

Supporting Information

Copper-Catalyzed Regiodivergent 1,4- and 1,6-Conjugate Silyl Addition to the Diendioates: Access to the Functionalized Allylsilanes

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I. General Information

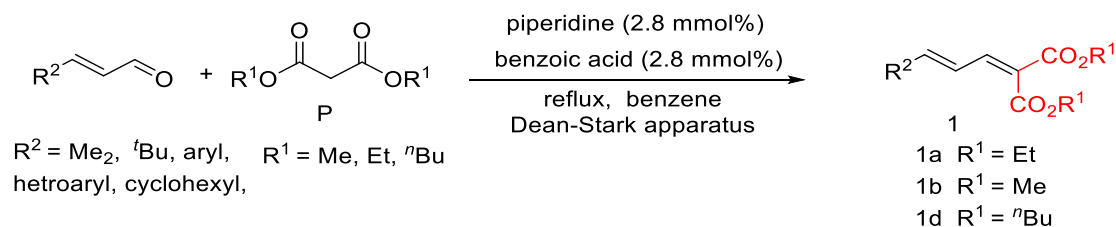
Dimethyl malonate, diethyl malonate, *i*-propyl malonate, *n*-butyl malonate, *t*-butyl malonate, Me₂PhSi-B(pin) and all phosphine ligands were purchased from commercial suppliers and used as received unless otherwise noted. All reactions were performed under argon atmosphere unless otherwise specified. All commercial solvents and reagents were employed without further purification. Reactions were monitored through analytical thin layer chromatography (SiO₂ 60 F-254 plates). The spots visualization were performed under UV radiation (254 nm), further visualization was possible using a basic solution of potassium permanganate. Flash chromatography was carried out using 200-300 mesh silica gel (SiO₂ 60) with distilled solvents. Proton nuclear magnetic resonance (¹H NMR) and Carbon nuclear magnetic resonance (¹³C NMR) spectra were recorded on Bruker Advance 400M NMR spectrometers. Chloroform-*d* was used as the solvent and SiMe₄ (TMS) as an internal standard. Chemical shifts for ¹H NMR spectra are reported as δ in units of parts per million (ppm) downfield from TMS (δ 0.00 ppm) and relative to the signal of chloroform-*d* (δ 7.260 ppm, singlet). Multiplicities are recorded as: *s* (singlet); *d* (doublet); *t* (triplet); *q* (quartet); *dd* (doublets of doublet); *m* (multiplets). Coupling constants are expressed as a *J* value in Hz. ¹³C NMR are reported as δ in units of parts per million (ppm) downfield from TMS (δ 0.00 ppm) and relative to the signal of chloroform-*d* (δ 77.03 ppm, triplet). Notable, splitting signals of the ¹³C nucleus was difficult to differentiate and ¹³C NMR signals were reported as a singlet. High resolution mass spectral analysis (HRMS) spectra were recorded on Water XEVO-G2 Q-TOF (Waters Corporation).

2. Experimental procedures

2.1 Procedure for synthesis of diendioates

All the diendioates were prepared according to the reported literature.^{1, 2, 3, 4} (**1a to 1s**):

Method A:



An oven-dried 100 mL round bottom flask with a mixture malonate **P** (14 mmol, 1 equiv), piperidine (2.8 mmol, 0.2 equiv), benzoic acid (2.8 mmol, 0.2 equiv) and benzene (32 mL) was

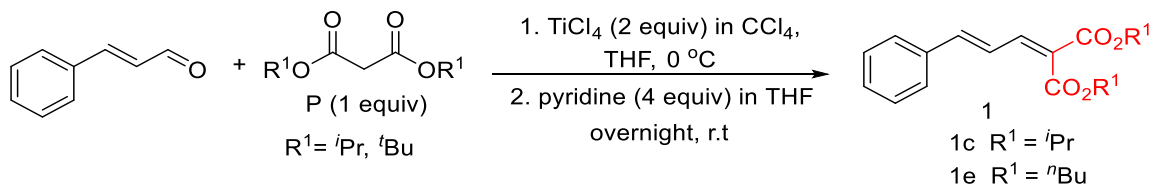
added the corresponding aldehyde (14 mmol, 1 equiv) under argon atmosphere. The mixture was refluxed for 3 to 6 h under a Dean-Stark apparatus. Then the reaction mixture was cooled to room temperature, washed with water, the aqueous phase was extracted with ethyl acetate (20 mL). The combined organic phase was dried over sodium sulfate (Na_2SO_4) and evaporated under reduced pressure to give the crude product, which was purified by flash column chromatography using petroleum ether/ethyl acetate (97:3) as eluent afforded the desired product (**1a**, **1b**, **1d**, **1e-1g**, **1i**, **1k-1v**) (60-86%).^{1,2}

Method B:



A flame-dried 50 mL round bottom flask charged with the catalytic amount of L-lysine (1 mmol, 20 mol%) in DMSO (10 mL, 0.5 M) and then the corresponding cinnamaldehyde (5 mmol), malonate (5 mmol) were added via syringe. The mixture was stirred at room temperature and until all the consumption of the starting material monitored by thin-layer chromatography (TLC). After the reaction was completed, the mixture was diluted with dichloromethane (60 mL) and washed with water (30 mL x 2). The mixture was evaporated under reduced pressure and the crude product was purified by silica gel flash column chromatography using petroleum ether/ethyl acetate (97:3) (**1h-1j**) (70-76%).³

Method C:

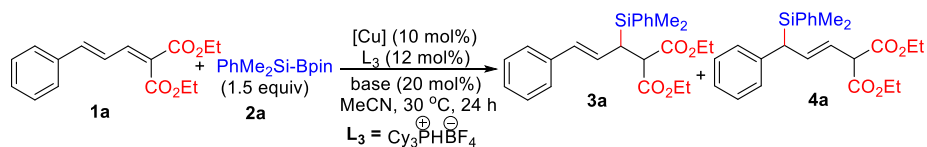


Malonate (6.0 mmol) and cinnamaldehyde (6.0 mmol) were added into a solution of TiCl_4 (12.0 mmol) in CCl_4 (4.0 mL) and THF (20 mL) at 0 °C. Then, pyridine (1.92 mL, 24.0 mmol) in THF (4 mL) was added slowly over 1 h. The reaction mixture was stirred at room temperature for overnight. The reaction mixture was quenched with water and then extracted with ethyl acetate, dried over MgSO_4 , filtered and evaporated under vacuum. The residue was

purified by silica gel flash column chromatography with petroleum ether/ethyl acetate (97:3) to afford the product (**1c-1e**) (65-69%).⁴

2.2 Optimization of reaction conditions

2.2.1 Optimization of reaction conditions for the 1,4-protosilylation of diendioates

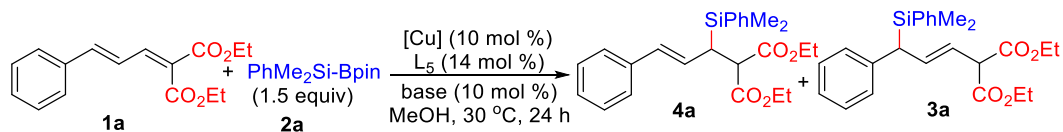


entry	cat. (10 mol %)	base (20 mol %)	ligand	solvent	r.r. (3a:4a) ^c	yield 3a (%) ^d
1	CuCN	LiO ^t Bu	-	CH ₃ CN	64:36	44
2	CuCN	LiO ^t Bu	L ₃	CH ₃ CN	80:20	78
3	CuCl	LiO ^t Bu	L ₃	CH ₃ CN	56:44	50
4	CuBr	LiO ^t Bu	L ₃	CH ₃ CN	68:32	66
5	CuI	LiO ^t Bu	L ₃	CH ₃ CN	65:35	63
6	CuTC	LiO ^t Bu	L ₃	CH ₃ CN	67:33	54
7	[Cu(CH ₃ CN) ₄][PF ₆]	LiO ^t Bu	L ₃	CH ₃ CN	74:26	70
8	Cu(OTf) ₂	LiO ^t Bu	L ₃	CH ₃ CN	70:30	64
9	CuCl ₂	LiO ^t Bu	L ₃	CH ₃ CN	69:31	66
10	CuSO ₄	LiO ^t Bu	L ₃	CH ₃ CN	66:34	58
11	Cu(OAc) ₂	LiO ^t Bu	L ₃	CH ₃ CN	65:35	52

^aReaction was performed according to following conditions: the mixture of **1a** (0.2 mmol), **2a** (0.3 mmol, 1.5 equiv), [Cu] (0.02 mmol, 0.1 equiv), **L**₃ (0.024 mmol, 0.12 equiv), LiO^tBu (0.04 mmol, 0.2 equiv), and Ar (1 atm) in MeCN (1 mL, 0.2 M) were stirred at 30 °C for 24 h.

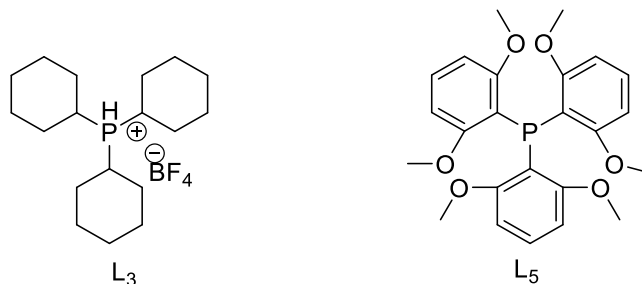
^cRegioselectivity ratio (**3a:4a**) determined by the crude ¹H NMR. ^dIsolated yields.

2.2.2 Optimization of reaction conditions for the 1,6-protosilylation of diendioates



entry	cat. (10 mol %)	base (10 mol %)	ligand (14 mol %)	solvent	r.r. (4a:3a) ^c	yield 4a (%) ^d
1	CuCN	LiO ^t Bu	-	MeOH	60:40	36
2	CuCN	LiO ^t Bu	L ₅	MeOH	80:20	72
3	CuCl	LiO ^t Bu	L ₅	MeOH	65:35	40
4	CuBr	LiO ^t Bu	L ₅	MeOH	67:33	43
5	CuI	LiO ^t Bu	L ₅	MeOH	77:23	68
6	CuTC	LiO ^t Bu	L ₅	MeOH	64:36	50
7	[Cu(CH ₃ CN) ₄][PF ₆]	LiO ^t Bu	L ₅	MeOH	62:38	45
8	Cu(OTf) ₂	LiO ^t Bu	L ₅	MeOH	60:40	33
9	CuCl ₂	LiO ^t Bu	L ₅	MeOH	65:35	38
10	Cu(OAc) ₂	LiO ^t Bu	L ₅	MeOH	78:22	64

^bReaction was performed according to following conditions: the mixture of **1a** (0.2 mmol), **2a** (0.3 mmol, 1.5 equiv), [Cu] (0.02 mmol, 0.1 equiv), **L₅** (0.028 mmol, 0.14 equiv), LiO^tBu (0.02 mmol, 0.1 equiv), and Ar (1 atm) in MeOH (1 ml, 0.2 M) were stirred at 30 °C for 24 h. ^cRegioselectivity ratio (**4a:3a**) determined by the crude ¹H NMR. ^dIsolated yields



2.3 Procedures for synthesis of 1,4- and 1,6-protosilylation adduct

2.3.1 Procedure for synthesis of the 1,4-protosilylation adduct

Method D: A dried 15 mL schlenk tube charged with a stir bar, MeCN (1.0 mL, 0.2 M) was added to a mixture of CuCN (1.8 mg, 0.02 mmol, 10 mol%) and **L₃** (11.1 mg, 0.024 mmol, 12 mol%) under argon atmosphere. The mixture was stirred for 40 minutes and followed by the addition of 2,2,6,6-tetramethylpiperidine (TMP) (5.6 mg, 0.04 mmol, 20 mol%), **1** (0.2 mmol, 1.0 equiv.) and [dimethylphenylsilyl pinacolatoboronate Me₂PhSi-B(pin)] **2a** (0.3 mmol, 1.5 equiv.). The reaction mixture was stirred at 30 °C for 24 h. The reaction mixture was diluted with ethyl acetate and the precipitate was removed by filtration through a celite pad of silica. Then the solvent was evaporated in vacuo and the crude product was purified by preparative thin layer chromatography (PTLC) (**3a-3v**).

2.3.2 Procedure for Synthesis of the 1,6-protosilylation adduct

Method E: A dried 15 mL schlenk tube charged with a stir bar, MeOH (1.0 mL, 0.2 M) was added to a mixture of CuCN (1.8 mg, 0.02 mmol, 10 mol%) and **L₅** (12.4 mg, 0.028 mmol, 14 mol%) under argon atmosphere. The mixture was stirred for 40 minutes and subsequently by the addition of TMP (2.8 mg, 0.02 mmol, 10 mol%), **1** (0.2 mmol, 1.0 equiv.) and [Me₂PhSi-B(pin)] **2a** (0.3 mmol, 1.5 equiv.). The reaction mixture was stirred at 30 °C for 24 h. The reaction mixture was diluted with ethyl acetate and the precipitate was removed by filtration through a celite pad of silica. Then the solvent was evaporated in vacuo and the crude product was obtained, which was confirmed by ¹H NMR. The crude product was purified by PTLC (**4a-4g, 4j-4l, 4o, 4q**). Some of 1,6-protosilylation product is very difficult to purify, therefore products (**4h, 4i, 4m, 4p, 4t, 4u, 4v**) were obtained in a mixture.

2.4 Synthetic applications of Compound (3a)

2.4.1 Reduction of esters to alcohols⁵

Method F: A dried 25 mL Schlenk tube was charged with **3a** (82.0 mg, 0.2 mmol) in dry DCM (2.0 mL, 0.1M) under argon atmosphere cooled to $-78\text{ }^{\circ}\text{C}$ for 10 min. Then, DIBAL-H (0.6 mL of a 1.5 M solution in toluene) was added dropwise over 5 min. After the cooling was removed and stirred for 12 h at ambient temperature. A saturated solution of potassium, sodium tartrate tetrahydrated (5 mL) was added and the resulting biphasic mixture stirred for further 6 h. The two phases were separated and the aqueous phase was extracted with DCM (3 x 5 mL). The combined organic phases were washed with brine, dried over anhydrous Na_2SO_4 . After the evaporation of the solvent in vacuo, the crude product was purified by PTLC as colorless oil **5** (45.3 mg, 0.139 mmol, 70% yield)

2.4.2 Desilylation

Method G: A dried 15 mL Schlenk tube was purged with argon and charged with **3a** (41.0 mg, 0.1 mmol), DMF (1.0 mL, 0.1 M) and K_2CO_3 (3.0 equiv., 0.041g). The resulting mixture was stirred at $30\text{ }^{\circ}\text{C}$ for 12 h. After the addition of aqueous solution of NH_4Cl and the mixture was extracted with DCM for 3 times, dried over anhydrous Na_2SO_4 , filtered and the solvent was evaporated in vacuo. The crude mixture was purified by PTLC as colorless oil **6** (18.0 mg, 0.065 mmol, 65% yield)

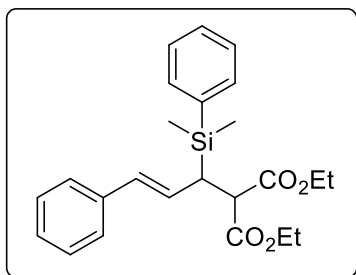
2.4.3 Conversion of silyl reagent to ester⁶

Method H: A flame dried 15 mL Schlenk tube was charged with tetrabutylammonium triphenyldifluorosilicate (TBAT) (1.1 equiv) under CO_2 atmosphere. The dry DMSO (0.1 M) was added to stirred to make a clear solution, then **3a** (1.0 equiv) in dry DMSO (0.1 M) was added *via* a syringe. The mixture was stirred at $30\text{ }^{\circ}\text{C}$ until all the consumption of **3a**. CH_3I (1.2 equiv) was then added and the reaction mixture was stirred for further 30 min. After the addition of water and the mixture was extracted with diethyl ether. The organic phase was washed with brine, dried over anhydrous Na_2SO_4 , filtered and the solvent was evaporated in vacuo. The crude mixture was purified by PTLC as colorless oil **7** (38.0 mg, 0.116 mmol, 58% yield)

3. Characterization Data and Spectra

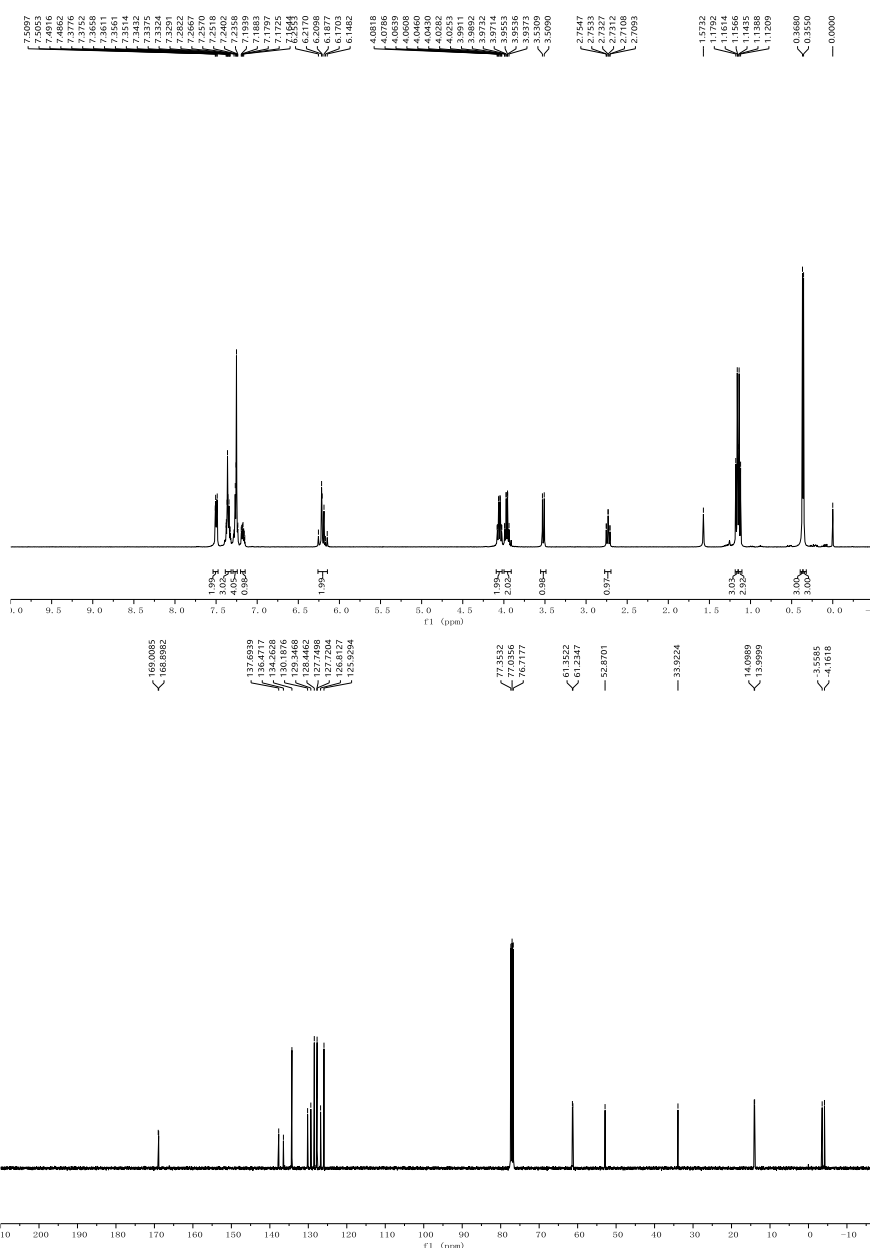
3.1 Characterization Data and Spectra of Products

Diethyl (*E*)-2-(1-(dimethyl(phenyl)silyl)-3-phenylallyl)malonate (**3a**)

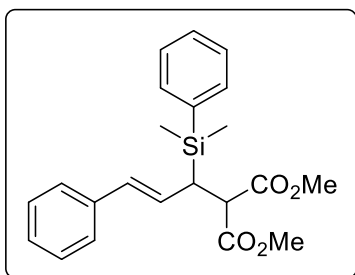


Following the Method D, **3a** was obtained as a colorless oil (70.8 mg, 0.172 mmol, 86%); ¹H NMR (400 MHz, CDCl₃): δ 7.48 – 7.50 (m, 2H), 7.38 – 7.33 (m, 3H), 7.29 – 7.24 (m, 4H), 7.19 – 7.15 (m, 1H), 6.26 – 6.14 (m, 2H), 4.08 – 4.02 (m, 2H), 3.99 – 3.93 (m, 2H), 3.52 (d, *J* = 8.8 Hz, 1H), 2.73 (ddd, *J* = 9.4, 8.8, 0.5 Hz, 1H), 1.16 (t, *J* = 7.1 Hz, 3H), 1.13 (t, *J* = 7.1 Hz, 3H), 0.37 (s, 3H), 0.36 (s, 3H) ppm; ¹³C NMR (101 MHz, CDCl₃): δ 169.01, 168.90, 137.69, 136.47, 134.26, 130.19, 129.35,

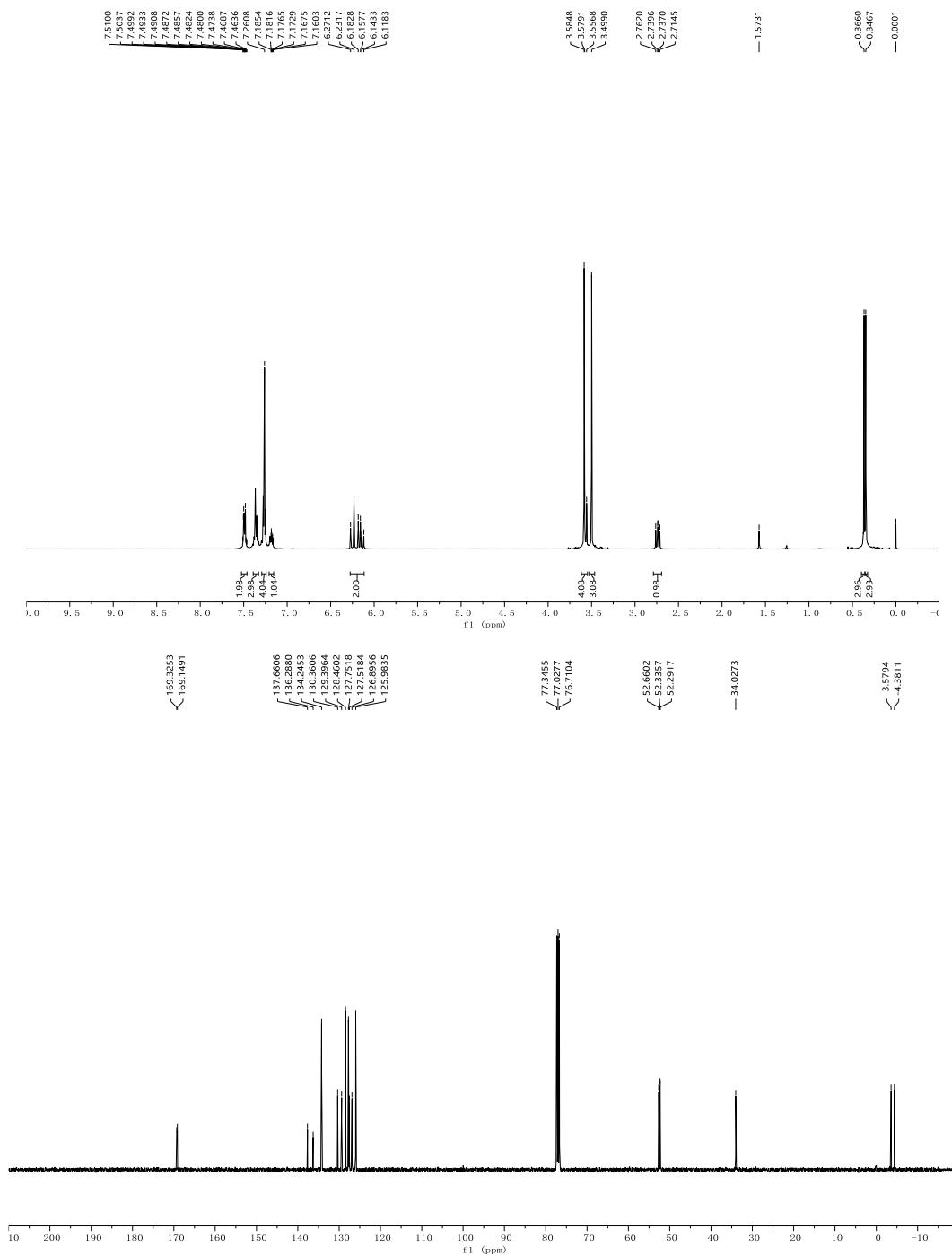
128.45, 127.75, 127.72, 126.81, 125.93, 61.35, 61.23, 52.87, 33.92, 14.10, 14.00, -3.56, -4.16 ppm; HRMS (ESI): *m/z* Calcd. for C₂₄ H₃₁ O₄ Si [M+H]⁺: 411.1986, found: 411.1989.



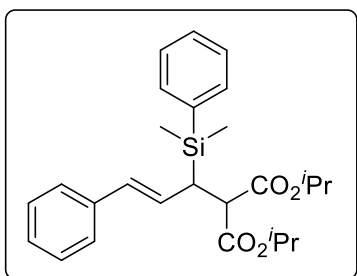
Dimethyl (*E*)-2-(1-(dimethyl(phenyl)silyl)-3-phenylallyl)malonate (**3b**)



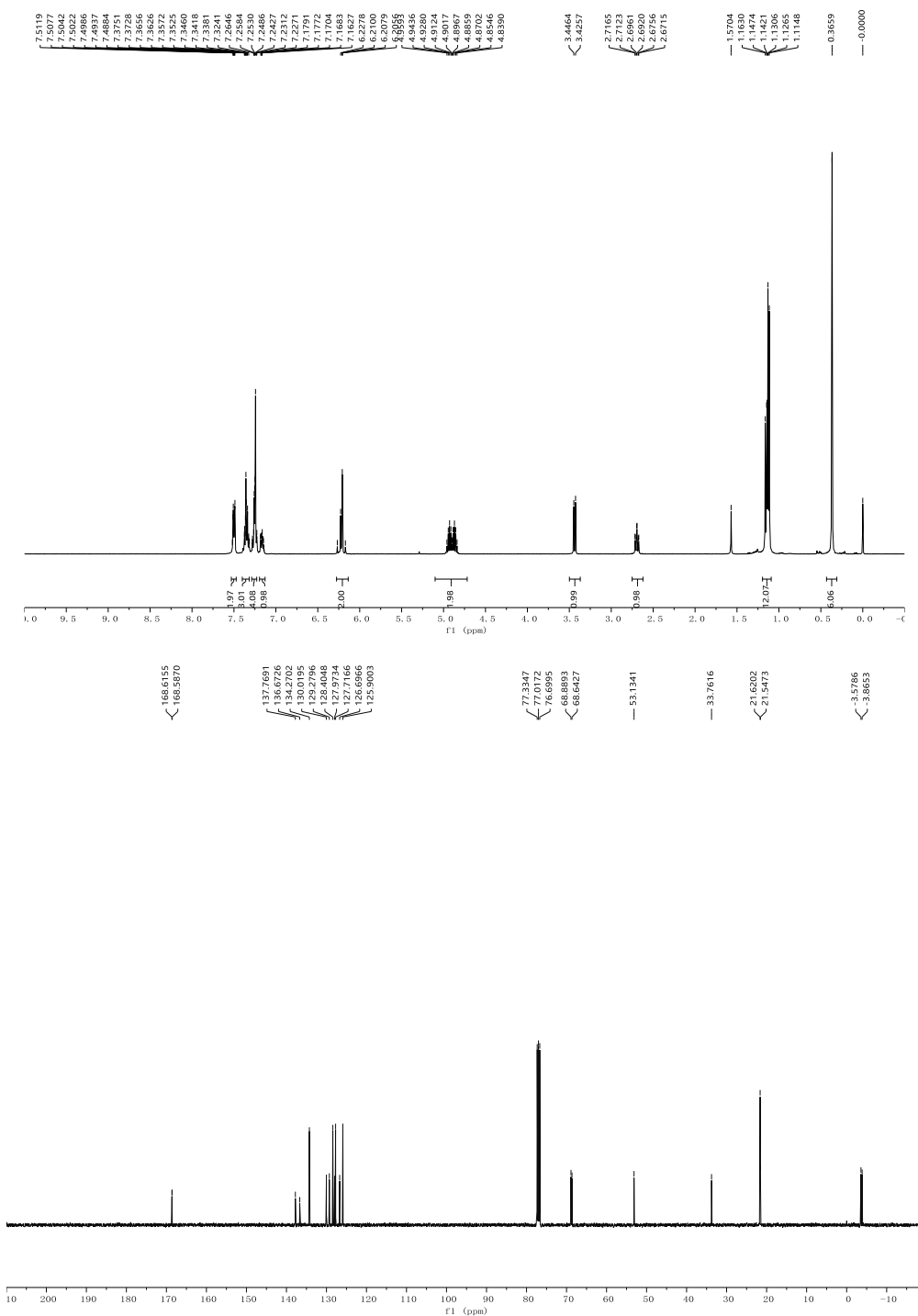
Following the Method D, **3b** was obtained as a colorless oil (62.8 mg, 0.165 mmol, 82%); **¹H NMR (400 MHz, CDCl₃)**: δ 7.53 – 7.46 (m, 2H), 7.38 – 7.32 (m, 3H), 7.29 – 7.24 (m, 4H), 7.20 – 7.16 (m, 1H), 6.28 – 6.11 (m, 2H), 3.58 – 3.55 (m, 4H), 3.50 (s, 3H), 2.73 (dd, *J* = 10.0, 9.1 Hz, 1H), 0.36 (s, 3H), 0.34 (s, 3H) ppm; **¹³C NMR (101 MHz, CDCl₃)**: δ 169.33, 169.15, 137.66, 136.29, 134.25, 130.36, 129.40, 128.46, 127.75, 127.52, 126.90, 125.98, 52.66, 52.34, 52.29, 34.03, -3.58, -4.38 ppm; **HRMS (ESI)**: *m/z* Calcd. for C₂₂H₂₇O₄Si [M+H]⁺: 383.1673, found: 383.1668.



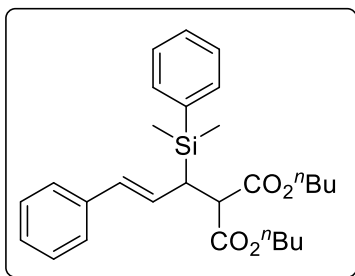
Diisopropyl (*E*)-2-(1-(dimethyl(phenyl)silyl)-3-phenylallyl)malonate (3c**)**



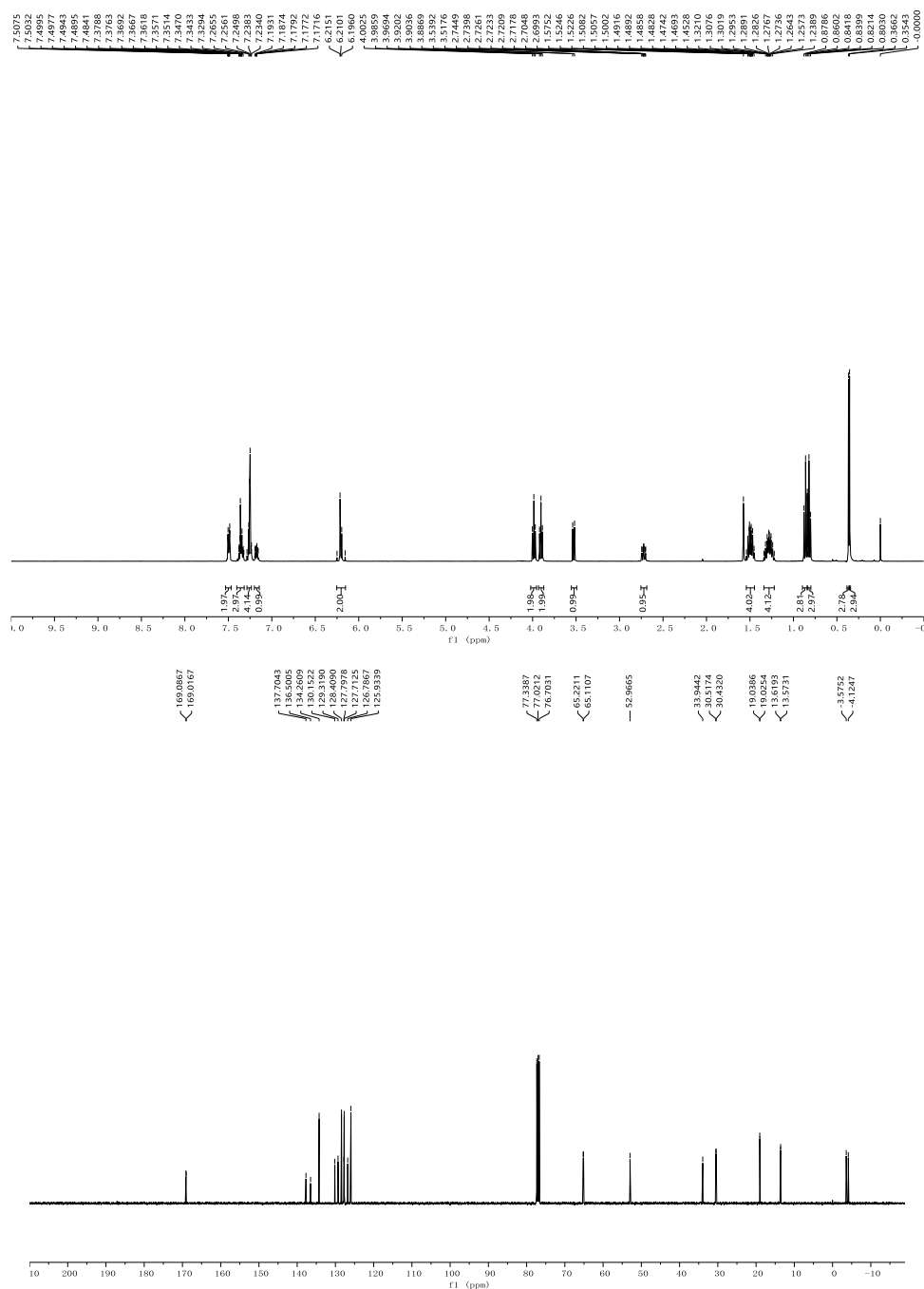
Following the Method D, **3c** was afforded as a colorless oil (67.8 mg, 0.155 mmol, 78%); **¹H NMR (400 MHz, CDCl₃)**: δ 7.53 – 7.47 (m, 2H), 7.40 – 7.32 (m, 3H), 7.29 – 7.23 (m, 4H), 7.19 – 7.13 (m, 1H), 6.28 – 6.14 (m, 2H), 4.99 – 4.84 (m, 2H), 3.44 (d, *J* = 8.3 Hz, 1H), 2.69 (ddd, *J* = 9.8, 8.2, 1.6 Hz, 1H), 1.20 – 1.09 (m, 12H), 0.36 (s, 6H) ppm; **¹³C NMR (101 MHz, CDCl₃)**: δ 168.62, 168.59, 137.77, 136.67, 134.27, 130.02, 129.28, 128.40, 127.97, 127.72, 126.70, 125.90, 68.89, 68.64, 53.13, 33.76, 21.62, 21.55, -3.58, -3.87 ppm; **HRMS (ESI)**: *m/z* Calcd. for C₂₆H₃₅O₄Si [M+H]⁺: 439.2299, found: 439.2292.



