

Copper-Catalysed, Diboron-Mediated *Cis*-Dideuterated Semihydrogenation of Alkynes with Heavy Water

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CONTENTS

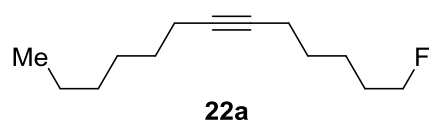
1. General Information	S2
2. Preparation of Alkynes Substrates	S2
3. General Procedure for the Synthesis of <i>cis</i> -Deuterated Olefins.....	S9
4. Reference	S42
5. Copies of NMR Spectra.....	S46

1. General Information

Unless otherwise noted, all reactions were performed under an argon atmosphere using flame-dried glassware. DMF were distilled over CaH₂. All new compounds were fully characterized. NMR-spectra were recorded on Bruker ARX-400 MHz or a ARX-500 Associated. Mass spectra were conducted at Micromass Q-ToF instrument (ESI) and Agilent Technologies 5973N (EI). All reactions were carried out in flame-dried reaction vessels (25 ML) with Teflon screw caps under argon. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. CuTc, Cu(OAc)₂ and Xantphos were purchased from Acros without further purification. LiO^tBu and B₂nep₂ were purchased from Sigma-Aldrich. All alkynes in Figure 2 (**1a-19a**) are known compounds, in which substrates **1a**, **3a**, **5a**, **11a**, **16a**, **18a**, **19a** are commercially available and others are synthesized by Sonogashira coupling according to the reported methods.^[1-3] In Figure 3, alkynes **20a**, **26a**, **28a**, **31a** are commercially available and other substrates including **21a**,^[4] **25a**,^[5] **29a**^[6] are known compounds. In scheme 2, **38**,^[11] **39**,^[12] are known compounds.

2. Preparation of unknown alkyne substrates

1-Fluorotridec-6-yne (**22a**)

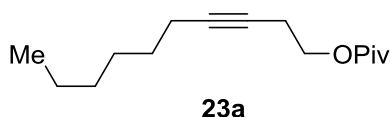


According to reported method,^[13] under an atmosphere of nitrogen, oct-1-yne (0.55 g, 5.0 mmol) was dissolved in 5 mL of THF and cooled to 0 °C. Methyllithium (3.2 mL, 5.0 mmol) was added followed by dropwise addition (via cannula) of a solution of 1-bromo-5-fluoropentane (0.84 g, 6.0 mmol) in 6.5 mL of HMPA. After addition of the 1-bromo-5-fluoropentane, the reaction was allowed to warm to room temperature and was complete by TLC in 1.5 h. Next, the reaction was diluted with 10 mL of water then extracted into pentane (2 x 15 mL). The combined organic extracts were dried over anhydrous MgSO₄, filtered, and then concentrated cold under reduced pressure to a crude transparent liquid. The crude material was

purified via silica gel chromatography to furnish of a colourless oil **22a** (0.7g, 73 %).

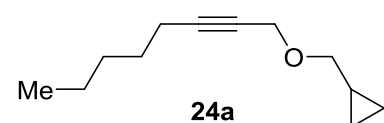
¹H NMR (400 MHz, CDCl₃) δ 4.49 (t, *J* = 6.2 Hz, 1H), 4.37 (t, *J* = 6.1 Hz, 1H), 2.14 (tdd, *J* = 9.5, 4.6, 2.4 Hz, 4H), 1.70 (ddd, *J* = 18.5, 13.9, 6.9 Hz, 2H), 1.54 – 1.42 (m, 6H), 1.40 – 1.24 (m, 6H), 0.88 (t, *J* = 7.0 Hz, 3H). **¹³C NMR (101 MHz, CDCl₃)** δ 84.0 (d, *J* = 165.1 Hz), 80.6, 79.6, 31.4, 30.0 (d, *J* = 19.6 Hz), 29.1, 28.7, 28.5, 24.4 (d, *J* = 5.5 Hz), 22.6, 18.8, 18.7, 14.0. **IR (film):** 3665, 2926, 1597, 1108, 754 cm⁻¹; **EI-MS (m/z, relative intensity):** 198 (M⁺, 30), 109 (38), 137 (13), 95 (50), 85 (94), 67 (100), 54 (67).

Dec-3-yn-1-yl pivalate (**23a**)



According to reported method,^[14] to a stirred solution of dec-3-yn-1-ol (154 mg, 1.0 mmol) in CH₂Cl₂ (4 mL) was added 4-dimethylaminopyridine (DMAP) (244 mg, 2.0 mmol) in one portion followed by pivaloyl chloride (148 μL, 1.2 mmol) in one portion. The resulting slurry was stirred overnight and then concentrated under reduced pressure. The resulting mixture was purified by flash chromatography eluting with ethyl acetate/petroleum ether to give ester as a colourless oil **23a** (219 mg, 92%). **¹H NMR (400 MHz, CDCl₃)** δ 4.11 (t, *J* = 6.9 Hz, 2H), 2.47 (tt, *J* = 6.9, 2.4 Hz, 2H), 2.12 (tt, *J* = 7.1, 2.4 Hz, 2H), 1.51 – 1.41 (m, 2H), 1.40 – 1.23 (m, 6H), 1.20 (s, 9H), 0.88 (t, *J* = 6.9 Hz, 3H). **¹³C NMR (101 MHz, CDCl₃)** δ 178.4, 81.9, 75.5, 62.7, 38.7, 31.4, 28.9, 28.5, 27.2, 22.6, 19.2, 18.6, 14.1. **IR (film):** 3696, 2924, 1735, 1646, 1266, 741 cm⁻¹; **EI-MS (m/z, relative intensity):** 238 (M⁺, 10), 121 (20), 79 (67), 57 (100).

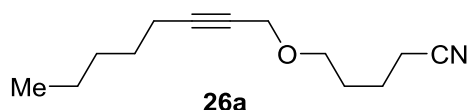
((oct-2-yn-1-yloxy)methyl)cyclopropane (**24a**)



To a 0 °C solution of oct-2-yn-1-ol (630 mg, 5.0 mmol) in THF (10 mL) was added NaH (240 mg, 6.0 mmol) under N₂ atmosphere. The reaction was then warmed to room temperature and stirred for 4 h after which (bromomethyl)cyclopropane (810 mg, 6.0 mmol) was added. The reaction was then warmed to 40 °C and stirred for 5 h

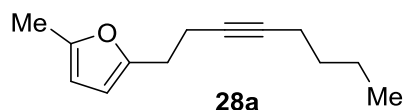
after which H₂O (5 mL) was added. The aqueous layer was extracted EtOAc (3 x 10 mL), and the combined organic layers were dried (Na₂SO₄) and concentrated. The resulting mixture was purified by flash chromatography eluting with ethyl acetate/petroleum ether to give as a colourless oil **24a** (810 mg, 90%). ¹H NMR (400 MHz, CDCl₃) δ 4.15 (t, *J* = 2.2 Hz, 2H), 3.33 (d, *J* = 7.0 Hz, 2H), 2.20 (tt, *J* = 7.2, 2.2 Hz, 2H), 1.55 – 1.46 (m, 2H), 1.40 – 1.27 (m, 4H), 1.12 – 0.98 (m, 1H), 0.89 (t, *J* = 7.1 Hz, 3H), 0.59 – 0.47 (m, 2H), 0.27 – 0.17 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 86.9, 76.0, 74.3, 58.1, 31.0, 28.3, 22.2, 18.7, 14.0, 10.3, 3.0. IR (film): 3451, 2924, 1638, 741 cm⁻¹; EI-MS (*m/z*, relative intensity): 180 (M⁺, 10), 165 (12), 109 (28), 95 (26), 79 (52), 67 (70), 55 (100).

5-(oct-2-yn-1-yloxy)pentanenitrile (**26a**)



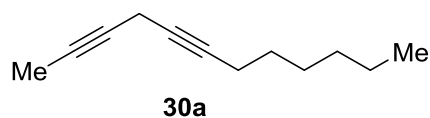
To a 0 °C solution of oct-2-yn-1-ol (630 mg, 5.0 mmol) in THF (10 mL) was added NaH (240 mg, 6.0 mmol) under N₂ atmosphere. The reaction was then warmed to room temperature and stirred for 4 h after which 5-bromopentanenitrile (960 mg, 6.0 mmol) was added. The reaction was then warmed to 40 °C and stirred for 5 h after which H₂O (5 mL) was added. The aqueous layer was extracted EtOAc (3 x 10 mL), and the combined organic layers were dried (Na₂SO₄) and concentrated. The resulting mixture was purified by flash chromatography eluting with ethyl acetate/petroleum ether to give **26a** as a yellow oil (880 mg, 85%). ¹H NMR (400 MHz, CDCl₃) δ 4.09 (t, *J* = 2.1 Hz, 2H), 3.51 (t, *J* = 5.7 Hz, 2H), 2.38 (t, *J* = 6.9 Hz, 2H), 2.20 (tt, *J* = 7.2, 2.1 Hz, 2H), 1.79 – 1.69 (m, 4H), 1.54 – 1.44 (m, 2H), 1.39 – 1.25 (m, 4H), 0.88 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 119.6, 87.1, 75.7, 68.3, 58.6, 31.0, 28.30, 28.20, 22.4, 22.1, 18.6, 16.8, 13.9. IR (film): 3451, 2922, 1638, 1518, 1440, 1349, 1265, 823, 755, 733 cm⁻¹; EI-MS (*m/z*, relative intensity): 207 (M⁺, 5), 192 (15), 151 (20), 136 (16), 109 (14), 82 (70), 55 (74).

2-methyl-5-(oct-3-yn-1-yl)furan (**28a**)



According to reported method,^[13] under an atmosphere of nitrogen, 2-(but-3-yn-1-yl)-5-methylfuran (605 mg, 5.0 mmol) was dissolved in 5 mL of THF and cooled to 0 °C. Methylolithium (3.2 mL, 5.0 mmol) was added followed by dropwise addition (via cannula) of a solution of 1-bromobutane (822 mg, 6.0 mmol) in 6.5 mL of HMPA. After addition of the 1-bromobutane, the reaction was allowed to warm to room temperature and was complete by TLC in 1.5 h. Next, the reaction was diluted with 10 mL of water then extracted into pentane (2 x 15 mL). The combined organic extracts were dried over anhydrous MgSO₄, filtered, and then concentrated cold under reduced pressure to a crude transparent liquid. The crude material was purified via silica gel chromatography to furnish of a colourless oil **28a** (665 mg; 70 % yield). ¹H NMR (400 MHz, CDCl₃) δ 5.94 (d, *J* = 2.9 Hz, 1H), 5.86 (dd, *J* = 2.8, 0.9 Hz, 1H), 2.78 (t, *J* = 7.6 Hz, 2H), 2.46 (tdd, *J* = 7.3, 4.8, 2.4 Hz, 2H), 2.26 (s, 3H), 2.16 (tt, *J* = 7.0, 2.4 Hz, 2H), 1.54 – 1.33 (m, 4H), 0.92 (t, *J* = 7.2 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 152.0, 150.4, 105.9, 105.8, 80.9, 79.0, 31.1, 28.2, 21.9, 18.4, 18.2, 13.6, 13.5. IR (film): 3451, 2944, 1639, 1440, 1156, 844, 766 cm⁻¹; EI-MS (*m/z*, relative intensity): 190 (M⁺, 100), 175 (20), 147 (30), 95 (10), 81 (60), 66 (40).

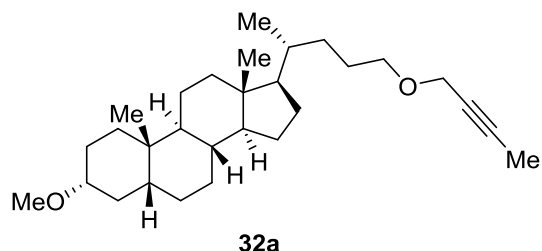
Dodeca-2,5-diyne (30a)



According to reported method,^[13] under an atmosphere of nitrogen, oct-1-yne (550 mg, 5.0 mmol) was dissolved in 5 mL of THF and cooled to 0 °C. Methylolithium (3.2 mL, 5.0 mmol) was added followed by dropwise addition (via cannula) of a solution of 1-bromobut-2-yne (792 mg, 6.0 mmol) in 6.5 mL of HMPA. After addition of the 1-bromobutane, the reaction was allowed to warm to room temperature and was complete by TLC in 1.5 h. Next, the reaction was diluted with 10 mL of water then extracted into pentane (2 x 15 mL). The combined organic extracts were dried over anhydrous MgSO₄, filtered, and then concentrated cold under reduced pressure to a crude transparent liquid. The crude material was purified via

silica gel chromatography to furnish of a light yellow oil **30a** (607 mg; 75 % yield). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 3.10 (dd, $J = 5.0, 2.5$ Hz, 2H), 2.15 (tt, $J = 7.2, 2.4$ Hz, 2H), 1.79 (t, $J = 2.6$ Hz, 3H), 1.51 – 1.46 (m, 2H), 1.31 – 1.26 (m, 6H), 0.89 (t, $J = 6.9$ Hz, 3H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 80.6, 75.8, 74.3, 73.6, 31.3, 28.7, 28.5, 22.5, 18.7, 14.0, 9.6, 3.5. **IR (film)**: 3746, 2921, 1736, , 1320, 884, 750 cm^{-1} ; **EI-MS (m/z, relative intensity)**: 162 (M^+ , 5), 147 (10), 133 (28), 105(50). 91 (100), 79 (22), 67 (18).

(3R,5R,8R,9S,10S,13R,14S,17R)-17-((R)-5-(but-2-yn-1-yloxy)pentan-2-yl)-3-methoxy-10,13-dimethylhexadecahydro-1H-cyclopenta[a]phenanthrene (32a)

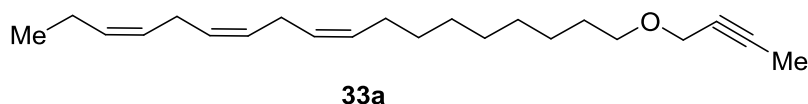


According to reported method ^[15] to a 0 °C solution of (R)-4-((3R,5R,8R,9S, 10S,13R,14S,17R)-3-methoxy-10,13-dimethylhexadecahydro-1H-cyclopenta[a]phenanthren-17-yl)pentanoic acid (3.12g, 8.0 mmol) in THF (10 mL) was added dropwise to a stirred suspension of LiAlH_4 (420 mg, 12.0 mmol) in THF (10 mL). The mixture was stirred at 0 °C for an additional hour and then allowed to slowly warm to room temperature. After 18 h, the reaction was quenched by slow dropwise addition of water. Once all bubbling had ceased, 10% aq H_2SO_4 was added. The layers were separated and the aqueous layer extracted with ethyl acetate. The combined organic layers were washed with brine, dried over Na_2SO_4 , filtered, and concentrated. This procedure provided (2.56 g 85% yield) of the desired alcohol, which was used without further purification.

To a 0 °C solution of alcohol (2.56g, 6.8 mmol) in THF (10 mL) was added NaH (324 mg, 8.1 mmol) under N_2 atmosphere. The reaction was then warmed to room temperature and stirred for 4h after which 1-bromobut-2-yne (1 g, 8.1 mmol) was added. The reaction was then warmed to 40 °C and stirred for 5 h after which H_2O (5 mL) was added. The aqueous layer was extracted EtOAc (3 x 10 mL), and the combined organic layers were dried Na_2SO_4 and concentrated. The resulting mixture

was purified by flash chromatography eluting with ethyl acetate/petroleum ether to give ester as light yellow viscous oil **32a** (1.8 g, 65%). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 4.07 (q, $J = 2.3$ Hz, 2H), 3.43 (td, $J = 6.9, 2.0$ Hz, 2H), 3.34 (s, 3H), 3.20 – 3.10 (m, 1H), 1.94 (dd, $J = 9.0, 6.3$ Hz, 1H), 1.91 – 1.71 (m, 7H), 1.71 – 1.48 (m, 5H), 1.48 – 1.28 (m, 8H), 1.30 – 1.18 (m, 4H), 1.15 – 0.99 (m, 6H), 0.91 (s, 6H), 0.63 (s, 3H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 82.0, 80.4, 75.4, 70.7, 58.5, 56.5, 56.2, 55.5, 42.7, 42.0, 40.3, 40.2, 35.8, 35.6, 35.3, 34.9, 32.7, 32.1, 28.3, 27.3, 26.8, 26.4, 26.2, 24.2, 23.4, 20.8, 18.5, 12.0, 3.6. **IR (film)**: 3674, 3450, 2923, 2852, 1631, 1455, 1372, 1262, 1101, 749, 472, 419 cm^{-1} **HRMS m/z (ESI) calcd for $\text{C}_{29}\text{H}_{48}\text{O}_2\text{Na}$ ($\text{M} + \text{Na}$) $^+$** : 451.3547, found 451.3542.

(3Z,6Z,9Z)-18-(but-2-yn-1-yloxy)octadeca-3,6,9-triene (33a)



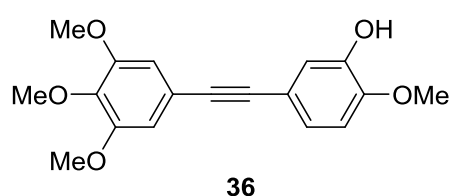
According to reported

method,^[15] to a 0 °C solution of Linolenic acid (2.78g, 10 mmol) in THF (10 mL) was added dropwise to a stirred suspension of LiAlH_4 (568 mg, 15 mmol) in THF (10 mL). The mixture was stirred at 0 °C for an additional hour and then allowed to slowly warm to room temperature. After 18 h, the reaction was quenched by slow dropwise addition of water. Once all bubbling had ceased, 10% aq H_2SO_4 was added. The layers were separated and the aqueous layer extracted with ethyl acetate. The combined organic layers were washed with brine, dried over Na_2SO_4 , filtered, and concentrated. This procedure provided (2.1 g 80% yield) of the desired alcohol, which was used without further purification.

To a 0 °C solution of alcohol (2.1g, 8.0 mmol) in THF (10 mL) was added NaH (384 mg, 9.6 mmol) under N_2 atmosphere. The reaction was then warmed to room temperature and stirred for 4 h after which 1-bromobut-2-yne (1.2g, 9.6 mmol) was added. The reaction was then warmed to 40 °C and stirred for 5 h after which H_2O (5 mL) was added. The aqueous layer was extracted EtOAc (3 x 10 mL), and the combined organic layers were dried (Na_2SO_4) and concentrated. The resulting mixture was purified by flash chromatography eluting with ethyl acetate/petroleum ether to

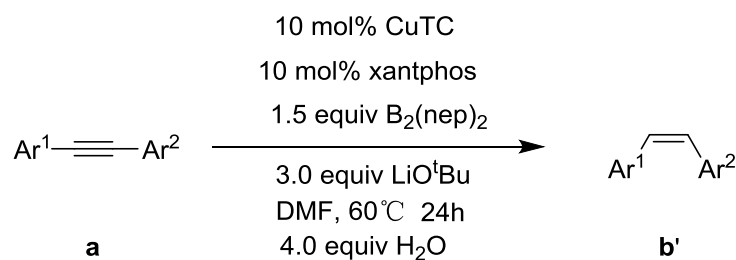
give ester as light yellow viscous oil **33a** (1.9g, 63%). ¹H NMR (400 MHz, CDCl₃) δ 5.44 – 5.24 (m, 6H), 4.06 (q, *J* = 2.3 Hz, 2H), 3.45 (t, *J* = 6.7 Hz, 2H), 2.79 (t, *J* = 6.0 Hz, 4H), 2.05 (dd, *J* = 14.8, 7.3 Hz, 4H), 1.83 (t, *J* = 2.3 Hz, 3H), 1.63 – 1.51 (m, 2H), 1.32 (dd, *J* = 14.0, 12.2 Hz, 10H), 0.96 (t, *J* = 7.5 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 131.8, 130.2, 128.2, 127.6, 127.0, 81.9, 75.3, 70.0, 58.5, 29.6, 29.5, 29.4, 29.4, 29.2, 27.2, 26.1, 25.5, 25.4, 20.5, 14.2, 3.5. IR (film): 3672, 3455, 2854, 1639, 1460, 1263, 750, 420 cm⁻¹; EI-MS (*m/z*, relative intensity): 316 (M⁺, 5), 263 (10), 161 (10), 133 (20), 121 (30), 115 (50), 93 (58), 79 (100), 67 (60).

2-methoxy-5-((3,4,5-trimethoxyphenyl)ethynyl)phenol (**36**)

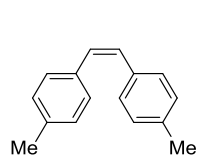
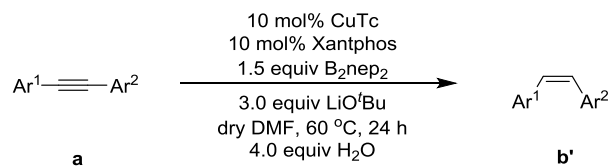


According to reported method,^[16] under N₂ alkyne **34** (0.65 g, 2.6 mmol) and phenol **35** (0.5 g, 2.6 mol), Pd(PPh₃)₄ (0.14 g, 0.52 mmol) and CuI (0.02 g, 0.13 mmol) were dissolved in THF(10 mL) and NEt₃(10 mL). heated to reflux and stirred for 4 h after which saturated NH₄Cl solution (5 mL) was added, the reaction was diluted with 10 mL of water then extracted into EtOAc (3 x 10 mL). The combined organic extracts were dried over anhydrous MgSO₄, filtered, and then concentrated cold under reduced pressure to a crude solid . The crude material was purified via silica gel chromatography to furnish of a light yellow solid **36** (0.58 g, 71%). ¹H NMR (400 MHz, CDCl₃) δ 7.12 – 7.02 (m, 2H), 6.81 (d, *J* = 8.3 Hz, 1H), 6.75 (s, 2H), 5.69 (s, 1H), 3.89 (s, 3H), 3.87 (s, 6H). 3.86 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 153.0, 147.0, 145.3, 138.6, 124.2, 118.5, 117.4, 115.9, 110.5, 108.6, 88.4, 87.8, 60.9, 56.1. IR (film): 3478, 2932, 2864, 1679, 1501, 1441, 1388, 1257, 1094, 660 cm⁻¹; HRMS *m/z* (ESI) calcd for C₁₈H₁₈O₅Na (M + Na)⁺: 337.1046, found 337.1050.

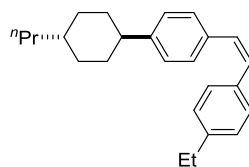
3. General procedure for the synthesis of *cis*-deuterated olefin



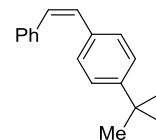
Reaction conditions A: The 25 mL Schlenk tube containing a stirring bar was added B₂nep₂ (68 mg, 0.3 mmol, 1.5 equiv). The tube was introduced in nitrogenfilled glovebox, and CuTc (3.8 mg, 10 mol %), Xantphos (11.6 mg, 10 mol %) and LiO^tBu (48.0 mg, 3.0 equiv) were added. The tube with the mixture was taken out of the glovebox. Then DMF (1mL) and H₂O (14 μL, 4.0 equiv)was added under argon. The formed mixture was stirred at 60 °C under Ar for 24 h as monitored by TLC and GC-MS. The solution was then cooled to room temperature. The crude product was purified by flash column chromatography on silica gel (PE/AcOEt) to afford the corresponding products.



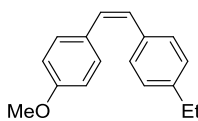
2b', 84% (> 99: 1)



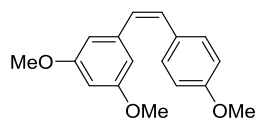
3b', 81% (> 99: 1)



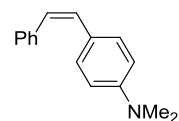
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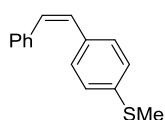
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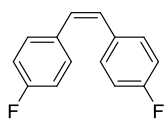
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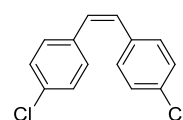
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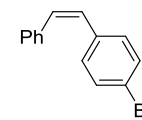
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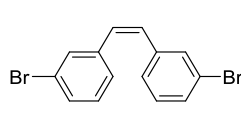
9b', 88% (> 99: 1)



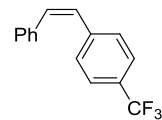
10b', 84% (> 99: 1)



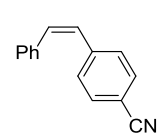
11b', 90% (> 99: 1)



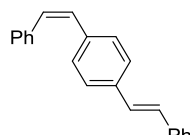
12b', 80% (> 99: 1)



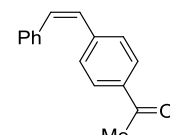
13b', 68% (> 99: 1)



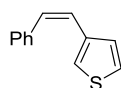
14b', 74% (> 99: 1)



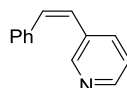
15b', 86% (> 99: 1)



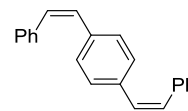
16b', 70% (> 99: 1)



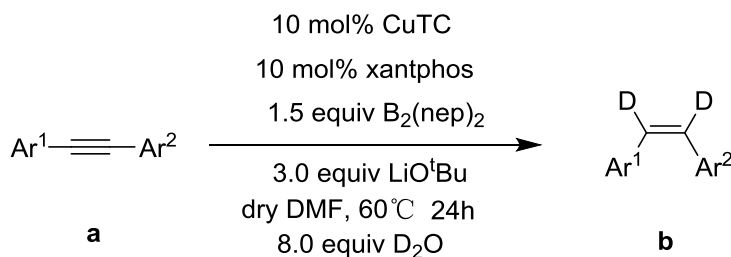
17b', 77% (> 99: 1)



18b', 73% (> 99: 1)

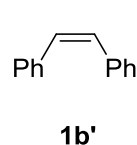


19b', 82% (> 99: 1)

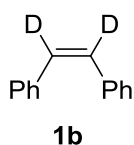


Reaction conditions B: The 25 mL Schlenk tube containing a stirring bar was introduced in nitrogen-filled glovebox was added B₂nep₂ (68 mg, 0.3 mmol, 1.5 equiv), CuTc (3.8 mg, 10 mol %), Xantphos (11.6 mg, 10 mol %), LiO^tBu (48.0 mg, 3.0 equiv) and dry DMF (1mL), D₂O (28 μL, 8.0 equiv). The formed mixture was stirred at 60 °C under Ar for 24 h as monitored by TLC and GC-MS. The solution was then cooled to room temperature. The crude product was purified by flash column chromatography on silica gel (PE/AcOEt) to afford the corresponding products.

(Z)-1,2-Diphenylethene (1b')^[18] & **(Z)-1,2-Diphenylethene-1,2-d2 (1b)**^[19]



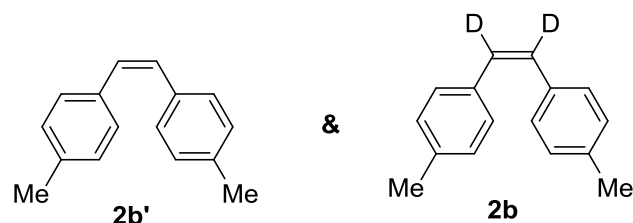
&



According to reaction conditions A, 0.2 mmol scale **1b'** was prepared from the 1,2-diphenylethyne (35.6 mg, 0.2 mmol). The formed mixture was stirred at 60 °C under Ar for 24 h as monitored by TLC and GC-MS. The solution was then cooled to room temperature, and the crude product was purified by flash column chromatography on silica gel to afford 31.4 mg (87%) of **1b'** as a colourless oil: ¹H NMR (500 MHz, CDCl₃) δ 7.32 – 7.20 (m, 10H), 6.64 (s, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 137.2, 130.2, 128.8, 128.2, 127.1. According to reaction conditions B, 0.2 mmol scale **1b** was prepared from the 1,2-diphenylethyne (35.6 mg, 0.2 mmol). The formed mixture was stirred at 60 °C under Ar for 24 h as monitored by TLC and GC-MS. The solution was then cooled to room temperature, and the crude product was purified by flash column chromatography on silica gel to afford 31.7 mg (84%) of **1b** as a colourless oil: ¹H NMR (400 MHz, CDCl₃) δ 7.28 – 6.99 (m, 10H), 6.52 (s, 0.08H). IR (film): 3022, 1739, 1492, 1443, 1024, 919, 750, 696 cm⁻¹; EI-MS (m/z, relative intensity): 182 (M⁺, 100), 167 (28), 153 (13), 116 (5), 103 (6), 90 (12), 77

(10), 52 (8). According to ^1H NMR, 94% deuterium incorporation at each vinylic position was generated in product **1b**.

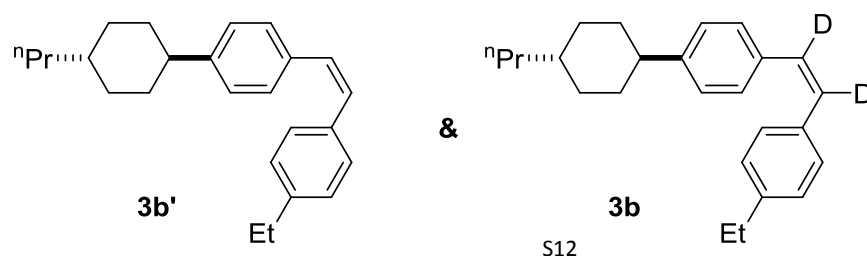
(Z)-1,2-Di-p-tolylene (2b') ^[20] & **(Z)-1,2-Di-p-tolylene-1,2-d2 (2b)**



According to reaction conditions **A**, 0.2 mmol scale **2b'** was prepared from the 1,2-di-p-tolylyne (41.2 mg, 0.2

mmol). The formed mixture was stirred at 60 °C under Ar for 24 h as monitored by TLC and GC-MS. The solution was then cooled to room temperature, and the crude product was purified by flash column chromatography on silica gel to afford 33.6 mg(81%) of **2b'** as a White solid. ^1H NMR (400 MHz, CDCl_3) δ 7.19 (d, $J = 8.1$ Hz, 4H), 7.06 (d, $J = 7.9$ Hz, 4H), 6.54 (s, 2H), 2.34 (s, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 136.7, 134.5, 129.5, 128.9, 128.7, 21.2. According to reaction conditions **B**, 0.2 mmol scale **2b** was prepared from the 1,2-di-p-tolylyne (41.2 mg, 0.2 mmol). The formed mixture was stirred at 60 °C under Ar for 24 h as monitored by TLC and GC-MS. The solution was then cooled to room temperature, and the crude product was purified by flash column chromatography on silica gel to afford 34 mg(81%) of **2b** as a White solid. ^1H NMR (400 MHz, CDCl_3) δ 7.18 (d, $J = 8.1$ Hz, 4H), 7.05 (d, $J = 7.9$ Hz, 4H), 6.53 (s, 0.02H) 2.33 (s, 6H). IR (film): 3012, 1739, 1511, 1443, 822, 481 cm^{-1} ; EI-MS (m/z, relative intensity): 210 (M^+ , 100), 195 (92), 178 (88), 165 (10), 152 (4), 115 (12), 89 (10), 65 (6). According to ^1H NMR, 99% deuterium incorporation at each vinylic position was generated in product **2b**.

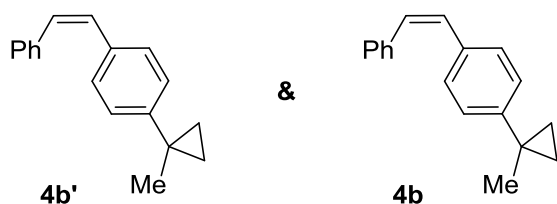
1-Ethyl-4-((Z)-4-(4-propylcyclohexyl)styryl)benzene (3b') & **1-Ethyl-4-((Z)-2-(4-(4-propylcyclohexyl)phenyl)vinyl-1,2-d2)benzene (3b)**



According to reaction conditions **A**, 0.2 mmol scale **3b'**

was prepared from the 1-ethyl-4-((4-((1*r*,4*s*)-4-propylcyclohexyl)phenyl)ethynyl)benzene (66.1 mg, 0.2 mmol). The formed mixture was stirred at 60 °C under Ar for 24 h as monitored by TLC and GC-MS. The solution was then cooled to room temperature, and the crude product was purified by flash column chromatography on silica gel to afford 66.1 mg (81%) of **3b'** as a White solid. **¹H NMR (500 MHz, CDCl₃)** δ 7.27 (dd, *J* = 8.3, 2.2 Hz, 4H), 7.18 – 7.00 (m, 4H), 6.57 (s, 2H), 2.68 (q, *J* = 7.6 Hz, 2H), 2.56 – 2.39 (m, 1H), 1.93 (td, *J* = 15.0, 3.1 Hz, 4H), 1.54 – 1.37 (m, 4H), 1.34 (m, 1H), 1.31 – 1.23 (m, 5H), 1.15 – 1.04 (m, 2H), 0.97 (t, *J* = 7.3 Hz, 3H). **¹³C NMR (126 MHz, CDCl₃)** δ 146.8, 143.0, 134.8, 134.8, 129.5, 129.4, 128.8, 128.7, 127.6, 126.6, 44.3, 39.7, 37.0, 34.2, 33.5, 28.6, 20.0, 15.4, 14.4. According to reaction conditions **B**, 0.2 mmol scale **3b** was prepared from the 1-ethyl-4-((4-((1*r*,4*s*)-4-propylcyclohexyl)phenyl)ethynyl)benzene (66.1 mg, 0.2 mmol). The formed mixture was stirred at 60 °C under Ar for 24 h as monitored by TLC and GC-MS. The solution was then cooled to room temperature, and the crude product was purified by flash column chromatography on silica gel to afford 66.1 mg (85%) of **3b** as a White solid. **¹H NMR (400 MHz, CDCl₃)** δ 7.27 (dd, *J* = 8.2, 1.8 Hz, 4H), 7.12 (d, *J* = 8.1 Hz, 4H), 6.56 (s, 0.06H), 2.68 (q, *J* = 7.6 Hz, 2H), 2.48 (tt, *J* = 12.2, 3.2 Hz, 1H), 2.01 – 1.86 (m, 4H), 1.55 – 1.38 (m, 4H), 1.37 – 1.32 (m, 1H), 1.32 – 1.24 (m, 5H), 1.17 – 1.03 (m, 2H), 0.96 (t, *J* = 7.3 Hz, 3H). **IR (film):** 2922, 2852, 1695, 1607, 1511, 1452, 1274, 1111, 961, 880, 830, 533 cm⁻¹; **EI-MS (m/z, relative intensity):** 334 (M⁺, 100), 247 (22), 234 (16), 219 (14), 207 (10), 179 (10), 141 (8), 129 (12), 115 (4), 91 (8), 55 (4). According to ¹H NMR, 97% deuterium incorporation at each vinylic position was generated in product **3b**.

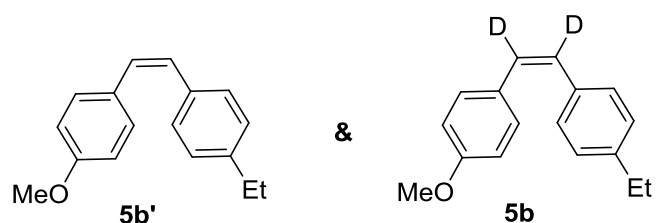
(Z)-1-Ethyl-4-(4-methoxystyryl)benzene (4b') & (Z)-1-(1-methylcyclopropyl)-4-(2-phenylvinyl-1,2-d₂)benzene (4b)



According to reaction conditions **A**, 0.2 mmol scale **4b'** was prepared from the 1-(1-methylcyclopropyl)-4-(phenylethynyl)benzene (46.4 mg, 0.2 mmol). The

formed mixture was stirred at 60 °C under Ar for 24 h as monitored by TLC and GC-MS. The solution was then cooled to room temperature, and the crude product was purified by flash column chromatography on silica gel to afford 42.1 mg (90%) of **4b'** as a White solid. ¹H NMR (400 MHz, CDCl₃) δ 7.32 – 7.21 (m, 5H), 7.21 – 7.17 (m, 2H), 7.13 – 7.06 (m, 2H), 6.57 (s, 2H), 1.41 (s, 3H), 0.87 (q, *J* = 4.2 Hz, 2H), 0.75 (q, *J* = 6.2, 4.2 Hz, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 146.1, 137.5, 134.1, 130.0, 129.5, 128.8, 128.7, 128.2, 127.0, 126.1, 25.2, 19.2, 16.1. According to reaction conditions **B**, 0.2 mmol scale **4b** was prepared from the 1-(1-methylcyclopropyl)-4-(phenylethynyl) benzene (46.4 mg, 0.2 mmol). The formed mixture was stirred at 60 °C under Ar for 24 h as monitored by TLC and GC-MS. The solution was then cooled to room temperature, and the crude product was purified by flash column chromatography on silica gel to afford 42.5 mg (90%) of **4b** as a White solid. ¹H NMR (400 MHz, CDCl₃) δ 7.31 – 7.18 (m, 5H), 7.17 – 7.14 (m, 2H), 7.08 – 7.04 (m, 2H), 6.53 (s, 0.1H), 1.37 (s, 3H), 0.84 (q, *J* = 4.2 Hz, 2H), 0.71 (q, *J* = 6.2, 4.2 Hz, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 146.1, 137.4, 134.1, 128.8, 128.7, 128.2, 127.0, 126.1, 25.2, 19.2, 16.1. IR (film): 3012, 1739, 1511, 1443, 822, 481 cm⁻¹; EI-MS (*m/z*, relative intensity): 210 (M⁺, 100), 195 (92), 178 (88), 165 (10), 152 (4), 115 (12), 89 (10), 65 (6). According to ¹H NMR, 95% deuterium incorporation at each vinylic position was generated in product **4b**.

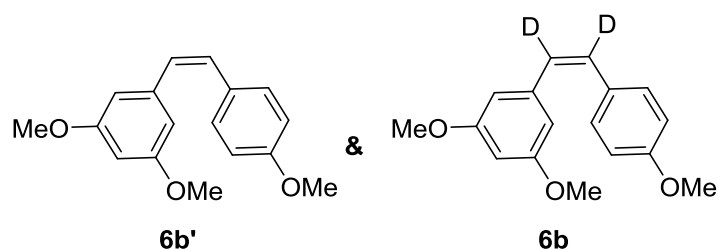
(Z)-1-Ethyl-4-(4-methoxystyryl)benzene (5b') & **(Z)-1-Ethyl-4-(2-(4-methoxyphenyl)vinyl-1,2-d₂)benzene (5b)**



According to reaction conditions **A**, 0.2 mmol scale **5b'** was prepared from the 1-ethyl-4-((4-methoxyphenyl)ethynyl)benzene (47.2 mg, 0.2 mmol). The formed mixture was stirred at 60 °C under Ar for 24 h as monitored by TLC and GC-MS. The solution was then cooled to room temperature, and the crude product was purified by flash column chromatography on silica gel to afford 40.8 mg (86%) of **5b'** as a White solid. ¹H NMR (400 MHz, CDCl₃) δ 7.32 –

7.19 (m, 4H), 7.11 (d, $J = 8.3$ Hz, 2H), 6.90 – 6.73 (m, 2H), 6.52 (s, 2H), 3.82 (s, 3H), 2.66 (q, $J = 7.6$ Hz, 2H), 1.27 (t, $J = 7.6$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 158.6, 143.0, 134.8, 130.0, 129.9, 129.1, 128.7, 127.7, 113.5, 55.1, 28.6, 15.4. According to reaction conditions **B**, 0.2 mmol scale **5b** was prepared from the 1-ethyl-4-((4-methoxyphenyl)ethynyl)benzene (47.2 mg, 0.2 mmol). The formed mixture was stirred at 60 °C under Ar for 24 h as monitored by TLC and GC-MS. The solution was then cooled to room temperature, and the crude product was purified by flash column chromatography on silica gel to afford 41.2 mg (86%) of **5b** as a White solid. ^1H NMR (400 MHz, CDCl_3) δ 7.19 – 7.08 (m, 4H), 6.98 (d, $J = 8.3$ Hz, 2H), 6.83 – 6.53 (m, 2H), 6.40 (s, 0.12H), 3.70 (s, 3H), 2.53 (q, $J = 7.6$ Hz, 2H), 1.14 (t, $J = 7.6$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 158.6, 143.0, 134.7, 130.1, 128.7, 127.7, 113.5, 55.2, 28.6, 15.4. IR (film): 2963, 2363, 1647, 1604, 1548, 1247, 1174, 1032, 844 cm^{-1} ; EI-MS (m/z , relative intensity): 240 (M^+ , 100), 225 (86), 211 (18), 196 (14), 180 (18), 167 (26), 154 (18), 123 (24), 112 (38), 90 (28), 77 (4). According to ^1H NMR, 94% deuterium incorporation at each vinylic position was generated in product **5b**.

(Z)-1,3-Dimethoxy-5-(4-methoxystyryl)benzene (6b')^[21] & (Z)-1,3-Dimethoxy-5-(2-(4-methoxyphenyl)vinyl-1,2-d₂)benzene (6b)

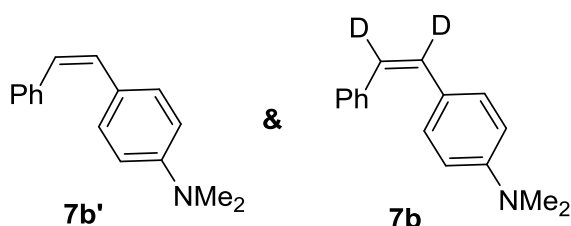


According to reaction conditions **A**, 0.2 mmol scale **6b'** was prepared from the 1,3-dimethoxy-5-((4-methoxyphenyl)ethynyl)

benzene (53.6 mg, 0.2 mmol). The formed mixture was stirred at 60 °C under Ar for 24 h as monitored by TLC and GC-MS. The solution was then cooled to room temperature, and the crude product was purified by flash column chromatography on silica gel to afford 48 mg (89%) of **6b'** as a light yellow solid. ^1H NMR (400 MHz, CDCl_3) δ 7.25 – 7.20 (m, 2H), 6.85 – 6.71 (m, 2H), 6.54 (d, $J = 12.3$ Hz, 1H), 6.45 (dd, $J = 7.2, 4.8$ Hz, 3H), 6.33 (t, $J = 2.3$ Hz, 1H), 3.79 (s, 3H), 3.68 (s, 6H). ^{13}C

NMR (101 MHz, CDCl₃) δ 160.5, 158.7, 139.4, 130.2, 130.1, 129.5, 128.6, 113.5, 106.6, 99.6, 55.2. According to reaction conditions **B**, 0.2 mmol scale **6b** was prepared from the 1,3-dimethoxy-5-((4-methoxyphenyl)ethynyl)benzene (53.6 mg, 0.2 mmol). The formed mixture was stirred at 60 °C under Ar for 24 h as monitored by TLC and GC-MS. The solution was then cooled to room temperature, and the crude product was purified by flash column chromatography on silica gel to afford 46.7 mg (86%) of **6b** as a light yellow solid. **¹H NMR (400 MHz, CDCl₃)** δ 7.33 – 7.10 (m, 2H), 6.78 (d, *J* = 8.8 Hz, 2H), 6.54 (d, *J* = 7.6 Hz, 1H), 6.45 (d, *J* = 2.3 Hz, 2H), 6.33 (t, *J* = 2.3 Hz, 1H), 3.68 (s, 6H). **IR (film)**: 3667, 2958, 1724, 1592, 1507, 1457, 1250, 1201, 1153, 1034, 841, 754 cm⁻¹ **HRMS m/z (ESI) calcd for C₁₇H₁₆D₂NaO₃ (M + Na)⁺**: 295.1274, found 295.1269. According to ¹H NMR, 94% deuterium incorporation at each vinylic position was generated in product **6b**.

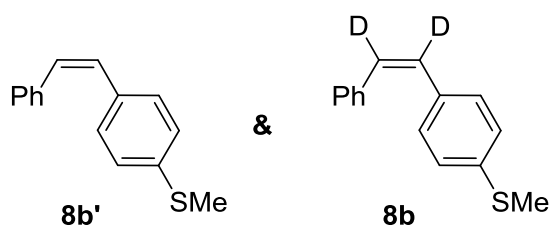
(Z)-N,N-Dimethyl-4-styrylaniline (7b')^[22] & (Z)-N,N-Dimethyl-4-(2-phenylvinyl-1,2-d₂)aniline (7b)



According to reaction conditions **A**, 0.2 mmol scale **7b'** was prepared from the N,N-dimethyl-4-(phenylethynyl)aniline (44.2 mg, 0.2 mmol). The formed mixture was stirred at 60 °C under Ar for 24 h as monitored by TLC and GC-MS. The solution was then cooled to room temperature, and the crude product was purified by flash column chromatography on silica gel to afford 31.5 mg (71%) of **7b'** as a light yellow solid. **¹H NMR (400 MHz, CDCl₃)** δ 7.37 – 7.30 (m, 2H), 7.27 – 7.21 (m, 2H), 7.20 – 7.14 (m, 3H), 6.56 (d, *J* = 8.9 Hz, 2H), 6.49 (d, *J* = 12.2 Hz, 1H), 6.41 (d, *J* = 12.2 Hz, 1H), 2.93 (s, 6H). **¹³C NMR (101 MHz, CDCl₃)** δ 149.5, 138.3, 130.2, 129.9, 128.8, 128.1, 126.8, 126.5, 111.8, 40.4. According to reaction conditions **B**, 0.2 mmol scale **7b** was prepared from the N,N-dimethyl-4-(phenylethynyl)aniline (44.2 mg, 0.2 mmol). The formed mixture was stirred at 60 °C under Ar for 24 h as monitored by TLC and GC-MS. The solution was then cooled to room temperature, and the crude product was purified by flash column chromatography on silica gel to afford 31.5 mg

(70%) of **7b** as a light yellow solid. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.33 (m, 2H), 7.25 – 7.22 (m, 2H), 7.18 – 7.14 (m, 3H), 6.57 (d, $J = 8.8$ Hz, 2H), 6.48 (s, 0.06H), 6.41 (s, 0.06H), 2.93 (s, 6H). **IR (film)**: 3693, 2922, 2653, 1815, 1518, 1266, 1022, 746 cm^{-1} . **HRMS m/z (ESI) calcd for $\text{C}_{16}\text{H}_{16}\text{D}_2\text{N}$ ($\text{M} + \text{H}$) $^+$** : 226.1559, found 226.1557. According to $^1\text{H NMR}$, 94% deuterium incorporation at each vinylic position was generated in product **7b**.

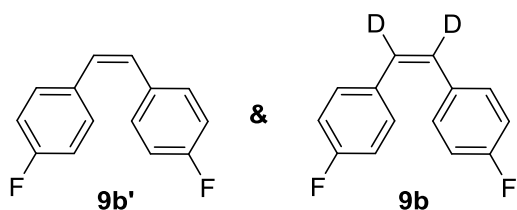
(Z)-methyl(4-styrylphenyl)sulfane (8b') & (Z)-Methyl(4-(2-phenylvinyl-1,2-d2)phenyl)sulfane (8b)



According to reaction conditions **A**, 0.2 mmol scale **8b'** was prepared from the methyl(4-(phenylethynyl)phenyl)sulfane (44.8 mg 0.2 mmol). The formed mixture

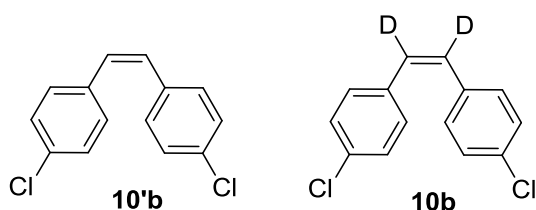
was stirred at 60 $^{\circ}\text{C}$ under Ar for 24 h as monitored by TLC and GC-MS. The solution was then cooled to room temperature, and the crude product was purified by flash column chromatography on silica gel to afford 37 mg (81%) of **8b'** as a White solid. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.27 – 7.21 (m, 4H), 7.21 – 7.18 (m, 1H), 7.17 – 7.13 (m, 2H), 7.12 – 7.05 (m, 2H), 6.56 (d, $J = 12.2$ Hz, 1H), 6.51 (d, $J = 12.2$ Hz, 1H), 2.45 (s, 3H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 137.3, 137.2, 133.9, 130.0, 129.5, 129.3, 128.8, 128.3, 127.1, 126.0, 15.6. According to reaction conditions **B**, 0.2 mmol scale **8b** was prepared from the methyl(4-(phenylethynyl)phenyl)sulfane (44.8 mg, 0.2 mmol). The formed mixture was stirred at 60 $^{\circ}\text{C}$ under Ar for 24 h as monitored by TLC and GC-MS. The solution was then cooled to room temperature, and the crude product was purified by flash column chromatography on silica gel to afford 37.2 mg (81%) of **8b** as a White solid. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.27 – 7.21 (m, 4H), 7.21 – 7.18 (m, 1H), 7.17 – 7.13 (m, 2H), 7.12 – 7.05 (m, 2H), 6.55 (s, 0.05H), 6.51 (s, 0.05H), 2.44 (s, 3H). **IR (film)**: 3693, 3021, 1753, 1491, 1263, 1026, 1022, 746 cm^{-1} ; **EI-MS (m/z, relative intensity)**: 228 (M^+ , 100), 213 (14), 180 (78), 169 (22), 105 (10), 90 (8), 77 (4). According to $^1\text{H NMR}$, 96% deuterium incorporation at each vinylic position was generated in product **8b**.

(Z)-1,2-Bis(4-fluorophenyl)ethane (9b')^[22] & (Z)-1,2-Bis(4-fluorophenyl)ethene-1,2-d₂ (9b)



According to reaction conditions **A**, 0.2 mmol scale **9b'** was prepared from the 1,2-bis(4-fluorophenyl)ethyne (42.8 mg, 0.2 mmol). The formed mixture was stirred at 60 °C under Ar for 24 h as monitored by TLC and GC-MS. The solution was then cooled to room temperature, and the crude product was purified by flash column chromatography on silica gel to afford 37.7 mg (88%) of **9b'** as a colourless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.23 – 7.14 (m, 4H), 6.98 – 6.86 (m, 4H), 6.55 (s, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 161.8 (d, *J* = 246.9 Hz), 132.9 (d, *J* = 3.4 Hz), 130.5 (d, *J* = 7.9 Hz), 129.1 (d, *J* = 1.0 Hz), 115.2 (d, *J* = 21.4 Hz). ¹⁹F NMR (377 MHz, CDCl₃) δ -114.46. According to reaction conditions **B**, 0.2 mmol scale **9b** was prepared from the 1,2-bis(4-fluorophenyl)ethyne (42.8 mg, 0.2 mmol). The formed mixture was stirred at 60 °C under Ar for 24 h as monitored by TLC and GC-MS. The solution was then cooled to room temperature, and the crude product was purified by flash column chromatography on silica gel to afford 36.6 mg (84%) of **9b** as a colourless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.23 – 7.15 (m, 4H), 7.02 – 6.81 (m, 4H), 6.54 (s, 0.1H). IR (film): 2923, 2326, 1647, 1604, 1508, 1247, 1174, 1032, 844 cm⁻¹; EI-MS (*m/z*, relative intensity): 218 (M⁺, 100), 197 (30), 185 (10), 171 (4), 121 (16), 108 (6), 75 (4). According to ¹H NMR, 95% deuterium incorporation at each vinylic position was generated in product **9b**.

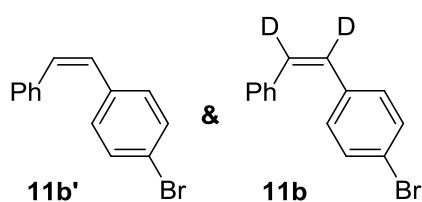
(Z)-1,2-Bis(4-chlorophenyl)ethane (10b')^[22] & (Z)-1,2-Bis(4-chlorophenyl)ethene-1,2-d₂ (10b)



According to reaction conditions **A**, 0.2 mmol scale **10b'** was prepared from the 1,2-bis(4-chlorophenyl)ethyne (49.4 mg, 0.2 mmol). The formed mixture was stirred at 60 °C under Ar for 24 h as monitored by TLC and GC-MS. The solution was

then cooled to room temperature, and the crude product was purified by flash column chromatography on silica gel to afford 41.7 mg (84%) of **10b'** as a White solid. ^1H NMR (400 MHz, CDCl_3) δ 7.23 – 7.18 (m, 4H), 7.17 – 7.12 (m, 4H), 6.56 (s, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 135.2, 133.0, 130.1, 129.6, 128.5. According to reaction conditions **B**, 0.2 mmol scale **10b** was prepared from the 1,2-bis(4-chlorophenyl)ethyne (49.4 mg, 0.2 mmol). The formed mixture was stirred at 60 °C under Ar for 24 h as monitored by TLC and GC-MS. The solution was then cooled to room temperature, and the crude product was purified by flash column chromatography on silica gel to afford 42.2 mg (84%) of **10b** as a White solid. ^1H NMR (400 MHz, CDCl_3) δ 7.23 – 7.19 (m, 4H), 7.18 – 7.13 (m, 4H), 6.56 (s, 0.08H). ^{13}C NMR (101 MHz, CDCl_3) δ 135.2, 133.0, 130.1, 128.5. IR (film): 3063, 2326, 1723, 1587, 1487, 1091, 1013, 849, 471 cm^{-1} ; EI-MS (m/z, relative intensity): 251 (M^+ , 50), 215 (20), 180 (100), 153 (6), 137 (4), 106 (8), 89 (14), 77 (6). According to ^1H NMR, 96% deuterium incorporation at each vinylic position was generated in product **10b**.

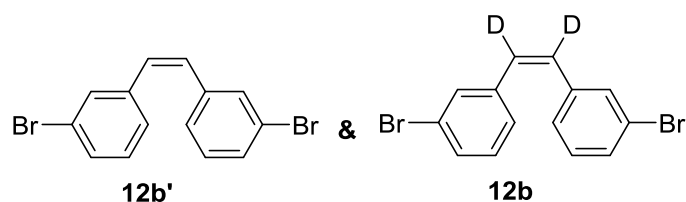
(Z)-1-Bromo-4-styrylbenzene (11b')^[23] & (Z)-1-Bromo-4-(2-phenylvinyl-1,2-d₂)benzene (11b)



According to reaction conditions **A**, 0.2 mmol scale **11b'** was prepared from the 1-bromo-4-(phenylethynyl)benzene (51.4 mg, 0.2 mmol). The formed mixture was stirred at 60 °C under Ar for 24 h as monitored by TLC and GC-MS. The solution was then cooled to room temperature, and the crude product was purified by flash column chromatography on silica gel to afford 46.2 mg (90%) of **11b'** as a White solid. ^1H NMR (400 MHz, CDCl_3) δ 7.38 (d, J = 8.4 Hz, 2H), 7.33 – 7.21 (m, 5H), 7.15 (d, J = 8.3 Hz, 2H), 6.68 (d, J = 12.2 Hz, 1H), 6.54 (d, J = 12.2 Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 136.8, 136.1, 131.3, 131.0, 130.5, 128.9, 128.8, 128.3, 127.3, 120.9. According to reaction conditions **B**, 0.2 mmol scale **11b** was prepared from the 1-bromo-4-(phenylethynyl)benzene (51.4 mg, 0.2 mmol). The formed mixture was

stirred at 60 °C under Ar for 24 h as monitored by TLC and GC-MS. The solution was then cooled to room temperature, and the crude product was purified by flash column chromatography on silica gel to afford 45.4 mg (87%) of **11b** as a White solid. ¹H NMR (400 MHz, CDCl₃) δ 7.25 (d, *J* = 8.6 Hz, 2H), 7.17 – 7.11 (m, 5H), 7.03 (d, *J* = 8.6 Hz, 2H), 6.55 (s, 0.05H), 6.42 (s, 0.05H). IR (film): 3021, 1484, 1070, 841, 744, 699, 446 cm⁻¹; EI-MS (*m/z*, relative intensity): 261 (M⁺, 36), 180 (100), 153 (12), 128 (4), 102 (6), 90 (18), 77 (10). According to ¹H NMR, 95% deuterium incorporation at each vinylic position was generated in product **11b**.

