Supporting Information for:

Palladium-Catalyzed Hydrocarbonylative Cyclization of 1,5-Dienes

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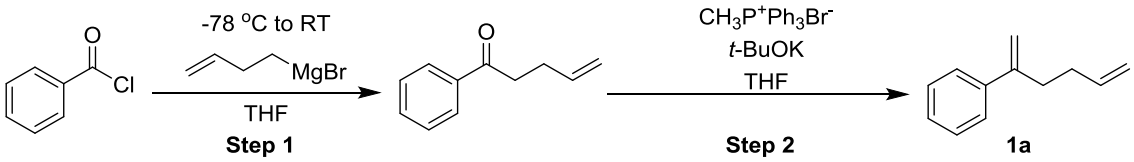
1. General experiment details and materials

Experimental: All non-aqueous reactions and manipulations were using standard Schlenk techniques. All solvents before use were dried and degassed by standard methods and stored under nitrogen atmosphere. All reactions were monitored by TLC with silica gel-coated plates. NMR spectra were recorded on BRUKER Avence III 400 MHz spectrometers. Chemical shifts were reported in parts per million (ppm) down field from TMS with the solvent resonance as the internal standard. Coupling constants (*J*) were reported in Hz and refered to apparent peak multiplications. High resolution mass spectra (HRMS) were recorded on Bruker MicroTOF-QII mass (ESI). GC analysis were performed on Agilent 7890B with Hp-5 column. GC-MS analysis were performed with Agilent 7890B/5975B GC-MS system. Dienes were synthesized according to the reported methods.[1]

2. Preparation and spectral data of 1,5-dienes

Method A: Synthesis of substrate 1a[1a]

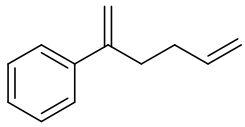


Step 1: To a mixture of the benzoyl chloride (4.6g, 33 mmol, 1.1 equiv) and CuI (279 mg, 1.5 mmol, 5mol%) in THF (45 mL) was added 0.5 M solution of 3-butenylmagnesium bromide in THF (60 mL, 30 mmol, 1.0 equiv.) at -78 ℃ dropwise. The reaction mixture was stirred at -78 ℃ for 1 hour and at room temperature overnight, before it was quenched by adding sat. aq. NH_4Cl solution. Then the aqueous solution was extracted with diethyl ether three times. The combined organic phases were dried over $MgSO_4$, filtered and removed in vacuo. The residue was purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (50/1) to afford 1-phenylpent-4-en-1-one (4.5 g, 94% yield).

Step 2: To a solution of methyltriphenylphosphonium bromide (25 mmol, 1.25 equiv.) in THF (80 mL) was added *t*-BuOK (24 mmol, 1.2 equiv.) at 0 ℃ and the resulting mixture was stirred for 30 minutes at 0 ℃. Then the solution of 1-phenylpent-4-en-1-one (20 mmol, 1.0 equiv.) in THF (20 mL) was added to the reaction mixture dropwise at 0 ℃. After 30 minutes, the ice bath was removed and the mixture was stirred overnight at room temperature, before it was quenched by adding sat. aq. NH_4Cl solution. Then the aqueous solution was extracted with diethyl ether three times. The combined organic phases were dried over $MgSO_4$, filtered and removed in vacuo. The residue was purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (100/1-50/1) to afford hexa-1,5-dien-2-ylbenzene **1a** (2.6 g, 82% yield).

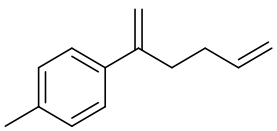
Other compounds including **1b**~**1n,** and **1p**, **1t** were prepared by method **A.**

Hexa-1,5-dien-2-ylbenzene (1a): Known compound.[1a] The title compound was

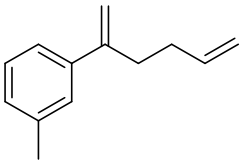


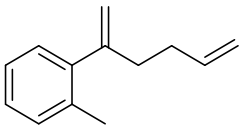
prepared according to the general procedure (Method **A**) and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (100/1) to give the colorless oil (2.6 g, 82% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.19-2.24 (m, 2H), 2.59 (t, *J* =7.6 Hz, 2H), 4.95-5,07 (m, 3H), 5.28 (s , 1H), 5.79-5.90 (m, 1H), 7.24-7.41 (m, 5H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 32.6, 34.9, 112.6, 114.9, 126.3, 127.5, 128.4, 138.3, 141.4, 148.1.

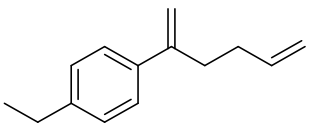
1-(hexa-1,5-dien-2-yl)-4-methylbenzene (1b): Known compound.[2a] The title



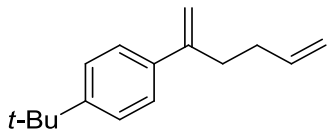
compound was prepared according to the general procedure (Method **A**) and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (100/1) to give the colorless oil (1.63 g, 41% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.18-2.23 (m, 2H), 2.33 (s, 3H), 2.57 (t, *J* = 7.6 Hz, 2H), 4.94-5.02 (m, 3H), 5.25 (d, *J* = 1.2 Hz, 1H), 5.78-5.88 (m, 1H), 7.11-7.13 (d, *J* = 8.0 Hz, 2H), 7.28-7.30(d, *J* = 8.0 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 21.2, 32.6, 34.9, 111.8, 114.8, 126.1, 129.1, 137.2, 138.4, 147.8.

1-(hexa-1,5-dien-2-yl)-3-methylbenzene (1c): The title compound was prepared according to the general procedure (Method **A**) and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (100/1) to give the colorless oil (1.3 g, 36% yield).  **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.18 (m, 2H), 2.36 (s, 3H), 2.58 (t, *J* = 8.0 Hz, 2H), 4.96-5.05 (m, 3H), 5.26 (s, 1H), 5.80-5.90 (m, 1H), 7.08-7.09 (m, 1H), 7.19-7.24 (m, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 21.7, 32.6, 34.9, 112.4, 114.8, 123.4, 127.0, 128.2, 128.3, 137.9, 138.4, 141.4, 148.2. **HRMS** (ESI) calcd. for $C_{13}H_{17}$ [M+H]: 173.1330, found: 173.1333.

1-(hexa-1,5-dien-2-yl)-2-methylbenzene (1d): The title compound was prepared according to the general procedure (Method **A**) and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (100/1) to give the colorless oil (4.3 g, 82% yield).  **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.12-2.17 (m, 2H), 2.29 (s, 3H), 2.42 (t, *J* = 7.6 Hz, 2H), 4.88-5.03 (m, 3H), 5.18 (m, 1H), 5.76-5.86 (m, 1H), 7.05-7.18 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 20.0, 32.1, 37.2, 114.2, 114.8, 125.5, 126.9, 128.5, 130.2, 135.0, 138.4, 143.0, 149.5. **HRMS** (ESI) calcd. for $C_{13}H_{17}$ [M+H]: 173.1330, found: 173.1329.

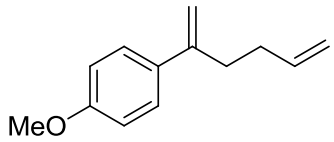
1-ethyl-4-(hexa-1,5-dien-2-yl)benzene (1e): The title compound was prepared according to the general procedure (Method **A**) and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (100/1) to give the colorless oil (1.2 g, 33% yield).  **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.23 (t, *J* = 7.6 Hz, 3H), 2.21 (q, *J* = 7.6 Hz, 2H), 2.57 (t, *J* = 7.6 Hz, 2H), 2.64 (q, *J* = 7.6 Hz, 2H), 4.94-5.02 (m, 3H), 5.26 (s, 1H), 5.79-5.89 (m, 1H), 7.15 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 15.7, 28.6, 32.6, 34.8, 111.9, 114.8, 126.2, 127.9, 138.4, 138.6, 143.6, 147.8. **HRMS** (ESI) calcd. for $C_{14}H_{19}$ [M+H]: 187.1487, found: 187.1474.

1-(tert-butyl)-4-(hexa-1,5-dien-2-yl)benzene (1f): The title compound was prepared



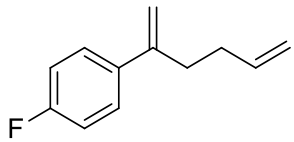
according to the general procedure (Method **A**) and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (100/1) to give the colorless oil (2.3 g, 58% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.32 (s, 9H), 2.20-2.26 (m, 2H), 2.56-2.60 (m, 2H), 4.95-5.05 (m, 3H), 5.28 (d, *J* = 1.6 Hz, 1H), 5.80-5.90 (m, 1H), 7.35 (m, 4H),; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 31.5, 32.7, 34.6, 34.7, 111.9, 114.8, 125.3, 125.8, 138.3, 138.4, 147.6, 150.5. **HRMS** (ESI) calcd. for $C_{16}H_{23}$ [M+H]: 215.1800, found: 215.1801.

1-(hexa-1,5-dien-2-yl)-4-methoxybenzene (1g): Known compound.[2b] The title



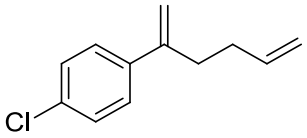
compound was prepared according to the general procedure (Method **A**) and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (50/1) to give the colorless oil (1.7 g, 65% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.18-2.23(m, 2H), 2.56 (t, *J* = 8.0 Hz, 2H), 3.79 (s, 3H), 4.94-5.03 (m, 3H), 5.21 (d, *J* = 1.2 Hz, 1H), 5.79-5.89 (m, 1H), 6.84-6.87 (m, 2H), 7.32-7.36 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 32.6, 34.9, 55.3, 111.0, 113.7, 114.8, 127.3, 133.7, 138.3, 147.3, 159.1.

1-fluoro-4-(hexa-1,5-dien-2-yl)benzene (1h): Known compound.[2b] The title

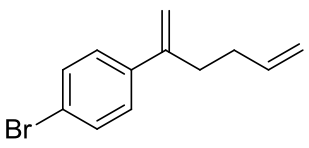


compound was prepared according to the general procedure (Method **A**) and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (100/1) to give the colorless oil (0.9 g, 48% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.16-2.22 (m, 2H), 2.56 (t, *J* = 8.4 Hz, 2H), 4.95-5.02 (m, 2H), 5.05 (d, *J* = 1.2 Hz, 1H), 5.22 (s, 1H), 5.77-5.87 (m, 1H), 6.98-7.02 (m, 2H), 7.33-7.37 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 32.5, 35.0, 112.6, 115.0, 115.3 (d, J_{C-F} = 20.0 Hz), 127.9 (d, J_{C-F} = 10.0 Hz), 137.4 (d, J_{C-F} = 10.0 Hz), 138.1, 147.0, 161.2, 163.6 (d, J_{C-F} = 240.0 Hz); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -115.3.

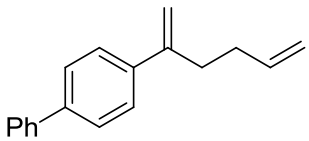
1-chloro-4-(hexa-1,5-dien-2-yl)benzene (1i): Known compound.[2b] The title compound was prepared according to the general procedure (Method **A**) and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (100/1) to give the colorless oil (1.95 g, 43% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.16-2.22 (m, 2H), 2.56 (t, *J* = 8.0 Hz, 2H), 4.95-5.02 (m, 2H), 5.08 (d, *J* = 1.2 Hz, 1H), 5.27 (s, 1H), 5.76-5.87 (m, 1H), 7.27-7.33 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 32.5, 34.8, 113.1, 115.0, 127.6, 128.5, 133.3, 138.0, 139.8, 146.9.



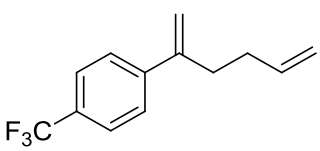
1-bromo-4-(hexa-1,5-dien-2-yl)benzene (1j): Known compound.[2c] The title compound was prepared according to the general procedure (Method **A**) and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (100/1) to give the colorless oil (2.5 g, 58% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.15-2.21 (m, 2H), 2.52-2.56 (m, 2H), 4.94-5.02 (m, 2H), 5.07-5.08 (m, 1H), 5.25-5.26 (m, 1H), 5.75-5.85 (m, 1H), 7.22-7.26 (m, 2H), 7.41-7.44 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 32.4, 34.7, 113.2, 115.1, 121.4, 127.9, 131.5, 138.0, 140.2, 146.9.



4-(hexa-1,5-dien-2-yl)-1,1'-biphenyl (1k): Known compound.[2b] The title compound was prepared according to the general procedure (Method **A**) and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (100/1) to give the a white solid (2.3 g, 60% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.23-2.28 (m, 2H), 2.61-2.65 (m, 2H), 4.96-5.05 (m, 2H), 2.61-2.65 (m, 2H), 5.10 (d, *J* = 1.2 Hz, 1H), 5.35 (d, *J* = 1.2 Hz, 1H), 5.81-5.91 (m, 1H), 7.32-7.36 (m, 1H), 7.41-7.49 (m, 4H), 7.55-7.61 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 32.6, 34.8, 112.6, 114.9, 126.6, 127.1, 127.1, 127.4, 128.9, 138.3, 140.2, 140.3, 140.9, 147.5.

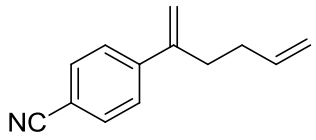


1-(hexa-1,5-dien-2-yl)-4-(trifluoromethyl)benzene (1l): Known compound.[2d] The title compound was prepared according to the general procedure (Method **A**) and purified by column

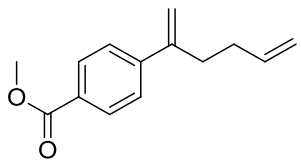


chromatography on silica gel and eluted with petroleum ether/ethyl acetate (50/1) to give the colorless oil (4.0 g, 75% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.17-2.22 (m, 2H), 2.60 (t, *J* = 7.6 Hz, 2H) , 4.96-5.02 (m, 2H), 5.16 (d, *J* = 1.2 Hz,1H), 5.33 (s, 1H) 5.76-5.87 (m, 1H), 7.47 (d, *J* = 8.0 Hz, 2H), 7.57 (d, *J* = 8.2 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 32.4, 34.7, 114.6, 115.2, 123.0, 125.4 (q, J_{C-F} = 4.0 Hz), 126.6, 129.5 (q, J_{C-F} = 32.0 Hz) , 137.8, 145.0, 147.0; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.5.

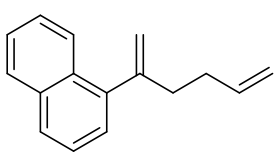
4-(hexa-1,5-dien-2-yl)benzonitrile (1m): The title compound was prepared according to the general procedure (Method **A**) and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (50/1) to give the colorless oil (3.8 g, 97% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.17-2.23 (m, 2H), 2.57-2.61 (m, 2H), 4.96-5.03 (m, 2H), 5.22 (d, *J* = 1.2 Hz, 1H), 5.38 (s, 1H), 5.76-5.86 (m, 1H), 7.47-7.50 (m, 2H), 7.61-7.63 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 32.3, 34.3, 111.0, 115.3, 115.5, 119.0, 126.9, 132.3, 137.5, 145.9, 146.5. **HRMS** (ESI) calcd. for $C_{13}H_{14}N$ [M+H]: 184.1126, found: 184.1122.



methyl 4-(hexa-1,5-dien-2-yl)benzoate (1n): The title compound was prepared according to the general procedure (Method **A**) and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (50/1) to give the colorless oil (3.8 g, 84% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.07-2.12 (m, 2H), 2.47-2.51 (m, 2H), 3.80 (s, 3H), 4.85-4.91 (m, 2H), 5.05 (d, *J* = 1.2 Hz, 1H), 5.26 (s, 1H), 5.66-5.76 (m, 1H), 7.34 (d, *J* = 8.4 Hz, 2H), 7.89 (d, *J* = 8.4 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 32.3, 34.5, 52.1, 114.4, 115.0, 126.1, 129.0, 129.7, 137.8, 145.8, 147.1, 166.9. **HRMS** (ESI) calcd. for $C_{14}H_{17}O_2$ [M+H]: 217.1229, found: 217.1227.

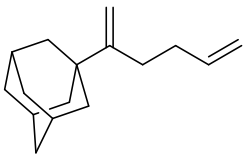


1-(hexa-1,5-dien-2-yl)naphthalene (1p): The title compound was prepared according to the general procedure (Method **A**) and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (50/1) to give the colorless oil (3.8 g, 84%



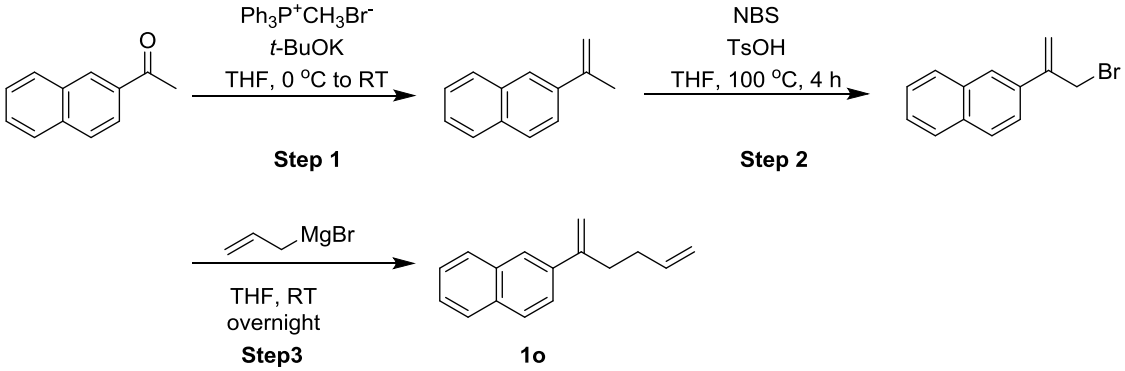
yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.14-2.20 (m, 2H), 2.60 (t, *J* = 8.0 Hz, 2H), 4.93-5.01 (m, 2H), 5.09 (s, 1H), 5.40 (t, *J* = 1.2 Hz, 1H), 5.76-5.87 (m, 1H), 7.25-7.27 (m, 1H), 7.38-7.46 (m, 3H), 7.73 (d, *J* = 8.0 Hz, 1H), 7.81-7.83 (m, 3H), 8.01-8.04 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 32.4, 38.0, 115.0, 125.2, 125.3, 125.8, 125.9, 125.9, 127.3, 128.4, 131.4, 133.8, 138.2, 141.3, 148.3. **HRMS** (ESI) calcd. for $C_{16}H_{17}$ [M+H]: 209.1330, found: 209.1323.

(1S,3s)-1-(hexa-1,5-dien-2-yl)adamantane (1t): The title compound was prepared



according to the general procedure (Method **A**) and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (100/1) to give the colorless oil (1.6 g, 48% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.64-1.73 (m, 12H), 2.00 (s, 3H), 2.07-2.11 (m, 2H), 2.16-2.22 (m, 2H), 4.71 (d, *J* = 1.2 Hz, 1H), 4.81 (s, 1H), 4.92-5.05 (m, 2H), 5.79-5.89 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 28.8, 29.6, 33.8, 37.1, 38.0, 41.2, 106.4, 114.4, 139.2, 158.1. **HRMS** (ESI) calcd. for $C_{16}H_{25}$ [M+H]: 217.1956, found: 217.1960.

Method B: Synthesis of substrate 1o[1b]



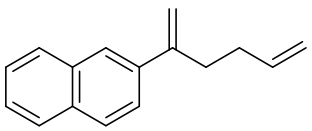
Step 1: In an oven dried flask, methyl triphenylphosphonium bromide (1.2 equiv.) was taken and THF (1.6 mL/mmol) was added. The suspension was cooled to 0 ℃, *t*-BuOK (1.2 equiv.) was added and the resulting yellow suspension was stirred at 0 ℃ for 30 minutes. To this suspension, a solution of ketone (1.0 equiv.) in THF (0.7 mL/mmol) was added dropwise and the resulting mixture was warmed gradually to

room temperature and stirred overnight. Reaction mixture was concentrated under reduced pressure and filtered over celite. The filtrate was concentrated under reduced pressure to yield yellow oil. The crude product was purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (100/1) to afford 2-(prop-1-en-2-yl)naphthalene (4.6 g, 89%).

Step 2: In an oven dried flask 2-(prop-1-en-2-yl)naphthalene (1.0 equiv.) was taken and to this dry THF (3.0 mL/mmol) was added. To the resulting solution N-Bromosuccinimide (1.05 equiv.) and TsOH (0.1 equiv.) was added and the solution was refluxed at 100 ℃ for 4 hours. Reaction mixture was cooled to room temperature and the reaction mixture was taken in petroleum ether (15 mL/mmol), washed with H_2O (15 mL × 3). Organic phase was dried over $MgSO_4$, concentrated under reduced pressure to obtain a yellow oil. The crude product was purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (100/1) to afford 2-(3-bromoprop-1-en-2-yl)naphthalene (3.2 g, 48%).

Step 3: To a solution of the 2-(3-bromoprop-1-en-2-yl)naphthalene (5 mmol, 1.0 equiv.) in THF (20 mL) was added 1 M solution of 3-butenylmagnesium bromide in diethyl ether (7.5 mL, 7.5 mmol, 1.5 equiv.) at room temperature. The reaction mixture was stirred at room temperature overnight, before it was quenched by adding sat. aq. NH_4Cl solution. Then the aqueous solution was extracted with diethyl ether three times. The combined organic phases were washed with sat. aq. $NaHCO_3$ solution and brine, dried over $MgSO_4$, filtered and removed in vacuo. The residue was purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (100/1) to afford 2-(hexa-1,5-dien-2-yl)naphthalene **1o** as a colorless oil (1.2 g, 44%).

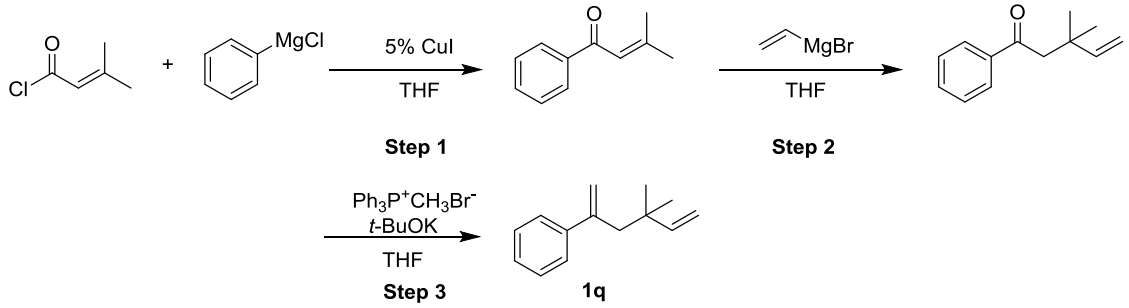
2-(hexa-1,5-dien-2-yl)naphthalene (1o): Known compound.[2b] The title compound



was prepared according to the general procedure (Method **B**) and purified by column chromatography to give the colorless oil (1.2 g, 44%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.14-2.20 (m, 2H), 2.60 (t, *J* = 8.0 Hz, 2H), 4.93-5.02 (m,, 2H), 5.09 (d, *J* = 2.0 Hz, 1H), 5.41 (m, 1H), 5.77-5.87 (m, 1H), 7.26-7.28 (m, 2H), 7.39-7.47 (m, 3H), 7.74 (d, *J* = 8.0 Hz, 1H),

7.81-7.85 (m, 1H), 8.00-8.03 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 32.4, 38.0, 115.0, 115.7, 125.2, 125.3, 125.8, 125.9, 125.9, 127.3, 128.4, 131.4, 133.8, 138.3, 141.3, 148.3.

Procedure C: Synthesis of substrate 1q

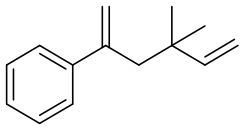


Step 1: To a mixture of the 3-methylbut-2-enoyl chloride (55 mmol, 1.1 equiv.) and CuI (465 mg, 2.5 mmol, 5 mol%) in THF (90 mL) was added 1 M solution of phenylmagnesium chloride in THF (50 mL, 50 mmol, 1.0 equiv.) at -78 ℃ dropwise. The reaction mixture was stirred at -78 ℃ for 1 hour and at room temperature overnight, before it was quenched by adding sat. aq. NH_4Cl solution. Then the aqueous solution was extracted with diethyl ether three times. The combined organic phases were dried over $MgSO_4$, filtered and removed in vacuo. The residue was was purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (50/1) to afford 3-methyl-1-phenylbut-2-en-1-one (5.0 g, 63% yield).

Step 2: To a solution of the 3-methyl-1-phenylbut-2-en-1-one (30 mmol, 1.0 equiv.) in THF (60 mL) was added 1 M solution of vinylmagnesium bromide in THF (45 mL, 45 mmol, 1.5 equiv.) at room temperature. The reaction mixture was stirred at room temperature overnight, before it was quenched by adding sat. aq. NH_4Cl solution. Then the aqueous solution was extracted with diethyl ether three times. The combined organic phases were washed with sat. aq. $NaHCO_3$ solution and brine, dried over $MgSO_4$, filtered and removed in vacuo. The residue was purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (50/1) to afford 3,3-dimethyl-1-phenylpent-4-en-1-one as a colorless oil (4.0 g, 70%).

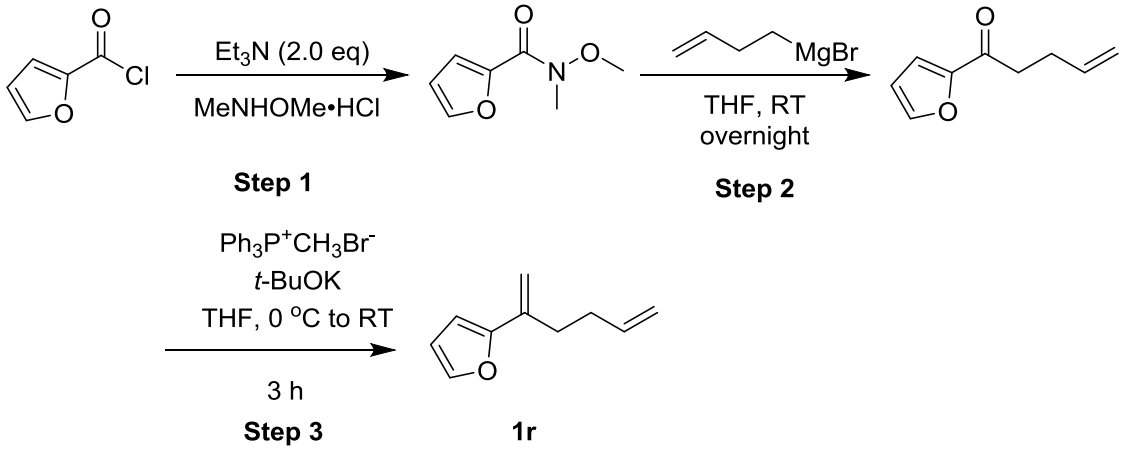
Step 3: To a solution of methyltriphenylphosphonium bromide (25 mmol, 1.25 equiv.) in THF (80 mL) was added *t*-BuOK (24 mmol, 1.2 equiv.) at 0 ℃ and the resulting mixture was stirred for 30 minutes at 0 ℃. Then the solution of 3,3-dimethyl-1-phenylpent-4-en-1-one (20 mmol, 1.0 equiv.) in THF (20 mL) was added to the reaction mixture dropwise at 0 ℃. After 30 minutes the ice bath was removed and the mixture was stirred overnight at room temperature, before it was quenched by adding sat. aq. NH_4Cl solution. Then the aqueous solution was extracted with diethyl ether three times. The combined organic phases were dried over $MgSO_4$, filtered and removed in vacuo. The residue was purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (100/1) to afford (4,4-dimethylhexa-1,5-dien-2-yl)benzene **1q** (2.6 g, 67%).

(4,4-dimethylhexa-1,5-dien-2-yl)benzene (1q): The title compound was prepared



according to the general procedure (Method **C**) and purified by column chromatography to give the colorless oil (2.6 g, 67%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 0.90 (s, 6H), 2.54 (s, 2H), 4.75-4.83 (m, 2H), 5.01 (t, *J* = 0.8 Hz, 1H), 5.24 (d, *J* = 2.0 Hz, 1H), 5.69-5.76 (m, 1H), 7.20-7.35 (m, 5H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 27.2, 37.7, 47.9, 109.9, 116.8, 126.8, 127.1, 128.2, 143.6, 146.8, 148.6. **HRMS** (ESI) calcd. for $C_{14}H_{19}$ [M+H]: 187.1487, found: 187.1490.

Procedure D: Synthesis of substrate 1r[1c]



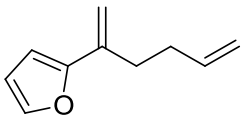
Step 1: Triethylamine (100 mmol, 2.0 equiv.) was slowly added to the mixture of furan-2-carbonyl chloride (50 mmol, 1.0 equiv.) and N,O-dimethylhydroxylamine hydrochloride (52.5 mmol, 1.05 equiv.) in dry CH_2Cl_2 at 0 ℃. The reaction mixture was allowed to warm up to room temperature and was stirred for 12 hours. After the addition of HCl (aq., 1.0 N, 100 mL), the phases were separated and the aqueous layer was extracted with CH_2Cl_2 (40 × 3 mL). The combined organic phases were dried over $MgSO_4$, filtered and then the solvent was removed in vacuo to afford the Weinreb amide. The crude product was purifiedby column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (2/1) to afford N-methoxy-N-methylfuran-2-carboxamide (6.4 g, 82%).

Step 2: A solution of 3-butenylmagnesium bromide (0.5 M in THF, 42 mmol, 1.05 equiv.) was added over 1 hour to the solution of N-methoxy-N-methylfuran-2-carboxamide (40 mmol, 1.0 equiv.) in dry THF at 0 ℃. The reaction mixture was allowed to warm up to room temperature and was stirred for 3 hours. The pH of the reaction mixture was adjusted to pH = 2 by the addition of HCl (aq., 1.0 N). The phases were separated and the aqueous layer was extracted with diethyl ether (30 × 3 mL). The combined organic phases were dried over $MgSO_4$, filtered and the solvent was removed in vacuo. The residue was purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (50/1) to afford 1-(furan-2-yl)pent-4-en-1-one (5 g, 83%).

Step 3: To a solution of methyltriphenylphosphonium bromide (41 mmol, 1.25 equiv.) in THF was added *t*-BuOK (40 mmol, 1.2 equiv.) at 0 ℃ and the resulting mixture was stirred for 30 minutes at 0 ℃. Then the solution of 1-(furan-2-yl)pent-4-en-1-one (33 mmol, 1.0 equiv.) in THF was added to the reaction mixture dropwise at 0 ℃. After 30 minutes the ice bath was removed and the mixture was stirred overnight at room temperature, before it was quenched by adding sat. aq. NH_4Cl solution. Then the aqueous solution was extracted with diethyl ether (30 × 3 mL). The combined organic phases were dried over $MgSO_4$, filtered and removed in vacuo. The residue was

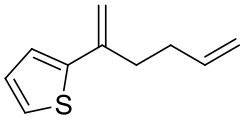
purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (100/1) to afford 2-(hexa-1,5-dien-2-yl)furan **1r** (3.5 g, 71%).

2-(hexa-1,5-dien-2-yl)furan (1r): The title compound was prepared according to the general procedure (Method **D**) and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (100/1) to give the colorless oil (3.5 g, 71%).



^{1}H NMR (400 MHz, $CDCl_3$) δ 2.30-2.35 (m, 2H), 2.43-2.47 (m, 2H), 4.97-5.08 (m, 3H), 5.54 (s, 1H), 5.82-5.92 (m, 1H), 6.30 (d, *J* = 3.2 Hz, 1H), 6.37-6.38 (m, 1H), 7.35 (d, *J* = 8.0Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 32.7, 32.9, 106.1, 109.6, 111.2, 115.0, 137.0, 138.2, 141.9, 154.7. **HRMS** (ESI) calcd. for $C_{10}H_{13}O$ [M+H]: 149.0966, found: 149.0961.

2-(hexa-1,5-dien-2-yl)thiophene (1s): The title compound was prepared according to the general procedure (Method **D**) and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (100/1) to give the colorless oil (5.8 g, 88%).



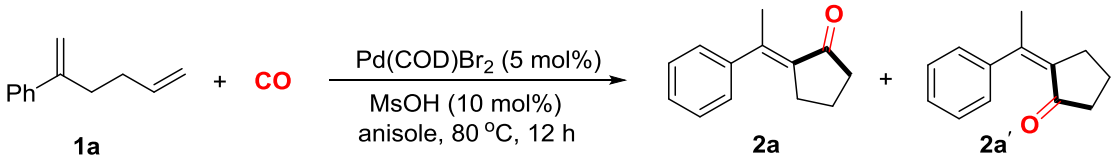
^{1}H NMR (400 MHz, $CDCl_3$) δ 2.30-2.36 (m, 2H), 2.56 (t, *J* = 6.8 Hz, 2H), 4.97-5.07 (m, 3H), 5.41 (s, 1H), 5.82-5.92 (m, 1H), 6.96-6.98 (m, 1H), 7.03-7.04 (m, 1H), 7.04-7.16 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 32.7, 35.0, 111.2, 115.1, 123.4, 124.3, 127.5, 138.1, 141.2, 145.4. **HRMS** (ESI) calcd. for $C_{10}H_{13}S$ [M+H]: 165.0738, found: 165.0732.

3. Optimization of the reaction conditions

In a glove box, a mixture of $Pd(COD)Br_2$ (7.5 mg, 0.02 mmol, 5 mol%), ligand (0.024 mmol), acid (0.04 mmol, 10 mol%), anisole (1.0 mL) was added into a dry glass vessel. The resulting mixture was stirred for 10 minutes at room temperature and then diene **1a** (63.2 mg, 0.4 mmol) was added into the reaction mixture. The glass vessel was put into an autoclave and then taken out from glove box. The autoclave was purged and charged with CO (20 atm). The reaction mixture was stirred at 80 ^{o}C for 12 hours. After the reaction finished, the autoclave was cooled to room temperature and the

pressure was carefully released in the fume hood. The combined yield (**2a** + **2a**′) based on the diene and the ratio (**2a/2a**′) of the crude reaction mixture was determined by GC and GC-MS analysis using *n*-dodecane as the internal standard, respectively.

Table S1. Screening of phosphine ligand [a]

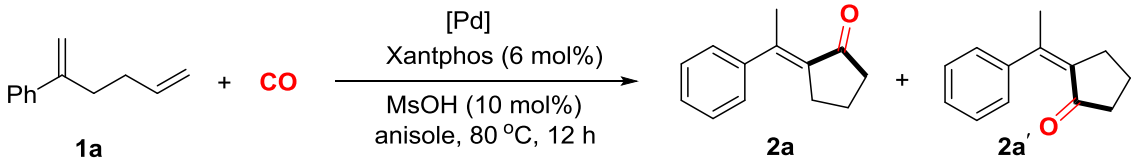


1a 2a 2a′

Entry	[Pd]	Ligand	CO (atm)	Yield(%) **2a** + **2a**′	**2a/2a**′
1	$Pd(COD)Br_2$	Xantphos	20	78	91:9
2	$Pd(COD)Br_2$	DPEphos	20	15	88:12
3	$Pd(COD)Br_2$	DPPF	20	0	-
4	$Pd(COD)Br_2$	DPPH	20	0	-
5	$Pd(COD)Br_2$	DPPPen	20	0	-
6	$Pd(COD)Br_2$	DPPB	20	0	-
7	$Pd(COD)Br_2$	DPPP	20	0	-
8	$Pd(COD)Br_2$	DPPE	20	0	-
9	$Pd(COD)Br_2$	DPPM	20	0	-
10	$Pd(COD)Br_2$	PPh_3	20	21	88:12
11	$Pd(COD)Br_2$	$P(2\text{-}MePh)_3$	20	trace	-
12	$Pd(COD)Br_2$	$P(4\text{-}MePh)_3$	20	trace	-
13	$Pd(COD)Br_2$	PCy_3	20	trace	-
14	$Pd(COD)Br_2$	Ruphos	20	trace	-
15	$Pd(COD)Br_2$	Dave Phos	20	trace	-
16	$Pd(COD)Br_2$	Xphos	20	trace	-

[a] Reaction conditions: **1a** (0.4 mmol), $Pd(COD)Br_2$ (0.02 mmol), MsOH (0.04 mmol), CO (20 atm), 80 °C, anisole (1.0 mL), 12 h, bidentate phosphine ligand (0.024 mmol) or monodentate phosphine ligand (0.04 mmol). The combined yield based on the diene and the ratio (**2a/2a**′) of the crude reaction mixture was determined by GC and GC-MS analysis using *n*-dodecane as the internal standard.

Table S2. Screening of palladium [a]



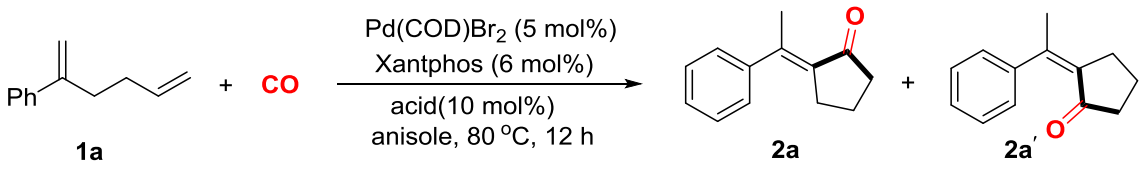
1a 2a 2a′

Entry	[Pd]	Ligand	CO (atm)	Yield (%)	**2a/2a**′

				2a + 2a′	
1	$Pd(COD)Br_2$	Xantphos	20	78	91:9
2	$PdCl_2$	Xantphos	20	58	90:10
3	$Pd(CH_3CN)_2Cl_2$	Xantphos	20	25	84:16
4	$Pd(PhCN)_2Cl_2$	Xantphos	20	65	88:12
5	$Pd(COD)Cl_2$	Xantphos	20	43	90:10
6	$PdBr_2$	Xantphos	20	62	89:11
7[b]	$Pd_2(dba)_3$	Xantphos	20	trace	-
8[b]	$[Pd(allyl)Cl]_2$	Xantphos	20	trace	-
9	-	Xantphos	20	0	-

[a] Reaction conditions: **1a** (0.4 mmol), [Pd] (0.02 mmol), Xantphos (0.024 mmol), MsOH (0.04 mmol), CO (20 atm), 80 °C, anisole (1.0 mL), 12 h. The combined yield based on the diene and the ratio (**2a/2a′**) of the crude reaction mixture was determined by GC and GC-MS analysis using *n*-dodecane as the internal standard. [b] [Pd] (0.01 mmol).

Table S3. Screening of acid [a]



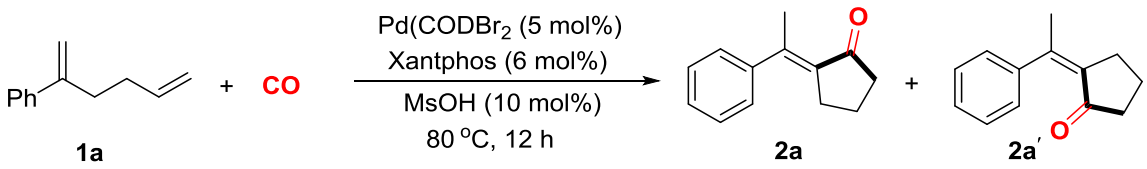
1a **2a** **2a′**

Entry	[Pd]	Ligand	Acid (10 mol%)	Yield (%) 2a + 2a′	2a/2a′
1	$Pd(COD)Br_2$	Xantphos	$MeSO_3H$	78	91:9
2	$Pd(COD)Br_2$	Xantphos	CH_3CO_2H	0	-
3	$Pd(COD)Br_2$	Xantphos	CF_3CO_2H	22	93:7
4	$Pd(COD)Br_2$	Xantphos	PivOH	trace	-
5	$Pd(COD)Br_2$	Xantphos	$PhCO_2H$	trace	-
6	$Pd(COD)Br_2$	Xantphos	NH_2SO_3H	trace	-
7	$Pd(COD)Br_2$	Xantphos	TsOH	54	91:9
8	$Pd(COD)Br_2$	Xantphos	$PhSO_3H$	73	91:9
9	$Pd(COD)Br_2$	Xantphos	NMP ·HCl	trace	-
10	$Pd(COD)Br_2$	Xantphos	NH_2OCH_3 ·HCl	0	-
11	$Pd(COD)Br_2$	Xantphos	NH_4Cl	0	-
12	$Pd(COD)Br_2$	Xantphos	$PhNHNH_2$ ·HCl	0	-
13	$Pd(COD)Br_2$	Xantphos	Et_3N ·HCl	0	-
14	$Pd(COD)Br_2$	Xantphos	$EtNH_2$ ·HCl	0	-
15	$Pd(COD)Br_2$	Xantphos	Et_2NH ·HCl	trace	-
16	$Pd(COD)Br_2$	Xantphos	Me_2NH ·HCl	trace	-

17	$Pd(COD)Br_2$	Xantphos	HCl ·NH_2NH_2 ·H	trace	-
18	$Pd(COD)Br_2$	Xantphos	Glycine	trace	-
19	$Pd(COD)Br_2$	Xantphos	Semicarbazide	trace	-
20	$Pd(COD)Br_2$	Xantphos	Py ·HCl	trace	-
21	$Pd(COD)Br_2$	Xantphos	$PhNH_2$ ·HCl	29	91:9
22	$Pd(COD)Br_2$	Xantphos	-	0	-

[a] Reaction conditions: **1a** (0.4 mmol), $Pd(COD)Br_2$ (0.02 mmol), Xantphos (0.024 mmol), Acid (0.04 mmol, 10 mol%), CO (20 atm), 80 °C, anisole (1.0 mL), 12 h. The combined yield based on the diene and the ratio (**2a**/**2a**′) of the crude reaction mixture was determined by GC and GC-MS analysis using *n*-dodecane as the internal standard.

Table S4. Screening of solvent [a]

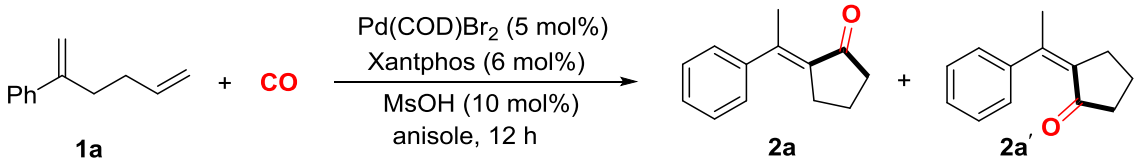


1a **2a** **2a′**

Entry	[Pd]	Ligand	Solvent	Yield (%) **2a** + **2a′**	**2a**/**2a′**
1	$Pd(COD)Br_2$	Xantphos	Anisole	78	91:9
2	$Pd(COD)Br_2$	Xantphos	Tol	76	91:9
3	$Pd(COD)Br_2$	Xantphos	Benzene	70	92:8
4	$Pd(COD)Br_2$	Xantphos	NMP	trace	-
5	$Pd(COD)Br_2$	Xantphos	DME	trace	-
6	$Pd(COD)Br_2$	Xantphos	CH_3CN	trace	-
7	$Pd(COD)Br_2$	Xantphos	dioxane	trace	-

[a] Reaction conditions: **1a** (0.4 mmol), $Pd(COD)Br_2$ (0.02 mmol), Xantphos (0.024 mmol), MsOH (0.04 mmol), CO (20 atm), 80 °C, Solvent (1.0 mL), 12 h. The combined yield based on the diene and the ratio (**2a**/**2a**′) of the crude reaction mixture was determined by GC and GC-MS analysis using *n*-dodecane as the internal standard.

Table S5. Screening of temperature [a]



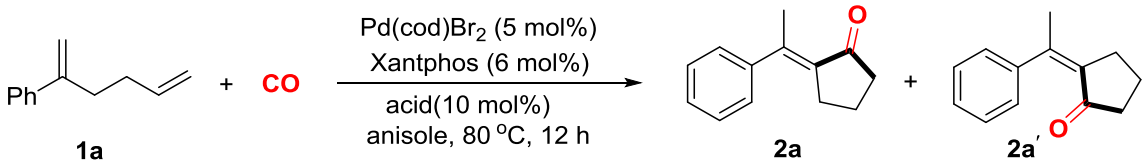
1a **2a** **2a′**

Entry	[Pd]	Ligand	T (°C)	Yield (%)	**2a**/**2a′**

				2a + 2a′	
1	$Pd(COD)Br_2$	Xantphos	100	48	93:7
2	$Pd(COD)Br_2$	Xantphos	80	78	91:9
3	$Pd(COD)Br_2$	Xantphos	60	43	93:7
4	$Pd(COD)Br_2$	Xantphos	40	12	90:10
5	$Pd(COD)Br_2$	Xantphos	25	0	-

[a] Reaction conditions: **1a** (0.4 mmol), $Pd(COD)Br_2$ (0.02 mmol), Xantphos (0.024 mmol), MsOH (0.04 mmol), CO (20 atm), 80 °C, anisole (1.0 mL), 12 h. The combined yield based on the diene and the ratio (**2a**/**2a′**) of the crude reaction mixture was determined by GC and GC-MS analysis using *n*-dodecane as the internal standard.

Table S6. Screening of concentration and catalyst loading [a]

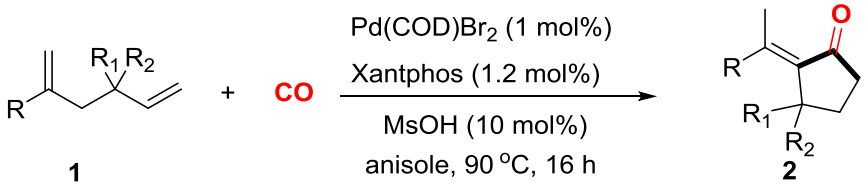


1a **2a** **2a′**

Entry	[Pd]	Ligand	anisole (mL)	CO (atm)	Yield(%) **2a + 2a′**	**2a/2a′**
1	$Pd(COD)Br_2$	Xantphos	1 mL	20	78	91:9
2	$Pd(COD)Br_2$	Xantphos	2 mL	20	71	92:8
3	$Pd(COD)Br_2$	Xantphos	3 mL	20	69	92:8
4[b]	$Pd(COD)Br_2$	Xantphos	2 mL	20	74	91:9
5[b]	$Pd(COD)Br_2$	Xantphos	2 mL	30	81	92:8

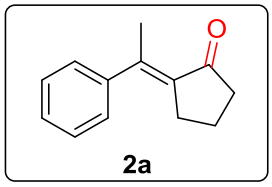
[a] Reaction conditions: **1a** (0.4 mmol), $Pd(COD)Br_2$ (0.02 mmol), Xantphos (0.024 mmol), MsOH (0.04 mmol), CO (20 atm), 80 °C, 12 h. The combined yield based on the alkene and the ratio (**2a**/**2a′**) of the crude reaction mixture was determined by GC and GC-MS analysis using *n*-dodecane as the internal standard. [b] **1a** (1.0 mmol), $Pd(COD)Br_2$ (0.01 mmol, 1 mol%), Xantphos (0.012 mmol, 1.2 mol%), MsOH (0.1 mmol, 10 mol%), CO (30 atm) , 90 °C, anisole (2.0 mL), 16 h.

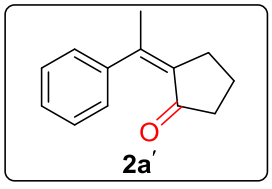
4. General procedure for the catalytic reaction and spectral data of products



In a glove box, a mixture of $Pd(COD)Br_2$ (3.7 mg, 0.01 mmol, 1 mol%), Xantphos (6.9 mg, 0.012 mmol), MsOH (6.5μL, 0.1 mmol), anisole (2.0 mL) was added into a dry glass vessel. The resulting mixture was stirred for 10 minutes at room temperature and then diene **1** (1.0 mmol) was added into the reaction mixture. The glass vessel was put into an autoclave and then taken out from glove box. The autoclave was purged and charged with CO (30 atm). The reaction mixture was stirred at 90 °C for 16 hours. After the reaction finished, the autoclave was cooled to room temperature and the pressure was carefully released in the fume hood. The ratio (E/Z) of the crude reaction mixture was determined by GC and GC-MS analysis. Then the corresponding reaction mixture was purified by flash column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (100/1-10/1) to give the desired products **2**.

(*E*)-2-(1-phenylethylidene)cyclopentan-1-one (2a): Known compound.[3] The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (100/1-30/1) to give a pale yellow solid, 135.2 mg, 73% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.76-1.82 (m, 2H) 2.38 (t, *J* = 7.6 Hz, 2H), 2.53 (t, *J* = 2.0 Hz 3H), 2.56-2.60 (m, 2H), 7.24-7.25 (m, 2H), 7.26-7.32 (m, 1H), 7.35-7.39 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 20.1, 20.5, 31.8, 40.7, 127.4, 127.9, 128.3, 132.8, 143.7, 147.7, 209.1. **HRMS** (ESI) calcd. for $C_{13}H_{15}O$ [M+H]: 187.1117, found: 187.1115.

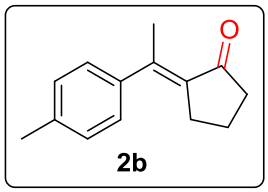




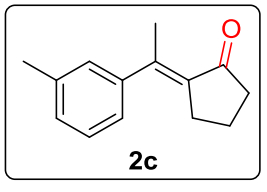
(*Z*)-2-(1-phenylethylidene)cyclopentan-1-one (2a′): Known compound.[5] The title compound was prepared according to the

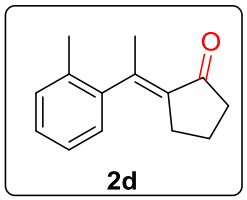
general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (100/1-30/1) to give a pale yellow solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.91-1.99 (m, 2H), 2.11 (t, *J* = 1.6 Hz, 3H), 2.31 (t, *J* = 8.0 Hz, 2H), 2.74-2.78 (m, 2H), 7.14-7.17 (m, 2H), 7.22-7.36 (m, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 19.4, 25.0, 30.1, 40.4, 127.4, 127.5, 127.9, 132.2, 141.8, 146.6, 205.1. **HRMS** (ESI) calcd. for $C_{13}H_{15}O$ [M+H]: 187.1123, found: 187.1122.

