

## Supporting Information

### Metal- and additive-free ipso-benzylation of arylsilanes to access diarylmethanes

Wanting Fu,<sup>a</sup>† Jialong Zhong,<sup>a</sup>† Shuang Lv,<sup>a</sup> Xinyu Song,<sup>a</sup> Yilin Xing,<sup>a</sup> and Zikun Wang<sup>\*a,b</sup>

<sup>a</sup> College of Chemistry and Materials Science, Hebei University, Baoding 071002, China. E-mail: wangzk@hbu.edu.cn.

<sup>b</sup> Key Laboratory of Medicinal Chemistry and Molecular Diagnosis of the Ministry of Education, Hebei University, Baoding 071002, China.

† These authors contributed equally to this work

# Content

|   |    |
|---|----|
| 1. General information .....  | 3  |
| 1.1 Solvents .....  | 3  |
| 1.2 Chromatography.....   | 3  |
| 1.3 Instrument characterization.....                                      | 3  |
| 1.4 Starting materials .....  | 4  |
| 2. Optimization of reaction conditionsa .....                             | 5  |
| 3. Experimental procedures.....   | 7  |
| 3.1 General synthesis method of raw material preparation.....             | 7  |
| 3.2 Preparation of new products.....                                      | 8  |
| 3.3 Pharmaceutical application .....                                      | 10 |
| 3.4 Enlargement reaction .....  | 12 |
| 4. Determination of reaction mechanism .....                              | 14 |
| 4.1 Necessity of benzyl fluoride in this reaction.....                    | 14 |
| 4.2 Applicability of other leaving groups in this reaction.....           | 15 |
| 4.3 Effect of different raw material concentrations on reaction rate..... | 16 |
| 4.4 Reaction process study .....  | 17 |
| 4.5 Interaction between hexafluoroisopropanol and benzyl fluoride .....   | 22 |
| 5. Characterization data of the products.....                             | 24 |
| 6. Copies of NMR spectra .....  | 39 |
| 7. References .....   | 96 |
| Appendix .....  | 99 |

# 1. General information

Unless mentioned otherwise, all air and moisture-insensitive reactions were carried out under an ambient atmosphere and monitored by thin-layer chromatography (TLC). High-resolution mass spectra were obtained using Q Exactive Plus from Thermo Concentration under reduced pressure was performed by rotary evaporation at 25 - 40 °C at an appropriate pressure. Purified compounds were further dried under vacuum ( $10^{-6}$  -  $10^{-3}$  bar). Yields refer to purified and spectroscopically pure compounds, unless otherwise stated.

## 1.1 Solvents

All reagents were purchased from Adamas, Kermel and DAMAO, and used without further purification.

## 1.2 Chromatography

All reagents were commercial and were used without further purification. Column chromatography was performed on silica gel (200-300 mesh) and reactions were monitored by thin-layer chromatography (TLC) using 254 nm UV light for visualization.

## 1.3 Instrument characterization

$^1\text{H}$  NMR,  $^{13}\text{C}$  NMR (400 MHz, 101 MHz, respectively) spectra were measured in  $\text{CDCl}_3$  recorded on Bruker Avance DPX 400 MHz spectrometer.  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR,  $^{19}\text{F}$  NMR (600 MHz, 151 MHz, 565 MHz respectively) spectra were measured in  $\text{CDCl}_3$  recorded on Bruker Avance DPX 600 MHz spectrometer. All chemical shifts ( $\delta$ ) were reported in ppm and coupling constants ( $J$ ) in Hz. NMR Spectra recorded in  $\text{CDCl}_3$  were referenced to tetramethylsilane at 0 ppm for  $^1\text{H}$  or referenced to residual  $\text{CHCl}_3$  at 77.16 ppm for  $^{13}\text{C}$ . The following abbreviations are used: m (multiplet), s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublets), etc. The high resolution mass spectra (HRMS) were measured on a Bruker Daltonics APEX II 47e spectrometer using electron spray ionization (APCI), the mass analyzer is a Fourier transform ion cyclotron resonance. GC-MS test in Agilent 7890B-5977B model gas

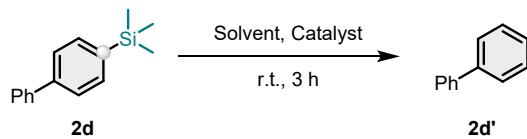
chromatography mass spectrometry instrument using 16-1050 amu, EI source, direct injection, mass analyzer for four bar mass analyzer.

#### **1.4 Starting materials**

All substrates were used as received from commercial suppliers, unless otherwise stated. Chemicals were purchased from Adamas Energy Chemical, Macklin and Aladdin.

## 2. Optimization of reaction conditions<sup>a</sup>

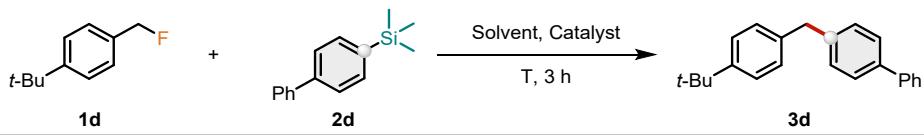
**Table S1:** Optimization of catalyst<sup>a</sup>:



| Entry | Solvent | Additive (10 mol%)                              | Yield (%) <sup>b</sup> |
|-------|---------|---|------------------------|
| 1     | HFIP    | --  | 0                      |
| 2     | HFIP    | FeCl <sub>3</sub>                               | 99                     |
| 3     | HFIP    | Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> | 0                      |
| 4     | HFIP    | Cu(OTf) <sub>2</sub>                            | 98                     |
| 5     | HFIP    | HCl (aq.)                                       | 97                     |
| 6     | HFIP    | AcOH  | 0                      |

<sup>a</sup> Reaction conditions: **2d** (0.5 mmol) and catalyst (0.05 mmol) were reacted in solvent (2 mL) at room temperature for 3 h. <sup>b</sup> Yield was isolated yield.

**Table S2:** Optimization of feed ratio; solvent and temperature<sup>a</sup>:



| Entry | 2d (equiv.) | Solvent      | Catalyst <sup>b</sup>                           | T (°C) | Yield (%) <sup>c</sup> |
|-------|-------------|--------------|---|--------|------------------------|
| 1     | 5           | HFIP         | --  | -10    | 0                      |
| 2     | 5           | HFIP         | --  | 0      | 73                     |
| 3     | 5           | HFIP         | --  | 23     | Mixture                |
| 4     | 1           | HFIP         | --  | 0      | 38                     |
| 5     | 2           | HFIP         | --  | 0      | 42                     |
| 6     | 3           | HFIP         | --  | 0      | 50                     |
| 7     | 4           | HFIP         | --  | 0      | 64                     |
| 8     | 5           | HFIP         | --  | 0      | 73                     |
| 9     | 6           | HFIP         | --  | 0      | 75                     |
| 10    | 5           | HFIP:DCM=1:1 | --  | 0      | 78                     |
| 11    | 5           | HFIP:DCM=2:1 | --  | 0      | 98                     |
| 12    | 5           | DCM          | --  | 0      | n.r.                   |
| 13    | 5           | DCM          | Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> | 0      | n.r.                   |
| 14    | 5           | THF          | --  | 0      | n.r.                   |
| 15    | 5           | TFE          | --  | 0      | n.r.                   |
| 16    | 5           | n-hexane     | --  | 0      | n.r.                   |
| 17    | 5           | n-hexane     | Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> | 0      | n.r.                   |
| 18    | 5           | MeCN         | --  | 0      | n.r.                   |
| 19    | 5           | MeCN         | Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> | 0      | n.r.                   |

<sup>a</sup> Reaction conditions: **1d** (0.3 mmol) and **2d** (1.5 mmol) were reacted in the mixture solvent of HFIP (2 mL) and DCM (1 mL) at 0 °C for 3 h. <sup>b</sup> Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> (0.015 mmol) as Catalyst. <sup>c</sup> Yield was isolated yield.

**Table S3:** Optimization of leaving group<sup>a</sup>:

Reaction scheme: **1** (t-Bu-phenyl-CH<sub>2</sub>-Y) + **2d** (Ph-phenyl-SiMe<sub>2</sub>) → **3d** (t-Bu-phenyl-CH<sub>2</sub>-Ph).

0 °C, 3 h

| Entry | Y                           | <b>2d</b> (equiv.) | Solvent | Yield (%) <sup>b</sup> |
|-------|-----------------------------|--------------------|---------|------------------------|
| 1     | OH                          | 5                  | HFIP    | 0                      |
| 2     | N <sub>3</sub> <sup>1</sup> | 5                  | HFIP    | 0                      |
| 3     | F                           | 5                  | HFIP    | 78                     |
| 4     | Cl                          | 5                  | HFIP    | Mixture                |
| 5     | Br                          | 5                  | HFIP    | Mixture                |
| 6     | OTf                         | 5                  | HFIP    | 0                      |

Below the table, structures 1d-1 to 1d-5 are shown, corresponding to entries 1-5 respectively:

1d-1: t-Bu-phenyl-CH<sub>2</sub>-Cl

1d-2: t-Bu-phenyl-CH<sub>2</sub>-Br

1d-3: t-Bu-phenyl-CH<sub>2</sub>-OH

1d-4: t-Bu-phenyl-CH<sub>2</sub>-OTf

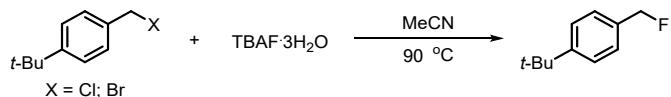
1d-5: t-Bu-phenyl-CH<sub>2</sub>-N<sub>3</sub>

<sup>a</sup> Reaction conditions: **1** (0.3 mmol) and **2d** (1.5 mmol) were reacted in the mixture solvent of HFIP (2 mL) at 0 °C for 3 h. <sup>b</sup> Yield was isolated yield.

### 3. Experimental procedures

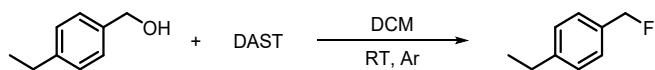
#### 3.1 General synthesis method of raw material preparation

General A synthesis method for preparation of fluorine raw materials:



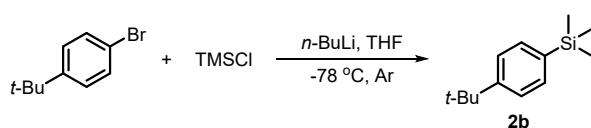
According to the literature report made,<sup>2</sup> a solution of benzylic bromide or benzyl chloride and tetrabutylammonium fluoride (either as trihydrate or tetrakis *tert*-butanol coordinated) in acetonitrile (0.1 M substrate concentration) was heated at reflux for 2 h, then cooled to room temperature. The solvent was removed in vacuo and the residue redissolved in DCM and filtered through a plug of silica eluting with diethyl ether. The solvent was removed in vacuo to give the benzylic fluoride product.

General B synthesis method for preparation of fluorine raw materials:



According to the literature report made,<sup>3</sup> in an Ar atmosphere, DAST (2.0 equiv.) was added dropwise to a stirring solution containing anhydrous CH<sub>2</sub>Cl<sub>2</sub> containing benzyl alcohol (1.0 equiv.) at 0 °C, and the reaction was transferred to room temperature overnight. After the reaction was completed, the crude mixture was quenched with saturated NaHCO<sub>3</sub> aqueous solution at 0 °C and extracted with Et<sub>2</sub>O. The merged organic layer is dried on Na<sub>2</sub>SO<sub>4</sub> and concentrated in vacuum. The crude product was purified by column chromatography.

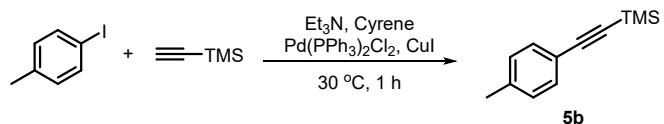
General C synthesis method of preparing aryl silane raw materials:



According to the literature report made,<sup>4</sup> an oven-dried Schlenk flask under Ar was charged with 1-bromo-4-*tert*-butylbenzene (1.00 equiv.) and anhydrous THF (0.50 M). The solution was cooled to -78 °C and after 10 min, *n*-butyllithium (1.60 M in hexanes; 1.20 equiv.) was added dropwise. Immediately or after 30 min at -78 °C, trimethylsilyl chloride (1.50 equiv.) was added dropwise. The solution was stirred

overnight, gradually warming up to rt. Water was added, the organic layer was separated, and the aqueous phase was extracted three times with  $\text{Et}_2\text{O}$ . Combined organic phases were washed with brine, dried over  $\text{MgSO}_4$ , filtered, and concentrated under reduced pressure. The crude product was purified by silica gel (eluent-n-hexane) column chromatography to obtain raw material **2b**.

General D synthesis method for the preparation of alkynylsilane raw materials:



According to the literature report made,<sup>5</sup> using  $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$  (2 mol %),  $\text{CuI}$  (4 mol%), Cyrene (0.5 mL, 0.5 M),  $\text{Et}_3\text{N}$  (1.1 equiv), 4-iodotoluene (1 equiv.), and ethynyltrimethylsilane (1.05 equiv.). After 1 h, the reaction mixture was purified by the general procedure (silica gel, petroleum ether 0 - 1%  $\text{Et}_2\text{O}$ ) to obtain raw material **5b**.

### 3.2 Preparation of new products

Synthesis of substrates **3a-3u**, **4a-4d**, **4i-4v**, **6a-6j**:



Under an ambient atmosphere, **2d** (0.34 g, 1.5 mmol) was added to a Schlenk tube equipped with a polytetrafluoroethylene-coated magnetic stir bar, and the reaction system was placed in an ice-water bath. Then 3 mL reaction solvent (HFIP, 2 mL and DCM, 1 mL) was added to the system until it was completely dissolved, followed by the addition of **1d** (0.05 g, 0.3 mmol). The reaction system was stirred at 0 °C for 3 hours, after the reaction was completed, and then  $\text{Cu}(\text{OTf})_2$  (0.01 g, 0.03 mmol) was added to the system to continue the reaction for 15 minutes. Then 20 mL of  $\text{CH}_2\text{Cl}_2$  was added to the reaction mixture. The organic layer was extracted with saturated aqueous  $\text{NaHCO}_3$  solution ( $3 \times 20$  mL). The combined organic layers were dried with anhydrous  $\text{Na}_2\text{SO}_4$  and filtered and solvent was removed under reduced pressure. The resulting crude product was purified by column chromatography on silica gel using petroleum ether : ethyl acetate = 80 : 1 as eluent to afford the product **3d** in the yield of

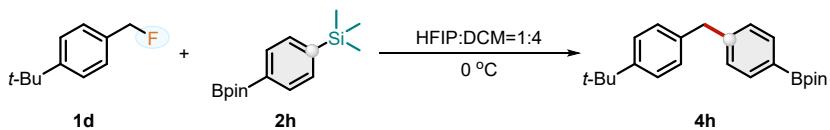
98% as a colorless oil.

Synthesis of substrates **4e-4g**:



In the atmosphere, **2f** (0.34 g, 1.5 mmol) was added to a Schrenk tube containing a polytetrafluoroethylene coated magnetic stirrer, and the reaction system was placed in an ice water bath. Then 3 mL reaction solvent (HFIP, 3 mL) was added to the system until completely dissolved, and then **1d** (0.05 g, 0.3 mmol) was added. The reaction system was stirred at 0 °C for 3 hours, after the reaction was completed, and then Cu(OTf)2 (0.01 g, 0.03 mmol) was added to the system to continue the reaction for 15 minutes. Then 20 mL of CH2Cl2 was added to the reaction mixture. The organic layer was extracted with saturated NaHCO3 aqueous solution (3 × 20 mL). The merged organic layer was dried with anhydrous Na2SO4, filtered, and decompressed to remove the solvent. The resulting crude product was purified by column chromatography on silica gel using petroleum ether : ethyl acetate = 80 : 1 as eluent to afford the product **4f** in the yield of 93% as a colorless oil.

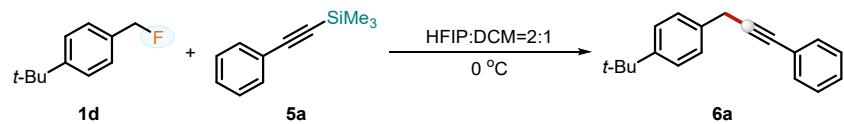
Synthesis of substrates **4h**:



In the atmosphere, **2h** (0.41 g, 1.5 mmol) was added to a Schrenk tube containing a polytetrafluoroethylene coated magnetic stirrer, and the reaction system was placed in an ice water bath. Then 3 mL reaction solvent (HFIP, 0.6 mL and DCM, 2.4 mL) was added to the system until completely dissolved, and then **1d** (0.05 g, 0.3 mmol) was added. The reaction system was stirred at 0 °C for 3 hours, after the reaction was completed, and then Cu(OTf)2 (0.01 g, 0.03 mmol) was added to the system to continue the reaction for 15 minutes. Then 20 mL of CH2Cl2 was added to the reaction mixture. The organic layer was extracted with saturated NaHCO3 aqueous solution (3 × 20 mL). The merged organic layer was dried with anhydrous Na2SO4, filtered, and

decompressed to remove the solvent. The resulting crude product was purified by column chromatography on silica gel using petroleum ether : ethyl acetate = 20 : 1 as eluent to afford the product **4h** in the yield of 46% as a white solid.

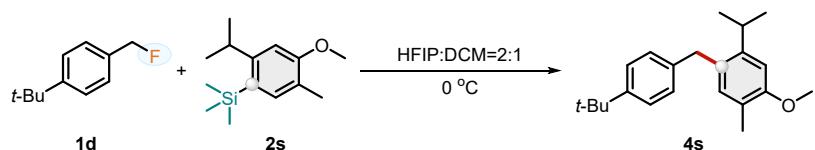
Synthesis of substrates **5a**:



In the atmosphere, **5a** (0.26 g, 1.5 mmol) was added to a Schrenk tube containing a polytetrafluoroethylene coated magnetic stirrer, and the reaction system was placed in an ice water bath. Then 3 mL reaction solvent (HFIP, 2 mL and DCM, 1 mL) was added to the system until completely dissolved, and then **1d** (0.05 g, 0.3 mmol) was added. The reaction system was stirred at 0 °C for 3 hours, after the reaction was completed, and then Cu(OTf)2 (0.01 g, 0.03 mmol) was added to the system to continue the reaction for 15 minutes. Then 20 mL of CH2Cl2 was added to the reaction mixture. The organic layer was extracted with saturated NaHCO3 aqueous solution (3 × 20 mL). The merged organic layer was dried with anhydrous Na2SO4, filtered, and decompressed to remove the solvent. The resulting crude product was purified by column chromatography on silica gel using petroleum ether : ethyl acetate = 80 : 1 as eluent to afford the product **6a** in the yield of 85% as a yellow oil.

### 3.3 Pharmaceutical application

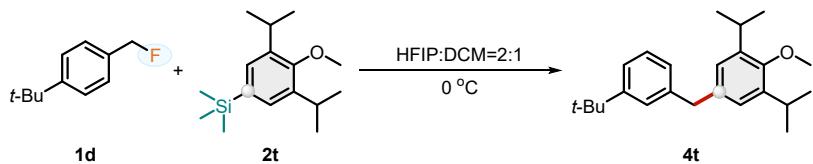
**Carvacrol:**



In the atmosphere, carvacrol derivatives **2s**<sup>6</sup> (0.35 g, 1.5 mmol) was added to a Schrenk tube containing a polytetrafluoroethylene coated magnetic stirrer, and the reaction system was placed in an ice water bath. Then 3 mL reaction solvent (HFIP, 2 mL and DCM, 1 mL) was added to the system until completely dissolved, and then **1d** (0.05 g, 0.3 mmol) was added. The reaction system was stirred at 0 °C for 3 hours, after the reaction was completed, and then Cu(OTf)2 (0.01 g, 0.03 mmol) was added to the system to continue the reaction for 15 minutes. Then 20 mL of CH2Cl2 was added to

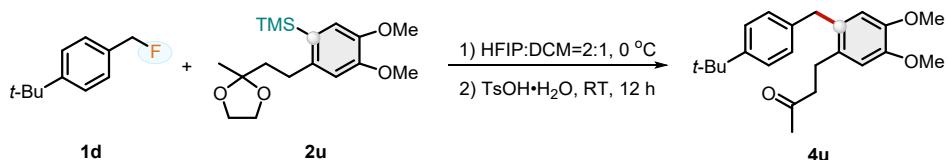
the reaction mixture. The organic layer was extracted with saturated  $\text{NaHCO}_3$  aqueous solution ( $3 \times 20$  mL). The merged organic layer was dried with anhydrous  $\text{Na}_2\text{SO}_4$ , filtered, and decompressed to remove the solvent. The resulting crude product was purified by column chromatography on silica gel using petroleum ether : ethyl acetate = 80 : 1 as eluent to afford the product **4s** in the yield of 71% as a white solid.

**Propofol:**



In the atmosphere, propofol derivative **2t**<sup>6</sup> (0.40 g, 1.5 mmol) was added to a Schrenk tube containing a polytetrafluoroethylene coated magnetic stirrer, and the reaction system was placed in an ice water bath. Then 3 mL reaction solvent (HFIP, 2 mL and DCM, 1 mL) was added to the system until completely dissolved, and then **1d** (0.05 g, 0.3 mmol) was added. The reaction system was stirred at 0 °C for 3 hours, after the reaction was completed, and then  $\text{Cu}(\text{OTf})_2$  (0.01 g, 0.03 mmol) was added to the system to continue the reaction for 15 minutes. Then 20 mL of  $\text{CH}_2\text{Cl}_2$  was added to the reaction mixture. The organic layer was extracted with saturated  $\text{NaHCO}_3$  aqueous solution ( $3 \times 20$  mL). The merged organic layer was dried with anhydrous  $\text{Na}_2\text{SO}_4$ , filtered, and decompressed to remove the solvent. The resulting crude product was purified by column chromatography on silica gel using petroleum ether : ethyl acetate = 80 : 1 as eluent to afford the product **4t** in the yield of 61% as a white solid.

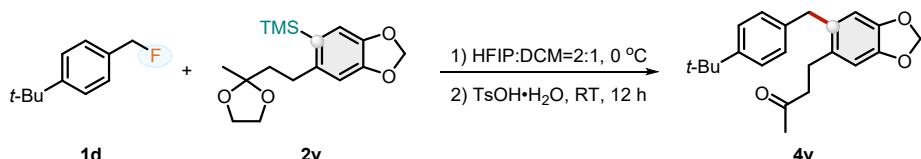
**Vanillylacetone acetone:**



In the atmosphere, piperonyl acetone derivatives **2u**<sup>6</sup> (0.46 g, 1.5 mmol) was added to a Schrenk tube containing a polytetrafluoroethylene coated magnetic stirrer, and the reaction system was placed in an ice water bath. Then 3 mL reaction solvent (HFIP 2 mL and DCM 1 mL) was added to the system until completely dissolved, and then p-tert-butylbenzyl fluoride (0.05 g, 0.3 mmol) was added. The reaction system was stirred

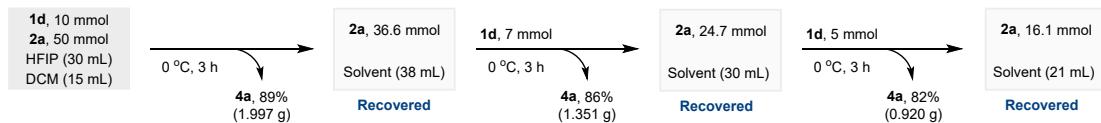
at 0 °C for 3 hours, after the reaction was completed, and then  $\text{TsOH} \cdot \text{H}_2\text{O}$  (0.01 g, 0.03 mmol) was added to the system to continue the reaction for 12 h. Then 20 mL of  $\text{CH}_2\text{Cl}_2$  was added to the reaction mixture. The organic layer was extracted with saturated  $\text{NaHCO}_3$  aqueous solution ( $3 \times 20$  mL). The merged organic layer was dried with anhydrous  $\text{Na}_2\text{SO}_4$ , filtered, and decompressed to remove the solvent. The resulting crude product was purified by column chromatography on silica gel using petroleum ether : ethyl acetate = 80 : 1 as eluent to afford the product **4u** in the yield of 62% as a white solid.

### Piperonyl acetone:



In the atmosphere, piperonyl acetone derivatives **2v**<sup>6</sup> (0.46 g, 1.5 mmol) was added to a Schrenk tube containing a polytetrafluoroethylene coated magnetic stirrer, and the reaction system was placed in an ice water bath. Then 3 mL reaction solvent (HFIP 2 mL and DCM 1 mL) was added to the system until completely dissolved, and then p-tert-butylbenzyl fluoride (0.05 g, 0.3 mmol) was added. The reaction system was stirred at 0 °C for 3 hours, after the reaction was completed, and then  $\text{TsOH} \cdot \text{H}_2\text{O}$  (0.01 g, 0.03 mmol) was added to the system to continue the reaction for 12 h. Then 20 mL of  $\text{CH}_2\text{Cl}_2$  was added to the reaction mixture. The organic layer was extracted with saturated  $\text{NaHCO}_3$  aqueous solution ( $3 \times 20$  mL). The merged organic layer was dried with anhydrous  $\text{Na}_2\text{SO}_4$ , filtered, and decompressed to remove the solvent. The resulting crude product was purified by column chromatography on silica gel using petroleum ether : ethyl acetate = 80 : 1 as eluent to afford the product **4v** in the yield of 64% as a white solid.

### 3.4 Enlargement reaction

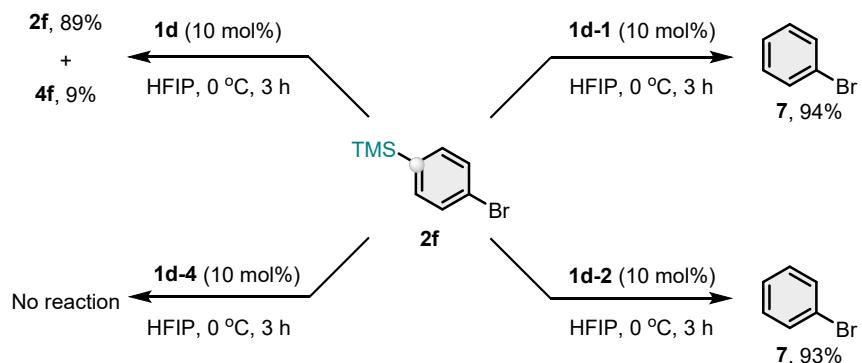


Under an ambient atmosphere, **2a** (7.52 g, 50 mmol) was added to a round-bottom

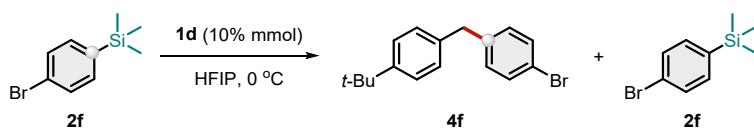
flask containing a polytetrafluoroethylene-coated magnetic stir bar, and the reaction system was placed in an ice water bath. Then, 45 mL of reaction solvent (HFIP, 30 mL, DCM, 15 mL) was added to the system. After it was completely dissolved, it was added for 1 d (1.66 g, 10 mmol). The reaction system was stirred at 0 °C for 3 hours, after the reaction was completed, The mixture of 2a and solvent (38 mL) was distilled by vacuum distillation, and the remaining mixture was separated and purified by column chromatography. The product 4a was obtained by using petroleum ether : ethyl acetate = 80 : 1 as eluent. After three consecutive reactions, the reaction efficiency was affected. Finally, the product 4a was obtained in an average yield of 86 %.

## 4. Determination of reaction mechanism

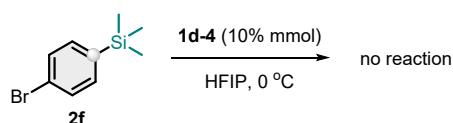
### 4.1 Necessity of benzyl fluoride in this reaction



**Figure S1.** Necessity of benzyl fluoride in this reaction

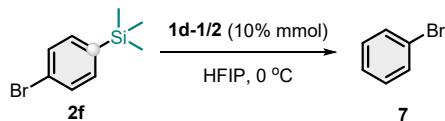


In the atmosphere, **2f** (0.23 g, 1 mmol) was added to a Schrenk tube containing a polytetrafluoroethylene coated magnetic stirrer, and the reaction system was placed in an ice water bath. Then 3 mL reaction solvent (HFIP, 3 mL) was added to the system until completely dissolved, and then **1d** (0.02 g, 0.1 mmol) was added. The reaction system was stirred at 0 °C for 3 hours, after the reaction was completed, the solvent was evaporated by rotary evaporation at low temperature, and then the system was separated by column chromatography. The target product **4f** was obtained in a yield of 9%, and the remaining **2f** was not involved in the reaction and successfully recovered.



In the atmosphere, **2f** (0.23 g, 1 mmol) was added to a Schrenk tube containing a polytetrafluoroethylene coated magnetic stirrer, and the reaction system was placed in an ice water bath. Then 3 mL reaction solvent (HFIP, 3 mL) was added to the system until completely dissolved, and then **1d-4**<sup>7</sup> (0.03 g, 0.1 mmol) was added. The reaction system was stirred at 0 °C for 3 hours, the reaction system was stirred at 0 °C for 3 hours, after the reaction was completed, the solvent was evaporated by rotary evaporation at low temperature, and then the system was separated by column

chromatography, the reactants were completely recovered.

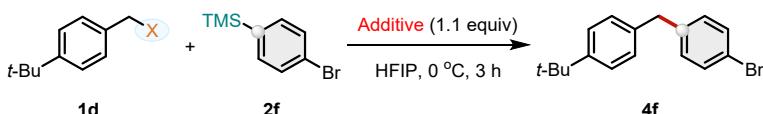


In the atmosphere, **2f** (0.23 g, 1 mmol) was added to a Schrenk tube containing a polytetrafluoroethylene coated magnetic stirrer, and the reaction system was placed in an ice water bath. Then 3 mL reaction solvent (HFIP, 3 mL) was added to the system until completely dissolved, and then **1d-1** or **1d-2** (0.1 mmol) was added. The reaction system was stirred at 0 °C for 3 hours, after the reaction was completed, the solvent was evaporated by rotary evaporation at low temperature, and then the system was separated by column chromatography, product **7** was collected and **2f** was not found.

## 4.2 Applicability of other leaving groups in this reaction

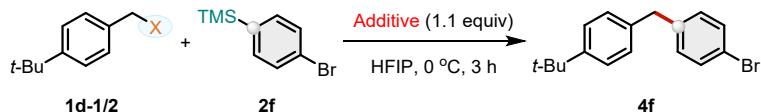
**Table S4:** Applicability of other leaving groups in this reaction

|             |    | Additive (1.1 equiv) | <b>4f</b>                        |                                  |
|-------------|----|----------------------|----------------------------------|----------------------------------|
| X           |    |                      | AgOAc                            | Et <sub>3</sub> N                |
| <b>1d</b>   | F  |                      | <b>4f</b> , 93%; <b>2f</b> , 81% | <b>4f</b> , 80%; <b>2f</b> , 83% |
| <b>1d-1</b> | Cl |                      | <b>4f</b> , 87%; <b>2f</b> , 82% | <b>4f</b> , 61%; <b>2f</b> , 87% |
| <b>1d-2</b> | Br |                      | <b>4f</b> , 84%; <b>2f</b> , 83% | <b>4f</b> , 59%; <b>2f</b> , 88% |



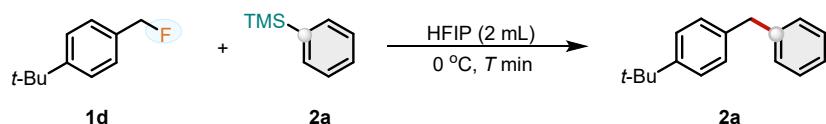
In the atmosphere, additive (Et<sub>3</sub>N or AgOAc, 0.33 mmol) and 1-bromo-4-trimethylsilylbenzene (0.34 g, 1.5 mmol) was added to a Schrenk tube containing a polytetrafluoroethylene coated magnetic stirrer, and the reaction system was placed in an ice water bath. Then 3 mL reaction solvent (HFIP, 3 mL) was added to the system until completely dissolved, and then **1d** (0.05 g, 0.3 mmol) was added. The reaction system was stirred at 0 °C for 3 hours. After the reaction was completed, 20 mL of CH<sub>2</sub>Cl<sub>2</sub> was added to the reaction mixture. The organic layer was extracted with saturated NaHCO<sub>3</sub> aqueous solution (3 × 20 mL). The merged organic layer was dried

with anhydrous  $\text{Na}_2\text{SO}_4$ , filtered, and decompressed to remove the solvent. The obtained crude product was purified by silica gel column chromatography, and the product **4f** was obtained, and the **2f** were all recovered.



In the atmosphere, additive ( $\text{Et}_3\text{N}$  or  $\text{AgOAc}$ , 0.33 mmol) and 1-bromo-4-trimethylsilylbenzene (0.34 g, 1.5 mmol) was added to a Schrenk tube containing a polytetrafluoroethylene coated magnetic stirrer, and the reaction system was placed in an ice water bath. Then 3 mL reaction solvent (HFIP, 3 mL) was added to the system until completely dissolved, and then **1d-1** or **1d-2** (0.3 mmol) was added. The reaction system was stirred at 0 °C for 3 hours. After the reaction was completed, 20 mL of  $\text{CH}_2\text{Cl}_2$  was added to the reaction mixture. The organic layer was extracted with saturated  $\text{NaHCO}_3$  aqueous solution ( $3 \times 20$  mL). The merged organic layer was dried with anhydrous  $\text{Na}_2\text{SO}_4$ , filtered, and decompressed to remove the solvent. The resulting crude product was purified by column chromatography on silica gel using petroleum ether : ethyl acetate = 80 : 1 as eluent to afford the product **4f** in the yield of as a colorless oil, the other **2f** are largely recovered.

#### 4.3 Effect of different raw material concentrations on reaction rate



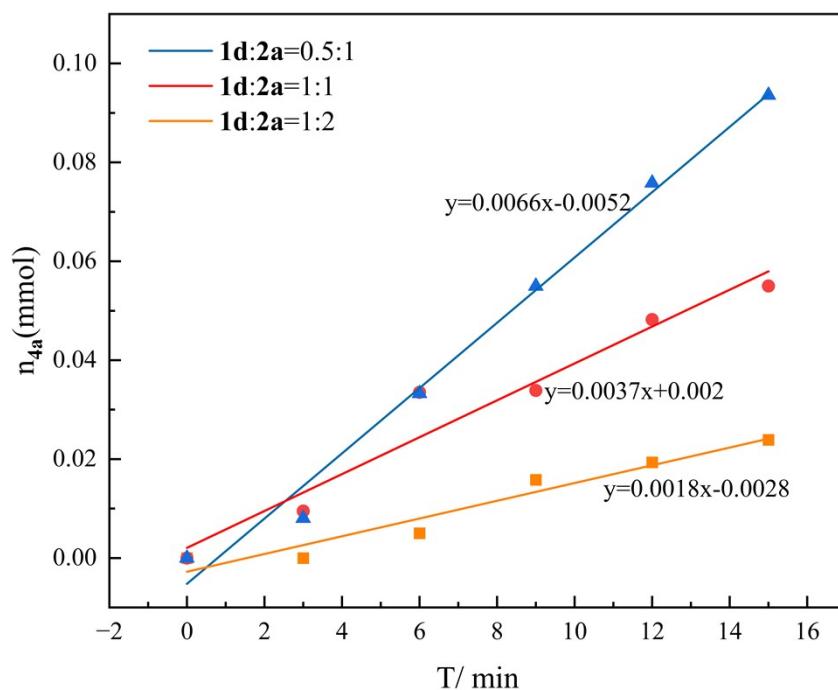
Under atmospheric conditions, **1d** was introduced into the **2a** system containing HFIP (2 mL) at 0 °C, dodecane was employed as an internal standard for quantification. Three sets of parallel experiments, each consisting of five replicates, were performed under varying molar numbers of **1d** : **2a** = 0.5 : 1, 1 : 1, and 1 : 2. See Appendix for specific data.

**Table S5:** Effect of different raw material concentrations on reaction rate

| T/ min | $n_1(\mathbf{1d}:\mathbf{2a} = 0.5:1)/$<br>mmol | $n_2(\mathbf{1d}:\mathbf{2a} = 1:1) /$<br>mmol | $n_3(\mathbf{1d}:\mathbf{2a} = 1:2) /$<br>mmol |
|--------|---|--|--|
|--------|---|--|--|

|    |         |        |         |
|----|---------|--------|---------|
| 0  | 0       | 0      | 0       |
| 3  | 0       | 0.0095 | 0.00803 |
| 6  | 0.005   | 0.0335 | 0.03326 |
| 9  | 0.01581 | 0.0339 | 0.05499 |
| 12 | 0.01934 | 0.0482 | 0.07583 |
| 15 | 0.02389 | 0.0550 | 0.0936  |

All samples were analyzed by gas chromatography-mass spectrometry (GC-MS).



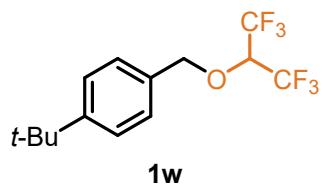
**Figure S2.** Effect of different raw material concentrations on reaction rate

#### 4.4 Reaction process study



In the atmosphere, **2f** (0.34 g, 1.5 mmol) was added to a Schrenk tube containing a polytetrafluoroethylene coated magnetic stirrer, and the reaction system was placed in an ice water bath. Then 3 mL reaction solvent (HFIP, 3 mL) was added to the system until completely dissolved, and then **1w**<sup>8</sup> (0.09 g, 0.3 mmol) was added. The reaction system was stirred at 0 °C for 3 hours, the reaction system was stirred at 0 °C for 3 hours, after the reaction was completed, the solvent was evaporated by rotary evaporation at low temperature, and then the system was separated by column

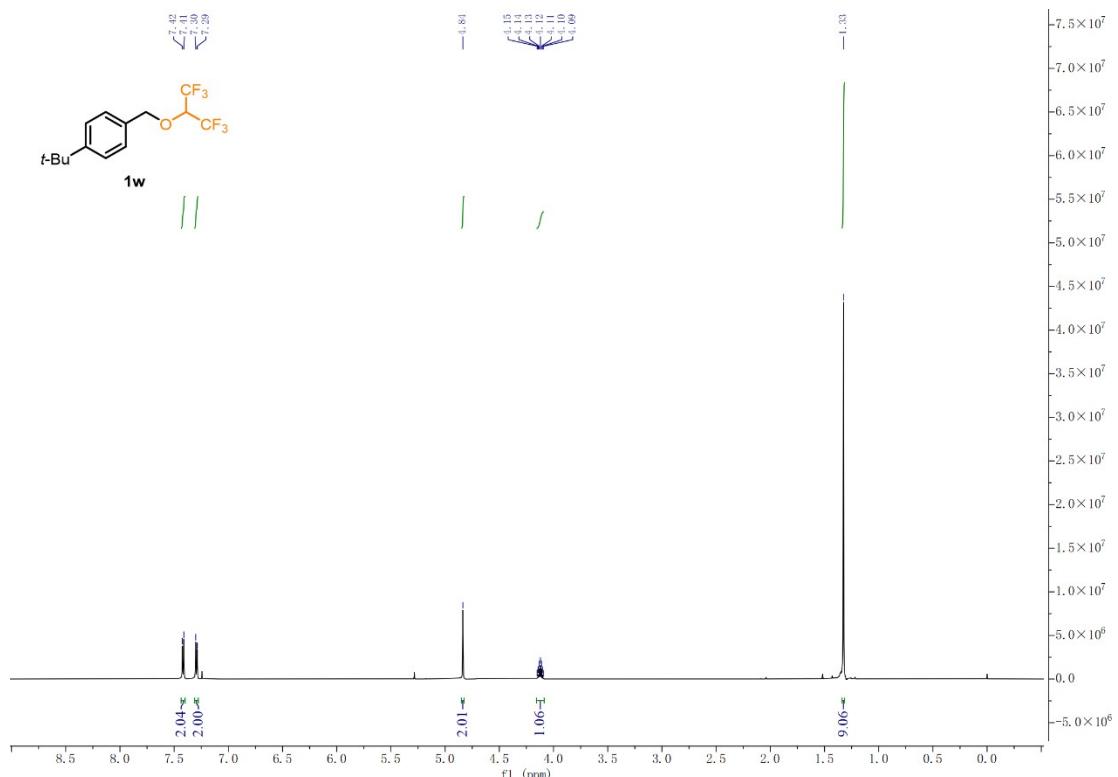
chromatography, the reactants were completely recovered.



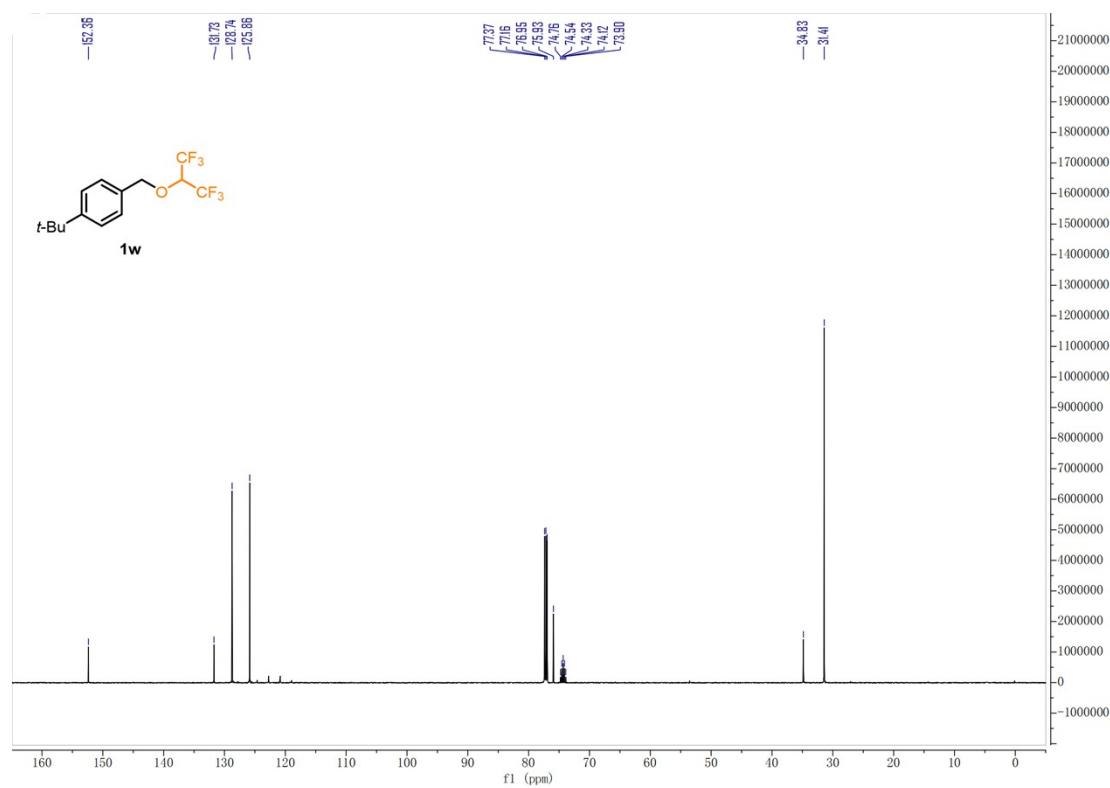
**1-(tert-butyl)-4-(((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)methyl)benzene (1w);**  
<sup>1</sup>**H NMR** (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.42 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 8.4 Hz, 2H), 4.84 (s, 2H), 4.15-4.09 (m, 1H), 1.33 (s, 9H); <sup>13</sup>**C NMR** (151 MHz, CDCl<sub>3</sub>)  $\delta$  152.36, 131.73, 128.74, 125.86, 77.37, 77.16, 76.95, 75.93, 74.76, 74.54, 74.33, 74.12, 73.90, 34.83, 31.41; <sup>19</sup>**F NMR** (565 MHz, CDCl<sub>3</sub>)  $\delta$  -73.50.

<sup>1</sup>**H NMR of 1w**

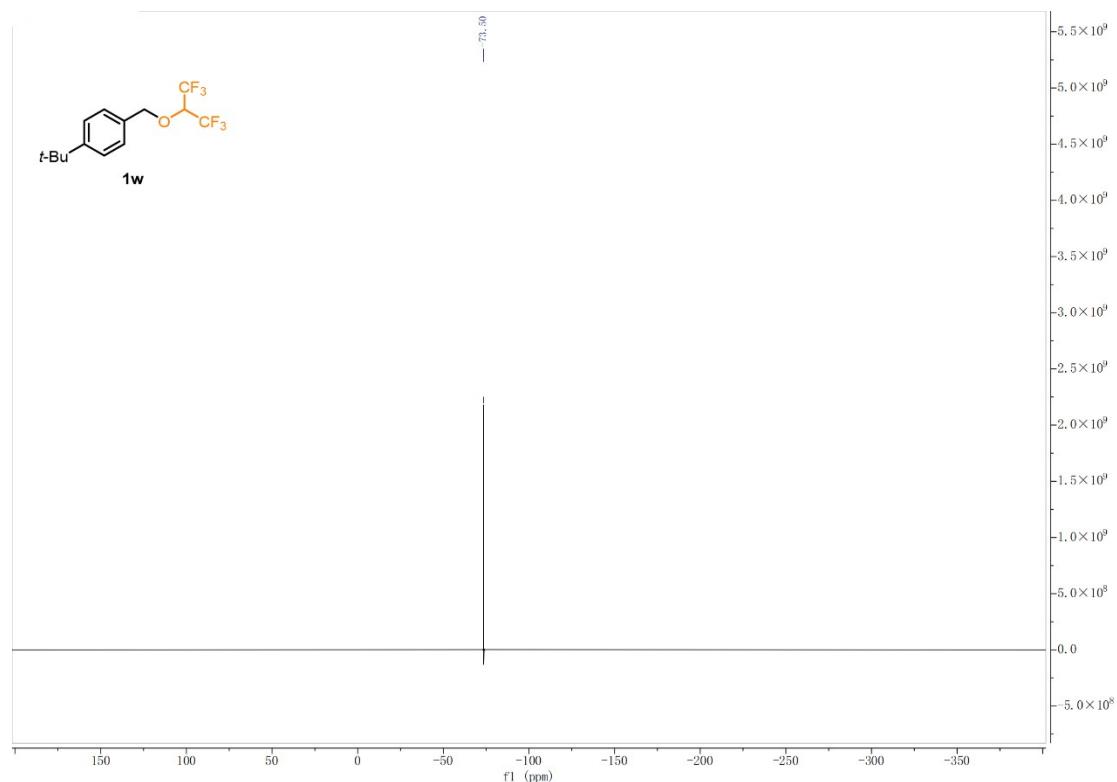
CDCl<sub>3</sub>, 600 MHz, 298 K

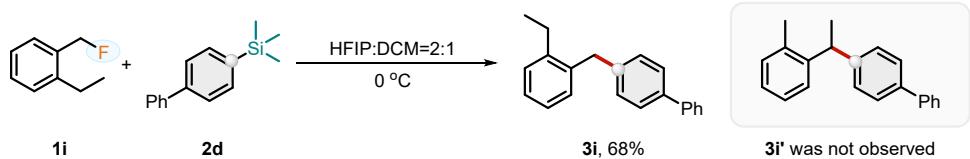


<sup>13</sup>C NMR of **1w**  
 $\text{CDCl}_3$ , 151 MHz, 298 K

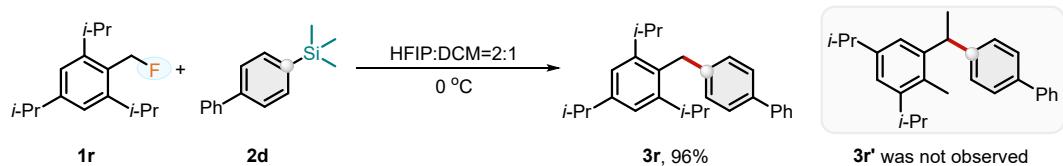


<sup>19</sup>F NMR of **1w**  
 $\text{CDCl}_3$ , 565 MHz, 298 K





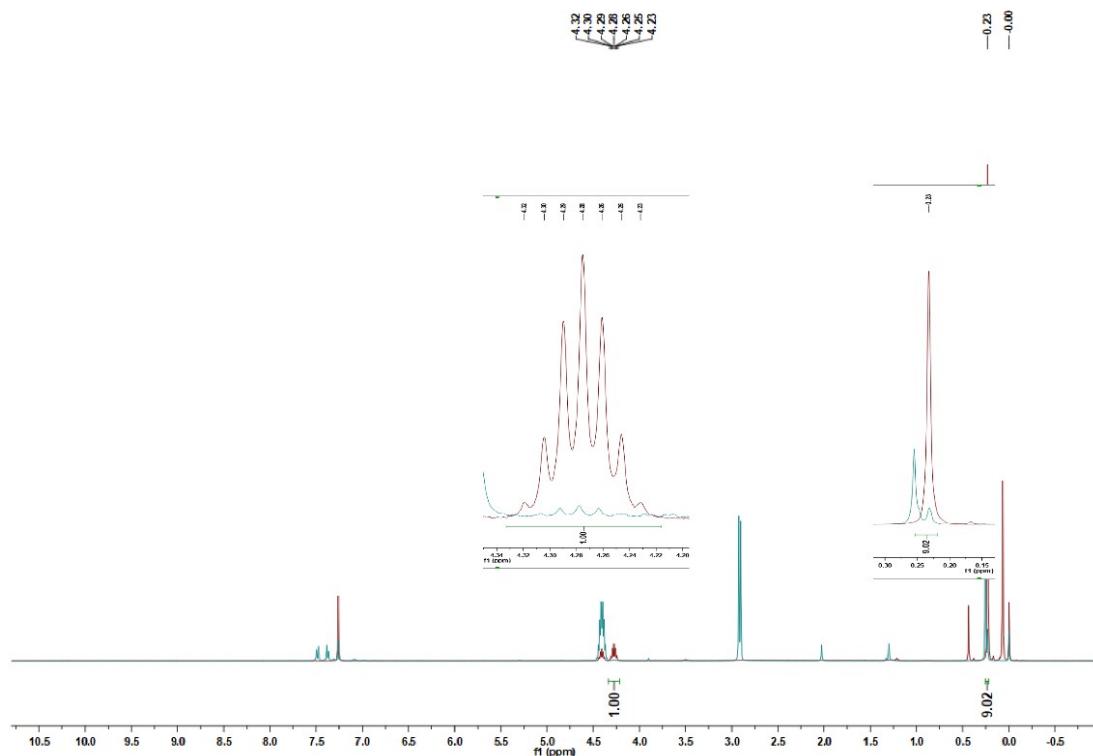
Under an ambient atmosphere, **2d** (0.34 g, 1.5 mmol) was added to a Schlenk tube equipped with a polytetrafluoroethylene-coated magnetic stir bar, and the reaction system was placed in an ice-water bath. Then 3 mL reaction solvent (HFIP, 2 mL and DCM, 1 mL) was added to the system until it was completely dissolved, followed by the addition of **1i** (0.05 g, 0.3 mmol). The reaction system was stirred at 0 °C for 3 hours, and then Cu(OTf)2 (0.01 g, 0.03 mmol) was added to the system to continue the reaction for 15 minutes. After the reaction was completed, 20 mL of CH2Cl2 was added to the reaction mixture. The organic layer was extracted with saturated aqueous NaHCO3 solution (3 × 20 mL). The combined organic layers were dried with anhydrous Na2SO4 and filtered and solvent was removed under reduced pressure. The resulting crude product was purified by column chromatography on silica gel using petroleum ether : ethyl acetate = 80 : 1 as eluent to afford the product **3i** in the yield of 68% as a colorless oil, and product **3i'** was not detected.



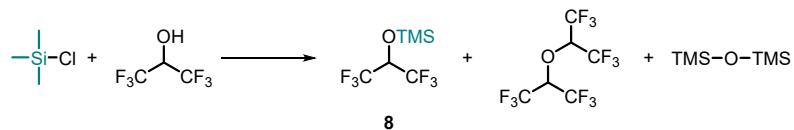
Under an ambient atmosphere, **2d** (0.34 g, 1.5 mmol) was added to a Schlenk tube equipped with a polytetrafluoroethylene-coated magnetic stir bar, and the reaction system was placed in an ice-water bath. Then 3 mL reaction solvent (HFIP, 2 mL and DCM, 1 mL) was added to the system until it was completely dissolved, followed by the addition of **1r** (0.05 g, 0.3 mmol). The reaction system was stirred at 0 °C for 3 hours, and then Cu(OTf)2 (0.01 g, 0.03 mmol) was added to the system to continue the reaction for 15 minutes. After the reaction was completed, 20 mL of CH2Cl2 was added to the reaction mixture. The organic layer was extracted with saturated aqueous NaHCO3 solution (3 × 20 mL). The combined organic layers were dried with anhydrous Na2SO4 and filtered and solvent was removed under reduced pressure. The resulting crude product was purified by column chromatography on silica gel using petroleum ether : ethyl acetate = 80 : 1 as eluent to afford the product **3r** in the yield of 96% as a colorless oil, and product **3r'** was not detected.

ether : ethyl acetate = 80 : 1 as eluent to afford the product **3r** in the yield of 96% as a colorless oil, and product **3r'** was not detected.

NMR monitoring of product **8**:



**Figure S3.** The NMR comparison diagram of product **8**

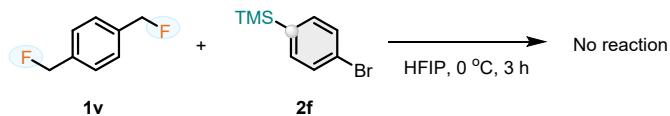


Under an ambient atmosphere, HFIP (0.17 g, 1 mmol) was added to a Schlenk tube equipped with a polytetrafluoroethylene-coated magnetic stir bar. Then add trimethylchlorosilane (0.11 g, 1 mmol). The reaction system was stirred at room temperature for 6 hours. After the reaction was completed, the solvent was dried and evaporated at low temperature, and the product **8** was generated by nuclear magnetic monitoring.

NMR data of product **8**:

**((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)trimethylsilane (8)<sup>9</sup>**, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 4.32 - 4.23 (m, 1H), 0.23 (s, 9H).

## 4.5 Interaction between hexafluoroisopropanol and benzyl fluoride

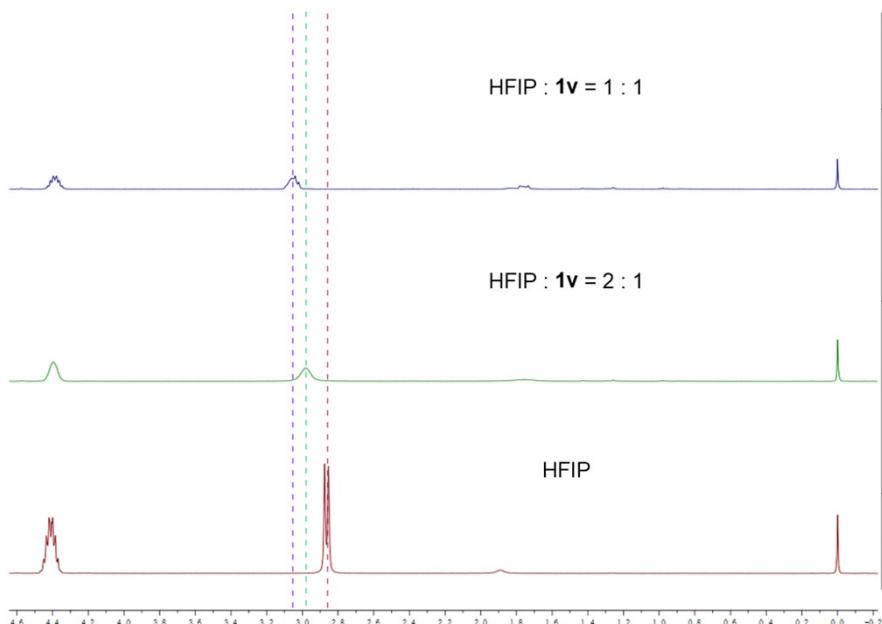


**Table S6:** NMR titration of **1v** and HFIP:

|                  | V <sub>(1v (μL))</sub> | V <sub>(HFIP(μL))</sub> |
|------------------|------------------------|-------------------------|
| <b>1v</b>        | 10                     | 0                       |
| HFIP             | 0                      | 10                      |
| <b>1v</b> : HFIP | 0.0121                 | 0.0105                  |
| <b>1v</b> : HFIP | 0.0121                 | 0.0211                  |

HFIP and  $\text{CDCl}_3$  were purchased commercially, **1v** was prepared according to the literature report. Four  $^1\text{H}$  NMR samples of 1 M stock solutions of HFIP and **1v** were prepared in 0.50 mL of  $\text{CDCl}_3$ , where the ratios of HFIP and **1v** are 1:1 and 2:1.

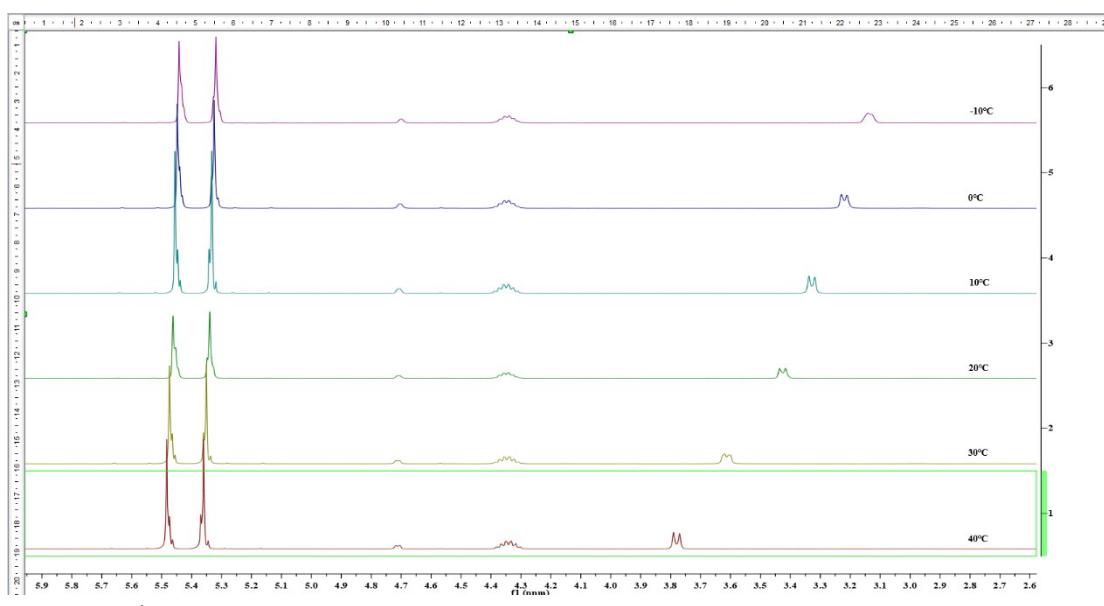
In order to evaluate the interaction between HFIP and **1v** (Table S6), HFIP was titrated with **1v** and the process was monitored by  $^1\text{H}$  NMR (Figure S4). An obviously downfield shift of the hydrogen of the OH moiety in HFIP was observed when HFIP was mixed with **1v**, indicating that the existence of hydrogen bonding interaction between HFIP and benzyl fluoride.



