
Supporting information for

***anti*-Hydroarylation of Activated Internal Alkynes: Merging Pd- and Energy Transfer Catalysis**

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1. General methods.

Dichloromethane, toluene, tetrahydrofuran, and acetonitrile were taken from a PureSolv MD purification system. Palladium (II) acetate, 1,2-(diphenylphosphino)ethane and boronic acids **2a-q** were purchased from commercial sources and used as received. Alkynes **1a**, **1b**, **4a**, **6a**, and **8a** were purchased from commercial sources and used as received. Deuteration of phenylboronic acid was carried out as described in the literature.¹ All reactions were carried out in anhydrous solvents and under argon atmosphere, unless otherwise noted. Column liquid chromatographies were performed on silica gel (230-400 mesh ASTM). TLC analysis was performed on 0.2 mm aluminium based plates (60 230-400 mesh). ¹H, ¹³C, ³¹P, and ¹⁹F NMR spectra were recorded in CDCl₃ solutions at 25 °C on AV-300, AVII-300 y AVIII-HD-300 (300, 75, 121, and 282 MHz, respectively) spectrometers (δ , ppm; J, Hz). ¹H and ¹³C NMR spectra were referenced using the solvent signal as internal standard. All ³¹P NMR spectra were referenced using H₃PO₄ (aq sol. 80 %) as internal standard. HRMS electron ionization (EI+), electrospray ionization (ESI+) and FAB mass spectra were recorded using an MicroToF Q, API-QToF ESI with a mass range from 20 to 3000 m/z and mass resolution 15000 (FWHM). Melting points were determined in open-end capillary tubes.

A custom-made photoreactor setup was used for the photocatalytic reactions developed by *Servicios Generales de Apoyo a la Investigación Experimental* (SEGAINVEX) at *Universidad Autónoma de Madrid* (UAM). Photochemical reactions were carried out using borosilicate glass vials. For reactions at room temperature, the vial was placed inside the fitted well in which irradiation takes place at 465 nm using 350 mW single LEDs located 1 cm beneath the base of the vial (see Figure S1A). Reaction temperature is kept at 20-25 °C using a recirculating chiller. For the reactions at higher temperatures, the vial was placed in a silicon oil bath at the required temperature and irradiated with a 34 W blue LEDs Kessil lamp (PR160L-440nm) located at 10 cm from the reaction vessel (see Figure S1B).

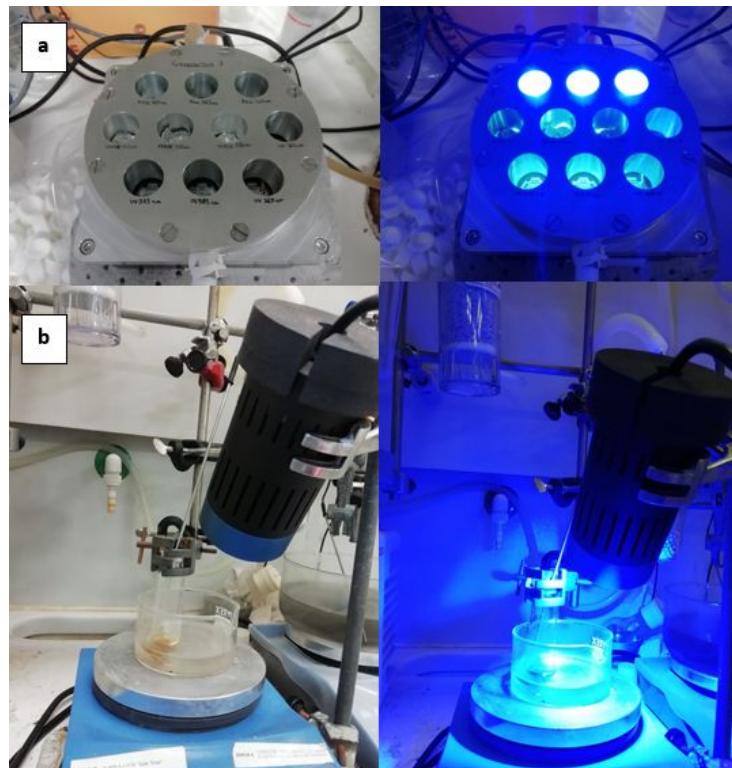
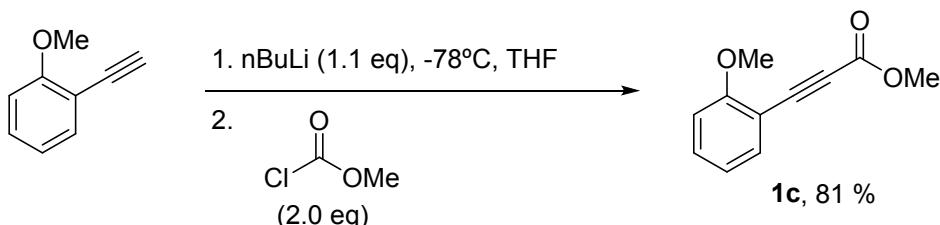


Figure S1. Experimental setup for reactions performed at (a) room temperature and (b) 60° or 80 °C using an oil bath.

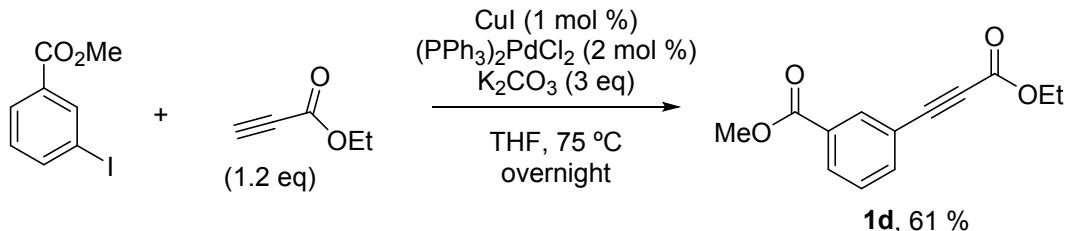
2. Synthesis of starting materials

Synthesis of methyl 3-(2-methoxyphenyl)propiolate (1c):



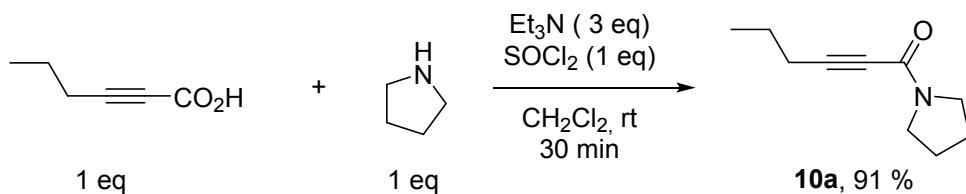
Substrate **1c** was synthesized according to the literature.² To a flame-dried round-bottom flask filled with argon were added methyl 1-ethynyl-2-methoxybenzene (1.29 mL, 10.0 mmol) and dry THF (30 mL). The mixture was then stirred at -78 °C for 5 min. After that ⁿBuLi (4.4 mL, 11.0 mmol, 2.5 M) was added dropwise via syringe. The reaction mixture was stirred at -78 °C for 30 min, followed by dropwise addition of methyl chloroformate (1.54 mL, 20.0 mmol) in THF (5.0 mL). The mixture was stirred at the same temperature for 1 h. When the raw material reacted completely, the reaction was quenched with saturated NH₄Cl aqueous. The layers were separated and extracted with ethyl acetate (20 mL×3). The combined organic layers were dried over anhydrous Na₂SO₄, filtered and concentrated by vacuo. The crude product was purified by column chromatograph over silica gel (cyclohexane: ethyl acetate=10:1) to afford the titled product as an oil (1.54 g, 81 % yield). ¹H NMR (300 MHz, CDCl₃): δ 7.47 (dd, J = 7.6, 1.7 Hz, 1H), 7.40 – 7.33 (m, 1H), 6.93 – 6.83 (m, 2H), 3.84 (s, 3H), 3.79 (s, 3H).

Synthesis of ethyl 3-(3-ethoxy-3-oxoprop-1-yn-1-yl)benzoate (1d):



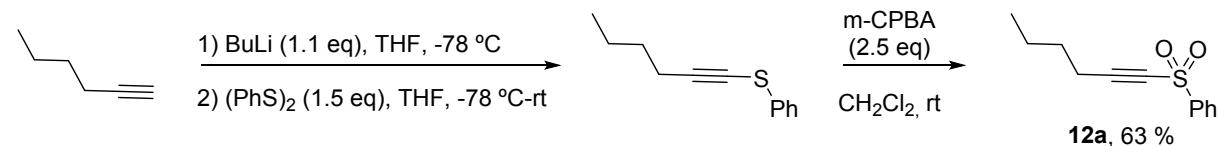
Following the procedure described in the literature,³ to a mixture of methyl-3-iodobenzoate (1.31 g, 5 mmol), ethyl propiolate (0.61 mL, 6 mmol) and (PPh₃)₂PdCl₂ (70 mg, 0.1 mmol) in THF (20 mL), K₂CO₃ (2.07 g, 15 mmol) was added. The reaction was stirred for 10 min at the room temperature, then CuI (9.52 mg, 0.05 mmol) was added slowly. Finally, the reaction was stirred overnight at 75 °C under a nitrogen atmosphere. Then the solution was filtered, the filtrate was concentrated under reduced pressure and the residue was purified by flash silica gel chromatography to give the titled product as a white solid (708 mg, 61% yield). ¹H NMR (300 MHz, CDCl₃): δ 8.25 (s, 1H), 8.10 (d, J = 7.8 Hz, 1H), 7.74 (d, J = 7.6 Hz, 1H), 7.46 (t, J = 7.8 Hz, 1H), 4.30 (q, J = 7.1 Hz, 2H), 3.92 (s, 3H), 1.35 (t, J = 7.1 Hz, 3H).

Synthesis of 1-(pyrrolidin-1-yl)hex-2-yn-1-one (10a):



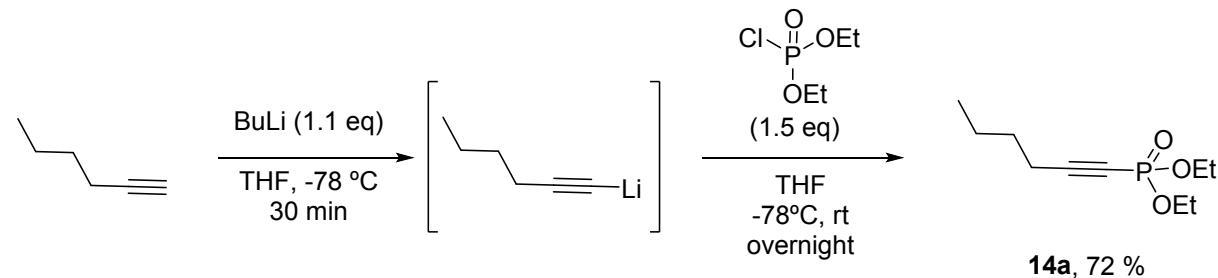
Following a modified procedure described in the literature,⁴ 2-hexynoic acid (0.305 mL, 2.7 mmol) was added to a solution of pyrrolidine (0.223 mL, 2.7 mmol) and Et₃N (1.12 mL, 8.1 mmol) in CH₂Cl₂ (50 mL). After that SOCl₂ (0.2 mL, 2.7 mmol) was added dropwise at 0 °C and the mixture was allowed to stir for 30 min at room temperature. The solvent was removed from vacuo to eliminate the unreacted SOCl₂, and the residue was dissolved in dichloromethane and washed with HCl 1 M. The organic phase was then washed with a solution of NaOH 1 M and finally with water until the pH becomes neutral. The organic phase was dried over MgSO₄, concentrated in the rotovap and the residue was purified by flash column chromatography to afford 406 mg (91 % yield) of the titled compound as an oil. ¹H-NMR (300 MHz, CDCl₃): δ 3.55 (t, *J* = 6.5 Hz, 1H), 3.39 (t, *J* = 6.2 Hz, 2H), 2.26 (t, *J* = 7.0 Hz, 2H), 1.92 – 1.74 (m, 4H), 1.63 – 1.41 (m, 2H), 0.95 (t, *J* = 7.4 Hz, 3H). ¹³C-NMR (75 MHz, CDCl₃): δ 152.9, 91.3, 75.3, 48.1, 45.1, 25.3, 24.7, 21.4, 20.8, 13.5. HRMS (EI+) m/z: [M]⁺ calcd for C₁₀H₁₅NO 165.1154; found 165.1159.

Synthesis of (hex-1-yn-1-ylsulfonyl)benzene (12a):



Following a modified procedure described in the literature,⁶ to a solution of 1-hexyne (0.7 mL, 6.1 mmol) in THF (20 mL) cooled to -78 °C was added ⁿBuLi (2.44 mL, 6.1 mmol, 2.5 M in hexane) dropwise. The resulting solution was stirred for 1 h and then warmed to rt, to which was added a premixed solution of phenyl disulfide (1.3 g, 6.1 mmol). The reaction was monitored by TLC. Upon completion, aqueous NH₄Cl was added to quench the reaction. The aqueous layer was extracted with hexanes (3 x 15 mL). The combined extracts were washed with brine and dried over MgSO₄. After rotary evaporation, the residue was further condensed under high vacuum to remove methyl phenyl sulfide and then purified by flash column chromatography (eluent: hexanes) to afford the corresponding alkynyl sulfide. 2.50 equiv. of *m*-CPBA was added at 0 °C to a solution of the sulfide (5 mmol) in dichloromethane (30 mL). The reaction mixture was stirred for 1 h at 0 °C and then for 12 h at room temperature. After reaction, the reaction mixture was washed with saturated aqueous NaHCO₃, dried over MgSO₄, and concentrated. The residue was purified by silica gel column chromatograph (cyclohexane/ethyl acetate, 6:1) to afford the desired sulfone 12a as an oil (854 mg, 63 % yield). ¹H-NMR (300 MHz, CDCl₃): δ 8.02 – 7.96 (m, 2H), 7.68 – 7.63 (m, 1H), 7.60 – 7.53 (m, 2H), 2.36 (t, *J* = 7.2 Hz, 2H), 1.53 (p, *J* = 7.2 Hz, 2H), 1.36 (h, *J* = 7.4 Hz, 2H), 0.88 (t, *J* = 7.4 Hz, 3H).

Synthesis of diethyl hex-1-yn-1-ylphosphonate (14a):



Following the procedure described in the literature,⁵ 1-hexyne (0.7 mL, 6.1 mmol) was placed in a 50 mL Schlenck tube under argon atmosphere and anhydrous THF was added (6 mL). After that a solution of BuLi in toluene (2.7 mL, 6.71 mmol) was added dropwise at -78 °C and was allowed to stir for 30 min. Finally, a solution of diethylchlorophosphosphate (1.33 mL, 9.15 mmol) in THF (5 mL) was added via syringe at -78 °C and the solution was stirred at this temperature for 1 h, followed by stirring at room temperature for overnight. The reaction was quenched with a saturated colution of NH₄Cl (15 mL) and the organic phase was extracted with water (15 mL), brine (15 mL) dried over MgSO₄ and the solvent was removed from vacuo. The residue was purified by flash column chromatography (cyclohexane:ethyl

acetate, 2:1) to afford 958 mg (72 % yield) of the titled compound as an oil. **¹H-NMR** (300 MHz, CDCl₃): δ 4.13 (m, 4H), 2.33 (td, *J* = 7.0, 4.4 Hz, 2H), 1.64 – 1.49 (m, 2H), 1.47-1.39 (m, 2H), 1.35 (t, *J* = 7.1 Hz, 6H), 0.91 (t, *J* = 7.2 Hz, 3H).

3. Pd-catalyzed hydroarylation of activated internal alkynes

3.1. Dual Pd/Ir-catalyzed (*Z*)-stereoselective hydroarylation.

3.1.1 General procedure for the Pd/Ir-Catalyzed *Z*-stereoselective hydroarylation of activated internal alkynes.

Formation of the pre-catalyst solution: $\text{Pd}(\text{OAc})_2$ (2.25 mg, 0.01 mmol) and dppe (3.98 mg, 0.01 mmol) were placed in a 5 mL vial provided with a magnetic stir and a septum. THF (0.5 mL) was added under argon atmosphere, and the mixture was stirred for 10 min to form a turbid orange mixture. Then, AcOH (2.3 μL , 0.04 mmol) was added and the solution quickly turned transparent, after which the mixture was allowed to stir for another 10 minutes at room temperature (see Figure S2).

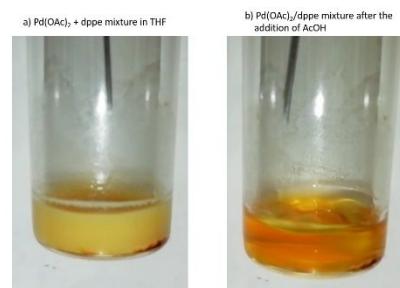


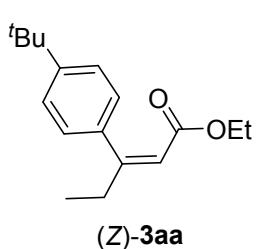
Figure S2. Formation of the pre-catalyst system.

Reaction set up: The solution containing the pre-catalyst mixture was added to a mixture of alkyne (0.2 mmol), the boronic acid (0.4 mmol), and $\text{Ir}(\text{ppy})_3$ (1.3 mg, 0.002 mmol) dissolved in THF (1 mL), under argon atmosphere. The mixture was allowed to stir at the temperature indicated in each case for 24 h under blue light irradiation (see Figure S1). Then, the reaction was diluted with 10 mL of AcOEt and washed with a 0.1 M solution of NaHCO_3 in brine (3x10 mL), and water until the pH becomes neutral. The organic phase was dried with Na_2SO_4 and concentrated in vacuo. The resulting residue was purified by column chromatography.

Notes:

- 1) It is important to pre-form the pre-catalyst to achieve complete conversions. A solution of the pre-catalyst must be added to the mixture of both alkyne and boronic acid in THF. **If the alkyne is not present in the reaction media, a black solution will form and the reproducibility will be lost.**
- 2) For the cyclization processes, water (0.15 mL) is added to the reaction vessel after the addition of the pre-catalyst system.
- 3) Cs_2CO_3 (130 mg, 0.4 mmol) is added when 2-aminophenylboronic acid hydrochloride substrates are used (indicated in each case).

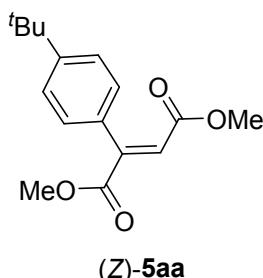
Ethyl (*Z*)-3-(4-(*tert*-butyl)phenyl)pent-2-enoate ((*Z*)-3aa):



Following the general procedure, the reaction between ethyl 2-pentynoate (26.4 μL , 0.2 mmol), 4-*tert*-butylphenyl boronic acid (71.2 mg, 0.4 mmol), $\text{Pd}(\text{OAc})_2$ (2.24 mg, 0.01 mmol), dppe (3.98 mg, 0.01 mmol), $\text{Ir}(\text{ppy})_3$ (1.3 mg, 0.002 mmol), and AcOH (2.3 μL , 0.04 mmol) in THF (1.5 mL) under blue light irradiation afforded the titled compound (49 mg, 92 % yield) as a colorless oil after flash column chromatography (cyclohexane:ethyl acetate, 20:1). **Note: the reaction at 1 mmol scale using ethyl 2-pentynoate (0.132 mL, 1 mmol), 4-*tert*-butylphenyl boronic acid (356 mg, 2 mmol), $\text{Pd}(\text{OAc})_2$ (11.2 mg, 0.05 mmol), dppe (19.9 mg, 0.05 mmol), $\text{Ir}(\text{ppy})_3$ (6.5 mg, 0.01 mmol), and AcOH (11.5 μL , 0.2 mmol) in THF (7.5 mL) under blue light irradiation afforded the titled compound as a colorless oil without a significant loss of reactivity (232 mg, 89 % yield).** $^1\text{H-NMR}$ (300 MHz, CDCl_3): δ 7.36 (d, $J = 8.5$ Hz, 2H), 7.11 (d, $J = 8.5$ Hz, 2H), 5.85 (s, 1H), 3.99 (q, $J = 7.1$ Hz, 2H), 2.46 (qd, $J = 7.3, 1.2$ Hz, 2H), 1.33 (s, 9H), 1.06 (t, $J = 7.4$ Hz, 3H), 1.05 (t, $J = 7.1$ Hz, 3H). $^{13}\text{C-NMR}$ (75 MHz, CDCl_3): δ 166.6, 161.2, 150.5,

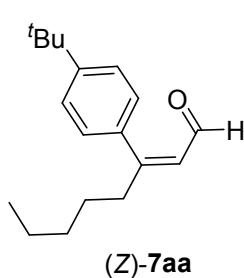
137.4, 126.9, 124.8, 116.1, 59.8, 34.7, 33.4, 31.5, 14.0, 12.4. **HRMS** (EI+) m/z: [M]⁺ calcd for C₁₇H₂₄O₂ 260.1776; found 260.1764.

Dimethyl 2-(4-(*tert*-butyl)phenyl)fumarate ((Z)-5aa):



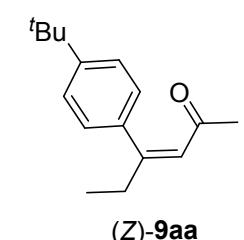
Following the general procedure, the reaction between dimethyl acetylendicarboxylate (24.6 μ L, 0.2 mmol), 4-*tert*-butylphenyl boronic acid (71.2 mg, 0.4 mmol), Pd(OAc)₂ (2.24 mg, 0.01 mmol), dppe (3.98 mg, 0.01 mmol), Ir(ppy)₃ (1.3 mg, 0.002 mmol), and AcOH (2.3 μ L, 0.04 mmol) in THF (1.5 mL) under blue light irradiation afforded the titled compound (49.7 mg, 90 % yield) as an oil after flash column chromatography (cyclohexane:ethyl acetate, 20:1). **¹H-NMR** (300 MHz, CDCl₃): δ 7.38 (d, *J* = 8.6 Hz, 2H), 7.19 (d, *J* = 8.6 Hz, 2H), 6.97 (s, 1H), 3.81 (s, 3H), 3.62 (s, 3H), 1.33 (s, 9H). **¹³C-NMR** (75 MHz, CDCl₃): δ 167.2, 165.9, 151.8, 144.4, 130.7, 128.8, 128.1, 124.9, 53.0, 51.9, 34.8, 31.4. **HRMS** (EI+) m/z: [M]⁺ calcd for C₁₆H₂₀O₄ 276.1362; found 276.1352.

(Z)-3-(4-(*tert*-butyl)phenyl)oct-2-enal ((Z)-7aa):



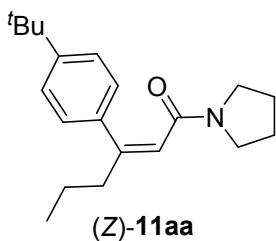
Following the general procedure, the reaction between 2-octynal (28.5 μ L, 0.2 mmol), 4-*tert*-butylphenyl boronic acid (71.2 mg, 0.4 mmol), Pd(OAc)₂ (2.24 mg, 0.01 mmol), dppe (3.98 mg, 0.01 mmol), Ir(ppy)₃ (1.3 mg, 0.002 mmol), and AcOH (2.3 μ L, 0.04 mmol) in THF (1.5 mL) under blue light irradiation afforded the titled compound (44.4 mg, 86 % yield) as a yellow oil after flash column chromatography (cyclohexane:ethyl acetate, 100:1). **¹H-NMR** (300 MHz, CDCl₃): δ 9.47 (d, *J* = 8.1 Hz, 1H), 7.41 (d, *J* = 8.2 Hz, 2H), 7.20 (d, *J* = 8.2 Hz, 2H), 6.09 (d, *J* = 8.1 Hz, 1H), 2.57 (t, *J* = 7.5 Hz, 2H), 1.35 (s, 9H), 1.33 – 1.22 (m, 6H), 0.86 (t, *J* = 6.9 Hz, 3H). **¹³C-NMR** (75 MHz, CDCl₃): δ 194.1, 167.0, 152.4, 135.0, 128.6, 128.4, 124, 39.7, 34.9, 31.5, 31.4, 27.4, 22.5, 14.1. **HRMS** (EI+) m/z: [M]⁺ calcd for C₁₈H₂₆O 258.1984; found 258.1978.

(Z)-4-(4-(*tert*-butyl)phenyl)hex-3-en-2-one ((Z)-9aa):



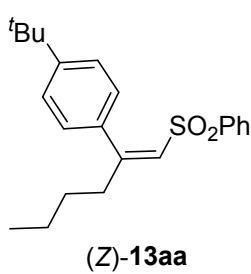
Following the general procedure, the reaction between 3-hexyn-2-one (21.4 μ L, 0.2 mmol), 4-*tert*-butylphenyl boronic acid (71.2 mg, 0.4 mmol), Pd(OAc)₂ (2.24 mg, 0.01 mmol), dppe (3.98 mg, 0.01 mmol), Ir(ppy)₃ (1.3 mg, 0.002 mmol), and AcOH (2.3 μ L, 0.04 mmol) in THF (1.5 mL) under blue light irradiation afforded the titled compound (42.4 mg, 92 % yield) as an oil after flash column chromatography (cyclohexane:ethyl acetate, 30:1). **¹H-NMR** (300 MHz, CDCl₃): 7.37 (d, *J* = 8.1 Hz, 2H), 7.09 (d, *J* = 8.1 Hz, 2H), 6.05 (s, 1H), 2.46 (q, *J* = 7.4 Hz, 2H), 1.77 (s, 3H), 1.33 (s, 9H), 1.05 (t, *J* = 7.4 Hz, 3H). **¹³C-NMR** (75 MHz, CDCl₃): δ 201.2, 158.7, 151.5, 137.4, 127.4, 127.1, 125.4, 34.8, 33.5, 31.5, 30.30, 12.5. **HRMS** (EI+) m/z: [M]⁺ calcd for C₁₆H₂₂O 230.1671; found 230.1680.

(Z)-3-(4-(*tert*-butyl)phenyl)-1-(pyrrolidin-1-yl)hex-2-en-1-one ((Z)-11aa):



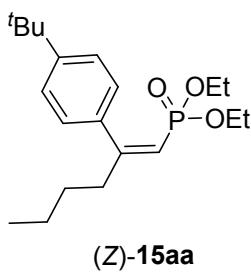
Following the general procedure, the reaction between 1-(pyrrolidin-1-yl)hex-2-yn-1-one **10a** (33 mg, 0.2 mmol), 4-*tert*-butylphenyl boronic acid (71.2 mg, 0.4 mmol), Pd(OAc)₂ (2.24 mg, 0.01 mmol), dppe (3.98 mg, 0.01 mmol), Ir(ppy)₃ (1.3 mg, 0.002 mmol), and AcOH (2.3 μ L, 0.04 mmol) in THF (1.5 mL) under blue light irradiation afforded the titled compound (52.7 mg, 88 % yield) as an oil after flash column chromatography (cyclohexane:ethyl acetate, 2:1). **¹H-NMR** (300 MHz, CDCl₃): δ 7.29 (d, *J* = 8.6 Hz, 2H), 7.20 (d, *J* = 8.6 Hz, 2H), 5.90 (s, 1H), 3.31 (t, *J* = 6.7 Hz, 2H), 3.01 (t, *J* = 6.4 Hz, 2H), 2.48 – 2.35 (m, 2H), 1.69 – 1.52 (m, 4H), 1.43 (m, 2H), 1.28 (s, 9H), 0.90 (t, *J* = 7.3 Hz, 3H). **¹³C-NMR** (75 MHz, CDCl₃): δ 167.5, 150.8, 147.9, 136.8, 127.2, 125.0, 121.0, 47.0, 45.2, 40.1, 34.6, 31.4, 25.8, 24.3, 21.4, 13.9. **HRMS** (EI+) m/z: [M]⁺ calcd for C₁₆H₂₂O 299.2249; found 299.2257.

(Z)-1-(*tert*-butyl)-4-(1-(phenylsulfonyl)hex-1-en-2-yl)benzene ((Z)-13aa):



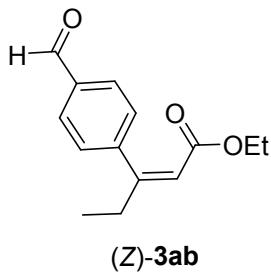
Following the general procedure, the reaction between (hex-1-yn-1-ylsulfonyl)benzene **12a** (44.5 mg, 0.2 mmol), 4-*tert*-butylphenyl boronic acid (71.2 mg, 0.4 mmol), Pd(OAc)₂ (2.24 mg, 0.01 mmol), dppe (3.98 mg, 0.01 mmol), Ir(ppy)₃ (1.3 mg, 0.002 mmol), and AcOH (2.3 μ L, 0.04 mmol) in THF (1.5 mL) under blue light irradiation afforded the titled compound (66.3 mg, 93 % yield) as an oil after flash column chromatography (cyclohexane:ethyl acetate, 6:1). **¹H-NMR** (300 MHz, CDCl₃): δ 7.46 – 7.36 (m, 3H), 7.25 – 7.18 (m, 4H), 6.90 (d, J = 8.5 Hz, 2H), 6.54 (t, J = 1.3 Hz, 1H), 2.36 (t, J = 6.8 Hz, 2H), 1.40 – 1.23 (m, 13H), 0.86 (t, J = 7.1 Hz, 3H). **¹³C-NMR** (75 MHz, CDCl₃): δ 159.3, 151.5, 141.6, 133.7, 132.5, 129.1, 128.4, 127.7, 127.6, 124.8, 40.6, 34.7, 31.5, 29.3, 22.2, 13.9. **HRMS** (APCI+) m/z: [M]⁺ calcd for C₂₂H₂₉O₂S 357.1883; found 357.1889.

Diethyl (Z)-(2-(4-(*Tert*-butyl)phenyl)hex-1-en-1-yl)phosphonate ((Z)-15aa):



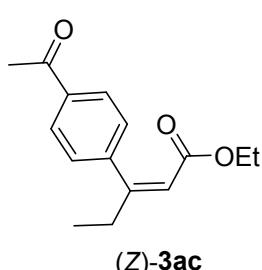
Following the general procedure, the reaction between diethyl hex-1-yn-1-ylphosphonate **14a** (43.6 mg, 0.2 mmol), 4-*tert*-butylphenyl boronic acid (71.2 mg, 0.4 mmol), Pd(OAc)₂ (2.24 mg, 0.01 mmol), dppe (3.98 mg, 0.01 mmol), Ir(ppy)₃ (1.3 mg, 0.002 mmol), and AcOH (2.3 μ L, 0.04 mmol) in THF (1.5 mL) under blue light irradiation afforded the titled compound (60.6 mg, 86 % yield) as an oil after flash column chromatography (cyclohexane:ethyl acetate, 1:1). **¹H-NMR** (300 MHz, CDCl₃): δ 7.35 (d, J = 8.6 Hz, 2H), 7.27 (d, J = 8.6 Hz, 2H), 5.65 (dt, J = 17.8, 1.2 Hz, 1H), 3.87 – 3.61 (m, 4H), 2.46 (t, J = 6.9 Hz, 2H), 1.43 – 1.24 (m, 4H), 1.30 (s, 9H), 1.02 (t, J = 7.1 Hz, 6H), 0.84 (d, J = 7.1 Hz, 3H). **¹³C-NMR** (75 MHz, CDCl₃): δ 163.4 (d, J = 4.0 Hz), 151.2, 137.2 (d, J = 7.9 Hz), 127.5 (d, J = 1.7 Hz), 124.8, 113.7 (d, J = 191.7 Hz), 61.3 (d, J = 6.0 Hz), 41.1 (d, J = 21.1 Hz), 34.8, 31.4, 29.8, 22.3, 16.1 (d, J = 6.9 Hz), 13.9. **³¹P NMR** (121 MHz, CDCl₃, H₃PO₄ as internal standard): 17.8 ppm. **HRMS** (EI+) m/z: [M]⁺ calcd for C₂₀H₃₃O₃P 352.2167; found 352.2163.

Ethyl (Z)-3-(4-formylphenyl)pent-2-enoate ((Z)-3ab):



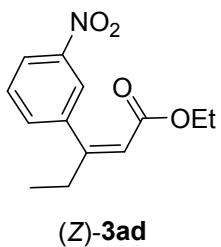
Following the general procedure, the reaction between ethyl 2-pentynoate (26.4 μ L, 0.2 mmol), 4-formylphenyl boronic acid (60 mg, 0.4 mmol), Pd(OAc)₂ (2.24 mg, 0.01 mmol), dppe (3.98 mg, 0.01 mmol), Ir(ppy)₃ (1.3 mg, 0.002 mmol), and AcOH (2.3 μ L, 0.04 mmol) in THF (1.5 mL) under blue light irradiation afforded the titled compound (41.3 mg, 89 % yield) as an oil after flash column chromatography (cyclohexane:ethyl acetate, 5:1). **¹H-NMR** (300 MHz, CDCl₃): δ 10.02 (s, 1H), 7.87 (d, J = 8.3 Hz, 2H), 7.31 (d, J = 8.3 Hz, 2H), 5.92 (t, J = 1.3 Hz, 1H), 3.98 (q, J = 7.1 Hz, 2H), 2.47 (qd, J = 7.4, 1.4 Hz, 2H), 1.07 (m, 6H). **¹³C-NMR** (75 MHz, CDCl₃): δ 192.0, 165.8, 160.0, 147.5, 135.5, 129.5, 127.9, 117.4, 60.1, 33.2, 14.1, 12.1. **HRMS** (EI+) m/z: [M]⁺ calcd for C₁₄H₁₆O₃ 232.1099; found 232.1105.

Ethyl (Z)-3-(4-acetylphenyl)pent-2-enoate ((Z)-3ac):



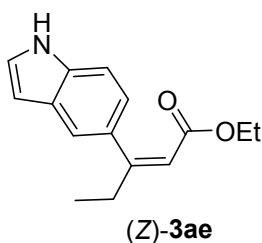
Following the general procedure, the reaction between ethyl 2-pentynoate (26.4 μ L, 0.2 mmol), 4-acetylphenyl boronic acid (65.6 mg, 0.4 mmol), Pd(OAc)₂ (2.24 mg, 0.01 mmol), dppe (3.98 mg, 0.01 mmol), Ir(ppy)₃ (1.3 mg, 0.002 mmol), and AcOH (2.3 μ L, 0.04 mmol) in THF (1.5 mL) under blue light irradiation afforded the titled compound (45.8 mg, 93 % yield) as an oil after flash column chromatography (cyclohexane:ethyl acetate, 4:1). **¹H-NMR** (300 MHz, CDCl₃): δ 7.95 (d, J = 8.1 Hz, 2H), 7.24 (d, J = 8.2 Hz, 2H), 5.91 (t, J = 1.4 Hz, 1H), 3.99 (q, J = 7.1 Hz, 2H), 2.60 (s, 3H), 2.45 (qd, J = 7.4, 1.4 Hz, 2H), 1.07 (m, 6H). **¹³C-NMR** (75 MHz, CDCl₃): δ 197.8, 165.9, 160.3, 145.9, 136.2, 128.1, 127.4, 117.1, 60.1, 33.3, 26.7, 14.1, 12.1. **HRMS** (EI+) m/z: [M]⁺ calcd for C₁₅H₁₈O₃ 246.1256; found 246.1251.

Ethyl (Z)-3-(3-nitrophenyl)pent-2-enoate ((Z)-3ad):



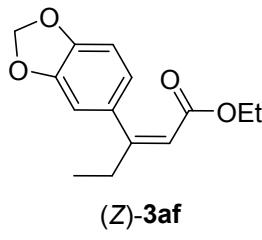
Following the general procedure, the reaction between ethyl 2-pentyneoate (26.4 μ L, 0.2 mmol), 3-nitrophenyl boronic acid (66.8 mg, 0.4 mmol), Pd(OAc)₂ (2.24 mg, 0.01 mmol), dppe (3.98 mg, 0.01 mmol), Ir(ppy)₃ (1.3 mg, 0.002 mmol), and AcOH (2.3 μ L, 0.04 mmol) in THF (1.5 mL) under blue light irradiation afforded the titled compound (45.4 mg, 91 % yield) as an oil after flash column chromatography (cyclohexane:ethyl acetate, 6:1). ¹H-NMR (300 MHz, CDCl₃): δ 8.23 – 8.14 (m, 1H), 8.08 – 7.99 (m, 1H), 7.60 – 7.42 (m, 2H), 5.97 (t, J = 1.4 Hz, 1H), 3.99 (q, J = 7.1 Hz, 2H), 2.49 (qd, J = 7.4, 1.4 Hz, 2H), 1.09 (m, 6H). ¹³C-NMR (75 MHz, CDCl₃): δ 165.6, 158.6, 148.1, 142.3, 133.6, 129.0, 122.6, 122.3, 118.0, 60.2, 33.3, 14.1, 12.0. HRMS (EI+) m/z: [M]⁺ calcd. for C₁₃H₁₅NO₄ 249.1001; found 249.0991.

Ethyl (Z)-3-(1*H*-indol-5-yl)pent-2-enoate ((Z)-3ae):



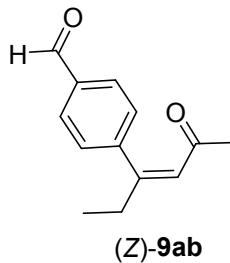
Following the general procedure, the reaction between ethyl 2-pentyneoate (26.4 μ L, 0.2 mmol), (1*H*-indol-5-yl)boronic acid (64.4 mg, 0.4 mmol), Pd(OAc)₂ (2.24 mg, 0.01 mmol), dppe (3.98 mg, 0.01 mmol), Ir(ppy)₃ (1.3 mg, 0.002 mmol), and AcOH (2.3 μ L, 0.04 mmol) in THF (1.5 mL) under blue light irradiation afforded the titled compound (38.5 mg, 84 % yield) as an oil after flash column chromatography (cyclohexane:ethyl acetate, 3:1). ¹H-NMR (300 MHz, CDCl₃): δ 8.27 (bs, 1H), 7.73 (bs, 1H), 7.37 – 7.23 (m, 2H), 7.20–7.16 (m, 1H), 6.53–6.50 (m, 1H), 6.04 (s, 1H), 4.17 (q, J = 7.1 Hz, 2H), 3.16 (q, J = 7.5 Hz, 2H), 1.27 (t, J = 7.1 Hz, 3H), 1.08 (t, J = 7.5 Hz, 3H). ¹³C-NMR (75 MHz, CDCl₃): δ 167.0, 163.8, 136.3, 133.0, 128.0, 125.2, 121.3, 119.5, 115.2, 111.1, 103.3, 59.8, 24.7, 14.5, 14.0. HRMS (EI+) m/z: [M+Na]⁺ calcd for C₁₅H₁₇NO₂Na 266.1151; found 266.1157.

Ethyl (Z)-3-(benzo[d][1,3]dioxol-5-yl)pent-2-enoate ((Z)-3af):



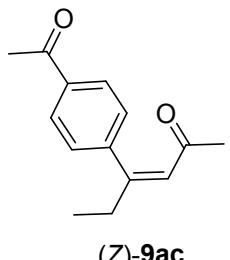
Following the general procedure, the reaction between ethyl 2-pentyneoate (26.4 μ L, 0.2 mmol), benzo[d][1,3]dioxol-5-ylboronic acid (66.4 mg, 0.4 mmol), Pd(OAc)₂ (2.24 mg, 0.01 mmol), dppe (3.98 mg, 0.01 mmol), Ir(ppy)₃ (1.3 mg, 0.002 mmol), and AcOH (2.3 μ L, 0.04 mmol) in THF (1.5 mL) under blue light irradiation afforded the titled compound (35.6 mg, 76 % yield) as an oil after flash column chromatography (cyclohexane:ethyl acetate, 3:1). ¹H-NMR (300 MHz, CDCl₃): δ 6.79 (d, J = 7.9 Hz, 1H), 6.68 – 6.59 (m, 2H), 5.96 (s, 2H), 5.83 (t, J = 1.2 Hz, 1H), 4.03 (q, J = 7.1 Hz, 2H), 2.42 (qd, J = 7.4, 1.3 Hz, 2H), 1.14 (t, J = 7.1 Hz, 3H), 1.04 (t, J = 7.4 Hz, 3H). ¹³C-NMR (75 MHz, CDCl₃): δ 166.4, 160.6, 147.3, 147.2, 134.1, 120.8, 116.4, 108.2, 108.1, 101.2, 59.9, 33.5, 14.2, 12.3. HRMS (EI+) m/z: [M+Na]⁺ calcd for C₁₄H₁₆O₄Na 271.0940; found 271.0949.

(Z)-4-(5-Oxohex-3-en-3-yl)benzaldehyde ((Z)-9ab):



Following the general procedure, the reaction between 3-hexyn-2-one (21.4 μ L, 0.2 mmol), 4-formylphenyl boronic acid (60 mg, 0.4 mmol), Pd(OAc)₂ (2.24 mg, 0.01 mmol), dppe (3.98 mg, 0.01 mmol), Ir(ppy)₃ (1.3 mg, 0.002 mmol), and AcOH (2.3 μ L, 0.04 mmol) in THF (1.5 mL) under blue light irradiation afforded the titled compound (36.8 mg, 91 % yield) as an oil after flash column chromatography (cyclohexane:ethyl acetate, 10:1). ¹H-NMR (300 MHz, CDCl₃): δ 10.02 (s, 1H), 7.88 (d, J = 8.3 Hz, 2H), 7.31 (d, J = 8.1 Hz, 2H), 6.18 (s, 1H), 2.46 (qd, J = 7.4, 1.3 Hz, 2H), 1.92 (s, 3H), 1.06 (t, J = 7.4 Hz, 3H). ¹³C-NMR (75 MHz, CDCl₃): δ 199.0, 191.8, 157.1, 147.3, 135.8, 129.8, 128.1, 126.6, 33.3, 30.9, 12.2. HRMS (APCI+) m/z: [M]⁺ calcd for C₁₃H₁₅O₂ 203.1067; found 203.1072.

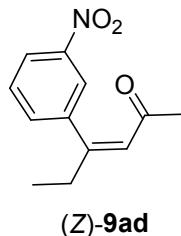
(Z)-4-(4-Acetylphenyl)hex-3-en-2-one ((Z)-9ac):



Following the general procedure, the reaction between 3-hexyn-2-one (21.4 μ L, 0.2 mmol), 4-acetylphenyl boronic acid (65.6 mg, 0.4 mmol), Pd(OAc)₂ (2.24 mg, 0.01 mmol), dppe (3.98 mg, 0.01 mmol), Ir(ppy)₃ (1.3 mg, 0.002 mmol), and

AcOH (2.3 μ L, 0.04 mmol) in THF (1.5 mL) under blue light irradiation afforded the titled compound (35.9 mg, 83 % yield) as an oil after flash column chromatography (cyclohexane:ethyl acetate, 3:1). **¹H-NMR** (300 MHz, CDCl₃): δ 7.95 (d, J = 8.4 Hz, 2H), 7.24 (d, J = 8.4 Hz, 2H), 6.15 (s, 1H), 2.60 (s, 3H), 2.45 (qd, J = 7.4, 1.2 Hz, 2H), 1.88 (s, 3H), 1.04 (t, J = 7.4 Hz, 3H). **¹³C-NMR** (75 MHz, CDCl₃): δ 199.3, 197.6, 157.3, 145.7, 136.6, 128.5, 127.7, 126.7, 33.4, 30.8, 26.7, 12.2. **HRMS** (EI+) m/z: [M]⁺ calcd for C₁₄H₁₆O₂ 216.1150; found 216.1156.

(Z)-4-(3-Nitrophenyl)hex-3-en-2-one ((Z)-9ad):



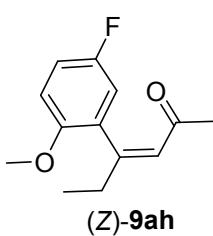
Following the general procedure, the reaction between 3-hexyn-2-one (21.4 μ L, 0.2 mmol), 3-nitrophenyl boronic acid (66.8 mg, 0.4 mmol), Pd(OAc)₂ (2.24 mg, 0.01 mmol), dppe (3.98 mg, 0.01 mmol), Ir(ppy)₃ (1.3 mg, 0.002 mmol), and AcOH (2.3 μ L, 0.04 mmol) in THF (1.5 mL) under blue light irradiation afforded the titled compound (32.4 mg, 74 % yield) as an oil after flash column chromatography (cyclohexane:ethyl acetate, 6:1). **¹H-NMR** (300 MHz, CDCl₃): δ 8.18 (ddd, J = 8.1, 2.2, 1.3 Hz, 1H), 8.01 (t, J = 1.8 Hz, 1H), 7.57 – 7.42 (m, 2H), 6.26 (s, 1H), 2.47 (qd, J = 7.4, 1.3 Hz, 2H), 2.03 (s, 3H), 1.07 (t, J = 7.4 Hz, 3H). **¹³C-NMR** (75 MHz, CDCl₃): δ 198.2, 156.0, 148.3, 142.3, 133.8, 129.3, 126.2, 122.8, 122.3, 33.4, 31.3, 12.1. **HRMS** (APCI+) m/z: [M]⁺ calcd for C₁₂H₁₄NO₃ 220.0968; found 220.0977.

(Z)-4-(3-Bromophenyl)hex-3-en-2-one ((Z)-9ag):



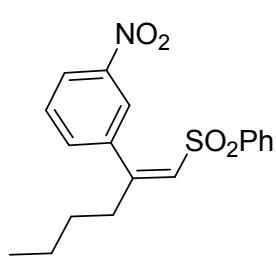
Following the general procedure, the reaction between 3-hexyn-2-one (21.4 μ L, 0.2 mmol), 3-bromophenyl boronic acid (80.3 mg, 0.4 mmol), Pd(OAc)₂ (2.24 mg, 0.01 mmol), dppe (3.98 mg, 0.01 mmol), Ir(ppy)₃ (1.3 mg, 0.002 mmol), and AcOH (2.3 μ L, 0.04 mmol) in THF (1.5 mL) under blue light irradiation afforded the titled compound (43.8 mg, 87 % yield) as an oil after flash column chromatography (cyclohexane:ethyl acetate, 6:1). **¹H-NMR** (300 MHz, CDCl₃): δ 7.51 – 7.41 (m, 1H), 7.32–7.29 (m, 1H), 7.27 – 7.18 (m, 1H), 7.08 (d, J = 7.7 Hz, 1H), 6.11 (s, 1H), 2.43 (q, J = 7.4 Hz, 2H), 1.87 (s, 3H), 1.04 (t, J = 7.4 Hz, 3H). **¹³C-NMR** (75 MHz, CDCl₃): δ 199.7, 156.6, 142.6, 131.1, 130.3, 130.0, 127.1, 126.3, 122.5, 33.5, 30.7, 12.2. **HRMS** (APCI+) m/z: [M]⁺ calcd for C₁₂H₁₄BrO 253.0223; found 253.0226.

(Z)-4-(5-Fluoro-2-methoxyphenyl)hex-3-en-2-one ((Z)-9ah):



Following the general procedure, the reaction between 3-hexyn-2-one (21.4 μ L, 0.2 mmol), (5-fluoro-2-methoxyphenyl)boronic acid (68 mg, 0.4 mmol), Pd(OAc)₂ (2.24 mg, 0.01 mmol), dppe (3.98 mg, 0.01 mmol), Ir(ppy)₃ (1.3 mg, 0.002 mmol), and AcOH (2.3 μ L, 0.04 mmol) in THF (1.5 mL) under blue light irradiation afforded the titled compound (35.6 mg, 80 % yield) as an oil after flash column chromatography (cyclohexane:ethyl acetate, 3:1). **¹H-NMR** (300 MHz, CDCl₃): δ 6.97 (ddd, J = 9.0, 8.0, 3.1 Hz, 1H), 6.83 (dd, J = 9.0, 4.3 Hz, 1H), 6.72 (dd, J = 8.5, 3.1 Hz, 1H), 6.15 (s, 1H), 3.76 (s, 3H), 2.41 (qd, J = 7.4, 1.3 Hz, 2H), 1.86 (s, 3H), 1.03 (t, J = 7.4 Hz, 3H). **¹³C-NMR** (75 MHz, CDCl₃): δ 199.2, 157.0 (d, J = 239.7 Hz), 154.5, 151.9 (d, J = 2.1 Hz), 131.0 (d, J = 7.5 Hz), 127.8, 115.9 (d, J = 23.7 Hz), 115.0 (d, J = 22.6 Hz), 111.9 (d, J = 8.3 Hz), 56.2, 32.5, 31.0, 12.1. **¹⁹F-NMR** (75 MHz, CDCl₃): δ -123.9. **HRMS** (ESI+) m/z: [M+Na]⁺ calcd for C₁₃H₁₅O₂FNa 245.0948; found 245.0942.

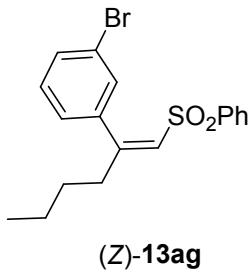
(Z)-1-Nitro-3-(1-(phenylsulfonyl)hex-1-en-2-yl)benzene ((Z)-13ad):



Following the general procedure, the reaction between (hex-1-yn-1-ylsulfonyl)benzene **12a** (44.5 mg, 0.2 mmol), 3-nitrophenyl boronic acid (66.8 mg, 0.4 mmol), Pd(OAc)₂ (2.24 mg, 0.01 mmol), dppe (3.98 mg, 0.01 mmol), Ir(ppy)₃ (1.3 mg, 0.002 mmol), and AcOH (2.3 μ L, 0.04 mmol) in THF (1.5 mL) under blue light irradiation afforded the titled compound (58 mg, 84 % yield) as a solid after flash column chromatography (cyclohexane:ethyl acetate, 6:1). **M.p.:** 77–80 °C. **¹H-NMR** (300 MHz, CDCl₃): δ 8.30 – 8.10 (m, 2H),

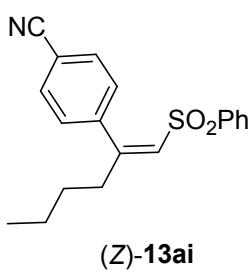
8.04 – 7.90 (m, 2H), 7.72 – 7.50 (m, 5H), 6.52 (s, 1H), 3.19 – 2.97 (m, 2H), 1.45 – 1.15 (m, 4H), 0.84 (t, J = 6.9 Hz, 3H). **$^{13}\text{C-NMR}$** (75 MHz, CDCl_3): δ 155.8, 148.6, 141.8, 141.2, 133.7, 132.8, 130.1, 130.0, 129.5, 127.5, 124.3, 121.8, 30.6, 30.3, 22.7, 13.9. **HRMS** (APCI+) m/z: [M]⁺ calcd for $\text{C}_{18}\text{H}_{20}\text{NO}_4\text{S}$ 346.1108; found 346.1101.

