

Transition-Metal-Free Regioselective Synthesis of

Alkylboronates from Arylacetylenes or Vinyl Arenes

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General information

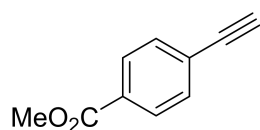
All experiments were conducted with a schlenk tube. Flash column chromatography was performed over silica gel (200-300 mesh). ^1H NMR spectra were recorded on a Bruker AVIII-500M spectrometers, chemical shifts (in ppm) were referenced to CDCl_3 ($\delta = 7.26$ ppm) and DMSO-d_6 ($\delta = 2.50$ ppm) as internal standards. ^{13}C NMR spectra were obtained by using the same NMR spectrometers and were calibrated with CDCl_3 ($\delta = 77.0$ ppm), DMSO-d_6 ($\delta = 39.6$ ppm). Unless otherwise noted, materials obtained from commercial suppliers were used without further purification, and the most starting materials were purchased from Adamas.

Procedure and characterization data for products

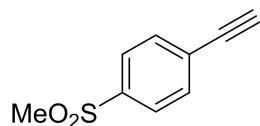
General Procedure A for the preparation of arylacetylene from aryl bromides and trimethylsilylacetylene: An oven-dried schlenk tube was charged with bromo-substrate (1 mmol), $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (14mg, 0.02 mmol) and CuI (7.6 mg, 0.04 mmol). The schlenk tube was taken to the glove box and dry THF (1 ml) was added to it. The tube was capped and taken out from the glove box. Triethylamine (216 μL , 1.55 mmol) was injected in it and trimethylsilylacetylene (176 μL , 1.25 mmol) was added to the reaction mixture slowly. The reaction mixture was stirred at room temperature for 24 hours. Upon completion, the reaction mixture was diluted with ethyl acetate, filtered through a silica gel plug, rinsed with ethyl acetate, and concentrated in vacuo. The crude reaction mixture was purified on silica gel.

Terminal alkyne was obtained through hydrolysis of 4-(trimethylsilyl)ethynyl-substrates. The TMS-ethynyl substrates were dissolved in 1.5 ml MeOH and anhydrous K_2CO_3 (2 eq) were added to it under N_2 atmosphere. The reaction mixture was stirred at room temperature for 3 h. Upon completion, the reaction mixture was diluted with ethyl acetate, filtered through a silica gel plug, rinsed with ethyl acetate, and concentrated in vacuo. The crude reaction mixture was purified on silica gel.¹

The following substrates were synthesized using this protocol.

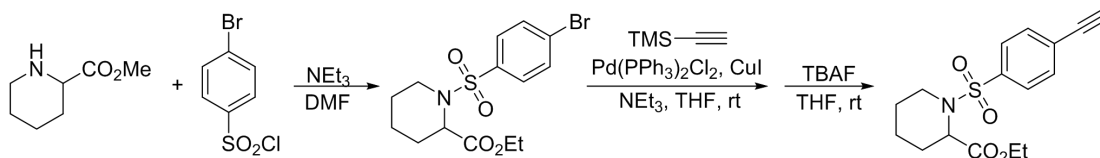


methyl 4-ethynylbenzoate (3034-86-4, 1k).² ^1H NMR (500 MHz, CDCl_3) δ 7.98 (d, $J = 8.5$ Hz, 2H), 7.53 (d, $J = 8.5$ Hz, 2H), 3.91 (s, 3H), 3.23 (s, 1H). ^{13}C NMR (125 MHz, CDCl_3) δ 166.3, 132.0, 130.1, 129.4, 126.7, 82.7, 80.0, 52.2.



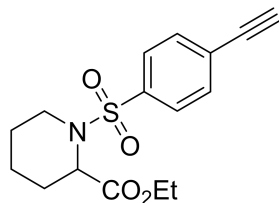
1-ethynyl-4-(methylsulfonyl)benzene (340771-31-5, 1m).³ ^1H NMR (500 MHz, CDCl_3) δ 7.89 (d, $J = 8.5$ Hz, 2H), 7.65 (d, $J = 8.5$ Hz, 2H), 3.29 (s, 1H), 3.04 (s, 3H). ^{13}C NMR (125 MHz, CDCl_3) δ 140.3, 132.9, 127.9, 127.3, 81.7, 81.2, 44.4.

Synthesis of terminal arylalkyne 4



Ethyl-1-((4-bromophenyl)sulfonyl)piperidine-2-carboxylate was prepared according to the literature procedure.⁴ Ethyl piperidine-2-carboxylate hydrochloride (0.79 g, 5 mmol) and 4-bromobenzenesulfonyl chloride (1.28 g, 5 mmol) were dissolved in 50 mL DMF. Triethylamine (3 eq) was then added dropwise. After stirring for 8 h at room temperature, the residue was suspended in 50 mL of ethyl acetate and washed with 2 M HCl (25 mL*3) and H₂O (25 mL). The organic layer was dried over anhydrous Na₂SO₄, and concentrated in vacuo. The crude reaction mixture was purified on silica gel.

An oven-dried schlenk tube was charged with bromo-substrate (1 mmol), Pd(PPh₃)₂Cl₂ (14mg, 0.02 mmol) and CuI (7.6 mg, 0.04 mmol). The tube was taken to the glove box and dry THF (1 mL) was added to it. The tube was capped and taken out from the glove box. Triethylamine (216 uL, 1.55 mmol) was injected in it and trimethylsilylacetylene (176 uL, 1.25 mmol) was added to the reaction mixture slowly. The reaction mixture was stirred at room temperature for 24 hours. Upon completion, the reaction mixture was diluted with ethyl acetate, filtered through a silica gel plug, rinsed with ethyl acetate, and concentrated in vacuo. The crude reaction mixture was purified on silica gel. The internal alkyne was dissolved with anhydrous THF (1 mL), and TBAF (1.5 mL, 1M in THF) was added. The resulting mixture was stirred at room temperature overnight. Upon completion, the reaction mixture was diluted with ethyl acetate, filtered through a silica gel plug, rinsed with ethyl acetate, and concentrated in vacuo. The crude reaction mixture was purified on silica gel.

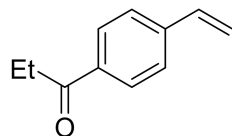


ethyl 1-((4-ethynylphenyl)sulfonyl)piperidine-2-carboxylate (4). Light yellow oil, ¹H NMR (500 MHz, CDCl₃) δ 7.73 (d, *J* = 8.0 Hz, 2H), 7.56 (d, *J* = 8.0 Hz, 2H), 4.71 (d, *J* = 5.5 Hz, 1H), 4.05-4.01 (m, 1H), 3.96-3.92 (m, 1H), 3.76 (dd, *J* = 13.0, 3.0 Hz, 1H), 3.23 (s, 1H), 3.22-3.17 (m, 1H), 2.13 (d, *J* = 13.5 Hz, 1H), 1.76-1.23 (m, 3H), 1.50 – 1.43 (m, 1H), 1.29 – 1.22 (m, 1H), 1.13 (t, *J* = 7.0 Hz, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 170.4, 140.0, 132.3, 127.0, 126.3, 82.1, 80.4, 61.1, 55.1, 42.7, 27.8, 24.7, 20.0, 14.0. HRMS (DART, *m/z*) calcd for [C₁₆H₁₉NO₄S + H⁺]: 327.1106; found: 322.1113.

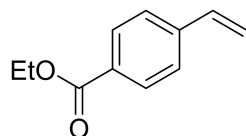
General Procedure B for the preparation of vinyl arenes from aryl bromides and vinyltrifluoroborate: A schlenk tube was charged with vinyltrifluoroborate (134 mg, 1 mmol), PdCl₂ (3.5 mg, 0.02 mmol), PPh₃ (16 mg, 0.04 mmol), Cs₂CO₃ (978 mg, 3 eq) and bromo-substrate (1 eq) in THF/H₂O (9:1) (2 mL) was heated at 85 °C under an N₂ atmosphere. The reaction mixture was stirred at 85 °C for 22 h, then cooled to room temperature and diluted with H₂O followed by extraction with CH₂Cl₂. The organic layer was dried over

anhydrous Na₂SO₄, and concentrated in vacuo. The crude reaction mixture was purified on silica gel.⁵

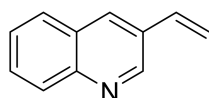
The following substrates were synthesized using this protocol.



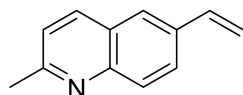
1-(4-vinylphenyl)propan-1-one (7646-72-2, 3s). Colorless oil, ¹H NMR (500 MHz, CDCl₃) δ 7.93 (d, *J* = 8.0 Hz, 2H), 7.48 (d, *J* = 8.0 Hz, 2H), 6.75 (dd, *J* = 17.5, 11.0 Hz, 1H), 5.87 (dd, *J* = 17.5, 0.5 Hz, 1H), 5.38 (d, *J* = 11.0 Hz, 1H), 2.99 (q, *J* = 7.2 Hz, 2H), 1.22 (t, *J* = 7.3 Hz, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 200.3, 141.8, 136.0, 135.9, 128.3, 126.3, 116.5, 31.8, 8.3.



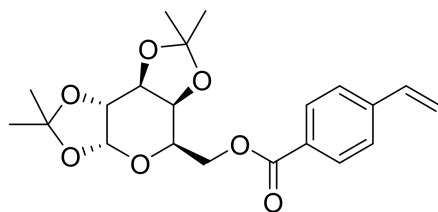
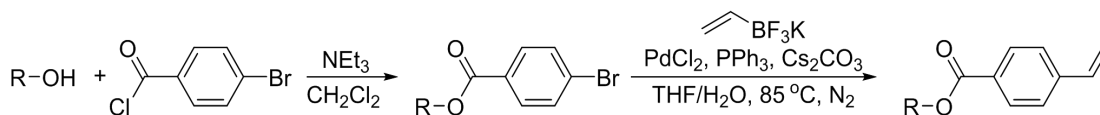
ethyl 4-vinylbenzoate (2715-43-7, 2t).⁶ Colorless oil, ¹H NMR (500 MHz, CDCl₃) δ 8.00 (d, *J* = 8.4 Hz, 2H), 7.45 (d, *J* = 8.3 Hz, 2H), 6.75 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.86 (d, *J* = 17.6 Hz, 1H), 5.37 (d, *J* = 10.9 Hz, 1H), 4.37 (q, *J* = 7.1 Hz, 2H), 1.39 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 166.4, 141.8, 136.0, 129.8, 129.6, 126.0, 116.3, 60.9, 14.3.



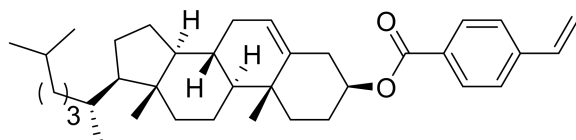
3-vinylquinoline (67752-31-2, 3p).⁷ Yellow oil, ¹H NMR (500 MHz, CDCl₃) δ 9.01 (d, *J* = 2.2 Hz, 1H), 8.16 – 8.00 (m, 2H), 7.79 (d, *J* = 8.1 Hz, 1H), 7.67 (ddd, *J* = 8.3, 6.9, 1.4 Hz, 1H), 7.58 – 7.47 (m, 1H), 6.86 (dd, *J* = 17.7, 11.0 Hz, 1H), 5.98 (d, *J* = 17.7 Hz, 1H), 5.45 (d, *J* = 11.0 Hz, 1H). ¹³C NMR (126 MHz, CDCl₃) δ 149.0, 147.5, 133.7, 132.5, 130.3, 129.3, 129.1, 127.9, 127.8, 126.9, 116.3.



2-methyl-6-vinylquinoline (1365842-17-6, 2o).⁸ Yellow oil, ¹H NMR (500 MHz, CDCl₃) δ 7.98 – 7.94 (m, 2H), 7.82-7.79 (m, 1H), 7.65-7.63 (m, 1H), 7.26 – 7.20 (m, 1H), 6.84 (dd, *J* = 17.5, 11.0 Hz, 1H), 5.85 (d, *J* = 17.5 Hz, 1H), 5.34 (d, *J* = 11.0 Hz, 1H), 2.71 (s, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 158.8, 147.6, 136.2, 136.1, 134.8, 128.7, 126.8, 126.4, 125.5, 122.3, 114.7, 25.2.

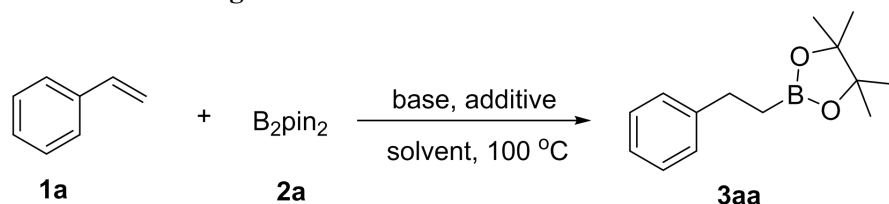


((3aR,5R,5aS,8aS,8bR)-2,2,7,7-tetramethyltetrahydro-5H-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-5-yl)methyl 4-vinylbenzoate. (64448-31-3, 6). A round-bottom flask was charged with 4-bromobenzoyl chloride (720 mg, 1.1 eq), 1,2:3,4-di-*O*-isopropylpyridene- α -D-galactopyranose (775 mg, 2.98 mmol), Et₃N (452 mg, 1.5 eq), and CH₂Cl₂ (100 mL). The reaction mixture was then filtered, and the filtrate was washed with 1M HCl. The organic layer was dried over anhydrous Na₂SO₄, and concentrated in vacuo, which was further purified by column chromatography to give a pure alkyl 4-bromobenzoate. The corresponding vinyl arene was prepared by using general procedure **B**. ¹H NMR (500 MHz, CDCl₃) δ 7.99 (d, *J* = 8.0 Hz, 2H), 7.43 (d, *J* = 8.0 Hz, 2H), 6.73 (dd, *J* = 17.5, 11.0 Hz, 1H), 5.84 (d, *J* = 17.5 Hz, 1H), 5.55 (d, *J* = 5.0 Hz, 1H), 5.36 (d, *J* = 11.0 Hz, 1H), 4.64 (dd, *J* = 8.0, 2.0 Hz, 1H), 4.51 (dd, *J* = 11.5, 4.5 Hz, 1H), 4.41 (dd, *J* = 11.5, 7.5 Hz, 1H), 4.34 – 4.30 (m, 2H), 4.18-4.15 (m, 1H), 1.50 (s, 3H), 1.46 (s, 3H), 1.34 (s, 3H), 1.32 (s, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 166.1, 141.9, 135.9, 129.9, 129.1, 126.0, 116.4, 109.6, 108.7, 96.2, 71.1, 70.7, 70.5, 66.1, 63.8, 25.9, 25.9, 24.9, 24.4.



(3S,8S,9S,10R,13R,14S,17R)-10,13-dimethyl-17-((R)-5-methylhexan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl 4-vinylbenzoate (111252-11-0, 8). A round-bottom flask was charged with 4-bromobenzoyl chloride (720 mg, 1.1 eq), cholestanol (1.16 g, 2.98 mmol), Et₃N (452 mg, 1.5 eq), and CH₂Cl₂ (100 mL). The reaction mixture was then filtered, and the filtrate was washed with 1M HCl. The organic layer was dried over anhydrous Na₂SO₄, and concentrated in vacuo, which was further purified by column chromatography to give a pure alkyl 4-bromobenzoate. The corresponding vinyl arene was prepared by using general procedure **B**. ¹H NMR (500 MHz, CDCl₃) δ 8.00 (d, *J* = 8.5 Hz, 2H), 7.45 (d, *J* = 8.5 Hz, 2H), 6.75 (dd, *J* = 17.5, 11.0 Hz, 1H), 5.86 (d, *J* = 17.5 Hz, 1H), 5.42 (d, *J* = 4.0 Hz, 1H), 5.37 (d, *J* = 11.0 Hz, 1H), 4.87-4.83 (m, 1H), 2.47 (d, *J* = 7.5 Hz, 2H), 2.04 – 1.97 (m, 3H), 1.94-1.89 (m, 1H), 1.86 – 1.82 (m, 1H), 1.75 – 1.72 (m, 1H), 1.58 – 1.46 (m, 5H), 1.28 – 1.09 (m, 13H), 1.07-0.97 (m, 7H), 0.95 (d, *J* = 6.5 Hz, 3H), 0.88 (d, *J* = 2.5 Hz, 3H), 0.86 (d, *J* = 2.5 Hz, 3H), 0.69 (s, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 165.7, 141.7, 139.7, 136.1, 129.9, 129.8, 126.0, 122.7, 116.3, 74.5, 56.7, 56.1, 50.1, 42.32 (s), 39.7, 39.5, 38.2, 37.0, 36.6, 36.2, 35.8, 31.9, 31.8, 29.7, 28.2, 28.0, 27.9, 24.3, 23.8, 22.8, 22.6, 21.0, 19.4, 18.7, 11.9.

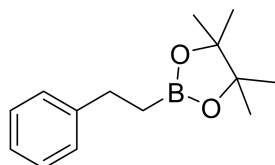
General Procedure C for the preparation of alkylboronates from terminal arylacetylenes and B₂Pin₂: In air, a 25 mL schlenk tube was charged with B₂Pin₂ (152 mg, 3 eq) and Cs₂CO₃ (260 mg, 4 eq). The flask was evacuated and filled with nitrogen for three cycles. CH₃CN (3 mL), arylalkyne (0.2 mmol) and CH₃OH (40 μ L, 5 eq) were added. The reaction was allowed to stir at 70 °C for 4 or 12 hours. Upon completion, the reaction mixture was diluted with ethyl acetate, filtered through a silica gel plug, rinsed with ethyl acetate, and concentrated in vacuo. The crude reaction mixture was purified on silica gel (petroleum ether: ethyl acetate = 50:1) to afford the desired product.

Table S1 Condition screening.


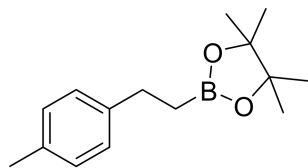
entry	base	additive	solvent	yield (%)
1	Cs ₂ CO ₃ (2.5 eq)	--	dioxane	64
2	K ^t -BuO (2.5 eq)	--	dioxane	11
3	Na ^t -BuO (2.5 eq)	--	dioxane	10
4	Na ₂ CO ₃ (2.5 eq)	--	dioxane	0
5	CsF (2.5 eq)	--	dioxane	59
6	K ₃ PO ₄ (2.5 eq)	--	dioxane	40
7	Cs₂CO₃ (2.5 eq)	MeOH (5 eq)	dioxane	99(89)
8	Cs ₂ CO ₃ (2.5eq)	MeOH (3 eq)	dioxane	89
9	Cs ₂ CO ₃ (2.0 eq)	MeOH (5 eq)	dioxane	82
10	Cs ₂ CO ₃ (2.5 eq)	MeOH (5 eq)	THF	73
11	Cs ₂ CO ₃ (2.5 eq)	MeOH (5 eq)	toluene	72
12	Cs ₂ CO ₃ (2.5 eq)	--	MeOH	61

condition: 1) styrene (0.2 mmol), B₂pin₂ (1.5 eq), solvent (2 mL), 100 °C, 12 h, N₂

General Procedure D for the preparation of alkylboronates from vinyl arenes and B₂Pin₂: In air, a 25 mL schlenk tube was charged with B₂pin₂ (76 mg, 1.5 eq) and Cs₂CO₃ (162 mg, 2.5 eq). The flask was evacuated and filled with nitrogen for three cycles. Dioxane (2 mL), vinyl arene (0.2 mmol) and CH₃OH (40 uL, 5 eq) were added. The reaction was allowed to stir at 100 °C for 12 hours. Upon completion, the reaction mixture was diluted with ethyl acetate, filtered through a silica gel plug, rinsed with ethyl acetate, and concentrated in vacuo. The crude reaction mixture was purified on silica gel (petroleum ether: ethyl acetate = 50:1) to afford the desired product.

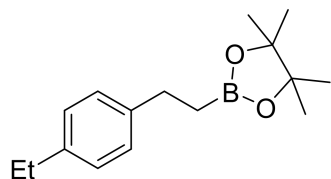


4,4,5,5-tetramethyl-2-phenethyl-1,3,2-dioxaborolane (165904-22-3, 2a).⁹ Colorless oil, ¹H NMR (500 MHz, CDCl₃) δ 7.28 – 7.21 (m, 4H), 7.17-7.14 (m, 1H), 2.75 (t, *J* = 8.0 Hz, 2H), 1.22 (s, 12H), 1.15 (t, *J* = 8.0 Hz, 2H). ¹³C NMR (125 MHz, CDCl₃) δ 144.4, 128.1, 128.0, 125.46 (s), 83.1, 29.9, 24.8.

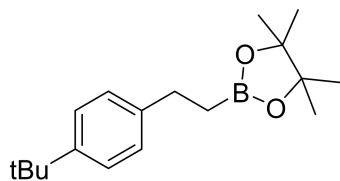


4,4,5,5-tetramethyl-2-(4-methylphenethyl)-1,3,2-dioxaborolane (444094-87-5, 2b).⁹

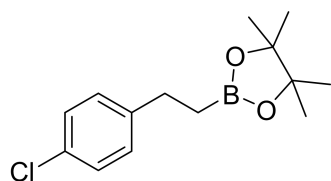
Colorless oil, ¹H NMR (500 MHz, CDCl₃) δ 7.12 (d, *J* = 8.0 Hz, 2H), 7.08 (d, *J* = 8.0 Hz, 2H), 2.72 (t, *J* = 8.0 Hz, 2H), 2.31 (s, 3H), 1.24 (s, 12H), 1.13 (t, *J* = 8.0 Hz, 2H). ¹³C NMR (125 MHz, CDCl₃) δ 141.3, 134.8, 128.8, 127.8, 83.0, 29.5, 24.8, 20.9.



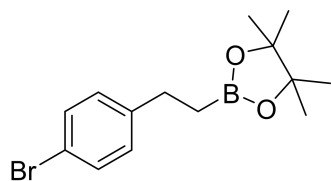
2-(4-ethylphenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2c). Colorless oil, ¹H NMR (500 MHz, CDCl₃) δ 7.15 (d, *J* = 8.0 Hz, 2H), 7.10 (d, *J* = 8.0 Hz, 2H), 2.72 (t, *J* = 8.0 Hz, 2H), 2.62 (q, *J* = 7.5 Hz, 2H), 1.23 (s, 12H), 1.22 (t, *J* = 7.5 Hz, 2H), 1.14 (t, *J* = 8.0 Hz, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 141.6, 141.3, 127.9, 127.6, 83.0, 29.5, 28.4, 24.8, 15.7. HRMS (EI, *m/z*) calcd for [C₁₆H₂₅BO₂]: 260.1948; found: 260.1950.



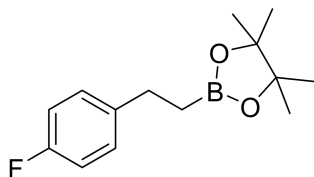
2-(4-(tert-butyl)phenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1073355-22-2, 2d).¹⁰ Colorless oil, ¹H NMR (500 MHz, CDCl₃) δ 7.30 (d, *J* = 8.0 Hz, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 2.73 (t, *J* = 8.0 Hz, 2H), 1.31 (s, 9H), 1.23 (s, 12H), 1.15 (t, *J* = 8.0 Hz, 2H). ¹³C NMR (125 MHz, CDCl₃) δ 148.2, 141.3, 127.6, 125.0, 83.0, 34.3, 31.4, 29.3, 24.8.



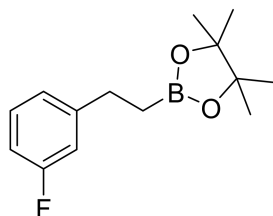
2-(4-chlorophenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (444094-88-6, 2e).⁹ Light yellow oil, ¹H NMR (500 MHz, CDCl₃) δ 7.21 (d, *J* = 8.5 Hz, 2H), 7.13 (d, *J* = 8.5 Hz, 2H), 2.71 (t, *J* = 8.0 Hz, 2H), 1.21 (s, 12H), 1.11 (t, *J* = 8.0 Hz, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 142.8, 131.1, 129.3, 128.2, 83.2, 29.3, 24.8.



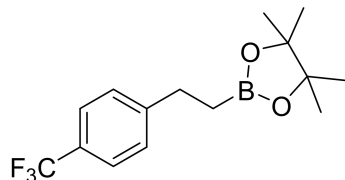
2-(4-bromophenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (748801-42-5, 2f).⁹ Light yellow oil, ¹H NMR (500 MHz, CDCl₃) δ 7.36 (d, *J* = 8.5 Hz, 2H), 7.08 (d, *J* = 8.5 Hz, 2H), 2.69 (t, *J* = 8.0 Hz, 2H), 1.21 (s, 12H), 1.11 (t, *J* = 8.0 Hz, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 143.3, 131.1, 129.9, 119.1, 83.2, 29.4, 24.8.



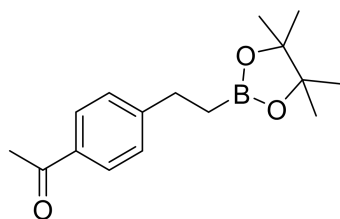
2-(4-fluorophenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1065498-70-5, 2g).⁹ Light yellow oil, ¹H NMR (500 MHz, CDCl₃, ppm) 7.17-7.14 (m, 2H), 6.95-6.91 (m, 2H), 2.71 (t, *J* = 8.0 Hz, 2H), 1.21 (s, 12H), 1.11 (t, *J* = 8.0 Hz). ¹³C NMR (125 MHz, CDCl₃, ppm) 161.1 (d, *J* = 241.3 Hz), 139.9 (d, *J* = 2.5 Hz), 129.3 (d, *J* = 7.5 Hz), 114.8 (d, *J* = 20.0 Hz), 83.1, 29.1, 24.8.



2-(3-fluorophenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1600527-27-2, 2h).⁹ Colorless oil, ¹H NMR (500 MHz, CDCl₃, ppm) 7.29-7.22(m, 1H), 6.99-6.97(m, 1H), 6.94-6.91(m, 1H), 6.86-6.82(m, 1H), 2.74 (t, *J* = 8.0 Hz, 2H), 1.22 (s, 12H), 1.13 (t, *J* = 8.0 Hz). ¹³C NMR (125 MHz, CDCl₃, ppm) 162.8 (d, *J* = 243.7 Hz), 147.0 (d, *J* = 7.5 Hz), 129.5 (d, *J* = 8.7 Hz), 123.6 (d, *J* = 3.7 Hz), 114.8 (d, *J* = 20.0 Hz), 83.2, 29.7 (d, *J* = 2.5 Hz), 24.8.

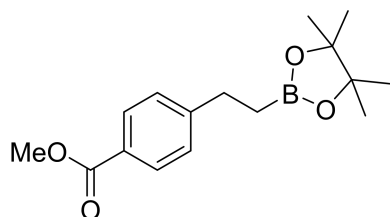


4,4,5,5-tetramethyl-2-(4-(trifluoromethyl)phenethyl)-1,3,2-dioxaborolane (1360649-56-4, 2i).¹¹ Light yellow oil, ¹H NMR (500 MHz, CDCl₃) δ 7.51 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 2.80 (t, *J* = 8.0 Hz, 2H), 1.21 (s, 12H), 1.15 (t, *J* = 8.0 Hz, 2H). ¹³C NMR (125 MHz, CDCl₃) δ 148.5, 128.3, 125.1 (q, *J* = 3.8 Hz), 83.2, 29.8, 24.8, 12.6.

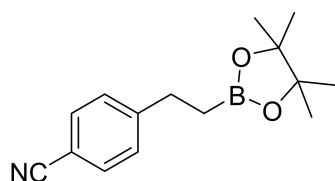


1-(4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)phenyl)ethan-1-one (2j), Colorless oil, ¹H NMR (500 MHz, CDCl₃) δ 7.86 (d, *J* = 8.5 Hz, 2H), 7.30 (d, *J* = 8.5 Hz, 2H), 2.79 (t, *J* = 8.0 Hz, 2H), 2.57 (s, 3H), 1.21 (s, 12H), 1.15 (t, *J* = 8.0 Hz, 2H). ¹³C NMR (125

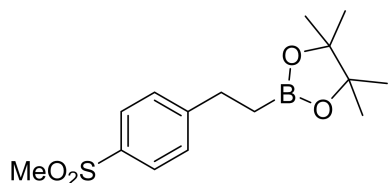
MHz, CDCl₃) δ 198.0, 150.3, 134.8, 128.4, 128.2, 83.2, 30.0, 26.5, 24.8. HRMS (EI, m/z) calcd for [C₁₆H₂₃BO₃ + Na⁺]: 297.1638; found: 297.1644.



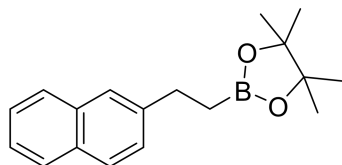
Methyl 4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)benzoate (1375536-90-5, 2k).¹⁰ Colorless oil, ¹H NMR (500 MHz, CDCl₃) δ 7.92 (d, *J* = 8.0 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 3.88 (s, 3H), 2.79 (t, *J* = 8.0 Hz, 2H), 1.20 (s, 12H), 1.14 (t, *J* = 8.0 Hz, 2H). ¹³C NMR (125 MHz, CDCl₃) δ 167.2, 149.9, 129.5, 128.0, 127.5, 83.2, 51.9, 30.0, 24.7.



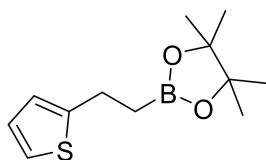
4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)benzonitrile (1375536-88-1, 2l).¹⁰ White solid, ¹H NMR (500 MHz, CDCl₃, ppm) δ 7.54 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 2.79 (t, *J* = 8.0 Hz, 2H), 1.20 (s, 12H), 1.13 (t, *J* = 8.0 Hz, 2H). ¹³C NMR (125 MHz, CDCl₃, ppm) δ 150.0, 132.0, 128.8, 119.2, 109.3, 83.3, 30.1, 24.8



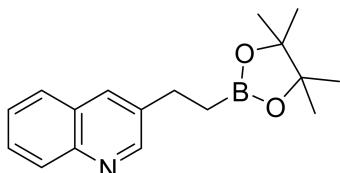
4,4,5,5-tetramethyl-2-(4-(methylsulfonyl)phenethyl)-1,3,2-dioxaborolane (2m). Light yellow oil, ¹H NMR (500 MHz, CDCl₃) δ 7.81 (d, *J* = 8.0 Hz, 2H), 7.39 (d, *J* = 8.0 Hz, 2H), 3.01 (s, 3H), 2.81 (t, *J* = 8.0 Hz, 2H), 1.20 (s, 12H), 1.13 (t, *J* = 8.0 Hz, 2H). ¹³C NMR (125 MHz, CDCl₃) δ 151.0, 137.7, 128.9, 127.28 (s), 83.3, 44.5, 29.9, 24.7. HRMS (ESI, m/z) calcd for [C₁₅H₂₄BO₄S + H⁺]: 311.1488; found: 311.1488.



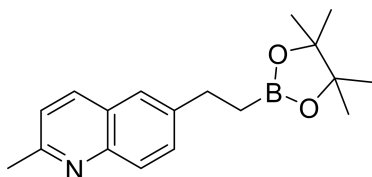
4,4,5,5-tetramethyl-2-(2-(naphthalen-2-yl)ethyl)-1,3,2-dioxaborolane (807611-10-5, 2n).⁹ Colorless oil, ¹H NMR (500 MHz, CDCl₃) δ 7.81 – 7.76 (m, 3H), 7.67 (s, 1H), 7.46 – 7.38 (m, 3H), 2.94 (t, *J* = 8.0 Hz, 2H), 1.26 (t, *J* = 8.0 Hz, 2H), 1.24 (s, 12H). ¹³C NMR (125 MHz, CDCl₃) δ 141.9, 133.6, 131.9, 127.6, 127.5, 127.4, 127.2, 125.7, 125.6, 124.9, 83.1, 30.1, 24.8.



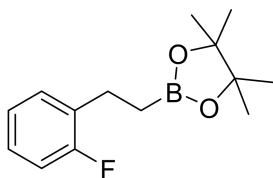
4,4,5,5-tetramethyl-2-(2-(thiophen-2-yl)ethyl)-1,3,2-dioxaborolane (1361022-77-6, 2o).¹² Light yellow, ¹H NMR (500 MHz, CDCl₃) δ 7.08 (dd, *J* = 5.5, 1.5 Hz, 1H), 6.88 (dd, *J* = 5.5, 3.5 Hz, 1H), 6.80 – 6.79 (m, 1H), 2.96 (t, *J* = 8.0 Hz, 2H), 1.23-1.22 (m, 15H). ¹³C NMR (125 MHz, CDCl₃) δ 147.7 126.5, 123.4, 122.6, 83.2, 24.8, 24.3.