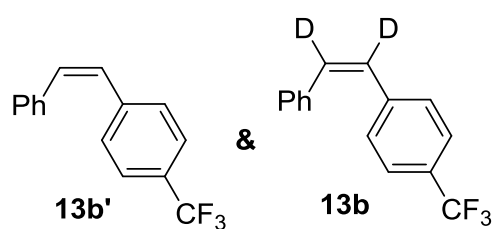
(Z)-1,2-Bis(3-bromophenyl)ethane (12b')^[24] & (Z)-1,2-Bis(3-bromophenyl)ethane -1,2-d₂ (12b)



According to reaction conditions **A**, 0.2 mmol scale **12b'** was prepared from the 1,2-bis(3-bromophenyl)ethyne

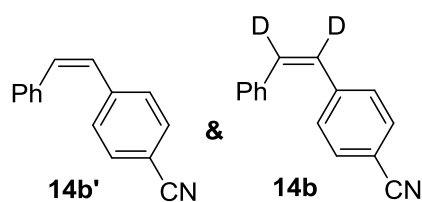
(67.2 mg, 0.2 mmol). The formed mixture was stirred at 60 °C under Ar for 24 h as monitored by TLC and GC-MS. The solution was then cooled to room temperature, and the crude product was purified by flash column chromatography on silica gel to afford 54.2 mg (80%) of **12b'** as a White solid. ¹H NMR (400 MHz, CDCl₃) δ 7.30 – 7.25 (m, 4H), 7.02 – 6.98 (m, 4H), 6.46 (s, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 135.6, 133.0, 131.7, 131.5, 130.4, 129.7, 121.2. According to reaction conditions **B**, 0.2 mmol scale **12b** was prepared from the 1,2-bis(3-bromophenyl)ethyne (67.2 mg, 0.2 mmol). The formed mixture was stirred at 60 °C under Ar for 24 h as monitored by TLC and GC-MS. The solution was then cooled to room temperature, and the crude product was purified by flash column chromatography on silica gel to afford 54.4 mg (80%) of **12b** as a White solid. ¹H NMR (400 MHz, CDCl₃) δ 7.42 – 7.32 (m, 4H), 7.16 – 7.06 (m, 4H), 6.56 (s, 1H). IR (film): 3066, 1757, 1070, 1556, 766 cm⁻¹; EI-MS (*m/z*, relative intensity): 340 (M⁺, 20), 259 (6), 180 (100), 153 (8), 129 (3), 90 (18), 77 (6). According to ¹H NMR, 94% deuterium incorporation at each vinylic position was generated in product **12b**.

(Z)-1-Styryl-4-(trifluoromethyl)benzene (13b')^[23] & (Z)-1-(2-phenylvinyl-1,2-d2)-4-(trifluoromethyl)benzene (13b)



According to reaction conditions **A**, 0.2 mmol scale **13b'** was prepared from the 1-(phenylethynyl)-4-(trifluoromethyl)benzene (49.2 mg, 0.2 mmol). The formed mixture was stirred at 60 °C under Ar for 24 h as monitored by TLC and GC-MS. The solution was then cooled to room temperature, and the crude product was purified by flash column chromatography on silica gel to afford 34 mg (68%) of **13b'** as a colourless oil. ¹H NMR (500 MHz, CDCl₃) δ 7.50 (d, *J* = 8.2 Hz, 2H), 7.36 (d, *J* = 8.5 Hz, 2H), 7.32 – 7.20 (m, 5H), 6.75 (d, *J* = 12.2 Hz, 1H), 6.62 (d, *J* = 12.2 Hz, 1H). ¹³C NMR (126 MHz, CDCl₃) δ 140.9, 136.5, 132.3, 129.1, 128.8, 128.7, 128.4, 125.4 (q, *J* = 3.8 Hz), 124.2 (q, *J* = 272.2 Hz). According to reaction conditions **B**, 0.2 mmol scale **13b** was prepared from the 1-(phenylethynyl)-4-(trifluoromethyl)benzene (49.2 mg, 0.2 mmol). The formed mixture was stirred at 60 °C under Ar for 24 h as monitored by TLC and GC-MS. The solution was then cooled to room temperature, and the crude product was purified by flash column chromatography on silica gel to afford 35.5 mg (71%) of **13b** as a colourless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.39 (d, *J* = 8.1 Hz, 2H), 7.26 (d, *J* = 8.0 Hz, 2H), 7.20 – 7.11 (m, 5H), 6.64 (s, 0.05H), 6.51 (s, 0.05H). IR (film): 3059, 1723, 1559, 1325, 1267, 1124, 752 cm⁻¹; EI-MS (*m/z*, relative intensity): 250 (M⁺, 100), 229 (10), 209 (8), 181 (92), 153 (4), 90 (8), 77 (6). According to ¹H NMR, 95% deuterium incorporation at each vinylic position was generated in product **13b**.

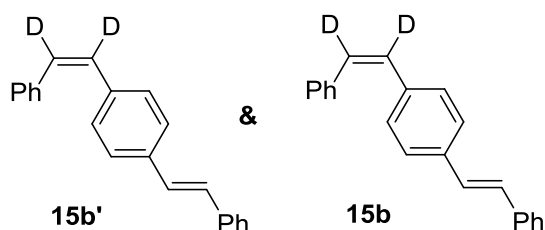
(Z)-4-Styrylbenzotrile (14b')^[25] & (Z)-4-(2-phenylvinyl-1,2-d2)benzotrile (14b)



According to reaction conditions **A**, 0.2 mmol scale **14b'** was prepared from the 4-(phenylethynyl)benzotrile (40.6 mg, 0.2 mmol). The formed mixture was stirred at 60 °C under Ar

for 24 h as monitored by TLC and GC-MS. The solution was then cooled to room temperature, and the crude product was purified by flash column chromatography on silica gel to afford 30.5 mg (74%) of **14b'** as a light yellow solid. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.52 (d, $J = 8.4$ Hz, 2H), 7.34 (d, $J = 8.1$ Hz, 2H), 7.30 – 7.26 (m, 3H), 7.23 – 7.20 (m, 2H), 6.79 (d, $J = 12.2$ Hz, 1H), 6.60 (d, $J = 12.2$ Hz, 1H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 142.0, 136.2, 133.3, 132.0, 129.5, 128.7, 128.5, 128.3, 127.8, 118.9, 110.4. According to reaction conditions **B**, 0.2 mmol scale **14b** was prepared from the 4-(phenylethynyl)benzotrile (40.6 mg, 0.2 mmol). The formed mixture was stirred at 60 °C under Ar for 24 h as monitored by TLC and GC-MS. The solution was then cooled to room temperature, and the crude product was purified by flash column chromatography on silica gel to afford 30.7 mg (74%) of **14b** as a light yellow solid. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.50 (d, $J = 8.4$ Hz, 2H), 7.32 (d, $J = 8.4$ Hz, 2H), 7.26 – 7.24 (m, 3H), 7.22 – 7.18 (m, 2H), 6.76 (s, 0.05H), 6.57 (s, 0.05H). IR (film): 3642, 2921, 2224, 1602, 1266, 833, 741 cm^{-1} ; EI-MS (m/z , relative intensity): 207 (M^+ , 100), 190 (46), 177 (18), 165 (16), 151 (8), 102 (8), 77 (6). According to $^1\text{H NMR}$, 95% deuterium incorporation at each vinylic position was generated in product **14b**.

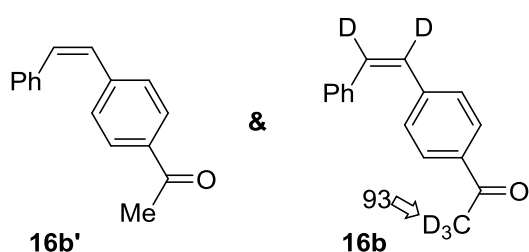
1-((E)-styryl)-4-((Z)-styryl)benzene (15b')^[26] & 1-((Z)-2-phenylvinyl-1,2-d₂)-4-((E)-styryl)benzene (15b)



According to reaction conditions **A**, 0.2 mmol scale **15b'** was prepared from the (*E*)-1-(phenylethynyl)-4-styryl benzene (56 mg, 0.2 mmol). The formed mixture was stirred at 60 °C under Ar for 24 h as monitored by TLC and GC-MS. The solution was then cooled to room temperature, and the crude product was purified by flash column chromatography on silica gel to afford 48.5 mg (86%) of **15b'** as a White solid. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.49 (d, $J = 7.4$ Hz, 2H), 7.39 – 7.31 (m, 4H), 7.30 – 7.22 (m, 8H), 7.12 – 7.01 (q, $J = 1.6$ Hz, 2H), 6.64 – 6.54 (q, $J = 4.8$ Hz, 2H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 137.3, 136.6, 136.1, 130.3, 129.9, 129.3, 128.9,

128.7, 128.6, 128.3, 128.3, 127.6, 127.2, 126.5, 126.3, According to reaction conditions **B**, 0.2 mmol scale **15b** was prepared from the (*E*)-1-(phenylethynyl)-4-styryl benzene (56 mg, 0.2 mmol). The formed mixture was stirred at 60 °C under Ar for 24 h as monitored by TLC and GC-MS. The solution was then cooled to room temperature, and the crude product was purified by flash column chromatography on silica gel to afford 48.8 mg (86%) of **15b** as a White solid. ¹H NMR (400 MHz, CDCl₃) δ 7.49 (d, *J* = 7.5 Hz, 2H), 7.40 – 7.32 (m, 4H), 7.31 – 7.21 (m, 8H), 7.13 – 7.00 (q, *J* = 1.6 Hz, 2H), 6.60 (s, 0.06H), 6.57 (s, 0.06H). IR (film): 3627, 2921, 2851, 1673, 1266, 964, 874, 823, 769, 699, 520 cm⁻¹; EI-MS (*m/z*, relative intensity): 284 (M⁺, 100), 267 (10), 241 (8), 204 (20), 192 (20), 178 (18), 142 (10), 126 (8), 103 (8), 77 (4). According to ¹H NMR, 94% deuterium incorporation at each vinylic position was generated in product **15b**.

(*Z*)-1-(4-styrylphenyl)ethan-1-one (**16b'**)^[27] & (*Z*)-1-(4-(2-phenylvinyl-1,2-d₂phenyl)ethan-1-one (**16b**)^[21]

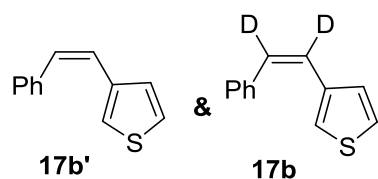


According to reaction conditions **A**, 0.2 mmol scale **16b'** was prepared from the 1-(4-(phenylethynyl)phenyl)ethan-1-one (44 mg, 0.2 mmol). The formed mixture was stirred at 60 °C under Ar for 24 h as

monitored by TLC and GC-MS. The solution was then cooled to room temperature, and the crude product was purified by flash column chromatography on silica gel to afford 31 mg (70%) of **16b'** as a White solid. ¹H NMR (400 MHz, CDCl₃) δ 7.84 (d, *J* = 8.4 Hz, 2H), 7.35 (d, *J* = 8.3 Hz, 2H), 7.25 (s, 5H), 6.75 (d, *J* = 12.3 Hz, 1H), 6.63 (d, *J* = 12.3 Hz, 1H), 2.59 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 197.6, 142.3, 136.6, 135.6, 132.4, 129.1, 129.0, 128.8, 128.4, 128.3, 127.5. According to reaction conditions **B**, 0.2 mmol scale **16b** was prepared from the 1-(4-(phenylethynyl)phenyl)ethan-1-one (44 mg, 0.2 mmol). The formed mixture was stirred at 60 °C under Ar for 24 h as monitored by TLC and GC-MS. The solution was then cooled to room temperature, and the crude product was purified by flash column

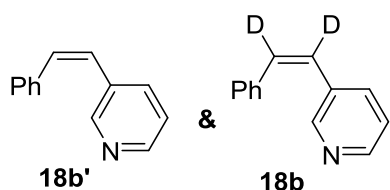
chromatography on silica gel to afford 31.4 mg (70%) of **16b** as a White solid. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.81 (d, $J = 8.5$ Hz, 2H), 7.33 (d, $J = 8.6$ Hz, 2H), 7.23 (s, 5H), 6.72 (d, $J = 4.9$ Hz, 0.15H), 6.61 (d, $J = 6.24$ Hz, 0.15H), 2.54 (dd, $J = 4.4, 2.2$ Hz, 0.21H). **IR (film)**: 2923, 1818, 1681, 1555, 1263, 964, 752, 700 cm^{-1} ; **EI-MS (m/z, relative intensity)**: 224 (M^+ , 50), 209 (100), 180 (80), 153 (12), 120 (4), 104 (10), 90 (14), 77 (8). According to $^1\text{H NMR}$, 85% deuterium incorporation at each vinylic position was generated in product **16b**.

(Z)-3-Styrylthiophene (17b') ^[25] & **(Z)-3-(2-phenylvinyl-1,2-d₂)thiophene (17b)**



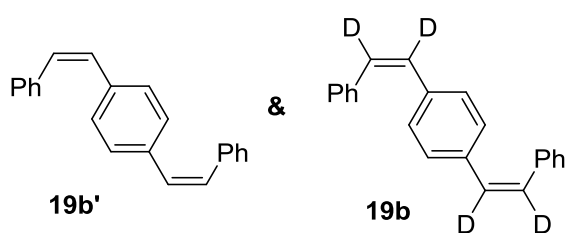
According to reaction conditions **A**, 0.2 mmol scale **17b'** was prepared from the 3-(phenylethynyl)thiophene (36.8 mg, 0.2 mmol). The formed mixture was stirred at 60 °C under Ar for 24 h as monitored by TLC and GC-MS. The solution was then cooled to room temperature, and the crude product was purified by flash column chromatography on silica gel to afford 28.7 mg (77%) of **17b'** as light yellow oil. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.32 – 7.27 (m, 4H), 7.27 – 7.22 (m, 2H), 7.15 – 7.08 (m, 2H), 6.86 (dd, $J = 4.9, 1.4$ Hz, 1H), 6.61 – 6.49 (q, $J = 1.7$ Hz, 2H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 138.2, 137.8, 129.5, 128.7, 128.3, 128.0, 127.2, 124.8, 124.4, 124.1. According to reaction conditions **B**, 0.2 mmol scale **17b** was prepared from the 3-(phenylethynyl)thiophene (36.8 mg, 0.2 mmol). The formed mixture was stirred at 60 °C under Ar for 24 h as monitored by TLC and GC-MS. The solution was then cooled to room temperature, and the crude product was purified by flash column chromatography on silica gel to afford 28.2 mg (75%) of **17b** as light yellow oil. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.32 – 7.27 (m, 4H), 7.27 – 7.20 (m, 2H), 7.14 – 7.09 (m, 2H), 6.87 (dd, $J = 4.8, 1.5$ Hz, 1H), 6.55 (d, $J = 6.9$ Hz, 0.1H). **IR (film)**: 3691, 2922, 1809, 1588, 1309, 1109, 1093, 1017, 802, 702, 585 cm^{-1} **HRMS m/z (ESI) calcd for $\text{C}_{12}\text{H}_9\text{D}_2\text{S}$ ($\text{M} + \text{H}$)⁺**: 189.0702 found 189.0703. According to $^1\text{H NMR}$, 85% deuterium incorporation at each vinylic position was generated in product **17b**.

(Z)-3-styrylpyridine (18b') ^[28] & **(Z)-3-(2-phenylvinyl-1,2-d₂)pyridine (18b)**



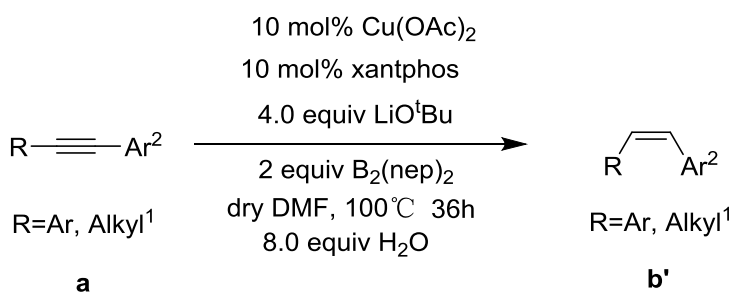
According to reaction conditions **A**, 0.2 mmol scale **18b'** was prepared from the 3-(phenylethynyl)pyridine (35.8 mg, 0.2 mmol). The formed mixture was stirred at 60 °C under Ar for 24 h as monitored by TLC and GC-MS. The solution was then cooled to room temperature, and the crude product was purified by flash column chromatography on silica gel to afford 26.5 mg (73%) of **18b'** as light yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 8.59 (d, *J* = 3.7 Hz, 1H), 7.56 – 7.39 (m, 1H), 7.28 – 7.23 (m, 5H), 7.16 (d, *J* = 7.9 Hz, 1H), 7.12 – 7.06 (m, 1H), 6.84 (d, *J* = 12.4 Hz, 1H), 6.70 (d, *J* = 12.4 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 149.6, 136.7, 135.6, 133.2, 130.5, 128.9, 128.3, 127.6, 123.8, 121.7. According to reaction conditions **B** 0.2 mmol scale **18b** was prepared from the 3-(phenylethynyl)pyridine (35.8 mg, 0.2 mmol). The formed mixture was stirred at 60 °C under Ar for 24 h as monitored by TLC and GC-MS. The solution was then cooled to room temperature, and the crude product was purified by flash column chromatography on silica gel to afford 26.7 mg (73%) of **18b** as light yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 8.61 (d, *J* = 4.0 Hz, 1H), 7.66 (td, *J* = 7.7, 1.8 Hz, 1H), 7.62 – 7.56 (m, 2H), 7.38 (dd, *J* = 11.5, 4.2 Hz, 3H), 7.30 (dd, *J* = 8.4, 6.3 Hz, 1H), 7.15 (dd, *J* = 7.0, 5.3 Hz, 1H). IR (film): 3627, 2921, 2851, 1637, 1266, 946, 874, 8237, 769, 699, 520 cm⁻¹ HRMS *m/z* (ESI) calcd for C₁₃H₉D₂NNa (M + Na)⁺: 206.0909, found 206.0913. According to ¹H NMR, >99% deuterium incorporation at each vinylic position was generated in product **18b**.

1,4-Di((Z)-styryl)benzene (19b') ^[26] & **1,4-Bis((Z)-2-phenylvinyl-1,2-d₂)benzene (19b)**

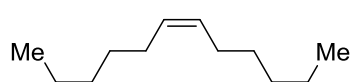
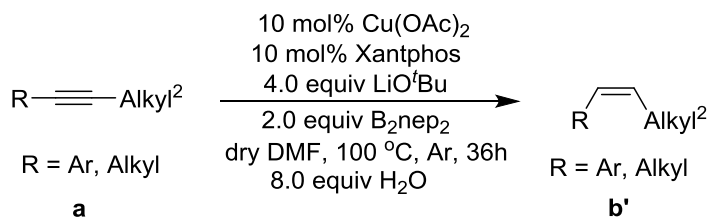


According to reaction conditions **A**, 0.2 mmol scale **19b'** was prepared from the 1,4-bis(phenylethynyl)benzene (55.7mg, 0.2 mmol). The formed mixture was stirred at 60 °C under Ar for 24 h as

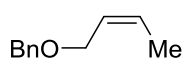
monitored by TLC and GC-MS. The solution was then cooled to room temperature, and the crude product was purified by flash column chromatography on silica gel to afford 45.2 mg (82%) of **19b'** as a White solid. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.36 – 7.20 (m, 10H), 7.17 (s, 4H), 6.66 – 6.57 (m, 4H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 137.3, 136.0, 130.3, 129.9, 128.8, 128.7, 128.2, 127.1. According to reaction conditions **B**, 0.2 mmol scale **19b** was prepared from the 1,4-bis(phenylethynyl)benzene (55.7 mg, 0.2 mmol). The formed mixture was stirred at 60 °C under Ar for 24 h as monitored by TLC and GC-MS. The solution was then cooled to room temperature, and the crude product was purified by flash column chromatography on silica gel to afford 45.8 mg (80%) of **19b** as a White solid. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.35 – 7.19 (m, 10H), 7.17 (d, $J = 1.2$ Hz, 4H), 6.62 (s, 0.16H), 6.59 (s, 0.16H). **IR (film)**: 3627, 2921, 2851, 1673, 1266, 964, 874, 823, 769, 699, 520 cm^{-1} **HRMS m/z (ESI) calcd for $\text{C}_{22}\text{H}_{15}\text{D}_2$ ($\text{M} + \text{H}$) $^+$** : 287.1732, found 287.1737. According to $^1\text{H NMR}$, 92% deuterium incorporation at each vinylic position was generated in product **19b**.



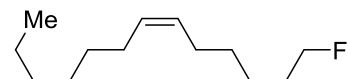
Reaction conditions C: The 25 mL Schlenk tube containing a stirring bar was added B_2nep_2 (90 mg, 0.4 mmol, 2.0 equiv). The tube was introduced in nitrogenfilled glovebox, and Cu(OAc)_2 (4 mg, 10 mol %), Xantphos (11.6 mg, 10 mol %) and LiO^tBu (64.0 mg, 4.0 equiv) were added. The tube with the mixture was taken out of the glovebox. Then DMF (1mL) and H_2O (28 μL , 8.0 equiv) was added under argon. The formed mixture was stirred at 100 °C under Ar for 36 h as monitored by TLC and GC-MS. The solution was then cooled to room temperature. The crude product was purified by flash column chromatography on silica gel (PE/AcOEt) to afford the corresponding products.



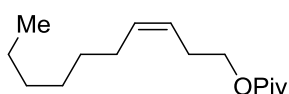
20b', 80% (> 99: 1)



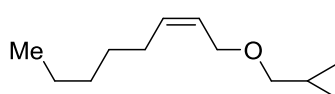
21b', 70% (> 99: 1)



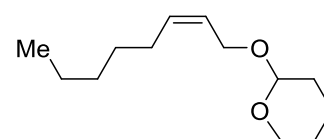
22b', 72% (> 99: 1)



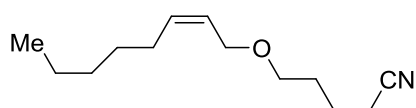
23b', 44% (> 99: 1)



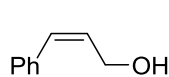
24b', 75% (> 99: 1)



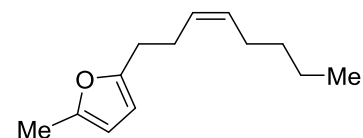
25b', 75% (> 99: 1)



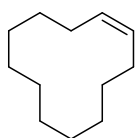
26b', 72% (> 99: 1)



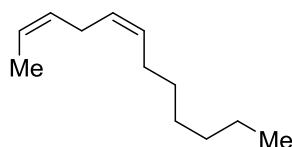
27b', 69% (> 99: 1)



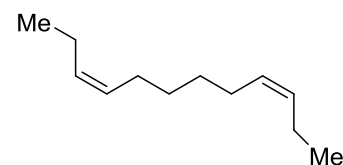
28b', 77% (> 99: 1)



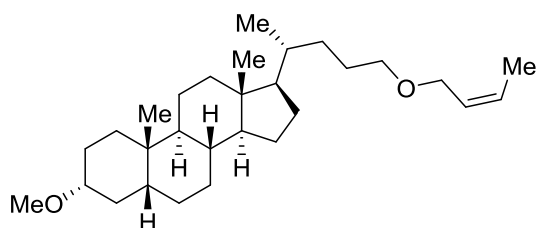
29b', 60% (> 99: 1)



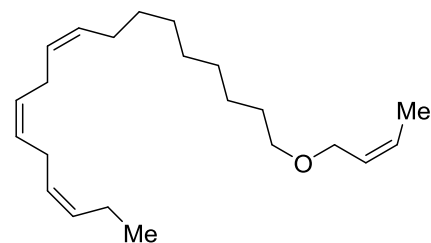
30b', 74% (> 99: 1)



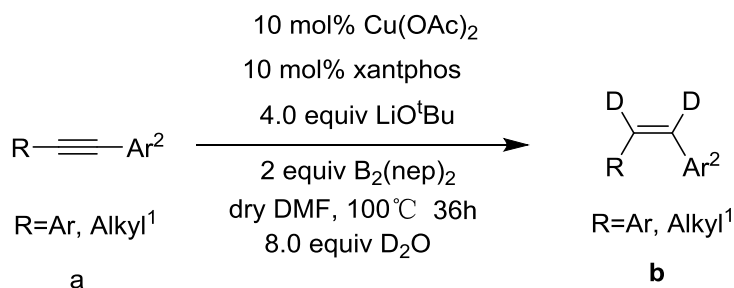
31b', 70% (> 99: 1)



32b', 62% (> 99: 1)

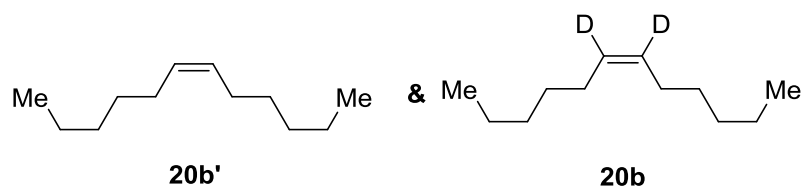


33b', 70% (> 99: 1)



Reaction conditions D: The 25 mL Schlenk tube containing a stirring bar was introduced in nitrogen-filled glovebox was added B₂nep₂ (90 mg, 0.4 mmol, 2.0 equiv), Cu(OAc)₂ (4 mg, 10 mol %), Xantphos (11.6 mg, 10 mol %) ,LiO^tBu (64.0 mg, 4.0 equiv) and dry DMF (1 mL), D₂O(28 μL, 8.0 equiv). The formed mixture was stirred at 100 °C under Ar for 36 h as monitored by TLC and GC-MS. The solution was then cooled to room temperature. The crude product was purified by flash column chromatography on silica gel (PE/AcOEt) to afford the corresponding products.

(Z)-Dodec-6-ene (20b')^[23] & (Z)-Dodec-6-ene-6,7-d₂ (20b)

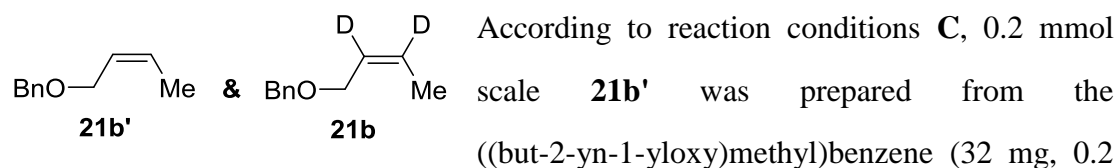


According to reaction conditions C, 0.2 mmol scale **20b'** was prepared from the

dodec-6-yne (33.2 mg, 0.2 mmol). The formed mixture was stirred at 100 °C under Ar for 36 h as monitored by TLC and GC-MS. The solution was then cooled to room temperature, and the crude product was purified by flash column chromatography on silica gel to afford 26.9 mg (80%) of **20b'** as a colourless oil. ¹H NMR (400 MHz, CDCl₃) δ 5.35 (ddd, *J* = 5.5, 4.4, 0.9 Hz, 2H), 2.02 (dd, *J* = 12.6, 6.9 Hz, 4H), 1.37 – 1.25 (m, 12H), 0.89 (t, *J* = 6.9 Hz, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 129.9, 31.5, 29.4, 27.2, 22.6, 14.1. According to reaction conditions D, 0.2 mmol scale **20b** was prepared from the dodec-6-yne (33.2 mg, 0.2 mmol). The formed mixture was stirred at 100 °C under Ar for 36 h as monitored by TLC and GC-MS. The solution was then cooled to room temperature, and the crude product was purified by flash column chromatography on silica gel to afford 27.2 mg (80%) of **20b** as a colourless oil. ¹H

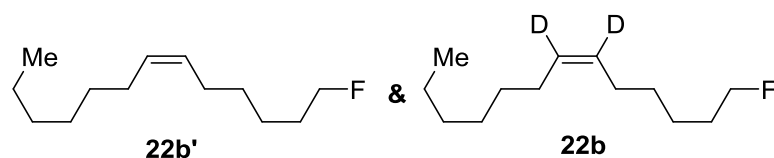
NMR (400 MHz, CDCl₃) δ 5.35 (d, $J = 0.9$ Hz, 0.08H), 2.01 (t, $J = 6.8$ Hz, 4H), 1.37 – 1.23 (m, 12H), 0.89 (t, $J = 6.9$ Hz, 6H). **IR (film):** 3523, 2921, 1639, 1267, 745 cm⁻¹; **EI-MS (m/z, relative intensity):** 170 (M⁺, 16), 141 (2), 126 (4), 98 (20), 84 (36), 70 (86), 56 (100). According to ¹H NMR, 96% deuterium incorporation at each vinylic position was generated in product **20b**.

(Z)-((but-2-en-1-yloxy)methyl)benzene (21b')^[29] & (Z)-(((but-2-en-1-yl-2,3-d₂)oxy)methyl)benzene (21b)



mmol). The formed mixture was stirred at 100 °C under Ar for 36 h as monitored by TLC and GC-MS. The solution was then cooled to room temperature, and the crude product was purified by flash column chromatography on silica gel to afford 22.7 mg (70%) of **21b'** as a colourless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.37 – 7.26 (m, 5H), 5.80 – 5.51 (m, 2H), 4.52 (s, 2H), 4.09 (dd, $J = 4.1, 3.3$ Hz, 2H), 1.65 (d, $J = 6.1$ Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 138.4, 128.3, 128.1, 127.8, 127.5, 126.8, 72.0, 65.4. According to reaction conditions **D**, 0.2 mmol scale **21b** was prepared from the ((but-2-yn-1-yloxy)methyl)benzene (32 mg, 0.2 mmol). The formed mixture was stirred at 100 °C under Ar for 36 h as monitored by TLC and GC-MS. The solution was then cooled to room temperature, and the crude product was purified by flash column chromatography on silica gel to afford 22.9 mg (70%) of **21b** as a colourless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.37 – 7.26 (m, 5H), 5.80 – 5.51 (m, 0.12H), 4.52 (s, 2H), 4.08 (d, $J = 0.6$ Hz, 2H), 1.64 (s, 3H). **IR (film):** 3602, 2931, 1635, 1457, 1383, 1265, 1200, 1124, 905, 811, 745 cm⁻¹; **EI-MS (m/z, relative intensity):** 164 (M⁺, 16), 141 (6), 123(4), 101 (18), 85 (100), 69 (48). According to ¹H NMR, 96% deuterium incorporation at each vinylic position was generated in product **21b**.

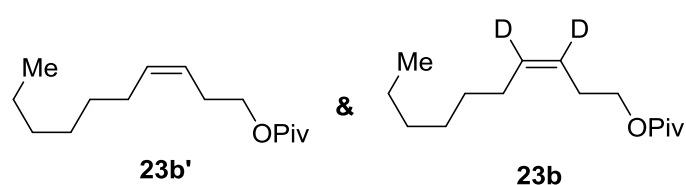
(Z)-1-Fluorotridec-6-ene (22b') & (Z)-1-Fluorotridec-6-ene-6,7-d₂ (22b)



According to reaction conditions **C**, 0.2 mmol scale **22b'** was

prepared from the 1-fluorotridec-6-yne (39.6 mg, 0.2 mmol). The formed mixture was stirred at 100 °C under Ar for 36 h as monitored by TLC and GC-MS. The solution was then cooled to room temperature, and the crude product was purified by flash column chromatography on silica gel to afford 28.3 mg (72%) of **22b'** as a colourless oil. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 5.45 – 5.27 (m, 2H), 4.50 (t, $J = 6.2$ Hz, 1H), 4.38 (t, $J = 6.2$ Hz, 1H), 2.03 (td, $J = 12.7, 6.3$ Hz, 4H), 1.80 – 1.61 (m, 2H), 1.46 – 1.37 (m, 4H), 1.31 (ddd, $J = 9.2, 8.7, 2.5$ Hz, 8H), 0.88 (t, $J = 6.9$ Hz, 3H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 130.3, 129.3, 84.2 (d, $J = 164.7$ Hz,), 31.8, 30.3 (d, $J = 19.5$ Hz,), 29.7, 29.3, 29.0, 27.2, 27.0, 24.8 (d, $J = 5.6$ Hz,), 22.6, 14.1. According to reaction conditions **D**, 0.2 mmol scale **22b** was prepared from the 1-fluorotridec-6-yne (39.6 mg, 0.2 mmol). The formed mixture was stirred at 100 °C under Ar for 36 h as monitored by TLC and GC-MS. The solution was then cooled to room temperature, and the crude product was purified by flash column chromatography on silica gel to afford 28.7 mg (71%) of **22b** as a colourless oil. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 5.35 (m, 0.06H), 4.50 (t, $J = 6.2$ Hz, 1H), 4.39 (t, $J = 6.1$ Hz, 1H), 2.15 (dddd, $J = 11.7, 7.2, 4.7, 2.3$ Hz, 4H), 1.80 – 1.62 (m, 2H), 1.53 – 1.44 (m, 5H), 1.42 – 1.21 (m, 7H), 0.89 (t, $J = 6.9$ Hz, 3H). IR (film): 3480, 2922, 1639, 1266, 1266, 741 cm^{-1} HRMS m/z (ESI) calcd for $\text{C}_{13}\text{H}_{22}\text{D}_2\text{FNa}$ ($\text{M} + \text{Na}$) $^+$: 225.1958, found 225.1954. According to $^1\text{H NMR}$, 94% deuterium incorporation at each vinylic position was generated in product **22b**.

(Z)-Dec-3-en-1-yl pivalate (23b') & (Z)-Dec-3-en-1-yl-3,4-d2 pivalate (23b)

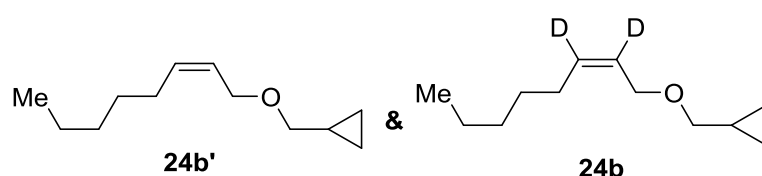


According to reaction conditions **C**, 0.2 mmol scale **23b'** was prepared from the dec-3-yn-1-yl pivalate (47.6

mg, 0.2 mmol). The formed mixture was stirred at 100 °C under Ar for 36 h as

monitored by TLC and GC-MS. The solution was then cooled to room temperature, and the crude product was purified by flash column chromatography on silica gel to afford 21 mg (44%) of **23b'** as a colourless oil. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 5.61 – 5.42 (m, 1H), 5.38 – 5.26 (m, 1H), 4.05 (t, $J = 6.8$ Hz, 2H), 2.41 – 2.32 (m, 2H), 2.04 (q, $J = 6.8$ Hz, 2H), 1.39 – 1.24 (m, 8H), 1.19 (s, 9H), $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 5.61 – 5.42 (m, 1H), 5.38 – 5.26 (m, 1H), 4.05 (t, $J = 6.8$ Hz, 2H), 2.41 – 2.32 (m, 2H), 2.04 (q, $J = 6.8$ Hz, 2H), 1.39 – 1.24 (m, 8H), 1.19 (s, 9H), 0.88 (t, $J = 6.9$ Hz, 3H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 178.6, 132.7, 124.4, 63.8, 38.7, 31.8, 29.6, 28.9, 27.3, 27.2, 26.9, 22.6, 14.0. According to reaction conditions **D**, 0.2 mmol scale **23b** was prepared from the dec-3-yn-1-yl pivalate (47.6 mg, 0.2 mmol). The formed mixture was stirred at 100 °C under Ar for 36 h as monitored by TLC and GC-MS. The solution was then cooled to room temperature, and the crude product was purified by flash column chromatography on silica gel to afford 21.3 mg (44%) of **23b** as a colourless oil. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 5.48 (t, $J = 7.2$ Hz, 0.04H), 5.33 (t, $J = 7.4$ Hz, 0.04H), 4.05 (t, $J = 6.8$ Hz, 2H), 2.36 (t, $J = 6.8$ Hz, 2H), 2.03 (t, $J = 6.8$ Hz, 2H), 1.35 – 1.24 (m, 8H), 1.19 (s, 9H), 0.88 (t, $J = 6.8$ Hz, 3H). IR (film): 3696, 2924, 1732, 1464, 1266, 741 cm^{-1} ; HRMS m/z (ESI) calcd for $\text{C}_{15}\text{H}_{26}\text{D}_2\text{O}_2\text{Na}$ ($M + \text{Na}$) $^+$: 265.2107, found 265.2102. According to $^1\text{H NMR}$, 96% deuterium incorporation at each vinylic position was generated in product **23b**.

(Z)-((oct-2-en-1-yloxy)methyl)cyclopropane (24b') & **(Z)-(((oct-2-en-1-yl-2,3-d2)oxy)methyl)cyclopropane (24b)**

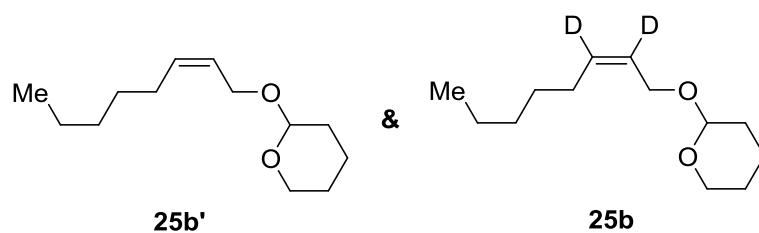


According to reaction conditions **C**, 0.2 mmol scale **24b'** was prepared from the ((oct-2-yn-1-

yloxy)methyl)cyclopropane (36 mg, 0.2 mmol). The formed mixture was stirred at 100 °C under Ar for 36 h as monitored by TLC and GC-MS. The solution was then cooled to room temperature, and the crude product was purified by flash column chromatography on silica gel to afford 27.3 mg (75%) of **24b'** as a colourless oil. $^1\text{H NMR}$

NMR (400 MHz, CDCl₃) δ 5.63 – 5.47 (m, 2H), 4.04 (d, J = 5.2 Hz, 2H), 3.25 (d, J = 6.9 Hz, 2H), 2.05 (dd, J = 14.0, 6.6 Hz, 2H), 1.42 – 1.22 (m, 6H), 1.12 – 1.00 (m, 1H), 0.88 (t, J = 6.8 Hz, 3H), 0.57 – 0.49 (m, 2H), 0.23 – 0.16 (m, 2H). **¹³C NMR (101 MHz, CDCl₃)** δ 133.5, 126.2, 74.9, 66.1, 31.4, 29.2, 27.5, 22.5, 14.0, 10.7, 3.0. According to reaction conditions **D**, 0.2 mmol scale **24b** was prepared from the ((non-2-yn-1-yloxy)methyl) cyclopropane (36 mg, 0.2 mmol). The formed mixture was stirred at 100 °C under Ar for 36 h as monitored by TLC and GC-MS. The solution was then cooled to room temperature, and the crude product was purified by flash column chromatography on silica gel to afford 29.6 mg (75%) of **24b** as a colourless oil. **¹H NMR (400 MHz, CDCl₃)** δ 5.57 (d, J = 5.6 Hz, 0.08H), 4.05 (s, 2H), 3.27 (d, J = 6.9 Hz, 2H), 2.06 (t, J = 7.1 Hz, 2H), 1.41 – 1.25 (m, 6H), 1.13 – 1.02 (m, 1H), 0.90 (dd, J = 9.1, 4.7 Hz, 3H), 0.59 – 0.50 (m, 2H), 0.27 – 0.16 (m, 2H). **IR (film):** 3451, 2068, 1638, 742 cm⁻¹; **HRMS m/z (ESI) calcd for C₁₂H₂₀D₂ONa (M + Na)⁺:** 207.1688, found 207.1688. According to ¹H NMR, 96% deuterium incorporation at each vinylic position was generated in product **24b**.

(Z)-2-(oct-2-en-1-yloxy)tetrahydro-2H-pyran (25b')^[30] & (Z)-2-((oct-2-en-1-yl-2,3- d2)oxy)tetrahydro-2H-pyran (25b)

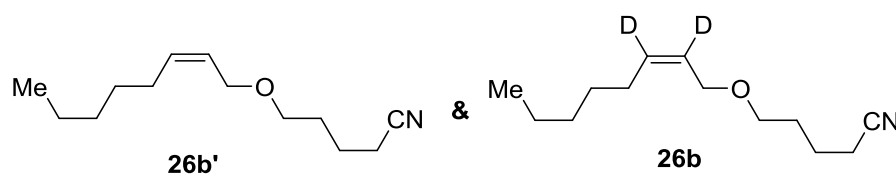


According to reaction conditions **C**, 0.2 mmol scale **25b'** was prepared from the 2-(oct-2-yn-1-

yloxy)tetrahydro-2H-pyran (42.7 mg, 0.2 mmol). The formed mixture was stirred at 100 °C under Ar for 36 h as monitored by TLC and GC-MS. The solution was then cooled to room temperature, and the crude product was purified by flash column chromatography on silica gel to afford 32 mg (75%) of **25b'** as a colourless oil. **¹H NMR (400 MHz, CDCl₃)** δ 5.68 – 5.46 (m, 2H), 4.76 – 4.52 (m, 1H), 4.39 – 4.17 (m, 1H), 4.15 – 3.97 (m, 1H), 3.89 (ddd, J = 11.3, 7.8, 3.4 Hz, 1H), 3.51 (ddd, J = 6.3, 5.8, 4.5 Hz, 1H), 2.07 (dd, J = 13.8, 6.7 Hz, 2H), 1.89 – 1.78 (m, 1H), 1.72 (ddt, J = 12.4, 8.7, 3.3 Hz, 1H), 1.59 – 1.50 (m, 4H), 1.37 – 1.23 (m, 6H), 0.88 (t, J = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 133.9, 125.9, 97.9, 62.8, 62.2, 31.4, 30.7, 29.2, 27.5, 25.5, 22.5, 19.5, 14.0. According to reaction conditions **D**, 0.2 mmol scale **25b** was prepared from the 2-(oct-2-yn-1-yloxy)tetrahydro-2H-pyran (42.7 mg, 0.2 mmol). The formed mixture was stirred at 100 °C under Ar for 36 h as monitored by TLC and GC-MS. The solution was then cooled to room temperature, and the crude product was purified by flash column chromatography on silica gel to afford 31.7 mg (74%) of **25b** as a colourless oil. ^1H NMR (400 MHz, CDCl_3) δ 5.58 (d, $J = 7.5$ Hz, 0.08H), 4.66 – 4.60 (m, 1H), 4.25 (d, $J = 12.1$ Hz, 1H), 4.07 (d, $J = 12.1$ Hz, 1H), 3.89 (ddd, $J = 11.2, 7.8, 3.3$ Hz, 1H), 3.58 – 3.47 (m, 1H), 2.07 (t, $J = 7.1$ Hz, 2H), 1.84 (ddd, $J = 15.4, 9.6, 4.8$ Hz, 1H), 1.72 (ddd, $J = 12.0, 6.0, 3.1$ Hz, 1H), 1.59 – 1.50 (m, 4H), 1.33 – 1.21 (m, 6H), 0.88 (t, $J = 6.8$ Hz, 3H). IR (film): 3451, 2065, 1638, 742 cm^{-1} ; EI-MS (m/z , relative intensity): 214 (M^+ , 3), 197 (2), 114 (8), 103 (12), 87(100), 72 (40), 58 (48). According to ^1H NMR, 96% deuterium incorporation at each vinylic position was generated in product **25b**.

(Z)-5-(oct-2-en-1-yloxy)pentanenitrile (26b') & **(Z)-5-((oct-2-en-1-yl-2,3-d₂)oxy)pentanenitrile (26b)**

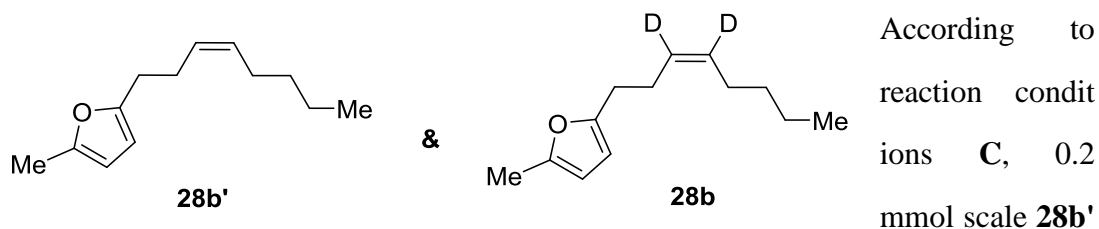


According to reaction conditions **C**, 0.2 mmol scale

26b' was prepared from the 5-(oct-2-yn-1-yloxy)pentanenitrile (41.4 mg, 0.2 mmol). The formed mixture was stirred at 100 °C under Ar for 36 h as monitored by TLC and GC-MS. The solution was then cooled to room temperature, and the crude product was purified by flash column chromatography on silica gel to afford 30.1 mg (72%) of **26b'** as a yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 5.67 – 5.38 (m, 2H), 4.00 (d, $J = 6.2$ Hz, 2H), 3.45 (t, $J = 5.7$ Hz, 2H), 2.38 (t, $J = 6.9$ Hz, 2H), 2.05 (q, $J = 7.1$ Hz, 2H), 1.85 – 1.66 (m, 4H), 1.40 – 1.21 (m, 6H), 0.88 (t, $J = 6.9$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 133.9, 125.8, 119.7, 68.8, 66.4, 31.4, 29.2, 28.6, 27.5, 22.6, 22.5, 17.0, 14.0. According to reaction conditions **D**, 0.2 mmol scale **26b** was prepared

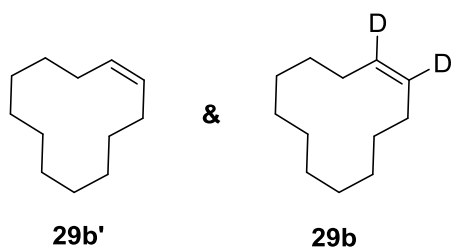
(film): 3452, 1636, 1268, 754 cm^{-1} ; **EI-MS (m/z, relative intensity):** 136 (M^+ , 12), 105 (18), 98 (22), 92(62), 73 (78), 61 (36), 56 (100). According to ^1H NMR, 68%, 84% deuterium incorporation at each vinylic position was generated in product **27b**

(Z)-2-Methyl-5-(oct-3-en-1-yl)furan (28b') & **(Z)-2-Methyl-5-(oct-3-en-1-yl-3,4-d2)furan (28b)**



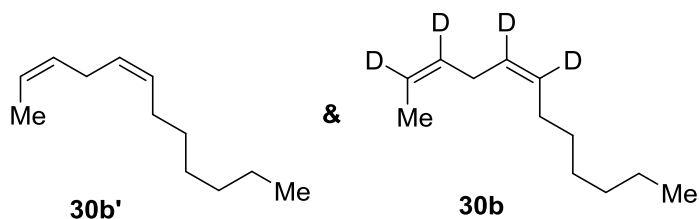
was prepared from the 2-methyl-5-(oct-3-yn-1-yl)furan (38 mg, 0.2 mmol). The formed mixture was stirred at 100 $^{\circ}\text{C}$ under Ar for 36 h as monitored by TLC and GC-MS. The solution was then cooled to room temperature, and the crude product was purified by flash column chromatography on silica gel to afford 29.6 mg (77%) of **28b'** as a colourless oil. ^1H NMR (400 MHz, CDCl_3) δ 6.02 – 5.67 (m, 2H), 5.55 – 5.22 (m, 2H), 2.60 (q, $J = 7.3$ Hz, 2H), 2.40 – 2.32 (m, 2H), 2.25 (s, 3H), 2.02 (d, $J = 6.2$ Hz, 2H), 1.31 (dq, $J = 7.1, 3.5$ Hz, 4H), 0.89 (t, $J = 7.0$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 154.0, 150.2, 130.9, 128.3, 105.8, 105.4, 31.84, 28.2, 26.9, 25.9, 22.3, 14.0, 13.5. According to reaction conditions **D**, 0.2 mmol scale **28b** was prepared from the 2-methyl-5-(oct-3-yn-1-yl)furan (38 mg, 0.2 mmol). The formed mixture was stirred at 100 $^{\circ}\text{C}$ under Ar for 36 h as monitored by TLC and GC-MS. The solution was then cooled to room temperature, and the crude product was purified by flash column chromatography on silica gel to afford 29.6 mg (77%) of **28b** as a colourless oil. ^1H NMR (400 MHz, CDCl_3) δ 5.96 – 5.73 (m, 2H), 5.40 – 5.35 (m, 0.18H), 2.61 (t, $J = 7.6$ Hz, 2H), 2.35 (t, $J = 7.6$ Hz, 2H), 2.25 (s, 3H), 2.01 (t, $J = 6.3$ Hz, 2H), 1.35 – 1.23 (dq, $J = 7.1, 3.5$ Hz, 4H), 0.89 (t, $J = 7.0$ Hz, 3H). **IR (film):** 3745, 3456, 2922, 2226, 1604, 1262, 862, 748, 697, 555, 419 cm^{-1} ; **EI-MS (m/z, relative intensity):** 194 (M^+ , 26), 177 (4), 151 (6), 95 (100). According to ^1H NMR, 90% deuterium incorporation at each vinylic position was generated in product **28b**.

(Z)-Cyclododecene (29b')^[32] & (Z)-Cyclododec-1-ene-1,2-d2 (29b)



According to reaction conditions **C**, 0.2 mmol scale **29b'** was prepared from the cyclododecyne (32.8 mg, 0.2 mmol) and B_2nep_2 (113 mg, 0.5 mmol, 2.5 equiv). The formed mixture was stirred at 100 °C under Ar for 36 h as monitored by TLC and GC-MS. The solution was then cooled to room temperature, and the crude product was purified by flash column chromatography on silica gel to afford 19.9 mg (60 %) of **29b'** as a colourless oil. 1H NMR (400 MHz, $CDCl_3$) δ 5.41 – 5.24 (m, 2H), 2.11 (q, $J = 6.4$ Hz, 4H), 1.44 (dt, $J = 11.7, 6.2$ Hz, 4H), 1.36 – 1.24 (m, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 130.4, 26.9, 24.6, 24.3, 23.9, 22.0. According to reaction conditions **D**, 0.2 mmol scale **29b** was prepared from the cyclododecyne (32.8 mg, 0.2 mmol) and B_2nep_2 (113 mg, 0.5 mmol, 2.5 equiv). The formed mixture was stirred at 100 °C under Ar for 36 h as monitored by TLC and GC-MS. The solution was then cooled to room temperature, and the crude product was purified by flash column chromatography on silica gel to afford 18.8 mg (56%) of **29b** as a colourless oil. 1H NMR (400 MHz, $CDCl_3$) δ 5.31 (m, 0.12H), 2.11 (t, $J = 6.4$ Hz, 4H), 1.50 – 1.39 (m, 4H), 1.39 – 1.17 (m, 12H). IR (film): 3451, 2925, 2854, 1634, 1460, 1265, 743 cm^{-1} ; EI-MS (m/z, relative intensity): 168 (M^+ , 12), 137 (18), 123 (20), 109 (66), 98 (72), 83 (100), 57 (58). According to 1H NMR, 91% deuterium incorporation at each vinylic position was generated in product **29b**.

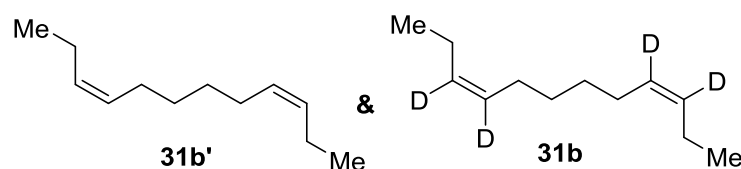
(2Z,5Z)-Dodeca-2,5-diene (30b') & (2Z,5Z)-Dodeca-2,5-diene-2,3,5,6-d4 (30b)



According to reaction conditions **C**, 0.2 mmol scale **30b'** was prepared from the dodeca-2,5-diyne (32.4 mg, 0.2 mmol). The formed mixture was stirred at 100 °C under Ar for 36 h as monitored by TLC and GC-MS. The solution was then cooled to room temperature, and the crude product was purified by flash column chromatography on silica gel to afford

24.5 mg (74 %) of **30b'** as a colourless oil. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 5.50 – 5.27 (m, 4H), 2.79 (t, $J = 6.7$ Hz, 2H), 2.06 (dd, $J = 13.5, 6.7$ Hz, 2H), 1.64 (d, $J = 6.5$ Hz, 3H), 1.36 – 1.23 (m, 8H), 0.88 (t, $J = 6.7$ Hz, 3H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 130.3, 129.9, 127.8, 123.9, 31.8, 29.6, 29.0, 27.2, 25.3, 22.6, 14.1, 12.7. According to reaction conditions **D**, 0.2 mmol scale **30b** was prepared from the dodeca-2,5-diyne (32.4mg, 0.2 mmol). The formed mixture was stirred at 100 °C under Ar for 36 h as monitored by TLC and GC-MS. The solution was then cooled to room temperature, and the crude product was purified by flash column chromatography on silica gel to afford 25.1 mg (74 %) of **30b** as a colourless oil. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 5.42 – 5.32 (m, 0.36H), 2.78 (s, 2H), 2.05 (t, $J = 6.5$ Hz, 2H), 1.63 (s, 3H), 1.31 – 1.25 (m, 8H), 0.88 (t, $J = 5.9$ Hz, 3H). **IR (film)**: 3446, 2926, 2855, 1632, 1457, 1262, 750 cm^{-1} ; **EI-MS (m/z, relative intensity)**: 170 (M^+ , 12), 126 (10), 112 (10), 99 (14), 84 (74), 69 (100), 57 (28). According to $^1\text{H NMR}$, 91% deuterium incorporation at each vinylic position was generated in product **30b**.

