Supporting Information

Dual silane-promoted palladium catalysis: synthesis of phenols from carbon dioxide and 1,4-enynes

Zhongrong Xu, Ting Zhao, Wenxin Jiang, Yanwei Ren, Chaorong Qi* and Huanfeng Jiang*

Key Lab of Functional Molecular Engineering of Guangdong Province, School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou 510640, China

E-mail: crqi@scut.edu.cn or jianghf@scut.edu.cn

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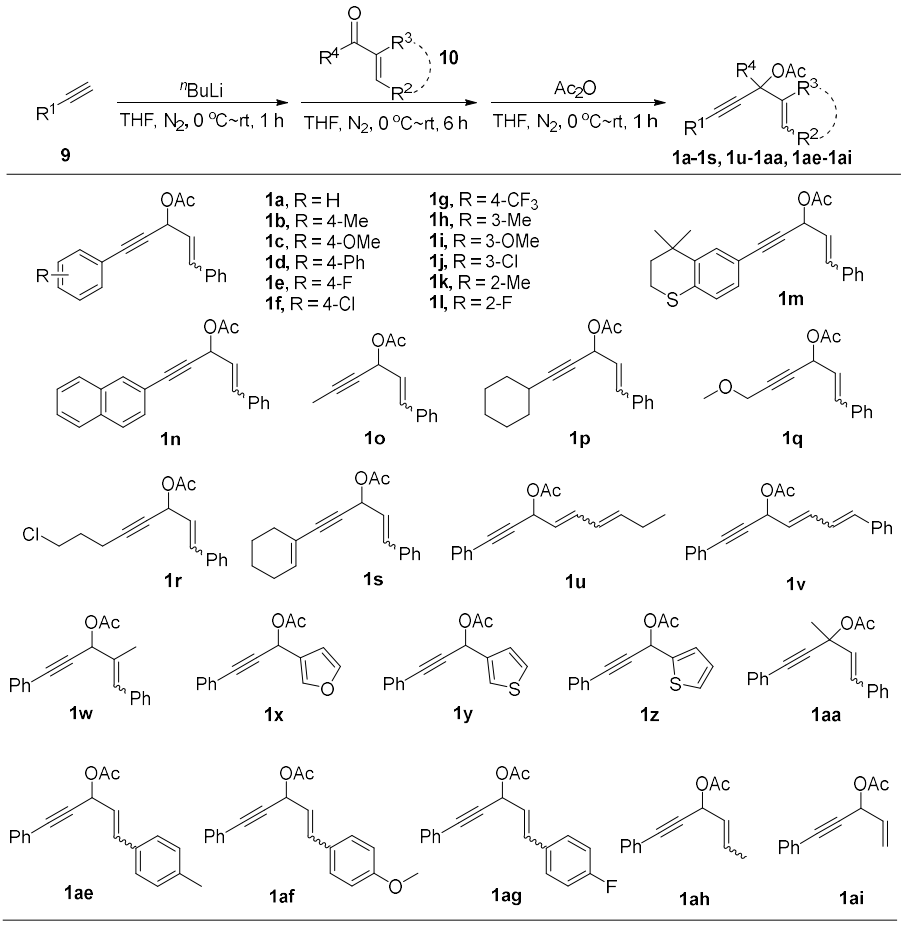
A General methods

^{1}H and ^{13}C NMR spectra were recorded by using a 400 MHz NMR spectrometer using $CDCl_3$ or DMSO-d_6 as solvent and TMS as an internal standard. The chemical shifts are referenced to signals at 7.26 and 77.0 ppm, respectively. The data of HRMS was carried out on a high-resolution mass spectrometer (LCMS-IT-TOF). GC-Mass analyses were conducted on a gas chromatograph-mass spectrometer (Trace 1300 ISQ) at an ionization voltage of 70 eV and equipped with a DB-WAX capillary column (internal diameter: 0.25 mm, length: 30 m). Melting points were determined with a digital melting point measuring instrument and are uncorrected. All the reaction temperatures reported are oil bath temperatures. The enynes **1a-1ak**, **3a**, **3b**, **4a**, **4b** were prepared according to the literature procedure.[1-4] Other reagents were commercially purchased and used without further purification.

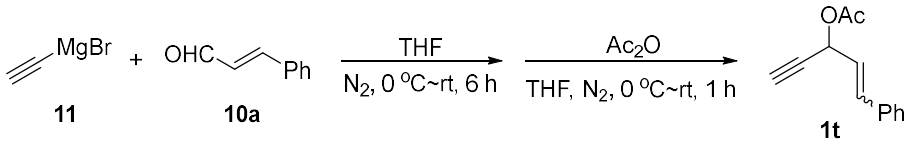
B Procedure for the preparation of enynes

i) Procedure for the preparation of 3-acetoxy 1,4-enynes **1a-1s, 1u-1aa, 1ae-1ai**.[1]



To a 100 mL two-necked round flask equipped with a stir bar was added alkyne **9** (6 mmol, 1.2 equiv). The vessel was then evacuated, refilled with nitrogen gas three times. Subsequently, dry THF (10 mL) was added via syringe under 0 °C. ^{n}BuLi (2.2 mL, 1.1 equiv, 2.5 M in THF) was added slowly to the vessel via syringe under 0 °C. The resulting mixture was stirred for 1 h at room temperature. Then α, β-unsaturated aldehyde/ketone **10** (5 mmol, 1 equiv) was dissolved in dry THF (10 mL) and added to the vessel via syringe under 0 °C. The resulting mixture was stirred for 6 h at room temperature. Ac_2O (6.5 mmol, 1.3 equiv) was dissolved in dry THF (10 mL) and added to the vessel via syringe under 0 °C. The resulting mixture was stirred for 1 h at room temperature. After the reaction was completed, saturated aqueous ammonium chloride (15 mL) was added to the mixture and the resulting aqueous phase was extracted with ethyl acetate (15 mL × 3). The organic phase was washed with water (15 mL × 3), dried over anhydrous Na_2SO_4 and then filtered. After removing the solvent under vacuum, the crude product was purified by column chromatography on silica gel using petroleum ether/ethyl acetate (v/v = 100:1–10:1) as the eluent to give the desired products **1a-1s**, **1u-1aa**, **1ae-1ai**.

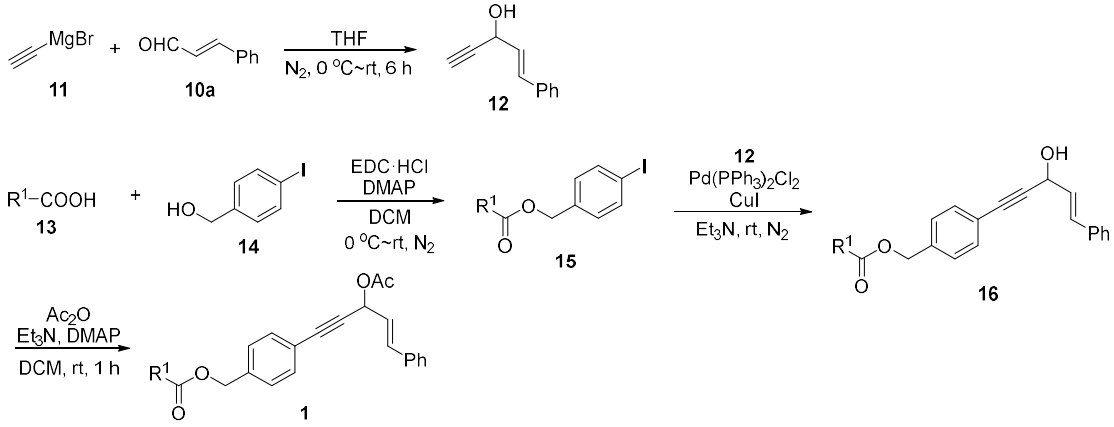
ii) Procedure for the preparation of 3-acetoxy 1,4-enyne **1t**.[1]

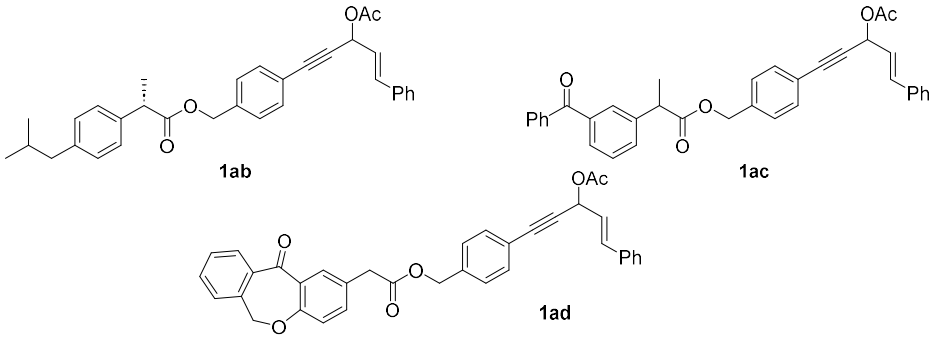


11 **10a** **1t**

To a 100 mL two-necked round flask equipped with a stir bar was evacuated, refilled with nitrogen gas three times. Subsequently, *trans*-cinnamaldehyde **10a** (5 mmol, 1 equiv) and dry THF (10 mL) were added via syringe. Ethynylmagnesium bromide **11** (12 mL, 1.2 equiv, 0.5 M in THF) was added slowly to the vessel via syringe under 0 °C. The resulting mixture was stirred for 6 h at room temperature. Then Ac_2O (6.5 mmol, 1.3 equiv) was dissolved in dry THF (10 mL) and added to the vessel via syringe under 0 °C. The resulting mixture was stirred for 1 h at room temperature. After the reaction was completed, saturated aqueous ammonium chloride (15 mL) was added to the mixture and the resulting aqueous phase was extracted with ethyl acetate (15 mL × 3). The organic phase was washed with water (15 mL × 3), dried over anhydrous Na_2SO_4 and then filtered. After removing the solvent under vacuum, the crude product was purified by column chromatography on silica gel using petroleum ether/ethyl acetate (v/v = 50:1) as the eluent to give the desired product **1t**.

iii) Procedure for the preparation of 3-acetoxy 1,4-enynes **1ab-1ad**.[1,2]





To a 100 mL two-necked round flask equipped with a stir bar was evacuated, refilled with nitrogen gas three times. Subsequently, *trans*-cinnamaldehyde **10a** (20 mmol, 1 equiv) and dry THF (10 mL) were added via syringe. Ethynylmagnesium bromide **11** (48 mL, 1.2 equiv, 0.5 M in THF) was added slowly to the vessel via syringe under 0 °C. The resulting mixture was stirred for 6 h at room temperature. After the reaction was completed, saturated aqueous ammonium chloride (20 mL) was added to the mixture and the resulting aqueous phase was extracted with ethyl acetate (20 mL × 3). The organic phase was washed with water (20 mL × 3), dried over anhydrous Na_2SO_4 and then filtered. After removing the solvent under vacuum, the crude product was purified by column chromatography on silica gel using petroleum ether/ethyl acetate (v/v = 5:1) as the eluent to give the desired enyne **12**.

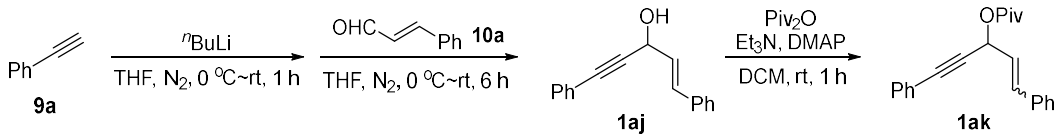
To a 100 mL two-necked round flask equipped with a stir bar were added carboxylic acid **13** (5.5 mmol, 1.1 eq), N'-(3-dimethylaminopropyl)-N-ethylcarbodimide (EDC·HCl) (15 mmol, 3 equiv) and 4-N,N-dimethylaminopyridine (DMAP) (11 mmol, 2.2 equiv). The vessel was then evacuated, refilled with nitrogen gas three times. Subsequently, alcohol **14** (5 mmol, 1 eq) was dissolved in dry DCM (25 mL) and added to the vessel via syringe at 0 °C. The resulting mixture was stirred at 0 °C for 1 h and then warmed to room temperature and stirred overnight. After the reaction was complete,

the mixture was diluted with saturated brine water (15 mL) and extracted with ethyl acetate (15 mL × 3). The organic phase was washed with water (15 mL × 3), dried over anhydrous Na_2SO_4 and then filtered. After removing the solvent under vacuum, crude product **15** was obtained and used in the next step without further purification.

To a 100 mL two-necked round flask equipped with a stir bar were added crude product **15** above, enyne **12** (5.5 mmol, 1.1 equiv), $Pd(PPh_3)_2Cl_2$ (0.05 mmol, 1 mol%) and CuI (0.1 mmol, 2 mol%). The vessel was then evacuated, refilled with nitrogen gas three times. Subsequently, Et_3N (20 mL) was added via syringe and the resulting mixture was stirred at room temperature overnight. After the reaction was completed, the mixture was diluted with saturated brine water (15 mL) and extracted with ethyl acetate (15 mL × 3). The organic phase was washed with water (15 mL × 3), dried over anhydrous Na_2SO_4 and then filtered. After removing the solvent under vacuum, crude enyne **16** was obtained and used in the next step without further purification.

To a 100 mL round flask equipped with a stir bar were added crude enyne **16** above, Ac_2O (7.5 mmol, 1.5 equiv), Et_3N (15 mmol, 3 equiv), DMAP (0.1 mmol, 0.02 equiv) and DCM (20 mL). The resulting mixture was stirred at room temperature for 1 h. After the reaction was completed, the reaction mixture was concentrated under reduced pressure to remove the solvent, and the crude product was purified by column chromatography on silica gel using petroleum ether/ethyl acetate (v/v = 10:1–3:1) as the eluent to give the desired products **1ab-1ad**.

iv) Procedure for the preparation of 1,4-enynes **1aj** and **1ak**.[1]

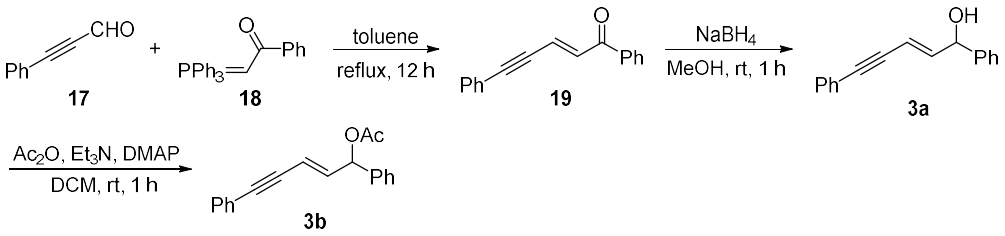


To a 100 mL two-necked round flask equipped with a stir bar was evacuated, refilled with nitrogen gas three times. Subsequently, Phenylacetylene **9a** (6 mmol, 1.2 equiv) and dry THF (10 mL) were added via syringe. *n*BuLi (2.2 mL, 1.1 equiv, 2.5 M in THF) was added slowly to the vessel via syringe under 0 °C. The resulting mixture was stirred for 1 h at room temperature. Then *trans*-cinnamaldehyde **10a** (5 mmol, 1 equiv) was dissolved in dry THF (10 mL) and added to the vessel via syringe under 0 °C. The resulting mixture was stirred for 6 h at room temperature. After the reaction was completed, saturated aqueous ammonium chloride (15 mL) was added to the mixture and the resulting aqueous phase was extracted with ethyl acetate (15 mL × 3). The organic phase

was washed with water (15 mL × 3), dried over anhydrous Na_2SO_4 and then filtered. After removing the solvent under vacuum, the crude product was purified by column chromatography on silica gel using petroleum ether/ethyl acetate (v/v = 10:1) as the eluent to give the desired enyne **1aj**.

To a 50 mL round flask equipped with a stir bar were added enyne **1aj** (3 mmol, 1 equiv), Piv_2O (4.5 mmol, 1.5 equiv), Et_3N (9 mmol, 3 equiv), DMAP (0.0.06 mmol, 0.02 equiv) and DCM (10 mL). The resulting mixture was stirred at room temperature for 1 h. After the reaction was completed, the reaction mixture was concentrated under reduced pressure to remove the solvent, and the crude product was purified by column chromatography on silica gel using petroleum ether/ethyl acetate (v/v = 50:1) as the eluent to give the desired product **1ak**.

v) Procedure for the preparation of enynes **3a** and **3b**.[1,3]



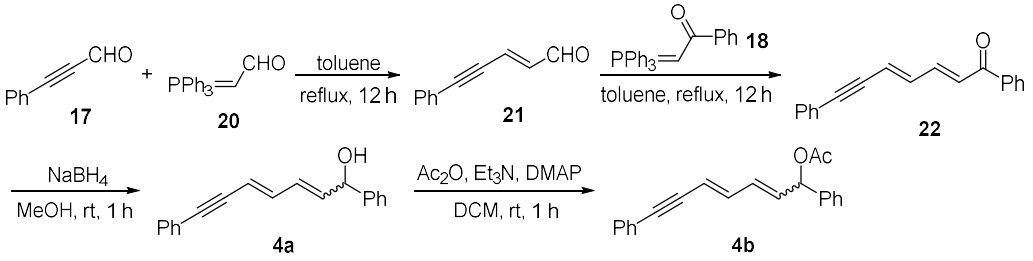
To a 100 mL round flask equipped with a stir bar were added 3-phenylpropiolaldehyde **17** (5 mmol, 1 equiv), Witting reagent **18** (5.5 mmol, 1.1 equiv) and toluene (15 mL). Then, the mixture was heated to reflux for 12 h. After cooling down to room temperature, the reaction mixture was concentrated under reduced pressure to remove the solvent, and the crude product was purified by column chromatography on silica gel using petroleum ether/ethyl acetate (v/v = 100:1) as the eluent to give the desired ketene **19**.

To a 50 mL round flask equipped with a stir bar were added ketene **19** (4 mmol, 1 equiv) and MeOH (15 mL). Subsequently, $NaBH_4$ (4 mmol, 1 equiv) was added slowly under 0 °C. The mixture was stirred at room temperature for 1 h. After the reaction was completed, the reaction mixture was concentrated under reduced pressure to remove the solvent, and the crude product was purified by column chromatography on silica gel using petroleum ether/ethyl acetate (v/v = 8:1) as the eluent to give the desired enyne **3a**.

To a 50 mL round flask equipped with a stir bar were added enyne **3a** (3 mmol, 1 equiv), Ac_2O (4.5 mmol, 1.5 equiv), Et_3N (9 mmol, 3 equiv), DMAP (0.06 mmol, 0.02 equiv) and DCM (10 mL). The resulting mixture was stirred at room temperature for 1 h. After the reaction was completed, the

reaction mixture was concentrated under reduced pressure to remove the solvent, and the crude product was purified by column chromatography on silica gel using petroleum ether/ethyl acetate (v/v = 50:1) as the eluent to give the desired product **3b**.

vi) Procedure for the preparation of enynes **4a**, **4b**.[1,3,4]



To a 100 mL round flask equipped with a stir bar were added 3-phenylpropiolaldehyde **17** (5 mmol, 1 equiv), Witting reagent **20** (5.5 mmol, 1.1 equiv) and toluene (15 mL). Then, the mixture was heated to reflux for 12 h. After cooling down to room temperature, the reaction mixture was concentrated under reduced pressure to remove the solvent, crude aldehyde **21** was obtained and used in the next step without further purification.

To a 100 mL round flask equipped with a stir bar were added crude aldehyde **21** above, Witting reagent **18** (5 mmol, 1 equiv) and toluene (15 mL). Then, the mixture was heated to reflux for 12 h. After cooling down to room temperature, the reaction mixture was concentrated under reduced pressure to remove the solvent, and the crude product was purified by column chromatography on silica gel using petroleum ether/ethyl acetate (v/v = 50:1) as the eluent to give the desired ketene **22**.

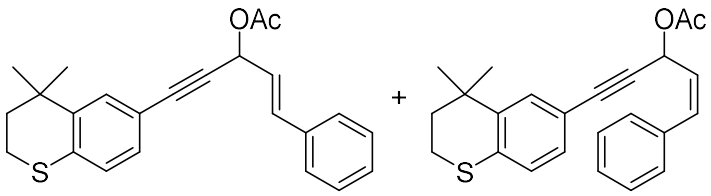
To a 50 mL round flask equipped with a stir bar were added ketene **22** (3 mmol, 1 equiv) and MeOH (10 mL). Subsequently, $NaBH_4$ (3 mmol, 1 equiv) was added slowly under 0 °C. The mixture was stirred at room temperature for 1 h. After the reaction was completed, the reaction mixture was concentrated under reduced pressure to remove the solvent, and the crude product was purified by column chromatography on silica gel using petroleum ether/ethyl acetate (v/v = 10:1) as the eluent to give the desired enyne **4a**.

To a 50 mL round flask equipped with a stir bar were added enyne **4a** (2 mmol, 1 equiv), Ac_2O (3 mmol, 1.5 equiv), Et_3N (6 mmol, 3 equiv), DMAP (0.04 mmol, 0.02 equiv) and DCM (10 mL). The resulting mixture was stirred at room temperature for 1 h. After the reaction was completed, the reaction mixture was concentrated under reduced pressure to remove the solvent, and the crude product was purified by column chromatography on silica gel using petroleum ether/ethyl acetate

(v/v = 50:1) as the eluent to give the desired product **4b**.

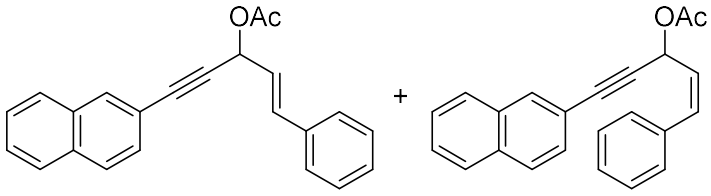
The analytic data of the new substrates are given as follows:

5-(4,4-Dimethylthiochroman-6-yl)-1-phenylpent-1-en-4-yn-3-yl acetate (1m)



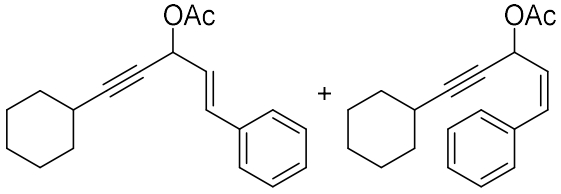
E: Z = 80:20. Eluent: V_{PE}/V_{EA} = 50:1. Brown liquid (1654.0 mg, 88% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.30 (m, 6.5H), 7.17 – 7.14 (dd, *J* = 8.4, 2.0 Hz, 0.2H), 7.09 – 7.00 (m, 1.8H), 6.38 – 6.29 (m, 1.5H), 6.07 – 5.84 (m, 1H), 3.06 – 3.00 (m, 2H), 2.13 (s, 2.9H), 1.98 – 1.90 (m, 2.1H), 1.34 (s, 1.2H), 1.31 (s, 4.8H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.7, 141.9, 139.6, 139.1, 138.2, 133.2, 129.63, 129.59, 128.9, 128.8, 128.62, 128.57, 128.3, 128.0, 127.1, 126.5, 126.4, 118.1, 112.5, 111.9, 96.7, 91.8, 86.1, 84.4, 75.3, 73.8, 37.1, 32.9, 32.8, 29.9, 23.14, 23.11, 21.2, 21.1. HRMS-ESI (*m/z*): calcd for $C_{24}H_{23}O_2S$ $[M - H]^+$: 375.1424; found: 375.1425.

5-(Naphthalen-2-yl)-1-phenylpent-1-en-4-yn-3-yl acetate (1n)



E: Z = 83:17. Eluent: V_{PE}/V_{EA} = 10:1. Brown liquid (1538.4 mg, 94% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 – 8.05 (m, 0.83H), 8.00 – 7.97 (m, 0.17H), 7.86 – 7.79 (m, 3H), 7.58 (dd, *J* = 8.5, 1.5 Hz, 1H), 7.55 – 7.47 (m, 4H), 7.44 – 7.42 (m, 0.6H), 7.38 (t, *J* = 7.3 Hz, 1.77H), 7.35 – 7.32 (m, 0.63H), 7.05 – 6.97 (m, 0.83H), 6.47 – 6.37 (m, 2H), 6.09 – 6.03 (m, 0.17H), 2.21 (s, 2.49H), 2.17 (s, 0.51H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.7, 140.3, 138.1, 135.6, 134.5, 132.9, 132.8, 132.7, 132.1, 131.4, 128.64, 128.57, 128.4, 128.3, 128.1, 127.9, 127.73, 127.68, 127.66, 127.1, 126.89, 126.86, 126.7, 126.55, 126.49, 123.9, 120.2, 119.2, 112.3, 91.7, 87.3, 87.2, 84.9, 75.2, 64.8, 21.1. HRMS-ESI (*m/z*): calcd for $C_{23}H_{17}O_2$ $[M - H]^+$: 325.1234; found: 325.1235.

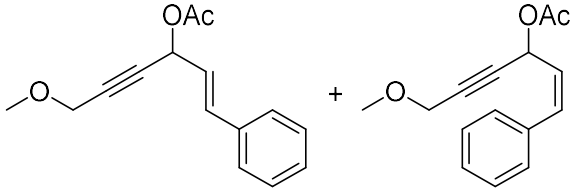
5-Cyclohexyl-1-phenylpent-1-en-4-yn-3-yl acetate (1p)



E: Z = 78:22. Eluent: V_{PE}/V_{EA} = 50:1. Orange liquid (1167.3 mg, 83% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.38 (m, 1.67H), 7.36 –

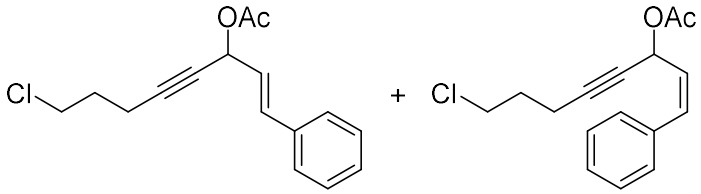
7.24 (m, 3.33H), 6.90 – 6.75 (m, 0.86H), 6.29 – 5.96 (m, 1.95H), 5.76 – 5.63 (m, 0.19H), 2.59 – 2.39 (m, 1H), 2.11 (s, 2.35H), 2.09 (s, 0.65H), 1.86 – 1.66 (m, 4H), 1.54 – 1.28 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.8, 138.6, 135.8, 134.0, 128.57, 128.56, 128.2, 127.1, 126.9, 124.7, 113.2, 92.4, 75.6, 75.4, 64.7, 32.5, 32.38, 32.36, 29.1, 25.8, 24.8, 21.20, 21.17. HRMS-ESI (*m/z*): calcd for $C_{19}H_{21}O_2$ $[M - H]^+$: 281.1547; found: 281.1548.

6-Methoxy-1-phenylhex-1-en-4-yn-3-yl acetate (1q)



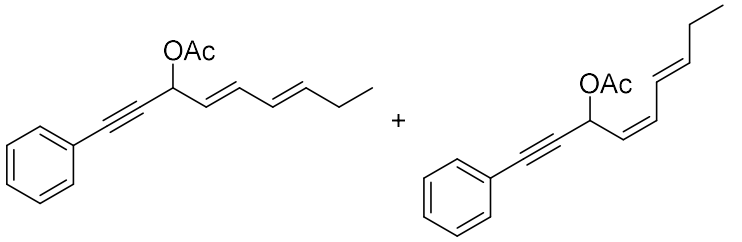
E: Z = 94:6. Eluent: V_{PE}/V_{EA} = 20:1. Brown liquid (525.1 mg, 43% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.39 (m, 2H), 7.35 – 7.28 (m, 3H), 6.85 (d, *J* = 15.7 Hz, 1H), 6.23 (dd, *J* = 15.7, 6.6 Hz, 1H), 6.15 – 6.06 (m, 1H), 4.20 (d, *J* = 1.5 Hz, 2H), 3.41 (s, 2.81H), 3.37 (s, 0.19H), 2.12 (s, 2.81H), 2.11 (s, 0.19H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.7, 135.6, 134.6, 128.6, 128.4, 126.9, 123.7, 83.0, 82.1, 64.2, 59.8, 57.7, 21.0. HRMS-ESI (*m/z*): calcd for $C_{15}H_{15}O_3$ $[M - H]^+$: 243.1027; found: 243.1026.

8-Chloro-1-phenyloct-1-en-4-yn-3-yl acetate (1r)



E: Z = 92:8. Eluent: V_{PE}/V_{EA} = 30:1. Orange liquid (1102.8 mg, 80% yield).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.26 (m, 5H), 6.84 (d, *J* = 15.7 Hz, 0.91H), 6.29 – 6.14 (m, 1.09H), 6.09 – 5.98 (m, 0.92H), 5.73 – 5.67 (m, 0.08H), 3.71 – 3.61 (m, 2H), 2.49 (td, *J* = 6.8, 1.9 Hz, 2H), 2.16 – 2.11 (s, 2.76H), 2.11 – 2.09 (s, 0.24H), 2.05 – 1.93 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.8, 139.5, 135.7, 134.2, 128.6, 128.4, 127.1, 126.9, 124.2, 112.6, 86.1, 76.8, 75.3, 64.6, 43.5, 31.0, 21.1, 16.8, 16.2. HRMS-ESI (*m/z*): calcd for $C_{16}H_{16}ClO_2$ $[M - H]^+$: 275.0844; found: 275.0847.

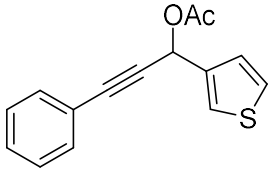
1-Phenylnona-4,6-dien-1-yn-3-yl acetate (1u)



E: Z = 81:19. Eluent: V_{PE}/V_{EA} = 50:1. Brown liquid (719.1 mg, 57% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.41 (m, 2H),

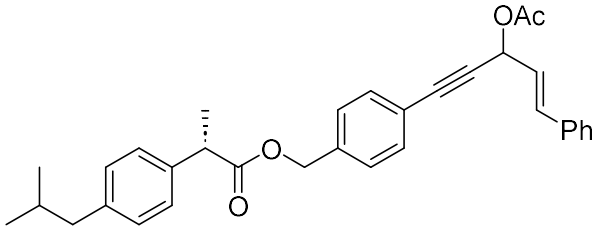
7.33 – 7.29 (m, 3H), 6.64 (dd, J = 15.5, 10.9 Hz, 1H), 6.37 – 6.27 (m, 1H), 5.87 – 5.70 (m, 2H), 5.39 – 5.17 (m, 1H), 2.07 (s, 2.44H), 2.07 (s, 0.56H), 1.73 – 1.61 (m, 2H), 0.91 (t, J = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 145.8, 140.6, 138.7, 133.9, 133.6, 131.6, 131.5, 131.3, 130.5, 128.33, 128.29, 128.2, 128.1, 123.3, 112.3, 111.2, 96.8, 92.4, 88.6, 87.8, 75.2, 70.7, 27.4, 21.4, 21.2, 20.4, 15.2, 9.4. HRMS-ESI (*m/z*): calcd for $C_{17}H_{19}O_2$ $[M + H]^+$: 255.1380; found: 255.1376.

3-Phenyl-1-(thiophen-3-yl)prop-2-yn-1-yl acetate (1y)



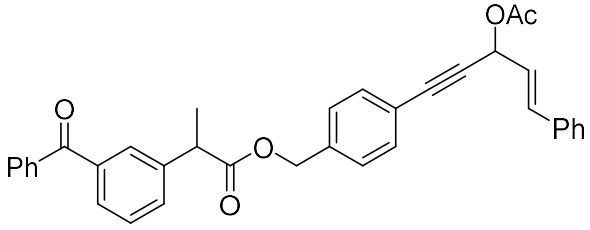
Eluent: V_{PE}/V_{EA} = 50:1. Brown solid (1135.2 mg, 89% yield), mp: 131–133 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, J = 2.7 Hz, 1H), 7.51 – 7.48 (m, 2H), 7.36 – 7.31 (m, 4H), 7.29 – 7.25 (m, 1H), 6.78 (s, 1H), 2.14 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.8, 137.9, 131.9, 128.8, 128.3, 126.8, 126.4, 124.7, 121.9, 86.2, 85.3, 61.5, 21.1. HRMS-ESI (*m/z*): calcd for $C_{15}H_{11}O_2S$ $[M – H]^+$: 255.0485; found: 255.0484.

4-((*E*)-3-acetoxy-5-phenylpent-4-en-1-yn-1-yl)benzyl (2*S*)-2-(4-isobutylphenyl)propanoate (1ab)



Eluent: V_{PE}/V_{EA} = 10:1. Orange liquid (1631.4mg, 66% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.38 (m, 4H), 7.38 – 7.29 (m, 3H), 7.21 – 7.15 (m, 4H), 7.12 – 7.08 (m, 2H), 6.97 – 6.84 (m, 1H), 6.39 – 6.26 (m, 2H), 5.10 (s, 2H), 3.76 (q, J = 7.1 Hz, 1H), 2.46 (d, J = 7.2 Hz, 2H), 2.15 (s, 3H), 1.90 – 1.81 (m, 1H), 1.51 (d, J = 7.2 Hz, 3H), 0.91 (d, J = 6.6 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.4, 169.8, 140.6, 137.4, 136.9, 135.7, 134.6, 132.0, 129.3, 128.6, 128.4, 127.5, 127.2, 126.9, 123.9, 121.7, 86.6, 84.9, 65.7, 64.7, 45.1, 45.0, 30.2, 22.3, 21.1, 18.3. HRMS-ESI (*m/z*): calcd for $C_{33}H_{35}O_4$ $[M + H]^+$: 495.2530; found: 495.2527.

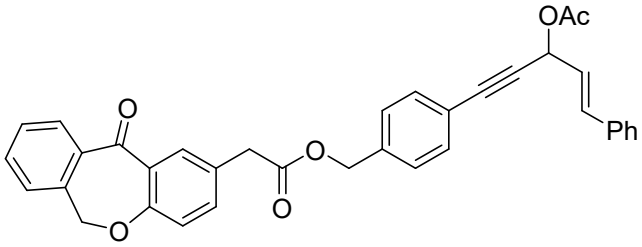
(*E*)-4-(3-acetoxy-5-phenylpent-4-en-1-yn-1-yl)benzyl 2-(3-benzoylphenyl)propanoate (1ac)



Eluent: V_{PE}/V_{EA} = 5:1. Brown liquid (1494.8 mg, 55% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 – 7.73 (m, 3H), 7.68 (d, J = 7.6 Hz, 1H), 7.58 (t, J = 7.4 Hz, 1H), 7.53 (d, J = 7.8 Hz, 1H), 7.50 – 7.40 (m, 7H), 7.37 – 7.27 (m, 3H), 7.20 (d, J = 8.1 Hz, 2H), 6.97 – 6.86 (m, 1H),

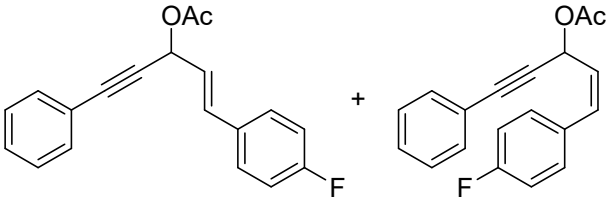
6.38 – 6.24 (m, 2H), 5.11 (s, 2H), 3.86 (q, J = 7.1 Hz, 1H), 2.15 (s, 3H), 1.56 (d, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.4, 173.7, 169.7, 140.5, 137.9, 137.4, 136.5, 135.6, 134.6, 132.5, 132.0, 131.4, 130.0, 129.2, 129.0, 128.6, 128.5, 128.4, 128.3, 127.7, 126.9, 123.8, 121.9, 86.5, 85.1, 66.0, 64.7, 45.3, 21.1, 18.3. HRMS-ESI (*m/z*): calcd for $C_{36}H_{31}O_5$ $[M + H]^+$: 543.2166; found: 543.2162.

(*E*)-4-(3-acetoxy-5-phenylpent-4-en-1-yn-1-yl)benzyl 2-(11-oxo-6,11-dihydrodibenzo[*b,e*]oxepin-2-yl)acetate (1ad)



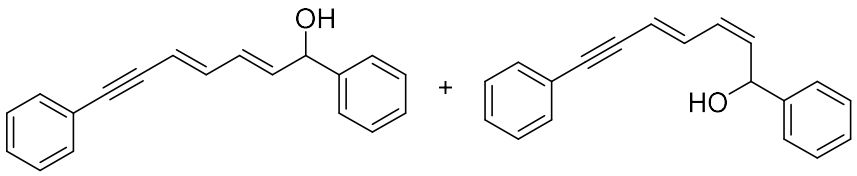
Eluent: V_{PE}/V_{EA} = 3:1. Brown liquid (678.5 mg, 24% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, J = 2.3 Hz, 1H), 7.91 – 7.87 (m, 1H), 7.58 – 7.53 (m, 1H), 7.49 – 7.40 (m, 6H), 7.37 – 7.32 (m, 3H), 7.31 – 7.27 (m, 3H), 7.03 (d, J = 8.5 Hz, 1H), 6.95 – 6.88 (m, 1H), 6.35 – 6.27 (m, 2H), 5.19 (s, 2H), 5.14 (s, 2H), 3.70 (s, 2H), 2.15 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.8, 171.1, 169.8, 160.5, 140.4, 136.4, 136.3, 135.7, 135.5, 134.6, 132.8, 132.5, 132.1, 129.5, 129.3, 128.6, 128.5, 128.0, 127.8, 127.5, 126.9, 125.1, 123.9, 122.0, 121.1, 86.6, 85.1, 73.6, 66.1, 64.7, 40.1, 21.1. HRMS-ESI (*m/z*): calcd for $C_{36}H_{29}O_6$ $[M + H]^+$: 557.1959; found: 557.1956.

1-(4-Fluorophenyl)-5-phenylpent-1-en-4-yn-3-yl acetate (1ag)



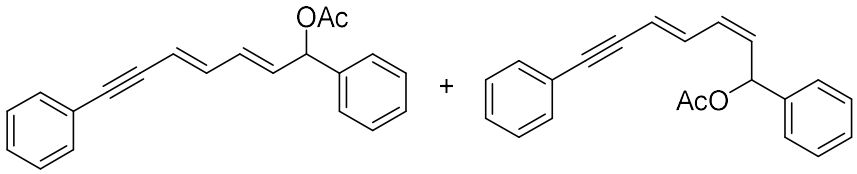
E: Z = 52:48. Eluent: V_{PE}/V_{EA} = 30:1. Brown liquid (1162.7 mg, 79% yield).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.48 (m, 1H), 7.44 – 7.39 (m, 2H), 7.38 – 7.29 (m, 4H), 7.10 – 7.00 (m, 2H), 6.89 (d, J = 15.2 Hz, 0.65H), 6.39 – 6.17 (m, 1.9H), 6.00 – 5.85 (m, 0.45H), 2.16 (s, 1.58H), 2.12 (s, 1.42H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.8, 169.7, 163.9 (d, J = 15.4 Hz), 161.5 (d, J = 14.6 Hz), 139.9, 134.0 (d, J = 3.3 Hz) 133.4, 131.9, 131.8 (d, J = 3.3 Hz), 131.5, 129.1 (d, J = 8.3 Hz), 128.9, 128.5 (d, J = 8.2 Hz), 128.4, 128.31, 128.29, 123.72, 123.70, 122.8, 121.9, 115.7 (d, J = 1.9 Hz), 115.5 (d, J = 2.0 Hz), 112.5, 91.5, 87.1, 86.6, 84.5, 74.5, 64.7, 21.1, 1.0. HRMS-ESI (*m/z*): calcd for $C_{19}H_{14}FO_2$ $[M – H]^+$: 293.0983; found: 293.0985.

1,7-Diphenylhepta-2,4-dien-6-yn-1-ol (4a)



E: Z = 83:17. Eluent: V_{PE}/V_{EA} = 10:1. Brown liquid (676.6 mg, 52% yield).[1]H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.42 (m, 2H), 7.41 – 7.36 (m, 4H), 7.35 – 7.29 (m, 4H), 6.95 (dd, *J* = 15.2 Hz, 10.8 Hz, 0.17H), 6.69 (dd, *J* = 15.5, 10.9 Hz, 0.83H), 6.50 – 6.36 (m, 1H), 6.12 – 5.97 (m, 1H), 5.87 (d, *J* = 15.5 Hz, 0.83H), 5.71 (d, *J* = 10.8 Hz, 0.17H), 5.40 – 5.22 (m, 1H), 2.18 (s, 0.83H), 1.68 (s, 0.17H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.34, 142.31, 140.7, 138.9, 138.4, 137.5, 131.5, 131.4, 129.7, 128.7, 128.6, 128.30, 128.28, 128.2, 127.9, 127.84, 127.78, 126.3, 123.3, 112.0, 110.1, 92.4, 88.7, 74.7, 74.5. HRMS-ESI (*m/z*): calcd for $C_{19}H_{17}O$ $[M + H]^+$: 261.1274; found: 261.1271.

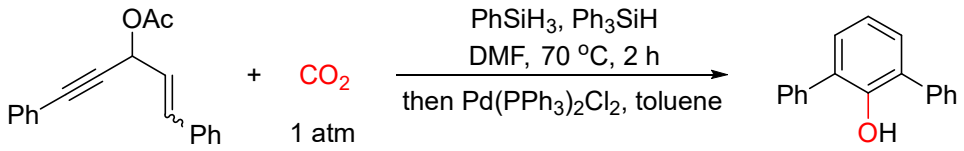
1,7-Diphenylhepta-2,4-dien-6-yn-1-yl acetate (4b)



E: Z = 70:30. Eluent: V_{PE}/V_{EA} = 50:1. Brown liquid (708.1 mg, 47% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.30 (m, 10H), 6.87 (dd, *J* = 15.6, 11.2 Hz, 0.3H), 6.66 (dd, *J* = 15.5, 10.9 Hz, 0.7H), 6.49 – 6.28 (m, 2H), 6.06 (dd, *J* = 15.2, 6.4 Hz, 0.3H), 5.96 (dd, *J* = 15.3, 6.5 Hz, 0.7H), 5.87 (d, *J* = 15.5 Hz, 0.7H), 5.71 (d, *J* = 10.4 Hz, 0.3H), 2.13 (s, 0.9H), 2.13 (s, 2.1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.9, 140.3, 138.78, 138.75, 138.4, 134.1, 133.3, 131.6, 131.47, 131.45, 129.4, 128.64, 128.62, 128.34, 128.30, 128.28, 128.25, 128.2, 127.15, 127.08, 123.20, 123.16, 112.9, 110.9, 96.4, 92.7, 88.5, 86.3, 75.7, 75.5, 21.3, 21.2. HRMS-ESI (*m/z*): calcd for $C_{21}H_{17}O_2$ $[M – H]^+$: 301.1234; found: 301.1236.

C Optimization of the reaction conditions

Table S1. Optimization of the amount of $PhSiH_3$ and Ph_3SiH[a]

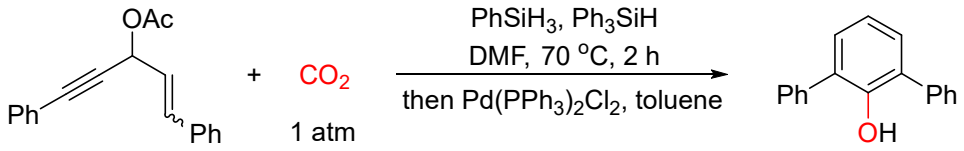


1a **2a**

Entry	Amount of $PhSiH_3$ (x eq)	Amount of $PhSiH_3$ (y eq)	Yield of **2a** (%)[b]
1	2.5	1.2	88
2	2	1.2	75
3	1.5	1.2	49
4	1	1.2	19
5	2.5	0.8	68
6	2.5	0.4	trace

[a]Reaction conditions: The mixture of CO_2 (1 atm), $PhSiH_3$ (x eq), Ph_3SiH (y eq), DMF (dry, 1 mL) was first stirred at 70 °C for 2 h; then another mixture of **1a** (0.2 mmol) and $Pd(PPh_3)_2Cl_2$ (10 mol%) in toluene (dry, 1 mL) was added dropwise with syringe and stirred for 12 h. [b]Yields were determined by GC-MS analysis with dodecane as internal standard.

Table S2. Optimization of the amount of $Pd(PPh_3)_2Cl_2$[a]

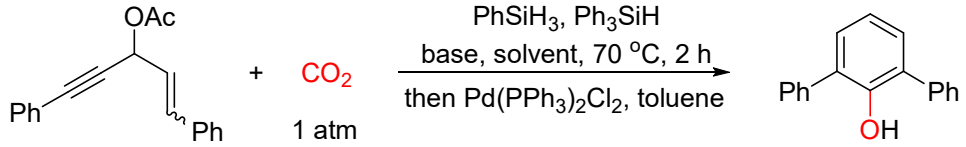


1a **2a**

Entry	Amount of $Pd(PPh_3)_2Cl_2$ (x mol%)	Yield of **2a** (%)[b]
1	10	88
2	8	77
3	5	71
4	2	54

[a]Reaction conditions: The mixture of CO_2 (1 atm), $PhSiH_3$ (2.5 eq), Ph_3SiH (1.2 eq), DMF (dry, 1 mL) was first stirred at 70 °C for 2 h; then another mixture of **1a** (0.2 mmol) and $Pd(PPh_3)_2Cl_2$ (x mol%) in toluene (dry, 1 mL) was added dropwise with syringe and stirred for 12 h. [b]Yields were determined by GC-MS analysis with dodecane as internal standard.