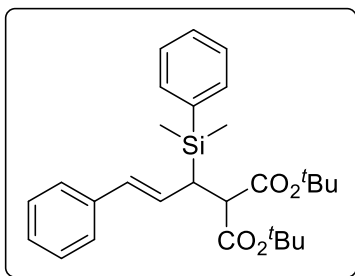
Dibutyl (*E*)-2-(1-(dimethyl(phenyl)silyl)-3-phenylallyl)malonate (3d**)**



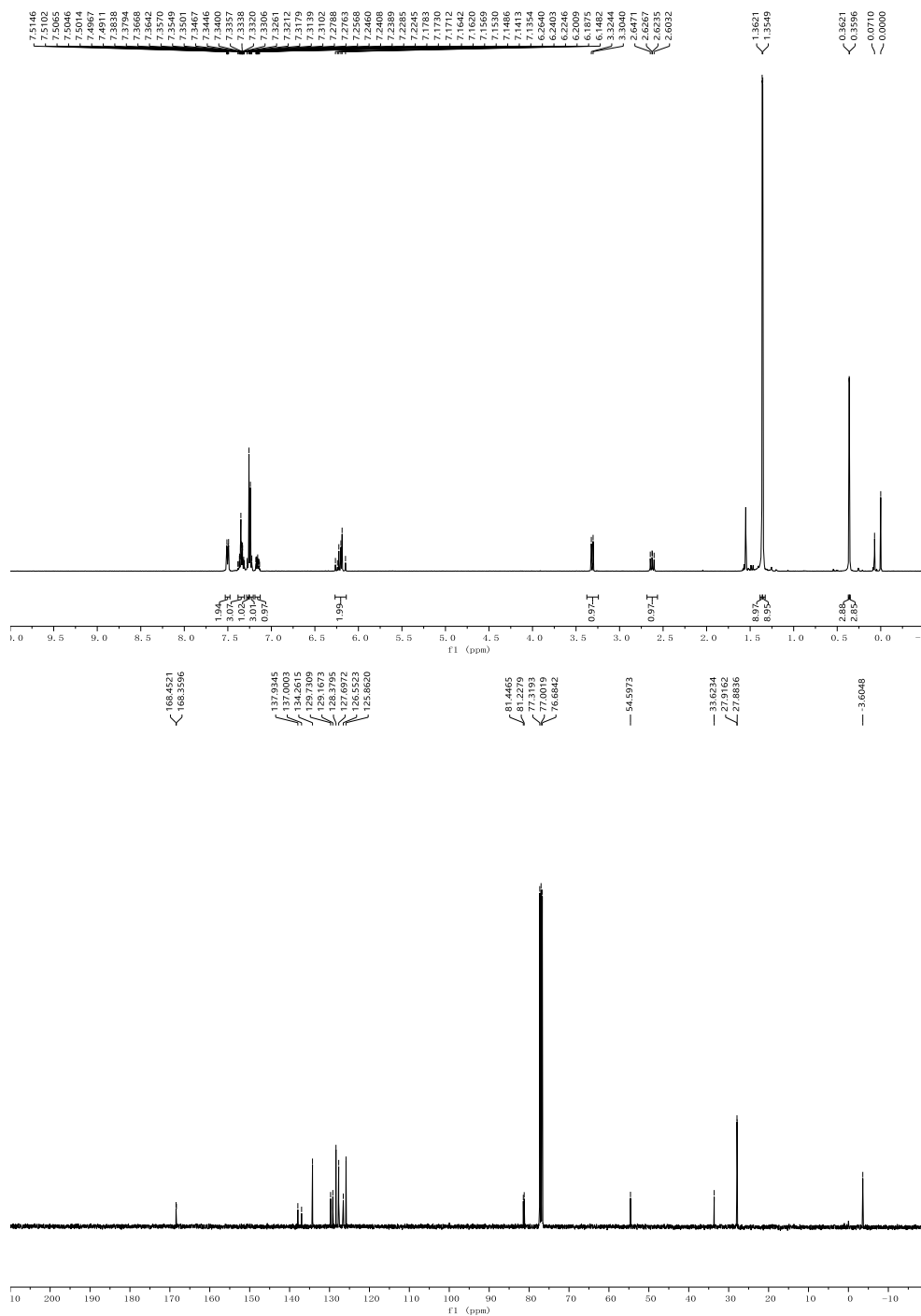
Following the Method D, **3d** was afforded as a colorless oil (74.6 mg, 0.160 mmol, 80%); **¹H NMR (400 MHz, CDCl₃)**: δ 7.53 – 7.47 (m, 2H), 7.40 – 7.32 (m, 3H), 7.29 – 7.23 (m, 4H), 7.19 – 7.15 (m, 1H), 6.25 – 6.15 (m, 2H), 3.99 (t, *J* = 6.6 Hz, 2H), 3.90 (t, *J* = 6.6 Hz, 2H), 3.53 (d, *J* = 8.6 Hz, 1H), 2.72 (ddd, *J* = 8.6, 7.5, 2.0 Hz, 1H), 1.54 – 1.45 (m, 4H), 1.34 – 1.22 (m, 4H), 0.86 (t, *J* = 7.2 Hz, 3H), 0.82 (t, *J* = 7.5 Hz, 3H), 0.36 (s, 3H), 0.35 (s, 3H) ppm; **¹³C NMR (101 MHz, CDCl₃)**: δ 169.09, 169.02, 137.70, 136.50, 134.26, 130.15, 129.32, 128.41, 127.80, 127.71, 126.79, 125.93, 65.22, 65.11, 52.97, 33.94, 30.52, 30.43, 19.04, 19.03, 13.62, 13.57, -3.58, -4.12 ppm; **HRMS (ESI)**: *m/z* Calcd. for C₂₈H₃₉O₄Si [M+H]⁺: 467.2612, found: 467.2614.



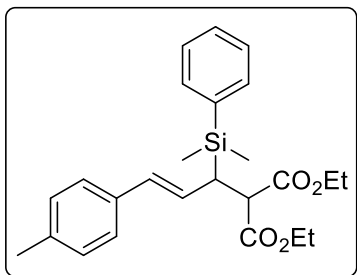
Di-tert-butyl (*E*)-2-(1-(dimethyl(phenyl)silyl)-3-phenylallyl)malonate (3e**)**



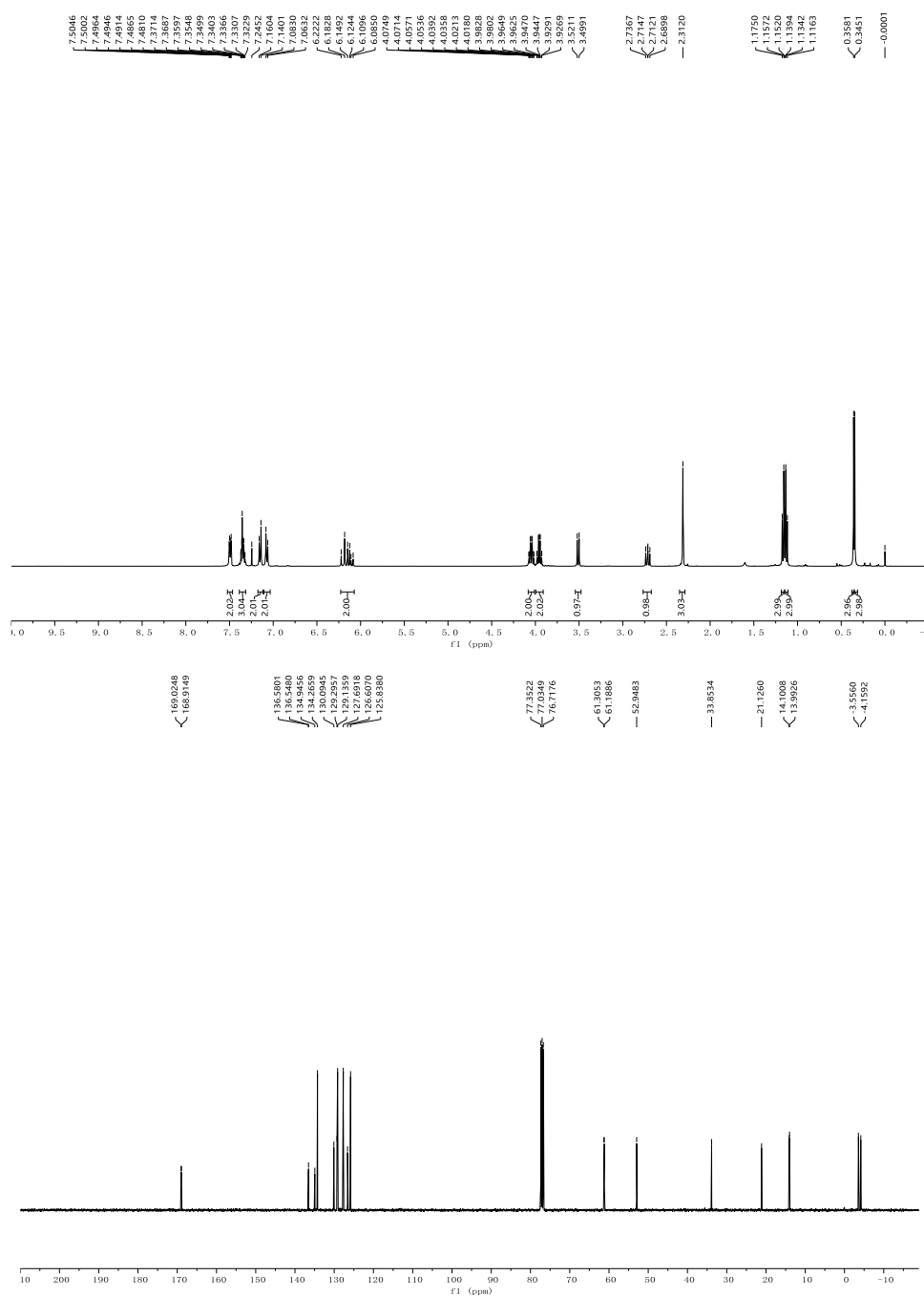
Following the Method **D**, **3e** was obtained as a light green oil (65.3 mg, 0.139 mmol, 70%); $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.53 – 7.48 (m, 2H), 7.38 – 7.31 (m, 3H), 7.28 – 7.26 (m, 1H), 7.25 – 7.21 (m, 3H), 7.19 – 7.13 (m, 1H), 6.33 – 6.09 (m, 2H), 3.31 (d, $J = 8.2$ Hz, 1H), 2.63 (dd, $J = 9.4$, 8.1 Hz, 1H), 1.36 (s, 9H), 1.35 (s, 9H), 0.36 (s, 3H), 0.35 (s, 3H) ppm; $^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 168.45, 168.36, 137.93, 137.00, 134.26, 129.73, 129.17, 128.38, 127.70, 126.55, 125.86, 81.45, 81.23, 54.60, 33.62, 27.92, 27.88, -3.60 ppm; **HRMS** (ESI): m/z Calcd. for $\text{C}_{28}\text{H}_{39}\text{O}_4\text{Si}$ $[\text{M}+\text{H}]^+$: 467.2612, found: 467.2603.



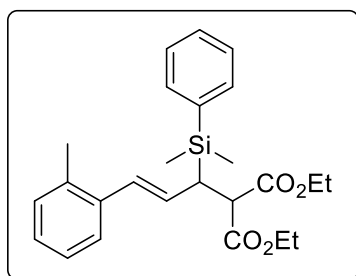
Diethyl (E)-2-(1-(dimethyl(phenyl)silyl)-3-(p-tolyl)allyl)malonate (3f)



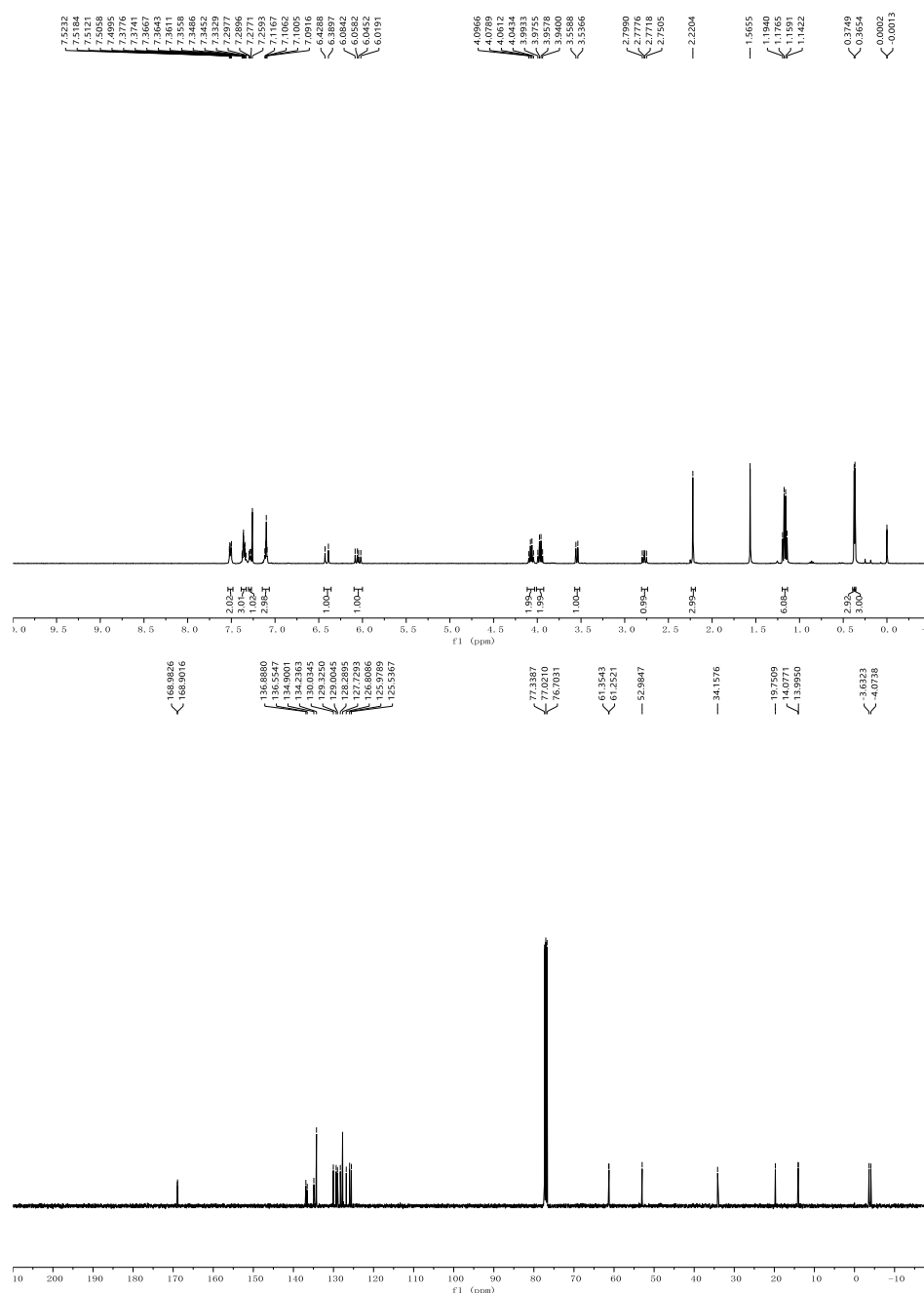
Following the Method D, **3f** was isolated as a light green oil (68.7 mg, 0.162 mmol, 81%); **¹H NMR (400 MHz, CDCl₃)**: δ 7.52 – 7.47 (m, 2H), 7.39 – 7.32 (m, 3H), 7.15 (d, *J* = 8.1 Hz, 2H), 7.07 (d, *J* = 7.9 Hz, 2H), 6.23 – 6.07 (m, 2H), 4.07 – 4.01 (m, 2H), 3.98 – 3.92 (m, 2H), 3.51 (d, *J* = 8.8 Hz, 1H), 2.71 (dd, *J* = 9.9, 8.9 Hz, 1H), 2.31 (s, 3H), 1.15 (t, *J* = 7.1 Hz, 3H), 1.13 (t, *J* = 7.1 Hz, 3H), 0.35 (s, 3H), 0.34 (s, 3H) ppm; **¹³C NMR (101 MHz, CDCl₃)**: δ 169.02, 168.91, 136.58, 136.55, 134.95, 134.27, 130.09, 129.30, 129.14, 127.69, 126.61, 125.84, 61.31, 61.19, 52.95, 33.85, 21.13, 14.10, 13.99, -3.56, -4.16. ppm; **HRMS (ESI)**: *m/z* Calcd. for C₂₅H₃₃O₄Si [M+H]⁺: 425.2143, found: 425.2135.



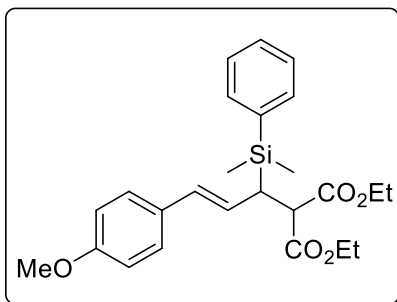
Diethyl (*E*)-2-(1-(dimethyl(phenyl)silyl)-3-(*o*-tolyl)allyl)malonate (3g**)**



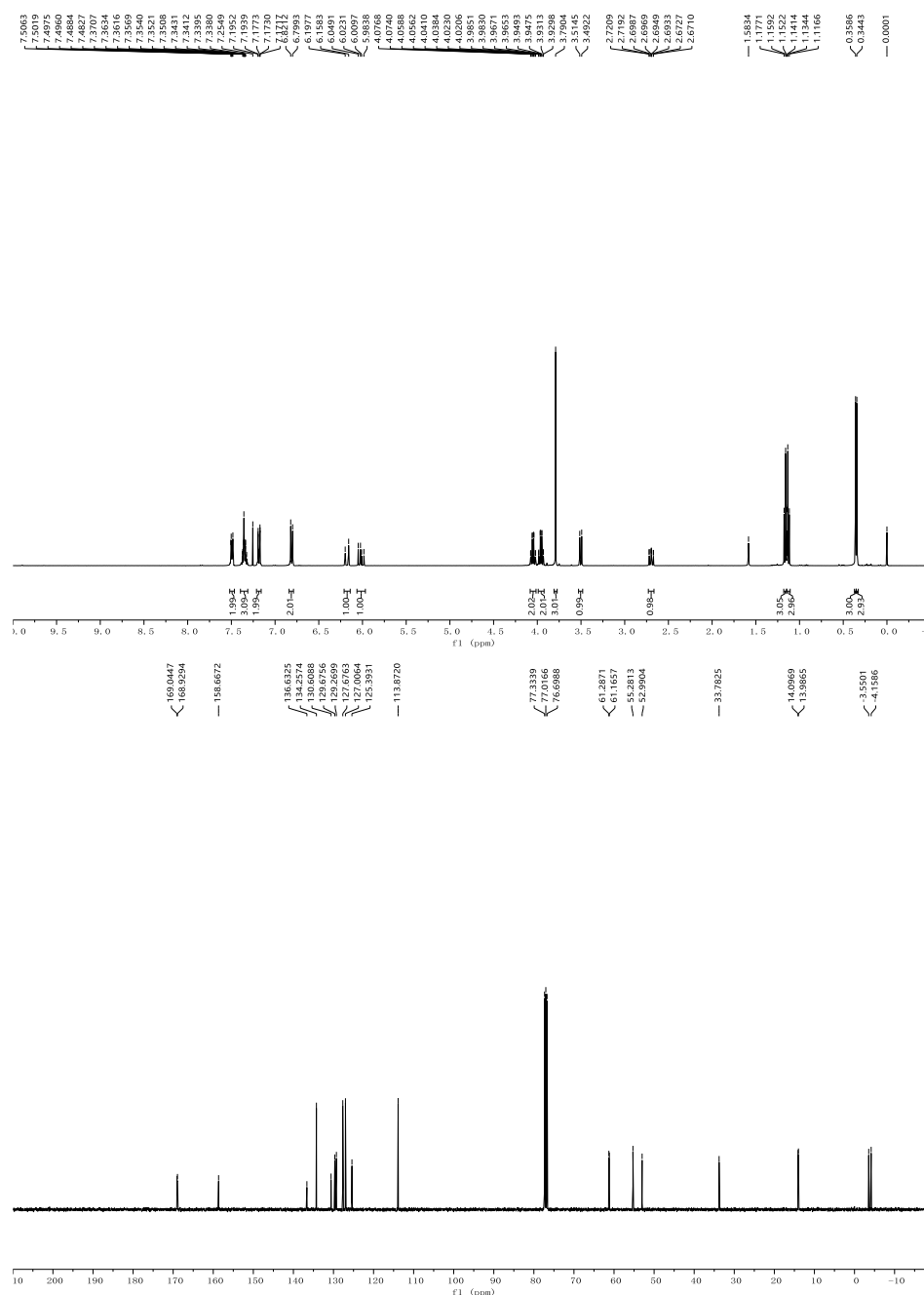
Following the Method D, **3g** was isolated as a light green oil (65.7 mg, 0.155 mmol, 78%); $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.52 – 7.49 (m, 2H), 7.39 – 7.33 (m, 3H), 7.30 – 7.27 (m, 1H), 7.11 – 7.09 (m, 3H), 6.41 (d, $J = 15.6$ Hz, 1H), 6.05 (dd, $J = 15.6, 10.4$ Hz, 1H), 4.07 (q, $J = 7.1$ Hz, 2H), 3.97 (q, $J = 7.1$ Hz, 2H), 3.55 (d, $J = 8.9$ Hz, 1H), 2.77 (dd, $J = 10.8, 8.6$ Hz, 1H), 2.22 (s, 3H), 1.19 – 1.14 (m, 6H), 0.37 (s, 3H), 0.36 (s, 3H) ppm; $^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 168.98, 168.90, 136.89, 136.55, 134.90, 134.24, 130.03, 129.33, 129.00, 128.29, 127.73, 126.81, 125.98, 125.54, 61.35, 61.25, 52.98, 34.16, 19.75, 14.08, 14.00, -3.63, -4.07 ppm; HRMS (ESI): m/z Calcd. for $\text{C}_{25}\text{H}_{33}\text{O}_4\text{Si}$ $[\text{M}+\text{H}]^+$: 425.2143, found: 425.2134.



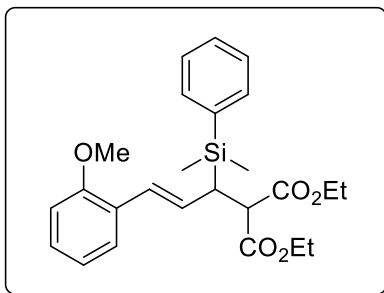
Diethyl (*E*)-2-(1-(dimethyl(phenyl)silyl)-3-(4-methoxyphenyl)allyl)malonate (**3h**)



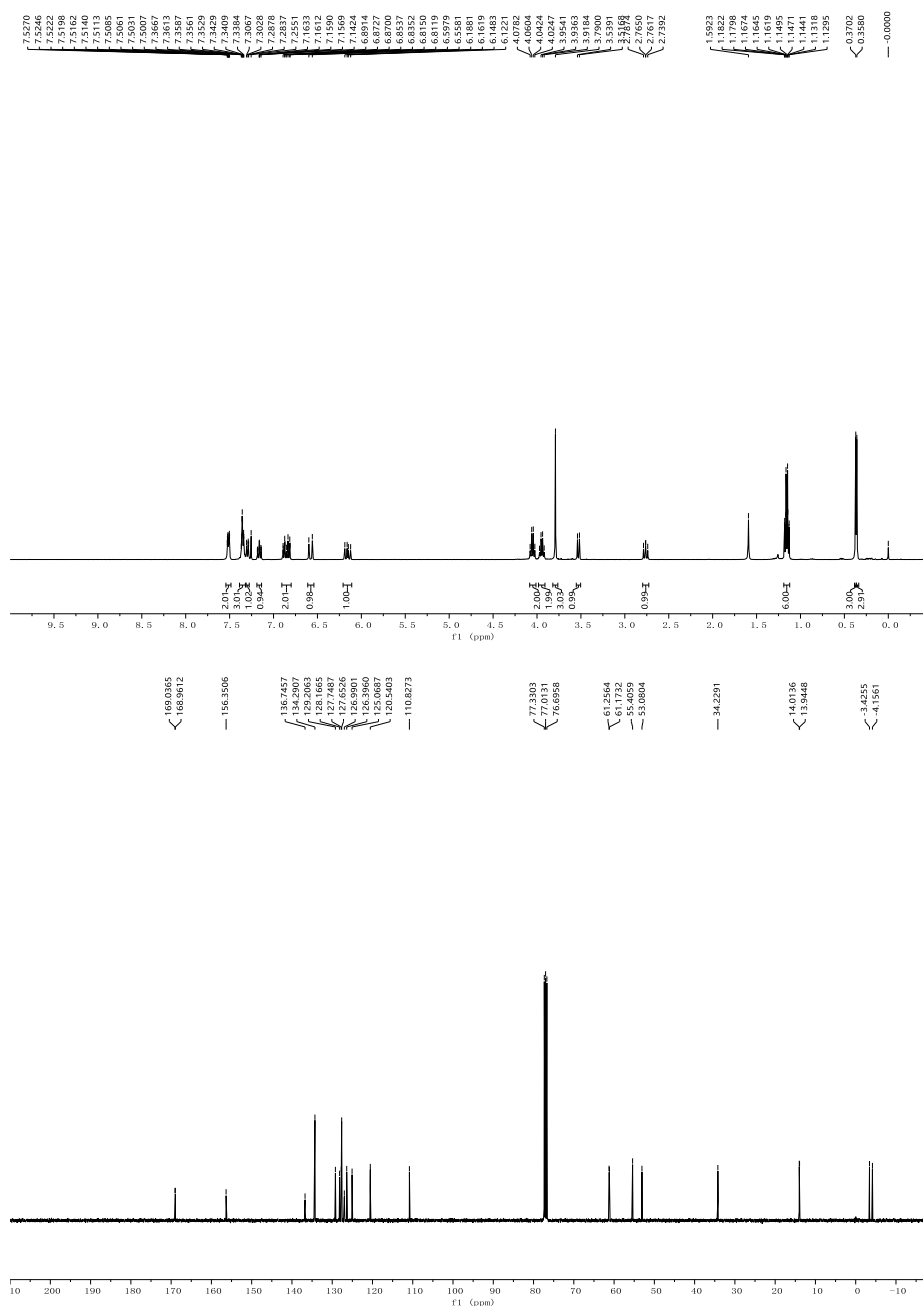
Following the Method D, **3h** was obtained as a light green oil (69.8 mg, 0.159 mmol, Yield: 79%); $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.52 – 7.47 (m, 2H), 7.40 – 7.31 (m, 3H), 7.21 – 7.16 (m, 2H), 6.81 (d, J = 8.8 Hz, 2H), 6.18 (d, J = 15.8 Hz, 1H), 6.02 (dd, J = 15.7, 10.4 Hz, 1H), 4.07 – 4.02 (m, 2H), 3.98 – 3.92 (m, 2H), 3.79 (s, 3H), 3.50 (d, J = 8.9 Hz, 1H), 2.69 (ddd, J = 9.5, 8.9, 0.6 Hz, 1H), 1.15 (t, J = 7.1 Hz, 3H), 1.13 (t, J = 7.1 Hz, 3H), 0.36 (s, 3H), 0.35 (s, 3H) ppm; $^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 169.04, 168.93, 158.67, 136.63, 134.26, 130.61, 129.68, 129.27, 127.68, 127.01, 125.39, 113.87, 61.29, 61.17, 55.28, 52.99, 33.78, 14.10, 13.99, -3.55, -4.16 ppm; HRMS (ESI): m/z Calcd. for $\text{C}_{25}\text{H}_{33}\text{O}_5\text{Si}$ $[\text{M}+\text{H}]^+$: 441.2092, found: 441.2083.



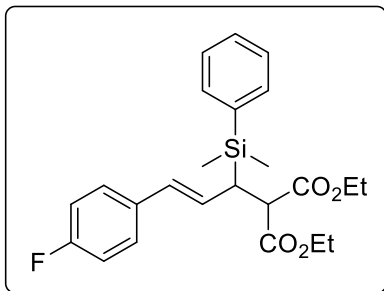
Diethyl (*E*)-2-(1-(dimethyl(phenyl)silyl)-3-(2-methoxyphenyl)allyl)malonate (**3i**)



Following the Method D, **3i** was isolated as a light green oil (65.5 mg, 0.148 mmol, Yield: 74%); $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.55 – 7.48 (m, 2H), 7.39 – 7.31 (m, 3H), 7.30 – 7.28 (m, 1H), 7.21 – 7.11 (m, 1H), 6.92 – 6.79 (m, 2H), 6.58 (d, $J = 15.9$ Hz, 1H), 6.16 (dd, $J = 15.9, 10.5$ Hz, 1H), 4.05 (q, $J = 7.1$ Hz, 2H), 3.95 (q, $J = 7.1$ Hz, 2H), 3.79 (s, 2H), 3.53 (d, $J = 8.9$ Hz, 1H), 2.76 (dd, $J = 10.3, 9.0$ Hz, 1H), 1.18 – 1.12 (m, 6H), 0.37 (s, 3H), 0.35 (s, 3H) ppm; $^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 169.04, 168.96, 156.35, 136.75, 134.29, 129.21, 128.17, 127.75, 127.65, 126.99, 126.40, 125.07, 120.54, 110.83, 61.26, 61.17, 55.41, 53.08, 34.23, 14.01, 13.94, -3.43, -4.16 ppm; HRMS (ESI): m/z Calcd. for $\text{C}_{25}\text{H}_{33}\text{O}_5\text{Si}$ $[\text{M}+\text{Na}]^+$: 441.2092, found: 441.2088.

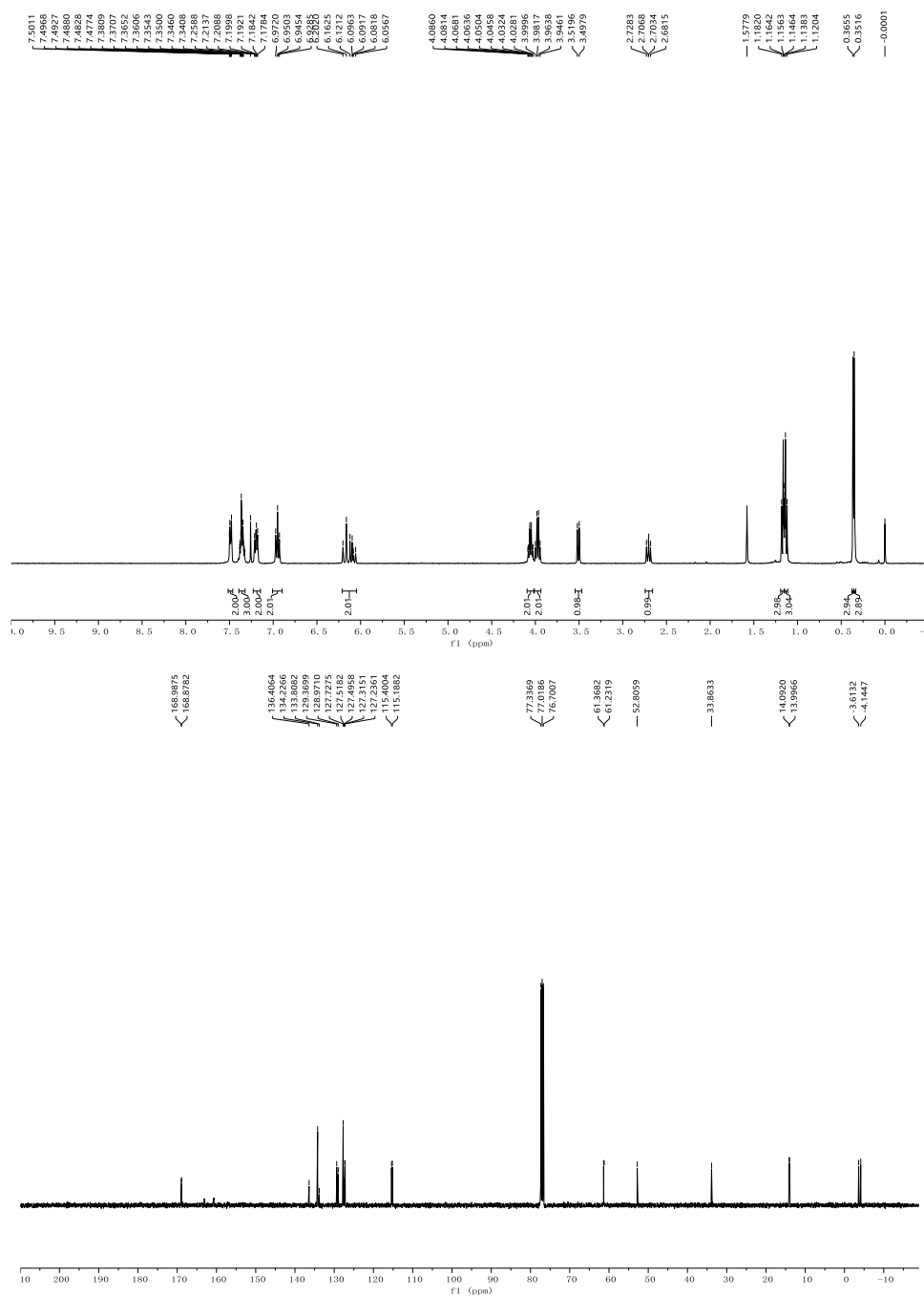


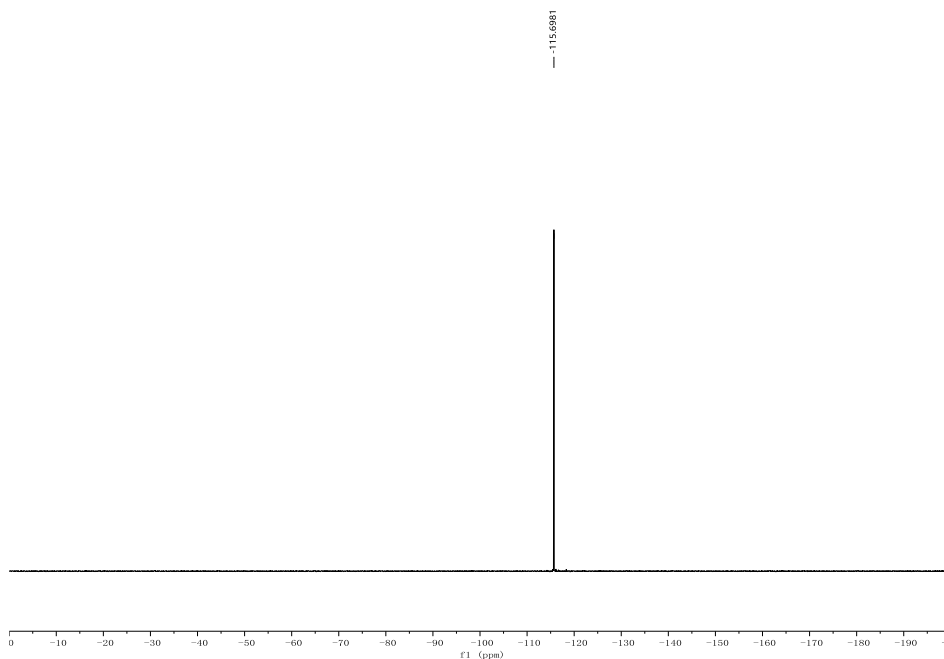
Diethyl (*E*)-2-(1-(dimethyl(phenyl)silyl)-3-(4-fluorophenyl)allyl)malonate (**3j**)



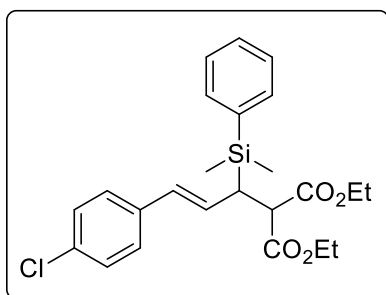
Following the Method D, **3j** was obtained as a colorless oil (71.8 mg, 0.168 mmol, Yield: 84%); **¹H NMR (400 MHz, CDCl₃)**: δ 7.52 – 7.46 (m, 2H), 7.39 – 7.32 (m, 3H), 7.23 – 7.15 (m, 2H), 7.01 – 6.90 (m, 2H), 6.21 – 6.05 (m, 2H), 4.08 – 4.02 (m, 2H), 3.97 (q, *J* = 7.1 Hz, 2H), 3.51 (d, *J* = 8.7 Hz, 1H), 2.71 (dd, *J* = 10.0, 8.7 Hz, 1H), 1.16 (t, *J* = 7.1 Hz, 3H), 1.13 (t, *J* = 7.1 Hz, 3H), 0.36 (s, 3H), 0.35 (s, 3H) ppm; **¹³C NMR (101 MHz, CDCl₃)**: δ 168.99, 168.88, 136.41, 134.23, 133.81, 129.37, 128.97, 127.73, 127.52, 127.50, 127.32, 127.24, 115.40, 115.19, 61.37,

61.23, 52.81, 33.86, 14.09, 14.00, -3.61, -4.14. ppm; **¹⁹F NMR (376 MHz, CDCl₃)**: δ -115.70 ppm; **HRMS (ESI)**: *m/z* Calcd. for C₂₄H₃₀O₄FSi [M+H]⁺: 429.1892, found: 429.1884.





