Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Access to α-all-carbon quaternary amides through the hydroamidation of allenes using DIBAL-H and isocyanates

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Supplementary Information

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1. General information

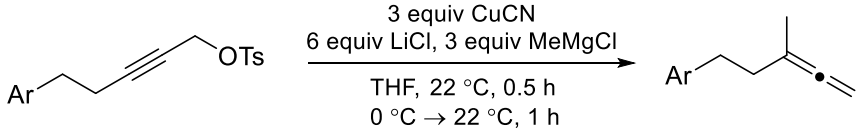
Infrared (IR) spectra were recorded on a ABB MB3000 FT-IR spectrophotometer, and are quoted in wavenumbers (cm^{-1}). Bands are characterized as strong (s), medium (m), and weak (w). ^{1}H NMR spectra were recorded a JEOL JNM-AL400 (400 MHz) spectrometer. Chemical shifts are reported in ppm from tetramethylsilane, with the solvent resonance as the internal standard ($CDCl_3$: δ 7.27 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, m = multiplet), coupling constants (Hz), and integration. ^{13}C NMR spectra were recorded on a JEOL JNM-AL400 (100 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard ($CDCl_3$: δ 77.00 ppm). ^{19}F NMR spectra were recorded on a Spinsolve 80 (75.2 Hz) spectrometer and reported in ppm from CFCl3 and are uncorrected. High-resolution mass spectra (HRMS) were performed at the Korea Basic Science Institute for technical assistance using an electron ionization (EI) or an electrospray ionization (ESI) time-of-flight mass spectrometer.

Unless otherwise noted, all reactions were carried out with distilled solvents under an atmosphere of dry N_2 in oven-dried (130 °C) glassware. Tetrahydrofuran was purified by distillation from Na immediately prior to use. DIBAL-H was purchased from Sigma-Aldrich Corporation and used as received. A variety of isocyanates were purchased from TCI, Alfa Aesar, Sigma-Aldrich Corporation and used as received. All work-up and purification procedures were carried out with reagent grade solvents in air. The NHC-CuCl complex was synthesized according to previously reported experimental procedures.[1]

2. Preparation of substrates

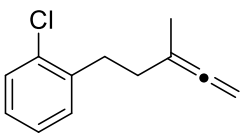
(1) 1,1-Disubsitutited allenes **1a-1m** were prepared according to reported experimental procedures.[2]

- **Representative experimental procedure for the synthesis of 1,1-disubsitutited allene:**

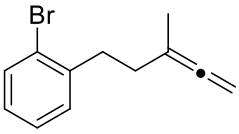


(1) W.-J. Yoo, T. V. Q. Nguyen and S. Kobayashi, *Angew. Chem., Int. Ed.*, 2014, **53**, 10213–10217.

(2) (a) S. Lee, S. Lee and Y. Lee, *Org. Lett*., 2020, **22**, 5806−5810; (b) A. Boreux, K. Indukuri, F. Gagosz and O. Riant, *ACS Catal.*, 2017, **7**, 8200−8204; (c) V. Gobé and X. Guinchard, *Chem. Eur. J.*, 2015, **21**, 8511–8520; (c) G. Mentink, J. H. Van Maarseveen and H. Hiemstra, *Org. Lett.*, 2002, **4**, 3497–3500.



1-Chloro-2-(3-methylpenta-3,4-dien-1-yl)benzene (1i). MeMgCl (3.0 M in THF, 1.50 mL, 4.50 mmol) was added dropwise to a solution of CuCN (403 mg, 4.50 mmol) and LiCl (382 mg, 9.00 mmol) in THF (13 mL) using a syringe at 22 °C under N_2. The solution was stirred for 0.5 h and allowed to cool to 0 °C in an ice bath. Then, a solution of 5-(2-chlorophenyl)pent-2-yn-1-yl 4-methylbenzenesulfonate (523 mg, 1.50 mmol) was added to THF (2 mL). The mixture was allowed to warm to room temperature and stirred for 1 h. Afterward, the resulting solution was allowed to cool to 0 °C, quenched with water (10 mL), and washed with diethyl ether (20 mL × 3). The organic layers were combined, dried over $MgSO_4$, filtered, and concentrated. The crude product was purified using silica gel column chromatography (100% hexanes), and the desired allene **1i** (275 mg, 1.43 mmol, 95%) was obtained as a colorless oil. **IR** (neat): 2978 (m), 2932 (m), 2862 (m), 1960 (m), 1744 (m), 1705 (s), 1443 (m), 1458 (m), 1049 (m), 1041 (m), 849 (s), 748 (s), 679 (s) cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.35 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.24-7.13 (m, 3H), 4.64 (sext, *J* = 3.0 Hz, 2H), 2.87 (t, *J* = 8.0 Hz, 2H), 2.27-2.21 (m, 2H), 1.75 (t, *J* = 3.0 Hz, 3H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 100 MHz): δ 206.1, 139.7, 133.9, 130.3, 129.4, 127.3, 126.7, 97.9, 74.7, 33.4, 31.8, 18.8; **HRMS** (EI) *m/z*: $[M]^+$ Calcd for $C_{12}H_{13}Cl$ 192.0706, Found 192.0700.

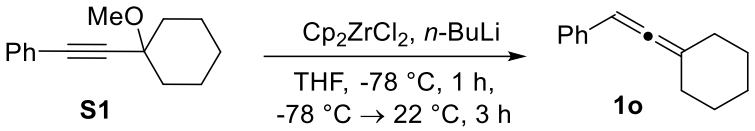


1-Bromo-2-(3-methylpenta-3,4-dien-1-yl)benzene (1j). Compound **1j** was synthesized from 5-(2-bromophenyl)pent-2-yn-1-yl 4-methylbenzenesulfonate (2.00 g, 5.09 mmol) in 90% yield (1.09 g, 4.58 mmol) as a colorless oil. The crude product was purified using silica gel column chromatography (100% hexanes). **IR** (neat): 2932 (m), 2361 (m), 2330 (m), 1960 (m), 1798 (m), 1744 (m), 1705 (m), 1443 (m), 1026 (m), 849 (s), 741 (s), 656 (m), 602 (m) cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.53 (d, *J* = 7.5 Hz, 1H), 7.26-7.21 (m, 2H), 7.09-7.03 (m, 1H), 4.65 (sext, *J* = 3.1 Hz, 2H), 2.87 (t, *J* = 8.2 Hz, 2H), 2.27-2.21 (m, 2H), 1 .76 (t, *J* = 3.0 Hz, 3H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 100 MHz): δ 206.2, 141.4, 132.7, 130.3, 127.5, 127.4, 124.4, 97.9, 74.7, 34.3, 33.5, 18.8; **HRMS** (EI) *m/z*: $[M]^+$ Calcd for $C_{12}H_{13}Br$ 236.0201, Found 236.0193.

(2) 1,1,3-Trisubstituted allenes **1n-1x** were prepared according to reported experimental procedures.[3]

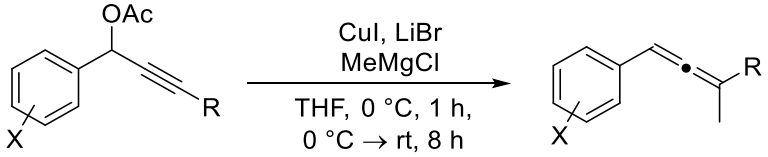
- **Experimental procedure for the synthesis of (2-cyclohexylidenevinyl)benzene (1o):**

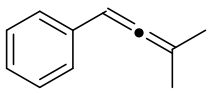
(3) (a) X. D. Vial, J. L. Mascarenas and M. I. Gulias, *Org. Lett.*, 2021, **23**, 5323−5328; (b) J. Eshon, C. R. Landis and J. M. Schomaker, *J. Org. Chem.*, 2017, **82**, 9270−9278; (c) C.-M. Ting, Y.-L. Hsu and R.-S. Liu, *Chem. Commun.*, 2012, **48**, 6577−6579.



n-BuLi (2.5 M in hexanes, 3.14 mL, 7.84 mmol) was added to a solution of Cp_2ZrCl_2 (2.29 g, 7.84 mmol) in THF (37.2 mL) at –78 °C (dry ice/acetone bath) under N_2 flow. After stirring for 1 h at the same temperature, a solution of ((1-methoxycyclohexyl)ethynyl)benzene (**S1**, 1.05 g, 4.90 mmol) in THF (2 mL) was added, and the mixture was allowed to warm to room temperature. The reaction mixture was stirred for 3 h and quenched by adding an aqueous solution of 1 N HCl (3 mL), followed by washing with ethyl ether (20 mL × 3). The organic layers were combined, washed with a saturated aqueous solution of $NaHCO_3$ (20 mL), dried over $MgSO_4$, filtered, and concentrated. The crude product was purified using silica gel column chromatography (100% hexanes), and the desired allene **1o** (704 mg, 3.82 mmol, 78%) was obtained as a colorless oil. This compound has been previously reported, and our experimental spectral data match the previously reported data.[4] **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.32-7.31 (m, 4H), 7.22-7.17 (m, 1H), 6.03-6.02 (m, 1H), 2.32-2.28 (m, 2H), 2.26-2.21 (m, 2H), 1.74-1.58 (m, 6H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 100 MHz): δ 199.6, 136.1, 128.5, 126.5, 126.3, 106.5, 92.3, 31.3, 27.7, 26.1.

▪ **Representative experimental procedure for the synthesis of 1,1,3-trisubsitutited allene:**

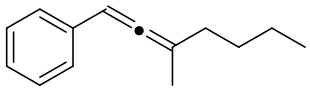




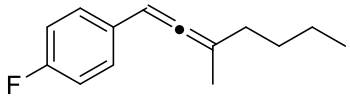
(3-Methylbuta-1,2-dien-1-yl)benzene (1n). MeMgCI (3.0 M in THF, 3.47 mL, 10.4 mmol) was added to a solution of CuI (3.05 g, 16.0 mmol) and LiBr (1.83 g, 21.1 mmol) in THF (24.5 mL) at 0 °C (ice bath) under N_2. The solution was stirred for 1 h before adding a solution of 1-phenylbut-2-yn-1-yl acetate (**S1**, 1.42 g, 7.50 mmol) in THF (2 mL). The reaction mixture was allowed to warm to 22 °C before being stirred for 8 h. The resulting solution was quenched by adding a saturated aqueous solution of Na_2CO_3 (50 mL) and washed with EtOAc (30 mL × 3). The organic layers were combined, dried over $MgSO_4$, filtered, and concentrated. The crude product was purified using silica gel column chromatography (100% hexanes), and the desired allene **1n** (898 mg, 6.23 mmol, 83%) was obtained as a colorless oil. This compound has been previously reported, and our experimental

(4) H. R. Yuan and J. B. Wang, *Org. Chem. Front.*, 2022, **9**, 5899−5905.

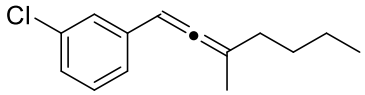
spectral data match the previously reported data.[3a] **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.46 (d, *J* = 4.0 Hz, 4H), 7.37-7.33 (m, 1H), 6.20-6.19 (m, 1H), 2.01 (s, 3H), 2.00 (s, 3H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 100 MHz): δ 203.0, 135.8, 128.3, 126.5, 126.3, 98.9, 92.5, 20.1.



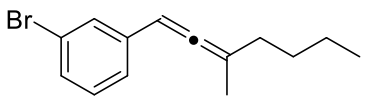
(3-Methylhepta-1,2-dien-1-yl)benzene (1p). This compound has been previously reported, and the spectral data match the described data.[3a] **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.31-7.28 (m, 4H), 7.20-7.18 (m, 1H), 6.06 (sext, *J* = 2.8 Hz, 1H), 2.11-2.07 (m, 2H), 1.82 (d, *J* = 2.7 Hz 3H), 1.50-1.44 (m, 2H), 1.40-1.34 (m, 2H), 0.91 (t, *J* = 7.1 Hz, 3H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 100 MHz): 202.6, 136.1, 128.5, 126.5, 126.3, 103.8, 93.7, 33.8, 29.7, 22.4, 18.8, 14.0.



1-Fluoro-4-(3-methylhepta-1,2-dien-1-yl)benzene (1q). Compound **1q** was synthesized from 1-(4-fluorophenyl)hept-2-yn-1-yl acetate (2.01 g, 8.10 mmol) in 84% yield (1.39 g, 6.80 mmol) as a colorless oil. The crude product was purified using silica gel column chromatography (100% hexanes). **IR** (neat): 2962 (w), 2932 (w), 2870 (w), 2361 (m), 1736 (m), 1605 (s), 1504 (w), 1458 (m), 1373 (s), 1296 (w), 1227 (mw), 1157 (s), 1095 (s), 964 (m), 849 (s) cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.27-7.24 (m, 2H), 7.03-6.99 (m, 2H), 6.06 (sext, *J* = 2.8 Hz, 1H), 2.12 (td, *J* = 7.5, 2.7 Hz, 2H), 1.84 (d, *J* = 3.2 Hz, 3H), 1.52-1.46 (m, 2H), 1.43-1.37 (m, 2H), 0.94 (t, *J* = 7.3 Hz, 3H); **^{13}C{1H} NMR** ($CDCl_3$, 100 MHz): δ 202.4, 162.8, 160.4 (d, $J_{C\text{-}F}$ = 244.7 Hz), 132.0, 127.8 (d, $J_{C\text{-}F}$ = 7.7 Hz), 115.3 (d, $J_{C\text{-}F}$ = 22.2 Hz), 104.0, 92.8, 33.8, 29.7, 22.4, 18.8, 13.9; ^{19}F NMR ($CDCl_3$, 75.2 Hz): δ -114.40; **HRMS** (EI) *m/z*: $[M]^+$ Calcd for $C_{14}H_{17}F$ 204.1314, Found 204.1309.