(3Z,9Z)-Dodeca-3,9-diene (31b') & **(3Z,9Z)-Dodeca-3,9-diene-3,4,9,10-d4 (31b)**

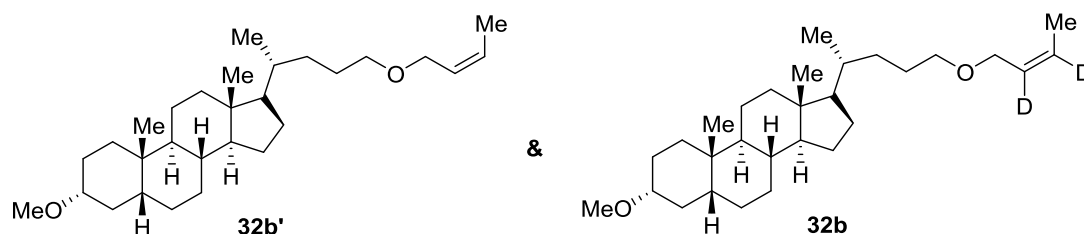


According to reaction conditions **C**, 0.2 mmol scale **31b'** was prepared

from the dodeca-3,9-diyne (32.4 mg, 0.2 mmol). The formed mixture was stirred at 100 °C under Ar for 36 h as monitored by TLC and GC-MS. The solution was then cooled to room temperature, and the crude product was purified by flash column chromatography on silica gel to afford 23.1 mg (70 %) of **31b'** as a colourless oil. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 5.49 – 5.11 (m, 4H), 2.04 (p, $J = 7.2$ Hz, 8H), 1.38 – 1.32 (m, 4H), 0.95 (t, $J = 7.5$ Hz, 6H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 131.6, 129.2, 29.4, 27.0, 20.5, 14.4. According to reaction conditions **D**, 0.2 mmol scale **31b** was prepared from the dodeca-3,9-diyne (32.4 mg, 0.2 mmol). The formed mixture was stirred at 100 °C under Ar for 36 h as monitored by TLC and GC-MS. The solution was then cooled to room temperature, and the crude product was purified by flash column chromatography on silica gel to afford 23.8 mg (70 %) of **31b** as a colourless

oil. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 5.34 (m, 0.32H), 2.03 (q, $J = 7.3$ Hz, 8H), 1.39 – 1.31 (m, 4H), 0.95 (t, $J = 7.5$ Hz, 6H). **IR (film)**: 3746, 3481, 2921, 3850, 1632, 1470, 1276, 750 cm^{-1} ; **EI-MS (m/z, relative intensity)**: 170 (M^+ , 2), 142 (4), 126 (28), 112 (40), 84 (74), 69 (100), 56 (62). According to $^1\text{H NMR}$, 92% deuterium incorporation at each vinylic position was generated in product **31b**.

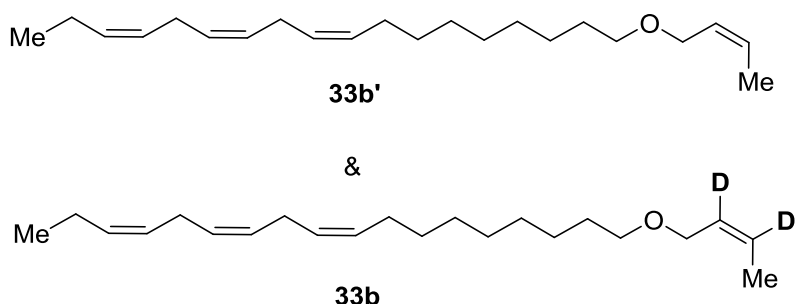
(3R,5R,8S,9S,10R,13R,14S,17S)-17-((R)-5-(((Z)-but-2-en-1-yl)oxy)pentan-2-yl)-3-methoxy-5,10,13-trimethylhexadecahydro-1H-cyclopenta[a]phenanthrene (32b')
& (3R,5R,8R,9S,10S,13R,14S,17S)-17-((R)-5-(((Z)-but-2-en-1-yl-2,3-d₂)oxy)pentan-2-yl)-3-methoxy-10,13-dimethylhexadecahydro-1H-cyclopenta[a]phenanthrene (32b).



According to reaction conditions **C**, 0.2 mmol scale **32b'** was prepared from the (3R,5R,8S,9S,10R,13R,14S,17S)-17-((R)-5-(but-2-yn-1-yloxy)pentan-2-yl)-3-methoxy-5,10,13-trimethylhexadecahydro-1H-cyclopenta[a]phenanthrene (88.4 mg, 0.2 mmol). The formed mixture was stirred at 100 °C under Ar for 36 h as monitored by TLC and GC-MS. The solution was then cooled to room temperature, and the crude product was purified by flash column chromatography on silica gel to afford 53 mg (62 %) of **32b'** as a light yellow oil. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 5.78 – 5.38 (m, 2H), 4.01 (d, $J = 6.4$ Hz, 2H), 3.43 – 3.31 (m, 5H), 3.19 – 3.10 (m, 1H), 1.98 – 1.91 (m, 1H), 1.89 – 1.72 (m, 4H), 1.71 – 1.62 (m, 5H), 1.62 – 1.50 (m, 2H), 1.49 – 1.29 (m, 8H), 1.29 – 1.16 (m, 4H), 1.15 – 0.96 (m, 6H), 0.96 – 0.86 (m, 7H), 0.63 (s, 3H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 127.4, 127.2, 80.4, 71.0, 60.0, 56.4, 56.1, 55.5, 42.6, 42.0, 40.3, 40.2, 35.8, 35.6, 35.3, 34.9, 32.7, 32.2, 28.3, 27.3, 26.7, 26.4, 26.3, 24.2, 23.4, 20.8, 18.6, 13.2, 12.0. According to reaction conditions **D**, 0.2 mmol scale **32b** was prepared from the (3R,5R,8S,9S,10R,13R,14S,17S)-17-((R)-5-(but-2-yn-1-yloxy)pentan-2-yl)-3-methoxy-5,10,13-trimethylhexadecahydro-1H-cyclopenta[a]phenant

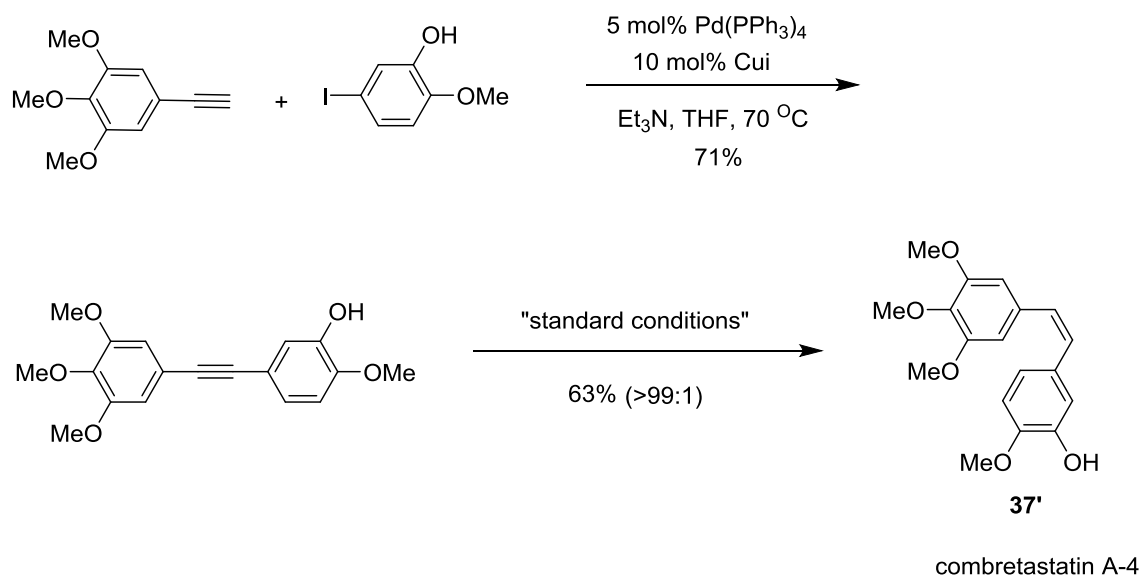
hrene (88.4 mg, 0.2 mmol). The formed mixture was stirred at 100 °C under Ar for 36 h as monitored by TLC and GC-MS. The solution was then cooled to room temperature, and the crude product was purified by flash column chromatography on silica gel to afford 53 mg (62 %) of **32b** as a light yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 5.70 – 5.52 (m, 0.2H), 4.01 (s, 2H), 3.44 – 3.27 (m, 5H), 3.23 – 3.06 (m, 1H), 2.02 – 1.91 (m, 1H), 1.81 (ddt, *J* = 24.9, 22.5, 10.6 Hz, 4H), 1.71 – 1.63 (m, 5H), 1.62 – 1.51 (m, 2H), 1.49 – 1.30 (m, 8H), 1.27 – 1.19 (m, 4H), 1.15 – 0.97 (m, 6H), 0.94 – 0.83 (m, 7H), 0.63 (s, 3H). IR (film): 3674, 3450, 2923, 2852, 1631, 1455, 1372, 1262, 1101, 749, 472, 419 cm⁻¹; HRMS *m/z* (ESI) calcd for C₂₉H₄₈D₂O₂Na (*M* + Na)⁺: 455.3829, found 455.3834. According to ¹H NMR, 90% deuterium incorporation at each vinylic position was generated in product **32b**.

(3Z,6Z,9Z)-18-(((Z)-but-2-en-1-yl)oxy)octadeca-3,6,9-triene (33b') & **(3Z,6Z,9Z)-18-(((Z)-but-2-en-1-yl-2,3-d₂)oxy)octadeca-3,6,9-triene (33b)**

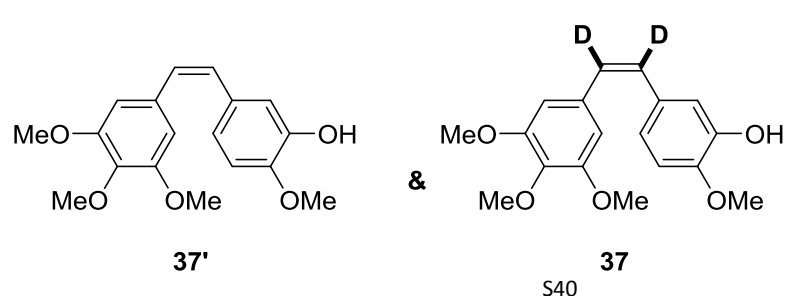


According to reaction conditions **C**, 0.2 mmol scale **33b'** was prepared from the (3Z,6Z,9Z)-18-(but-2-yn-1-yloxy)octadeca-3,6,9-triene (63.2 mg, 0.2 mmol). The formed mixture was stirred at 100 °C under Ar for 36 h as monitored by TLC and GC-MS. The solution was then cooled to room temperature, and the crude product was purified by flash column chromatography on silica gel to afford 44.6 mg (70 %) of **33b'** as a light yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 5.72 – 5.51 (m, 2H), 5.45 – 5.25 (m, 6H), 4.07 – 3.97 (m, 2H), 3.41 (t, *J* = 6.7 Hz, 2H), 2.81 (t, *J* = 6.0 Hz, 4H), 2.14 – 1.99 (m, 4H), 1.70 – 1.63 (m, 3H), 1.57 (dd, *J* = 14.2, 7.0 Hz, 2H), 1.41 – 1.22 (m, 10H), 0.97 (t, *J* = 7.5 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 131.9, 130.3, 128.2, 128.1, 127.6, 127.5, 127.2, 127.1, 70.4, 66.0, 29.8, 29.6, 29.5, 29.4, 29.2, 27.2, 26.2, 25.6, 25.5, 20.5, 14.3, 13.1. According to reaction conditions **D**, 0.2 mmol scale

33b was prepared from the (3Z,6Z,9Z)-18-(but-2-yn-1-yloxy)octadeca-3,6,9-triene (63.2 mg, 0.2 mmol). The formed mixture was stirred at 100 °C under Ar for 36 h as monitored by TLC and GC-MS. The solution was then cooled to room temperature, and the crude product was purified by flash column chromatography on silica gel to afford 44.9 mg (70 %) of **33b** as a light yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 5.64-5.56 (m, 0.18H), 5.45 – 5.25 (m, 6H), 4.02 (s, 2H), 3.41 (t, *J* = 6.7 Hz, 2H), 2.81 (t, *J* = 6.0 Hz, 4H), 2.10 – 2.01 (m, 4H), 1.64 – 1.50 (m, 5H), 1.30 (s, 10H), 0.97 (t, *J* = 7.5 Hz, 3H). IR (film): 3672, 3453, 2922, 2852, 1631, 1470, 1263, 750, 472, 420 cm⁻¹; EI-MS (*m/z*, relative intensity): 320 (M⁺, 2), 291 (4), 263 (20), 207 (12) 175 (6), 163 (4), 149 (12), 135 (20), 121 (22), 108 (42), 93 (52), 79 (100), 67 (68), 57 (54). According to ¹H NMR, 91% deuterium incorporation at each vinylic position was generated in product **33b**.



Combretastatin CA-4 (**37'**)^[16] & d₂-Combretastatin CA-4 (**37**)



According to reaction conditions A, 0.2 mmol scale **37'** was prepared from the

2-methoxy-5-((3,4,5-trimethoxyphenyl)ethynyl)phenol (62.8 mg, 0.2 mmol). The formed mixture was stirred at 60 °C under Ar for 48 h as monitored by TLC and GC-MS. The solution was then cooled to room temperature, and the crude product was purified by flash column chromatography on silica gel to afford 39.8 mg (63%) of **37'** as a light yellow solid. ¹H NMR (400 MHz, CDCl₃) δ 6.92 (d, J = 2.0 Hz, 1H), 6.80 (dd, J = 8.3, 1.9 Hz, 1H), 6.73 (d, J = 8.3 Hz, 1H), 6.52 (s, 2H), 6.47 (d, J = 12.2 Hz, 1H), 6.41 (d, J = 12.2 Hz, 1H), 5.54 (s, 1H), 3.86 (s, 3H), 3.84 (s, 3H), 3.70 (s, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 152.8, 145.7, 145.2, 137.1, 132.7, 130.6, 129.4, 129.0, 121.1, 115.0, 110.3, 106.0, 60.9, 55.9, 55.9. According to reaction conditions **B**, 0.2 mmol scale **45a** was prepared from the 2-methoxy-5-((3,4,5-trimethoxyphenyl)ethynyl)phenol (63.2 mg, 0.2 mmol). The formed mixture was stirred at 60 °C under Ar for 48 h as monitored by TLC and GC-MS. The solution was then cooled to room temperature, and the crude product was purified by flash column chromatography on silica gel to afford 40.1 mg (63%) of **37** as a light yellow solid. ¹H NMR (400 MHz, CDCl₃) δ 6.93 (d, J = 2.0 Hz, 1H), 6.80 (dd, J = 8.3, 2.0 Hz, 1H), 6.73 (d, J = 8.3 Hz, 1H), 6.53 (s, 2H), 6.46 (d, J = 3.8 Hz, 0.09H), 6.41 (d, J = 5.2 Hz, 0.09H), 5.53 (s, 1H), 3.87 (s, 3H), 3.84 (s, 3H), 3.70 (s, 6H). IR (film): 3747, 3453, 2921, 2852, 1632, 1579, 1506, 1456, 1415, 1276, 1126, 1008, 750, 457, 420 cm⁻¹; HRMS m/z (ESI) calcd for C₁₈H₁₈D₂O₅Na (M + Na)⁺: 341.1328, found 341.1325. According to ¹H NMR, 91% deuterium incorporation at each vinylic position was generated in product **37**.

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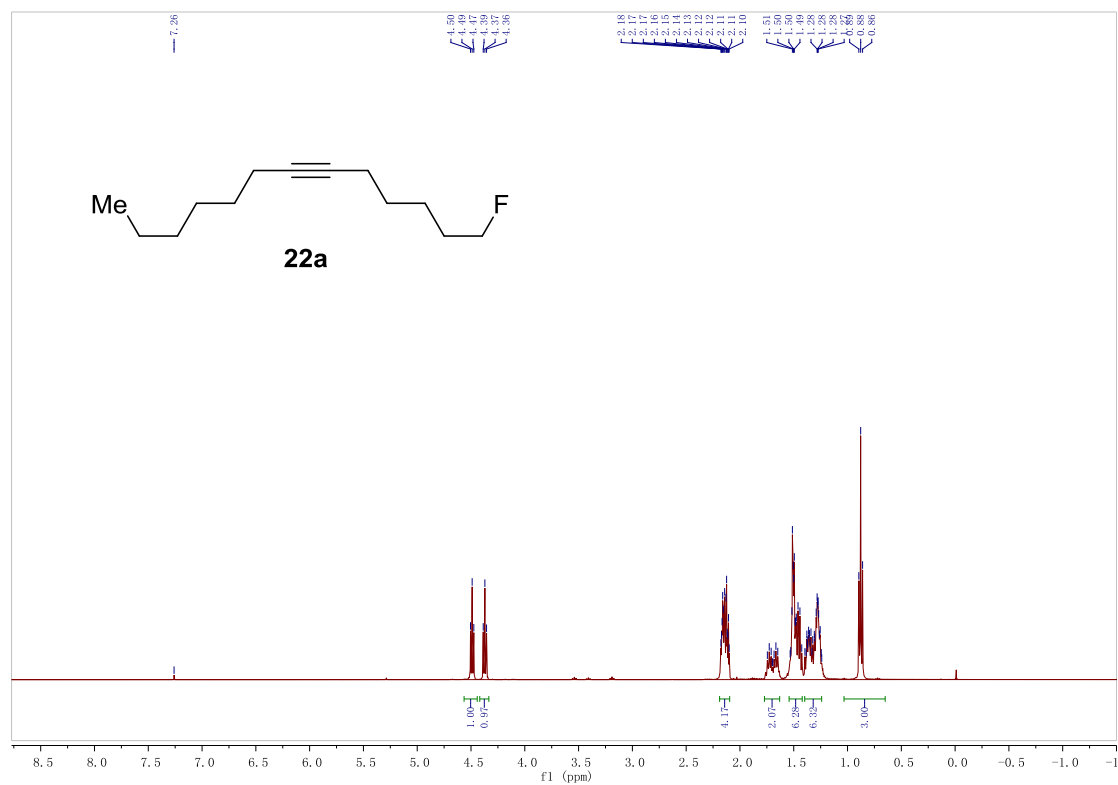
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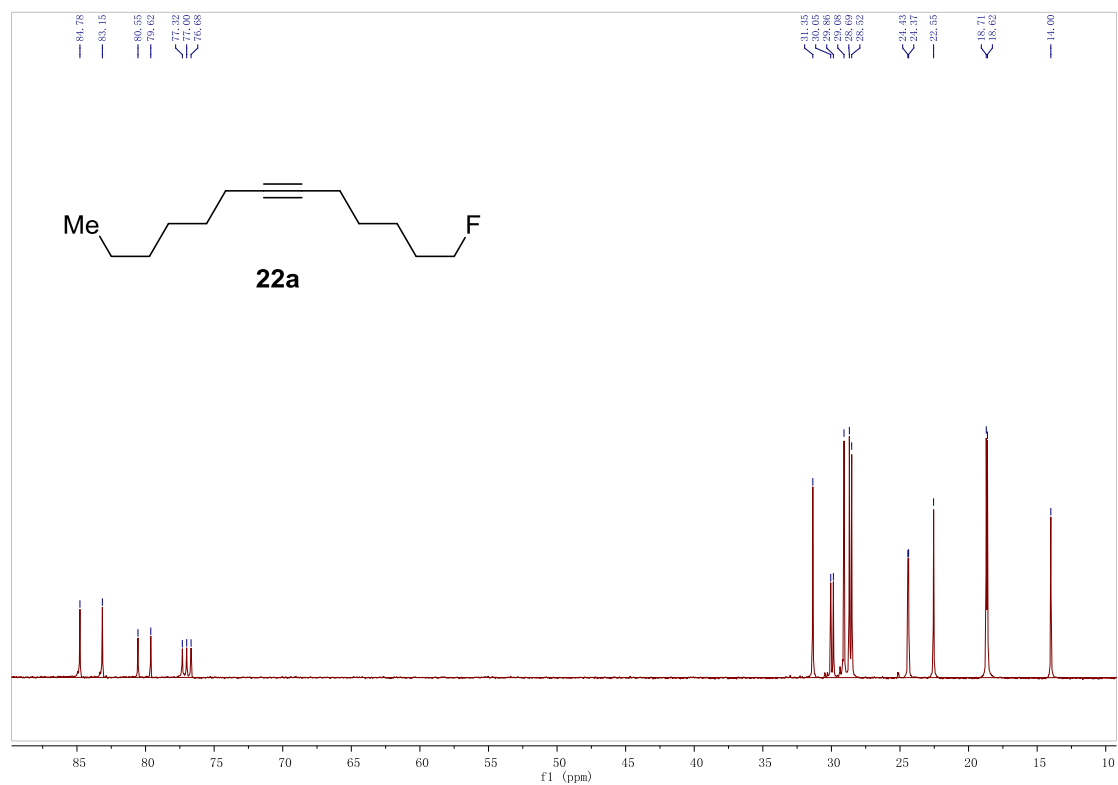
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5. Copies of NMR Spectra

