Supporting Information

Synthesis of Highly Substituted Racemic and Enantioenriched Allenylsilanes via Copper-Catalyzed Hydrosilylation of (*Z*)-2-Alken-4-ynoates with Silylboronate

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General Information:

Experiments involving moisture and/or air sensitive components were performed in oven-dried glassware under a positive pressure of argon using dry solvents. Et_3N was fractionally distilled. Other reagents were commercially purchased and were used as received without further purification for the reactions

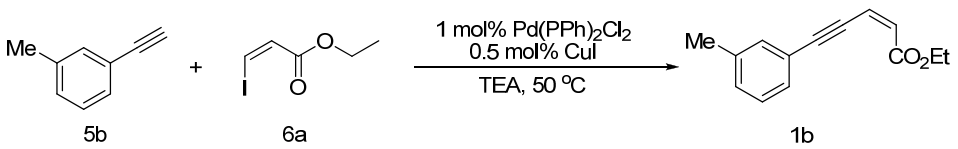
Proton nuclear magnetic resonance (^{1}H NMR) and carbon nuclear magnetic resonance (^{13}C NMR) spectroscopy were performed on a Bruker Advance 400M NMR spectrometers. Chemical shifts ^{1}H NMR spectra are reported as in units of parts per million (ppm) downfield from $SiMe_4$ (0.0) and relative to the signal of chloroform-*d* (*J* = 7.264, singlet). Multiplicities were given as: s (singlet); d (doublet); t (triplet); q (quartet); dd (doublet of doublets); dt (doublet of triplets); m (multiplets) and etc. The number of protons (n) for a given resonance is indicated by nH. Coupling constants are reported as a *J* value in Hz. Carbon nuclear magnetic resonance spectra (^{13}C NMR) are reported as d in units of parts per million (ppm) downfield from $SiMe_4$ (0.0) and relative to the signal of chloroform-*d* (*J* = 77.03, triplet).

High resolution mass spectral analysis (HRMS) was performed on Water XEVO G2 Q-TOF (Waters Corporation).The enantiomeric excesses were determined by HPLC analysis on Chiral Daicel Chiralpak OD-H, IC, columns.

1. Experimental Procedure：

1.1 Procedures for synthesis of the enynoates.

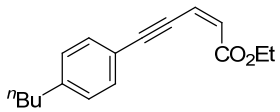
All (*Z*)-2-alken-4-ynoates were prepared according to the reported literatures.[1-3]



5b 6a 1b

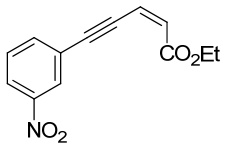
1b was synthesized according to the reported procedures:[2] To a mixture of (*Z*)-ethyl 3-iodoacrylate **6a** (1.13 g, 5 mmol, 1.0 equiv), $PdCl_2(PPh_3)_2$ (35.6 mg, 0.05 mmol, 1.0 mol%), CuI (4.9 mg, 0.025 mmol, 0.5 mol%) and TEA (20 mL) were added the corresponding alkyne **5b** (639 mg, 5.5 mmol, 1.1 equiv). The mixture was stirred at 50 °C until the starting material **6a** was completely consumed (monitored by TLC). Then the mixture was cooled to room temperature and diluted with diethyl ether (15 mL). Then the solution was washed with saturated ammonium chloride twice (10 mL×2). The aqueous layer was extracted with diethyl ether (10 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and evaporated in vacuo, the residue was purified by column chromatography (PE/EA = 97:3) to afford the product **1b** (921 mg, 86%) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39 - 7.31 (m, 2H), 7.27 - 7.14 (m, 2H), 6.36 (d, *J* = 11.4 Hz, 1H), 6.12 (d, *J* = 11.4 Hz, 1H), 4.27 (q, *J* = 7.1 Hz, 2H), 2.34 (s, 3H), 1.34 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.87, 138.08, 132.58, 130.11, 129.16, 128.26, 128.03, 122.95, 122.44, 101.52, 86.04, 60.43, 21.17, 14.31.

HRMS (ESI): m/z calculated for $C_{14}H_{14}O_2Na$ $[M+Na]^+$: 237.0891, found: 237.0896.



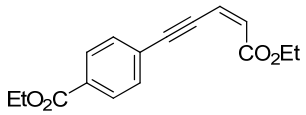
1e: To a mixture of (*Z*)-ethyl 3-iodoacrylate **6a** (1.13g, 5 mmol, 1.0 equiv), $PdCl_2(PPh_3)_2$ (35.6 mg, 0.05 mmol, 1.0 mol%), CuI (4.9 mg, 0.025 mmol, 0.5 mol%) and TEA (20 mL) were added the corresponding alkyne **5e** (871 mg, 5.5 mmol, 1.1 equiv). The mixture was stirred at 50 °C and dealt with according to the similar procedures as **1b** to give the product **1e** (1.06 g, 83%) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 - 7.42 (m, 2H), 7.20 - 7.10 (m, 2H), 6.36 (d, *J* = 11.4 Hz, 1H), 6.10 (d, *J* = 11.4 Hz, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 2.68 - 2.56 (m, 2H), 1.67 - 1.54 (m, 2H), 1.39 - 1.30 (m,5H), 0.92 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.93, 144.53, 132.02, 128.52, 127.70, 123.05, 119.78, 101.73, 85.99, 60.40, 35.67, 33.31, 22.30, 14.32 ,13.91.

HRMS (ESI): m/z calculated for $C_{17}H_{20}O_2Na$ $[M+Na]^+$: 279.1361, found: 279.1364.



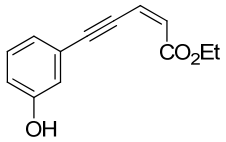
1g: To a mixture of (*Z*)-ethyl 3-iodoacrylate **6a** (1.13g, 5 mmol, 1.0 equiv), $PdCl_2(PPh_3)_2$ (35.6 mg, 0.05 mmol, 1.0 mol%), CuI (4.9 mg, 0.025 mmol, 0.5 mol%) and TEA (20 mL) were added the corresponding alkyne **5g** (810 mg, 5.5 mmol, 1.1 equiv). The mixture was stirred at 50 °C and dealt with according to the similar procedures as **1b** to give the product **1g** (932 mg, 76 %) as light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.41 - 8.33 (m, 1H), 8.21 (ddd, *J* = 8.3, 2.2, 1.1 Hz, 1H), 7.85 - 7.82 (m, 1H), 7.59 - 7.51 (m, 1H), 6.37 (d, *J* = 11.5 Hz, 1H), 6.24 (d, *J* = 11.5 Hz, 1H), 4.28 (q, *J* = 7.1 Hz, 2H), 1.34 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.47, 148.11, 137.59, 130.03, 129.45, 126.62, 124.46, 123.68, 121.78, 97.67, 88.24, 60.66, 14.26.

HRMS (ESI): m/z calculated for $C_{13}H_{11}NO_4Na$ $[M+Na]^+$: 286.0586, found: 286.0582.



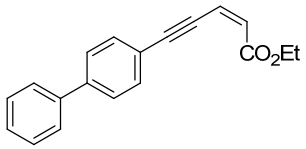
1l: To a mixture of (*Z*)-ethyl 3-iodoacrylate **6a** (1.13 g, 5 mmol, 1.0 equiv), $PdCl_2(PPh_3)_2$ (35.6 mg, 0.05 mmol, 1.0 mol%), CuI (4.9 mg, 0.025 mmol, 0.5 mol%) and TEA (20 mL) were added the corresponding alkyne **5l** (958 mg, 5.5 mmol, 1.1 equiv). The mixture was stirred at 50 °C and dealt with according to the similar procedures as **1b** to give the product **1l** (1.02 g, 75%) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 - 7.98 (m, 2H), 7.65 - 7.53 (m, 2H), 6.37 (d, *J* = 11.5 Hz, 1H), 6.19 (d, *J* = 11.5 Hz, 1H), 4.38 (q, *J* = 7.1 Hz, 2H), 4.27 (q, *J* = 7.1 Hz, 2H), 1.40 (t, *J* = 7.1 Hz, 3H), 1.33 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.91, 164.64, 131.84, 130.62, 129.45, 129.25, 127.09, 122.28, 99.81, 88.63, 61.20, 60.56, 14.29, 14.27.

HRMS (ESI): m/z calculated for $C_{16}H_{16}O_4Na$ $[M+Na]^+$: 295.0546, found: 295.0954.



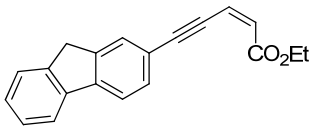
1p: To a mixture of (*Z*)-ethyl 3-iodoacrylate **6a** (1.13 g, 5 mmol, 1.0 equiv), $PdCl_2(PPh_3)_2$ (35.6 mg, 0.05 mmol, 1.0 mol%), CuI (4.9 mg, 0.025 mmol, 0.5 mol%) and TEA (20 mL) were added the corresponding alkyne **5p** (550 mg, 5.5 mmol, 1.1 equiv). The mixture was stirred at 50 °C and dalt with according to the similar procedures as **1b** to give the product **1p** (865 mg, 80%) as a brown solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.19 - 7.12 (m, 1H), 7.08 - 7.03 (m, 1H), 7.00 (dd, *J* = 2.5, 1.4 Hz, 1H), 6.86 (ddd, *J* = 8.1, 2.6, 1.0 Hz, 1H), 6.37 (d, *J* = 11.4 Hz, 1H), 6.14 (d, *J* = 11.4 Hz, 1H), 5.58 (broad, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 1.33 (t, *J* = 7.1 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.36, 155.95, 129.60, 127.97, 124.25, 123.51, 123.31, 118.72, 117.02, 101.45, 85.99, 60.77, 14.25.

HRMS (ESI): m/z calculated for $C_{13}H_{12}O_3Na$ $[M+Na]^+$: 239.0684, found:239.0681.

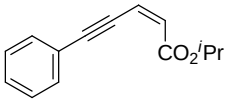


1r: To a mixture of (*Z*)-ethyl 3-iodoacrylate **6a** (1.13g, 5 mmol, 1.0 equiv), $PdCl_2(PPh_3)_2$ (35.6 mg, 0.05 mmol, 1.0 mol%), CuI (4.9 mg, 0.025 mmol, 0.5 mol%) and TEA (20 mL) were added the corresponding alkyne **5r** (980 mg, 5.5 mmol, 1.1 equiv). The mixture was stirred at 50 °C and dealt with according the similar procedures as **1b** to give the product **1r** (1.16 g, 84%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 - 7.54 (m, 6H), 7.51 - 7.41 (m, 2H), 7.41 - 7.32 (m, 1H), 6.39 (d, *J* = 11.4 Hz, 1H), 6.15 (d, *J* = 11.4 Hz, 1H), 4.28 (q, *J* = 7.1 Hz, 2H), 1.35 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.88, 141.91, 140.17, 132.52, 128.87, 128.16, 127.80, 127.11, 127.05, 122.85, 121.52, 101.17, 87.10, 60.47, 14.34.

HRMS (ESI): m/z calculated for $C_{19}H_{16}O_2Na$ $[M+Na]^+$: 299.1048, found:299.1054.

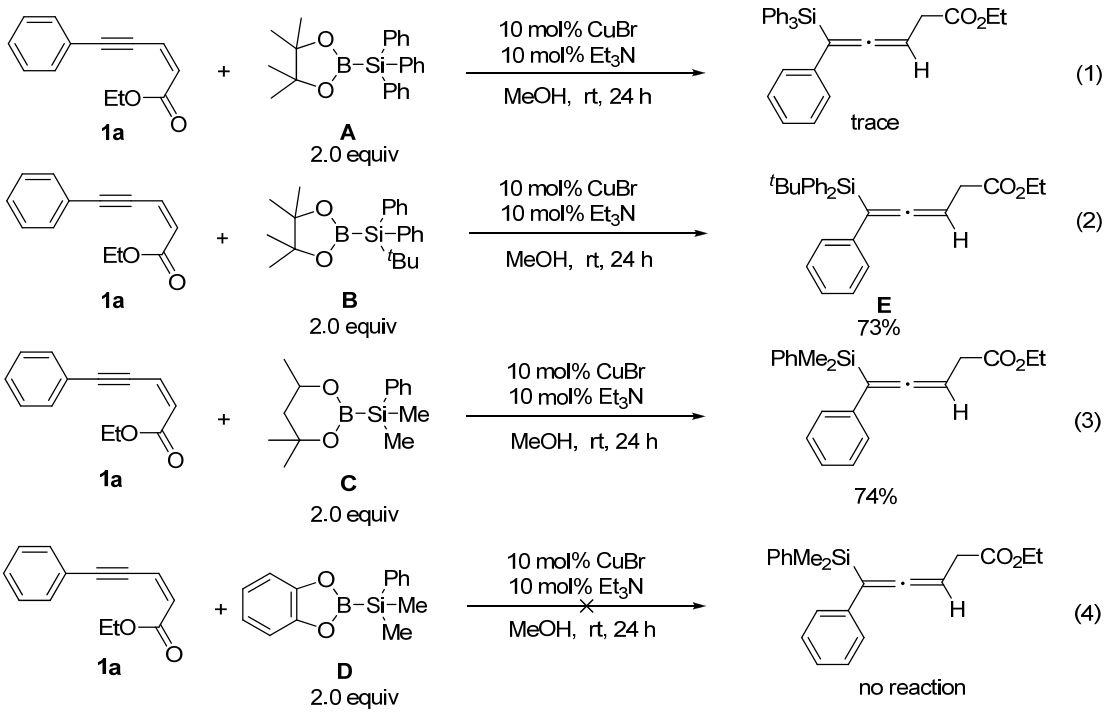


1s: To a mixture of (*Z*)-ethyl 3-iodoacrylate **6a** (1.13g, 5 mmol, 1.0 equiv), $PdCl_2(PPh_3)_2$ (35.6 mg, 0.05 mmol, 1.0 mol%), CuI (4.9 mg, 0.025 mmol, 0.5 mol%) and TEA (20 mL) were added the corresponding alkyne **5s** (1.05 g, 5.5 mmol, 1.1 equiv). The mixture was stirred at 50 °C and dealt with according to the similar procedures as **1b** to give product **1s** (1.04g 72%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 - 7.71 (m, 3H), 7.62 - 7.51 (m, 2H), 7.44 - 7.30 (m, 2H), 6.39 (d, *J* = 11.4 Hz, 1H), 6.13 (d, *J* = 11.4 Hz, 1H), 4.29 (q, *J* = 7.1 Hz, 2H), 3.90 (s, 2H), 1.35 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.96, 143.73, 143.18, 142.87, 140.91, 131.11, 128.73, 127.73, 127.42, 126.96, 125.12, 123.10, 120.61, 120.35, 119.83, 102.34, 86.67, 60.43, 36.71, 14.35.
HRMS (ESI): m/z calculated for $C_{20}H_{16}O_2Na$ $[M+Na]^+$: 311.1048, found:311.1054.

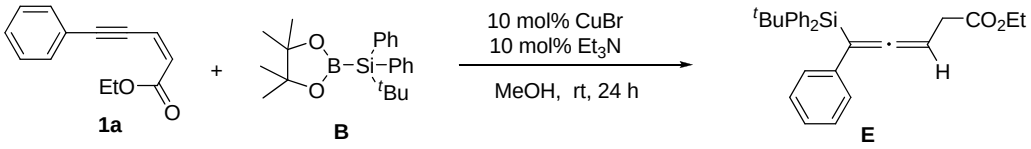


1ad: To a mixture of (Z)-iPr-3-iodoacrylate **6c** (1.2 g, 5 mmol, 1.0 equiv), $PdCl_2(PPh_3)_2$ (35.6 mg, 0.05 mmol, 1.0 mol%), CuI (4.9 mg, 0.025 mmol, 0.5 mol%) and TEA (20 mL) were added the corresponding alkyne **5a** (566 mg, 5.5 mmol, 1.1 equiv). The mixture was stirred at 50 °C and dealt with the similar procedures as **1b** to give the product **1ad** (804 mg, 75%) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59 - 7.51 (m, 2H), 7.41 - 7.31 (m, 3H), 6.34 (d, *J* = 11.5 Hz, 1H), 6.11 (d, *J* = 11.5 Hz, 1H), 5.15 (m, 1H), 1.31 (d, *J* = 6.5 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.39, 131.99, 129.11, 128.79, 128.37, 122.71, 122.44, 100.94, 86.37, 67.91, 21.97.
HRMS (ESI): m/z calculated for $C_{14}H_{14}O_2Na$ $[M+Na]^+$: 237.0891, found:237.0896.

1.2 The results of reactions between different silylboronates with 1a.



Procedures for the reaction between 1a and silylboronate B:

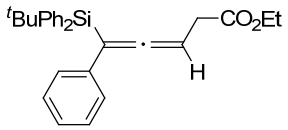


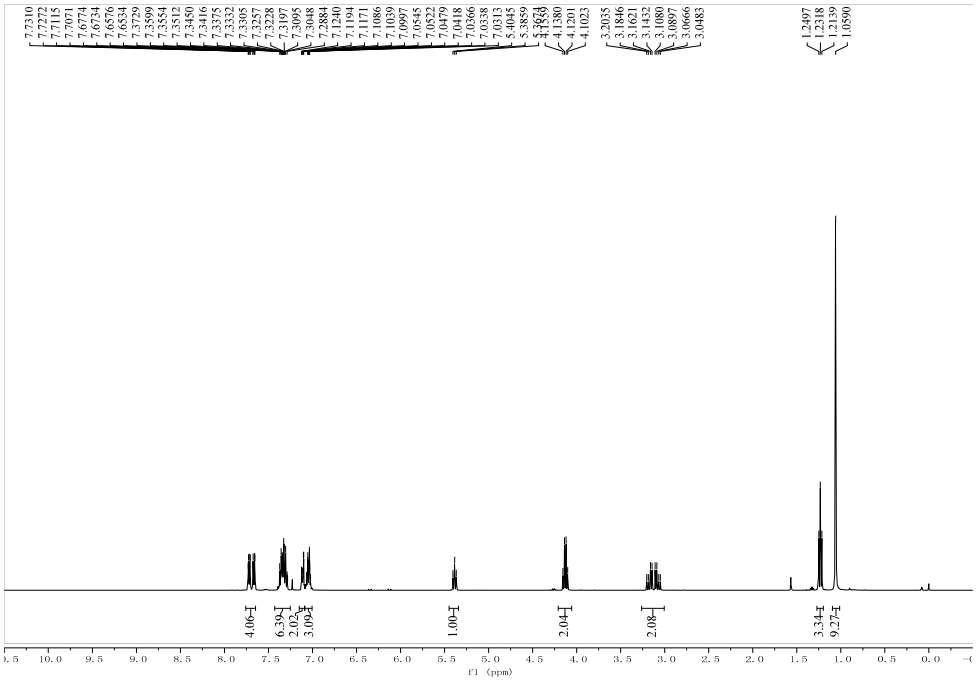
In an oven dried 15 mL Schlenk tube equipped with a stirring bar, 0.02 mmol (2.9 mg, 10 mol%) CuBr, 0.02 mmol (2.1 mg, 10 mol%) Et_3N, were dissolved in 1 mL of dry MeOH under argon atmosphere. The solution was stirred for 5 min at room temperature. Then 0.2 mmol **1** (40.4 mg, 1.0 equiv) enyens, 0.4 mmol (2.0 equiv, 146.7 mg) ^{t}BuPh$_2$Si-Bpin was added to the tube under Ar atmosphere. The final solution was continued to stir for 24 h at room temperature. Then the solution was diluted with DCM and filtered through Celite. The final filtrate was concentrated under vacuum to afford the crude product which was isolated through flash column chromatography (Eluent: PE/Et_2O = 97:3) to furnish the related product **3** (64.1 mg, 73%) as colorless oil.

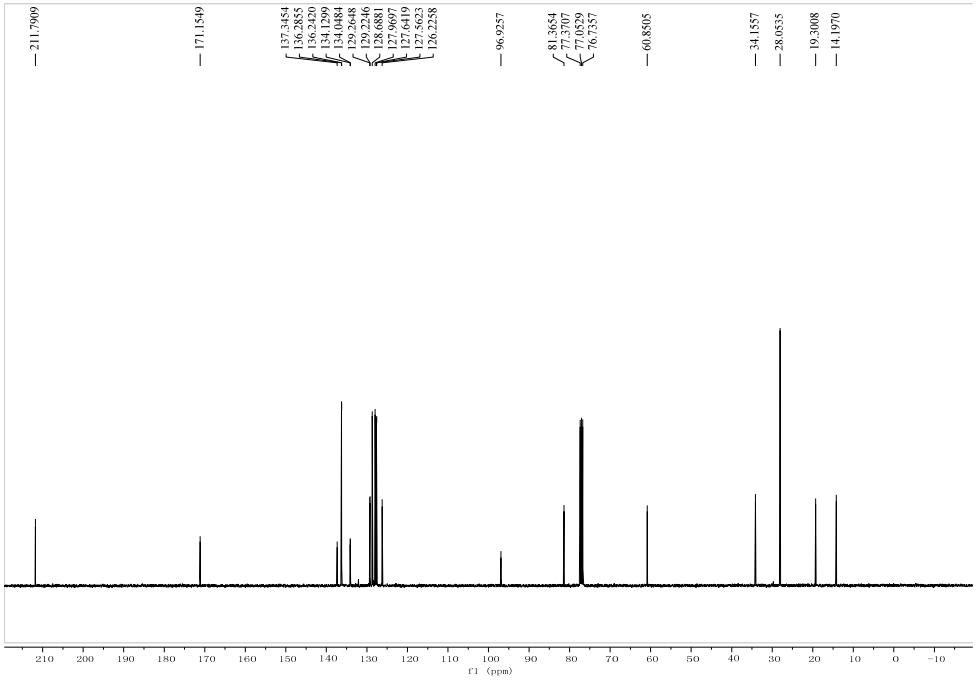
^{1}HNMR (400 MHz, $CDCl_3$): δ 7.72 (dd, J = 8.0, 1.6 Hz, 2H), 7.67 (dd, J = 8.0, 1.6 Hz, 2H), 7.43-7.25 (m, 6H), 7.15-7.09 (m, 2H), 7.09-7.00 (m, 3H), 5.39 (t, J = 7.4 Hz,

1H), 4.13 (q, *J* = 7.1 Hz, 2H), 3.26- 3.01 (m, 2H), 1.23 (t, *J* = 7.1 Hz, 3H), 1.06 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 211.8, 171.2, 137.3, 136.3, 136.2, 134.1, 134.0, 129.3, 129.2, 128.7, 127.9, 127.6, 127.5, 126.2, 96.9, 81.4, 60.8, 34.2, 28.05, 19.3, 14.2.

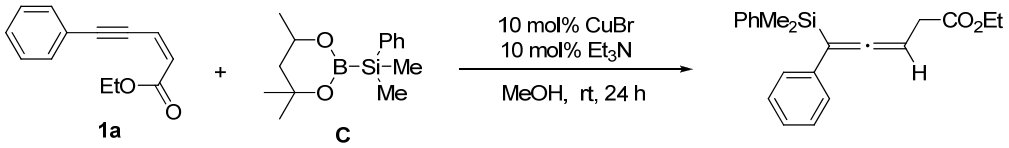
HRMS (ESI): m/z calculated for $C_{29}H_{23}O_2Si$ $[M+H]^+$: 441.2250 found: 441.2248.





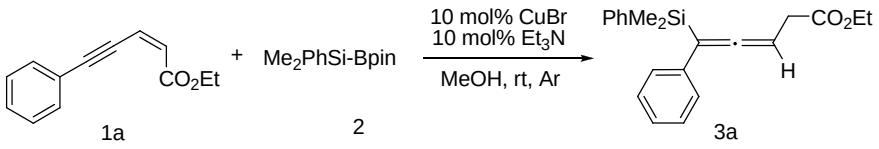


Procedures for the reaction between 1a and silylboronate C:



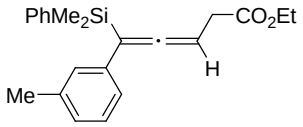
In an oven dried 15 mL Schlenk tube equipped with a stirring bar, 0.02 mmol (2.9 mg, 10 mol%) CuBr, 0.02 mmol (2.1 mg, 10 mol%) Et_3N, were dissolved in 1 mL of dry MeOH under argon atmosphere. The solution was stirred for 5 min at room temperature. Then 0.2 mmol **1a** (40.4 mg, 1.0 equiv), 0.4 mmol **C** (105 mg, 2.0 equiv) was added to the tube under Ar atmosphere. The final solution was continued to stir for 24 h at room temperature. Then the solution was diluted with DCM and filtered through Celite. The final filtrate was concentrated under vacuum to afford the crude product which was isolated through flash column chromatography (Eluent: PE/Et_2O = 97:3) to furnish the related product (50.1 mg, 74% yield) as colorless oil.

1.3 Procedures for synthesis of allenylsilanes:



3a: In an oven dried 15 mL Schlenk tube equipped with a stirring bar, 0.02 mmol (2.9 mg, 10 mol%) CuBr and 0.02 mmol (2.1 mg, 10 mol%) Et_3N were added into 1 mL of dry MeOH under argon atmosphere. The solution was stirred for 5min at room temperature. Then 0.2 mmol **1a** (40.4 mg, 1.0 equiv) and 0.4 mmol (2.0 equiv, 105 mg) Me_2PhSi-Bpin were added to the tube in sequence under argon atmosphere. The final solution was continued to stir for 24 hours at room temperature. Then the solution was diluted with DCM and filtered through Celite. The final filtrate was concentrated under vacuum to afford the crude product which was purified through flash column chromatography (Eluent: PE/Et_2O = 97:3) to furnish the related product **3a** (62. 0 mg, 92%) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$):δ 7.61 - 7.55 (m, 2H), 7.36 - 7.32 (m, 3H), 7.24 - 7.17 (m, 4H), 7.16 - 7.10 (m, 1H), 5.37 (t, *J* = 7.4 Hz, 1H), 4.15 (q, *J* = 7.1 Hz, 2H), 3.15 (dd, *J* = 16.2, 7.2 Hz, 1H), 3.07 (dd, *J* = 16.2, 7.6 Hz, 1H), 1.25 (t, *J* = 7.1 Hz, 3H), 0.46 (s, 3H), 0.45 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 211.53, 173.26, 139.94, 138.32, 135.72, 131.03, 130.18, 129.78, 129.71, 128.24, 101.61, 82.96, 62.64, 36.08, 16.02, 0.00, -0.06.

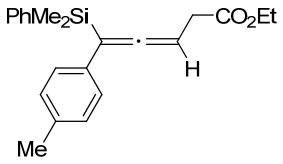
HRMS (ESI): m/z calculated for $C_{21}H_{24}O_2SiNa$ $[M+Na]^+$: 359.1443, found: 359.1443.



3b: In an oven dried 15 mL Schlenk tube equipped with a stirring bar, 0.02 mmol (2.9 mg, 10 mol%) CuBr, and 0.02 mmol (2.1 mg, 10 mol%) Et_3N were added into 1 mL of dry MeOH under Ar atmosphere. The solution was stirred for 5 min at room temperature. Then 0.2 mmol **1c** (42.9 mg, 1.0 equiv), 0.4 mmol (105 mg, 2.0 equiv) $SiMe_2Ph$-Bpin was added to the tube under argon atmosphere. The final solution was continued to stir for 24 hours at room temperature. Then the solution was diluted with DCM and filtered through Celite. The final filtrate was concentrated under vacuum to

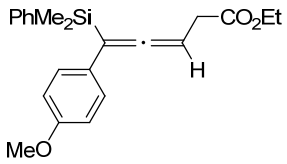
afford the crude product which was isolated through flash column chromatography (Eluent: PE/Et_2O = 97:3) to furnish the related product **3b** (64.1 mg) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ7.54 - 7.47 (m, 2H), 7.31 - 7.25 (m, 3H), 7.02 - 6.98 (m, 2H), 6.91 - 6.86 (m, 2H), 5.27 (t, *J* = 7.4 Hz, 1H), 4.07 (q, *J* = 7.2 Hz, 2H), 3.04 (dd, *J* = 16.2, 7.2 Hz, 1H), 2.99 (dd, *J* = 16.2, 7.6 Hz, 1H), 2.17 (s, 3H), 1.17 (t, *J* = 7.1 Hz, 3H), 0.38 (s, 3H), 0.38 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 211.47, 173.36, 140.10, 139.79, 138.26, 135.79, 131.07, 130.58, 130.10, 129.75, 129.13, 126.92, 101.66, 82.89, 62.68, 36.18, 23.30, 16.09, 0.09, 0.00.

HRMS (ESI): m/z calculated for $C_{22}H_{26}O_2SiNa$ $[M+Na]^+$: 373.1600 found: 373.1612.



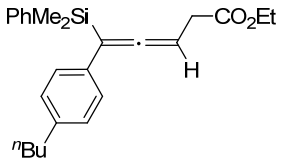
3c: In an oven dried 15 mL Schlenk tube equipped with a stirring bar, 0.02 mmol (2.9 mg, 10 mol%) CuBr and 0.02 mmol (2.1 mg, 10 mol%) Et_3N were added into 1 mL of dry MeOH under argon atmosphere. The solution was stirred for 5 min at room temperature. Then 0.2 mmol **1c** (42.9 mg, 1.0 equiv) and 0.4 mmol (105 mg, 2.0 equiv) Me_2PhSi-Bpin were added to the tube under argon atmosphere. The final solution was continued to stir for 24 hours at room temperature. Then the solution was diluted with DCM and filtered through Celite. The final filtrate was concentrated under vacuum to afford the crude product which was isolated through flash column chromatography (Eluent: PE/Et_2O = 97:3) to furnish the related product **3c** (57.5 mg, 92%) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 - 7.38 (m, 2H), 7.17 - 7.13 (m, 3H), 6.92 (d, *J* = 8.1 Hz, 2H), 6.82 (d, *J* = 8.1 Hz, 2H), 5.15 (t, *J* = 7.4 Hz, 1H), 3.96 (q, *J* = 7.1 Hz, 2H), 2.92 (dd, *J* = 16.2, 7.2 Hz, 1H), 2.87 (dd, *J* = 16.2, 7.6 Hz, 1H), 2.08 (s, 3H), 1.06 (t, *J* = 7.1 Hz, 3H), 0.26 (s, 3H), 0.26 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 211.38, 173.37, 140.13, 138.00, 135.77, 135.23, 131.03,130.97, 129.74,129.70, 101.31, 82.96, 62.65, 22.96, 15.97,0.08, 0.00.

HRMS (ESI): m/z calculated for $C_{22}H_{26}O_2SiNa$ $[M+Na]^+$: 373.1600 found: 373.1604.



3d: In an oven dried 15 mL Schlenk tube equipped with a stirring bar, 0.02 mmol (2.9 mg, 10 mol%) CuBr and 0.02 mmol (2.1 mg, 10 mol%) Et_3N were added into 1 mL of dry MeOH under argon atmosphere. The solution was stirred for 5 min at room temperature. Then 0.2 mmol **1d** (46.1 mg, 1.0 equiv) and 0.4 mmol (105 mg, 2.0 equiv) Me_2PhSi-Bpin were added to the tube under argon atmosphere. The final solution was continued to stir for 24 hours at room temperature. Then the solution was diluted with DCM and filtered through Celite. The final filtrate was concentrated under vacuum to afford the crude product which was isolated through flash column chromatography (Eluent: PE/Et_2O = 97:3) to furnish the related product **3d** (63.2 mg) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 - 7.49 (m, 2H), 7.28 - 7.25 (m, 3H), 7.09 - 7.06 (m, 2H), 6.69 - 6.66 (m, 2H), 5.27 (t, *J* = 7.3 Hz, 1H), 4.08 (q, *J* = 7.1 Hz, 2H), 3.66 (s, 3H), 3.04 (dd, *J* = 16.2, 7.2 Hz, 1H), 2.99 (dd, *J* = 16.2, 7.6 Hz, 1H), 1.17 (t, *J* = 7.1 Hz, 3H), 0.38 (s, 3H), 0.38 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 211.11, 173.39, 160.15, 140.10, 135.75, 131.04, 130.86, 130.34, 129.75, 115.72, 100.88, 83.04, 62.63, 57.06, 36.26, 16.13, 0.07, 0.00.

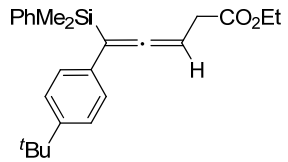
HRMS (ESI): m/z calculated for $C_{22}H_{26}O_3SiNa$ $[M+Na]^+$: 385.1549, found: 385.1542.



3e: In an oven dried 15 mL Schlenk tube equipped with a stirring bar, 0.02 mmol (2.9 mg, 10 mol%) CuBr and 0.02 mmol (2.1 mg, 10 mol%) Et_3N were added into 1 mL of dry MeOH under argon atmosphere. The solution was stirred for 5 min at room temperature. Then 0.2 mmol **1e** (51.3 mg, 1.0 equiv) and 0.4 mmol (105 mg, 2.0 equiv) Me_2PhSi-Bpin were added to the tube under argon atmosphere. The final solution was continued to stir for 24 hours at room temperature. Then the solution was diluted with DCM and filtered through Celite. The final filtrate was concentrated

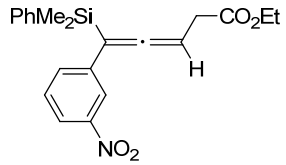
under vacuum to afford the crude product which was isolated through flash column chromatography (Eluent: PE/Et_2O = 97:3) to furnish the related product **3e** (63.1 mg) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 - 7.58 (m, 2H), 7.38 - 7.34 (m, 3H), 7.15 - 7.13 (m, 2H), 7.04 - 7.00 (m, 2H), 5.36 (t, *J* = 7.4 Hz, 1H), 4.17 (q, *J* = 6.9 Hz, 2H), 3.13 (dd, *J* = 16.2, 7.2 Hz, 1H), 3.07 (dd, *J* = 16.2, 7.6 Hz, 1H), 2.58 - 2.51 (m, 2H), 1.58 - 1.51 (m, 2H), 1.35 - 1.29 (m, 2H), 1.26 (t, *J* = 7.3 Hz, 3H) 0.90 (t, *J* = 7.3 Hz, 3H), 0.47 (s, 3H), 0.47(s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 211.33, 173.29, 142.97, 140.07, 135.68, 135.26, 130.92, 130.22, 129.64, 129.57, 101.23, 82.87, 62.56, 37.00, 36.12, 35.30, 24.11, 15.97, 15.71, 0.00. -0.07.

HRMS (ESI): m/z calculated for $C_{25}H_{32}O_2SiNa$ $[M+Na]^+$: 415.2069, found: 415.2079.

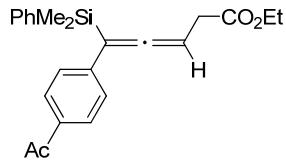


3f: In an oven dried 15 mL Schlenk tube equipped with a stirring bar, 0.02 mmol (2.9 mg, 10 mol%) CuBr and 0.02 mmol (2.1 mg, 10 mol%) Et_3N were added into 1 mL of dry MeOH under argon atmosphere. The solution was stirred for 5 min at room temperature. Then 0.2 mmol **1f** (51.3 mg, 1.0 equiv) and 0.4 mmol (105 mg, 2.0 equiv) Me_2PhSi-Bpin were added to the tube under argon atmosphere. The final solution was continued to stir for 24 hours at room temperature. Then the solution was diluted with DCM and filtered through Celite. The final filtrate was concentrated under vacuum to afford the crude product which was isolated through flash column chromatography (Eluent: PE/Et_2O = 97:3) to furnish the related product **3f** (63.8 mg) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63 - 7.56 (m, 2H), 7.40 - 7.31 (m, 3H), 7.26 - 7.20 (m, 2H), 7.20 - 7.12 (m, 2H), 5.35 (t, *J* = 7.4 Hz, 1H), 4.15 (q, *J* = 7.1 Hz, 2H), 3.11 (dd, *J* = 16.2, 7.2 Hz, 1H), 3.06 (dd, *J* = 16.2, 7.6 Hz, 1H), 1.27 - 1.23 (m, 12H), 0.46 (s, 3H), 0.46 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 211.52, 173.30, 151.19, 140.16, 135.73, 135.07, 130.97, 129.69, 129.40, 127.14, 101.14, 82.95, 62.60, 36.23, 36.17, 33.10, 16.02, 0.07, 0.00.

HRMS (ESI): m/z calculated for $C_{25}H_{32}O_2SiNa$ $[M+Na]^+$: 415.2069, found: 415.2074.



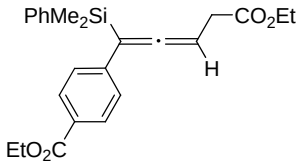
3g: In an oven dried 15 mL Schlenk tube equipped with a stirring bar, 0.02 mmol (2.9 mg, 10 mol%) CuBr and 0.02 mmol (2.1 mg, 10 mol%) Et_3N were added into 1 mL of dry MeOH under argon atmosphere. The solution was stirred for 5 min at room temperature. Then 0.2 mmol **1g** (49.1 mg, 1.0 equiv) and 0.4 mmol (2.0 equiv, 105 mg) Me_2PhSi-Bpin were added to the tube under argon atmosphere. The final solution was continued to stir for 24 hours at room temperature. Then the solution was diluted with DCM and filtered through Celite. The final filtrate was concentrated under vacuum to afford the crude product which was isolated through flash column chromatography (Eluent: PE/Et_2O = 97:3) to furnish the related product **3g** (43.1 mg) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00 (s, 1H), 7.89 (d, *J* = 8.1 Hz, 1H), 7.52 - 7.46 (m, 2H), 7.40 (d, *J* = 7.8 Hz, 1H), 7.32 - 7.22 (m, 4H), 5.40 (t, *J* = 7.4 Hz, 1H), 4.10 (q, *J* = 7.1 Hz, 2H), 3.08 (dd, *J* = 16.2, 7.2 Hz, 1H), 3.03 (dd, *J* = 16.2, 7.6 Hz, 1H), 1.18 (t, *J* = 7.1 Hz, 3H), 0.42 (s, 3H), 0.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 212.43, 173.10, 150.48, 140.96, 139.05, 135.93, 135.86, 131.73, 131.21, 130.23, 124.73, 123.31, 101.11, 84.39, 63.10, 36.00, 16.29, 0.02, 0.01.
HRMS (ESI): m/z calculated for $C_{21}H_{23}NO_4SiNa$ $[M+Na]^+$: 404.1294, found: 404.1298.



3h: In an oven dried 15 mL Schlenk tube equipped with a stirring bar, 0.02 mmol (2.9 mg, 10 mol%) CuBr and 0.02 mmol (2.1 mg, 10 mol%) Et_3N were added into 1 mL of dry MeOH under argon atmosphere. The solution was stirred for 5 min at room temperature. Then 0.2 mmol **1h** (48.5 mg, 1.0 equiv) and 0.4 mmol (2.0 equiv, 105

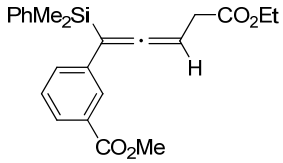
mg) Me_2PhSi-Bpin were added to the tube under argon atmosphere. The final solution was continued to stir for 24 hours at room temperature. Then the solution was diluted with DCM and filtered through Celite. The final filtrate was concentrated under vacuum to afford the crude product which was isolated through flash column chromatography (Eluent: PE/Et_2O = 97:3) to furnish the related product **3h** (48.1 mg) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80-7.78 (m, 2H), 7.68 - 7.55 (m, 2H), 7.40 - 7.34(m, 3H), 7.30 - 7.28 (m, 2H), 5.43 (t, *J* = 7.4 Hz, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 3.14 (dd, *J* = 16.2, 7.2 Hz, 1H), 3.09 (dd, *J* = 16.2, 7.6 Hz, 1H), 2.53 (s, 3H), 1.25 (d, *J* = 7.1 Hz, 3H), 0.47 (s, 3H), 0.47 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 212.58, 199.57, 173.17, 144.06, 139.55, 137.11, 135.84, 135.50, 131.43, 130.50, 130.01, 101.73, 83.84, 62.97, 36.14, 28.13, 16.46, 0.08, 0.00.

HRMS (ESI): m/z calculated for $C_{23}H_{26}O_3SiNa$ $[M+Na]^+$: 401.1549, found: 401.1551.

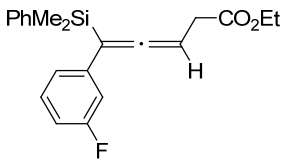


3i: In an oven dried 15 mL Schlenk tube equipped with a stirring bar, 0.02 mmol (2.9 mg, 10 mol%) CuBr and 0.02 mmol (2.1 mg, 10 mol%) Et_3N were added into 1 mL of dry MeOH under argon atmosphere. The solution was stirred for 5 min at room tem. Then 0.2 mmol **1i** (54.5 mg, 1.0 equiv), 0.4 mmol (105 mg, 2.0 equiv) Me_2PhSi-Bpin were added to the tube under argon atmosphere. The final solution was continued to stir for 24 hours at room temperature. Then the solution was diluted with DCM and filtered through Celite. The final filtrate was concentrated under vacuum to afford the crude product which was isolated through flash column chromatography (Eluent: PE/Et_2O = 97:3) to furnish the related product **3i** (64.1 mg) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 - 7.84 (m, 2H), 7.59 - 7.53 (m, 2H), 7.40 - 7.34 (m, 3H), 7.29 - 7.23 (m, 2H), 5.42 (t, *J* = 7.4 Hz, 1H), 4.33 (q, *J* = 7.1 Hz, 2H), 4.16 (q, *J* = 7.1 Hz, 2H), 3.14 (dd, *J* = 16.2, 7.2 Hz, 1H), 3.08 (dd, *J* = 16.2, 7.6 Hz, 1H), 1.35 (t, *J* = 7.1 Hz, 3H), 1.26 (t, *J* = 7.1 Hz, 3H), 0.47 (s, 3H), 0.47 (s, 3H). ^{13}C NMR

(100 MHz, $CDCl_3$): δ 212.35, 173.12, 168.38, 143.61, 139.52, 135.77, 131.55, 131.32, 130.29, 129.92, 129.73, 101.64, 83.51, 62.82, 62.71, 35.92, 16.24, 16.13, 0.00, -0.08.
HRMS (ESI): m/z calculated for $C_{24}H_{28}O_4SiNa$ $[M+Na]^+$: 431.1655, found: 431.1655.