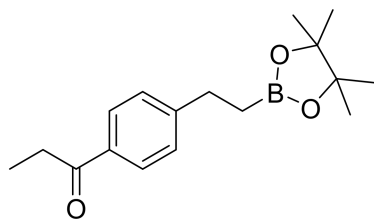
3-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)quinolone (2p). Yellow solid, ¹H NMR (500 MHz, CDCl₃) δ 8.81 (d, *J* = 2.0 Hz, 1H), 8.06 (d, *J* = 8.0 Hz, 1H), 7.94 (d, *J* = 1.5 Hz, 1H), 7.74 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.64-7.61 (m, 1H), 7.51-7.47 (m, 1H), 2.93 (t, *J* = 8.0 Hz, 2H), 1.24 (t, *J* = 8.0 Hz, 2H), 1.20 (s, 12H). ¹³C NMR (125 MHz, CDCl₃) δ 152.1, 146.6, 136.9, 133.6, 129.0, 128.4, 128.2, 127.3, 126.4, 83.3, 27.3, 24.8. HRMS (EI, *m/z*) calcd for [C₁₇H₂₂BNO₂ + H⁺]: 284.1822; found: 289.1865.



2-methyl-6-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)quinolone (2q). White solid, ¹H NMR (500 MHz, CDCl₃, ppm) δ 7.95 (d, *J* = 8.5 Hz, 1H), 7.90 (d, *J* = 9.0 Hz, 1H), 7.56-7.55 (m, 2H), 7.22 (d, *J* = 8.5 Hz, 1H), 2.91 (t, *J* = 8.0 Hz, 2H), 2.71 (s, 3H), 1.22 (t, *J* = 8.0 Hz, 2H), 1.19(s, 12H). ¹³C NMR (125 MHz, CDCl₃, ppm) δ 157.9, 146.5, 141.8, 135.7, 130.8, 128.2, 126.4, 125.2, 121.8, 83.1, 29.8, 25.2, 24.8. HRMS (EI, *m/z*) calcd for [C₁₈H₂₄BNO₂ + H⁺]: 298.1978; found: 298.1978.

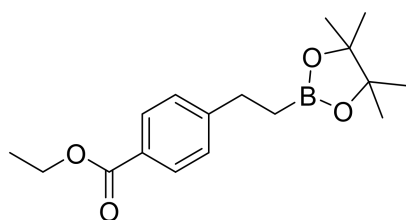


2-(2-(2-fluorophenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1700308-87-7, 2r).¹³ Colorless oil, ¹H NMR (500 MHz, CDCl₃, ppm) 7.24-7.21(m, 1H), 7.15-7.11(m, 1H), 7.04-7.01(m, 1H), 6.99-6.95(m, 1H), 2.77 (t, *J* = 8.0 Hz, 2H), 1.22 (s, 12H), 1.14 (t, *J* = 8.0 Hz). ¹³C NMR (125 MHz, CDCl₃, ppm) 161.0 (d, *J* = 243.7 Hz), 131.1 (d, *J* = 16.3 Hz), 130.0 (d, *J* = 5.0 Hz), 123.7 (d, *J* = 3.7 Hz), 115.0(d, *J* = 21.3 Hz), 83.1, 24.8, 23.1 (d, *J* = 1.3 Hz).

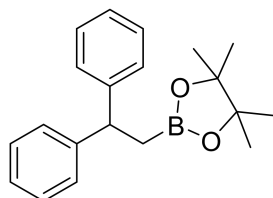


1-(4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)phenyl)propan-1-one (2s).

Colorless oil, $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.86 (d, $J = 8.5$ Hz, 2H), 7.28 (d, $J = 8.5$ Hz, 2H), 2.97 (q, $J = 7.3$ Hz, 2H), 2.78 (t, $J = 8.0$ Hz, 2H), 1.21 (s, 12H), 1.20 (t, $J = 7.5$ Hz, 2H), 1.14 (t, $J = 8.0$ Hz, 2H). $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 200.6, 150.0, 134.52 (s), 128.2, 128.1, 83.2, 31.6, 30.0, 24.8, 8.3. HRMS (EI, m/z) calcd for $[\text{C}_{17}\text{H}_{25}\text{BO}_3 + \text{H}^+]$: 289.1975; found: 289.1975.

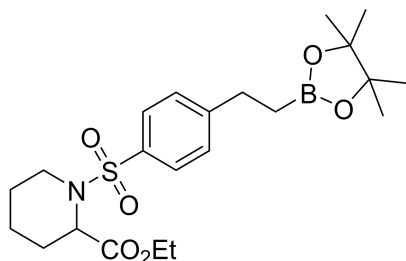


ethyl 4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)benzoate (2t). Colorless oil, $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.93 (d, $J = 8.0$ Hz, 2H), 7.27 (d, $J = 8.0$ Hz, 2H), 7.27 (d, $J = 7.8$ Hz, 2H), 4.35 (q, $J = 7.0$ Hz, 2H), 2.79 (t, $J = 8.0$ Hz, 2H), 1.37 (t, $J = 7.1$ Hz, 3H), 1.37 (t, $J = 7.0$ Hz, 3H), 1.21 (s, 12H), 1.14 (t, $J = 8.0$ Hz, 2H). $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 166.8, 149.8, 129.5, 127.9, 127.8, 83.2, 60.7, 30.0, 24.8, 14.3. HRMS (EI, m/z) calcd for $[\text{C}_{17}\text{H}_{25}\text{BO}_4 + \text{H}^+]$: 327.1744; found: 327.1774.



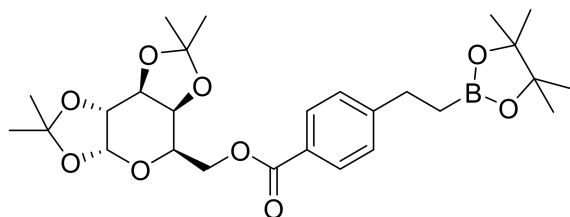
2-(2,2-diphenylethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1609554-12-2, 2u).¹⁴

Colorless oil, $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.28-7.23 (m, 8H), 7.15-7.12 (m, 2H), 4.28 (t, $J = 8.5$ Hz, 1H), 1.60 (d, $J = 8.5$ Hz, 2H), 1.05 (s, 12H). $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 146.6, 128.2, 127.6, 125.9, 83.1, 46.5, 24.6.

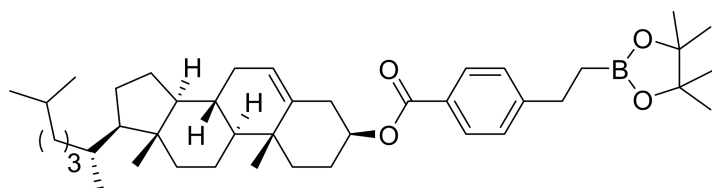


Ethyl 1-((4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)phenyl)sulfonyl)piperidine-2-carboxylate (5). Colorless oil, $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.67 (d, $J = 8.0$ Hz, 2H), 7.30 (d, $J = 8.0$ Hz, 2H), 4.70 (d, $J = 5.0$ Hz, 1H), 4.06 – 3.99 (m, 1H), 3.94-3.88 (m, 1H), 3.75– 3.72 (m, 1H), 3.24-3.18 (m, 1H), 2.78 (t, $J = 8.0$ Hz, 2H), 2.10 (dd, $J = 13.5, 1.5$ Hz,

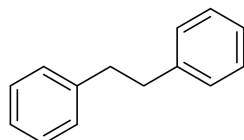
1H), 1.75 – 1.61 (m, 3H), 1.51 – 1.41 (m, 1H), 1.33 – 1.24 (m, 1H), 1.21 (s, 12H), 1.14 – 1.11 (m, 5H). ¹³C NMR (125 MHz, CDCl₃) δ 170.7, 149.4, 137.2, 128.4, 127.3, 83.3, 61.0, 55.0, 42.5, 29.8, 27.8, 24.8, 24.7, 20.0, 14.0. HRMS (ESI, m/z) calcd for [C₂₂H₃₄BNO₆S + H⁺]: 452.2278; found: 452.2276.



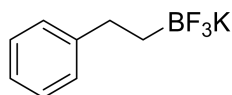
((3aR,5R,5aS,8aS,8bR)-2,2,7,7-tetramethyltetrahydro-5H-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-5-yl)methyl 4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)benzoate (7). Colorless oil, ¹H NMR (500 MHz, CDCl₃) δ 7.94 (d, *J* = 8.5 Hz, 2H), 7.26 (d, *J* = 8.5 Hz, 2H), 5.55 (d, *J* = 5.0 Hz, 1H), 4.64 (dd, *J* = 8.0, 2.5 Hz, 1H), 4.51 (dd, *J* = 11.5, 5.0 Hz, 1H), 4.39 (dd, *J* = 11.5, 7.5 Hz, 1H), 4.34 – 4.31 (m, 2H), 4.18-4.15 (m, 1H), 2.75 (t, *J* = 8.0 Hz, 2H), 1.50 (s, 3H), 1.47 (s, 3H), 1.35 (s, 3H), 1.33 (s, 3H), 1.21 (s, 12H), 1.14 (t, *J* = 8.0 Hz, 2H). ¹³C NMR (125 MHz, CDCl₃) δ 166.5, 150.0, 129.7, 128.0, 127.4, 109.6, 108.8, 96.3, 83.2, 71.1, 70.7, 70.5, 66.1, 63.6, 30.0, 26.0, 25.9, 25.0, 24.8, 24.5. HRMS (ESI, m/z) calcd for [C₂₇H₃₉BO₉ + H⁺]: 519.2765; found: 519.2761.



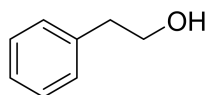
(3S,8S,9S,10R,13R,14S,17R)-10,13-dimethyl-17-((R)-4-methylpentan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl 4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)benzoate (9). White solid, ¹H NMR (500 MHz, CDCl₃) δ 7.93 (d, *J* = 8.5 Hz, 2H), 7.26 (d, *J* = 8.5 Hz, 2H), 5.41 (d, *J* = 3.5 Hz, 1H), 4.86-4.81 (m, 1H), 2.79 (m, *J* = 8.0 Hz, 2H), 2.45 (d, *J* = 7.5 Hz, 2H), 2.03-1.96 (m, 3H), 1.92 – 1.82 (m, 2H), 1.80 – 1.70 (m, 1H), 1.64-1.24 (m, 12H), 1.21 (s, 12H), 1.16-1.09 (m, 7H), 1.06 (s, 3H), 1.04-0.97 (m, 4H), 0.92 (d, *J* = 7.0 Hz, 3H), 0.87 (d, *J* = 2.0 Hz, 3H), 0.86 (d, *J* = 2.0 Hz, 3H), 0.69 (s, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 166.1, 149.7, 139.7, 129.5, 128.2, 127.9, 122.6, 83.2, 74.3, 56.7, 56.1, 50.0, 42.3, 39.7, 39.5, 38.2, 37.0, 36.6, 36.2, 35.8, 31.9, 31.8, 30.0, 28.2, 28.0, 27.9, 24.8, 24.3, 23.8, 22.8, 22.5, 21.0, 19.4, 18.7, 11.9. HRMS (ESI, m/z) calcd for [C₄₂H₆₅BO₄ + Na⁺]: 667.4874; found: 667.4870.



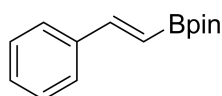
1,2-diphenylethane(103-29-7, 10).¹⁵ White solid, ¹H NMR (500 MHz, CDCl₃) δ 7.32-7.28 (m, 4H), 7.23-7.20 (m, 6H), 2.95 (s, 4H). ¹³C NMR (125 MHz, CDCl₃) δ 141.8, 128.4, 128.3, 125.9, 37.9.



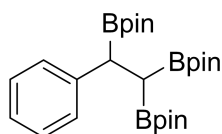
trifluoro(phenethyl)-14-borane, potassium salt (329976-74-1,11).¹⁶ White solid, ¹H NMR (500 MHz, DMSO) δ 7.20 – 7.12 (m, 4H), 7.06-7.03 (m, 1H), 2.42 (s, 2H), 0.30 (s, 2H). ¹³C NMR (125 MHz, DMSO) δ 148.1, 127.9, 127.7, 124.4, 32.2. ¹⁹F NMR (471 MHz, DMSO) δ -137.8.



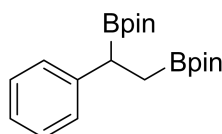
2-phenylethan-1-ol (60-12-8, 12).¹⁷ Colorless oil, ¹H NMR (500 MHz, CDCl₃) δ 7.34 – 7.31 (m, 2H), 7.26 – 7.23 (m, 3H), 3.84 (t, *J* = 6.5 Hz, 2H), 2.87 (t, *J* = 6.5 Hz, 2H). ¹³C NMR (125 MHz, CDCl₃) δ 138.5, 129.0, 128.5, 126.4, 63.6, 39.1.



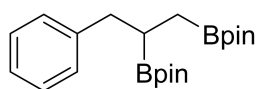
(E)-4,4,5,5-tetramethyl-2-styryl-1,3,2-dioxaborolane (78782-27-1, 13).¹⁸ Colorless oil, ¹H NMR (500 MHz, CDCl₃) δ 7.49 (d, *J* = 7.0 Hz, 2H), 7.40 (d, *J* = 18.5 Hz, 1H), 7.35 – 7.27 (m, 3H), 6.17 (d, *J* = 18.5 Hz, 1H), 1.32 (s, 12H). ¹³C NMR (125 MHz, CDCl₃) δ 149.5, 137.4, 128.9, 128.5, 127.0, 83.3, 24.8.



2,2'-((phenyl(4,4,5,5-tetramethyl-1,3-dioxolan-2-yl)boranyl)methylene)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (1638158-49-2, 14).¹⁹ Light yellow oil, ¹H NMR (500 MHz, CDCl₃) δ 7.21 – 7.14 (m, 4H), 7.04-7.01 (m, 1H), 2.66 (d, *J* = 13.0 Hz, 1H), 1.44 (d, *J* = 13.0 Hz, 1H), 1.24 (s, 6H), 1.23 (s, 6H), 1.15 (s, 6H), 1.13 (s, 6H), 0.94 (s, 6H), 0.92 (s, 6H). ¹³C NMR (125 MHz, CDCl₃) δ 145.3, 128.5, 127.8, 124.6, 83.0, 83.0, 82.6, 24.8, 24.8, 24.6, 24.4, 24.3, 24.2.



2,2'-(1-phenylethane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (189885-64-1, 15).²⁰ white solid, ¹H NMR (500 MHz, CDCl₃) δ 7.22 (d, *J* = 4.5 Hz, 4H), 7.12 – 7.07 (m, 1H), 2.52 (dd, *J* = 11.0, 6.0 Hz, 1H), 1.38 (dd, *J* = 16.0, 11.0 Hz, 1H), 1.20 (s, 12H), 1.19 (s, 6H), 1.17 (s, 6H), 1.11 (dd, *J* = 16.0, 5.5 Hz, 1H). ¹³C NMR (125 MHz, CDCl₃) δ 145.3, 128.1, 127.9, 124.9, 83.2, 83.0, 24.9, 24.7, 24.6, 24.4.



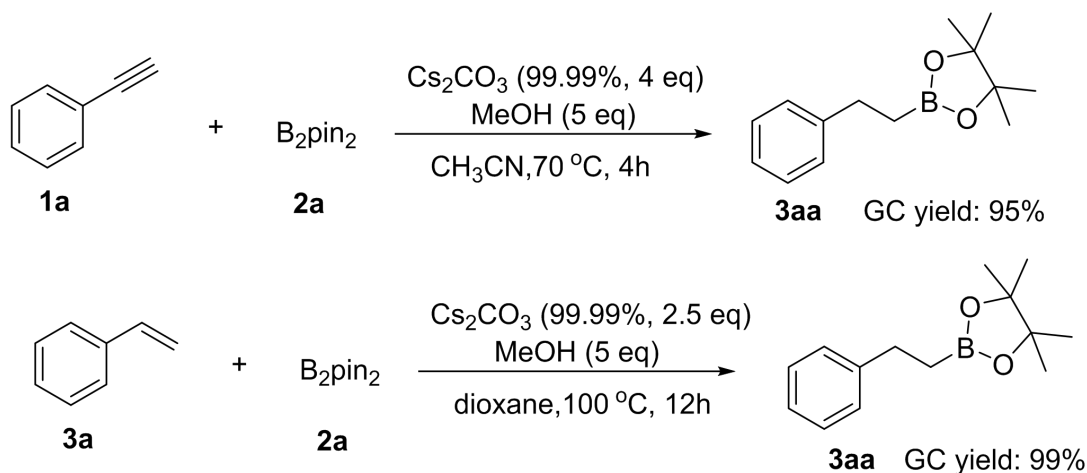
2,2'-(3-phenylpropane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (1172611-59-4, 19).²¹ Colorless oil. ¹H NMR (500 MHz, CDCl₃) δ 7.24-7.18 (m, 4H),

7.14-7.11 (m, 1H), 2.79 (dd, $J = 13.0, 7.0$ Hz, 1H), 2.60 (dd, $J = 13.5, 8.5$ Hz, 1H), 1.49 (s, 1H), 1.22 (s, 12H), 1.19 (s, 6H), 1.16 (s, 6H), 0.82 (d, $J = 7.5$ Hz, 2H). ^{13}C NMR (125 MHz, CDCl_3) δ 142.3, 129.1, 127.9, 125.4, 82.9, 82.8, 39.5, 24.9, 24.8, 24.8, 24.7.

Trace Transition Metal Analysis/Exclusion

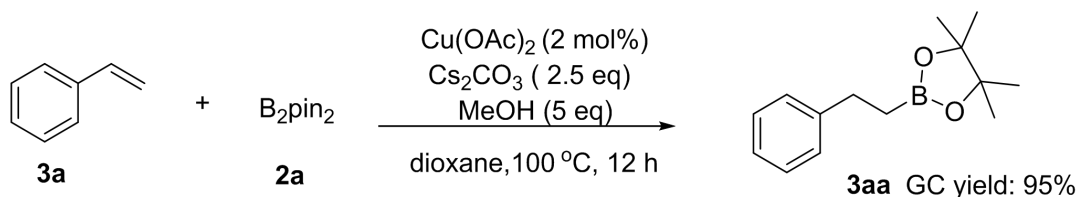
In order to rule out the possibility of the trace amount of transition metal in the reaction mixture, three different strategies have been performed:

1) 99.99% purity of Cs_2CO_3 was used in the two standard conditions and the results were listed below:



As we can see, with high purity of Cs_2CO_3 , desired product **3aa** were obtained in very high GC yields, which are consistent to the results listed in the manuscript with regular Cs_2CO_3 . So we have reasons to believe that this IS a transition-metal FREE reaction.

2) On the other hand, since copper salt was widely used as a catalyst in the borylation of unsaturated compounds, 2 mol% of $\text{Cu}(\text{OAc})_2$ was added as a catalyst in the standard condition of styrene, the desired product **3aa** was obtained in 95% in GC, which is consistent to the result without copper catalyst in our manuscript, therefore once again it suggested that the transformation in our manuscript is a transition-metal free reaction.



3) ICP-MS was used to analyze trace metal in B_2pin_2 and Cs_2CO_3 and the results were listed below:

B_2pin_2 (152.4 mg, 0.6 mmol) include 27Al (1.8 ug), 56Fe(8.0 ug), 60Ni(0.2 ug), 63Cu(0.35 ug), Zn(1.4 ug), 195Pt(0.0 ug), 208Pb(0.06 ug);

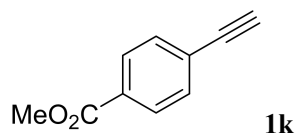
Cs_2CO_3 (259.2 mg, 0.8 mmol) include 27Al (0.7 ug), 56Fe(0.9 ug), 60Ni(0.05 ug), 63Cu(0.12 ug), Zn(0.5 ug), 195Pt(0.0 ug), 208Pb(0.04 ug)

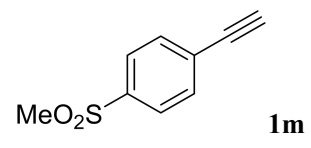
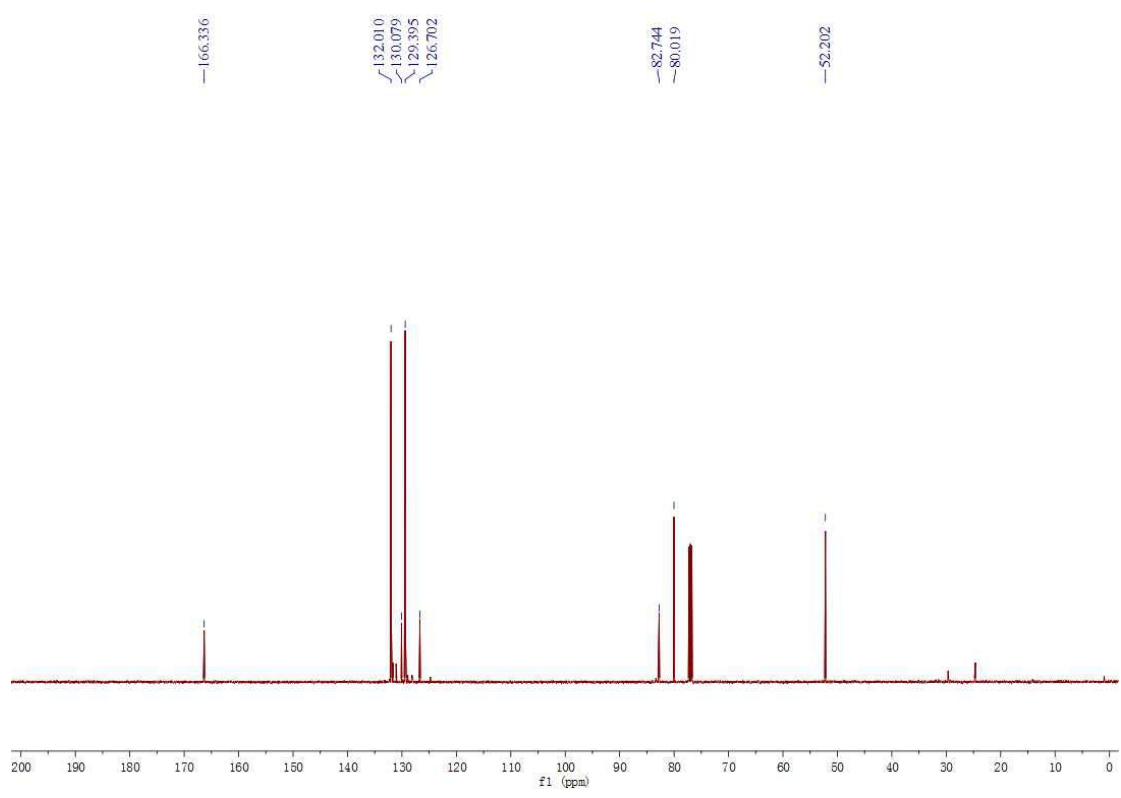
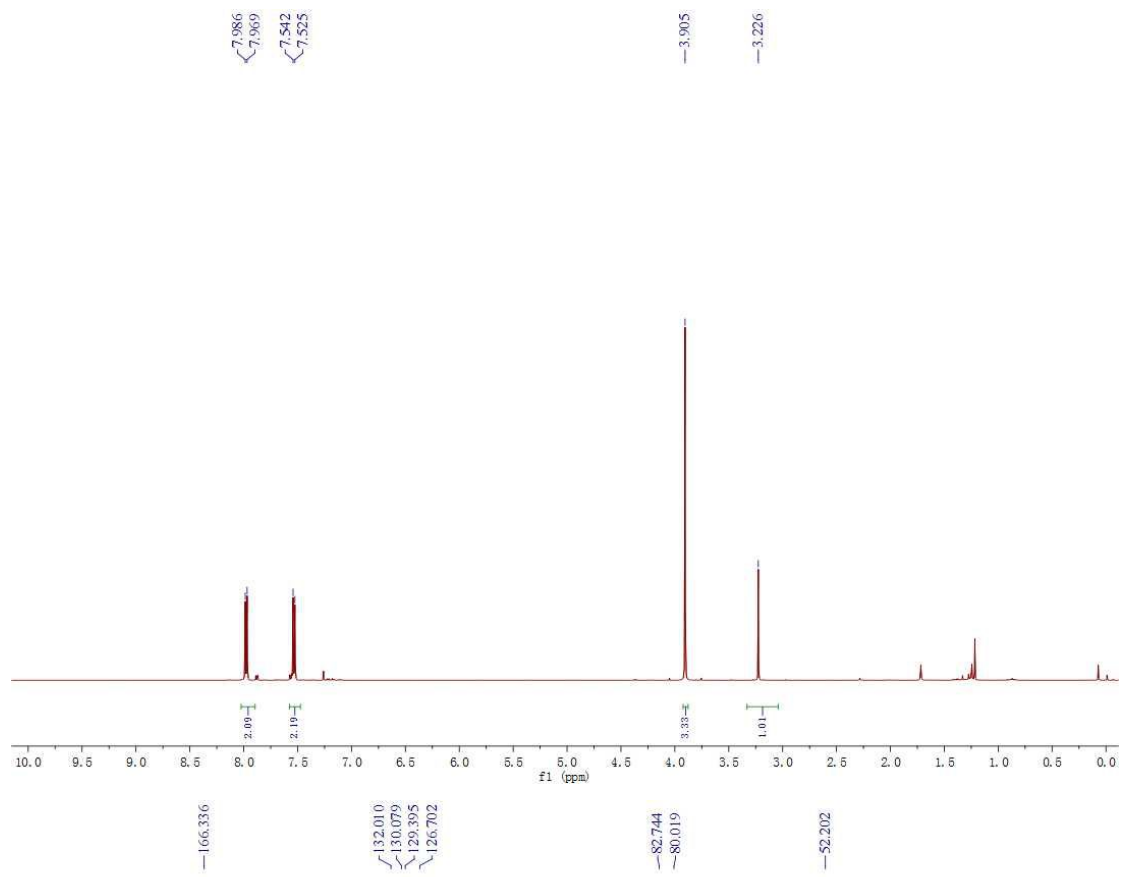
From all the above three strategies, it indicates that this is a transition metal-free methods and base/MeOH combination play key role for the success of the reaction.