(Z)-1-Bromo-3-(1-(phenylsulfonyl)hex-1-en-2-yl)benzene ((Z)-13ag):



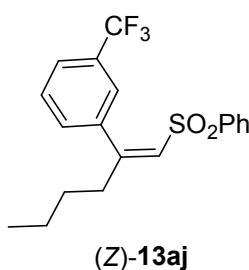
Following the general procedure, the reaction between (hex-1-yn-1-ylsulfonyl)benzene **12a** (44.5 mg, 0.2 mmol), 3-bromophenyl boronic acid (80.3 mg, 0.4 mmol), $\text{Pd}(\text{OAc})_2$ (2.24 mg, 0.01 mmol), dppe (3.98 mg, 0.01 mmol), $\text{Ir}(\text{ppy})_3$ (1.3 mg, 0.002 mmol), and AcOH (2.3 μL , 0.04 mmol) in THF (1.5 mL) under blue light irradiation afforded the titled compound (69.8 mg, 92 % yield) as an oil after flash column chromatography (cyclohexane:ethyl acetate, 6:1). **$^1\text{H-NMR}$** (300 MHz, CDCl_3): δ 7.55 – 7.47 (m, 3H), 7.38–7.20 (m, 3H), 7.16 (td, J = 7.8, 1.9 Hz, 1H), 7.07 – 6.99 (m, 1H), 6.95 (dd, J = 3.5, 1.7 Hz, 1H), 6.54 (s, 1H), 2.34 (t, J = 6.5 Hz, 2H), 1.43 – 1.15 (m, 4H), 0.86 (t, J = 6.1 Hz, 3H). **$^{13}\text{C-NMR}$** (75 MHz, CDCl_3): δ 157.0, 141.4, 138.8, 133.1, 131.4, 130.0, 129.8, 129.6, 128.8, 127.7, 126.8, 122.1, 40.5, 29.1, 22.2, 13.8. **HRMS** (APCI+) m/z: [M]⁺ calcd for $\text{C}_{18}\text{H}_{20}\text{BrO}_2\text{S}$ 379.0362; found 379.0355.

(Z)-4-(1-(Phenylsulfonyl)hex-1-en-2-yl)benzonitrile ((Z)-13ai):



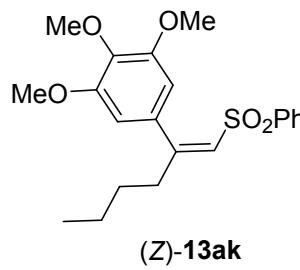
Following the general procedure, the reaction between (hex-1-yn-1-ylsulfonyl)benzene **12a** (44.5 mg, 0.2 mmol), 4-cyanophenyl boronic acid (58.8 mg, 0.4 mmol), $\text{Pd}(\text{OAc})_2$ (2.24 mg, 0.01 mmol), dppe (3.98 mg, 0.01 mmol), $\text{Ir}(\text{ppy})_3$ (1.3 mg, 0.002 mmol), and AcOH (2.3 μL , 0.04 mmol) in THF (1.5 mL) under blue light irradiation afforded the titled compound (59.2 mg, 91 % yield) as an oil after flash column chromatography (cyclohexane:ethyl acetate, 6:1). **$^1\text{H-NMR}$** (300 MHz, CDCl_3): δ 7.61 – 7.50 (m, 5H), 7.42 (m, 2H), 7.16 (d, J = 8.3 Hz, 2H), 6.54 (s, 1H), 2.37 (t, J = 7.2 Hz, 2H), 1.38 – 1.17 (m, 4H), 0.86 (t, J = 7.0 Hz, 3H). **$^{13}\text{C-NMR}$** (75 MHz, CDCl_3): δ 156.2, 141.9, 141.4, 133.4, 131.8, 129.8, 129.1, 128.5, 127.6, 118.6, 112.3, 40.3, 29.1, 22.2, 13.8. **HRMS** (APCI+) m/z: [M]⁺ calcd for $\text{C}_{19}\text{H}_{20}\text{O}_2\text{S}$ 326.1209; found 326.1220.

(Z)-1-(1-(Phenylsulfonyl)hex-1-en-2-yl)-3-(trifluoromethyl)benzene ((Z)-13aj):



Following the general procedure, the reaction between (hex-1-yn-1-ylsulfonyl)benzene **12a** (44.5 mg, 0.2 mmol), 3-(trifluoromethyl)phenyl boronic acid (76 mg, 0.4 mmol), $\text{Pd}(\text{OAc})_2$ (2.24 mg, 0.01 mmol), dppe (3.98 mg, 0.01 mmol), $\text{Ir}(\text{ppy})_3$ (1.3 mg, 0.002 mmol), and AcOH (2.3 μL , 0.04 mmol) in THF (1.5 mL) under blue light irradiation afforded the titled compound (56.1 mg, 79% yield) as an oil after flash column chromatography (cyclohexane:ethyl acetate, 6:1). **$^1\text{H-NMR}$** (300 MHz, CDCl_3): δ 7.60–7.41 (m, 5H), 7.37 – 7.30 (m, 3H), 7.08 (s, 1H), 6.61 (s, 1H), 2.38 (t, J = 7.2 Hz, 2H), 1.37 – 1.23 (m, 4H), 0.86 (t, J = 6.2 Hz, 3H). **$^{13}\text{C-NMR}$** (75 MHz, CDCl_3): δ 157.1, 141.4, 137.6, 133.2, 131.7, 130.47 (m), 130.0, 128.9, 128.6, 127.5, 125.2 (q, J = 3.7 Hz), 123.96 (q, J = 3.7 Hz), 40.5, 29.1, 22.1, 13.8. **$^{19}\text{F-NMR}$** (75 MHz, CDCl_3): δ -62.7. **HRMS** (EI+) m/z: [M]⁺ calcd for $\text{C}_{19}\text{H}_{19}\text{F}_3\text{O}_2\text{S}$ 368.1058; found 368.1044.

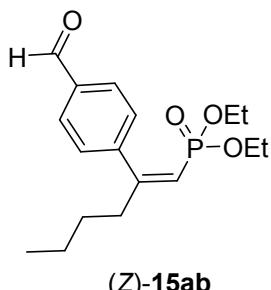
(Z)-1,2,3-Trimethoxy-5-(1-(phenylsulfonyl)hex-1-en-2-yl)benzene ((Z)-13ak):



Following the general procedure, the reaction between (hex-1-yn-1-ylsulfonyl)benzene **12a** (44.5 mg, 0.2 mmol), (3,4,5-trimethoxyphenyl)boronic acid (84.8 mg, 0.4 mmol), $\text{Pd}(\text{OAc})_2$ (2.24 mg, 0.01 mmol), dppe (3.98 mg, 0.01 mmol), $\text{Ir}(\text{ppy})_3$ (1.3 mg, 0.002 mmol), and AcOH (2.3 μL , 0.04 mmol) in THF (1.5 mL) under blue light irradiation

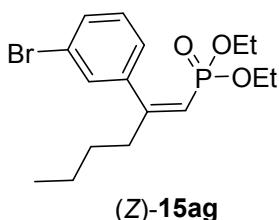
afforded the titled compound (62.4 mg, 80 % yield) as an oil after flash column chromatography (cyclohexane:ethyl acetate, 6:1). **¹H-NMR** (300 MHz, CDCl₃): δ 7.50 – 7.36 (m, 3H), 7.32 – 7.21 (m, 2H), 6.54 (s, 1H), 6.13 (s, 2H), 3.83 (s, 3H), 3.71 (s, 6H), 2.34 (t, J = 6.8 Hz, 2H), 1.42 – 1.17 (m, 4H), 0.85 (t, J = 7.0 Hz, 3H). **¹³C-NMR** (75 MHz, CDCl₃): δ 158.7, 152.7, 141.5, 138.0, 132.5, 131.9, 129.7, 128.4, 127.8, 105.2, 60.9, 56.1, 40.2, 29.3, 22.2, 13.8. **HRMS** (ESI+) m/z: [M+Na]⁺ calcd for C₂₁H₂₆O₅SnA 413.1393; found 413.1380.

Diethyl (Z)-(2-(4-formylphenyl)hex-1-en-1-yl)phosphonate ((Z)-15ab):



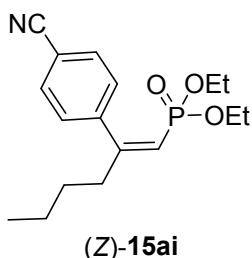
Following the general procedure, the reaction between diethyl hex-1-yn-1-ylphosphonate **14a** (43.6 mg, 0.2 mmol), 4-formylphenyl boronic acid (58.8 mg, 0.4 mmol), Pd(OAc)₂ (2.24 mg, 0.01 mmol), dppe (3.98 mg, 0.01 mmol), Ir(ppy)₃ (1.3 mg, 0.002 mmol), and AcOH (2.3 μL, 0.04 mmol) in THF (1.5 mL) under blue light irradiation afforded the titled compound (56.4 mg, 87 % yield) as an oil after flash column chromatography (cyclohexane:ethyl acetate, 2:1). **¹H-NMR** (300 MHz, CDCl₃): δ 10.02 (s, 1H), 7.88 (d, J = 8.0 Hz, 2H), 7.48 (d, J = 8.1 Hz, 2H), 5.79 (d, J = 17.0 Hz, 1H), 4.01 – 3.72 (m, 4H), 2.49 (t, J = 6.7 Hz, 2H), 1.44 – 1.27 (m, 4H), 1.11 (t, J = 7.1 Hz, 6H), 0.87 (t, J = 6.9 Hz, 3H). **¹³C-NMR** (75 MHz, CDCl₃): δ 192.0, 162.1 (d, J = 3.5 Hz), 146.7 (d, J = 7.9 Hz), 136.0, 129.5, 128.5 (d, J = 1.8 Hz), 115.6 (d, J = 190.8 Hz), 61.6 (d, J = 6.1 Hz), 41.2 (d, J = 20.7 Hz), 29.6, 22.3, 16.3 (d, J = 6.5 Hz), 13.9. **³¹P NMR** (121 MHz, CDCl₃, H₃PO₄ as internal standard): 16.2 ppm. **HRMS** (APCI+) m/z: [M]⁺ calcd for C₁₇H₂₆O₄P 325.1563; found 325.1559.

Diethyl (Z)-(2-(3-bromophenyl)hex-1-en-1-yl)phosphonate ((Z)-15ag):



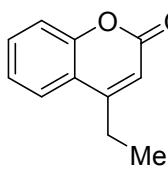
Following the general procedure, the reaction between diethyl hex-1-yn-1-ylphosphonate **14a** (43.6 mg, 0.2 mmol), 3-bromophenyl boronic acid (80.3 mg, 0.4 mmol), Pd(OAc)₂ (2.24 mg, 0.01 mmol), dppe (3.98 mg, 0.01 mmol), Ir(ppy)₃ (1.3 mg, 0.002 mmol), and AcOH (2.3 μL, 0.04 mmol) in THF (1.5 mL) under blue light irradiation afforded the titled compound (63.1 mg, 84 % yield) as an oil after flash column chromatography (cyclohexane:ethyl acetate, 2:1). **¹H-NMR** (300 MHz, CDCl₃): δ 7.51 (m, 2H), 7.35 – 7.25 (m, 2H), 5.79 (dt, J = 17.3, 1.3 Hz, 1H), 4.02 – 3.78 (m, 4H), 2.51 (t, J = 6.8 Hz, 2H), 1.53 – 1.31 (m, 4H), 1.20 (t, J = 7.1 Hz, 6H), 0.94 (t, J = 7.0 Hz, 3H). **¹³C-NMR** (75 MHz, CDCl₃): δ 161.7 (d, J = 3.4 Hz), 142.3 (d, J = 7.9 Hz), 131.1, 130.6 (d, J = 1.8 Hz), 129.6, 126.5 (d, J = 1.8 Hz), 122.0, 115.3 (d, J = 191.1 Hz), 61.5 (d, J = 6.1 Hz), 41.2 (d, J = 20.7 Hz), 29.6, 22.2, 16.3 (d, J = 6.7 Hz), 13.9. **³¹P NMR** (121 MHz, CDCl₃, H₃PO₄ as internal standard): 16.6 ppm. **HRMS** (EI+) m/z: [M]⁺ calcd for C₁₇H₂₆O₄P 374.0646; found 374.0657.

Diethyl (Z)-(2-(4-cyanophenyl)hex-1-en-1-yl)phosphonate ((Z)-15ai):



Following the general procedure, the reaction between diethyl hex-1-yn-1-ylphosphonate **14a** (43.6 mg, 0.2 mmol), 4-cyanophenyl boronic acid (58.8 mg, 0.4 mmol), Pd(OAc)₂ (2.24 mg, 0.01 mmol), dppe (3.98 mg, 0.01 mmol), Ir(ppy)₃ (1.3 mg, 0.002 mmol), and AcOH (2.3 μL, 0.04 mmol) in THF (1.5 mL) under blue light irradiation afforded the titled compound (57.8 mg, 90 % yield) as an oil after flash column chromatography (cyclohexane:ethyl acetate, 1:1). **¹H-NMR** (300 MHz, CDCl₃): δ 7.63 (d, J = 8.5 Hz, 2H), 7.40 (d, J = 8.5 Hz, 2H), 5.76 (dt, J = 16.6, 1.3 Hz, 1H), 3.94 – 3.67 (m, 4H), 2.44 (t, J = 6.7 Hz, 2H), 1.39 – 1.23 (m, 4H), 1.11 (t, J = 7.1 Hz, 6H), 0.85 (t, J = 7.1 Hz, 3H). **¹³C-NMR** (75 MHz, CDCl₃): δ 161.2 (d, J = 3.3 Hz), 145.1 (d, J = 7.8 Hz), 131.8, 128.6 (d, J = 1.8 Hz), 118.7, 117.4, 113.4 (d, J = 223.6 Hz), 61.6 (d, J = 6.1 Hz), 41.0 (d, J = 20.5 Hz), 29.5, 22.2, 16.3 (d, J = 6.5 Hz), 13.8. **³¹P NMR** (121 MHz, CDCl₃, H₃PO₄ as internal standard): 15.7 ppm. **HRMS** (EI+) m/z: [M]⁺ calcd for C₁₇H₂₄NO₃P 321.1494; found 321.1500.

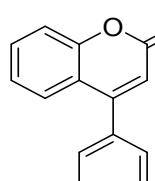
4-Ethyl-2*H*-chromen-2-one (3al):



Following the general procedure, the reaction between ethyl 2-pentynoate (26.4 μL, 0.2 mmol), 2-hydroxyphenyl boronic acid (55.2 mg, 0.4 mmol), Pd(OAc)₂ (2.24 mg,

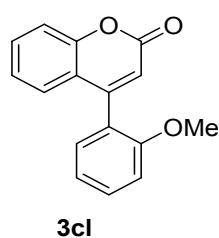
0.01 mmol), dppe (3.98 mg, 0.01 mmol), Ir(ppy)₃ (1.3 mg, 0.002 mmol), and AcOH (2.3 μ L, 0.04 mmol) in THF (1.5 mL), and H₂O (0.15 mL) under blue light irradiation afforded the titled compound (32.4 mg, 93 % yield) as an oil after flash column chromatography (cyclohexane:ethyl acetate, 20:1). **M.p.:** 60–62 °C. **¹H-NMR** (300 MHz, CDCl₃): δ 7.63 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.50 (ddd, *J* = 8.6, 7.3, 1.5 Hz, 1H), 7.35 – 7.24 (m, 2H), 6.28 (s, 1H), 2.81 (qd, *J* = 7.4, 1.2 Hz, 2H), 1.32 (t, *J* = 7.4 Hz, 3H). **¹³C-NMR** (75 MHz, CDCl₃): δ 161.2, 157.5, 153.7, 131.6, 124.3, 124.2, 119.4, 117.4, 113.1, 24.7, 12.2. **HRMS** (APCI+) m/z: [M]⁺ calcd for C₁₁H₁₁O₂ 175.0754; found 175.0759.

4-Phenyl-2*H*-chromen-2-one (3bl):



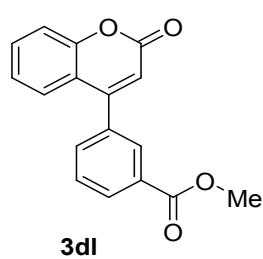
Following the general procedure, the reaction between methyl phenylpropiolate (29.5 μ L, 0.2 mmol), 2-hydroxyphenyl boronic acid (55.2 mg, 0.4 mmol), Pd(OAc)₂ (2.24 mg, 0.01 mmol), dppe (3.98 mg, 0.01 mmol), Ir(ppy)₃ (1.3 mg, 0.002 mmol), and AcOH (2.3 μ L, 0.04 mmol) in THF (1.5 mL), and H₂O (0.15 mL) under blue light irradiation afforded the titled compound (40.4 mg, 91 % yield) as a white solid after flash column chromatography (cyclohexane:ethyl acetate, 10:1). **M.p.:** 89–92 °C. **¹H-NMR** (300 MHz, CDCl₃): δ 7.61 – 7.35 (m, 8H), 7.35 – 7.13 (m, 1H), 6.38 (s, 1H). **¹³C-NMR** (75 MHz, CDCl₃): δ 160.8, 155.8, 154.3, 135.3, 132.0, 129.8, 129.0, 128.5, 127.1, 124.3, 119.1, 117.5, 115.3. **HRMS** (APCI+) m/z: [M]⁺ calcd for C₁₅H₁₁O₂ 223.0754; found 223.0755.

4-(2-Methoxyphenyl)-2*H*-chromen-2-one (3cl):



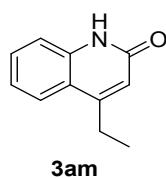
Following the general procedure, the reaction between methyl (2-methoxy)phenylpropiolate (38.04 mg, 0.2 mmol), 2-hydroxyphenyl boronic acid (55.2 mg, 0.4 mmol), Pd(OAc)₂ (2.24 mg, 0.01 mmol), dppe (3.98 mg, 0.01 mmol), Ir(ppy)₃ (1.3 mg, 0.002 mmol), and AcOH (2.3 μ L, 0.04 mmol) in THF (1.5 mL), and H₂O (0.15 mL) under blue light irradiation afforded the titled compound (40.3 mg, 80 % yield) as a brown solid after flash column chromatography (cyclohexane:ethyl acetate, 10:1). **M.p.:** 260 °C (decomposition before melting). **¹H-NMR** (300 MHz, CDCl₃): δ 7.57 – 7.43 (m, 2H), 7.38 (d, *J* = 7.9 Hz, 1H), 7.29 – 6.95 (m, 5H), 6.37 (s, 1H), 3.75 (s, 3H). **¹³C-NMR** (75 MHz, CDCl₃): δ 161.2, 156.6, 153.9, 131.6, 131.1, 130.2, 127.4, 124.3, 124.0, 121.1, 119.6, 117.1, 116.4, 111.3, 55.6. **HRMS** (ESI+) m/z: [M+Na]⁺ calcd for C₁₆H₁₂O₃Na 275.0678; found 275.0674.

Methyl 3-(2-oxo-2*H*-chromen-4-yl)benzoate (3dl):



Following the general procedure, the reaction between ethyl (3-carbomethoxy)phenylpropiolate (43.6 mg, 0.2 mmol), 2-hydroxyphenyl boronic acid (55.2 mg, 0.4 mmol), Pd(OAc)₂ (2.24 mg, 0.01 mmol), dppe (3.98 mg, 0.01 mmol), Ir(ppy)₃ (1.3 mg, 0.002 mmol), and AcOH (2.3 μ L, 0.04 mmol) in THF (1.5 mL), and H₂O (0.15 mL) under blue light irradiation afforded the titled compound (42.6 mg, 76 % yield) as an oil after flash column chromatography (cyclohexane:ethyl acetate, 5:1). **¹H-NMR** (300 MHz, CDCl₃): δ 8.25 – 8.18 (m, 1H), 8.15 (s, 1H), 7.69 – 7.61 (m, 2H), 7.57 (ddd, *J* = 8.6, 7.3, 1.4 Hz, 1H), 7.42 (ddd, *J* = 7.6, 5.4, 1.0 Hz, 2H), 7.29 – 7.20 (m, 1H), 6.40 (s, 1H), 3.95 (s, 3H). **¹³C-NMR** (75 MHz, CDCl₃): δ 166.4, 160.6, 154.7, 154.3, 135.6, 132.8, 132.3, 131.1, 130.9, 129.7, 129.3, 126.8, 124.5, 118.8, 117.6, 115.9, 52.6. **HRMS** (ESI+) m/z: [M+Na]⁺ calcd for C₁₇H₁₂O₄Na 303.0627; found 303.0636.

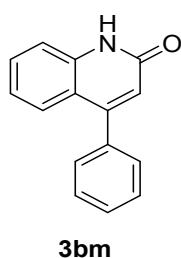
4-Ethylquinolin-2(*H*)-one (3am):



Following the general procedure, the reaction between ethyl 2-pentynoate (26.4 μ L, 0.2 mmol), 2-aminophenyl boronic acid hydrochloride (69.4 mg, 0.4 mmol), Cs₂CO₃ (130 mg, 0.4 mmol), Pd(OAc)₂ (2.24 mg, 0.01 mmol), dppe (3.98 mg, 0.01 mmol), Ir(ppy)₃ (1.3 mg, 0.002 mmol), and AcOH (2.3 μ L, 0.04 mmol) in THF (1.5 mL), and H₂O (0.15 mL) at 60 °C under blue light irradiation afforded the titled compound (28.4 mg, 82 % yield) as an orange solid after flash column chromatography (cyclohexane:ethyl acetate,

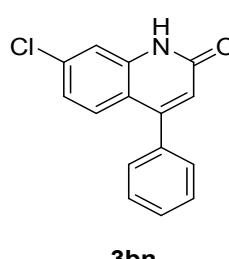
2:1). **M.p.**: 185–188 °C. **¹H-NMR** (300 MHz, CDCl₃): δ 12.67 (s, 1H), 7.72 (d, *J* = 8.1 Hz, 1H), 7.48 (d, *J* = 3.5 Hz, 2H), 7.38 – 7.03 (m, 1H), 6.62 (s, 1H), 2.91 (q, *J* = 7.4 Hz, 2H), 1.36 (t, *J* = 7.4 Hz, 3H). **¹³C-NMR** (75 MHz, CDCl₃): δ 164.9, 154.6, 138.7, 130.4, 124.1, 122.6, 120.0, 118.6, 117.0, 25.2, 13.0. **HRMS** (ESI+) m/z: [M+Na]⁺ calcd for C₁₁H₁₁NONa 196.0732; found 196.0740.

4-Phenylquinolin-2(1*H*)-one (**3bm**):



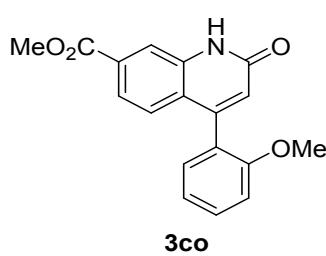
Following the general procedure, the reaction between methyl phenylpropiolate (29.5 μL, 0.2 mmol), 2-aminophenyl boronic acid hydrochloride (69.4 mg, 0.4 mmol), Cs₂CO₃ (130 mg, 0.4 mmol), Pd(OAc)₂ (2.24 mg, 0.01 mmol), dppe (3.98 mg, 0.01 mmol), Ir(ppy)₃ (1.3 mg, 0.002 mmol), and AcOH (2.3 μL, 0.04 mmol) in THF (1.5 mL), and H₂O (0.15 mL) at 60 °C under blue light irradiation afforded the titled compound (41.2 mg, 93 % yield) as a solid after flash column chromatography (cyclohexane:ethyl acetate, 2:1). **M.p.**: 256–259 °C **¹H-NMR** (300 MHz, CDCl₃): δ 12.63 (s, 1H), 7.69 – 7.41 (m, 8H), 7.27 – 7.04 (m, 1H), 6.71 (s, 1H). **¹³C-NMR** (75 MHz, CDCl₃): δ 153.7, 139.1, 137.3, 130.9, 129.0, 128.9, 128.8, 126.9, 122.7, 119.8, 116.8. **HRMS** (ESI+) m/z: [M+Na]⁺ calcd for C₁₅H₁₁NONa 244.0732; found 244.0736.

7-Chloro-4-phenylquinolin-2(1*H*)-one (**3bn**):



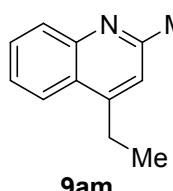
Following the general procedure, the reaction between methyl phenylpropiolate (29.5 μL, 0.2 mmol), 2-amino-4-chlorophenyl boronic acid pinacol ester (101 mg, 0.4 mmol), Cs₂CO₃ (130 mg, 0.4 mmol), Pd(OAc)₂ (2.24 mg, 0.01 mmol), dppe (3.98 mg, 0.01 mmol), Ir(ppy)₃ (1.3 mg, 0.002 mmol), and AcOH (2.3 μL, 0.04 mmol) in THF (1.5 mL), and H₂O (0.15 mL) at 60 °C under blue light irradiation afforded the titled compound (44 mg, 86 % yield) as a solid after flash column chromatography (cyclohexane:ethyl acetate, 2:1). **¹H-NMR** (300 MHz, CDCl₃): δ 12.56 (s, 1H), 7.59 – 7.35 (m, 7H), 7.12 (dd, *J* = 8.7, 1.4 Hz, 1H), 6.68 (s, 1H). **¹³C-NMR** (75 MHz, CDCl₃): δ 153.2, 139.6, 137.0, 136.7, 129.1, 128.8 (3C), 128.1, 123.3, 120.8 (bs), 118.2, 116.2. **HRMS** (ESI+) m/z: [M+Na]⁺ calcd for C₁₅H₁₀NOClNa 278.0343; found 278.0346.

Methyl 4-(2-methoxyphenyl)-2-oxo-1,2-dihydroquinoline-7-carboxylate (**3co**):



Following the general procedure, the reaction between methyl (2-methoxy)phenylpropiolate (38.04 mg, 0.2 mmol), 2-amino-4-(carbomethoxy)phenyl boronic acid hydrochloride (93 mg, 0.4 mmol), Cs₂CO₃ (130 mg, 0.4 mmol), Pd(OAc)₂ (2.24 mg, 0.01 mmol), dppe (3.98 mg, 0.01 mmol), Ir(ppy)₃ (1.3 mg, 0.002 mmol), and AcOH (2.3 μL, 0.04 mmol) in THF (1.5 mL), and H₂O (0.15 mL) at 60 °C under blue light irradiation afforded the titled compound (45.6 mg, 74 % yield) as a solid after flash column chromatography (cyclohexane:ethyl acetate, 2:1). **M.p.**: 234–238 °C. **¹H-NMR** (300 MHz, CDCl₃): δ 12.35 (s, 1H), 8.11 (d, *J* = 1.3 Hz, 1H), 7.74 (dd, *J* = 8.4, 1.5 Hz, 1H), 7.62 – 7.40 (m, 1H), 7.40 – 7.20 (m, 2H), 7.20 – 6.98 (m, 2H), 6.78 (s, 1H), 3.95 (s, 3H), 3.74 (s, 3H). **¹³C-NMR** (75 MHz, CDCl₃): δ 166.5, 164.3, 156.7, 150.6, 138.2, 131.7, 130.7, 130.6, 127.4, 125.7, 124.0, 123.3, 122.8, 121.1, 117.8, 111.3, 55.6, 52.6. **HRMS** (ESI+) m/z: [M+Na]⁺ calcd for C₁₈H₁₅NO₄Na 332.0893; found 332.0900.

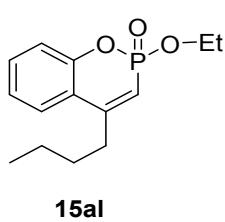
4-Ethyl-2-methylquinoline (**9am**):



Following the general procedure, the reaction between 3-hexyn-2-one (21.4 μL, 0.2 mmol), 2-aminophenylboronic acid hydrochloride (69.4 mg, 0.4 mmol), Pd(OAc)₂ (2.24 mg, 0.01 mmol), dppe (3.98 mg, 0.01 mmol), Ir(ppy)₃ (1.3 mg, 0.002 mmol), and AcOH (2.3 μL, 0.04 mmol) in THF (1.5 mL) under blue light irradiation afforded the titled compound (428.82.4 mg, 84 % yield) as an oil after flash column chromatography (cyclohexane:ethyl acetate, 10:1). **¹H-NMR** (300 MHz, CDCl₃): 8.01 (ddd, *J* = 8.5, 5.0, 1.1 Hz, 1H), 7.66 (ddd, *J* = 8.4, 6.9, 1.5 Hz, 1H), 7.49 (ddd,

J = 8.3, 6.9, 1.3 Hz, 1H), 7.15 (s, 1H), 3.08 (q, *J* = 7.5 Hz, 2H), 2.72 (s, 3H), 1.39 (t, *J* = 7.5 Hz, 3H). ¹³C-NMR (75 MHz, CDCl₃): δ 159.0, 149.9, 148.1, 129.5, 129.1, 125.9, 125.5, 123.4, 120.8, 25.5, 25.1, 14.2. HRMS (APCI+) m/z: [M]⁺ calcd for C₁₂H₁₄N 172.1121; found 172.1127.

4-Butyl-2-ethoxy-2*H*-benzo[e][1,2]oxaphosphinine 2-oxide (15al):

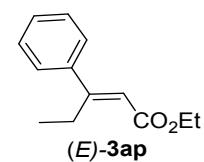


Following the general procedure, the reaction between diethyl hex-1-yn-1-ylphosphonate **14a** (43.6 mg, 0.2 mmol), 2-hydroxyphenyl boronic acid (55.2 mg, 0.4 mmol), Pd(OAc)₂ (2.24 mg, 0.01 mmol), dppe (3.98 mg, 0.01 mmol), Ir(ppy)₃ (1.3 mg, 0.002 mmol), and AcOH (2.3 μL, 0.04 mmol) in THF (1.5 mL) and H₂O (0.15 mL) under blue light irradiation at 80 °C afforded the titled compound (36.7 mg, 69 % yield) as an oil after flash column chromatography (cyclohexane:ethyl acetate, 2:1). ¹H-NMR (300 MHz, CDCl₃): δ 7.56 – 7.48 (m, 1H), 7.41 – 7.32 (m, 1H), 7.21 – 7.12 (m, 2H), 5.97 (d, *J* = 17.2 Hz, 1H), 4.16 (dq, *J* = 9.2, 7.1 Hz, 2H), 2.78 – 2.56 (m, 2H), 1.68 – 1.54 (m, 2H), 1.50–1.37 (m, 2H), 1.33 (t, *J* = 7.1 Hz, 3H), 0.95 (t, *J* = 7.3 Hz, 3H). ¹³C-NMR (75 MHz, CDCl₃): δ 156.2, 151.7 (d, *J* = 8.1 Hz), 131.1, 126.2 (d, *J* = 0.9 Hz), 123.7, 121.4 (d, *J* = 16.9 Hz), 119.5 (d, *J* = 7.7 Hz), 109.1 (d, *J* = 176.1 Hz), 63.0 (d, *J* = 6.6 Hz), 34.8 (d, *J* = 18.4 Hz), 30.3, 22.6, 16.6 (d, *J* = 6.0 Hz), 14.0. ³¹P NMR (121 MHz, CDCl₃, H₃PO₄ as internal standard): 10.2 ppm. HRMS (ESI+) m/z: [M+Na]⁺ calcd for C₁₄H₁₉O₃PNa 289.0964; found 289.0969.

4 Mechanistic experiments

4.1 Role of AcOH, trapping and deuteration experiments

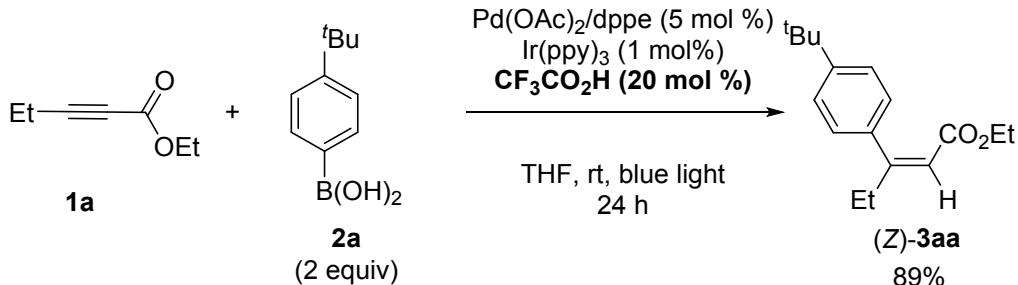
4.1.1 Synthesis of (*E*)-ethyl 3-phenylpent-2-enoate ((*E*)-3ap) in the absence of AcOH:



Pd(OAc)₂ (2.25 mg, 0.01 mmol) and dppe (3.98 mg, 0.01 mmol) were placed in a 5 mL vial provided with a magnetic stir and a septum. THF (0.5 mL) was added under argon atmosphere, and the mixture was stirred for 18 h (overnight) until the formation of a transparent orange mixture. This solution was added to a solution containing a mixture of ethyl 2-pentynoate (0.2 mmol) and phenylboronic acid (0.4 mmol) solved in THF (1 mL), under argon atmosphere. The mixture was allowed to stir at room temperature for overnight. Then, the reaction was diluted with 10 mL of AcOEt and extracted with a saturated solution of NaHCO₃ in brine (3x10 mL), and water until the pH becomes neutral. The organic phase was dried with Na₂SO₄ and concentrated in vacuo. The resulting residue was purified by column chromatography (cyclohexane:ethyl acetate, 10:1) to afford the titled compound as an oil (37 mg, 93 % yield). ¹H-NMR (300 MHz, CDCl₃): δ 7.48 – 7.41 (m, 2H), 7.36 (m, 3 H), 6.02 (s, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 3.11 (q, *J* = 7.5 Hz, 2H), 1.32 (t, *J* = 7.1 Hz, 3H), 1.08 (t, *J* = 7.5 Hz, 3H). The spectroscopic data matches the reported compound.⁷

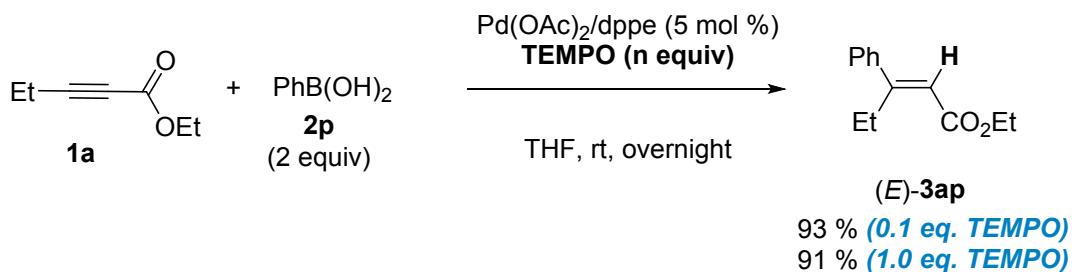
Effect of the acid in the reaction: CF₃CO₂H vs CH₃CO₂H.

To evaluate the effect of other acids more than AcOH, we carried out the reaction between ethyl 2-pentynoate (26.4 μL, 0.2 mmol), 4-*tert*-butylphenyl boronic acid (71.2 mg, 0.4 mmol), Pd(OAc)₂ (2.24 mg, 0.01 mmol), dppe (3.98 mg, 0.01 mmol), Ir(ppy)₃ (1.3 mg, 0.002 mmol), and CF₃CO₂H (3 μL, 0.04 mmol) in THF (1.5 mL) under blue light irradiation affording (*Z*)-3aa with comparable efficiency than that reported using AcOH (46 mg, 89 % yield) as an oil after flash column chromatography.

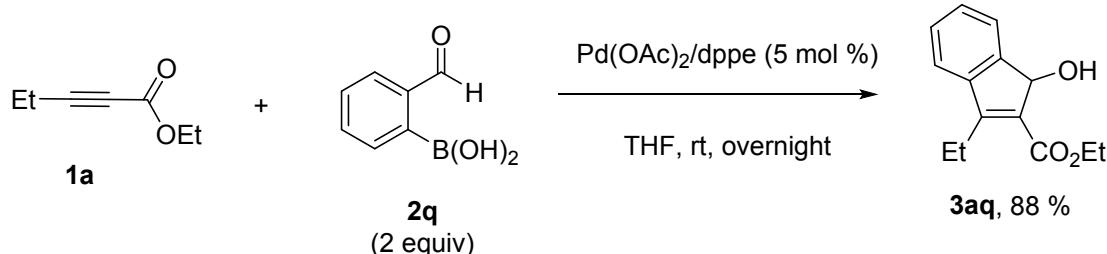


4.1.2 Study of the (*E*)-hydroarylation in presence of TEMPO and intramolecular trapping

Following the typical procedure for the (*E*)-hydroarylation in presence of TEMPO, (*E*)-3ap was obtained as an oil without a significant loss of reactivity, neither with 0.1 eq. nor with 1 eq. of TEMPO:



Intramolecular trapping of the alkenyl-Pd intermediate:



Pd(OAc)₂ (2.25 mg, 0.01 mmol) and dppe (3.98 mg, 0.01 mmol) were placed in a 5 mL vial provided with a magnetic stir and a septum. THF (0.5 mL) was added under argon atmosphere, and the mixture was stirred for 18 h (overnight) until the formation of a transparent orange mixture. This solution was added to a solution containing a mixture of ethyl 2-pentynoate (0.2 mmol) and 2-formylphenylboronic acid (0.4 mmol) solved in THF (1 mL), under argon atmosphere. The mixture was allowed to stir at room temperature for overnight. Then, the reaction was diluted with 10 mL of AcOEt and extracted with a saturated solution of NaHCO₃ in brine (3x10 mL), and water until the pH becomes neutral. The organic phase was dried with Na₂SO₄ and concentrated in vacuo. The resulting residue was purified by column chromatography (cyclohexane:ethyl acetate, 3:1) to afford the titled compound as a white solid (40.9 mg, 88 % yield). **M.p.**: 97-99 °C. **¹H-NMR** (300 MHz, CDCl₃): δ 7.64-7.56 (m, 1H), 7.47 – 7.35 (m, 3H), 5.39 (s, 1H), 4.35 (q, *J* = 7.1 Hz, 2H), 3.34 (s, 1H), 3.09-2.89 (m, 2H), 1.39 (t, *J* = 7.1 Hz, 3H), 1.24 (t, *J* = 7.6 Hz, 3H). **¹³C-NMR** (75 MHz, CDCl₃): δ 165.6, 158.6, 145.1, 141.6, 131.5, 129.0, 128.7, 124.2, 121.5, 75.9, 60.4, 19.9, 14.4, 13.2. **HRMS** (APCI+) m/z: [M+H]⁺ calcd for C₁₄H₁₇O₃ 233.1172; found 233.1176.

4.1.3 Deuteration experiments

Following the procedure described above, the corresponding boron-precursor and the deuterium source (indicated in each case) were used for the deuteration experiments. The integrals for selected reference signals are integrated and indicated in each case. The allylic signal was used as internal standard.

Studies with D₂O:

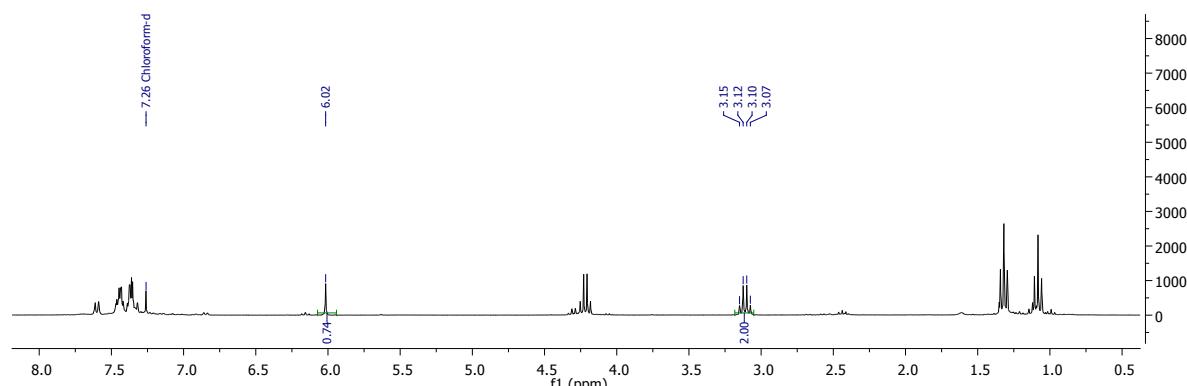
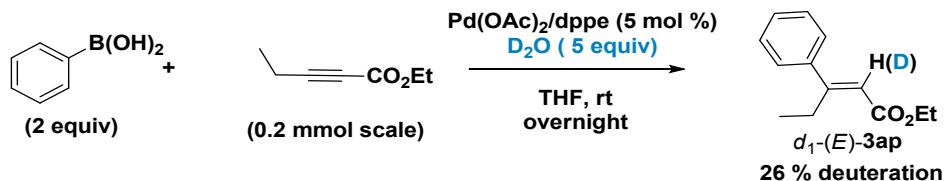


Figure S3. ¹H NMR spectrum (300 MHz, CDCl₃) of the reaction crude between PhB(OH)₂ and **1a** in presence of D₂O (5.0 equiv).

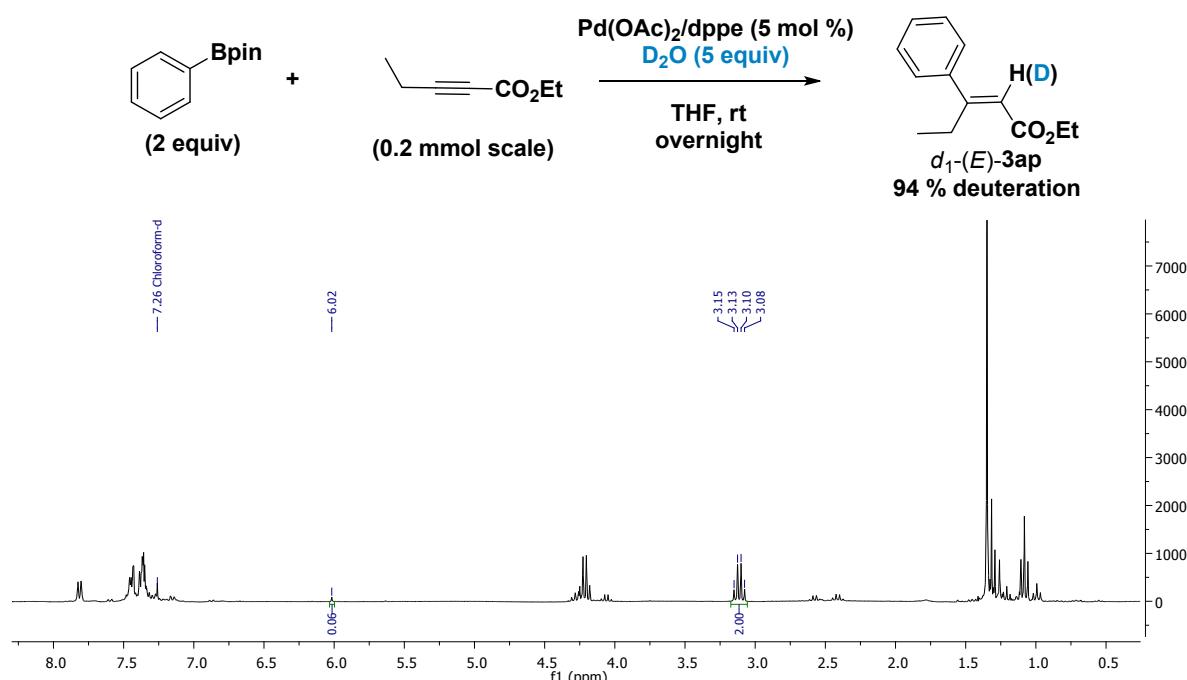
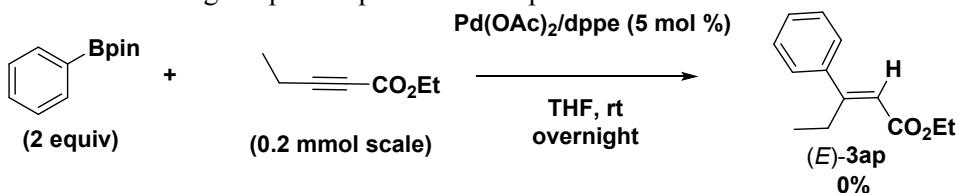


Figure S4. ¹H NMR spectrum (300 MHz, CDCl₃) of the reaction crude between PhBpin and **1a** in presence of D₂O (5.0 equiv).

Additionally, the reaction between **1a** and PhBpin in absence of H₂O did not take place, indicating that water may release PhB(OH)₂, which is the active species in the reaction media. This result suggests the crucial role of the OH during the protodepalladation step in the reaction mechanism.



Studies with AcOD:

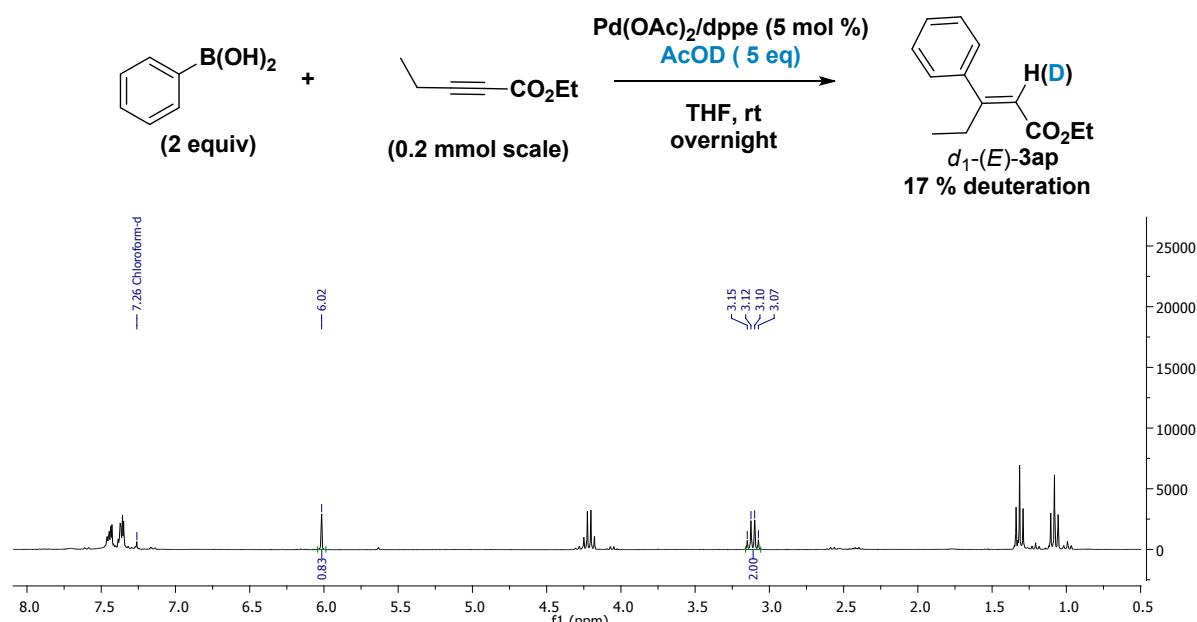
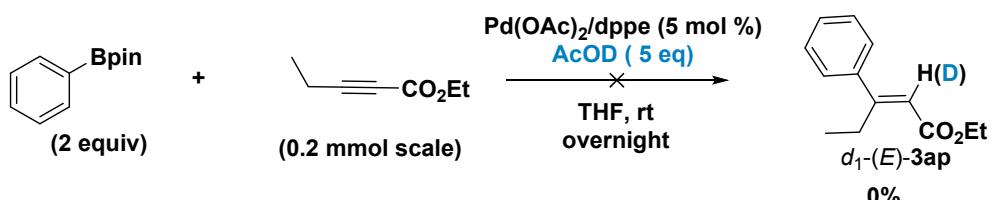


Figure S5. ¹H NMR spectrum (300 MHz, CDCl₃) of the reaction crude between PhB(OH)₂ and **1a** in presence of AcOD (5.0 equiv).

Similarly to previous experiments, the reaction with PhBpin and AcOD, which is not able to generate PhB(OH)₂ in the reaction media, did not take place:



Studies with PhB(OD)₂:

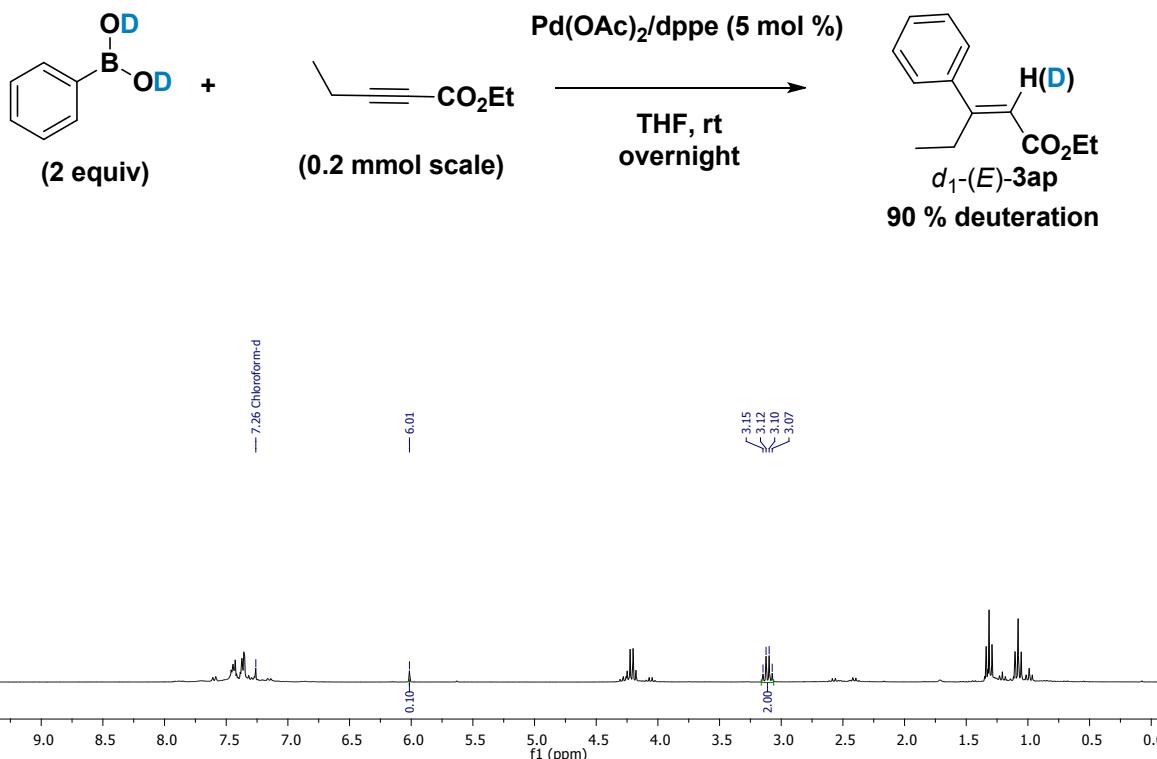


Figure S6. ¹H NMR spectrum (300 MHz, CDCl₃) of the reaction crude between PhB(OD)₂ and **1a**.