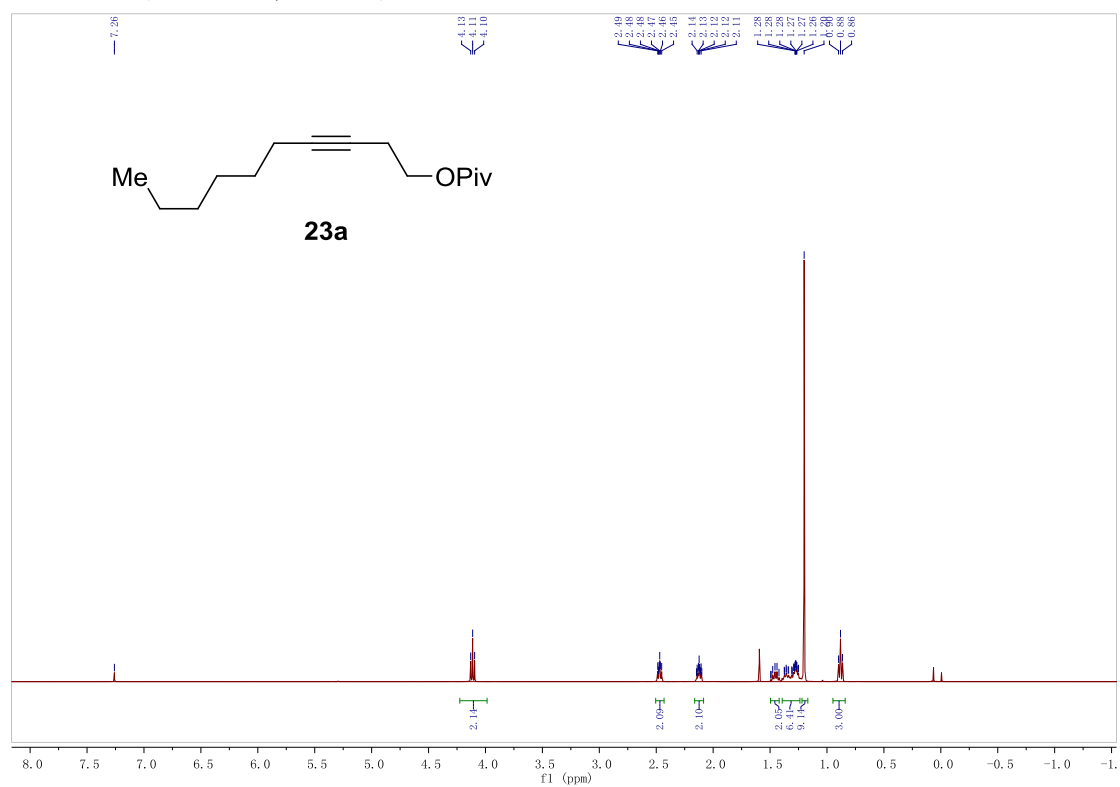
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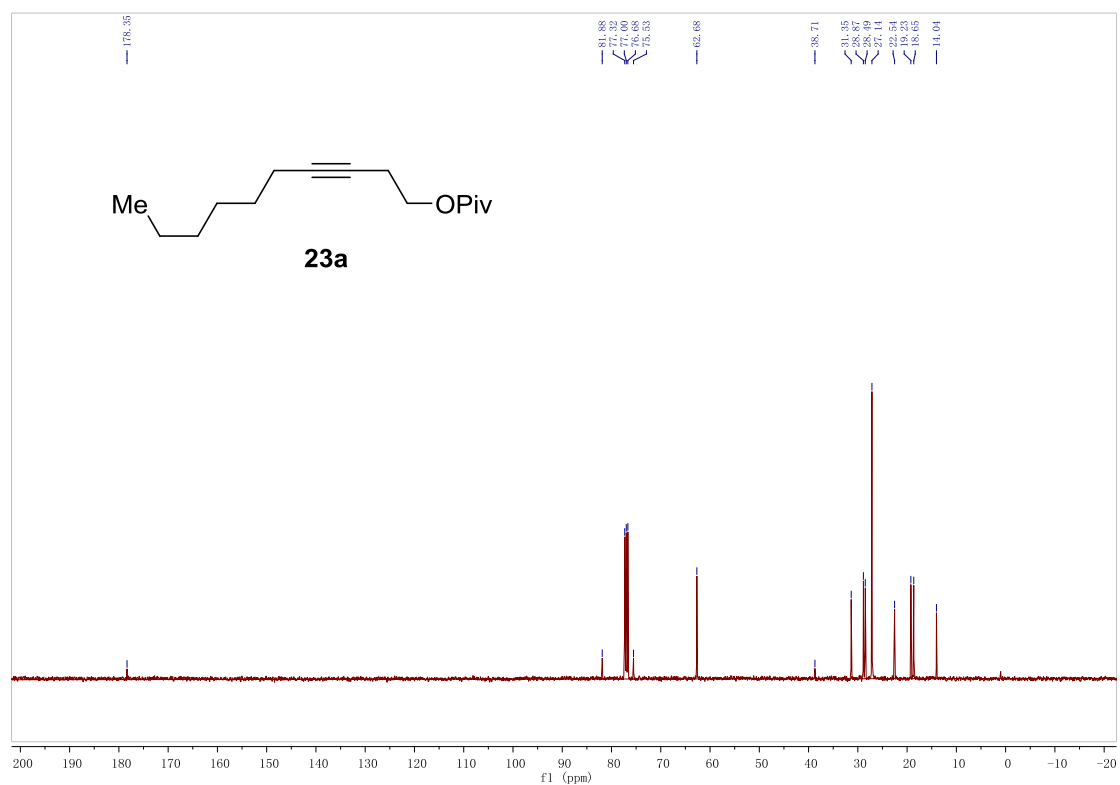
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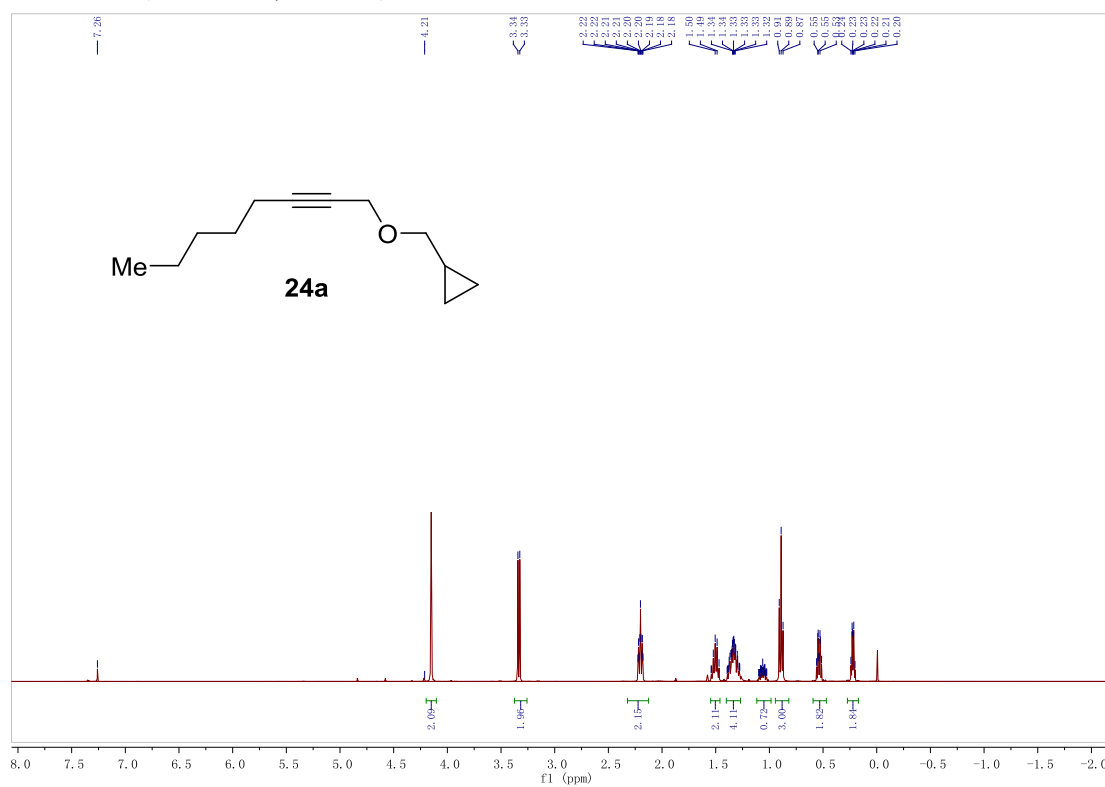
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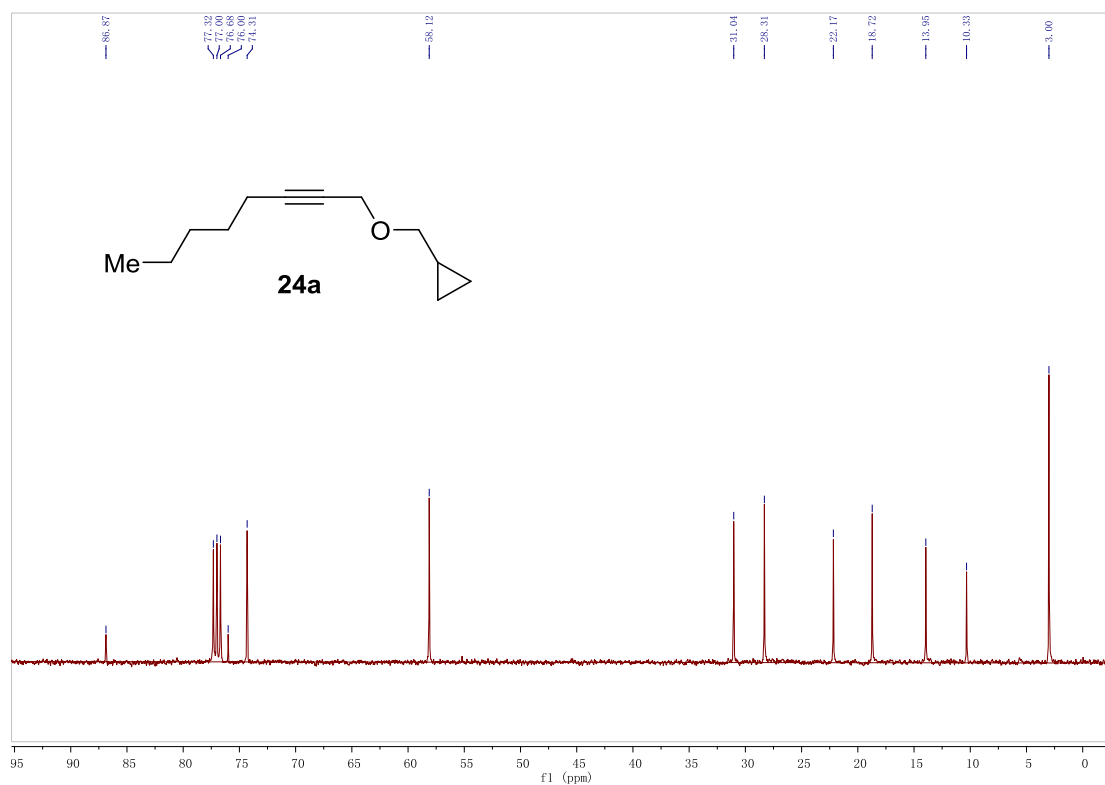
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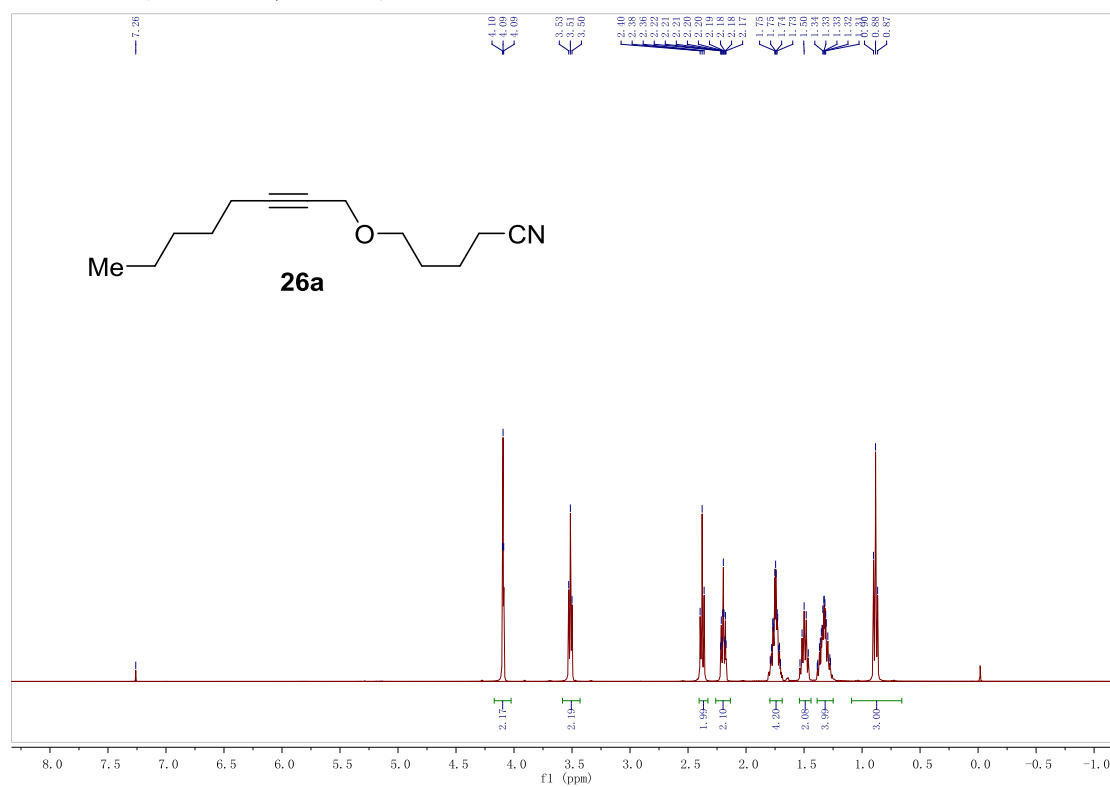
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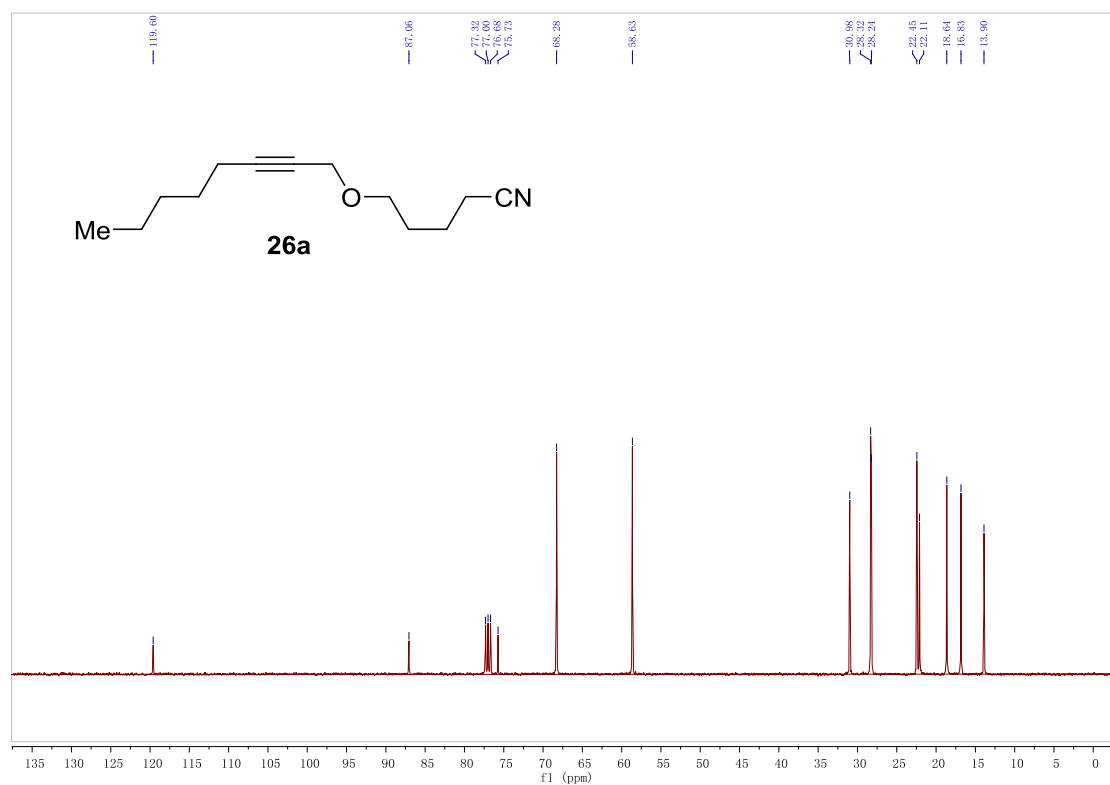
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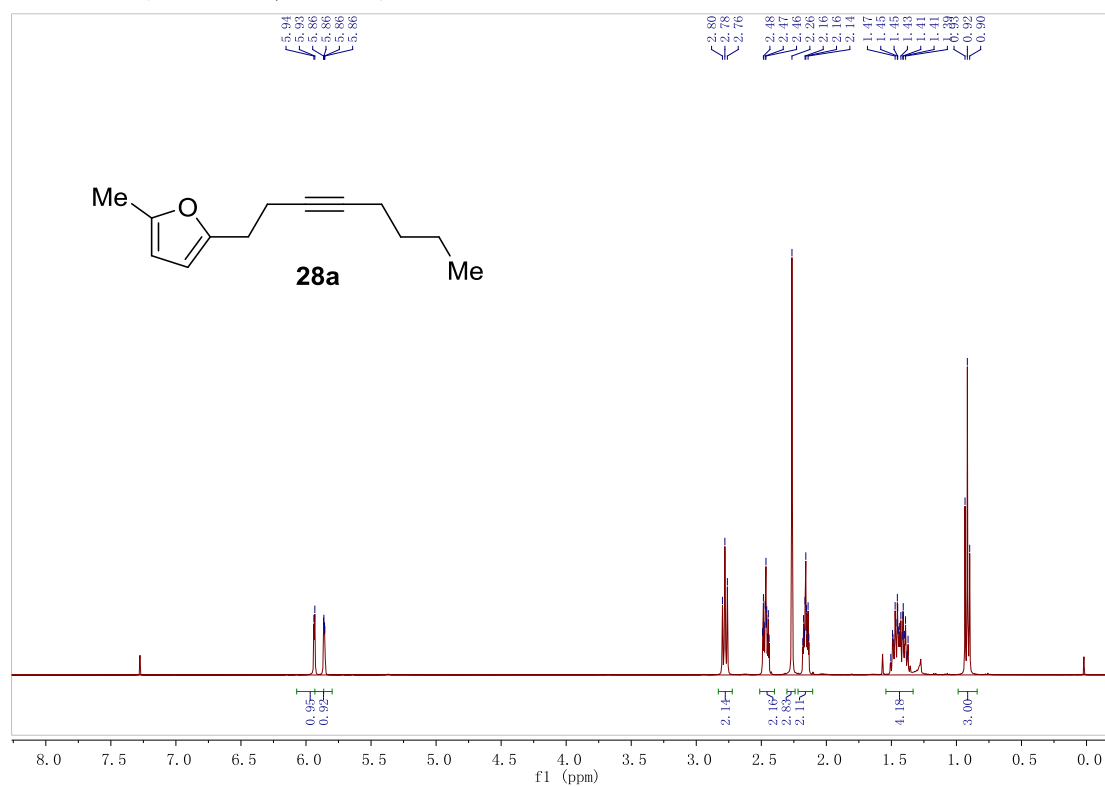
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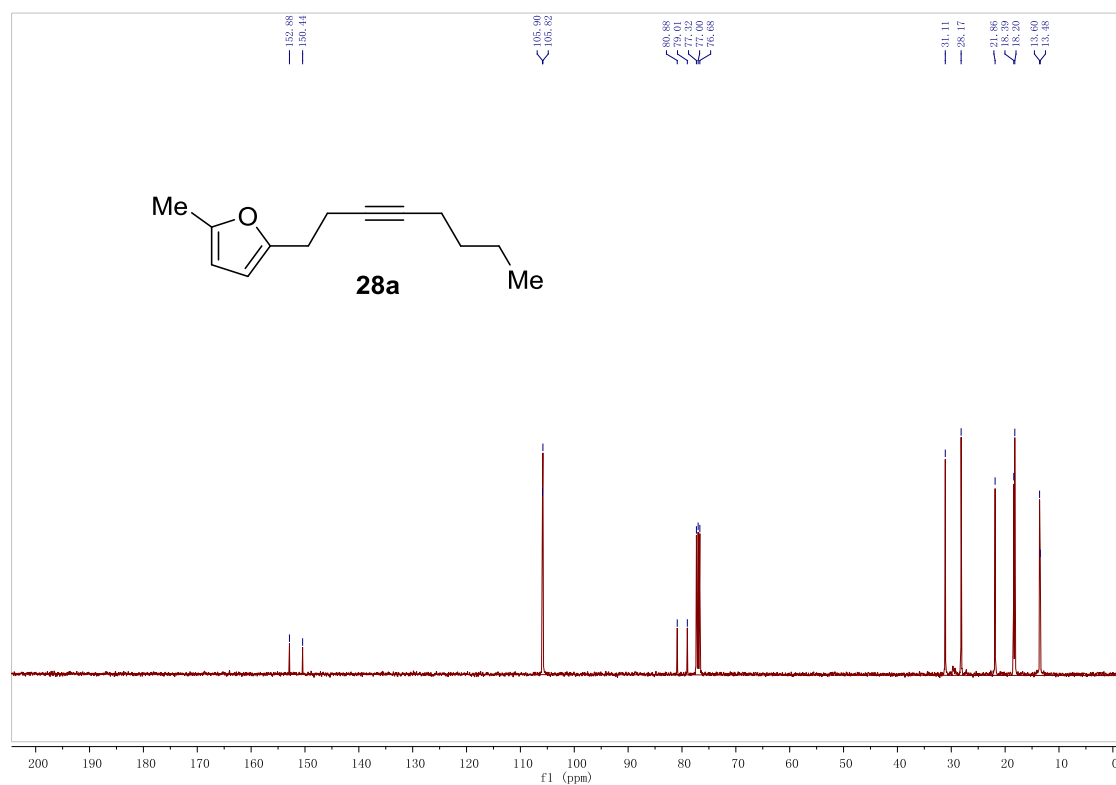
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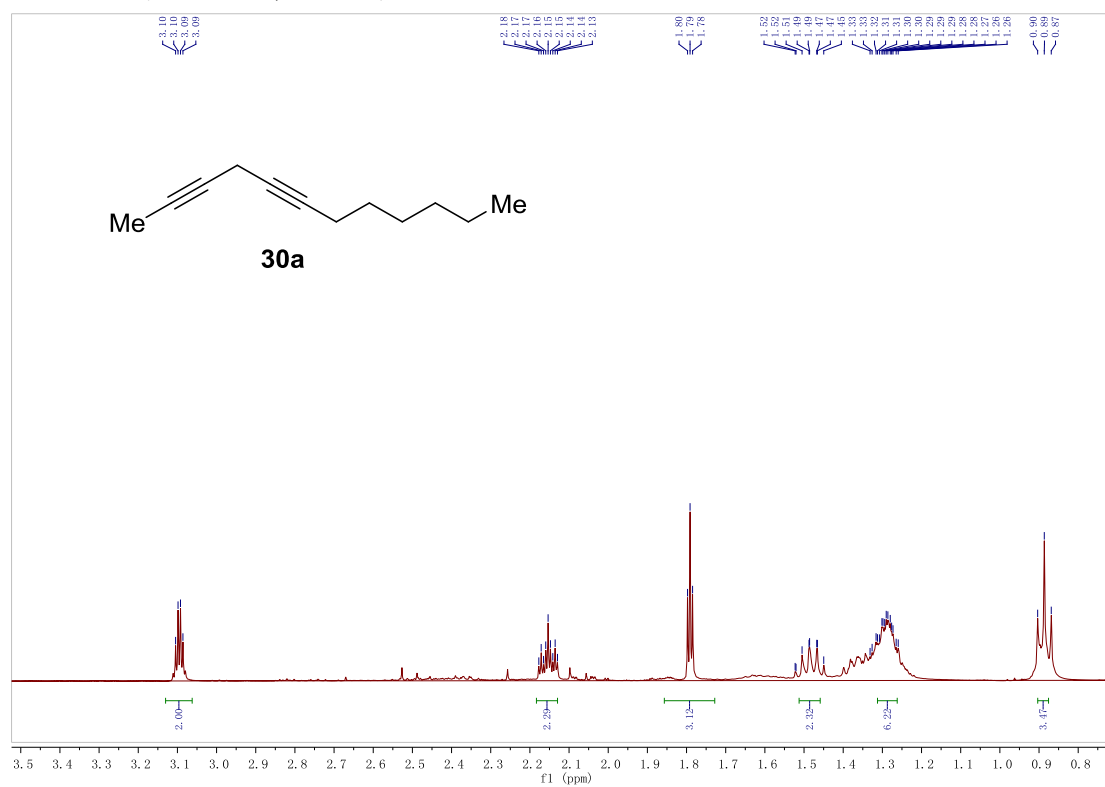
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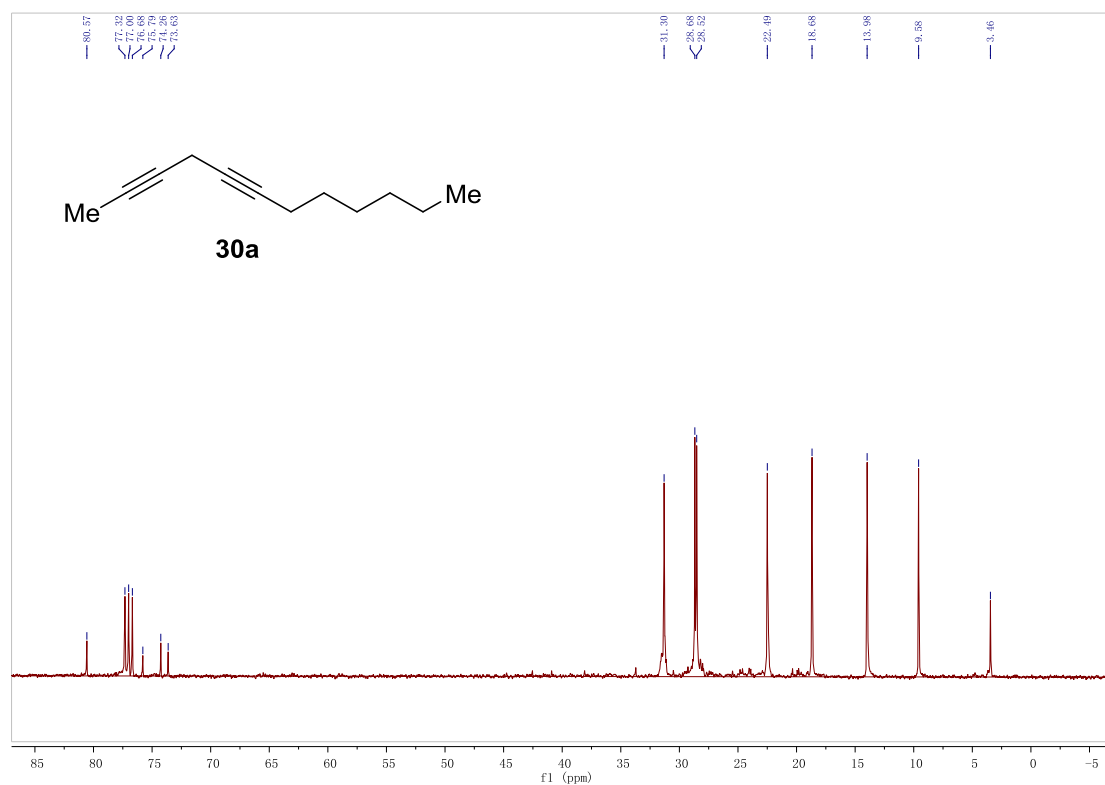
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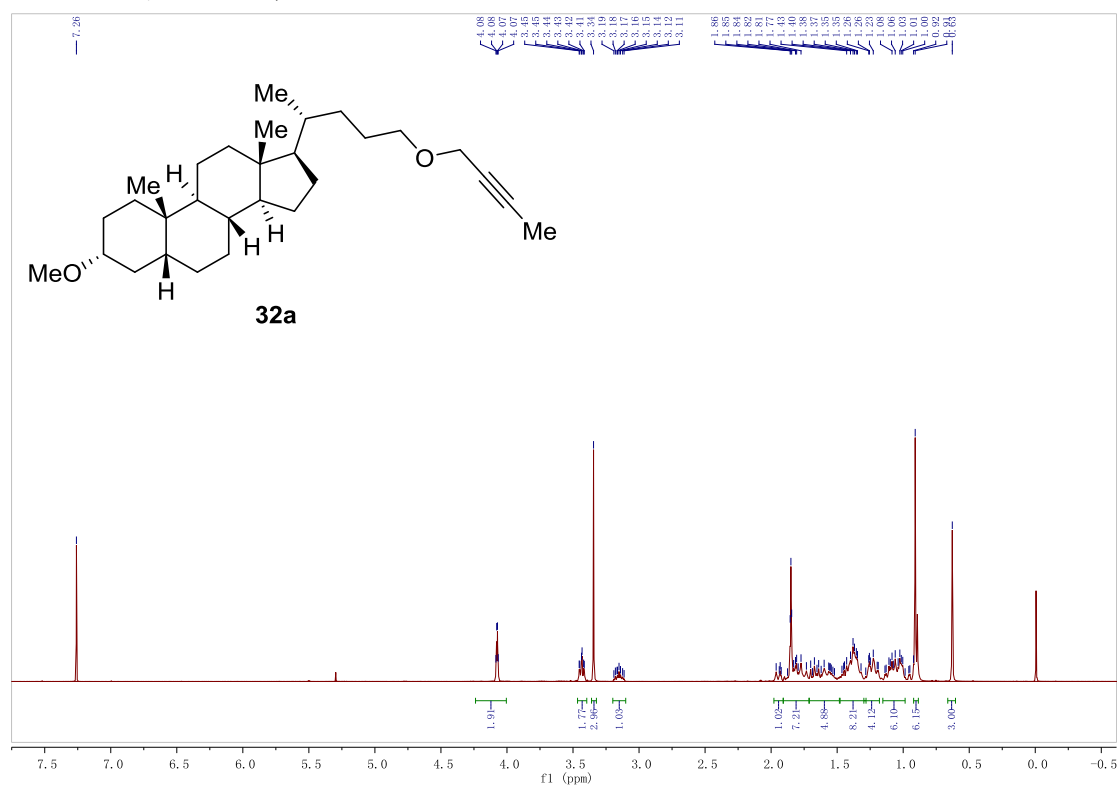
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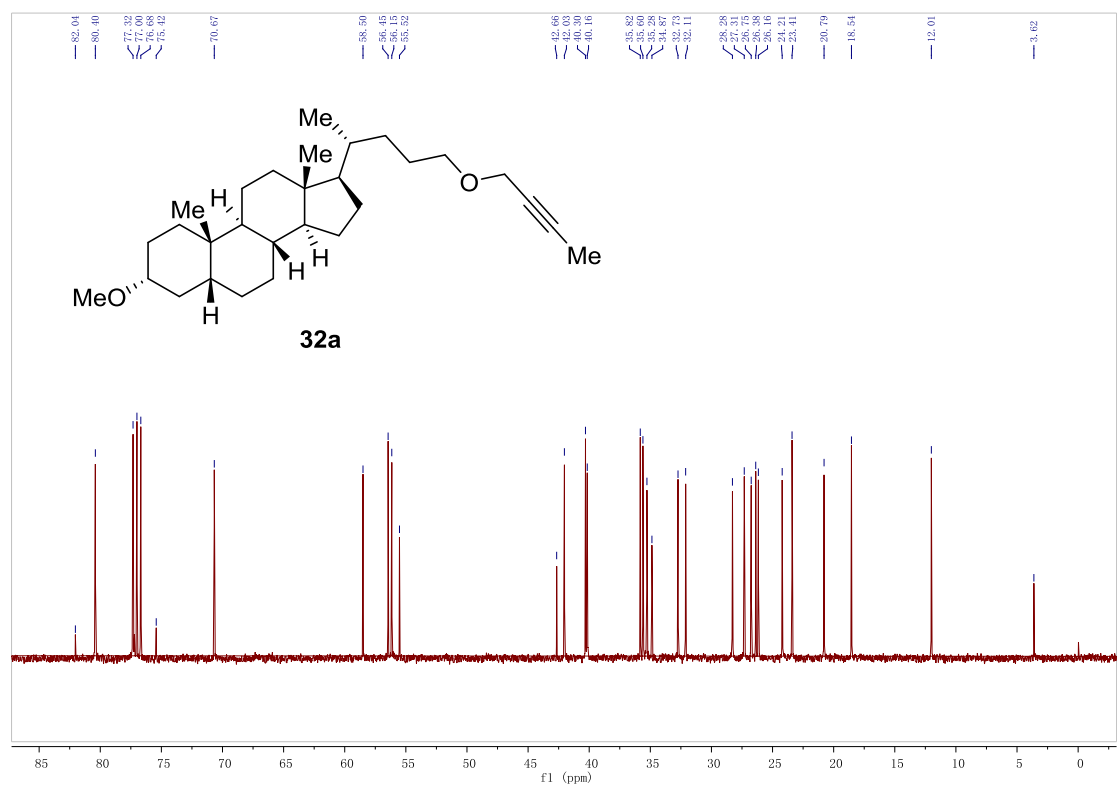
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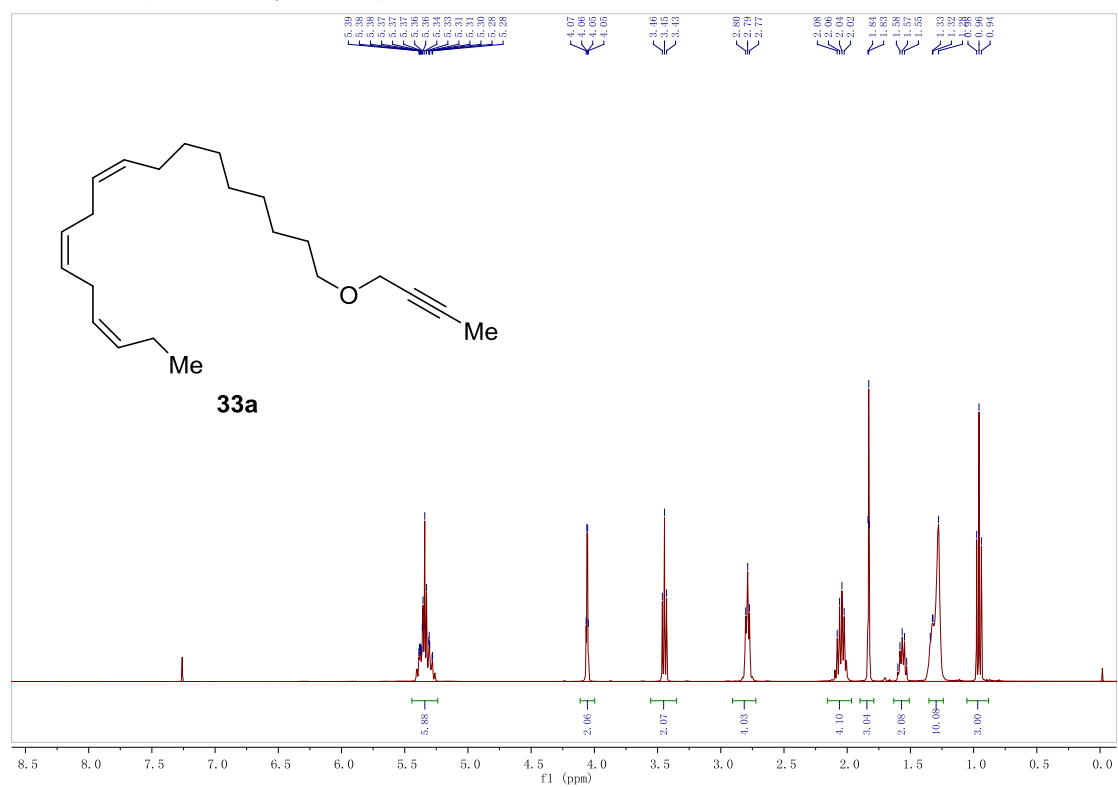
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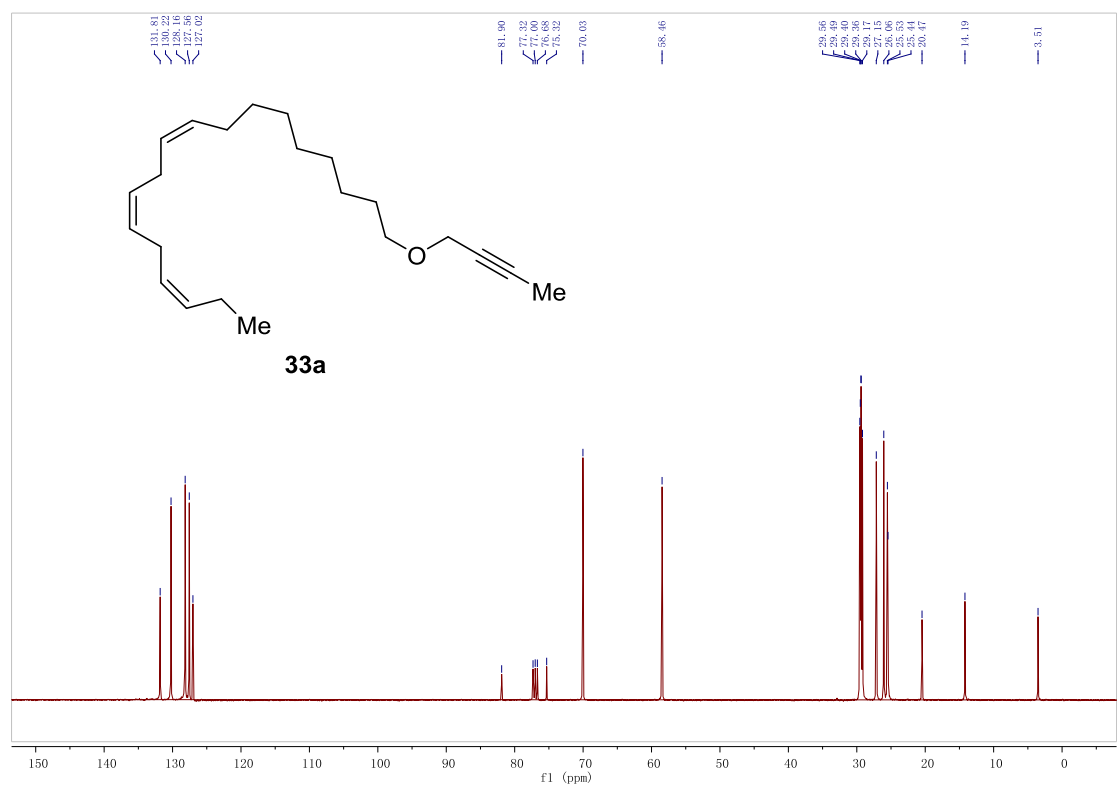
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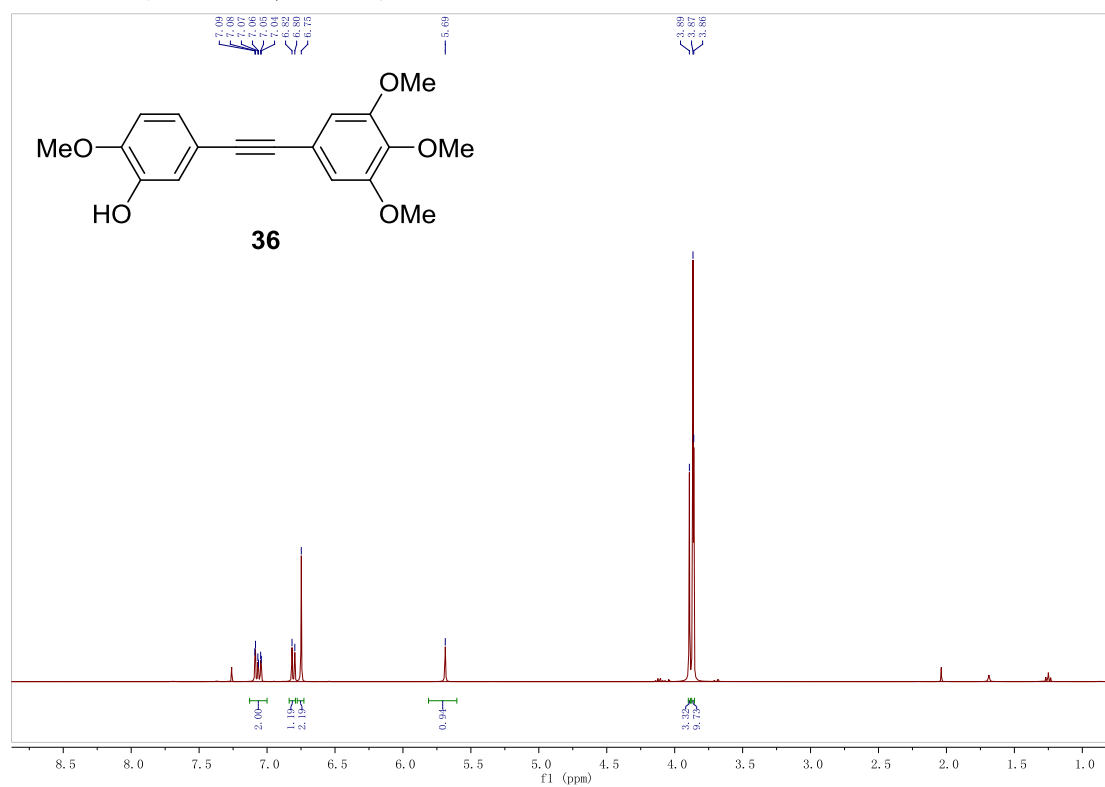
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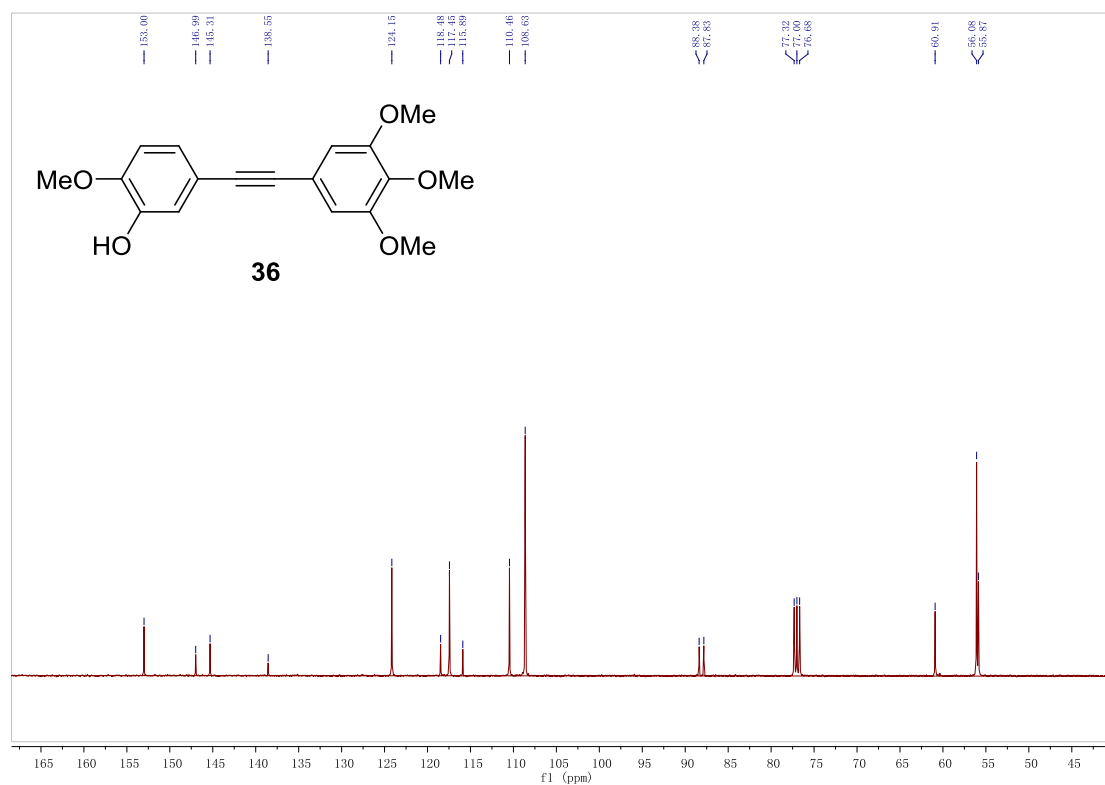
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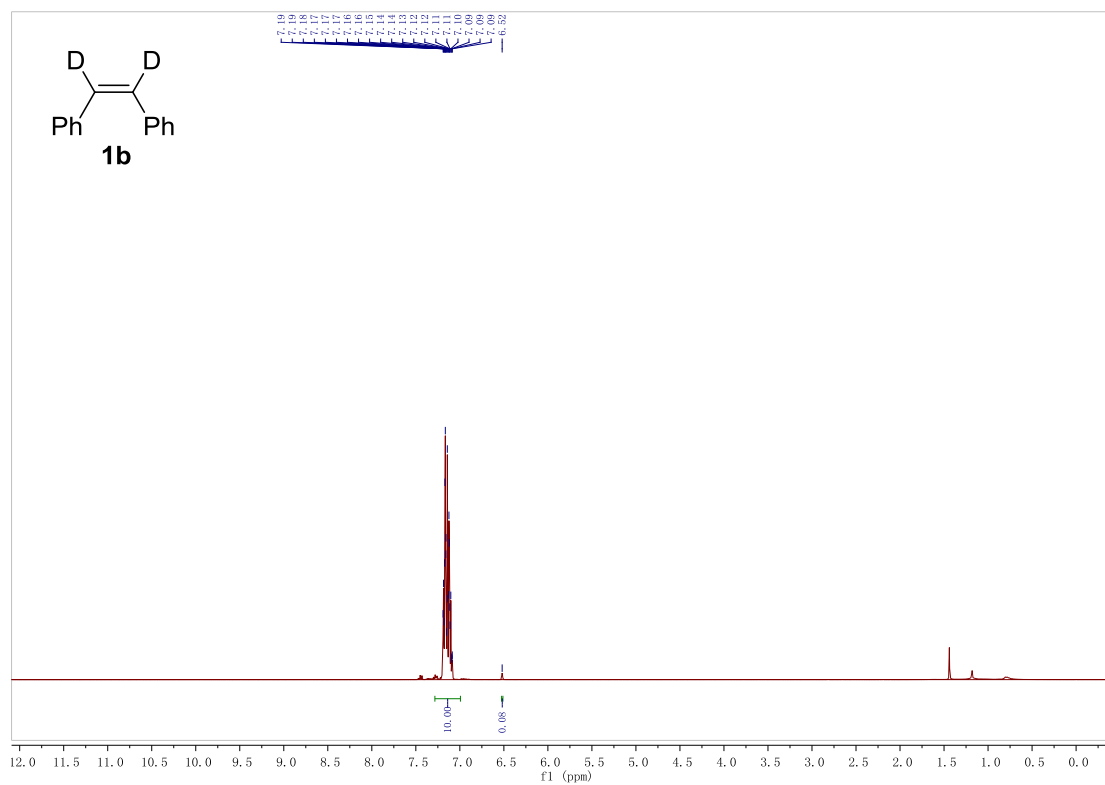
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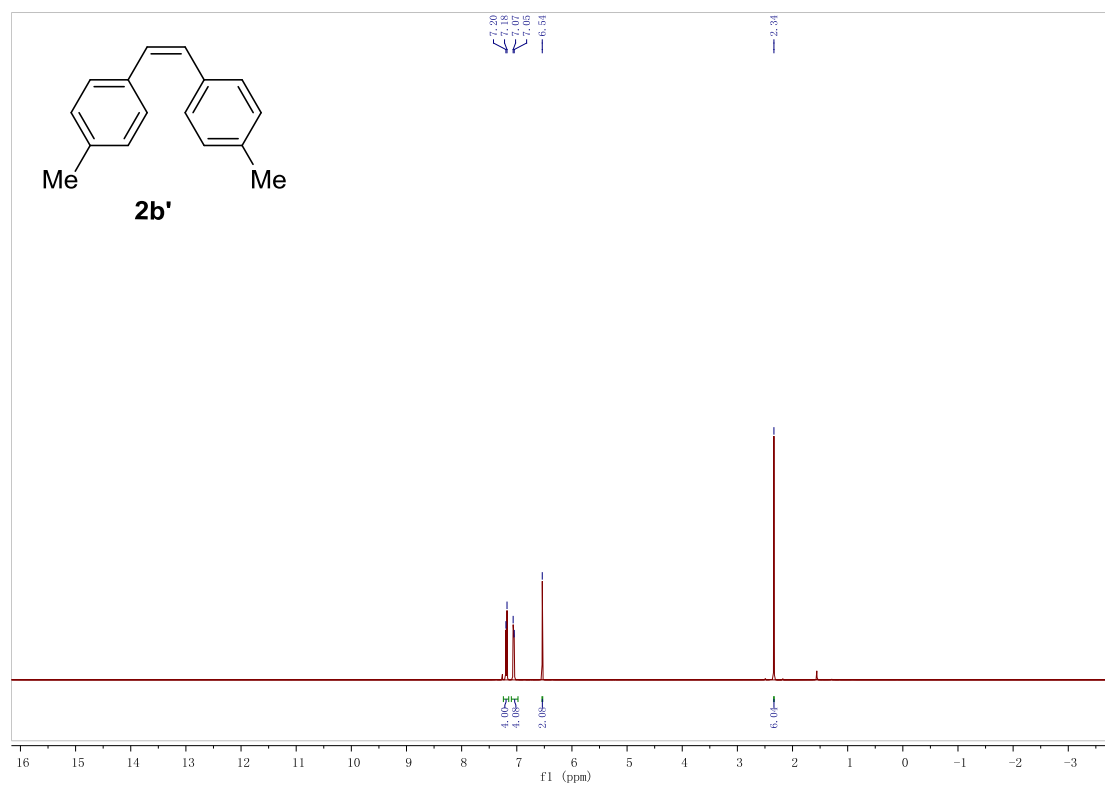
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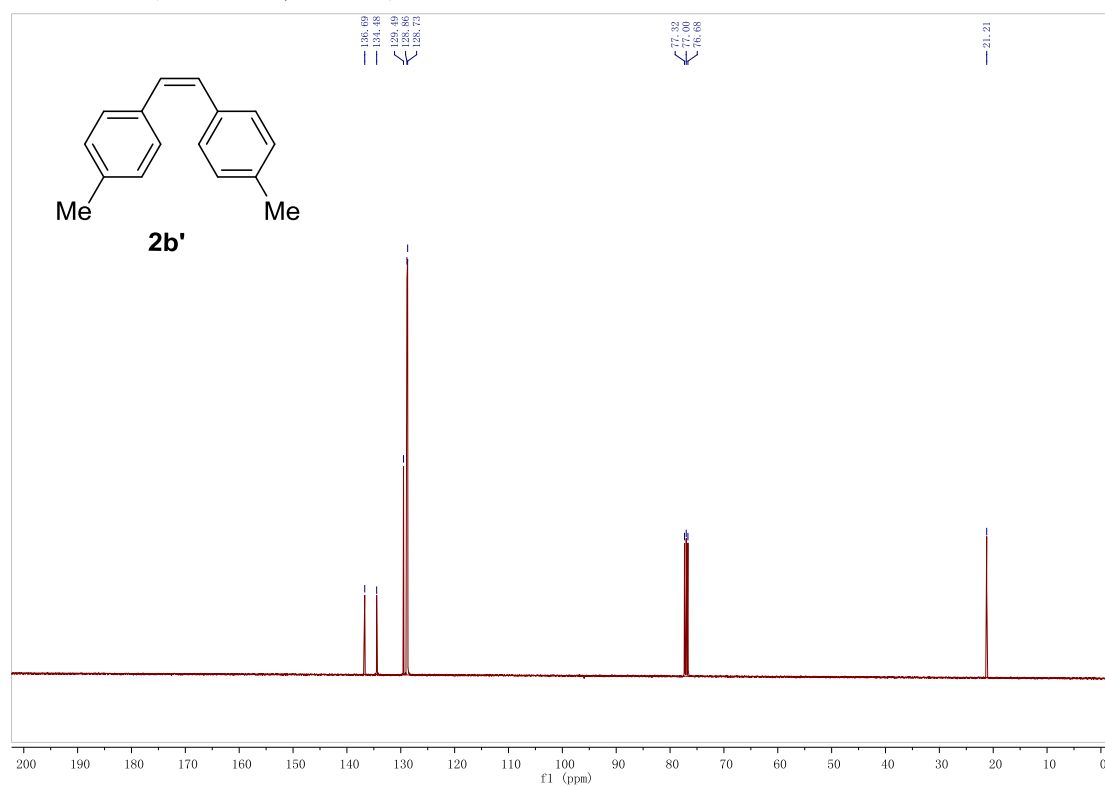
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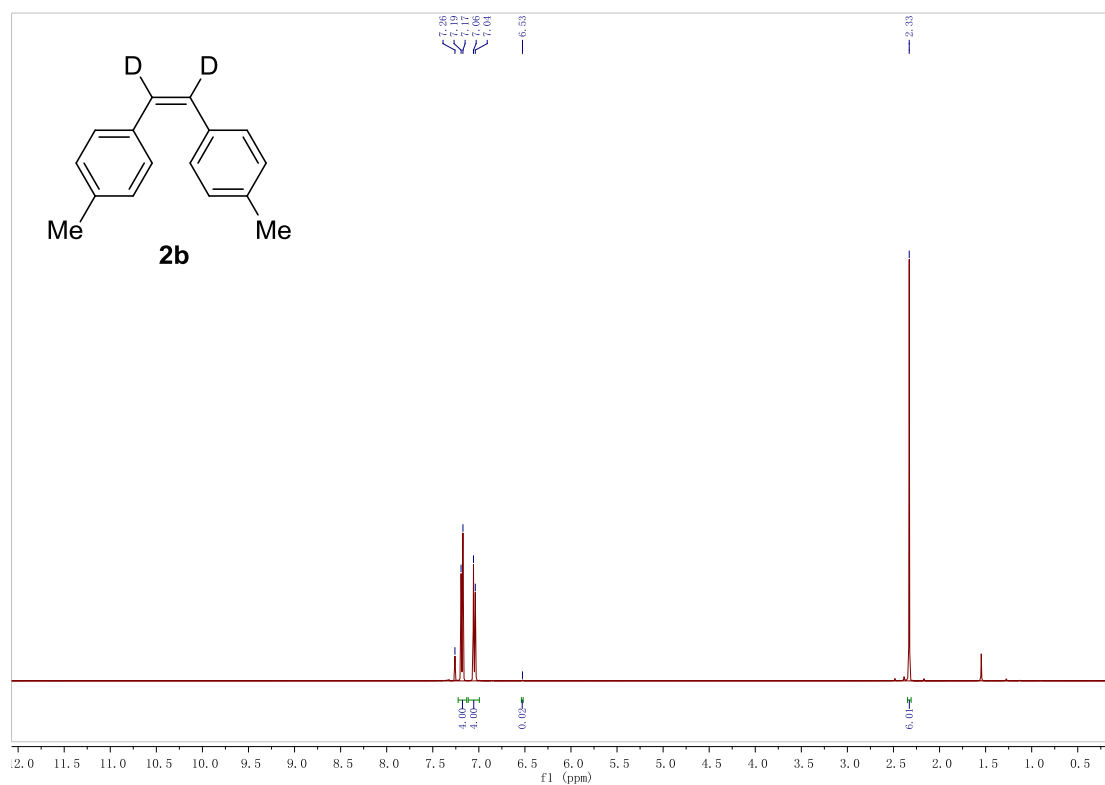
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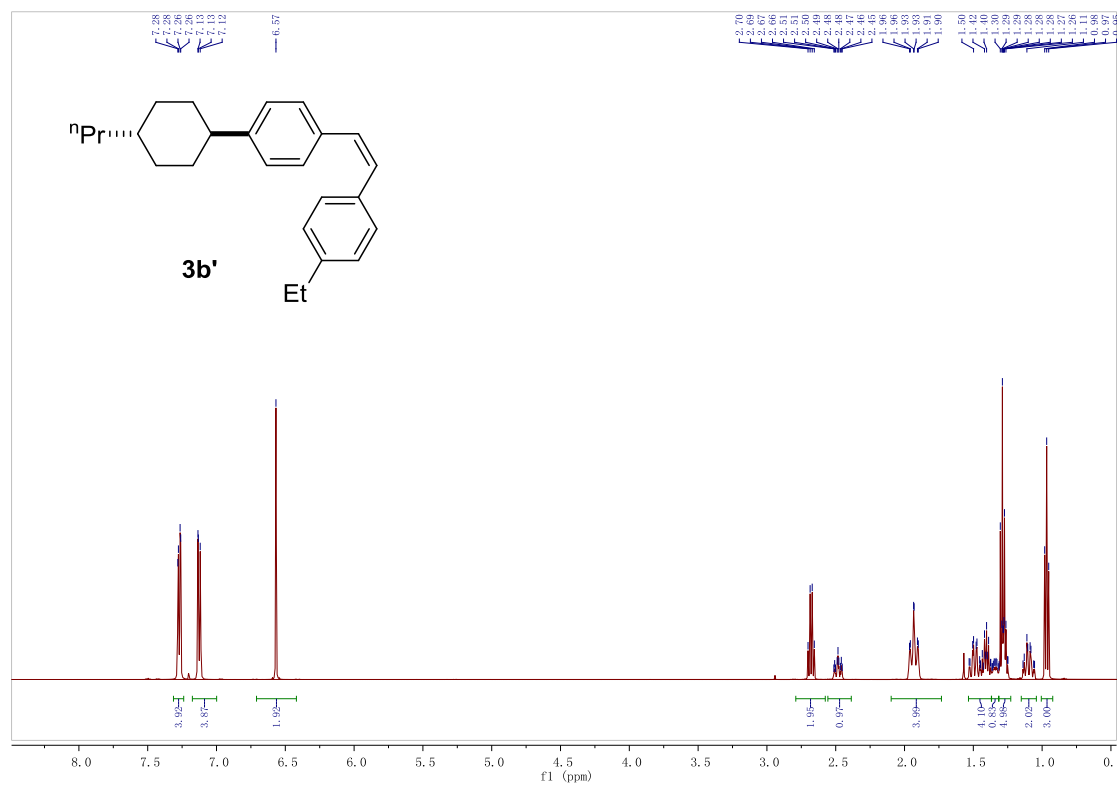
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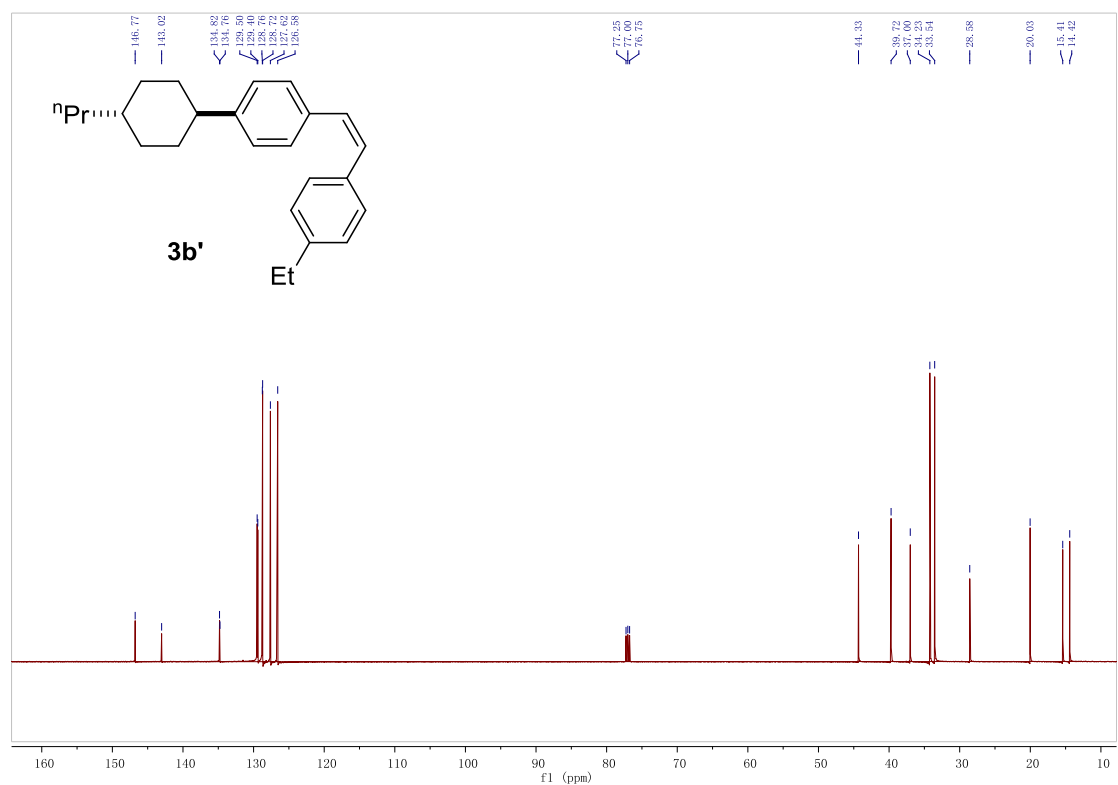
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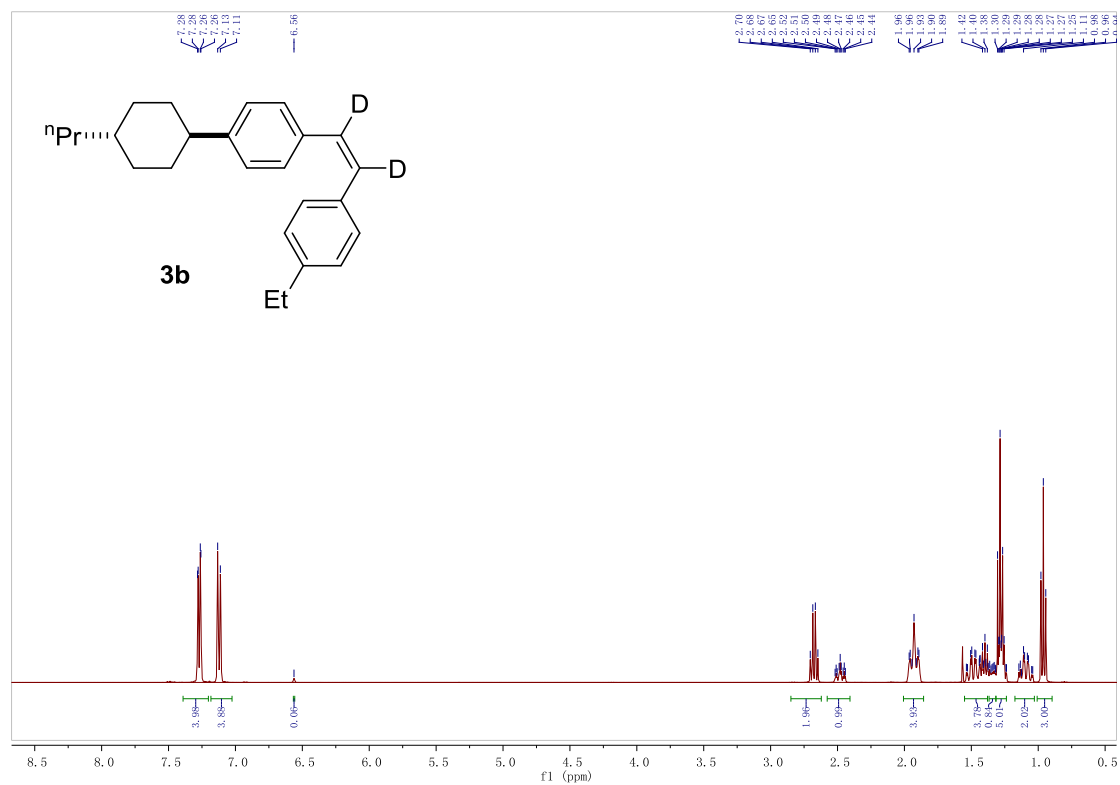
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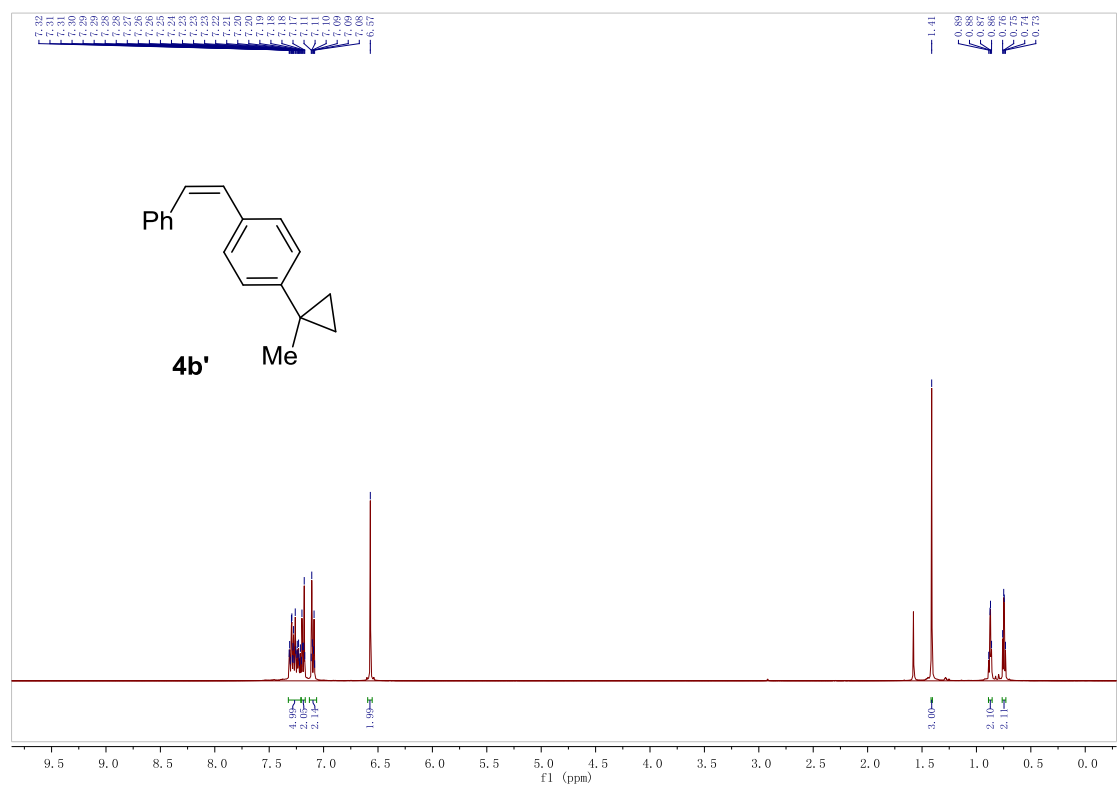
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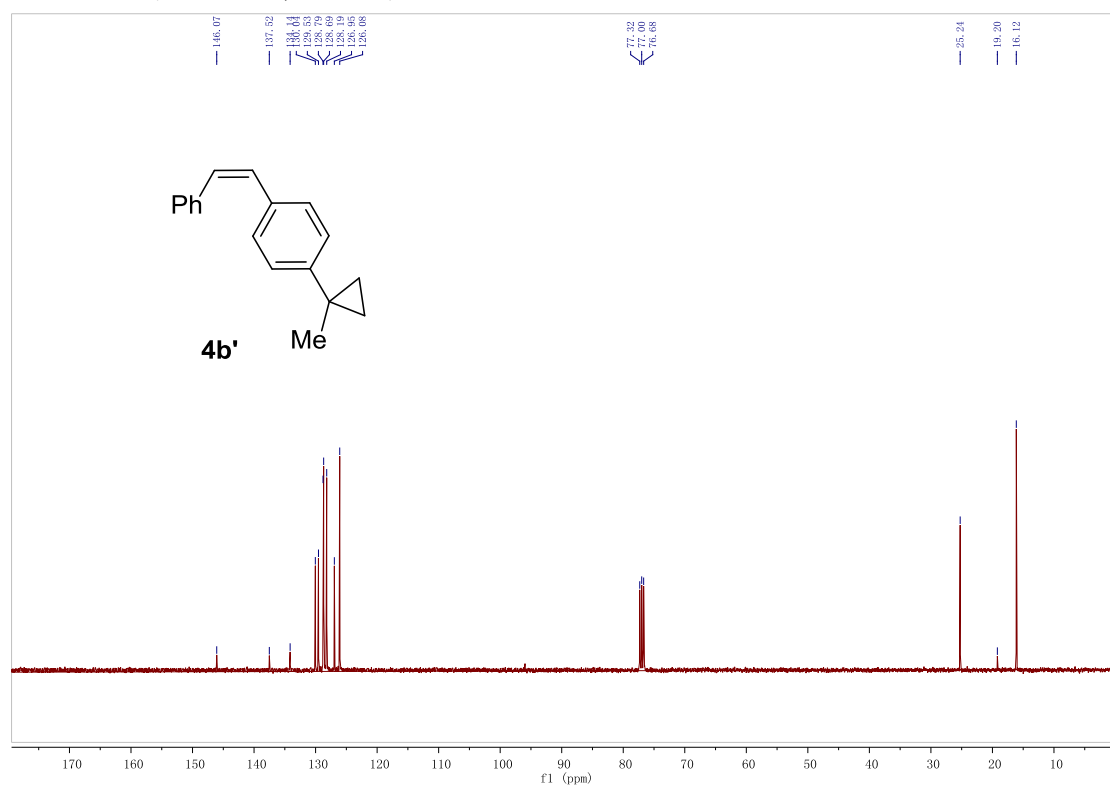
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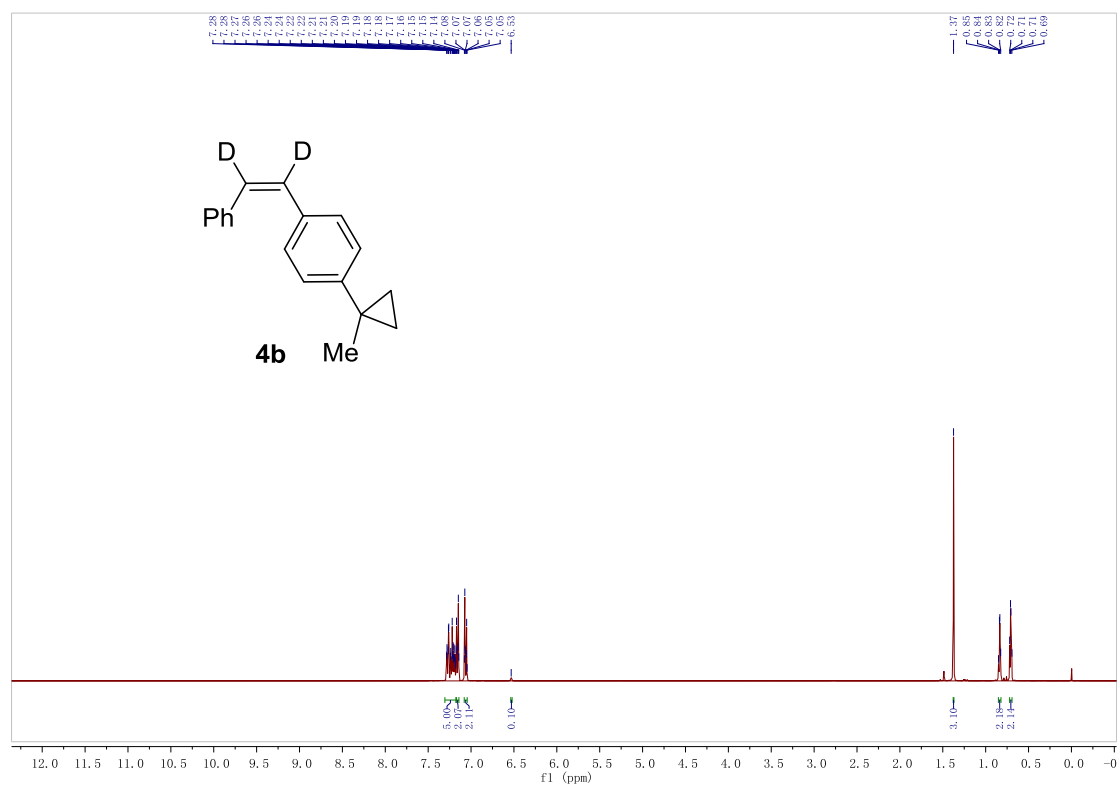
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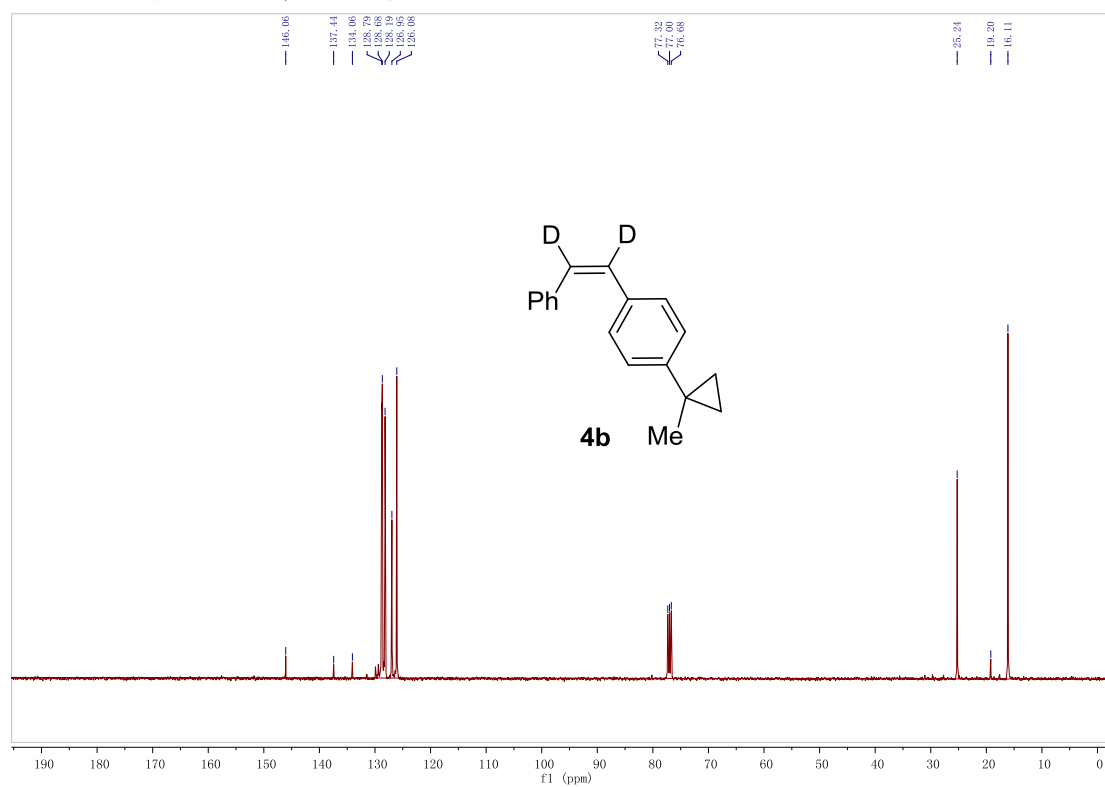
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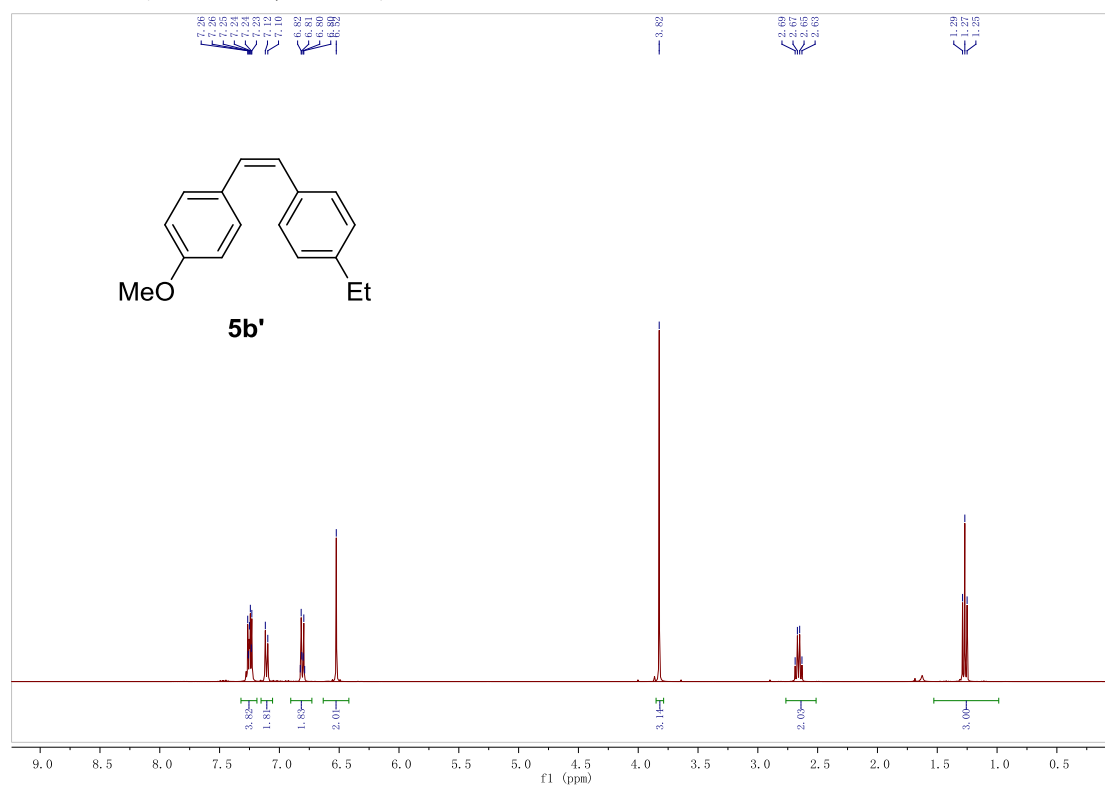
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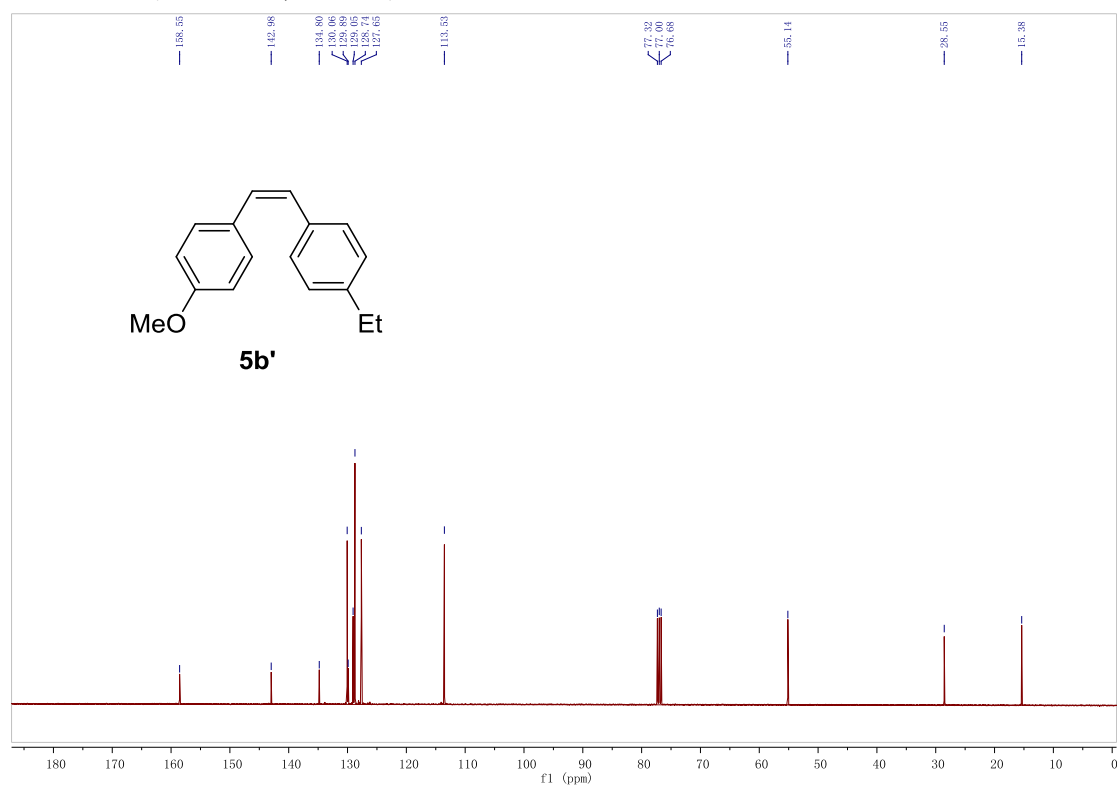
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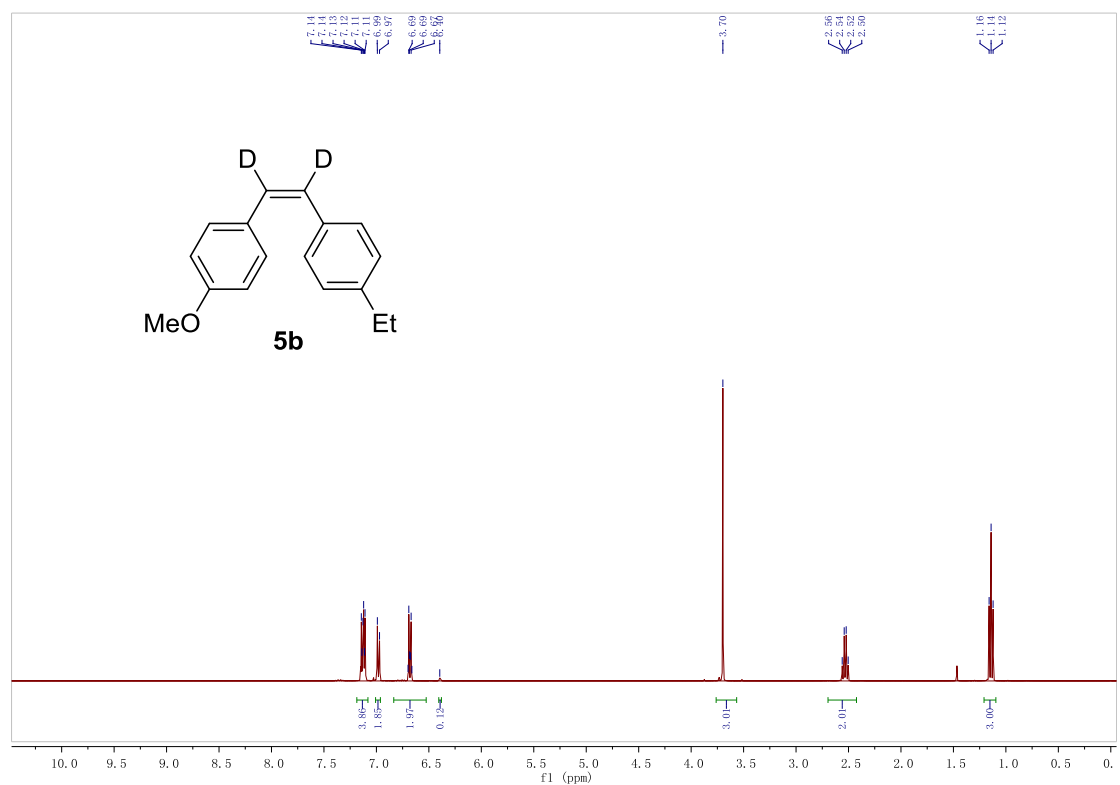
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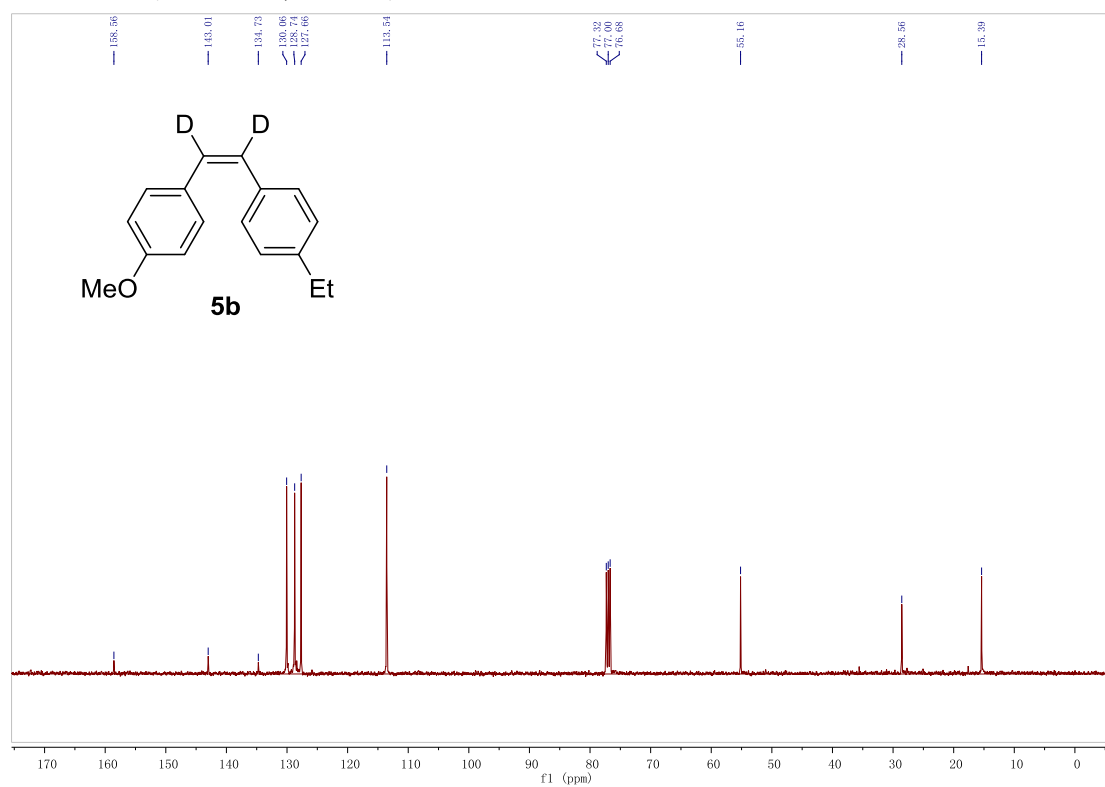
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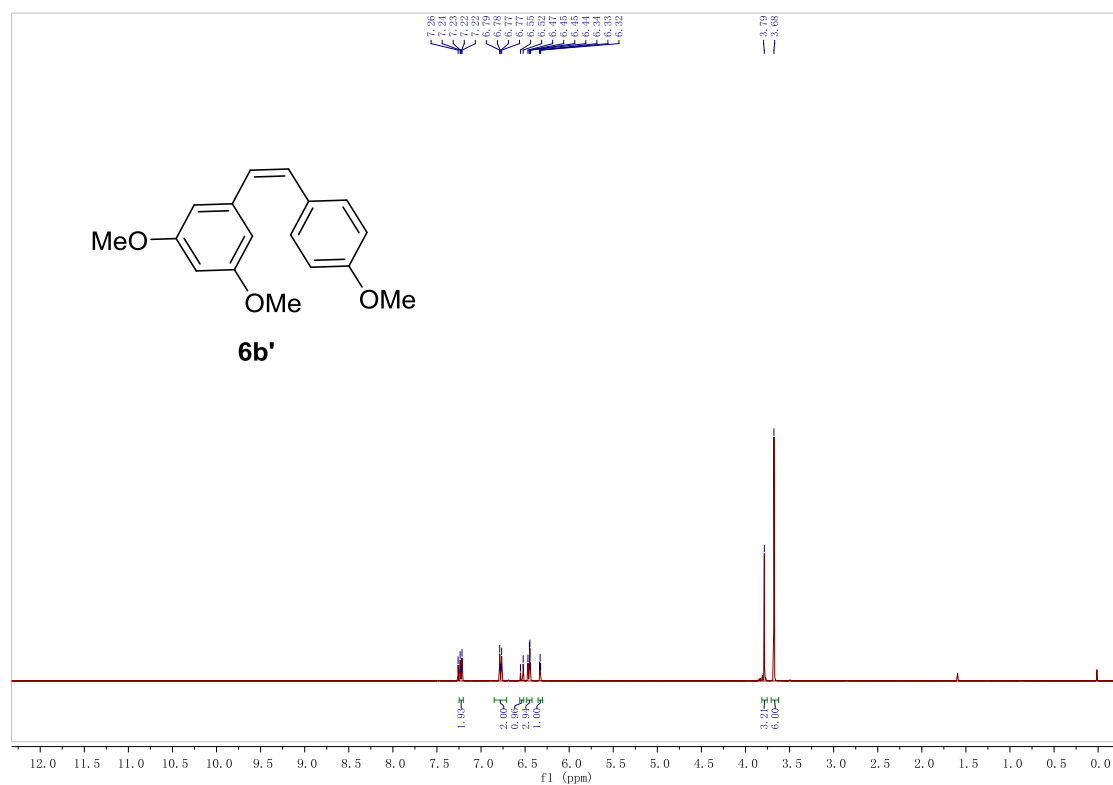
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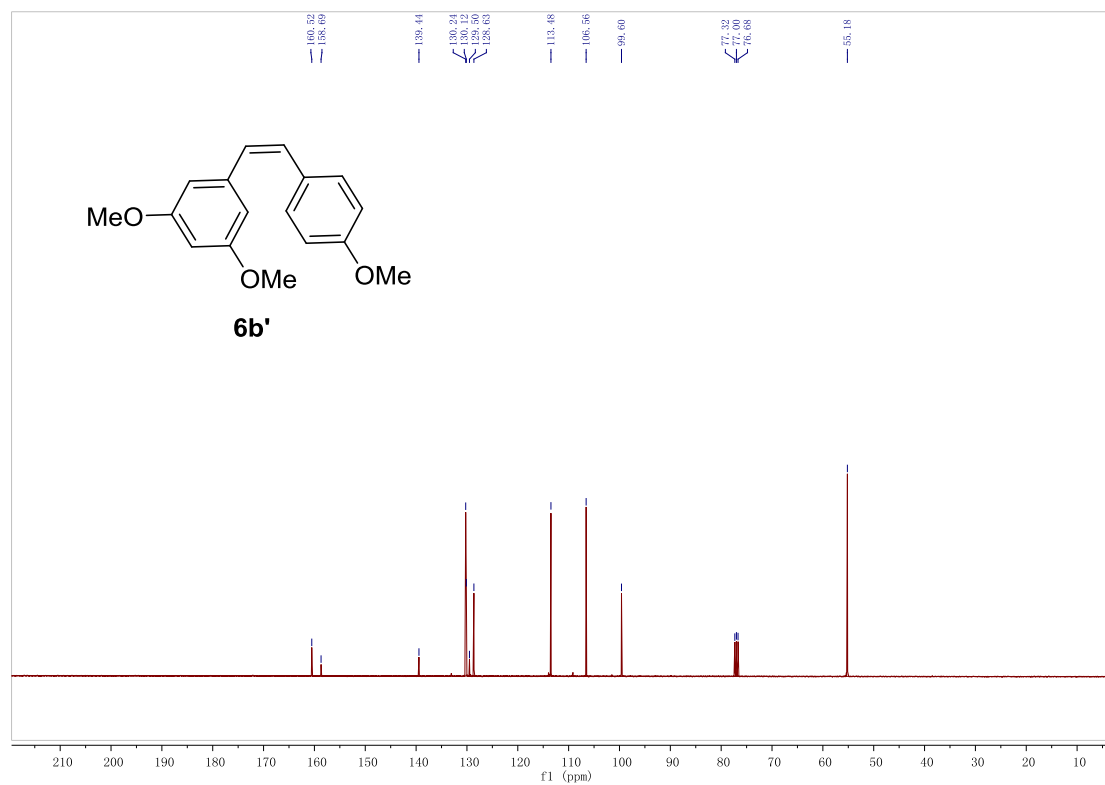
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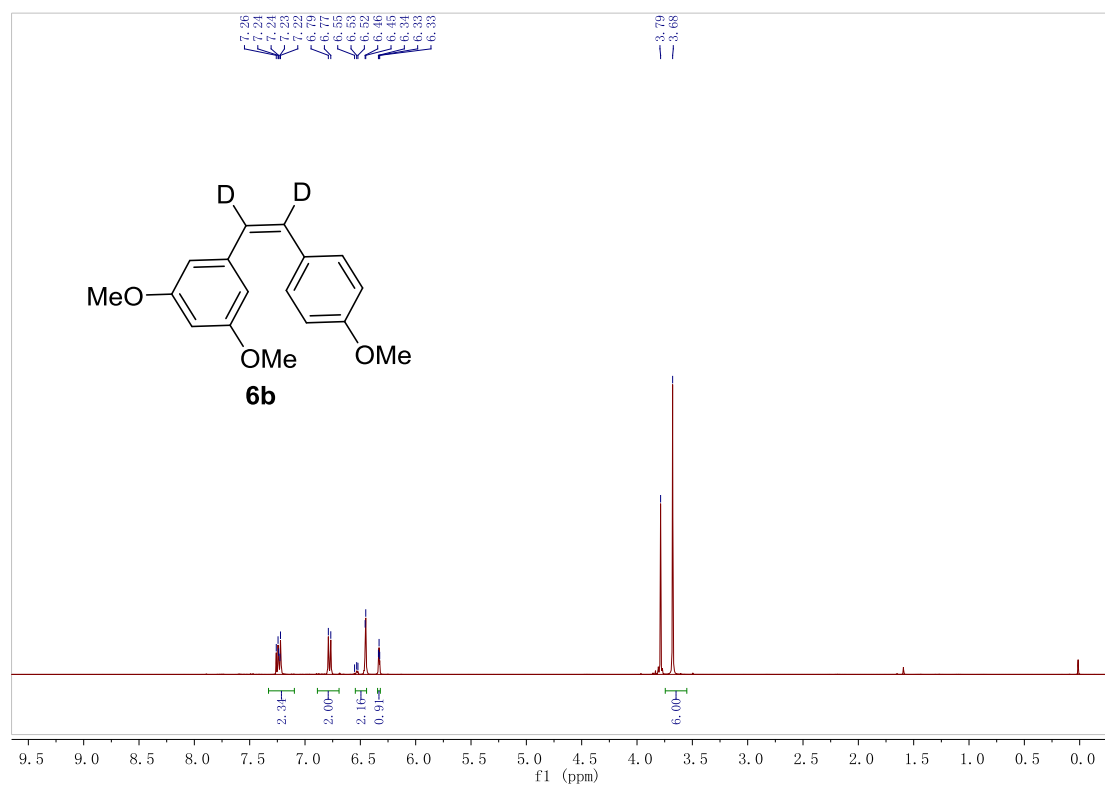
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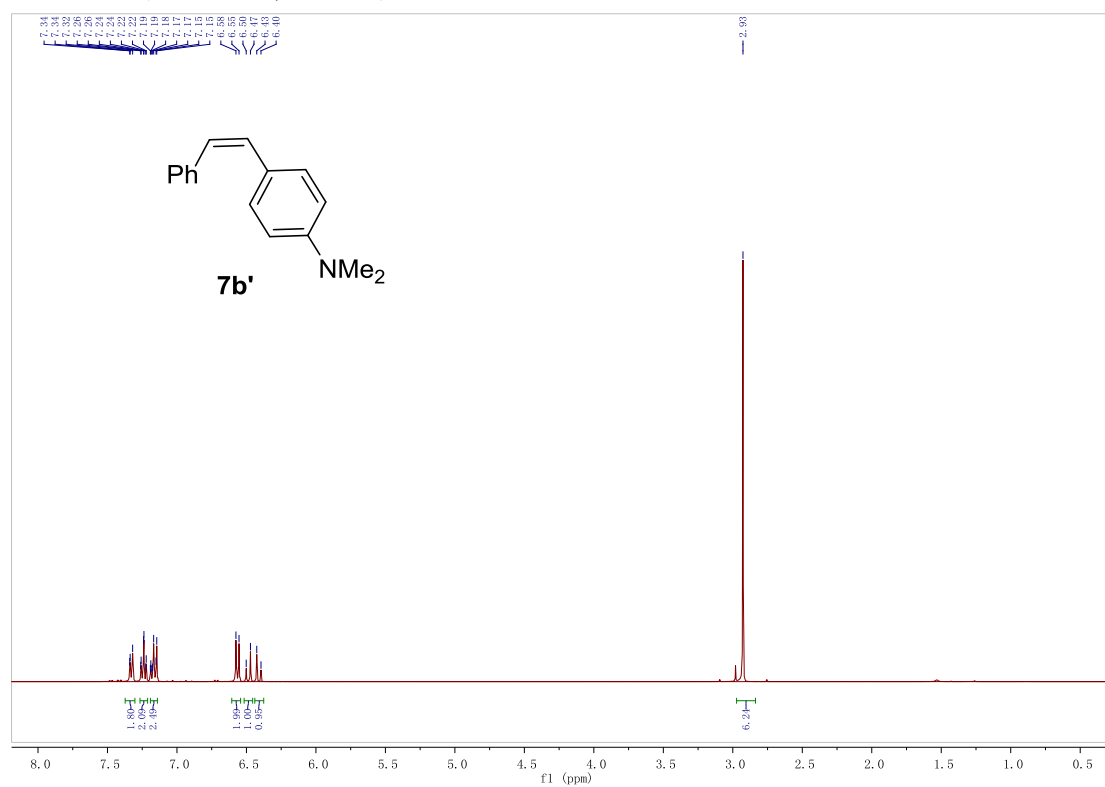
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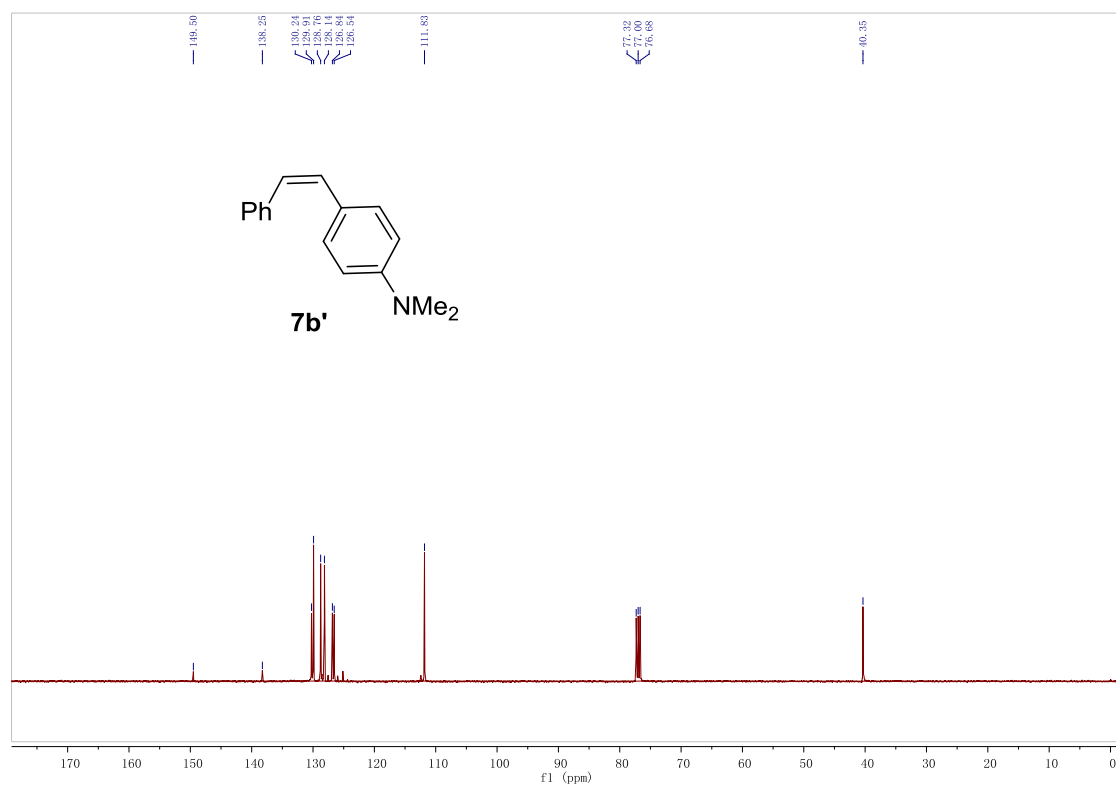
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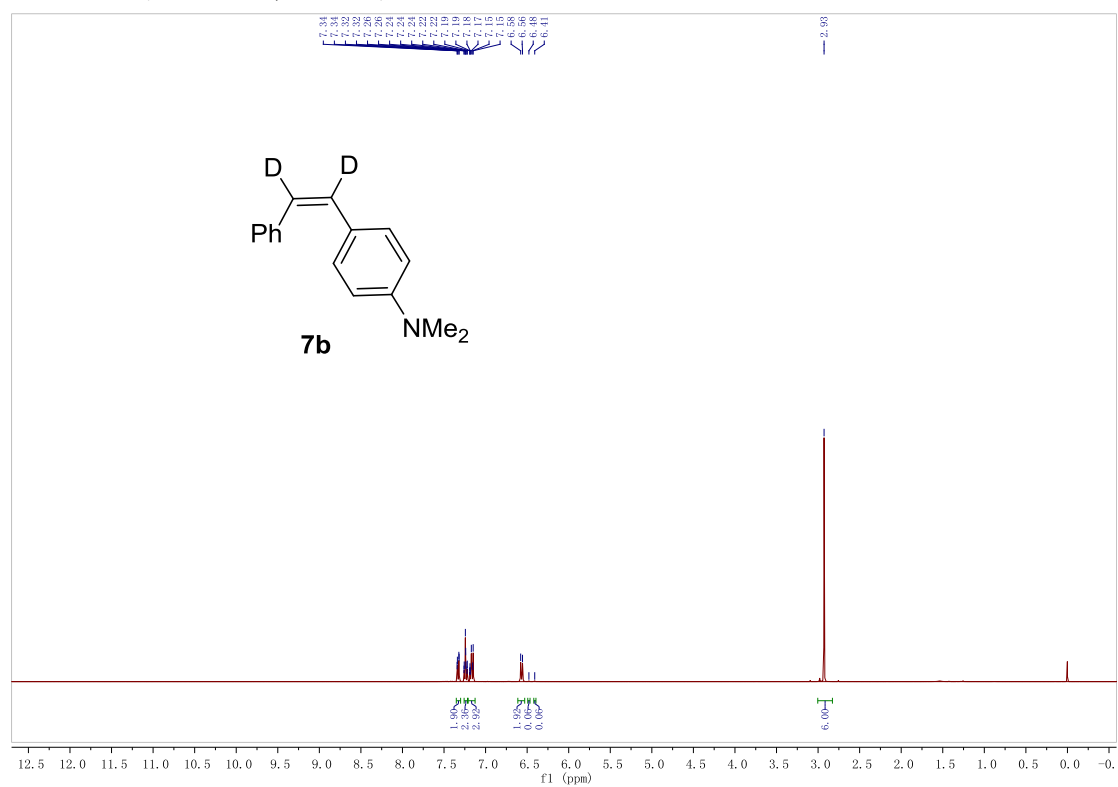
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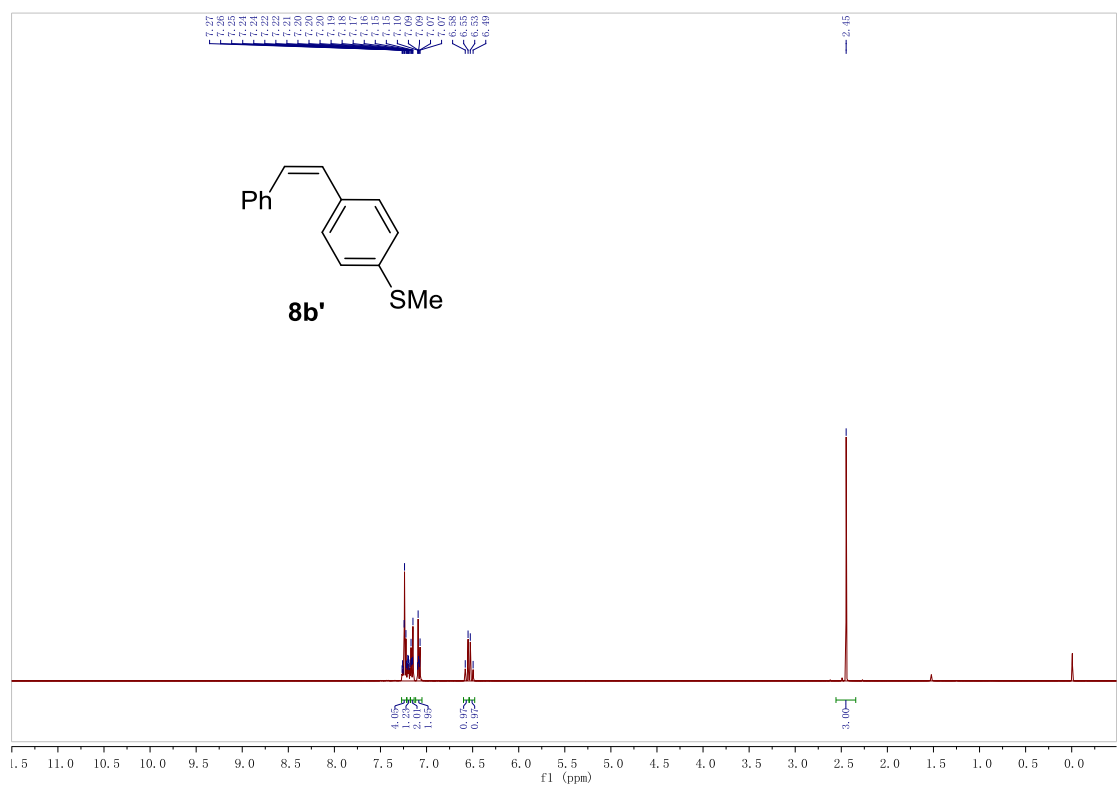
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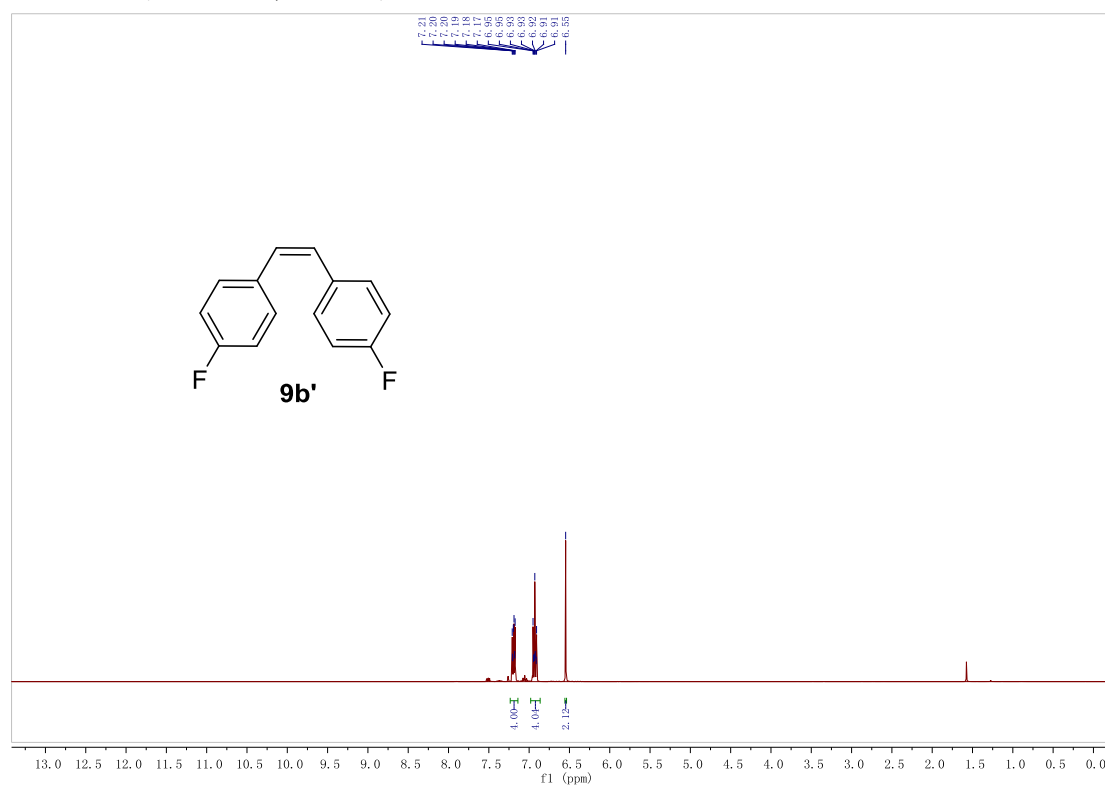
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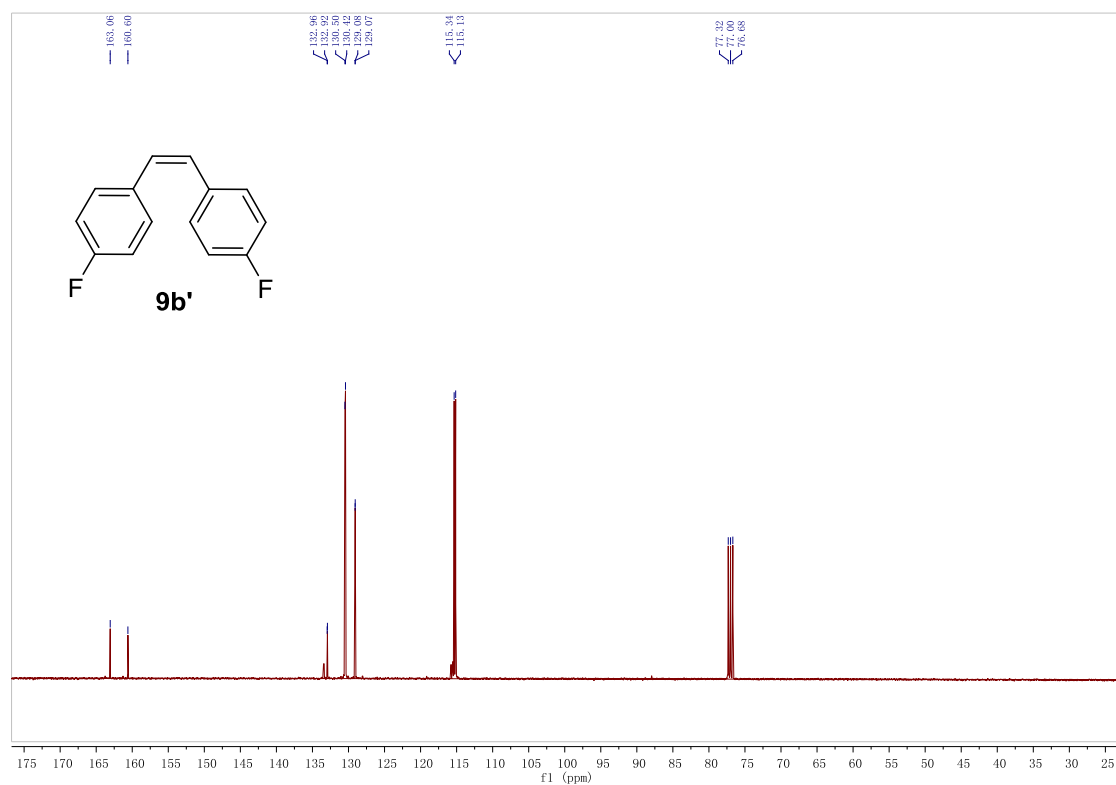
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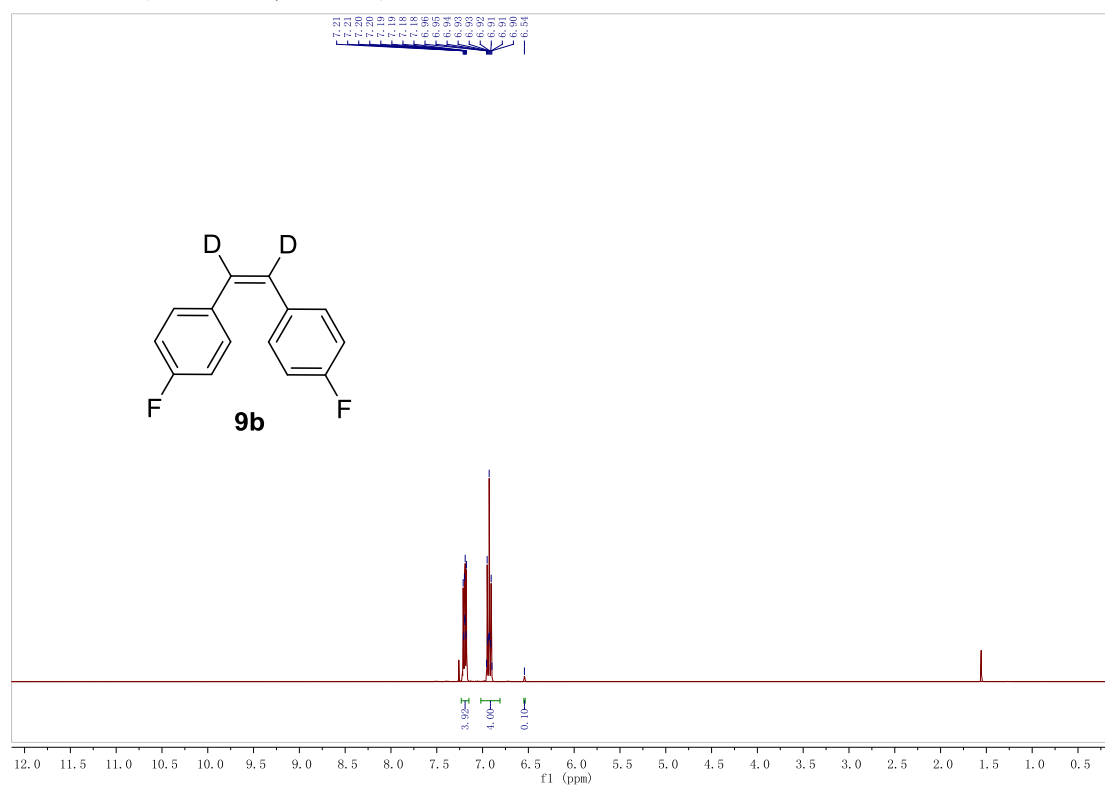
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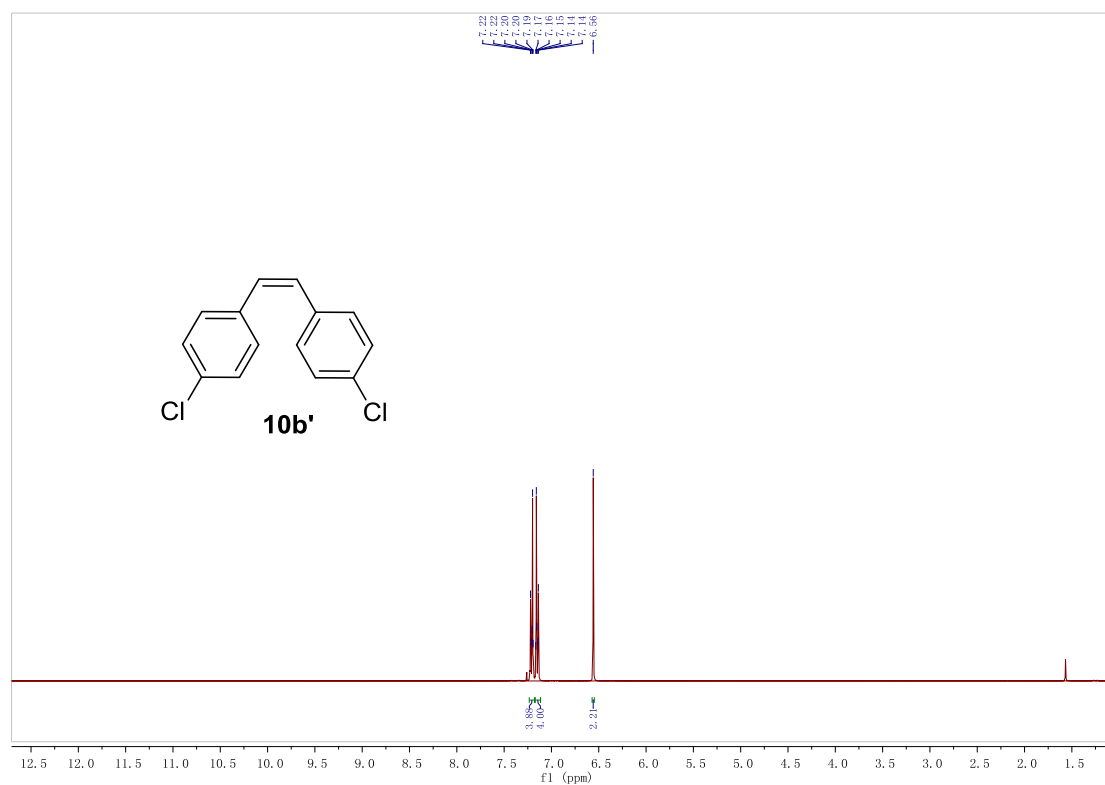
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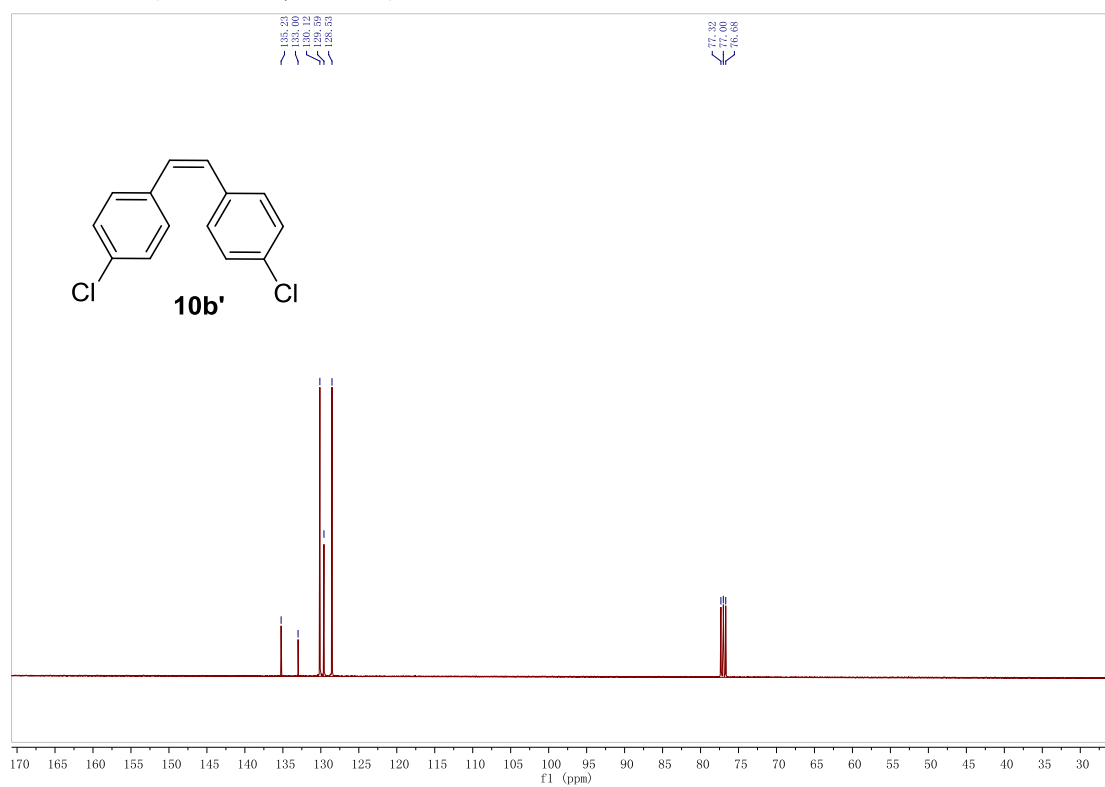
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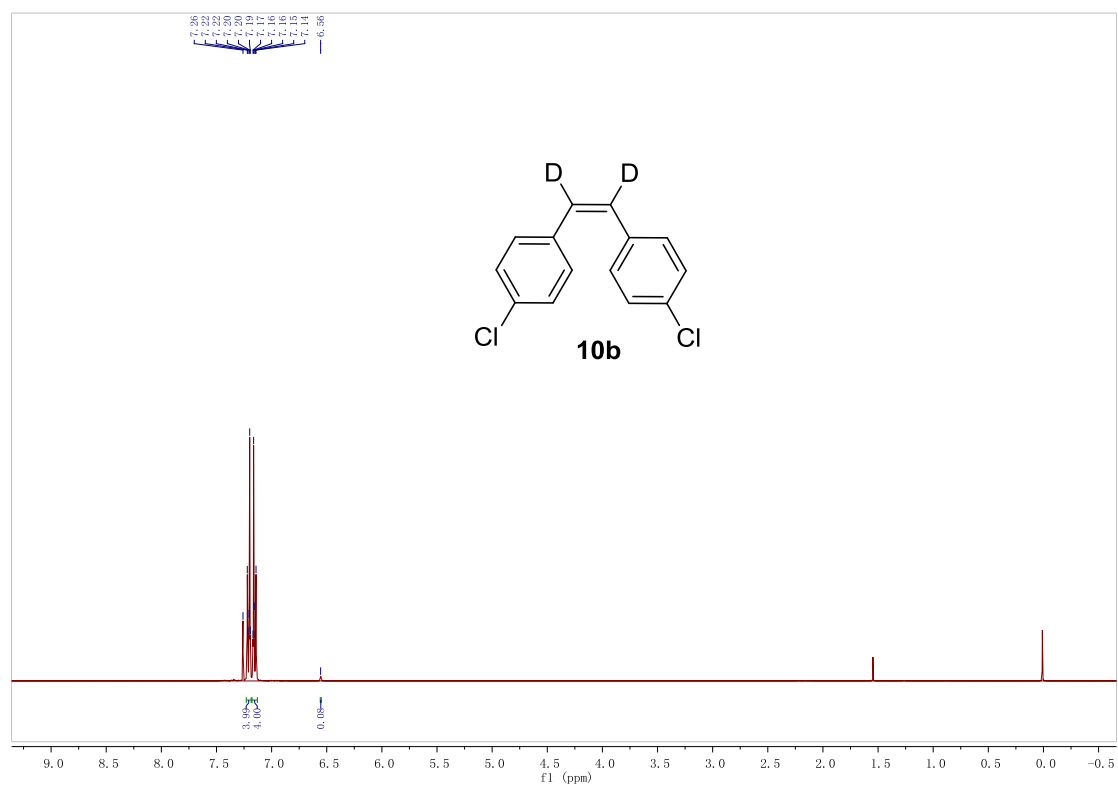
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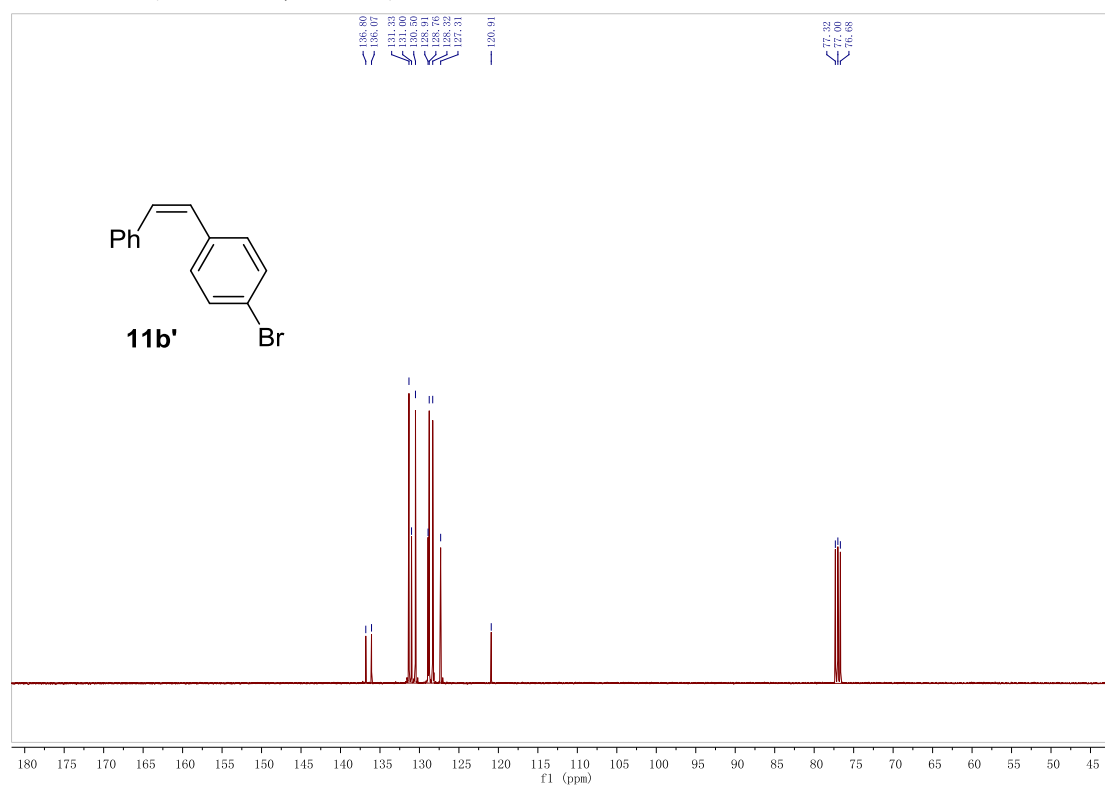
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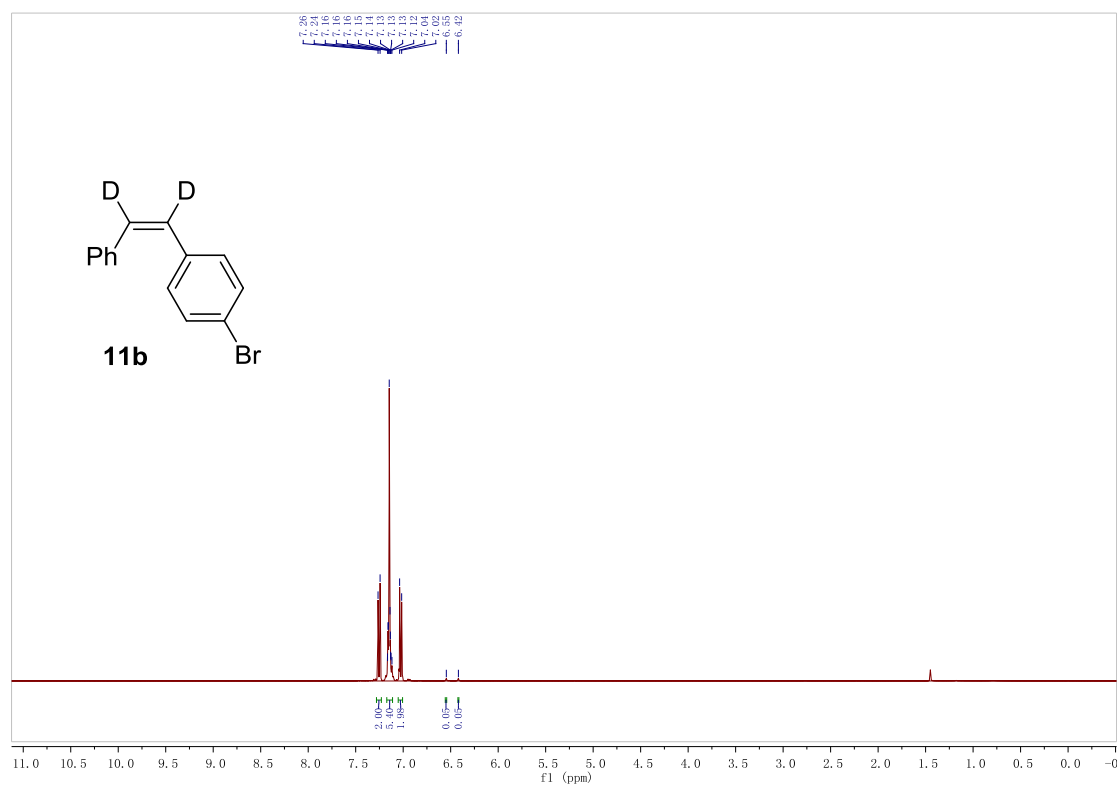
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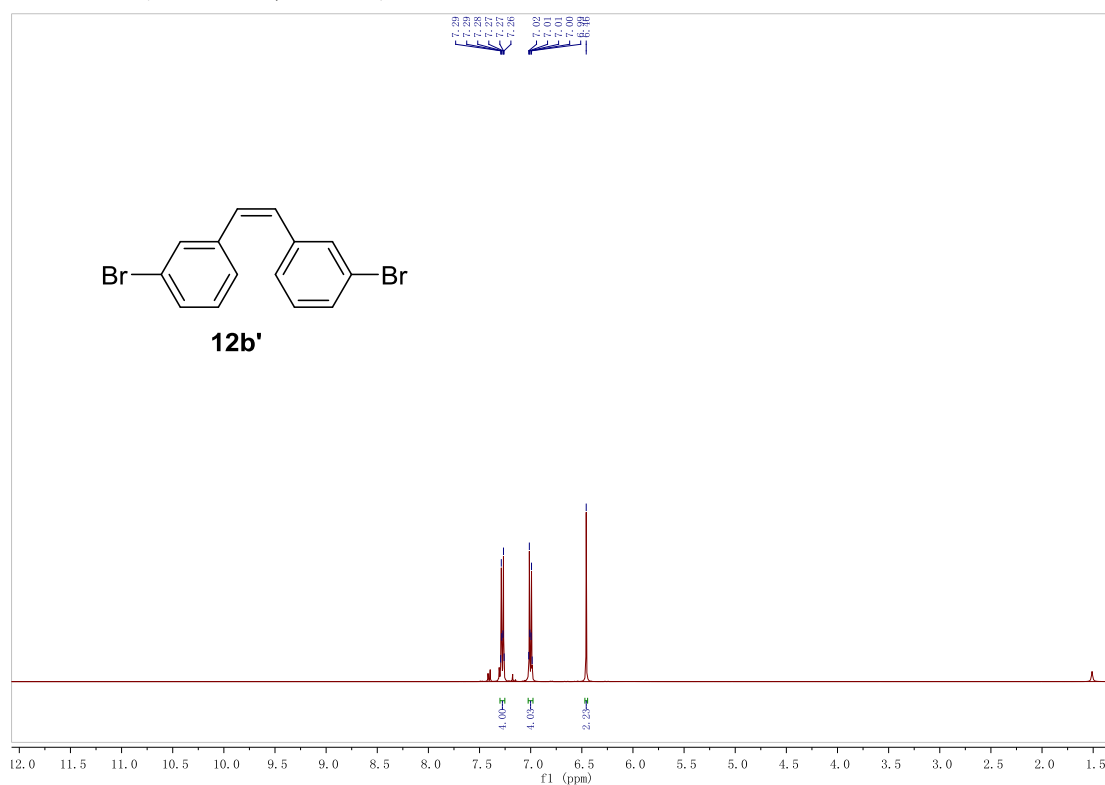
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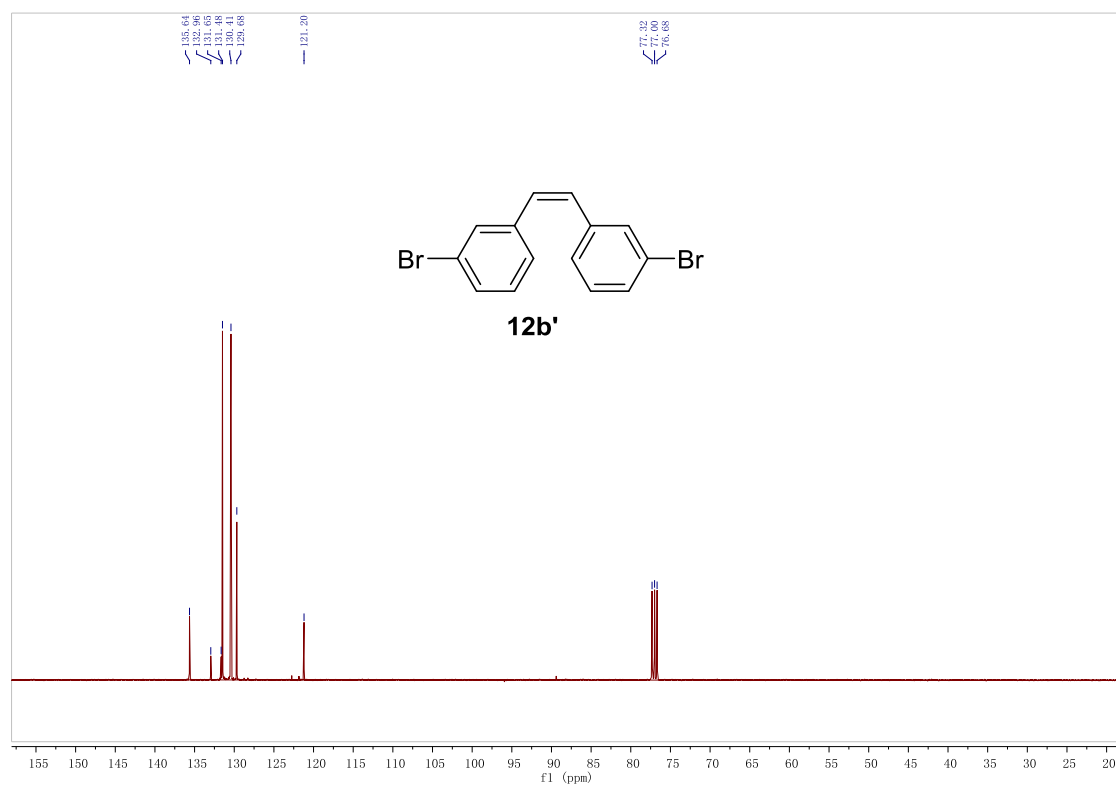
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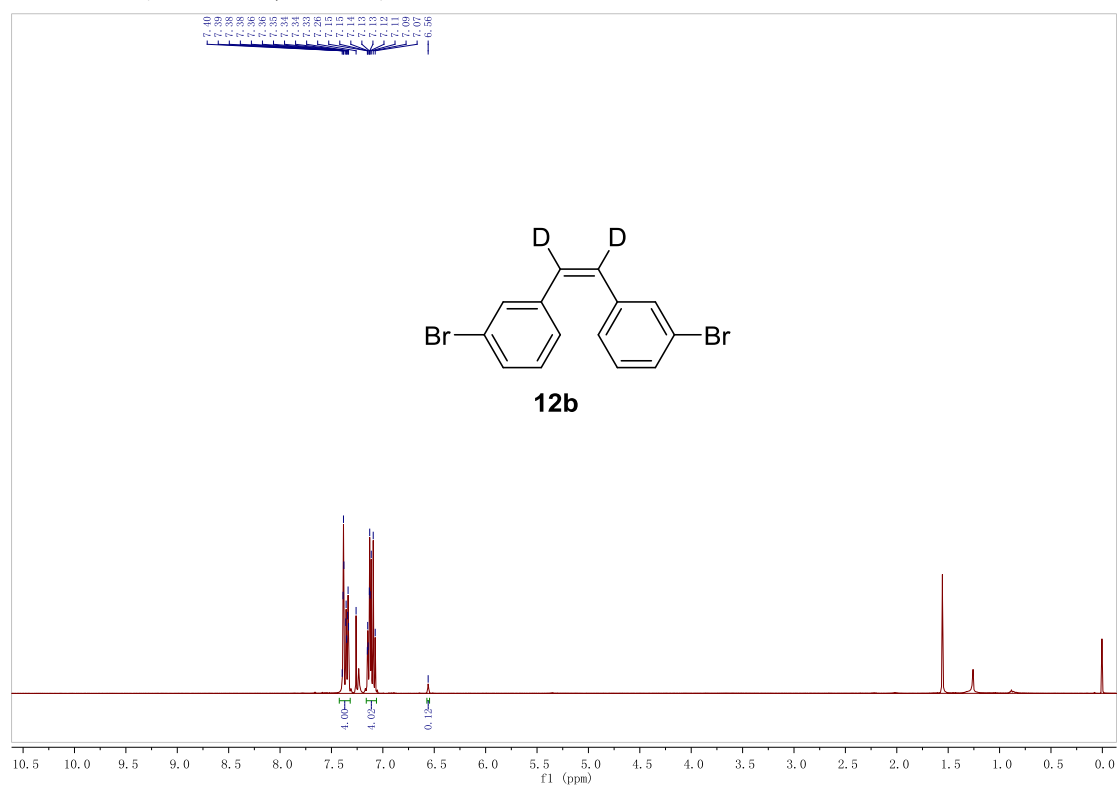
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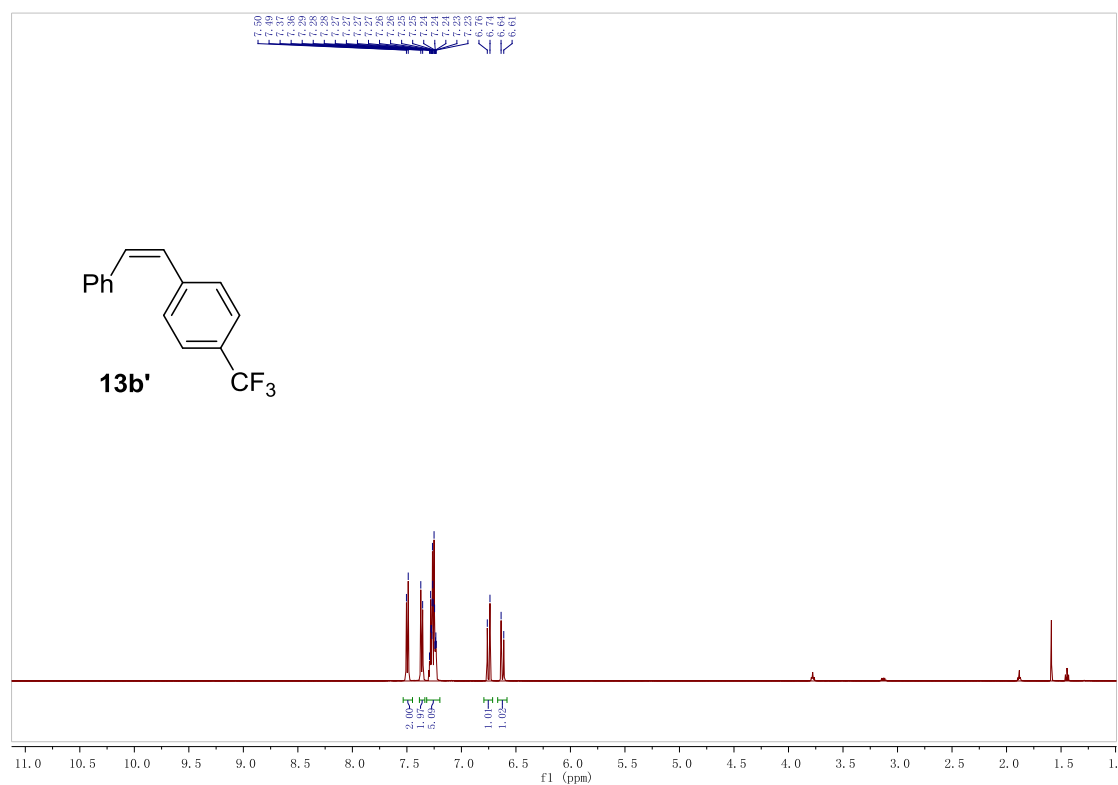
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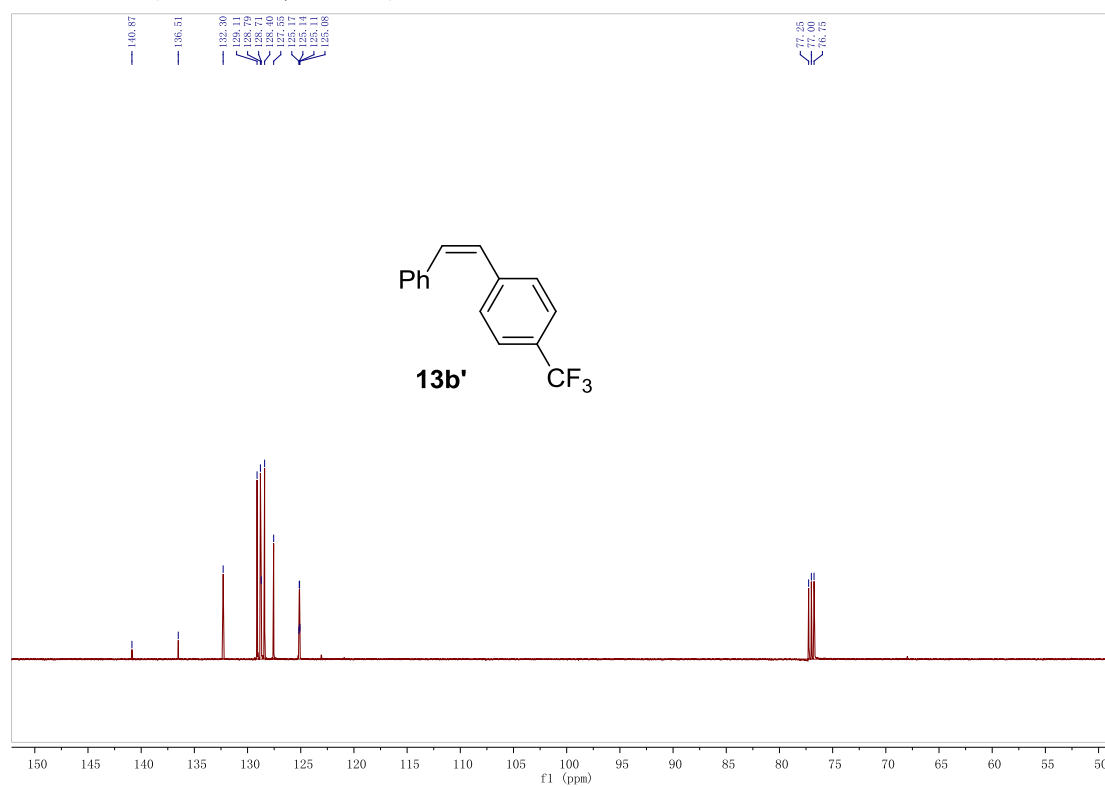
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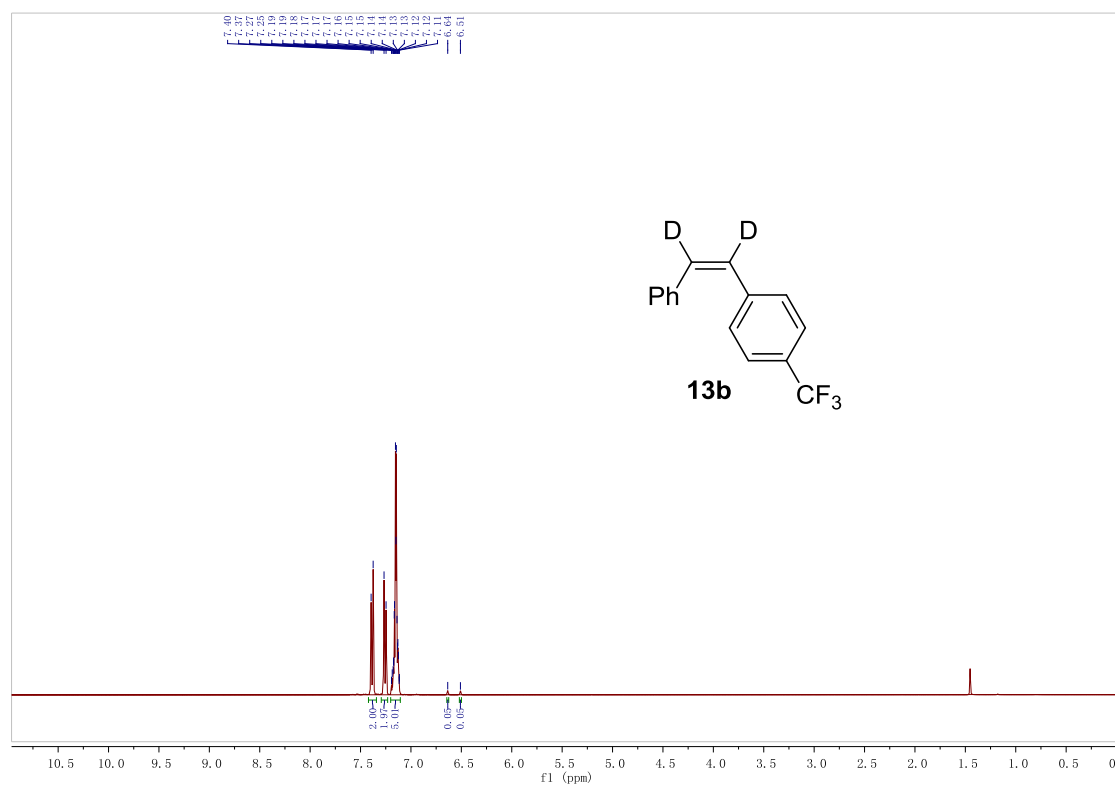
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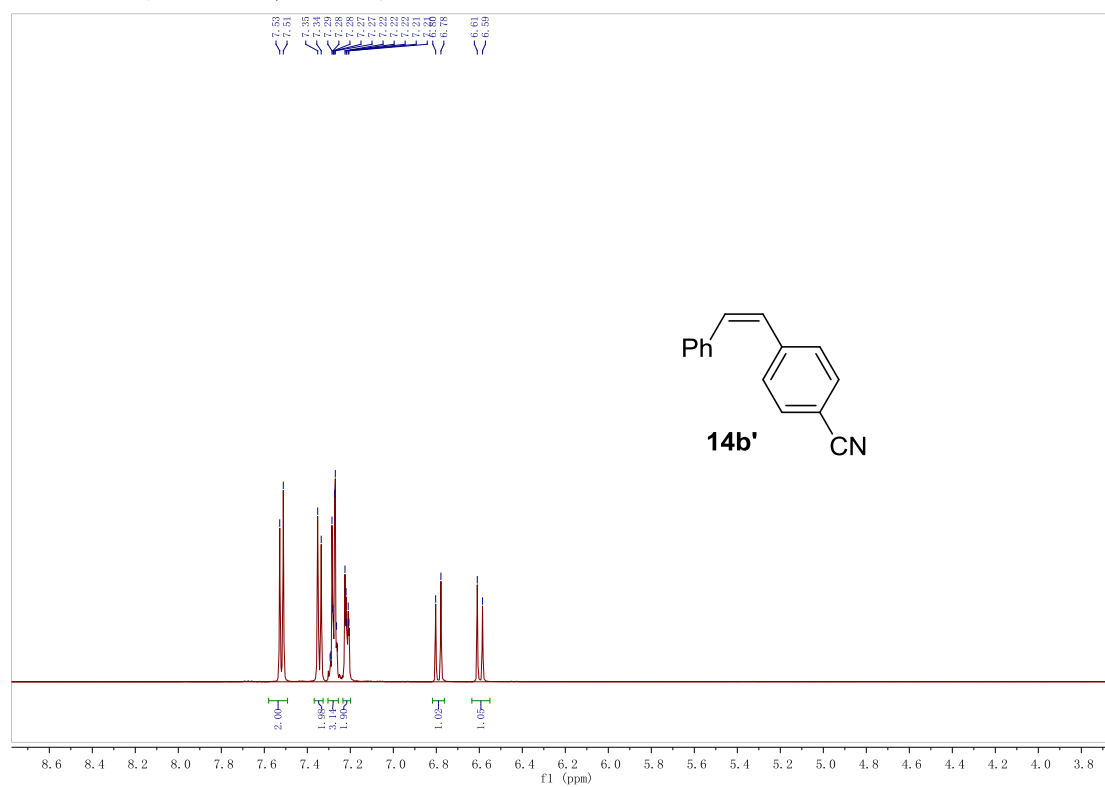
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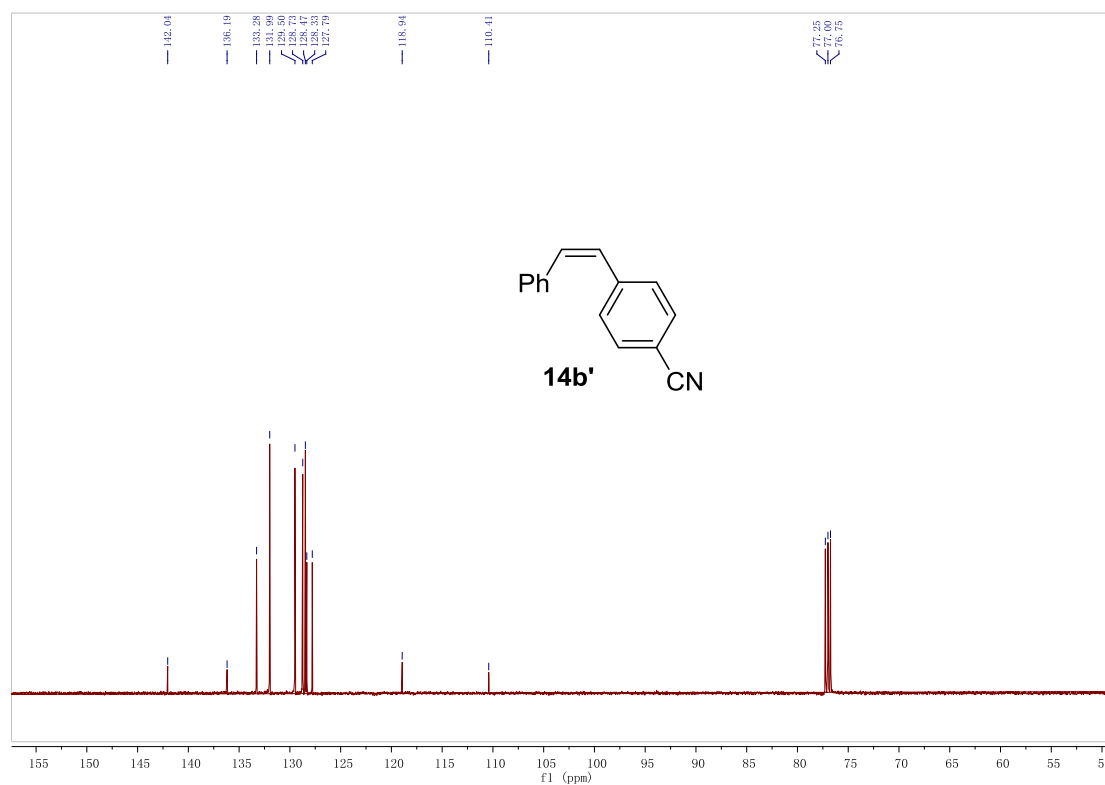
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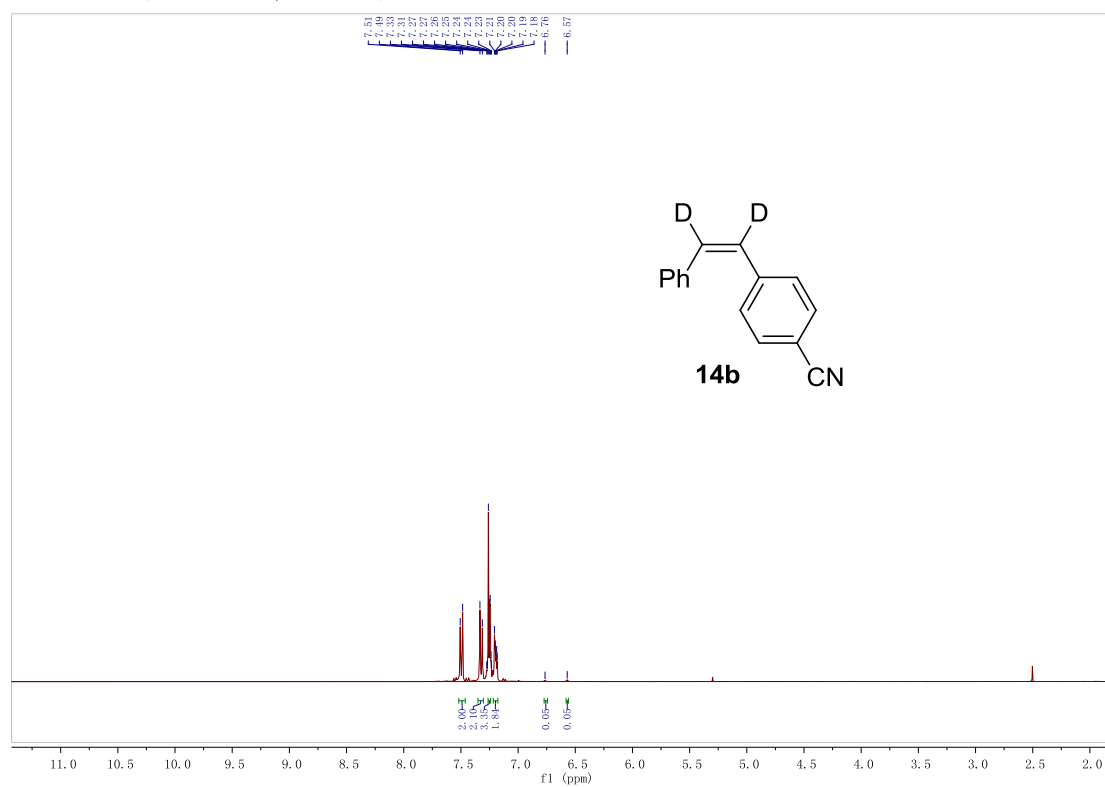
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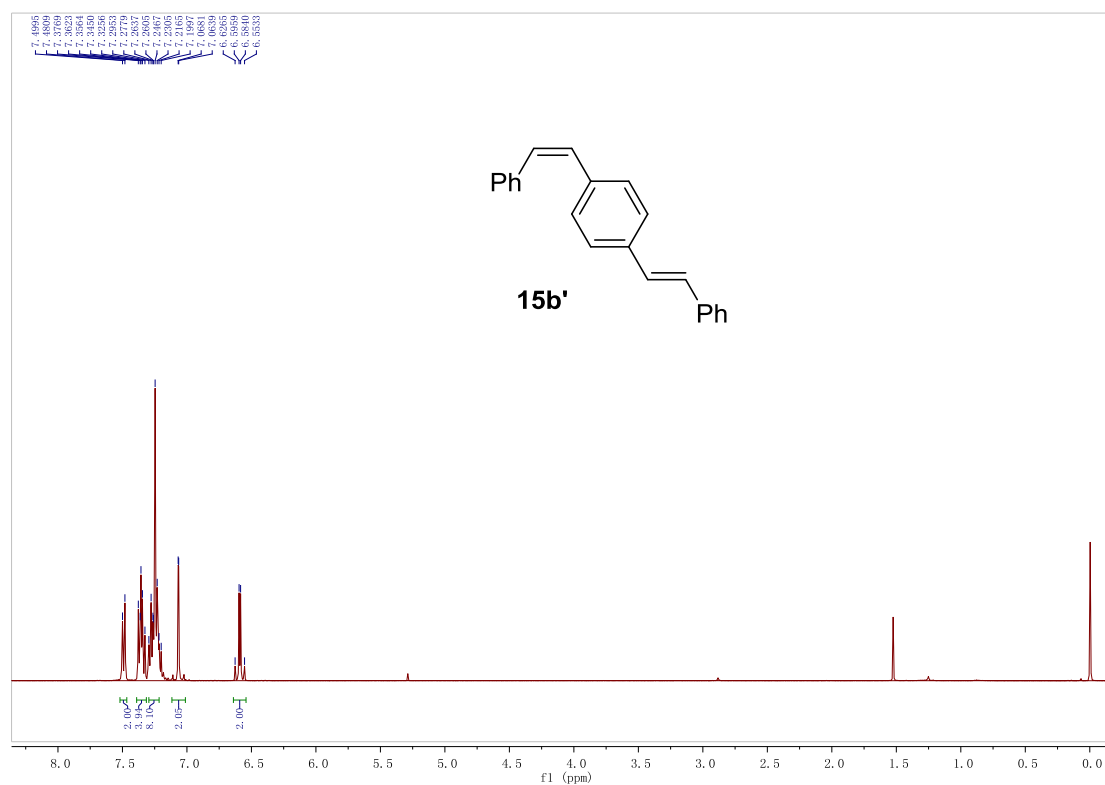
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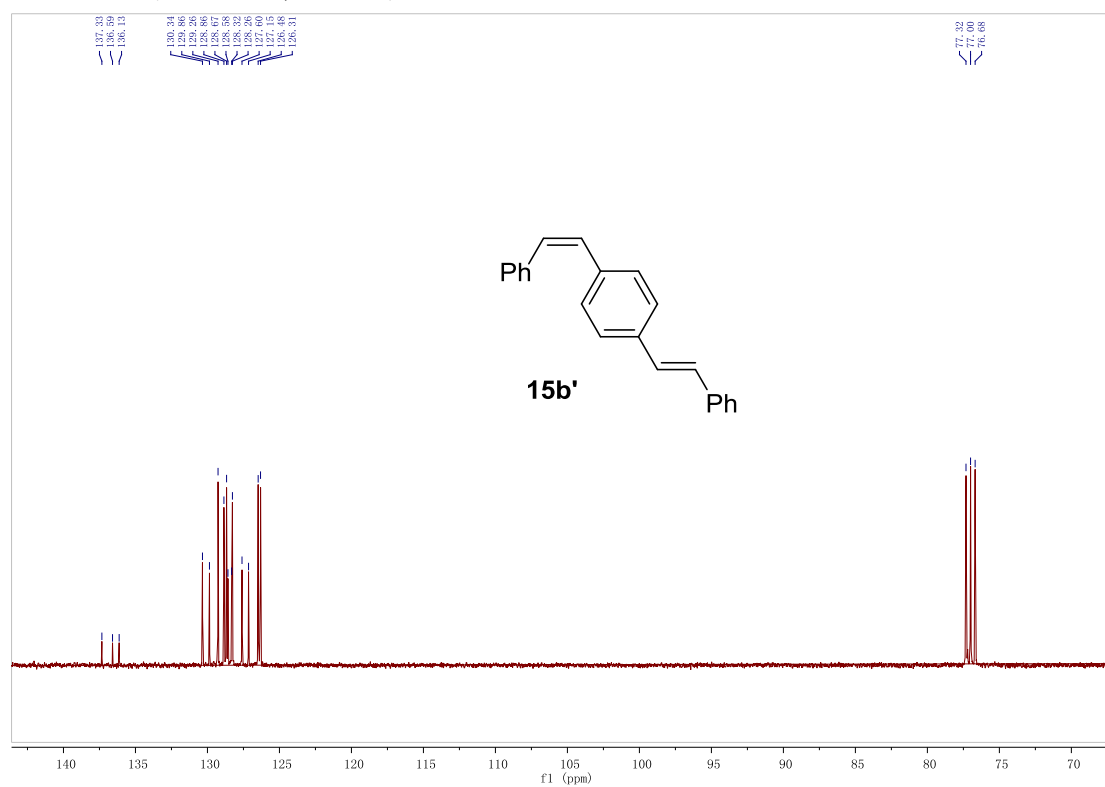
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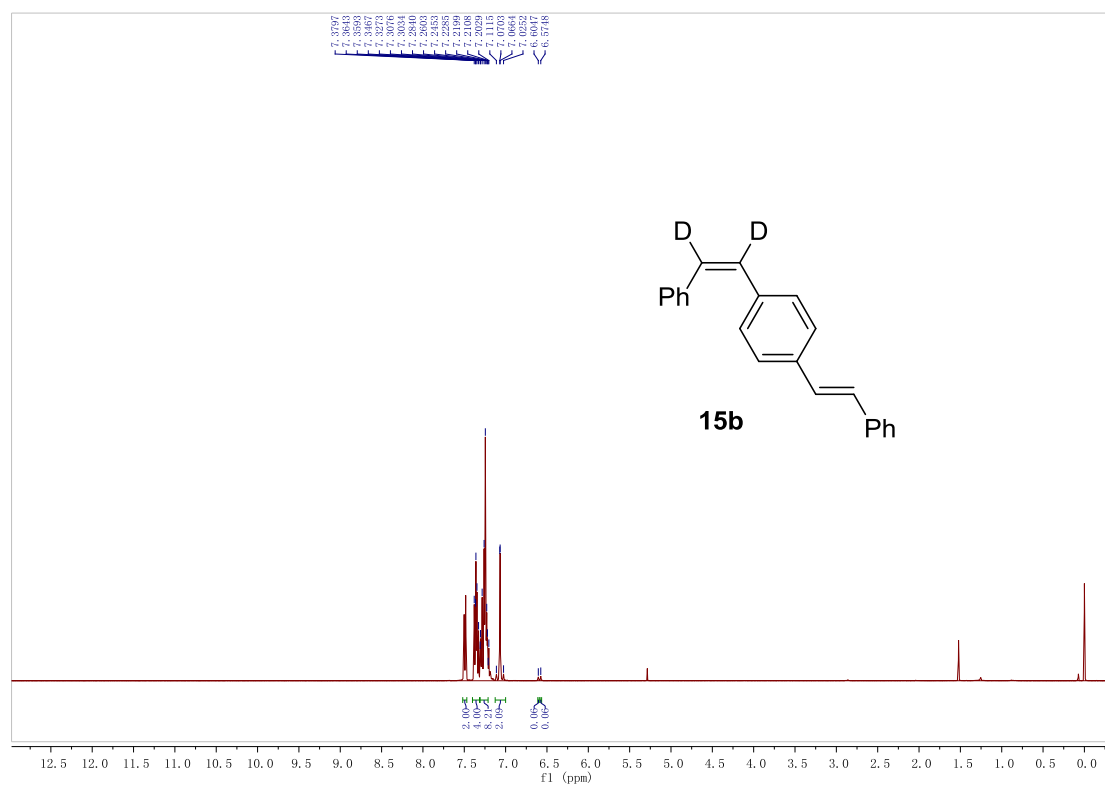
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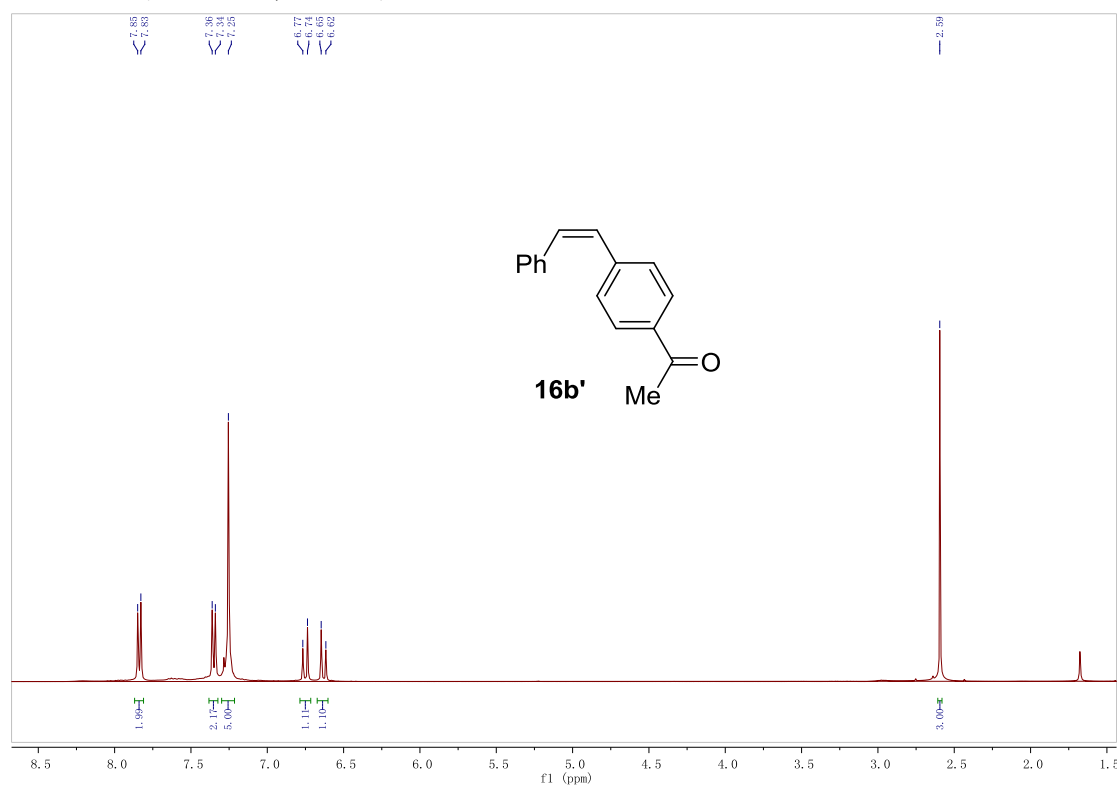
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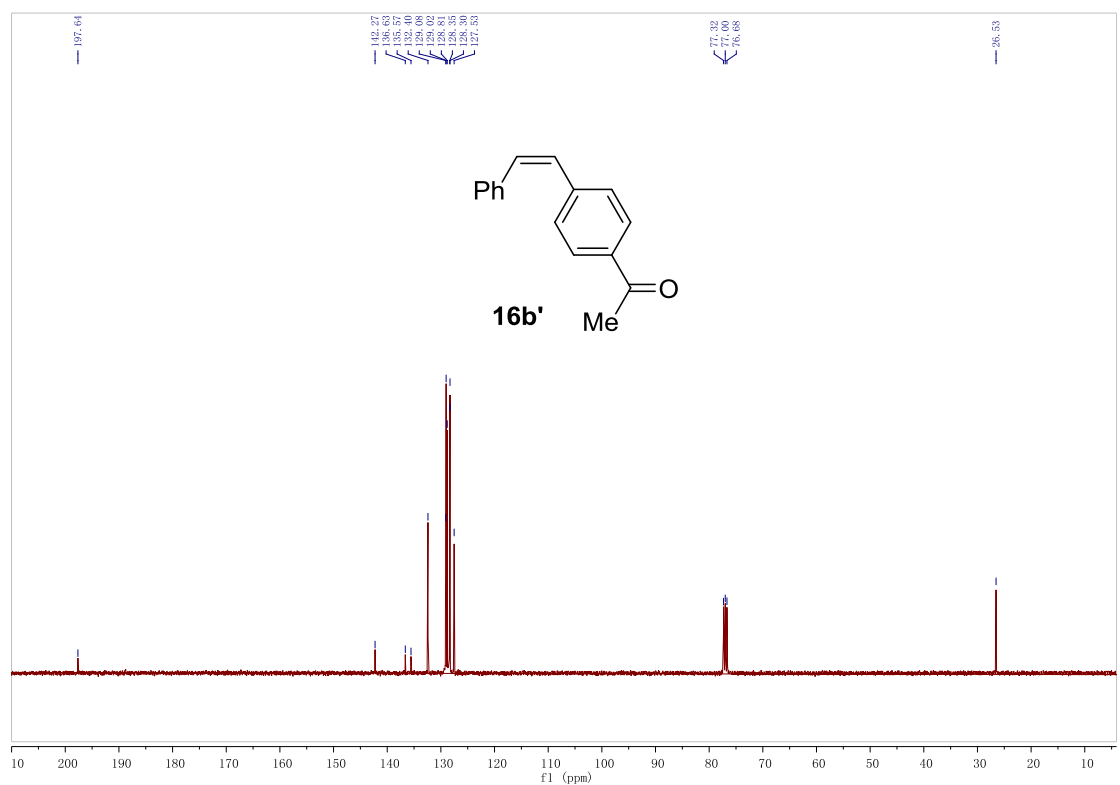
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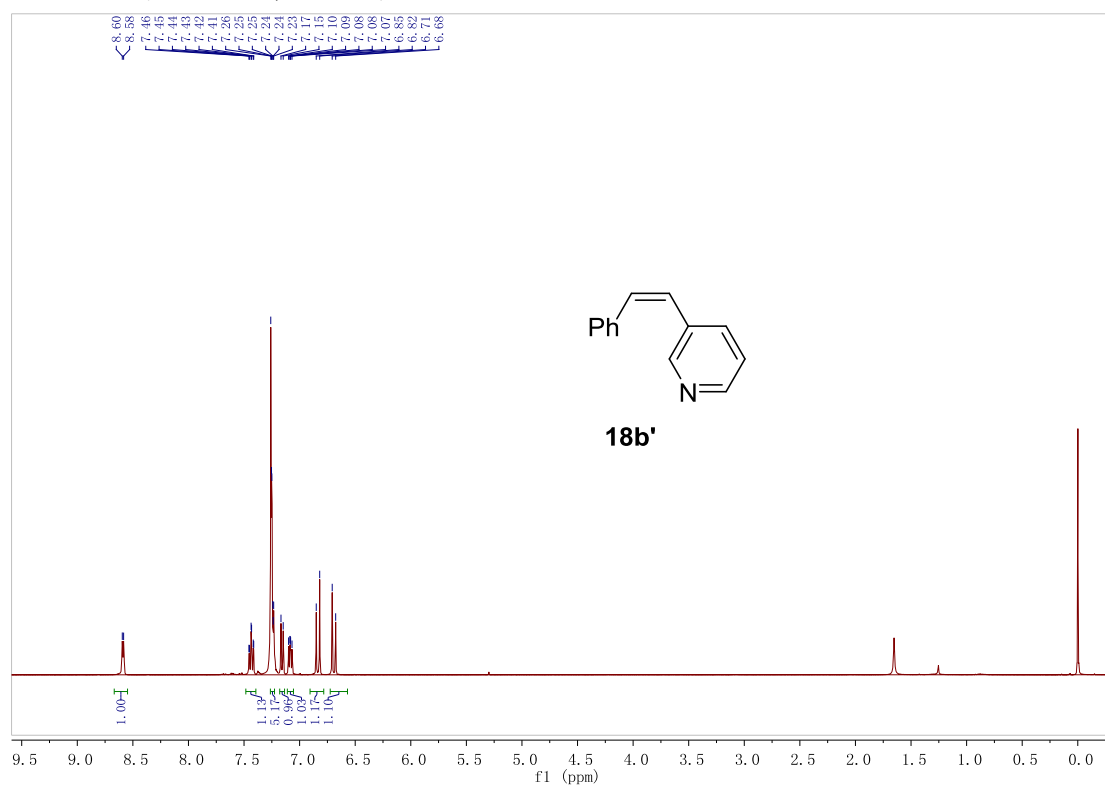
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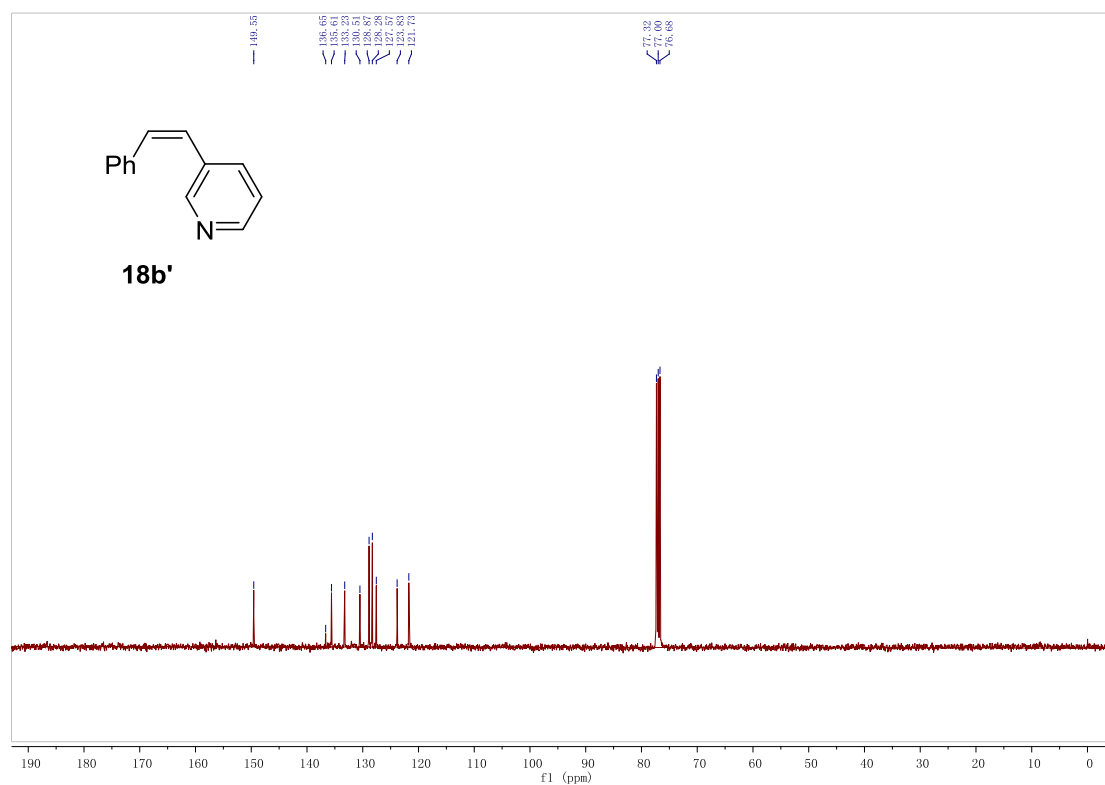
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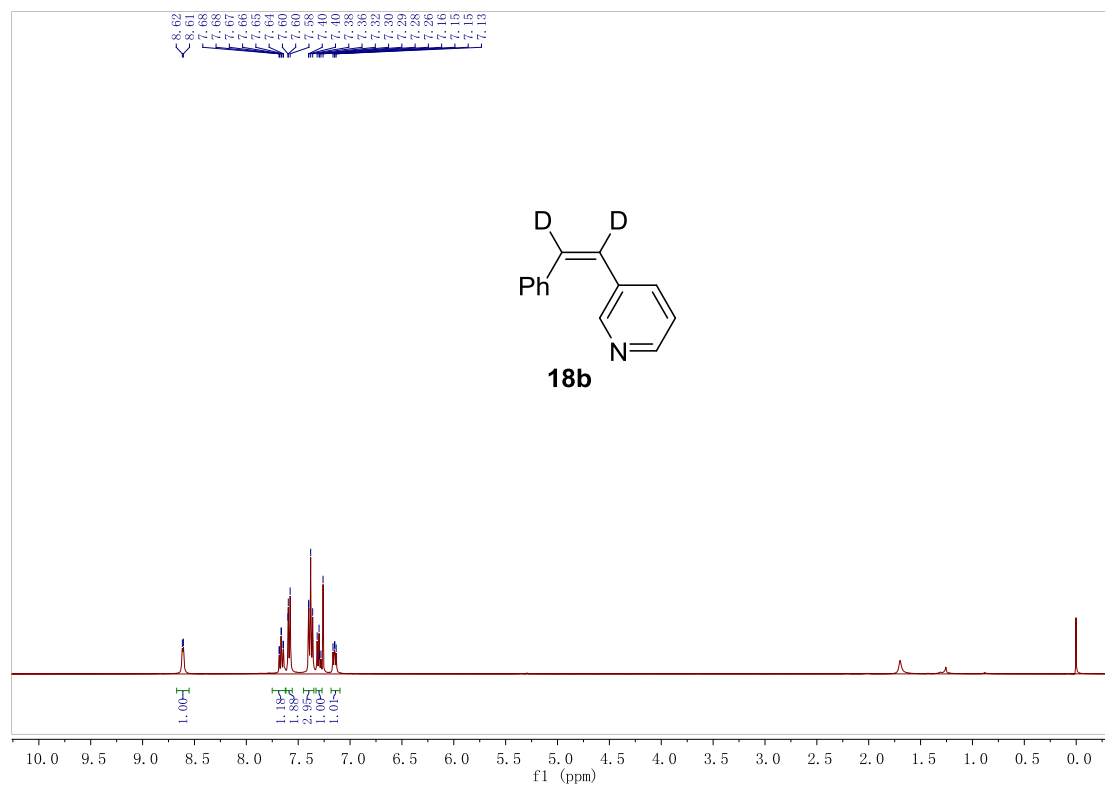
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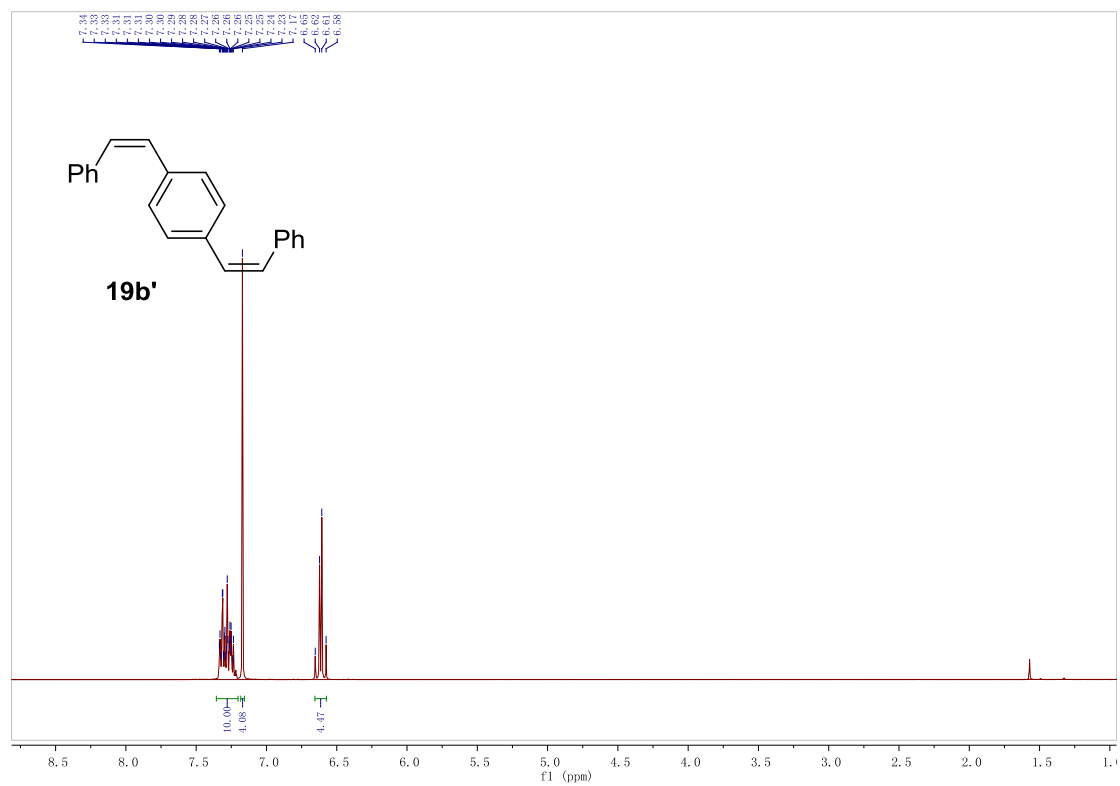
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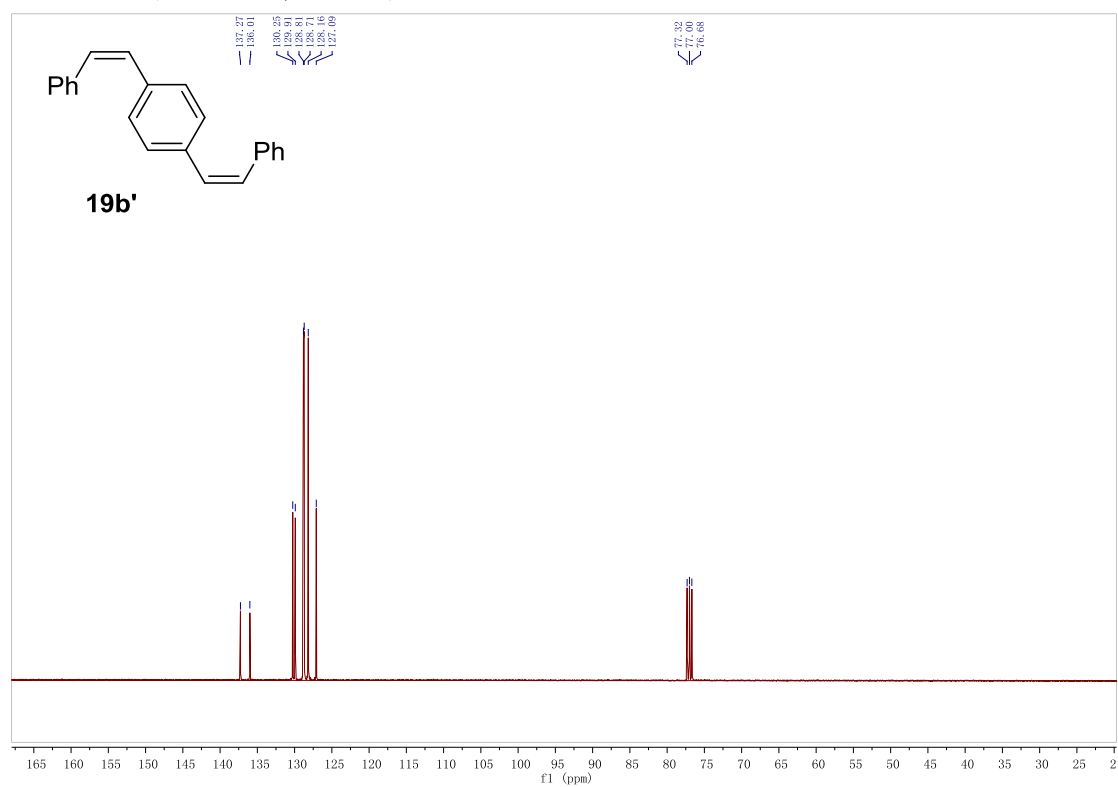
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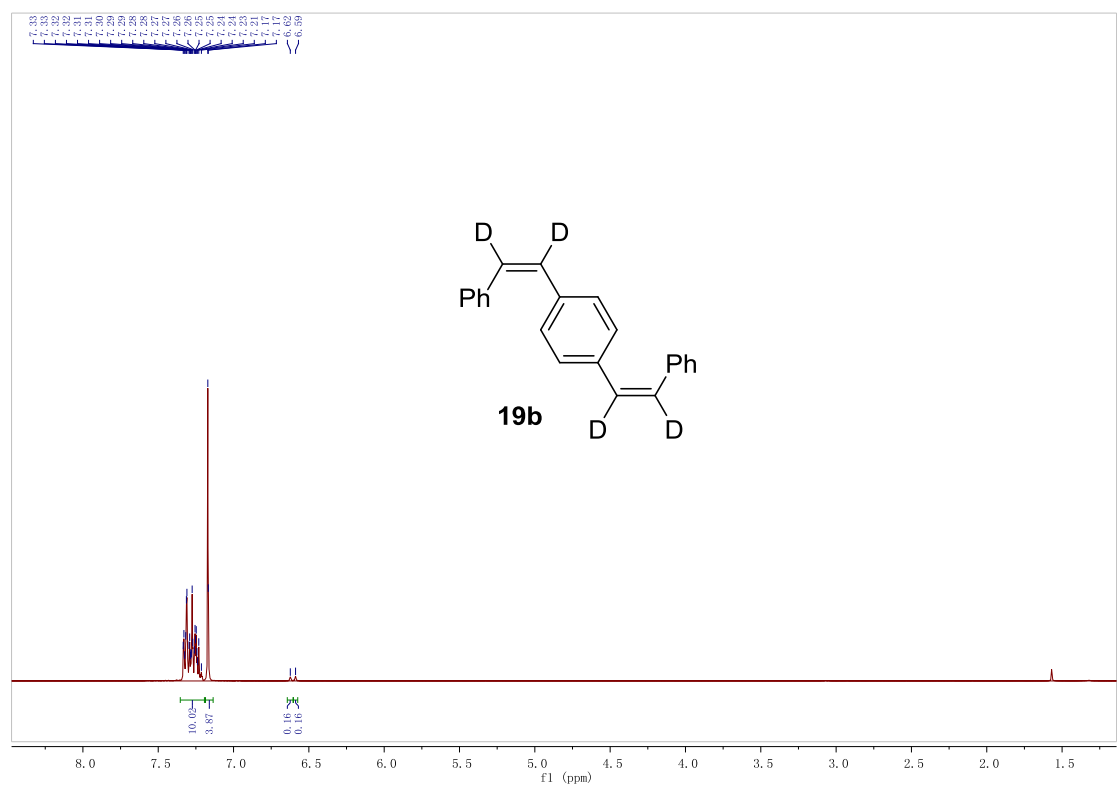
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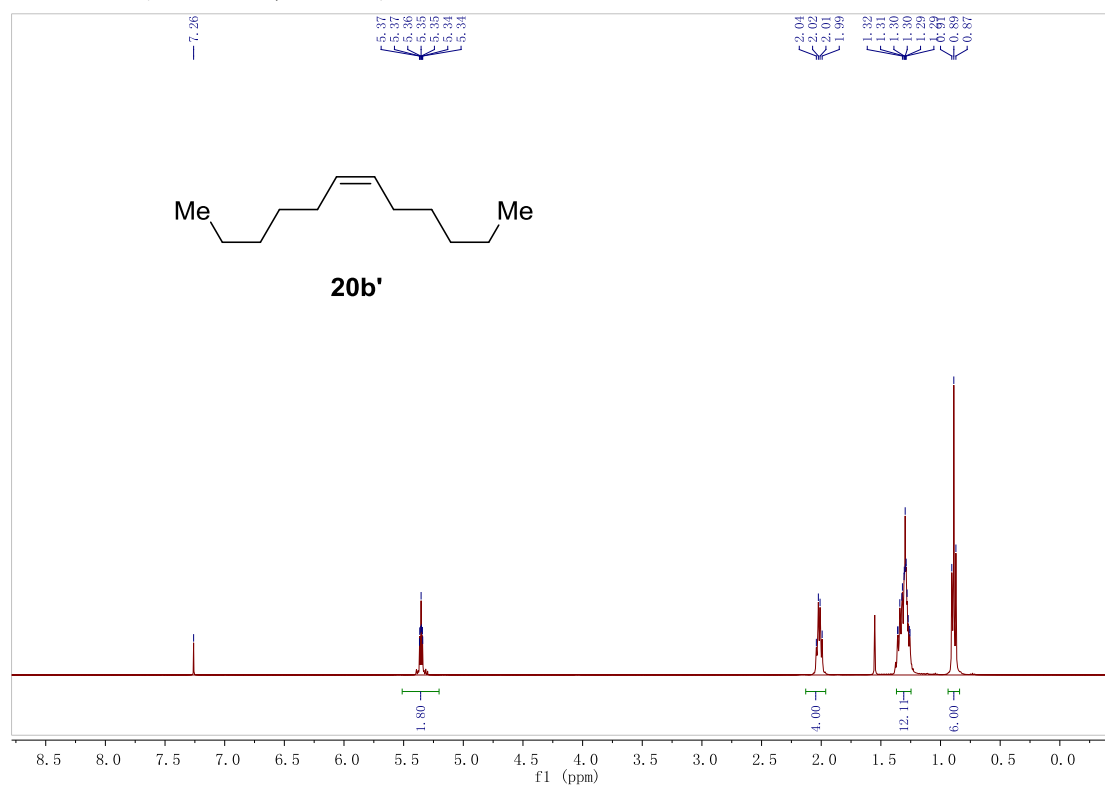
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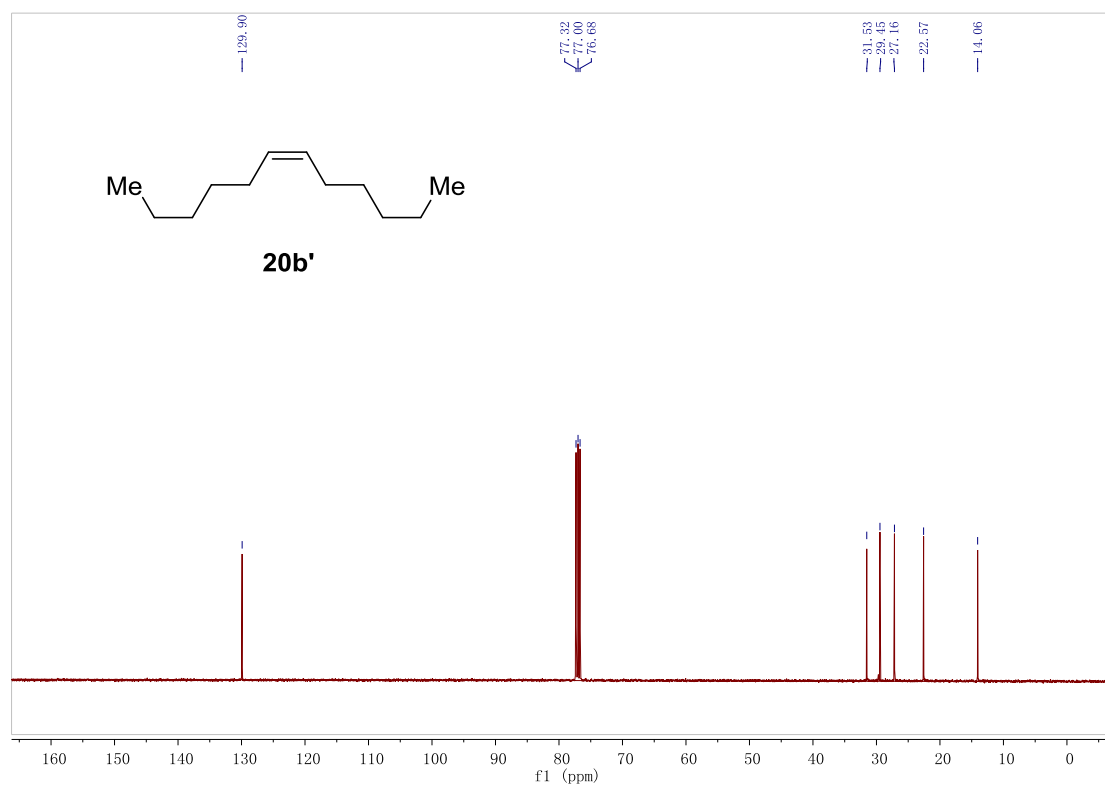
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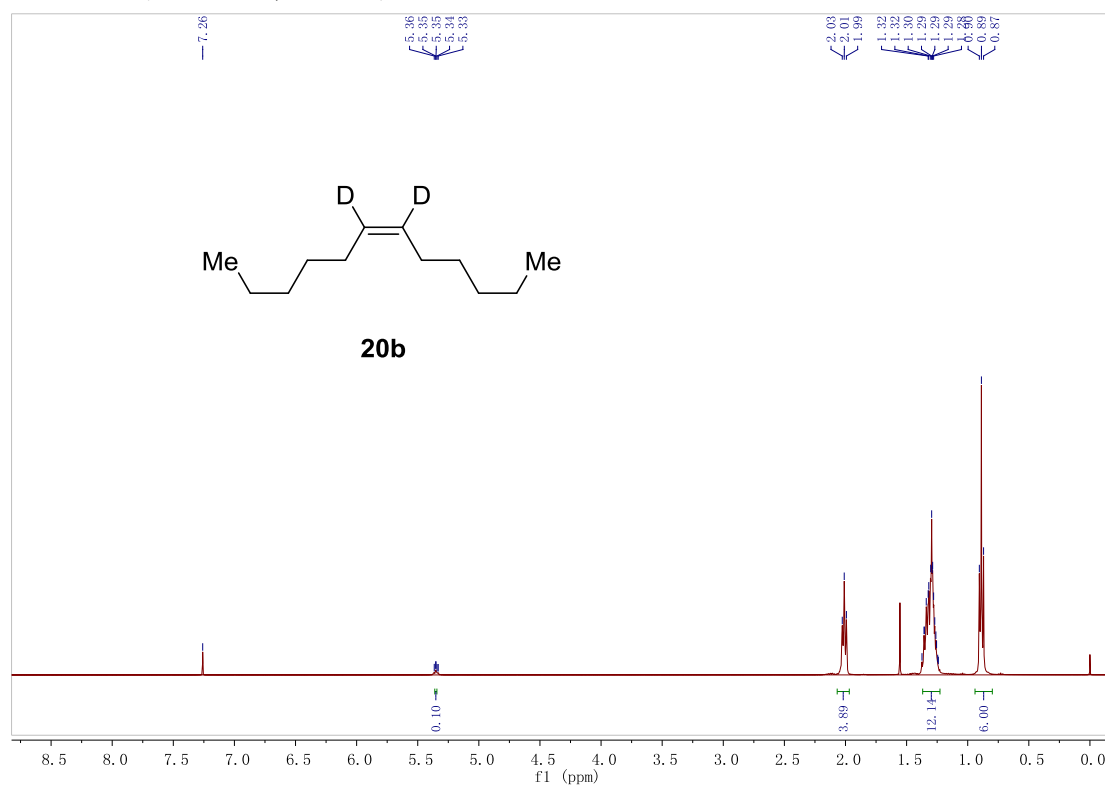
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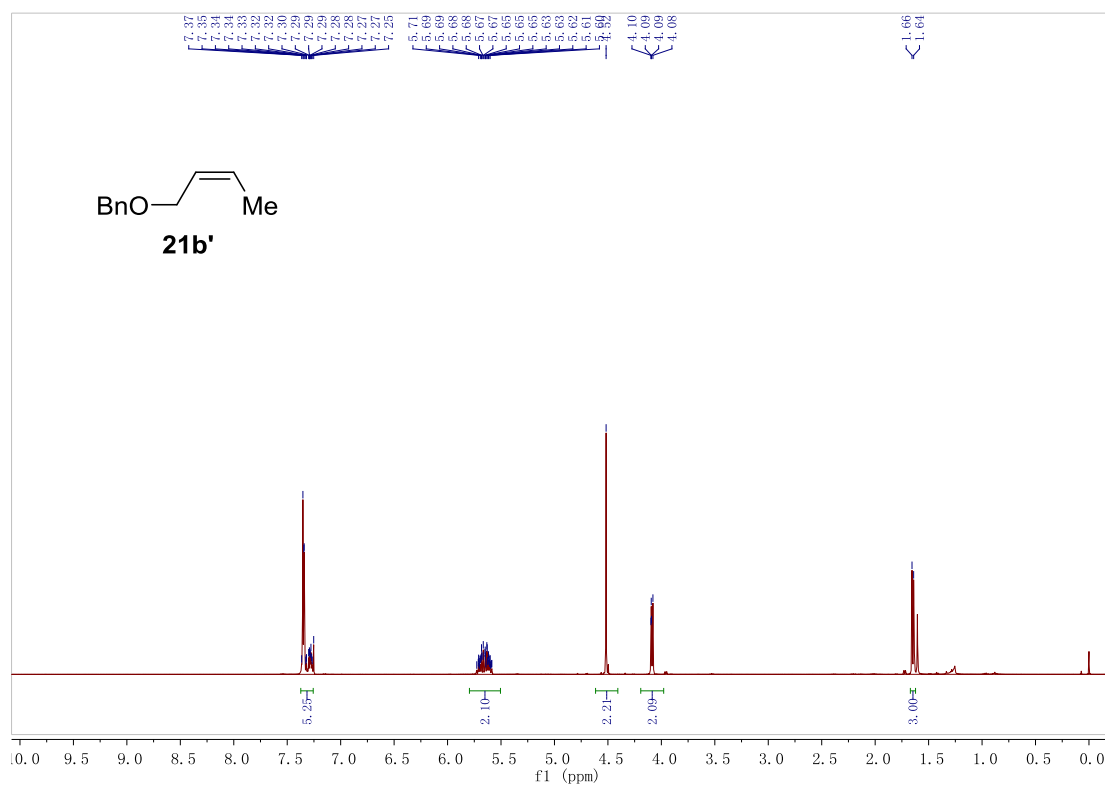
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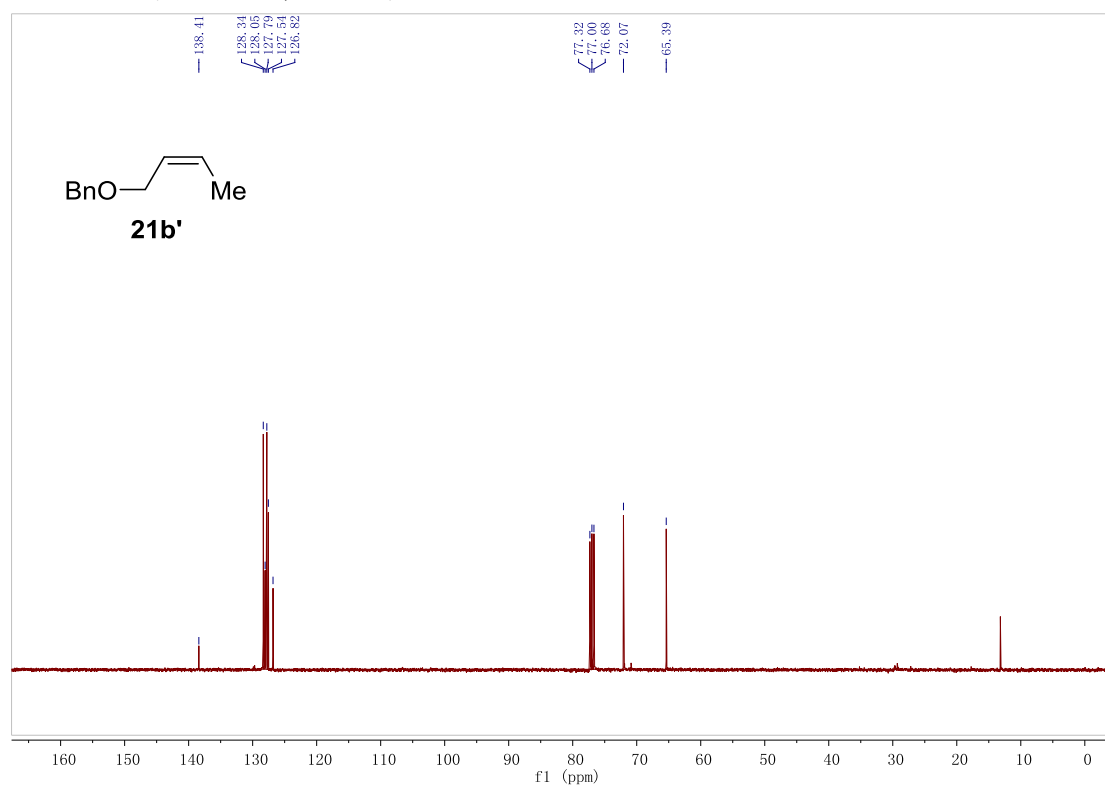
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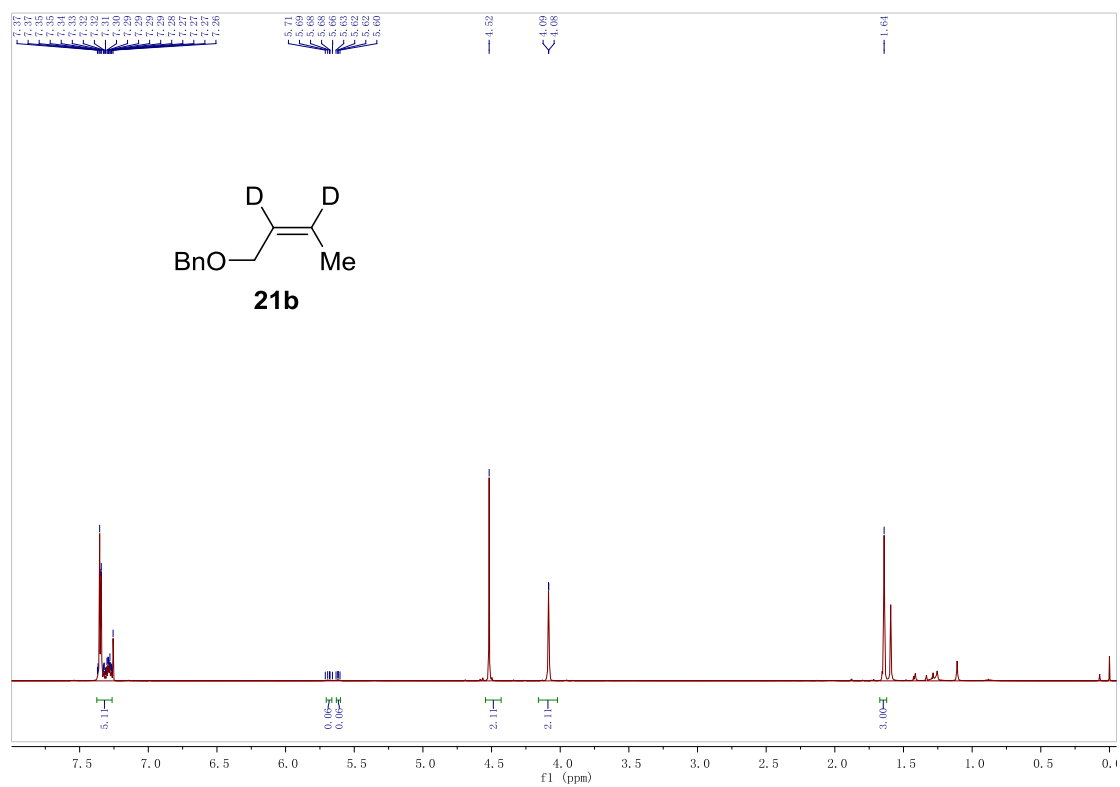
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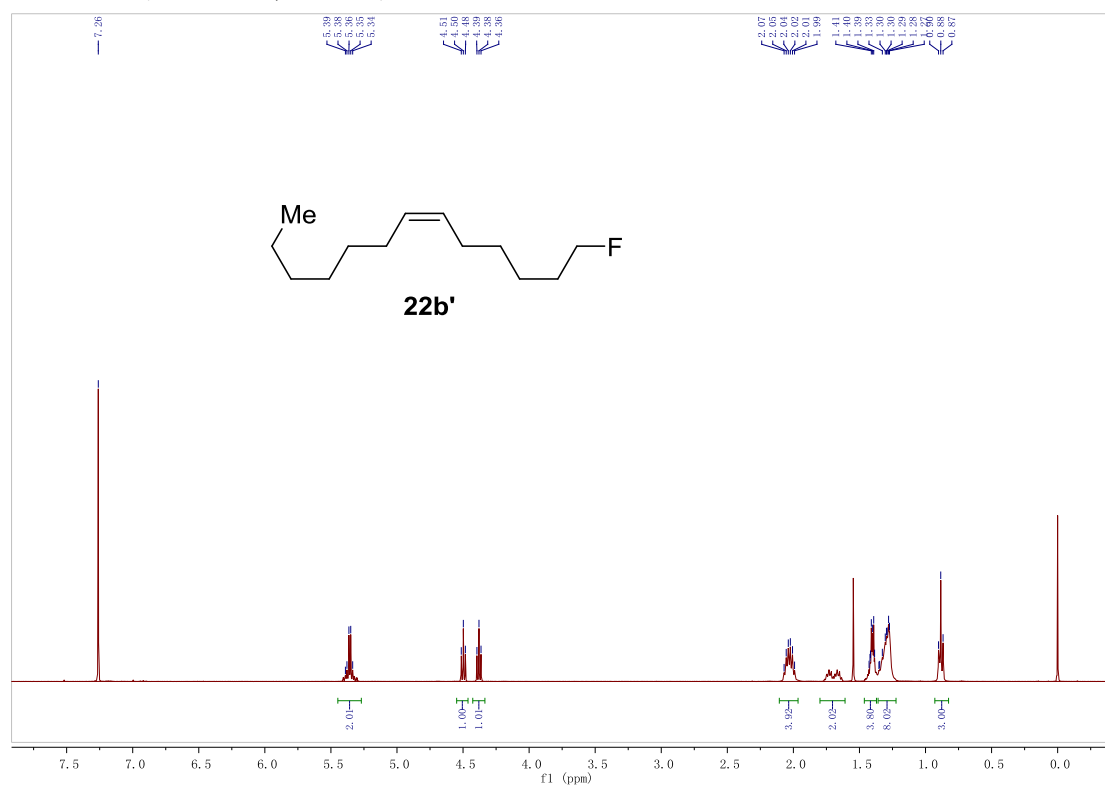
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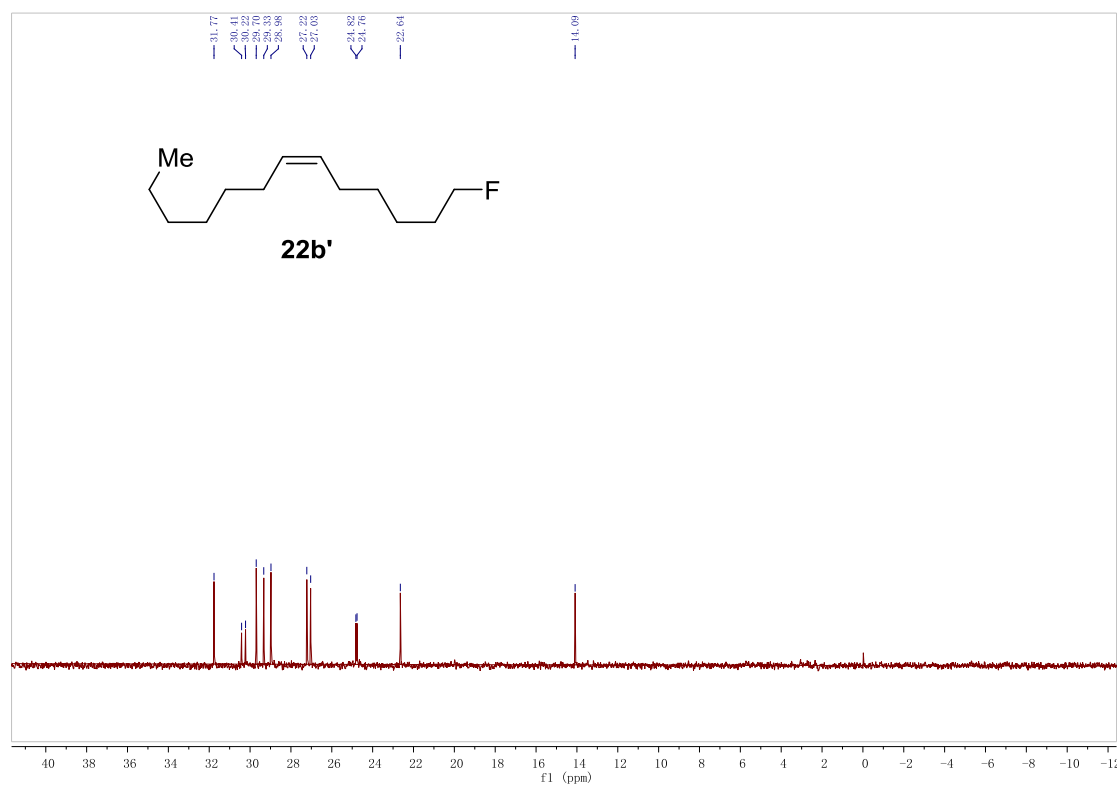
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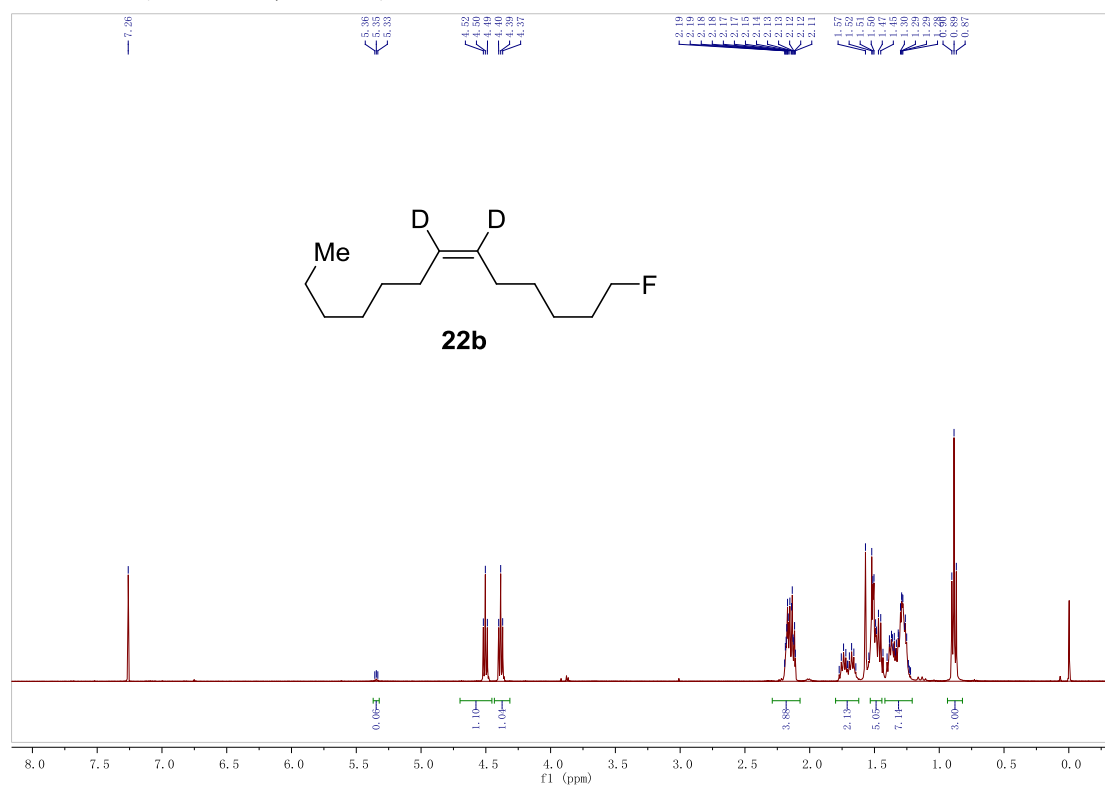
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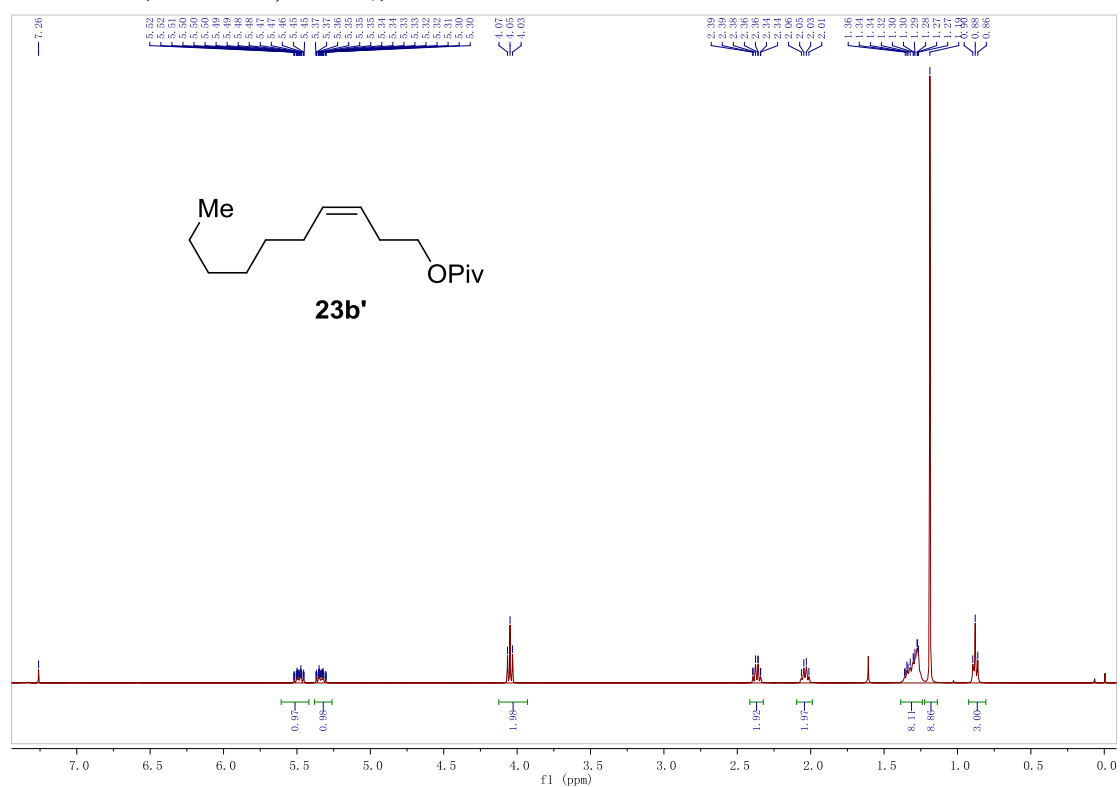
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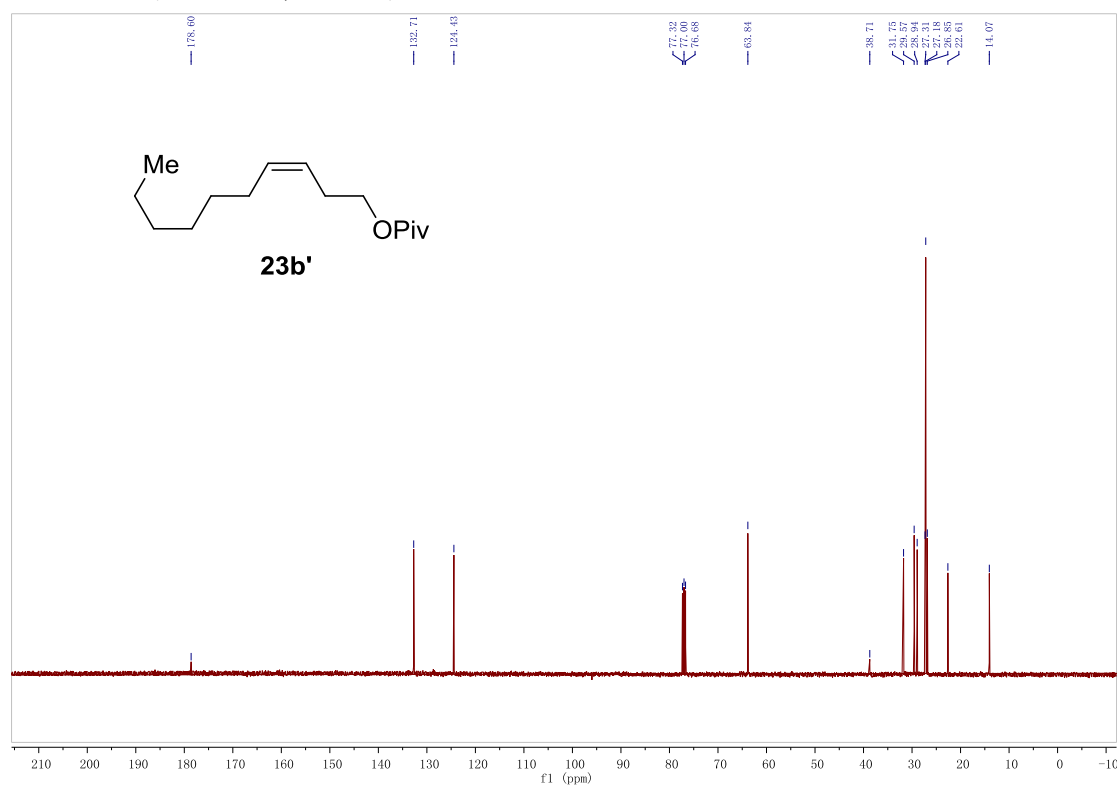
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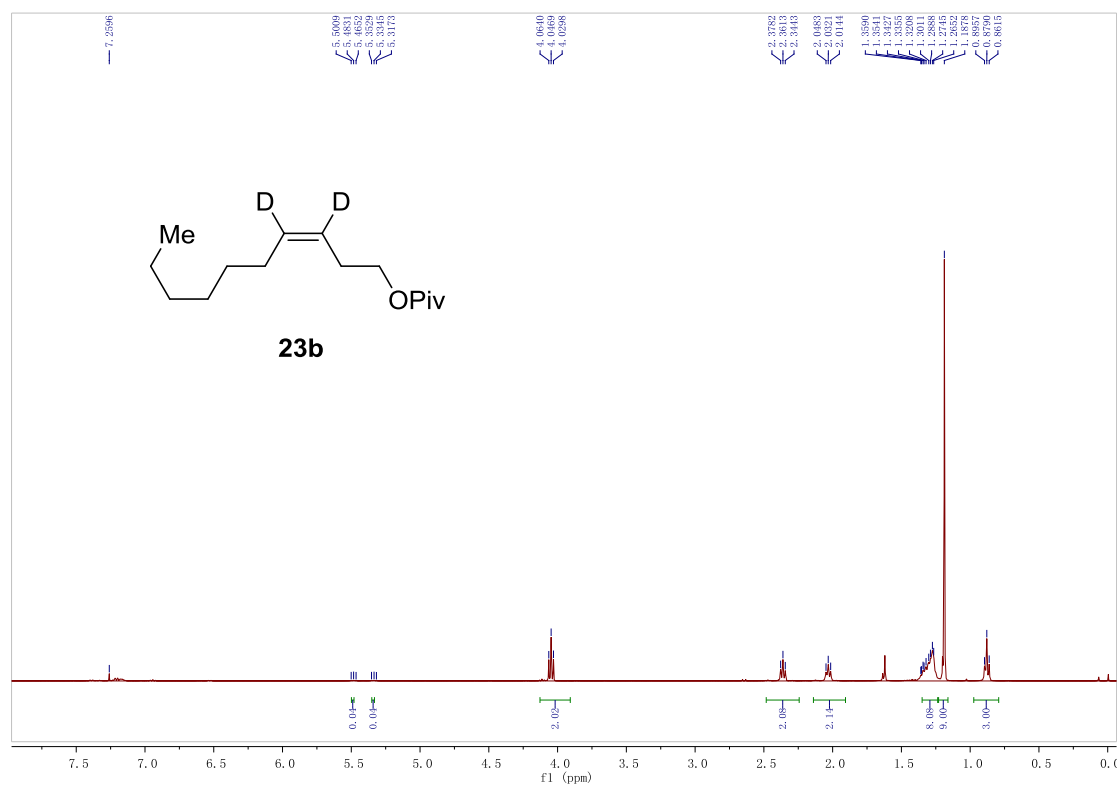
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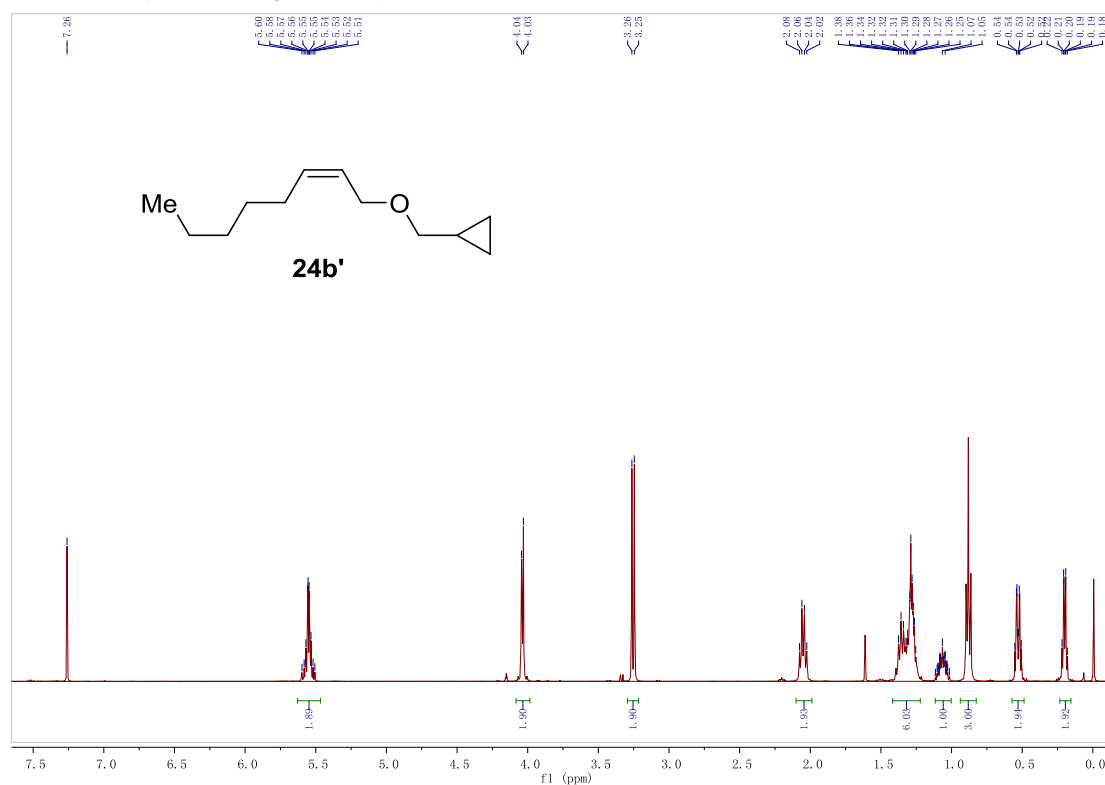
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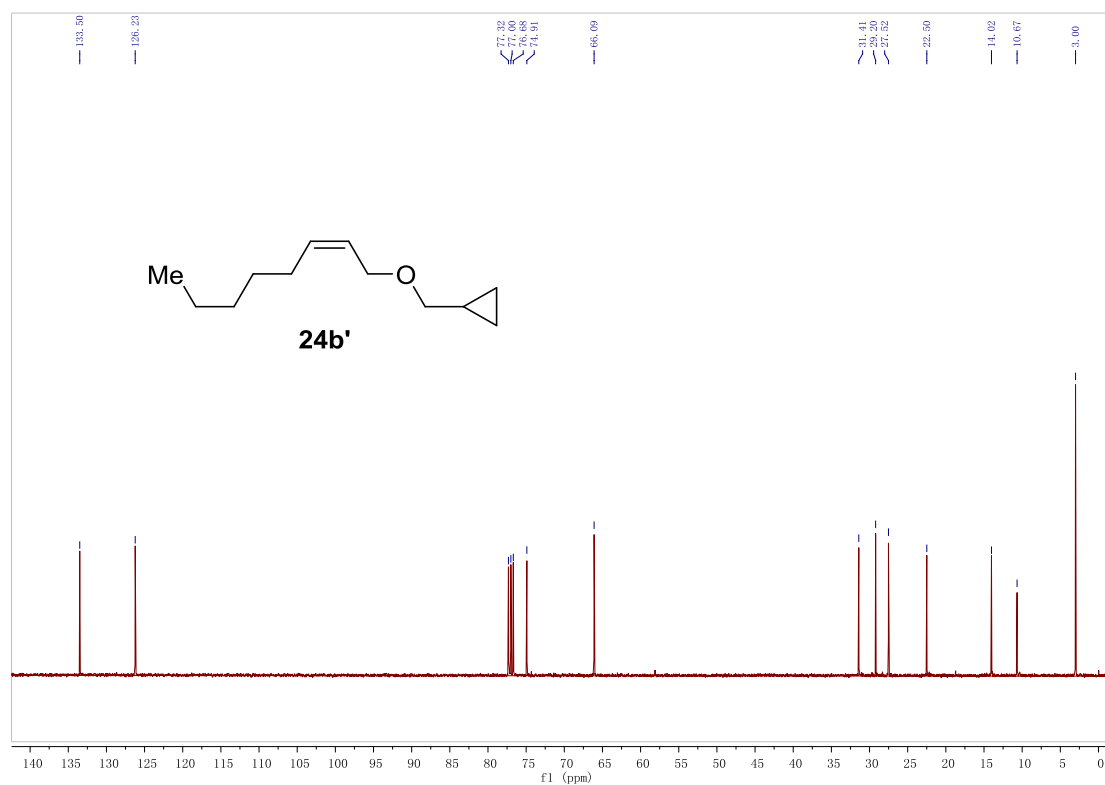
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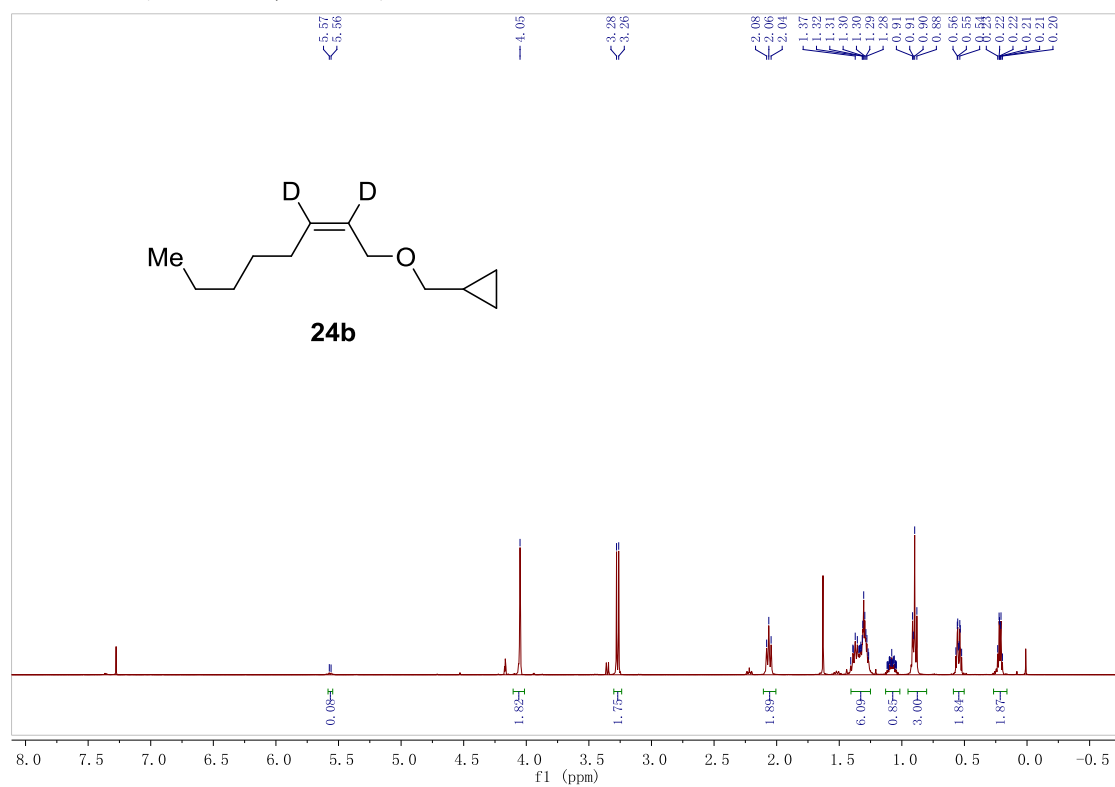
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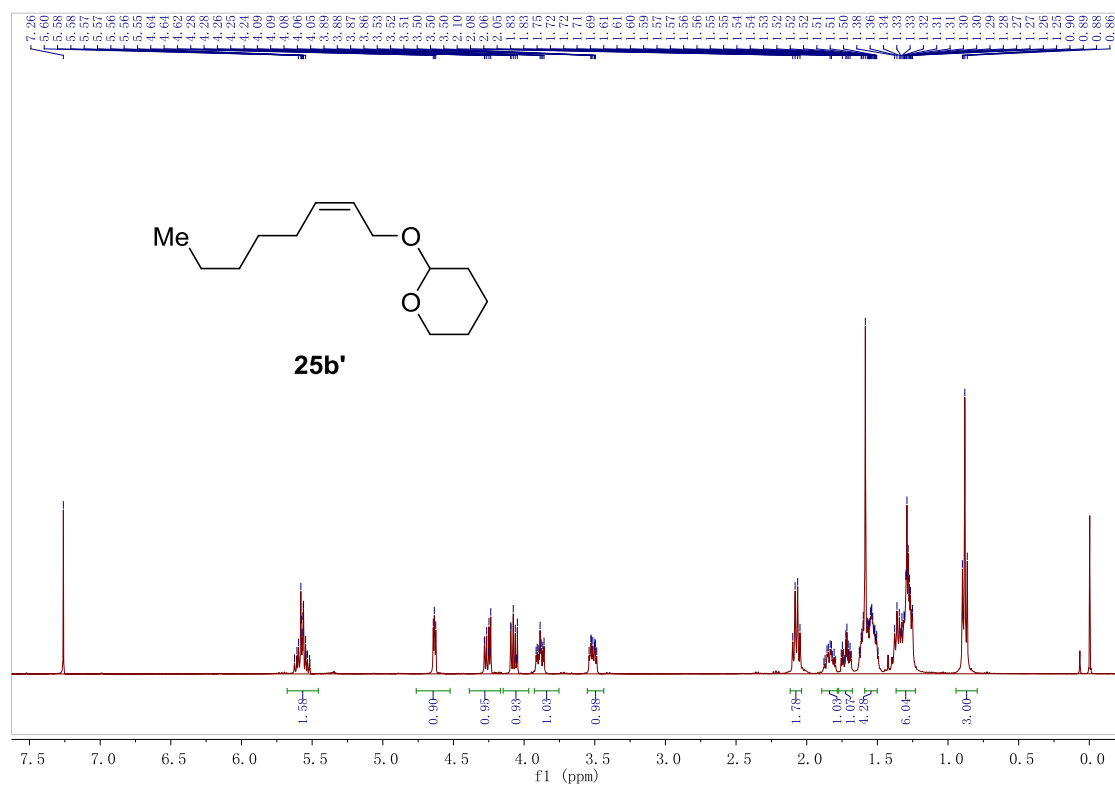
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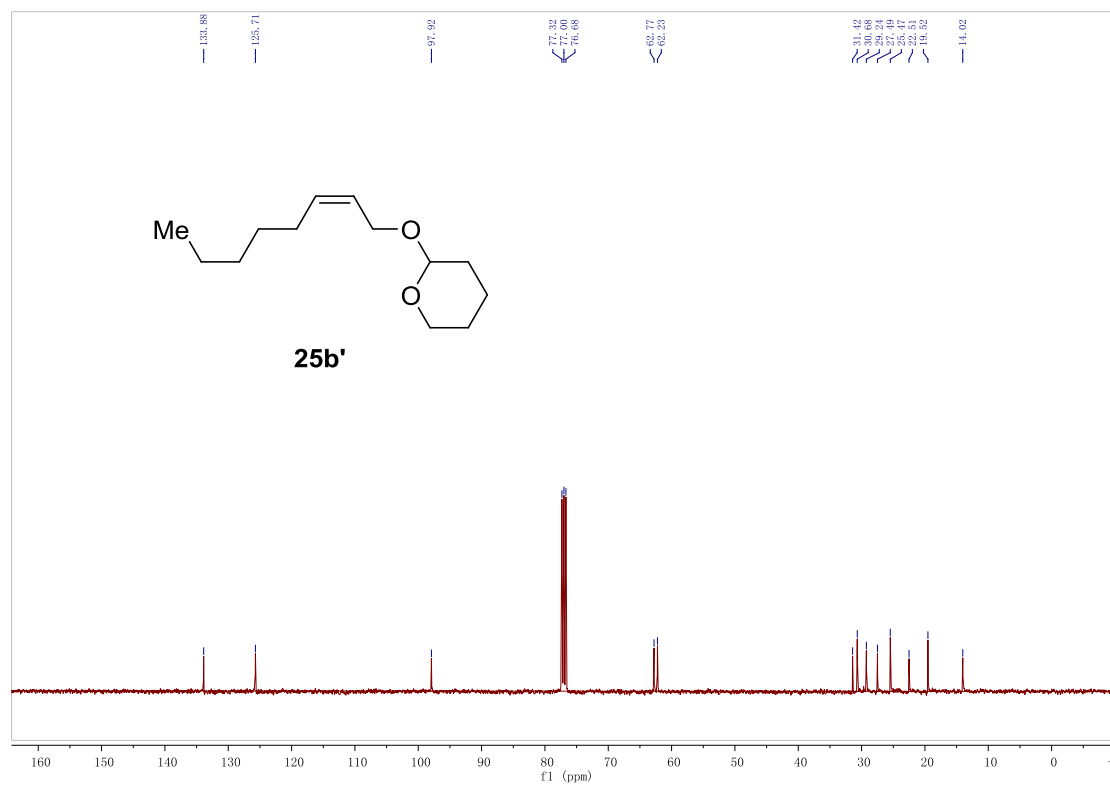
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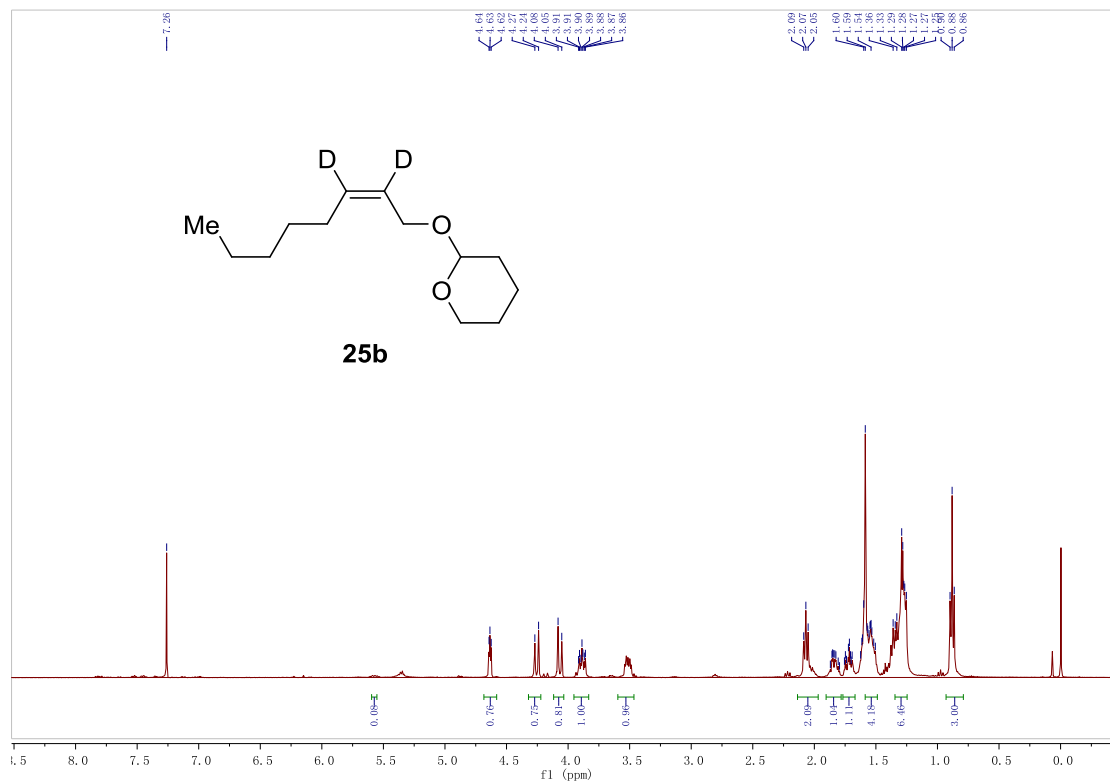
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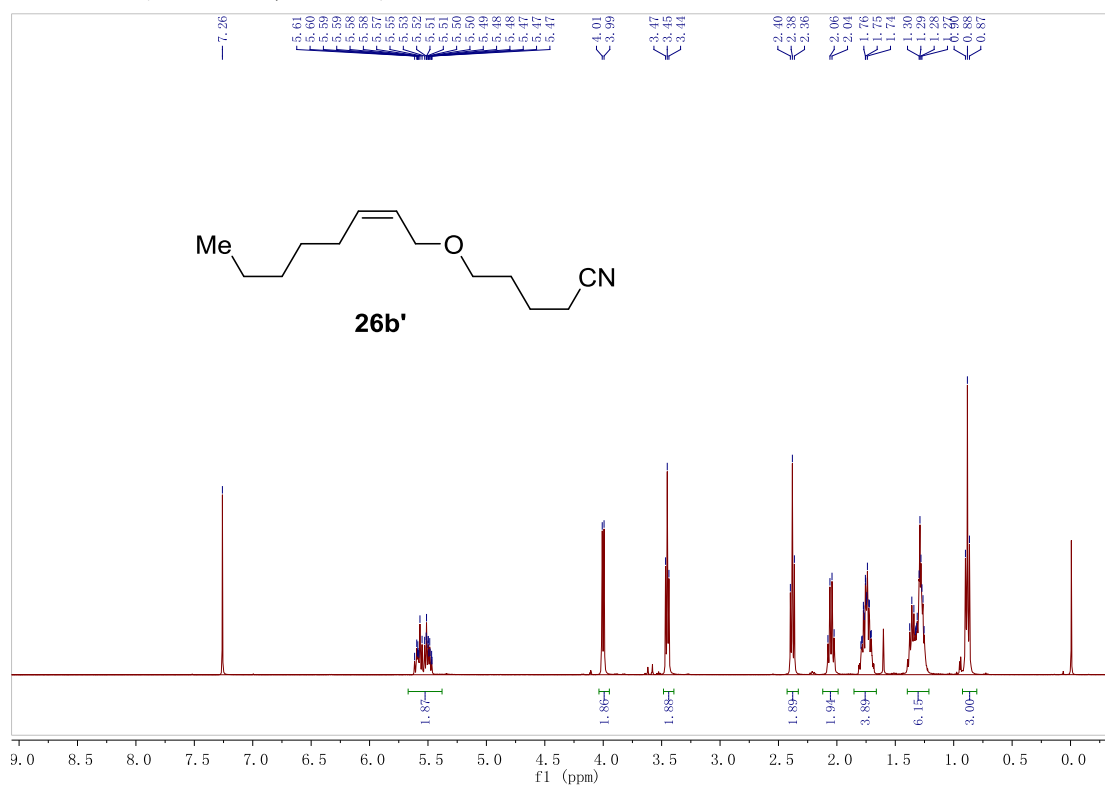
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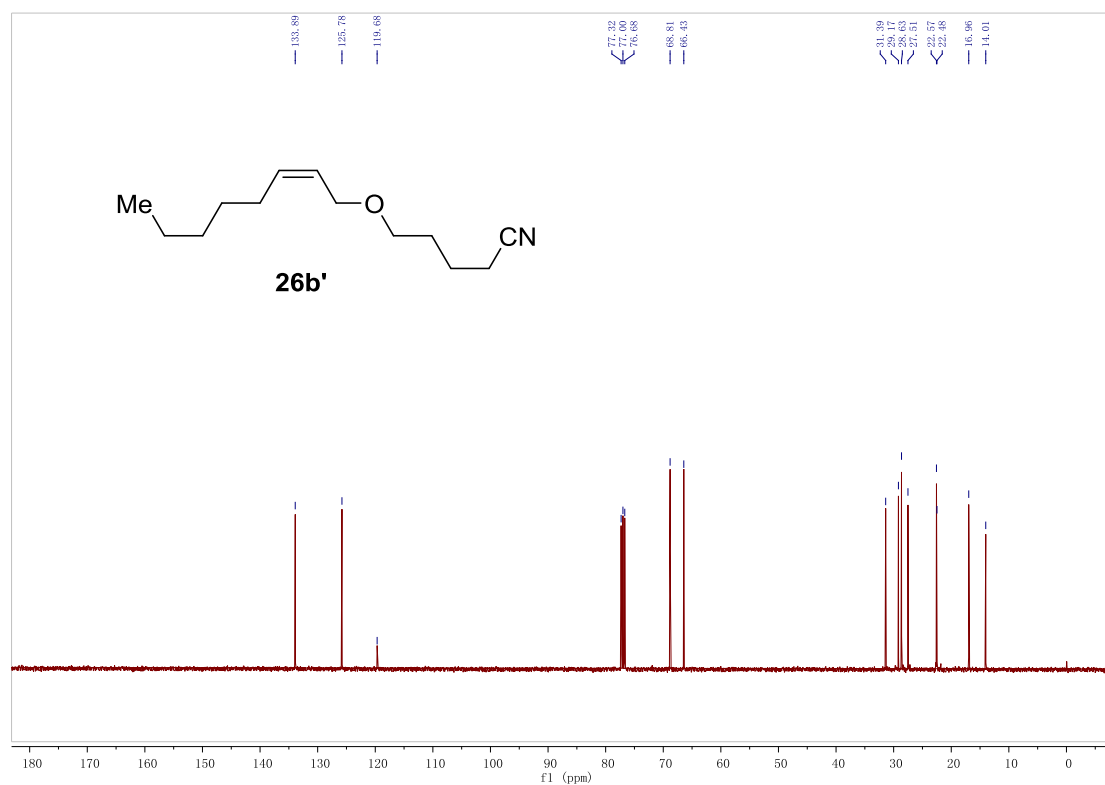
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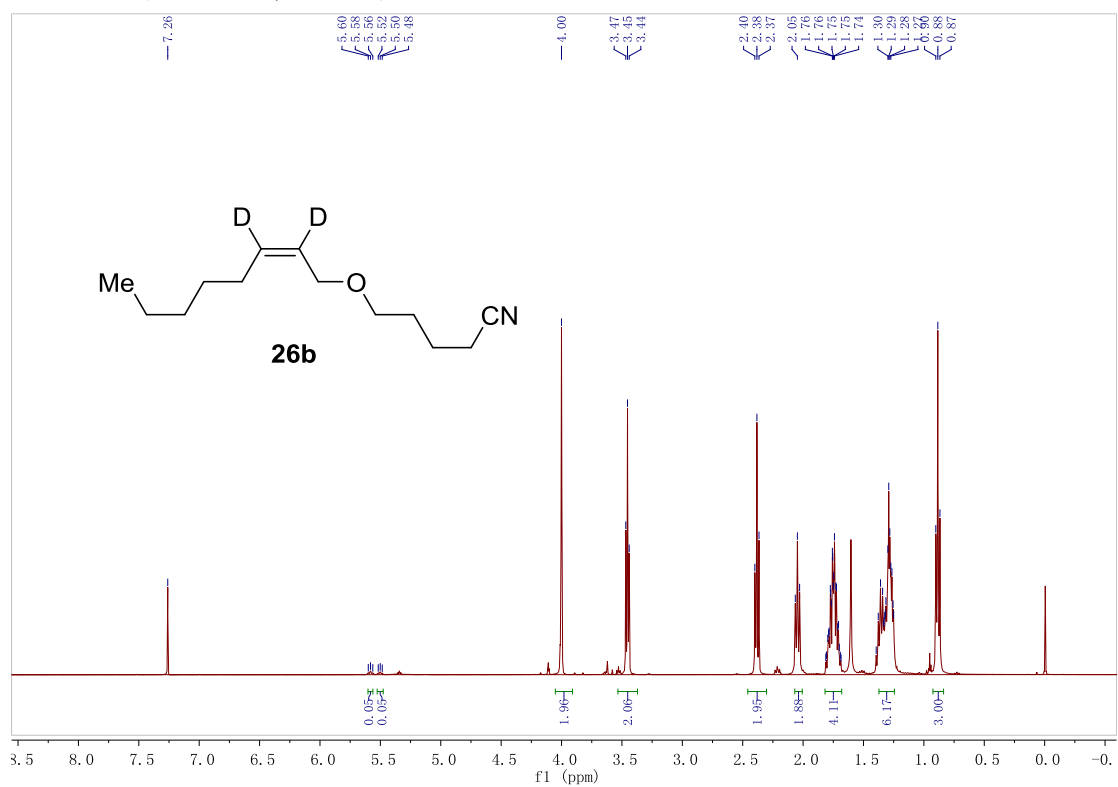
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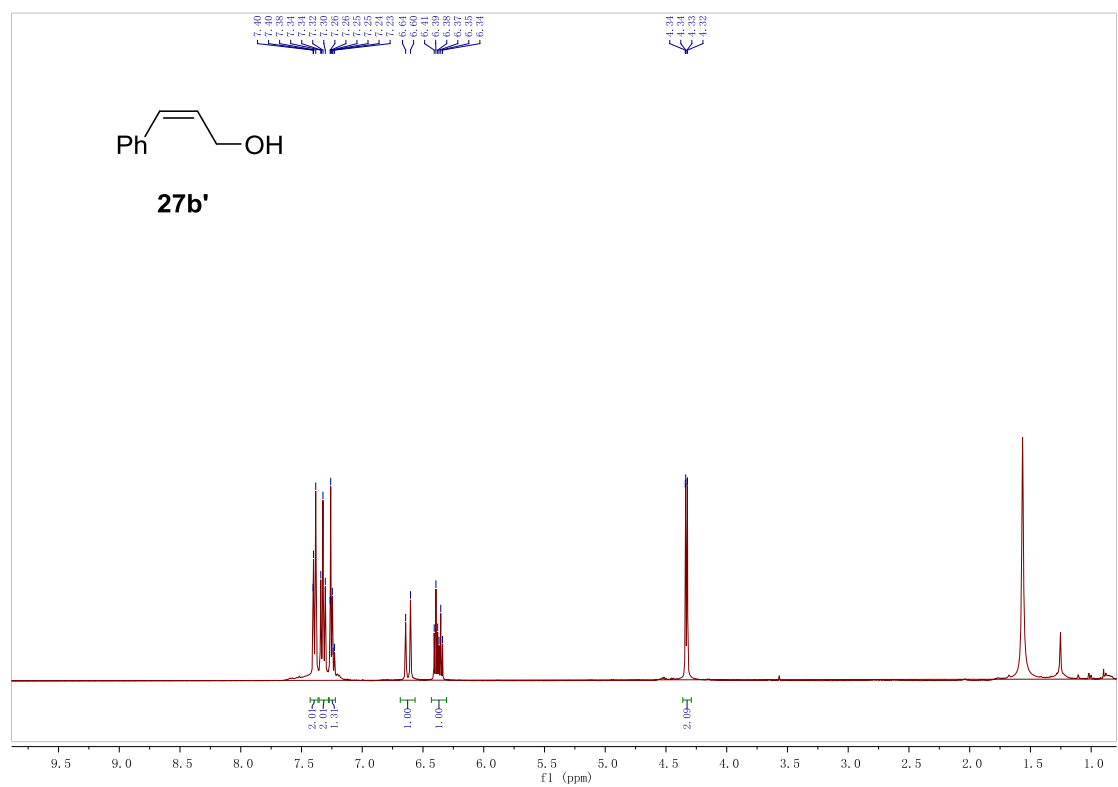
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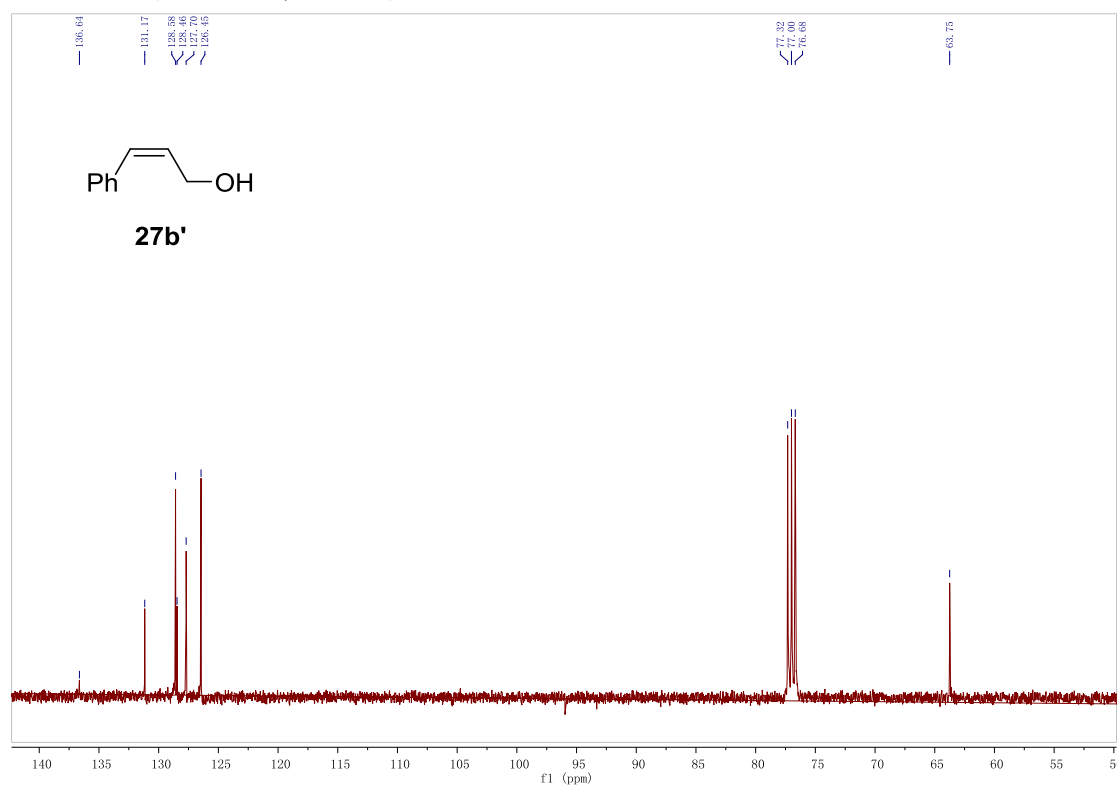
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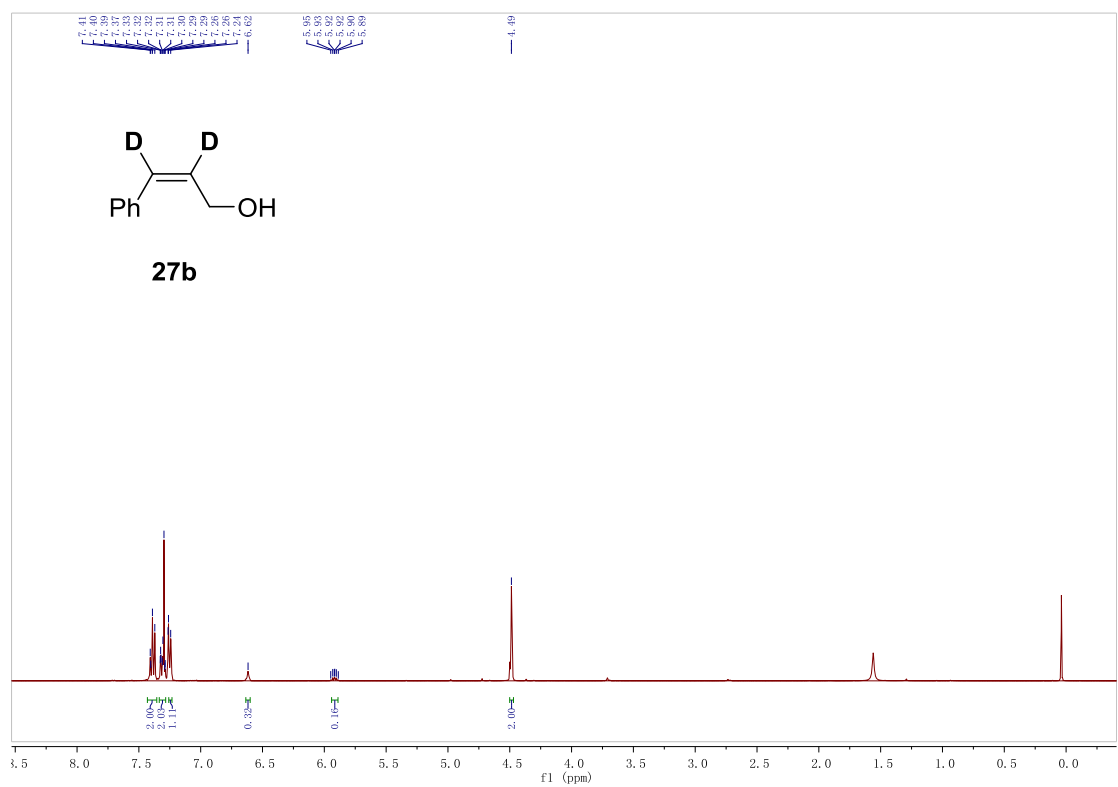
¹H NMR (400 MHz, CDCl₃)