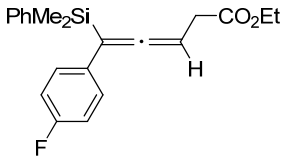


3j: In an oven dried 15 mL Schlenk tube equipped with a stirring bar, 0.02 mmol (2.9 mg, 10 mol%) CuBr and 0.02 mmol (2.1 mg, 10 mol%) Et_3N were added into 1 mL of dry MeOH under argon atmosphere. The solution was stirred for 5 min at room temperature. Then 0.2 mmol **1j** (51.7 mg, 1.0 equiv), 0.4 mmol (105 mg, 2.0 equiv) Me_2PhSi-Bpin were added to the tube under argon atmosphere. The final solution was continued to stir for 24 hours at room temperature. Then the solution was diluted with DCM and filtered through Celite. The final filtrate was concentrated under vacuum to afford the crude product which was isolated through flash column chromatography (Eluent: PE/Et_2O = 97:3) to furnish the related product **3j** (72.8 mg) as colorless oil. ^1H NMR (400 MHz, $CDCl_3$) : δ 7.82 - 7.81 (m, 1H), 7.73 - 7.71 (m, 1H), 7.53 - 7.47 (m, 2H), 7.28 (dd, *J* = 5.1, 1.9 Hz, 5H), 7.21 - 7.14 (m, 1H), 5.33 (t, *J* = 7.4 Hz, 1H), 4.08 (q, *J* = 7.1 Hz, 2H), 3.78 (s, 3H), 3.06 (dd, *J* = 16.2, 7.2 Hz, 1H), 3.00 (dd, *J* = 16.2, 7.2 Hz, 1H), 1.17 (t, *J* = 7.1 Hz, 3H), 0.40 (s, 3H), 0.40 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 211.79, 173.24, 168.96, 139.60, 139.12, 135.88, 134.29, 132.28, 131.32, 131.02, 130.36, 129.93, 129.52, 101.49, 83.51, 62.85, 54.02, 36.11, 16.18, -0.00, -0.12.
HRMS (ESI): m/z calculated for $C_{23}H_{26}O_4SiNa$ $[M+Na]^+$: 417.1498, found: 417.1504.



3k: In an oven dried 15 mL Schlenk tube equipped with a stirring bar, 0.02 mmol (2.9 mg, 10 mol%) CuBr and 0.02 mmol (2.1 mg, 10 mol%) Et_3N were added into 1 mL of dry MeOH under argon atmosphere. The solution was stirred for 5 min at room temperature. Then 0.2 mmol **1k** (42.7 mg, 1.0 equiv), 0.4 mmol (105 mg, 2.0 equiv) Me_2PhSi-Bpin were added to the tube under argon atmosphere. The final solution was continued to stir for 48 h at room temperature. Then the solution was diluted with DCM and filtered through Celite. The final filtrate was concentrated under vacuum to afford the crude product which was isolated through flash column chromatography (Eluent: PE/Et_2O = 97:3) to furnish the related product **3k** (60.8 mg) as colorless oil. ^1H NMR (400 MHz, $CDCl_3$): δ 7.59 - 7.56 (m, 2H), 7.38 - 7.35 (m, 3H), 7.18 - 7.12 (m, 1H), 6.97 - 6.93 (m, 2H), 6.86 - 6.81 (m, 1H), 5.41 (t, *J* = 7.4 Hz, 1H), 4.17 (q, *J* = 7.2 Hz, 2H), 3.14 (dd, *J* = 16.2, 7.2 Hz, 1H), 3.08 (dd, *J* = 16.2, 7.6 Hz, 1H) 1.27 (t, *J* = 7.1 Hz, 3H), 0.47 (s, 3H), 0.47 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 211.92, 173.21, 164.80 (d, *J* = 245.4 Hz), 141.02 (d, *J* = 7.5 Hz), 139.62, 135.83, 131.61 (d, *J* = 8.3 Hz), 131.35, 129.96, 125.60 (d, *J* = 2.8 Hz), 116.65 (d, *J* = 21.9 Hz), 115.29 (d, *J* = 21.3 Hz), 101.32, 83.56, 62.89, 36.07, 16.16, 0.06, 0.00.

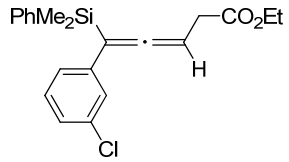
HRMS (ESI): m/z calculated for $C_{21}H_{23}FO_2SiNa$ $[M+Na]^+$: 377.1349, found: 377.1341



3l: In an oven dried 15 mL Schlenk tube equipped with a stirring bar, 0.02 mmol (2.9 mg, 10 mol%) CuBr and 0.02 mmol (2.1 mg, 10 mol%) Et_3N were added into 1 mL of dry MeOH under argon atmosphere. The solution was stirred for 5 min at room temperature. Then 0.2 mmol **1l** (42.7 mg, 1.0 equiv), 0.4 mmol (105 mg, 2.0 equiv) Me_2PhSi-Bpin were added to the tube under argon atmosphere. The final solution was continued to stir for 48 h at room temperature. Then the solution was diluted with DCM and filtered through Celite. The final filtrate was concentrated under vacuum to afford the crude product which was isolated through flash column chromatography (Eluent: PE/Et_2O = 97:3) to furnish the related product **3l** (60.1 mg) as colorless oil.

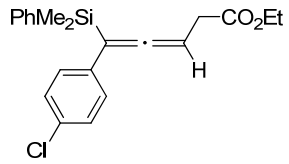
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 - 7.55 (m, 2H), 7.37 - 7.34 (m, 3H), 7.17 - 7.14 (m, 2H), 6.92 - 6.86 (m, 2H), 5.37 (t, *J* = 7.4 Hz, 1H), 4.16 (q, *J* = 7.1 Hz, 2H), 3.12 (dd, *J* = 16.2, 7.2 Hz, 1H), 3.07 (dd, *J* = 16.2, 7.2 Hz, 1H), 1.25 (t, *J* = 7.1 Hz, 3H), 0.45 (s, 3H), 0.45 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 211.57, 173.36, 163.58 (d, *J* = 245.6 Hz), 139.82, 135.85, 134.36 (d, *J* = 3.3 Hz), 131.41, 131.33, 129.96, 117.23 (d, *J* = 21.4 Hz), 100.94, 83.32, 62.84, 36.21, 16.18, 0.06, 0.00.

HRMS (ESI): m/z calculated for $C_{21}H_{23}FO_2SiNa$ $[M+Na]^+$: 377.1349, found: 377.1355.



3m: In an oven dried 15 mL Schlenk tube equipped with a stirring bar, 0.02 mmol (2.9 mg, 10 mol%) CuBr and 0.02 mmol (2.1 mg, 10 mol%) Et_3N were added into 1 mL of dry MeOH under argon atmosphere. The solution was stirred for 5 min at room temperature. Then 0.2 mmol **1m** (47.0 mg, 1.0 equiv), 0.4 mmol (105 mg, 2.0 equiv) Me_2PhSi-Bpin were added to the tube under argon atmosphere. The final solution was continued to stir for 48 hours at room temperature. Then the solution was diluted with DCM and filtered through Celite. The final filtrate was concentrated under vacuum to afford the crude product which was isolated through flash column chromatography (Eluent: PE/Et_2O = 97:3) to furnish the related product **3m** (60.4 mg) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59 - 7.57(m, 2H), 7.39 - 7.37 (m, 3H), 7.26 - 7.25 (m, 1H), 7.12 - 7.11(m, 2H), 7.06 - 7.02 (m, 1H), 5.41 (t, *J* = 7.4 Hz, 1H), 4.22 - 4.15 (m, 2H), 3.14 (dd, *J* = 16.2, 7.2 Hz, 1H), 3.09 (dd, *J* = 16.2, 7.6 Hz, 1H), 1.27 (t, *J* = 7.1 Hz, 3H), 0.48 (s, 3H), 0.48 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 211.83 , 173.15, 140.57, 139.51, 136.16, 135.78, 131.41, 131.33, 129.92, 129.87, 128.43, 127.94, 101.13, 83.56, 62.86, 36.03, 16.14, 0.00, -0.07.

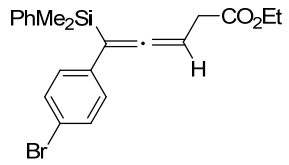
HRMS (ESI): m/z calculated for $C_{21}H_{23}ClO_2SiNa$ $[M+Na]^+$: 393.1053, found: 393.1054.



3n: In an oven dried 15 mL Schlenk tube equipped with a stirring bar, 0.02 mmol (2.9 mg, 10 mol%) CuBr and 0.02 mmol (2.1 mg, 10 mol%) Et_3N were added into 1 mL of dry MeOH under argon atmosphere. The solution was stirred for 5 min at room temperature. Then 0.2 mmol **1n** (47.0 mg, 1.0 equiv) and 0.4 mmol (2.0 equiv, 105 mg) Me_2PhSi-Bpin were added to the tube under argon atmosphere. The final solution was continued to stir for 24 hours at room temperature. Then the solution was diluted with DCM and filtered through Celite. The final filtrate was concentrated under vacuum to afford the crude product which was isolated through flash column chromatography (Eluent: PE/Et_2O = 97:3) to furnish the related product **3n** (68.6 mg) as colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49 - 7.47 (m 2H), 7.30 - 7.27 (m, 3H), 7.09 - 7.04 (m, 4H), 5.31 (t, *J* = 7.4 Hz, 1H), 4.08 (q, *J* = 7.1 Hz, 2H), 3.05 (dd, *J* = 16.2, 7.2 Hz, 1H), 3.00 (dd, *J* = 16.2, 7.6Hz, 1H), 1.18 (t, *J* = 7.1 Hz, 3H), 0.38 (s, 3H), 0.38 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 211.70, 173.21, 139.63, 136.99, 135.78, 134.12, 131.30, 131.10, 130.43, 129.92, 100.96, 83.44, 62.87, 36.04, 16.06, 0.00, -0.08.

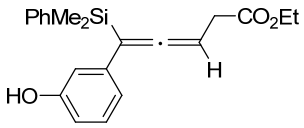
HRMS (ESI): m/z calculated for $C_{21}H_{23}ClO_2SiNa$ $[M+Na]^+$: 393.1053, found: 393.1048.



3o: In an oven dried 15 mL Schlenk tube equipped with a stirring bar, 0.02 mmol (2.9 mg, 10 mol%) CuBr and 0.02 mmol (2.1 mg, 10 mol%) Et_3N were added into 1 mL of dry MeOH under argon atmosphere. The solution was stirred for 5 min at room temperature. Then 0.2 mmol **1o** (55.9 mg, 1.0 equiv) and 0.4 mmol (105 mg, 2.0 equiv) Me_2PhSi-Bpin were added to the tube under argon atmosphere. The final solution was continued to stir for 48 hours at room temperature. Then the solution was diluted with DCM and filtered through Celite. The final filtrate was concentrated

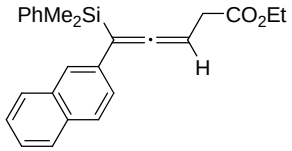
under vacuum to afford the crude product which was isolated through flash column chromatography (Eluent: PE/Et_2O = 97:3) to furnish the related product **3o** (70.1 mg) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57 - 7.53 (m, 2H), 7.39 - 7.34 (m, 3H), 7.33 - 7.31 (m, 1H), 7.30 - 7.29 (m, 1H), 7.09 - 7.04 (m, 2H), 5.37 (t, *J* = 7.4 Hz, 1H), 4.16 (q, *J* = 7.1 Hz, 2H), 3.12 (dd, *J* = 16.2, 7.2 Hz, 1H), 3.07 (dd, *J* = 16.2, 7.6 Hz, 1H), 1.25 (t, *J* = 7.1 Hz, 3H), 0.45 (s, 3H), 0.45 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 211.75, 173.27, 139.68, 137.58, 135.85, 133.45, 131.54, 131.39, 130.00, 122.32, 101.11, 83.56, 62.89, 36.09, 16.22, 0.08, 0.00.

HRMS (ESI): m/z calculated for $C_{21}H_{23}$ BrO_2SiNa $[M+Na]^+$: 437.0548, found: 437.0550.

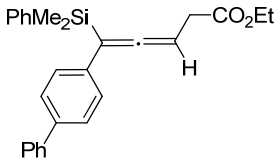


3p: In an oven dried 15 mL Schlenk tube equipped with a stirring bar, 0.02 mmol (2.9 mg, 10 mol%) CuBr and 0.02 mmol (2.1 mg, 10 mol%) Et_3N were added into 1 mL of dry MeOH under argon atmosphere. The solution was stirred for 5 min at room temperature. Then 0.2 mmol **1p** (43.3 mg, 1.0 equiv) and 0.4 mmol (105 mg, 2.0 equiv) Me_2PhSi-Bpin were added to the tube under argon atmosphere. The final solution was continued to stir for 48 hours at room temperature. Then the solution was diluted with DCM and filtered through Celite. The final filtrate was concentrated under vacuum to afford the crude product which was isolated through flash column chromatography (Eluent: PE/Et_2O = 97:3) to furnish the related product **3p** (59.9 mg) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 - 7.57 (m, 2H), 7.39 - 7.33 (m, 3H), 7.08 - 7.04 m, 1H), 6.80 - 6.73 (m, 2H), 6.67 - 6.64 (m, 1H), 5.77 (s, 1H), 5.35 (t, *J* = 7.4 Hz, 1H), 4.16 (q, *J* = 7.1 Hz, 2H), 3.12 (dd, *J* = 16.2, 7.2 Hz, 1H), 3.07 (dd, *J* = 16.2, 7.6 Hz, 1H), 1.26 (t, *J* = 7.1 Hz, 4H), 0.47 (s, 3H), 0.47 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 211.64, 173.80, 157.62, 139.88, 135.73, 131.31, 131.07, 129.74, 129.59, 122.23, 116.55, 115.55, 101.53, 82.93, 62.91, 36.07, 15.98, 0.00.

HRMS (ESI): m/z calculated for $C_{21}H_{24}O_3SiNa$ $[M+Na]^+$: 375.1392, found: 375.1401.



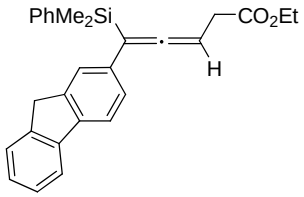
3q: In an oven dried 15 mL Schlenk tube equipped with a stirring bar, 0.02 mmol (2.9 mg, 10 mol%) CuBr and 0.02 mmol (2.1 mg, 10 mol%) Et_3N were added into 1 mL of dry MeOH under argon atmosphere. The solution was stirred for 5 min at room temperature. Then 0.2 mmol **1q** (50.1 mg, 1.0 equiv), 0.4 mmol (105 mg, 2.0 equiv) Me_2PhSi-Bpin were added to the tube under argon atmosphere. The final solution was continued to stir for 24 hours at room temperature. Then the solution was diluted with DCM and filtered through Celite. The final filtrate was concentrated under vacuum to afford the crude product which was isolated through flash column chromatography (Eluent: PE/Et_2O = 97:3) to furnish the related product **3q** (72.9 mg) as colorless oil.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 - 7.64 (m, 1H), 7.61 (d, *J* = 8.2 Hz, 1H), 7.57 - 7.52 (m, 3H), 7.48 (d, *J* = 1.2 Hz, 1H), 7.37 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.32 - 7.26 (m, 5H), 5.36 (t, *J* = 7.4 Hz, 1H), 4.09 (q, *J* = 7.1 Hz, 2H), 3.09 (dd, *J* = 16.2, 7.2 Hz, 1H), 3.03 (dd, *J* = 16.2, 7.6 Hz, 1H), 1.19 (d, *J* = 7.1 Hz, 3H), 0.44 (s, 3H), 0.44 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 212.00, 173.23, 139.93, 135.76, 135.72, 135.26, 133.98, 131.10, 129.76, 129.72, 129.63, 129.31, 128.36, 128.29, 127.74, 127.36, 101.84 , 83.29, 62.65, 36.10, 16.03 , 0.09, 0.00.
HRMS (ESI): m/z calculated for $C_{25}H_{26}O_2SiNa$ $[M+Na]^+$: 409.1600, found: 409.1602.



3r: In an oven dried 15 mL Schlenk tube equipped with a stirring bar, 0.02 mmol (2.9 mg, 10 mol%) CuBr and 0.02 mmol (2.1 mg, 10 mol%) Et_3N, were added into 1 mL of dry MeOH under argon atmosphere. The solution was stirred for 5 min at room temperature. Then 0.2 mmol **1r** (55.3 mg, 1.0 equiv) and 0.4 mmol (2.0 equiv, 105 mg) Me_2PhSi-Bpin were added to the tube under argon atmosphere. The final solution was continued to stir for 48 hours at room temperature. Then the solution

was diluted with DCM and filtered through Celite. The final filtrate was concentrated under vacuum to afford the crude product which was isolated through flash column chromatography (Eluent: PE/Et_2O = 97:3) to furnish the related product **3r** (69.5 mg) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 - 7.59 (m, 2H), 7.55 - 7.51 (m, 2H), 7.45 - 7.43 (m, 2H), 7.41 - 7.34 (m, 5H), 7.31 - 7.28 (m, 3H), 5.40 (t, *J* = 7.4 Hz, 1H), 4.16 (q, *J* = 7.1 Hz, 2H), 3.14 (dd, *J* = 16.2, 7.2 Hz, 1H), 3.09 (dd, *J* = 16.2, 7.6 Hz, 1H), 1.26 (t, *J* = 7.1 Hz, 3H), 0.49 (s, 3H), 0.49 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 211.73, 173.23, 142.58, 141.06, 139.92, 137.32, 135.75, 131.10, 130.54, 130.18, 129.77, 128.96, 128.91, 128.70, 101.29, 83.19, 62.67, 36.09, 16.05, 0.08, 0.00.

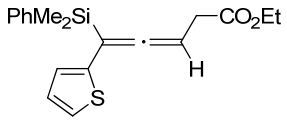
HRMS (ESI): m/z calculated for $C_{27}H_{28}O_2SiNa$ $[M+Na]^+$: 435.1756, found: 435.1765.



3s: In an oven dried 15 mL Schlenk tube equipped with a stirring bar, 0.02 mmol (2.9 mg, 10 mol%) CuBr and 0.02 mmol (2.1 mg, 10 mol%) Et_3N were added into 1 mL of dry MeOH under argon atmosphere. The solution was stirred for 5 min at room temperature. Then 0.2 mmol **1s** (58.0 mg, 1.0 equiv), 0.4 mmol (105 mg, 2.0 equiv) Me_2PhSi-Bpin were added to the tube under argon atmosphere. The final solution was continued to stir for 48 hours at room temperature. Then the solution was diluted with DCM and filtered through Celite. The final filtrate was concentrated under vacuum to afford the crude product which was isolated through flash column chromatography (Eluent: PE/Et_2O = 97:3) to furnish the related product **3s** (64.7 mg) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 7.5 Hz, 1H), 7.61 - 7.58 (m, 3H), 7.47 (d, *J* = 7.1 Hz, 1H), 7.42 (s, 1H), 7.36 - 7.31(m, 4H), 7.26 - 7.19 (m, 2H), 5.40 (t, *J* = 7.4 Hz, 1H), 4.16 (q, *J* = 7.1 Hz, 2H), 3.79 (s, 2H), 3.20 - 3.06 (m, 2H), 1.25 (t, *J* = 7.1 Hz, 3H), 0.49 (s, 6H), 0.49 (s, 3H). ^{13}C NMR (100 MHz,$CDCl_3$): δ 211.38, 173.14, 145.17, 144.96, 143.13, 141.86, 139.88, 136.67, 135.61, 130.90, 129.59, 128.38,

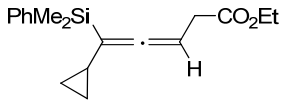
128.37, 128.17, 126.61, 126.24, 121.39, 121.35, 101.81, 82.90, 62.49, 38.53, 36.02, 15.91, 0.00, -0.08.

HRMS (ESI): m/z calculated for $C_{28}H_{28}O_2SiNa$ $[M+Na]^+$: 447.1756, found:447.1773.



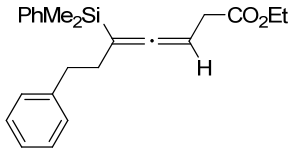
3t: In an oven dried 15 mL Schlenk tube equipped with a stirring bar, 0.02 mmol (2.9 mg, 10 mol%) CuBr and 0.02 mmol (2.1 mg, 10 mol%) Et_3N were added into 1 mL of dry MeOH under argon atmosphere. The solution was stirred for 5 min at room temperature. Then 0.2 mmol **1t** (41.3 mg, 1.0 equiv), 0.4 mmol (105 mg, 2.0 equiv) Me_2PhSi-Bpin was added to the tube under argon atmosphere. The final solution was continued to stir for 72 hours at room temperature. Then the solution was diluted with DCM and filtered through Celite. The final filtrate was concentrated under vacuum to afford the crude product which was isolated through flash column chromatography (Eluent: PE/Et_2O = 97:3) to furnish the related product **3t** (42 mg) as colorless oil. ^1H NMR (400 MHz, $CDCl_3$): δ 7.63 - 7.60 (m, 2H), 7.41 - 7.34 (m, 3H), 7.11 - 7.10 (m, 1H), 6.83 (dd, *J* = 5.2, 3.6 Hz, 1H), 6.69 - 6.68 (m, 1H), 5.43 (t, *J* = 7.4 Hz, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.14 (dd, *J* = 16.2, 7.2 Hz, 1H), 3.08 (dd, *J* = 16.2, 7.6 Hz, 1H) 1.27 (t, *J* = 7.1 Hz, 3H), 0.52 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 211.13, 173.28, 142.19, 139.47, 136.07, 131.50, 130.01, 129.35, 127.24, 126.52, 96.80, 84.22, 62.95, 36.33, 16.32, 0.09, 0.00.

HRMS (ESI): m/z calculated for $C_{19}H_{22}O_2SiNa$ $[M+Na]^+$: 387.1756, found:387.1747.



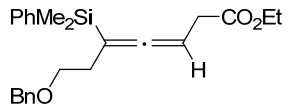
3u: In an oven dried 15 mL Schlenk tube equipped with a stirring bar, 0.02 mmol (2.9 mg, 10 mol%) CuBr and 0.02 mmol (2.1 mg, 10 mol%) Et_3N were added into 1 mL of dry MeOH under argon atmosphere. The solution was stirred for 5 min at room temperature. Then 0.2 mmol **1u** (32.8 mg, 1.0 equiv), 0.4 mmol (105 mg, 2.0 equiv) Me_2PhSi-Bpin were added to the tube under argon atmosphere. The final solution was

continued to stir for 24 hours at room temperature. Then the solution was diluted with DCM and filtered through Celite. The final filtrate was concentrated under vacuum to afford the crude product which was isolated through flash column chromatography (Eluent: PE/Et_2O = 97:3) to furnish the related product **3u** (52.8 mg) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) : δ 7.59 - 7.56 (m, 2H), 7.37 - 7.34 (m, 3H), 5.06 (td, *J* = 7.3, 1.8 Hz, 1H), 4.14 (q, *J* = 7.1 Hz, 2H), 2.95 (dd, *J* = 16.2, 7.2 Hz, 1H), 2.90 (dd, *J* = 16.2, 7.6 Hz, 1H), 1.26 (t, *J* = 7.1 Hz, 4H), 1.07 - 1.00 (m, 1H), 0.64 - 0.60 (m, 2H), 0.46 - 0.34 (m, 8H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 204.78, 171.75, 138.00, 133.89, 129.08, 127.71, 101.14, 81.45, 60.63, 34.79, 14.21, 9.56, 8.22, 7.82, -2.83, -2.89.
HRMS (ESI): m/z calculated for $C_{18}H_{24}O_2SiNa$ $[M+Na]^+$: 323.1443, found:323.1442.



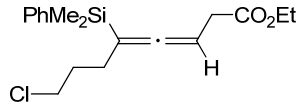
3v: In an oven dried 15 mL Schlenk tube equipped with a stirring bar, 0.02 mmol (2.9 mg, 10 mol%) CuBr and 0.02 mmol (2.1 mg, 10 mol%) Et_3N were added into 1 mL of dry MeOH under argon atmosphere. The solution was stirred for 5 min at room temperature. Then 0.2 mmol **1v** (45.6 mg, 1.0 equiv), 0.4 mmol (105 mg, 2.0 equiv) Me_2PhSi-Bpin were added to the tube under argon atmosphere. The final solution was continued to stir for 24 h at room temperature. Then the solution was diluted with DCM and filtered through Celite. The final filtrate was concentrated under vacuum to afford the crude product which was isolated through flash column chromatography (Eluent: PE/Et_2O = 97:3) to furnish the related product **3v** (64.4 mg) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53 - 7.48 (m, 2H), 7.36 - 7.33 (m, 3H), 7.24 - 7.20 (m, 2H), 7.17 - 7.13 (m, 1H), 7.10 - 7.05 (m, 2H), 5.06 - 5.01 (m, 1H), 4.14 (q, *J* = 7.1 Hz, 2H), 2.93 (dd, *J* = 16.2, 7.2 Hz, 1H), 2.91 (dd, *J* = 16.2, 7.6 Hz, 1H), 2.70 - 2.67 (m, 2H), 2.24 - 2.19 (m, 2H), 1.25 (t, *J* = 7.1 Hz, 4H), 0.36 (s, 3H), 0.36 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 206.86, 171.86, 142.12, 137.75, 133.84, 129.18, 128.47, 128.20, 127.82, 125.73, 96.31 , 80.26, 60.64, 35.14, 34.61, 30.89, 14.26, -3.08, -3.16.

HRMS (ESI): m/z calculated for $C_{24}H_{28}O_2SiNa$ $[M+Na]^+$: 387.1756, found: 387.1747.



3w: In an oven dried 15 mL Schlenk tube equipped with a stirring bar, 0.02 mmol (2.9 mg, 10 mol%) CuBr and 0.02 mmol (2.1 mg, 10 mol%) Et_3N were dissolved in 1 mL of dry MeOH under argon atmosphere. The solution was stirred for 5 min at room temperature. Then 0.2 mmol **1w** (51.7 mg, 1.0 equiv) and 0.4 mmol (105 mg, 2.0 equiv) Me_2PhSi-Bpin were added to the tube under argon atmosphere. The final solution was continued to stir for 24 hours at room temperature. Then the solution was diluted with DCM and filtered through Celite. The final filtrate was concentrated under vacuum to afford the crude product which was isolated through flash column chromatography (Eluent: PE/Et_2O = 97:3) to furnish the related product **3w** (72.8 mg) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 - 7.47 (m, 2H), 7.35 - 7.23 (m, 8H), 5.08 - 4.97 (m, 1H), 4.42 (s, 2H), 4.12 (q, *J* = 7.1 Hz, 2H), 3.51 (t, *J* = 7.2 Hz, 2H), 2.95 (d, *J* = 7.4 Hz, 2H), 2.25 (td, *J* = 7.3, 2.9 Hz, 2H), 1.24 (t, *J* = 7.1 Hz, 3H), 0.36 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 206.89, 171.77, 138.50, 137.62, 133.83, 129.19, 128.32, 127.81, 127.64, 127.48, 93.23, 79.71, 72.86, 69.75, 60.65, 34.56, 29.31, 14.24, -3.13, -3.02.

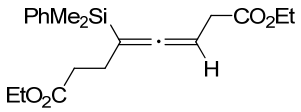
HRMS (ESI): m/z calculated for C_{24} $H_{30}O_3SiNa$ $[M+Na]^+$: 417.1862, found: 417.1858.



3x: In an oven dried 15 mL Schlenk tube equipped with a stirring bar, 0.02 mmol (2.9 mg, 10 mol%) CuBr and 0.02 mmol (2.1 mg, 10 mol%) Et_3N and were added into 1 mL of dry MeOH under argon atmosphere. The solution was stirred for 5 min at room temperature. Then 0.2 mmol **1x** (40.2 mg, 1.0 equiv), 0.4 mmol (105 mg, 2.0 equiv) Me_2PhSi-Bpin were added to the tube under argon atmosphere. The final solution was

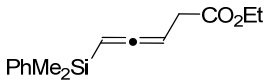
continued to stir for 24 h at room temperature. Then the solution was diluted with DCM and filtered through Celite. The final filtrate was concentrated under vacuum to afford the crude product which was isolated through flash column chromatography (Eluent: PE/Et_2O = 97:3) to furnish the related product **3x** (55.7 mg) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 - 7.50 (m, 2H), 7.36 - 7.35(m, 3H), 5.08 - 5.02 (m, 1H), 4.14 (q, *J* = 7.1 Hz, 2H), 3.49 (t, *J* = 6.5 Hz, 2H), 2.97 (dd, *J* = 7.4, 2.1 Hz, 2H), 2.08 - 2.04 (m, 2H), 1.91 - 1.84 (m, 2H), 1.26 (t, *J* = 7.1 Hz, 3H), 0.38 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 206.49, 171.69, 137.51, 133.75, 129.23, 127.83, 95.66, 80.36, 60.70, 44.51, 34.59, 31.58, 26.20, 14.22, -3.15, -3.21.

HRMS (ESI): m/z calculated for $C_{18}H_{25}ClO_2SiNa$ $[M+Na]^+$: 359.1210, found: 359.1203.

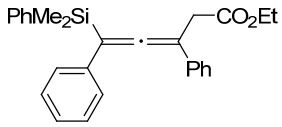


3y: In an oven dried 15 mL Schlenk tube equipped with a stirring bar, 0.02 mmol (2.9 mg, 10 mol%) CuBr and 0.02 mmol (2.1 mg, 10 mol%) Et_3N were added into 1 mL of dry MeOH under argon atmosphere. The solution was stirred for 5 min at room temperature. Then 0.2 mmol **1y** (44.9 mg, 1.0 equiv), 0.4 mmol (105 mg, 2.0 equiv) Me_2PhSi-Bpin were added to the tube under argon atmosphere. The final solution was continued to stir for 24 hours at room temperature. Then the solution was diluted with DCM and filtered through Celite. The final filtrate was concentrated under vacuum to afford the crude product which was isolated through flash column chromatography (Eluent: PE/Et_2O = 97:3) to furnish the related product **3y** (66.2 mg) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 - 7.49 (m, 2H), 7.40 - 7.29 (m, 3H), 5.12 - 5.01 (m, 1H), 4.21 - 4.04 (m, 4H), 2.95 (dd, *J* = 7.3, 2.7 Hz, 2H), 2.44 - 2.40 (m, 2H), 2.26 - 2.17 (m, 2H), 1.28 - 1.20 (m, 6H), 0.38 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 206.19, 173.21, 171.65, 137.44, 133.80, 129.23, 127.83, 96.03, 81.13, 60.67, 60.23, 34.58, 33.28, 24.02, 14.20, 14.13, -3.19, -3.25.

HRMS (ESI): m/z calculated for $C_{20}H_{28}O_4SiNa$ $[M+Na]^+$: 383.1655, found: 383.1651.



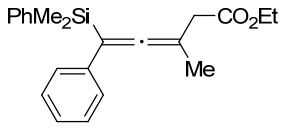
3z: In an oven dried 15 mL Schlenk tube equipped with a stirring bar, 0.02 mmol (2.9 mg, 10 mol%) CuBr and 0.02 mmol (2.1 mg, 10 mol%) Et_3N were added into 1 mL of dry MeOH under argon atmosphere. The solution was stirred for 5 min at room temperature. Then 0.2 mmol **1z** (24.9 mg, 1.0 equiv), 0.4 mmol (105 mg, 2.0 equiv) Me_2PhSi-Bpin were added to the tube under argon atmosphere. The final solution was continued to stir for 24 hours at room temperature. Then the solution was diluted with DCM and filtered through Celite. The final filtrate was concentrated under vacuum to afford the crude product which was isolated through flash column chromatography (Eluent: PE/Et_2O = 97:3) to furnish the related product **3z** (43.0 mg) as colorless oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.58 - 7.49 (m, 2H), 7.37 - 7.34 (m,3H), 5.17 - 5.14 (m, 1H), 4.99 (q, *J* = 7.3 Hz, 1H), 4.14 (q, *J* = 7.1 Hz, 2H), 3.00 - 2.97 (m, 2H), 1.25 (t, *J* = 7.1 Hz, 3H), 0.37 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 213.47, 174.09, 140.60, 136.04, 131.60, 130.22, 84.69, 79.91, 63.13, 36.33, 16.64, 0.02, 0.00.
HRMS (ESI): m/z calculated for $C_{15}H_{20}O_2SiNa$ $[M+Na]^+$: 283.1130, found: 283.1129.



3aa: In an oven dried 15 mL Schlenk tube equipped with a stirring bar, 0.02 mmol (2.9 mg, 10 mol%) CuBr and 0.02 mmol (2.1 mg, 10 mol%) Et_3N were added into 1 mL of dry MeOH under argon atmosphere. The solution was stirred for 5 min at room temperature. Then 0.2 mmol **1aa** (55.3 mg, 1.0 equiv), 0.4 mmol (105 mg, 2.0 equiv) Me_2PhSi-Bpin were added to the tube under argon atmosphere. The final solution was continued to stir for 24 hours at room temperature. Then the solution was diluted with DCM and filtered through Celite. The final filtrate was concentrated under vacuum to afford the crude product which was isolated through flash column chromatography (Eluent: PE/Et_2O = 97:3) to furnish the related product **3aa** (71.7 mg) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 - 7.60 (m, 2H), 7.43 - 7.28 (m, 9H), 7.24 - 7.12

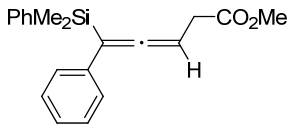
(m, 4H), 4.11 (qd, *J* = 7.1, 1.7 Hz, 2H), 3.61 - 3.45 (m, 2H), 1.16 (t, *J* = 7.1 Hz, 3H), 0.52 (s, 3H), 0.51 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 212.71, 172.87, 139.63, 137.53, 137.14, 135.62, 130.97, 130.28, 130.14, 129.86, 129.63, 128.41, 128.26, 126.92, 104.82, 99.12, 62.62, 38.51, 15.76, 0.00, -0.07.

HRMS (ESI): m/z calculated for $C_{27}H_{28}O_2SiNa$ $[M+Na]^+$: 435.1756, found: 435.1762.



3ab: In an oven dried 15 mL Schlenk tube equipped with a stirring bar, 0.02 mmol (2.9 mg, 10 mol%) CuBr and 0.02 mmol (2.1 mg, 10 mol%) Et_3N were added into 1 mL of dry MeOH under argon atmosphere. The solution was stirred for 5 min at room temperature. Then 0.2 mmol **1ab** (42.9 mg, 1.0 equiv), 0.4 mmol (105 mg, 2.0 equiv) Me_2PhSi-Bpin were added to the tube under argon atmosphere. The final solution was continued to stir for 24 hours at room temperature. Then the solution was diluted with DCM and filtered through Celite. The final filtrate was concentrated under vacuum to afford the crude product which was isolated through flash column chromatography (Eluent: PE/Et_2O = 97:3) to furnish the related product **3ab** (49.5 mg) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60 - 7.57 (m, 2H), 7.36 - 7.34 (m, 3H), 7.24 - 7.17 (m, 4H), 7.13 - 7.09 (m, 1H), 4.13 (qd, *J* = 7.1, 0.9 Hz, 2H), 3.04 (s, 2H), 1.85 (s, 3H), 1.22 (t, *J* = 7.1 Hz, 3H), 0.453 (s, 3H), 0.448 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 210.98, 173.04, 140.47, 139.23, 135.77, 130.99, 130.19, 129.91, 129.75, 128.09, 100.69, 92.45, 62.61, 41.70, 20.12, 16.09, 0.22, 0.00.

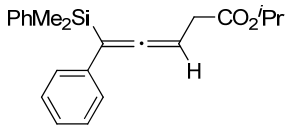
HRMS (ESI): m/z calculated for $C_{22}H_{26}O_2SiNa$ $[M+Na]^+$: 373.1600, found:373.1605.



3ac: In an oven dried 15 mL Schlenk tube equipped with a stirring bar, 0.02 mmol (2.9 mg, 10 mol%) CuBr and 0.02 mmol (2.1 mg, 10 mol%) Et_3N were added into 1 mL of dry MeOH under argon atmosphere. The solution was stirred for 5 min at room

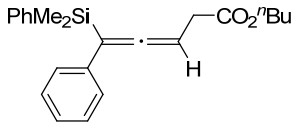
temperature. Then 0.2 mmol **1ac** (37.2 mg, 1.0 equiv), 0.4 mmol (105 mg, 2.0 equiv) Me_2PhSi-Bpin were added to the tube under argon atmosphere. The final solution was continued to stir for 24 hours at room temperature. Then the solution was diluted with DCM and filtered through Celite. The final filtrate was concentrated under vacuum to afford the crude product which was isolated through flash column chromatography (Eluent: PE/Et_2O = 97:3) to furnish the related product **3ac** (61.8 mg) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60 - 7.57 (m, 2H), 7.38 - 7.35 (m, 3H), 7.22 - 7.21 (m, 4H), 7.17 - 7.12 (m, 1H), 5.37 (t, *J* = 7.4 Hz, 1H), 3.70 (s, 3H), 3.14 (dd, *J* = 16.2, 7.2 Hz, 1H), 3.09 (dd, *J* = 16.2, 7.6 Hz, 1H), 0.473 (s, 3H), 0.468 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 211.56, 173.77, 139.99, 138.37, 135.81, 131.13, 130.29, 129.86, 129.80, 128.35, 101.83, 82.88, 53.81, 35.85, 0.06, 0.00.

HRMS (ESI): m/z calculated for $C_{20}H_{22}O_2SiNa$ $[M+Na]^+$: 345.1287, found:345.1289.



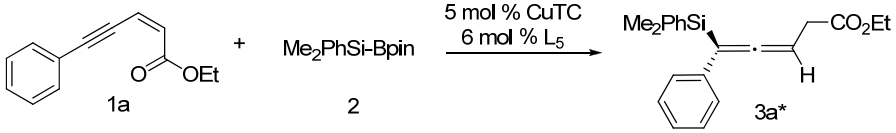
3ad: In an oven dried 15 mL Schlenk tube equipped with a stirring bar, 0.02 mmol (2.9 mg, 10 mol%) CuBr and 0.02 mmol (2.1 mg, 10 mol%) Et_3N were added in 1 mL of dry MeOH under argon atmosphere. The solution was stirred for 5 min at room temperature. Then 0.2 mmol **1ad** (42.9 mg, 1.0 equiv), 0.4 mmol (105 mg, 2.0 equiv) Me_2PhSi-Bpin were added to the tube under argon atmosphere. The final solution was continued to stir for 48 hours at room temperature. Then the solution was diluted with DCM and filtered through Celite. The final filtrate was concentrated under vacuum to afford the crude product which was isolated through flash column chromatography (Eluent: PE/Et_2O = 97:3) to furnish the related product **3ad** (55.5 mg) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60 - 7.57(m, 2H), 7.36 - 7.34 (m, 3H), 7.24 - 7.18 (m, 4H), 7.14 - 7.10 (m, 1H), 5.37 (t, *J* = 7.4 Hz, 1H), 5.03 (m, 1H), 3.16 - 3.00 (m, 2H), 1.24 - 1.22 (m, 7H), 0.47 (s, 3H), 0.46 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 211.54, 172.73, 139.94, 138.33, 135.69, 131.00, 130.14, 129.76, 129.69, 128.19, 101.47, 83.07, 70.02, 36.41, 23.62, 0.00, -0.05.

HRMS (ESI): m/z calculated for $C_{22}H_{26}O_2SiNa$ $[M+Na]^+$: 373.1600, found:373.1607.



3ae: In an oven dried 15 mL Schlenk tube equipped with a stirring bar, 0.02 mmol (2.9 mg, 10 mol%) CuBr and 0.02 mmol (2.1 mg, 10 mol%) Et_3N were added into 1 mL of dry MeOH under argon atmosphere. The solution was stirred for 5 min at room temperature. Then 0.2 mmol **1ae** (45.7 mg, 1.0 equiv), 0.4 mmol (105 mg, 2.0 equiv) Me_2PhSi-Bpin were added to the tube under argon atmosphere. The final solution was continued to stir for 24 hours at room temperature. Then the solution was diluted with DCM and filtered through Celite. The final filtrate was concentrated under vacuum to afford the crude product which was isolated through flash column chromatography (Eluent: PE/Et_2O = 97:3) to furnish the related product **3ae** (68.3 mg) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60 - 7.55 (m, 2H), 7.36 - 7.32 (m, 3H), 7.23 - 7.17 (m, 4H), 7.14 - 7.10 (m, 1H), 5.36 (t, *J* = 7.4 Hz, 1H), 4.10 (t, *J* = 6.7 Hz, 2H), 3.13 (dd, *J* = 16.2, 7.2 Hz, 1H), 3.07 (dd, *J* = 16.2, 7.6 Hz, 1H), 1.65 - 1.55 (m, 2H), 1.37 (dq, *J* = 14.6, 7.3 Hz, 2H), 0.91 (t, *J* = 7.4 Hz, 3H), 0.463 (s, 3H), 0.457 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 211.50, 173.32, 139.92, 138.31, 135.70, 131.02, 130.17, 129.77, 129.70, 128.22, 101.60, 82.98, 66.55, 36.08, 32.45, 20.94, 15.52, 0.00, -0.08. HRMS (ESI): m/z calculated for $C_{23}H_{28}O_2SiNa$ $[M+Na]^+$: 387.1756, found:387.1765.

1.4 Procedure for synthesis of enantioenriched allenylsilanes.



3a*: In an oven dried 15 mL Schlenk tube equipped with a stirring bar, 0.01mmol (1.9 mg, 5 mol%) CuTC and 0.012 mmol (3.6 mg, 6 mol%) ligand L_5 were added into 1 mL of dry ^{t}AmOH under argon atmosphere. The mixture was stirred for 1 hour at room temperature to form a light green solution. Then the tube was cooled to 0 ^{o}C, and 0.2 mmol **1a** (40.4 mg 1.0 equiv,) and 0.3 mmol (79 mg, 1.5 equiv) Me_2PhSi-Bpin were added to the tube under argon atmosphere. It was continued to

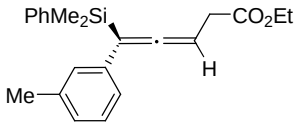
stir for 48 hours at 0 ^{o}C. Then the final deep green solution was concentrated under vacuum to afford the crude product which was isolated through flash column chromatography (Eluent: PE/Et_2O = 97:3) to furnish the related product **3a*** (54.1 mg, 80%) as colorless oil.

$[\alpha]_D^{25}$ +42.3^{o} (c = 1.59, $CHCl_3$)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 - 7.55 (m, 2H), 7.36 - 7.32 (m, 3H), 7.24 - 7.17 (m, 4H), 7.16 - 7.10 (m, 1H), 5.37 (t, *J* = 7.4 Hz, 1H), 4.15 (q, *J* = 7.1 Hz, 2H), 3.15 (dd, *J* =16.2, 7.2 Hz, 1H), 3.07 (dd, *J* =16.2, 7.6 Hz, 1H), 1.25 (t, *J* = 7.1 Hz, 3H), 0.463 (s, 3H), 0.458 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 211.53, 173.26, 139.94, 138.32, 135.72, 131.03, 130.18, 129.78, 129.71, 128.24, 101.61, 82.96, 62.64, 36.08, 16.02, 0.00, -0.06.

92% ee, HPLC, IC, Hexane:^{i}PrOH = 200:1, 0.6 mL/min: 22.4 min (major), 21.4 min (minor).

HRMS (ESI): m/z calculated for $C_{21}H_{24}O_2SiNa$ $[M+Na]^{+}$:359.1443, found: 359.1443.



3b***:** In an oven dried 15 mL Schlenk tube equipped with a stirring bar, 0.01mmol (1.9 mg, 5 mol%) CuTC and 0.012 mmol (3.6 mg, 6 mol%) ligand L_5 were added into 1 mL of dry ^{t}AmOH under argon atmosphere. The mixture was stirred for 1 hour at room temperature to form a light green solution. Then the tube was cooled to -5 ^{o}C, and 0.2 mmol **1b** (1.0 equiv, 42.9 mg) and 0.3 mmol (1.5 equiv, 79 mg) Me_2PhSi-Bpin were added to the tube under argon atmosphere. It was continued to stir for 72 h at -5 ^{o}C. Then the final deep green solution was concentrated under vacuum to afford the crude product which was isolated through flash column chromatography (Eluent: PE/Et_2O = 97:3) to furnish the related product **3b*** (61.6mg, 87%) as colorless oil.