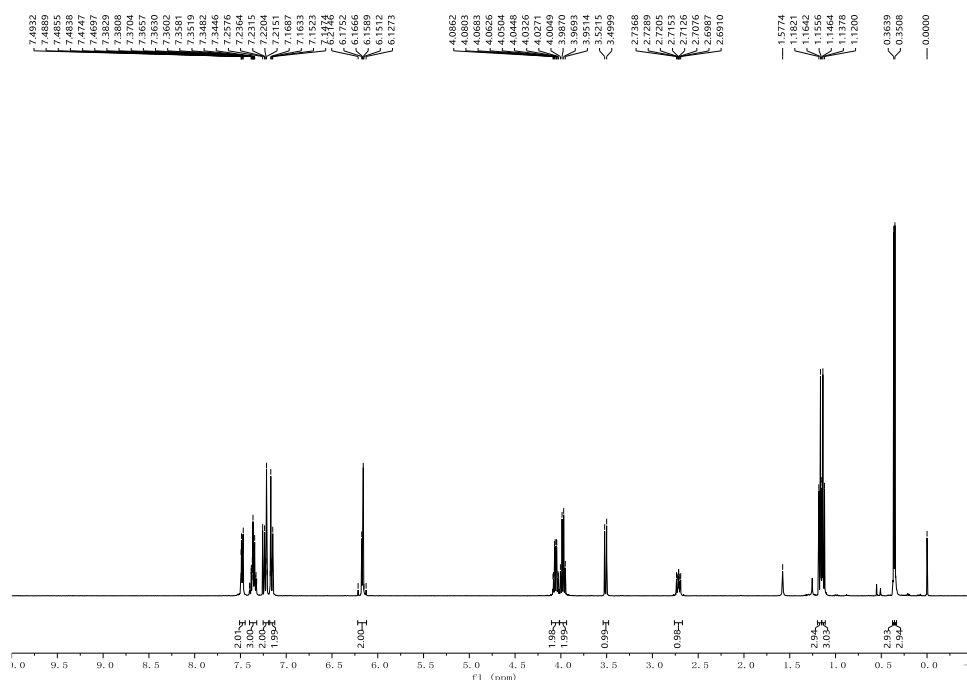
Diethyl (*E*)-2-(3-(4-chlorophenyl)-1-(dimethyl(phenyl)silyl)allyl)malonate (**3k**)

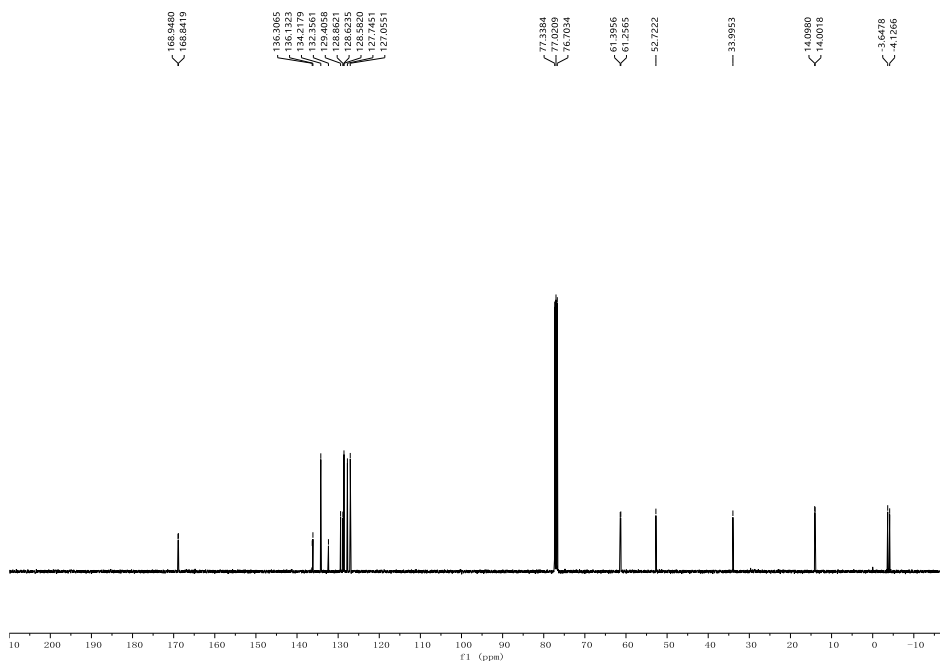


Following the Method D, **3k** was obtained as a colorless oil (77.7 mg, 0.175 mmol, Yield: 88%); ¹H NMR (400 MHz, CDCl₃): δ 7.51 – 7.45 (m, 2H), 7.40 – 7.32 (m, 3H), 7.25 – 7.19 (m, 2H), 7.18 – 7.13 (m, 2H), 6.22 – 6.12 (m, 2H), 4.08 – 4.02 (m, 2H), 3.98 (q, *J* = 7.1 Hz, 2H), 3.51 (d, *J* = 8.6 Hz, 1H), 2.73 – 2.69 (m, 1H), 1.16 (t, *J* = 7.1 Hz, 3H), 1.13 (t, *J* = 7.1 Hz, 3H), 0.36 (s, 3H), 0.35 (s, 3H) ppm; ¹³C NMR (101 MHz, CDCl₃): δ 168.95, 168.84, 136.31, 136.13, 134.22, 132.36,

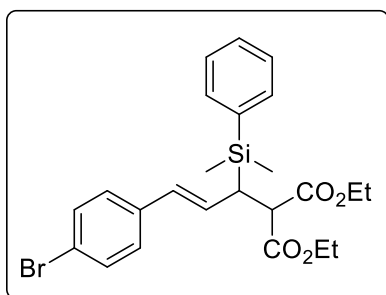
129.41, 128.86, 128.62, 128.58, 127.75, 127.06, 61.40, 61.26, 52.72, 34.00, 14.10, 14.00, -3.65, -4.13 ppm;

HRMS (ESI): *m/z* Calcd. for C₂₄H₃₀O₄Cl Si [M+H]⁺: 445.1596, found: 445.1590.



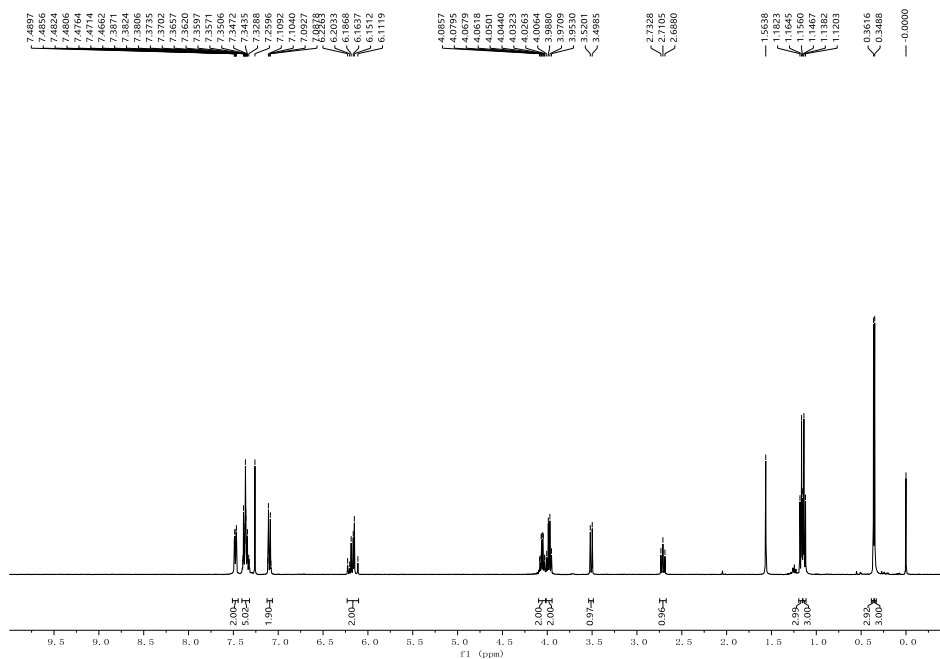


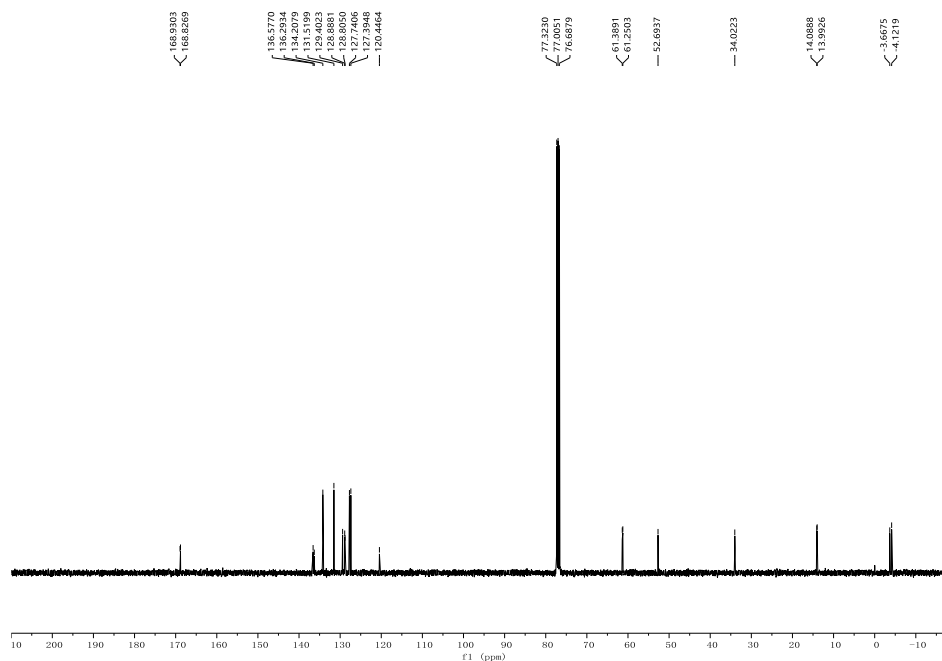
Diethyl (*E*)-2-(3-(4-bromophenyl)-1-(dimethyl(phenyl)silyl)allyl)malonate (**3I**)



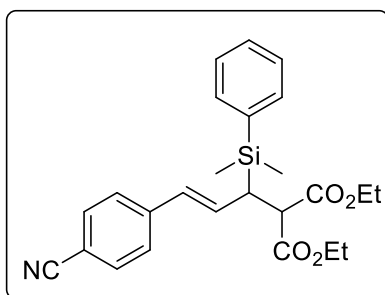
Following the Method D, **3I** was obtained as a colorless oil (79.8 mg, 0.163 mmol, Yield: 82%); ¹H NMR (400 MHz, CDCl₃): δ 7.51 – 7.45 (m, 2H), 7.41 – 7.32 (m, 5H), 7.12 – 7.07 (m, 2H), 6.23 – 6.10 (m, 2H), 4.08 – 4.02 (m, 2H), 3.98 (q, *J* = 7.3 Hz, 2H), 3.51 (d, *J* = 8.7 Hz, 1H), 2.71 (dd, *J* = 8.9, 9.0 Hz, 1H), 1.16 (t, *J* = 7.1 Hz, 3H), 1.13 (t, *J* = 7.1 Hz, 3H), 0.36 (s, 3H), 0.34 (s, 3H) ppm; ¹³C NMR (101 MHz, CDCl₃):

δ 168.93, 168.83, 136.58, 136.29, 134.21, 131.52, 129.40, 128.89, 128.80, 127.74, 127.39, 120.45, 61.39, 61.25, 52.69, 34.02, 14.09, 13.99, -3.67, -4.12 ppm; **HRMS (ESI):** *m/z* Calcd. for C₂₄H₃₀O₄BrSi [M+H]⁺: 489.1091, found: 489.1089.



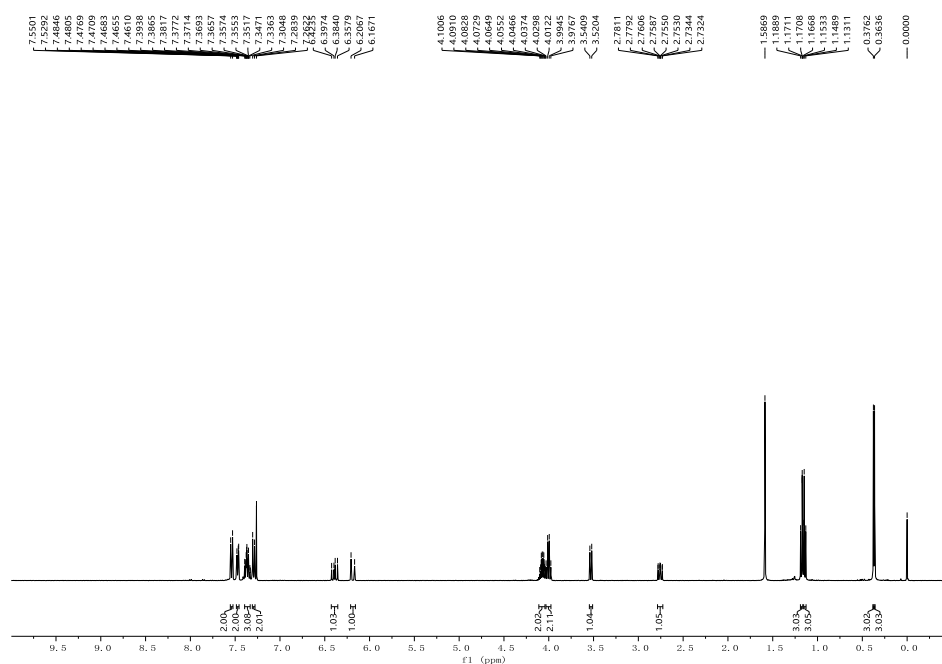


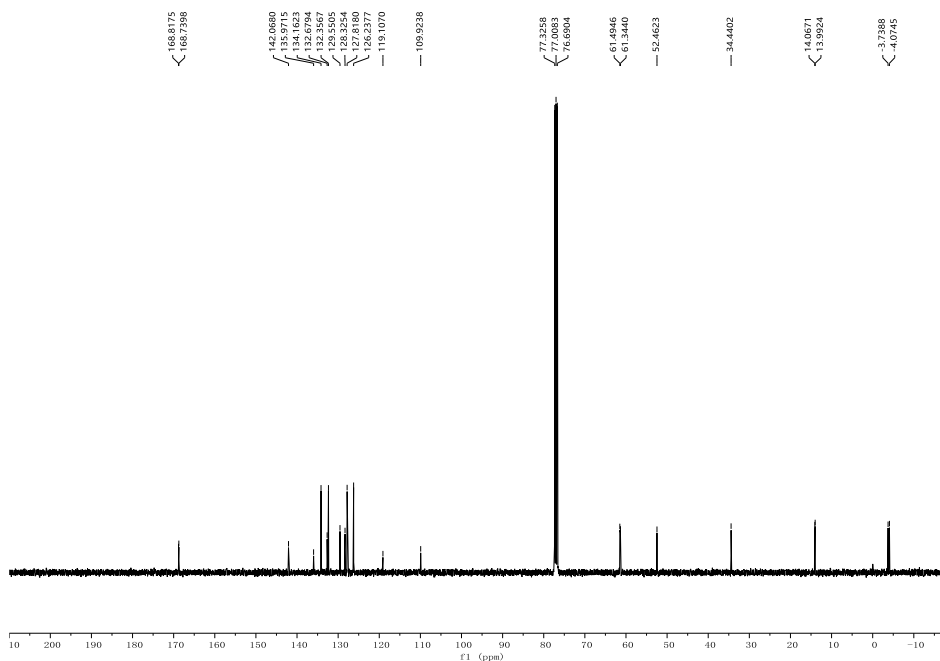
Diethyl (*E*)-2-(3-(4-cyanophenyl)-1-(dimethyl(phenyl)silyl)allyl)malonate (**3m**)



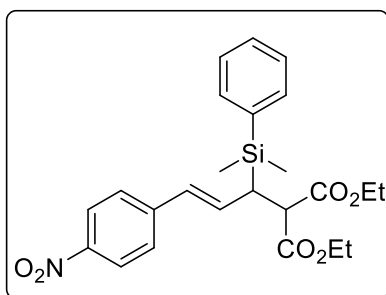
Following the Method D, **3m** was obtained as a light brownish oil (69.8 mg, 0.160 mmol, Yield: 80%); $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.54 (d, $J = 8.4$ Hz, 2H), 7.49 – 7.46 (m, 2H), 7.39 – 7.33 (m, 3H), 7.29 (d, $J = 8.4$ Hz, 2H), 6.39 (dd, $J = 15.8, 10.4$ Hz, 1H), 6.19 (d, $J = 15.9$ Hz, 1H), 4.10 – 4.02 (m, 2H), 4.00 (q, $J = 7.1$ Hz, 2H), 3.53 (d, $J = 8.2$ Hz, 1H), 2.76 (ddd, $J = 10.5, 8.2, 0.8$ Hz, 1H), 1.17 (t, $J = 7.1$ Hz, 3H), 1.14 (t, $J = 7.1$ Hz, 3H), 0.37 (s, 3H), 0.36 (s, 3H) ppm; $^{13}\text{C NMR}$ (101

MHz, CDCl_3): δ 168.82, 168.74, 142.07, 135.97, 134.16, 132.68, 132.36, 129.55, 128.33, 127.82, 126.24, 119.11, 109.92, 61.49, 61.34, 52.46, 34.44, 14.07, 13.99, -3.74, -4.07 ppm; **HRMS (ESI)**: m/z Calcd. for $\text{C}_{25}\text{H}_{30}\text{O}_4\text{NSi}$ $[\text{M}+\text{H}]^+$: 436.1939, found: 436.1936.



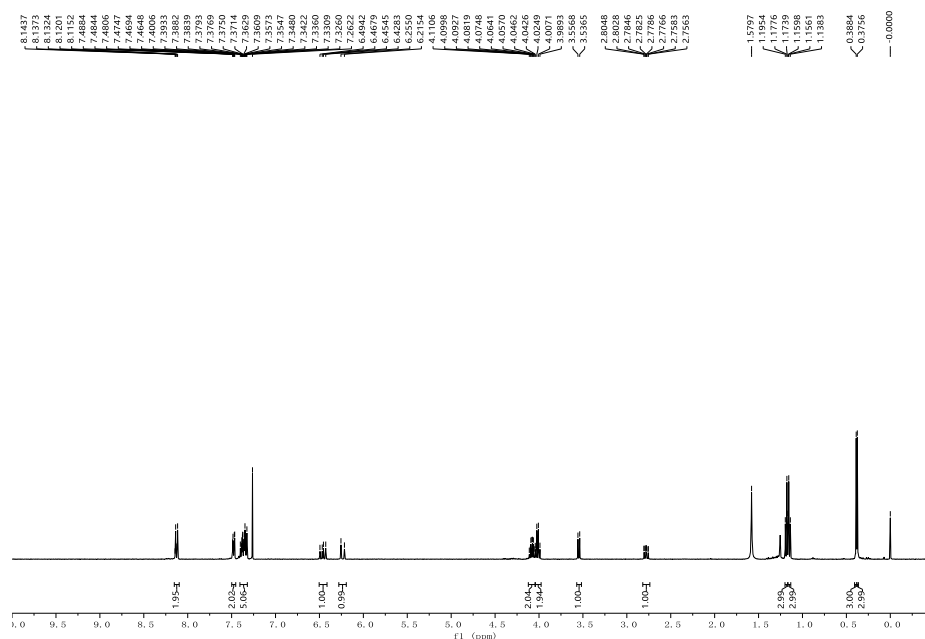


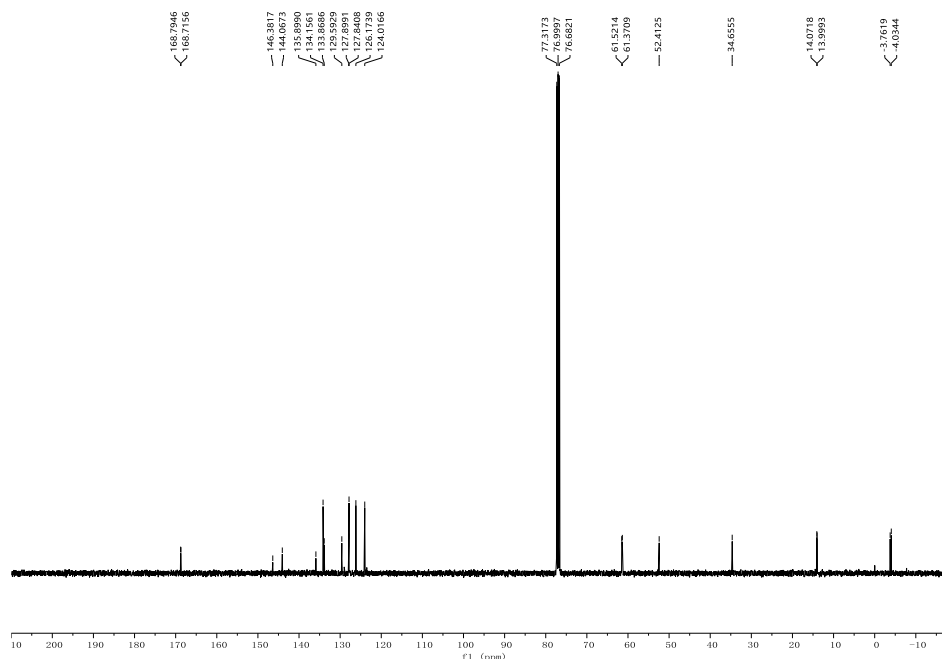
Diethyl (*E*)-2-(1-(dimethyl(phenyl)silyl)-3-(4-nitrophenyl)allyl)malonate (**3n**)



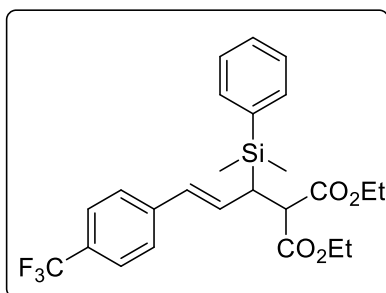
Following the Method D, **3n** was obtained as a light brown oil (64.8 mg, 0.142 mmol, Yield: 71%); ¹H NMR (400 MHz, CDCl₃): δ 8.15 – 8.10 (m, 2H), 7.50 – 7.45 (m, 2H), 7.41 – 7.32 (m, 5H), 6.46 (dd, *J* = 15.8, 10.5 Hz, 1H), 6.24 (d, *J* = 15.8 Hz, 1H), 4.11 – 4.04 (m, 2H), 4.01 (q, *J* = 7.1 Hz, 2H), 3.55 (d, *J* = 8.1 Hz, 1H), 2.78 (ddd, *J* = 10.5, 8.1, 0.8 Hz, 1H), 1.17 (t, *J* = 7.1 Hz, 3H), 1.15 (t, *J* = 7.1 Hz, 3H), 0.38 (s, 3H), 0.37 (s, 3H) ppm; ¹³C NMR (101 MHz, CDCl₃): δ 168.79,

168.72, 146.38, 144.07, 135.90, 134.16, 133.87, 129.59, 127.90, 127.84, 126.17, 124.02, 61.52, 61.37, 52.41, 34.66, 14.07, 14.00, -3.76, -4.03 ppm; HRMS (ESI): *m/z* Calcd. for C₂₄H₃₀O₆NSi [M+H]⁺: 456.1836, found: 456.1827.



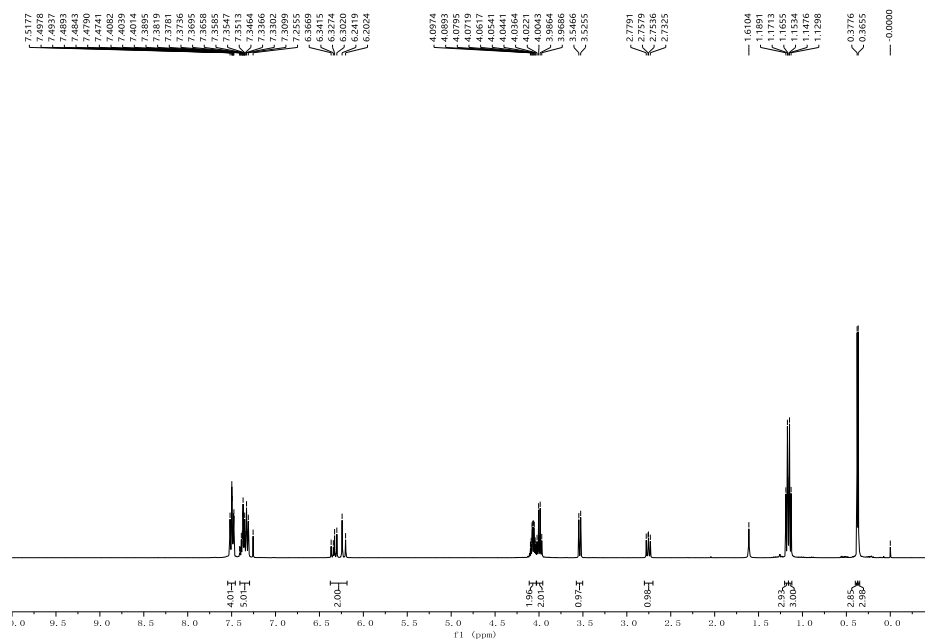


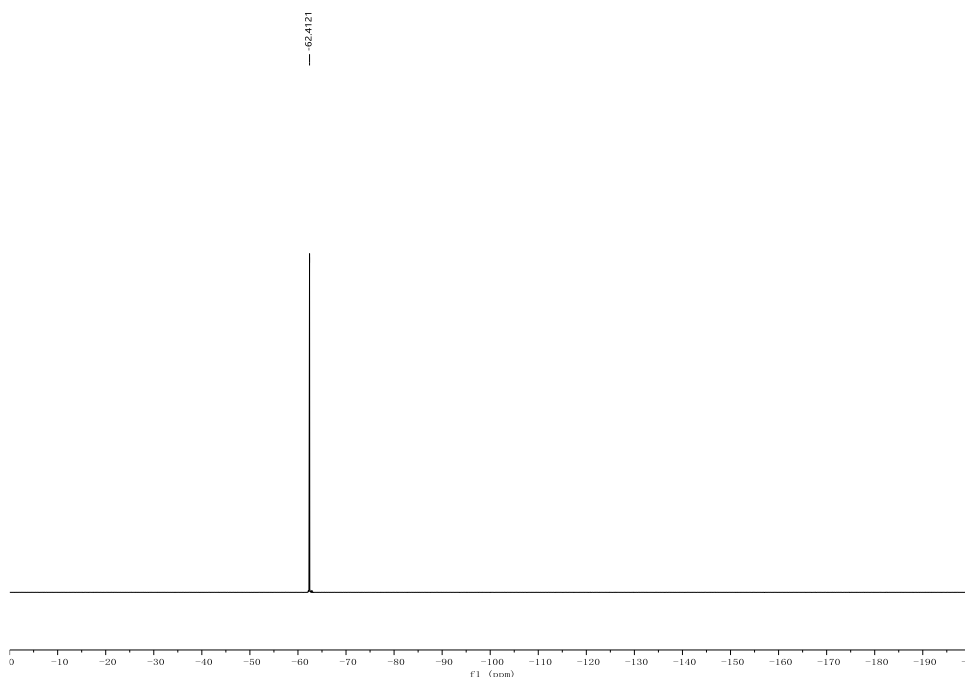
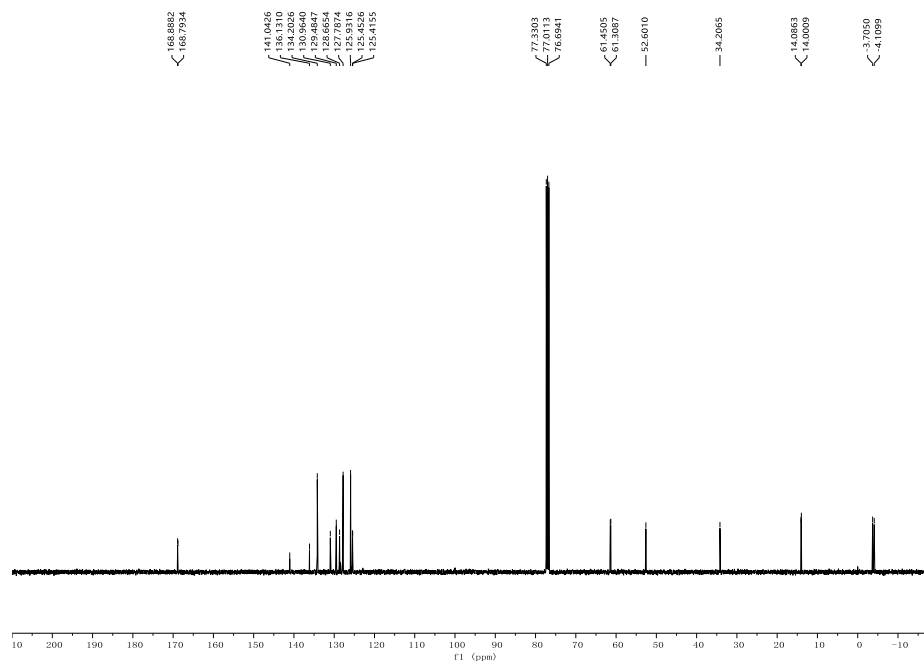
Diethyl (*E*)-2-(1-(dimethyl(phenyl)silyl)-3-(4-(trifluoromethyl)phenyl)allyl)malonate (**3o**)



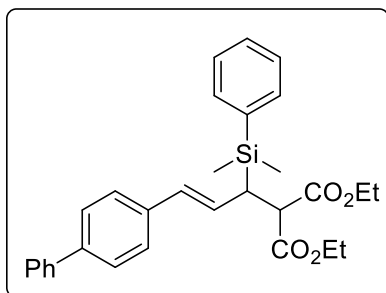
Following the Method D, **3o** was obtained as a brownish oil (74.6 mg, 0.156 mmol, Yield: 78%); ¹H NMR (400 MHz, CDCl₃): δ 7.54 – 7.46 (m, 4H), 7.41 – 7.30 (m, 5H), 6.38 – 6.19 (m, 2H), 4.09 – 4.03 (m, 2H), 4.00 (q, *J* = 7.1 Hz, 2H), 3.54 (d, *J* = 8.4 Hz, 1H), 2.76 (dd, *J* = 10.2, 8.5 Hz, 1H), 1.17 (t, *J* = 7.1 Hz, 3H), 1.14 (t, *J* = 7.1 Hz, 3H) 0.37 (s, 3H), 0.36 (s, 3H) ppm; ¹³C NMR (101 MHz, CDCl₃): δ 168.89, 168.79, 141.04, 136.13, 134.20, 130.96, 129.48, 128.67, 127.79, 125.93, 125.45, 125.42, 61.45, 61.31, 52.60, 34.21, 14.09, 14.00, -3.70,

-4.11 ppm; ¹⁹F NMR (376 MHz, CDCl₃): δ -62.41 ppm; HRMS (ESI): *m/z* Calcd. for C₂₅H₃₀O₄F₃Si [M+H]⁺: 479.1860, found: 479.1862.



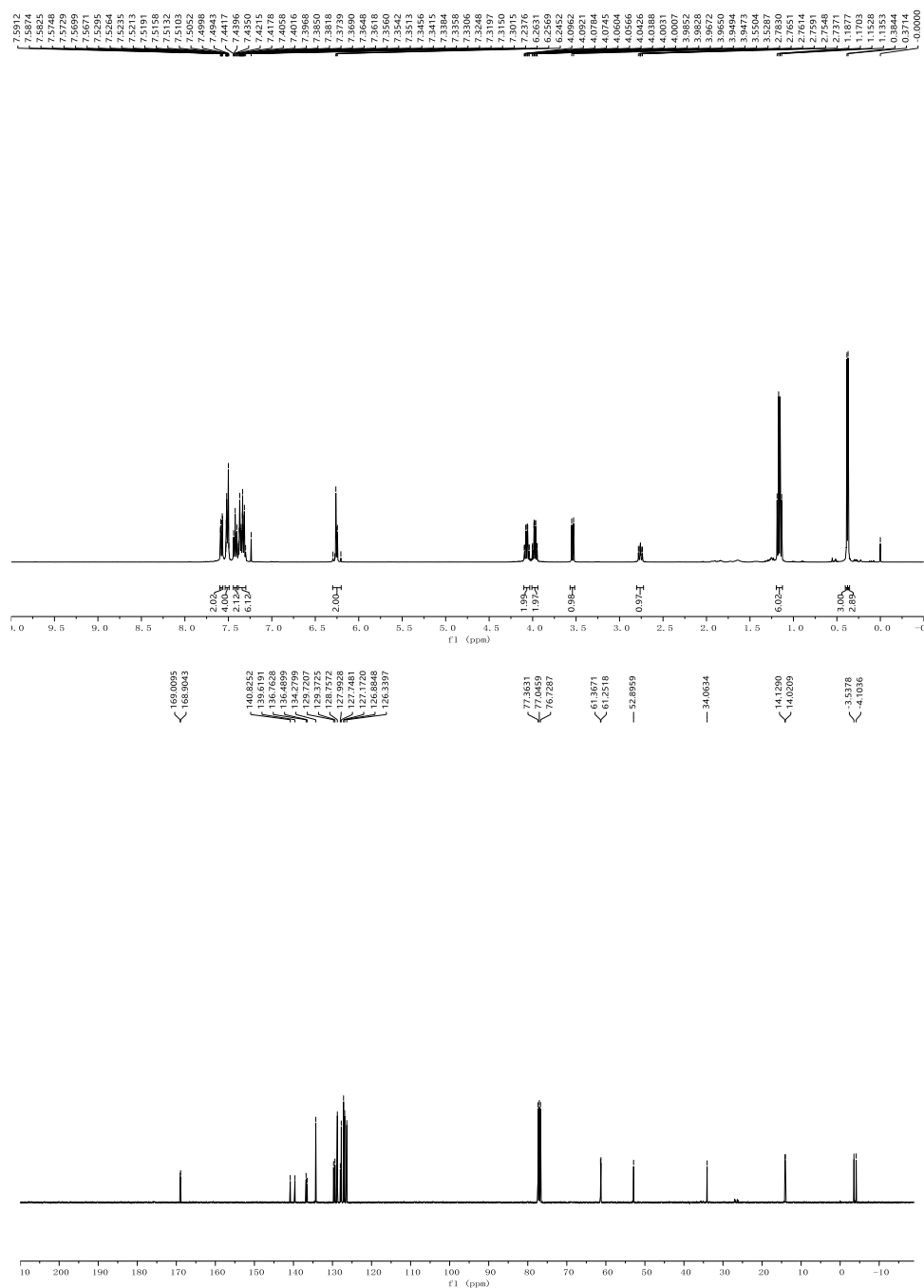


Diethyl (*E*)-2-(3-([1,1'-biphenyl]-4-yl)-1-(dimethyl(phenyl)silyl)allyl)malonate (**3p**)

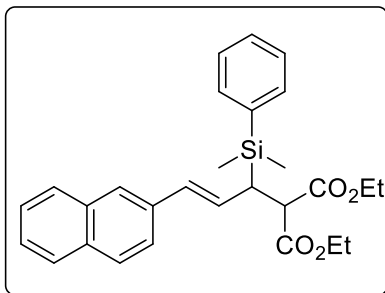


Following the Method D, **3p** was obtained as a white solid (78.8 mg, 0.162 mmol, Yield: 81%); $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.60 – 7.56 (m, 2H), 7.54 – 7.49 (m, 4H), 7.44 – 7.39 (m, 2H), 7.38 – 7.30 (m, 6H), 6.30 – 6.20 (m, 2H), 4.09 – 4.03 (m, 2H), 4.00 – 3.94 (m, 2H), 3.54 (d, $J = 8.7$ Hz, 1H), 2.76 (ddd, $J = 8.8, 7.1, 2.5$ Hz, 1H), 1.18 – 1.13 (m, 6H), 0.38 (s, 3H), 0.37 (s, 3H) ppm; $^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 169.01, 168.90, 140.83, 139.62, 136.76, 136.49, 134.28, 129.72, 129.37, 128.76, 127.99, 127.75, 127.17, 126.88, 126.34, 61.37, 61.25,

52.90, 34.06, 14.13, 14.02, -3.54, -4.10 ppm; **HRMS (ESI)**: m/z Calcd. for $\text{C}_{30}\text{H}_{35}\text{O}_4\text{Si}$ $[\text{M}+\text{H}]^+$: 487.2299, found: 487.2297.