**Figure S4.** Comparison of **1v** and HFIP NMR titration spectra

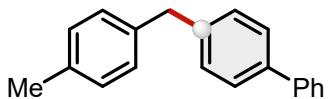
In the atmospheric atmosphere, mix HFIP (0.5 mmol) and **1v** (0.5 mmol) in a molar

ratio of 1:1 to the sample. After mixing evenly, 13  $\mu$ L of the mixed sample was taken with a pipette and transferred to a nuclear magnetic tube, and 0.6 mL of  $\text{CDCl}_3$  was added for later use. The nuclear magnetic tubes were placed in a low-temperature nuclear magnetic field, and nuclear magnetic monitoring was performed at different temperatures of -10 °C, 0 °C, 10 °C, 20 °C, 30 °C and 40 °C. It is evident that the chemical shift of the H proton at the benzyl position of **1v** (the rightmost peak in **Figure S5**) exhibits a continuous variation with changing temperature, indicating that an intermolecular interaction between the benzyl fluoride and the HFIP mediated by F–H bonding.

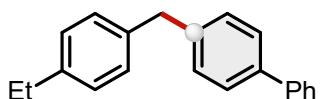


**Figure S5.**  $^1\text{H}$ -NMR experiments of the interaction between HFIP and **1v** at different temperatures.

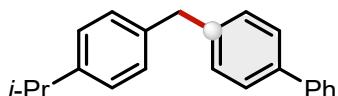
## 5. Characterization data of the products



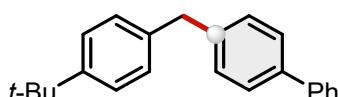
**4-(4-methylbenzyl)-1,1'-biphenyl (3a)**<sup>10</sup>, white solid; 99% yield; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.54 (d, *J* = 7.6 Hz, 2H), 7.49 (d, *J* = 6.8 Hz, 2H), 7.39 (t, *J* = 7.0 Hz, 2H), 7.29 (t, *J* = 7.2 Hz, 1H), 7.23 (d, *J* = 7.4 Hz, 2H), 7.09 (s, 4H), 3.96 (s, 2H), 2.30 (s, 3H); **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 141.00, 140.53, 138.91, 137.93, 135.58, 129.22, 129.18, 128.81, 128.68, 127.15, 127.01, 126.97, 41.13, 21.00; **HRMS** (APCI) m/z calculated C<sub>20</sub>H<sub>17</sub><sup>−</sup> [M-H]<sup>−</sup> 257.1325, found 257.1338.



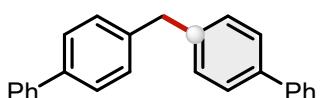
**4-(4-ethylbenzyl)-1,1'-biphenyl (3b)**, white solid; 87% yield; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.54 (d, *J* = 7.6 Hz, 2H), 7.49 (d, *J* = 7.8 Hz, 2H), 7.38 (t, *J* = 6.8 Hz, 2H), 7.29 (d, *J* = 6.4 Hz, 1H), 7.23 (d, *J* = 6.6 Hz, 2H), 7.12 (s, 4H), 3.96 (s, 2H), 2.60 (q, *J* = 7.6 Hz, 2H), 1.21 (t, *J* = 7.6 Hz, 3H); **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 141.99, 141.01, 140.49, 138.92, 138.18, 129.26, 128.84, 128.68, 127.97, 127.15, 127.01, 126.97, 41.17, 28.43, 15.60; **HRMS** (APCI) m/z calculated C<sub>21</sub>H<sub>19</sub><sup>−</sup> [M-H]<sup>−</sup> 271.1481, found 271.1496.



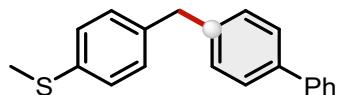
**4-(4-isopropylbenzyl)-1,1'-biphenyl (3c)**, colorless oil; 98% yield; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.55 (d, *J* = 7.6 Hz, 2H), 7.50 (d, *J* = 7.8 Hz, 2H), 7.39 (t, *J* = 6.8 Hz, 2H), 7.30 (d, *J* = 6.4 Hz, 1H), 7.25 (d, *J* = 6.6 Hz, 2H), 7.14 (s, 4H), 3.97 (s, 2H), 2.90 - 2.83 (m, 1H), 1.22 (d, *J* = 6.8 Hz, 6H); **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 146.63, 141.03, 140.46, 138.94, 138.31, 129.30, 128.80, 128.68, 127.16, 127.01, 126.98, 126.53, 41.17, 33.68, 24.03; **HRMS** (APCI) m/z calculated C<sub>22</sub>H<sub>21</sub><sup>−</sup> [M-H]<sup>−</sup> 285.1638, found 285.1654.



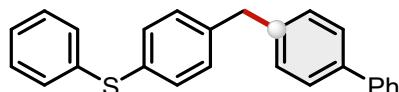
**4-(4-(tert-butyl)benzyl)-1,1'-biphenyl (3d)**<sup>10</sup>, colorless oil; 98% yield; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.56 (d, *J* = 7.4 Hz, 2H), 7.50 (d, *J* = 8.2 Hz, 2H), 7.40 (t, *J* = 7.6 Hz, 2H), 7.33 - 7.25 (m, 5H), 7.15 (d, *J* = 8.2 Hz, 2H), 3.98 (s, 2H), 1.30 (d, *J* = 2.6 Hz, 9H); **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 148.88, 141.01, 140.39, 138.93, 137.94, 129.32, 128.69, 128.51, 127.16, 127.02, 126.98, 125.39, 41.05, 34.35, 31.38; **HRMS** (APCI) m/z calculated C<sub>23</sub>H<sub>23</sub><sup>−</sup> [M-H]<sup>−</sup> 299.1794, found 299.1810.



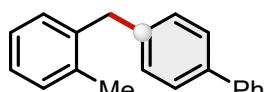
**di([1,1'-biphenyl]-4-yl)methane (3e)**<sup>10</sup>, brown solid; 97% yield; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.57 (d, *J* = 6.4 Hz, 4H), 7.53 (d, *J* = 7.6 Hz, 4H), 7.41 (t, *J* = 7.2 Hz, 4H), 7.30 (t, *J* = 9.6 Hz, 6H), 4.05 (s, 2H); **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 140.96, 140.11, 139.11, 133.78, 129.33, 129.02, 128.71, 127.26, 127.08, 127.00, 126.34, 41.22; **HRMS** (APCI) m/z calculated C<sub>25</sub>H<sub>19</sub><sup>-</sup> [M-H]<sup>-</sup> 319.1481, found 319.1498.



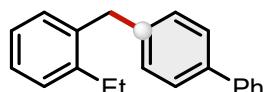
**(4-([1,1'-biphenyl]-4-ylmethyl)phenyl)(methyl)sulfane (3f)**, white solid; 53% yield; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.55 (d, *J* = 7.8 Hz, 2H), 7.49 (d, *J* = 6.8 Hz, 2H), 7.39 (t, *J* = 7.2 Hz, 2H), 7.30 (t, *J* = 7.2 Hz, 1H), 7.23 - 7.18 (m, 4H), 7.13 (d, *J* = 7.8 Hz, 2H), 3.95 (s, 2H), 2.43 (s, 3H); **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 140.87, 140.05, 139.03, 138.00, 135.81, 129.42, 129.20, 128.68, 127.17, 127.07, 126.94, 40.95, 16.11; **HRMS** (APCI) m/z calculated C<sub>20</sub>H<sub>17</sub>S<sup>-</sup> [M-H]<sup>-</sup> 289.1045, found 289.1061.



**(4-([1,1'-biphenyl]-4-ylmethyl)phenyl)(phenyl)sulfane (3g)**, white solid; 42% yield; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.56 (d, *J* = 7.6 Hz, 2H), 7.52 (d, *J* = 6.4 Hz, 2H), 7.42 (t, *J* = 6.8 Hz, 2H), 7.35 - 7.20 (m, 10H), 7.17 (d, *J* = 8.0 Hz, 2H), 3.99 (s, 2H); **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 140.90, 140.34, 139.73, 139.21, 136.29, 132.87, 131.71, 130.52, 129.82, 129.31, 129.11, 128.72, 127.27, 127.12, 127.00, 126.77, 41.14; **HRMS** (APCI) m/z calculated C<sub>25</sub>H<sub>19</sub>S<sup>-</sup> [M-H]<sup>-</sup> 351.1202, found 351.1217.

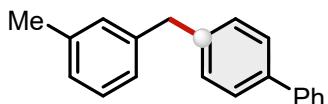


**4-(2-methylbenzyl)-1,1'-biphenyl (3h)**<sup>11</sup>, colorless oil; 70% yield; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.56 (d, *J* = 7.6 Hz, 2H), 7.49 (d, *J* = 6.4 Hz, 2H), 7.41 (t, *J* = 7.6 Hz, 2H), 7.31 (t, *J* = 7.4 Hz, 1H), 7.19 - 7.15 (m, 6H), 4.02 (s, 2H), 2.27 (s, 3H); **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 140.99, 139.51, 138.86, 138.80, 136.63, 130.32, 129.95, 129.11, 128.70, 127.10, 127.03, 126.97, 126.51, 126.03, 39.08, 19.70; **HRMS** (APCI) m/z calculated C<sub>20</sub>H<sub>17</sub><sup>-</sup> [M-H]<sup>-</sup> 257.1325, found 257.1338.

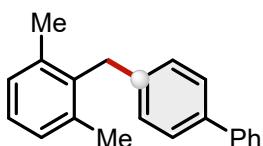


**4-(2-ethylbenzyl)-1,1'-biphenyl (3i)**, colorless oil; 68% yield; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.56 (d, *J* = 7.2 Hz, 2H), 7.49 (d, *J* = 7.6 Hz, 2H), 7.41 (t, *J* = 7.2 Hz, 2H), 7.34 - 7.29 (m, 1H), 7.22 - 7.14 (m, 6H), 4.06 (s, 2H), 2.64 (q, *J* = 7.6 Hz, 2H), 1.17 (t, *J* = 7.4 Hz, 3H); **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 142.42, 140.97, 140.04, 138.82, 138.04, 130.31, 129.09, 128.69, 128.45, 127.07, 127.03, 126.96, 126.70, 125.92, 38.37,

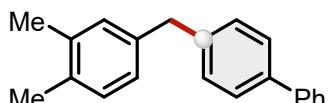
25.74, 14.83; **HRMS** (APCI)  $m/z$  calculated  $C_{21}H_{19}^-$  [M-H] $^-$  271.1481, found 271.1496.



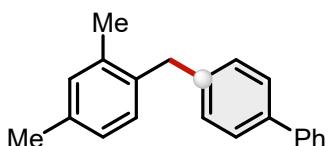
**4-(3-methylbenzyl)-1,1'-biphenyl (3j)**<sup>12</sup>, colorless oil; 48% yield; **<sup>1</sup>H NMR** (400 MHz,  $CDCl_3$ )  $\delta$  7.57 (d,  $J$  = 7.6 Hz, 2H), 7.51 (d,  $J$  = 7.2 Hz, 2H), 7.41 (t,  $J$  = 7.4 Hz, 2H), 7.32 (d,  $J$  = 7.2 Hz, 1H), 7.25 (d,  $J$  = 8.0 Hz, 2H), 7.19 (t,  $J$  = 7.4 Hz, 1H), 7.03 (d,  $J$  = 8.6 Hz, 3H), 3.98 (s, 2H), 2.32 (s, 3H); **<sup>13</sup>C NMR** (101 MHz,  $CDCl_3$ )  $\delta$  141.01, 140.90, 140.37, 138.96, 138.10, 129.72, 129.28, 128.70, 128.39, 127.18, 127.04, 126.99, 126.89, 125.98, 41.52, 21.41; **HRMS** (APCI)  $m/z$  calculated  $C_{20}H_{17}^-$  [M-H] $^-$  257.1325, found 257.1338. **HRMS** (APCI)  $m/z$  calculated  $C_{20}H_{17}^-$  [M-H] $^-$  257.1325, found 257.1338.



**4-(2,6-dimethylbenzyl)-1,1'-biphenyl (3k)**<sup>13</sup>, white solid; 90% yield; **<sup>1</sup>H NMR** (400 MHz,  $CDCl_3$ )  $\delta$  7.55 (d,  $J$  = 7.6 Hz, 2H), 7.46 (d,  $J$  = 6.8 Hz, 2H), 7.41 (t,  $J$  = 6.8 Hz, 2H), 7.31 (t,  $J$  = 7.2 Hz, 1H), 7.08 (d,  $J$  = 7.2 Hz, 5H), 4.10 (s, 2H), 2.28 (s, 6H); **<sup>13</sup>C NMR** (101 MHz,  $CDCl_3$ )  $\delta$  141.00, 138.91, 138.70, 137.16, 136.77, 128.68, 128.25, 128.14, 127.09, 126.99, 126.94, 126.36, 34.70, 20.26; **HRMS** (APCI)  $m/z$  calculated  $C_{21}H_{19}^-$  [M-H] $^-$  271.1481, found 271.1495.

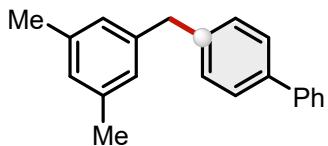


**4-(3,4-dimethylbenzyl)-1,1'-biphenyl (3l)**, white solid; 77% yield; **<sup>1</sup>H NMR** (400 MHz,  $CDCl_3$ )  $\delta$  7.56 (d,  $J$  = 7.8 Hz, 2H), 7.50 (d,  $J$  = 7.8 Hz, 2H), 7.41 (t,  $J$  = 7.6 Hz, 2H), 7.31 (d,  $J$  = 6.2 Hz, 1H), 7.26 - 7.22 (m, 2H), 7.06 (d,  $J$  = 6.6 Hz, 1H), 7.00 (s, 1H), 6.96 (s, 1H), 3.94 (s, 2H), 2.23 (s, 6H); **<sup>13</sup>C NMR** (101 MHz,  $CDCl_3$ )  $\delta$  141.06, 140.66, 138.89, 138.41, 136.62, 134.26, 130.25, 129.74, 129.22, 128.68, 127.16, 126.99, 126.29, 41.16, 19.76, 19.31; **HRMS** (APCI)  $m/z$  calculated  $C_{21}H_{19}^-$  [M-H] $^-$  271.1481, found 271.1495.

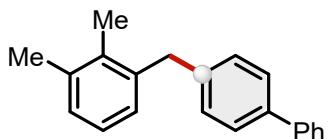


**4-(2,4-dimethylbenzyl)-1,1'-biphenyl (3m)**<sup>14</sup>, white solid; 72% yield; **<sup>1</sup>H NMR** (400 MHz,  $CDCl_3$ )  $\delta$  7.55 (d,  $J$  = 7.8 Hz, 2H), 7.48 (d,  $J$  = 7.2 Hz, 2H), 7.39 (t,  $J$  = 7.4 Hz, 2H), 7.29 (t,  $J$  = 7.2 Hz, 1H), 7.17 (d,  $J$  = 7.2 Hz, 2H), 7.03 - 6.96 (m, 3H), 3.97 (s, 2H), 2.30 (s, 3H), 2.22 (s, 3H); **<sup>13</sup>C NMR** (101 MHz,  $CDCl_3$ )  $\delta$  141.02, 139.82, 138.76,

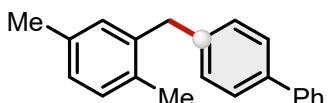
136.39, 135.95, 135.74, 131.15, 129.90, 129.04, 128.68, 127.07, 126.99, 126.95, 126.64, 38.67, 20.94, 19.61; **HRMS** (APCI)  $m/z$  calculated  $C_{21}H_{19}^-$  [M-H] $^-$  271.1481, found 271.1495.



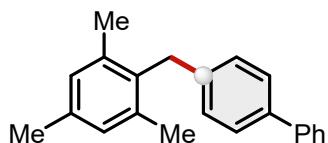
**4-(3,5-dimethylbenzyl)-1,1'-biphenyl (3n)**<sup>14</sup>, white solid; 71% yield;  **$^1H$  NMR** (400 MHz,  $CDCl_3$ )  $\delta$  7.56 (d,  $J$  = 7.8 Hz, 2H), 7.50 (d,  $J$  = 7.2 Hz, 2H), 7.40 (t,  $J$  = 7.6 Hz, 2H), 7.31 (d,  $J$  = 7.4 Hz, 1H), 7.25 (d,  $J$  = 7.2 Hz, 2H), 6.84 (s, 3H), 3.93 (s, 2H), 2.28 (s, 6H);  **$^{13}C$  NMR** (101 MHz,  $CDCl_3$ )  $\delta$  141.03, 140.84, 140.49, 138.90, 137.98, 129.26, 128.69, 127.79, 127.15, 127.01, 126.98, 126.78, 41.46, 21.27; **HRMS** (APCI)  $m/z$  calculated  $C_{21}H_{19}^-$  [M-H] $^-$  271.1481, found 271.1495.



**4-(2,3-dimethylbenzyl)-1,1'-biphenyl (3o)**<sup>14</sup>, white solid; 88% yield;  **$^1H$  NMR** (400 MHz,  $CDCl_3$ )  $\delta$  7.55 (d,  $J$  = 7.8 Hz, 2H), 7.48 (d,  $J$  = 6.8 Hz, 2H), 7.40 (t,  $J$  = 7.0 Hz, 2H), 7.30 (t,  $J$  = 7.2 Hz, 1H), 7.17 (d,  $J$  = 7.2 Hz, 2H), 7.07 - 7.02 (m, 3H), 4.04 (s, 2H), 2.29 (s, 3H), 2.16 (s, 3H);  **$^{13}C$  NMR** (101 MHz,  $CDCl_3$ )  $\delta$  141.01, 139.91, 138.77, 138.58, 137.04, 135.21, 129.00, 128.68, 128.30, 128.08, 127.07, 127.00, 126.96, 125.45, 39.68, 20.69, 15.44; **HRMS** (APCI)  $m/z$  calculated  $C_{21}H_{19}^-$  [M-H] $^-$  271.1481, found 271.1495.

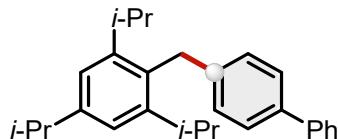


**4-(2,5-dimethylbenzyl)-1,1'-biphenyl (3p)**, white solid; 99% yield;  **$^1H$  NMR** (400 MHz,  $CDCl_3$ )  $\delta$  7.56 (d,  $J$  = 7.6 Hz, 2H), 7.49 (d,  $J$  = 6.6 Hz, 2H), 7.41 (t,  $J$  = 7.2 Hz, 2H), 7.31 (t,  $J$  = 7.2 Hz, 1H), 7.18 (d,  $J$  = 7.2 Hz, 2H), 7.06 (d,  $J$  = 7.2 Hz, 1H), 6.97 (d,  $J$  = 6.6 Hz, 2H), 3.98 (s, 2H), 2.30 (s, 3H), 2.22 (s, 3H);  **$^{13}C$  NMR** (101 MHz,  $CDCl_3$ )  $\delta$  141.01, 139.67, 138.78, 138.55, 135.43, 133.44, 130.76, 130.22, 129.07, 128.69, 127.15, 127.08, 127.02, 126.97, 39.05, 20.98, 19.23; **HRMS** (APCI)  $m/z$  calculated  $C_{21}H_{19}^-$  [M-H] $^-$  271.1481, found 271.1495.

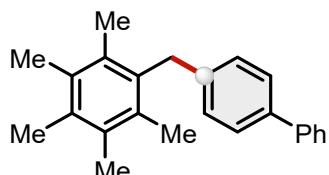


**4-(2,4,6-trimethylbenzyl)-1,1'-biphenyl (3q)**<sup>11</sup>, white solid; 97% yield;  **$^1H$  NMR** (400 MHz,  $CDCl_3$ )  $\delta$  7.53 (d,  $J$  = 7.8 Hz, 2H), 7.44 (d,  $J$  = 7.2 Hz, 2H), 7.38 (t,  $J$  = 7.4 Hz,

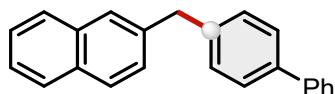
2H), 7.28 (t,  $J$  = 7.0 Hz, 1H), 7.06 (d,  $J$  = 7.6 Hz, 2H), 6.89 (s, 2H), 4.04 (s, 2H), 2.29 (s, 3H), 2.22 (s, 6H);  **$^{13}\text{C}$  NMR** (101 MHz,  $\text{CDCl}_3$ )  $\delta$  141.03, 139.22, 138.61, 136.98, 135.69, 133.67, 128.91, 128.66, 128.23, 127.05, 126.92, 34.35, 20.90, 20.15; **HRMS** (APCI) m/z calculated  $\text{C}_{22}\text{H}_{21}^-$  [M-H]<sup>-</sup> 285.1649, found 285.1651.



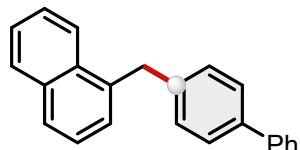
**4-(2,4,6-triisopropylbenzyl)-1,1'-biphenyl (3r)**, colorless oil; 96% yield;  **$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.55 (d,  $J$  = 7.2 Hz, 2H), 7.47 (d,  $J$  = 7.6 Hz, 2H), 7.38 (t,  $J$  = 7.2 Hz, 2H), 7.28 (d,  $J$  = 6.8 Hz, 1H), 7.09 - 7.06 (m, 4H), 4.15 (s, 2H), 3.13 - 3.02 (m, 2H), 2.95 - 2.90 (m, 1H), 1.29 (d,  $J$  = 6.6 Hz, 6H), 1.16 (d,  $J$  = 6.2 Hz, 12H);  **$^{13}\text{C}$  NMR** (101 MHz,  $\text{CDCl}_3$ )  $\delta$  147.40, 147.03, 141.01, 140.64, 138.46, 130.58, 128.67, 128.32, 126.92, 126.90, 121.04, 34.17, 32.69, 29.65, 24.11, 24.22; **HRMS** (APCI) m/z calculated  $\text{C}_{28}\text{H}_{33}^-$  [M-H]<sup>-</sup> 369.2588, found 369.2593.



**4-(2,3,4,5,6-pentamethylbenzyl)-1,1'-biphenyl (3s)**, white solid; 95% yield;  **$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.54 (d,  $J$  = 7.6 Hz, 2H), 7.45 (d,  $J$  = 7.8 Hz, 2H), 7.39 (t,  $J$  = 7.4 Hz, 2H), 7.29 (t,  $J$  = 6.8 Hz, 1H), 7.10 (d,  $J$  = 7.6 Hz, 2H), 4.14 (s, 2H), 2.28 (s, 3H), 2.25 (s, 6H), 2.20 (s, 6H);  **$^{13}\text{C}$  NMR** (101 MHz,  $\text{CDCl}_3$ )  $\delta$  141.08, 139.75, 138.52, 133.69, 133.17, 132.77, 132.52, 128.65, 128.33, 127.04, 126.93, 35.80, 16.96, 16.88; **HRMS** (APCI) m/z calculated  $\text{C}_{24}\text{H}_{25}^-$  [M-H]<sup>-</sup> 313.1962, found 313.1963.

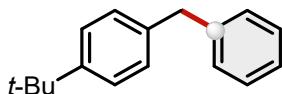


**2-([1,1'-biphenyl]-4-ylmethyl)naphthalene (3t)**<sup>11</sup>, white solid; 69% yield;  **$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.78 (t,  $J$  = 8.6 Hz, 3H), 7.66 (s, 1H), 7.56 (d,  $J$  = 7.6 Hz, 2H), 7.52 (d,  $J$  = 6.8 Hz, 2H), 7.46 - 7.39 (m, 4H), 7.35 - 7.28 (m, 4H), 4.17 (s, 2H);  **$^{13}\text{C}$  NMR** (101 MHz,  $\text{CDCl}_3$ )  $\delta$  140.95, 140.09, 139.10, 138.46, 133.61, 132.10, 129.40, 128.71, 128.14, 127.62, 127.55, 127.22, 127.13, 127.08, 127.00, 126.00, 125.38, 41.73; **HRMS** (APCI) m/z calculated  $\text{C}_{23}\text{H}_{17}^-$  [M-H]<sup>-</sup> 293.1336, found 293.1339.

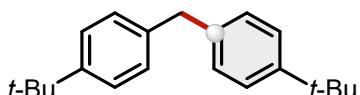


**1-([1,1'-biphenyl]-4-ylmethyl)naphthalene (3u)**<sup>11</sup>, white solid; 64% yield;  **$^1\text{H}$  NMR**

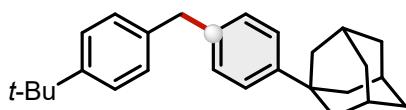
(400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.05 - 7.99 (m, 1H), 7.90 - 7.82 (m, 1H), 7.77 (d,  $J = 8.2$  Hz, 1H), 7.54 (d,  $J = 7.6$  Hz, 2H), 7.49 - 7.37 (m, 7H), 7.34 - 7.29 (m, 2H), 7.25 (d,  $J = 7.2$  Hz, 2H), 4.48 (s, 2H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  140.94, 139.74, 138.97, 136.49, 133.94, 132.12, 129.09, 128.69, 127.36, 127.21, 127.16, 127.04, 126.96, 126.00, 125.57, 124.27, 38.68; HRMS (APCI) m/z calculated  $\text{C}_{23}\text{H}_{17}^-$  [M-H]<sup>-</sup> 293.1336, found 293.1339.



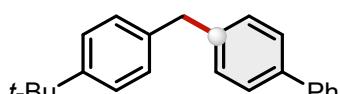
**1-benzyl-4-(*tert*-butyl)benzene (**4a**)**<sup>15</sup>, colorless oil; 94% yield;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.31 - 7.26 (m, 4H), 7.23 - 7.16 (m, 3H), 7.12 (d,  $J = 8.2$  Hz, 2H), 3.95 (s, 2H), 1.30 (s, 9H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  148.79, 141.25, 138.05, 128.94, 128.47, 128.40, 125.97, 125.32, 41.40, 34.34, 31.37; HRMS (APCI) m/z calculated  $\text{C}_{17}\text{H}_{19}^-$  [M-H]<sup>-</sup> 223.1481, found 223.1482.



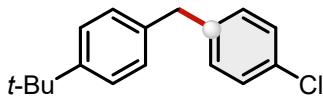
**bis(4-(*tert*-butyl)phenyl)methane (**4b**)**<sup>11</sup>, white solid; 78% yield;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.30 (d,  $J = 8.2$  Hz, 4H), 7.13 (d,  $J = 8.2$  Hz, 4H), 3.92 (s, 2H), 1.30 (s, 18H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  148.70, 138.23, 128.51, 125.30, 40.89, 34.34, 31.39; HRMS (APCI) m/z calculated  $\text{C}_{21}\text{H}_{27}^-$  [M-H]<sup>-</sup> 279.2118, found 279.2122.



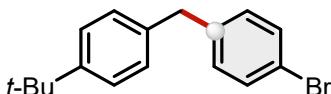
**1-(4-(*tert*-butyl)benzyl)phenyladamantane (**4c**)**, white solid; 66% yield;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.28 (t,  $J = 9.4$  Hz, 4H), 7.14 (d,  $J = 6.6$  Hz, 4H), 3.91 (s, 2H), 2.07 (s, 3H), 1.89 (s, 6H), 1.75 (s, 6H), 1.29 (s, 9H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  149.00, 148.68, 138.29, 138.26, 128.56, 128.52, 125.28, 124.86, 43.22, 40.95, 36.81, 35.86, 34.33, 31.39, 28.96; HRMS (APCI) m/z calculated  $\text{C}_{27}\text{H}_{33}^-$  [M-H]<sup>-</sup> 357.2588, found 357.2589.



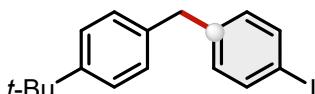
**4-(4-(*tert*-butyl)benzyl)-1,1'-biphenyl (**4d**)**<sup>10</sup>, colorless oil; 98% yield;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.56 (d,  $J = 7.4$  Hz, 2H), 7.50 (d,  $J = 8.2$  Hz, 2H), 7.40 (t,  $J = 7.6$  Hz, 2H), 7.33 - 7.25 (m, 5H), 7.15 (d,  $J = 8.2$  Hz, 2H), 3.98 (s, 2H), 1.30 (s, 9H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  148.88, 141.01, 140.39, 138.93, 137.94, 129.32, 128.69, 128.51, 127.16, 127.02, 126.98, 125.39, 41.05, 34.35, 31.38; HRMS (APCI) m/z calculated  $\text{C}_{23}\text{H}_{23}^-$  [M-H]<sup>-</sup> 299.1794, found 299.1810.



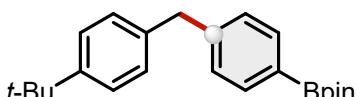
**1-(*tert*-butyl)-4-(4-chlorobenzyl)benzene (4e)<sup>16</sup>**, colorless oil; 84% yield; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.30 (d, *J* = 8.2 Hz, 2H), 7.23 (d, *J* = 8.2 Hz, 2H), 7.14 - 7.05 (m, 4H), 3.90 (s, 2H), 1.29 (s, 9H); **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 149.06, 139.72, 137.48, 131.76, 130.26, 128.49, 128.41, 125.43, 40.70, 34.36, 31.35; **HRMS** (APCI) m/z calculated C<sub>17</sub>H<sub>18</sub>Cl<sup>+</sup> [M-H]<sup>-</sup> 257.1102, found 257.1106.



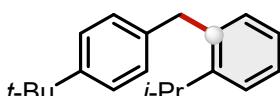
**1-bromo-4-(4-(*tert*-butyl)benzyl)benzene (4f)<sup>16</sup>**, colorless oil; 92% yield; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.38 (d, *J* = 6.8 Hz, 2H), 7.30 (d, *J* = 6.4 Hz, 2H), 7.06 (t, *J* = 8.8 Hz, 4H), 3.88 (s, 2H), 1.30 (s, 9H); **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 149.05, 140.22, 137.36, 131.43, 130.66, 128.41, 125.42, 119.81, 40.75, 34.34, 31.35; **HRMS** (APCI) m/z calculated C<sub>17</sub>H<sub>18</sub>Br<sup>+</sup> [M-H]<sup>-</sup> 301.0597, found 301.0601.



**1-(*tert*-butyl)-4-(4-iodobenzyl)benzene (4g)<sup>16</sup>**, yellow oil; 61% yield; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.59 (d, *J* = 8.2 Hz, 2H), 7.30 (d, *J* = 8.2 Hz, 2H), 7.08 (d, *J* = 8.2 Hz, 2H), 6.95 (d, *J* = 8.2 Hz, 2H), 3.88 (s, 2H), 1.30 (s, 9H); **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 149.11, 140.95, 137.44, 137.34, 131.03, 128.42, 125.44, 91.19, 40.88, 34.37, 31.35; **HRMS** (APCI) m/z calculated C<sub>17</sub>H<sub>18</sub>I<sup>+</sup> [M-H]<sup>-</sup> 349.0459, found 349.0449.

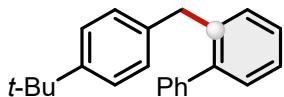


**2-(4-(*tert*-butyl)benzyl)phenyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4h)**, white solid; 46% yield; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.74 (d, *J* = 7.8 Hz, 2H), 7.28 (d, *J* = 8.2 Hz, 2H), 7.22 (d, *J* = 7.8 Hz, 2H), 7.09 (d, *J* = 8.2 Hz, 2H), 3.95 (s, 2H), 1.32 (s, 12H), 1.29 (s, 9H); **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 148.83, 144.57, 137.84, 134.98, 128.44, 125.32, 83.62, 41.63, 34.33, 31.36, 24.83; **HRMS** (APCI) m/z calculated C<sub>23</sub>H<sub>32</sub>BO<sub>2</sub><sup>+</sup> [M+H]<sup>+</sup> 350.2526, found 350.2523.

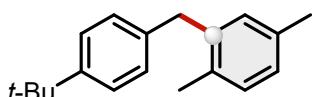


**1-(4-(*tert*-butyl)benzyl)-2-isopropylbenzene (4i)<sup>16</sup>**, colorless oil; 91% yield; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.29 (d, *J* = 7.4 Hz, 2H), 7.13 (s, 6H), 3.91 (s, 2H), 2.96 - 2.77 (m, 1H), 1.29 (s, 9H), 1.22 (d, *J* = 6.2 Hz, 6H); **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 148.70, 146.45, 138.61, 138.30, 128.80, 128.49, 126.44, 125.29, 41.02, 34.34, 33.68, 31.40,

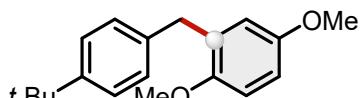
24.05; **HRMS** (APCI)  $m/z$  calculated  $C_{20}H_{27}^+ [M+H]^+$  267.2107, found 267.2109.



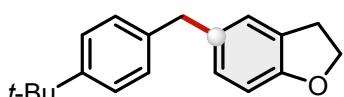
**2-(4-(*tert*-butyl)benzyl)-1,1'-biphenyl (4j)**<sup>16</sup>, yellow solid; 93% yield; **<sup>1</sup>H NMR** (400 MHz,  $CDCl_3$ )  $\delta$  7.57 (d,  $J$  = 7.4 Hz, 2H), 7.51 (d,  $J$  = 8.0 Hz, 2H), 7.41 (t,  $J$  = 7.6 Hz, 2H), 7.33 - 7.24 (m, 5H), 7.16 (d,  $J$  = 8.2 Hz, 2H), 3.99 (s, 2H), 1.31 (s, 9H); **<sup>13</sup>C NMR** (101 MHz,  $CDCl_3$ )  $\delta$  148.91, 141.03, 140.41, 138.95, 137.95, 129.33, 128.69, 128.51, 127.17, 127.02, 126.99, 125.40, 41.06, 34.37, 31.38; **HRMS** (APCI)  $m/z$  calculated  $C_{23}H_{23}^- [M-H]^-$  299.1794, found 299.1810.



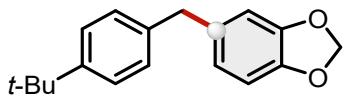
**2-(4-(*tert*-butyl)benzyl)-1,4-dimethylbenzene (4k)**<sup>17</sup>, colorless oil; 79% yield; **<sup>1</sup>H NMR** (400 MHz,  $CDCl_3$ )  $\delta$  7.28 (d,  $J$  = 7.4 Hz, 2H), 7.04 (d,  $J$  = 7.4 Hz, 3H), 6.95 (s, 2H), 3.91 (s, 2H), 2.28 (s, 3H), 2.20 (s, 3H), 1.29 (s, 9H); **<sup>13</sup>C NMR** (101 MHz,  $CDCl_3$ )  $\delta$  148.56, 138.84, 137.42, 135.31, 133.39, 130.75, 130.13, 128.24, 126.99, 125.21, 38.82, 34.31, 31.38, 20.98, 19.23; **HRMS** (APCI)  $m/z$  calculated  $C_{19}H_{23}^- [M-H]^-$  251.1805, found 251.1806.



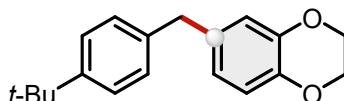
**2-(4-(*tert*-butyl)benzyl)-1,4-dimethoxybenzene (4l)**<sup>18</sup>, colorless oil; 82% yield; **<sup>1</sup>H NMR** (400 MHz,  $CDCl_3$ )  $\delta$  7.28 (d,  $J$  = 7.6 Hz, 2H), 7.14 (d,  $J$  = 7.8 Hz, 2H), 6.79 (d,  $J$  = 8.6 Hz, 1H), 6.71 - 6.67 (m, 2H), 3.91 (s, 2H), 3.78 (s, 3H), 3.72 (s, 3H), 1.29 (s, 9H); **<sup>13</sup>C NMR** (101 MHz,  $CDCl_3$ )  $\delta$  153.48, 151.68, 148.54, 137.60, 131.15, 128.54, 125.19, 116.91, 111.34, 111.02, 56.04, 55.61, 35.33, 34.32, 31.40; **HRMS** (APCI)  $m/z$  calculated  $C_{19}H_{23}O_2^- [M-H]^-$  283.1693, found 283.1693.



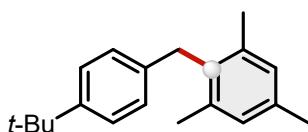
**5-(4-(*tert*-butyl)benzyl)-2,3-dihydrobenzofuran (4m)**, colorless oil; 47% yield; **<sup>1</sup>H NMR** (400 MHz,  $CDCl_3$ )  $\delta$  7.30 (d,  $J$  = 7.2 Hz, 2H), 7.11 (d,  $J$  = 7.6 Hz, 2H), 7.02 (s, 1H), 6.94 (d,  $J$  = 8.2 Hz, 1H), 6.70 (d,  $J$  = 8.0 Hz, 1H), 4.53 (t,  $J$  = 8.2 Hz, 2H), 3.87 (s, 2H), 3.16 (t,  $J$  = 8.6 Hz, 2H), 1.30 (s, 9H); **<sup>13</sup>C NMR** (101 MHz,  $CDCl_3$ )  $\delta$  158.40, 148.71, 138.76, 133.30, 128.37, 128.32, 127.12, 125.41, 125.31, 108.96, 71.15, 40.81, 34.34, 31.39, 29.80; **HRMS** (APCI)  $m/z$  calculated  $C_{19}H_{21}O^- [M-H]^-$  265.1587, found 265.1587.



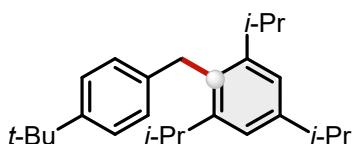
**5-(4-(*tert*-butyl)benzyl)benzo-[1,3]dioxole (4n)**, colorless oil; 63% yield; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.30 (d, *J* = 6.8 Hz, 2H), 7.10 (d, *J* = 7.2 Hz, 2H), 6.73 (d, *J* = 8.2 Hz, 1H), 6.66 (s, 2H), 5.89 (s, 2H), 3.85 (s, 2H), 1.29 (s, 9H); **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 148.87, 147.63, 145.77, 138.19, 135.17, 128.35, 125.35, 121.69, 109.43, 108.11, 100.77, 41.08, 34.35, 31.37; **HRMS** (APCI) m/z calculated C<sub>18</sub>H<sub>19</sub>O<sub>2</sub><sup>+</sup> [M-H]<sup>-</sup> 267.1390, found 267.1393.



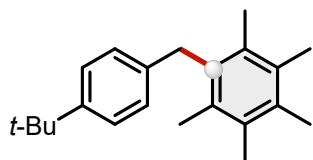
**6-(4-(*tert*-butyl)benzyl)-2,3-dihydrobenzo-[1,4]dioxine (4o)**, colorless oil; 42% yield; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.29 (d, *J* = 6.8 Hz, 2H), 7.11 (d, *J* = 6.8 Hz, 2H), 6.77 (d, *J* = 8.0 Hz, 1H), 6.67 (d, *J* = 10.2 Hz, 2H), 4.22 (s, 4H), 3.83 (s, 2H), 1.29 (s, 9H); **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 148.76, 143.29, 141.76, 138.19, 134.71, 128.40, 125.32, 121.80, 117.55, 117.07, 64.38, 64.29, 40.66, 34.34, 31.38; **HRMS** (APCI) m/z calculated C<sub>19</sub>H<sub>21</sub>O<sub>2</sub><sup>+</sup> [M-H]<sup>-</sup> 281.2486, found 281.2487.



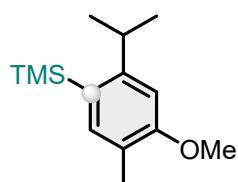
**2-(4-(*tert*-butyl)benzyl)-1,3,5-trimethylbenzene (4p)**<sup>19</sup>, colorless oil; 74% yield; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.23 (d, *J* = 7.2 Hz, 2H), 6.94 (d, *J* = 7.6 Hz, 2H), 6.87 (s, 2H), 3.97 (s, 2H), 2.28 (s, 3H), 2.20 (s, 6H), 1.27 (s, 9H); **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 148.36, 136.94, 135.49, 134.11, 128.83, 127.48, 125.18, 34.27, 34.19, 31.39, 20.89, 20.19; **HRMS** (APCI) m/z calculated C<sub>20</sub>H<sub>27</sub><sup>+</sup> [M+H]<sup>+</sup> 267.2107, found 267.2107.



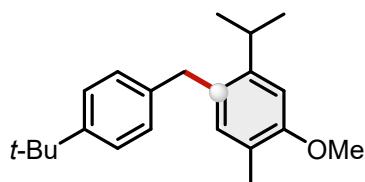
**2-(4-(*tert*-butyl)benzyl)-1,3,5-triisopropylbenzene (4q)**, colorless oil; 87% yield; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.25 (d, *J* = 7.2 Hz, 2H), 7.03 (s, 2H), 6.95 (d, *J* = 7.4 Hz, 2H), 4.08 (s, 2H), 3.11 - 3.02 (m, 2H), 2.94 - 2.87 (m, 1H), 1.29 (s, 15H), 1.14 (d, *J* = 6.2 Hz, 12H); **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 148.28, 147.34, 146.81, 138.29, 131.05, 127.55, 125.06, 120.93, 34.29, 34.16, 32.51, 31.41, 29.57, 24.19, 24.11; **HRMS** (APCI) m/z calculated C<sub>26</sub>H<sub>37</sub><sup>+</sup> [M-H]<sup>-</sup> 349.2890, found 349.2890.



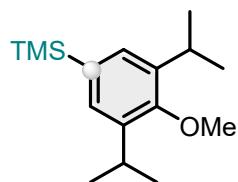
**1-(4-(*tert*-butyl)benzyl)-2,3,4,5,6-pentamethylbenzene (4r)**, white solid; 93% yield; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.23 (d, *J* = 7.8 Hz, 2H), 6.96 (d, *J* = 7.6 Hz, 2H), 4.06 (s, 2H), 2.23 (s, 9H), 2.17 (s, 6H), 1.28 (s, 9H); **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 148.23, 137.44, 134.10, 132.71, 132.39, 128.93, 127.55, 125.14, 35.61, 34.25, 31.39, 20.52, 16.93, 16.88, 16.85, 15.87; **HRMS** (APCI) m/z calculated C<sub>22</sub>H<sub>29</sub><sup>+</sup> [M-H]<sup>-</sup> 293.2264, found 293.2264.



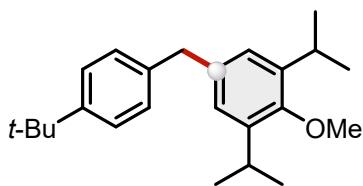
**Carvacrol derivatives** **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.18 (s, 1H), 6.77 (s, 1H), 3.85 (s, 3H), 3.17 - 3.11 (m, 1H), 2.19 (s, 3H), 1.27 (d, *J* = 6.8 Hz, 6H), 0.30 (s, 9H); **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 159.03, 154.54, 136.57, 127.58, 123.38, 106.85, 55.04, 33.75, 24.74, 15.88, 0.61; **HRMS** (APCI) m/z calculated C<sub>14</sub>H<sub>25</sub>OSi<sup>+</sup> [M+H]<sup>+</sup> 238.1747, found 238.1748.



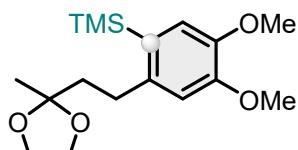
**1-(4-(*tert*-butyl)benzyl)-2-isopropyl-4-methoxy-5-methylbenzene (4s)**, white solid; 71% yield; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.27 (d, *J* = 8.2 Hz, 2H), 7.03 (d, *J* = 8.2 Hz, 2H), 6.89 (s, 1H), 6.75 (s, 1H), 3.93 (s, 2H), 3.83 (s, 3H), 3.15 - 3.08 (m, 1H), 2.15 (s, 3H), 1.29 (s, 9H), 1.14 (d, *J* = 6.8 Hz, 6H); **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 156.55, 148.44, 145.51, 138.68, 132.84, 128.96, 128.02, 125.14, 123.70, 107.10, 55.31, 37.28, 34.30, 31.39, 29.16, 23.88, 15.73; **HRMS** (APCI) m/z calculated C<sub>22</sub>H<sub>31</sub>O<sup>+</sup> [M+H]<sup>+</sup> 311.2369, found 311.2370.



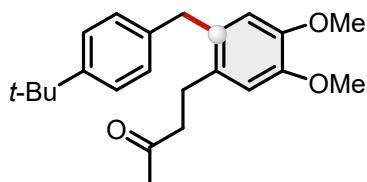
**Propofol derivatives** **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.25 (s, 2H), 3.75 (s, 3H), 3.37 - 3.30 (m, 2H), 1.25 (d, *J* = 6.8 Hz, 12H), 0.26 (s, 9H); **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 155.34, 140.66, 135.62, 129.13, 62.14, 26.47, 24.08, -0.87; **HRMS** (APCI) m/z calculated C<sub>16</sub>H<sub>29</sub>OSi<sup>+</sup> [M+H]<sup>+</sup> 265.1982, found 265.1986.



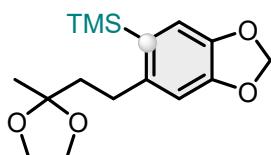
**5-(4-(*tert*-butyl)benzyl)-1,3-diisopropyl-2-methoxybenzene (4t)**, white solid; 61% yield; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.31 (d, *J* = 8.2 Hz, 2H), 7.12 (d, *J* = 8.2 Hz, 2H), 6.92 (s, 2H), 3.90 (s, 2H), 3.72 (s, 3H), 3.35 - 3.27 (m, 2H), 1.30 (s, 9H), 1.20 (d, *J* = 6.8 Hz, 12H); **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 152.75, 148.61, 141.41, 136.66, 129.13, 128.28, 125.23, 124.67, 62.21, 41.29, 34.34, 31.39, 26.48, 24.06; **HRMS** (APCI) m/z calculated C<sub>24</sub>H<sub>35</sub>O<sup>+</sup> [M+H]<sup>+</sup> 339.2682, found 339.2685.



**(4,5-dimethoxy-2-(2-(2-methyl-1,3-dioxolan-2-yl)ethyl)phenyl)trimethylsilane (2u)**; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 6.94 (s, 1H), 6.74 (s, 1H), 4.00 (d, *J* = 4.2 Hz, 4H), 3.87 (d, *J* = 1.6 Hz, 6H), 2.85 - 2.73 (m, 2H), 1.99 - 1.92 (m, 2H), 1.39 (s, 3H), 0.33 (s, 9H); **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 149.85, 146.30, 141.15, 128.88, 117.14, 112.10, 109.62, 64.84, 55.88, 55.65, 42.19, 29.93, 24.16, 0.40; **HRMS** (APCI) m/z calculated C<sub>17</sub>H<sub>29</sub>O<sub>4</sub>Si<sup>+</sup> [M+H]<sup>+</sup> 325.1829, found 325.1830.

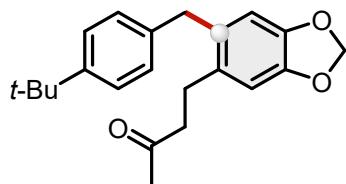


**4-(2-(4-(*tert*-butyl)benzyl)-4,5-dimethoxyphenyl)butan-2-one (4u)**, white solid; 62% yield; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.30 (d, *J* = 12.6 Hz, 2H), 7.03 (d, *J* = 8.2 Hz, 2H), 6.68 (d, *J* = 6.2 Hz, 2H), 3.92 (s, 2H), 3.85 (s, 6H), 2.85 - 2.76 (m, 4H), 1.99 (s, 3H), 1.29 (s, 9H); **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 207.93, 148.90, 146.10, 145.85, 137.80, 132.47, 131.78, 128.19, 125.33, 110.74, 109.37, 56.04, 55.61, 44.70, 38.33, 34.34, 31.37, 29.89, 26.64; **HRMS** (APCI) m/z calculated C<sub>23</sub>H<sub>31</sub>O<sub>3</sub><sup>+</sup> [M+H]<sup>+</sup> 355.2268, found 355.2263.

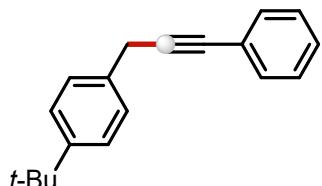


**trimethyl(6-(2-(2-methyl-1,3-dioxolan-2-yl)ethyl)benzo-[1,3]dioxol-5-yl)silane (2v)**; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 6.91 (s, 1H), 6.73 (s, 1H), 5.90 (s, 2H), 3.97 (t, *J* = 8.8 Hz, 4H), 2.80 - 2.72 (m, 2H), 1.95 - 1.87 (m, 2H), 1.38 (s, 3H), 0.31 (s, 9H); **<sup>13</sup>C NMR**

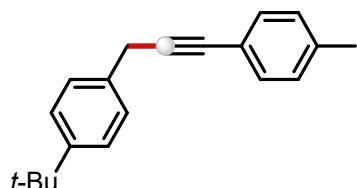
**NMR** (101 MHz, CDCl<sub>3</sub>) δ 148.55, 145.25, 142.32, 130.22, 113.37, 109.58, 109.41, 100.57, 64.82, 42.01, 30.03, 24.14, 0.41; **HRMS** (APCI) m/z calculated C<sub>16</sub>H<sub>25</sub>O<sub>4</sub>Si<sup>+</sup> [M+H]<sup>+</sup> 309.1517, found 309.1515.



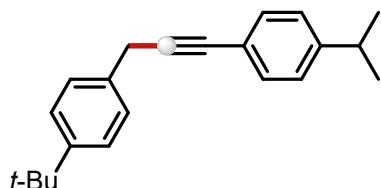
**4-(6-(4-(*tert*-butyl)benzyl)benzo-[1,3]dioxol-5-yl)butan-2-one (4v)**, white solid; 62% yield; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.28 (d, *J* = 9.2 Hz, 2H), 7.03 (d, *J* = 7.8 Hz, 2H), 6.64 (s, 2H), 5.90 (s, 2H), 3.88 (s, 2H), 2.80 - 2.74 (m, 2H), 2.41 (t, *J* = 7.8 Hz, 2H), 2.01 (s, 3H), 1.29 (s, 9H); **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 207.93, 148.90, 146.10, 145.85, 137.80, 132.47, 131.78, 128.19, 125.33, 110.74, 109.37, 100.79, 44.70, 38.33, 34.34, 31.37, 29.89, 26.64; **HRMS** (APCI) m/z calculated C<sub>22</sub>H<sub>27</sub>O<sub>3</sub><sup>+</sup> [M+H]<sup>+</sup> 339.1955, found 339.1961.



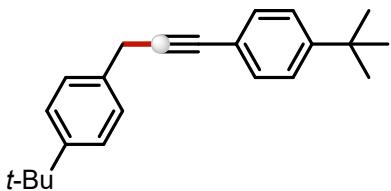
**1-(*tert*-butyl)-4-(3-phenylprop-2-yn-1-yl)benzene (6a)**<sup>20</sup>, yellow oil; 85% yield; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.46 - 7.43 (m, 2H), 7.37 (s, 4H), 7.31 - 7.27 (m, 3H), 3.81 (s, 2H), 1.32 (s, 9H); **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 149.53, 133.71, 131.61, 128.19, 127.73, 127.63, 125.46, 123.72, 87.80, 82.38, 34.43, 31.37, 25.22; **HRMS** (APCI) m/z calculated C<sub>19</sub>H<sub>19</sub><sup>-</sup> [M-H]<sup>-</sup> 247.1492, found 247.1495.



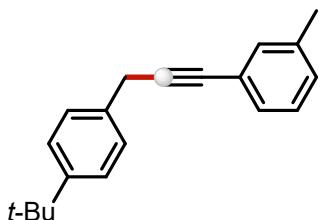
**1-(*tert*-butyl)-4-(3-(p-tolyl)prop-2-yn-1-yl)benzene (6b)**, yellow oil; 62% yield; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.34 (d, *J* = 11.8 Hz, 5H), 7.25 (s, 1H), 7.10 (d, *J* = 7.4 Hz, 2H), 3.79 (s, 2H), 2.33 (s, 3H), 1.32 (s, 9H); **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 149.48, 137.72, 133.87, 131.49, 128.95, 127.63, 125.44, 120.66, 86.98, 82.44, 34.42, 31.38, 25.24, 21.41; **HRMS** (APCI) m/z calculated C<sub>20</sub>H<sub>21</sub><sup>-</sup> [M-H]<sup>-</sup> 261.1649, found 261.1652.



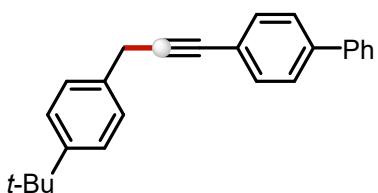
**1-(*tert*-butyl)-4-(3-(4-isopropylphenyl)prop-2-yn-1-yl)benzene (6c)**, yellow oil; 59% yield; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.36 (d, *J* = 9.6 Hz, 6H), 7.15 (d, *J* = 6.8 Hz, 2H), 3.79 (s, 2H), 2.92 - 2.85 (m, 1H), 1.32 (s, 9H), 1.23 (d, *J* = 6.8 Hz, 6H); **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 149.46, 148.66, 133.89, 131.59, 127.62, 126.32, 125.42, 121.05, 86.91, 82.51, 34.42, 34.00, 31.38, 25.24, 23.81; **HRMS** (APCI) m/z calculated C<sub>22</sub>H<sub>25</sub><sup>+</sup> [M-H]<sup>-</sup> 289.1962, found 289.1967.



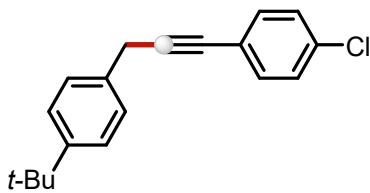
**4,4'-(prop-1-yne-1,3-diyl)bis(*tert*-butylbenzene) (6d)**, yellow oil; 55% yield; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.40 - 7.34 (m, 6H), 7.31 (d, *J* = 6.8 Hz, 2H), 3.79 (s, 2H), 1.31 (d, *J* = 6.6 Hz, 18H); **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 150.90, 149.46, 133.89, 131.32, 127.63, 125.42, 125.18, 120.74, 86.99, 82.46, 34.68, 34.42, 31.38, 31.18, 25.24; **HRMS** (APCI) m/z calculated C<sub>23</sub>H<sub>27</sub><sup>+</sup> [M-H]<sup>-</sup> 303.2118, found 303.2123.



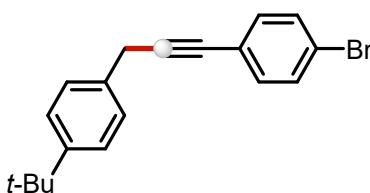
**1-(3-(*tert*-butyl)phenyl)prop-1-yn-1-yl-3-methylbenzene (6e)**, yellow oil; 58% yield; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.36 (m, 4H), 7.25 (t, *J* = 6.6 Hz, 2H), 7.18 (t, *J* = 7.6 Hz, 1H), 7.09 (d, *J* = 7.4 Hz, 1H), 3.79 (s, 2H), 2.32 (s, 3H), 1.32 (s, 9H); **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 149.51, 137.84, 133.79, 132.24, 128.66, 128.62, 128.10, 127.63, 125.45, 123.54, 87.39, 82.54, 34.43, 31.38, 25.22, 21.20; **HRMS** (APCI) m/z calculated C<sub>20</sub>H<sub>23</sub><sup>+</sup> [M+H]<sup>+</sup> 263.1794, found 263.1793.



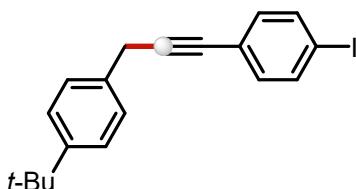
**4-(3-(*tert*-butyl)phenyl)prop-1-yn-1-yl-1,1'-biphenyl (6f)**, white solid; 68% yield; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.58 (d, *J* = 7.8 Hz, 2H), 7.55 - 7.49 (m, 5H), 7.43 (t, *J* = 6.8 Hz, 2H), 7.37 (s, 4H), 3.83 (s, 2H), 1.33 (s, 9H); **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 149.57, 140.47, 133.71, 132.04, 128.81, 127.66, 127.49, 126.99, 126.89, 126.66, 125.49, 122.70, 88.52, 82.26, 34.44, 31.38, 25.32; **HRMS** (APCI) m/z calculated C<sub>25</sub>H<sub>23</sub><sup>+</sup> [M-H]<sup>-</sup> 323.1805, found 323.1810.



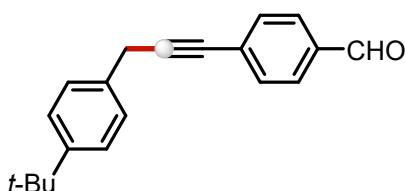
**1-(tert-butyl)-4-(3-(4-chlorophenyl)prop-2-yn-1-yl)benzene (6g)**, yellow oil; 91% yield; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.36 - 7.31 (m, 6H), 7.26 (d, *J* = 8.8 Hz, 2H), 3.78 (s, 2H), 1.32 (s, 9H); **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 149.65, 133.69, 133.45, 132.85, 128.51, 127.62, 125.51, 122.25, 88.93, 81.29, 34.44, 31.36, 25.22; **HRMS** (APCI) m/z calculated C<sub>19</sub>H<sub>18</sub>Cl<sup>−</sup> [M-H]<sup>−</sup> 281.1102, found 281.1107.



**1-bromo-4-(3-(4-(tert-butyl)phenyl)prop-1-yn-1-yl)benzene (6h)**, colorless oil; 89% yield; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.42 (d, *J* = 6.2 Hz, 2H), 7.37 (d, *J* = 6.4 Hz, 2H), 7.35 - 7.27 (m, 4H), 3.78 (s, 2H), 1.33 (s, 9H); **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 149.66, 133.40, 133.09, 131.43, 127.62, 125.52, 122.70, 121.86, 89.14, 81.35, 34.44, 31.36, 25.25; **HRMS** (APCI) m/z calculated C<sub>19</sub>H<sub>18</sub>Br<sup>−</sup> [M-H]<sup>−</sup> 325.0597, found 325.0603.