(*E*)-2-(1-(*p*-tolyl)ethylidene)cyclopentan-1-one (2b): The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (100/1-30/1) to give the pale yellow oil, 146.1 mg, 73% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.74-1.82 (m, 2H), 2.35-2.39 (m, 5H), 2.52 (t, *J* = 2.0 Hz, 3H), 2.57-2.61 (m, 2H), 7.15-7.19 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 19.9, 20.4, 21.3, 31.9, 40.6, 127.3, 128.9, 132.4, 137.8, 140.6, 147.6, 208.9. **HRMS** (ESI) calcd. for $C_{14}H_{17}O$ [M+H]: 201.1274, found: 201.1276.



(*E*)-2-(1-(*m*-tolyl)ethylidene)cyclopentan-1-one (2c): The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (100/1-30/1) to give the pale yellow oil, 141.7 mg, 71% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.75-1.82 (m, 2H) , 2.35-2.39 (m, 5H), 2.52 (t, *J* = 2.0 Hz, 3H), 2.55-2.60 (m, 2H) , 7.03-7.06 (m, 2H), 7.10-7.13 (m, 1H), 7.24-7.27 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 20.1, 20.4, 21.5, 31.8, 40.6, 124.4, 127.9, 128.2, 128.6, 132.5, 137.9, 143.6, 147.8, 209.0. **HRMS** (ESI) calcd. for $C_{14}H_{17}O$ [M+H]: 201.1274, found: 201.1275.

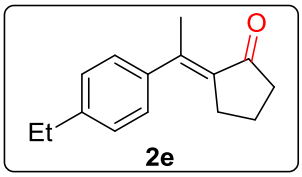




(*E*)-2-(1-(*o*-tolyl)ethylidene)cyclopentan-1-one (2d): The title compound was prepared according to the general procedure and

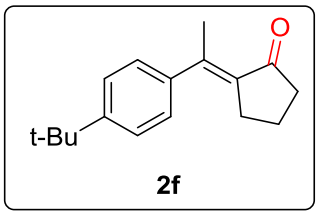
purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (100/1-30/1) to give the pale yellow oil, 101.0 mg, 50% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.76-1.84 (m, 2H), 2.19-2.23 (m, 4H), 2.26-2.33 (m, 1H), 2.37-2.42 (m, 5H), 6.94-6.98 (m, 1H), 7.17-7.22 (m, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 19.1, 20.0, 20.3, 30.6, 40.8, 126.1, 126.1, 127.3, 130.4, 132.9, 133.2, 143.6, 148.7, 208.8. **HRMS** (ESI) calcd. for $C_{14}H_{17}O$ [M+H]: 201.1274, found: 201.1275.

(*E*)-2-(1-(4-ethylphenyl)ethylidene)cyclopentan-1-one (2e): The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (100/1-30/1) to give the pale yellow oil, 162.4 mg, 76% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.25 (t, *J* = 7.6 Hz, 3H), 1.75-1.82 (m, 2H), 2.37 (t, *J* = 7.6 Hz, 2H), 2.52 (t, *J* = 2.0 Hz, 3H), 2.58-2.69 (m, 4H), 7.20-7.26 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 15.5, 20.0, 20.6, 28.7, 32.1, 40.7, 127.5, 127.7, 132.5, 140.8, 144.2, 209.2. **HRMS** (ESI) calcd. for $C_{15}H_{19}O$ [M+H]: 215.1430, found: 215.1430.



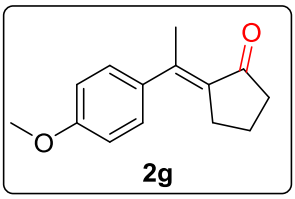
2e

(*E*)-2-(1-(4-(tert-butyl)phenyl)ethylidene)cyclopentan-1-one (2f): The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (100/1-30/1) to give a pale yellow solid, 178.2 mg, 74% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.34 (s, 9H), 1.75-1.83 (m, 2H), 2.38 (t, *J* = 7.6 Hz, 2H), 2.53 (t, *J* = 2.0 Hz, 3H), 2.61-2.65 (m, 2H), 7.21-7.23 (m, 2H), 7.37-7.41 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 19.9, 20.6, 31.4, 32.2, 34.8, 40.7, 125.1, 127.3, 132.5, 140.5, 147.6, 151.1, 209.2. **HRMS** (ESI) calcd. for $C_{17}H_{23}O$ [M+H]: 243.1743, found: 243.1746.



2f

(*E*)-2-(1-(4-methoxyphenyl)ethylidene)cyclopentan-1-one (2g): The title compound



was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (100/1-10/1) to give a pale yellow solid, 116.5 mg, 54% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.75-1.82 (m, 2H), 2.37 (t, *J* = 7.6 Hz, 2H), 2.52 (t, *J* = 2.0 Hz, 3H), 2.60-2.65 (m, 2H), 3.83 (s, 3H), 6.88-6.92 (m, 2H), 7.22-7.27 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 19.9, 20.6, 32.2, 40.6, 55.4, 113.6, 129.1, 132.2, 135.8, 147.2, 159.4, 208.9. **HRMS** (ESI) calcd. for $C_{14}H_{17}O_2$ [M+H]: 217.1228, found: 217.1226.

The compound was also confirmed by single-crystal X-ray analysis

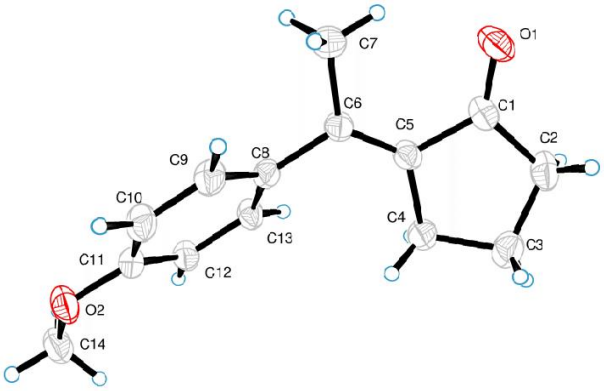
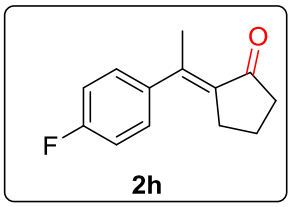


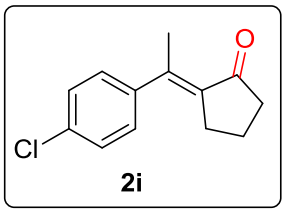
Figure S1. ORTEP drawing of complex **2g**

(*E*)-2-(1-(4-fluorophenyl)ethylidene)cyclopentan-1-one (2h): The title compound



was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (100/1-20/1) to give the pale yellow oil, 110.2 mg, 54% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.77-1.84 (m, 2H), 2.39 (t, *J* = 7.2 Hz, 2H), 2.51 (t, *J* = 2.0 Hz, 3H), 2.54-2.59 (m, 2H), 7.03-7.09 (m, 2H), 7.22-7.26 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 20.1, 20.5, 31.9, 40.6, 115.4 (d, $J_{C\text{-}F}$ = 20.0 Hz), 129.3 (d, $J_{C\text{-}F}$ = 10.0 Hz), 133.0, 139.6 (d, $J_{C\text{-}F}$ = 10.0 Hz), 146.5, 163.5 (d, $J_{C\text{-}F}$ = 240.0 Hz), 208.9; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -113.62. **HRMS** (ESI) calcd. for $C_{13}H_{14}FO$ [M+H]: 205.1029, found: 205.1024.

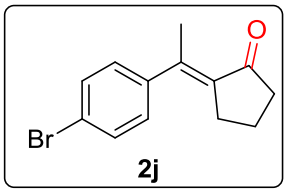
(*E*)-2-(1-(4-chlorophenyl)ethylidene)cyclopentan-1-one (2i): The title compound



2i

was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (100/1-20/1) to give the pale yellow oil, 136.5 mg, 62% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.77-1.84 (m, 2H), 2.38 (t, *J* = 8.0 Hz, 2H), 2..50 (t, *J* = 2.0 Hz, 3H), 2.53-2.58 (m, 2H), 7.18-7.21 (m, 2H), 7.33-7.36 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 19.8, 20.4, 31.8, 40.5, 128.5, 128.8, 133.1, 133.7, 141.9, 146.1, 208.7. **HRMS** (ESI) calcd. for $C_{13}H_{14}ClO$ [M+H]: 221.0728, found: 221.0728.

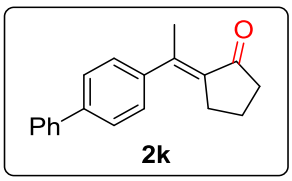
(*E*)-2-(1-(4-bromophenyl)ethylidene)cyclopentan-1-one (2j): The title compound



2j

was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (100/1-20/1) to give a pale yellow solid, 158.8 mg, 60% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.77-1.84 (m, 2H), 2.38 (t, *J* = 7.6 Hz, 2H), 2.49 (t, *J* = 2.0 Hz, 3H), 2.53-2.58 (m, 2H), 7.12-7.15 (m, 2H), 7.48-7.52 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 19.7, 20.3, 31.7, 40.5, 121.9, 129.1, 131.5, 133.1, 142.4, 146.0, 208.7. **HRMS** (ESI) calcd. for $C_{13}H_{13}BrNaO$ [M+Na]: 287.0042, found: 287.0037.

(*E*)-2-(1-([1,1'-biphenyl]-4-yl)ethylidene)cyclopentan-1-one (2k): The title

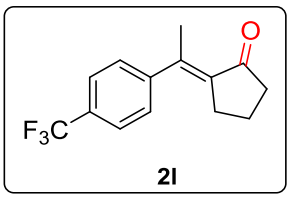


2k

compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (100/1-30/1) to give a white solid, 163.1 mg, 62% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.77-1.84 (m, 2H), 2.39 (t, *J* = 7.6 Hz, 2H), 2.56 (t, *J* = 2.0 Hz, 3H), 2.62-2.66 (m, 2H), 7.32-7.37 (m, 3H), 7.42-7.46 (m, 2H), 7.58-7.62 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 19.9, 20.6, 32.1, 40.7, 127.0, 127.2, 127.7, 128.0, 129.0,

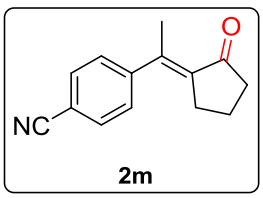
132.9, 140.6, 140.8, 142.4, 147.1, 209.1. **HRMS** (ESI) calcd. for $C_{19}H_{18}NaO$ [M+Na]: 285.1250, found: 285.1248.

(*E*)-2-(1-(4-(trifluoromethyl)phenyl)ethylidene)cyclopentan-1-one (2l): The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (100/1-10/1) to give a pale yellow solid, 117.6 mg, 46% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.79-1.86 (m, 2H), 2.41 (t, *J* = 8.0 Hz, 2H), 2.52-2.56 (m, 5H), 7.36 (q, *J* = 8.0 Hz, 2H), 7.64 (q, *J* = 8.0 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 19.8, 20.3, 31.6, 40.6, 122.8, 125.4 (d, J_{C-F} = 4.0 Hz), 129.9 (d, J_{C-F} = 32.0 Hz), 130.1, 130.4, 133.7, 145.8, 147.2, 208.8. **HRMS** (ESI) calcd. for $C_{14}H_{13}F_3NaO$ [M+Na]: 277.0811, found: 277.0808.



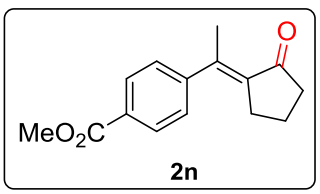
2l

(*E*)-4-(1-(2-oxocyclopentylidene)ethyl)benzonitrile (2m): The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (100/1-10/1) to give a pale yellow solid, 69.8 mg, 33% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.80-1.87 (m, 2H), 2.41 (t, *J* = 7.6 Hz, 2H), 2.51-2.55 (m, 5H), 7.35-7.37 (d, *J* =8.0 Hz, 2H), 7.68-7.70 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 19.6, 20.3, 31.6, 40.5, 111.6, 118.7, 128.2, 132.3, 134.0, 145.0, 148.2, 208.6. **HRMS** (ESI) calcd. for $C_{14}H_{13}NNaO$ [M+Na]: 234.0889, found: 234.0888.



2m

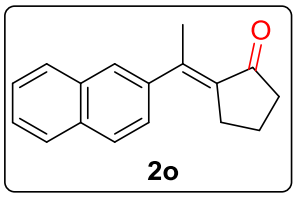
Methyl (*E*)-4-(1-(2-oxocyclopentylidene)ethyl)benzoate (2n): The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (100/1-10/1) to give a pale yellow solid, 138.3 mg, 57% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.78-1.85 (m, 2H), 2.39 (t, *J* =8.0 Hz, 2H), 2.53-2.67 (m, 5H), 3.93 (d,



2n

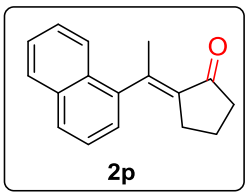
J =0.8 Hz, 3H), 7.31-7.33 (m, 2H), 8.04-8.06 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 19.8, 20.4, 31.6, 40.6, 52.3, 127.4, 129.5, 129.7, 133.4, 146.3, 148.2, 166.8, 208.9. **HRMS** (ESI) calcd. for $C_{15}H_{16}NaO_3$ [M+Na]: 267.0992, found: 267.0989.

(*E*)-2-(1-(naphthalen-2-yl)ethylidene)cyclopentan-1-one (2o): The title compound

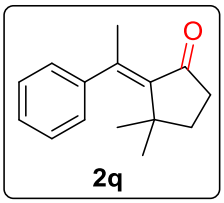


was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (100/1-30/1) to give a pale yellow solid, 156.0 mg, 66% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.76-1.83 (m, 2H), 2.40 (t, *J* = 7.6 Hz, 2H), 2.58-2.64 (m, 5H), 7.36-7.38 (m, 1H), 7.47-7.51 (m, 2H), 7.69-7.70 (m, 1H), 7.81-7.84 (m, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 20.1, 20.5, 31.9, 40.6, 125.4, 126.5, 127.8, 128.0, 128.2, 132.8, 133.1, 133.1, 141.0, 147.5, 208.9. **HRMS** (ESI) calcd. for $C_{17}H_{16}NaO$ [M+Na]: 259.1093, found: 259.1086.

(*E*)-2-(1-(naphthalen-1-yl)ethylidene)cyclopentan-1-one (2p): The title compound



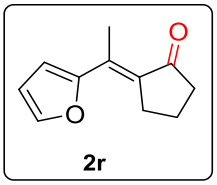
was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (100/1-30/1) to give a pale yellow solid, 117.9 mg, 50% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.71-1.79(m, 2H), 2.12-2.29(m, 2H), 2.43 (t, *J* =7.6 Hz, 2H), 2.60 (t, *J* = 2.0 Hz, 3H), 7.19-7.21 (m, 1H), .7.45-7.51 (m, 3H), 7.70-7.72 (m, 1H), 7.79 (d, *J* =8.4Hz, 1H), 7.86-7.89 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 19.9, 21.1, 30.8, 40.8, 123.6, 125.0, 125.7, 126.1, 126.5, 127.7, 128.7, 129.2, 133.8, 134.3, 141.8, 147.3, 208.9. **HRMS** (ESI) calcd. for $C_{17}H_{16}NaO$ [M+Na]: 259.1093, found: 259.1092.



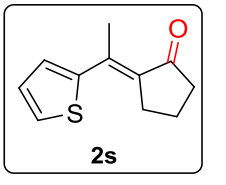
(*E*)-3,3-dimethyl-2-(1-phenylethylidene)cyclopentan-1-one (2q): The title compound was prepared according to the general procedure and purified by column chromatography on silica gel

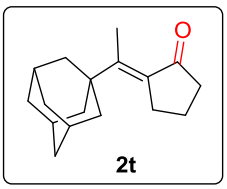
and eluted with petroleum ether/ethyl acetate (100/1-30/1) to give a pale yellow solid, 120.1 mg, 56% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 0.87 (s, 6H), 1.65 (t, *J* = 7.6 Hz, 2H), 2.38 (t, *J* = 8.0 Hz, 2H), 2.44 (s, 3H), 7.08-7.11 (m, 2H), 7.27-7.36 (m, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 24.1, 29.2, 37.1, 37.4, 42.0, 127.0, 127.2, 128.0, 140.8, 143.8, 149.9, 210.2. **HRMS** (ESI) calcd. for $C_{15}H_{19}O$ [M+H]: 215.1430, found: 215.1434.

(*E*)-2-(1-(furan-2-yl)ethylidene)cyclopentan-1-one (2r): The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (100/1-20/1) to give the pale yellow oil, 75.4 mg, 43% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.89-1.97 (m, 2H), 2.38 (t, *J* =8.0Hz, 2H), 2.54 (t, *J* =2.0Hz, 3H), 2.95-2.99 (m, 2 H), 6.51 (dd, J_1 =3.6Hz, J_2 =1.6Hz, 1H), 6.69 (d, *J* =3.6Hz, 1H) 7.55 (d, *J* =1.6Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 14.9, 20.0, 32.4, 40.5, 112.1, 114.2, 129.7, 134.0, 144.0, 155.1, 209.5. **HRMS** (ESI) calcd. for $C_{11}H_{13}O_2$ [M+H]: 177.0916, found: 177.0899.



(*E*)-2-(1-(thiophen-2-yl)ethylidene)cyclopentan-1-one (2s): The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (100/1-20/1) to give a pale yellow solid, 108.0mg, 56% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.90-1.97 (m, 2H), 2.41 (t, *J* =8.0Hz, 2H), 2.68 (t, *J* = 2.0 Hz, 3H), 2.92-2.96 (m, 2H), 7.11-7.14 (m, 1H), 7.34-7.35 (m, 1H), 7.46-7.47 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 19.0, 20.2, 33.2, 40.7, 127.5, 128.1, 129.2, 131.0, 139.2, 145.7, 208.9. **HRMS** (ESI) calcd. for $C_{11}H_{12}ONaS$ [M+H]: 215.0509, found: 215.0494.

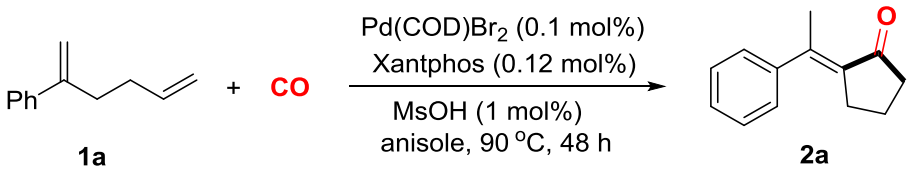




(*E*)-2-(1-((1S,3s)-adamantan-1-yl)ethylidene)cyclopentan-1-one (2t): The title compound was prepared according to the general

procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (100/1-30/1) to give the pale yellow oil, 67.1mg, 28% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.71 (br, 6H), 1.78-1.84 (m, 2H), 1.89-1.99 (br, 6H), 2.0 (s, 3H), 2.20-2.25 (m, 5H), 2.86-2.90 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 15.7, 20.5, 28.9, 32.2, 36.9 39.4, 39.7, 40.7, 131.4, 159.3, 210.5. **HRMS** (ESI) calcd. for $C_{17}H_{25}O$ [M+H]: 245.1900, found: 245.1892.

5. Gram-scale synthesis of 2a



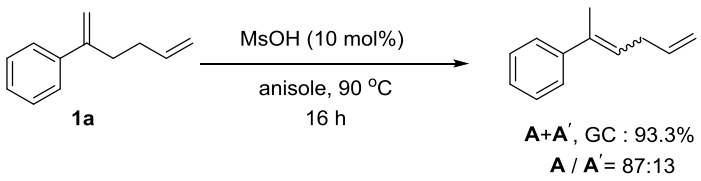
In a glove box, a mixture of $Pd(COD)Br_2$ (3.7 mg, 0.01 mmol, 0.1 mol%), Xantphos (6.9 mg, 0.012 mmol, 0.12 mol%), MsOH (6.5 μL, 0.1 mmol, 1 mol%), anisole (10.0 mL) was added into a 50 mL round-bottomed flask. The resulting mixture was stirred for 10 minutes at room temperature and then 1,5-diene **1a** (10 mmol) was added into the reaction mixture. The round-bottomed flask was put into an autoclave and then taken out from glove box. The autoclave was purged and charged with CO (30 atm). The reaction mixture was stirred at 90 °C for 48 hours. After the reaction finished, the autoclave was cooled to room temperature and the pressure was carefully released in the fume hood, solvent was removed under reduced pressure. The ratio (**2a**/**2a′**) of the crude reaction mixture was determined by GC and GC-MS. Then the corresponding reaction mixture was purified by flash column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (100/1-30/1) to give the desired products **2a (**910.1 mg, 49% yield), **2a**/**2a′** = 91 : 9.

6. Mechanistic studies

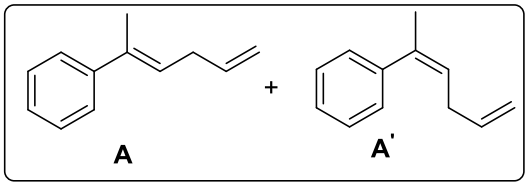
6.1 Reaction of 1a under MsOH

MsOH (6.5μL, 0.1 mmol), 1,5-diene **1a** (1.0 mmol), anisole (2.0 mL) were added to a 25 mL flame-dried Young-type tube under nitrogen atmosphere. The reaction

mixture was stirred for 16 hour at 90 °C. After the reaction finished, the solvent was removed under reduced pressure. The combined yield (**A + A′**) based on the diene and the ratio (**A**/**A′**) of the crude reaction mixture was determined by GC and GC-MS analysis using *n*-dodecane as the internal standard. Then the corresponding reaction mixture was purified by flash column chromatography on silica gel and eluted with petroleum to give the desired products **A + A′**.



Hexa-2,5-dien-2-ylbenzene (A+A′): A colorless oil. **(*E*)-hexa-2,5-dien-2-ylbenzene**

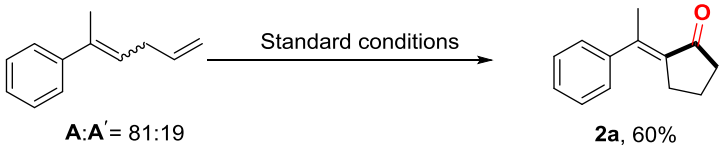


(**A**): Known compound.[4] **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 2.03-2.04 (m, 3H), 2.94-2.97 (m, 2H), 5.00-5.12 (m, 2H), 5.77-5.93 (m, 2H), 7.20-7.40 (m, 5H); **(*Z*)-hexa-2,5-dien-2-ylbenzene** (**A′**): Known compound.[4] **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 2.04-2.05 (m, 3H), 2.70-2.74 (m, 2H), 4.95-5.05 (m, 2H), 5.47-5.51 (m, 1H), 5.76-5.86 (m, 1H), 7.17-7.34 (m, 5H).

6.2 Cyclocarbonylation of 1,4-diene (A+A′)

In a glove box, a mixture of $Pd(COD)Br_2$ (3.7 mg, 0.01 mmol, 1 mol%), Xantphos (6.9 mg, 0.012 mmol), MsOH (6.5 μL, 0.1 mmol), anisole (2 mL) was added into a dry glass vessel. The resulting mixture was stirred for 10 minutes at room temperature and then 1,4-diene (**A**:**A′= 81**:**19**) (1.0 mmol) was added into the reaction mixture. The glass vessel was put into an autoclave and then taken out from glove box. The autoclave was purged and charged with CO (30 atm). The reaction mixture was stirred at 90 °C for 16 hours. After the reaction finished, the autoclave was cooled to room temperature and the pressure was carefully released in the fume hood. The ratio (**2a**/**2a′**)

of the crude reaction mixture was determined by GC and GC-MS. Then the corresponding reaction mixture was purified by flash column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (100/1-30/1) to give the desired products **2a** (111.4 mg, 60% yield), **2a**/**2a′** = 91 : 9.



6.3 Reaction profile

In a glove box, a mixture of $Pd(COD)Br_2$ (11.1 mg, 0.03 mmol, 1 mol%), Xantphos (20.7 mg, 0.036 mmol), MsOH (19.2 μL, 0.1 mmol), anisole (15 mL) was added into a PTFE vessel. The resulting mixture was stirred for 10 minutes at room temperature and then diene **1a** (3.0 mmol) was added into the reaction mixture. The PTFE vessel was put into an autoclave and then taken out from glove box. The autoclave was purged and charged with CO (30 atm). The reaction mixture was stirred at 90 ^{o}C. Yields were determined by GC and GC-MS analysis using *n*-dodecane as the internal standard.

Table S7 Reaction profile of Pd-catalyzed hydrocarbonylative cyclization of **1a**.

t (min)	**1a** (%)	**A** (%)	**2a** (%)	**A′** (%)
0	100	0	0	0
20	94.5	5.5	0	0
60	74.5	19.4	2.3	1.0
100	58.7	31.5	2.7	1.1
140	47.5	40.0	2.7	2.0
200	26.0	55.7	6.3	2.3
260	17.6	59.3	9.3	2.6
320	13.7	59.3	11.9	2.6
380	10.5	55.5	17.5	2.8
440	8.1	52.9	21.2	2.7
500	6.6	46.2	28.0	2.6
560	5.6	40.8	33.2	2.5
620	4.9	38.2	36.7	2.3
680	4.2	32.8	42.2	2.2
740	3.6	29.5	45.2	2.0
800	3.2	25.1	49.5	1.7
860	2.5	20.5	54.3	1.7
920	2.4	19.4	55.5	1.7
980	2.3	17.9	57.0	1.6

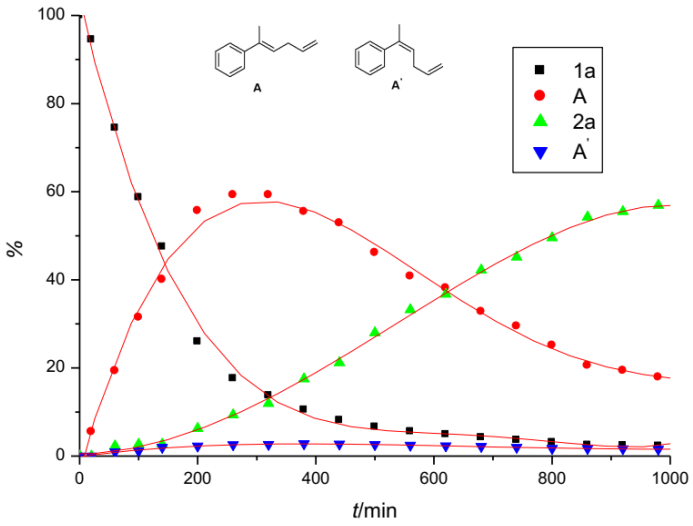


Figure S2 Reaction profile of Pd-catalyzed hydrocarbonylative cyclization of **1a**.

7. References

(1) (a) Imai, M.; Tanaka, M.; Tanaka, K.; Yamamoto, Y.; Imai-Ogata, N.; Shimowatari, M.; Nagumo, S.; Kawahara, No.; Suemune, H. Double-Chelation-Assisted Rh-Catalyzed Intermolecular Hydroacylation between Salicylaldehydes and 1,4-Penta- or 1,5-Hexadienes. *J. Org. Chem*. **2004**, *69*, 1144. (b) Jiang, B.; Meng, F.; Liang, Q.; Xu, Y.; Loh, T-P. Palladium-Catalyzed Direct Intramolecular C–N Bond Formation: Access to Multisubstituted Dihydropyrroles. *Org. Lett.* **2017**, *19*, 914. (c) Uehara, K. B.; Wagner, C.; Vogler, T.; Luftmann, H.; Studer, A. Poly(vinyl ketone)s by Controlled Boron Group Transfer Polymerization (BGTP). *Angew. Chem. Int. Ed.* **2010**, *49*, 3073.

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8. Copies for ^{1}H NMR, ^{19}F NMR and ^{13}C NMR of materials and products

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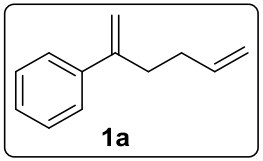

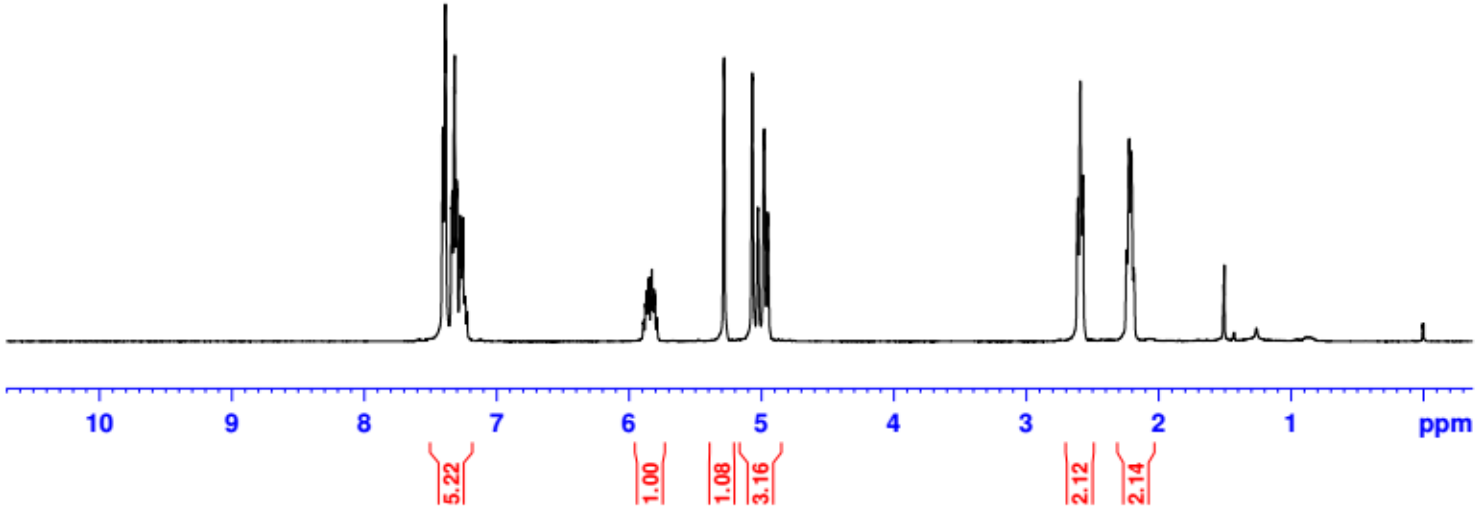

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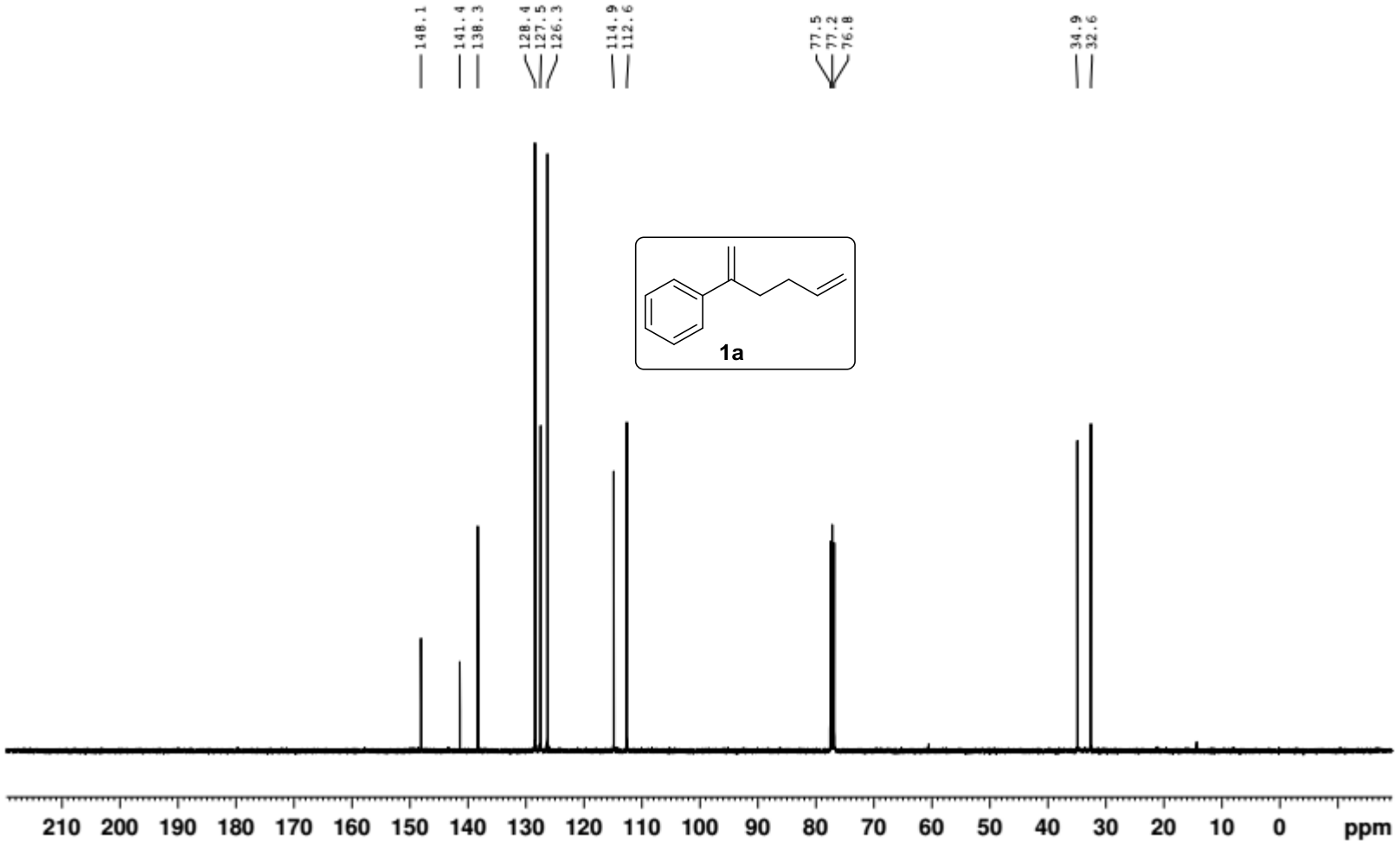

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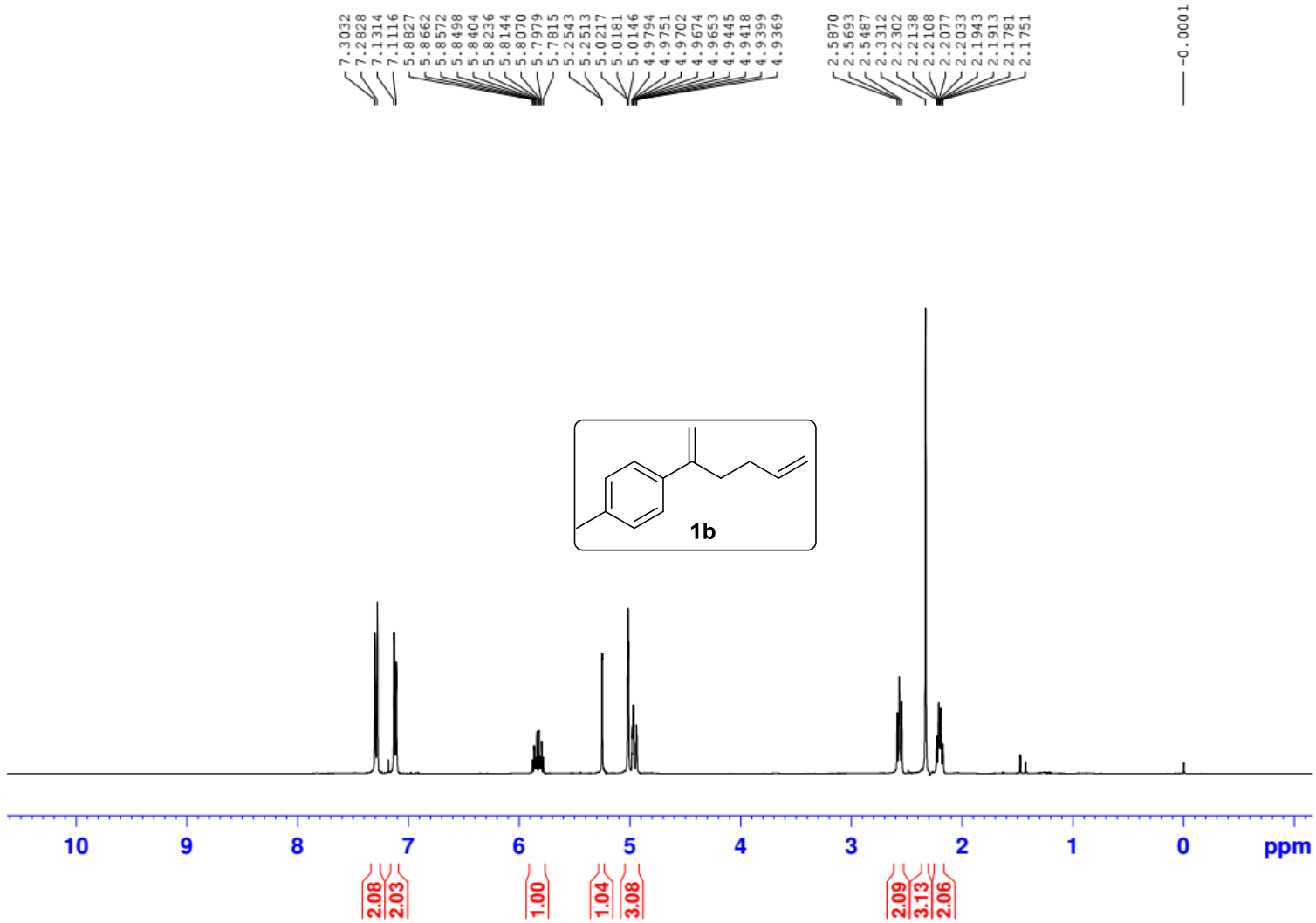

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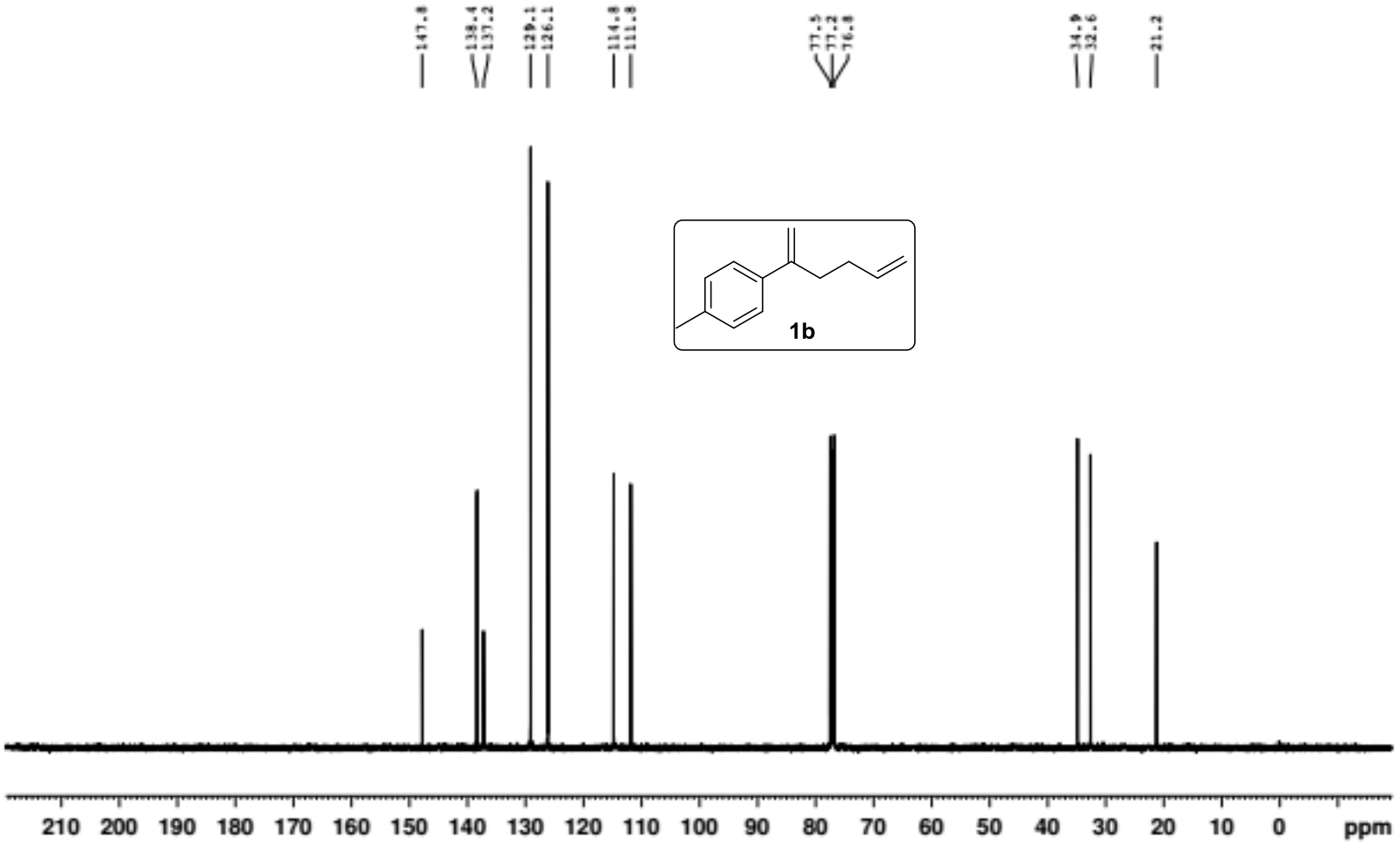

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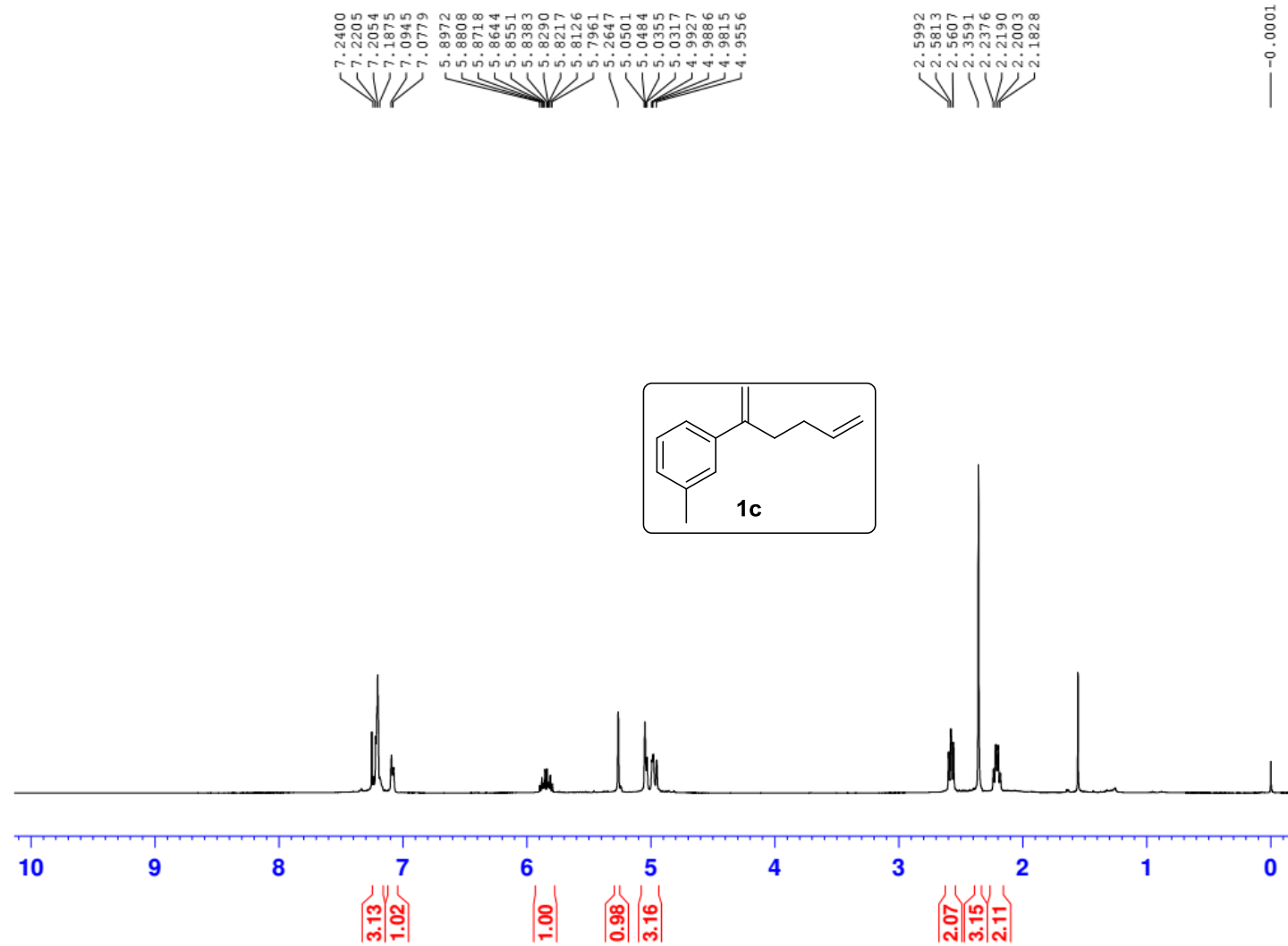

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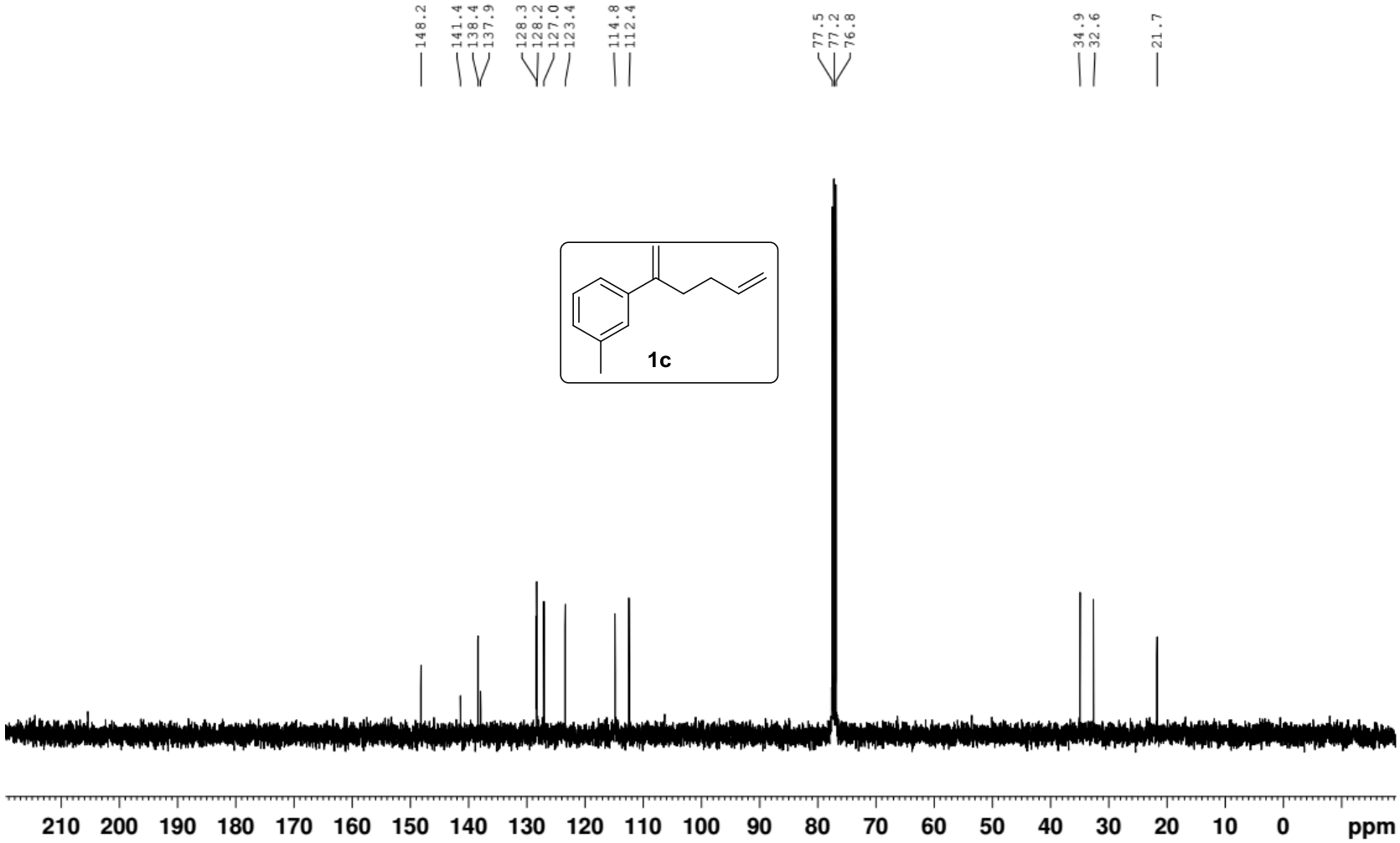