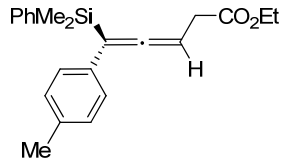
$[\alpha]_D^{25}$ +60.5^{o} (c = 2.35, $CHCl_3$)

^{1}H NMR (400 MHz, $CDCl_3$): δ7.54 - 7.47 (m, 2H), 7.31 - 7.25 (m, 3H), 7.02 - 6.98 (m, 2H), 6.91 - 6.86 (m, 2H), 5.27 (t, *J* = 7.4 Hz, 1H), 4.07 (q, *J* = 7.2 Hz, 2H), 3.04

(dd, J = 16.2, 7.2 Hz, 1H), 2.99 (dd, J = 16.2, 7.6 Hz, 1H), 2.17 (s, 3H), 1.17 (t, J = 7.1 Hz, 3H), 0.384 (s, 3H), 0.378 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 211.47, 173.36, 140.10, 139.79, 138.26, 135.79, 131.07, 130.58, 130.10, 129.75, 129.13, 126.92, 101.66, 82.89, 62.68, 36.18, 23.30, 16.09 , 0.09, 0.00.

92% ee, HPLC, OD-H, Hexane:^{i}PrOH = 250:1, 0.7 mL/min: 27.2 min (major), 21.7 min (minor).

HRMS (ESI): m/z calculated for $C_{22}H_{26}O_2SiNa$ $[M+Na]^+$:373.1600, found: 373.1612.



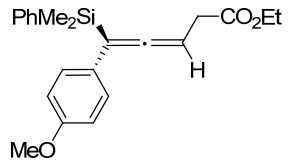
3c*: In an oven dried 15 mL Schlenk tube equipped with a stirring bar, 0.01mmol (1.9 mg, 5 mol%) CuTC and 0.012 mmol (3.6 mg, 6 mol%) ligand L_5 were added into 1 mL of dry ^{t}AmOH under argon atmosphere. The mixture was stirred for 1 hour at room temperature to form a light green solution. Then the tube was cooled to 0 ^{o}C, and 0.2 mmol **1c** (1.0 equiv, 42.9 mg) and 0.3 mmol (1.5 equiv, 79 mg) Me_2PhSi-Bpin were added to the tube under argon atmosphere. It was continued to stir for 48 hours at 0 ^{o}C. Then the final deep green solution was concentrated under vacuum to afford the crude product which was isolated through flash column chromatography (Eluent: PE/Et_2O = 97:3) to furnish the related product **3c*** (58.1 mg, 87%) as colorless oil.

$[\alpha]_D^{25}$ +39.4^{o} (c = 2.36, $CHCl_3$)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 - 7.38 (m, 2H), 7.17 - 7.13 (m, 3H), 6.92 (d, J = 8.1 Hz, 2H), 6.82 (d, J = 8.1 Hz, 2H), 5.15 (t, J = 7.4 Hz, 1H), 3.96 (q, J = 7.1 Hz, 2H), 2.92 (dd, J = 16.2, 7.2 Hz, 1H), 2.87 (dd, J = 16.2, 7.6 Hz, 1H), 2.08 (s, 3H), 1.06 (t, J = 7.1 Hz, 3H), 0.26 (s, 3H), 0.26 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 211.38, 173.37, 140.13, 138.00, 135.77, 135.23, 131.03,130.97, 129.74,129.70, 101.31, 82.96, 62.65, 22.96, 15.97,0.08, 0.00.

91% ee, HPLC, OD-H, Hexane:^{i}PrOH = 300:1, 0.6 mL/min: 21.8 min (major), 21.6 min (minor).

HRMS (ESI): m/z calculated for $C_{22}H_{26}O_2SiNa$ $[M+Na]^+$:373.1600, found: 373.1604.

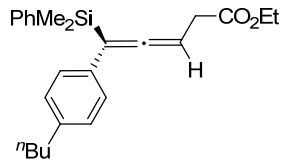


3d*: In an oven dried 15 mL Schlenk tube equipped with a stirring bar, 0.01mmol (1.9 mg, 5 mol%) CuTC and 0.012 mmol (3.6 mg, 6 mol%) ligand L_5 were added into 1 mL of dry ^{t}AmOH under argon atmosphere. The mixture was stirred for 1 hour at room temperature to form a light green solution. Then the tube was cooled to 0 ^{o}C, and 0.2 mmol **1d** (1.0 equiv, 46.1 mg), 0.3 mmol (1.5 equiv, 79 mg) Me_2PhSi-Bpin were added to the tube under argon atmosphere. It was continued to stir for 48 hours at 0 ^{o}C. Then the final deep green solution was concentrated under vacuum to afford the crude product which was isolated through flash column chromatography (Eluent: PE/Et_2O = 97:3) to furnish the related product **3d*** (52.9 mg, 72%) as colorless oil. $[\alpha]_D^{25}$ +42.3^o (c = 1.58, $CHCl_3$)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 - 7.49 (m, 2H), 7.28 - 7.25 (m, 3H), 7.09 - 7.06 (m, 2H), 6.69 - 6.66 (m, 2H), 5.27 (t, *J* = 7.3 Hz, 1H), 4.08 (q, *J* = 7.1 Hz, 2H), 3.66 (s, 3H), 3.04 (dd, *J* = 16.2, 7.2 Hz, 1H), 2.99 (dd, *J* =16.2, 7.6 Hz, 1H), 1.17 (t, *J* = 7.1 Hz, 3H), 0.38 (s, 3H), 0.38 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 211.11, 173.39, 160.15, 140.10, 135.75, 131.04,130.86,130.34, 129.75, 115.72, 100.88, 83.04, 62.63, 57.06, 36.26, 16.13, 0.07, 0.00.

90% ee, HPLC, OD-H, Hexane:^{i}PrOH = 250:1, 0.7 mL/min, 60.1min (major), 55.7 min (minor).

HRMS (ESI): m/z calculated for $C_{22}H_{26}O_3SiNa$ $[M+Na]^+$:385.1549, found: 385.1512.



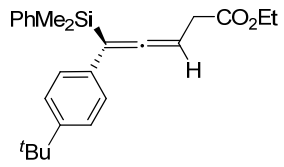
3e*: In an oven dried 15 mL Schlenk tube equipped with a stirring bar, 0.01mmol (1.9 mg, 5 mol%) CuTC, 0.012 mmol (3.6 mg, 6 mol%) ligand L_5 were added into 1 mL of dry ^{t}AmOH under argon atmosphere. The mixture was stirred for 1 hour at room temperature to form a light green solution. Then the tube was cooled to -5 ^{o}C,

and 0.2 mmol **1e** (1.0 equiv, 51.3 mg), 0.3 mmol (1.5 equiv, 79 mg) Me_2PhSi-Bpin were added to the tube under argon atmosphere. It was continued to stir for 48 hours at -5 ^oC. Then the final deep green solution was concentrated under vacuum to afford the crude product which was isolated through flash column chromatography (Eluent: PE/Et_2O = 97:3) to furnish the related product **3e*** (57.1 mg, 73%) as colorless oil. $[\alpha]_D^{25}$ +36.7^o (c = 2.59, $CHCl_3$).

^1H NMR (400 MHz, $CDCl_3$) δ 7.60 - 7.58 (m, 2H), 7.38 - 7.34 (m, 3H), 7.15 - 7.13 (m, 2H), 7.04 - 7.00 (m, 2H), 5.36 (t, *J* = 7.4 Hz, 1H), 4.17 (q, *J* = 6.9 Hz, 2H), 3.13 (dd, *J* = 16.2, 7.2 Hz, 1H), 3.07(dd, *J* = 16.2, 7.6 Hz, 1H), 2.58 - 2.51 (m, 2H), 1.58 - 1.51 (m, 2H), 1.35 - 1.29 (m, 2H), 1.26 (t, *J* = 7.3 Hz, 3H), 0.90 (t, *J* = 7.3 Hz, 3H), 0.47 (s, 3H), 0.47 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 211.33, 173.29, 142.97, 140.07, 135.68, 135.26, 130.92, 130.22, 129.64, 129.57, 101.23, 82.87, 62.56, 37.00, 36.12, 35.30, 24.11, 15.97, 15.71, 0.00. -0.07.

93% ee, HPLC, OD-H, Hexane:^{i}PrOH = 250:1, 0.7 mL/min: 23.0 min (major), 25.1 min (minor).

HRMS (ESI): m/z calculated for $C_{25}H_{32}O_2SiNa$ $[M+Na]^+$:415.2069, found: 415.2079.

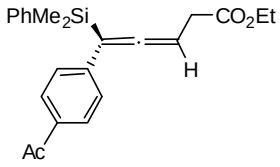


3f***:** In an oven dried 15 mL Schlenk tube equipped with a stirring bar, 0.01mmol (1.9 mg, 5 mol%) CuTC, 0.012 mmol (3.6 mg, 6 mol%) ligand L_5 were added into 1 mL of dry ^{t}AmOH under argon atmosphere. The mixture was stirred for 1 hour at room temperature to form a light green solution. Then the tube was cooled to 0 ^oC, and 0.2 mmol **1f** (1.0 equiv, 51.3 mg), 0.3 mmol (1.5 equiv, 79 mg) Me_2PhSi-Bpin were added to the tube under argon atmosphere. It was continued to stir for 48 hours at 0 ^oC. Then the final deep green solution was concentrated under vacuum to afford the crude product which was isolated through flash column chromatography (Eluent: PE/Et_2O = 97:3) to furnish the related product **3e*** (55.9 mg, 71%) as colorless oil. $[\alpha]_D^{25}$ +39.4^o (c = 2.36, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63 - 7.56 (m, 2H), 7.40 - 7.31 (m, 3H), 7.26 - 7.20 (m, 2H), 7.20 - 7.12 (m, 2H), 5.35 (t, *J* = 7.4 Hz, 1H), 4.15 (q, *J* = 7.1 Hz, 2H), 3.11(dd, *J* = 16.2, 7.2 Hz, 1H), 3.06 (dd, *J* = 16.2, 7.6 Hz, 1H), 1.27 - 1.23 (m, 12H), 0.46 (s, 3H), 0.46 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 211.52, 173.30, 151.19, 140.16, 135.73, 135.07, 130.97, 129.69, 129.40, 127.14, 101.14, 82.95, 62.60, 36.23, 36.17, 33.10, 16.02, 0.07, 0.00.

91% ee, HPLC, OD-H, Hexane:^{i}PrOH = 300:1, 0.6 mL/min: 12.0 min (major), 13.1 min (minor).

HRMS (ESI): m/z calculated for $C_{25}H_{32}O_2SiNa$ $[M+Na]^+$:415.2069, found: 415.2074.



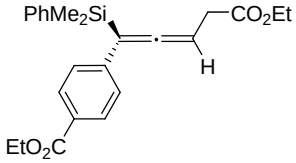
3h*: In an oven dried 15 mL Schlenk tube equipped with a stirring bar, 0.01mmol (1.9 mg, 5 mol%) CuTC, 0.012 mmol (3.6 mg, 6 mol%) ligand L_5 were added into 1 mL of dry ^{t}AmOH under argon atmosphere. The mixture was continued to stir for 1 hour at room temperature to form a light green solution. Then the tube was cooled to 0 ^{o}C, and 0.2 mmol **1h** (1.0 equiv, 48.5 mg), 0.3 mmol (1.5 equiv, 79 mg) Me_2PhSi-Bpin were added to the tube under argon atmosphere. It was continued to stir for 72 hours at 0 ^{o}C. Then the final deep green solution was concentrated under vacuum to afford the crude product which was isolated through flash column chromatography (Eluent: PE/Et_2O = 97:3) to furnish the related product **3h*** (48.3 mg, 64%) as colorless oil.

$[\alpha]_D^{25}$ +61.5^o (c = 1.53, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 - 7.78 (m, 2H), 7.68 - 7.55 (m, 2H), 7.40 - 7.34 (m, 3H), 7.30 - 7.28 (m, 2H), 5.43 (t, *J* = 7.4 Hz, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 3.14 (dd, *J* = 16.2, 7.2 Hz, 1H), 3.09 (dd, *J* = 16.2, 7.6 Hz, 1H), 2.53 (s, 3H), 1.25 (d, *J* = 7.1 Hz, 3H), 0.47 (s, 3H), 0.47 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 212.58, 199.57, 173.17, 144.06, 139.55, 137.11, 135.84, 135.50, 131.43 , 130.50, 130.01, 101.73, 83.84, 62.97, 36.14, 28.13, 16.46, 0.08, 0.00.

93% ee, HPLC, IC, Hexane:^{i}PrOH = 99:1, 0.6 mL/min: 42.4 min (major), 38.9 min (minor).

HRMS (ESI): m/z calculated for $C_{23}H_{26}O_3SiNa$ $[M+Na]^+$: 401.1549, found: 401.1551.

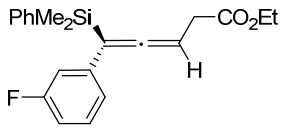


3i*: In an oven dried 15 mL Schlenk tube equipped with a stirring bar, 0.01mmol (1.9 mg, 5 mol%) CuTC, 0.012 mmol (3.6 mg, 6 mol%) ligand L_5 were added into 1 mL of dry ^{t}AmOH under argon atmosphere. The mixture was stirred for 1 hour at room temperature to form a light green solution. Then the tube was cooled to -5 ^{o}C, and 0.2 mmol **1i** (1.0 equiv, 54.5 mg), 0.3 mmol (1.5 equiv, 79 mg) Me_2PhSi-Bpin were added to the tube under argon atmosphere. It was continued to stir for 72 hours at -5 ^{o}C. Then the final deep green solution was concentrated under vacuum to afford the crude product which was isolated through flash column chromatography (Eluent: PE/Et_2O = 97:3) to furnish the related product **3i*** (59.8 mg, 74%) as colorless oil. $[\alpha]_D^{25}$ +58.2^{o} (c = 2.22, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 - 7.84 (m, 2H), 7.59 - 7.53 (m, 2H), 7.40 - 7.34 (m, 3H), 7.29 - 7.23 (m, 2H), 5.42 (t, *J* = 7.4 Hz, 1H), 4.33 (q, *J* = 7.1 Hz, 2H), 4.16 (q, *J* = 7.1 Hz, 2H), 3.14 (dd, *J* = 16.2, 7.2 Hz, 1H), 3.08 (dd, *J* = 16.2, 7.6 Hz, 1H), 1.35 (t, *J* = 7.1 Hz, 3H), 1.26 (t, *J* = 7.1 Hz, 3H), 0.47 (s, 3H), 0.47 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) : δ 212.35, 173.12, 168.38, 143.61, 139.52, 135.77, 131.55, 131.32, 130.29, 129.92,129.73, 101.64, 83.51, 62.82, 62.71, 35.92, 16.24, 16.13, 0.00, -0.08.

90% ee, HPLC, OD-H, Hexane:^{i}PrOH = 250:1, 0.7 mL/min, 34.2 min (major), 31.9 min (minor).

HRMS (ESI): m/z calculated for $C_{24}H_{28}O_4SiNa$ $[M+Na]^+$: 431.1655, found: 431.1655.

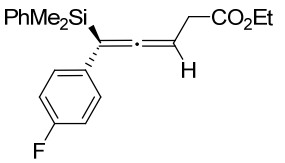


3k*: In an oven dried 15 mL Schlenk tube equipped with a stirring bar, 0.01mmol (1.9 mg, 5 mol%) CuTC, 0.012 mmol (3.6 mg, 6 mol%) ligand L_5 were added into 1 mL of dry ^{t}AmOH under argon atmosphere. The mixture was stirred for 1 hour at room temperature to form a light green solution. Then the tube was cooled to -5 ^{o}C, and 0.2 mmol **1k** (1.0 equiv 43.7 mg), 0.3 mmol (1.5 equiv, 79 mg) Me_2PhSi-Bpin were added to the tube under argon atmosphere. It was continued to stir for 72 hours at -5 ^{o}C. Then the final deep green solution was concentrated under vacuum to afford the crude product which was isolated through flash column chromatography (Eluent: PE/Et_2O = 97:3) to furnish the related product **3k*** (54.1 mg, 76%) as colorless oil. $[\alpha]_D^{25}$ +43.9^o (c = 2.02, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59 - 7.56 (m, 2H), 7.38 - 7.35 (m, 3H), 7.18 - 7.12 (m,1H), 6.97 - 6.93 (m, 2H), 6.86 - 6.81 (m, 1H), 5.41 (t, *J* = 7.4 Hz, 1H), 4.17 (q, *J* = 7.2 Hz, 2H), 3.14 (dd, *J* = 16.2, 7.2 Hz, 1H), 3.08 (dd, *J* = 16.2, 7.6 Hz, 1H), 1.27 (t, *J* = 7.1 Hz, 3H), 0.47 (s, 3H), 0.47 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 211.92, 173.21, 164.80 (d, *J* = 245.4 Hz), 141.02 (d, *J* = 7.5 Hz), 139.62, 135.83, 131.61 (d, *J* = 8.3 Hz), 131.35, 129.96, 125.60 (d, *J* = 2.8 Hz), 116.65 (d, *J* = 21.9 Hz), 115.29 (d, *J* = 21.3 Hz), 101.32 , 83.56, 62.89, 36.07, 16.16, 0.06, 0.00.

91% ee, HPLC, OD-H, Hexane:^{i}PrOH = 250:1, 0.7 mL/min, 37.0 min (major), 32.3 min (minor).

HRMS (ESI): m/z calculated for $C_{21}H_{23}FO_2SiNa$ $[M+Na]^+$:377.1349, found: 377.1341.



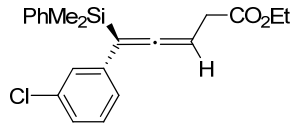
3l*: In an oven dried 15 mL Schlenk tube equipped with a stirring bar, 0.01mmol (1.9 mg, 5 mol%) CuTC, 0.012 mmol (3.6 mg, 6 mol%) ligand L_5 were added into 1 mL of dry ^{t}AmOH under argon atmosphere. The mixture was stirred for 1 hour at room

temperature to form a light green solution. Then the tube was cooled to -5 ^{o}C, and 0.2 mmol **1l** (1.0 equiv, 43.7 mg), 0.3 mmol (1.5 equiv, 79 mg) Me_2PhSi-Bpin were added to the tube under argon atmosphere. It was continued to stir for 96 hours at -5 ^{o}C. Then the final deep green solution was concentrated under vacuum to afford the crude product which was isolated through flash column chromatography (Eluent: PE/Et_2O = 97:3) to furnish the related product **3l*** (64.1 mg, 90%) as colorless oil. $[\alpha]_D^{25}$ +47.2^{o} (c = 2.20, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 - 7.55 (m, 2H), 7.37 - 7.34 (m, 3H), 7.17 - 7.14 (m, 2H), 6.92 - 6.86 (m, 2H), 5.37 (t, *J* = 7.4 Hz, 1H), 4.16 (q, *J* = 7.1 Hz, 2H), 3.12 (dd, *J* = 16.2, 7.2 Hz, 1H), 3.07 (dd, *J* = 16.2, 7.2 Hz, 1H), 1.25 (t, *J* = 7.1 Hz, 3H), 0.45 (s, 3H), 0.45 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 211.57, 173.36, 163.58 (d, *J* = 245.6 Hz), 139.82, 135.85, 134.36 (d, *J* = 3.3 Hz), 131.41, 131.33, 129.96, 117.23 (d, *J* = 21.4 Hz), 100.94, 83.32, 62.84, 36.21, 16.18, 0.06, 0.00.

90% ee, HPLC, OD-H, Hexane:^{i}PrOH = 250:1, 0.6 mL/min, 18.1 min (major), 18.7 min (minor).

HRMS (ESI): m/z calculated for $C_{21}H_{23}FO_2SiNa$ $[M+Na]^{+}$: 377.1349, found: 377.1355.

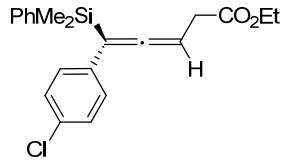


3m*: In an oven dried 15 mL Schlenk tube equipped with a stirring bar, 0.01mmol (1.9 mg, 5 mol%) CuTC, 0.012 mmol (3.6 mg, 6 mol%) ligand L_5 were added into 1 mL of dry ^{t}AmOH under argon atmosphere. The mixture was stirred for 1 hour at room temperature to form a light green solution. Then the tube was cooled to -5 ^{o}C, and 0.2 mmol **1m** (1.0 equiv, 47.0 mg), 0.3 mmol (1.5 equiv, 79 mg) Me_2PhSi-Bpin were added to the tube under argon atmosphere. It was continued to stir for 72 hours at -5 ^{o}C. Then the final deep green solution was concentrated under vacuum to afford the crude product which was isolated through flash column chromatography (Eluent: PE/Et_2O = 97:3) to furnish the related product **3m*** (62.9 mg, 85%) as colorless oil. $[\alpha]_D^{25}$ +54.7^{o} (c = 2.04, $CHCl_3$)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59 - 7.57(m, 2H), 7.39 - 7.37 (m, 3H), 7.26 - 7.25 (m, 1H), 7.12 - 7.11(m, 2H), 7.06 - 7.02 (m, 1H), 5.41 (t, *J* = 7.4 Hz, 1H), 4.22 - 4.15 (m, 2H), 3.14 (dd, *J* = 16.2, 7.2 Hz, 1H), 3.09 (dd, *J* = 16.2, 7.6 Hz, 1H), 1.27 (t, *J* = 7.1 Hz, 3H), 0.48 (s, 3H), 0.48 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 211.83, 173.15, 140.57, 139.51, 136.16, 135.78, 131.41, 131.33, 129.92, 129.87, 128.43, 127.94, 101.13, 83.56, 62.86, 36.03, 16.14, 0.00, -0.07.

92% ee, HPLC, OD-H, Hexane:^{i}PrOH = 250:1, 0.7 mL/min, 41.4 min (major), 30.6 min (minor).

HRMS (ESI): m/z calculated for $C_{21}H_{23}ClO_2SiNa$ $[M+Na]^+$: 393.1053, found: 393.1054.



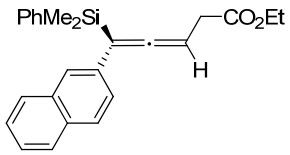
3n*: In an oven dried 15 mL Schlenk tube equipped with a stirring bar, 0.01mmol (1.9 mg, 5 mol%) CuTC, 0.012 mmol (3.6 mg, 6 mol%) ligand L_5 were added into 1 mL of dry ^{t}AmOH under argon atmosphere. The mixture was continued to stir for 1 hour at room temperature to form a light green solution. Then the tube was cooled to -5 ^{o}C, and 0.2 mmol **1n** (1.0 equiv, 47.0 mg), 0.3 mmol (1.5 equiv, 79 mg) Me_2PhSi-Bpin were added to the tube under argon atmosphere. It was continued to stir for 96 hours at -5 ^{o}C. Then the final deep green solution was concentrated under vacuum to afford the crude product which was isolated through flash column chromatography (Eluent: PE/Et_2O = 97:3) to furnish the related product **3n*** (61.6 mg, 83%) as colorless oil.

$[\alpha]_D^{25}$ +53.7^o (c = 2.40, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49 - 7.47 (m 2H), 7.30 - 7.27(m, 3H), 7.09 - 7.04 (m, 4H), 5.31 (t, *J* = 7.4 Hz, 1H), 4.08 (q, *J* = 7.1 Hz, 2H), 3.05 (dd, *J* = 16.2, 7.2 Hz, 1H), 3.00 (dd, *J* = 16.2, 7.6Hz, 1H), 1.18 (t, *J* = 7.1 Hz, 3H), 0.38 (s, 3H), 0.38 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 211.70, 173.21, 139.63, 136.99, 135.78, 134.12, 131.30, 131.10, 130.43, 129.92, 100.96, 83.44, 62.87, 36.04, 16.06, 0.00, -0.08.

90% ee, HPLC, OD-H, Hexane:^{i}PrOH = 550:1, 0.5 mL/min, 36.7 min (major), 40.1 min (minor).

HRMS (ESI): m/z calculated for $C_{21}H_{23}ClO_2SiNa$ $[M+Na]^+$:393.1053, found: 393.1048.



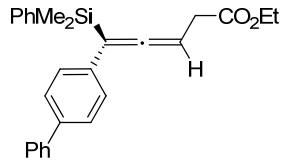
3q*: In an oven dried 15 mL Schlenk tube equipped with a stirring bar, 0.01mmol (1.9 mg, 5 mol%) CuTC, 0.012 mmol (3.6 mg, 6 mol%) ligand L_5 were added into 1 mL of dry ^{t}AmOH under argon atmosphere. The mixture was stirred for one hour at room temperature to form a light green solution. Then the tube was cooled to 0 ^{o}C, and 0.2 mmol **1q** (1.0 equiv 50.1 mg), 0.3 mmol (1.5 equiv, 79 mg) Me_2PhSi-Bpin were added to the tube under argon atmosphere. It was continued to stir for 48 hours at 0 ^{o}C. Then the final deep green solution was concentrated under vacuum to afford the crude product which was isolated through flash column chromatography (Eluent: PE/Et_2O = 97:3) to furnish the related product **3q*** **(**54.6 mg, 71%） as colorless oil. $[\alpha]_D^{25}$ +50^{o} (c = 0.55, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 - 7.64 (m, 1H), 7.61 (d, *J* = 8.2 Hz, 1H), 7.57 - 7.52 (m, 3H), 7.48 (d, *J* = 1.2 Hz, 1H), 7.37 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.32 - 7.26 (m, 5H), 5.36 (t, *J* = 7.4 Hz, 1H), 4.09 (q, *J* = 7.1 Hz, 2H), 3.09 (dd, *J* = 16.2, 7.2 Hz, 1H), 3.03 (dd, *J* = 16.2, 7.6 Hz, 1H), 1.19 (d, *J* = 7.1 Hz, 3H), 0.44 (s, 3H), 0.44 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 212.00, 173.23, 139.93, 135.76, 135.72, 135.26, 133.98, 131.10, 129.76, 129.72, 129.63, 129.31, 128.36, 128.29, 127.74, 127.36, 101.84 , 83.29, 62.65, 36.10, 16.03 , 0.09, 0.00.

93% ee, HPLC, IC, Hexane:EA = 200:1, 0.6 mL/min, 18.2 min (major), 20.2 min (minor).

HRMS (ESI): m/z calculated for $C_{25}H_{26}O_2SiNa$ $[M+Na]^+$: 409.1600, found:409.1602.



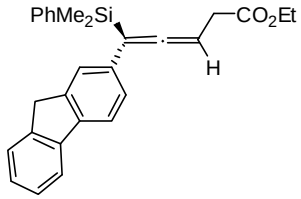
3r*: In an oven dried 15 mL Schlenk tube equipped with a stirring bar, 0.01mmol (1.9 mg, 5 mol%) CuTC, 0.012 mmol (3.6 mg, 6 mol%) ligand L_5 were added into 1 mL of dry ^{t}AmOH under argon atmosphere. The mixture was stirred for one hour at room temperature to form a light green solution. Then the tube was cooled to -5 ^{o}C, and 0.2 mmol **1r** (1.0 equiv, 55.3 mg), 0.3 mmol (1.5 equiv, 79 mg) Me_2PhSi-Bpin were added to the tube under argon atmosphere. It was continued to stir for 72 hours at -5 ^{o}C. Then the final deep green solution was concentrated under vacuum to afford the crude product which was isolated through flash column chromatography (Eluent: PE/Et_2O = 97:3) to furnish the related product **3r*** (61.9, 75%) as colorless oil.

$[\alpha]_D^{25}$ +66.3^{o} (c = 2.32, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 - 7.59 (m, 2H), 7.55 - 7.51 (m, 2H), 7.45 - 7.43 (m, 2H), 7.41 - 7.34 (m, 5H), 7.31 - 7.28 (m, 3H), 5.40 (t, *J* = 7.4 Hz, 1H), 4.16 (q, *J* = 7.1 Hz, 2H), 3.14 (dd, *J* = 16.2, 7.2 Hz, 1H), 3.09 (dd, *J* = 16.2, 7.6 Hz, 1H), 1.26 (t, *J* = 7.1 Hz, 3H), 0.49 (s, 3H), 0.49 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 211.73, 173.23, 142.58, 141.06, 139.92, 137.32, 135.75, 131.10, 130.54, 130.18, 129.77, 128.96, 128.91, 128.70, 101.29, 83.19, 62.67, 36.09, 16.05, 0.08, 0.00.

90% ee, HPLC, OD-H, Hexane:^{i}PrOH = 200:1, 0.6 mL/min, 15.2min (major), 16.5 min (minor).

HRMS (ESI): m/z calculated for $C_{27}H_{28}O_2SiNa$ $[M+Na]^+$: 435.1756, found: 435.1765.



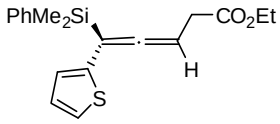
3s*: In an oven dried 15 mL Schlenk tube equipped with a stirring bar, 0.01mmol (1.9 mg, 5 mol%) CuTC, 0.012 mmol (3.6 mg, 6 mol%) ligand L_5 were added into 1 mL

of dry ^{t}AmOH under argon atmosphere. The mixture was stirred for one hour at room temperature to form a light green solution. Then the tube was cooled to -5 ^{o}C, and 0.2 mmol **1s** (1.0 equiv, 58.0 mg), 0.3 mmol (1.5 equiv, 79 mg) Me_2PhSi-Bpin were added to the tube under argon atmosphere. It was continued to stir for 72 hours at -5 ^{o}C. Then the final deep green solution was concentrated under vacuum to afford the crude product which was isolated through flash column chromatography (Eluent: PE/Et_2O = 97:3) to furnish the related product **3s*** (53.5 mg, 63%) as colorless oil. $[\alpha]_D^{25}$ +59.6^{o} (c = 1.90, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 7.5 Hz, 1H), 7.61 - 7.58 (m, 3H), 7.47 (d, *J* = 7.1 Hz, 1H), 7.42 (s, 1H), 7.36 - 7.31(m, 4H), 7.26 - 7.19 (m, 2H), 5.40 (t, *J* = 7.4 Hz, 1H), 4.16 (q, *J* = 7.1 Hz, 2H), 3.79 (s, 2H), 3.20 - 3.06 (m, 2H), 1.25 (t, *J* = 7.1 Hz, 3H), 0.49 (s, 6H), 0.49 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 211.38, 173.14, 145.17, 144.96, 143.13, 141.86, 139.88, 136.67, 135.61, 130.90, 129.59, 128.38, 128.37, 128.17, 126.61, 126.24, 121.39, 121.35, 101.81, 82.90, 62.49, 38.53, 36.02, 15.91, 0.00, -0.08.

91% ee, HPLC, AS-H , Hexane:^{i}PrOH = 330:1, 0.4 mL/min, 20.9 min (major), 23.1 min (minor).

HRMS (ESI): m/z calculated for $C_{28}H_{28}O_2SiNa$ $[M+Na]^{+}$: 447.1756, found:447.1773.



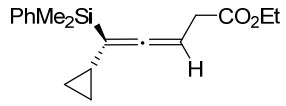
3t***:** In an oven dried 15 mL Schlenk tube equipped with a stirring bar, 0.01mmol (1.9 mg, 5 mol%) CuTC, 0.012 mmol (3.6 mg, 6 mol%) ligand L_5 were added into 1 mL of dry ^{t}AmOH under argon atmosphere. The mixture was stirred for one hour at room temperature to form a light green solution. Then the tube was cooled to -5 ^{o}C, and 0.2 mmol **1t** (1.0 equiv, 41.3 mg), 0.3 mmol (1.5 equiv, 79 mg) Me_2PhSi-Bpin were added to the tube under argon atmosphere. It was continued to stir for 72 hours at -5 ^{o}C. Then the final deep green solution was concentrated under vacuum to afford the crude product which was isolated through flash column chromatography (Eluent:

PE/Et_2O = 97:3) to furnish the related product **3t*** (35.6 mg, 52%) as colorless oil. $[\alpha]_D^{25}$ +81.7° (c = 1.67, $CHCl_3$).

^1H NMR (400 MHz, $CDCl_3$) δ 7.63 - 7.60 (m, 2H), 7.41 - 7.34 (m, 3H), 7.11 - 7.10 (m, 1H), 6.83 (dd, *J* = 5.2, 3.6 Hz, 1H), 6.69 - 6.68 (m, 1H), 5.43 (t, *J* = 7.4 Hz, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.14 (dd, *J* = 16.2, 7.2 Hz, 1H), 3.08 (dd, *J* = 16.2, 7.6 Hz, 1H) 1.27 (t, *J* = 7.1 Hz, 3H), 0.52 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 211.13, 173.28, 142.19, 139.47, 136.07, 131.50, 130.01, 129.35, 127.24, 126.52, 96.80, 84.22, 62.95, 36.33, 16.32, 0.09, 0.00.

90% ee, HPLC, OD-H , Hexane:^{i}PrOH = 250:1, 0.6 mL/min, 36.9 min (major), 32.0 min (minor).

HRMS (ESI): m/z calculated for $C_{19}H_{22}O_2SiNa$ $[M+Na]^+$: 387.1756, found: 387.1747.

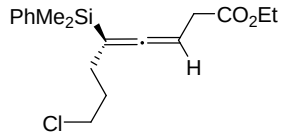


3u*: In an oven dried 15 mL Schlenk tube equipped with a stirring bar, 0.01mmol (1.9 mg, 5 mol%) CuTC, 0.012 mmol (3.6 mg, 6 mol%) ligand L_5 were added into 1 mL of dry ^{t}AmOH under argon atmosphere. The mixture was stirred for one hour at room temperature to form a light green solution. Then the tube was cooled to -5 °C, and 0.2 mmol **1u** (1.0 equiv, 32.8 mg), 0.3 mmol (1.5 equiv, 79 mg) Me_2PhSi-Bpin were added to the tube under argon atmosphere. It was continued to stir for 72 hours at -5 °C. Then the final deep green solution was concentrated under vacuum to afford the crude product which was isolated through flash column chromatography (Eluent: PE/Et_2O = 97:3) to furnish the related product **3u*** (47.4 mg, 75%) as colorless oil. $[\alpha]_D^{25}$ +4.2° (c = 1.71, $CHCl_3$).

^1H NMR (400 MHz, $CDCl_3$): δ 7.59 - 7.56 (m, 2H), 7.37 - 7.34 (m, 3H), 5.06 (td, *J* = 7.3, 1.8 Hz, 1H), 4.14 (q, *J* = 7.1 Hz, 2H), 2.95 (dd, *J* = 16.2, 7.2 Hz, 1H), 2.90 (dd, *J* = 16.2, 7.6 Hz, 1H), 1.26 (t, *J* = 7.1 Hz, 4H), 1.07 - 1.00 (m, 1H), 0.64 - 0.60 (m, 2H), 0.46 - 0.34 (m, 8H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 204.78, 171.75, 138.00, 133.89, 129.08, 127.71, 101.14, 81.45, 60.63, 34.79, 14.21, 9.56, 8.22, 7.82, -2.83, -2.89.

73% ee, HPLC, IC, Hexane:^{i}PrOH = 300:1, 0.6 mL/min, 18.8 min (major), 17.9 min (minor).

HRMS (ESI): m/z calculated for $C_{18}H_{24}O_2SiNa$ $[M+Na]^+$: 323.1443, found: 323.1442.



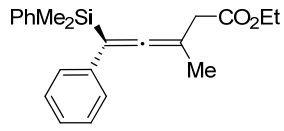
3x*: In an oven dried 15 mL Schlenk tube equipped with a stirring bar, 0.01mmol (1.9 mg, 5 mol%) CuTC, 0.012 mmol (3.6 mg, 6 mol%) ligand L_5 were added into 1 mL of dry ^{t}AmOH under argon atmosphere. The mixture was stirred for one hour at room temperature to form a light green solution. Then the tube was cooled to -5 ^{o}C, and 0.2 mmol **1x** (1.0 equiv, 40.2 mg), 0.3 mmol (1.5 equiv, 79 mg) Me_2PhSi-Bpin were added to the tube under argon atmosphere. It was continued to stir for 72 hours at -5 ^{o}C. Then the final deep green solution was concentrated under vacuum to afford the crude product which was isolated through flash column chromatography (Eluent: PE/Et_2O = 97:3) to furnish the related product **3x*** (51.0 mg, 76%) as colorless oil.

$[\alpha]_D^{25}$ -0.95^{o} (c = 2.33, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 - 7.50 (m, 2H), 7.36 - 7.35(m, 3H), 5.08 - 5.02 (m, 1H), 4.14 (q, *J* = 7.1 Hz, 2H), 3.49 (t, *J* = 6.5 Hz, 2H), 2.97 (dd, *J* = 7.4, 2.1 Hz, 2H), 2.08 - 2.04 (m, 2H), 1.91 - 1.84 (m, 2H), 1.26 (t, *J* = 7.1 Hz, 3H), 0.38 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 206.49, 171.69, 137.51, 133.75, 129.23, 127.83, 95.66, 80.36, 60.70, 44.51, 34.59, 31.58, 26.20, 14.22, -3.15, -3.21.

68% ee, HPLC, IC , Hexane:^{i}PrOH = 300:1, 0.6 mL/min, 49.3 min (major), 50.5 min (minor).

HRMS (ESI): m/z calculated for $C_{18}H_{25}ClO_2SiNa$ $[M+Na]^+$:359.1210, found: 359.1203.



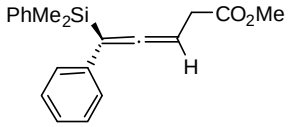
3ab*: In an oven dried 15 mL Schlenk tube equipped with a stirring bar, 0.01mmol (1.9 mg, 5 mol%) CuTC, 0.012 mmol (3.6 mg, 6 mol%) ligand L_5 were added into 1 mL of dry ^{t}AmOH under argon atmosphere. The mixture was stirred for one hour at room temperature to form a light green solution. Then the tube was cooled to 0 ^{o}C, and 0.2 mmol **1ab** (1.0 equiv 42.9 mg), 0.3 mmol (1.5 equiv, 79 mg) Me_2PhSi-Bpin were added to the tube under argon atmosphere. It was continued to stir for 48 hours at 0 ^{o}C. Then the final deep green solution was concentrated under vacuum to afford the crude product which was isolated through flash column chromatography (Eluent: PE/Et_2O = 97:3) to furnish the related product **3ab*** (52.1 mg, 74%) as colorless oil.

$[\alpha]_D^{25}$ +6.2^o (c = 2.70, $CHCl_3$)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60 - 7.57 (m, 2H), 7.36 - 7.34 (m, 3H), 7.24 - 7.17 (m, 4H), 7.13 - 7.09 (m, 1H), 4.13 (qd, *J* = 7.1, 0.9 Hz, 2H), 3.04 (s, 2H), 1.85 (s, 3H), 1.22 (t, *J* = 7.1 Hz, 3H), 0.453 (s, 3H), 0.448 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 210.98, 173.04, 140.47, 139.23, 135.77, 130.99, 130.19, 129.91, 129.75, 128.09, 100.69, 92.45, 62.61, 41.70, 20.12, 16.09, 0.22, 0.00.

36% ee, HPLC, AS-H , Hexane:^{i}PrOH = 99:1, 0.6 mL/min, 13.0 min (major), 16.3 min (minor).

HRMS (ESI): m/z calculated for $C_{22}H_{26}O_2SiNa$ $[M+Na]^+$:373.1600, found:373.1605.



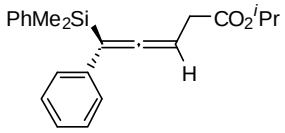
3ac*: In an oven dried 15 mL Schlenk tube equipped with a stirring bar, 0.01mmol (1.9 mg, 5 mol%) CuTC, 0.012 mmol (3.6 mg, 6 mol%) ligand L_5 were dissolved in 1 mL of dry ^{t}AmOH under argon atmosphere. The mixture was stirred for one hour at room temperature to form a light green solution. Then the tube was cooled to 0 ^{o}C, and 0.2 mmol **1ac** (1.0 equiv, 37.2 mg), 0.3 mmol (1.5 equiv, 79 mg) Me_2PhSi-Bpin were added to the tube under argon atmosphere. It was continued to stir for 48 hours at 0 ^{o}C. Then the final deep green solution was concentrated under vacuum to afford the crude product which was isolated through flash column chromatography (Eluent: PE/Et_2O = 97:3) to furnish the related product **3ac*** (52.3 mg，81%）as colorless oil.

$[\alpha]_D^{25}$ +61.5^o (c = 2.14, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$):δ 7.60 - 7.57 (m, 2H), 7.38 - 7.35 (m, 3H), 7.22 - 7.21 (m, 4H), 7.17 - 7.12 (m, 1H), 5.37 (t, *J* = 7.4 Hz, 1H), 3.70 (s, 3H), 3.14 (dd, *J* = 16.2, 7.2 Hz, 1H), 3.09 (dd, *J* = 16.2, 7.6 Hz, 1H), 0.473 (s, 3H), 0.468 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 211.56, 173.77, 139.99, 138.37, 135.81, 131.13, 130.29, 129.86, 129.80, 128.35, 101.83, 82.88, 53.81, 35.85, 0.06, 0.00.

94% ee, HPLC, IC , Hexane:^{i}PrOH = 300:1, 0.6 mL/min, 15.1 min (major), 13.5 min (minor).

HRMS (ESI): m/z calculated for $C_{20}H_{22}O_2SiNa$ $[M+Na]^+$:345.1287, found:345.1289.



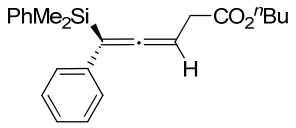
3ad*: In an oven dried 15 mL Schlenk tube equipped with a stirring bar, 0.01mmol (1.9 mg, 5 mol%) CuTC, 0.012 mmol (3.6 mg, 6 mol%) ligand L_5 were added in 1 mL of dry ^{t}AmOH under argon atmosphere. The mixture was stirred for one hour at room temperature to form a light green solution. Then the tube was cooled to -5 ^{o}C, and 0.2 mmol **1ad** (1.0 equiv, 42.9 mg), 0.3 mmol (1.5 equiv, 79 mg) Me_2PhSi-Bpin were added to the tube under argon atmosphere. It was continued to stir for 72 hours at -5 ^{o}C. Then the final deep green solution was concentrated under vacuum to afford the crude product which was isolated through flash column chromatography (Eluent: PE/Et_2O = 97:3) to furnish the related product **3ad*** (52 mg, 74%) as colorless oil.

$[\alpha]_D^{25}$ +43.6^o (c = 2.07, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60 - 7.57(m, 2H), 7.36 - 7.34 (m, 3H), 7.24 - 7.18 (m, 4H), 7.14 - 7.10 (m, 1H), 5.37 (t, *J* = 7.4 Hz, 1H), 5.03 (sep, *J* = 6.3 Hz, 1H), 3.16 - 3.00 (m, 2H), 1.24 - 1.22 (m, 7H), 0.47 (s, 3H), 0.46 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 211.54, 172.73, 139.94, 138.33, 135.69, 131.00, 130.14, 129.76, 129.69, 128.19, 101.47, 83.07, 70.02, 36.41, 23.62, 0.00, -0.05.

