Transition-Metal-Free Regioselective and Stereoselective C(sp^2)-C(sp^3) Coupling of Enamides with Ethers or Alkanes via Photoredox-Catalyzed Cross-Dehydrogenative Coupling Reactions

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Supporting Information

Table of Contents

General Information **S-2**

General Procedures for the Synthesis of *β*-alkylated Enamides 2 ..... **S-3**

General Procedures for the Synthesis of *β*-alkylated Enamides 4 ..... **S-3**

Method A **S-3**

Method B **S-3**

Method C **S-4**

Analytical Data for the *β*-alkylated Enamides **S-4**

Synthetic Applications **S-23**

(a) Gram-Scale Synthesis of Enamide 2a **S-23**

(b) The Palladium-Catalyzed Heck-Coupling Reaction **S-24**

(c) Hydrolysis of *β*-alkylated Enamide 2a **S-25**

(d) Conversion of Stereochemistry of Enamides **S-26**

(e) The Synthesis of *α*-acyloxyketone **S-27**

(f) Cleavage of *N*-Boc Group **S-28**

Mechanistic Studies **S-28**

(a) Trapping Experiment with 2,2,6,6-Tetramethylpiperidin-1-oxyl (TEMPO) **S-28**

(b) Trapping Experiment with Ethene-1,1-Diyldibenzene **S-29**

(c) Intermolecular Kinetic Isotopic Effect (KIE) Study **S-30**

(d) Quantum Yield Measurement **S-32**

(e)Stern-Volmer Experiments **S-34**

References **S-36**

^{1}H NMR, ^{19}F NMR and ^{13}C NMR Spectra of Products **S-37**

General Information

All photoredox-catalyzed reactions were carried out in oven-dried Schlenk tubes under nitrogen atmosphere using anhydrous solvent purchased from Energy Chemical. All enamides or enecarbamates were prepared using existing methods.[1] ^{1}H, ^{19}F, ^{13}C NMR spectra were recorded in $CDCl_3$ on Bruker Avance 400 MHz spectrometers. Data are reported in the following order: chemical shift (δ) in ppm; multiplicities are indicated s (singlet), d (doublet), t (triplet), dd (doublet of doublets), m (multiplet); coupling constants (J) are in Hertz (Hz). NMR spectra were taken using TMS (^{1}H, δ = 0), $CDCl_3$ (^{1}H, δ = 7.26), and $CDCl_3$ (^{13}C, CPD δ = 77.16) as the internal standards, respectively. HRMS were obtained on an IonSpec FT-ICR mass spectrometer with ESI resource. Column chromatography was generally performed on silica gel (300-400 mesh) and reactions were monitored by thin layer chromatography (TLC) using UV light to visualize the course of the reactions.

The photoredox-catalyzed transformations were carried out in a customized dark cassette equipped with three 80 W blue LEDs lamp from different directions for irradiation along with an electronic cooling fan for heat dissipation (**Figure S1**). A magnetic hotplate stirrer was placed in the dark cassette for stirring. The reaction vessel was placed in the center of the stirrer so that the average distance from the lamp to the reaction medium was 10 cm. The 80 W blue LEDs were purchased from Ctech Global Pte Ltd (Singapore) with the maximum absorption wavelength of 460-465 nm. The borosilicate made reaction vessels (Schlenk tubes) were all purchased from Synthware Glassware.

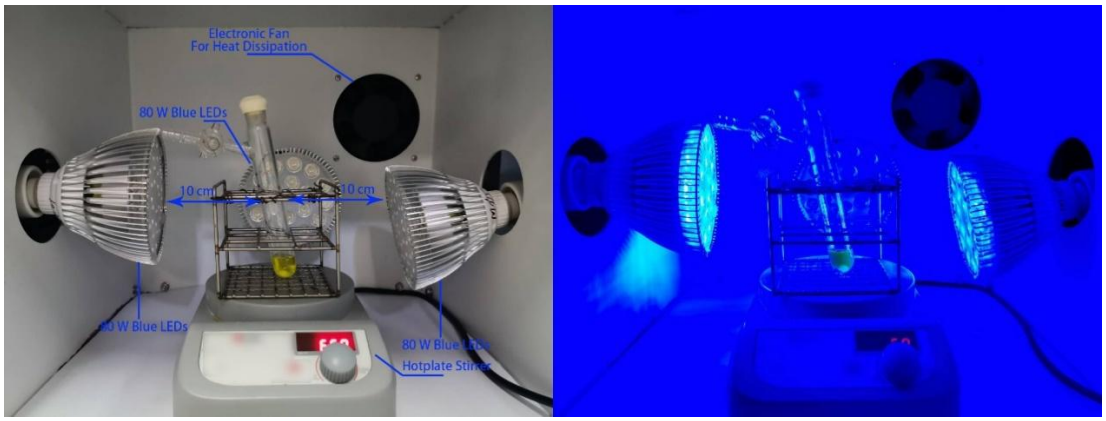
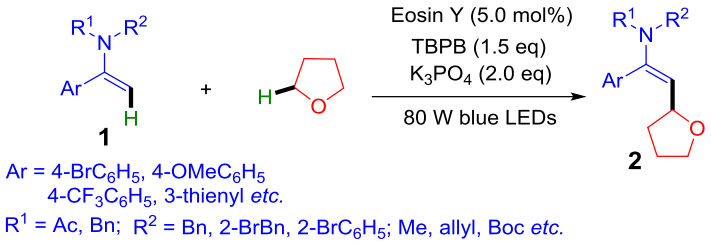


Figure S1 The customized dark cassette equipped with 80 W blue LEDs lamps

Abbreviations: Bn = benzyl, Ac = acetyl, DMA = dimethylacetamide, THF = Tetrahydrofuran, TBPB = *tert*-Butyl peroxybenzoate, Boc = *t*-butoxycarbonyl, TEMPO = 2,2,6,6-tetramethylpiperidinooxy.

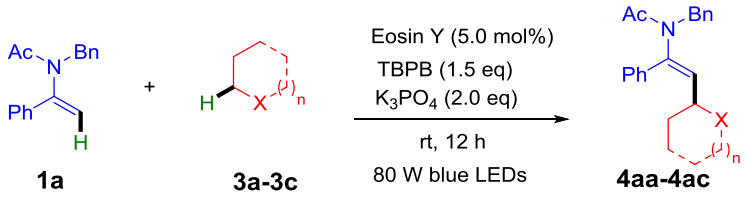
General Procedures for the Synthesis of *β*-alkylated Enamides 2



Method A:

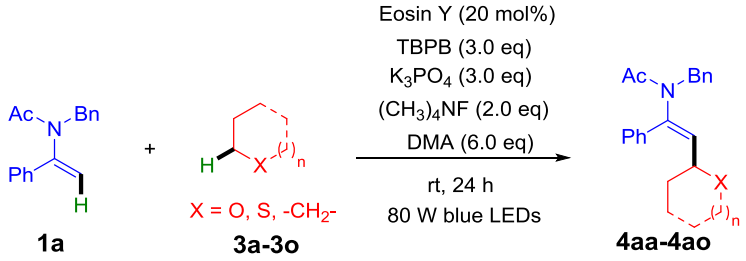
Enamides or enecarbamates **1** (0.3 mmol), Eosin Y (0.015 mmol, 5.0 mol%) and K_3PO_4 (0.6 mmol, 2.0 eq) were added sequentially into Schlenk tube under nitrogen, the tube was then capped with a rubber stopper. TBPB (90 μL, 0.45 mmol, 1.5 eq) and THF (1.5 mL) were then added by syringe. The resulting mixture was stirred under 80 W blue LEDs irradiation. Upon completion of the reaction as monitored by TLC, the solvent was removed under vacuum and the residue was purified by flash silica gel column chromatography using petroleum ether/ethyl acetate (10:1 *v*/*v*) as eluent to afford pure products **2a-2z**, **2aa-2ag.**

General Procedures for the Synthesis of *β*-alkylated Enamides 4



Method A:

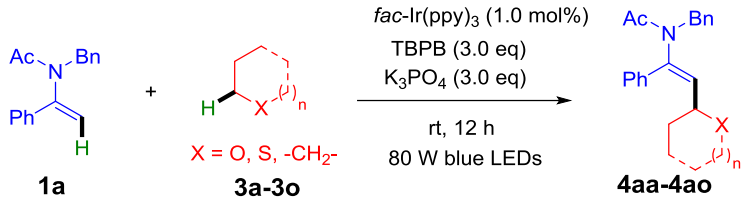
Enamide **1a** (0.3 mmol), Eosin Y (0.015 mmol, 5.0 mol%) and K_3PO_4 (0.6 mmol, 2.0 eq) were added sequentially into Schlenk tube under nitrogen, the tube was then capped with a rubber stopper. TBPB (90 μL, 0.45 mmol, 1.5 eq) and ethers **3a-3c** (1.5 mL) were then added by syringe. The resulting mixture was stirred under 80 W blue LEDs irradiation. Upon completion of the reaction as monitored by TLC, the solvent was removed under vacuum and the residue was purified by flash silica gel column chromatography using petroleum ether/ethyl acetate (10:1 *v*/*v*) as eluent to afford pure products **4aa-4ac.**



Method B

Enamide **1a** (0.3 mmol), K_3PO_4 (0.9 mmol, 3.0 eq), tetramethylammonium fluoride (0.6 mmol,

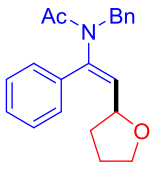
2.0 eq) and Eosin Y (0.06 mmol, 20 mol%) were added sequentially into Schlenk tube under nitrogen, the tube was then capped with a rubber stopper. TBPB (180 μL, 0.9 mmol, 3.0 eq), dimethylacetamide (1.8 mmol, 6.0 eq) and ethers **3a-3j** (or alkanes **3k-3o**) (1.5 mL) were then added by syringe. The resulting mixture was stirred under 80 W blue LEDs irradiation for 24 h. Upon completion of the reaction as monitored by TLC, the solvent was removed under vacuum and the residue was purified by flash silica gel column chromatography using petroleum ether/ethyl acetate (10:1 *v*/*v*) as eluent to afford pure products **4aa-4ao.**



Method C

Enamide **1a** (0.3 mmol), *fac*-Ir(ppy)$_3$ (0.003 mmol, 1.0 mol%) and K_3PO_4 (0.9 mmol, 3.0 eq) were added sequentially into Schlenk tube under nitrogen, the tube was then capped with a rubber stopper. TBPB (180 μL, 0.9 mmol, 3.0 eq) and **3d-3o** (1.5 mL) were then added by syringe. The resulting mixture was stirred under 80 W blue LEDs irradiation for 12 h. Upon completion of the reaction as monitored by TLC, the solvent was removed under vacuum and the residue was purified by flash silica gel column chromatography using petroleum ether/ethyl acetate (10:1 *v*/*v*) as eluent to afford pure products **4ad-4ao.**

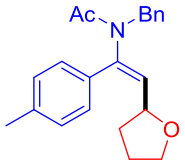
Analytical Data for the *β*-alkylated Enamides



2a

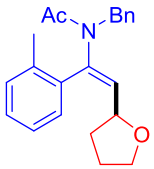
(*E*)-*N*-benzyl-*N*-(1-phenyl-2-(tetrahydrofuran-2-yl)vinyl)acetamide (2a): 87 mg, 90% yield. Colorless oil. Eluents for flash column chromatography petroleum ether/ethyl acetate (10:1 *v*/*v*). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.44 – 7.36 (m, 3H), 7.32 – 7.17 (m, 7H), 5.30 (d, J = 9.4 Hz, 1H), 4.78 (d, J = 14.3 Hz, 1H), 4.40 (q, J = 7.6 Hz, 1H), 4.26 (d, J = 14.3 Hz, 1H), 3.82 (q, J = 7.4 Hz, 1H), 3.70 (q, J = 7.3 Hz, 1H), 2.26 (s, 3H), 2.08 – 1.98 (m, 1H), 1.94 – 1.79 (m, 2H), 1.54 – 1.41 (m, 1H).^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 171.0, 140.5, 137.1, 134.4, 132.4, 129.04, 128.96, 128.7,

128.5, 128.2, 127.2, 75.1, 68.1, 49.3, 32.6, 26.1, 22.3. HRMS m/z: calcd for $C_{21}H_{23}NNaO_2^+$ $[M+Na]^+$ 344.1621, found: 344.1606.



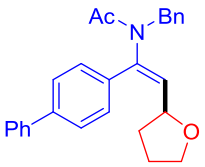
2b

(*E*)-*N*-benzyl-*N*-(2-(tetrahydrofuran-2-yl)-1-(p-tolyl)vinyl)acetamide (2b): 87 mg, 86% yield. Colorless oil. Eluents for flash column chromatography petroleum ether/ethyl acetate (10:1 *v*/*v*). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.31 – 7.12 (m, 9H), 5.25 (d, J = 9.4 Hz, 1H), 4.76 (d, J = 14.1 Hz, 1H), 4.40 (q, J = 8.1 Hz, 1H), 4.26 (d, J = 14.2 Hz, 1H), 3.82 (q, J = 8.0 Hz, 1H), 3.70 (q, J = 8.0 Hz, 1H), 2.39 (s, 3H), 2.24 (s, 3H), 2.09 – 1.97 (m, 1H), 1.94 – 1.80 (m, 2H), 1.54 – 1.39 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 171.1, 140.5, 139.1, 137.1, 131.8, 131.4, 129.2, 128.9, 128.6, 128.1, 127.2, 75.2, 68.0, 49.3, 32.6, 26.1 22.3, 21.2. HRMS m/z: calcd for $C_{22}H_{25}NNaO_2^+$ $[M+Na]^+$ 358.1778, found: 358.1765.



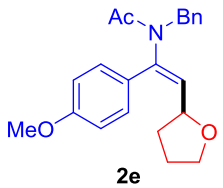
2c

(*E*)-*N*-benzyl-*N*-(2-(tetrahydrofuran-2-yl)-1-(o-tolyl)vinyl)acetamide (2c): 50 mg, 50% yield. Colorless oil. Eluents for flash column chromatography petroleum ether/ethyl acetate (10:1 *v*/*v*). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.31 – 7.16 (m, 6H), 7.11 (d, J = 6.8 Hz, 3H), 5.47 (d, J = 9.5 Hz, 1H), 4.47 (d, J = 15.1 Hz, 1H), 4.38 (d, J = 15.1 Hz, 1H), 4.12 – 4.03 (m, 1H), 3.87 – 3.79 (m, 1H), 3.68 – 3.61 (m, 1H), 2.39 (s, 3H), 2.20 (s, 3H), 1.97 – 1.86 (m, 2H), 1.84 – 1.75 (m, 1H), 1.59 – 1.48 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 170.7, 140.4, 137.4, 137.0, 133.6, 130.7, 130.7, 130.6, 128.9, 128.1, 127.9, 126.9, 125.7, 75.8, 67.9, 48.3, 32.1, 26.0, 22.6, 19.8. HRMS m/z: calcd for $C_{22}H_{25}NNaO_2^+$ $[M+Na]^+$ 358.1778, found: 358.1766.



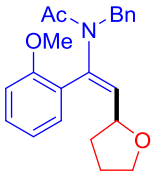
2d

(*E*)-*N*-(1-([1,1'-biphenyl]-4-yl)-2-(tetrahydrofuran-2-yl)vinyl)-*N*-benzylacetamide (2d): 107 mg, 90 % yield. Colorless oil. Eluents for flash column chromatography petroleum ether/ethyl acetate (10:1 *v*/*v*). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.63 – 7.59 (m, 4H), 7.47 (t, J = 7.6 Hz, 2H), 7.40 – 7.32 (m, 3H), 7.31 – 7.20 (m, 5H), 5.33 (d, J = 9.4 Hz, 1H), 4.79 (d, J = 14.3 Hz, 1H), 4.50 – 4.43 (m, 1H), 4.35 (d, J = 14.3 Hz, 1H), 3.88 – 3.81 (m, 1H), 3.76 – 3.69 (m, 1H), 2.24 (s, 3H), 2.10 – 2.01 (m, 1H), 1.94 – 1.83 (m, 2H), 1.57 – 1.45 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 171.0, 141.8, 140.4, 140.0, 137.2, 133.3, 132.4, 129.1, 129.0, 128.8, 128.2, 127.7, 127.22, 127.18, 127.0, 75.2, 68.1, 49.4, 32.6, 26.1, 22.4. HRMS m/z: calcd for $C_{27}H_{27}NNaO_2^+$ $[M+Na]^+$ 420.1934, found: 420.1944.



2e

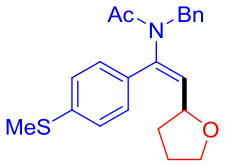
(*E*)-*N*-benzyl-*N*-(1-(4-methoxyphenyl)-2-(tetrahydrofuran-2-yl)vinyl)acetamide (2e): 76 mg, 72% yield. Colorless oil. Eluents for flash column chromatography petroleum ether/ethyl acetate (10:1 *v*/*v*). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.30 – 7.16 (m, 7H), 6.95 – 6.87 (m, 2H), 5.22 (d, J = 9.3 Hz, 1H), 4.73 (d, J = 14.3 Hz, 1H), 4.44 – 4.35 (m, 1H), 4.29 (d, J = 14.3 Hz, 1H), 3.87 – 3.78 (m, 4H), 3.74 – 3.66 (m, 1H), 2.19 (s, 3H), 2.07 – 1.96 (m, 1H), 1.92 – 1.80 (m, 2H), 1.52 – 1.41 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 170.7, 160.1, 140.6, 137.4, 130.9, 130.1, 129.0, 128.1, 127.1, 126.8, 113.9, 75.3, 68.0, 55.3, 49.2, 32.6, 26.1, 22.3. HRMS m/z: calcd for $C_{22}H_{25}NNaO_3^+$ $[M+Na]^+$ 374.1727, found: 374.1721.



2f

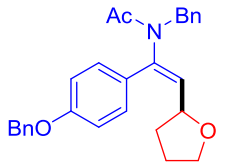
(*E*)-*N*-benzyl-*N*-(1-(2-methoxyphenyl)-2-(tetrahydrofuran-2-yl)vinyl)acetamide (2f): 70 mg, 66% yield. Colorless oil. Eluents for flash column chromatography petroleum ether/ethyl acetate (10:1 *v*/*v*). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.37 – 7.30 (m, 1H), 7.26 – 7.12 (m, 5H), 7.05 (dd, J = 7.5, 1.8

Hz, 1H), 6.93 (td, J = 7.4, 1.0 Hz, 1H), 6.85 (d, J = 8.0 Hz, 1H), 5.39 (d, J = 9.3 Hz, 1H), 4.67 (d, J = 14.8 Hz, 1H), 4.28 – 4.12 (m, 2H), 3.86 – 3.78 (m, 1H), 3.74 (s, 3H), 3.69 – 3.61 (m, 1H), 2.34 (s, 3H), 2.00 – 1.73 (m, 3H), 1.56 – 1.45 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 171.3, 157.6, 138.9, 137.8, 132.4, 132.2, 130.4, 128.5, 127.9, 126.7, 123.0, 120.1, 110.8, 75.7, 68.0, 55.1, 48.5, 32.2, 26.0, 22.5. HRMS m/z: calcd for $C_{22}H_{25}NNaO_3^+$ $[M+Na]^+$ 374.1727, found: 374.1708.



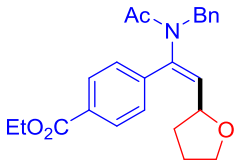
2g

(*E*)-*N*-benzyl-*N*-(1-(4-(methylthio)phenyl)-2-(tetrahydrofuran-2-yl)vinyl)acetamide (2g): 61 mg, 55 % yield. Colorless oil. Eluents for flash column chromatography petroleum ether/ethyl acetate (10:1 *v*/*v*). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.30 – 7.22 (m, 5H), 7.21 – 7.16 (m, 4H), 5.27 (d, J = 9.3 Hz, 1H), 4.73 (d, J = 14.3 Hz, 1H), 4.42 – 4.28 (m, 2H), 3.86 – 3.79 (m, 1H), 3.74 – 3.66 (m, 1H), 2.51 (s, 3H), 2.19 (s, 3H), 2.07 – 1.97 (m, 1H), 1.93 – 1.78 (m, 2H), 1.54 – 1.41 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 170.7, 140.4, 140.1, 137.3, 131.9, 131.06, 129.1, 129.0, 128.2, 127.2, 125.9, 75.2, 68.0, 49.3, 32.6, 26.1, 22.3, 15.2. HRMS m/z: calcd for $C_{22}H_{25}NNaO_2S^+$ $[M+Na]^+$ 390.1498, found: 390.1488.



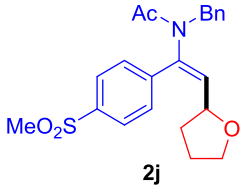
2h

(*E*)-*N*-benzyl-*N*-(1-(4-(benzyloxy)phenyl)-2-(tetrahydrofuran-2-yl)vinyl)acet-amide (2h): 67 mg, 52% yield. Colorless oil. Eluents for flash column chromatography petroleum ether/ethyl acetate (10:1 *v*/*v*). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.48 – 7.32 (m, 5H), 7.30 – 7.16 (m, 7H), 7.01 – 6.95 (m, 2H), 5.22 (d, J = 9.3 Hz, 1H), 5.09 (s, 2H), 4.74 (d, J = 14.3 Hz, 1H), 4.39 (dt, J = 9.2, 7.1 Hz, 1H), 4.29 (d, J = 14.3 Hz, 1H), 3.87 – 3.78 (m, 1H), 3.75 – 3.65 (m, 1H), 2.19 (s, 3H), 2.06 – 1.95 (m, 1H), 1.93 – 1.80 (m, 2H), 1.53 – 1.40 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 170.7, 159.3, 140.6, 137.4, 136.5, 131.0, 130.1, 129.0, 128.6, 128.2, 128.1, 127.5, 127.2, 127.1, 114.8, 75.3, 70.1, 68.0, 49.3, 32.7, 26.2, 22.4. HRMS m/z: calcd for $C_{28}H_{29}NNaO_3^+$ $[M+Na]^+$ 450.2040, found: 450.2053.



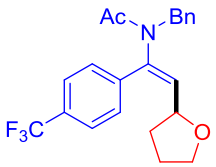
2i

Ethyl (*E*)-4-(1-(*N*-benzylacetamido)-2-(tetrahydrofuran-2-yl)vinyl)benzoate (2i): 104 mg, 88% yield. Colorless oil. Eluents for flash column chromatography petroleum ether/ethyl acetate (10:1 *v*/*v*). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 8.06 (d, J = 8.3 Hz, 2H), 7.36 – 7.21 (m, 5H), 7.20 – 7.14 (m, 2H), 5.40 (d, J = 9.4 Hz, 1H), 4.76 (d, J = 14.4 Hz, 1H), 4.44 – 4.24 (m, 4H), 3.87 – 3.79 (m, 1H), 3.75 - 3.66 (m, 1H), 2.20 (s, 3H), 2.08 – 1.98 (m, 1H), 1.95 – 1.83 (m, 2H), 1.55 – 1.45 (m, 1H), 1.41 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 170.6, 165.9, 140.0, 139.0, 137.0, 133.7, 130.9, 129.7, 128.9, 128.7, 128.2, 127.3, 75.0, 68.1, 61.1, 49.5, 32.6, 26.1, 22.3, 14.2. HRMS m/z: calcd for $C_{24}H_{27}NNaO_4^+$ $[M+Na]^+$ 416.1832, found: 416.1841.



2j

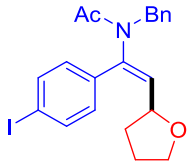
(*E*)-*N*-benzyl-*N*-(1-(4-(methylsulfonyl)phenyl)-2-(tetrahydrofuran-2-yl)vinyl)acetamide (2j): 85 mg, 71% yield. Yellow solid. Eluents for flash column chromatography petroleum ether/ethyl acetate (10:1 *v*/*v*). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.94 (d, J = 8.3 Hz, 2H), 7.46 – 7.43 (m, 2H), 7.30 – 7.23 (m, 3H), 7.19 – 7.14 (m, 2H), 5.47 (d, J = 9.4 Hz, 1H), 4.73 (d, J = 14.3 Hz, 1H), 4.43 – 4.25 (m, 2H), 3.89 – 3.81 (m, 1H), 3.77 – 3.69 (m, 1H), 3.09 (s, 3H), 2.19 (s, 3H), 2.08 – 2.00 (m, 1H), 1.97 – 1.83 (m, 2H), 1.51 (dq, J = 12.3, 7.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 170.4, 140.7, 140.3, 139.3, 136.8, 134.7, 129.6, 128.9, 128.3, 127.6, 127.4, 74.7, 68.2, 49.6, 44.3, 32.6, 26.1, 22.3. HRMS m/z: calcd for $C_{22}H_{25}NNaO_4S^+$ $[M+Na]^+$ 422.1397, found: 422.1372.



2k

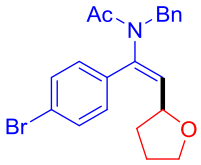
(*E*)-*N*-benzyl-*N*-(2-(tetrahydrofuran-2-yl)-1-(4-(trifluoromethyl)phenyl)vinyl)-acetamide (2k): 103 mg, 88% yield. Yellow oil. Eluents for flash column chromatography petroleum ether/ethyl acetate (10:1 *v*/*v*). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.64 (d, J = 8.2 Hz, 2H), 7.37 (d, J = 8.0 Hz, 2H), 7.31 – 7.23 (m, 3H), 7.20 – 7.14 (m, 2H), 5.42 (d, J = 9.4 Hz, 1H), 4.72 (d, J = 14.4 Hz, 1H,), 4.42 – 4.26

(m, 2H), 3.88 – 3.79 (m, 1H), 3.76 – 3.66 (m, 1H), 2.20 (s, 3H), 2.09 – 1.99 (m, 1H), 1.94 – 1.83 (m, 2H), 1.50 (dq, J = 12.1, 7.9 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 170.5, 139.7, 138.3, 137.0, 133.9, 130.93 (p, J = 32.3 Hz), 129.1, 128.9, 128.3, 127.4, 125.52 (p, J = 4.0 Hz), 123.75 (p, J = 270.3 Hz), 74.9, 68.2, 49.5, 32.6, 26.1, 22.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ ppm -62.65. HRMS m/z: calcd for $C_{22}H_{22}F_3NNaO_2^+$ $[M+Na]^+$ 412.1495, found: 412.1485.



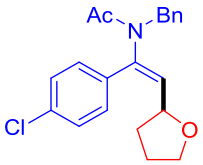
2l

(*E*)-*N*-benzyl-*N*-(1-(4-iodophenyl)-2-(tetrahydrofuran-2-yl)vinyl)acetamide (2l): 114 mg, 85% yield. White solid. Eluents for flash column chromatography petroleum ether/ethyl acetate (10:1 *v*/*v*). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.72 (d, J = 8.4 Hz, 2H), 7.33 – 7.23 (m, 3H), 7.20 – 7.14 (m, 2H), 6.99 (d, J = 8.4 Hz, 2H), 5.32 (d, J = 9.4 Hz, 1H), 4.71 (d, J = 14.4 Hz, 1H), 4.44 – 4.22 (m, 2H), 3.88 – 3.78 (m, 1H), 3.76 – 3.64 (m, 1H), 2.19 (s, 3H), 2.07 – 1.94 (m, 1H), 1.92 – 1.80 (m, 2H), 1.54 – 1.40 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 170.7, 140.0, 137.7, 137.0, 134.1, 132.8, 130.4, 128.9, 128.2, 127.3, 95.1, 75.0, 68.1, 49.4, 32.6, 26.1, 22.3. HRMS m/z: calcd for $C_{21}H_{22}INNaO_2^+$ $[M+Na]^+$ 470.0587, found: 470.0571.



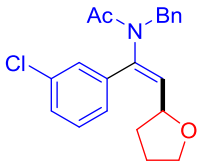
2m

(*E*)-*N*-benzyl-*N*-(1-(4-bromophenyl)-2-(tetrahydrofuran-2-yl)vinyl)acetamide (2m): 106 mg, 88% yield. Colorless oil. Eluents for flash column chromatography petroleum ether/ethyl acetate (10:1 *v*/*v*). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.52 (d, J = 8.0 Hz, 2H), 7.32 – 7.10 (m, 7H), 5.33 (d, J = 9.4 Hz, 1H), 4.72 (d, J = 14.4 Hz, 1H), 4.38 – 4.26 (m, 2H), 3.88 – 3.78 (m, 1H), 3.75 – 3.66 (m, 1H), 2.20 (s, 3H), 2.07 – 1.96 (m, 1H), 1.94 – 1.79 (m, 2H), 1.54 – 1.42 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 170.6, 139.8, 137.0, 133.4, 132.8, 131.7, 130.2, 128.9, 128.2, 127.3, 123.2, 75.0, 68.1, 49.3, 32.6, 26.1, 22.3. HRMS m/z: calcd for $C_{21}H_{22}{}^{79}BrNNaO_2^+$ $[M+Na]^+$ 422.0726, found: 422.0717.



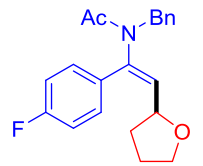
2n

(*E*)-*N*-benzyl-*N*-(1-(4-chlorophenyl)-2-(tetrahydrofuran-2-yl)vinyl)acetamide (2n): 94 mg, 88% yield. Light yellow oil. Eluents for flash column chromatography petroleum ether/ethyl acetate (10:1 *v*/*v*). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.36 (d, J = 8.4 Hz, 2H), 7.31 – 7.15 (m, 7H), 5.33 (d, J = 9.4 Hz, 1H), 4.72 (d, J = 14.4 Hz, 1H), 4.37 – 4.28 (m, 2H), 3.86 – 3.79 (m, 1H), 3.74 – 3.67 (m, 1H), 2.19 (s, 3H), 2.06 – 1.96 (m, 1H), 1.94 – 1.81 (m, 2H), 1.48 (dq, J = 12.0, 7.9 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 170.5, 139.8, 137.1, 135.0, 133.0, 132.7, 130.0, 128.9, 128.8, 128.2, 127.3, 75.0, 68.1, 49.3, 32.6, 26.1, 22.3. HRMS m/z: calcd for $C_{21}H_{22}{}^{35}ClNNaO_2^+$ $[M+Na]^+$ 378.1231, found: 378.1227.



2o

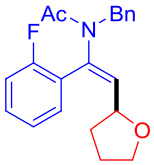
(*E*)-*N*-benzyl-*N*-(1-(3-chlorophenyl)-2-(tetrahydrofuran-2-yl)vinyl)acetamide (2o): 88 mg, 82% yield. Light yellow oil. Eluents for flash column chromatography petroleum ether/ethyl acetate (10:1 *v*/*v*). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.38 – 7.31 (m, 2H), 7.31 – 7.14 (m, 7H), 5.35 (d, J = 9.4 Hz, 1H), 4.75 (d, J = 14.3 Hz, 1H), 4.40 – 4.24 (m, 2H), 3.87 – 3.79 (m, 1H), 3.75 – 3.67 (m, 1H), 2.20 (s, 3H), 2.08 – 1.98 (m, 1H), 1.92 – 1.82 (m, 2H), 1.48 (dq, J = 12.1, 7.9 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 170.5, 139.5, 137.0, 136.5, 134.6, 133.3, 129.8, 129.1, 128.9, 128.5, 128.2, 127.3, 127.0, 74.9, 68.1, 49.4, 32.6, 26.1, 22.3. HRMS m/z: calcd for $C_{21}H_{22}{}^{35}ClNNaO_2^+$ $[M+Na]^+$ 378.1231, found: 378.1217.



2p

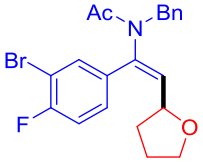
(*E*)-*N*-benzyl-*N*-(1-(4-fluorophenyl)-2-(tetrahydrofuran-2-yl)vinyl)acetamide (2p): 82 mg, 81% yield. Yellow oil. Eluents for flash column chromatography petroleum ether/ethyl acetate (10:1 *v*/*v*). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.30 – 7.21 (m, 5H), 7.20 – 7.14 (m, 2H), 7.11 – 7.04 (m, 2H) 5.31 (d, J = 9.4 Hz, 1H), 4.71 (d, J = 14.3 Hz, 1H), 4.39 – 4.27 (m, 2H), 3.87 – 3.78 (m, 1H), 3.75 – 3.66

(m, 1H), 2.19 (s, 3H), 2.06 – 1.96 (m, 1H), 1.94 – 1.82 (m, 2H), 1.55 – 1.44 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 170.5, 162.89 (d, J = 248.0 Hz), 140.0, 137.2, 132.1, 130.6, 130.5, 128.9, 128.2, 127.2, 115.58 (d, J = 21.0 Hz), 75.1, 68.0, 49.3, 32.6, 26.1, 22.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ ppm -111.53. HRMS m/z: calcd for $C_{21}H_{22}FNNaO_2^+$ $[M+Na]^+$ 362.1527, found: 362.1516.



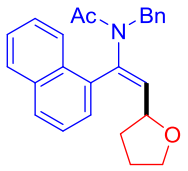
2q

(*E*)-*N*-benzyl-*N*-(1-(2-fluorophenyl)-2-(tetrahydrofuran-2-yl)vinyl)acetamide (2q): 66 mg, 65% yield. Yellow oil. Eluents for flash column chromatography petroleum ether/ethyl acetate (10:1 *v*/*v*). **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 7.41- 7.32 (m, 1H), 7.30 – 7.12 (m, 7H), 7.12 – 7.05 (m, 1H), 5.44 (d, J = 9.4 Hz, 1H), 4.76 (d, J = 14.6 Hz, 1H), 4.26 – 4.14 (m, 2H), 3.84 – 3.76 (m, 1H), 3.71 – 3.63 (m, 1H), 2.29 (s, 3H), 2.06 – 1.96 (m, 1H), 1.92 – 1.77 (m, 2H), 1.49 (dq, J = 12.3, 7.9 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ ppm 170.6, 160.15 (d, J = 248.0 Hz), 137.3, 135.1, 134.5, 131.37 (d, J = 3.0 Hz), 130.90 (d, J = 9.0 Hz), 128.7, 128.1, 127.0, 124.08 (d, J = 3.0 Hz), 122.20 (d, J = 14.0 Hz), 116.01 (d, J = 22.0 Hz), 75.37 (d, J = 1.0 Hz), 68.0, 48.7, 31.9, 26.0, 22.24 (d, J = 2.0 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$) δ ppm -112.70. **HRMS** m/z: calcd for $C_{21}H_{22}FNNaO_2^+$ $[M+Na]^+$ 362.1527, found: 362.1506.



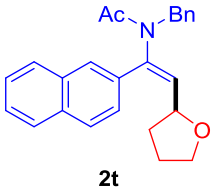
2r

(*E*)-*N*-benzyl-*N*-(1-(3-bromo-4-fluorophenyl)-2-(tetrahydrofuran-2-yl)vinyl)acetamide (2r): 107 mg, 85% yield. Yellow oil. Eluents for flash column chromatography petroleum ether/ethyl acetate (10:1 *v*/*v*). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.41 (dd, J = 6.5, 2.2 Hz, 1H), 7.31 – 7.10 (m, 7H), 5.35 (d, J = 9.3 Hz, 1H), 4.71 (d, J = 14.3 Hz, 1H), 4.42 – 4.25 (m, 2H), 3.88 – 3.79 (m, 1H), 3.76 – 3.67 (m, 1H), 2.18 (s, 3H), 2.08 – 1.97 (m, 1H), 1.94 – 1.83 (m, 2H), 1.49 (dq, J = 12.0, 7.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 170.4, 159.1 (d, J = 250.0 Hz), 138.9, 136.99, 133.5, 133.1, 132.2(d, J = 3.0 Hz), 129.6 (d, J = 7.0 Hz), 128.9, 128.3, 127.4, 116.5 (d, J = 22.0 Hz), 109.4 (d, J = 21.0 Hz), 74.8, 68.1, 49.5, 32.5, 26.1, 22.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ ppm -105.55. HRMS m/z: calcd for $C_{21}H_{21}{}^{79}BrFNNaO_2^+$ $[M+Na]^+$ 440.0632, found: 440.0621.



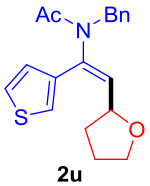
2s

(*E*)-*N*-benzyl-*N*-(1-(naphthalen-1-yl)-2-(tetrahydrofuran-2-yl)vinyl)acetamide (2s): 45 mg, 40% yield. Colorless oil. Eluents for flash column chromatography petroleum ether/ethyl acetate (10:1 *v*/*v*). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 8.15 – 7.60 (m, 3H), 7.54 – 7.43 (m, 3H), 7.37- 7.29 (m, 1H), 7.28 – 7.16 (m, 3H), 7.15 – 6.99 (m, 2H), 5.69 (d, J = 4.0 Hz, 1H), 5.06 – 3.87 (m, 3H), 3.85 – 3.72 (m, 1H), 3.61 – 3.49 (m, 1H), 2.52 (s, 3H), 1.92 – 1.76 (m, 2H), 1.73 – 1.61 (m, 1H), 1.60 – 1.46 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 171.0, 137.4, 133.5, 132.8, 132.0, 129.5, 128.5, 128.2, 127.4, 127.0, 126.6, 126.2, 125.1, 125.0, 75.8, 67.9, 48.6, 31.7, 26.0, 22.6. HRMS m/z: calcd for $C_{25}H_{25}NNaO^+$ $[M+Na]^+$ 394.1778, found: 394.1785.



2t

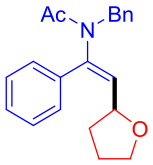
(*E*)-*N*-benzyl-*N*-(2-(naphthalen-1-yl)-2-(tetrahydrofuran-2-yl)vinyl)acetamide (2t): 91 mg, 82% yield. Colorless oil. Eluents for flash column chromatography petroleum ether/ethyl acetate (10:1 *v*/*v*). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.92 – 7.82 (m, 3H), 7.72 (s, 1H), 7.58 – 7.50 (m, 2H), 7.37 (dd, J = 8.5, 1.8 Hz, 1H), 7.32 – 7.19 (m, 5H), 5.41 (d, J = 9.3 Hz, 1H), 4.76 (d, J = 14.3 Hz, 1H), 4.54 – 4.29 (m, 2H), 3.92 – 3.79 (m, 1H), 3.76 – 3.66 (m, 1H), 2.28 (s, 3H), 2.11 – 2.01 (m, 1H), 1.97 – 1.81 (m, 2H), 1.61 – 1.47 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 170.9, 140.8, 137.2, 133.3, 132.8, 132.5, 131.9, 128.9, 128.5, 128.3, 128.24, 128.19, 127.6, 127.2, 126.8, 126.6, 125.7, 75.3, 68.1, 49.4, 32.7, 26.1, 22.5. HRMS m/z: calcd for $C_{25}H_{26}NO_2^+$ $[M+H]^+$ 372.1958, found: 372.1971.



2u

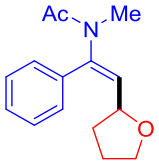
(*E*)-*N*-benzyl-*N*-(2-(tetrahydrofuran-2-yl)-1-(thiophen-3-yl)vinyl)acetamide (2u): 82 mg, 83% yield. Colorless oil. Eluents for flash column chromatography petroleum ether/ethyl acetate (10:1 *v*/*v*). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.37 – 7.19 (m, 7H), 7.04 – 6.98 (m, 1H), 5.26 (d, J = 9.0 Hz, 1H), 4.83 (d, J = 14.2 Hz, 1H), 4.53 (q, J = 7.0 Hz, 1H), 4.36 (d, J = 14.2 Hz, 1H), 3.87 – 3.79 (m, 1H),

3.77 – 3.69 (m, 1H), 2.14 (s, 3H), 2.10 – 2.00 (m, 1H), 1.94 – 1.84 (m, 2H), 1.47 (dq, J = 12.2, 7.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 170.4, 137.4, 136.4, 136.3, 132.2, 129.1, 128.2, 127.3, 127.2, 126.2, 125.7, 74.9, 68.0, 49.8, 22.2. HRMS m/z: calcd for $C_{19}H_{21}NNaO_2S^+$ $[M+Na]^+$ 350.1185, found: 350.1166.



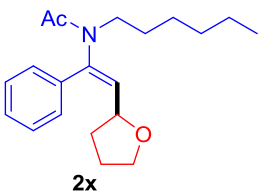
2v

(*E*)-*N*-(4-chlorobenzyl)-*N*-(1-phenyl-2-(tetrahydrofuran-2-yl)vinyl)acetamide (2v): 82 mg, 77 % yield. Light yellow oil. Eluents for flash column chromatography petroleum ether/ethyl acetate (10:1 *v*/*v*). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.42-7.39 (m, 3H), 7.28-7.22 (m, 4H), 7.15-7.12 (m, 2H), 5.32-5.29 (d, J=9.4 Hz, 1H), 4.65-4.61 (d, J=14.4 Hz, 1H), 4.43-4.37(m, 1H), 4.30-4.26(d, J=14.4 Hz, 1H), 3.87-3.69 (m, 2H), 2.23(s, 3H), 2.09-2.01 (m, 1H), 1.94-1.83 (m, 2H), 1.56-1.47 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 170.79, 140.73, 135.76, 134.23, 132.99, 132.21, 130.34, 129.86, 129.15, 128.62, 128.30, 75.15, 68.09, 48.53, 32.66, 26.15, 22.23. HRMS m/z: calcd for $C_{21}H_{23}ClNO_2^+$ $[M + H]^+$ 356.1412, found 356.1424.



2w

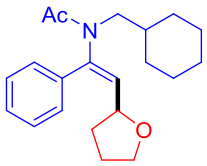
(*E*)-*N*-methyl-*N*-(1-phenyl-2-(tetrahydrofuran-2-yl)vinyl)acetamide (2w): 66 mg, 90% yield. Colorless oil. Eluents for flash column chromatography petroleum ether/ethyl acetate (10:1 *v*/*v*). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.43 – 7.31 (m, 5H), 5.62 (d, J = 9.5 Hz, 1H), 4.50 – 4.41 (m, 1H), 3.99 – 3.91 (m, 1H), 3.83 – 3.75 (m, 1H), 2.97 (s, 3H), 2.18 – 2.10 (m, 4H), 2.07 – 1.91 (m, 2H), 1.76 – 1.66 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 170.9, 143.7, 134.6, 129.4, 129.05, 128.96, 128.6, 75.3, 68.2, 35.0, 32.8, 26.3, 22.1. HRMS m/z: calcd for $C_{15}H_{19}NNaO_2^+$ $[M+Na]^+$ 268.1308, found: 268.1303.



2x

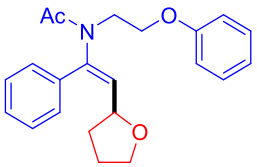
(*E*)-*N*-hexyl-*N*-(1-phenyl-2-(tetrahydrofuran-2-yl)vinyl)acetamide (2x): 74 mg, 78% yield.

Colorless oil. Eluents for flash column chromatography petroleum ether/ethyl acetate (10:1 *v*/*v*). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.45 – 7.28 (m, 5H), 5.56 (d, J = 9.4 Hz, 1H), 4.53 – 4.39 (m, 1H), 4.00 – 3.90 (m, 1H), 3.84 – 3.72 (m, 1H), 3.40 – 3.12 (m, 2H), 2.19 (s, 3H), 2.16 – 1.87 (m, 3H), 1.75 – 1.65 (m, 1H), 1.53 – 1.42 (m, 2H), 1.30 – 1.16 (m, 6H), 0.84 (t, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 170.4, 141.8, 134.5, 130.8, 128.9, 128.6, 128.4, 75.4, 68.1, 45.4, 32.7, 31.4, 27.4, 26.3, 26.2, 22.44, 22.37, 13.9. HRMS m/z: calcd for $C_{20}H_{29}NNaO_2^+$ $[M+Na]^+$ 338.2091, found: 338.2086.



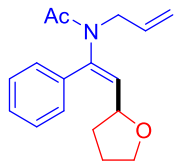
2y

(*E*)-*N*-(cyclohexylmethyl)-*N*-(1-phenyl-2-(tetrahydrofuran-2-yl)vinyl)acetamide (2y): 69 mg, 70% yield. Colorless oil. Eluents for flash column chromatography petroleum ether/ethyl acetate (10:1 *v*/*v*). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.44 – 7.34 (m, 3H), 7.33 – 7.27 (m, 2H), 5.59 (d, J = 9.4 Hz, 1H), 4.52 – 4.38 (m, 1H), 4.00 – 3.90 (m, 1H), 3.83 – 3.73 (m, 1H), 3.23 – 2.99 (m, 2H), 2.23 (s, 3H), 2.18 – 1.88 (m, 3H), 1.76 – 1.48 (m, 7H), 1.28 – 1.08 (m, 3H), 0.98 – 0.83 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 170.9, 142.2, 134.4, 131.0, 129.0, 128.7, 128.5, 75.5, 68.1, 50.8, 36.4, 32.8, 30.75, 30.71, 26.4, 26.3, 25.8, 22.5. HRMS m/z: calcd for $C_{21}H_{29}NNaO_2^+$ $[M+Na]^+$ 350.2091, found: 350.2085.



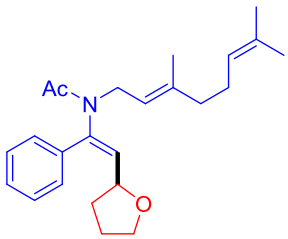
2z

(*E*)-*N*-(2-phenoxyethyl)-*N*-(1-phenyl-2-(tetrahydrofuran-2-yl)vinyl)acetamide (2z): 79 mg, 75% yield. Colorless oil. Eluents for flash column chromatography petroleum ether/ethyl acetate (10:1 *v*/*v*). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.45 – 7.33 (m, 5H), 7.25 (t, J = 7.9 Hz, 2H), 6.92 (t, J = 7.3 Hz, 1H), 6.85 (d, J = 8.0 Hz, 2H), 5.66 (d, J = 9.5 Hz, 1H), 4.46 (q, J = 7.3 Hz, 1H), 4.12 – 3.95 (m, 2H), 3.90 (q, J = 7.2 Hz, 1H), 3.78 (dd, J = 14.8, 7.2 Hz, 2H), 3.68-3.62 (m, 1H), 2.20 (s, 3H), 2.16 – 2.06 (m, 1H), 2.02-1.85 (m, 2H), 1.71 – 1.61 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 171.26, 158.40, 142.05, 134.52, 131.17, 129.35, 129.09, 128.75, 128.56, 120.66, 114.34, 75.31, 68.12, 65.05, 45.65, 32.71, 26.29, 22.38. HRMS m/z: calcd for $C_{22}H_{26}NO_3^+$ $[M + H]^+$ 352.1907, found 352.1917.



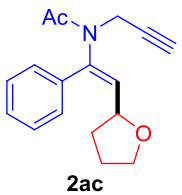
2aa

(*E*)-*N*-allyl-*N*-(1-phenyl-2-(tetrahydrofuran-2-yl)vinyl)acetamide (2aa): 63 mg, 77% yield. Colorless oil. Eluents for flash column chromatography petroleum ether/ethyl acetate (10:1 *v*/*v*). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.46-7.34 (m, 3H), 7.33-7.28 (m, 2H), 5.84 – 5.73 (m, 1H), 5.59 (d, J = 9.4 Hz, 1H), 5.10 (d, J = 10.1 Hz, 1H), 5.02 (d, J = 17.1 Hz, 1H), 4.44 (q, J = 7.7 Hz, 1H), 4.02-3.89 (m, 3H), 3.77 (q, J = 7.5 Hz, 1H), 2.18 (s, 3H), 2.15 – 2.08 (m, 1H), 2.06-1.98 (m, 1H), 1.95-1.87 (m, 1H), 1.67-1.65 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 170.52, 141.55, 134.66, 132.85, 131.21, 129.00, 128.69, 128.48, 117.77, 75.40, 68.14, 48.93, 32.84, 26.24, 22.32. HRMS m/z: calcd for $C_{17}H_{22}NO_2^+$ $[M + H]^+$ 272.1645, found 272.1640.



2ab

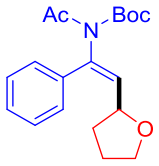
***N*-((*E*)-3,7-dimethylocta-2,6-dien-1-yl)-*N*-((*E*)-1-phenyl-2-(tetrahydrofuran-2-yl)vinyl) acetamide (2ab):** 66 mg, 60% yield. Colorless oil. Eluents for flash column chromatography petroleum ether/ethyl acetate (10:1 *v*/*v*). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.39-7.37 (m, 3H), 7.34 – 7.30 (m, 2H), 5.56 (d, J = 9.4 Hz, 1H), 5.20 (t, J = 7.1 Hz, 1H), 5.07 (t, J = 6.2 Hz, 1H), 4.46 (q, J = 7.5 Hz, 1H), 4.04 (dd, J = 14.5, 6.7 Hz, 1H), 3.96-3.89 (m, 2H), 3.77 (q, J = 7.8 Hz, 1H), 2.14 (s, 3H), 2.06-1.87 (m, 7H), 1.73-1.71 (m, 1H), 1.68 (s, 3H), 1.60 (s, 3H), 1.44 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 170.39, 141.77, 139.17, 134.82, 131.46, 130.95, 128.88, 128.77, 128.37, 123.99, 119.13, 75.34, 68.09, 44.01, 39.51, 32.81, 26.47, 26.27, 25.63, 22.38, 17.62, 16.01. HRMS m/z: calcd for $C_{24}H_{34}NO_2^+$ $[M + H]^+$ 368.2584, found 368.2569.