Table S3. Optimization of solvent and base for the first step of the reaction[a]

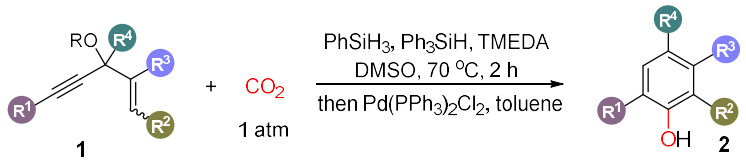


1a **2a**

Entry	Solvent	Base	Yield of **2a** (%)[b]
1	DMSO	Et_3N	32
2	DMSO	TMEDA	43
3	DMSO	TBD	ND
4	DMSO	DBU	ND
5	DMSO	DBN	trace
6	DMSO	DIPEA	21
7[c]	DMSO	TMEDA	78
8[d]	DMSO	TMEDA	82
9[e]	DMSO	TMEDA	85 (79)
10[f]	DMSO	TMEDA	64
11[g]	DMSO	TMEDA	33
12	DMSO	-	trace
13[e]	toluene	TMEDA	ND
14[e]	EtOAc	TMEDA	ND
15[e]	2-Me-THF	TMEDA	ND
16[e]	cyrene	TMEDA	15
17	DMF	-	88 (81)
18	DMA	-	79
19	NMP	-	82

[a]Reaction conditions: The mixture of CO_2 (1 atm), $PhSiH_3$ (2.5 eq), Ph_3SiH (1.2 eq), base (2 eq), solvent (dry, 1 mL) was first stirred at 70 °C for 2 h; then another mixture of **1a** (0.2 mmol) and $Pd(PPh_3)_2Cl_2$ (10 mol%) in toluene (dry, 1 mL) was added dropwise with syringe and stirred for 12 h. [b]Yields were determined by GC-MS analysis with dodecane as internal standard. Number in parentheses is the yield of isolated product. [c]TMEDA (30 mol%). [d]TMEDA (25 mol%). [e]TMEDA (20 mol%). [f]TMEDA (15 mol%). [g]TMEDA (10 mol%). TMEDA = N,N,N',N'-Tetramethylethylenediamine. TBD = 1,5,7-Triazabicyclo[4.4.0]dec-5-ene. DBU = 1,8-Diazabicyclo[5.4.0]undec-7-ene. DBN = 1,5-Diazabicyclo[4.3.0]non-5-ene. DIPEA = N,N-Diisopropylethylamine.

D General procedure for the synthesis of substituted phenols 2



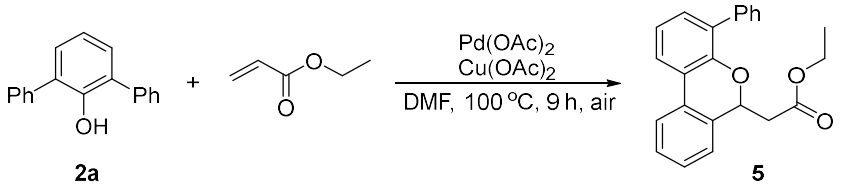
To a 25 mL oven-dried Schlenk tube equipped with a magnetic stirring bar was added Ph_3SiH (0.24 mmol, 1.2 equiv). The tube was then evacuated, refilled with CO_2 (1 atm) three times, and charged with dry DMSO (1 mL), TMEDA (0.04 mmol, 20 mol%) and $PhSiH_3$ (0.5 mmol, 2.5 equiv) successively via a syringe. The mixture was stirred at 70 °C for 2 h. Subsequently, 1,4-enyne **1** (0.2 mmol, 1 equiv) and $Pd(PPh_3)_2Cl_2$ (0.02 mmol, 10 mol%) were dissolved in dry toluene (1 mL) and added to the vessel via syringe. The mixture was stirred at 70 °C for 12 h. After cooling down to room temperature, the mixture was diluted with saturated brine water (10 mL) and extracted with ethyl acetate (10 mL × 3). The organic phase was washed with water (10 mL × 3), dried over anhydrous Na_2SO_4 and then filtered. After removing the solvent under vacuum, the crude product was purified by column chromatography on silica gel using petroleum ether/ethyl acetate (v/v = 50:1 – 3:1) as the eluent to give the desired product **2**. (Noted: DMSO was purged with CO_2 for 5 min prior to use).

E Procedure for the reaction of 2a on a 3 mmol scale

To a 100 mL oven-dried Schlenk tube equipped with a magnetic stirring bar was added Ph_3SiH (3.6 mmol, 1.2 equiv). The tube was then evacuated, refilled with CO_2 (1 atm) three times, and charged with dry DMSO (5 mL), TMEDA (0.6 mmol, 20 mol%) and $PhSiH_3$ (6 mmol, 2 equiv) successively via a syringe. The mixture was stirred at 70 °C for 4 h. Subsequently, **1a** (3 mmol, 1 equiv) and $Pd(PPh_3)_2Cl_2$ (0.15 mmol, 5 mol%) were dissolved in dry toluene (5 mL) and added to the vessel via syringe. The mixture was stirred at 70 °C for 12 h. After cooling down to room temperature, the mixture was diluted with saturated brine water (15 mL) and extracted with ethyl acetate (15 mL × 3). The organic phase was washed with water (15 mL × 3), dried over anhydrous Na_2SO_4 and then filtered. After removing the solvent under vacuum, the crude product was purified by column chromatography on silica gel using petroleum ether/ethyl acetate (v/v = 50:1) as the eluent to give the desired product **2a**. (Noted: DMSO was purged with CO_2 for 5 min prior to use).

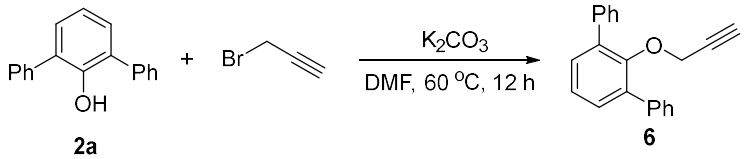
F Procedure for the synthesis of products 5-7

i) Procedure for the synthesis of 5



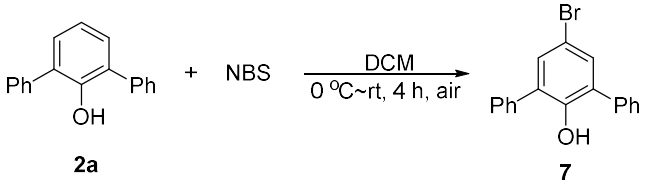
To a 15 mL test tube equipped with a magnetic stirring bar were added **2a** (0.2 mmol, 1 equiv), ethyl acrylate (0.24 mmol, 1.2 equiv), $Pd(OAc)_2$ (0.01 mmol, 5 mol%), $Cu(OAc)_2$ (0.01 mmol, 5 mol%) and DMF (2 mL). The mixture was stirred at 100 °C for 9 h. After cooling down to room temperature, the mixture was diluted with saturated brine water (10 mL) and extracted with ethyl acetate (10 mL × 3). The organic phase was washed with water (10 mL × 3), dried over anhydrous Na_2SO_4 and then filtered. After removing the solvent under vacuum, the crude product was purified by column chromatography on silica gel using petroleum ether/ethyl acetate (v/v = 30:1) as the eluent to give the desired product **5**.

ii) Procedure for the synthesis of 6



To a 15 mL test tube equipped with a magnetic stirring bar were added **2a** (0.2 mmol, 1 equiv), 3-bromopropyne (0.26 mmol, 1.3 equiv), K_2CO_3 (0.24 mmol, 1.2 equiv) and DMF (dry, 2 mL). The reaction mixture was stirred at 60 °C for 12 h. After cooling down to room temperature, the mixture was diluted with saturated brine water (10 mL) and extracted with ethyl acetate (10 mL × 3). The organic phase was washed with water (10 mL × 3), dried over anhydrous Na_2SO_4 and then filtered. After removing the solvent under vacuum, the crude product was purified by column chromatography on silica gel using petroleum ether/ethyl acetate (v/v = 200:1) as the eluent to give the desired product **6**.

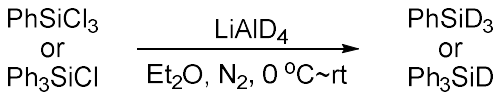
iii) Procedure for the synthesis of 7



To a 15 mL test tube equipped with a magnetic stirring bar were added **2a** (0.2 mmol, 1 equiv) and NBS (0.3 mmol, 1.3 equiv). Subsequently, DCM (2 mL) was added under 0 °C. The reaction mixture was stirred at rome temperature for 4 h. After the reaction was completed, the reaction mixture was concentrated under reduced pressure to remove the solvent, and the crude product was purified by column chromatography on silica gel using petroleum ether/ethyl acetate (v/v = 30:1) as the eluent to give the desired product **7**.

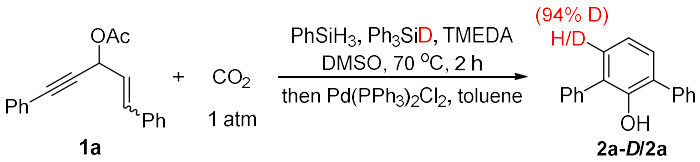
G Deuterium-labeling study

i) Procedure for the synthesis of $PhSiD_3$ or Ph_3SiD

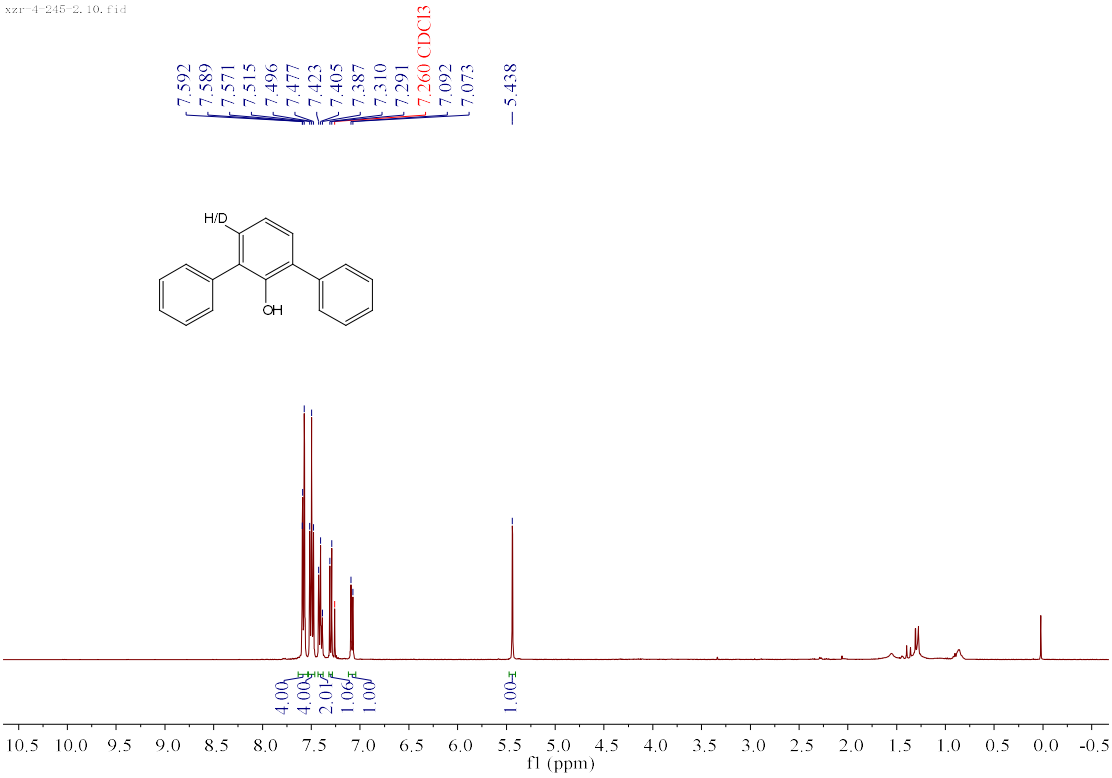


In a glove box, $LiAlD_4$ (5 mmol, 1 equiv) was added to a 100 mL round flask equipped with a rubber stopper and a magnetic stirring bar. After the flask was taken out of the glovebox, Et_2O (30 mL) was added successively under 0 °C. $PhSiCl_3$ or Ph_3SiCl (5 mmol, 1 equiv) was added slowly to the vessel via syringe under 0 °C. After the reaction was completed, the resulting suspension was filtered through celite and cooled to 0 °C. The filtrate was quenched by the dropwise addition of chilled H_2O (30 mL) with vigorous stirring and extracted with Et_2O (20 mL × 3). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated in vacuo under 0~5 °C to provide $PhSiD_3$ or Ph_3SiD.

ii) D-labeling study



400 MHz ^{1}H NMR Spectrum of **2a-*D*/2a** in $CDCl_3$**:**



H X-ray crystal structure and data for product 2m

Single-crystal X-ray diffraction data for **2m** was collected on an X-ray diffractometer operated at 90 kV and 50 mA using MoKα radiation (λ = 0.71073 Å) at 100 K. All empirical absorption corrections were performed using the CrystalClear program. The structure was solved by a direct method and refined on F^2 by the full-matrix least squares technique using the SHELXTL-97 program package. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms attached to carbon were placed in geometrically idealized positions and refined using a riding model. The X-ray crystal structure of product **2m** is shown in **Figure S1**, and the crystallographic data for product **2m** is given in **Table S4**.

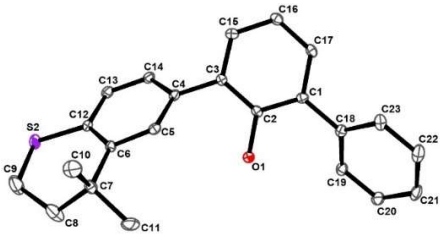


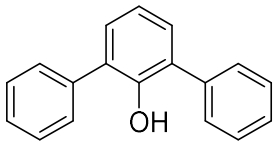
Figure S1. The X-ray crystal structure for product **2m**.

Table S4. Crystal data and structure refinements for **2m**

Empirical formula	$C_{23}H_{22}OS$
Formula weight	346.14
Temperature	100 K
Wavelength	0.71073 *Å*
Crystal system, space group	Orthorhombic, P $2_12_12_1$
Unit cell dimensions	a=6.4582(7) *Å* alpha=90 deg.
	b=12.2794(10) *Å* beta=90 deg.
	c=22.668(2) *Å* gamma=90 deg.
Volume	1797.6(3) $Å^3$
Z, Calculated density	4, 1.280 g/cm^3
Absorption coefficient	0.188 mm^{-1}
F(000)	736.0
Crystal size	0.12 × 0.06 × 0.05 mm^3
Theta range for data collection	4.89 to 52.796 deg.
Limiting indices	$-8 \le h \le 8$, $-15 \le k \le 15$, $-28 \le l \le 26$
Reflections collected / unique	12590 / 3655
Completeness to theta = 26.32	99%
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3655/0/229
Goodness-of-fit on F^2	1.061
Final R indices [I>2sigma(I)]	R_1 = 0.0704, wR_2 = 0.1310
R indices (all data)	R_1 = 0.1170, wR_2 = 0.1552

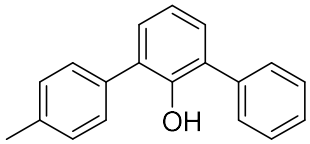
I Analytical data

[1,1':3',1''-Terphenyl]-2'-ol (2a)



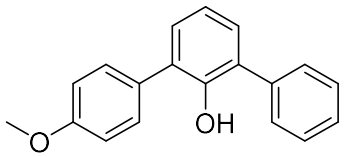
Eluent: V_{PE}/V_{EA} = 50:1. White solid (38.9 mg, 79% yield), mp: 104 – 105 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.55 (m, 4H), 7.55 – 7.47 (m, 4H), 7.45 – 7.38 (m, 2H), 7.31 (d, J = 7.6 Hz, 2H), 7.09 (t, 1H), 5.45 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.3, 137.5, 129.9, 129.3, 128.8, 128.7, 127.6, 120.7.

4-Methyl-[1,1':3',1''-terphenyl]-2'-ol (2b) (from 1b)



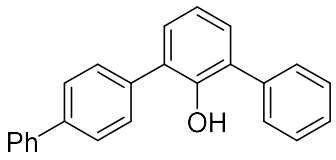
Eluent: V_{PE}/V_{EA} = 50:1. Brown liquid (39.0 mg, 75% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.58 (m, 2H), 7.54 – 7.47 (m, 4H), 7.44 – 7.39 (m, 1H), 7.36 – 7.28 (m, 4H), 7.09 (t, J = 7.6 Hz, 1H), 5.46 (s, 1H), 2.45 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.3, 137.7, 137.4, 134.5, 129.84, 129.77, 129.6, 129.3, 129.2, 128.73, 128.69, 128.6, 127.5, 120.6, 21.2.

4-Methoxy-[1,1':3',1''-terphenyl]-2'-ol (2c) (from 1c)



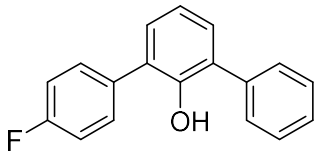
Eluent: V_{PE}/V_{EA} = 20:1. White solid (46.9 mg, 85% yield), mp: 112 – 114 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.55 (m, 2H), 7.54 – 7.46 (m, 4H), 7.43 – 7.39 (m, 1H), 7.28 (d, J = 7.6 Hz, 2H), 7.10 – 7.01 (m, 3H), 5.43 (s, 1H), 3.87 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.1, 149.3, 137.7, 130.5, 129.8, 129.7, 129.6, 129.3, 128.8, 128.6, 128.4, 127.5, 120.6, 114.3, 55.3.

[1,1':3',1'':4'',1'''-Quaterphenyl]-2'-ol (2d)



Eluent: V_{PE}/V_{EA} = 20:1. White solid (47.0 mg, 73% yield), mp: 106 – 108 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 – 7.72 (m, 2H), 7.71 – 7.66 (m, 4H), 7.62 – 7.58 (m, 2H), 7.55 – 7.47 (m, 4H), 7.45 – 7.36 (m, 3H), 7.32 (dd, J = 7.6, 1.8 Hz, 1H), 7.12 (t, J = 7.6 Hz, 1H), 5.49 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.4, 140.6, 140.4, 137.4, 136.6, 130.0, 129.9, 129.7, 129.3, 128.9, 128.80, 128.78, 128.3, 127.7, 127.5, 127.4, 127.1, 120.8.

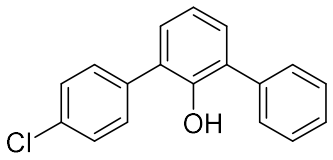
4-Fluoro-[1,1':3',1''-terphenyl]-2'-ol (2e) (from 1e)



Eluent: V_{PE}/V_{EA} = 30:1. Brown liquid (40.7 mg, 77% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.48 (m, 6H), 7.45 – 7.39 (m, 1H), 7.28 (d, J = 7.7 Hz, 2H), 7.20 – 7.13 (m, 2H), 7.08 (t, J = 7.6 Hz, 1H),

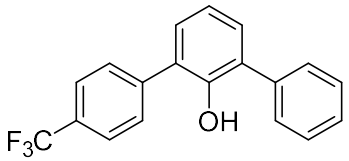
5.37 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.3 (d, J = 246.8 Hz), 149.2, 137.2, 133.6 (d, J = 3.3 Hz), 131.1, 131.0, 130.1, 129.9, 129.3, 129.1, 128.3 (d, J = 105.4 Hz), 127.9, 120.7, 115.6, 115.4. HRMS-ESI (*m/z*): calcd for $C_{18}H_{12}FO$ $[M - H]^+$: 263.0878; found: 263.0878.

4-Chloro-[1,1':3',1''-terphenyl]-2'-ol (2f)



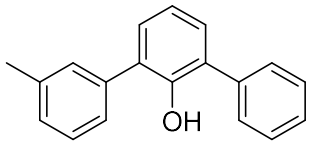
Eluent: V_{PE}/V_{EA} = 50:1. Brown liquid (42.6 mg, 76% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.49 (m, 6H), 7.48 – 7.41 (m, 3H), 7.29 (d, J = 7.6 Hz, 2H), 7.12 – 7.05 (m, 1H), 5.39 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.2, 137.0, 136.2, 133.4, 130.7, 130.02, 129.97, 129.2, 129.1, 128.9, 128.7, 127.9, 127.5, 120.8.

4-(Trifluoromethyl)-[1,1':3',1''-terphenyl]-2'-ol (2g)



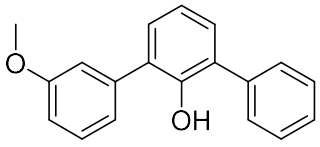
Eluent: V_{PE}/V_{EA} = 50:1. Yellow liquid (31.4 mg, 50% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 – 7.70 (m, 4H), 7.55 – 7.50 (m, 4H), 7.47 – 7.42 (m, 1H), 7.33 – 7.29 (m, 2H), 7.10 (t, J = 7.6 Hz, 1H), 5.40 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.3, 141.7, 136.8, 130.4, 130.2, 129.7, 129.4, 129.3 (d, J = 32.2 Hz), 129.2, 129.0, 128.2, 127.4, 125.3 (q, J = 3.8 Hz), 124.3 (d, J = 272.1 Hz), 120.9.

3-Methyl-[1,1':3',1''-terphenyl]-2'-ol (2h)



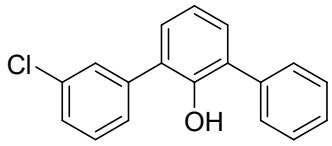
Eluent: V_{PE}/V_{EA} = 30:1. Orange liquid (39.1 mg, 75% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.59 (m, 2H), 7.53 – 7.48 (m, 2H), 7.44 – 7.37 (m, 4H), 7.33 – 7.29 (m, 2H), 7.27 – 7.22 (m, 1H), 7.09 (t, J = 7.6 Hz, 1H), 5.48 (s, 1H), 2.46 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.3, 138.6, 137.7, 137.4, 130.0, 129.9, 129.8, 129.3, 128.83, 128.81, 128.69, 128.65, 128.5, 127.5, 126.3, 120.6, 21.5.

3-Methoxy-[1,1':3',1''-terphenyl]-2'-ol (2i)



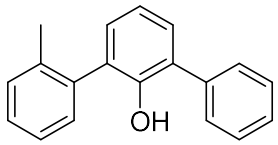
Eluent: V_{PE}/V_{EA} = 20:1. White solid (45.8 mg, 83% yield), mp: 120 – 121 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.56 (m, 2H), 7.52 – 7.47 (m, 2H), 7.44 – 7.39 (m, 2H), 7.33 – 7.29 (m, 2H), 7.16 (d, J = 7.6 Hz, 1H), 7.13 – 7.11 (m, 1H), 7.08 (t, J = 7.6 Hz, 1H), 6.96 (dd, J = 8.1, 2.3 Hz, 1H), 5.51 (s, 1H), 3.86 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.0, 149.3, 138.8, 137.6, 130.1, 130.0, 129.7, 129.3, 128.7, 128.5, 127.5, 121.5, 120.6, 114.7, 113.5, 55.3.

3-Chloro-[1,1':3',1''-terphenyl]-2'-ol (2j)



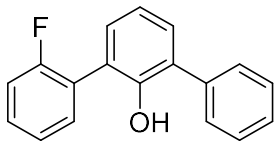
Eluent: V_{PE}/V_{EA} = 30:1. Orange liquid (45.9 mg, 82% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.58 (m, 1H), 7.57 – 7.45 (m, 5H), 7.45 – 7.34 (m, 3H), 7.29 (d, J = 7.7 Hz, 2H), 7.08 (t, J = 7.6 Hz, 1H), 5.40 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.2, 139.6, 137.0, 134.4, 130.2, 130.0, 129.7, 129.6, 129.3, 129.2, 128.9, 128.0, 127.5, 127.4, 120.8. HRMS-ESI (*m/z*): calcd for $C_{18}H_{12}ClO$ [M – H]$^+$: 279.0582; found: 279.0583.

2-Methyl-[1,1':3',1''-terphenyl]-2'-ol (2k)



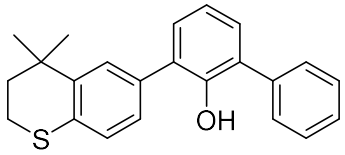
Eluent: V_{PE}/V_{EA} = 50:1. Orange liquid (40.1 mg, 77% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.58 (m, 2H), 7.51 – 7.45 (m, 2H), 7.41 – 7.30 (m, 6H), 7.15 (dd, J = 7.5, 1.8 Hz, 1H), 7.07 (t, J = 7.5 Hz, 1H), 5.07 (s, 1H), 2.25 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.4, 137.8, 137.3, 136.3, 130.5, 130.4, 130.0, 129.7, 129.3, 128.6, 128.5, 128.33, 128.25, 127.4, 126.3, 120.4, 19.9. HRMS-ESI (*m/z*): calcd for $C_{19}H_{15}O$ [M – H]$^+$: 259.1128; found: 259.1128.

2-Fluoro-[1,1':3',1''-terphenyl]-2'-ol (2l)



Eluent: V_{PE}/V_{EA} = 20:1. Yellow liquid (36.4 mg, 69% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.51 (m, 2H), 7.50 – 7.34 (m, 5H), 7.32 – 7.15 (m, 4H), 7.06 (t, J = 7.6 Hz, 1H), 5.29 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.0 (d, J = 245.8 Hz), 149.7, 137.2, 131.9 (d, J = 3.4 Hz), 130.7 (d, J = 1.4 Hz), 130.4, 129.6 (d, J = 8.2 Hz), 129.3, 129.0, 128.7, 127.8, 125.2 (d, J = 16.0 Hz), 124.2 (d, J = 10.4 Hz), 123.0, 120.5, 115.9 (d, J = 22.2 Hz). HRMS-ESI (*m/z*): calcd for $C_{18}H_{12}FO$ [M – H]$^+$: 263.0878; found: 263.0877.

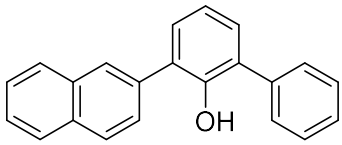
3-(4,4-Dimethylthiochroman-6-yl)-[1,1'-biphenyl]-2-ol (2m)



Eluent: V_{PE}/V_{EA} = 30:1. White solid (50.5 mg, 73% yield), mp: 128 – 130 °C.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.55 (m, 3H), 7.53 – 7.47 (m, 2H), 7.43 – 7.38 (m, 1H), 7.32 – 7.20 (m, 4H), 7.08 (t, J = 7.6 Hz, 1H), 5.44 (s, 1H), 3.11 – 3.06 (m, 2H), 2.05 – 1.98 (m, 2H), 1.39 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.3, 142.4, 137.7, 133.0, 131.7, 129.8, 129.7, 129.3, 128.72, 128.69, 128.6,

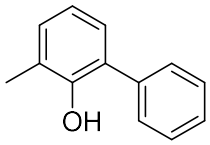
127.53, 127.45, 127.0, 126.9, 120.6, 37.5, 33.1, 30.2, 23.1. HRMS-ESI (*m/z*): calcd for $C_{23}H_{21}OS$ $[M - H]^+$: 345.1319; found: 345.1320.

3-(Naphthalen-2-yl)-[1,1'-biphenyl]-2-ol (2n)



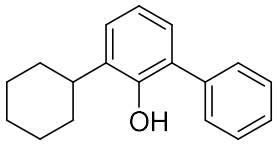
Eluent: V_{PE}/V_{EA} = 40:1. Brown liquid (39.1 mg, 66% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 – 8.04 (m, 1H), 7.98 (d, J = 8.5 Hz, 1H), 7.96 – 7.88 (m, 2H), 7.74 (dd, J = 8.5, 1.8 Hz, 1H), 7.66 – 7.60 (m, 2H), 7.58 – 7.49 (m, 4H), 7.46 – 7.40 (m, 2H), 7.36 (dd, J = 7.6, 1.7 Hz, 1H), 7.14 (t, J = 7.6 Hz, 1H), 5.55 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.5, 137.5, 135.1, 133.5, 132.6, 130.2, 130.0, 129.3, 128.85, 128.82, 128.7, 128.4, 128.09, 128.05, 127.68, 127.66, 127.5, 126.4, 126.2, 120.8. HRMS-ESI (*m/z*): calcd for $C_{22}H_{15}O$ $[M - H]^+$: 295.1128; found: 295.1129.

3-Methyl-[1,1'-biphenyl]-2-ol (2o) (from 1o)



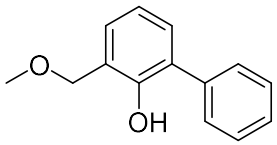
Eluent: V_{PE}/V_{EA} = 30:1. Orange liquid (27.6 mg, 75% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.45 (m, 4H), 7.44 – 7.39 (m, 1H), 7.18 – 7.13 (m, 1H), 7.09 (dd, J = 7.6, 1.3 Hz, 1H), 6.91 (t, J = 7.5 Hz, 1H), 5.26 (s, 1H), 2.33 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.5, 137.3, 130.5, 129.3, 129.1, 127.8, 127.7, 127.6, 124.6, 120.2, 16.2.

3-Cyclohexyl-[1,1'-biphenyl]-2-ol (2p)



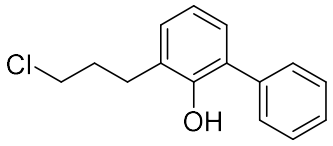
Eluent: V_{PE}/V_{EA} = 50:1. Brown liquid (36.3 mg, 72% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.43 (m, 4H), 7.43 – 7.38 (m, 1H), 7.21 (dd, J = 7.6, 1.4 Hz, 1H), 7.07 (dd, J = 7.5, 1.6 Hz, 1H), 6.96 (t, J = 7.6 Hz, 1H), 5.27 (s, 1H), 3.03 – 2.91 (m, 1H), 1.98 – 1.82 (m, 4H), 1.80 – 1.74 (m, 1H), 1.50 – 1.38 (m, 4H), 1.33 – 1.28 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.5, 137.5, 135.4, 134.2, 129.4, 129.3, 127.9, 127.4, 126.4, 120.4, 37.4, 33.1, 27.1, 26.4.

3-(Methoxymethyl)-[1,1'-biphenyl]-2-ol (2q)



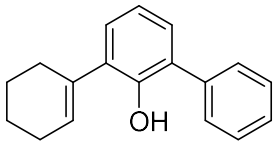
Eluent: V_{PE}/V_{EA} = 30:1. Yellow liquid (22.3 mg, 52% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, J = 7.6 Hz, 2H), 7.49 (s, 1H), 7.45 (t, J = 7.6 Hz, 2H), 7.35 (t, J = 7.3 Hz, 1H), 7.29 (d, J = 7.5 Hz, 1H), 7.08 (d, J = 7.4 Hz, 1H), 6.95 (t, J = 7.5 Hz, 1H), 4.71 (s, 2H), 3.47 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.8, 137.8, 130.6, 129.4, 129.2, 128.3, 127.8, 127.1, 122.7, 119.9, 73.7, 58.2.

3-(3-Chloropropyl)-[1,1'-biphenyl]-2-ol (2r)



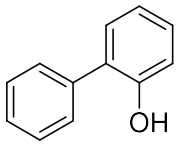
Eluent: V_{PE}/V_{EA} = 50:1. Orange liquid (27.0 mg, 55% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.39 (m, 5H), 7.17 (dd, J = 7.5, 1.5 Hz, 1H), 7.12 (dd, J = 7.6, 1.6 Hz, 1H), 6.94 (t, J = 7.5 Hz, 1H), 5.32 (s, 1H), 3.61 (t, J = 6.6 Hz, 2H), 2.86 (t, 2H), 2.16 (p, J = 6.7 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.3, 137.1, 130.0, 129.4, 129.1, 128.2, 128.0, 127.3, 120.4, 44.8, 32.4, 27.7. HRMS-ESI (*m/z*): calcd for $C_{15}H_{16}ClO$ $[M + H]^+$: 247.0884; found: 247.0882.

2,3,4,5-Tetrahydro-[1,1':3',1''-terphenyl]-2'-ol (2s)



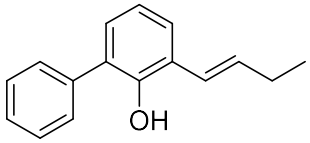
Eluent: V_{PE}/V_{DCM} = 50:1. Brown liquid (25.0 mg, 50% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.52 (m, 2H), 7.48 – 7.42 (m, 2H), 7.35 (t, J = 7.3 Hz, 1H), 7.19 (dd, J = 7.5, 1.5 Hz, 1H), 7.10 (dd, J = 7.6, 1.5 Hz, 1H), 6.96 (t, J = 7.6 Hz, 1H), 5.96 – 5.90 (m, 1H), 5.79 (s, 1H), 2.38 – 2.31 (m, 2H), 2.26 – 2.19 (m, 2H), 1.85 – 1.78 (m, 2H), 1.76 – 1.69 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.9, 138.2, 135.4, 130.7, 129.3, 129.1, 128.4, 128.20, 128.18, 127.7, 127.2, 120.1, 29.8, 25.5, 23.0, 21.9. HRMS-ESI (*m/z*): calcd for $C_{18}H_{17}O$ $[M – H]^+$: 249.1285; found: 249.1283.

[1,1'-Biphenyl]-2-ol (2t)



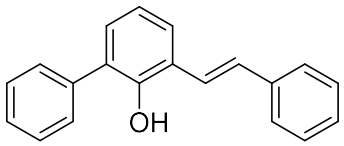
Eluent: V_{PE}/V_{EA} = 8:1. White solid (10.2 mg, 30% yield), mp: 60 – 61 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.45 (m, 4H), 7.42 – 7.37 (m, 1H), 7.29 – 7.22 (m, 2H), 7.02 – 6.96 (m, 2H), 5.20 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.4, 137.0, 130.2, 129.3, 129.15, 129.07, 128.1, 127.9, 120.8, 115.8.

(*E*)-3-(but-1-en-1-yl)-[1,1'-biphenyl]-2-ol (2u)



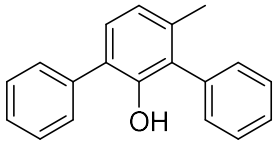
Eluent: V_{PE}/V_{EA} = 50:1. Yellow liquid (19.3 mg, 43% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.44 (m, 4H), 7.43 – 7.37 (m, 2H), 7.09 (d, J = 7.5 Hz, 1H), 6.94 (t, J = 7.6 Hz, 1H), 6.70 (d, J = 15.9 Hz, 1H), 6.37 – 6.26 (m, 1H), 5.36 (s, 1H), 2.28 (p, J = 7.2 Hz, 2H), 1.12 (t, J = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.2, 137.2, 134.5, 129.3, 129.2, 128.6, 128.4, 127.9, 126.4, 125.3, 123.3, 120.5, 26.5, 13.8. HRMS-ESI (*m/z*): calcd for $C_{16}H_{15}O$ $[M – H]^+$: 223.1128; found: 223.1125.

(*E*)-3-styryl-[1,1'-biphenyl]-2-ol (2v)



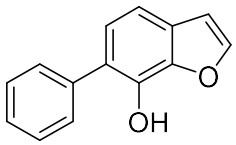
Eluent: V_{PE}/V_{EA} = 50:1. Brown solid (20.1 mg, 37% yield), mp: 70 – 72 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (dd, J = 7.8, 1.4 Hz, 1H), 7.58 – 7.47 (m, 7H), 7.46 – 7.42 (m, 1H), 7.39 – 7.34 (m, 2H), 7.29 – 7.24 (m, 1H), 7.20 (d, J = 16.5 Hz, 1H), 7.16 (dd, J = 7.5, 1.6 Hz, 1H), 7.02 (t, J = 7.6 Hz, 1H), 5.51 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.9, 137.8, 136.8, 129.7, 129.5, 129.3, 129.2, 128.6, 128.2, 127.5, 126.6, 126.3, 124.8, 123.4, 120.6. HRMS-ESI (*m/z*): calcd for $C_{20}H_{15}O$ [M – H]$^+$: 271.1128; found: 271.1129.

4'-Methyl-[1,1':3',1''-terphenyl]-2'-ol (2w)



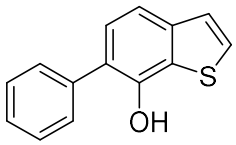
Eluent: V_{PE}/V_{EA} = 50:1. Yellow liquid (40.1 mg, 77% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.58 (m, 2H), 7.56 – 7.51 (m, 2H), 7.48 – 7.43 (m, 3H), 7.39 – 7.34 (m, 3H), 7.26 (d, J = 7.8 Hz, 1H), 6.97 (d, J = 7.8 Hz, 1H), 5.03 (s, 1H), 2.14 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.6, 138.0, 136.8, 135.7, 130.2, 129.4, 129.25, 129.23, 128.6, 128.4, 128.0, 127.1, 125.7, 122.0, 20.4.

6-Phenylbenzofuran-7-ol (2x)



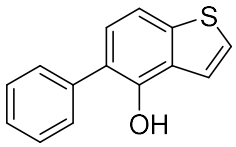
Eluent: V_{PE}/V_{EA} = 10:1. Brown liquid (31.1 mg, 74% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, J = 2.1 Hz, 1H), 7.60 – 7.55 (m, 2H), 7.53 – 7.48 (m, 2H), 7.42 – 7.37 (m, 1H), 7.25 – 7.17 (m, 2H), 6.81 (d, J = 2.1 Hz, 1H), 5.49 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.5, 143.6, 138.1, 137.1, 129.4, 129.0, 128.6, 127.5, 125.2, 123.7, 113.0, 107.2.

6-Phenylbenzo[*b*]thiophen-7-ol (2y)



Eluent: V_{PE}/V_{EA} = 15:1. Brown liquid (20.3 mg, 45% yield).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.51 (m, 4H), 7.51 – 7.47 (m, 2H), 7.46 – 7.41 (m, 1H), 7.36 (d, J = 5.4 Hz, 1H), 7.28 (d, J = 8.1 Hz, 1H), 5.76 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.0, 141.5, 136.8, 129.6, 129.3, 127.9, 127.5, 127.3, 127.0, 124.1, 121.7, 116.2. HRMS-ESI (*m/z*): calcd for $C_{14}H_9OS$ [M – H]$^+$: 225.0380; found: 225.0376.

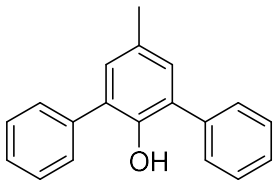
5-Phenylbenzo[*b*]thiophen-4-ol (2z)



Eluent: V_{PE}/V_{EA} = 15:1. Brown liquid (25.8 mg, 57% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.49 (m, 6H), 7.45 – 7.42 (m, 1H), 7.40 (d, J = 5.5

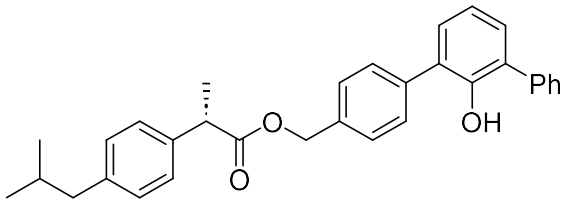
Hz, 1H), 7.24 (d, J = 8.2 Hz, 1H), 5.70 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.4, 141.1, 137.0, 129.5, 129.4, 129.3, 127.8, 126.7, 125.4, 121.8, 120.6, 114.8. HRMS-ESI (*m/z*): calcd for $C_{14}H_9OS$ $[M - H]^+$: 225.0380; found: 225.0377.

5'-Methyl-[1,1':3',1''-terphenyl]-2'-ol (2aa)



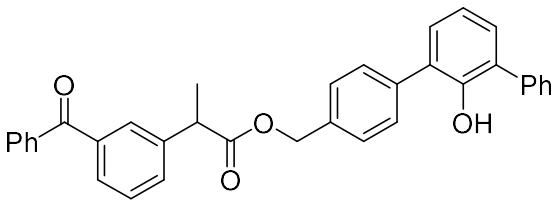
Eluent: V_{PE}/V_{EA} = 50:1. White solid (47.2 mg, 91% yield), mp: 79 – 81 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.57 (m, 1H), 7.56 – 7.55 (m, 2H), 7.50 – 7.46 (m, 4H), 7.40 – 7.37 (m, 2H), 7.24 (t, J = 7.5 Hz, 1H), 7.11 (s, 2H), 5.26 (s, 1H), 2.37 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.0, 137.7, 135.1, 130.5, 129.8, 129.3, 128.8, 128.5, 127.7, 127.5, 20.5.

(2'-Hydroxy-[1,1':3',1''-terphenyl]-4-yl)methyl (*S*)-2-(4-isobutylphenyl)propanoate (2ab)



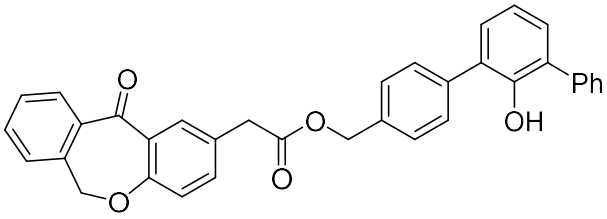
Eluent: V_{PE}/V_{EA} = 10:1. Yellow liquid (72.4 mg, 78% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.47 (m, 6H), 7.44 – 7.40 (m, 1H), 7.35 (d, J = 8.1 Hz, 2H), 7.32 – 7.24 (m, 4H), 7.13 (d, J = 8.0 Hz, 2H), 7.09 (t, J = 7.6 Hz, 1H), 5.41 (s, 1H), 5.25 – 5.13 (m, 2H), 3.81 (q, J = 7.1 Hz, 1H), 2.49 (d, J = 7.2 Hz, 2H), 1.94 – 1.83 (m, 1H), 1.56 (d, J = 7.2 Hz, 3H), 0.94 (d, J = 6.6 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.5, 149.3, 140.6, 137.5, 137.38, 137.36, 135.4, 130.0, 129.9, 129.4, 129.30, 129.28, 128.9, 128.8, 128.2, 128.1, 127.7, 127.2, 120.7, 66.0, 45.1, 45.0, 30.1, 22.3, 18.4. HRMS-ESI (*m/z*): calcd for $C_{32}H_{31}O_3$ $[M - H]^+$: 463.2279; found: 463.2274.

(2'-Hydroxy-[1,1':3',1''-terphenyl]-4-yl)methyl 2-(3-benzoylphenyl)propanoate (2ac)



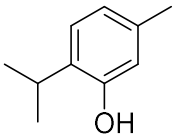
Eluent: V_{PE}/V_{EA} = 5:1. Yellow liquid (82.9 mg, 81% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 – 7.74 (m, 3H), 7.70 – 7.65 (m, 1H), 7.60 – 7.38 (m, 12H), 7.36 (d, J = 8.1 Hz, 2H), 7.30 – 7.23 (m, 2H), 7.06 (t, J = 7.6 Hz, 1H), 5.49 (s, 1H), 5.19 (s, 2H), 3.89 (q, J = 7.2 Hz, 1H), 1.58 (d, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.5, 173.8, 149.3, 140.7, 137.9, 137.7, 137.4, 135.0, 132.5, 131.5, 130.05, 129.99, 129.96, 129.5, 129.3, 129.2, 129.0, 128.9, 128.8, 128.5, 128.32, 128.26, 128.2, 127.7, 120.7, 66.3, 45.4, 18.4. HRMS-ESI (*m/z*): calcd for $C_{35}H_{27}O_4$ $[M - H]^+$: 511.1915; found: 511.1910.

(2'-Hydroxy-[1,1':3',1''-terphenyl]-4-yl)methyl 2-(11-oxo-6,11-dihydrodibenzo[*b,e*]oxepin-2-yl)acetate (2ad)



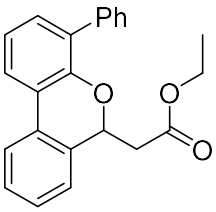
Eluent: V_{PE}/V_{EA} = 3:1. Brown liquid (89.4 mg, 85% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, J = 2.3 Hz, 1H), 7.91 – 7.85 (m, 1H), 7.59 – 7.53 (m, 5H), 7.51 – 7.43 (m, 6H), 7.42 – 7.39 (m, 1H), 7.36 (d, J = 7.4 Hz, 1H), 7.28 (d, J = 7.5 Hz, 2H), 7.09 – 7.02 (m, 2H), 5.48 (s, 1H), 5.20 (d, J = 9.7 Hz, 4H), 3.72 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.9, 171.3, 160.5, 149.3, 140.4, 137.8, 137.4, 136.4, 135.5, 135.0, 132.7, 132.4, 130.02, 129.99, 129.6, 129.5, 129.3, 129.2, 128.9, 128.8, 128.6, 128.2, 127.8, 127.7, 127.6, 125.1, 121.1, 120.7, 73.6, 66.5, 40.2. HRMS-ESI (*m/z*): calcd for $C_{35}H_{25}O_5$ $[M - H]^+$: 525.1707; found: 525.1703.

2-Isopropyl-5-methylphenol (thymol, 2ae)



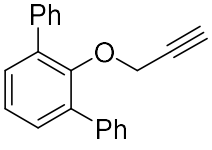
Eluent: V_{PE}/V_{EA} = 50:1. White solid (6.6 mg, 22% yield), mp: 55 – 56 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10 (d, J = 7.8 Hz, 1H), 6.75 (d, J = 7.8 Hz, 1H), 6.59 (s, 1H), 4.64 (s, 1H), 3.24 – 3.12 (m, 1H), 2.29 (s, 3H), 1.26 (d, J = 6.9 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.5, 136.6, 131.3, 126.2, 121.7, 116.0, 26.7, 22.7, 20.8.