4.2 Determination of the Kinetic Isotope Effect (KIE).

For the determination of the KIE the reaction between phenylboronic acid PhB(OH)₂ and its deuterated analogue, PhB(OD)₂, was monitored by ¹H NMR (300 MHz, CDCl₃) with an initial concentration of the alkyne **1a** [alkyne **1a**]₀ = 0.1 M in THF-*d*₈. Methyl 3,5-dinitrobenzoate was used as internal standard. The kinetic measurements were performed on an AVIII-HD-300 spectrometer taking a ¹H NMR (300 MHz) spectrum each 5 minutes during the first 2 hours of reaction, and each 15 minutes after the first 2 hours during a total reaction time of 10 h. Each experiment (with PhB(OH)₂ or PhB(OD)₂) was recorded by independent experiments in order to determine the presence of a primary KIE (Figure S7).

Table S1. Kinetic measurements for the reaction with PhB(OH)₂ and PhB(OD)₂ by independent experiments. The concentration of the product is given in each case.

Time (min)	[alkene-H]	[alkene-D]
0	0	0
5	0	0
10	0	0
15	0	0
20	0,00478469	0,0014
25	0,00526316	0,0014
30	0,0062201	0,0016
35	0,0062201	0,0024
40	0,00669856	0,0028
45	0,00789474	0,0028
50	0,0076555	0,003

55	0,00813397	0,0032
60	0,00885167	0,0038
65	0,00909091	0,004
70	0,00956938	0,004
75	0,01052632	0,004
80	0,01100478	0,0042
85	0,01148325	0,0042
90	0,01196172	0,0042
95	0,01244019	0,0044
100	0,01244019	0,0046
105	0,01291866	0,0048
110	0,01363636	0,0048
115	0,01411483	0,0052
120	0,0145933	0,0052
125	0,0145933	0,0056
140	0,015311	0,0066
155	0,01674641	0,007
170	0,01794258	0,007
185	0,01866029	0,007
200	0,02033493	0,0074
215	0,0208134	0,0082
230	0,02200957	0,0088
245	0,02200957	0,009
260	0,02344498	0,009
275	0,02416268	0,0096
290	0,02416268	0,0102
305	0,02488038	0,0102
320	0,02559809	0,0106
335	0,02607656	0,011
350	0,02655502	0,011
365	0,0277512	0,0116
380	0,02727273	0,0118
395	0,02822967	0,0124
410	0,02822967	0,0126
425	0,02822967	0,0124
440	0,0284689	0,0128
455	0,02894737	0,013
470	0,02870813	0,0132
485	0,02966507	0,0136
500	0,03062201	0,0138
515	0,03086124	0,014
530	0,03181818	0,0142
545	0,03157895	0,0142
560	0,03181818	0,0146
575	0,03205742	0,015
590	0,03277512	0,0152

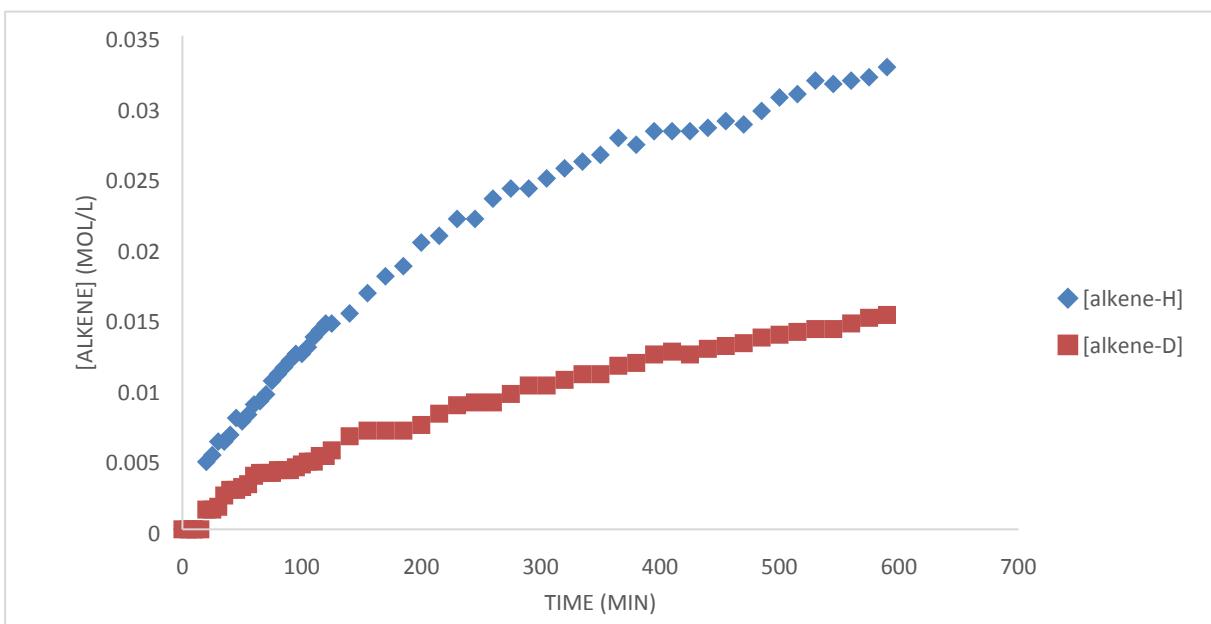


Figure S7. Concentration of the product as a function of the time. In blue, the reaction with $\text{PhB}(\text{OH})_2$, in red the reaction with $\text{PhB}(\text{OD})_2$.

Taking the linear region of the graphic (Figure S8), to consider the steady-state approximation, the corresponding k-values for the H- and the D-experiments can be obtained:

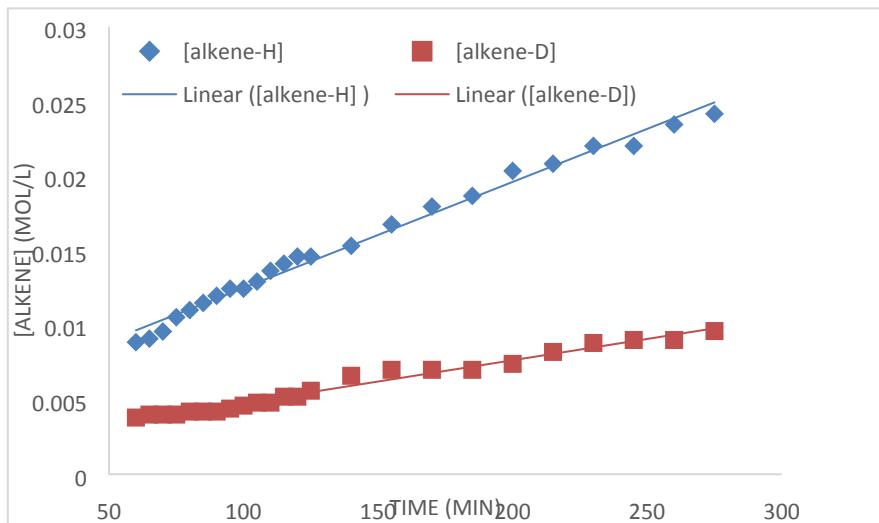


Figure S8. Linear region.

Thus, the KIE value in this case is given by the expression:

$$KIE = \frac{k_H}{k_D} = \frac{\text{slope} - H}{\text{slope} - D} = \frac{7 \cdot 10^{-5} \text{ M/min}}{3 \cdot 10^{-5} \text{ M/min}} \approx 2.3$$

4.3 Determination of Z:E selectivity in hydroarylation of 3-arylpropiolates

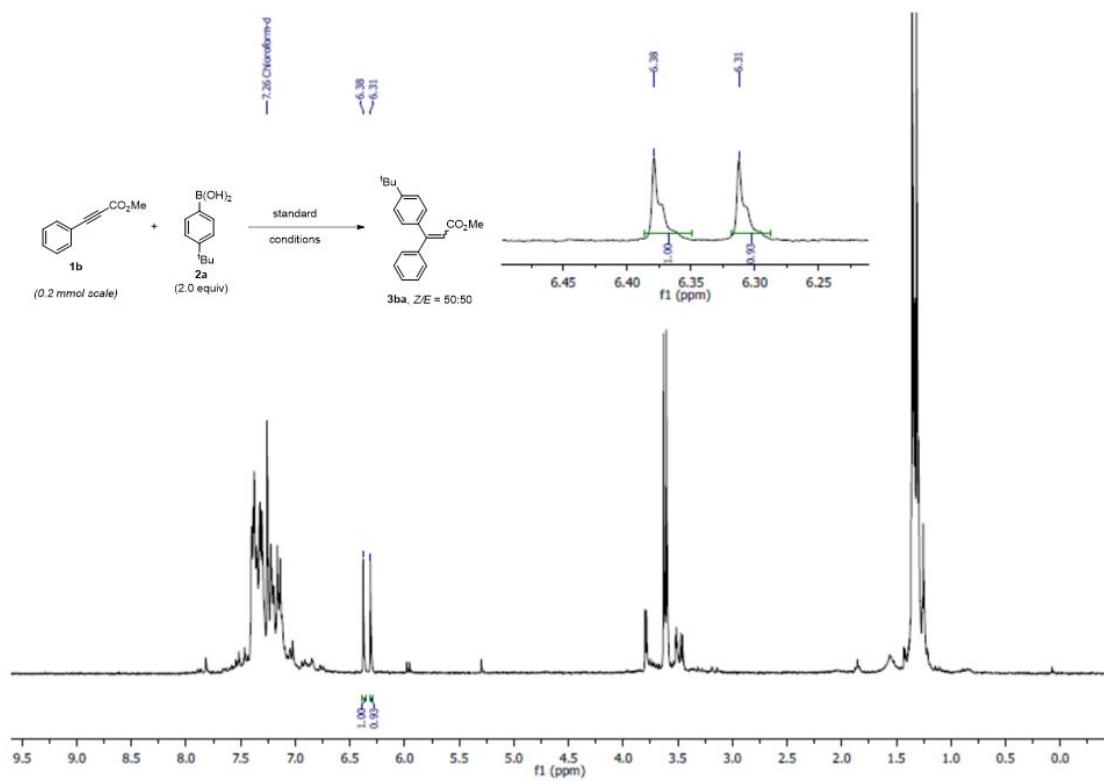


Figure S9. ^1H NMR spectrum (300 MHz, CDCl_3) of the reaction crude between **1b** and **2a**

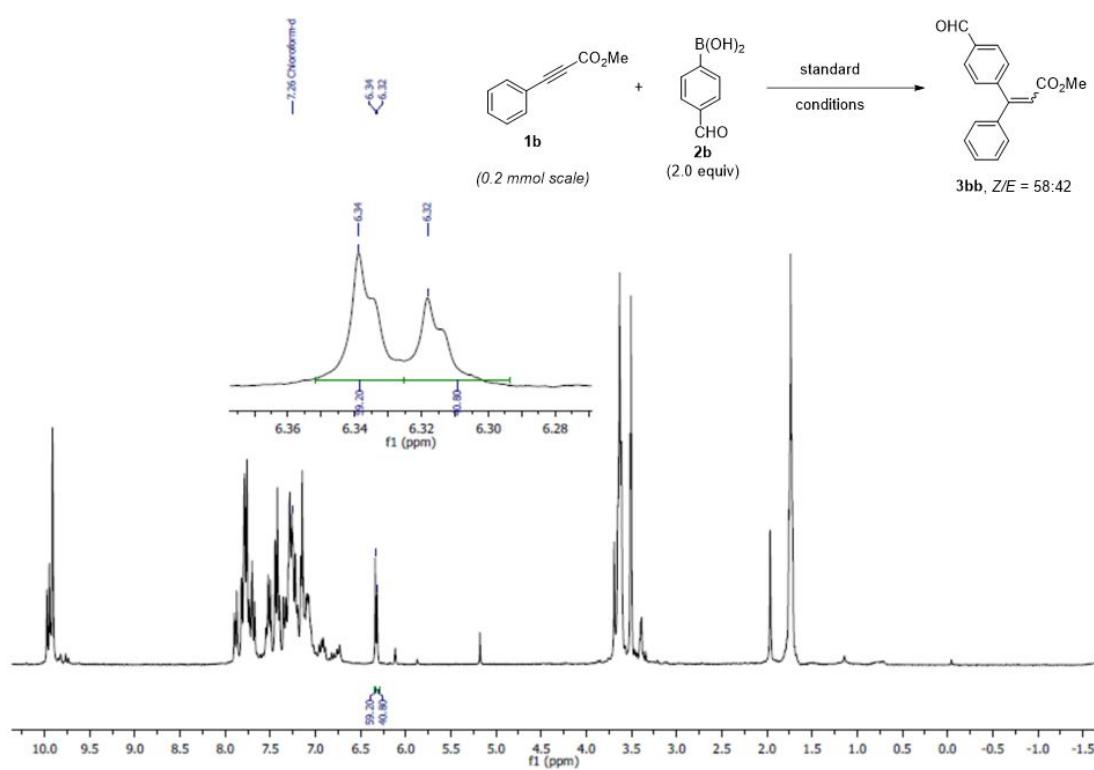


Figure S10. ^1H NMR spectrum (300 MHz, CDCl_3) of the reaction crude between **1b** and **2b**

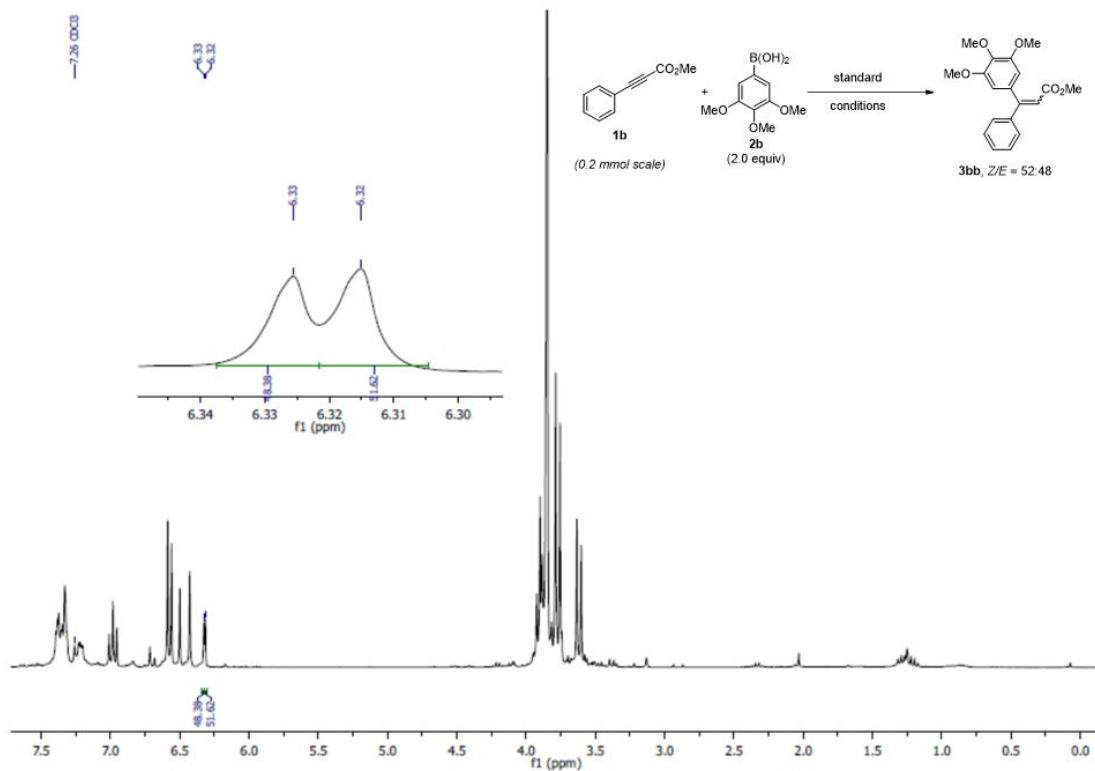


Figure S11. ^1H NMR spectrum (300 MHz, CDCl_3) of the reaction crude between **1b** and **2k**

5 Determination of the stereochemistry

The (*Z*)-configuration of the alkenes was determined performing quantitative nOe experiments. The corresponding correlation between the olefinic and the allylic protons is given in each case:

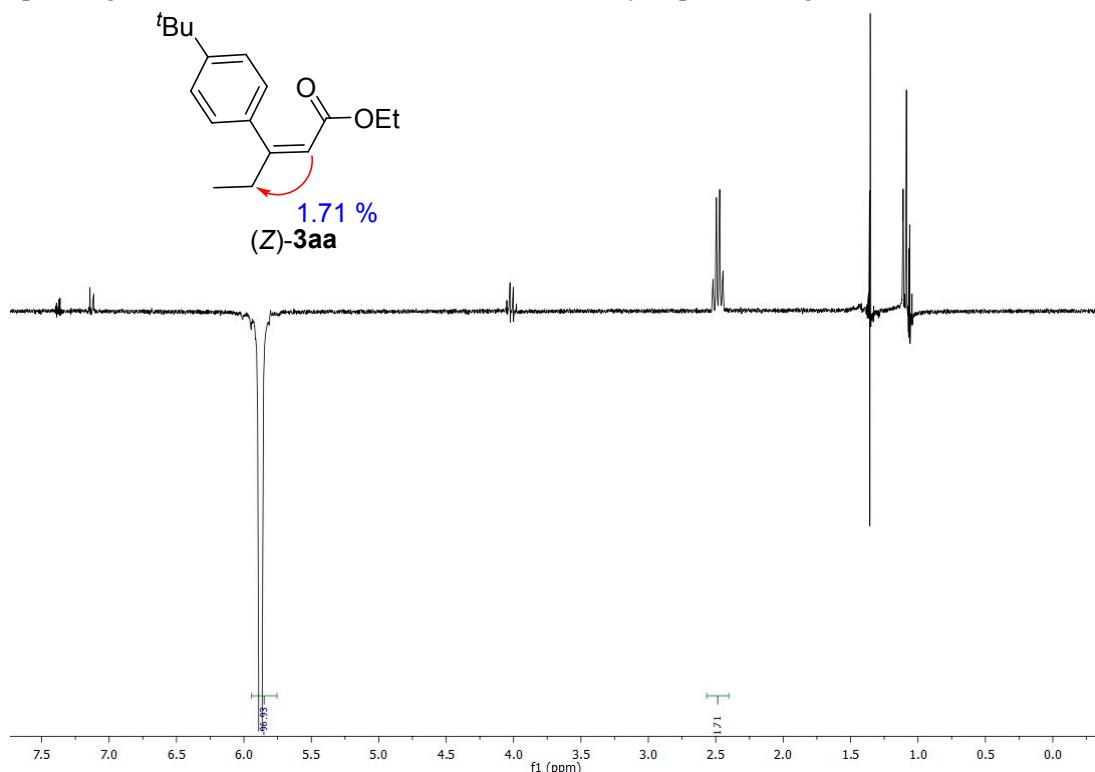


Figure S12. nOe experiment by ¹H NMR (300 MHz, CDCl₃) of (Z)-3aa.

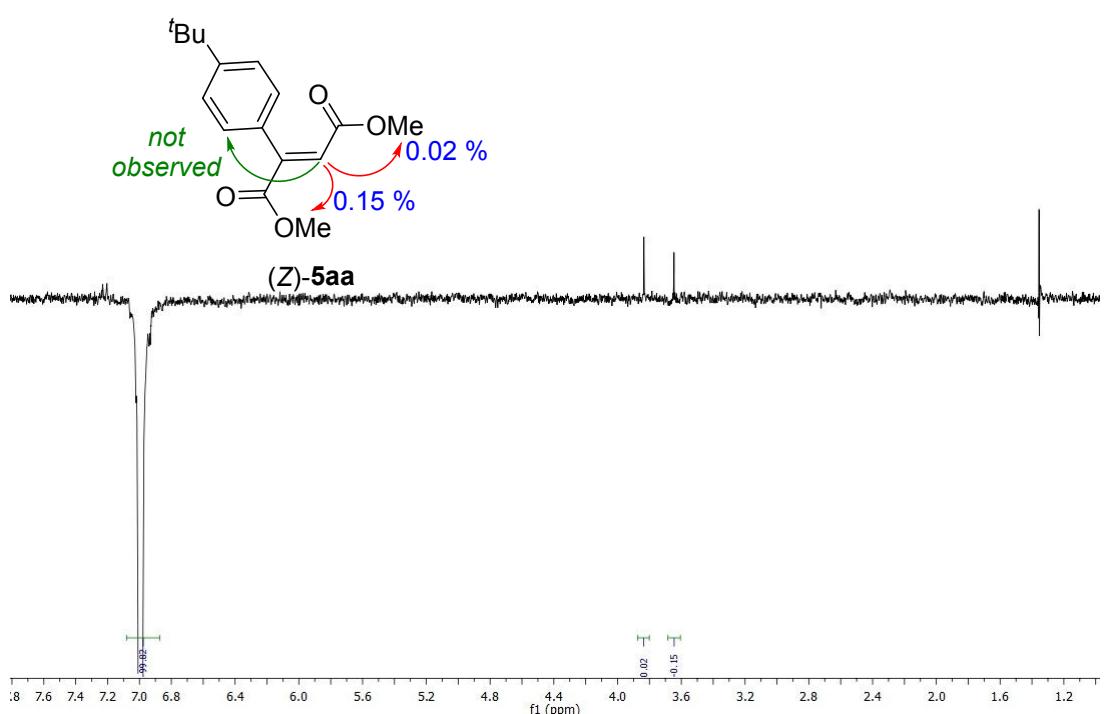


Figure S13. nOe experiment by ¹H NMR (300 MHz, CDCl₃) of (Z)-5aa.

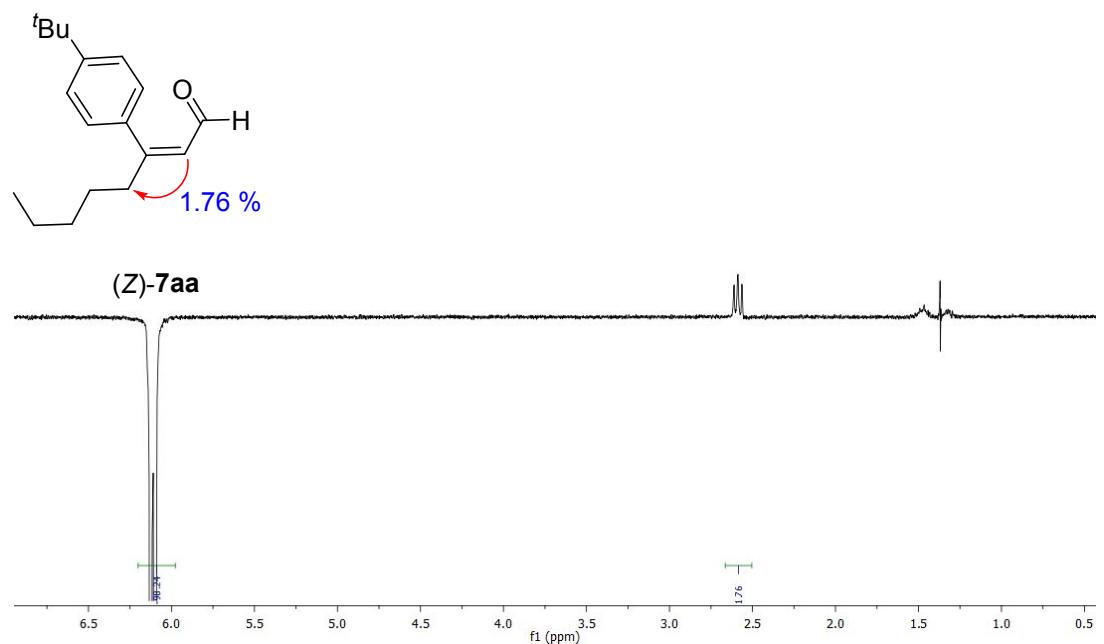


Figure S14. nOe experiment by ¹H NMR (300 MHz, CDCl₃) of (Z)-7aa.

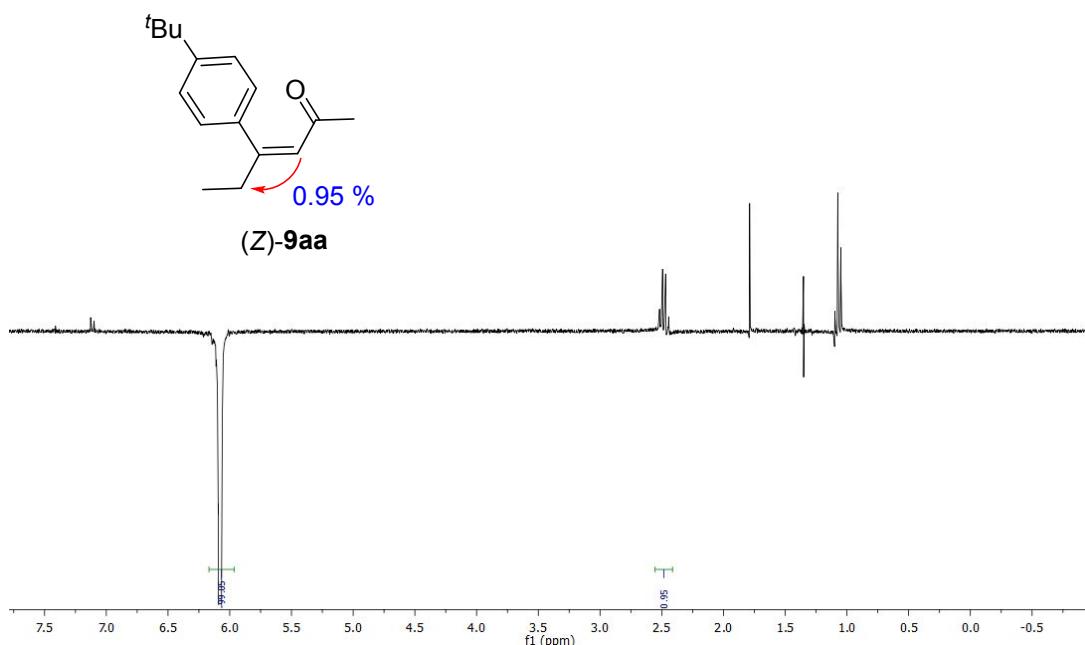


Figure S15. nOe experiment by ^1H NMR (300 MHz, CDCl_3) of (Z)-9aa.

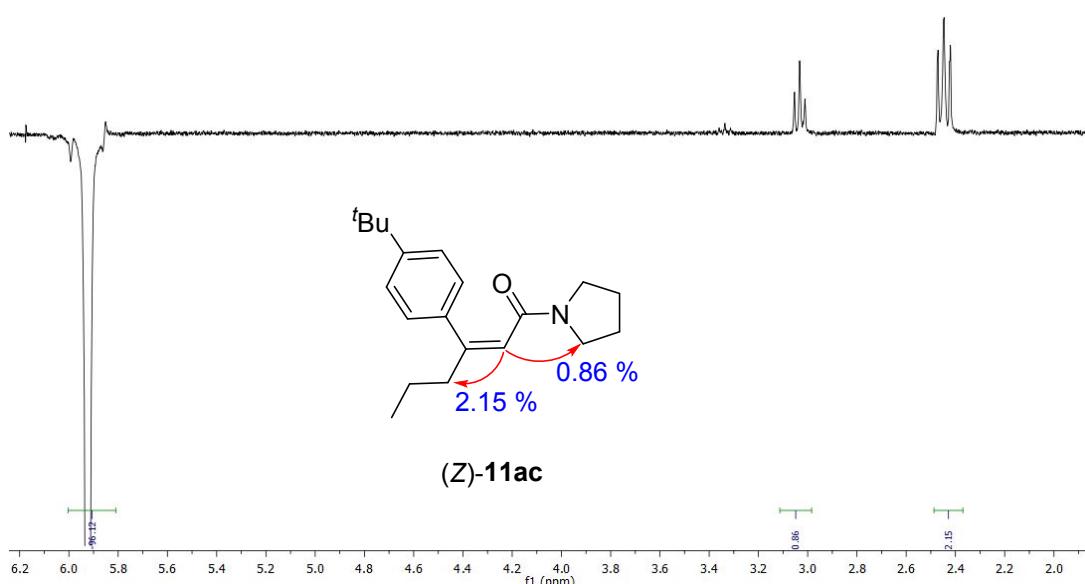


Figure S16. nOe experiment by ^1H NMR (300 MHz, CDCl_3) of (*Z*)-11ac.

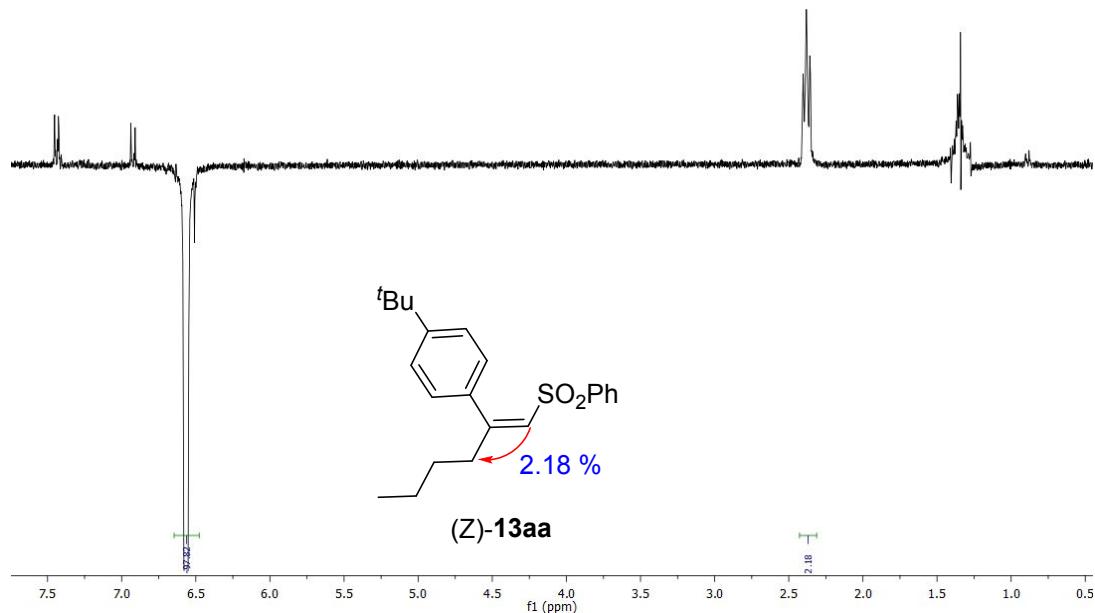


Figure S17. nOe experiment by ^1H NMR (300 MHz, CDCl_3) of (Z)-13aa.

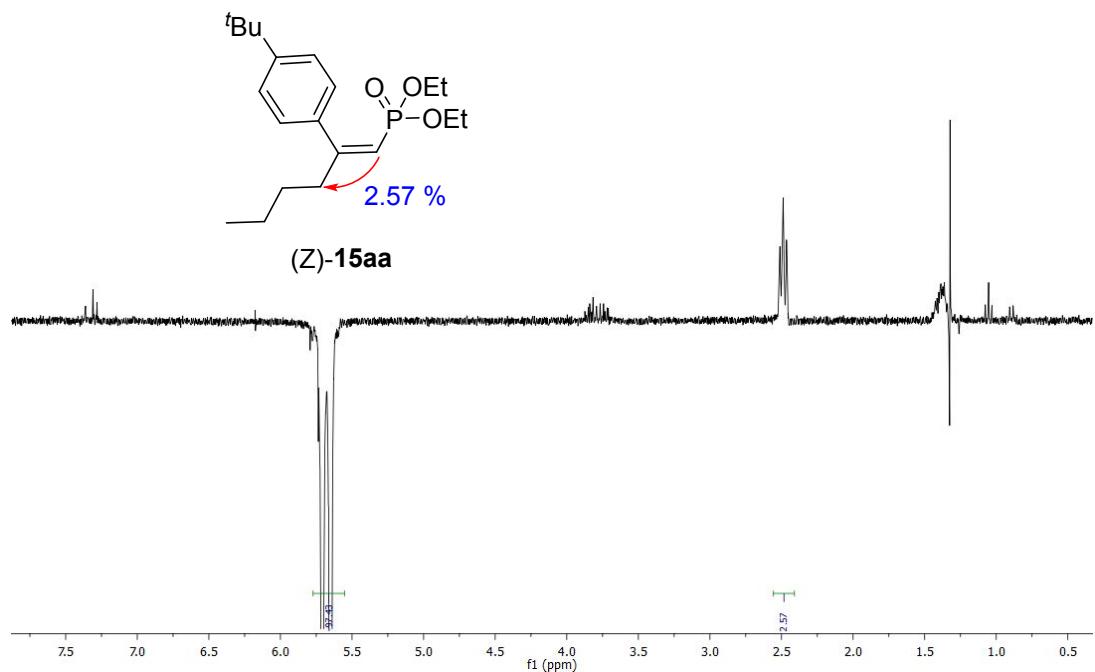


Figure S18. nOe experiment by ^1H NMR (300 MHz, CDCl_3) of (Z)-15aa.

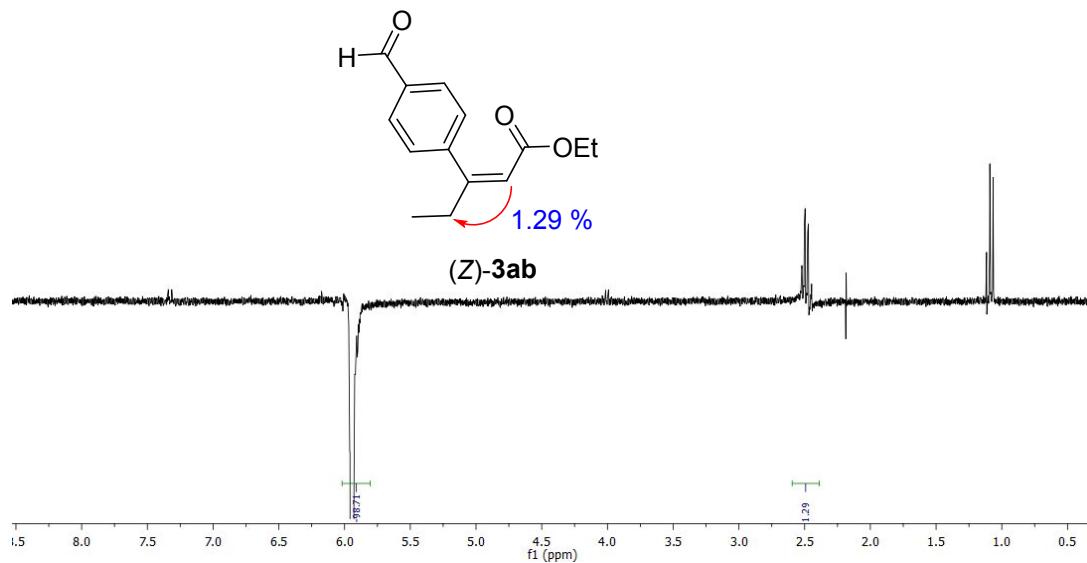


Figure S19. nOe experiment by ^1H NMR (300 MHz, CDCl_3) of (Z)-3ab.

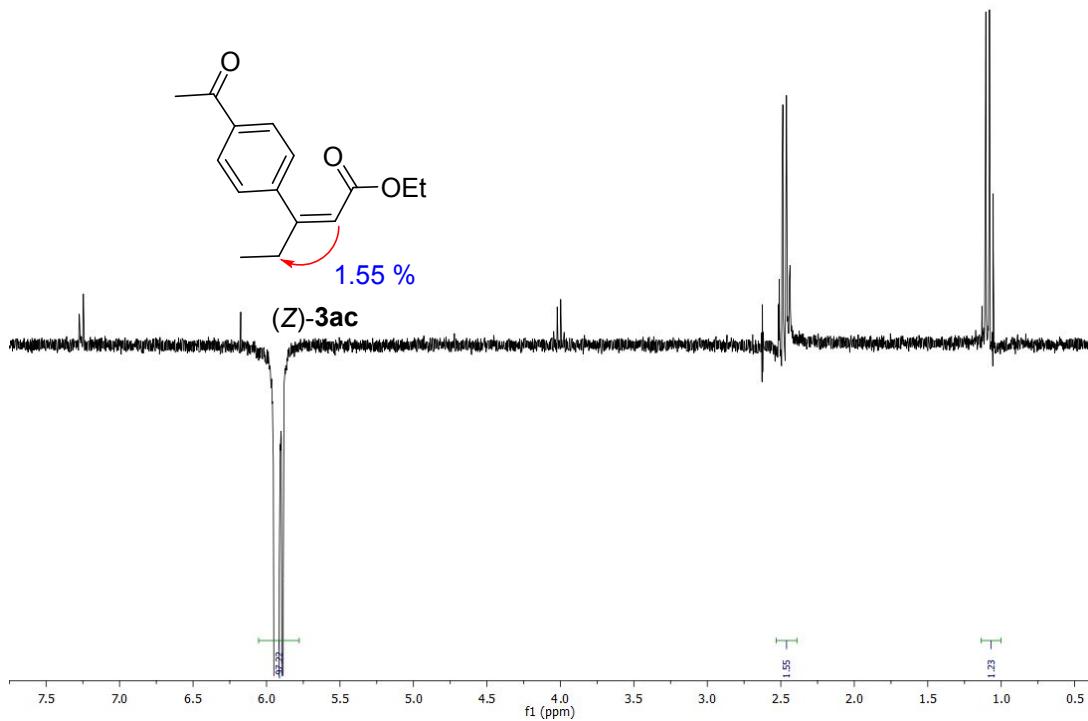


Figure S20. nOe experiment by ^1H NMR (300 MHz, CDCl_3) of (Z)-3ac.

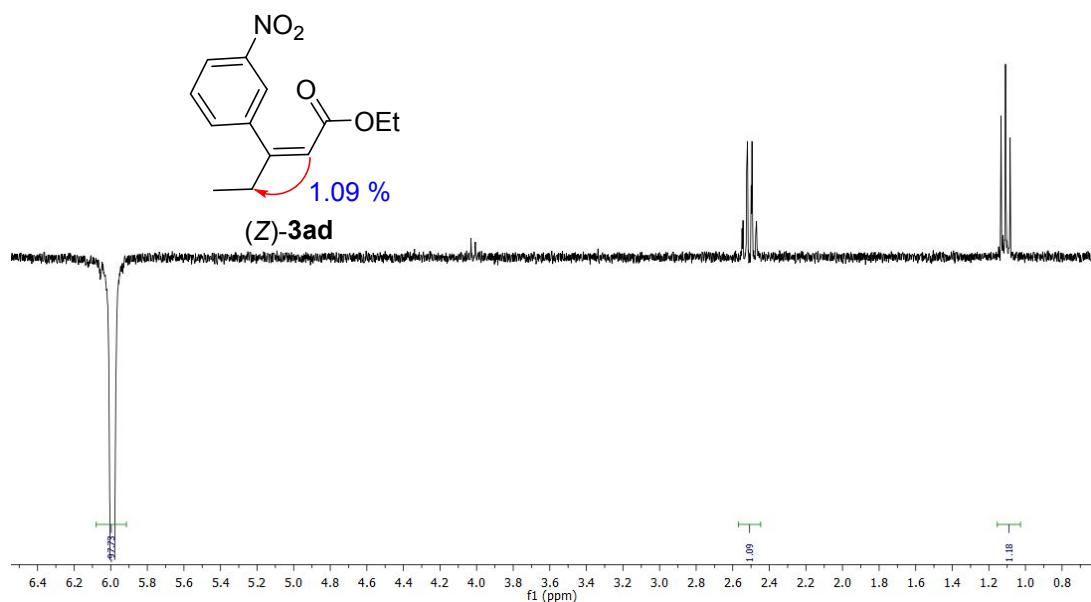


Figure S21. nOe experiment by ¹H NMR (300 MHz, CDCl₃) of (Z)-3ad.

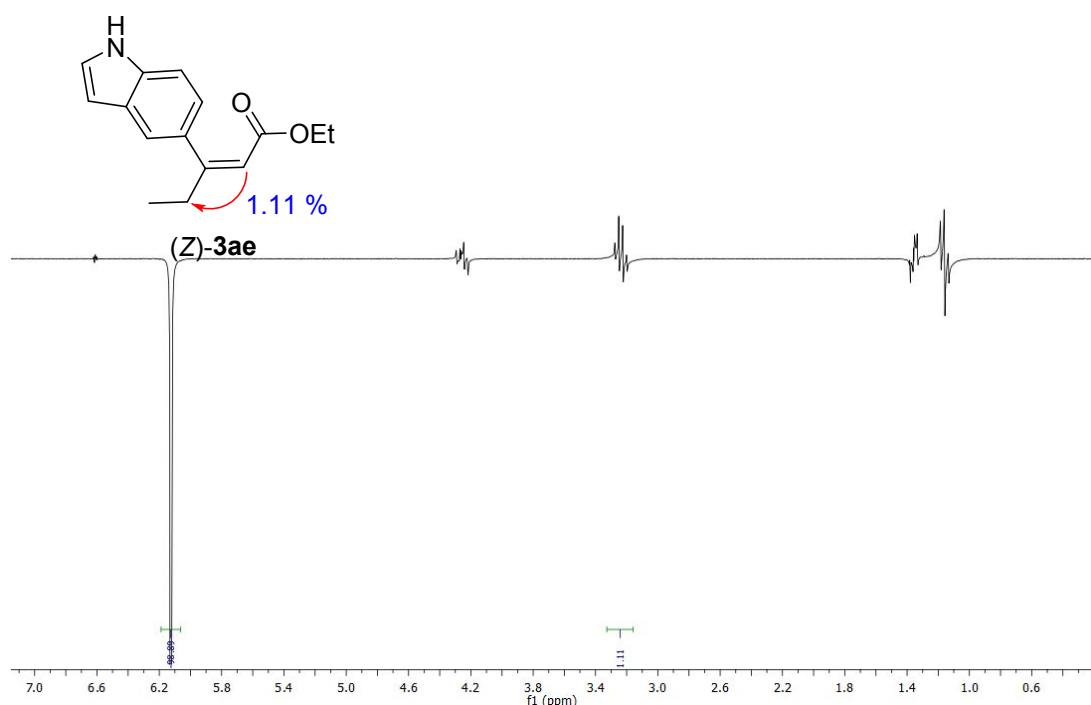


Figure S22. nOe experiment by ¹H NMR (300 MHz, CDCl₃) of (Z)-3ae.

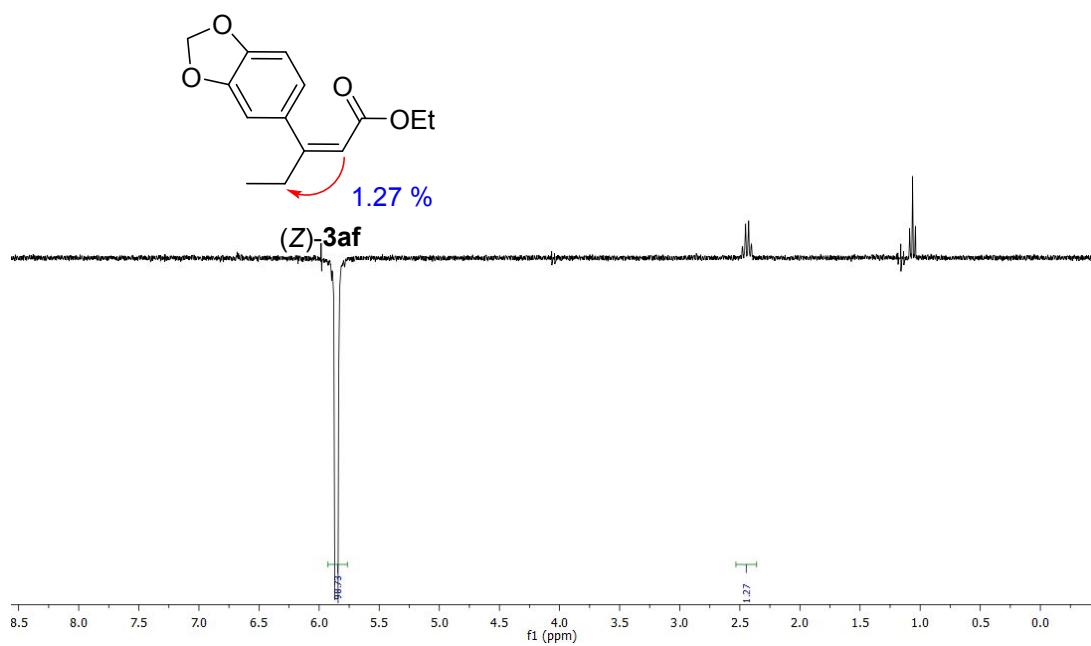


Figure S23. nOe experiment by ^1H NMR (300 MHz, CDCl_3) of $(\text{Z})\text{-3af}$.

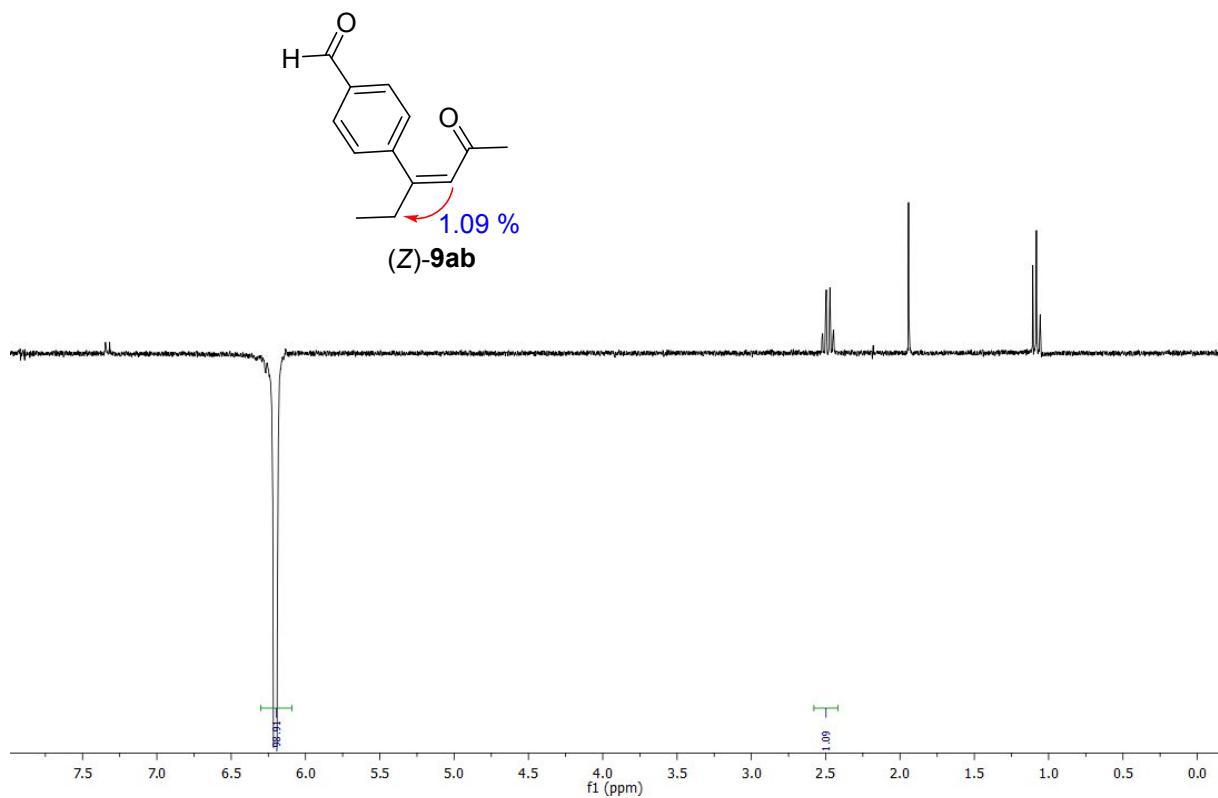


Figure S24. nOe experiment by ^1H NMR (300 MHz, CDCl_3) of $(\text{Z})\text{-9ab}$.

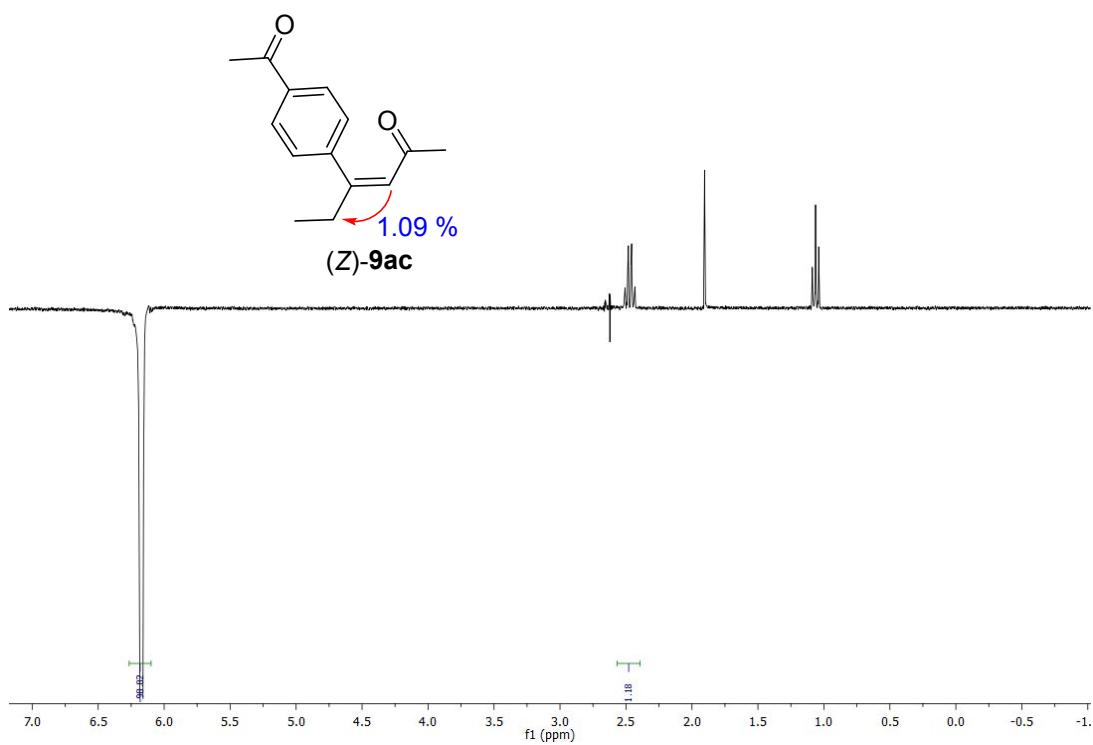


Figure S25. nOe experiment by ^1H NMR (300 MHz, CDCl_3) of $(\text{Z})\text{-9ac}$.