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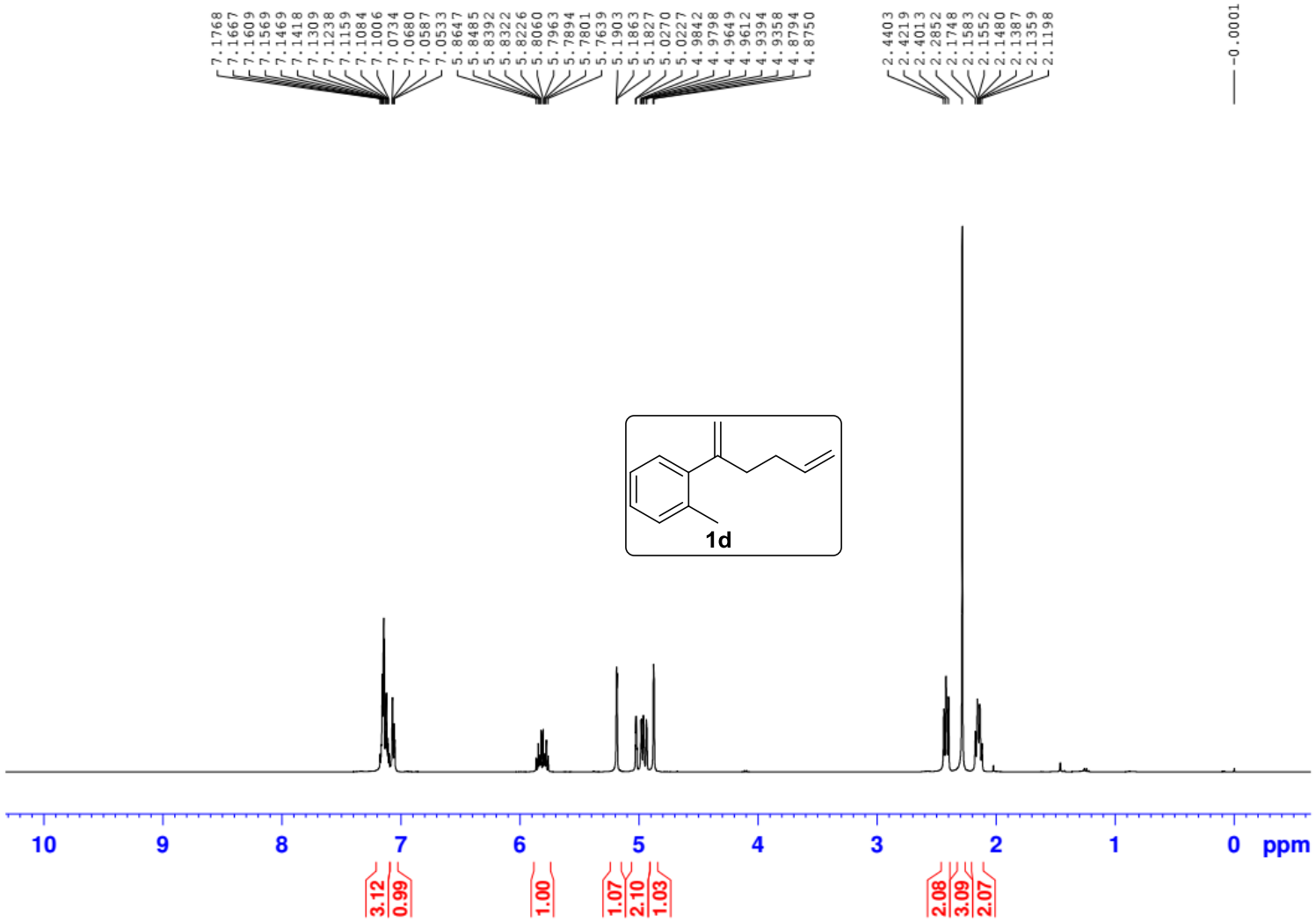

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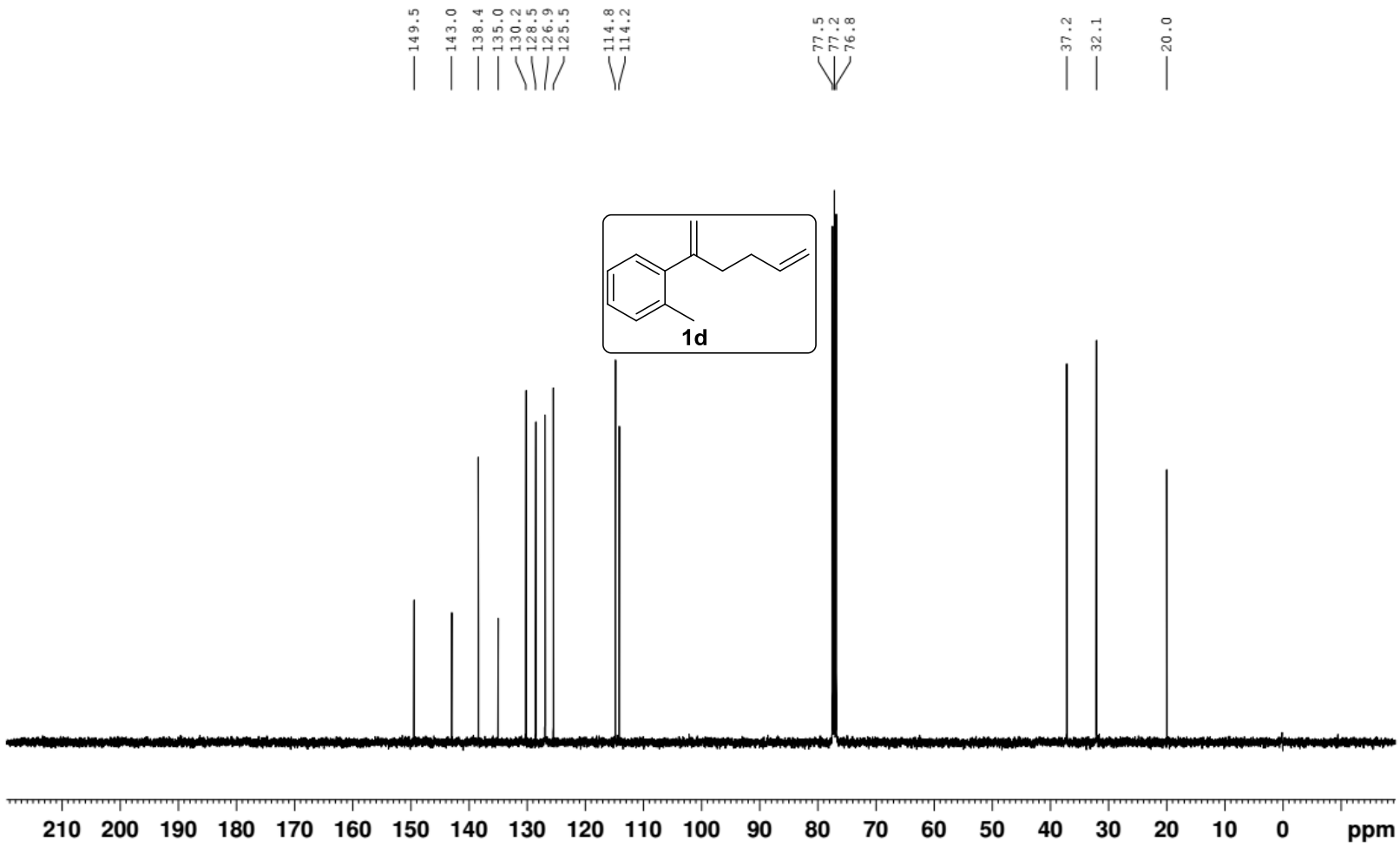

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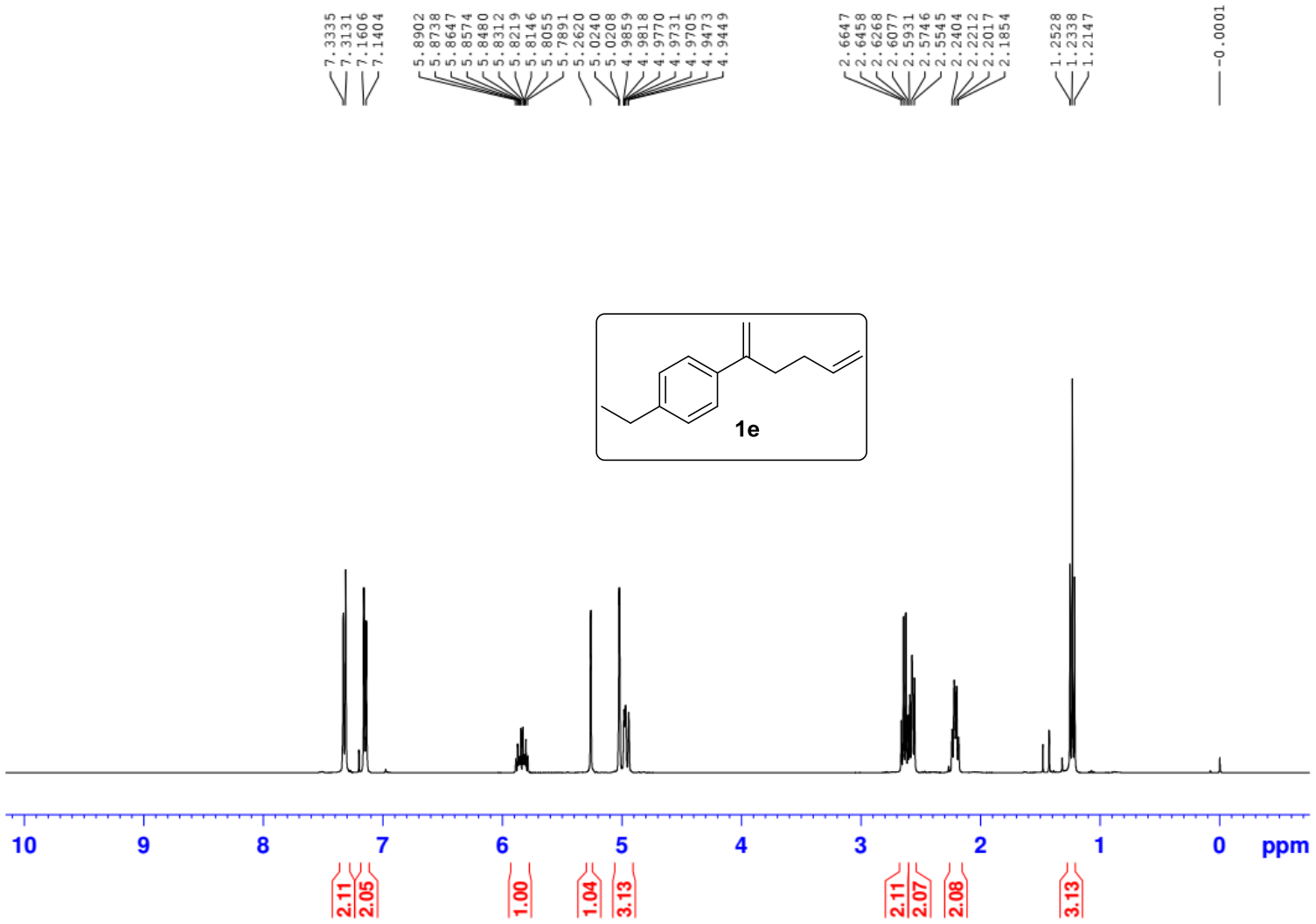

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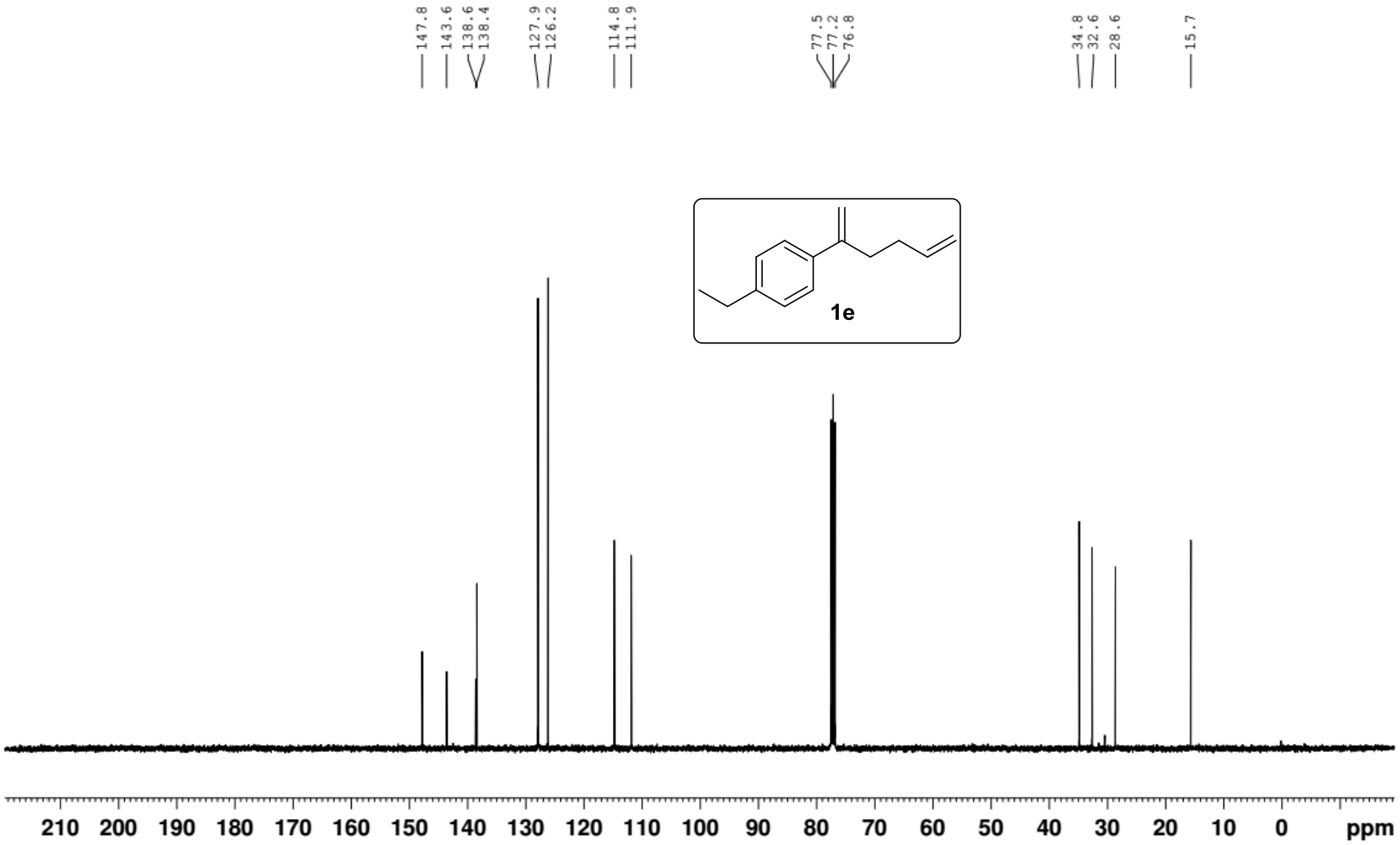

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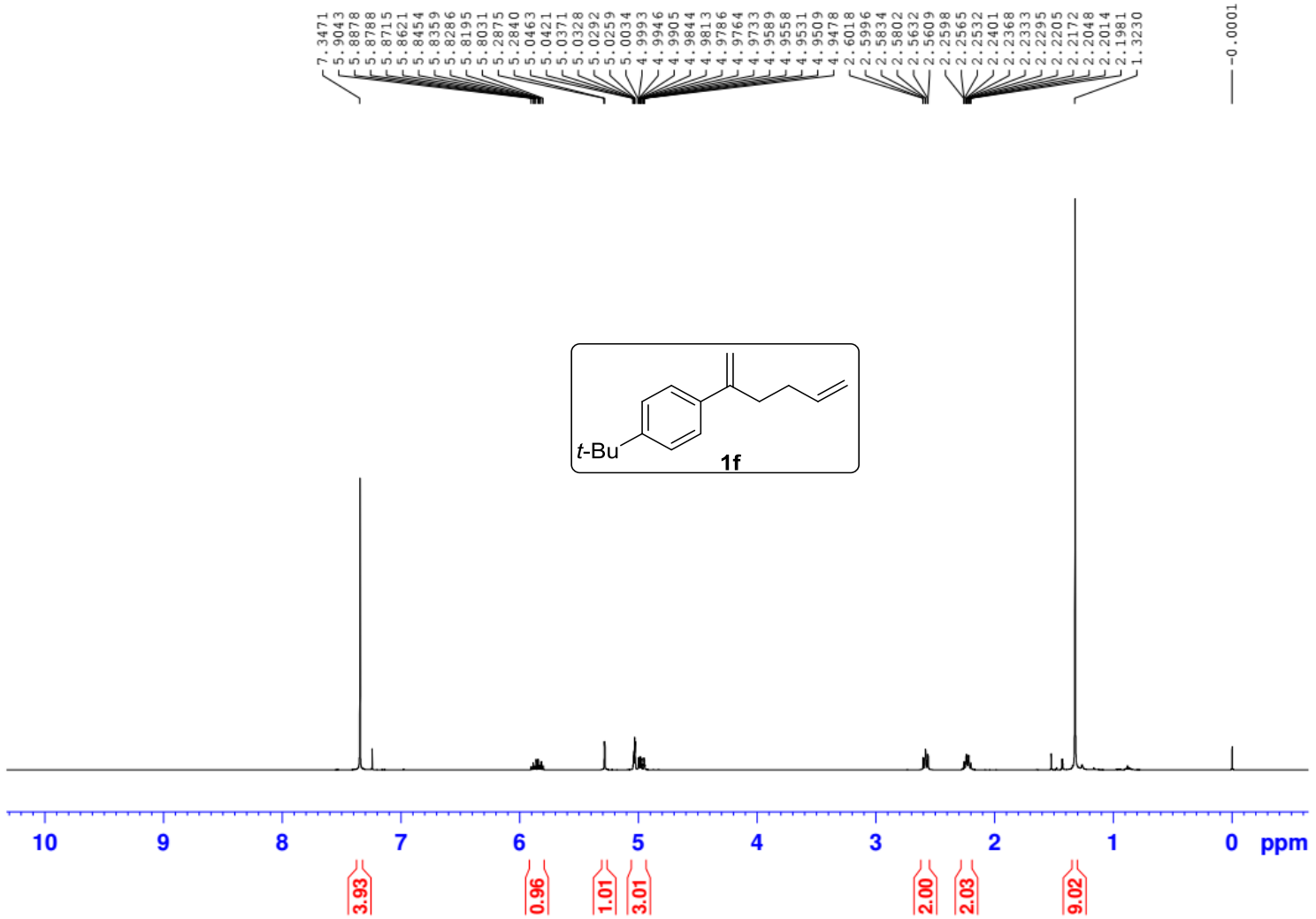

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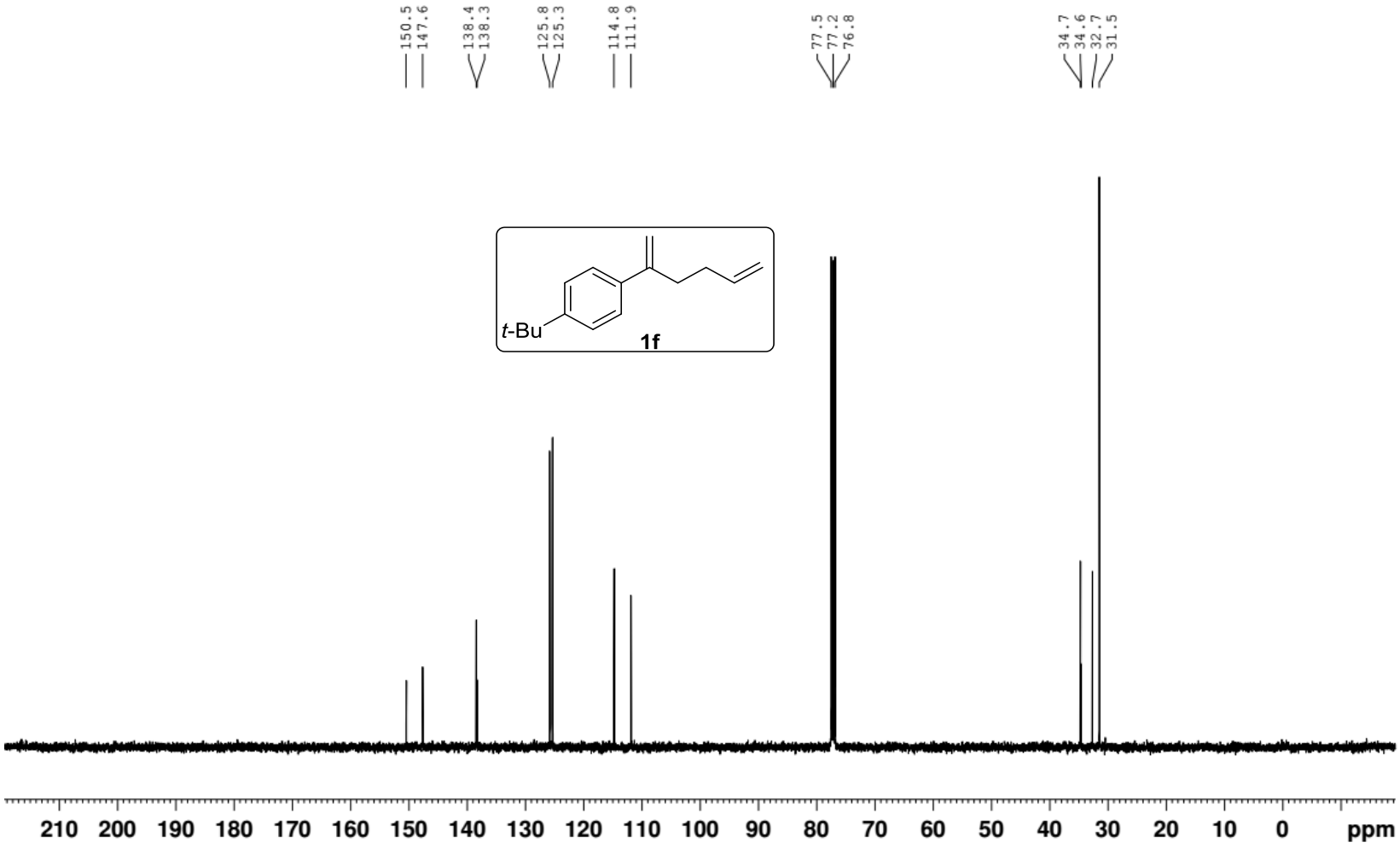

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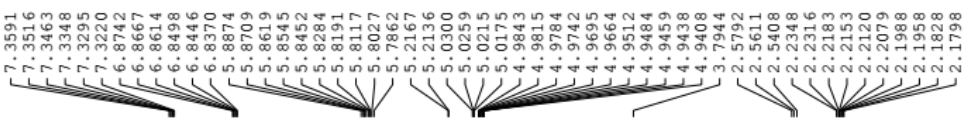

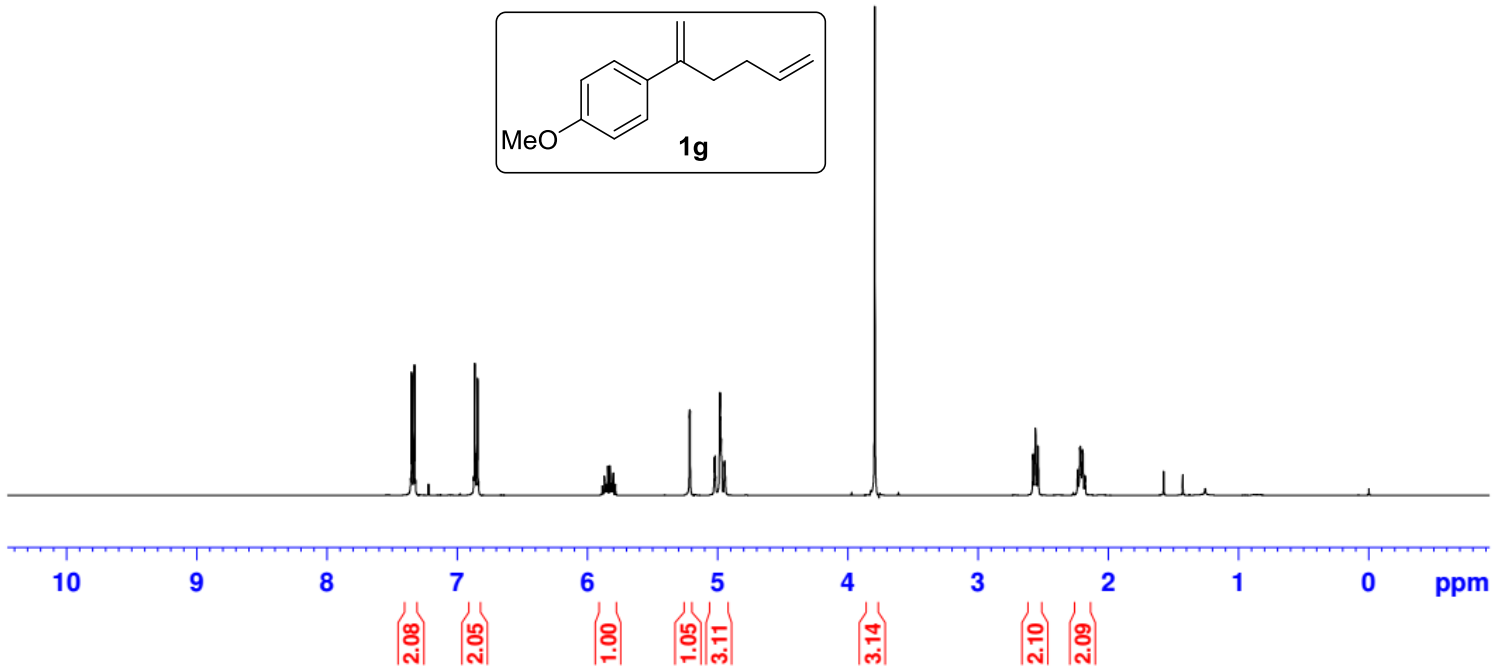

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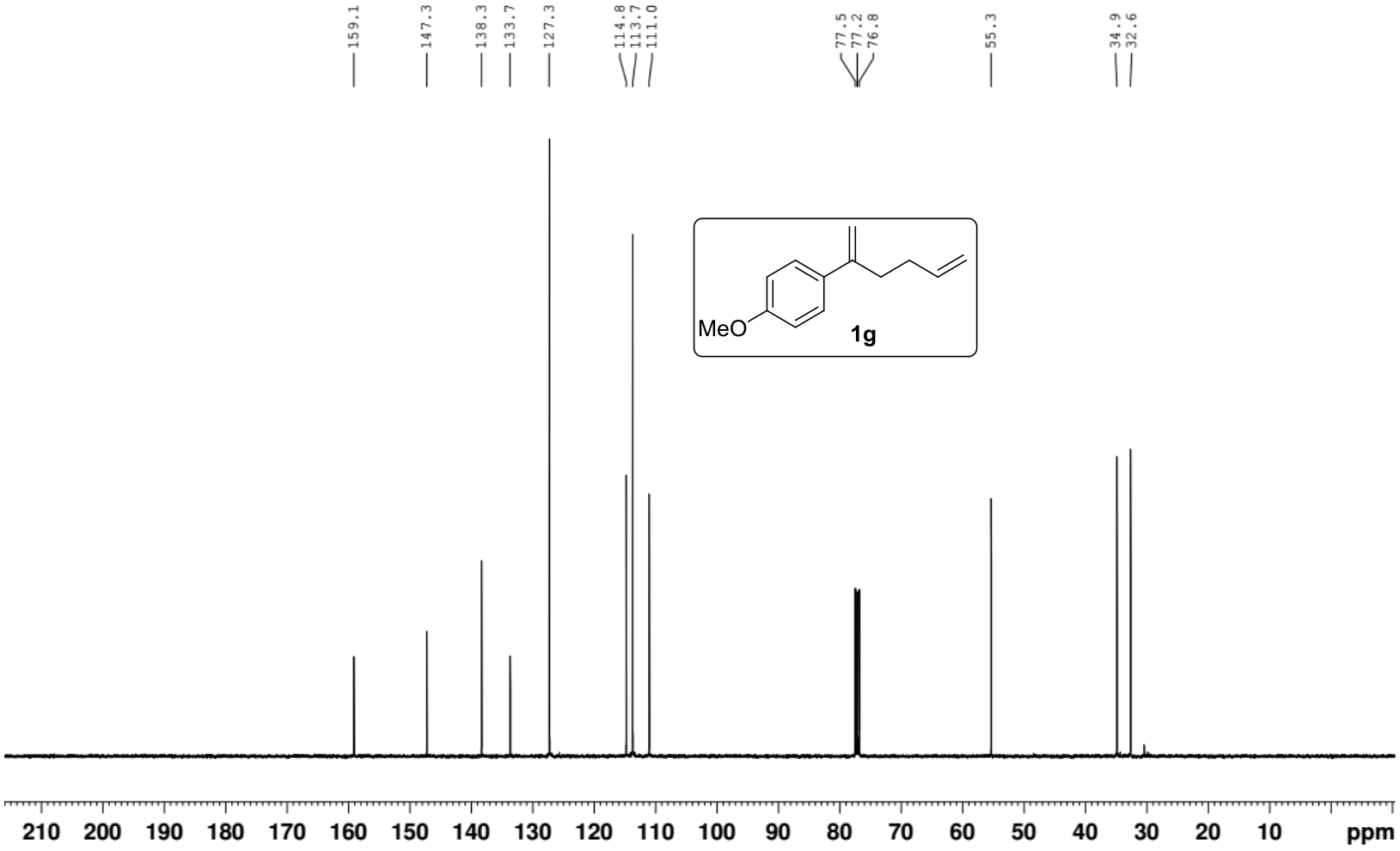

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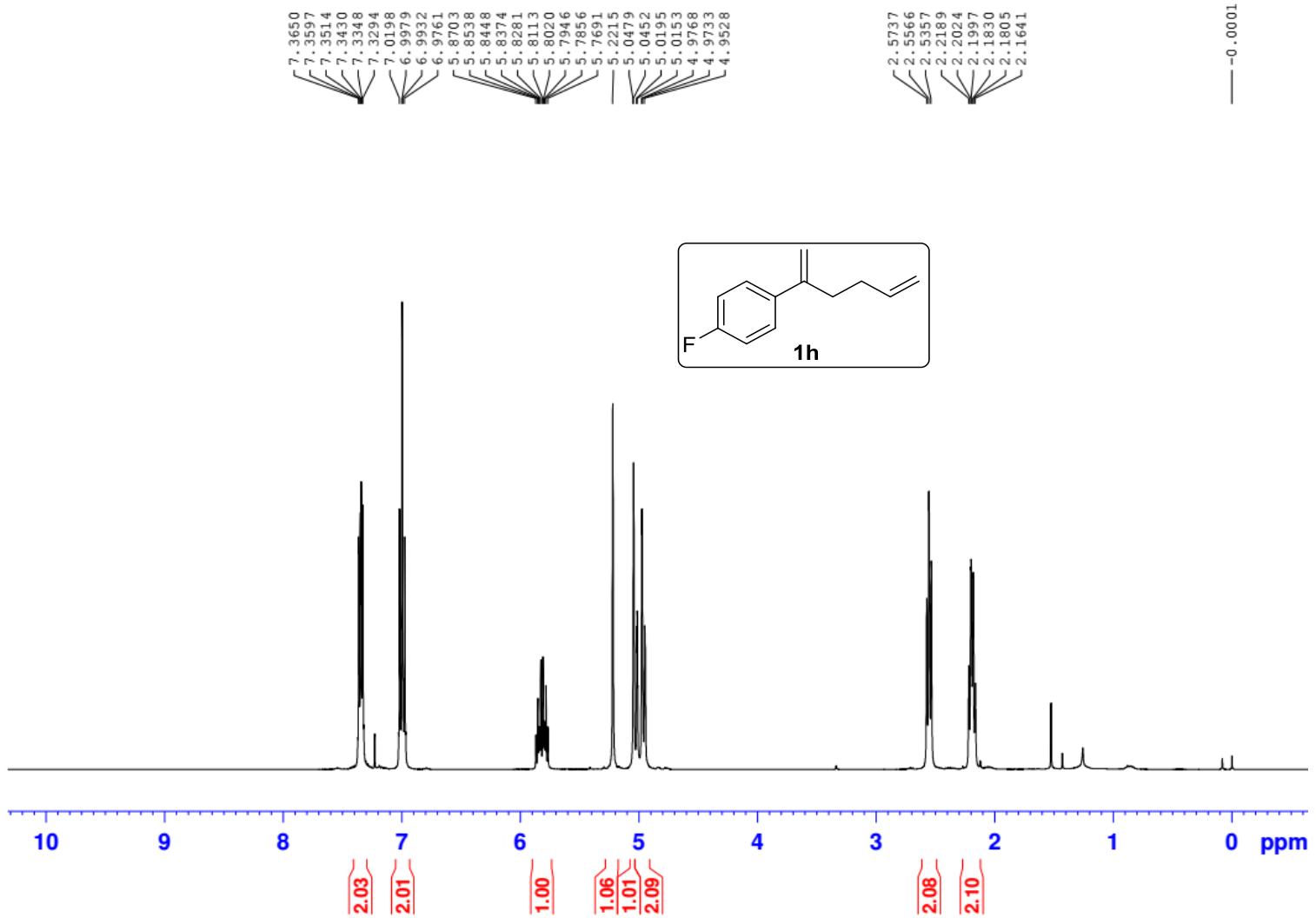

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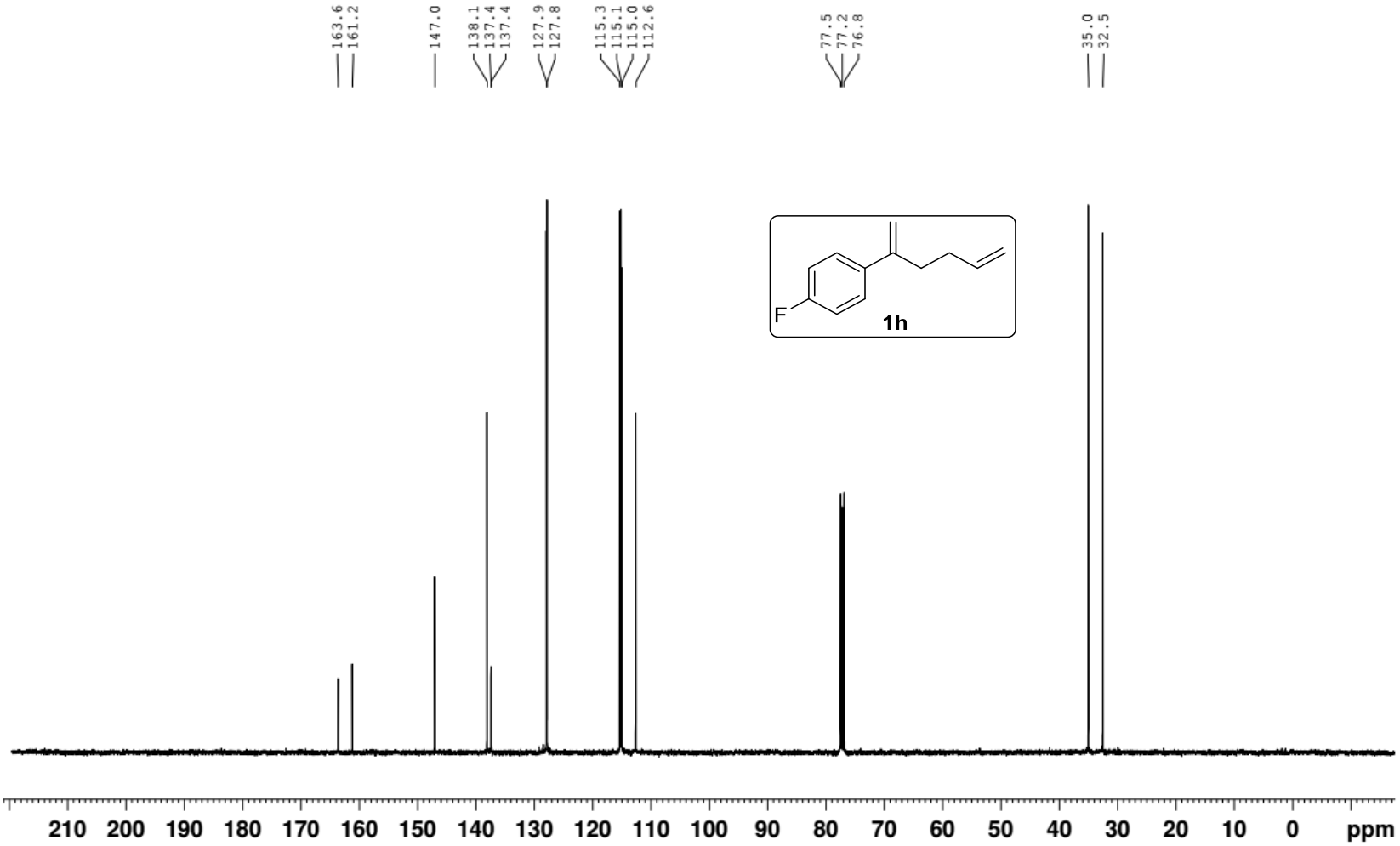

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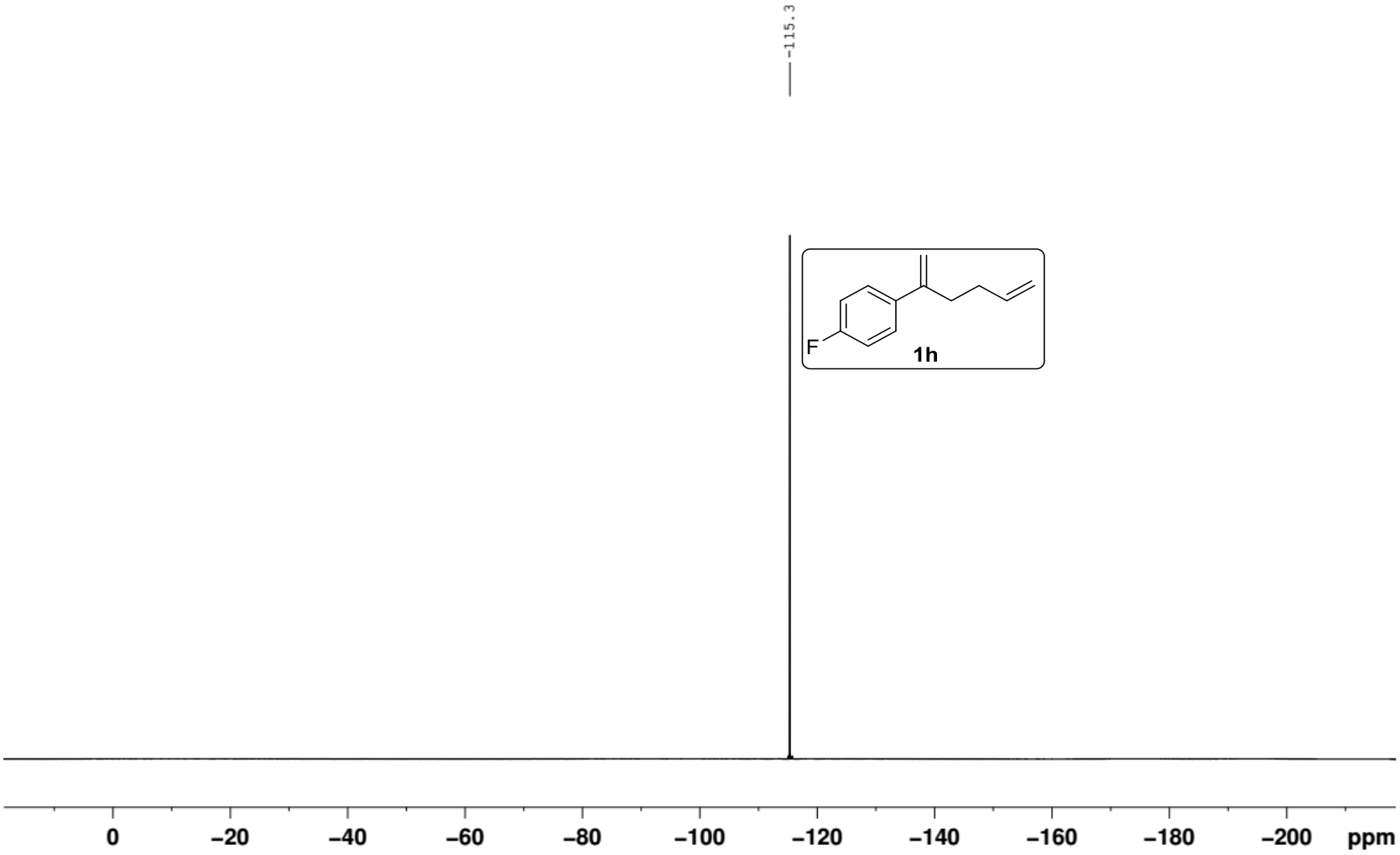

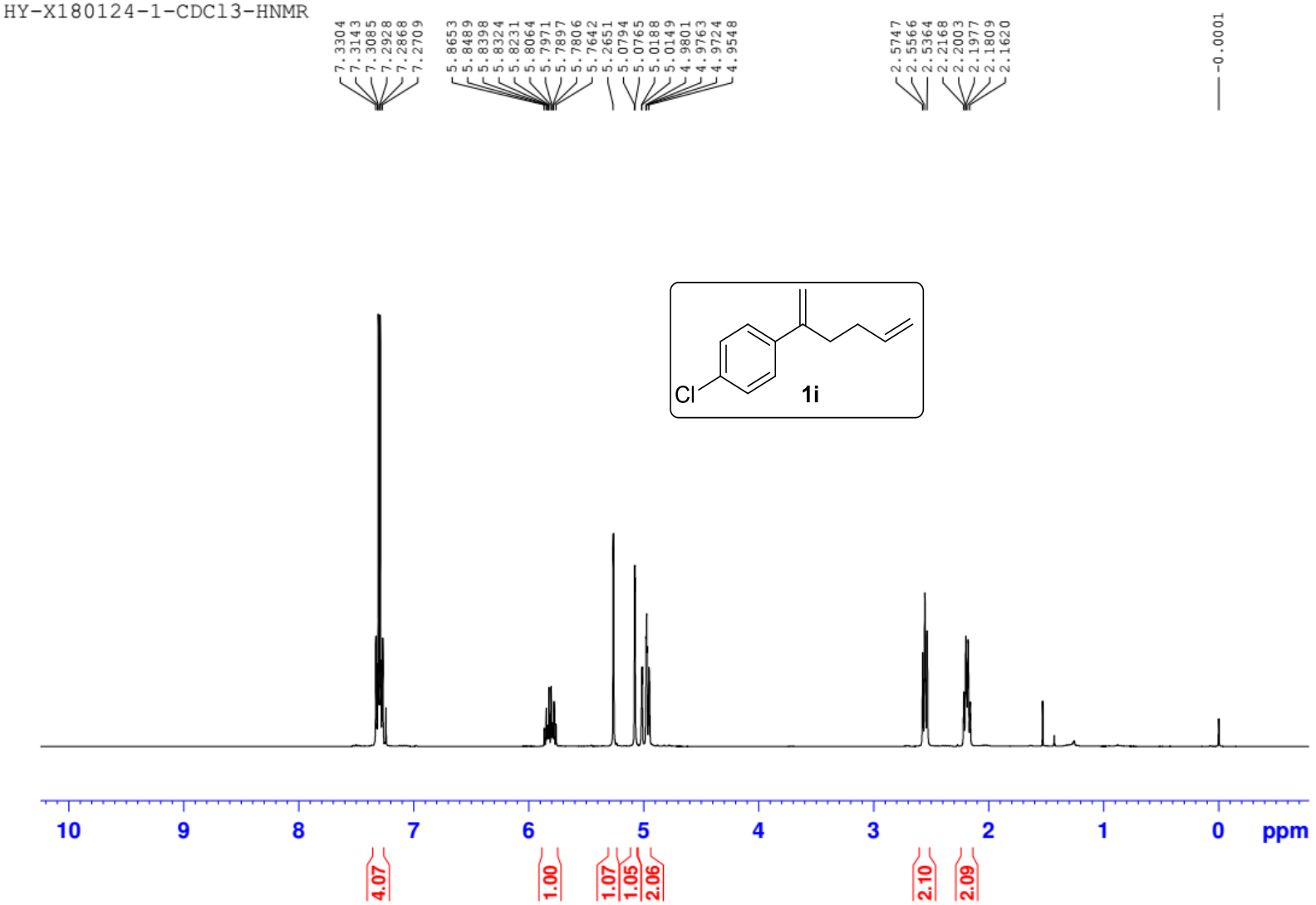
HY-X180124-1-CDCl3-HNMR
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5.7642
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2.1809
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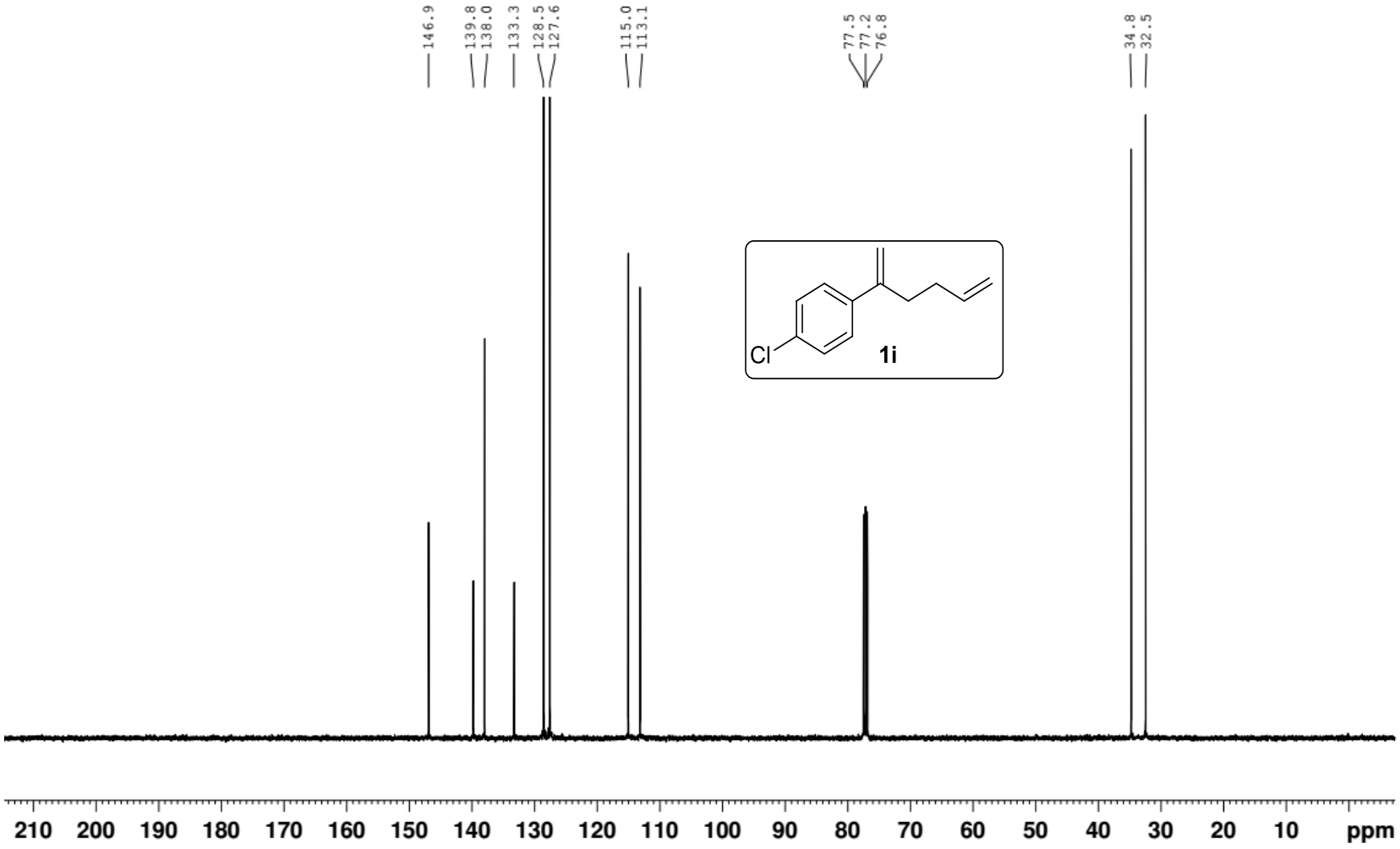
HY-X180124-1-CDCl3-CNMR



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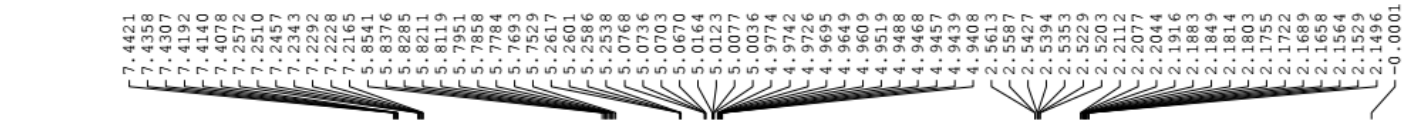