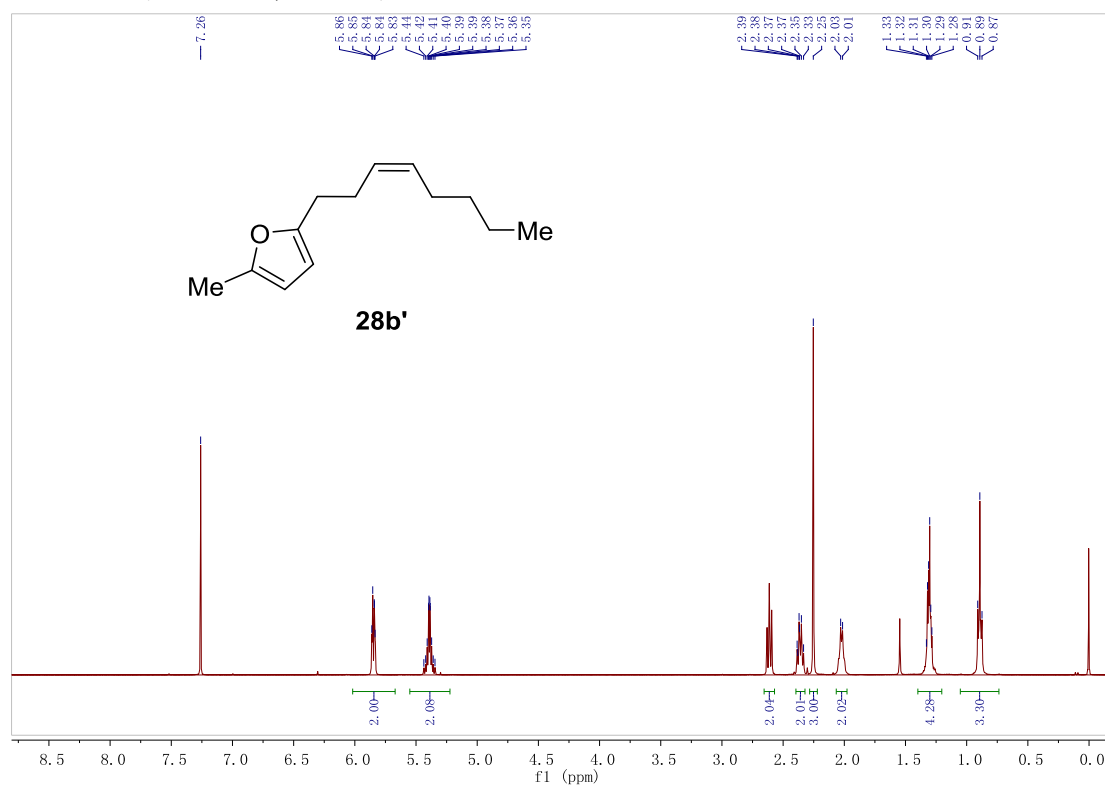
¹³C NMR (400 MHz, CDCl₃)