91% ee, HPLC, OD-H, Hexane:^{i}PrOH = 250:1, 0.7 mL/min, 26.6 min (major), 25.8 min (minor).

HRMS (ESI): m/z calculated for $C_{22}H_{26}O_2SiNa$ $[M+Na]^+$: 373.1600, found:373.1607.



3ae*: In an oven dried 15 mL Schlenk tube equipped with a stirring bar, 0.01mmol (1.9 mg, 5 mol%) CuTC, 0.012 mmol (3.6 mg, 6 mol%) ligand L_5 were dissolved in 1 mL of dry ^{t}AmOH under argon atmosphere. The mixture was stirred for one hour at room temperature to form a light green solution. Then the tube was cooled to 0 ^{o}C, and 0.2 mmol **1ae** (1.0 equiv, 45.7 mg), 0.3 mmol (1.5 equiv, 79 mg) Me_2PhSi-Bpin were added to the tube under argon atmosphere. It was continued to stir for 48 hours at 0 ^{o}C. Then the final deep green solution was concentrated under vacuum to afford the crude product which was isolated through flash column chromatography (Eluent: PE/Et_2O = 97:3) to furnish the related product **3ae*** (54.7 mg, 75%) as colorless oil. $[\alpha]_D^{25}$ +24.0^o (c = 2.12, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60 - 7.55 (m, 2H), 7.36 - 7.32 (m, 3H), 7.23 - 7.17 (m, 4H), 7.14 - 7.10 (m, 1H), 5.36 (t, *J* = 7.4 Hz, 1H), 4.10 (t, *J* = 6.7 Hz, 2H), 3.13 (dd, *J* = 16.2, 7.2 Hz, 1H), 3.07 (dd, *J* = 16.2, 7.6 Hz, 1H), 1.65 - 1.55 (m, 2H), 1.37 (dq, *J* = 14.6, 7.3 Hz, 2H), 0.91 (t, *J* = 7.4 Hz, 3H), 0.463 (s, 3H), 0.457 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 211.50, 173.32, 139.92, 138.31, 135.70, 131.02, 130.17, 129.77, 129.70, 128.22, 101.60, 82.98, 66.55, 36.08, 32.45, 20.94, 15.52, 0.00, -0.08.

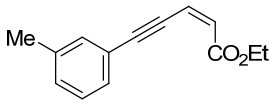
91% ee, HPLC, IC , Hexane:^{i}PrOH = 300:1, 0.6 mL/min, 51.1min (major), 49.6 min (minor).

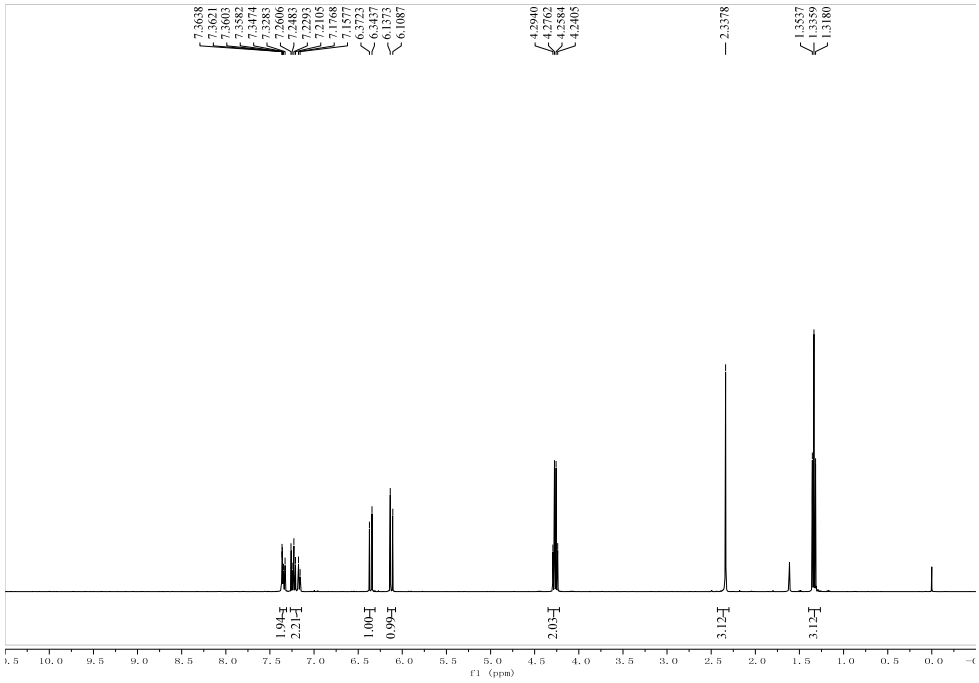
HRMS (ESI): m/z calculated for $C_{23}H_{28}O_2SiNa$ $[M+Na]^+$:387.1756, found:387.1765.

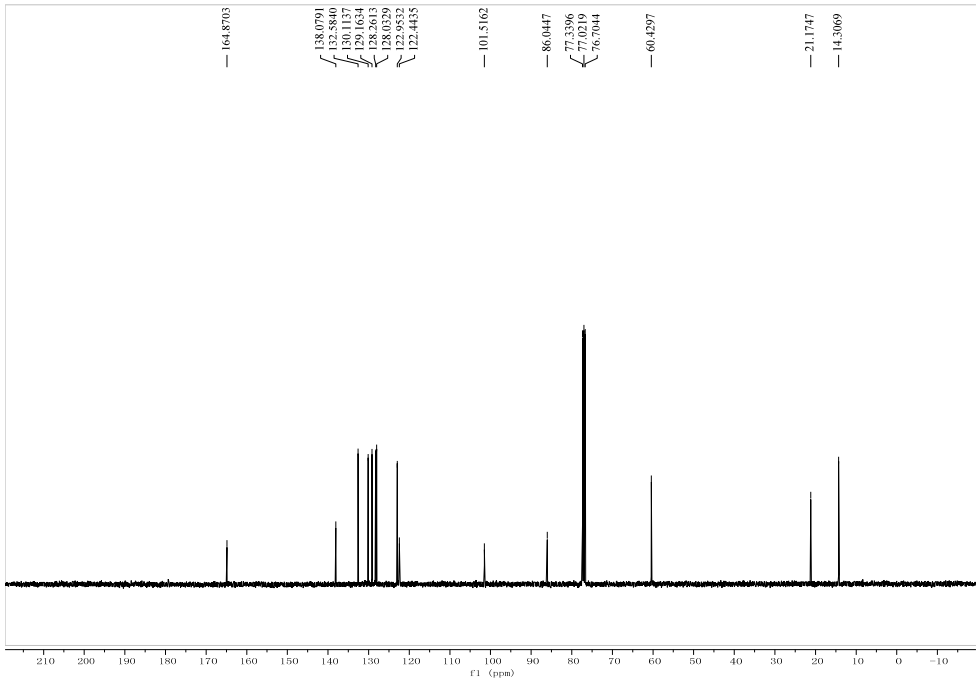
2. References

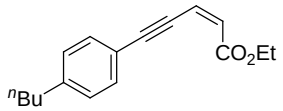
1. Takeuchi, R.; Tanabe,K.; Tanaka, S. *J. Org. Chem.* **2000**, *65*, 1558-1561.
2. Bates, C.G.; Saejueng, P.; Venkataraman. D. *Org. Lett.* **2004**, *6*, 1441-1444.
3. Tian, P.-P.; Cai, S.-H.; Liang, Q.-J.; Zhou, X.-Y.; Xu, Y.-H.; Loh. T. P. *Org. Lett.* **2015**, *17*, 1636-1639.

3. ^{1}H NMR, ^{13}C NMR and HPLC Spectra of the Enynoates and Products





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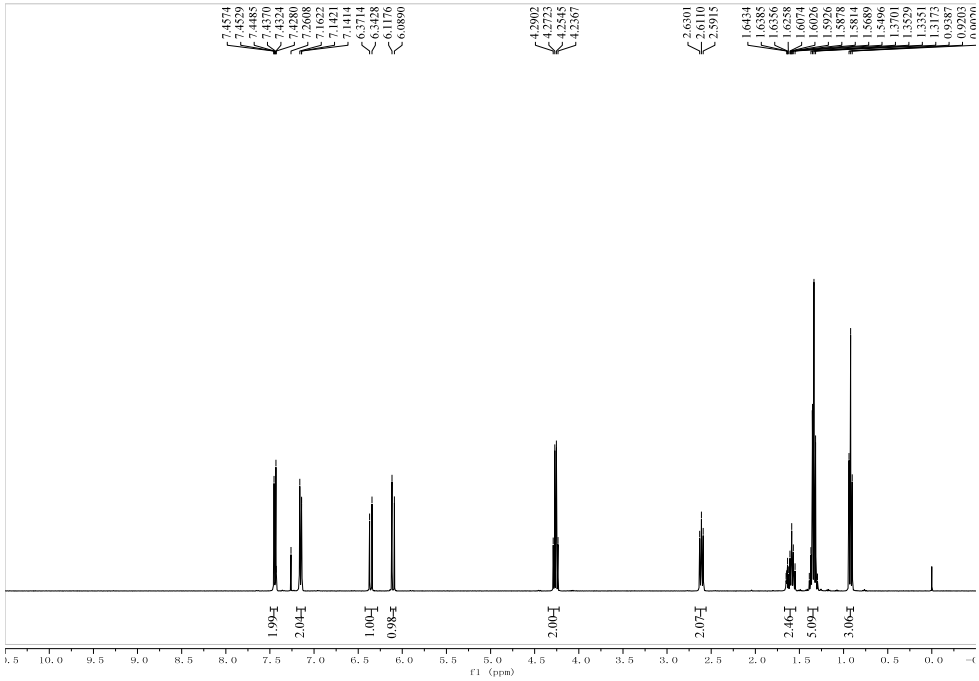
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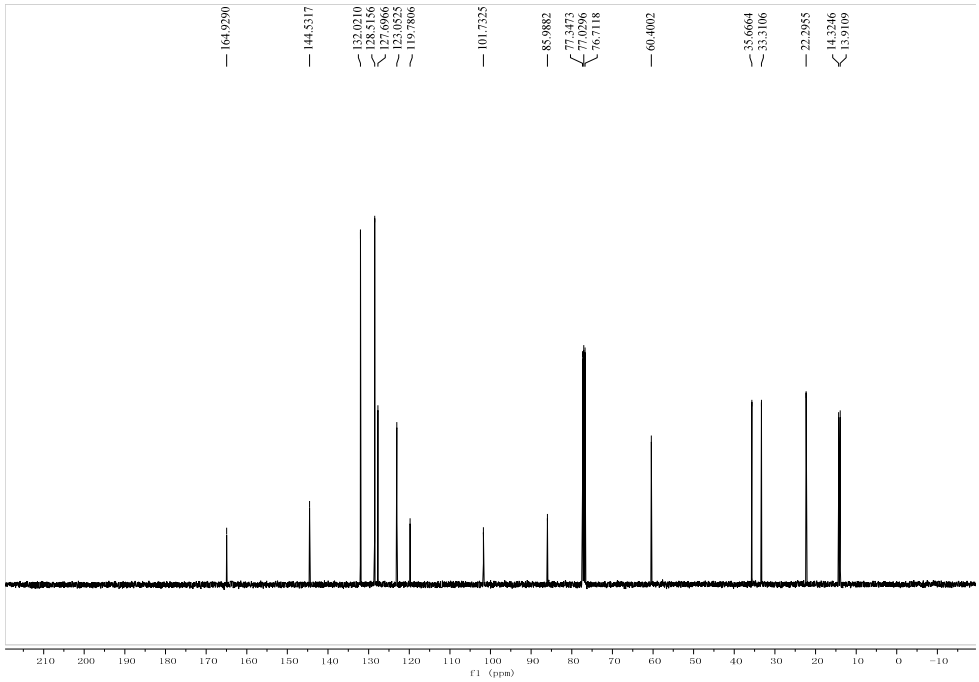
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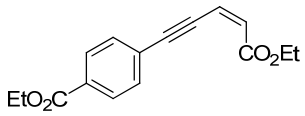
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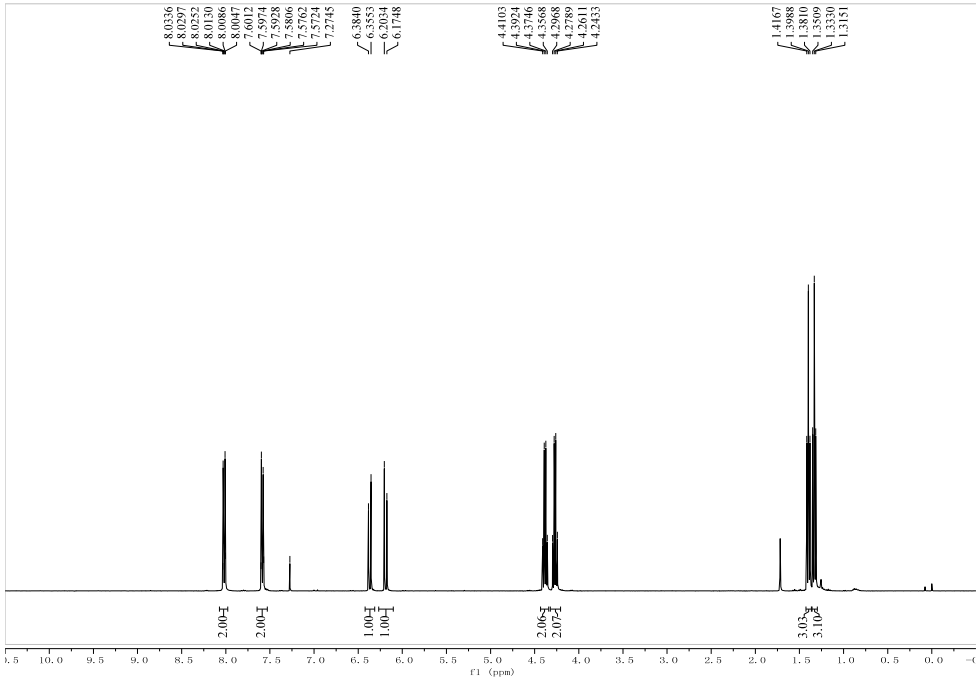
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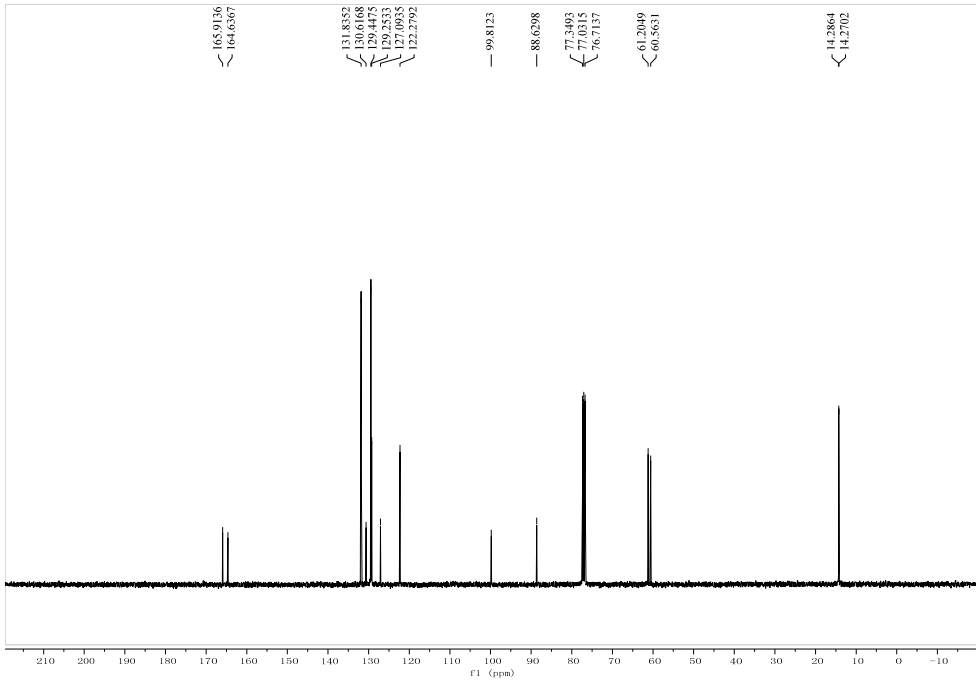
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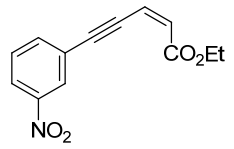
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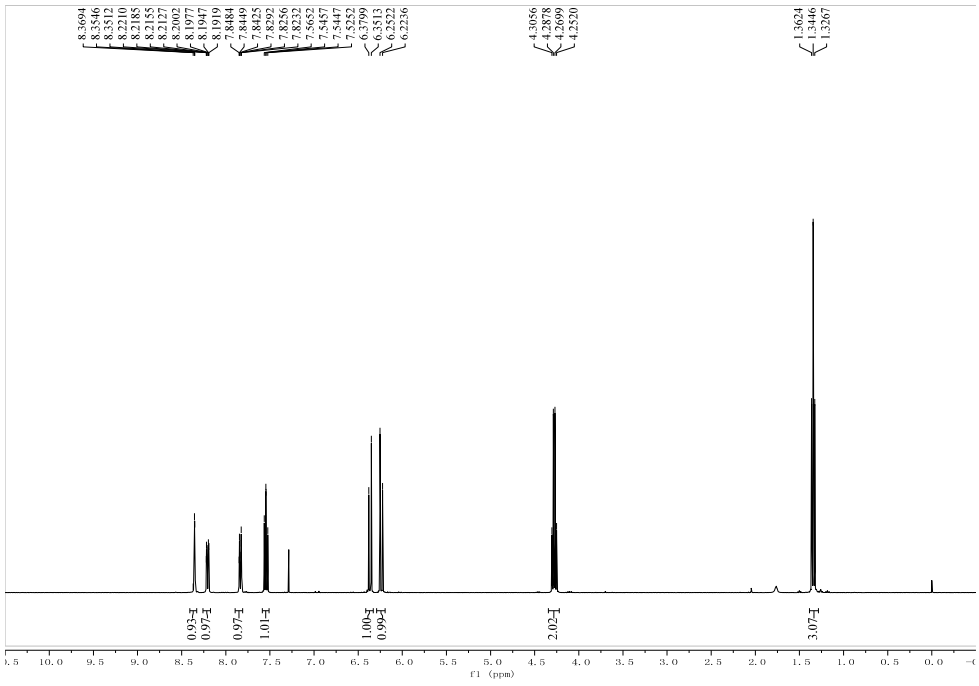
NO2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7.8292
7.8256
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7.5447
7.5252
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6.3513
6.2522
6.2236
4.3056
4.2878
4.2699
4.2520
1.3624
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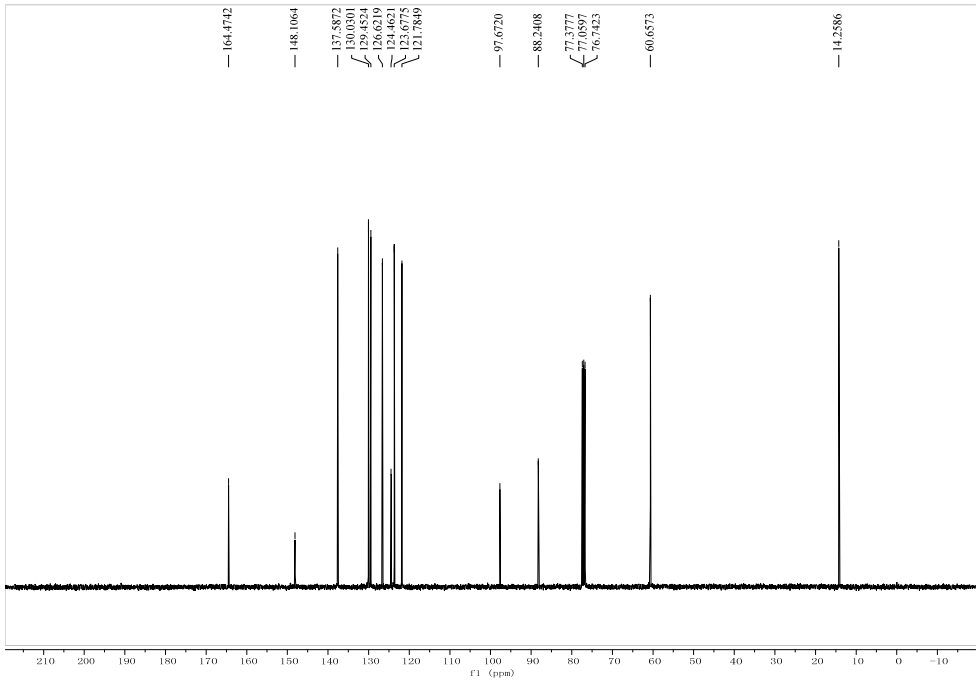
0.97
0.97
1.01
1.00
0.99
2.02
3.07
f1 (ppm)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121.7849
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88.2408
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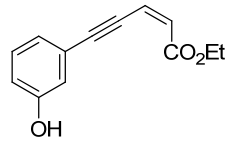
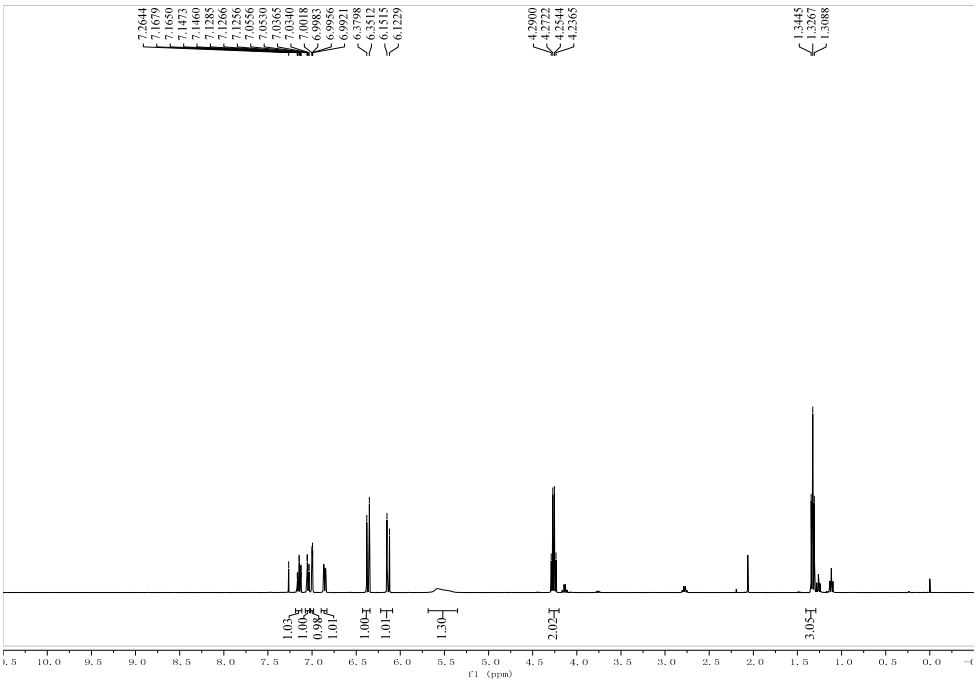
77.0597
76.7423
60.6573
14.2586
f1 (ppm)


CO2Et
OH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7.0340
7.0018
6.9983
6.9956
6.9921
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6.3512
6.1515
6.1229
4.2900
4.2722
4.2544
4.2365
1.3445
1.3267
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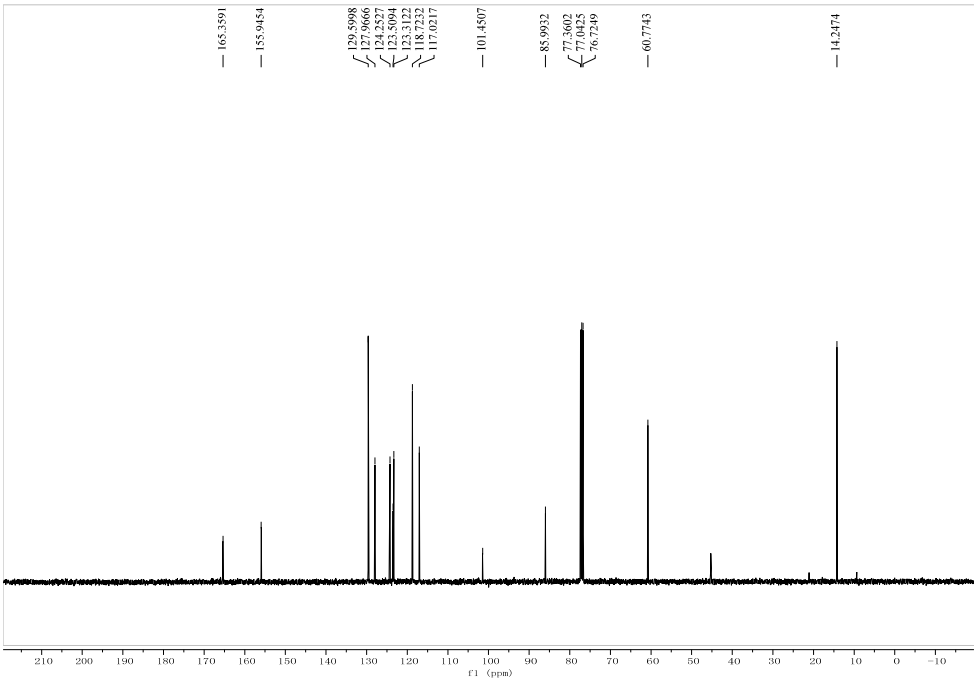
1.01
1.00
1.01
1.30
2.02
3.05
f1 (ppm)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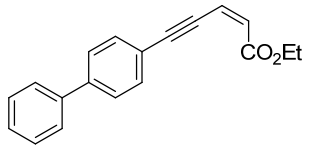
60.7743
14.2474
f1 (ppm)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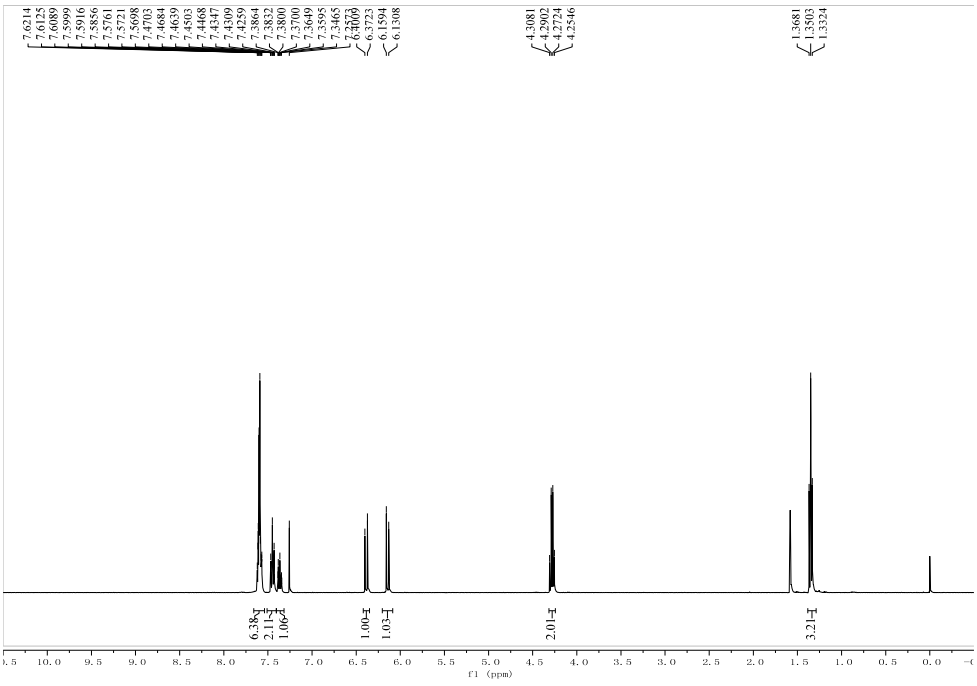
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7.4468
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7.4309
7.4259
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7.3832
7.3700
7.3649
7.3595
7.3465
6.4009
6.3723
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6.1308
4.3081
4.2902
4.2724
4.2546
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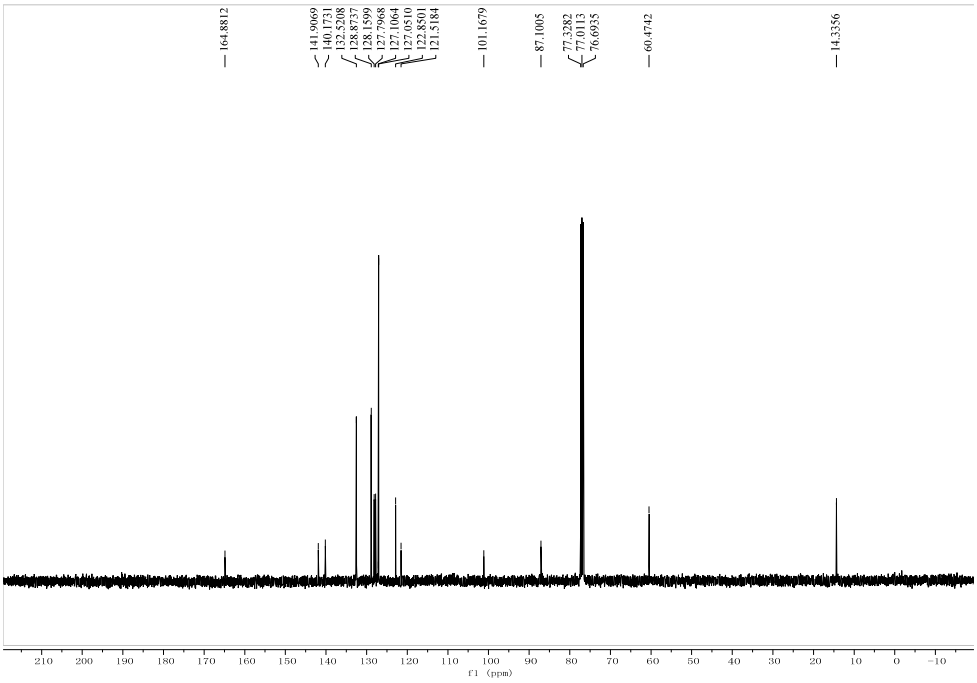
3.21
f1 (ppm)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128.1599
127.7968
127.1064
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122.8501
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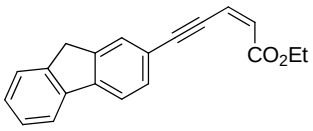
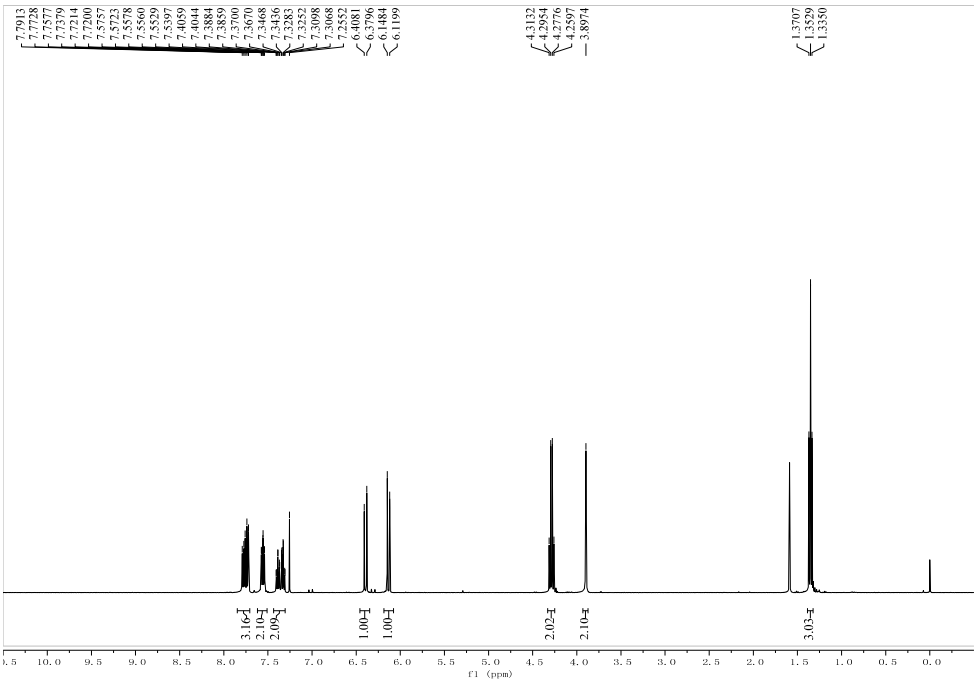
87.1005
77.3282
77.0113
76.6935
60.4742
14.3356
f1 (ppm)


CO2Et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7.5529
7.5397
7.4059
7.4044
7.3884
7.3859
7.3700
7.3670
7.3468
7.3436
7.3283
7.3252
7.3098
7.3068
7.2552
6.4081
6.3796
6.1484
6.1199
4.3132
4.2954
4.2776
4.2597
3.8974
1.3707
1.3529
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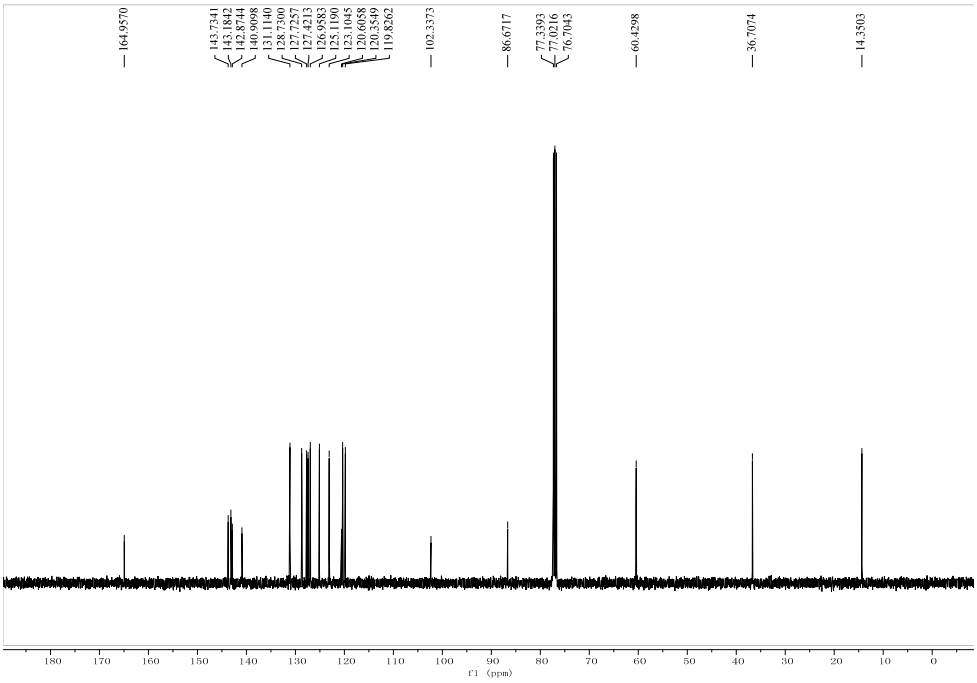
2.10
2.09
1.00
1.00
2.02
2.10
3.03
f1 (ppm)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125.1190
123.1045
120.6058
120.3549
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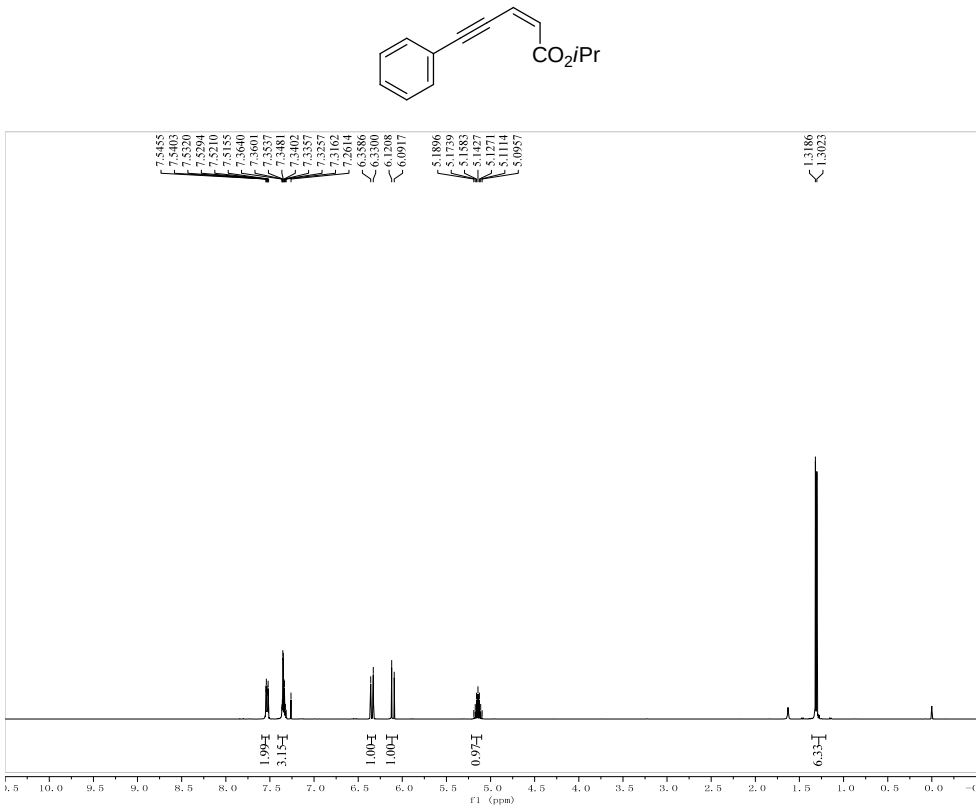
102.3373
86.6717
77.3393
77.0216
76.7043
60.4298
36.7074
14.3503
f1 (ppm)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7.3257
7.3162
7.2614
6.3586
6.3300
6.1208
6.0917
5.1896
5.1739
5.1583
5.1427
5.1271
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1.00
1.00
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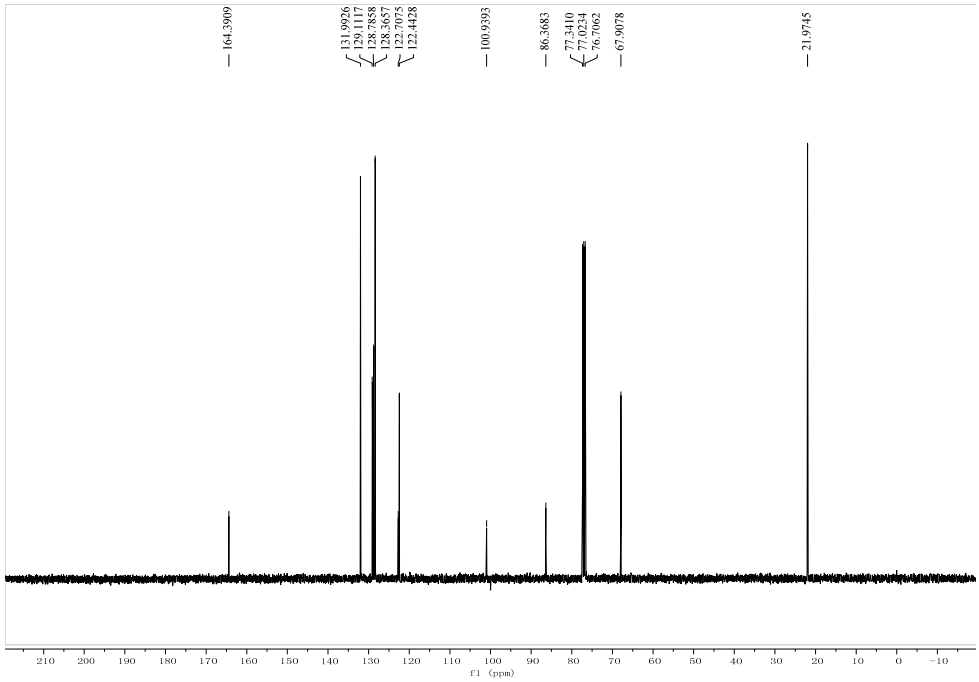
6.33
f1 (ppm)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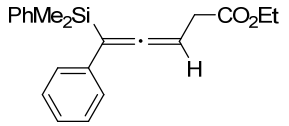
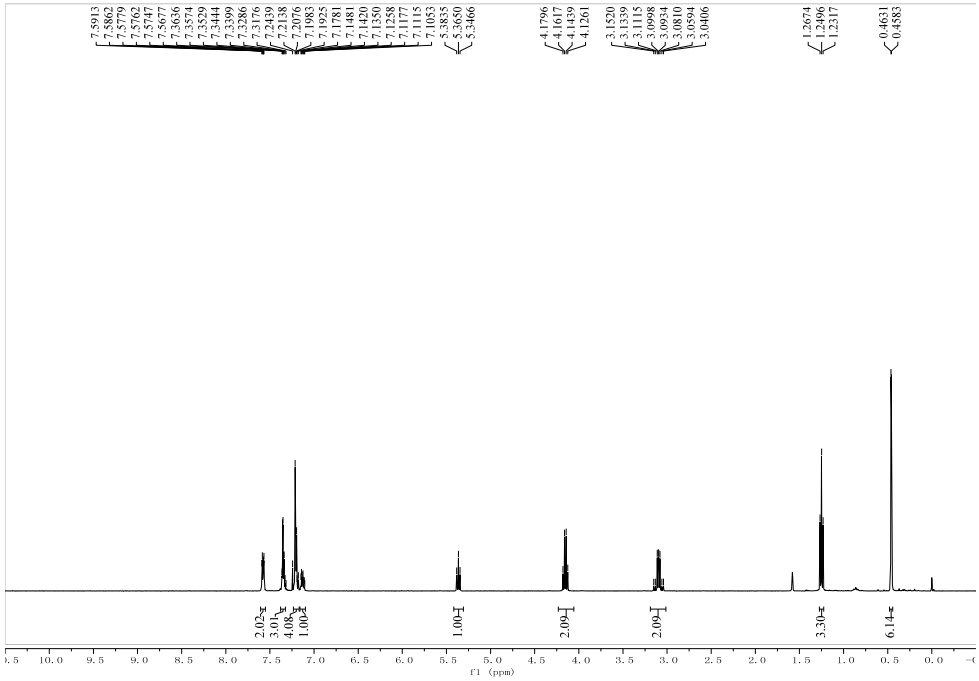
76.7062
67.9078
21.9745
f1 (ppm)