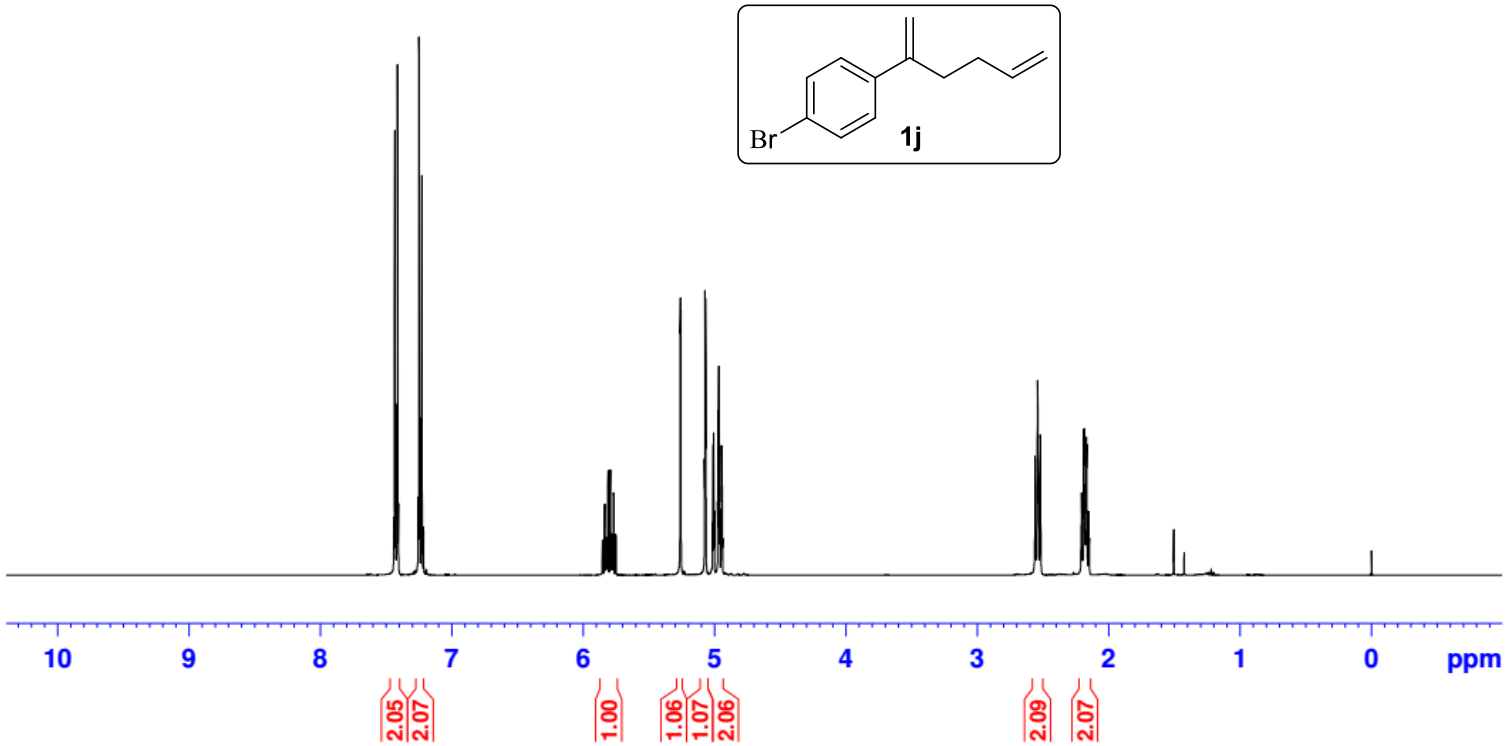

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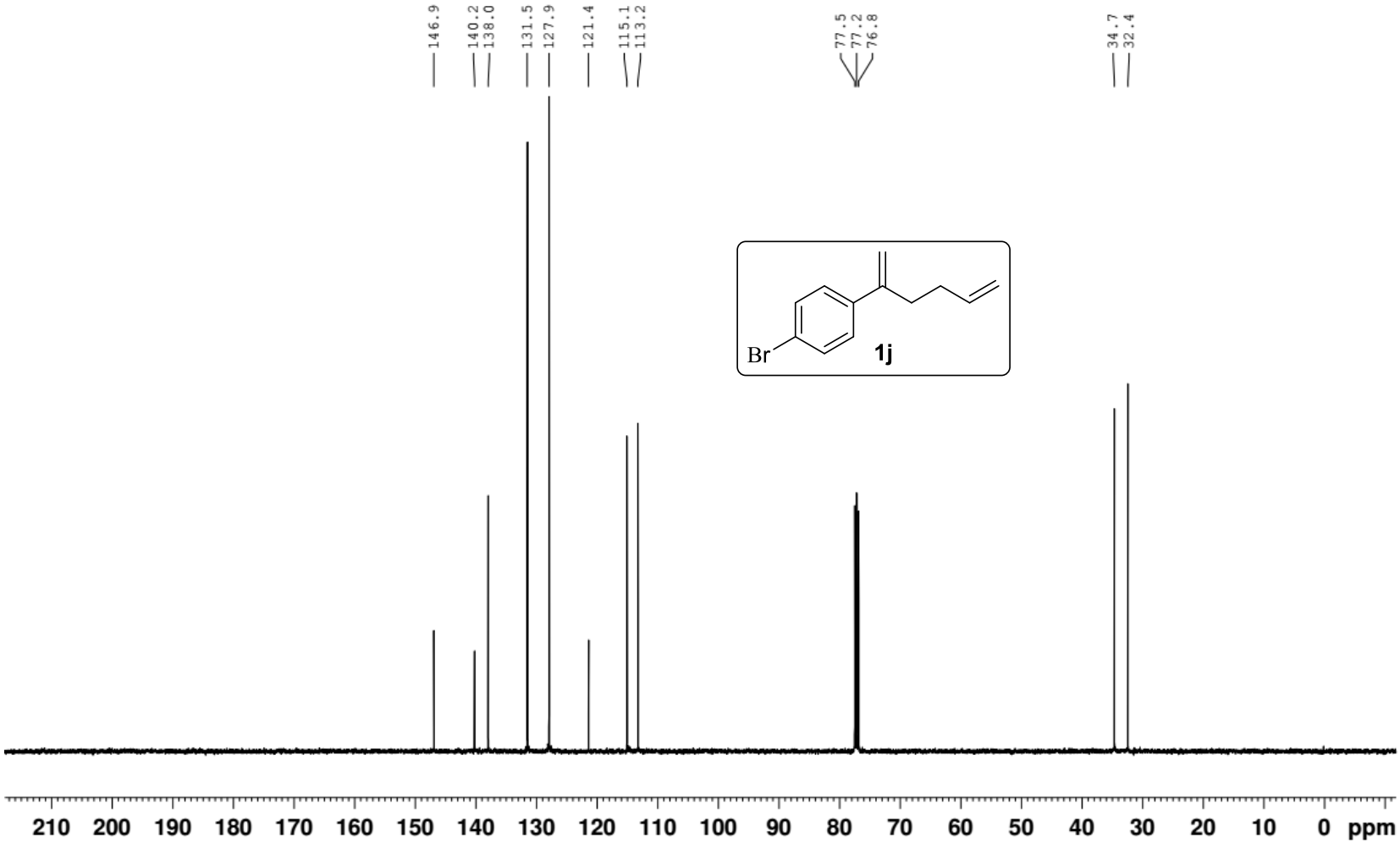
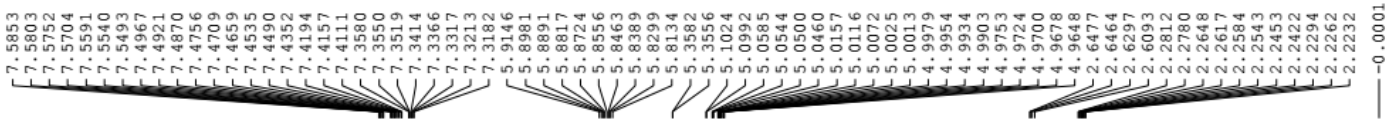
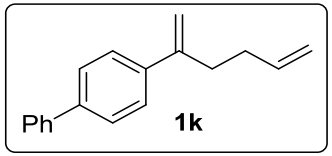
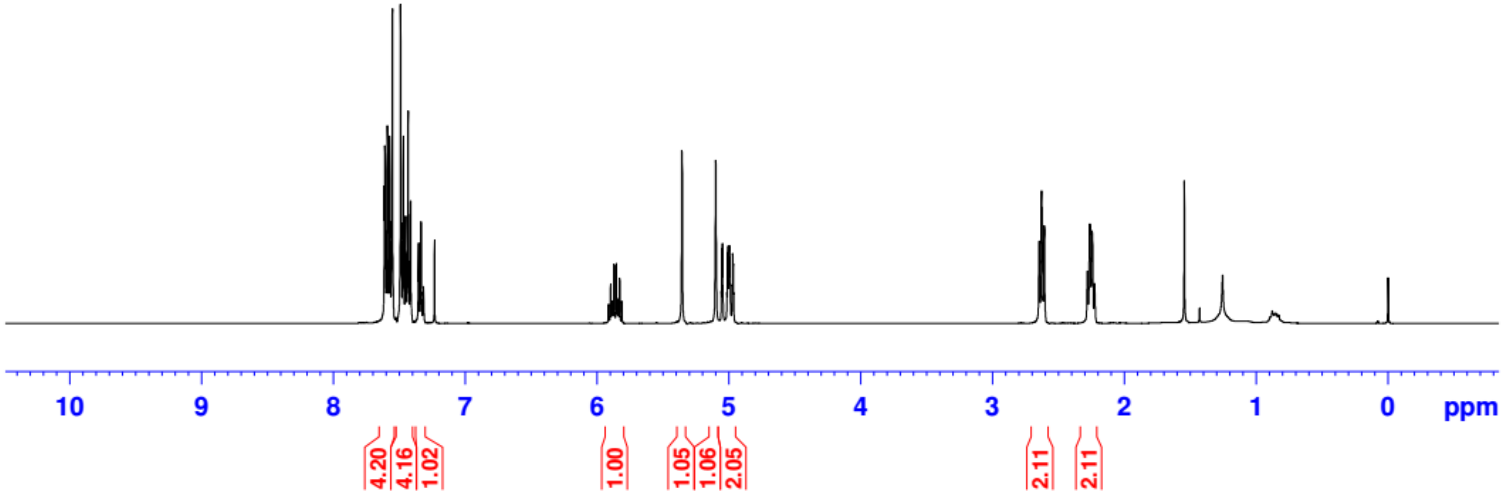


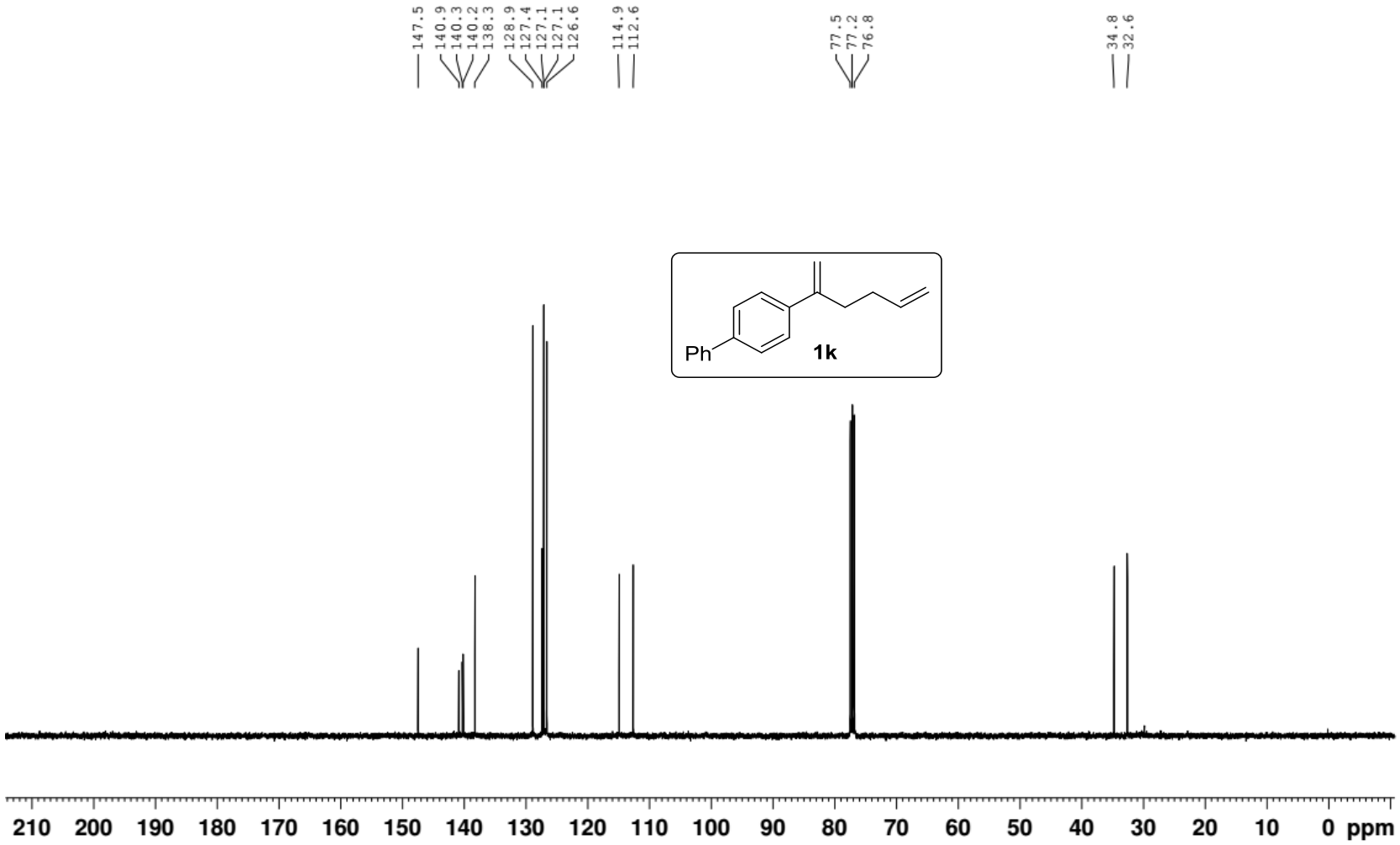
HY-X180424-1-CDCl3-HNMR



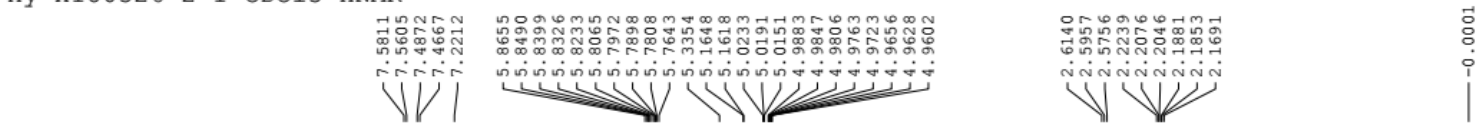


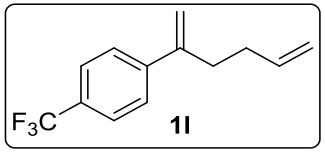


HY-X180424-1-CDCl3-CNMR



hy-x180326-2-1-CDCl3-HNMR





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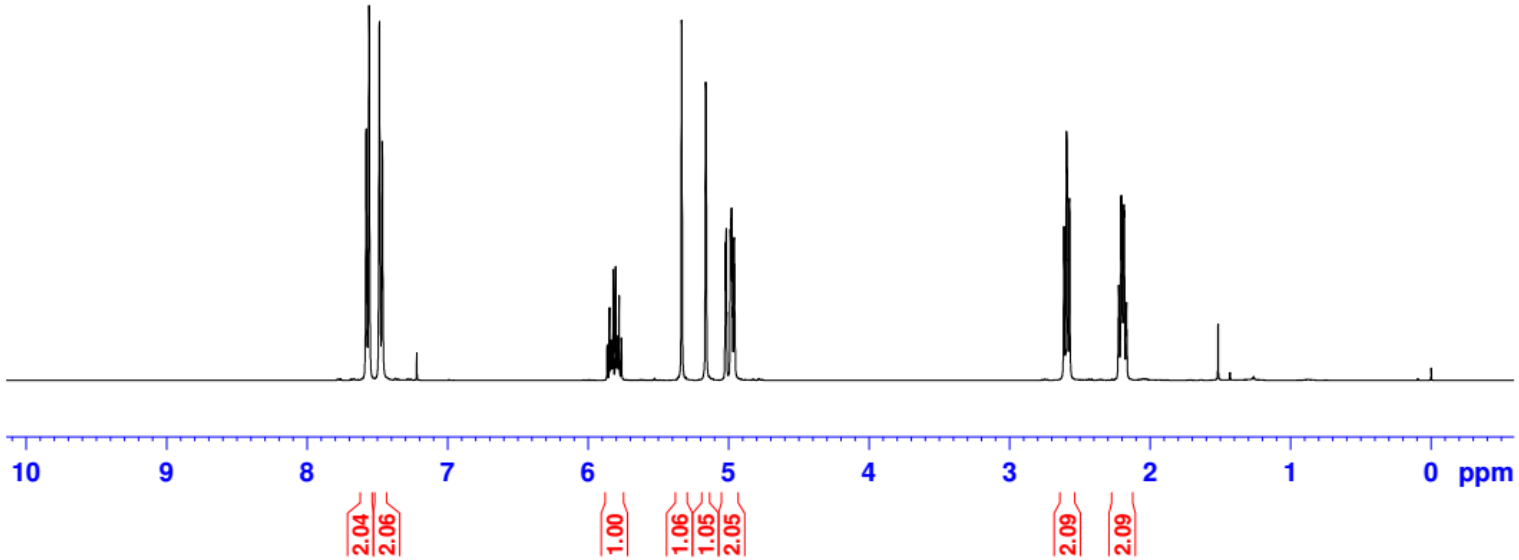
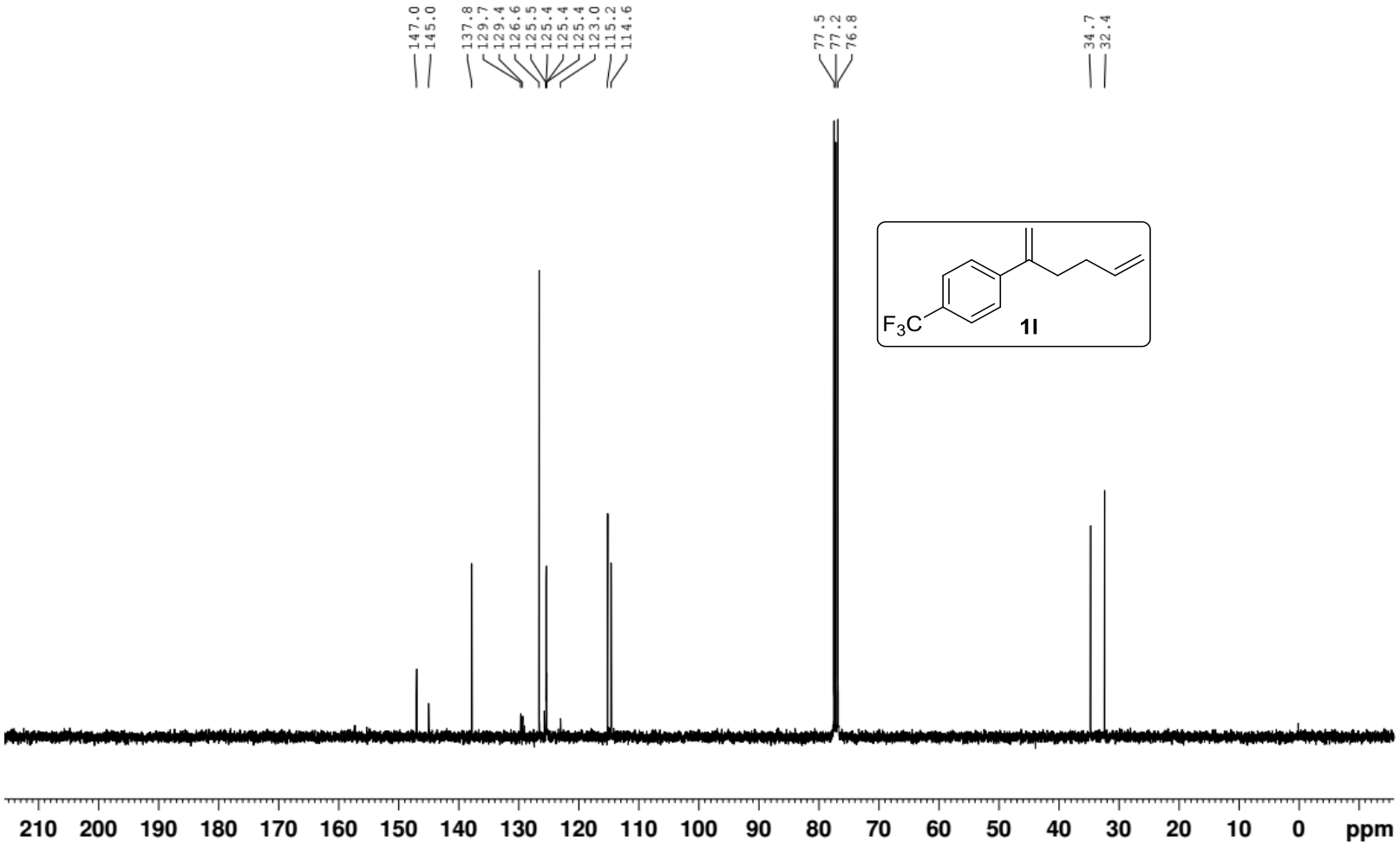
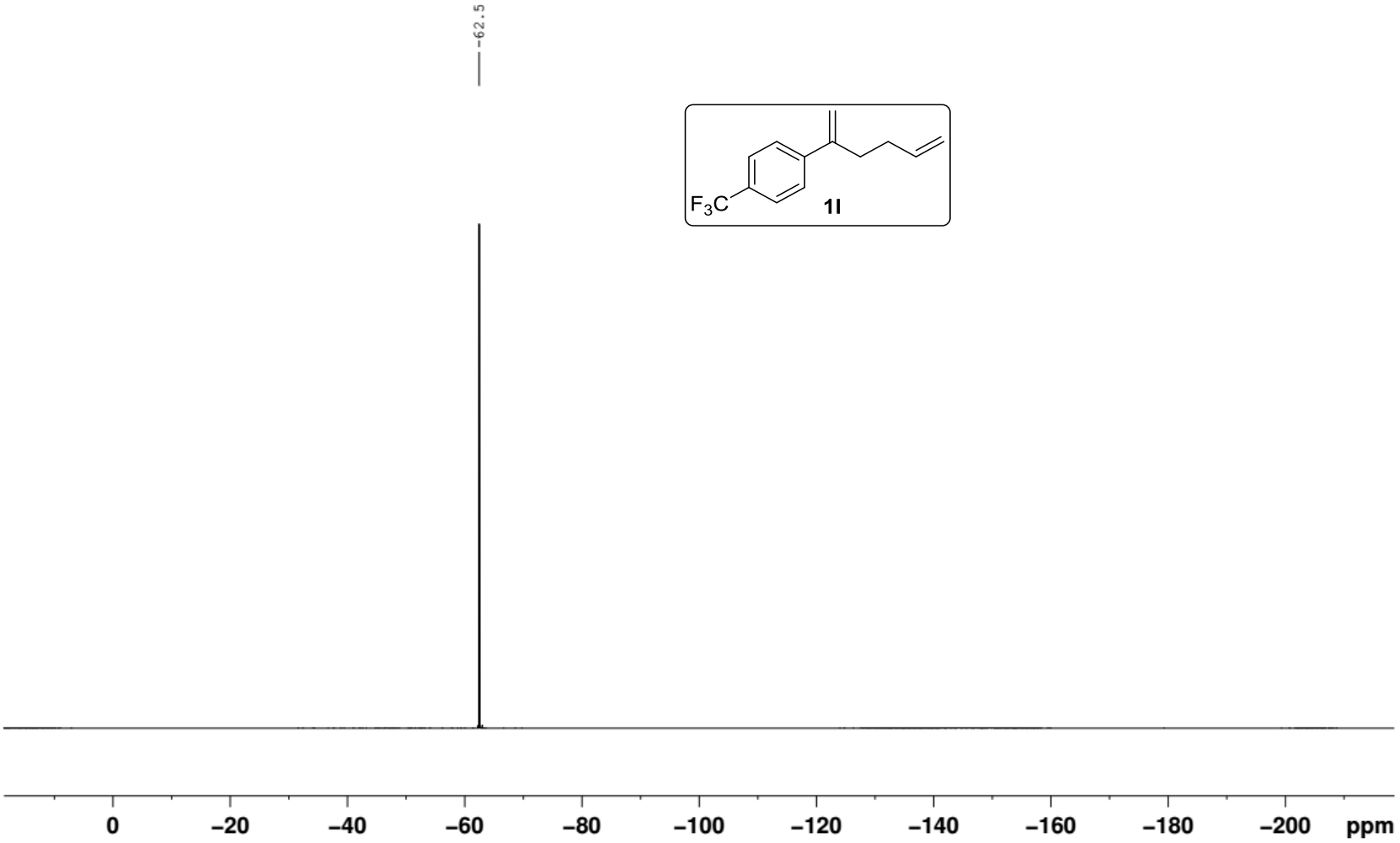


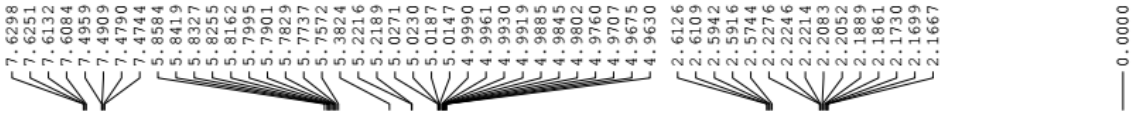
HY-X180326-2-1-CDCl3-CNMR

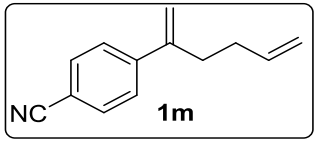


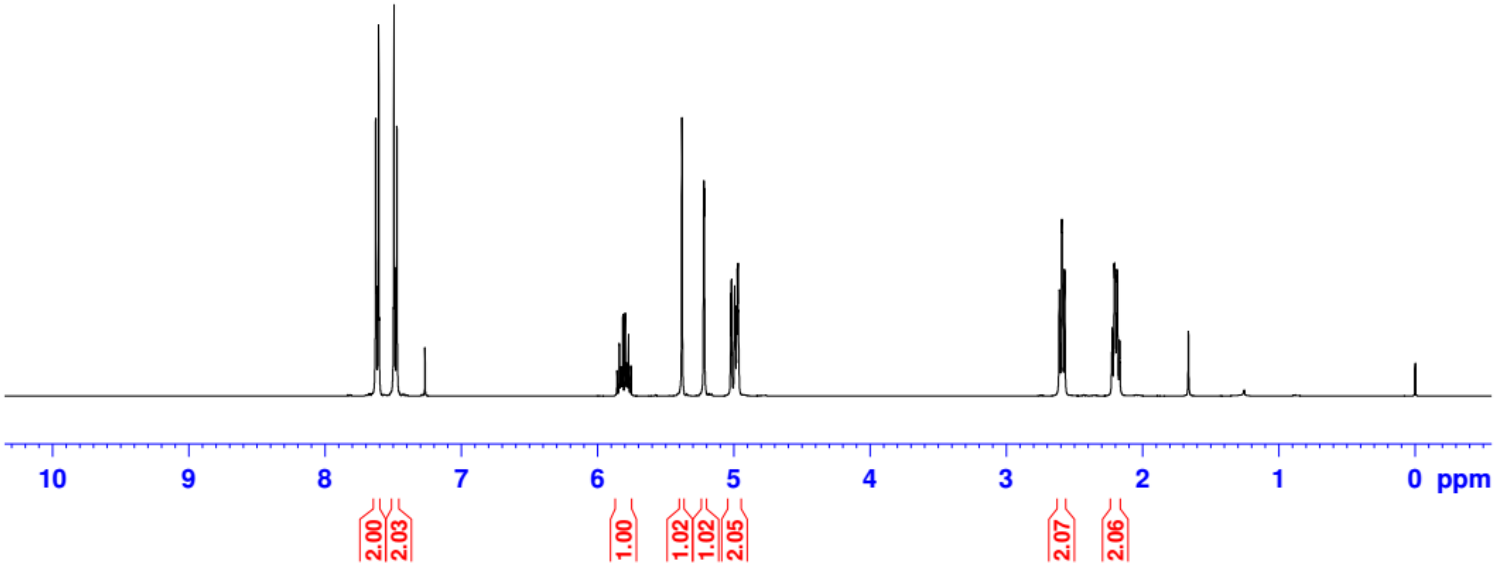
HY-X180326-2-1-CDCl3-FNMR



HY-X180321-1-CDCl3-HNMR







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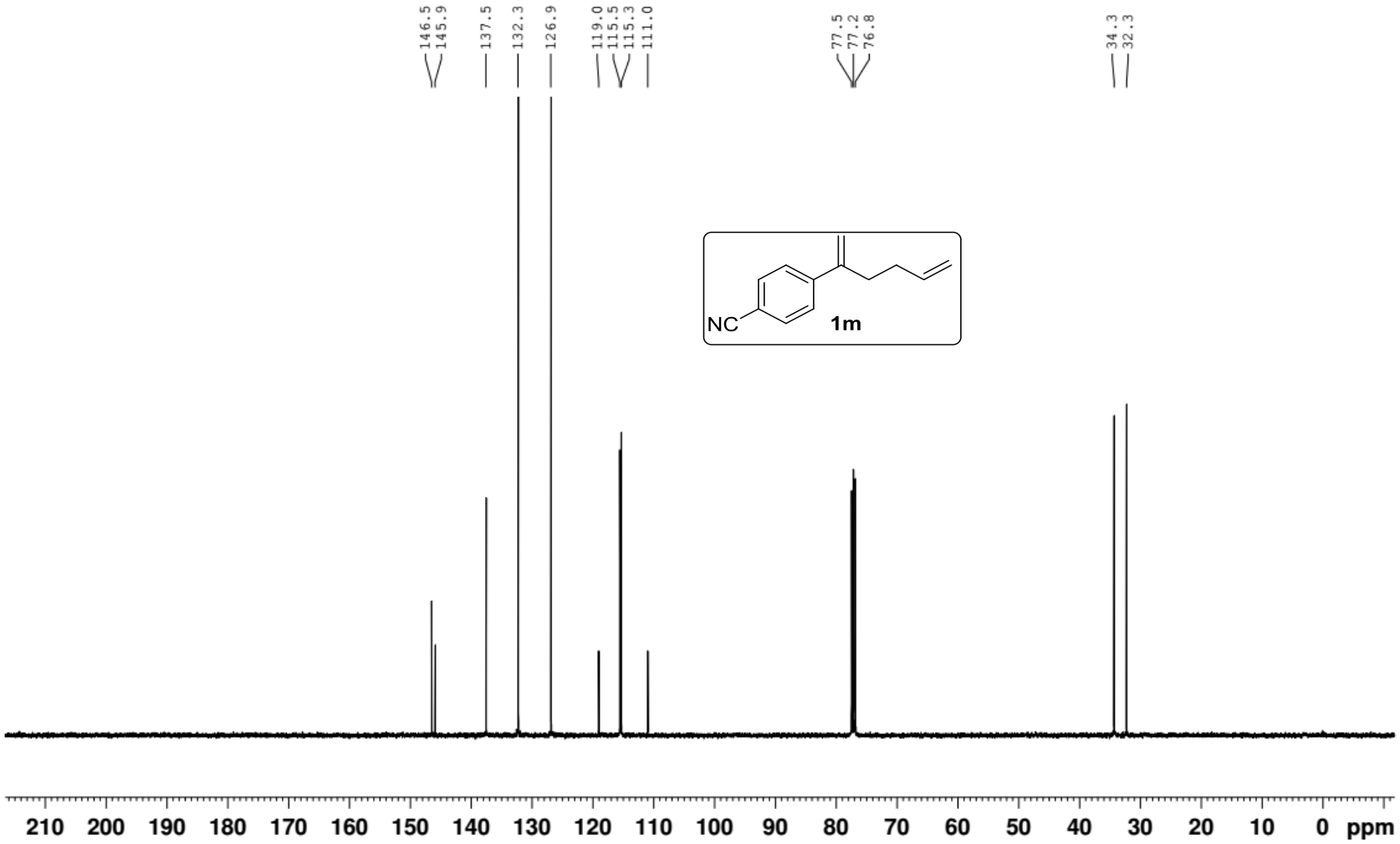
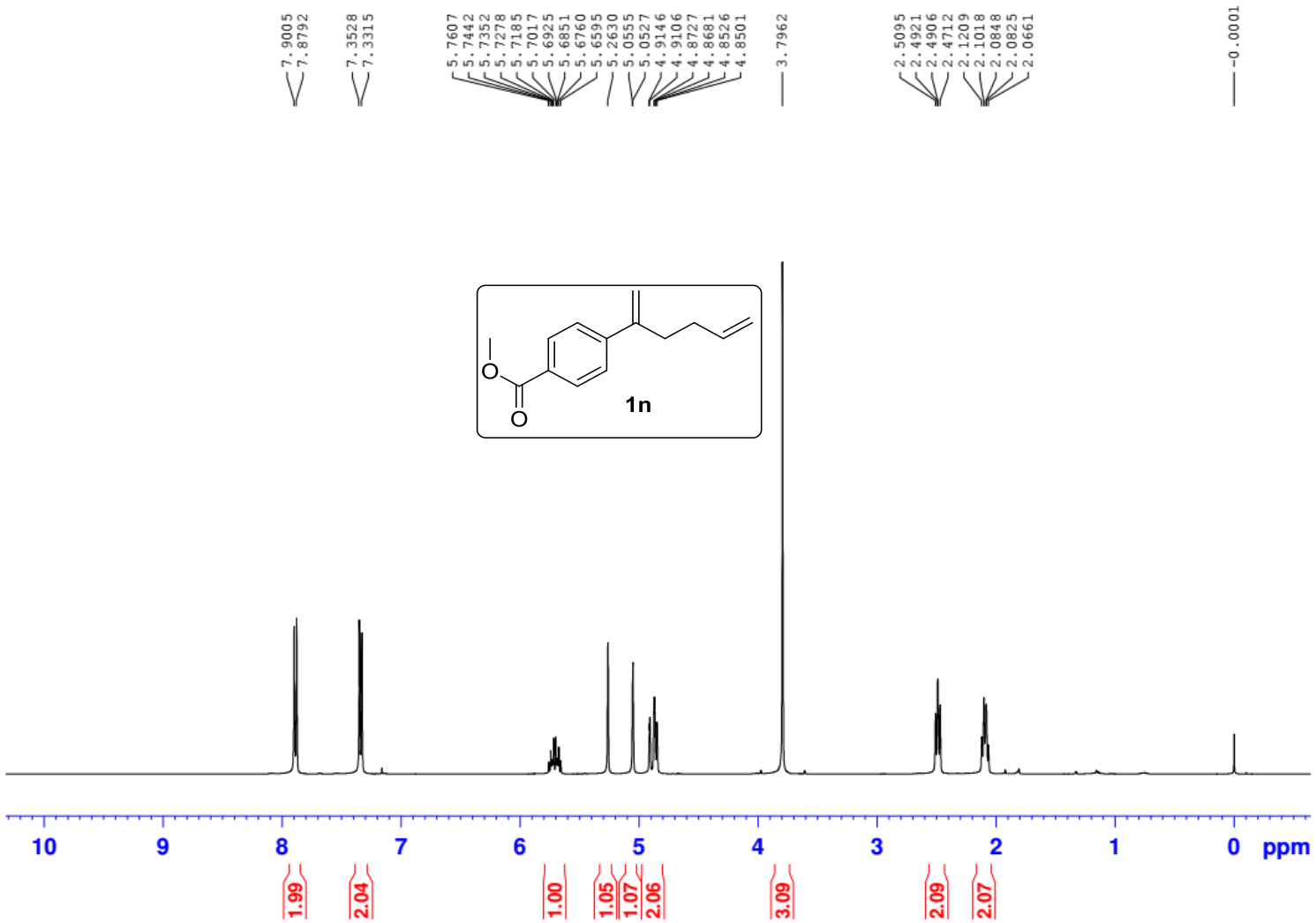


HY-X180408-1-CDCl3-HNMR



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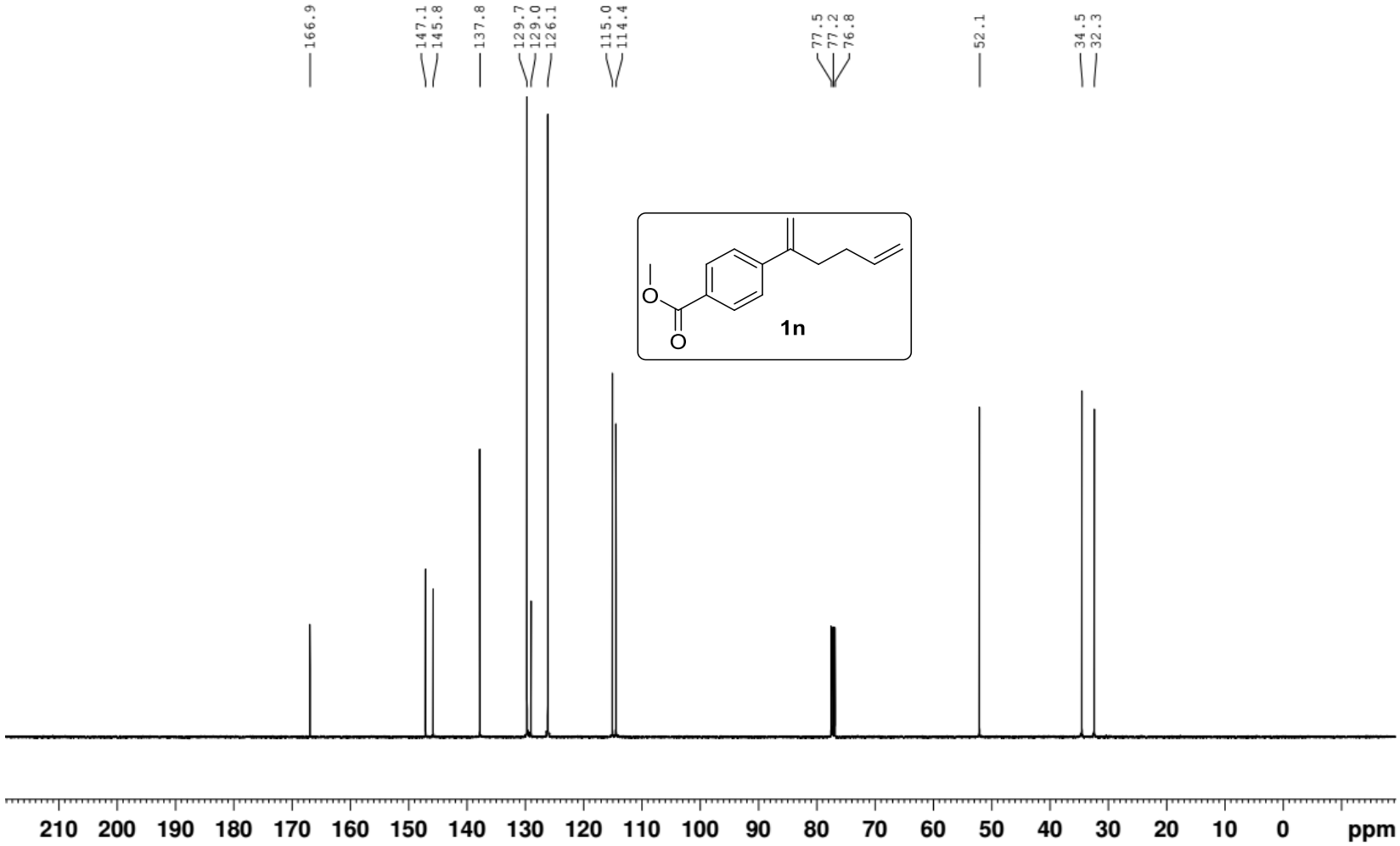
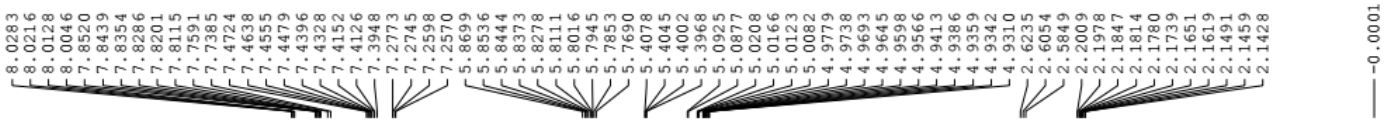
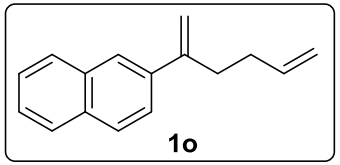
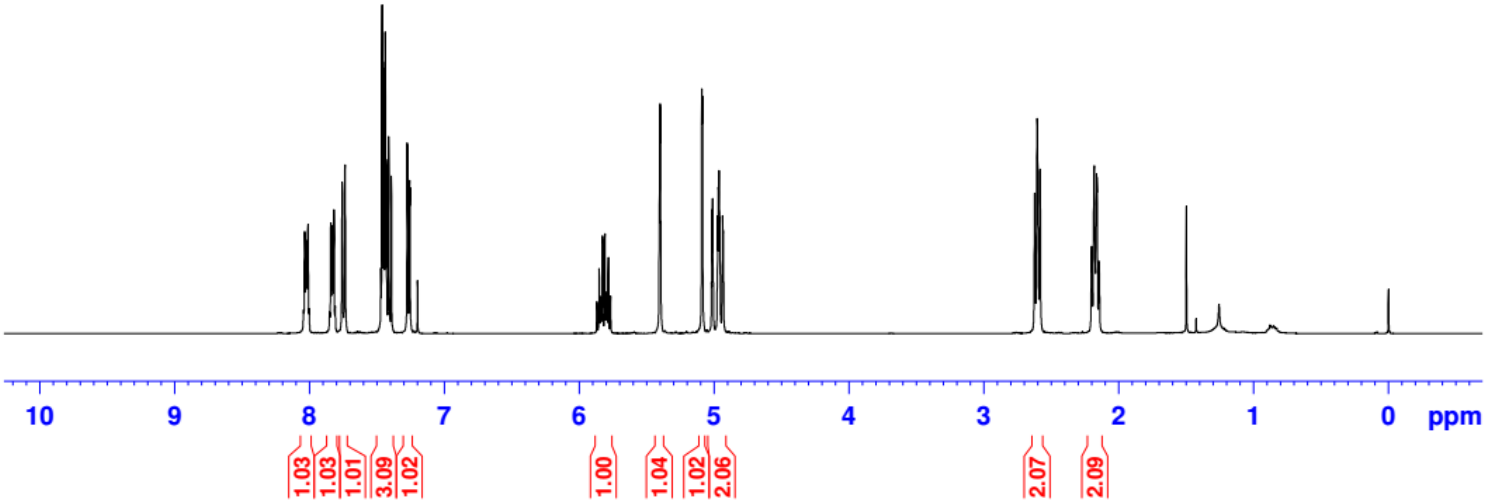


HY-X180226-1-CDC13-HNMR







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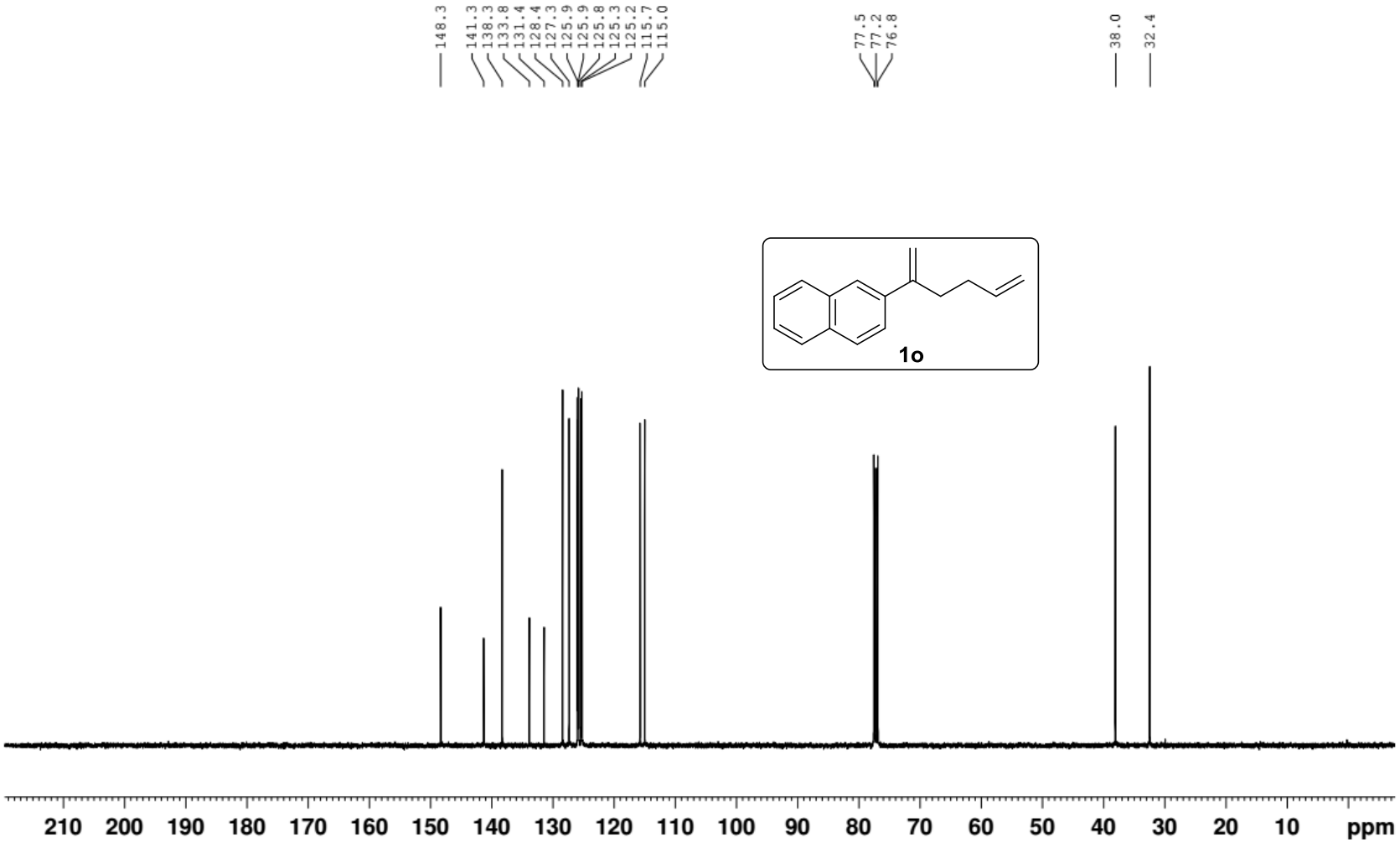
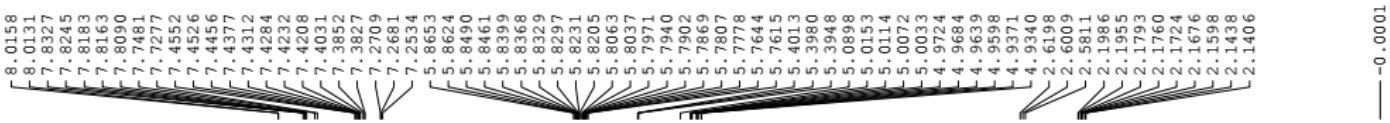
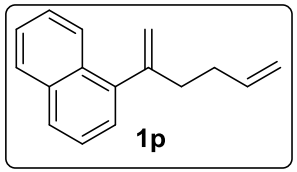
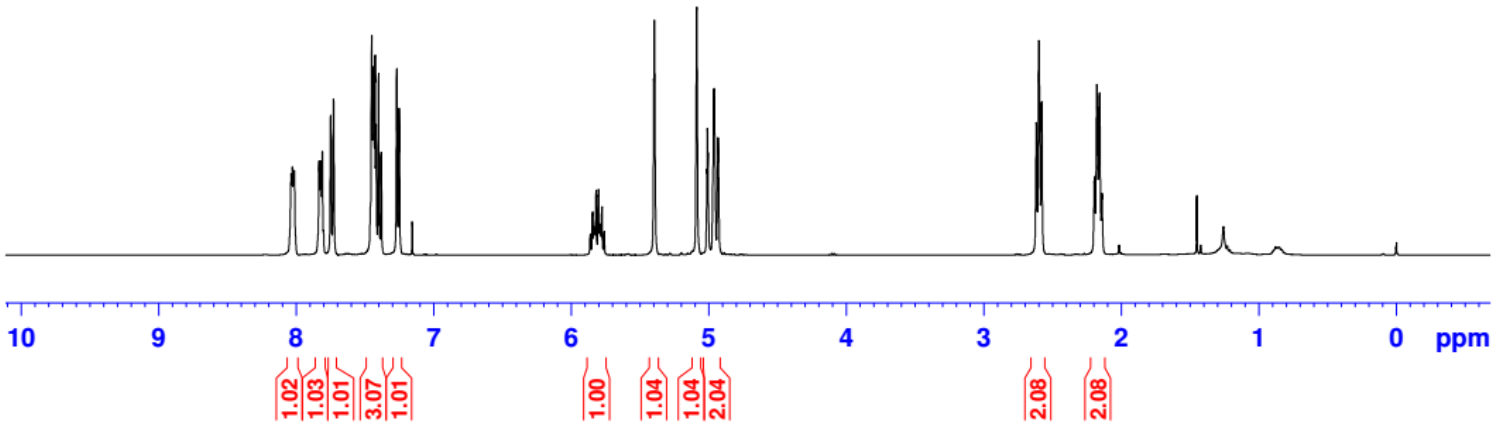


