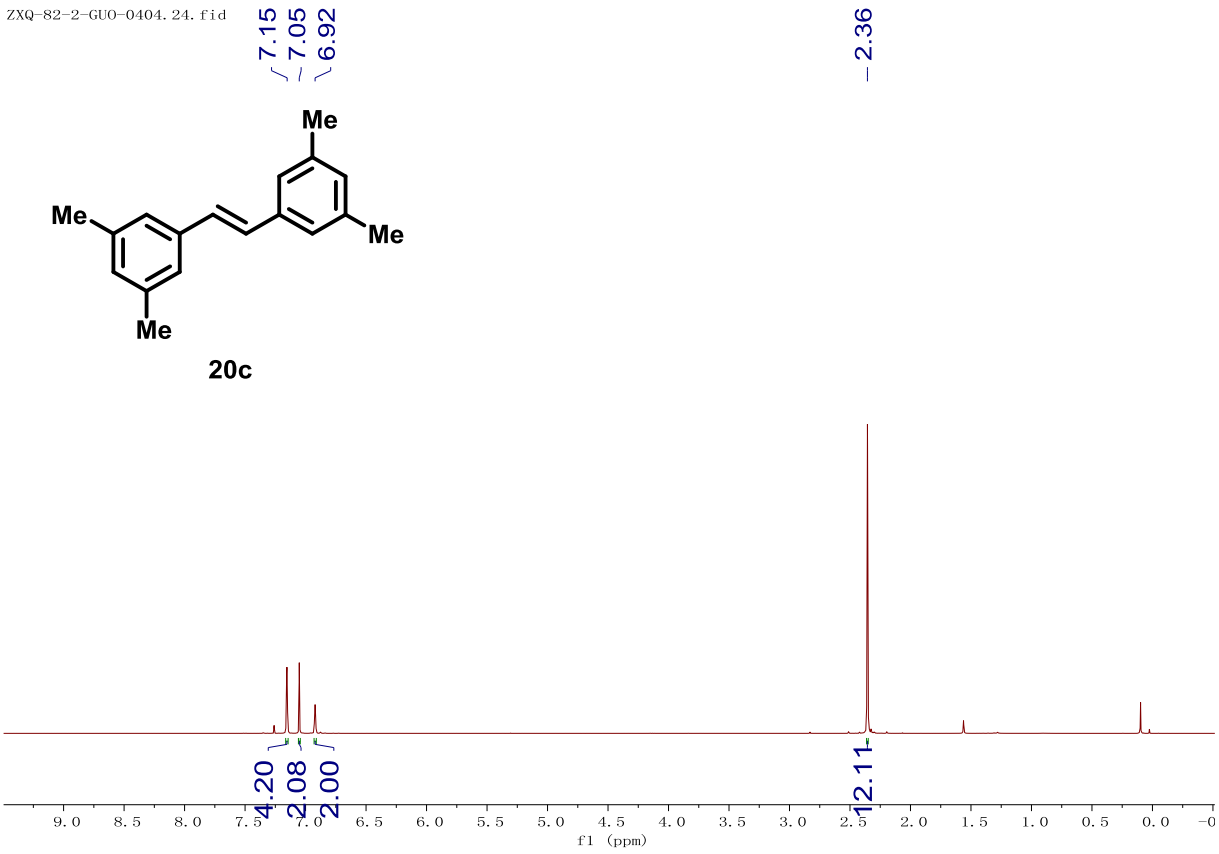
^{1}H NMR for **19a** and **19c**



^{13}C NMR for **19a** and **19c**



^{1}H NMR for **20c**



^{13}C NMR for **20c**