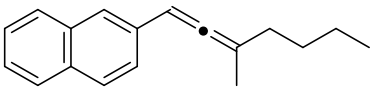


1-Chloro-3-(3-methylhepta-1,2-dien-1-yl)benzene (1r). Compound **1r** was synthesized from 1-(3-chlorophenyl)hept-2-yn-1-yl acetate (741 mg, 2.80 mmol) in 93% yield (574 mg, 2.60 mmol) as a colorless oil. The crude product was purified using silica gel column chromatography (100% hexanes). **IR** (neat): 3055 (w), 2955 (m), 2932 (w), 2862 (m), 2361 (m), 1952 (m), 1736 (w), 1589 (s), 1474 (s), 1443 (s), 1373 (s), 1273 (s), 1196 (s), 1119 (s), 1080 (s), 879 (s), 687 (s) cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.27-7.25 (m, 1H), 7.23-7.19 (m, 1H), 7.14-7.12 (m, 2H), 6.00 (sext, *J* = 2.7 Hz, 1H), 2.11-2.06 (m, 2H), 1.81 (d, *J* = 2.3 Hz, 3H), 1.50-1.42 (m, 2H), 1.41-1.34 (m, 2H), 0.90 (t, *J* = 6.9 Hz, 3H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 100 MHz): δ 203.0, 138.2, 134.4, 129.6, 126.3, 124.6, 104.4, 92.9, 33.7, 29.6, 22.4, 18.7, 13.9; **HRMS** (EI) *m/z*: $[M]^+$ Calcd for $C_{14}H_{17}Cl$ 220.1019, Found 220.1014.

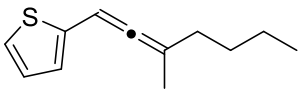


1-Bromo-3-(3-methylhepta-1,2-dien-1-yl)benzene (1s): Compound **1s** was synthesized from 1-(3-bromophenyl)hept-2-yn-1-yl acetate (928 mg, 3.00 mmol) in 81% yield (644 mg, 2.43 mmol) as a colorless oil. The crude product was purified using

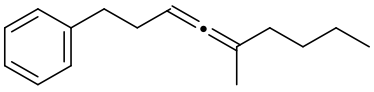
silica gel column chromatography (100% hexanes).This compound has been previously reported, and the spectral data match the described data.[5] **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.41 (s, 1H), 7.31-7.27 (m, 1H), 7.19-7.13 (m, 2H), 5.99 (sext, *J* = 2.9 Hz, 1H), 2.12-2.06 (m, 2H), 1.82 (d, *J* = 2.7 Hz, 3H), 1.50-1.42 (m, 2H), 1.43-1.33 (m, 2H), 0.91 (t, *J* = 7.1 Hz, 3H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 100 MHz): 203.0, 138,5, 130.0, 129.2, 129.1, 125.1, 122.7, 104.5, 92.7, 33.6, 29.5, 22.4, 18.8, 13.9.



2-(3-Methylhepta-1,2-dien-1-yl)naphthalene (1t). Compound **1t** was synthesized from 1-(naphthalen-2-yl)hept-2-yn-1-yl acetate (841 mg, 3.00 mmol) in 90% yield (638 mg, 2.70 mmol) as a colorless oil. The crude product was purified using silica gel column chromatography (100% hexanes). **IR** (neat): 3055 (w), 2970 (m), 2932 (w), 2862 (m), 2361 (m), 2168 (m), 2160 (w), 1952 (s), 1744 (s), 1626 (s), 1597 (s), 1443 (s), 1366 (s), 1211 (s), 1119 (s), 1072 (m), 1018 (m), 949 (s), 895 (s), 864 (s), 818 (s), 741 (s) cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.80-7.75 (m, 3H), 7.63 (d, *J* = 1.4 Hz, 1H), 7.50-7.39 (m, 3H), 6.24 (sext, *J* = 2.8 Hz, 1H), 2.16-2.11 (m, 2H), 1.86 (d, *J* = 2.7 Hz, 3H), 1.55-1.47 (m, 2H), 1.44-1.34 (m, 2H), 0.91 (t, *J* = 7.3 Hz, 3H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 100 MHz): δ 203.3, 133.8, 133.7, 132.4, 128.0, 127.7, 127.6, 126.1, 125.3, 125.0, 124.8, 104.0, 94.1, 33.8, 29.7, 22.5, 18.9, 13.9; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{18}H_{21}$ 237.1643, Found 237.1640.



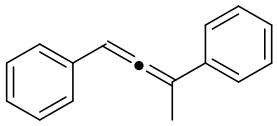
2-(3-Methylhepta-1,2-dien-1-yl)thiophene (1u). Compound **1u** was synthesized from 1-(thiophen-2-yl)hept-2-yn-1-yl acetate (236 mg, 1.00 mmol) in 77% yield (148 mg, 0.770 mmol) as a colorless oil. The crude product was purified using silica gel column chromatography (100% hexanes). **IR** (neat): 3070 (w), 2955 (s), 2924 (s), 2870 (m), 2361 (m), 1651 (m), 1458 (w), 1366 (m), 1296 (m), 1227 (m), 895 (s), 694 (s) cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.13 (dd, *J* = 5.0, 0.9 Hz, 1H), 7.00 (dd, *J* = 5.3, 3.4 Hz, 1H), 6.90-6.88 (m, 1H), 6.30 (sext, *J* = 2.8 Hz, 1H), 2.11 (td, *J* = 7.3, 2.7 Hz, 2H), 1.83 (d, *J* = 2.7 Hz, 3H), 1.55-1.47 (m, 2H), 1.45-1.38 (m, 2H), 0.94 (t, *J* = 7.1 Hz, 3H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 100 MHz): δ 202.0, 141.2, 127.3, 123.7,123.6, 104.2, 88.1, 33.9, 29.6, 22.4, 18.9, 13.9; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{12}H_{17}S$ 193.1051, Found 193.1054.



(5-Methylnona-3,4-dien-1-yl)benzene (1w). Compound **1w** was synthesized from 1-phenylnon-4-yn-3-yl acetate (698mg, 2.70 mmol) in 84% yield (487 mg, 2.27 mmol) as a colorless oil. The crude product was purified using silica gel column chromatography (100% hexanes). This compound has been previously reported, and the spectral data

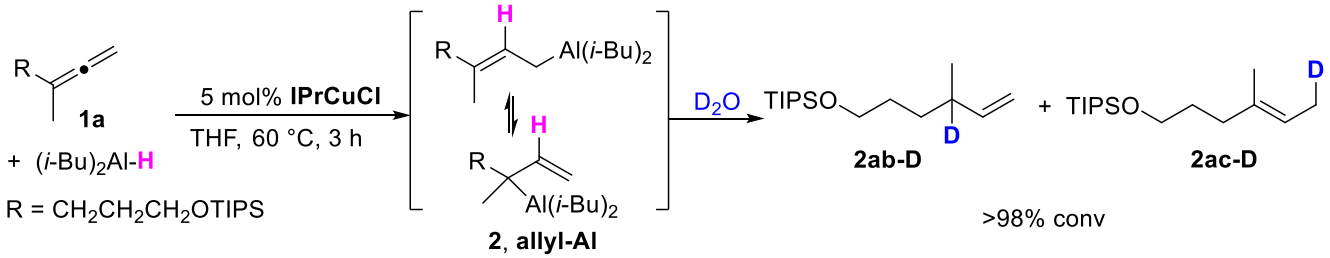
(5) J. Q. Kuang, X. J. Tang and S. M. Ma, *Org. Chem. Front.,* 2015, **2**, 470−475.

match the described data.[6] **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.34-7.30 (m, 2H), 7.25-7.20 (m, 3H), 5.10 (qq, *J* = 6.2, 2.8 Hz, 1H), 2.76 (t, *J* = 7.8 Hz, 2H), 2.36-2.31 (m, 2H), 1.96-1.92 (m, 2H), 1.67 (d, *J* = 2.7 Hz, 3H), 1.43-1.33 (m, 4H), 0.95 (t, *J* = 7.1 Hz, 3H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 100 MHz): 201.4, 142.1, 128.5, 128.2, 125.7, 99.8, 89.4, 35.6, 33.7, 31.1, 29.7, 22.3, 19.2, 14.0.



Buta-1,2-diene-1,3-diyldibenzene (1x). Compound **1x** was synthesized from 1,3-diphenylprop-2-yn-1-yl acetate (250 mg, 1.00 mmol) in 96% yield (198 mg, 0.960 mmol) as a yellow oil. The crude product was purified using silica gel column chromatography (100% hexanes). This compound has been previously reported, and the spectral data match the described data.[4] **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.56-7.54 (m, 2H), 7.44-7.37 (m, 6H), 7.33-7.27 (m, 2H), 6.56 (q, *J* = 2.7 Hz, 1H), 2.31 (d, *J* = 2.7 Hz, 3H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 100 MHz): 206.8, 136.3, 134.5, 128.7, 128.4, 127.0, 126.9 126.8, 125.8, 104.5, 96.6, 16.7.

3. Cu-Catalyzed hydroalumination of allene 1a with diisobutylaluminum hydride

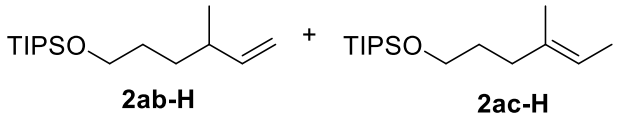


The formation of allylaluminum reagent **2** was deduced by analysis of ^{1}H NMR spectra of protonated and deuterated products. In ^{1}H NMR spectra, it was found that the ratio of regioisomers varied depending upon the quenching conditions (1 N HCl quenching: **2ab-H**:**2ac-H**=>98:<2, D_2O quenching: **2ab-D**:**2ac-D**=50:50).

In a glove box, **IPrCuCl** (7.32 mg, 1.50×10^{-2} mmol) was added to a vial (8 mL) charged with a magnetic stir bar. Then, the vial was sealed with a cap (phenolic open-top cap with gray PTFE/silicone) and removed from the glove box. After purging the vial with N_2 gas for 5 min, THF (1.0 mL) and diisobutylaluminum hydride (54.0 μL, 0.300 mmol) were added. The mixture was premixed for 10 min and a solution of triisopropyl((4-methylhexa-4,5-dien-1-yl)oxy)silane (**1a**, 80.6 mg, 0.300 mmol) in THF (0.5 mL) was added. The reaction mixture was stirred at 60 °C on a preheated heating block for 3 h.

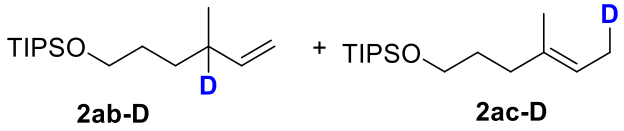
(6) R. J. Sharma and L. J. Williams, *Org. Lett.*, 2013, **15**, 2202−2205.

Afterward, the reaction solution was quenched by adding an aqueous solution of 1 N HCl (1 mL), followed by washing with ethyl acetate (1 mL × 3). The organic layers were combined, dried over $MgSO_4$, filtered, and concentrated in vacuo. The crude product was purified using silica gel column chromatography (100% hexanes) to afford the *protonated* product **2a-H** (**2ab-H**:**2ac-H**=>98:<2, 79.5 mg, 0.294 mmol, 98%) as a colorless oil.



2ab-H **2ac-H**

Triisopropyl((4-methylhex-5-en-1-yl)oxy)silane (2ab-H). **IR** (neat): 3070 (w), 2947 (s), 2870 (s), 2731 (w), 1636 (w), 1466 (m), 1389 (w), 1250 (w), 1095 (s), 1003 (m), 895 (s), 787 (m), 679 (s) cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 5.70 (ddd, *J* = 17.4, 10.1, 7.3 Hz, 1H), 4.99-4.90 (m, 2H), 3.67 (t, *J* = 6.6 Hz, 2H), 2.13 (spt, *J* = 6.9 Hz, 1H), 1.60-1.49 (m, 2H), 1.39-1.31 (m, 2H), 1.12-1.04 (m, 21H), 1.00 (d, *J* = 6.9 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 144.7, 112.5, 63.5, 37.6, 32.7, 30.7, 20.2, 18.0, 11.9; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{16}H_{35}OSi$ 271.2457, Found 271.2439.



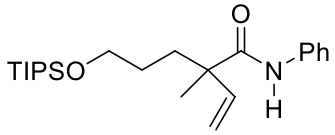
2ab-D **2ac-D**

Triisopropyl((4-methylhex-5-en-1-yl-4-*d*)oxy)silane (2a-D). The reaction was quenched by adding D_2O and washed with EtOAc (2 x 1 mL). The organic layers were combined, dried over $MgSO_4$, filtered, and concentrated in vacuo. The crude product was purified using silica gel column chromatography (100% hexanes) to afford the *deuterated* product **2a-D** (**2ab-D**:**2ac-D**=1:1, 80.0 mg, 0.295 mmol, 98%) as a colorless oil. **IR** (neat): 3070 (w), 2947 (s), 2870 (s), 2731 (w), 1636 (w), 1466 (m), 1389 (w), 1250 (w), 1111 (s), 1003 (m), 879 (s), 787 (w), 679 (s) cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$), a 1:1 mixture of regioisomers: δ 5.70 (dd, *J* = 17.2, 10.3 Hz, 0.5H), 5.22 (t, *J* = 6.4 Hz, 0.5H), 4.99-4.90 (m, 1H), 3.69-3.64 (m, 2H), 2.12-2.02 (m, 1H), 1.69-1.61 (m, 2.5H), 1.58-1.50 (m, 2H), 1.36-1.32 (m, 1H), 1.14-1.04 (m, 21H), 0.99 (s, 1.5H); **^{13}C NMR** (100 MHz, $CDCl_3$), a 1:1 mixture of regioisomers: δ 144.7, 135.6, 118.2, 112.4, 63.5, 63.1, 35.8, 32.6, 31.4, 31.2, 30.6, 27.7, 23.4, 20.1, 18.0, 15.6, 12.0, 11.9; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{16}H_{34}DOSi$ 272.2520, Found 275.2503.