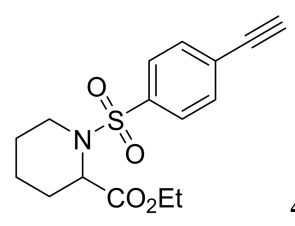
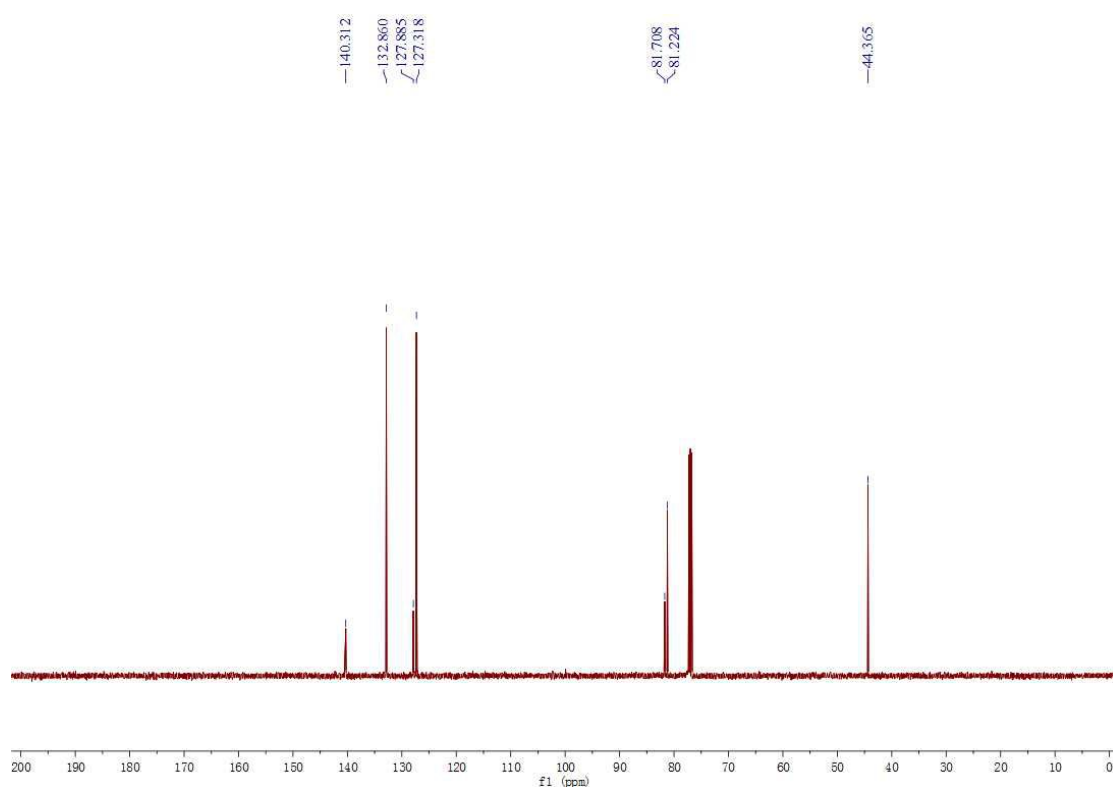
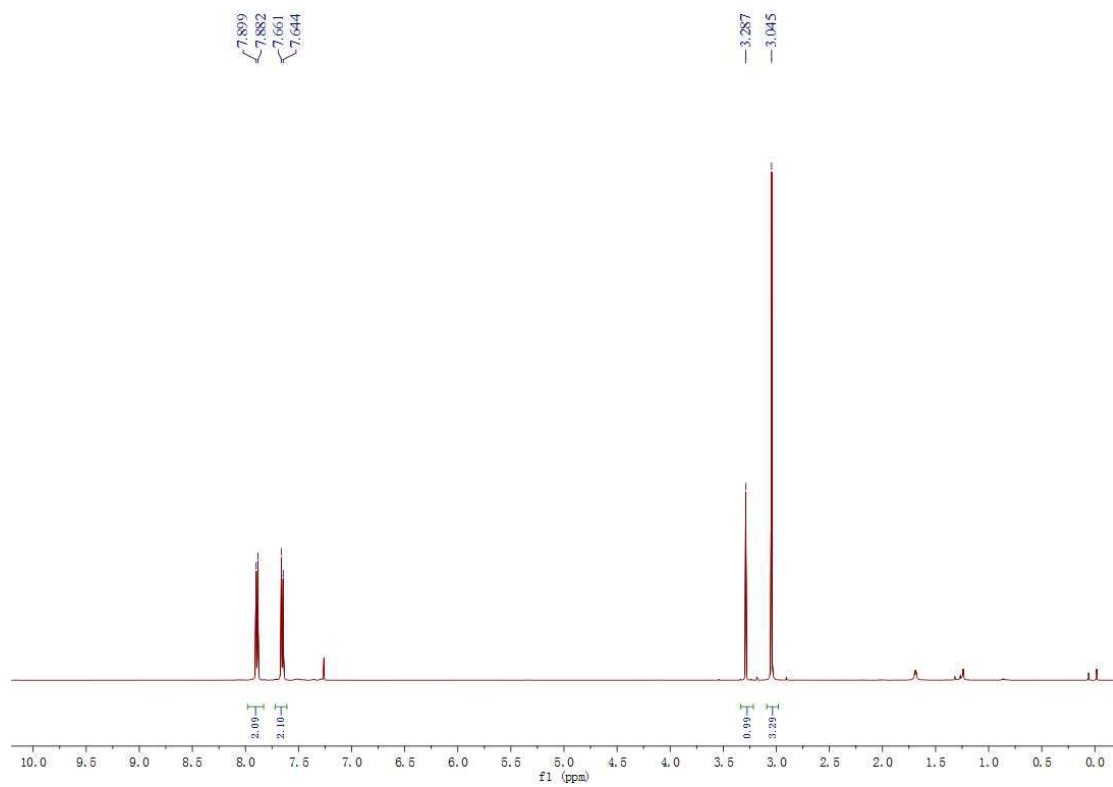
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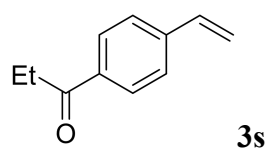
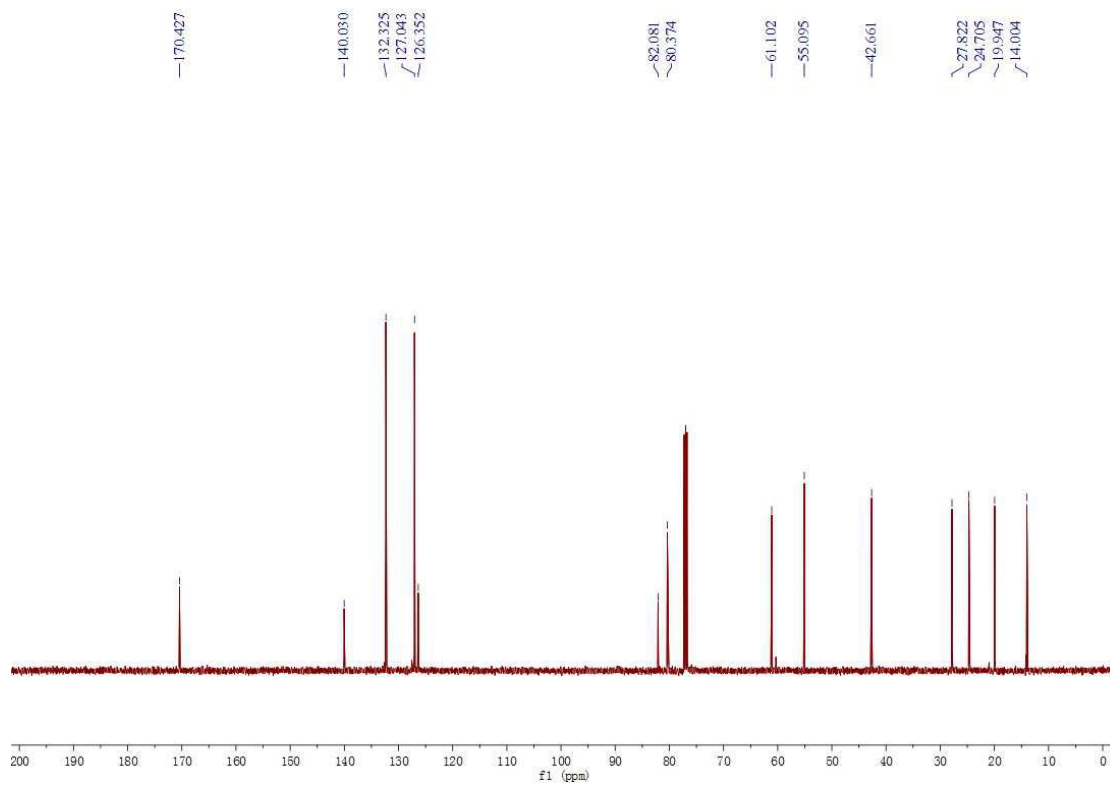
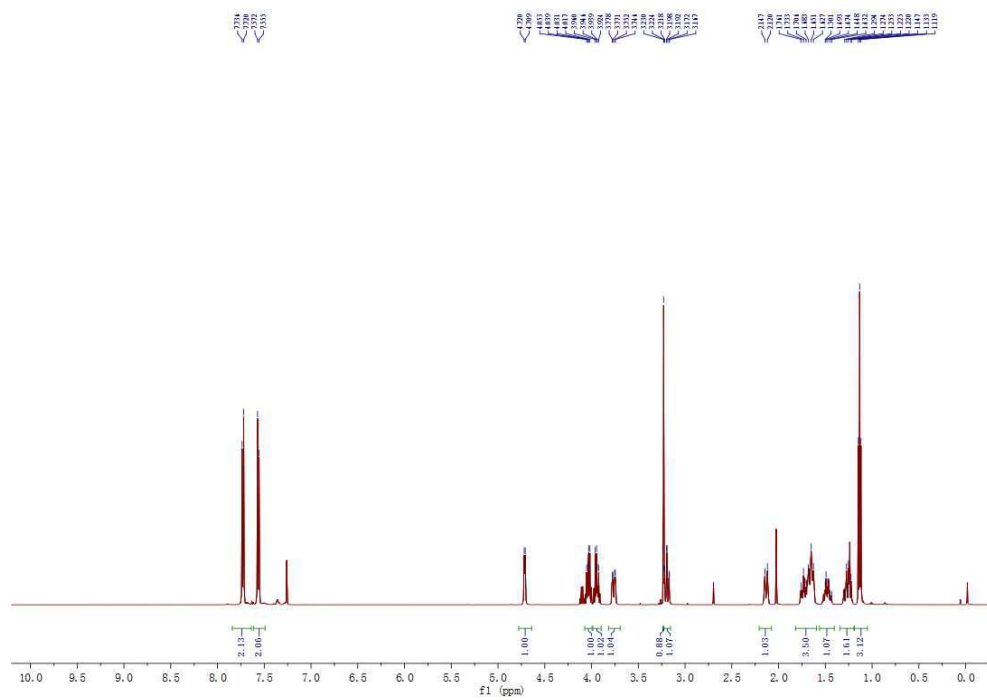
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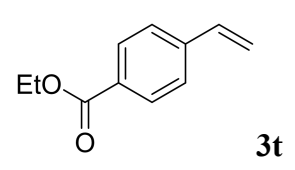
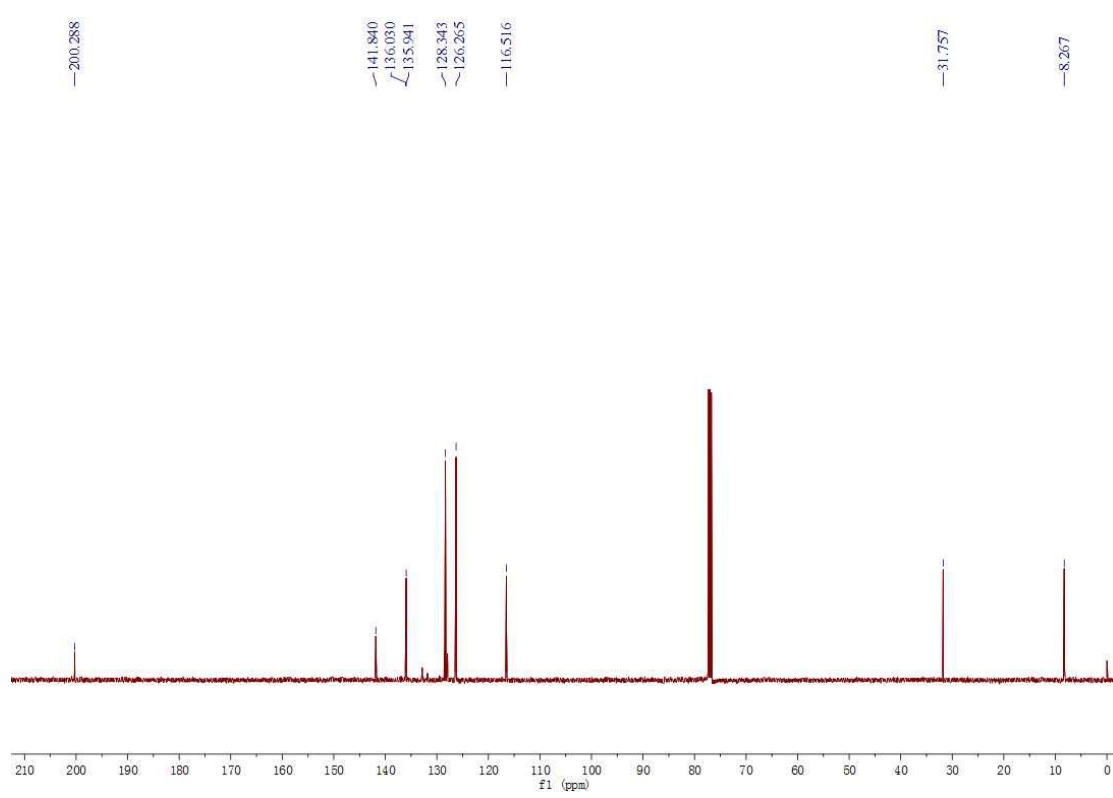
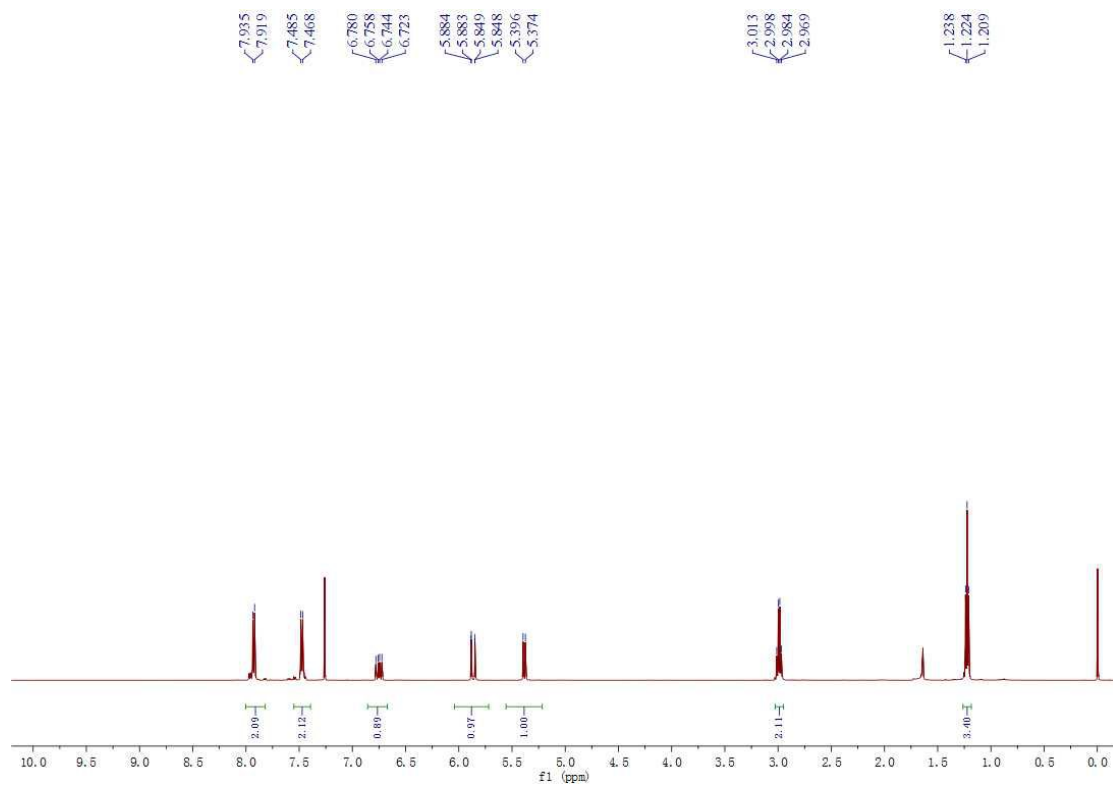


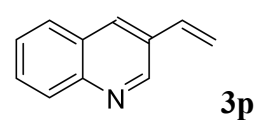
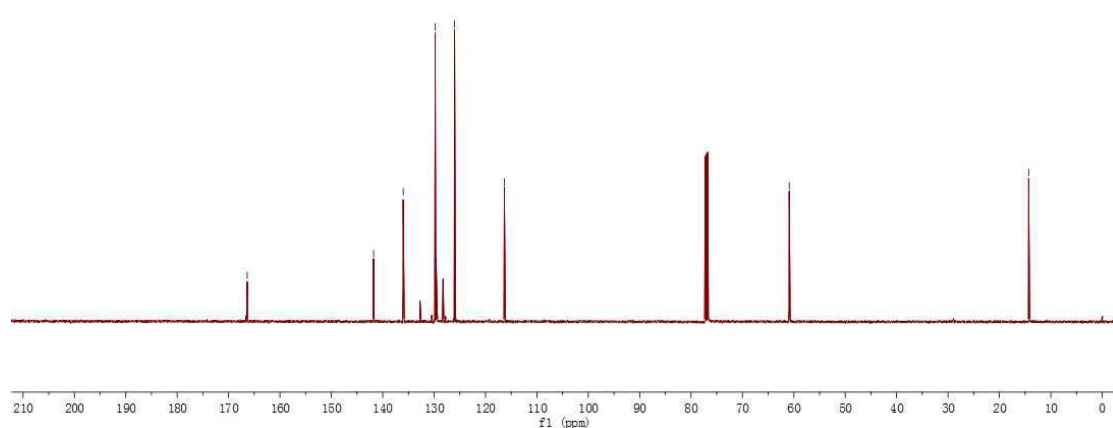
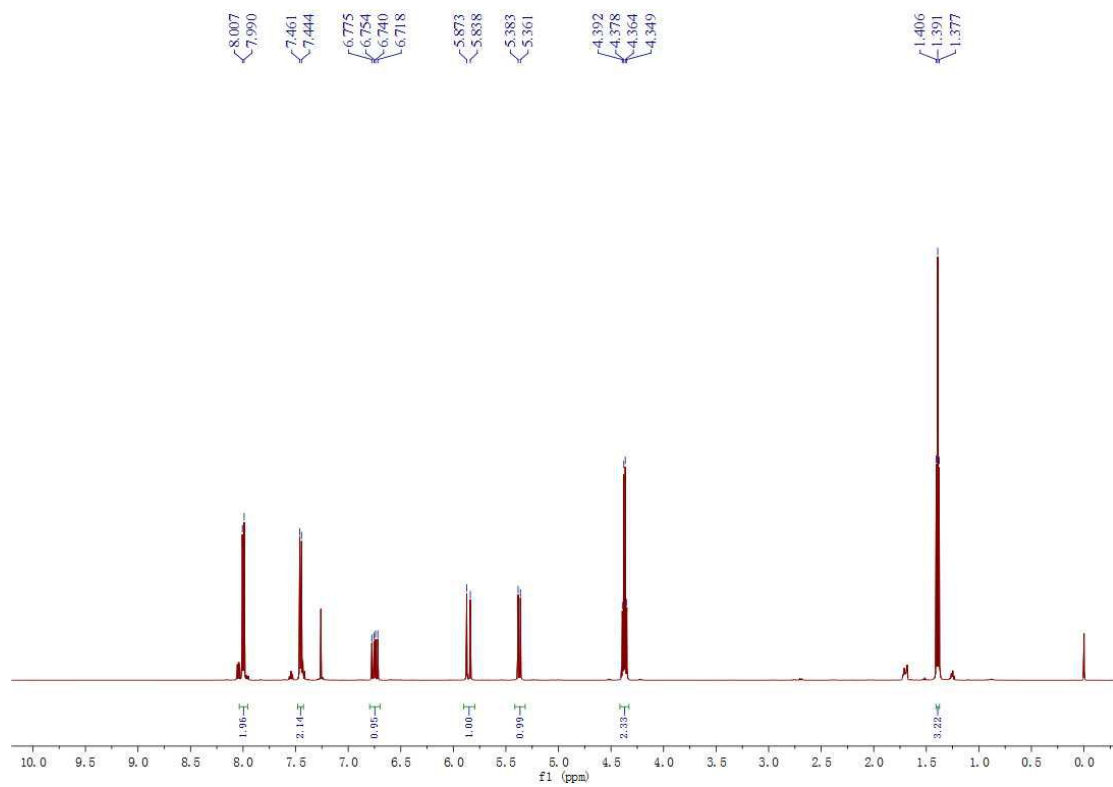


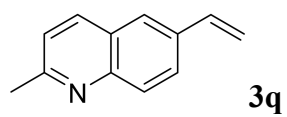
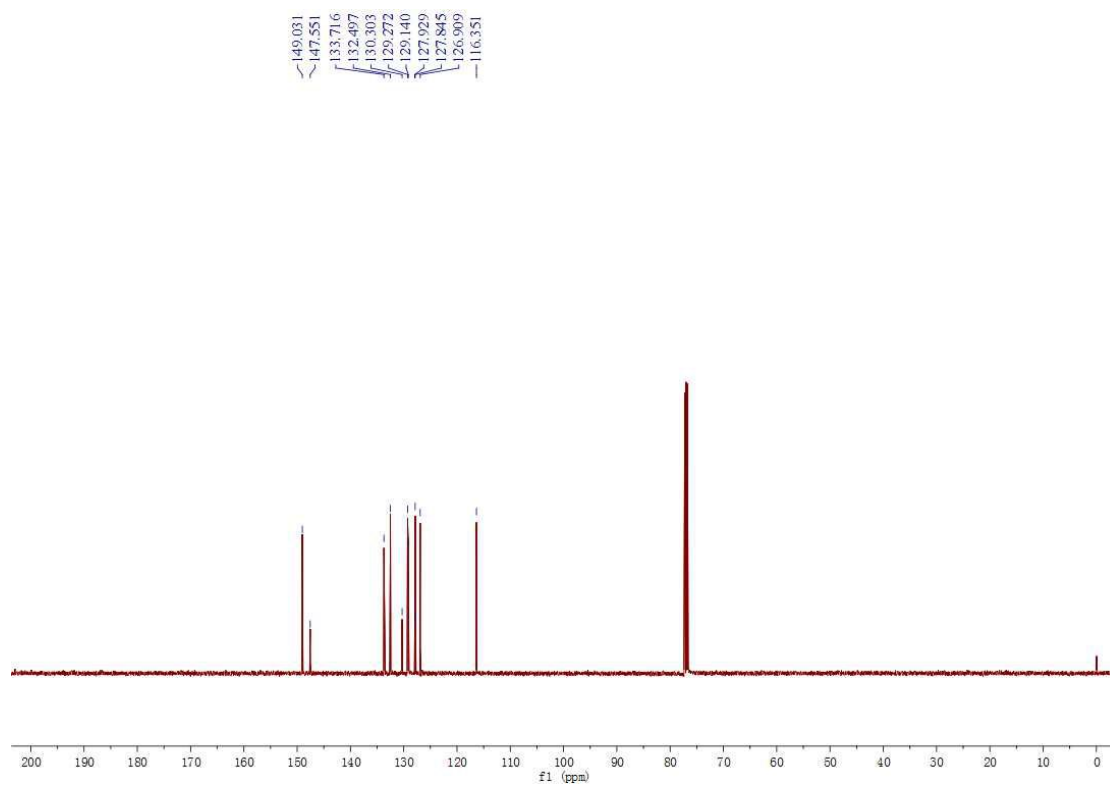
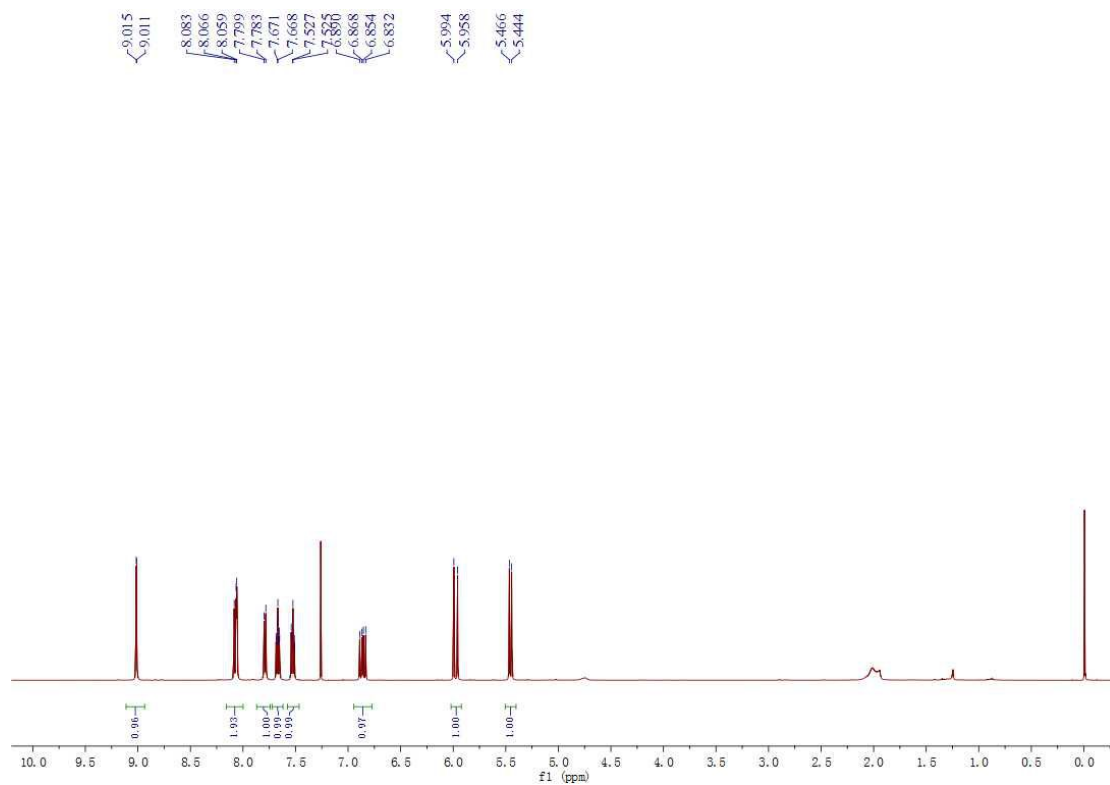


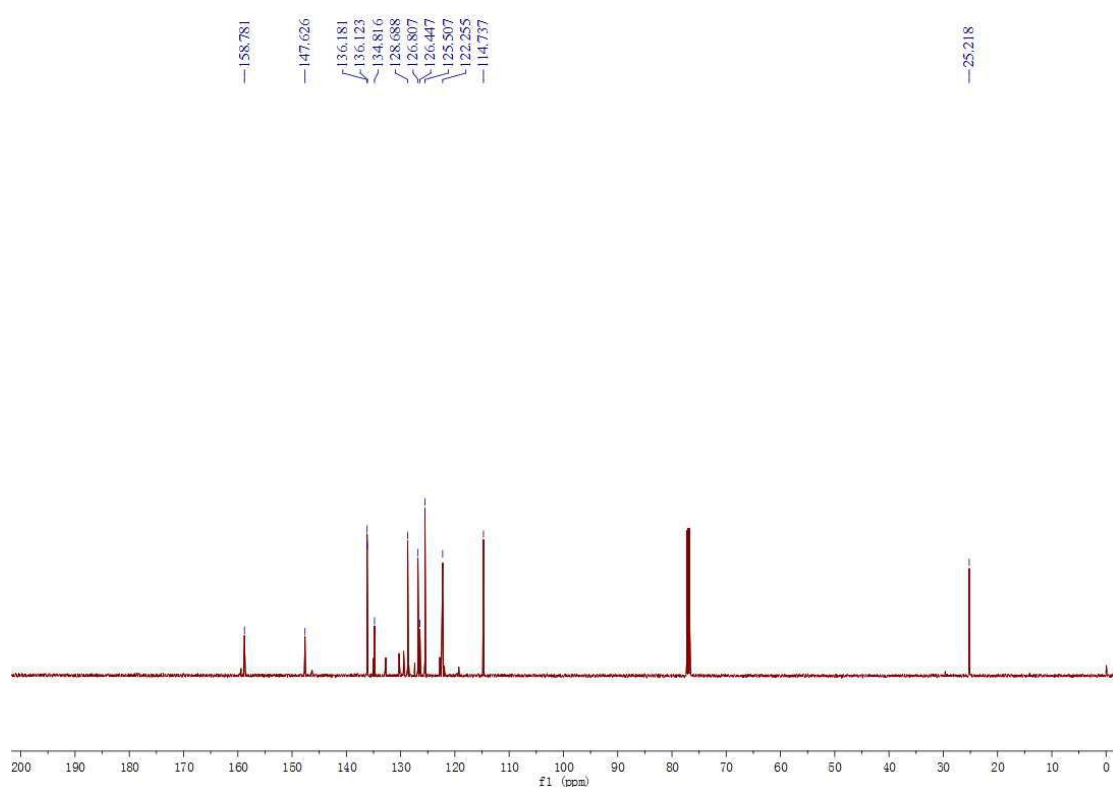
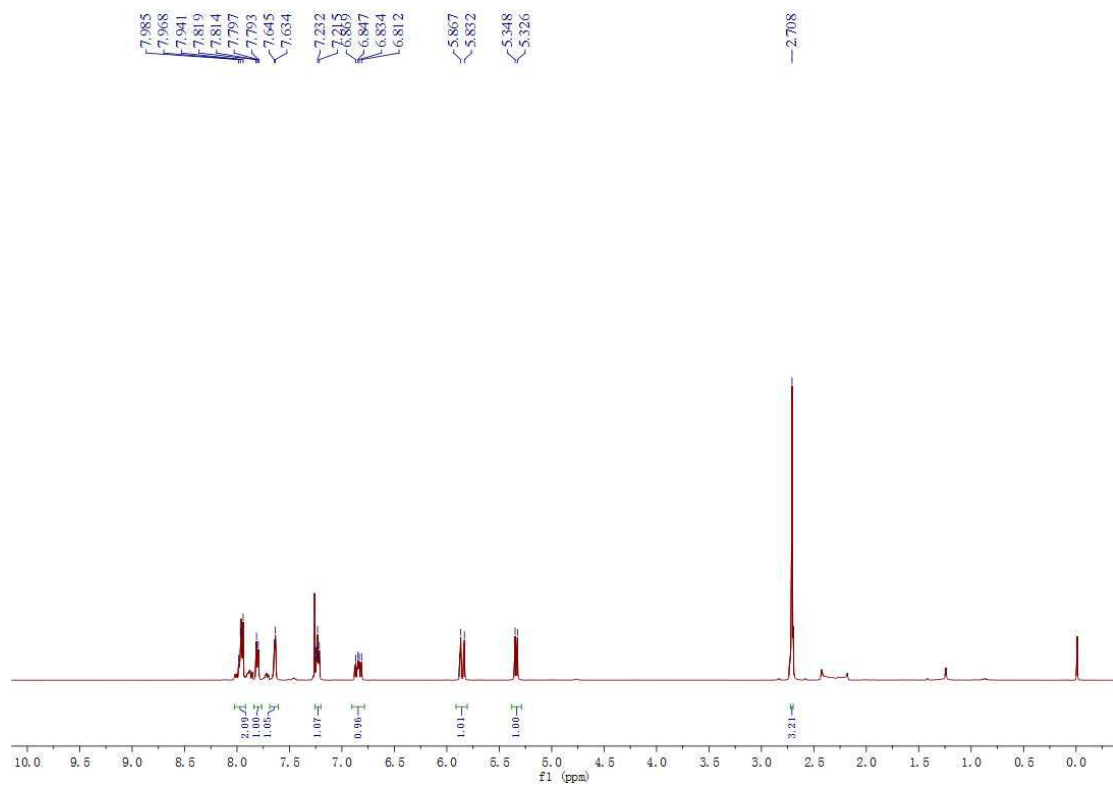
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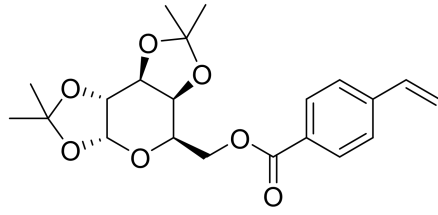




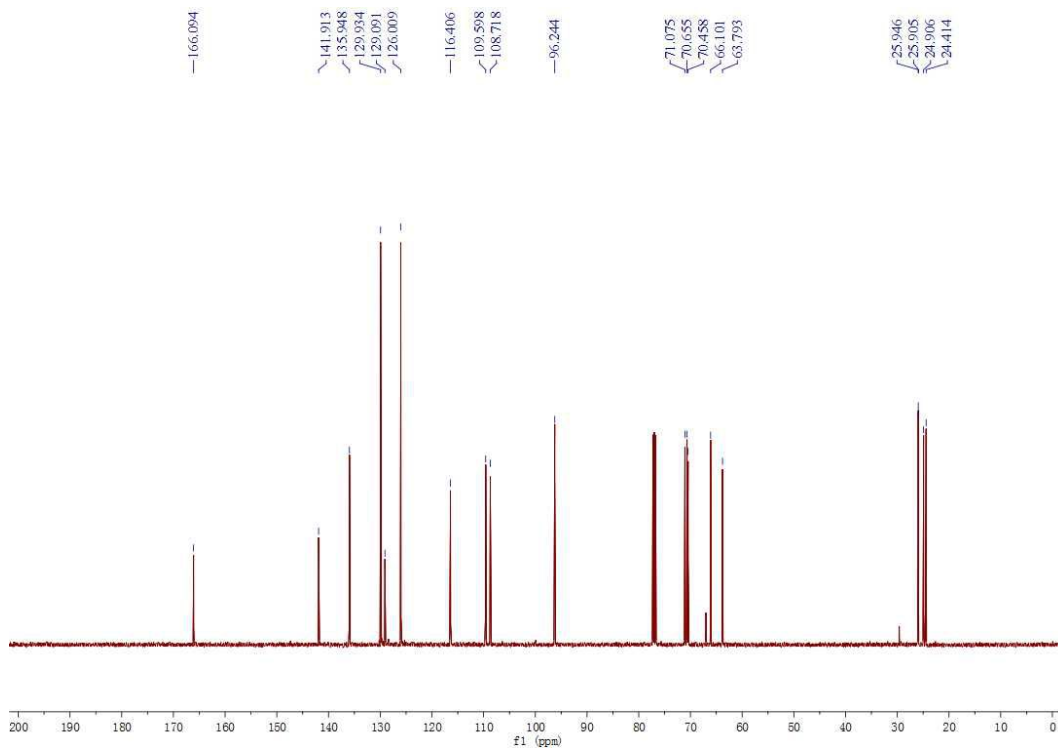
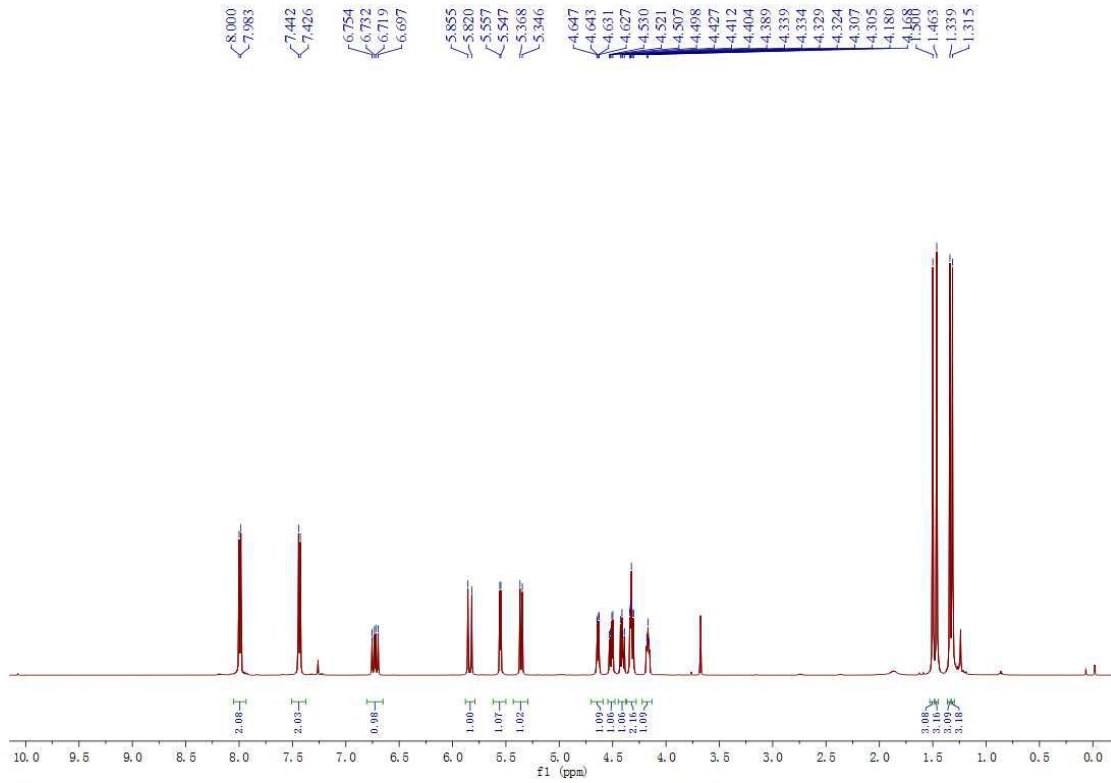