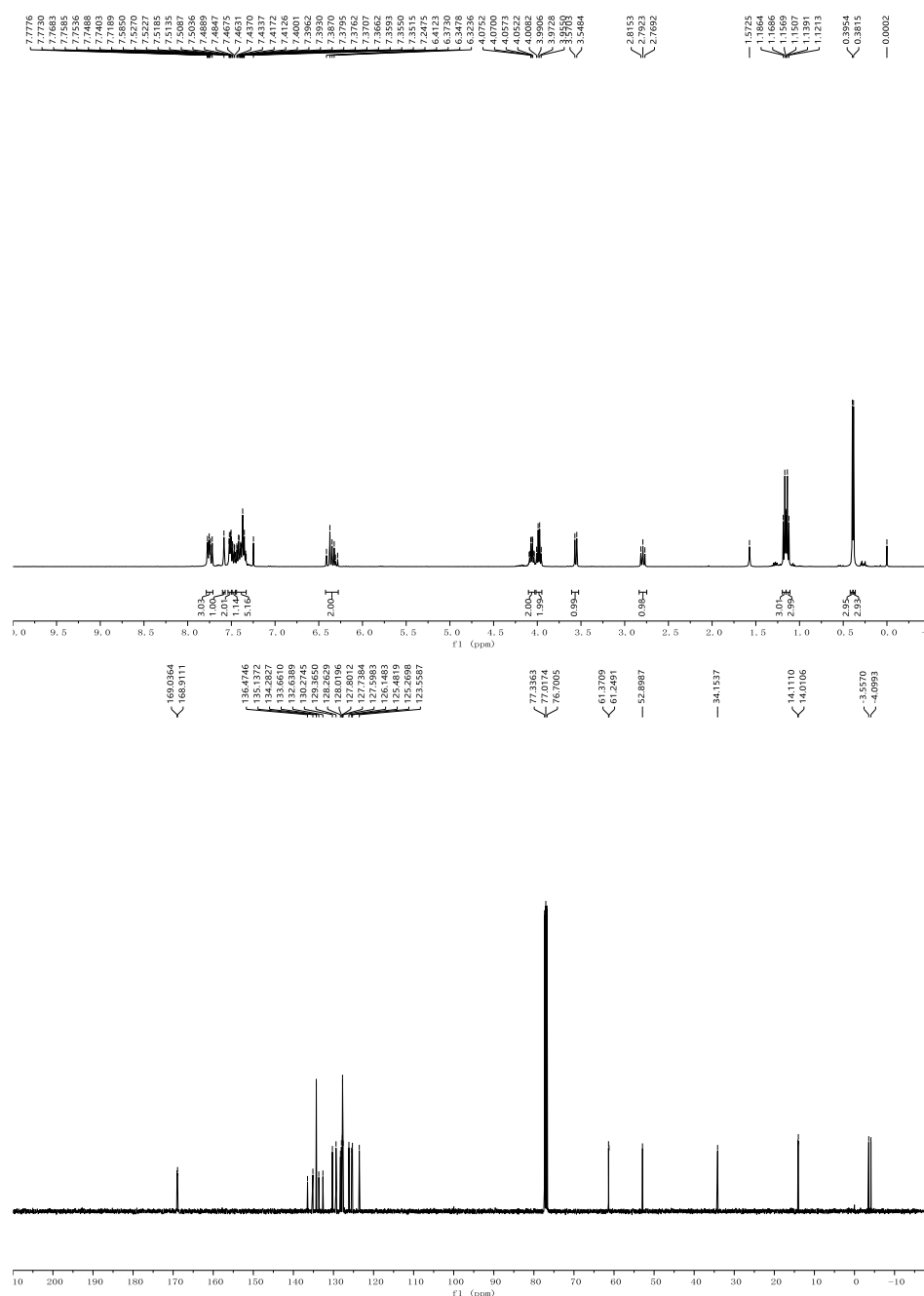


Diethyl (*E*)-2-(1-(dimethyl(phenyl)silyl)-3-(naphthalen-2-yl)allyl)malonate (**3q**)

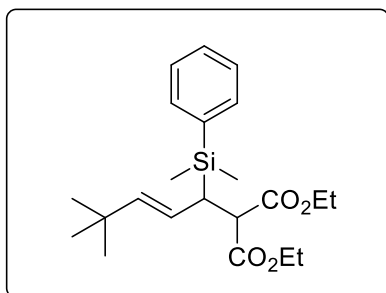


Following the Method D, **3q** was obtained as a light brown solid (76.8 mg, 0.167 mmol, Yield: 84%); **¹H NMR (400 MHz, CDCl₃):** δ 7.79 – 7.71 (m, 3H), 7.59 (s, 1H), 7.54 – 7.50 (m, 2H), 7.48 – 7.45 (m, 1H), 7.44 – 7.33 (m, 5H), 6.42 – 6.28 (m, 2H), 4.09 – 4.03 (m, 2H), 3.98 (q, *J* = 7.1 Hz, 2H), 3.56 (d, *J* = 8.8 Hz, 1H), 2.79 (dd, *J* = 9.1, 9.3 Hz, 1H), 1.16 (t, *J* = 7.1 Hz, 3H), 1.13 (t, *J* = 7.1 Hz, 3H), 0.39 (s, 3H), 0.38 (s, 3H) ppm; **¹³C NMR (101 MHz, CDCl₃):** δ 169.04, 168.91, 136.47, 135.14, 134.28, 133.66, 132.64, 130.27, 129.36, 128.26, 128.02, 127.80, 127.74, 127.60, 126.15, 125.48, 125.27, 123.56, 61.37, 61.25, 52.90, 34.15, 14.11, 14.01, -3.56, -4.10 ppm; **HRMS (ESI):** *m/z* Calcd.

for C₂₈H₃₃O₄Si [M+H]⁺: 461.2143, found: 461.2138.

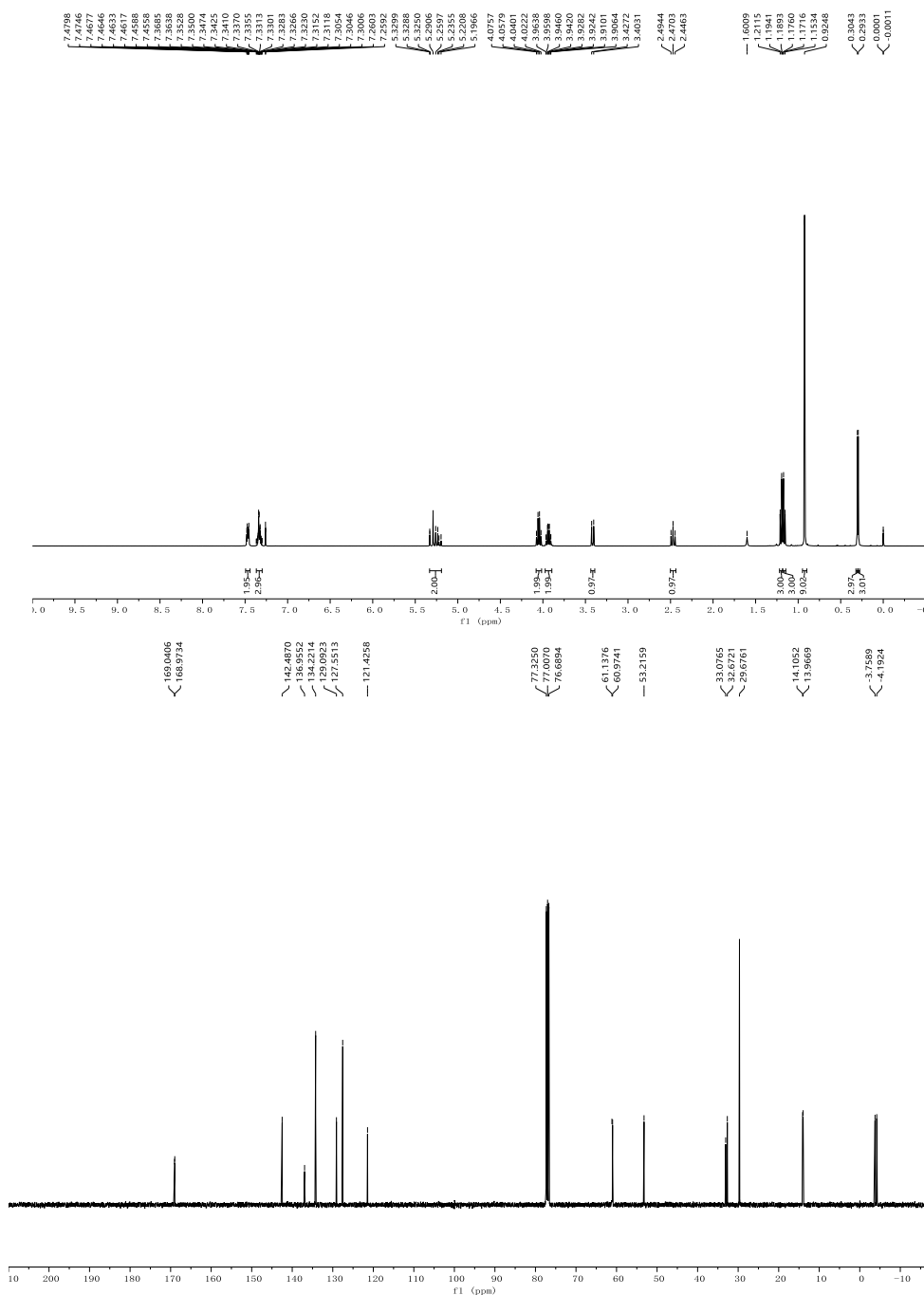


Diethyl (E)-2-(1-(dimethyl(phenyl)silyl)-4,4-dimethylpent-2-en-1-yl)malonate (**3r**)

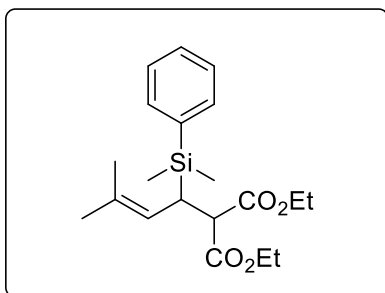


Following the Method D, **3r** was obtained as a colorless oil (59.5 mg, 0.152 mmol, Yield: 76%); ¹H NMR (400 MHz, CDCl₃): δ 7.49 – 7.44 (m, 2H), 7.37 – 7.30 (m, 3H), 5.33 – 5.19 (m, 2H), 4.05 (q, *J* = 7.1 Hz, 2H), 3.96 – 3.90 (m, 2H), 3.42 (d, *J* = 9.6 Hz, 1H), 2.47 (dd, *J* = 9.6, 9.6 Hz, 1H), 1.19 (t, *J* = 7.1 Hz, 3H), 1.17 (t, *J* = 7.1 Hz, 3H), 0.92 (s, 9H), 0.30 (s, 3H), 0.29 (s, 3H) ppm; ¹³C NMR (101 MHz, CDCl₃): δ 169.04, 168.97, 142.49, 136.96, 134.22, 129.09, 127.55, 121.43, 61.14,

60.97, 53.22, 33.08, 32.67, 29.68, 14.11, 13.97, -3.76, -4.19 ppm; **HRMS (ESI)**: *m/z* Calcd. for C₂₂H₃₅O₄Si [M+H]⁺: 391.2299, found: 391.2296.



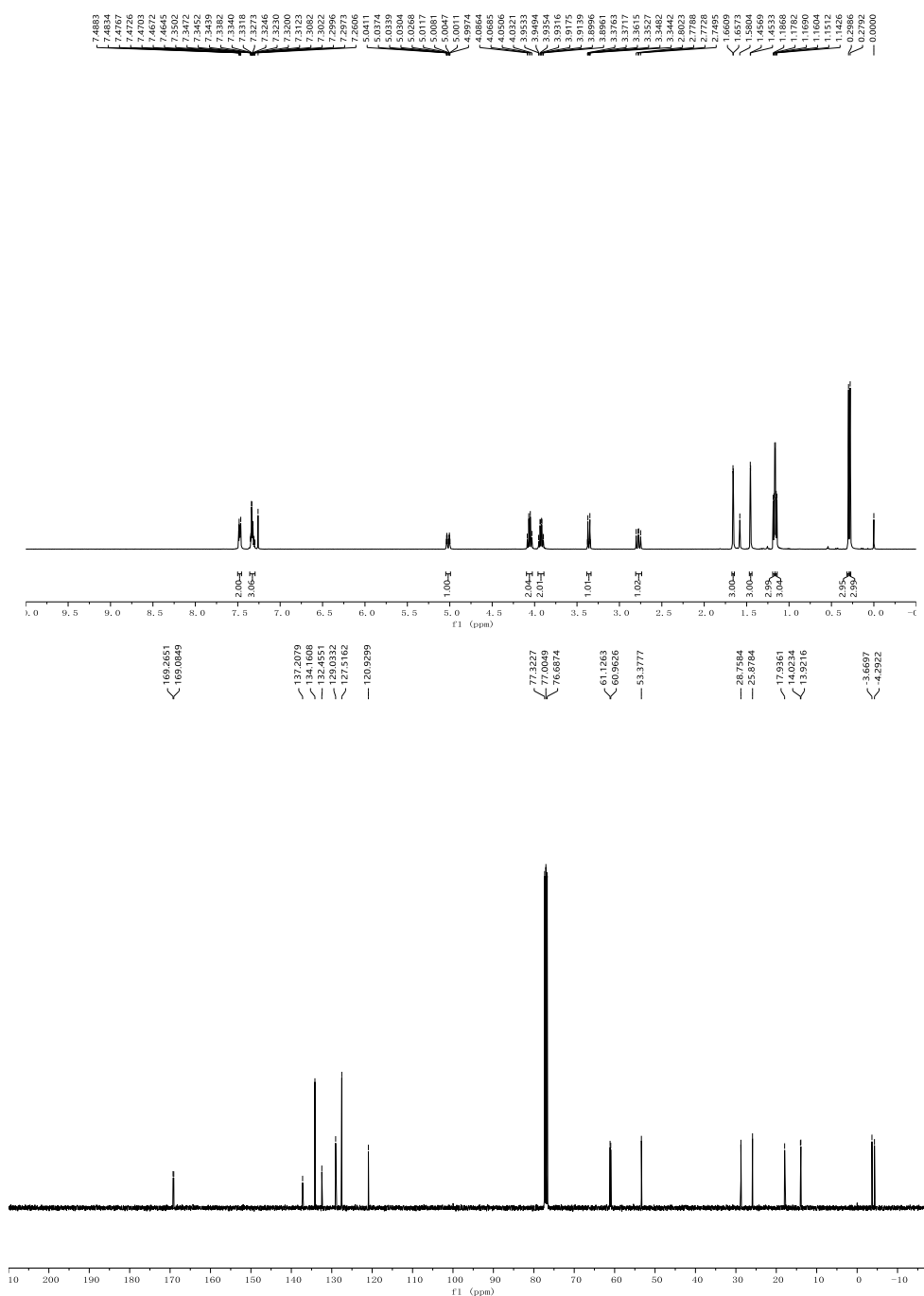
Diethyl-2-(1-(dimethyl(phenyl)silyl)-3-methylbut-2-en-1-yl)malonate (**3s**)



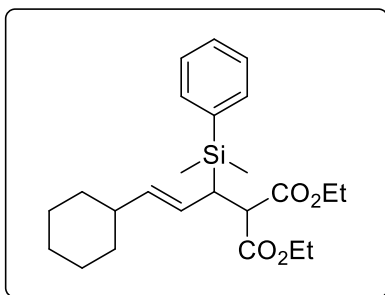
Following the Method D, **3s** was isolated as a colorless oil (52.2 mg, 0.144 mmol, Yield: 72%); ¹H NMR (400 MHz, CDCl₃): δ 7.50 – 7.45 (m, 2H), 7.36 – 7.30 (m, 3H), 5.04 – 4.99 (m, 1H), 4.06 (q, *J* = 7.3 Hz, 2H), 3.95 – 3.89 (m, 2H), 3.36 (d, *J* = 9.4 Hz, 1H), 2.78 (dd, *J* = 11.7, 9.4 Hz, 1H), 1.66 (d, *J* = 1.4 Hz, 3H), 1.46 (d, *J* = 1.4 Hz, 3H), 1.17 (t, *J* = 3.4 Hz, 3H), 1.15 (t, *J* = 3.4 Hz, 3H), 0.29 (s, 3H), 0.27 (s, 3H) ppm; ¹³C NMR (101 MHz, CDCl₃): δ 169.27, 169.08, 137.21, 134.16,

132.46, 129.03, 127.52, 120.93, 61.13, 60.96, 53.38, 28.76, 25.88, 17.94, 14.02, 13.92, -3.67, -4.29 ppm;

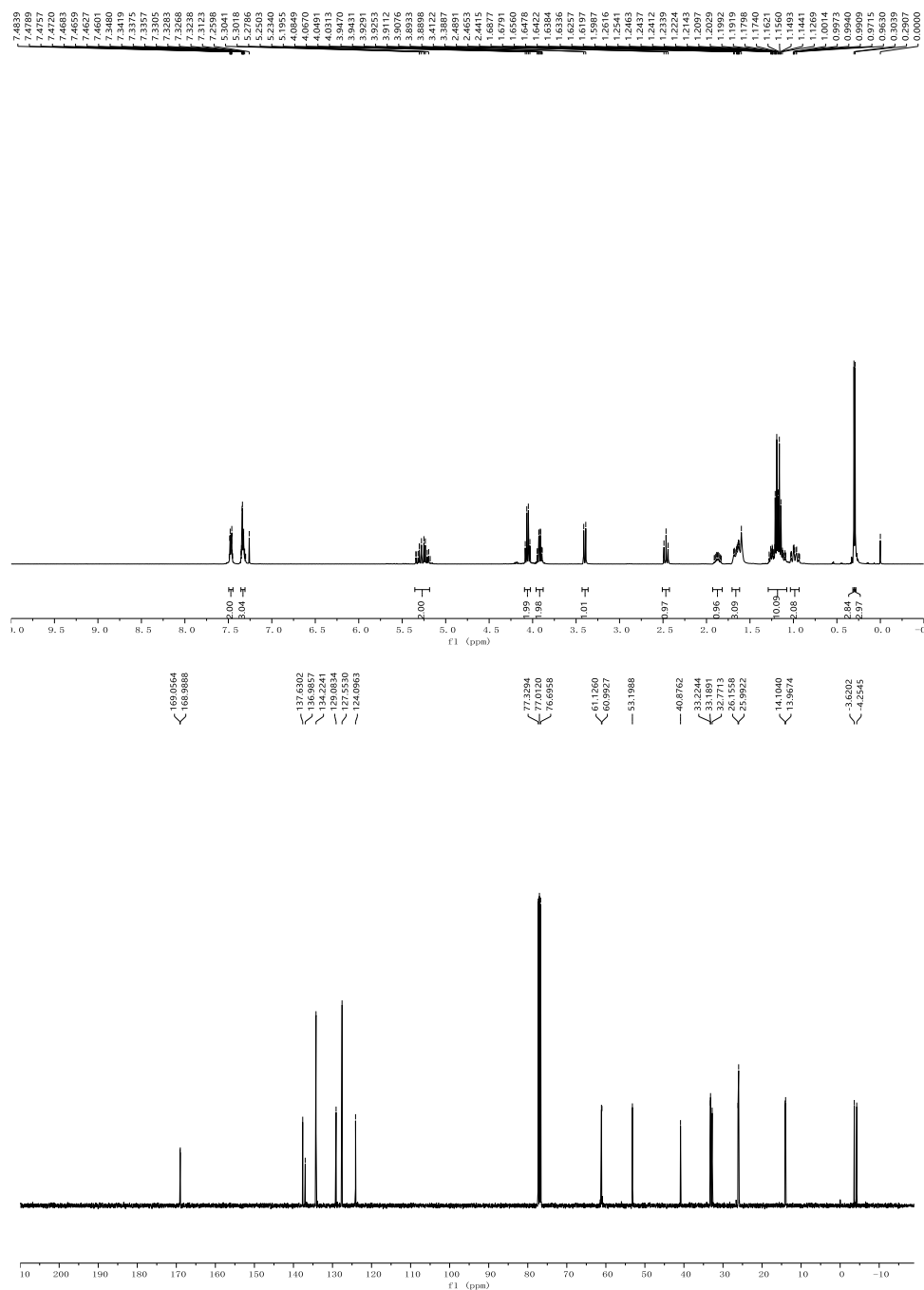
HRMS (ESI): *m/z* Calcd. for C₂₀H₃₁O₄Si [M+H]⁺: 363.1986, found: 363.1980.



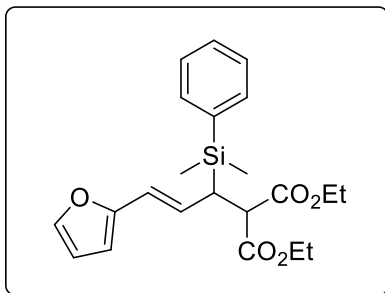
Diethyl (*E*)-2-(3-cyclohexyl-1-(dimethyl(phenyl)silyl)allyl)malonate (**3t**)



Following the Method D, **3t** was obtained as a light green oil (65.7 mg, 0.158 mmol, Yield: 79%); ¹H NMR (400 MHz, CDCl₃): δ 7.50 – 7.45 (m, 2H), 7.36 – 7.31 (m, 3H), 5.35 – 5.19 (m, 2H), 4.06 (q, *J* = 7.1 Hz, 2H), 3.94 – 3.88 (m, 2H), 3.40 (d, *J* = 9.4 Hz, 1H), 2.47 (dd, *J* = 9.6, 9.4 Hz, 1H), 1.91 – 1.83 (m, 1H), 1.71 – 1.62 (m, 3H), 1.29 – 1.08 (m, 10H), 1.03 – 0.93 (m, 2H), 0.30 (s, 3H), 0.29 (s, 3H) ppm; ¹³C NMR (101 MHz, CDCl₃): δ 169.06, 168.99, 137.63, 136.99, 134.22, 129.08, 127.55, 124.10, 61.13, 60.99, 53.20, 40.88, 33.22, 33.19, 32.77, 26.16, 25.99, 14.10, 13.97, -3.62, -4.25 ppm; HRMS (ESI): *m/z* Calcd. for C₂₄H₃₇O₄Si [M+H]⁺: 417.2456, found: 417.2449.



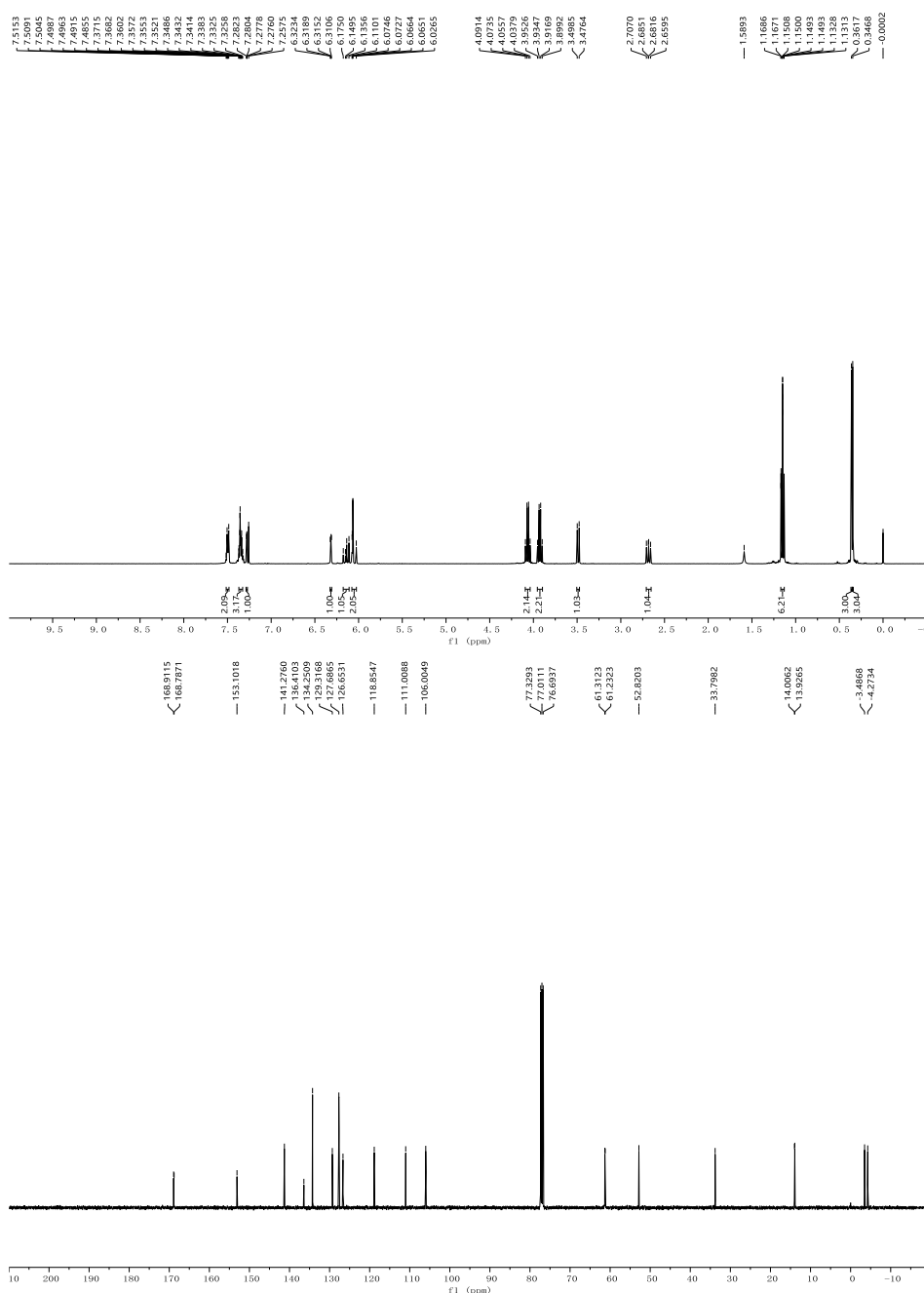
Diethyl (*E*)-2-(1-(dimethyl(phenyl)silyl)-3-(furan-2-yl)allyl)malonate (**3u**)



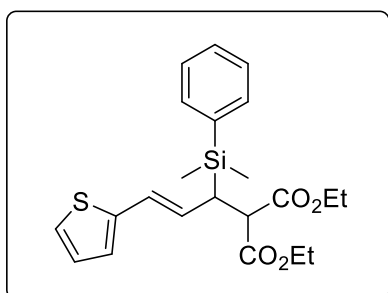
Following the Method D, **3u** was obtained as a light brown oil (63.6 mg, 0.159 mmol, Yield: 80%); **¹H NMR (400 MHz, CDCl₃):** δ 7.51 – 7.48 (m, 2H), 7.37 – 7.33 (m, 3H), 7.32 – 7.25 (m, 1H), 6.32 (dd, J = 3.3, 1.8 Hz, 1H), 6.14 (dd, J = 15.8, 10.2 Hz, 1H), 6.08 – 6.02 (m, 2H), 4.06 (q, J = 7.1 Hz, 2H), 3.93 (q, J = 7.1 Hz, 2H), 3.49 (d, J = 8.8 Hz, 1H), 2.68 (dd, J = 10.2, 8.8 Hz, 1H), 1.17 – 1.13 (m, 6H), 0.36 (s, 3H), 0.35 (s, 3H) ppm; **¹³C NMR (101 MHz, CDCl₃):** δ 168.91, 168.79,

153.10, 141.28, 136.41, 134.25, 129.32, 127.69, 126.65, 118.85, 111.01, 106.00, 61.31, 61.23, 52.82, 33.80, 14.01, 13.93, -3.49, -4.27 ppm; **HRMS (ESI):** m/z Calcd. for C₂₂H₂₉O₅Si [M+H]⁺: 401.1779, found:

401.1773.

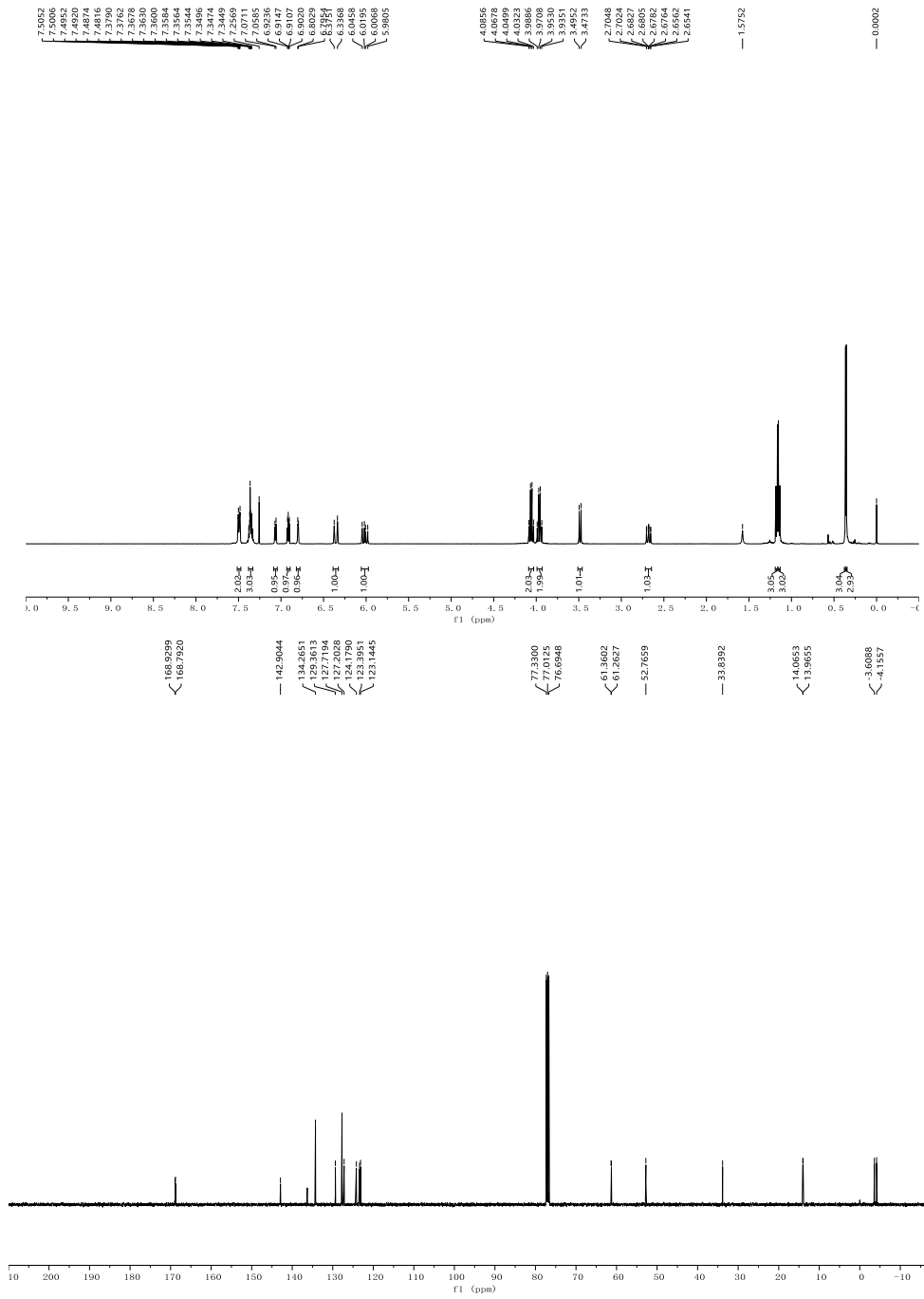


Diethyl (*E*)-2-(1-(dimethyl(phenyl)silyl)-3-(thiophen-2-yl)allyl)malonate (**3v**)



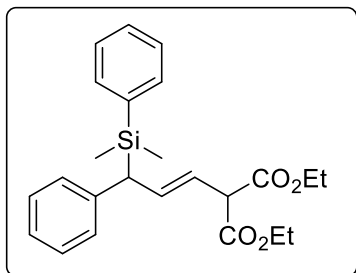
Following the Method D, **3v** was isolated as a brown oil (65.7 mg, 0.158 mmol, Yield: 79%) **¹H NMR (400 MHz, CDCl₃):** δ 7.51 – 7.47 (m, 2H), 7.38 – 7.33 (m, 3H), 7.06 (d, J = 5.0 Hz, 1H), 6.91 (dd, J = 5.1, 3.5 Hz, 1H), 6.80 (d, J = 3.4 Hz, 1H), 4.06 (q, J = 7.1 Hz, 2H), 3.96 (q, J = 7.1 Hz, 2H), 3.48 (d, J = 8.8 Hz, 1H), 2.68 (ddd, J = 10.6, 8.9, 0.9 Hz, 1H), 1.17 (t, J = 4.3 Hz, 3H), 1.14 (t, J = 4.3 Hz, 3H), 0.36 (s, 3H), 0.36 (s, 3H) ppm; **¹³C NMR (101 MHz, CDCl₃):** δ 168.93,

168.79, 142.90, 134.27, 129.36, 127.72, 127.20, 124.18, 123.40, 123.14, 61.36, 61.26, 52.77, 33.84, 14.07, 13.97, -3.61, -4.16 ppm; **HRMS (ED):** m/z Calcd. for C₂₂H₂₉O₄SSi [M+H]⁺: 417.155, found: 417.1546.