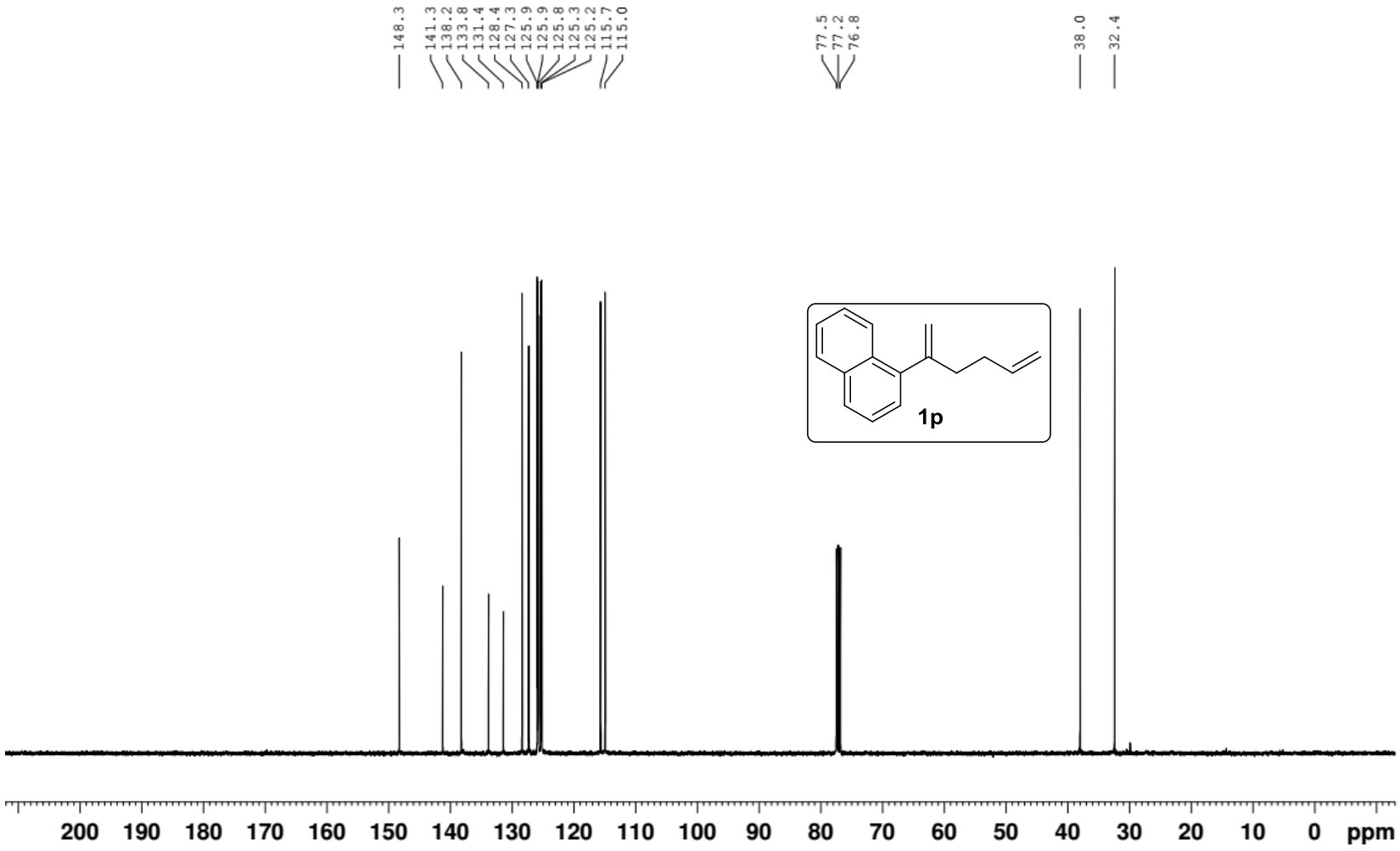
HY-X180424-1-CDCl3-HNMR



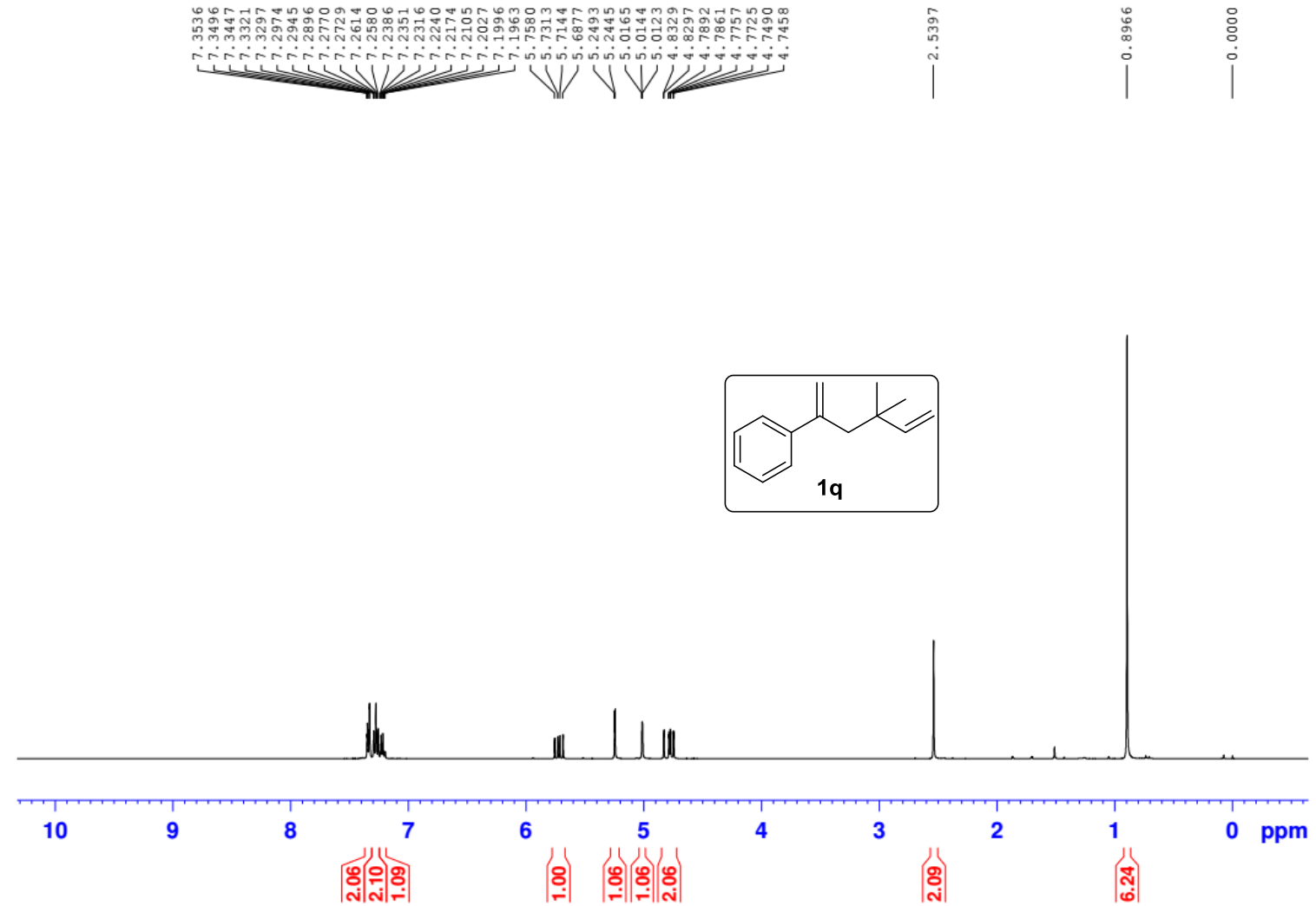




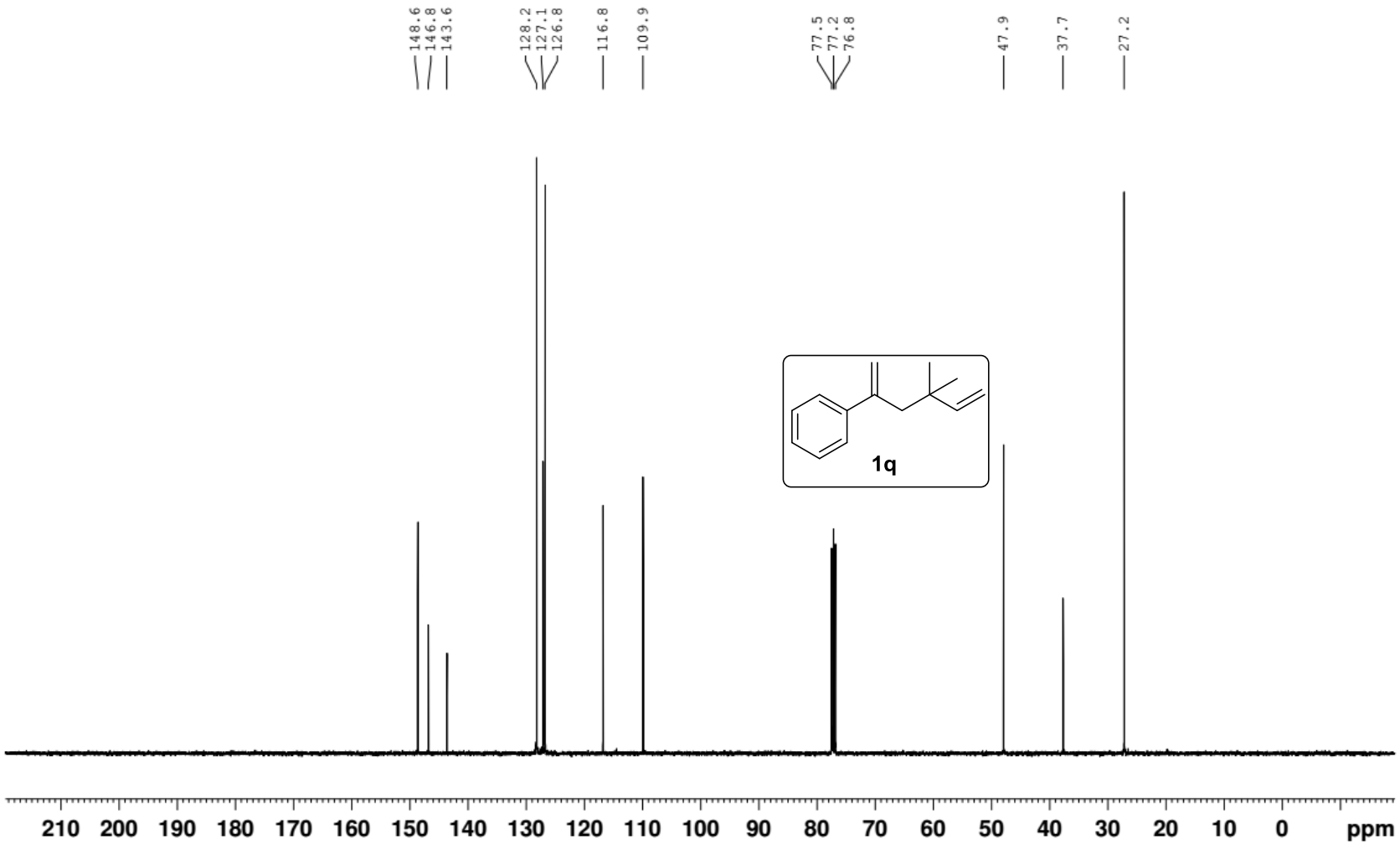
HY-X180424-2-CDCl3-CNMR



HY-X180430-1-CDCl3-HNMR



HY-X180430-1-CDCl3-CNMR



HY-X180401-2-CDCl3-HNMR

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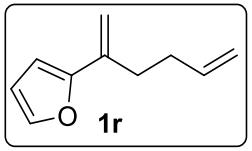
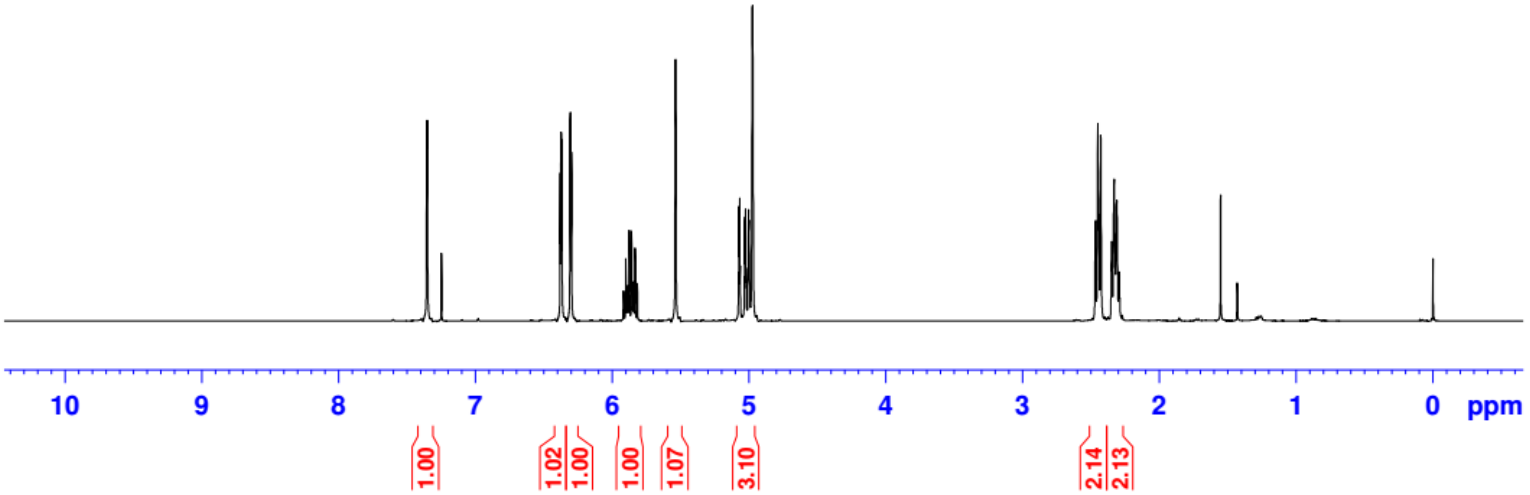
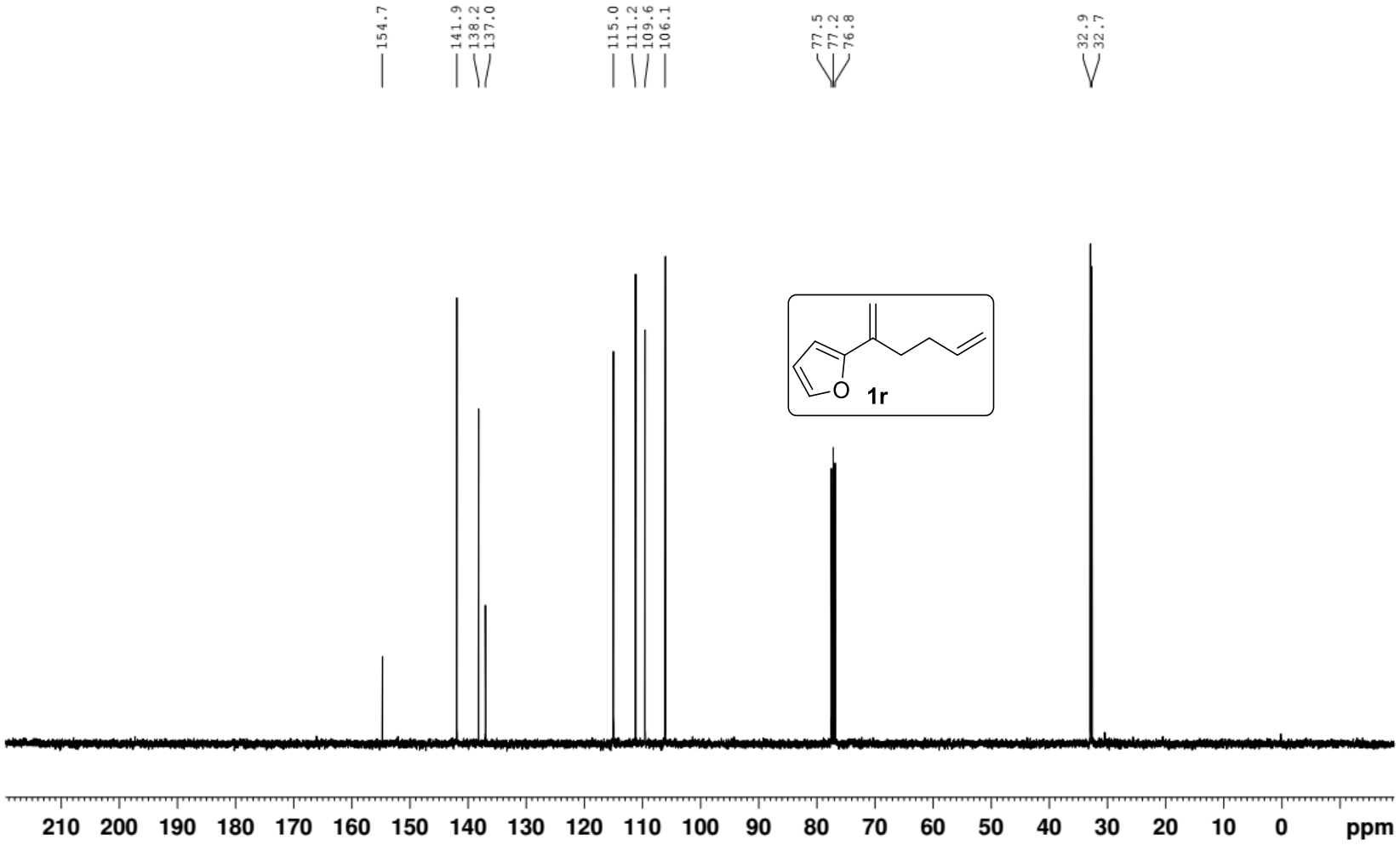
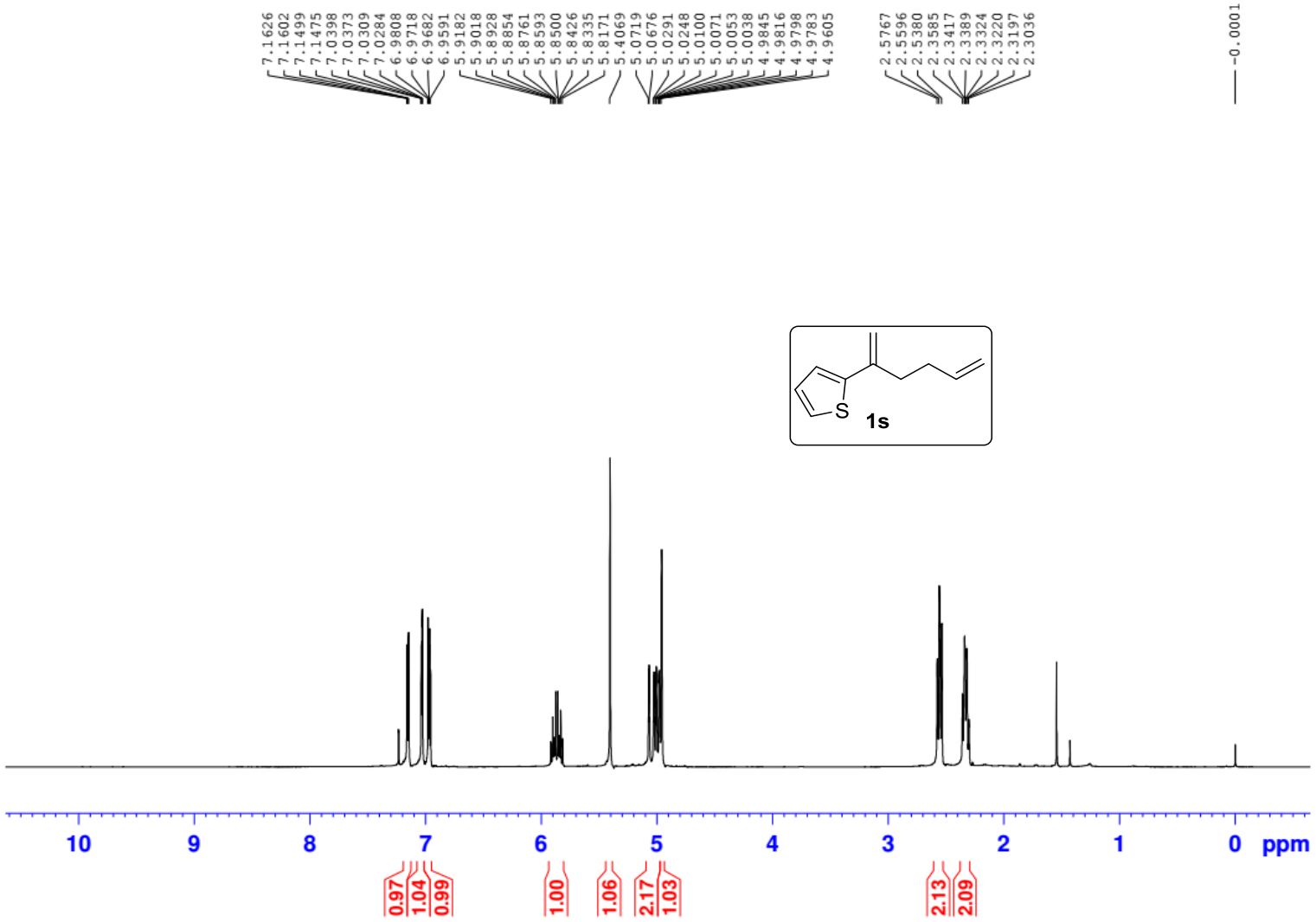




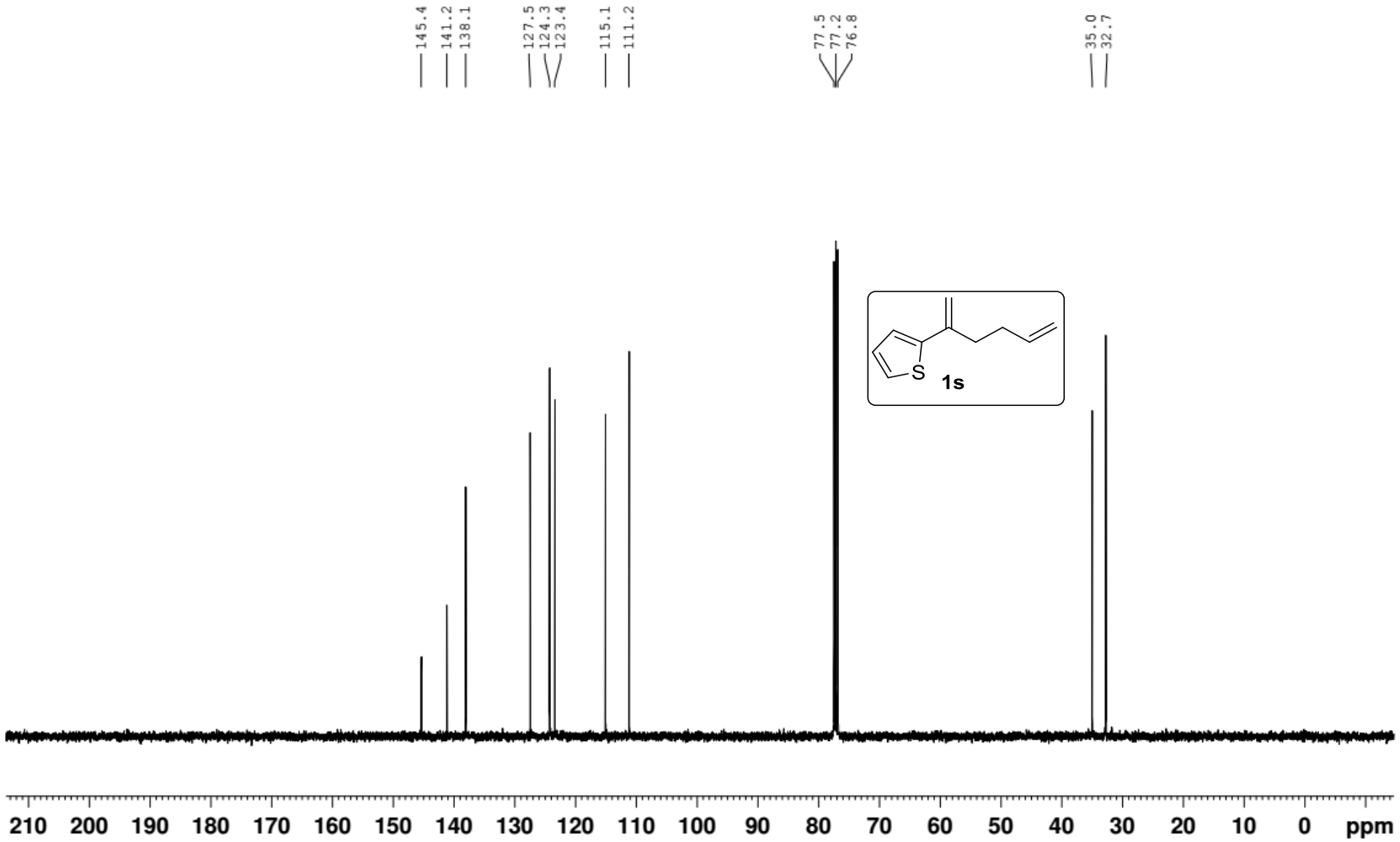
HY-X180401-2-CDCl3-CNMR



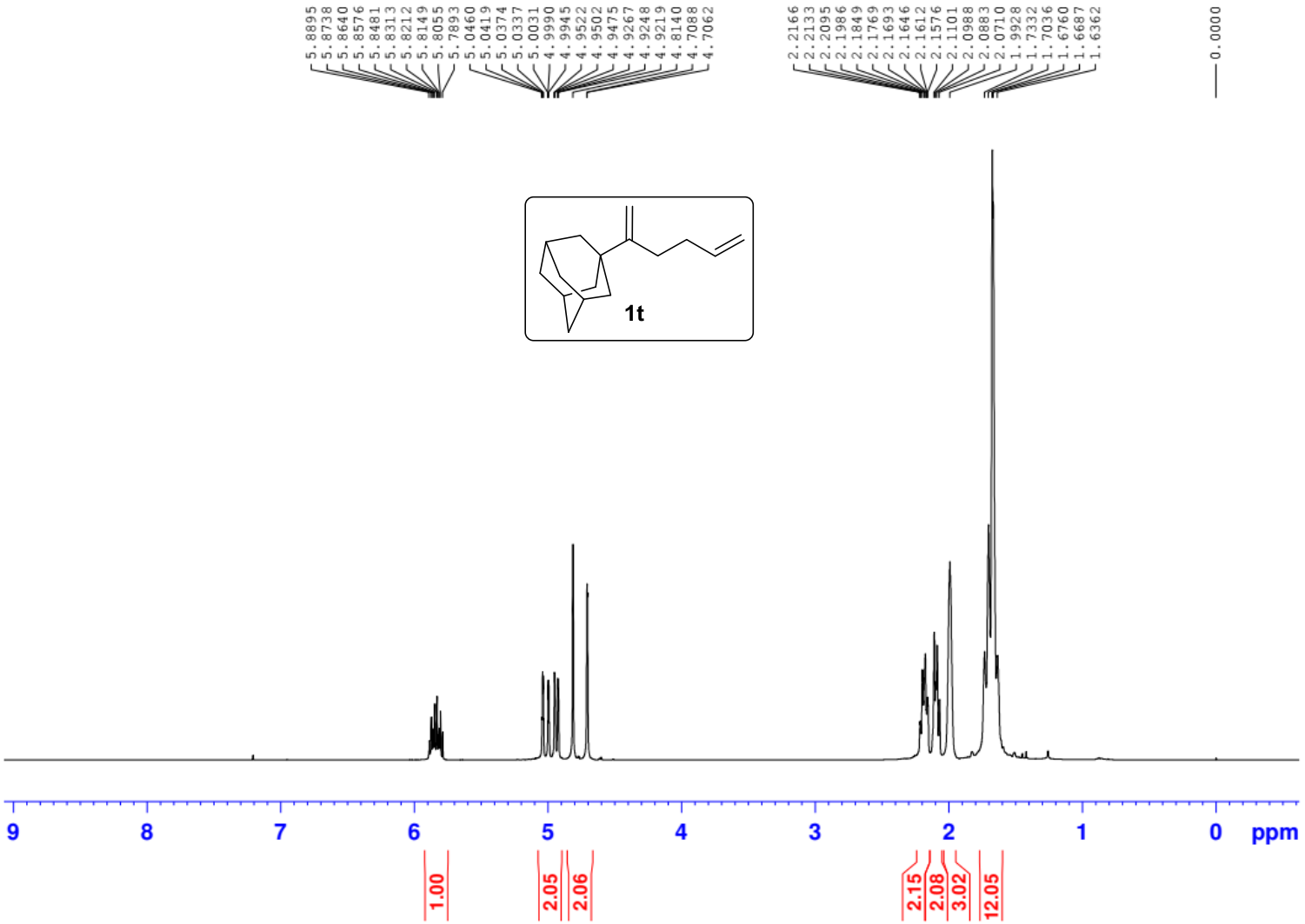
HY-X180401-3-CDCl3-HNMR



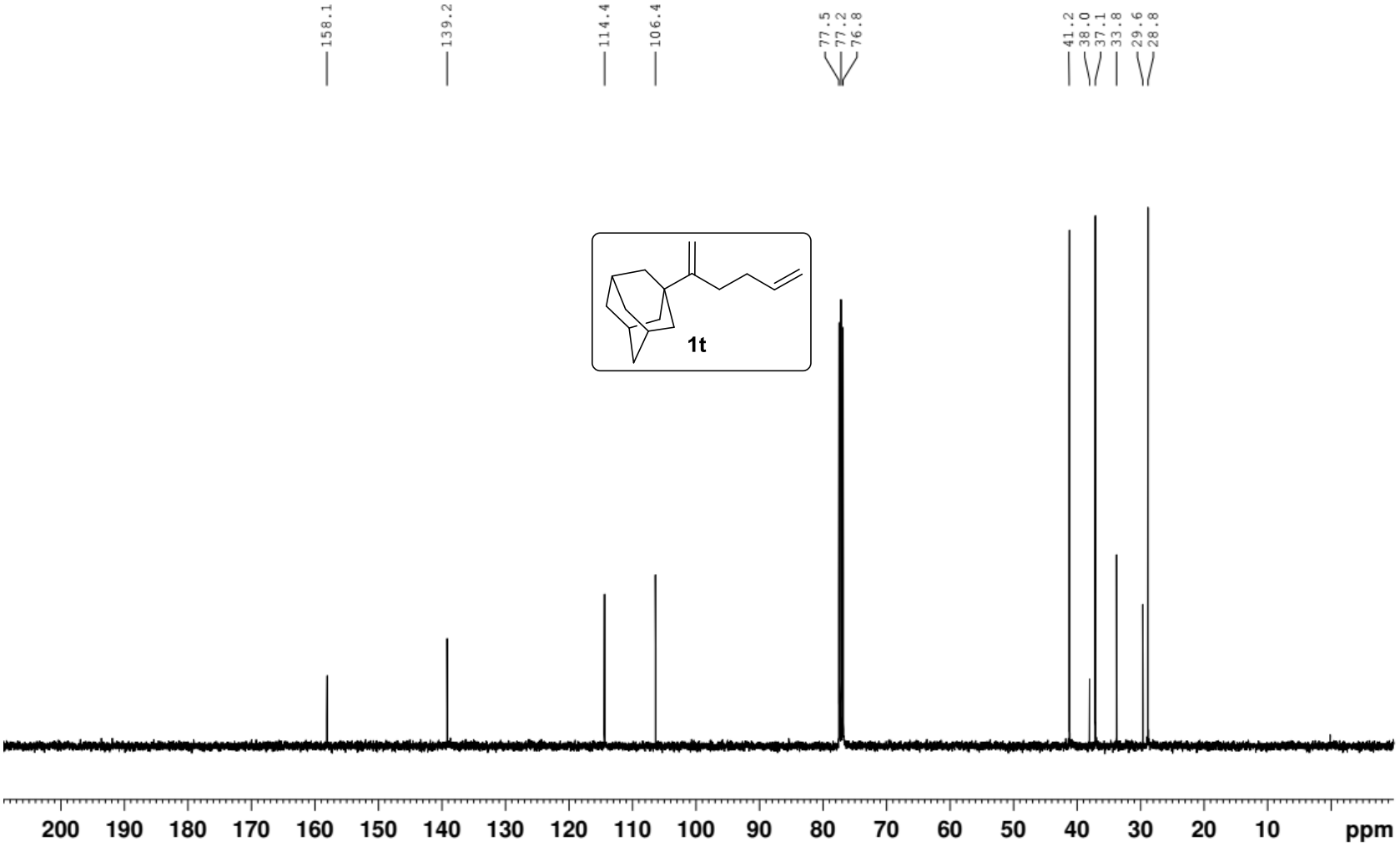
HY-X180401-3-CDCl3-CNMR



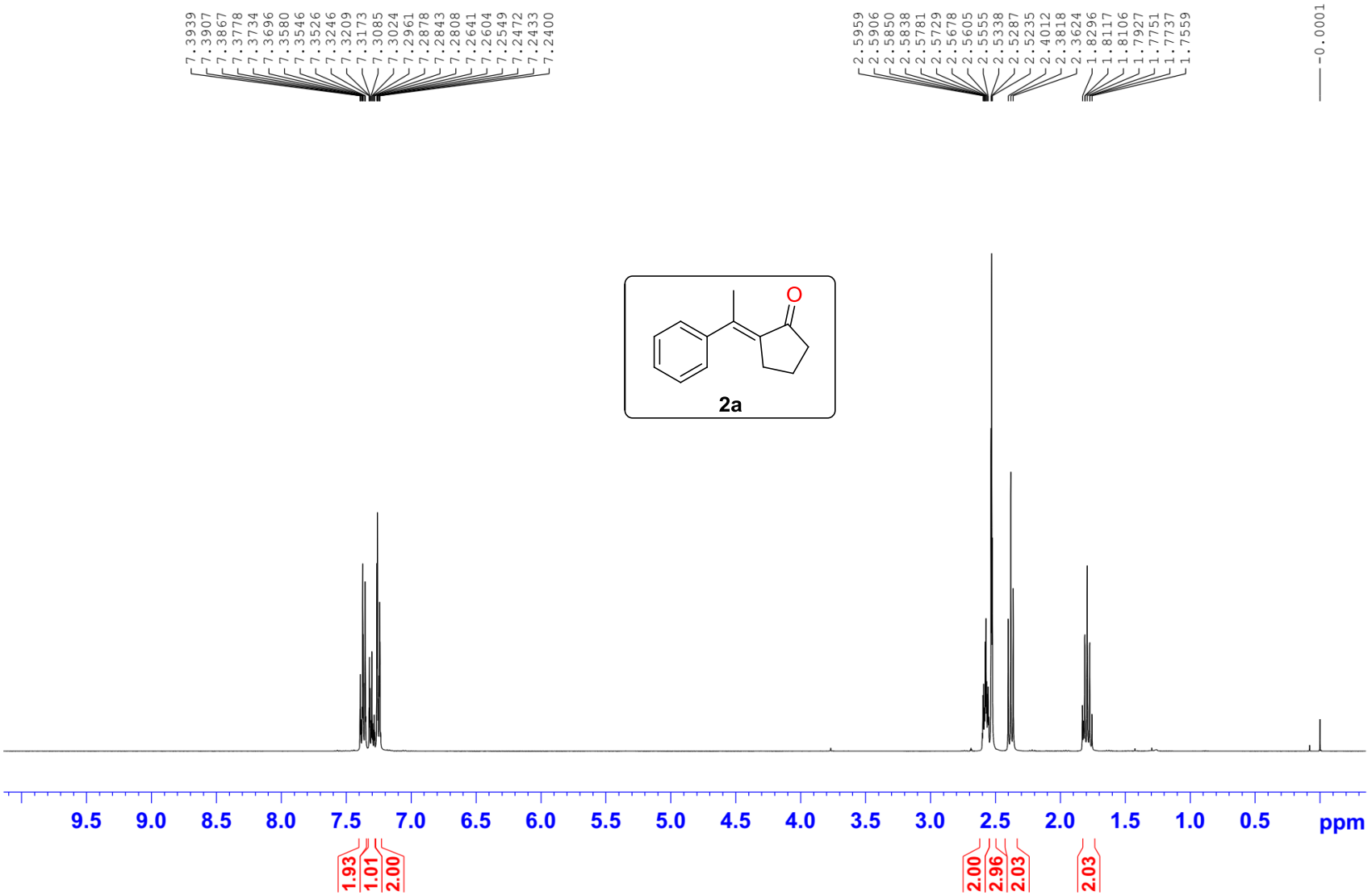
HY-X180318-1-CDCl3-HNMR



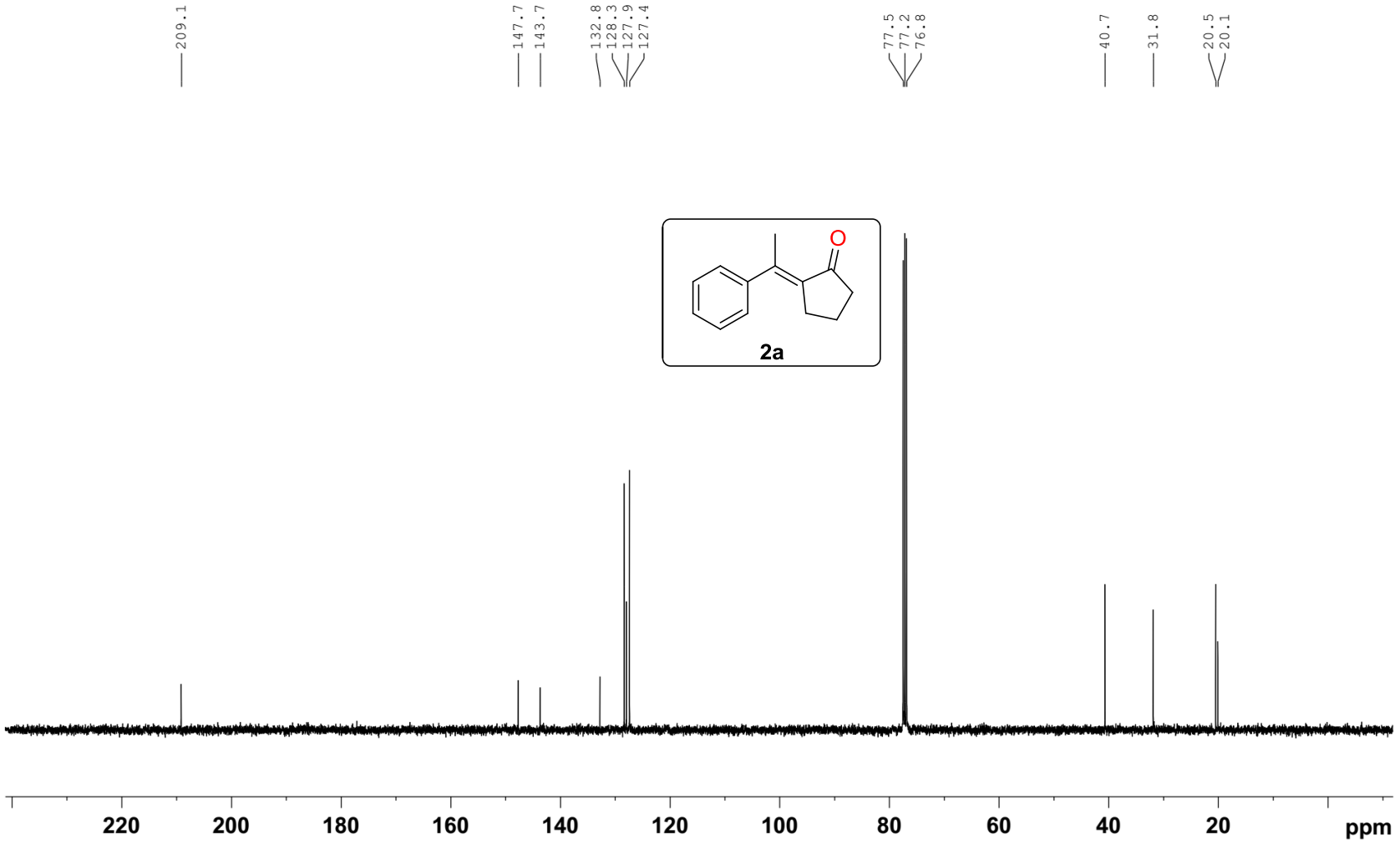
HY-X180318-1-CDCl3-CNMR



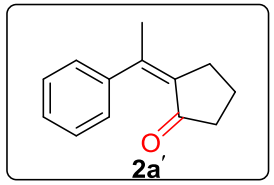
GB-X180129-1-0-HNMR

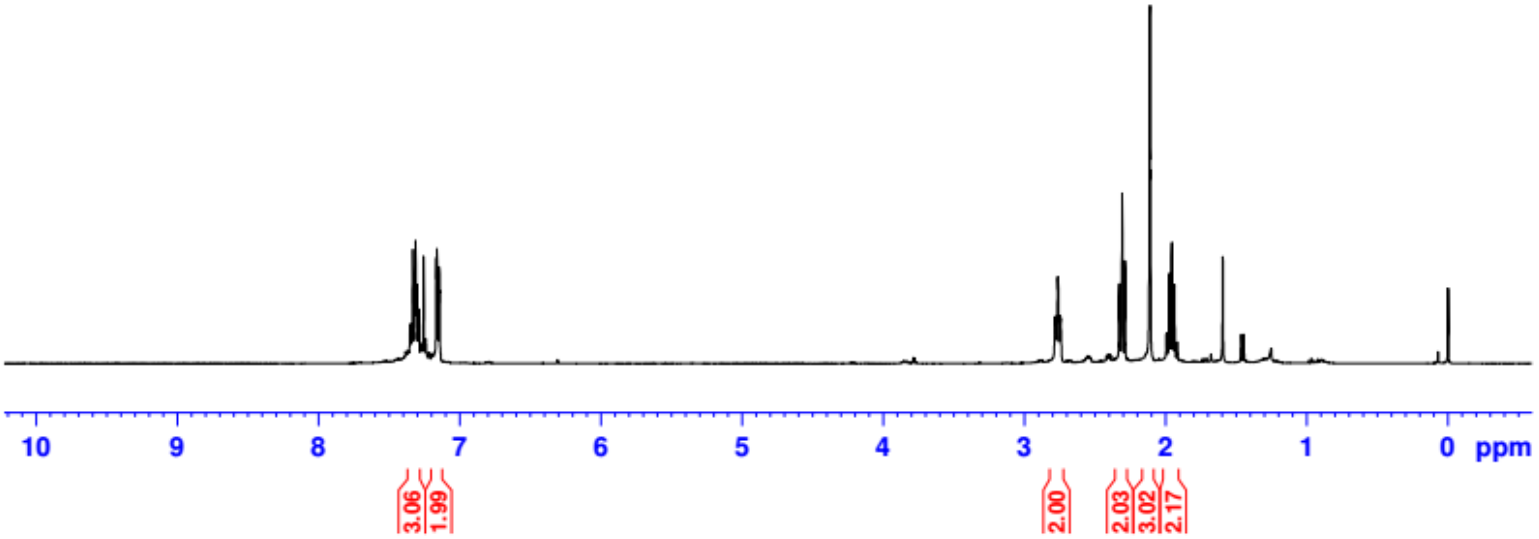


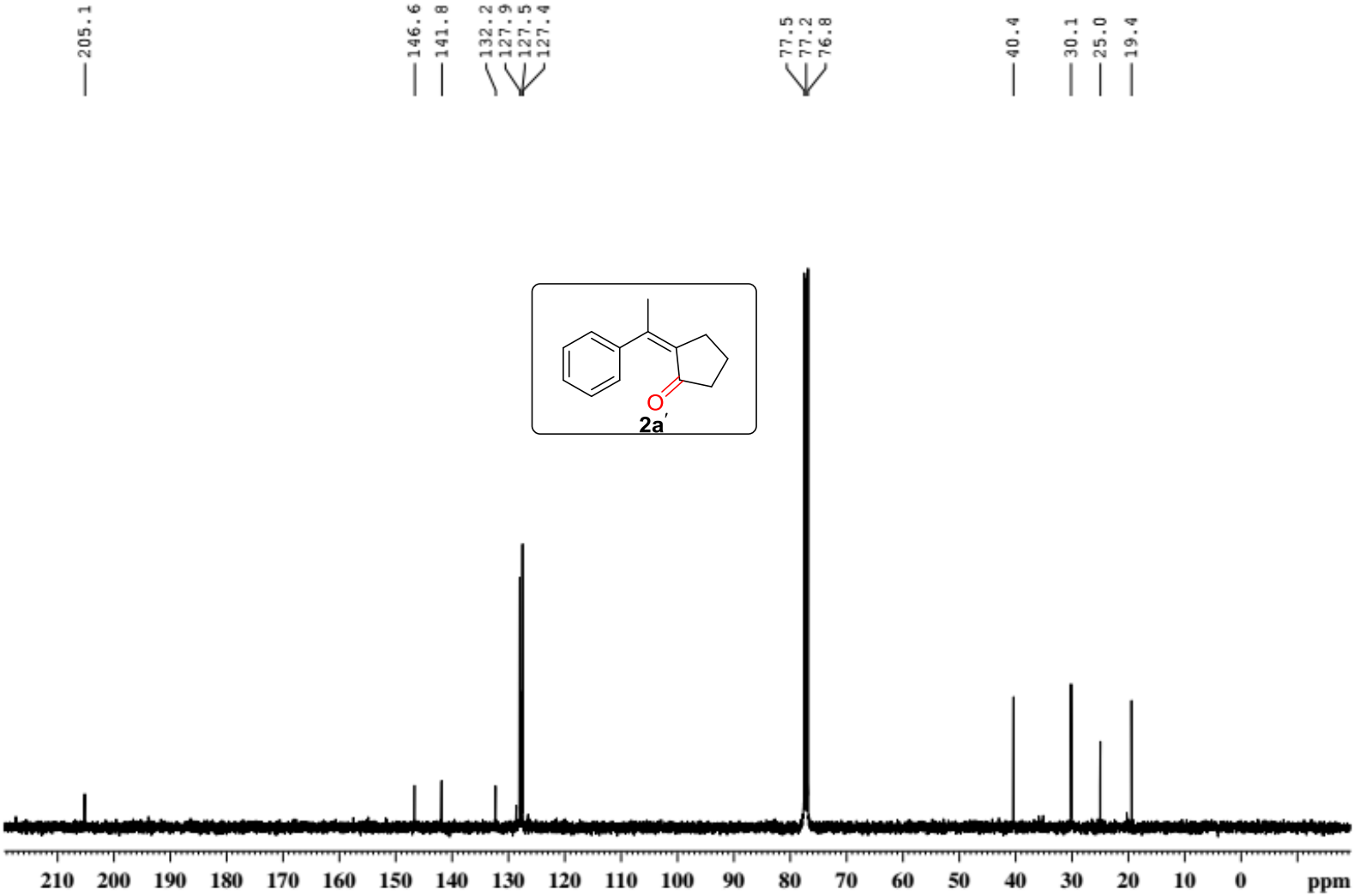
GB-X180129-1-0-CNMR



ZSC-X18X25-2a-cis-CDCl3-HNMR



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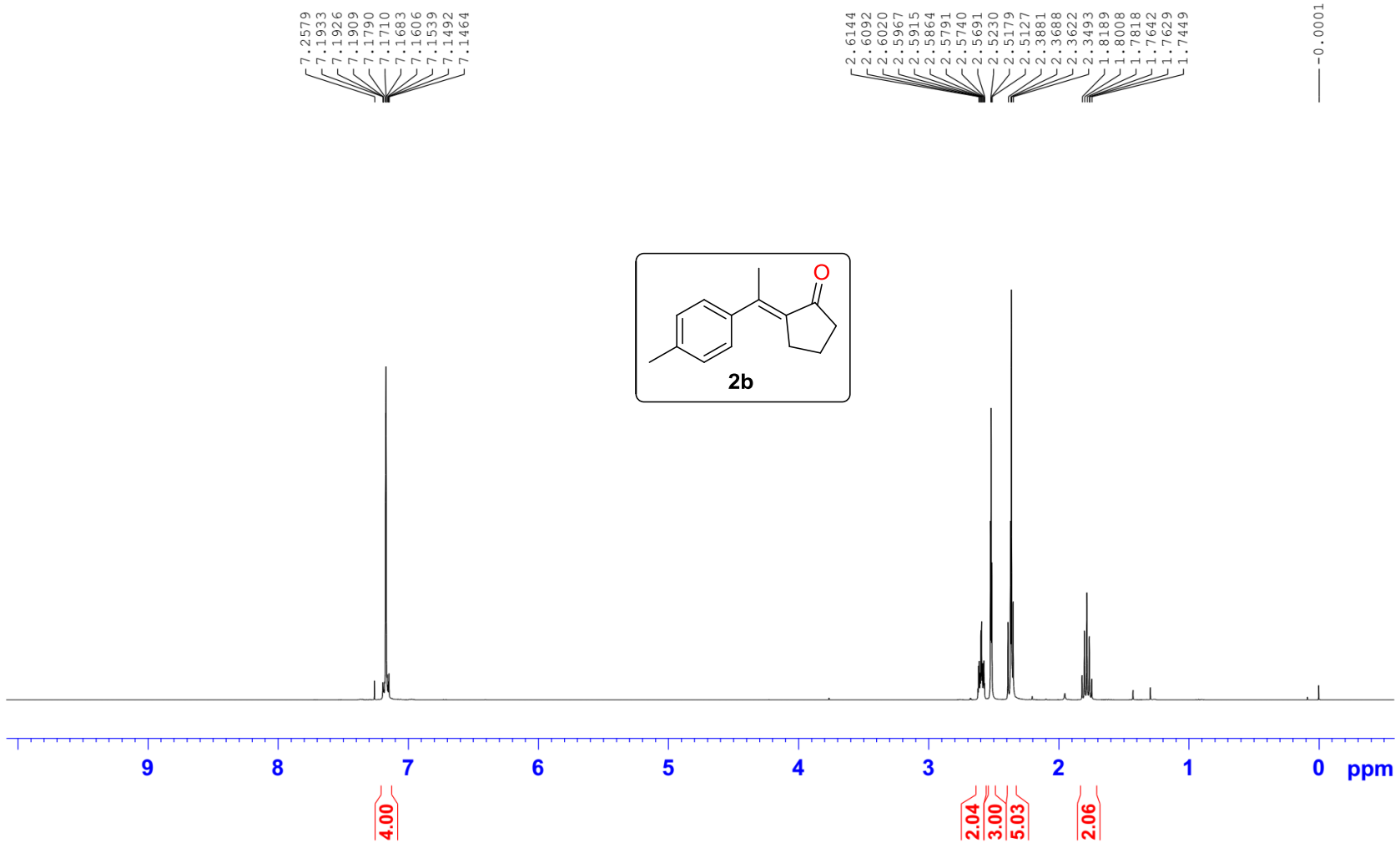
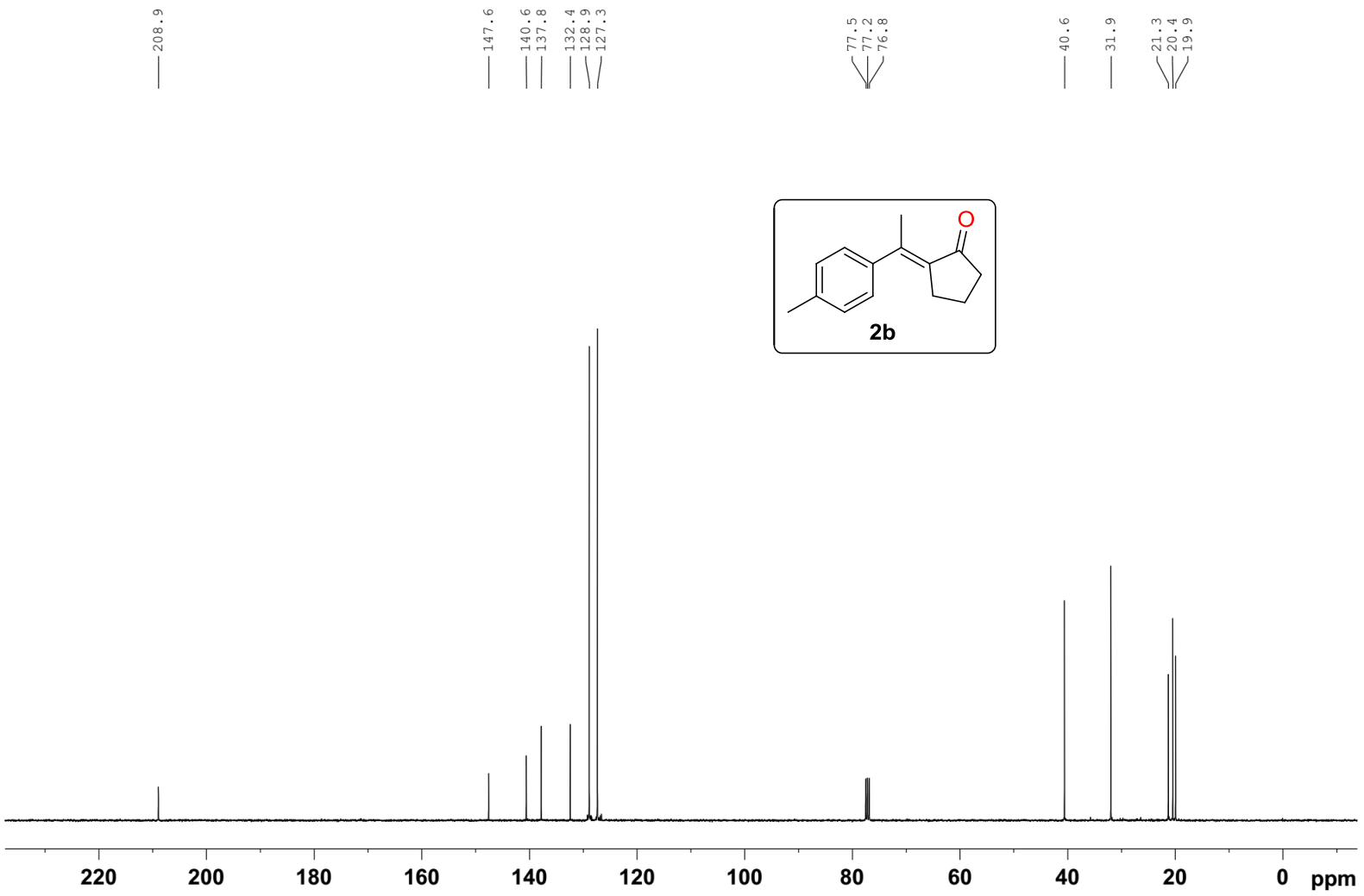
141.8
132.2
127.9
127.5
127.4
77.5
77.2
76.8
40.4
30.1
25.0
19.4
O
2a'
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