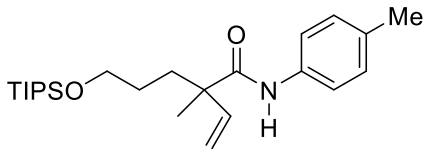
4. General procedure for the synthesis of β,γ-unsaturated α-quaternary amides

In a glove box, **IPrCuCl** (7.32 mg, 1.50×10^{-2} mmol) was added to a vial (8 mL) charged with a magnetic stir bar. Then, the vial was sealed with a cap (phenolic open-top cap with gray PTFE/silicone) and removed from the glove box. After purging the vial with N_2 gas for 5 min, THF (1.0 mL) and diisobutylaluminum hydride (54.0 µL, 0.300 mmol) were added. The mixture was premixed for 10 min and a solution of triisopropyl((4-methylhexa-4,5-dien-1-yl)oxy)silane (**1a**, 80.6 mg, 0.300 mmol) in THF (0.5 mL) was added. The reaction mixture was stirred at 60 °C on a preheated heating block for 3 h. Phenyl isocyanate (**3a**, 28.0 µL, 0.250 mmol) was added via a syringe to the solution, which was stirred at 60 °C for an additional 2 h. Afterward, the reaction solution was quenched by adding an aqueous solution of 1 N HCl (1 mL), followed by washing with ethyl acetate (1 mL × 3). The organic layers were combined, dried over $MgSO_4$, filtered, and concentrated in vacuo. The crude product was purified using silica gel column chromatography (EtOAc:hexanes = 1:20) to produce the desired product **4aa** (95.6 mg, 0.245 mmol, 98% yield) as a colorless oil.

5. Characterization data for all products

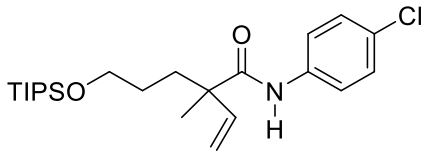


2-Methyl-*N*-phenyl-5-((triisopropylsilyl)oxy)-2-vinylpentanamide (4aa). **IR** (neat): 2939 (m), 2862 (m), 1666 (m), 1597 (m), 1520 (s), 1443 (s), 1381 (m), 1311 (m), 1242 (m), 1103 (s), 879 (m), 687 (s) cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.50 (d, *J* = 8.2 Hz, 2H), 7.47 (br s, 1H), 7.31 (t, *J* = 8.0 Hz, 2H), 7.10 (t, *J* = 7.3 Hz, 1H), 6.12 (dd, *J* =17.6, 10.7 Hz, 1H), 5.41 (d, *J* = 10.5 Hz, 1H), 5.39 (d, *J* = 17.9 Hz, 1H), 3.70 (t, *J* = 6.4 Hz, 2H), 1.89-1.81 (m, 2H), 1.61-1.54 (m, 2H), 1.37 (s, 3H) 1.08-1.05 (m, 21H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 100 MHz): δ 173.6, 141.9, 137.9, 128.8, 124.1, 119.7, 116.4, 63.4, 49.5, 34.1, 27.9, 21.8, 18.0, 11.9; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{23}H_{40}NO_2Si$ 390.2828, Found 390.2826.

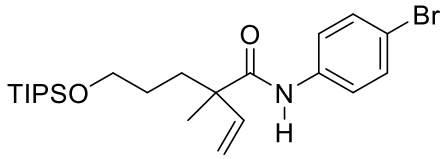


2-Methyl-*N*-(*p*-tolyl)-5-((triisopropylsilyl)oxy)-2-vinylpentanamide (4ab). Compound **4ab** was synthesized from triisopropyl((4-methylhexa-4,5-diene-1-yl)oxy)silane (**1a**, 80.6 mg, 0.300 mmol) and

p-tolyl isocyanate (**3b**, 32.0 μL, 0.250 mmol) in 95% yield (95.9 mg, 0.238 mmol) as a light yellow solid. The crude product was purified using silica gel column chromatography (EtOAc:hexanes = 1:20). **mp** 40-41 °C; **IR** (neat): 3317 (w), 2939 (m), 2870 (m), 1659 (s), 1605 (s), 1520 (s), 1466 (m), 1404 (m), 1319 (m), 1242 (m), 1188 (w), 1103 (s), 818 (s), 679 (s) cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.44 (br s, 1H), 7.37 (d, *J* = 8.7 Hz, 2H), 7.11 (d, *J* = 8.7 Hz, 2H), 6.11 (dd, *J* = 17.6, 10.7 Hz, 1H), 5.39 (d, *J* = 11.0 Hz, 1H), 5.38 (d, *J* = 17.4 Hz, 1H), 3.70 (t, *J* = 6.4 Hz, 2H), 2.31 (s, 3H), 1.87-1.80 (m, 2H), 1.58-1.53 (m, 2H), 1.36 (s, 3H), 1.07-1.03 (m, 21H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 100 MHz): δ 173.5, 141.8, 135.2, 133.7, 129.3, 119.7, 116.5, 63.4, 49.4, 34.0, 27.9, 21.8, 20.8, 18.0, 11.8; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{24}H_{42}NO_2Si$ 404.2985, Found 404.2986.

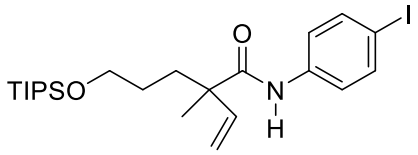


***N*-(4-Chlorophenyl)-2-methyl-5-((triisopropylsilyl)oxy)-2-vinylpentanamide (4ac)**. Compound **4ac** was synthesized from triisopropyl((4-methylhexa-4,5-diene-1-yl)oxy)silane (**1a**, 80.6 mg, 0.300 mmol) and 4-chlorophenyl isocyanate (**3c**, 38.4 mg, 0.250 mmol) in 94% yield (100 mg, 0.236 mmol) as a white solid. The crude product was purified using silica gel column chromatography (EtOAc:hexanes = 1:20). **mp** 109-110 °C; **IR** (neat): 3317 (w), 2947 (m), 2870 (m), 1659 (s), 1597 (m), 1528 (m), 1497 (m), 1389 (m), 1304 (m), 1242 (m), 1095 (s), 995 (m), 825 (s), 679 (s) cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.45 (br s, 1H), 7.42 (d, *J* = 8.7 Hz, 2H), 7.23 (d, *J* = 8.7 Hz, 2H), 6.08 (dd, *J* = 17.6, 10.7 Hz, 1H), 5.37 (dd, *J* = 17.4, 10.1 Hz, 2H), 3.68 (t, *J* = 6.4 Hz, 2H), 1.89-1.74 (m, 2H), 1.57-1.51 (m, 2H), 1.34 (s, 3H), 1.10-0.97 (m, 21H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 100 MHz): δ 173.7, 141.7, 136.5, 129.1, 128.8, 120.9, 116.7, 63.4, 49.5, 34.1, 27.9, 21.8, 18.0, 11.9; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{23}H_{39}ClNO_2Si$ 424.2439, Found 424.2438.

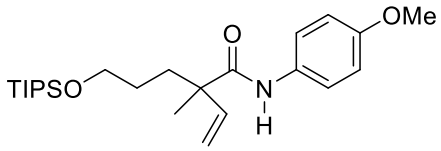


***N*-(4-Bromophenyl)-2-methyl-5-((triisopropylsilyl)oxy)-2-vinylpentanamide (4ad)**. Compound **4ad** was synthesized from triisopropyl((4-methylhexa-4,5-diene-1-yl)oxy)silane (**1a**, 80.6 mg, 0.300 mmol) and 4-bromophenyl isocyanate (**3d**, 49.2 mg, 0.250 mmol) in 95% yield (111 mg, 0.238 mmol) as a white solid. The crude product was purified using silica gel column chromatography (EtOAc:hexanes = 1:20). **mp** 128-129 °C; **IR** (neat): 3294 (w), 2939 (m), 2862 (m), 1659 (s), 1589 (m), 1520 (s), 1489 (s), 1389

(m), 1311 (m), 1242 (m), 1103 (s), 918 (m), 825 (s), 679 (s) cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.46 (br s, 1H), 7.43-7.38 (m, 4H), 6.10 (dd, *J* = 17.6, 10.7 Hz, 1H), 5.40 (d, *J* = 10.5 Hz, 1H), 5.38 (d, *J* = 17.4 Hz, 1H), 3.70 (t, *J* = 6.4 Hz, 2H), 1.91-1.76 (m, 2H), 1.59-1.51 (m, 2H), 1.36 (s, 3H), 1.12-1.00 (m, 21H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 100 MHz): δ 173.7, 141.7, 137.0, 131.8, 121.2, 116.7, 116.7, 63.4, 49.6, 34.1, 27.9, 21.8, 18.0, 11.9; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{23}H_{39}BrNO_2Si$ 468.1933, Found 468.1931.

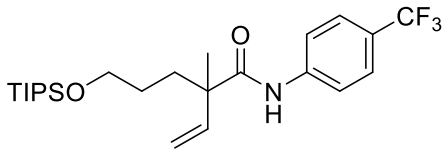


***N*-(4-Iodophenyl)-2-methyl-5-((triisopropylsilyl)oxy)-2-vinylpentanamide (4ae)**. Compound **4ae** was synthesized from triisopropyl((4-methylhexa-4,5-diene-1-yl)oxy)silane (**1a**, 80.6 mg, 0.300 mmol) and 4-iodophenyl isocyanate (**3e**, 61.3 mg, 0.250 mmol) in 92% yield (119 mg, 0.231 mmol) as a white solid. The crude product was purified using silica gel column chromatography (EtOAc:hexanes = 1:20). **mp** 131-132 °C; **IR** (neat): 3310 (w), 2939 (m), 2870 (m), 1659 (s), 1589 (m), 1520 (s), 1489 (s), 1389 (m), 1311 (m), 1242 (m), 1103 (s), 879 (m), 818 (s), 679 (s) cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.57 (d, *J* = 9.1 Hz, 2H), 7.43 (br s, 1H), 7.26 (d, *J* = 8.7 Hz, 2H), 6.08 (dd, *J* = 17.6, 10.7 Hz, 1H), 5.37 (d, *J* = 11.0 Hz, 1H), 5.35 (d, *J* = 17.8 Hz, 1H), 3.71-3.63 (m, 2H), 1.89-1.74 (m, 2H), 1.58-1.49 (m, 2H), 1.33 (s, 3H), 1.10-0.97 (m, 21H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 100 MHz): δ 173.7, 141.7, 137.8, 137.7, 121.5, 116.7, 87.2, 63.4, 49.6, 34.1, 27.9, 21.8, 18.0, 11.9; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{23}H_{39}INO_2Si$ 516.1795, Found 516.1794.

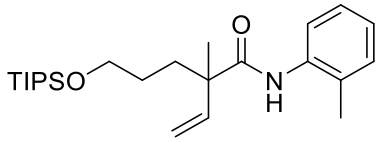


***N*-(4-Methoxyphenyl)-2-methyl-5-((triisopropylsilyl)oxy)-2-vinylpentanamide (4af)**. Compound **4af** was synthesized from triisopropyl((4-methylhexa-4,5-diene-1-yl)oxy)silane (**1a**, 80.6 mg, 0.300 mmol) and 4-methoxyphenyl isocyanate (**3f**, 33.0 μL, 0.250 mmol) in 95% yield (100 mg, 0.239 mmol) as a colorless oil. The crude product was purified using silica gel column chromatography (EtOAc:hexanes = 1:20). **IR** (neat): 3356 (w), 2970 (m), 2862 (m), 1659 (s), 1605 (w), 1512 (s), 1466 (m), 1381 (m), 1296 (m), 1242 (s), 1111 (s), 918 (m), 825 (m), 679 (s) cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.38 (br s, 1H), 7.36 (d, *J* = 9.1 Hz, 2H), 6.81 (d, *J* = 9.1 Hz, 2H), 6.09 (dd, *J* = 17.6, 10.7 Hz, 1H), 5.34 (d, *J* = 11.0 Hz, 1H), 5.33 (d, *J* = 17.4 Hz, 1H), 3.75 (s, 3H), 3.67 (t, *J* = 6.4 Hz, 2H), 1.86-1.75 (m, 2H), 1.58-1.50 (m,

2H), 1.33 (s, 3H), 1.08-0.98 (m, 21H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 100 MHz): δ 173.4, 156.2, 141.9, 131.0, 121.5, 116.2, 113.9, 63.4, 55.3, 49.2, 34.1, 27.9, 21.8, 17.9, 11.9; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{24}H_{42}NO_3Si$ 420.2934, Found 420.2935.

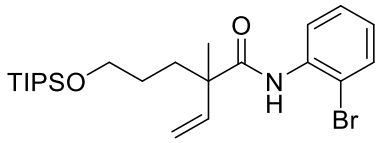


2-Methyl-*N*-(4-(trifluoromethyl)phenyl)-5-((triisopropylsilyl)oxy)-2-vinylpentanamide (4ag). Compound **4ag** was synthesized from triisopropyl((4-methylhexa-4,5-diene-1-yl)oxy)silane (**1a**, 80.6 mg, 0.300 mmol) and 4-(trifluoromethyl)phenyl isocyanate (**3g**, 62.0 μL, 0.250 mmol) in 69% yield (79.0 mg, 0.173 mmol) as a white solid. The crude product was purified using silica gel column chromatography (EtOAc:hexanes = 1:20). **mp** 41-42 °C; **IR** (neat): 3325 (w), 2947 (m), 2870 (w), 1666 (m), 1605 (m), 1528 (s), 1466 (w), 1404 (m), 1319 (s), 1250 (w), 1165 (m), 1111 (s), 679 (s) cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.63 (d, *J* =8.7 Hz, 3H), 7.56 (d, *J* = 8.7 Hz, 2H), 6.12 (dd, *J* = 17.6, 10.7 Hz, 1H), 5.44 (d, *J* = 10.6 Hz, 1H), 5.41 (d, *J* = 17.4 Hz, 1H), 3.70 (t, *J* = 6.4 Hz, 2H), 1.90-1.81 (m, 2H), 1.59-1.53 (m, 2H), 1.38 (s, 3H), 1.07-1.02 (m, 21H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 100 MHz): δ 174.0, 141.6, 140.9, 126.2 (q, J_{C-F} = 3.9 Hz), 125.9 (q, J_{C-F} = 32.7 Hz), 121.3 (q, J_{C-F} = 271.6 Hz), 119.2, 117.0, 63.4, 49.8, 34.1, 27.9, 21.8, 18.0, 11.9; ^{19}F NMR ($CDCl_3$, 75.2 Hz): δ -60.01; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{24}H_{39}F_3NO_2Si$ 458.2702, Found 458.2702.