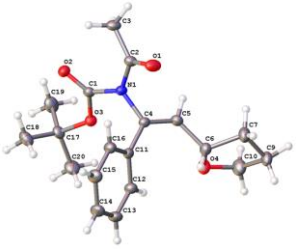
2ac

(*E*)-*N*-(1-phenyl-2-(tetrahydrofuran-2-yl) vinyl)-*N*-(prop-2-yn-1-yl)acetamide (2ac): 50 mg, 62% yield. Colorless oil. Eluents for flash column chromatography petroleum ether/ethyl acetate (10:1 *v*/*v*).

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.42 – 7.33 (m, 5H), 5.75 (d, J = 9.4 Hz, 1H), 4.48 (dt, J = 9.2, 7.2 Hz, 1H), 4.28 (dd, J = 17.2, 2.3 Hz, 1H), 4.11 (dd, J = 17.3, 2.4 Hz, 1H), 3.99 – 3.92 (m, 1H), 3.79 (td, J = 7.9, 6.0 Hz, 1H), 2.20 (t, J = 2.4 Hz, 1H), 2.18 – 2.16 (m, 1H), 2.15 (s, 3H), 2.09 – 1.97 (m, 2H), 1.96 – 1.88 (m, 1H), 1.76 – 1.72 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 170.58, 141.05, 134.41, 131.77, 129.33, 128.90, 128.71, 78.90, 75.49, 71.86, 68.38, 36.19, 33.05, 26.44, 22.38. HRMS m/z: calcd for $C_{17}H_{20}NO_2^+$ $[M + H]^+$ 270.1489, found 270.1479.

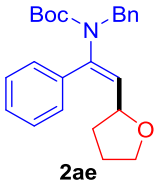


2ad



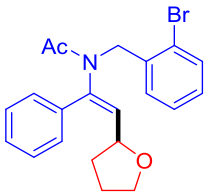
CCDC (2102570)

***Tert*-butyl (*E*)-acetyl(1-phenyl-2-(tetrahydrofuran-2-yl)vinyl)carbamate (2ad)**: 78 mg, 78% yield (*E*/*Z* = 88:12). White solid. Eluents for flash column chromatography petroleum ether/ethyl acetate (10:1 *v*/*v*). For major *E*-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.39 – 7.29 (m, 5H), 5.58 (d, J = 9.4 Hz, 1H), 4.47 (q, J = 8.4, 7.9 Hz, 1H), 3.97 -3.88 (m, 1H), 3.80 – 3.71 (m, 1H), 2.52 (s, 3H), 2.15 – 2.04 (m, 1H), 2.02 – 1.81 (m, 2H), 1.77 – 1.63 (m, 1H), 1.32 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 172.9, 152.5, 138.0, 136.2, 131.7, 128.8, 128.2, 128.0, 83.1, 75.5, 68.1, 32.6, 27.6, 26.3, 26.2. HRMS m/z: calcd for $C_{19}H_{25}NNaO_4^+$ $[M+Na]^+$ 354.1676, found: 354.1663. [For *Z*-isomer: ^{1}H NMR 6.07 (d, J = 8.2 Hz, 0.14H), 4.39 (q, J = 7.8, 7.4 Hz, 0.14H), 2.62 (s, 0.42H), 1.28 (s, 1.26H).]



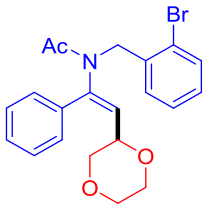
2ae

***Tert*-butyl (*E*)-benzyl(1-phenyl-2-(tetrahydrofuran-2-yl)vinyl)carbamate (2ae)**: 61 mg, 54% yield. Colorless solid. Eluents for flash column chromatography petroleum ether/ethyl acetate (10:1 *v*/*v*). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm7.34 – 7.18 (m, 10H), 5.45 (d, J = 9.4 Hz, 1H), 4.77 – 4.59 (m, 2H), 4.28 (ddd, J = 9.3, 7.8, 6.4 Hz, 1H), 3.90 – 3.81 (m, 1H), 3.74 – 3.64 (m, 1H), 2.04 – 1.76 (m, 3H), 1.57 (dt, J = 11.7, 8.2 Hz, 1H), 1.23 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 154.8, 142.4, 138.6, 137.2, 128.6, 128.4, 128.1, 128.0, 127.9, 127.1, 126.5, 80.4, 75.9, 67.9, 53.1, 32.9, 28.0, 26.2. HRMS m/z: calcd for $C_{24}H_{29}NNaO_3^+$ $[M+Na]^+$ 402.2040, found: 402.2058.



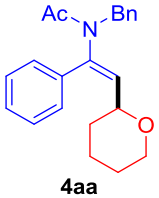
2af

(*E*)-*N*-(2-bromobenzyl)-*N*-(1-phenyl-2-(tetrahydrofuran-2-yl)vinyl)acetamide (2af): 88 mg, 73% yield. Colorless oil. Eluents for flash column chromatography petroleum ether/ethyl acetate (10:1 *v*/*v*). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.48 (d, J = 7.7 Hz, 1H), 7.42 – 7.34 (m, 3H), 7.26 – 7.19 (m, 4H), 7.13 – 7.05 (m, 1H), 5.49 (d, J = 9.3 Hz, 1H), 4.95 (d, J = 15.1 Hz, 1H), 4.50 – 4.35 (m, 2H), 3.89 – 3.79 (m, 1H), 3.75 – 3.65 (m, 1H), 2.25 (s, 3H), 2.08 – 1.96 (m, 1H), 1.96 – 1.79 (m, 2H), 1.56 –1.44 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 171.0, 140.8, 136.3, 134.4, 132.5, 132.1, 130.6, 129.0, 128.7, 128.4, 127.3, 123.8, 75.2, 68.1, 49.5, 32.6, 26.1, 22.3. HRMS m/z: calcd for $C_{21}H_{22}{}^{79}BrNNaO_2^+$ $[M+Na]^+$ 422.0726, found: 422.0717.



2ag

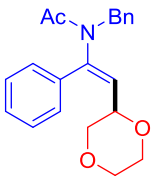
(*E*)-*N*-(2-(1,4-dioxan-2-yl)-1-phenylvinyl)-*N*-(2-bromobenzyl)acetamide (2ag): 76 mg, 61% yield. Colorless oil. Eluents for flash column chromatography petroleum ether/ethyl acetate (10:1 *v*/*v*). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.49 (d, J = 7.9 Hz, 1H), 7.43 – 7.38 (m, 3H), 7.29 – 7.17 (m, 4H), 7.10 (td, J = 7.5, 2.1 Hz, 1H), 5.39 (d, J = 9.4 Hz, 1H), 4.88 (d, J = 15.1 Hz, 1H), 4.55 (d, J = 15.2 Hz, 1H), 4.20 (td, J = 9.5, 2.6 Hz, 1H), 3.73-3.71 (m, 1H), 3.67 – 3.56 (m, 4H), 3.28 (dd, J = 11.5, 9.7 Hz, 1H), 2.22 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 171.60, 144.84, 136.98, 135.09, 133.53, 131.47, 130.40, 129.76, 129.59, 129.36, 128.24, 127.33, 124.68, 73.03, 70.54, 66.97, 66.60, 50.54, 23.20. HRMS m/z: calcd for $C_{21}H_{23}BrNO_3^+$ $[M + H]^+$ 416.0856, found 416.0868.



4aa

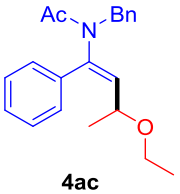
(*E*)-*N*-benzyl-*N*-(1-phenyl-2-(tetrahydro-2*H*-pyran-2-yl)vinyl)acetamide (4aa): **Method A:** 67 mg, 67% yield. Colorless oil. Eluents for flash column chromatography petroleum ether/ethyl acetate (10:1 *v*/*v*). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.42 – 7.37 (m, 3H), 7.33 – 7.16 (m, 7H), 5.34 (d, J =

9.3 Hz, 1H), 4.56 (d, J = 14.4 Hz, 1H), 4.47 (d, J = 14.4 Hz, 1H), 3.97 – 3.87 (m, 2H), 3.37 (td, J = 11.5, 2.5 Hz, 1H), 2.19 (s, 3H), 1.63 – 1.20 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 170.7, 141.2, 137.4, 134.9, 131.9, 129.1, 128.9, 128.6, 128.2, 127.2, 74.4, 67.7, 49.5, 31.7, 25.5, 22.8, 22.4. HRMS m/z: calcd for $C_{22}H_{25}NNaO_2^+$ $[M+Na]^+$ 358.1778, found: 358.1773.



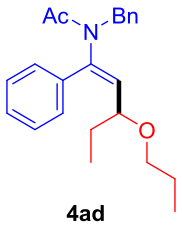
4ab

(*E*)-*N*-(2-(1,4-dioxan-2-yl)-1-phenylvinyl)-*N*-benzylacetamide (4ab): **Method A:** 82 mg, 81% yield. Colorless oil. Eluents for flash column chromatography petroleum ether/ethyl acetate (10:1 *v*/*v*). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.42 – 7.38 (m, 3H), 7.29 – 7.21 (m, 5H), 7.18 – 7.13 (m, 2H), 5.21 (d, J = 9.5 Hz, 1H), 4.62 (d, J = 14.4 Hz, 1H), 4.39 (d, J = 14.4 Hz, 1H), 4.18 (td, J = 9.5, 2.6 Hz, 1H), 3.72 – 3.56 (m, 5H), 3.29 – 3.20 (m, 1H), 2.18 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 170.5, 143.8, 137.1, 134.3, 129.5, 128.8, 128.8, 128.5, 128.3, 127.3, 126.5, 72.1, 69.7, 66.1, 65.6, 49.3, 22.3. HRMS m/z: calcd for $C_{21}H_{23}NNaO_3^+$ $[M+Na]^+$ 360.1570, found: 360.1581.



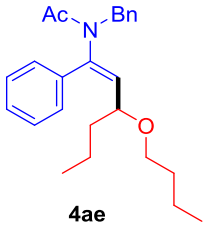
4ac

(*E*)-*N*-benzyl-*N*-(3-ethoxy-1-phenylbut-1-en-1-yl)acetamide (4ac): **Method A:** 43 mg, 44% yield ; **Method B:** 72 mg, 74% yield. Colorless oil. Eluents for flash column chromatography petroleum ether/ethyl acetate (10:1 *v*/*v*). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.44 – 7.36 (m, 3H), 7.32 – 7.14 (m, 7H), 5.24 (d, J = 9.5 Hz, 1H), 4.65 (d, J = 14.4 Hz, 1H), 4.37 (d, J = 14.4 Hz, 1H), 4.15 – 4.05 (m, 1H), 3.29 – 3.11 (m, 2H), 2.26 (s, 3H), 1.14 (d, J = 6.4 Hz, 3H), 1.05 (t, J = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 170.3, 139.8, 137.2, 135.0, 134.6, 128.9, 128.7, 128.6, 128.2, 127.2, 71.1, 63.5, 48.8, 22.4, 21.0, 15.3. HRMS m/z: calcd for $C_{21}H_{25}NNaO_2^+$ $[M+Na]^+$ 346.1778, found: 346.1785.



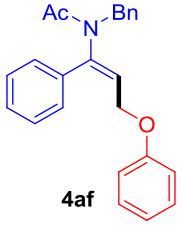
4ad

(*E*)-*N*-benzyl-*N*-(1-phenyl-3-propoxypent-1-en-1-yl)acetamide (4ad): **Method B:** 62 mg, 59% yield; **Method C:** 69 mg, 65% yield. Colorless oil. Eluents for flash column chromatography petroleum ether/ethyl acetate (10:1 *v*/*v*). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.44 – 7.37 (m, 3H), 7.31 – 7.14 (m, 7H), 5.22 (d, J = 9.7 Hz, 1H), 4.68 (d, J = 14.4 Hz, 1H), 4.32 (d, J = 14.4 Hz, 1H), 3.90 – 3.79 (m, 1H), 3.17 – 3.08 (m, 1H), 3.03 – 2.94 (m, 1H), 2.29 (s, 3H), 1.57 – 1.46 (m, 1H), 1.45 – 1.34 (m, 3H), 0.79 (dt, J = 9.9, 7.4 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 140.4, 137.3, 134.7, 134.0, 128.92, 128.87, 128.64, 128.62, 128.2, 127.2, 76.3, 70.00, 48.5, 28.3, 23.0, 22.4, 10.6, 9.6. HRMS m/z: calcd for $C_{23}H_{29}NNaO_2^+$ $[M+Na]^+$ 374.2091, found: 374.2081.



4ae

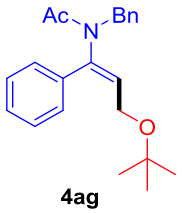
(*E*)-*N*-benzyl-*N*-(3-butoxy-1-phenylhex-1-en-1-yl)acetamide (4ae): **Method B:** 73 mg, 64% yield; **Method C:** 81 mg, 71% yield. Colorless oil. Eluents for flash column chromatography petroleum ether/ethyl acetate (10:1 *v*/*v*). **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 7.44 – 7.36 (m, 3H), 7.31 – 7.14 (m, 7H), 5.22 (d, J = 9.7 Hz, 1H), 4.70 (d, J = 14.4 Hz, 1H), 4.31 (d, J = 14.4 Hz, 1H), 3.96 – 3.86 (m, 1H), 3.22 – 3.12 (m, 1H), 3.05 – 2.96 (m, 1H), 2.29 (s, 3H), 1.54 – 1.44 (m, 1H), 1.40 – 1.10 (m, 7H), 0.81 (dt, J = 10.1, 7.2 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ ppm 170.3, 140.2, 137.3, 134.7, 134.3, 128.9, 128.9, 128.6, 128.2, 127.2, 74.7, 68.1, 48.6, 37.4, 31.9, 22.4, 19.3, 18.4, 13.9, 13.8. **HRMS** m/z: calcd for $C_{25}H_{33}NNaO_2^+$ $[M+Na]^+$ 402.2404, found: 402.2413.



4af

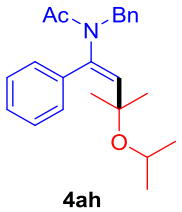
(*E*)-*N*-benzyl-*N*-(3-phenoxy-1-phenylprop-1-en-1-yl)acetamide (4af): Method B: 49 mg, 46% yield; Method C: 60 mg, 56% yield. Colorless oil. Eluents for flash column chromatography petroleum

ether/ethyl acetate (10:1 *v*/*v*). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.45 – 7.41 (m, 3H), 7.29 – 7.15 (m, 9H), 6.92 (tt, J = 7.4, 1.0 Hz, 1H), 6.74 – 6.69 (m, 2H), 5.63 (t, J = 6.7 Hz, 1H), 4.62 (d, J = 6.7 Hz, 2H), 4.55 (s, 2H), 2.14 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 170.7, 157.9, 142.7, 137.2, 134.3, 129.5, 129.4, 128.8, 128.5, 128.3, 127.3, 126.6, 121.1, 114.8, 64.1, 49.5, 22.3. HRMS m/z: calcd for $C_{24}H_{23}NNaO_2^+$ $[M+Na]^+$ 380.1621, found: 380.1612.



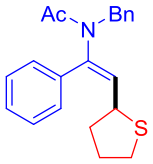
4ag

(*E*)-*N*-benzyl-*N*-(3-(tert-butoxy)-1-phenylprop-1-en-1-yl)acetamide (4ag): Method B: 53 mg, 52% yield; Method C: 59 mg, 58% yield. Colorless oil. Eluents for flash column chromatography petroleum ether/ethyl acetate (10:1 *v*/*v*). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.42 – 7.35 (m, 3H), 7.30 – 7.17 (m, 7H), 5.54 (t, J = 6.8 Hz, 1H), 4.54 (s, 2H), 3.97 (d, J = 6.8 Hz, 2H), 2.20 (s, 3H), 1.11 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm171.0, 140.6, 137.4, 134.7, 129.7, 128.9, 128.8, 128.53, 128.49, 128.2, 127.1, 73.4, 58.6, 49.6, 27.5, 22.4. HRMS m/z: calcd for $C_{22}H_{27}NNaO_2^+$ $[M+Na]^+$ 360.1934, found: 360.1917.



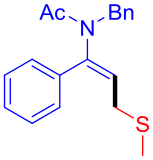
4ah

(*E*)-*N*-benzyl-*N*-(3-isopropoxy-3-methyl-1-phenylbut-1-en-1-yl)acetamide (4ah): **Method B:** 51 mg, 48% yield; **Method C:** 70 mg, 66% yield. Colorless oil. Eluents for flash column chromatography petroleum ether/ethyl acetate (10:1 *v*/*v*). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.40 – 7.33 (m, 5H), 7.31 – 7.20 (m, 5H), 5.43 (s, 1H), 4.47 (s, 2H), 3.55 – 3.45 (m, 1H), 2.35 (s, 3H), 1.05 (s, 6H), 0.93 (d, J = 6.1 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 170.3, 139.4, 138.5, 137.4, 135.2, 129.6, 128.9, 128.8, 128.3, 128.1, 127.2, 74.4, 65.6, 47.9, 28.2, 24.8, 22.4. HRMS m/z: calcd for $C_{23}H_{29}NNaO_2^+$ $[M+Na]^+$ 374.2091, found: 374.2075.



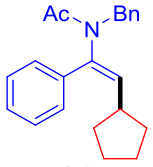
4ai

(*E*)-*N*-benzyl-*N*-(1-phenyl-2-(tetrahydrothiophen-2-yl)vinyl)acetamide (4ai): **Method B:** 46 mg, 45% yield; **Method C:** 53 mg, 52% yield. Colorless oil. Eluents for flash column chromatography petroleum ether/ethyl acetate (10:1 *v*/*v*). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.44 – 7.36 (m, 3H), 7.31 – 7.23 (m, 5H), 7.21 – 7.16 (m, 2H), 5.25 (d, J = 10.8 Hz, 1H), 4.58 (d, J = 14.2 Hz, 1H), 4.37 (d, J = 14.2 Hz, 1H), 4.18 – 4.04 (m, 1H), 2.96 – 2.78 (m, 2H), 2.20 (s, 3H), 2.14 – 2.02 (m, 2H), 1.90 – 1.77 (m, 1H), 1.56 – 1.44 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 170.7, 138.3, 137.3, 134.5, 133.2, 129.1, 128.8, 128.72, 128.70, 128.2, 127.2, 49.1, 46.1, 38.1, 33.3, 30.9, 22.4. HRMS m/z: calcd for $C_{21}H_{23}NNaOS^+$ $[M+Na]^+$ 360.1393, found: 360.1379.



4aj

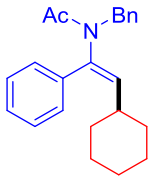
(*E*)-*N*-benzyl-*N*-(3-(methylthio)-1-phenylprop-1-en-1-yl)acetamide (4aj): **Method B:** 30 mg, 32 % yield; **Method C:** 42 mg, 45% yield. Colorless oil. Eluents for flash column chromatography petroleum ether/ethyl acetate (10:1 *v*/*v*). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.45 – 7.37 (m, 3H), 7.32 – 7.23 (m, 5H), 7.21 – 7.17 (m, 2H), 5.43 (t, J = 8.2 Hz, 1H), 4.50 (s, 2H), 3.21 (d, J = 8.2 Hz, 2H), 2.26 (s, 3H), 1.92 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 170.6, 140.5, 137.3, 134.2, 129.0, 128.9, 128.8, 128.7, 128.3, 127.5, 127.2, 49.0, 31.8, 22.3, 15.2. HRMS m/z: calcd for $C_{19}H_{21}NNaOS^+$ $[M+Na]^+$ 334.1236, found: 334.1231.



4ak

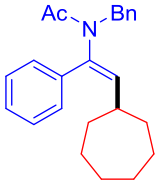
(*E*)-*N*-benzyl-*N*-(2-cyclopentyl-1-phenylvinyl)acetamide (4ak): **Method B:** 48 mg, 50% yield; **Method C:** 57 mg, 59% yield. Colorless oil. Eluents for flash column chromatography petroleum ether/ethyl acetate (10:1 *v*/*v*). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.43 – 7.32 (m, 3H), 7.30 – 7.17 (m, 7H), 5.12 (d, J = 10.6 Hz, 1H), 4.46 (s, 2H), 2.68 (dp, J = 10.4, 8.1 Hz, 1H), 2.21 (s, 3H), 1.79 – 1.69 (m, 2H), 1.64 – 1.45 (m, 4H), 1.23 – 1.09 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 170.7, 138.1,

137.5, 136.5, 135.2, 129.1, 128.53, 128.47, 128.3, 128.0, 127.1, 48.7, 38.8, 33.5, 25.3, 22.1. HRMS m/z: calcd for $C_{22}H_{26}NO^+$ $[M+H]^+$ 320.2009, found: 320.2014.



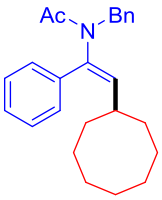
4al

(*E*)-*N*-benzyl-*N*-(2-cyclohexyl-1-phenylvinyl)acetamide (4al): **Method B:** 57 mg, 57% yield; **Method C:** 74 mg, 74% yield. Colorless oil. Eluents for flash column chromatography petroleum ether/ethyl acetate (10:1 *v*/*v*). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.43 – 7.35 (m, 3H), 7.29 – 7.21 (m, 5H), 7.18 (dd, J = 7.7, 1.7 Hz, 2H), 5.06 (d, J = 10.8 Hz, 1H), 4.45 (s, 2H), 2.32 (qt, J = 11.2, 3.4 Hz, 1H), 2.21 (s, 3H), 1.66 – 1.54 (m, 5H), 1.24 – 1.07 (m, 3H), 1.05 – 0.92 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 170.7, 138.6, 137.4, 136.7, 135.3, 129.2, 128.6, 128.42, 128.41, 128.0, 127.1, 48.7, 37.0, 32.5, 25.7, 25.2, 22.2. HRMS m/z: calcd for $C_{23}H_{28}NO^+$ $[M+H]^+$ 334.2165, found: 334.2169.



4am

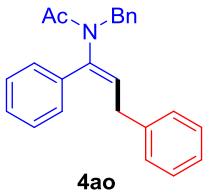
(*E*)-*N*-benzyl-*N*-(2-cycloheptyl-1-phenylvinyl)acetamide (4am): **Method B:** 69 mg, 66% yield; **Method C:** 74 mg, 71% yield. Colorless oil. Eluents for flash column chromatography petroleum ether/ethyl acetate (10:1 *v*/*v*). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.43 – 7.33 (m, 3H), 7.30 – 7.16 (m, 7H), 5.14 (d, J = 11.1 Hz, 1H), 4.45 (s, 2H), 2.56 – 2.40 (m, 1H), 2.22 (s, 3H), 1.66 – 1.30 (m, 10H), 1.26 – 1.15 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 170.6, 139.2, 137.4, 135.2, 134.9, 129.2, 128.5, 128.4, 128.3, 128.0, 127.1, 48.6, 38.3, 34.3, 28.2, 26.0, 22.3. HRMS m/z: calcd for $C_{24}H_{29}NNaO^+$ $[M+Na]^+$ 370.2141, found: 370.2150.



4an

(*E*)-*N*-benzyl-*N*-(2-cyclooctyl-1-phenylvinyl)acetamide (4an): **Method B:** 74 mg, 68% yield;

Method C: 90 mg, 83% yield. Colorless oil. Eluents for flash column chromatography petroleum ether/ethyl acetate (10:1 *v*/*v*). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.43 – 7.33 (m, 3H), 7.30 – 7.16 (m, 7H), 5.15 (d, J = 11.1 Hz, 1H), 4.45 (s, 2H), 2.55 (qd, J = 8.9, 4.5 Hz, 1H), 2.22 (s, 3H), 1.64 – 1.22 (m, 14H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 170.6, 139.3, 137.4, 135.1, 134.9, 129.1, 128.49, 128.47, 128.3, 128.0, 127.1, 48.6, 36.3, 31.7, 26.9, 26.0, 24.6 22.3. HRMS m/z: calcd for $C_{25}H_{31}NNaO^+$ $[M+Na]^+$ 384.2298, found: 384.2282.

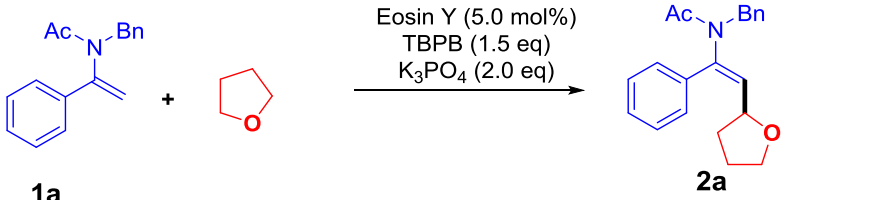


4ao

(*E*)-*N*-benzyl-*N*-(1,3-diphenylprop-1-en-1-yl)acetamide (4ao): **Method B:** 46 mg, 45% yield; **Method C:** 51 mg, 50% yield. Colorless oil. Eluents for flash column chromatography petroleum ether/ethyl acetate (10:1 *v*/*v*). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.41 – 7.37 (m, 3H), 7.30 – 7.25 (m, 5H), 7.22 – 7.17 (m, 5H), 6.87 – 6.82 (m, 2H), 5.50 (t, J = 8.1 Hz, 1H), 4.53 (s, 2H), 3.50 (d, J = 8.1 Hz, 2H), 2.23 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 170.7, 139.4, 139.2, 137.5, 134.4, 130.1, 129.1, 128.8, 128.7, 128.52, 128.49, 128.3, 128.0, 127.2, 126.2, 48.6, 34.4, 22.3. HRMS m/z: calcd for $C_{24}H_{24}NO^+$ $[M+H]^+$ 342.1852, found: 342.1837.

Synthetic Applications

(a) Gram-scale Synthesis of Enamide 2a



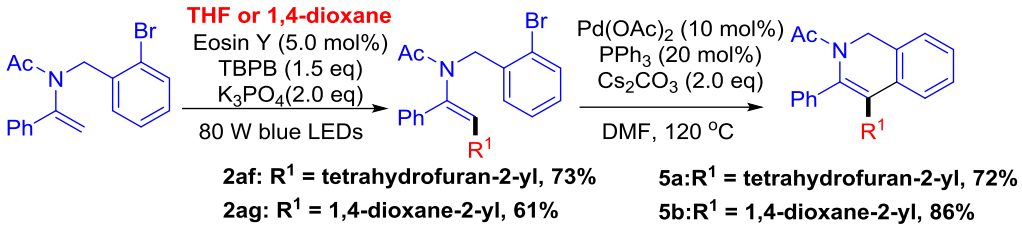
1a
1.01 g

2a
80 W blue LEDs: 0.92 g, 72%
90 W Kessil Lamp: 1.04 g, 81%

Enamide **1a** (1.01 g, 4.0 mmol), Eosin Y (0.2 mmol, 5.0 mol%), K_3PO_4 (8.0 mmol, 2.0 eq) were added sequentially into an oven-dried Schlenk tube under nitrogen atmosphere, the tube was then capped with a rubber stopper. TBPB (1.2 mL, 6.0 mmol, 1.5 eq) and THF (20.0 mL) were then added by syringe. The resulting mixture was allowed to stir at room temperature under 80 W blue LEDs irradiation for 12 hours. Upon completion of the reaction as monitored by TLC, the solvent was removed under vacuum and the residue was purified by flash silica gel column chromatography using petroleum ether/ethyl acetate (10:1 *v*/*v*) as eluent to afford pure products **2a** in 72% yield (0.92 g).

Alternatively, upon the employment of a 90 W Kessil A360X LED lamp instead of the 80 W blue LEDs, the desired product **2a** could be obtained in 81% yield (1.04 g).

(b) The Palladium-Catalyzed Heck-Coupling Reaction[2]

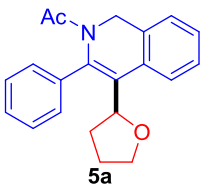


2af: R^1 = tetrahydrofuran-2-yl, 73% **5a:R^1 = tetrahydrofuran-2-yl, 72%**

2ag: R^1 = 1,4-dioxane-2-yl, 61% **5b:R^1 = 1,4-dioxane-2-yl, 86%**

N-(2-bromobenzyl)-*N*-(1-phenylvinyl)acetamide (0.3 mmol), *fac*-Ir(ppy)$_3$ (0.003 mmol, 1.0 mol%), K_3PO_4 (0.9 mmol, 3.0 eq) were added sequentially into Schlenk tube under nitrogen, the tube was then capped with a rubber stopper. TBPB (180 μL, 0.9 mmol, 3.0 eq) and THF (1.5 mL) were then added by syringe. The resulting mixture was allowed to stir at room temperature under 80 W blue LEDs irradiation. Upon completion of the reaction as monitored by TLC, the solvent was removed under vacuum and the residue was purified by flash silica gel column chromatography using petroleum ether/ethyl acetate (10:1 *v*/*v*) as eluent to afford pure products **2af, 2ag**.

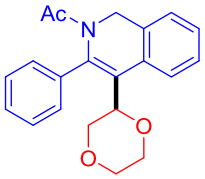
(*E*)-*N*-(2-bromobenzyl)-*N*-(1-phenyl-2-(tetrahydrofuran-2-yl)vinyl)acetamide **2af** (0.2 mmol), $Pd(OAc)_2$ (0.02 mmol), PPh_3 (0.04 mmol) and Cs_2CO_3 (0.24 mmol) were added sequentially into a oven-dried Schlenk tube under nitrogen atmosphere, then the tube was capped with a rubber stopper. DMF was added by syringe. The resulting mixture was allowed to stir at 120 °C in the oil bath. Upon completion of the reaction as monitored by TLC, the solvent was removed under vacuum and the residue was purified by flash silica gel column chromatography using petroleum ether/ethyl acetate (30:1 *v*/*v*) as eluent to afford pure products **5a**.



5a

1-(3-phenyl-4-(tetrahydrofuran-2-yl)isoquinolin-2(1*H*)-yl)ethan-1-one (5a): 46 mg, 72% yield. White solid. Eluents for flash column chromatography petroleum ether/ethyl acetate (30:1 *v*/*v*). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.75 – 7.68 (m, 1H), 7.56 (d, J = 6.9 Hz, 2H), 7.47 – 7.35 (m, 3H), 7.31 – 7.21 (m, 3H), 5.57 (d, J = 14.0 Hz, 1H), 4.70 (dd, J = 8.9, 7.0 Hz, 1H), 4.30 (d, J = 14.2 Hz, 1H), 4.25 – 4.17 (m, 1H), 3.79 (q, J = 7.4 Hz, 1H), 2.16 – 1.91 (m, 3H), 1.89 – 1.77 (m, 1H), 1.42 (s,

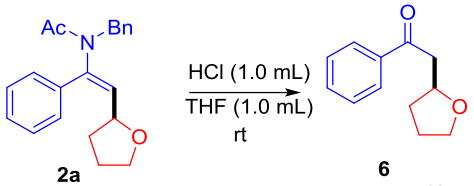
3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 171.4, 140.5, 136.7, 134.7, 131.9, 130.0, 128.8, 128.5, 127.3, 127.0, 125.2, 125.0, 124.8, 78.4, 68.1, 46.5, 30.4, 26.4, 24.3. HRMS m/z: calcd for $C_{21}H_{22}NO_2^+$ $[M+H]^+$ 320.1645, found: 320.1652.



5b

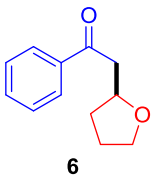
1-(4-(1,4-dioxan-2-yl)-3-phenylisoquinolin-2(1*H*)-yl)ethan-1-one (5b): 58mg, 86% yield. White solid. Eluents for flash column chromatography petroleum ether/ethyl acetate (30:1 *v*/*v*). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 8.10 (d, J = 7.7 Hz, 1H), 7.55 (d, J = 6.3 Hz, 2H), 7.47-4.40 (m, 4H), 7.35-7.29 (m, 1H), 7.25 (s, 1H), 5.71 (d, J = 14.1 Hz, 1H), 4.65 (dd, J = 10.4, 2.8 Hz, 1H), 4.13 – 3.92 (m, 3H), 3.89 – 3.78 (m, 2H), 3.73 (t, J = 9.5 Hz, 1H), 3.42 (dd, J = 11.7, 2.6 Hz, 1H), 1.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 171.31, 141.77, 136.31, 134.15, 131.89, 129.77, 129.29, 128.78, 127.54, 127.17, 125.81, 125.29, 122.82, 76.16, 69.21, 67.01, 66.22, 46.48, 29.64, 24.44. HRMS m/z: calcd for $C_{21}H_{22}NO_3^+$ $[M + H]^+$ 336.1594, found 336.1584.

(c) Hydrolysis of *β*-alkylated Enamides 2a



2a **6**
38 mg, 66%

(*E*)-*N*-benzyl-*N*-(1-phenyl-2-(tetrahydrofuran-2-yl)vinyl)acetamide **2a** (0.3 mmol) was added into a tube. Then THF (1.0 mL) and concentrated hydrochloric acid (1.0 mL) were added sequentially by syringe. The resulting mixture was stirred at room temperature. Upon completion of the reaction as monitored by TLC, the solvent was removed under vacuum and the residue was purified by flash silica gel column chromatography using petroleum ether/ethyl acetate (20:1 *v*/*v*) as eluent to afford pure products **6**.

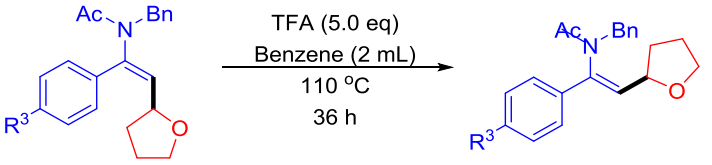


6

1-phenyl-2-(tetrahydrofuran-2-yl)ethan-1-one (6): 38 mg, 66% yield. Light yellow oil. Eluents for

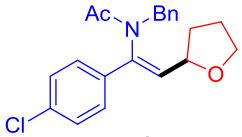
flash column chromatography petroleum ether/ethyl acetate (20:1 *v*/*v*). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 8.00 – 7.93 (m, 2H), 7.61 – 7.52 (m, 1H), 7.51 – 7.43 (m, 2H), 4.41 (q, J = 6.8 Hz, 1H), 3.89 (q, J = 7.4, 6.7 Hz, 1H), 3.75 (q, J = 7.5 Hz, 1H), 3.40 (ddd, J = 16.3, 6.1, 1.2 Hz, 1H), 3.06 (ddd, J = 16.3, 6.7, 1.0 Hz, 1H), 2.25 – 2.15 (m, 1H), 1.98 – 1.88 (m, 2H), 1.57 (dq, J = 12.3, 7.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 198.4, 136.9, 133.0, 128.5, 128.1, 75.3, 67.8, 44.6, 31.6, 25.6. HRMS m/z: calcd for $C_{12}H_{14}NaO_2^+$ $[M+Na]^+$ 213.0886, found: 213.0892.

(d) Conversion of Stereochemistry of Enamides



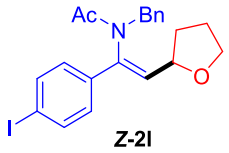
2 ***Z*-2n:** R^3=Cl, 75%
***Z*-2l:** R^3=I, 75%

0.3 mmol (1.0 eq) of the enamide **2** was dissolved in dry benzene (2.0 mL) in a screw cap vial. 102.6 mg (1.5 mmol, 5.0 eq) of trifluoroacetic acid were then added to the solution and the vial was heated to 110 °C using a magnetic hotplate stirrer equipped with an oil bath. Upon completion of the reaction as monitored by TLC, the solvent was removed under vacuum and the residue was purified by flash silica gel column chromatography using petroleum ether/ethyl acetate (10:1 *v*/*v*) as eluent to afford pure products **7**.



***Z*-2n**

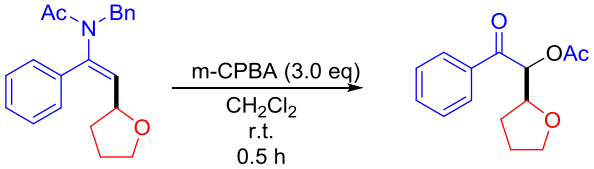
(*Z*)-*N*-benzyl-*N*-(1-(4-chlorophenyl)-2-(tetrahydrofuran-2-yl)vinyl)acetamide (*Z*-2n): 81 mg, 75 % yield. Light yellow oil. Eluents for flash column chromatography petroleum ether/ethyl acetate (10:1 *v*/*v*). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.42 – 7.28 (m, 5H), 7.22 (s, 4H), 5.92 (d, J = 9.6 Hz, 1H), 5.59 (d, J = 13.8 Hz, 1H), 3.87 (q, J = 8.0 Hz, 1H), 3.75 (q, J = 7.3 Hz, 1H), 3.63 (q, J = 7.1 Hz, 1H), 3.46 (d, J = 13.8 Hz, 1H), 2.20 (s, 3H), 1.64 – 1.54 (m, 1H), 1.06 – 0.97 (m, 1H), 0.83 – 0.76 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 171.07, 138.40, 136.86, 134.86, 133.85, 130.98, 129.96, 129.22, 128.36, 127.71, 127.15, 75.03, 68.13, 48.63, 31.63, 26.01, 21.57. HRMS m/z: calcd for $C_{21}H_{23}ClNO_2^+$ $[M + H]^+$ 356.1412, found 356.1421.



Z-2l

(*Z*)-*N*-benzyl-*N*-(1-(4-iodophenyl)-2-(tetrahydrofuran-2-yl)vinyl)acetamide (*Z*-2l): 101 mg, 75 % yield. White solid. Eluents for flash column chromatography petroleum ether/ethyl acetate (10:1 *v*/*v*). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.74 (d, J = 8.6 Hz, 2H), 7.27 (d, J = 2.4 Hz, 2H), 7.25 – 7.19 (m, 3H), 7.16 – 7.11 (m, 2H), 5.94 (d, J = 9.7 Hz, 1H), 5.59 (d, J = 13.9 Hz, 1H), 3.90 – 3.81 (m, 1H), 3.75 (q, J = 7.1 Hz, 1H), 3.62 (td, J = 8.0, 5.8 Hz, 1H), 3.45 (d, J = 13.9 Hz, 1H), 2.19 (s, 3H), 1.81 – 1.69 (m, 1H), 1.66 – 1.51 (m, 2H), 1.05 – 0.96 (m, 1H), 0.84 – 0.71 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 171.07, 138.54, 138.13, 136.84, 134.92, 131.09, 129.95, 128.36, 127.71, 127.57, 94.76, 75.00, 68.13, 48.62, 31.58, 26.00, 21.56. HRMS m/z: calcd for $C_{21}H_{23}INO_2^+$ $[M + H]^+$ 448.0768, found 448.0775.

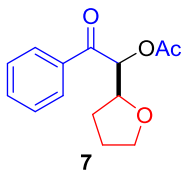
(e) The Synthesis of *α*-acyloxyketone



2a

7
32 mg, 65 %

Enamide **2a** (0.2 mmol) was added into a reaction tube. *m*-CPBA (3.0 eq) was then added to the stirred solution of the enamide in CH_2Cl_2 at 0 ^{o}C and the resultant suspension was stirred for 30 min before warming to room temperature. The resulting mixture was stirred at room temperature. Upon completion, the solvent was then removed under vacuum. The residue was purified directly by silica gel chromatography, eluting with petroleum ether/ethyl acetate (50:1 *v*/*v*) to give *α*-acyloxyketone **7.**

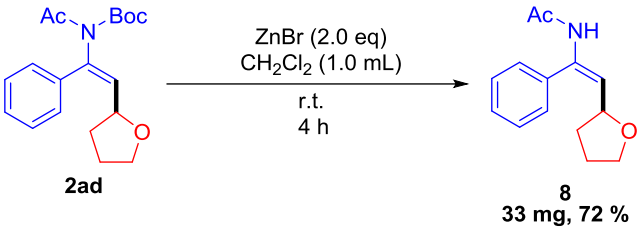


7

2-oxo-2-phenyl-1-(tetrahydrofuran-2-yl)ethyl acetate (7): 32 mg, 65 % yield. Colorless oil. Eluents for flash column chromatography petroleum ether/ethyl acetate (50:1 *v*/*v*). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 8.00 (d, J = 8.4 Hz, 2H), 7.63 – 7.55 (m, 1H), 7.52 – 7.44 (m, 2H), 6.01 (d, J = 4.5 Hz, 1H), 4.37 (q, J = 6.0 Hz, 1H), 3.89 (q, J = 6.8, 5.6 Hz, 1H), 3.75 (q, J = 7.5 Hz, 1H), 2.17 – 2.16 (m, 3H), 2.07 – 1.95 (m, 2H), 1.97 – 1.81 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 195.36, 170.31, 135.32,

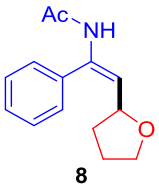
133.65, 128.71, 128.56, 77.47, 76.54, 69.05, 26.64, 25.81, 20.69. HRMS m/z: calcd for $C_{14}H_{17}O_4^+$ [M + H]$^+$ 249.1121, found 249.1135.

(f) Cleavage of *N*-Boc Group[3]



2ad **8**
33 mg, 72 %

Enamide **2ad** (0.2 mmol) was added into a reaction tube. $ZnBr_2$ (90.1 mg, 0.4 mmol) and CH_2Cl_2 (1 mL) were then added sequentially. The resulting mixture was stirred at room temperature for 4 hours. Upon completion as monitored by TLC, the solvent was then removed under vacuum. The residue was purified directly by silica gel chromatography, eluting with petroleum ether/ethyl acetate (5:1 *v*/*v*) to give **8**.

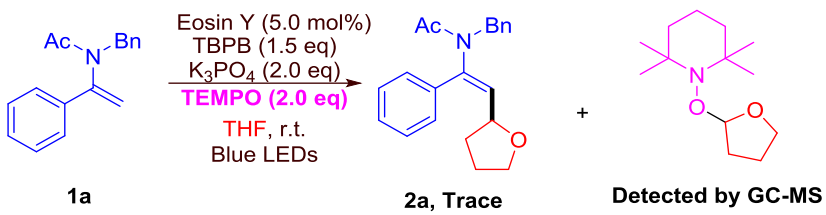


8

(*E*)-*N*-(1-phenyl-2-(tetrahydrofuran-2-yl)vinyl)acetamide (8): 33 mg, 72 % yield. Colorless oil. Eluents for flash column chromatography petroleum ether/ethyl acetate (5:1 *v*/*v*). **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 7.78 (s, 1H), 7.37 (d, J = 5.5 Hz, 3H), 7.31 (dd, J = 10.6, 5.0 Hz, 2H), 5.63 (d, J = 7.1 Hz, 1H), 4.63 – 4.53 (m, 1H), 3.91 (q, J = 7.2 Hz, 1H), 3.82 – 3.79 (m, 1H), 2.26 – 2.17 (m, 1H), 2.13 (s, 3H), 1.98 – 1.91 (m, 2H), 1.78 – 1.60 (m, 1H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ ppm 137.07, 136.63, 128.76, 128.26, 125.89, 123.37, 75.67, 68.02, 33.02, 31.75, 26.39, 25.95, 23.53. **HRMS** m/z: calcd for $C_{14}H_{18}NO_2^+$ [M + H]$^+$ 232.1332, found 232.1317.

Mechanistic Studies

(a) Trapping Experiment with 2,2,6,6-Tetramethylpiperidin-1-oxyl (TEMPO)



1a **2a, Trace** **Detected by GC-MS**

Enamide **1a** (0.2 mmol), Eosin Y (0.01 mmol, 5 mol%), K_3PO_4 (0.4 mmol, 2.0 eq) and TEMPO (0.4 mmol, 2.0 eq) were added sequentially into Schlenk tube under nitrogen, the tube was then capped with a rubber stopper. TBPB (60 μL, 0.3 mmol, 1.5 eq) and THF (1.0 mL) were then added by syringe. The resulting mixture was allowed to stir at room temperature under 80 W blue LEDs irradiation for 12 hours. Then solvent was removed under vacuum and the residue was determined by ^{1}H NMR analysis of the crude reaction mixture by using mesitylene as an internal standard. The adduct of the α-alkoxy alkyl radical species with TEMPO has been detected by GC-MS, as shown in **Figure S2**.

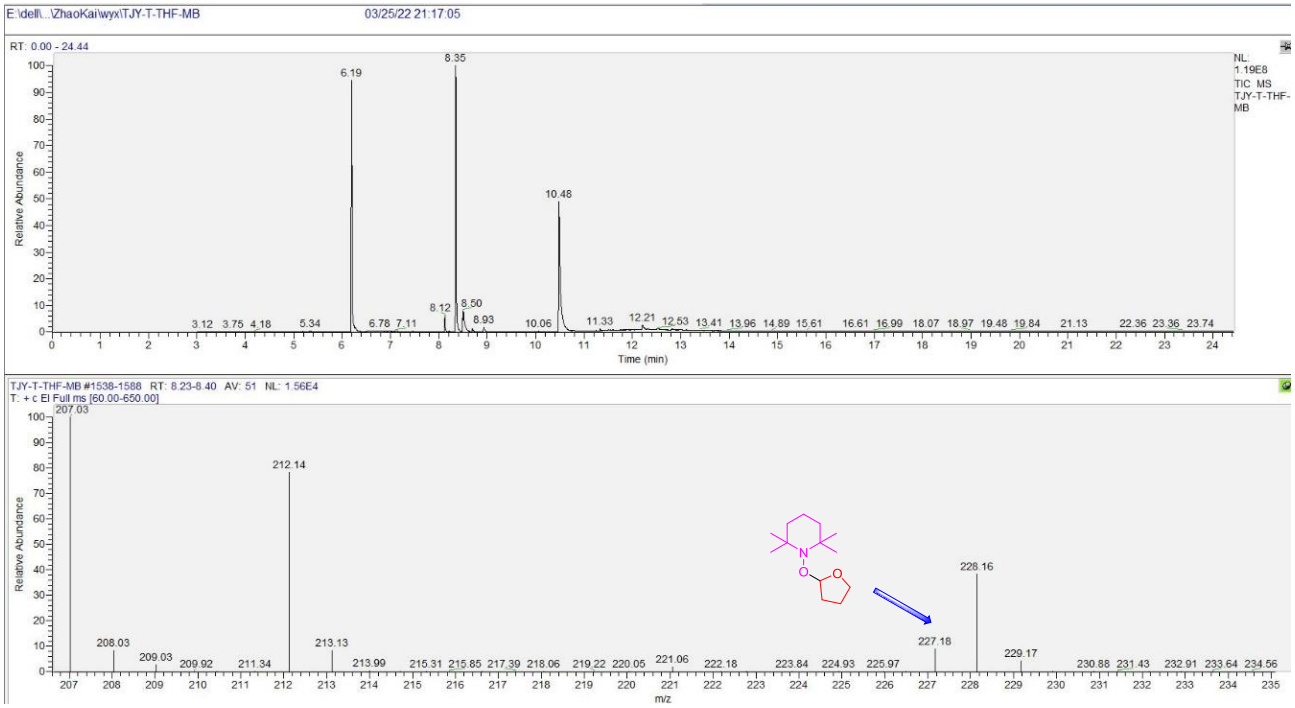
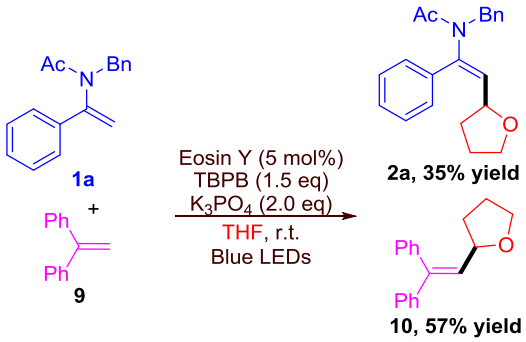


Figure S2 The GC-MS Spectra for the Radical-Trapping Experiment with TEMPO

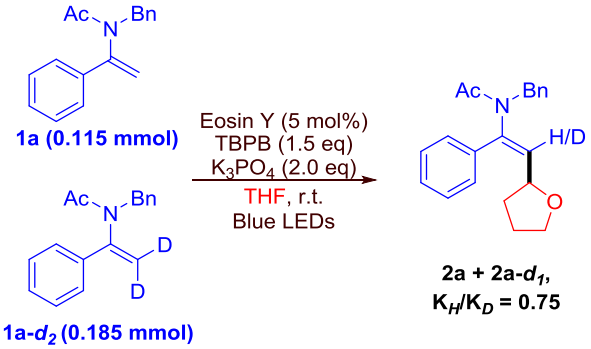
(b) Trapping Experiment with Ethene-1,1-diyldibenzene



Enamide **1a** (0.2 mmol), Eosin Y (0.01 mmol, 5 mol%), K_3PO_4 (0.4 mmol, 2.0 eq) were added sequentially into Schlenk tube under nitrogen, the tube was then capped with a rubber stopper. Ethene-1,1-diyldibenzene **10** (0.2 mmol), TBPB (60 μL, 0.3 mmol, 1.5 eq) and THF (1.0 mL) were then added by syringe. The resulting mixture was allowed to stir at room temperature under 80 W blue LEDs

irradiation for 12 hours. Then solvent was removed under vacuum and the residue was determined by NMR analysis of the crude reaction mixture by using mesitylene as an internal standard.