**1-(tert-butyl)-4-(3-(4-iodophenyl)prop-2-yn-1-yl)benzene (6i)**, colorless oil; 78% yield; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.63 (d, *J* = 8.2 Hz, 2H), 7.37 (d, *J* = 6.4 Hz, 2H), 7.33 (d, *J* = 8.2 Hz, 2H), 7.16 (d, *J* = 8.2 Hz, 2H), 3.78 (s, 2H), 1.33 (s, 9H); **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 149.66, 137.34, 133.38, 133.20, 127.62, 125.52, 123.28, 93.42, 89.45, 81.47, 34.44, 31.36, 25.27; **HRMS** (APCI) m/z calculated C<sub>19</sub>H<sub>20</sub>I<sup>+</sup> [M+H]<sup>+</sup> 375.0604, found 375.0603.



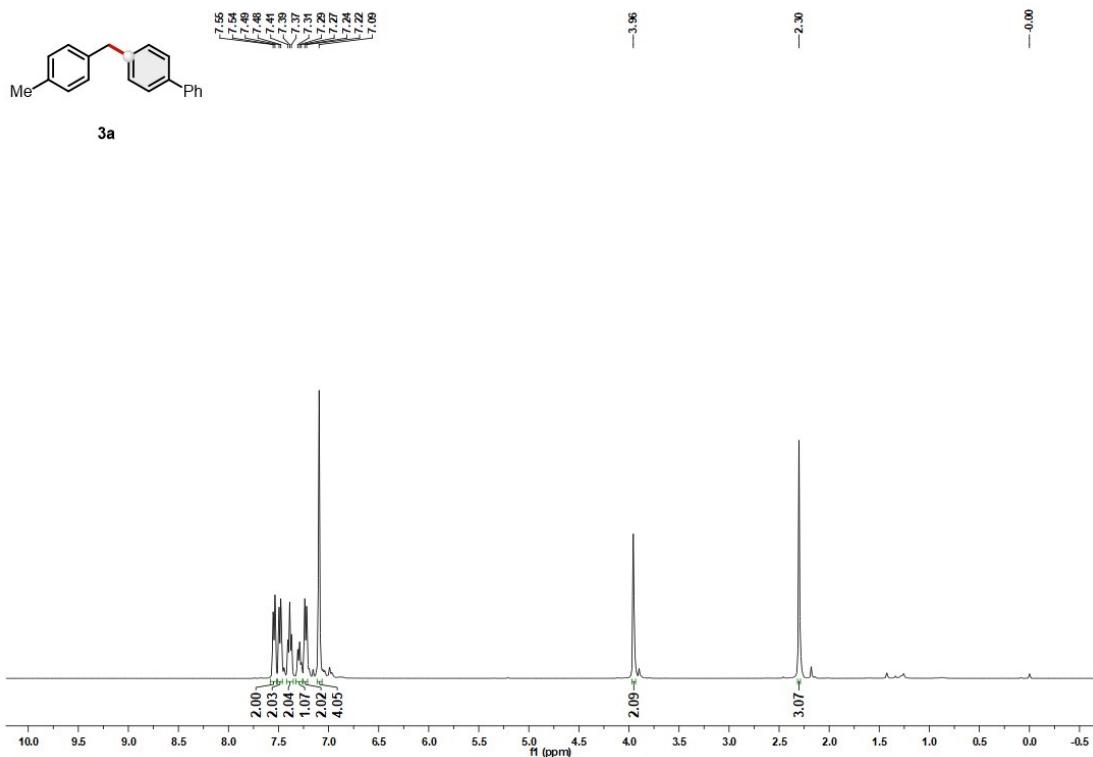
**4-(3-(4-(tert-butyl)phenyl)prop-1-yn-1-yl)benzaldehyde (6j)**, colorless oil; 72% yield; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 9.99 (s, 1H), 7.81 (d, *J* = 7.0 Hz, 2H), 7.58 (d, *J* = 7.2 Hz, 2H), 7.38 (d, *J* = 6.8 Hz, 2H), 7.33 (d, *J* = 7.2 Hz, 2H), 3.83 (s, 2H), 1.33 (s, 9H); **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 191.48, 149.81, 135.13, 133.05, 132.17, 130.17, 129.49, 127.64, 125.59, 92.56, 81.76, 34.46, 31.36, 25.37; **HRMS** (APCI) m/z

calculated C<sub>20</sub>H<sub>21</sub><sup>+</sup> [M+H]<sup>+</sup> 277.1587, found 277.158.

## 6. Copies of NMR spectra

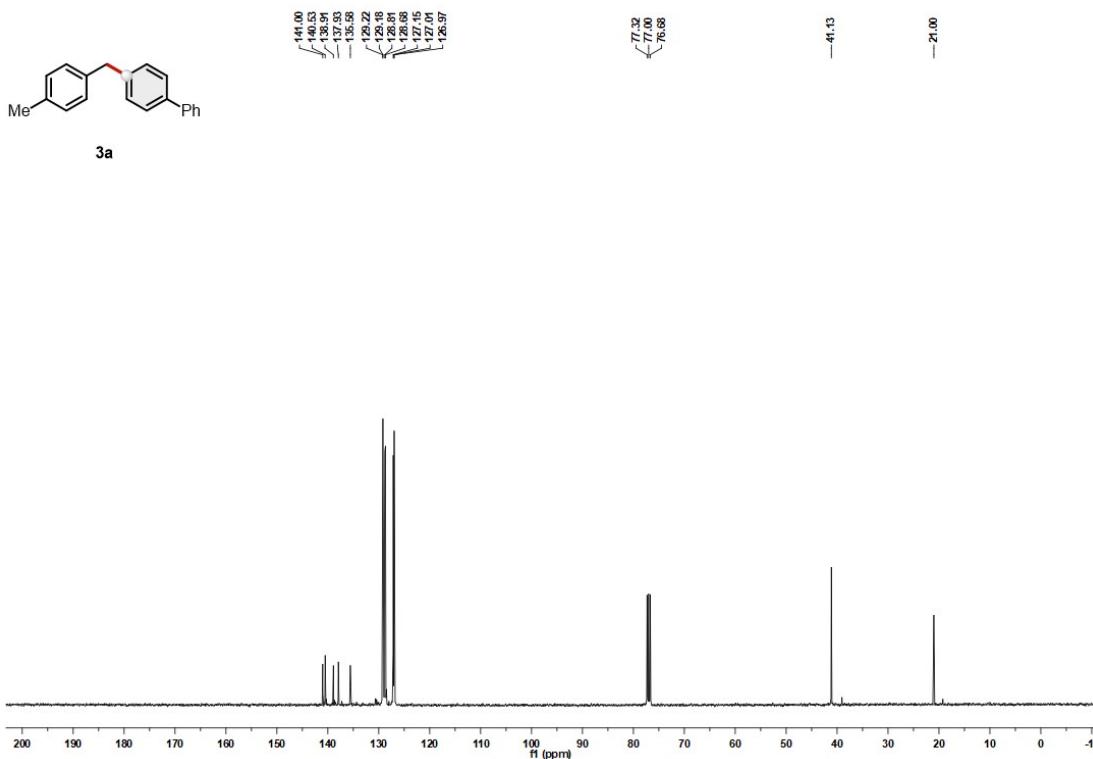
<sup>1</sup>H NMR of **3a**

CDCl<sub>3</sub>, 400 MHz, 298 K

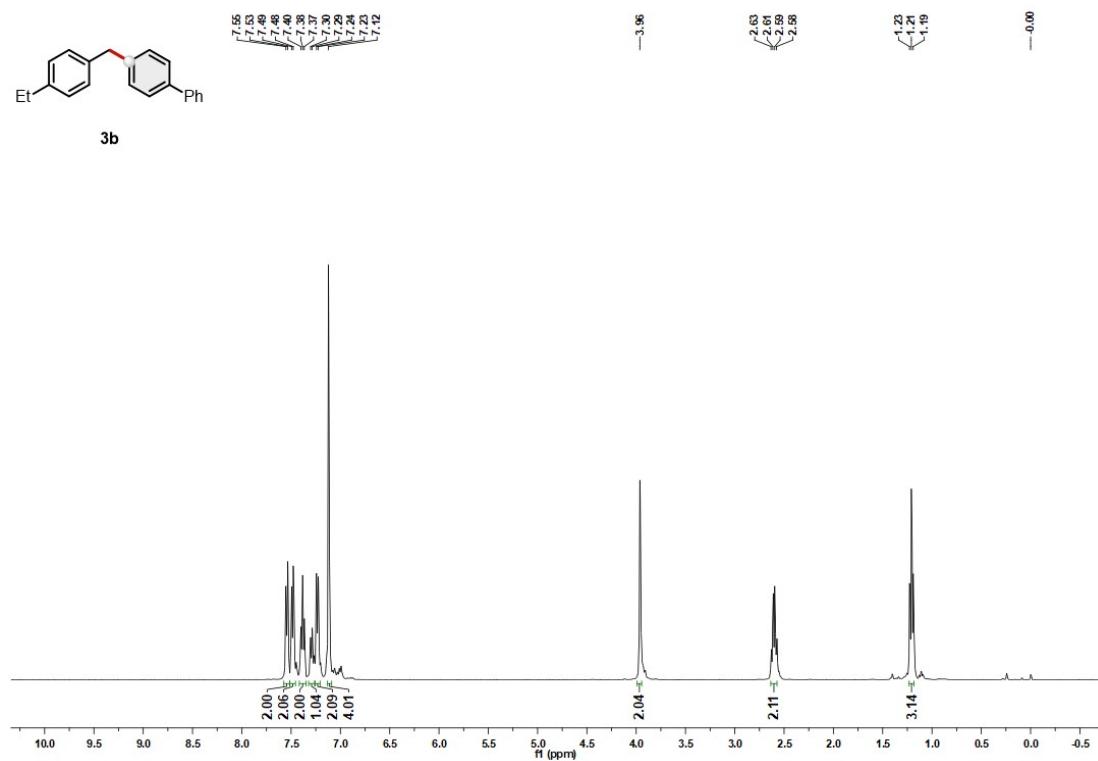
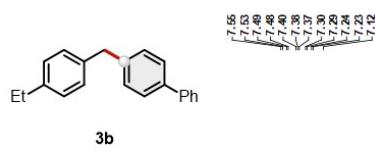


<sup>13</sup>C NMR of **3a**

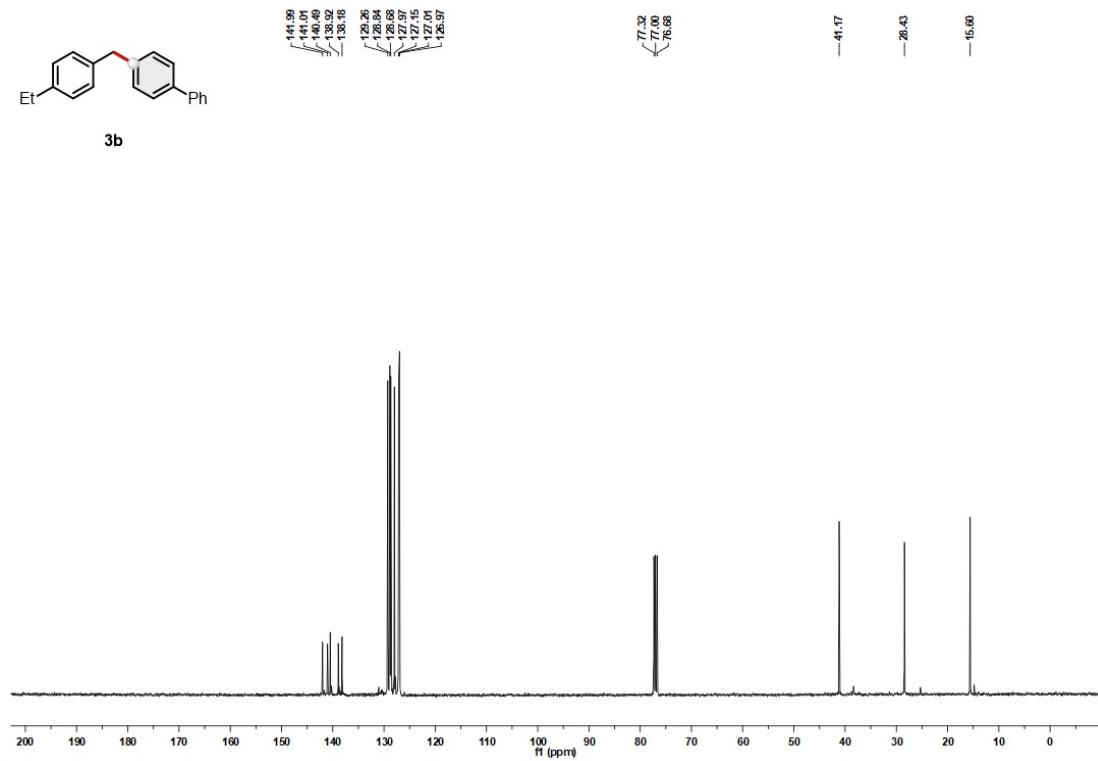
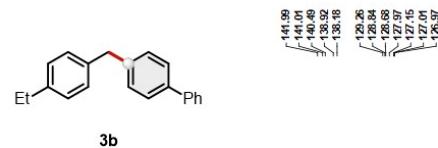
CDCl<sub>3</sub>, 101 MHz, 298 K



<sup>1</sup>H NMR of **3b**  
 $\text{CDCl}_3$ , 400 MHz, 298 K

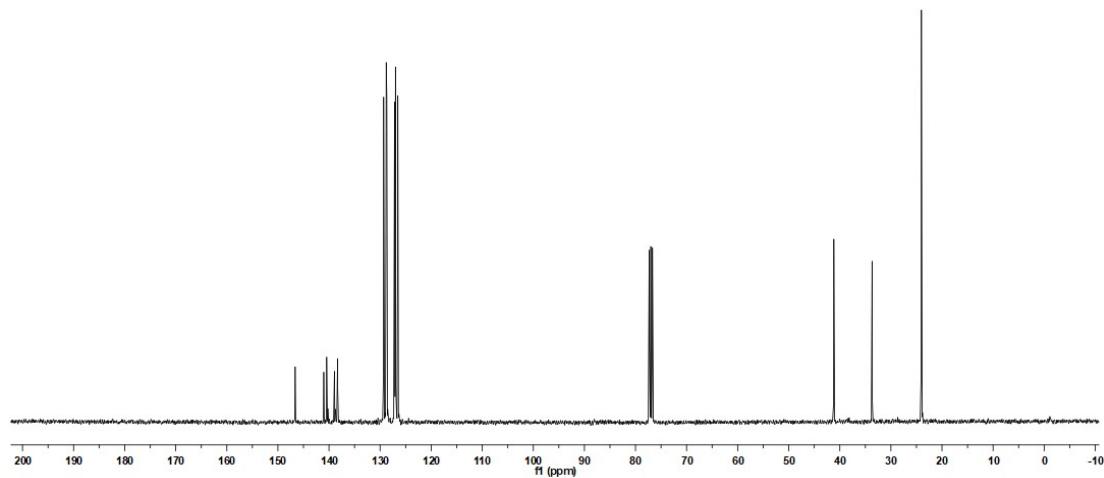
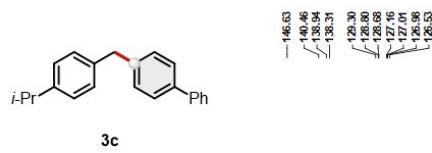


### <sup>13</sup>C NMR of **3b**



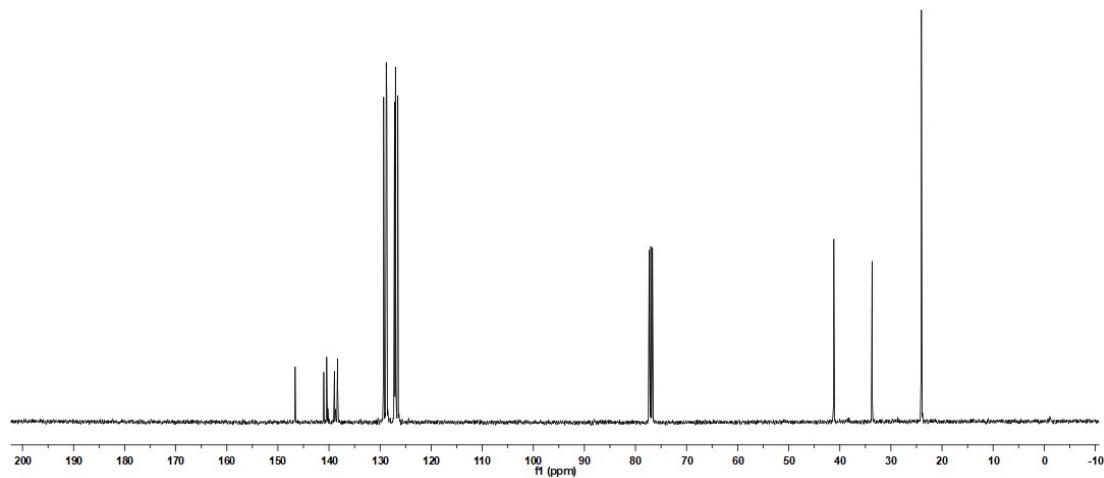
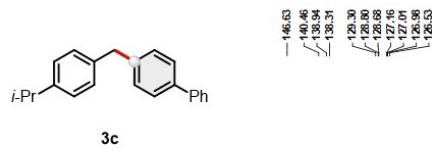
### <sup>1</sup>H NMR of 3c

CDCl<sub>3</sub>, 400 MHz, 298 K

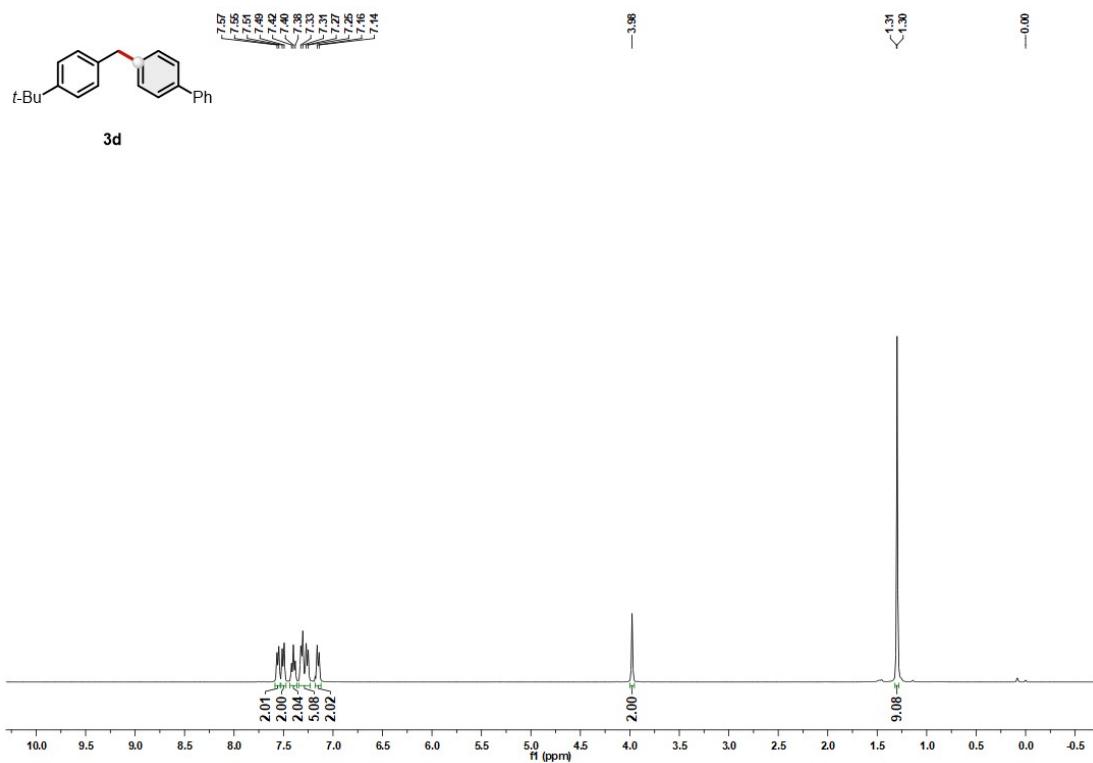


### <sup>13</sup>C NMR of 3c

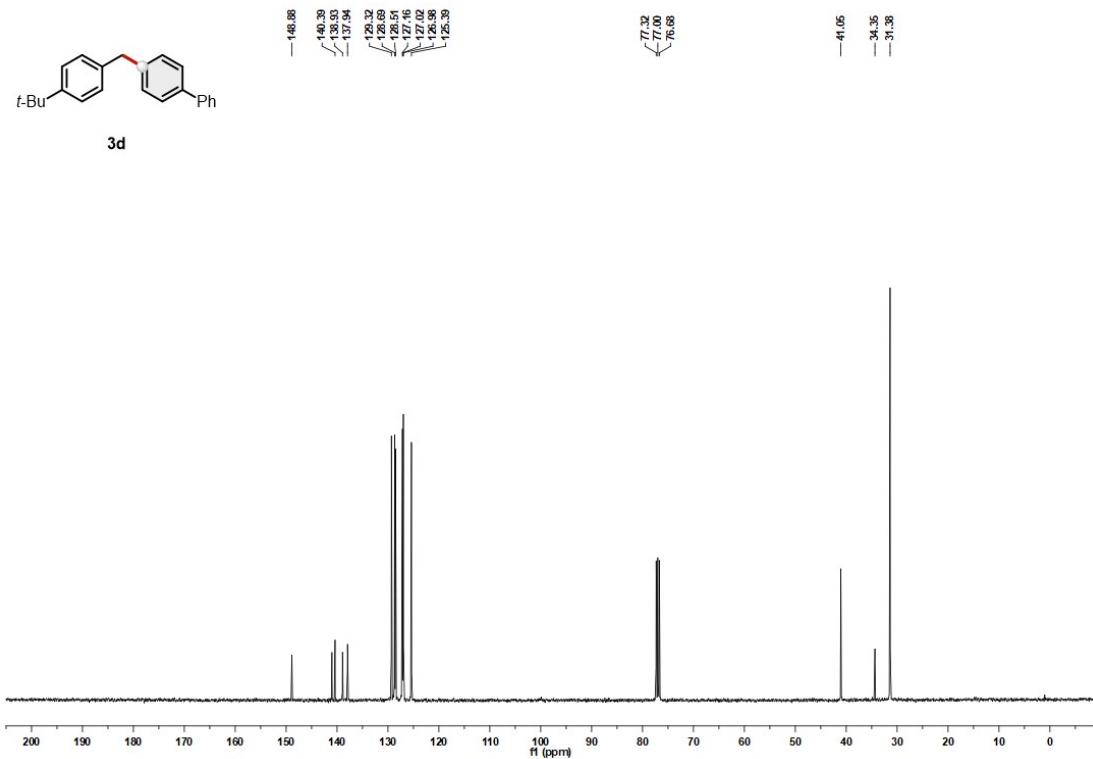
CDCl<sub>3</sub>, 101 MHz, 298 K



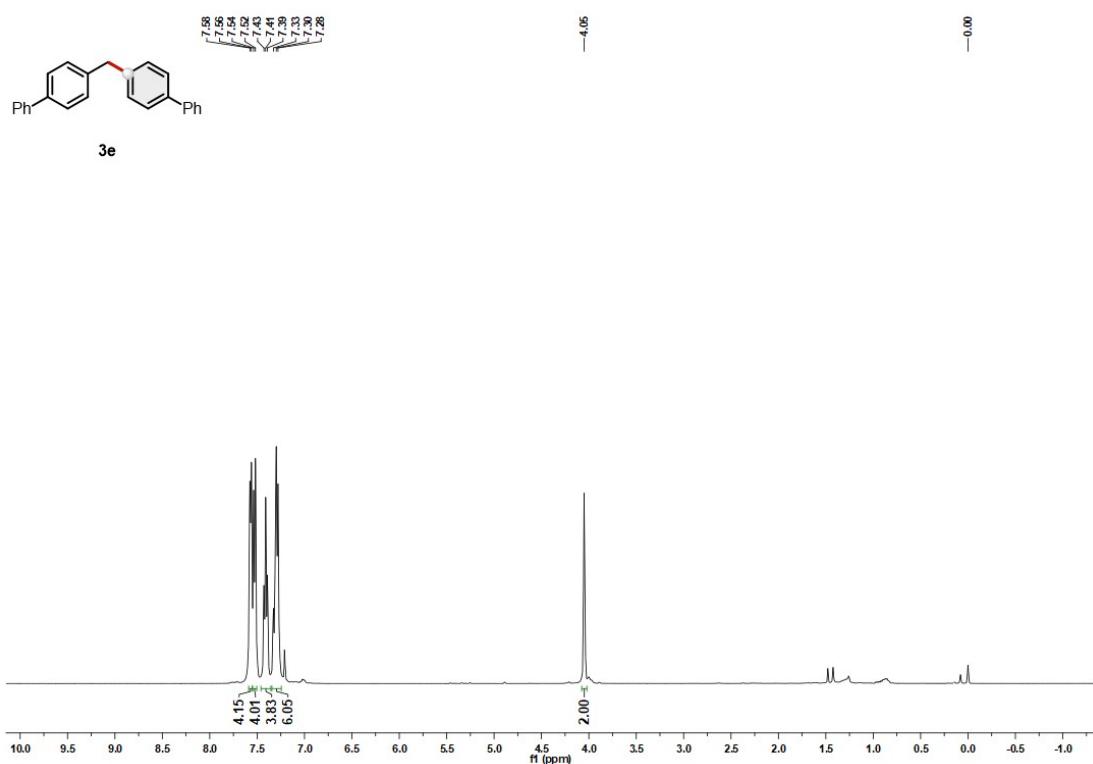
<sup>1</sup>H NMR of **3d**  
CDCl<sub>3</sub>, 400 MHz, 298 K



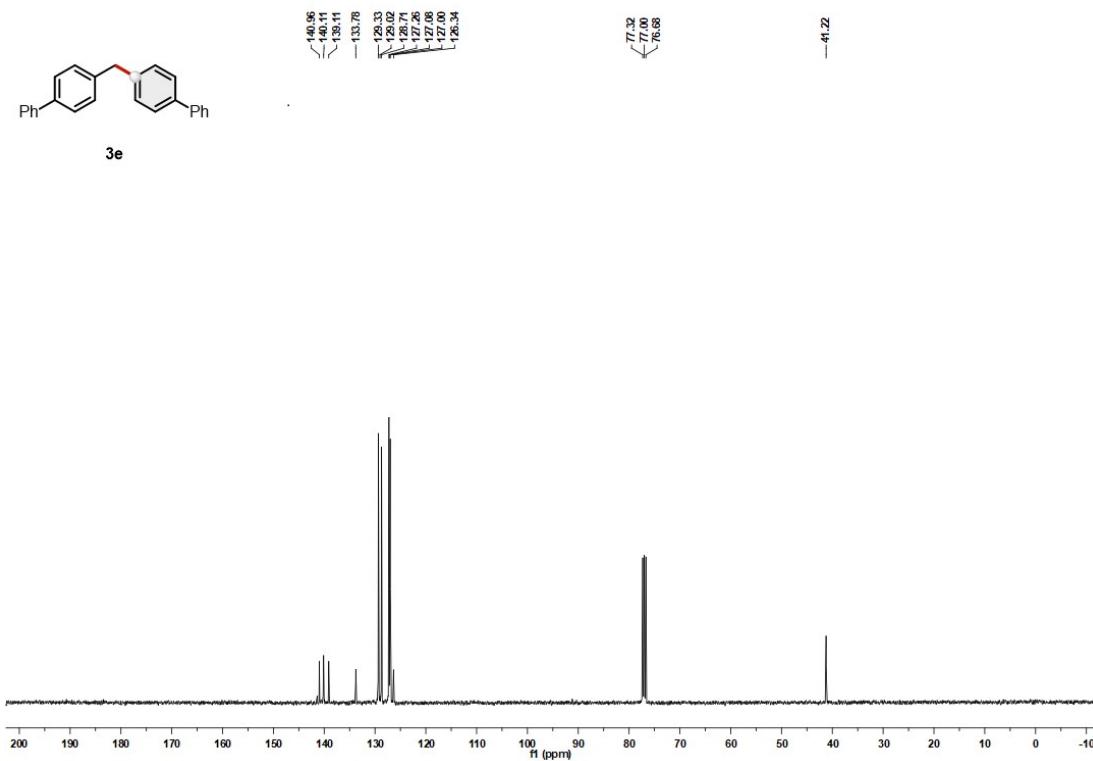
<sup>13</sup>C NMR of **3d**  
CDCl<sub>3</sub>, 101 MHz, 298 K



<sup>1</sup>H NMR of **3e**  
CDCl<sub>3</sub>, 400 MHz, 298 K

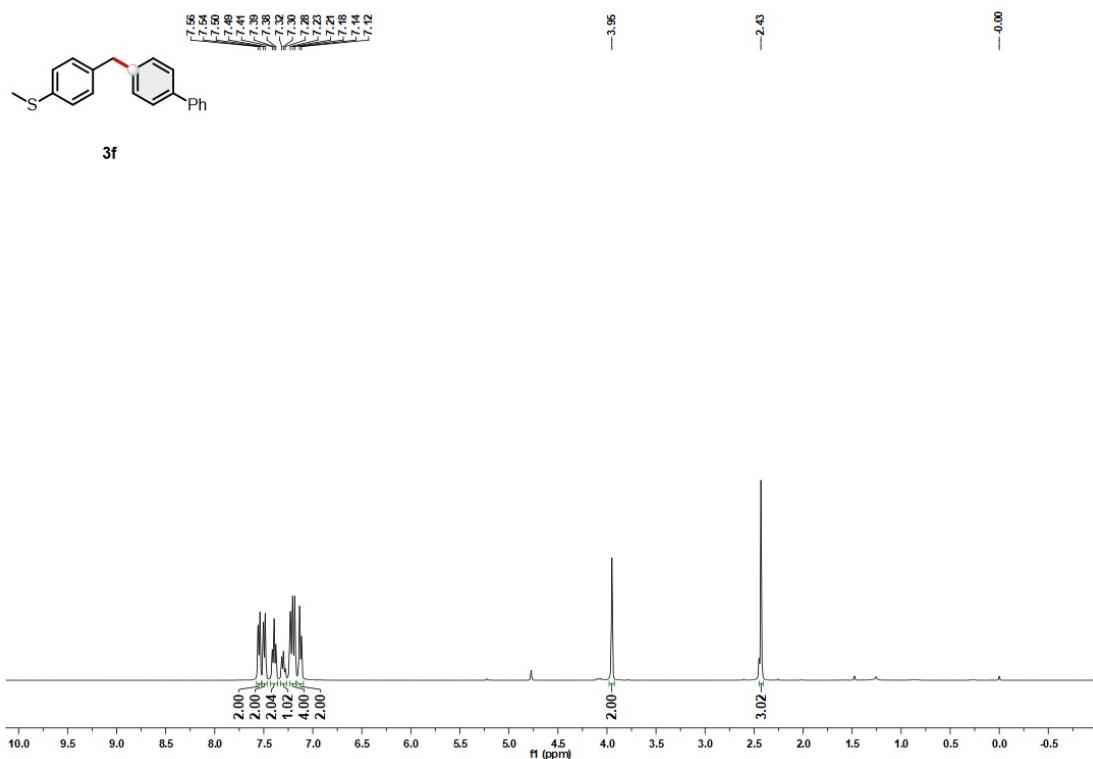


<sup>13</sup>C NMR of **3e**  
CDCl<sub>3</sub>, 101 MHz, 298 K



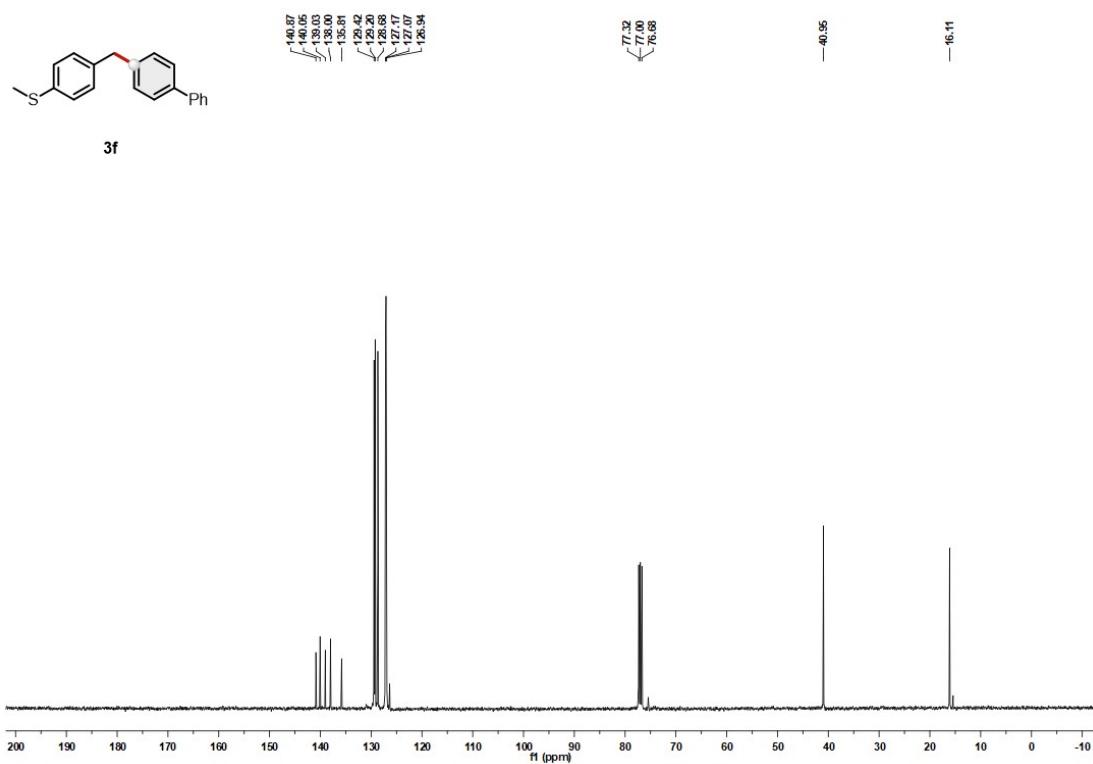
<sup>1</sup>H NMR of **3f**

CDCl<sub>3</sub>, 400 MHz, 298 K

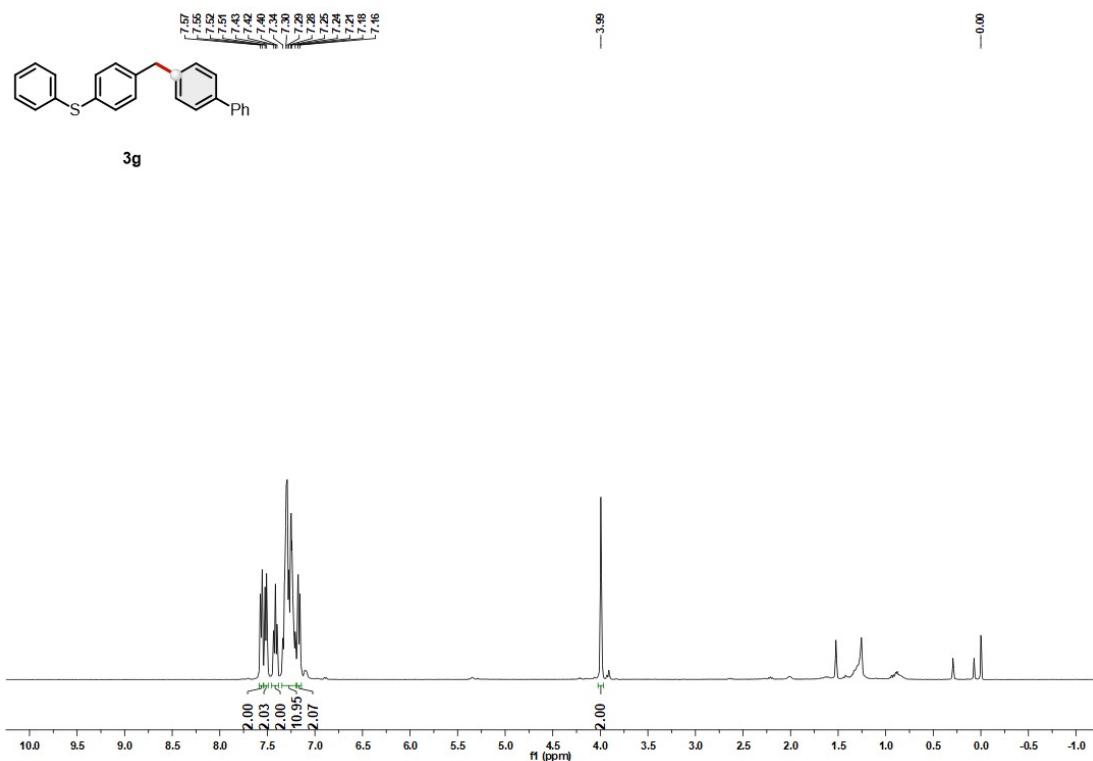


<sup>13</sup>C NMR of **3f**

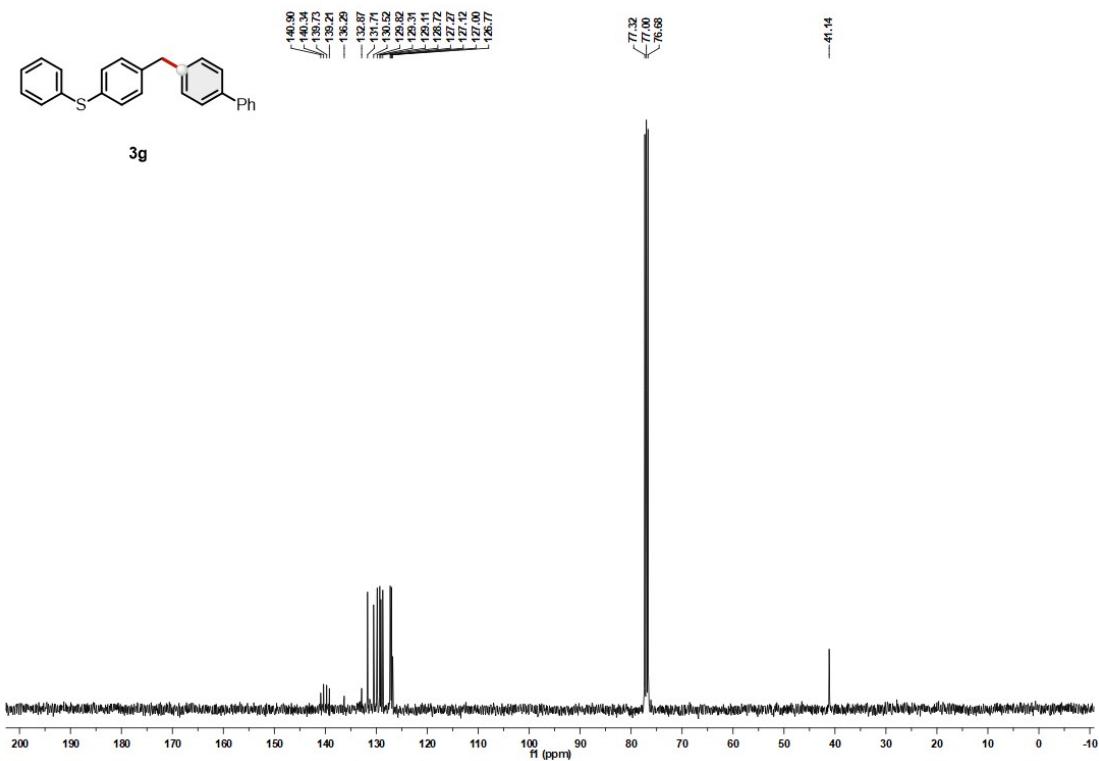
CDCl<sub>3</sub>, 101 MHz, 298 K



<sup>1</sup>H NMR of **3g**  
CDCl<sub>3</sub>, 400 MHz, 298 K

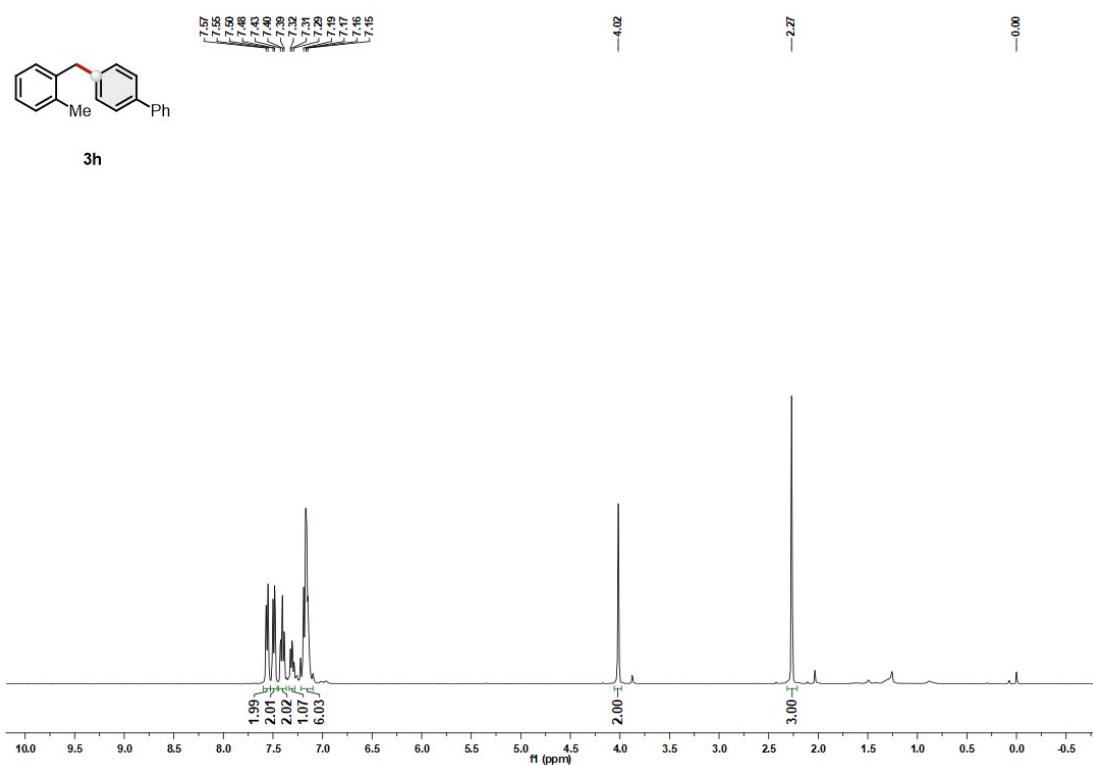


<sup>13</sup>C NMR of **3g**  
CDCl<sub>3</sub>, 101 MHz, 298 K



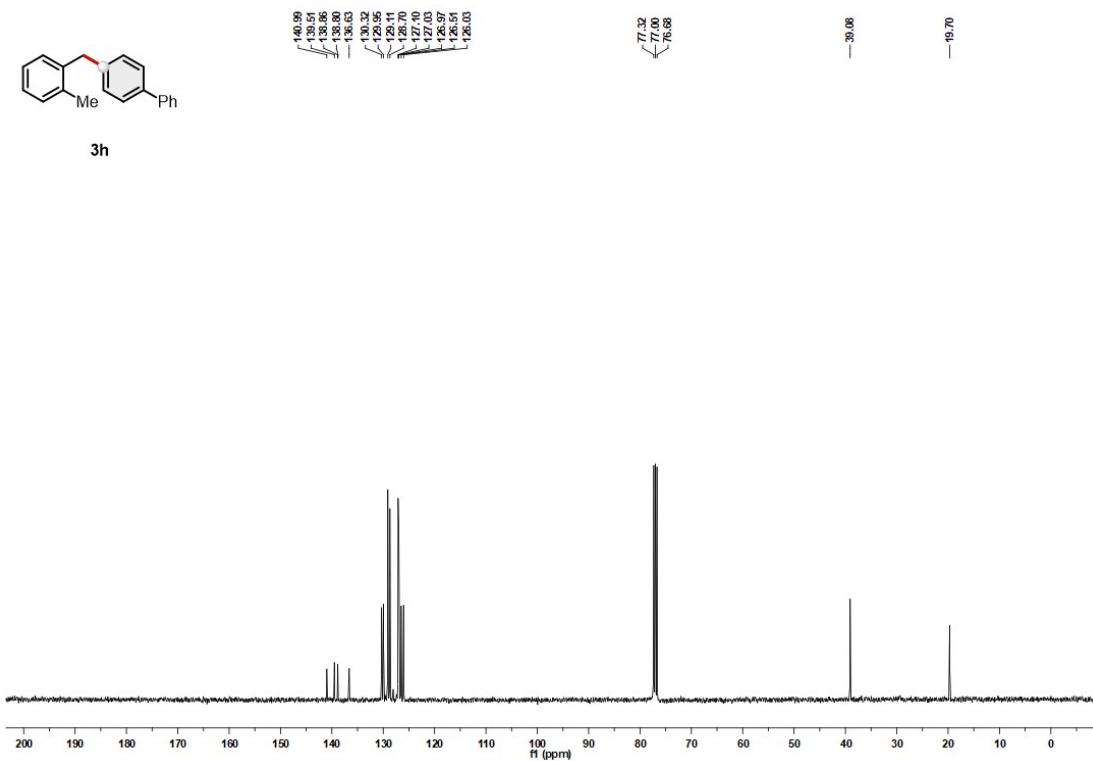
<sup>1</sup>H NMR of **3h**

CDCl<sub>3</sub>, 400 MHz, 298 K



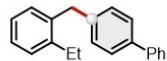
<sup>13</sup>C NMR of **3h**

CDCl<sub>3</sub>, 101 MHz, 298 K

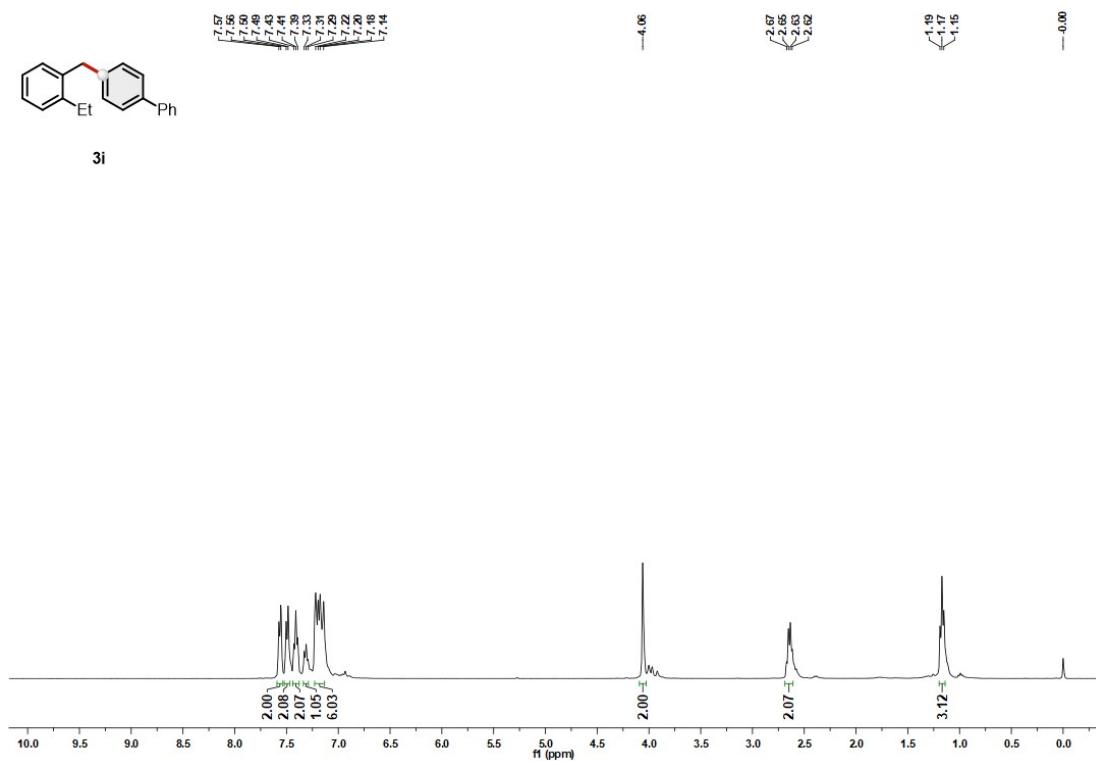


### <sup>1</sup>H NMR of 3i

CDCl<sub>3</sub>, 400 MHz, 298 K

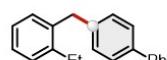


3i

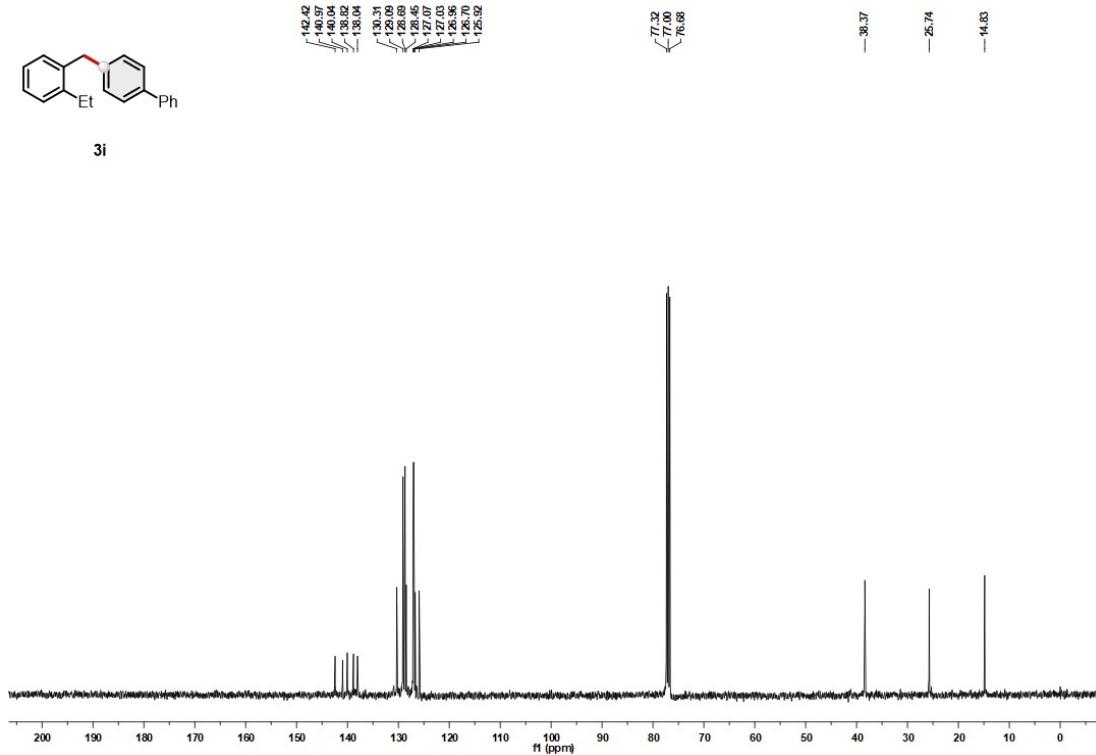


### <sup>13</sup>C NMR of 3i

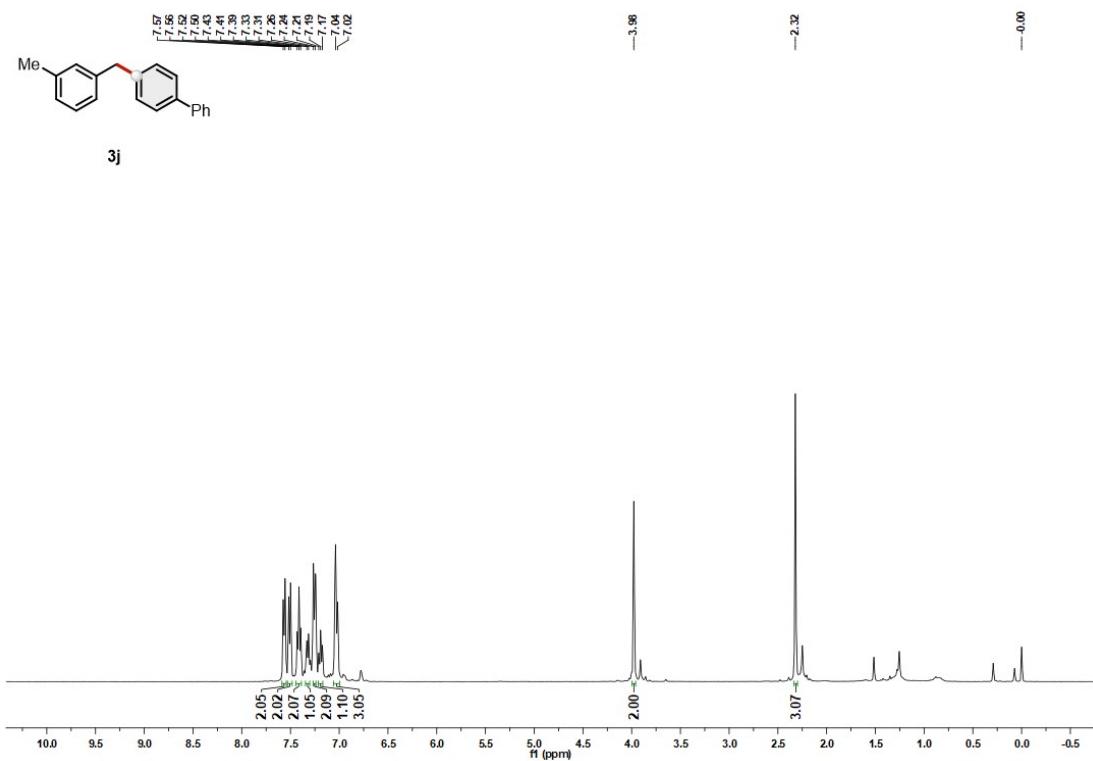
CDCl<sub>3</sub>, 101 MHz, 298 K



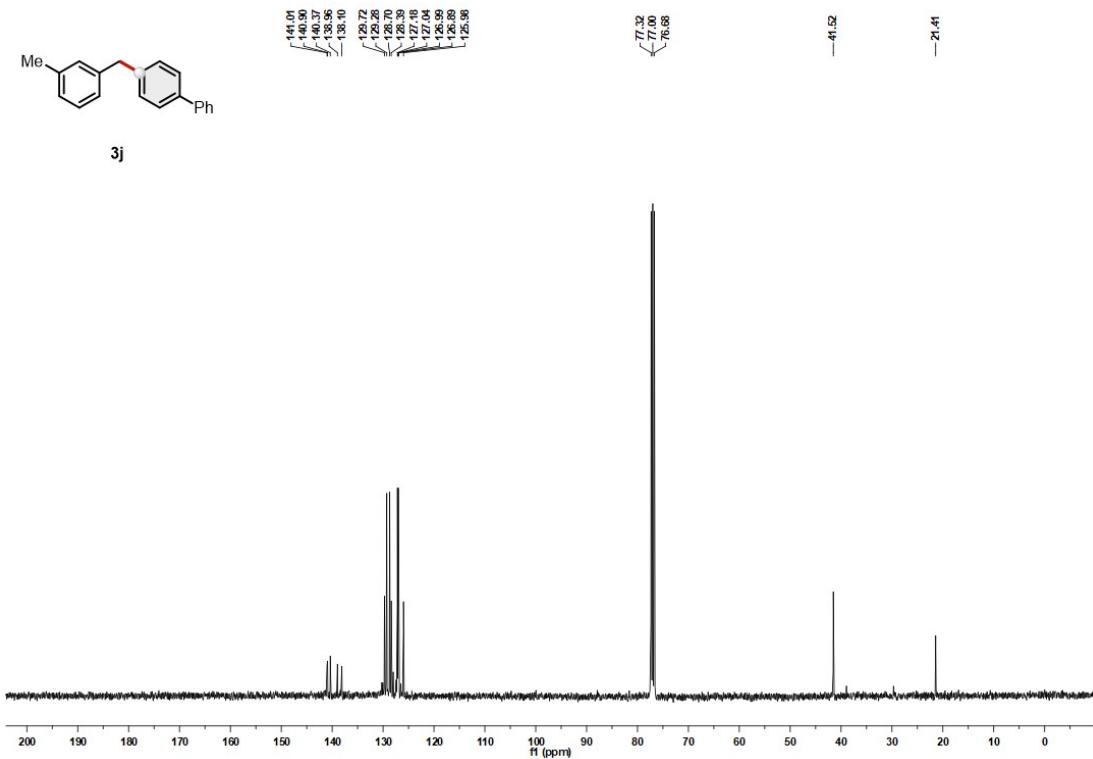
3i



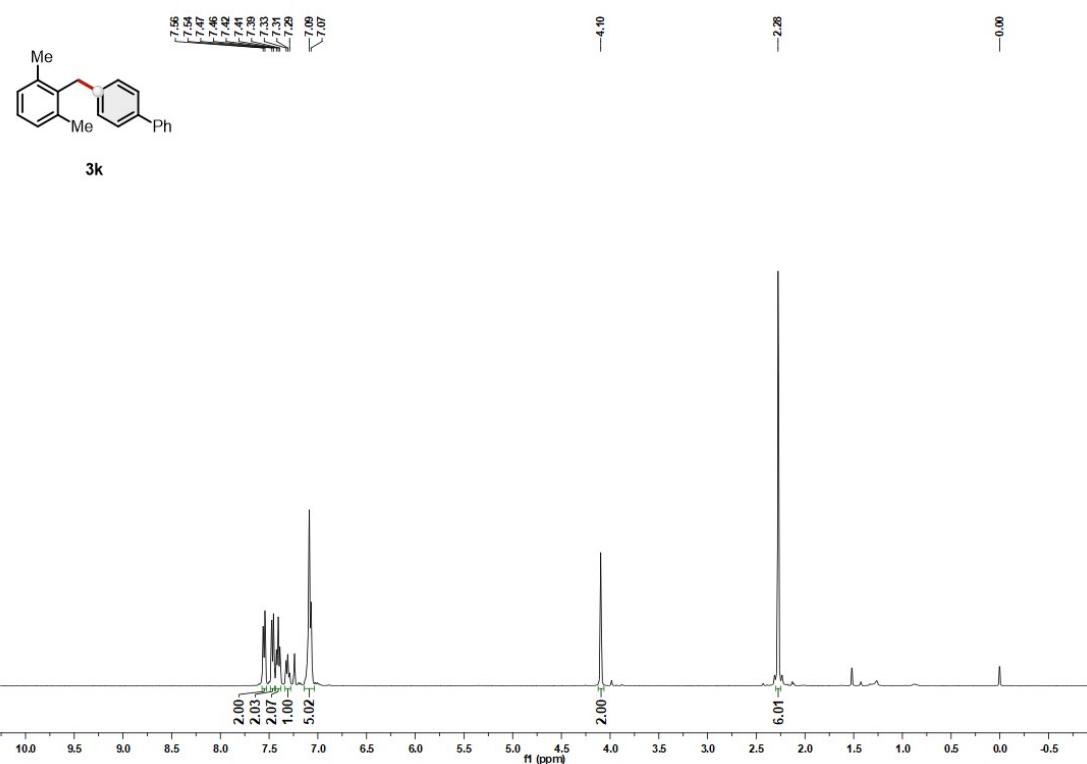
<sup>1</sup>H NMR of **3j**  
CDCl<sub>3</sub>, 400 MHz, 298 K