Ethyl 2-(4-phenyl-6*H*-benzo[*c*]chromen-6-yl)acetate (5)



Eluent: V_{PE}/V_{EA} = 30:1. Brown liquid (27.9 mg, 41% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 – 7.73 (m, 2H), 7.54 (d, J = 7.2 Hz, 2H), 7.44 – 7.38 (m, 3H), 7.36 – 7.29 (m, 3H), 7.20 – 7.12 (m, 2H), 5.71 (dd, J = 9.2, 4.9 Hz, 1H), 3.97 – 3.80 (m, 2H), 2.92 (dd, J = 15.1, 9.2 Hz, 1H), 2.73 (dd, J = 15.1, 4.9 Hz, 1H), 1.09 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.1, 149.2, 137.7, 133.1, 131.6, 130.9, 129.47, 129.46, 128.6, 127.9, 127.8, 126.9, 124.3, 122.70, 122.67, 122.5, 122.0, 74.2, 60.7, 39.8, 13.9. HRMS-ESI (*m/z*): calcd for $C_{23}H_{19}O_3$ $[M - H]^+$: 343.1340; found: 343.1341.

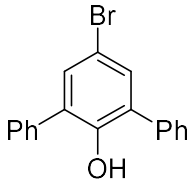
2'-(Prop-2-yn-1-yloxy)-1,1':3',1''-terphenyl (6)



Eluent: V_{PE}/V_{EA} = 200:1. Colorless liquid (46.9 mg, 83% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 – 7.65 (m, 4H), 7.50 – 7.45 (m, 4H), 7.43 – 7.37 (m, 4H), 7.31 (dd, J = 8.3, 6.7 Hz, 1H), 3.96 (d, J = 2.4 Hz, 2H), 2.15 (t, J = 2.4 Hz,

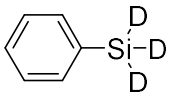
1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.4, 138.4, 136.1, 130.3, 129.5, 128.2, 127.2, 124.9, 78.6, 74.6, 59.8. HRMS-ESI (*m/z*): calcd for $C_{21}H_{17}O$ $[M + H]^+$: 285.1274; found: 285.1271.

5'-Bromo-[1,1':3',1''-terphenyl]-2'-ol (7)



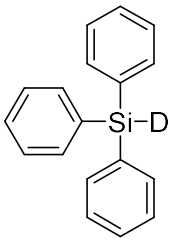
Eluent: V_{PE}/V_{EA} = 30:1. Brown liquid (42.3 mg, 65% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.52 (m, 4H), 7.52 – 7.48 (m, 4H), 7.46 – 7.39 (m, 4H), 5.41 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.5, 136.2, 132.2, 130.6, 129.2, 128.9, 128.1, 112.7.

Phenylsilane-*d*$_3$



Colourless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.58 (m, 2H), 7.45 – 7.35 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.8, 129.8, 128.1.

Triphenylsilane-*d*



Colourless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.58 (m, 6H), 7.47 – 7.37 (m, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.8, 133.3, 129.8, 128.0.

J Reference

1 X.-Z. Shu, X.-Y. Liu, H.-Q. Xiao, K.-G. Ji, L.-N. Guo, C.-Z. Qi, Y.-M. Liang, *Adv. Synth. Catal.*, 2007, **349**, 2493.

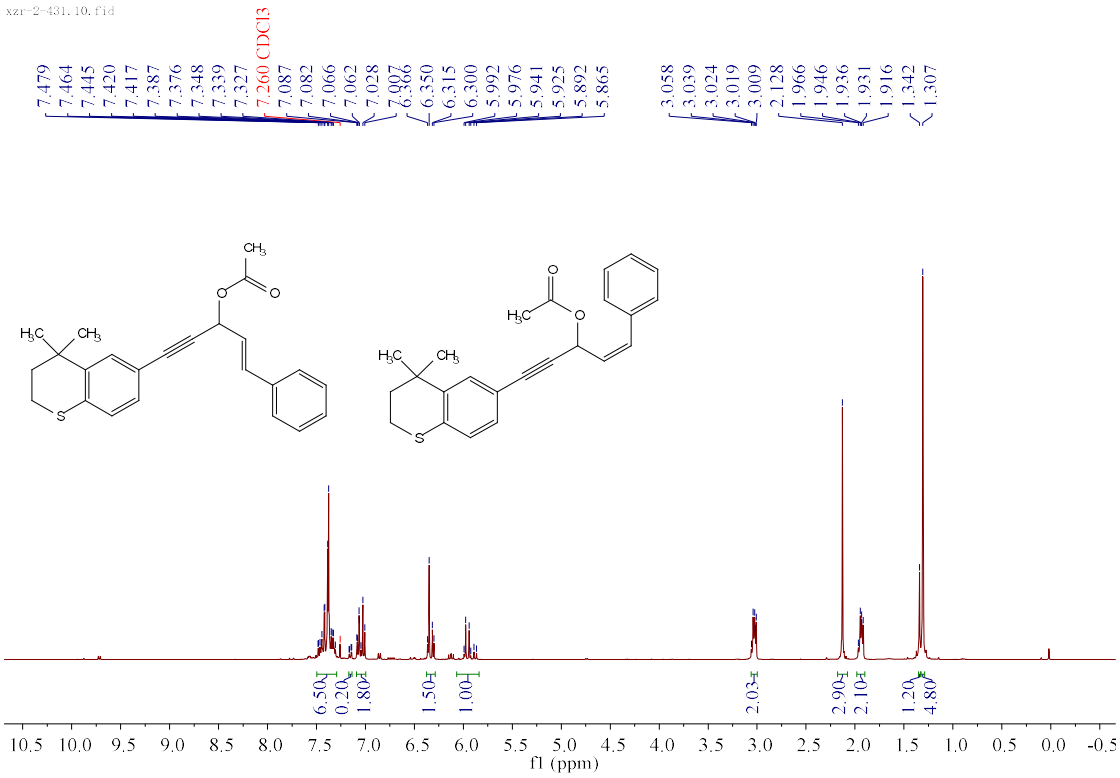
2 Z. Xu, J. Huang, T. Zhao, Y. Ren, H. Jiang, C. Qi, *Adv. Synth. Catal.*, 2025, **367**, e202500201.

3 R. Zhang, J. Xu, S. Liu, S. Si, J. Chen, L. Wang, W.-W. Chen, B. Zhao, *J. Am. Chem. Soc.*, 2024, **146**, 25927.

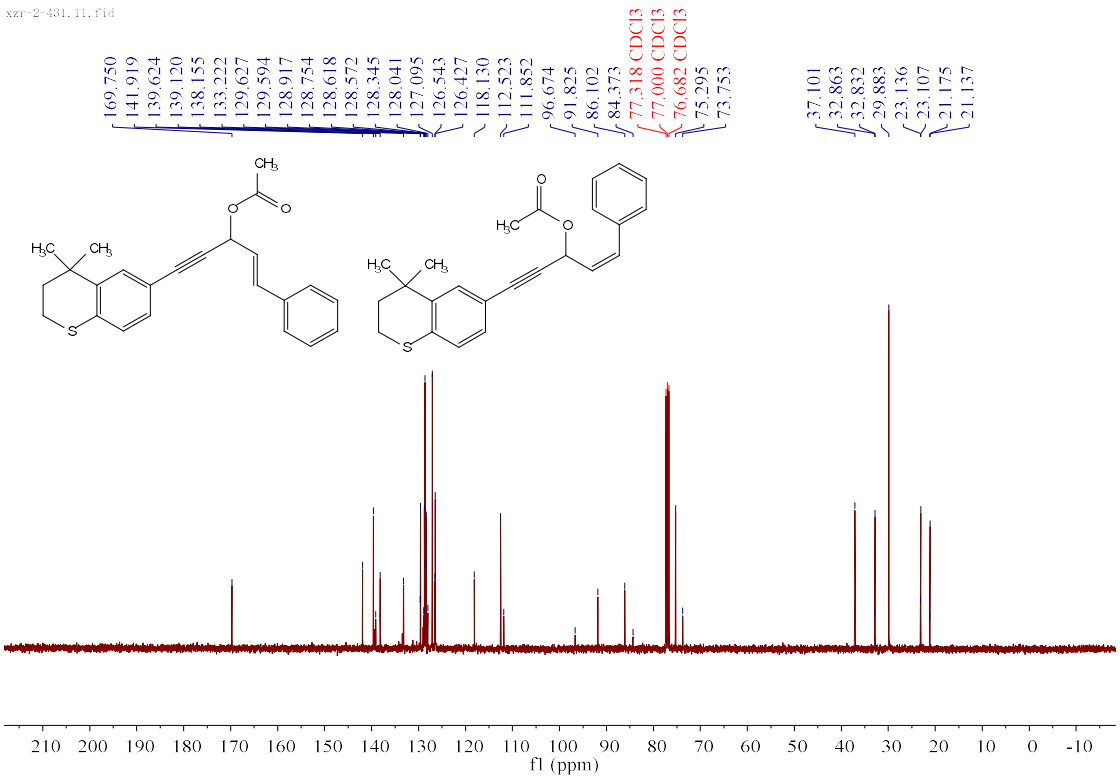
4 W. Cai, Y. Huang, *Angew. Chem. Int. Ed.*, 2023, **62**, e202310133.

K NMR Spectra

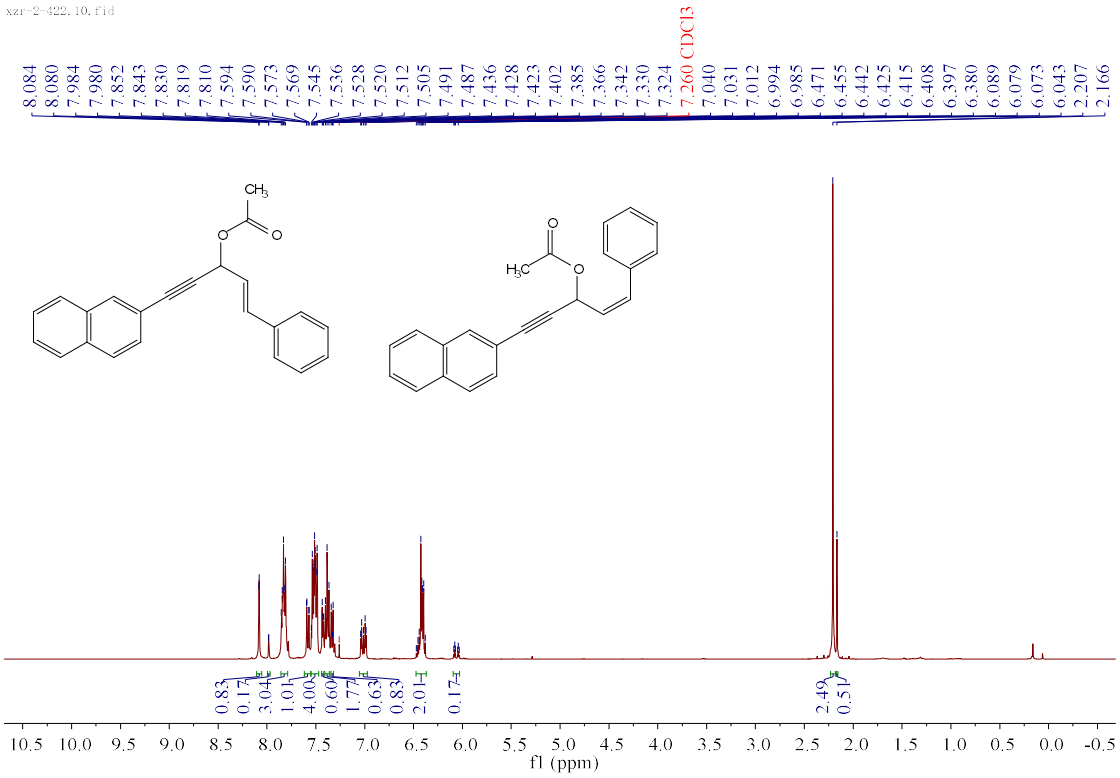
400 MHz ^{1}H NMR Spectrum of 1m in $CDCl_3$



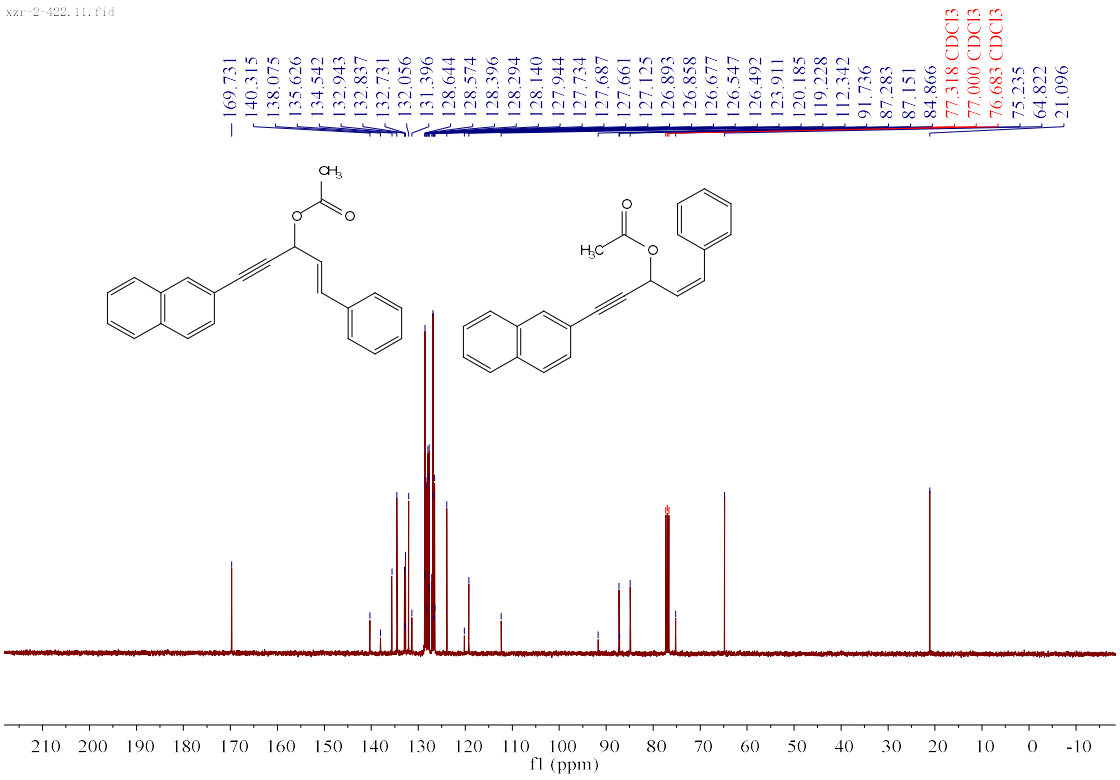
100 MHz ^{13}C NMR Spectrum of 1m in $CDCl_3$



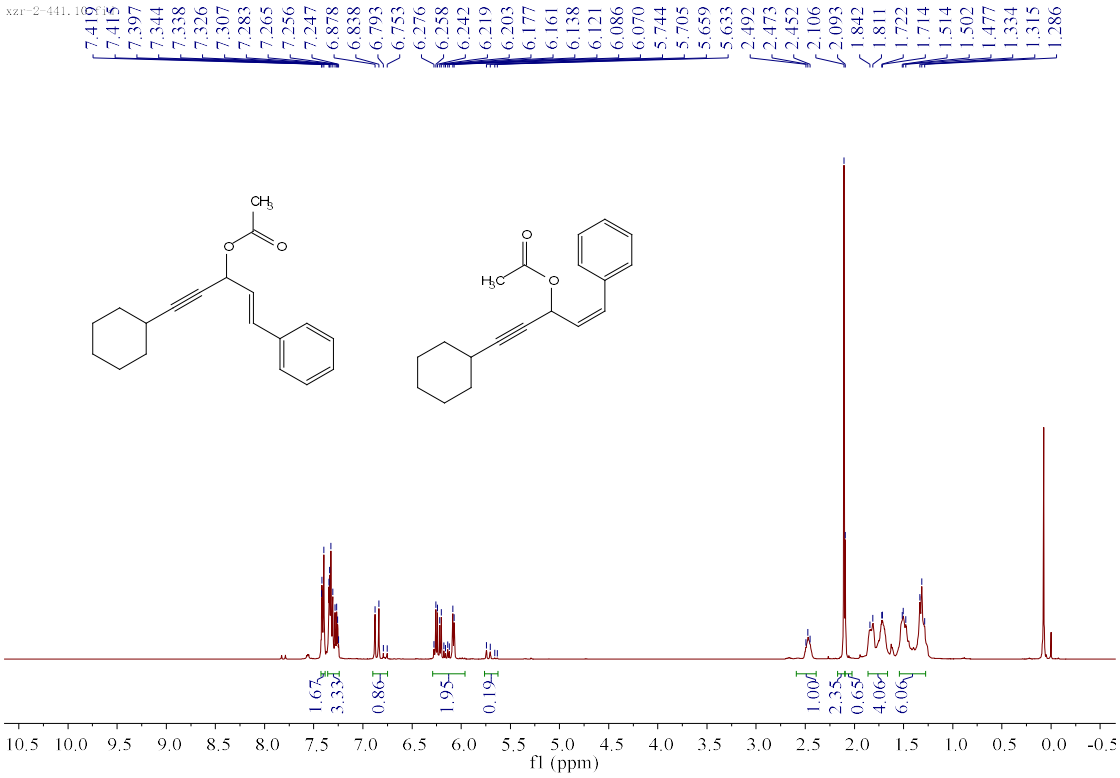
400 MHz ^{1}H NMR Spectrum of 1n in $CDCl_3$



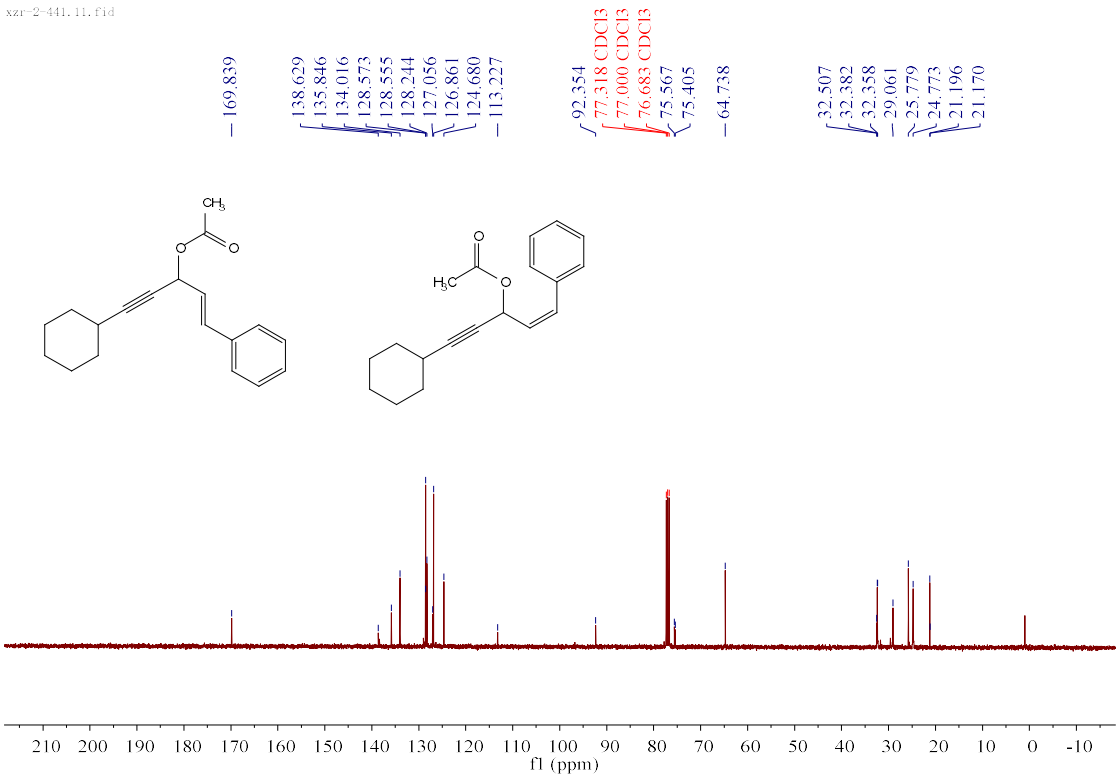
100 MHz ^{13}C NMR Spectrum of 1n in $CDCl_3$



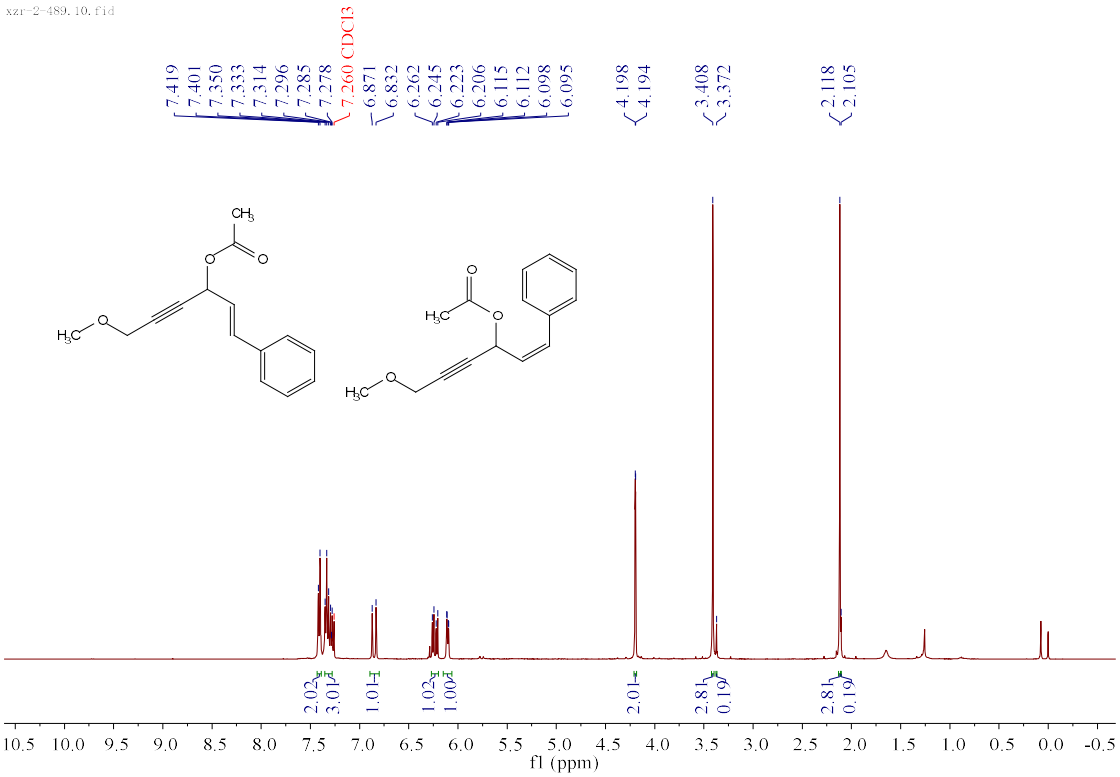
400 MHz ^{1}H NMR Spectrum of 1p in $CDCl_3$



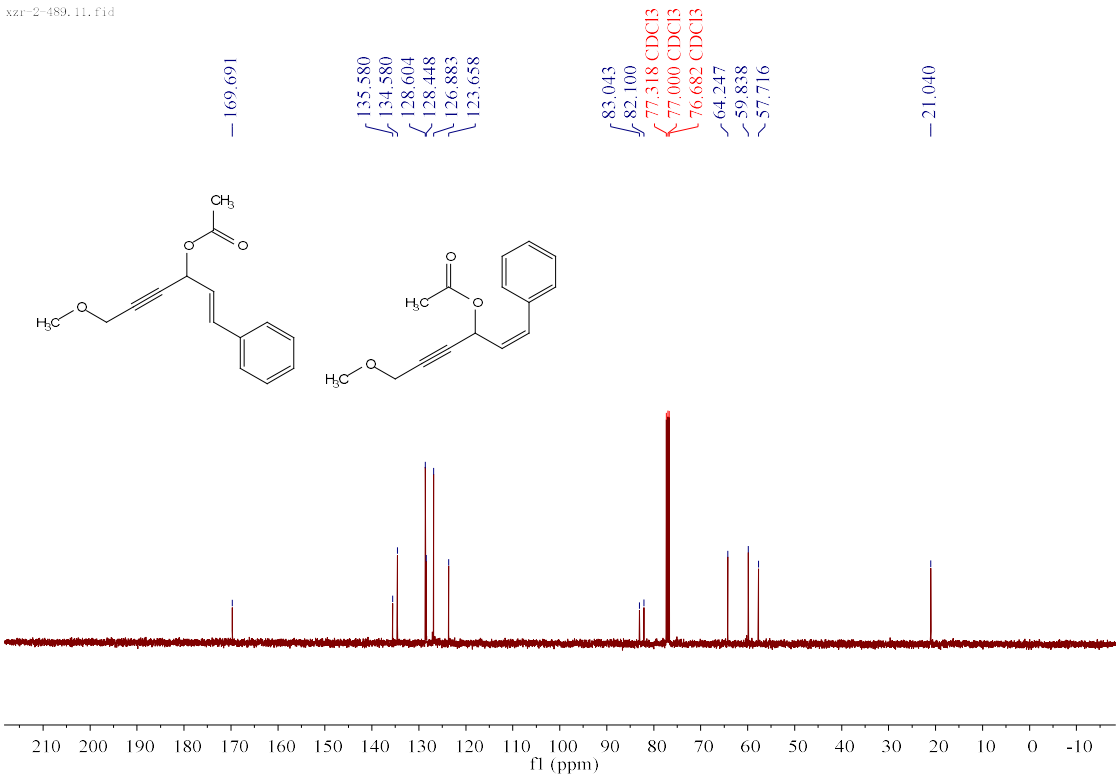
100 MHz ^{13}C NMR Spectrum of 1p in $CDCl_3$



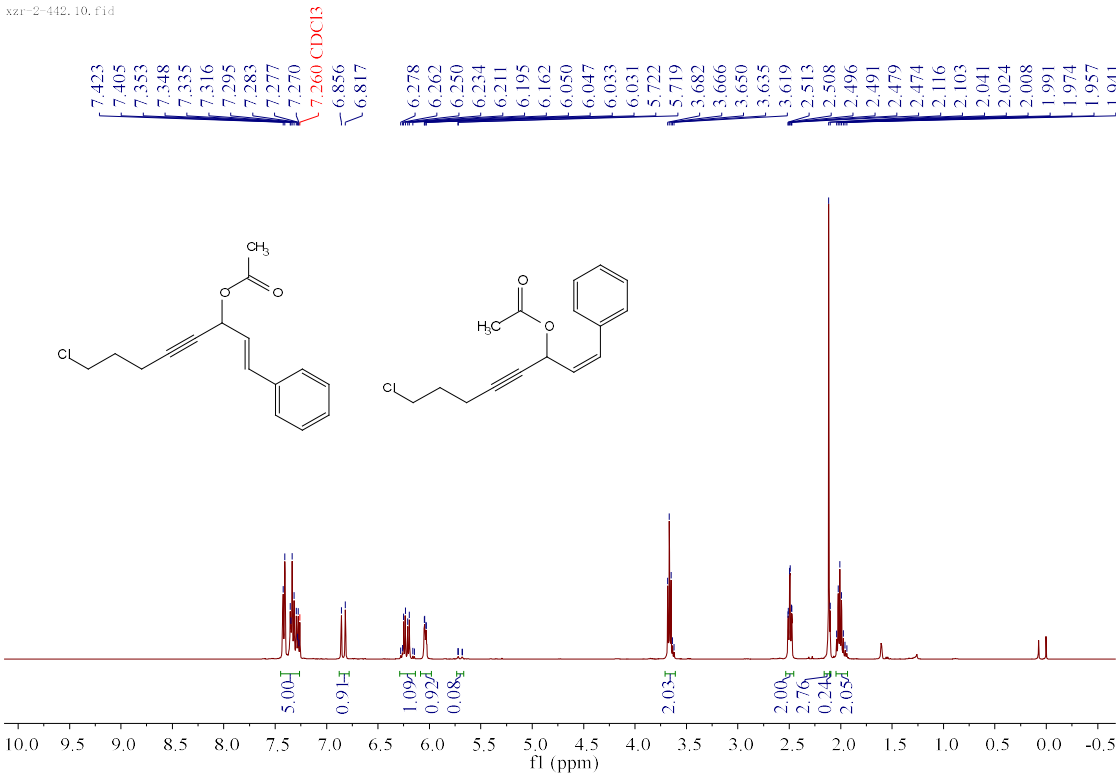
400 MHz ^{1}H NMR Spectrum of 1q in $CDCl_3$



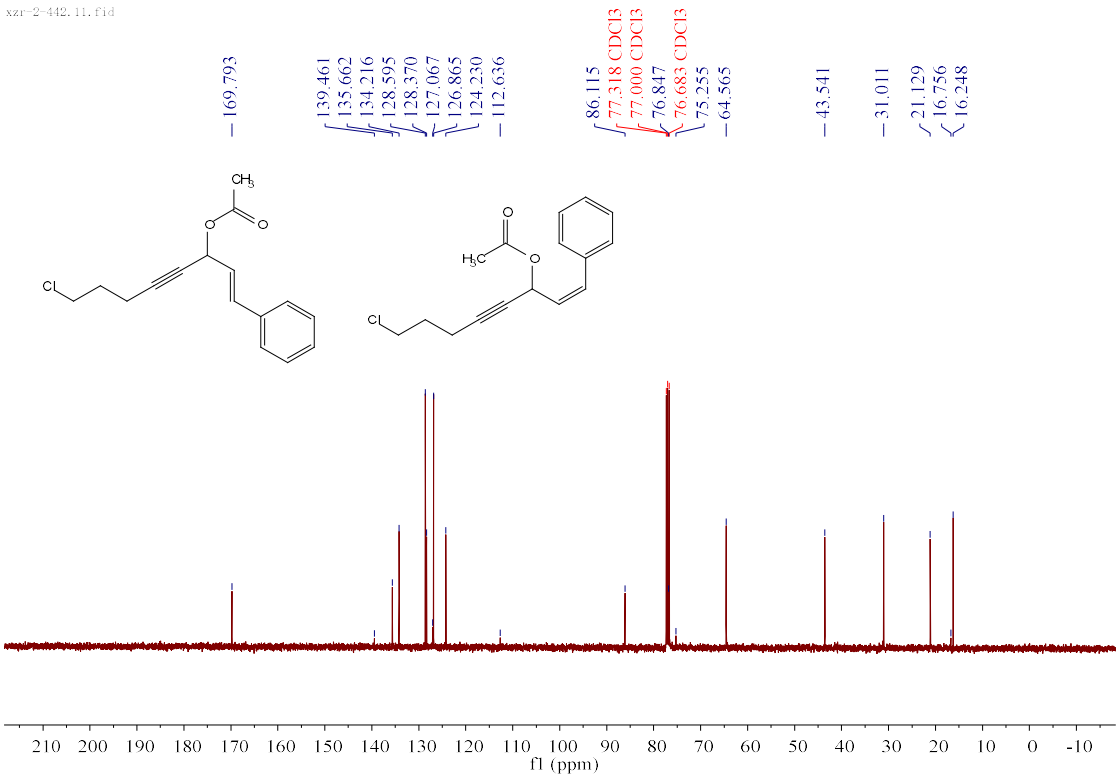
100 MHz ^{13}C NMR Spectrum of 1q in $CDCl_3$



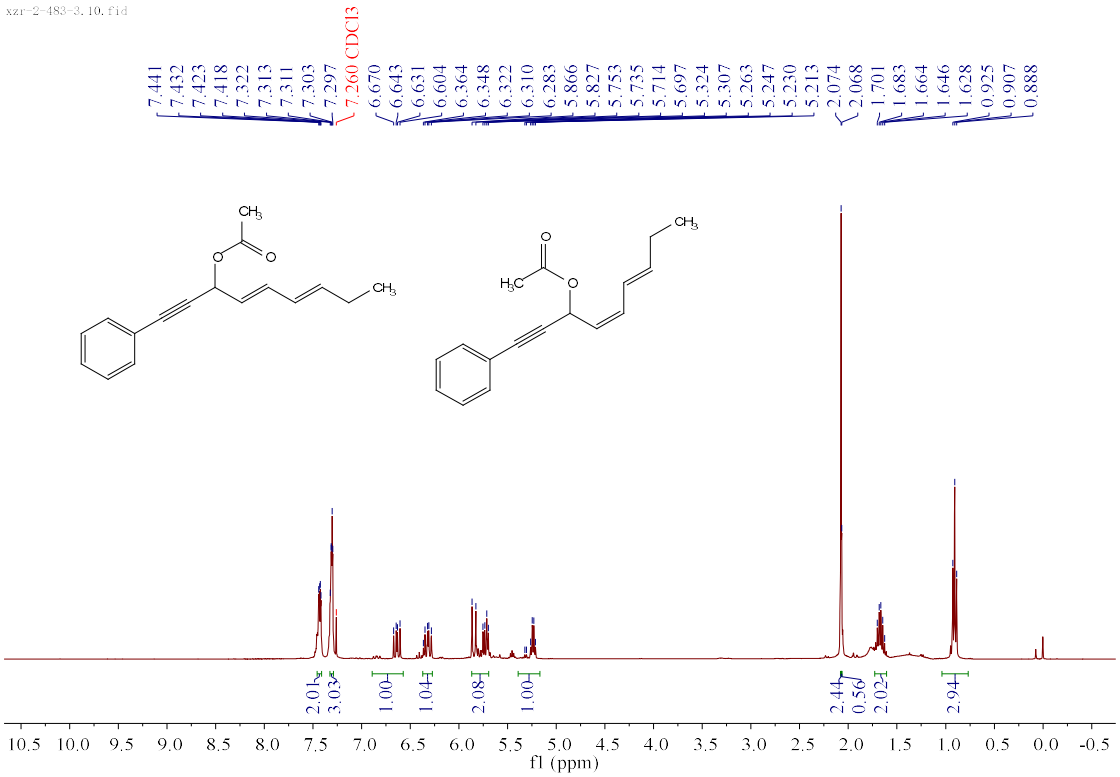
400 MHz ^{1}H NMR Spectrum of 1r in $CDCl_3$



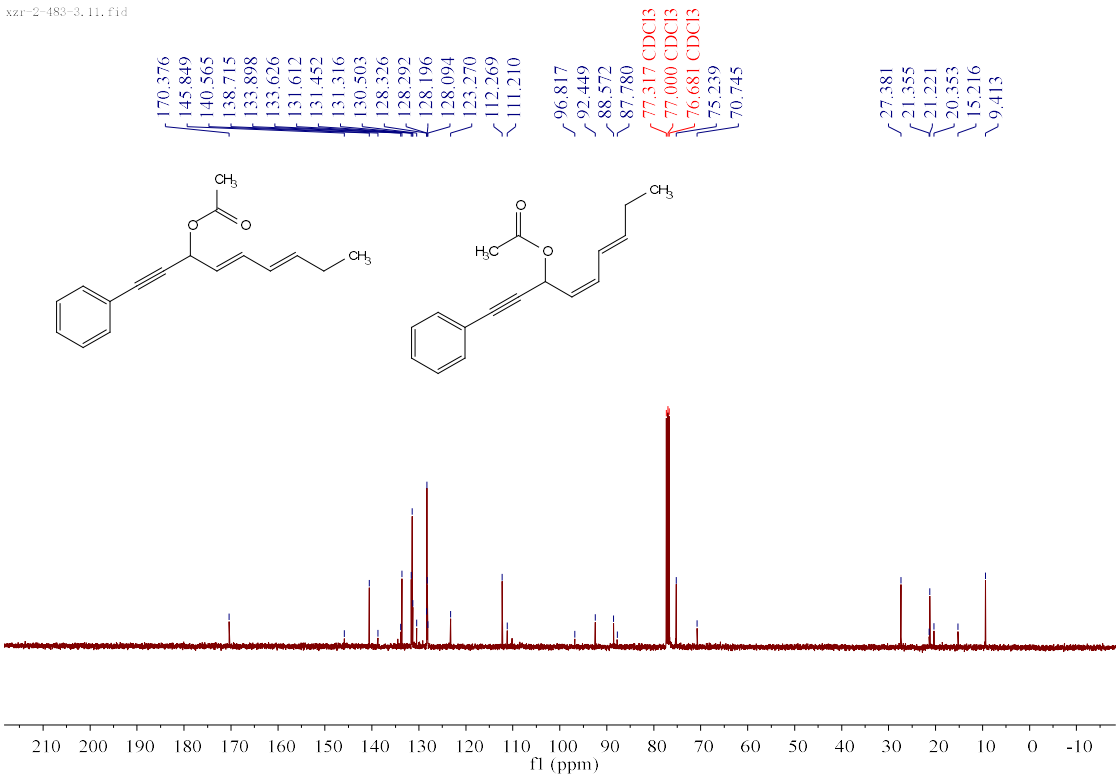
100 MHz ^{13}C NMR Spectrum of 1r in $CDCl_3$



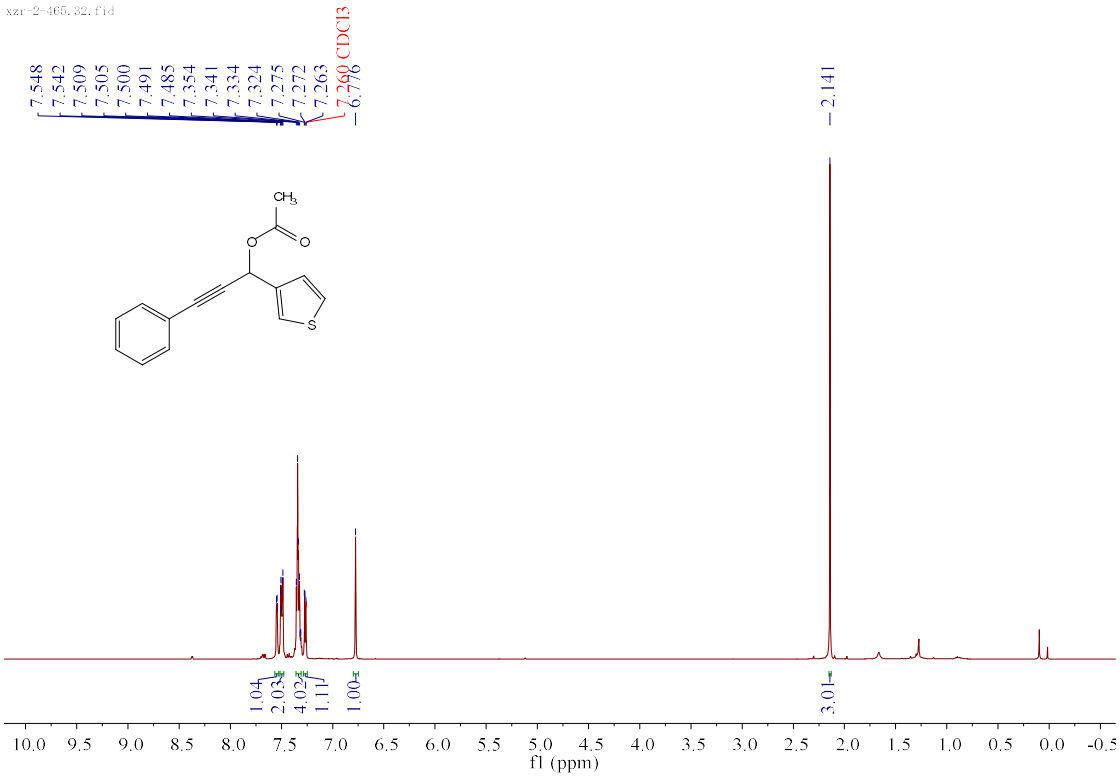
400 MHz ^{1}H NMR Spectrum of 1u in $CDCl_3$



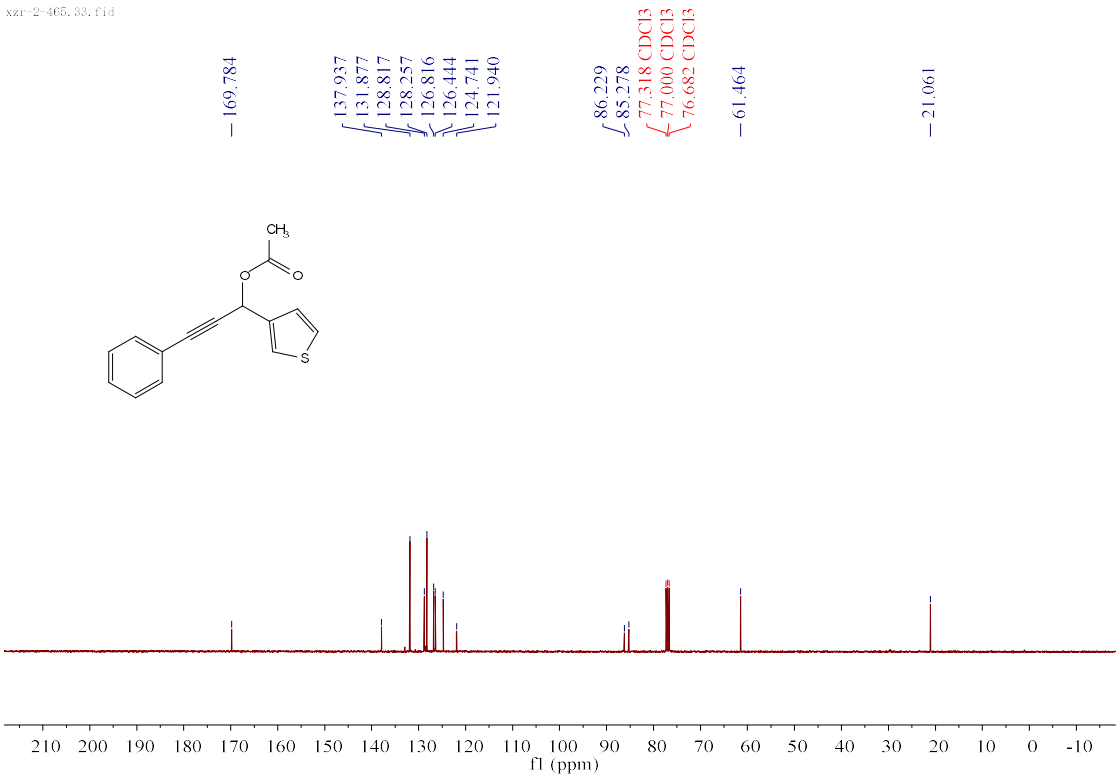
100 MHz ^{13}C NMR Spectrum of 1u in $CDCl_3$



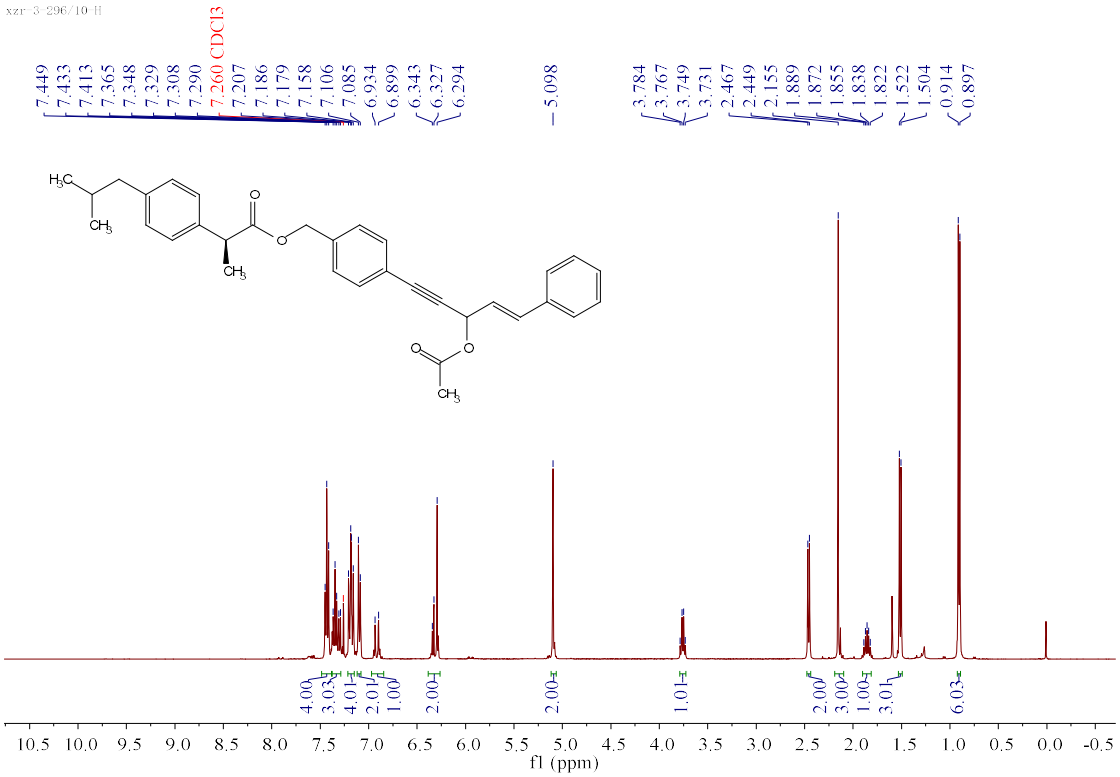
400 MHz ^{1}H NMR Spectrum of 1y in $CDCl_3$