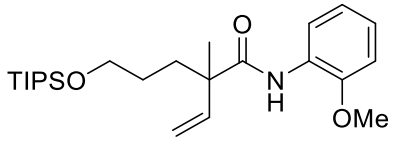


2-Methyl-*N*-(*o*-tolyl)-5-((triisopropylsilyl)oxy)-2-vinylpentanamide (4ah). Compound **4ah** was synthesized from triisopropyl((4-methylhexa-4,5-diene-1-yl)oxy)silane (**1a**, 80.6 mg, 0.300 mmol) and *o*-tolyl isocyanate (**3h**, 31.0 μL, 0.250 mmol) in 78% yield (79.2 mg, 0.196 mmol) as a colorless oil. The crude product was purified using silica gel column chromatography (EtOAc:hexanes = 1:20). **IR** (neat): 3325 (w), 2939 (m), 2862 (m), 1682 (s), 1589 (m), 1512 (m), 1458 (s), 1381 (m), 1250 (s), 1103 (s), 918 (m), 748 (s) cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.93 (d, *J* = 7.8 Hz, 1H), 7.46 (br s, 1H), 7.21 (t, *J* = 7.8 Hz, 1H), 7.16 (d, *J* = 7.8 Hz, 1H), 7.05 (t, *J* = 7.8 Hz, 1H), 6.18 (dd, *J* = 17.8, 10.5 Hz, 1H), 5.43 (d, *J* = 17.3 Hz, 1H), 5.43 (d, *J* = 11.4 Hz, 1H), 3.72 (t, *J* = 6.4 Hz, 2H), 2.20 (s, 3H), 1.94-1.81 (m, 2H), 1.63-1.55 (m, 2H), 1.40 (s, 3H), 1.12-1.06 (m, 21H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 100 MHz): δ 173.4, 142.1, 135.8, 130.2, 128.1, 126.7, 124.6, 121.9, 116.4, 63.4, 49.6, 34.0, 27.9, 21.8, 17.9, 17.6, 11.8; **HRMS**

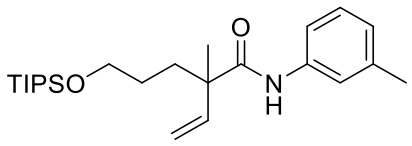
(ESI) *m/z*: $[M+H]^+$ Calcd for $C_{24}H_{42}NO_2Si$ 404.2985, Found 404.2986.



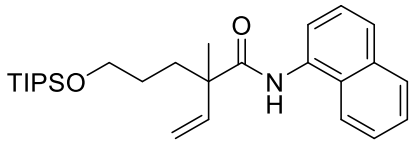
***N*-(2-Bromophenyl)-2-methyl-5-((triisopropylsilyl)oxy)-2-vinylpentanamide (4ai)**. Compound **4ai** was synthesized from triisopropyl((4-methylhexa-4,5-diene-1-yl)oxy)silane (**1a**, 80.6 mg, 0.300 mmol) and 2-bromophenyl isocyanate (**3i**, 31.0 µL, 0.250 mmol) in 82% yield (96.1 mg, 0.205 mmol) as a light greenish oil. The crude product was purified using silica gel column chromatography (EtOAc:hexanes = 1:20). **IR** (neat): 3371 (w), 2947 (m), 2862 (m), 1697 (s), 1589 (m), 1512 (s), 1435 (m), 1389 (m), 1296 (m), 1103 (s), 879 (m), 748 (s) cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 8.39 (dd, *J* = 8.2, 1.8 Hz, 1H), 8.15 (br s, 1H), 7.50 (dd, *J* = 8.2, 1.4 Hz, 1H), 7.29 (t, *J* = 8.0 Hz, 1H), 6.94 (dt, *J* = 7.8, 1.9 Hz, 1H), 6.14 (dd, *J* = 17.4, 11.0 Hz, 1H), 5.45 (d, *J* = 10.1 Hz, 1H), 5.44 (d, *J* = 17.8 Hz, 1H), 3.71 (t, *J* = 6.4 Hz, 2H), 1.94-1.81 (m, 2H), 1.61-1.54 (m, 2H), 1.40 (s, 3H), 1.13-1.00 (m, 21H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 100 MHz): δ 173.8, 141.4, 135.8, 132.1, 128.2, 124.8, 121.4, 116.8, 113.6, 63.4, 49.9, 34.2, 27.9, 21.8, 18.0, 11.9; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{23}H_{39}BrNO_2Si$ 468.1933, Found 468.1933.



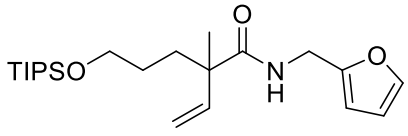
***N*-(2-Methoxyphenyl)-2-methyl-5-((triisopropylsilyl)oxy)-2-vinylpentanamide (4aj)**. Compound **4aj** was synthesized from triisopropyl((4-methylhexa-4,5-diene-1-yl)oxy)silane (**1a**, 80.6 mg, 0.300 mmol) and 2-methoxyphenyl isocyanate (**3j**, 33.0 µL, 0.250 mmol) in 62% yield (65.1 mg, 0.155 mmol) as a colorless oil. The crude product was purified using silica gel column chromatography (EtOAc:hexanes = 1:20). **IR** (neat): 3387 (w), 2939 (m), 2862 (m), 1674 (m), 1605 (w), 1528 (s), 1458 (s), 1381 (w), 1250 (m), 1103 (s), 926 (s), 748 (s), 679 (s) cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 8.39 (dd, *J* = 8.0, 1.6 Hz, 1H), 8.25 (br s, 1H), 7.03 (td, *J* = 7.8, 1.8 Hz, 1H), 6.95 (t, *J* = 7.8, 1.4 Hz, 1H), 6.85 (dd, *J* = 8.2, 1.4 Hz, 1H), 6.13 (dd, *J* = 17.2, 11.2 Hz, 1H), 5.40-5.35 (m, 2H), 3.86 (s, 3H), 3.70 (t, *J* = 6.4 Hz, 2H), 1.88-1.81 (m, 2H), 1.60-1.54 (m, 2H), 1.38 (s, 3H), 1.08-1.02 (m, 21H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 100 MHz): δ 173.5, 148.0, 141.7, 127.7, 123.4, 121.0, 119.3, 116.1, 109.7, 63.5, 55.7, 49.8, 34.2, 27.9, 21.7, 18.0, 11.9; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{24}H_{42}NO_3Si$ 420.2934, Found 420.2933.



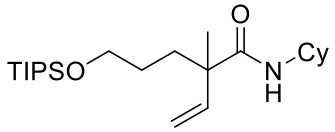
2-Methyl-*N*-(*m*-tolyl)-5-((triisopropylsilyl)oxy)-2-vinylpentanamide (4ak). Compound **4ak** was synthesized from triisopropyl((4-methylhexa-4,5-diene-1-yl)oxy)silane (**1a**, 80.6 mg, 0.300 mmol) and *m*-tolyl isocyanate (**3k**, 33.0 μL, 0.250 mmol) in 95% yield (96.2 mg, 0.238 mmol) as a white solid. The crude product was purified using silica gel column chromatography (EtOAc:hexanes = 1:20). **mp** 63-64 °C; **IR** (neat): 3325 (w), 2947 (m), 2862 (w), 2361 (m), 2168 (m), 2129 (m), 1744 (s), 1659 (m), 1589 (m), 1535 (m), 1458 (w), 1427 (m), 1366 (s), 1304 (m), 1211 (m), 1103 (m), 1003 (mw), 918 (m), 887 (m), 779 (m), 725 (m), 687 (m) cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.42 (s, 1H), 7.38 (s, 1H), 7.26 (d, *J* = 9.6, 1H), 7.19 (t, *J* = 7.4 Hz, 1H), 6.92 (d, *J* = 7.3 Hz, 1H), 6.12 (dd, *J* = 17.4, 11.0 Hz, 1H), 5.41-5.36 (m, 2H), 3.70 (t, *J* = 6.4 Hz, 2H) 2.33 (s, 3H), 1.88-1.80 (m, 2H), 1.60-1.54 (m, 2H), 1.36 (s, 3H), 1.11-1.02 (m, 21H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 100 MHz): δ 173.6, 141.9, 138.9, 137.8, 128.7, 125.0, 120.3, 116.7, 116.5, 63.5, 49.6, 34.1, 28.0, 21.9, 21.4, 18.0, 11.9; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{24}H_{42}NO_2Si$ 404.2985, Found 404.2984.



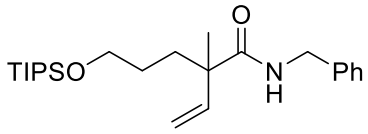
2-Methyl-*N*-(naphthalene-1-yl)-5-((triisopropylsilyl)oxy)-2-vinylpentanamide (4al). Compound **4al** was synthesized from triisopropyl((4-methylhexa-4,5-diene-1-yl)oxy)silane (**1a**, 80.6 mg, 0.300 mmol) and 1-naphthyl isocyanate (**3l**, 36.0 μL, 0.250 mmol) in 84% yield (92.3 mg, 0.210 mmol) as a white solid. The crude product was purified using silica gel column chromatography (EtOAc:hexanes = 1:20). **mp** 68-69 °C; **IR** (neat): 3279 (w), 2939 (m), 2862 (m), 1659 (s), 1528 (s), 1466 (m), 1389 (w), 1273 (m), 1095 (s), 795 (s), 687 (s) cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 8.05 (t, *J* = 3.7 Hz, 2H), 7.88-7.86 (m, 1H), 7.72-7.67 (m, 2H), 7.53-7.46 (m, 3H), 6.31 (dd, *J* = 17.8, 10.5 Hz, 1H), 5.54 (d, *J* = 17.4 Hz, 1H), 5.54 (d, *J* = 11.0 Hz, 1H), 3.75 (t, *J* = 6.4 Hz, 2H), 2.00-1.93 (m, 2H), 1.68-1.64 (m, 2H), 1.48 (s, 3H), 1.09-1.04 (m, 21H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 100 MHz): δ 173.9, 142.2, 134.0, 132.3, 128.8, 126.8, 126.2, 125.8, 125.8, 125.2, 120.0, 119.8, 116.8, 63.5, 49.8, 34.1, 28.0, 22.0, 18.0, 11.9; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{27}H_{42}NO_2Si$ 440.2985, Found 440.2984.



***N*-(Furan-2-ylmethyl)-2-methyl-5-((triisopropylsilyl)oxy)-2-vinylpentanamide (4am)**. Compound **4am** was synthesized from triisopropyl((4-methylhexa-4,5-diene-1-yl)oxy)silane (**1a**, 80.6 mg, 0.300 mmol) and furfuryl isocyanate (**3m**, 27.0 μL, 0.250 mmol) in 81% yield (79.9 mg, 0.203 mmol) as a yellow oil. The crude product was purified using silica gel column chromatography (EtOAc:hexanes = 1:20). **IR** (neat): 3356 (m), 2947 (s), 2862 (s), 2361 (m), 1659 (s), 1520 (s), 1466 (m), 1381 (w), 1250 (m), 1098 (s), 1011 (m), 918 (m), 879 (m), 679 (s) cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.34 (t, *J* = 0.9 Hz, 1H), 6.31 (t, *J* = 2.7 Hz, 1H), 6.19 (dd, *J* = 3.2, 0.9 Hz, 1H), 6.04 (br s, 1H), 5.99 (dd, *J* = 17.6, 10.7 Hz, 1H), 5.26 (d, *J* = 10.5 Hz, 1H), 5.24 (d, *J* = 17.4 Hz, 1H), 4.40 (d, *J* = 5.5 Hz, 2H), 3.66 (t, *J* = 6.4 Hz, 2H), 1.82-1.66 (m, 2H), 1.54-1.44 (m, 2H), 1.27 (s, 3H), 1.10-1.02 (m, 21H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 100 MHz): δ 175.3, 151.4, 142.1, 141.8, 115.8, 110.3, 107.1, 63.5, 48.5, 36.7, 34.2, 27.9, 21.6, 18.0, 11.9; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{22}H_{40}NO_3Si$ 394.2777, Found 394.2776.