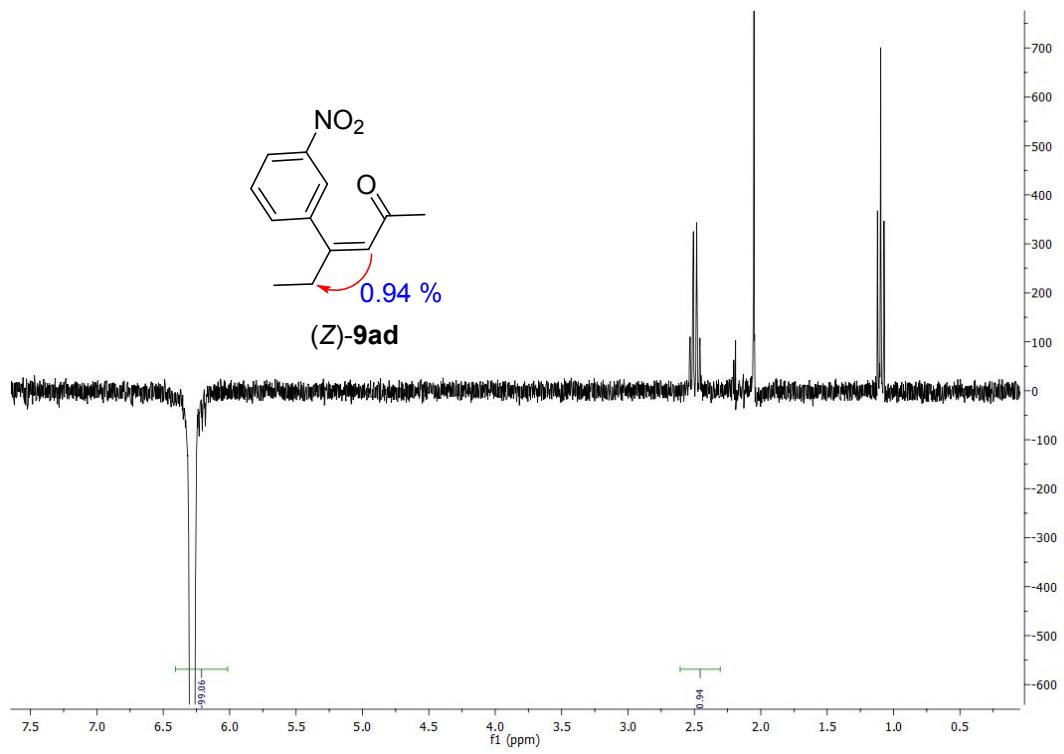


Figure S26. nOe experiment by ^1H NMR (300 MHz, CDCl_3) of $(\text{Z})\text{-9ad}$.

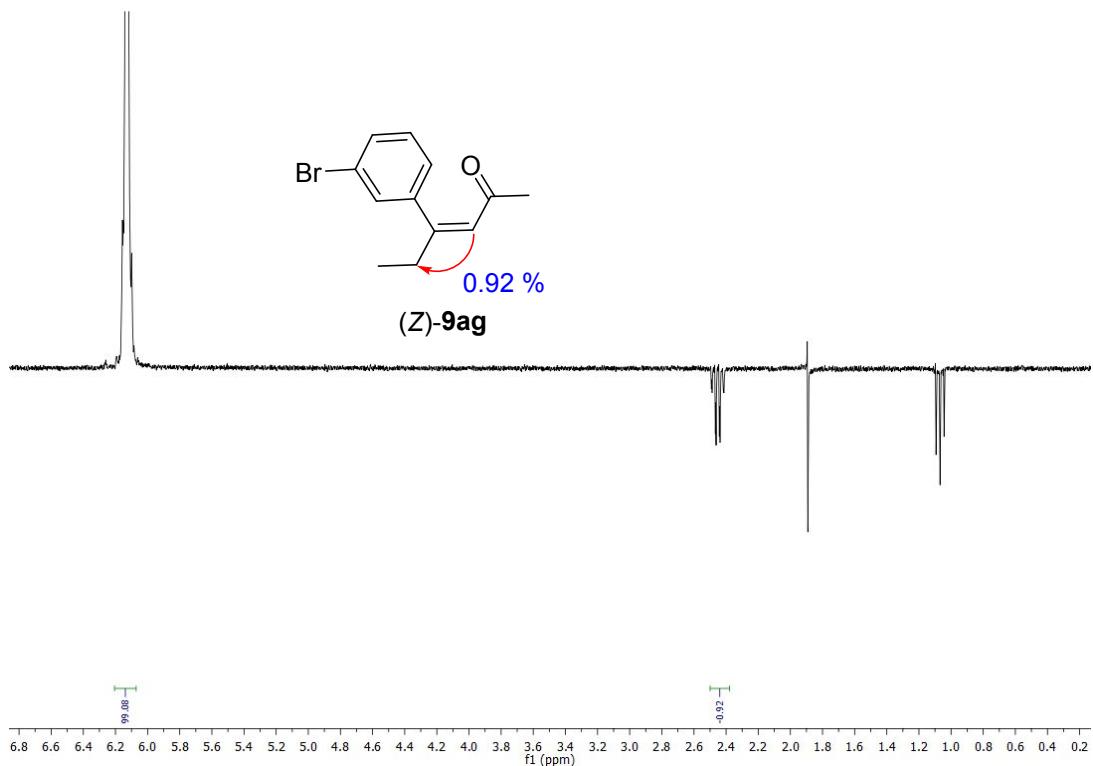


Figure S27. nOe experiment by ^1H NMR (300 MHz, CDCl_3) of (Z)-9ag.

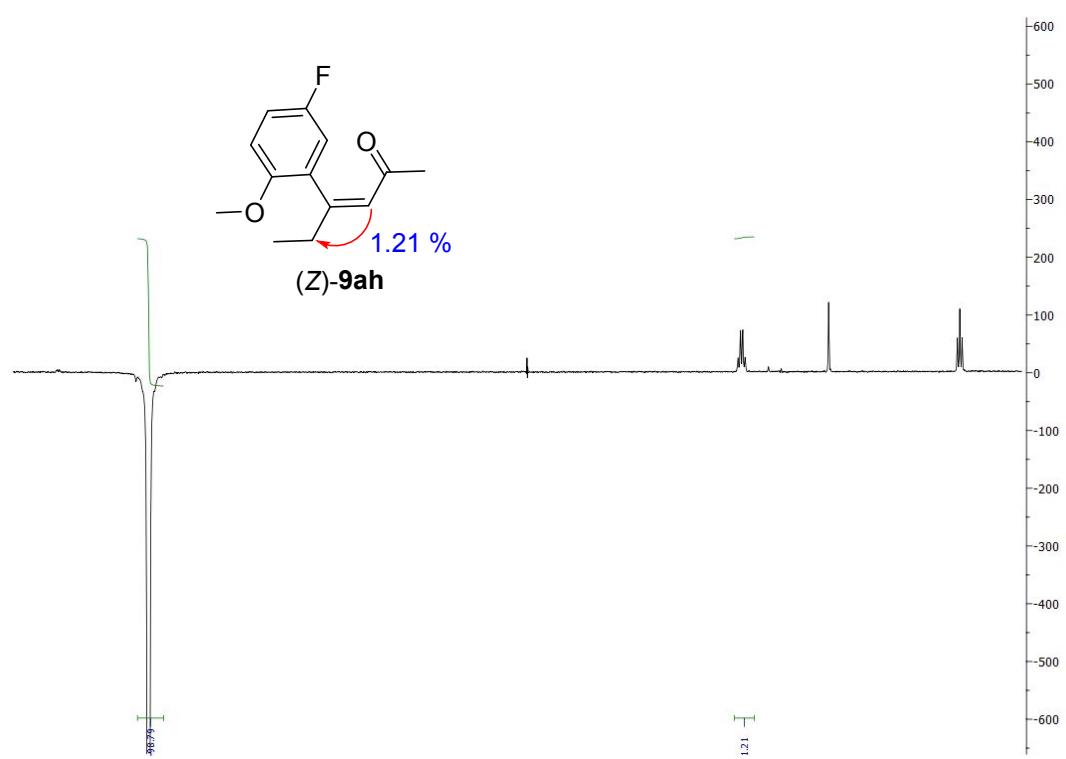


Figure S28. nOe experiment by ^1H NMR (300 MHz, CDCl_3) of (Z)-9ah.

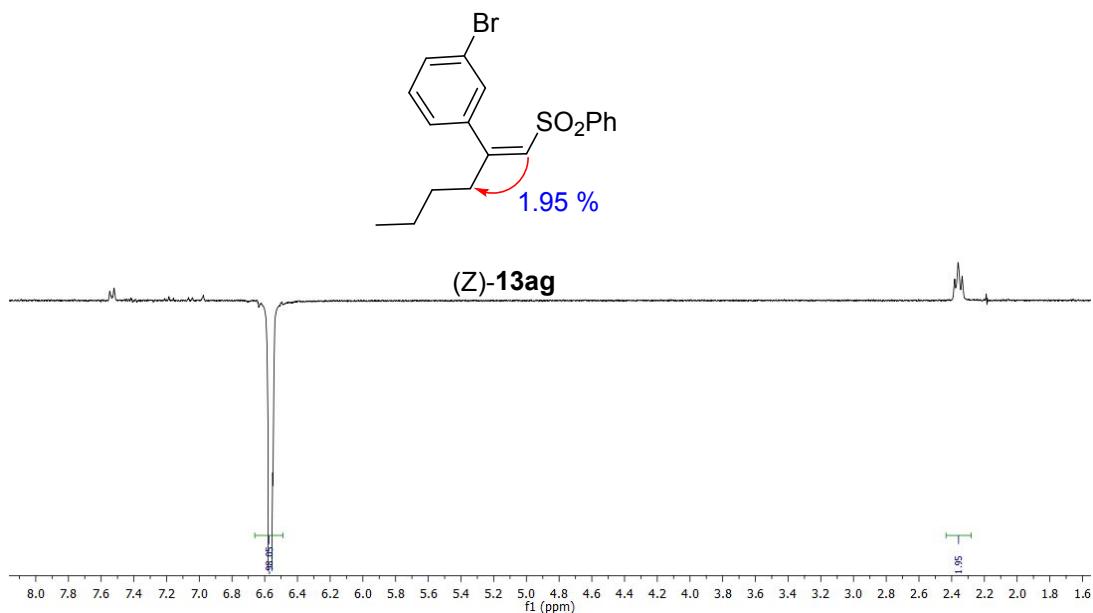


Figure S29. nOe experiment by ^1H NMR (300 MHz, CDCl_3) of (Z)-13ag.

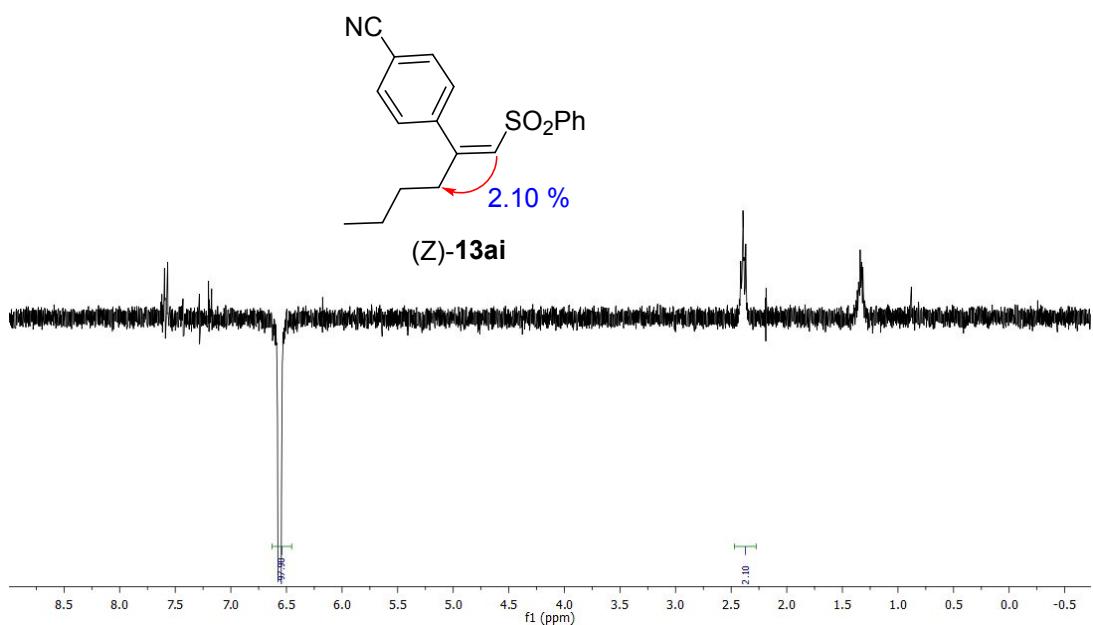


Figure S30. nOe experiment by ^1H NMR (300 MHz, CDCl_3) of (Z)-13ai.

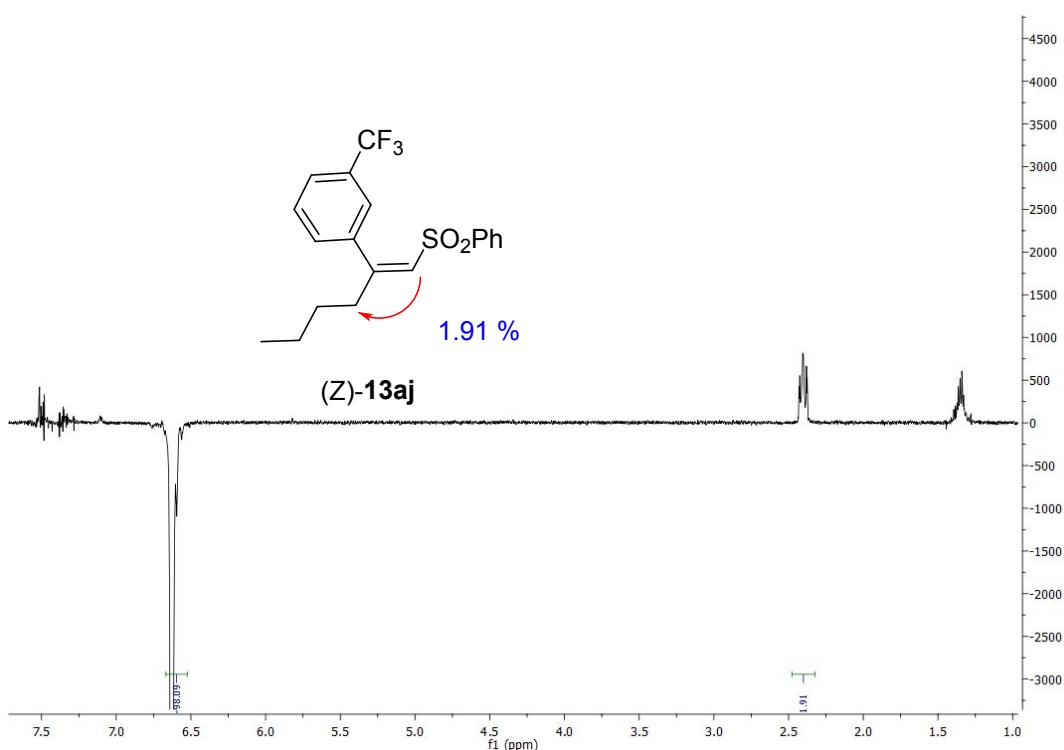


Figure S31. nOe experiment by ^1H NMR (300 MHz, CDCl_3) of **(Z)-13aj**.

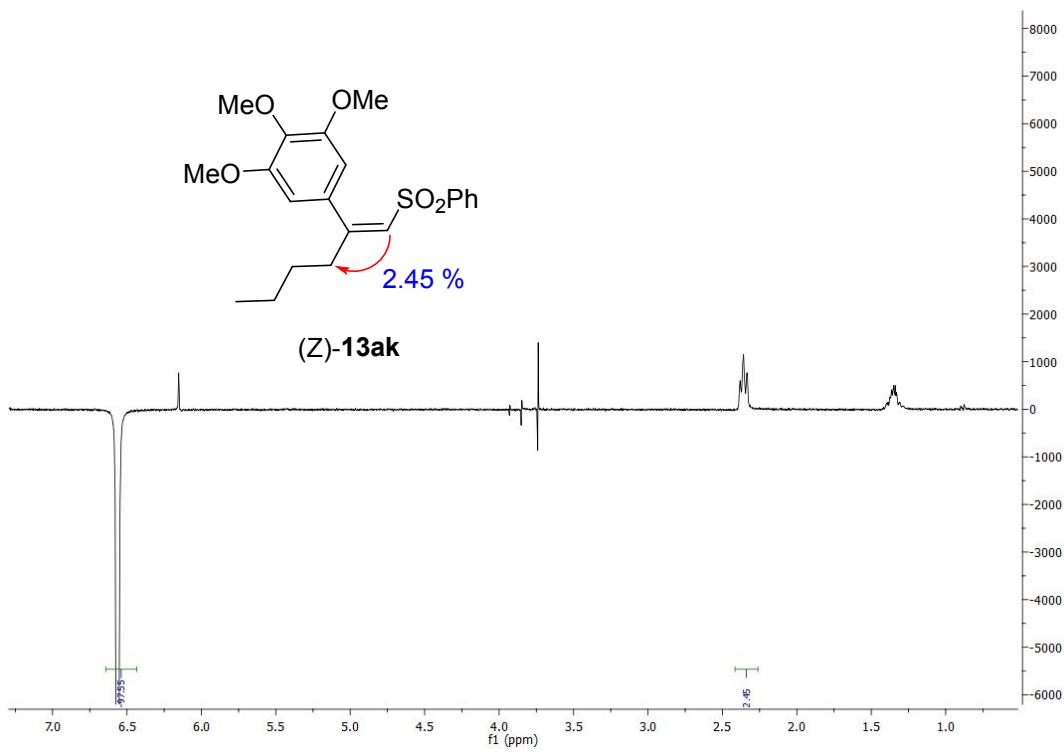


Figure S32. nOe experiment by ^1H NMR (300 MHz, CDCl_3) of **(Z)-13ak**.

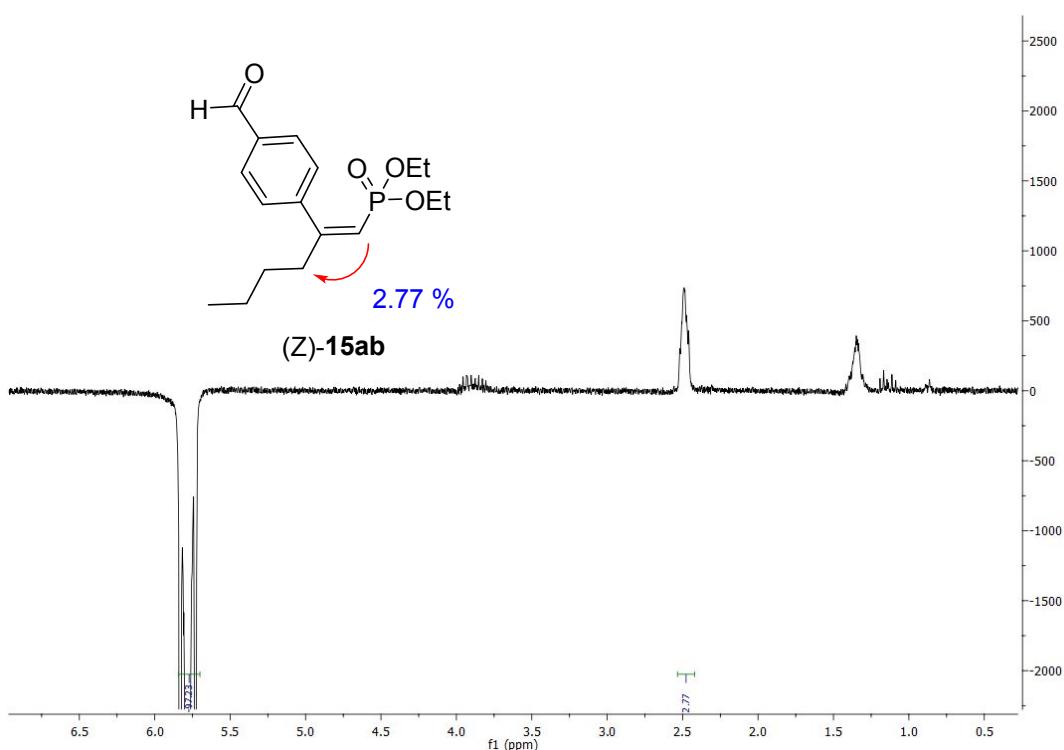


Figure S33. nOe experiment by ^1H NMR (300 MHz, CDCl_3) of **(Z)-15ab**.

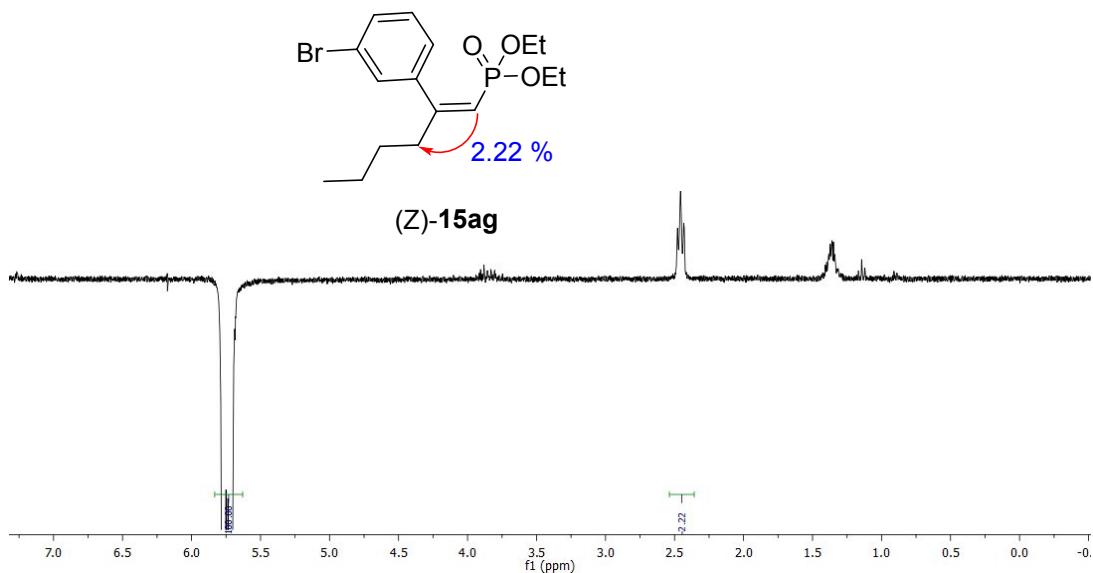


Figure S34. nOe experiment by ^1H NMR (300 MHz, CDCl_3) of **(Z)-15ag**.

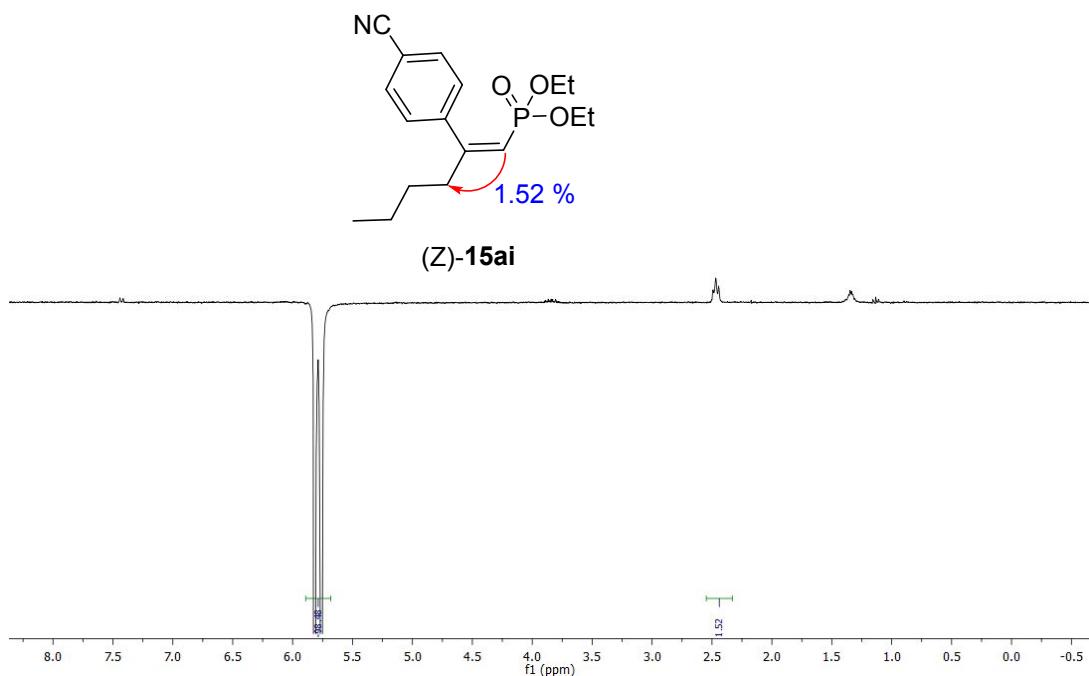


Figure S35. nOe experiment by ^1H NMR (300 MHz, CDCl_3) of (Z)-15ai.

6 References

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7 NMR spectra

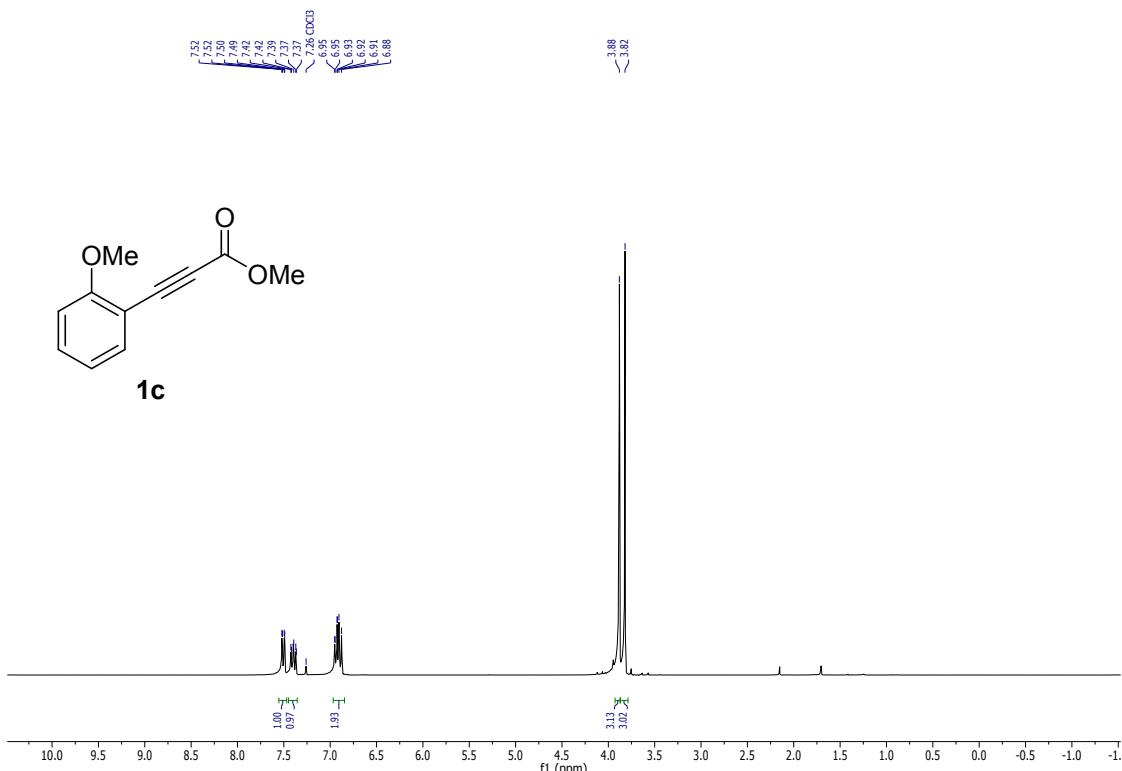


Figure S37. ¹H NMR (300 MHz, CDCl₃) of **1c**.

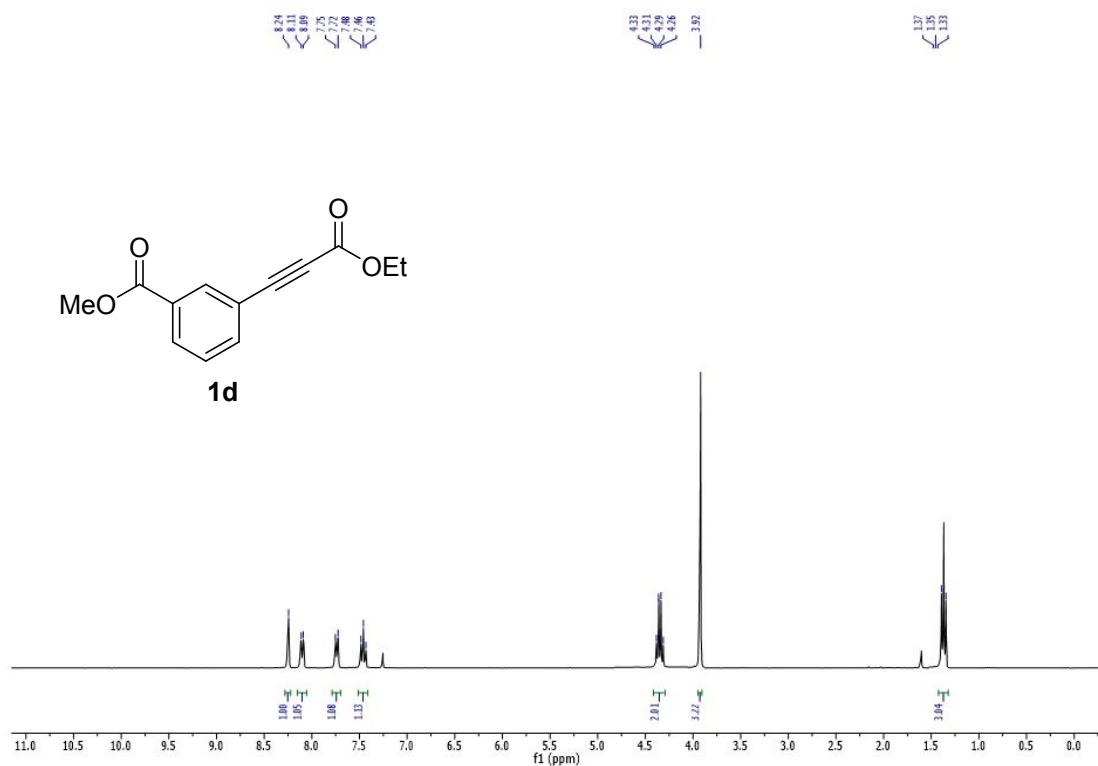


Figure S37. ¹H NMR (300 MHz, CDCl₃) of **1c**.

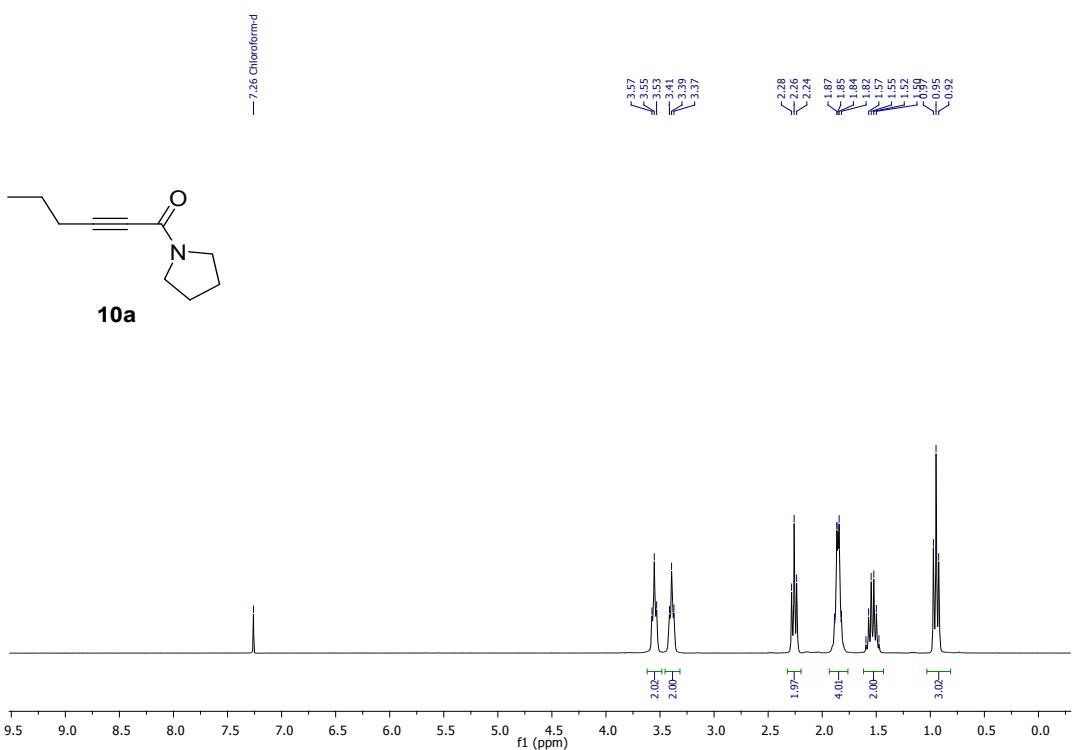


Figure S37. ^1H NMR (300 MHz, CDCl_3) of **10a**.

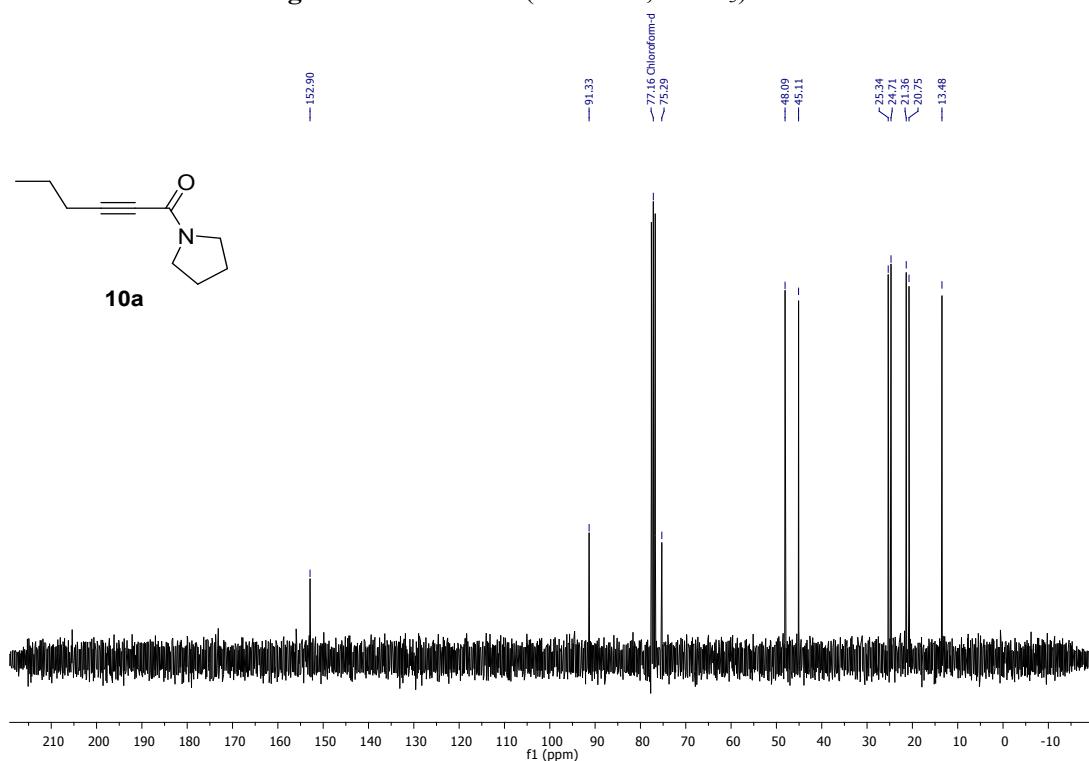


Figure S38. ^{13}C NMR (75 MHz, CDCl_3) of **10a**

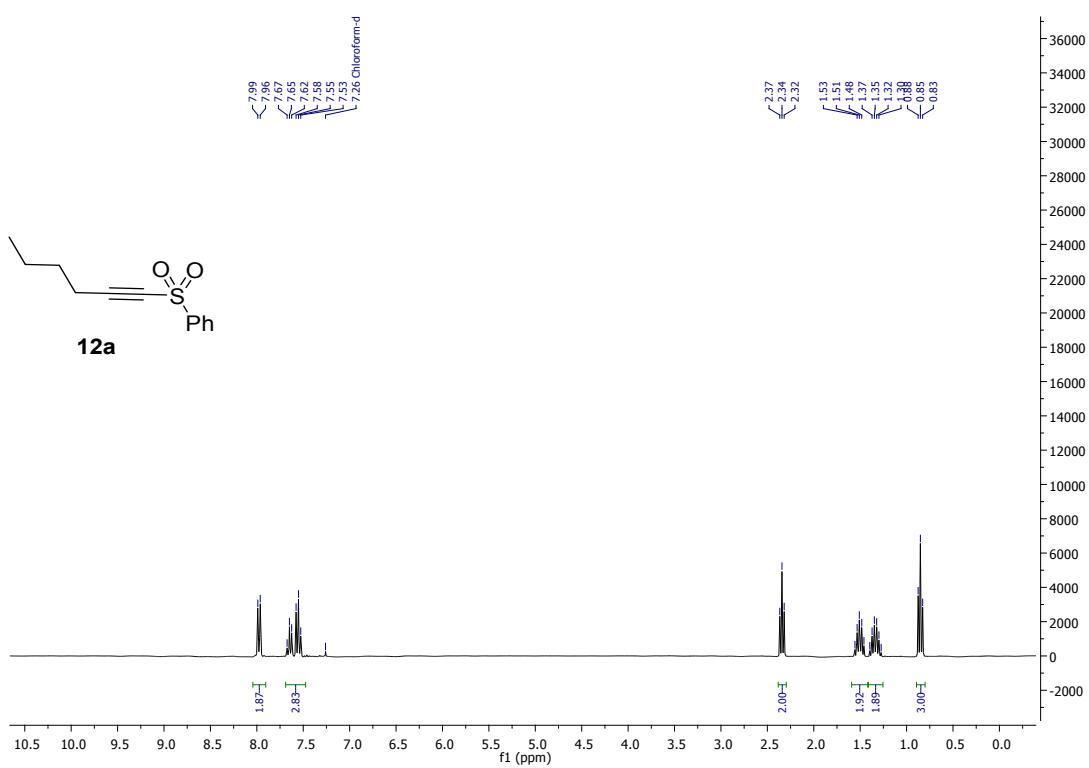


Figure S39. ^1H NMR (300 MHz, CDCl_3) of **12a**.

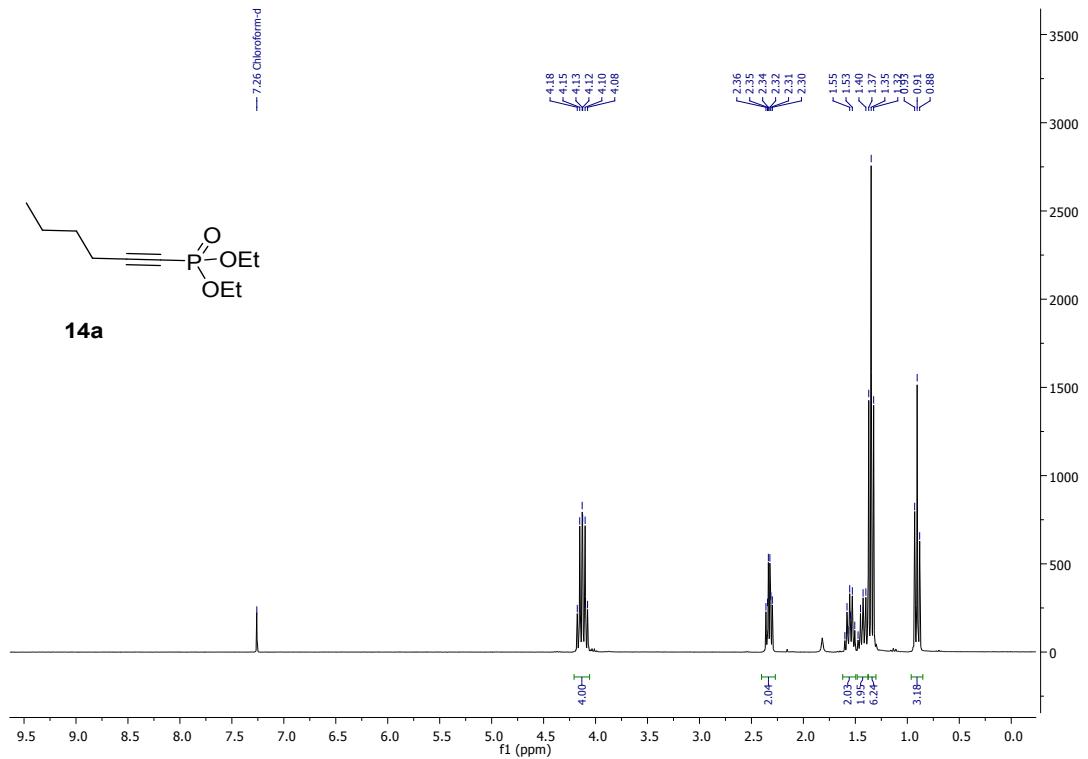


Figure S39. ^1H NMR (300 MHz, CDCl_3) of **14a**.

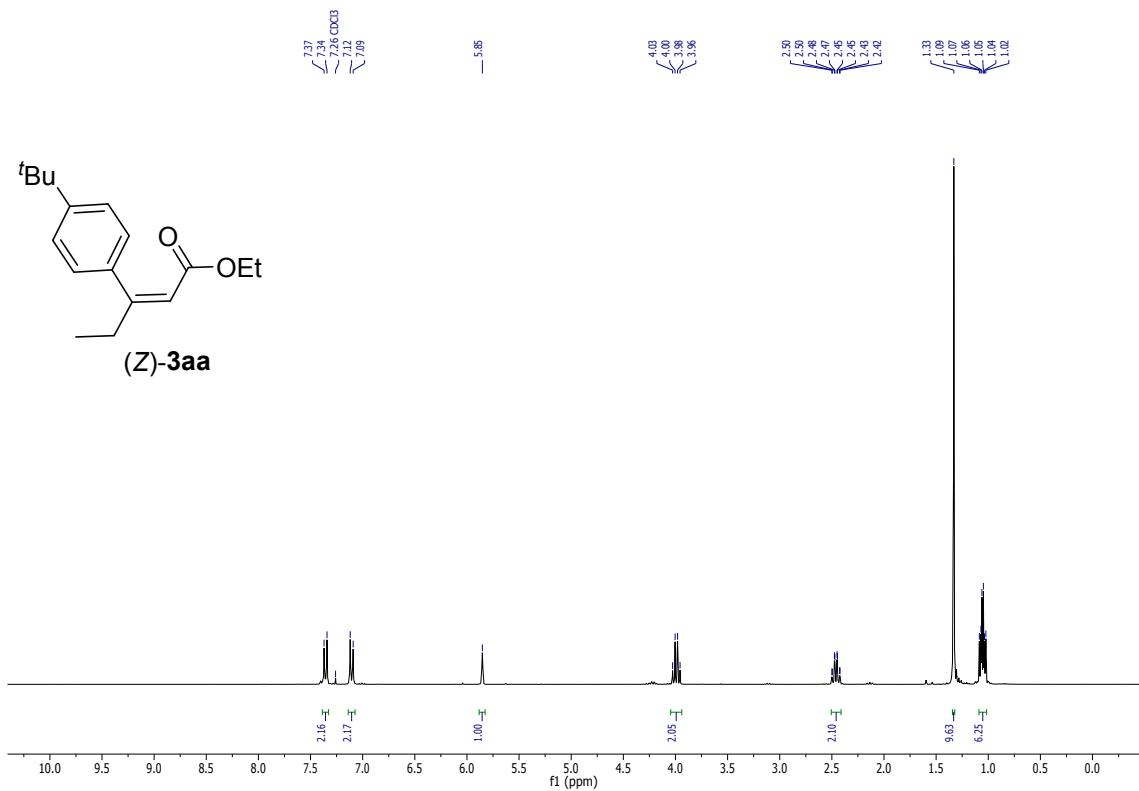


Figure S40. ¹H NMR (300 MHz, CDCl₃) of (Z)-3aa.

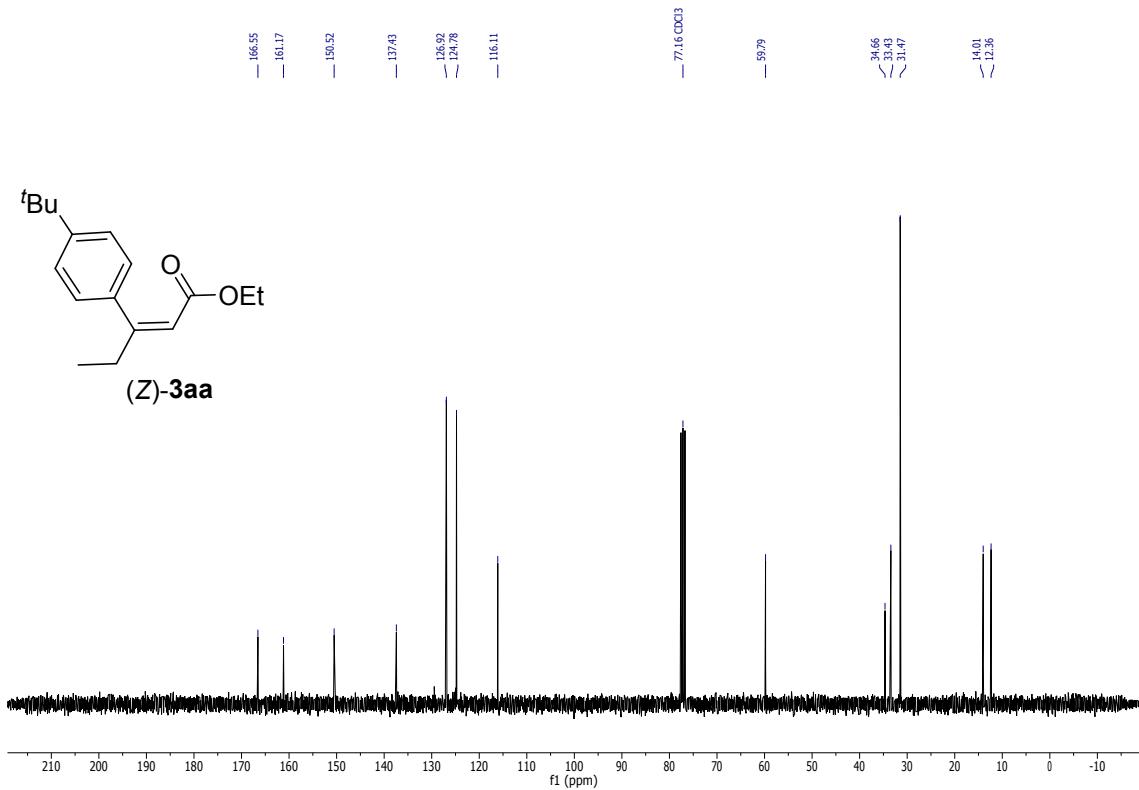


Figure S41. ¹³C NMR (75 MHz, CDCl₃) of (Z)-3aa.

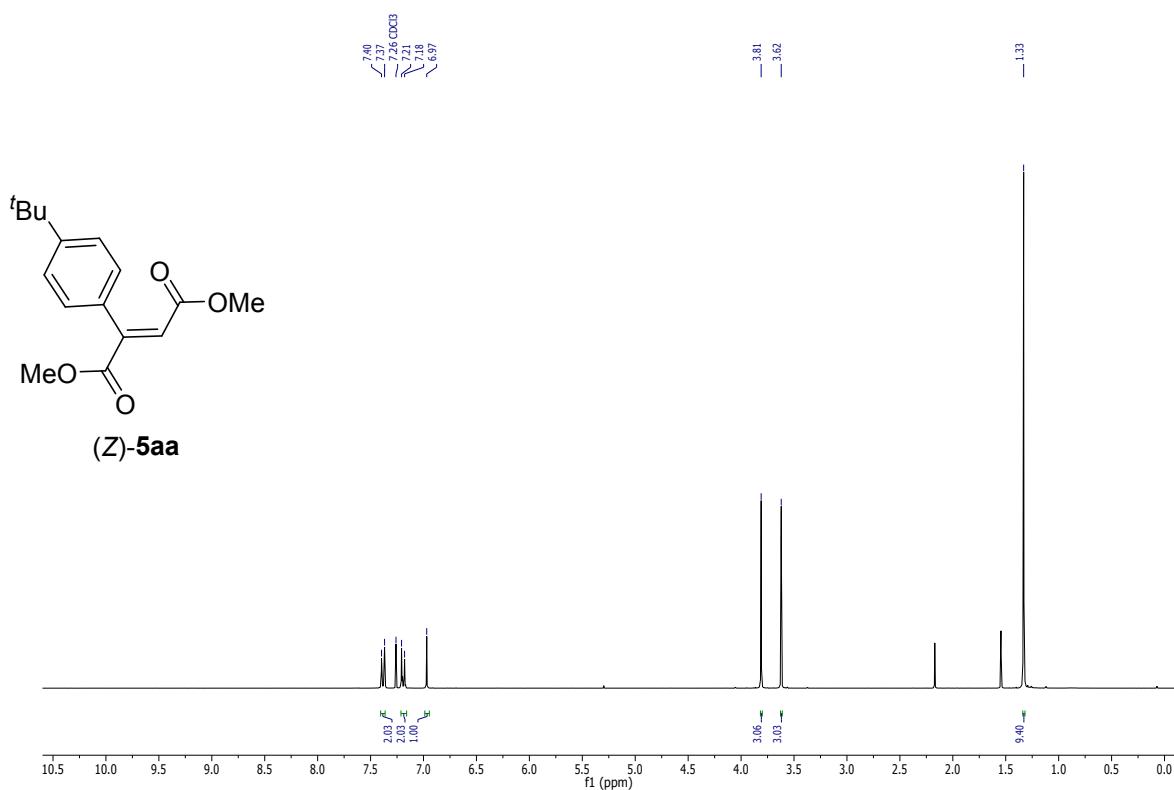


Figure S42. ¹H NMR (300 MHz, CDCl₃) of (Z)-5aa.