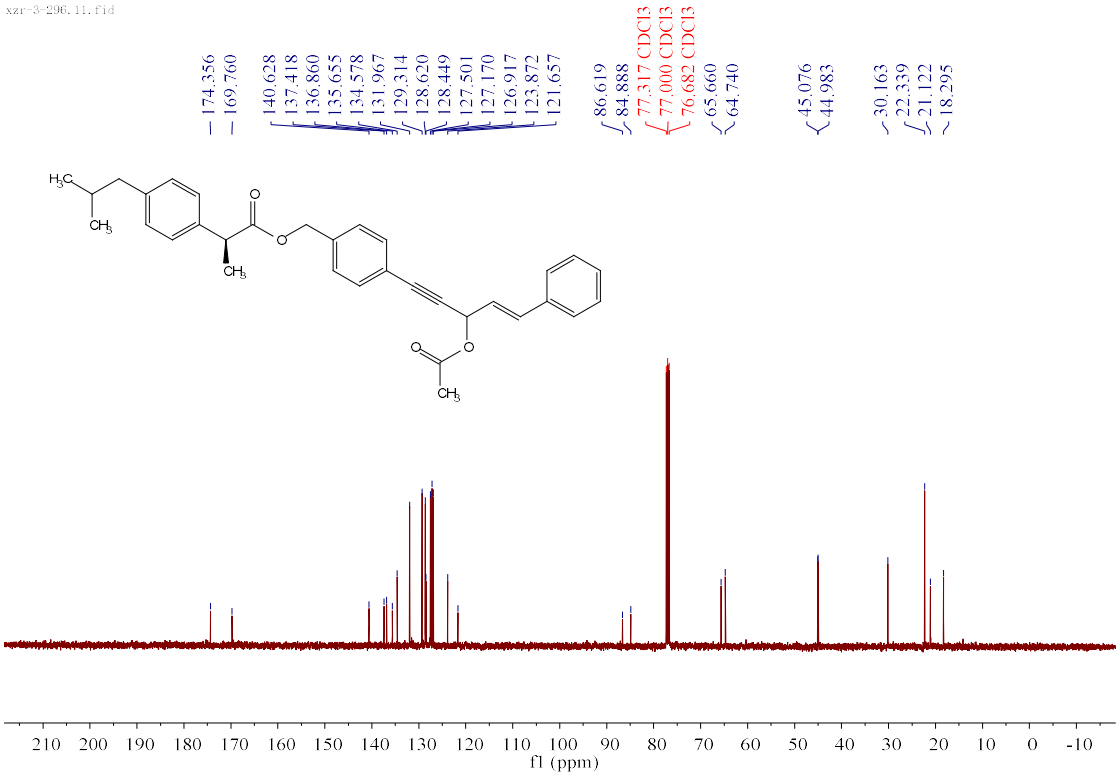
100 MHz ^{13}C NMR Spectrum of 1y in $CDCl_3$



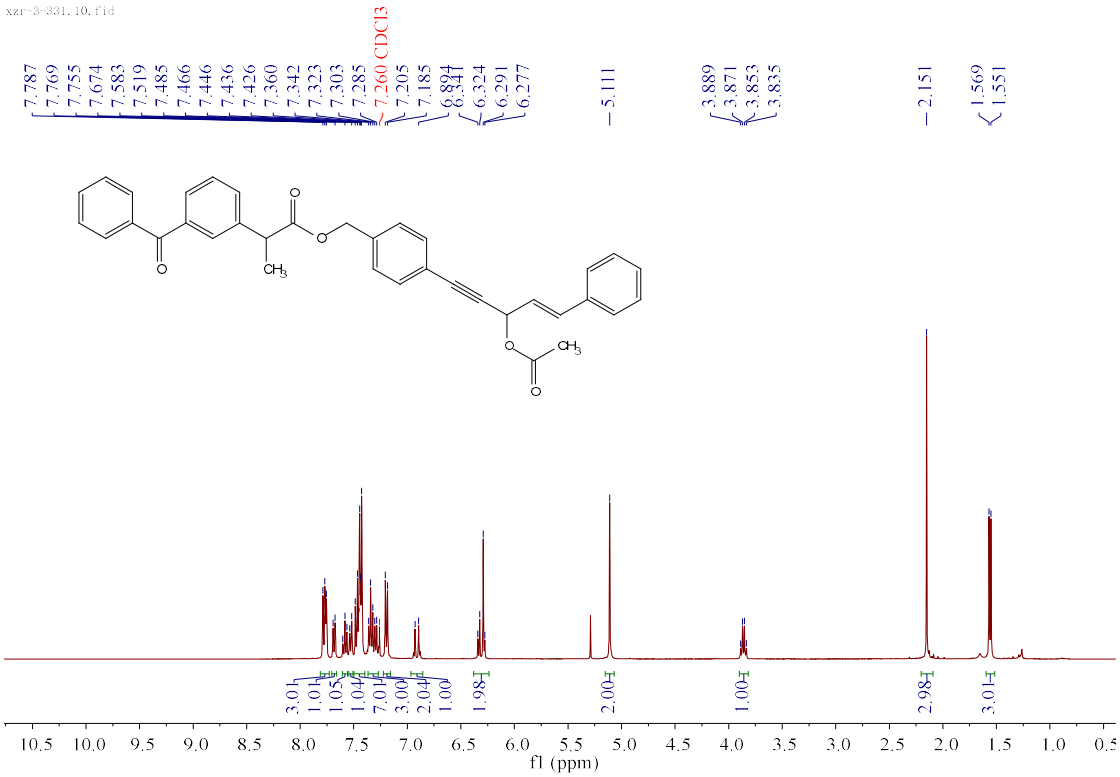
400 MHz ^{1}H NMR Spectrum of 1ab in $CDCl_3$



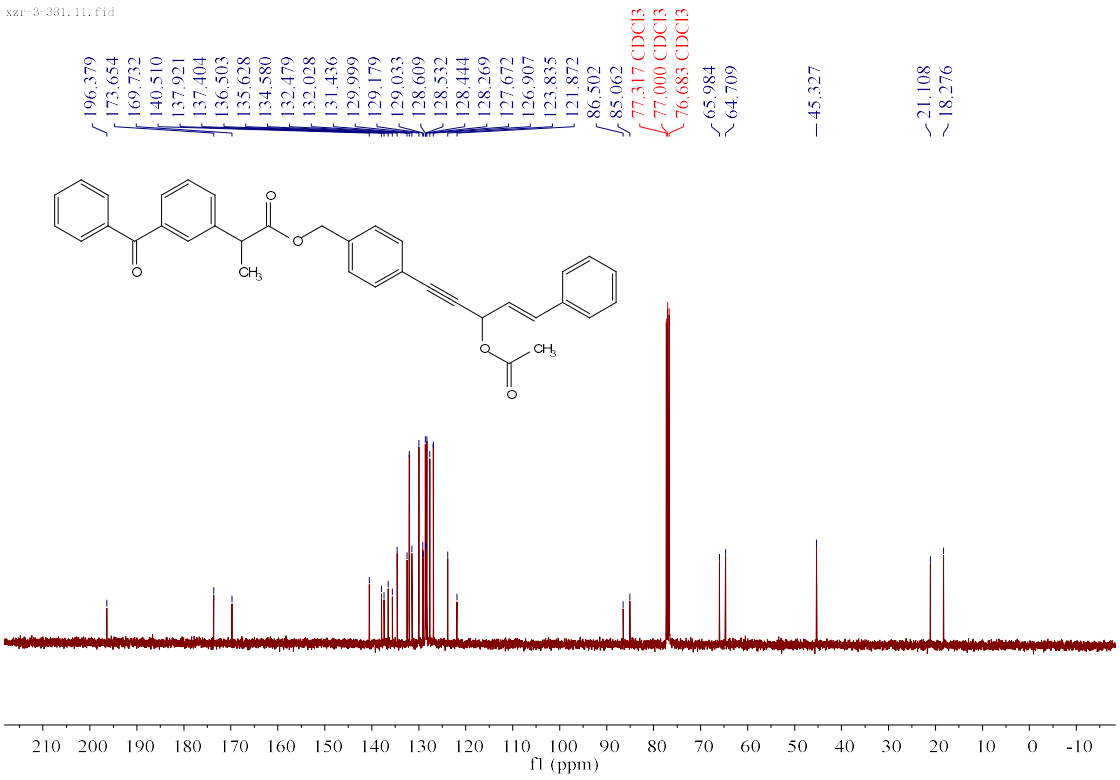
100 MHz ^{13}C NMR Spectrum of 1ab in $CDCl_3$



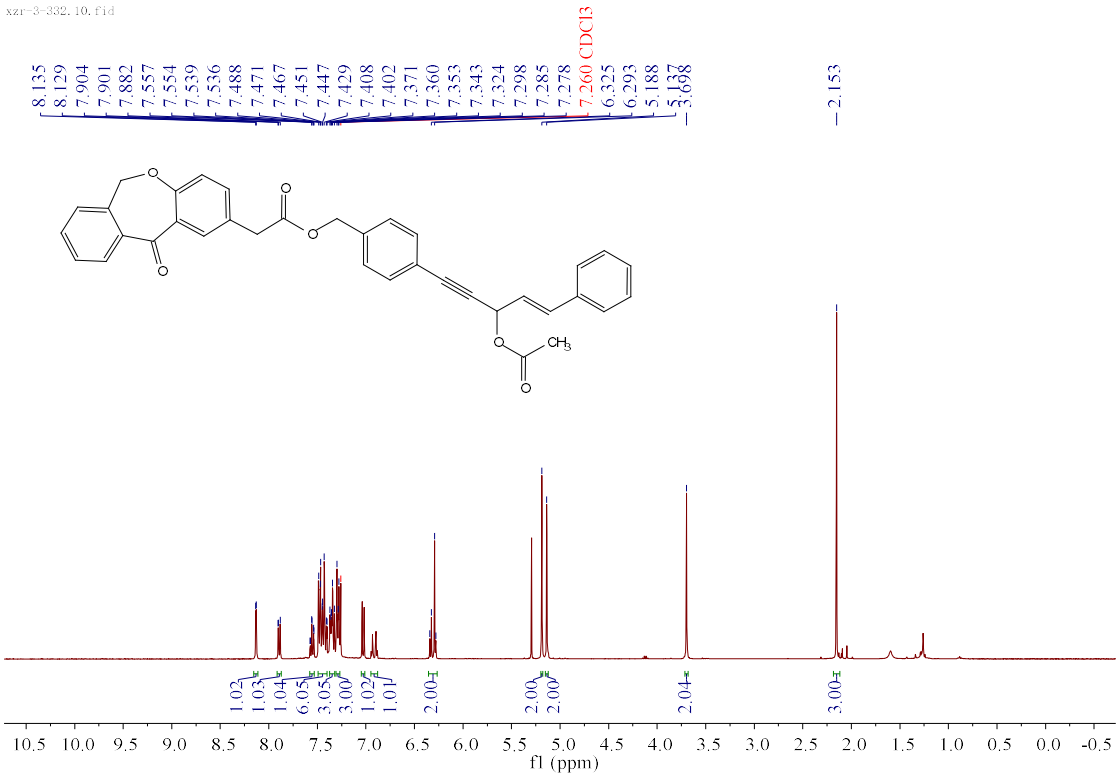
400 MHz ^{1}H NMR Spectrum of 1ac in $CDCl_3$



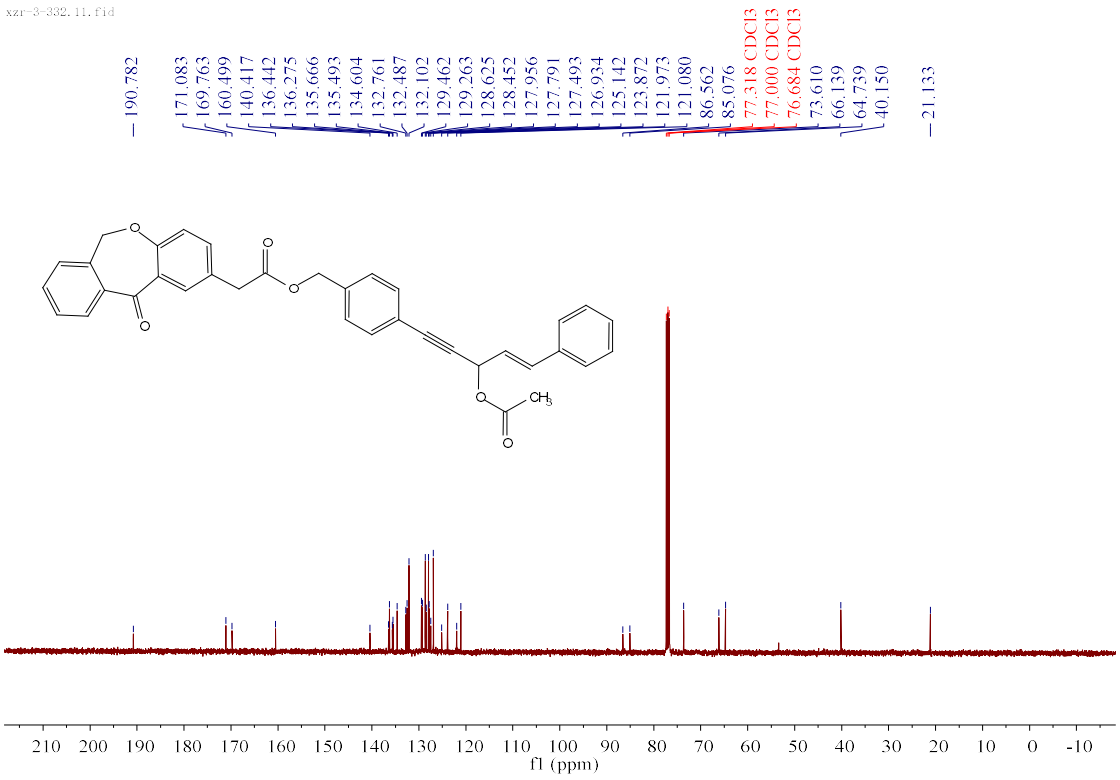
100 MHz ^{13}C NMR Spectrum of 1ac in $CDCl_3$



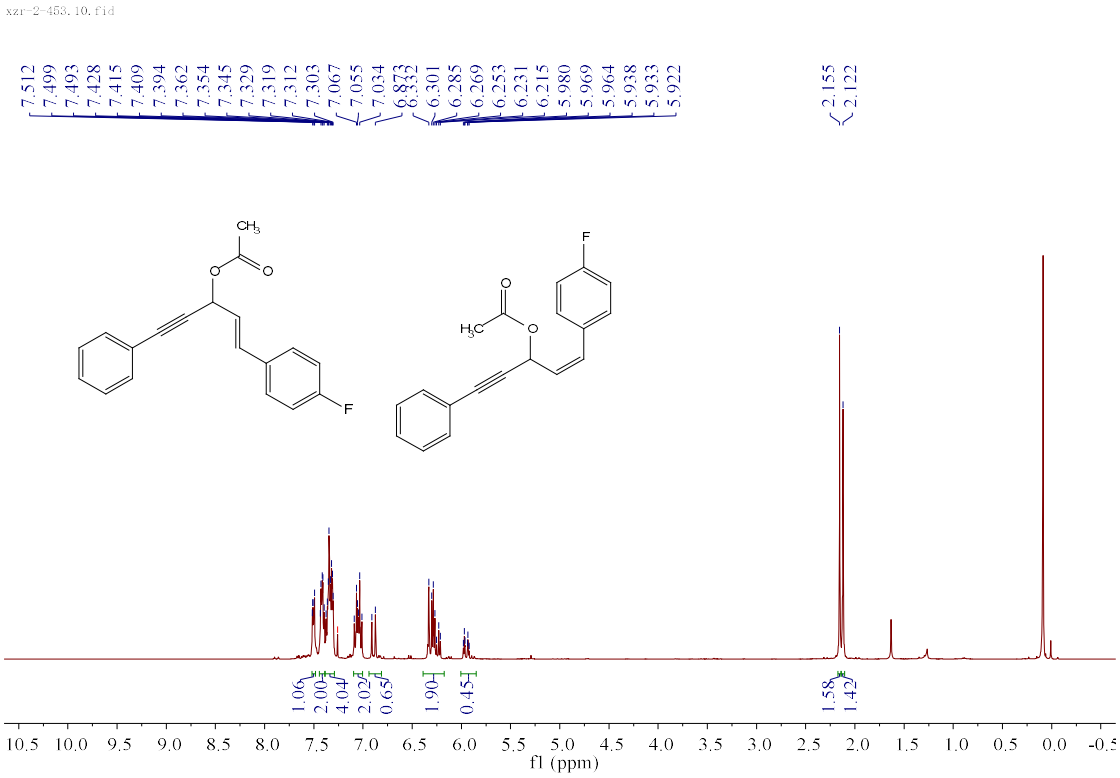
400 MHz ^{1}H NMR Spectrum of 1ad in $CDCl_3$



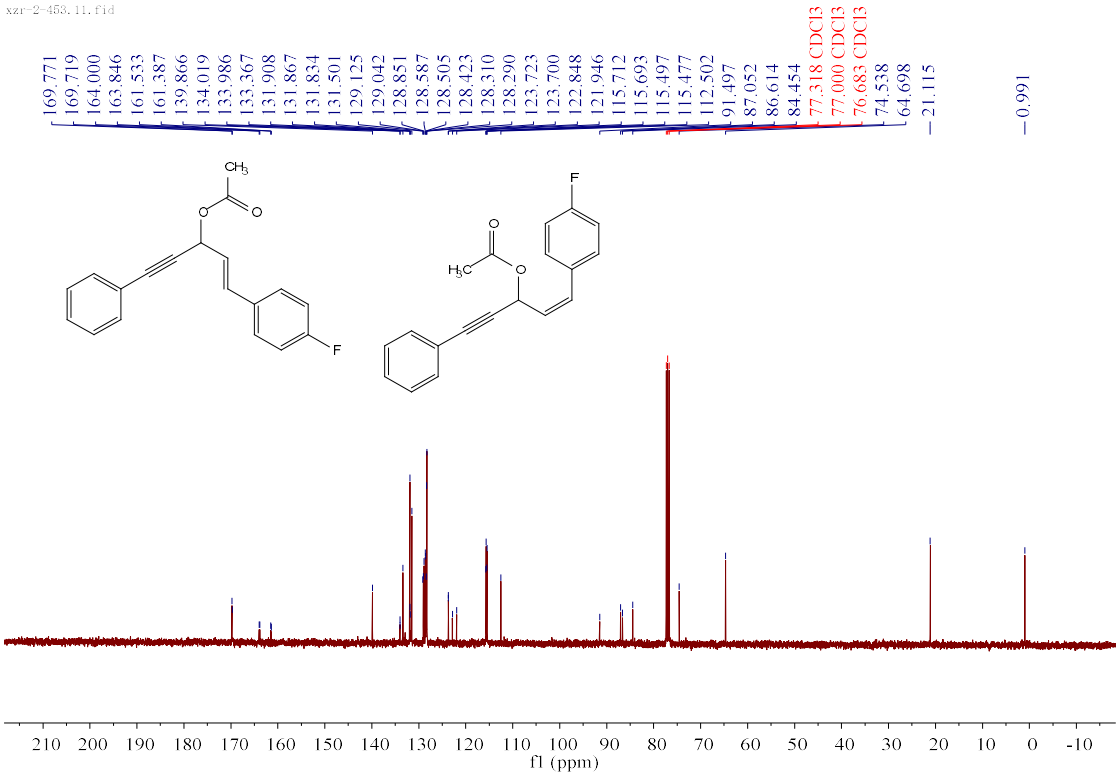
100 MHz ^{13}C NMR Spectrum of 1ad in $CDCl_3$



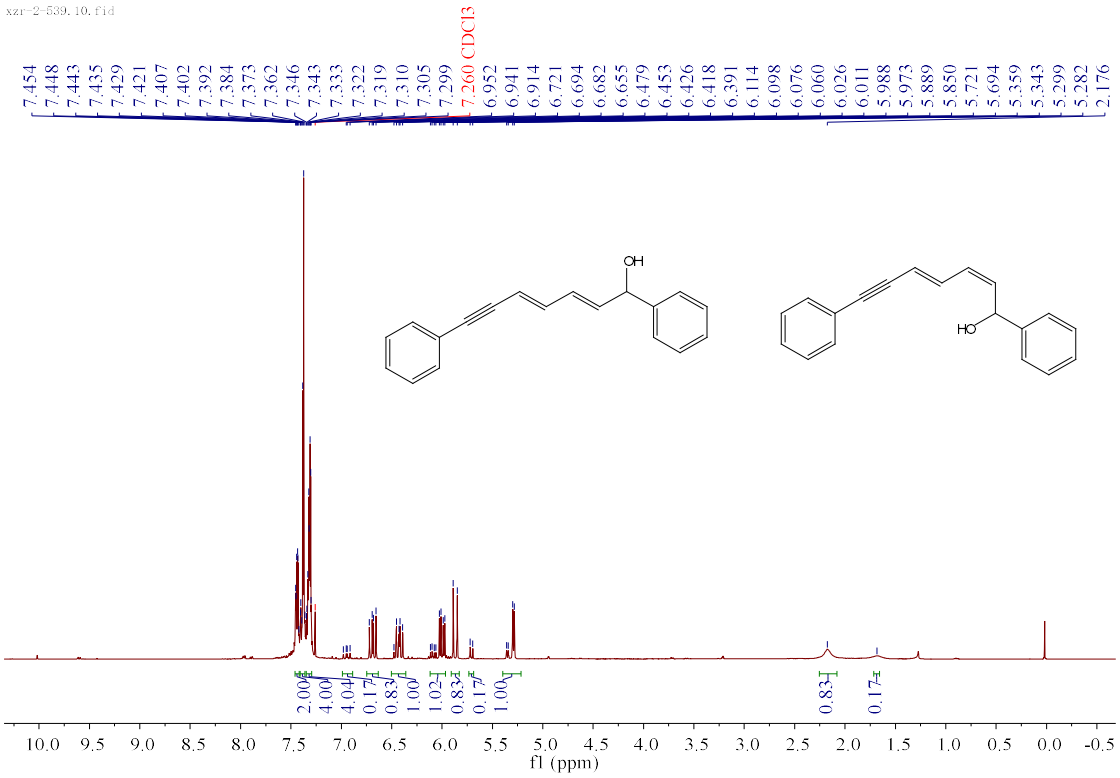
400 MHz ^{1}H NMR Spectrum of 1ag in $CDCl_3$



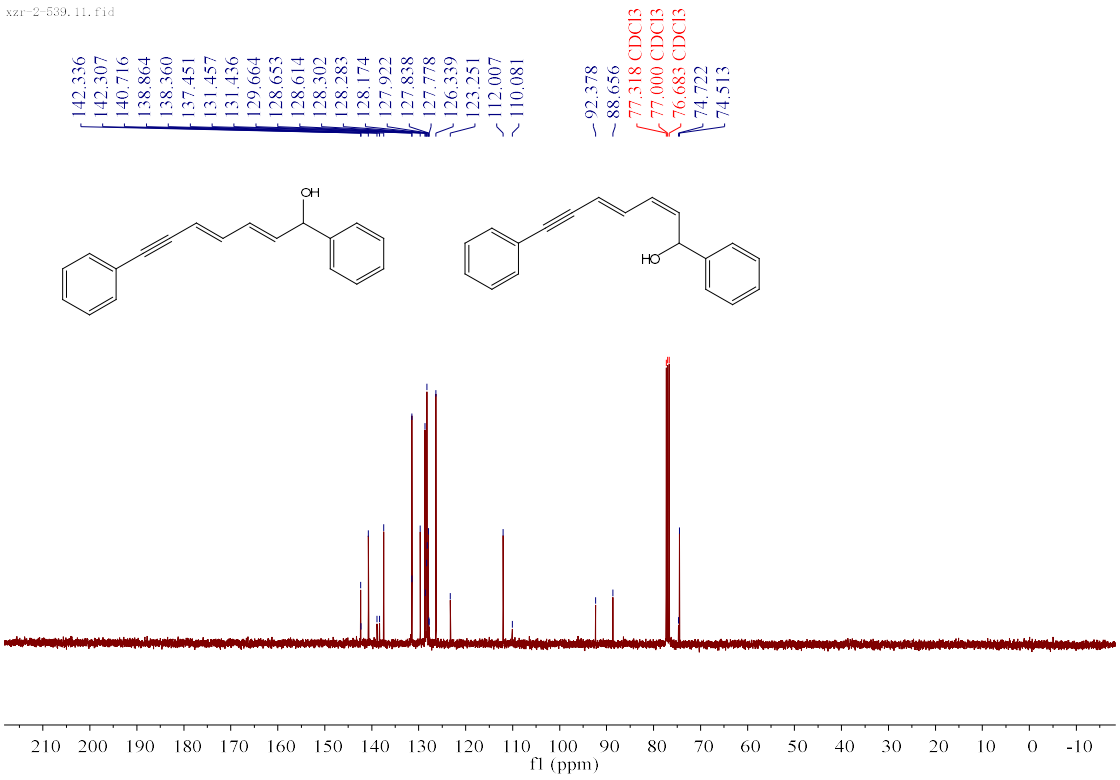
100 MHz ^{13}C NMR Spectrum of 1ag in $CDCl_3$



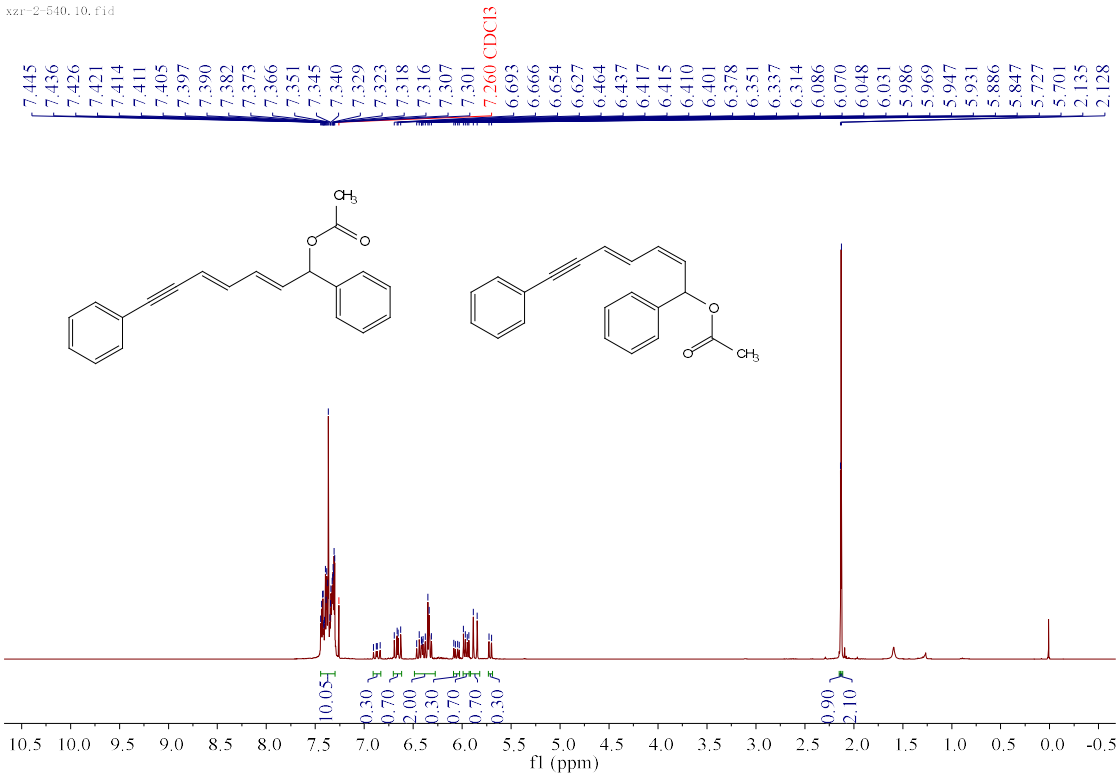
400 MHz ^{1}H NMR Spectrum of 4a in $CDCl_3$



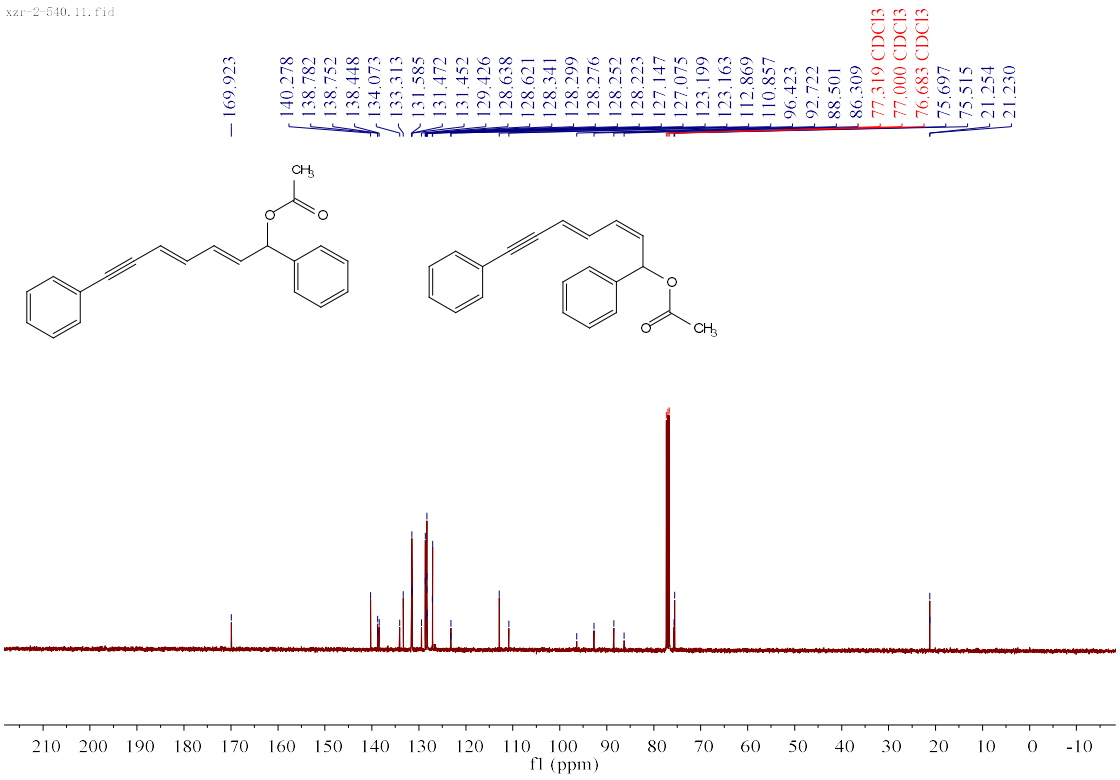
100 MHz ^{13}C NMR Spectrum of 4a in $CDCl_3$



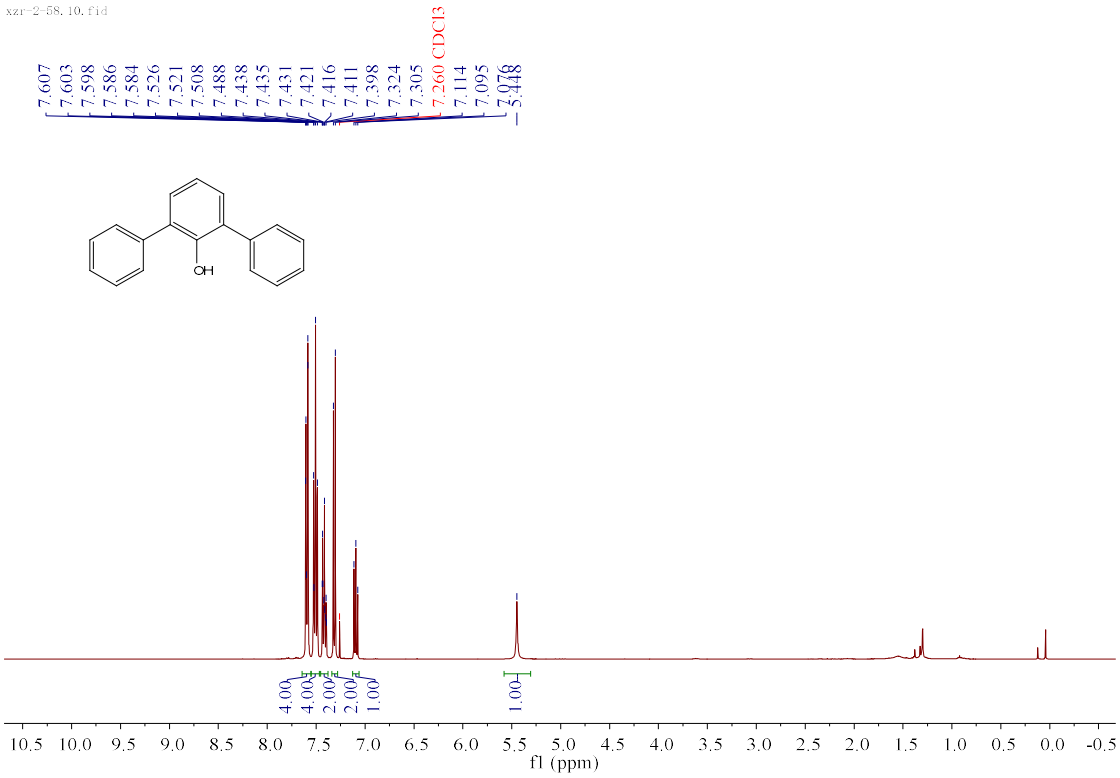
400 MHz ^{1}H NMR Spectrum of 4b in $CDCl_3$



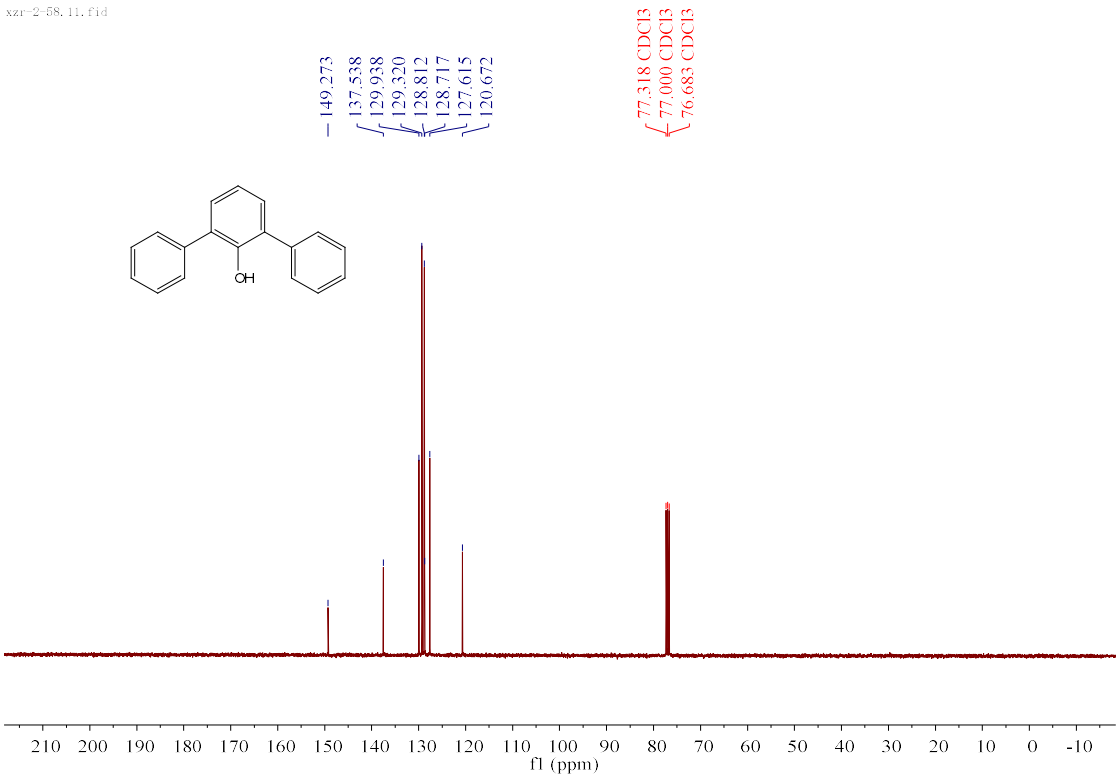
100 MHz ^{13}C NMR Spectrum of 4b in $CDCl_3$



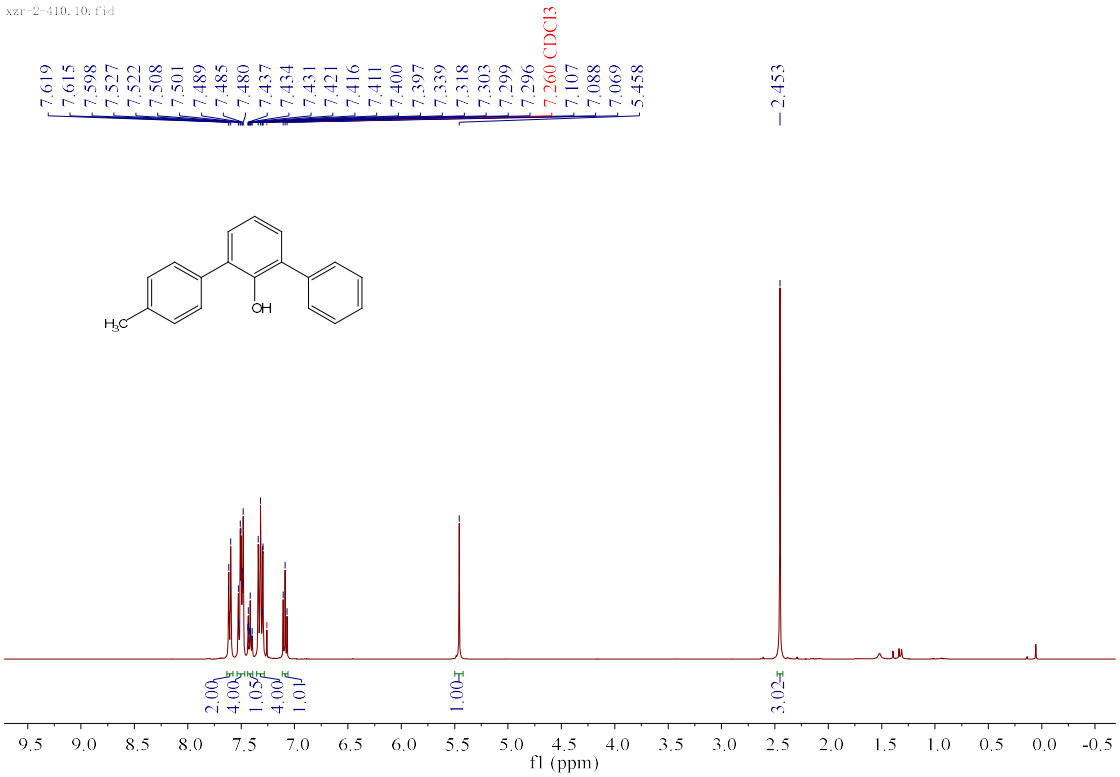
400 MHz ^{1}H NMR Spectrum of 2a in $CDCl_3$



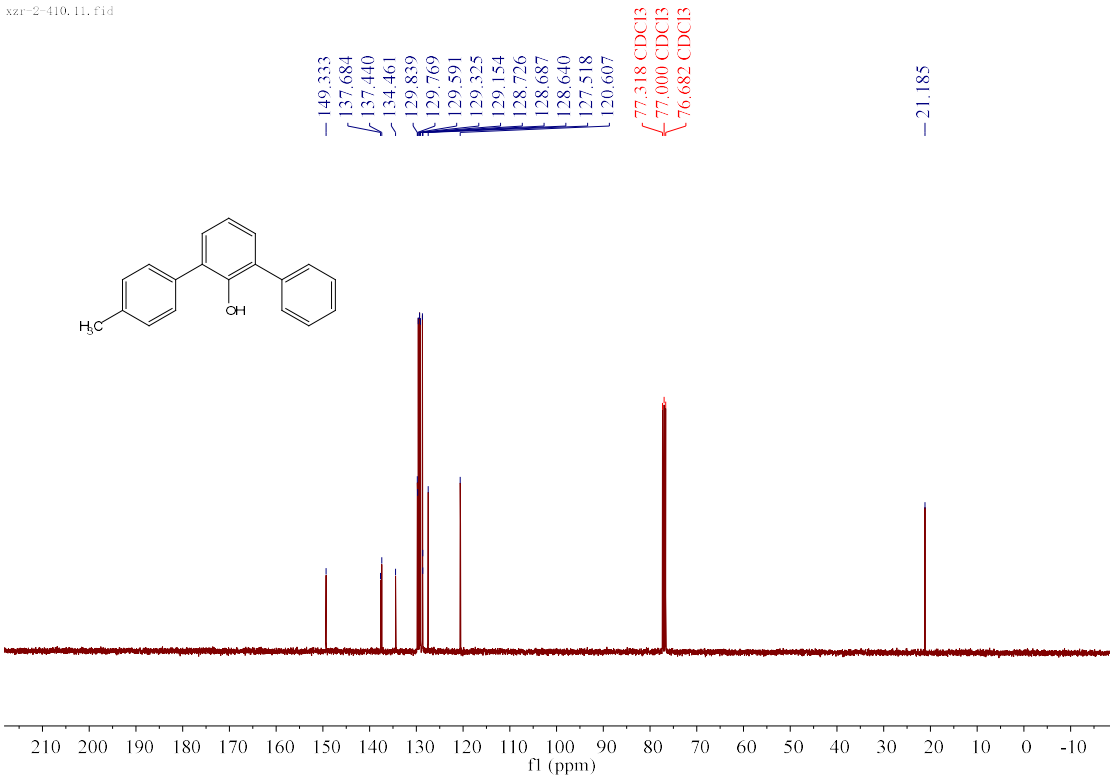
100 MHz ^{13}C NMR Spectrum of 2a in $CDCl_3$



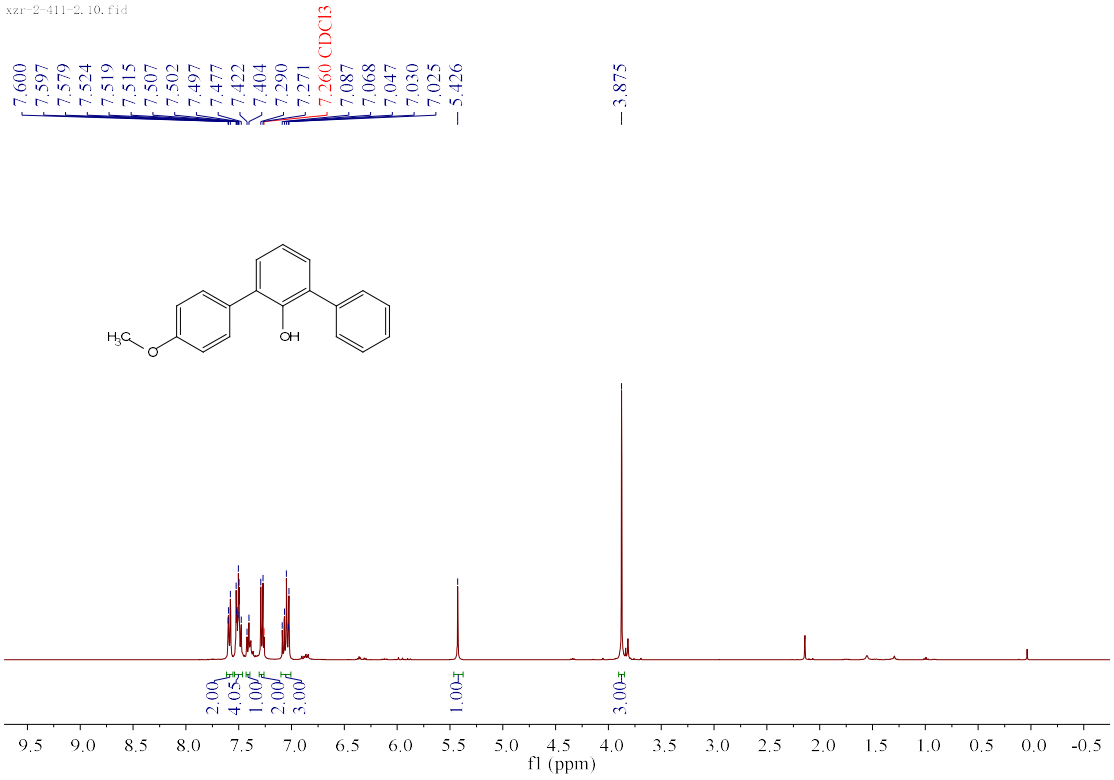
400 MHz ^{1}H NMR Spectrum of 2b in $CDCl_3$



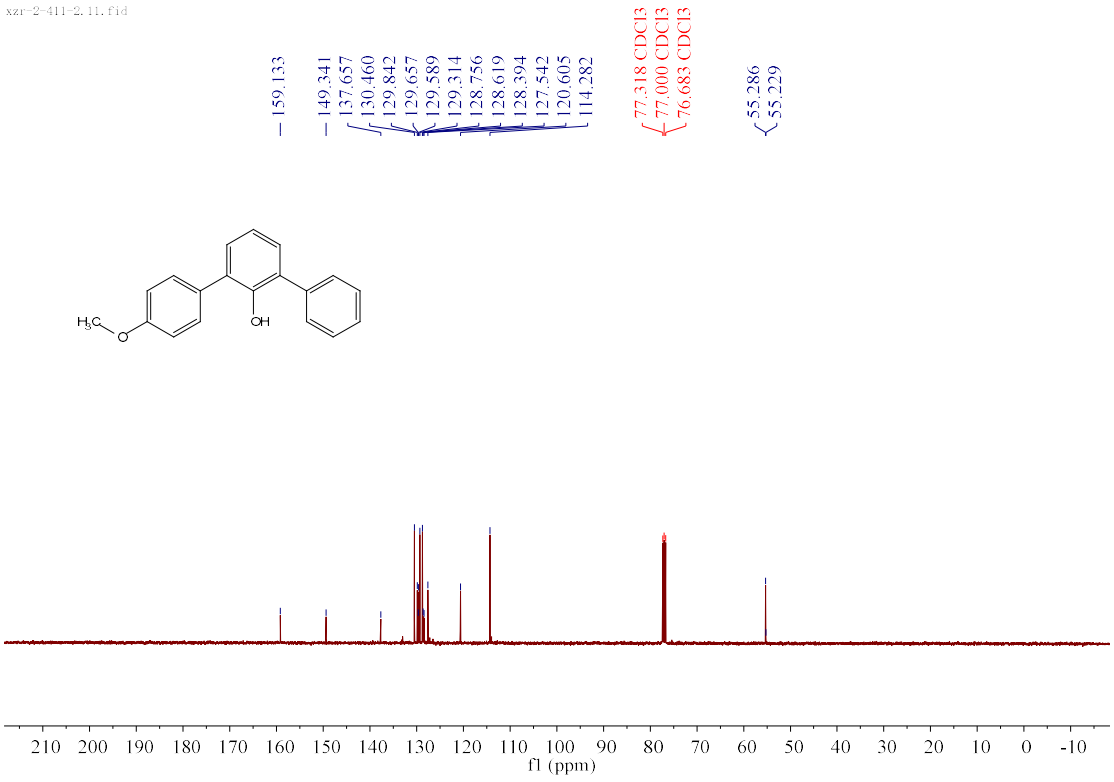
100 MHz ^{13}C NMR Spectrum of 2b in $CDCl_3$