(c) Intermolecular Kinetic Isotopic Effect (KIE) Study

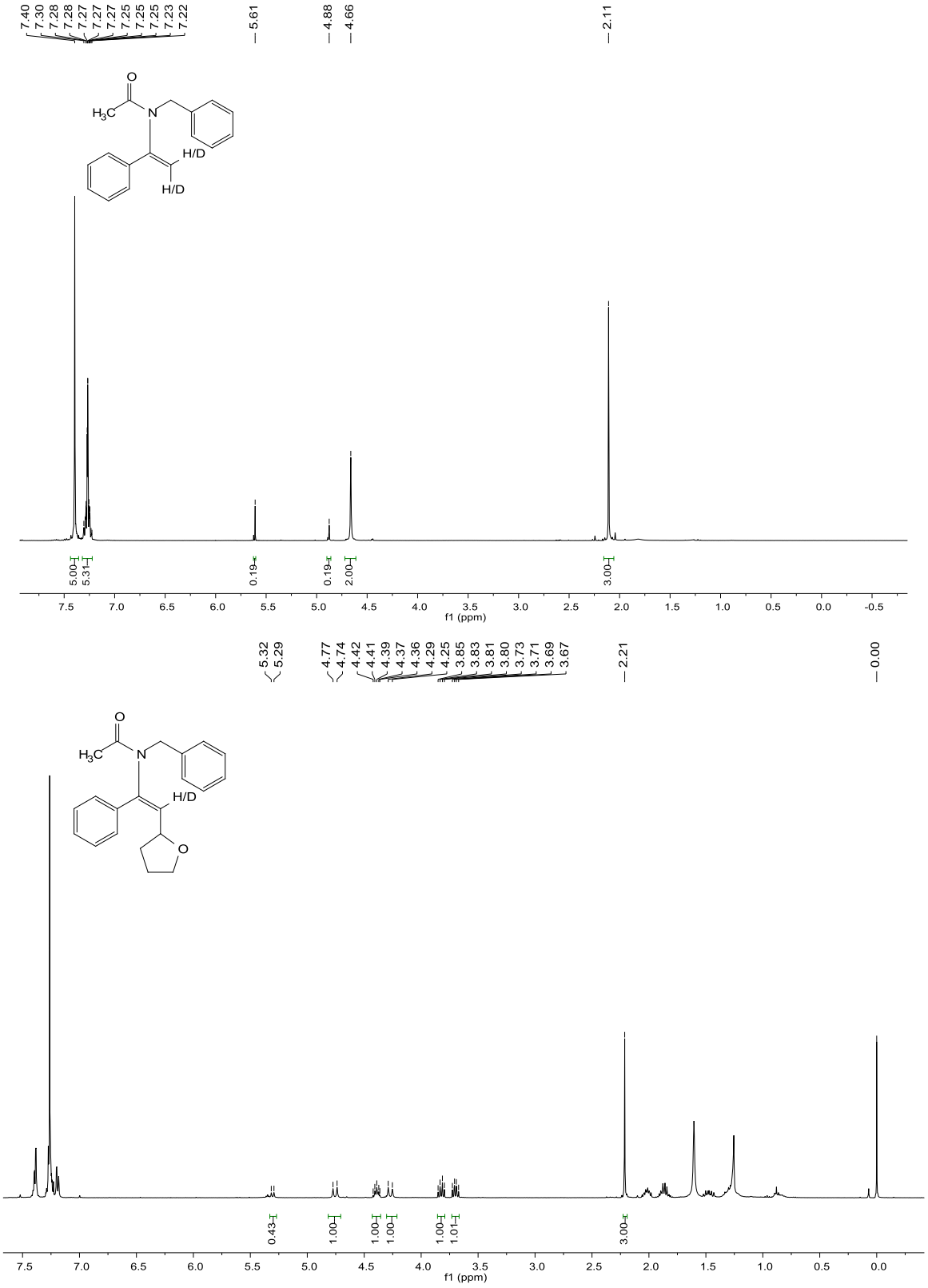


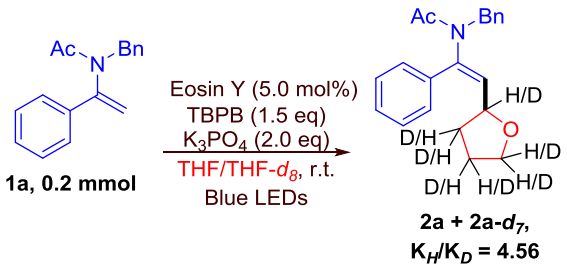
Enamide **1a-*d*$_2$** was prepared according to the literatures,[1b,4] as a light yellow oil with 81% deuterium. Enamide **1a** (0.115 mmol), **1a-*d*$_2$** (0.185 mmol), Eosin Y (0.01 mmol, 5 mol%), K_3PO_4 (0.4 mmol, 2.0 eq) were added sequentially into an oven-dried Schlenk tube under nitrogen atmosphere, the tube was then capped with a rubber stopper. TBPB (60 μL, 0.3 mmol, 1.5 eq) and THF (1 mL) were then added by syringe. The resulting mixture was allowed to stir at room temperature under 80 W blue LEDs irradiation for 1 hours. The product was isolated through thin-layer chromatography (petroleum ether/ethyl acetate (5: 1 *v*/*v*) to afford crude mixture (10% yield) as light yellow oil. The KIE value (K_H/K_D = 0.75) was determined from the ^{1}H NMR.

In consideration of the 81% deuterated ratio of **1a-*d*$_2$**, 0.185 mmol of **1a-*d*$_2$** (a H-D mixture containing 81% deuterated enamide and 19% undeuterated one) was added along with 0.118 mmol of undeuterated enamide **1a** in the same reaction vessel, so that the real amount of pure deuterated enamide (and its undeuterated competitor) was calculated to be 0.2 mmol approximately. The ratio of deuterated enamide **2a-*d*$_1$** *vs* **2a** in the isolated mixture was 57:43 as determined by ^{1}H NMR, thus giving a calculated K_H/K_D = 0.43/0.57 = 0.75.

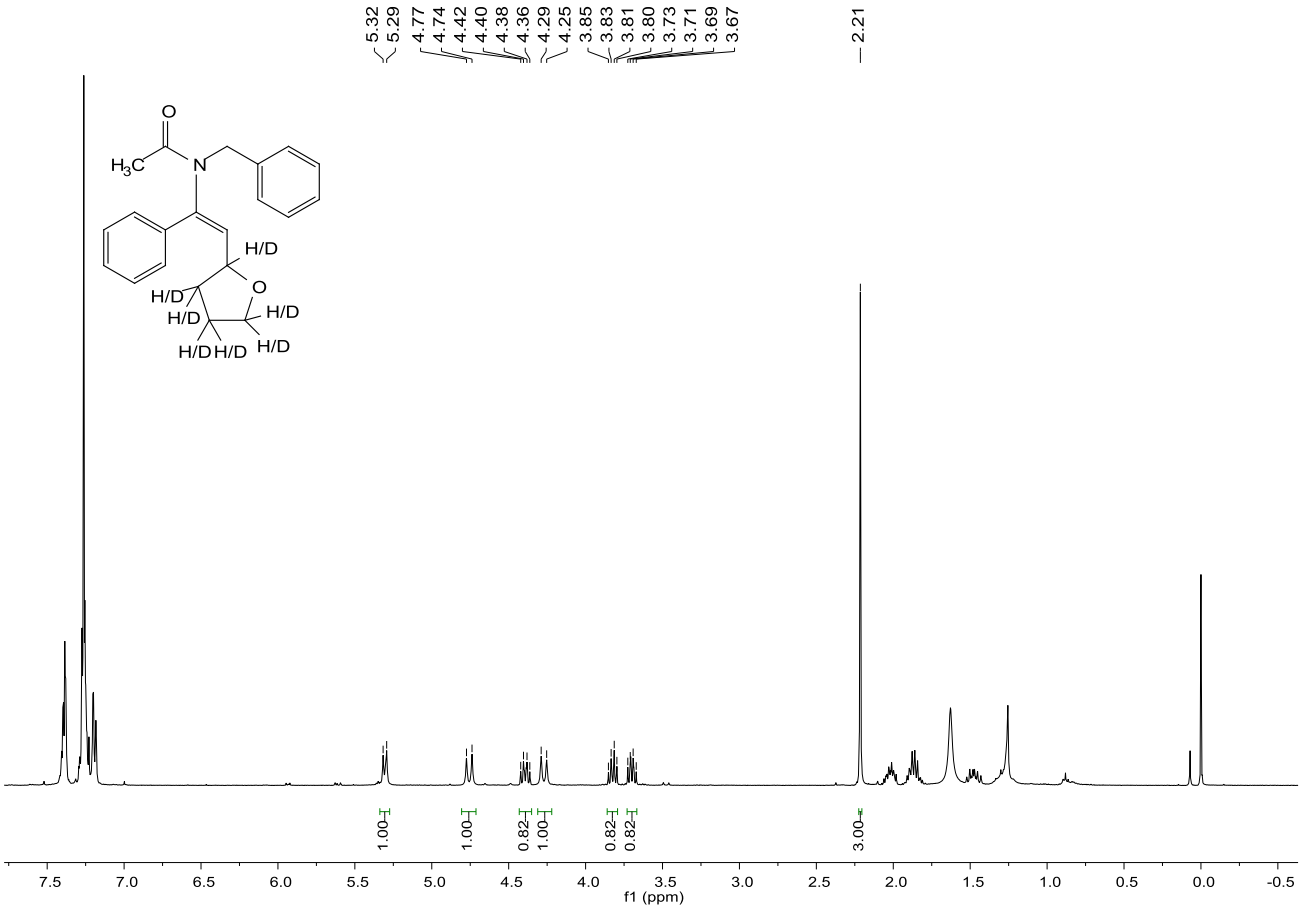
Notably, an inverse secondary KIE (KIE<1) is observed, which might be attributed to the change of the hybridization state of the olefinic carbon of the substrate. Based on the mechanism as depicted in Scheme 4, the addition of the alkyl radical species to the double bonds of enamides to form intermediate **A** changes the hybridization state of the *β*-olefinic carbon from sp^2 to sp^3, leading to an increase of the force constant of the C-H or C-D bonds bending vibrations (which means the C-H bending vibrations became more rigid and difficult). In this pattern, the difference between the zero-point energy in the transition state (ΔG_{TS}) (between the H-containing compound and a D-containing one) is greater than the difference between the starting enamide substrates (ΔG_s), implying that the

reaction rate of a deuterium-labelled substrate would surpass the rate of the non-deuterium one at a relatively low conversion, resulting to an inverse KIE of 0.75.





Enamide **1a** (0.2 mmol), Eosin Y (0.01 mmol, 5.0 mol%), K_3PO_4 (0.4 mmol, 2.0 eq) were added sequentially into Schlenk tube under nitrogen, the tube was then capped with a rubber stopper. TBPB (60 μL, 0.3 mmol, 1.5 eq), THF (0.5 mL) and THF-d_8 (0.5 mL) were then added by syringe. The resulting mixture was allowed to stir at room temperature under 80 W blue LEDs irradiation for 1 hours. The product was isolated through thin-layer chromatography (petroleum ether/ethyl acetate = 5/1 as developing solvent) to afford crude mixture (10% yield) as light yellow oil. The ratio of deuterated enamide **2a-*d*$_7$** *vs* **2a** in the isolated mixture was 82:18 as determined by ^{1}H NMR. The KIE value (K_H/K_D = 0.82/0.18 = 4.56) was determined from the ^{1}H NMR.



(d) Quantum Yield Measurement

In order to determine whether a radical-chain reaction is involved, the quantum yield measurement was conducted, which gives the quantum yield (Φ) of the photoreaction of 1.02, implying that the reaction is highly possible to proceed in a photoredox catalytic pathway rather than

a radical-chain mechanism.

The actinometry measurements were done as follows based on previous literature[5] :

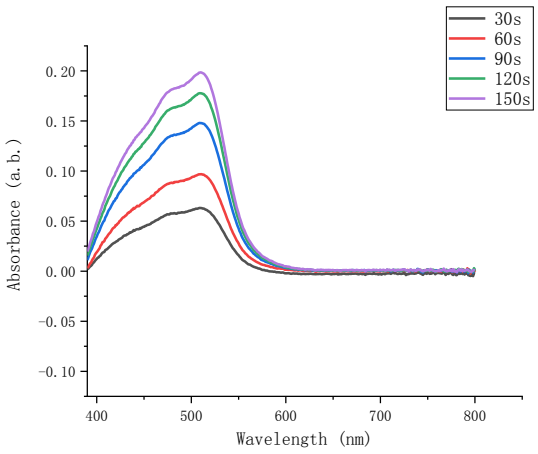
(i) The actinometry measurements were determined by standard ferrioxalate actinometry. A solution of ferrioxalate was prepared by dissolving 73.7 mg of potassium ferrioxalate hydrate and 67.0 μL of concentrated sulfuric acid in a 25.0 mL volumetric flask and filled to the mark with water (HPLC grade). A buffered solution of phenanthroline was prepared by dissolving 25.0 mg of phenanthroline, 5.2 g of sodium acetate and 0.56 mL of concentrated sulfuric acid in a 50.0 mL volumetric flask and filled to the mark with water (HPLC grade). Both solutions were stored in the dark.

(ii) The actinometry solutions (V_1, 1.0 mL) were irradiated with 80 W blue LEDs for specified time intervals (30 s, 60 s, 90 s, 120 s, and 150 s). After irradiation, 40.0 μL (V_2) of the actionmeter solutions were removed and placed in 10.0 mL (V_3) volumetric flasks. 1.5 mL of buffered solutions were added to these flasks and filled to the mark with water (HPLC grade). The UV-Vis spectra of actinometry samples were recorded for each time interval (**Figure S3, a**). The absorbance of the actinometry solutions were monitored at 510 nm. A non-irradiated sample was also prepared and the absorbance at 510 nm measured in cuvette (l = 1 cm). ε is the molar absorptivity at 510 nm (11,100 L mol^{-1} cm^{-1}). Based on the data, we got the graph (**Figure S3, b**).

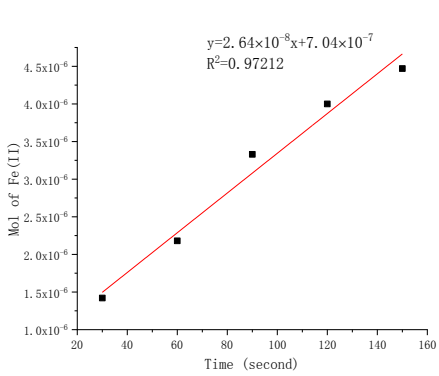
$$\text{mol } Fe^{2+} = \frac{V_1 \times V_3 \times \Delta A\ (510\ nm)}{10^3 \times V_2 \times I \times \varepsilon\ (510\ nm)} = \frac{1\ mL \times 10\ mL \times \Delta A\ (510\ nm)}{10^3 \times (40 \times 10^{-3}\ mL) \times 1\ cm \times 11100} = \frac{\Delta A\ (510\ nm)}{44400} = 2.64 \times 10^{-8}$$

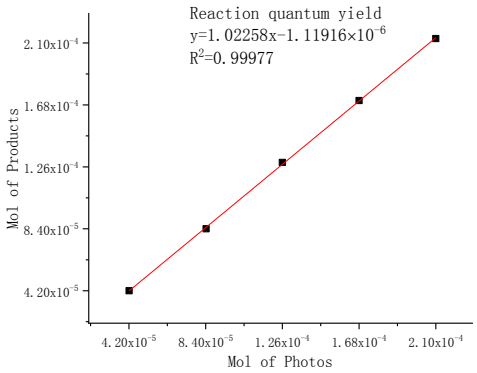
The quantum yield for Fe^{2+} ($\Phi_{Fe^{2+}}$= 1.13), F = mol Fe^{2+}/$\Phi_{Fe^{2+}}$.Then, the irradiated light intensity was estimated to 2.64×10^{-8} einstein S^{-1} by using $K_3[Fe(C_2O_4)_3]$ as an actinometer.

(iii) For five clean tubes, according to the general procedure, the 0.3 mmol scale model reaction solution was irradiated with 80 W blue LEDs for specified time intervals (30 min, 60 min, 90 min, 120 min and 150 min). The moles of products formed were determined by ^1H NMR yield with mesitylene as reference standard. The number of moles of products (y axis) per unit time is related to the number of photons (x axis, calculated from the light intensity) (**Figure S3, c**). The slope gives the quantum yield (Φ) of the photoreaction, 1.02.



a)





b) **c)**

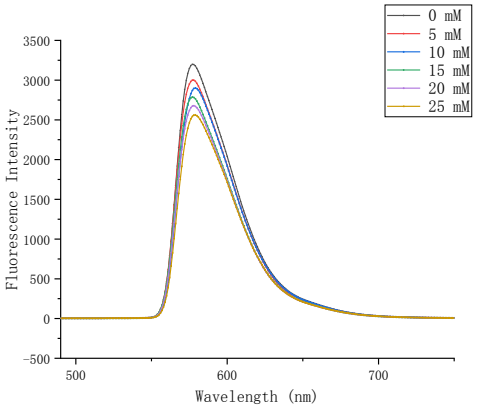
Figure S3. The UV-Vis spectra and data of quantum yield measurement

(e) Stern-Volmer Experiments

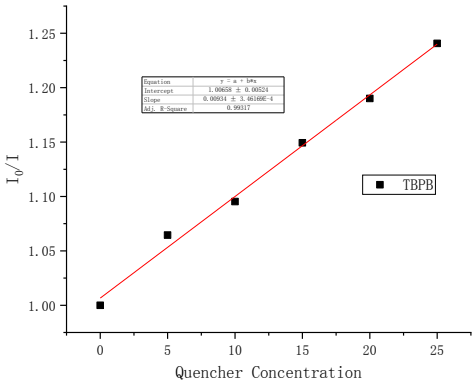
The Stern-Volmer fluorescence quenching experiments of Eosin Y with different oxidants was conducted by the following procedures. Firstly, the emission and excitation spectra of the photocatalyst Eosin Y was investigated. The luminescence quenching experiment was taken using an F97 pro Fluorescence spectrophotometer (Shanghai, China). A solution of Eosin Y (1.0 mM) in DMSO was chosen as the model. The excitation wavelength was 451 nm and the emission intensity was collected at 578 nm.

Next, the fluorescence quenching experiments of Eosin Y with different oxidants such as TBPB, TBHP, DTBP and BPO were conducted respectively: In a typical experiment, 1.0 mL of solution of Eosin Y (1.0 mM) in DMSO was added to the appropriate amount of quencher in a screw-top 1.0 cm quartz cuvette, 1 M solution of the quencher (oxidants) was added into the cuvette by 5 μL, and the emission of the sample was collected (**Figure S4a, S4c, S4e, S4g**). The solution was excited at λ = 451 nm (excitation maximum of Eosin Y) and the emission intensity at 578 nm (emission maximum

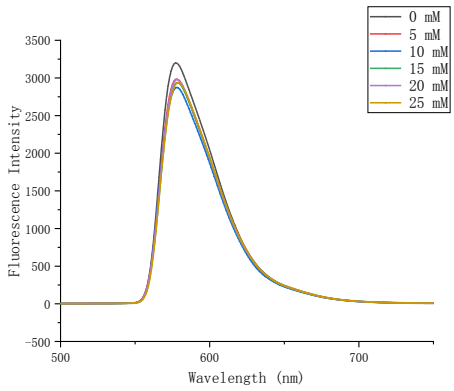
of Eosin Y) was observed (**Figure S4b, S4d, S4f, S4h**). Linear quenching was observed when TBPB and BPO were used as the oxidants (**Figure S4b** and **S4h**), while no quenching was observed when TBHP and DTBP were employed as the oxidant (**Figure S4d** and **S4f**).



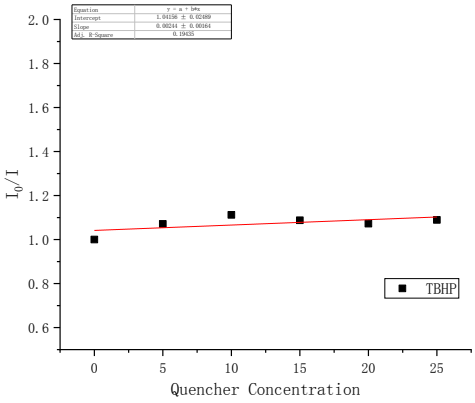
a) The fluorescence emission spectra of Eosin Y with different concentration of added quencher (TBPB) excited at 451 nm.



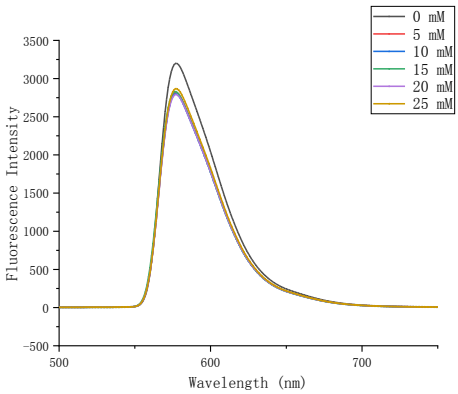
b) Eosin Y emission quenching by TBPB. Linear quenching is observed.



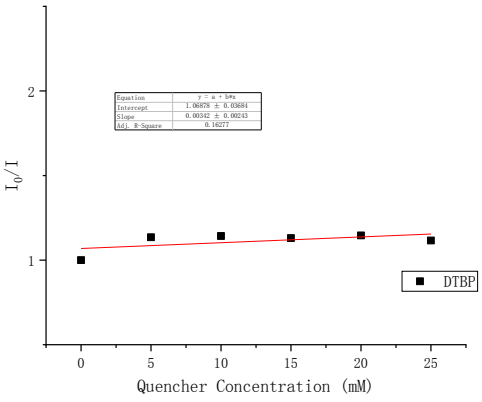
c) The fluorescence emission spectra of Eosin Y with different concentration of added quencher (TBHP) excited at 451 nm.



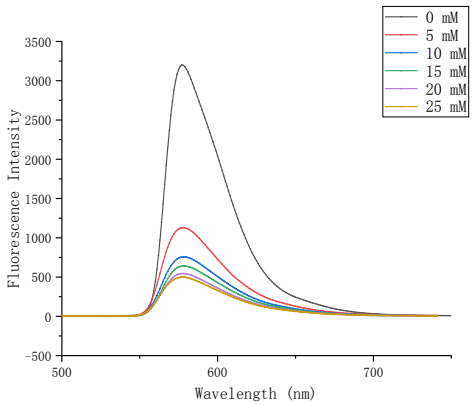
d) Eosin Y emission quenching by TBHP. No quenching was observed.



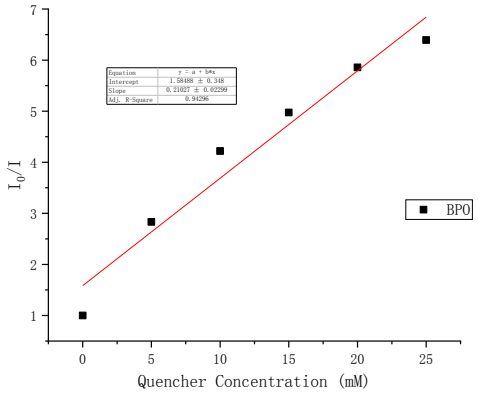
e) The fluorescence emission spectra of Eosin Y with different concentration of added quencher (DTBP) excited at 451 nm.



f) Eosin Y emission quenching by DTBP. No quenching was observed.



g) The fluorescence emission spectra of Eosin Y with different concentration of added quencher (DTBP) excited at 451 nm.



h) Eosin Y emission quenching by BPO. Linear quenching is observed.

Figure S4 Stern-Volmer Experiments

Stern–Volmer fluorescence quenching experiments demonstrated that the emission intensity of excited Eosin Y diminished in the presence of TBPB and BPO, indicating that the excited Eosin Y* might be oxidatively quenched by TBPB and BPO.

References

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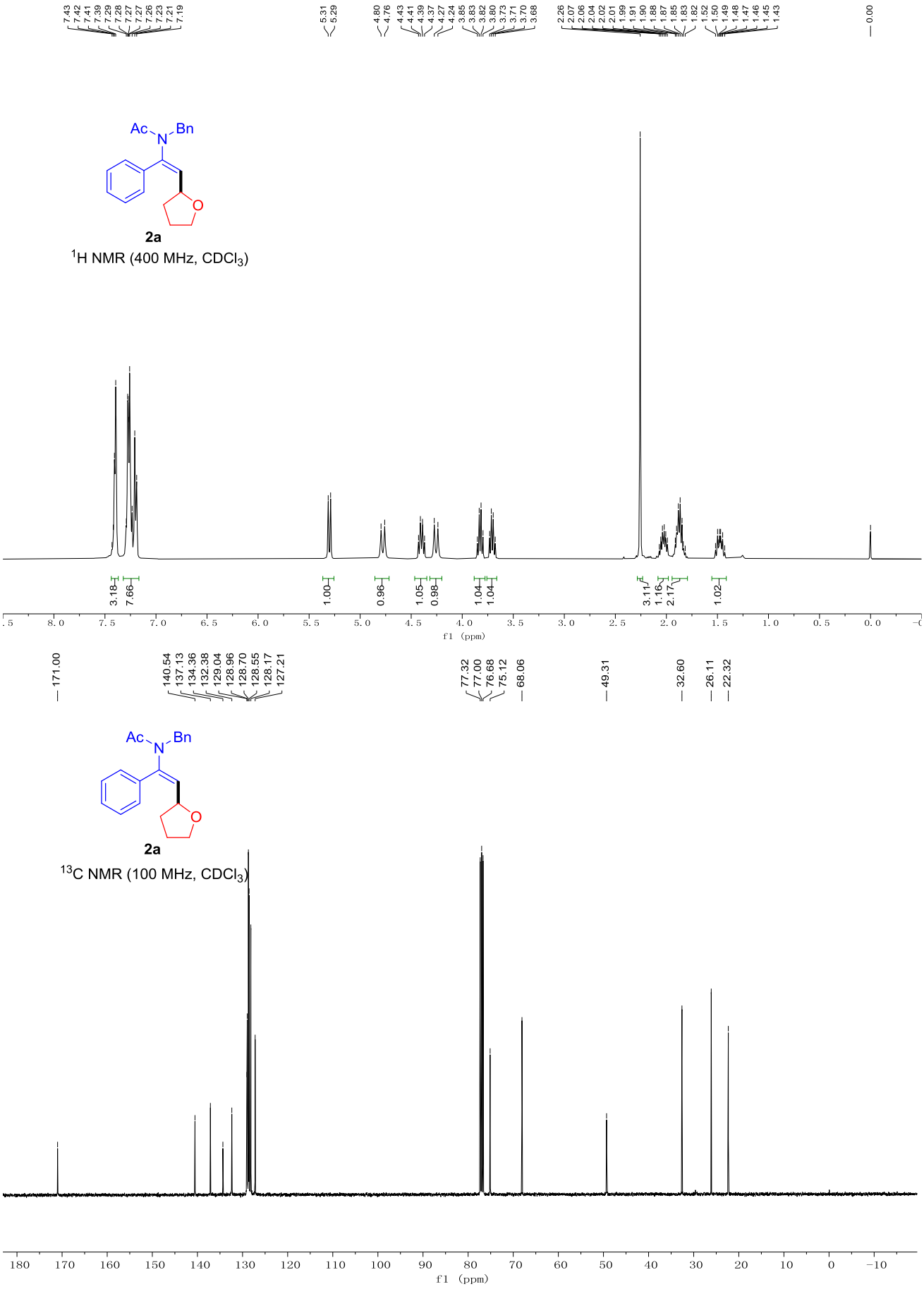
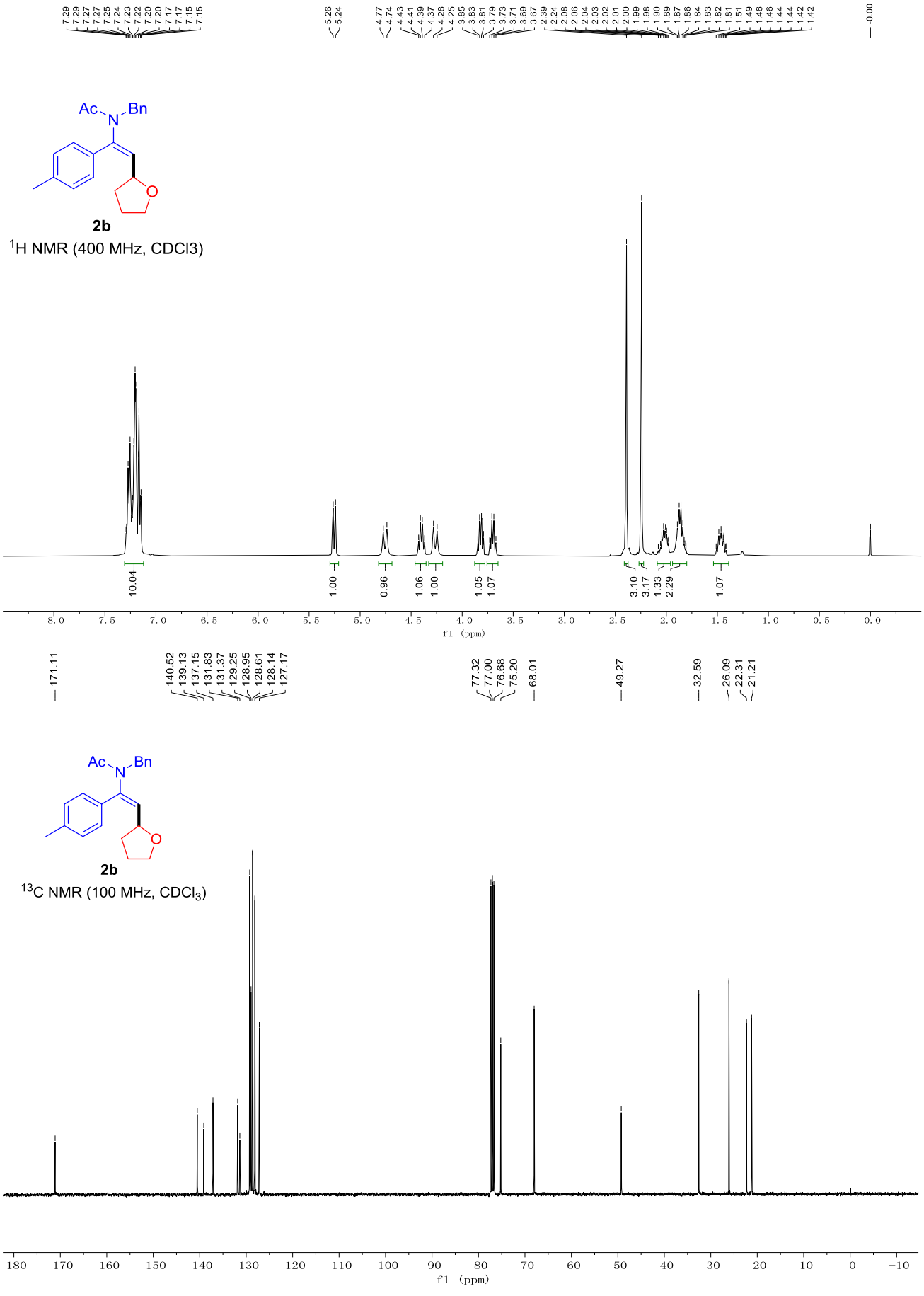
^{1}H NMR, ^{19}F NMR and ^{13}C NMR Spectra of Products

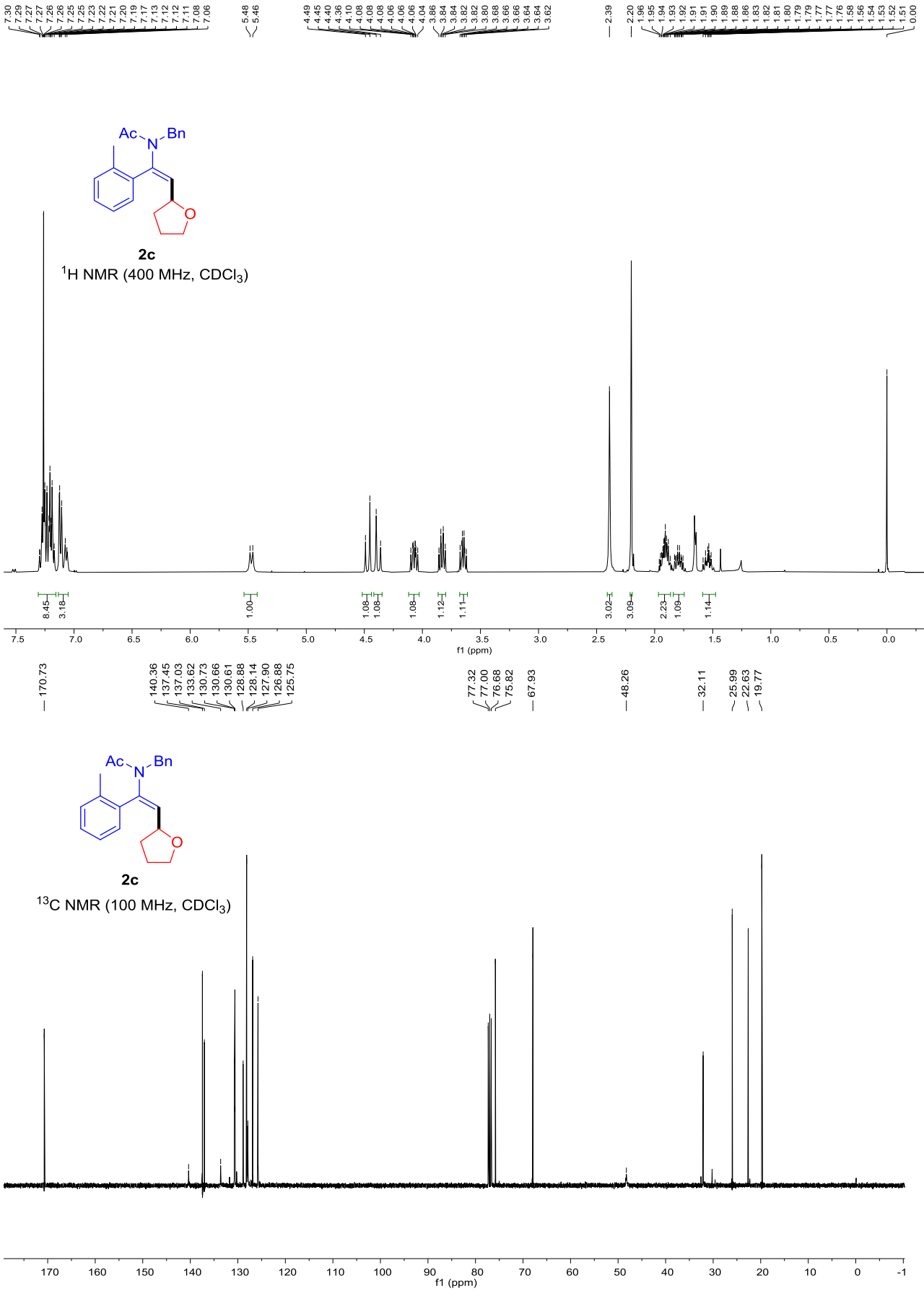
(*E*)-*N*-benzyl-*N*-(1-phenyl-2-(tetrahydrofuran-2-yl)vinyl)acetamide (**2a**)



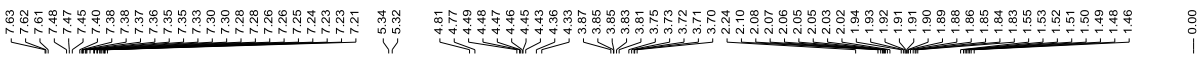
(*E*)-*N*-benzyl-*N*-(2-(tetrahydrofuran-2-yl)-1-(p-tolyl)vinyl)acetamide (**2b**)

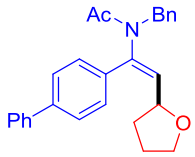


(*E*)-*N*-benzyl-*N*-(2-(tetrahydrofuran-2-yl)-1-(o-tolyl)vinyl)acetamide (**2c**)



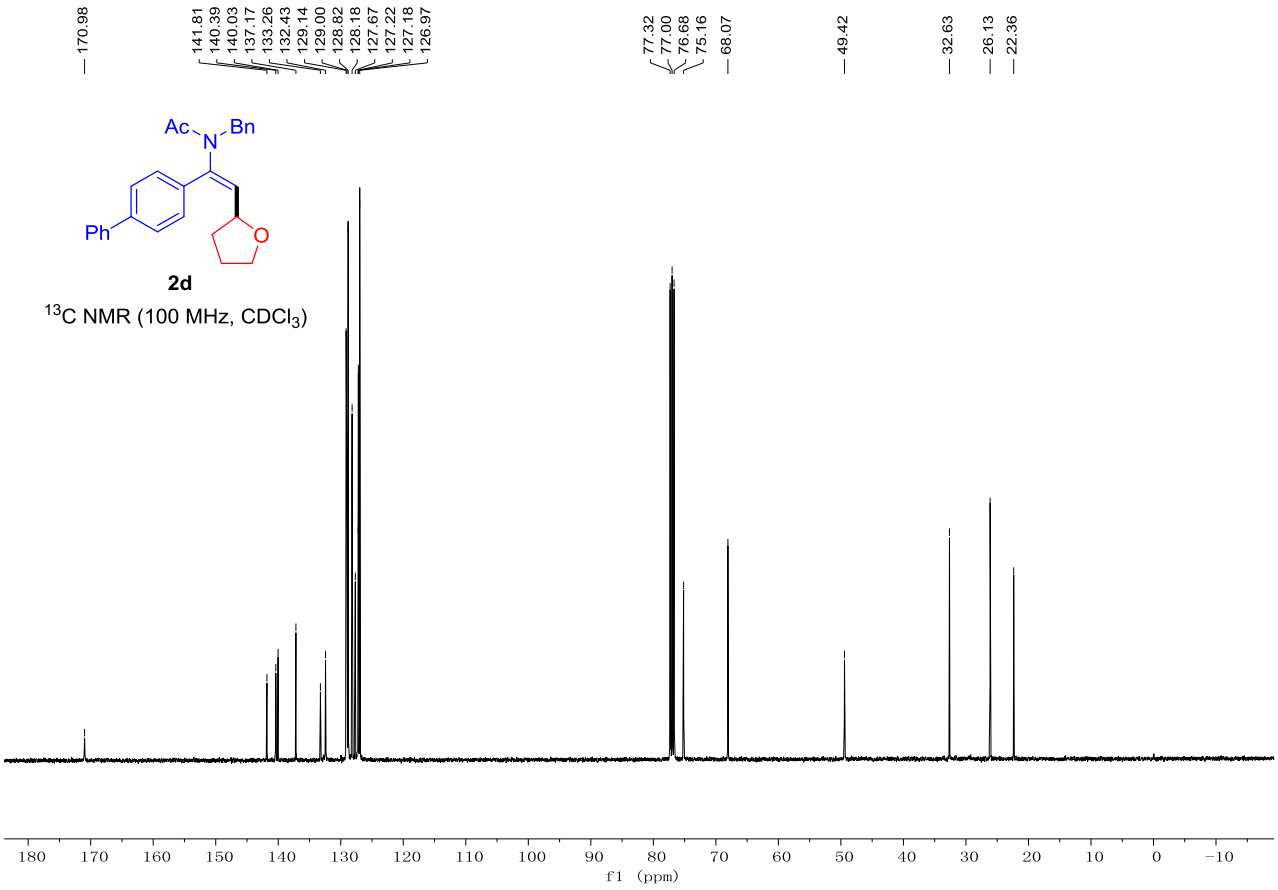
(*E*)-*N*-(1-([1,1'-biphenyl]-4-yl)-2-(tetrahydrofuran-2-yl)vinyl)-*N*-benzylacetamide (**2d**)





2d

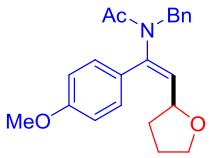
^{1}H NMR (400 MHz, $CDCl_3$)



2d

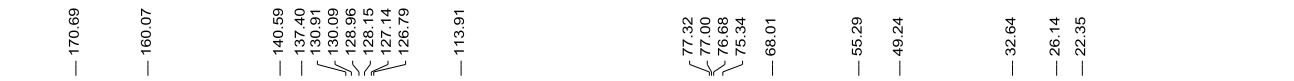
^{13}C NMR (100 MHz, $CDCl_3$)

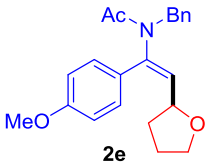
(*E*)-*N*-benzyl-*N*-(1-(4-methoxyphenyl)-2-(tetrahydrofuran-2-yl)vinyl)acetamide (**2e**)



2e

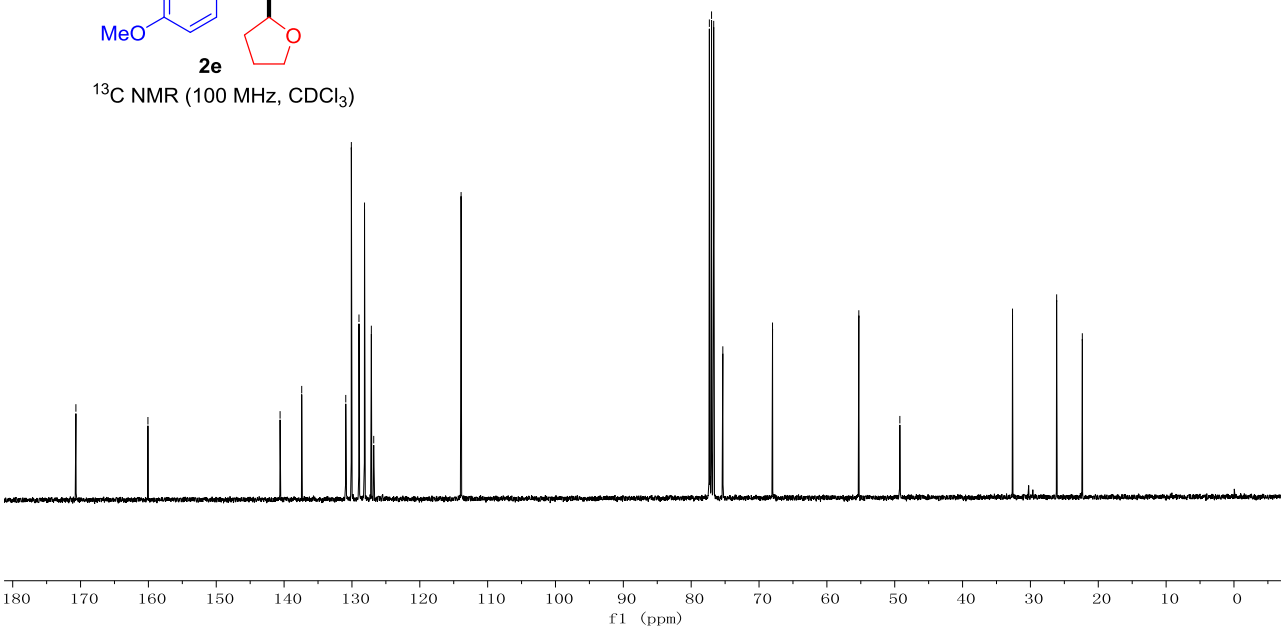
^{1}H NMR (400 MHz, $CDCl_3$)



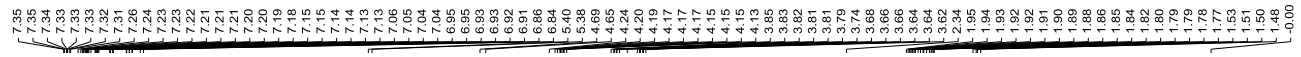


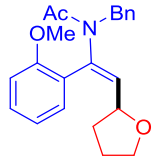
2e

^{13}C NMR (100 MHz, $CDCl_3$)



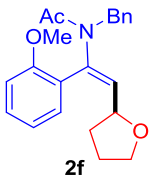
(*E*)-*N*-benzyl-*N*-(1-(2-methoxyphenyl)-2-(tetrahydrofuran-2-yl)vinyl)acetamide (**2f**)





2f

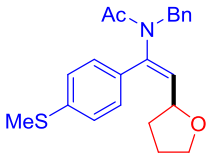
^{1}H NMR (400 MHz, $CDCl_3$)



2f

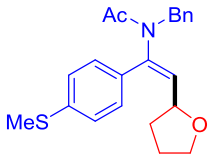
^{13}C NMR (100 MHz, $CDCl_3$)

(*E*)-*N*-benzyl-*N*-(1-(4-(methylthio)phenyl)-2-(tetrahydrofuran-2-yl)vinyl)acetamide (**2g**)



2g

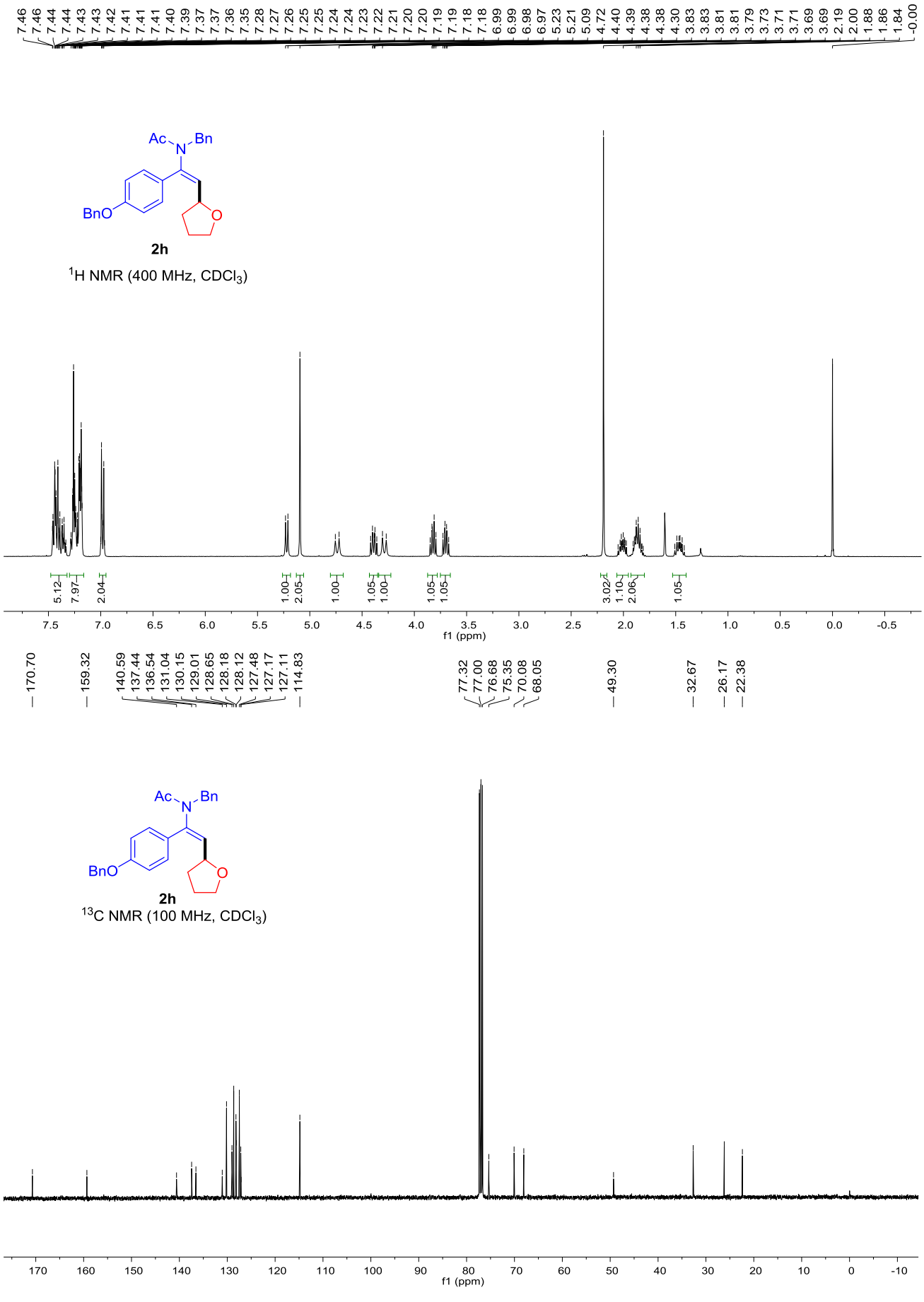
^{1}H NMR (400 MHz, $CDCl_3$)