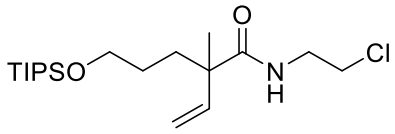


***N*-Cyclohexyl-2-methyl-5-((triisopropylsilyl)oxy)-2-vinylpentanamide (4an)**. Compound **4an** was synthesized from triisopropyl((4-methylhexa-4,5-diene-1-yl)oxy)silane (**1a**, 80.6 mg, 0.300 mmol) and cyclohexyl isocyanate (**3n**, 32.0 μL, 0.250 mmol) in 92% yield (91.3 mg, 0.231 mmol) as a sticky oil. The crude product was purified using silica gel column chromatography (EtOAc:hexanes = 1:20). **IR** (neat): 3348 (w), 2939 (s), 2662 (s), 2361 (m), 1636 (s), 1512 (s), 1458 (s), 1381 (m), 1250 (w), 1219 (w), 1103 (s), 1011 (w), 918 (w), 802 (w) cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 5.97 (dd, *J* = 17.6, 10.7 Hz, 1H), 5.56 (d, *J* = 8.0 Hz, 1H), 5.23 (d, *J* = 9.6 Hz, 1H), 5.22 (d, *J* = 17.9 Hz, 1H), 3.76-3.68 (m, 1H), 3.66 (t, *J* = 6.4 Hz, 2H), 1.84 (d, *J* = 8.7 Hz, 2H), 1.76-1.56 (m, 5H), 1.52-1.44 (m, 2H), 1.39-1.27 (m, 3H), 1.23 (s, 3H), 1.19-1.10 (m, 2H), 1.08-1.00 (m, 21H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 100 MHz): 174.4, 142.3, 115.4, 63.6, 48.4, 34.2, 33.0, 32.9, 27.9, 25.5, 24.7, 21.7, 18.0, 11.9; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{23}H_{46}NO_2Si$ 396.3298, Found 396.3297.

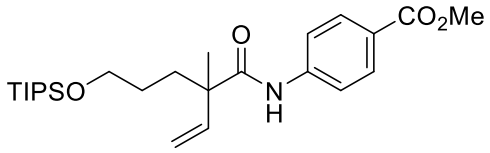


***N*-Benzyl-2-methyl-5-((triisopropylsilyl)oxy)-2-vinylpentanamide (4ao)**. Compound **4ao** was synthesized from triisopropyl((4-methylhexa-4,5-diene-1-yl)oxy)silane (**1a**, 80.6 mg, 0.300 mmol) and benzyl isocyanate (**3o**, 31.0 μL, 0.250 mmol) in 80% yield (80.8 mg, 0.200 mmol) as a yellow oil. The crude product was purified using silica gel column chromatography (EtOAc:hexanes = 1:20). **IR** (neat):

3333 (w), 3032 (w), 2970 (m), 1643 (s), 1528 (s), 1458 (m), 1381 (w), 1257 (m), 1003 (m), 879 (m), 679 (s) cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.33-7.27 (m, 3H), 7.23 (t, *J* = 7.8 Hz, 2H), 6.03-5.96 (m, 2H), 5.23 (d, *J* = 10.5 Hz, 1H), 5.22 (d, *J* = 17.4 Hz, 1H), 4.40 (d, *J* = 5.9 Hz, 2H), 3.66 (t, *J* = 6.4 Hz, 2H), 1.81-1.70 (m, 2H), 1.58-1.47 (m, 2H), 1.29 (s, 3H), 1.09-1.03 (m, 21H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 100 MHz): δ 175.4, 141.9, 138.5, 128.6, 127.5, 127.3, 115.8, 63.5, 48.6, 43.6, 34.2, 27.9, 21.7, 18.0, 11.9; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{24}H_{42}NO_2Si$ 404.2985, Found 404.2985.

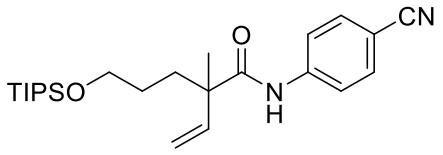


***N*-(2-Chloroethyl)-2-methyl-5-((triisopropylsilyl)oxy)-2-vinylpentanamide (4ap)**. Compound **4ap** was synthesized from triisopropyl((4-methylhexa-4,5-diene-1-yl)oxy)silane (**1a**, 134 mg, 0.500 mmol) and 2-chloroethyl isocyanate (**3p**, 22.0 μL, 0.250 mmol) in 87% yield (81.9 mg, 0.218 mmol) as a greenish oil. The crude product was purified using silica gel column chromatography (EtOAc:hexanes = 1:10). **IR** (neat): 3371 (w), 2970 (s), 2870 (s), 2361 (m), 1651 (s), 1520 (m), 1466 (m), 1381 (w), 1250 (m), 1111 (s), 1065 (m), 1003 (m), 879 (m), 679 (s) cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 6.18 (br s, 1H), 6.00 (dd, *J* = 17.7, 10.8 Hz, 1H), 5.29 (d, *J* = 10.1 Hz, 1H), 5.27 (d, *J* = 17.4 Hz, 1H), 3.67 (t, *J* = 6.4 Hz, 2H), 3.61-3.59 (m, 2H), 3.56 (t, *J* = 5.5 Hz, 2H), 1.80-1.67 (m, 2H), 1.54-1.46 (m, 2H), 1.28 (s, 3H), 1.09-1.03 (m, 21H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 100 MHz): δ 175.7, 141.7, 115.9, 63.5, 48.6, 44.0, 41.3, 34.2, 27.9, 21.7, 18.0, 11.9; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{19}H_{39}ClNO_2Si$ 376.2439, Found 376.2437.

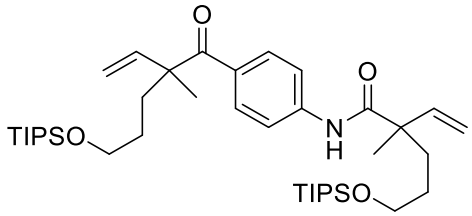


Methyl 4-(2-methyl-5-((triisopropylsilyl)oxy)-2-vinylpentanamido)benzoate (4aq). Compound **4aq** was synthesized from triisopropyl((4-methylhexa-4,5-diene-1-yl)oxy)silane (**1a**, 67.1 mg, 0.250 mmol) and methyl 4-isocyanatobenzoate (**3q**, 88.6 mg, 0.500 mmol) in 86% yield (96.7 mg, 0.216 mmol) as a yellow oil. The crude product was purified using silica gel column chromatography (EtOAc:hexanes = 1:40). **IR** (neat): 3379 (w), 2970 (m), 2870 (m), 1620 (s), 1666 (m), 1597 (m), 1528 (s), 1435 (m), 1404 (m), 1284 (s), 1173 (m), 1111 (s), 679 (s) cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 8.00 (d, *J* = 8.7 Hz, 2H), 7.63 (br s, 1H), 7.58 (d, *J* = 8.7 Hz, 2H), 6.11 (dd, *J* = 17.6, 10.7 Hz, 1H), 5.43 (d, *J* = 11.0 Hz, 1H), 5.41 (d, *J* = 17.8 Hz, 1H), 3.90 (s, 3H), 3.70 (t, *J* = 6.2 Hz, 2H), 1.93-1.76 (m, 2H), 1.59-1.52 (m, 2H), 1.37

(s, 3H), 1.11-1.01 (m, 21H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 100 MHz): δ 173.9, 166.6, 142.0, 141.6, 130.8, 125.5, 118.7, 117.0, 63.4, 52.0, 49.8, 44.0, 27.9, 21.8, 18.0, 11.9; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{25}H_{42}NO_4Si$ 448.2883, Found 448.2882.

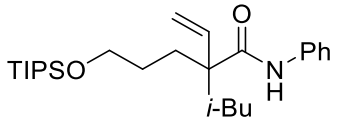


***N*-(4-Cyanophenyl)-2-methyl-5-((triisopropylsilyl)oxy)-2-vinylpentanamide (4ar)**. Compound **4ar** was synthesized from triisopropyl((4-methylhexa-4,5-diene-1-yl)oxy)silane (**1a**, 67.1 mg, 0.250 mmol) and 4-cyanophenyl isocyanate (**3r**, 72.1 mg, 0.500 mmol) in 83% yield (86.4 mg, 0.208 mmol) as a yellow oil. The crude product was purified using silica gel column chromatography (EtOAc:hexanes = 1:20). **IR** (neat): 3371 (m), 2939 (m), 2862 (s), 2361 (m), 1690 (s), 1512 (s), 1466 (m), 1311 (m), 1250 (m), 1173 (m), 1111 (m), 1003 (w), 841 (m), 679 (s) cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.65-7.58 (m, 5H), 6.10 (dd, *J* = 17.6, 10.7 Hz, 1H), 5.44 (d, *J* = 10.5 Hz, 1H), 5.42 (d, *J* = 17.9 Hz, 1H), 3.70 (t, *J* = 6.6 Hz, 2H), 1.92-1.78 (m, 2H), 1.58-1.51 (m, 2H), 1.37 (s, 3H), 1.11-1.00 (m, 21H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 100 MHz): δ 174.1, 141.9, 141.4, 133.2, 119.4, 118.8, 117.2, 107.0, 63.3, 49.8, 33.9, 27.9, 21.7, 18.0, 11.9; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{24}H_{39}N_2O_2Si$ 415.2781, Found 415.2780.

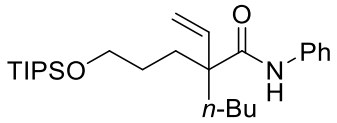


2-Methyl-*N*-(4-(2-methyl-5-((triisopropylsilyl)oxy)-2-vinylpentanoyl)phenyl)-5-((triisopropylsilyl)oxy)-2-vinylpentanamide (5ar). Compound **5ar** was synthesized from triisopropyl((4-methylhexa-4,5-diene-1-yl)oxy)silane (**1a**, 134 mg, 0.500 mmol) and 4-cyanophenyl isocyanate (**3r**, 36.0 mg, 0.250 mmol) in 70% yield (121 mg, 0.176 mmol) as a yellow oil. The crude product was purified using silica gel column chromatography (EtOAc:hexanes = 1:30). **IR** (neat): 3394 (w), 2947 (m), 2862 (s), 1674 (s), 1512 (s), 1381 (m), 1311 (m), 1242 (m), 1180 (m), 1103 (s), 995 (m), 879 (m), 679 (s) cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.89 (d, *J* = 8.7 Hz, 2H), 7.57 (br s, 1H), 7.50 (d, *J* = 8.7 Hz, 2H), 6.16 (dd, *J* = 17.8, 11.0 Hz, 1H), 6.10 (dd, *J* = 17.4, 11.0 Hz, 1H), 5.41 (d, *J* = 10.1 Hz, 1H), 5.39 (d, *J* = 17.4 Hz, 1H), 5.22 (d, *J* = 10.5 Hz, 1H), 5.18 (d, *J* = 16.9 Hz, 1H), 3.69 (t, *J* = 6.4 Hz, 2H), 3.60 (t, *J* = 6.4 Hz, 2H), 2.01-1.94 (m, 1H), 1.89-1.77 (m, 3H), 1.58-1.49 (m, 4H), 1.36 (s, 3H), 1.35 (s, 3H), 1.11-0.98 (m, 42H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 100 MHz): δ 202.7, 173.8, 143.3, 141.6, 140.9,

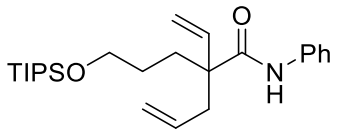
132.6, 130.7, 118.2, 116.9, 114.7, 63.5, 63.4, 53.1, 49.7, 35.1, 34.0, 27.9, 27.7, 23.2, 21.8, 18.0, 18.0, 11.9, 11.9; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{40}H_{72}NO_4Si_2$ 686.5000, Found 686.4998.



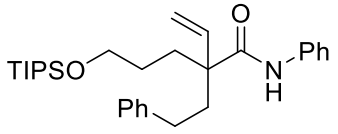
2-Isobutyl-*N*-phenyl-5-((triisopropylsilyl)oxy)-2-vinylpentanamide (4ba). Compound **4ba** was synthesized from triisopropyl((6-methyl-4-vinylideneheptyl)oxy)silane (**1b**, 93.2 mg, 0.300 mmol) and phenyl isocyanate (**3a**, 27.0 µL, 0.250 mmol) in 72% yield (77.8 mg, 0.180 mmol) as a colorless oil. The crude product was purified using silica gel column chromatography (EtOAc:hexanes = 1:20). **IR** (neat): 3384 (w), 2947 (m), 2870 (s), 2361 (m), 1659 (s), 1520 (s), 1443 (m), 1311 (m), 1242 (m), 1103 (s), 918 (m), 748 (m), 687 (s) cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.49 (d, *J* = 7.8 Hz, 2H), 7.48 (br s, 1H), 7.31 (t, *J* = 7.8 Hz, 2H), 7.09 (t, *J* = 7.3 Hz, 1H), 6.12 (dd, *J* = 17.8, 11.0 Hz, 1H), 5.43 (d, *J* = 10.5 Hz, 1H), 5.40 (d, *J* = 17.4 Hz, 1H), 3.69 (td, *J* = 6.3, 3.0 Hz, 2H), 1.98-1.90 (m, 1H), 1.86-1.68 (m, 4H), 1.58-1.50 (m, 2H), 1.11-1.03 (m, 21H), 0.93 (d, *J* = 5.9 Hz, 6H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 100 MHz): δ 173.1, 141.3, 137.8, 128.9, 124.1, 119.6, 116.7, 63.4, 52.6, 44.4, 31.8, 27.7, 24.5, 24.2, 18.0, 11.9; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{26}H_{46}NO_2Si$ 432.3298, Found 432.3297.