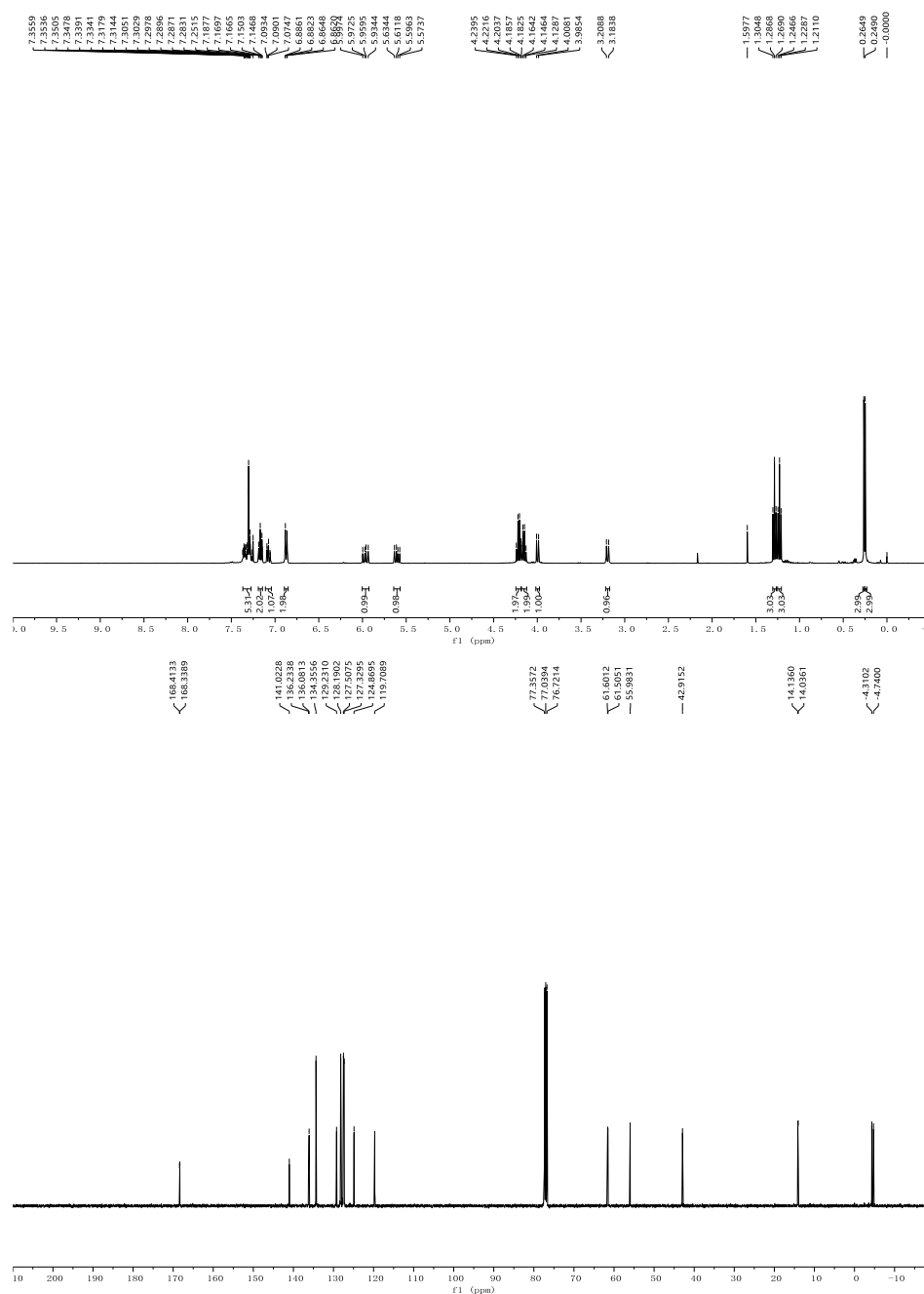
3.2 Characterization Data and Spectra of 1,6-addition Products

Diethyl (*E*)-2-(3-(dimethyl(phenyl)silyl)-3-phenylprop-1-en-1-yl)malonate (**4a**)

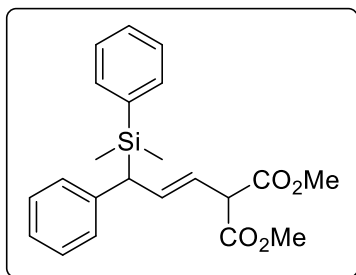


Following the Method E, **4a** was isolated as a colorless oil. (67.5 g, 0.164 mmol, 82%); ¹H NMR (400 MHz, CDCl₃): δ 7.36 – 7.27 (m, 5H), 7.19 – 7.15 (m, 2H), 7.11 – 7.04 (m, 1H), 6.89 – 6.85 (m, 2H), 5.96 (dd, *J* = 15.2, 10.0 Hz, 1H), 5.60 (dd, *J* = 15.2, 9.1 Hz, 1H), 4.21 (q, *J* = 7.1 Hz, 2H), 4.15 (q, *J* = 7.1 Hz, 2H), 4.00 (d, *J* = 9.1 Hz, 1H), 3.20 (d, *J* = 10.0 Hz, 1H), 1.29 (t, *J* = 7.2 Hz, 3H), 1.23 (t, *J* = 7.1 Hz, 3H), 0.26 (s, 3H), 0.25 (s, 3H) ppm; ¹³C NMR (101 MHz, CDCl₃): δ 168.41, 168.34, 141.02, 136.23, 136.08, 134.36, 129.23, 128.19, 127.51, 127.33, 124.87,

119.71, 61.60, 61.51, 55.98, 42.92, 14.14, 14.04, -4.31, -4.74 ppm; HRMS (ESI): *m/z* Calcd. for C₂₄H₃₁O₄Si [M+H]⁺: 411.1986, found: 411.1992.

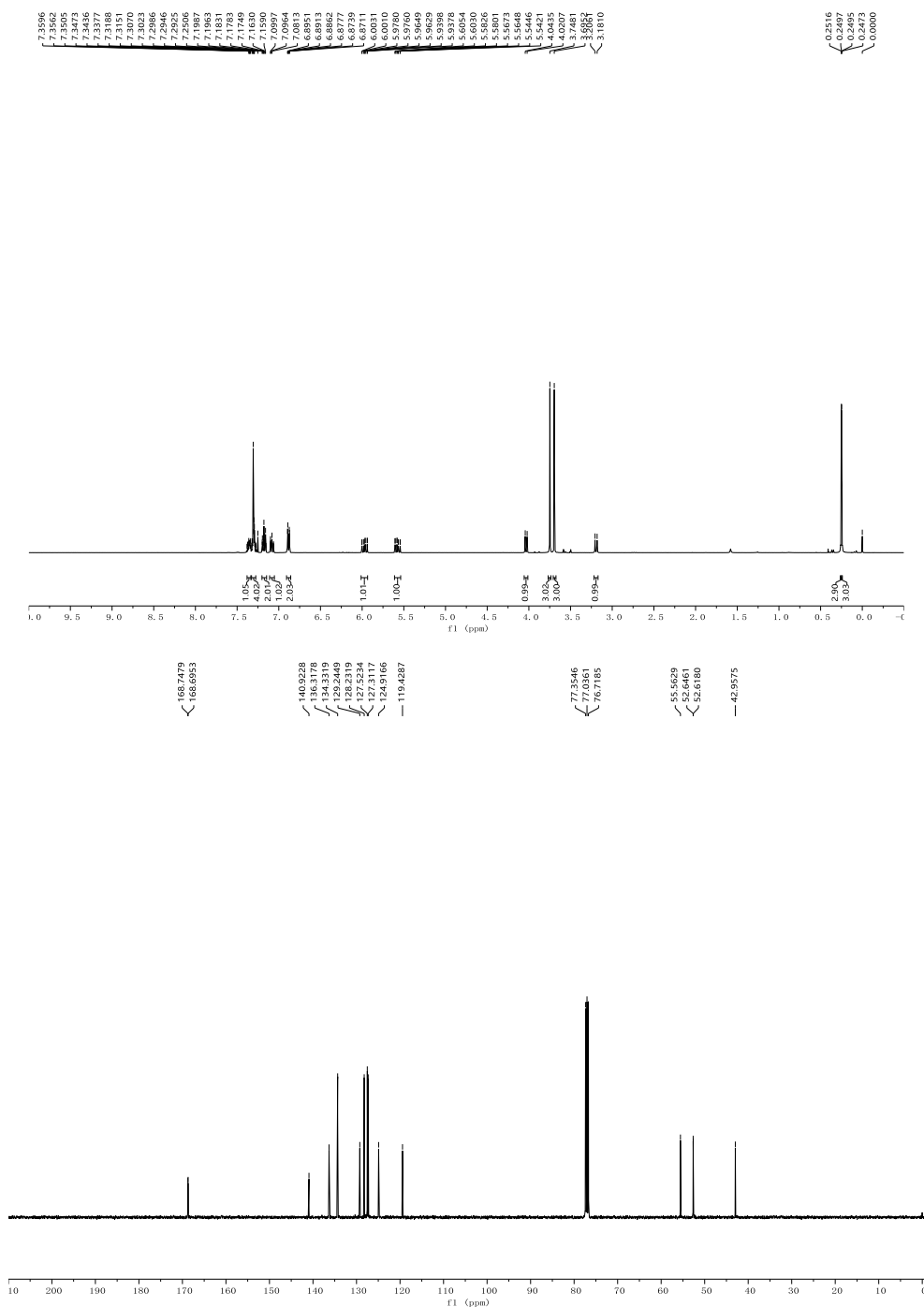


Dimethyl (*E*)-2-(3-(dimethyl(phenyl)silyl)-3-phenylprop-1-en-1-yl)malonate (**4b**)

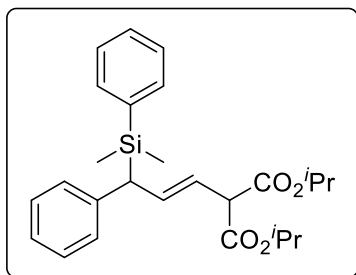


Following the Method E, **4b** was isolated as a colorless oil (58.3 mg, 0.152 mmol, 76%); ¹H NMR (400 MHz, CDCl₃): δ 7.38 – 7.34 (m, 1H), 7.33 – 7.28 (m, 4H), 7.20 – 7.15 (m, 2H), 7.11 – 7.05 (m, 1H), 6.91 – 6.86 (m, 2H), 5.97 (ddd, *J* = 15.3, 10.0, 0.8 Hz, 1H), 5.57 (ddd, *J* = 15.2, 9.1, 1.0 Hz, 1H), 4.03 (d, *J* = 9.2 Hz, 1H), 3.75 (s, 3H), 3.70 (s, 3H), 3.19 (d, *J* = 10.0 Hz, 1H), 0.25 (s, 3H), 0.25 (s, 3H) ppm; ¹³C NMR (101 MHz, CDCl₃): δ 168.75, 168.70, 140.92, 136.32, 134.33, 129.24, 128.23,

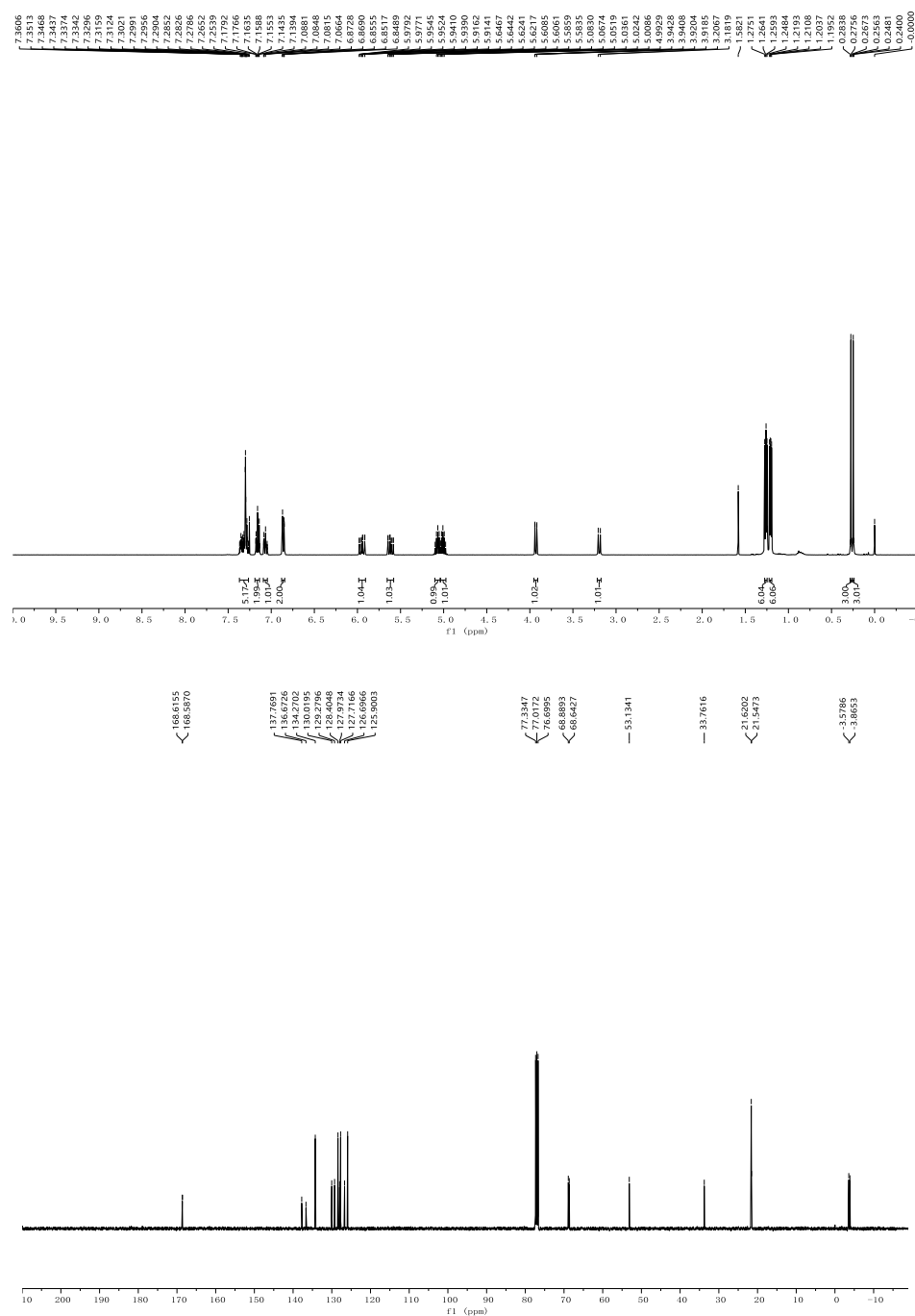
127.52, 127.31, 124.92, 119.43, 55.56, 52.65, 52.62, 42.96, -4.31, -4.87 ppm; HRMS (ESI): *m/z* Calcd. for C₂₂H₂₇O₄Si [M+H]⁺: 383.1673, found: 383.1670.



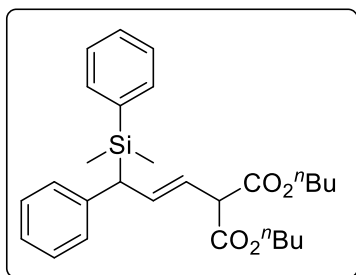
Diisopropyl (*E*)-2-(3-(dimethyl(phenyl)silyl)-3-phenylprop-1-en-1-yl)malonate (**4c**)



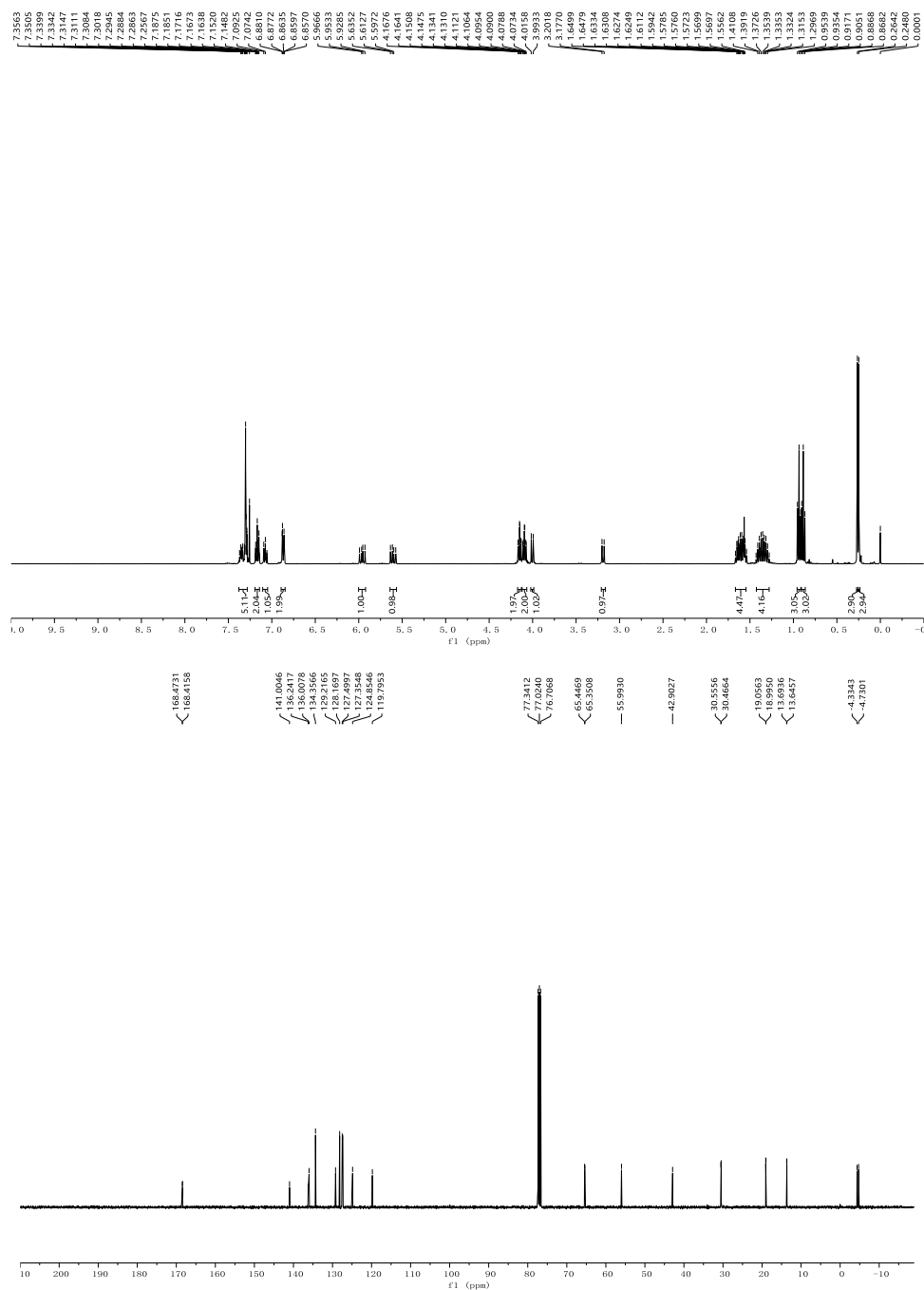
Following the Method E, **4c** was obtained as colorless oil (61.3 mg, 0.140 mmol, 70%); ¹H NMR (400 MHz, CDCl₃): δ 7.37 – 7.26 (m, 5H), 7.19 – 7.14 (m, 2H), 7.09 – 7.05 (m, 1H), 6.88 – 6.84 (m, 2H), 5.95 (ddd, *J* = 15.3, 9.9, 0.8 Hz, 1H), 5.62 (ddd, *J* = 15.3, 9.0, 1.0 Hz, 1H), 5.10 – 5.04 (m, 1H), 5.04 – 4.97 (m, 1H), 3.93 (dd, *J* = 8.9, 0.8 Hz, 1H), 3.19 (d, *J* = 9.9 Hz, 1H), 1.27 – 1.24 (m, 6H), 1.21 – 1.19 (m, 6H), 0.28 (s, 3H), 0.25 (s, 3H) ppm; ¹³C NMR (101 MHz, CDCl₃): δ 167.97, 167.91, 141.11, 136.26, 135.89, 134.39, 129.21, 128.14, 127.49, 127.35, 124.82, 119.90, 69.10, 68.94, 56.39, 42.87, 21.70, 21.67, 21.61, 21.57, -4.30, -4.61 ppm; HRMS (ESI): *m/z* Calcd. for C₂₆H₃₅O₄Si [M+H]⁺: 439.2299, found: 439.2294.



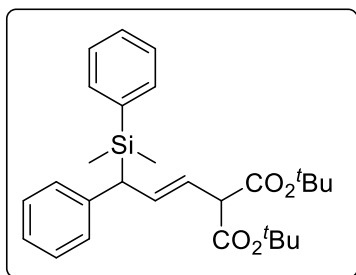
Dibutyl (*E*)-2-(3-(dimethyl(phenyl)silyl)-3-phenylprop-1-en-1-yl)malonate (**4d**)



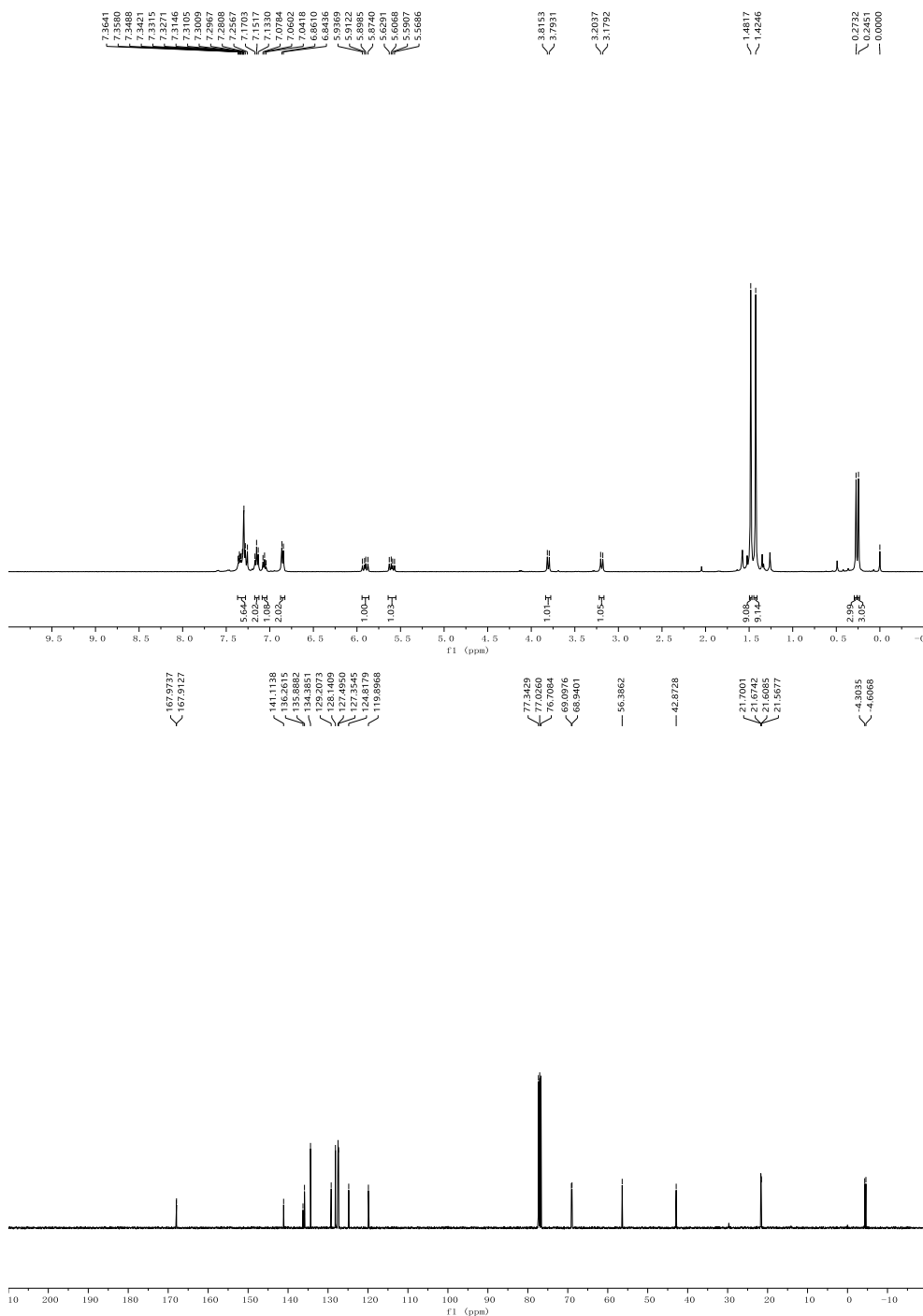
Following the method E, **4d** was obtained as colorless oil (67.3 mg, 0.144 mmol, 72%); ¹H NMR (400 MHz, CDCl₃): δ 7.37 – 7.28 (m, 5H), 7.19 – 7.14 (m, 2H), 7.10 – 7.05 (m, 1H), 6.89 – 6.85 (m, 2H), 5.96 (dd, *J* = 15.3, 10.0 Hz, 1H), 5.60 (dd, *J* = 15.3, 9.1 Hz, 1H), 4.16 – 4.13 (m, 2H), 4.11 – 4.07 (m, 2H), 4.00 (d, *J* = 9.0 Hz, 1H), 3.19 (d, *J* = 9.9 Hz, 1H), 1.67 – 1.55 (m, 4H), 1.43 – 1.28 (m, 4H), 0.94 (t, *J* = 7.4 Hz, 3H), 0.89 (t, *J* = 7.4 Hz, 3H), 0.26 (s, 3H), 0.25 (s, 3H) ppm; ¹³C NMR (101 MHz, CDCl₃): δ 168.47, 168.42, 141.00, 136.24, 136.01, 134.36, 129.22, 128.17, 127.50, 127.35, 124.85, 119.80, 65.45, 65.35, 55.99, 42.90, 30.56, 30.47, 19.06, 18.99, 13.69, 13.65, -4.33, -4.73 ppm; HRMS (ESI): *m/z* Calcd. for C₂₈H₃₉O₄Si [M+H]⁺: 467.2612, found: 467.2618.



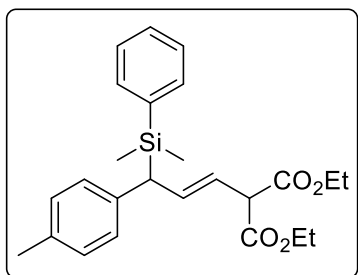
Di-tert-butyl (*E*)-2-(3-(dimethyl(phenyl)silyl)-3-phenylprop-1-en-1-yl)malonate (**4e**)



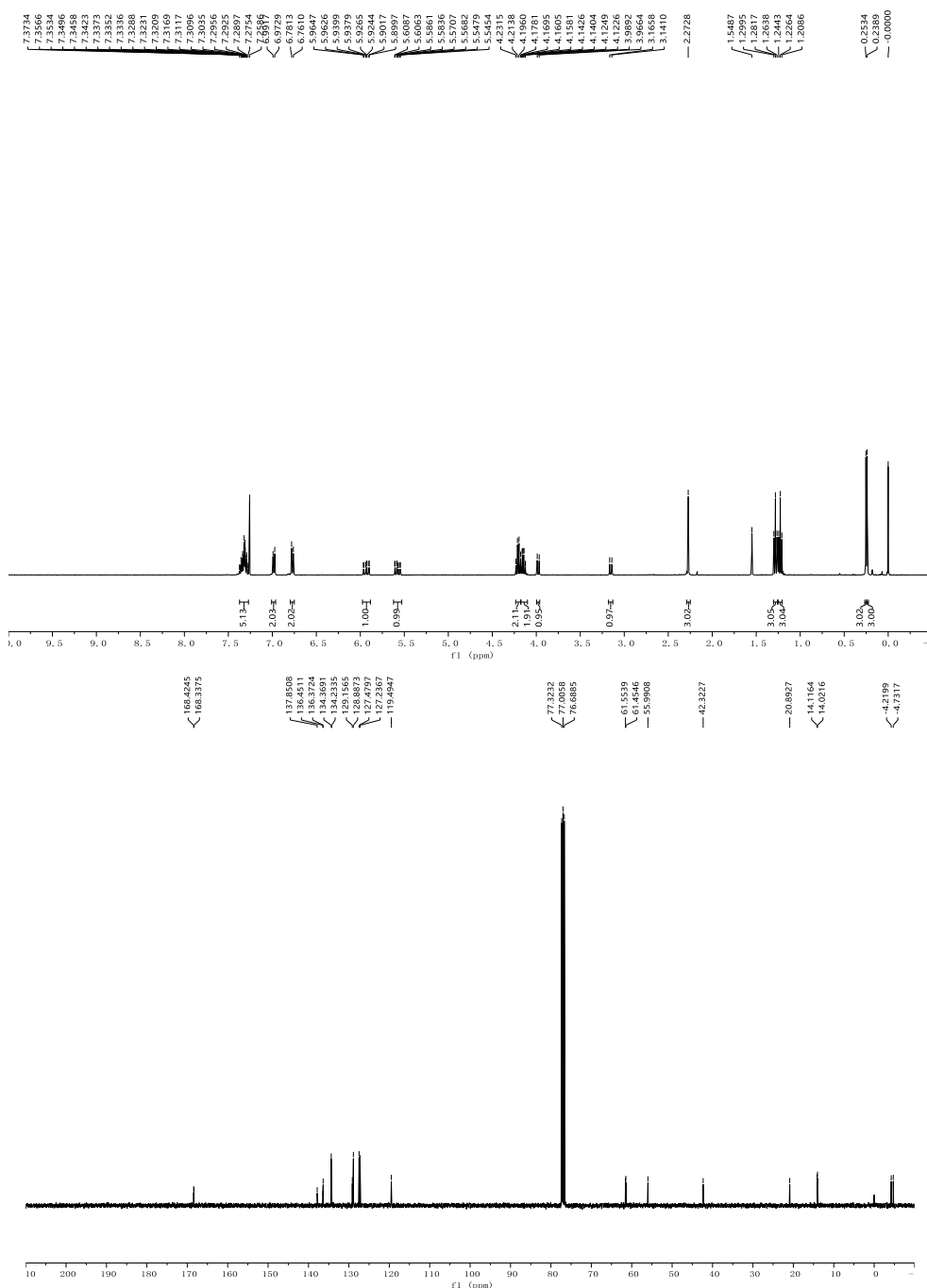
Following the Method E, **4e** was obtained as light green oil (55.5 mg, 0.119 mmol, 60%); ¹H NMR (400 MHz, CDCl₃): δ 7.36 – 7.28 (m, 6H), 7.15 (dd, *J* = 7.4, 7.5 Hz, 2H), 7.06 (dd, *J* = 7.3, 7.3 Hz, 1H), 6.85 (d, *J* = 7.0 Hz, 2H), 5.91 (dd, *J* = 15.3, 9.8 Hz, 1H), 5.60 (dd, *J* = 15.3, 8.9 Hz, 1H), 3.80 (d, *J* = 8.9 Hz, 1H), 3.19 (d, *J* = 9.8 Hz, 1H), 1.48 (s, 9H), 1.42 (s, 9H), 0.27 (s, 3H), 0.25 (s, 3H) ppm; ¹³C NMR (101 MHz, CDCl₃): δ 167.73, 167.72, 141.25, 136.34, 135.28, 134.40, 129.17, 128.10, 127.49, 127.38, 124.75, 120.55, 81.61, 81.51, 58.08, 42.81, 28.19, 28.11, 27.96, 27.90, 27.83, 27.73, -4.27, -4.54 ppm; HRMS (ESI): *m/z* Calcd. for C₂₈H₃₉O₄Si [M+H]⁺: 467.2612, found: 467.2605.



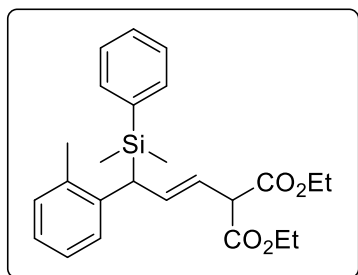
Diethyl (*E*)-2-(3-(dimethyl(phenyl)silyl)-3-(*p*-tolyl)prop-1-en-1-yl)malonate (**4f**)



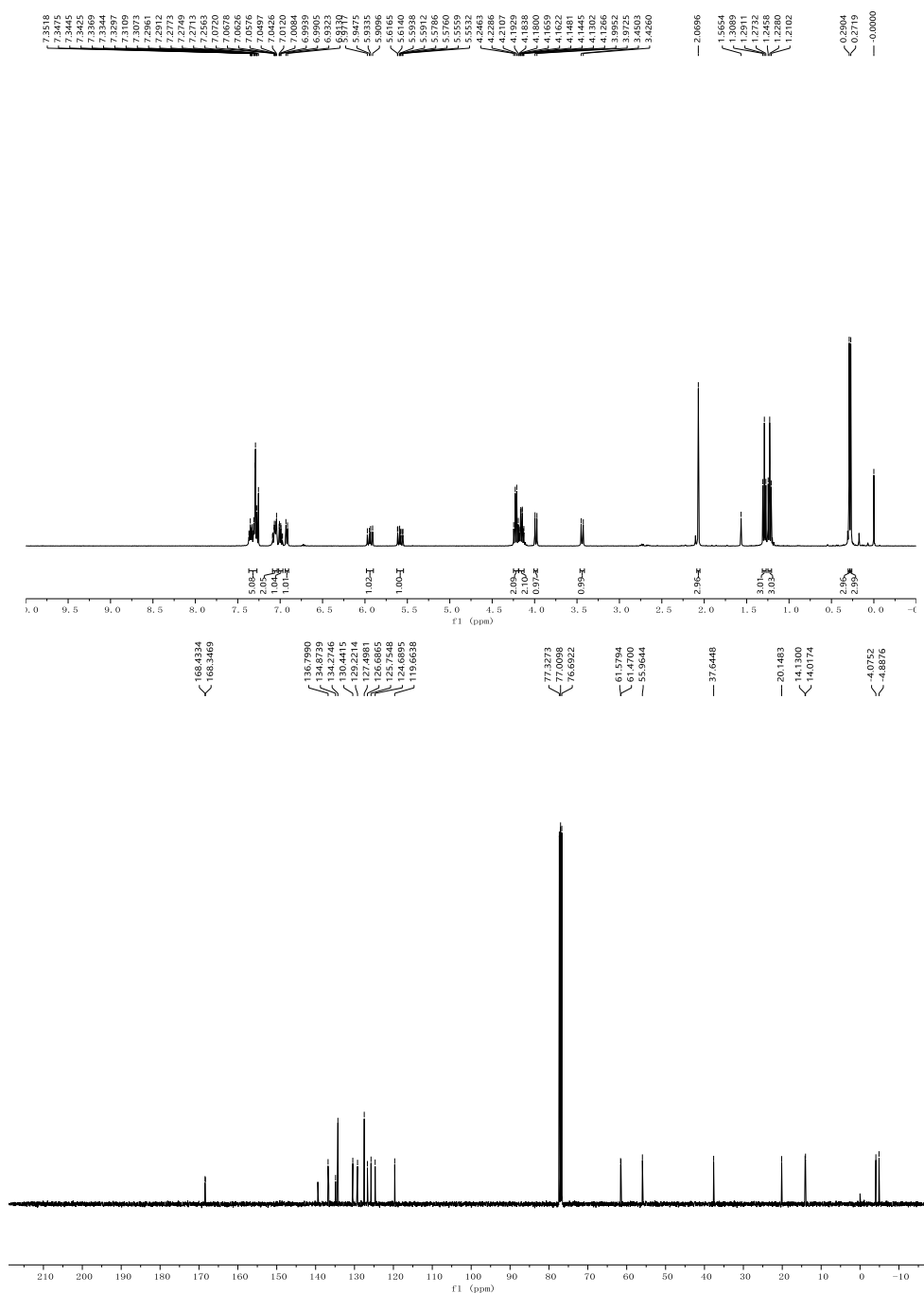
Following the Method E, **4f** was obtained as light greenish oil (62.8 mg, 0.148 mmol, 74%) as light yellow solid; $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.39 – 7.25 (m, 5H), 6.98 (d, $J = 7.5$ Hz, 2H), 6.77 (d, $J = 8.1$ Hz, 2H), 5.93 (ddd, $J = 15.3, 9.9, 0.8$ Hz, 1H), 5.58 (ddd, $J = 15.3, 9.1, 1.0$ Hz, 1H), 4.20 (q, $J = 7.1$ Hz, 2H), 4.15 – 4.12 (m, 2H), 3.98 (d, $J = 9.1$ Hz, 1H), 3.15 (d, $J = 9.9$ Hz, 1H), 2.27 (s, 3H), 1.28 (t, $J = 7.1$ Hz, 3H), 1.23 (t, $J = 7.1$ Hz, 3H), 0.25 (s, 3H), 0.24 (s, 3H) ppm; $^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 168.42, 168.34, 137.85, 136.45, 136.37, 134.37, 134.23, 129.16, 128.89, 127.48, 127.24, 119.49, 61.55, 61.45, 55.99, 42.32, 20.89, 14.12, 14.02, -4.22, -4.73 ppm; **HRMS (ESI)**: m/z Calcd. for $\text{C}_{25}\text{H}_{33}\text{O}_4\text{Si}$ $[\text{M}+\text{H}]^+$: 425.2143, found: 425.2134.