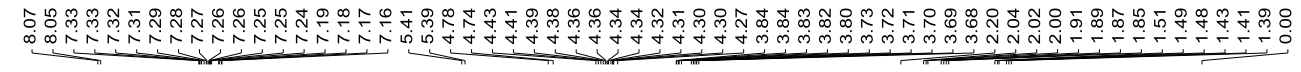
2g

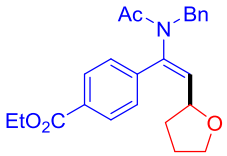
^{13}C NMR (100 MHz, $CDCl_3$)

(*E*)-*N*-benzyl-*N*-(1-(4-(benzyloxy)phenyl)-2-(tetrahydrofuran-2-yl)vinyl)acet-amide (**2h**)



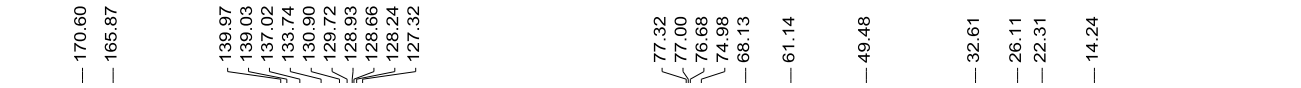
Ethyl (*E*)-4-(1-(*N*-benzylacetamido)-2-(tetrahydrofuran-2-yl)vinyl)benzoate (**2i**)

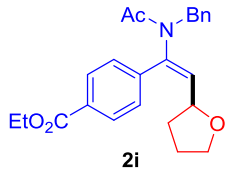




2i

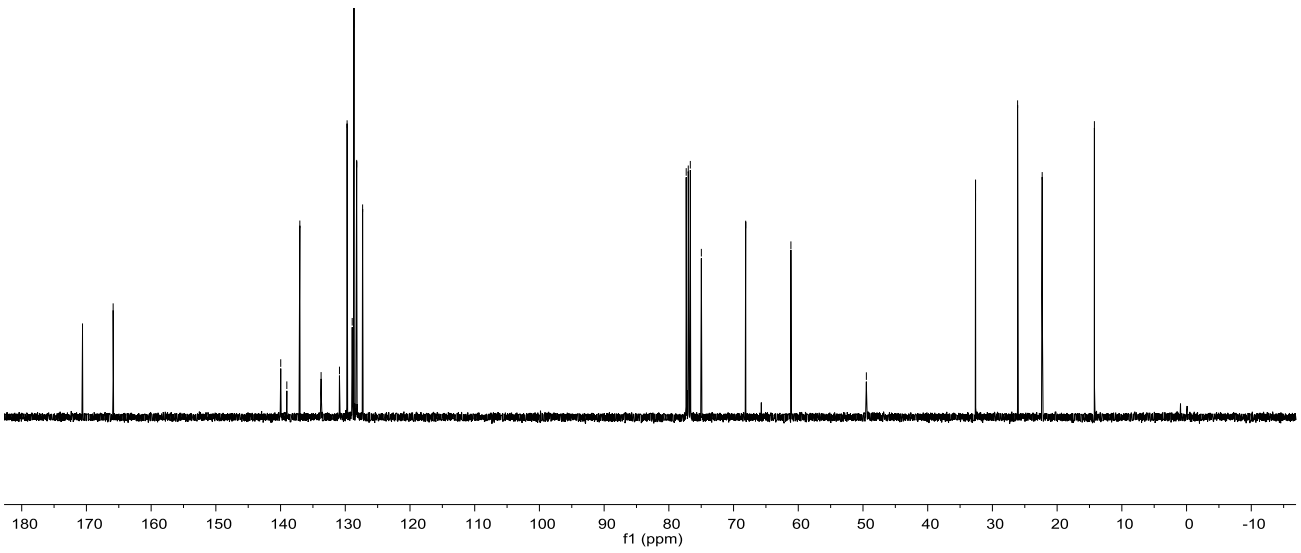
^{1}H NMR (400 MHz, $CDCl_3$)



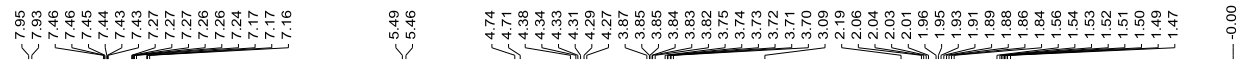


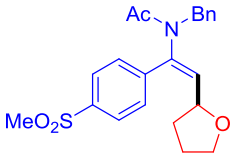
2i

^{13}C NMR (100 MHz, $CDCl_3$)



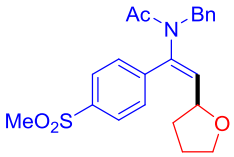
(*E*)-*N*-benzyl-*N*-(1-(4-(methylsulfonyl)phenyl)-2-(tetrahydrofuran-2-yl)vinyl)acetamide (**2j**)





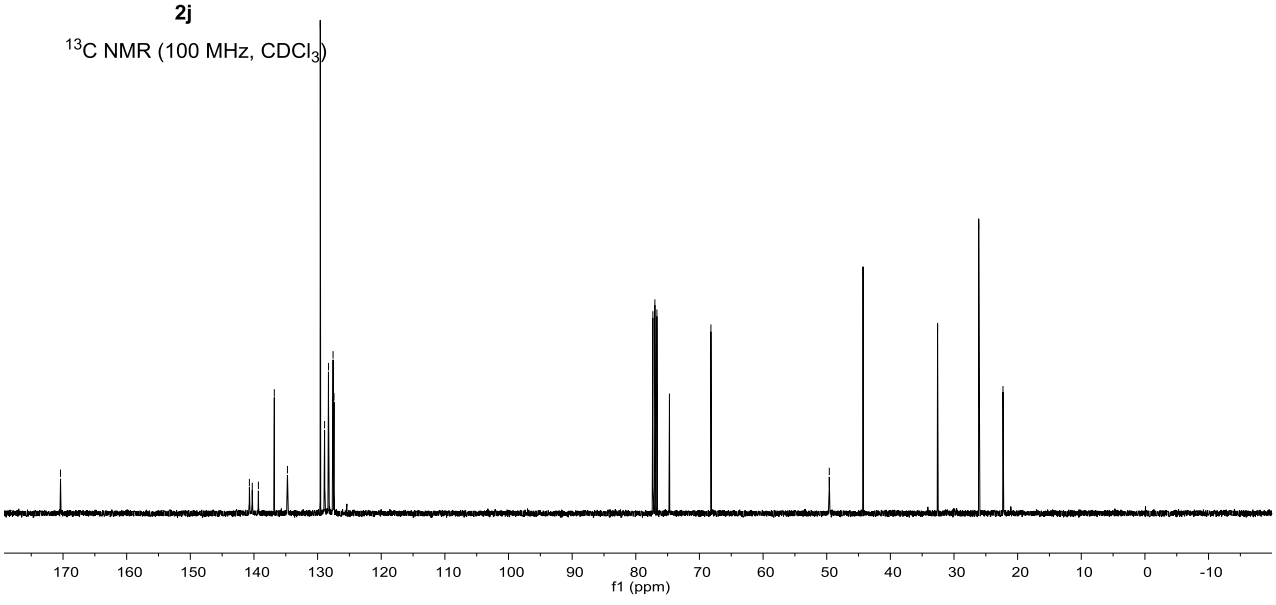
2j

^{1}H NMR (400 MHz, $CDCl_3$)

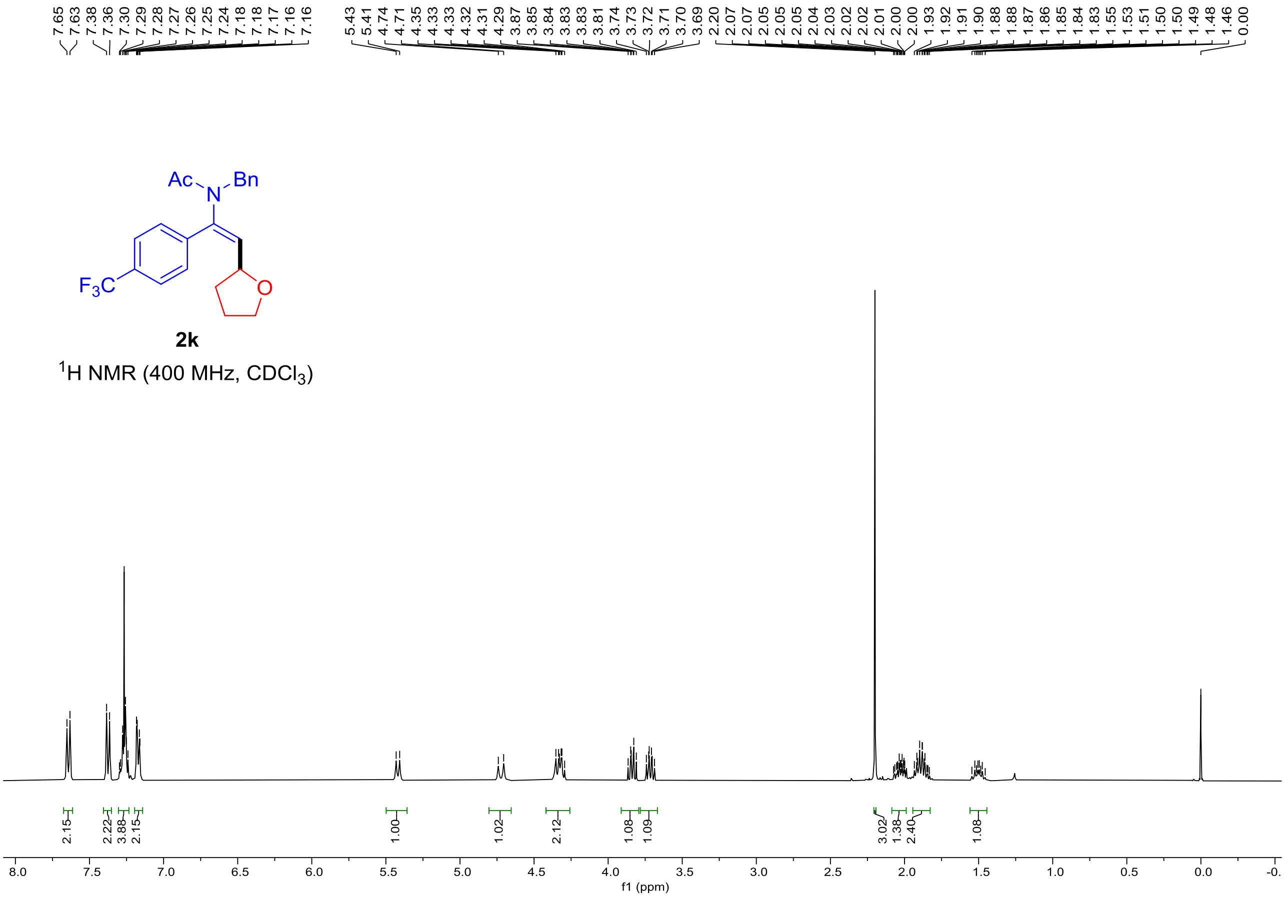


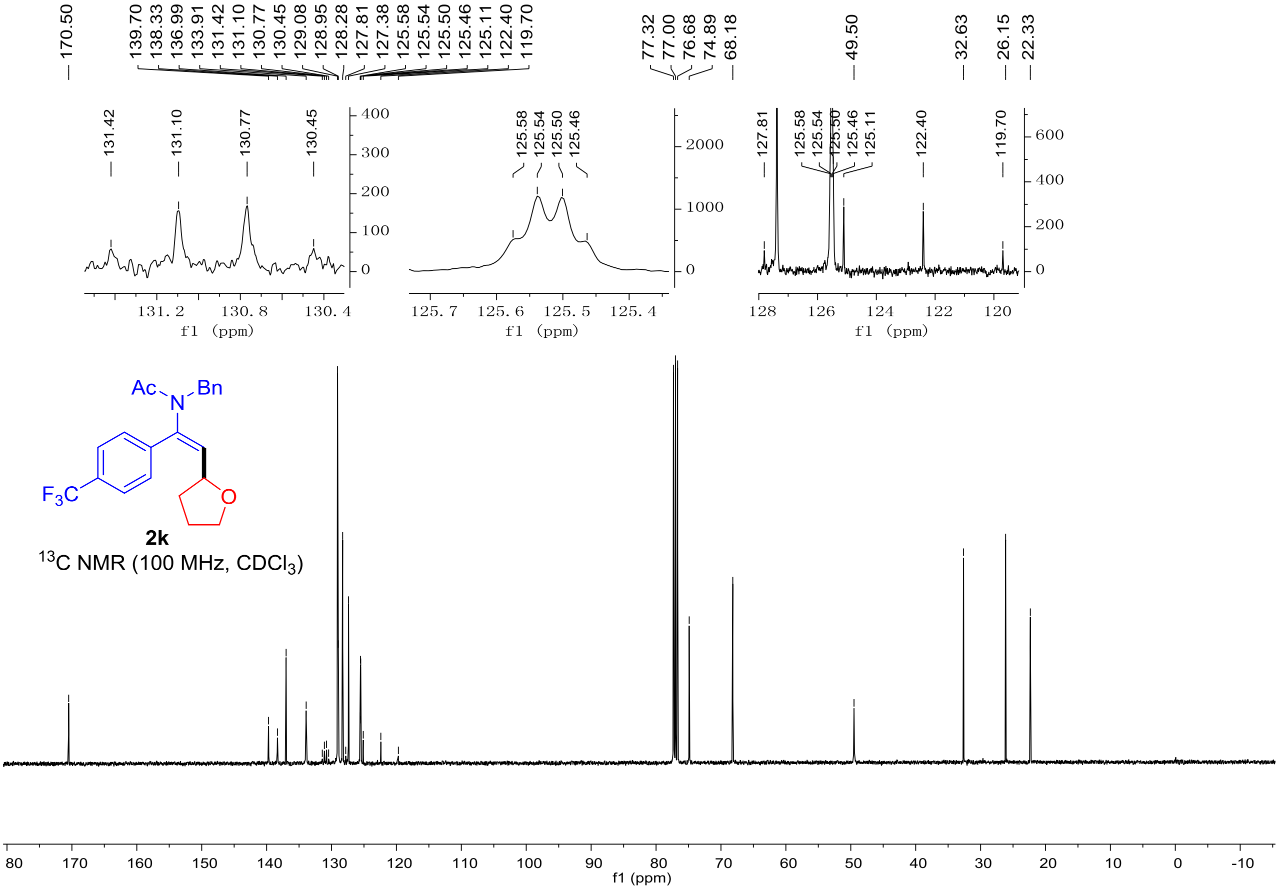
2j

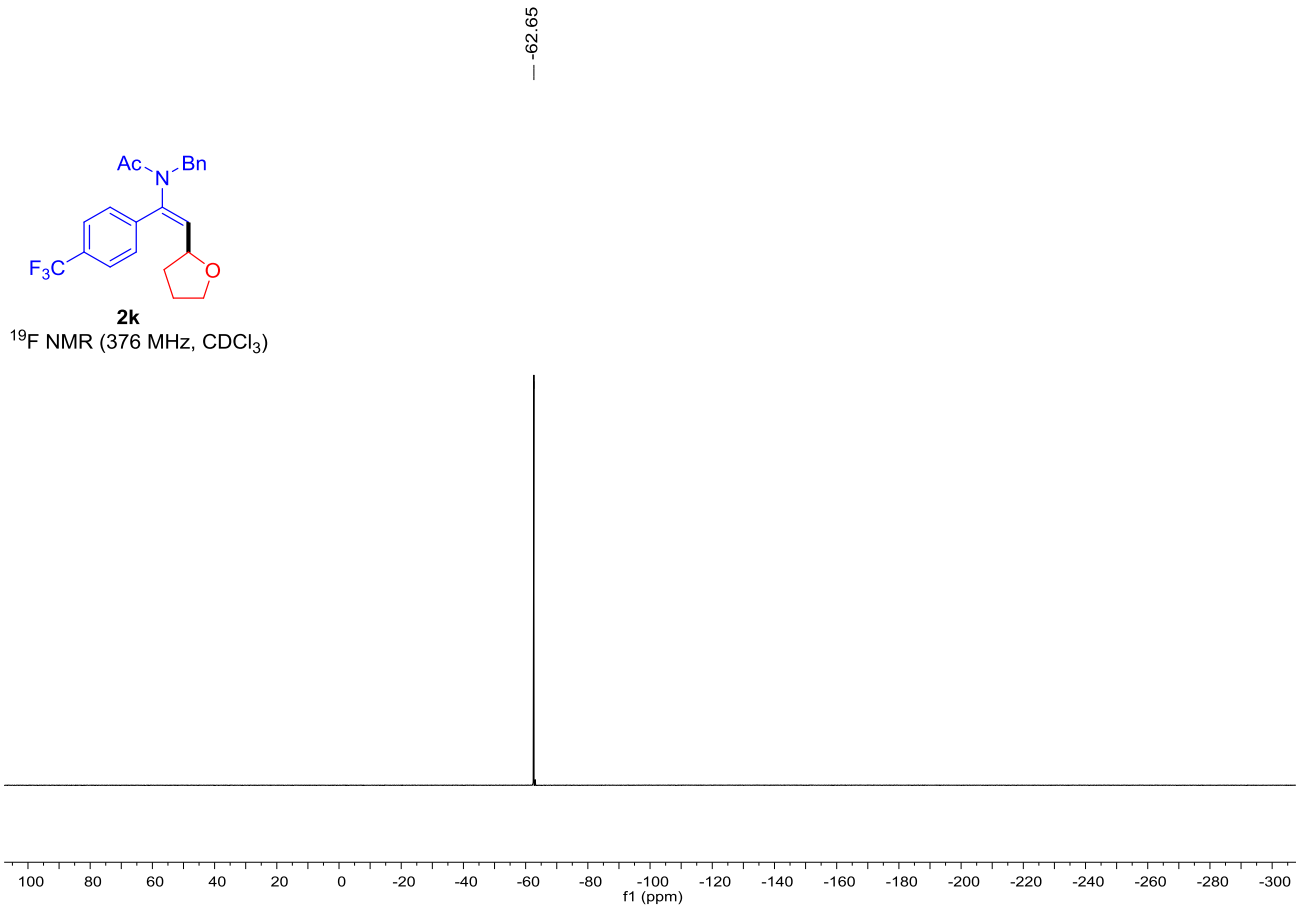
^{13}C NMR (100 MHz, $CDCl_3$)



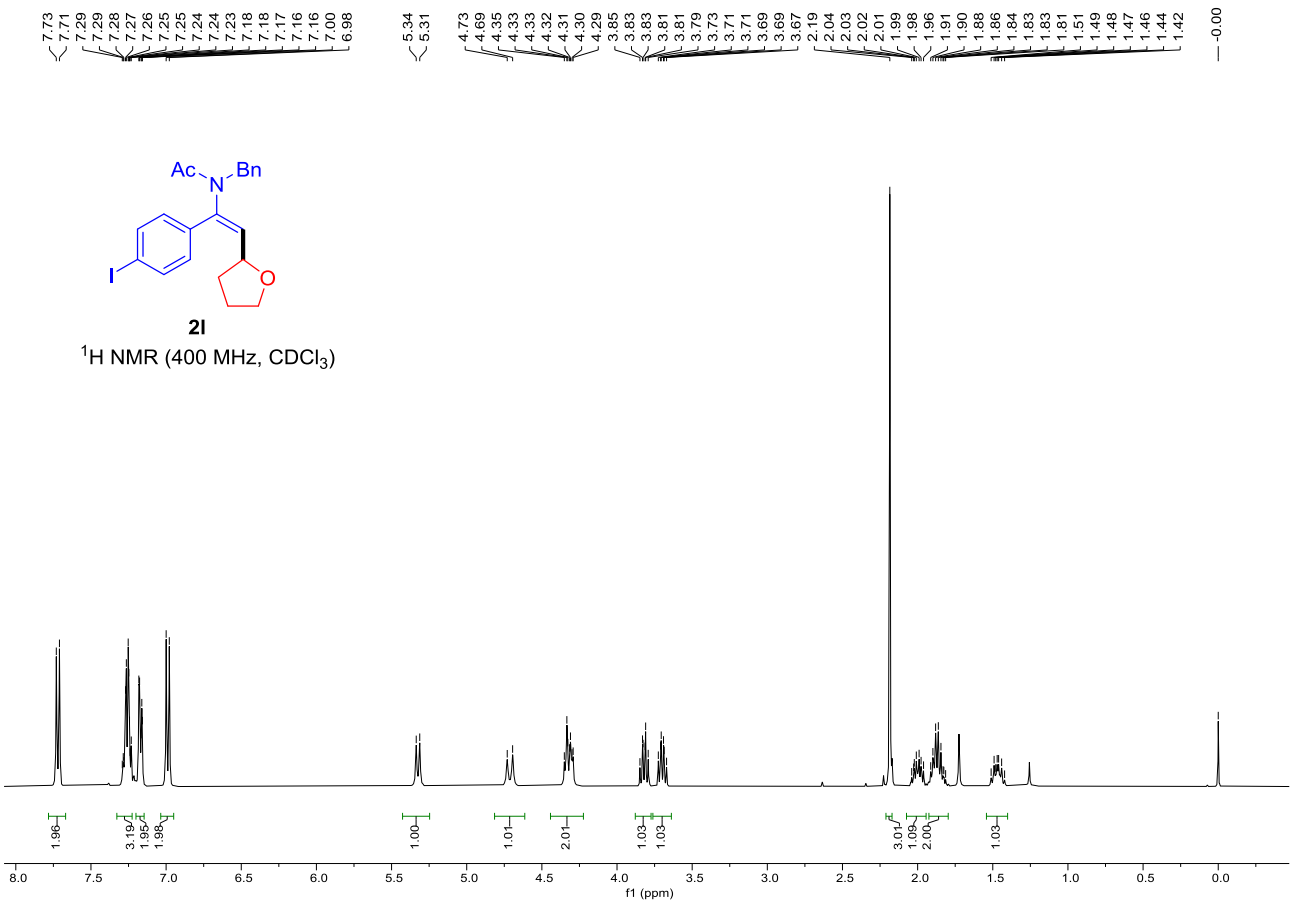
(*E*)-*N*-benzyl-*N*-(2-(tetrahydrofuran-2-yl)-1-(4-(trifluoromethyl)phenyl)vinyl)-acetamide (**2k**)

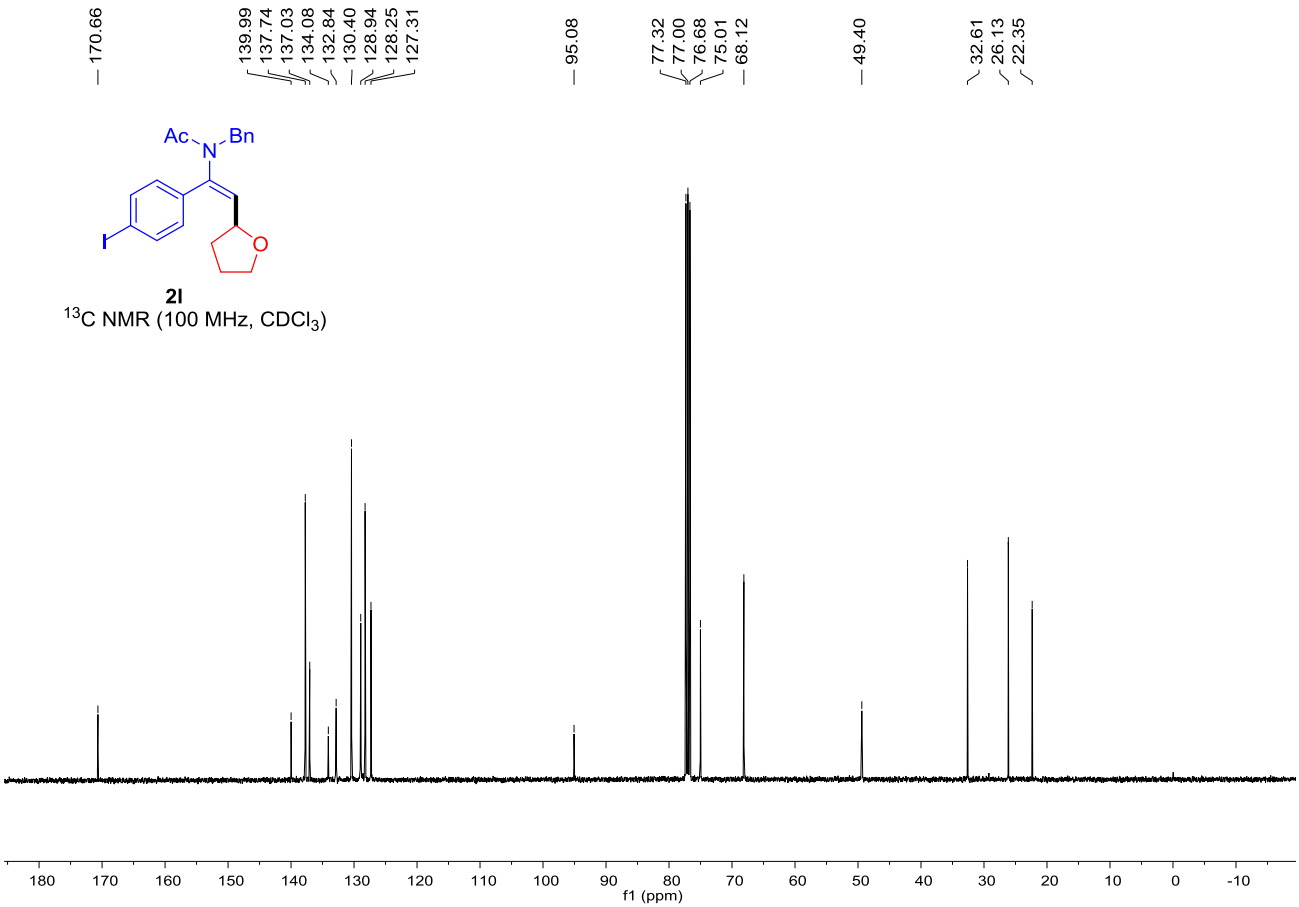






(*E*)-*N*-benzyl-*N*-(1-(4-iodophenyl)-2-(tetrahydrofuran-2-yl)vinyl)acetamide (**2l**)

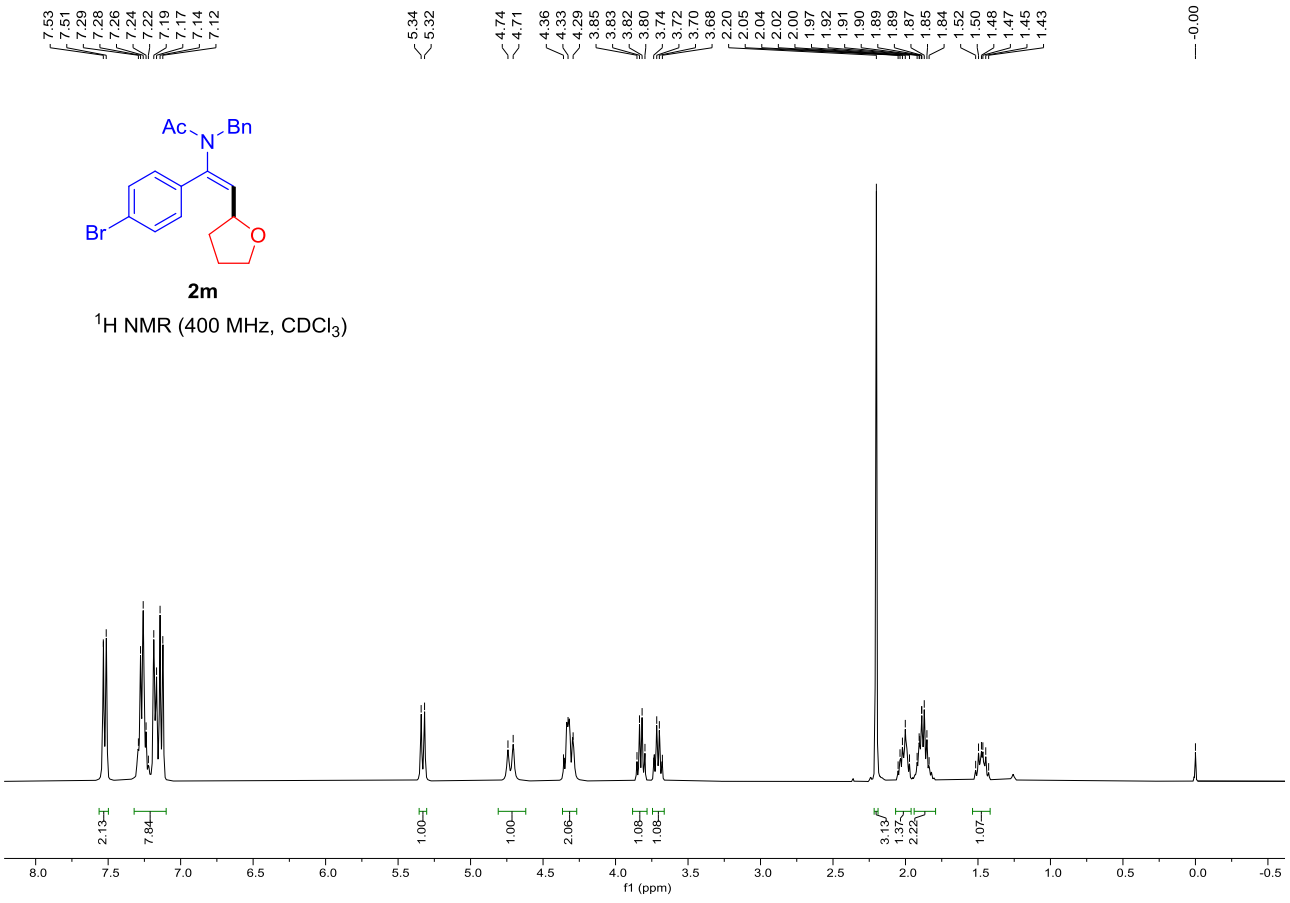




2l

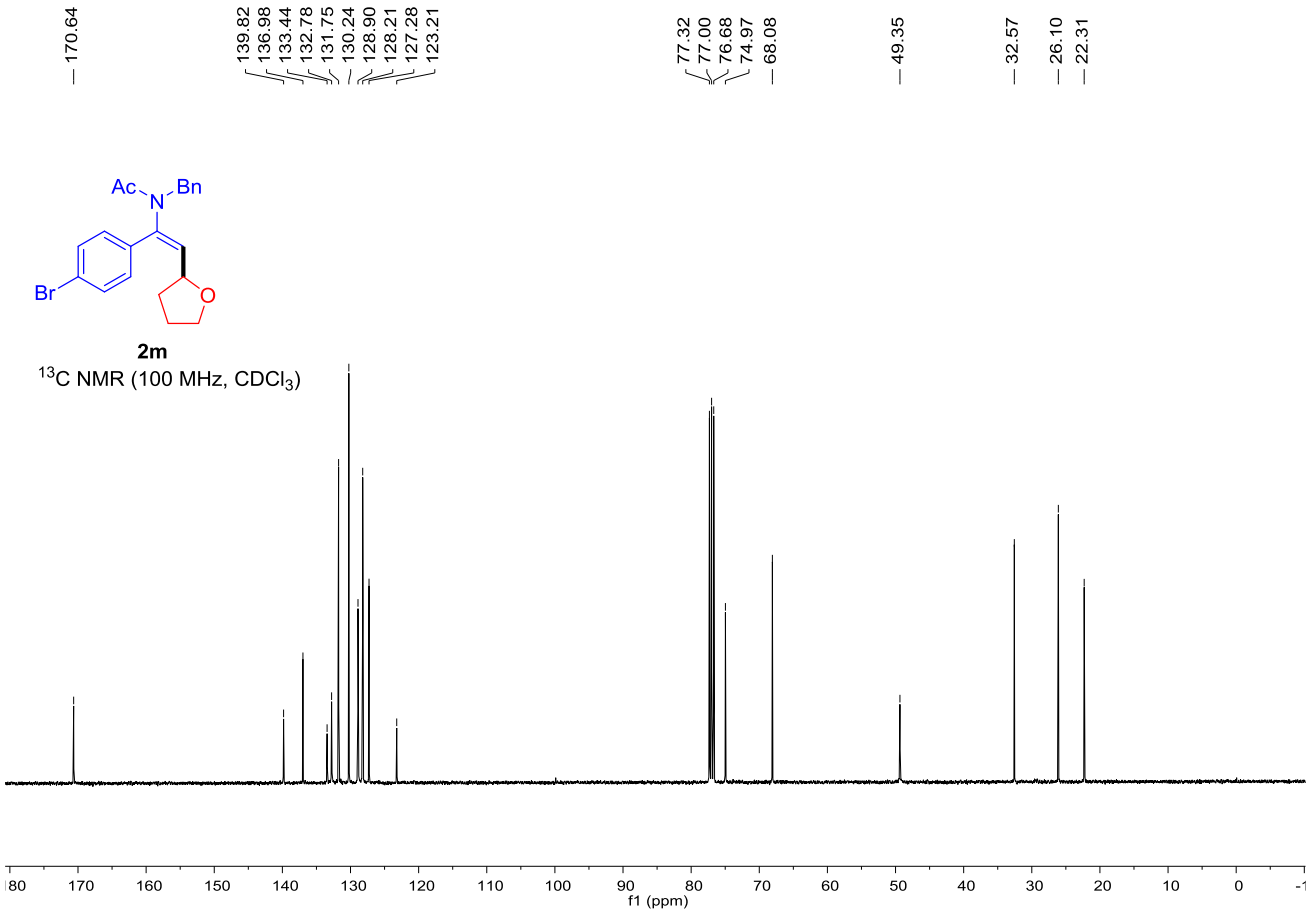
^{13}C NMR (100 MHz, $CDCl_3$)

(*E*)-*N*-benzyl-*N*-(1-(4-bromophenyl)-2-(tetrahydrofuran-2-yl)vinyl)acetamide (**2m**)

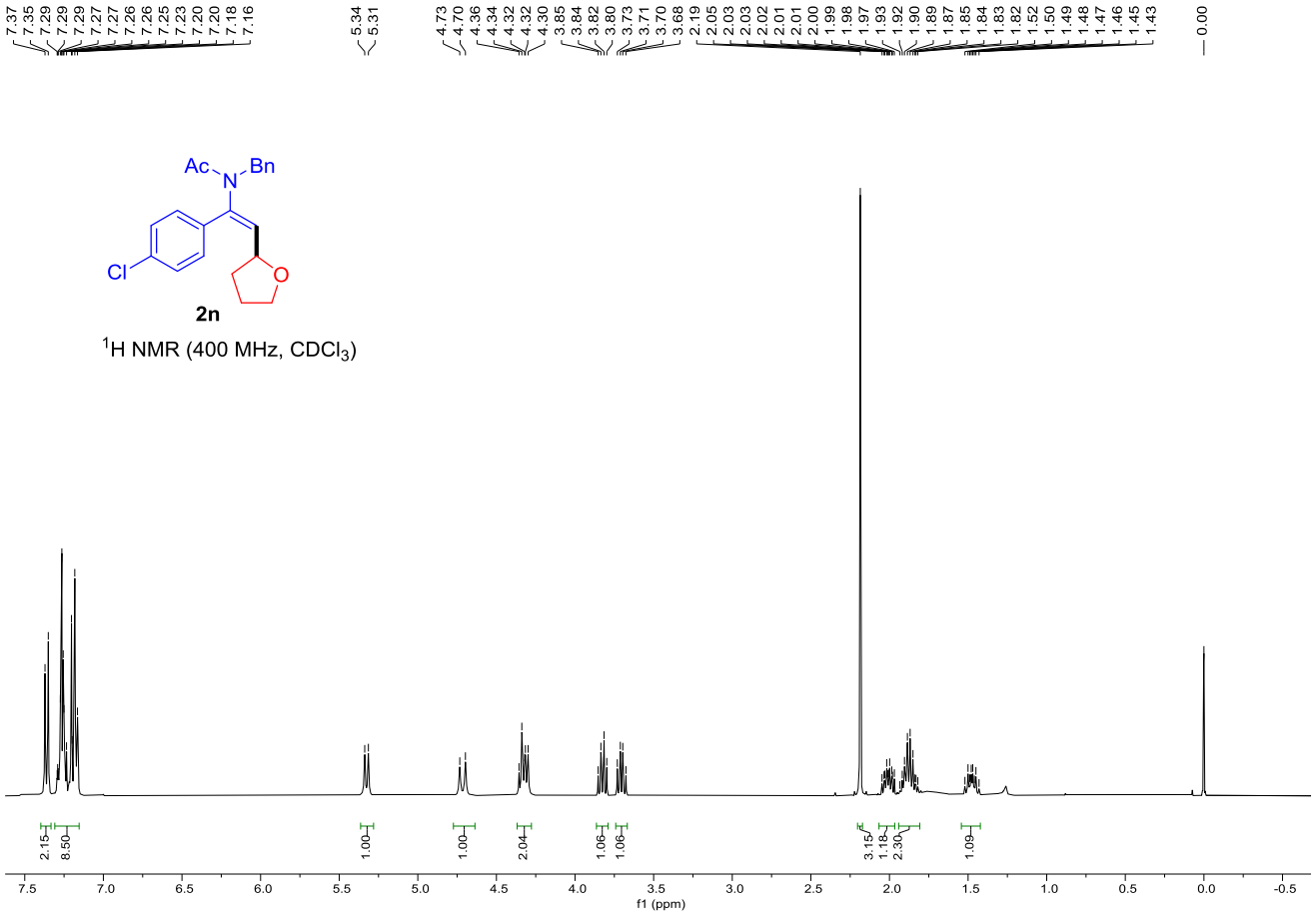


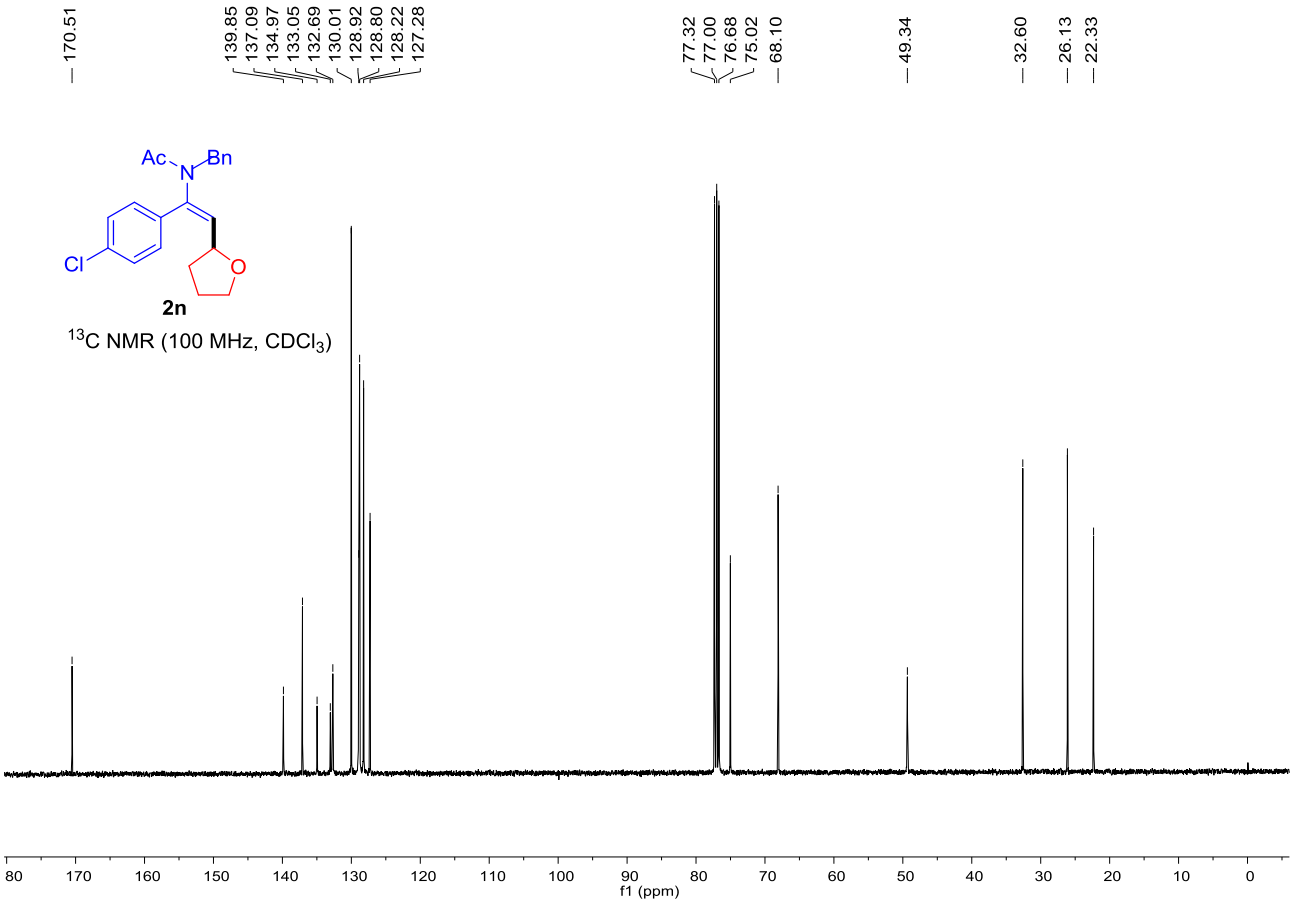
2m

^{1}H NMR (400 MHz, $CDCl_3$)

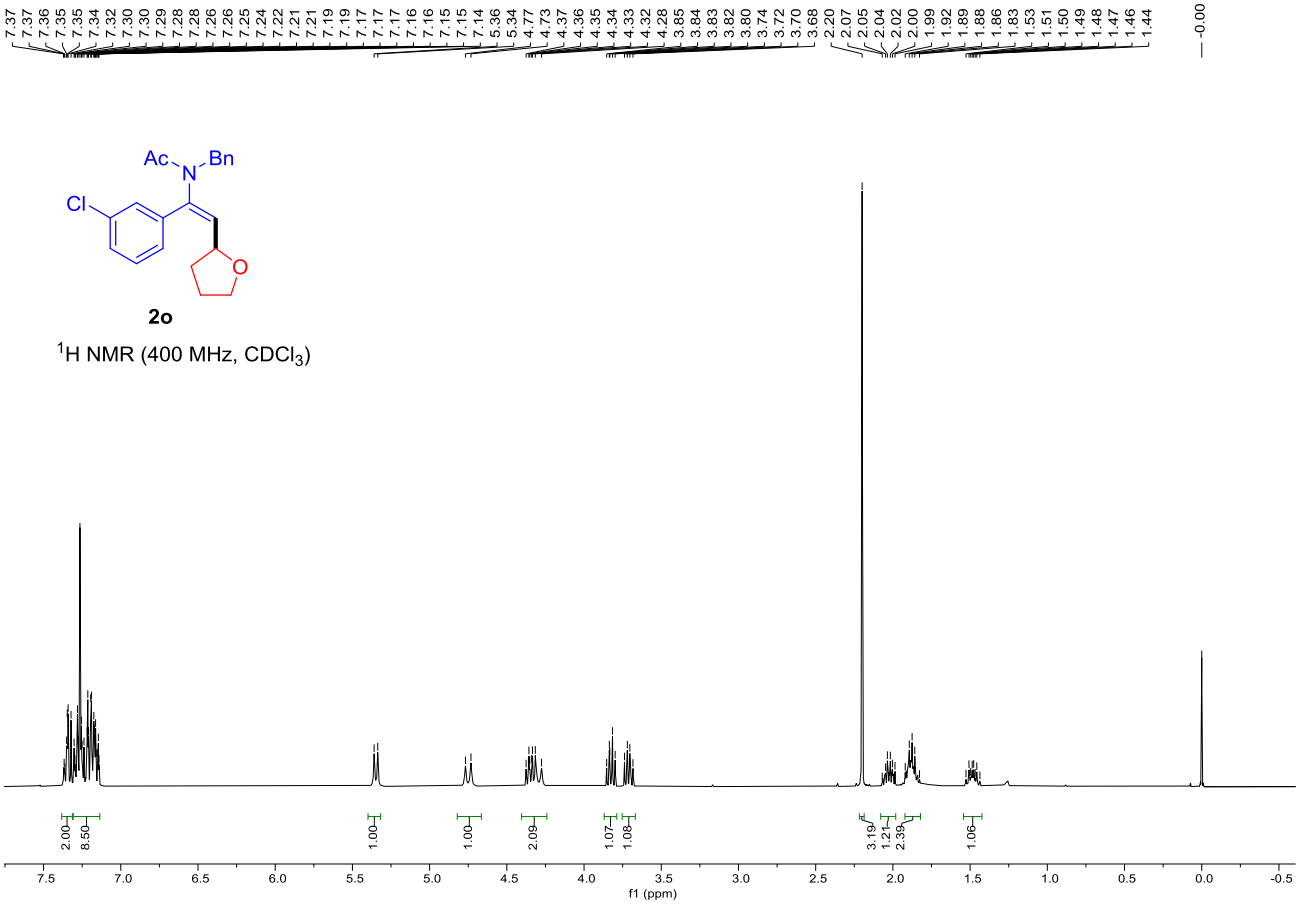


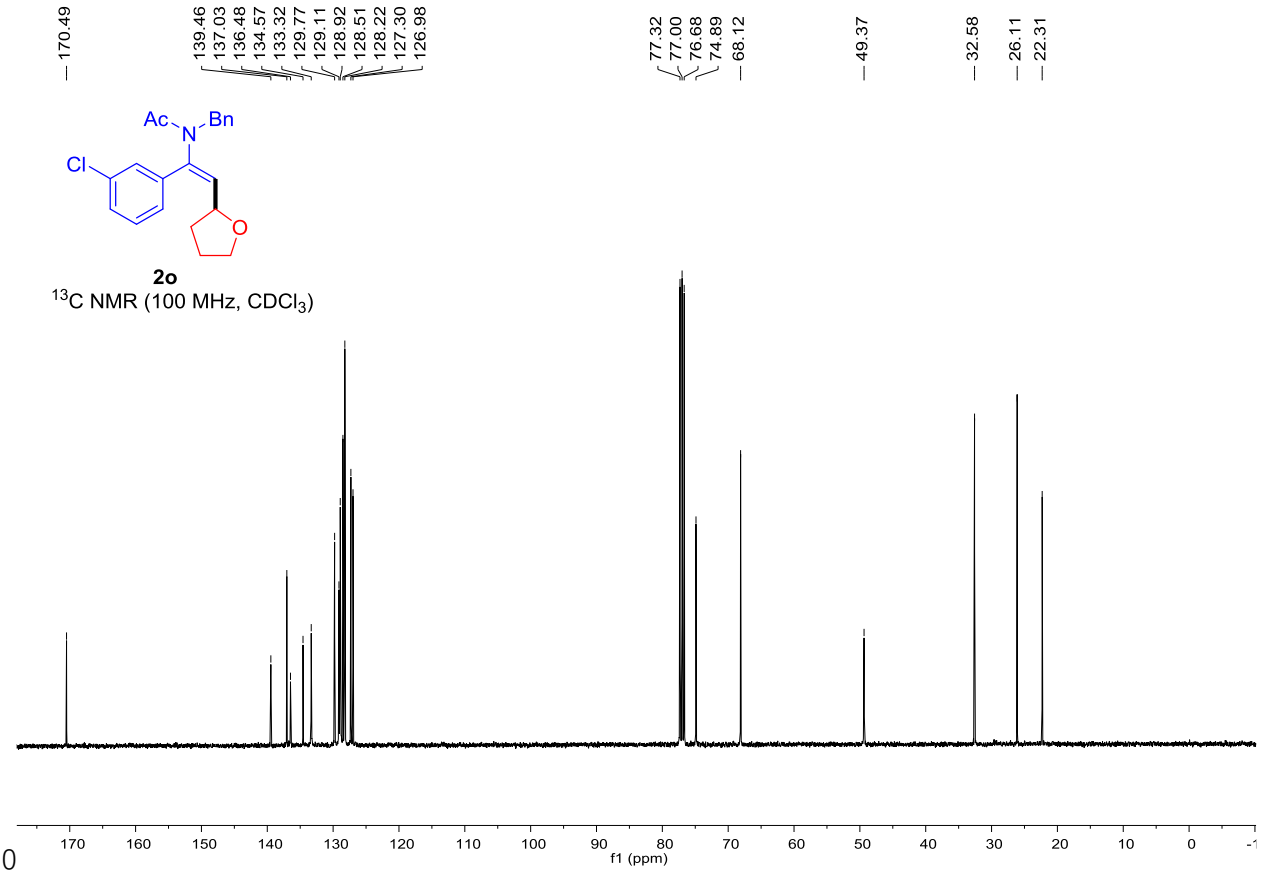
(*E*)-*N*-benzyl-*N*-(1-(4-chlorophenyl)-2-(tetrahydrofuran-2-yl)vinyl)acetamide (**2n**)