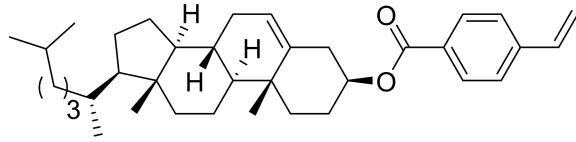




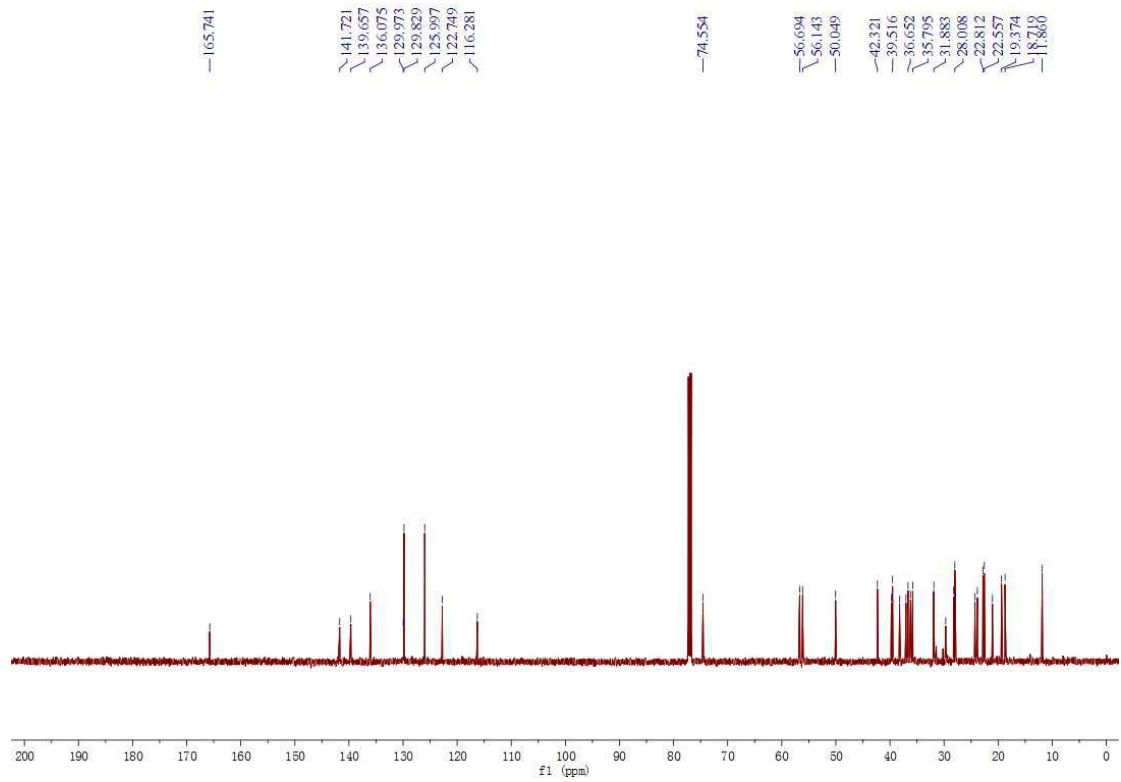
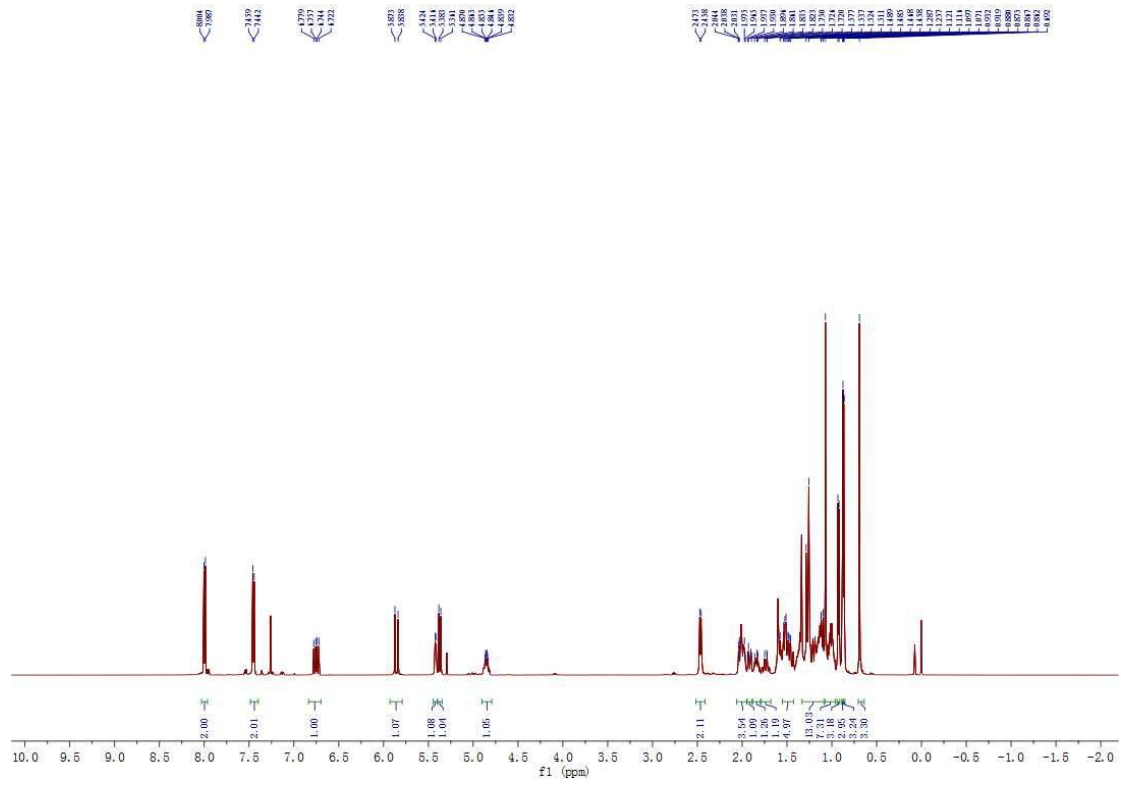


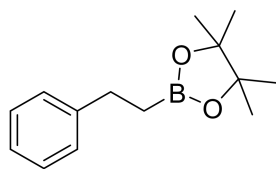
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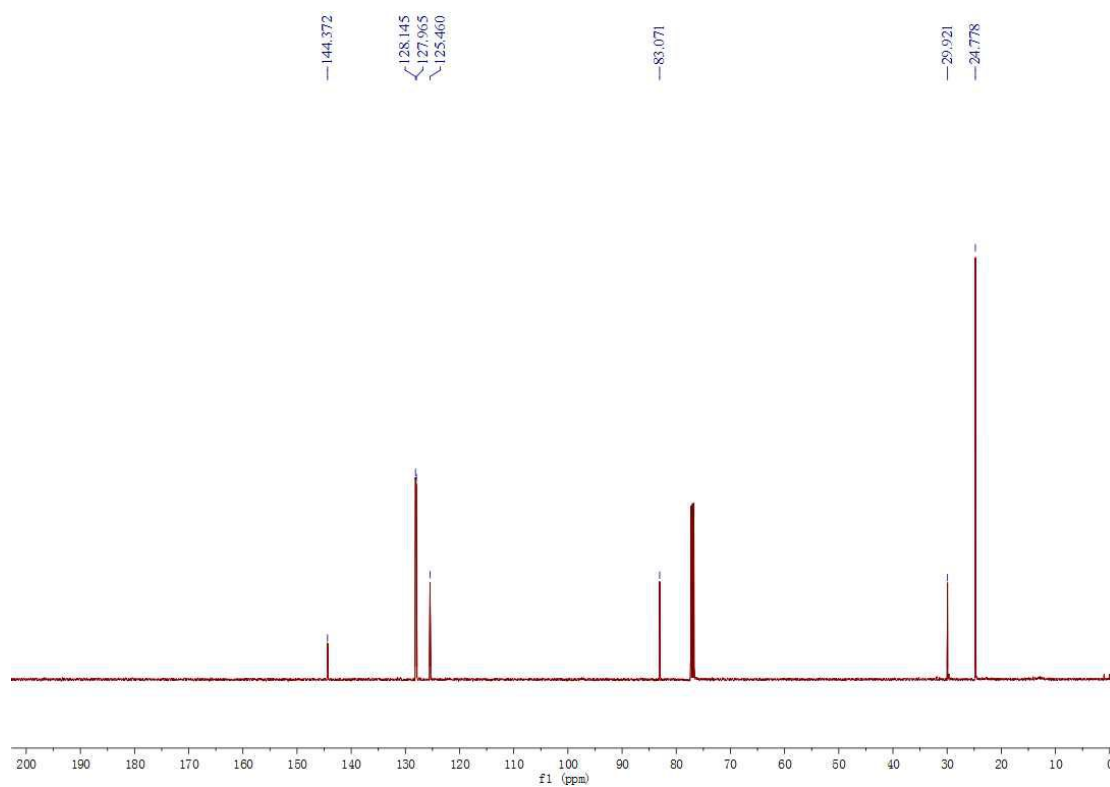
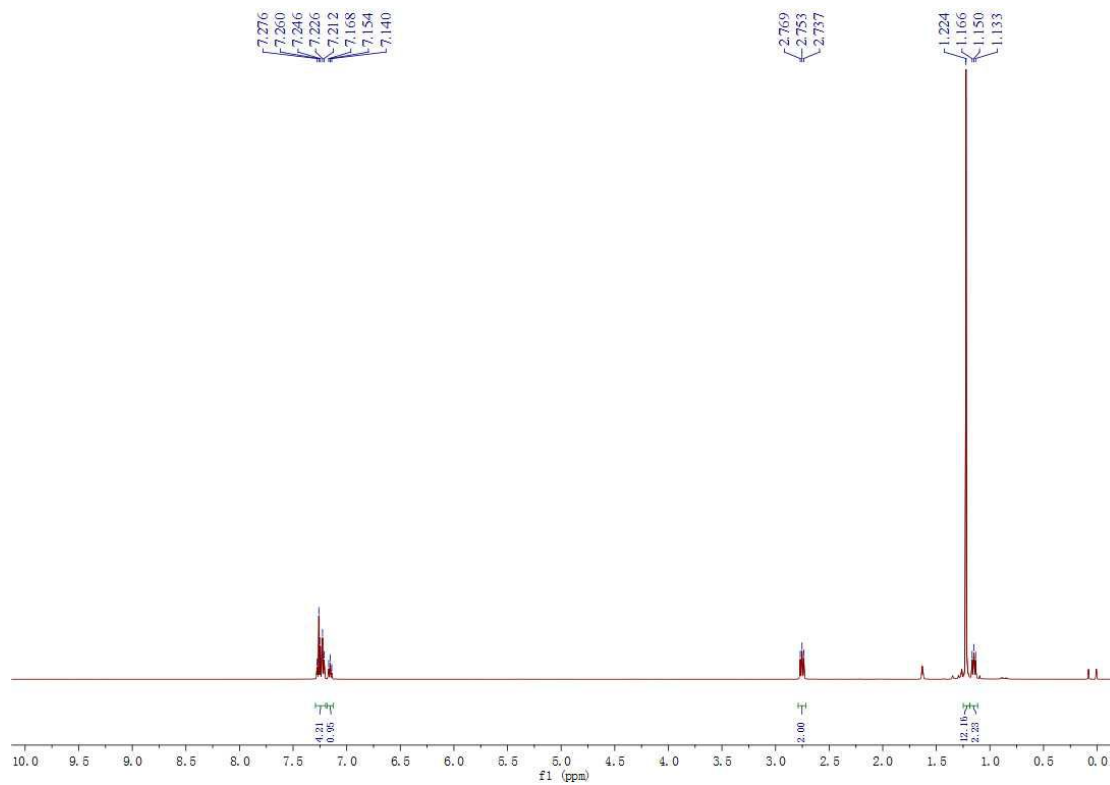


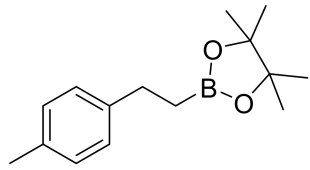
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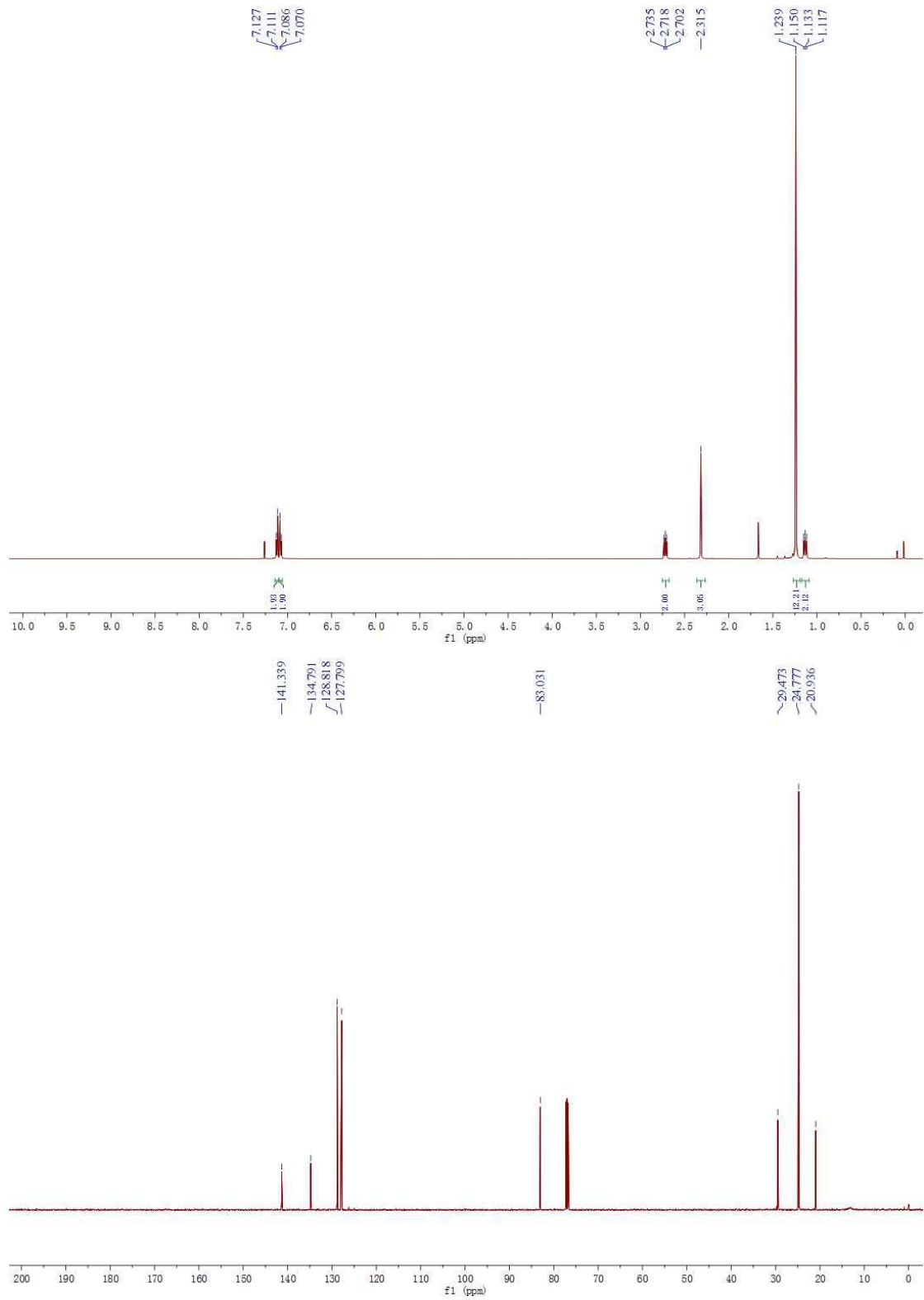


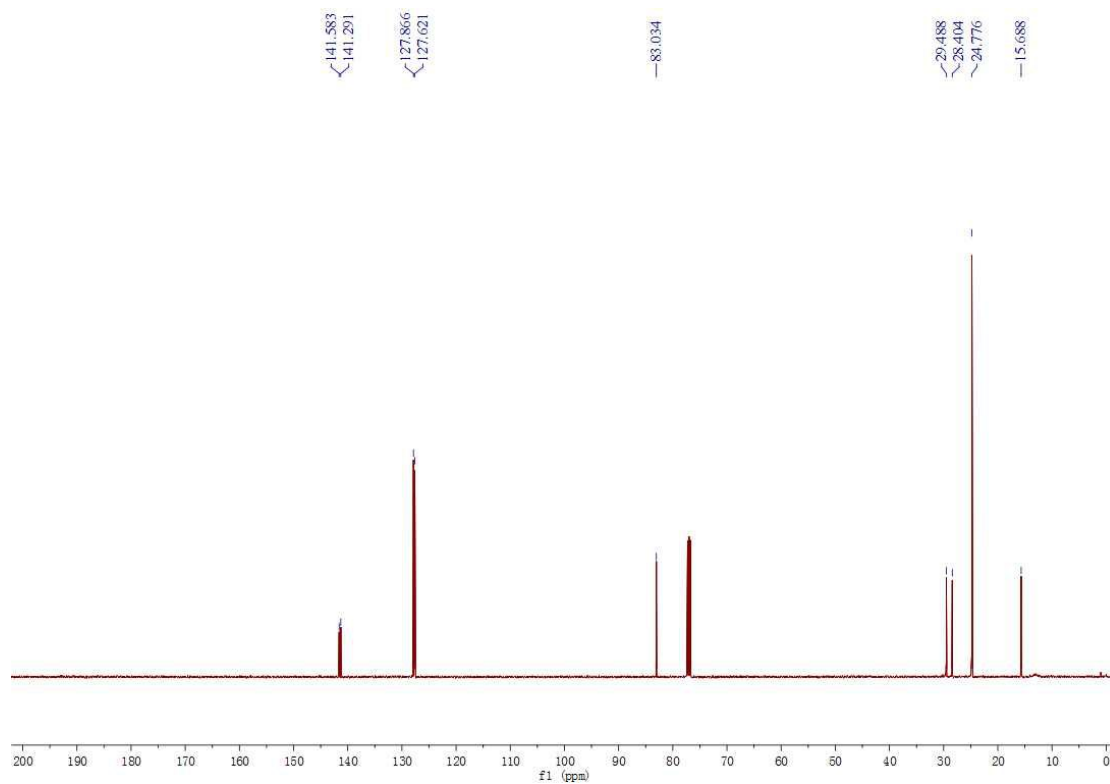
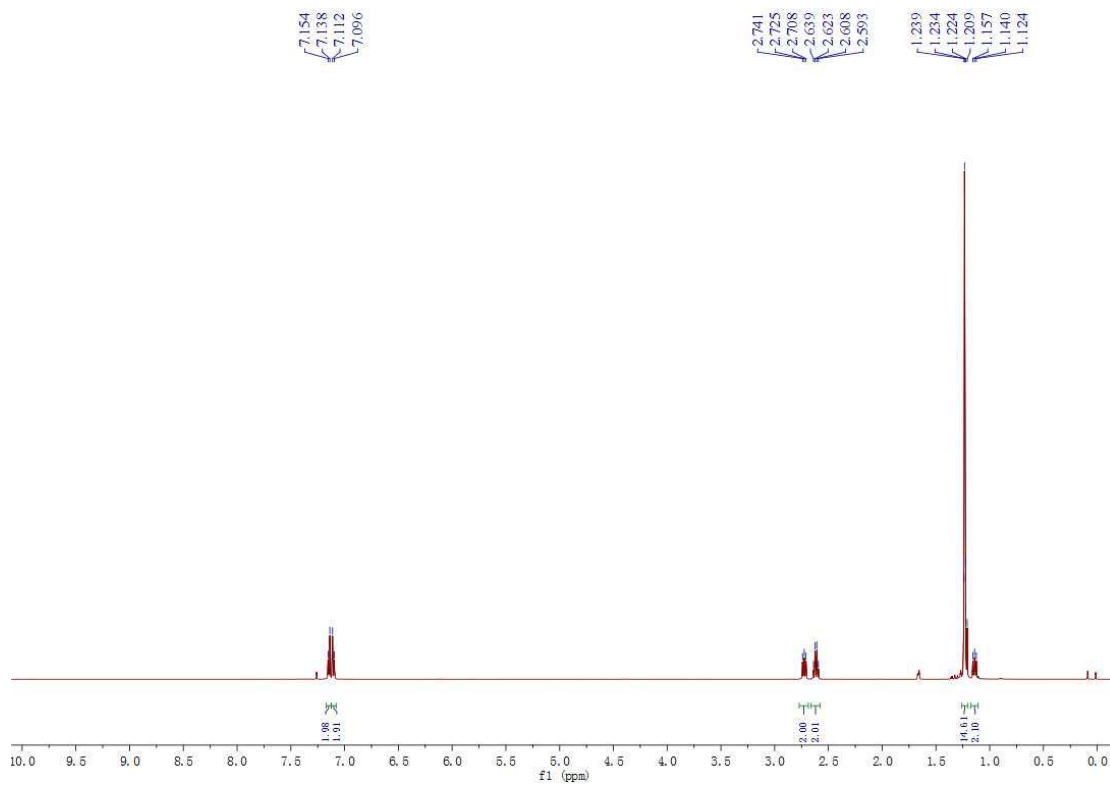
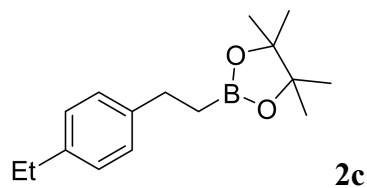
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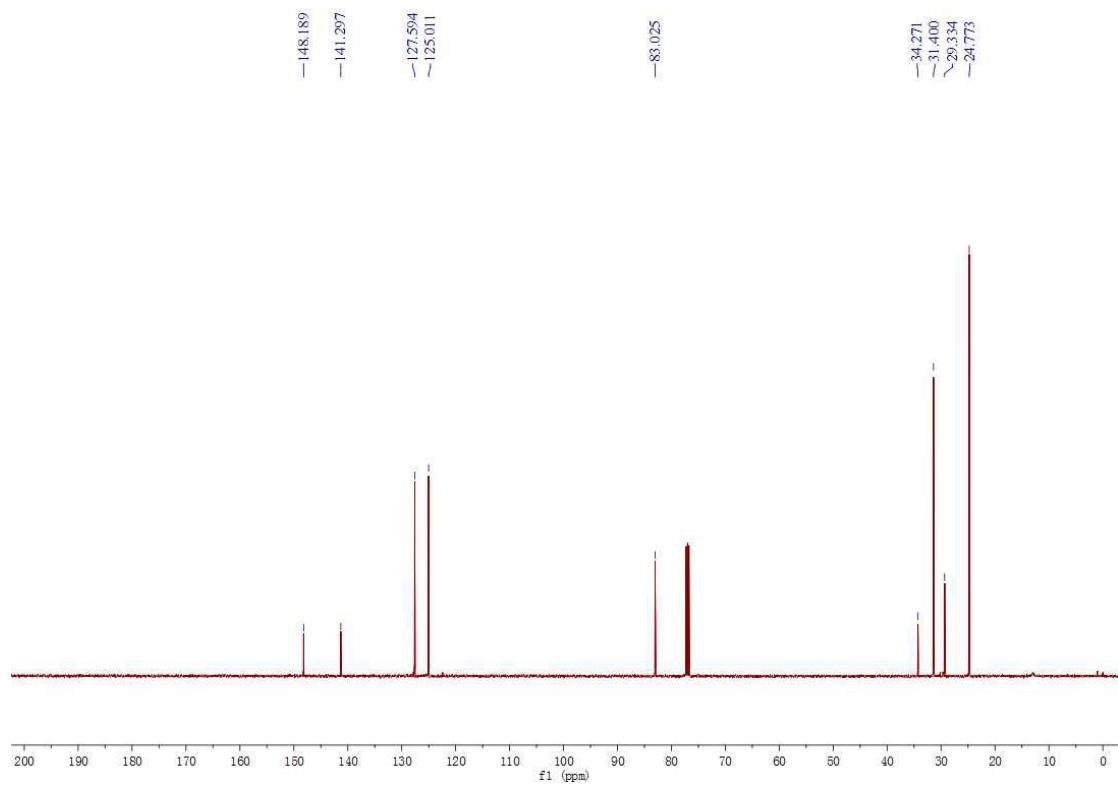
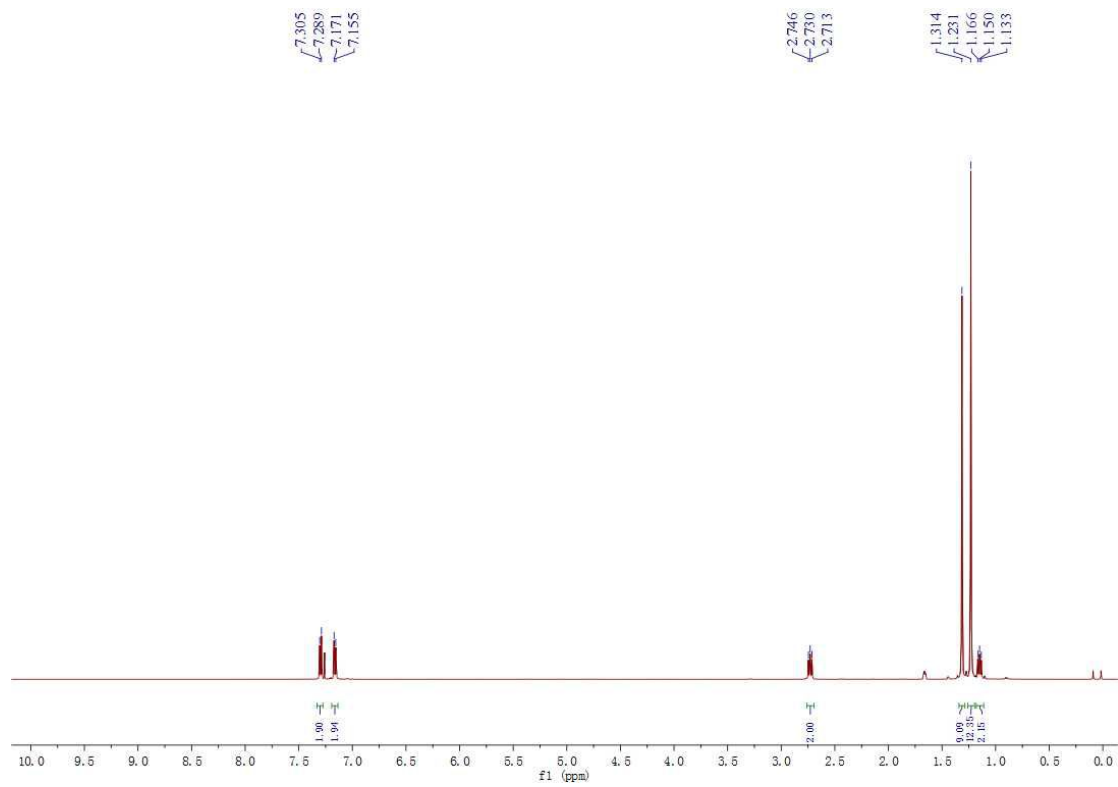
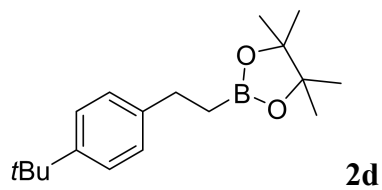


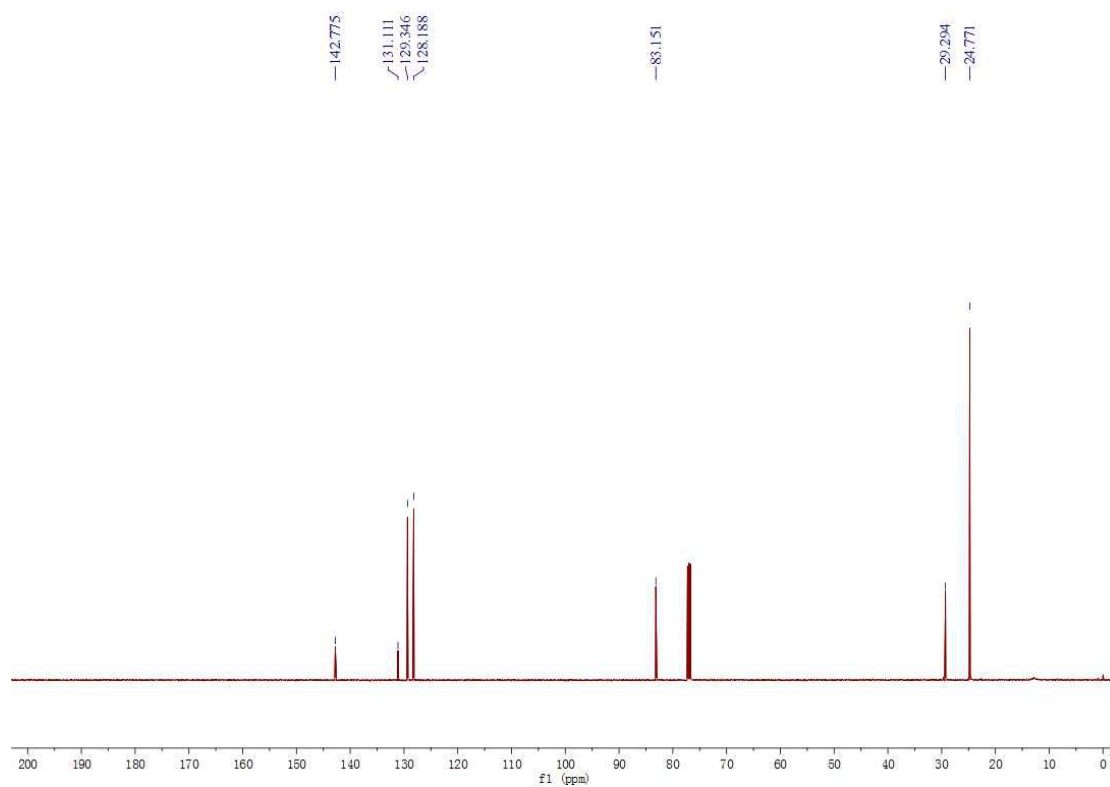
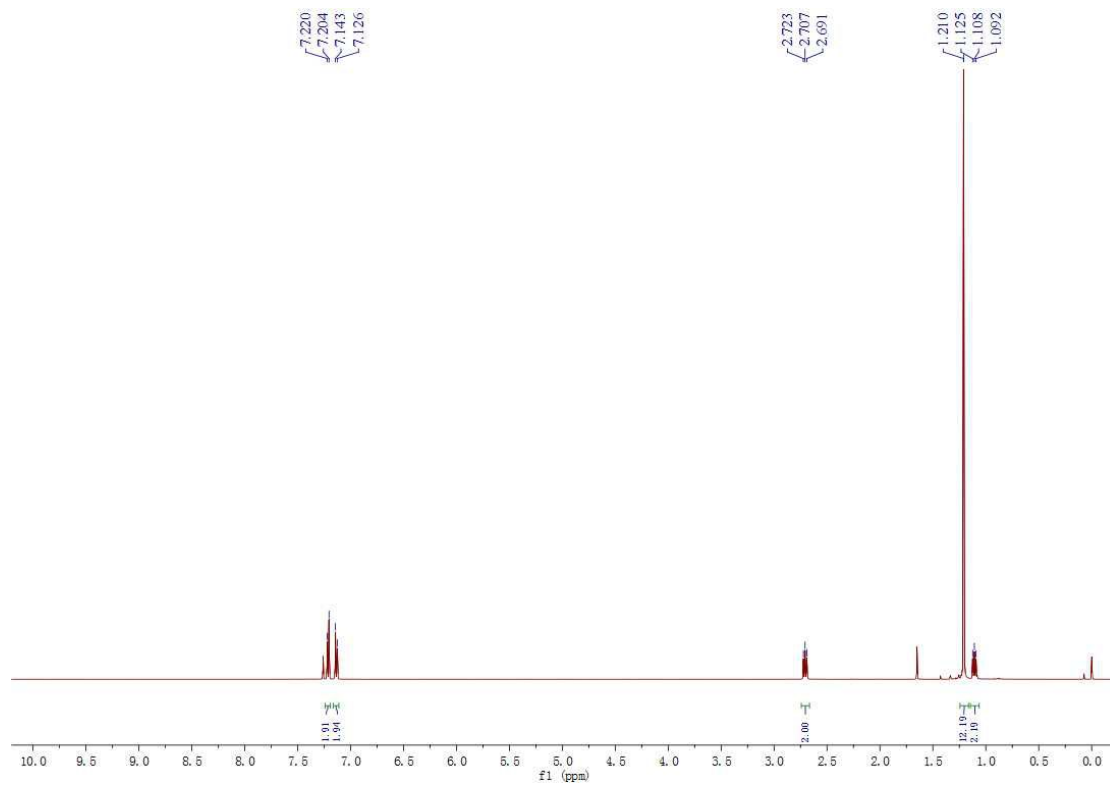
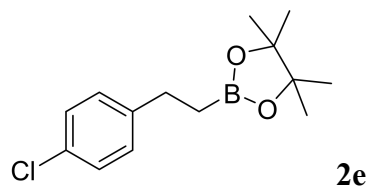