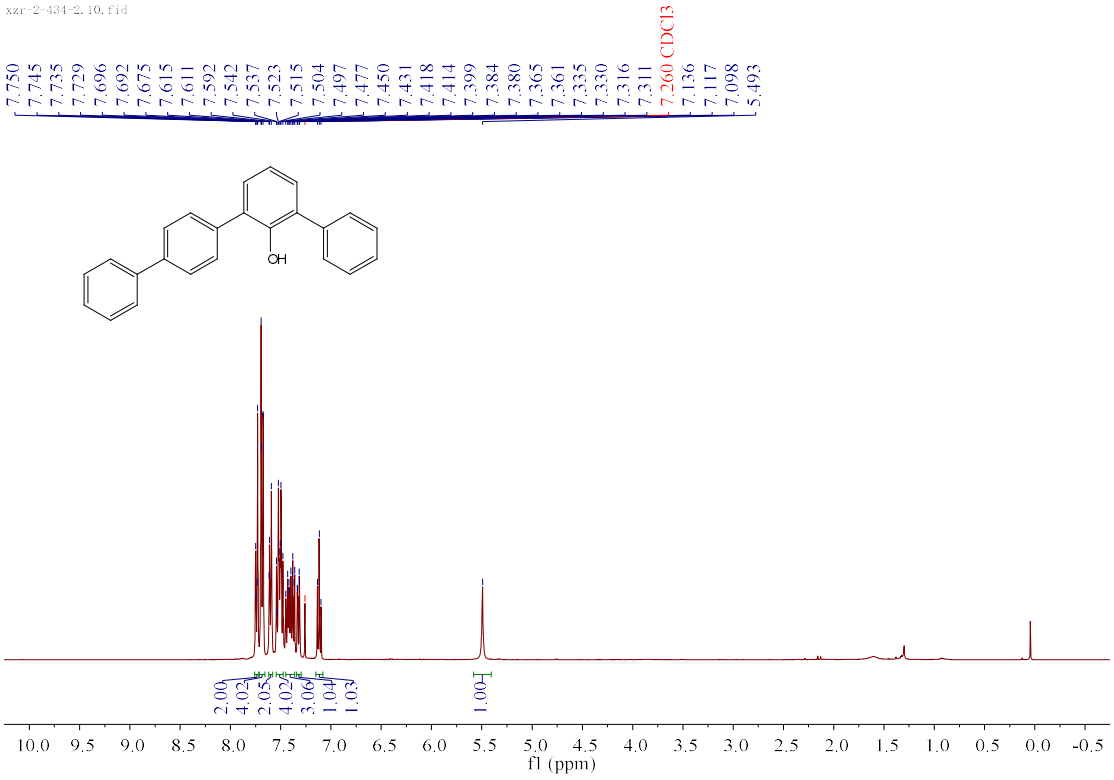
400 MHz ^{1}H NMR Spectrum of 2c in $CDCl_3$



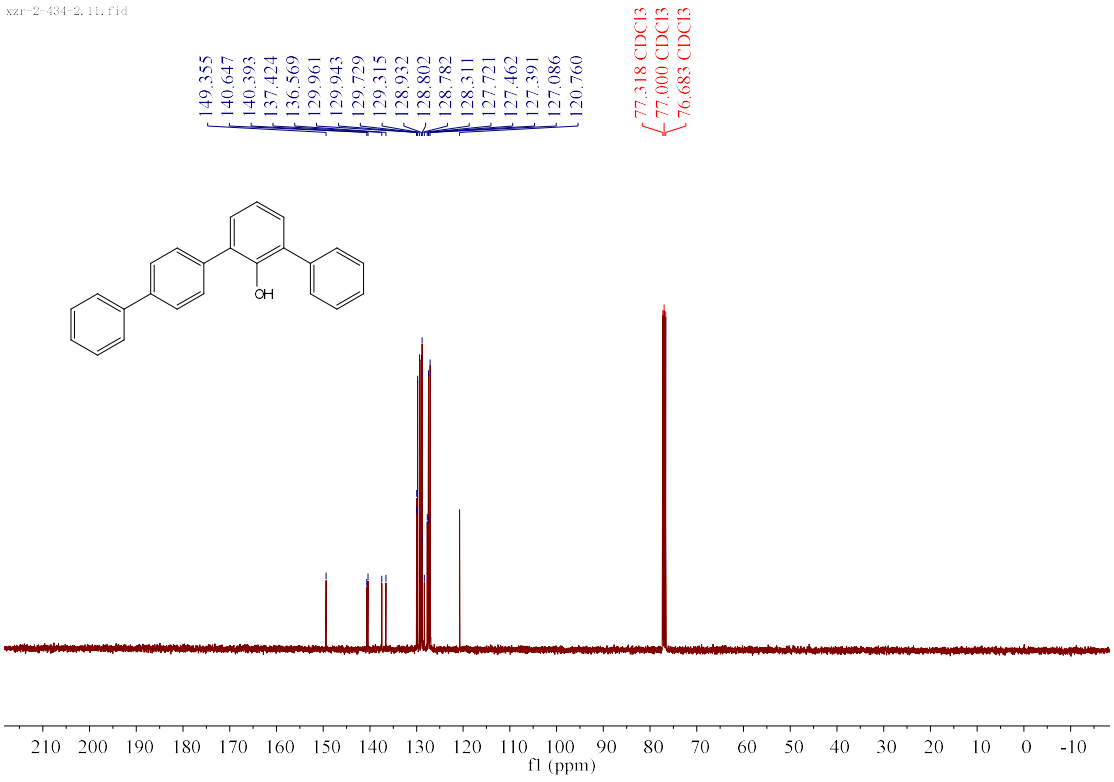
100 MHz ^{13}C NMR Spectrum of 2c in $CDCl_3$



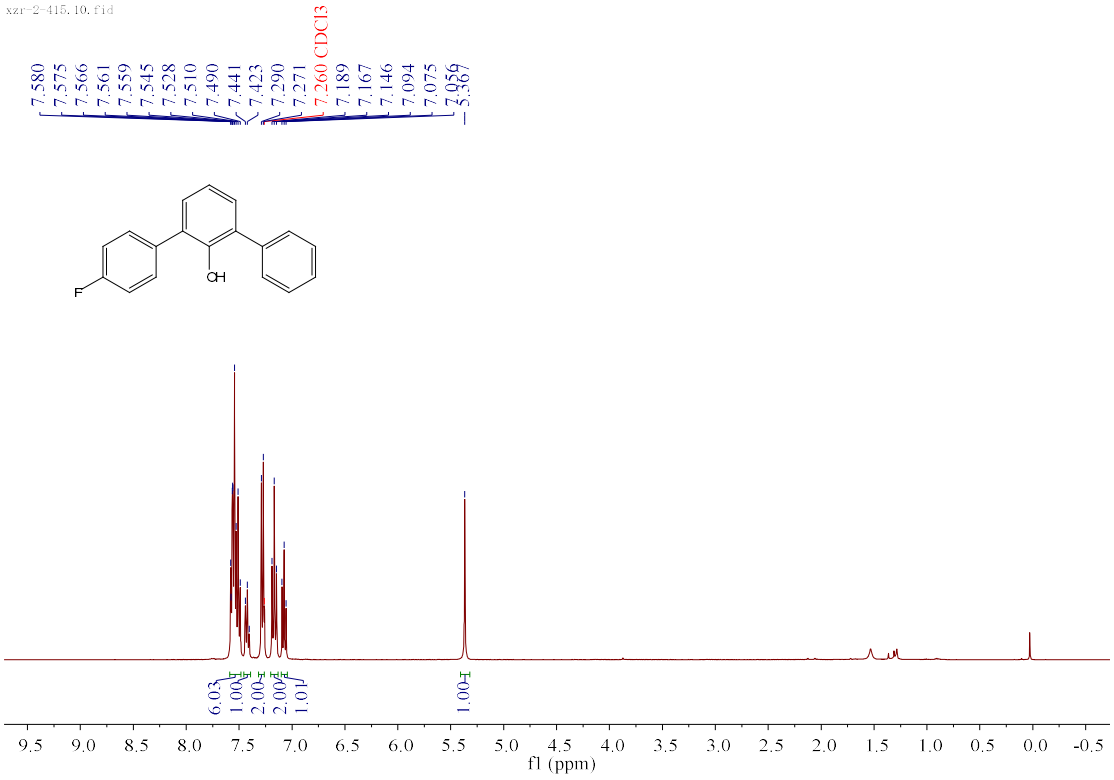
400 MHz ^{1}H NMR Spectrum of 2d in $CDCl_3$



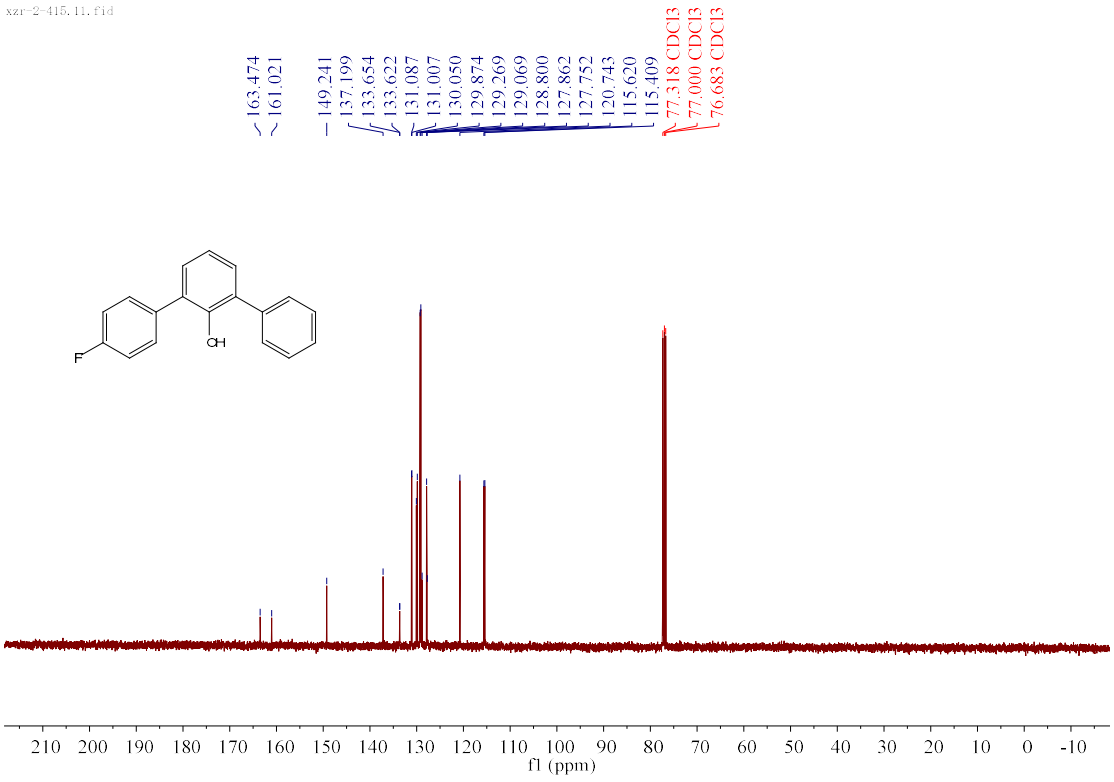
100 MHz ^{13}C NMR Spectrum of 2d in $CDCl_3$



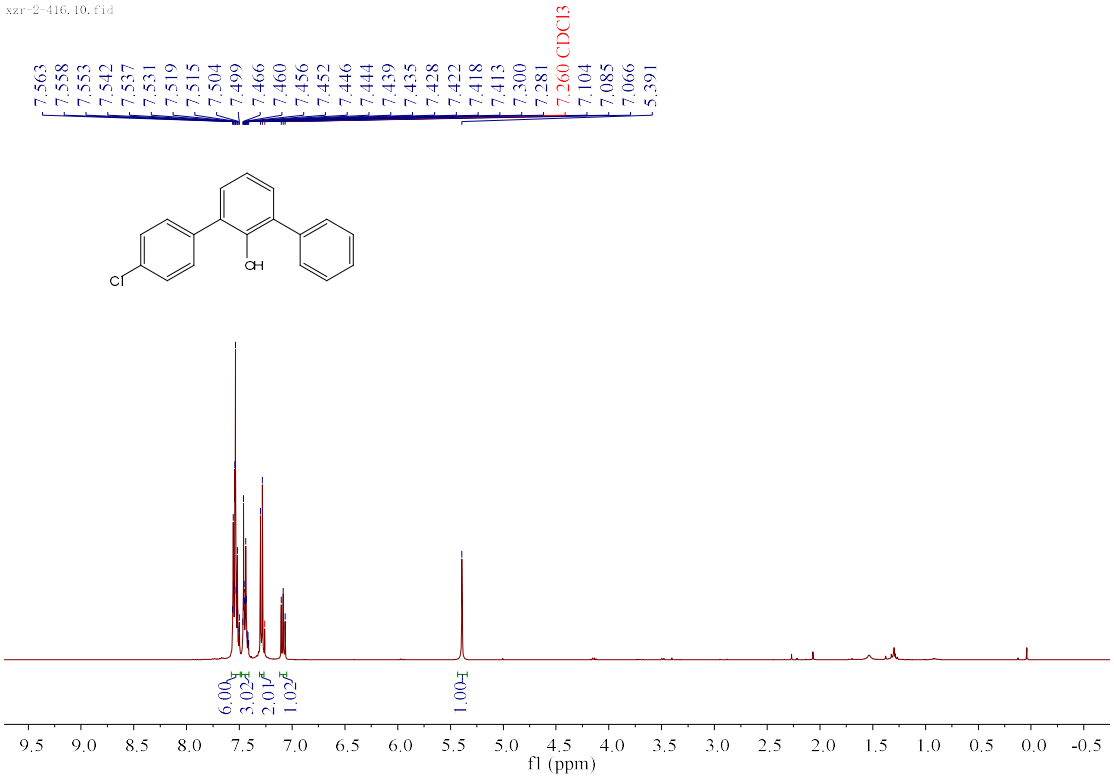
400 MHz ^{1}H NMR Spectrum of 2e in $CDCl_3$



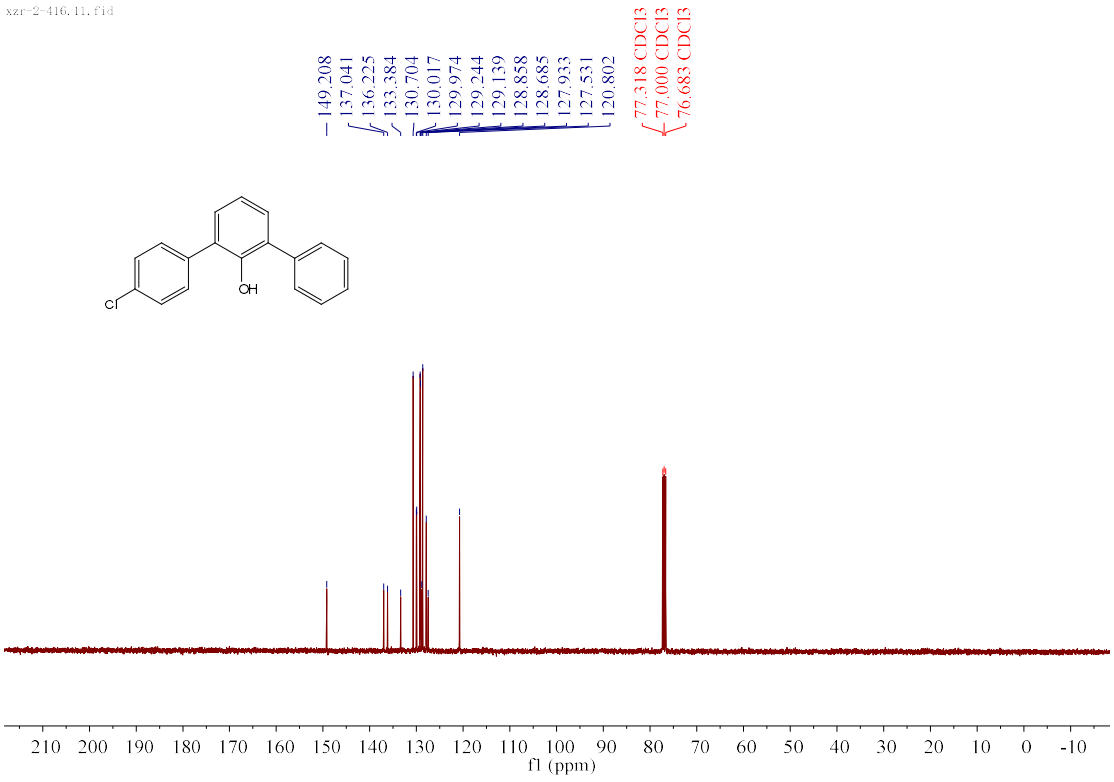
100 MHz ^{13}C NMR Spectrum of 2e in $CDCl_3$



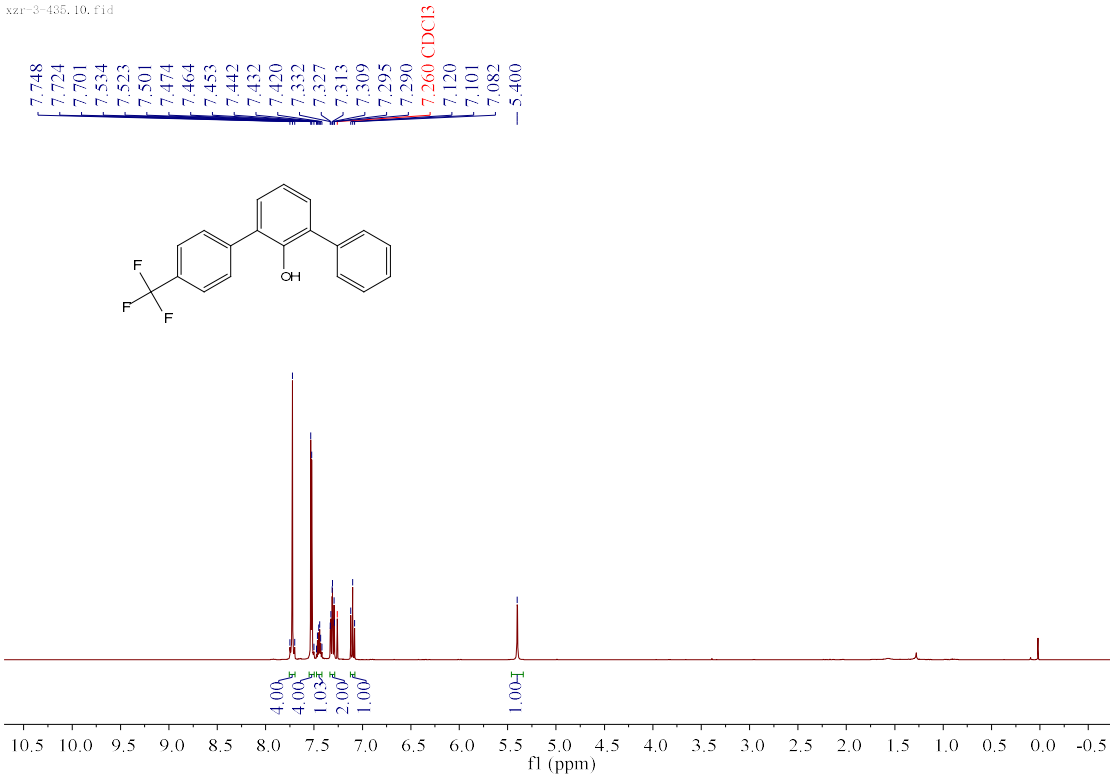
400 MHz ^{1}H NMR Spectrum of 2f in $CDCl_3$



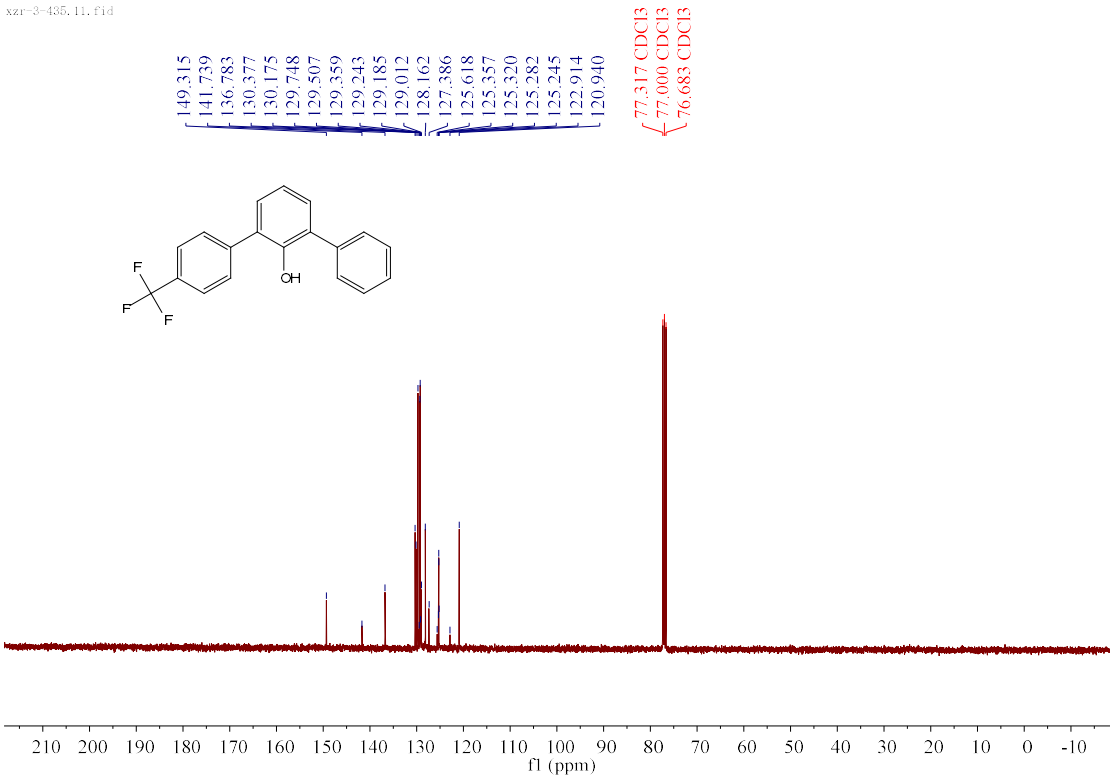
100 MHz ^{13}C NMR Spectrum of 2f in $CDCl_3$



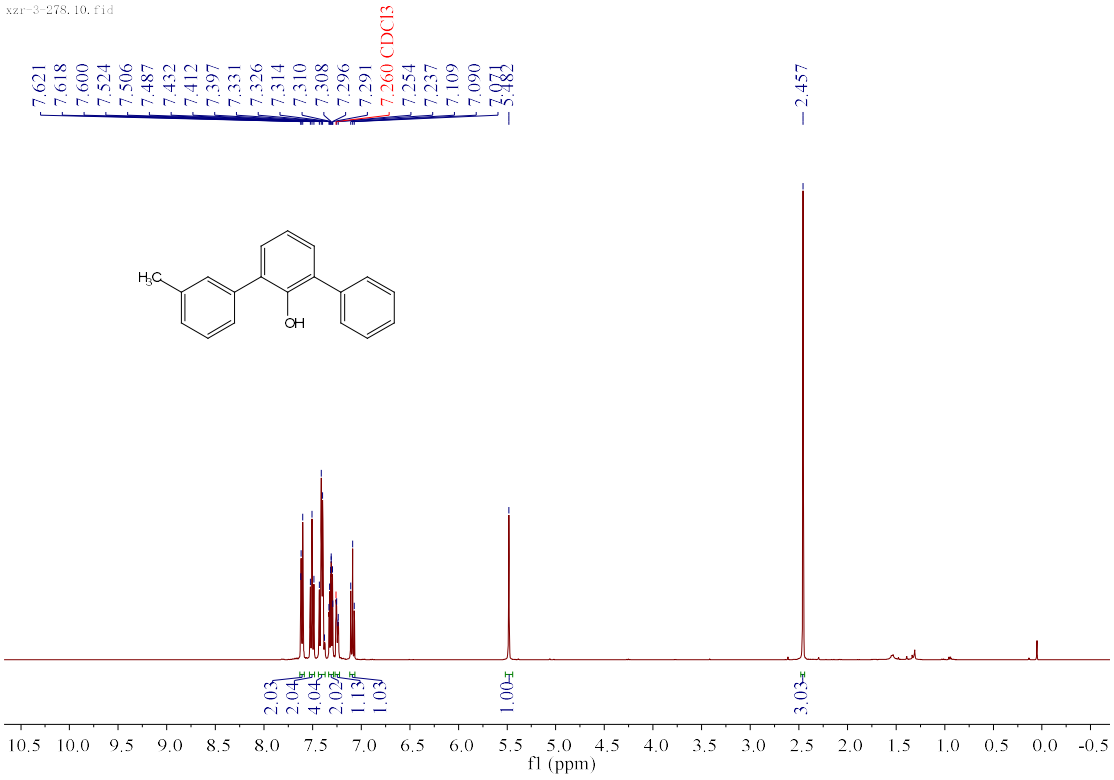
400 MHz ^{1}H NMR Spectrum of 2g in $CDCl_3$



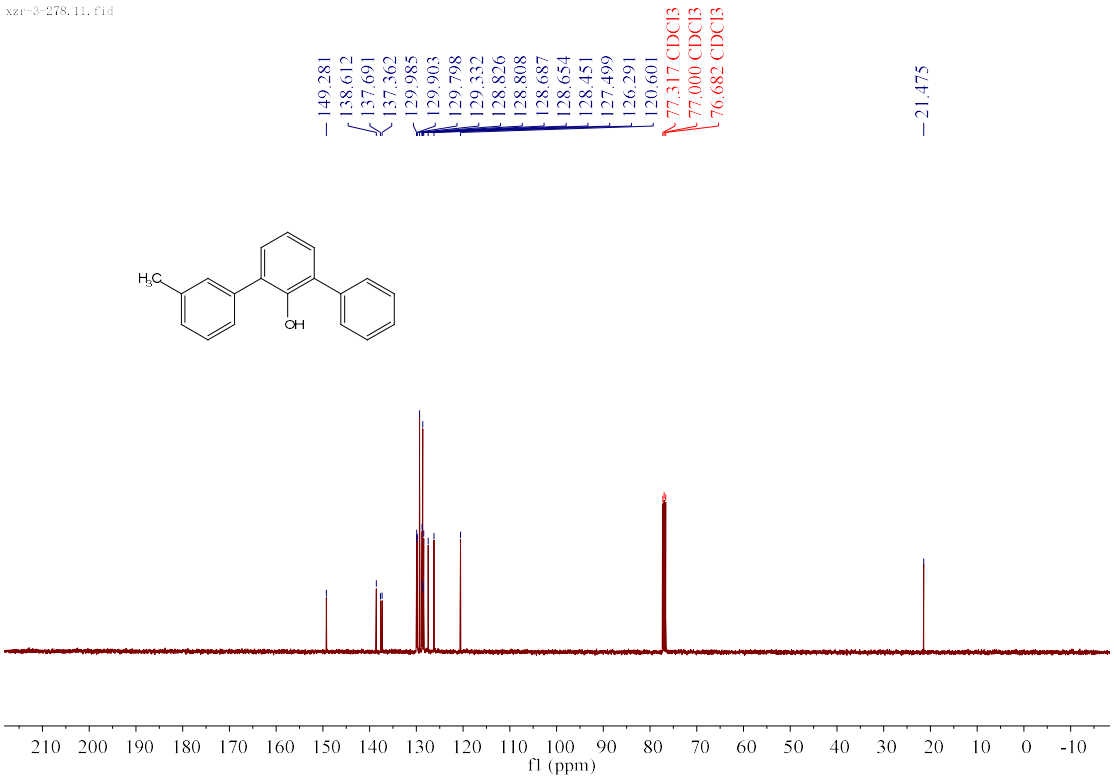
100 MHz ^{13}C NMR Spectrum of 2g in $CDCl_3$



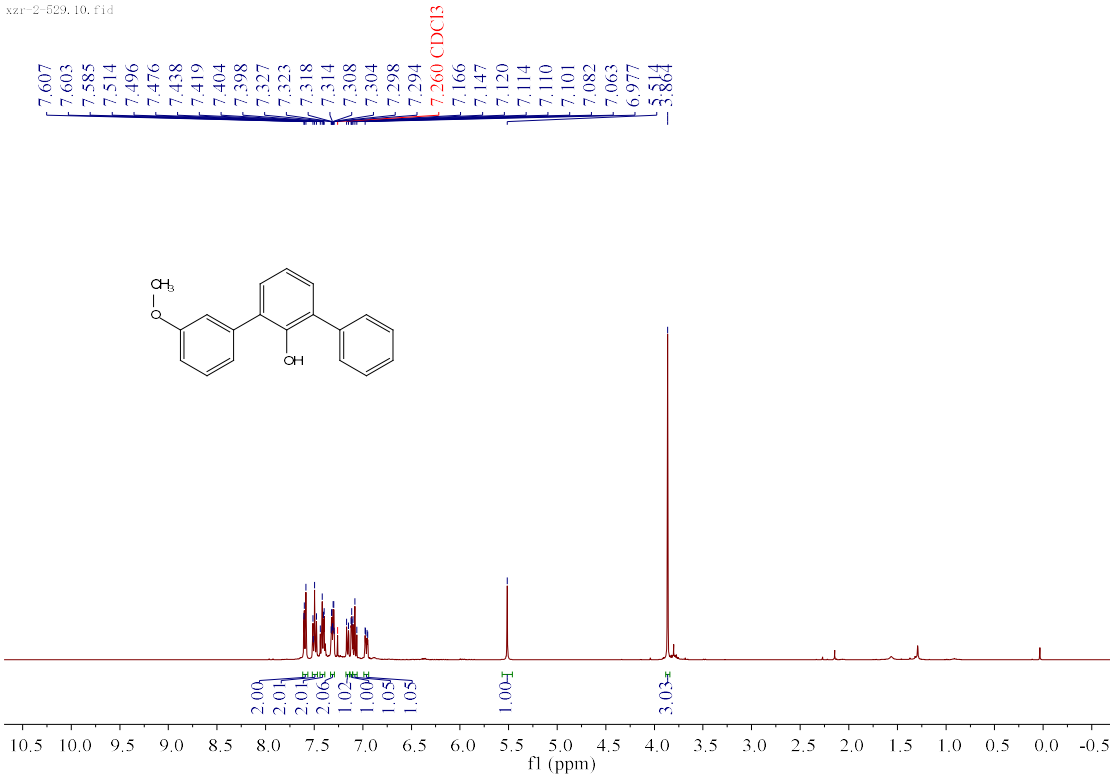
400 MHz ^{1}H NMR Spectrum of 2h in $CDCl_3$



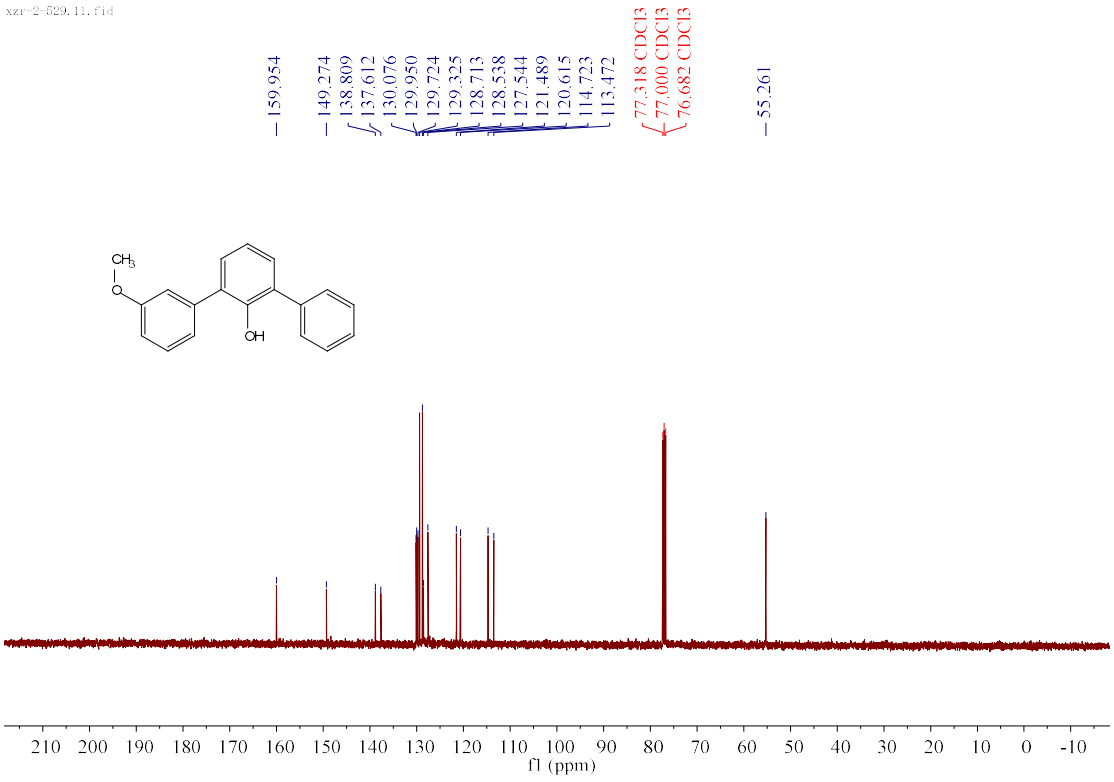
100 MHz ^{13}C NMR Spectrum of 2h in $CDCl_3$



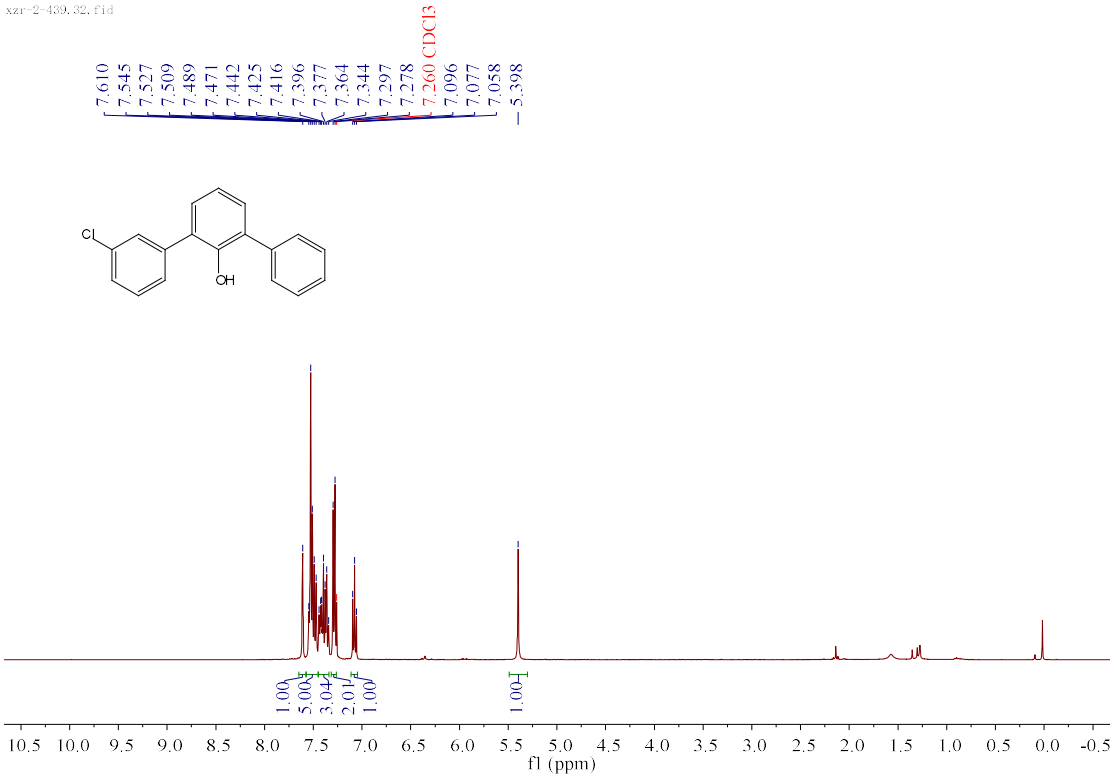
400 MHz ^{1}H NMR Spectrum of 2i in $CDCl_3$



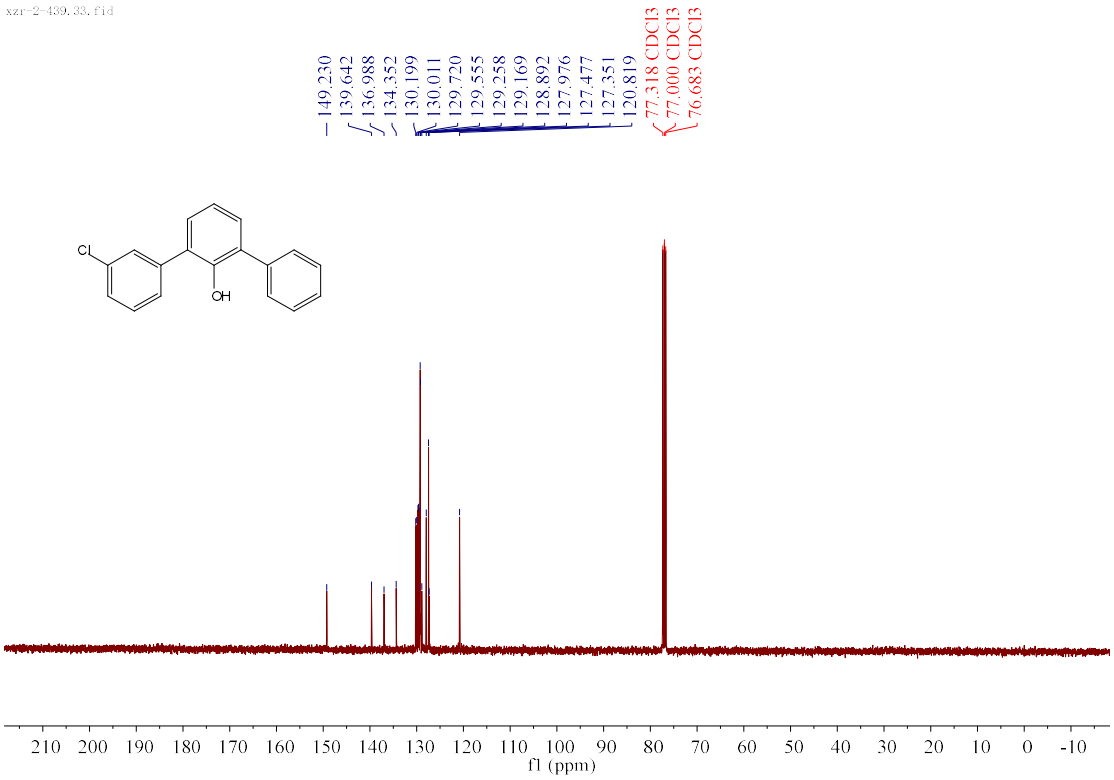
100 MHz ^{13}C NMR Spectrum of 2i in $CDCl_3$



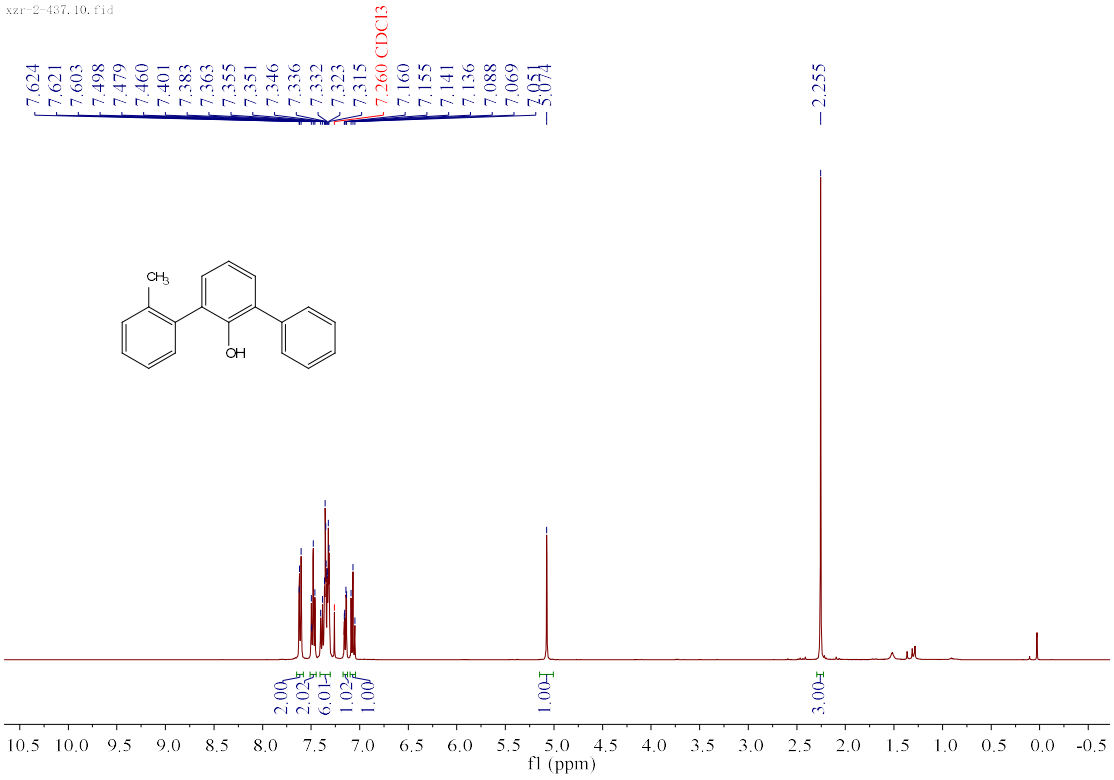
400 MHz ^{1}H NMR Spectrum of 2j in $CDCl_3$



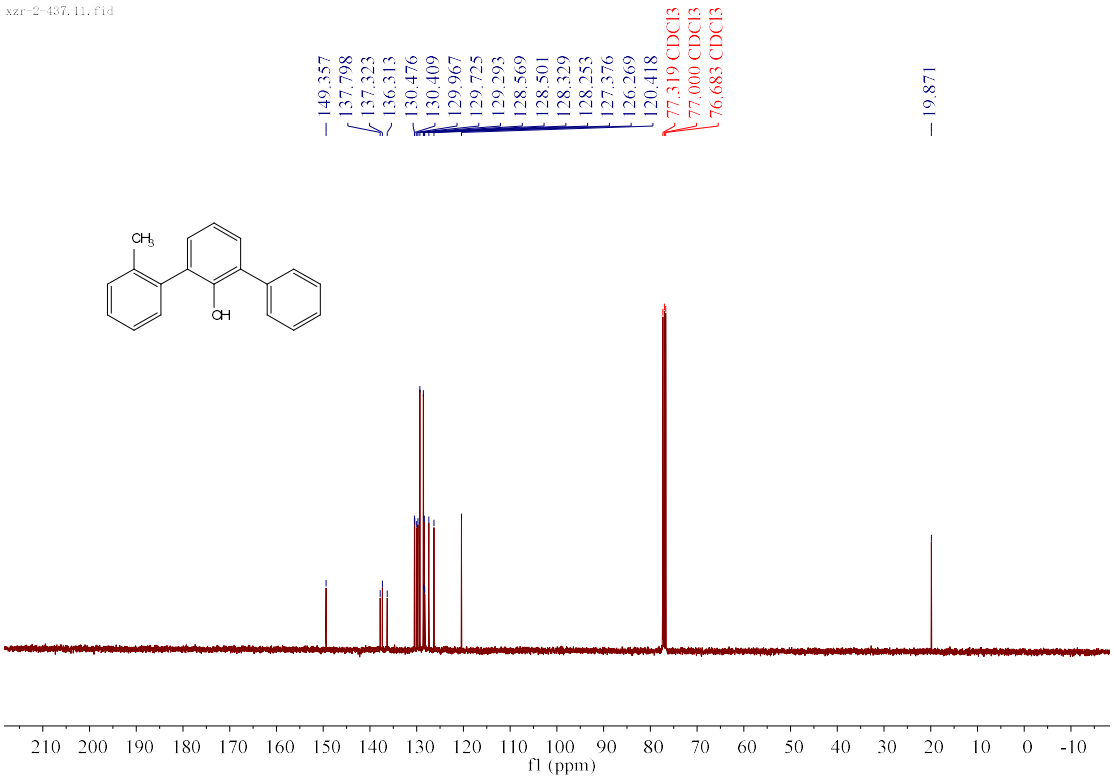
100 MHz ^{13}C NMR Spectrum of 2j in $CDCl_3$