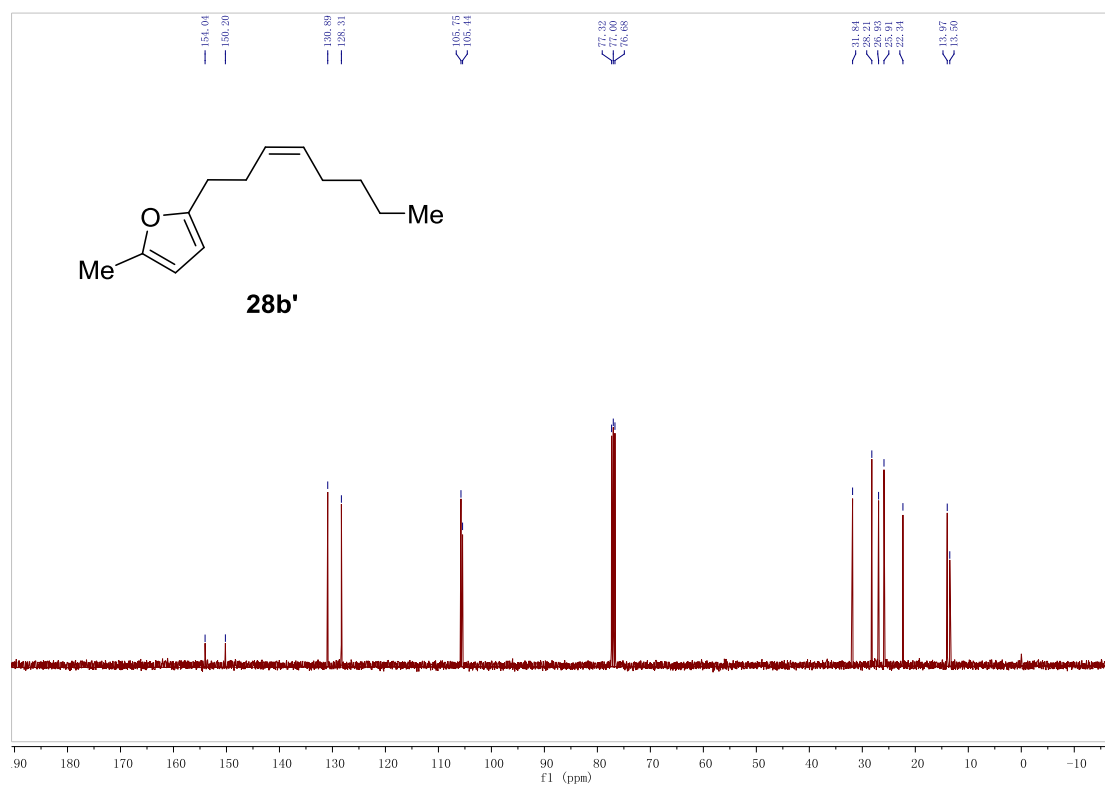
¹H NMR (400 MHz, CDCl₃)