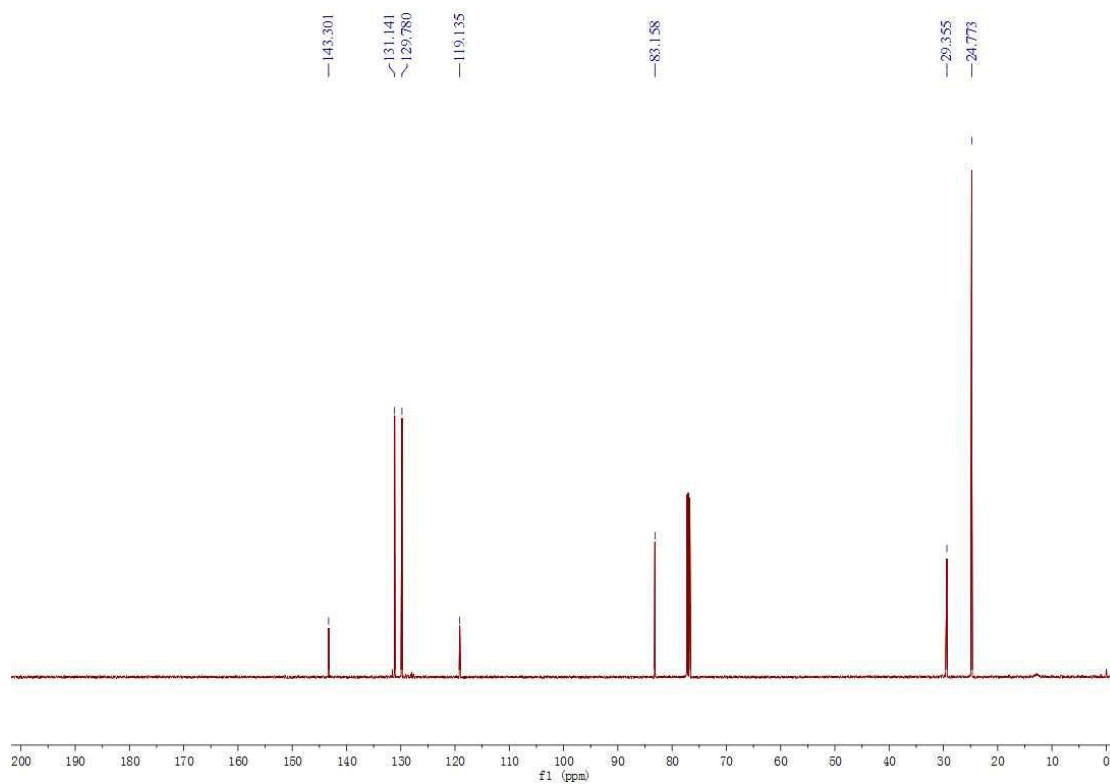
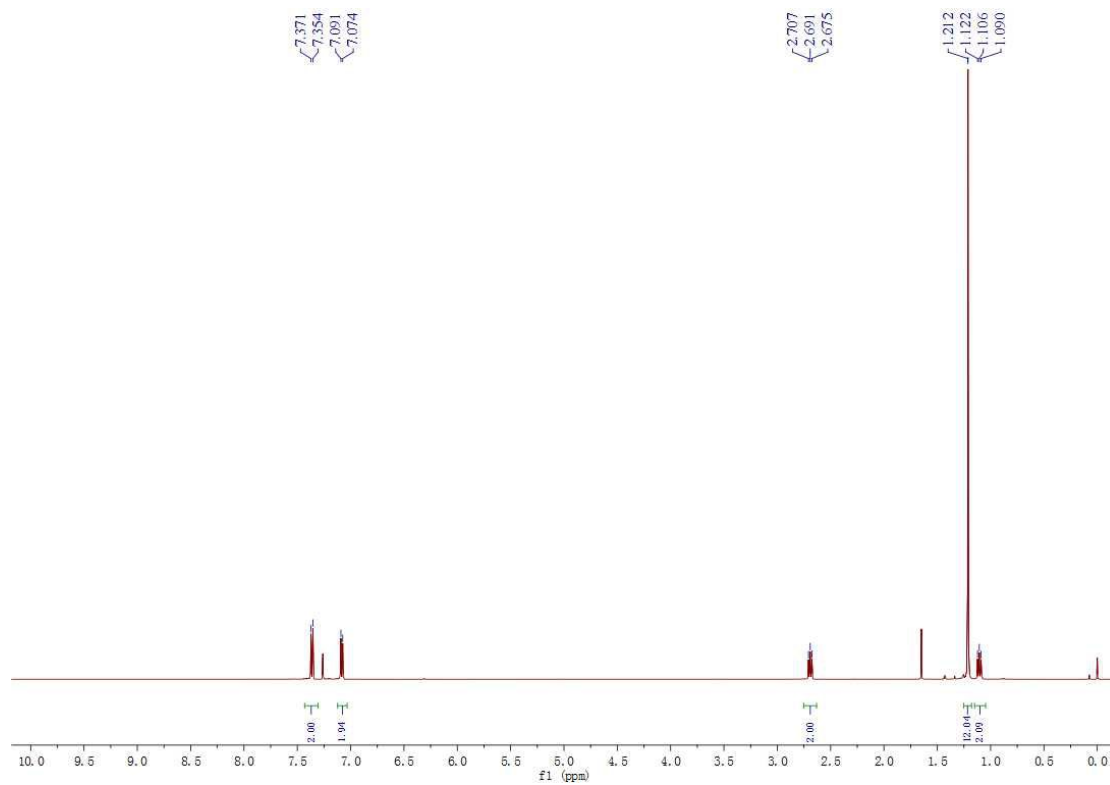
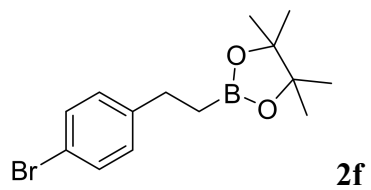
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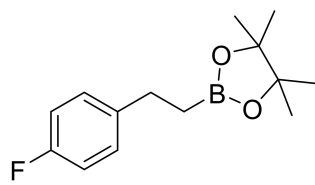




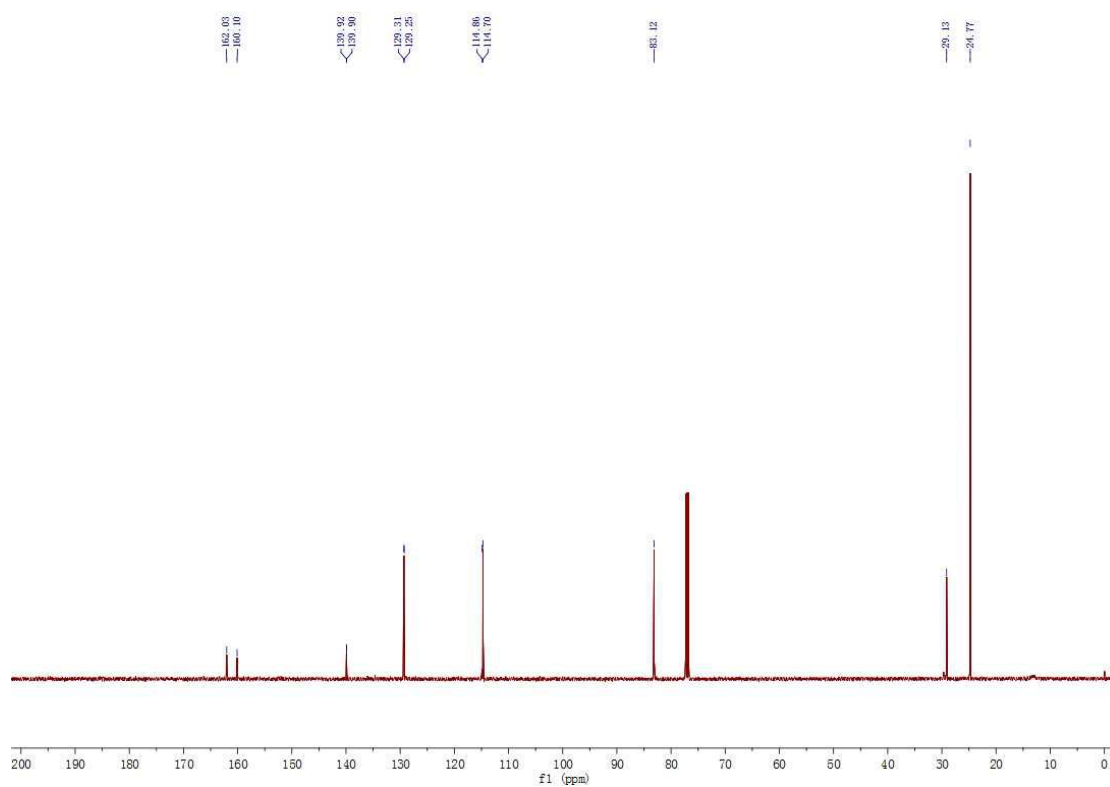
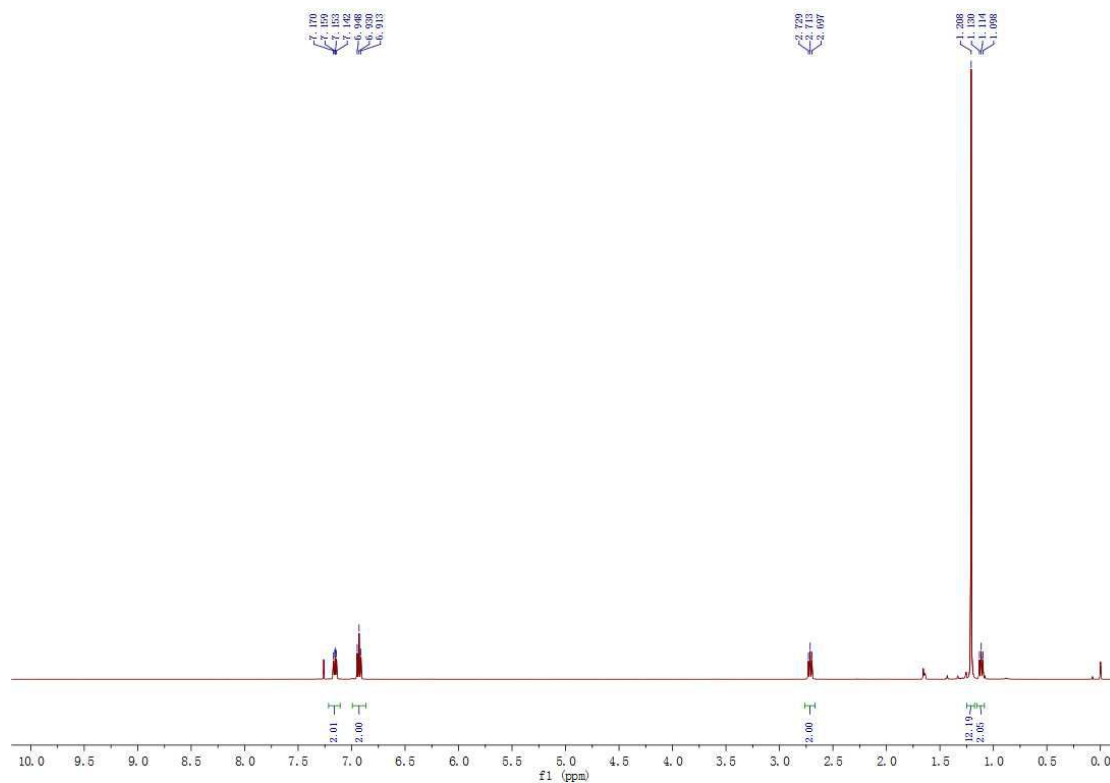


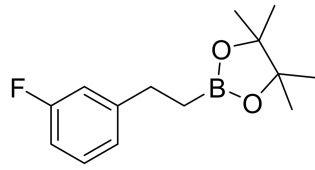




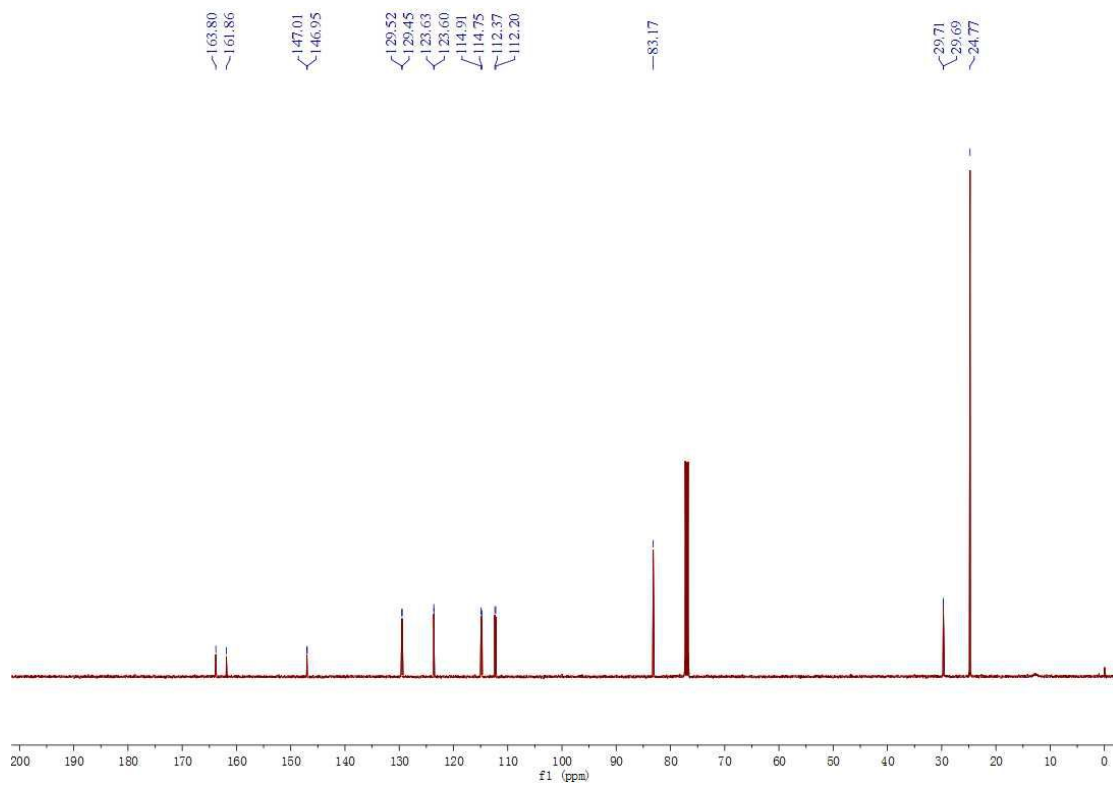
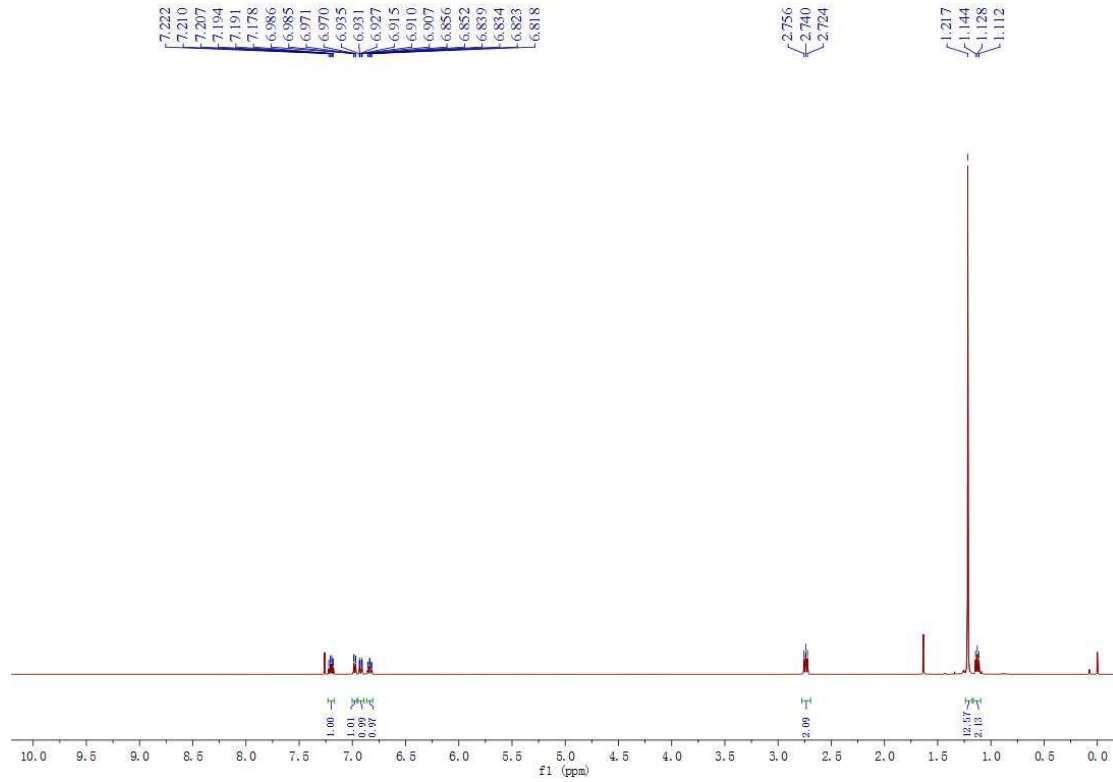


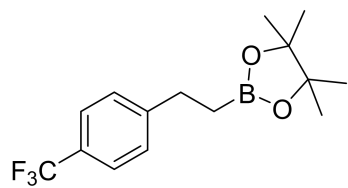
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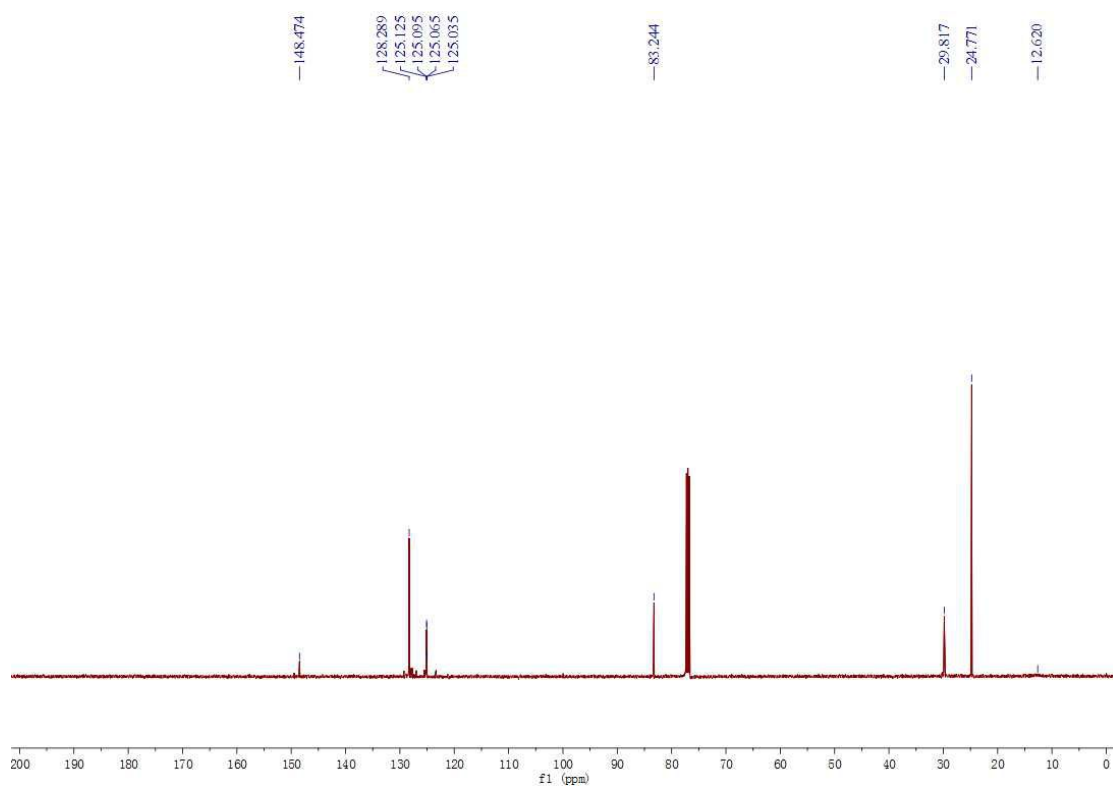
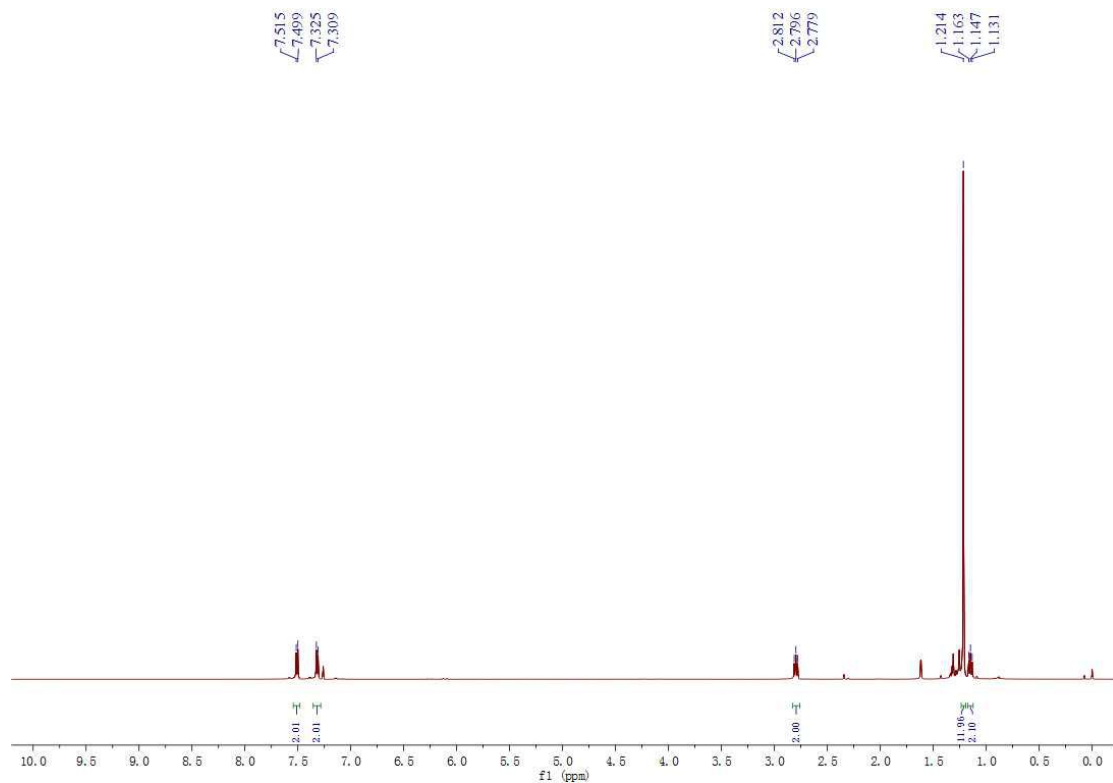


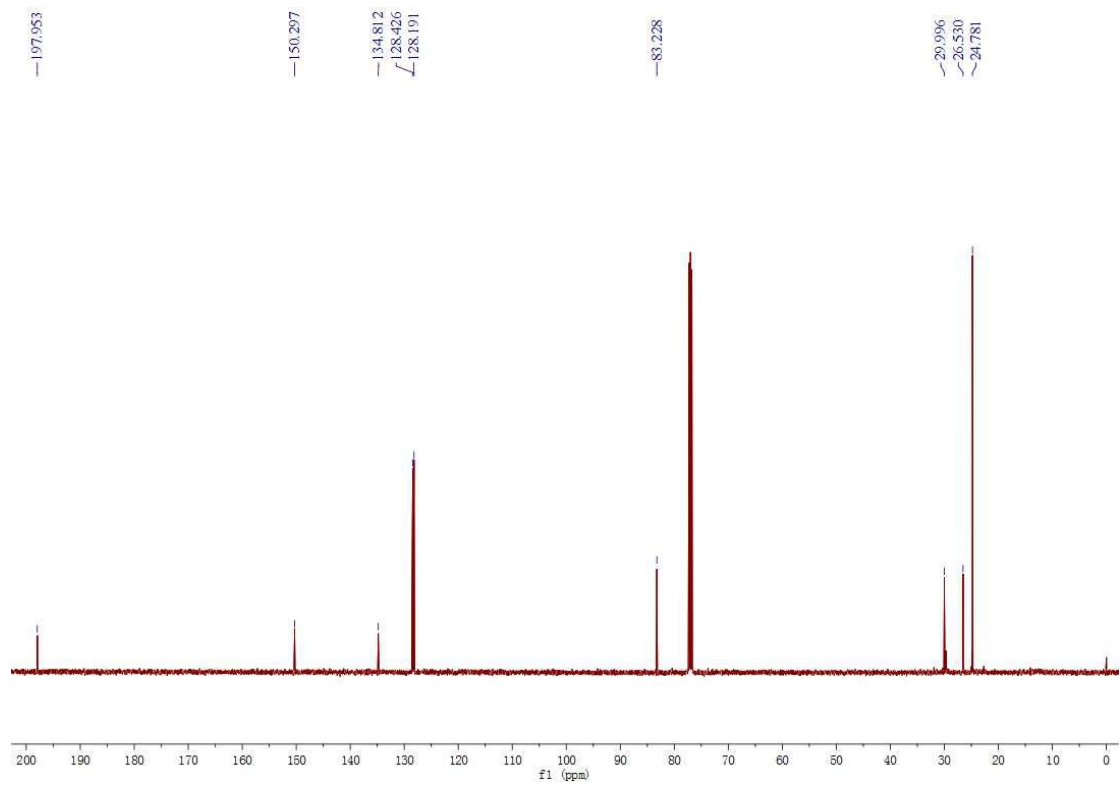
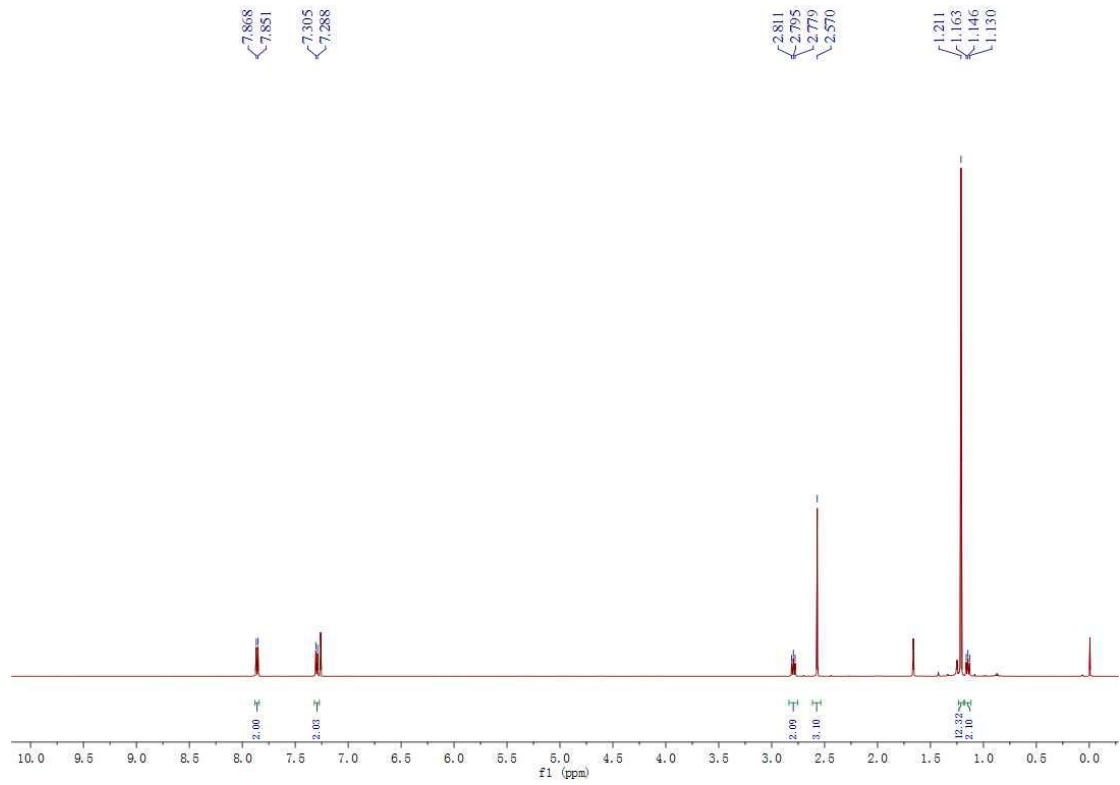
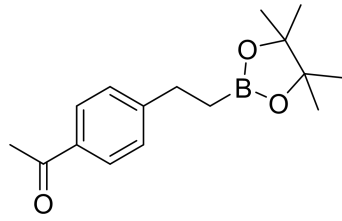
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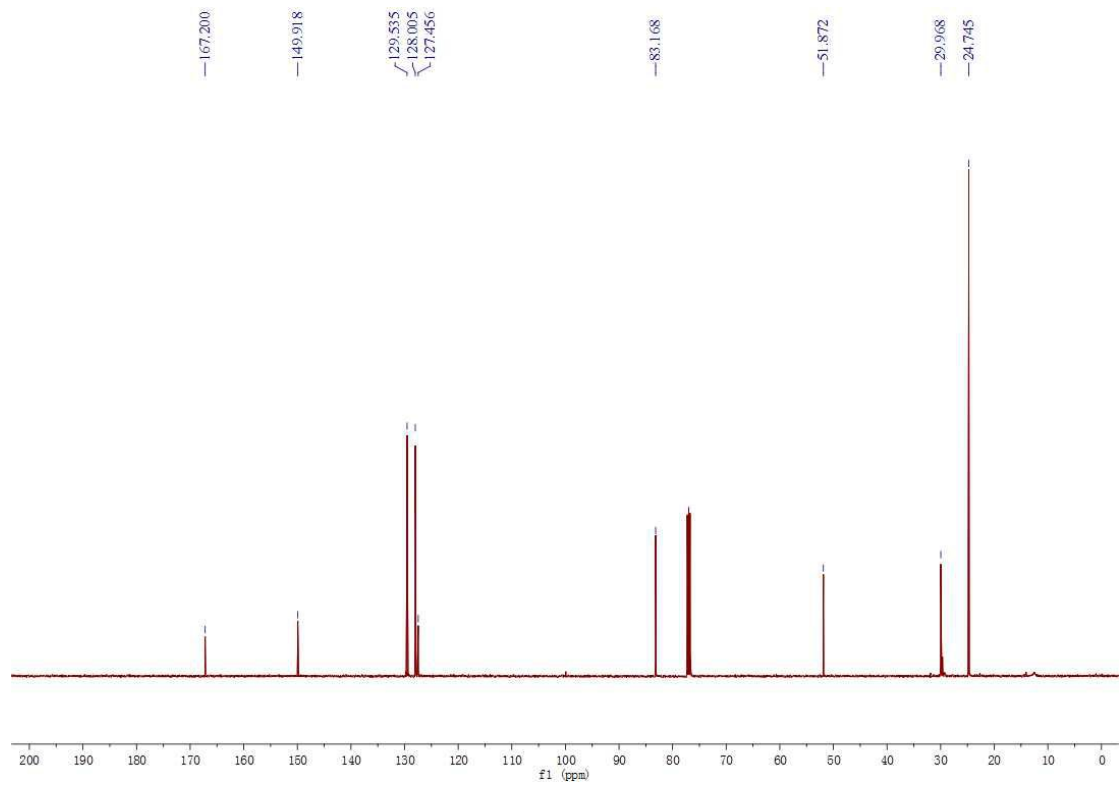
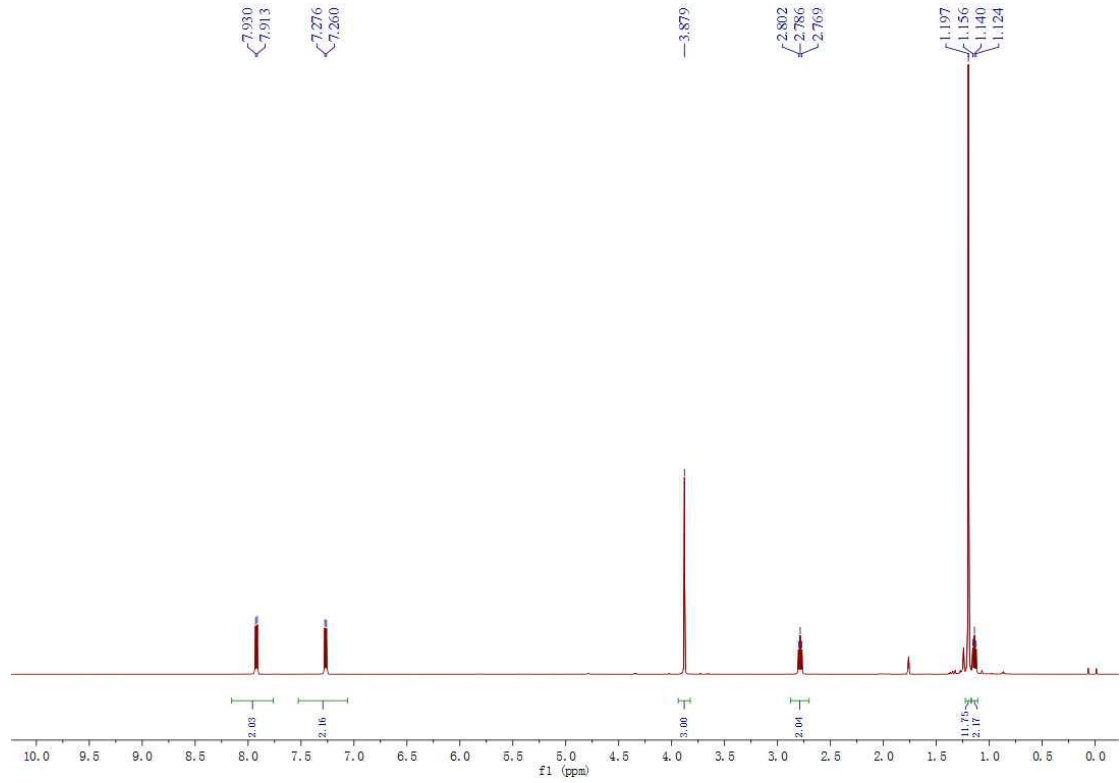
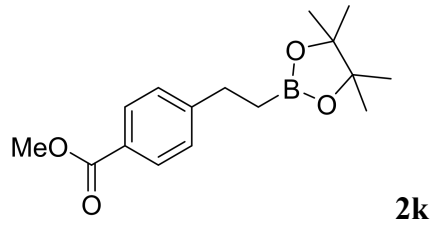