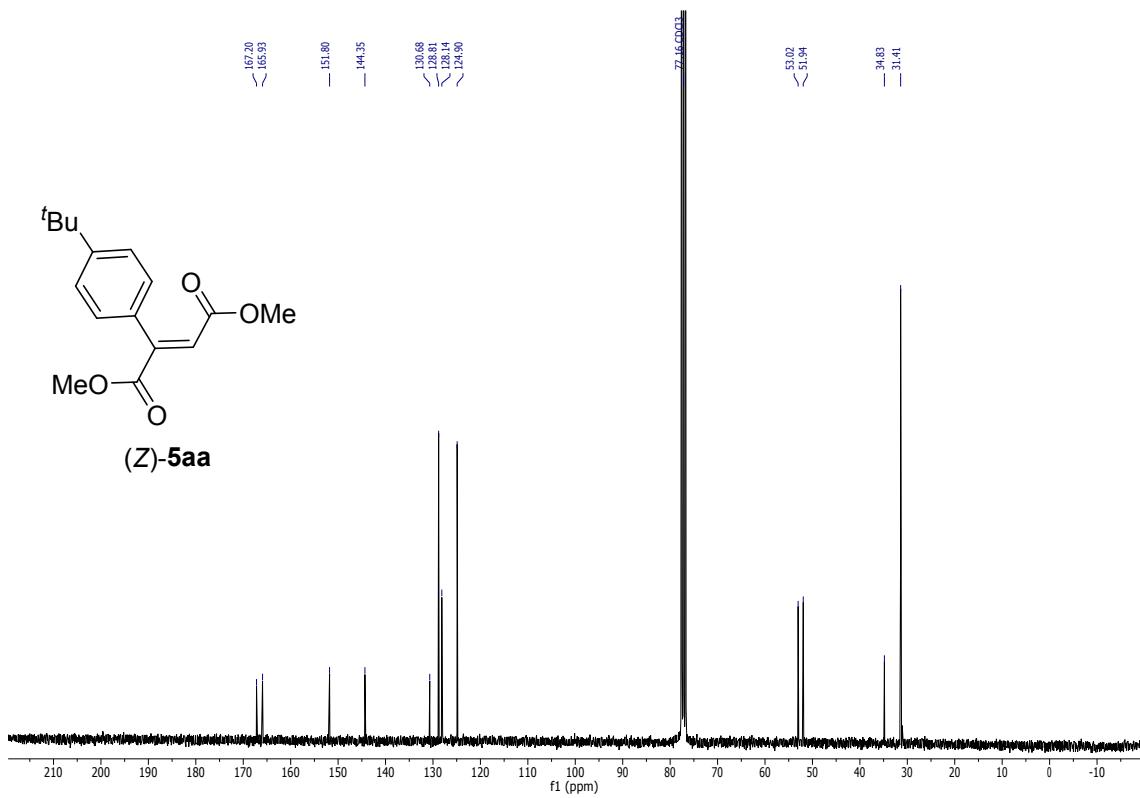


Figure S43. ¹³C NMR (75 MHz, CDCl₃) of (Z)-5aa.

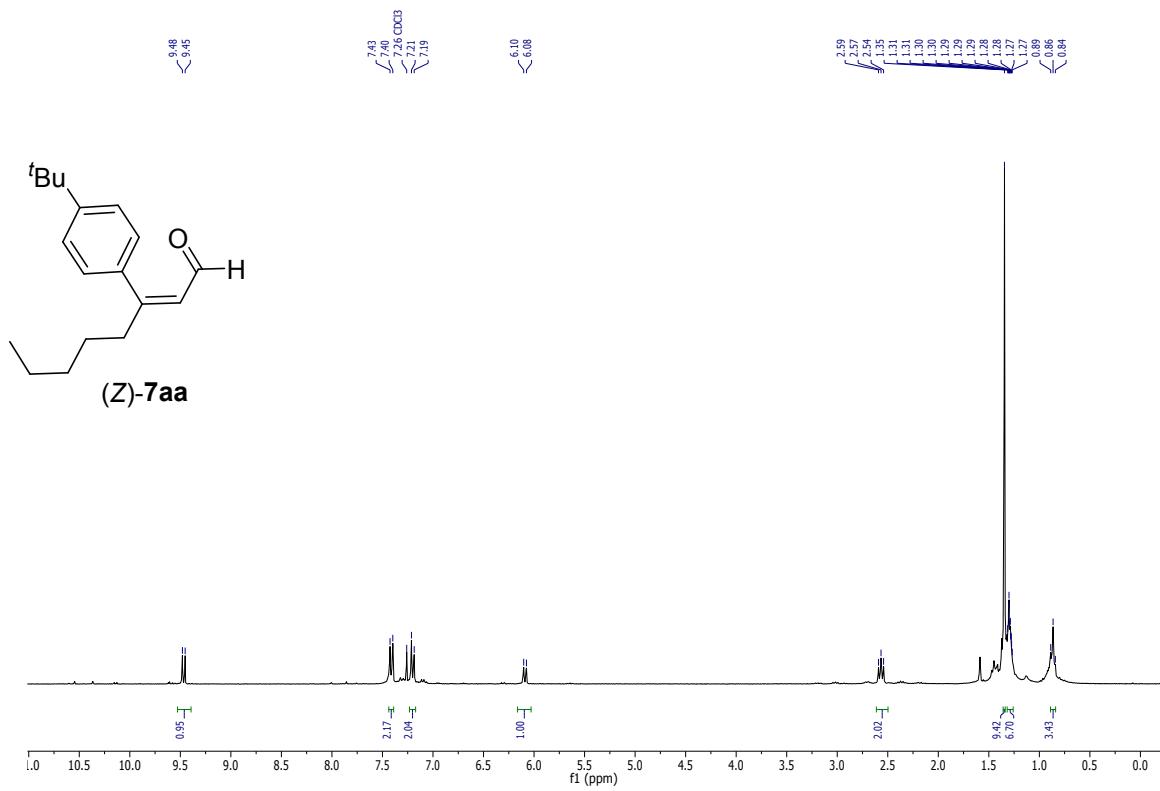


Figure S44. ^1H NMR (300 MHz, CDCl_3) of (Z)-7aa.

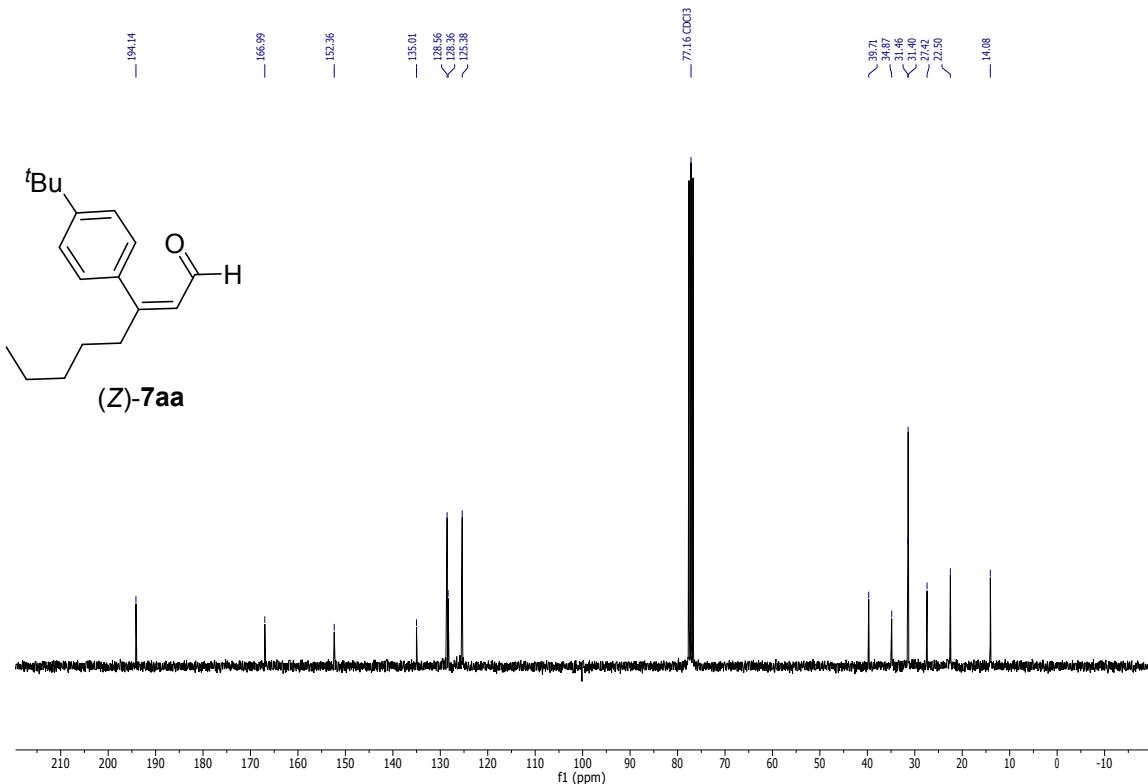


Figure S45. ^{13}C NMR (75 MHz, CDCl_3) of (Z)-7aa.

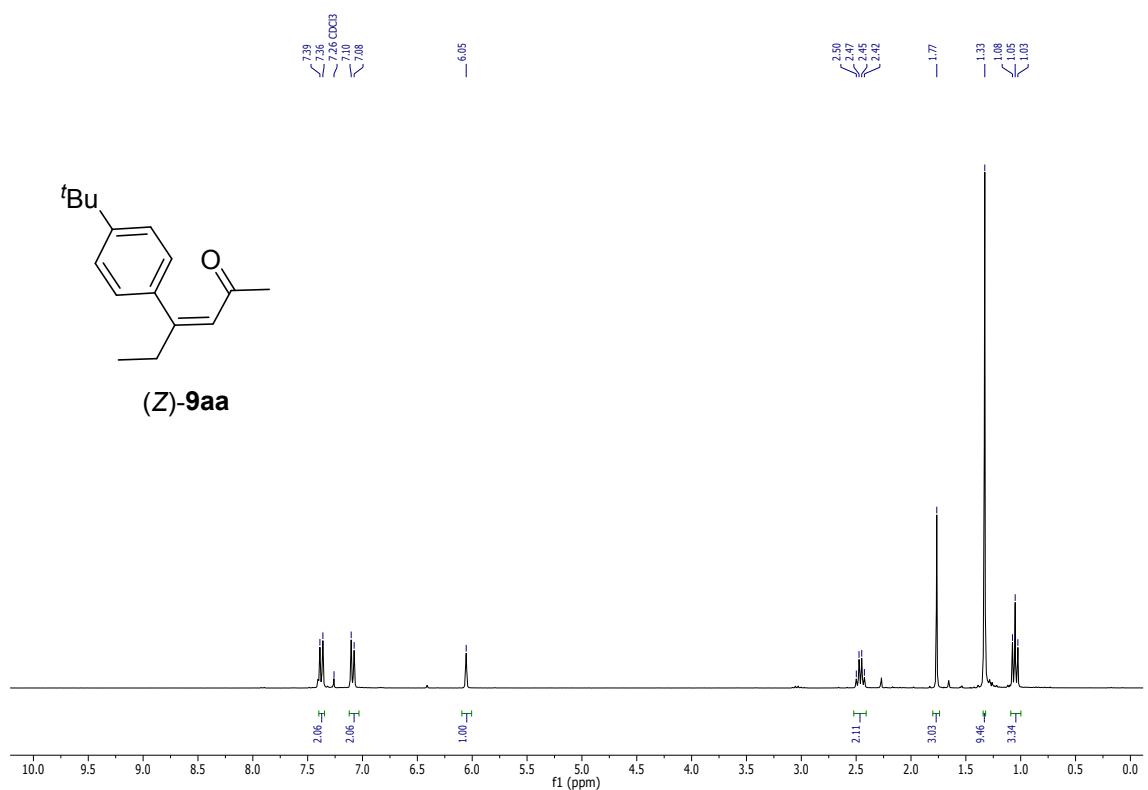


Figure S46. ¹H NMR (300 MHz, CDCl₃) of (Z)-9aa.

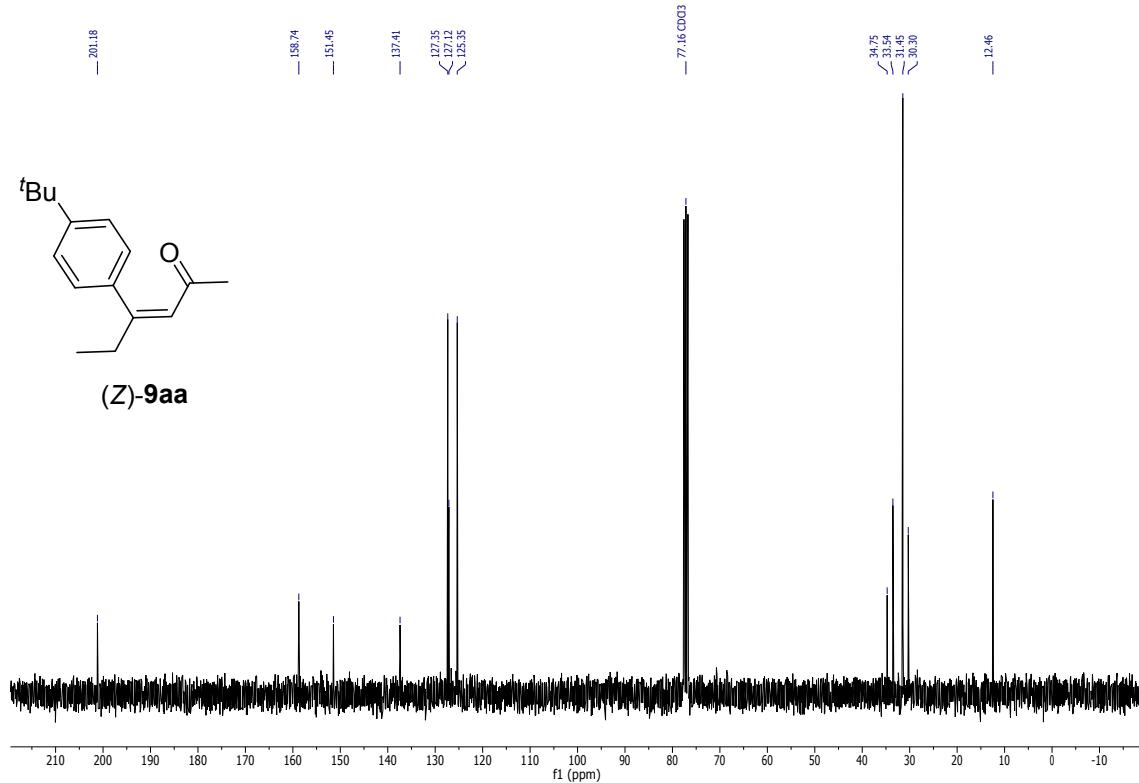


Figure S47. ¹³C NMR (75 MHz, CDCl₃) of (Z)-9aa.



Figure S48. ^1H NMR (300 MHz, CDCl_3) of (Z)-11aa.

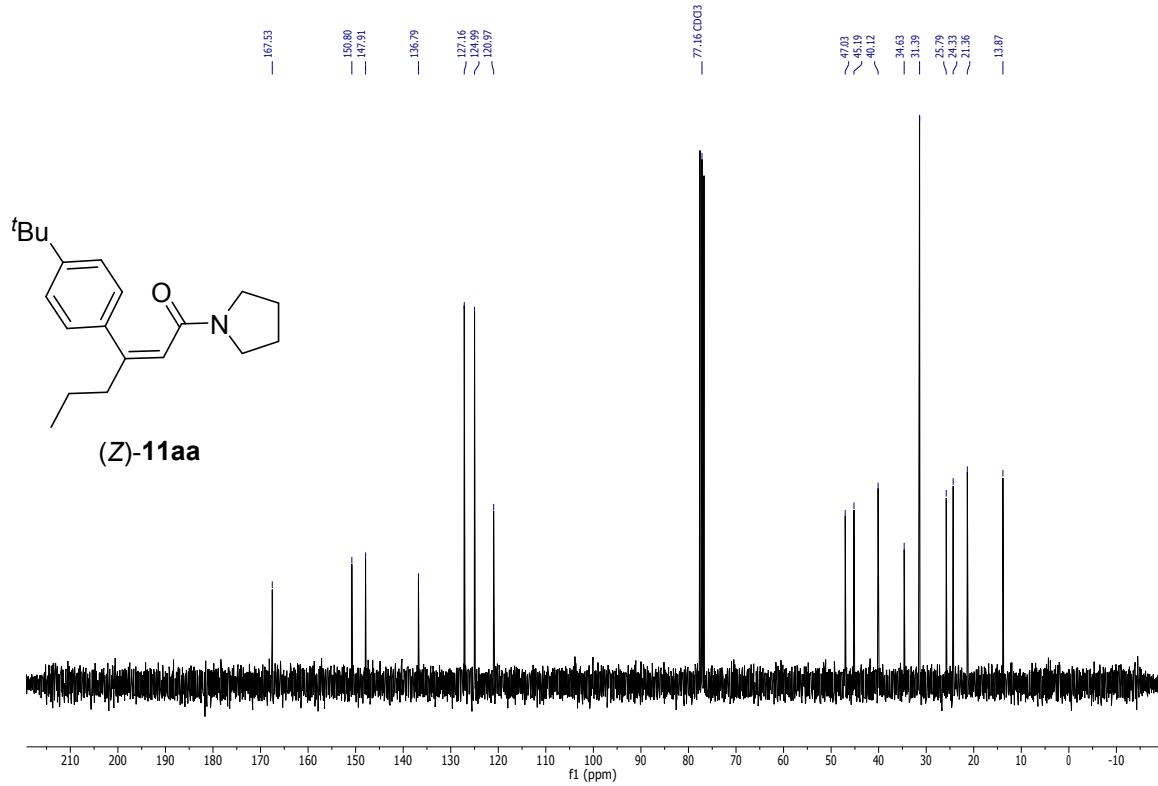


Figure S49. ^{13}C NMR (75 MHz, CDCl_3) of (Z)-11aa.

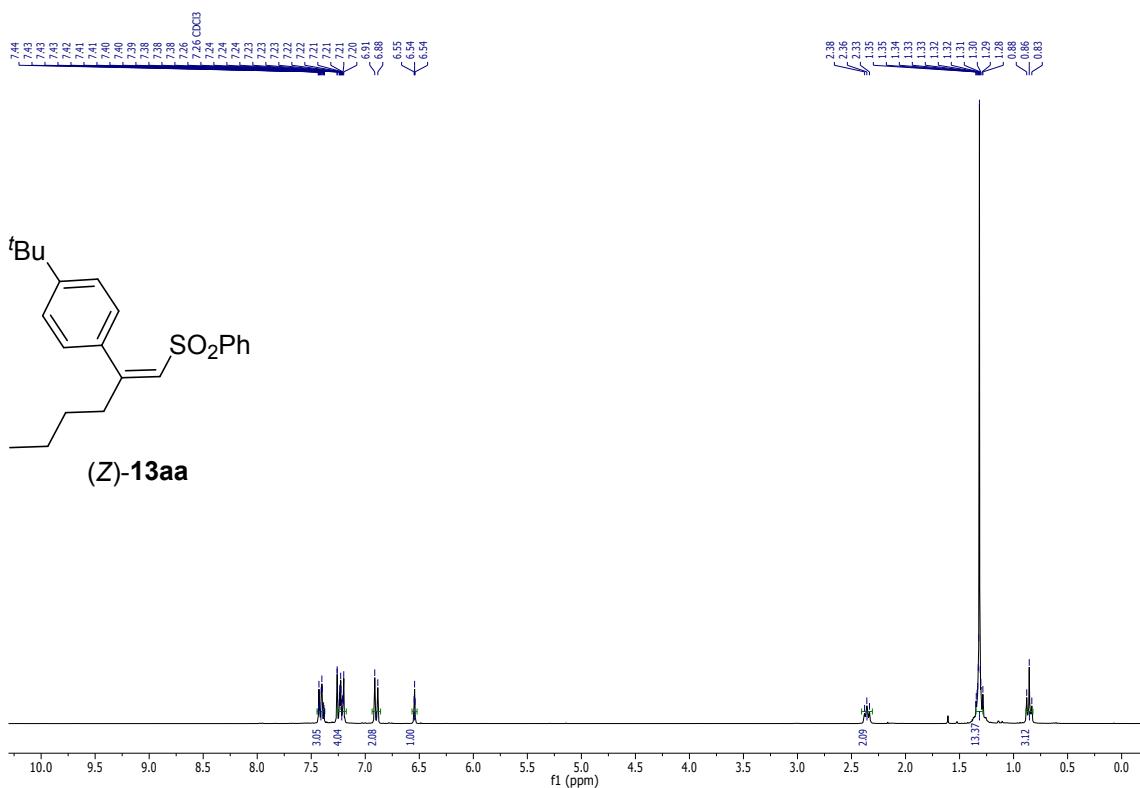


Figure S50. ¹H NMR (300 MHz, CDCl₃) of (Z)-13aa.

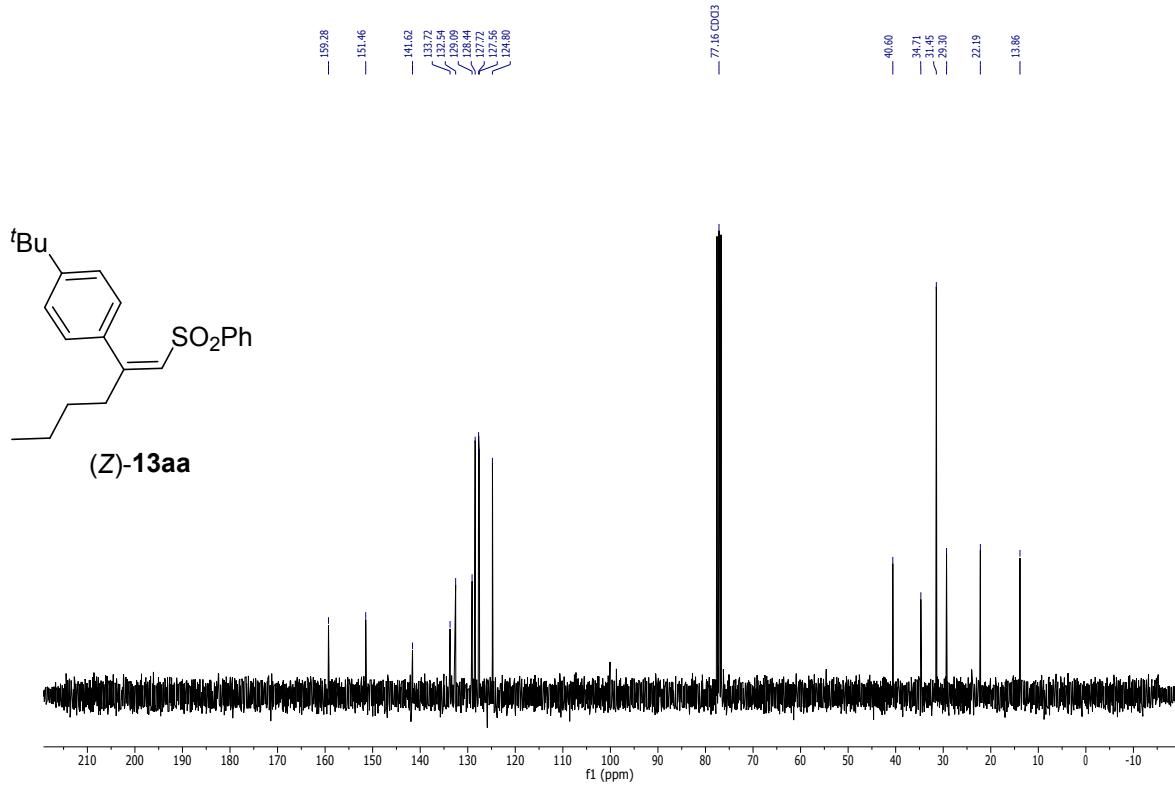


Figure S51. ¹³C NMR (75 MHz, CDCl₃) of (Z)-13aa.

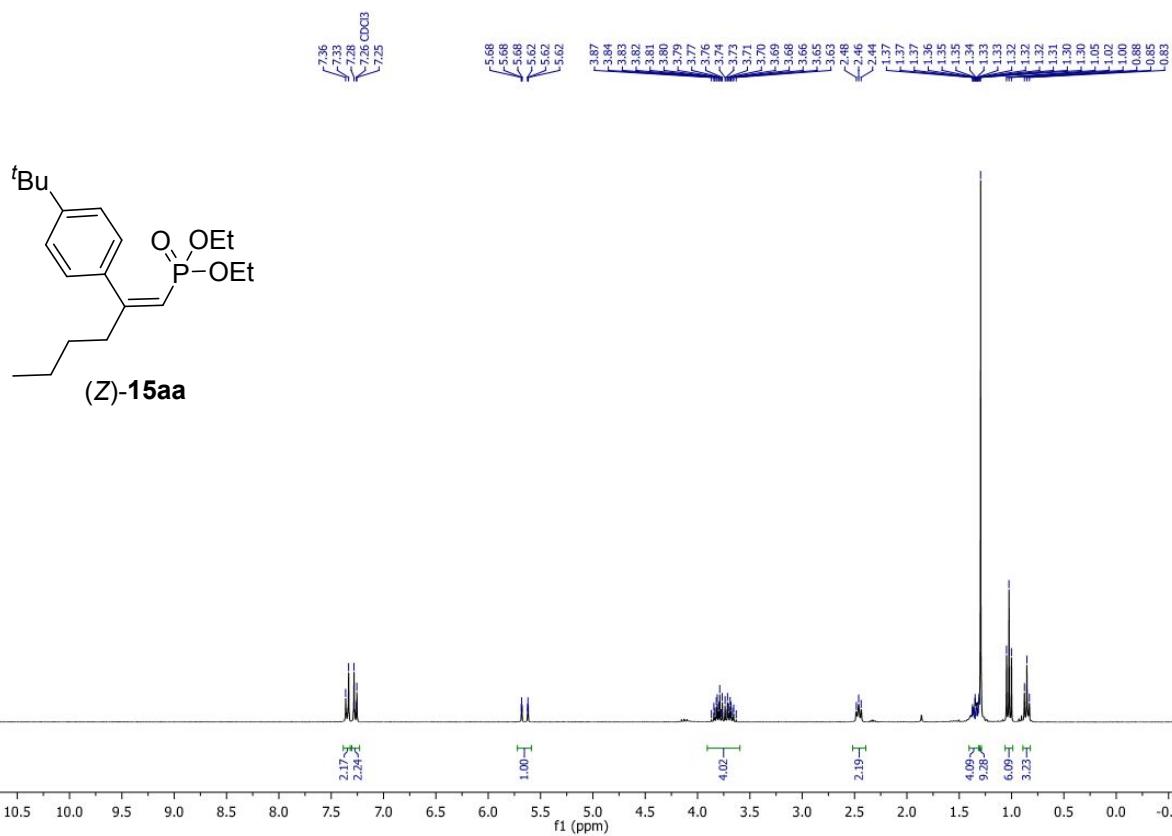


Figure S52. ^1H NMR (300 MHz, CDCl_3) of (Z)-15aa.

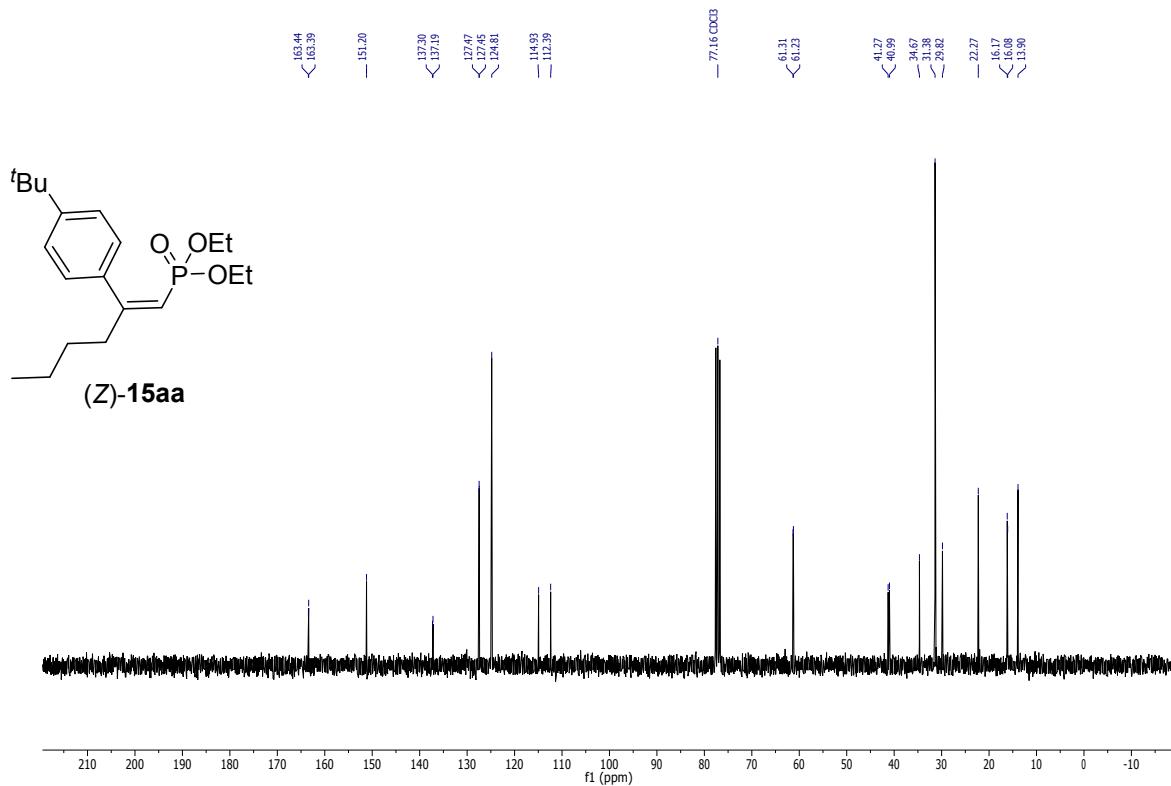


Figure S53. ^{13}C NMR (75 MHz, CDCl_3) of (Z)-15aa.

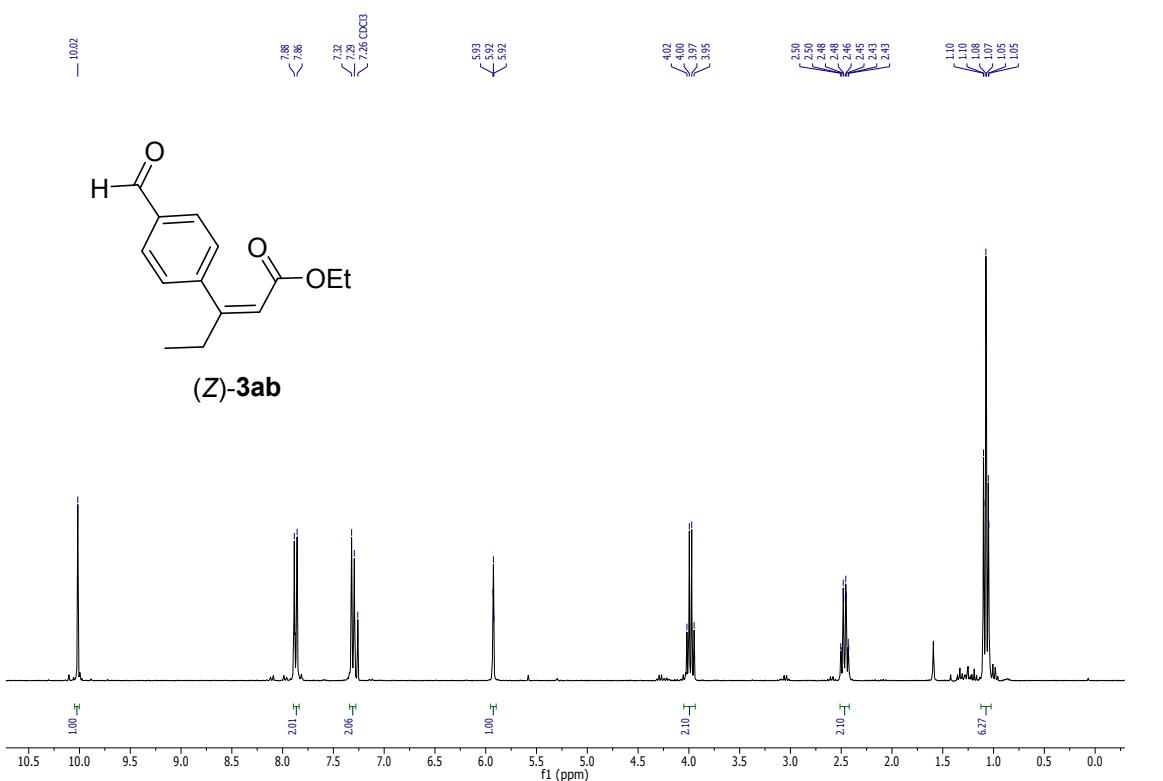


Figure S54. ^1H NMR (300 MHz, CDCl_3) of (Z)-3ab.

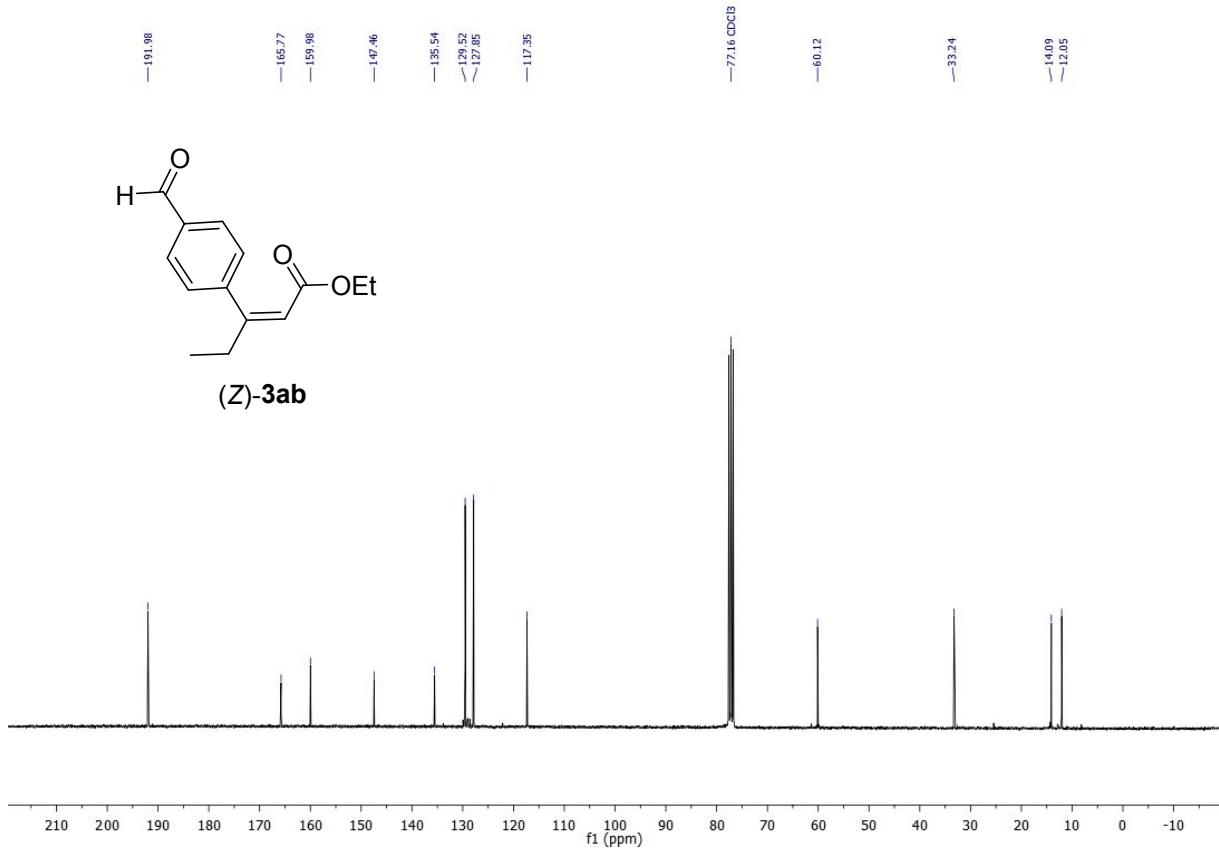


Figure S55. ^{13}C NMR (75 MHz, CDCl_3) of (Z)-3ab.

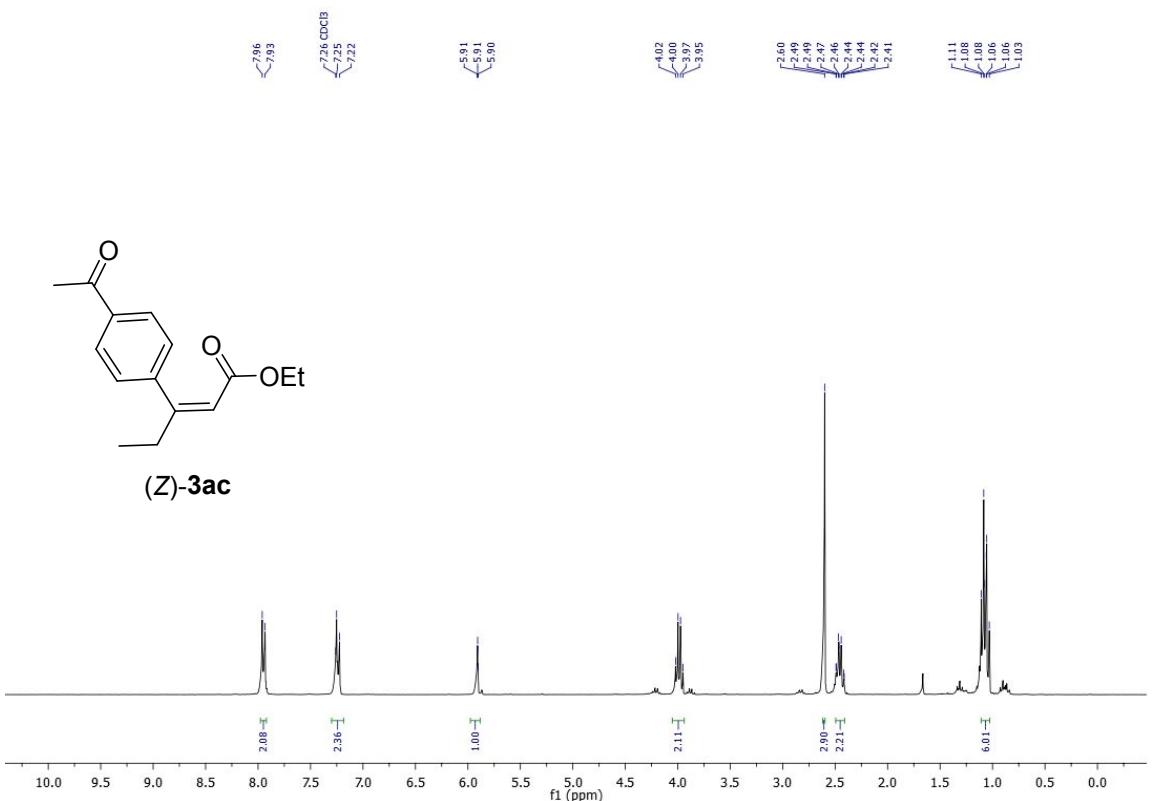


Figure S56. ^1H NMR (300 MHz, CDCl_3) of (Z)-3ac.

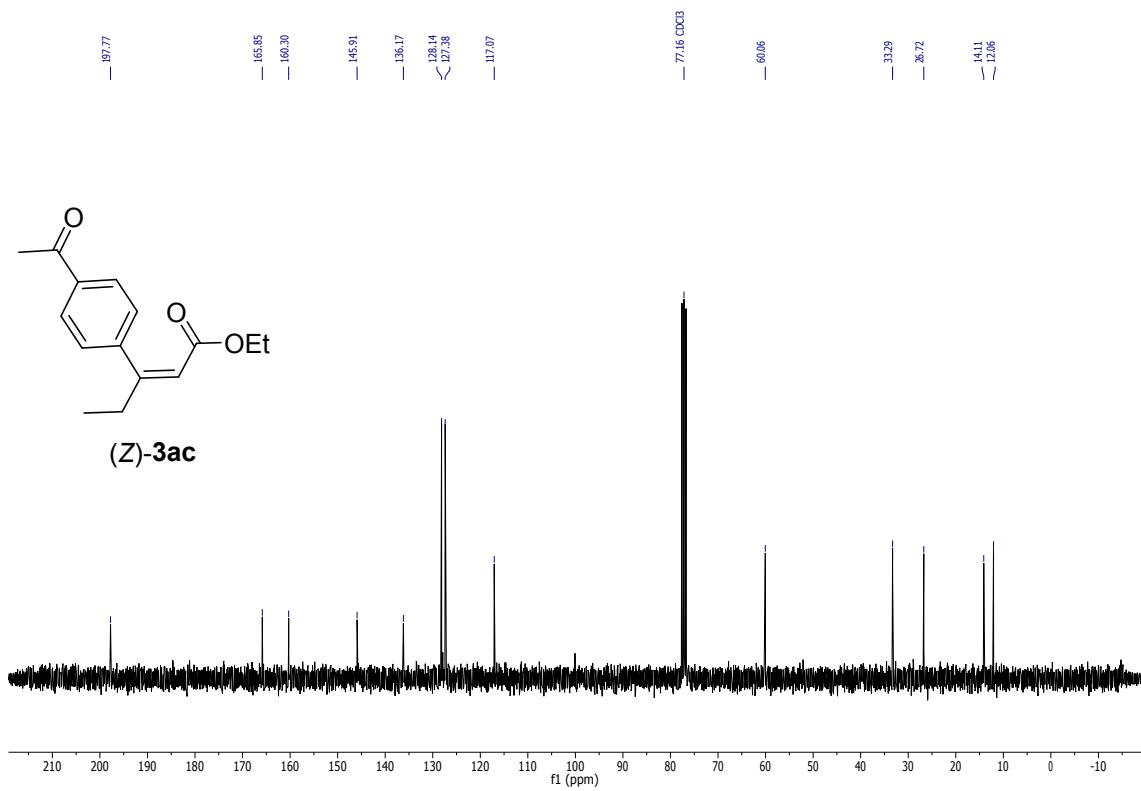


Figure S57. ^{13}C NMR (75 MHz, CDCl_3) of (Z)-3ac.

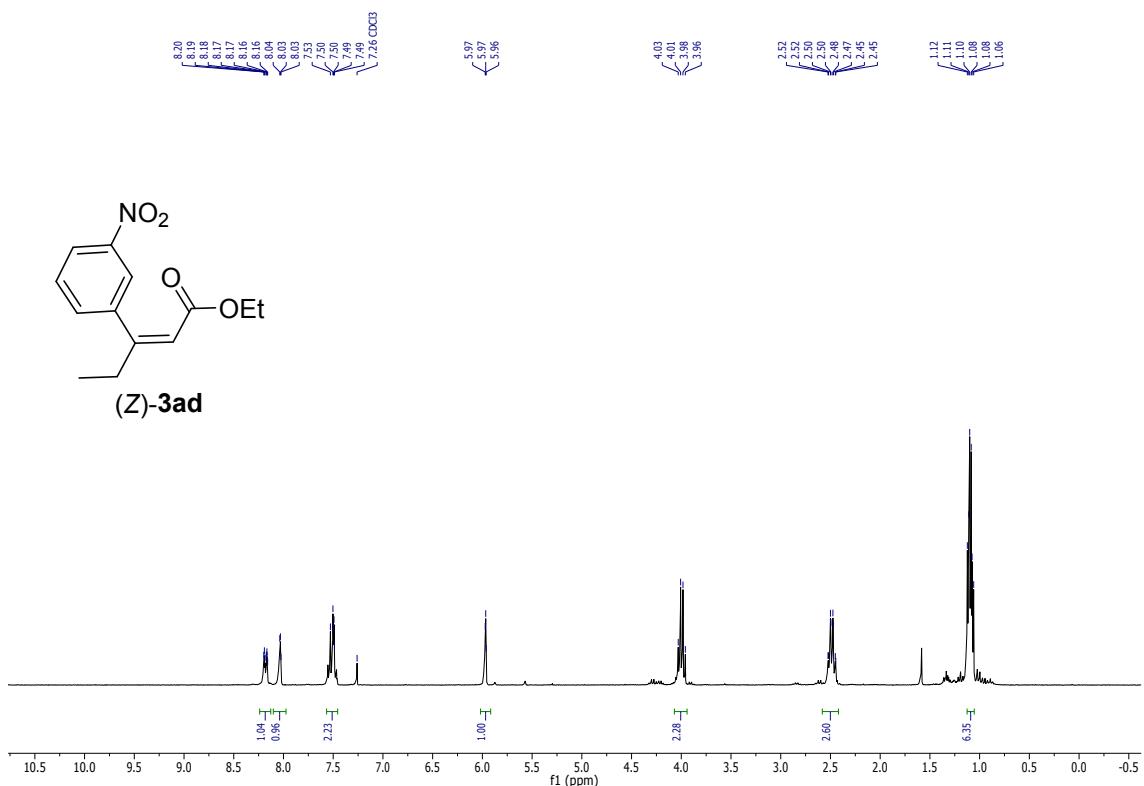


Figure S58. ^1H NMR (300 MHz, CDCl_3) of (*Z*)-3ad.

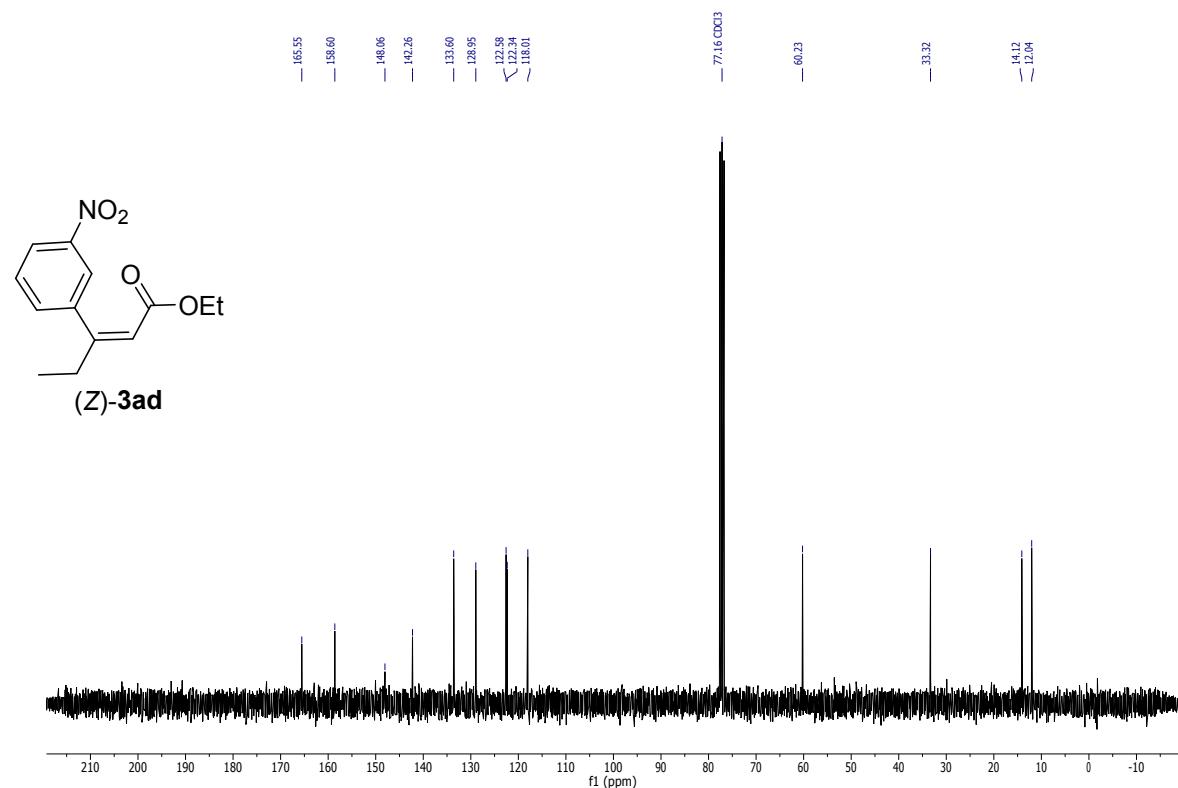


Figure S59. ^{13}C NMR (75 MHz, CDCl_3) of (Z)-3ad.

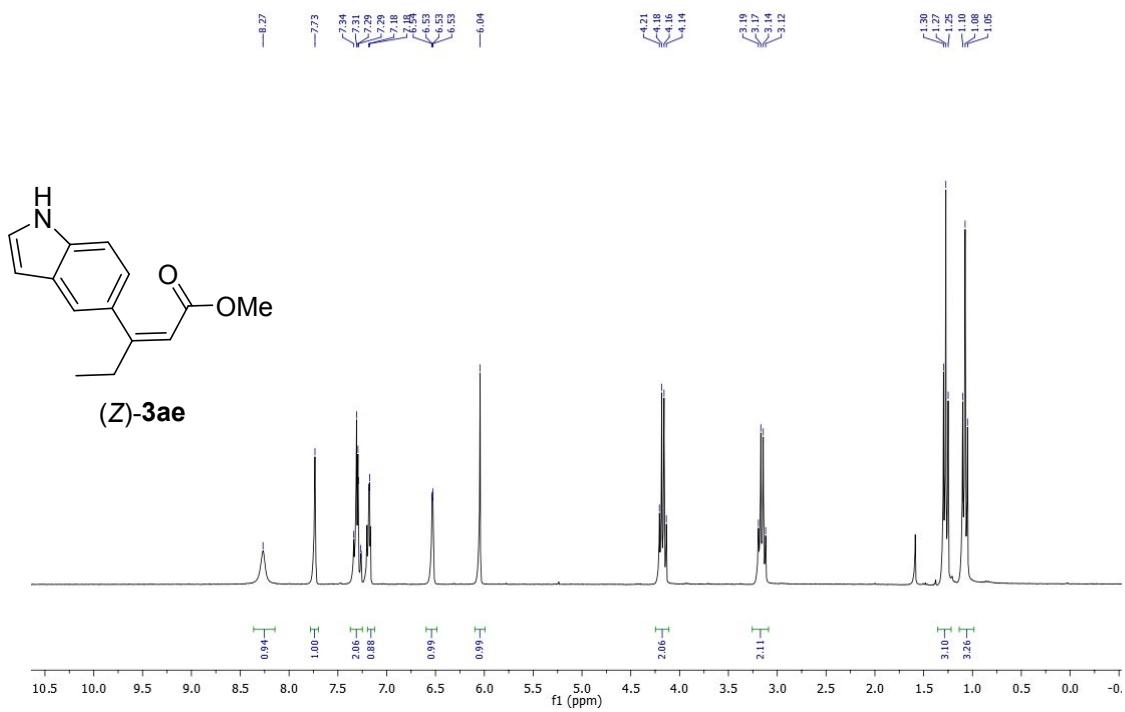


Figure S60. ^1H NMR (300 MHz, CDCl_3) of (Z)-3ae.