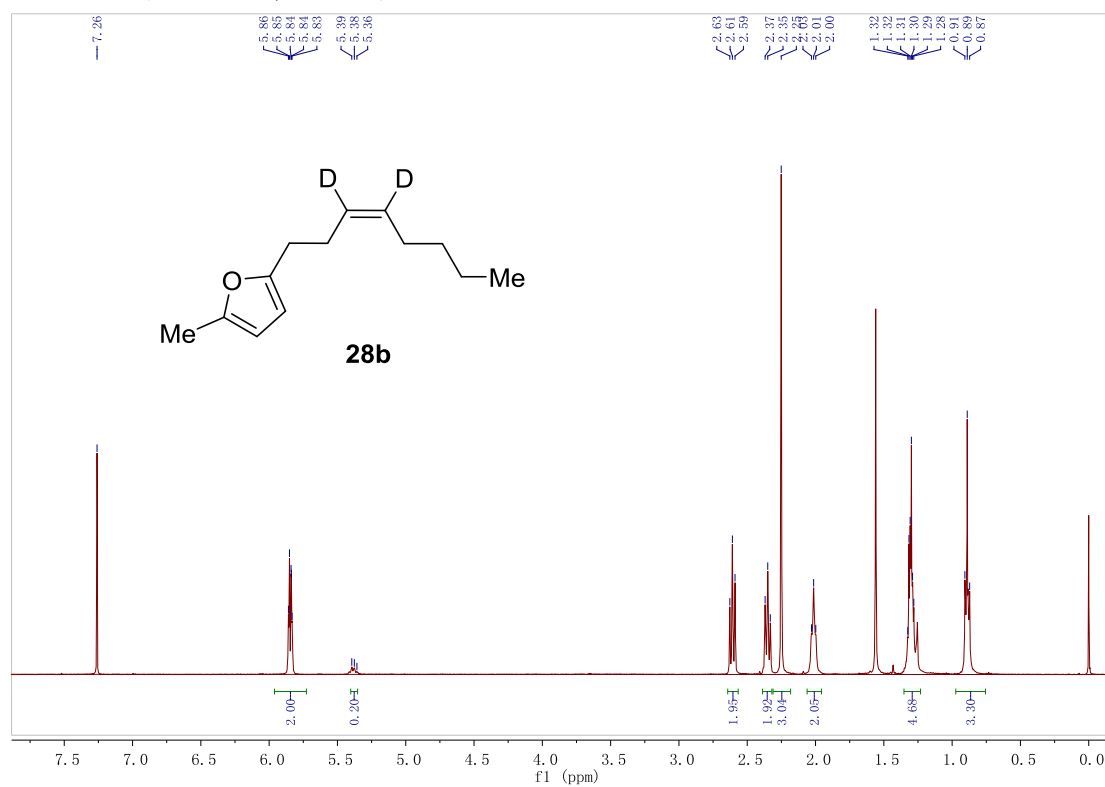
¹H NMR (400 MHz, CDCl₃)