(*E*)-*N*-benzyl-*N*-(1-(3-chlorophenyl)-2-(tetrahydrofuran-2-yl)vinyl)acetamide (**2o**)



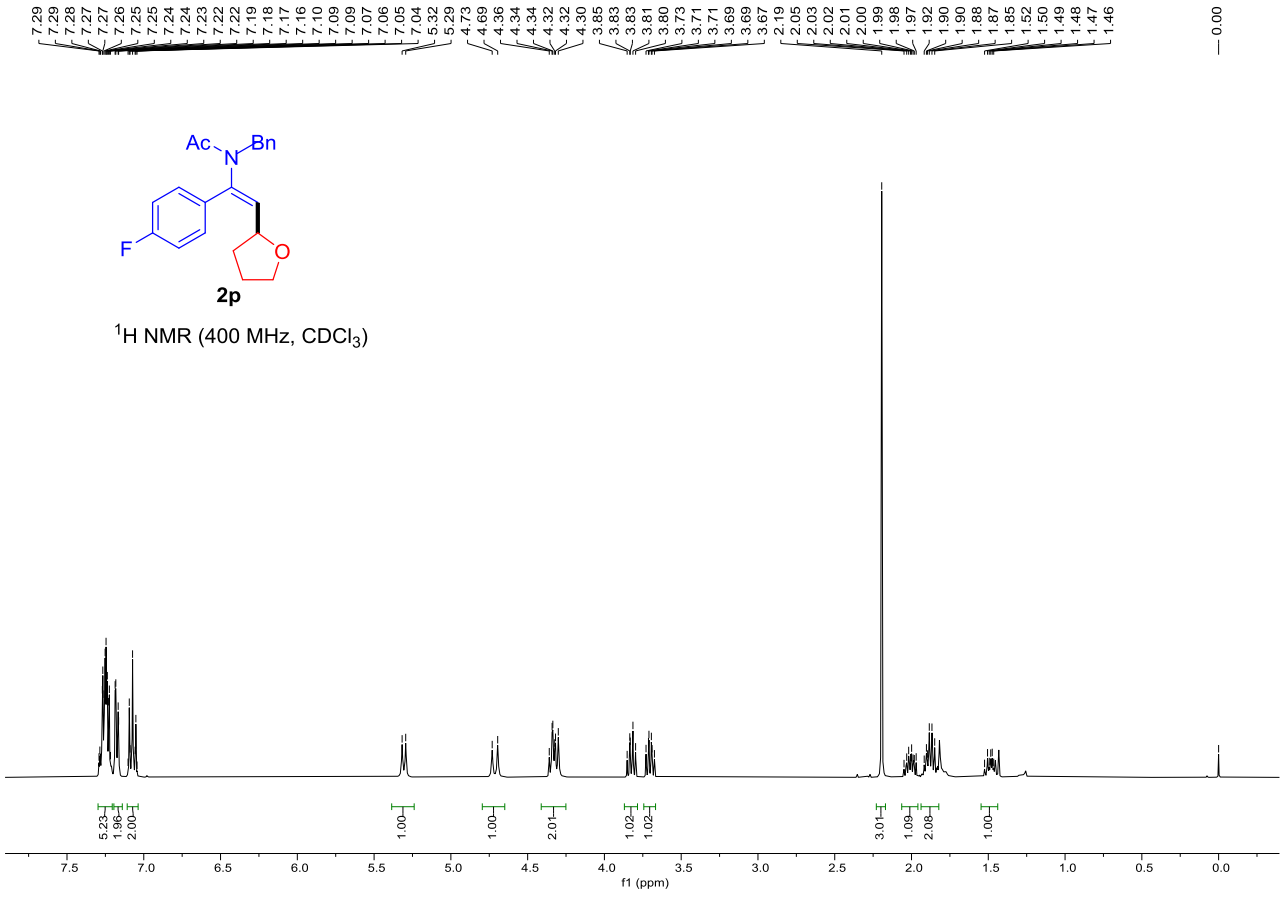


2o

^{13}C NMR (100 MHz, $CDCl_3$)

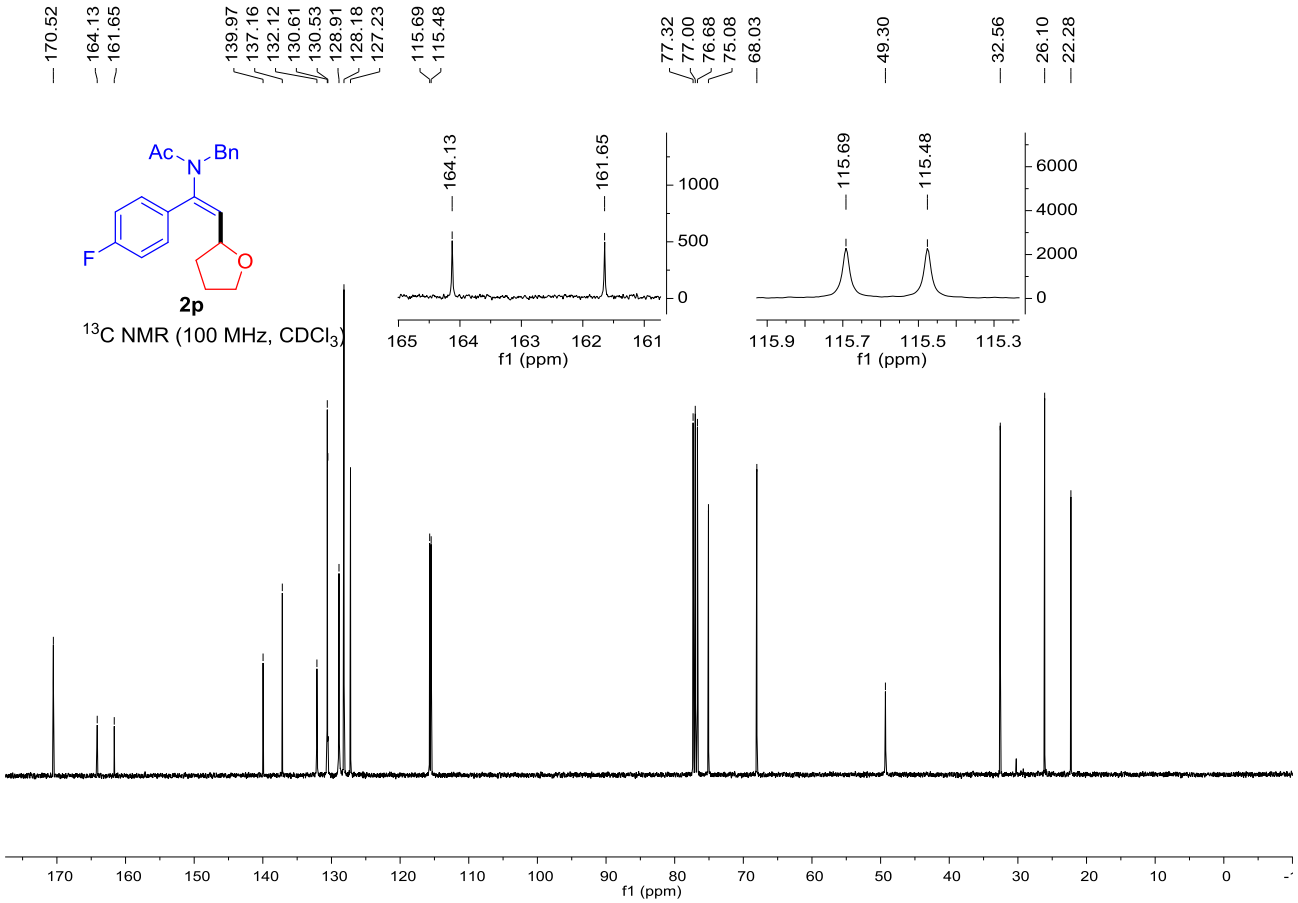
90

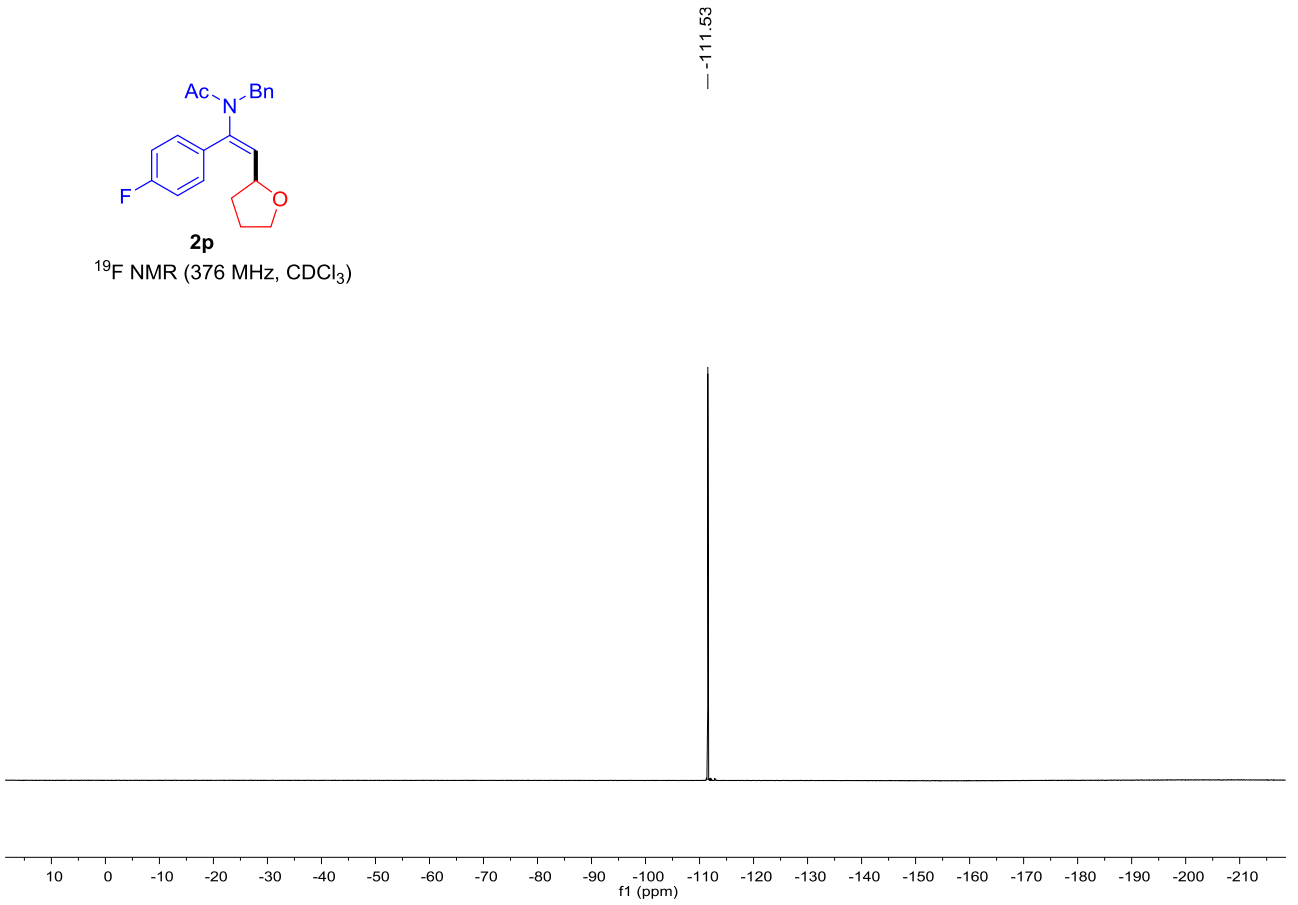
(*E*)-*N*-benzyl-*N*-(1-(4-fluorophenyl)-2-(tetrahydrofuran-2-yl)vinyl)acetamide (**2p**)



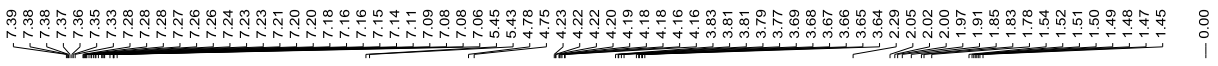
2p

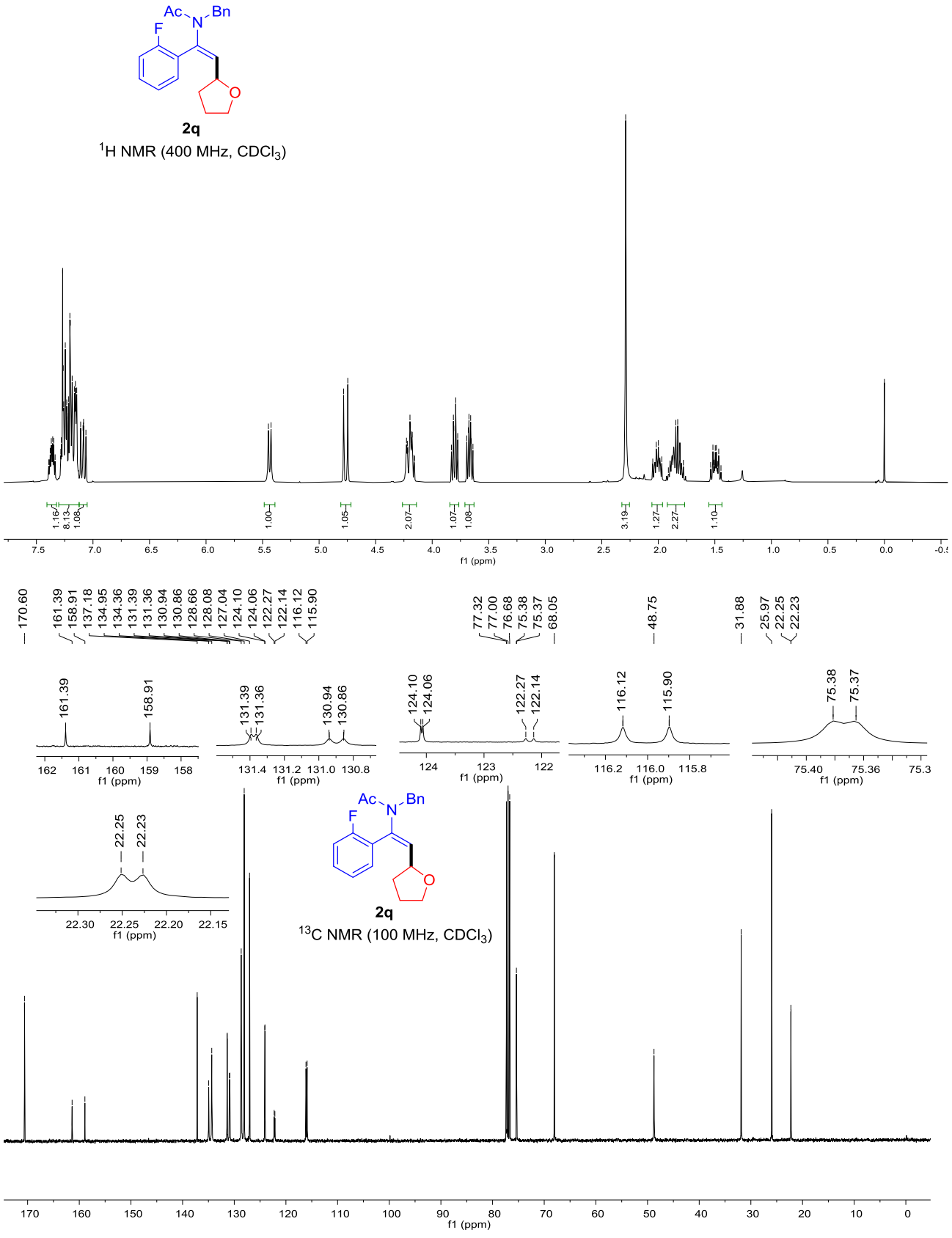
^{1}H NMR (400 MHz, $CDCl_3$)

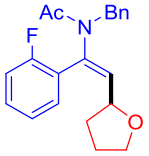

170.52
164.13
161.65
139.97
137.16
132.12
130.61
130.53
128.91
128.18
127.23
115.69
115.48
77.32
77.00
76.68
75.08
68.03
49.30
32.56
26.10
22.28
Ac
N
Bn
F
O
2p
13C NMR (100 MHz, CDCl3)
f1 (ppm)


-111.53
Ac
N
Bn
F
O
2p
19F NMR (376 MHz, CDCl3)
f1 (ppm)

(*E*)-*N*-benzyl-*N*-(1-(2-fluorophenyl)-2-(tetrahydrofuran-2-yl)vinyl)acetamide (**2q**)



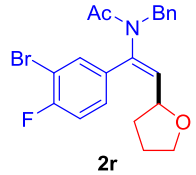




2q

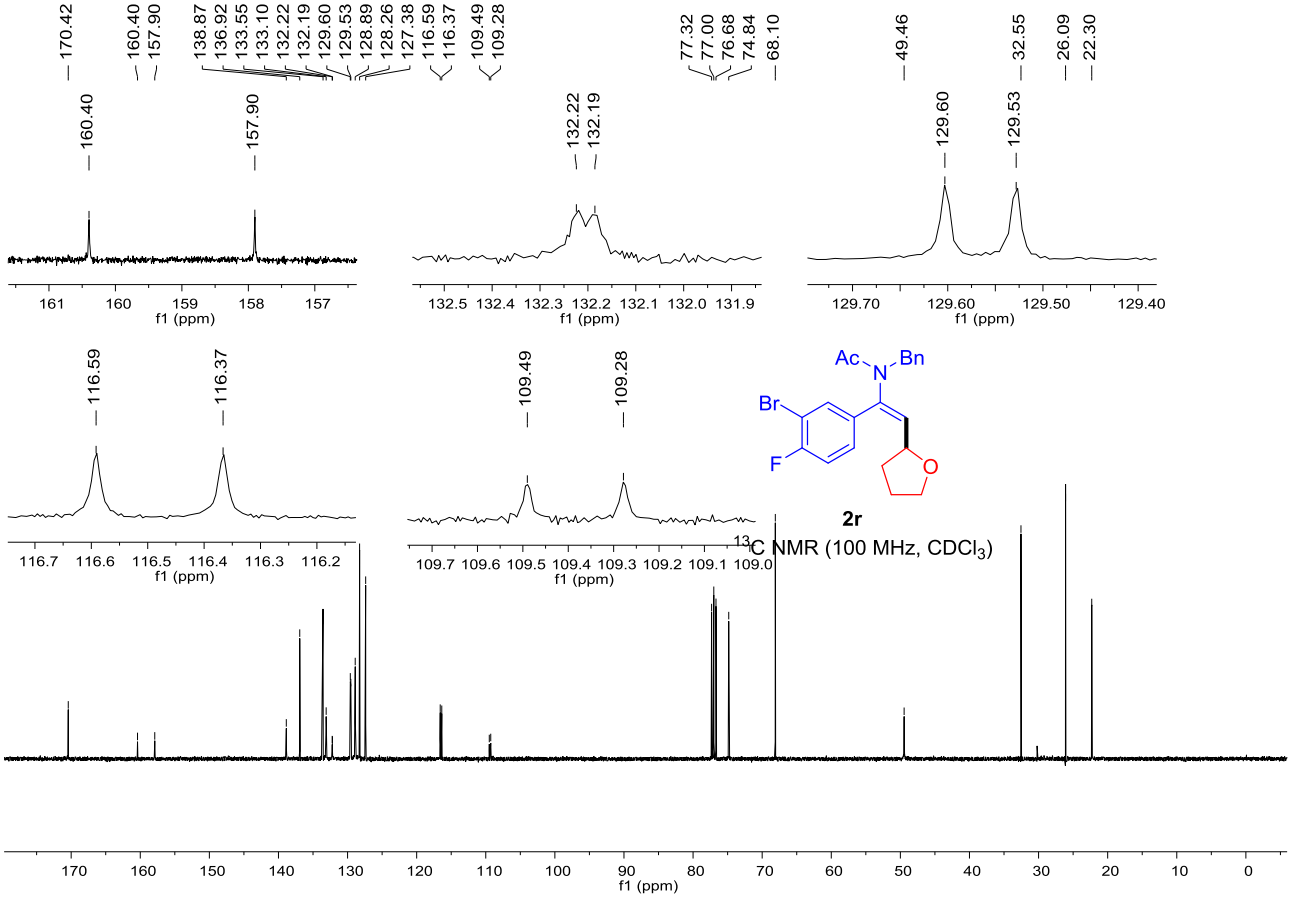
^{19}F NMR (376 MHz, $CDCl_3$)

(*E*)-*N*-benzyl-*N*-(1-(3-bromo-4-fluorophenyl)-2-(tetrahydrofuran-2-yl)vinyl)acetamide (**2r**)



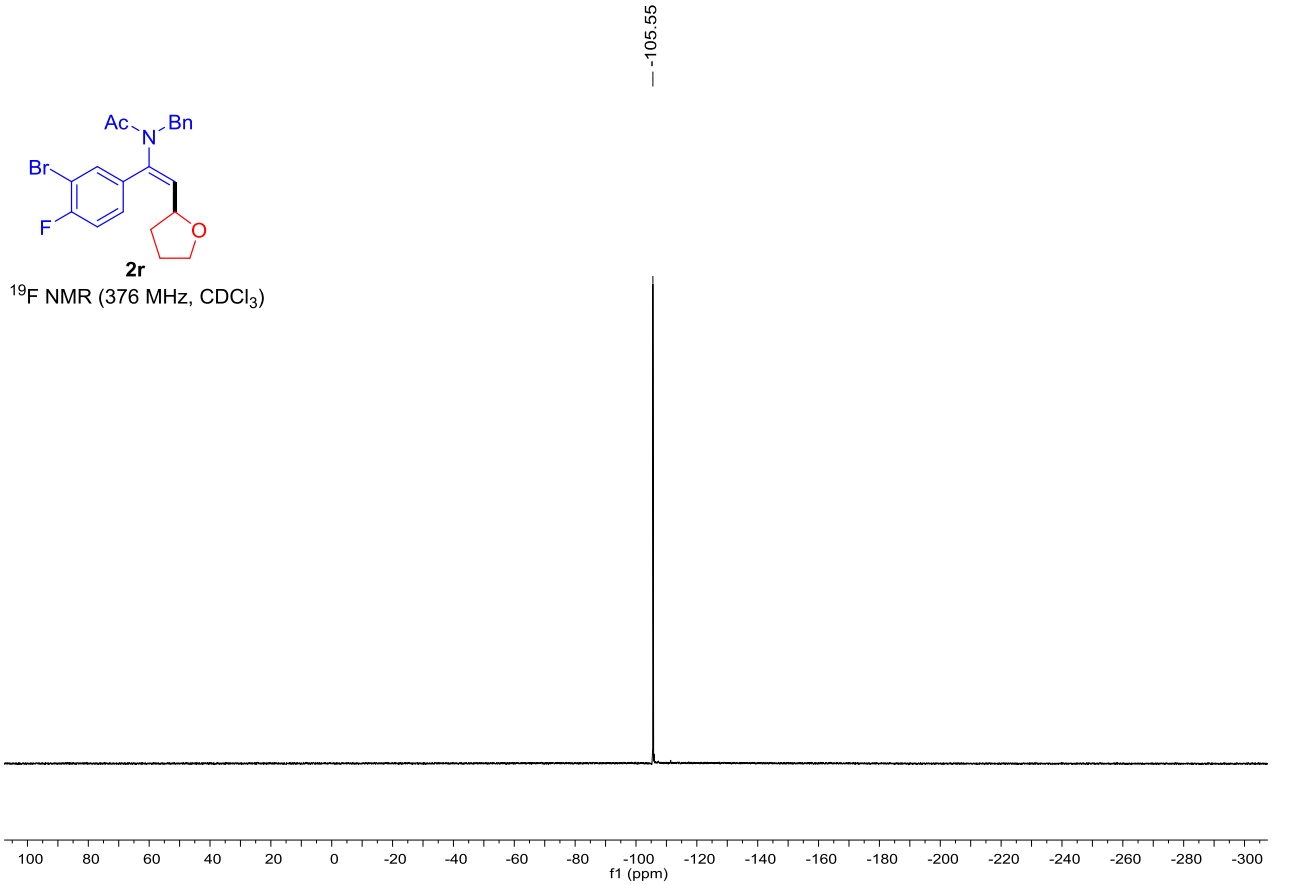
2r

^{1}H NMR (400 MHz, $CDCl_3$)



2r

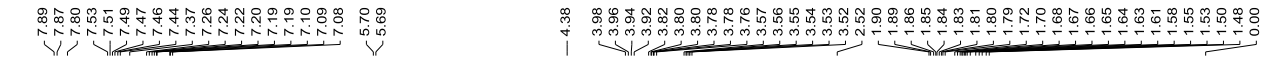
^{13}C NMR (100 MHz, $CDCl_3$)

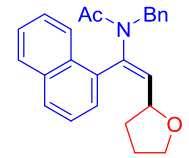


2r

^{19}F NMR (376 MHz, $CDCl_3$)

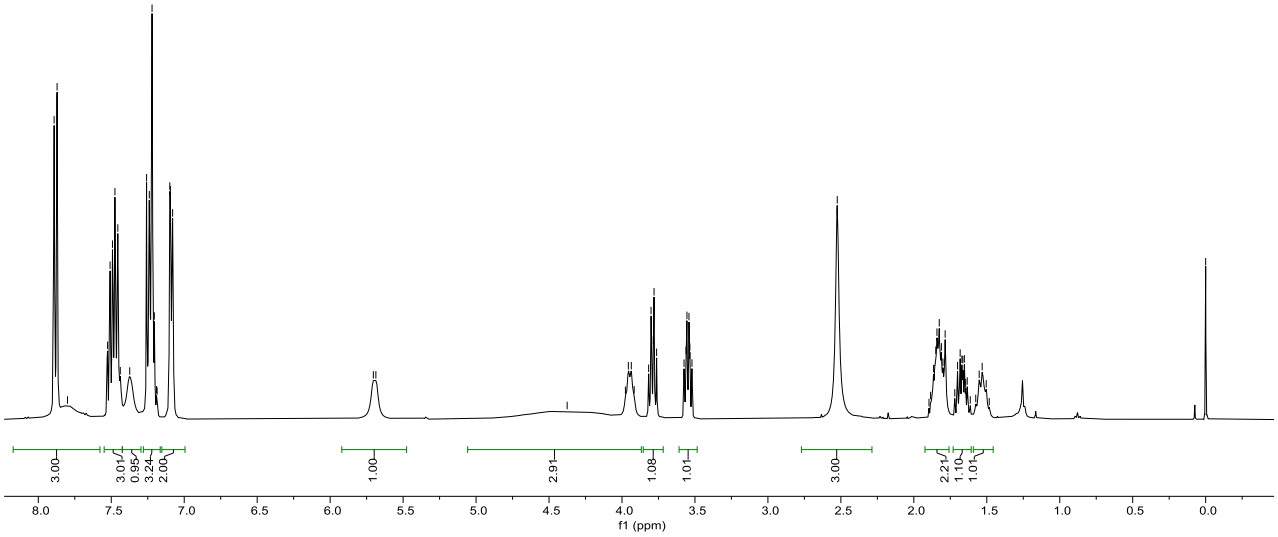
(*E*)-*N*-benzyl-*N*-(1-(naphthalen-1-yl)-2-(tetrahydrofuran-2-yl)vinyl)acetamide (**2s**)

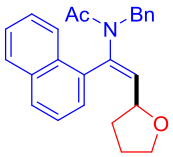




2s

^{1}H NMR (400 MHz, $CDCl_3$)

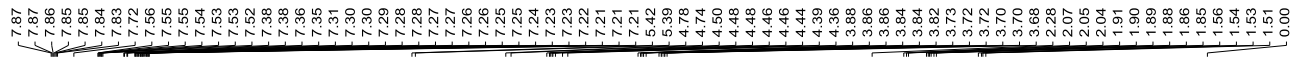


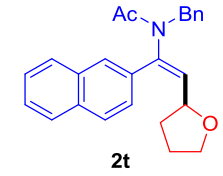


2s

^{13}C NMR (100 MHz, $CDCl_3$)

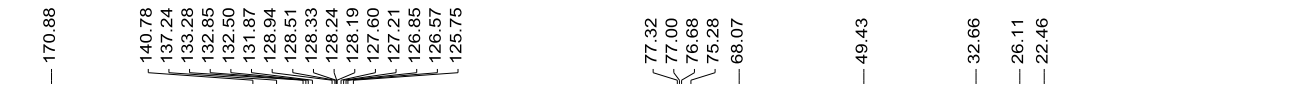
(*E*)-*N*-benzyl-*N*-(2-(naphthalen-1-yl)-2-(tetrahydrofuran-2-yl)vinyl)acetamide (**2t**)

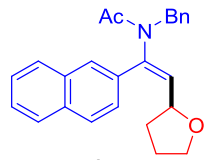




2t

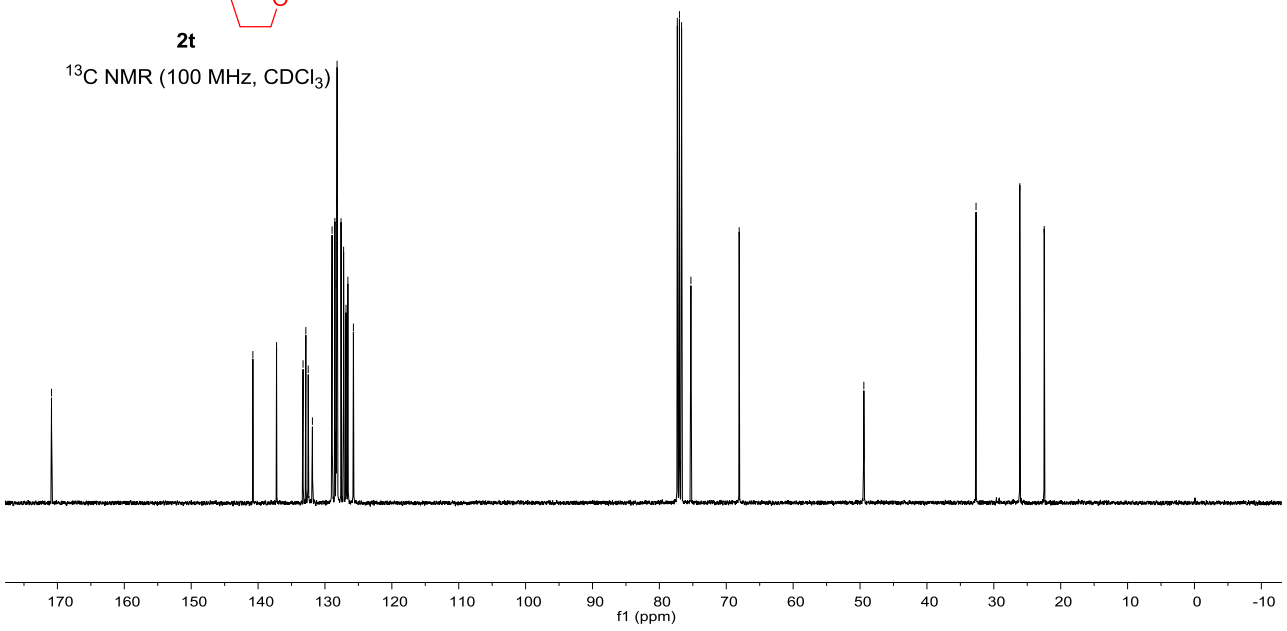
^{1}H NMR (400 MHz, $CDCl_3$)



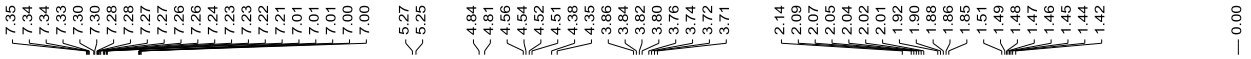


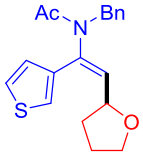
2t

^{13}C NMR (100 MHz, $CDCl_3$)



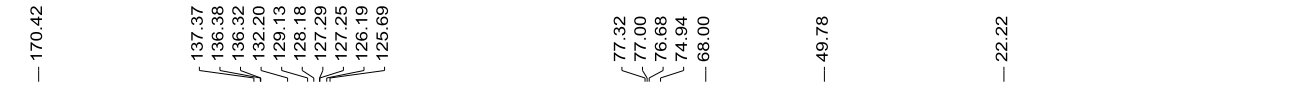
(*E*)-*N*-benzyl-*N*-(2-(tetrahydrofuran-2-yl)-1-(thiophen-3-yl)vinyl)acetamide (**2u**)

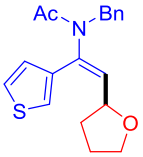




2u

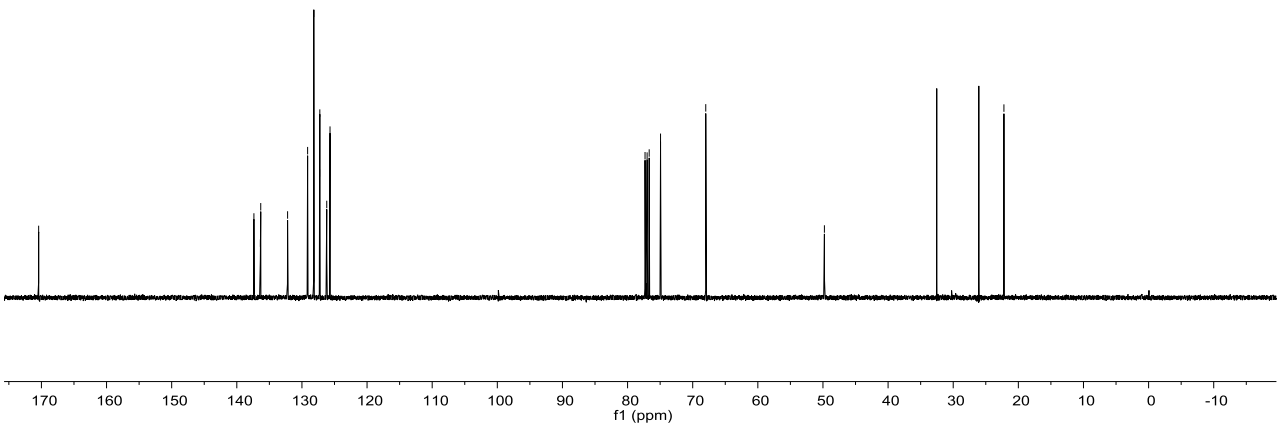
^{1}H NMR (400 MHz, $CDCl_3$)



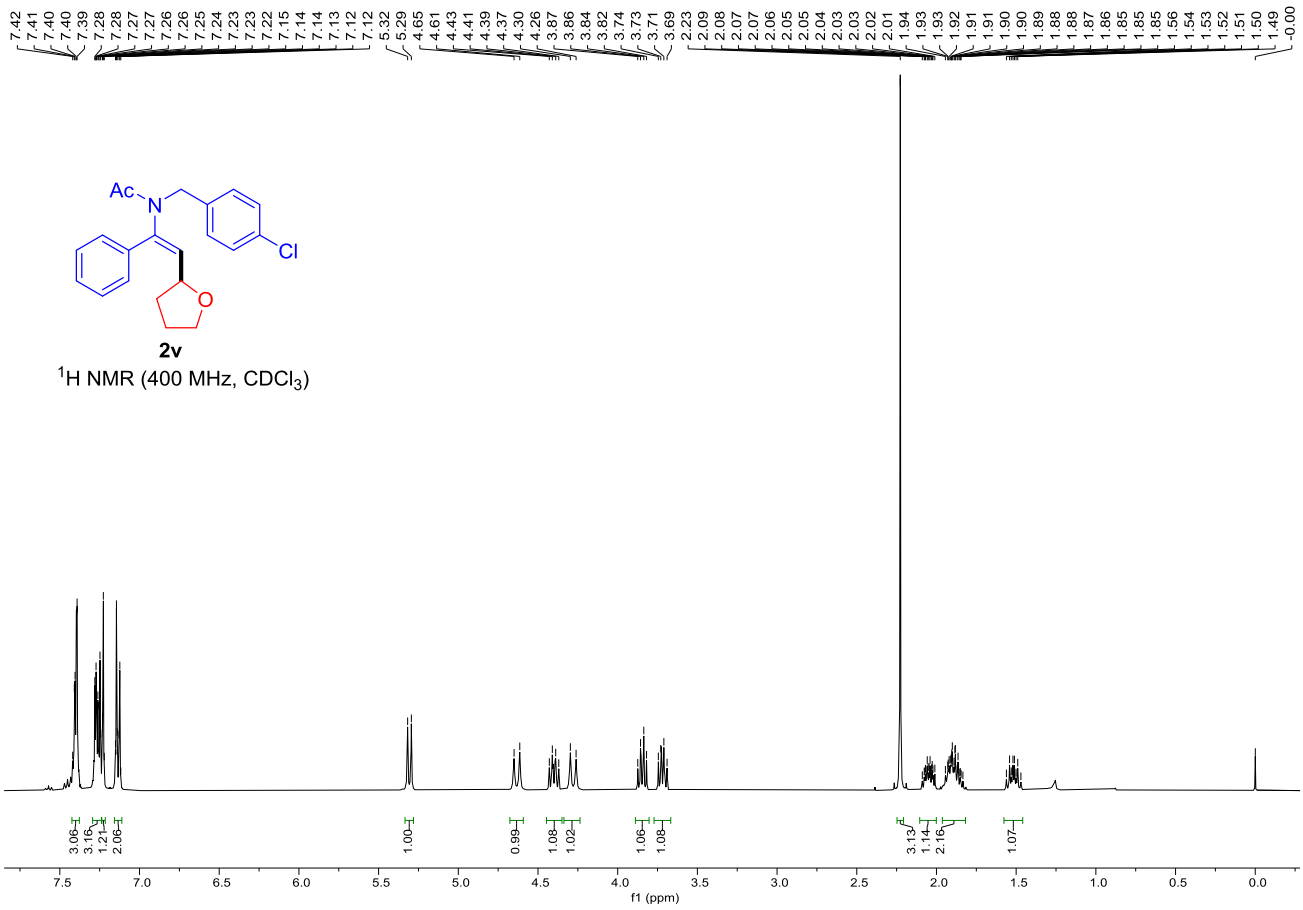


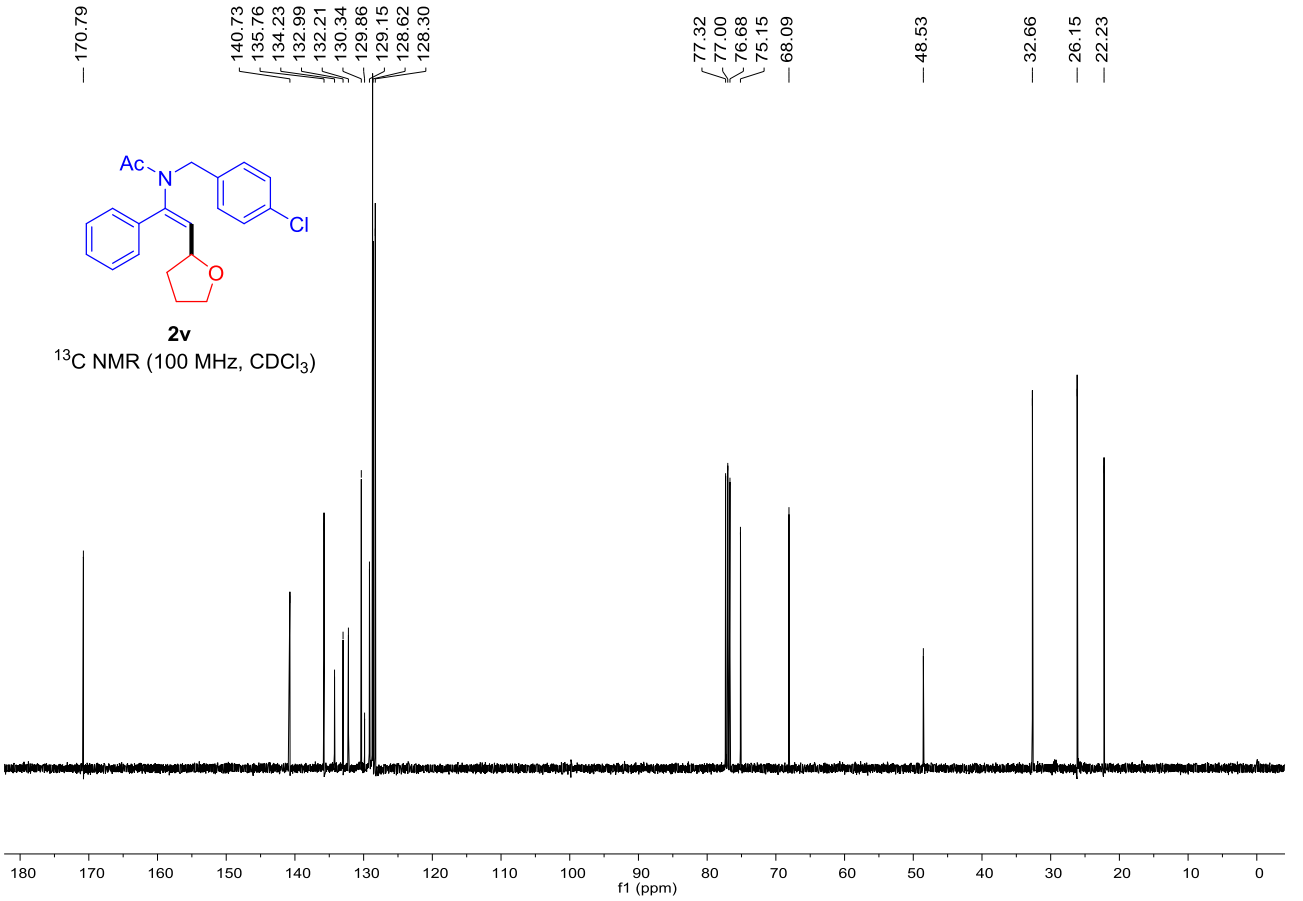
2u

^{13}C NMR (100 MHz, $CDCl_3$)

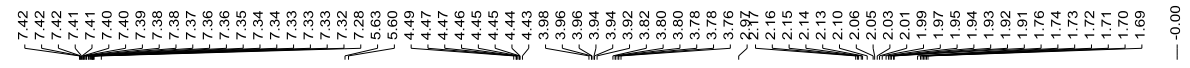


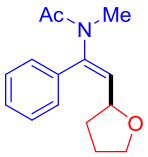
(*E*)-*N*-(4-chlorobenzyl)-*N*-(1-phenyl-2-(tetrahydrofuran-2-yl)vinyl)acetamide (**2v**)





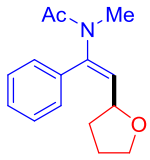
(*E*)-*N*-methyl-*N*-(1-phenyl-2-(tetrahydrofuran-2-yl)vinyl)acetamide (**2w**)





2w

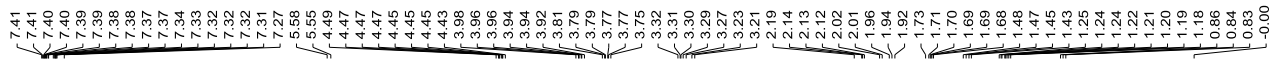
^{1}H NMR (400 MHz, $CDCl_3$)

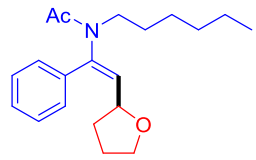


2w

^{13}C NMR (100 MHz, $CDCl_3$)

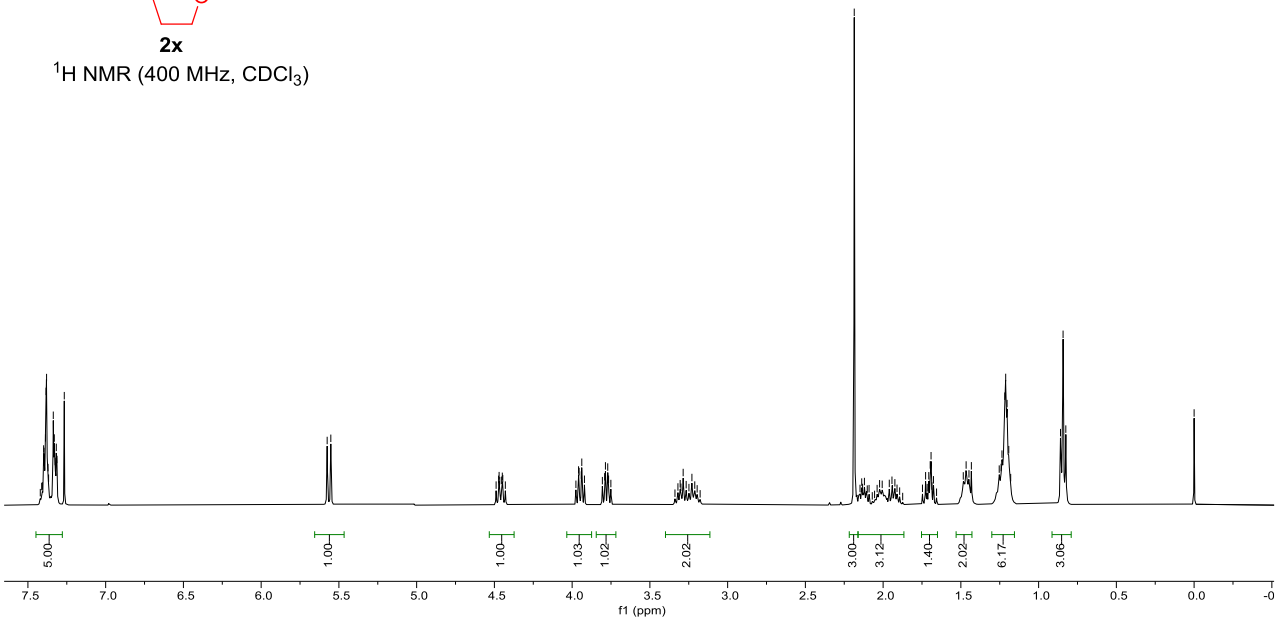
(*E*)-*N*-hexyl-*N*-(1-phenyl-2-(tetrahydrofuran-2-yl)vinyl)acetamide (**2x**)

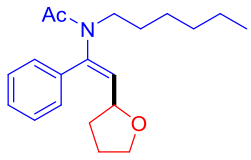




2x

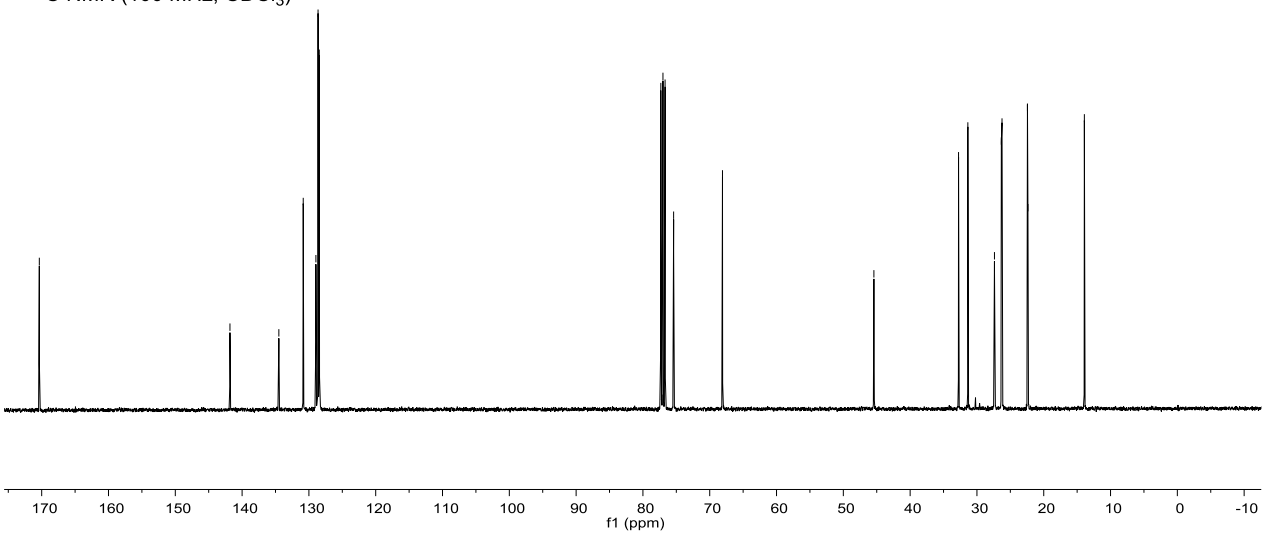
^{1}H NMR (400 MHz, $CDCl_3$)