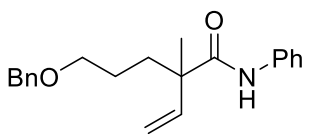
***N*-Phenyl-2-(3-((triisopropylsilyl)oxy)propyl)-2-vinylhexanamide (4ca)**. Compound **4ca** was synthesized triisopropyl((4-vinylideneoctyl)oxy)silane (**1c**, 93.2 mg, 0.300 mmol) and phenyl isocyanate (**3a**, 27.0 µL, 0.250 mmol) in 97% yield (105 mg, 0.243 mmol) as a white solid. The crude product was purified using silica gel column chromatography (EtOAc:hexanes = 1:20). **mp** 72-73 °C; **IR** (neat): 3325 (w), 2947 (m), 2862 (w), 2361 (s), 2168 (m), 2129 (m), 1744 (s), 1682 (m), 1597 (m), 1528 (m), 1435 (w), 1366 (m), 1311 (s), 1211 (m), 1103 (m), 1003 (mw), 918 (m), 887 (m), 748 (m), 687 (m) cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.49 (dd, *J* = 8.7, 0.9 Hz, 2H), 7.45 (s, 1H), 7.31 (d, *J* = 7.8 Hz, 2H), 7.10 (t, *J* = 7.3 Hz, 1H), 6.07 (dd, *J* = 17.8, 11.0 Hz, 1H), 5.41 (dd, *J* = 17.0, 11.0 Hz, 2H), 3.70 (t, *J* = 6.2 Hz, 2H) 1.91-1.72 (m, 4H), 1.59-1.51 (m, 2H), 1.34-1.24 (m, 4H), 1.11-1.02 (m, 21H), 0.90 (t, *J* = 7.1 Hz, 3H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 100 MHz): δ 173.0, 141.2, 137.9, 128.9, 124.1, 119.7, 117.0, 63.5, 52.8, 34.8, 31.1, 27.7, 26.2, 23.3, 18.0, 14.0, 11.9; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{26}H_{46}NO_2Si$ 432.3298, Found 432.3297.



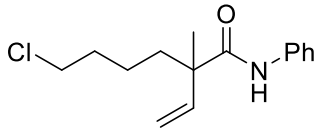
***N*-Phenyl-2-(3-((triisopropylsilyl)oxy)propyl)-2-vinylpent-4-enamide (4da)**. Compound **4da** was synthesized from triisopropyl((4-vinylidenehept-6-en-1-yl)oxy)silane (**1d**, 88.4 mg, 0.300 mmol) and phenyl isocyanate (**3a**, 27.0 μL, 0.250 mmol) in 83% yield (86.3 mg, 0.208 mmol) as a colorless oil. The crude product was purified using silica gel column chromatography (EtOAc:hexanes = 1:20). **IR** (neat): 3394 (w), 2978 (m), 2847 (s), 2361 (m), 1666 (s), 1520 (m), 1435 (m), 1311 (m), 1242 (m), 1119 (s), 995 (s), 787 (m), 679 (s) cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.51 (br s, 1H), 7.49 (d, *J* = 7.8 Hz, 2H), 7.31 (t, *J* = 7.8 Hz, 2H), 7.10 (t, *J* = 7.3 Hz, 1H), 6.09 (dd, *J* = 17.6, 10.7 Hz, 1H), 5.78 (td, *J* = 17.2, 7.3 Hz, 1H), 5.47 (d, *J* = 11.0 Hz, 1H), 5.42 (d, *J* = 17.4 Hz, 1H), 5.15-5.09 (m, 2H), 3.70 (td, *J* = 6.3, 2.5 Hz, 2H), 2.56 (t, *J* = 7.5 Hz, 2H), 1.93-1.78 (m, 2H), 1.62-1.55 (m, 2H), 1.11-0.98 (m, 21H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 100 MHz): δ 172.3, 140.4, 137.7, 133.7, 128.9, 124.2, 119.7, 118.3, 117.4, 63.3, 52.6, 39.5, 31.2, 27.5, 18.0, 11.8; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{25}H_{42}NO_2Si$ 416.2985, Found 416.2984.



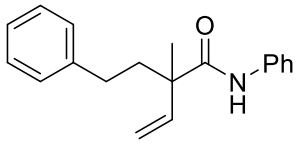
2-Phenethyl-*N*-phenyl-5-((triisopropylsilyl)oxy)-2-vinylpentanamide (4ea). Compound **4ea** was synthesized from triisopropyl((4-phenethylhexa-4,5-dien-1-yl)oxy)silane (**1e**, 108 mg, 0.300 mmol) and phenyl isocyanate (**3a**, 27.0 μL, 0.250 mmol) in 99% yield (119 mg, 0.248 mmol) as a colorless oil. The crude product was purified using silica gel column chromatography (EtOAc:hexanes = 1:20). **IR** (neat): 3402 (w), 2978 (m), 2862 (s), 1690 (s), 1605 (m), 1435 (m), 1311 (w), 1242 (w), 1119 (s), 1018 (m), 879 (m), 748 (m), 694 (s) cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.53 (d, *J* = 7.8 Hz, 2H), 7.54 (s, 1H), 7.35 (t, *J* = 7.8 Hz, 2H), 7.29 (d, *J* = 7.3 Hz, 2H), 7.22 (d, *J* = 7.3 Hz, 3H), 7.13 (t, *J* = 7.3 Hz, 1H), 6.17 (dd, *J* = 17.6, 10.7 Hz, 1H), 5.53 (d, *J* = 11.0 Hz, 1H), 5.48 (d, *J* = 17.4 Hz, 1H), 3.74 (t, *J* = 5.9 Hz, 2H), 2.66-2.61 (m, 2H), 2.11-2.07 (m, 2H), 2.04-1.99 (m, 1H), 1.95-1.87 (m, 1H), 1.65-1.58 (m, 2H), 1.15-1.04 (m, 21H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 100 MHz): δ 172.5, 142.2, 140.7, 137.7, 128.9, 128.4, 128.3, 125.8, 124.2, 119.7, 117.5, 63.3, 52.9, 37.2, 31.2, 30.5, 27.6, 18.0, 11.9; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{30}H_{46}NO_2Si$ 480.3298, Found 480.3295.



5-(Benzyloxy)-2-methyl-*N*-phenyl-2-vinylpentanamide (4fa). Compound **4fa** was synthesized from (((4-methylhexa-4,5-diene-1-yl)oxy)methyl)benzene (**1f**, 60.7 mg, 0.300 mmol) and phenyl isocyanate (**3a**, 27.0 μL, 0.250 mmol) in 98% yield (78.9 mg, 0.244 mmol) as a colorless oil. The crude product was purified using silica gel column chromatography (EtOAc:hexanes = 1:20). **IR** (neat): 3340 (w), 2978 (w), 2862 (w), 1666 (s), 1597 (m), 1520 (s), 1443 (s), 1373 (w), 1311 (m), 1242 (w), 1095 (s), 926 (m), 748 (s), 694 (s) cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.52 (br s, 1H), 7.50 (dd, *J* = 8.7, 0.9 Hz, 2H), 7.36-7.29 (m, 7H), 7.11 (t, *J* = 7.8 Hz, 1H), 6.13 (t, *J* = 17.6, 10.7 Hz, 1H), 5.41 (d, *J* = 10.5 Hz, 1H), 5.38 (d, *J* = 17.8 Hz, 1H), 4.52 (s, 2H), 3.51 (t, *J* = 6.4 Hz, 2H), 1.91-1.85 (m, 2H), 1.69-1.64 (m, 2H), 1.39 (s, 3H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 100 MHz): δ 173.5, 141.6, 138.4, 137.8, 128.9, 128.3, 127.6, 127.5, 124.1, 119.6, 116.6, 72.9, 70.4, 49.5, 34.3, 24.8, 21.8; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{21}H_{26}NO_2$ 324.1964, Found 324.1963.

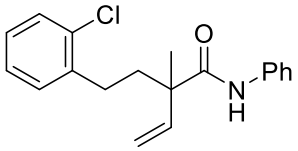


6-Chloro-2-methyl-*N*-phenyl-2-vinylhexanamide (4ga). Compound **4ga** was synthesized from 7-chloro-3-methylhepta-1,2-diene (**1g**, 43.4 mg, 0.300 mmol) and phenyl isocyanate (**3a**, 27.0 μL, 0.250 mmol) in 89% yield (59.1 mg, 0.222 mmol) as a colorless oil. The crude product was purified using silica gel column chromatography (EtOAc:hexanes = 1:20). **IR** (neat): 3333 (w), 2978 (m), 2870 (m), 1674 (s), 1597 (s), 1528 (s), 1311 (m), 1242 (w), 1119 (m), 1011 (m), 926 (m), 748 (s), 694 (s) cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.50 (d, *J* = 7.8 Hz, 2H), 7.47 (br s, 1H), 7.32 (t, *J* = 7.8 Hz, 2H), 7.11 (t, *J* = 7.4 Hz, 1H), 6.13 (dd, *J* = 17.6, 10.7 Hz, 1H), 5.43 (d, *J* = 10.5 Hz, 1H), 5.39 (d, *J* = 17.8 Hz, 1H), 3.55 (t, *J* = 6.6 Hz, 2H), 1.84-1.75 (m, 4H), 1.54-1.42 (m, 2H), 1.38 (s, 3H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 100 MHz): δ 173.5, 141.4, 137.7, 128.9, 124.3, 119.6, 117.0, 49.7, 44.8, 37.2, 32.9, 21.8, 21.7; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{15}H_{21}ClNO$ 266.1312, Found 266.1311.

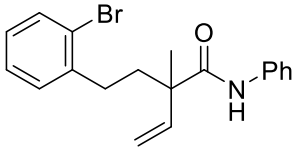


2-Methyl-2-phenethyl-*N*-phenylbut-3-enamide (4ha). Compound **4ha** was synthesized from (3-methylpenta-3,4-dien-1-yl)benzene (**1h**, 47.5 mg, 0.300 mmol) and phenyl isocyanate (**3a**, 27.0 μL, 0.250 mmol) in 93% yield (64.7 mg, 0.232 mmol) as a white solid. The crude product was purified using silica gel column chromatography (EtOAc:hexanes = 1:20). **mp** 83-84 °C; **IR** (neat): 3325 (w), 2939 (w), 1659 (s), 1597 (s), 1535 (s), 1435 (s), 1319 (m), 1234 (m), 1180 (w), 918 (s), 748 (s), 694 (s) cm^{-1}; **^{1}H**

NMR ($CDCl_3$, 400 MHz): δ 7.55-7.53 (m, 3H), 7.37-7.28 (m, 4H), 7.24-7.19 (m, 3H), 7.13 (t, *J* = 7.3 Hz, 1H), 6.23 (dd, *J* = 17.4, 11.0 Hz, 1H), 5.48 (dd, *J* = 11.0, 0.9 Hz, 1H), 5.45 (dd, *J* = 17.4, 0.9 Hz, 1H), 2.68-2.63 (m, 2H), 2.12-2.07 (m, 2H), 1.47 (s, 3H); **$^{13}C\{^1H\}$ NMR** ($CDCl_3$, 100 MHz): δ 173.3, 142.1, 141.5, 137.8, 128.9, 128.4, 128.3, 125.8, 124.3, 119.7, 116.9, 49.8, 40.1, 30.8, 21.9; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{19}H_{22}NO$ 280.1701, Found 280.1700.

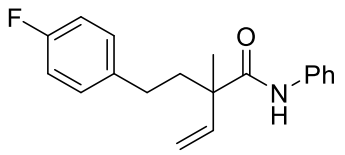


2-(2-Chlorophenethyl)-2-methyl-*N*-phenylbut-3-enamide (4ia). Compound **4ia** was synthesized from 1-chloro-2-(3-methylpenta-3,4-dien-1-yl)benzene (**1i**, 57.8 mg, 0.300 mmol) and phenyl isocyanate (**3a**, 27.0 μL, 0.250 mmol) in 92% yield (72.1 mg, 0.230 mmol) as a white solid. The crude product was purified using silica gel column chromatography (EtOAc:hexanes = 1:20). **mp** 64-65 °C; **IR** (neat): 3340 (w), 1659 (s), 1597 (s), 1535 (s), 1497 (m), 1435 (m), 1319 (m), 1250 (m), 1173 (m), 1041 (m), 918 (m), 748 (s), 694 (s) cm^{-1}; **^1H NMR** ($CDCl_3$, 400 MHz): δ 7.57-7.50 (m, 3H), 7.36-7.32 (m, 3H), 7.27-7.25 (m, 1H), 7.19 (td, *J* = 7.4, 1.6 Hz, 1H), 7.16-7.10 (m, 2H), 6.23 (dd, *J* = 17.4, 11.0 Hz, 1H), 5.49 (d, *J* = 17.4 Hz, 1H), 5.45 (d, *J* = 10.1 Hz, 1H), 2.81-2.69 (m, 2H), 2.13-1.98 (m, 2H), 1.49 (s, 3H); **$^{13}C\{^1H\}$ NMR** ($CDCl_3$, 100 MHz): δ 173.2, 141.3, 139.6, 137.7, 133.7, 130.4, 129.4, 128.9, 127.4, 126.7, 124.2, 119.7, 117.0, 49.8, 38.0, 28.7, 21.6; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{19}H_{21}ClNO$ 314.1312, Found 314.1313.

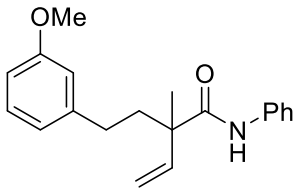


2-(2-Bromophenethyl)-2-methyl-*N*-phenylbut-3-enamide (4ja). Compound **4ja** was synthesized from 1-bromo-2-(3-methylpenta-3,4-dien-1-yl)benzene (**1j**, 71.1 mg, 0.300 mmol) and phenyl isocyanate (**3a**, 27.0 μL, 0.250 mmol) in 98% yield (87.8 mg, 0.245 mmol) as a white solid. The crude product was purified using silica gel column chromatography (EtOAc:hexanes = 1:20). **mp** 78-79 °C; **IR** (neat): 3333 (w), 2932 (w), 1659 (s), 1597 (s), 1535 (s), 1497 (m), 1435 (m), 1319 (s), 1250 (m), 1173 (m), 1018 (m), 918 (s), 748 (s) cm^{-1}; **^1H NMR** ($CDCl_3$, 400 MHz): δ 7.55-7.51 (m, 4H), 7.34 (t, *J* = 7.8 Hz, 2H), 7.28-7.22 (m, 2H), 7.12 (t, *J* = 7.5 Hz, 1H), 7.09-7.04 (m, 1H), 6.25 (dd, *J* = 17.4, 11.0 Hz, 1H), 5.49 (d, *J* = 17.4 Hz, 1H), 5.46 (d, *J* = 10.1 Hz, 1H), 2.83-2.70 (m, 2H), 2.13-1.97 (m, 2H), 1.49 (s, 3H); **$^{13}C\{^1H\}$ NMR** ($CDCl_3$, 100 MHz): δ 173.2, 141.4, 141.3, 137.7, 132.7, 130.4, 128.9, 127.7, 127.6, 124.2, 124.2,

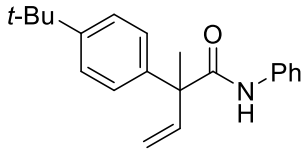
119.7, 117.0, 49.7, 38.2, 31.3, 21.6; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{19}H_{21}BrNO$ 358.0807, Found 358.0807.