PhMe2Si
CO2Et
H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7.3444
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7.3286
7.3176
7.2439
7.2138
7.2076
7.1983
7.1925
7.1781
7.1481
7.1420
7.1350
7.1258
7.1177
7.1115
7.1053
5.3835
5.3650
5.3466
4.1796
4.1617
4.1439
4.1261
3.1520
3.1339
3.1115
3.0998
3.0934
3.0810
3.0594
3.0406
1.2674
1.2496
1.2317
0.4631
0.4583
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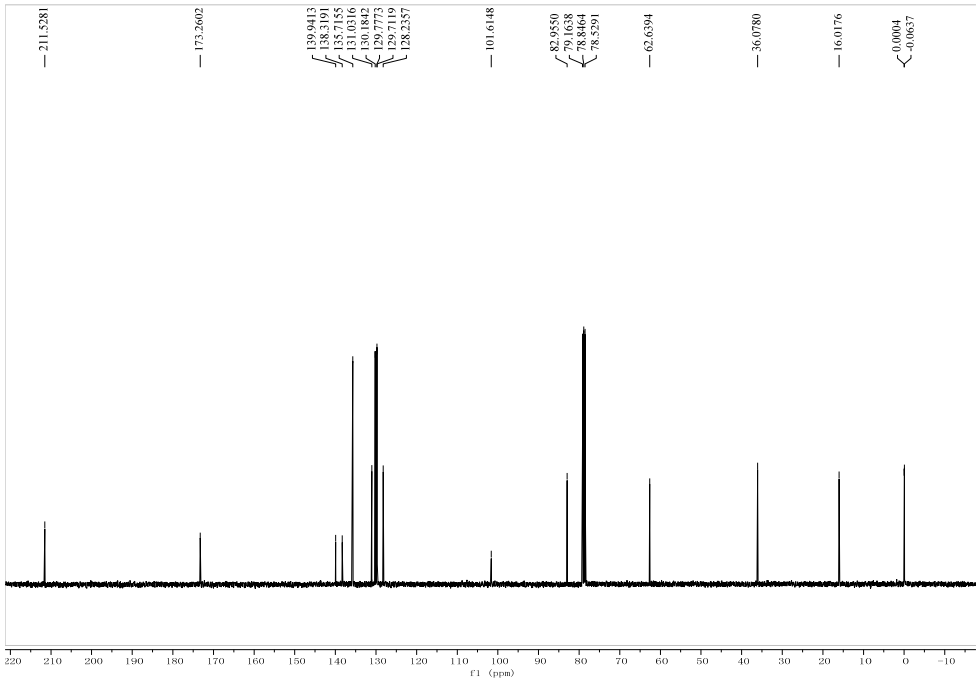
3.01
4.08
1.00
1.00
2.09
2.09
3.30
6.14
f1 (ppm)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101.6148
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16.0176
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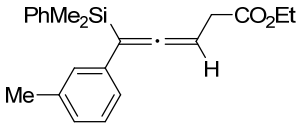
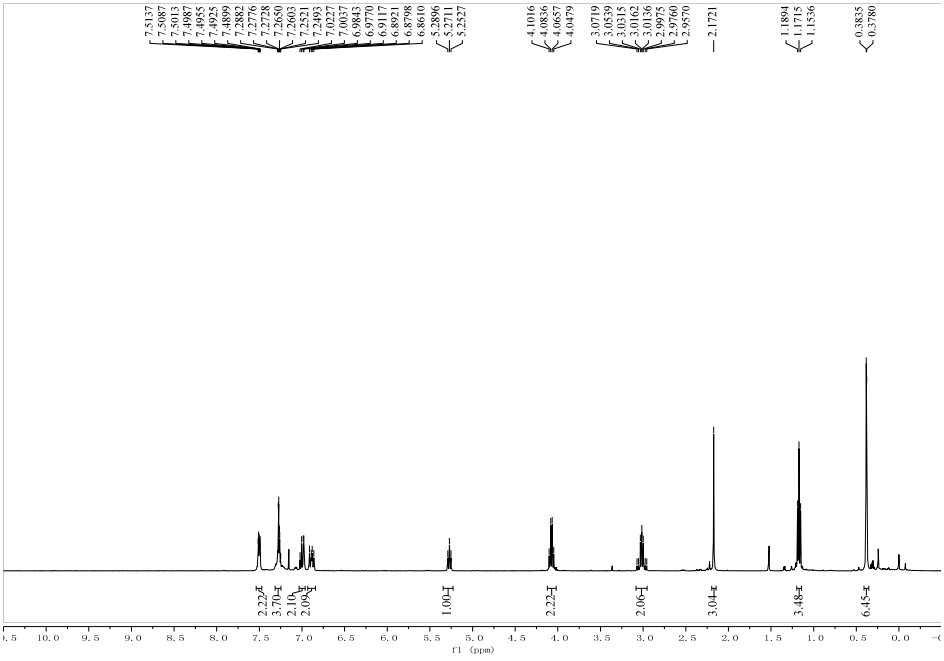
f1 (ppm)


PhMe2Si
CO2Et
H
Me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7.2521
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7.0227
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6.8798
6.8610
5.2896
5.2771
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3.0539
3.0315
3.0162
3.0136
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2.9570
2.1721
1.1894
1.1715
1.1536
0.3835
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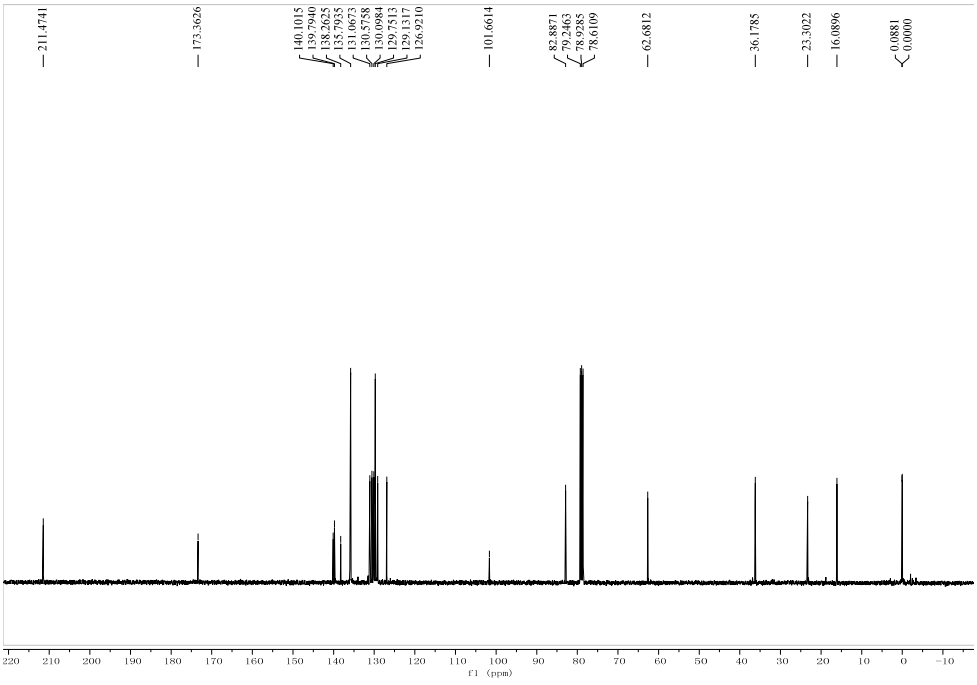
f1 (ppm)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126.9210
101.6614
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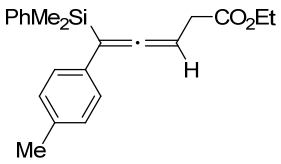
f1 (ppm)


PhMe2Si
CO2Et
H
Me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7.1440
7.1327
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6.8107
5.1726
5.1542
5.1358
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3.9691
3.9514
3.9336
2.9508
2.9326
2.9104
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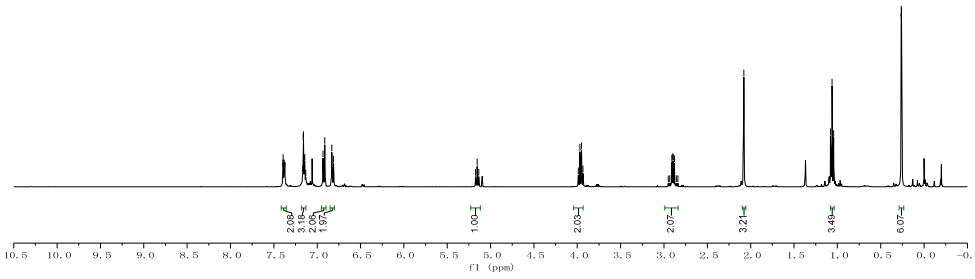
0.2594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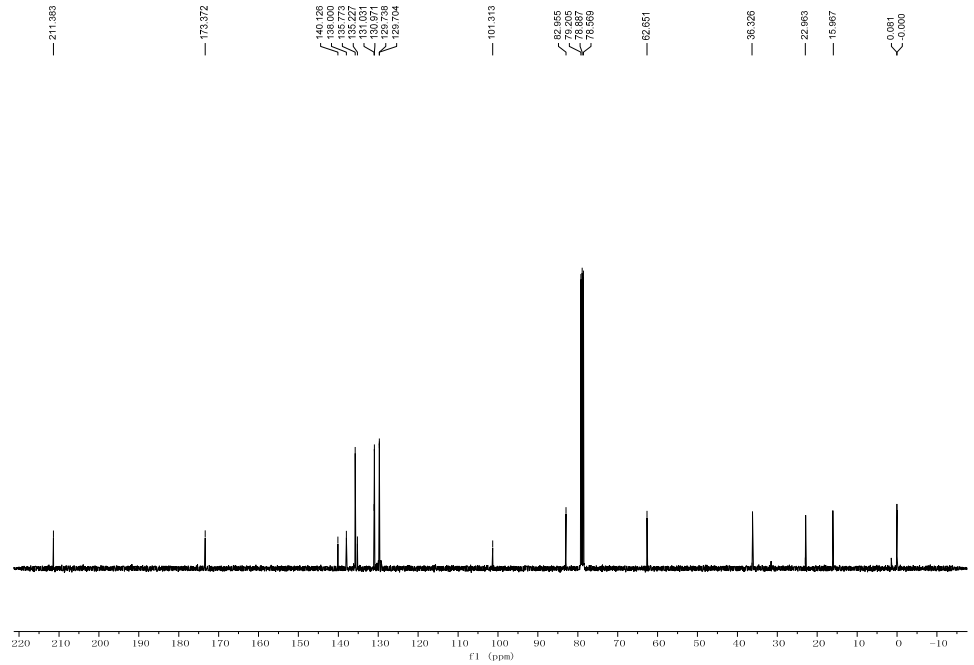
6.07
f1 (ppm)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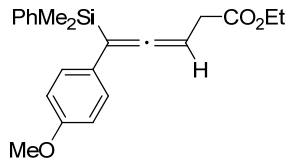
f1 (ppm)


PhMe2Si
CO2Et
H
MeO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5.2774
5.2541
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4.0675
4.0497
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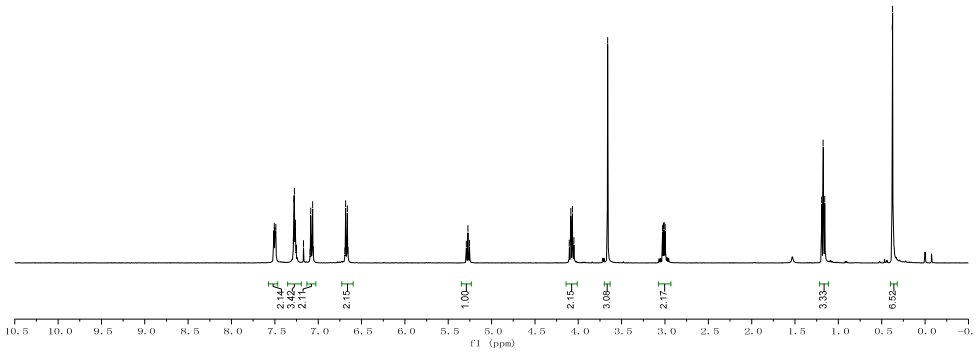
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3.06
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6.52
f1 (ppm)


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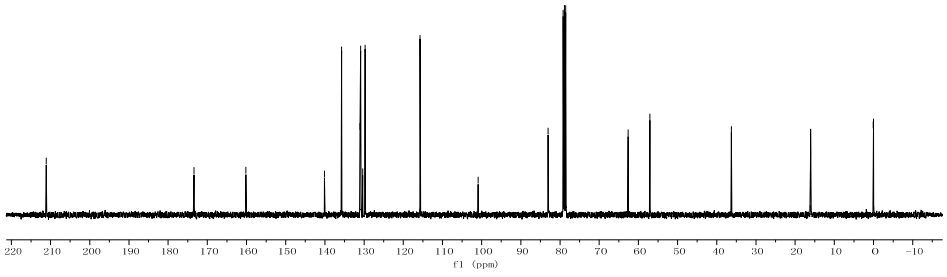
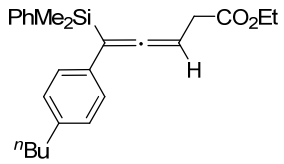
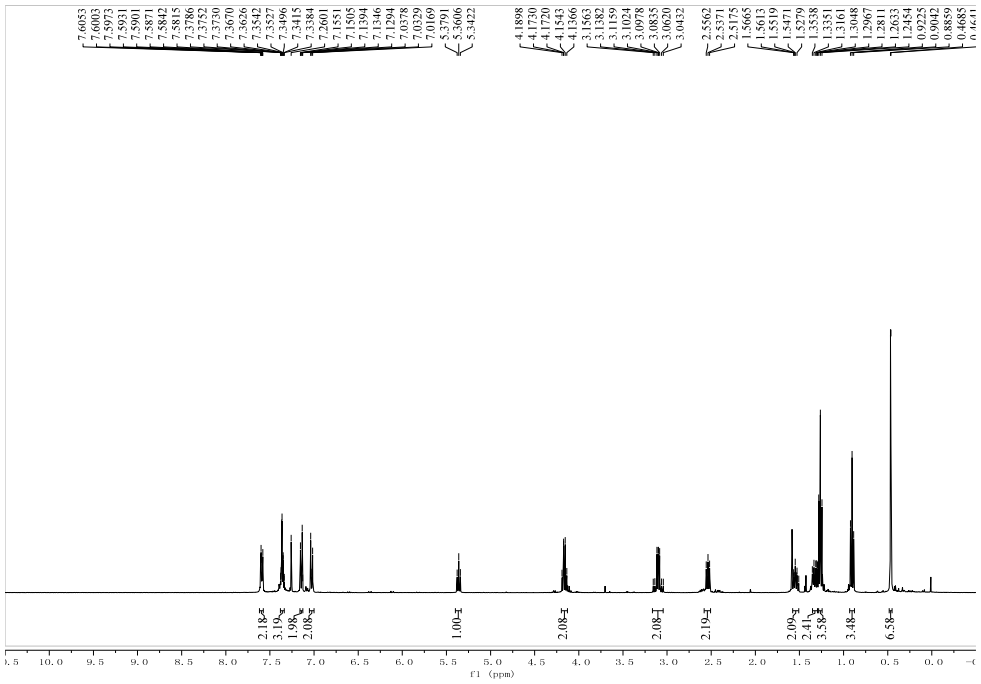

f1 (ppm)


PhMe2Si
CO2Et
H
nBu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7.1294
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1.2811
1.2633
1.2454
0.9225
0.9042
0.8859
0.4685
2.18
3.19
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2.08
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2.08
2.08
2.19
2.09
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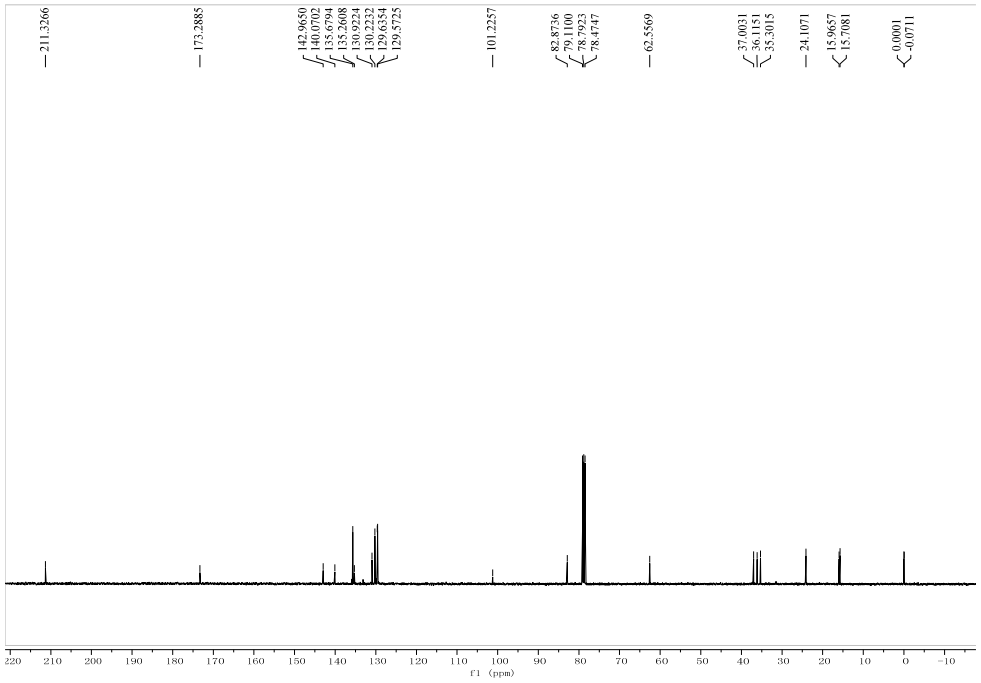
6.58
f1 (ppm)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82.8736
79.1100
78.7923
78.4747
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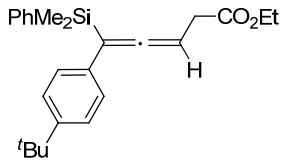
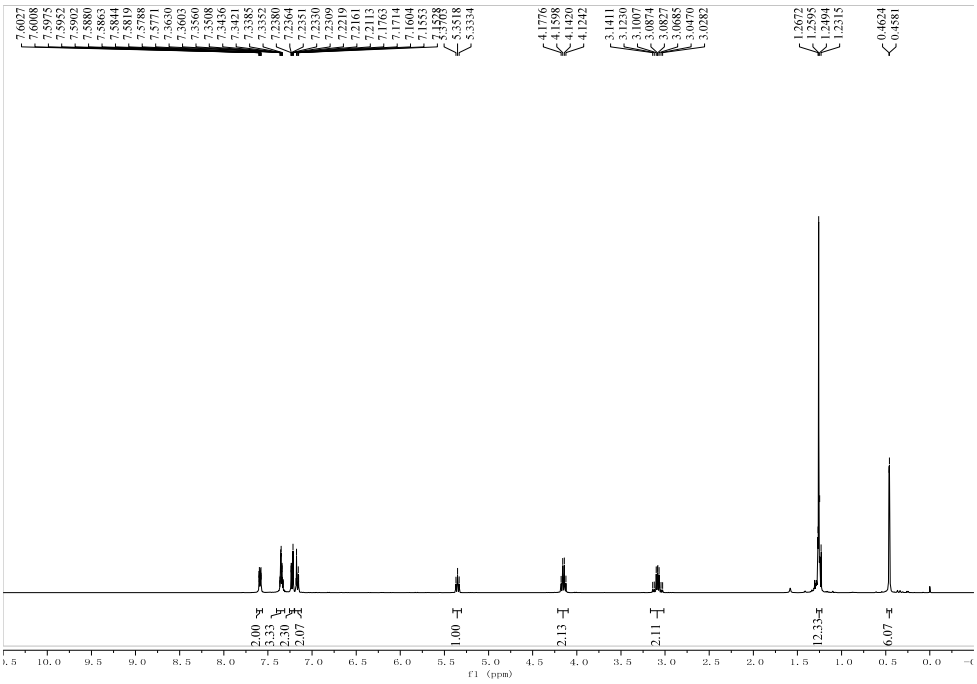
-0.0711
f1 (ppm)


PhMe2Si
CO2Et
H
tBu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3.0470
3.0282
1.2672
1.2595
1.2494
1.2315
0.4624
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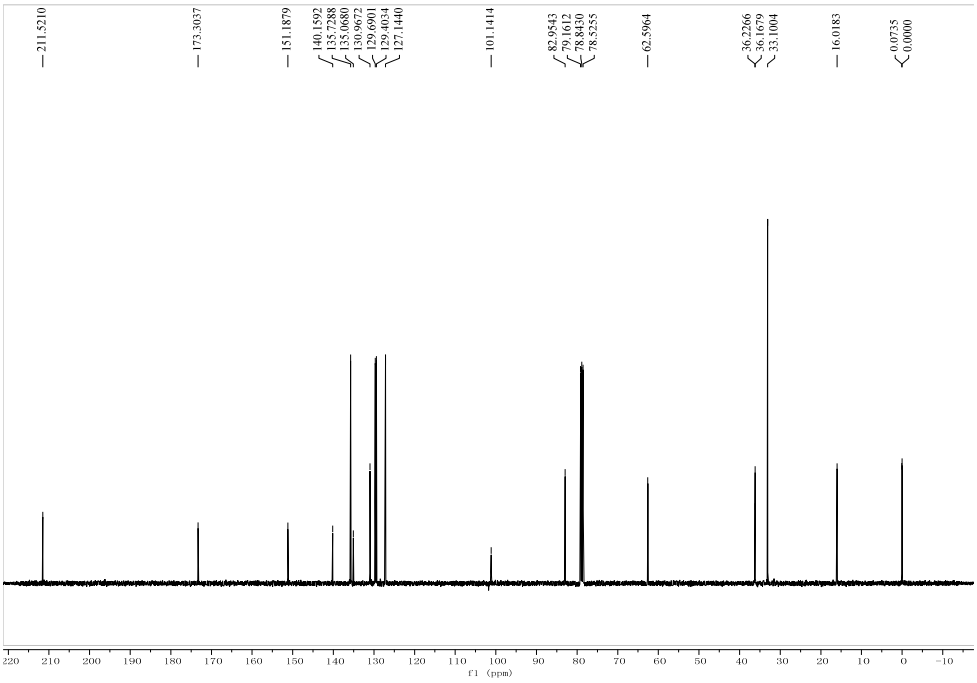
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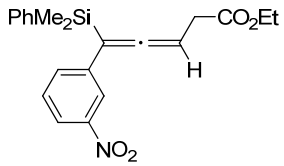
0.0000
f1 (ppm)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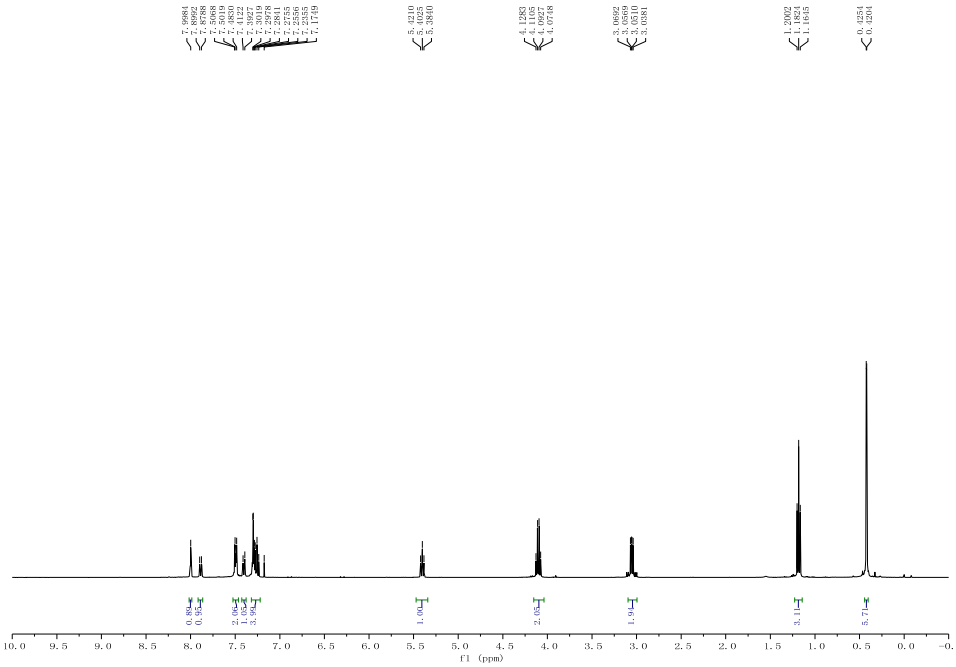
NO2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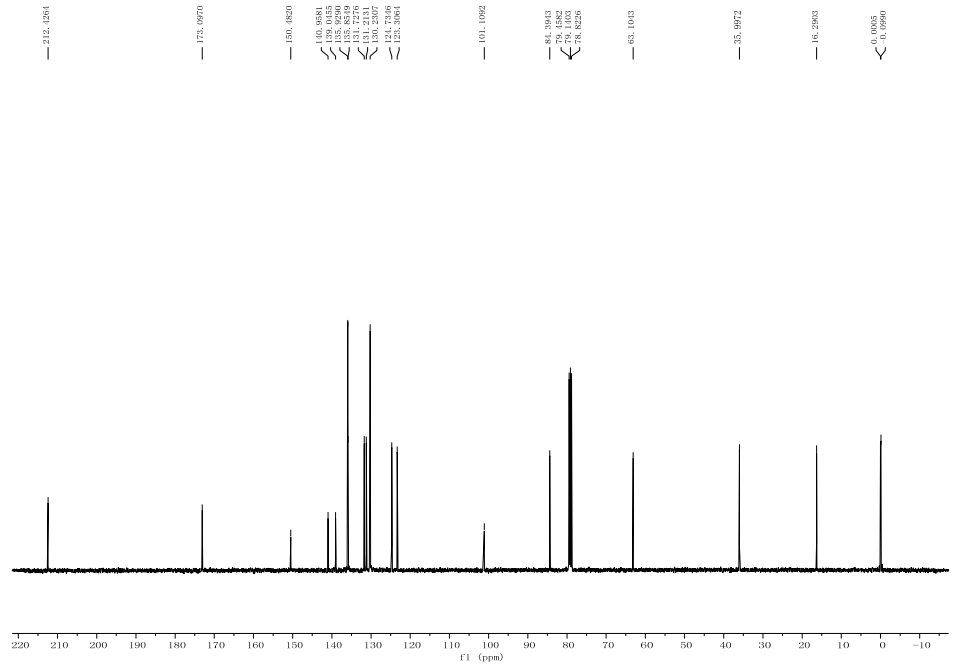
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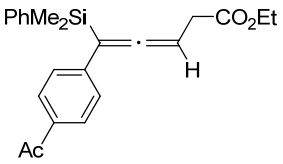
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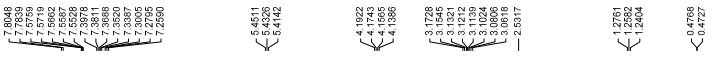
Ac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7.2590
5.4511
5.4295
5.4142
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3.1728
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3.1232
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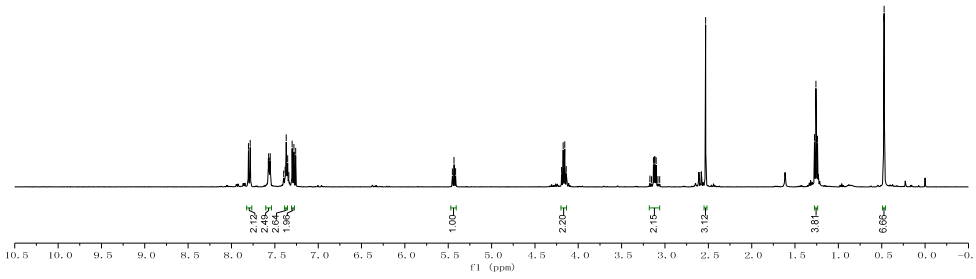
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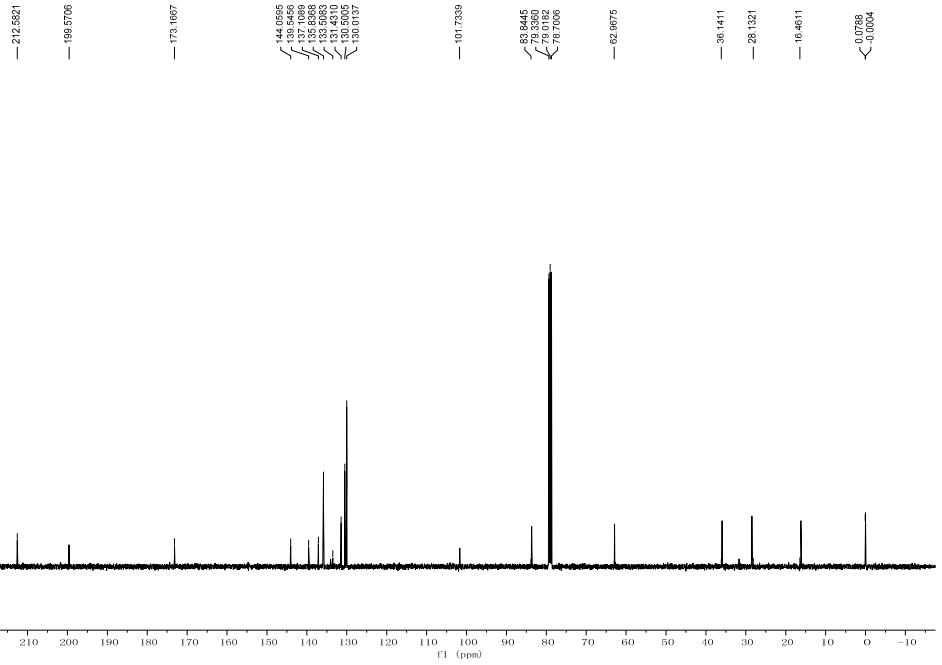
f1 (ppm)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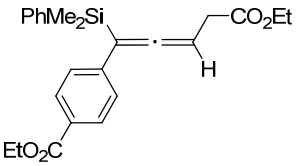
f1 (ppm)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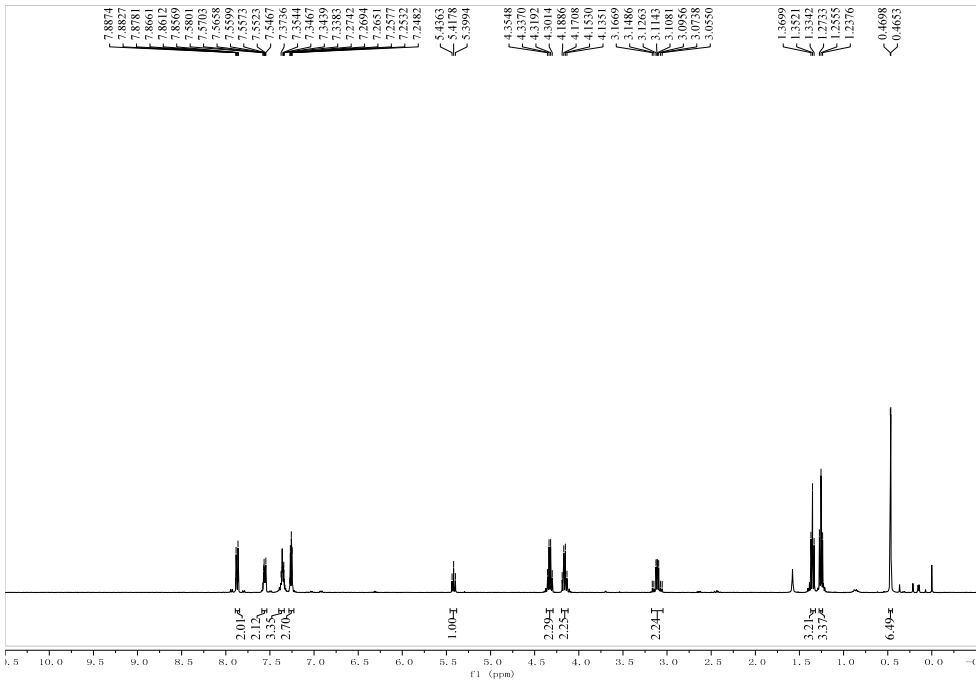
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7.3439
7.3383
7.2742
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7.2577
7.2532
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4.3014
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4.1708
4.1530
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3.1143
3.1081
3.0956
3.0738
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1.3521
1.3342
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1.2555
1.2376
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0.4653
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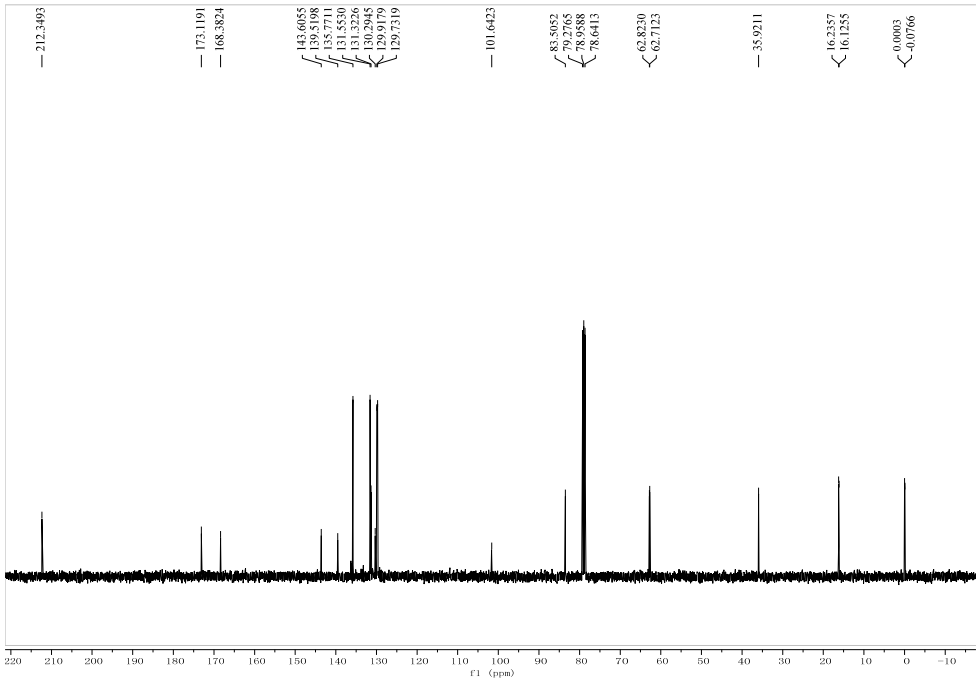
f1 (ppm)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83.5052
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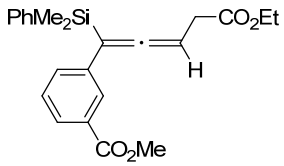
f1 (ppm)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CO2Et
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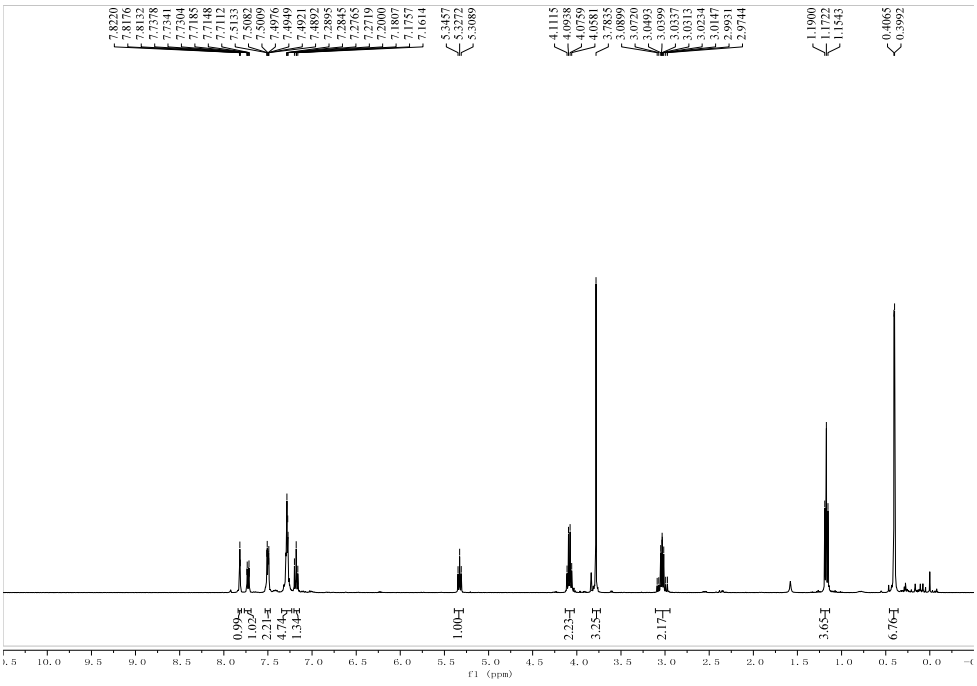
CO2Me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3.0720
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3.0399
3.0337
3.0133
3.0034
3.0147
2.9931
2.9744
1.1900
1.1722
1.1543
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0.3992
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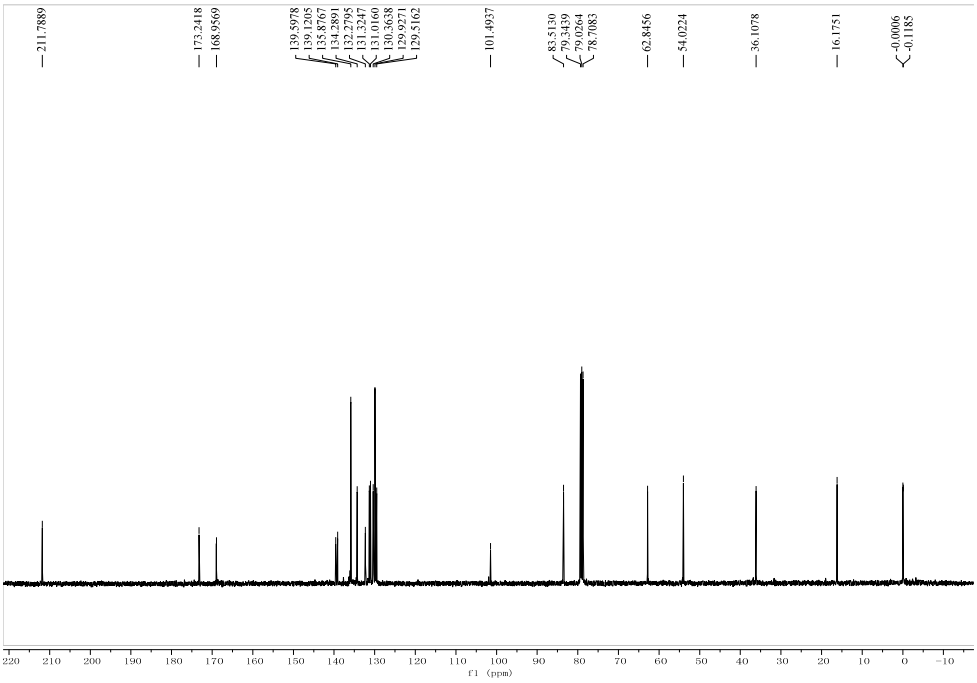
f1 (ppm)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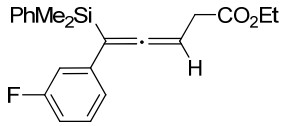
f1 (ppm)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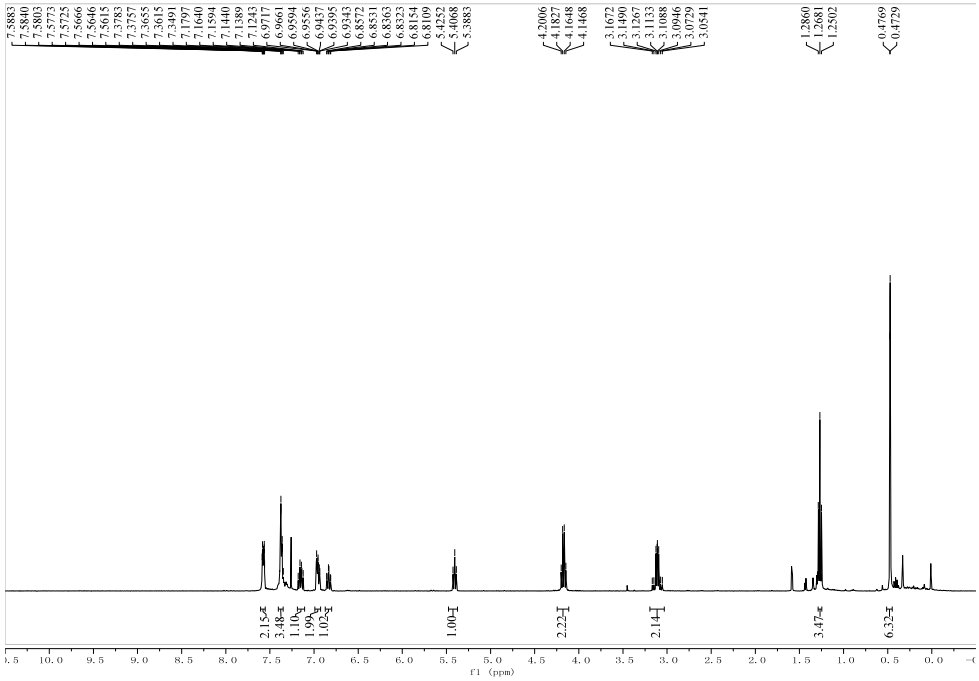
CO2Et
H
F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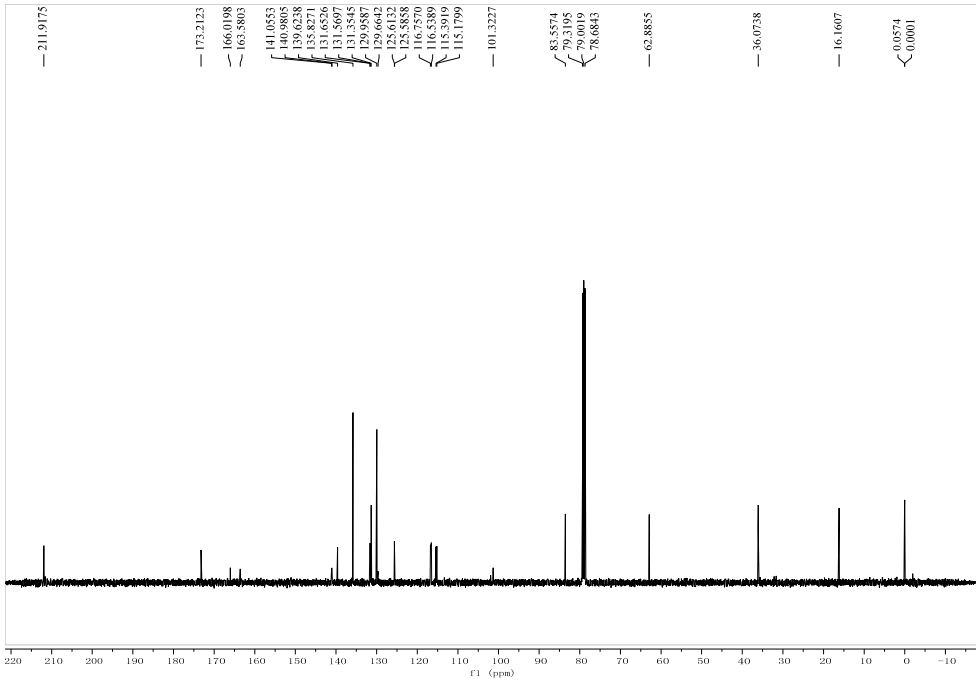
f1 (ppm)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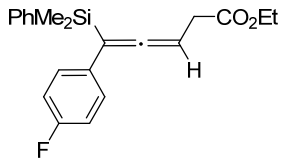
0.0001
f1 (ppm)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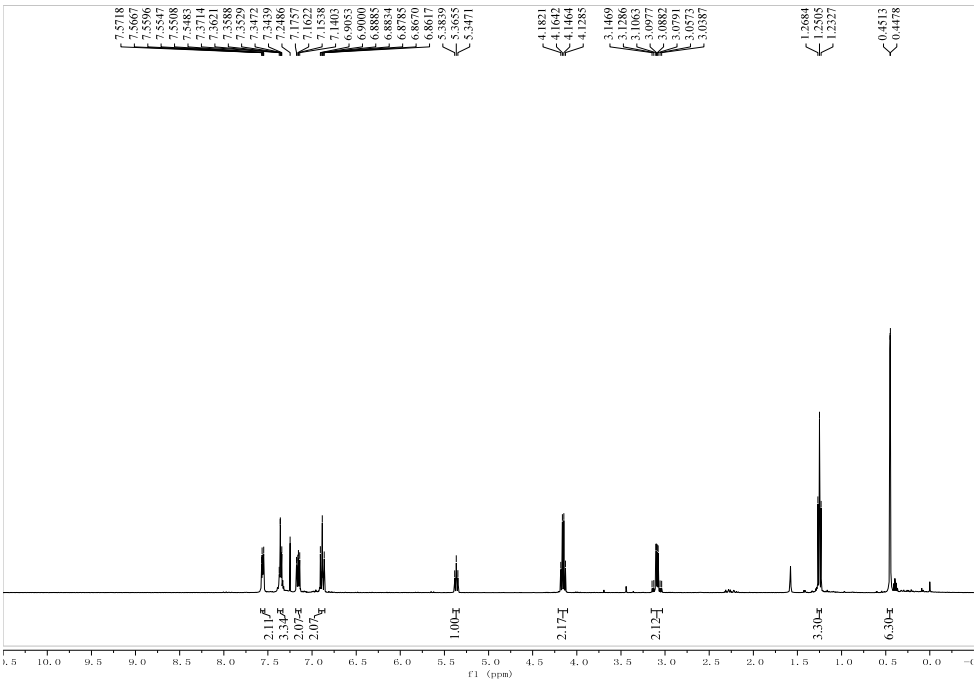
CO2Et
H
F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2.07
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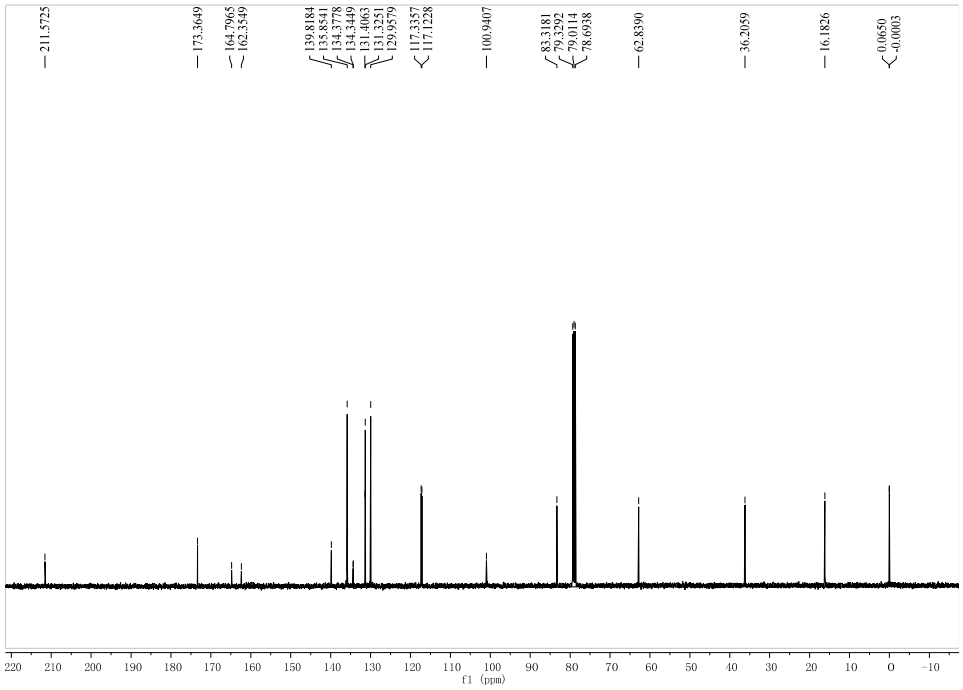
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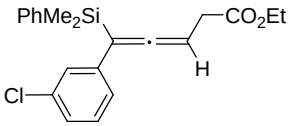
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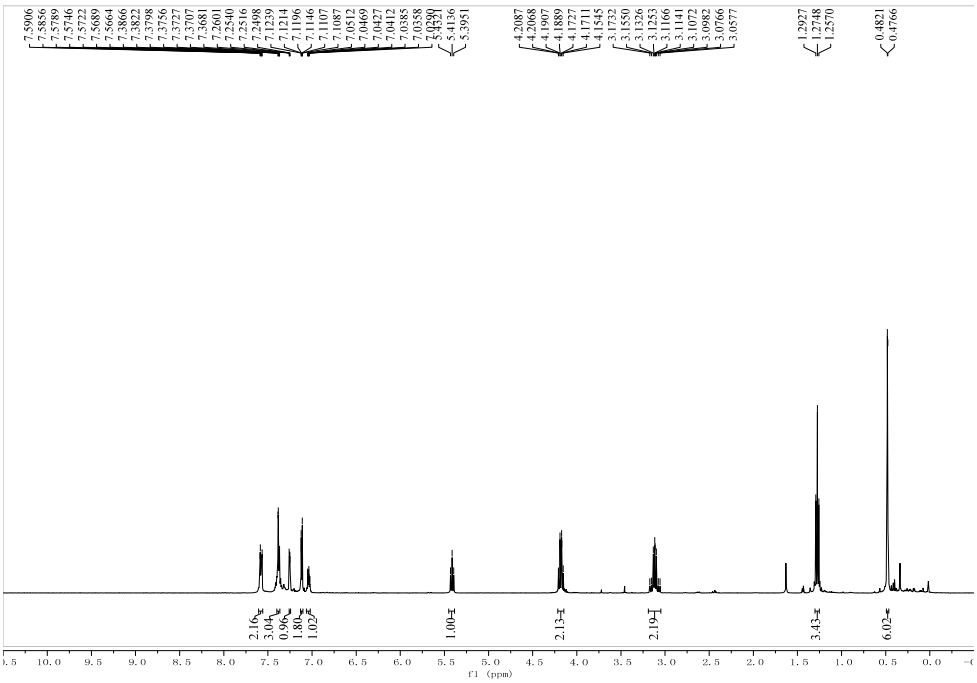
Cl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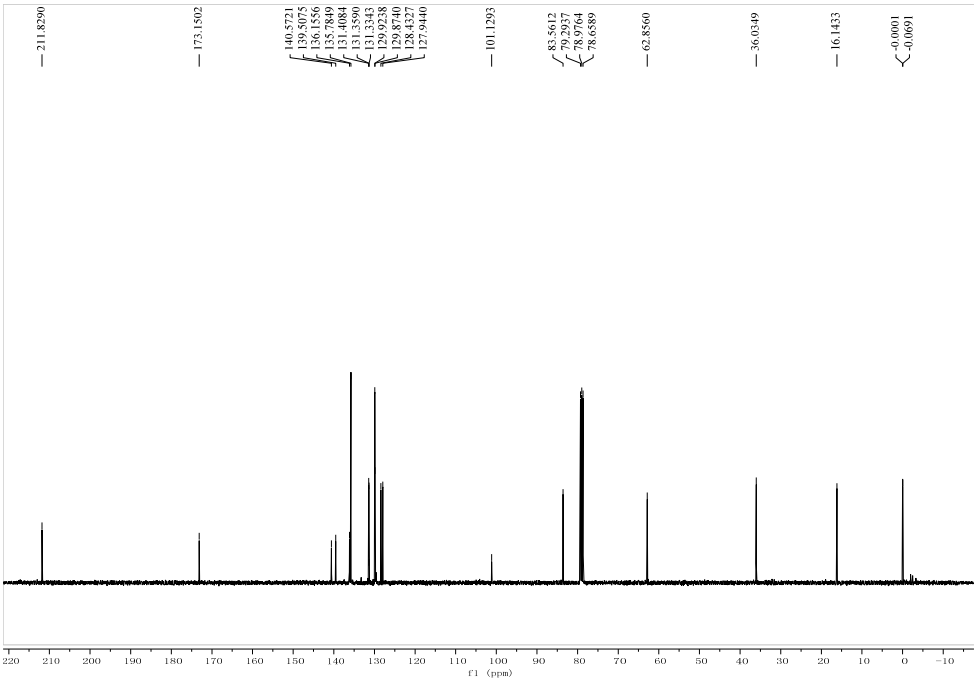
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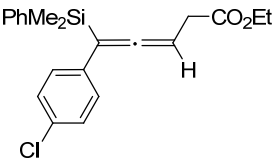
PhMe2Si
CO2Et
H
Cl