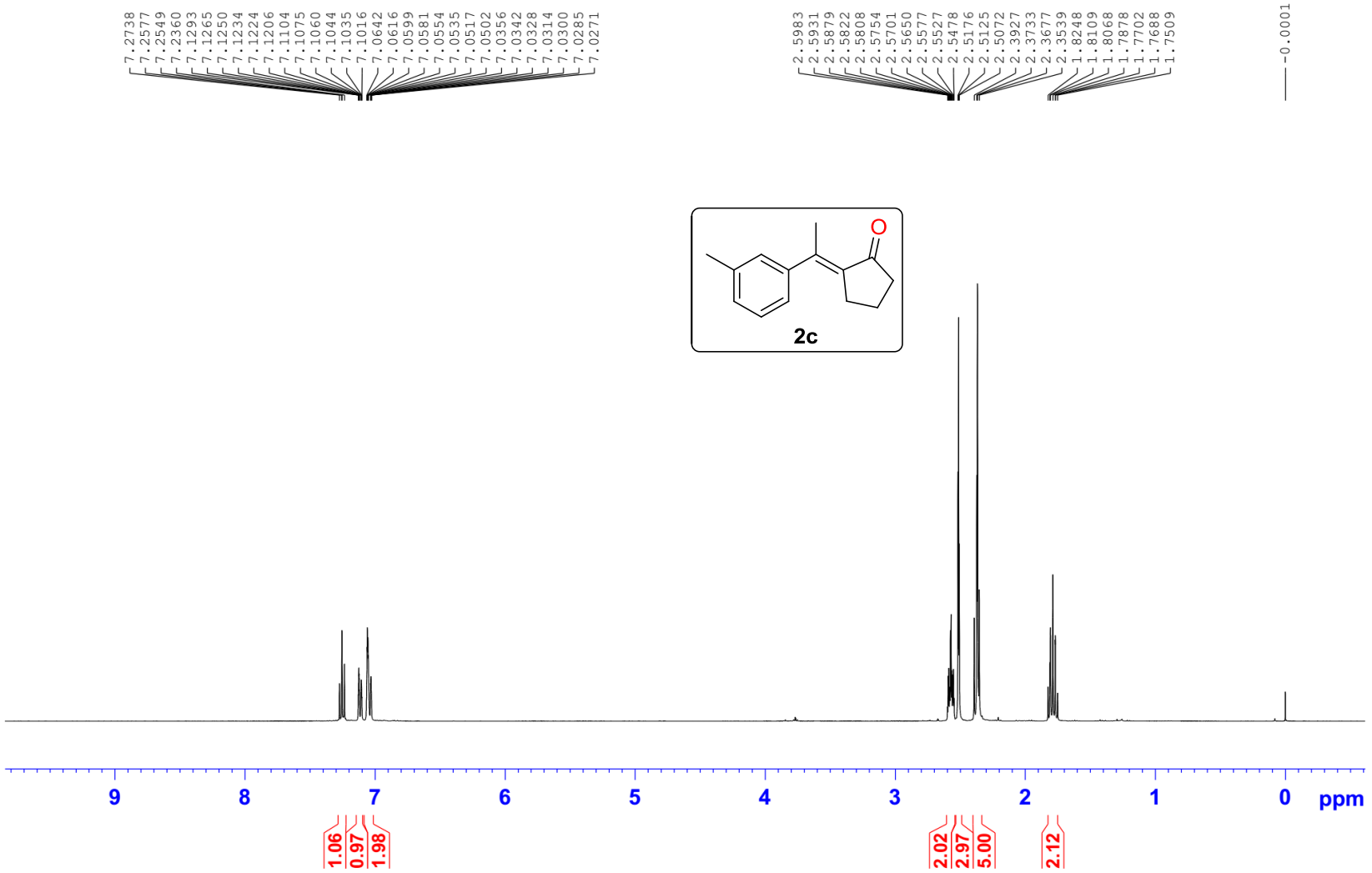
GB-X180129-1-1-HNMR



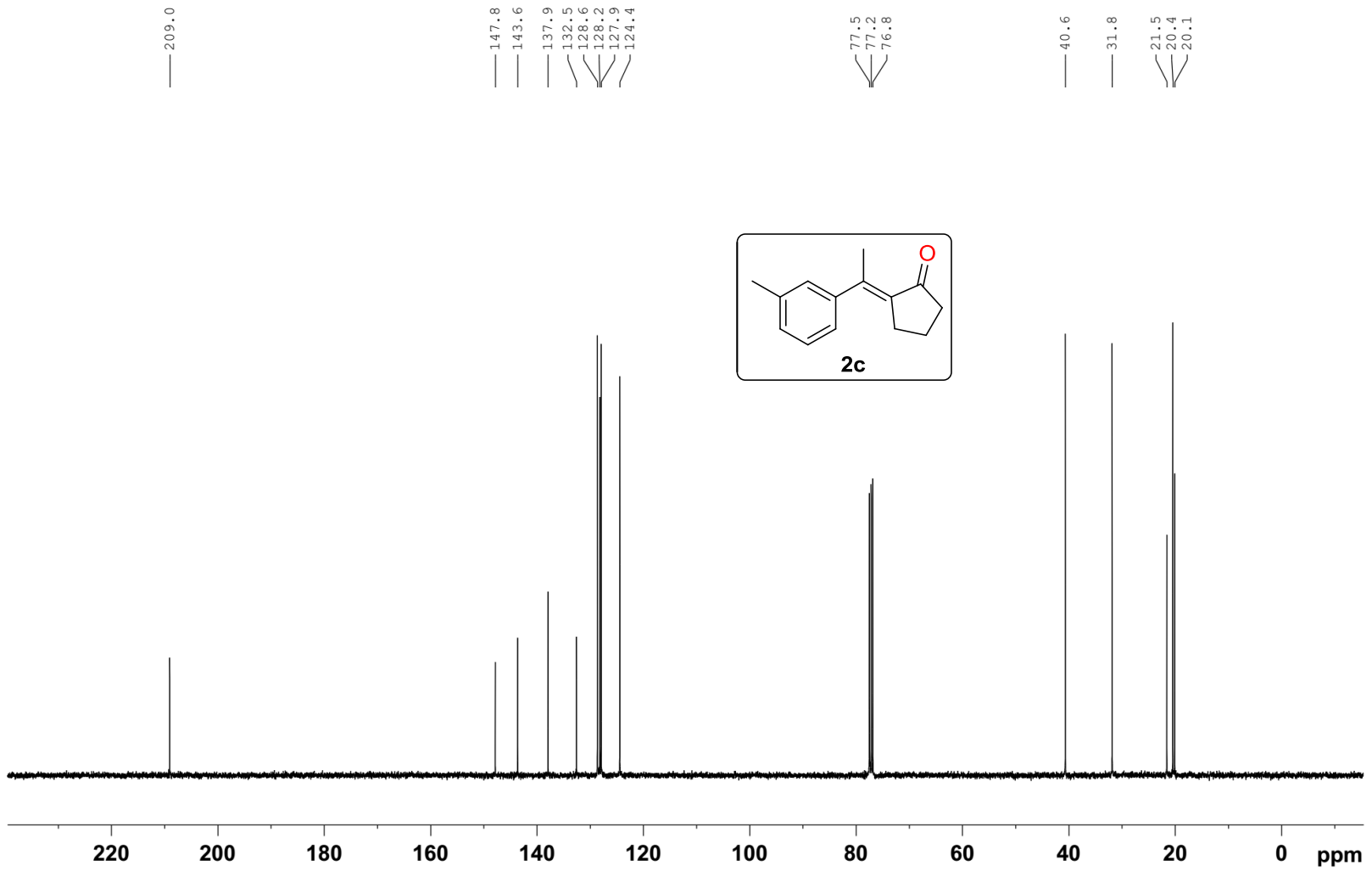
GB-X180129-1-1-CNMR



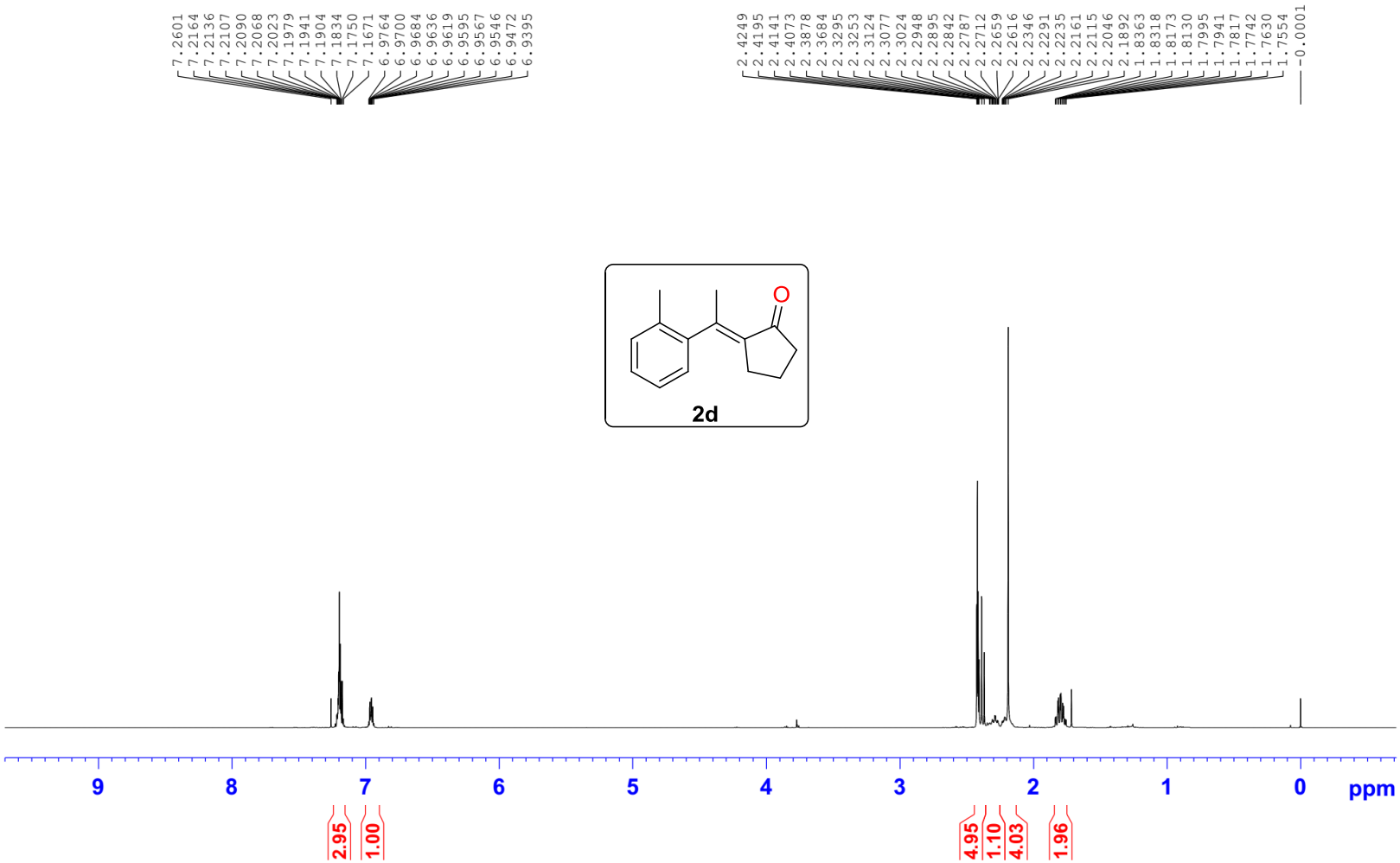
GB-X180129-1-2-3Me-HNMR



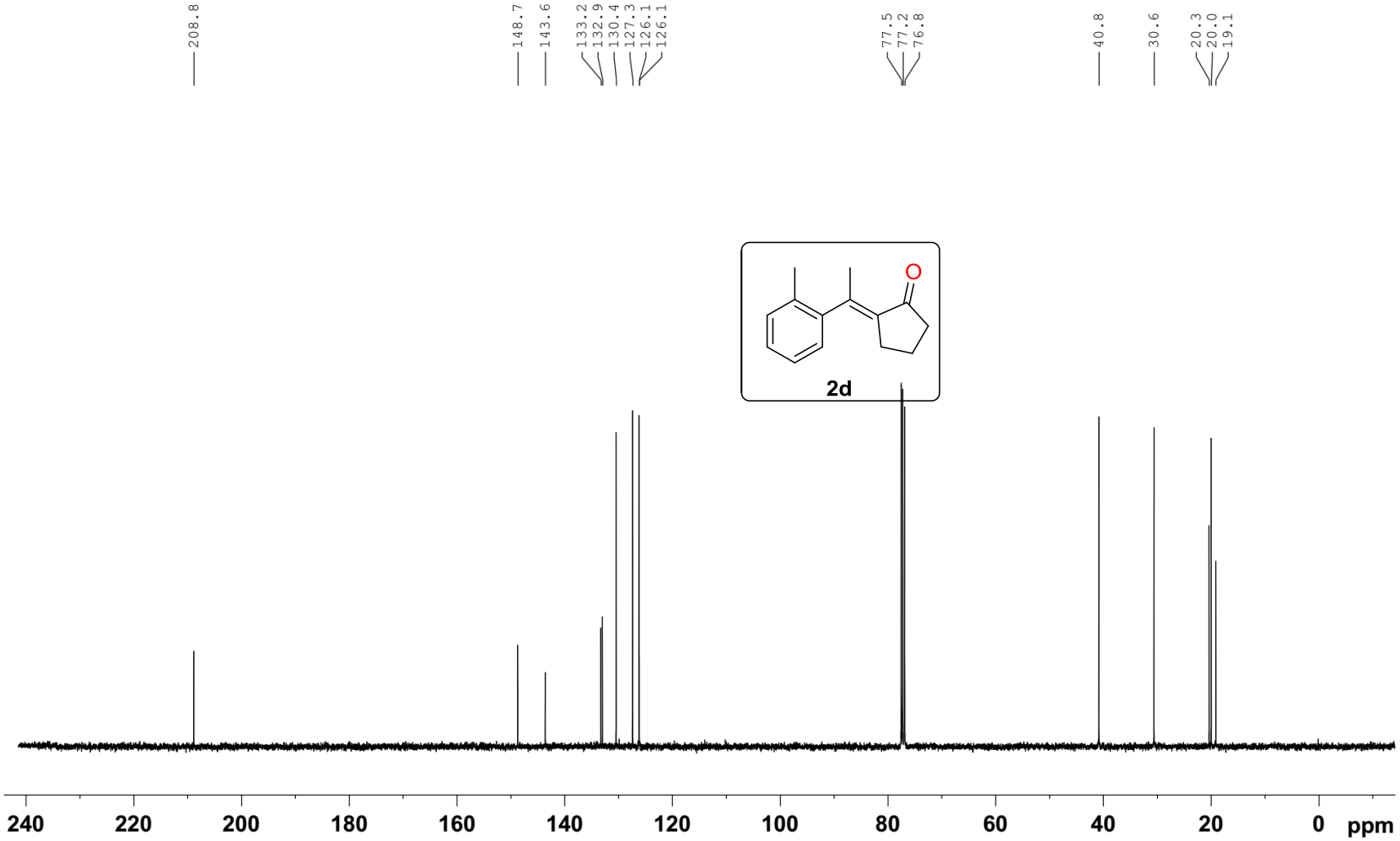
GB-X180129-1-2-3Me-CNMR



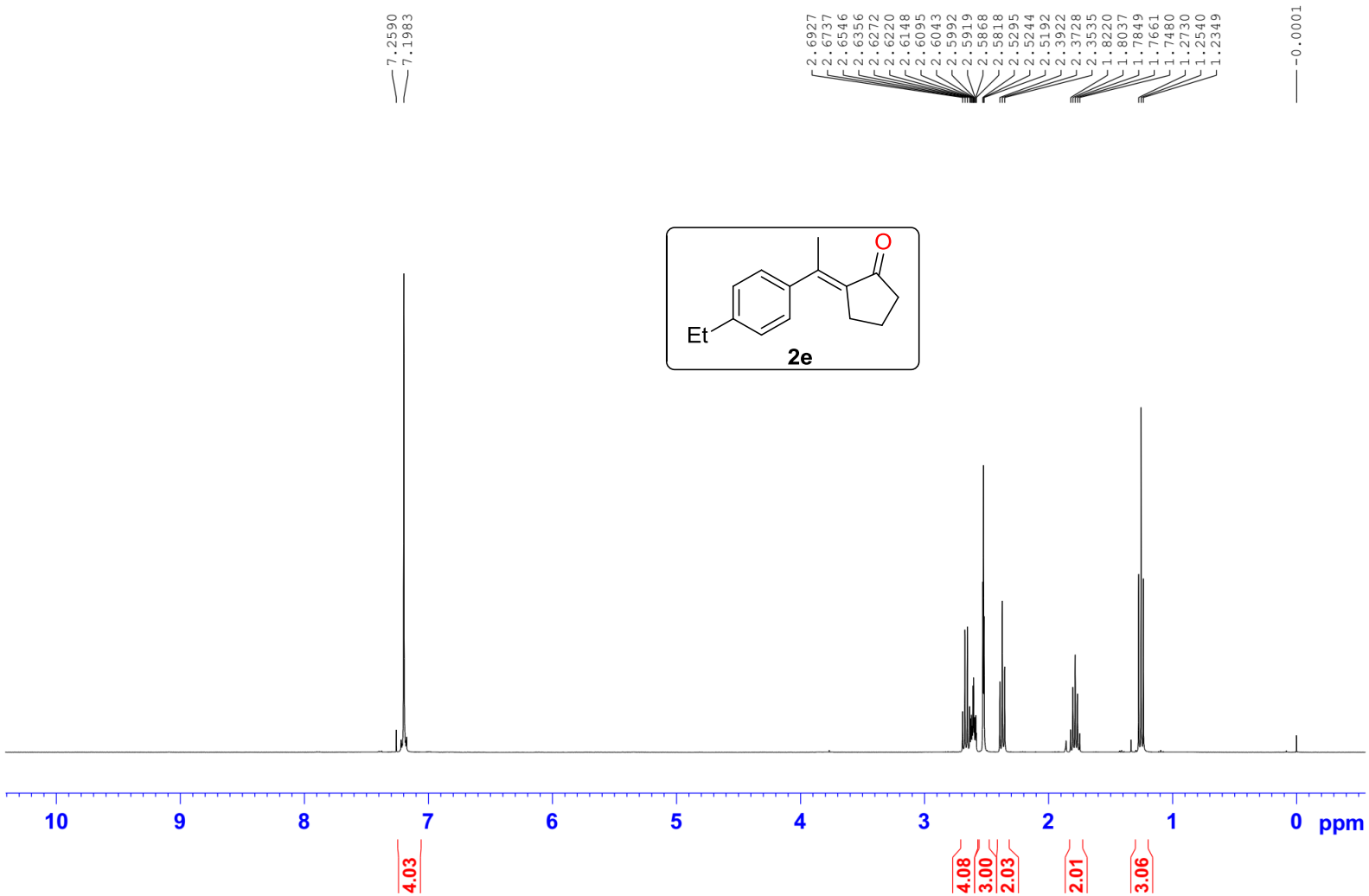
GB-X180308-1-4-2Me-HNMR



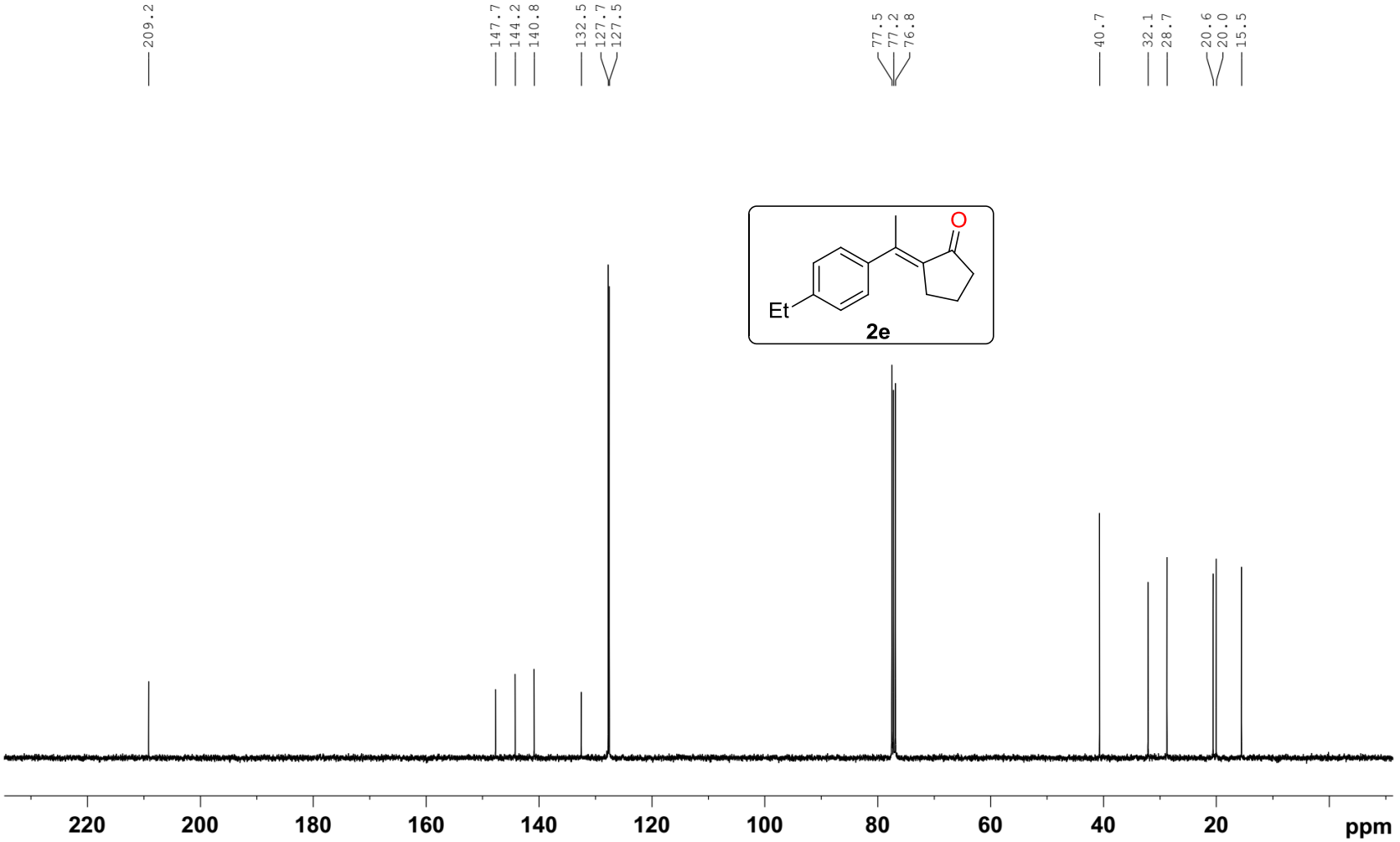
GB-X180308-1-4-2Me-CNMR



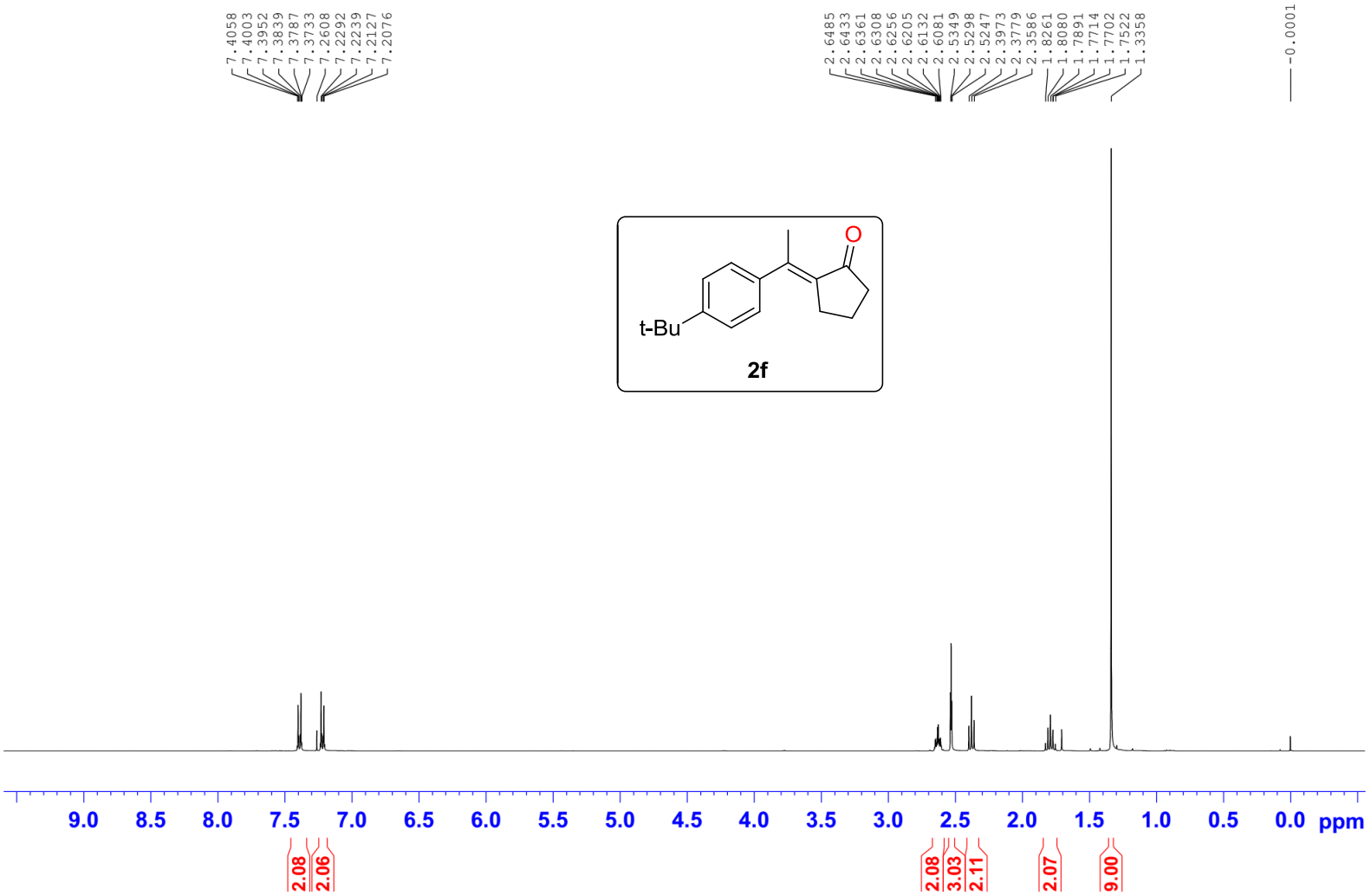
GB-X180129-1-4-HNMR



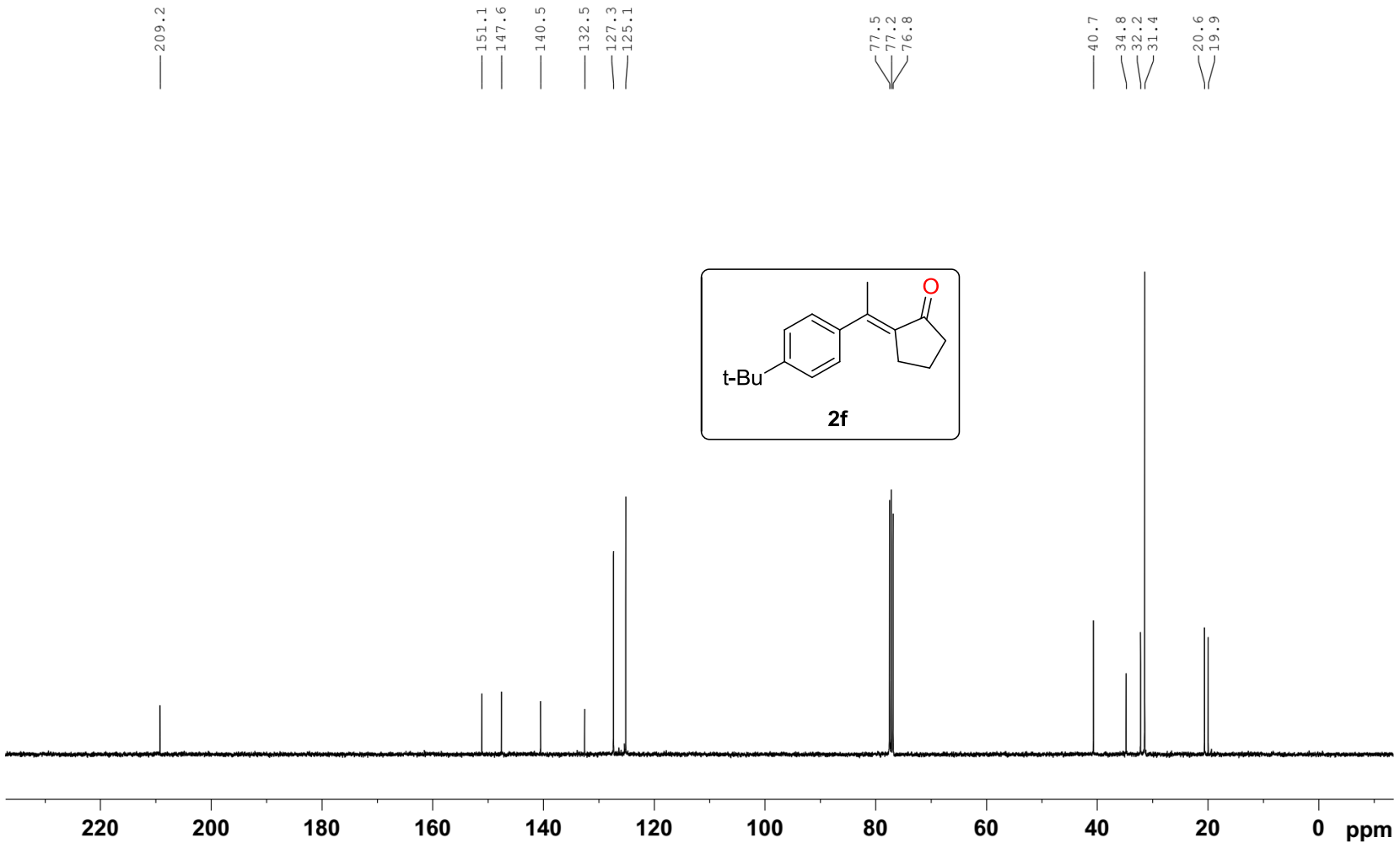
GB-X180129-1-4-4Et-CNMR



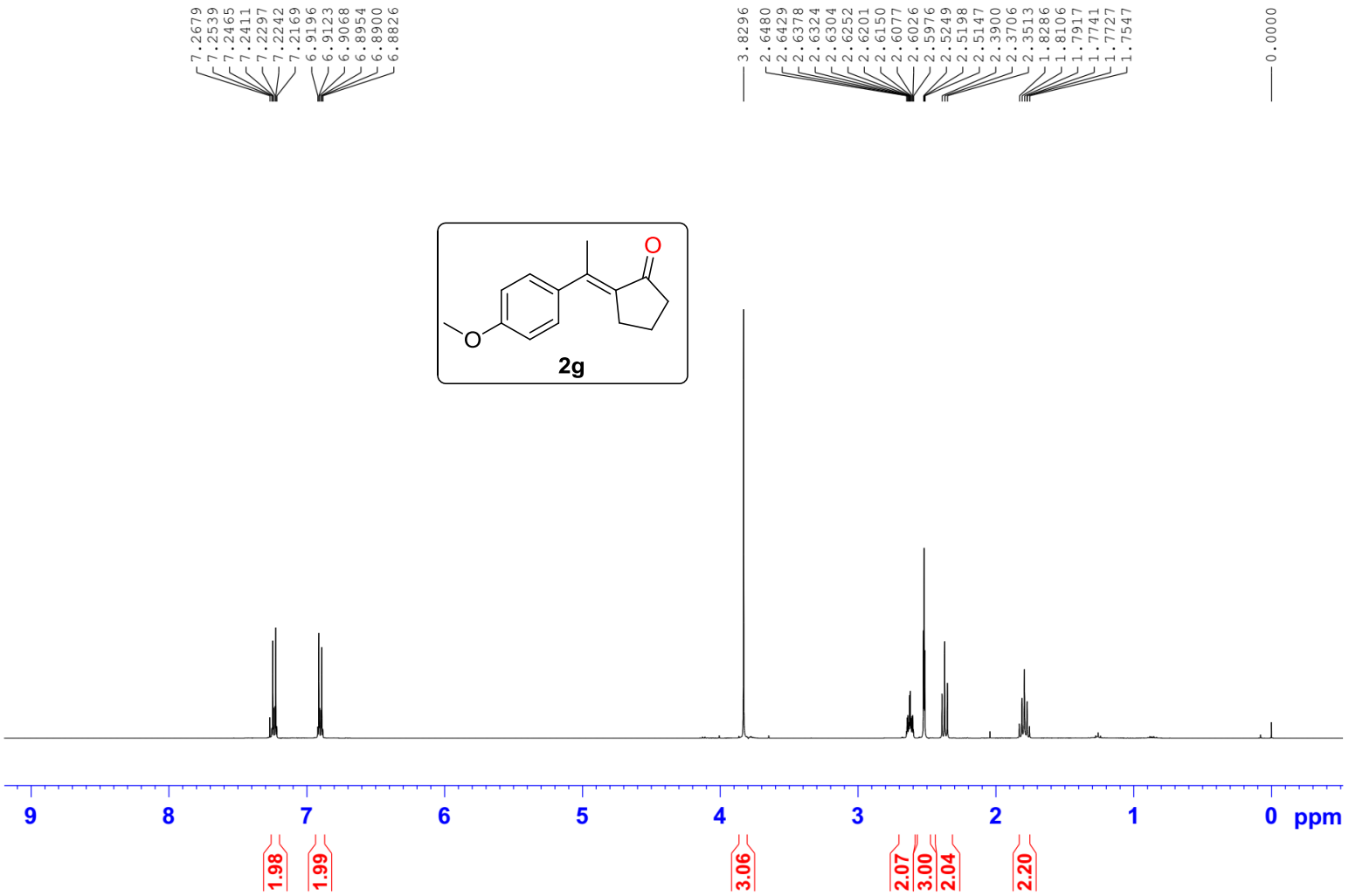
GB-X180129-1-5-HNMR



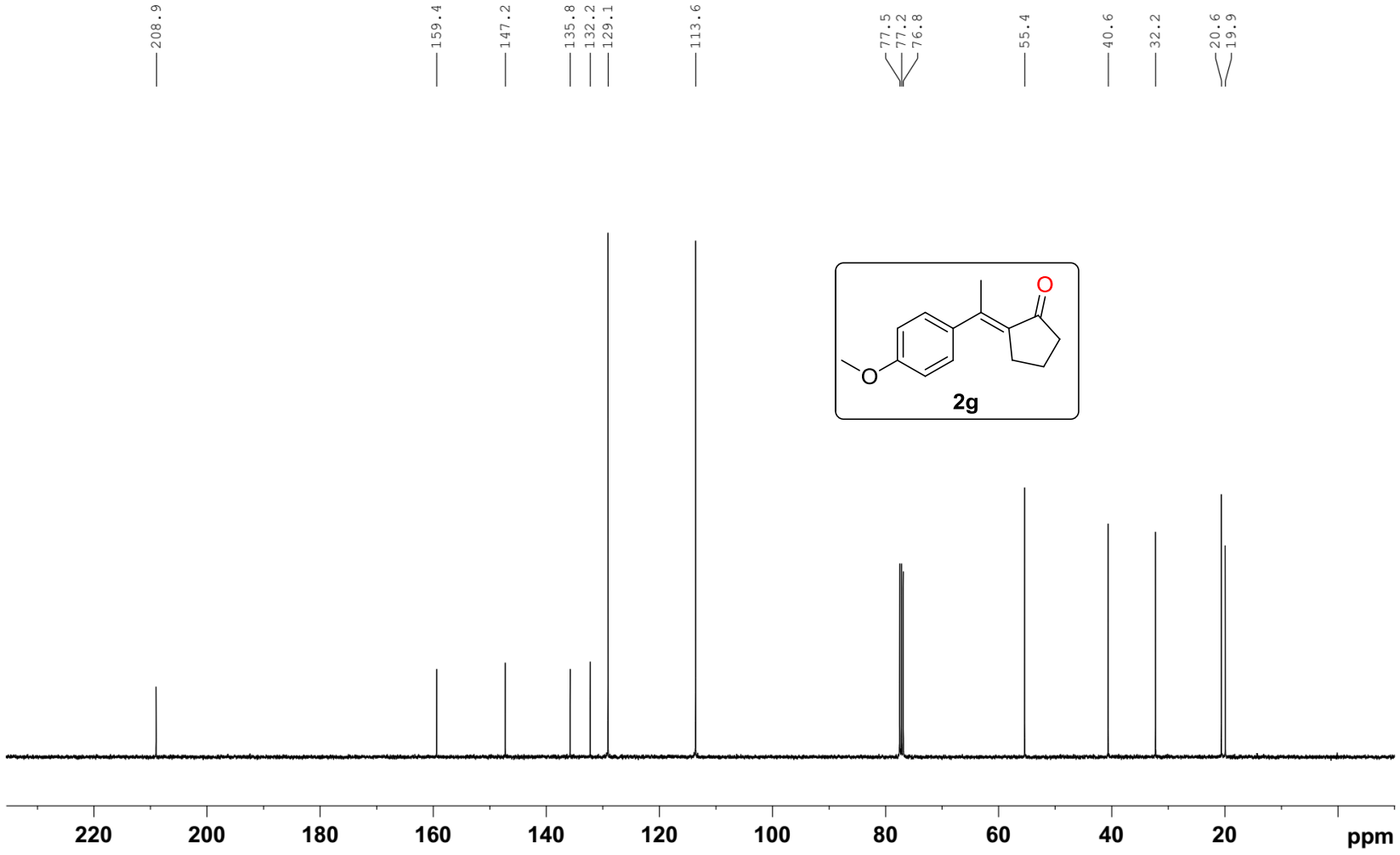
GB-X180129-1-5-CNMR



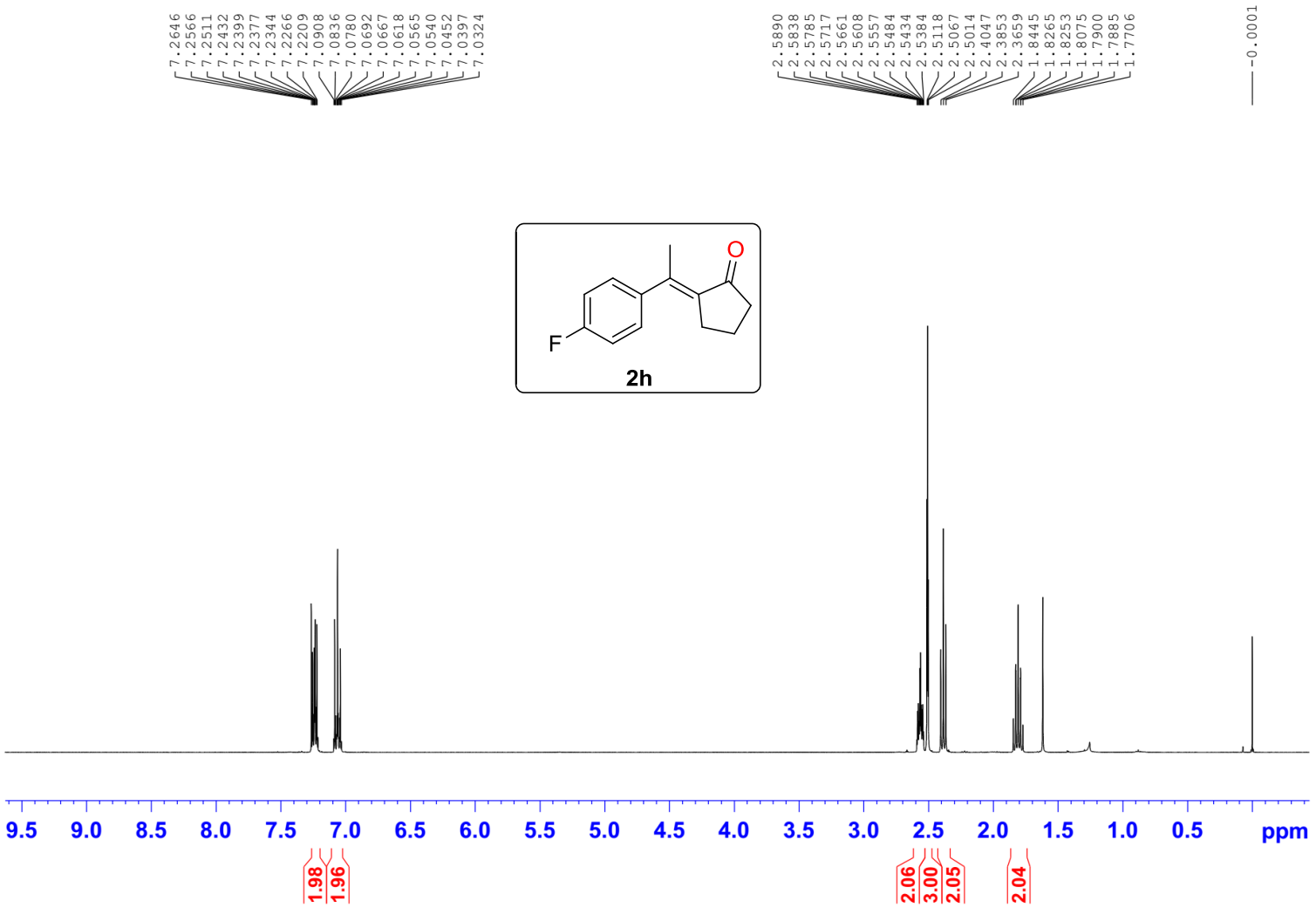
GB-X180614-4MeO-HNMR



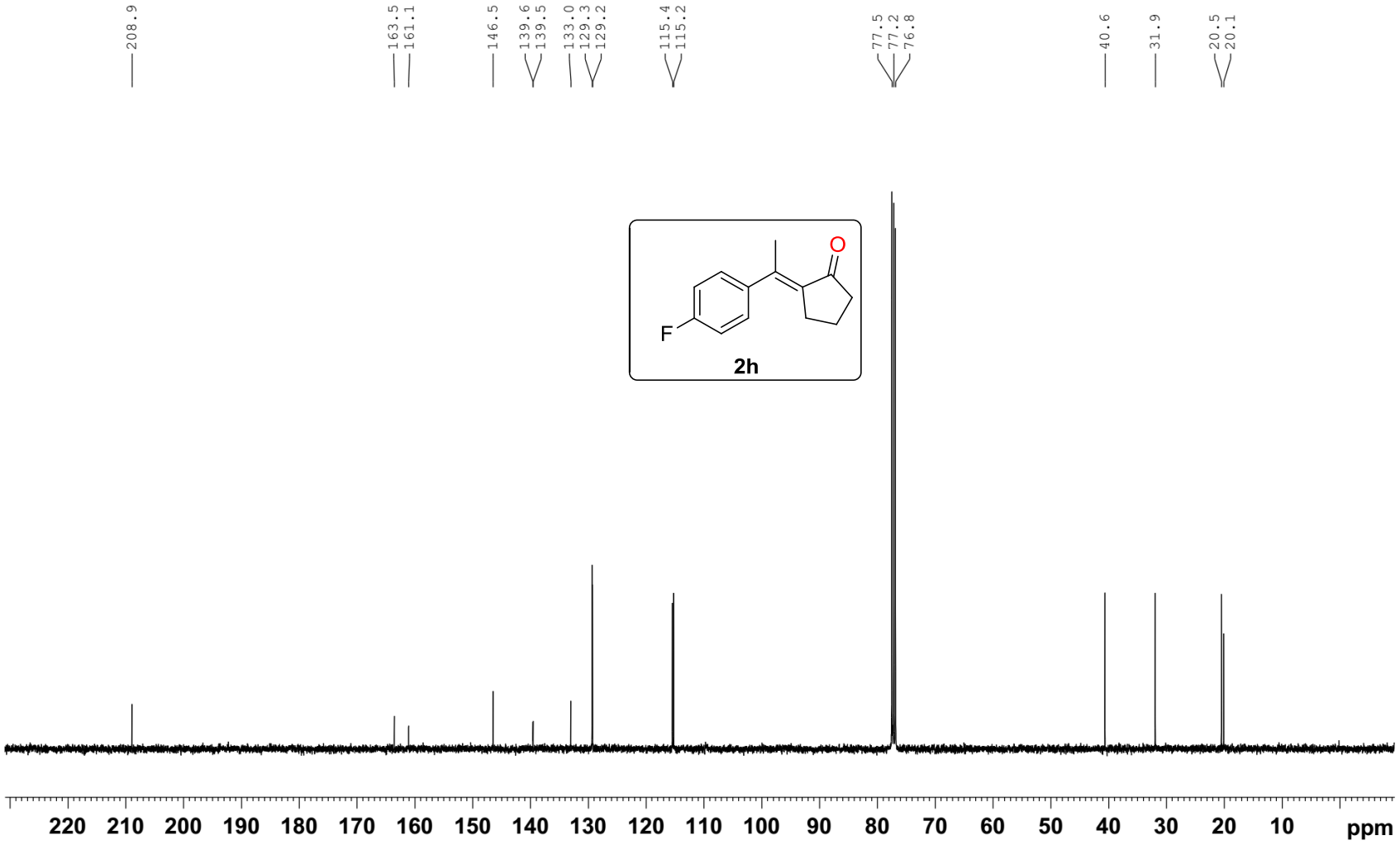
GB-X180614-4MeO-CNMR



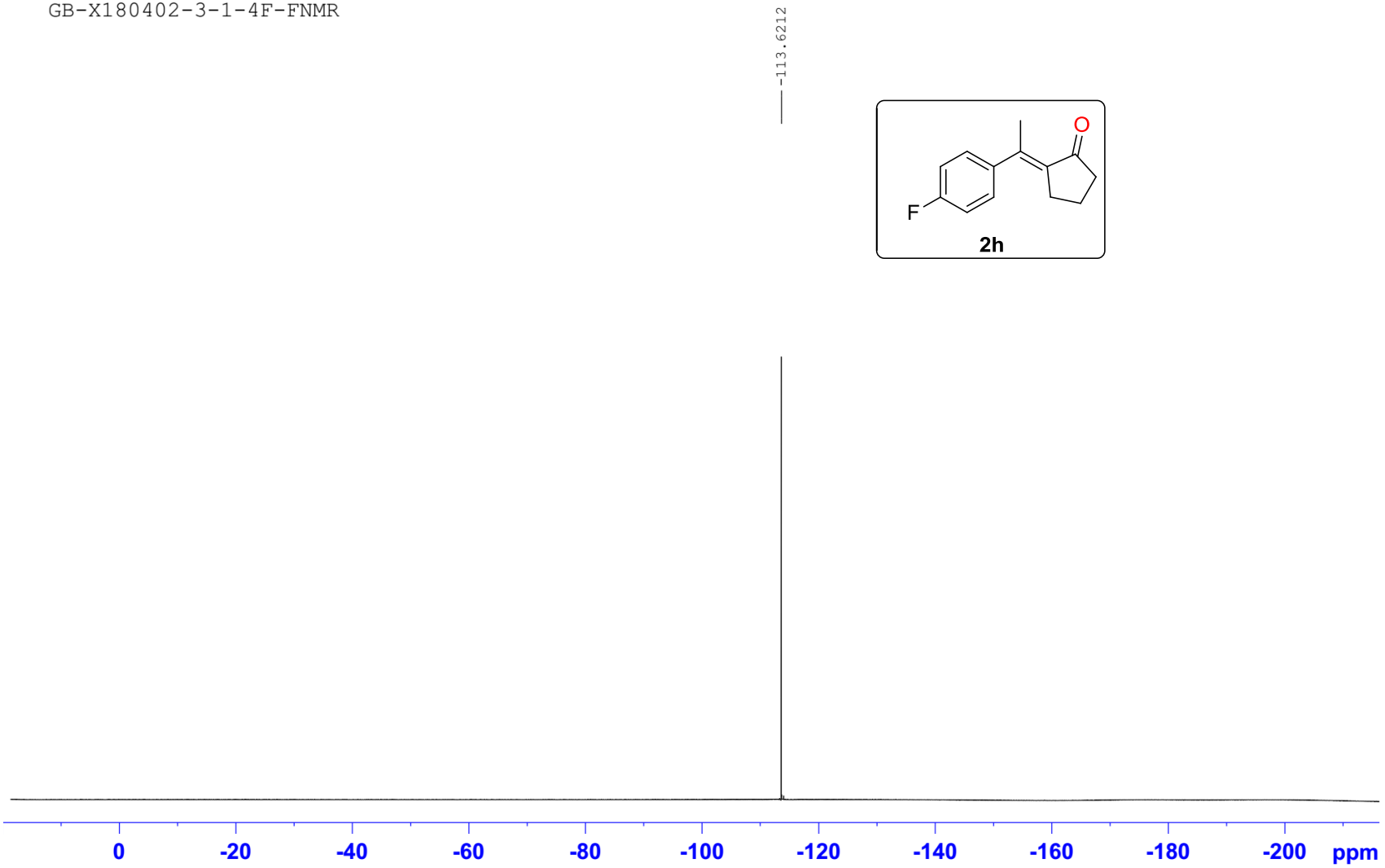
GB-X180402-3-1-4F-HNMR



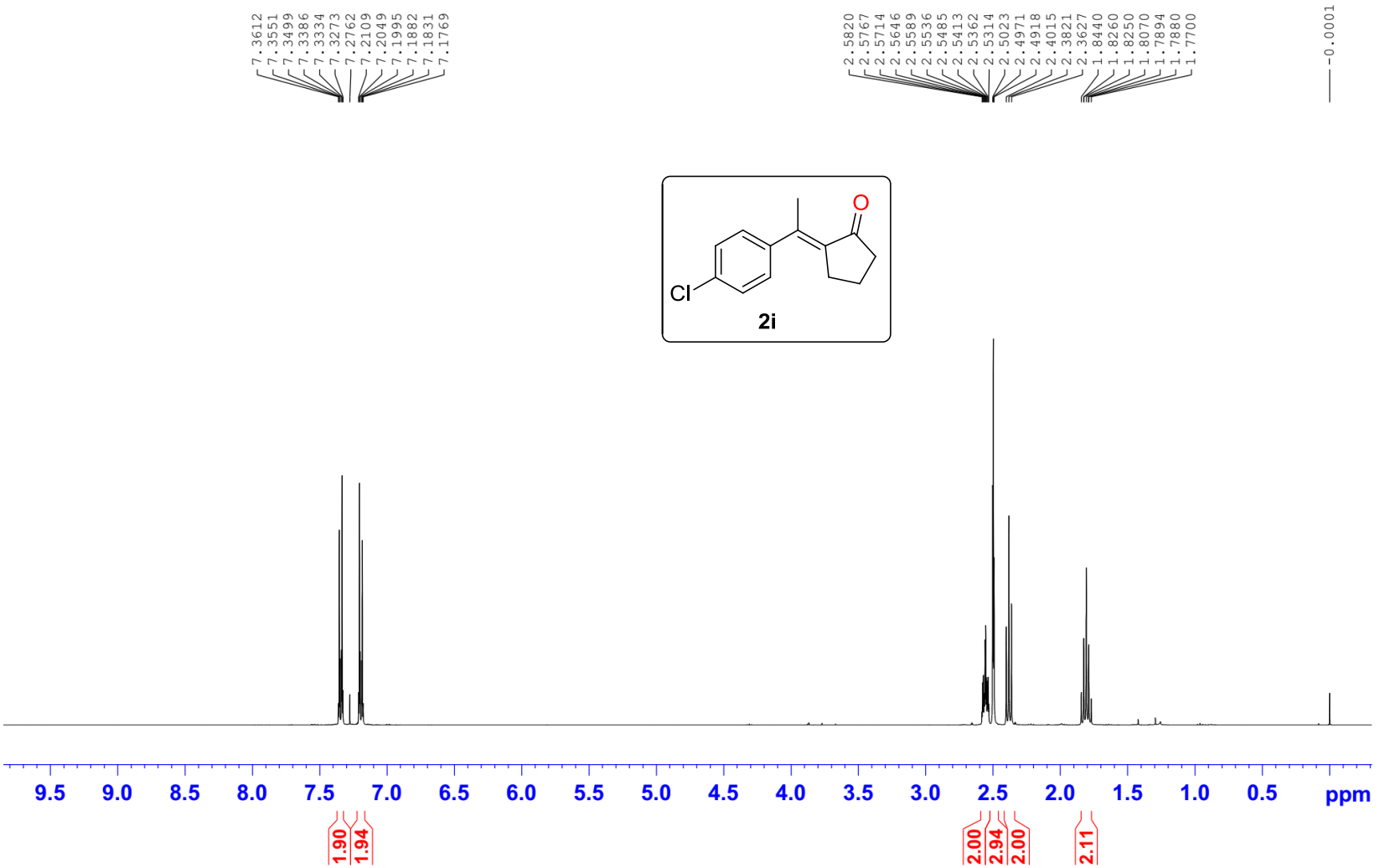
GB-X180402-3-1-4F-CNMR



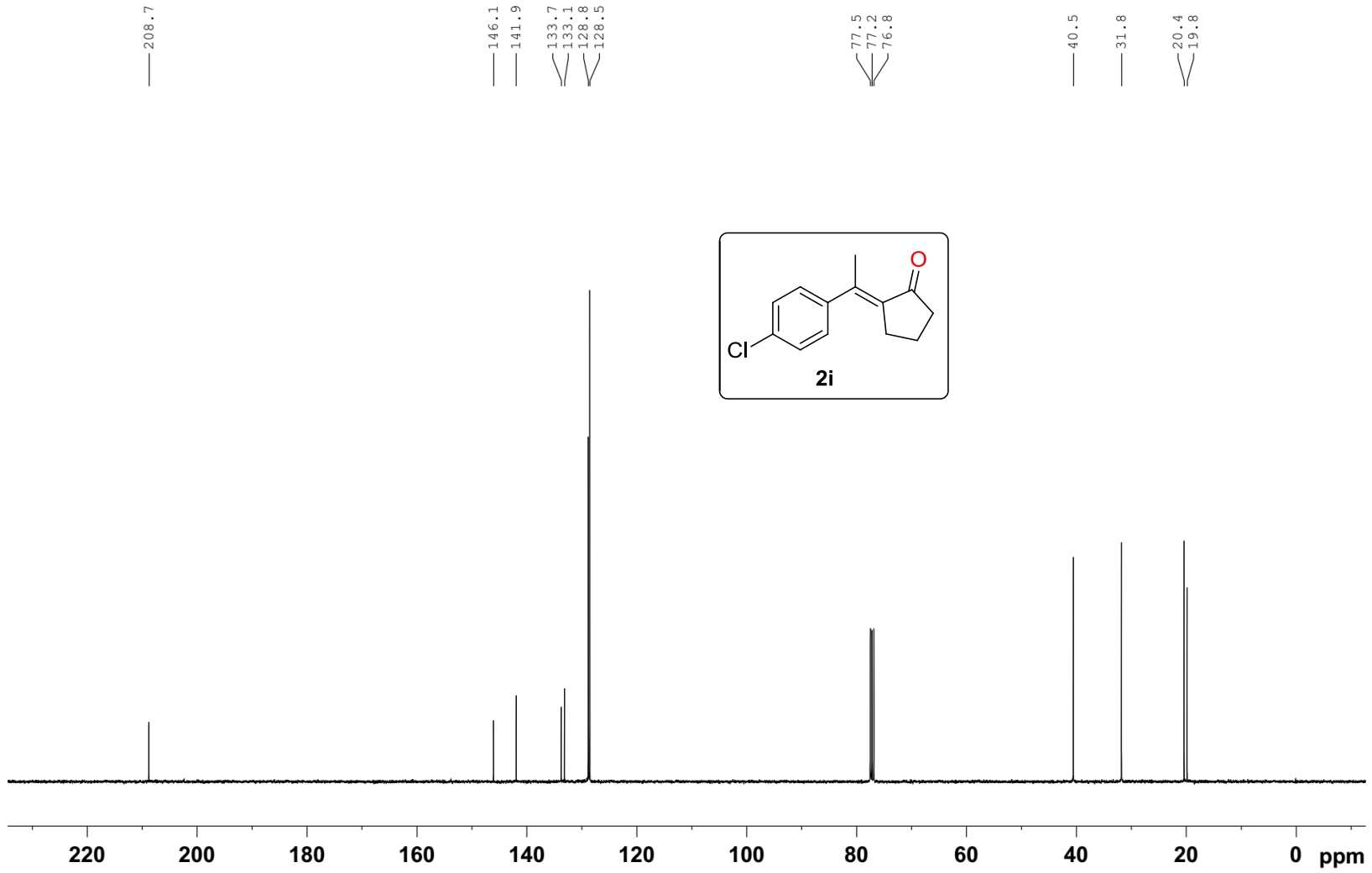
GB-X180402-3-1-4F-FNMR



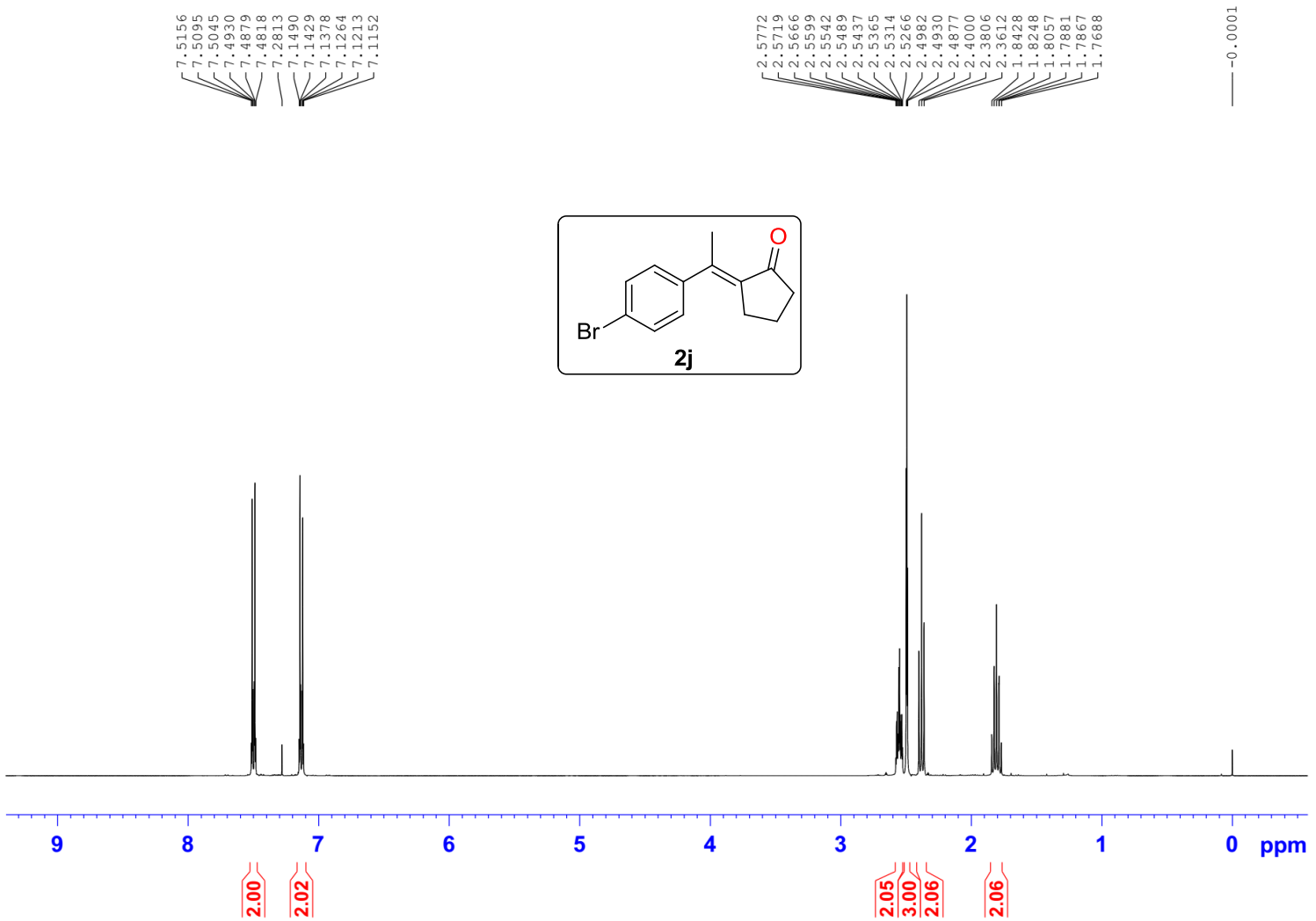
GB-X180129-1-7-4Cl-HNMR