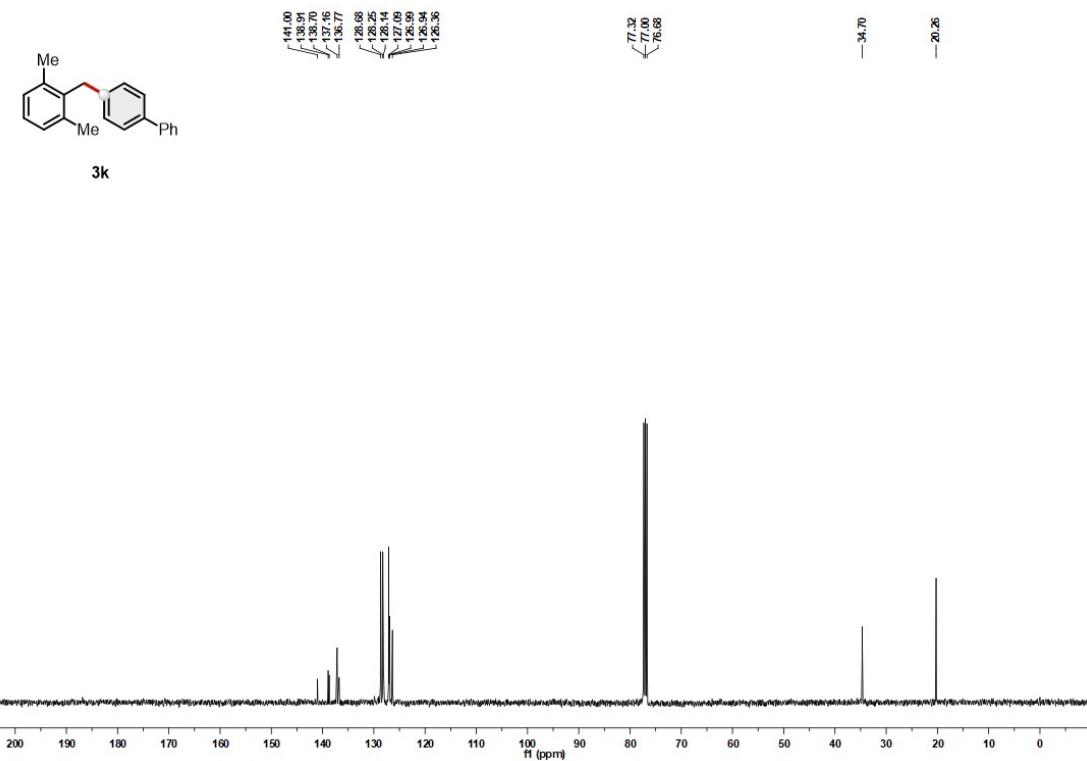
<sup>13</sup>C NMR of **3j**  
CDCl<sub>3</sub>, 101 MHz, 298 K



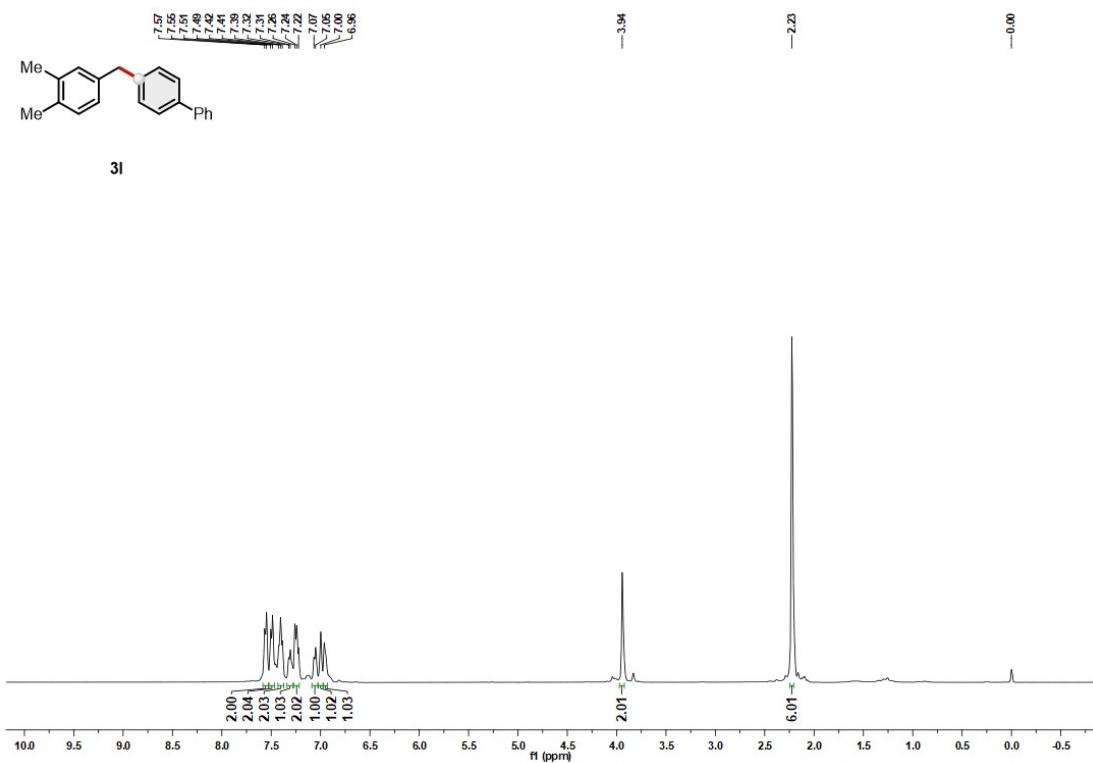
<sup>1</sup>H NMR of **3k**  
CDCl<sub>3</sub>, 400 MHz, 298 K



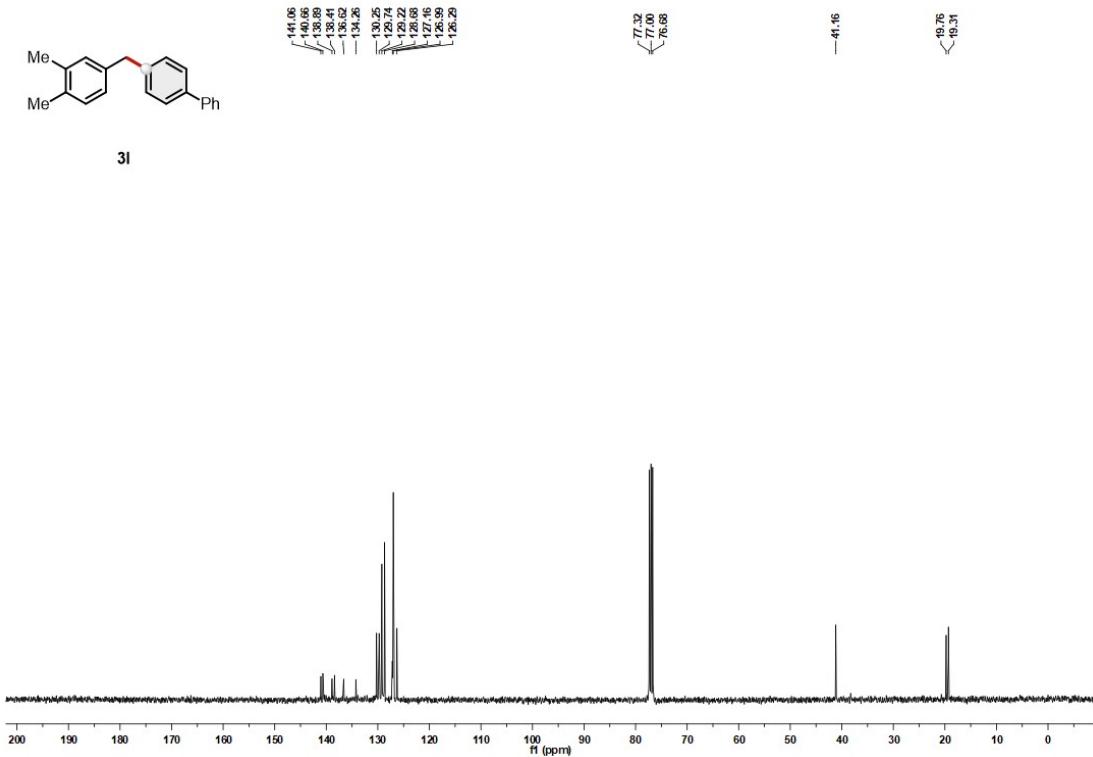
<sup>13</sup>C NMR of **3k**  
CDCl<sub>3</sub>, 101 MHz, 298 K



<sup>1</sup>H NMR of **3l**  
CDCl<sub>3</sub>, 400 MHz, 298 K

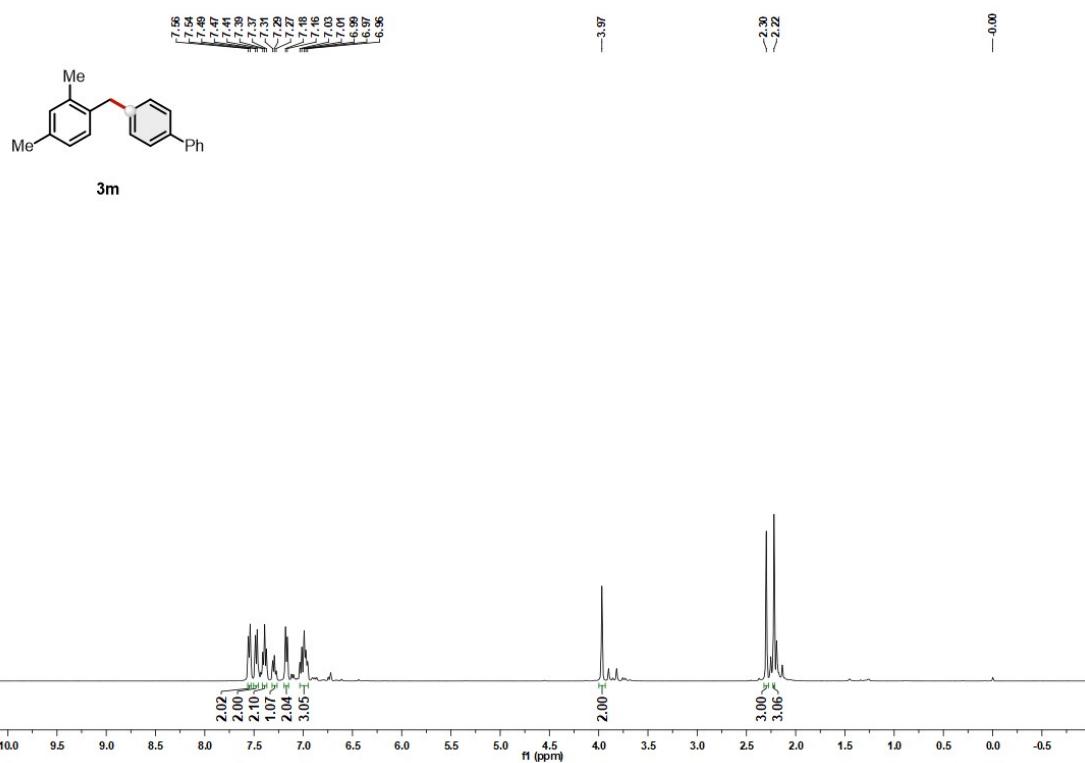


<sup>13</sup>C NMR of **3l**  
CDCl<sub>3</sub>, 101 MHz, 298 K



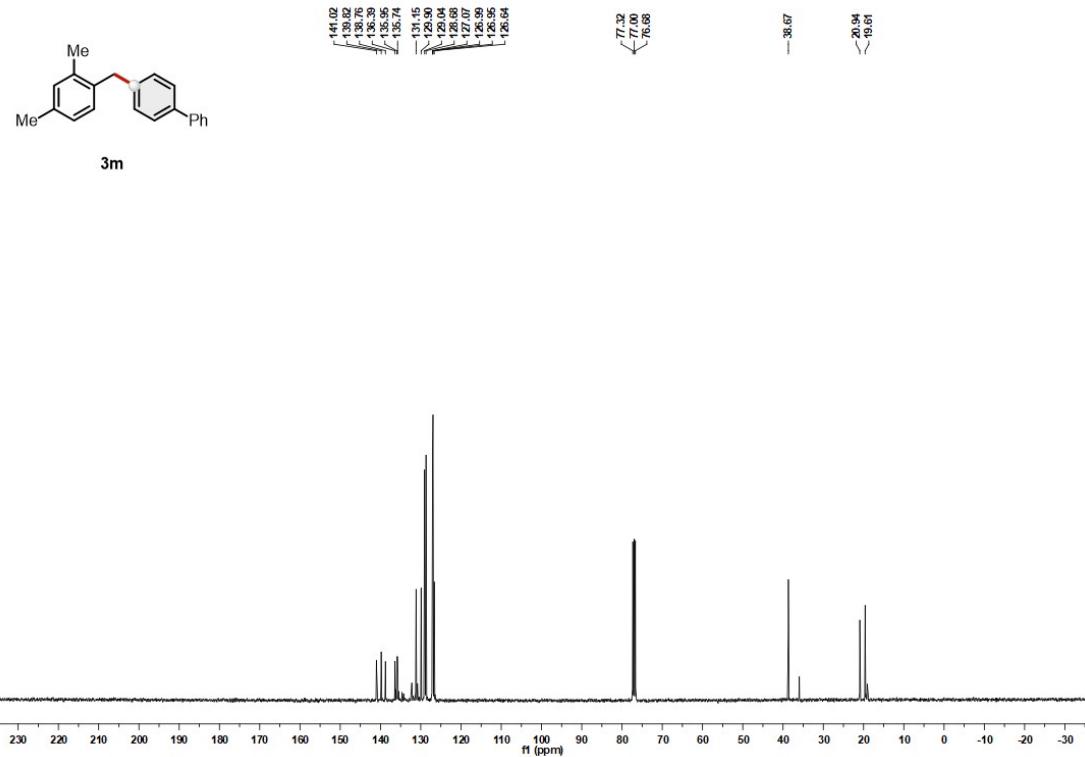
### <sup>1</sup>H NMR of 3m

CDCl<sub>3</sub>, 400 MHz, 298 K



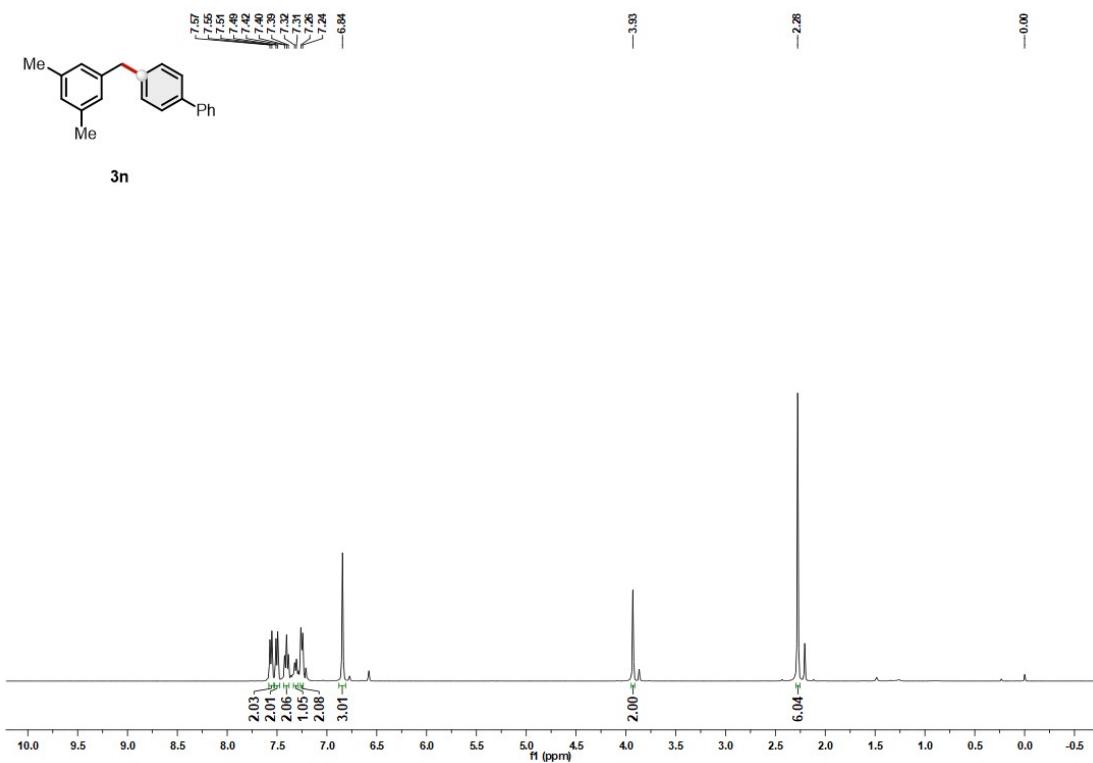
### <sup>13</sup>C NMR of 3m

CDCl<sub>3</sub>, 101 MHz, 298 K



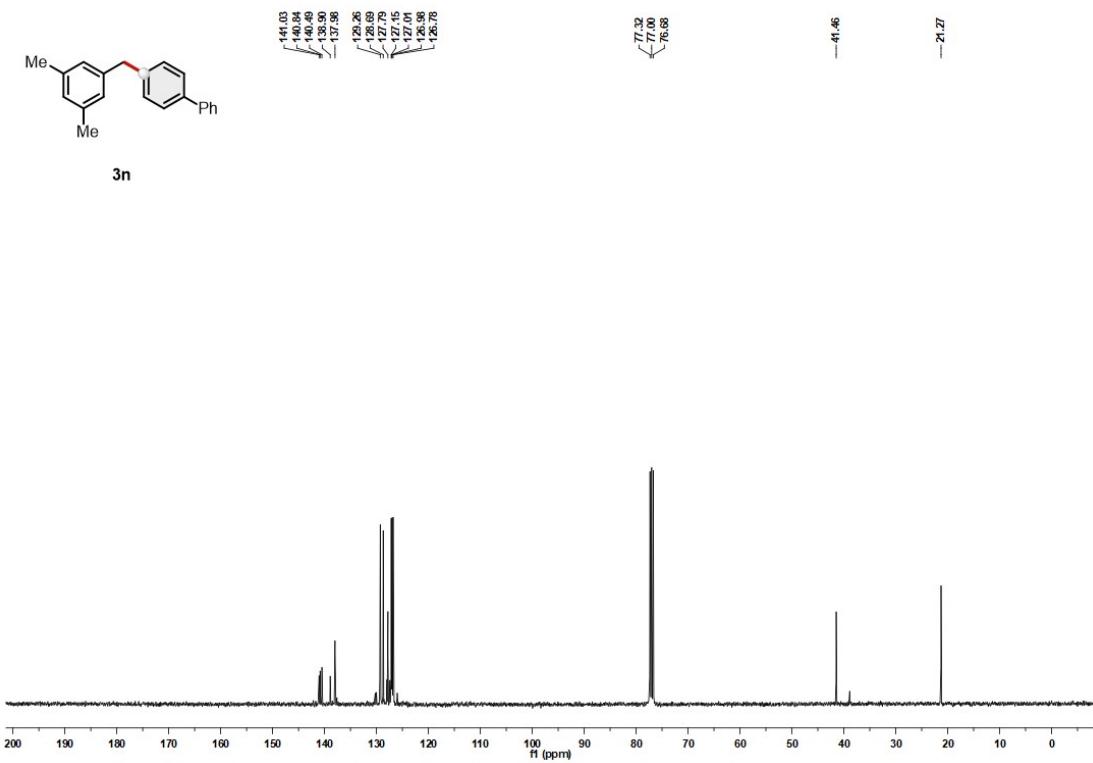
<sup>1</sup>H NMR of **3n**

CDCl<sub>3</sub>, 400 MHz, 298 K



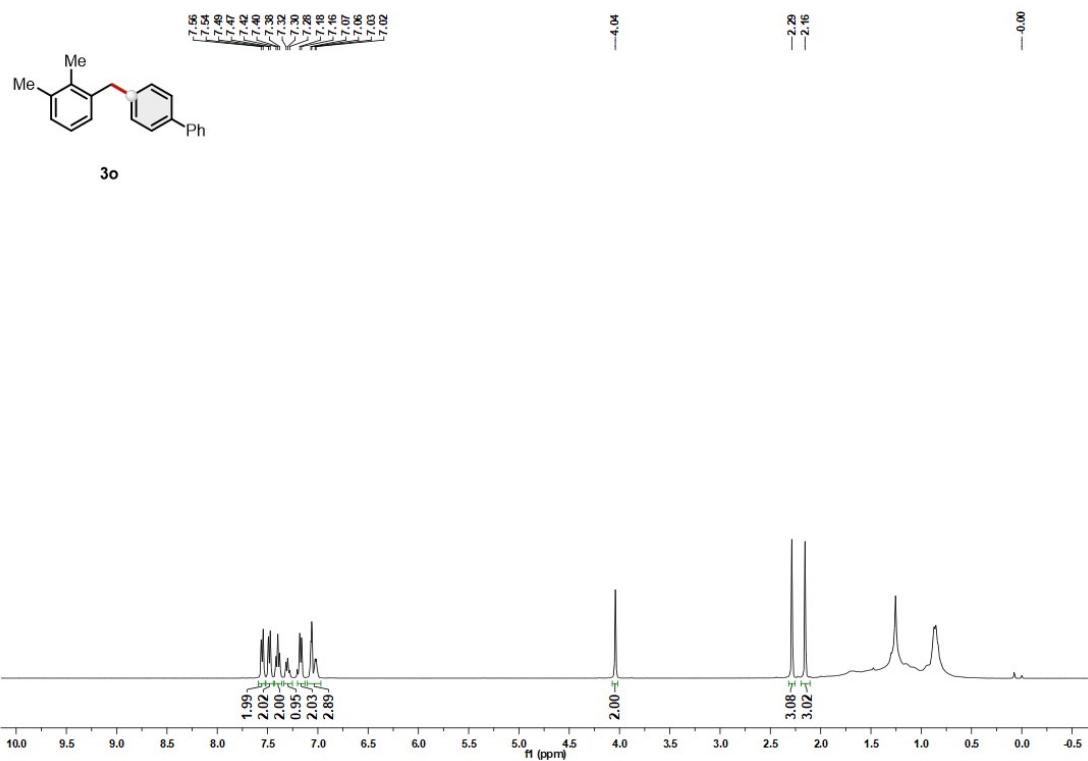
<sup>13</sup>C NMR of **3n**

CDCl<sub>3</sub>, 101 MHz, 298 K



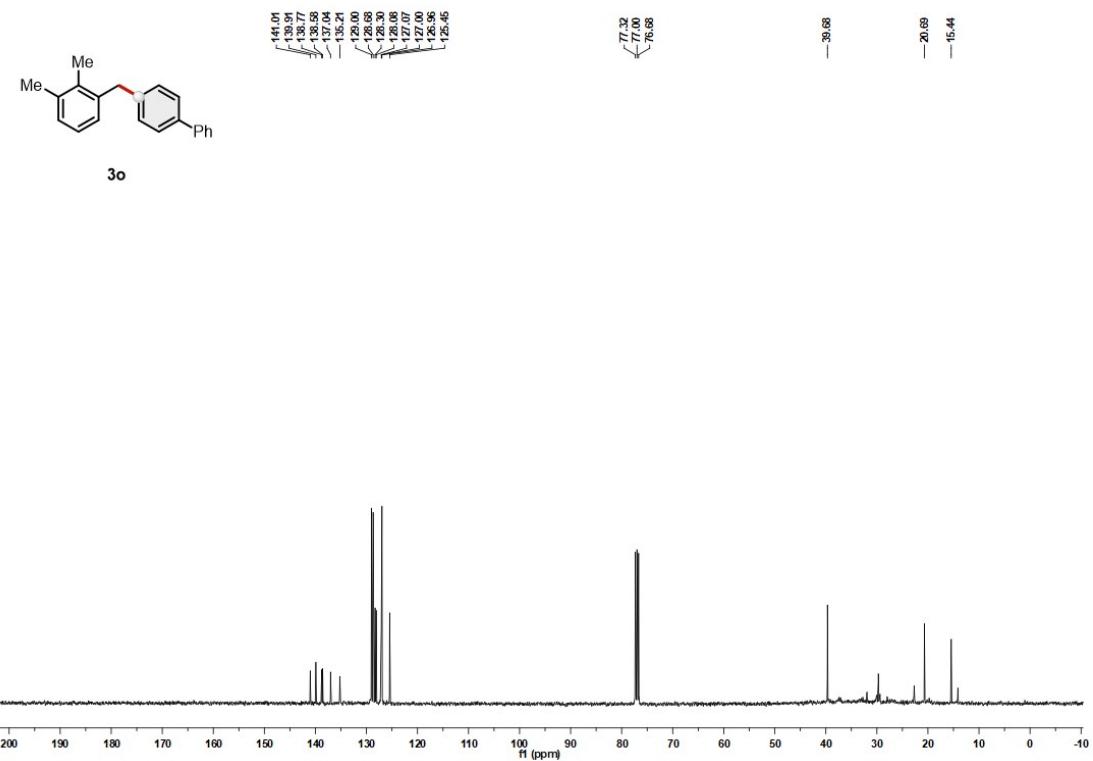
<sup>1</sup>H NMR of **3o**

CDCl<sub>3</sub>, 400 MHz, 298 K

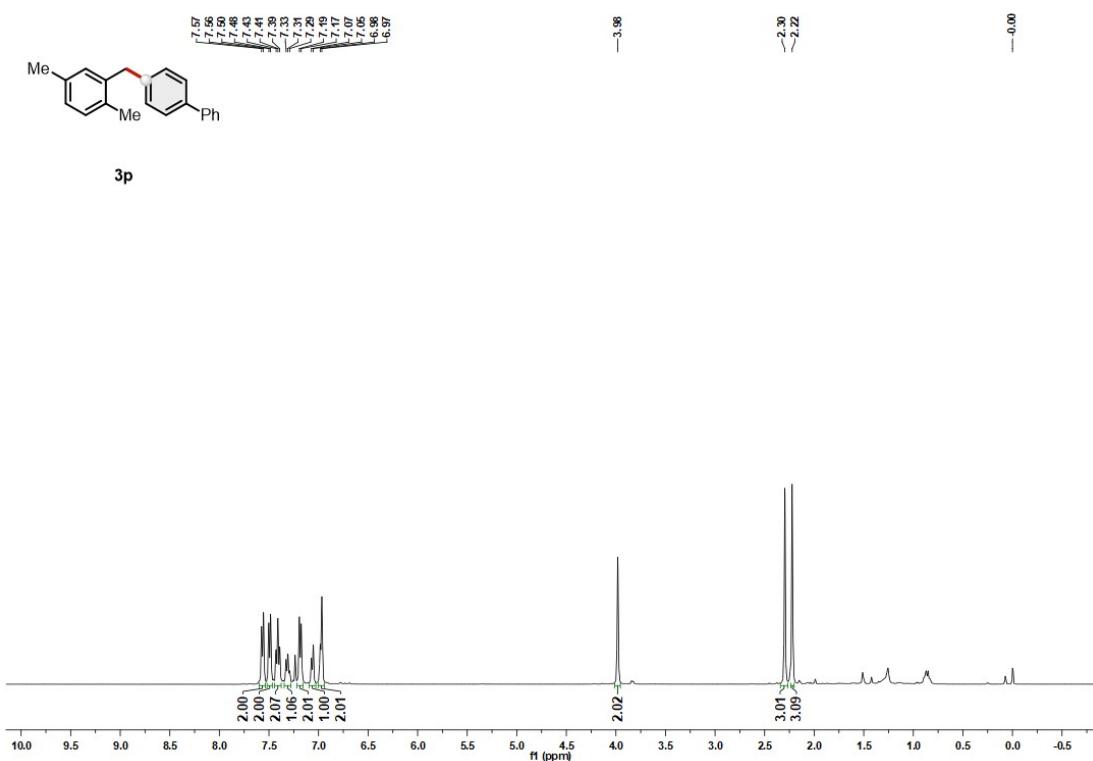


<sup>13</sup>C NMR of **3o**

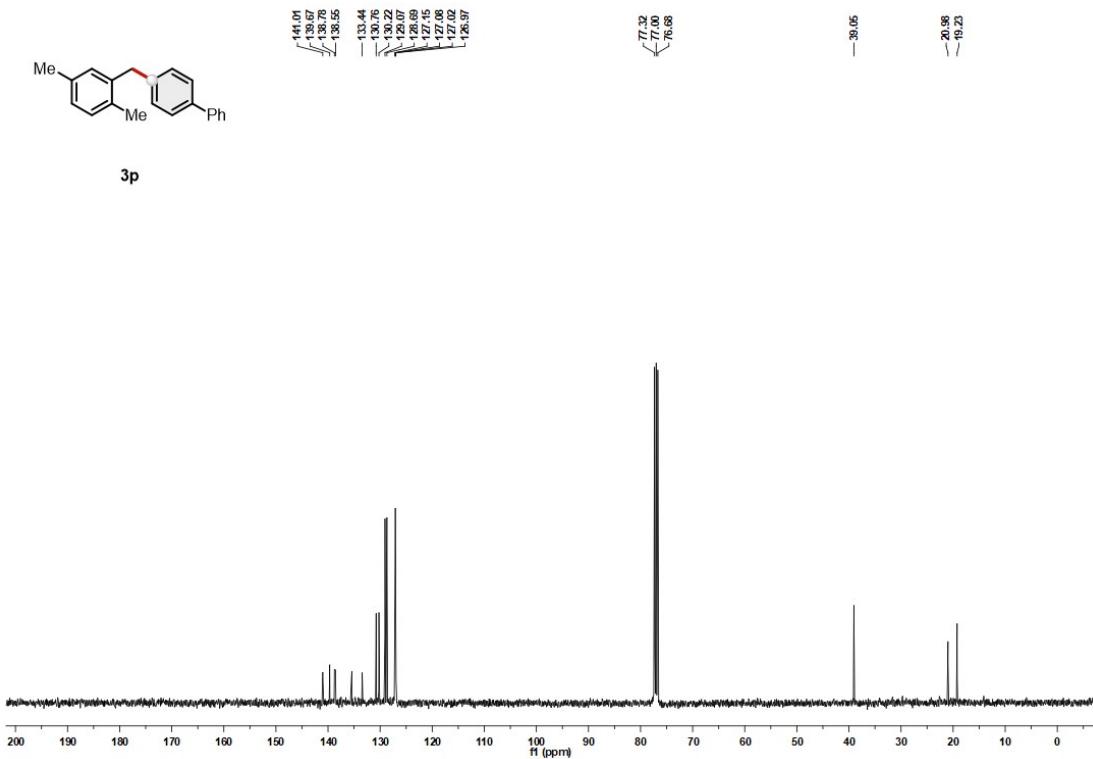
CDCl<sub>3</sub>, 101 MHz, 298 K



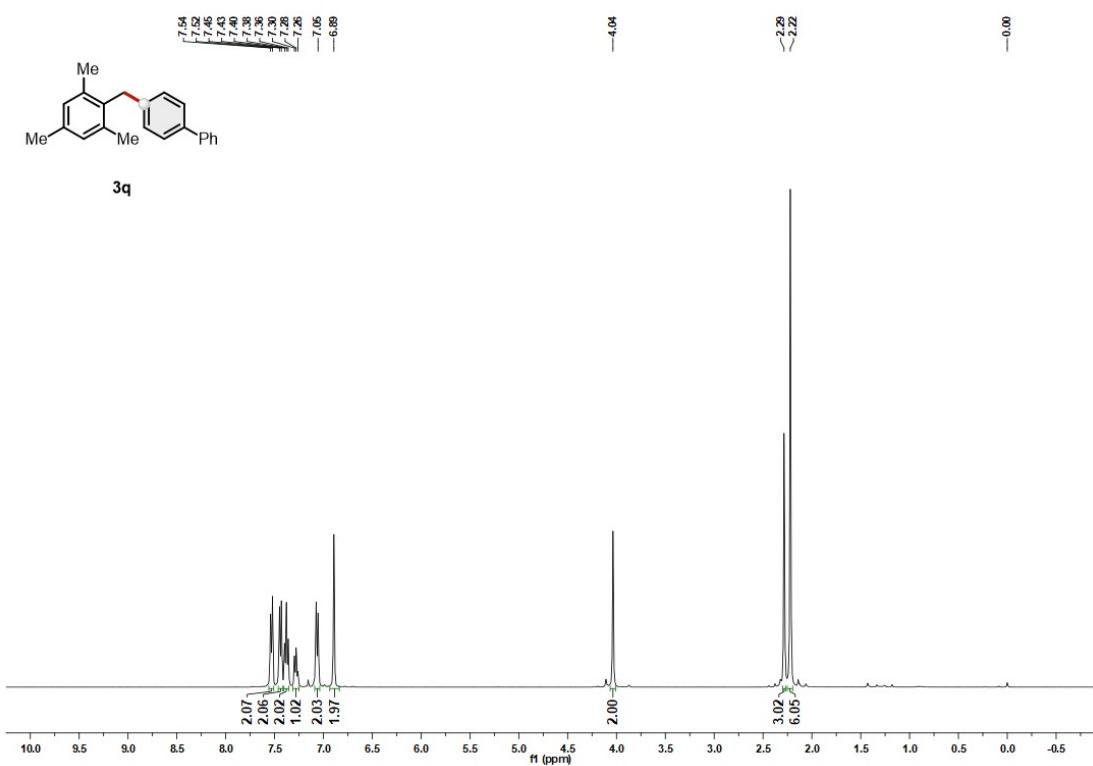
<sup>1</sup>H NMR of **3p**  
 $\text{CDCl}_3$ , 400 MHz, 298 K



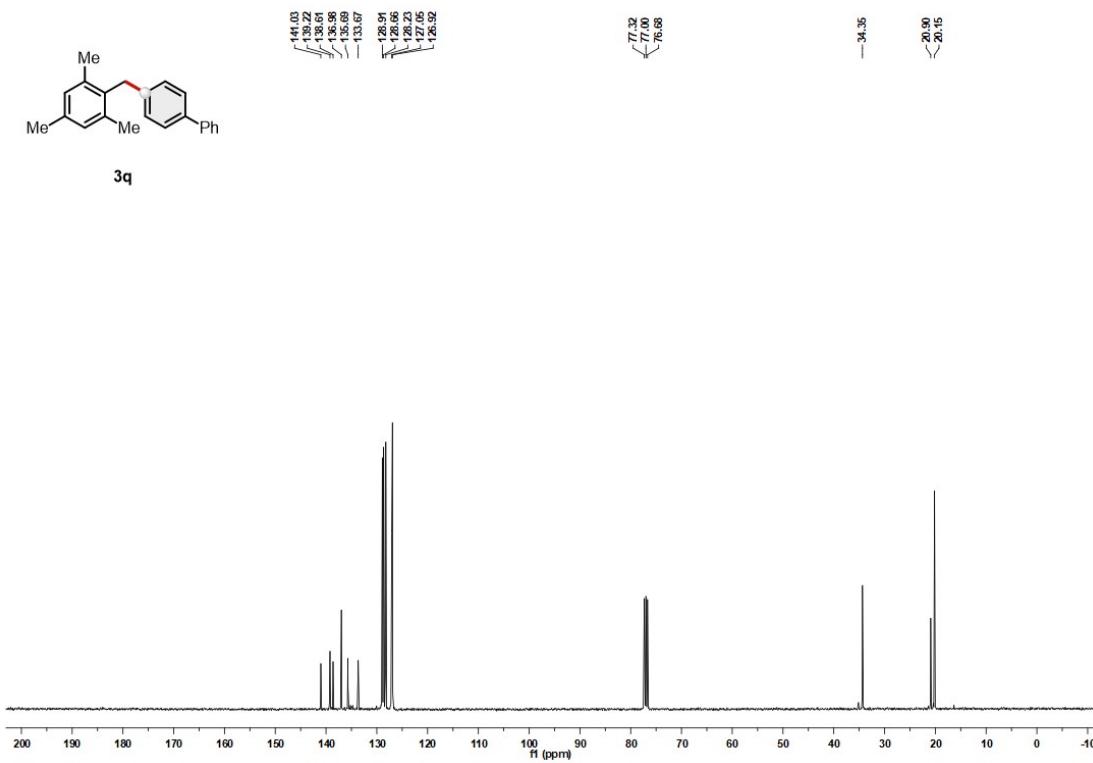
<sup>13</sup>C NMR of **3p**  
 $\text{CDCl}_3$ , 101 MHz, 298 K



<sup>1</sup>H NMR of **3q**  
 $\text{CDCl}_3$ , 400 MHz, 298 K

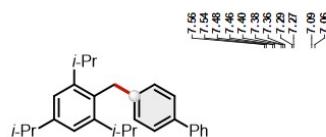


<sup>13</sup>C NMR of **3q**  
 $\text{CDCl}_3$ , 101 MHz, 298 K

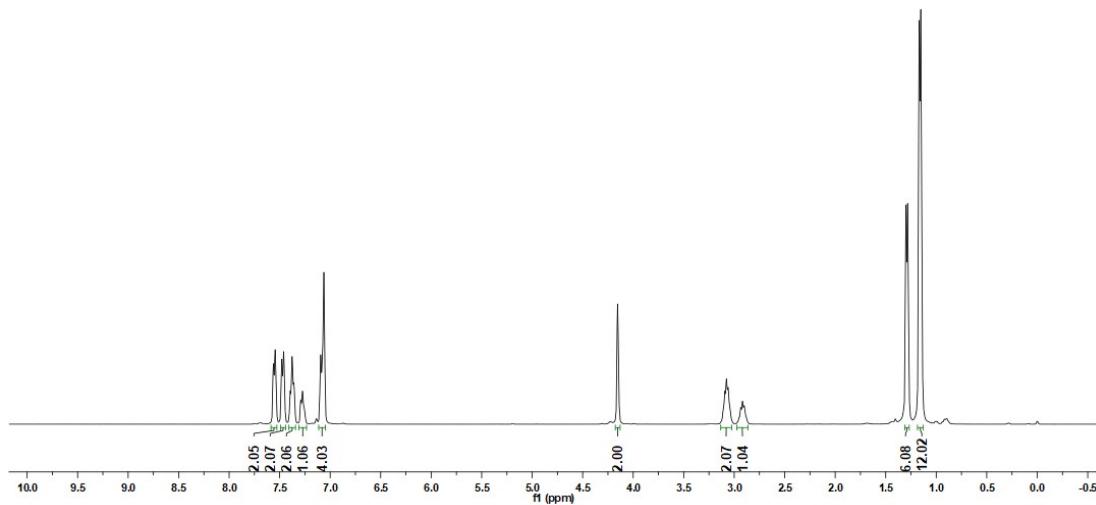


### <sup>1</sup>H NMR of 3r

CDCl<sub>3</sub>, 400 MHz, 298 K

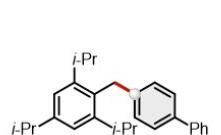


3r

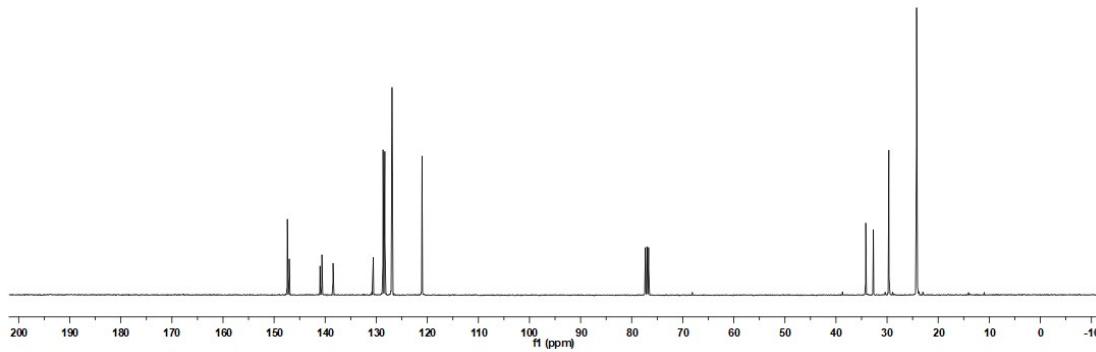


### <sup>13</sup>C NMR of 3r

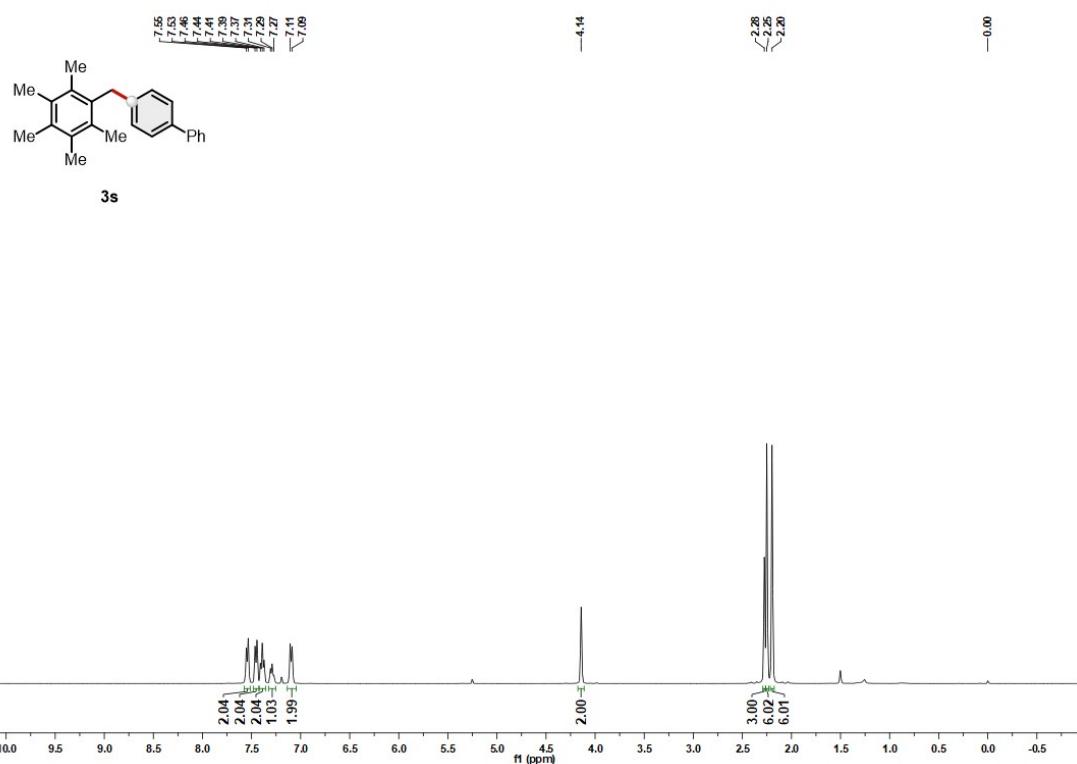
CDCl<sub>3</sub>, 101 MHz, 298 K



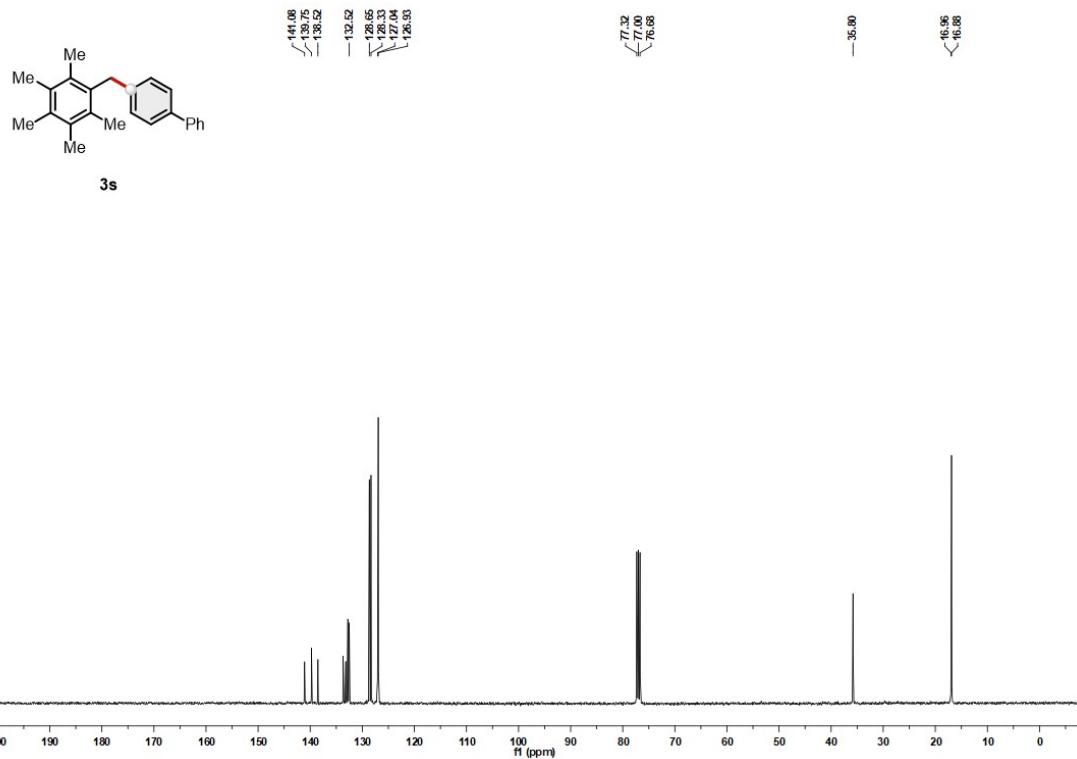
3r



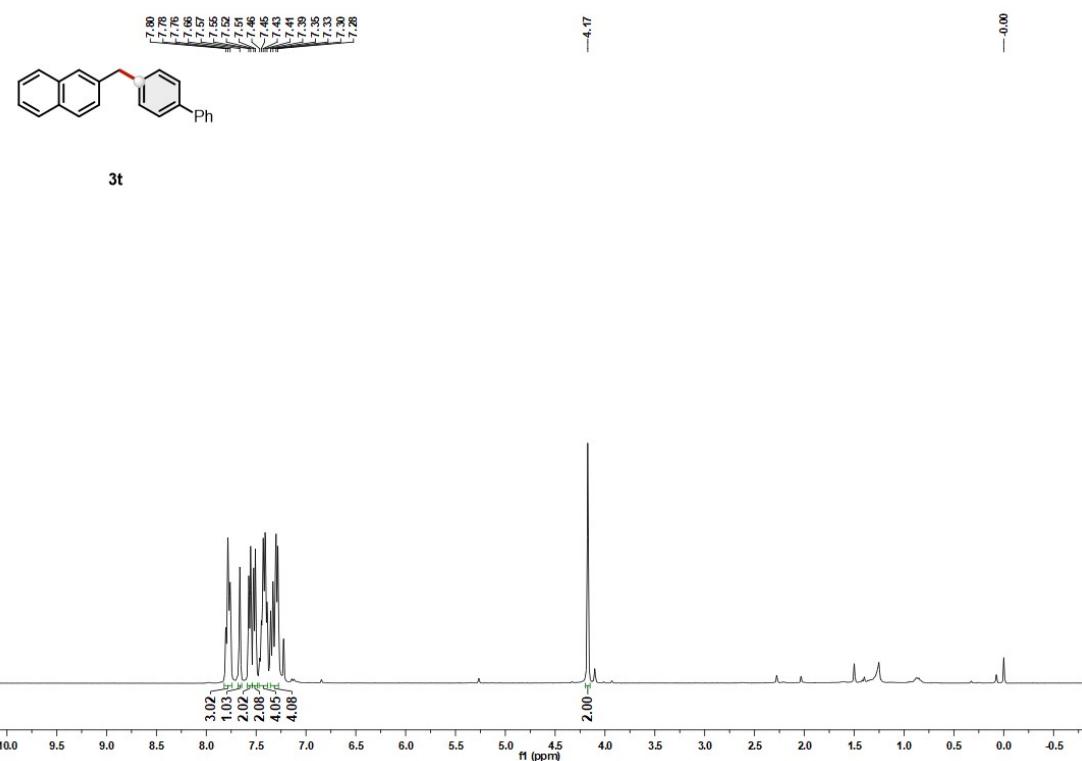
<sup>1</sup>H NMR of **3s**  
 $\text{CDCl}_3$ , 400 MHz, 298 K



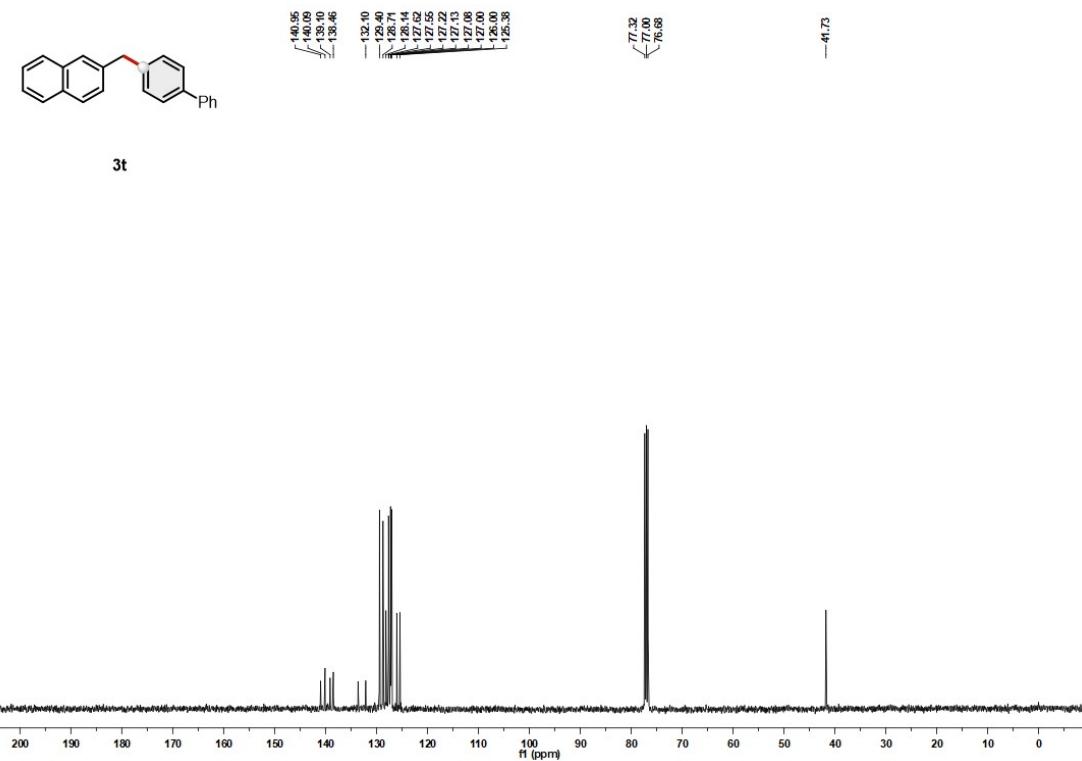
<sup>13</sup>C NMR of **3s**  
 $\text{CDCl}_3$ , 101 MHz, 298 K