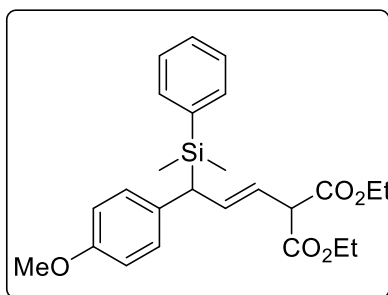
Diethyl (*E*)-2-(3-(dimethyl(phenyl)silyl)-3-(*o*-tolyl)prop-1-en-1-yl)malonate (4g)



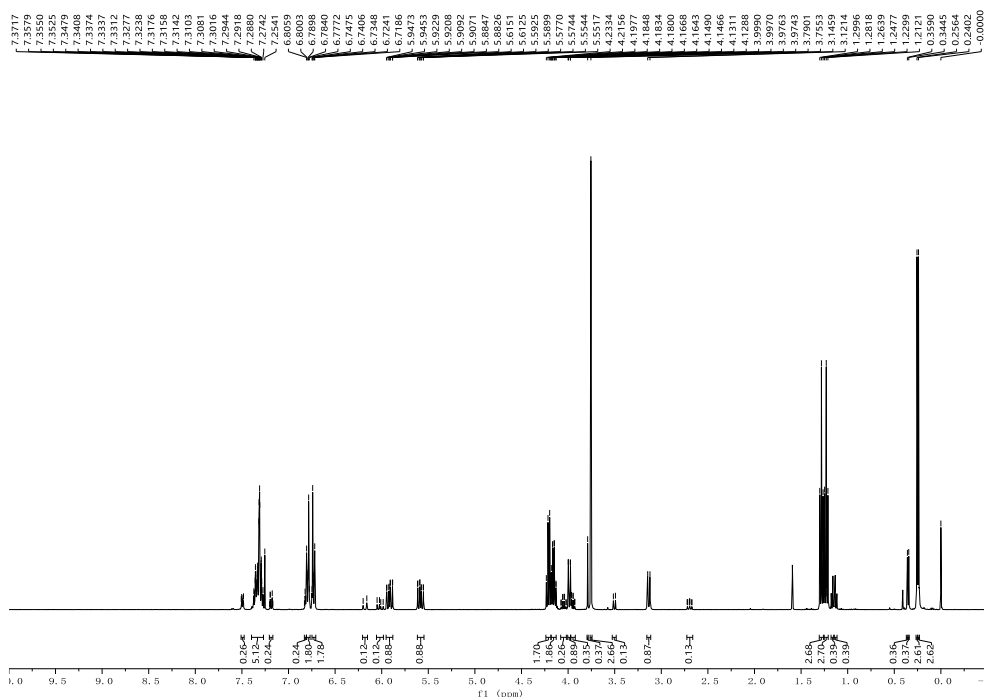
Following the Method E, **4g** was obtained as light green oil (54.5 mg, 0.128 mmol, 64%); $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.35 – 7.27 (m, 5H), 7.09 – 7.03 (m, 2H), 7.02 – 6.97 (m, 1H), 6.92 (d, $J = 7.7$ Hz, 1H), 5.94 (dd, $J = 15.2, 9.6$ Hz, 1H), 5.58 (ddd, $J = 15.2, 9.1, 1.0$ Hz, 1H), 4.22 (q, $J = 7.1$ Hz, 2H), 4.18 – 4.12 (m, 2H), 3.98 (d, $J = 9.1$ Hz, 1H), 3.44 (d, $J = 9.7$ Hz, 1H), 2.07 (s, 3H), 1.29 (t, $J = 7.1$ Hz, 3H), 1.23 (t, $J = 7.1$ Hz, 3H), 0.29 (s, 3H), 0.27 (s, 3H) ppm; $^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 168.43, 168.35, 136.80, 134.87, 134.27, 130.44, 129.22, 127.50, 126.69, 125.75, 124.69, 119.66, 61.58, 61.47, 55.96, 37.64, 20.15, 14.13, 14.02, -4.08, -4.89 ppm; **HRMS (ESI)**: m/z Calcd. for $\text{C}_{25}\text{H}_{33}\text{O}_4\text{Si}$ $[\text{M}+\text{H}]^+$: 425.2143, found: 425.2136.

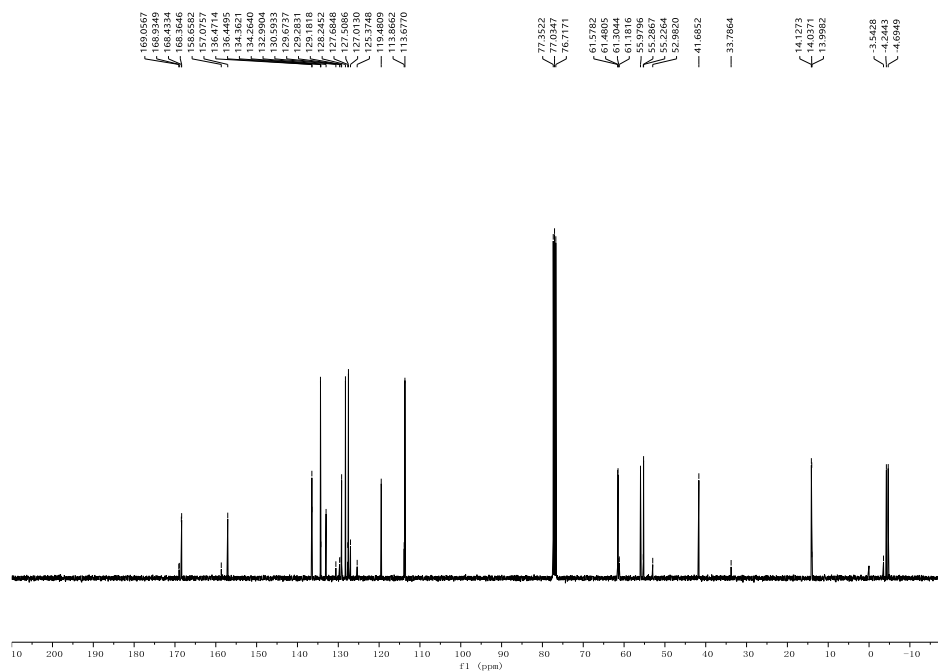


Diethyl (*E*)-2-(3-(dimethyl(phenyl)silyl)-3-(4-methoxyphenyl)prop-1-en-1-yl) malonate (4h**)**

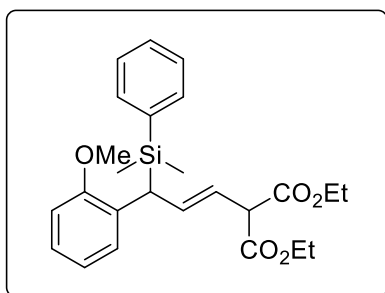


Following the Method E, the mixture of **4h** and **3h** were obtained as a greenish oil (67.3 mg, 0.151 mmol, Yield: 76%); The 1,6 (**4h**) and 1,4 (**3h**) addition ratio was determined after purification to be approximately 88:12 by ¹H NMR. ¹H NMR (400 MHz, CDCl₃): δ 7.50 – 7.48 (m, 2H × 0.12), 7.37 – 7.25 (m, 5H), 7.20 – 7.16 (m, 2H × 0.12), 6.81 – 6.82 (m, 2H × 0.12), 6.80 – 6.77 (m, 2H × 0.88) 6.75 – 6.71 (m, 2H × 0.88), 6.18 (d, *J* = 15.8 Hz, 1H × 0.12), 6.02 (dd, *J* = 15.7, 10.4 Hz, 1H × 0.12), 5.91 (ddd, *J* = 15.3, 9.8, 0.8 Hz, 1H × 0.88), 5.58 (ddd, *J* = 15.3, 9.1, 1.0 Hz, 1H × 0.88), 4.22 (q, *J* = 7.1 Hz, 2H × 0.88), 4.18 – 4.13 (m, 2H × 0.88), 4.05 (m, 2H × 0.12), 3.99 (dd, *J* = 9.1, 0.8 Hz, 1H × 0.88), 3.96 (m, 2H × 0.12), 3.79 (s, 3H × 0.12), 3.76 (s, 3H × 0.88), 3.50 (d, *J* = 8.9 Hz, 1H × 0.12), 3.13 (d, *J* = 9.8 Hz, 1H × 0.88), 2.69 (ddd, *J* = 9.5, 8.9, 0.6 Hz, 1H × 0.12), 1.28 (t, *J* = 7.1 Hz, 3H × 0.88), 1.23 (t, *J* = 7.1 Hz, 3H × 0.88), 1.15 (t, *J* = 7.1 Hz, 3H × 0.12), 1.13 (t, *J* = 7.1 Hz, 3H × 0.12), 0.36 (s, 3H × 0.12), 0.35 (s, 3H × 0.12), 0.25 (s, 3H × 0.88), 0.24 (s, 3H × 0.88) ppm; ¹³C NMR (101 MHz, CDCl₃): δ 169.06, 168.93, 168.43, 168.36, 158.66, 157.08, 136.47, 136.45, 134.36, 134.26, 132.99, 130.59, 129.67, 129.28, 129.18, 128.25, 127.68, 127.51, 127.01, 125.37, 119.48, 113.87, 113.68, 61.58, 61.48, 61.30, 61.18, 55.98, 55.29, 55.23, 52.98, 41.69, 33.79, 14.13, 14.04, 14.00, -3.54, -4.24, -4.69 ppm; HRMS (ESI): *m/z* Calcd. for C₂₅H₃₃O₅Si [M+H]⁺: 441.2092, found: 441.2093.

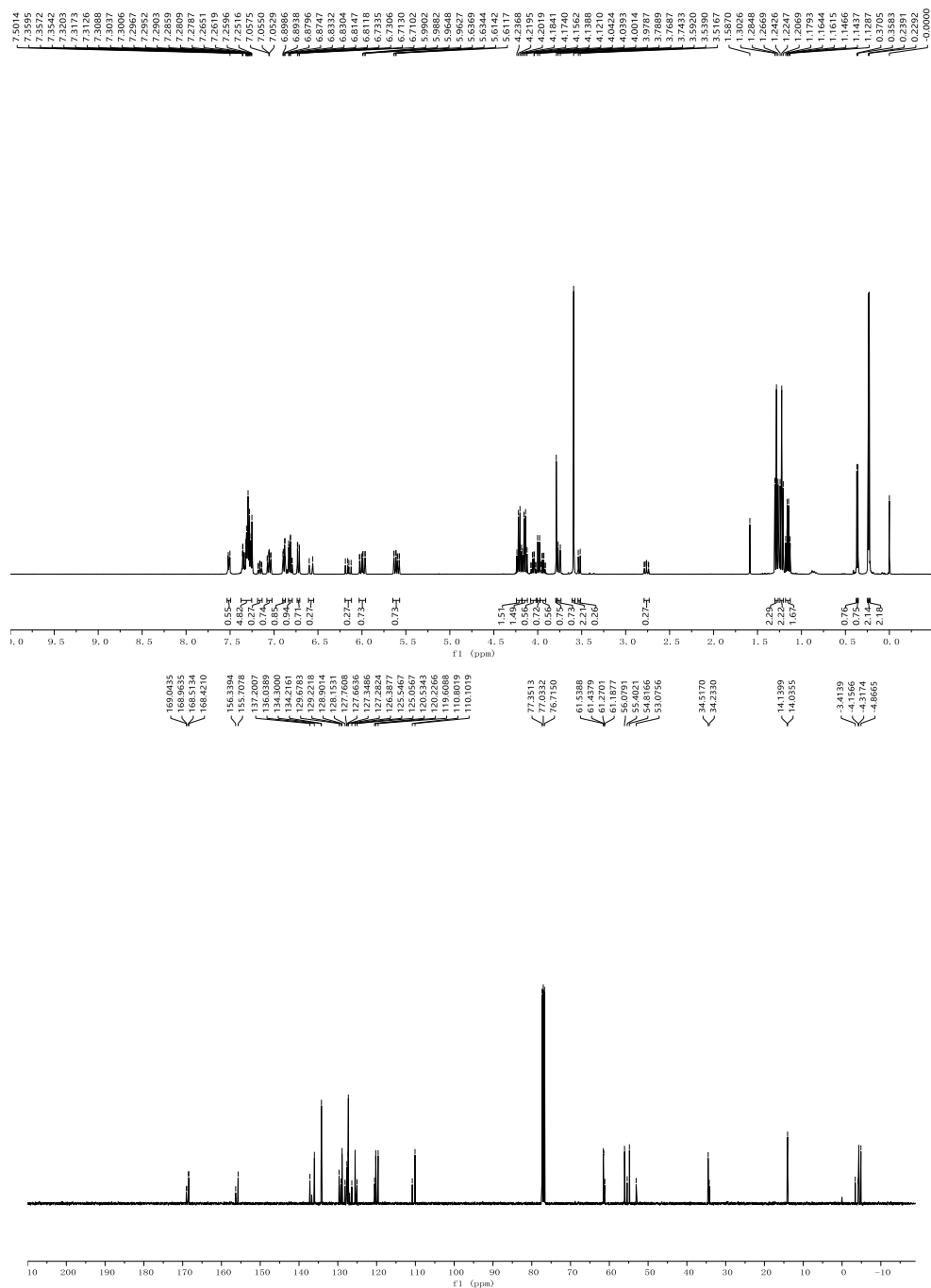




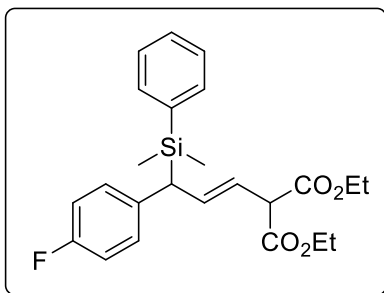
Diethyl (E)-2-(3-(dimethyl(phenyl)silyl)-3-(2-methoxyphenyl)prop-1-en-1-yl)malonate (4i)



Following the Method E, the mixture of **4i** and **3i** were obtained as a greenish oil (61.5mg, 0.139 mmol, Yield: 70%); The 1,6 (**4i**) and 1,4 (**3i**) addition ratio was determined after purification to be approximately 73:27 by ¹H NMR. ¹H NMR (400 MHz, CDCl₃): δ 7.52 – 7.50 (m, 2H × 0.27), 7.35 – 7.25 (m, 5H), 7.18 – 7.13 (m, 1H × 0.27), 7.07 – 7.03 (m, 1H × 0.73), 6.89 – 6.87 (m, 1H × 0.73), 6.83 – 6.79 (m, 3H × 0.27), 6.72 (dd, *J* = 8.2, 1.1 Hz, 1H × 0.73), 6.58 (d, *J* = 15.9 Hz, 1H × 0.27), 6.16 (dd, *J* = 15.9, 10.5 Hz, 1H × 0.27), 6.00 (ddd, *J* = 15.3, 10.1, 0.8 Hz, 1H × 0.73), 5.61 (ddd, *J* = 15.2, 9.1, 1.0 Hz, 1H × 0.73), 4.21 (q, *J* = 7.1 Hz, 2H × 0.73), 4.15 (q, *J* = 7.1 Hz, 2H × 0.73), 4.07 – 4.02 (m, 2H × 0.27), 3.98 (d, *J* = 8.9 Hz, 1H × 0.73), 3.96 – 3.91 (m, 1H × 0.27), 3.78 (s, 3H × 0.27), 3.75 (d, *J* = 10.2 Hz, 1H × 0.73), 3.59 (s, 3H × 0.73), 3.52 (d, *J* = 8.9 Hz, 1H × 0.27), 2.76 (ddd, *J* = 9.9, 8.9, 0.9 Hz, 1H × 0.27), 1.28 (t, *J* = 7.1 Hz, 3H × 0.73), 1.22 (t, *J* = 7.1 Hz, 3H × 0.73), 1.17 – 1.12 (m, 6H × 0.27), 0.37 (s, 3H × 0.27), 0.35 (s, 3H × 0.27), 0.24 (s, 3H × 0.73), 0.23 (s, 3H × 0.73) ppm; ¹³C NMR (101 MHz, CDCl₃): δ 169.04, 168.96, 168.51, 168.42, 156.34, 155.71, 137.20, 136.04, 134.30, 134.22, 129.68, 129.22, 128.90, 128.15, 127.76, 127.66, 127.35, 127.28, 126.39, 125.55, 125.06, 120.53, 120.23, 119.61, 110.80, 110.10, 61.54, 61.44, 61.27, 61.19, 56.08, 55.40, 54.82, 53.08, 34.52, 34.23, 14.14, 14.04, -3.41, -4.16, -4.32, -4.87 ppm; HRMS (ESI): *m/z* Calcd. for C₂₅H₃₃O₅Si [M+Na]⁺: 441.2092, found: 441.2084.



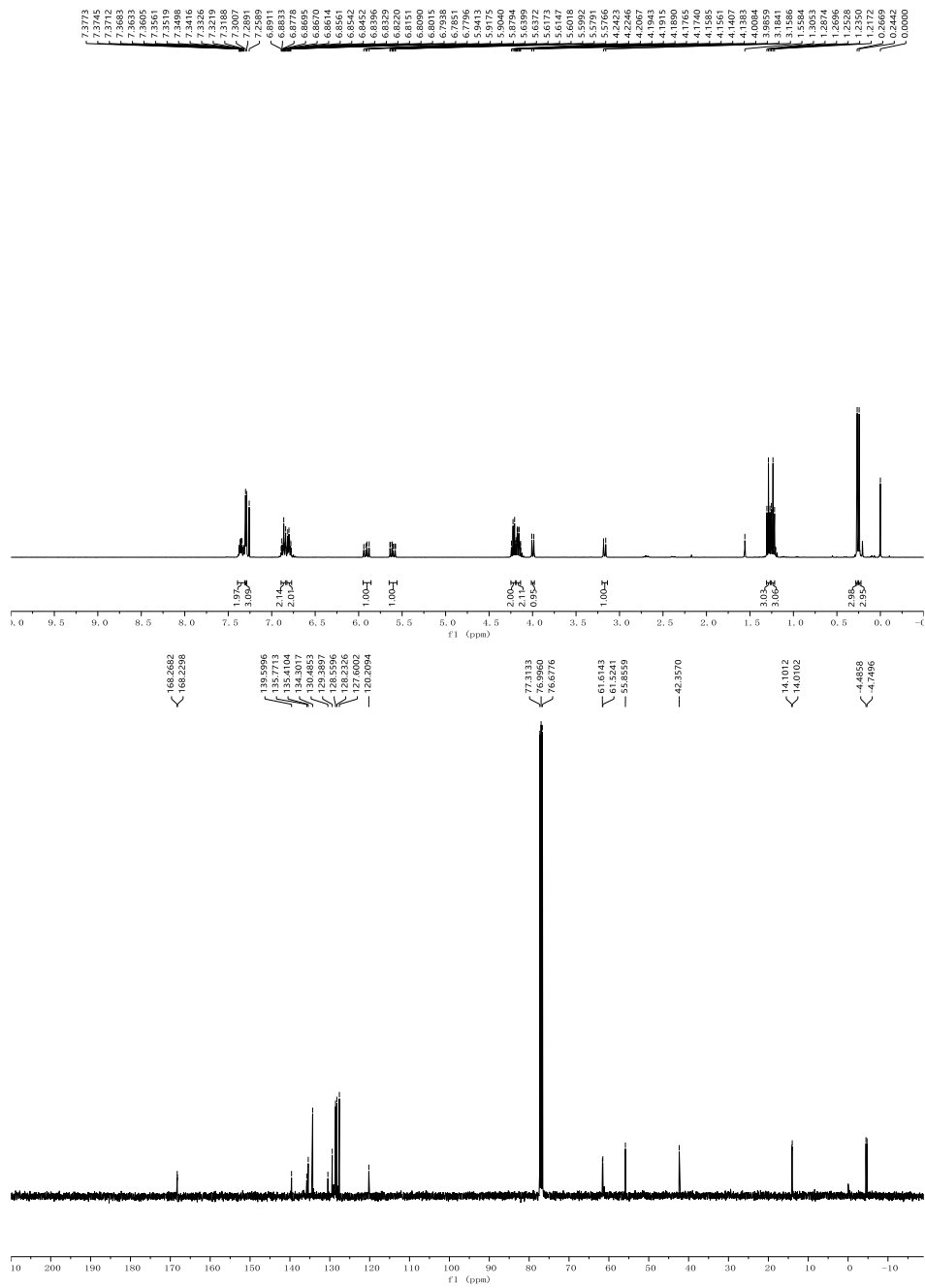
Diethyl (*E*)-2-(3-(dimethyl(phenyl)silyl)-3-(4-fluorophenyl)prop-1-en-1-yl)malonate (**4j**)

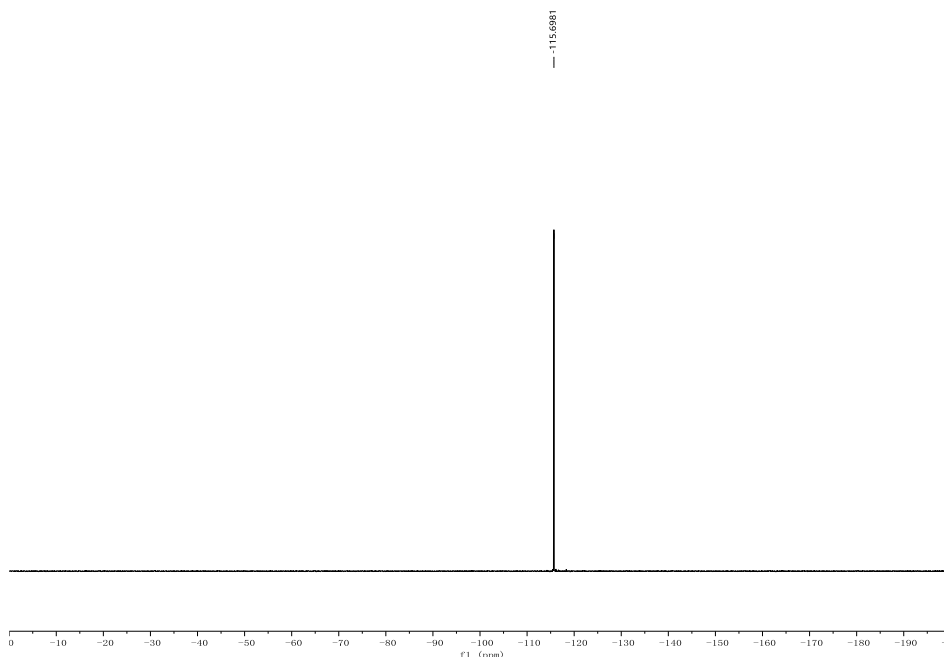


Following the Method E, **4j** was obtained as a light green oil (61.7 mg, 0.144 mmol, Yield: 72%); ^1H NMR (400 MHz, CDCl_3): δ 7.39 – 7.31 (m, 2H), 7.29 (d, J = 4.6 Hz, 3H), 6.89 – 6.84 (m, 2H), 6.83 – 6.77 (m, 2H), 5.91 (dd, J = 15.1, 9.7 Hz, 1H), 5.61 (ddd, J = 15.2, 9.0, 1.0 Hz, 1H), 4.22 (q, J = 7.1 Hz, 2H), 4.19 – 4.13 (m, 2H), 4.00 (d, J = 9.0 Hz, 1H), 3.17 (d, J = 10.2 Hz, 1H), 1.29 (t, J = 7.2 Hz, 3H), 1.24 (t, J = 7.1 Hz, 3H), 0.27 (s, 3H), 0.24 (s, 3H) ppm; ^{13}C NMR (101 MHz, CDCl_3):

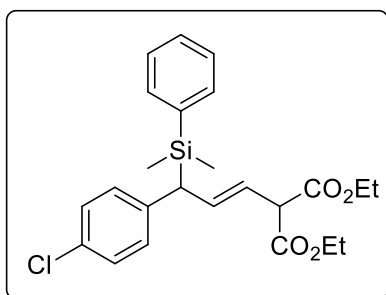
δ 168.27, 168.23, 139.60, 135.77, 135.41, 134.30, 130.49, 129.39, 128.56, 128.23, 127.60, 120.21, 61.61, 61.52, 55.86, 42.36, 14.10, 14.01, -4.49, -4.75. ppm; ^{19}F NMR (376 MHz, CDCl_3): δ -115.70 ppm; HRMS (ESI): m/z Calcd. for $\text{C}_{24}\text{H}_{30}\text{O}_4\text{FSi}$ [$\text{M}+\text{H}$] $^+$: 429.1892, found:

429.1886.



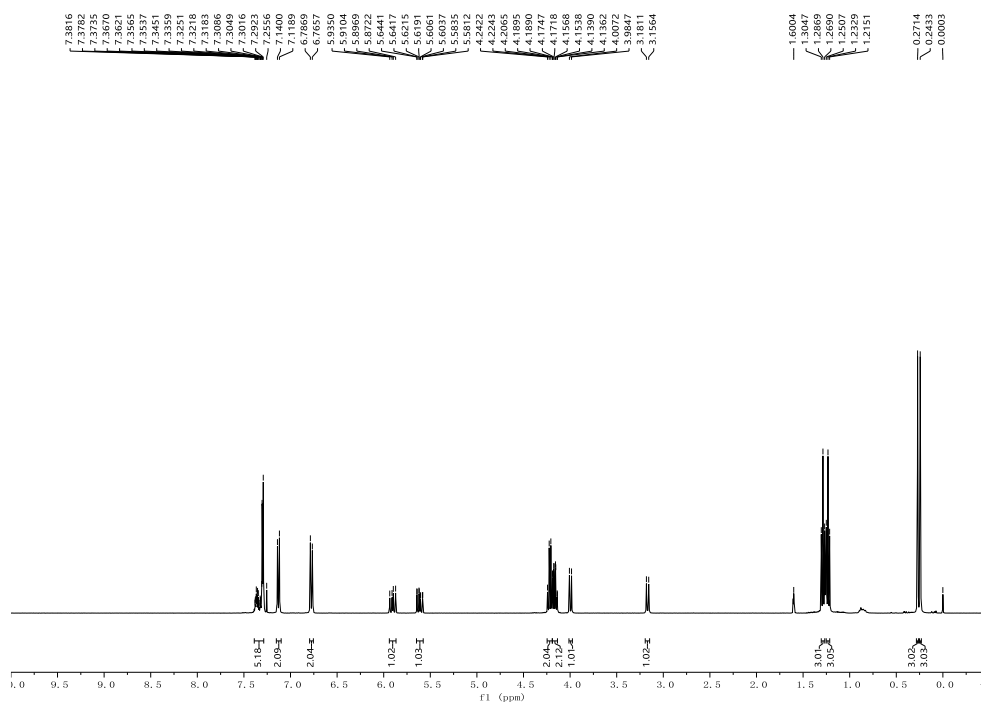


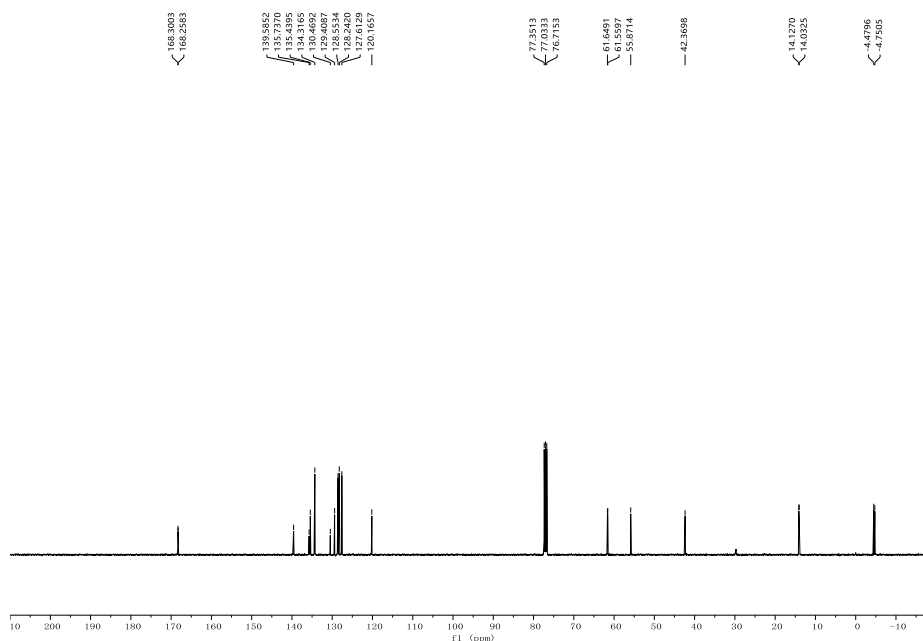
Diethyl (*E*)-2-(3-(4-chlorophenyl)-3-(dimethyl(phenyl)silyl)prop-1-en-1-yl)malonate (**4k**)



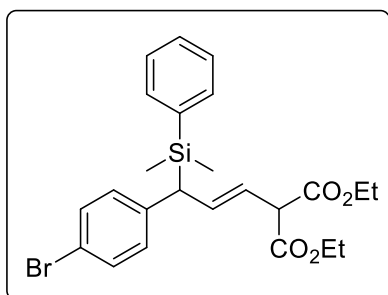
Following the Method E, **4k** was obtained as a light brown oil (62.5 mg, 0.14 mmol, Yield: 70%); $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.39 – 7.29 (m, 5H), 7.13 (d, $J = 8.4$ Hz, 2H), 6.78 (d, $J = 8.5$ Hz, 2H), 5.90 (dd, $J = 15.2, 9.9$ Hz, 1H), 5.61 (ddd, $J = 15.2, 9.0, 1.0$ Hz, 1H), 4.25 – 4.19 (m, 2H), 4.19 – 4.14 (m, 2H), 4.00 (d, $J = 9.0$ Hz, 1H), 3.17 (d, $J = 9.9$ Hz, 1H), 1.29 (t, $J = 7.1$ Hz, 3H), 1.23 (t, $J = 7.1$ Hz, 3H), 0.27 (s, 3H), 0.24 (s, 3H) ppm; $^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 168.30, 168.26, 139.59, 135.74, 135.44, 134.32, 130.47, 129.41, 128.55,

128.24, 127.61, 120.17, 61.65, 61.56, 55.87, 42.37, 14.13, 14.03, -4.48, -4.75 ppm; **HRMS (ESI)**: m/z Calcd. for $\text{C}_{24}\text{H}_{30}\text{O}_4\text{Cl Si}$ $[\text{M}+\text{H}]^+$: 445.1596, found: 445.1589.



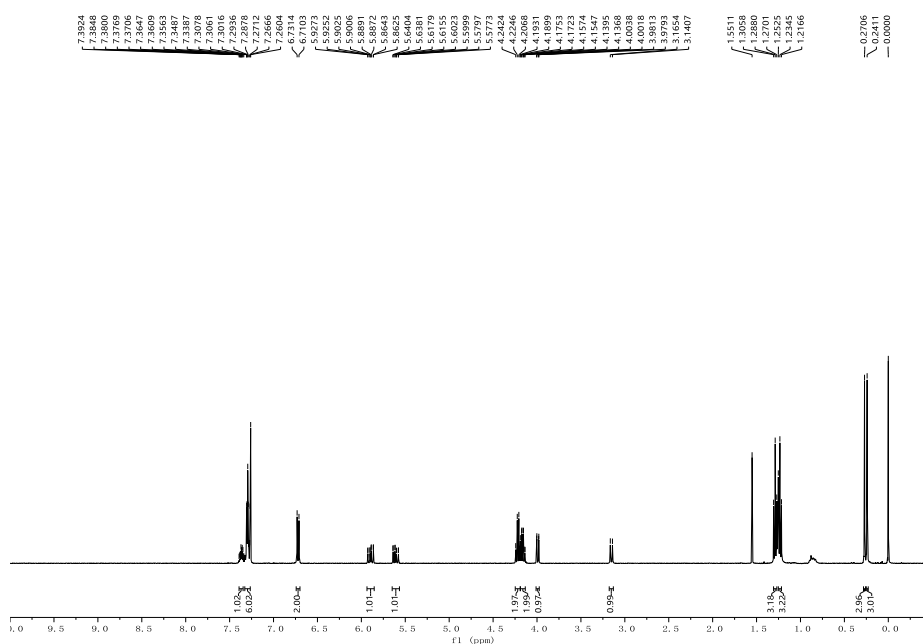


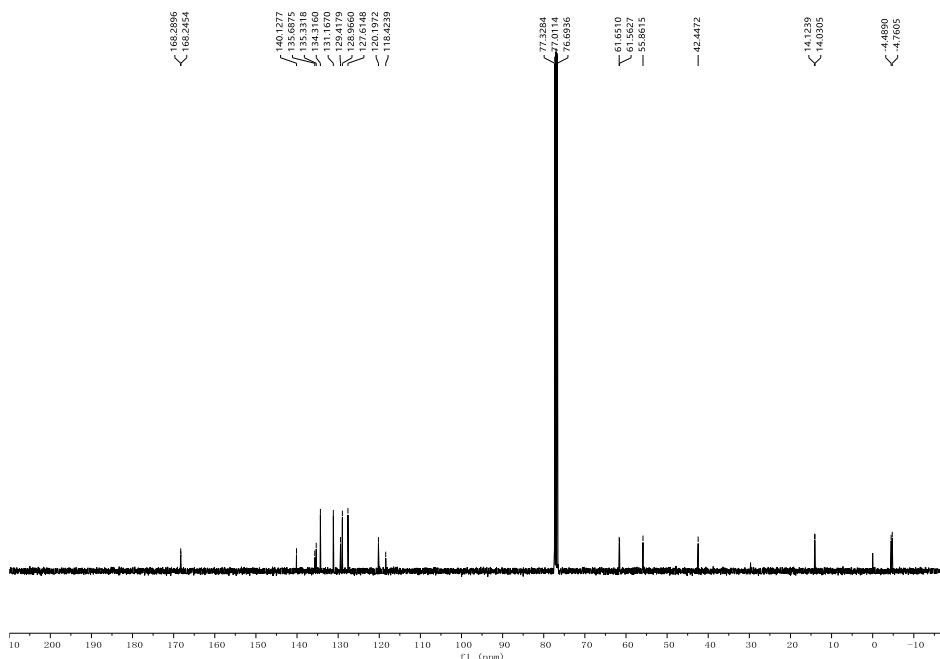
Diethyl (*E*)-2-(3-(4-bromophenyl)-3-(dimethyl(phenyl)silyl)prop-1-en-1-yl)malonate (**4I**)



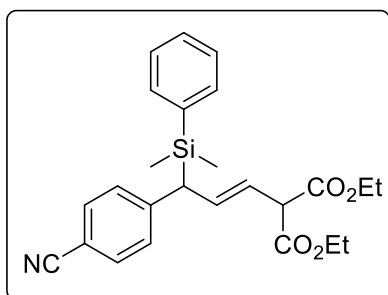
Following the general procedure, **4I** was obtained as a brown solid (62.5 mg, 0.128 mmol, Yield: 64%); ¹H NMR (400 MHz, CDCl₃): δ 7.39 – 7.33 (m, 1H), 7.30 – 7.27 (m, 6H), 6.72 (d, *J* = 8.5 Hz, 2H), 5.89 (ddd, *J* = 15.3, 9.9, 0.8 Hz, 1H), 5.61 (ddd, *J* = 15.3, 9.0, 1.0 Hz, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 4.18 – 4.13 (m, 2H), 3.99 (dd, *J* = 9.0, 0.8 Hz, 1H), 3.15 (d, *J* = 9.9 Hz, 1H), 1.28 (t, *J* = 7.1 Hz, 3H), 1.23 (t, *J* = 7.1 Hz, 3H), 0.27 (s, 3H), 0.24 (s, 3H) ppm; ¹³C NMR (101 MHz, CDCl₃): δ 168.29, 168.25, 140.13, 135.69, 135.33, 134.32, 131.17,

129.42, 128.97, 127.61, 120.20, 118.42, 61.65, 61.56, 55.86, 42.45, 14.12, 14.03, -4.49, -4.76 ppm; HRMS (ESI): *m/z* Calcd. for C₂₄H₃₀O₄BrSi [M+H]⁺: 489.1091, found: 489.1086.