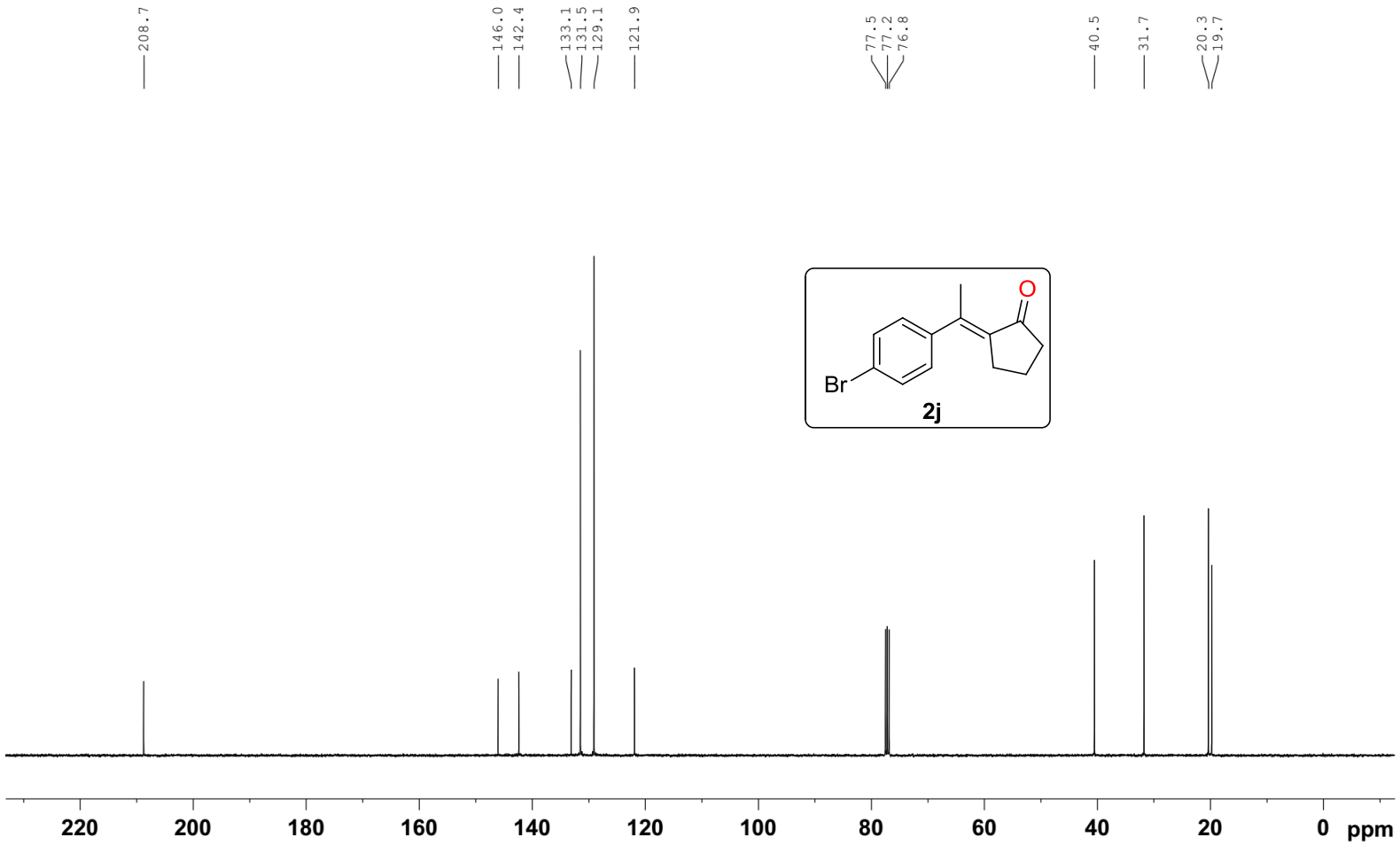
GB-X180129-1-7-4Cl-CNMR



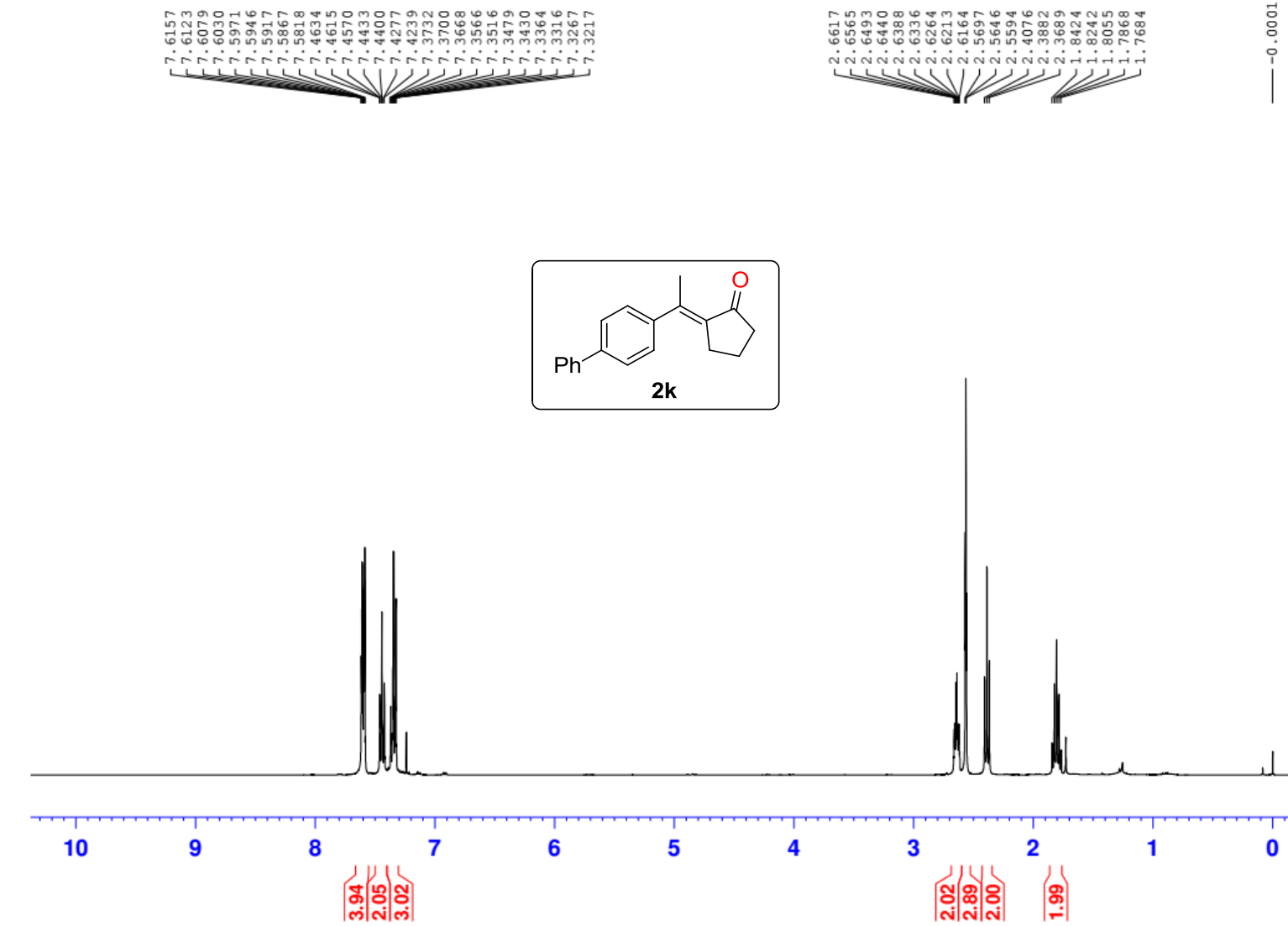
GB-X180614-4Br-HNMR



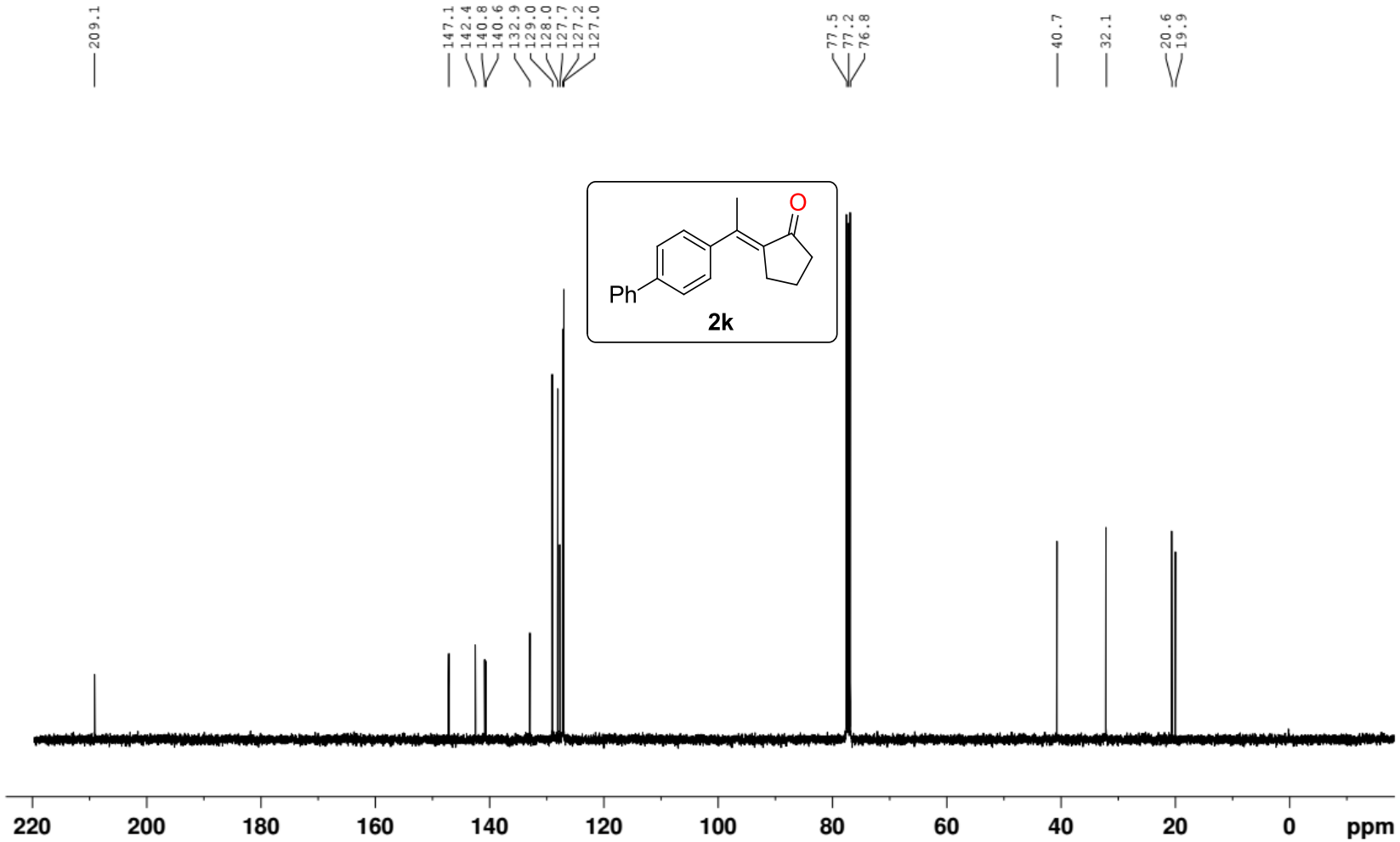
GB-X180614-4Br-CNMR



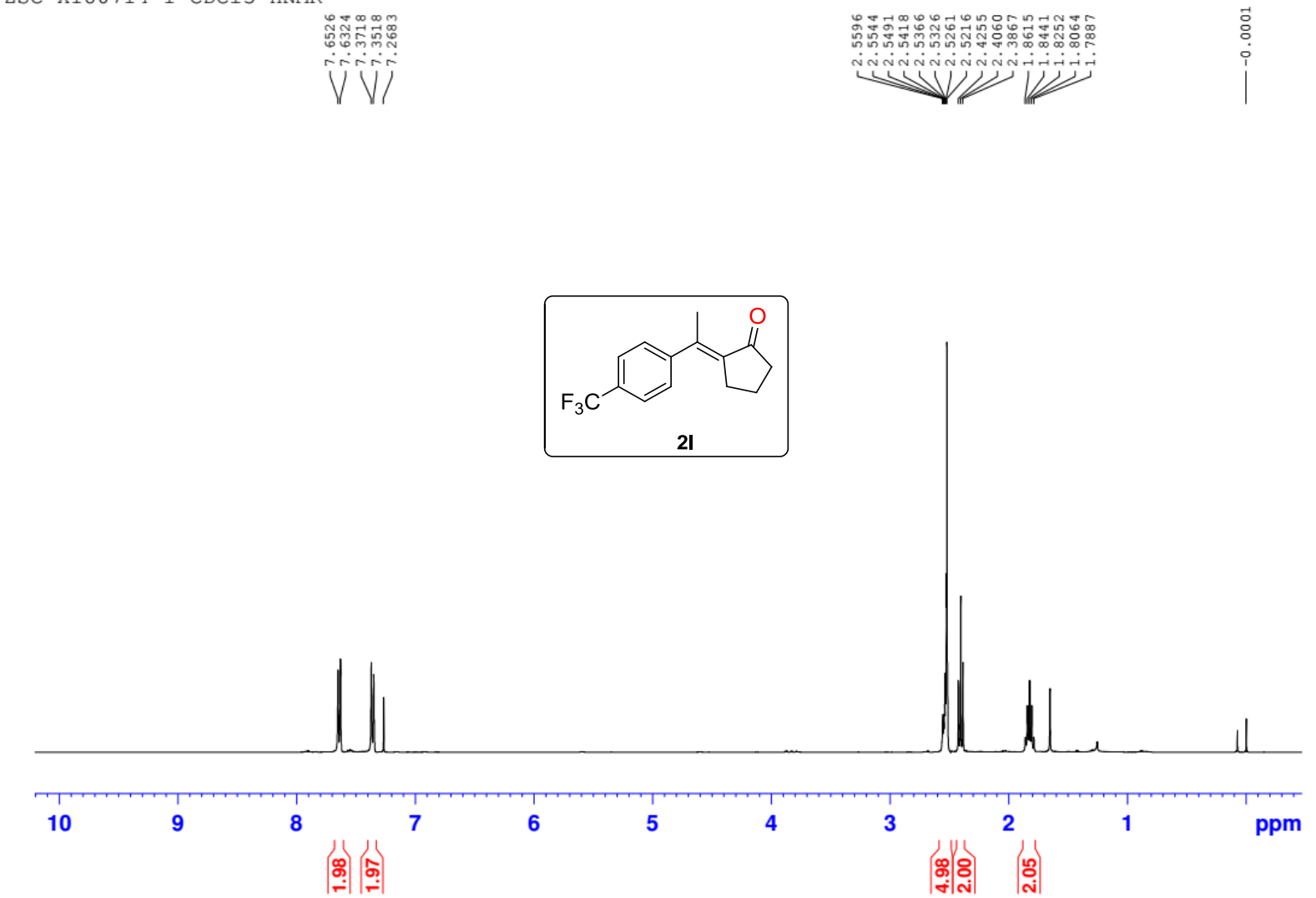
zsc-x180711-5-CDCl3-HNMR



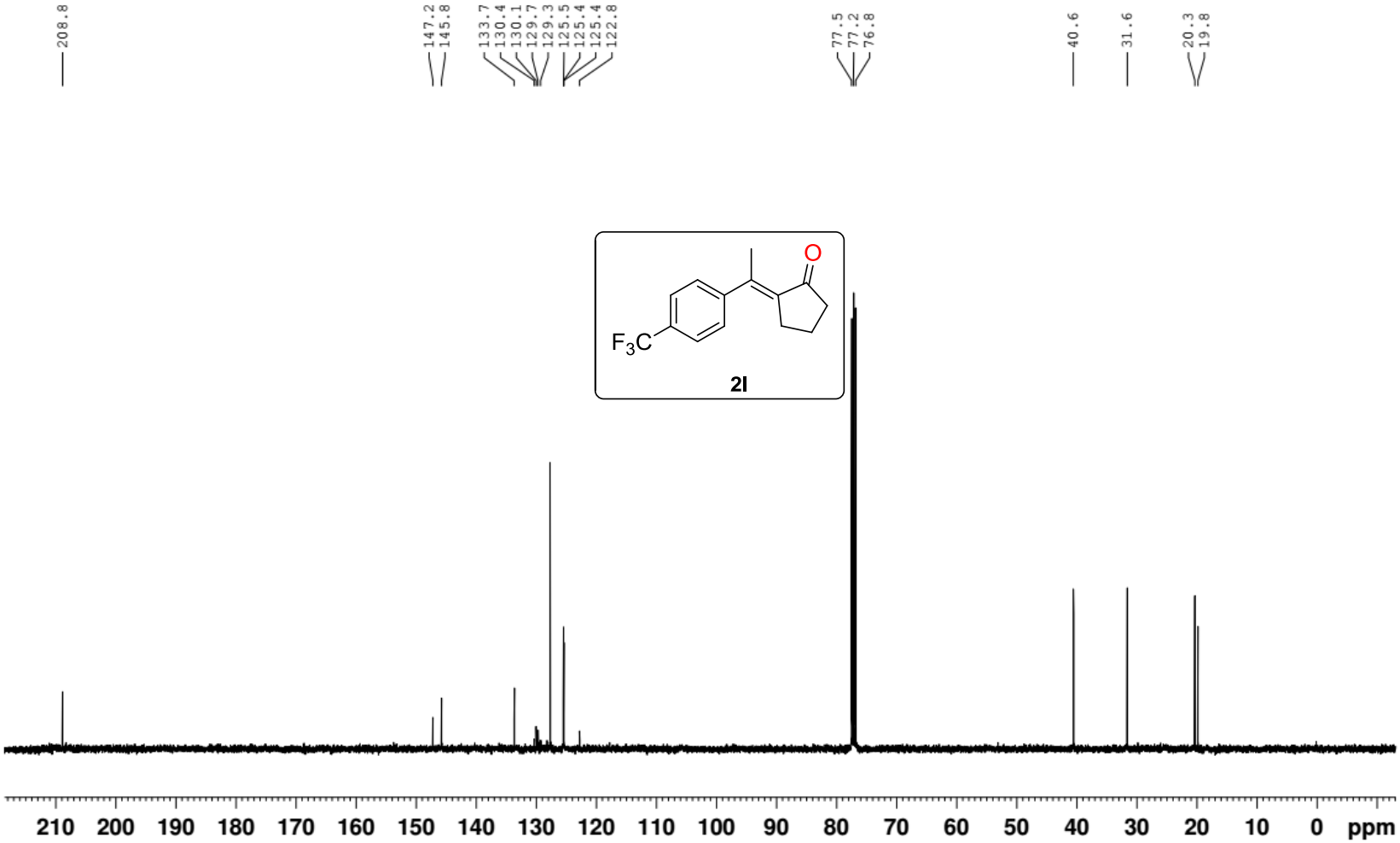
ZSC-X180711-1-5-CDCl3-CNMR



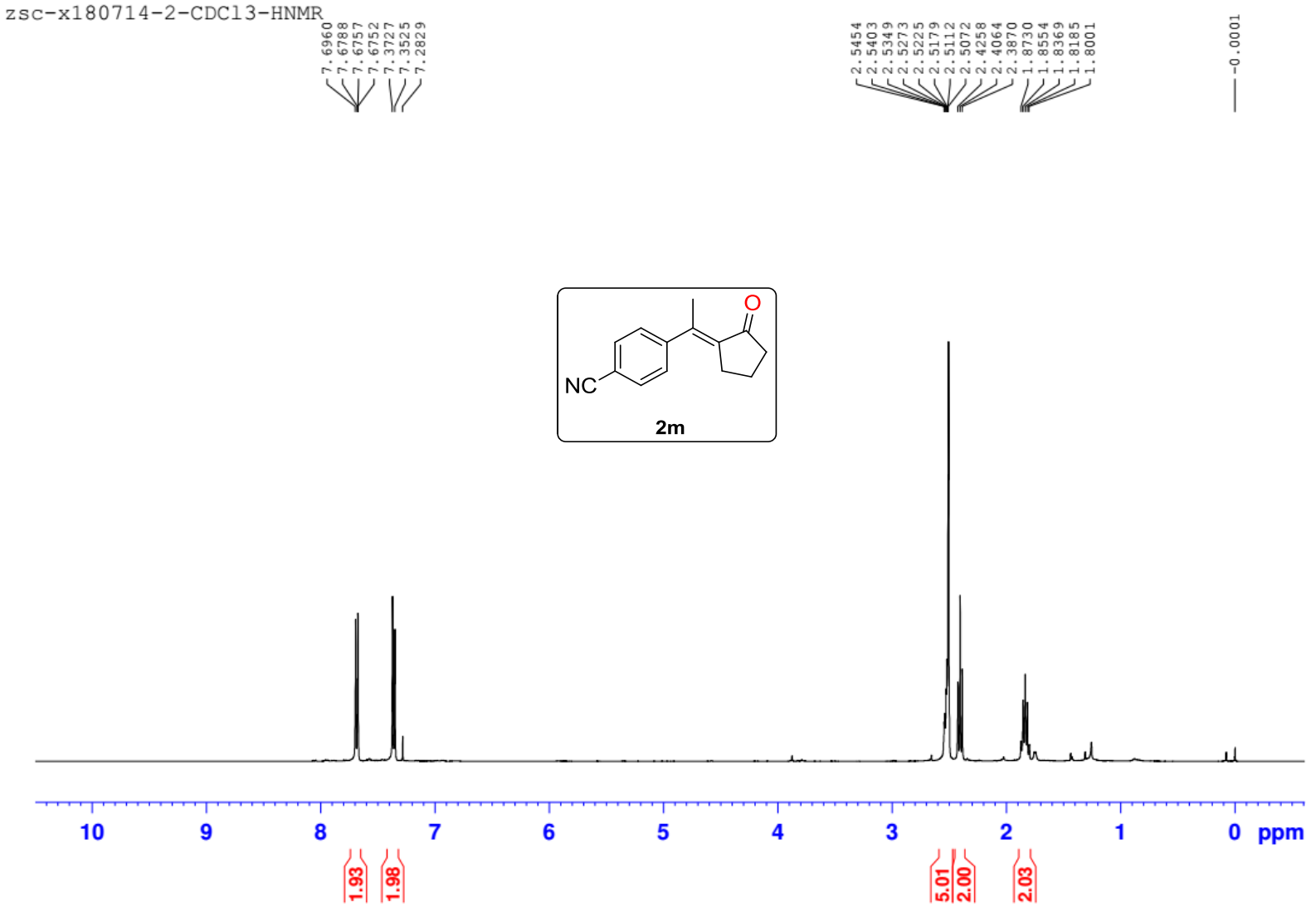
ZSC-X180714-1-CDCl3-HNMR

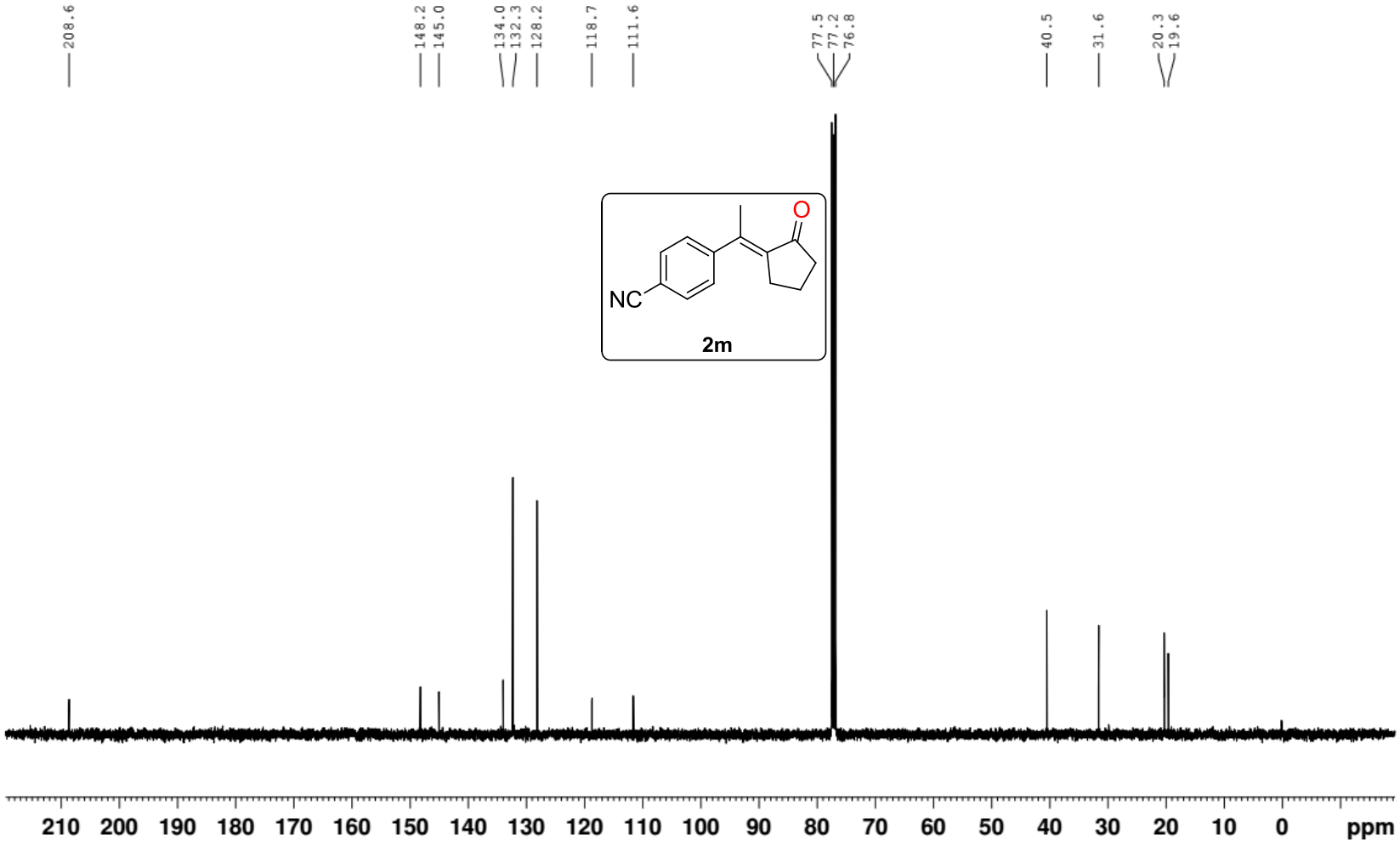


ZSC-X180714-1-CDCl3-CNMR

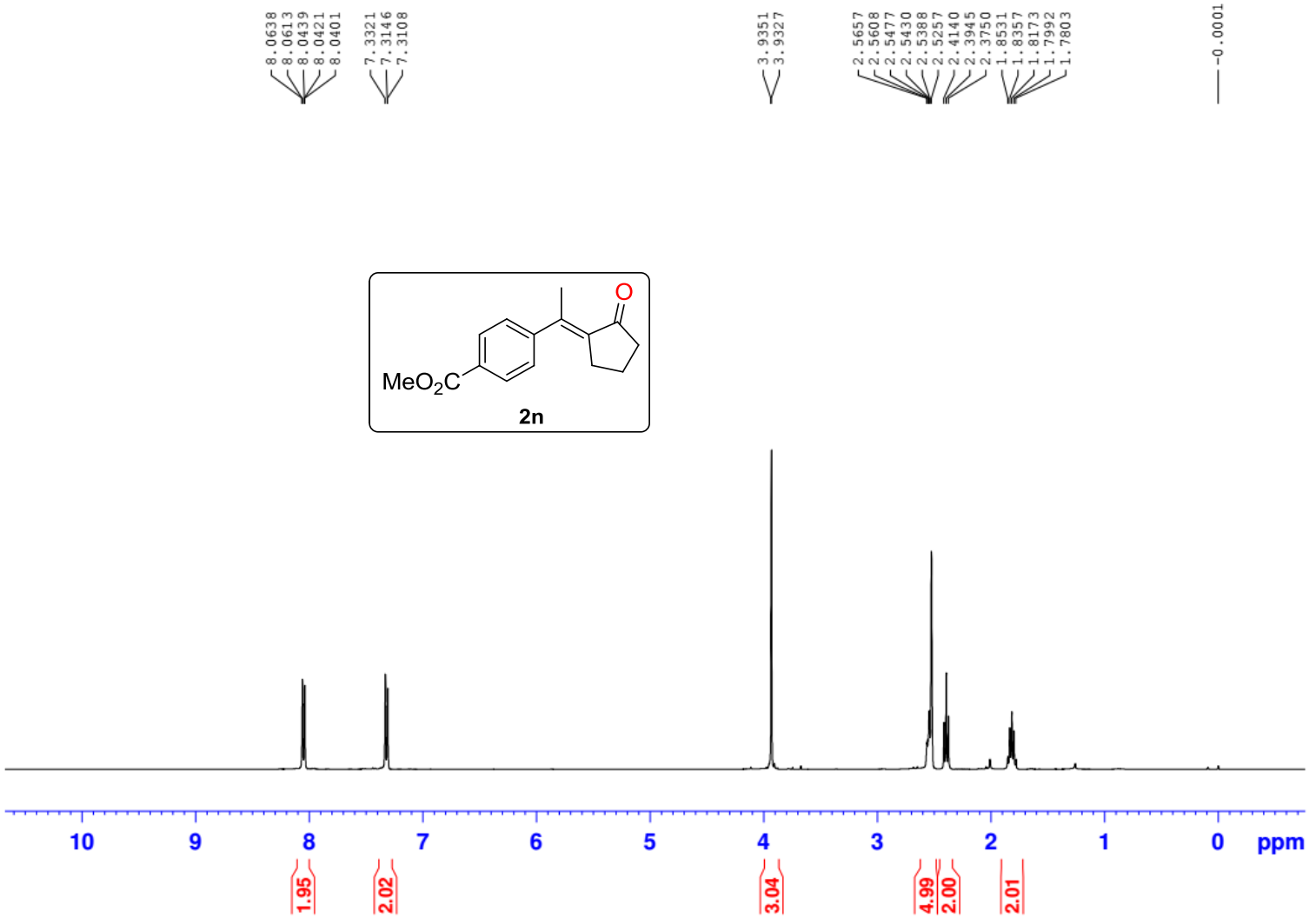


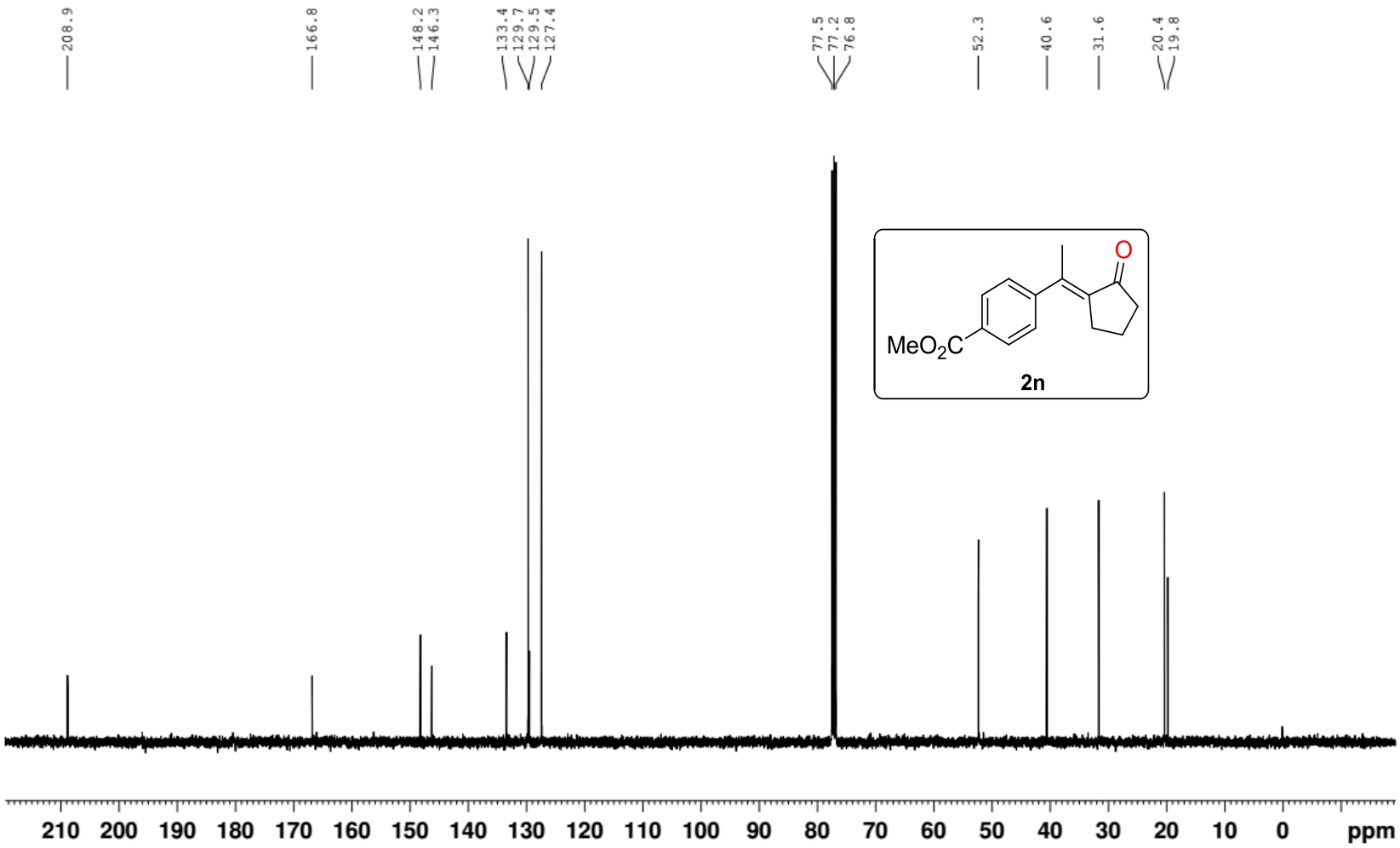
ZSC-X180714-1-CDCl3-f-NMR


zsc-x180714-2-CDCl3-HNMR
7.6960
7.6788
7.6757
7.6752
7.3727
7.3525
7.2829
2.5454
2.5403
2.5349
2.5273
2.5225
2.5179
2.5112
2.5072
2.4258
2.4064
2.3870
1.8730
1.8554
1.8369
1.8185
1.8001
-0.0001
O
NC
2m
10
9
8
7
6
5
4
3
2
1
0
ppm
1.93
1.98
5.01
2.00
2.03

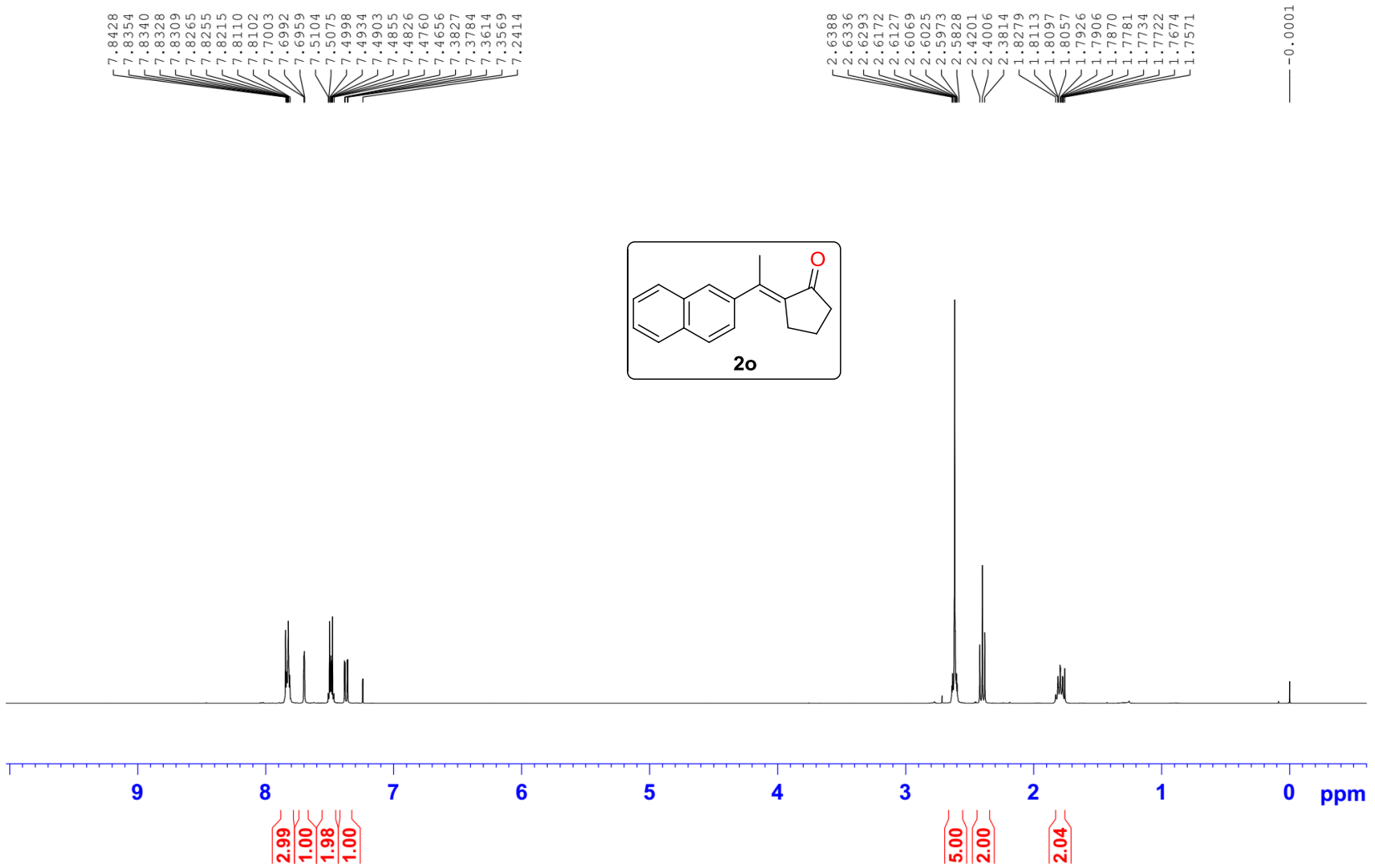

ZSC-X180714-2-CDCl3-CNMR
208.6
148.2
145.0
134.0
132.3
128.2
118.7
111.6
77.5
77.2
76.8
40.5
31.6
20.3
19.6
O
NC
2m
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