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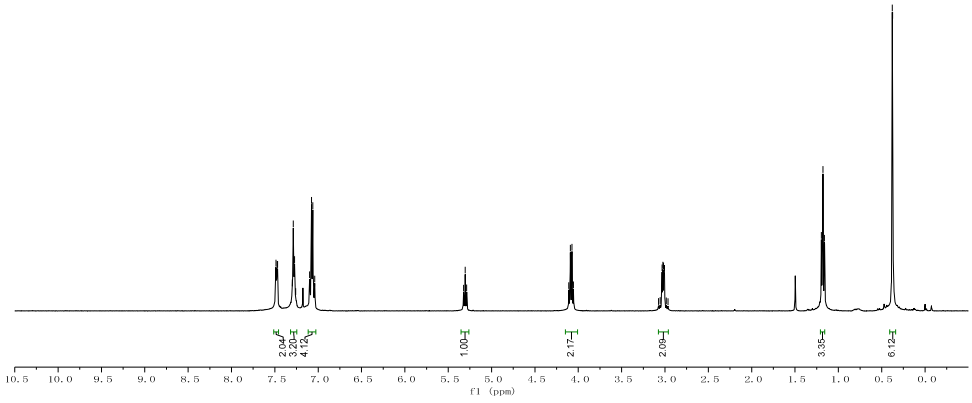
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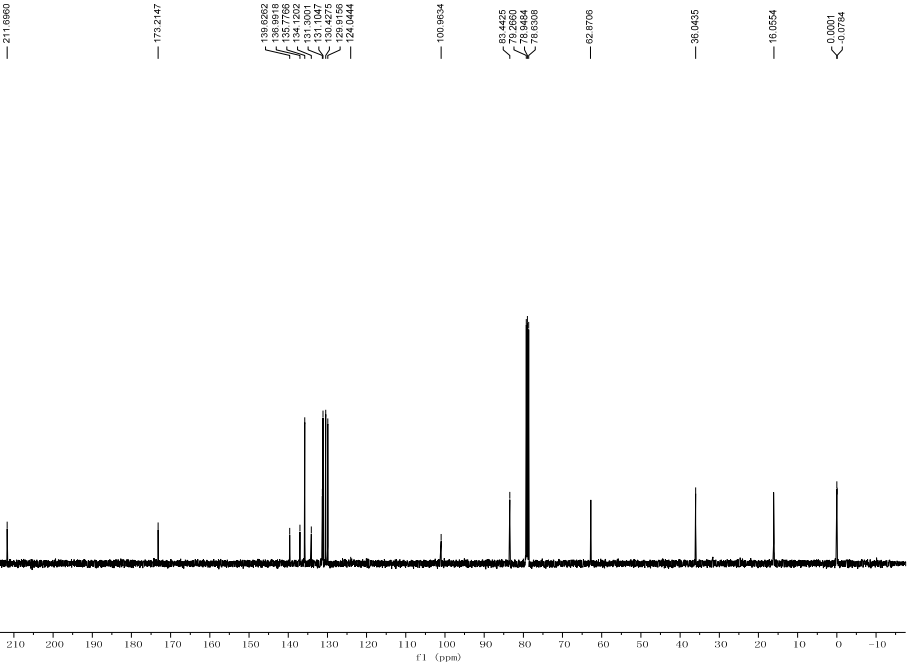
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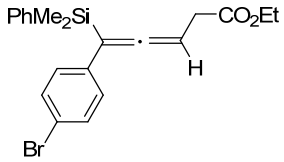
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CO2Et
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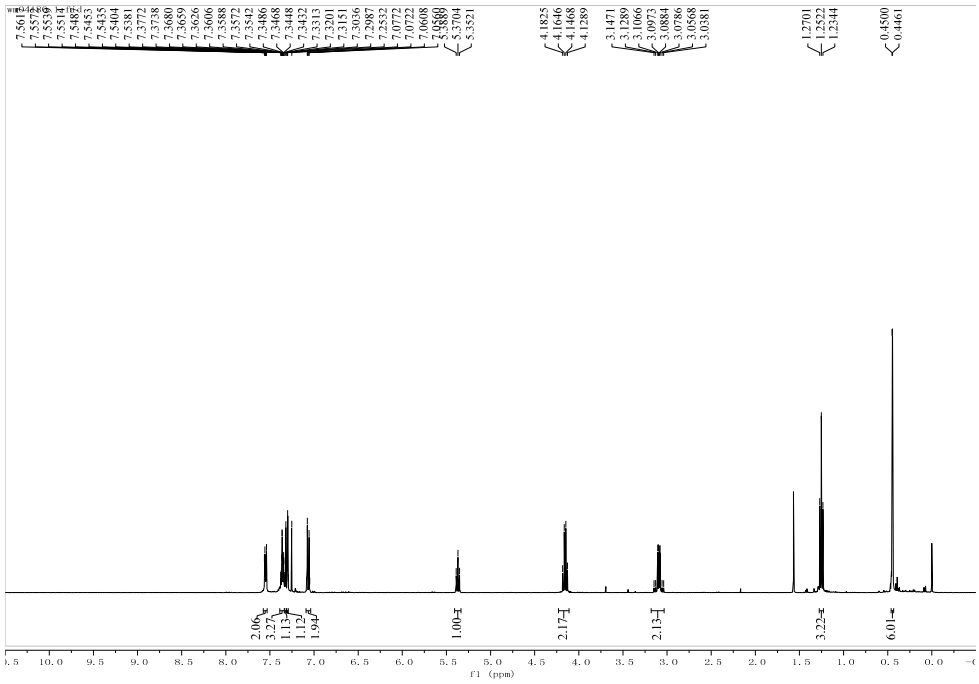
Br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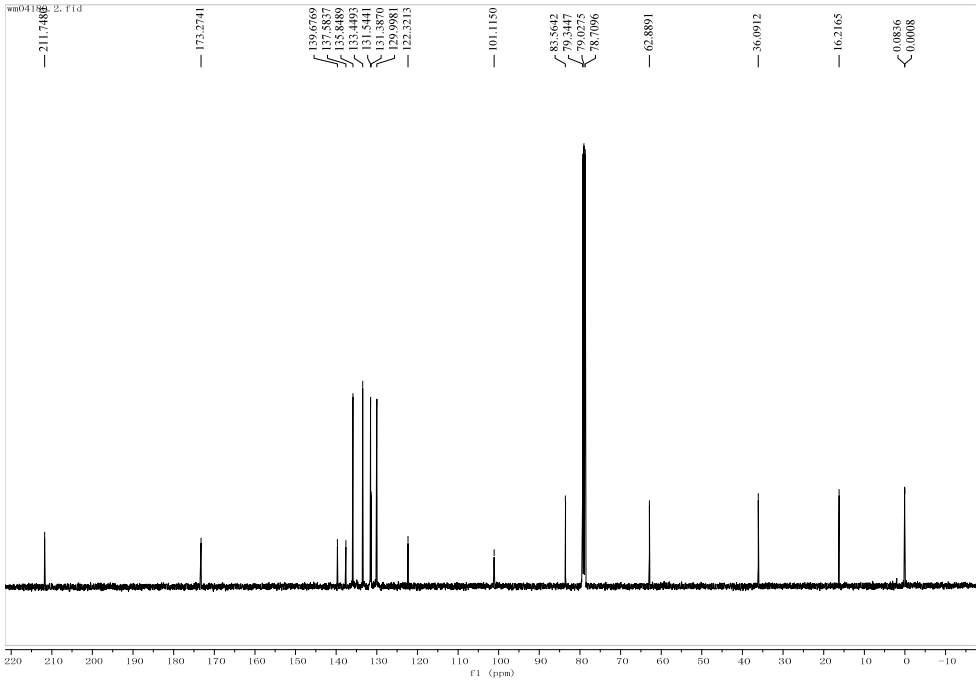
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101.1150
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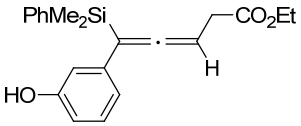
0.0008
f1 (ppm)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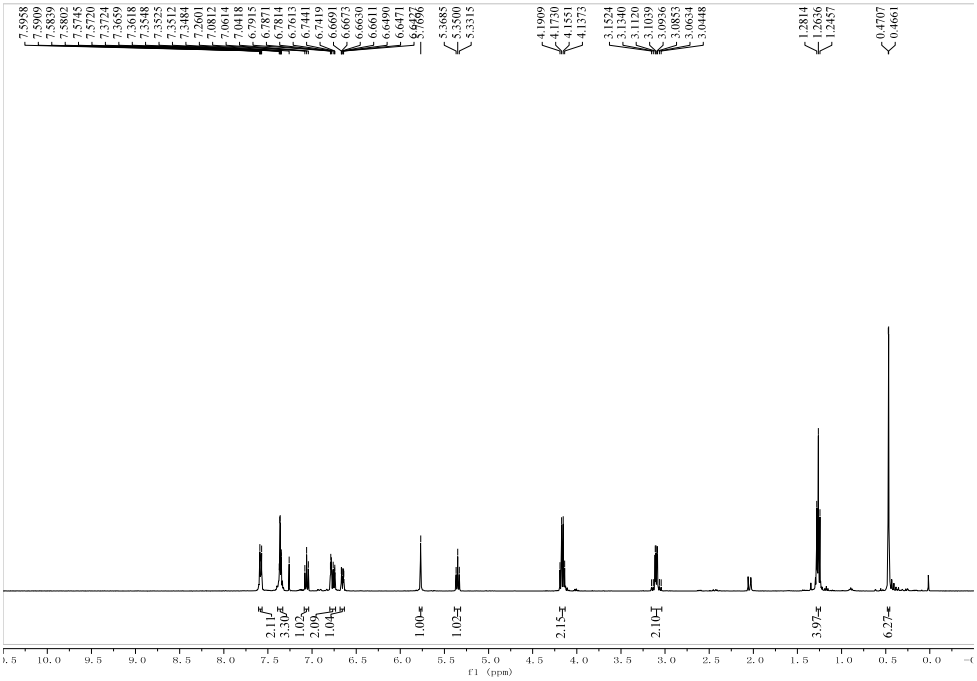
CO2Et
H
HO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6.4866
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5.3500
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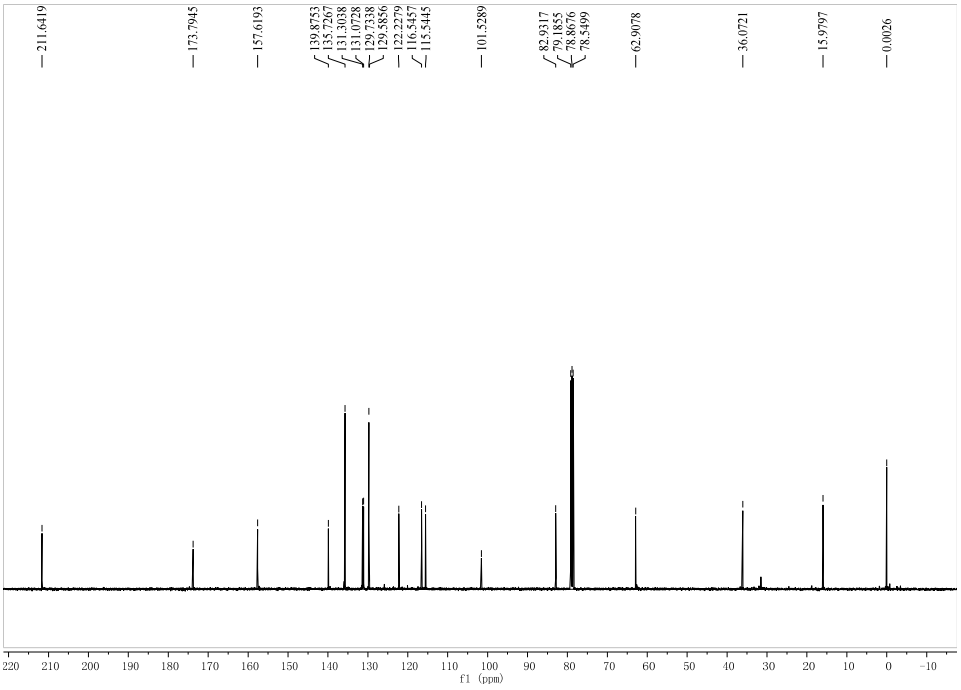
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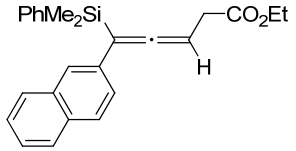
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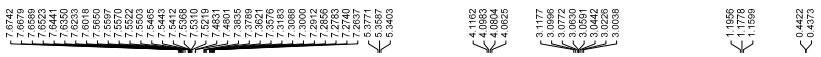
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7.2740
7.2677
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4.0804
4.0625
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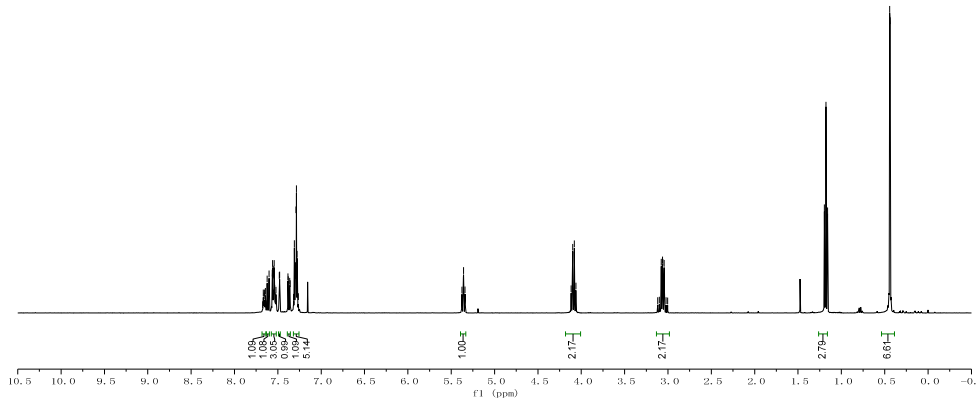
0.4373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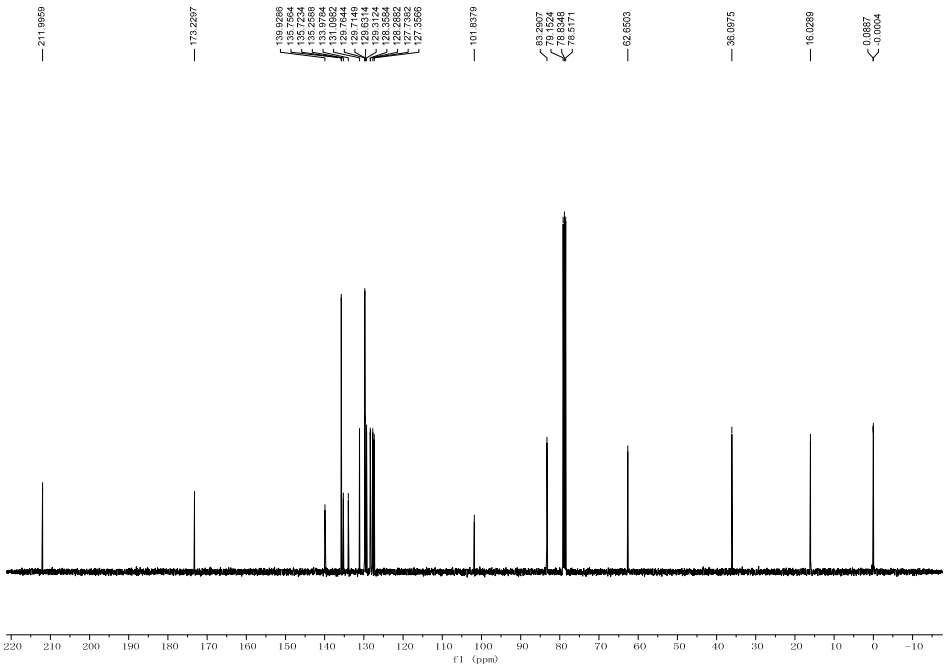
f1 (ppm)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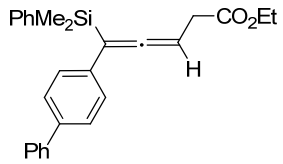
-0.0004
f1 (ppm)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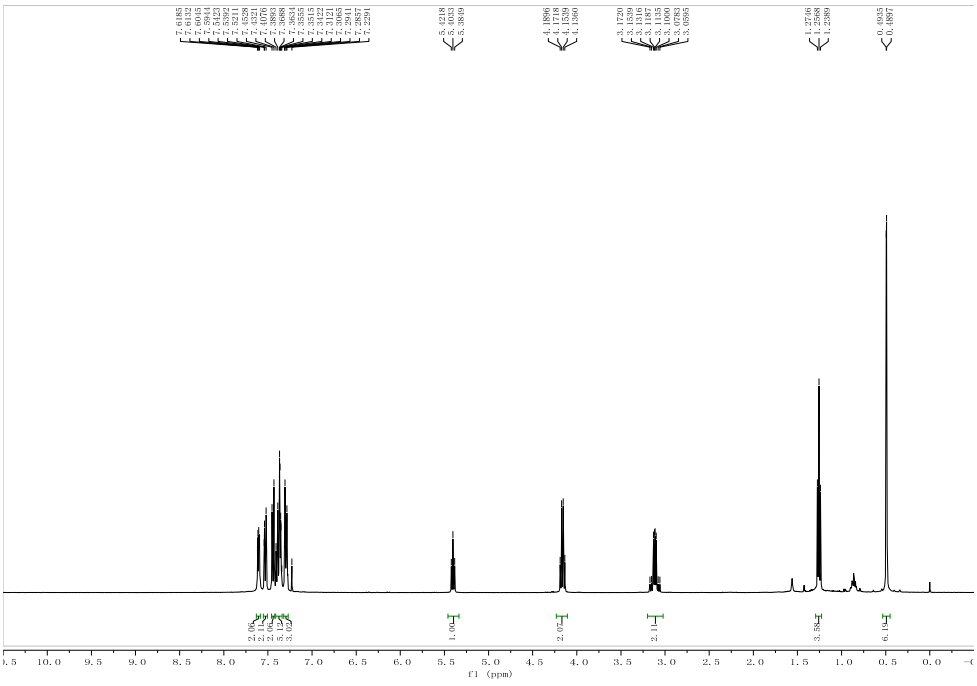
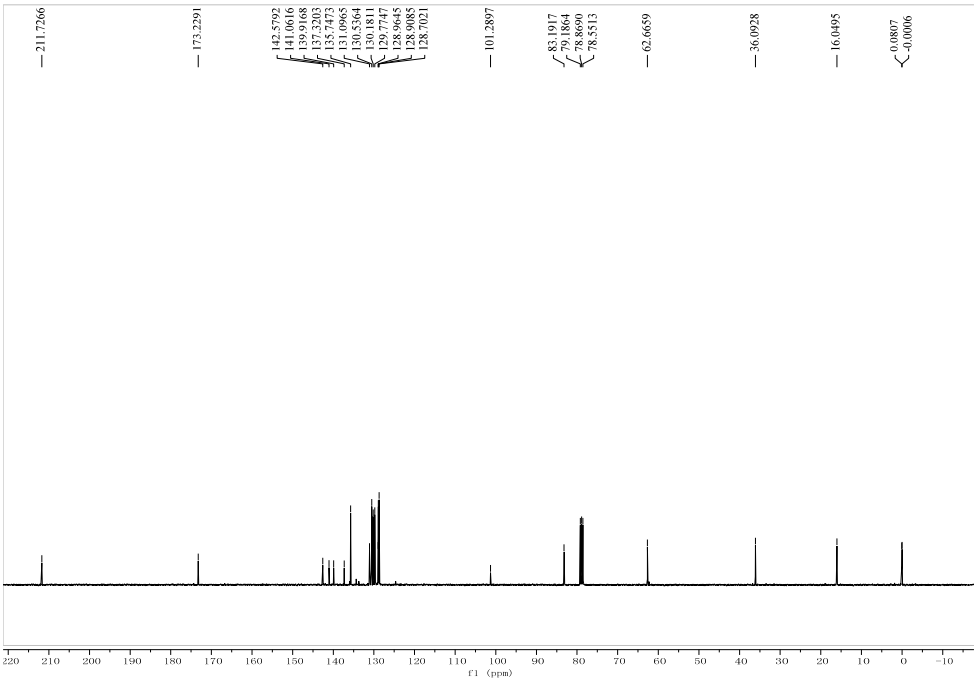
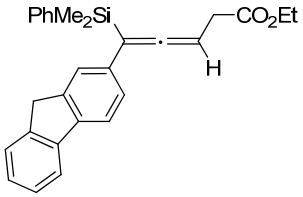
CO2Et
H
Ph



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CO2Et
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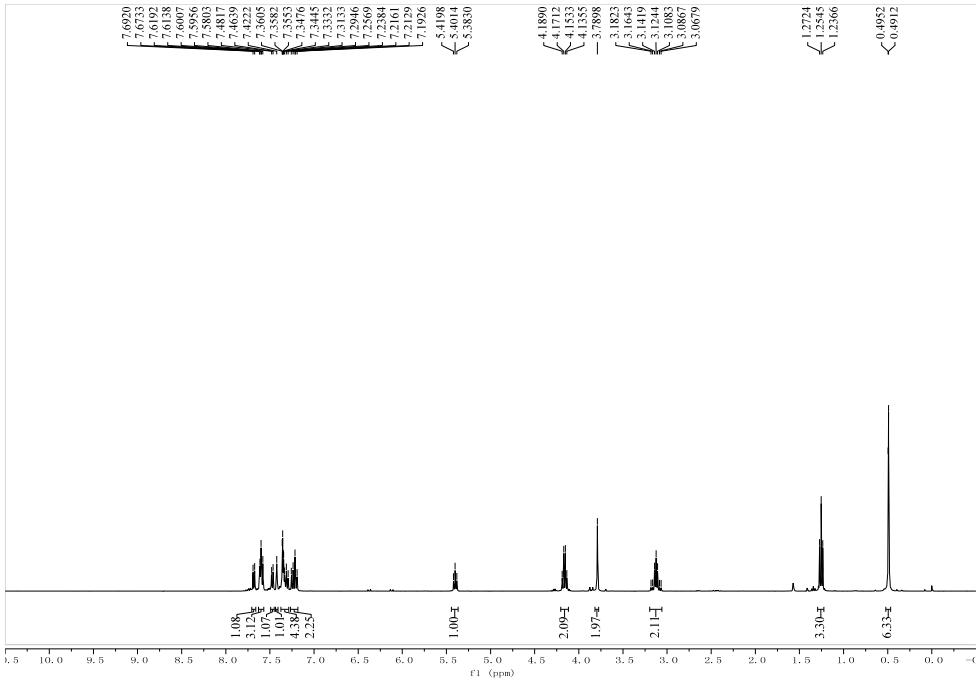
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7.3445
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7.3133
7.2946
7.2669
7.2384
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7.1926
5.4198
5.4014
5.3830
4.1890
4.1712
4.1533
4.1355
3.7898
3.1823
3.1643
3.1419
3.1244
3.1083
3.0867
3.0679
1.2724
1.2545
1.2366
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0.4912
1.08
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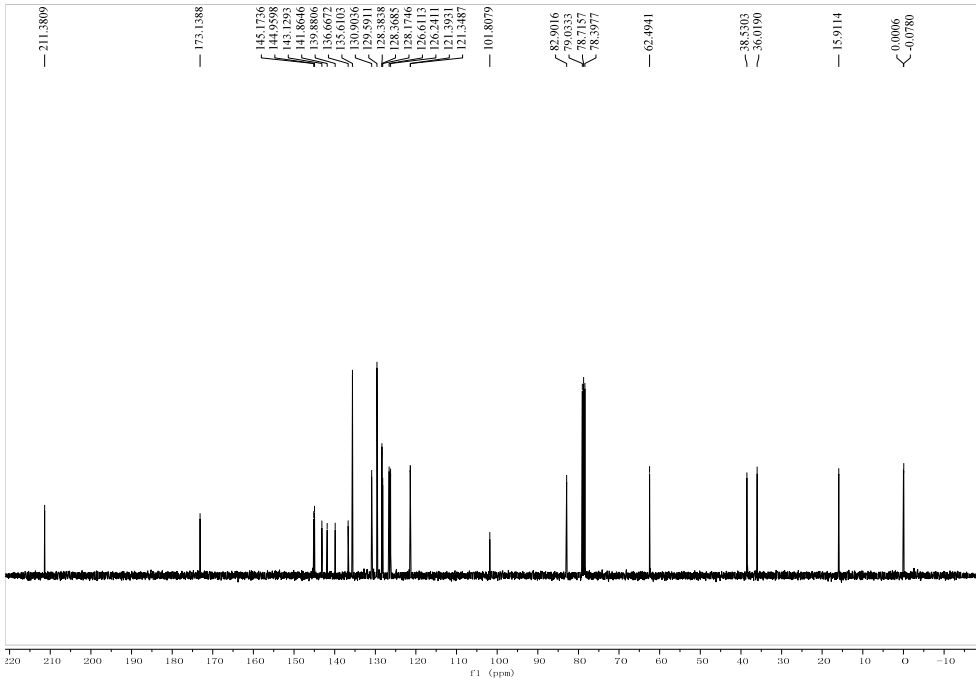
6.33
f1 (ppm)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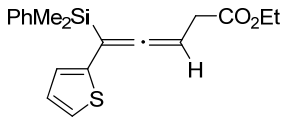
f1 (ppm)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CO2Et
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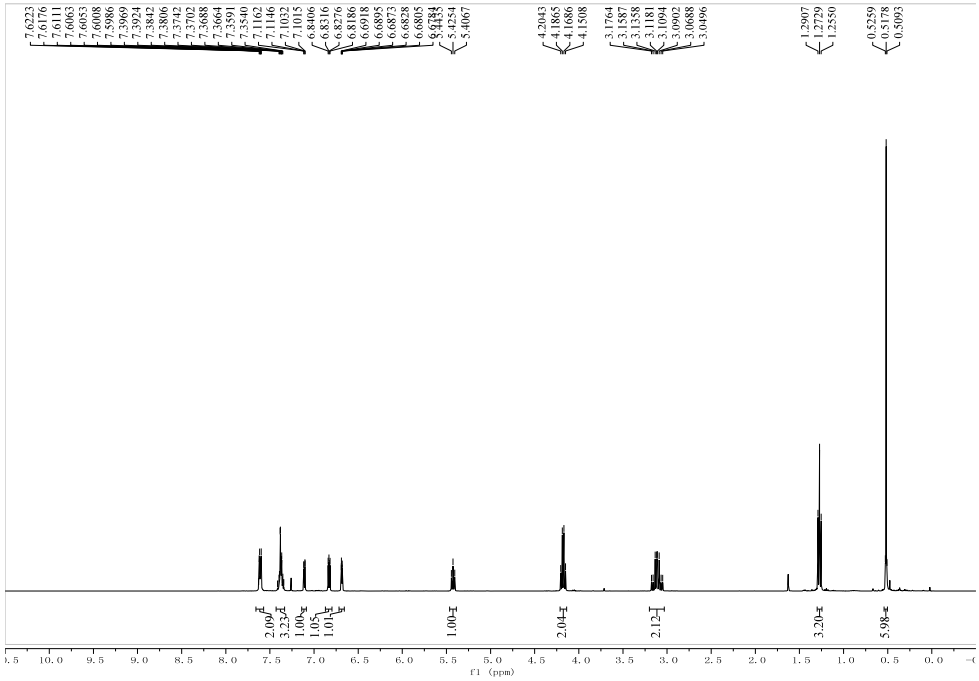
S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7.3540
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6.6784
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5.4354
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3.1764
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3.1181
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3.0496
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1.00
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2.12
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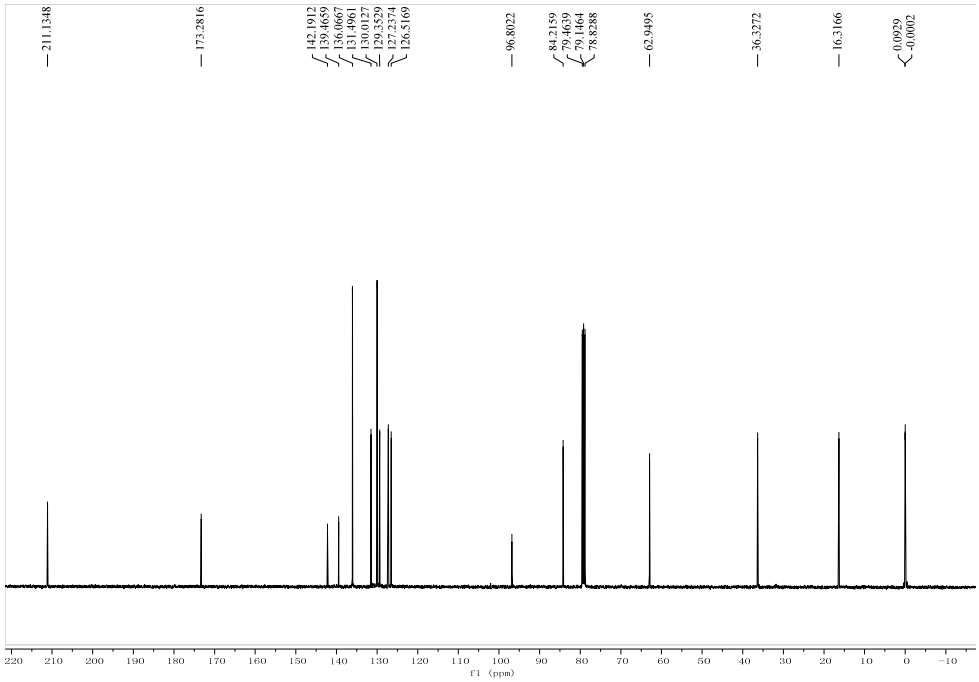
f1 (ppm)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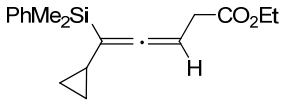
f1 (ppm)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CO2Et
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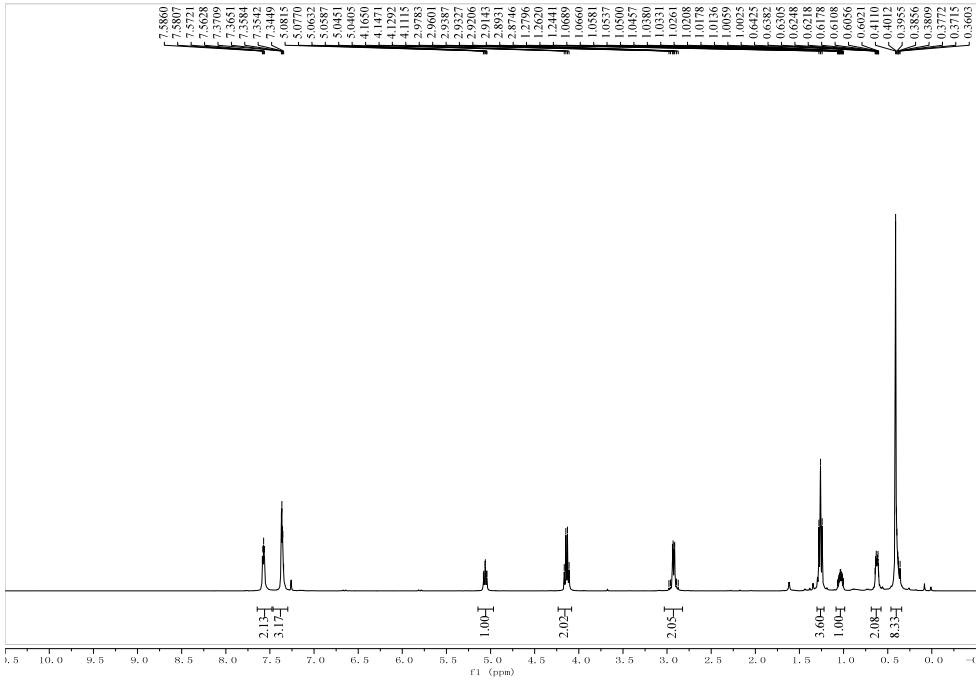
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5.0405
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1.0331
1.0261
1.0208
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0.6108
0.6056
0.6021
0.4110
0.4012
0.3955
0.3856
0.3699
0.3772
0.3715
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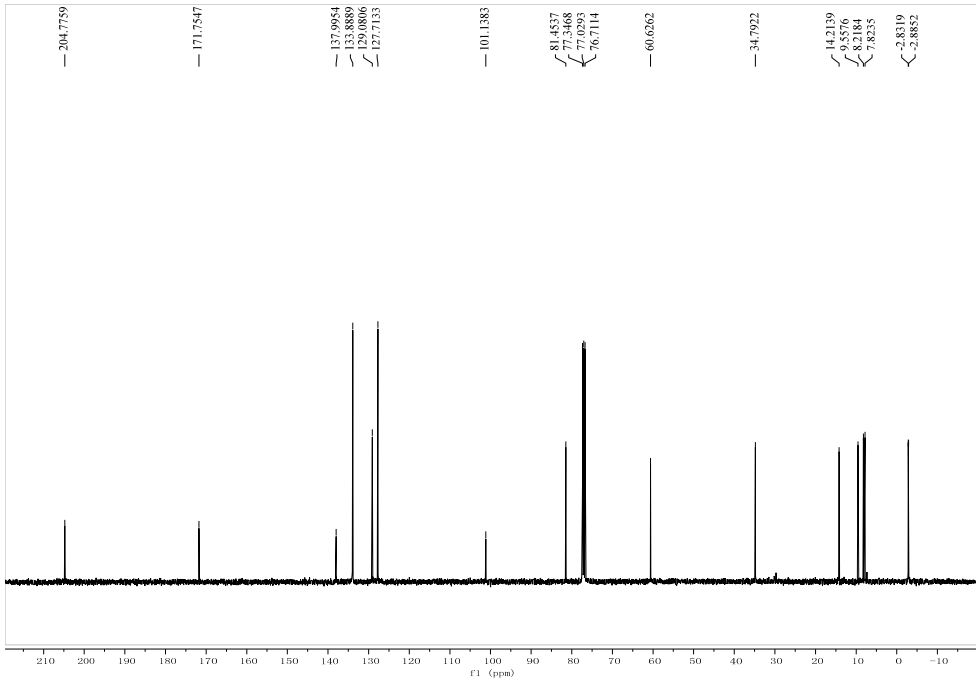
1.00
2.08
8.33
f1 (ppm)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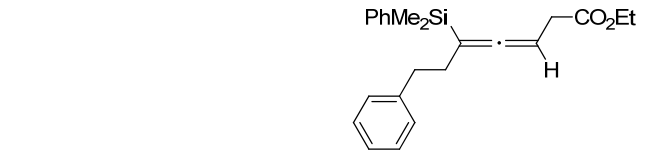
f1 (ppm)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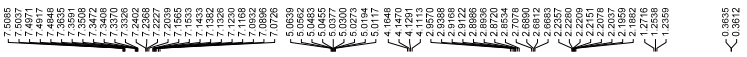