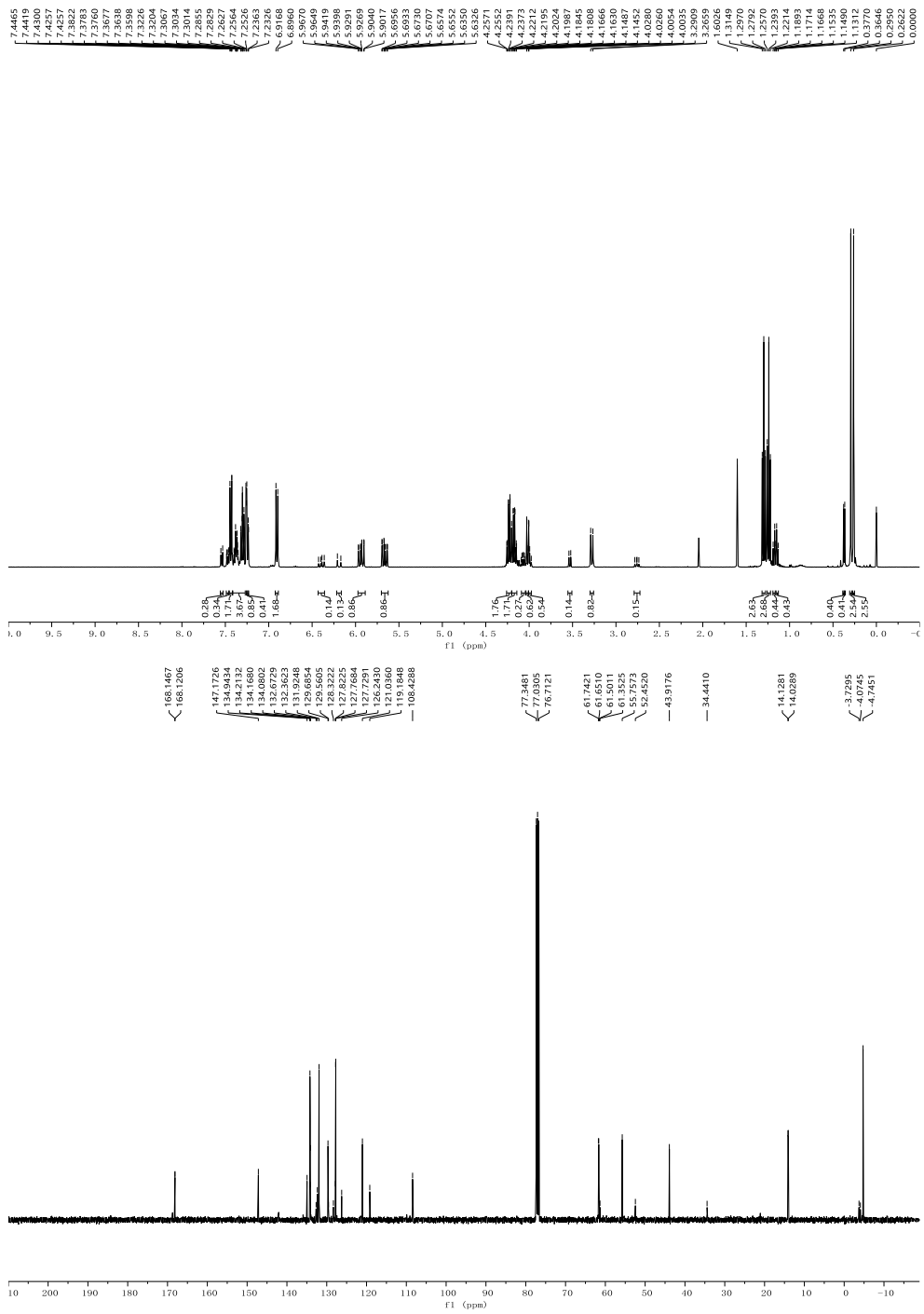


Diethyl (*E*)-2-(3-(4-cyanophenyl)-3-(dimethyl(phenyl)silyl)prop-1-en-1-yl)malonate (**4m**)

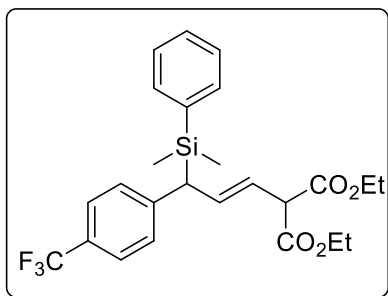


Following the Method E, the mixture of **4m** and **3m** were obtained as a greenish oil (67.7 mg, 0.155 mmol, Yield: 78%); The 1,6 (**4m**) and 1,4 (**3m**) addition ratio was determined after purification to be approximately 86:14 by ^1H NMR. ^1H NMR (400 MHz, CDCl_3): δ 7.54 (d, $J = 8.4$ Hz, $2\text{H} \times 0.14$), 7.49 – 7.46 (m, $2\text{H} \times 0.14$), 7.45 – 7.42 (m, $2\text{H} \times 0.86$), 7.40 – 7.29 (m, 3H), 7.25 (d, $J = 1.5$ Hz, $1\text{H} \times 0.86$), 7.23 (d, $J = 1.5$ Hz, $2\text{H} \times 0.14$), 6.90 (d, $J = 8.4$ Hz, $1\text{H} \times 0.86$), 6.39 (dd, $J = 15.8, 10.4$ Hz, $1\text{H} \times 0.14$), 6.19 (d, $J = 15.9$ Hz, $1\text{H} \times 0.14$),

5.93 (ddd, $J = 10.8, 10.0, 0.8$ Hz, $1\text{H} \times 0.86$), 5.66 (ddd, $J = 9.9, 9.0, 0.9$ Hz, $1\text{H} \times 0.86$), 4.25 – 4.21 (m, $2\text{H} \times 0.86$), 4.19 – 4.14 (m, $2\text{H} \times 0.86$), 4.09 – 4.04 (m, $2\text{H} \times 0.14$), 4.02 (d, $J = 0.8$ Hz, $1\text{H} \times 0.86$), 4.01 – 3.97 (m, $2\text{H} \times 0.14$), 3.53 (d, $J = 8.2$ Hz, $1\text{H} \times 0.14$), 3.28 (d, $J = 10.1$ Hz, $1\text{H} \times 0.86$), 2.76 (dd, $J = 10.4, 8.2$ Hz, $1\text{H} \times 0.14$), 1.29 (t, $J = 7.1$ Hz, $3\text{H} \times 0.86$), 1.23 (t, $J = 7.1$ Hz, $3\text{H} \times 0.86$), 1.17 (t, $J = 7.1$ Hz, $3\text{H} \times 0.14$), 1.14 (t, $J = 7.1$ Hz, $3\text{H} \times 0.14$), 0.37 (s, $3\text{H} \times 0.14$), 0.36 (s, $3\text{H} \times 0.14$), 0.29 (s, $3\text{H} \times 0.86$), 0.26 (s, $3\text{H} \times 0.86$) ppm; ^{13}C NMR (101 MHz, CDCl_3): δ 168.15, 168.12, 147.17, 134.94, 134.21, 134.17, 134.08, 132.67, 132.36, 131.92, 129.69, 129.56, 128.32, 127.82, 127.77, 127.73, 126.24, 121.04, 119.18, 108.43, 61.74, 61.65, 61.50, 61.35, 55.76, 52.45, 43.92, 34.44, 14.13, 14.03, -3.73, -4.07, -4.75 ppm; HRMS (ESI): m/z Calcd. for $\text{C}_{25}\text{H}_{30}\text{O}_4\text{NSi}$ $[\text{M}+\text{H}]^+$: 436.1939, found: 436.1933.

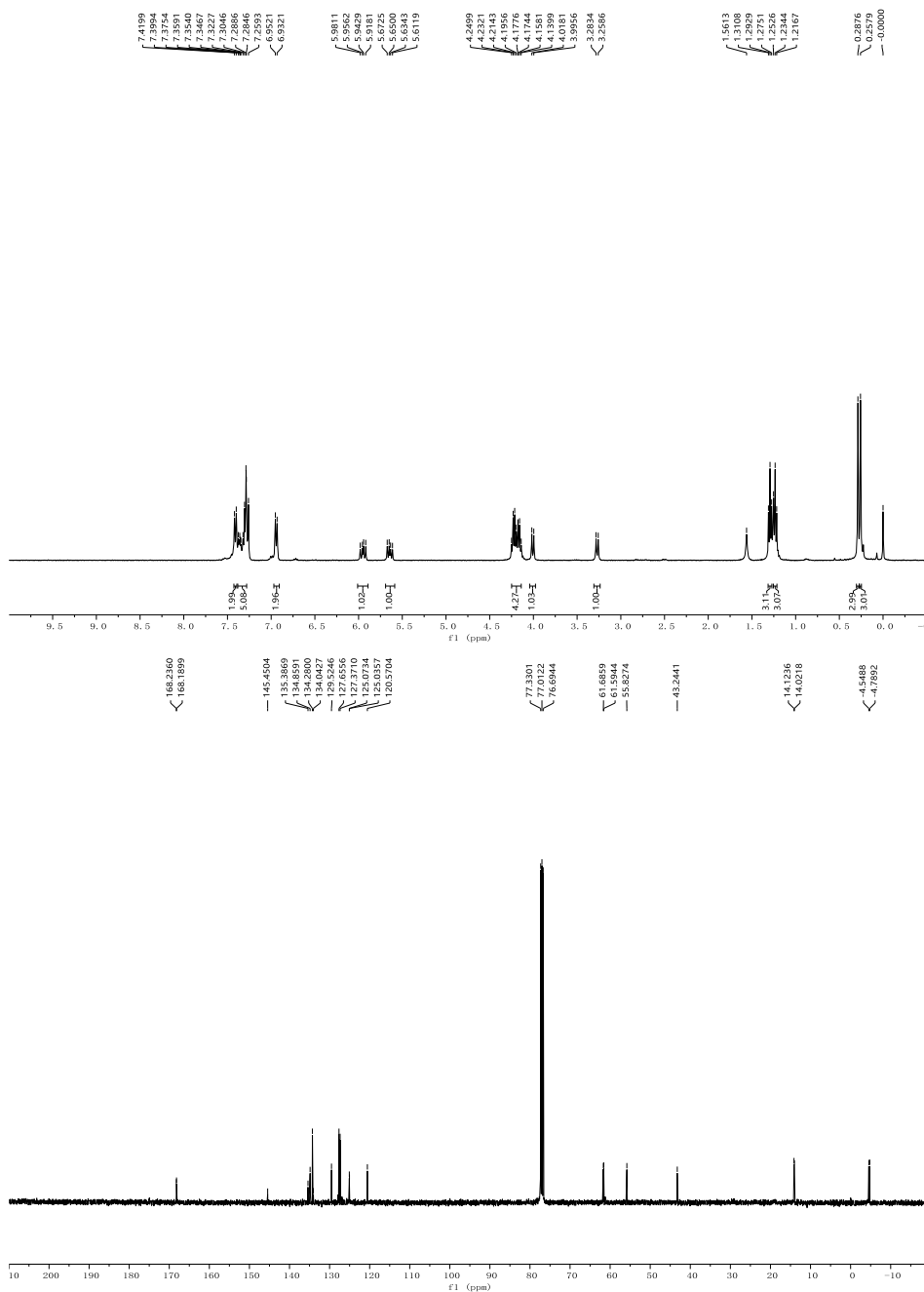


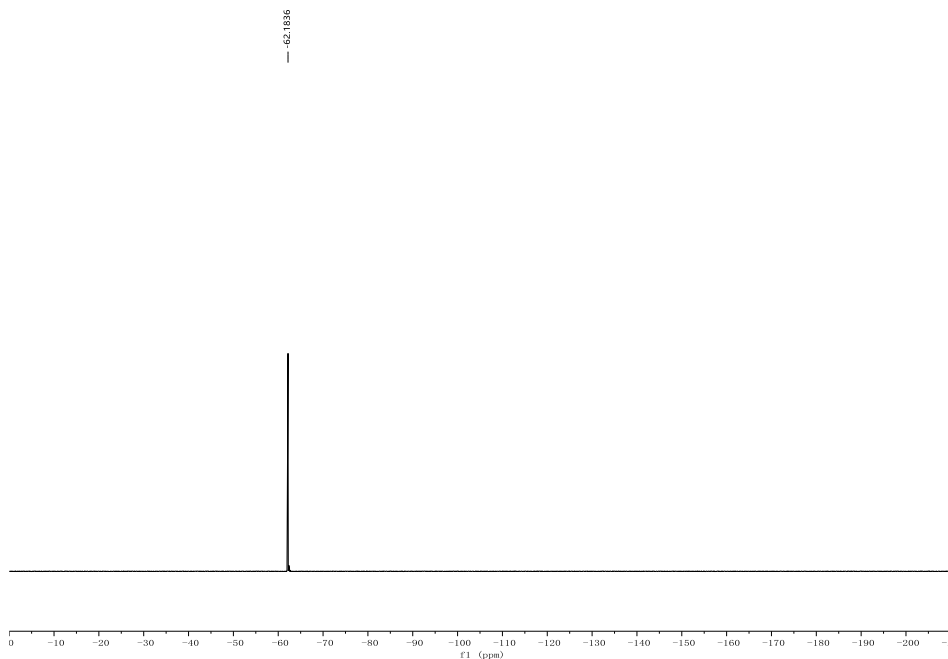
Diethyl (E)-2-(3-(dimethyl(phenyl)silyl)-3-(4-(trifluoromethyl)phenyl)prop-1-en-1-yl)malonate (4o)



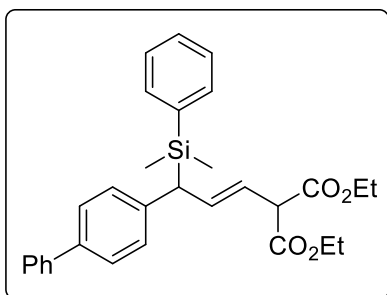
Following the Method E, **4o** was obtained as a colorless oil (64.3 mg, 0.134 mmol, Yield: 67%); ¹H NMR (400 MHz, CDCl₃): 7.41 (d, *J* = 8.2 Hz, 2H), 7.38 – 7.28 (m, 5H), 6.94 (d, *J* = 8.0 Hz, 2H), 5.95 (dd, *J* = 15.3, 9.9 Hz, 1H), 5.64 (dd, *J* = 15.3, 9.0 Hz, 1H), 4.25 – 4.14 (m, 4H), 4.01 (d, *J* = 9.0 Hz, 1H), 3.27 (d, *J* = 9.9 Hz, 1H), 1.29 (t, *J* = 7.1 Hz, 3H), 1.23 (t, *J* = 7.2 Hz, 3H), 0.29 (s, 3H), 0.26 (s, 3H). ppm; ¹³C NMR (101 MHz, CDCl₃): δ 168.24, 168.19, 145.45, 135.39, 134.86, 134.28, 134.04, 129.52, 127.66, 127.37, 125.07, 125.04, 120.57, 61.69,

61.59, 55.83, 43.24, 14.12, 14.02, -4.55, -4.79 ppm; ¹⁹F NMR (376 MHz, CDCl₃): δ -62.18 ppm; HRMS (ESI): *m/z* Calcd. for C₂₅H₃₀O₄F₃ Si [M+H]⁺: 479.1860, found: 479.1866.



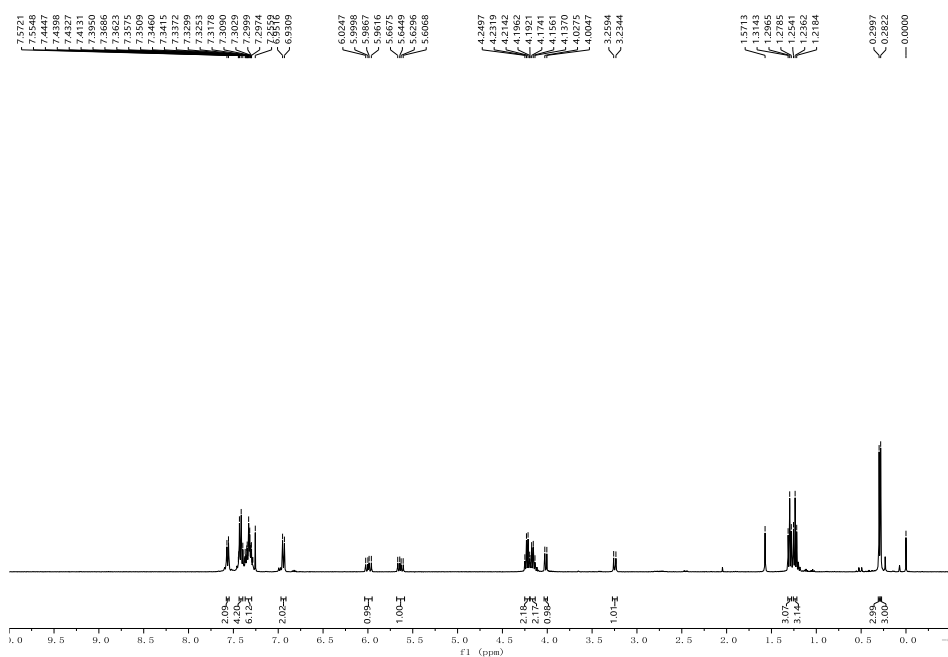


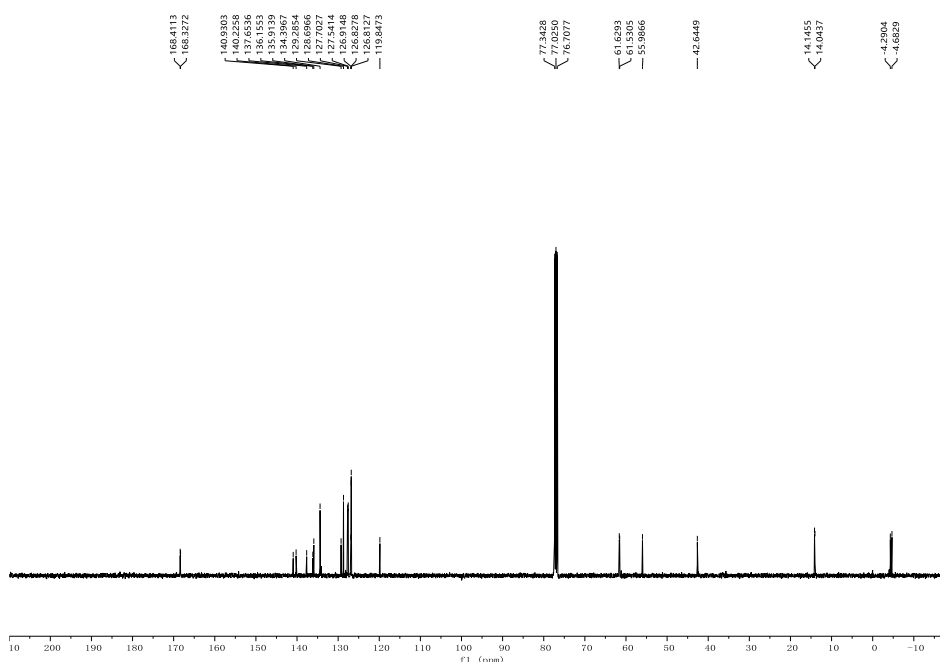
Diethyl (*E*)-2-(3-([1,1'-biphenyl]-4-yl)-3-(dimethyl(phenyl)silyl)prop-1-en-1-yl)malonate (**4p**)



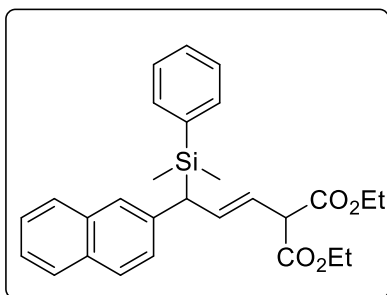
Following the Method E, **4p** was obtained as a white solid (68.5 mg, 0.140 mmol, Yield: 70%); **¹H NMR (400 MHz, CDCl₃):** δ 7.56 (d, *J* = 6.9 Hz, 2H), 7.44 – 7.34 (m, 4H), 7.37 – 7.30 (m, 6H), 6.94 (d, *J* = 8.2 Hz, 2H), 5.99 (dd, *J* = 15.2, 10.0 Hz, 1H), 5.64 (dd, *J* = 15.2, 9.1 Hz, 1H), 4.22 (q, *J* = 7.2 Hz, 2H), 4.16 (q, *J* = 7.4 Hz, 2H), 4.02 (d, *J* = 9.1 Hz, 1H), 3.25 (d, *J* = 10.0 Hz, 1H), 1.30 (t, *J* = 7.2 Hz, 3H), 1.24 (t, *J* = 7.1 Hz, 3H), 0.30 (s, 3H), 0.28 (s, 3H) ppm; **¹³C NMR (101 MHz, CDCl₃):** δ 168.41, 168.33, 140.93, 140.23, 137.65, 136.16,

135.91, 134.40, 129.29, 128.70, 127.70, 127.54, 126.91, 126.83, 126.81, 119.85, 61.63, 61.53, 55.99, 42.64, 14.15, 14.04, -4.29, -4.68 ppm; **HRMS (ESI):** *m/z* Calcd. for C₃₀H₃₅O₄Si [M+H]⁺: 487.2299, found: 487.2295.



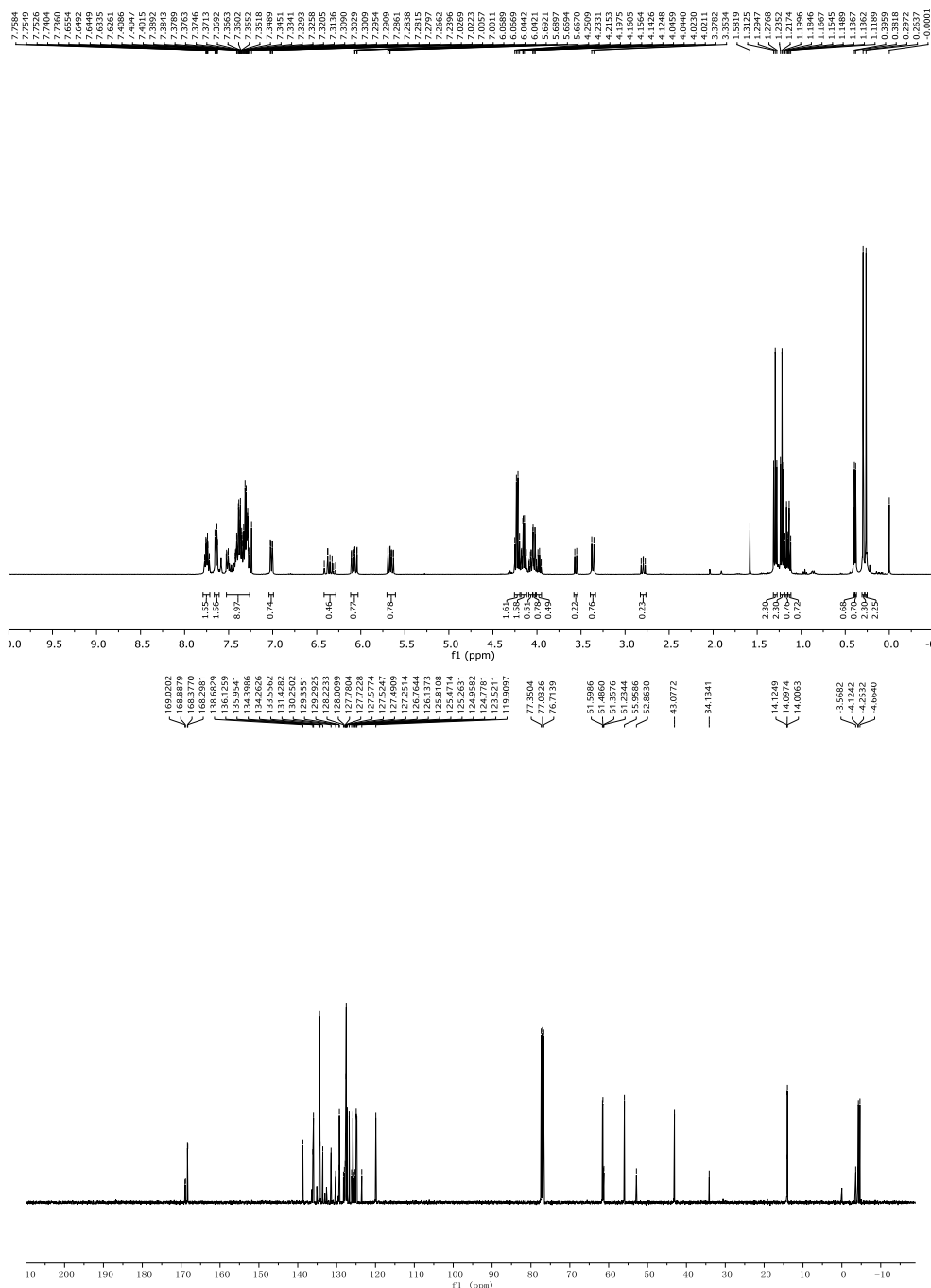


Diethyl (E)-2-(3-(dimethyl(phenyl)silyl)-3-(naphthalen-2-yl)prop-1-en-1-yl)malonate (**4q**)



Following the Method E, the mixture of **4q** and **3q** were obtained as a light brownish solid (73.5 mg, 0.159 mmol, Yield: 80%); The 1,6 (**4q**) and 1,4 (**3q**) addition ratio was determined after purification to be approximately 77:23 by ^1H NMR. ^1H NMR (400 MHz, CDCl_3): δ 7.77 – 7.71 (m, 2H), 7.65 – 7.62 (m, 2H), 7.54 – 7.27 (m, 8H), 7.01 (dd, $J = 8.5, 1.8$ Hz, $1\text{H} \times 0.77$), 6.41 – 6.28 (m, $2\text{H} \times 0.23$), 6.08 (ddd, $J = 10.8, 10.0, 0.88$ Hz, $1\text{H} \times 0.77$), 5.66 (ddd, $J = 10.0, 9.1, 1.0$ Hz, $1\text{H} \times 0.77$), 4.22 (q, $J = 7.1$ Hz, $2\text{H} \times 0.77$), 4.17 – 4.12 (m, Hz, $2\text{H} \times$

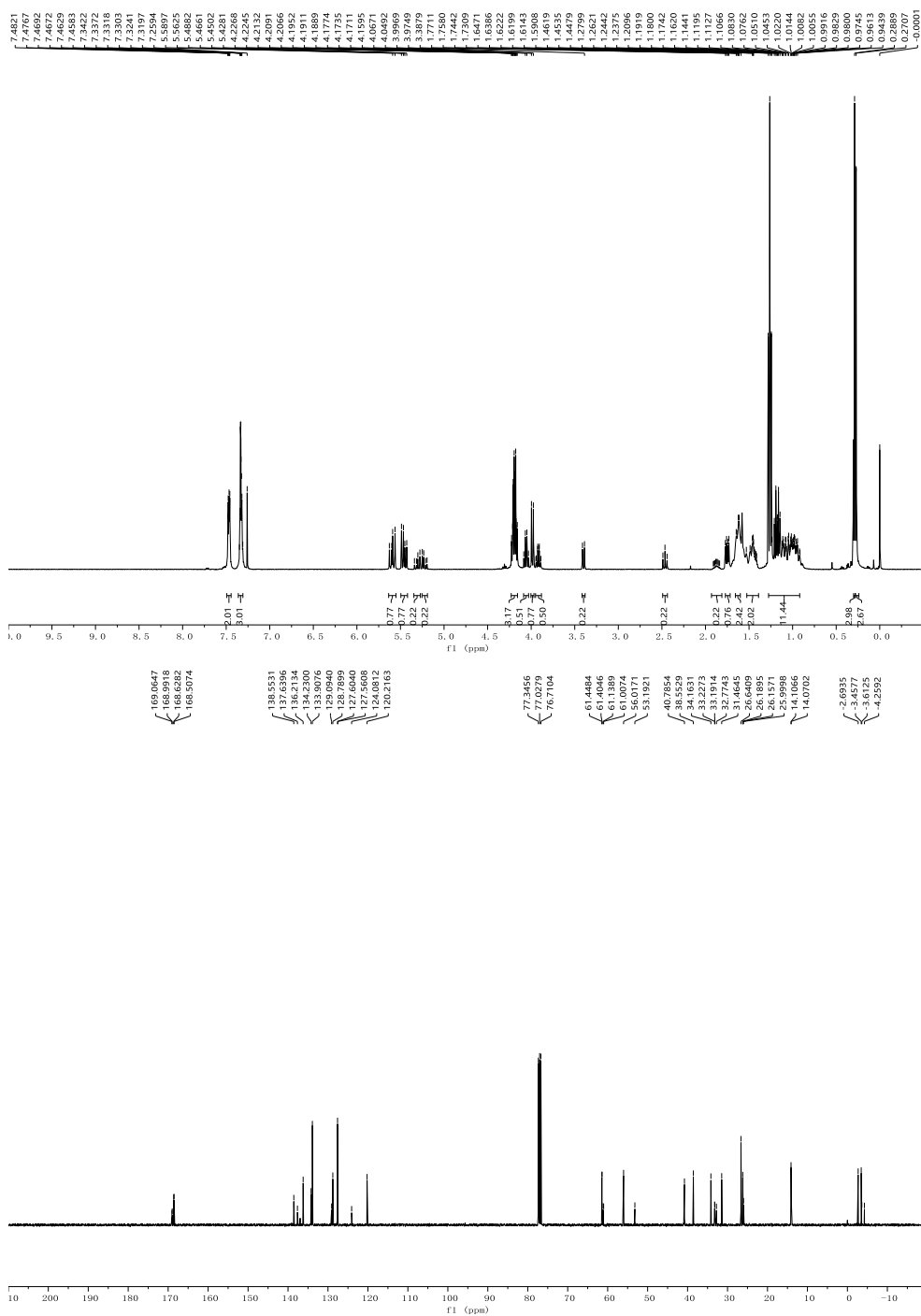
0.77), 4.09 – 4.04 (m, $2\text{H} \times 0.23$), 4.03 (dd, $J = 9.1, 0.7$ Hz, $1\text{H} \times 0.77$), 3.98 (q, $J = 7.1$ Hz, $2\text{H} \times 0.23$), 3.56 (d, $J = 8.8$ Hz, $1\text{H} \times 0.23$), 3.35 (d, $J = 9.9$ Hz, $1\text{H} \times 0.77$), 2.79 (dd, $J = 9.7, 8.7$ Hz, $1\text{H} \times 0.23$), 1.29 (t, $J = 7.1$ Hz, $3\text{H} \times 0.77$), 1.21 (t, $J = 7.2$ Hz, $3\text{H} \times 0.77$), 1.16 (t, $J = 7.1$ Hz, $3\text{H} \times 0.23$), 1.13 (t, $J = 7.1$ Hz, $3\text{H} \times 0.23$), 0.39 (s, $3\text{H} \times 0.23$), 0.38 (s, $3\text{H} \times 0.23$), 0.29 (s, $3\text{H} \times 0.77$), 0.26 (s, $3\text{H} \times 0.77$) ppm; ^{13}C NMR (101 MHz, CDCl_3): δ 169.02, 168.89, 168.38, 168.30, 138.68, 136.13, 135.95, 134.40, 134.26, 133.56, 131.43, 130.25, 129.36, 129.29, 128.22, 128.01, 127.78, 127.72, 127.58, 127.52, 127.49, 127.25, 126.76, 126.14, 125.81, 125.47, 125.26, 124.96, 124.78, 123.52, 119.91, 61.60, 61.49, 61.36, 61.23, 55.96, 52.86, 43.08, 34.13, 14.12, 14.10, 14.01, -3.57, -4.12, -4.25, -4.66 ppm; HRMS (ESI): m/z Calcd. for $\text{C}_{28}\text{H}_{33}\text{O}_4\text{Si}$ [$\text{M}+\text{H}$] $^+$: 461.2143, found: 461.2136.



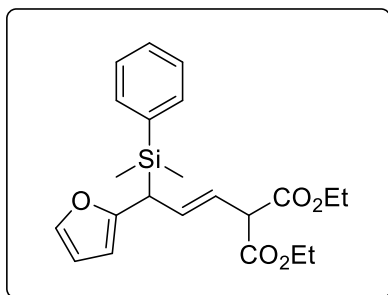
Diethyl (*E*)-2-(3-cyclohexyl-3-(dimethyl(phenyl)silyl)prop-1-en-1-yl)malonate (**4t**)

Following the Method E, the mixture of **4t** and **3t** were obtained as a light greenish oil (65.8 mg, 0.158 mmol, Yield: 79%); The 1,6 (**4t**) and 1,4 (**3t**) addition ratio was determined after purification to be approximately 77:23 by ¹H NMR. ¹H NMR (400 MHz, CDCl₃): δ 7.48 – 7.45 (m, 2H), 7.34 – 7.30 (m, 3H), 5.58 (dd, *J* = 15.2, 10.7 Hz, 1H × 0.77), 5.45 (dd, *J* = 15.3, 8.8 Hz, 1H × 0.77), 5.30 (dd, *J* = 15.6, 9.8 Hz, 1H × 0.22), 5.22 (dd, *J* = 15.3, 6.4 Hz, 1H × 0.22), 4.22 – 4.15 (m, 4H × 0.77), 4.05 (q, *J* = 7.2 Hz, 2H × 0.22), 3.98 (d, *J* = 8.8 Hz, 1H × 0.77), 3.94 – 3.88 (m, 2H × 0.22), 3.40 (d, *J* = 9.3 Hz, 1H × 0.22), 2.46 (t, *J* = 9.6 Hz, 1H × 0.22), 1.75 (dd, *J* = 10.2, 5.7 Hz, 1H × 0.77), 1.64 – 1.59 (m, 2H), 1.48 – 1.41 (m, 2H), 1.27 – 0.91 (m, 12H), 0.28 (s,

6H), 0.27 (s, 6H) ppm; ¹³C NMR (101 MHz, CDCl₃): δ 169.06, 168.99, 168.63, 168.51, 138.55, 137.64, 136.21, 134.23, 133.91, 129.09, 128.79, 127.60, 127.56, 124.08, 120.22, 61.45, 61.40, 61.14, 61.01, 56.02, 53.19, 40.79, 38.55, 34.16, 33.23, 33.19, 32.77, 31.46, 26.64, 26.19, 26.16, 26.00, 14.11, 14.07, -2.69, -3.46, -3.61, -4.26 ppm; HRMS (ESI): m/z Calcd. for C₂₄H₃₇O₄Si [M+H]⁺: 417.2456, found: 417.2448.