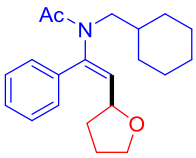


2x

^{13}C NMR (100 MHz, $CDCl_3$)

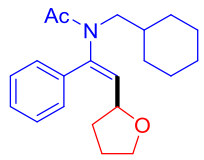


(*E*)-*N*-(cyclohexylmethyl)-*N*-(1-phenyl-2-(tetrahydrofuran-2-yl)vinyl)acetamide (**2y**)



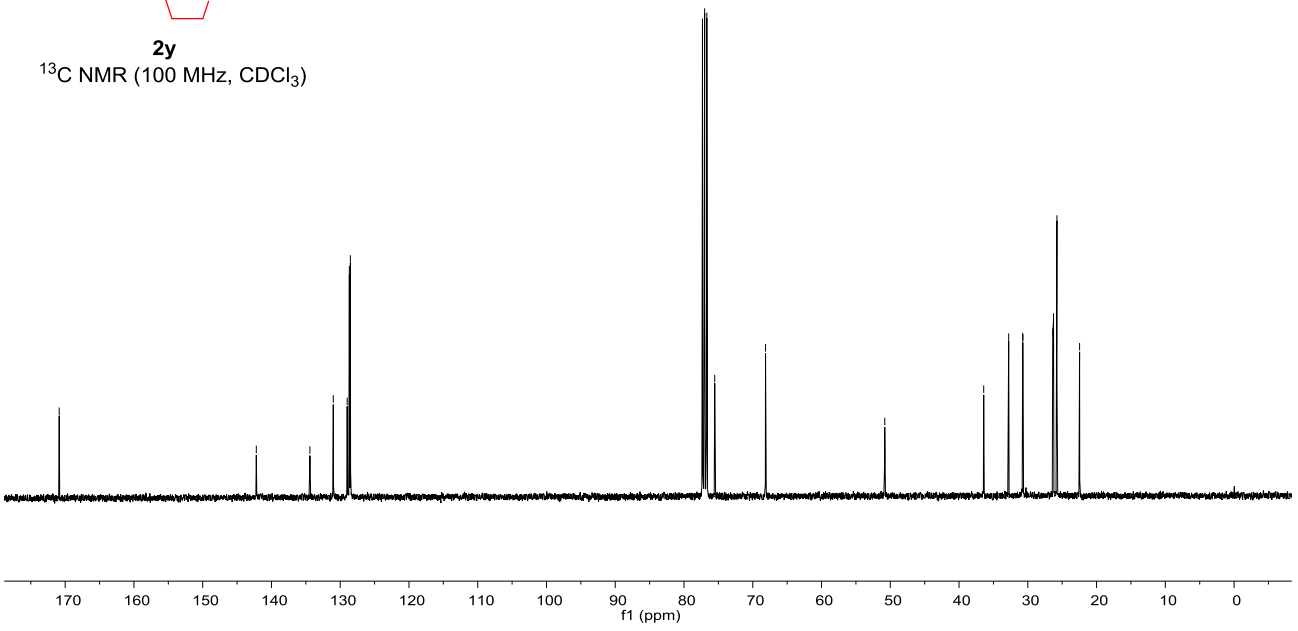
2y

^{1}H NMR (400 MHz, $CDCl_3$)

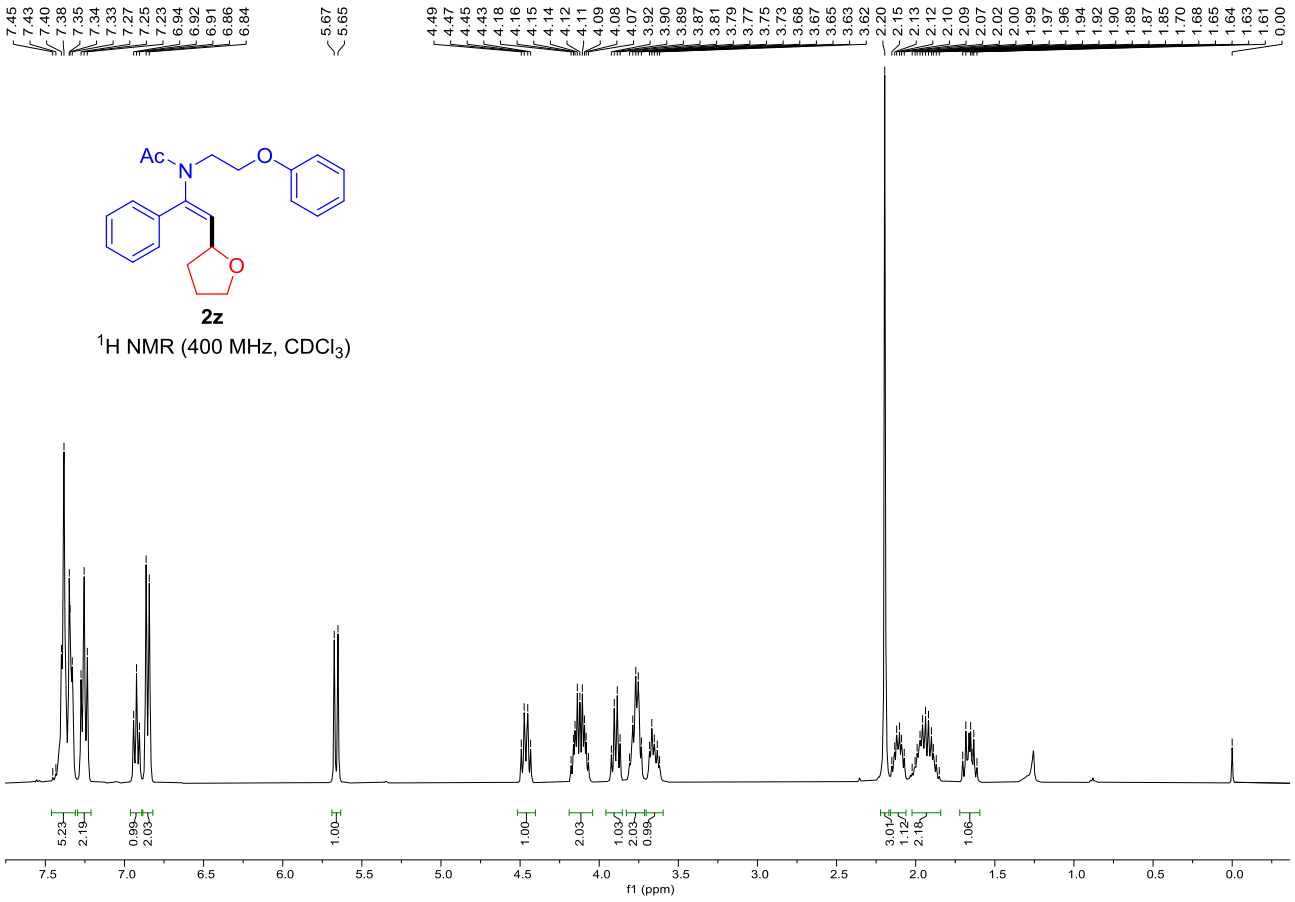


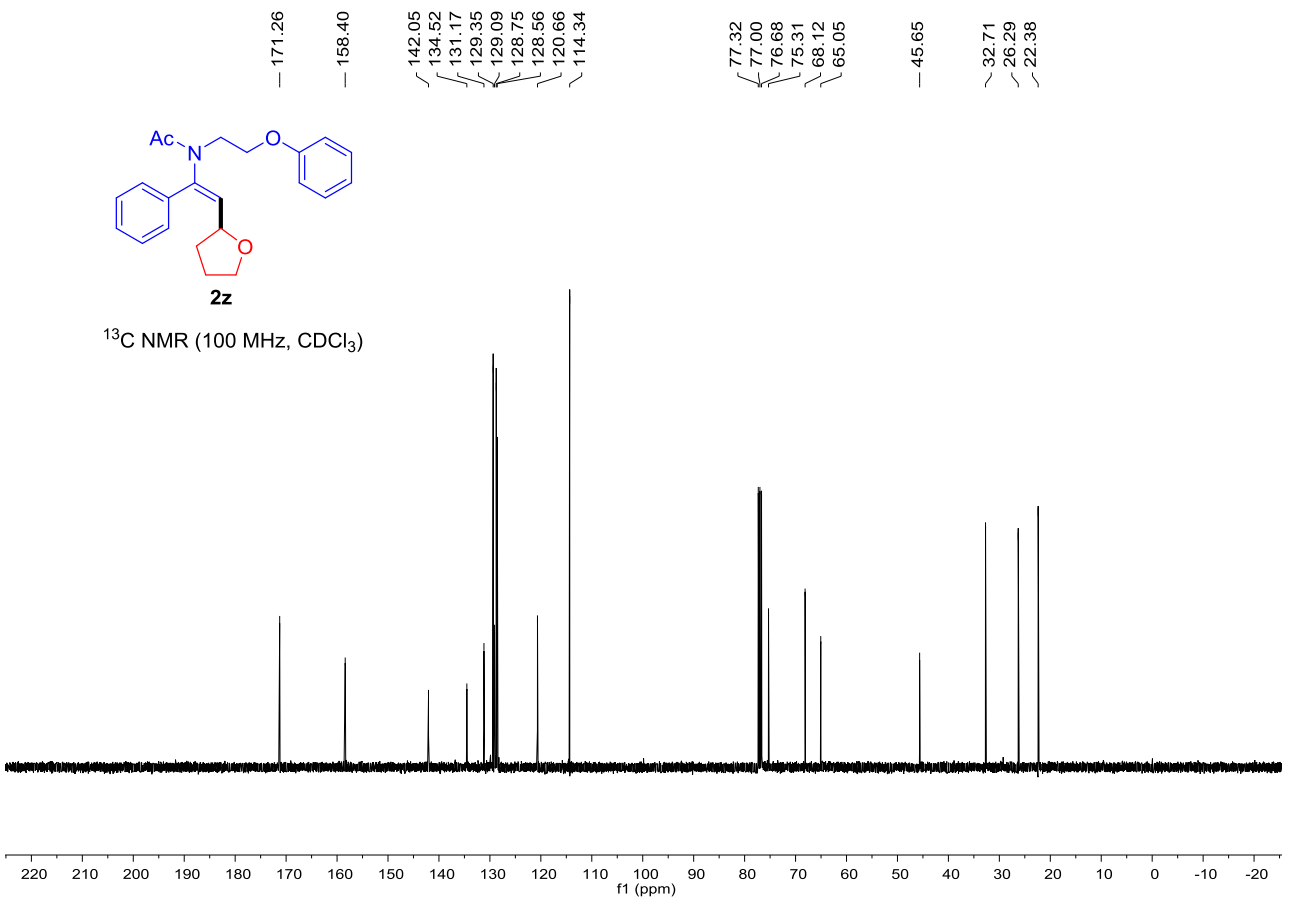
2y

^{13}C NMR (100 MHz, $CDCl_3$)

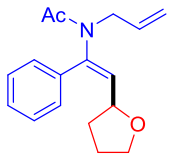


(*E*)-*N*-(2-phenoxyethyl)-*N*-(1-phenyl-2-(tetrahydrofuran-2-yl)vinyl)acetamide (**2z**)



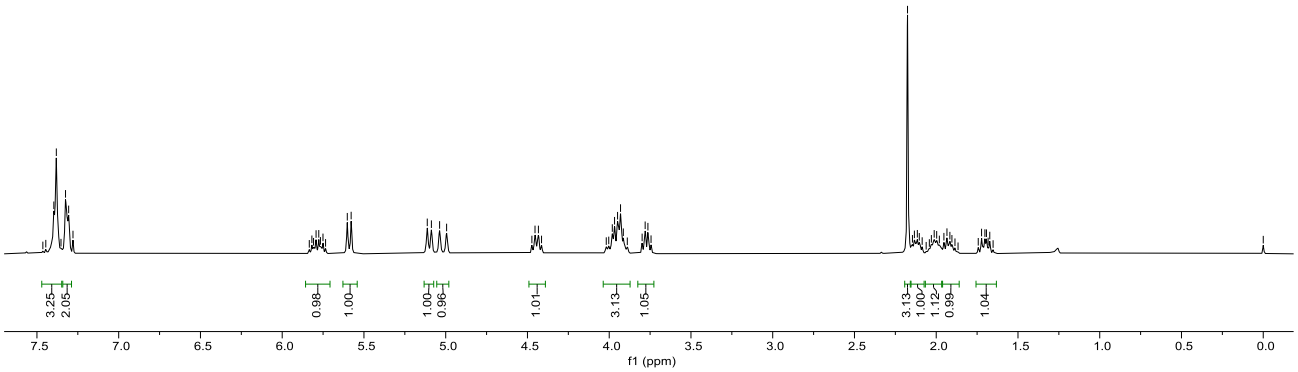


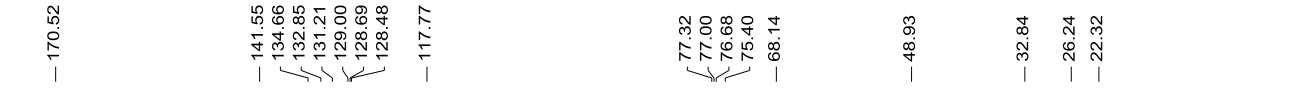
(*E*)-*N*-allyl-*N*-(1-phenyl-2-(tetrahydrofuran-2-yl)vinyl)acetamide (**2aa**)

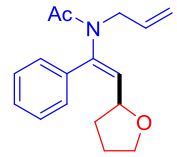


2aa

^{1}H NMR (400 MHz, $CDCl_3$)

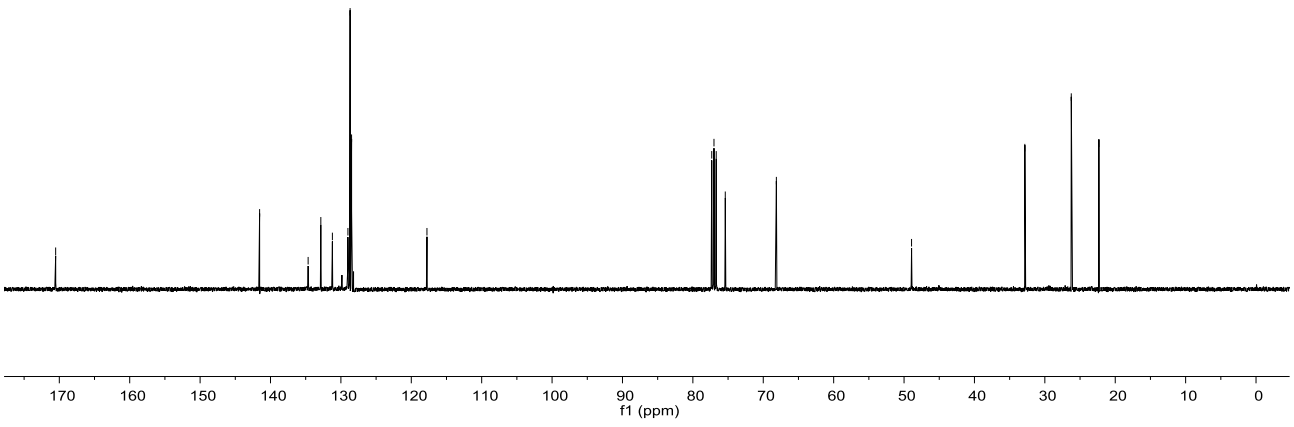




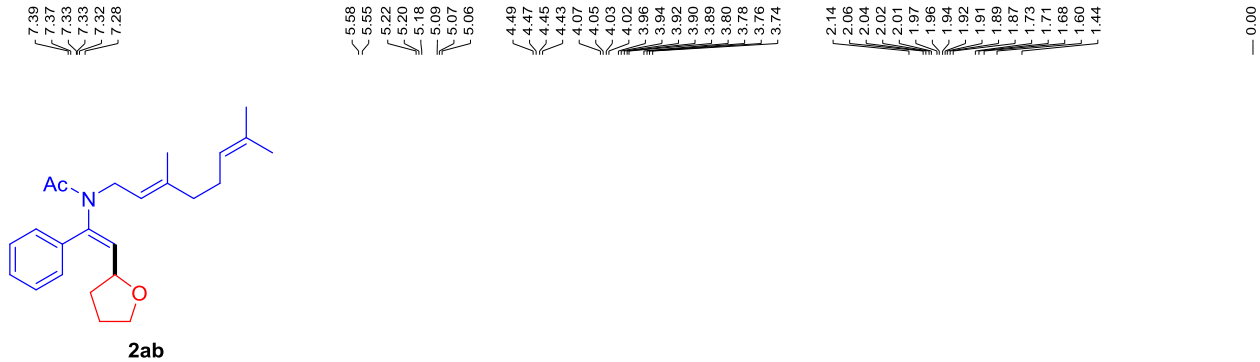


2aa

^{13}C NMR (100 MHz, $CDCl_3$)

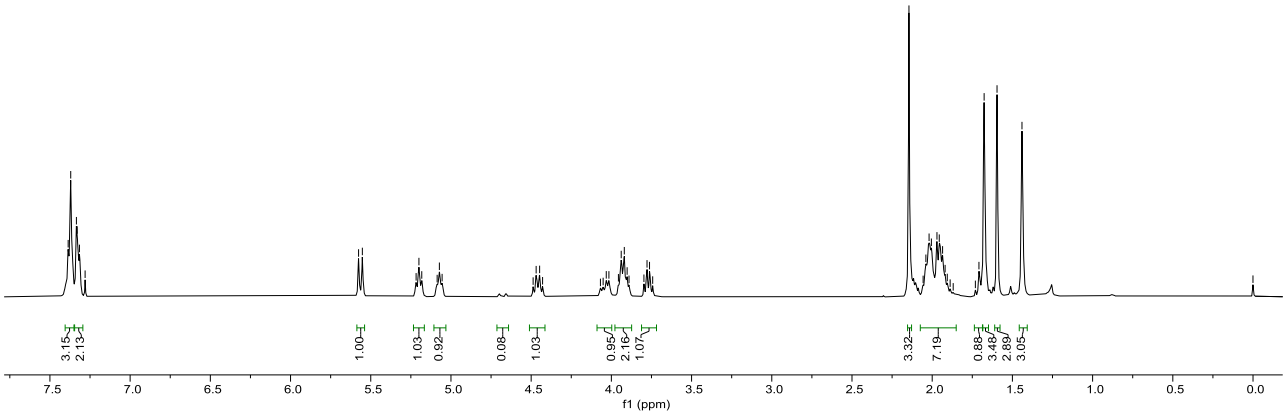


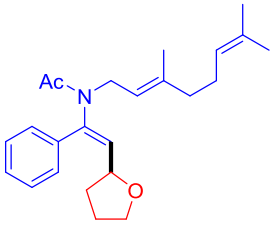
N-((*E*)-3,7-dimethylocta-2,6-dien-1-yl)-*N*-((*E*)-1-phenyl-2-(tetrahydrofuran-2-yl)vinyl)acetamide (**2ab**)



2ab

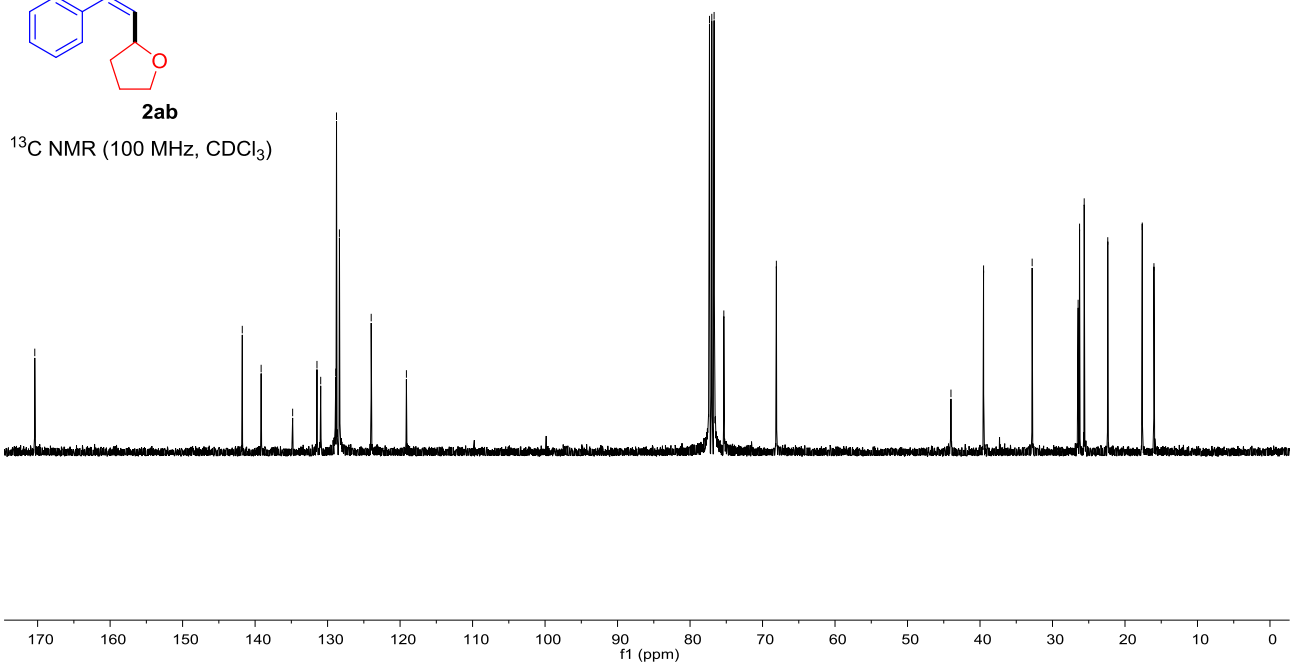
^{1}H NMR (400 MHz, $CDCl_3$)



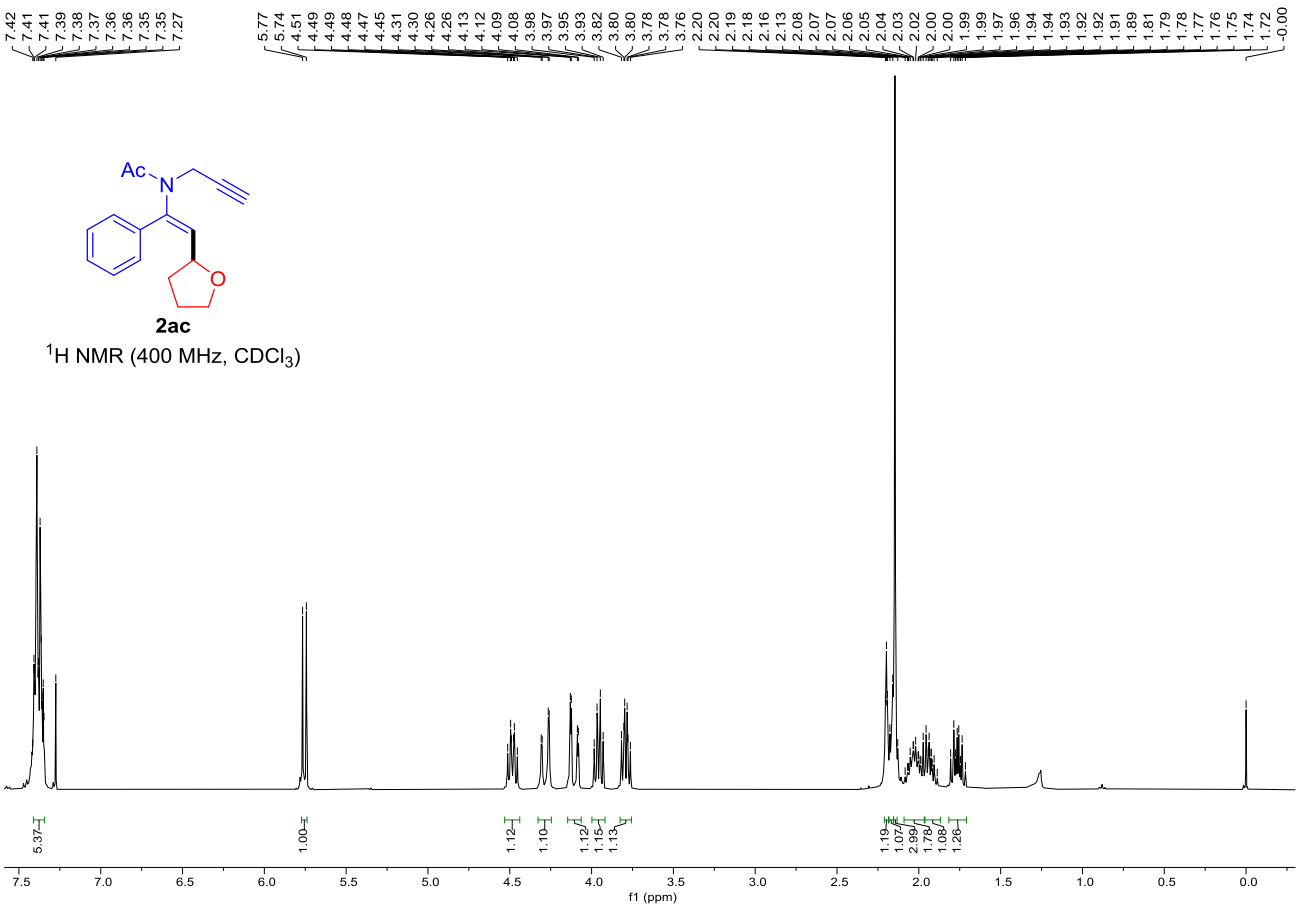


2ab

^{13}C NMR (100 MHz, $CDCl_3$)

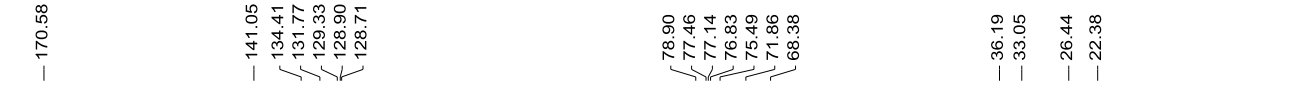


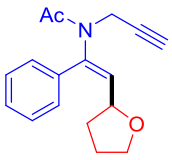
(*E*)-*N*-(1-phenyl-2-(tetrahydrofuran-2-yl) vinyl)-*N*-(prop-2-yn-1-yl)acetamide (**2ac**)



2ac

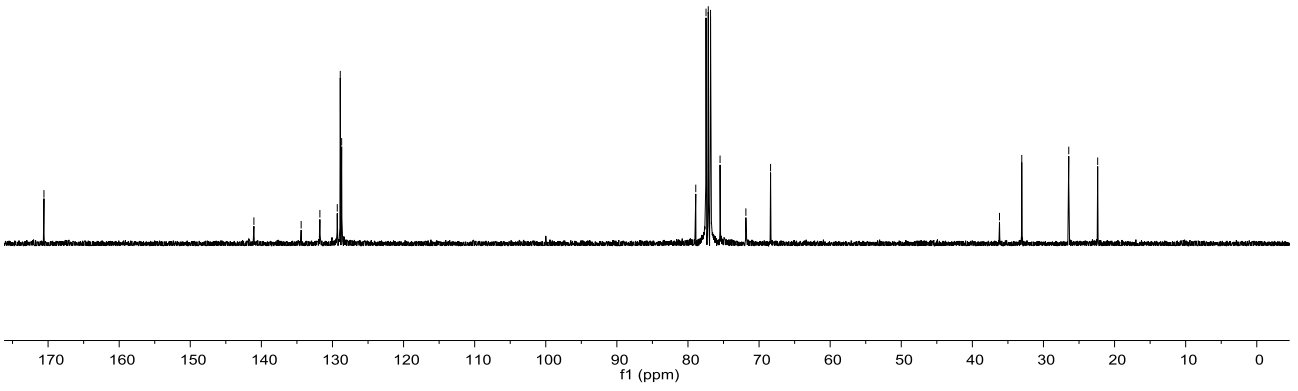
^{1}H NMR (400 MHz, $CDCl_3$)



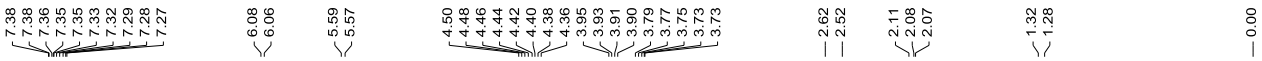


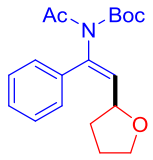
2ac

^{13}C NMR (100 MHz, $CDCl_3$)



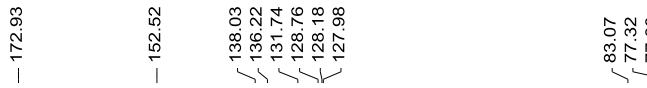
Tert-butyl (*E*)-acetyl(1-phenyl-2-(tetrahydrofuran-2-yl)vinyl)carbamate (**2ad**)

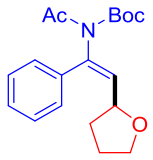




2ad

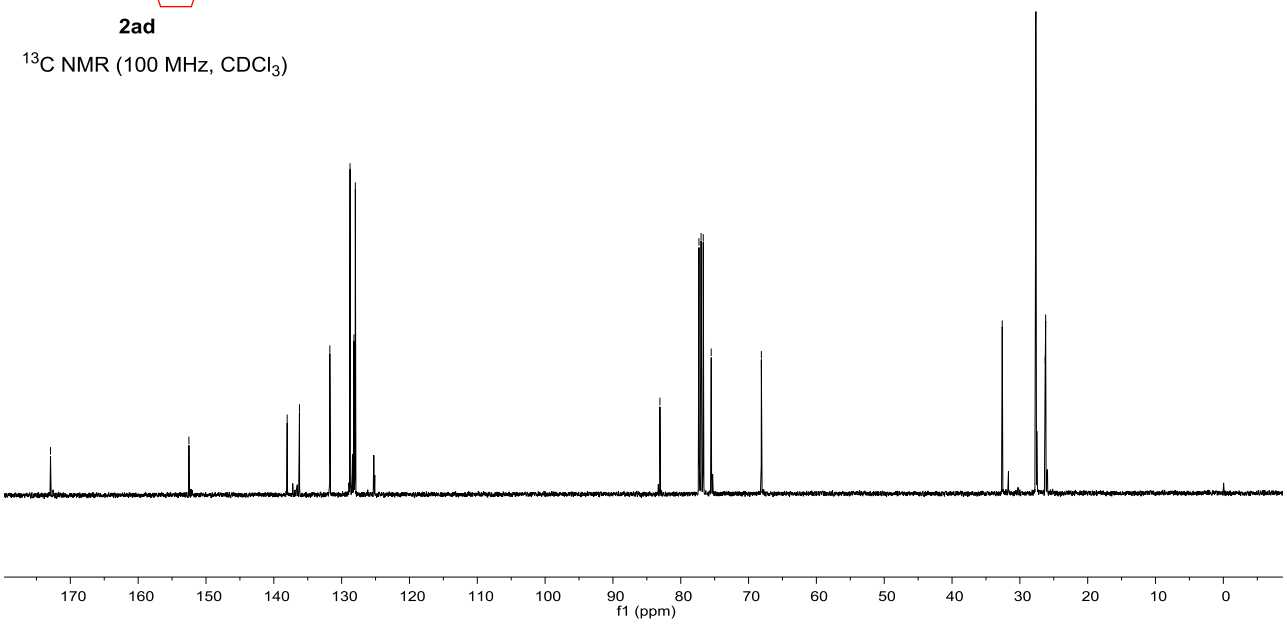
^{1}H NMR (400 MHz, $CDCl_3$)



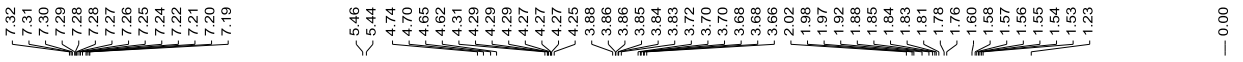


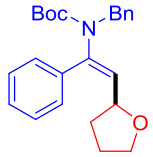
2ad

^{13}C NMR (100 MHz, $CDCl_3$)



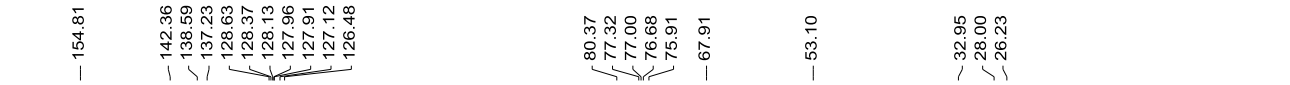
Tert-butyl (*E*)-benzyl(1-phenyl-2-(tetrahydrofuran-2-yl)vinyl)carbamate (**2ae**)

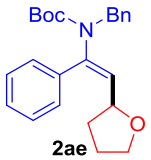




2ae

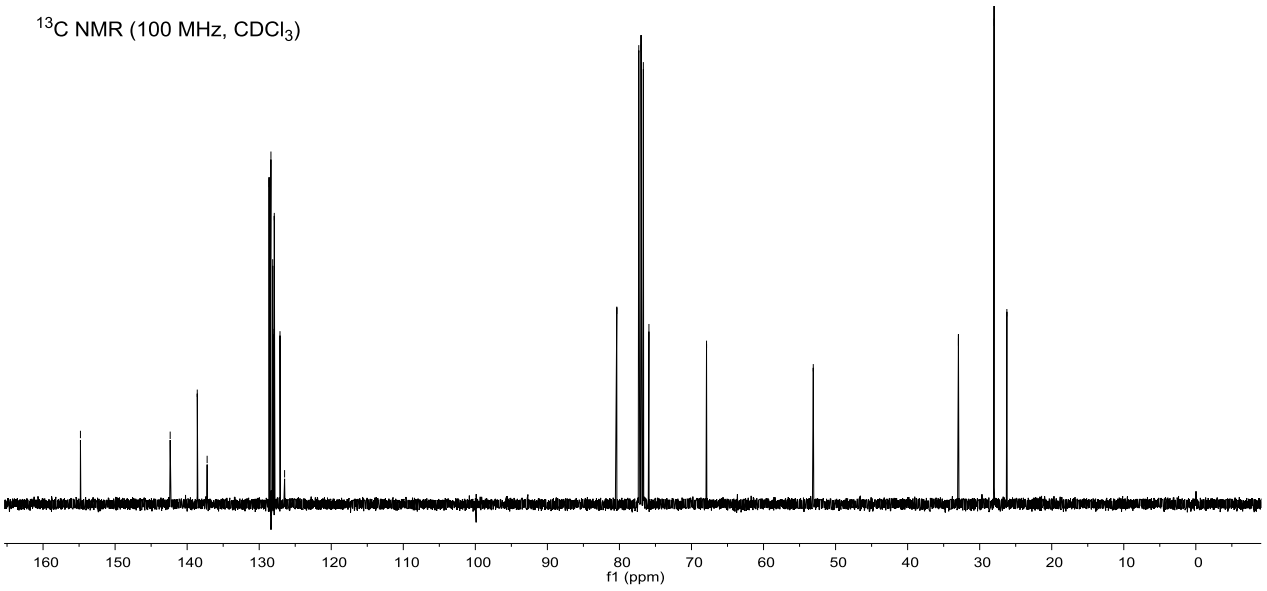
^{1}H NMR (400 MHz, $CDCl_3$)



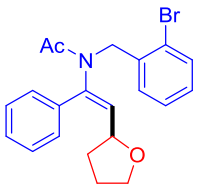


2ae

^{13}C NMR (100 MHz, $CDCl_3$)

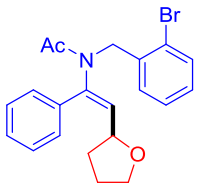


(*E*)-*N*-(2-bromobenzyl)-*N*-(1-phenyl-2-(tetrahydrofuran-2-yl)vinyl)acetamide (**2af**)



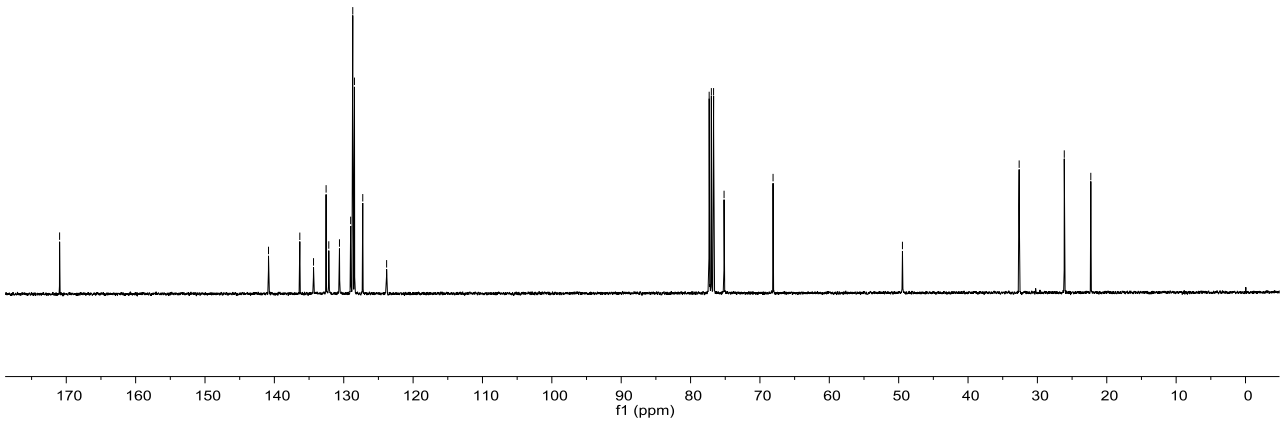
2af

^{1}H NMR (400 MHz, $CDCl_3$)

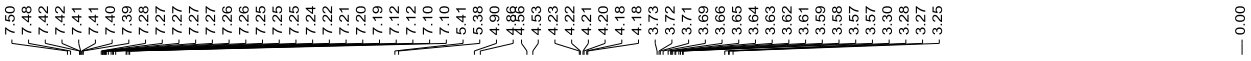


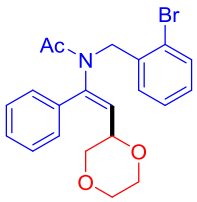
2af

^{13}C NMR (100 MHz, $CDCl_3$)



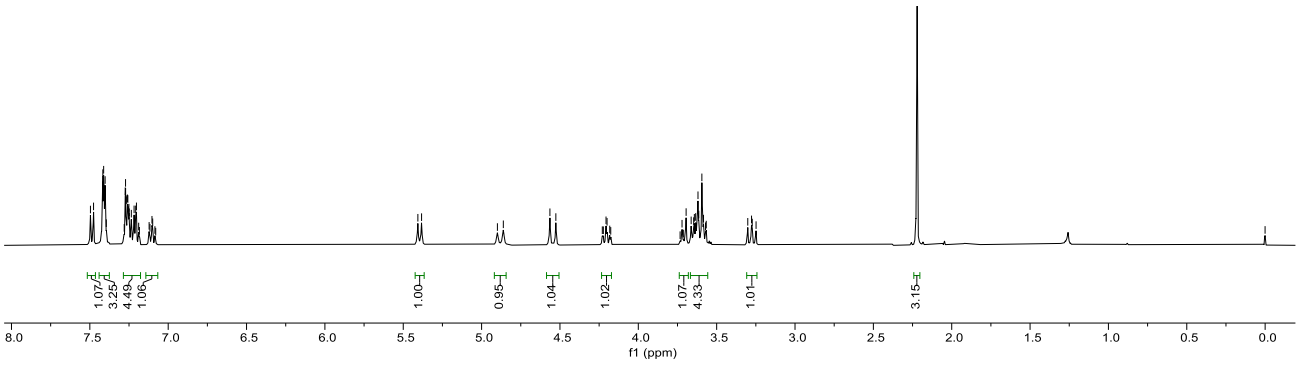
(*E*)-*N*-(2-(1,4-dioxan-2-yl)-1-phenylvinyl)-*N*-(2-bromobenzyl)acetamide (**2ag**)

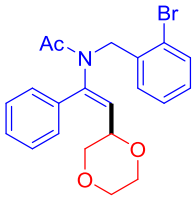




2ag

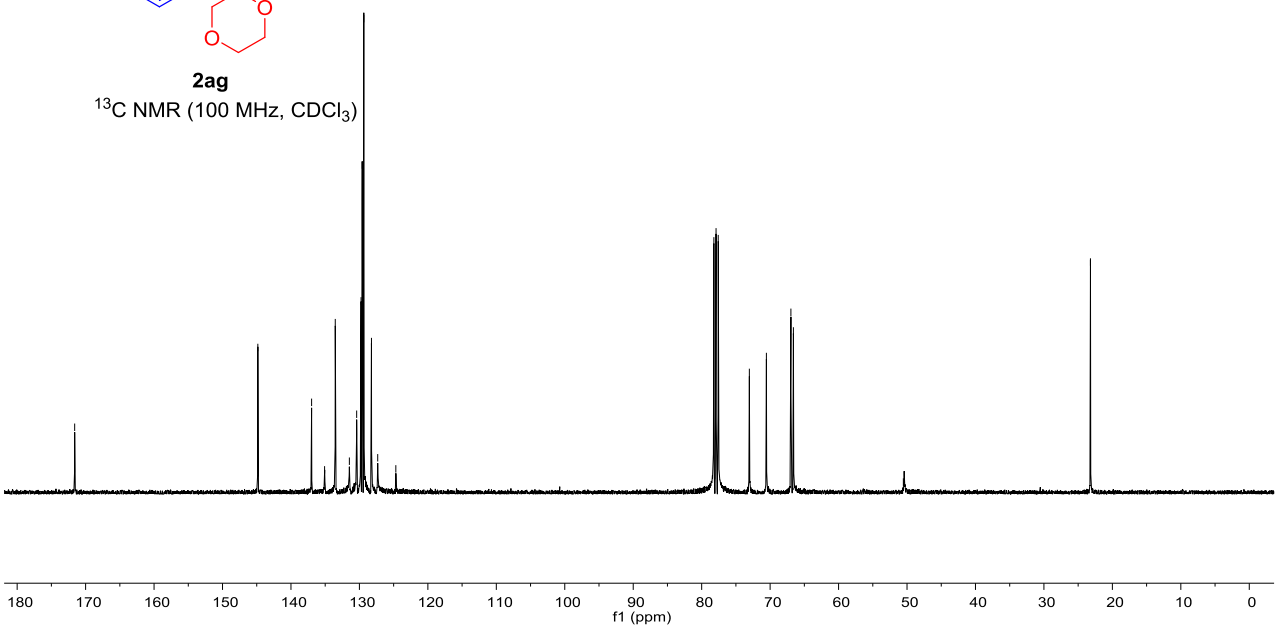
^{1}H NMR (400 MHz, $CDCl_3$)



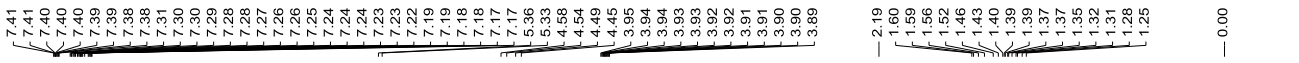


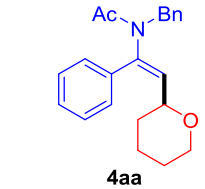
2ag

^{13}C NMR (100 MHz, $CDCl_3$)



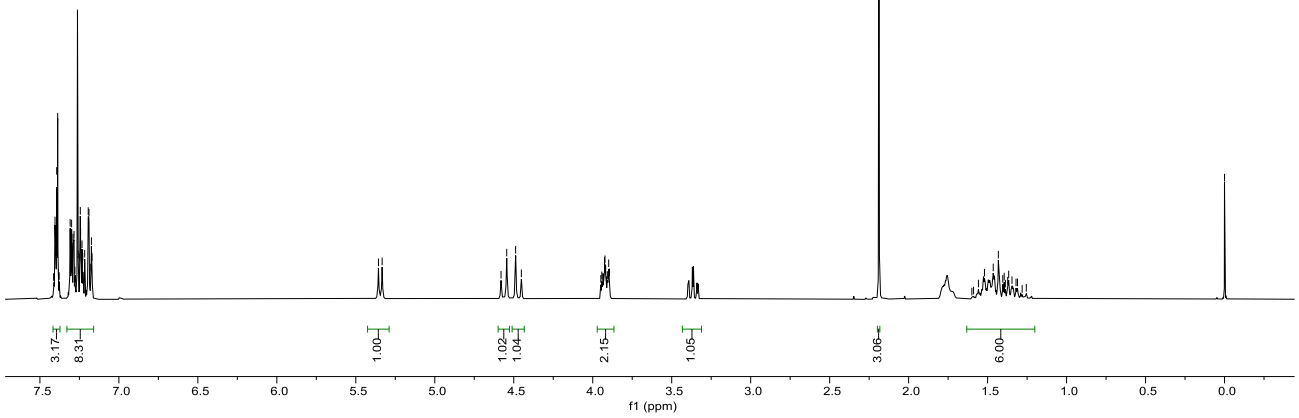
(*E*)-*N*-benzyl-*N*-(1-phenyl-2-(tetrahydro-2H-pyran-2-yl)vinyl)acetamide (**4aa**)

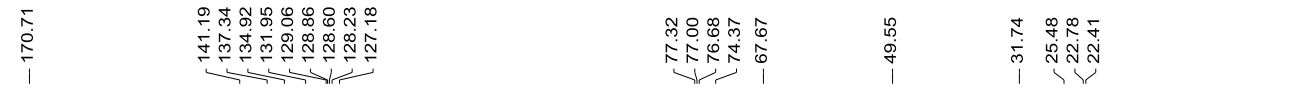


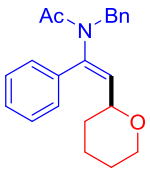


4aa

^{1}H NMR (400 MHz, $CDCl_3$)



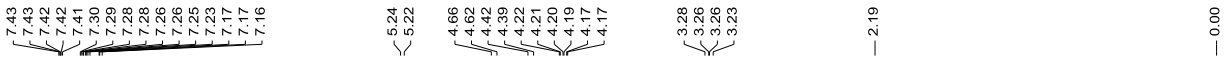


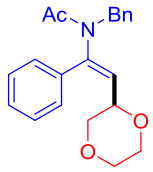


4aa

^{13}C NMR (100 MHz, $CDCl_3$)

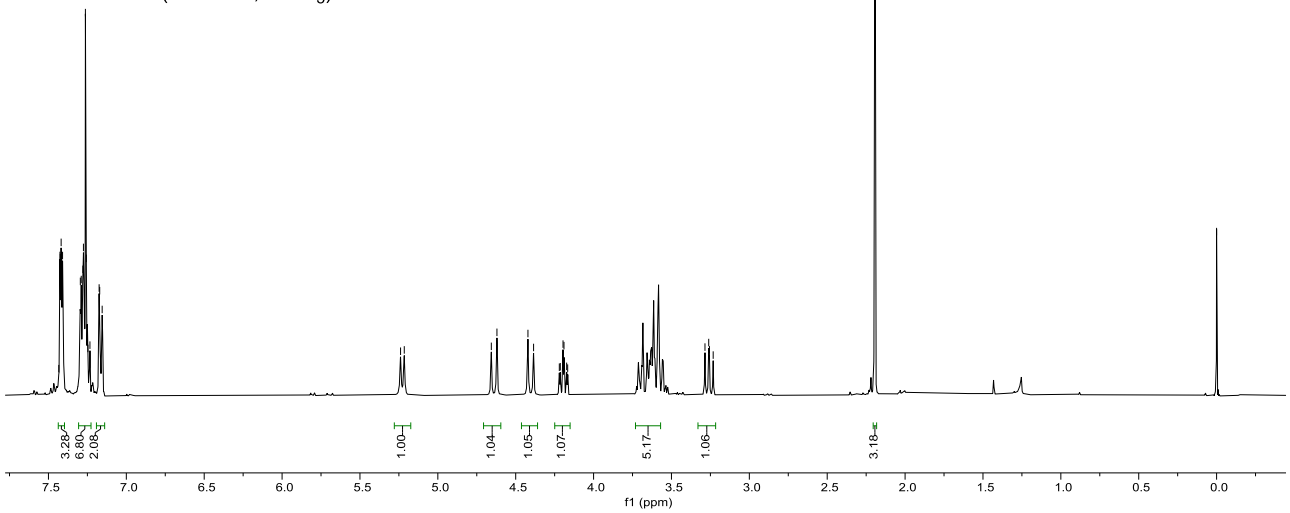
(*E*)-*N*-(2-(1,4-dioxan-2-yl)-1-phenylvinyl)-*N*-benzylacetamide (**4ab**)