<sup>1</sup>H NMR of **3t**  
 $\text{CDCl}_3$ , 400 MHz, 298 K

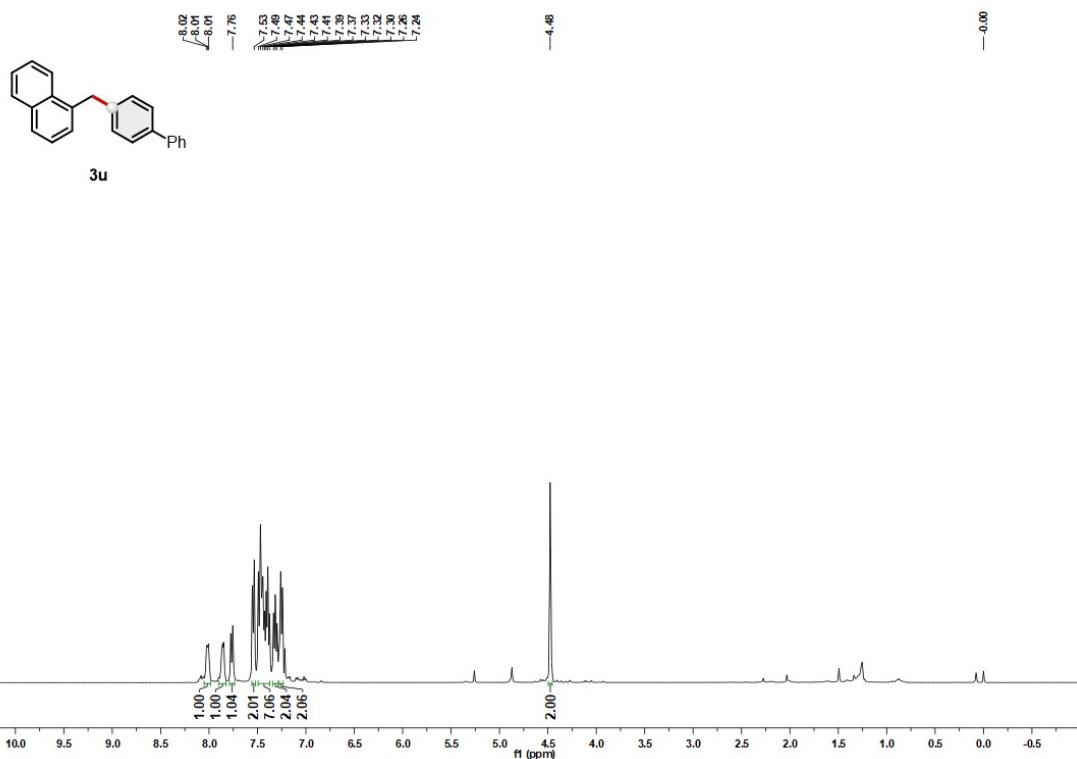


<sup>13</sup>C NMR of **3t**  
 $\text{CDCl}_3$ , 101 MHz, 298 K



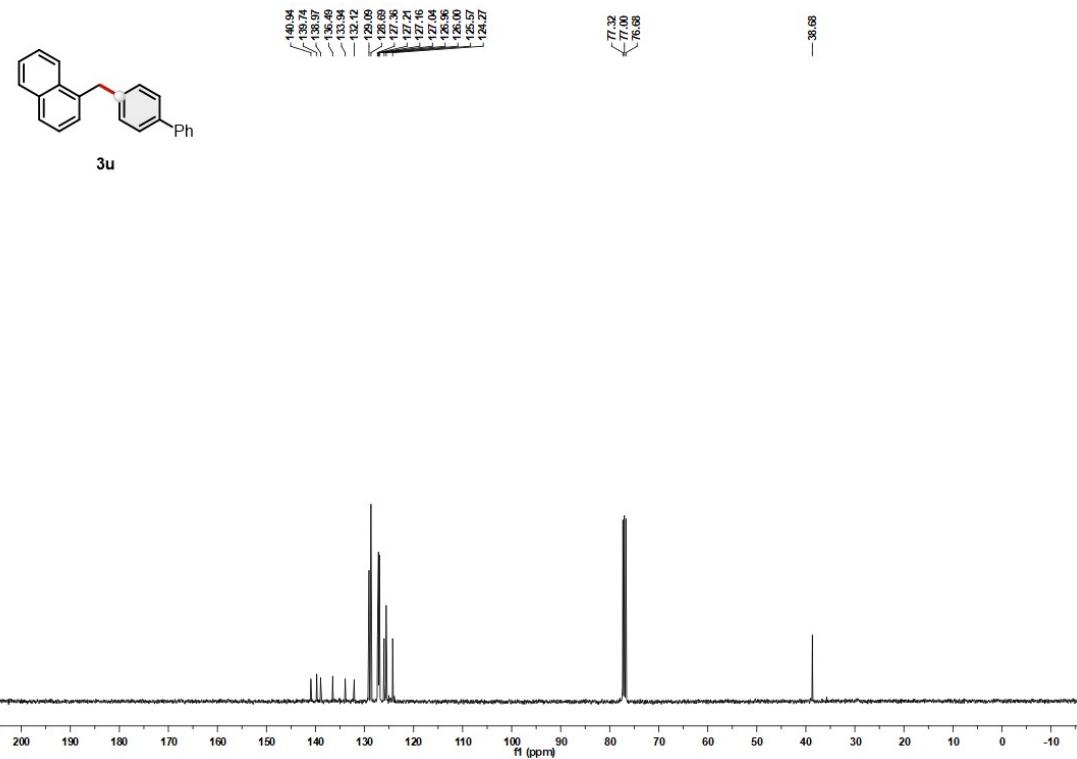
<sup>1</sup>H NMR of **3u**

CDCl<sub>3</sub>, 400 MHz, 298 K



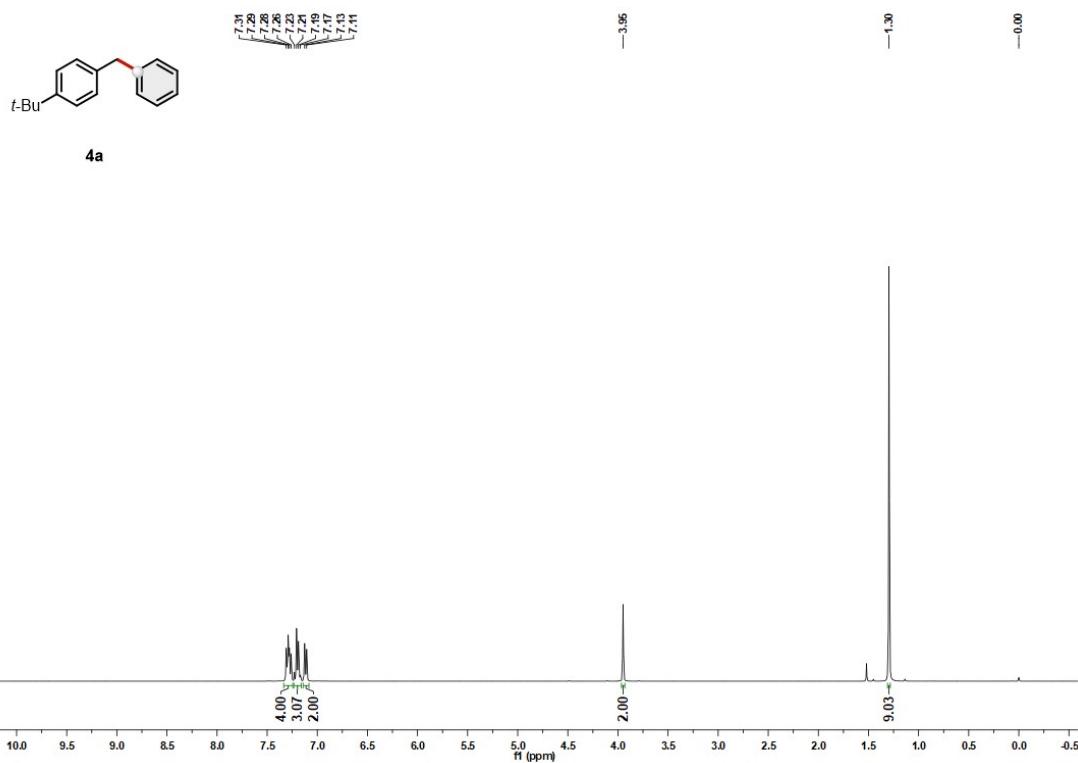
<sup>13</sup>C NMR of **3u**

CDCl<sub>3</sub>, 101 MHz, 298 K



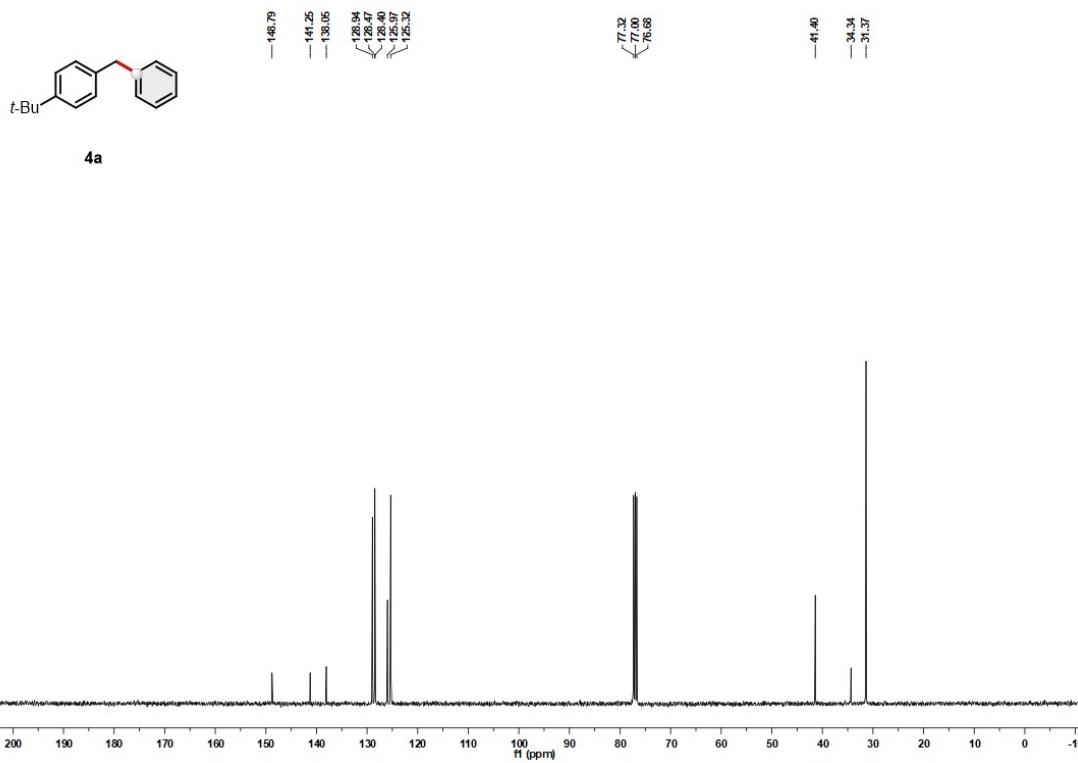
<sup>1</sup>H NMR of **4a**

CDCl<sub>3</sub>, 400 MHz, 298 K



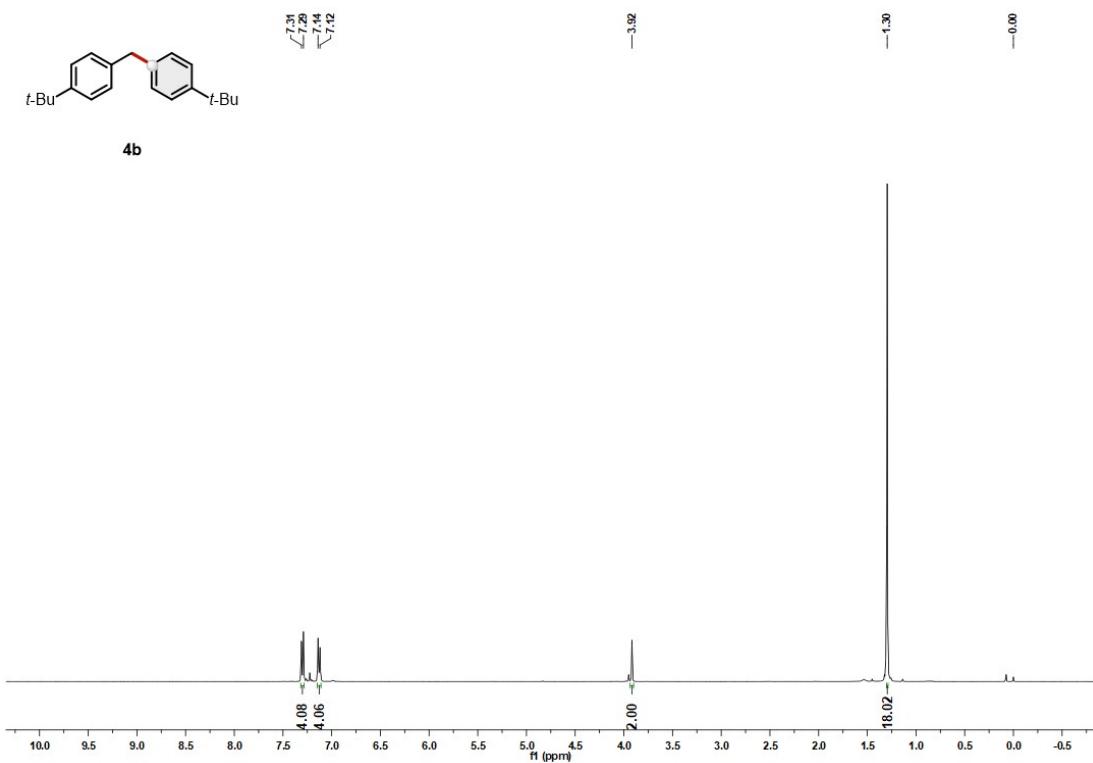
<sup>13</sup>C NMR of **4a**

CDCl<sub>3</sub>, 101 MHz, 298 K



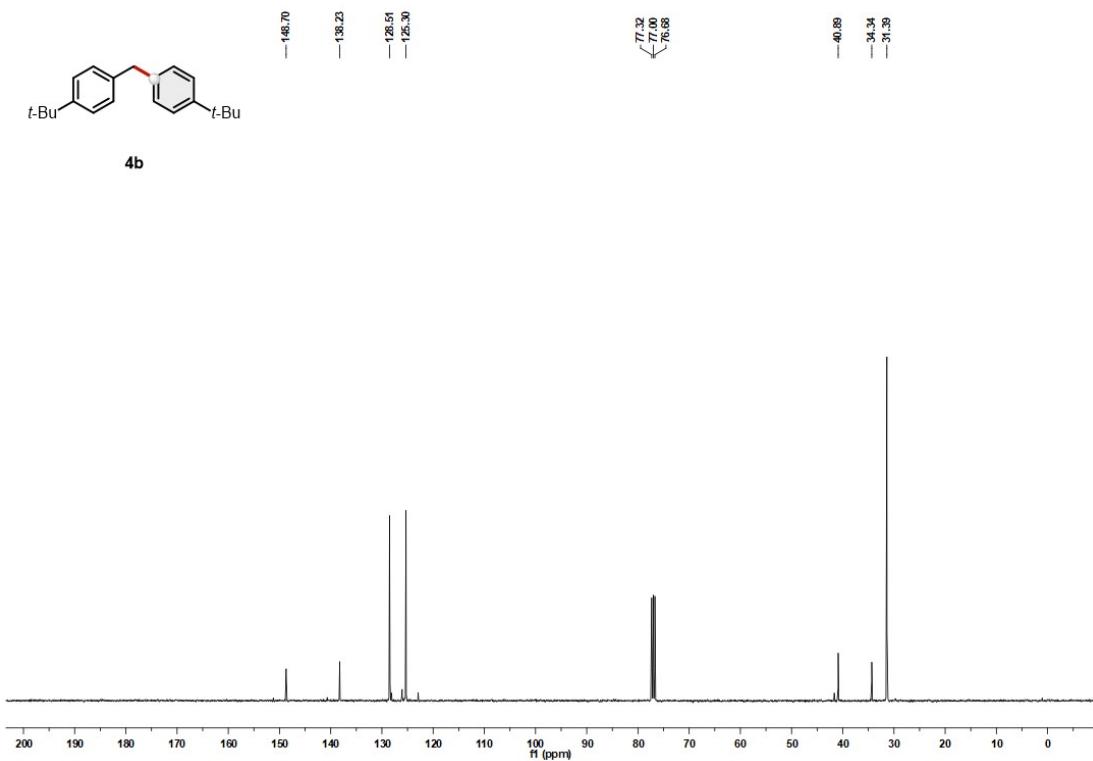
<sup>1</sup>H NMR of **4b**

CDCl<sub>3</sub>, 400 MHz, 298 K

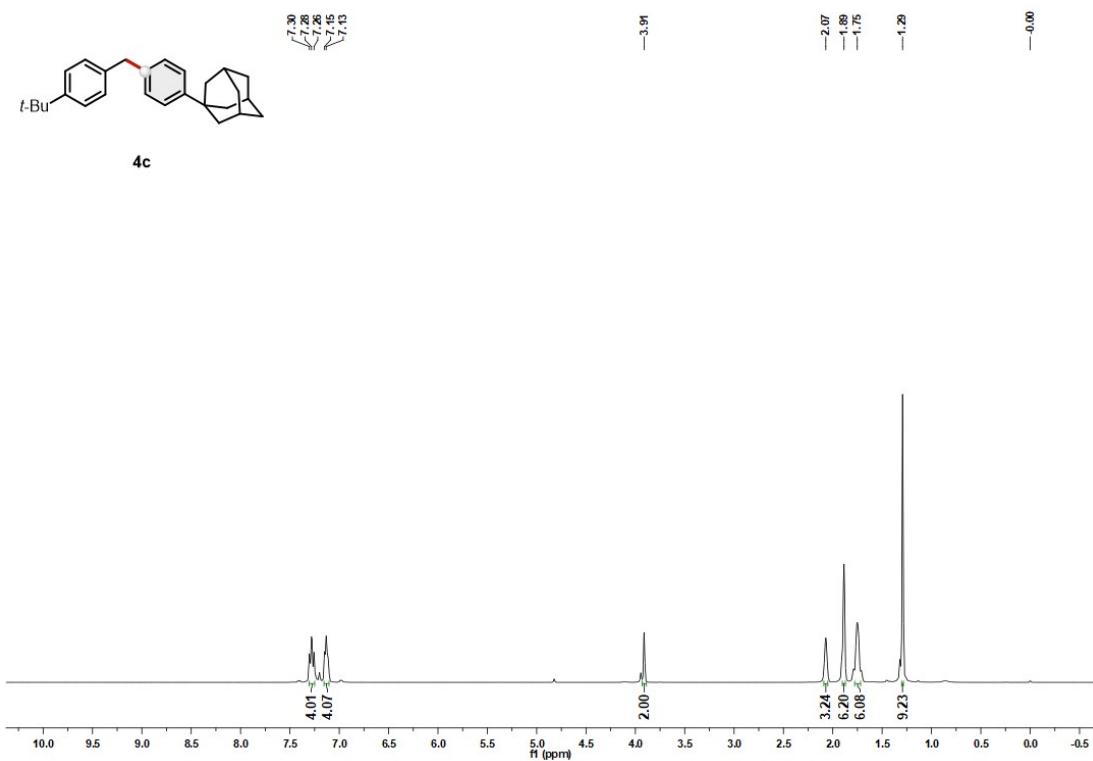


<sup>13</sup>C NMR of **4b**

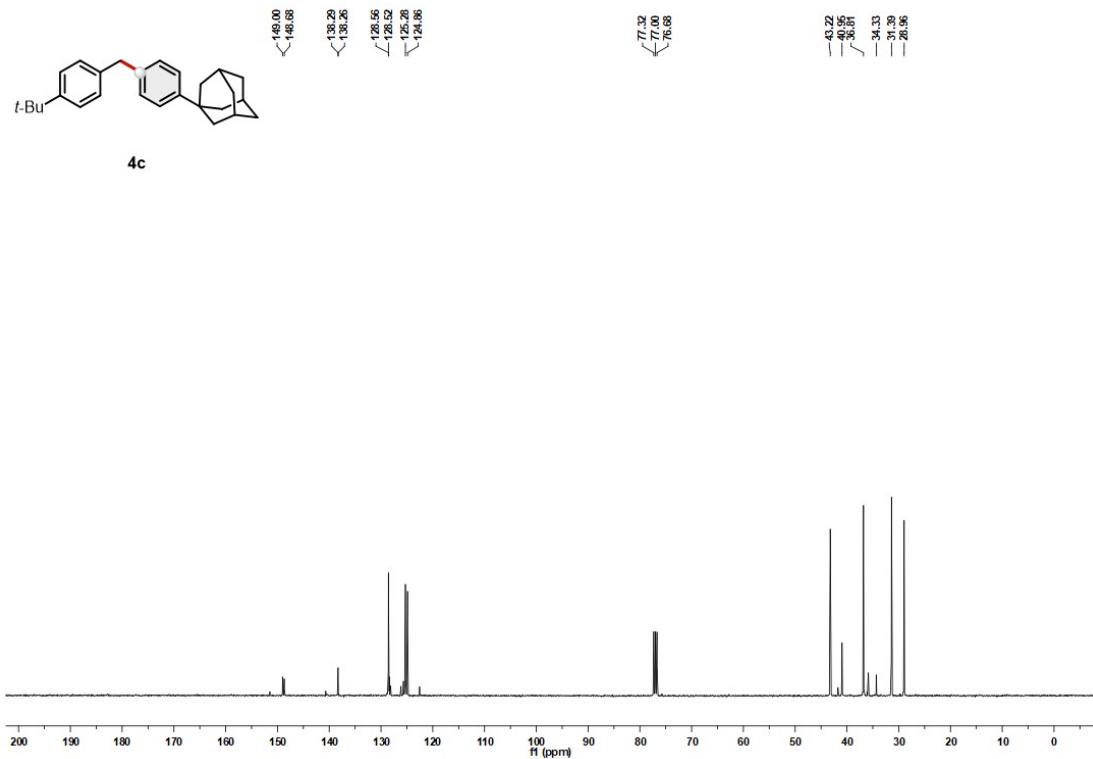
CDCl<sub>3</sub>, 101 MHz, 298 K



<sup>1</sup>H NMR of **4c**  
CDCl<sub>3</sub>, 400 MHz, 298 K

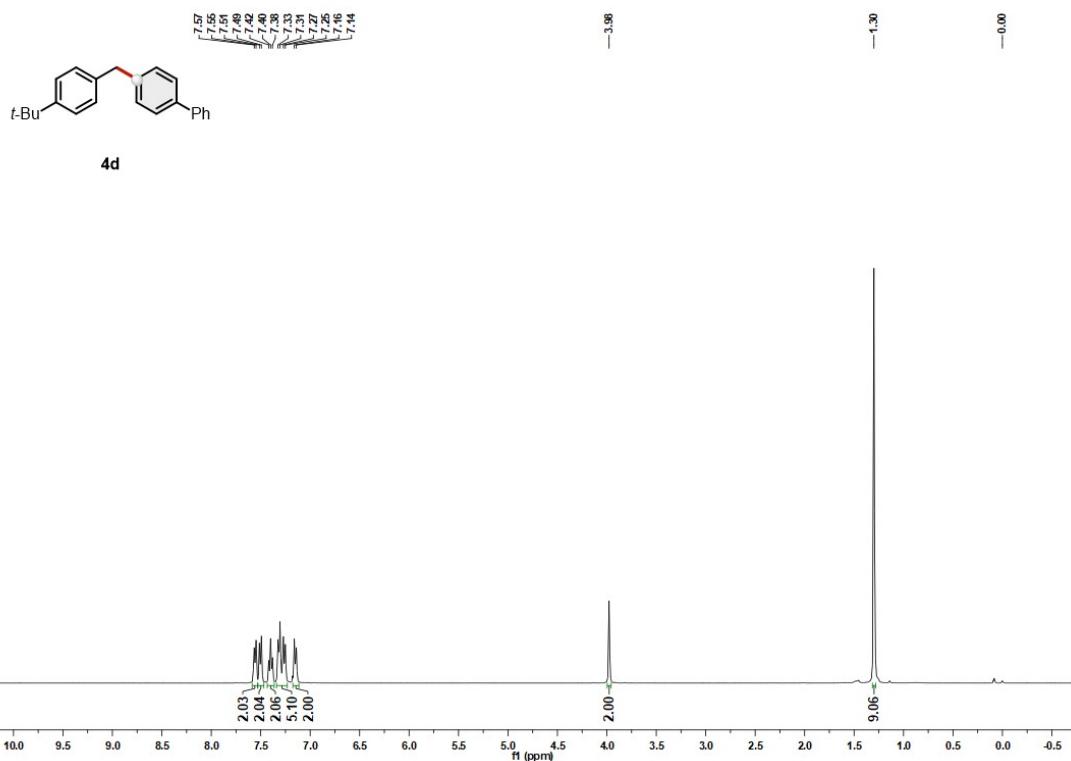


<sup>13</sup>C NMR of **4c**  
CDCl<sub>3</sub>, 101 MHz, 298 K



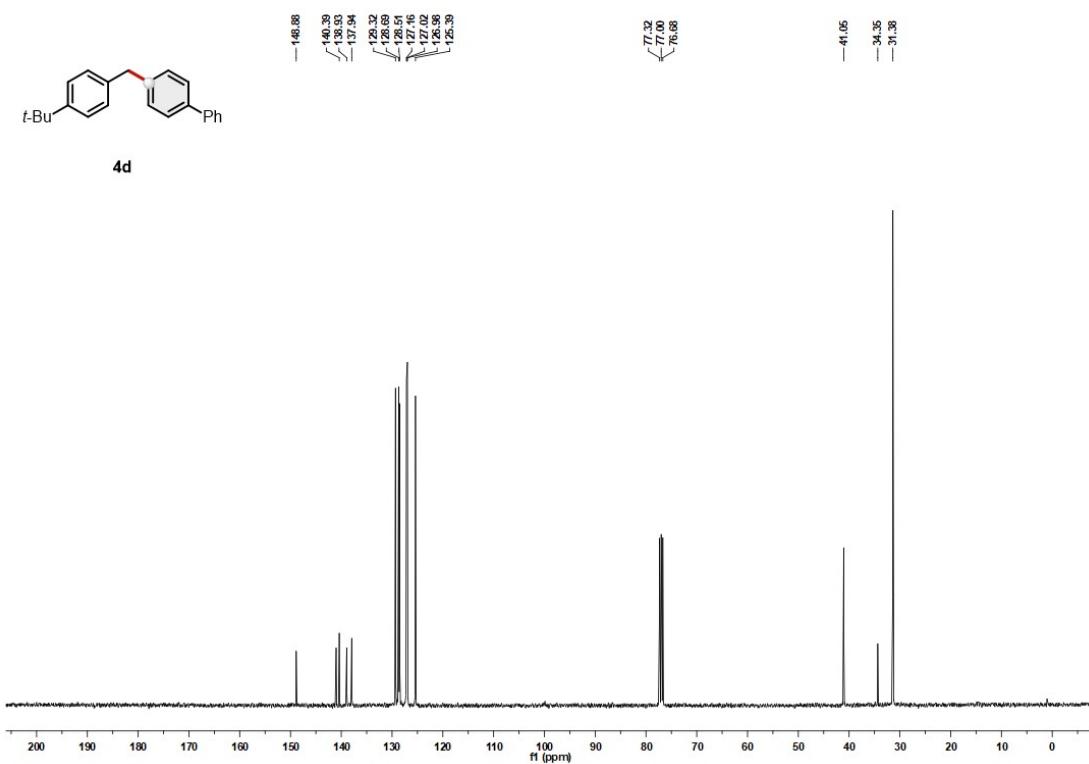
<sup>1</sup>H NMR of **4d**

CDCl<sub>3</sub>, 400 MHz, 298 K



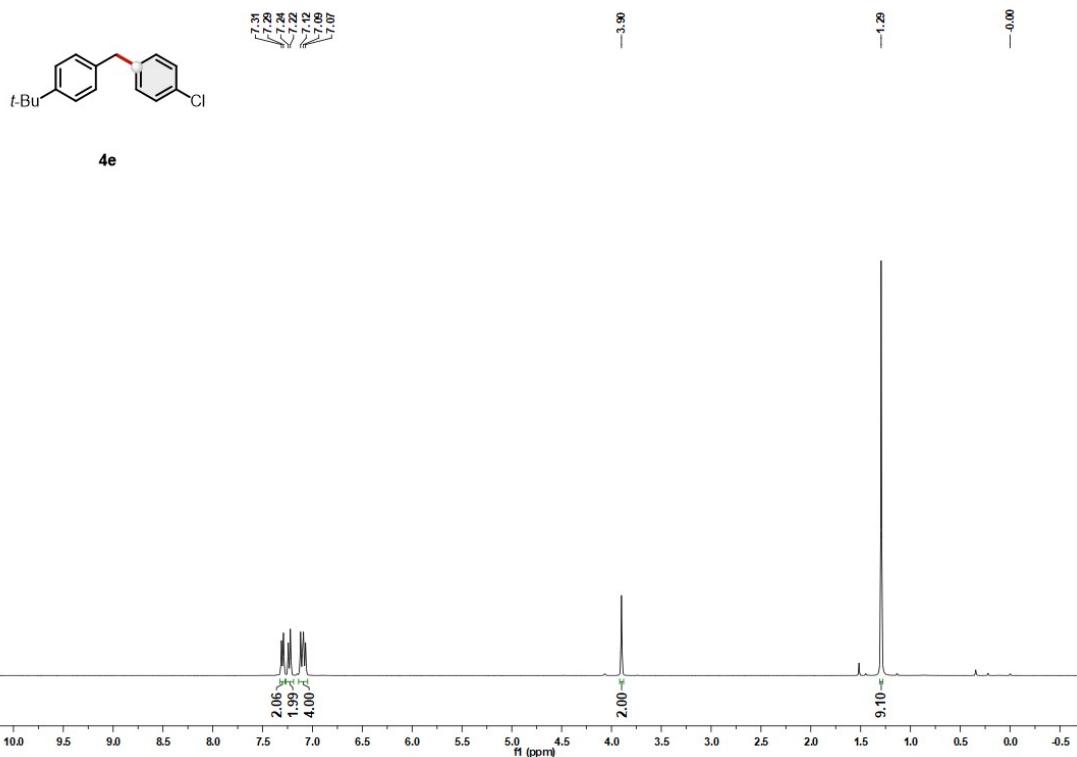
<sup>13</sup>C NMR of **4d**

CDCl<sub>3</sub>, 101 MHz, 298 K



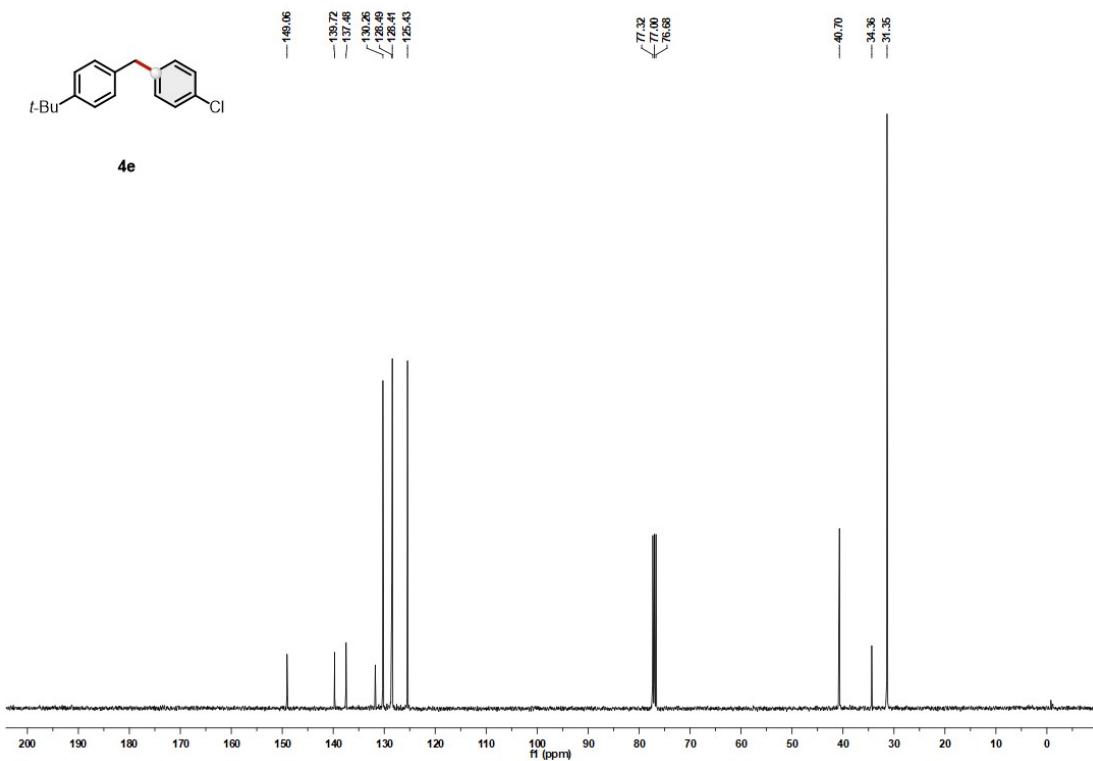
<sup>1</sup>H NMR of **4e**

CDCl<sub>3</sub>, 400 MHz, 298 K



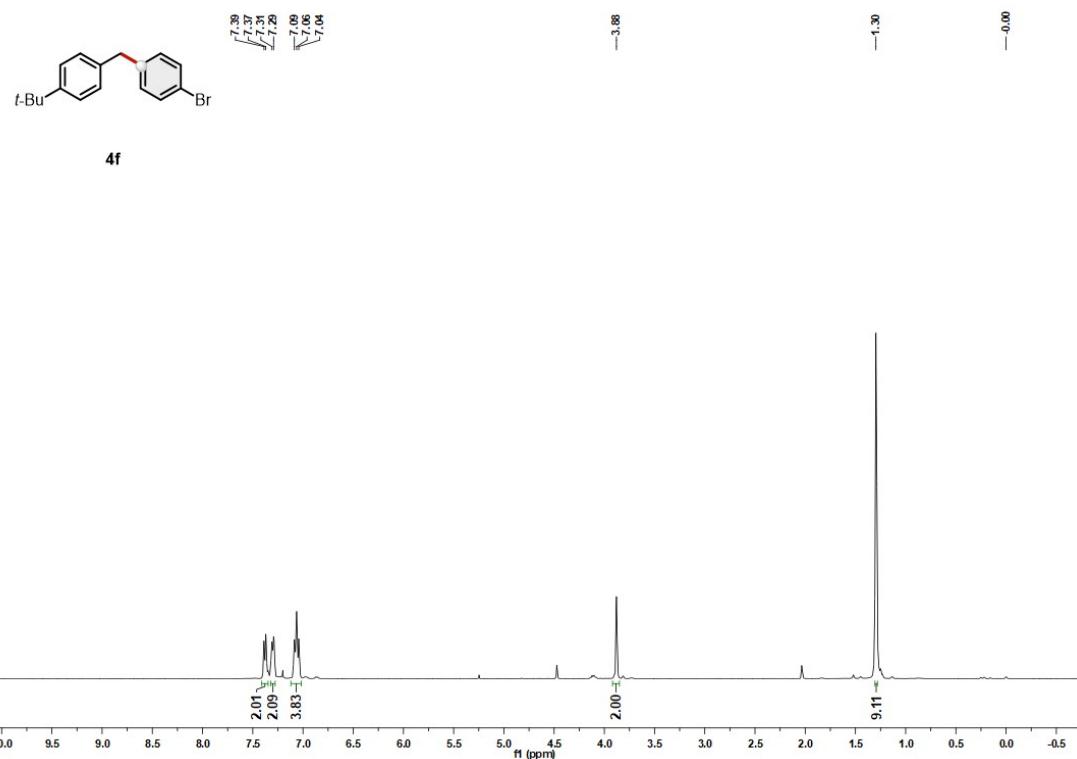
<sup>13</sup>C NMR of **4e**

CDCl<sub>3</sub>, 101 MHz, 298 K



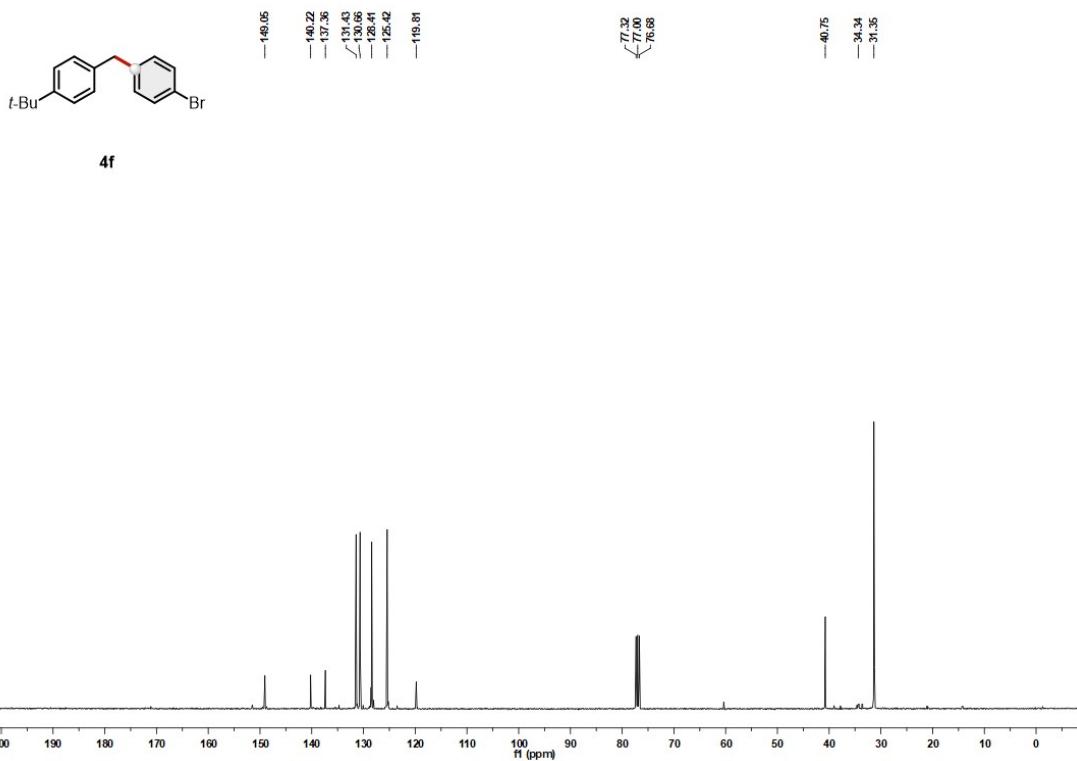
<sup>1</sup>H NMR of **4f**

CDCl<sub>3</sub>, 400 MHz, 298 K

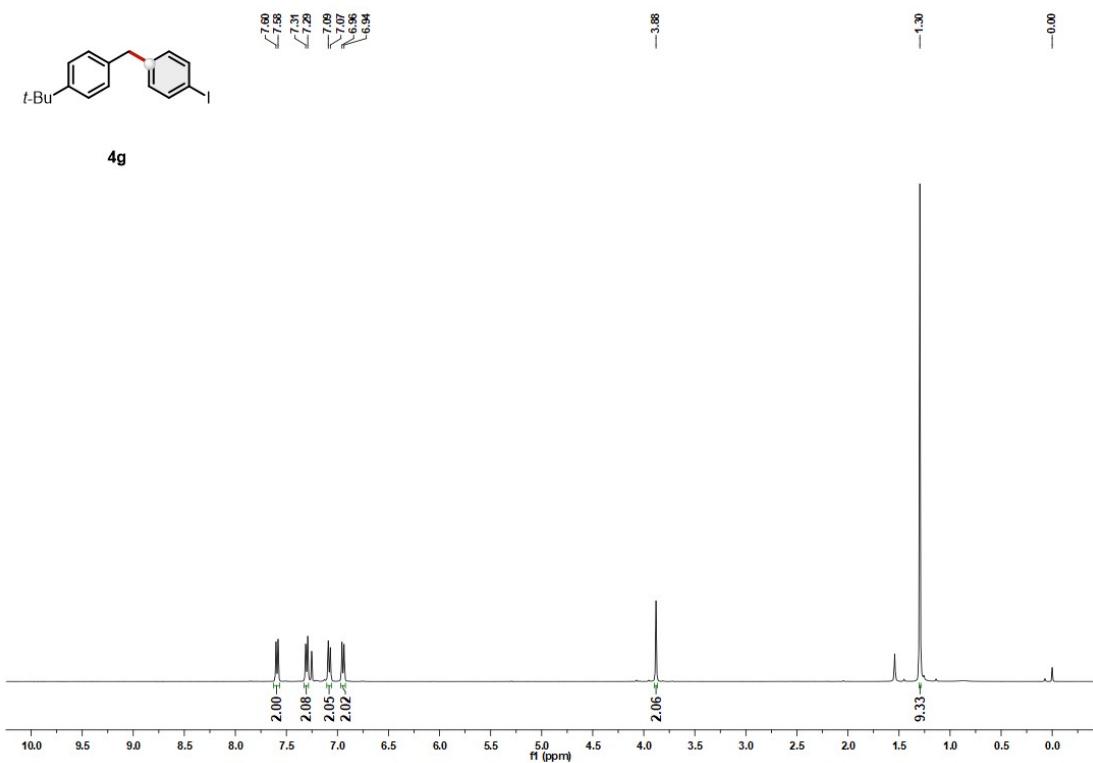


<sup>13</sup>C NMR of **4f**

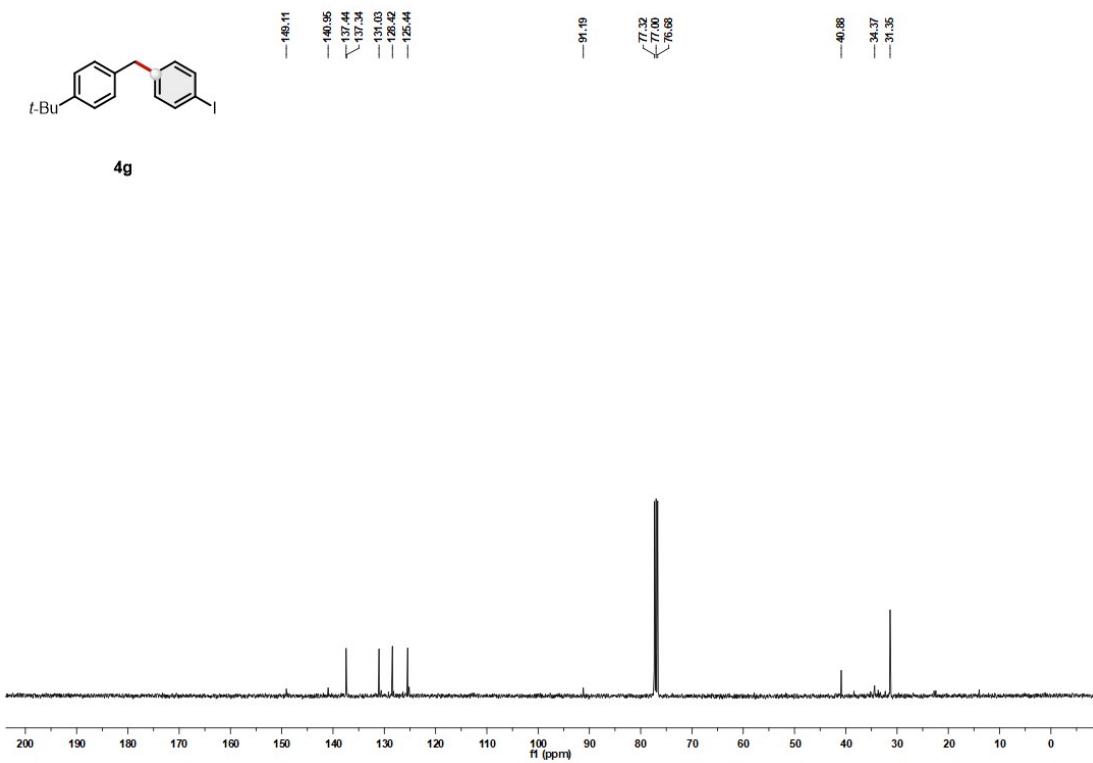
CDCl<sub>3</sub>, 101 MHz, 298 K



<sup>1</sup>H NMR of **4g**  
CDCl<sub>3</sub>, 400 MHz, 298 K

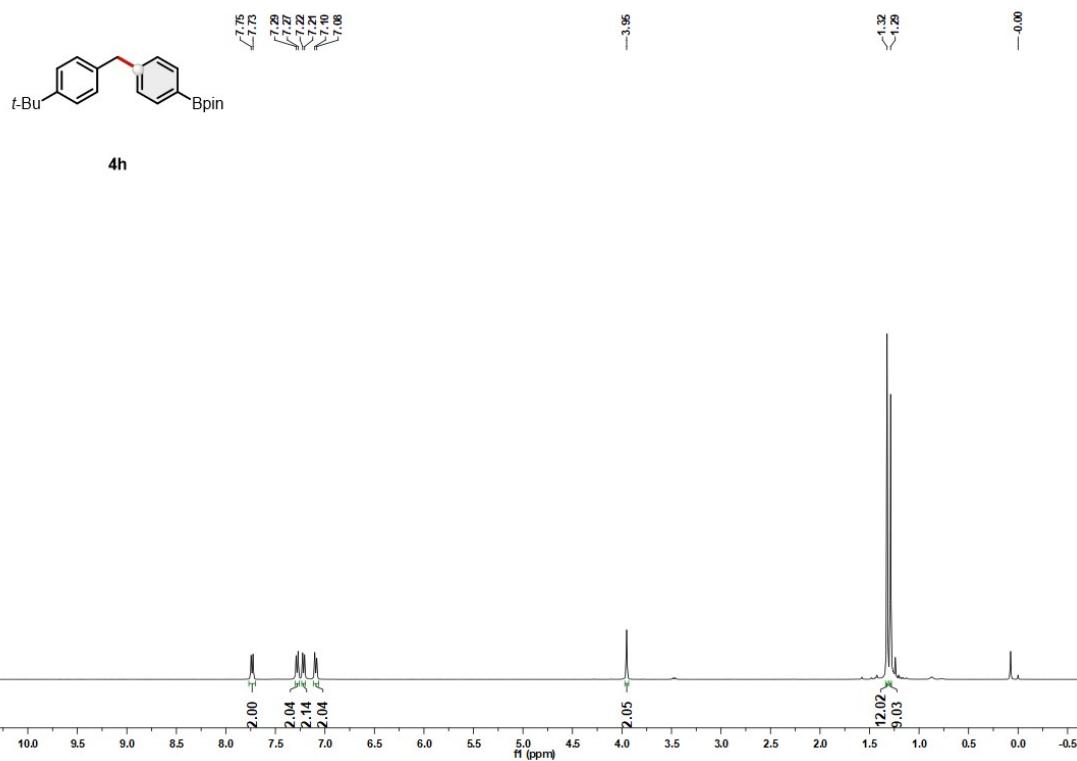


<sup>13</sup>C NMR of **4g**  
CDCl<sub>3</sub>, 101 MHz, 298 K



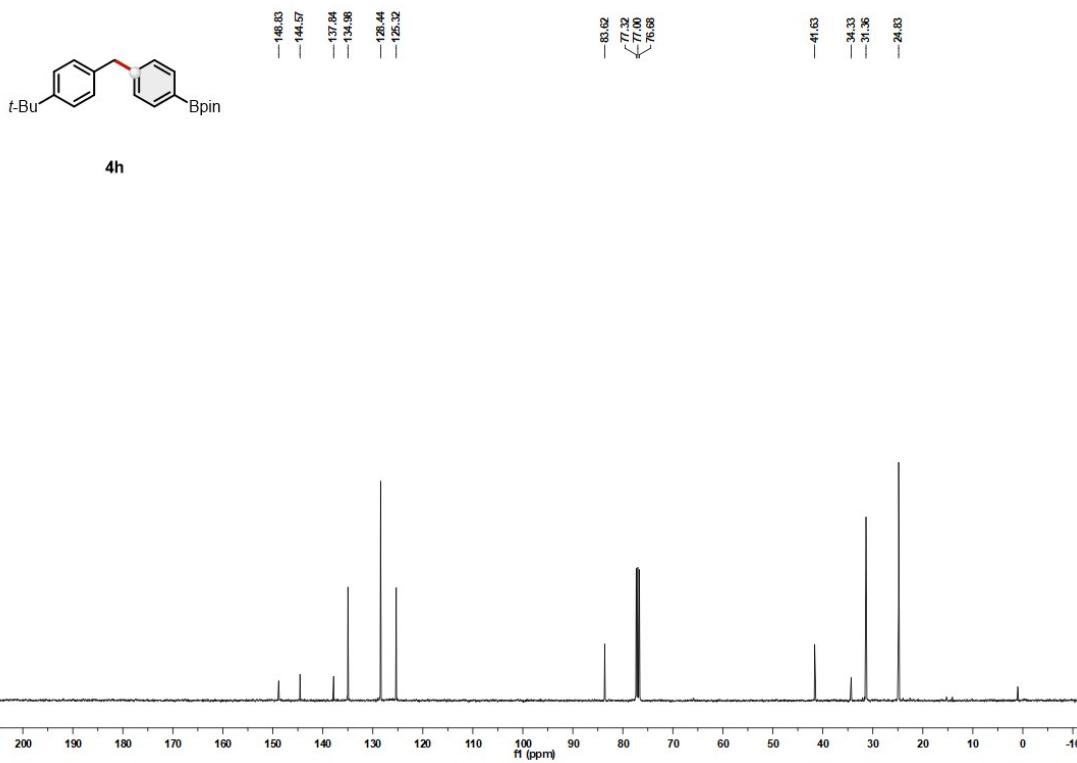
<sup>1</sup>H NMR of **4h**

CDCl<sub>3</sub>, 400 MHz, 298 K

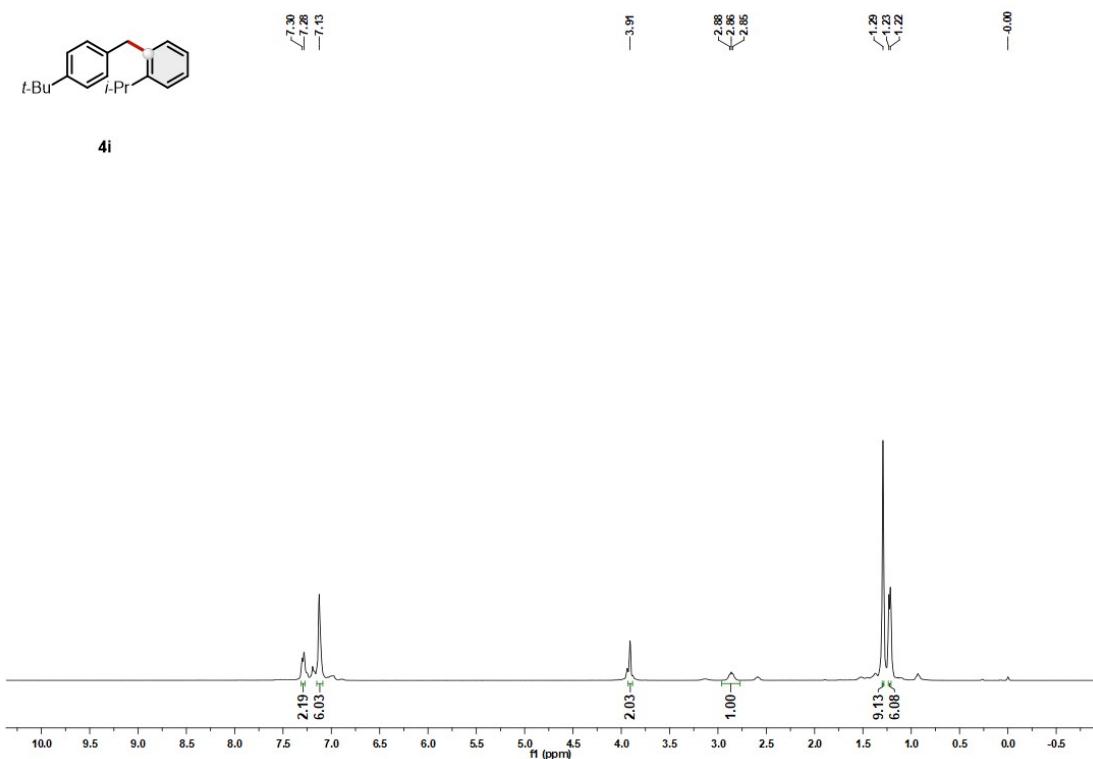


<sup>13</sup>C NMR of **4h**

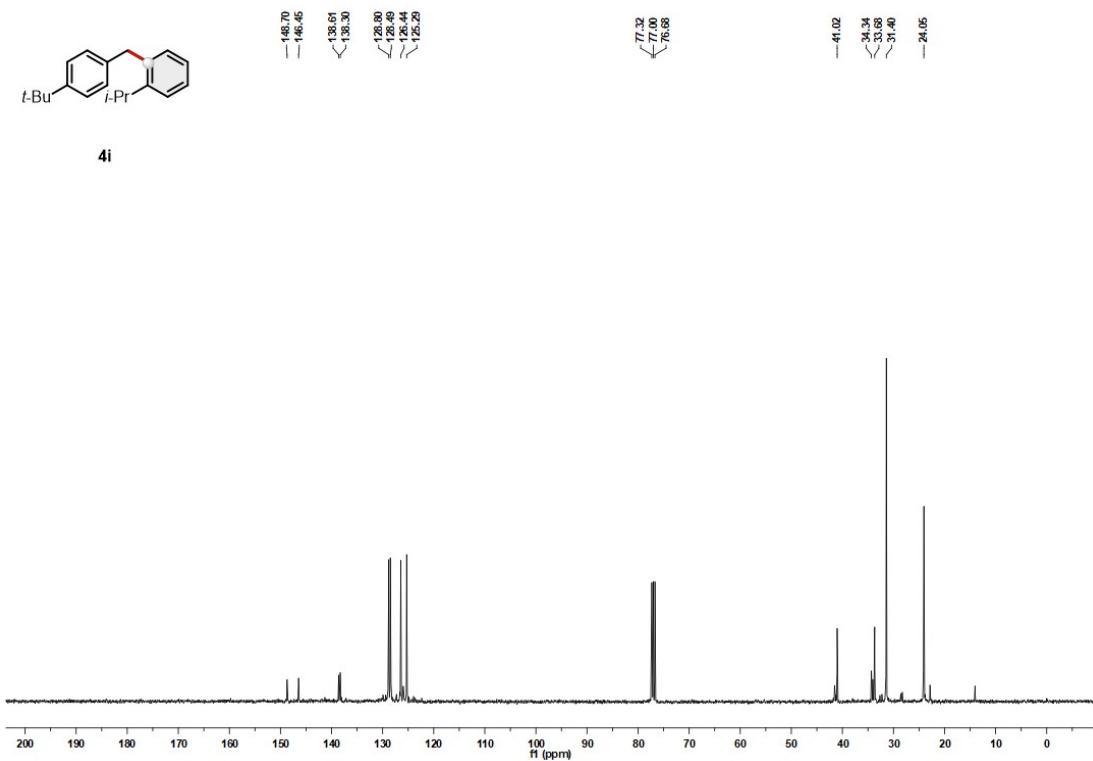
CDCl<sub>3</sub>, 101 MHz, 298 K



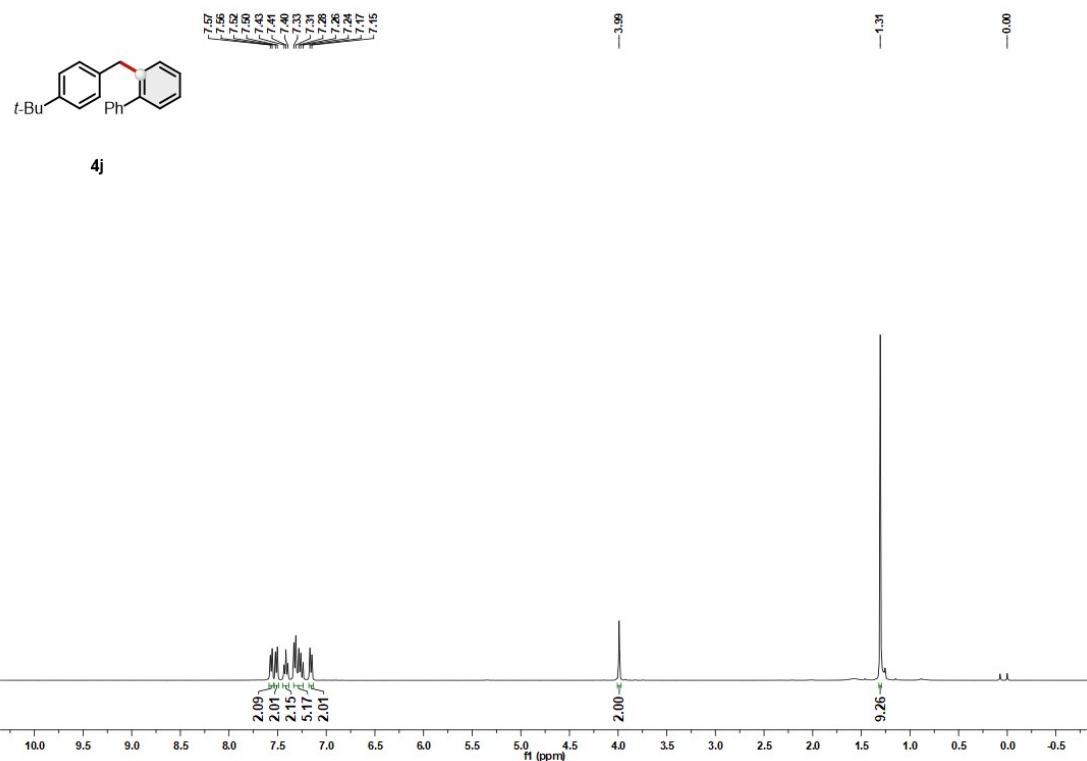
<sup>1</sup>H NMR of **4i**  
 $\text{CDCl}_3$ , 400 MHz, 298 K



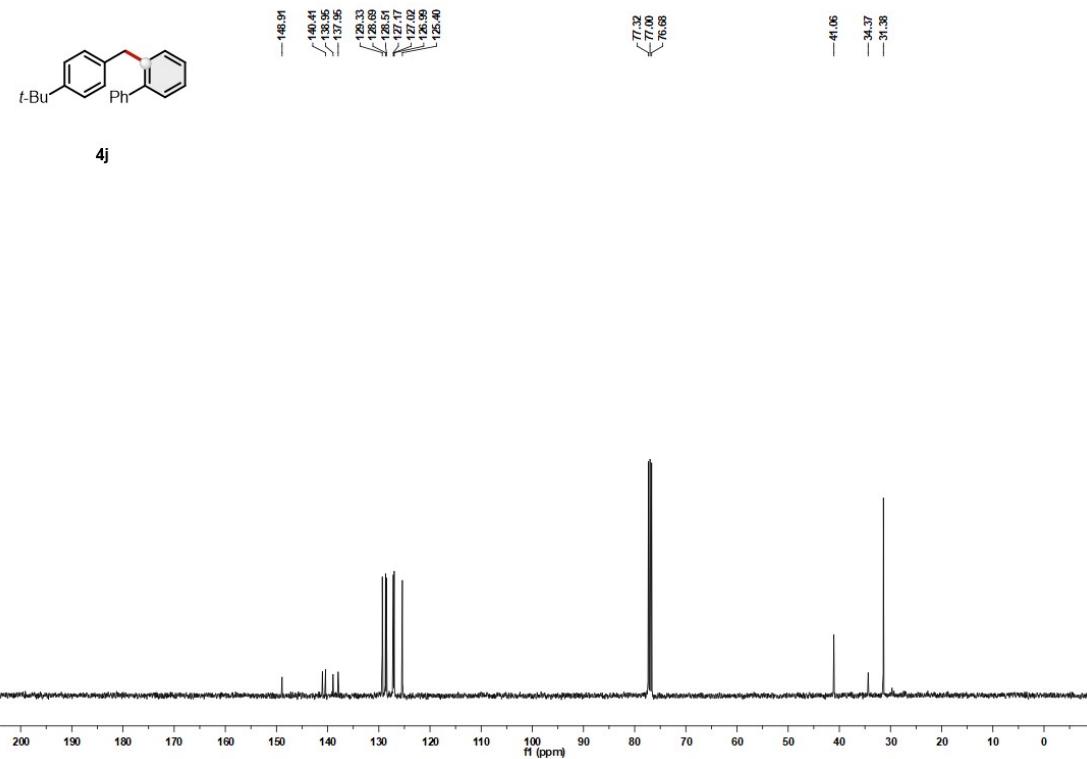
<sup>13</sup>C NMR of **4i**  
 $\text{CDCl}_3$ , 101 MHz, 298 K