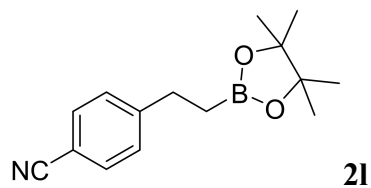


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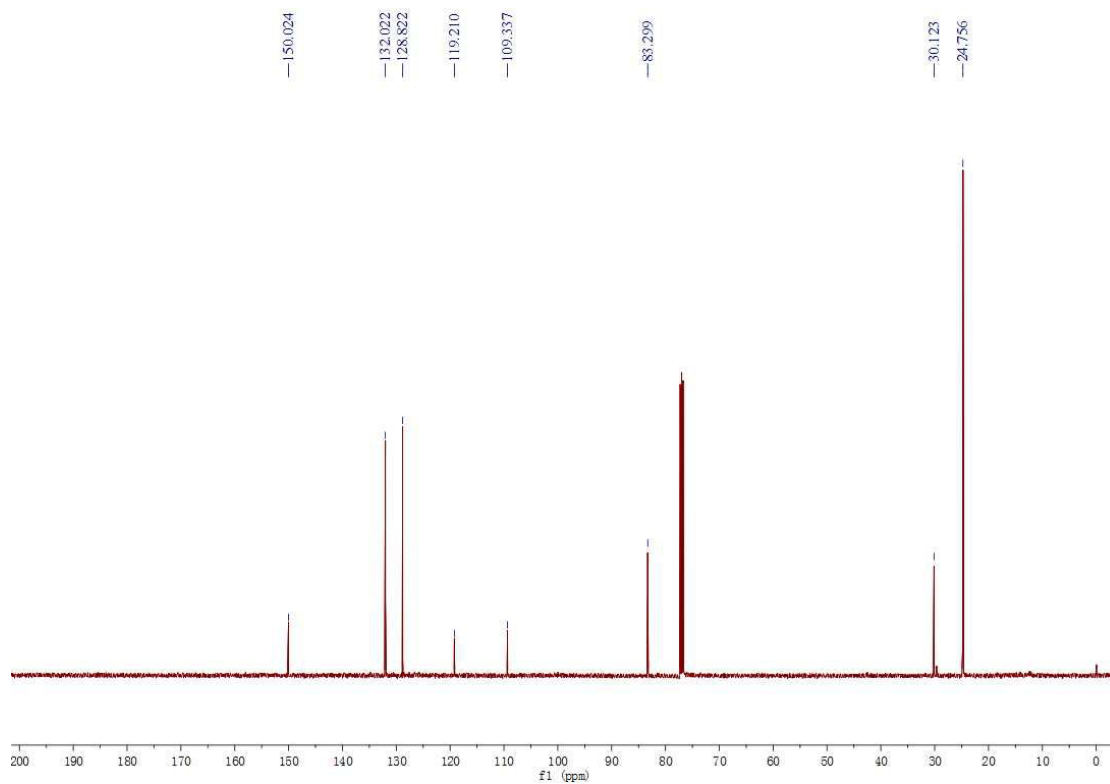
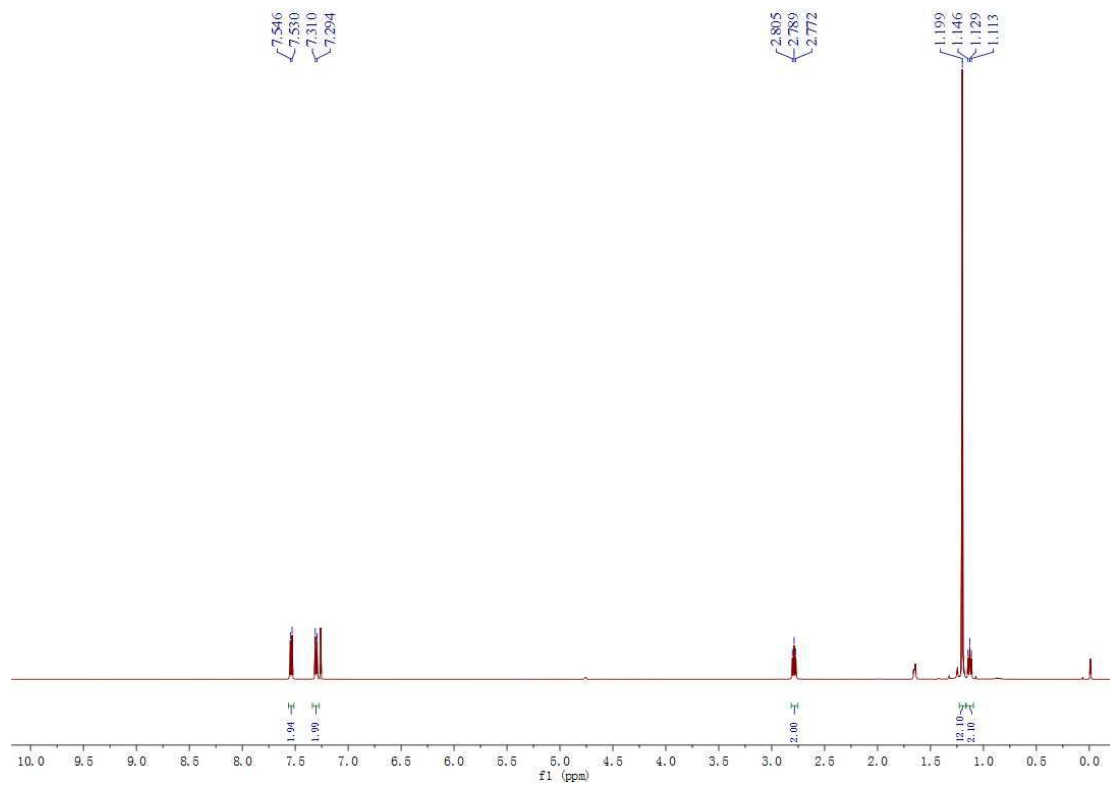


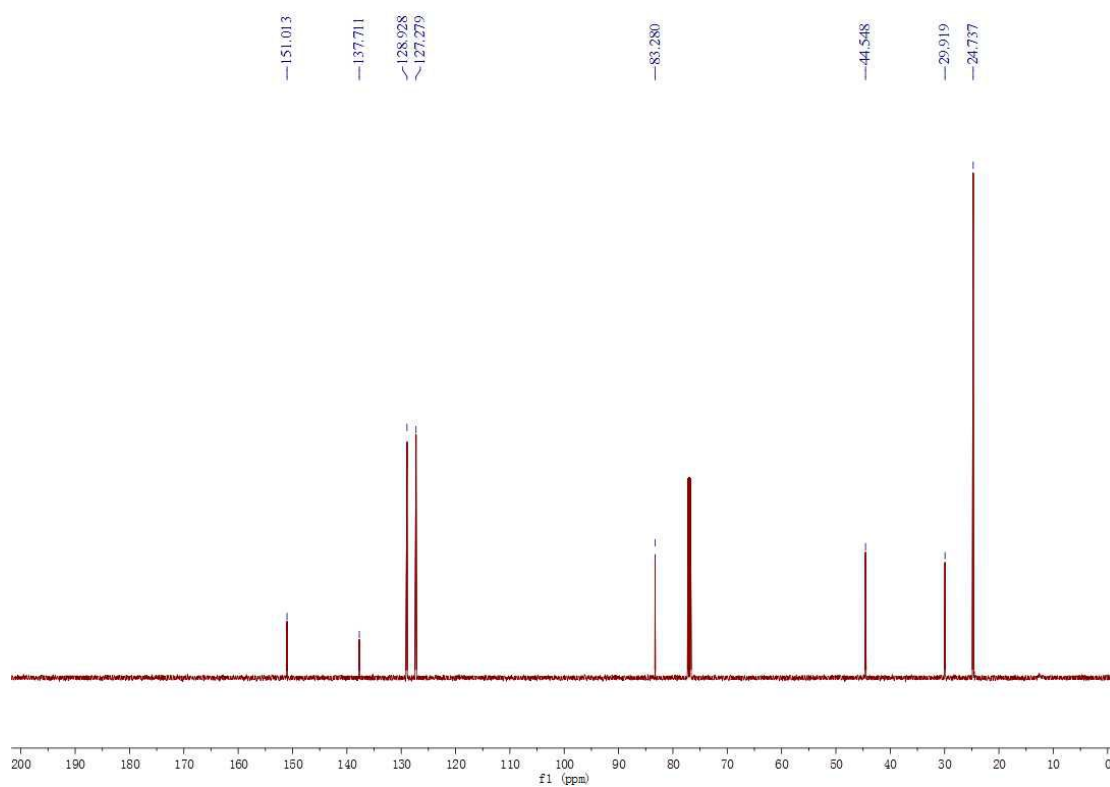
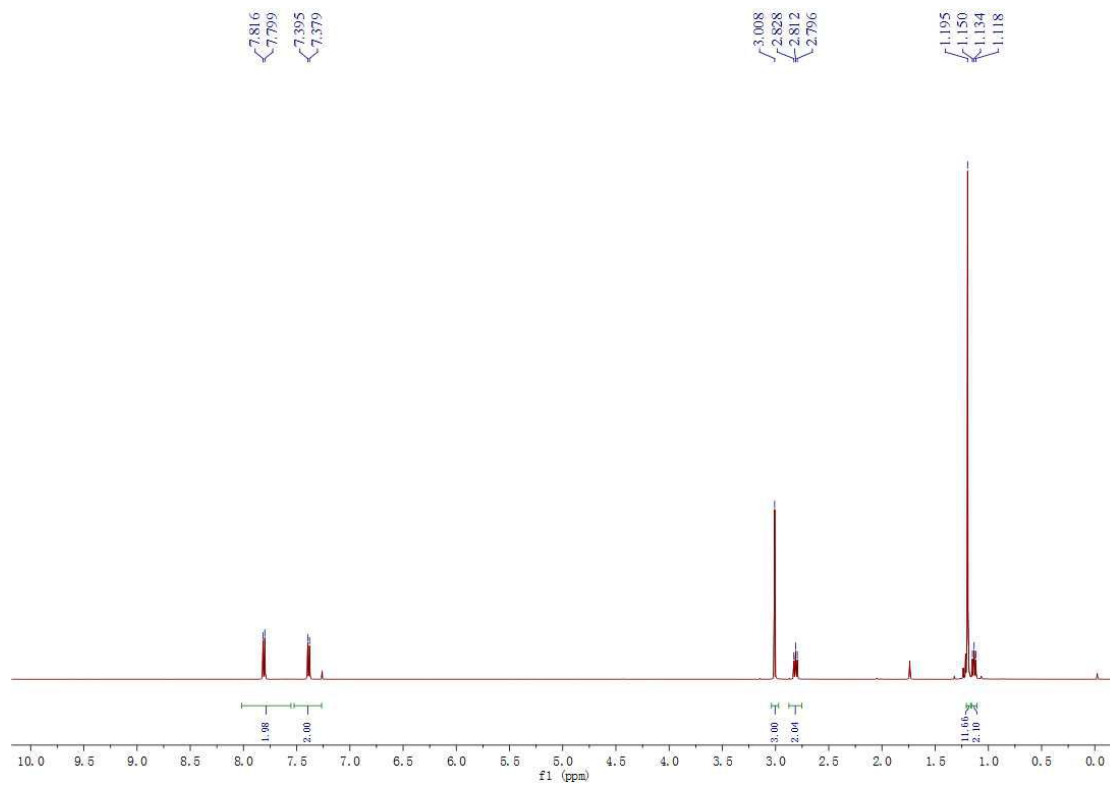
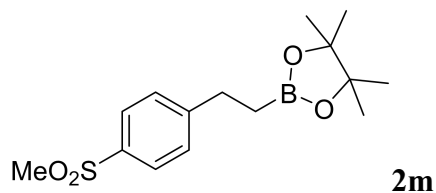


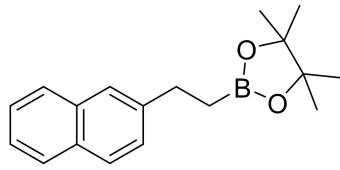




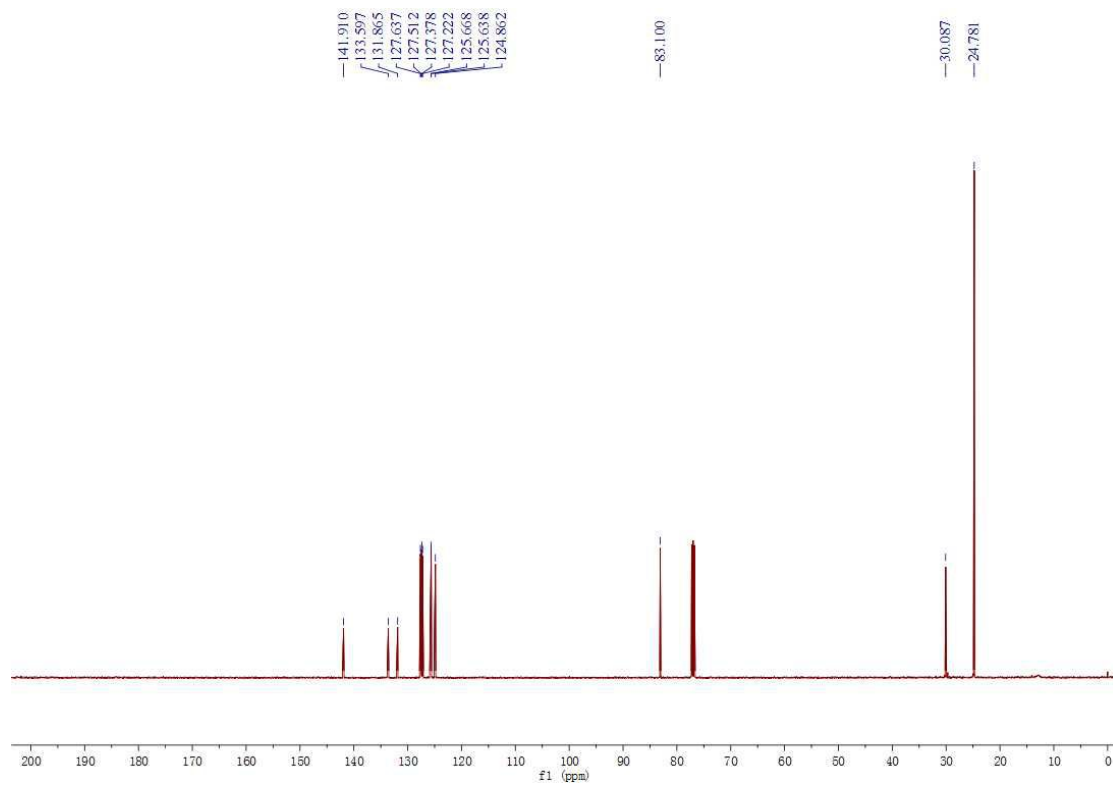
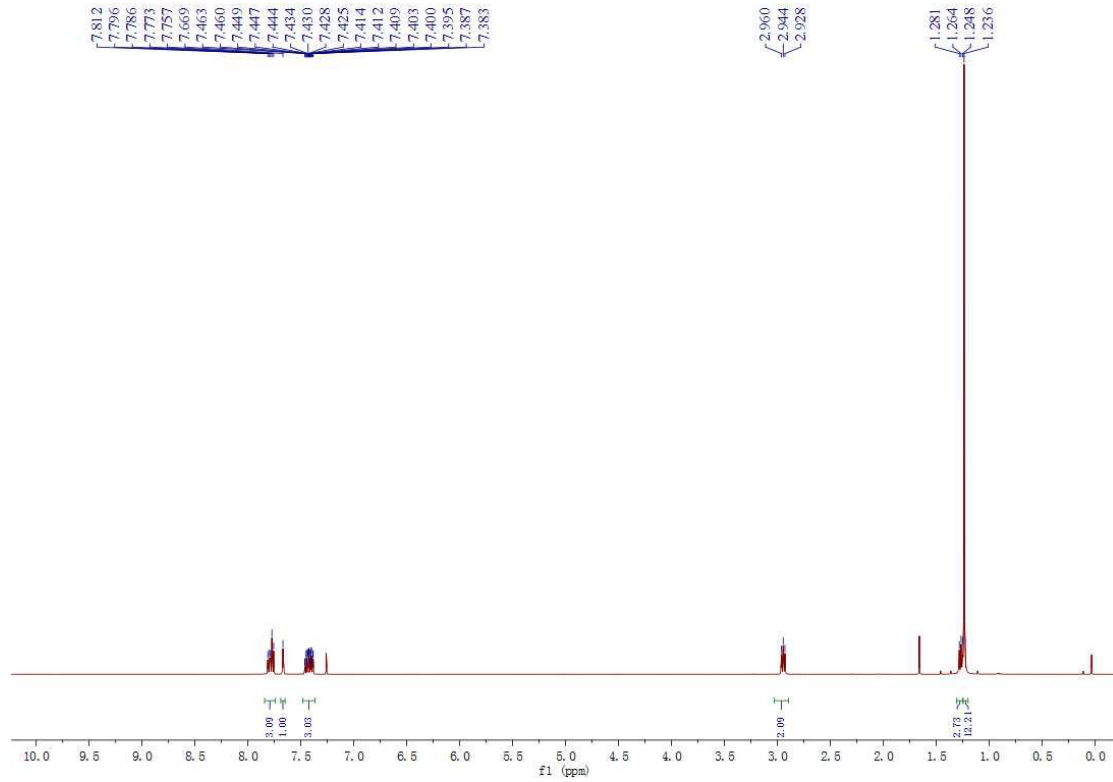
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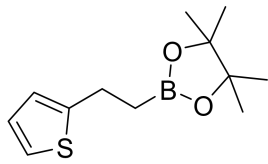




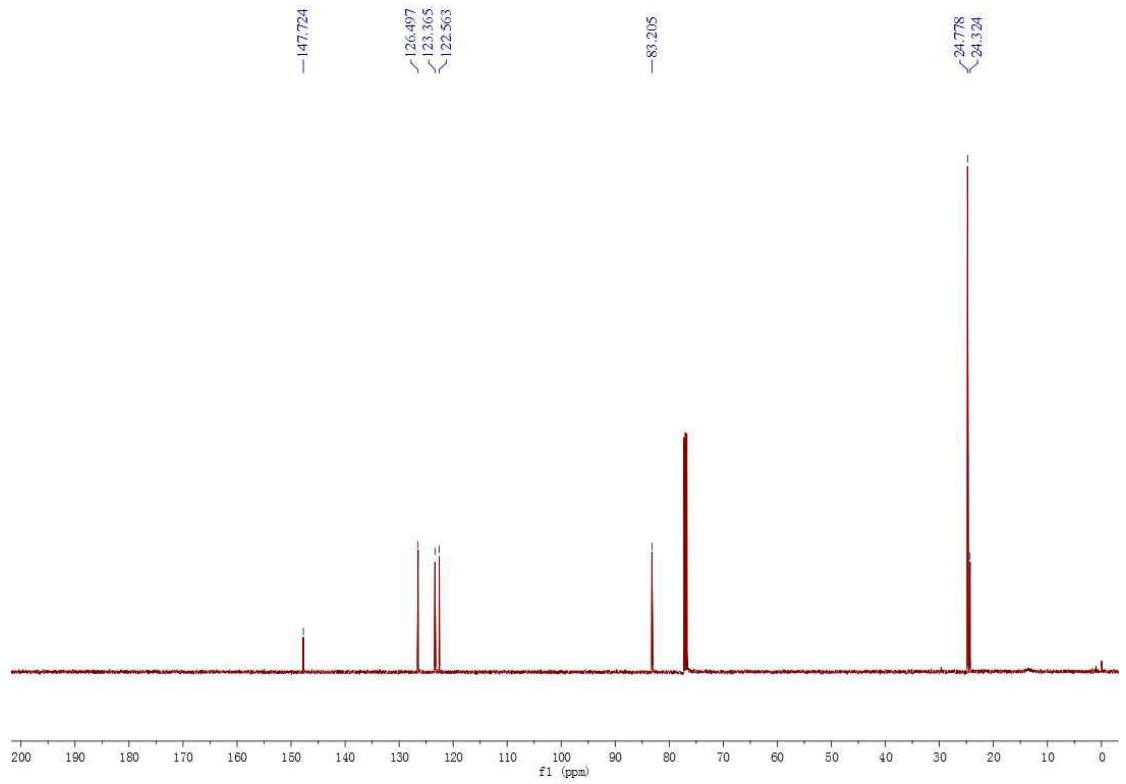
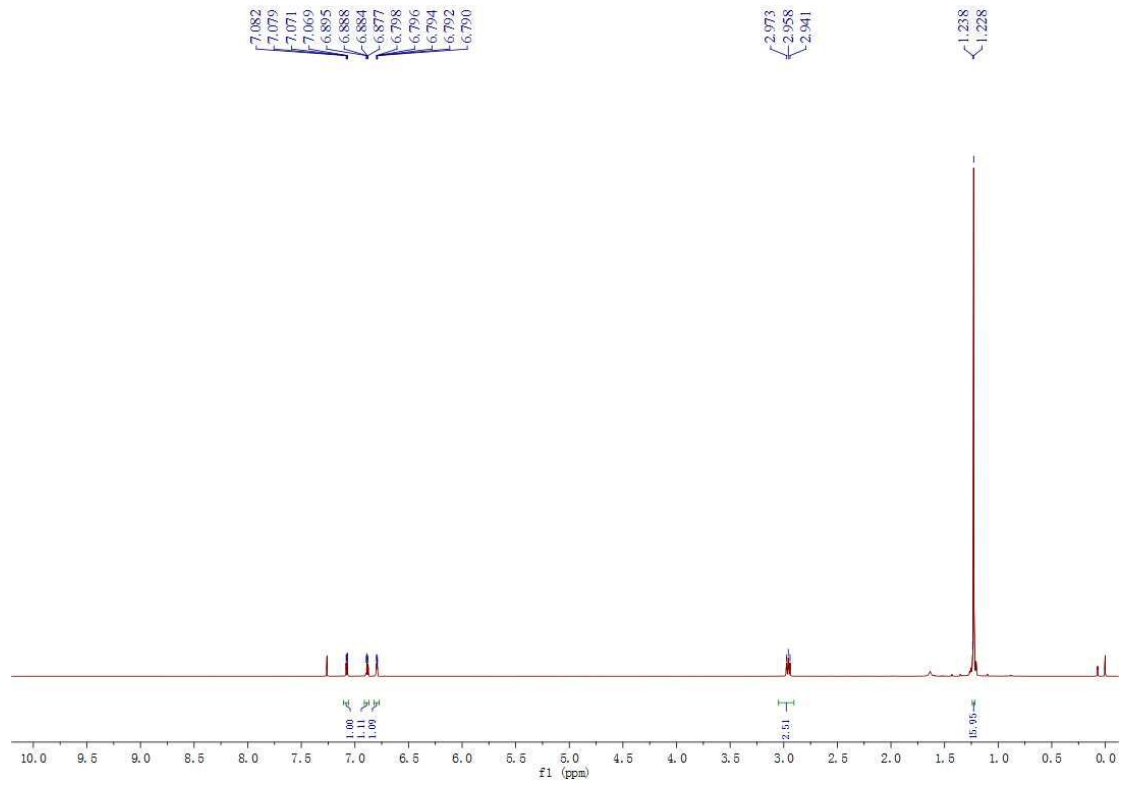


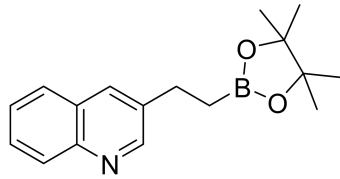
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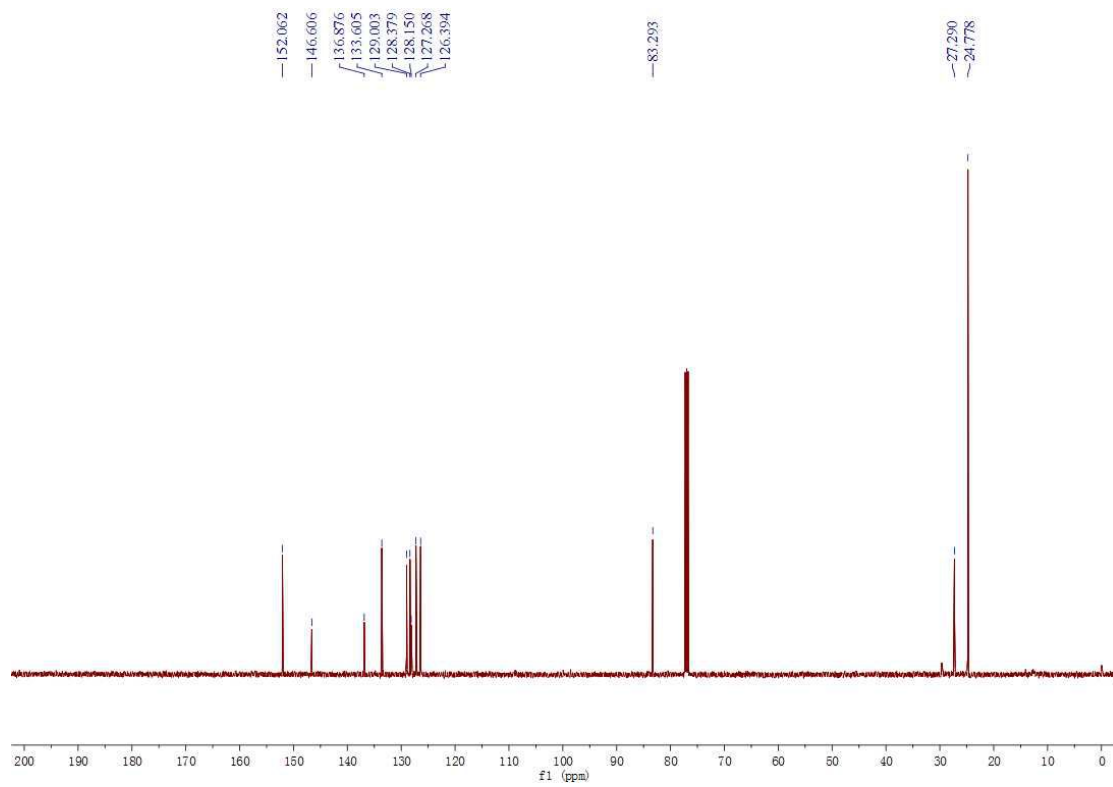
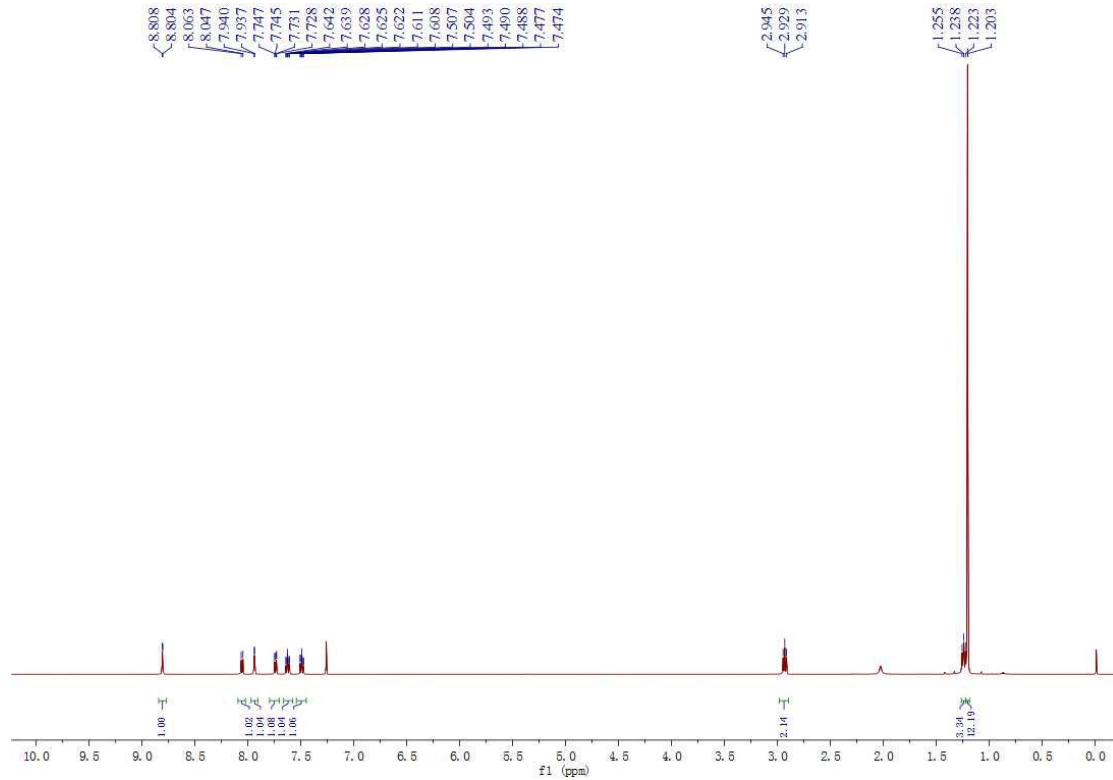


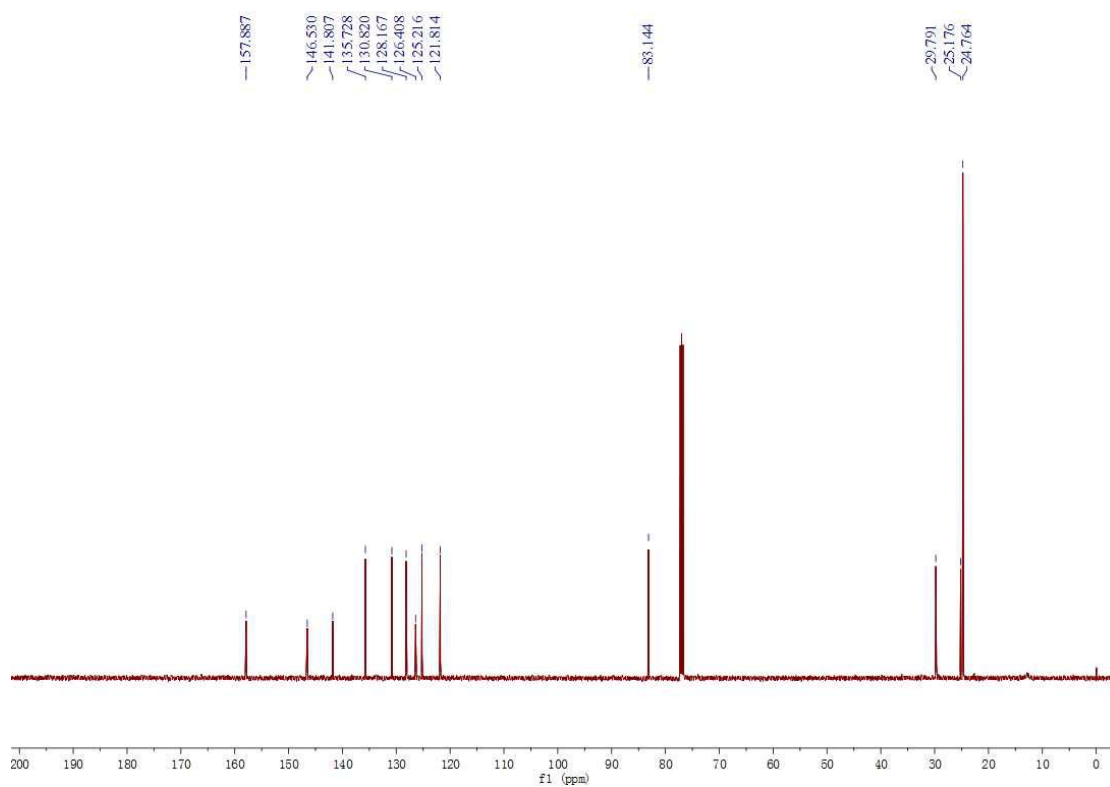
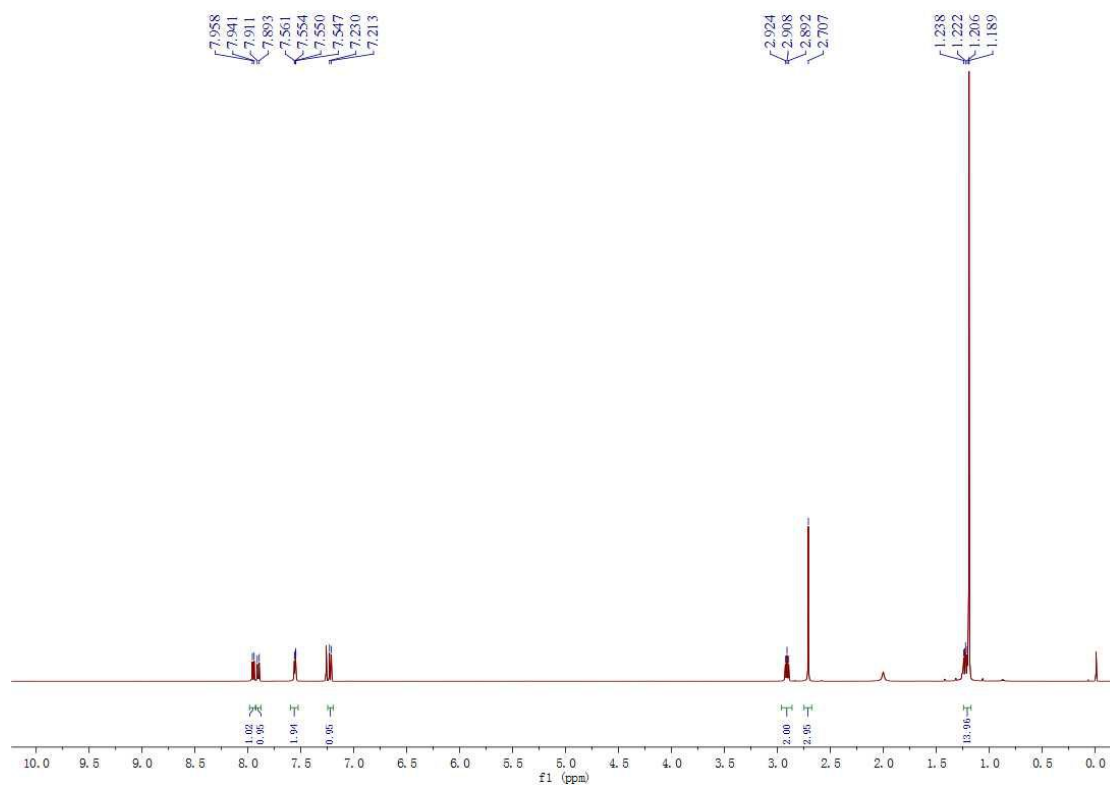
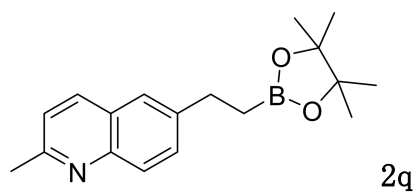
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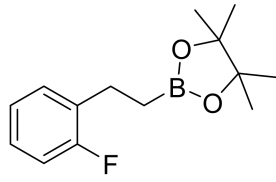