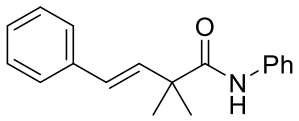
2-(4-Fluorophenylethyl)-2-methyl-*N*-phenylbut-3-enamide (4ka). Compound **4ka** was synthesized from 1-fluoro-4-(3-methylpenta-3,4-dien-1-yl)benzene (**1k**, 52.9 mg, 0.300 mmol) and phenyl isocyanate (**3a**, 27.0 μL, 0.250 mmol) in 89% yield (66.5 mg, 0.224 mmol) as a white solid. The crude product was purified using silica gel column chromatography (EtOAc:hexanes = 1:20). **mp** 77-78 °C; **IR** (neat): 3340 (m), 2986 (w), 2939 (w), 1659 (s), 1597 (s), 1535 (s), 1504 (s), 1435 (s), 1311 (m), 1219 (s), 1088 (w), 1003 (w), 918 (s), 756 (s), 694 (s) cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.54-7.50 (m, 3H), 7.34 (t, *J* = 8.0 Hz, 2H), 7.18-7.10 (m, 3H), 6.97 (t, *J* = 8.9 Hz, 2H), 6.21 (dd *J* = 17.6, 10.7 Hz, 1H), 5.49-5.42 (m, 2H), 2.64-2.59 (m, 2H), 2.07-2.03 (m, 2H), 1.45 (s, 3H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 100 MHz): δ 173.2, 161.2 (d, $J_{C\text{-}F}$ = 243.7 Hz), 141.3, 137.7, 137.6 (d, $J_{C\text{-}F}$ = 2.9 Hz), 129.6 (d, $J_{C\text{-}F}$ = 7.7 Hz), 128.9, 124.3, 119.7, 117.1, 115.0 (d, $J_{C\text{-}F}$ = 21.2 Hz), 49.8, 40.2, 30.0, 21.9; ^{19}F NMR ($CDCl_3$, 75.2 Hz): δ -68.61; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{19}H_{21}FNO$ 298.1607, Found 298.1607.



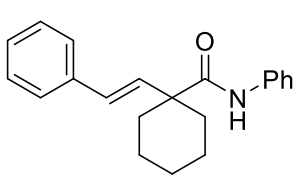
2-(3-Methoxyphenethyl)-2-methyl-*N*-phenylbut-3-enamide (4la). Compound **4la** was synthesized from 1-methoxy-3-(3-methylpenta-3,4-dien-1-yl)benzene (**1l**, 56.5 mg, 0.300 mmol) and phenyl isocyanate (**3a**, 27.0 μL, 0.250 mmol) in 89% yield (68.9 mg, 0.223 mmol) as a light yellow oil. The crude product was purified using silica gel column chromatography (EtOAc:hexanes = 1:20). **IR** (neat): 3340 (m), 2978 (m), 2870 (m), 1666 (s), 1597 (s), 1520 (s), 1435 (s), 1311 (m), 1257 (s), 1157 (s), 1049 (m), 926 (s), 748 (s), 694 (s) cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.54-7.52 (m, 3H), 7.34 (t, *J* = 8.0 Hz, 2H), 7.22 (d, *J* = 7.8 Hz, 1H), 7.13 (t, *J* = 7.3 Hz, 1H), 6.82 (d, *J* = 8.2 Hz, 1H), 6.75 (m, 2H), 6.22 (dd, *J* = 17.4, 11.0 Hz, 1H), 5.48 (d, *J* = 11.0 Hz, 1H), 5.45 (d, *J* = 17.9 Hz, 1H), 3.80 (s, 3H), 2.65-2.61 (m, 2H), 2.11-2.07 (m, 2H), 1.46 (s, 3H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 100 MHz): δ 173.3, 159.6, 143.7, 141.4, 137.7, 129.3, 128.9, 124.3, 120.7, 119.7, 117.0, 113.9, 111.2, 55.1, 49.8, 39.9, 30.9, 21.9; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{20}H_{24}NO_2$ 310.1807, Found 310.1806.



2-(4-(*tert*-Butyl)phenyl)-2-methyl-*N*-phenylbut-3-enamide (4ma). Compound **4ma** was synthesized from 1-(buta-2,3-dien-2-yl)-4-(*tert*-butyl)benzene (**1m**, 55.9 mg, 0.300 mmol) and phenyl isocyanate (**3a**, 27.0 μL, 0.250 mmol) in 59% yield (45.1 mg, 0.147 mmol) as a white solid. The crude product was purified using silica gel column chromatography (EtOAc:hexanes = 1:20). **mp** 112-113 °C; **IR** (neat): 3310 (m), 3063 (w), 2962 (m), 1659 (s), 1597 (m), 1535 (s), 1443 (m), 1319 (m), 1250 (m), 1111 (m), 1018 (m), 926 (m), 833 (s), 687 (s) cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.46-7.40 (m, 4H), 7.34-7.28 (m, 4H), 7.17 (br s, 1H), 7.09 (t, *J* = 7.5 Hz, 1H), 6.39 (dd, *J* = 17.4, 11.0 Hz, 1H), 5.37 (d, *J* = 10.7 Hz, 1H), 5.21 (d, *J* = 17.4 Hz, 1H), 1.75 (s, 3H), 1.34 (s, 9H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 100 MHz): δ 173.0, 150.3, 141.8, 139.8, 137.8, 128.9, 127.0, 125.8, 124.3, 119.7, 116.3, 55.1, 34.5, 31.3, 24.6; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{21}H_{26}NO$ 308.2014, Found 308.2015.

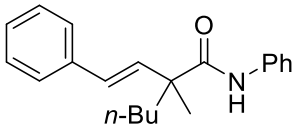


(*E*)-2,2-Dimethyl-*N*,4-diphenylbut-3-enamide (4na). Compound **4na** was synthesized from (3-methylbuta-1,2-dien-1-yl)benzene (**1n**, 43.3 mg, 0.300 mmol) and phenyl isocyanate (**3a**, 27.0 μL, 0.250 mmol) in 71% yield (46.9 mg, 0.177 mmol) as a white solid. The crude product was purified using silica gel column chromatography (EtOAc:hexanes = 1:40). **mp** 90-91 °C; **IR** (neat): 3286 (m), 2970 (m), 1659 (s), 1597 (s), 1520 (s), 1497 (m), 1435 (m), 1311 (m), 1242 (m), 1149 (m), 1034 (m), 972 (m), 748 (s), 687 (s) cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.52-7.47 (m, 5H), 7.39 (t, *J* = 7.5 Hz, 2H), 7.33-7.29 (m, 3H), 7.11 (t, *J* = 7.3 Hz, 1H), 6.70 (d, *J* = 16.0 Hz, 1H), 6.49 (d, *J* = 16.0 Hz, 1H), 1.53 (s, 6H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 100 MHz): δ 174.2, 137.8, 136.3, 133.9, 130.3, 128.9, 128.7, 128.0, 126.4, 124.2, 119.7, 46.0, 25.2; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{18}H_{20}NO$ 266.1545, Found 266.1545.

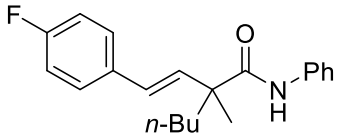


(*E*)-*N*-Phenyl-1-styrylcyclohexane-1-carboxamide (4oa). Compound **4oa** was synthesized from (2-cyclohexylidenevinyl)benzene (**1o**, 55.3 mg, 0.300 mmol) and phenyl isocyanate (**3a**, 27.0 μL, 0.250 mmol) in 76% yield (58.2 mg, 0.191 mmol) as a white solid. The crude product was purified using silica

gel column chromatography (EtOAc:hexanes = 1:40). **mp** 91-92 °C; **IR** (neat): 3286 (m), 2932 (m), 1651 (s), 1597 (m), 1528 (s), 1443 (m), 1311 (m), 1250 (m), 1165 (m), 1080 (m), 1034 (m), 972 (m), 748 (s), 694 (s) cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.55 (br s, 1H), 7.49 (d, *J* = 6.9 Hz, 2H), 7.44 (d, *J* = 7.8 Hz, 2H), 7.36 (t, *J* = 7.1 Hz, 2H), 7.28 (t, *J* = 7.8 Hz, 3H), 7.07 (t, *J* = 7.3 Hz, 1H), 6.64 (d, *J* = 16.5 Hz, 1H), 6.28 (d, *J* = 16.5 Hz, 1H), 2.20-2.14 (m, 2H), 1.88-1.85 (m, 2H), 1.65-1.45 (m, 6H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 100 MHz): δ 173.5, 137.9, 136.6, 133.2, 131.9, 128.9, 128.7, 127.9, 126.3, 124.1, 119.8, 50.2, 33.8, 25.6, 22.4; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{21}H_{24}NO$ 306.1858, Found 306.1859.

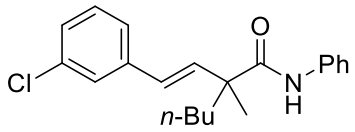


(*E*)-2-Methyl-*N*-phenyl-2-styrylhexanamide (4pa). Compound **4pa** was synthesized from (3-methylhepta-1,2-dien-1-yl)benzene (**1p**, 55.9 mg, 0.300 mmol) and phenyl isocyanate (**3a**, 27.0 μL, 0.250 mmol) in 77% yield (59.2 mg, 0.193 mmol) as a white solid. The crude product was purified using silica gel column chromatography (EtOAc:hexanes = 1:40). **mp** 96-97 °C; **IR** (neat): 3279 (m), 2962 (m), 1659 (s), 1597 (m), 1520 (s), 1435 (m), 1311 (m), 1242 (m), 1149 (m), 1134 (m), 1080 (m), 972 (m), 748 (s), 694 (s) cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.52-7.47 (m, 5H), 7.40 (t, *J* = 7.5 Hz, 2H), 7.32 (t, *J* = 7.5 Hz, 3H), 7.11 (t, *J* = 7.3 Hz, 1H), 6.68 (d, *J* = 16.4 Hz, 1H), 6.50 (d, *J* = 16.4 Hz, 1H), 1.89 (t, *J* = 7.5 Hz, 2H), 1.51 (s, 3H), 1.38-1.36 (m, 4H), 0.95 (t, *J* = 7.4 Hz, 3H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 100 MHz): δ 174.1, 138.0, 136.7, 133.2, 131.2, 129.1, 128.9, 128.1, 126.6, 124.4, 120.0, 49.6, 38.7, 26.9, 23.4, 22.7, 14.2; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{21}H_{26}NO$ 308.2014, Found 308.2015.

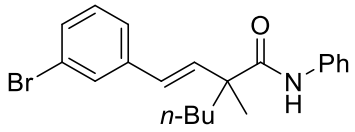


(*E*)-2-(4-Fluorostyryl)-2-methyl-*N*-phenylhexanamide (4qa). Compound **4qa** was synthesized from 1-fluoro-4-(3-methylhepta-1,2-dien-1-yl)benzene (**1q**, 61.3 mg, 0.300 mmol) and phenyl isocyanate (**3a**, 27.0 μL, 0.250 mmol) in 92% yield (74.9 mg, 0.230 mmol) as a white solid. The crude product was purified using silica gel column chromatography (EtOAc:hexanes = 1:20). **mp** 117-118 °C; **IR** (neat): 3279 (m), 2970 (m), 1659 (s), 1597 (m), 1512 (s), 1443 (m), 1311 (m), 1227 (s), 1157 (m), 972 (m), 818 (m), 756 (s), 702 (s) cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.50 (d, *J* = 7.8 Hz, 2H), 7.45 (br s, 1H), 7.43 (dd, *J* = 8.7, 5.5 Hz, 2H), 7.31 (t, *J* = 8.0 Hz, 2H), 7.12-7.04 (m, 3H), 6.62 (d, *J* = 16.5 Hz, 1H), 6.40 (d, *J* = 16.5 Hz, 1H), 1.87 (t, *J* = 7.5 Hz, 2H), 1.49 (s, 3H), 1.39-1.34 (m, 4H), 0.94 (t, *J* = 6.9 Hz, 3H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 100 MHz): δ 173.8, 162.5 (d, $J_{C\text{-}F}$ = 247.6 Hz), 137.8, 132.8 (d, $J_{C\text{-}F}$ = 2.9 Hz),

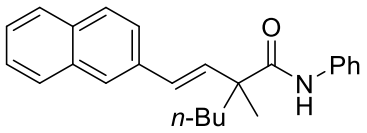
132.7 (d, $J_{C\text{-}F}$ = 3.9 Hz), 129.7, 128.9, 127.9 (d, $J_{C\text{-}F}$ = 7.7 Hz), 124.2, 119.8, 115.6 (d, $J_{C\text{-}F}$ = 21.2 Hz), 49.3, 38.6, 26.7, 23.2, 22.4, 14.0; ^{19}F NMR ($CDCl_3$, 75.2 Hz): δ -68.54; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{21}H_{25}FNO$ 326.1920, Found 326.1920.