<sup>1</sup>H NMR of **4j**  
 $\text{CDCl}_3$ , 400 MHz, 298 K

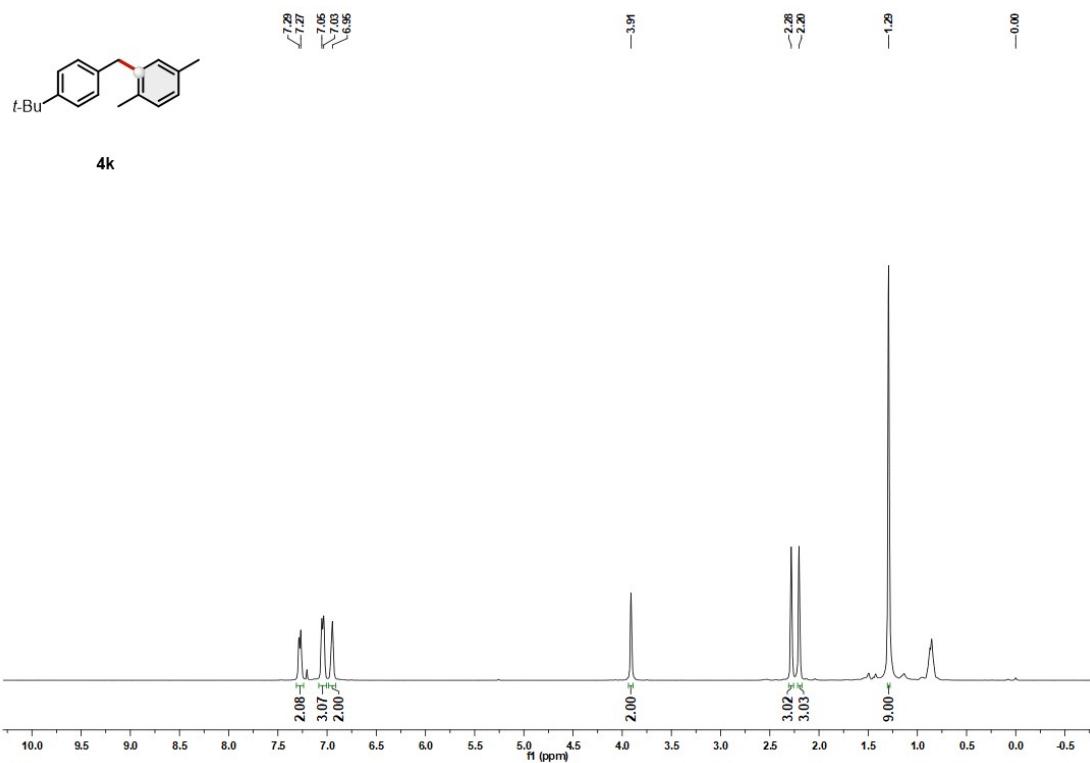


<sup>13</sup>C NMR of **4j**  
 $\text{CDCl}_3$ , 101 MHz, 298 K



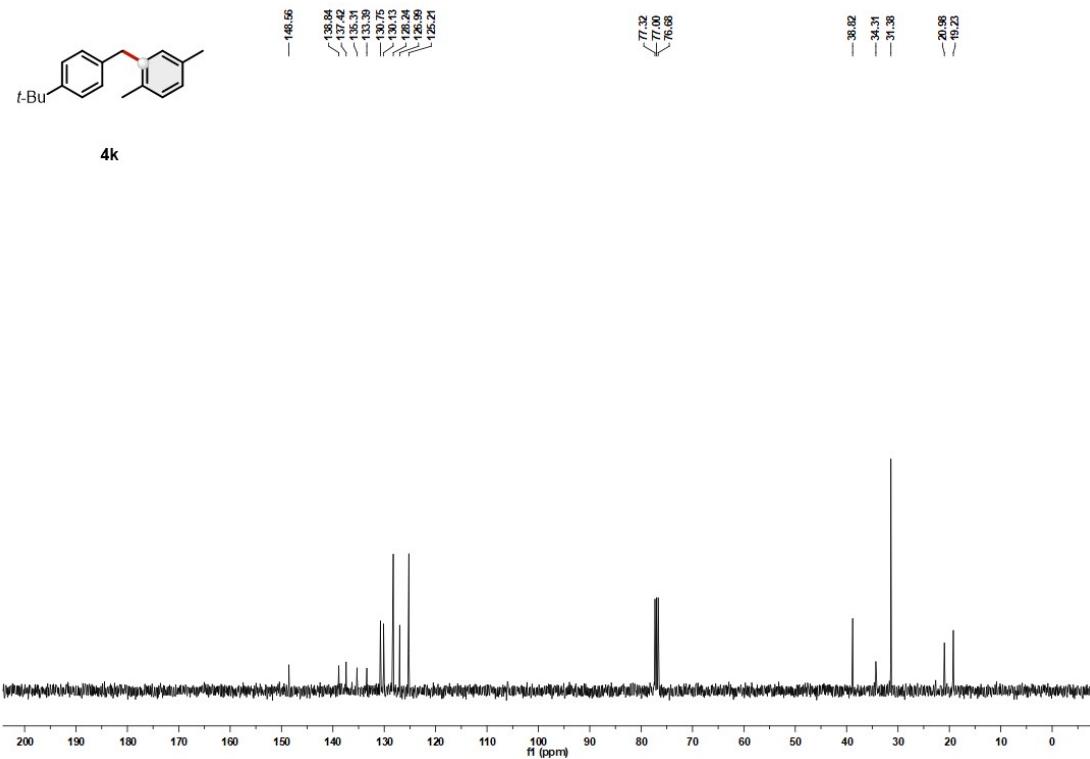
<sup>1</sup>H NMR of **4k**

CDCl<sub>3</sub>, 400 MHz, 298 K

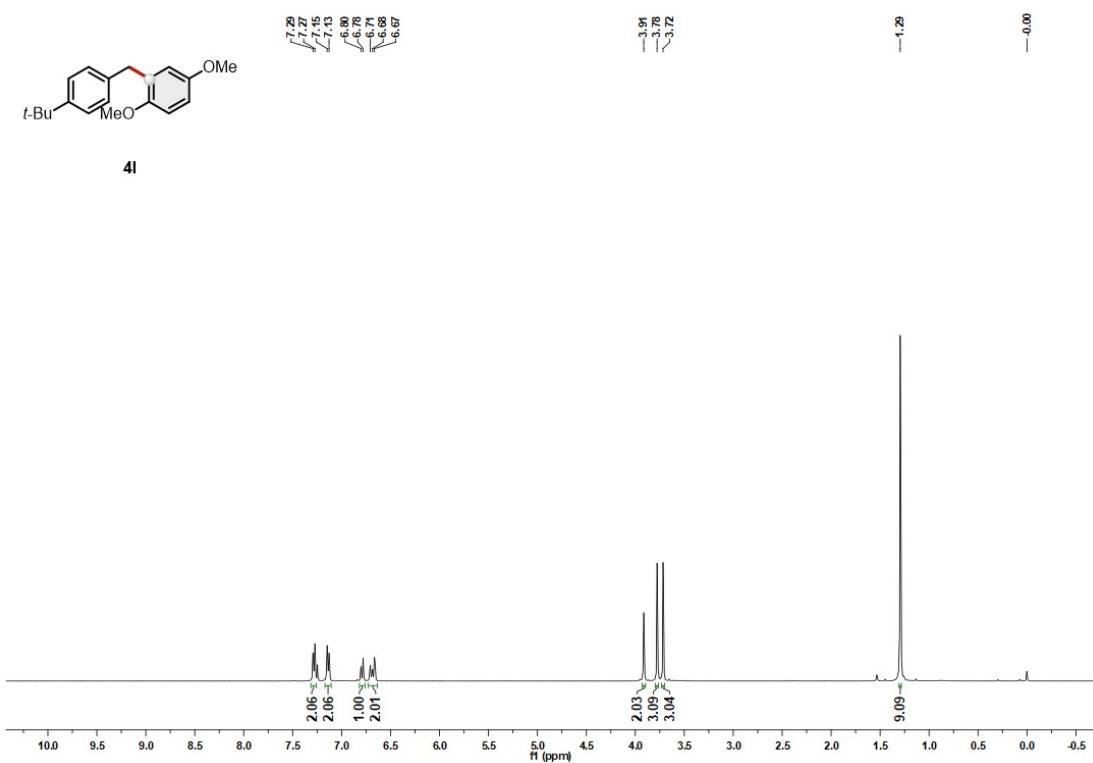


<sup>13</sup>C NMR of **4k**

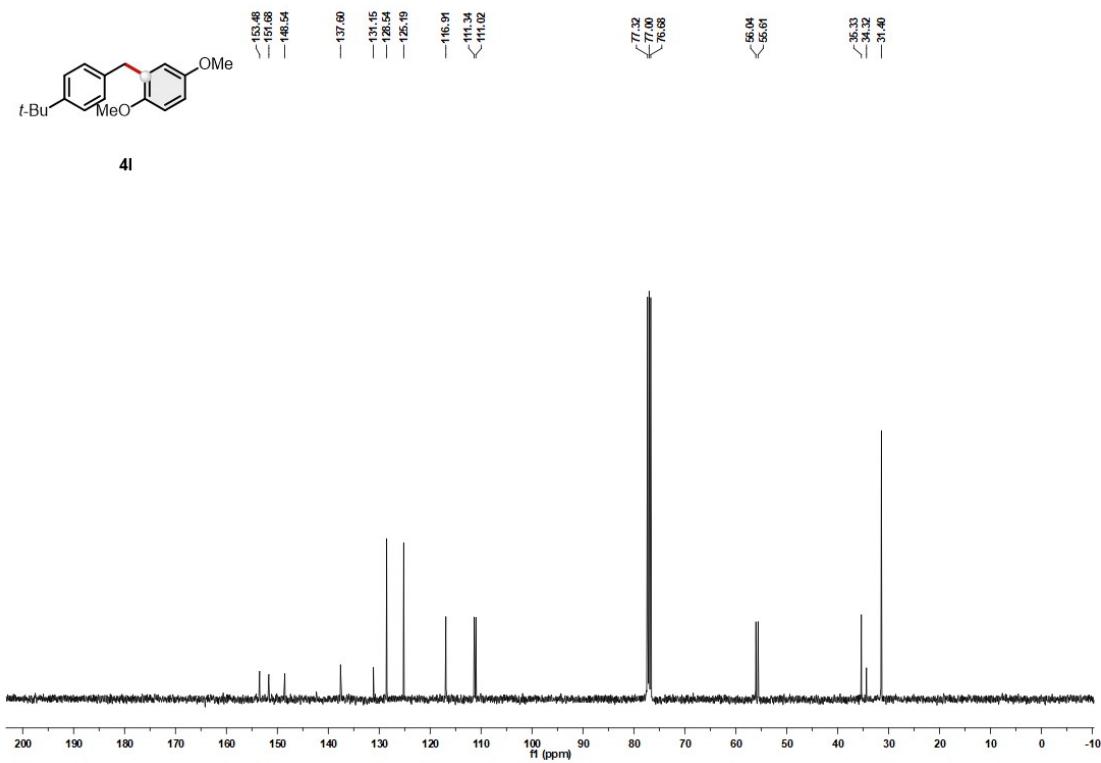
CDCl<sub>3</sub>, 101 MHz, 298 K



<sup>1</sup>H NMR of **4I**  
 $\text{CDCl}_3$ , 400 MHz, 298 K

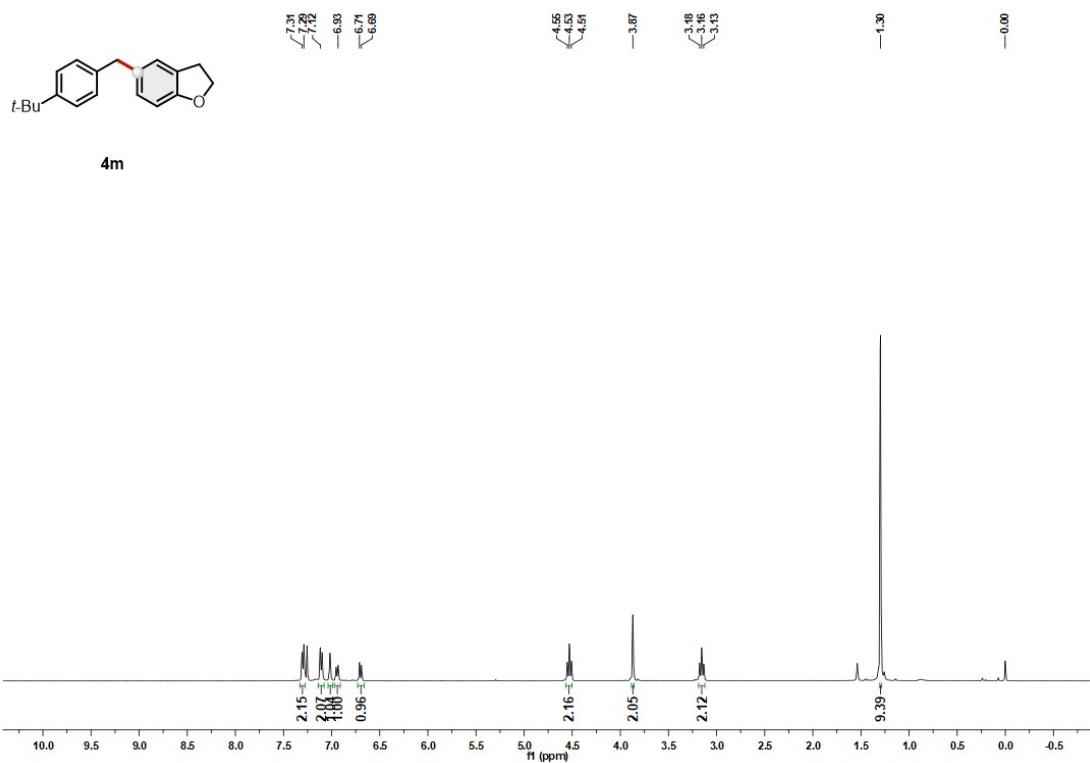


<sup>13</sup>C NMR of **4I**  
 $\text{CDCl}_3$ , 101 MHz, 298 K



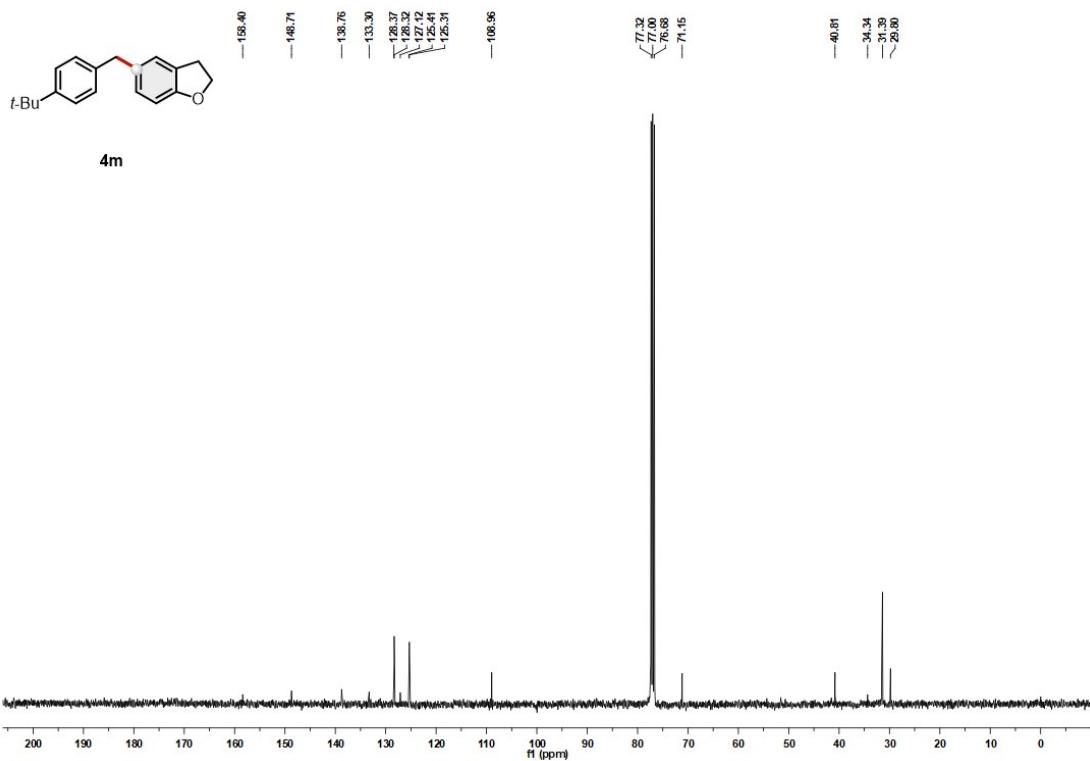
<sup>1</sup>H NMR of **4m**

CDCl<sub>3</sub>, 400 MHz, 298 K



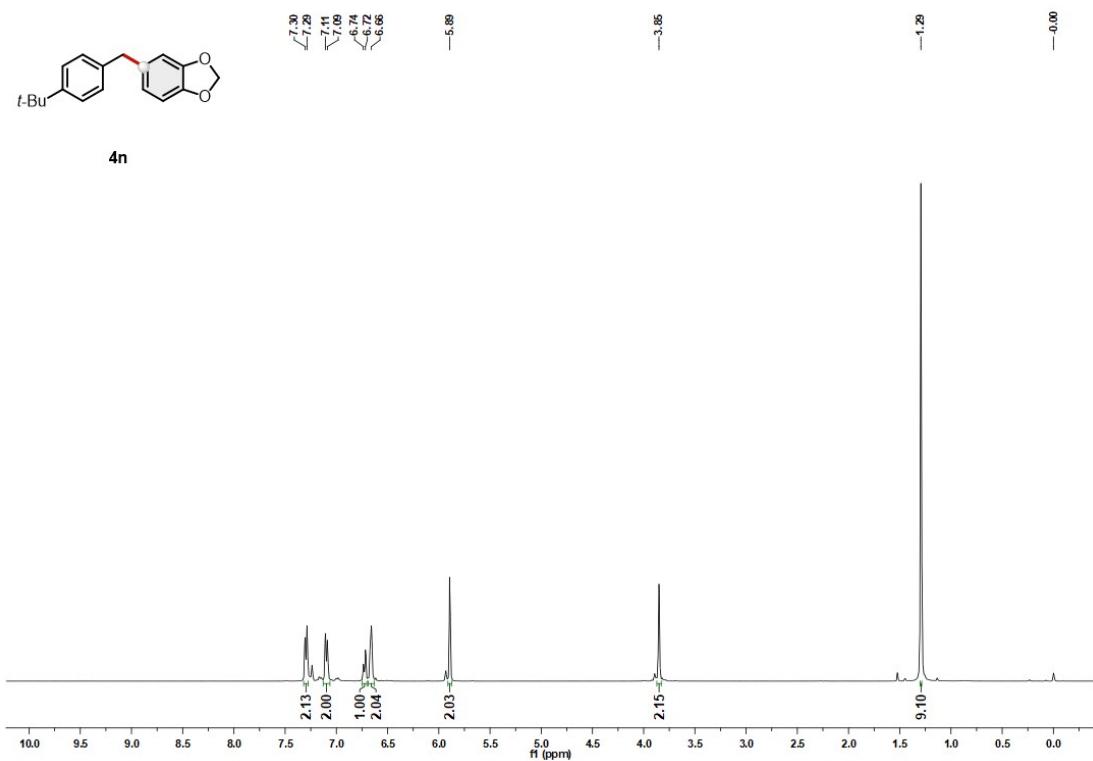
<sup>13</sup>C NMR of **4m**

CDCl<sub>3</sub>, 101 MHz, 298 K



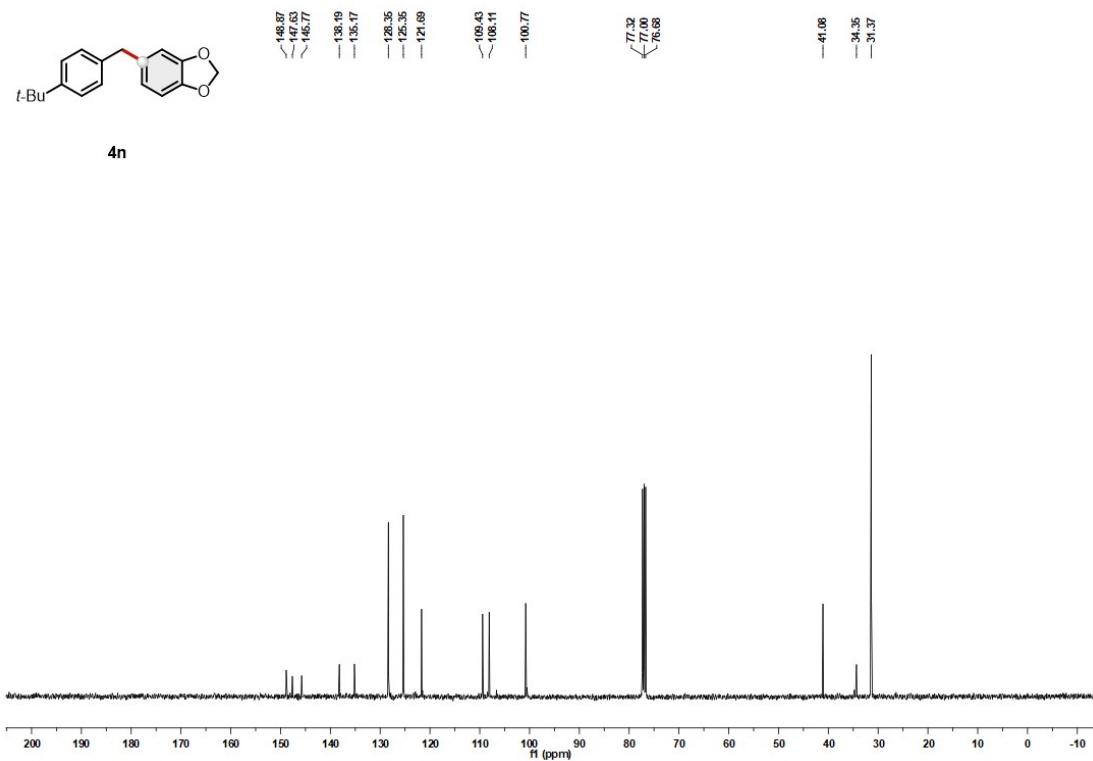
<sup>1</sup>H NMR of **4n**

CDCl<sub>3</sub>, 400 MHz, 298 K



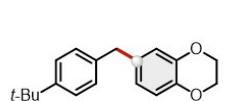
<sup>13</sup>C NMR of **4n**

CDCl<sub>3</sub>, 101 MHz, 298 K

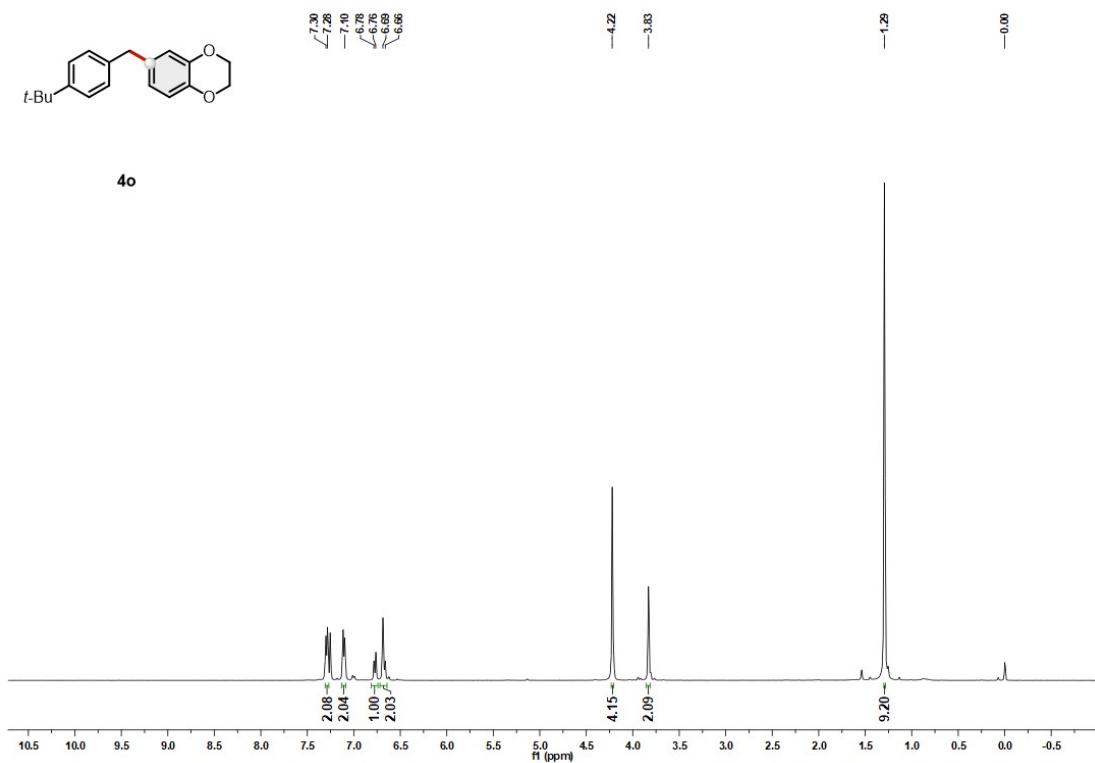


### <sup>1</sup>H NMR of **4o**

CDCl<sub>3</sub>, 400 MHz, 298 K

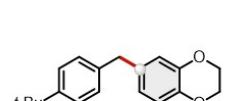


40

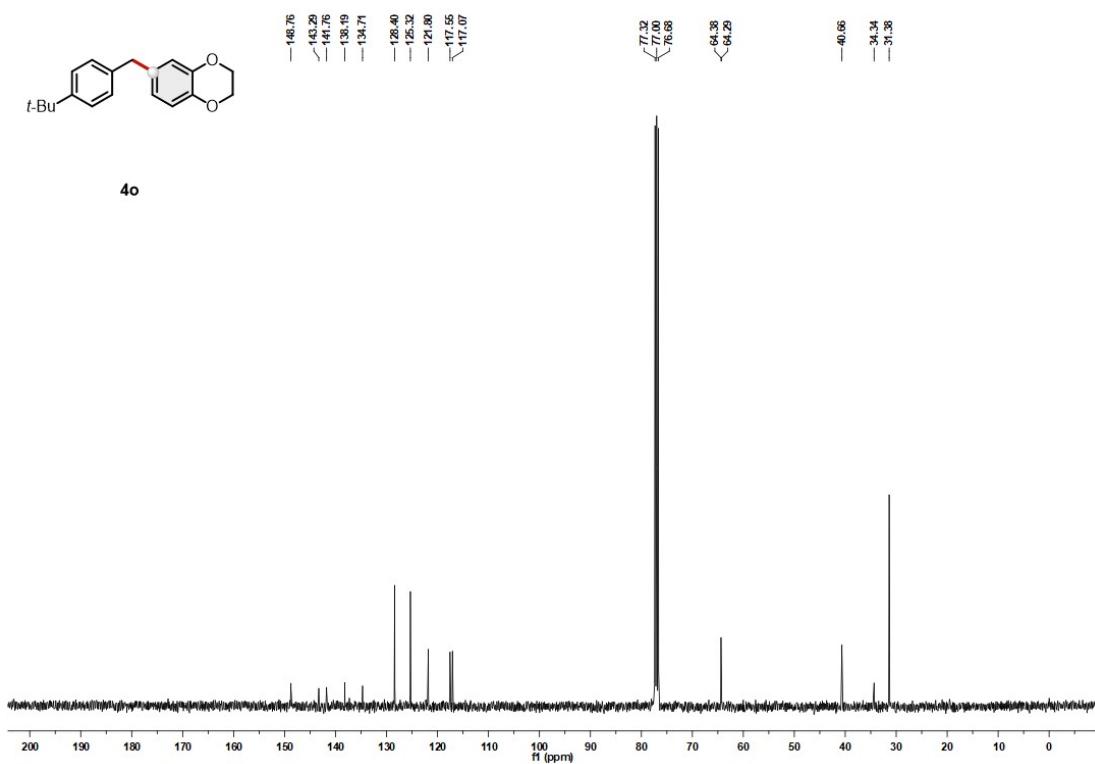


### <sup>13</sup>C NMR of **4o**

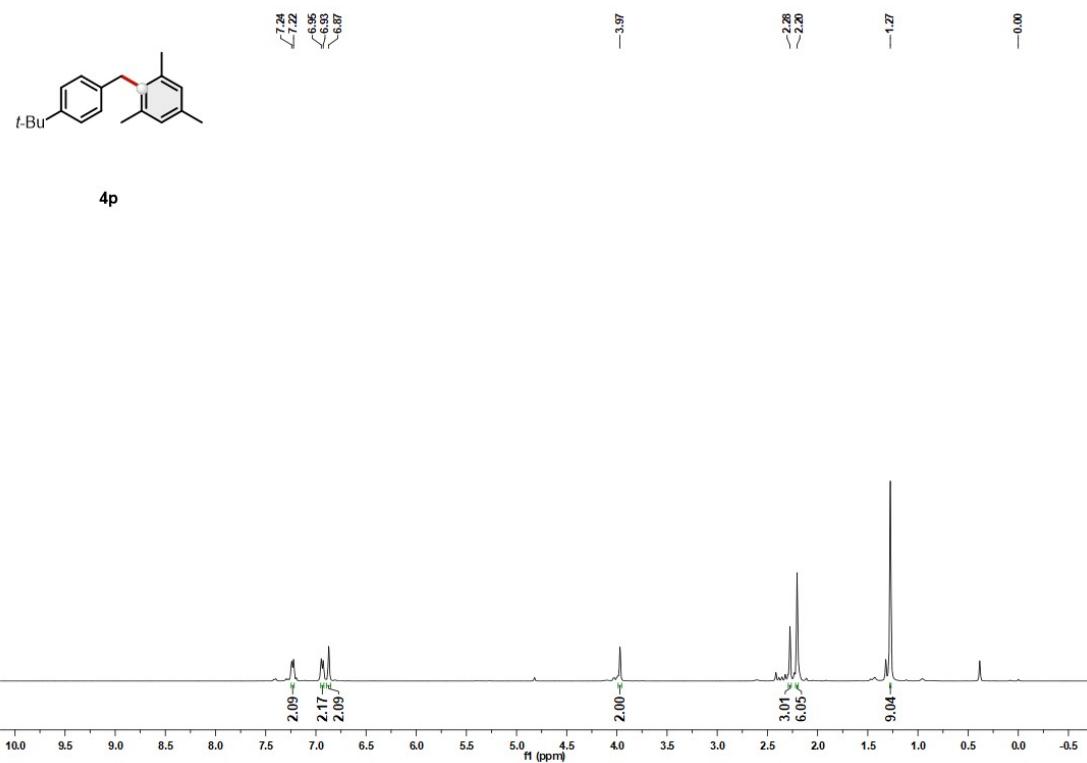
CDCl<sub>3</sub>, 101 MHz, 298 K



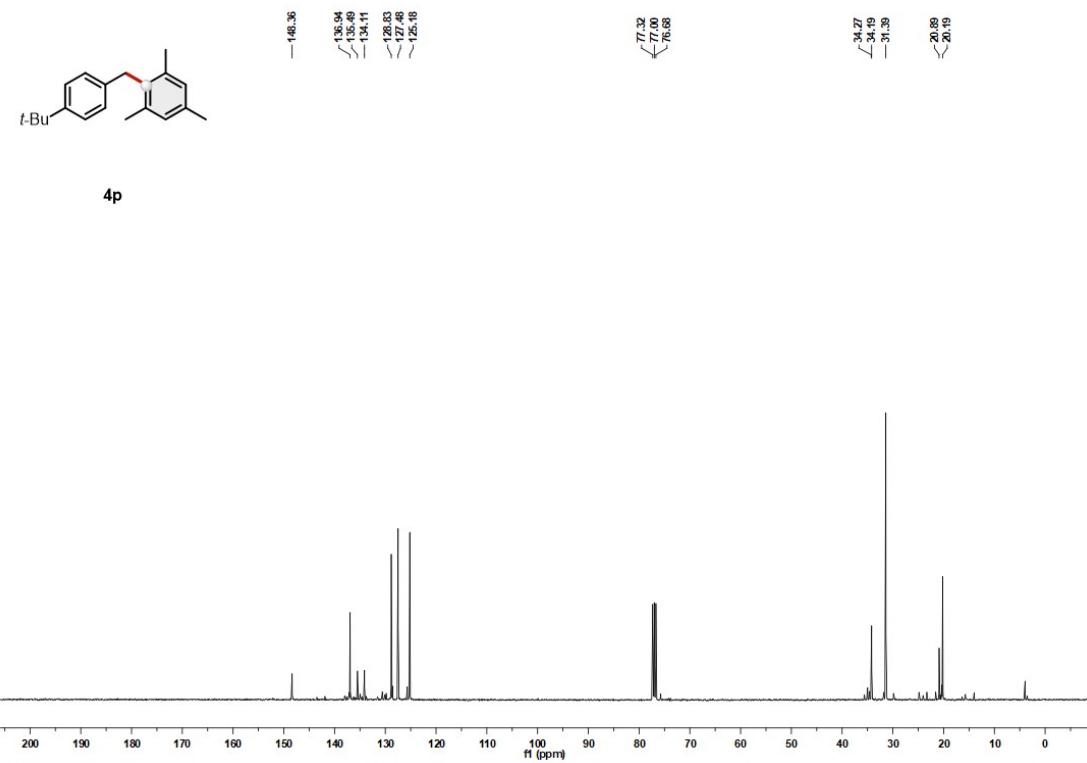
40



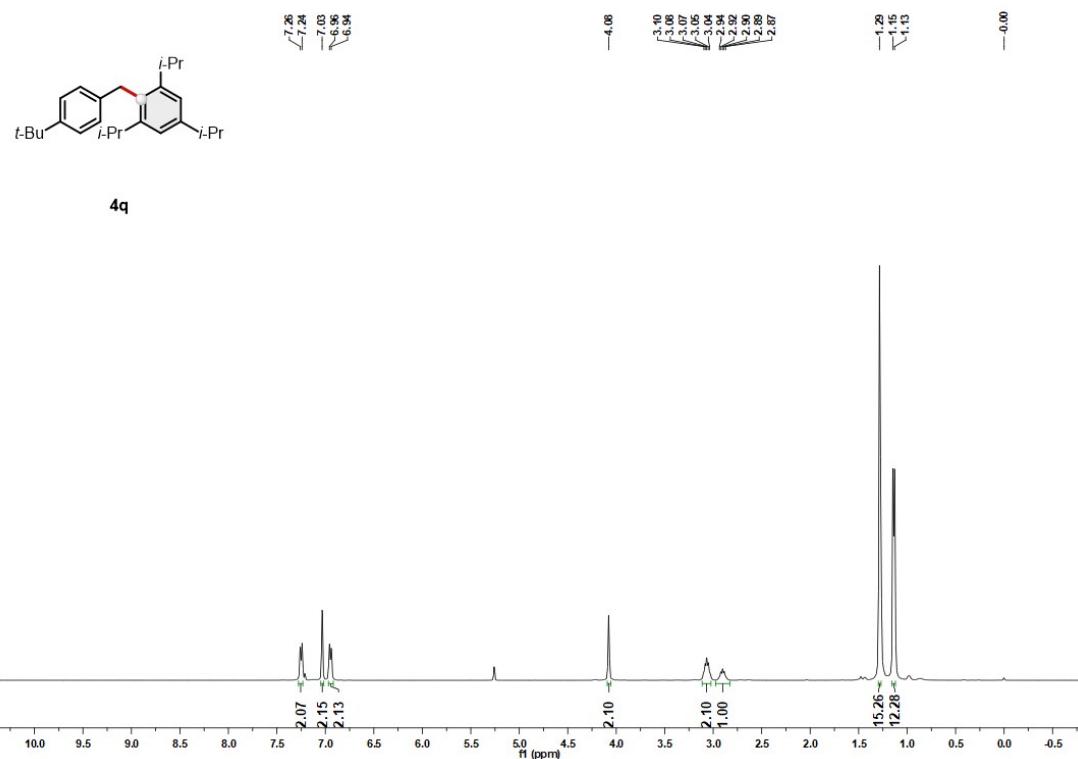
<sup>1</sup>H NMR of **4p**  
CDCl<sub>3</sub>, 400 MHz, 298 K



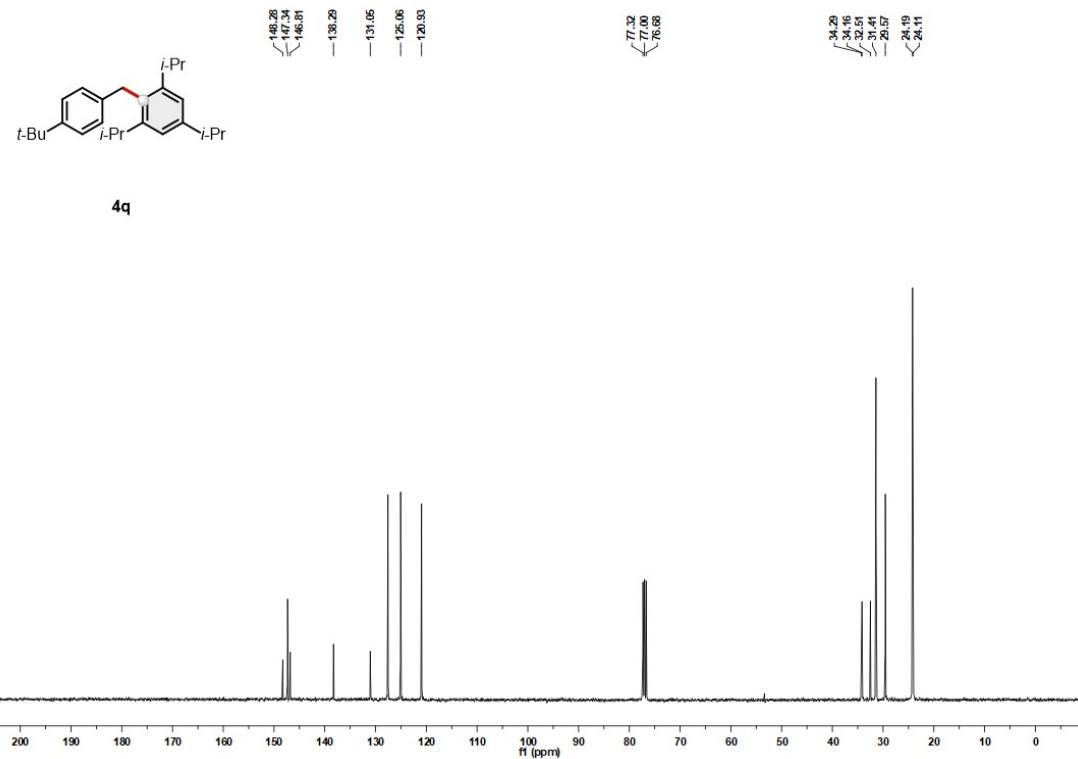
<sup>13</sup>C NMR of **4p**  
CDCl<sub>3</sub>, 101 MHz, 298 K



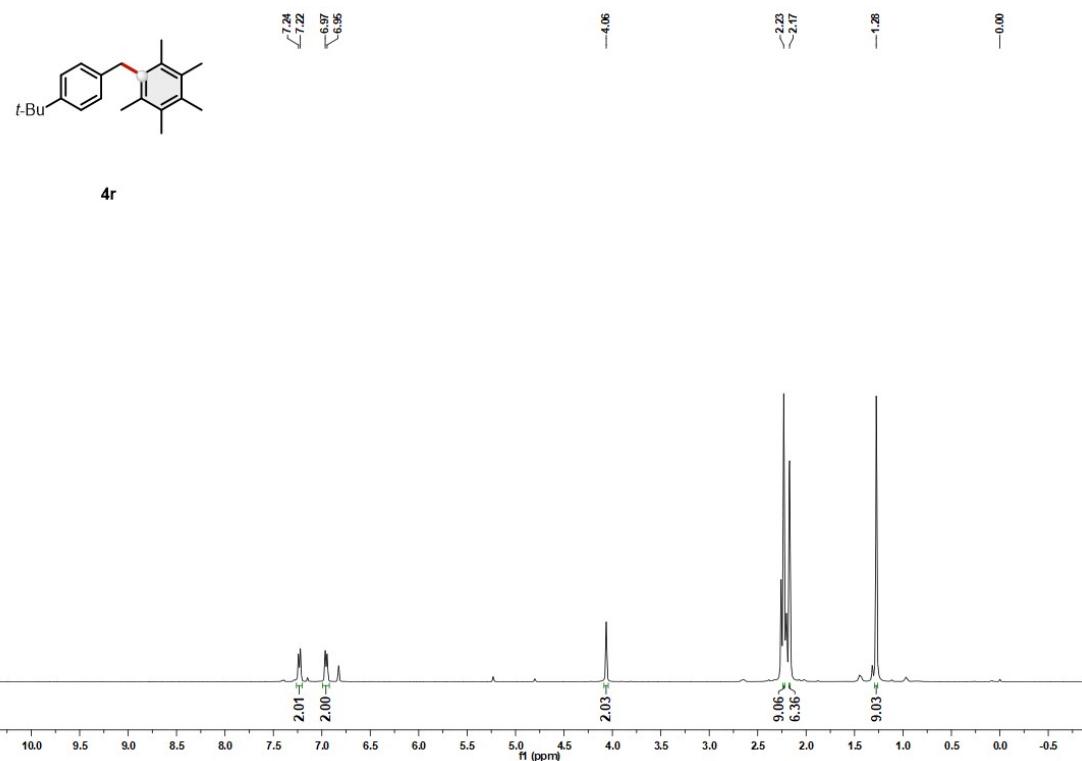
<sup>1</sup>H NMR of **4q**  
 $\text{CDCl}_3$ , 400 MHz, 298 K



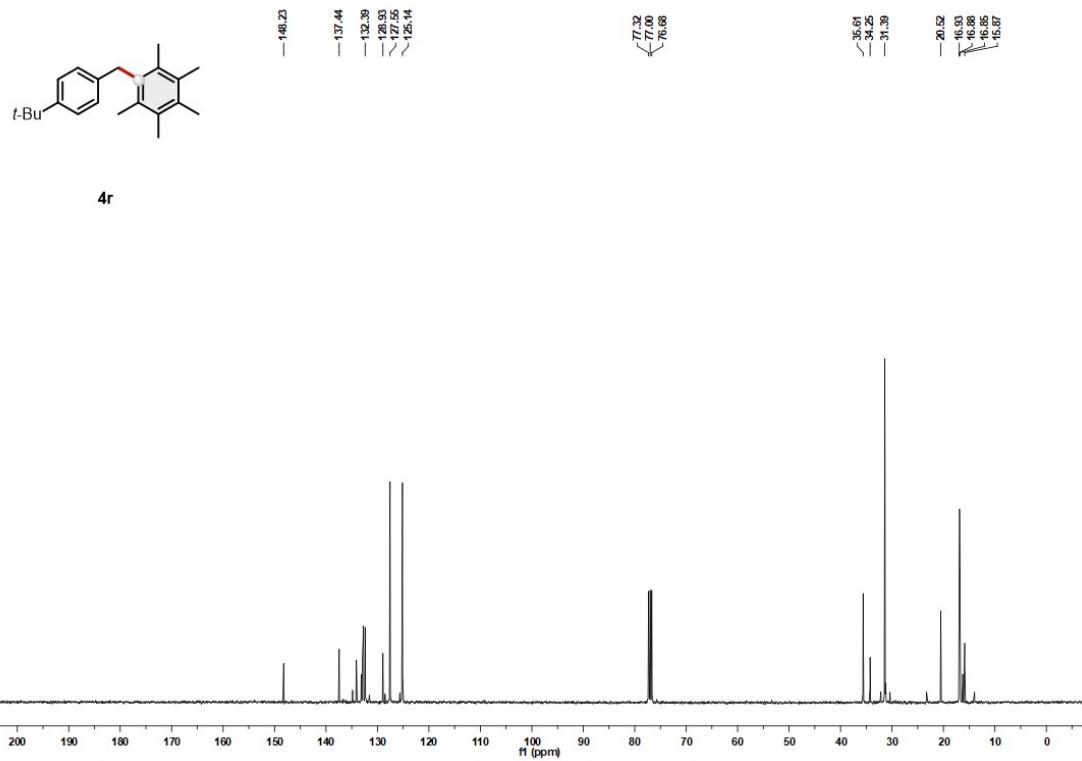
<sup>13</sup>C NMR of **4q**  
 $\text{CDCl}_3$ , 101 MHz, 298 K



<sup>1</sup>H NMR of **4r**  
CDCl<sub>3</sub>, 400 MHz, 298 K

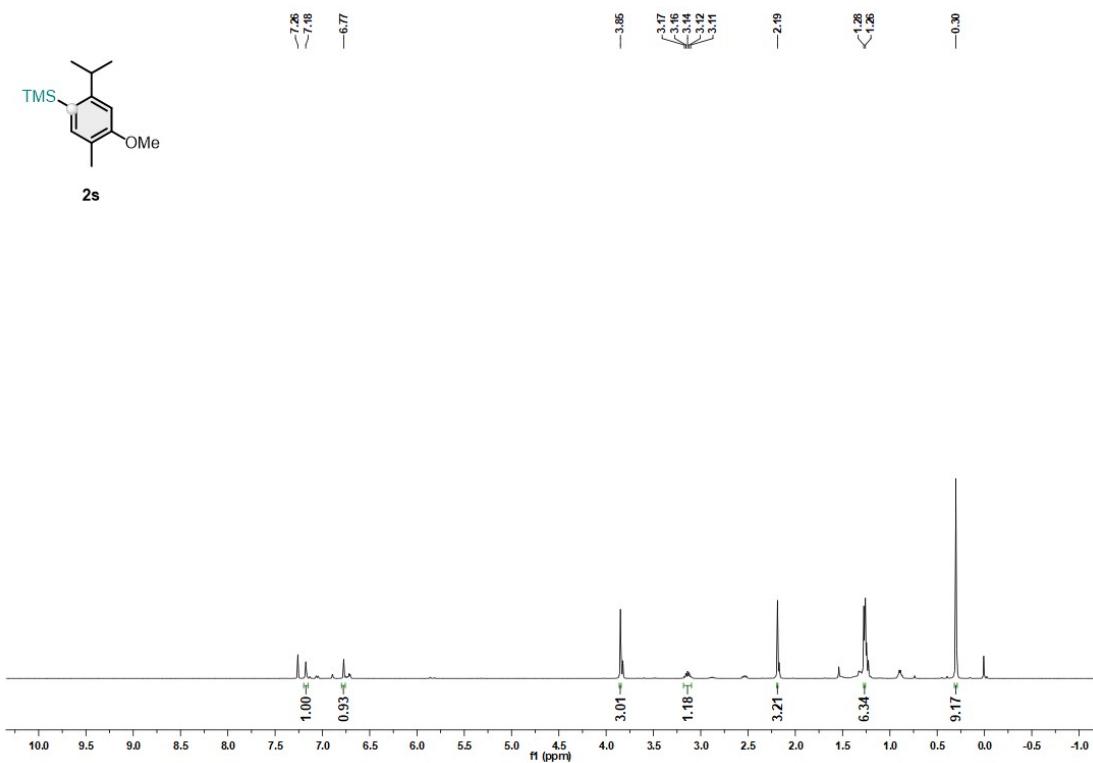


<sup>13</sup>C NMR of **4r**  
CDCl<sub>3</sub>, 101 MHz, 298 K



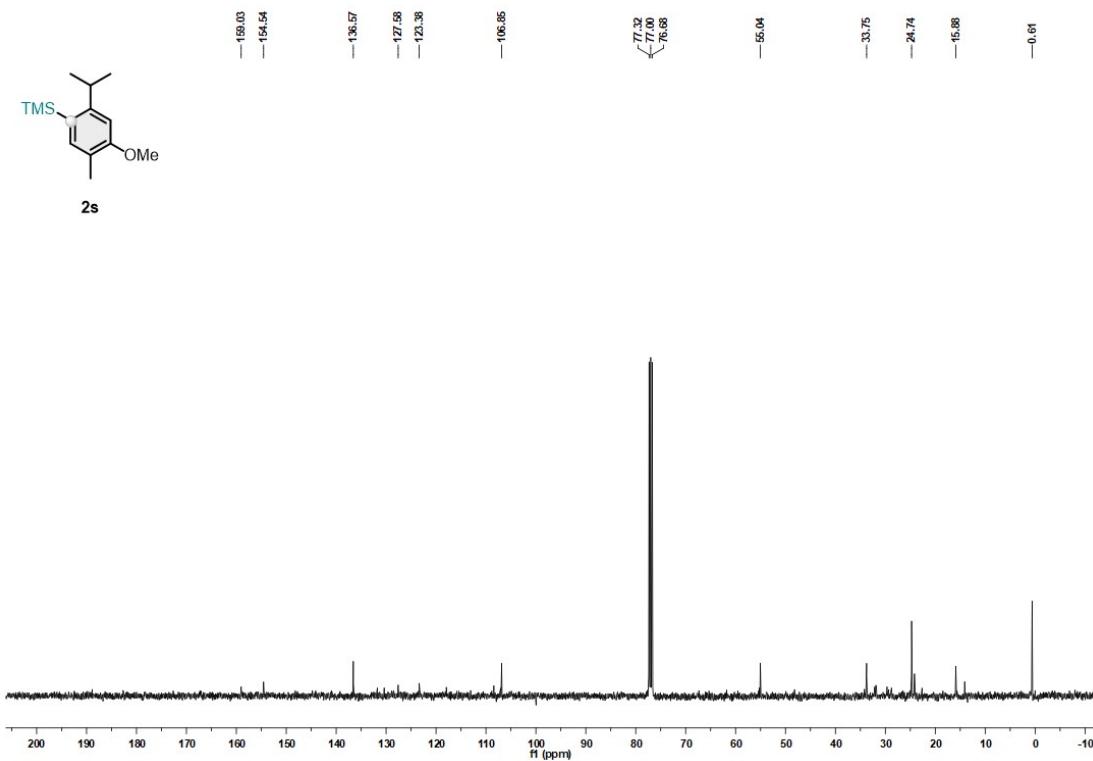
<sup>1</sup>H NMR of **2s**

CDCl<sub>3</sub>, 400 MHz, 298 K



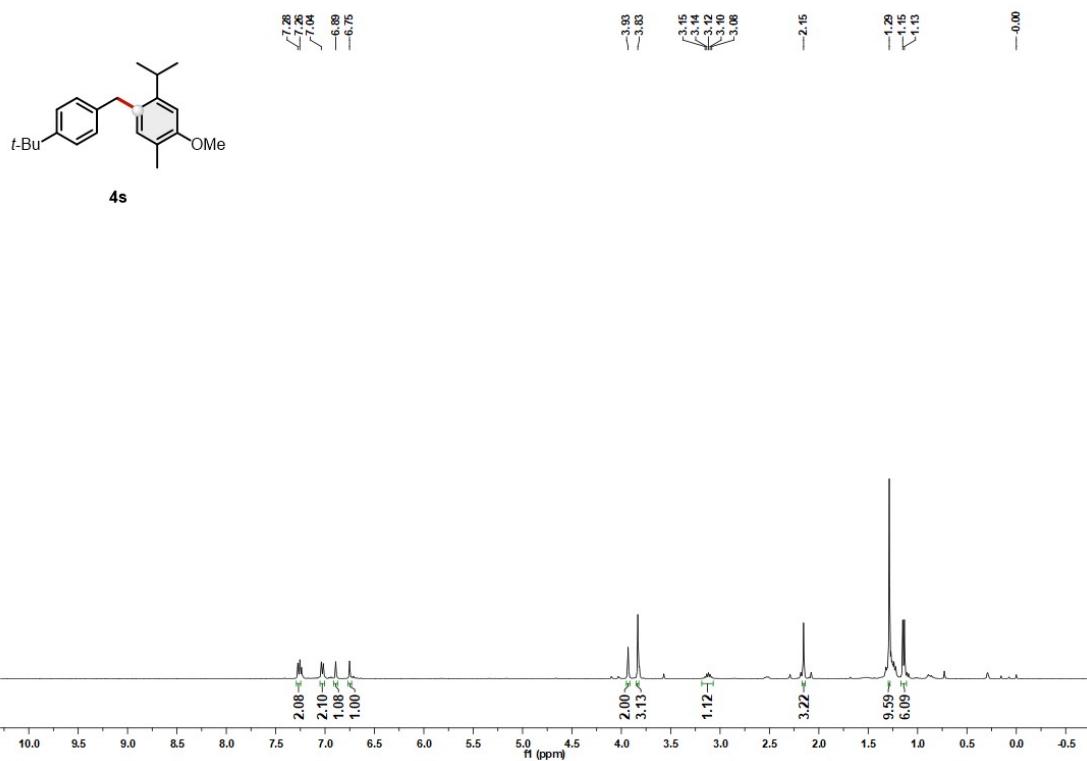
<sup>13</sup>C NMR of **2s**

CDCl<sub>3</sub>, 101 MHz, 298 K



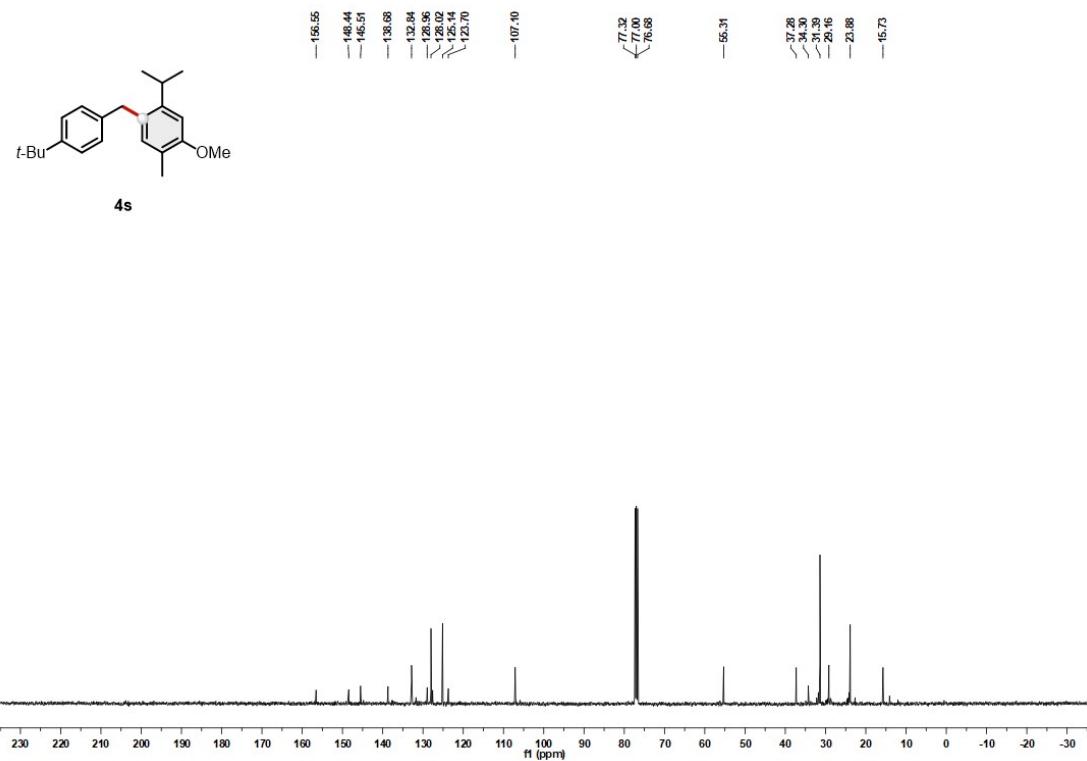
<sup>1</sup>H NMR of **4s**

CDCl<sub>3</sub>, 400 MHz, 298 K

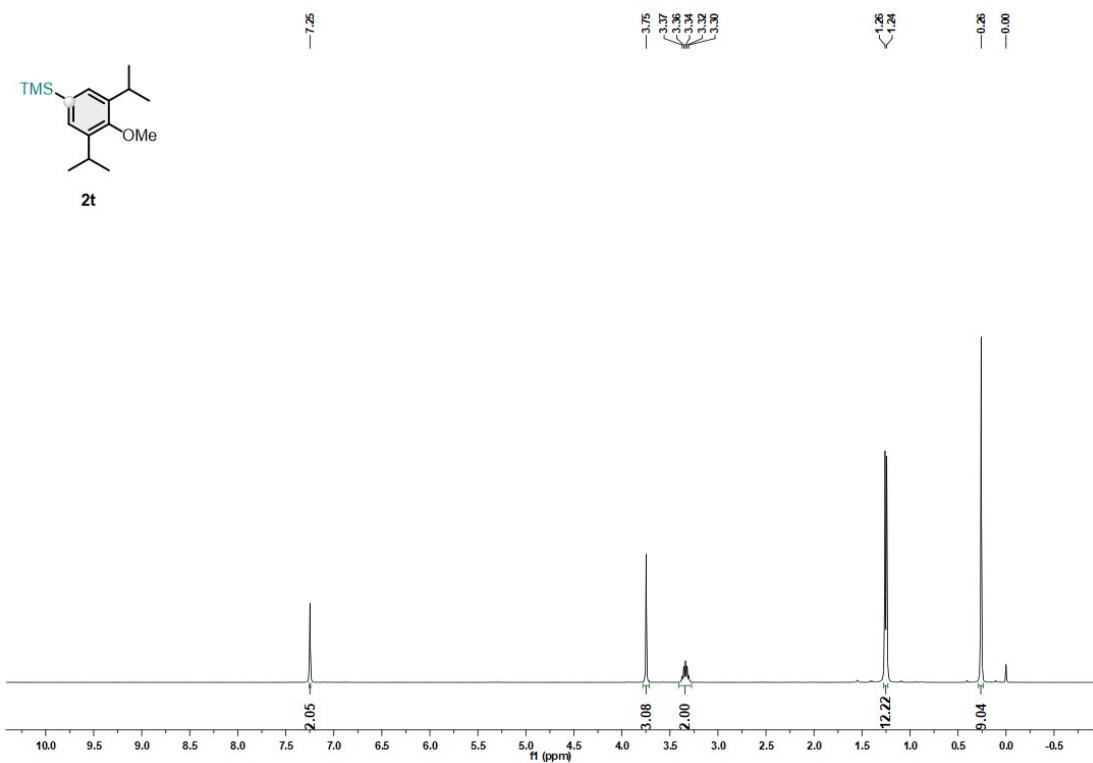


<sup>13</sup>C NMR of **4s**

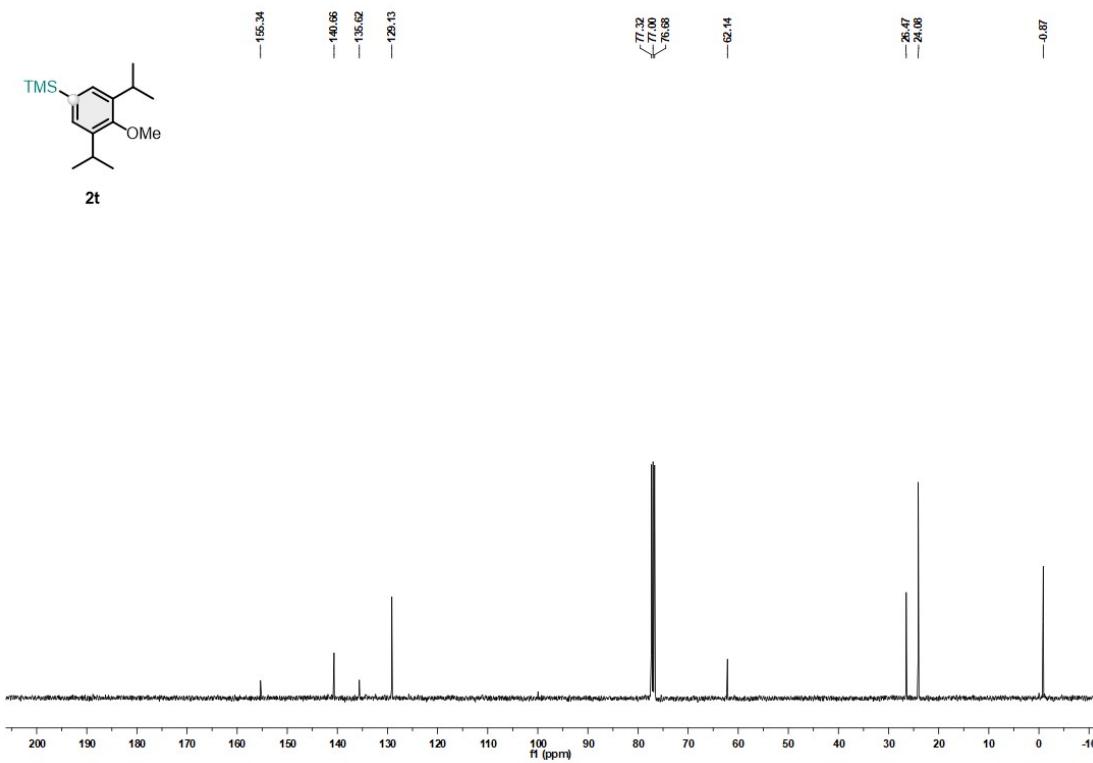
CDCl<sub>3</sub>, 101 MHz, 298 K



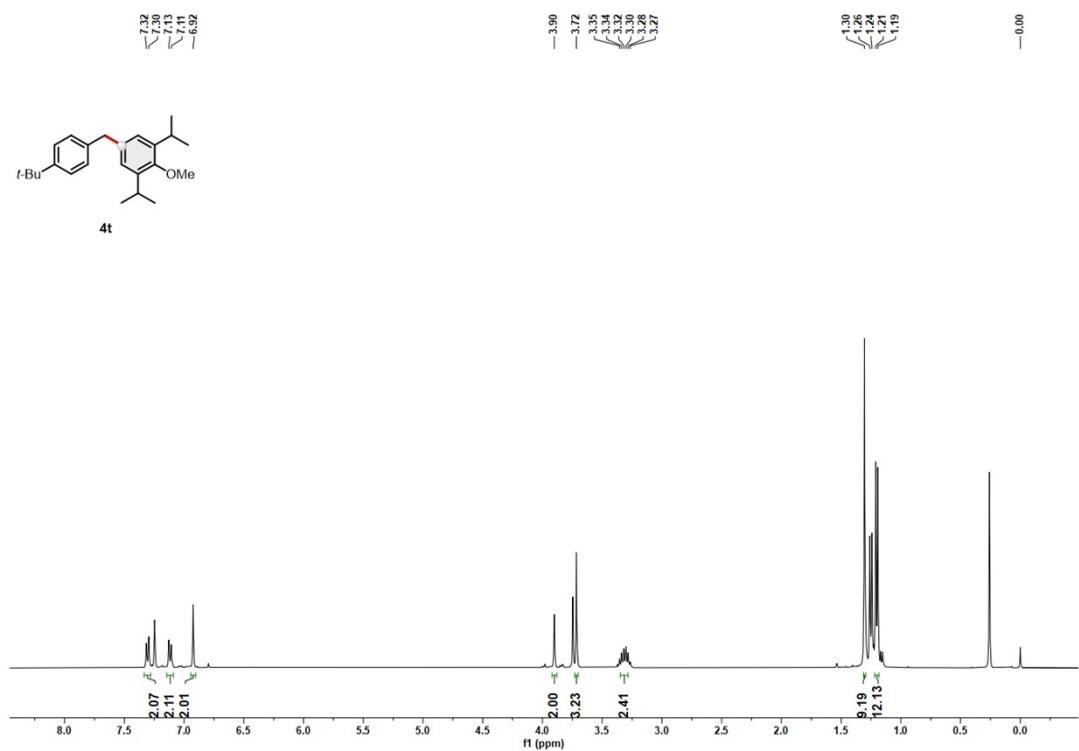
<sup>1</sup>H NMR of **2t**  
CDCl<sub>3</sub>, 400 MHz, 298 K