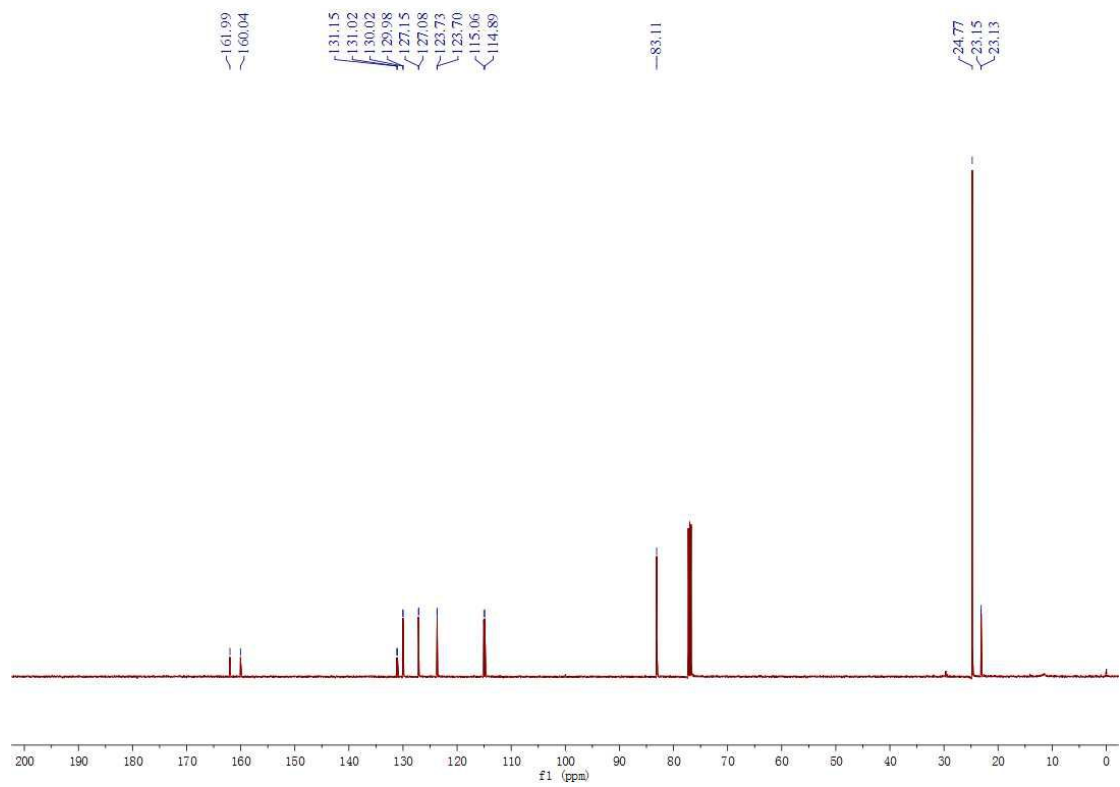
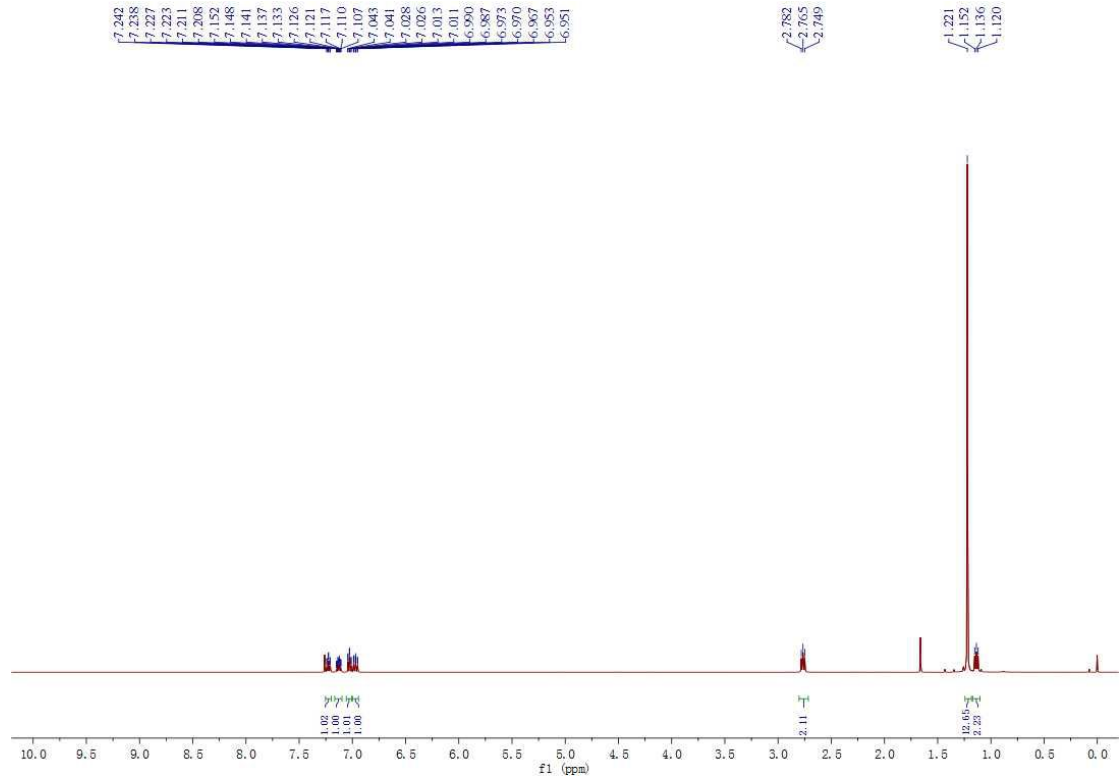
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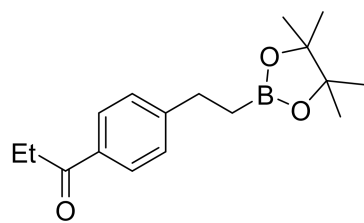




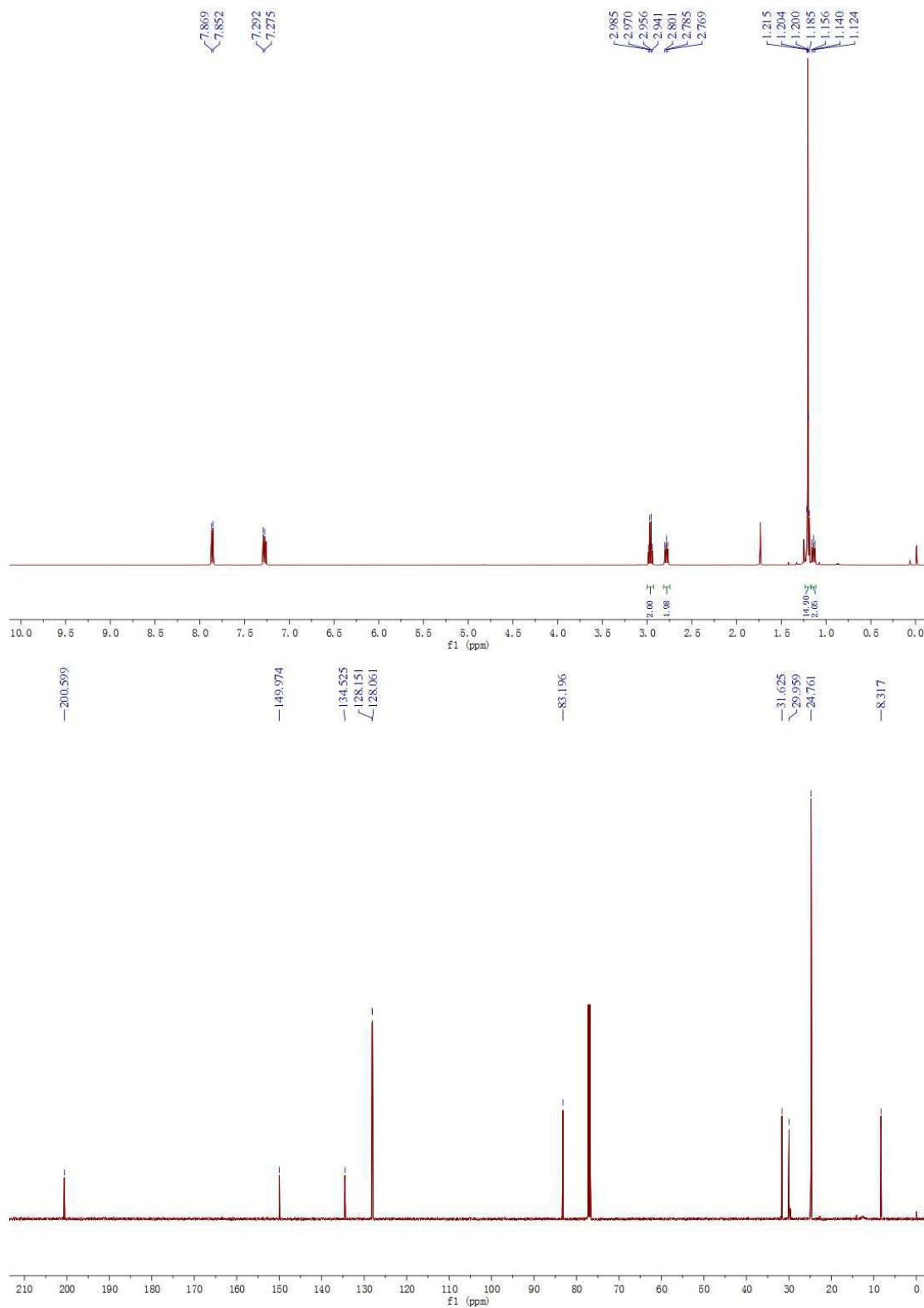


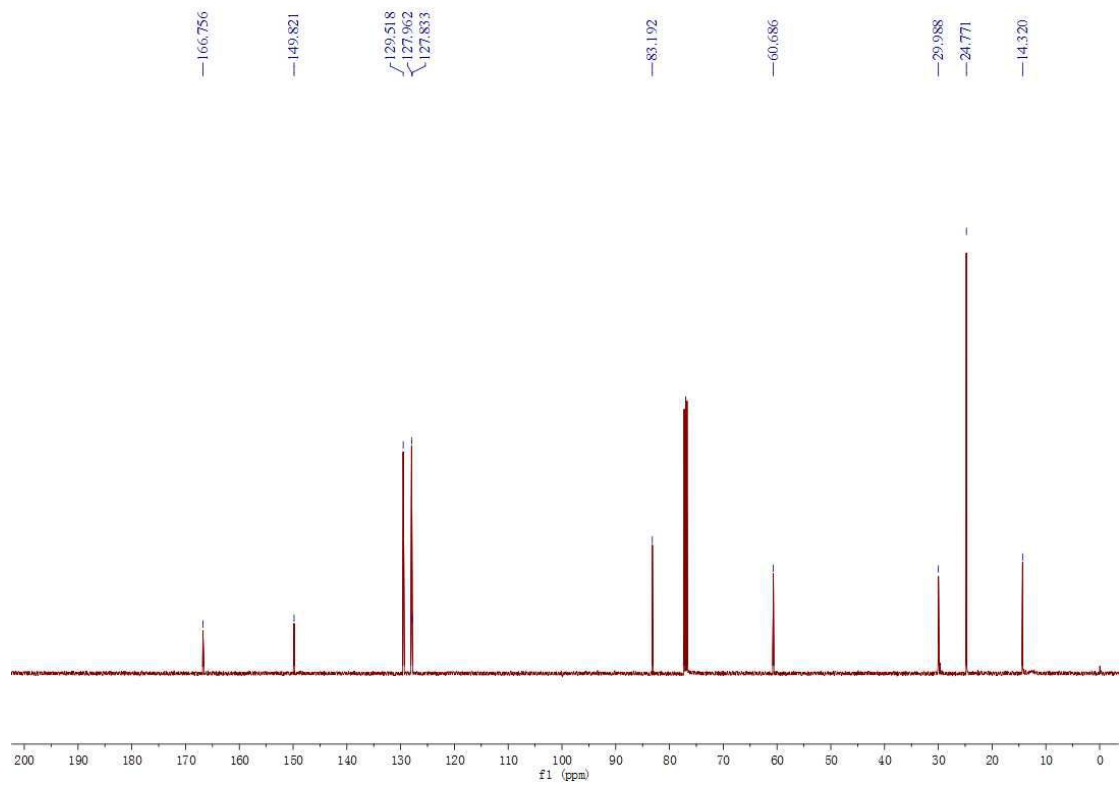
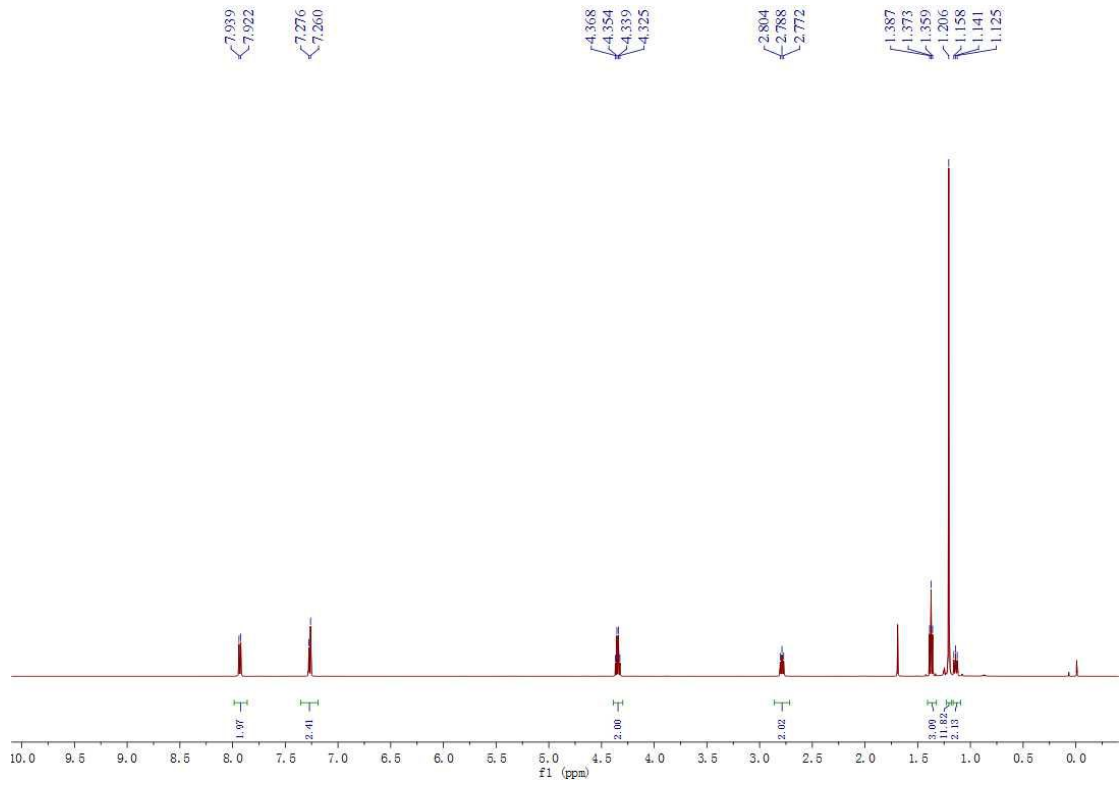
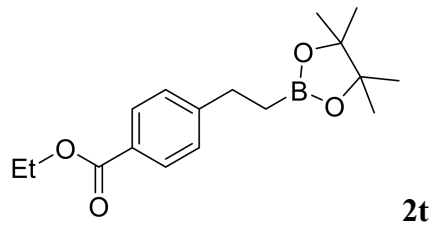
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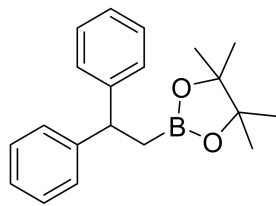




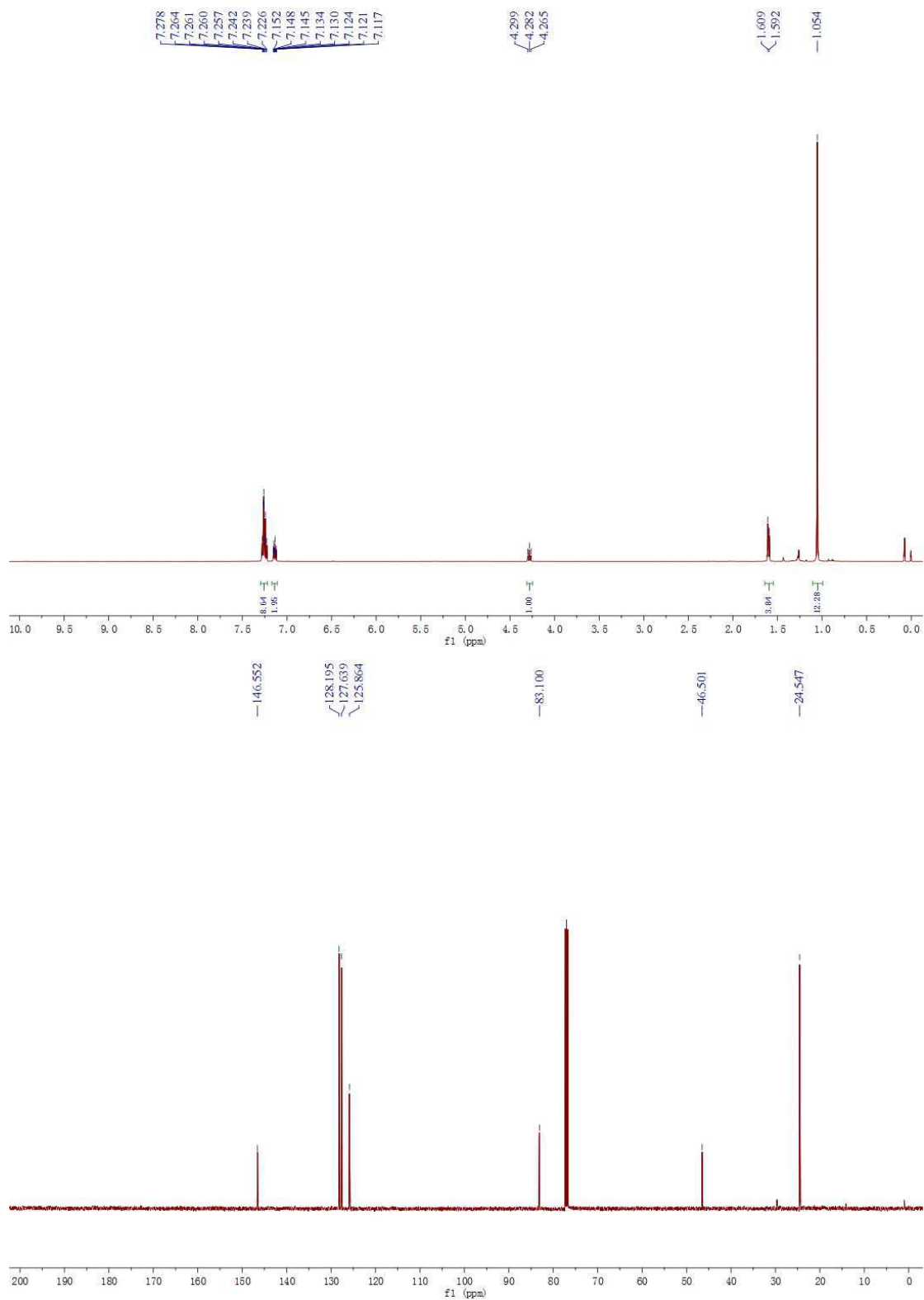
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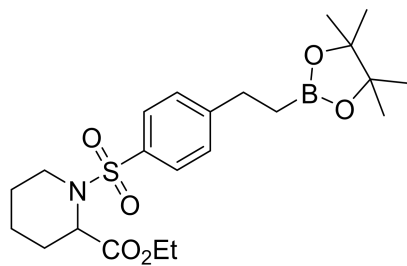




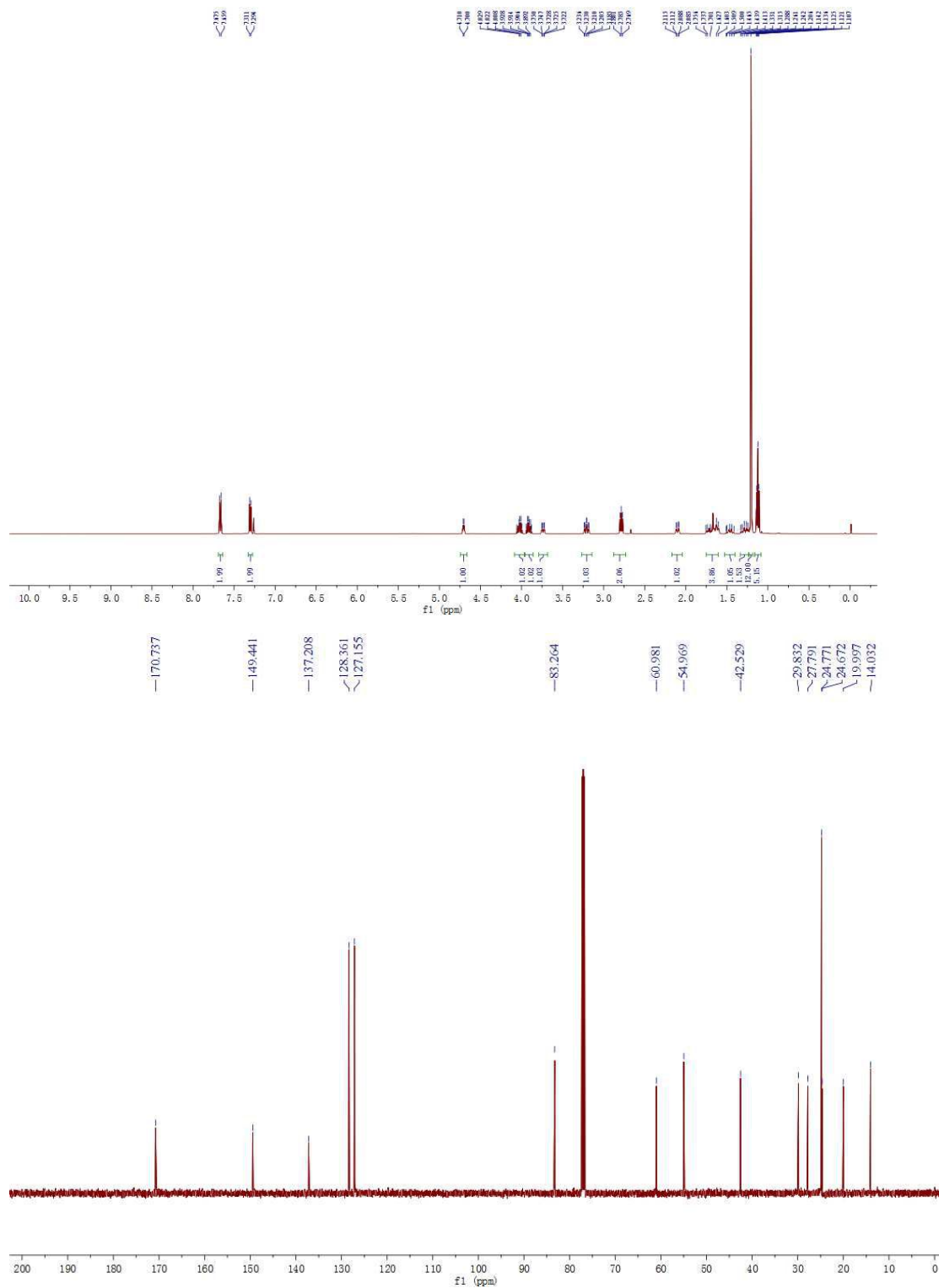


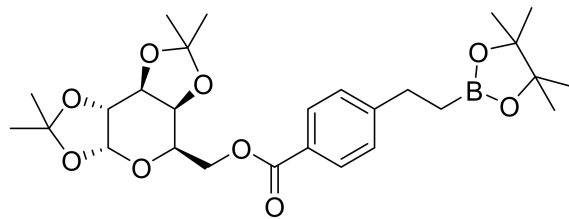
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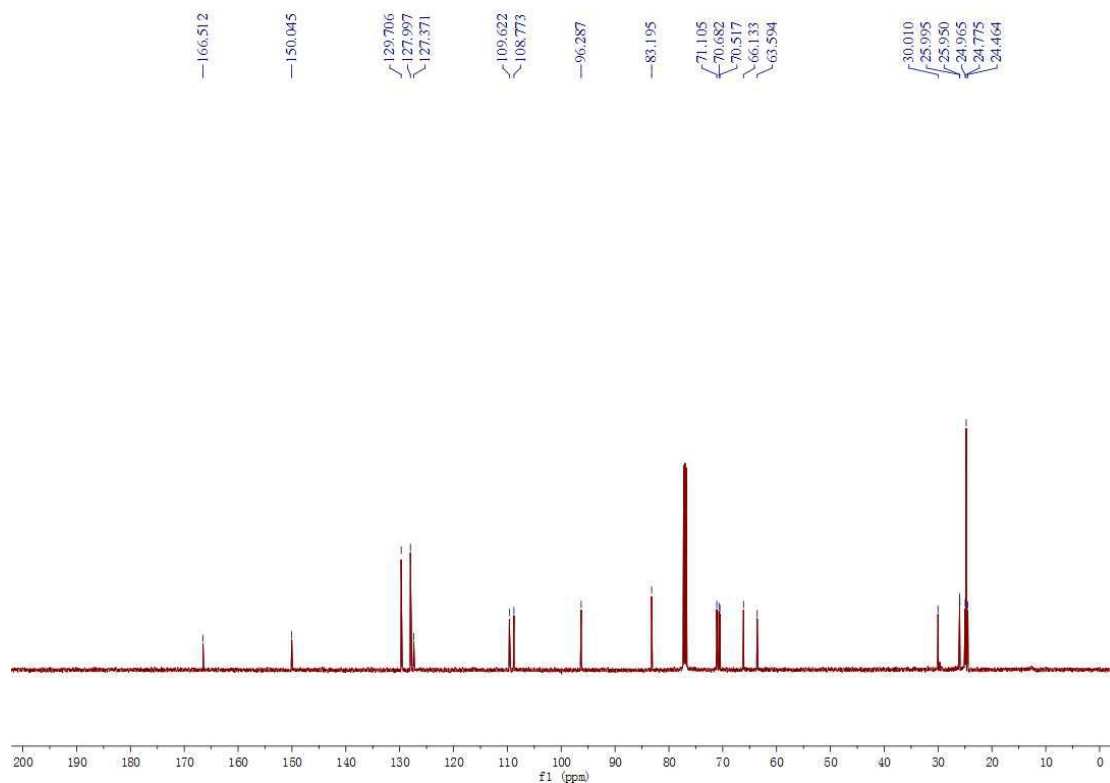
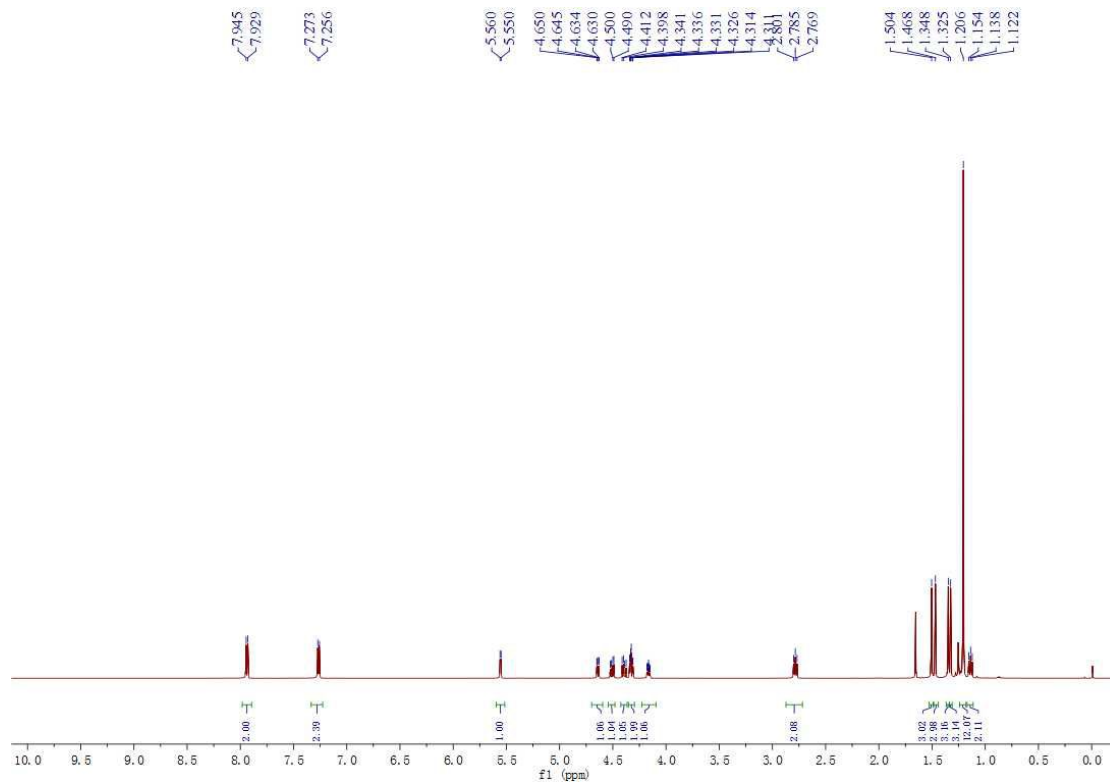