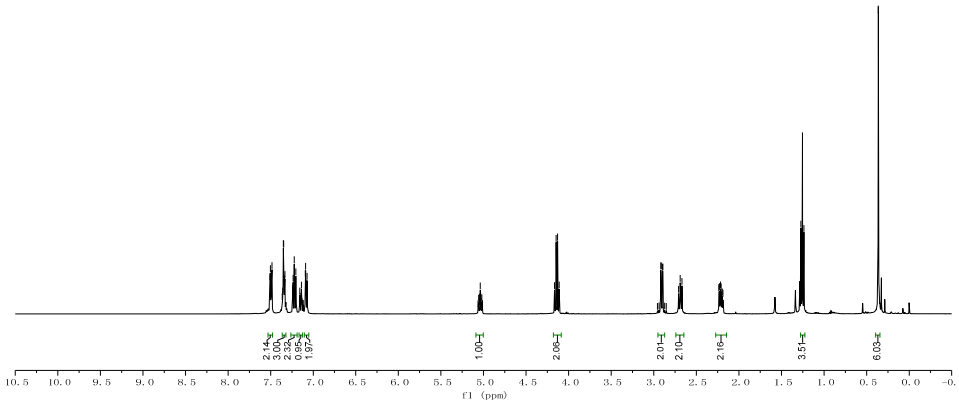
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2.01
2.10
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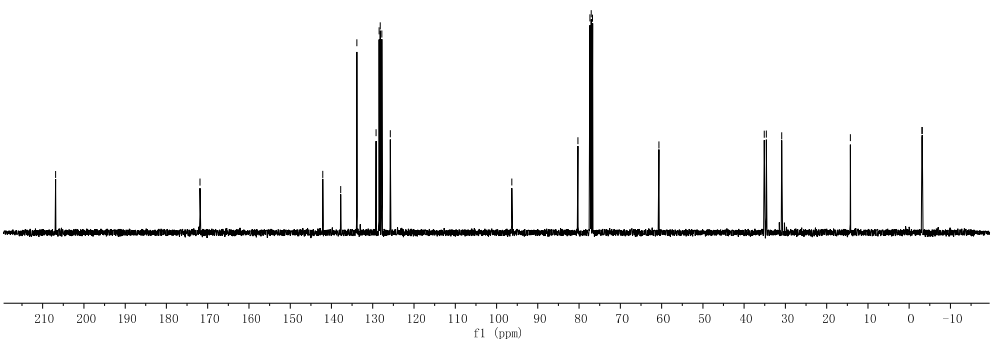
f1 (ppm)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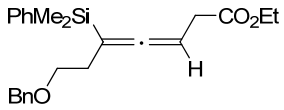
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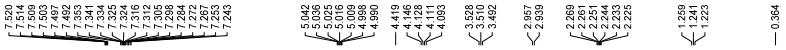
BnO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5.025
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4.128
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3.492
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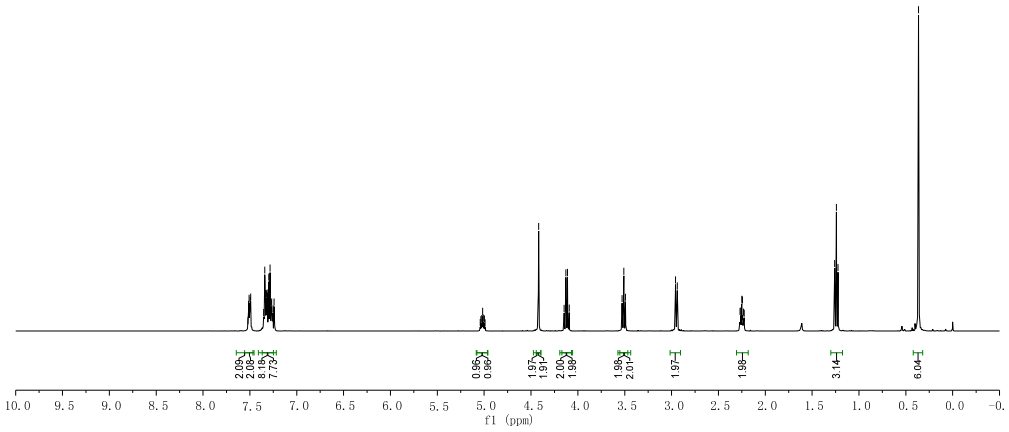
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1.98
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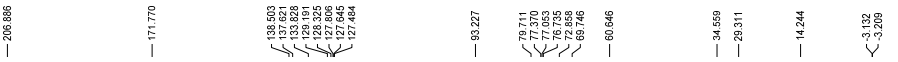
f1 (ppm)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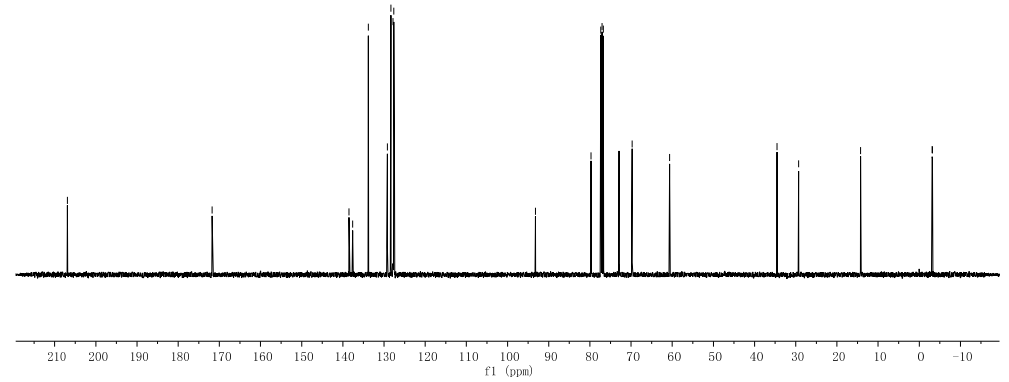
-3.209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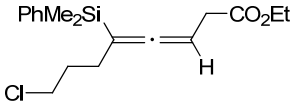
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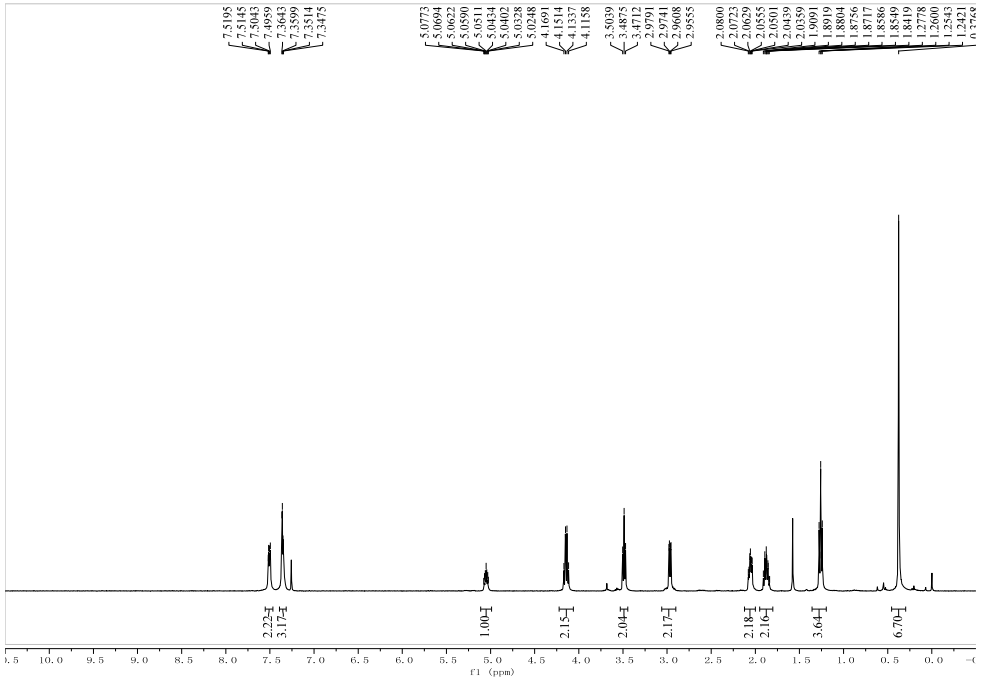
CO2Et
H
Cl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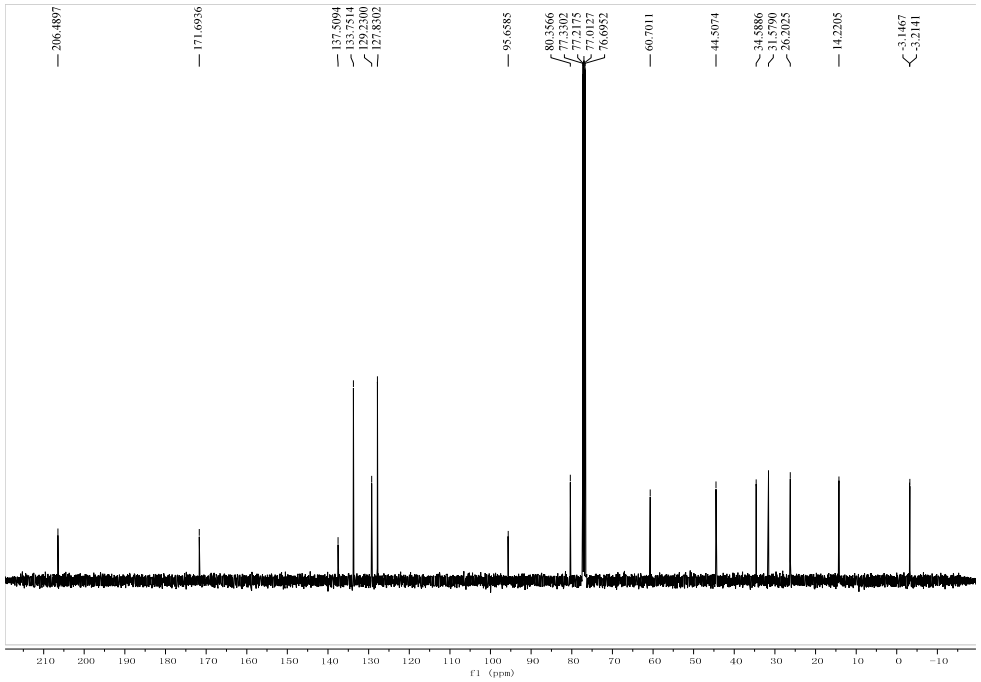
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76.6952
60.7011
44.5074
34.5886
31.5790
26.2025
14.2205
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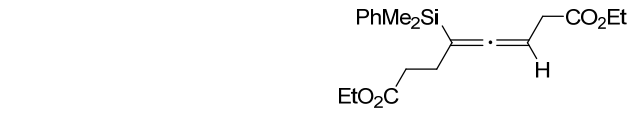
f1 (ppm)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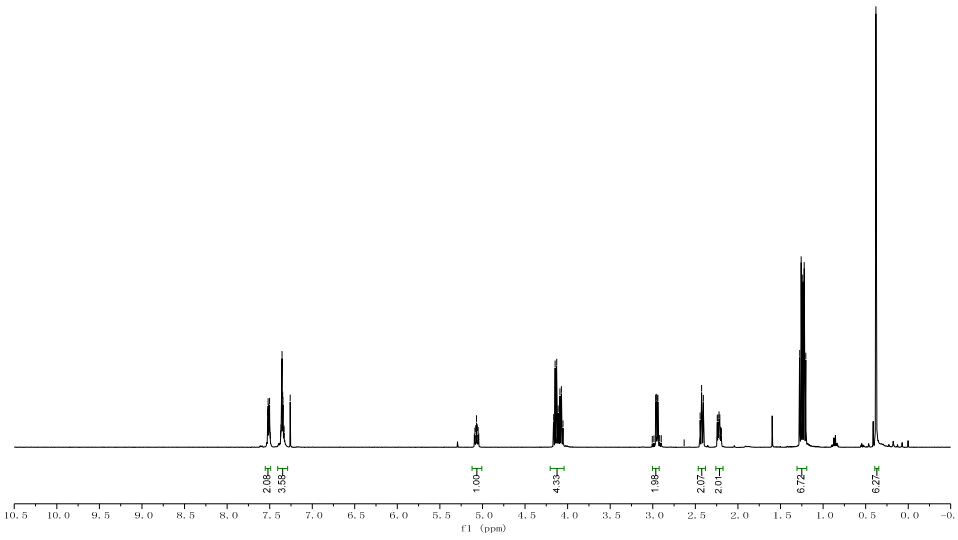
H
EtO2C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3.58
1.00
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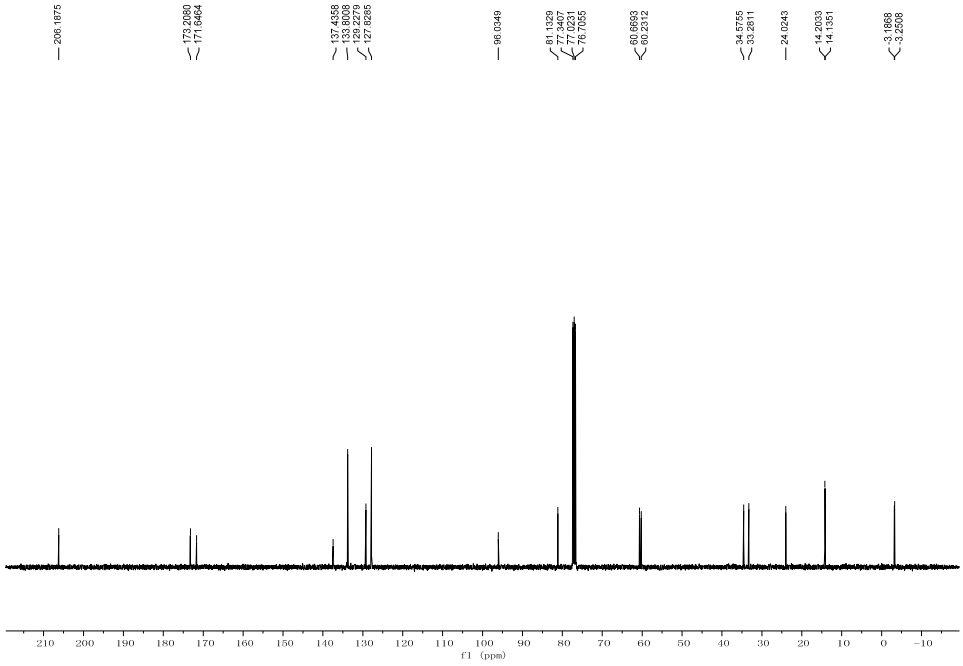
1.99
2.07
2.01
6.72
6.27
f1 (ppm)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133.8000
129.2279
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96.0349
81.1329
77.3407
77.0251
76.7095
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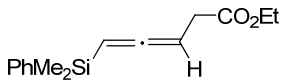
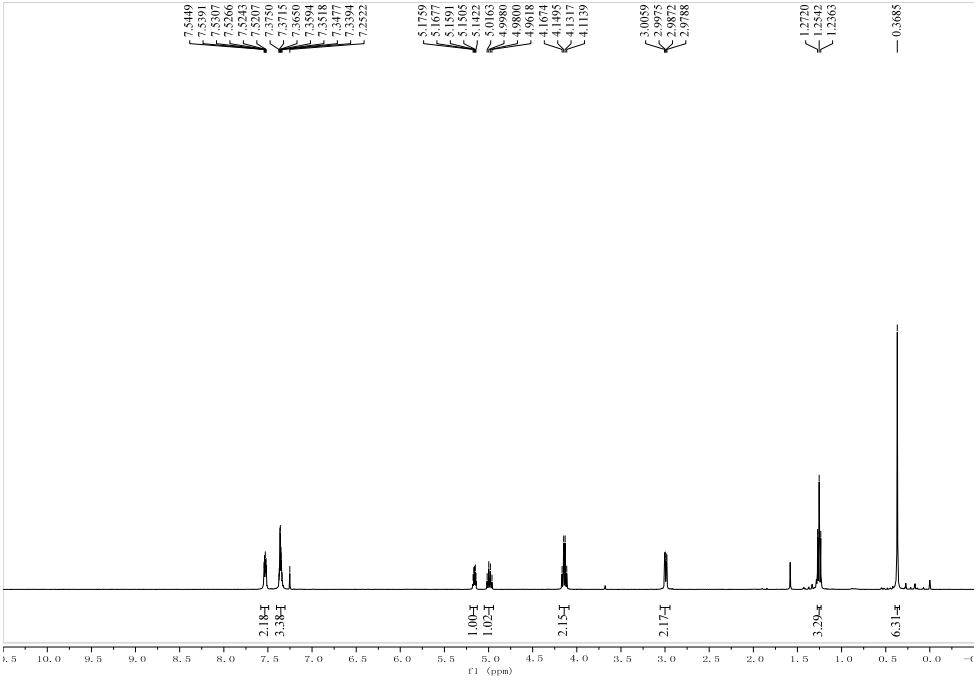
60.2312
34.5755
33.2811
24.0243
14.2033
14.1351
-3.1868
-3.2508
f1 (ppm)


CO2Et
PhMe2Si
H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7.5207
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7.3660
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7.3518
7.3477
7.3394
7.2522
5.1759
5.1677
5.1591
5.1505
5.1422
5.0163
4.9980
4.9800
4.9618
4.1674
4.1495
4.1317
4.1139
3.0059
2.9975
2.9872
2.9788
1.2720
1.2542
1.2363
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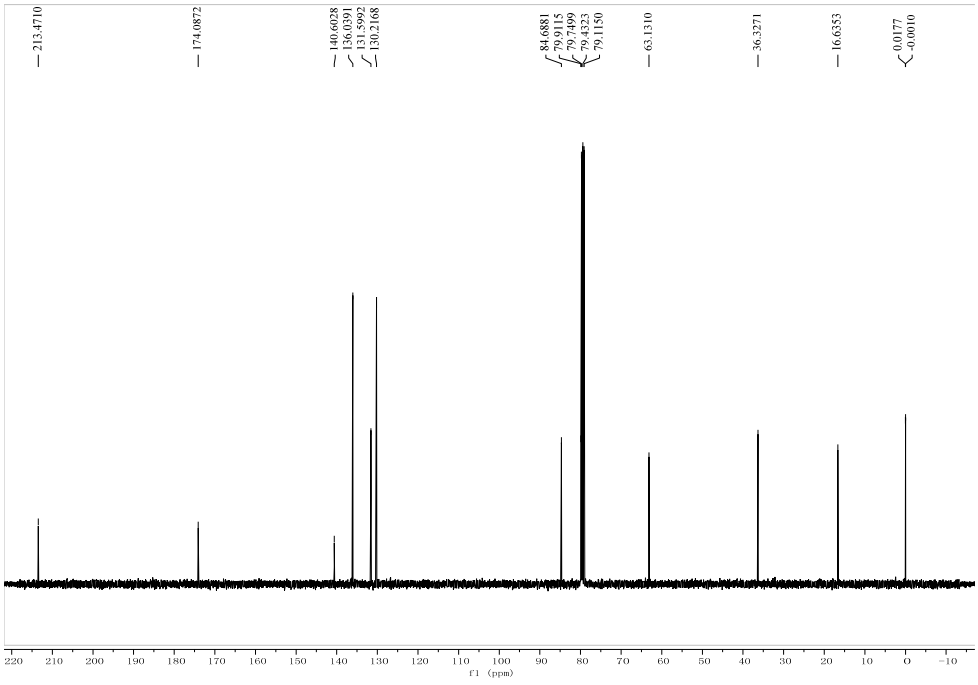
2.18
3.38
1.00
1.02
2.15
2.17
3.29
6.31
f1 (ppm)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79.1150
63.1310
36.3271
16.6353
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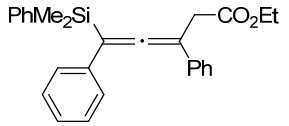
-0.0010
f1 (ppm)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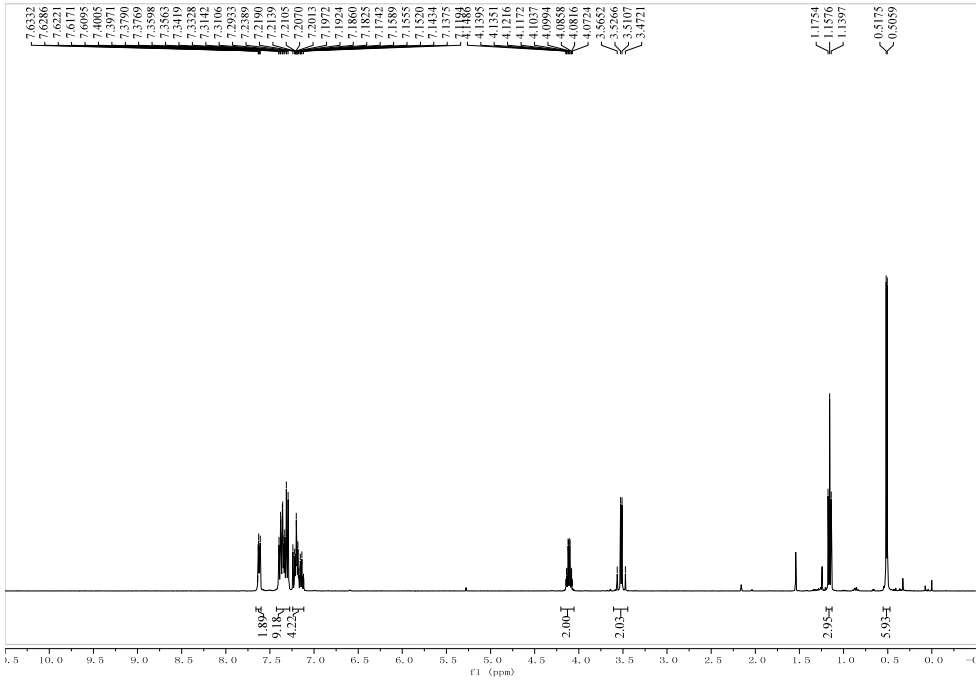
CO2Et
Ph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7.6171
7.6095
7.4005
7.3971
7.3790
7.3769
7.3598
7.3563
7.3419
7.3328
7.3142
7.3106
7.2933
7.2389
7.2190
7.2139
7.2105
7.2070
7.2013
7.1972
7.1924
7.1860
7.1825
7.1742
7.1589
7.1555
7.1520
7.1434
7.1375
4.1395
4.1351
4.1216
4.1172
4.1037
4.0994
4.0858
4.0816
4.0724
3.5652
3.5266
3.5107
3.4721
1.1754
1.1576
1.1397
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0.5059
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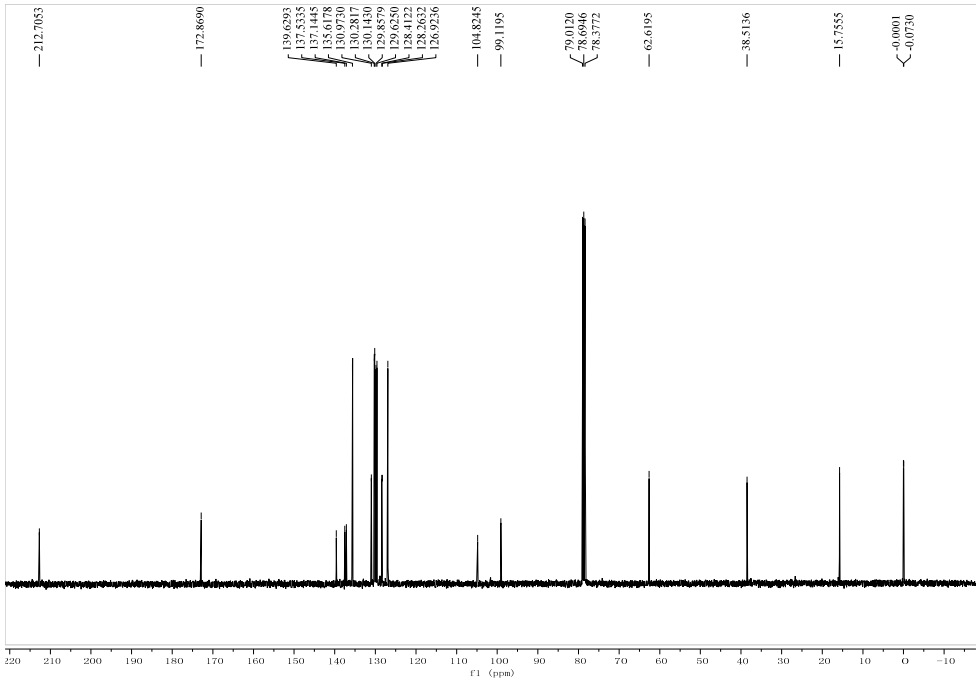
9.18
4.22
2.00
2.03
2.95
5.93
f1 (ppm)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135.6178
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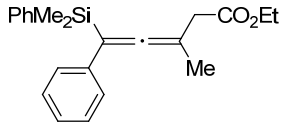
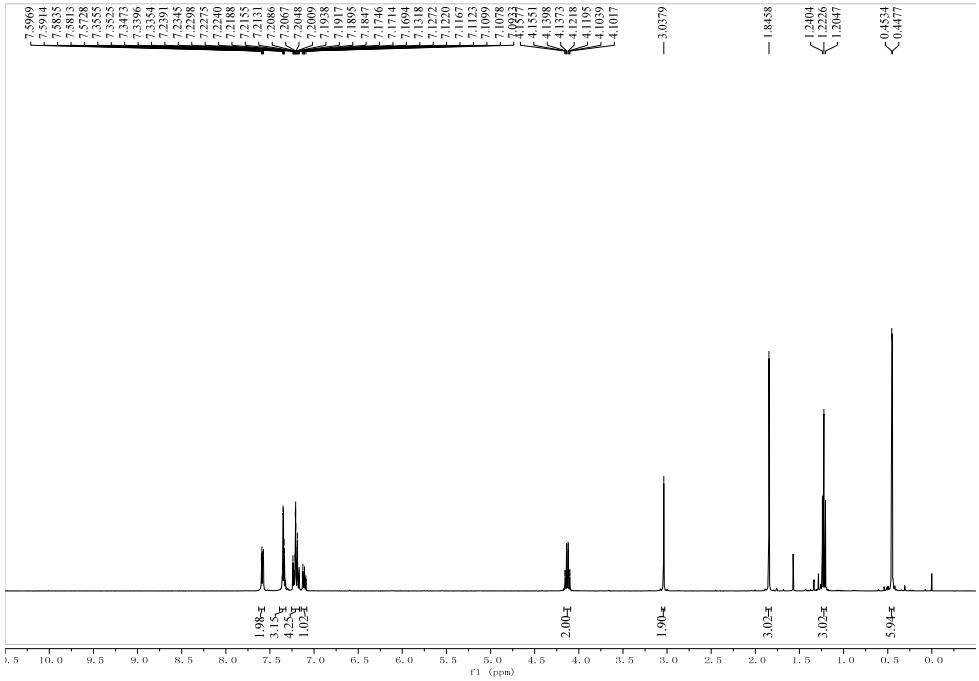
130.2817
130.1450
129.8579
129.6250
128.4122
128.2632
126.9236
104.8245
99.1195
79.0120
78.6946
78.3772
62.6195
38.5136
15.7555
-0.0001
-0.0730
f1 (ppm)


PhMe2Si
CO2Et
Me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7.3525
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7.2391
7.2345
7.2298
7.2275
7.2240
7.2188
7.2155
7.2131
7.2086
7.2067
7.2048
7.2009
7.1938
7.1917
7.1895
7.1847
7.1746
7.1714
7.1694
7.1318
7.1272
7.1220
7.1167
7.1123
7.1099
7.1078
4.1551
4.1398
4.1373
4.1218
4.1195
4.1039
4.1017
3.0379
1.8458
1.2404
1.2226
1.2047
0.4534
0.4477
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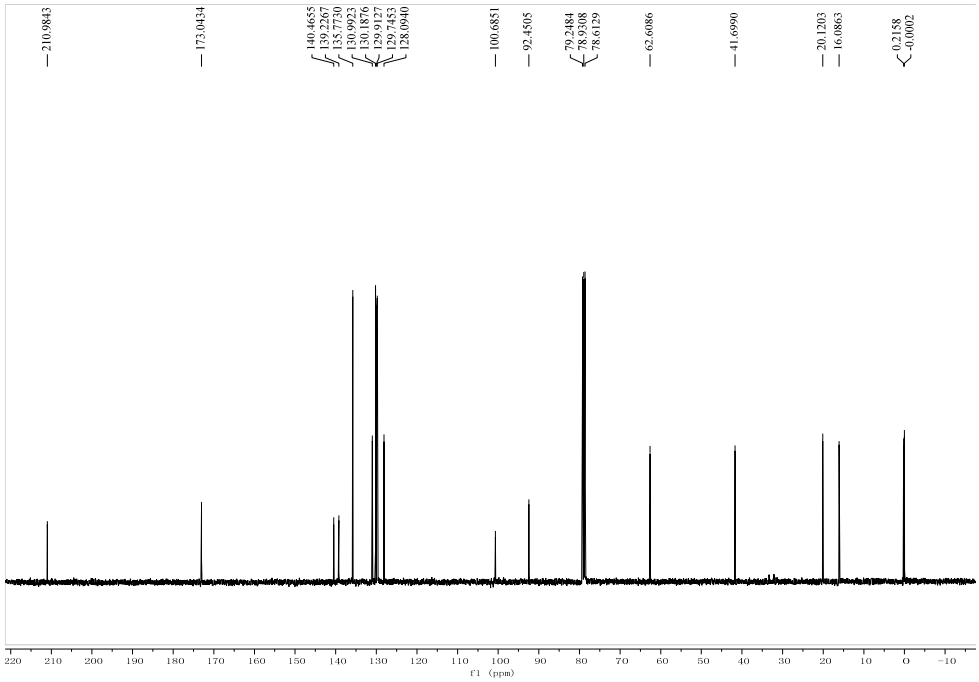
3.15
4.25
1.02
2.00
1.90
3.02
3.02
5.94
f1 (ppm)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135.7730
130.0923
130.1876
129.9127
129.7453
128.0940
100.6851
92.4505
79.2484
78.9308
78.6129
62.6086
41.6990
20.1203
16.0863
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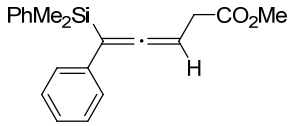
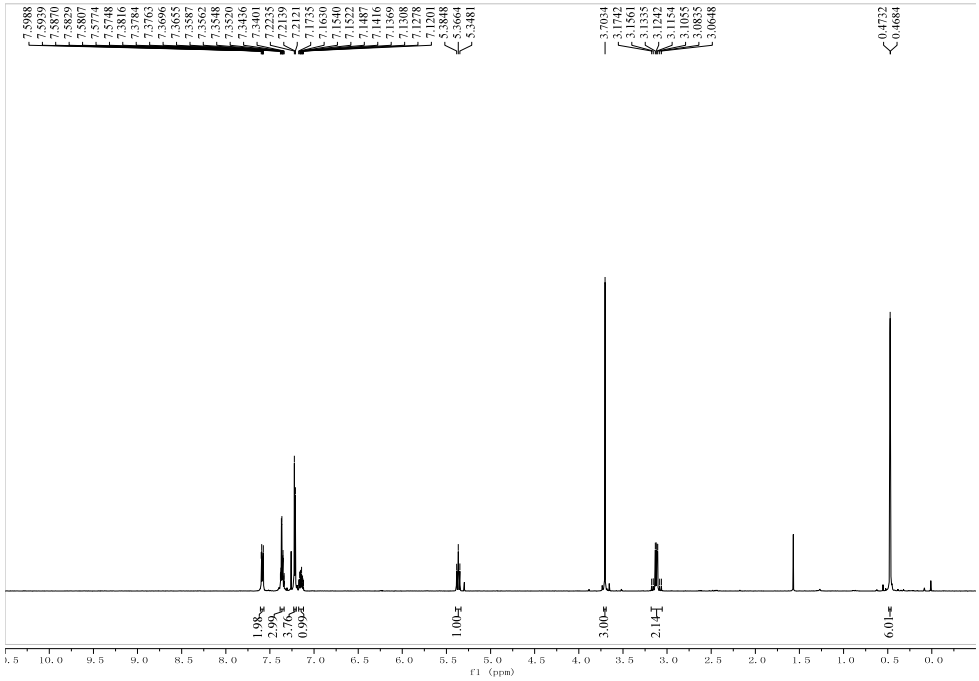
-0.0002
f1 (ppm)


PhMe2Si
CO2Me
H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7.3655
7.3587
7.3562
7.3520
7.3486
7.3440
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7.2139
7.2121
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7.1540
7.1522
7.1487
7.1416
7.1369
7.1308
7.1278
7.1201
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5.3664
5.3481
3.7034
3.1742
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3.1242
3.1154
3.1055
3.0835
3.0648
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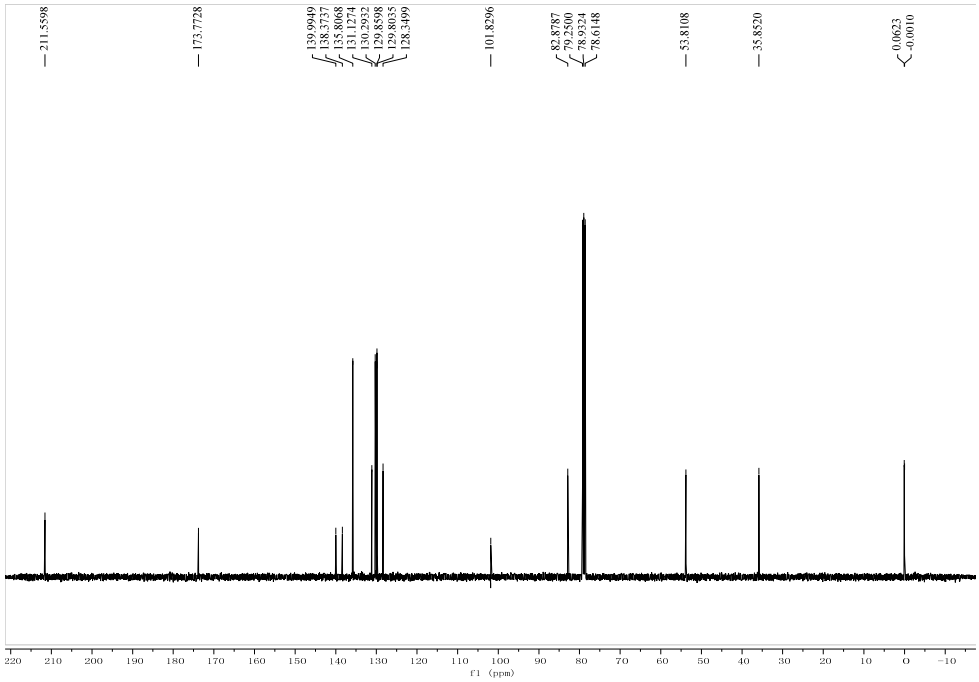
2.99
3.76
0.99
1.00
3.00
2.14
6.01
f1 (ppm)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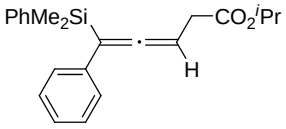
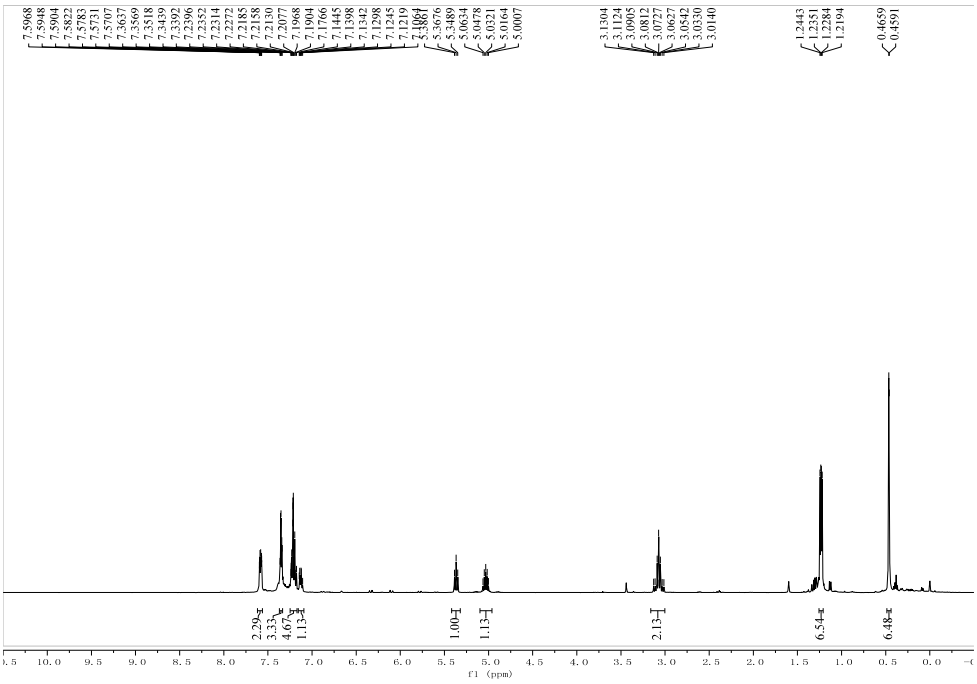
79.2500
78.9324
78.6148
53.8108
35.8520
0.0623
-0.0010
f1 (ppm)


PhMe2Si
CO2iPr
H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7.3439
7.3392
7.2396
7.2352
7.2314
7.2272
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7.2158
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7.2077
7.1968
7.1904
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7.1342
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3.0727
3.0627
3.0542
3.0330
3.0140
1.2443
1.2351
1.2284
1.2194
0.4659
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3.33
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1.13
1.00
1.13
2.13
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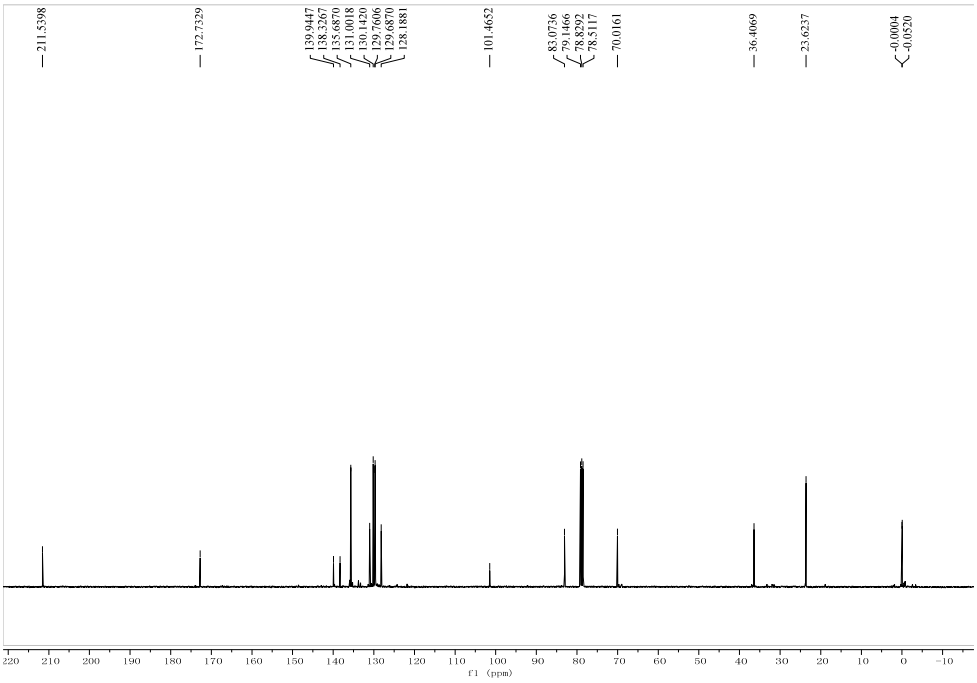
6.48
f1 (ppm)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101.4652
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78.8292
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23.6237
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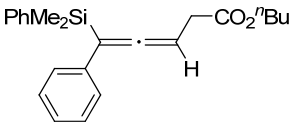
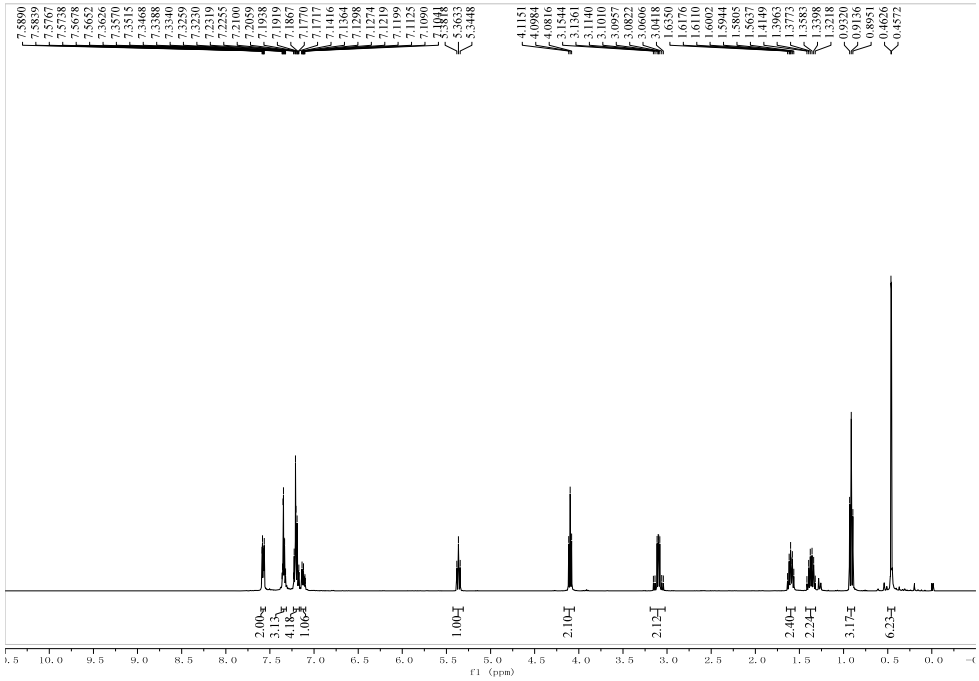
f1 (ppm)