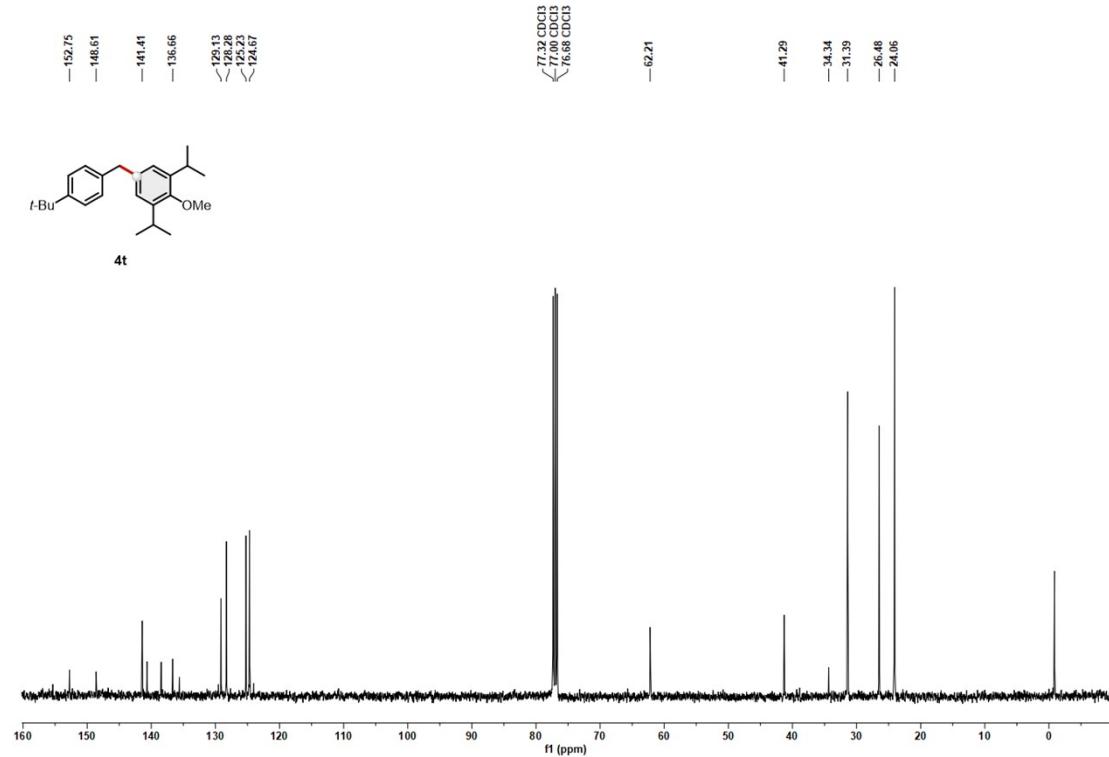
<sup>13</sup>C NMR of **2t**  
CDCl<sub>3</sub>, 101 MHz, 298 K



<sup>1</sup>H NMR of **4t**  
 $\text{CDCl}_3$ , 400 MHz, 298 K

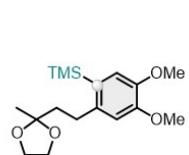


<sup>13</sup>C NMR of **4t**  
 $\text{CDCl}_3$ , 101 MHz, 298 K

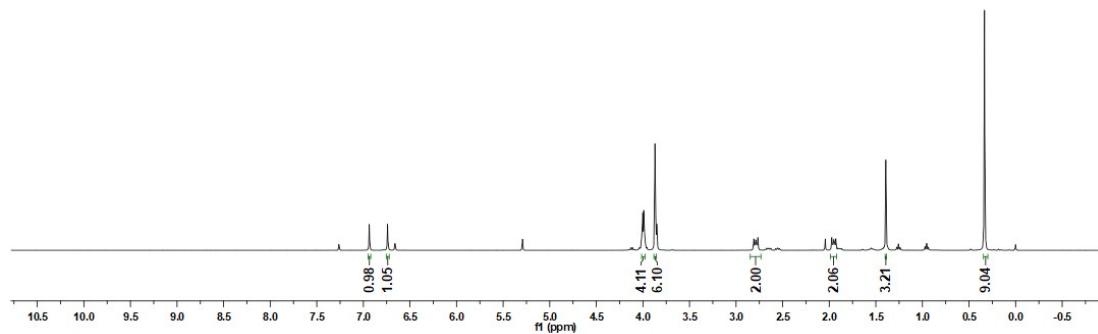


### <sup>1</sup>H NMR of **2u**

CDCl<sub>3</sub>, 400 MHz, 298 K

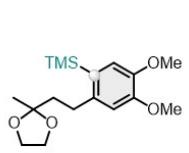


2u

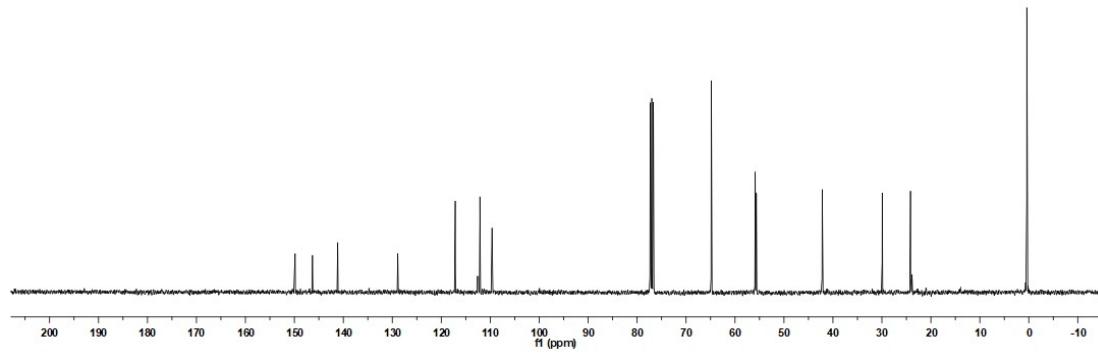


### <sup>13</sup>C NMR of **2u**

CDCl<sub>3</sub>, 101 MHz, 298 K

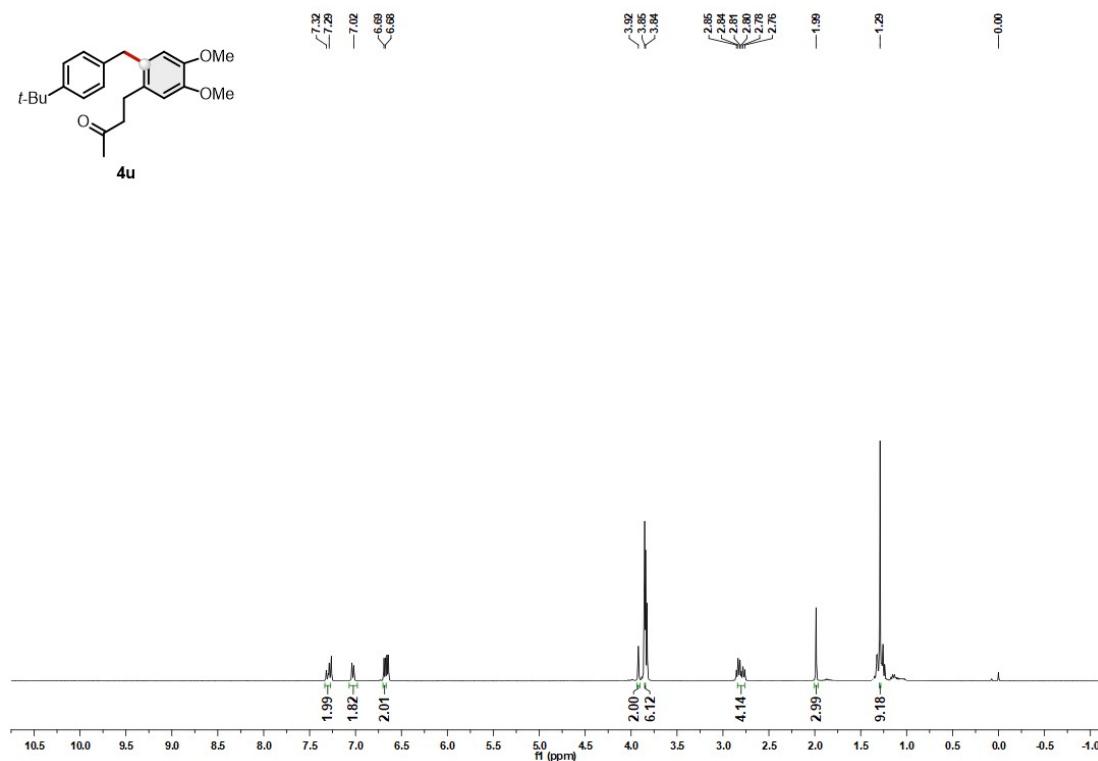
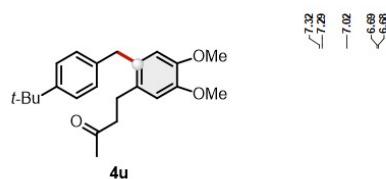


2u



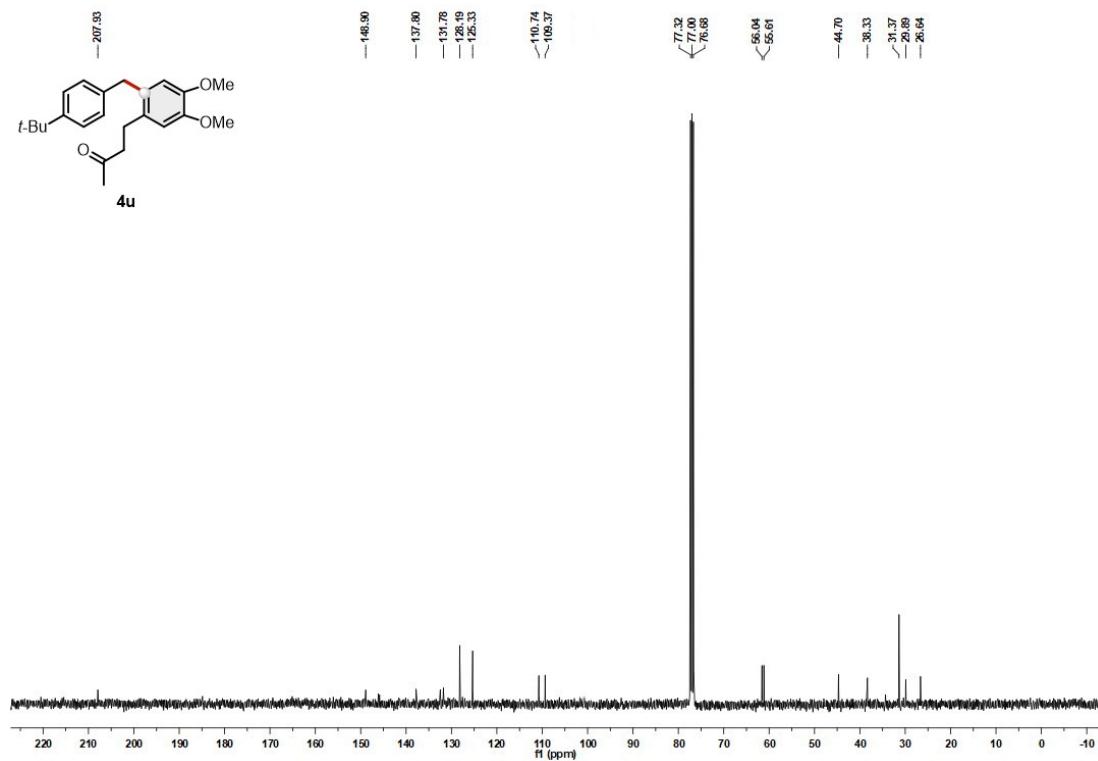
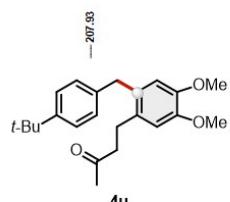
### <sup>1</sup>H NMR of 4u

CDCl<sub>3</sub>, 400 MHz, 298 K

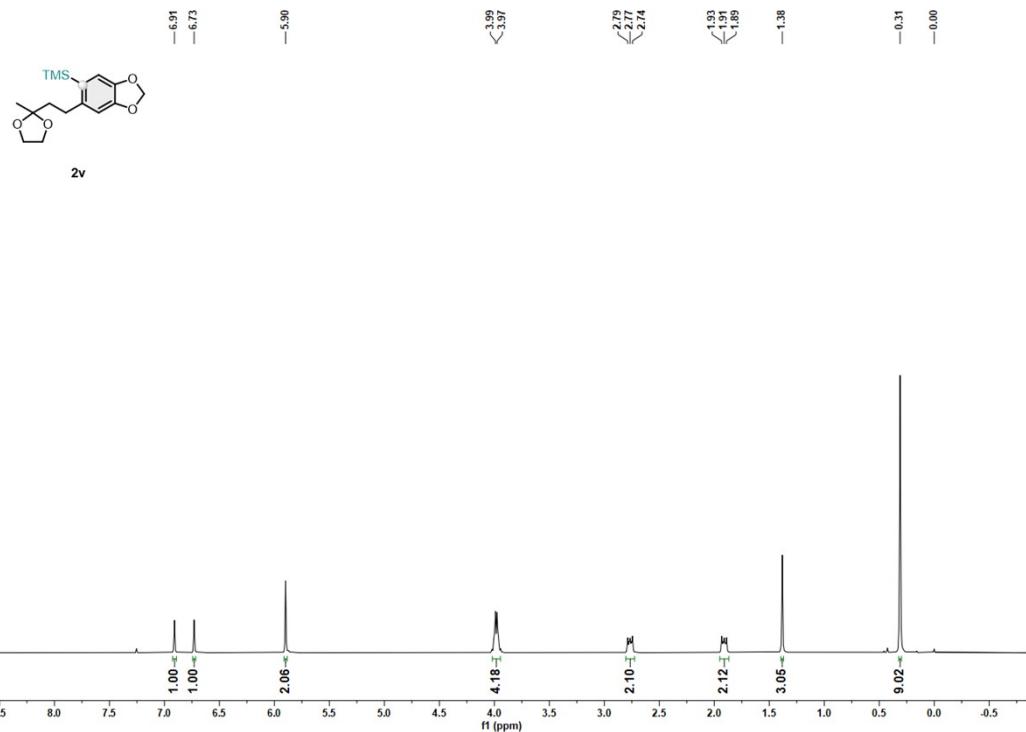


### <sup>13</sup>C NMR of 4u

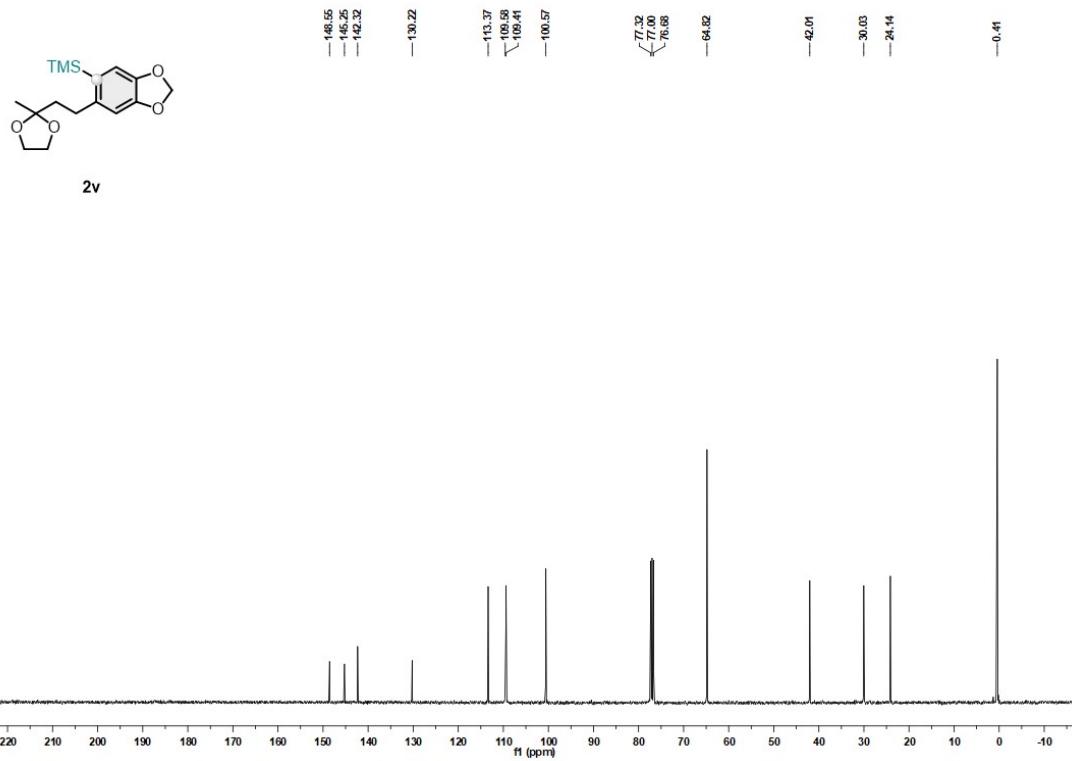
CDCl<sub>3</sub>, 101 MHz, 298 K



<sup>1</sup>H NMR of **2v**  
 $\text{CDCl}_3$ , 400 MHz, 298 K

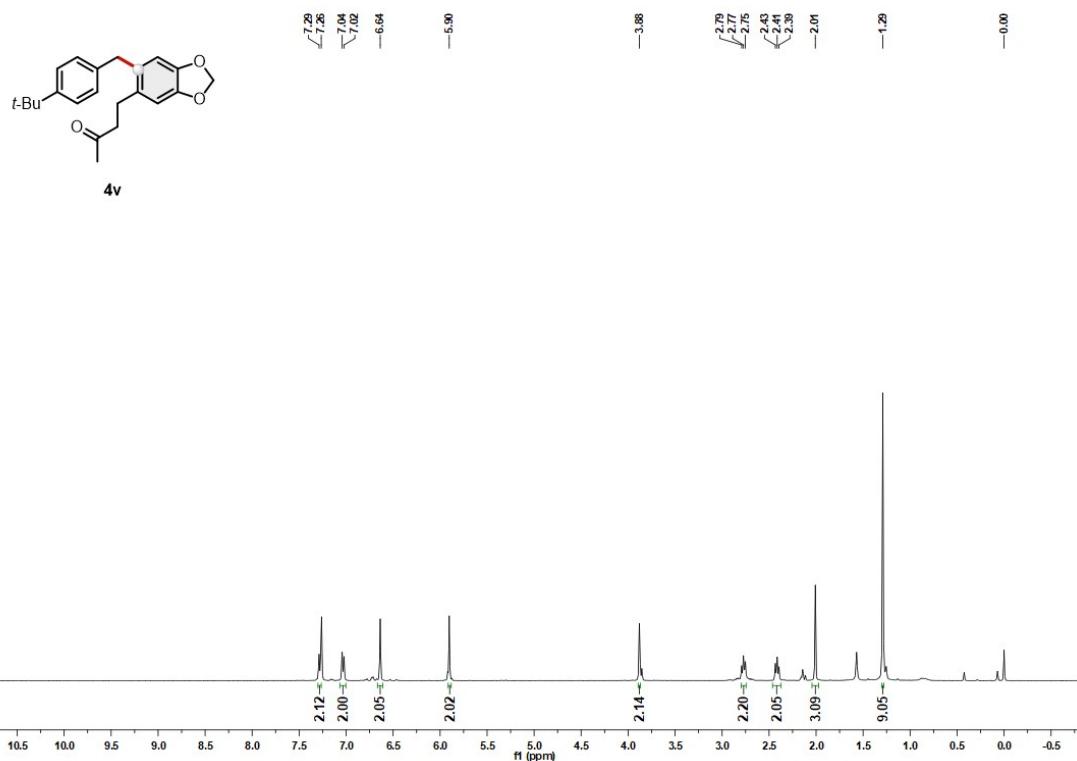


<sup>13</sup>C NMR of **2v**  
 $\text{CDCl}_3$ , 101 MHz, 298 K



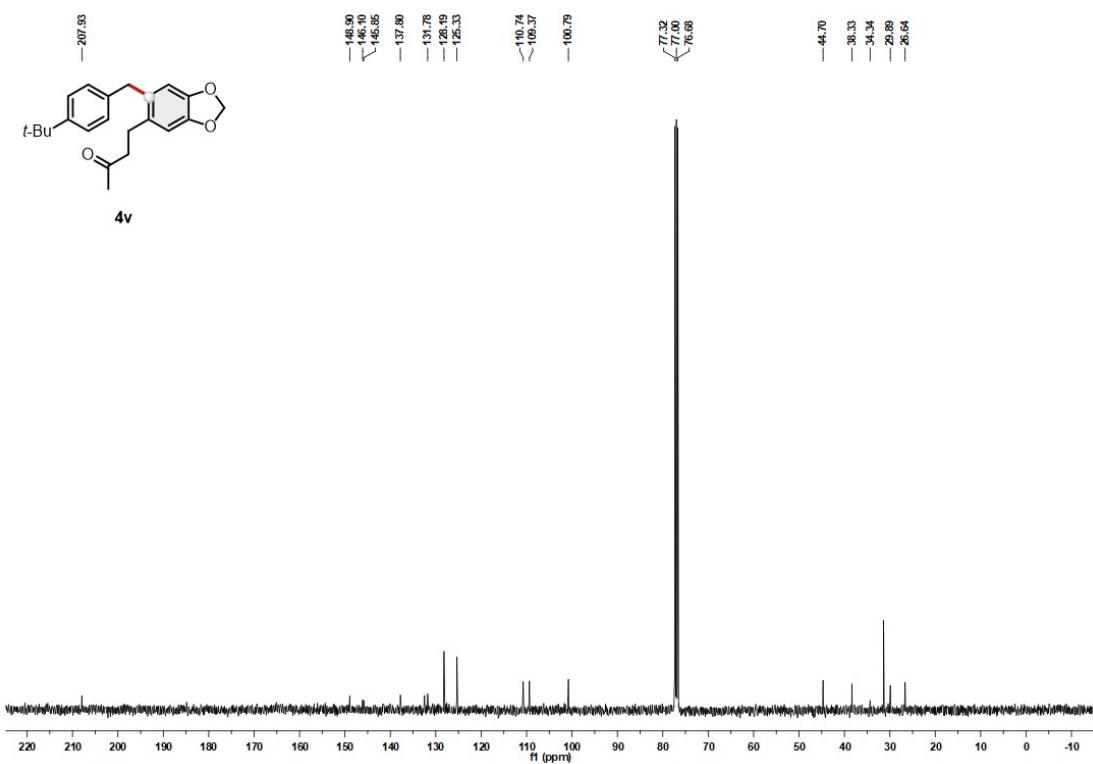
<sup>1</sup>H NMR of **4v**

CDCl<sub>3</sub>, 400 MHz, 298 K



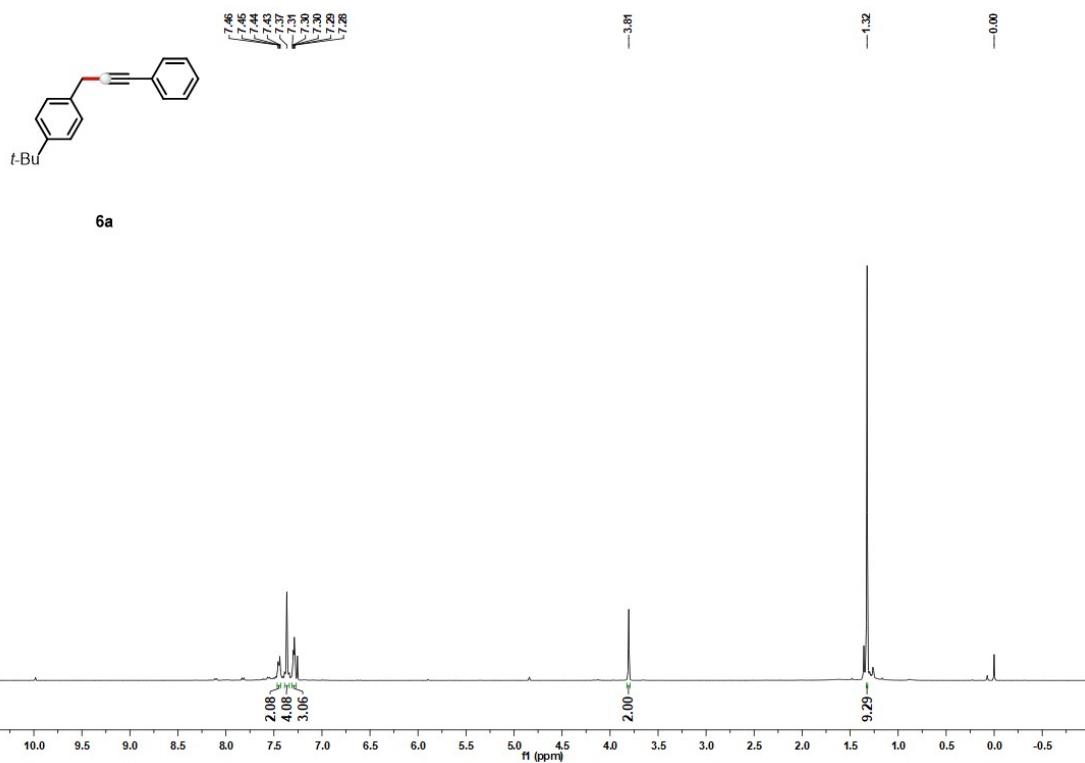
<sup>13</sup>C NMR of **4v**

CDCl<sub>3</sub>, 101 MHz, 298 K



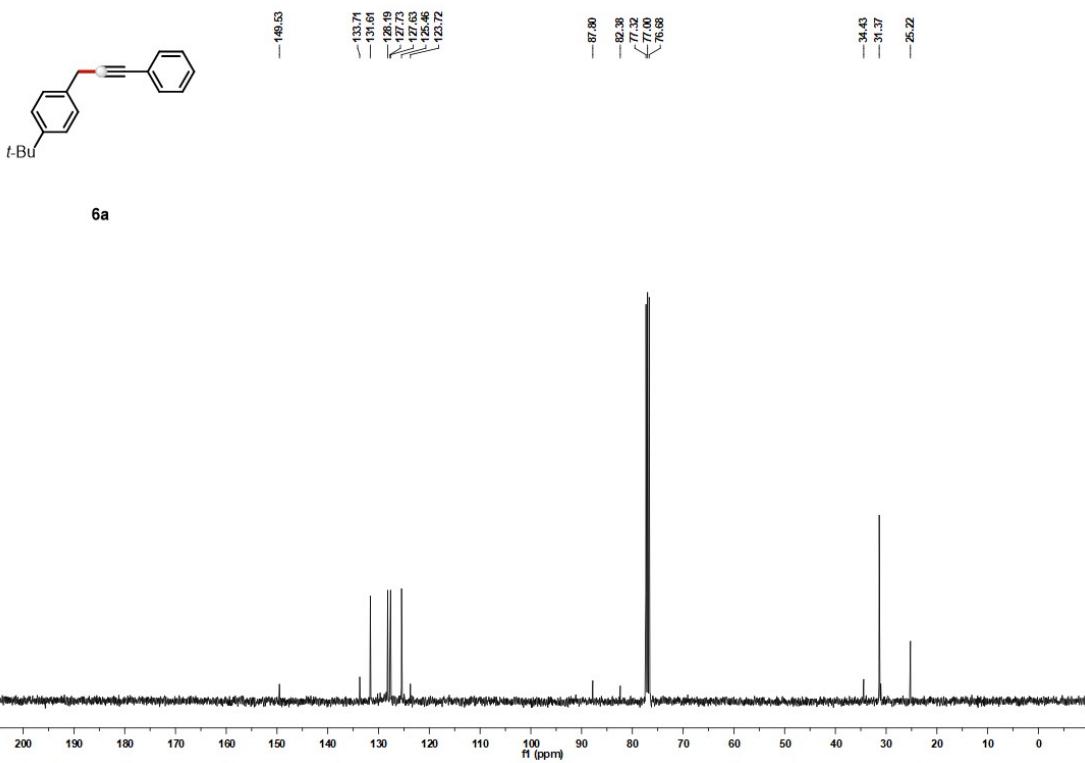
<sup>1</sup>H NMR of **6a**

CDCl<sub>3</sub>, 400 MHz, 298 K



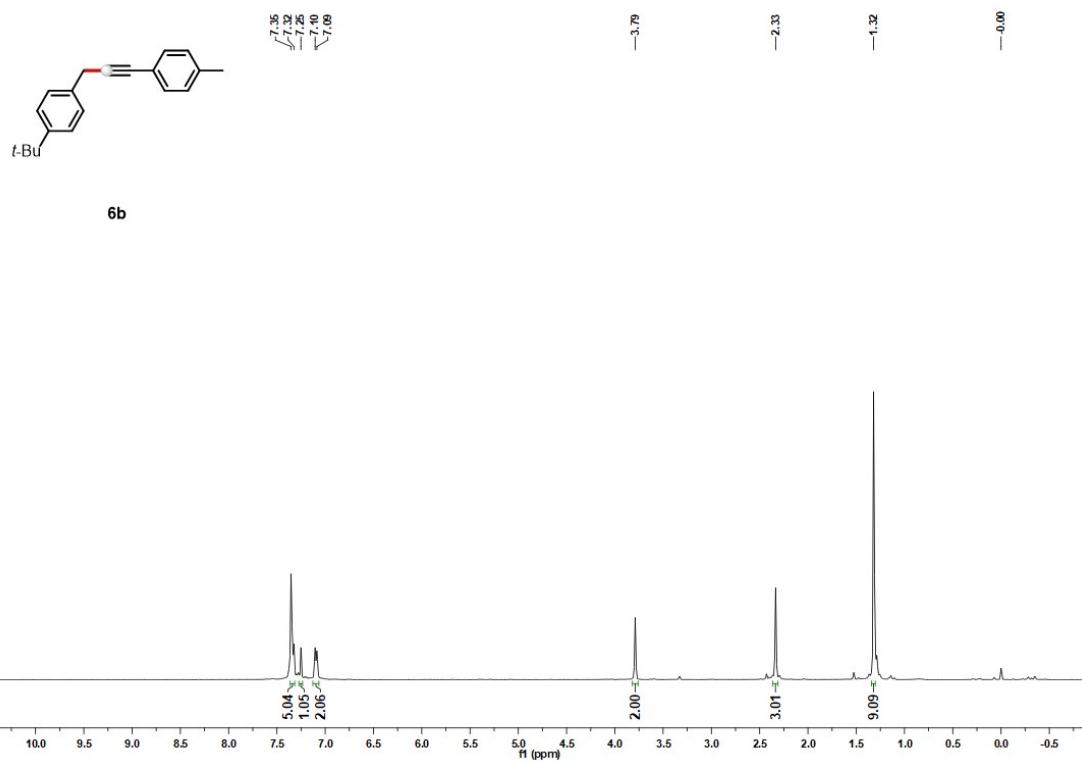
<sup>13</sup>C NMR of **6a**

CDCl<sub>3</sub>, 101 MHz, 298 K



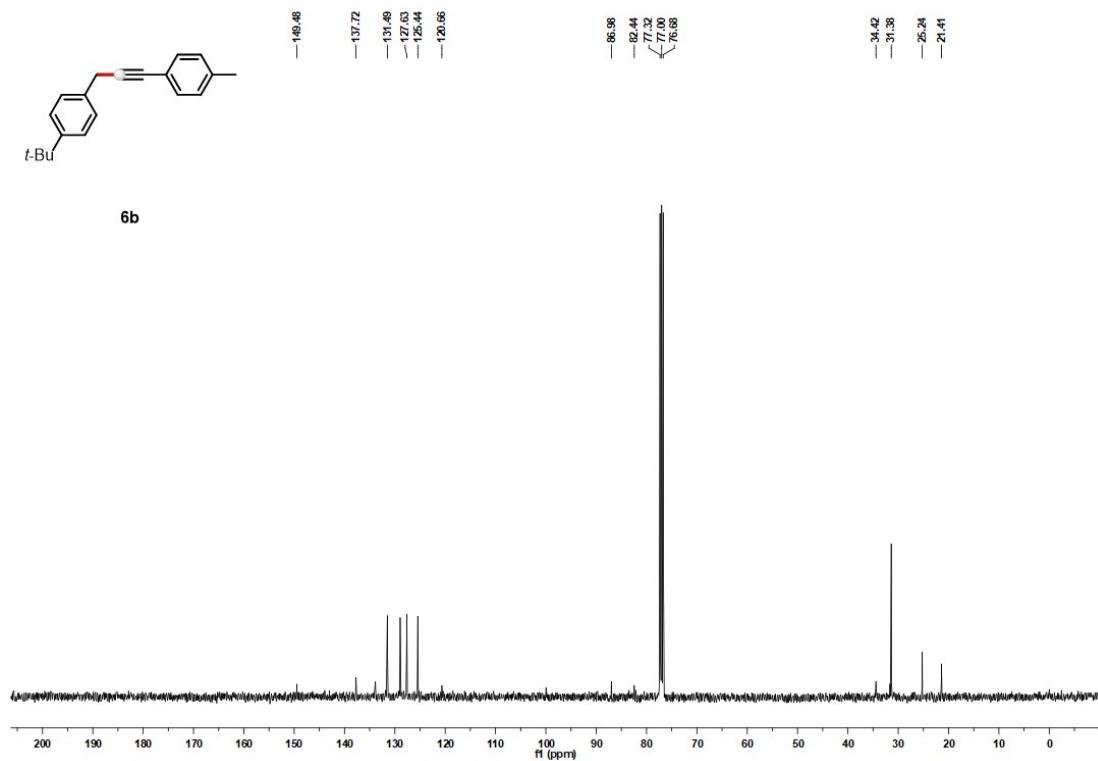
<sup>1</sup>H NMR of **6b**

CDCl<sub>3</sub>, 400 MHz, 298 K



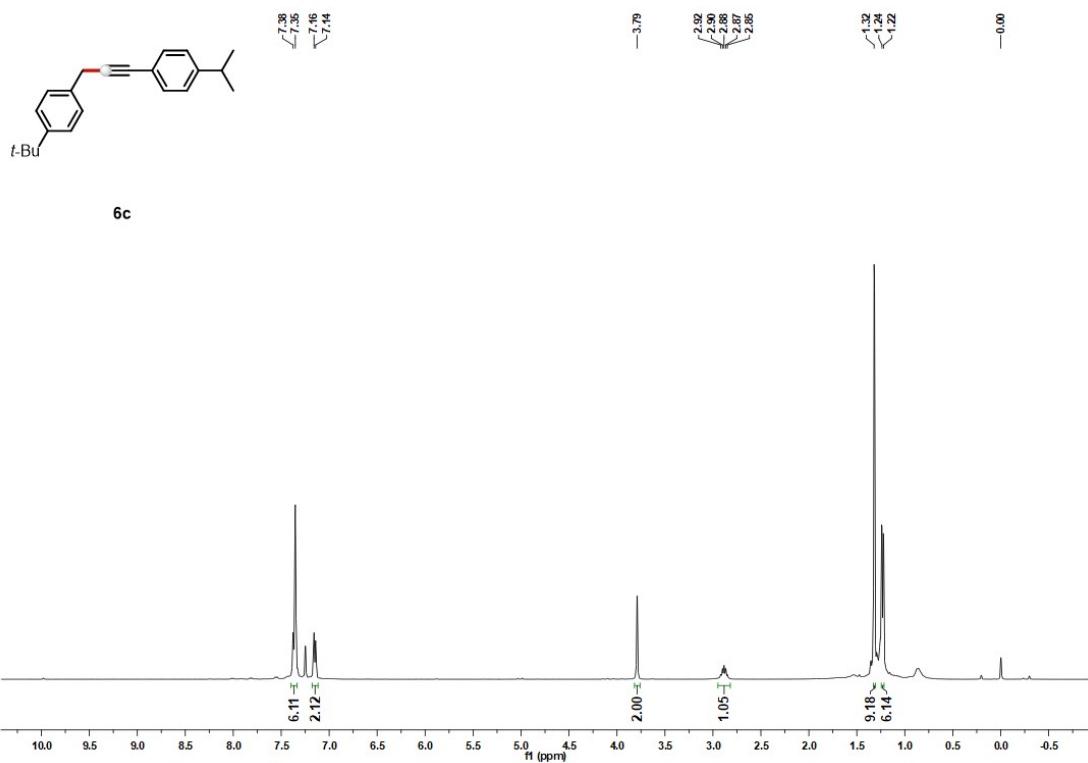
<sup>13</sup>C NMR of **6b**

CDCl<sub>3</sub>, 101 MHz, 298 K



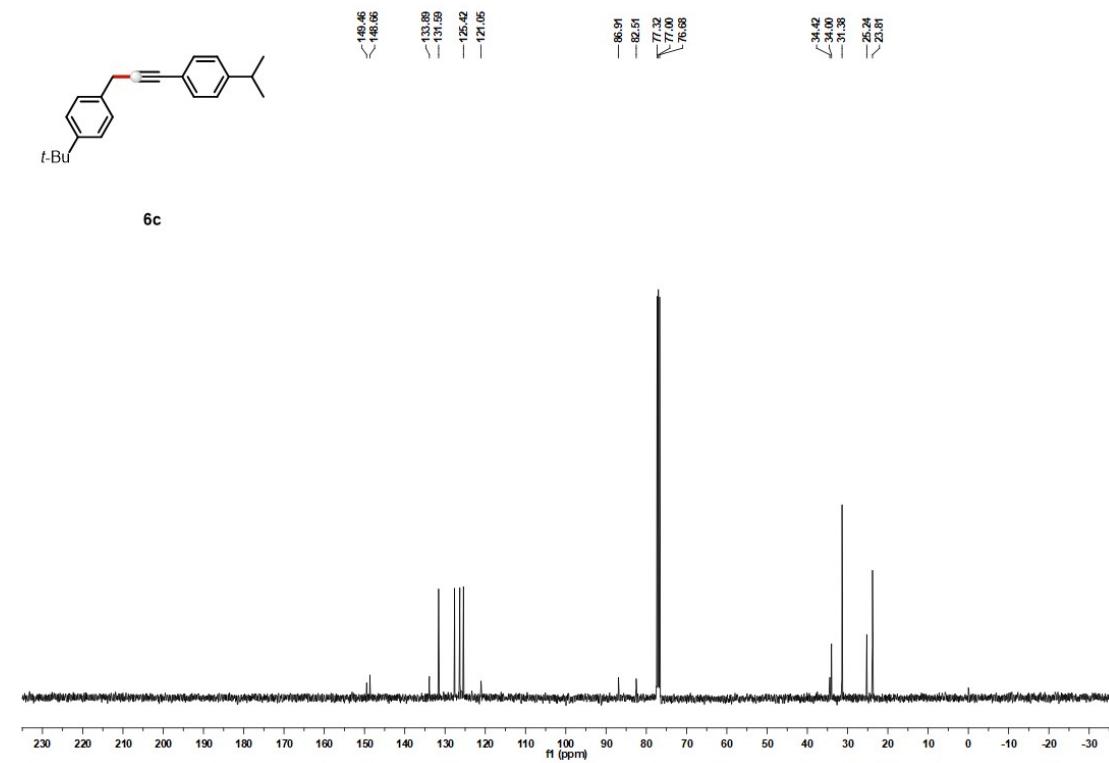
<sup>1</sup>H NMR of **6c**

CDCl<sub>3</sub>, 400 MHz, 298 K



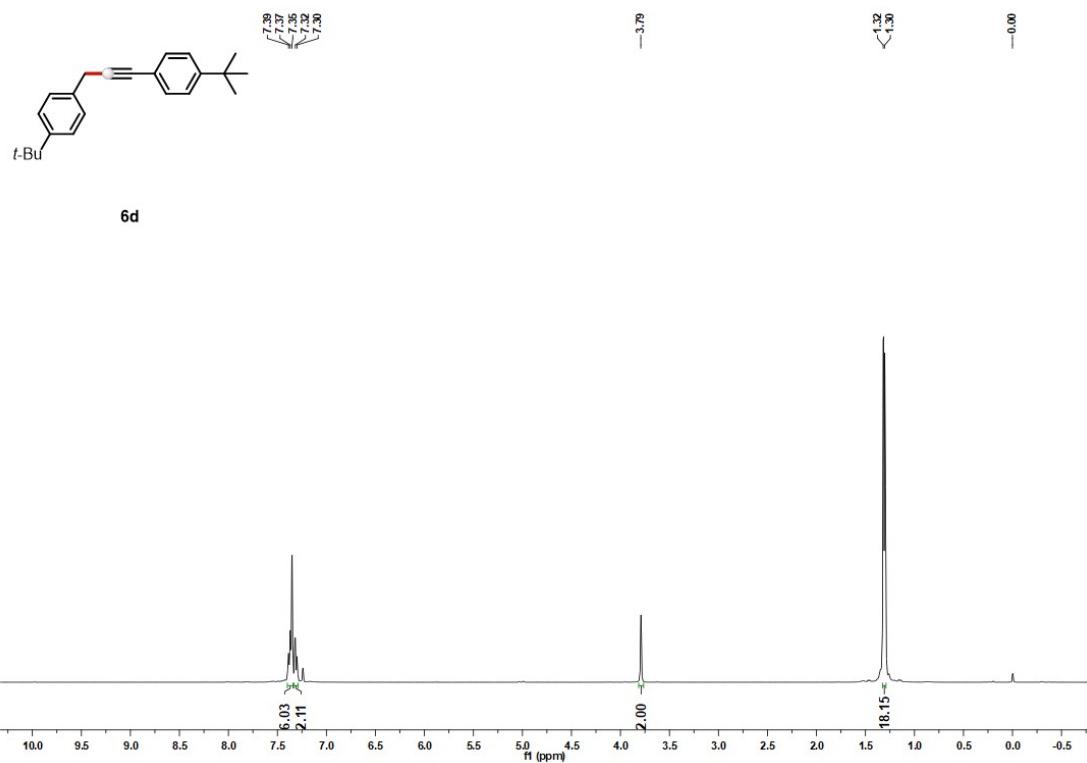
<sup>13</sup>C NMR of **6c**

CDCl<sub>3</sub>, 101 MHz, 298 K



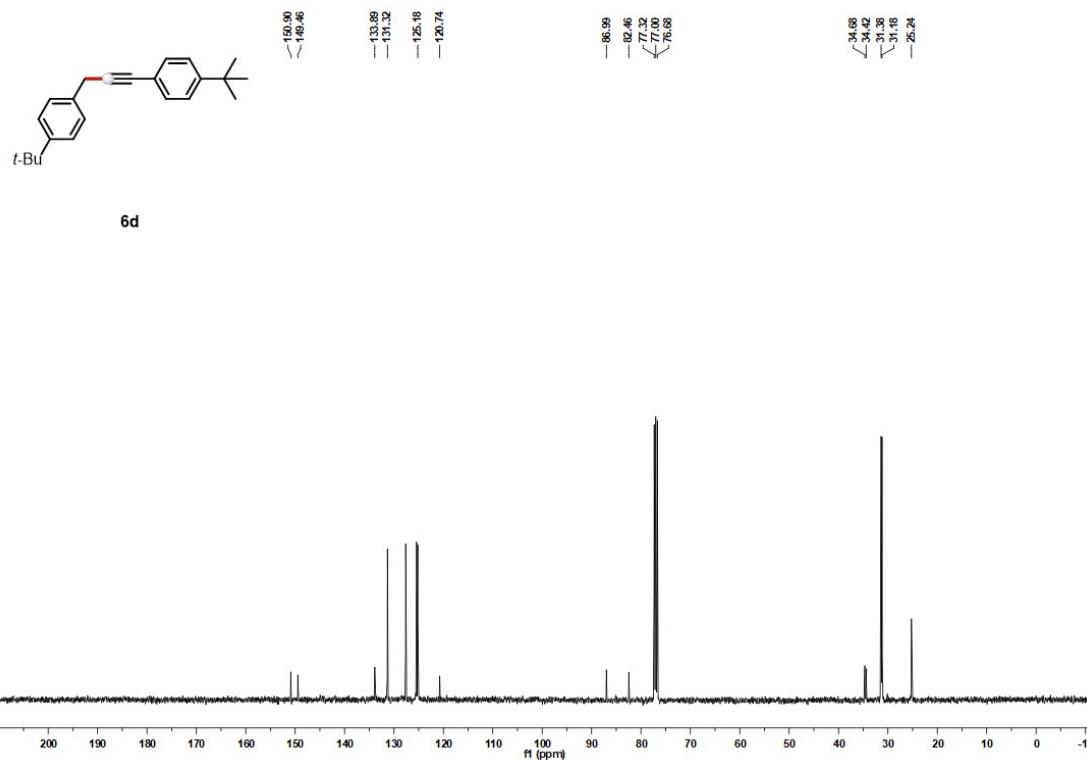
<sup>1</sup>H NMR of **6d**

CDCl<sub>3</sub>, 400 MHz, 298 K



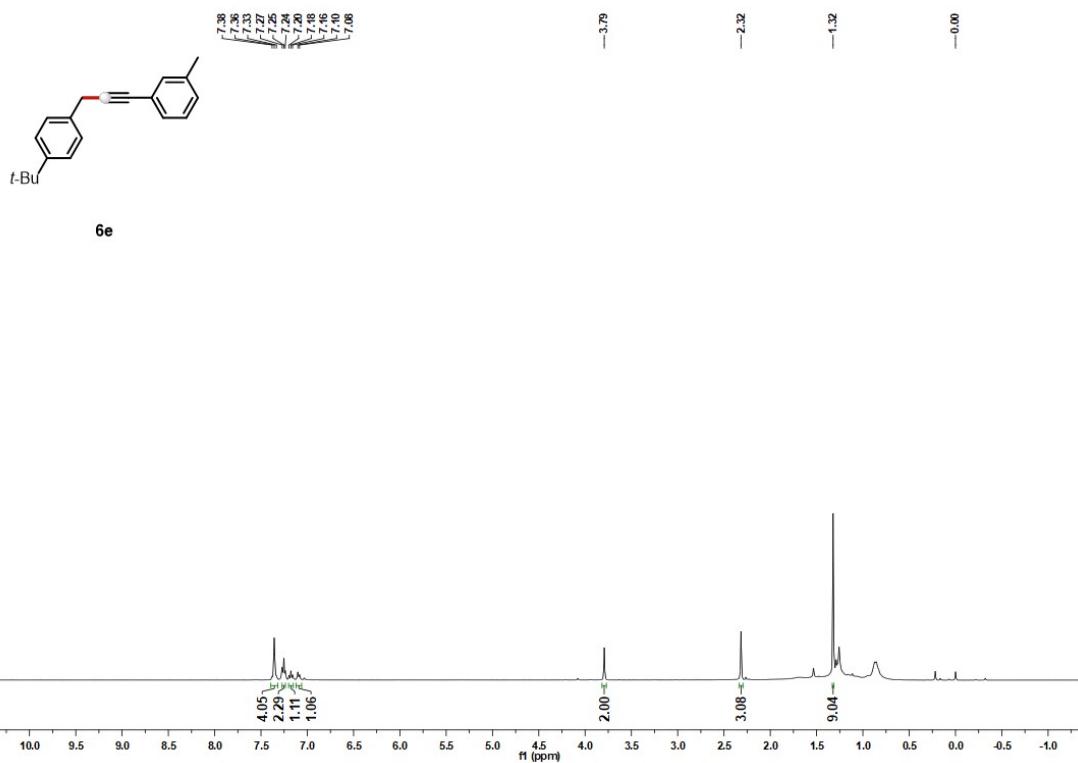
<sup>13</sup>C NMR of **6d**

CDCl<sub>3</sub>, 101 MHz, 298 K



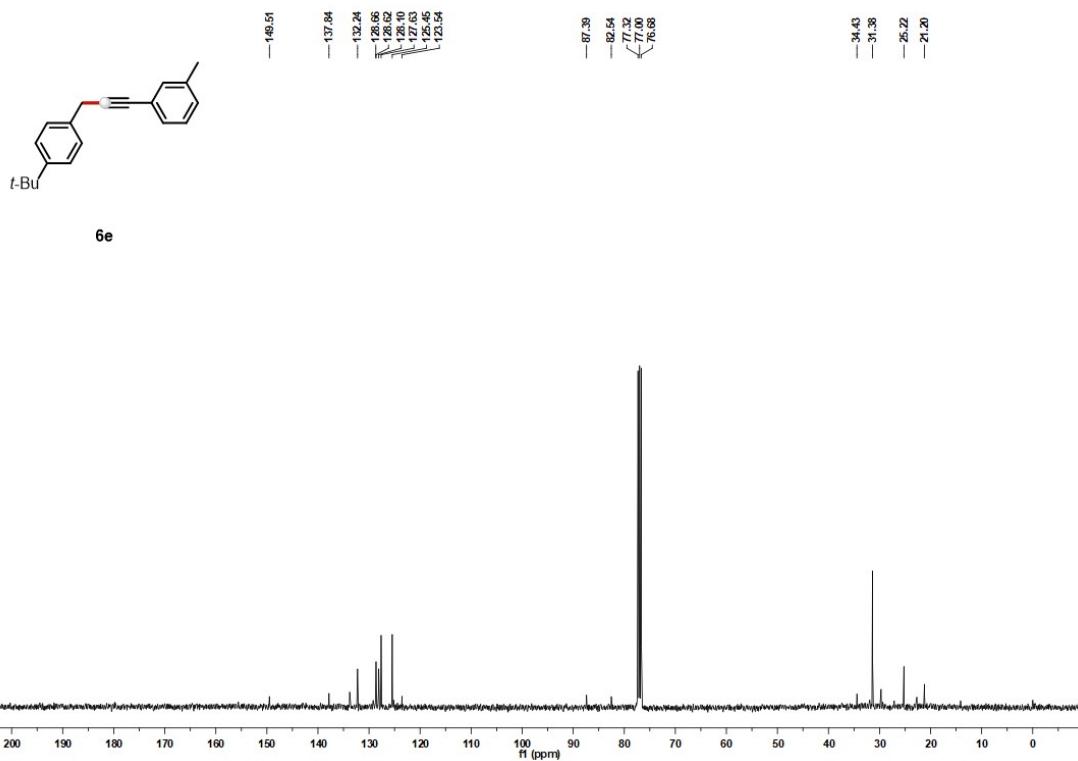
<sup>1</sup>H NMR of **6e**

CDCl<sub>3</sub>, 400 MHz, 298 K



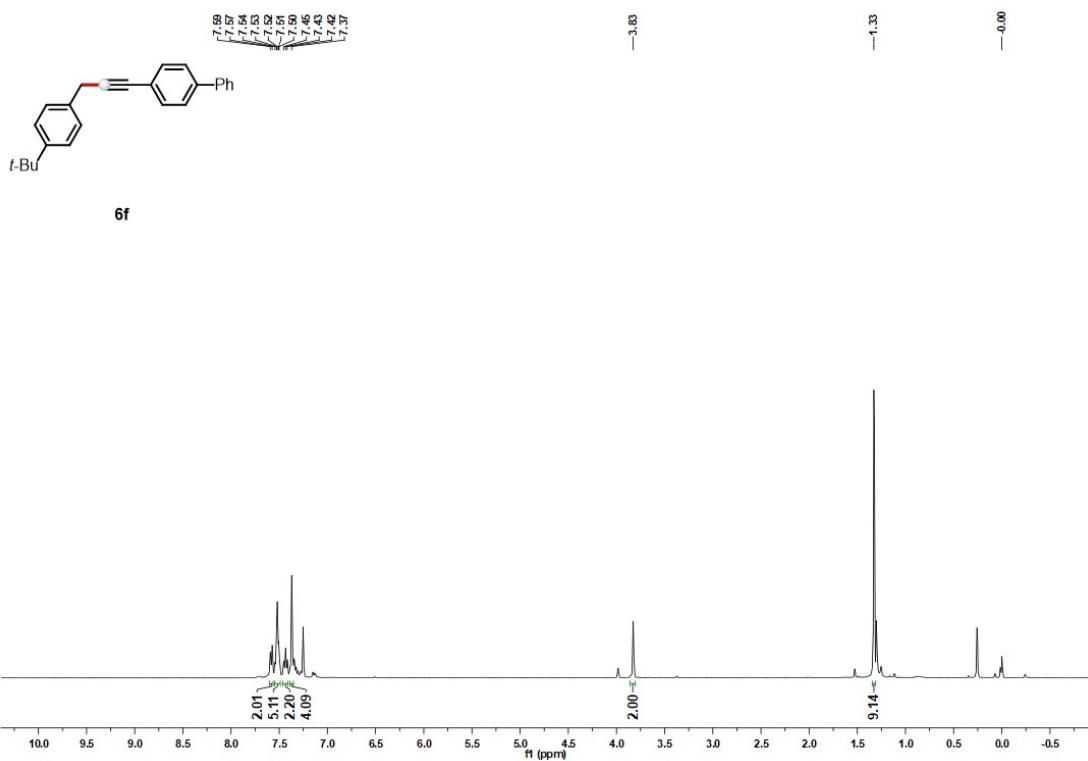
<sup>13</sup>C NMR of **6e**

CDCl<sub>3</sub>, 101 MHz, 298 K



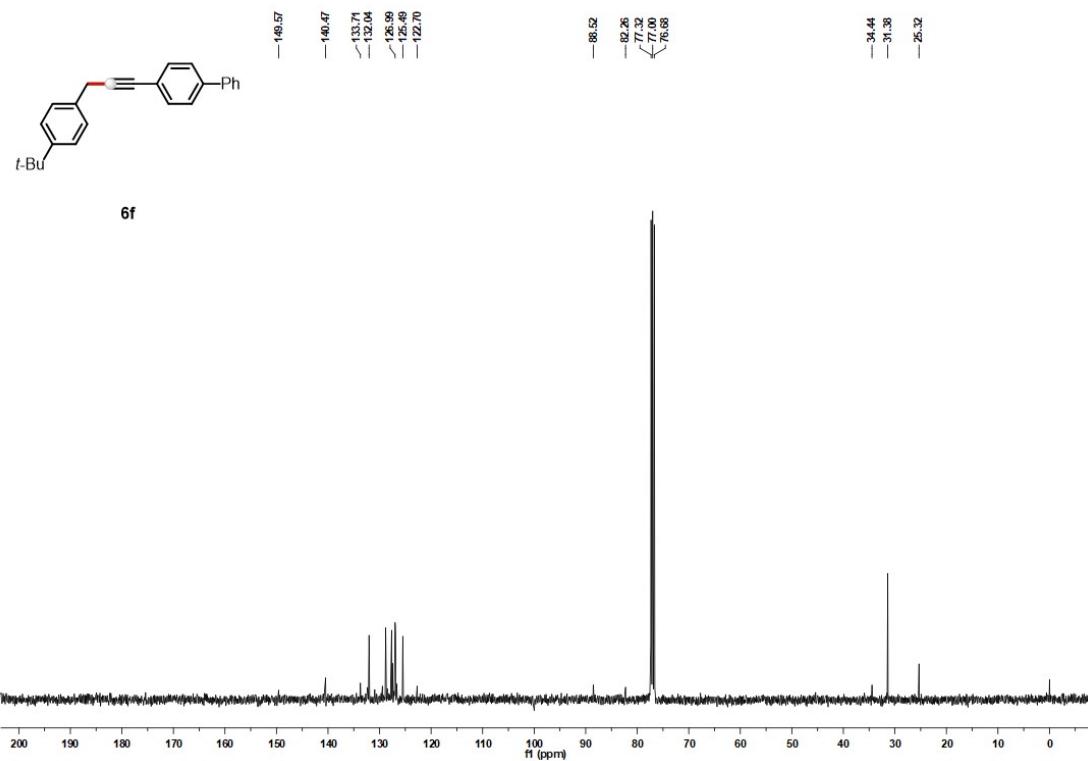
<sup>1</sup>H NMR of **6f**

CDCl<sub>3</sub>, 400 MHz, 298 K

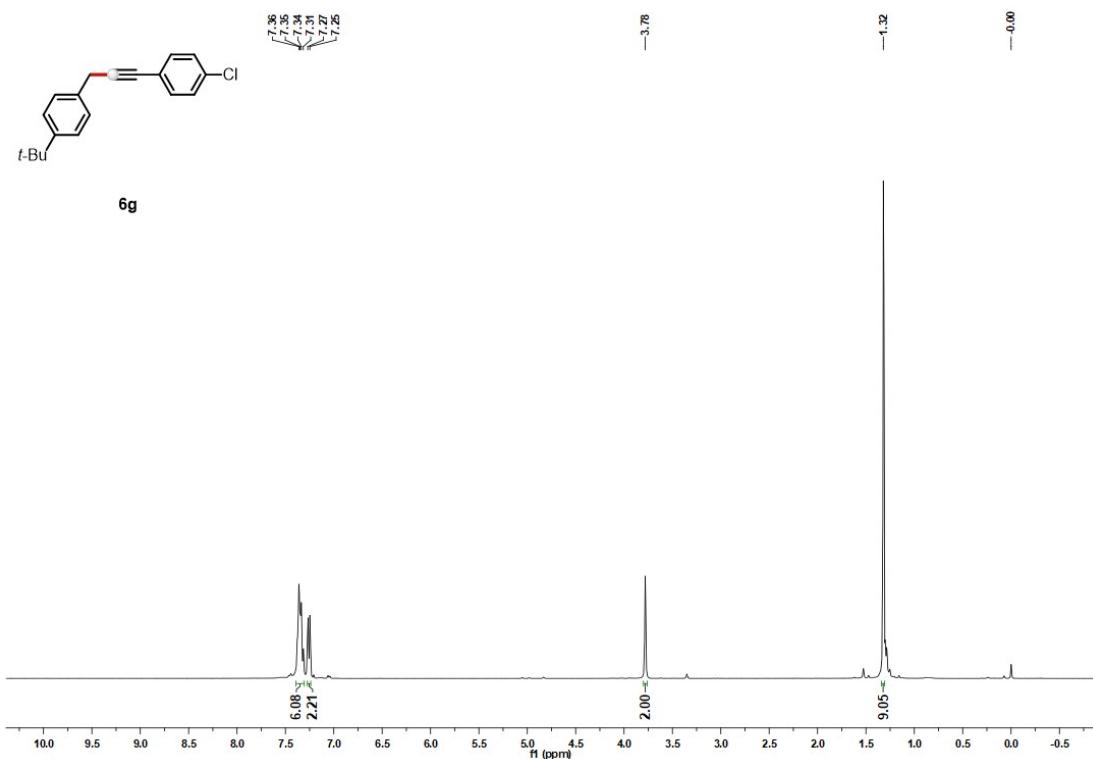


<sup>13</sup>C NMR of **6f**

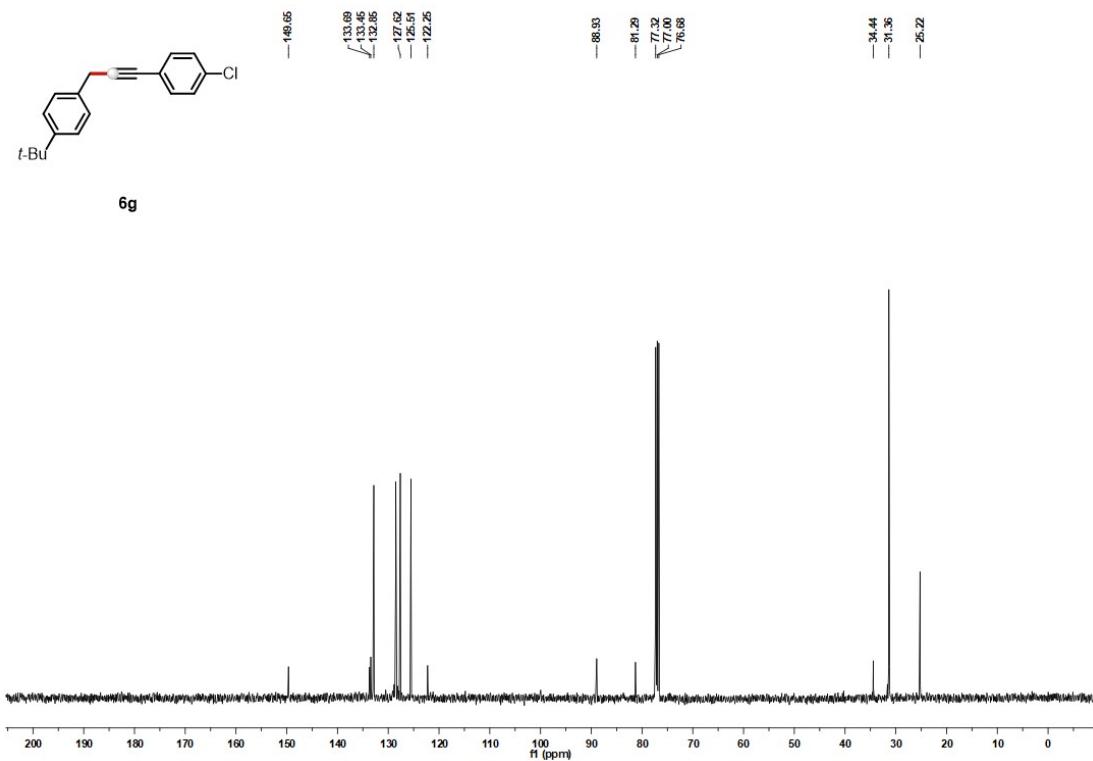
CDCl<sub>3</sub>, 101 MHz, 298 K



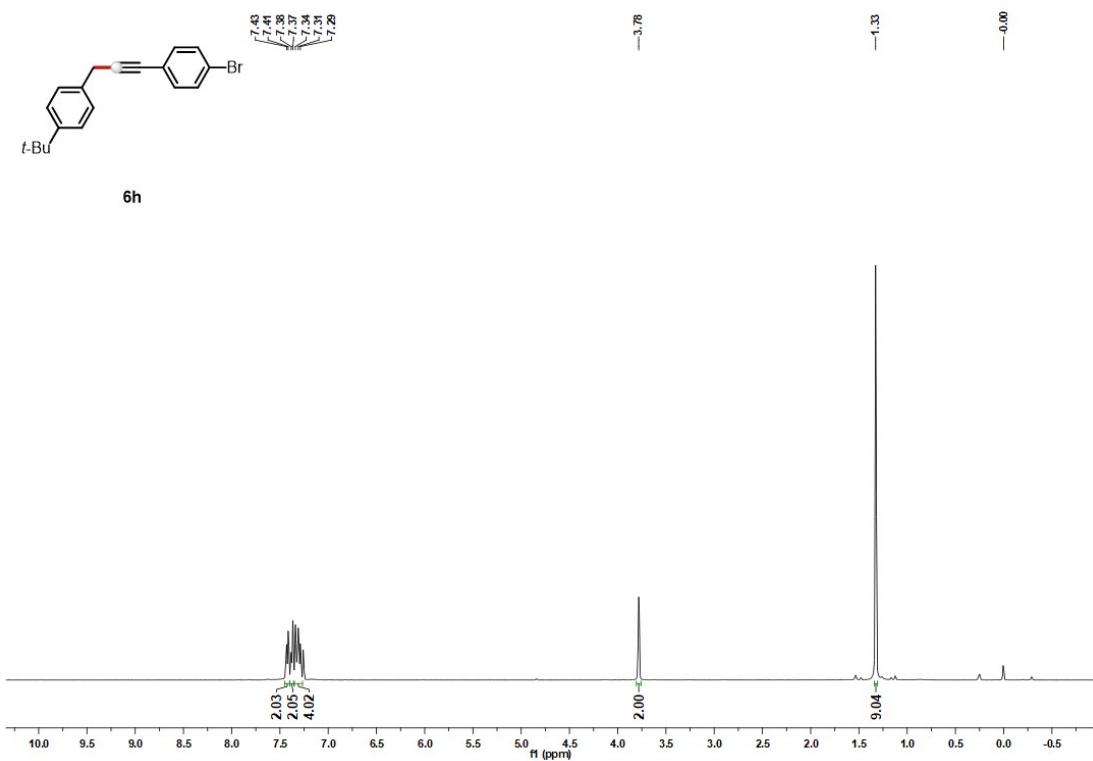
<sup>1</sup>H NMR of **6g**  
CDCl<sub>3</sub>, 400 MHz, 298 K