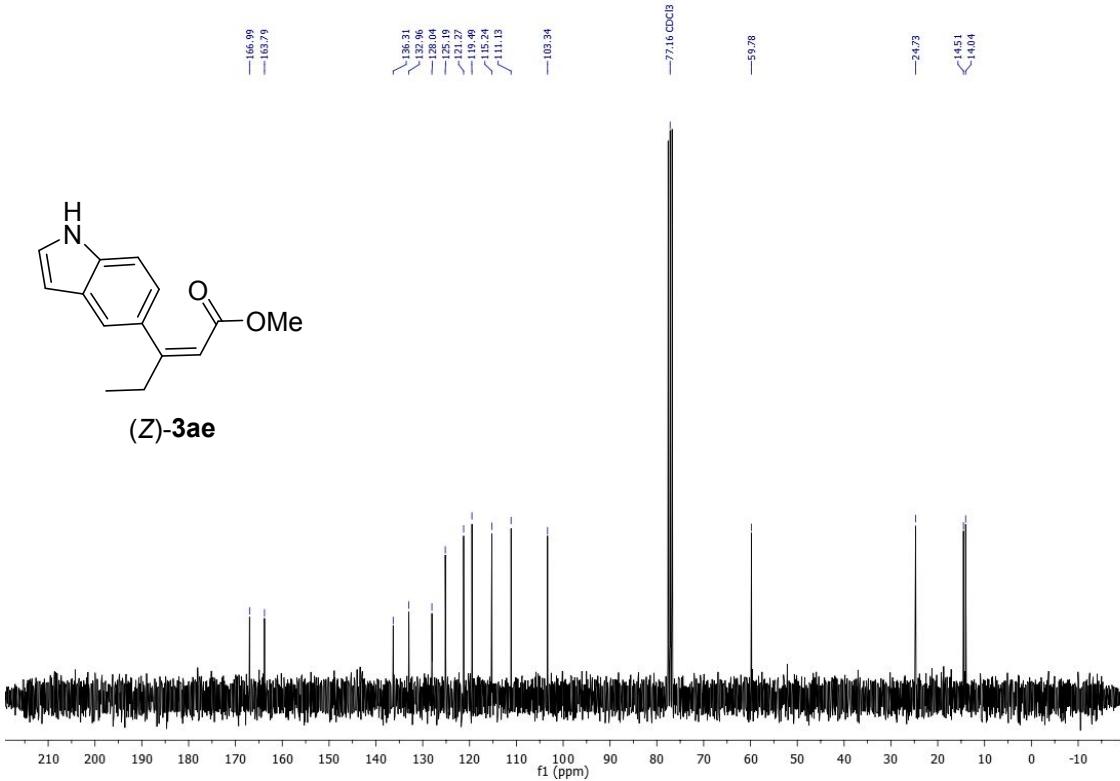


Figure S61. ^{13}C NMR (75 MHz, CDCl_3) of (Z)-3ae.

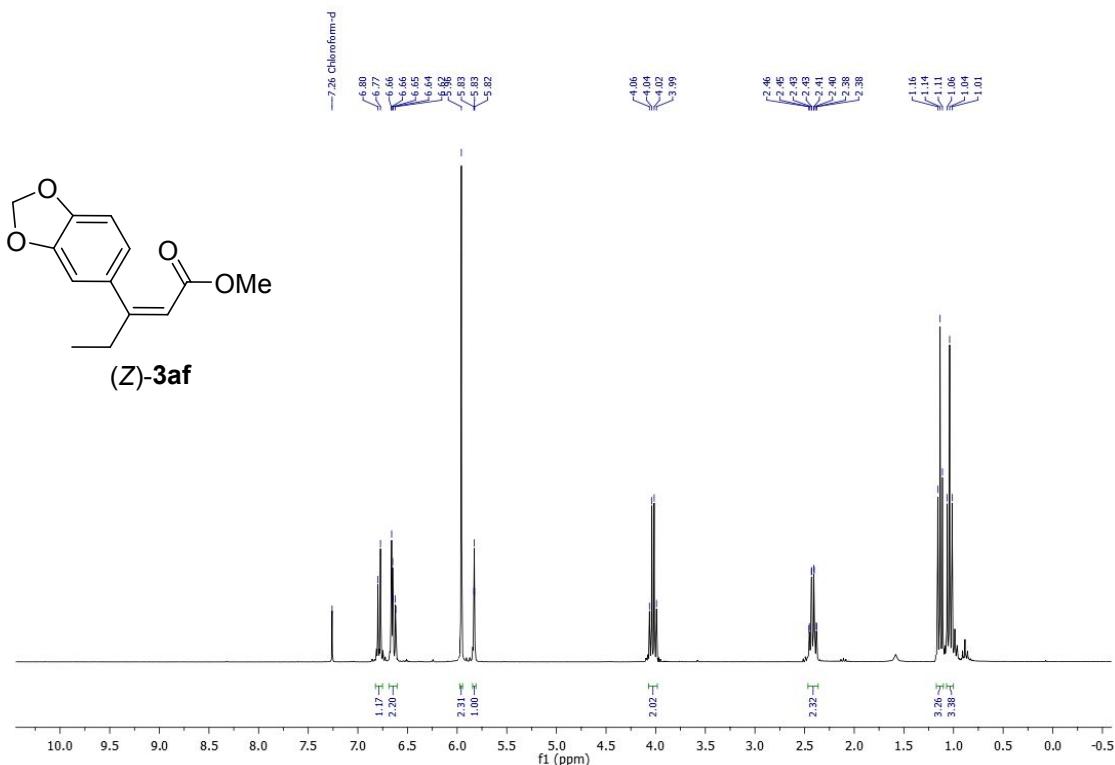


Figure S62. ^1H NMR (300 MHz, CDCl_3) of (Z)-3af.

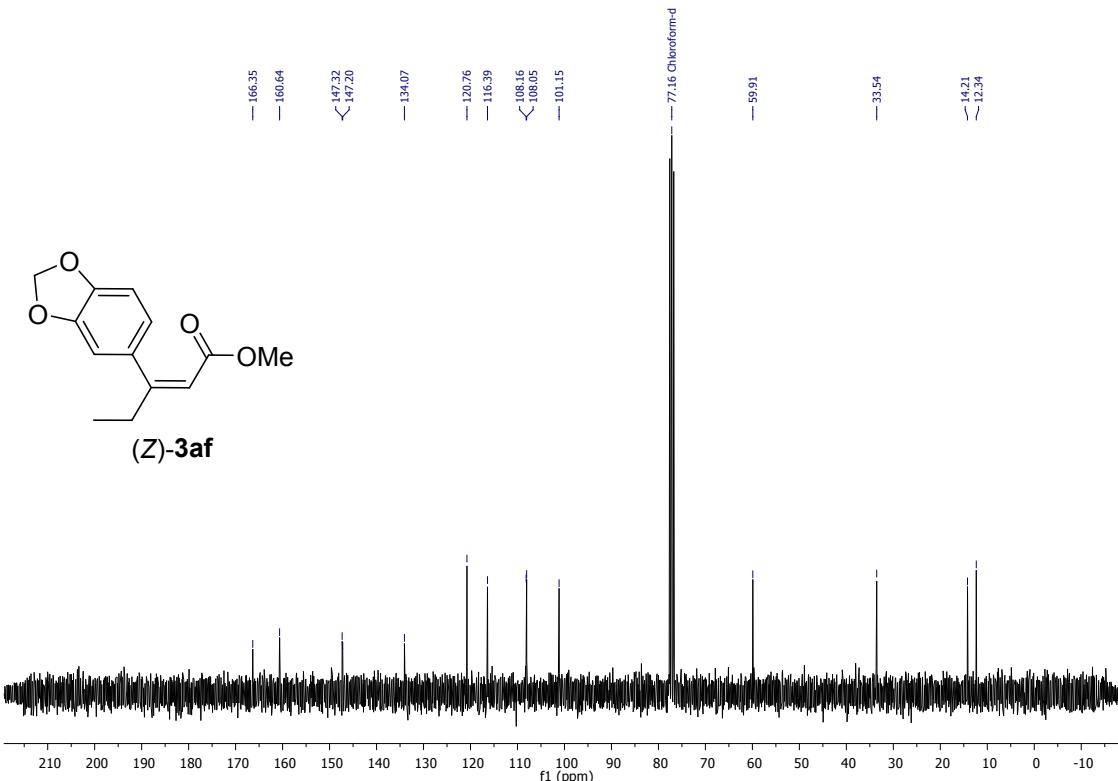
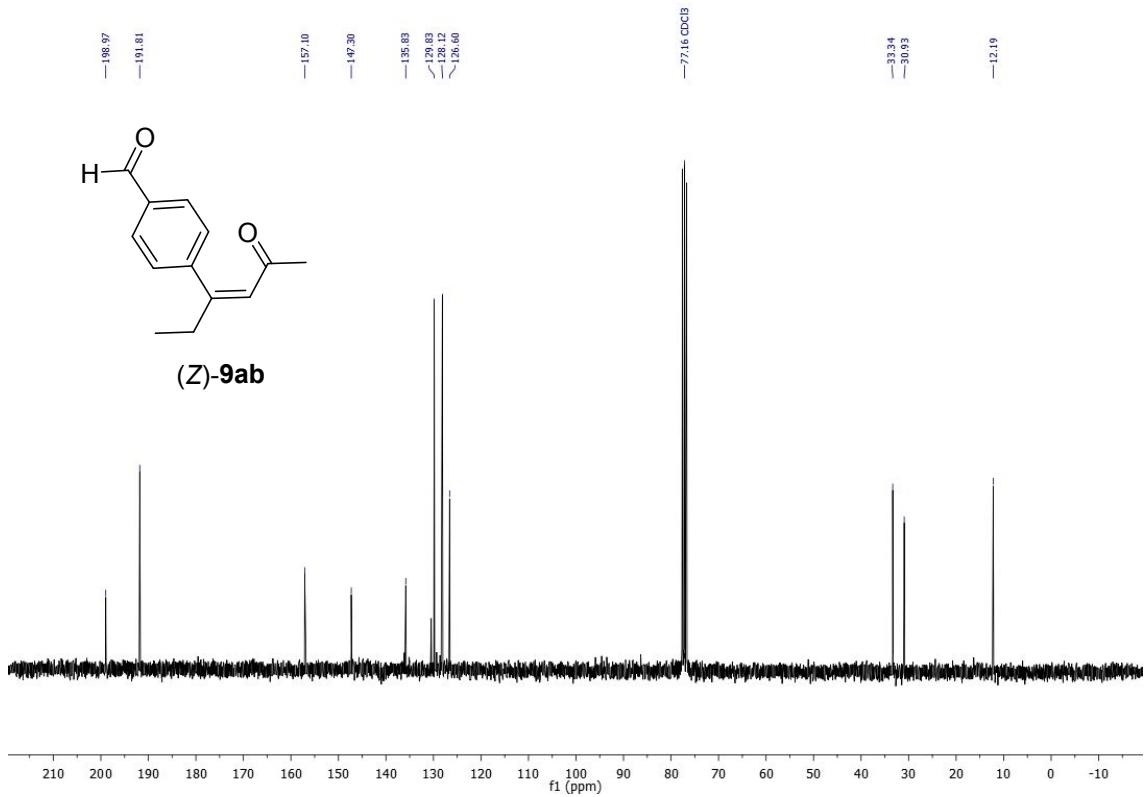
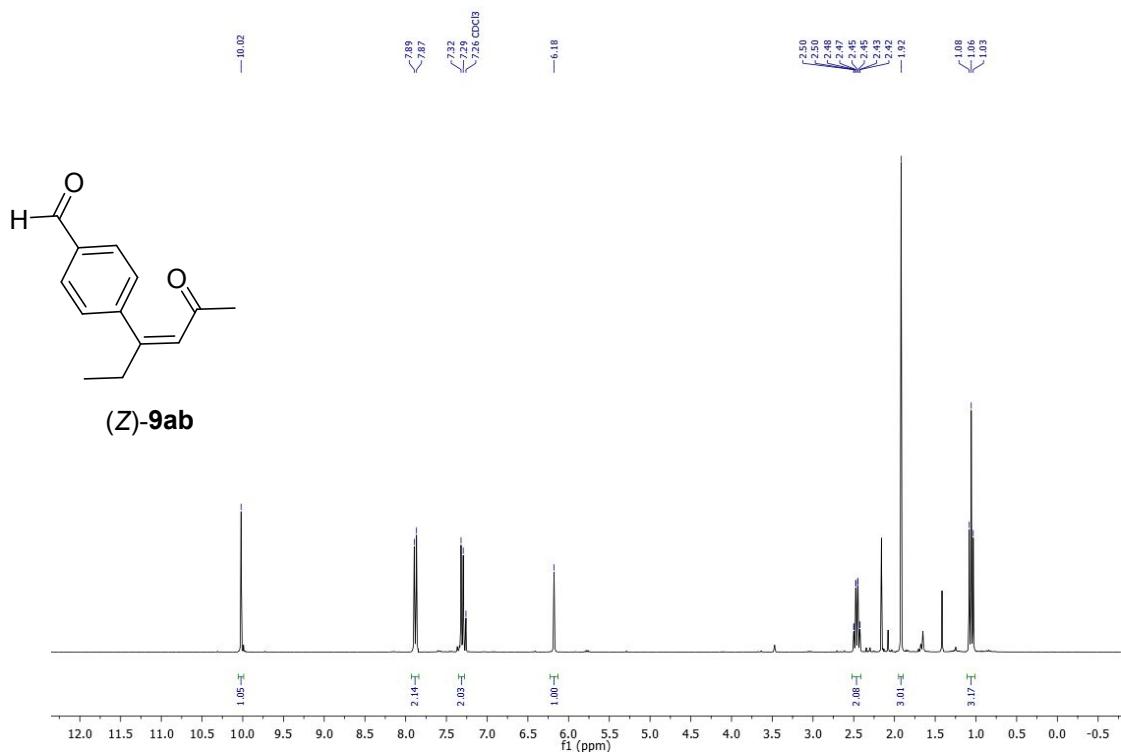
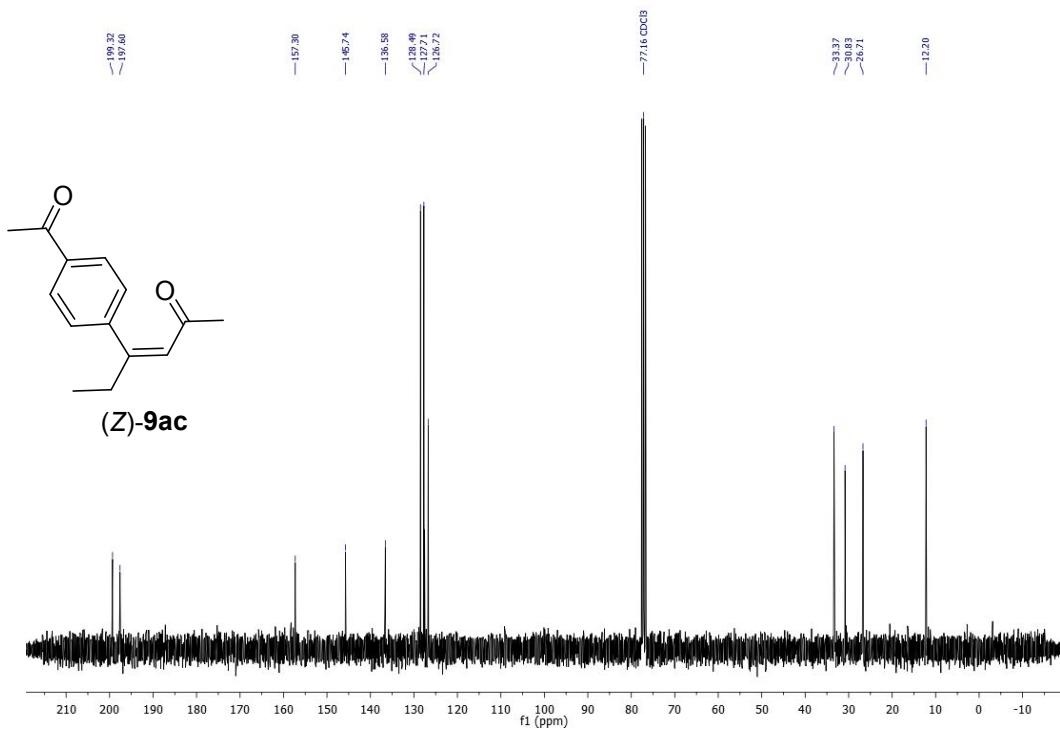
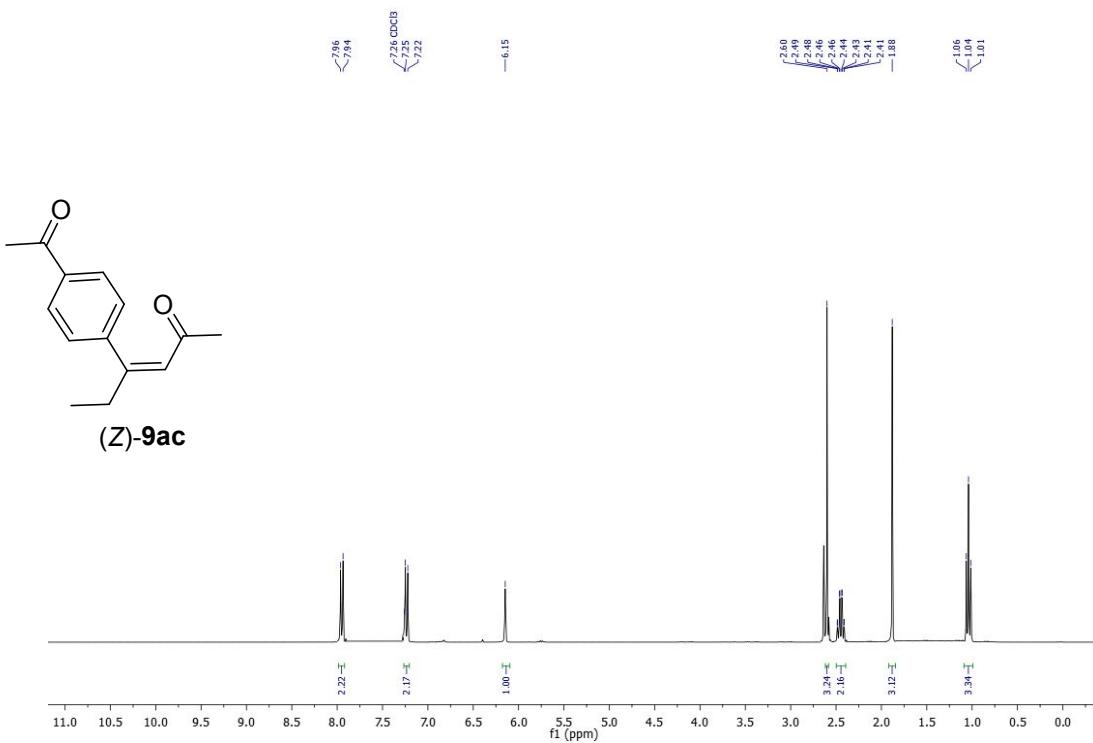


Figure S63. ^{13}C NMR (75 MHz, CDCl_3) of (*Z*)-3af.





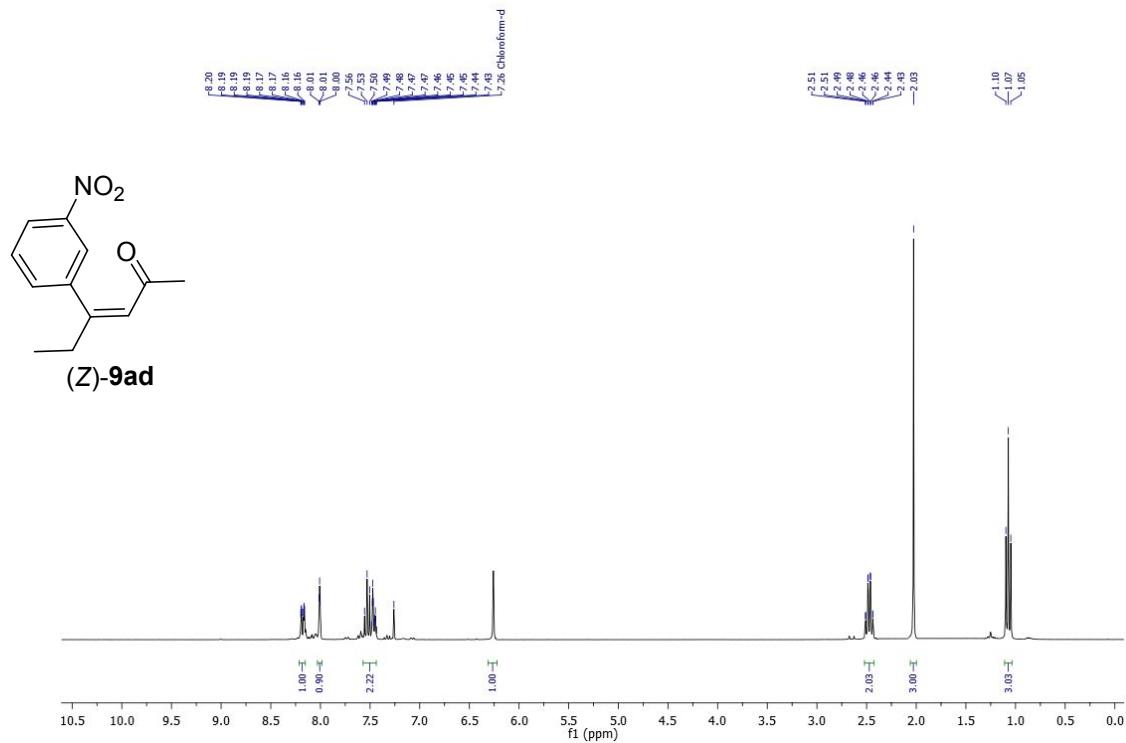


Figure S68. ^1H NMR (300 MHz, CDCl_3) of (Z)-9ad.

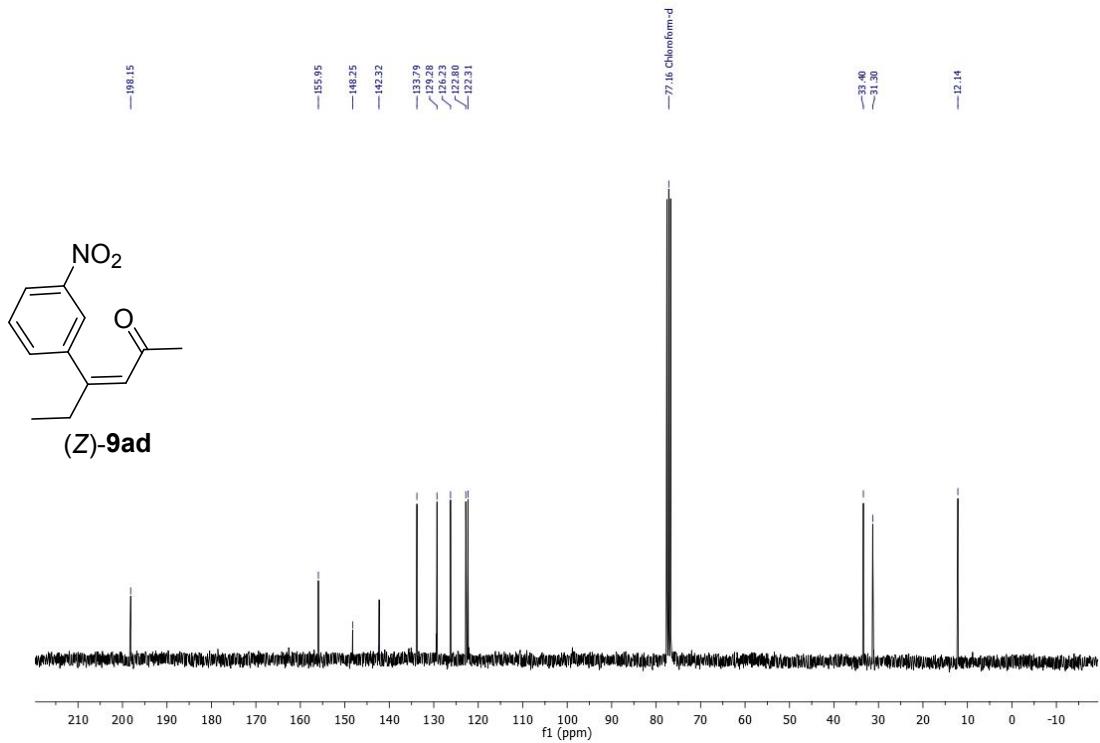


Figure S69. ^{13}C NMR (75 MHz, CDCl_3) of (Z)-9ad.

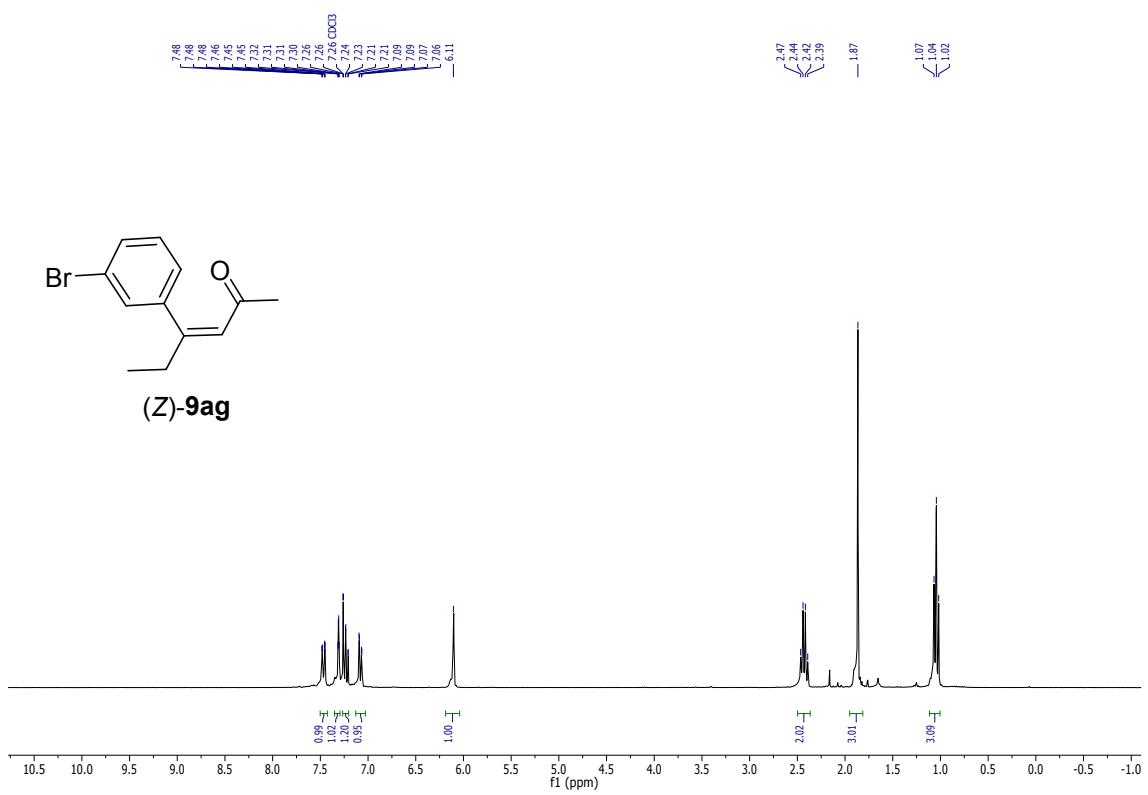


Figure S70. ^1H NMR (300 MHz, CDCl_3) of (Z)-9ag.

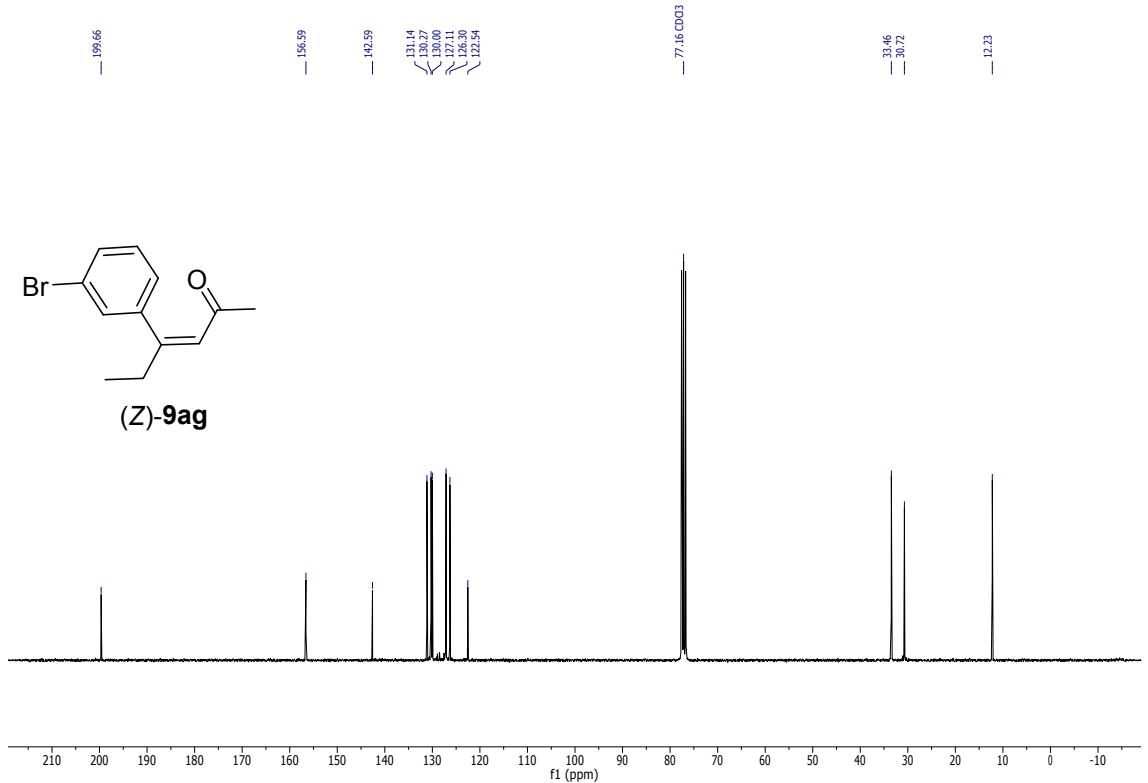


Figure S71. ^{13}C NMR (75 MHz, CDCl_3) of (Z)-9ag.

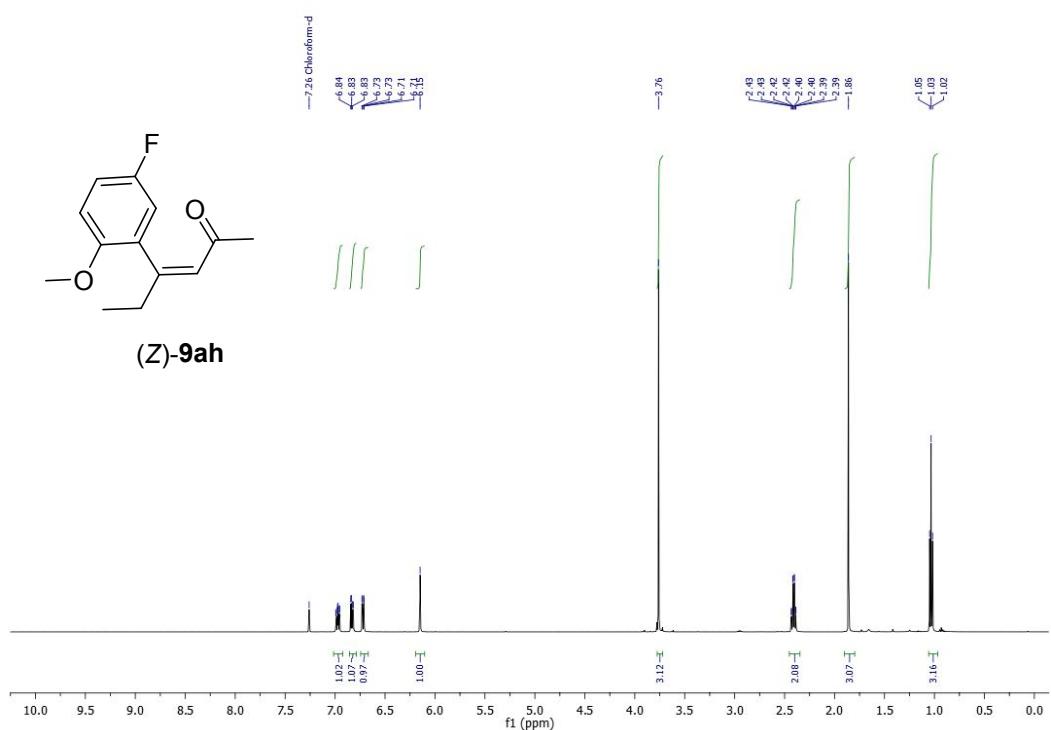


Figure S72. ¹H NMR (300 MHz, CDCl₃) of (Z)-9ah.

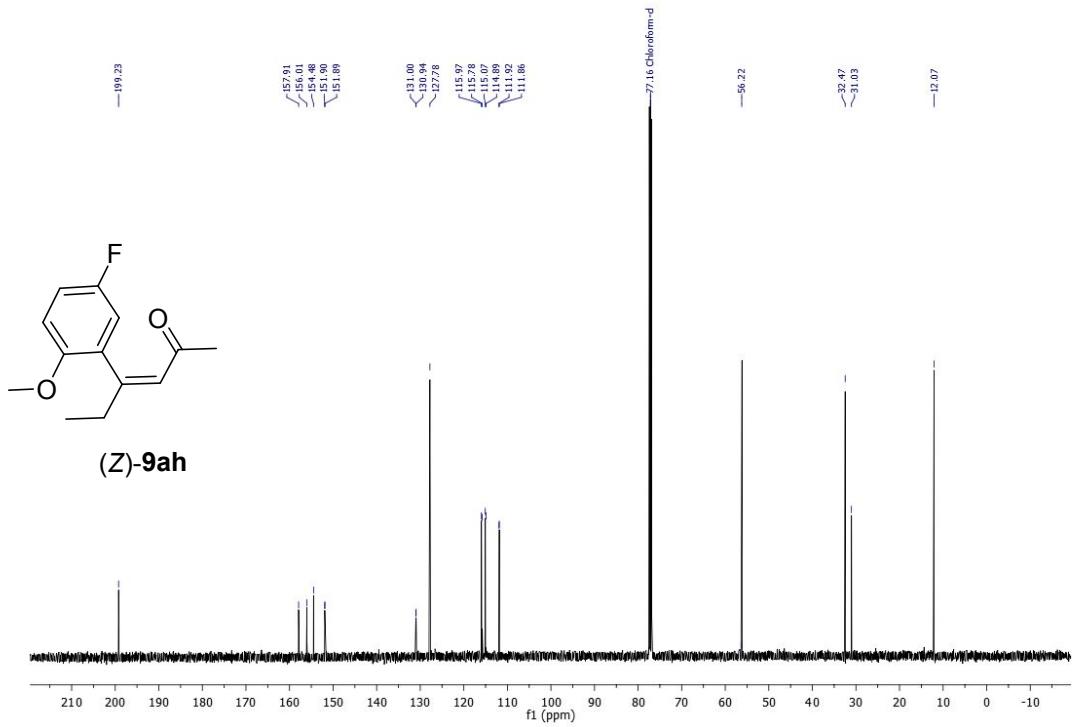


Figure S73. ¹³C NMR (75 MHz, CDCl₃) of (Z)-9ah.

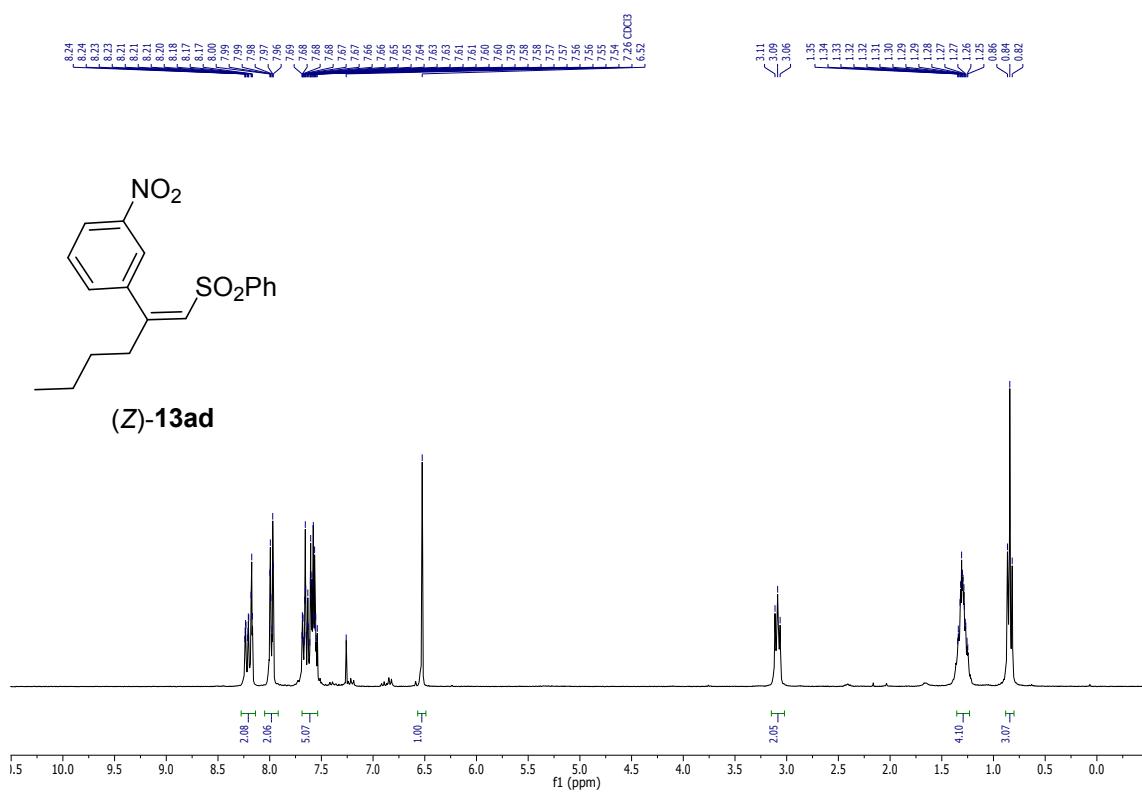


Figure S74. ^1H NMR (300 MHz, CDCl_3) of (Z)-13ad.

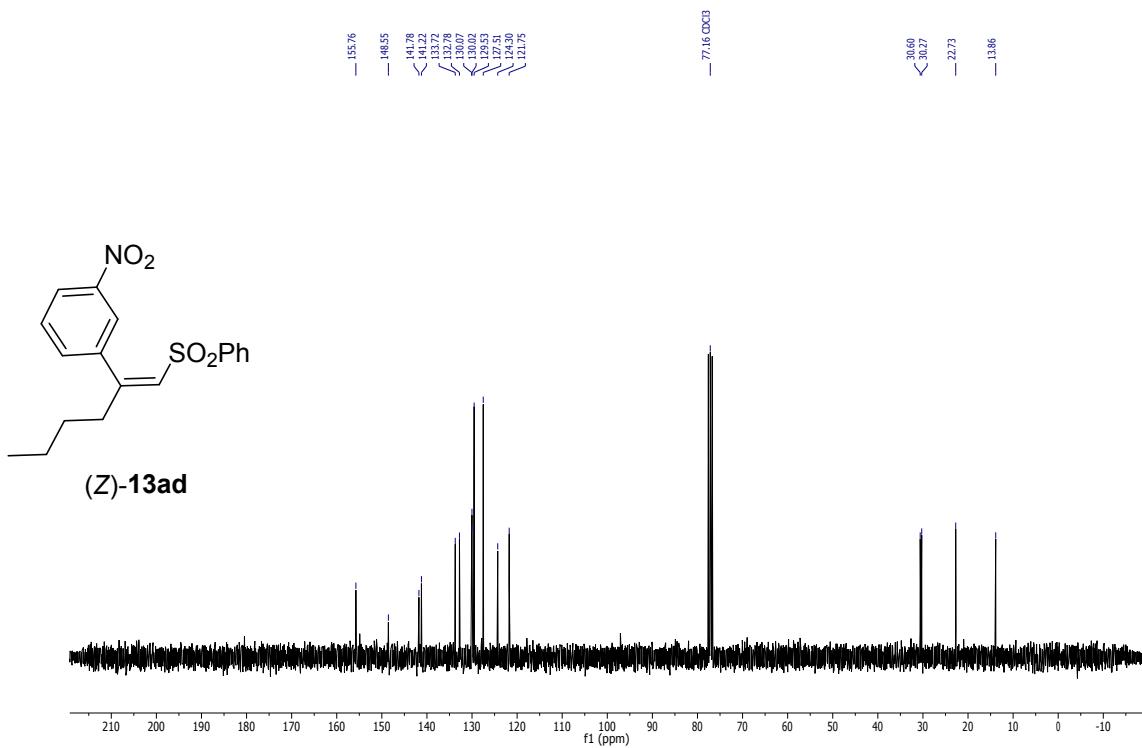


Figure S75. ^{13}C NMR (75 MHz, CDCl_3) of (Z)-13ad.

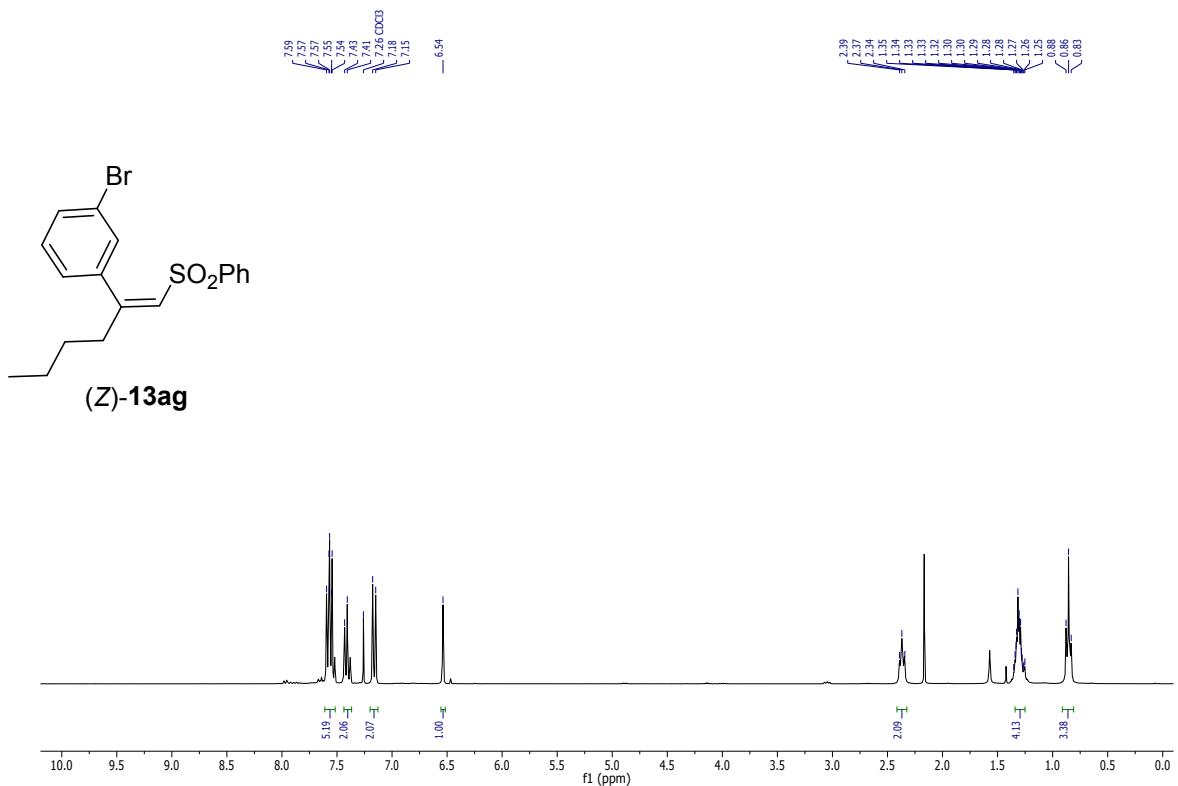


Figure S76. ^1H NMR (300 MHz, CDCl_3) of (Z)-13ag.

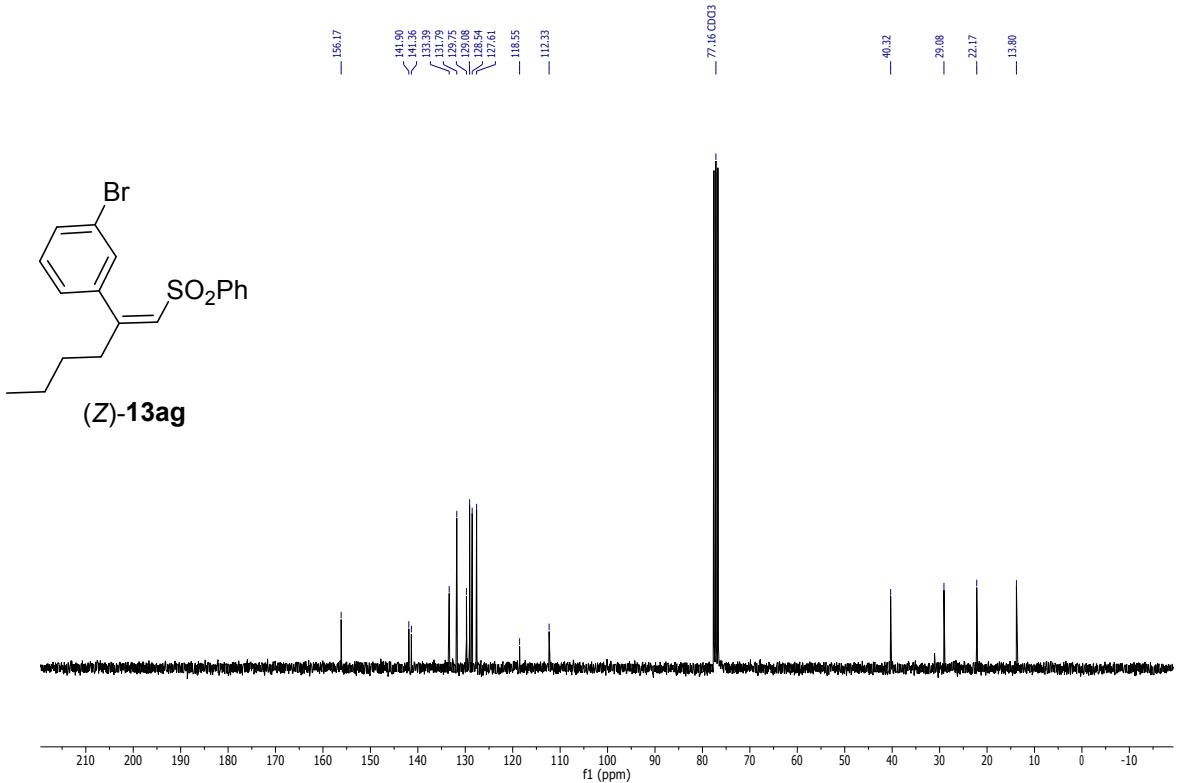


Figure S77. ^{13}C NMR (75 MHz, CDCl_3) of (Z)-13ag.

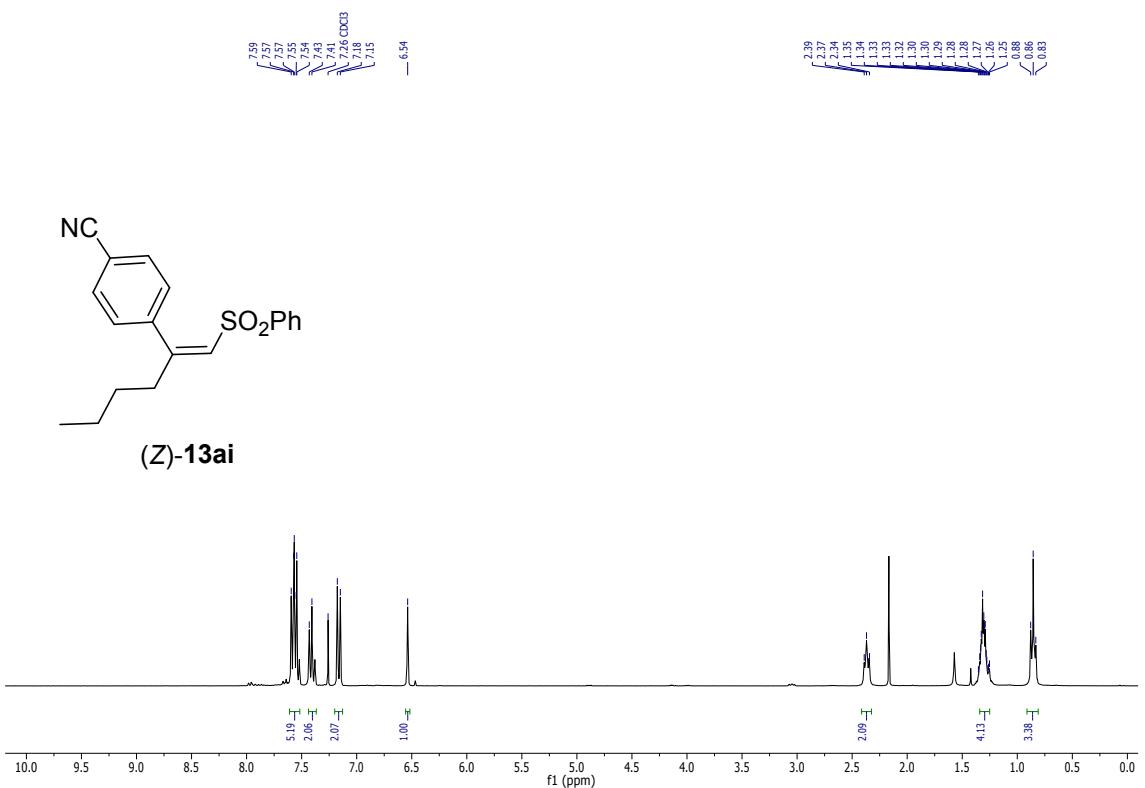


Figure S78. ^1H NMR (300 MHz, CDCl_3) of (Z)-13ai.