ZSC-X180714-6-CDCL3-HNMR

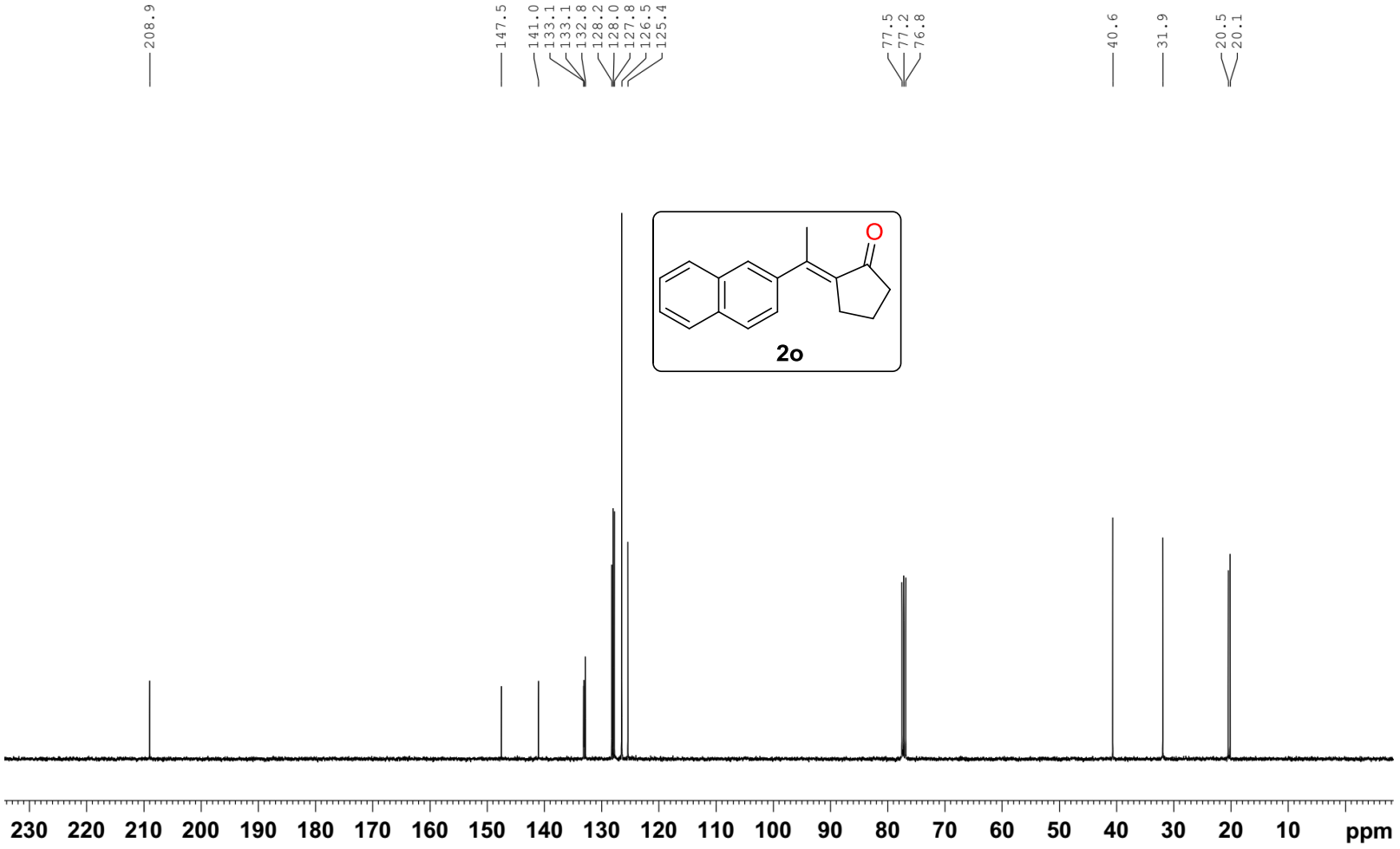



ZSC-X180714-6-CDCl3-CNMR
208.9
166.8
148.2
146.3
133.4
129.7
129.5
127.4
77.5
77.2
76.8
52.3
40.6
31.6
20.4
19.8
O
MeO2C
2n
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

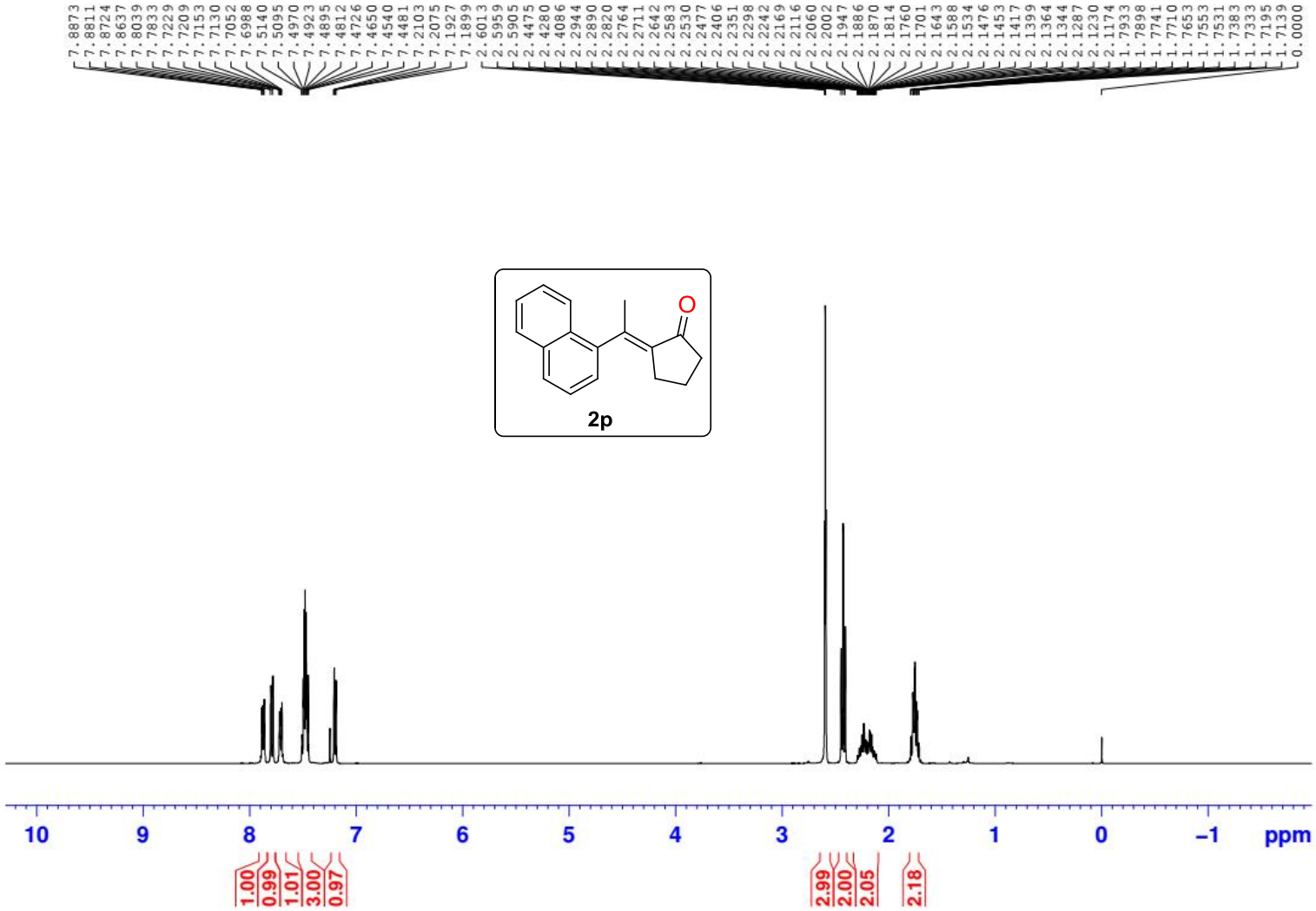
GB-X180308-1-1-2Na-HNMR



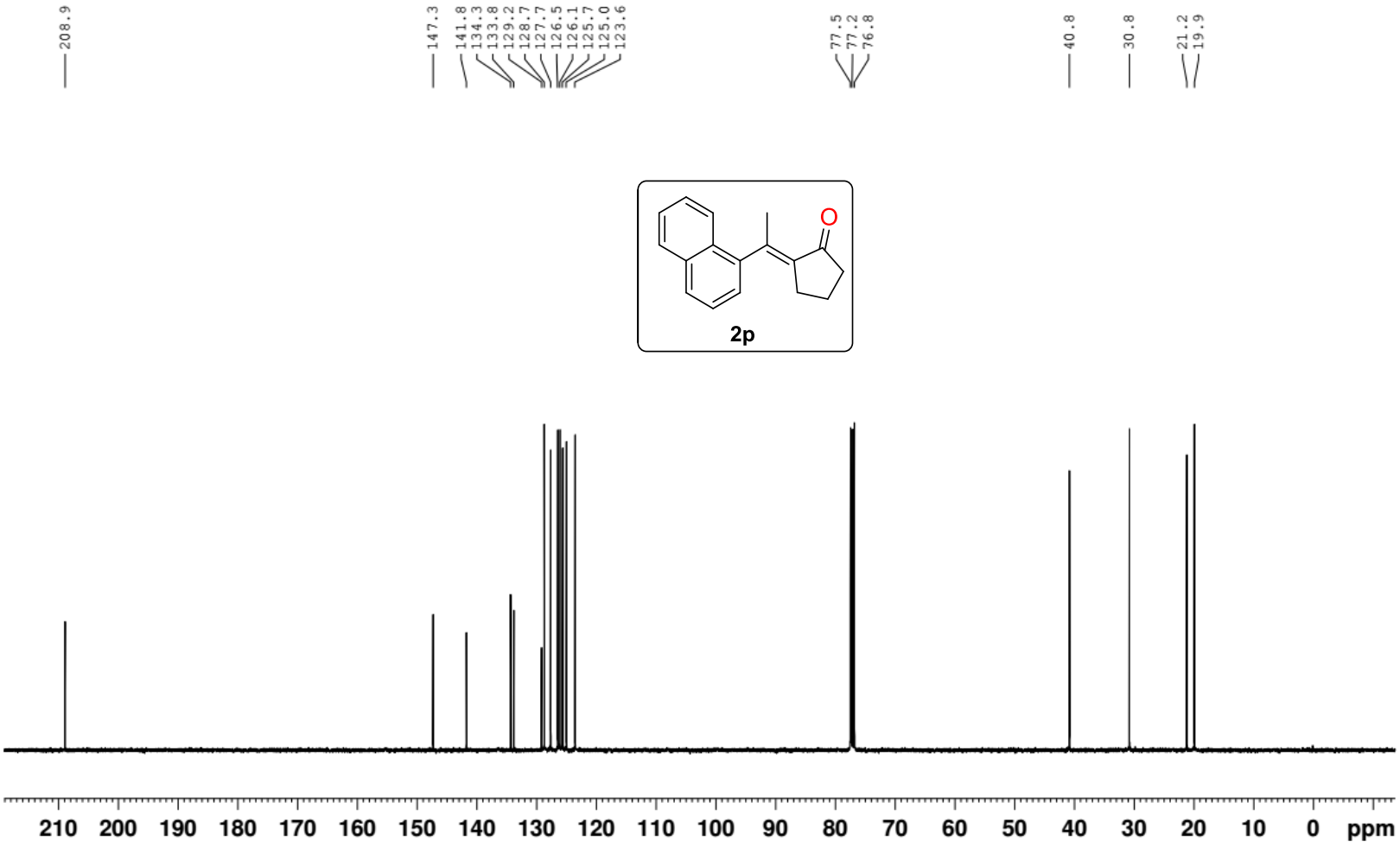
GB-X180308-1-1-2Na-CNMR



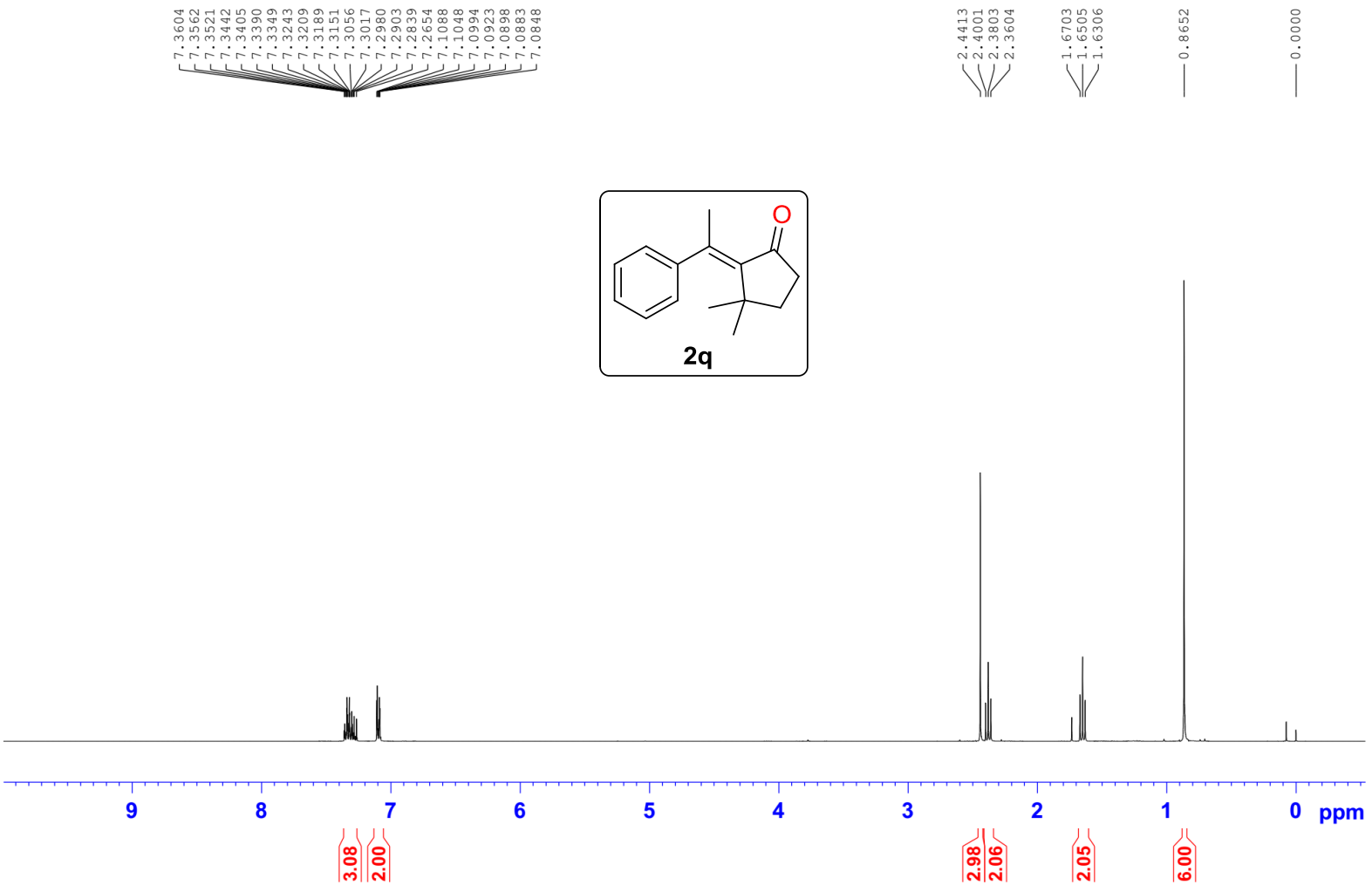
ZSC-X180717-2-CDCl3-HNMR



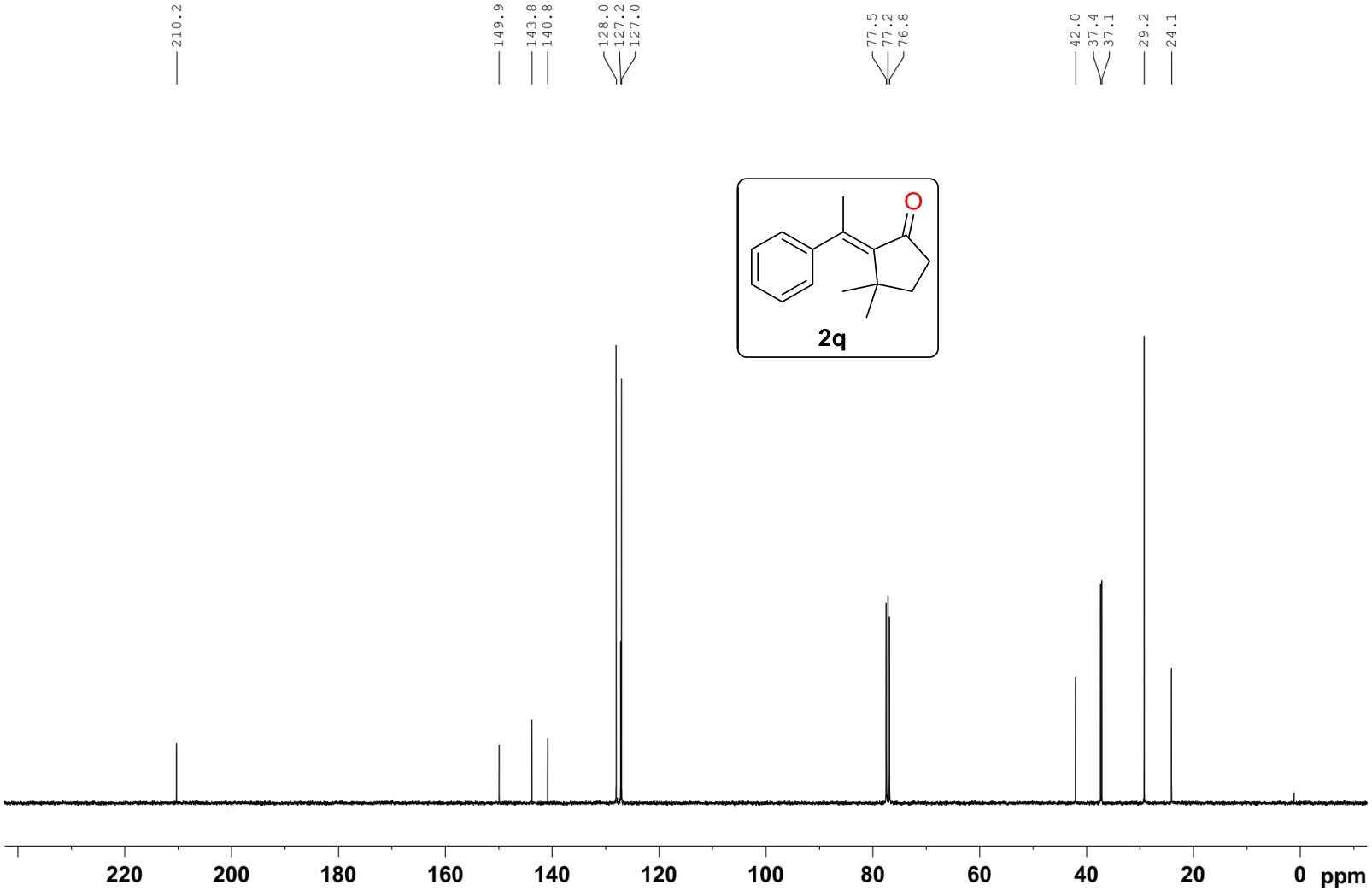
ZSC-X180717-2-CDCl3-CNMR

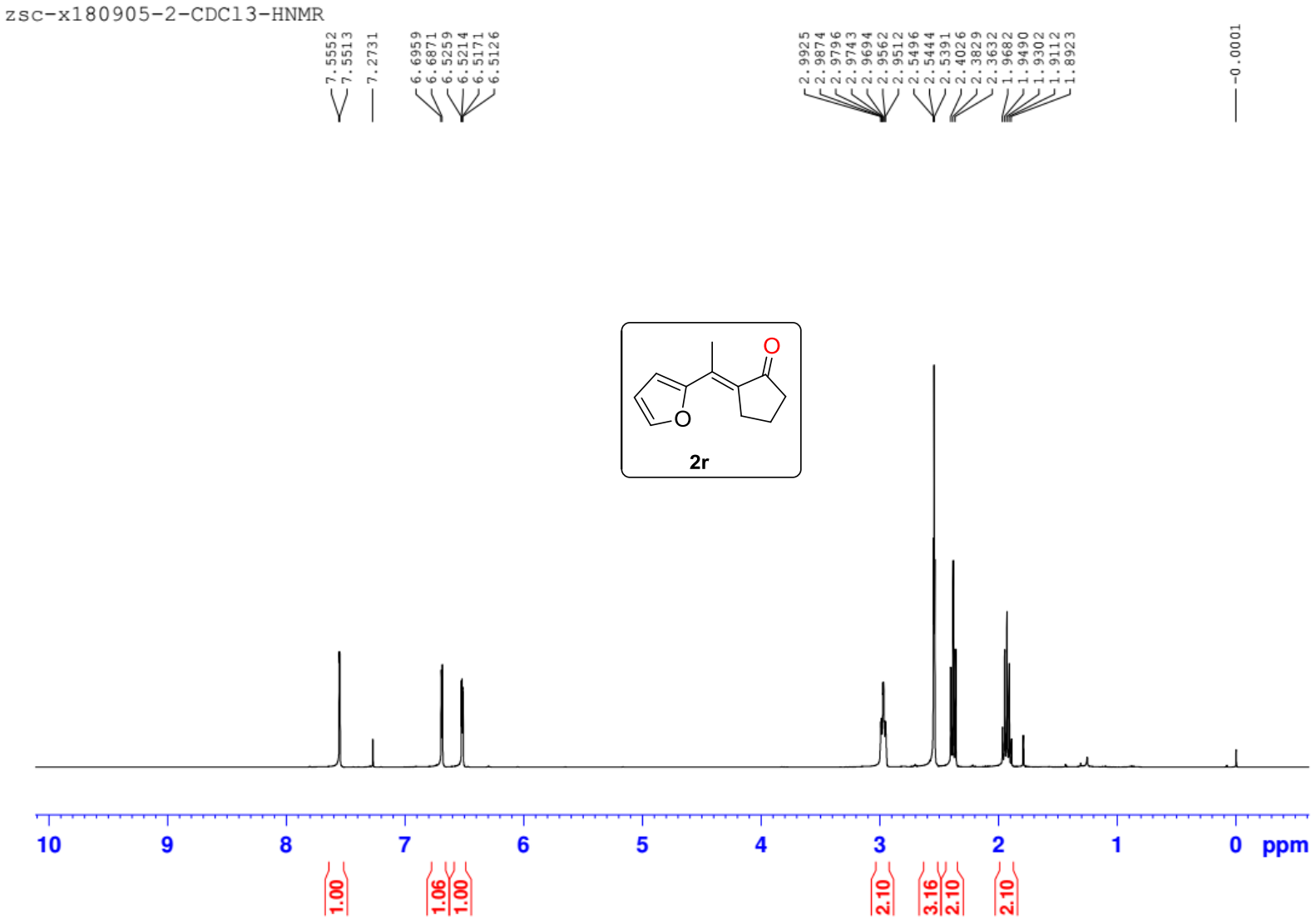


GB-X180614-1-2-MeMe-HNMR

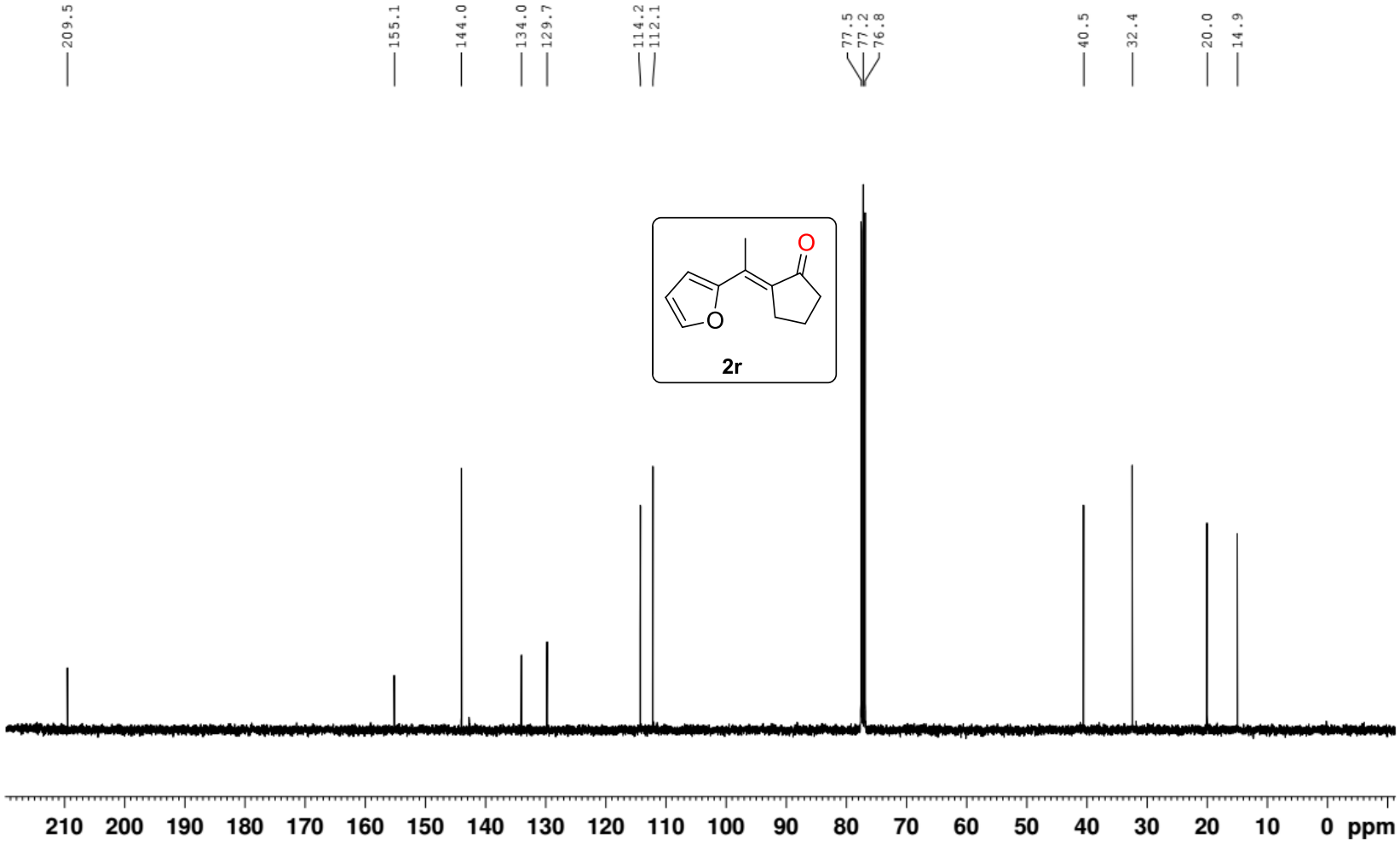


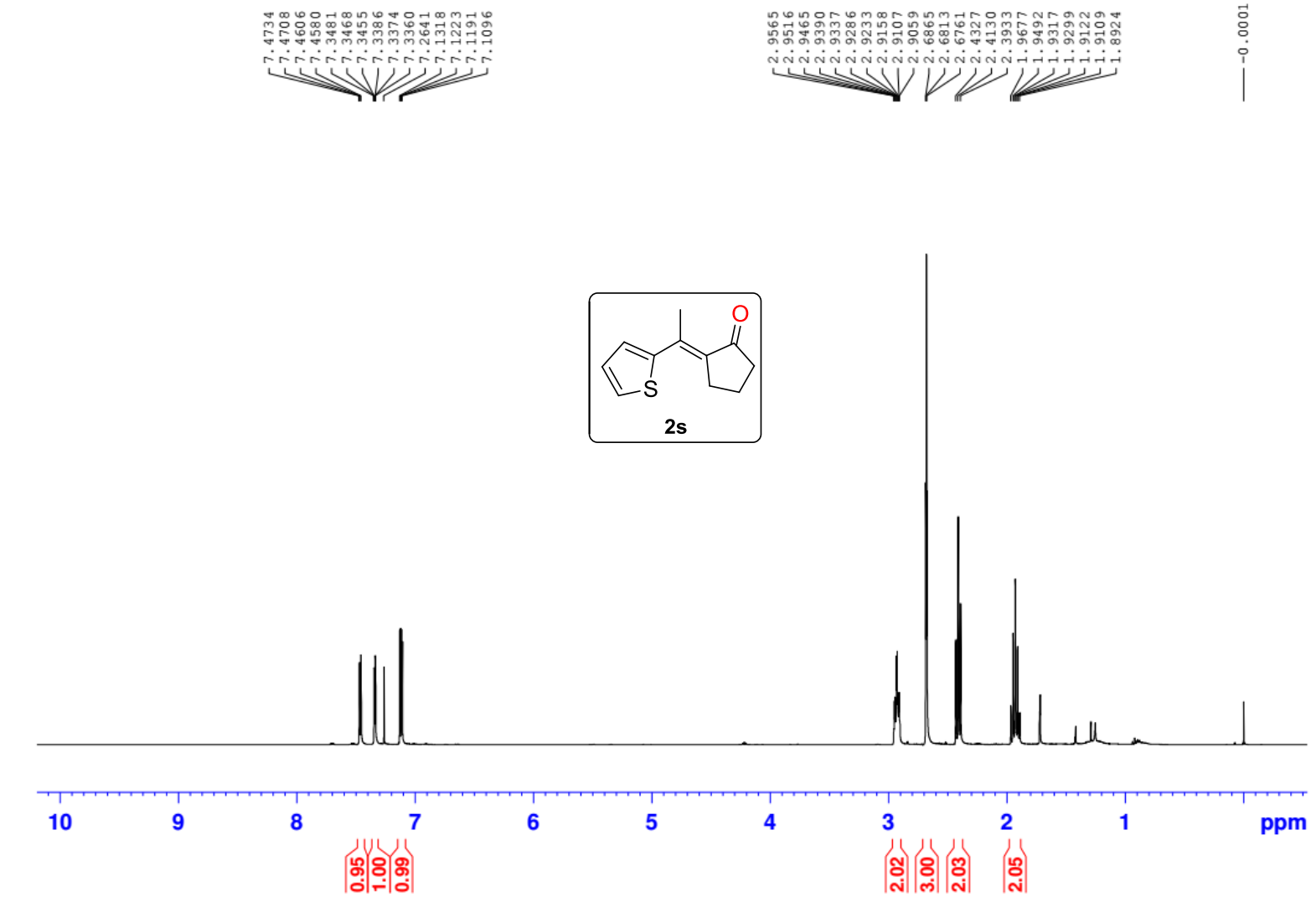
GB-X180614-1-2-MeMe-CNMR

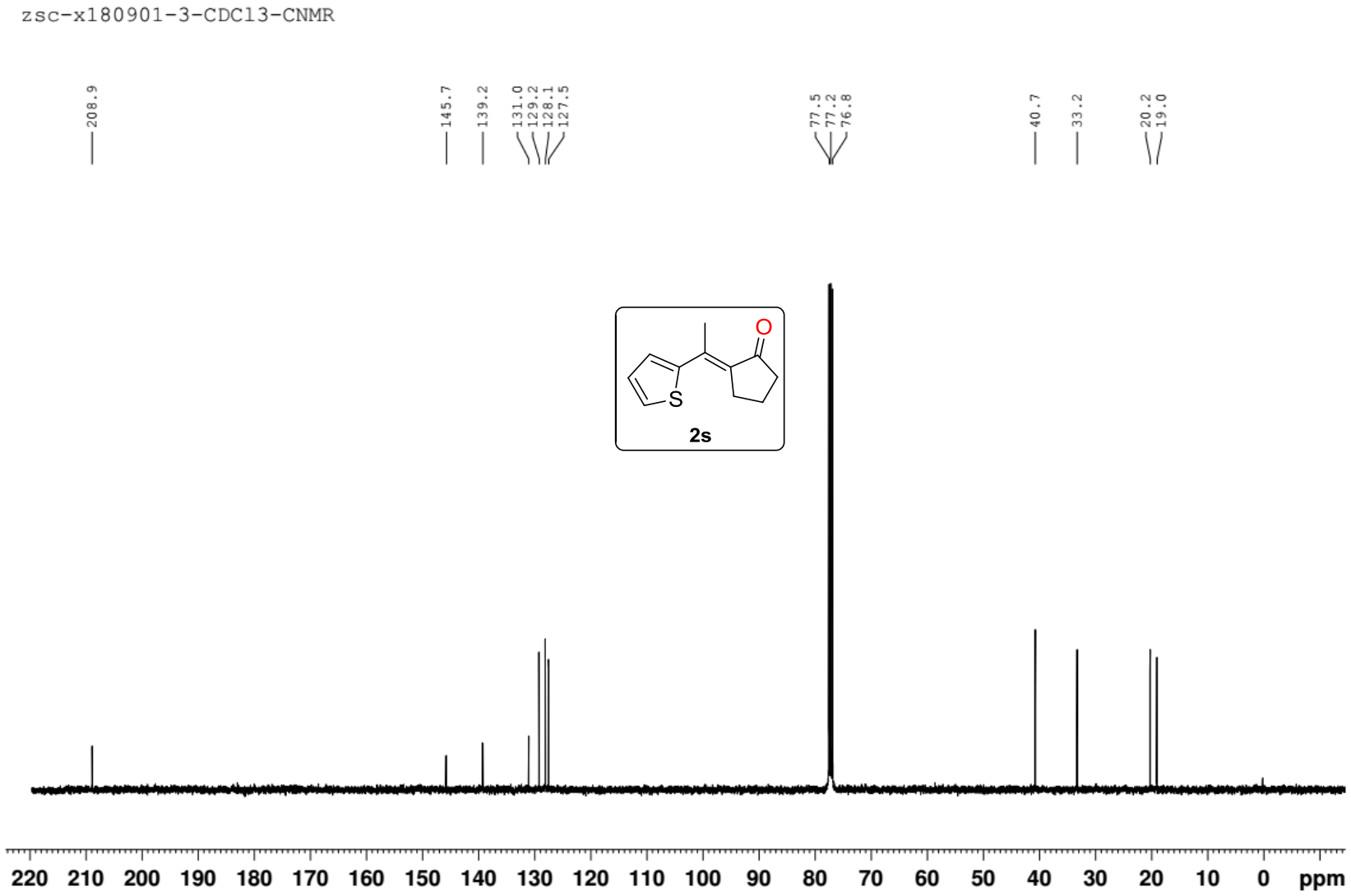



zsc-x180905-2-CDCl3-HNMR
7.5552
7.5513
7.2731
6.6959
6.6871
6.5259
6.5214
6.5171
6.5126
2.9925
2.9874
2.9796
2.9743
2.9694
2.9562
2.9512
2.5496
2.5444
2.5391
2.4026
2.3829
2.3632
1.9682
1.9490
1.9302
1.9112
1.8923
-0.0001
O
O
2r
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.06
1.00
2.10
3.16
2.10
2.10

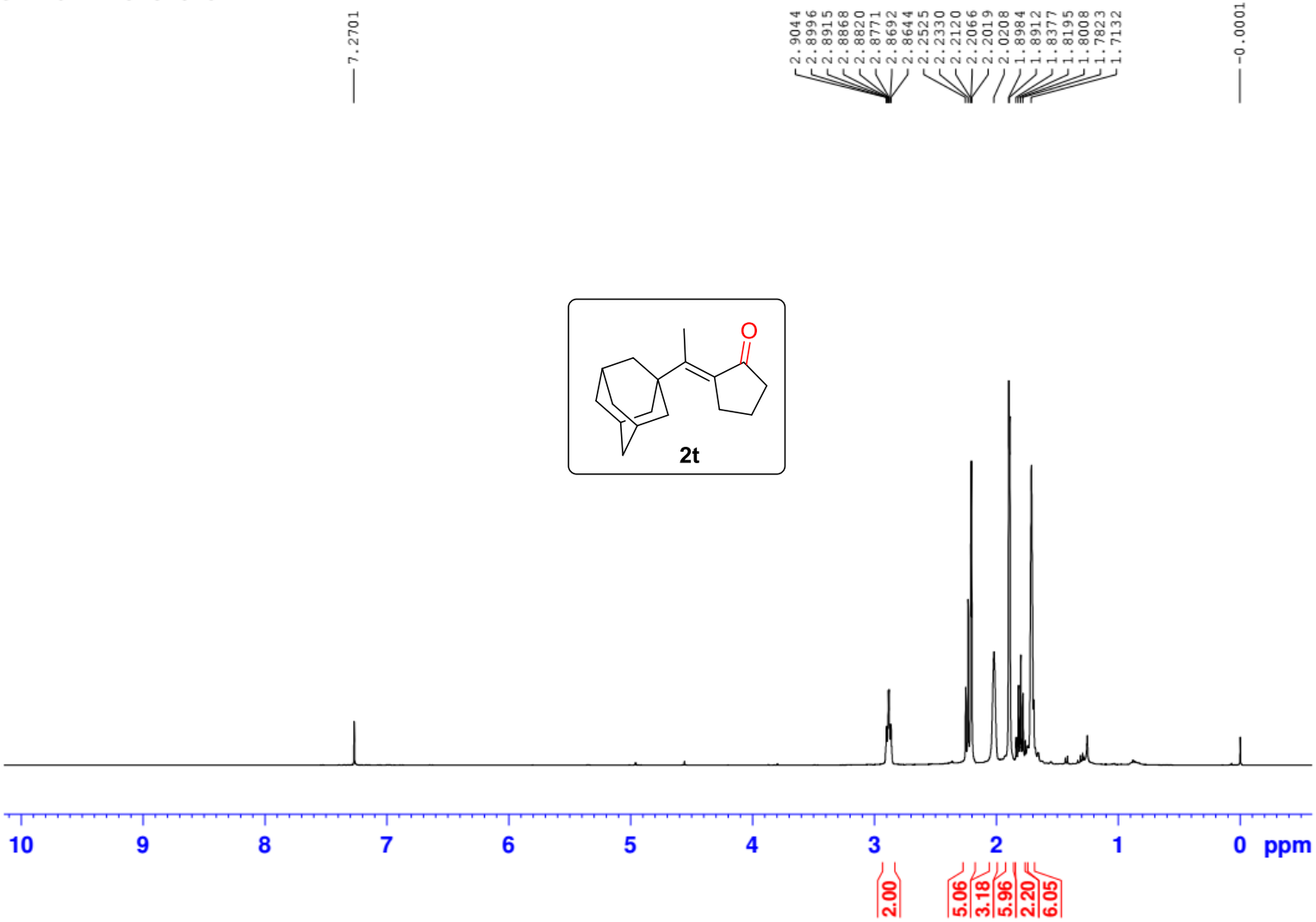
ZSC-X180905-2-CDCl3-CNMR

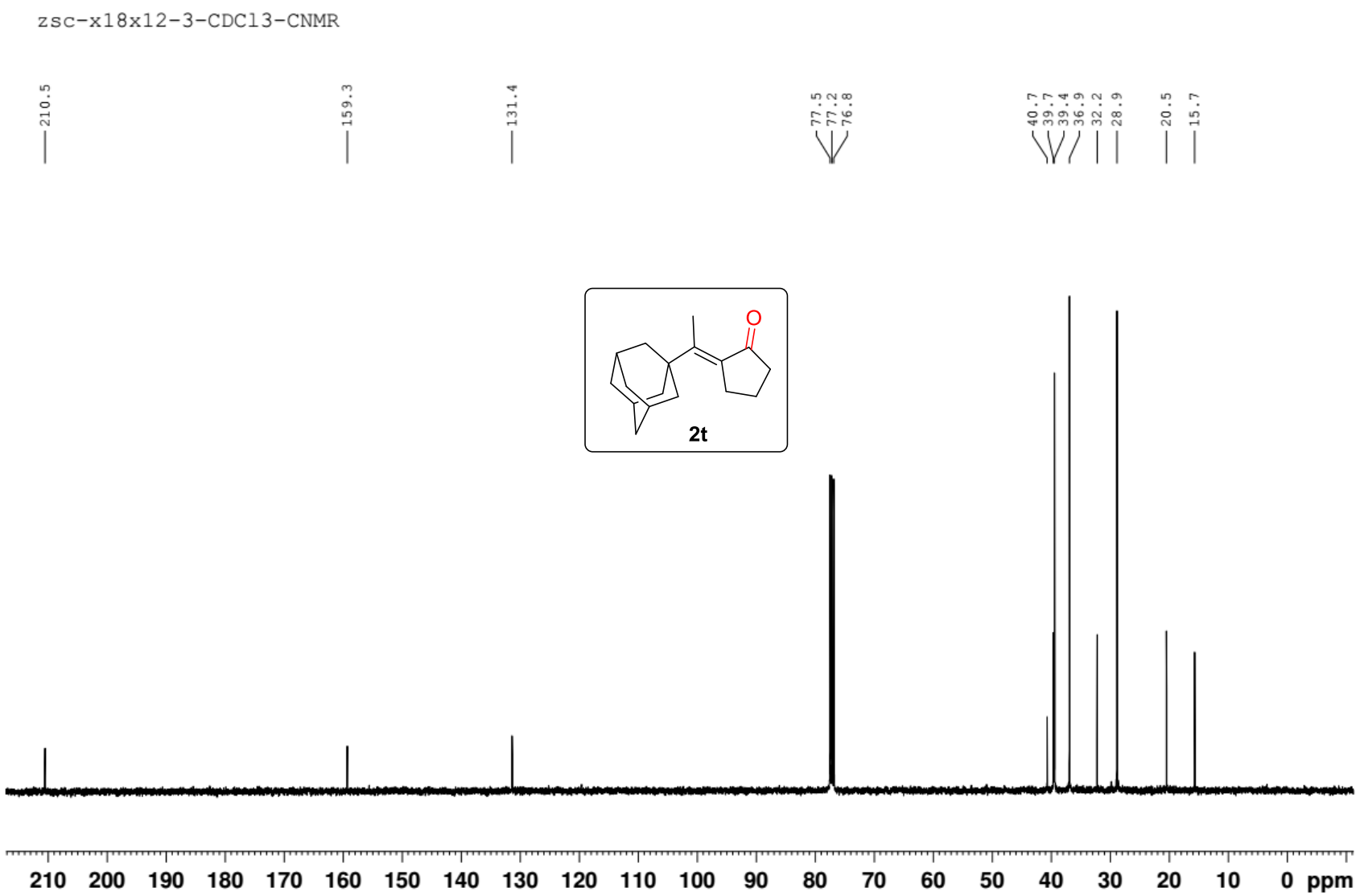



zsc-x180901-3-CDCl3-HNMR
7.4734
7.4708
7.4606
7.4580
7.3481
7.3468
7.3455
7.3386
7.3374
7.3360
7.2641
7.1318
7.1223
7.1191
7.1096
2.9565
2.9516
2.9465
2.9390
2.9337
2.9286
2.9233
2.9158
2.9107
2.9059
2.6865
2.6813
2.6761
2.4327
2.4130
2.3933
1.9677
1.9492
1.9317
1.9299
1.9122
1.9109
1.8924
-0.0001
O
S
2s
10
9
8
7
6
5
4
3
2
1
ppm
0.95
1.00
0.99
2.02
3.00
2.03
2.05

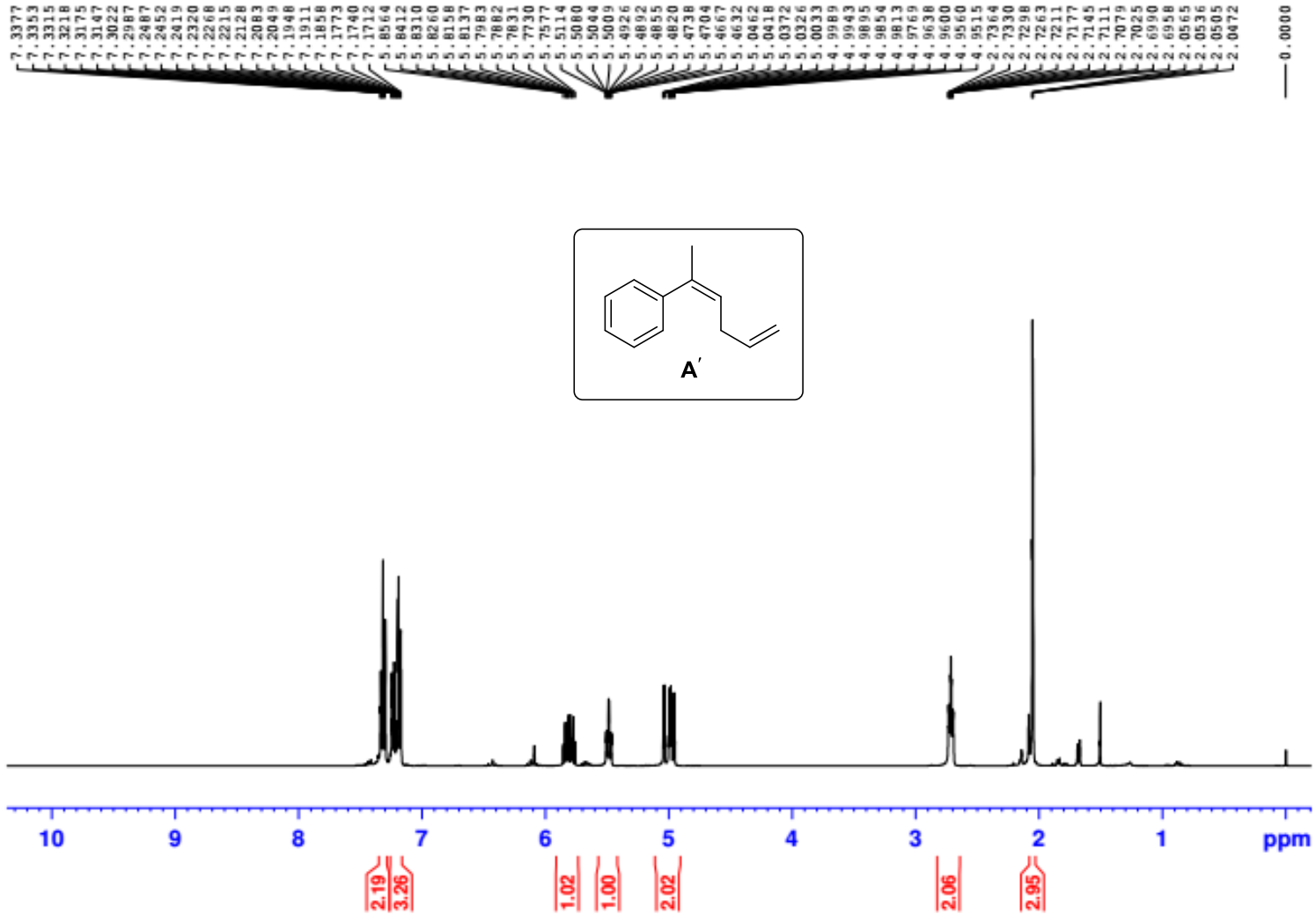

zsc-x180901-3-CDCl3-CNMR
208.9
145.7
139.2
131.0
129.2
128.1
127.5
77.5
77.2
76.8
40.7
33.2
20.2
19.0
O
S
2s
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

zsc-x18x12-3-CDCl3-HNMR

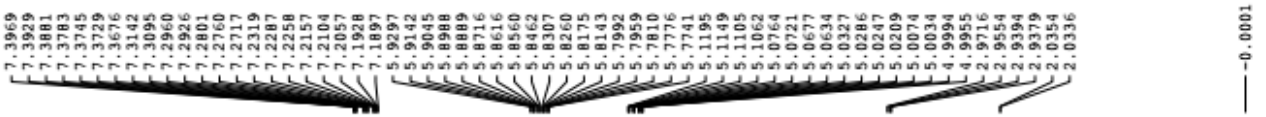


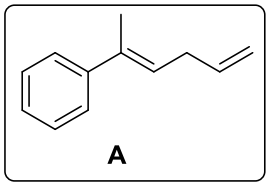

zsc-x18x12-3-CDCl3-CNMR
210.5
159.3
131.4
77.5
77.2
76.8
40.7
39.7
39.4
36.9
32.2
28.9
20.5
15.7
O
2t
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

ZSC-X180813-1-CDCl3-HNMR



zsc-x180907-2-3-CDCl3-HNMR





A