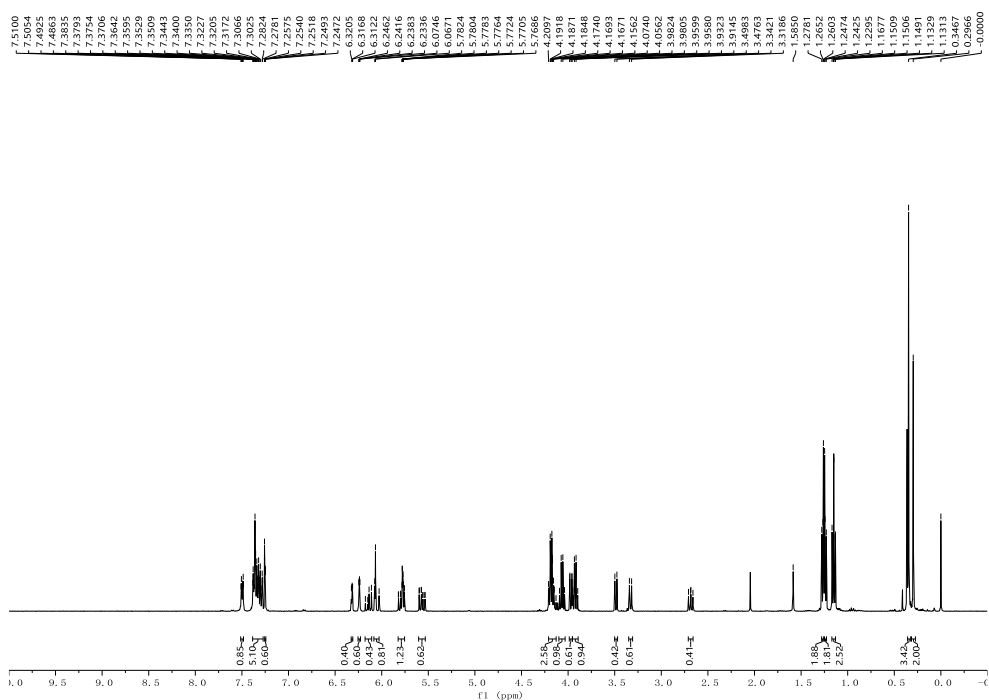


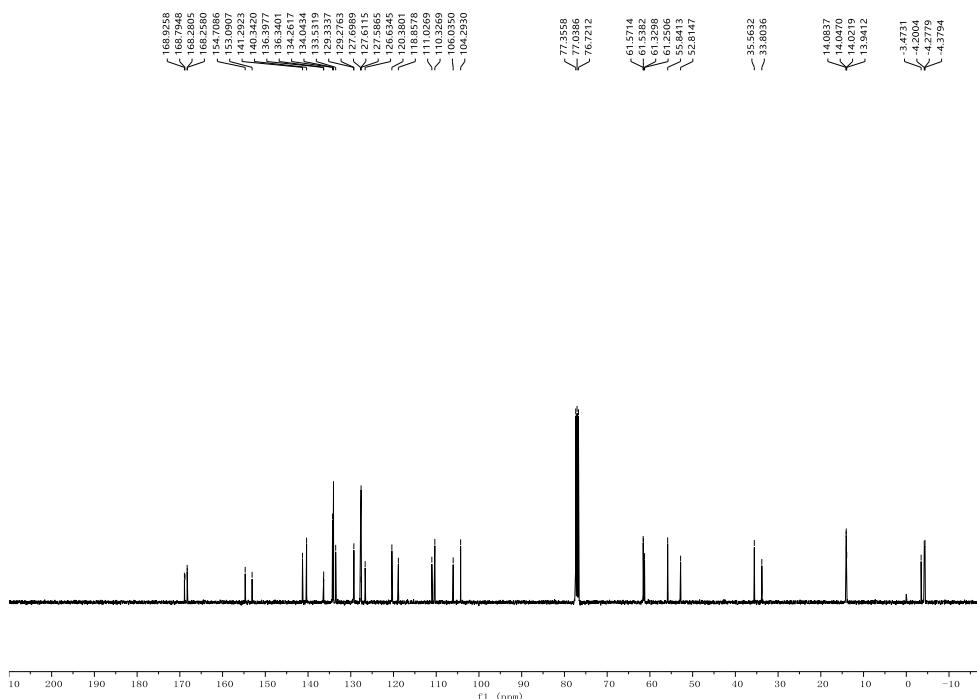
Diethyl (E)-2-(3-(dimethyl(phenyl)silyl)-3-(furan-2-yl)prop-1-en-1-yl)malonate (**4u**)



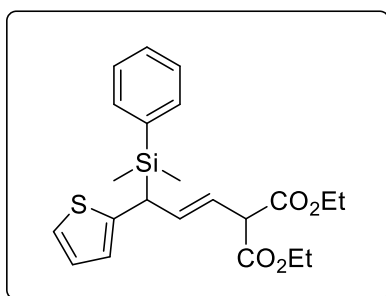
Following the Method E, the mixture of **4u** and **3u** were obtained as a light brownish oil (66.7 mg, 0.166 mmol, Yield: 83%). The 1,6 (**4u**) and 1,4 (**3u**) addition ratio was determined after purification to be approximately 60:40 by $^1\text{H NMR}$. $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.51 – 7.48 (m, $2\text{H} \times 0.40$), 7.39 – 7.27 (m, 5H), 7.25 (dd, $J = 1.9, 0.9$ Hz, $1\text{H} \times 0.60$), 6.32 (dd, $J = 3.3, 1.8$ Hz, $1\text{H} \times 0.40$), 6.24 (dd, $J = 3.2, 1.9$ Hz, $1\text{H} \times 0.60$), 6.14 (dd, $J = 15.8, 10.2$ Hz, $1\text{H} \times 0.40$), 6.07 – 6.02 (m, $1\text{H} \times 0.40$), 5.82 – 5.75 (m, $2\text{H} \times 0.60$), 5.57 (ddd, $J = 15.4,$

9.0, 1.0 Hz, $1\text{H} \times 0.60$), 4.21 – 4.13 (m, $4\text{H} \times 0.60$), 4.07 (q, $J = 7.1$ Hz, $2\text{H} \times 0.40$), 3.97 (dd, $J = 9.0, 0.8$ Hz, $1\text{H} \times 0.60$), 3.92 (q, $J = 7.1$ Hz, $2\text{H} \times 0.40$), 3.48 (d, $J = 8.8$ Hz, $1\text{H} \times 0.40$), 3.33 (d, $J = 9.4$ Hz, $1\text{H} \times 0.60$), 2.68 (dd, $J = 10.2, 8.8$ Hz, $1\text{H} \times 0.40$), 1.26 (t, $J = 5.1$ Hz, $3\text{H} \times 0.60$), 1.24 (t, $J = 5.1$ Hz, $3\text{H} \times 0.60$), 1.16 – 1.13 (m, $6\text{H} \times 0.40$), 0.34 (s, $6\text{H} \times 0.40$), 0.29 (s, $6\text{H} \times 0.60$) ppm; $^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 168.93, 168.79, 168.28, 168.26, 154.71, 153.09, 141.29, 140.34, 136.40, 136.34, 134.26, 134.04, 133.53, 129.33, 129.28, 127.70, 127.61, 127.59, 126.63, 120.38, 118.86, 111.03, 110.33, 106.04, 104.29, 61.57, 61.54, 61.33, 61.25, 55.84, 52.81, 35.56, 33.80, 14.08, 14.05, 14.02, 13.94, -3.47, -4.20, -4.28, -4.38 ppm; HRMS (ESI): m/z Calcd. for $\text{C}_{22}\text{H}_{29}\text{O}_5\text{Si}$ $[\text{M}+\text{H}]^+$: 401.1779, found: 401.1771.

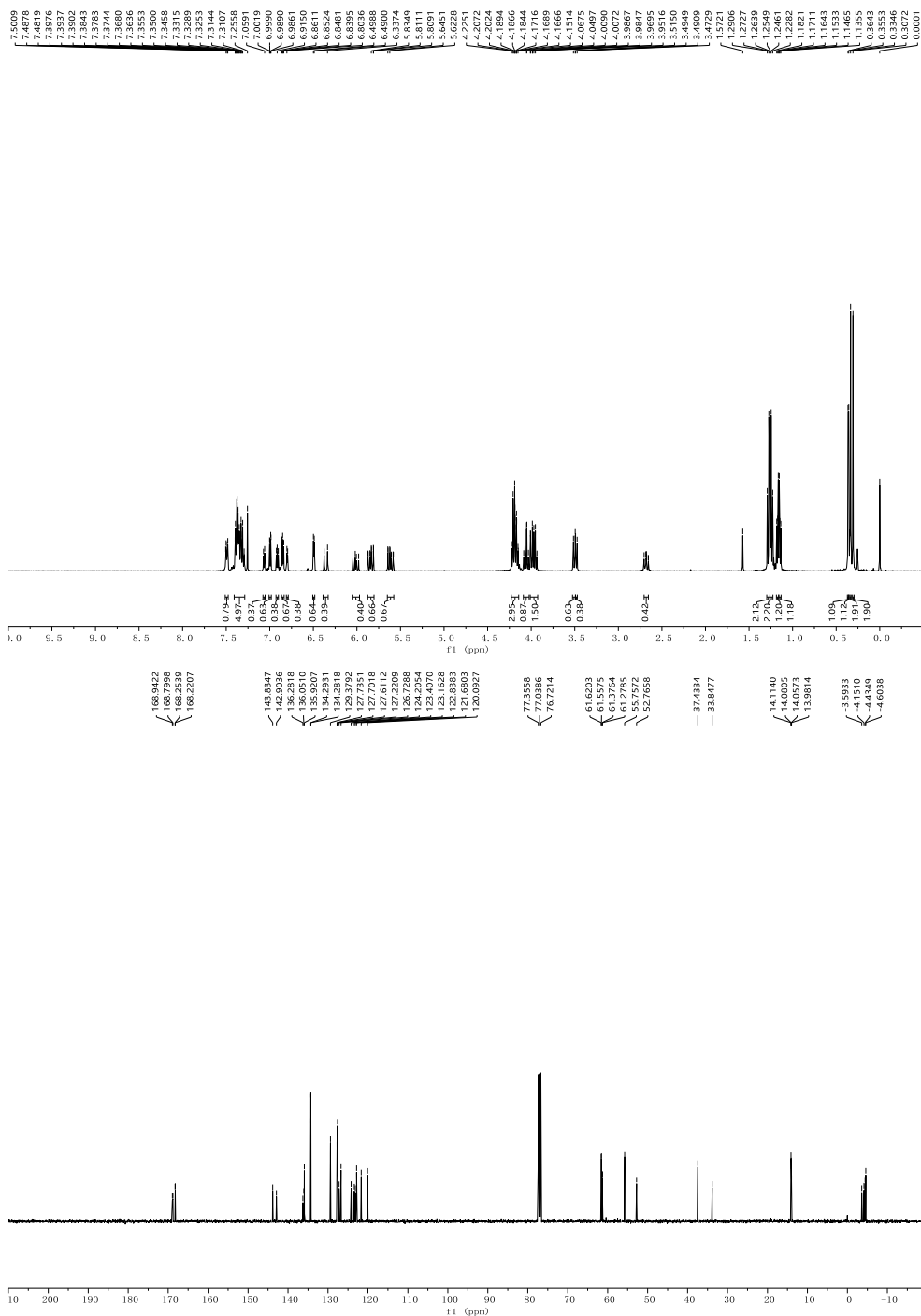




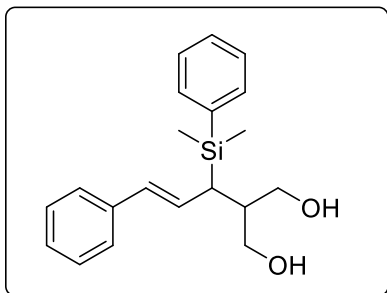
Diethyl (*E*)-2-(3-(dimethyl(phenyl)silyl)-3-(thiophen-2-yl)prop-1-en-1-yl)malonate (**4v**)



Following the Method E, the mixture of **4v** and **3v** were obtained as a brownish oil (66.4 mg, 0.159 mmol, Yield: 80%). The 1,6 (**4v**) and 1,4 (**3v**) addition ratio was determined after purification to be approximately 63:37 by ¹H NMR (400 MHz, CDCl₃): δ 7.51 – 7.48 (m, 2H × 0.37), 7.41 – 7.29 (m, 5H), 7.06 (d, *J* = 5.0 Hz, 1H × 0.37), 6.99 (dd, *J* = 5.2, 1.1 Hz, 1H × 0.63), 6.91 (dd, *J* = 5.1, 3.5 Hz, 1H × 0.37), 6.85 (dd, *J* = 5.2, 3.5 Hz, 1H × 0.63), 6.80 (d, *J* = 3.4 Hz, 1H × 0.37), 6.49 (d, *J* = 3.5 Hz, 1H × 0.63), 5.84 (ddd, *J* = 15.3, 9.5, 0.8 Hz, 1H × 0.63), 5.61 (ddd, *J* = 15.2, 8.9, 1.0 Hz, 1H × 0.63), 4.23 – 4.14 (m, 3H × 0.63), 4.06 (q, *J* = 7.1 Hz, 2H × 0.37), 4.01 – 3.93 (m, 3H), 3.50 (d, *J* = 8.1 Hz, 1H × 0.63), 3.48 (d, *J* = 7.1 Hz, 1H × 0.37), 2.68 (ddd, *J* = 10.6, 8.9, 0.9 Hz, 1H × 0.37), 1.28 (t, *J* = 3.5 Hz, 3H × 0.63), 1.24 (t, *J* = 3.5 Hz, 3H × 0.63), 1.17 (t, *J* = 4.4 Hz, 3H × 0.37), 1.14 (t, *J* = 4.4 Hz, 3H × 0.37), 0.36 (s, 3H × 0.63), 0.35 (s, 3H × 0.63), 0.33 (s, 3H × 0.37), 0.31 (s, 3H × 0.37) ppm; ¹³C NMR (101 MHz, CDCl₃): δ 168.94, 168.80, 168.25, 168.22, 143.83, 142.90, 136.28, 136.05, 135.92, 134.29, 134.28, 129.38, 127.74, 127.70, 127.61, 127.22, 126.73, 124.21, 123.41, 123.16, 122.84, 121.68, 120.09, 61.62, 61.56, 61.38, 61.28, 55.76, 52.77, 37.43, 33.85, 14.11, 14.08, 14.06, 13.98, -3.59, -4.15, -4.43, -4.60 ppm; HRMS (ESI): *m/z* Calcd. for C₂₂H₂₉O₄SSi [M+H]⁺: 417.155, found: 417.1549.

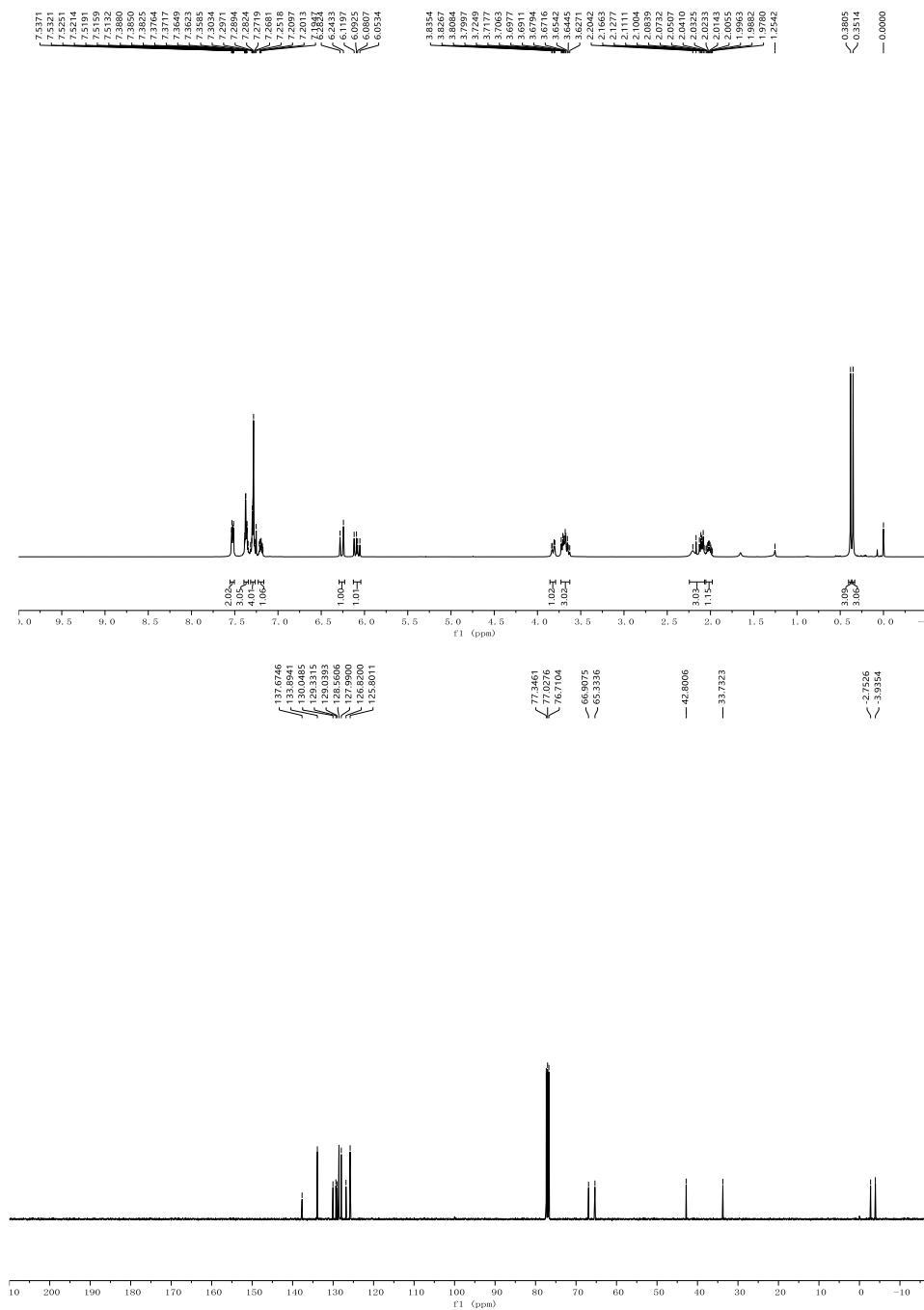


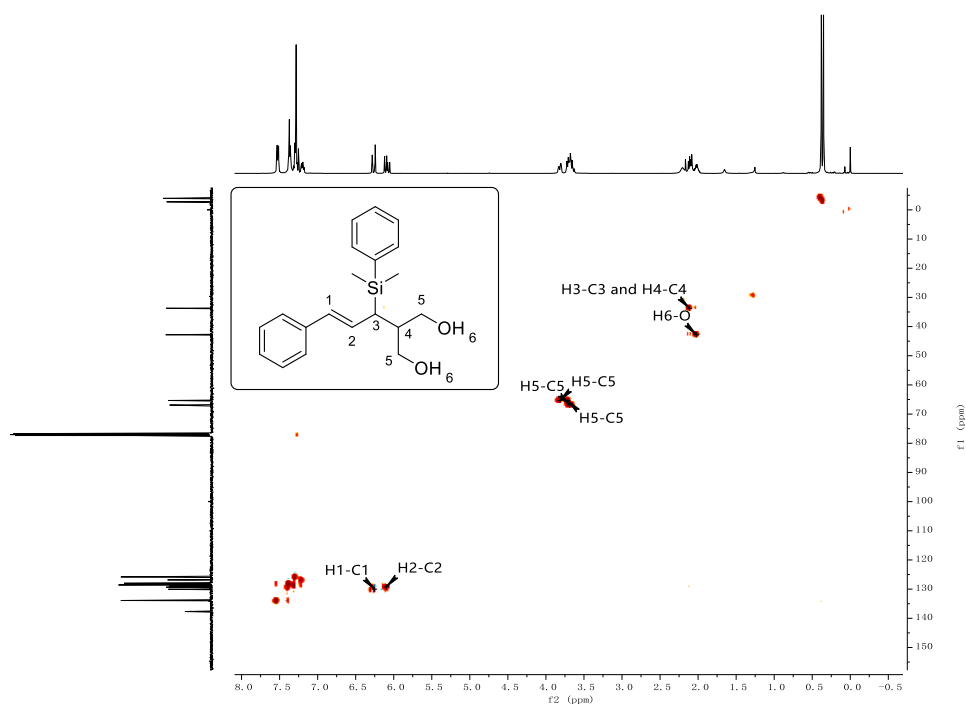
3.3 Characterization Data and Spectra of Synthetic Applications (*E*)-2-(1-(dimethyl(phenyl)silyl)-3-phenylallyl)propane-1,3-diol (**5**)



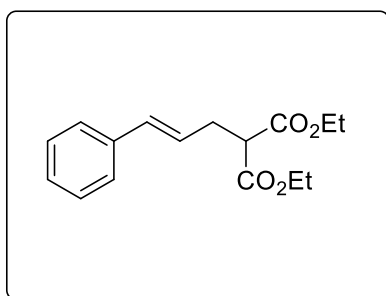
Following the Method F, **5** was obtained as a colorless oil (45.3 mg, 0.139 mmol, Yield: 70%). **¹H NMR (400 MHz, CDCl₃):** δ 7.55 – 7.50 (m, 2H), 7.39 – 7.34 (m, 3H), 7.31 – 7.28 (m, 4H), 7.21 – 7.17 (m, 1H), 6.26 (d, J = 15.6 Hz, 1H), 6.09 (dd, J = 15.6, 10.9 Hz, 1H), 3.82 (dd, J = 10.8, 3.5 Hz, 1H), 3.73 – 3.63 (m, 3H), 2.24 – 2.07 (m, 3H), 2.06 – 1.97 (m, 1H), 0.38 (s, 3H), 0.35 (s, 3H) ppm; **¹³C NMR (101 MHz, CDCl₃):** δ 137.67, 133.89, 130.05, 129.33, 129.04, 128.56, 127.99, 126.82, 125.80, 66.91, 65.33, 42.80, 33.73, -2.75, -3.94 ppm; **HRMS**

(ESI): m/z Calcd. for C₂₀H₂₇O₂Si [M+H]⁺: 327.1775, found: 327.1768.

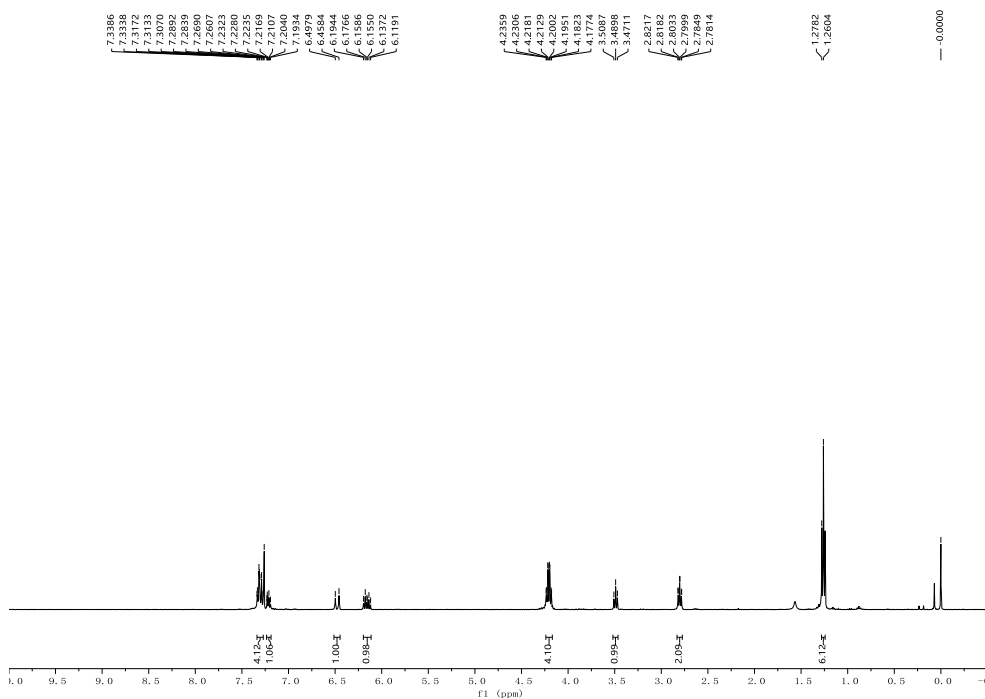


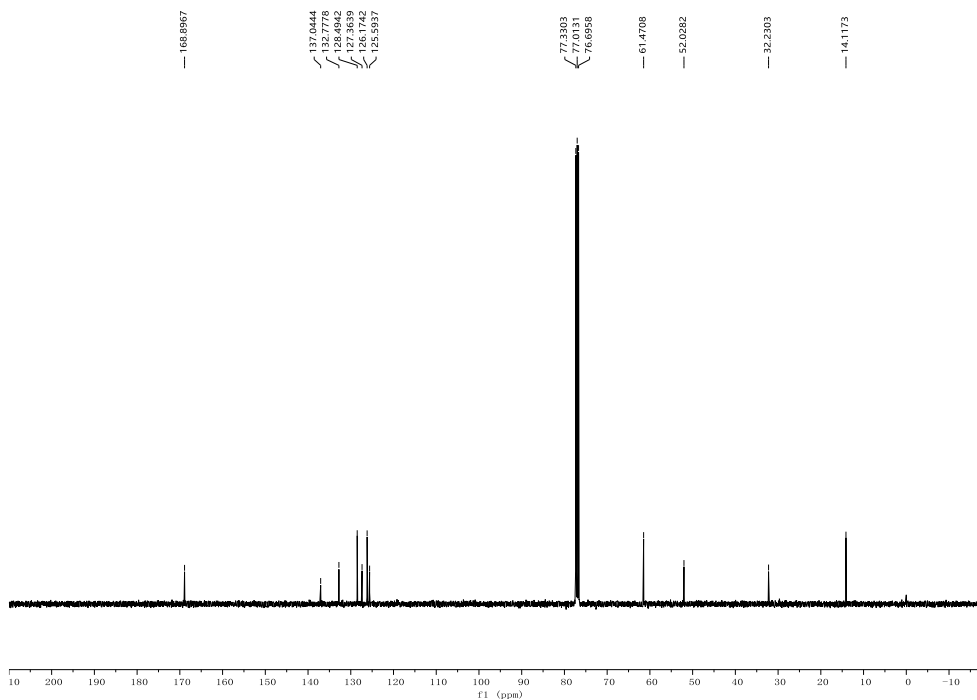


Diethyl 2-cinnamylmalonate (**6**)

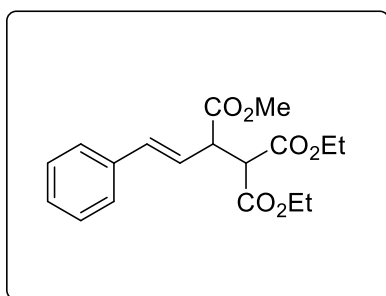


Following the Method G, **6** was obtained as a colorless oil (18.0 mg, 0.065 mmol, 65% yield). $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.34 – 7.27 (m, 4H), 7.24 – 7.19 (m, 1H), 6.48 (d, $J = 15.8$ Hz, 1H), 6.19 – 6.11 (m, 1H), 4.23 – 4.17 (m, 4H), 3.49 (t, $J = 7.5$ Hz, 1H), 2.82 – 2.78 (m, 2H), 1.27 – 1.24 (m, 6H) ppm; $^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 168.90, 137.04, 132.78, 128.49, 127.36, 126.17, 125.59, 61.47, 52.03, 32.23, 14.12 ppm; **HRMS (ESI)**: m/z Calcd. for $\text{C}_{16}\text{H}_{21}\text{O}_4$ $[\text{M}+\text{H}]^+$: 277.1434, found: 277.1436.



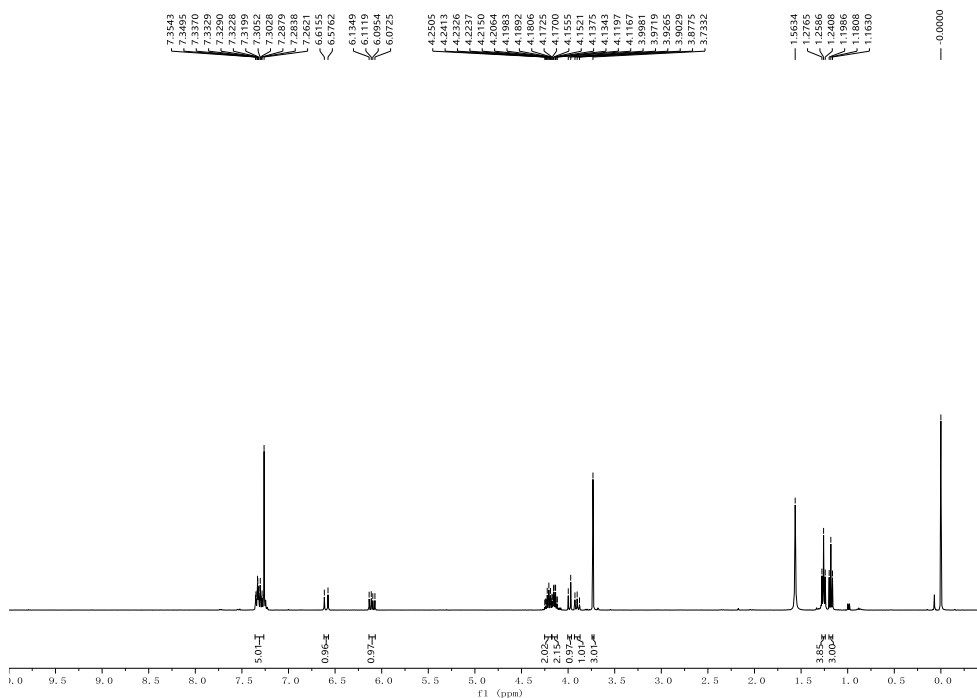


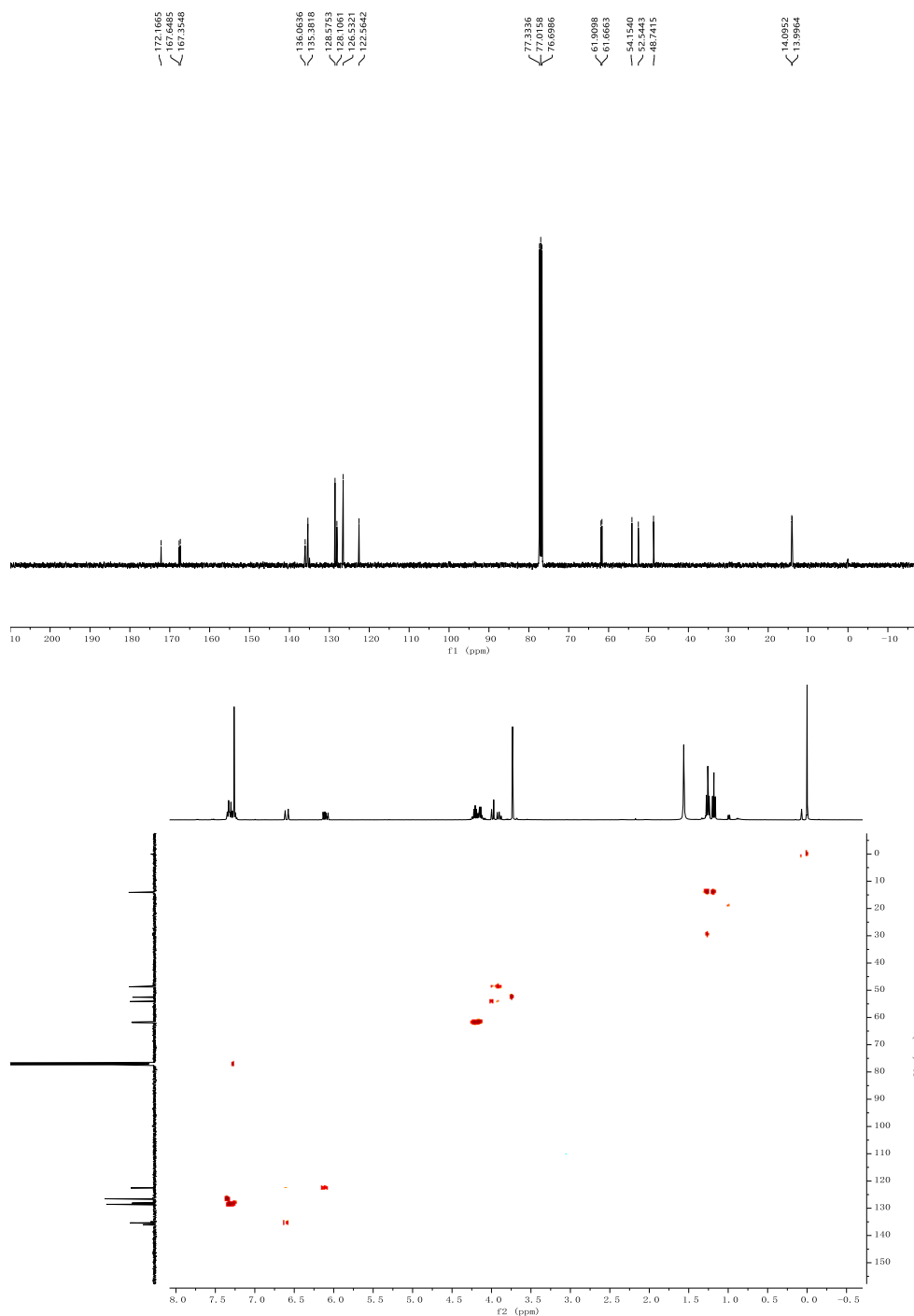
1,1-diethyl 2-methyl (*E*)-4-phenylbut-3-ene-1,1,2-tricarboxylate (7)



Following the Method H, **7** was obtained as a colorless oil (39.4 mg, 0.118 mmol, Yield: 58%). ¹H NMR (400 MHz, CDCl₃): δ 7.36 – 7.27 (m, 5H), 6.60 (d, *J* = 15.7 Hz, 1H), 6.10 (dd, *J* = 15.8, 9.2 Hz, 1H), 4.25 – 4.18 (m, 2H), 4.17 – 4.11 (m, 2H), 3.99 (d, *J* = 10.5 Hz, 1H), 3.93 – 3.87 (m, 1H), 3.73 (s, 3H), 1.26 (t, *J* = 7.1 Hz, 4H), 1.18 (t, *J* = 7.1 Hz, 3H) ppm; ¹³C NMR (101 MHz, CDCl₃): δ 172.17, 167.65, 167.35, 136.06, 135.38, 128.58, 128.11, 126.53, 122.56, 61.91, 61.67, 54.15, 52.54, 48.74, 14.10, 14.00 ppm; HRMS (ESI): *m/z* Calcd. for

C₁₈H₂₃O₆ [M+H]⁺: 335.1489, found: 335.1482.





5. References

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