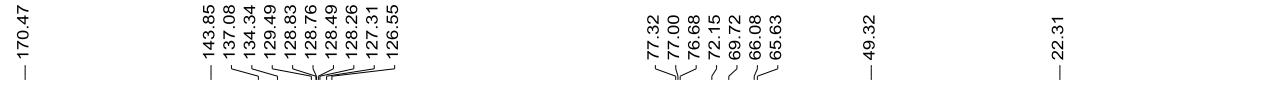


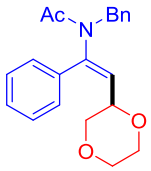


4ab

^{1}H NMR (400 MHz, $CDCl_3$)

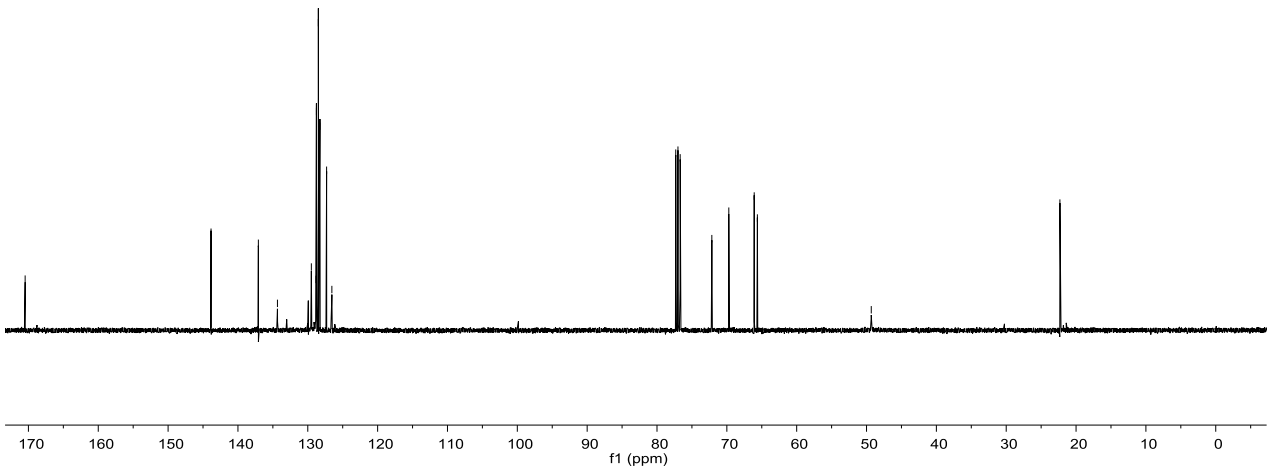




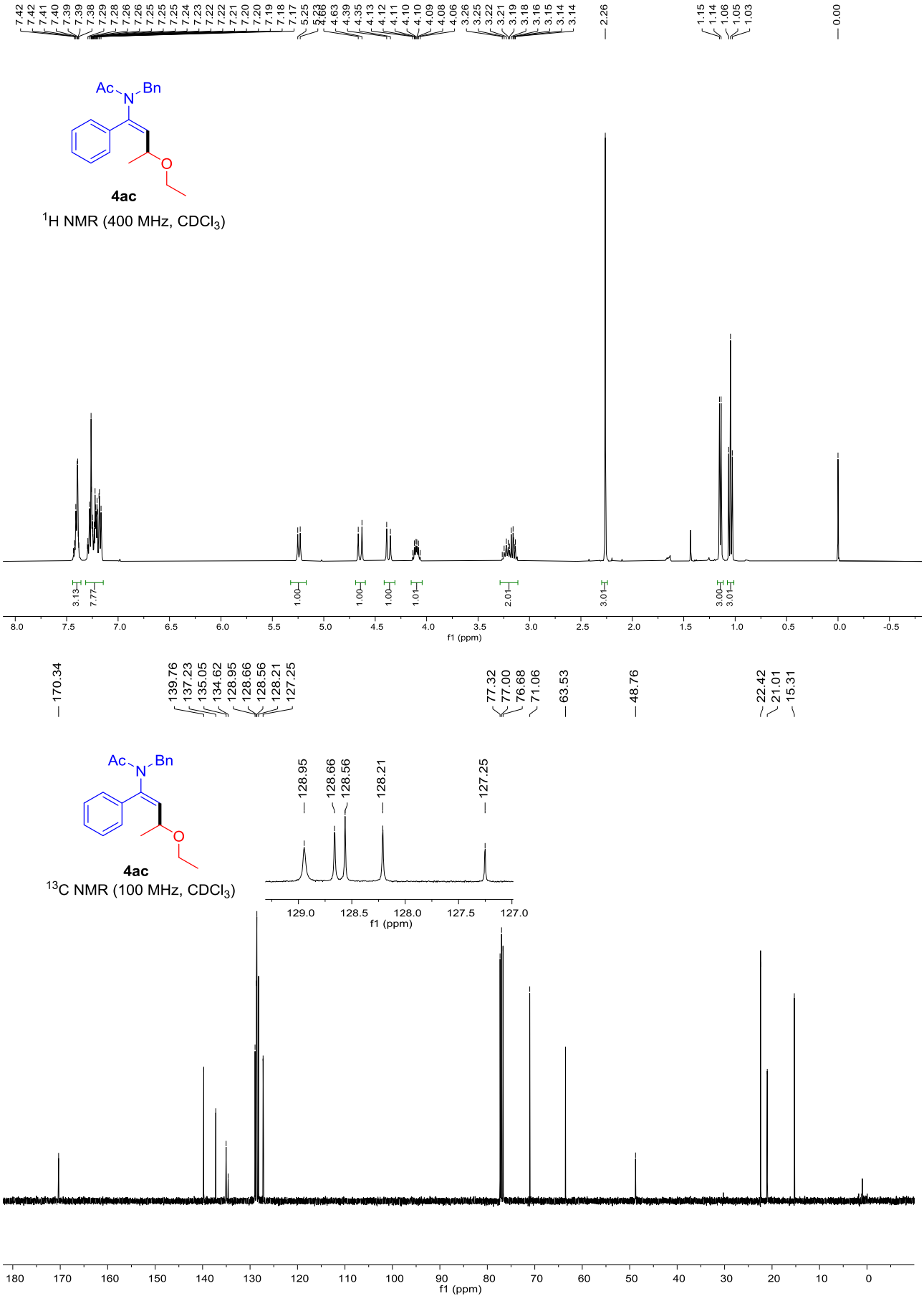


4ab

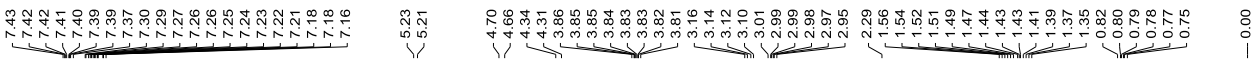
^{13}C NMR (100 MHz, $CDCl_3$)

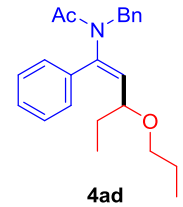


(*E*)-*N*-benzyl-*N*-(3-ethoxy-1-phenylbut-1-en-1-yl)acetamide (**4ac**)



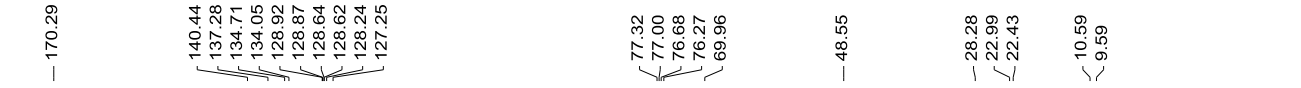
(*E*)-*N*-benzyl-*N*-(1-phenyl-3-propoxypent-1-en-1-yl)acetamide (**4ad**)

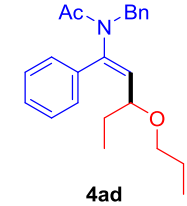




4ad

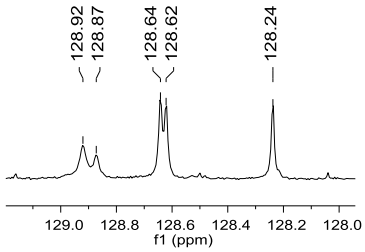
^{1}H NMR (400 MHz, $CDCl_3$)

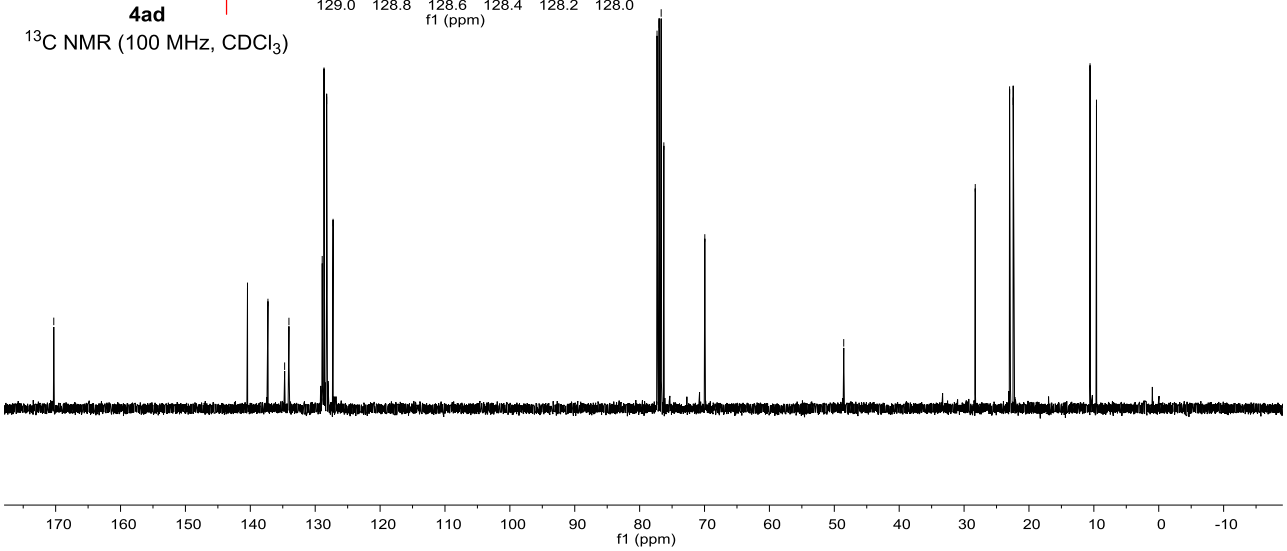




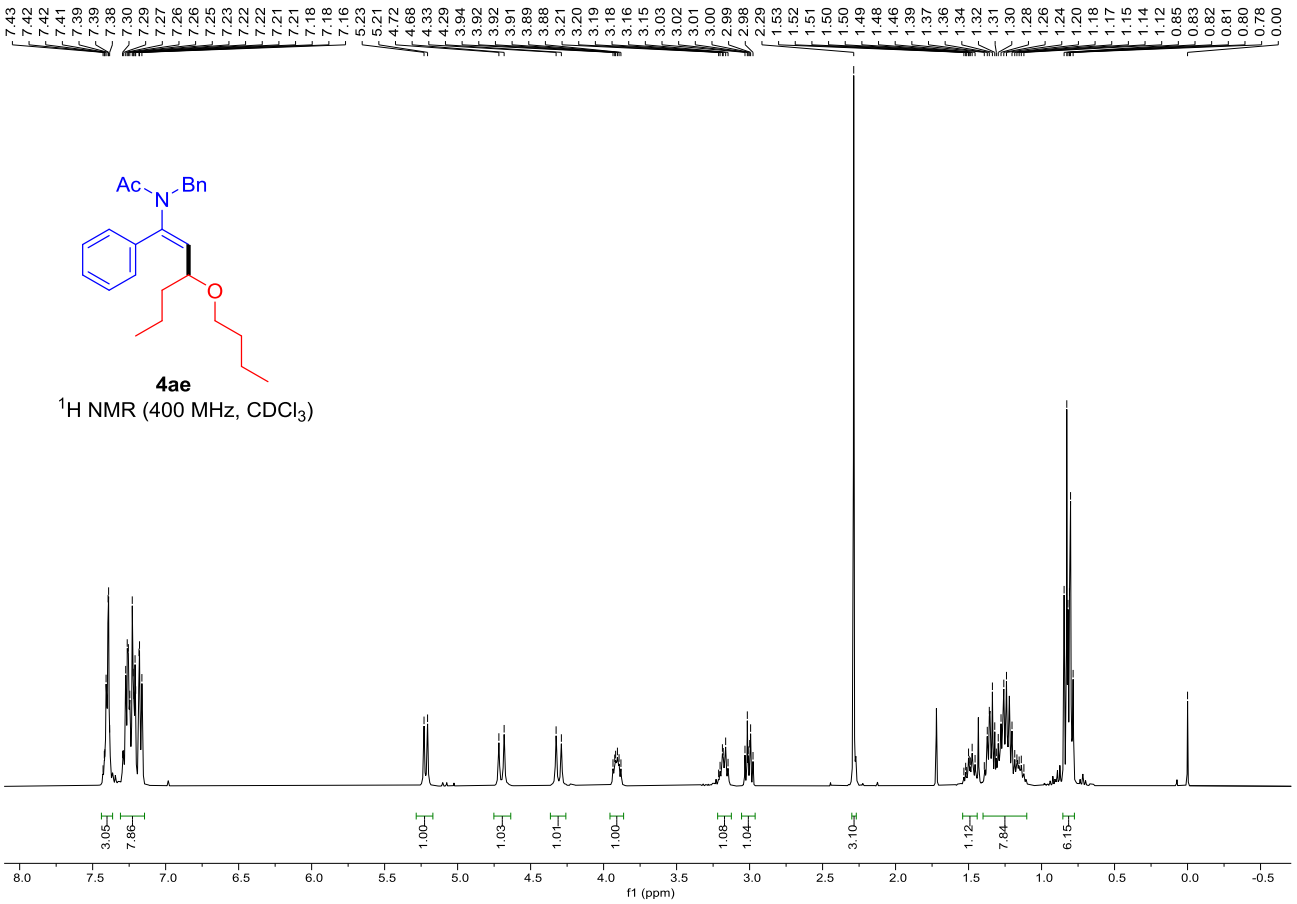
4ad

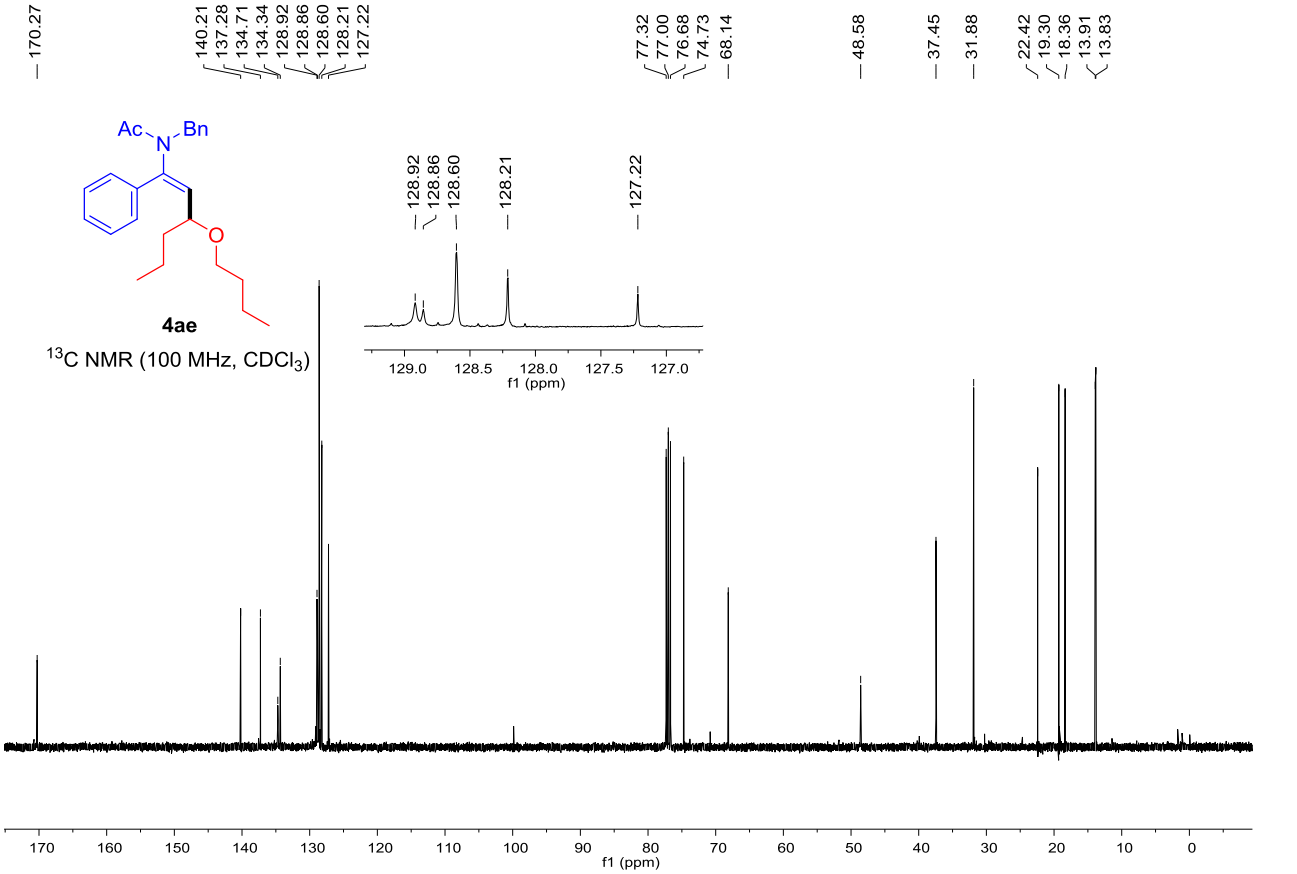
^{13}C NMR (100 MHz, $CDCl_3$)



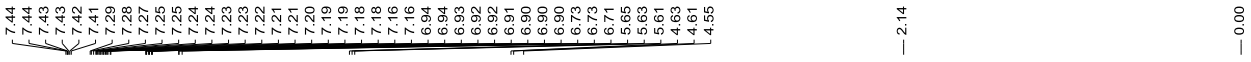


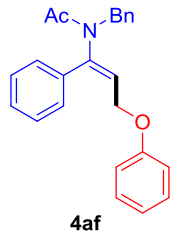
(*E*)-*N*-benzyl-*N*-(3-butoxy-1-phenylhex-1-en-1-yl)acetamide (**4ae**)





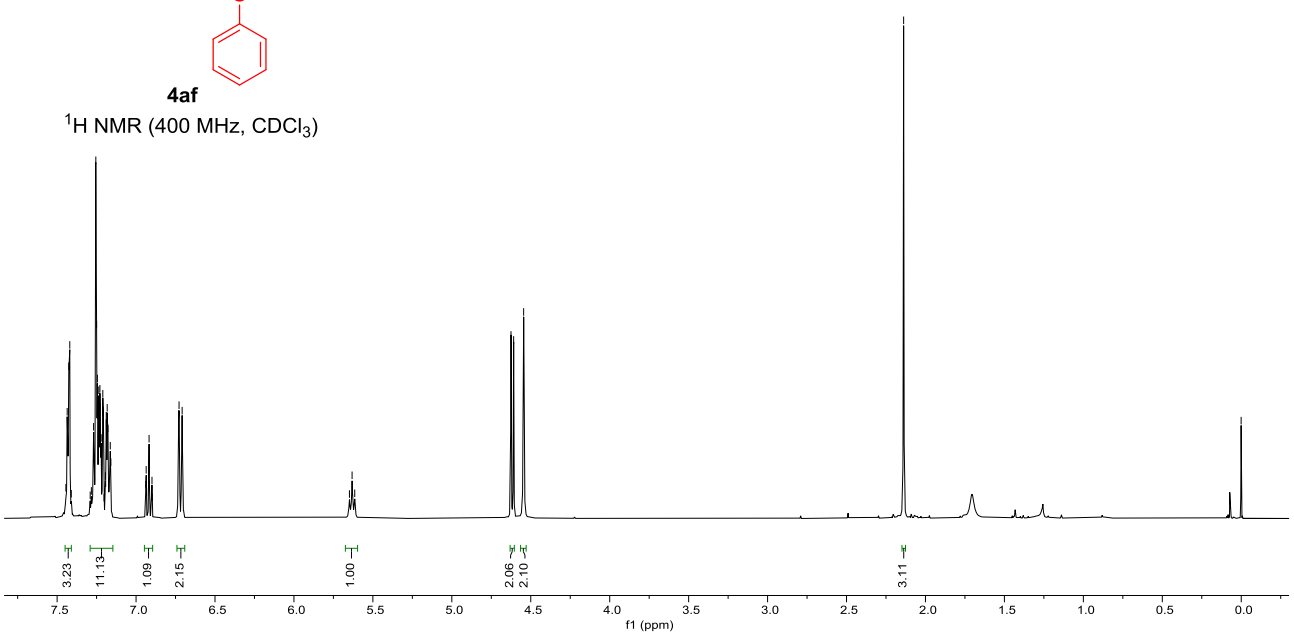
(*E*)-*N*-benzyl-*N*-(3-phenoxy-1-phenylprop-1-en-1-yl)acetamide (**4af**)

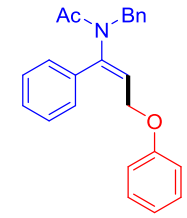




4af

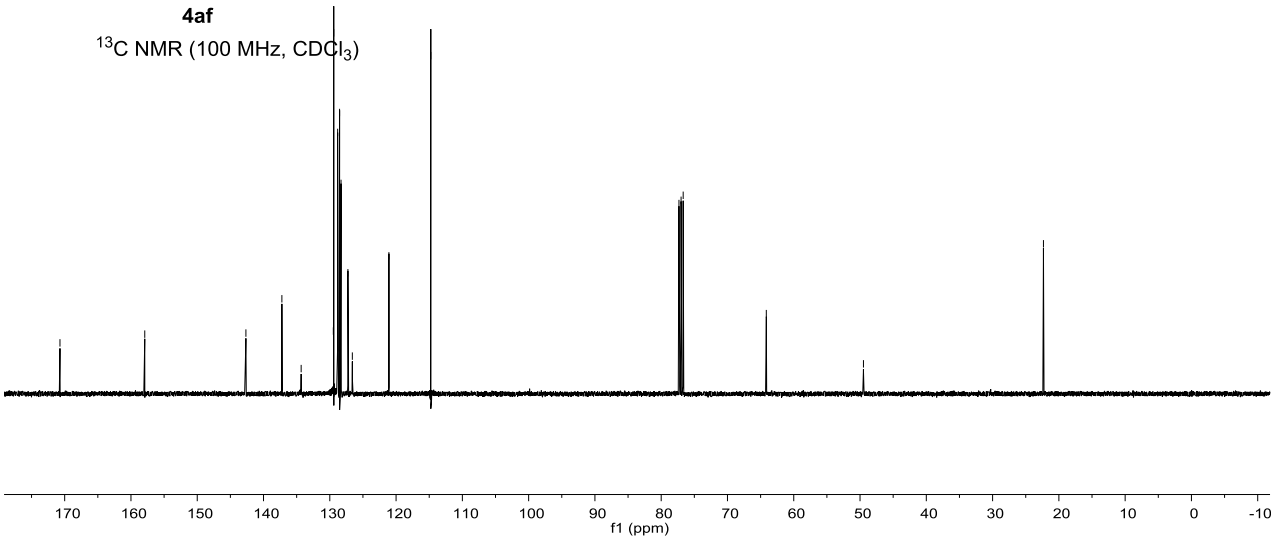
^{1}H NMR (400 MHz, $CDCl_3$)



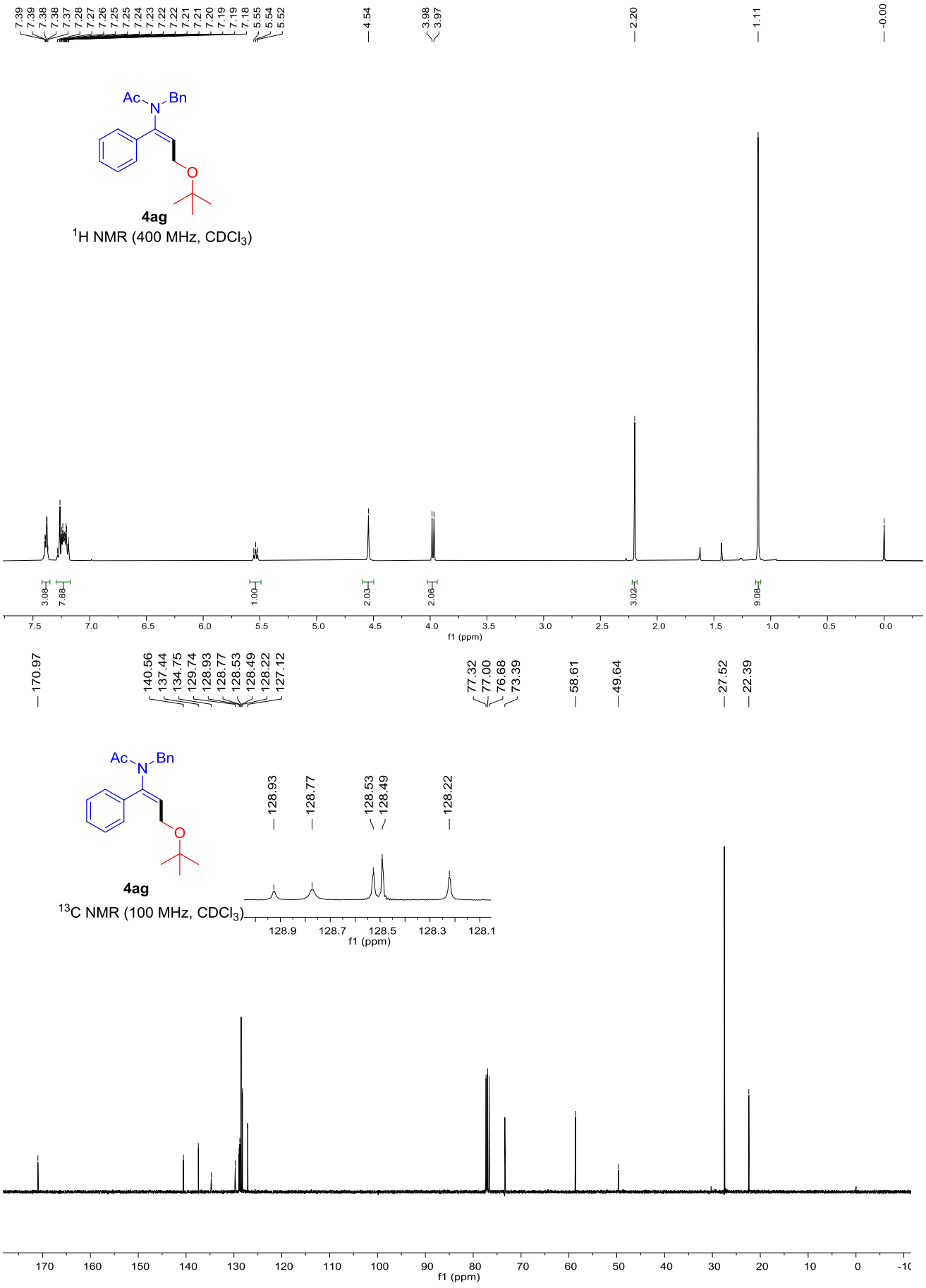


4af

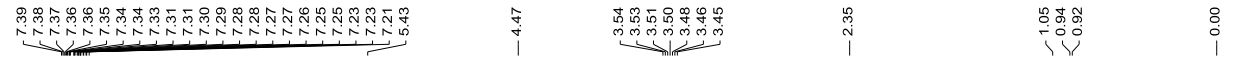
^{13}C NMR (100 MHz, $CDCl_3$)

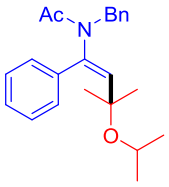


(*E*)-*N*-benzyl-*N*-(3-(tert-butoxy)-1-phenylprop-1-en-1-yl)acetamide (**4ag**)



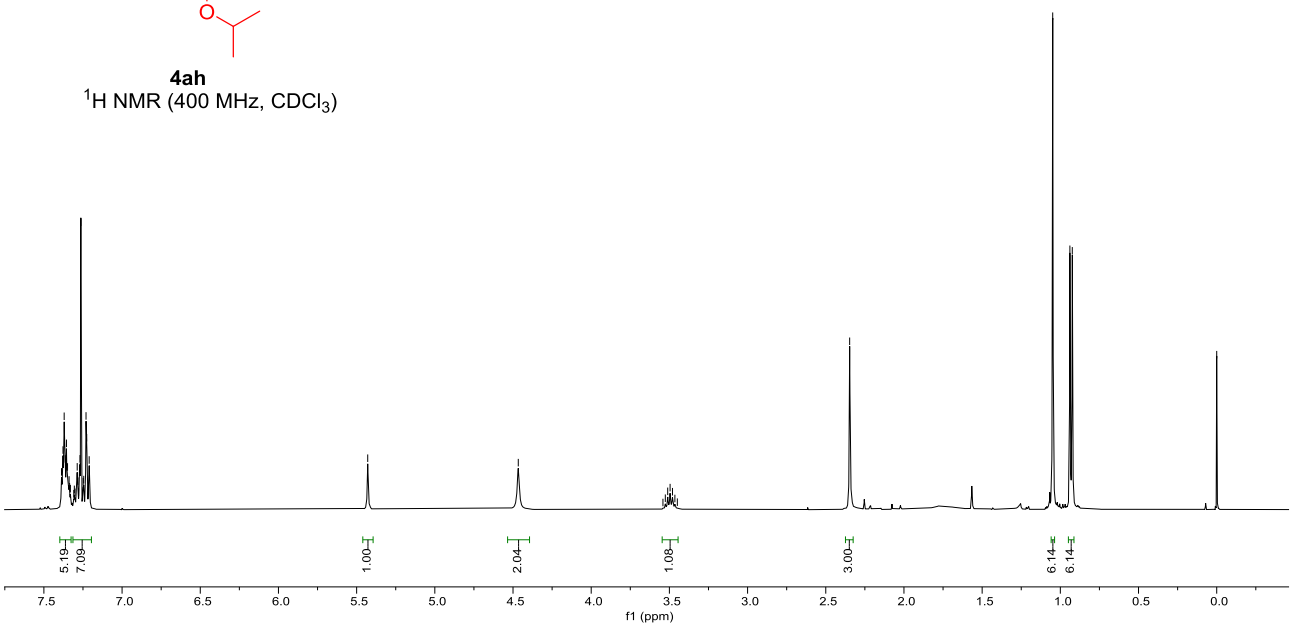
(*E*)-*N*-benzyl-*N*-(3-isopropoxy-3-methyl-1-phenylbut-1-en-1-yl)acetamide (**4ah**)

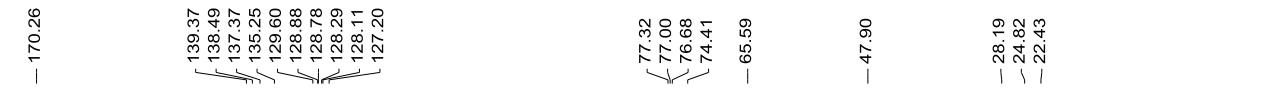


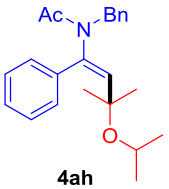


4ah

^{1}H NMR (400 MHz, $CDCl_3$)

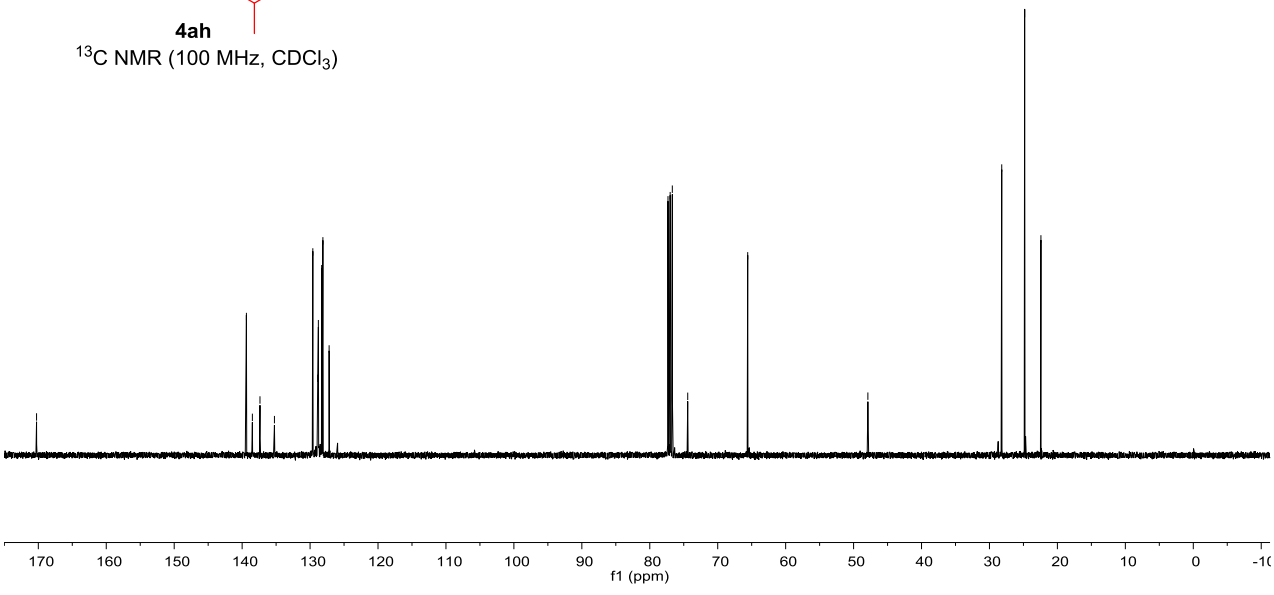




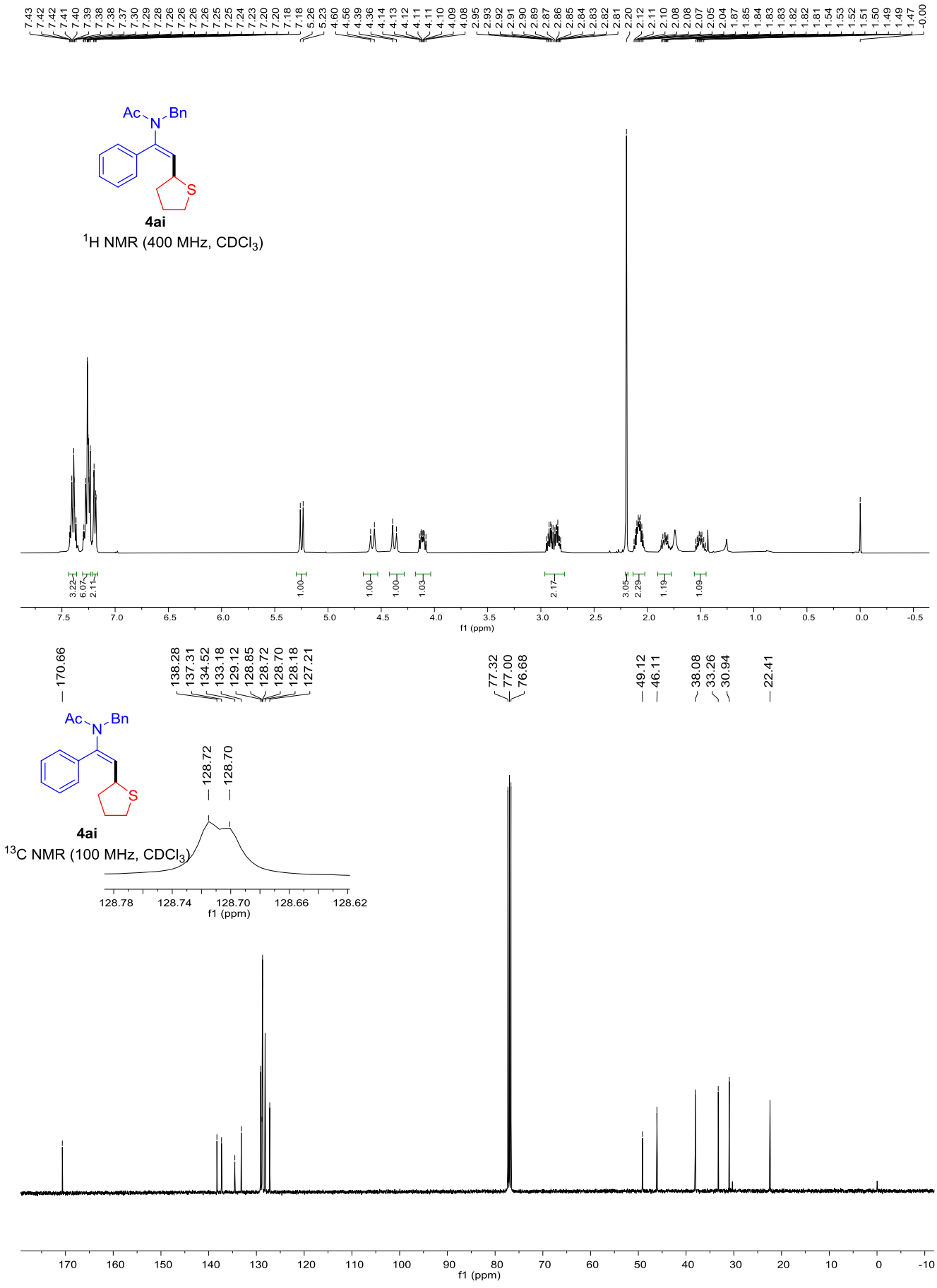


4ah

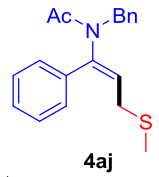
^{13}C NMR (100 MHz, $CDCl_3$)



(*E*)-*N*-benzyl-*N*-(1-phenyl-2-(tetrahydrothiophen-2-yl)vinyl)acetamide (**4ai**)

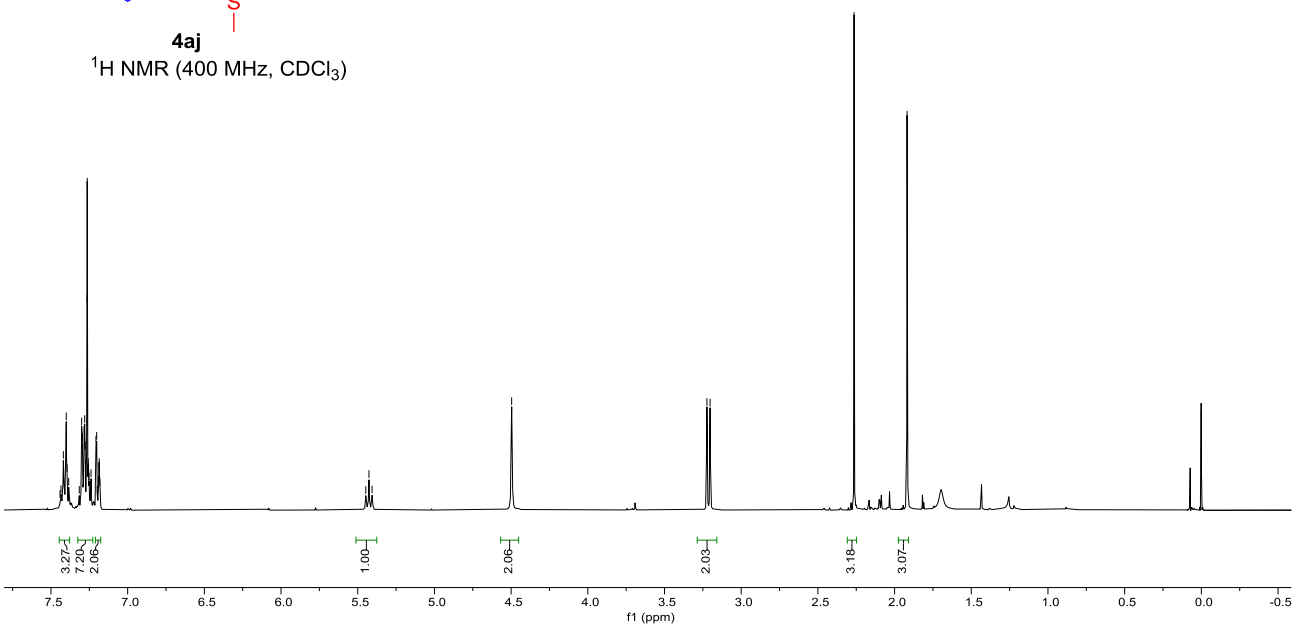


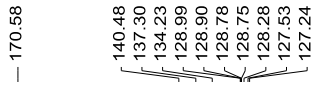
(*E*)-*N*-benzyl-*N*-(3-(methylthio)-1-phenylprop-1-en-1-yl)acetamide (**4aj**)

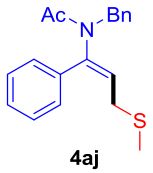


4aj

^{1}H NMR (400 MHz, $CDCl_3$)

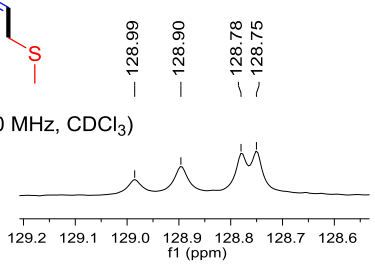




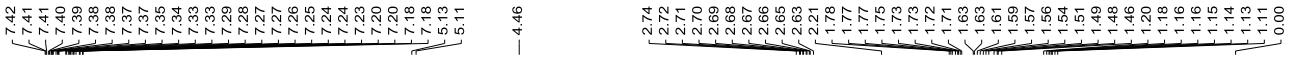


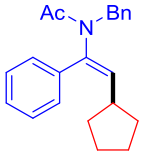
4aj

^{13}C NMR (100 MHz, $CDCl_3$)



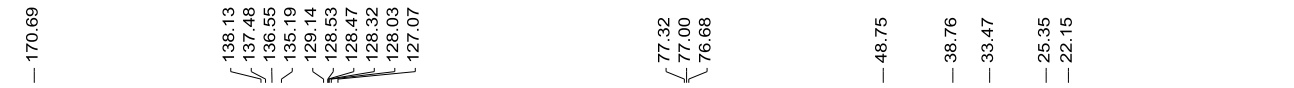
(*E*)-*N*-benzyl-*N*-(2-cyclopentyl-1-phenylvinyl)acetamide (**4ak**)

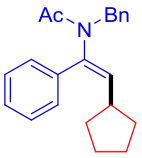




4ak

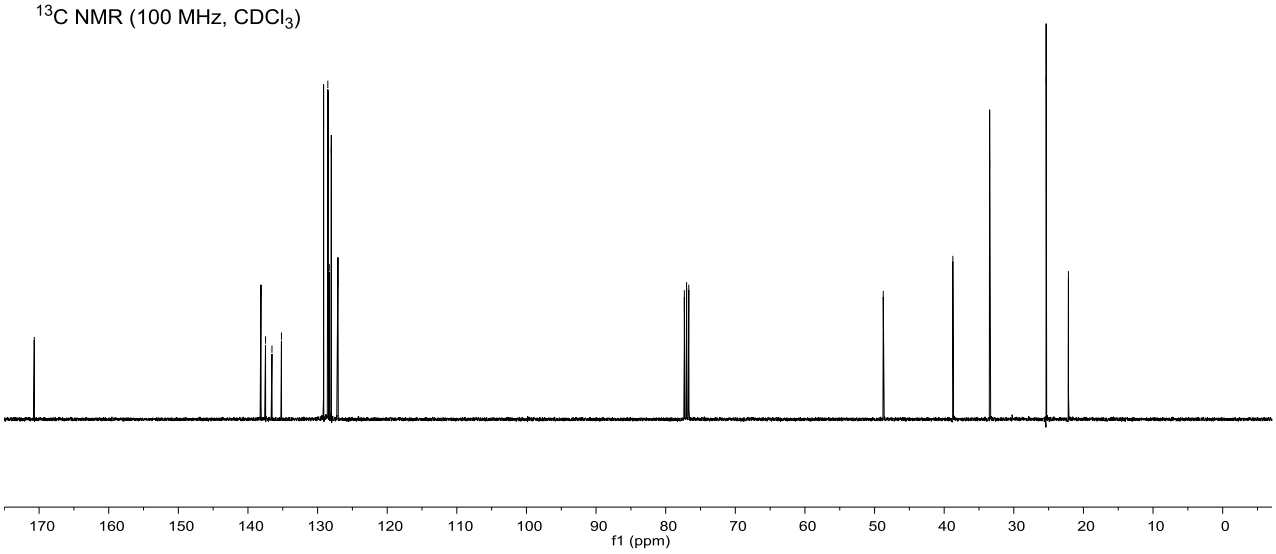
^{1}H NMR (400 MHz, $CDCl_3$)



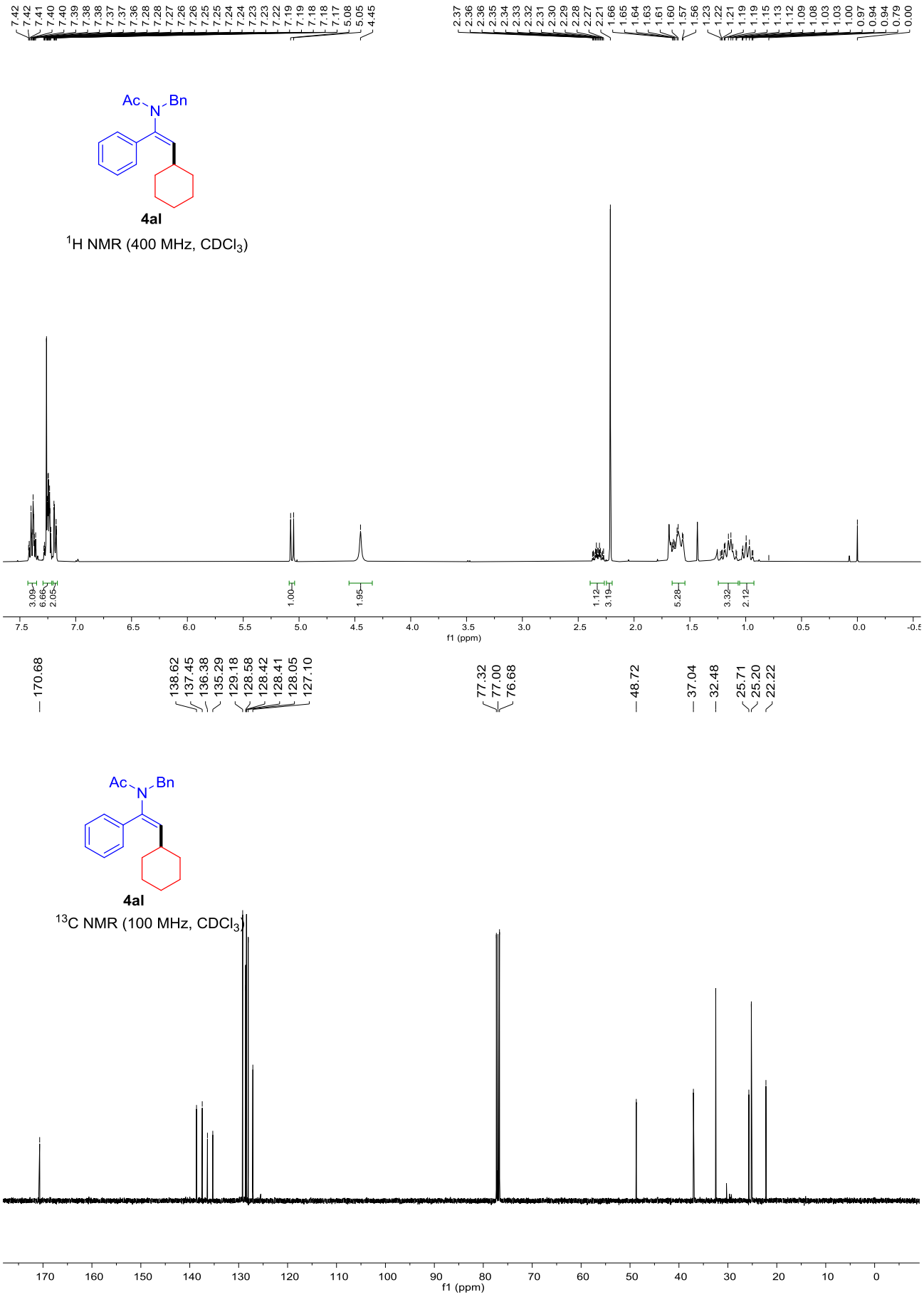


4ak

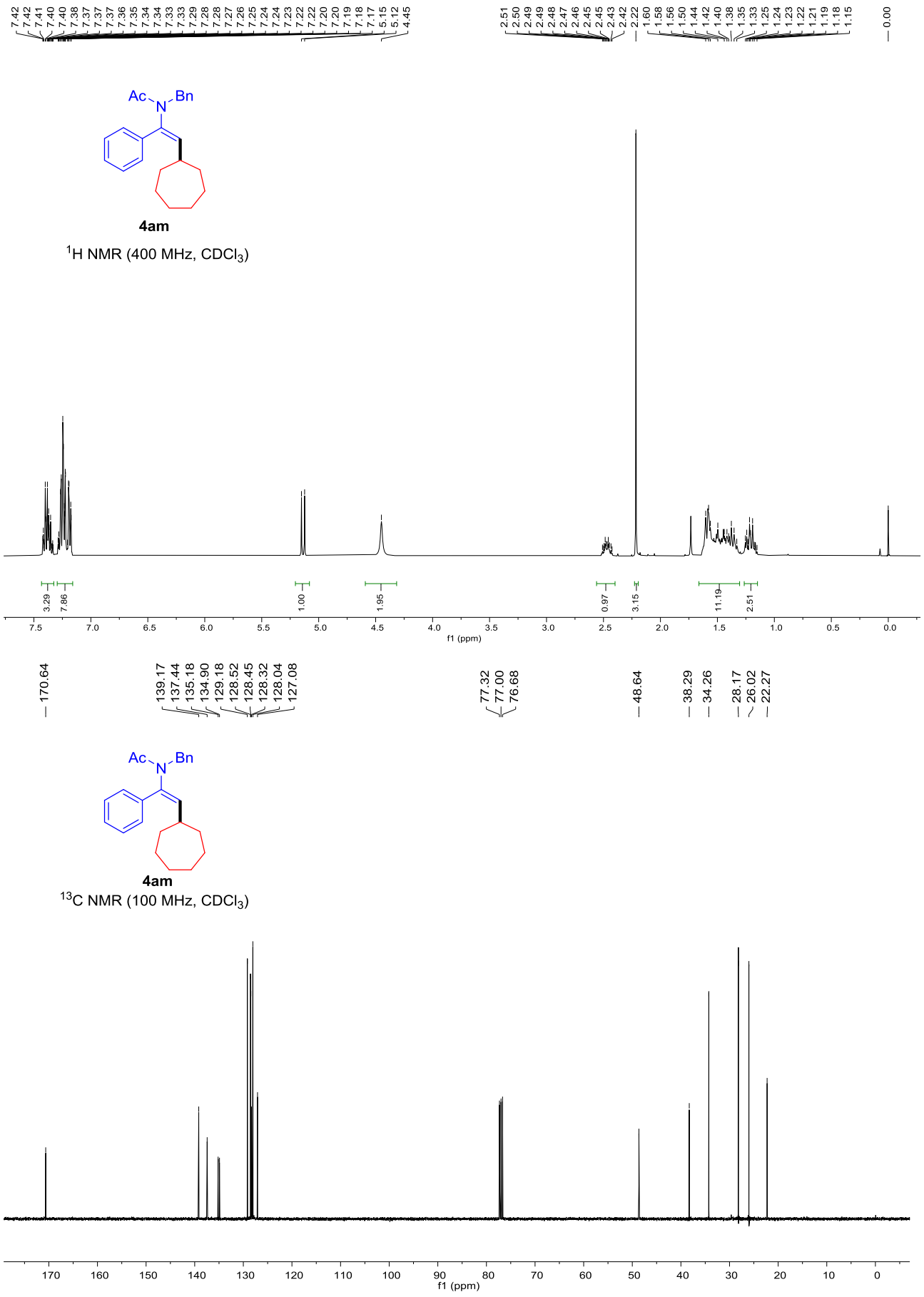
^{13}C NMR (100 MHz, $CDCl_3$)