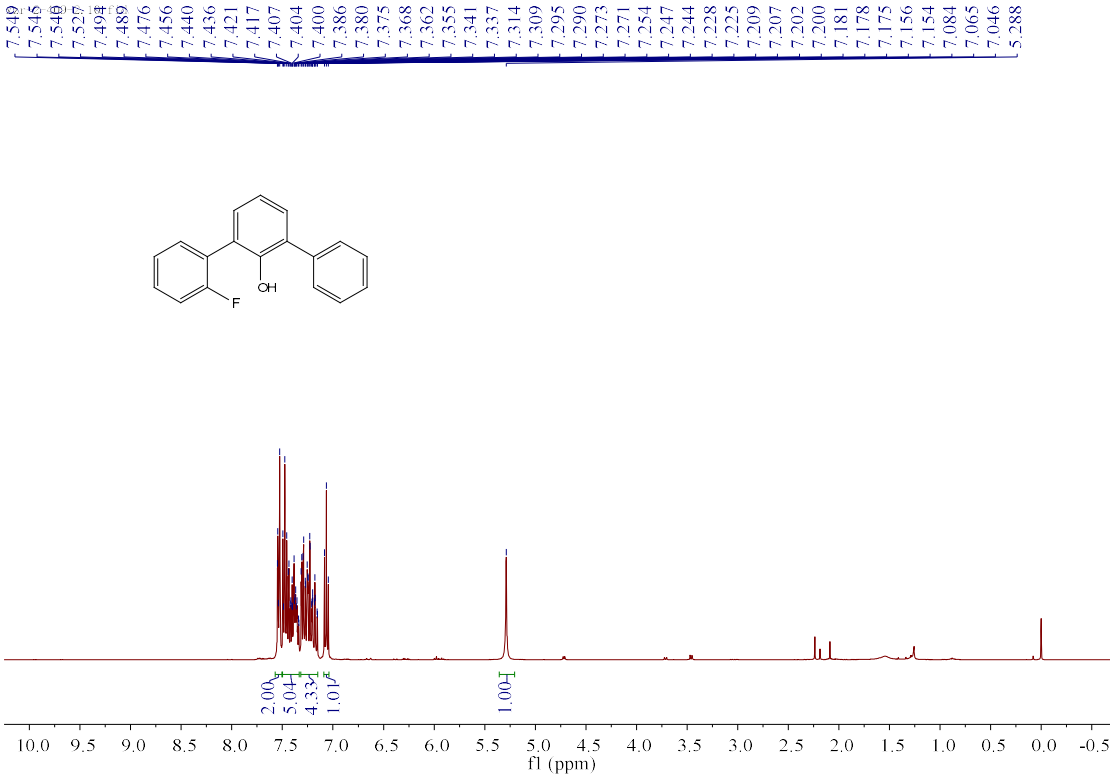
400 MHz ^{1}H NMR Spectrum of 2k in $CDCl_3$



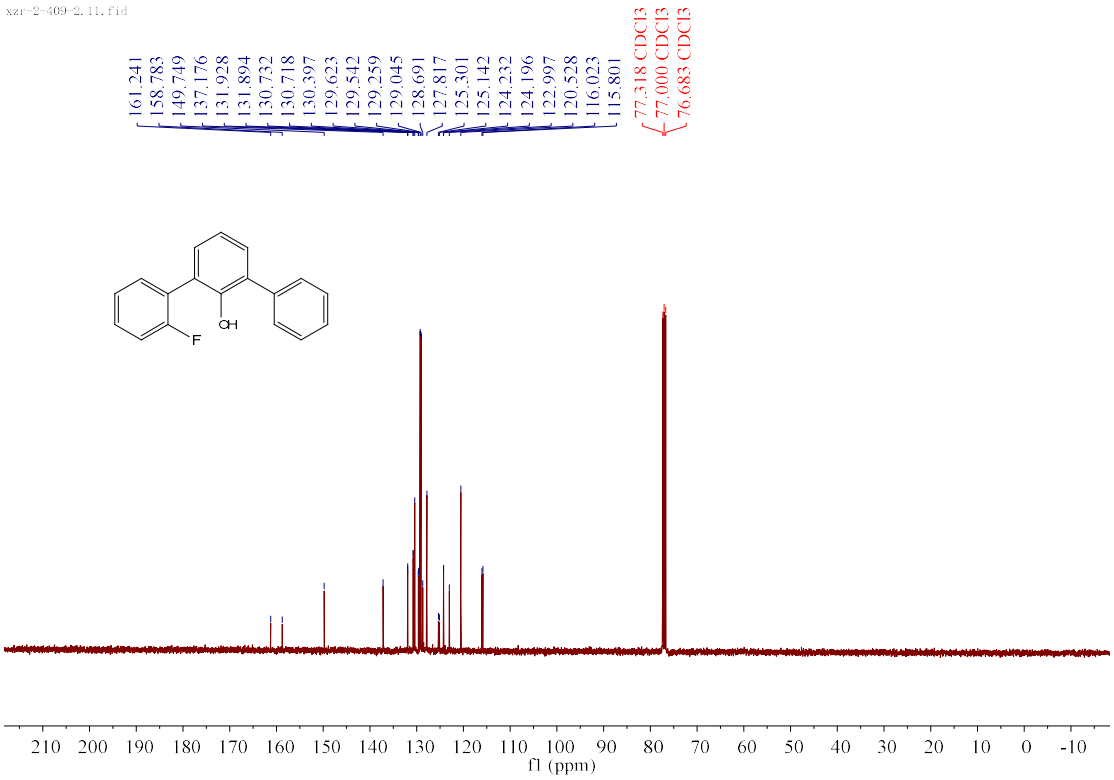
100 MHz ^{13}C NMR Spectrum of 2k in $CDCl_3$



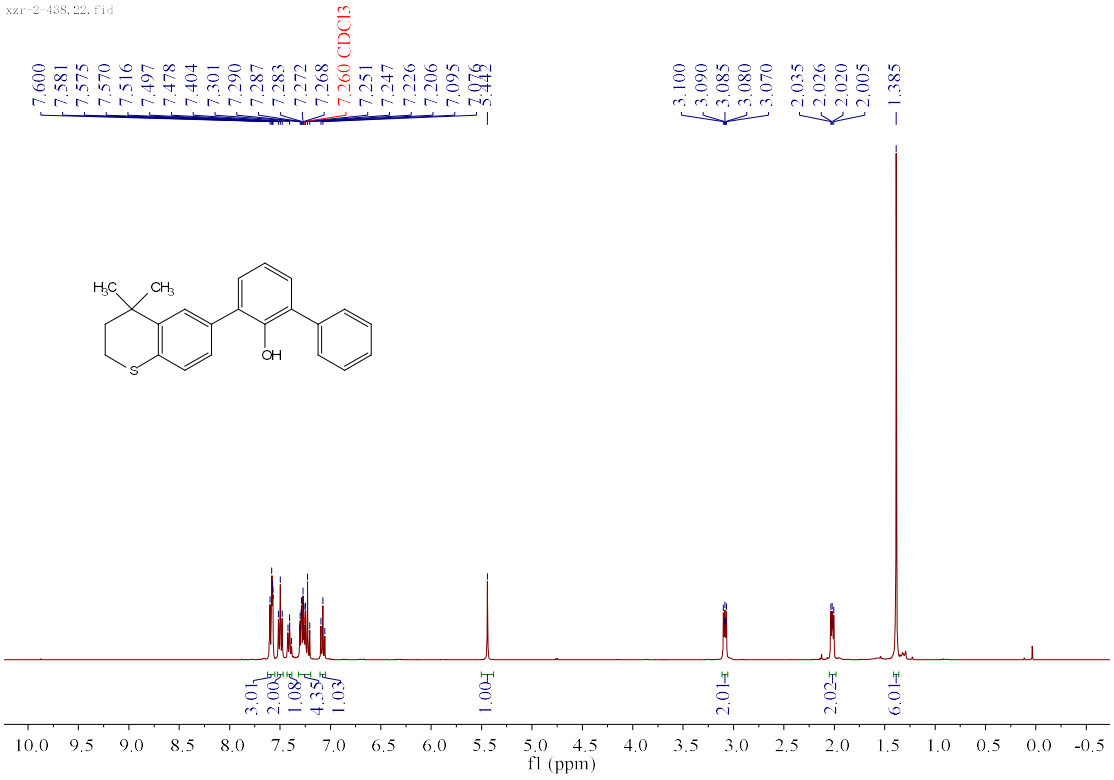
400 MHz ^{1}H NMR Spectrum of 2l in $CDCl_3$



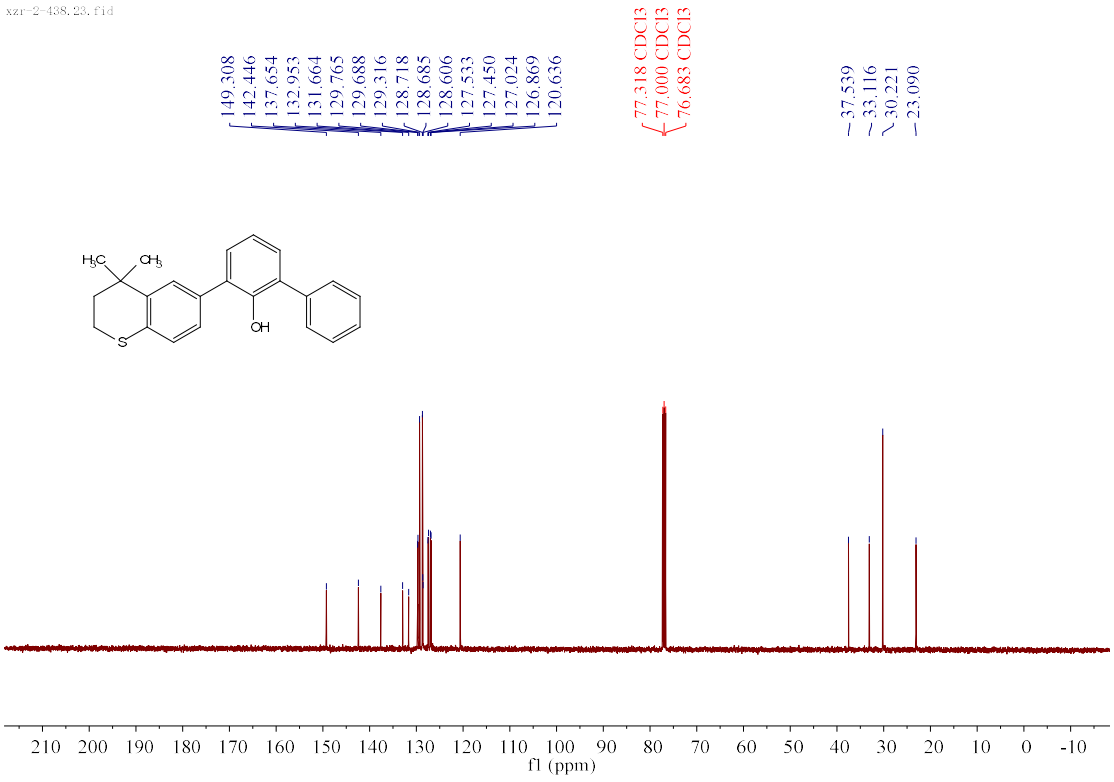
100 MHz ^{13}C NMR Spectrum of 2l in $CDCl_3$



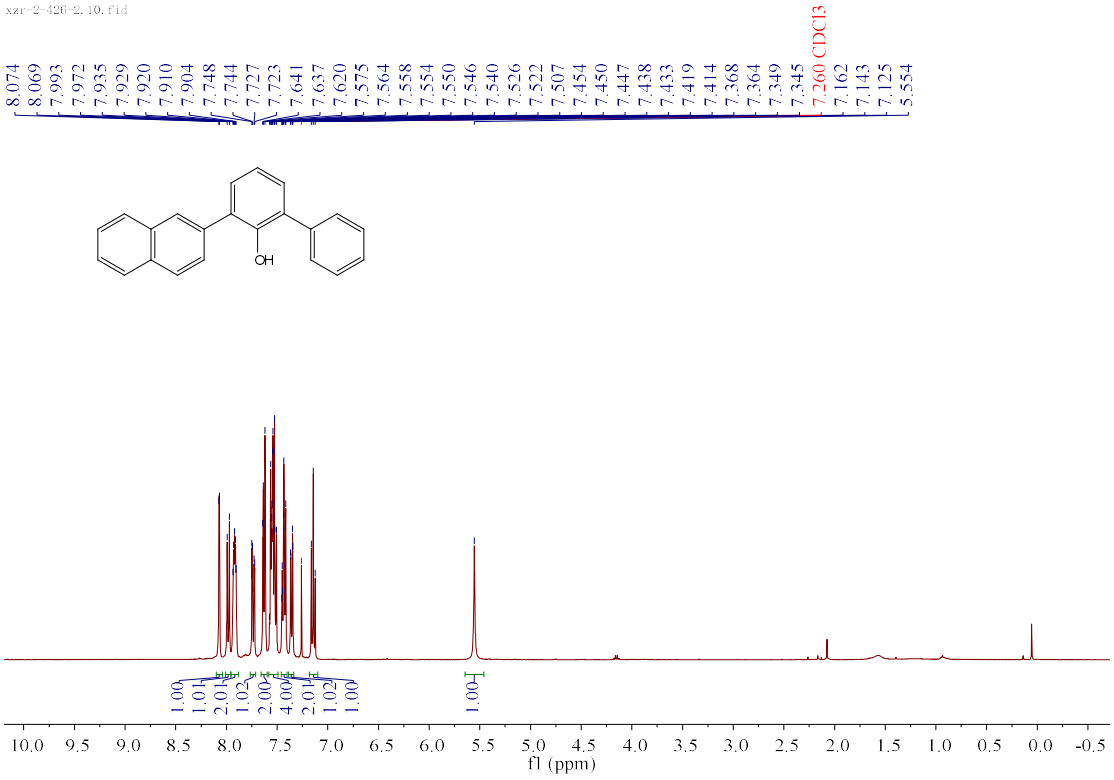
400 MHz ^{1}H NMR Spectrum of 2m in $CDCl_3$



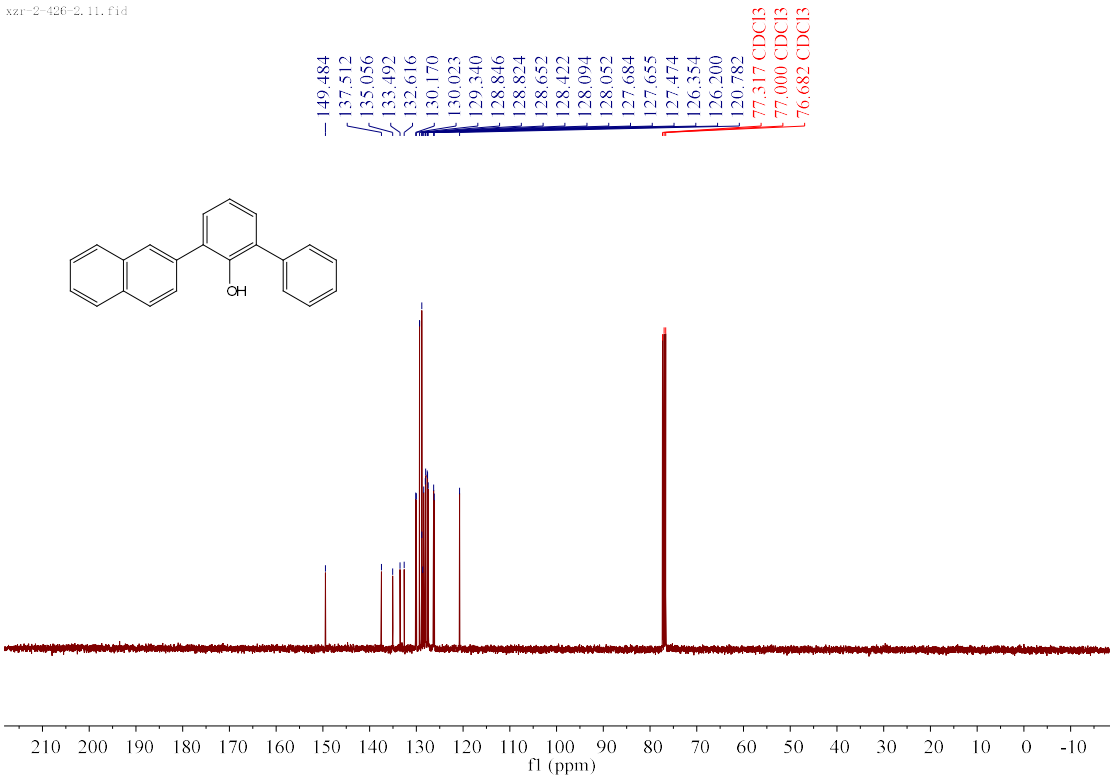
100 MHz ^{13}C NMR Spectrum of 2m in $CDCl_3$



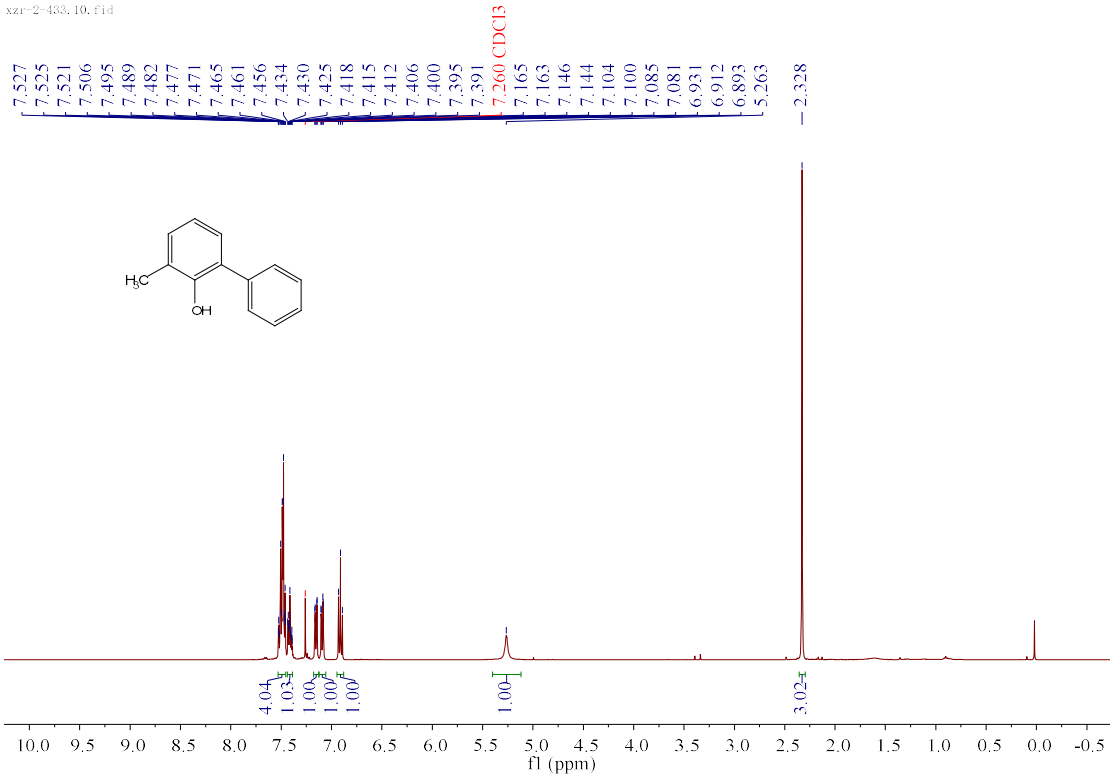
400 MHz ^{1}H NMR Spectrum of 2n in $CDCl_3$



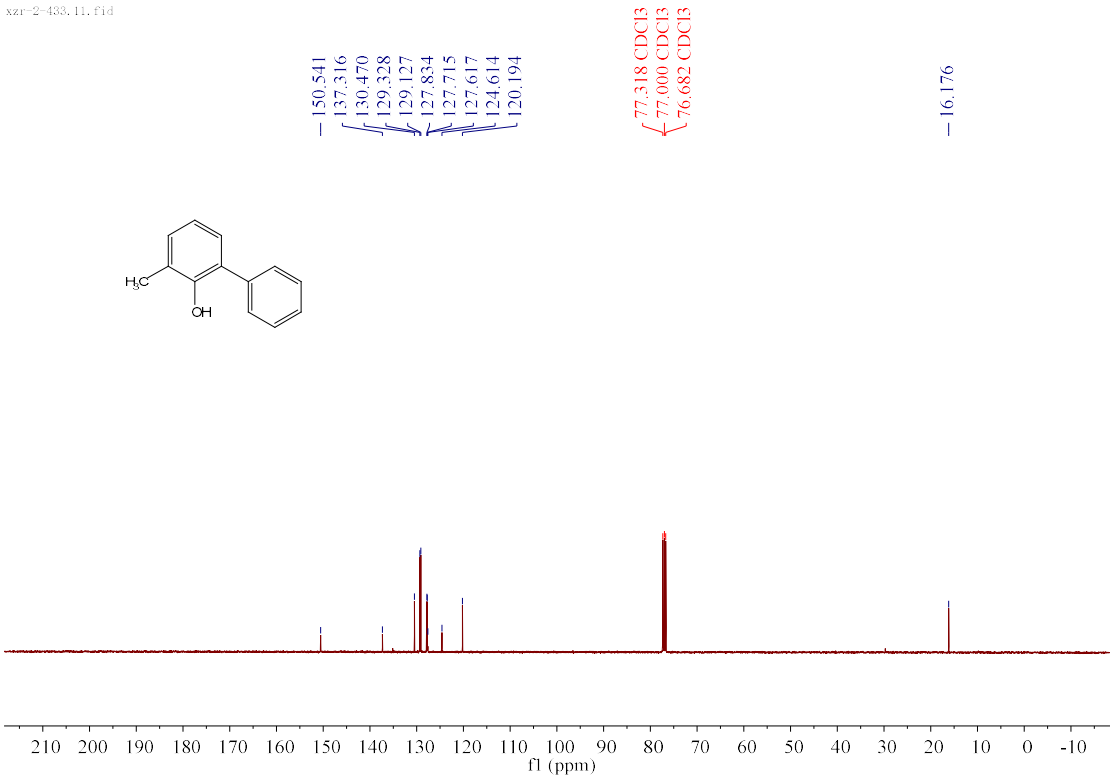
100 MHz ^{13}C NMR Spectrum of 2n in $CDCl_3$



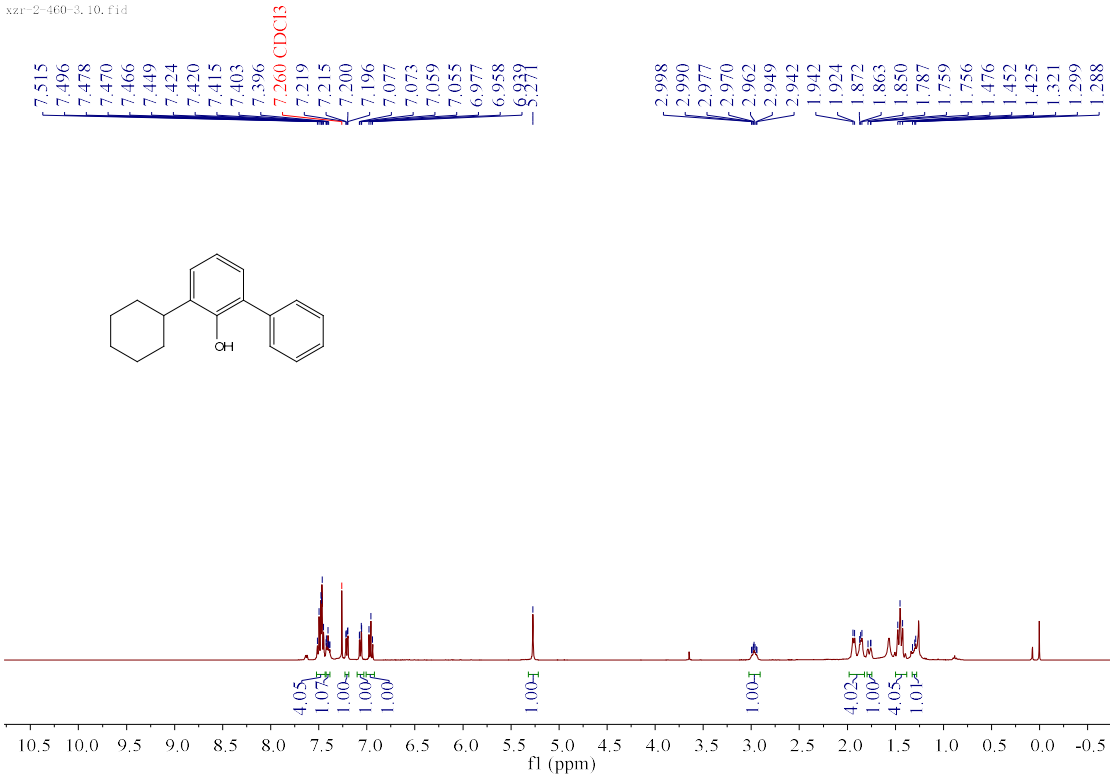
400 MHz ^{1}H NMR Spectrum of 2o in $CDCl_3$



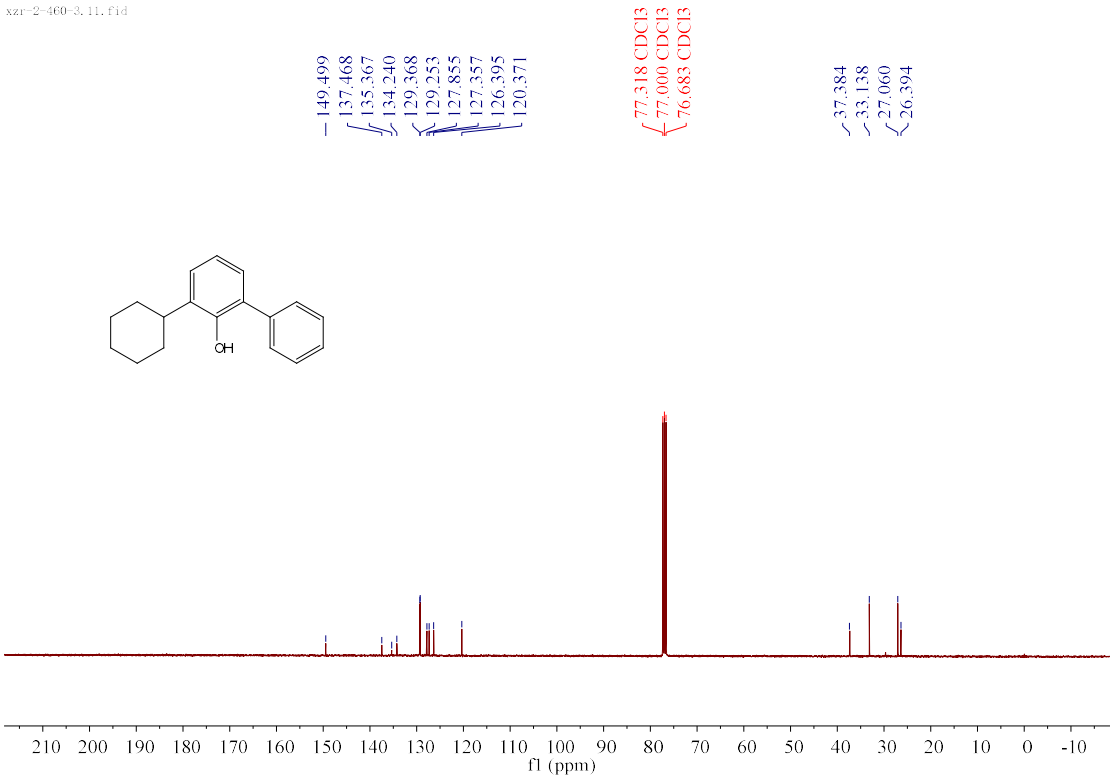
100 MHz ^{13}C NMR Spectrum of 2o in $CDCl_3$



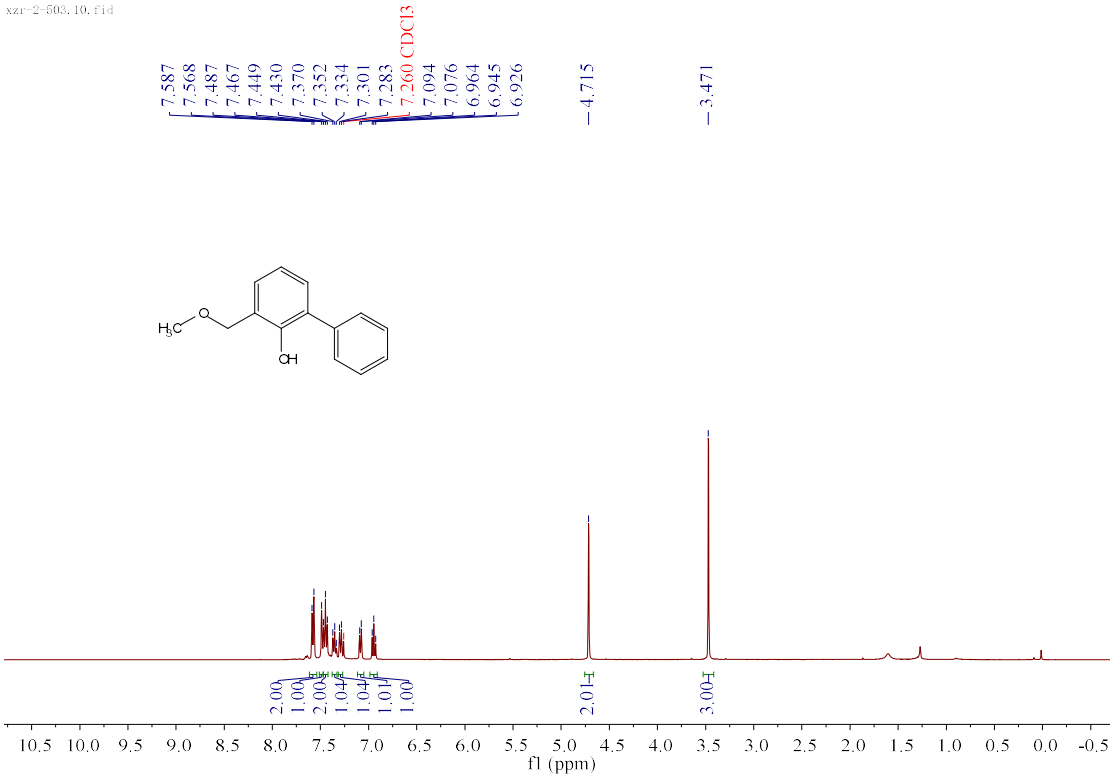
400 MHz ^{1}H NMR Spectrum of 2p in $CDCl_3$



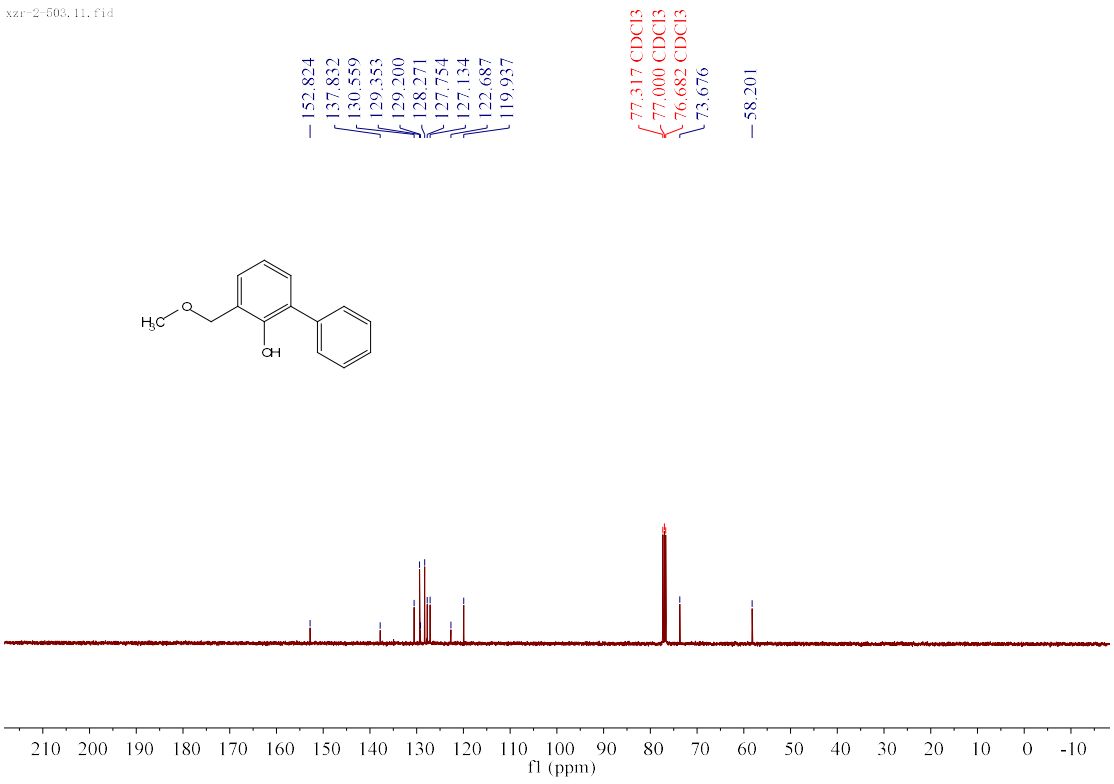
100 MHz ^{13}C NMR Spectrum of 2p in $CDCl_3$



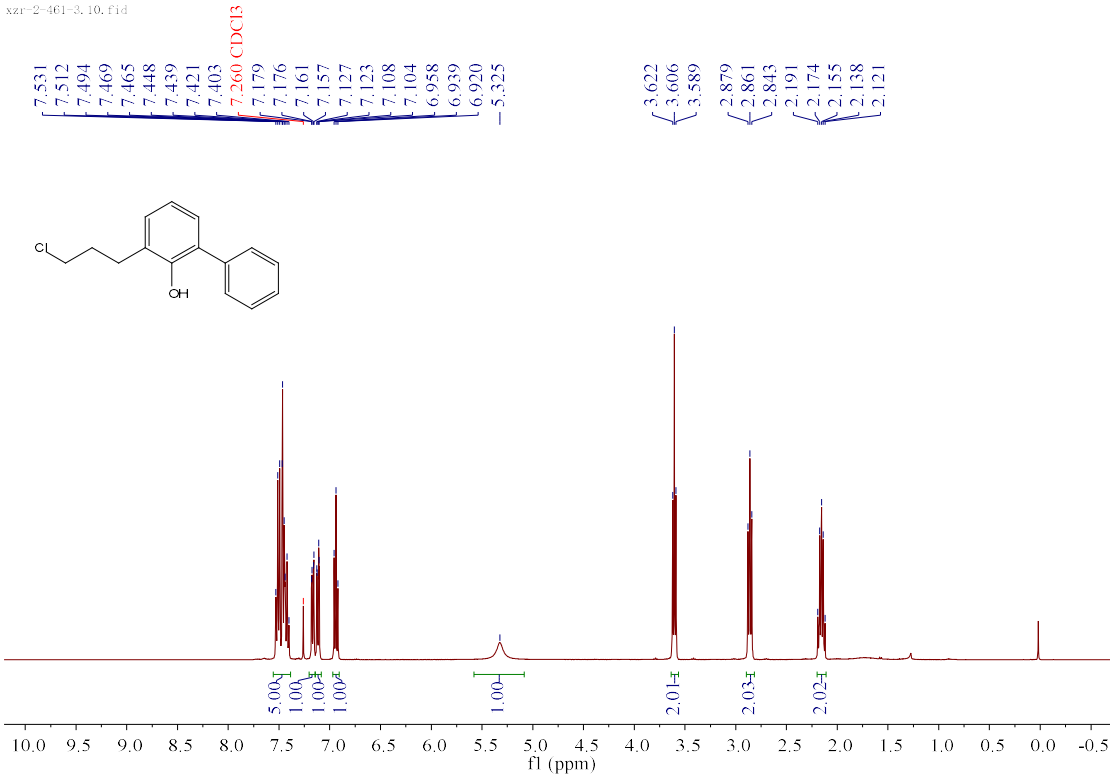
400 MHz ^{1}H NMR Spectrum of 2q in $CDCl_3$



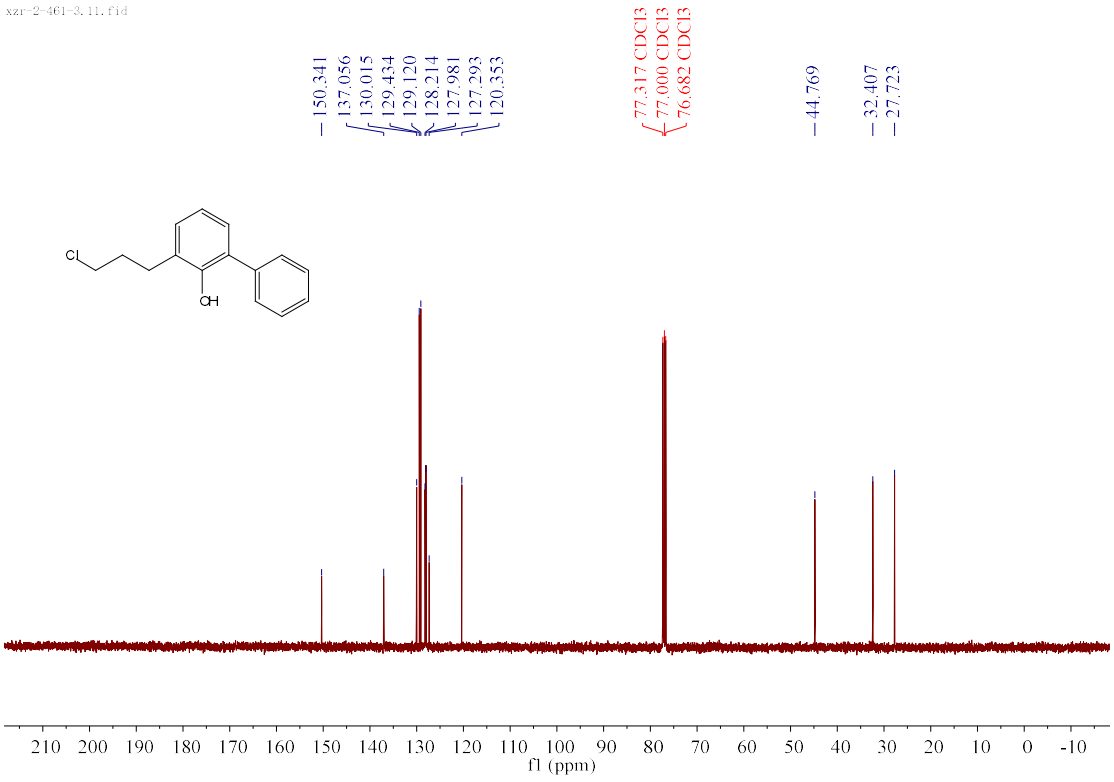
100 MHz ^{13}C NMR Spectrum of 2q in $CDCl_3$



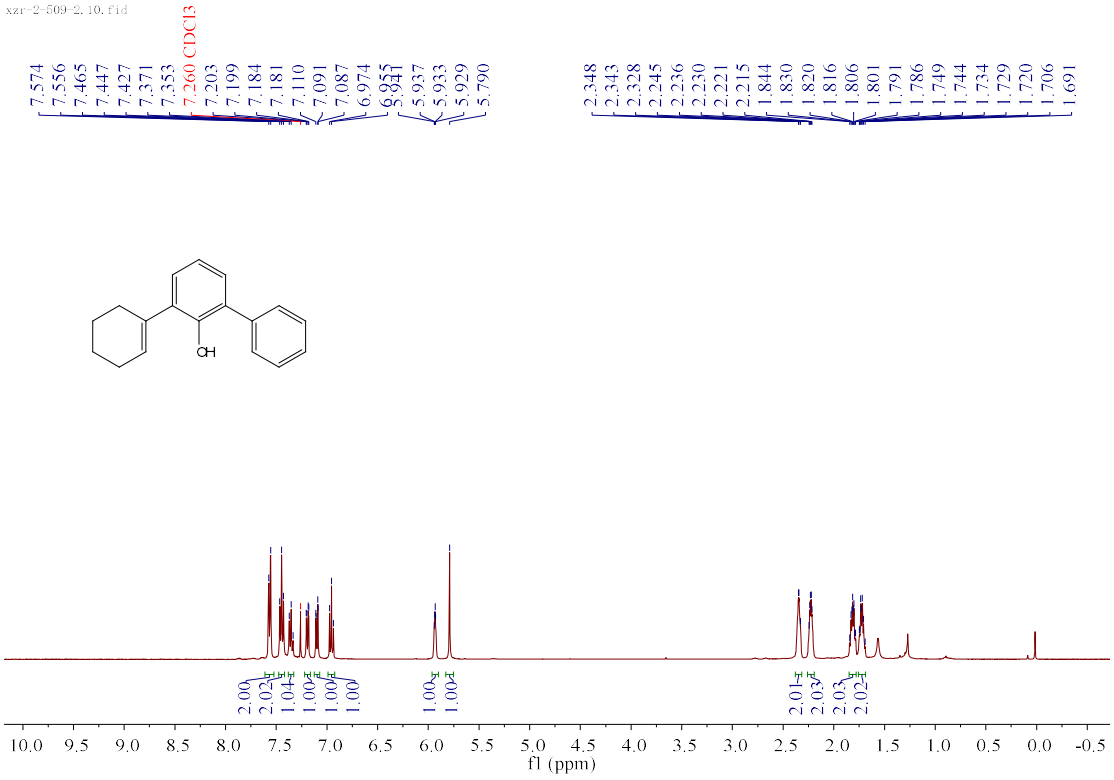
400 MHz ^{1}H NMR Spectrum of 2r in $CDCl_3$



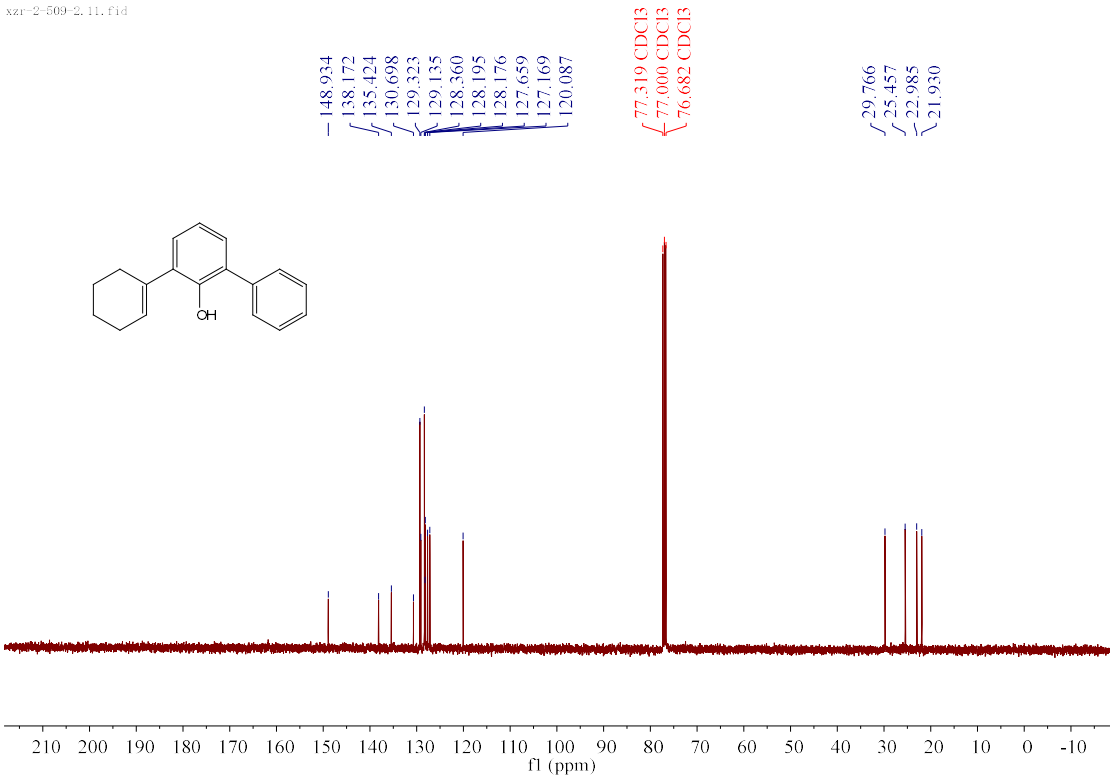
100 MHz ^{13}C NMR Spectrum of 2r in $CDCl_3$