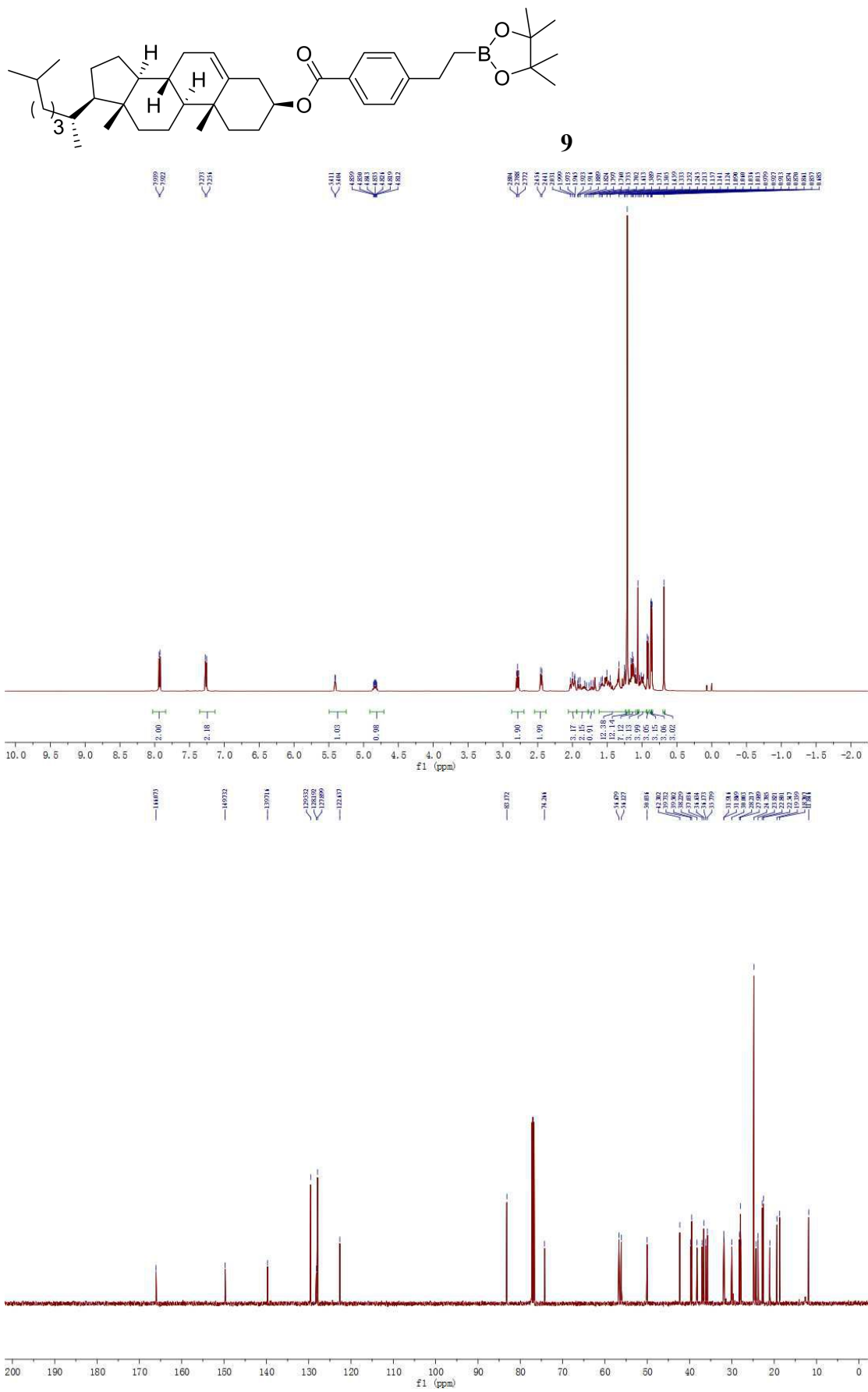
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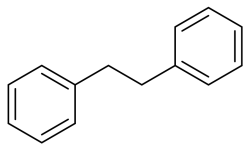




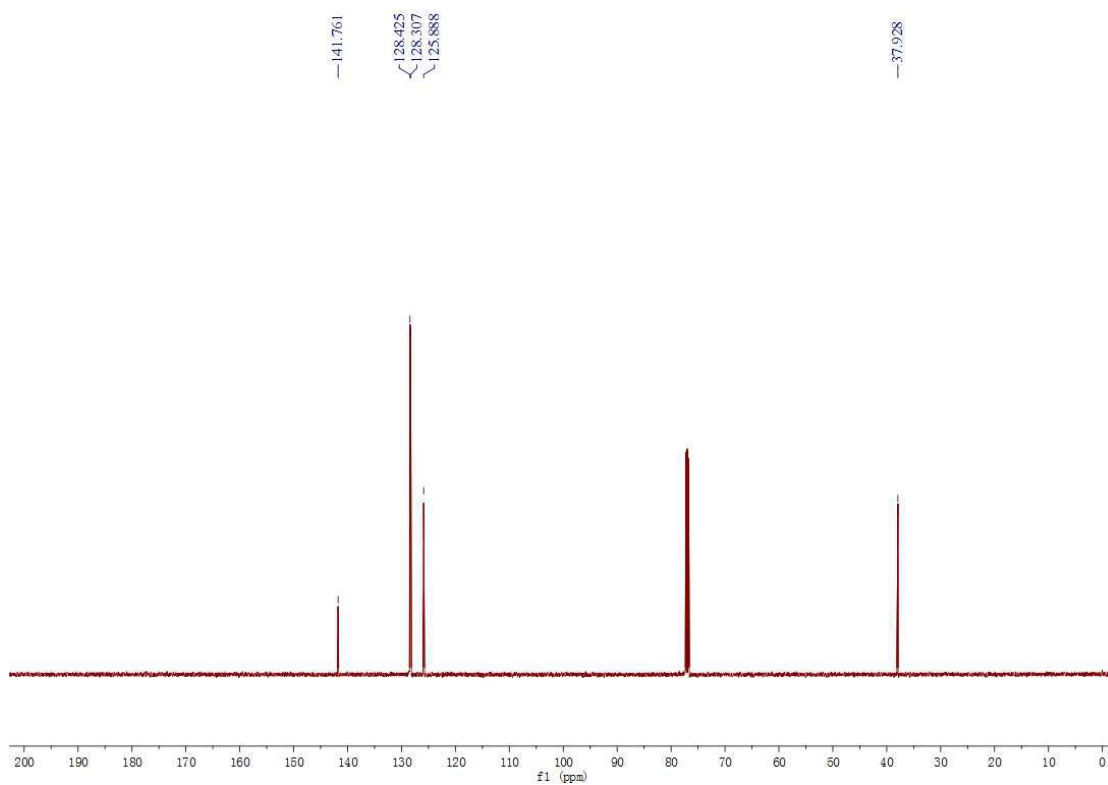
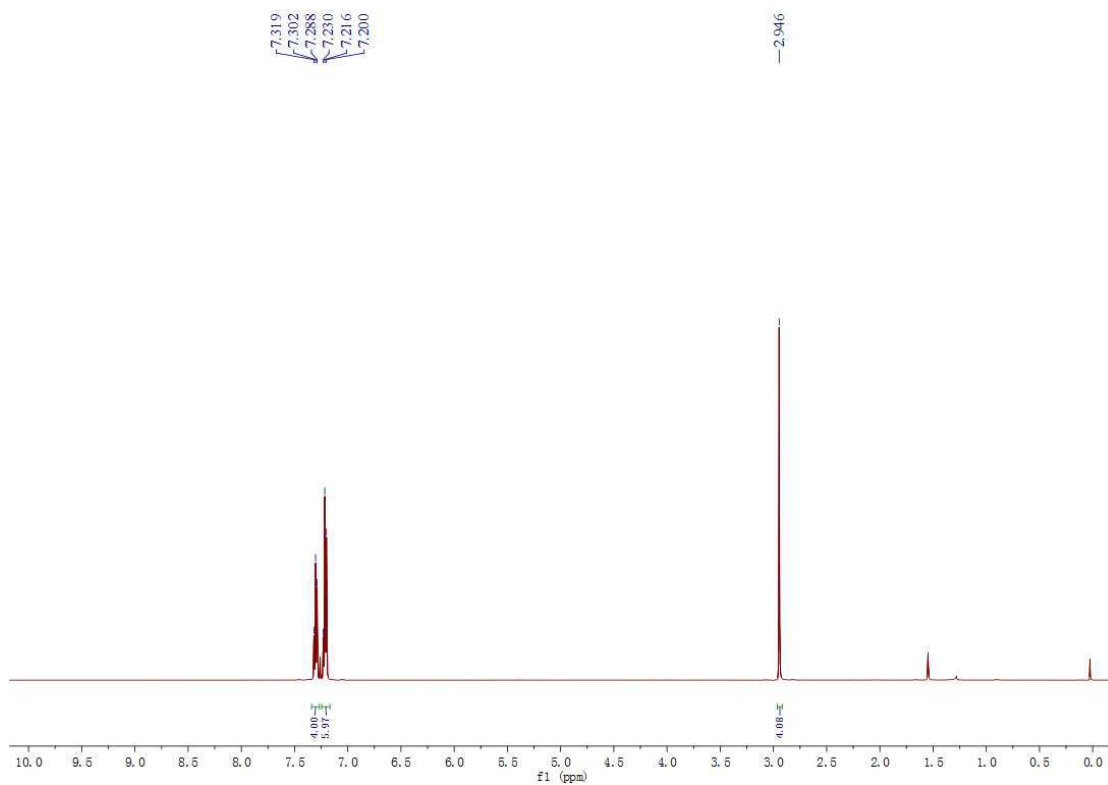
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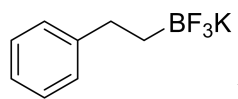




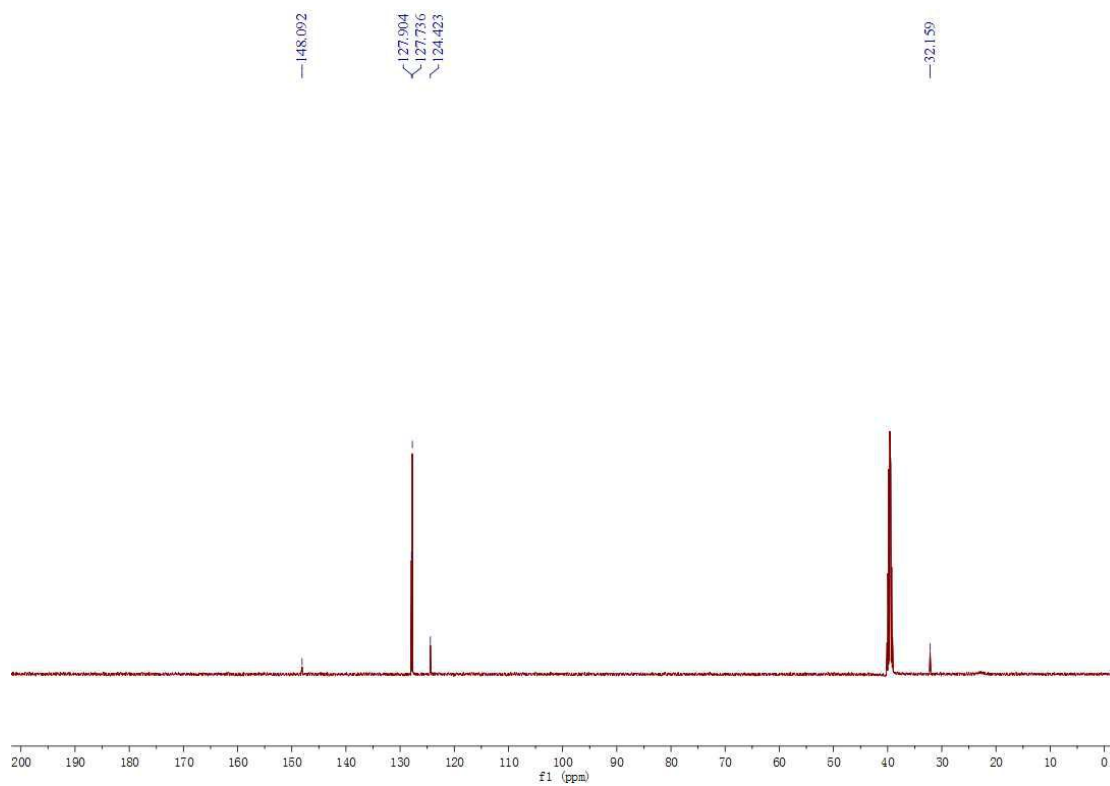
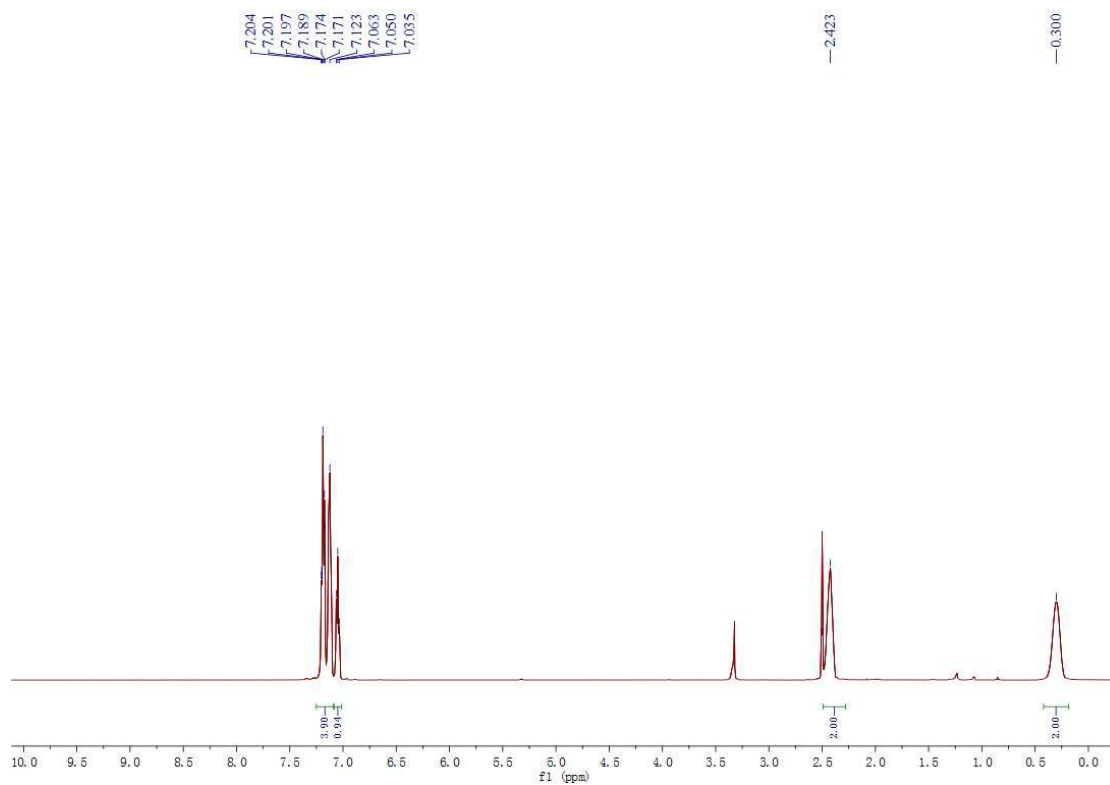


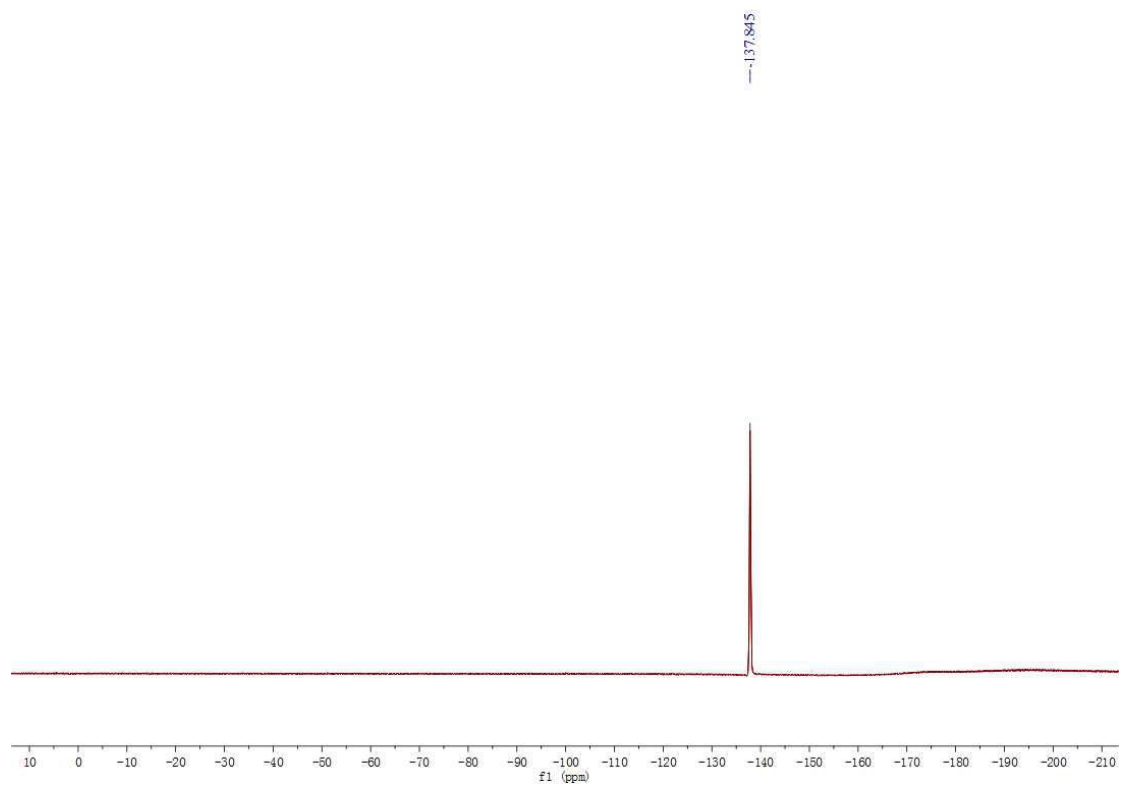
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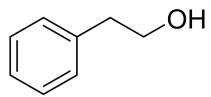




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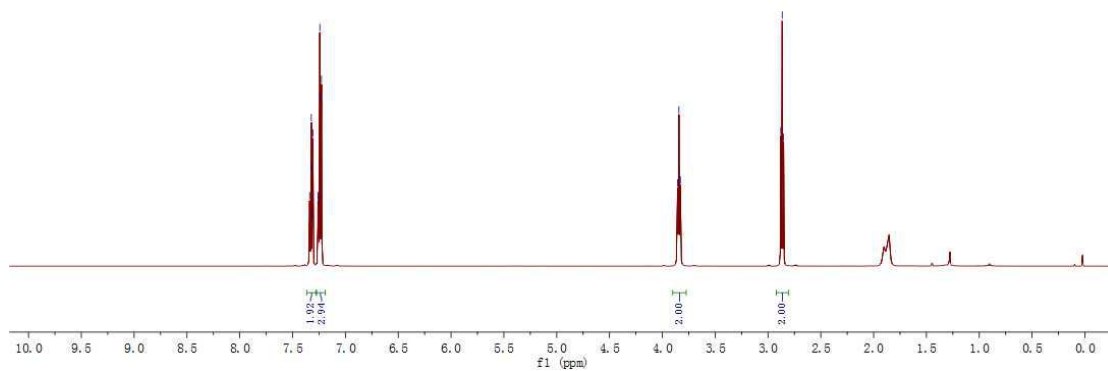


13

7.338
7.326
7.323
7.313
7.308
7.260
7.255
7.253
7.242
7.240
7.227

3.856
3.843
3.830

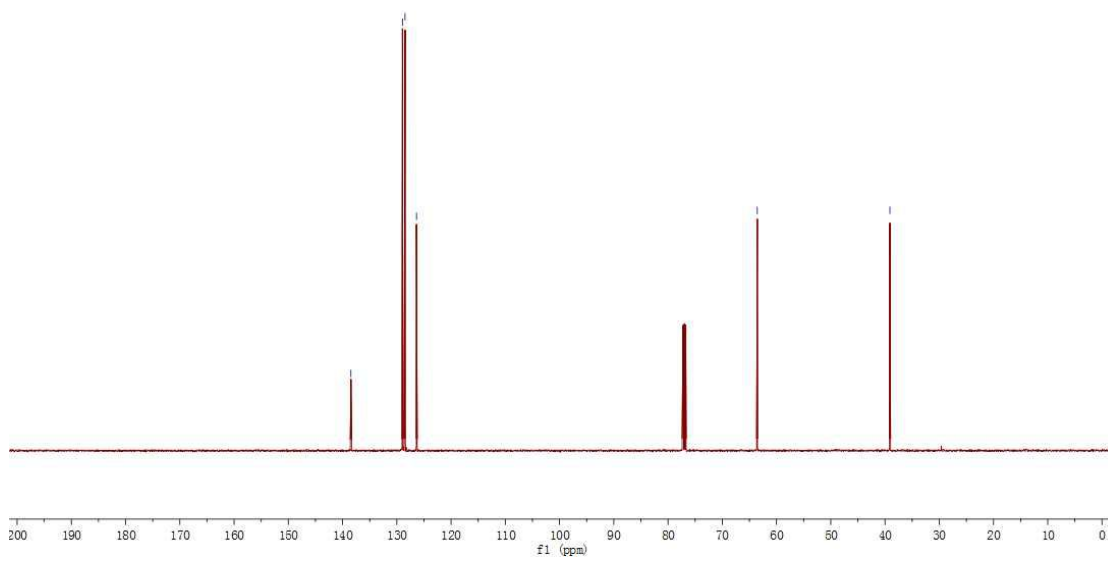
2.879
2.865
2.852

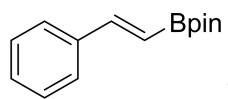


138.462
128.961
128.482
126.368

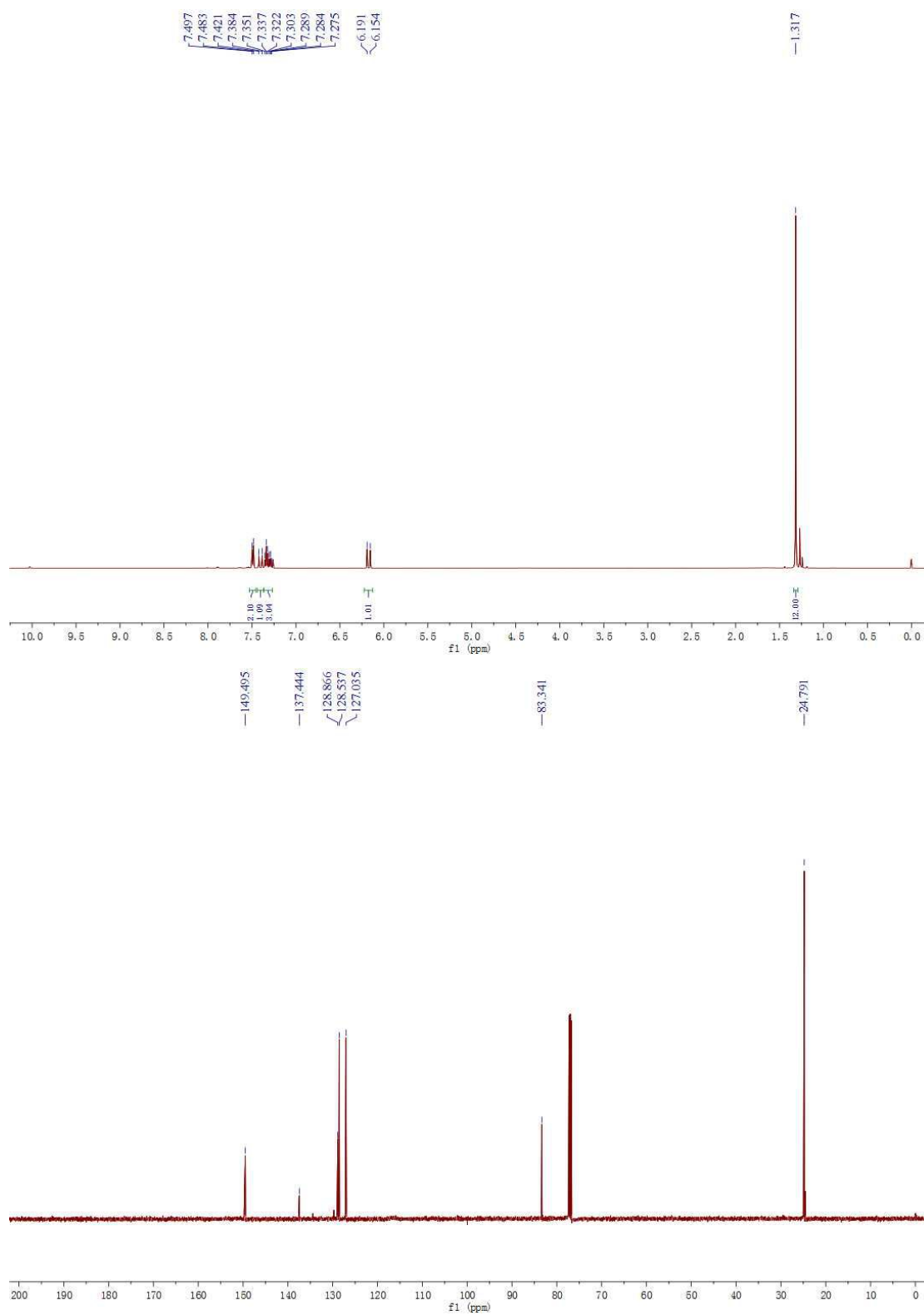
63.547

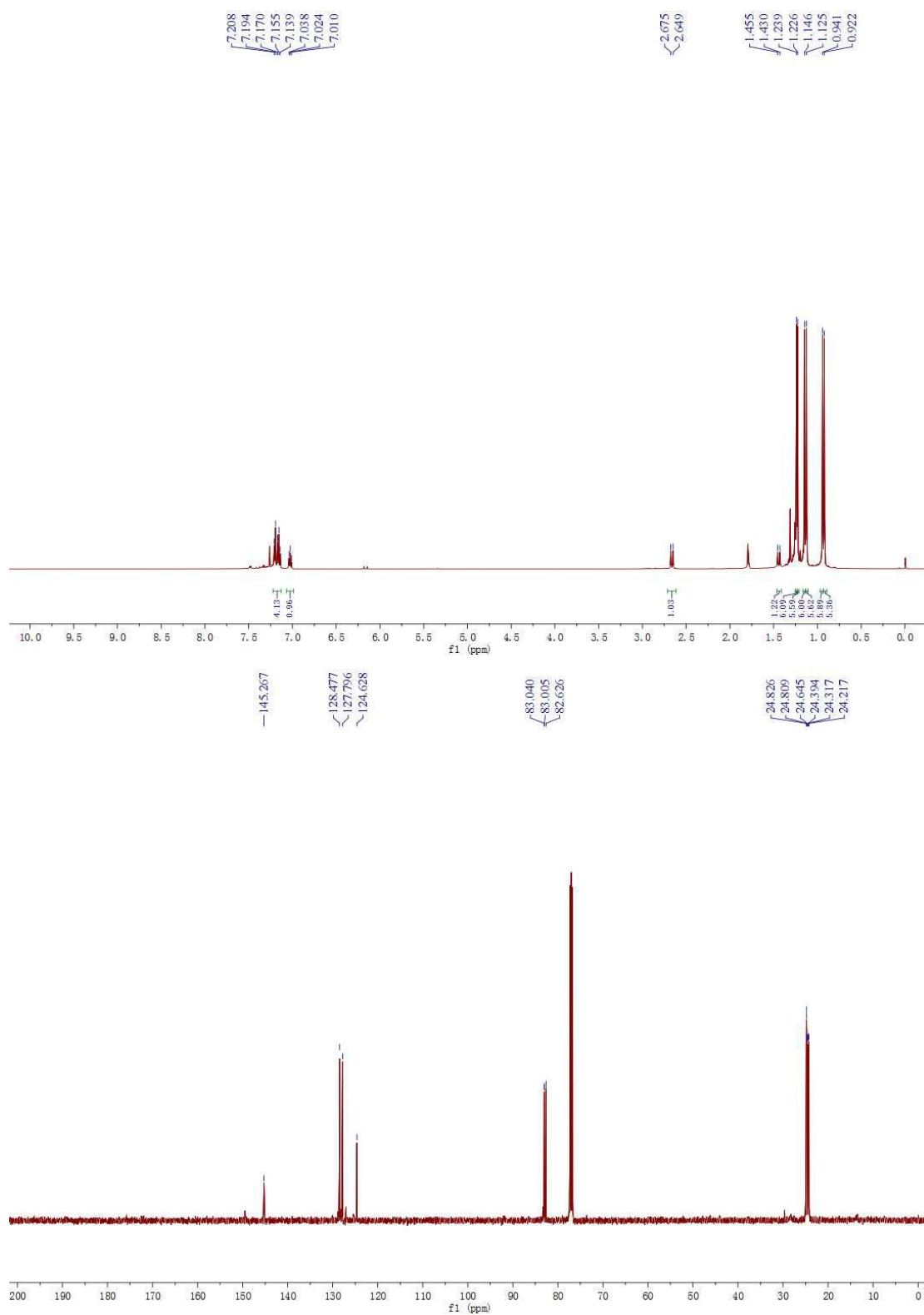
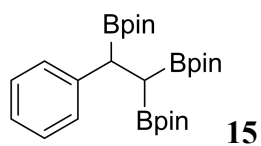
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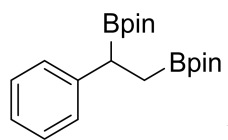




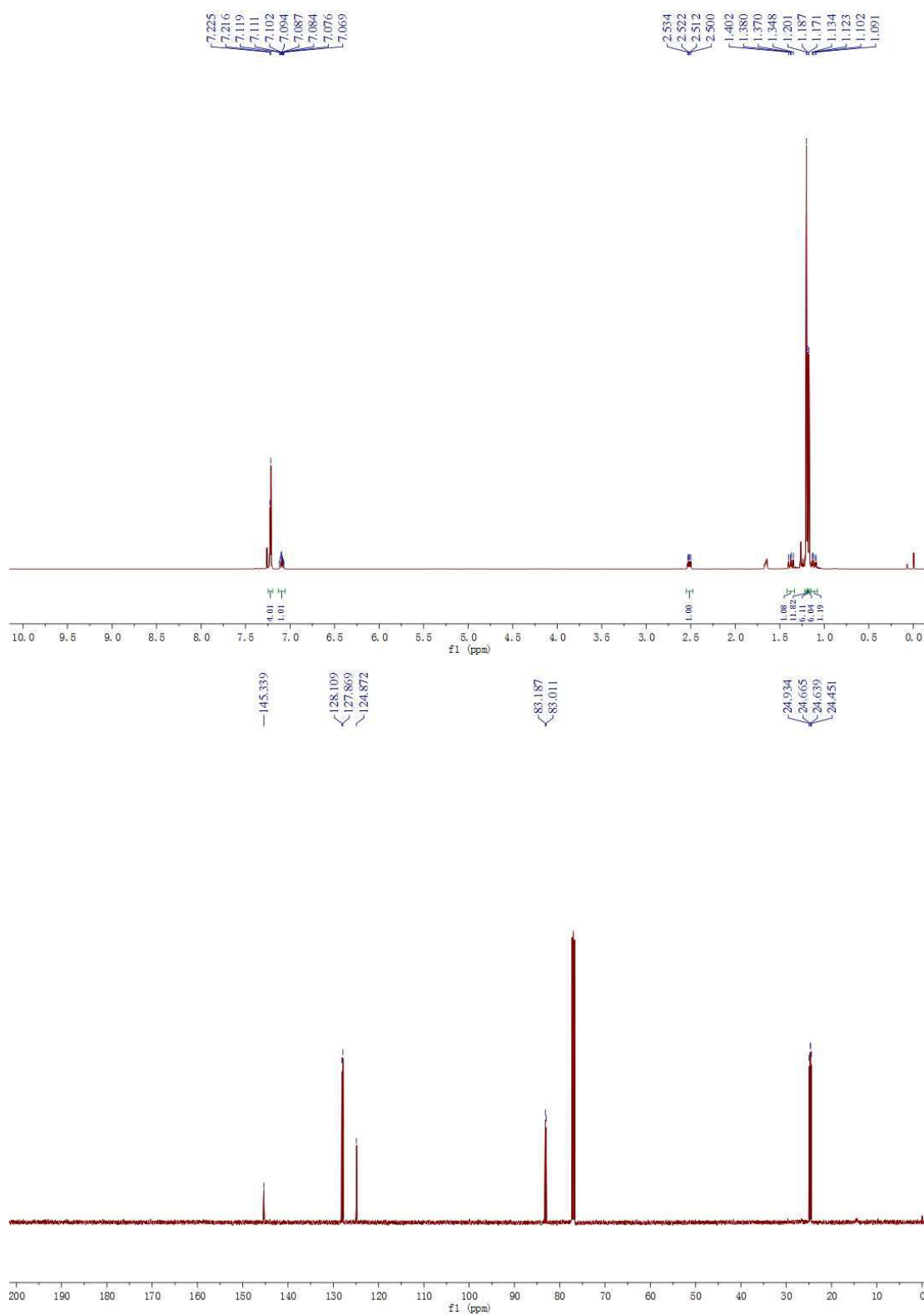
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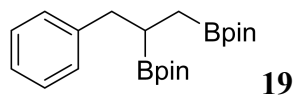






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