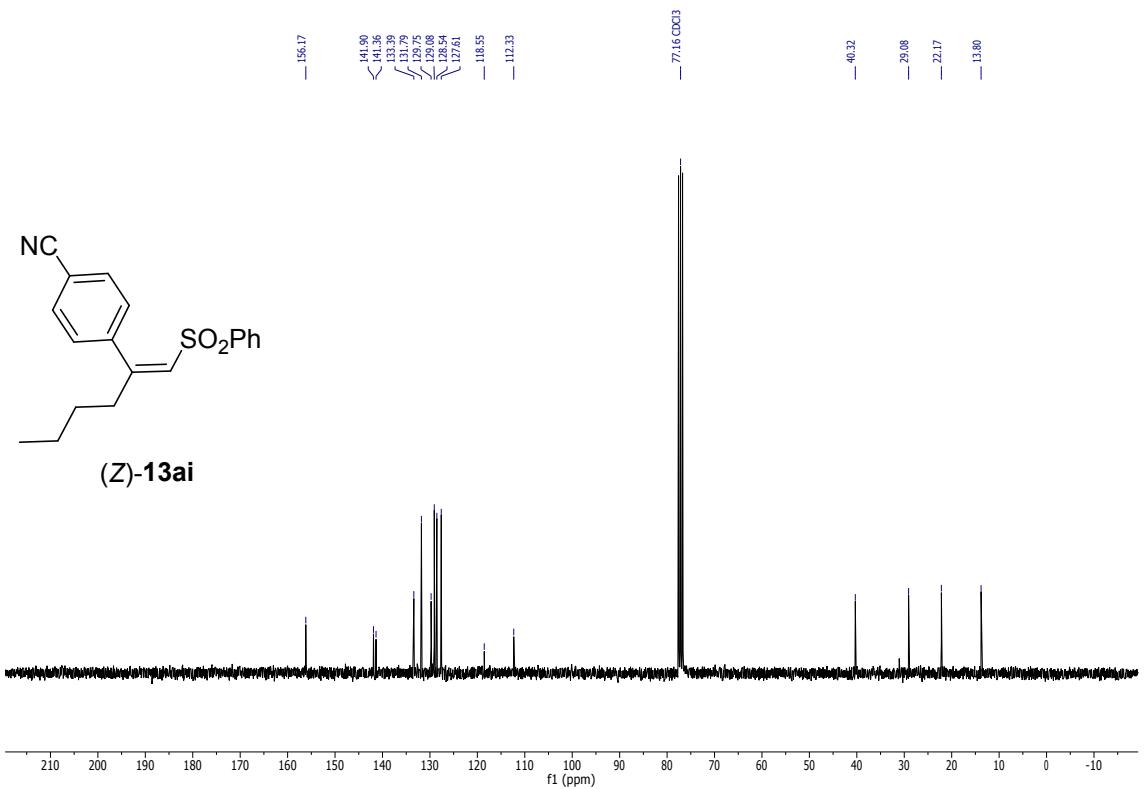


Figure S79. ^{13}C NMR (75 MHz, CDCl_3) of (Z)-13ai.

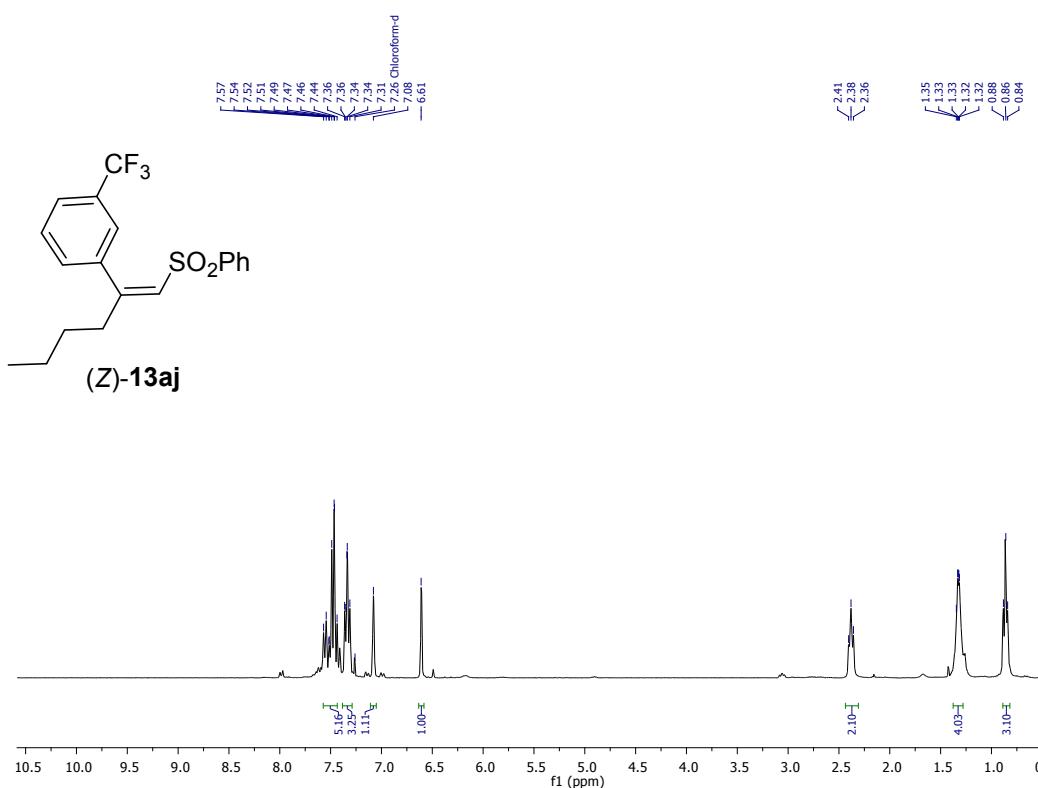


Figure S80. ^1H NMR (300 MHz, CDCl_3) of (Z)-13aj.

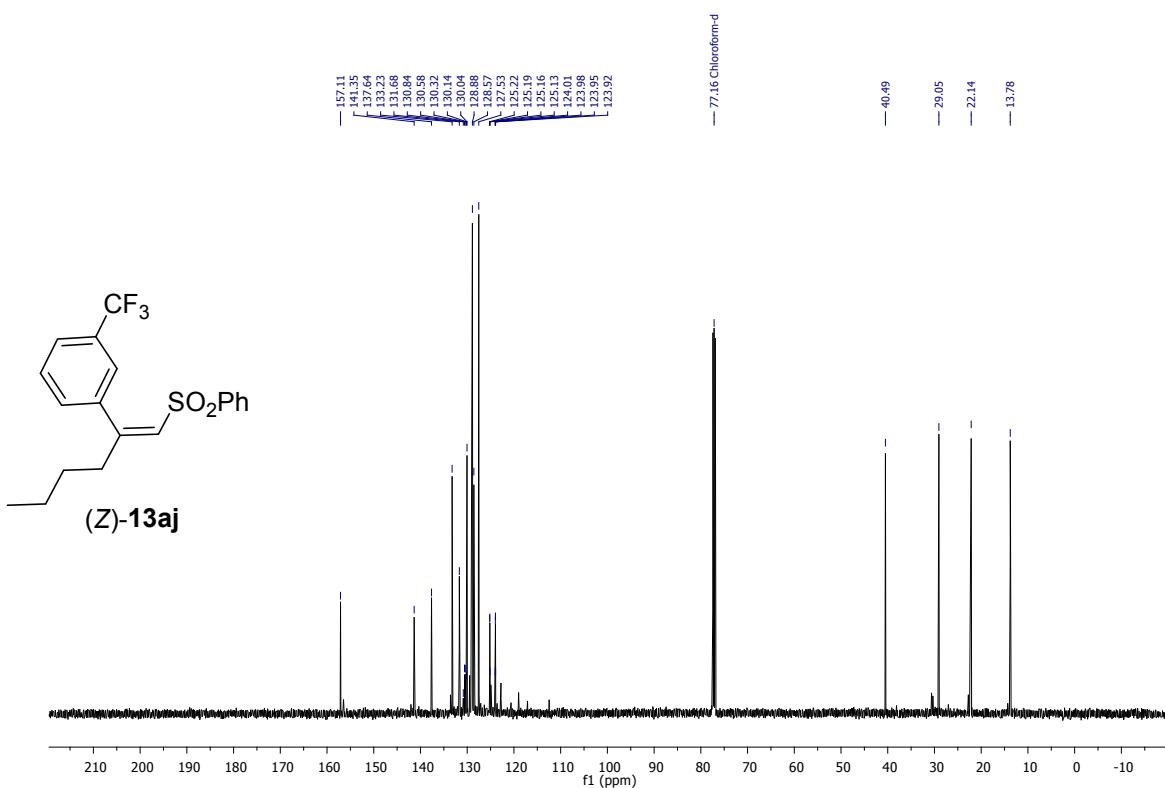


Figure S81. ^{13}C NMR (75 MHz, CDCl_3) of (Z)-13aj.

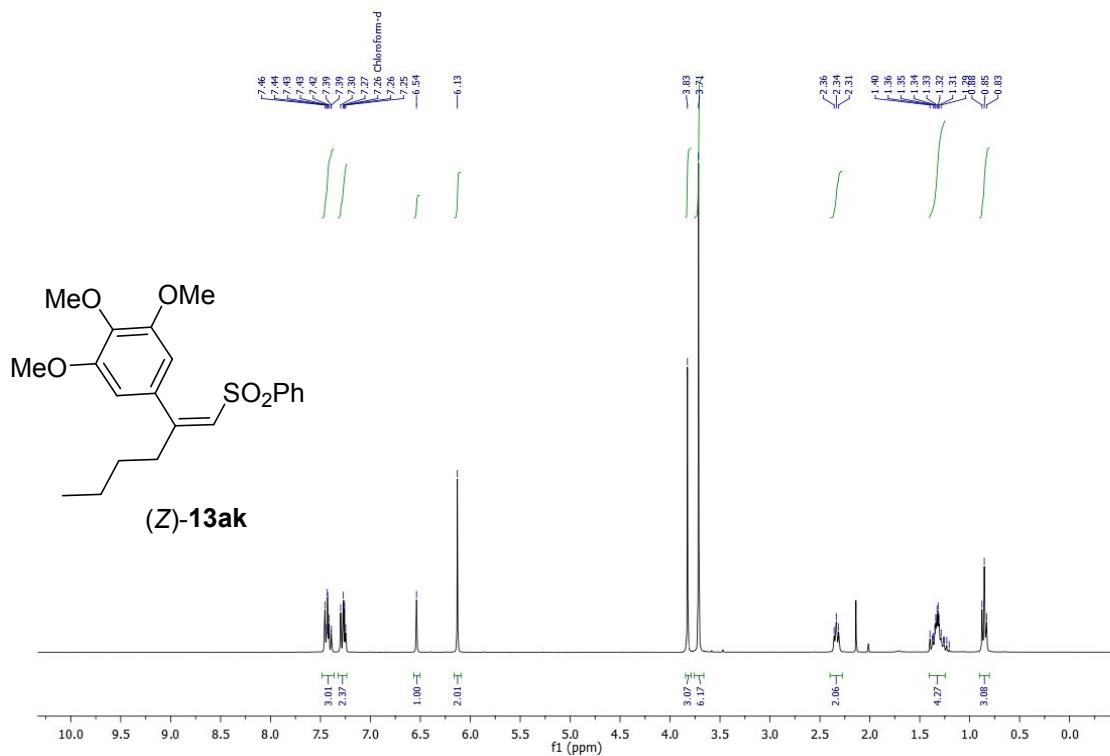


Figure S82. ^1H NMR (300 MHz, CDCl_3) of (Z)-13ak.

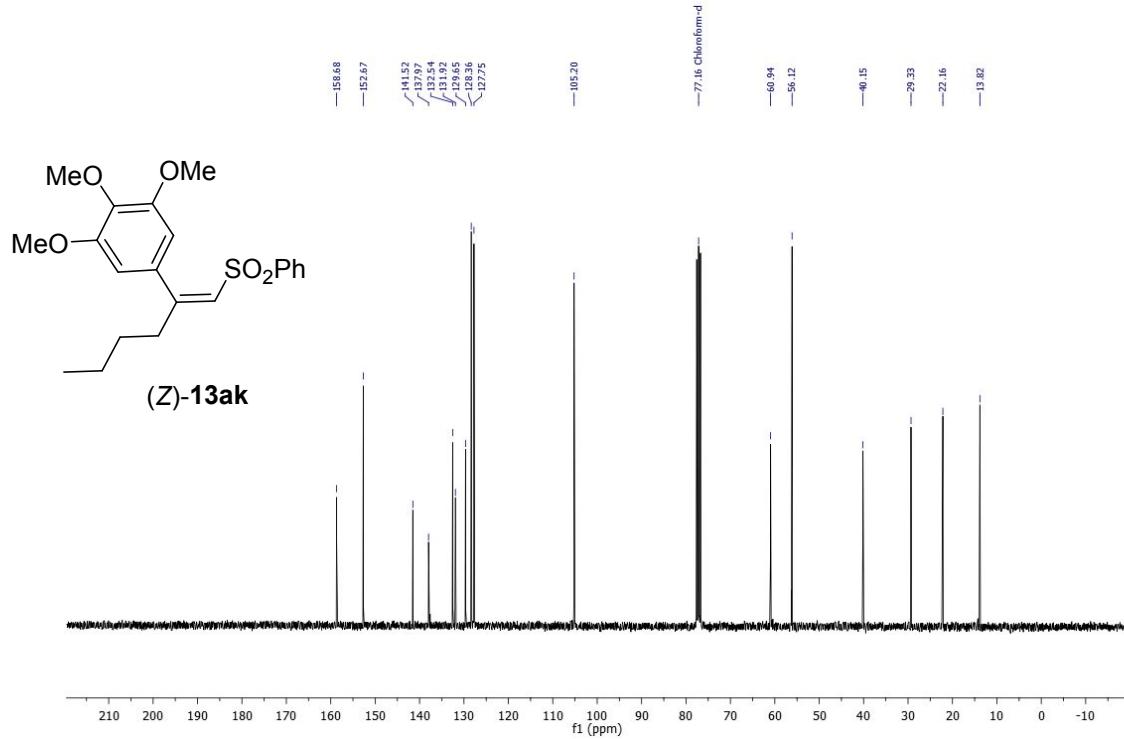


Figure S83. ^{13}C NMR (75 MHz, CDCl_3) of (Z)-13ak.

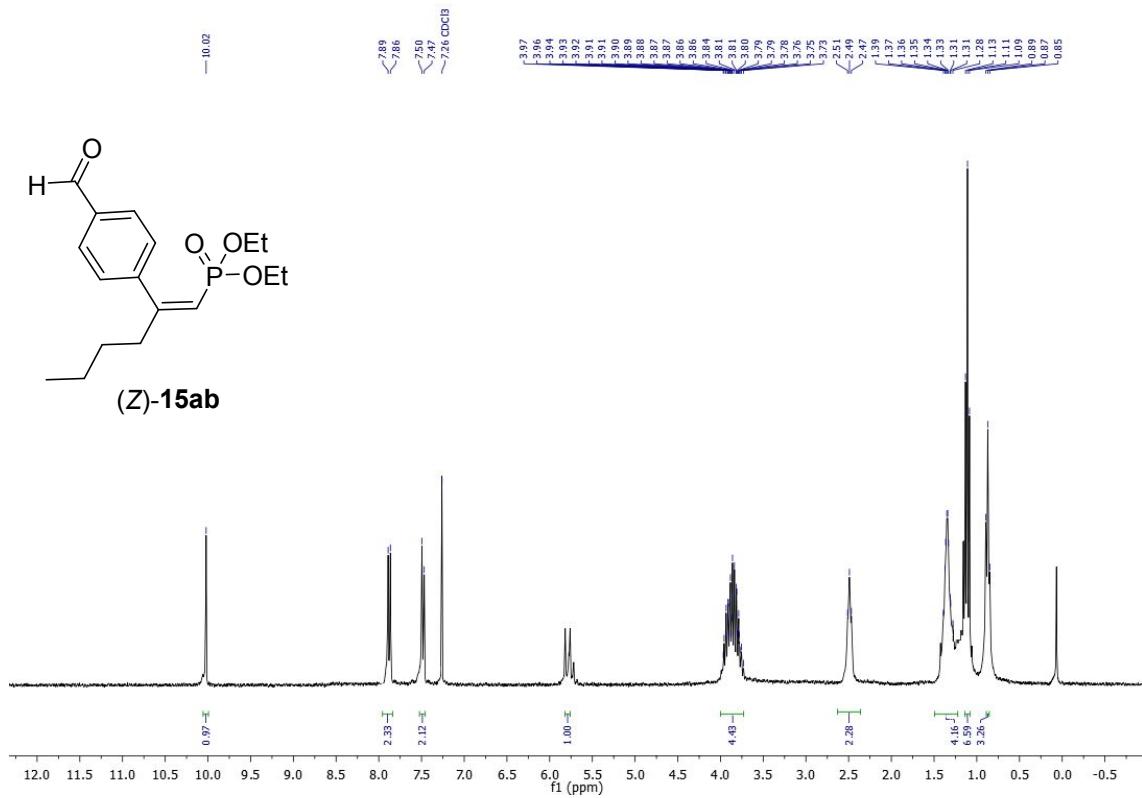


Figure S84. ^1H NMR (300 MHz, CDCl_3) of (Z)-15ab.

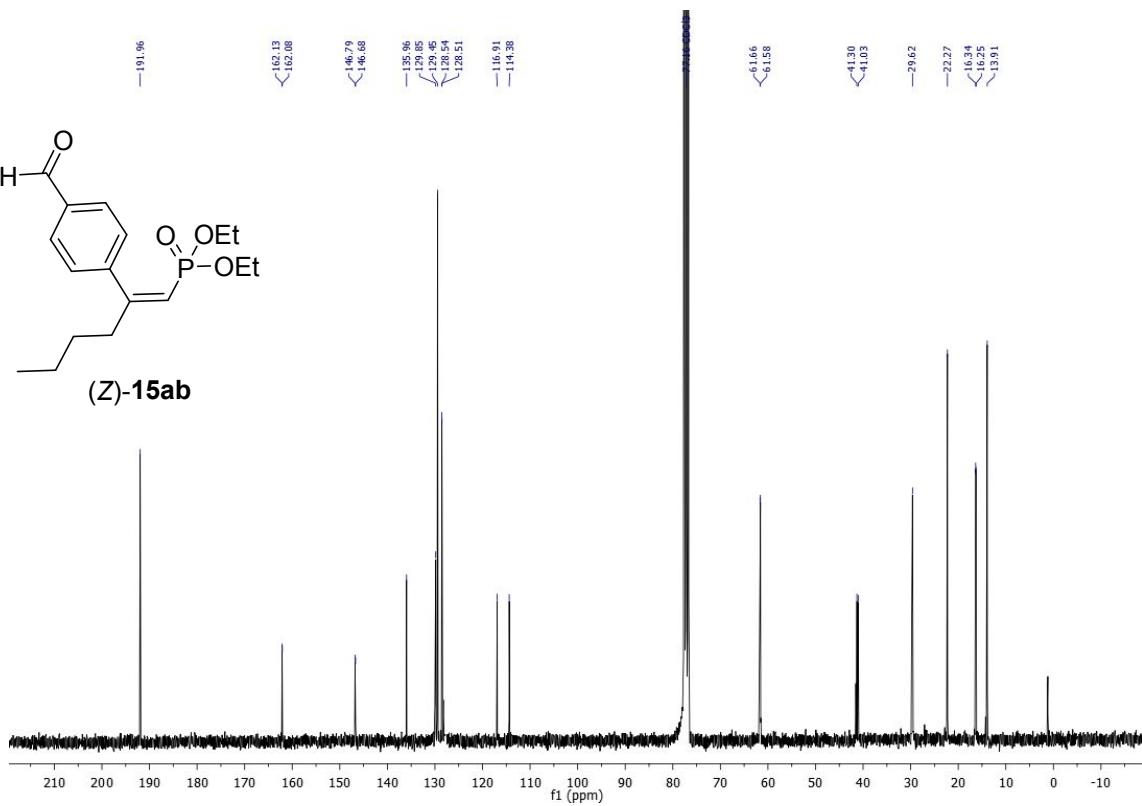


Figure S85. ^{13}C NMR (75 MHz, CDCl_3) of (Z)-15ab.

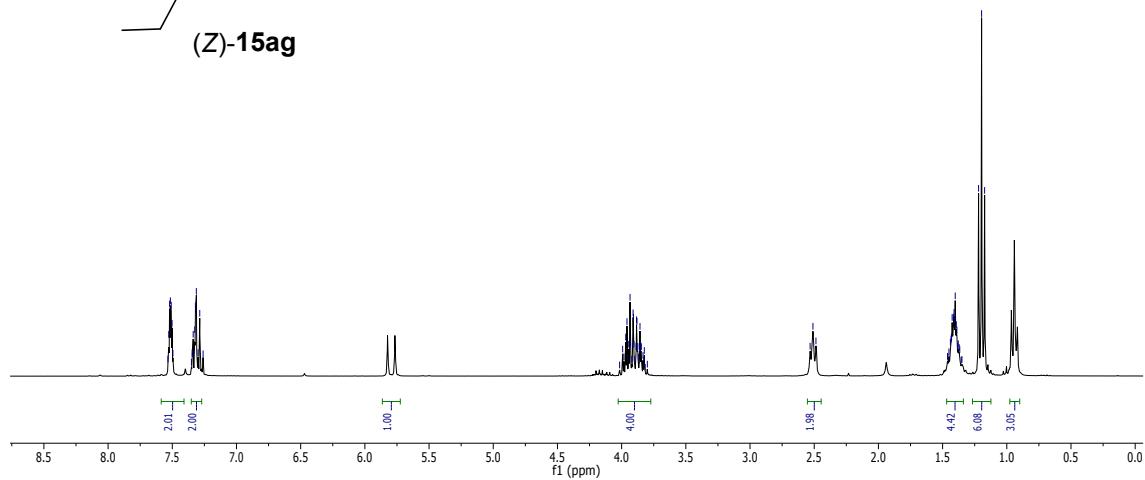
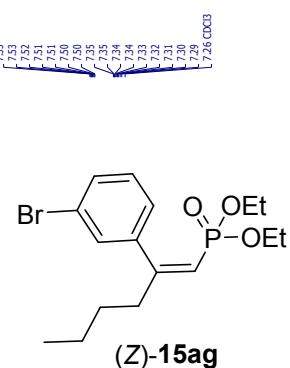


Figure S86. ^1H NMR (300 MHz, CDCl_3) of (Z)-15ag.

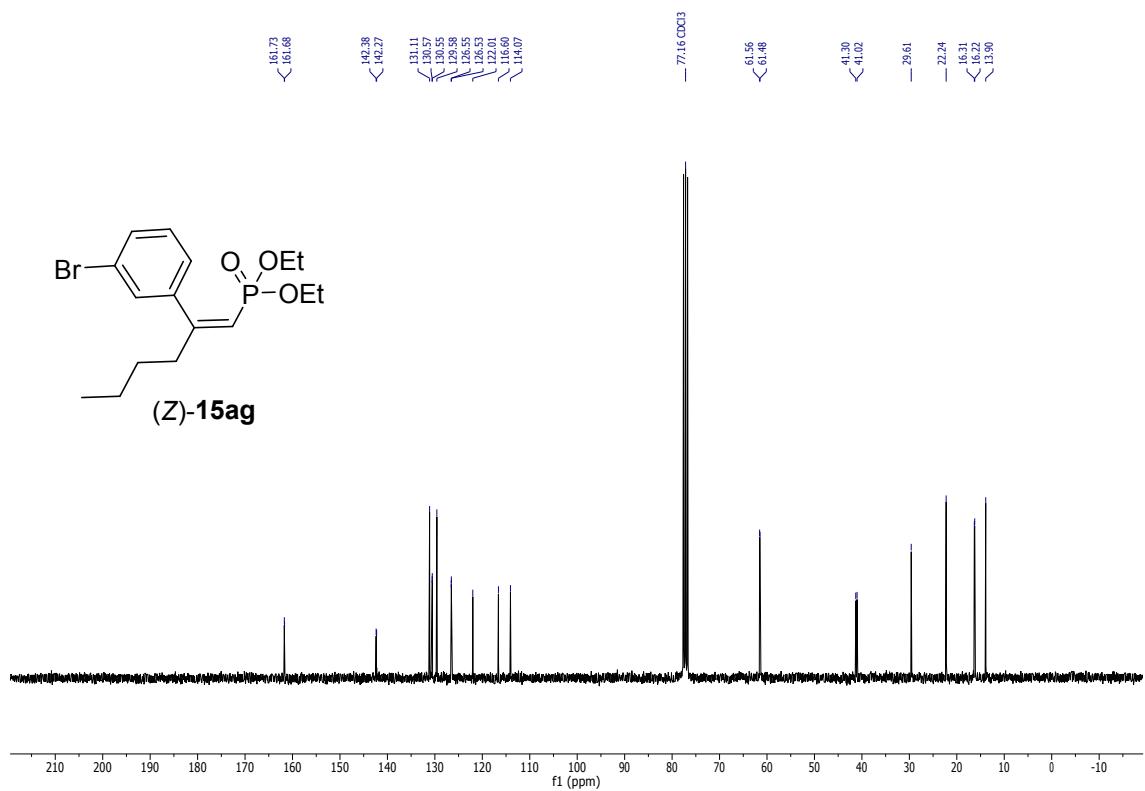
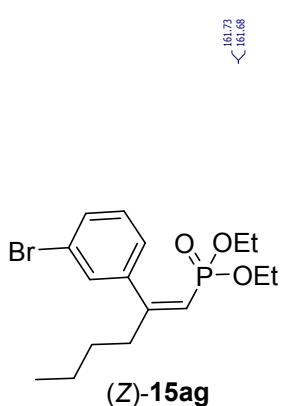


Figure S87. ^{13}C NMR (75 MHz, CDCl_3) of (Z)-15ag.

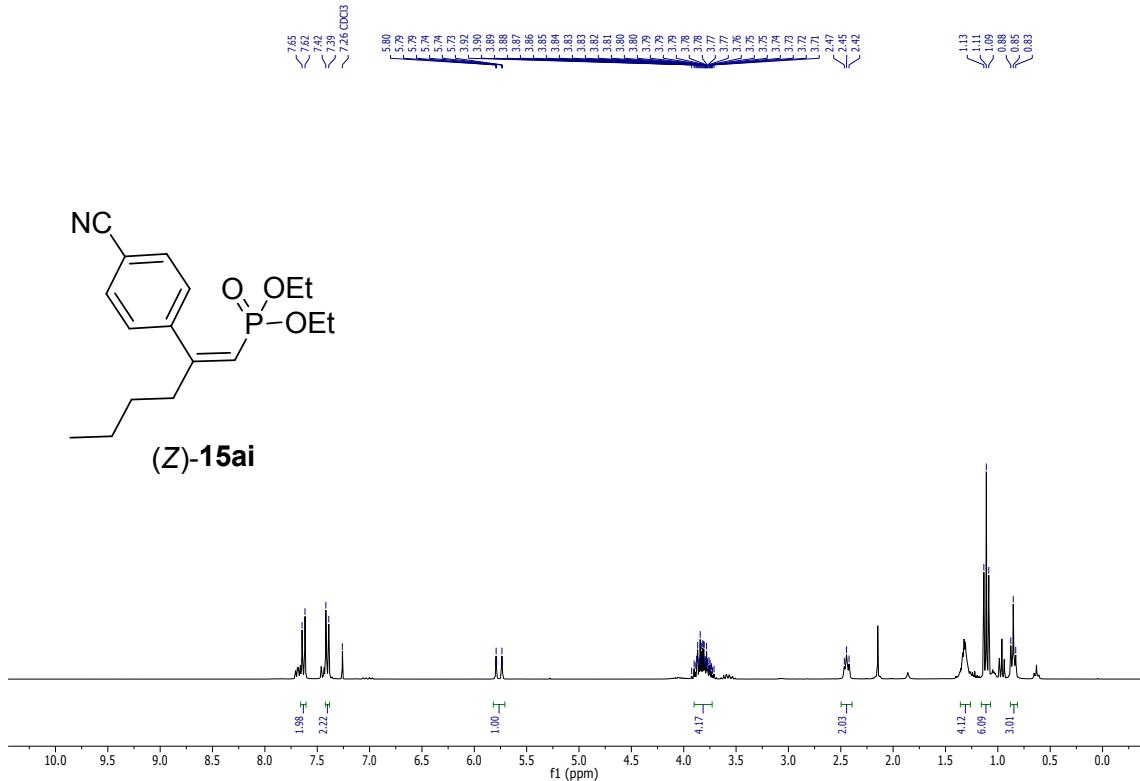
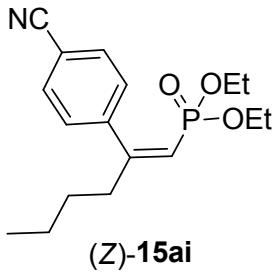


Figure S88. ^1H NMR (300 MHz, CDCl_3) of (Z)-15ai.

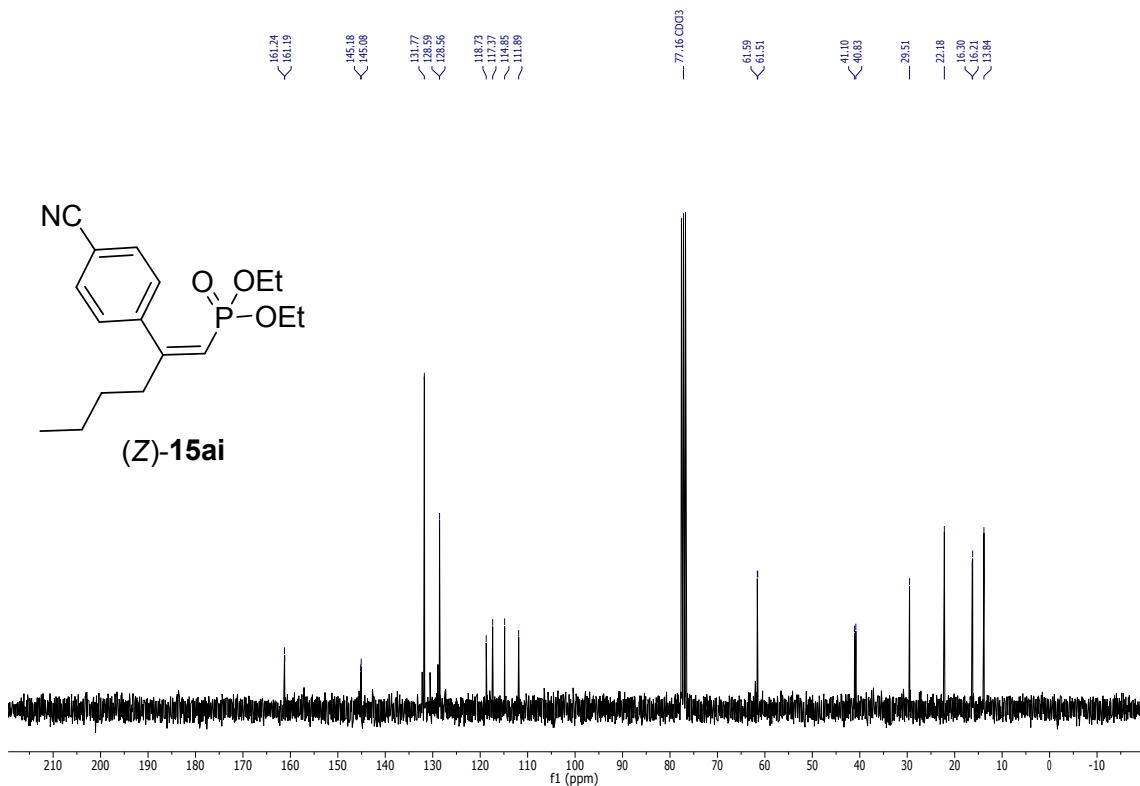
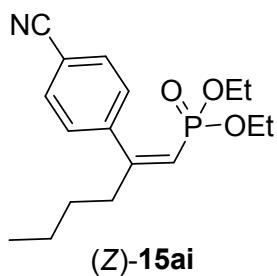
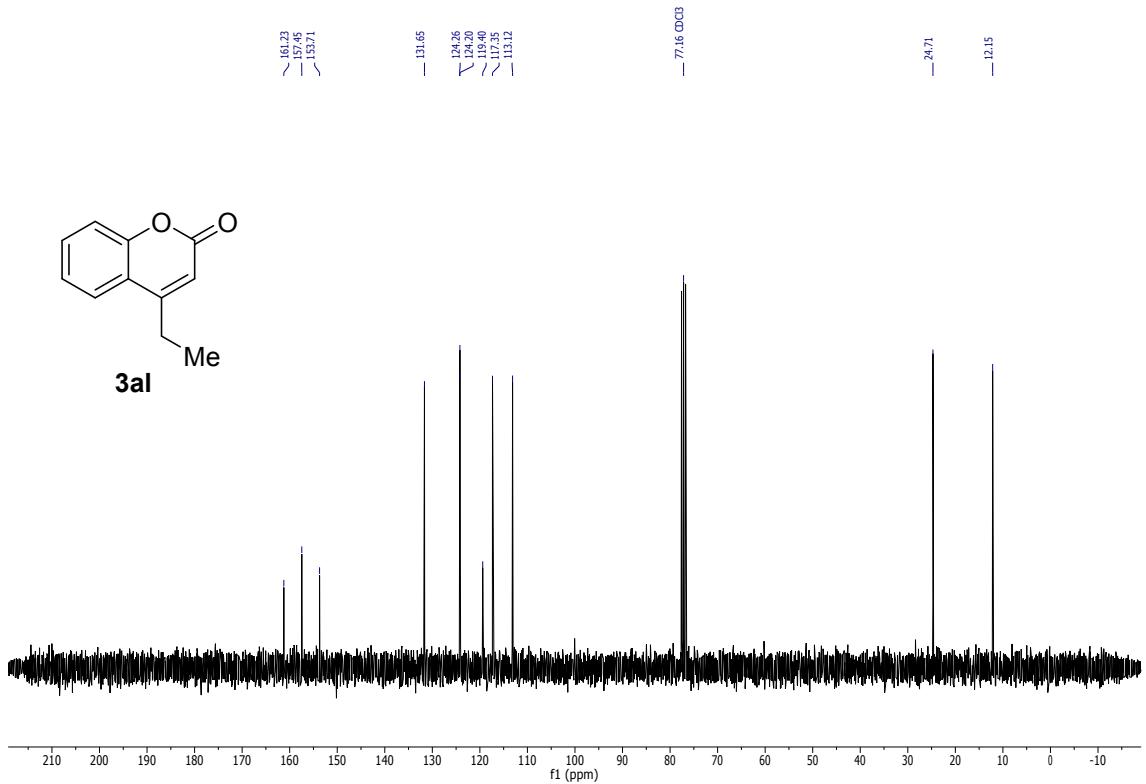
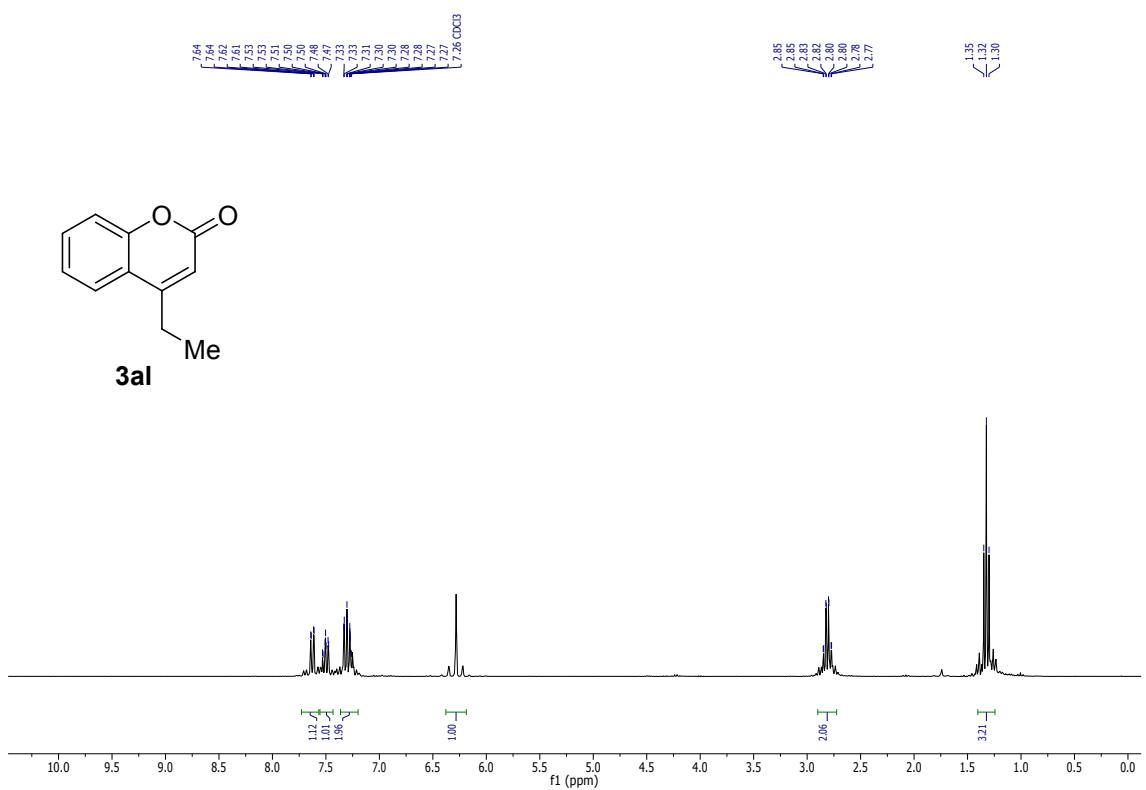


Figure S89. ^{13}C NMR (75 MHz, CDCl_3) of (Z)-15ai.



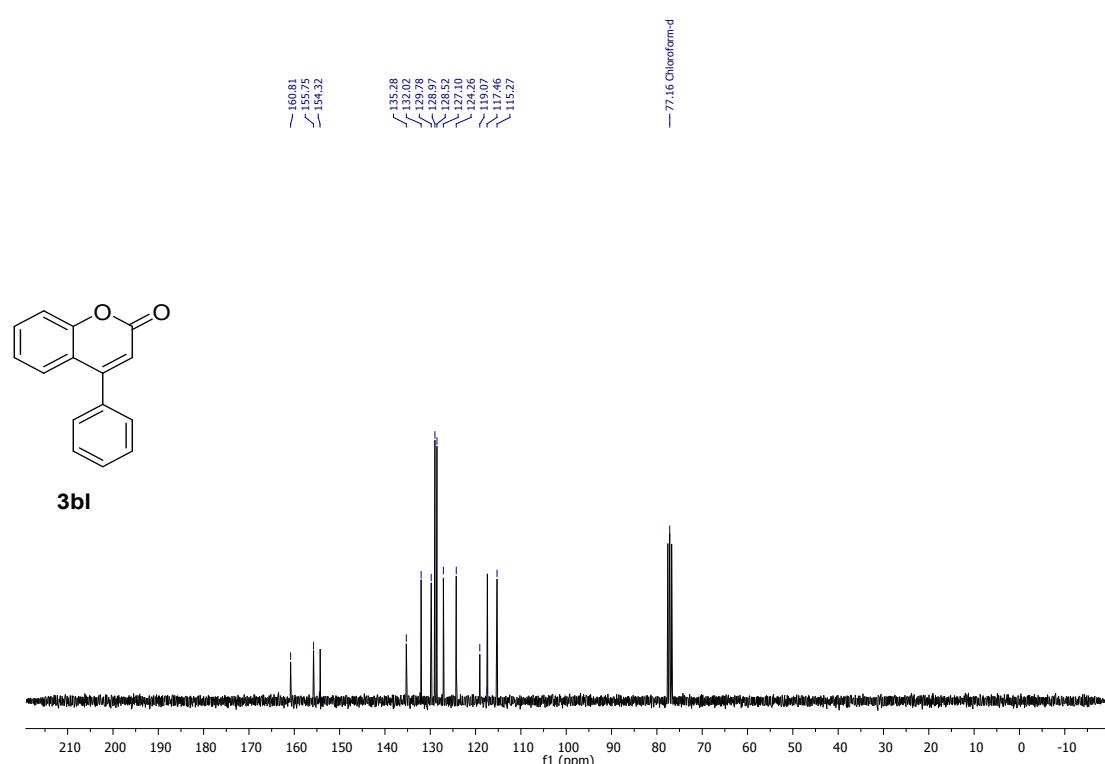
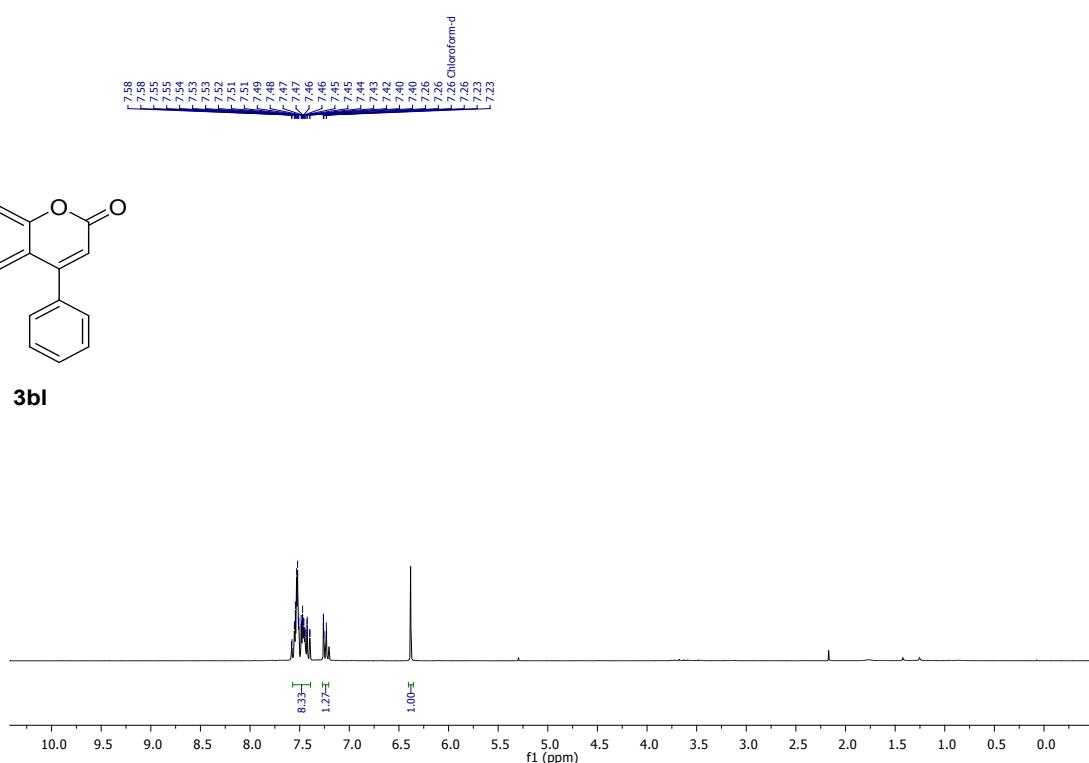
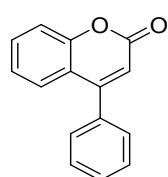
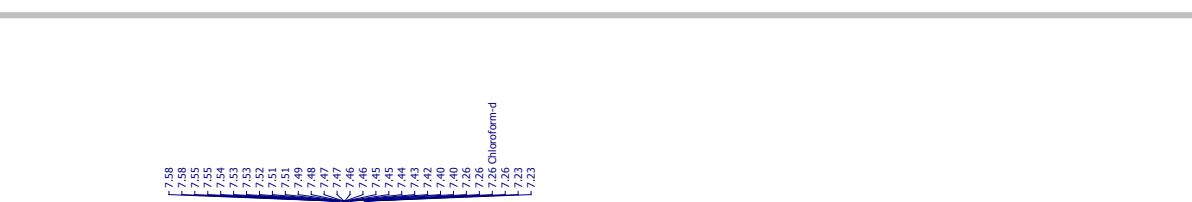


Figure S93. ^{13}C NMR (75 MHz, CDCl_3) of **3bl**.

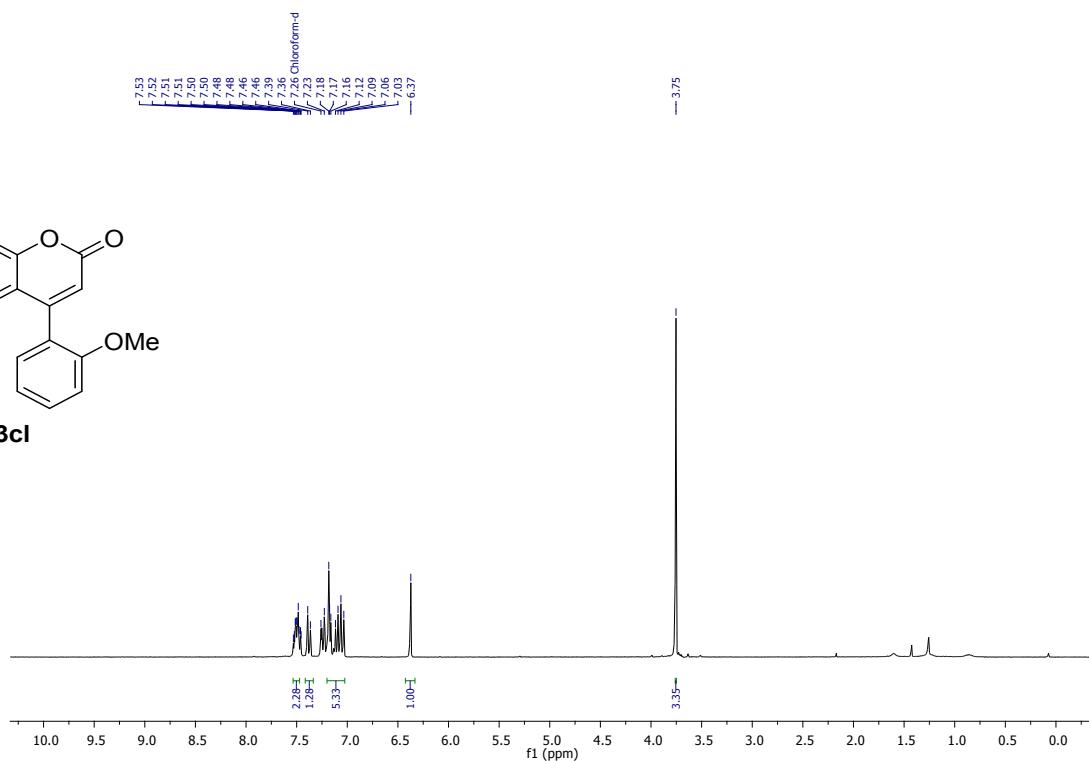
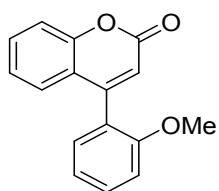
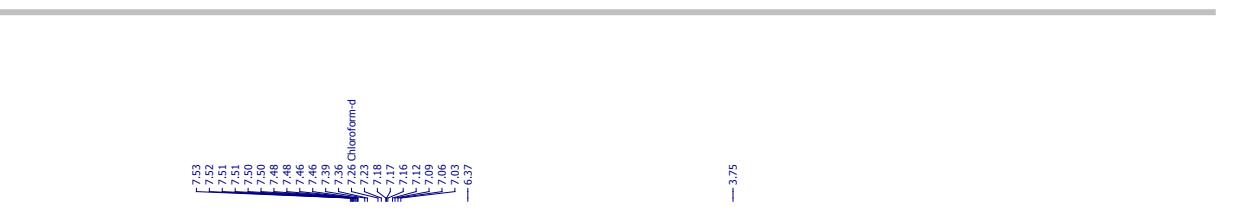


Figure S94. ^1H NMR (300 MHz, CDCl_3) of **3cl**.

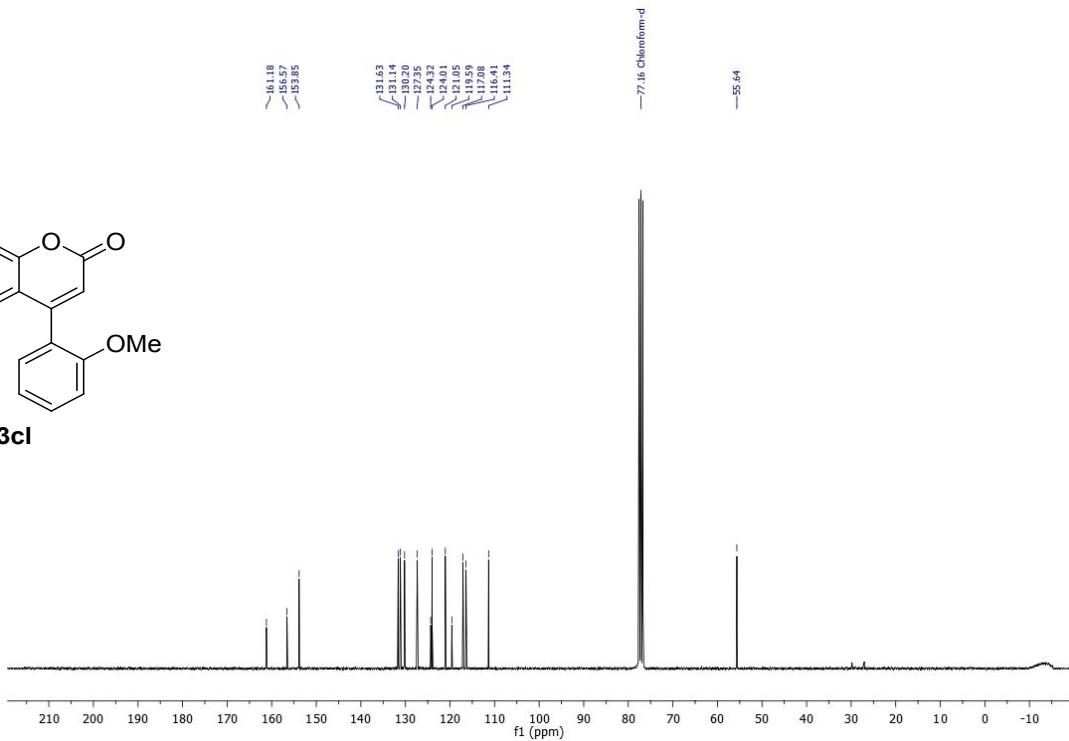
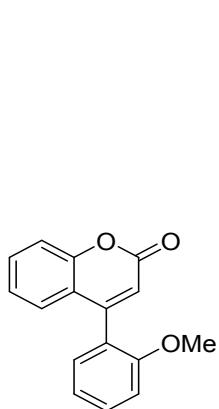


Figure S95. ^{13}C NMR (75 MHz, CDCl_3) of **3cl**.