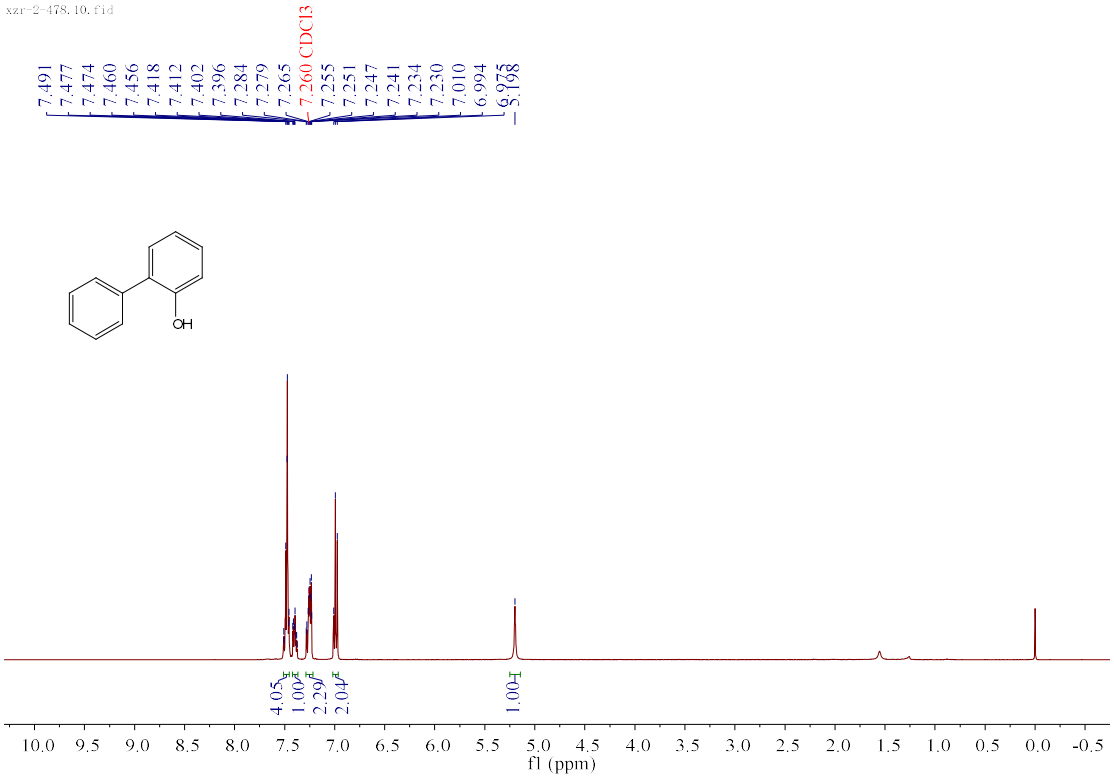
400 MHz ^{1}H NMR Spectrum of 2s in $CDCl_3$



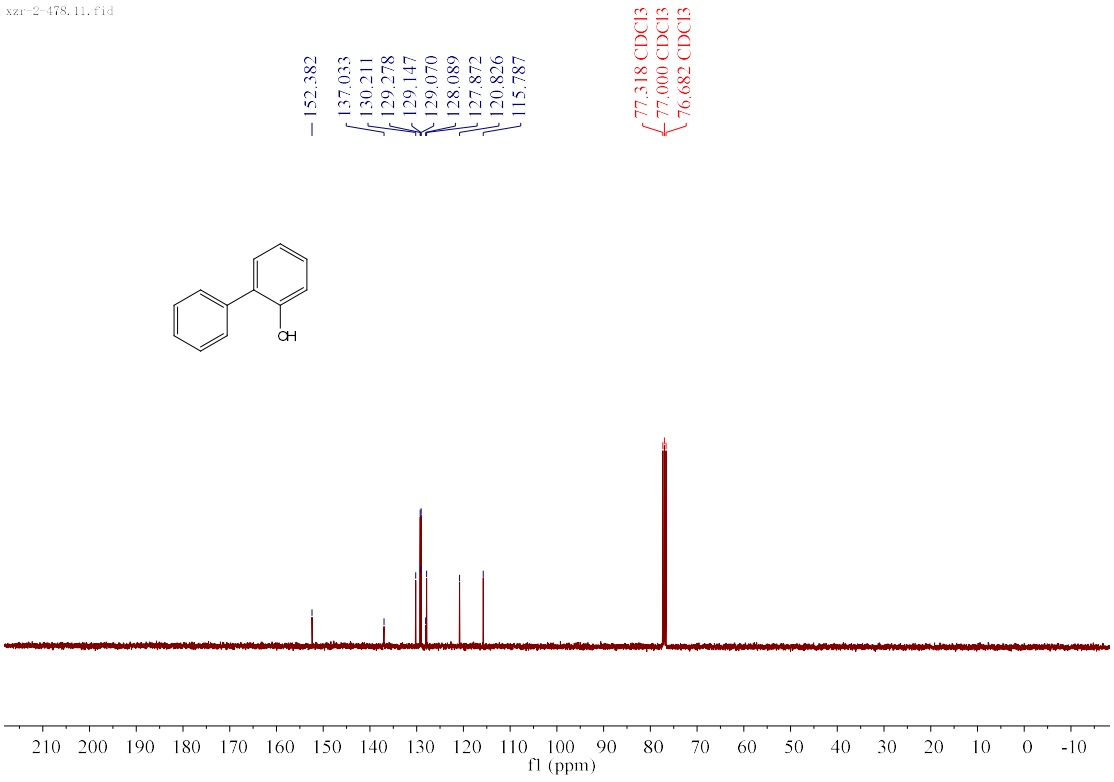
100 MHz ^{13}C NMR Spectrum of 2s in $CDCl_3$



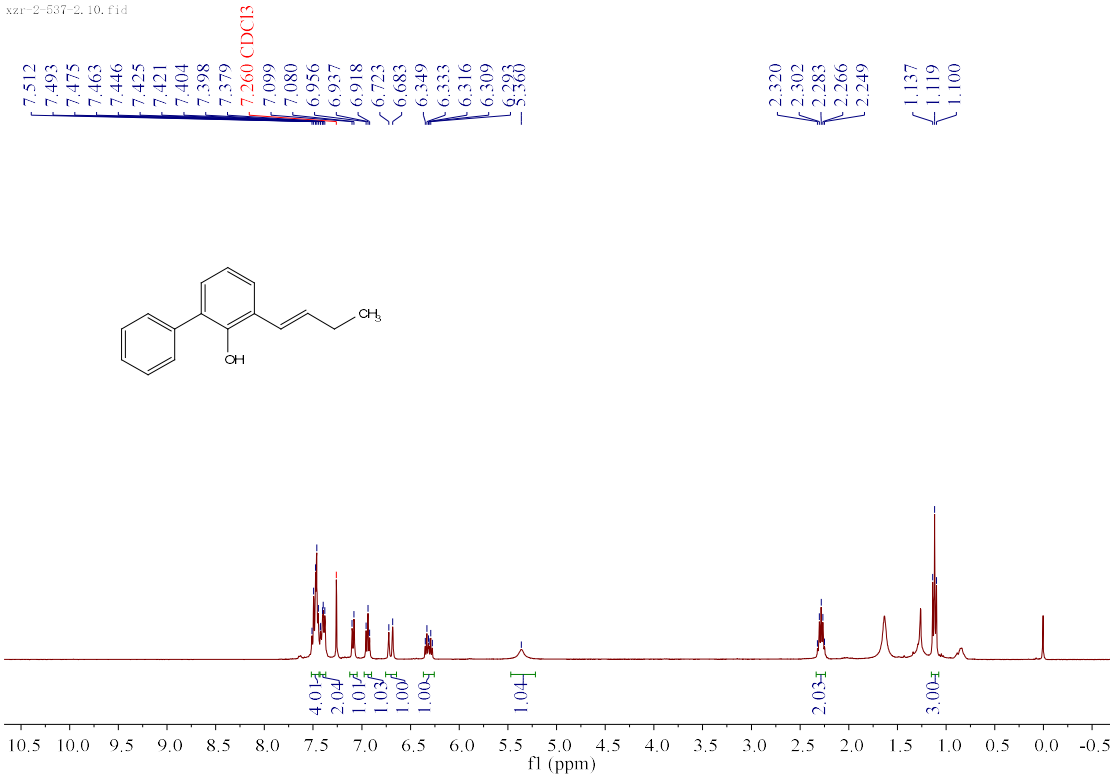
400 MHz ^{1}H NMR Spectrum of 2t in $CDCl_3$



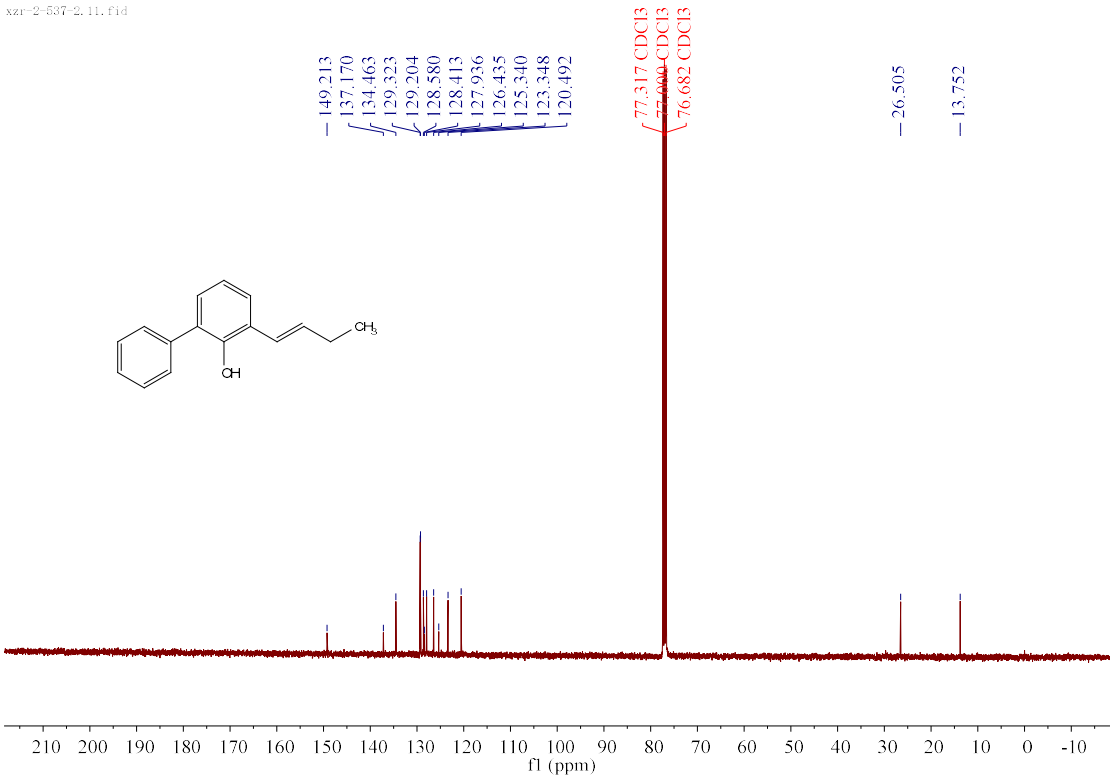
100 MHz ^{13}C NMR Spectrum of 2t in $CDCl_3$



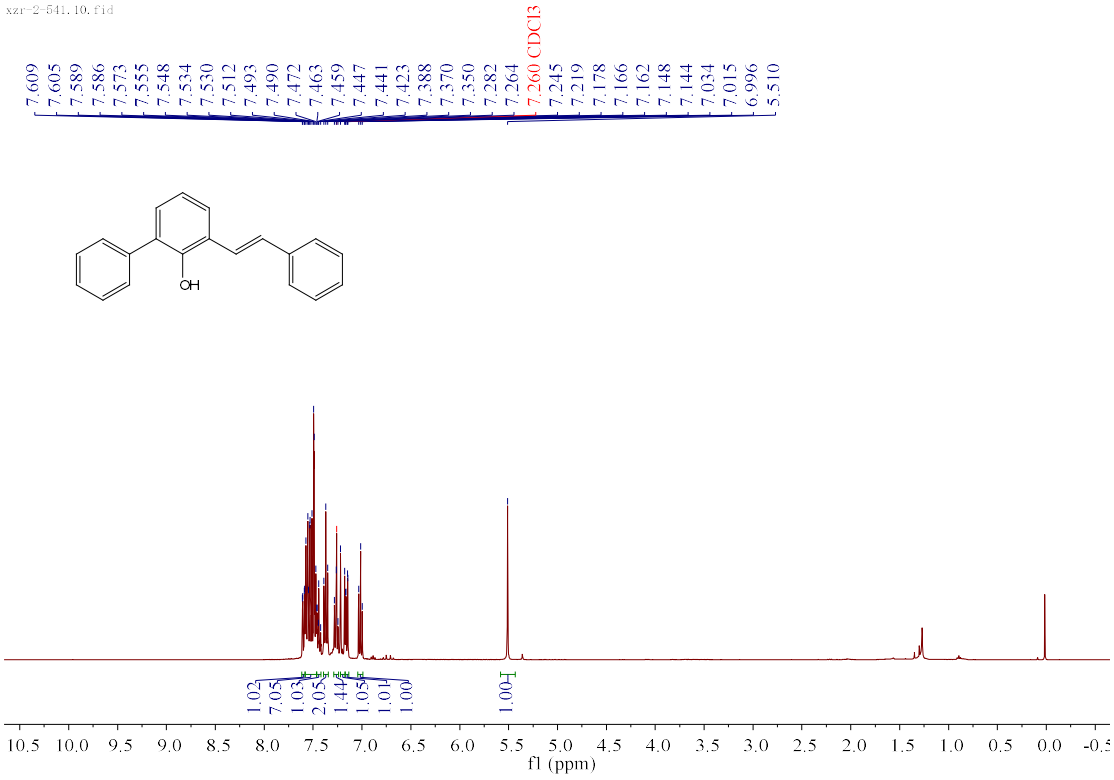
400 MHz ^{1}H NMR Spectrum of 2u in $CDCl_3$



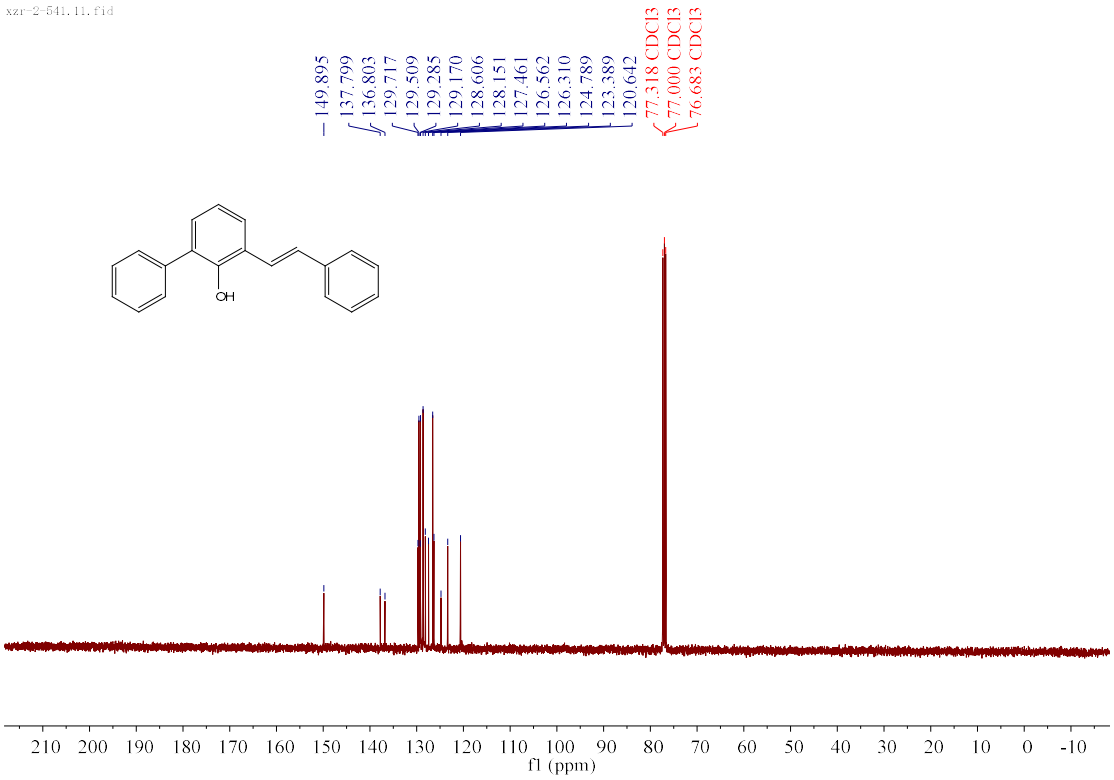
100 MHz ^{13}C NMR Spectrum of 2u in $CDCl_3$



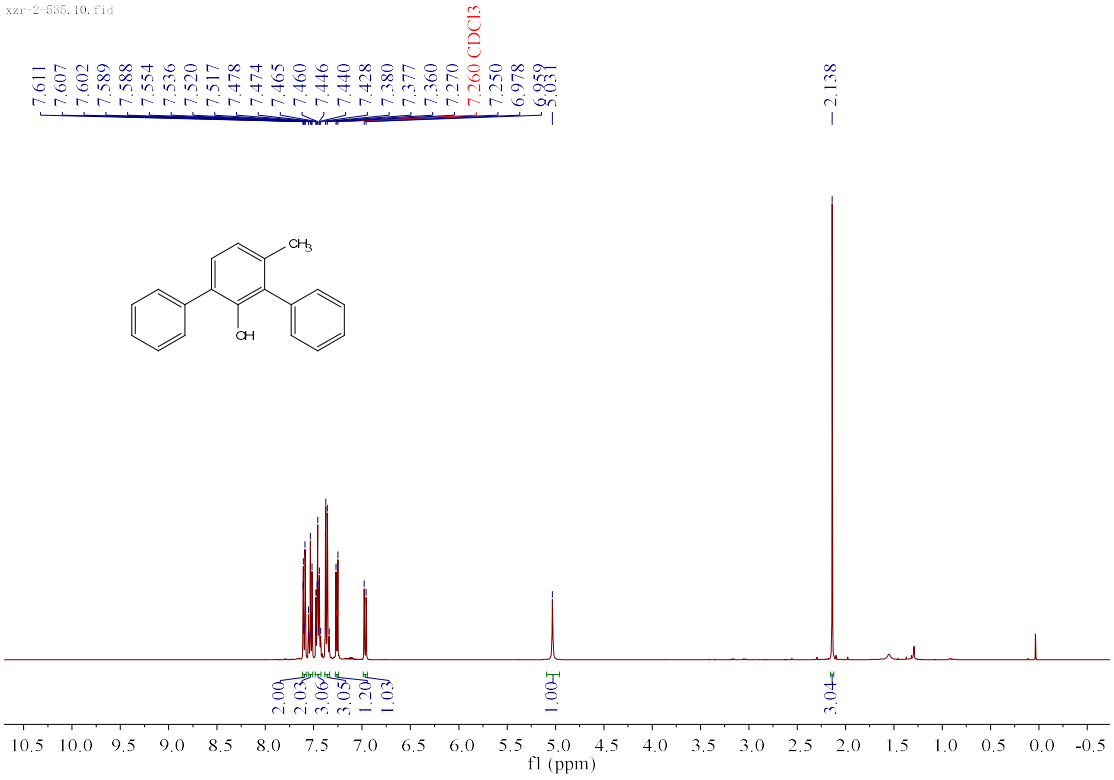
400 MHz ^{1}H NMR Spectrum of 2v in $CDCl_3$



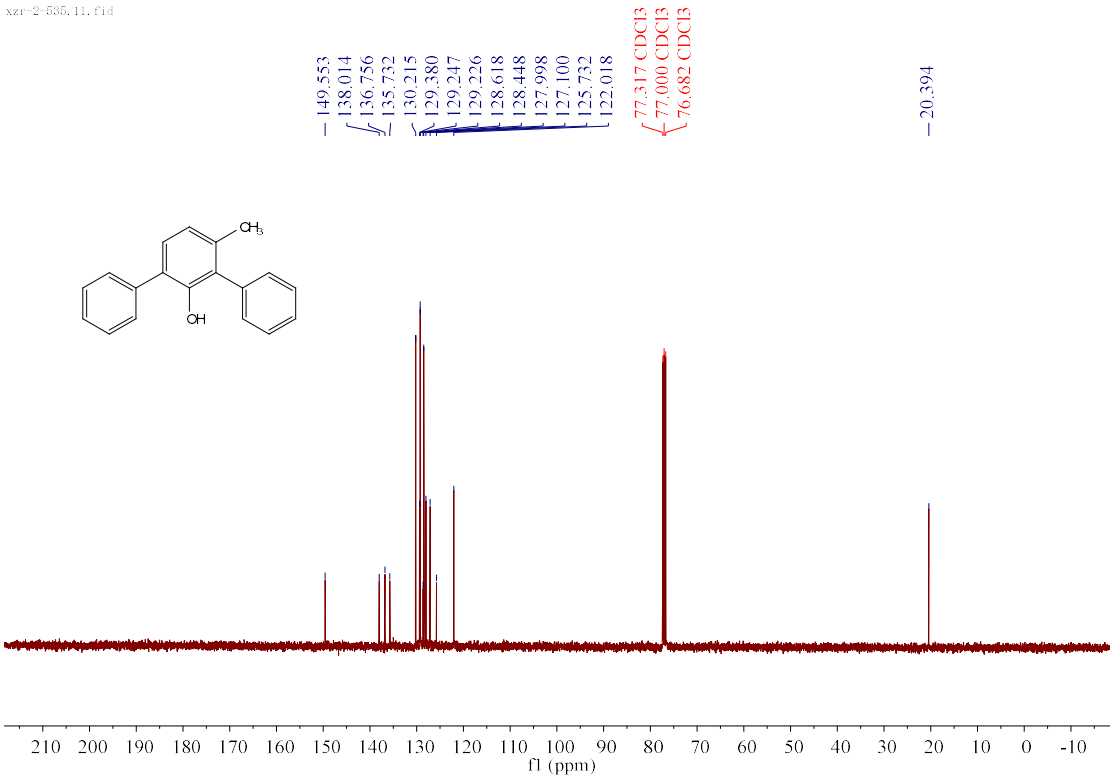
100 MHz ^{13}C NMR Spectrum of 2v in $CDCl_3$



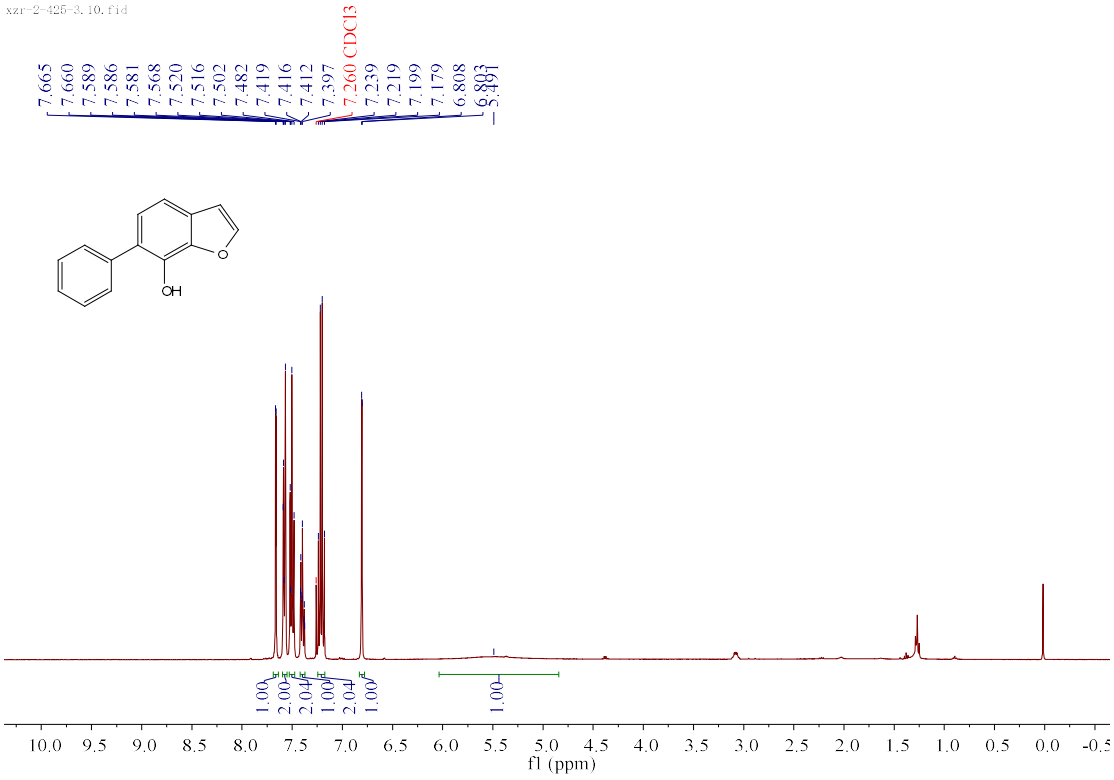
400 MHz ^{1}H NMR Spectrum of 2w in $CDCl_3$



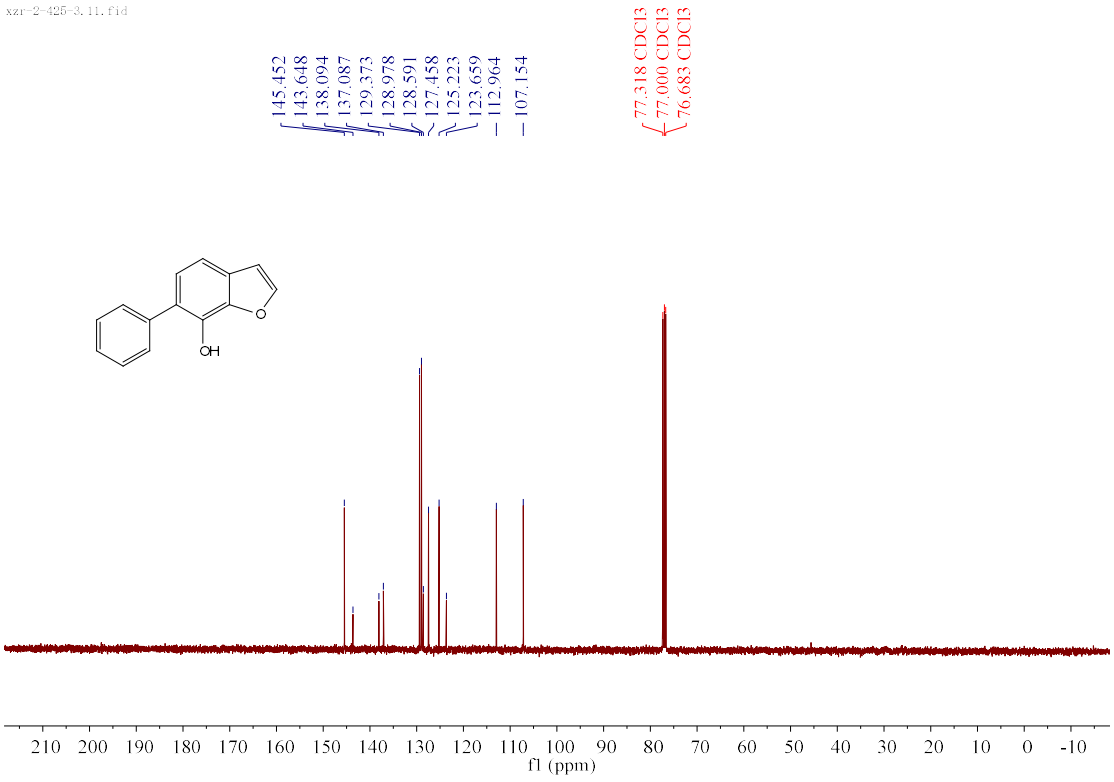
100 MHz ^{13}C NMR Spectrum of 2w in $CDCl_3$



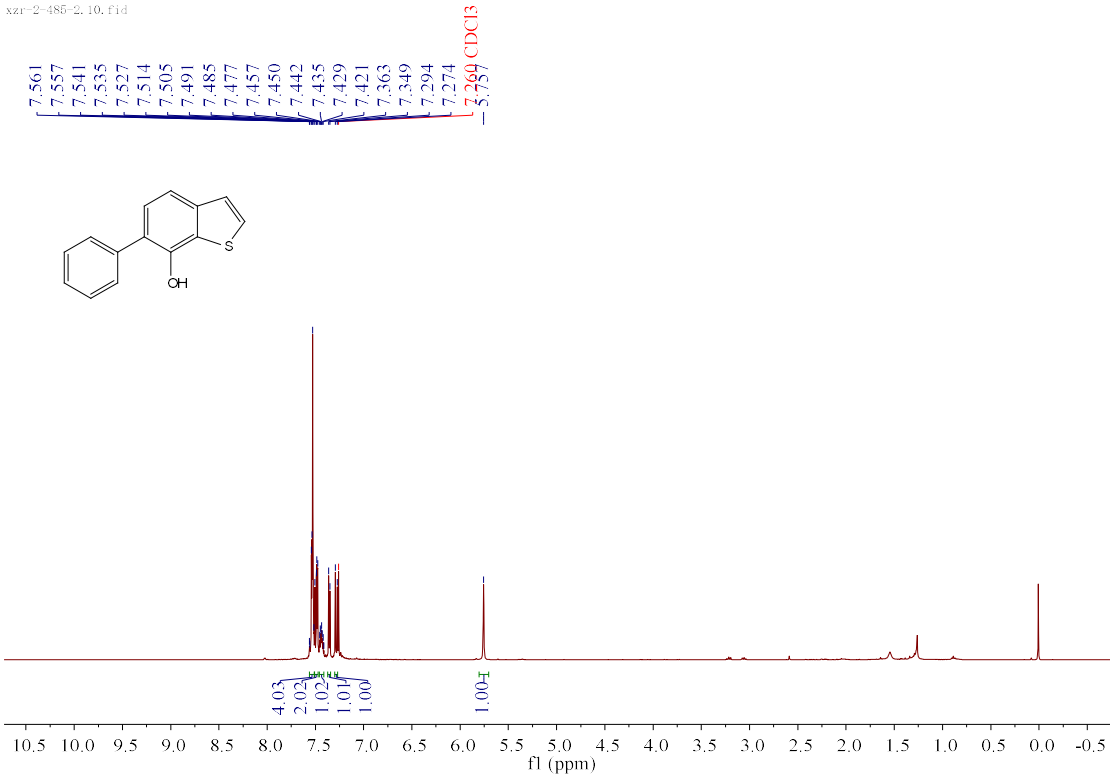
400 MHz ^{1}H NMR Spectrum of 2x in $CDCl_3$



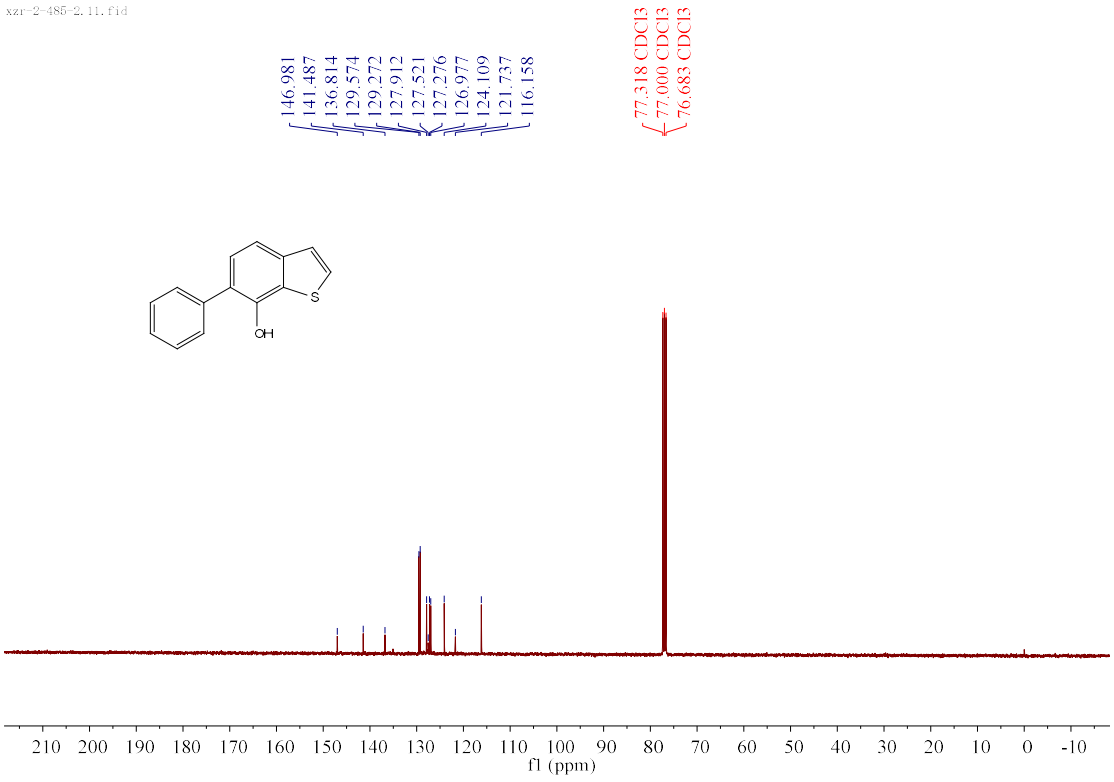
100 MHz ^{13}C NMR Spectrum of 2x in $CDCl_3$



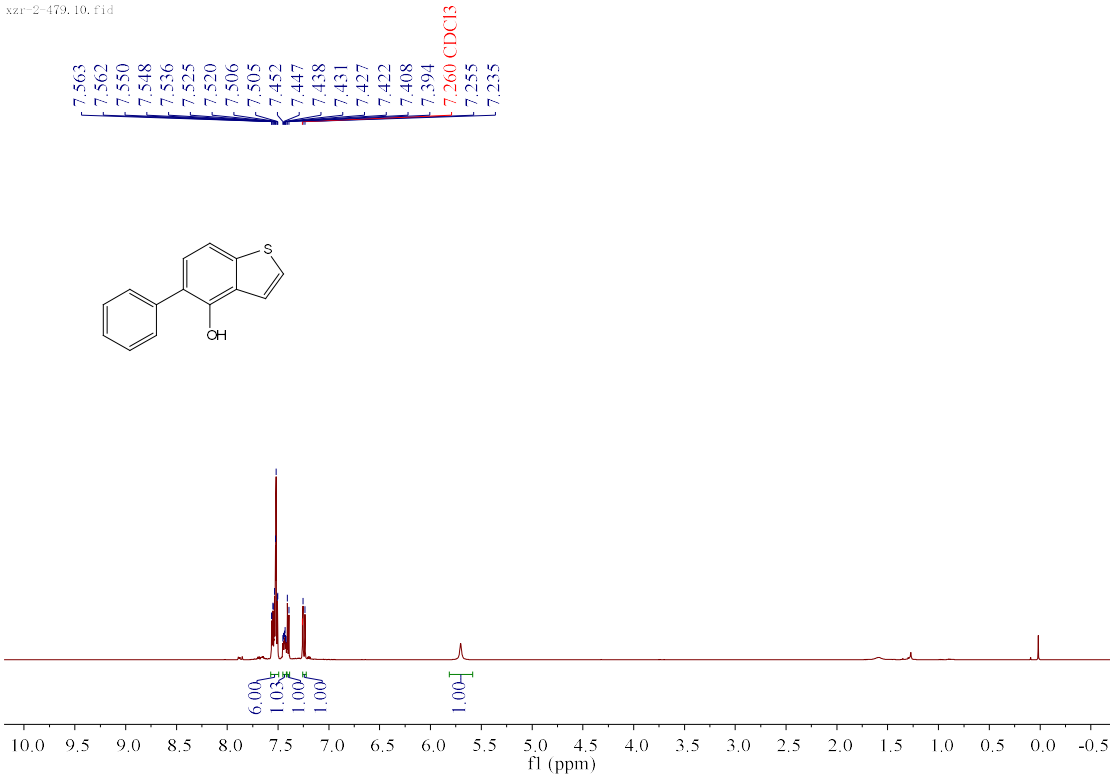
400 MHz ^{1}H NMR Spectrum of 2y in $CDCl_3$



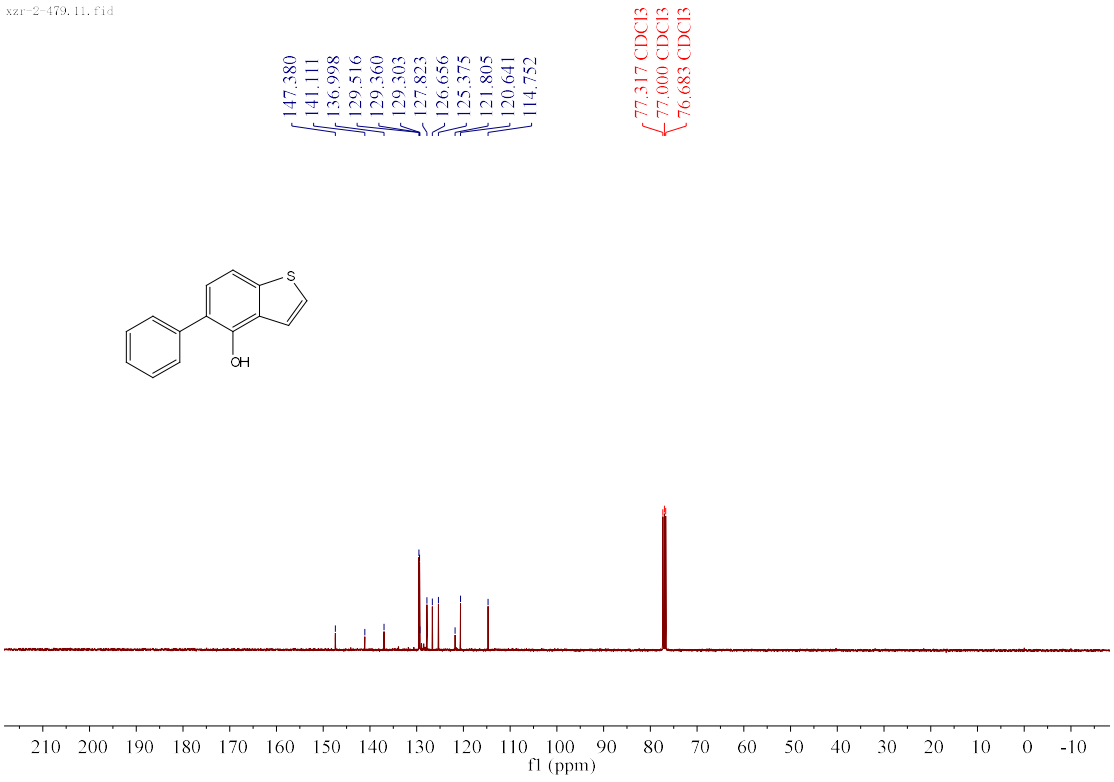
100 MHz ^{13}C NMR Spectrum of 2y in $CDCl_3$



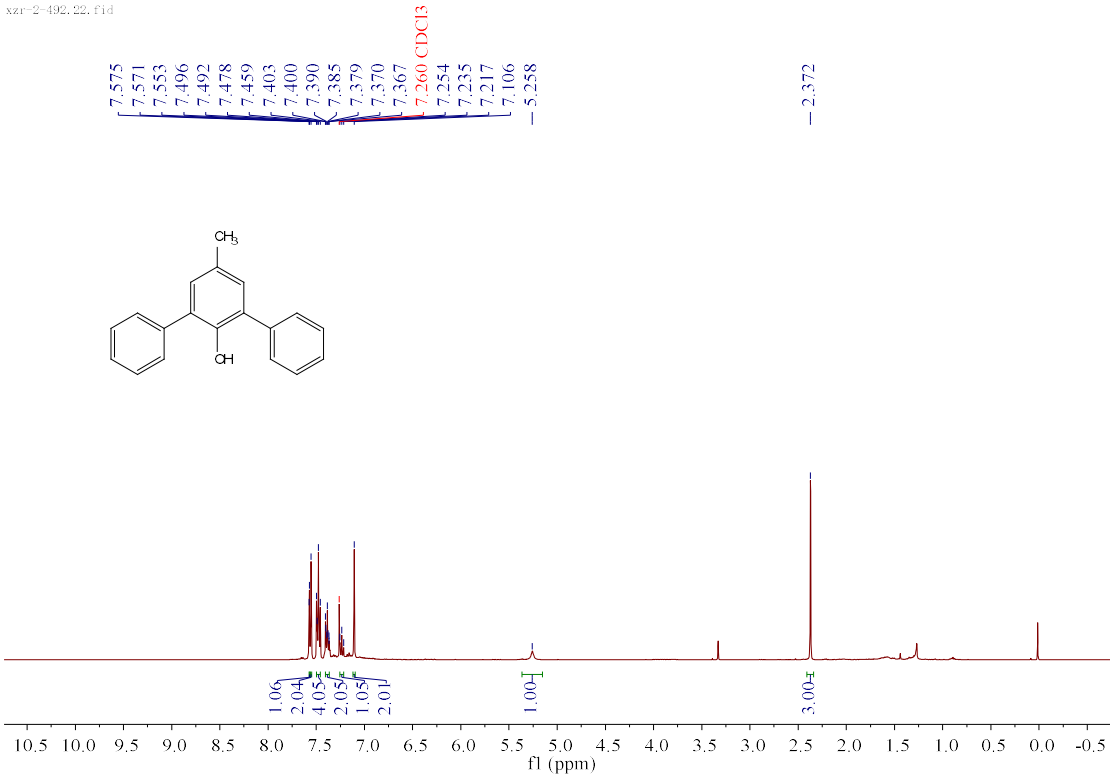
400 MHz ^{1}H NMR Spectrum of 2z in $CDCl_3$



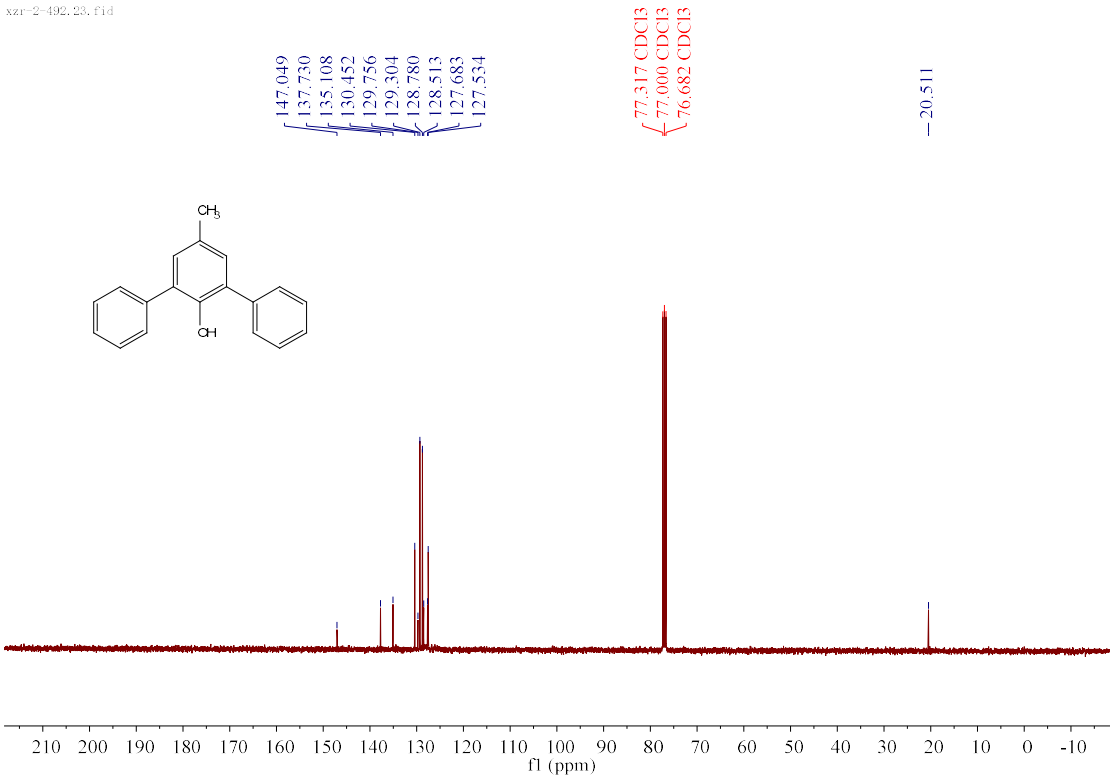
100 MHz ^{13}C NMR Spectrum of 2z in $CDCl_3$



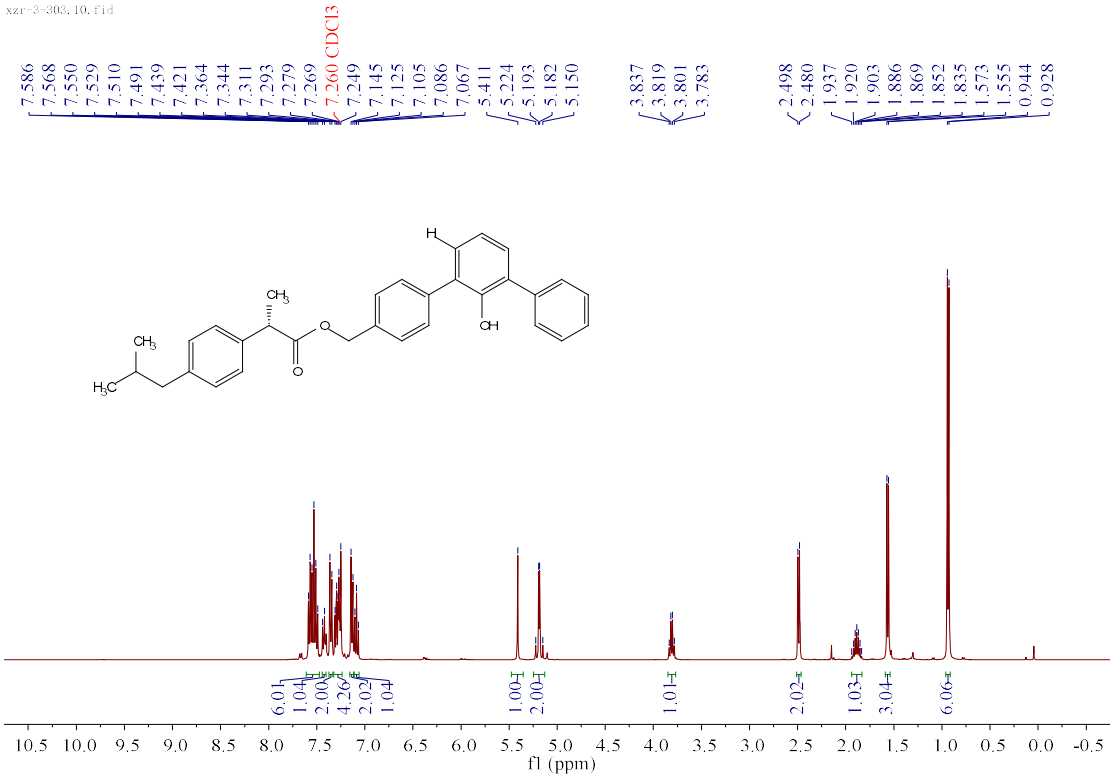
400 MHz ^{1}H NMR Spectrum of 2aa in $CDCl_3$