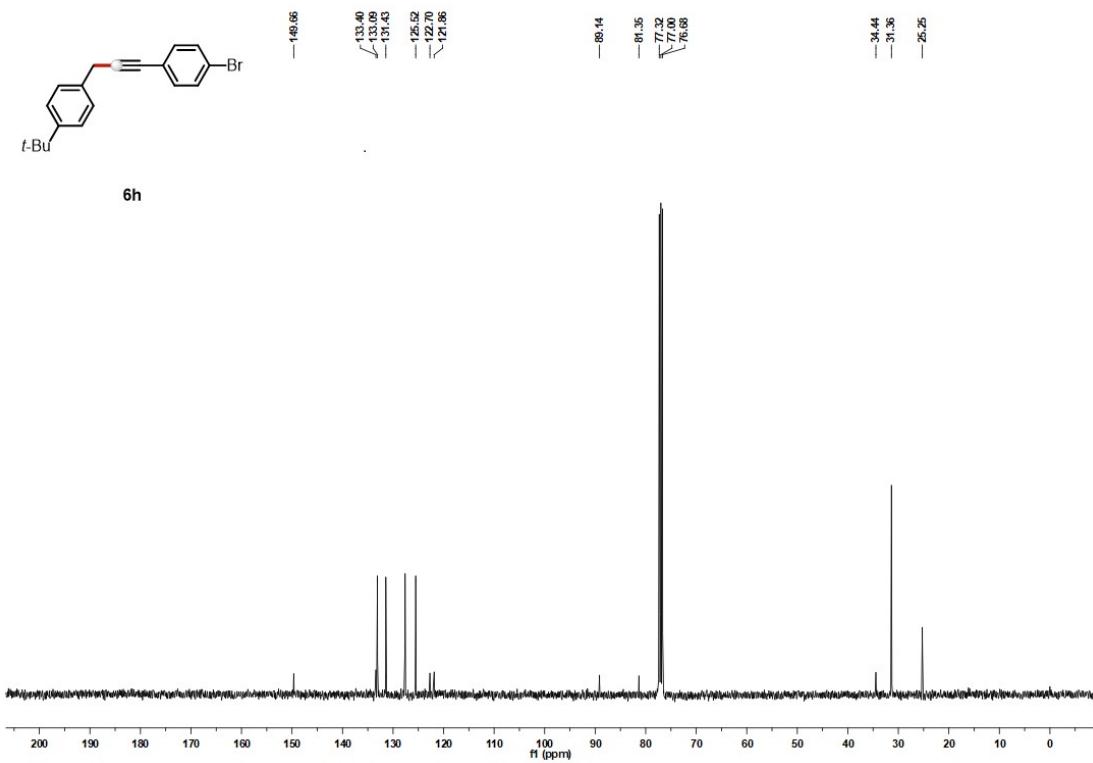
<sup>13</sup>C NMR of **6g**  
CDCl<sub>3</sub>, 101 MHz, 298 K



<sup>1</sup>H NMR of **6h**  
CDCl<sub>3</sub>, 400 MHz, 298 K

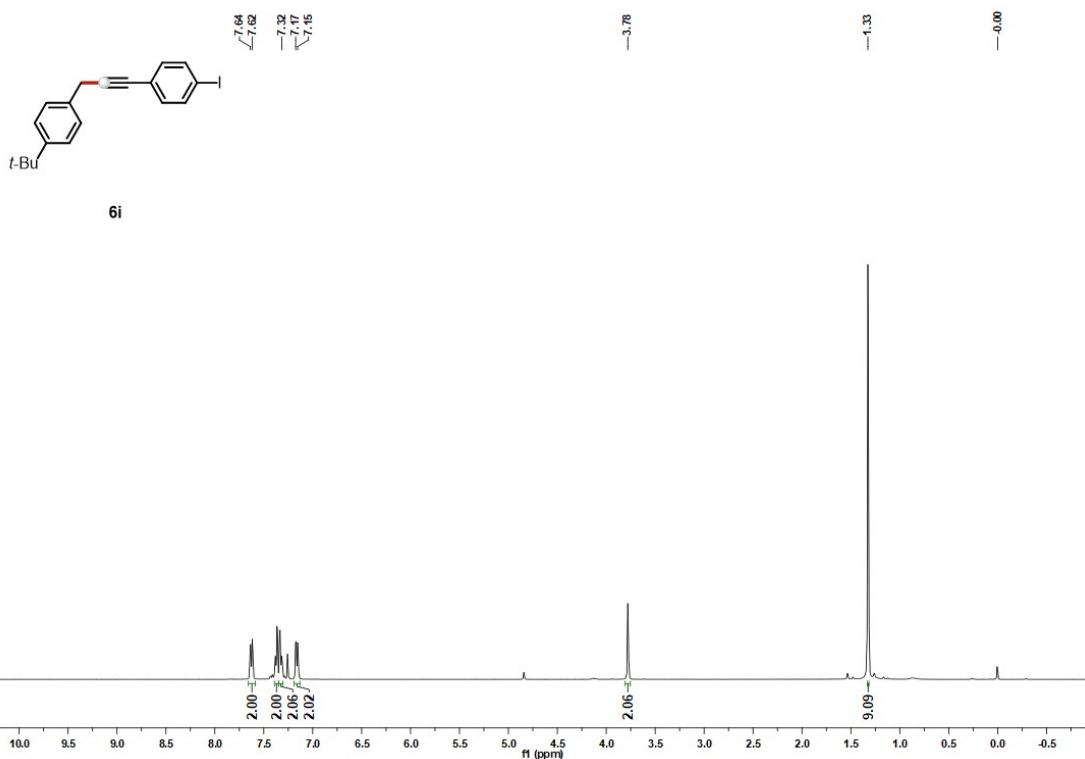


<sup>13</sup>C NMR of **6h**  
CDCl<sub>3</sub>, 101 MHz, 298 K



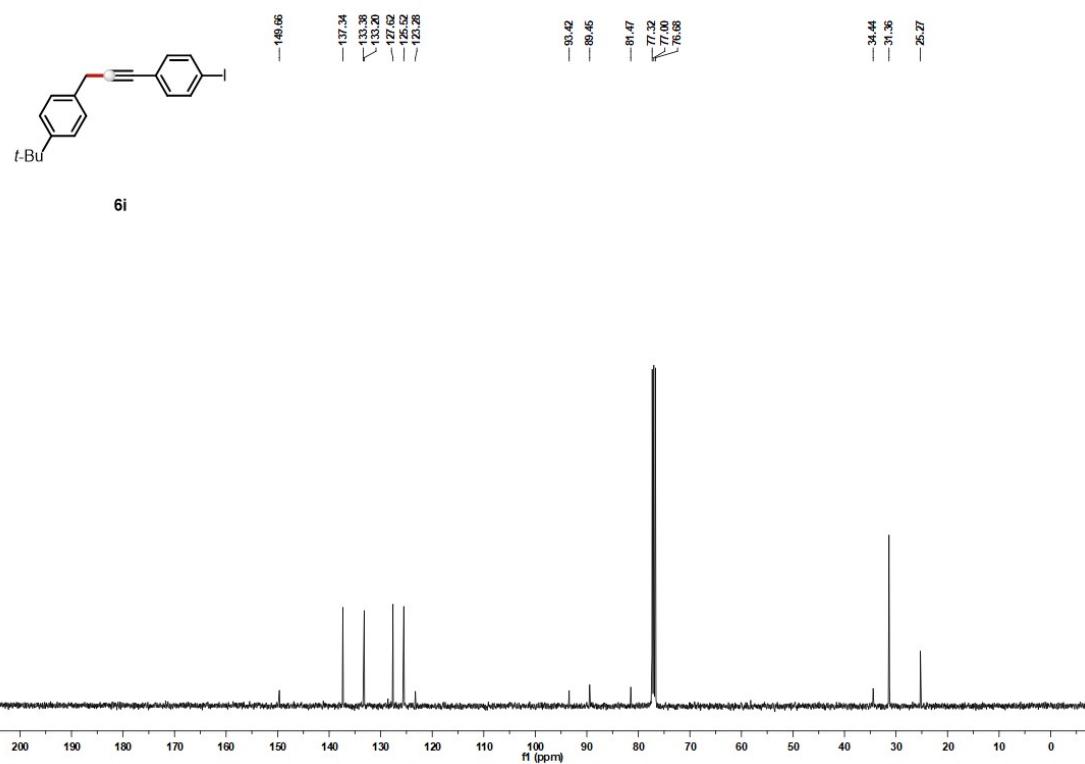
<sup>1</sup>H NMR of **6i**

CDCl<sub>3</sub>, 400 MHz, 298 K

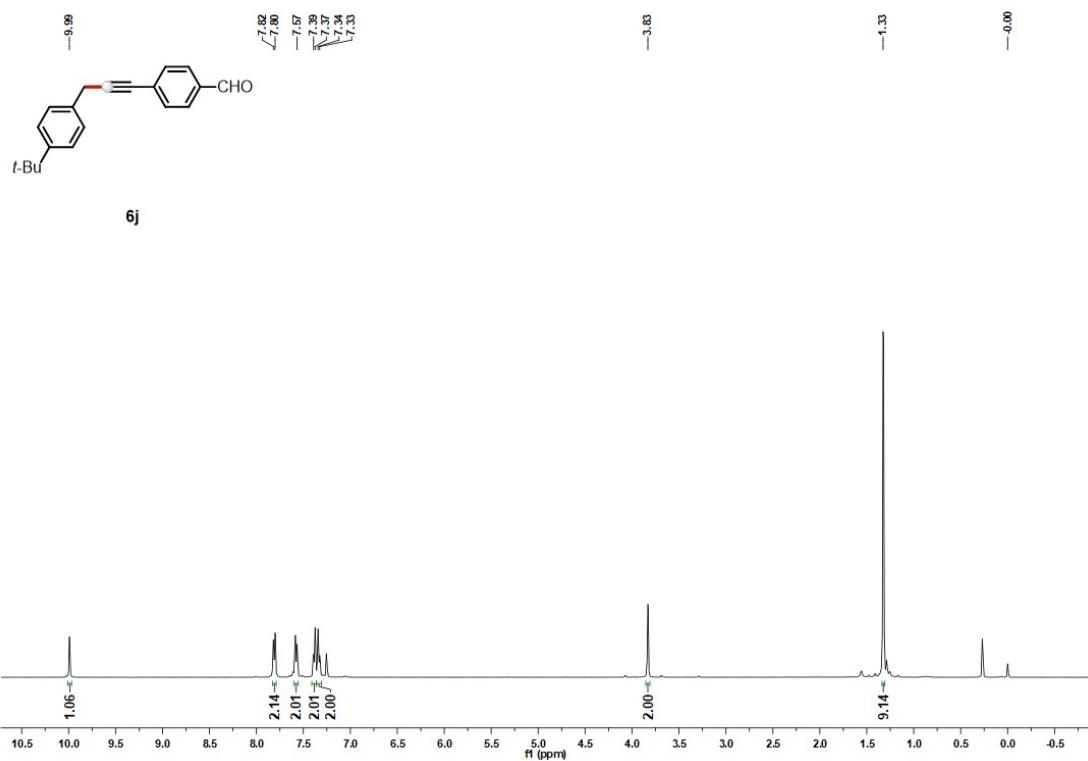


<sup>13</sup>C NMR of **6i**

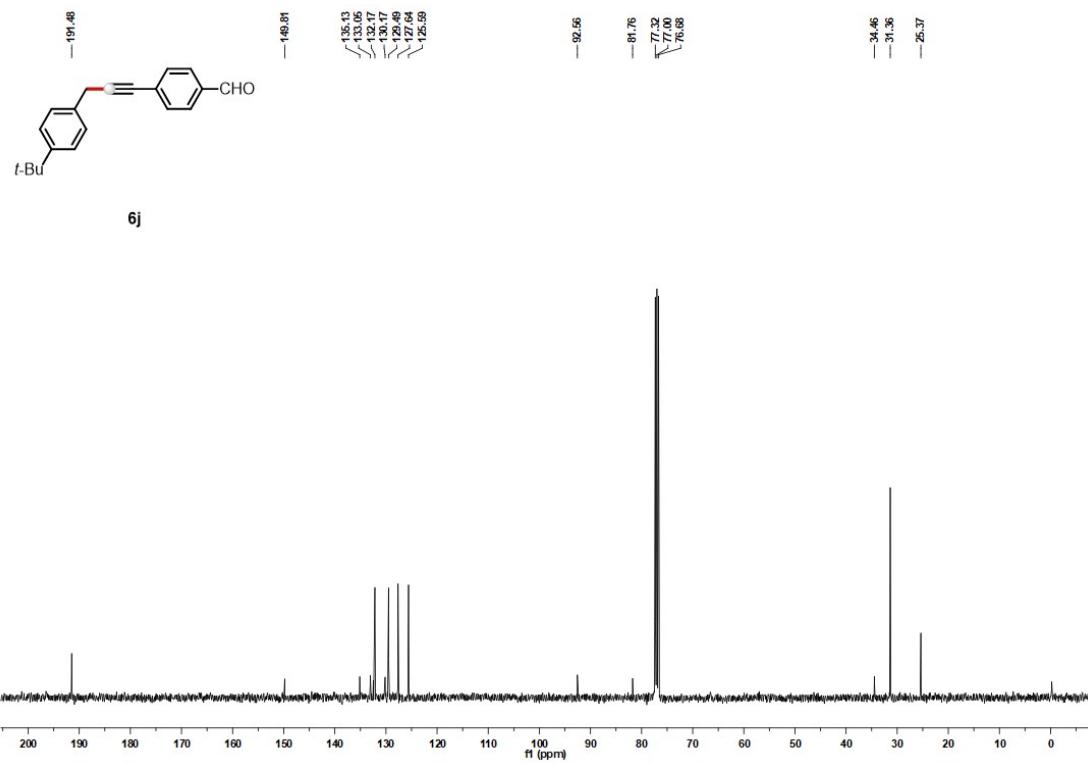
CDCl<sub>3</sub>, 101 MHz, 298 K



<sup>1</sup>H NMR of **6j**  
 $\text{CDCl}_3$ , 400 MHz, 298 K



<sup>13</sup>C NMR of **6j**  
 $\text{CDCl}_3$ , 101 MHz, 298 K



## 7. References

1. Robinson, S. W.; Mustoe, C. L.; White, N. G. Evidence for Halogen Bond Covalency in Acyclic and Interlocked Halogen-Bonding Receptor Anion Recognition. *Journal of the American Chemical Society* **2015**, *137* (1), 499-507.
2. Blessley, G.; Holden, P.; Walker, M. Palladium-Catalyzed Substitution and Cross-Coupling of Benzylic Fluorides. *Organic Letters* **2012**, *14* (11), 2754-2757.
3. Lal, G. S.; Pez, G. P.; Pesaresi, R. J. Bis(2-methoxyethyl)aminosulfur trifluoride: A new broad-spectrum deoxofluorinating agent with enhanced thermal stability. *Journal of Organic Chemistry* **1999**, *64* (19), 7048-7054.
4. Mosiagin, I.; Fernandes, A. J.; Budinska, A. Catalytic ipso-Nitration of Organosilanes Enabled by Electrophilic N Nitrosaccharin Reagent. *Angewandte Chemie-International Edition* **2023**, *62* (41).
5. Wilson, K. L.; Kennedy, A. R.; Murray, J. Scope and limitations of a DMF bio-alternative within Sonogashira cross-coupling and Cacchi-type annulation. *Beilstein Journal of Organic Chemistry* **2016**, *12*, 2005-2011.
6. (a) Tang, R.-J.; Milcent, T.; Crousse, B. Regioselective Halogenation of Arenes and Heterocycles in Hexafluoroisopropanol. *Journal of Organic Chemistry* **2018**, *83* (2), 930-938. (b) Srikrishna, A.; Viswajanani, R. Tri-*n*-butylstannyll chloride-sodium cyanoborohydride mediated regioselective reductive demethoxylation of alkyl methyl ketals. *Journal of the Indian Chemical Society* **2000**, *77* (11-12), 621-625.
7. Kong, X.; Chen, Y.; Liu, Q. Selective Fluorosulfonylation of Thianthrenium Salts Enabled by Electrochemistry. *Organic Letters* **2023**, *25* (4), 581-586.
8. Yu, C.; Huang, R.; Patureau, F. W. Direct Dehydrogenative Access to Unsymmetrical Phenones. *Angewandte Chemie-International Edition* **2022**, *61* (20).
9. Seifert, F. U.; Röschenenthaler, G.-V. Additionen von trimethylsilylphosphiten an pentafluoraceteton. *Journal of Fluorine Chemistry* **1994**, *68* (2), 169-174.
10. Zhang, D.; Xu, Z.; Tang, T.; Le, L.; Wang, C.; Kambe, N.; Qiu, R. Pd-Catalyzed

Cross-Coupling of Sb-Aryl Stibines with Halogenomethyl Arenes to Give Unsymmetric Diarylmethanes. *Organic Letters* **2022**, *24* (17), 3155-3160.

11. Chen, Y. G.; Wang, X.; He, X.; An, Q.; Zuo, Z. W. Photocatalytic Dehydroxymethylative Arylation by Synergistic Cerium and Nickel Catalysis. *Journal of the American Chemical Society* **2021**, *143* (13), 4896-4902.
12. Wang, X. X.; Xu, B. B.; Song, W. T.; Sun, K. X.; Lu, J. M. N-heterocyclic carbene-palladium(II)-1-methylimidazole complex-catalyzed Suzuki-Miyaura coupling of benzyl sulfonates with arylboronic acids. *Organic & Biomolecular Chemistry* **2015**, *13* (17), 4925-4930.
13. Li, J. S.; Kang, T. F.; Xiao, Y.; Li, Z. Y.; Xiao, Y. L.; Yan, Y. G.; Song, G. Y.; Li, G.; Dong, J. Y.; Wang, C.; et al. The Multiple Roles of Bipyridine-Nickel(II) Complex in Versatile Photoredox C(sp<sub>2</sub>)-C(sp<sub>3</sub>) Cross-Coupling. *Ac<sub>s</sub> Catalysis* **2025**, *15* (4), 3328-3338.
14. Forster, F.; Metsänen, T. T.; Irran, E.; Hrobárik, P.; Oestreich, M. Cooperative Al-H Bond Activation in DIBAL-H: Catalytic Generation of an Alumenium-Ion-Like Lewis Acid for Hydrodefluorinative Friedel-Crafts Alkylation. *Journal of the American Chemical Society* **2017**, *139* (45), 16334-16342.
15. Guo, J.; Bamford, K. L.; Stephan, D. W. 9-Borabicyclo 3.3.1 nonane-induced Friedel-Crafts benzylation of arenes with benzyl fluorides. *Organic & Biomolecular Chemistry* **2019**, *17* (21), 5258-5261.
16. Charboneau, D. J.; Huang, H.; Barth, E. L.; Germe, C. C.; Hazari, N.; Mercado, B. Q.; Uehling, M. R.; Zultanski, S. L. Tunable and Practical Homogeneous Organic Reductants for Cross-Electrophile Coupling. *Journal of the American Chemical Society* **2021**, *143* (49), 21024-21036.
17. Champagne, P. A.; Benhassine, Y.; Desroches, J.; Paquin, J.-F. Friedel-Crafts Reaction of Benzyl Fluorides: Selective Activation of C-F Bonds as Enabled by Hydrogen Bonding. *Angewandte Chemie-International Edition* **2014**, *53* (50), 13835-13839.
18. Desroches, J.; Champagne, P. A.; Benhassine, Y.; Paquin, J.-F. In situ activation of benzyl alcohols with XtalFluor-E: formation of 1,1-diarylmethanes and 1,1,1-

triarylmethanes through Friedel-Crafts benzylation *Organic & Biomolecular Chemistry* **2015**, *13* (8), 2243-2246.

19. Lv, F.; Xiao, J.; Xiang, J.; Guo, F.; Tang, Z.-L.; Han, L.-B. Conversion of Aryl Aldehydes to Benzyl Iodides and Diarylmethanes by  $H_3PO_3/I_2$ . *Journal of Organic Chemistry* **2021**, *86* (3), 3081-3088.

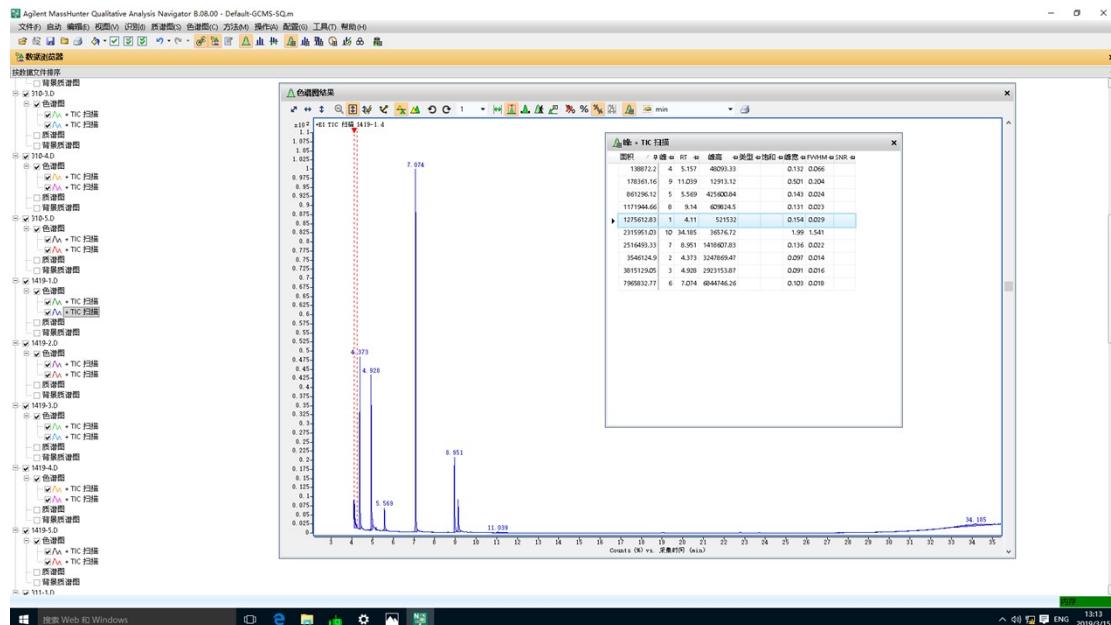
20. Biradar, D. B.; Gau, H.-M. Simple and efficient nickel-catalyzed cross-coupling reaction of alkynylalanes with benzylic and aryl bromides. *Chemical Communications* **2011**, *47* (37), 10467-10469.

## Appendix

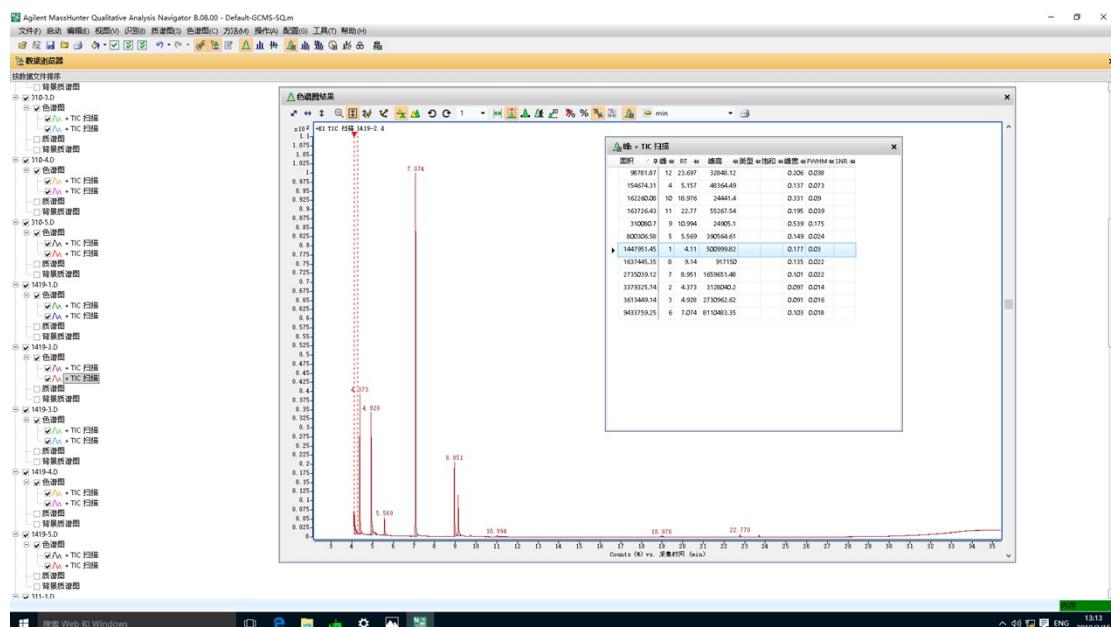
The following is the GC-MS raw data

$$\mathbf{1d} : \mathbf{2a} = 0.5 : 1$$

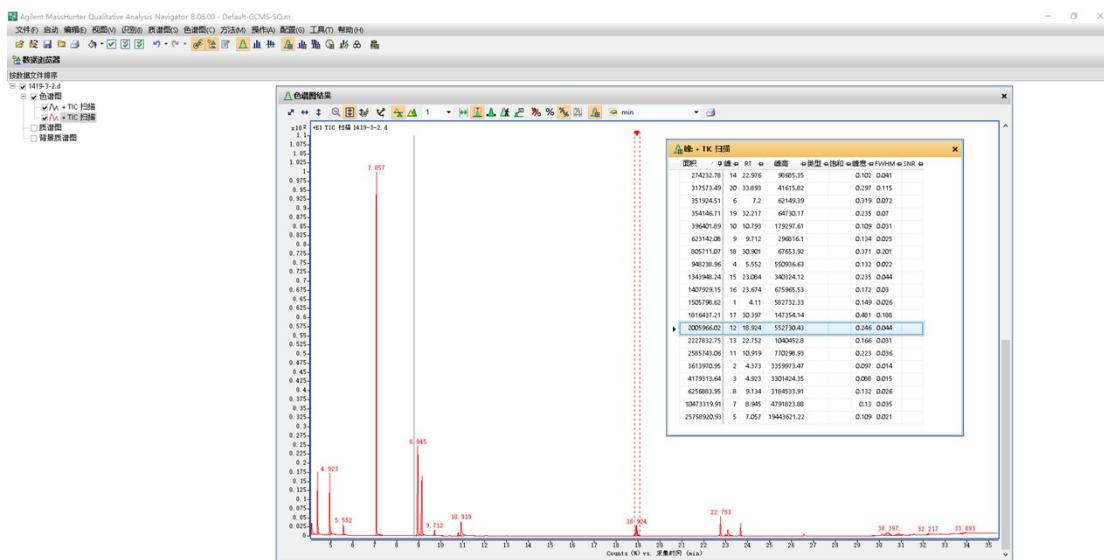
T=3 min



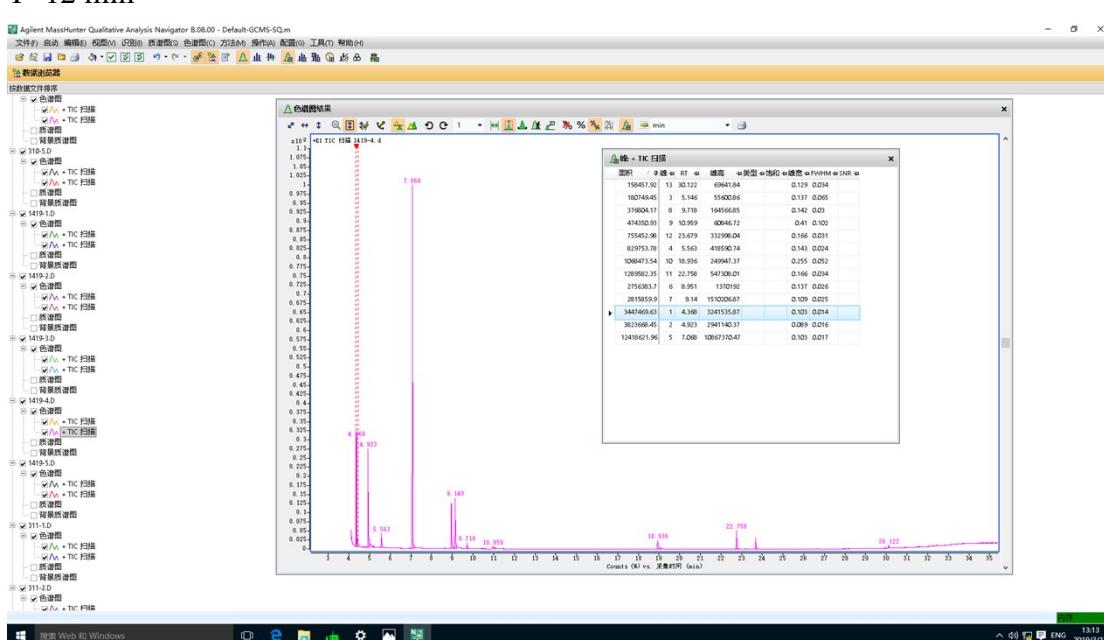
T=6 min



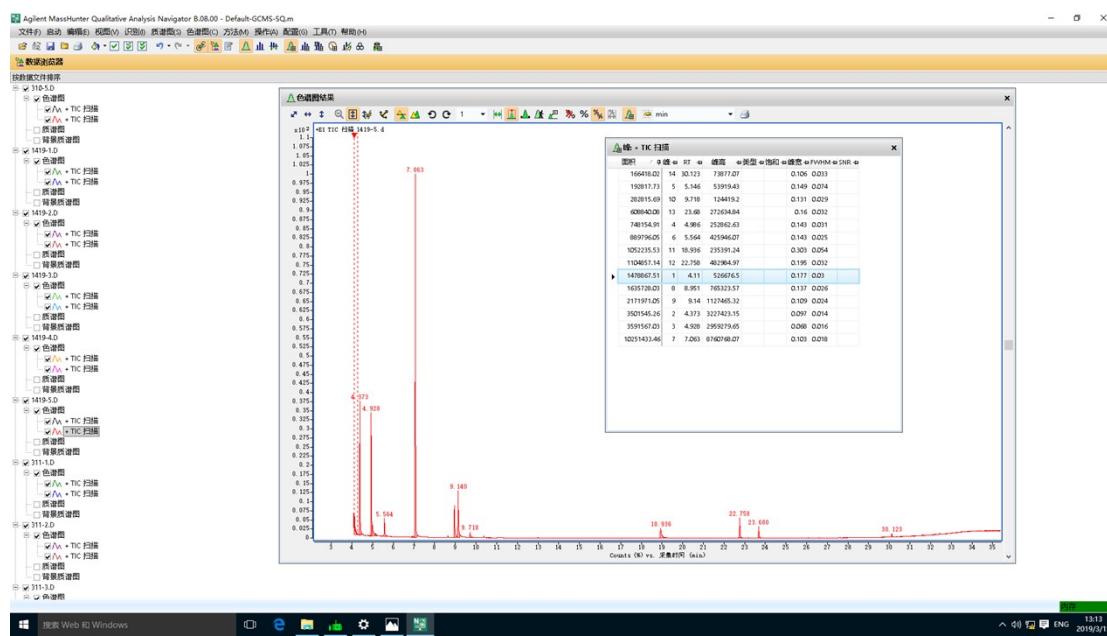
T=9 min



T=12 min

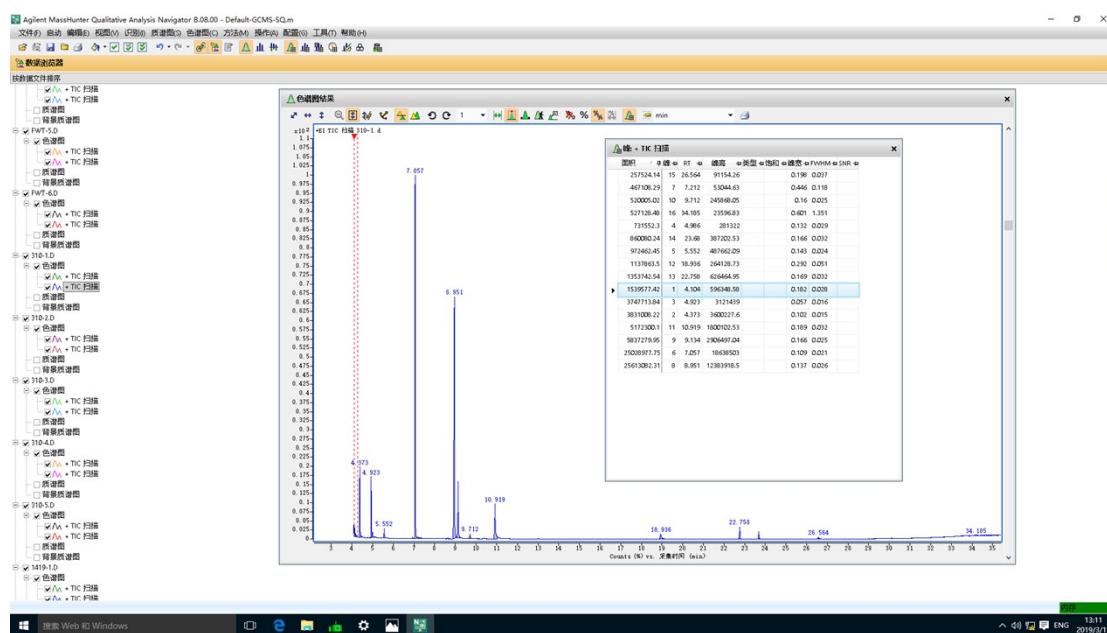


T=15 min

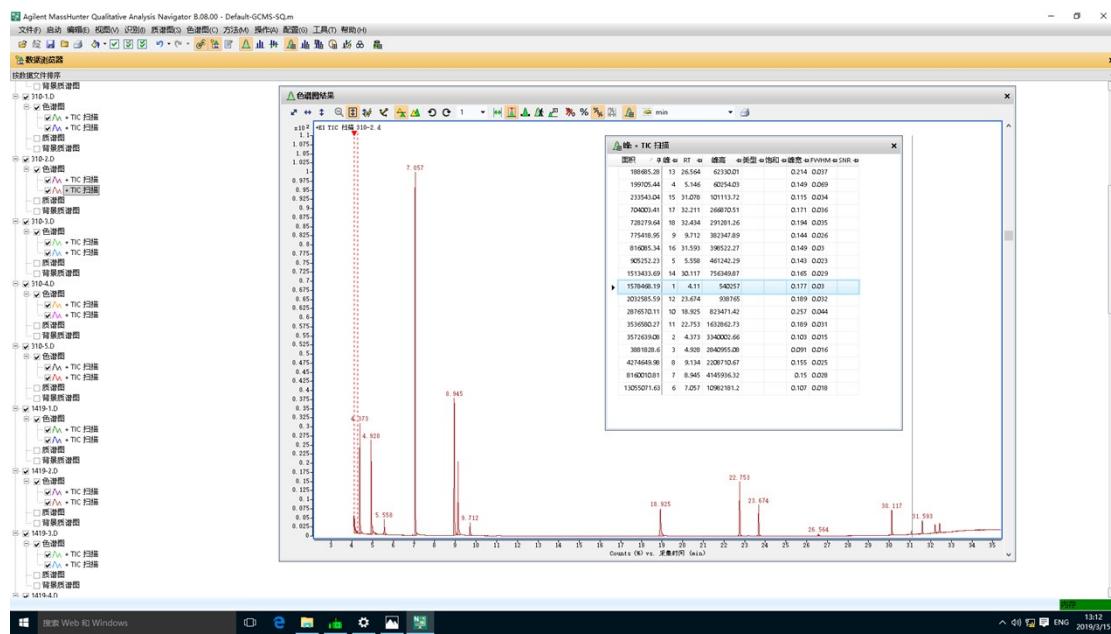


1d : 2a = 1 : 1

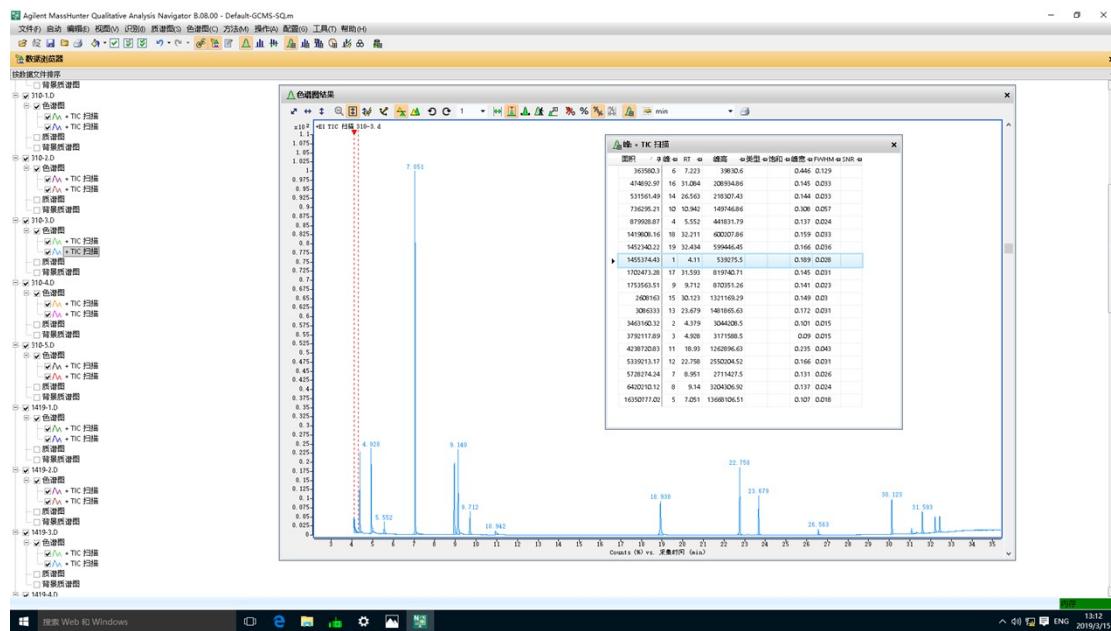
T=3 min



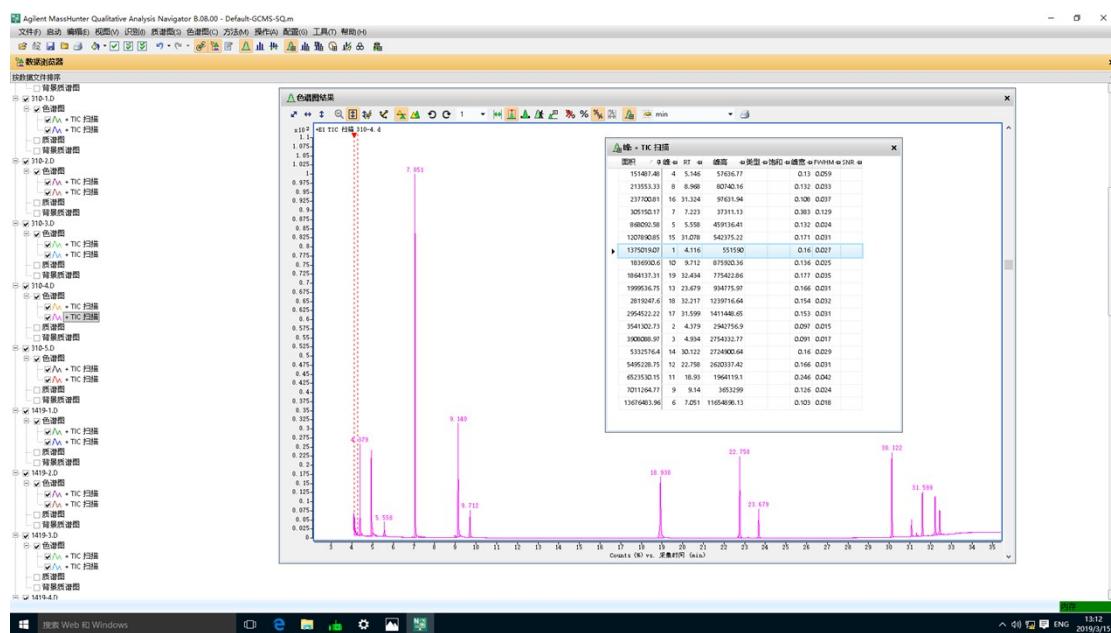
T=6 min



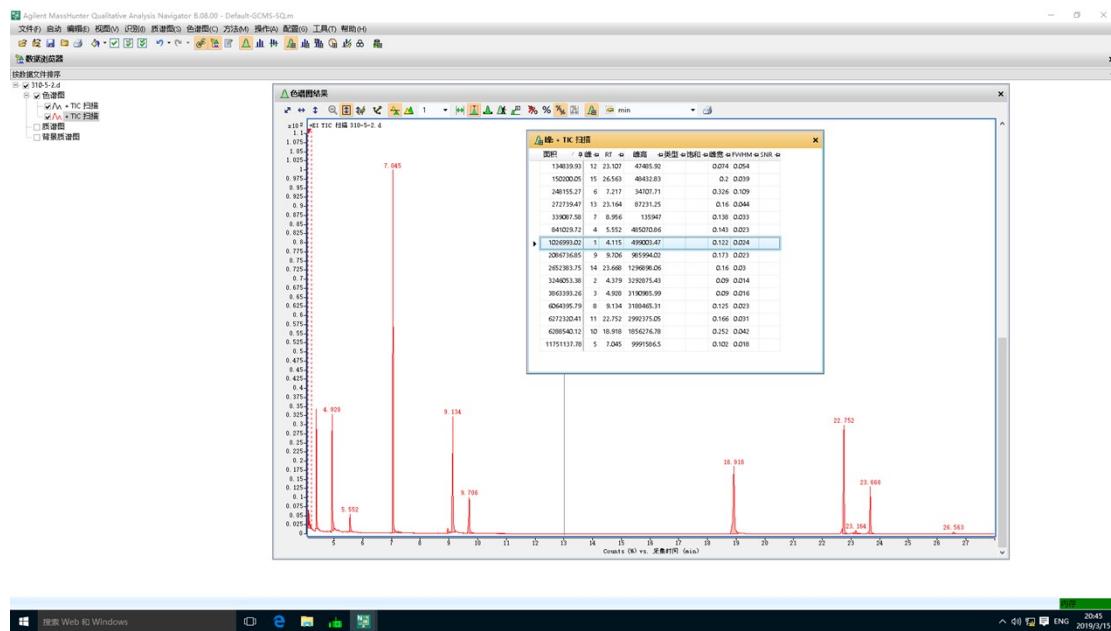
T=9 min



T=12 min

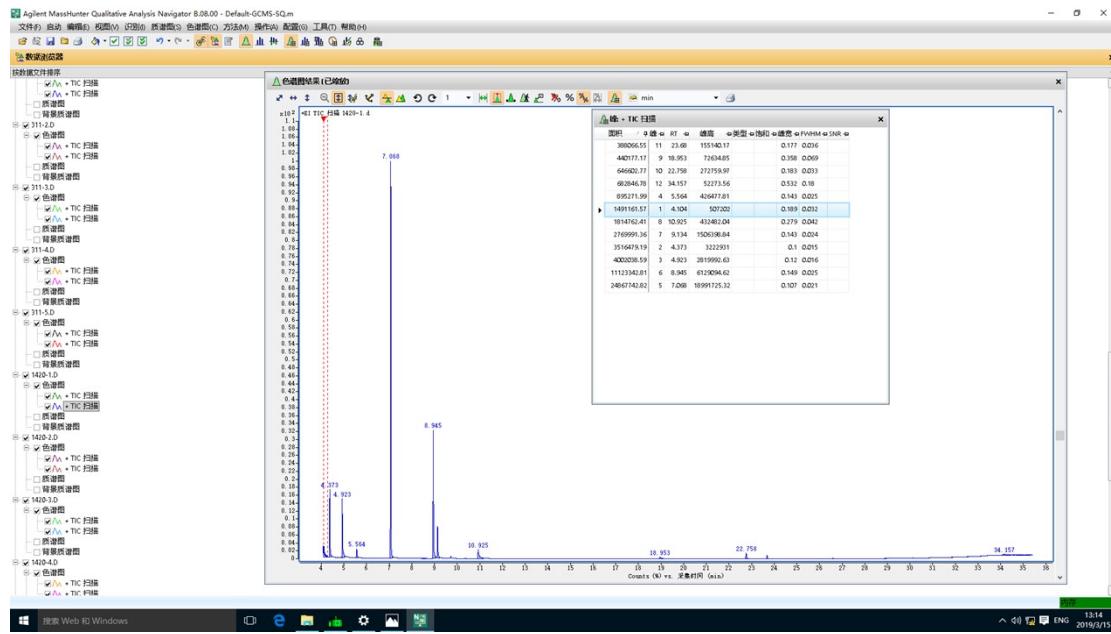


T=15 min

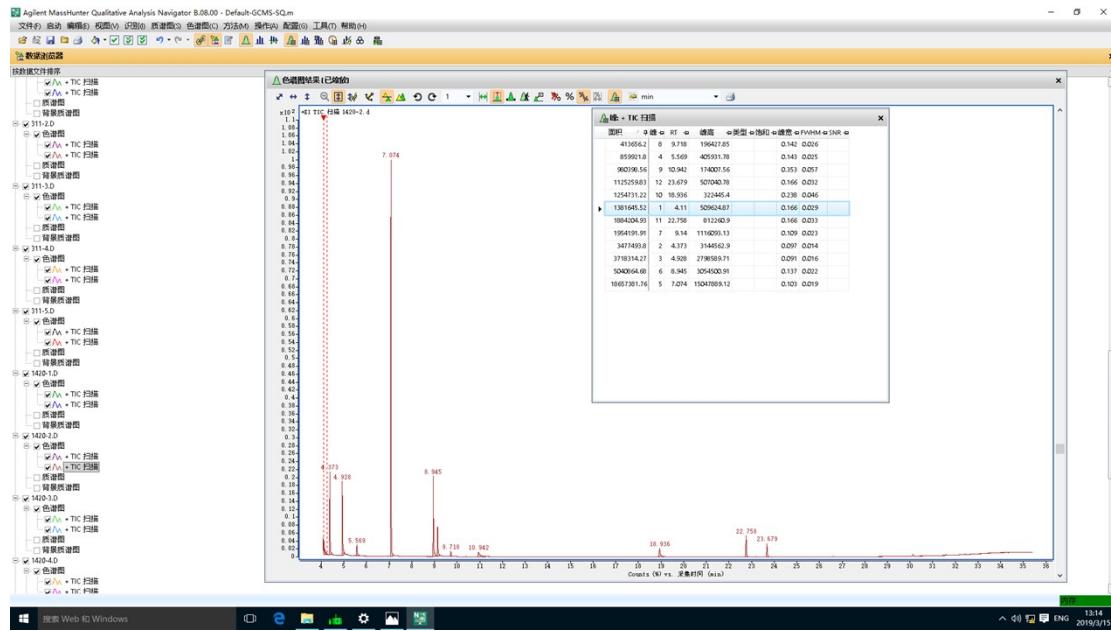


$$1\mathbf{d} : 2\mathbf{a} = 1 : 2$$

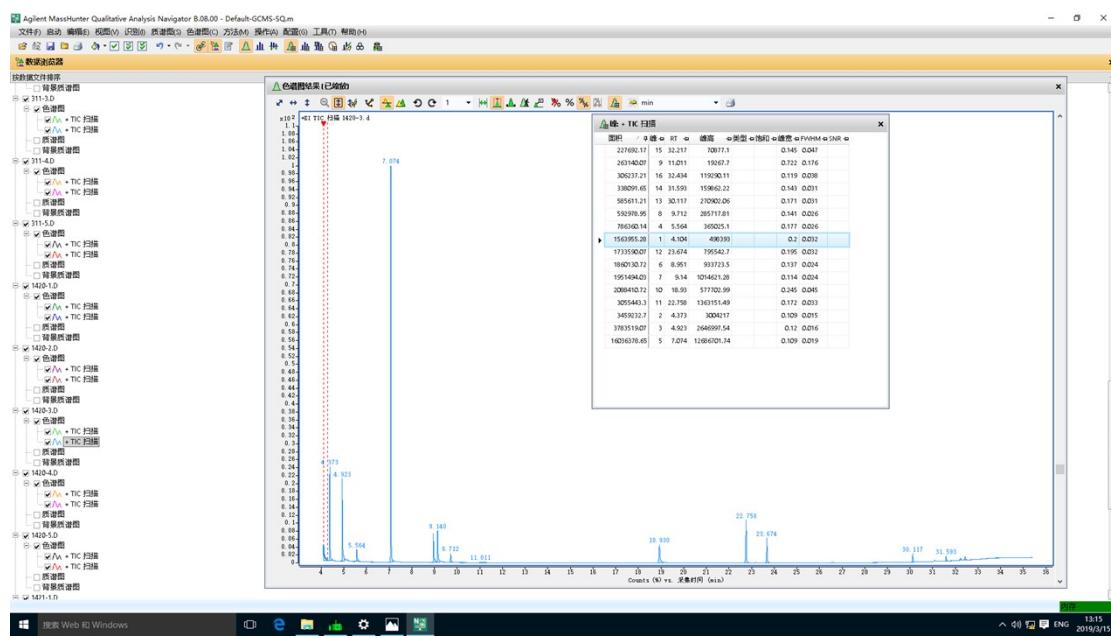
T=3 min



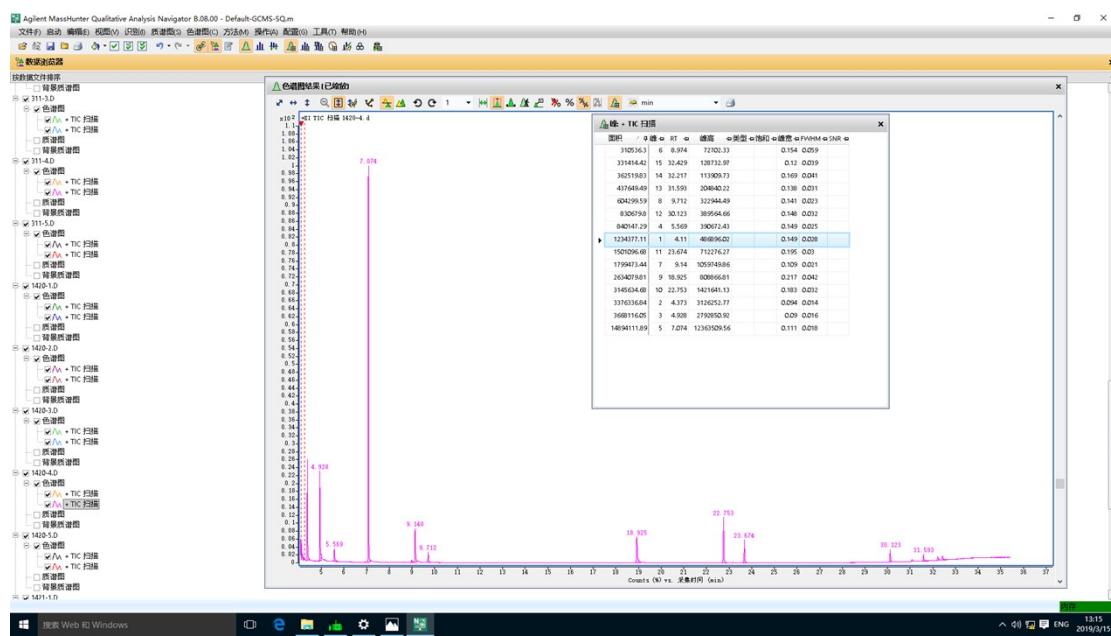
T=6 min



T=9 min



T=12 min



T=15 min