PhMe2Si
CO2nBu
H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7.3388
7.3340
7.3259
7.3230
7.2319
7.2255
7.2100
7.2059
7.1938
7.1919
7.1867
7.1770
7.1717
7.1416
7.1364
7.1298
7.1274
7.1219
7.1199
7.1125
7.1090
5.3818
5.3633
5.3448
4.1151
4.0984
4.0816
3.1544
3.1361
3.1140
3.1010
3.0957
3.0822
3.0606
3.0418
1.6350
1.6176
1.6110
1.6002
1.5944
1.5805
1.3637
1.4149
1.3963
1.3773
1.3583
1.3398
1.3218
0.9230
0.9136
0.8951
0.4626
0.4572
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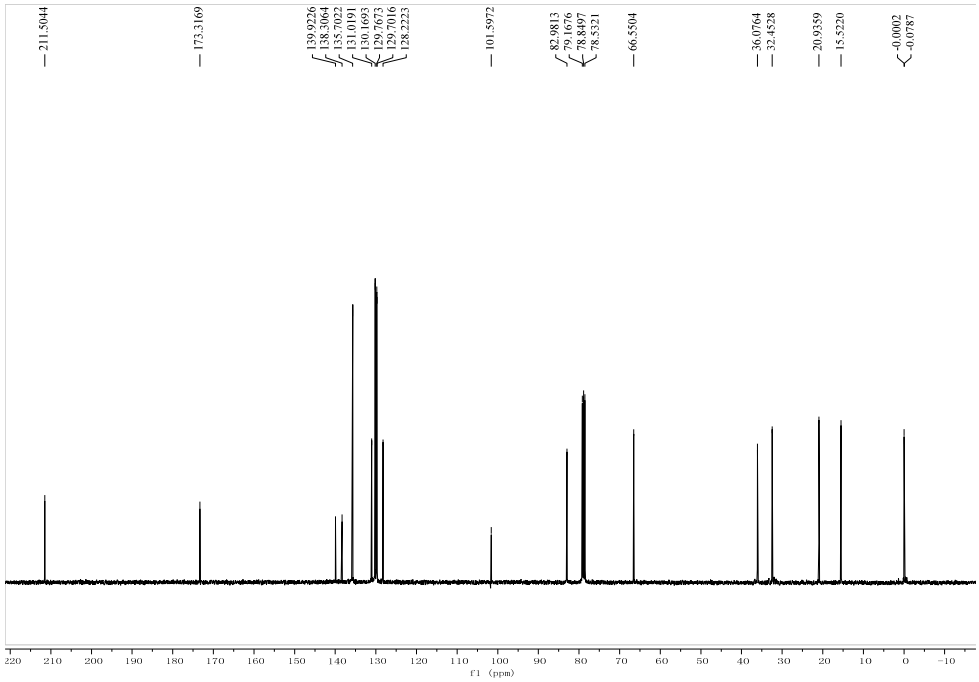
3.13
4.18
1.06
1.00
2.10
2.12
2.40
2.24
3.17
6.23
f1 (ppm)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101.5972
82.9813
79.1676
78.8497
78.5321
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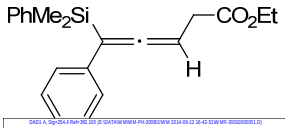
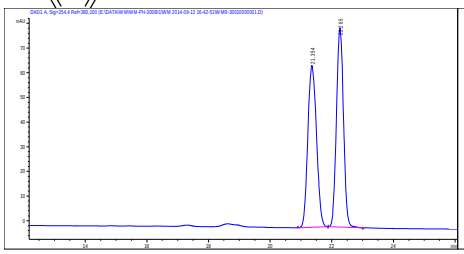
32.4528
20.9359
15.5220
-0.0002
-0.0787
f1 (ppm)

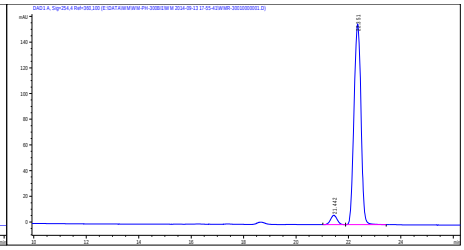
HPLC for chiral allenylsilane





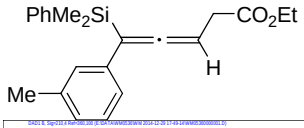
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

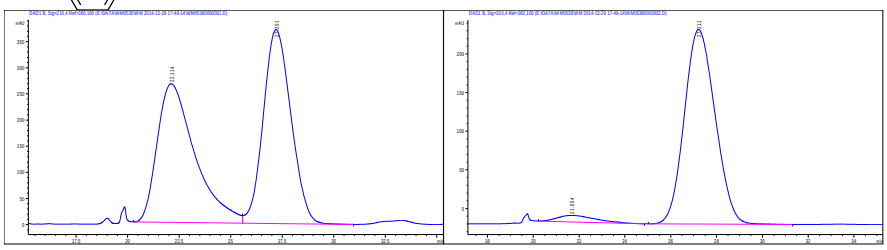
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.354	BB	0.3129	1286.00977	65.55194	50.0475
2	22.265	BB	0.2515	1283.56885	80.70587	49.9525
Totals :				2569.57861	146.25781	



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.442	BB	0.2760	127.03123	7.26643	4.2104
2	22.351	BB	0.2980	2890.07813	156.09740	95.7896
Totals :				3017.10936	163.36383	



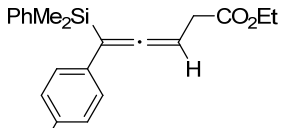


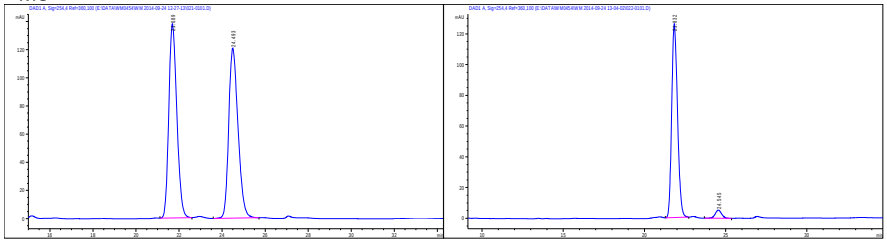
Signal 2: DAD1 B, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.114	BV	1.8886	3.37817e4	265.12143	49.3282
2	27.201	VB	1.4509	3.47018e4	371.13174	50.6718
Totals :				6.84834e4	636.25317	

Signal 2: DAD1 B, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.654	BB	1.3490	959.69135	8.33680	3.9124
2	27.211	BB	1.4685	2.35699e4	251.68980	96.0876
Totals :				2.45296e4	260.02660	



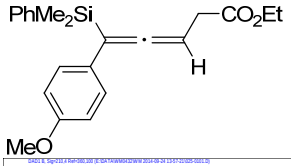


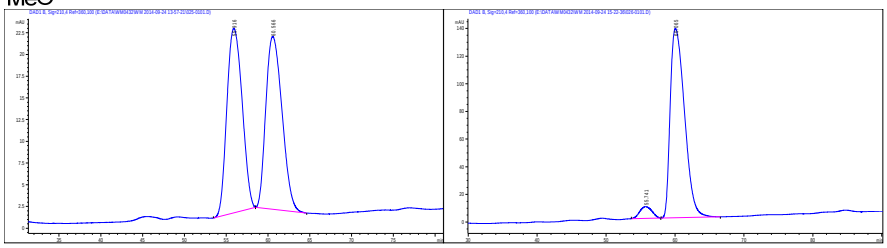
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.689	BB	0.3996	3566.28784	137.97507	49.5867
2	24.493	BB	0.4663	3625.74023	120.75926	50.4133
Totals :				7192.02808	258.73433	

Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.832	BB	0.3874	3148.87622	126.07990	95.6191
2	24.545	BB	0.4182	144.26875	5.28990	4.3809
Totals :				3293.14497	131.36980	



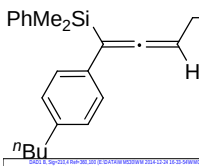


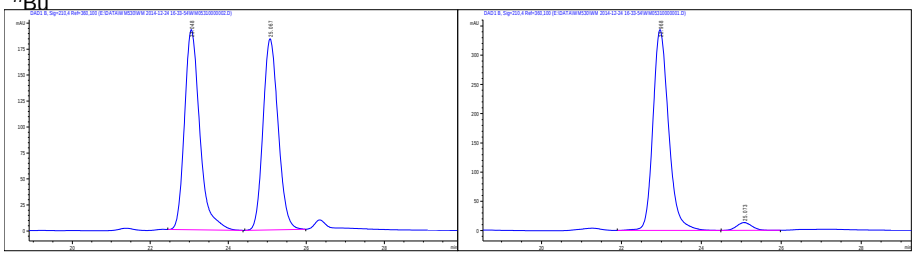
Signal 2: DAD1 B, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	55.916	BB	1.9766	2697.56128	21.22772	50.1588
2	60.566	BB	1.9772	2680.48242	19.87842	49.8412
Totals :				5378.04370	41.10614	

Signal 2: DAD1 B, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	55.741	MM R	1.5056	1051.19055	8.46832	5.0606
2	60.065	BB	2.2519	1.97209e4	136.95995	94.9394
Totals :				2.07721e4	145.42826	



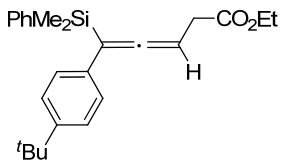


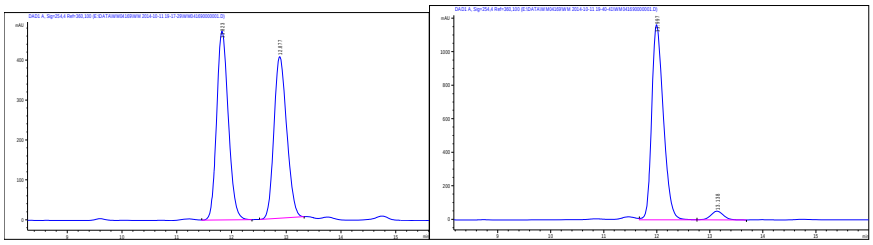
Signal 2: DAD1 B, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.048	BB	0.4161	5250.86572	192.60344	51.4024
2	25.067	BB	0.4207	4964.34912	184.04930	48.5976
Totals :				1.02152e4	376.65274	

Signal 2: DAD1 B, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.968	BB	0.4173	9341.26270	343.43756	96.3814
2	25.073	BB	0.4135	350.71884	13.22050	3.6186
Totals :				9691.98154	356.65807	



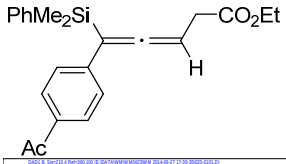


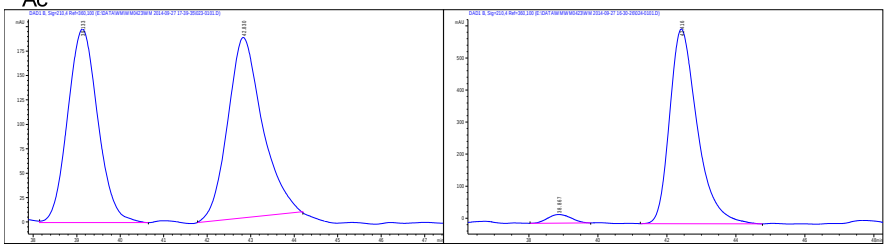
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.823	VB	0.2313	7018.46631	472.40195	51.6914
2	12.877	BB	0.2531	6559.15430	404.71805	48.3086
Totals :				1.35776e4	877.12000	

Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.997	VV	0.2352	1.78847e4	1164.22034	95.3726
2	13.138	VB	0.2570	867.75684	51.91274	4.6274
Totals :				1.87525e4	1216.13308	



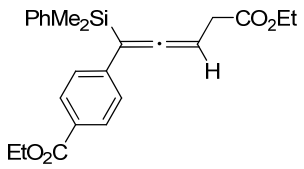


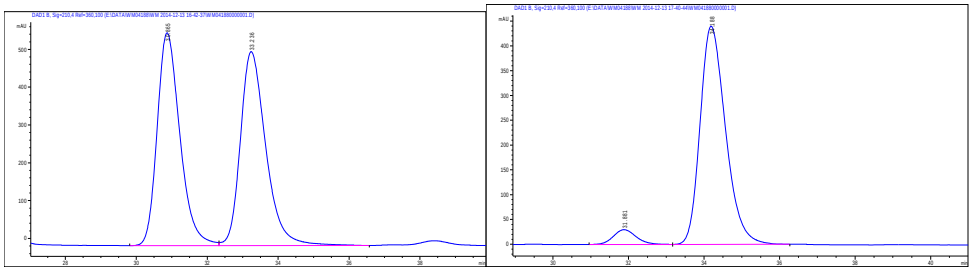
Signal 2: DAD1 B, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	39.133	VB	0.7493	9528.21289	198.05148	48.4283
2	42.830	MM R	0.9181	1.01467e4	184.19614	51.5717
Totals :				1.96749e4	382.24762	

Signal 2: DAD1 B, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	38.867	BB	0.7589	1245.06531	26.65984	3.5559
2	42.416	BB	0.8448	3.37687e4	607.19452	96.4441
Totals :				3.50138e4	633.85436	



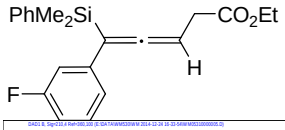


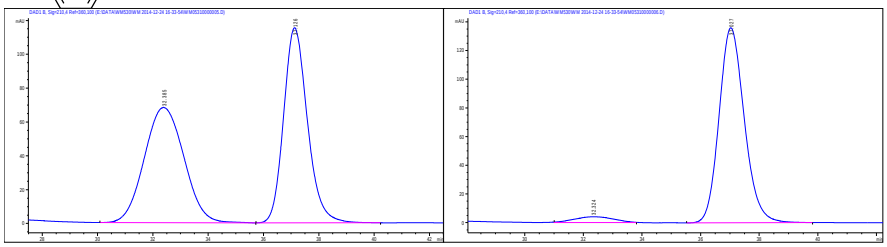
Signal 2: DAD1 B, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	30.865	BV	0.6837	2.50661e4	562.67657	49.5443
2	33.236	VB	0.7610	2.55272e4	512.62451	50.4557
Totals :				5.05933e4	1075.30109	

Signal 2: DAD1 B, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	31.881	MM	0.6324	1084.56628	28.58165	5.0982
2	34.188	MM	0.7684	2.01888e4	437.90866	94.9018
Totals :				2.12734e4	466.49031	

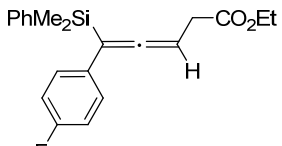


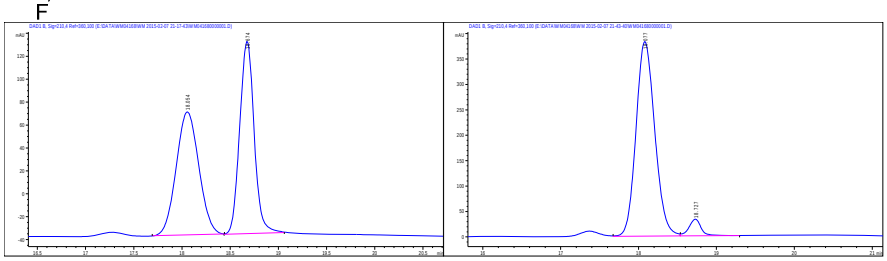


Signal 2: DAD1 B, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	32.385	BB	1.5615	6779.71533	68.09615	49.5457
2	37.126	BB	0.9229	6904.03955	115.25564	50.4543
Totals :				1.36838e4	183.35178	

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	32.324	MM R	1.5606	376.04007	4.01595	4.4190
2	37.027	BB	0.9282	8133.50684	135.90018	95.5810
Totals :				8509.54691	139.91613	



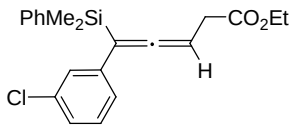


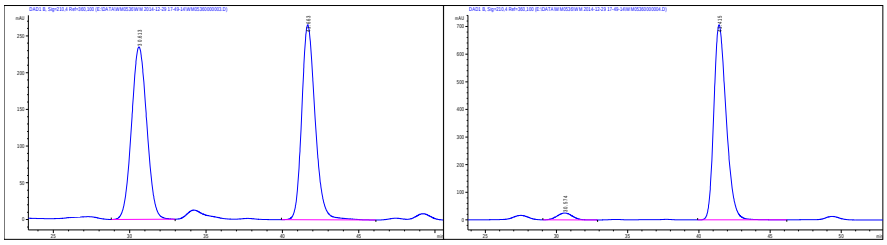
Signal 2: DAD1 B, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.054	MM R	0.2714	1747.65857	107.30874	49.9679
2	18.674	MM R	0.1738	1749.90588	167.82521	50.0321
Totals :				3497.56445	275.13395	

Signal 2: DAD1 B, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.077	VV	0.2616	6420.84766	382.96121	94.7884
2	18.727	VB	0.1662	353.02951	32.64647	5.2116
Totals :				6773.87717	415.60769	



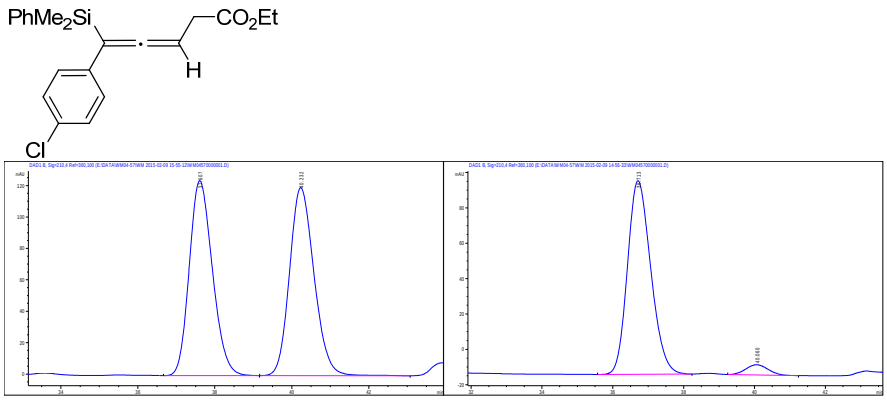


Signal 2: DAD1 B, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	30.613	BB	1.0859	1.62941e4	234.71832	50.0661
2	41.663	BB	0.9388	1.62511e4	265.22906	49.9339
Totals :				3.25453e4	499.94739	

Signal 2: DAD1 B, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	30.574	BB	1.1348	1838.88354	24.80824	4.1294
2	41.415	BB	0.9318	4.26925e4	705.71790	95.8706
Totals :				4.45314e4	730.52613	

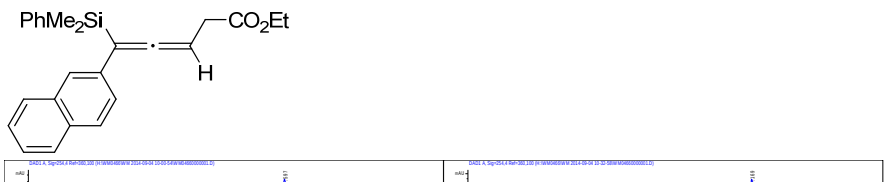


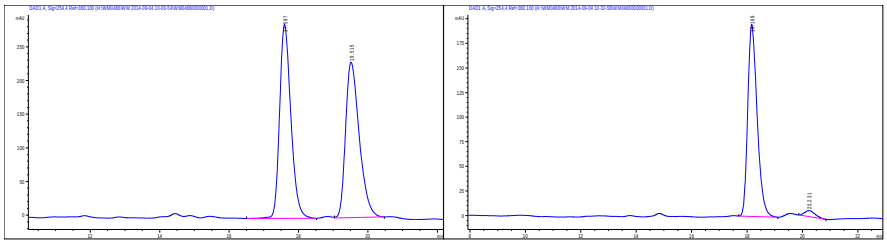
Signal 2: DAD1 B, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	37.607	BB	0.6453	5181.97363	124.06824	49.4344
2	40.232	BB	0.6888	5300.54492	119.66532	50.5656
Totals :				1.04825e4	243.73356	

Signal 2: DAD1 B, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	36.713	BB	0.7094	5003.88184	109.43909	95.1983
2	40.060	BB	0.6742	252.38898	5.74917	4.8017
Totals :				5256.27081	115.18826	



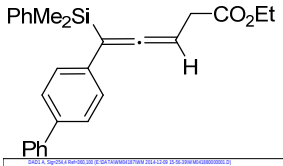


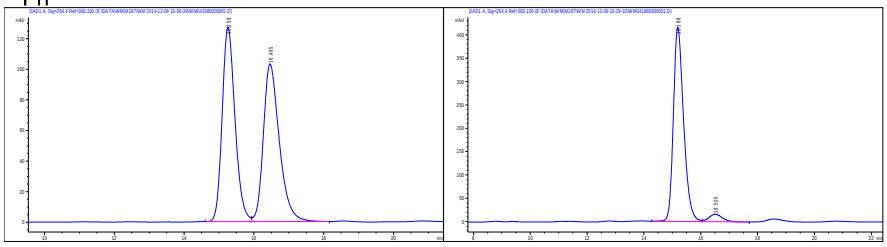
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.597	BB	0.3498	6513.97119	288.04388	50.7785
2	19.515	VB	0.4190	6314.22412	230.92447	49.2215
Totals :				1.28282e4	518.96835	

Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.169	BB	0.3641	4617.32471	195.09680	96.7236
2	20.231	BB	0.4146	156.40437	5.99048	3.2764
Totals :				4773.72908	201.08729	



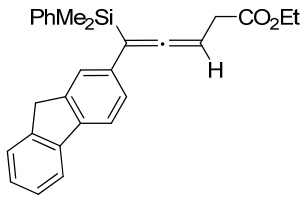


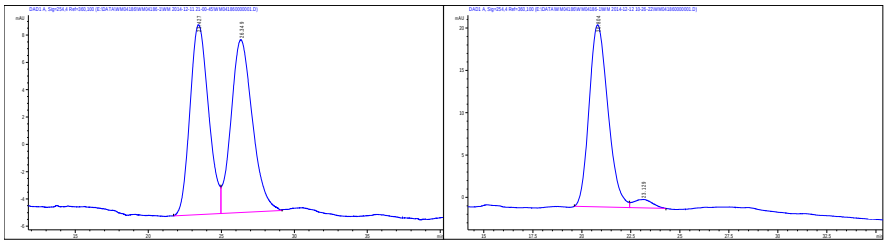
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.259	BV	0.3916	3243.51953	127.16936	49.7793
2	16.465	VB	0.4824	3272.27466	103.05710	50.2207
Totals :				6515.79419	230.22646	

Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.188	BV	0.3838	1.04129e4	416.37518	95.1790
2	16.505	VB	0.4990	527.43781	16.15190	4.8210
Totals :				1.09403e4	432.52708	



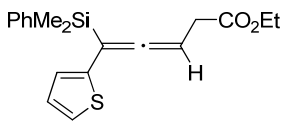


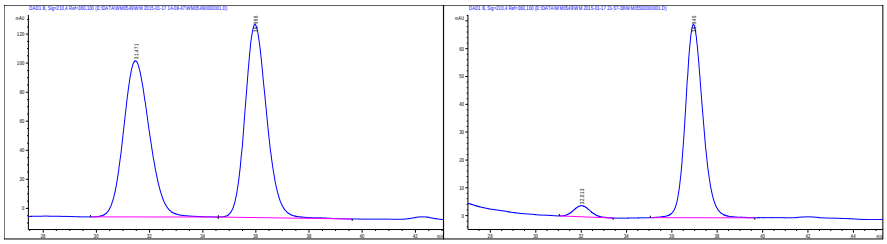
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.427	MF R	1.4750	1229.45691	13.89245	48.8172
2	26.349	FM R	1.6993	1289.03662	12.64289	51.1828
Totals :				2518.49353	26.53534	

Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.804	MF R	1.1117	1432.39026	21.47523	95.5894
2	23.129	FM R	1.1199	66.09176	9.83630e-1	4.4106
Totals :				1498.48202	22.45886	



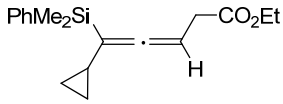


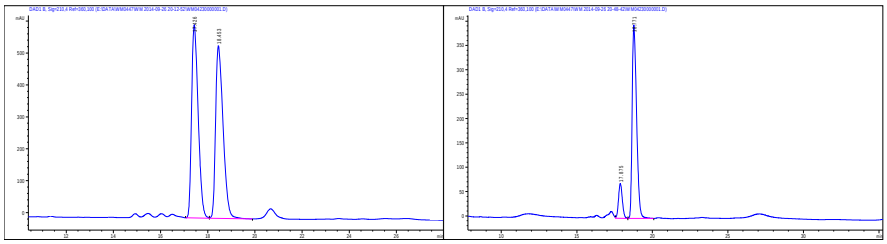
Signal 2: DAD1 B, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	31.471	BB	1.0533	7275.27393	107.53164	49.0921
2	35.966	BB	0.8722	7544.35840	132.92227	50.9079
Totals :				1.48196e4	240.45391	

Signal 2: DAD1 B, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	32.013	BB	0.7401	203.99904	3.99288	5.1631
2	36.945	BB	0.8276	3747.11523	69.43748	94.8369
Totals :				3951.11427	73.43035	



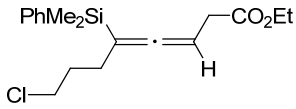


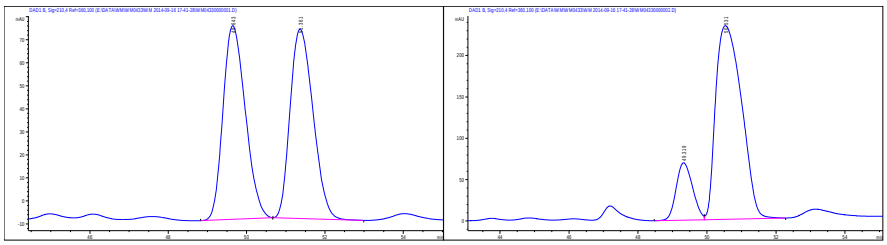
Signal 2: DAD1 B, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.426	BV	0.3050	1.17653e4	604.57373	49.6154
2	18.453	VB	0.3460	1.19477e4	540.25183	50.3846
Totals :				2.37130e4	1144.82556	

Signal 2: DAD1 B, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.875	VB	0.2717	1245.76013	71.36281	13.3103
2	18.771	BB	0.3186	8113.60693	396.76343	86.6897
Totals :				9359.36707	468.12624	



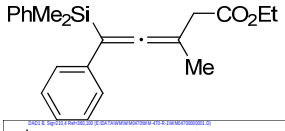


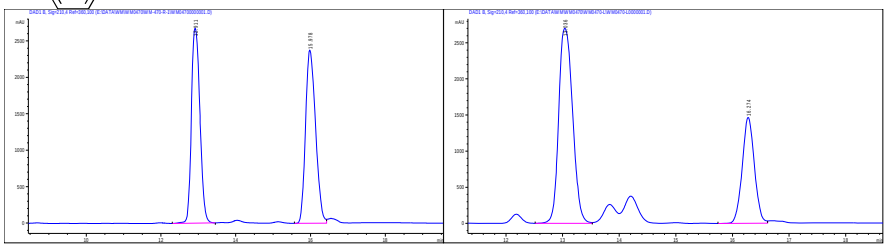
Signal 2: DAD1 B, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	49.319	BV	0.5236	2288.06104	69.23113	15.8424
2	50.531	VB	0.8941	1.21546e4	233.96143	84.1576
Totals :				1.44427e4	303.19256	

Signal 2: DAD1 B, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	49.319	BV	0.5236	2288.06104	69.23113	15.8424
2	50.531	VB	0.8941	1.21546e4	233.96143	84.1576
Totals :				1.44427e4	303.19256	



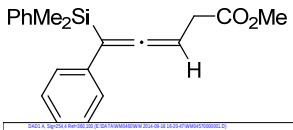


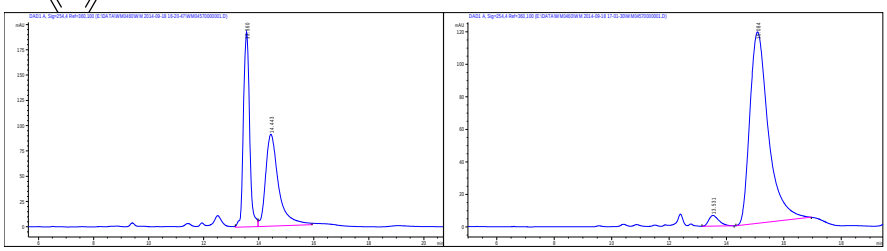
Signal 2: DAD1 B, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.911	BB	0.2488	4.23571e4	2674.21411	48.8188
2	15.978	BV	0.2899	4.44068e4	2377.54517	51.1812
Totals :				8.67639e4	5051.75928	

Signal 2: DAD1 B, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.036	BV	0.2692	4.61007e4	2700.50464	67.7912
2	16.274	BV	0.2281	2.19033e4	1467.94019	32.2088
Totals :				6.80040e4	4168.44482	



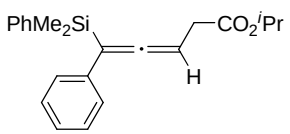


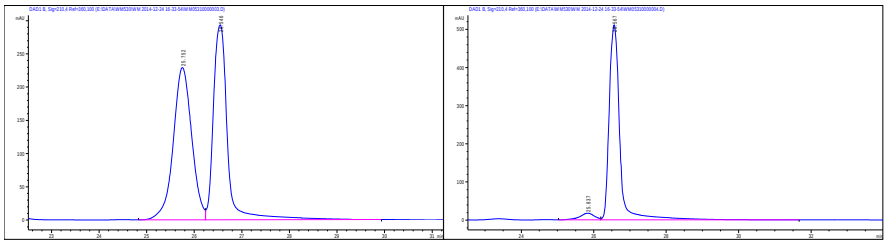
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.560	BV	0.2503	3006.10669	192.39133	50.6007
2	14.443	MM R	0.5393	2934.72852	90.69703	49.3993
Totals :				5940.83521	283.08836	

Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.531	BB	0.3761	160.93994	6.56205	2.9567
2	15.084	MM R	0.7455	5282.23047	118.09123	97.0433
Totals :				5443.17041	124.65328	



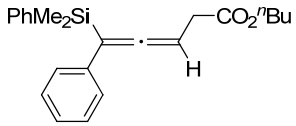


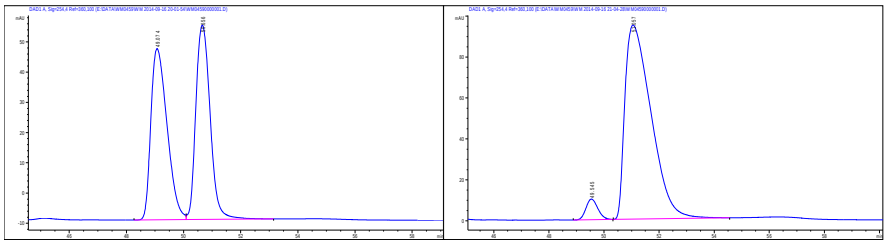
Signal 2: DAD1 B, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.752	BV	0.4149	6183.56494	229.09872	50.6115
2	26.546	VB	0.3241	6034.14160	293.16403	49.3885
Totals :				1.22177e4	522.26276	

Signal 2: DAD1 B, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.837	BV	0.4212	489.96878	17.46968	4.4787
2	26.567	VB	0.3226	1.04500e4	510.96277	95.5213
Totals :				1.09400e4	528.43245	





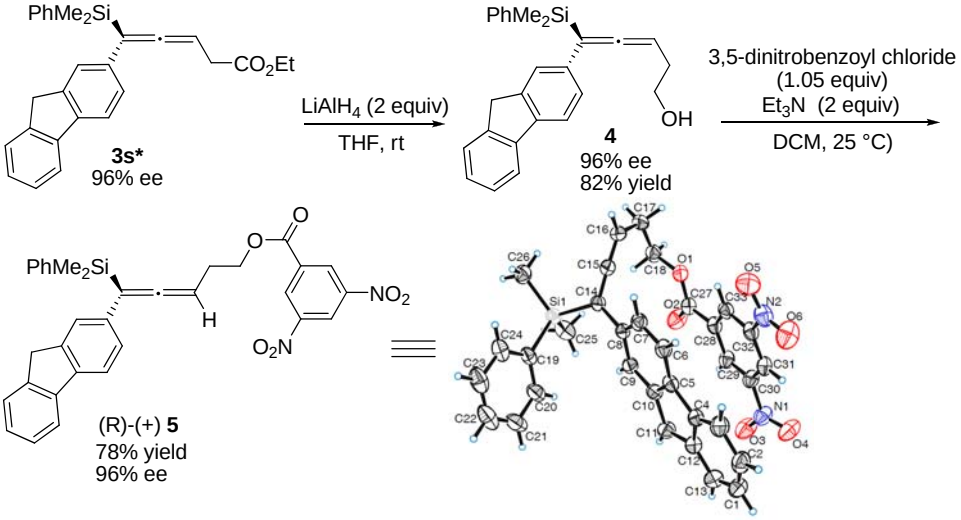
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	49.074	BV	0.6235	2229.79028	56.62008	49.9018
2	50.656	VB	0.5562	2238.56616	64.28928	50.0982
Totals :				4468.35645	120.90936	

Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	49.545	BB	0.4655	302.33047	10.09297	4.6291
2	51.057	BB	1.0367	6228.77637	94.78144	95.3709
Totals :				6531.10684	104.87441	

4. Determination of the Absolute Configuration of Compound 3s*.



In an oven dried 10 mL round bottom flask equipped with a stirring bar, 0.4 mmol (175.8 mg, 1 equiv) was dissolved in 4 mL of dry THF under argon atmosphere. The solution was added $LiAlH_4$ (30.4 mg, 2 equiv) in four batches at 0°C. The final solution was continued to stir for 5 hours at room temperature. Then the reaction was quenched with water and excess amount of saturated potassium sodium tartrate was introduced, and the solution was stirred for 30 minutes at room temperature. The final solution was extracted with ethyl acetate (10 mL×2), and the combined organic layer was washed with saturated brine (5 mL) and dried over anhydrous Na_2SO_4. The final filtrate was concentrated under vacuum to afford the crude product which was isolated through flash column chromatography (Eluent: PE/EA = 80:20) to furnish the related product **4** (130.5 mg, 82% yield) as yellow oil.

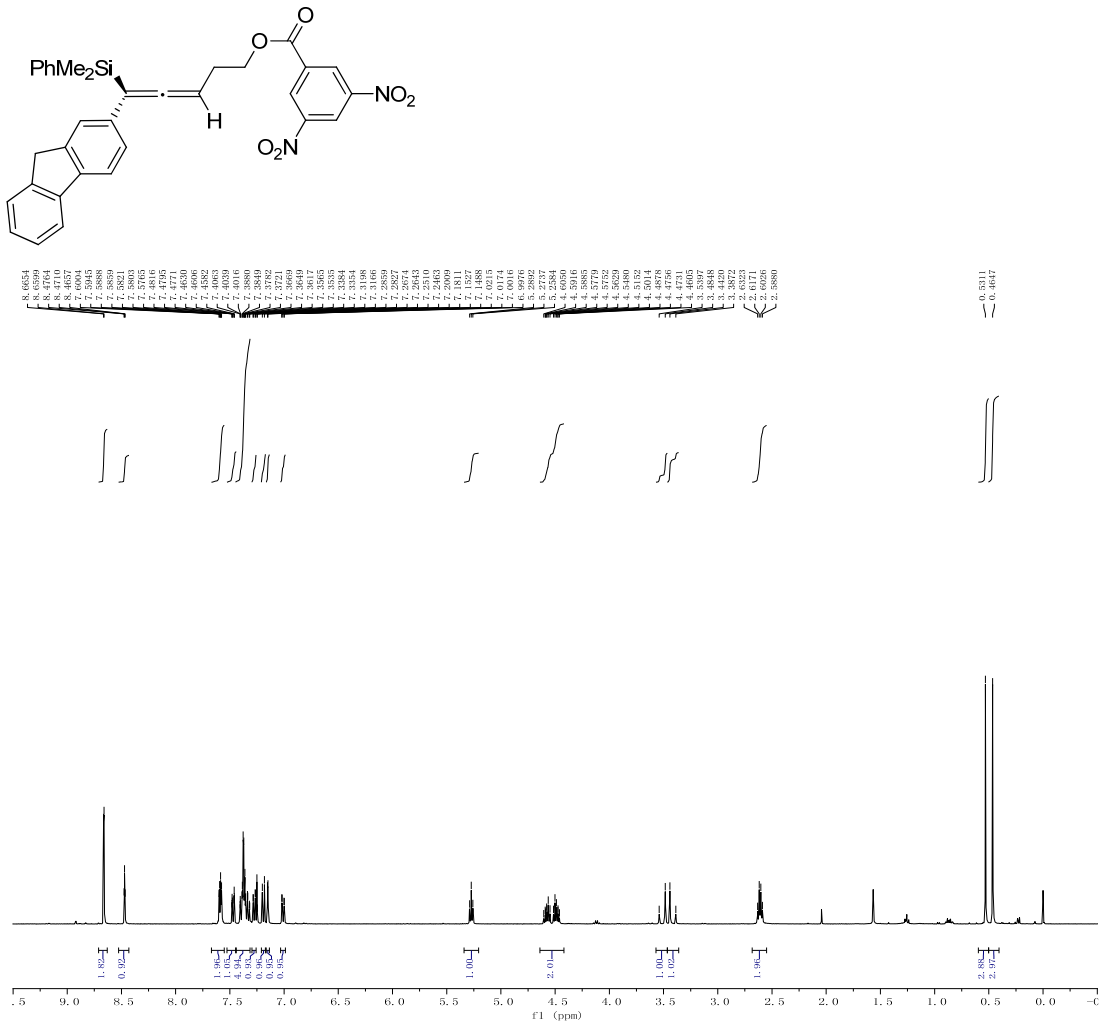
To a solution of 3,5-dinitrobenzoyl chloride (79.5 mg, 1.05 equiv) and alcohol **4** (130.5 mg, 1 equiv) with trace amount of DMAP in dichloromethane (2 mL) was added Et_3N (66.5 mg, 2 equiv) dropwise. The resulting mixture was stirred for 1 hour at room temperature, the final solution was directly subjected to column chromatography on silica gel (elution with PE:EA = 90:10) for purification of the crude product. The compound **5** was isolated (151.4 mg, 78% yield) as a bright yellow solide. ^{1}HNMR (400 MHz, $CDCl_3$): δ 8.66 (d, J = 2.2 Hz, 2H), 8.47 (t, J = 2.2 Hz, 1H), 7.60-7.57 (m, 2H), 7.48-7.45 (m, 1H), 7.40-7.31 (m, 5H), 7.27 (dd, J = 7.4, 1.3 Hz, 1H), 7.19 (d, J = 7.9 Hz, 1H), 7.15 (s, 1H), 7.01 (dd, J = 7.9, 1.6 Hz, 1H),

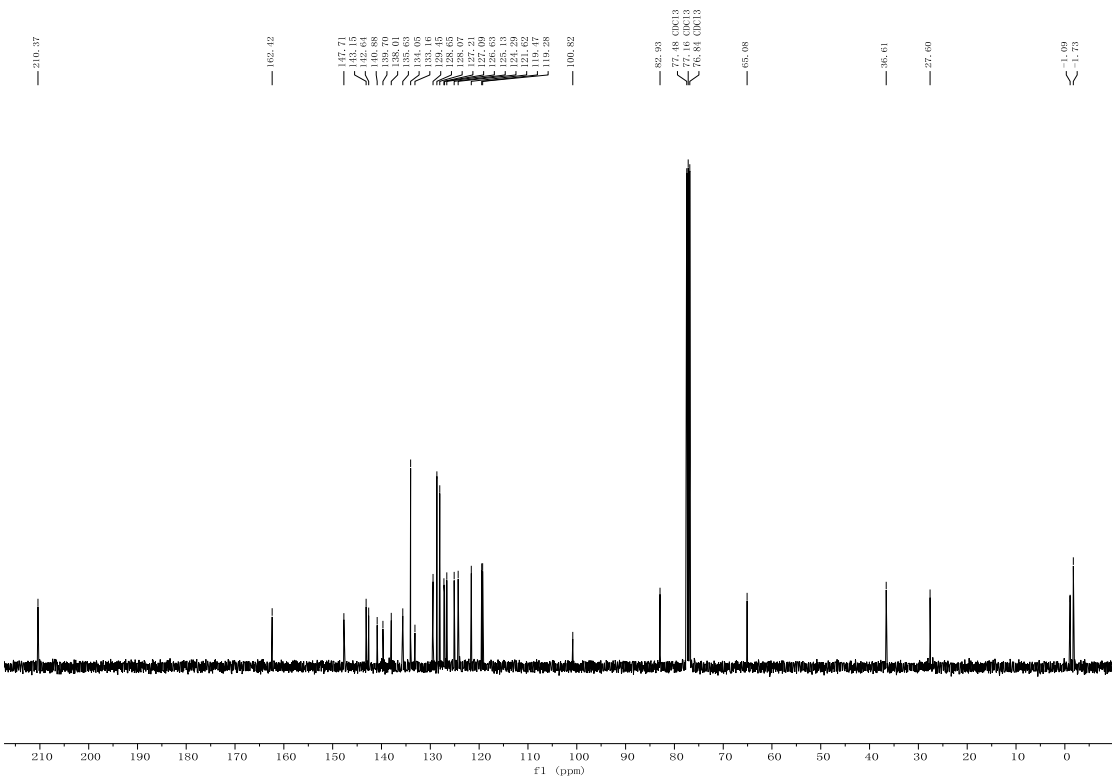
5.27 (t, *J* = 6.2 Hz, 1H). 4.60-4.46 (m, 2H), 3.50 (d, *J* = 22 Hz, 1H), 3.41 (d, *J* = 22 Hz, 1H), 2.60 (q, *J* = 6.1 Hz, 2H), 0.53 (s, 3H), 0.46 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 210.3, 162.4, 147.7, 143.1, 142.6, 140.8, 139.7, 138.0, 135.6. 134.0, 133.1, 129.4, 128.6, 128.0, 127.2, 127.0, 126.6, 125.1, 124.2, 121.6, 119.4, 119.2, 100.8, 82.9, 65.0, 36.6, 27.6, -1.0, -1.7..

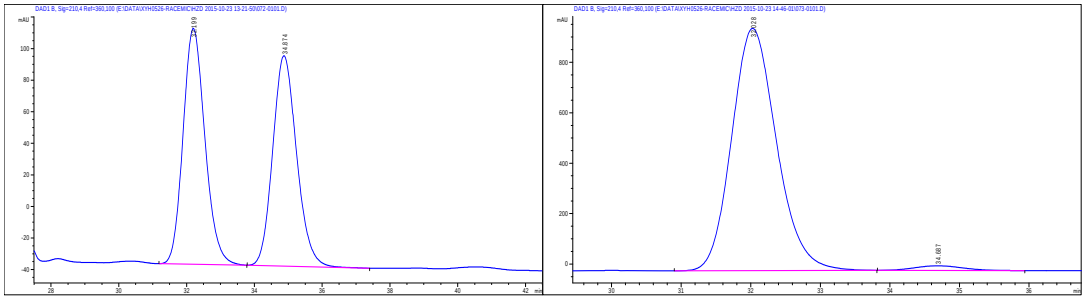
$[\alpha]_D^{25}$ +1.63^o (c = 1.00, $CHCl_3$).

96% ee, HPLC, IC, Hexane:^{i}PrOH = 94:6, 0.6 mL/min, 32.0 min (major), 34.6 min (minor).

HRMS (ESI): m/z calculated for $C_{33}H_{28}O_6N_2SiNa$ $[M+Na]^+$: 599.1614 found: 599.1606.







Signal 2: DAD1 B, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	32.199	BB	0.6874	6706.54883	149.48610	50.6045
2	34.874	BB	0.7529	6546.32178	133.30595	49.3955
Totals :				1.32529e4	282.79205	

Signal 2: DAD1 B, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	32.028	BB	0.6904	4.29782e4	959.82495	97.9911
2	34.687	BB	0.7160	881.06775	18.48867	2.0089
Totals :				4.38593e4	978.31362	