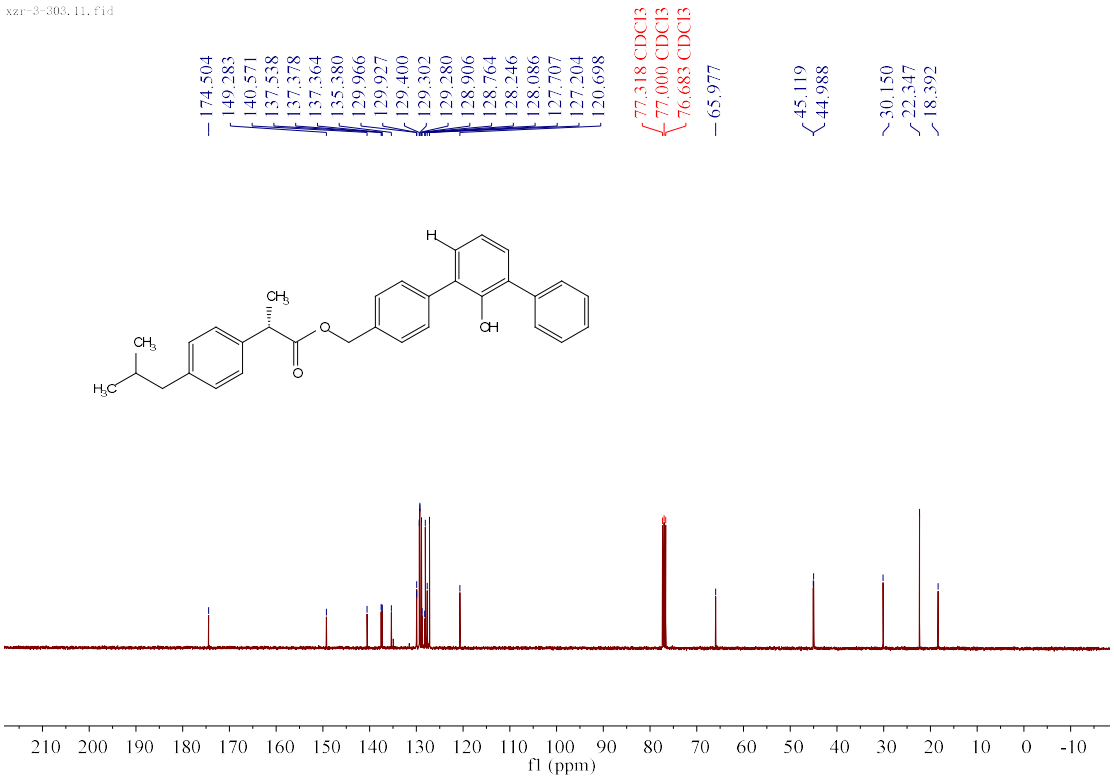
100 MHz ^{13}C NMR Spectrum of 2aa in $CDCl_3$



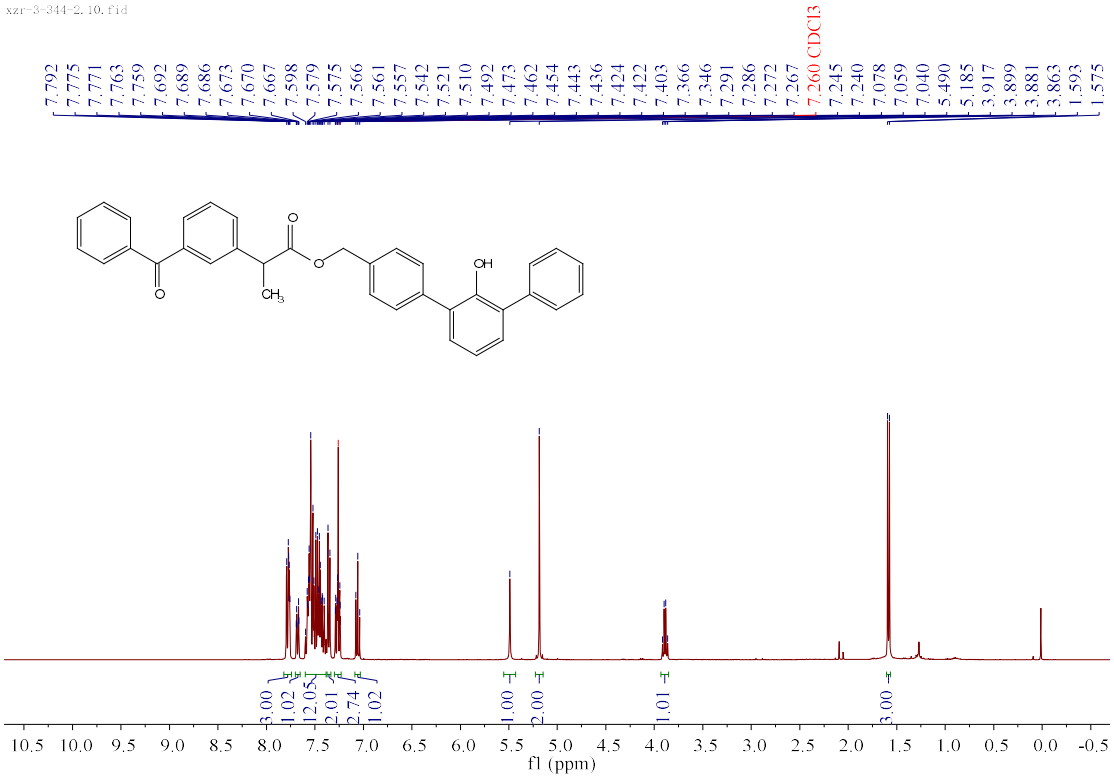
400 MHz ^{1}H NMR Spectrum of 2ab in $CDCl_3$



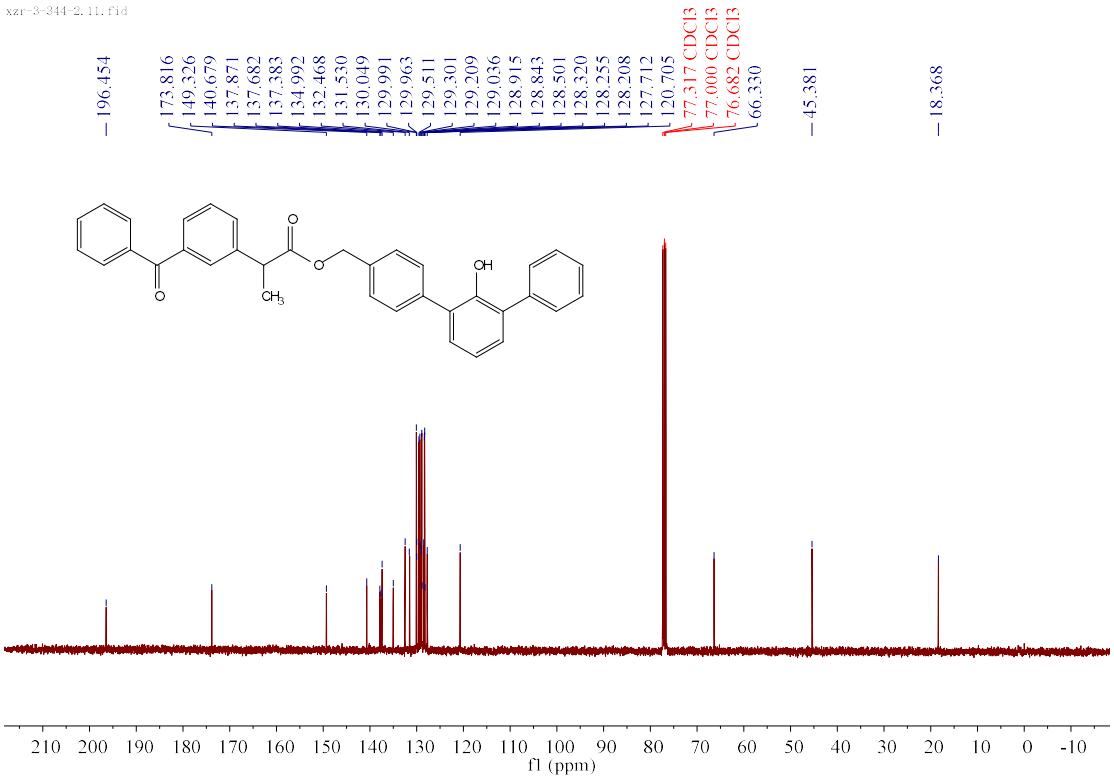
100 MHz ^{13}C NMR Spectrum of 2ab in $CDCl_3$



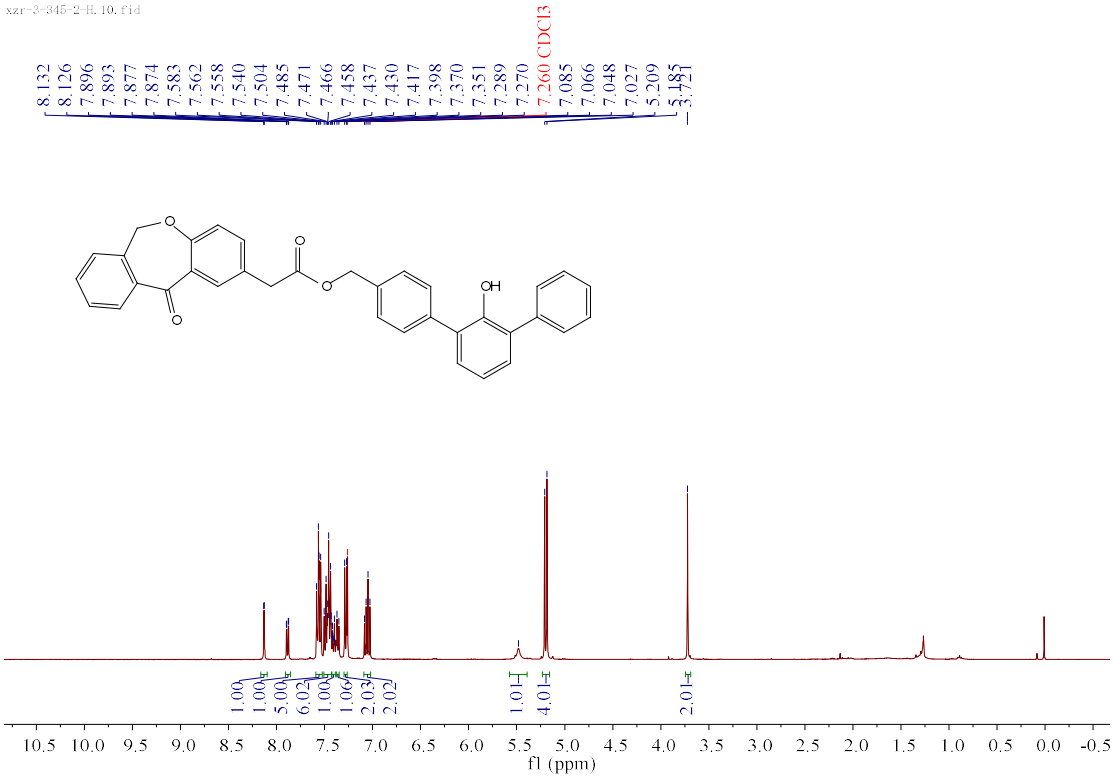
400 MHz ^{1}H NMR Spectrum of 2ac in $CDCl_3$



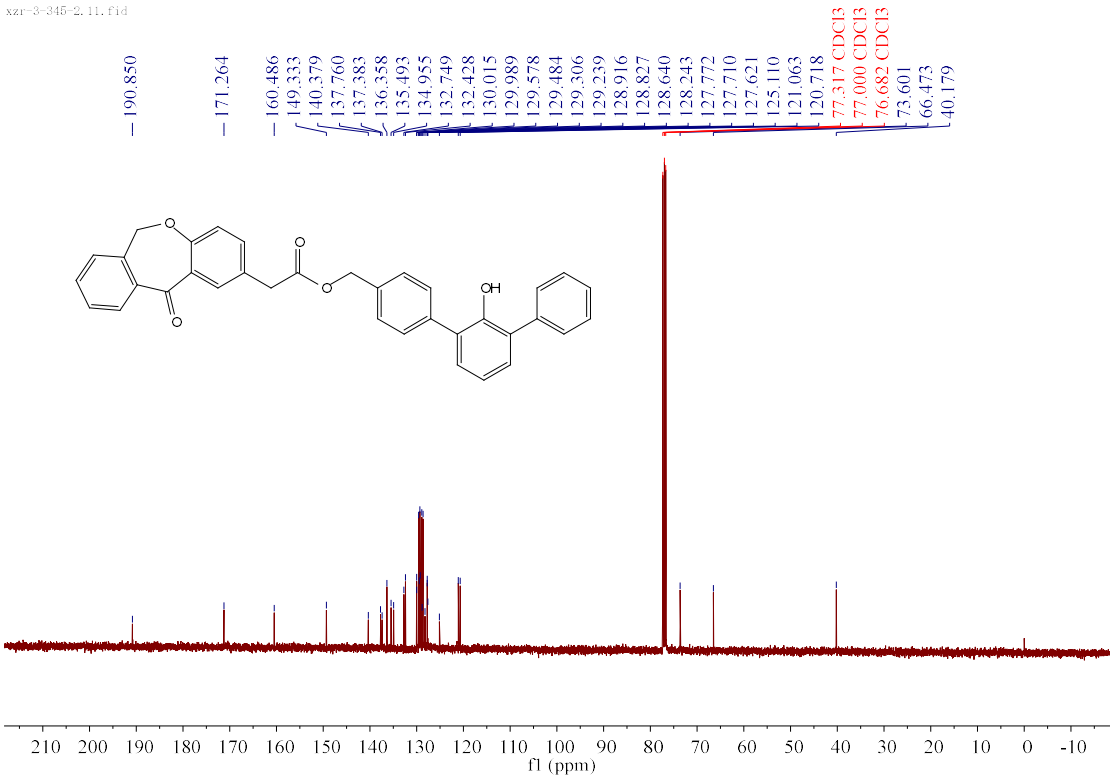
100 MHz ^{13}C NMR Spectrum of 2ac in $CDCl_3$



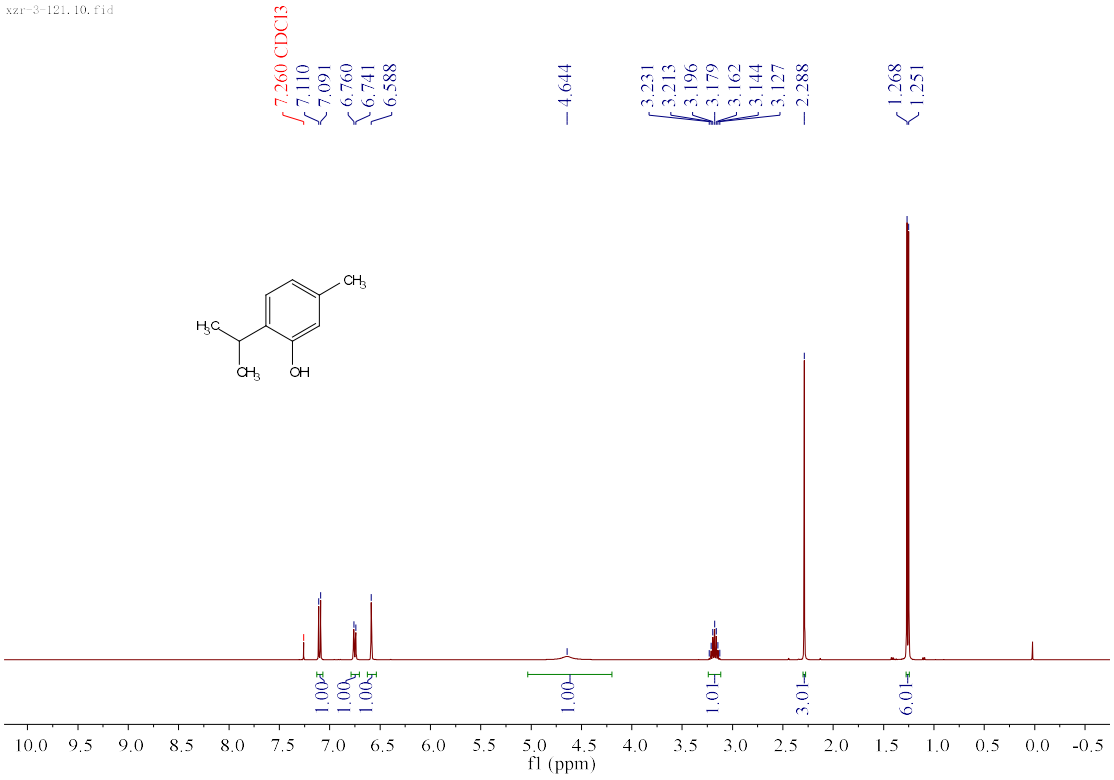
400 MHz ^{1}H NMR Spectrum of 2ad in $CDCl_3$



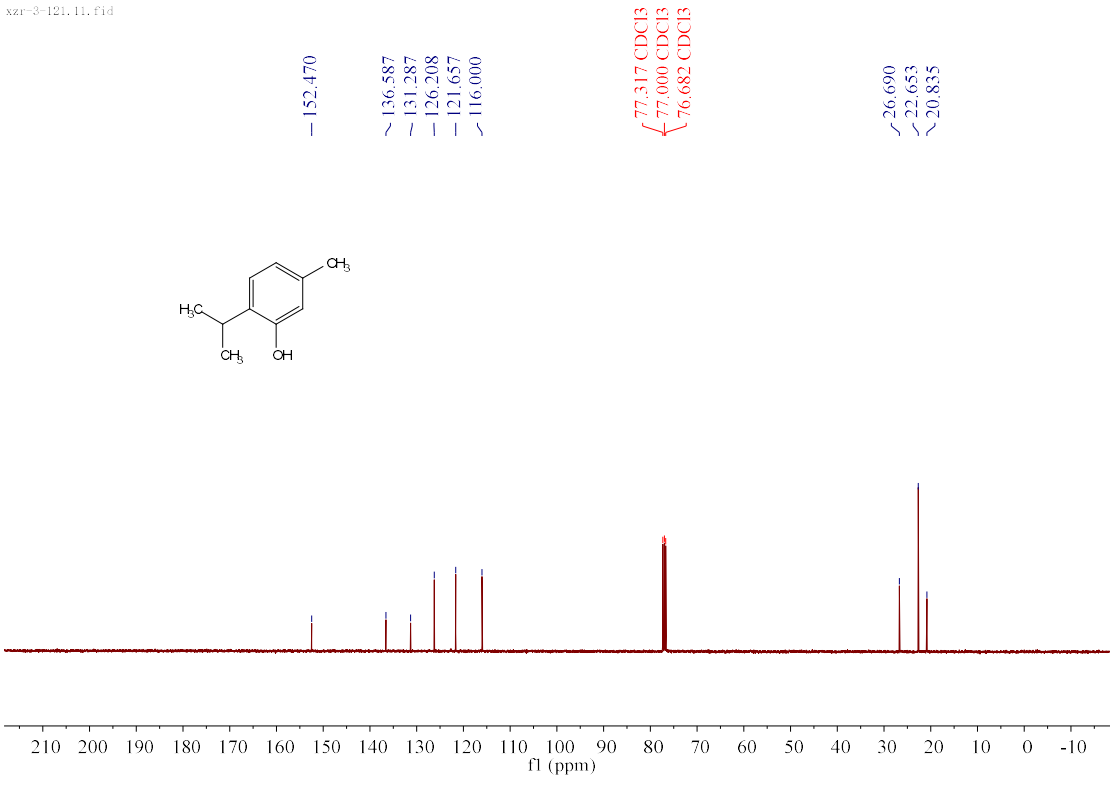
100 MHz ^{13}C NMR Spectrum of 2ad in $CDCl_3$



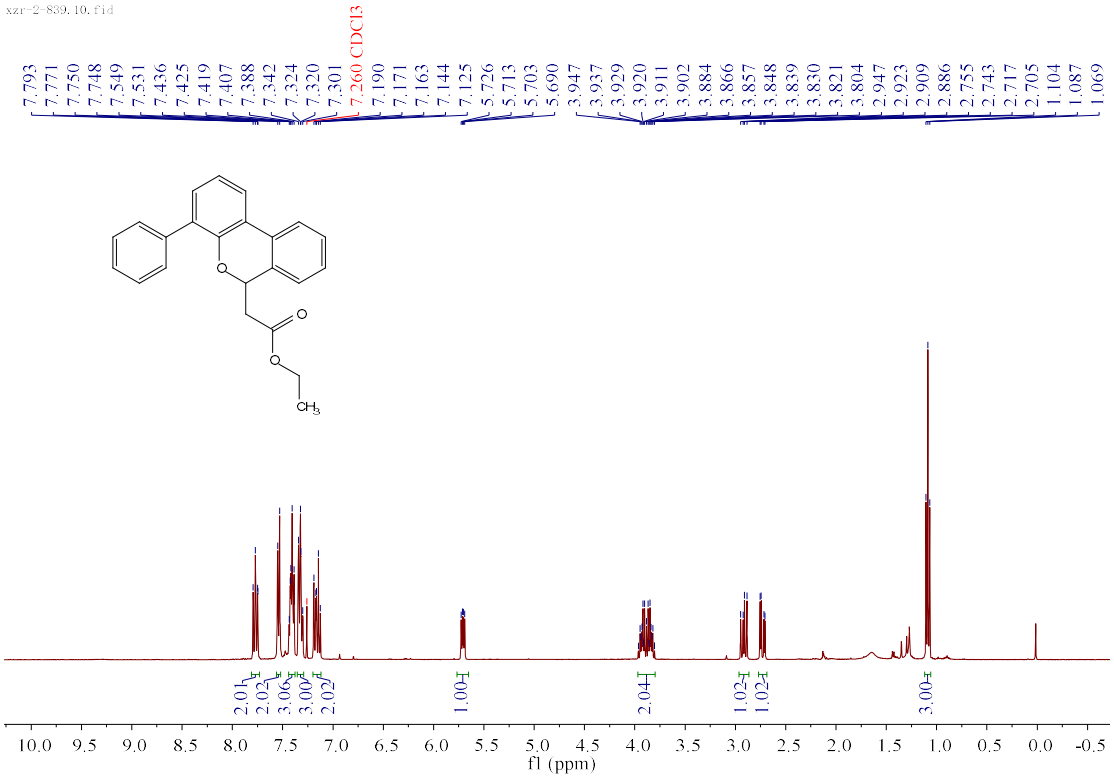
400 MHz ^{1}H NMR Spectrum of 2ae in $CDCl_3$



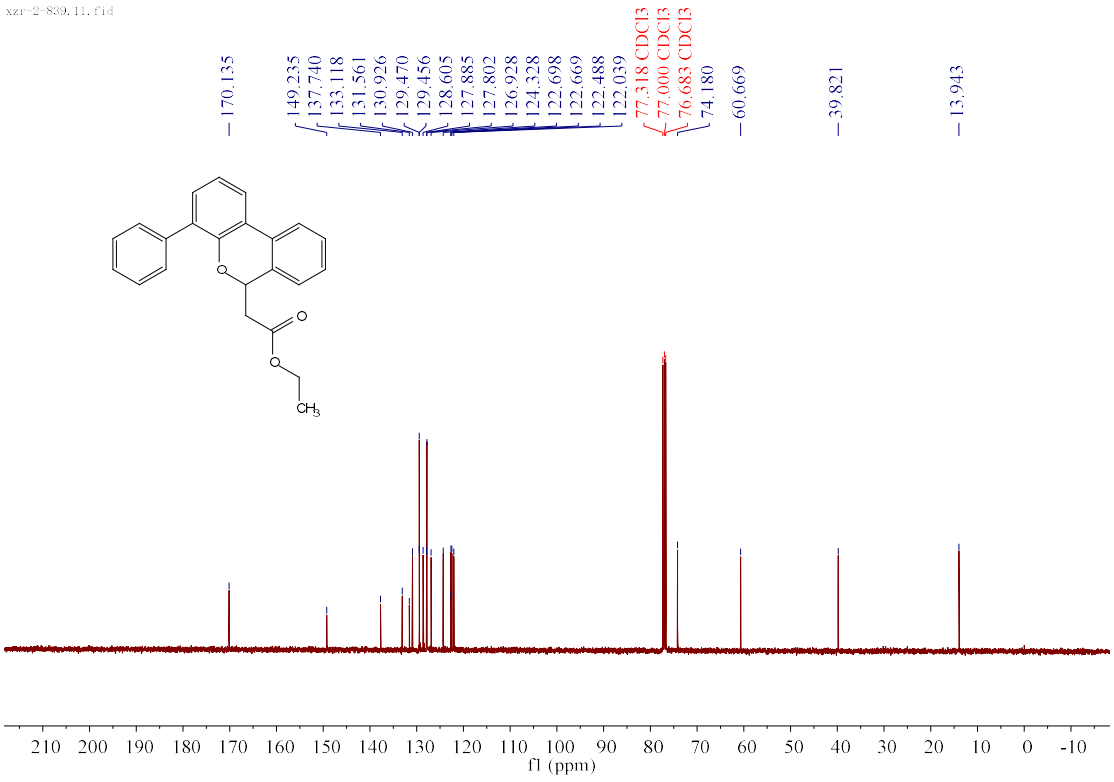
100 MHz ^{13}C NMR Spectrum of 2ae in $CDCl_3$



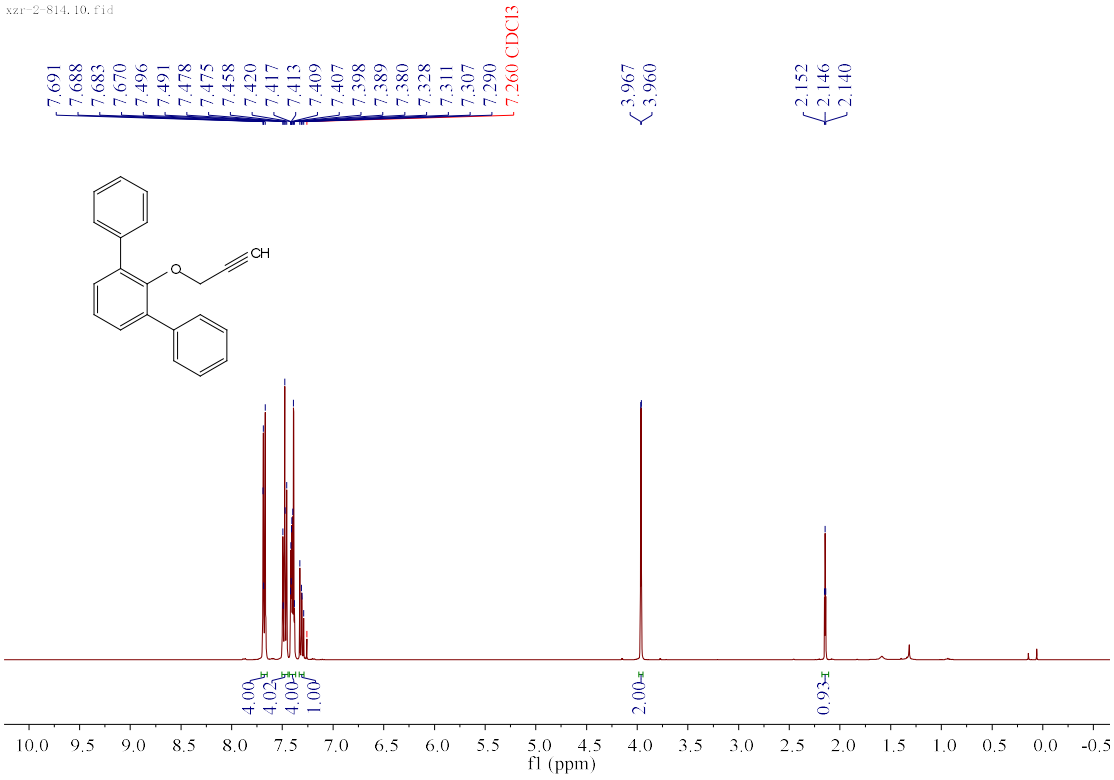
400 MHz ^{1}H NMR Spectrum of 5 in $CDCl_3$



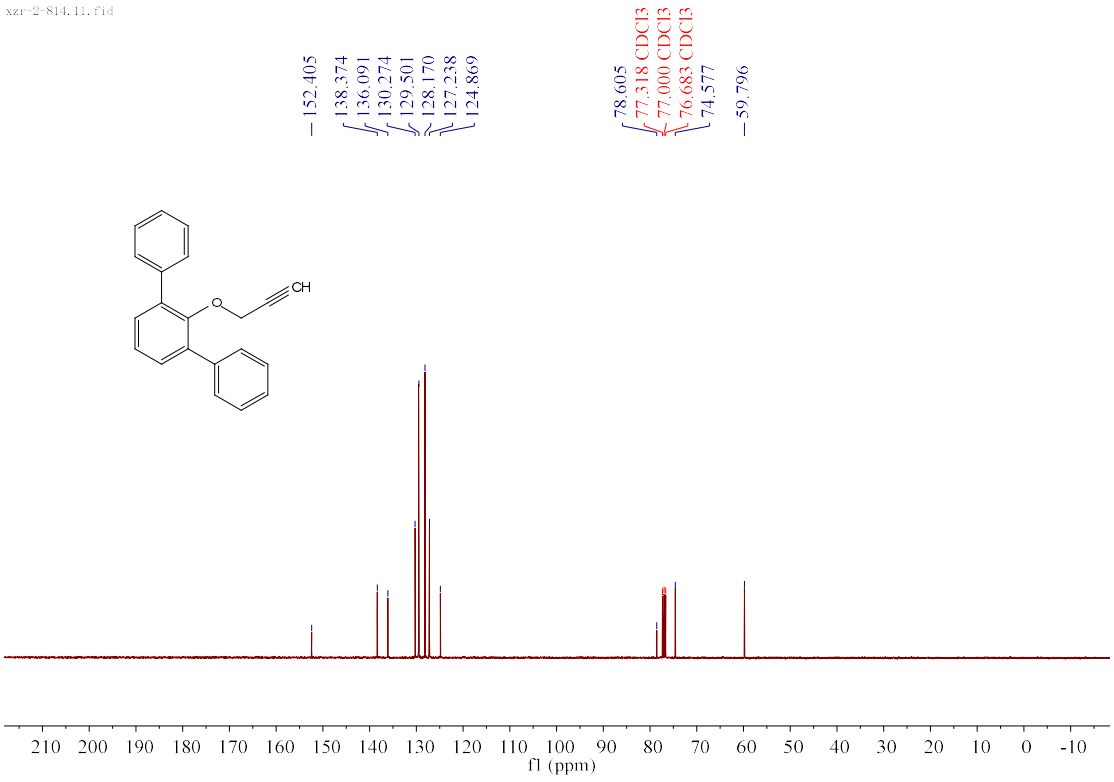
100 MHz ^{13}C NMR Spectrum of 5 in $CDCl_3$



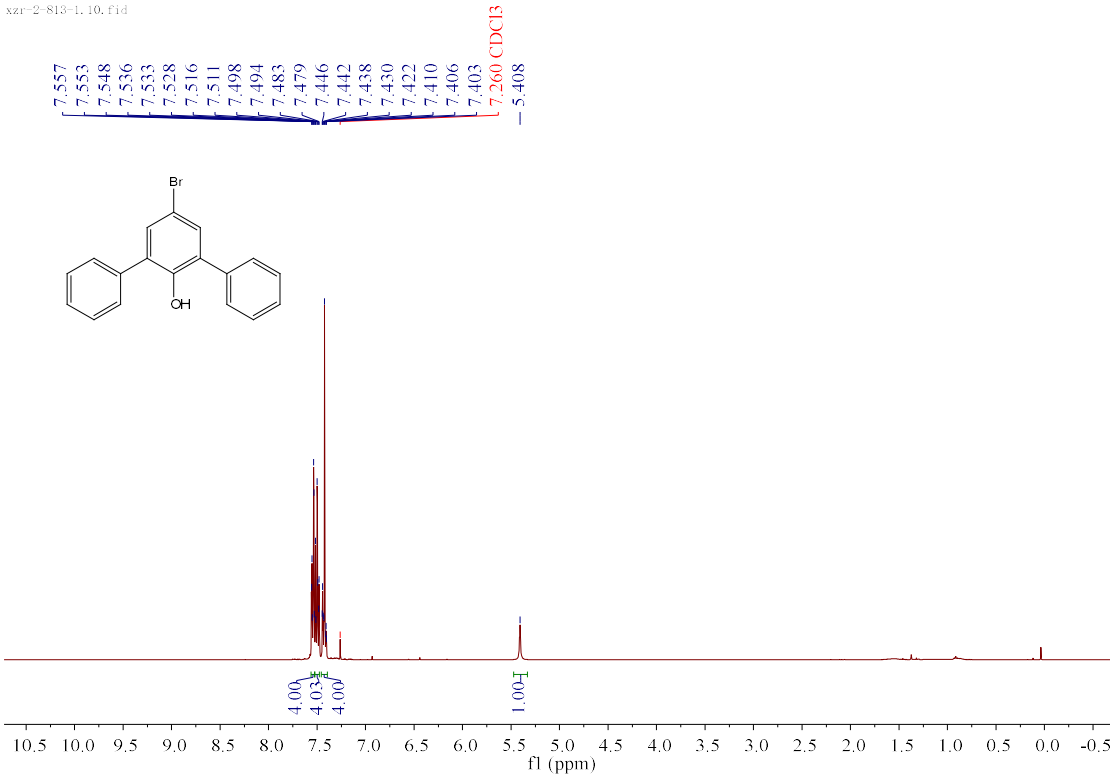
400 MHz ^{1}H NMR Spectrum of 6 in $CDCl_3$



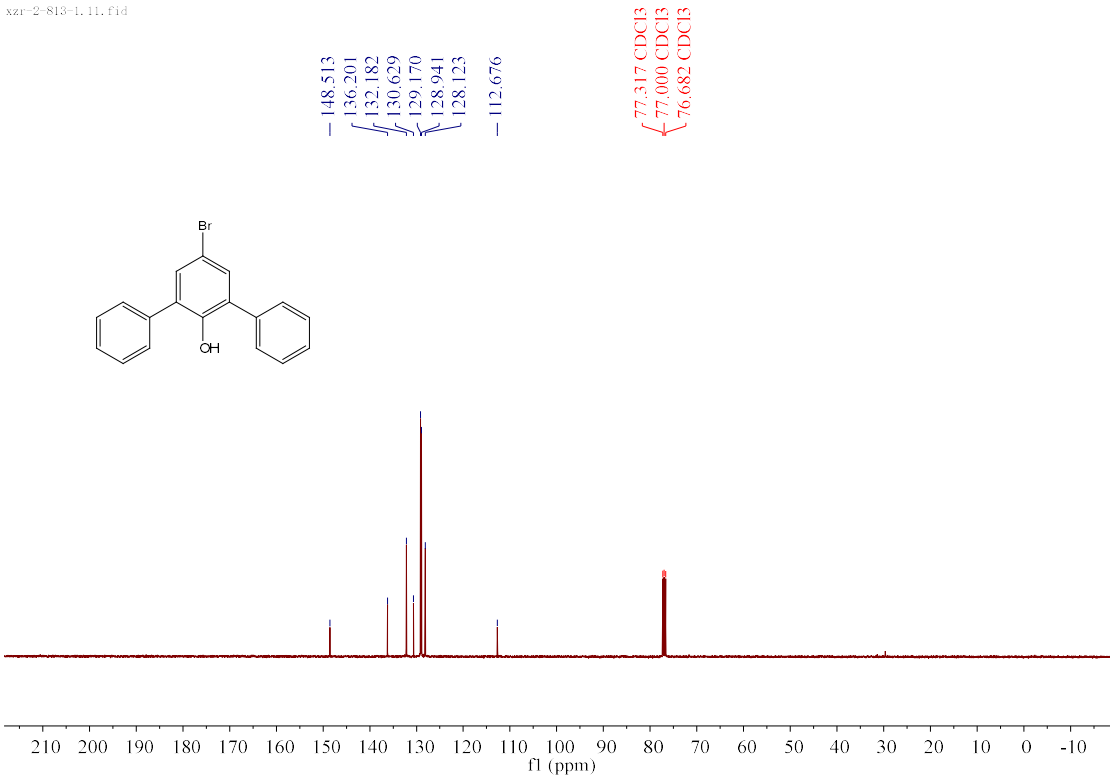
100 MHz ^{13}C NMR Spectrum of 6 in $CDCl_3$



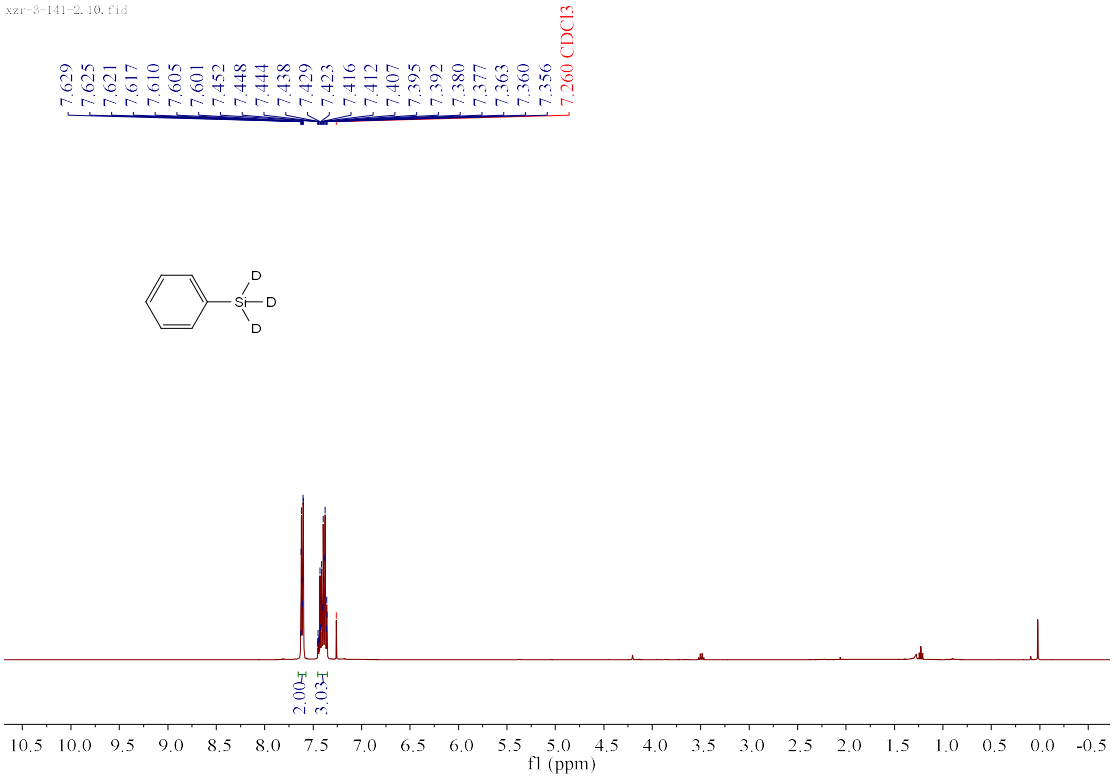
400 MHz ^{1}H NMR Spectrum of 7 in $CDCl_3$



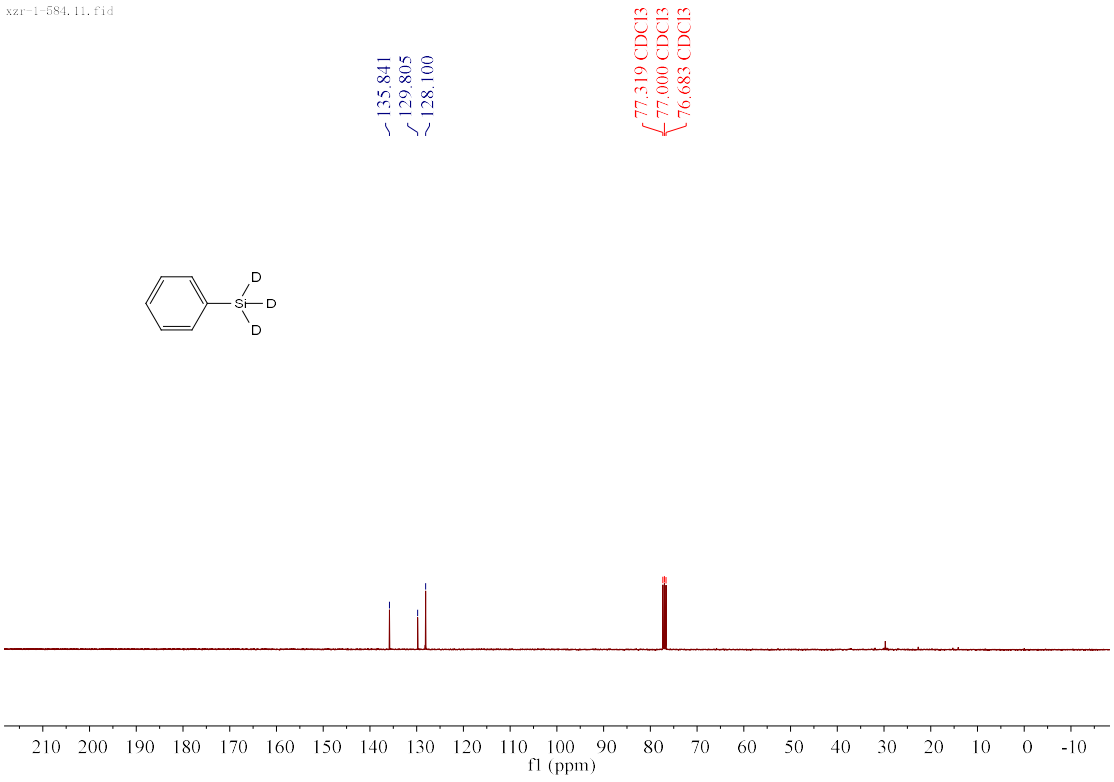
100 MHz ^{13}C NMR Spectrum of 7 in $CDCl_3$



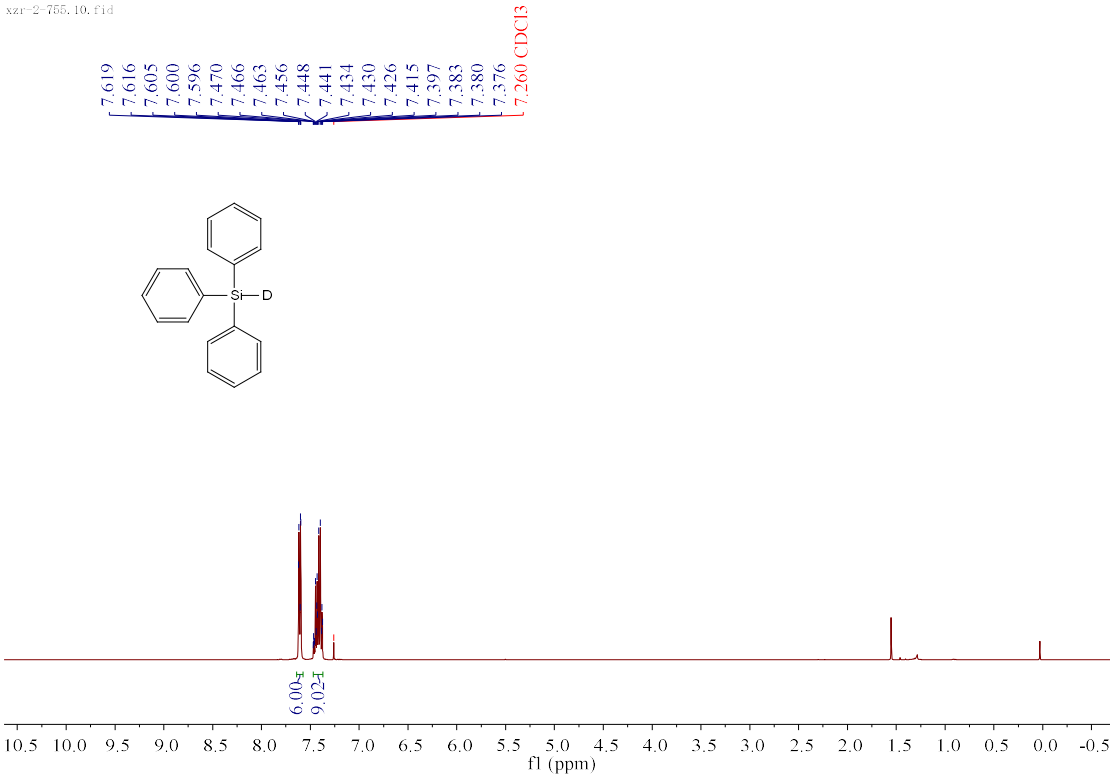
400 MHz ^{1}H NMR Spectrum of $PhSiD_3$ in $CDCl_3$



100 MHz ^{13}C NMR Spectrum of $PhSiD_3$ in $CDCl_3$



400 MHz ^{1}H NMR Spectrum of Ph_3SiD in $CDCl_3$



100 MHz ^{13}C NMR Spectrum of Ph_3SiD in $CDCl_3$