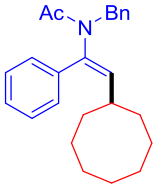
(*E*)-*N*-benzyl-*N*-(2-cyclohexyl-1-phenylvinyl)acetamide (**4al**)



(*E*)-*N*-benzyl-*N*-(2-cycloheptyl-1-phenylvinyl)acetamide (**4am**)

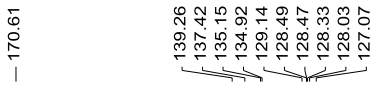


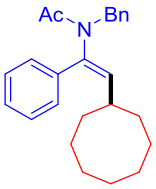
(*E*)-*N*-benzyl-*N*-(2-cyclooctyl-1-phenylvinyl)acetamide (**4an**)



4an

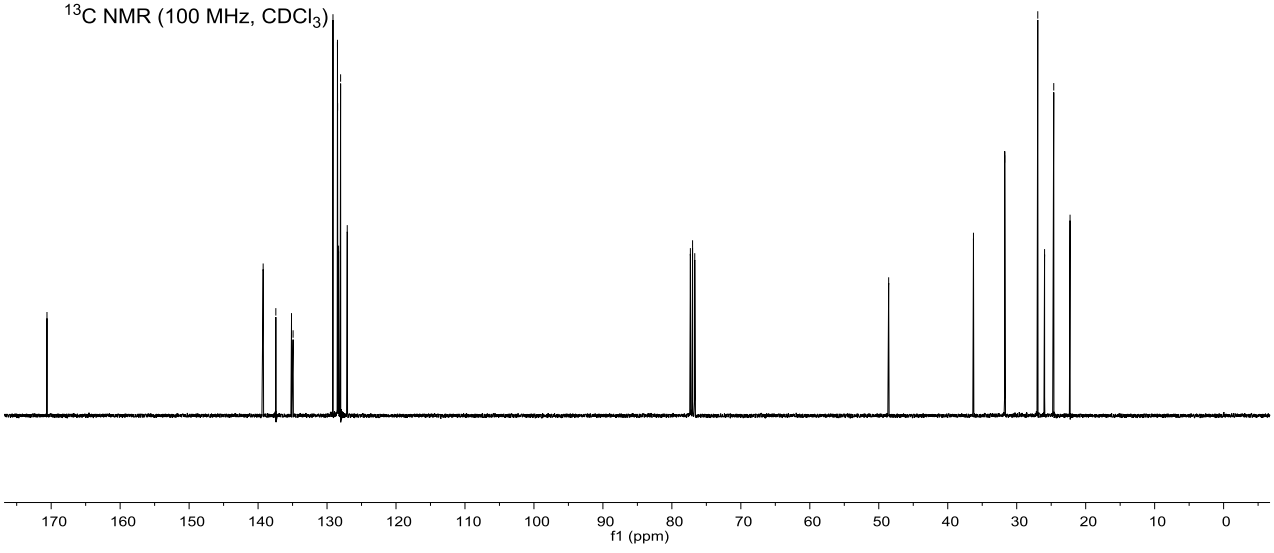
^{1}H NMR (400 MHz, $CDCl_3$)



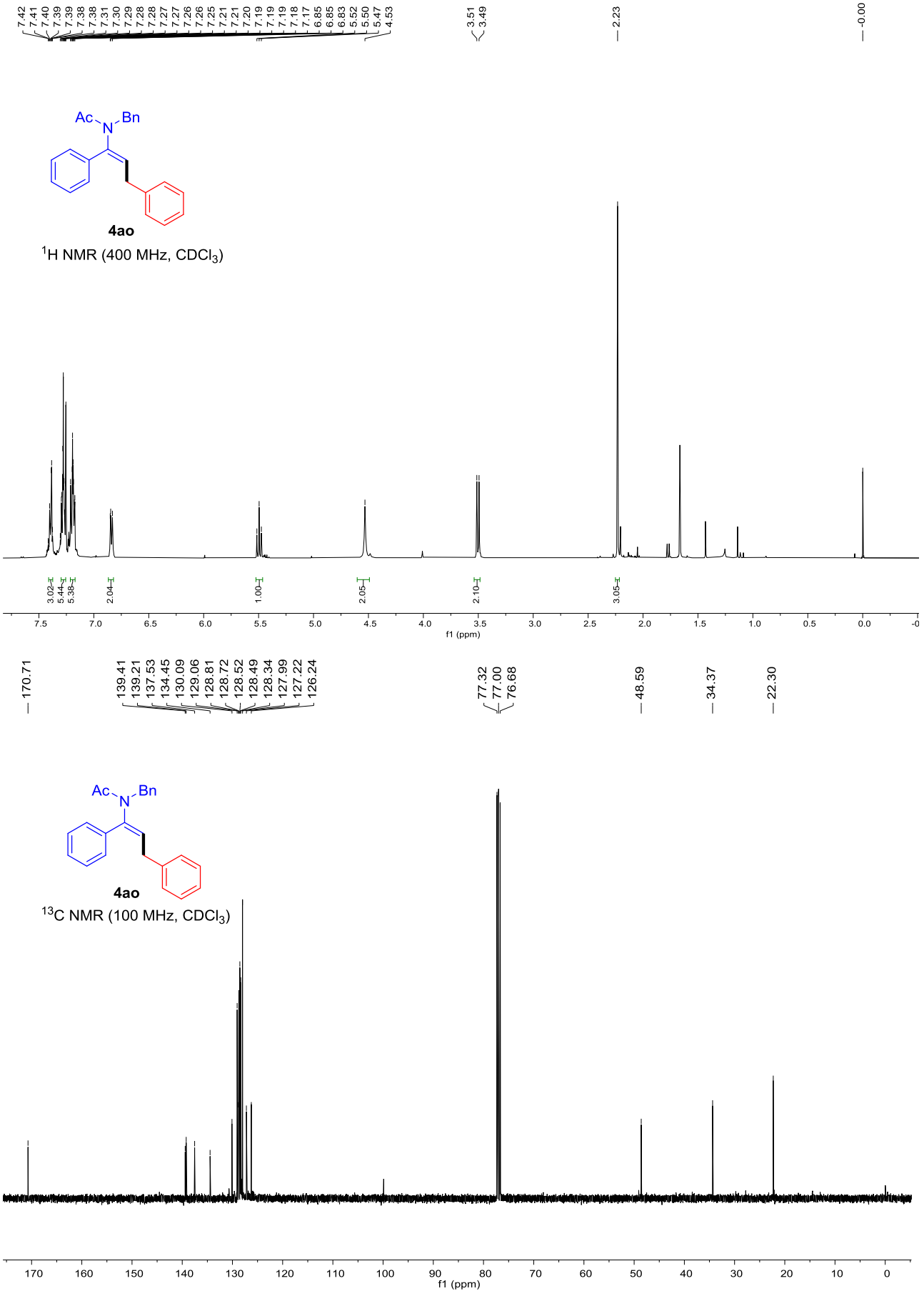


4an

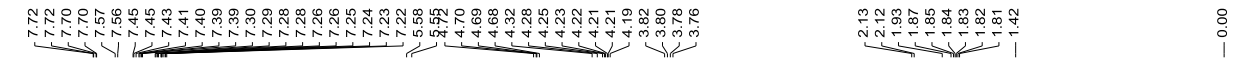
^{13}C NMR (100 MHz, $CDCl_3$)

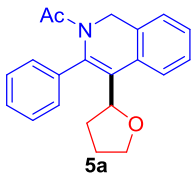


(*E*)-*N*-benzyl-*N*-(1,3-diphenylprop-1-en-1-yl)acetamide (**4ao**)



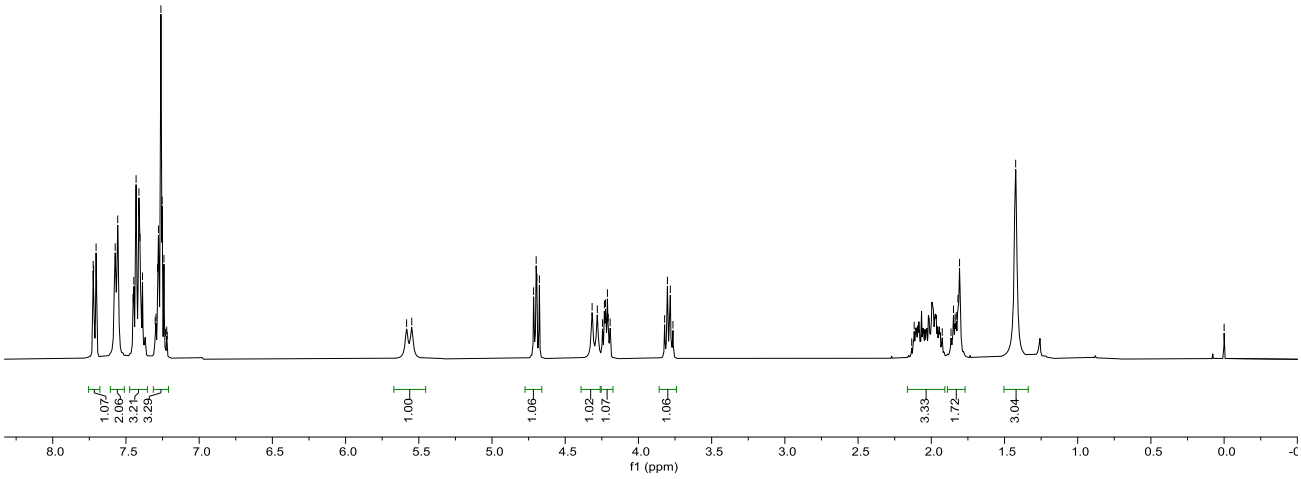
1-(3-phenyl-4-(tetrahydrofuran-2-yl)isoquinolin-2(1*H*)-yl)ethan-1-one (**5a**)

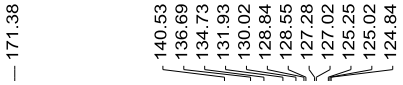


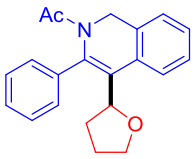


5a

^{1}H NMR (400 MHz, $CDCl_3$)

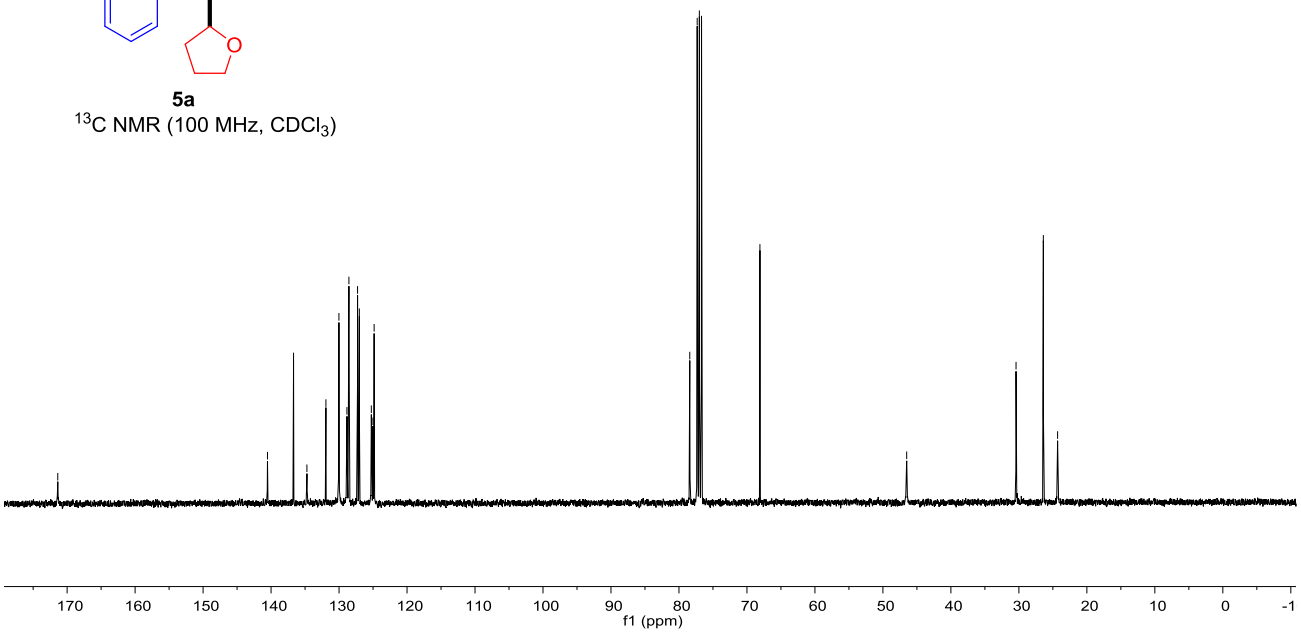




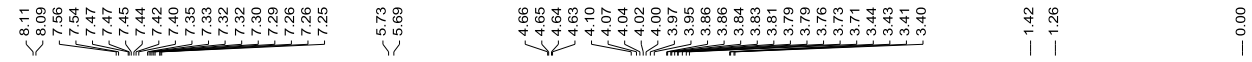


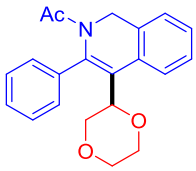
5a

^{13}C NMR (100 MHz, $CDCl_3$)



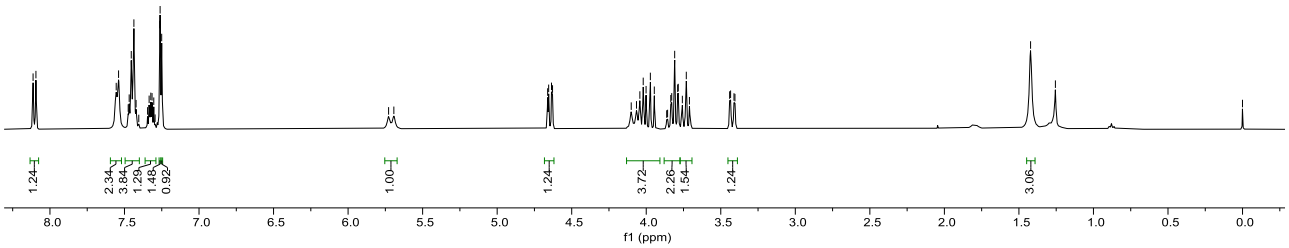
1-(4-(1,4-dioxan-2-yl)-3-phenylisoquinolin-2(1*H*)-yl)ethan-1-one (**5b**)

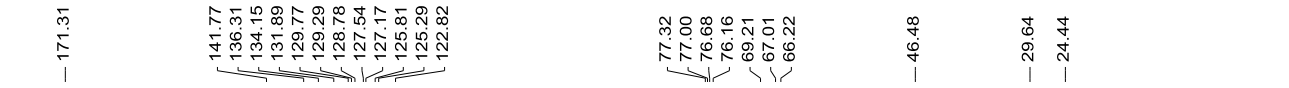


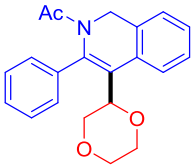


5b

^{1}H NMR (400 MHz, $CDCl_3$)

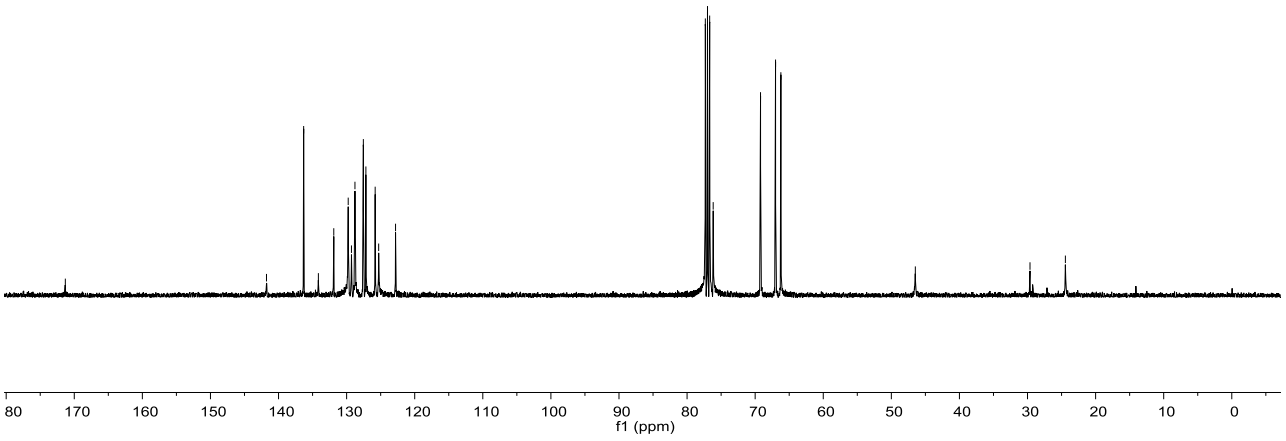




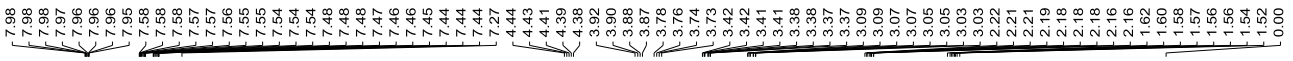


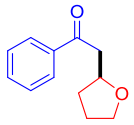
5b

^{13}C NMR (100 MHz, $CDCl_3$)



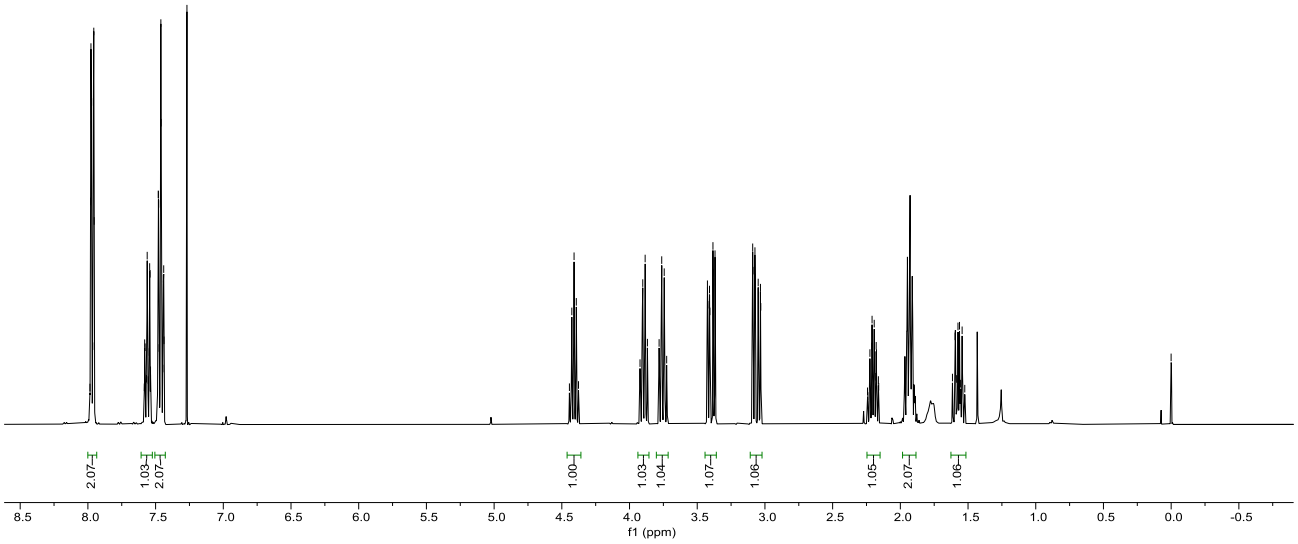
1-phenyl-2-(tetrahydrofuran-2-yl)ethan-1-one (**6**)

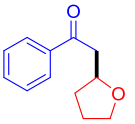




6

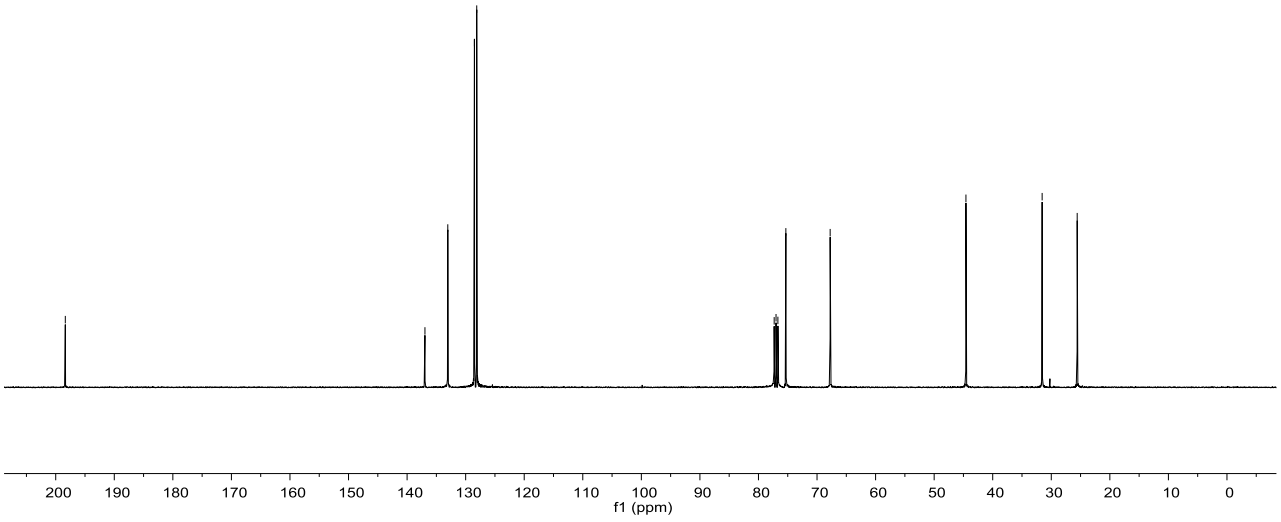
^{1}H NMR (400 MHz, $CDCl_3$)



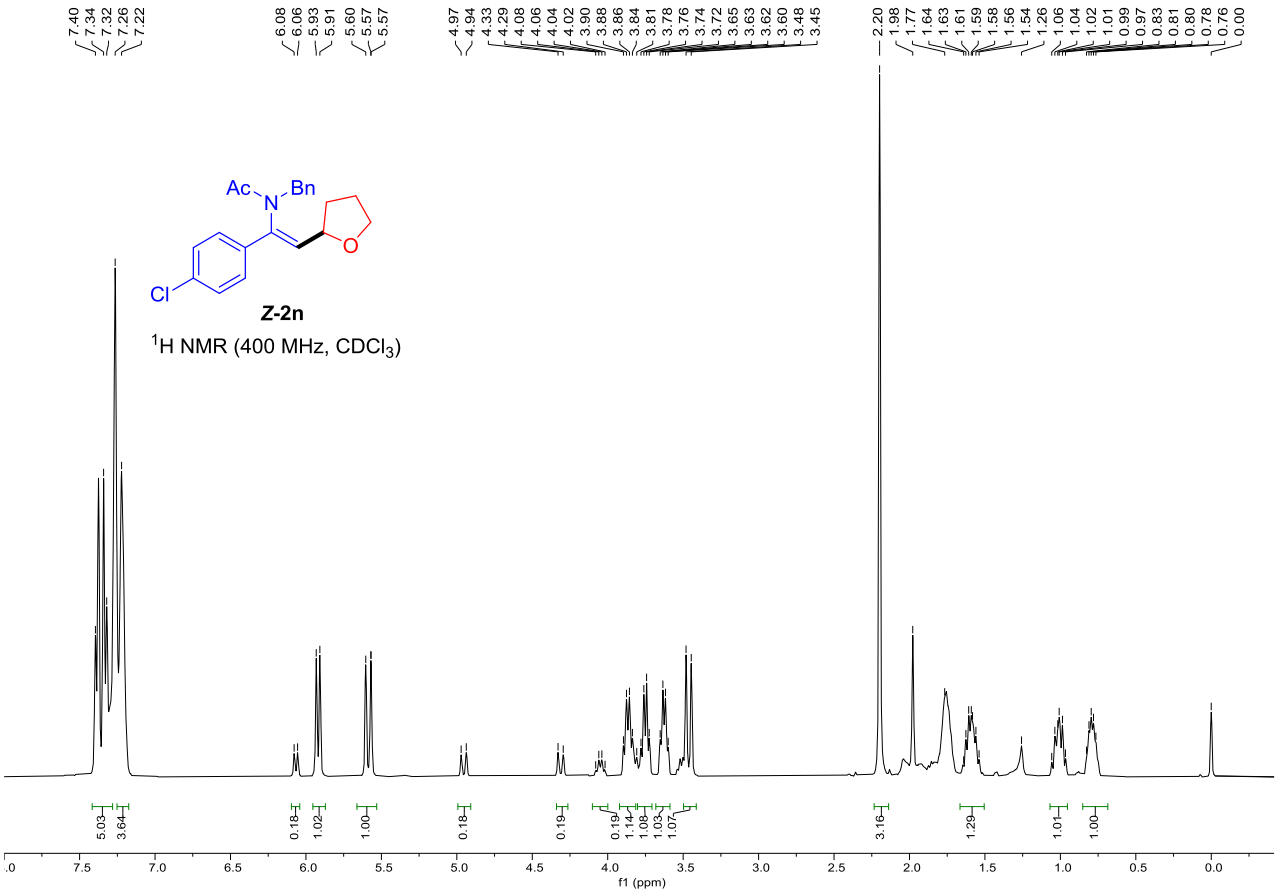


6

^{13}C NMR (100 MHz, $CDCl_3$)

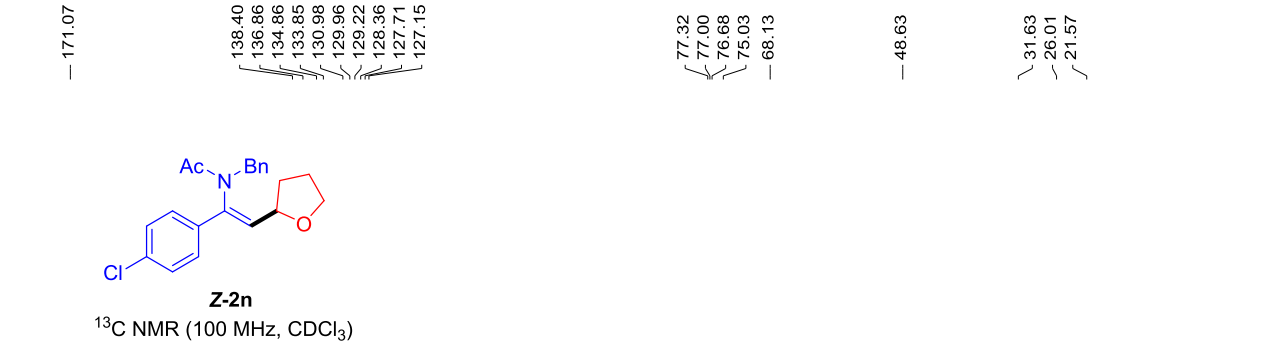


(*Z*)-*N*-benzyl-*N*-(1-(4-chlorophenyl)-2-(tetrahydrofuran-2-yl)vinyl)acetamide (***Z*-2n**)



***Z*-2n**

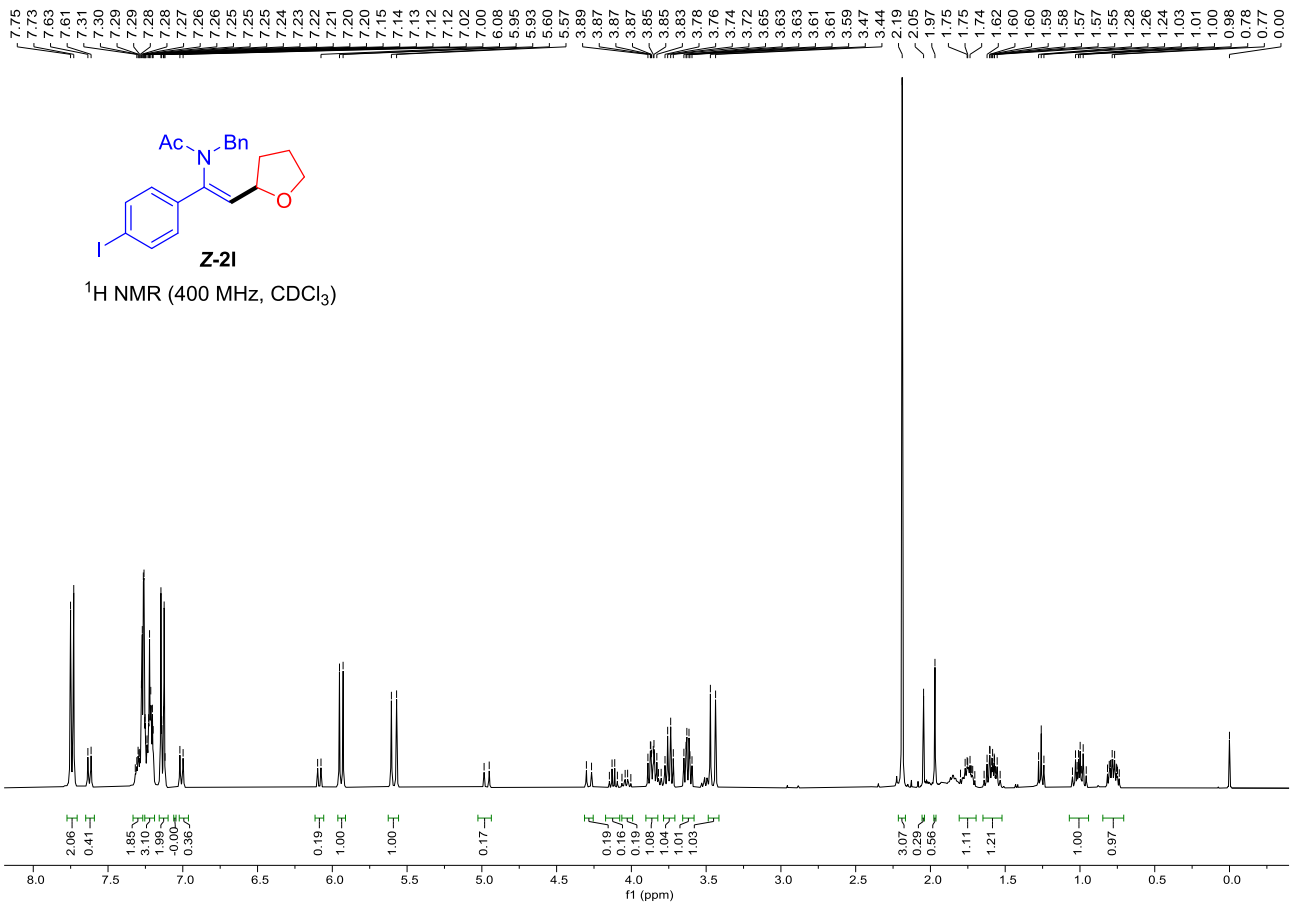
^{1}H NMR (400 MHz, $CDCl_3$)



***Z*-2n**

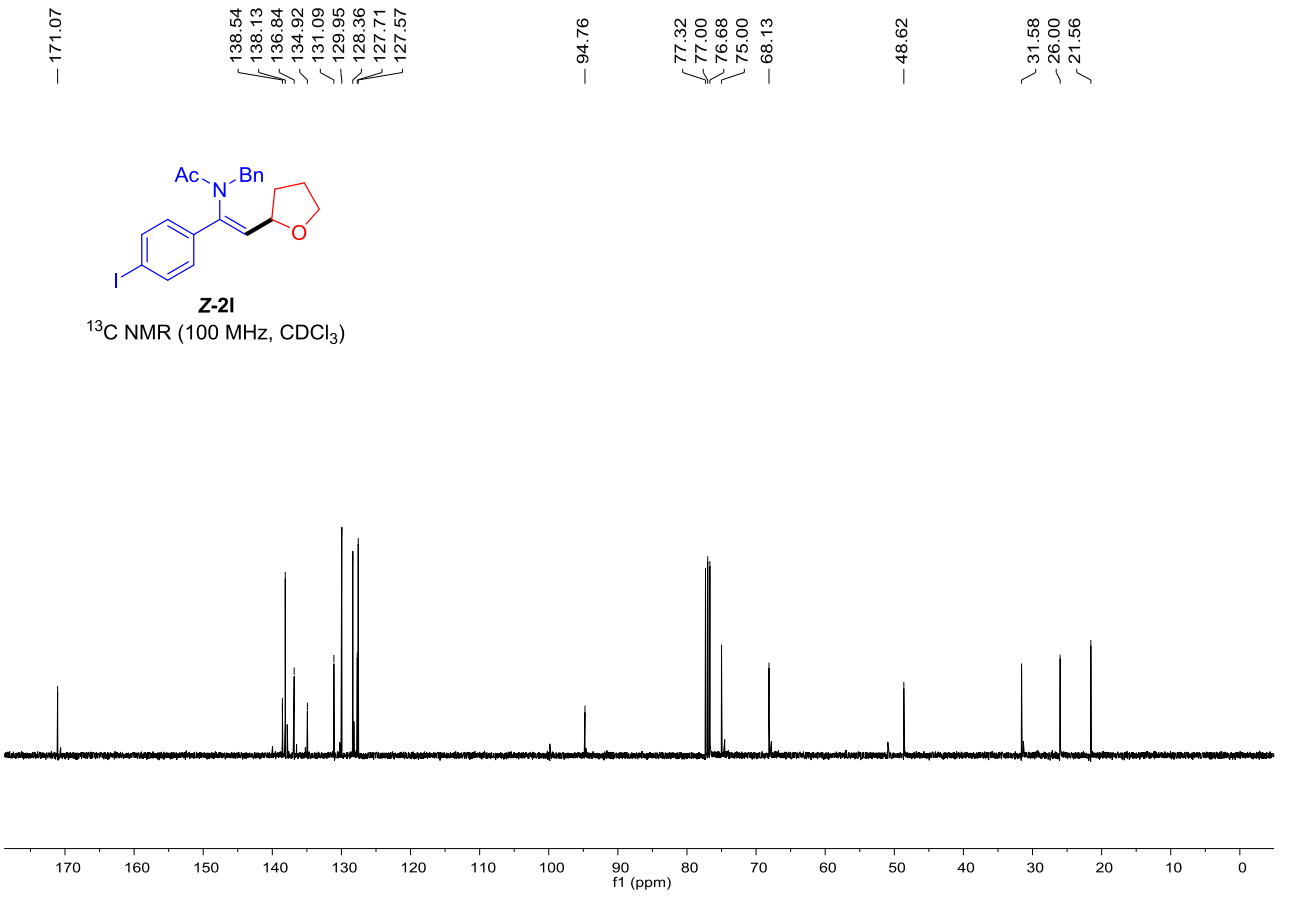
^{13}C NMR (100 MHz, $CDCl_3$)

(*Z*)-*N*-benzyl-*N*-(1-(4-iodophenyl)-2-(tetrahydrofuran-2-yl)vinyl)acetamide (***Z*-2l**)



***Z*-2l**

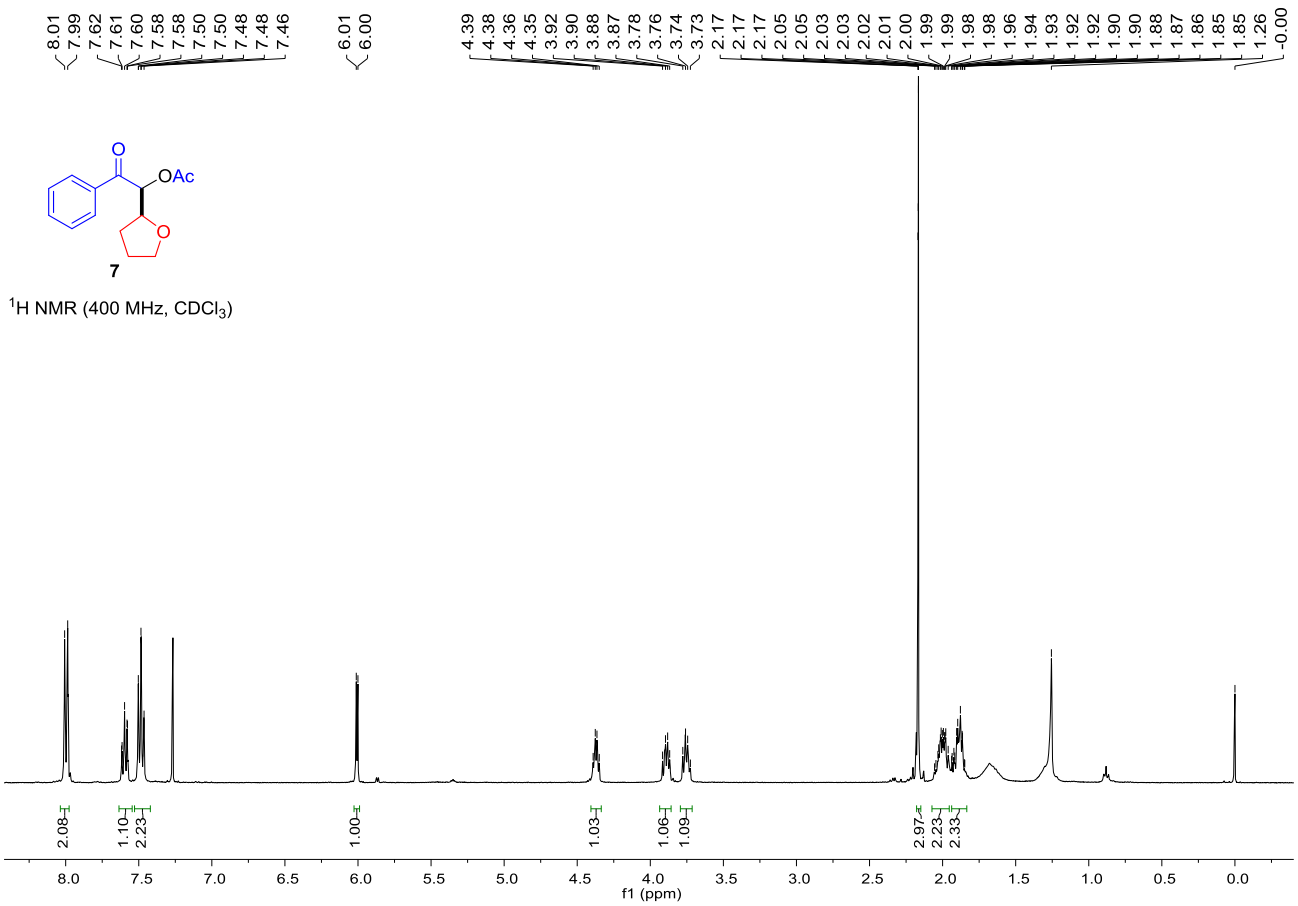
^{1}H NMR (400 MHz, $CDCl_3$)



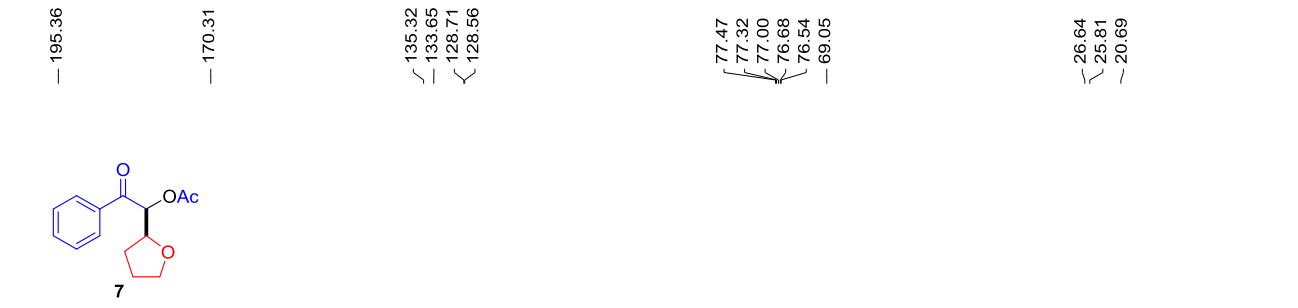
***Z*-2l**

^{13}C NMR (100 MHz, $CDCl_3$)

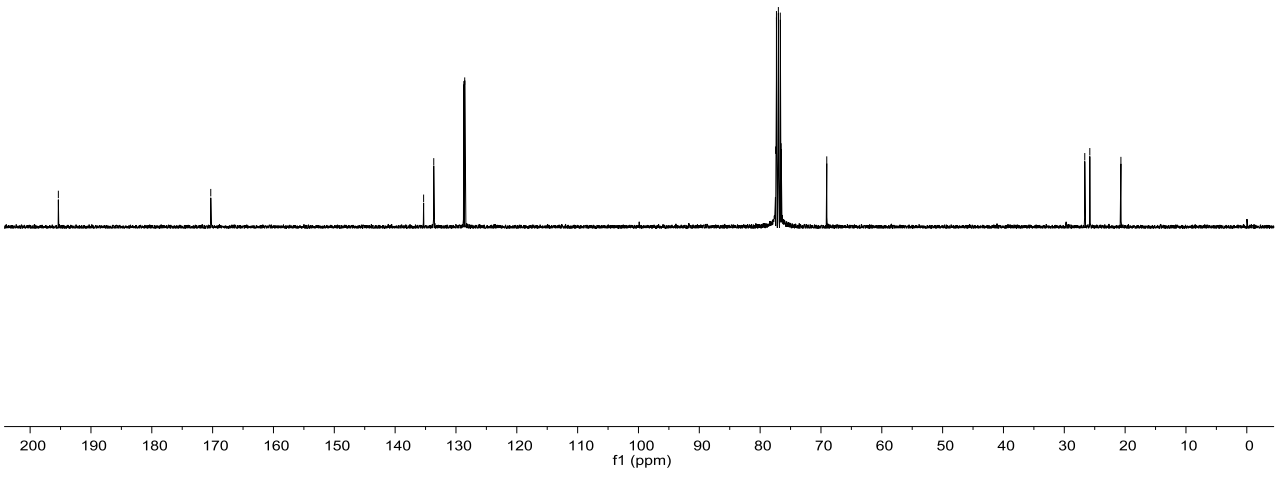
2-oxo-2-phenyl-1-(tetrahydrofuran-2-yl)ethyl acetate (**7**)



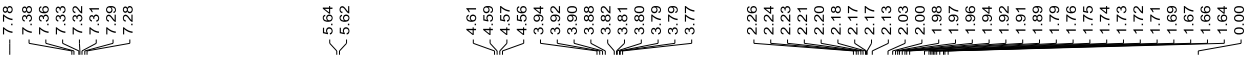
^{1}H NMR (400 MHz, $CDCl_3$)

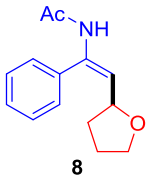


^{13}C NMR (100 MHz, $CDCl_3$)



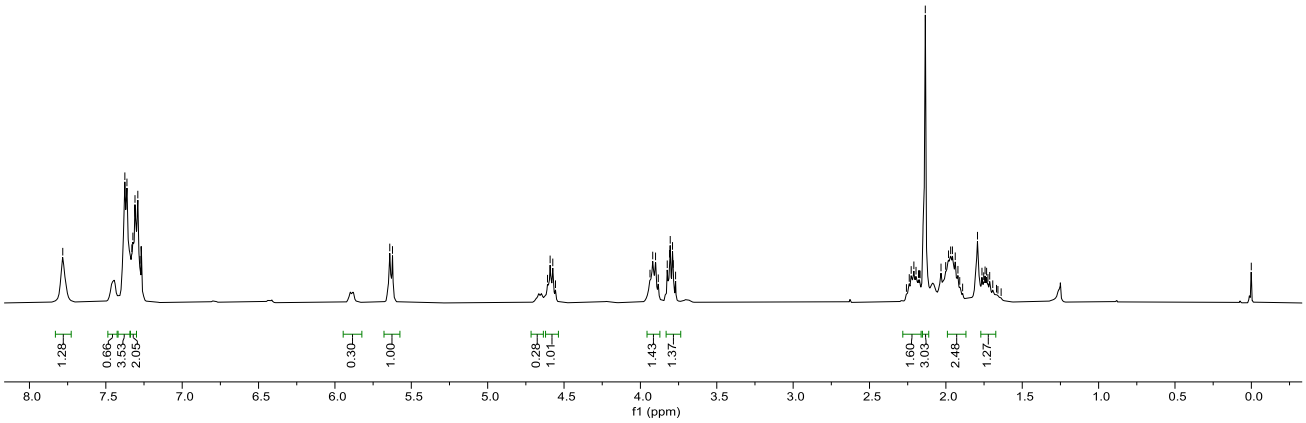
(*E*)-*N*-(1-phenyl-2-(tetrahydrofuran-2-yl)vinyl)acetamide (**8**)

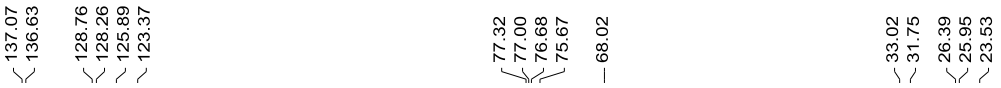


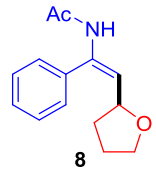


8

^{1}H NMR (400 MHz, $CDCl_3$)







8

^{13}C NMR (100 MHz, $CDCl_3$)