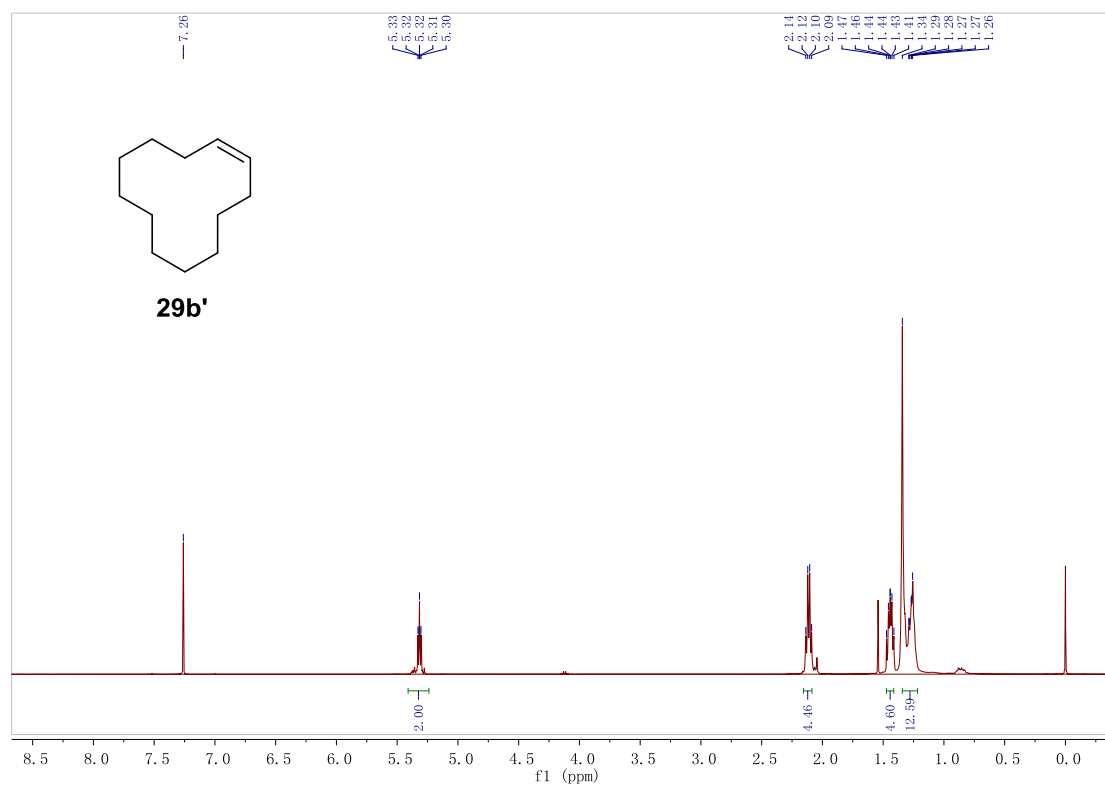
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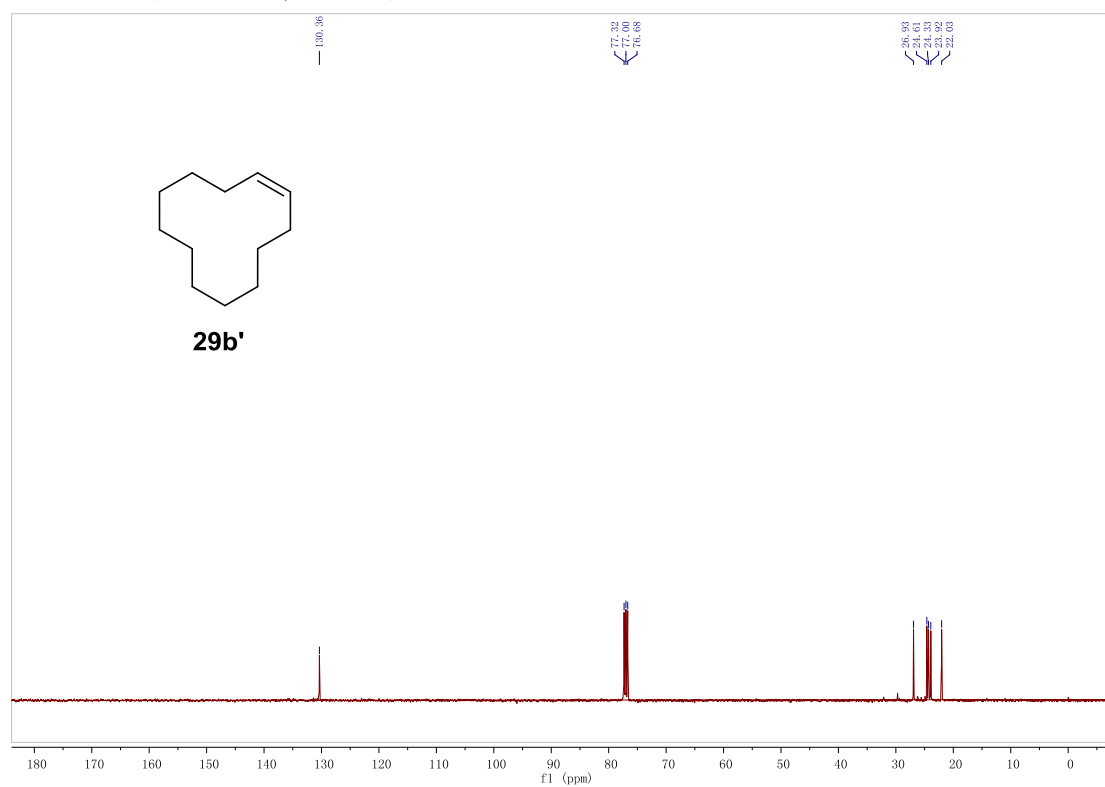
¹H NMR (400 MHz, CDCl₃)



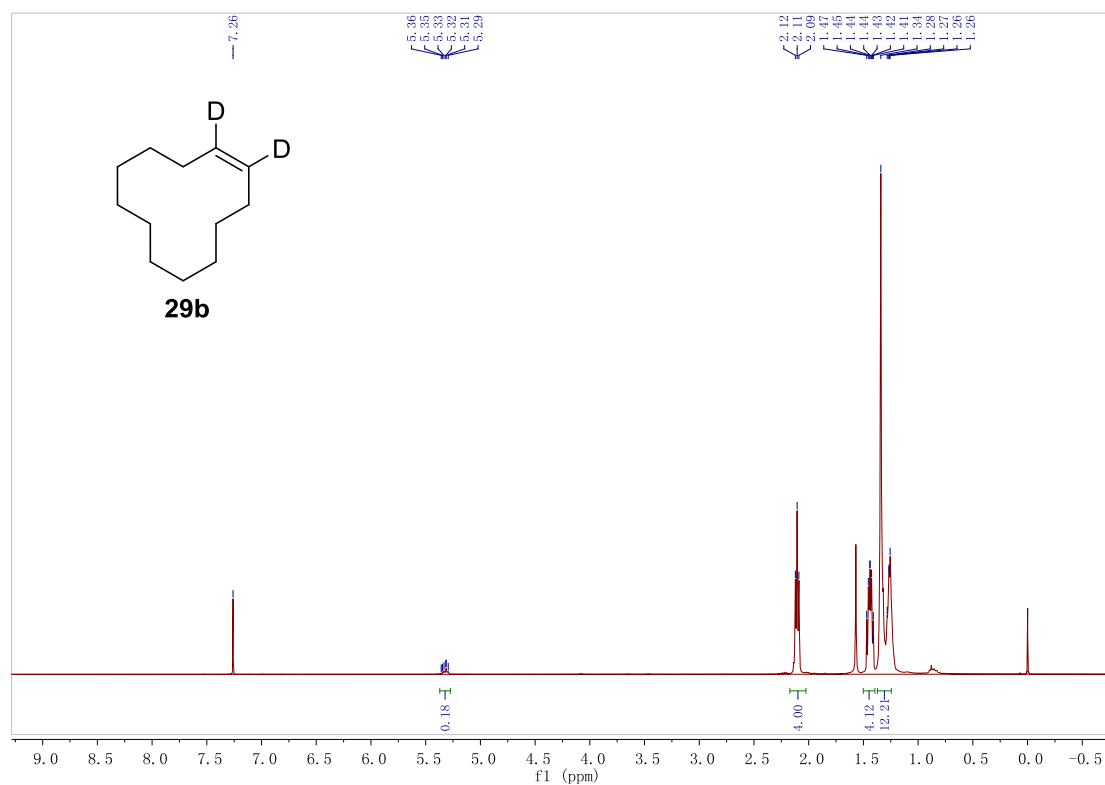
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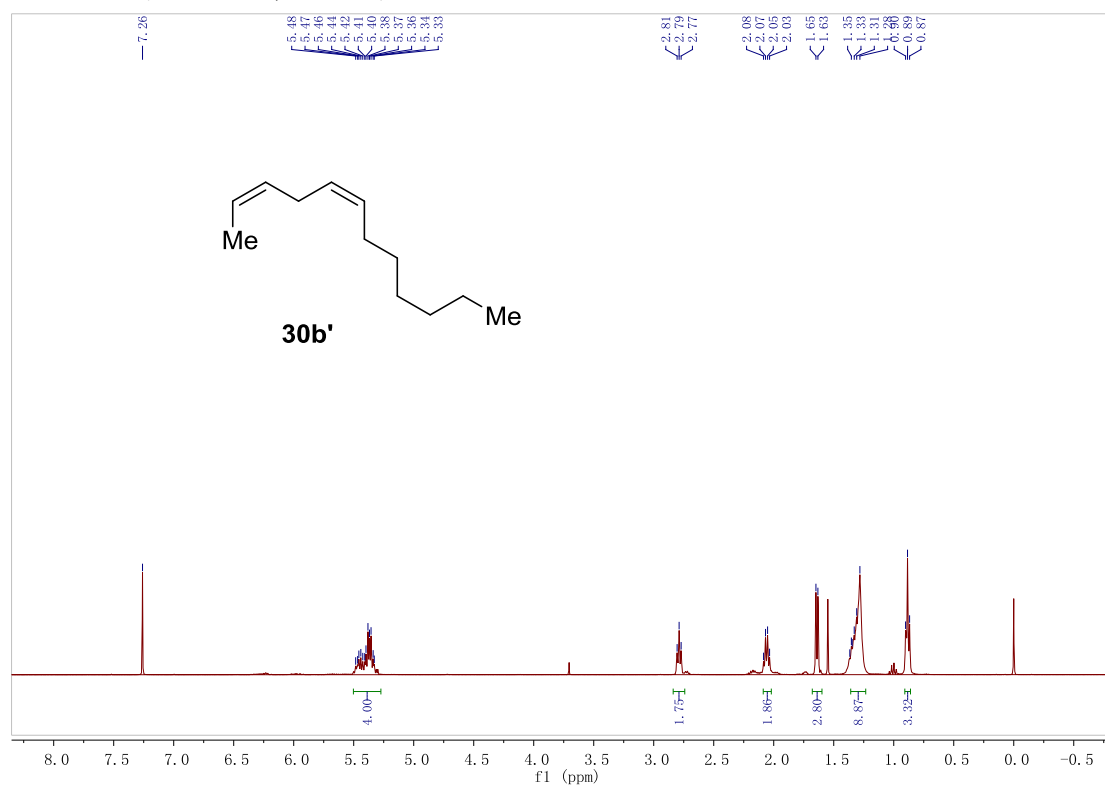
¹³C NMR (400 MHz, CDCl₃)



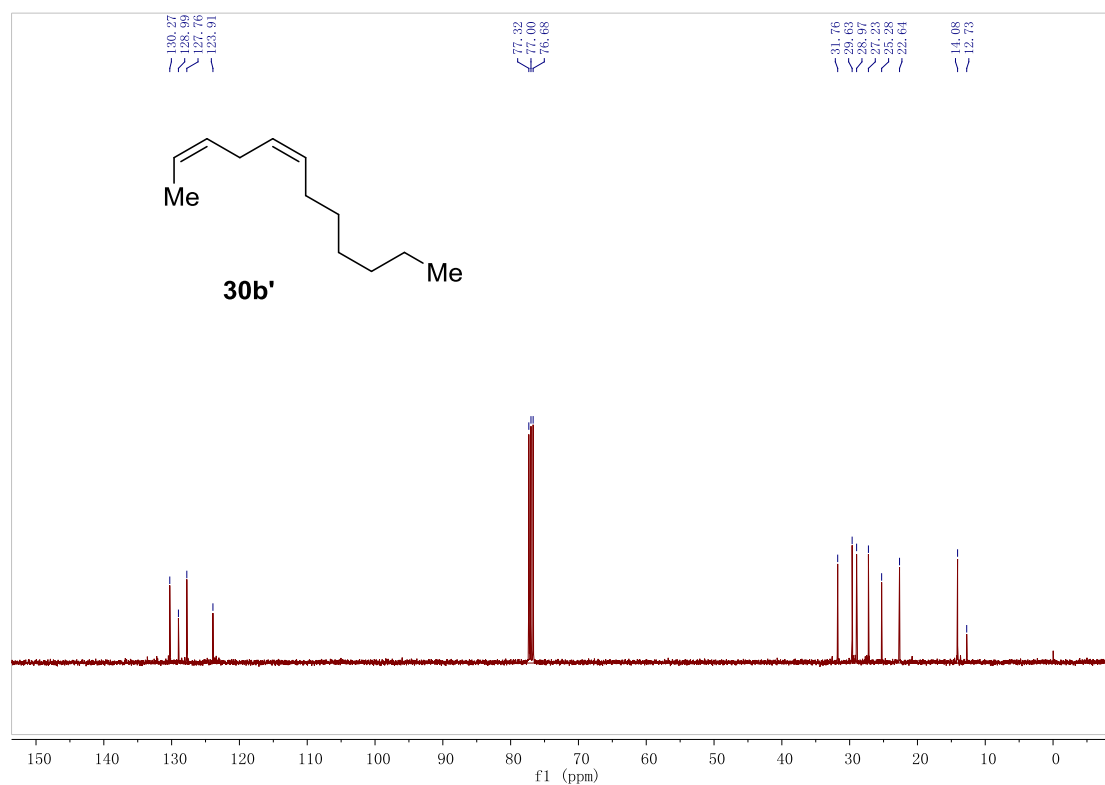
¹H NMR (400 MHz, CDCl₃)



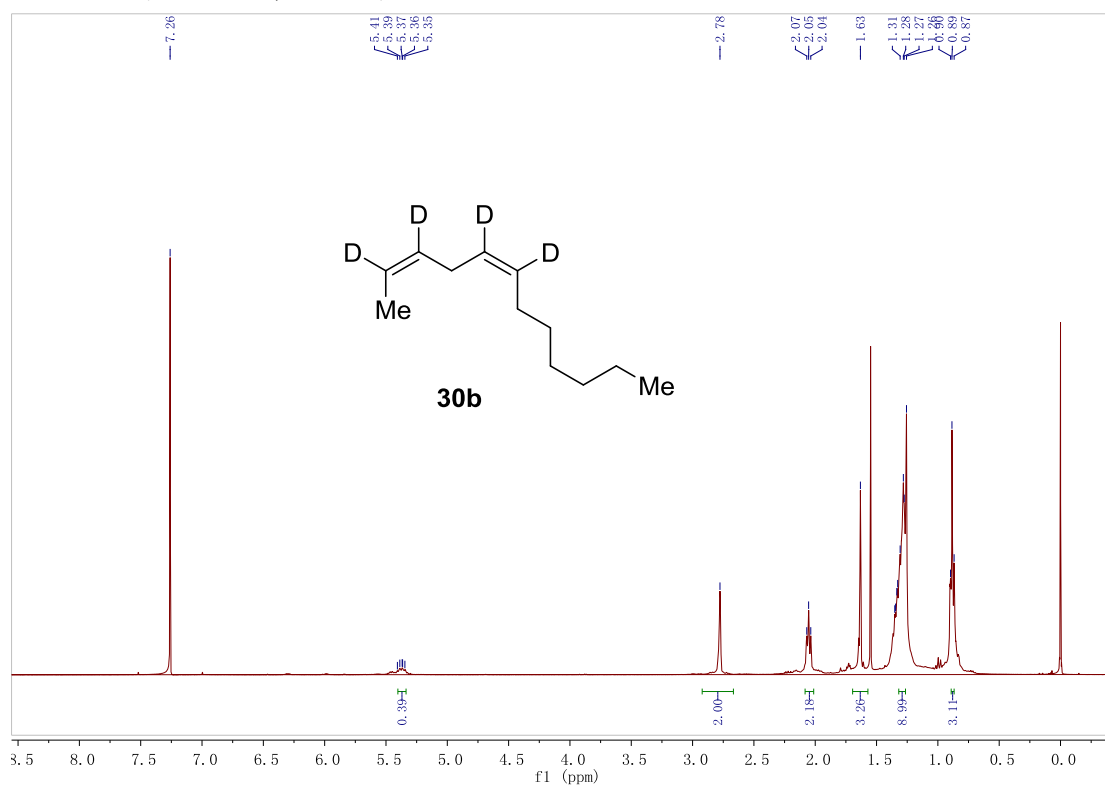
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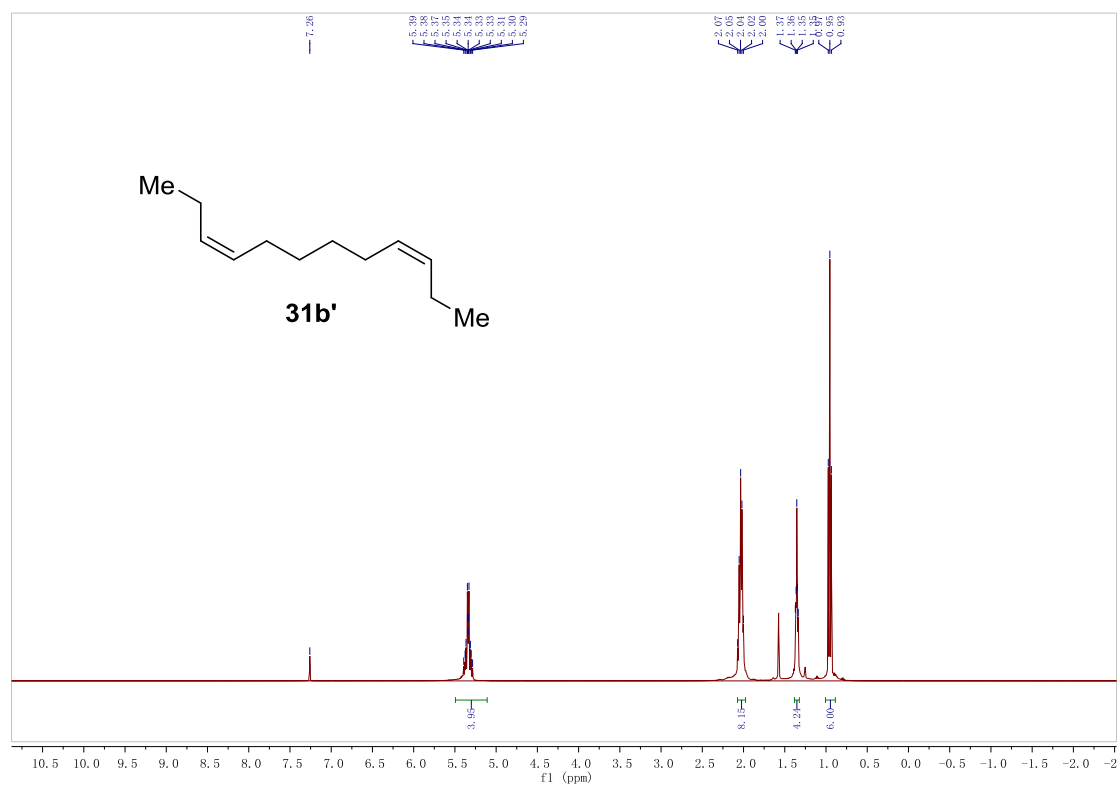
¹³C NMR (400 MHz, CDCl₃)



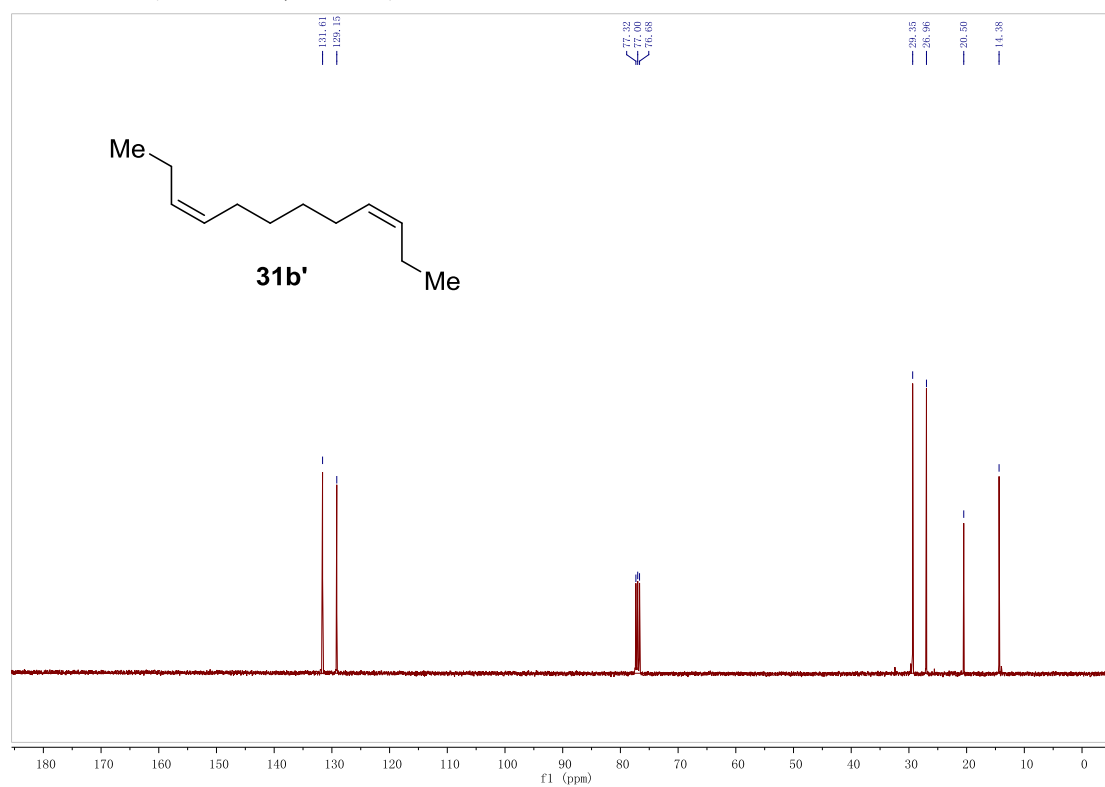
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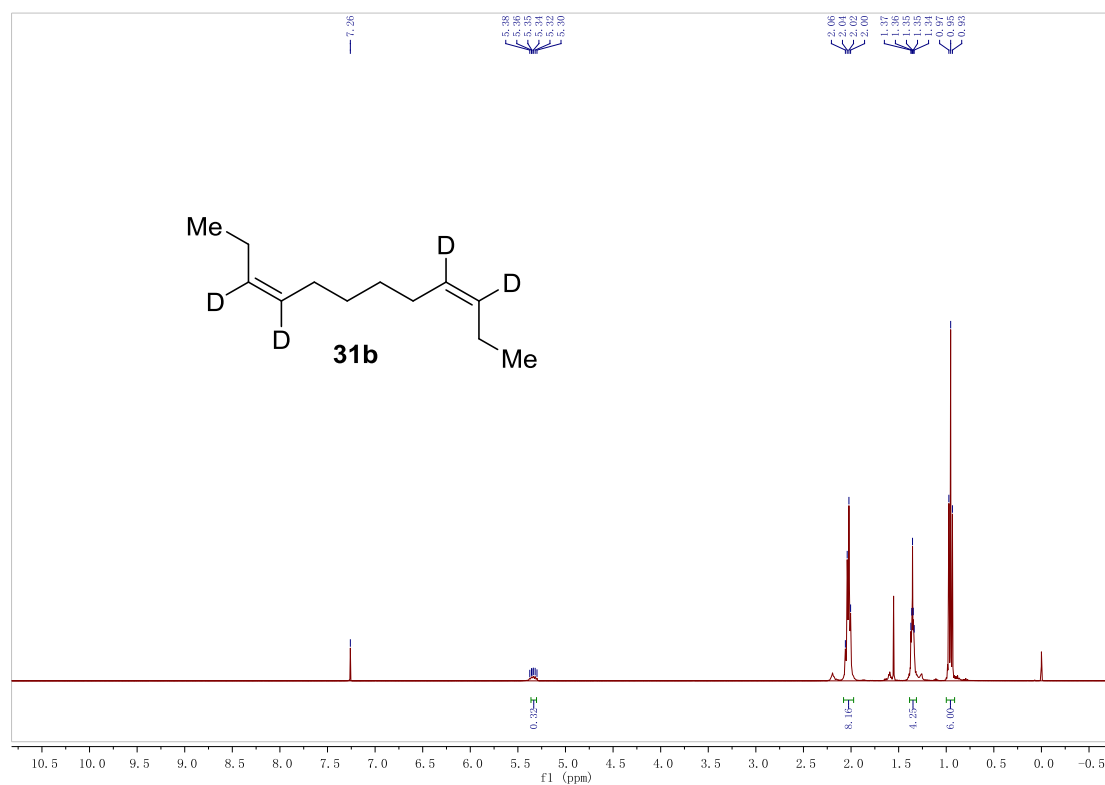
¹H NMR (400 MHz, CDCl₃)



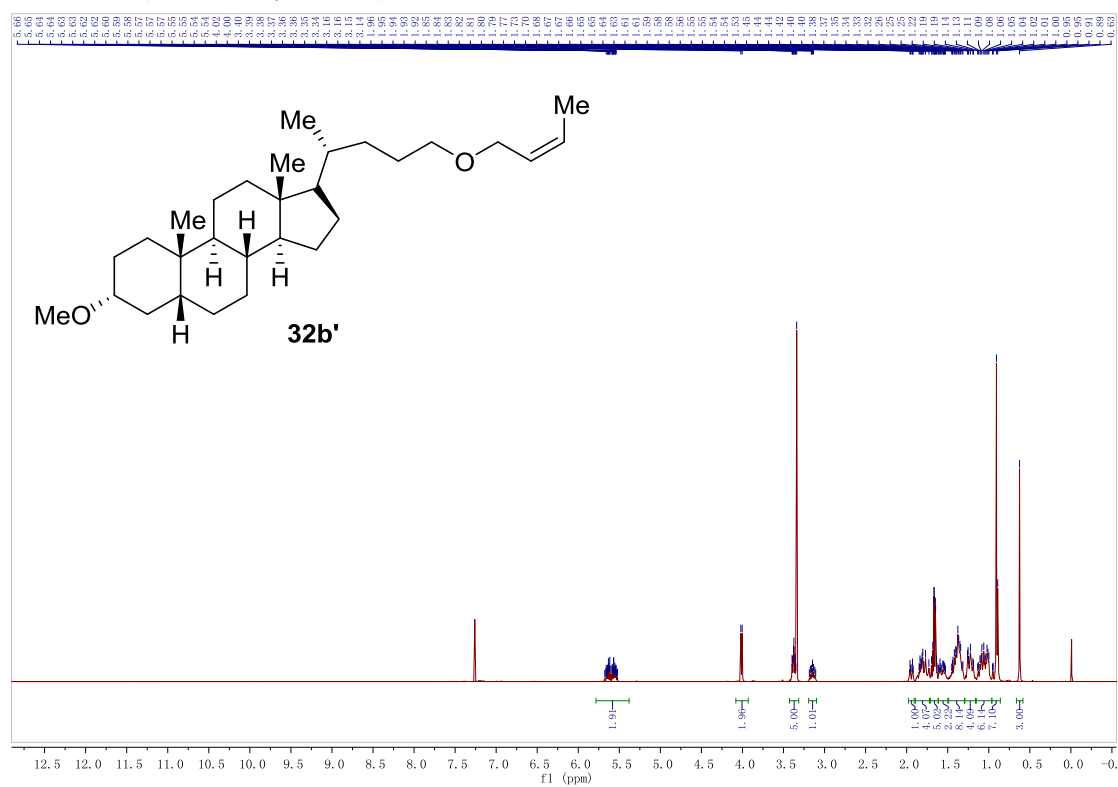
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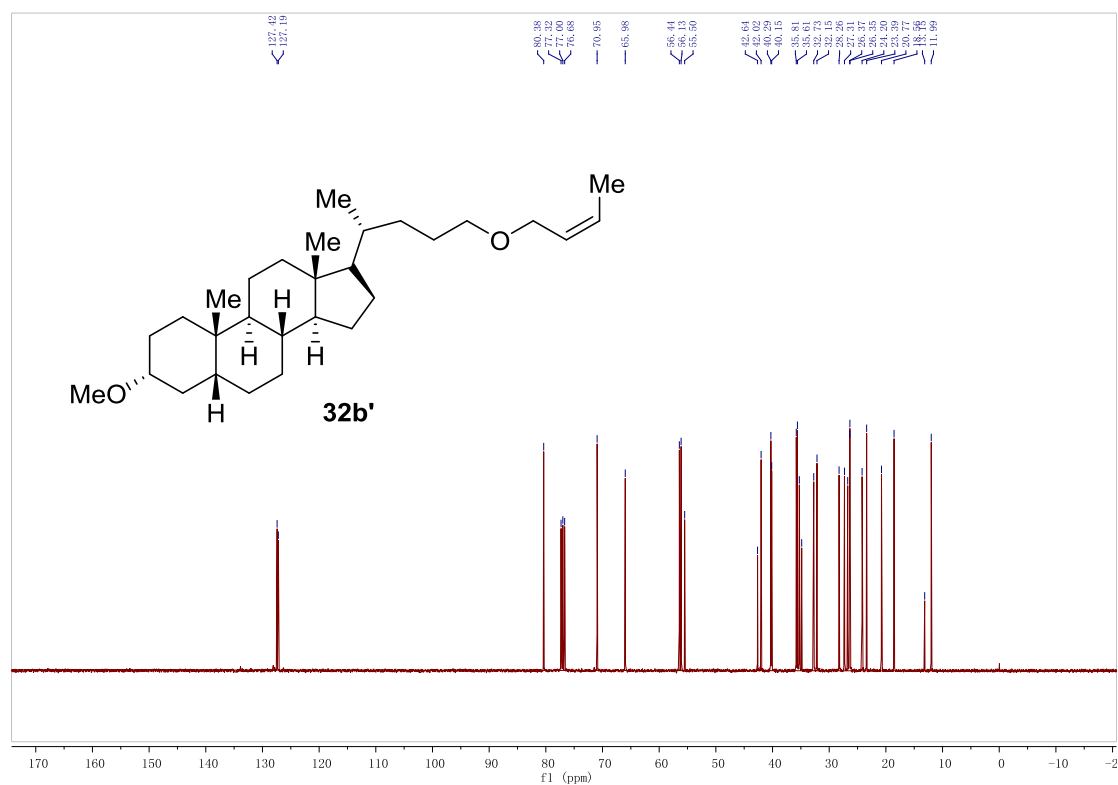
¹H NMR (400 MHz, CDCl₃)



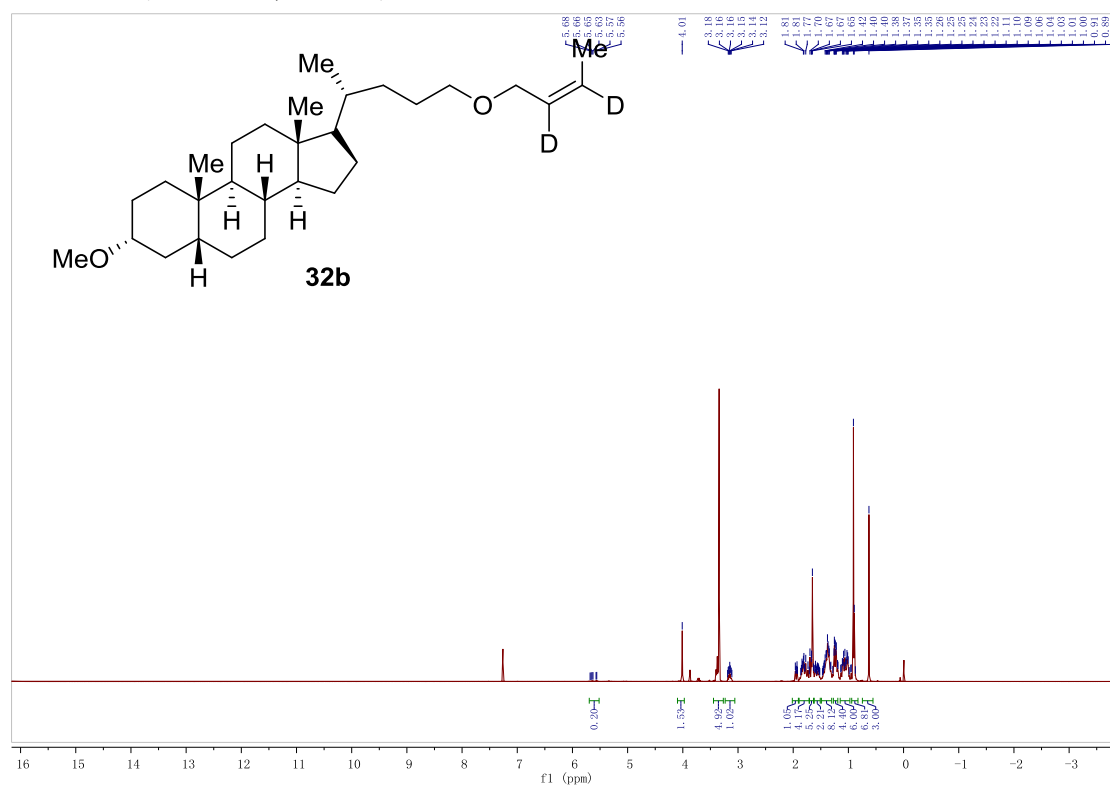
¹H NMR (400 MHz, CDCl₃)



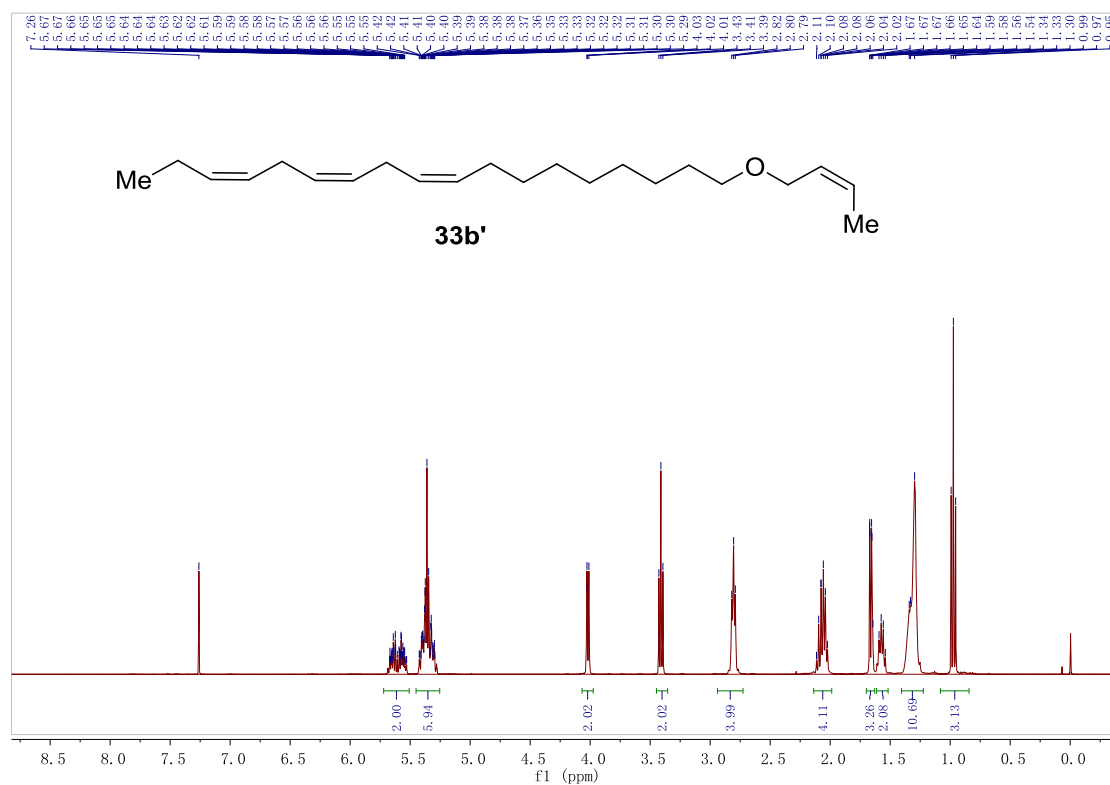
¹³C NMR (400 MHz, CDCl₃)



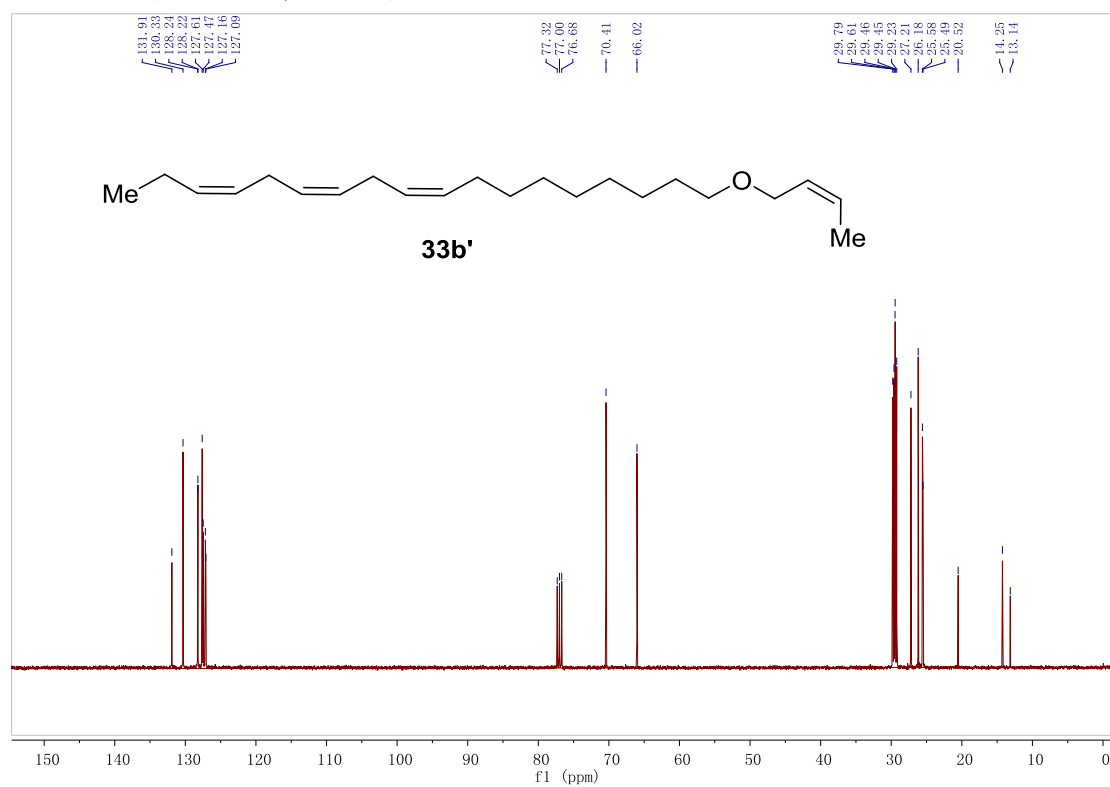
¹H NMR (400 MHz, CDCl₃)



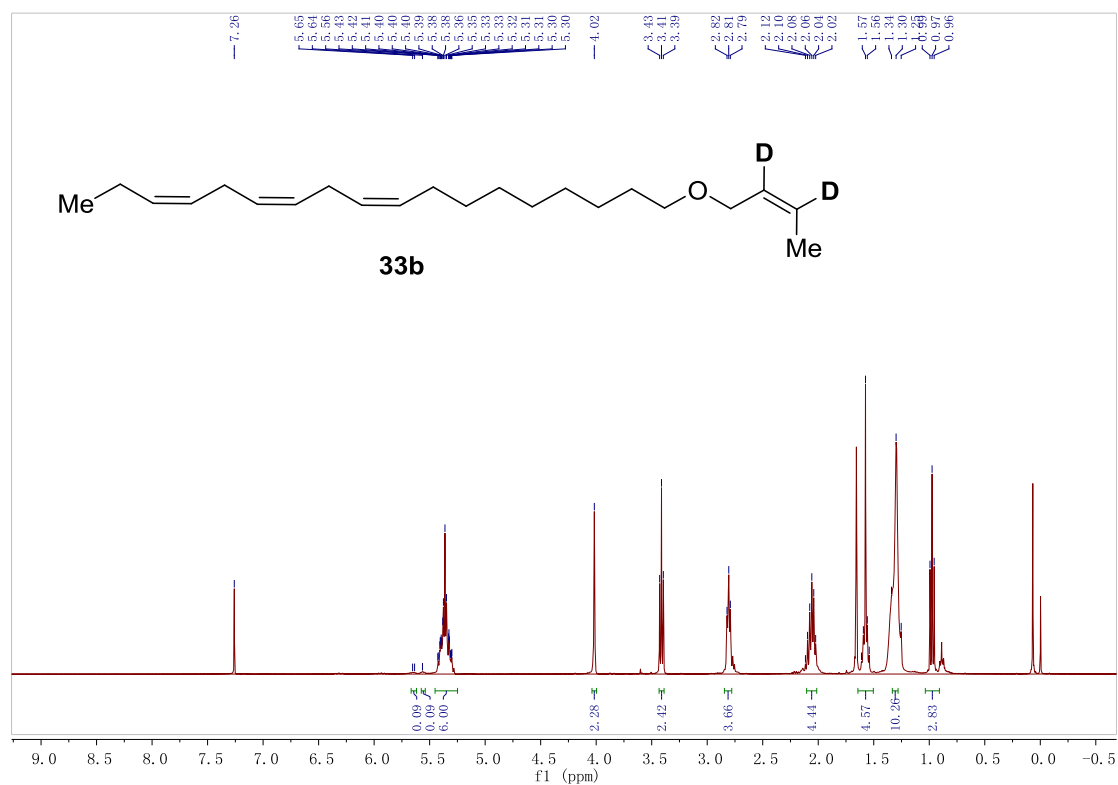
¹H NMR (400 MHz, CDCl₃)



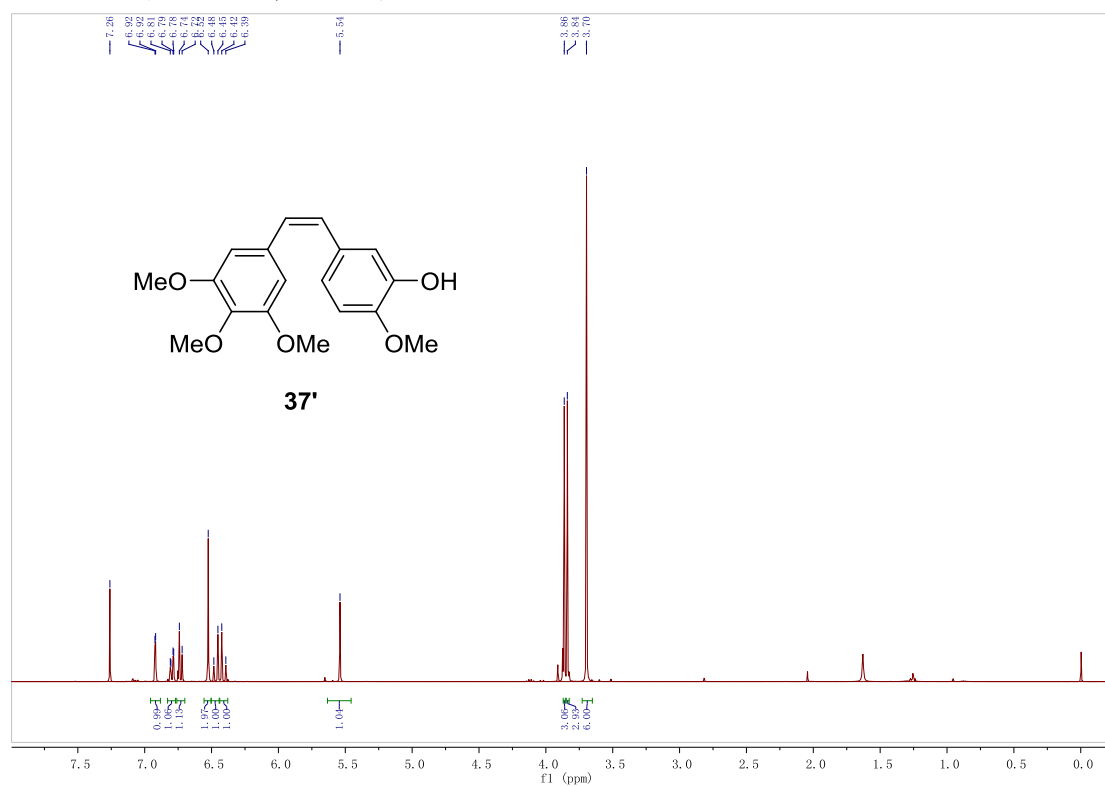
^{13}C NMR (400 MHz, CDCl_3)



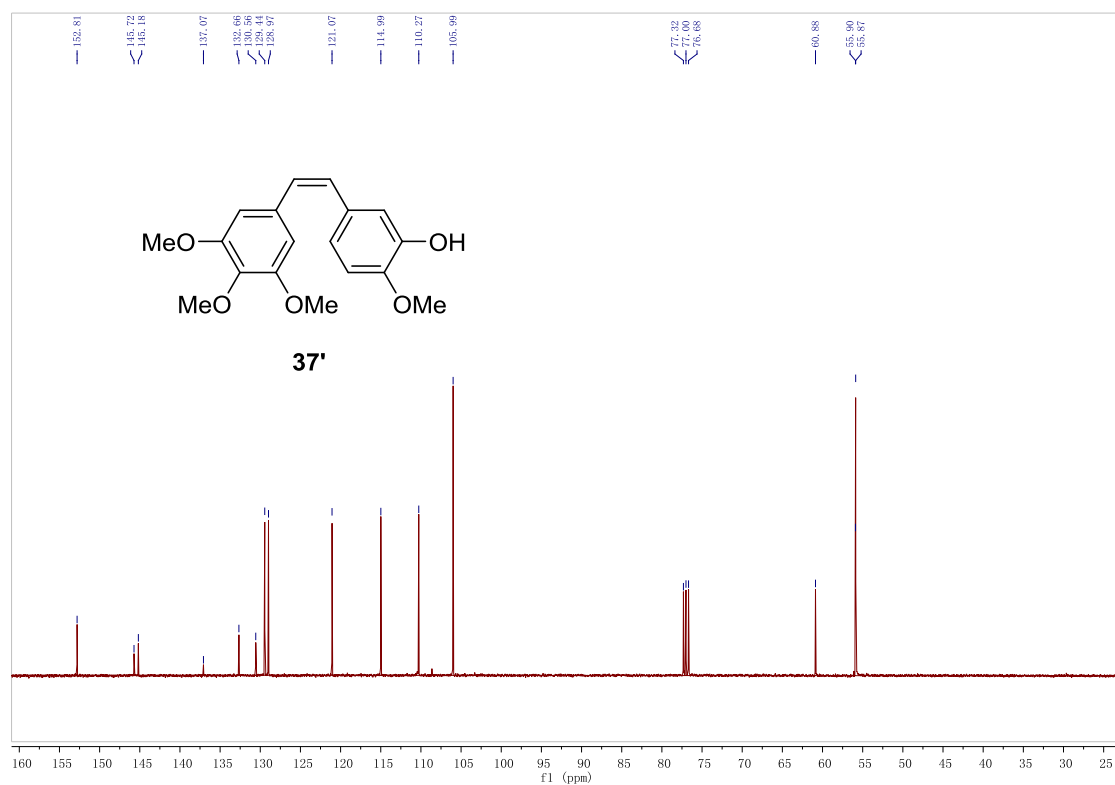
^1H NMR (400 MHz, CDCl_3)



¹H NMR (400 MHz, CDCl₃)



¹³C NMR (400 MHz, CDCl₃)



¹H NMR (400 MHz, CDCl₃)