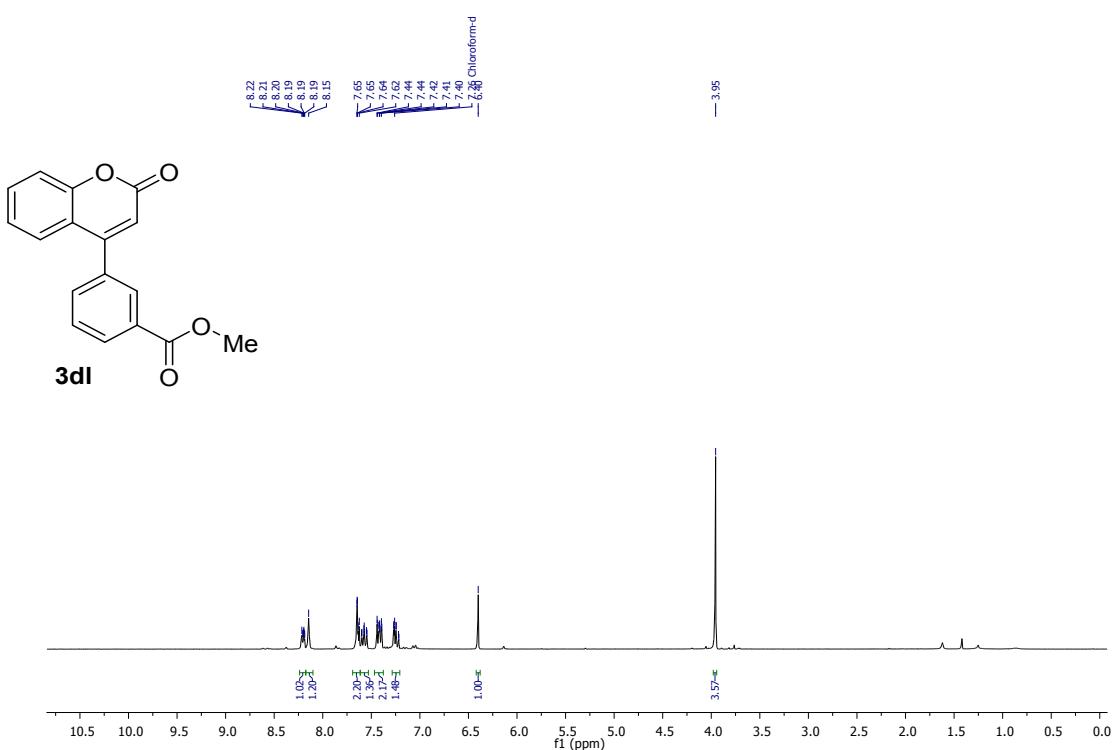


Figure S96. ^1H NMR (300 MHz, CDCl_3) of **3dl**.

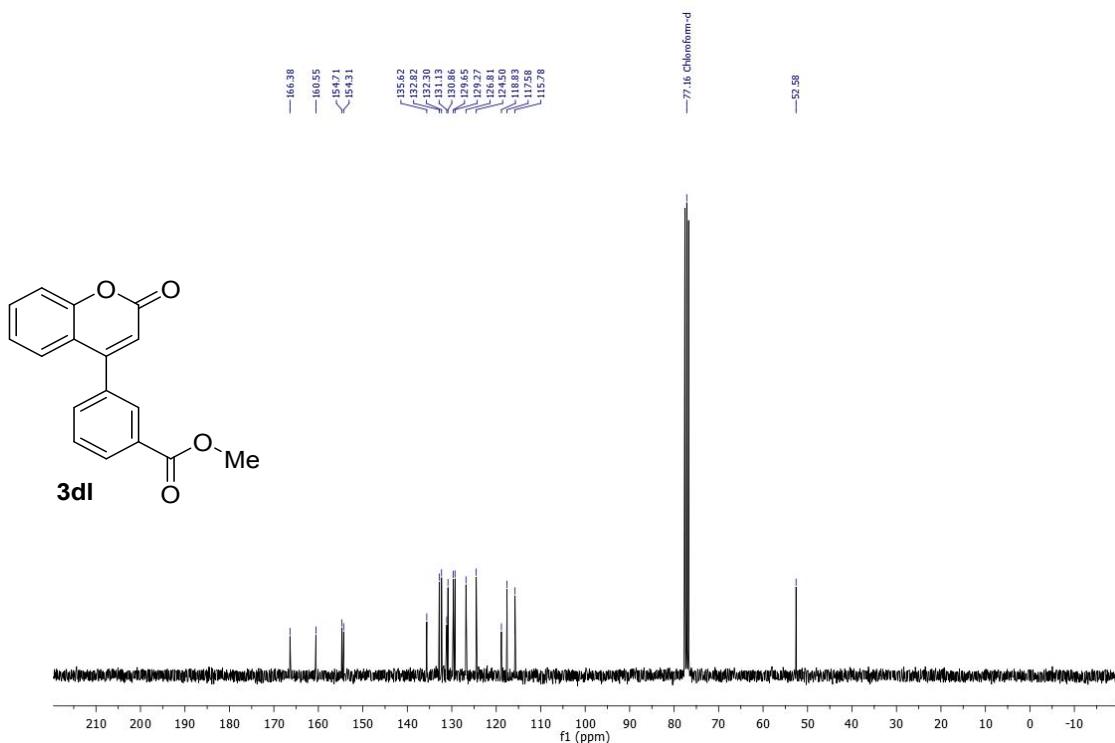


Figure S97. ^{13}C NMR (75 MHz, CDCl_3) of **3dl**.

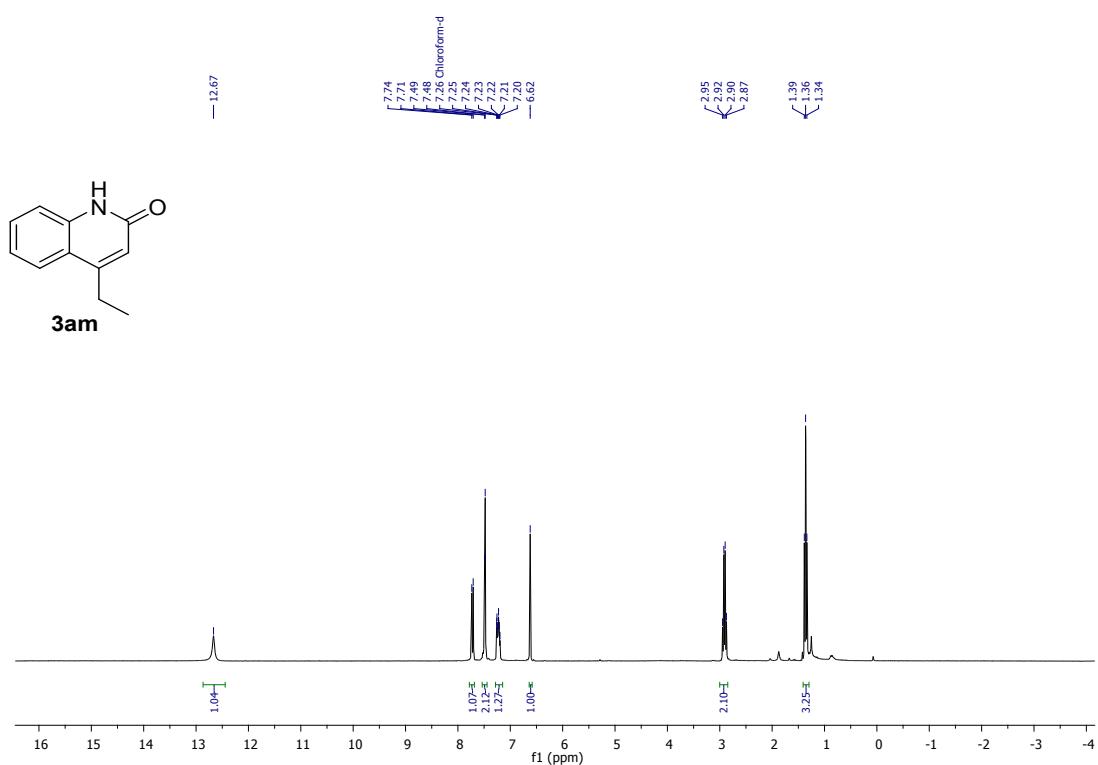


Figure S98. ^1H NMR (300 MHz, CDCl_3) of **3am**.

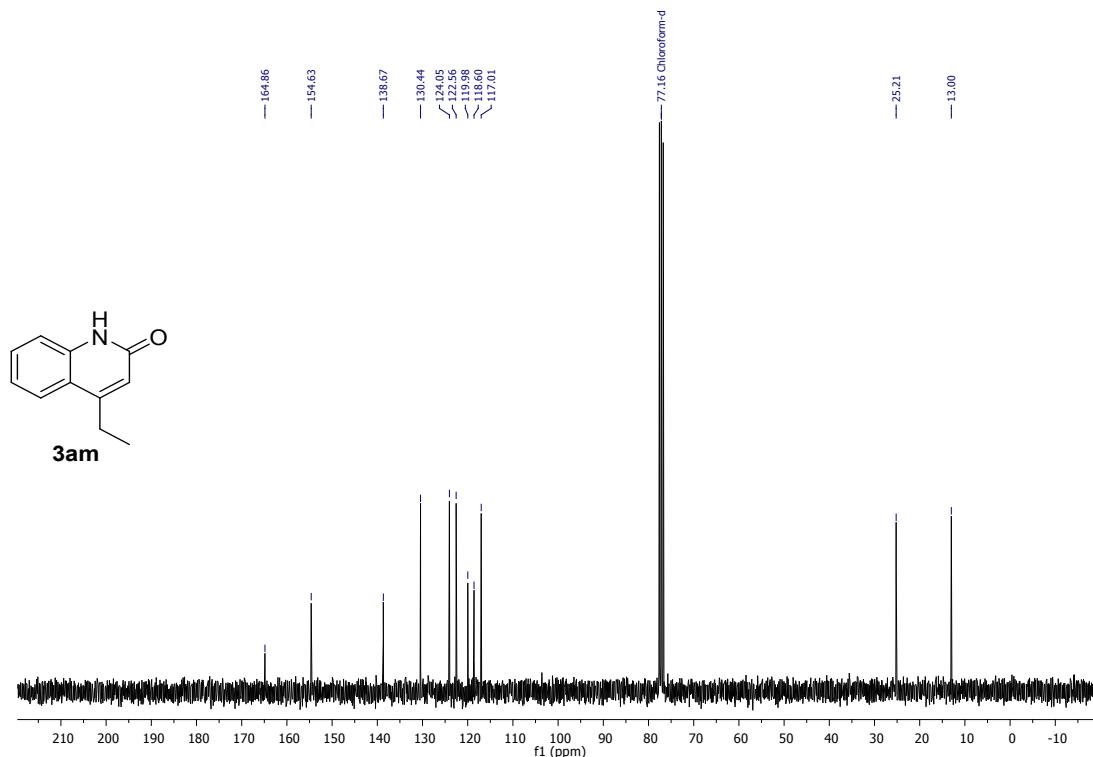


Figure S99. ^{13}C NMR (75 MHz, CDCl_3) of **3am**.

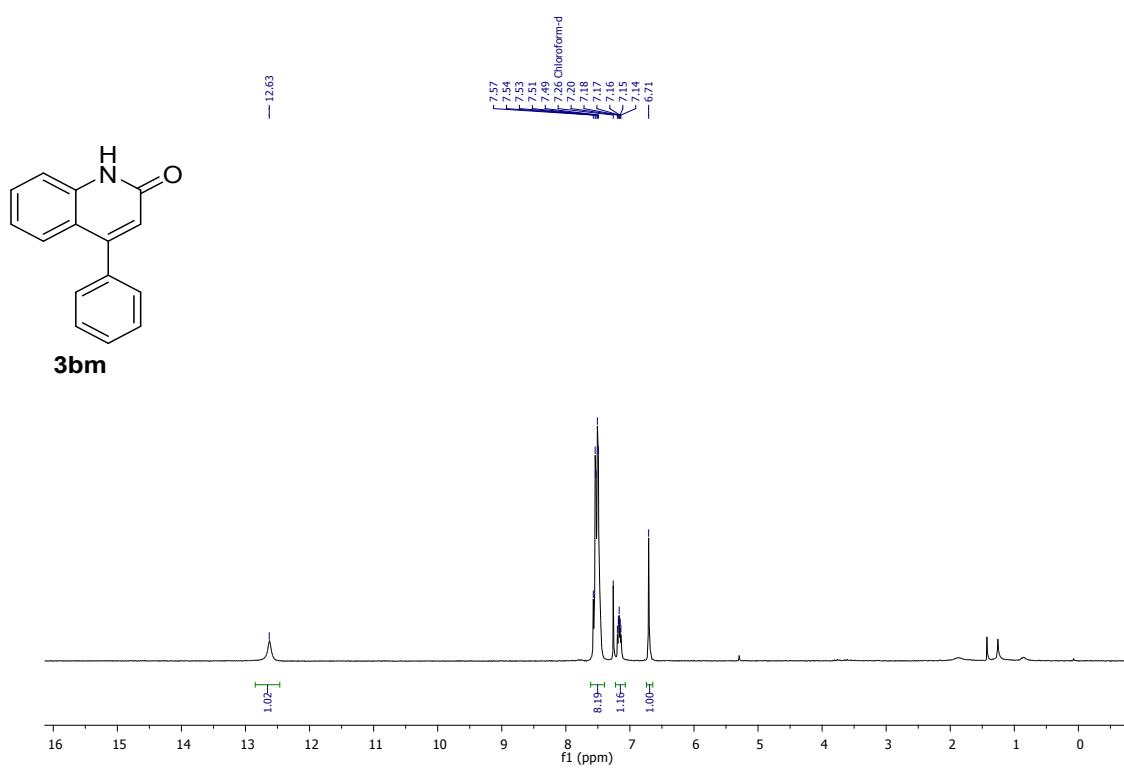


Figure S100. ^1H NMR (300 MHz, CDCl_3) of **3bm**.

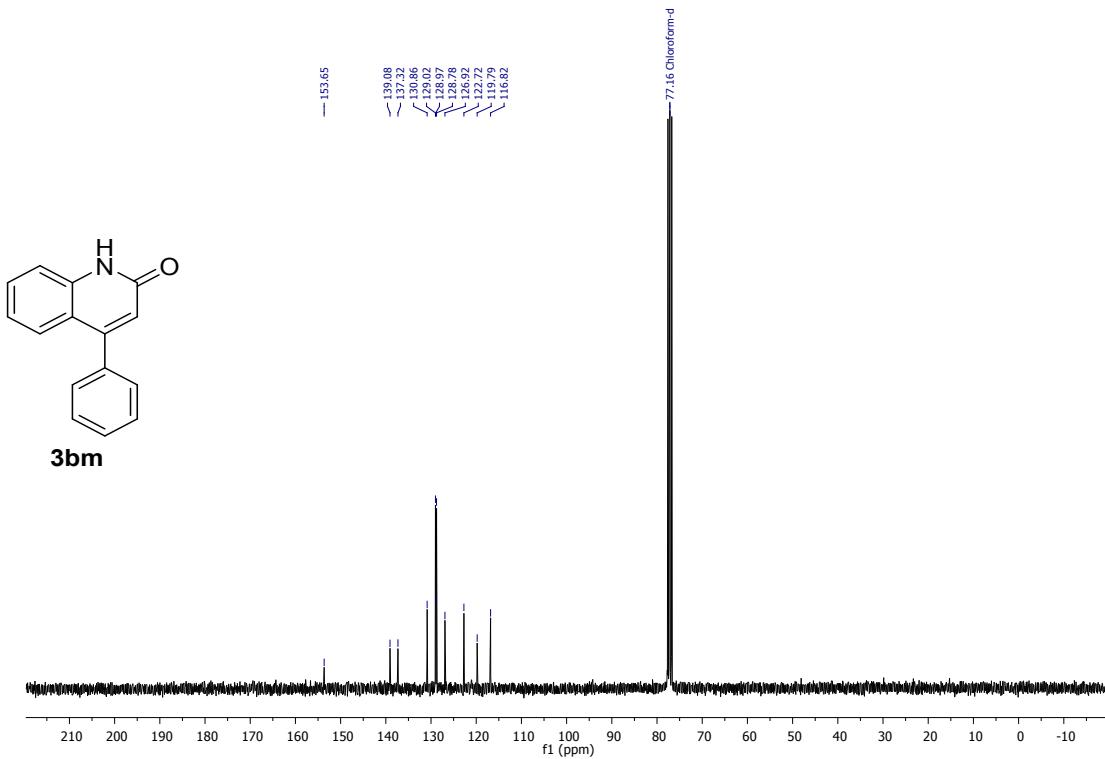


Figure S101. ^{13}C NMR (75 MHz, CDCl_3) of **3bm**.

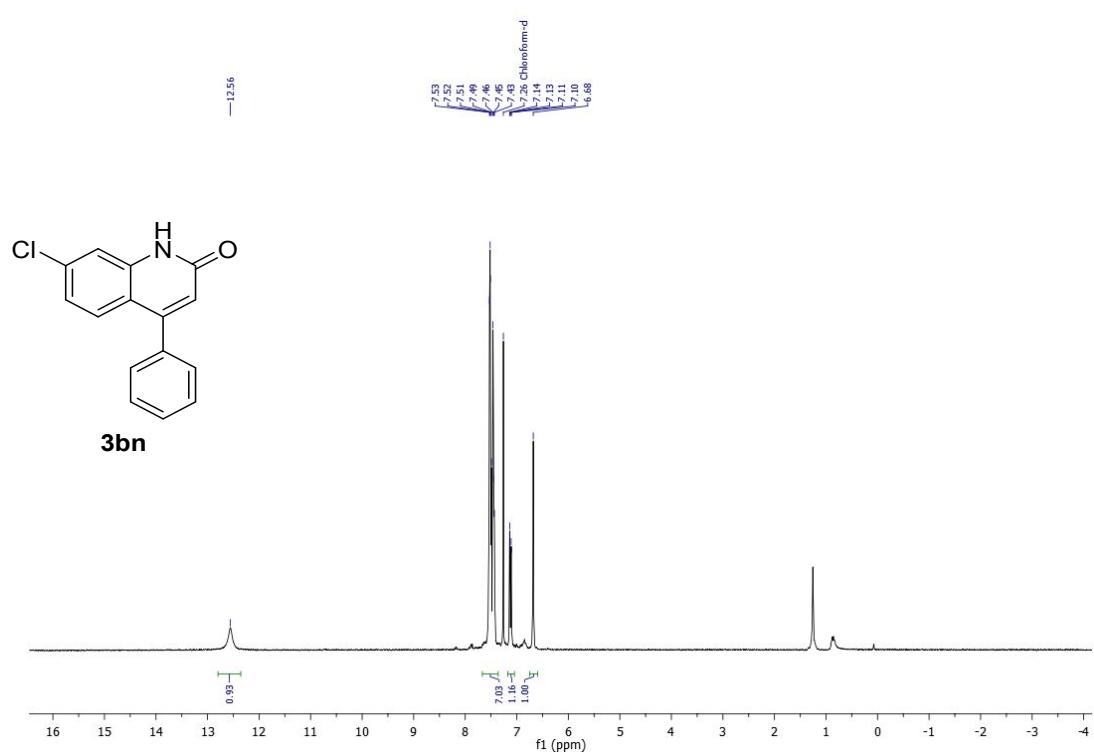


Figure S102. ¹H NMR (300 MHz, CDCl₃) of **3bn**.

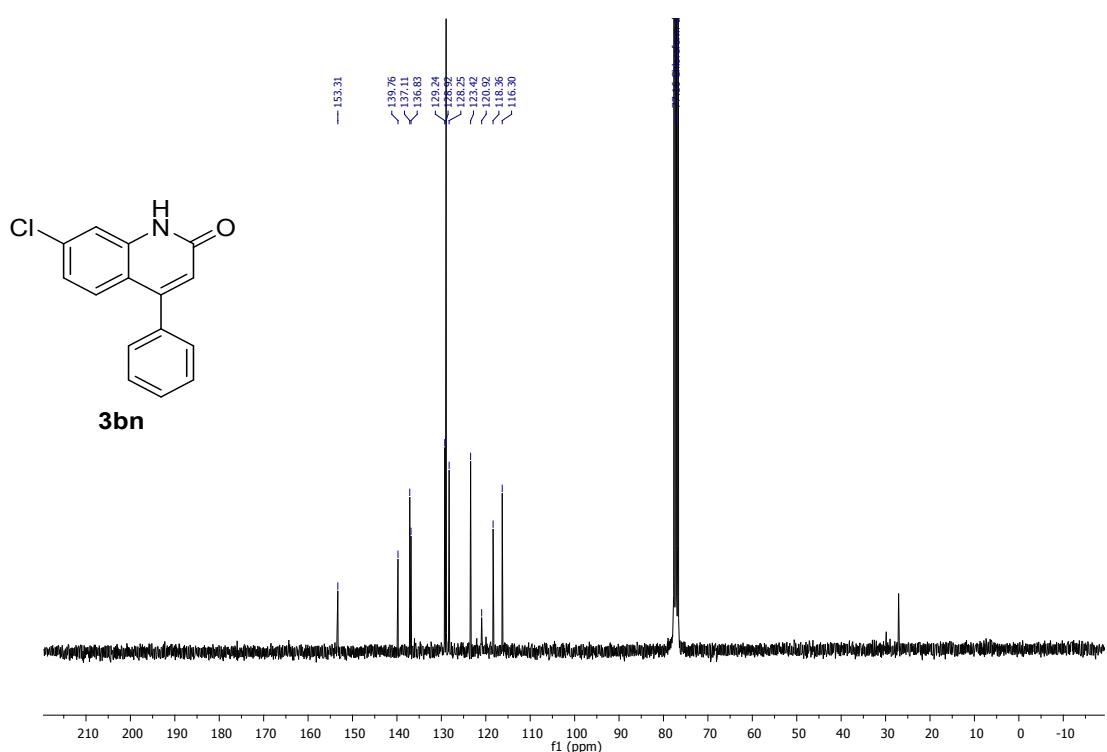


Figure S103. ¹³C NMR (75 MHz, CDCl₃) of **3bn**.

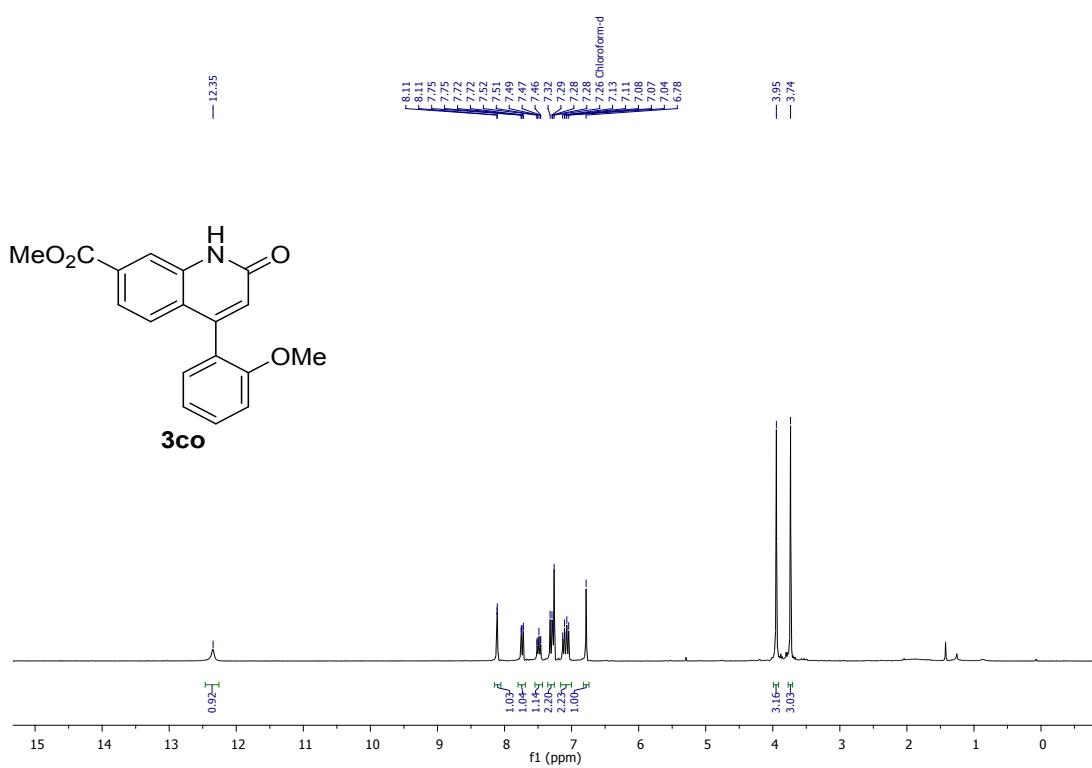


Figure S104. ^1H NMR (300 MHz, CDCl_3) of **3co**.

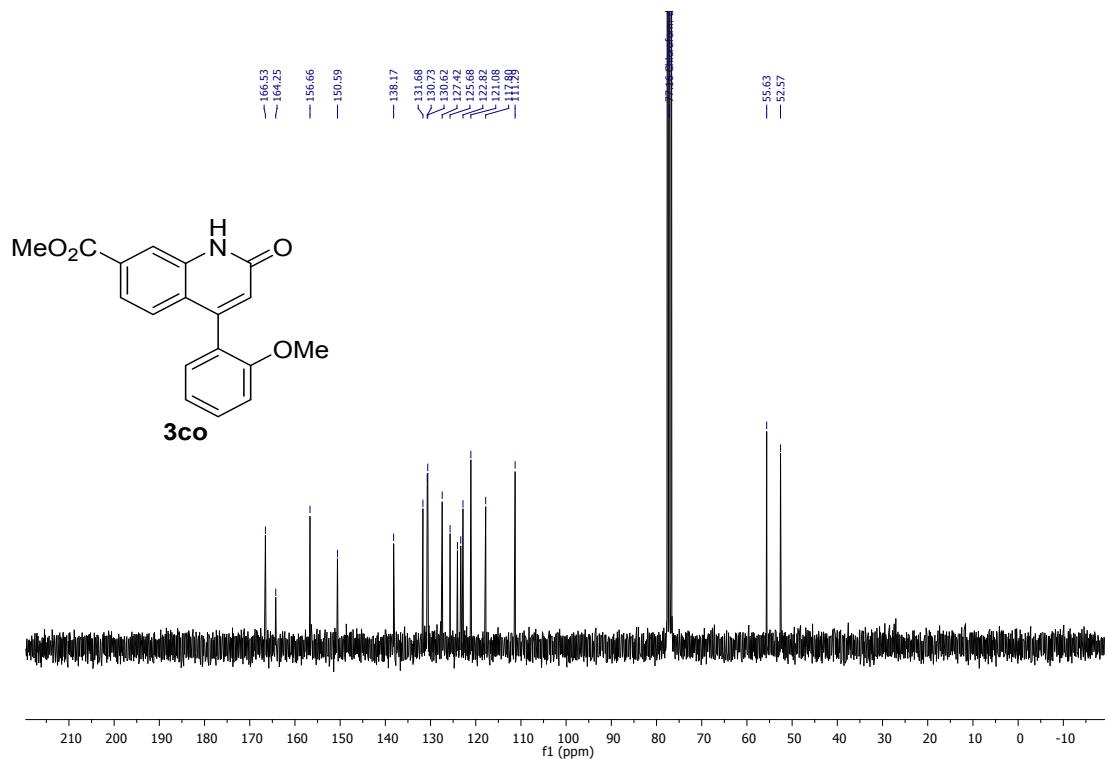


Figure S105. ^{13}C NMR (75 MHz, CDCl_3) of **3co**.

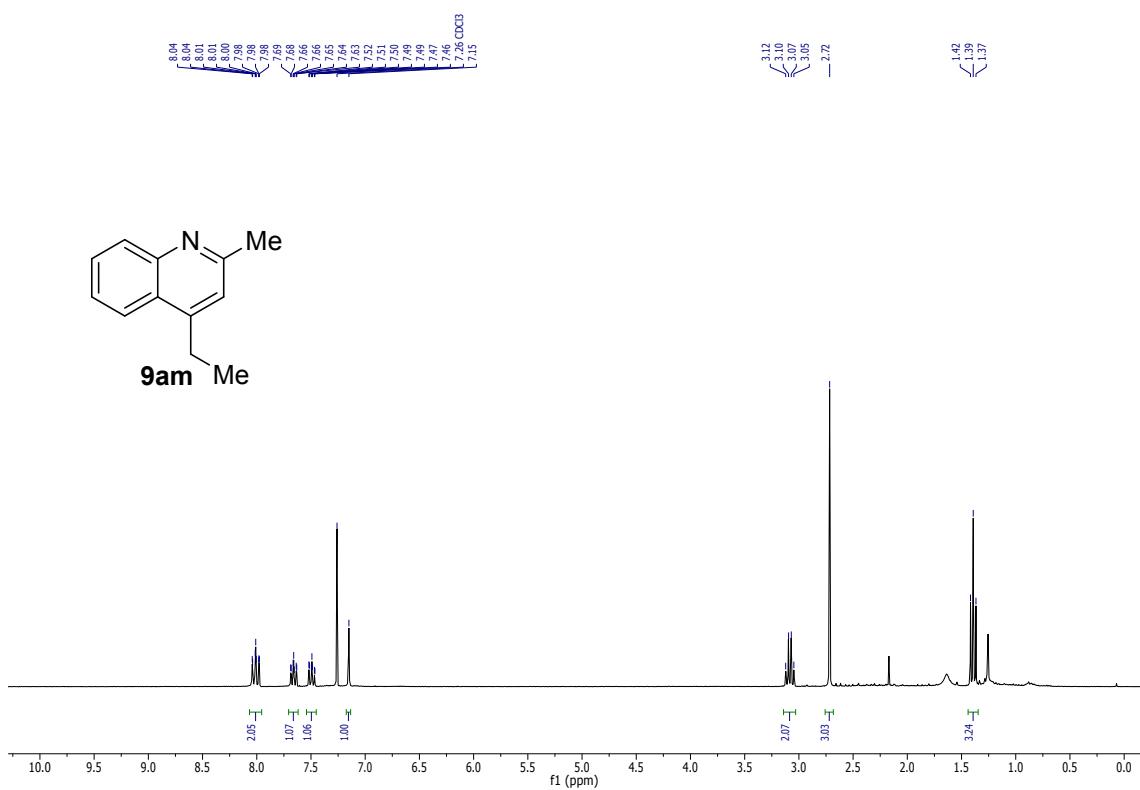


Figure S106. ^1H NMR (300 MHz, CDCl_3) of **9am**.

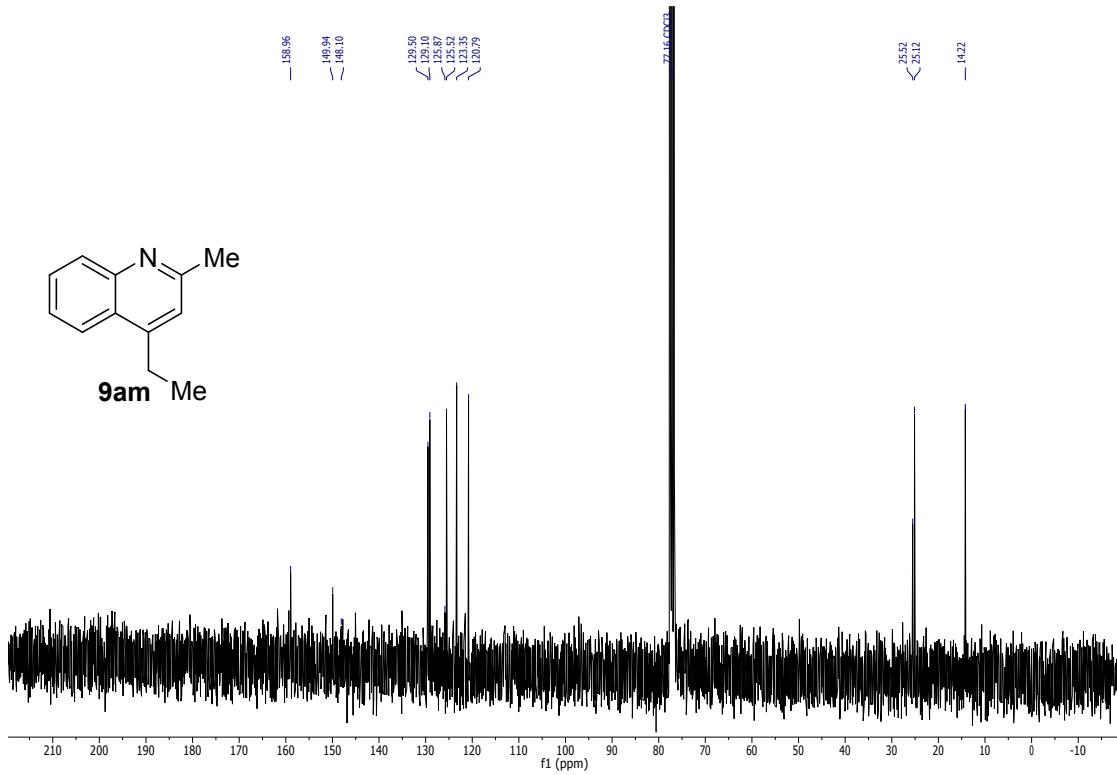


Figure S107. ^{13}C NMR (75 MHz, CDCl_3) of **9am**.

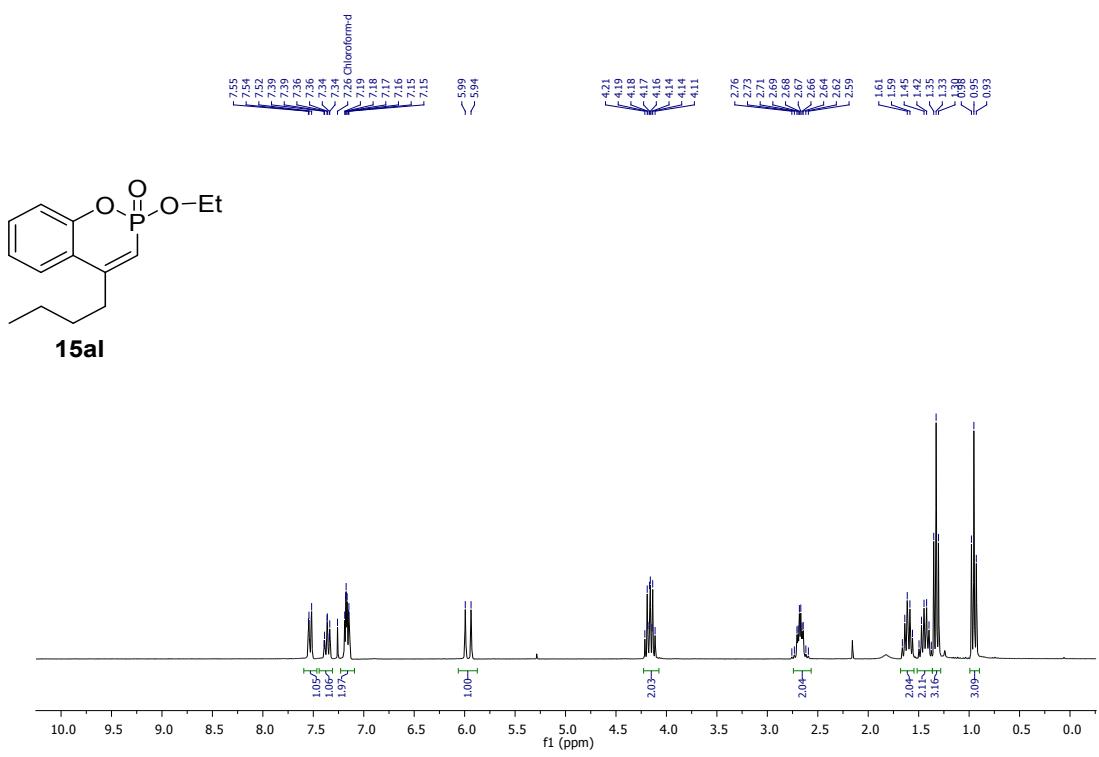


Figure S108. ¹H NMR (300 MHz, CDCl₃) of **15al**.

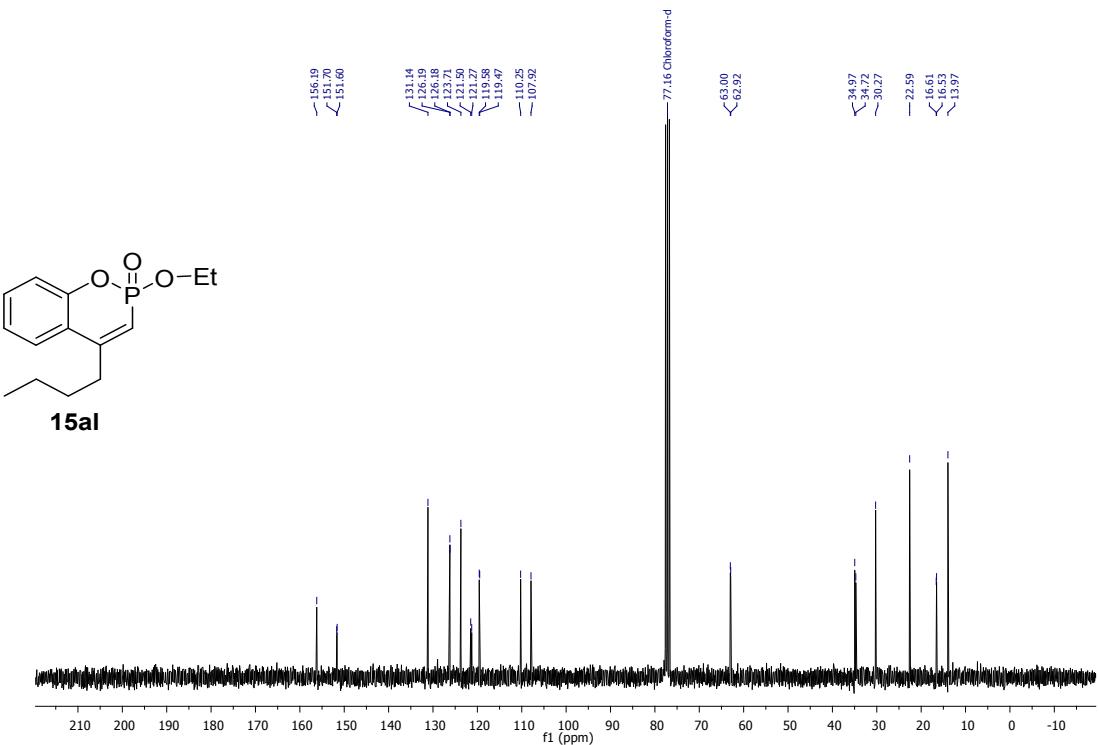


Figure S109. ¹³C NMR (75 MHz, CDCl₃) of **15al**.

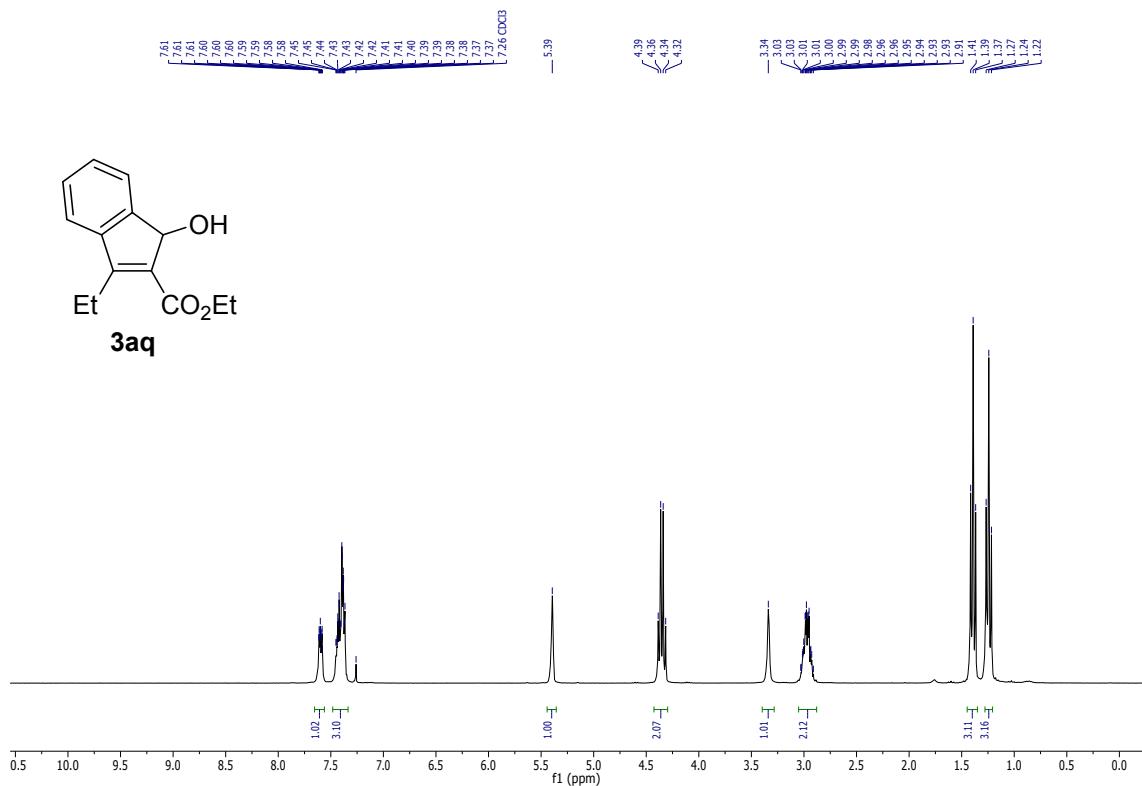
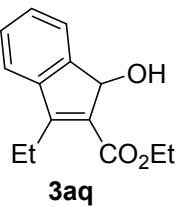


Figure S110. ^1H NMR (300 MHz, CDCl_3) of **3aq**.

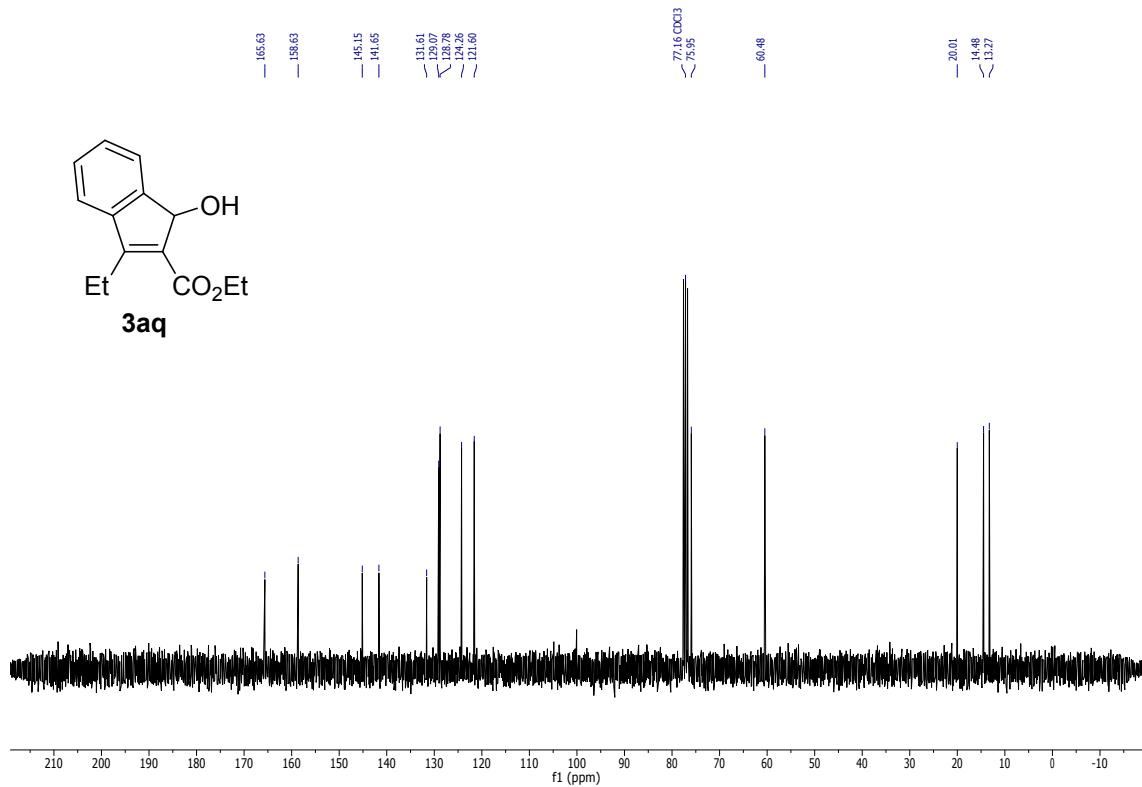
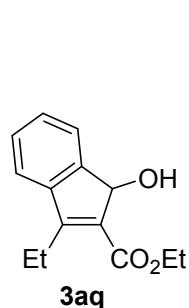


Figure S111. ^{13}C NMR (75 MHz, CDCl_3) of **3aq**.

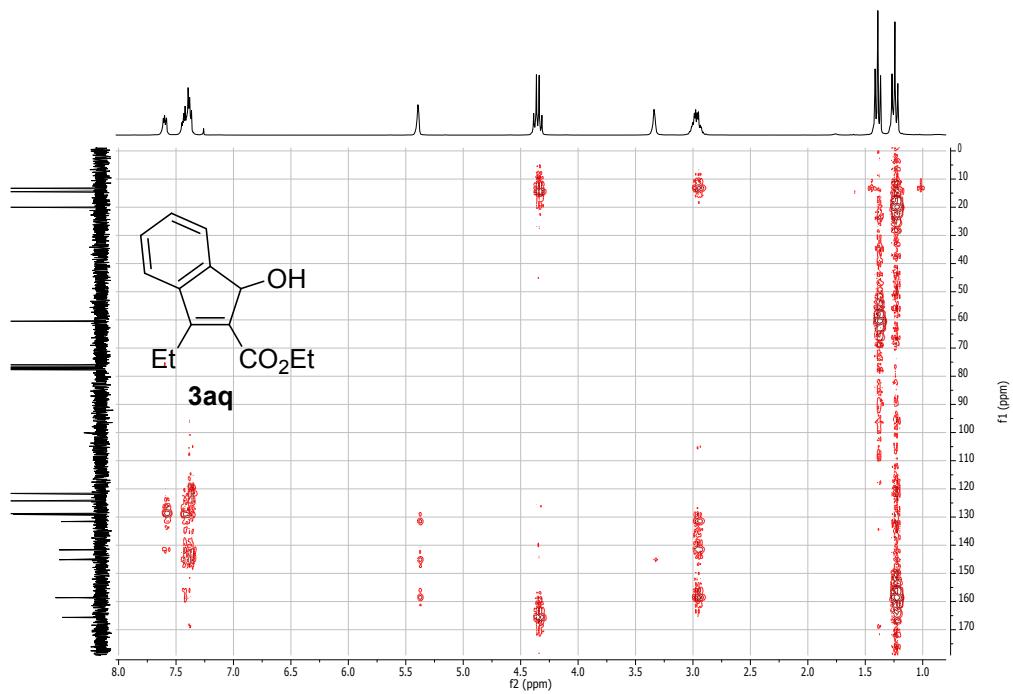


Figure S112. HMQC spectrum of **3aq**.

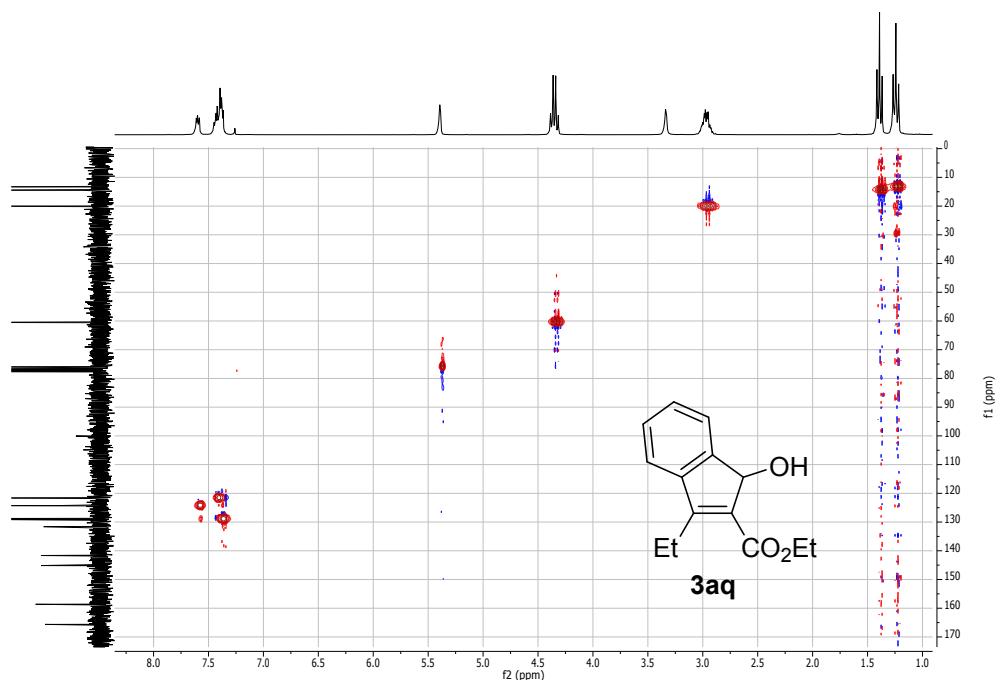


Figure S113. HSQC spectrum of **3aq**.