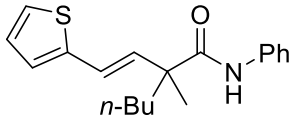
(*E*)-2-(3-Chlorostyryl)-2-methyl-*N*-phenylhexanamide (4ra). Compound **4ra** was synthesized from 1-chloro-3-(3-methylhepta-1,2-dien-1-yl)benzene (**1r**, 66.2 mg, 0.300 mmol) and phenyl isocyanate (**3a**, 27.0 μL, 0.250 mmol) in 81% yield (69.2 mg, 0.202 mmol) as a colorless oil. The crude product was purified using silica gel column chromatography (EtOAc:hexanes = 1:40). **IR** (neat): 3348 (m), 2970 (m), 1666 (s), 1597 (s), 1520 (s), 1443 (m), 1311 (m), 1242 (m), 1119 (s), 1034 (m), 972 (m), 756 (s), 694 (s) cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.47 (d, *J* = 8.2 Hz, 2H), 7.42 (s, 1H), 7.37 (br s, 1H), 7.31-7.25 (m, 5H), 7.08 (t, *J* = 7.3 Hz, 1H), 6.57 (d, *J* = 16.4 Hz, 1H), 6.47 (d, *J* = 16.4 Hz, 1H), 1.86-1.82 (m, 2H), 1.46 (s, 3H), 1.36-1.33 (m, 2H), 1.25 (t, *J* = 7.1 Hz, 2H), 0.96 (t, *J* = 6.6 Hz, 3H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 100 MHz): δ 173.5, 138.4, 137.7, 134.7, 129.9, 129.6, 128.9, 127.9, 126.3, 124.6, 124.3, 120.1, 119.8, 49.4, 38.6, 26.7, 23.2, 22.3, 14.0; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{21}H_{25}ClNO$ 342.1625, Found 342.1624.



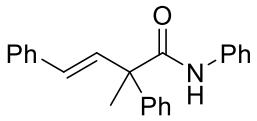
(*E*)-2-(3-Bromostyryl)-2-methyl-*N*-phenylhexanamide (4sa). Compound **4sa** was synthesized from 1-bromo-3-(3-methylhepta-1,2-dien-1-yl)benzene (**1s**, 79.6 mg, 0.300 mmol) and phenyl isocyanate (**3a**, 27.0 μL, 0.250 mmol) in 94% yield (90.8 mg, 0.235 mmol) as a colorless oil. The crude product was purified using silica gel column chromatography (EtOAc:hexanes = 1:40). **IR** (neat): 3325 (m), 2978 (m), 1666 (s), 1597 (s), 1520 (s), 1443 (m), 1312 (m), 1242 (m), 1126 (m), 1072 (m), 972 (m), 748 (s), 694 (s) cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.61 (s, 1H), 7.50 (d, *J* = 7.8 Hz, 2H), 7.43-7.30 (m, 5H), 7.24 (t, *J* = 7.8 Hz, 1H), 7.11 (t, *J* = 7.3 Hz, 1H), 6.58 (d, *J* = 16.5 Hz, 1H), 6.49 (d, *J* = 16.5 Hz, 1H), 1.88-1.85 (m, 2H), 1.48 (s, 3H), 1.38-1.32 (m, 4H), 0.93 (t, *J* = 6.6 Hz, 3H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 100 MHz): δ 173.5, 138.6, 137.7, 134.7, 130.8, 130.2, 129.5, 129.2, 128.9, 125.1, 124.3, 122.9, 119.8, 49.4, 38.5, 26.7, 23.2, 22.3, 14.0; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{21}H_{25}BrNO$ 386.1120, Found 386.1122.



(*E*)-2-Methyl-2-(2-(naphthalen-2-yl)vinyl)-*N*-phenylhexanamide (4ta). Compound **4ta** was synthesized from 2-(3-methylhepta-1,2-dien-1-yl)naphthalene (**1t**, 70.9 mg, 0.300 mmol) and phenyl isocyanate (**3a**, 27.0 μL, 0.250 mmol) in 90% yield (80.4 mg, 0.225 mmol) as a colorless oil. The crude product was purified using silica gel column chromatography (EtOAc:hexanes = 1:40). **IR** (neat): 3340 (m), 2970 (m), 1666 (s), 1597 (m), 1520 (s), 1443 (m), 1311 (m), 1242 (m), 1119 (m), 972 (m), 810 (m), 748 (s), 694 (s) cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.88-7.84 (m, 4H), 7.69 (d, *J* = 8.7 Hz, 1H), 7.55-7.48 (m, 5H), 7.32 (t, *J* = 7.3 Hz, 2H), 7.11 (t, *J* = 7.6 Hz, 1H), 6.85 (d, *J* = 16.5 Hz, 1H), 6.63 (d, *J* = 16.5 Hz, 1H), 1.95-1.91 (m, 2H), 1.56 (s, 3H), 1.42-1.39 (m, 4H), 0.98-0.95 (m, 3H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 100 MHz): δ 174.0, 137.8, 133.8, 133.5, 133.2, 133.0, 131.1, 128.9, 128.4, 127.9, 127.7, 126.5, 126.5, 126.1, 124.2, 123.2, 119.7, 49.5, 38.6, 26.7, 23.3, 22.5, 14.0; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{25}H_{28}NO$ 358.2171, Found 358.2170.

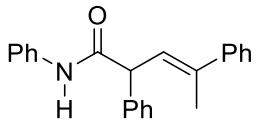


(*E*)-2-Methyl-*N*-phenyl-2-(2-(thiophen-2-yl)vinyl)hexanamide (4ua). Compound **4ua** was synthesized from 2-(3-methylhepta-1,2-dien-1-yl)thiophene (**1u**, 57.7 mg, 0.300 mmol) and phenyl isocyanate (**3a**, 27.0 μL, 0.250 mmol) in 82% yield (64.3 mg, 0.205 mmol) as a white solid. The crude product was purified using silica gel column chromatography (EtOAc:hexanes = 1:30). **mp** 115-116 °C; **IR** (neat): 3294 (m), 2970 (m), 1659 (s), 1597 (m), 1520 (s), 1445 (m), 1311 (m), 1242 (m), 1126 (m), 964 (m), 810 (m), 748 (s), 702 (s) cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.50 (d, *J* = 7.8 Hz, 2H), 7.43 (br s, 1H), 7.31 (t, *J* = 8.0 Hz, 2H), 7.22 (d, *J* = 5.0 Hz, 1H), 7.10 (t, *J* = 7.8 Hz, 1H), 7.04-7.01 (m, 2H), 6.78 (d, *J* = 16.5 Hz, 1H), 6.30 (d, *J* = 16.4 Hz, 1H), 1.86-1.82 (m, 2H), 1.46 (s, 3H), 1.39-1.31 (m, 4H), 0.93 (t, *J* = 6.9 Hz, 3H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 100 MHz): δ 173.7, 141.7, 137.8, 132.4, 128.9, 127.6, 126.1, 124.6, 124.5, 124.3, 119.8, 49.4, 38.6, 26.7, 23.2, 22.5, 14.0; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{19}H_{24}NOS$ 314.1579, Found 314.1580.

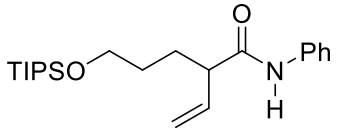


(*E*)-2-Methyl-*N*,2,4-triphenylbut-3-enamide (4xa-1). Compound **4xa-1** was synthesized from buta-

1,2-diene-1,3-diyldibenzene (**1x**, 61.9 mg, 0.300 mmol) and phenyl isocyanate (**3a**, 27.0 μL, 0.250 mmol) in 39% yield (31.9 mg, 0.0974 mmol) as a white foaming. The crude product was purified using silica gel column chromatography (EtOAc:hexanes = 1:40). **IR** (neat): 3032 (m), 2986 (m), 1728 (s), 1674 (s), 1520 (s), 1443 (m), 1311 (m), 1211 (m), 1072 (m), 972 (m), 910 (m), 748 (s), 694 (s) cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.48-7.41 (m, 8H), 7.37-7.29 (m, 6H), 7.21 (br s, 1H), 7.11 (t, *J* = 7.5 Hz, 1H), 6.78 (d, *J* = 16.5 Hz, 1H), 6.48 (d, *J* = 16.1 Hz, 1H), 1.87 (s, 3H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 100 MHz): δ 172.9, 143.3, 137.7, 136.6, 133.4, 129.7, 129.3, 128.9, 128.6, 127.9, 127.5, 127.5, 126.5, 124.4, 119.7, 55.1, 25.4; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{23}H_{22}NO$ 328.1701, Found 328.1701.



(*E*)-*N*,2,4-triphenylpent-3-enamide (4xa-2). Compound **4xa-2** was synthesized from buta-1,2-diene-1,3-diyldibenzene (**1x**, 61.9 mg, 0.300 mmol) and phenyl isocyanate (**3a**, 27.0 μL, 0.250 mmol) in 35% yield (28.6 mg, 0.0873 mmol) as a white solid. The crude product was purified using silica gel column chromatography (EtOAc:hexanes = 1:40). **mp** 130-131 °C**; IR** (neat): 3294 (m), 3063 (m), 1659 (s), 1597 (s), 1543 (s), 1497 (m), 1375 (m), 1250 (m), 1080 (m), 1026 (m), 887 (m), 756 (s), 694 (s) cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.50-7.37 (m, 9H), 7.35-7.28 (m, 6H), 7.11 (t, *J* = 7.4 Hz, 1H), 6.33 (dd, *J* = 9.1, 1.4 Hz, 1H), 4.72 (d, *J* = 8.7 Hz, 1H), 2.16 (s, 3H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 100 MHz): δ 170.4, 142.7, 139.5, 139.2, 137.7, 129.1, 128.9, 128.3, 128.1, 127.5, 127.4, 125.9, 125.3, 124.4, 119.8, 53.8, 16.6; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{23}H_{22}NO$ 328.1701, Found 328.1702.



***N*-Phenyl-5-((triisopropylsilyl)oxy)-2-vinylpentanamide (4ya)**. Compound **4ya** was synthesized from (hexa-4,5-dien-1-yloxy)triisopropylsilane (**1y**, 127.2 mg, 0.500 mmol) and phenyl isocyanate (**3a**, 27.0 μL, 0.250 mmol) in 90% yield (84.5 mg, 0.225 mmol) as a colorless oil. The crude product was purified using silica gel column chromatography (EtOAc:hexanes = 1:30). **IR** (neat): 3302 (m), 2939 (m), 2862 (m), 1659 (s), 1605 (m), 1543 (s), 1443 (m), 1103 (s), 995 (m), 879 (m), 748 (s), 687 (s) cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.51 (d, *J* = 7.8 Hz, 2H), 7.32 (t, *J* = 7.8 Hz, 2H), 7.32 (br s, 1H), 7.11 (d, *J* = 7.3 Hz, 1H), 5.99-5.90 (m, 1H), 5.31-5.27 (2H), 3.79-3.69 (m, 2H), 3.04 (q, *J* = 7.4 Hz, 1H), 2.06-1.99 (m, 1H), 1.75-1.58 (m, 3H), 1.15-1.03 (m, 21H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 100 MHz): δ 171.3, 137.8, 137.1, 129.0, 124.2, 119.7, 118.4, 63.2, 52.6, 30.4, 28.2, 18.0, 12.0; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for

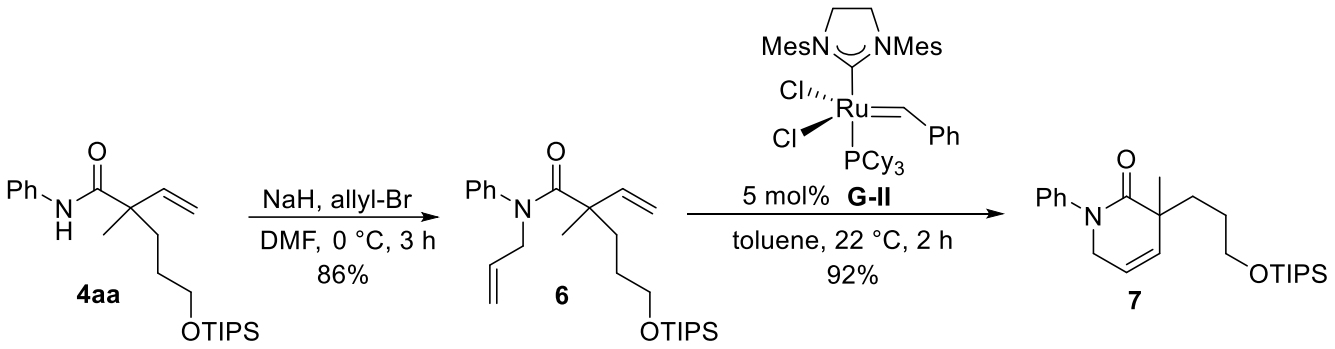
$C_{22}H_{38}NO_2Si$ 376.2672, Found 376.2653.

6. Procedure for gram-scale reaction

In a glove box, IPrCuCl (97.5 mg, 0.200 mmol) was added to a round bottomed flask (100 mL) charged with a magnetic stir bar, and the flask was sealed with a rubber septum equipped with a reflux condenser and removed from the glove box. After purging the flask with N_2 gas for 5 min, THF (13.3 mL) and diisobutylaluminum hydride (0.713 mL, 4.00 mmol) were added. The reaction mixture was premixed for 10 min and a solution of triisopropyl((4-methylhexa-4,5-dien-1-yl)oxy)silane (**1a**, 1.07 g, 4.00 mmol) in THF (6.7 mL) was added. The reaction solution was stirred at 60 °C on a preheated heating block for 3 h. Then, phenyl isocyanate (**3a**, 0.362 mL, 3.33 mmol) was added slowly via a syringe to the solution, which was stirred at 60 °C for an additional 2 h. The resulting solution was quenched by adding an aqueous solution of 1 N HCl (13 mL), followed by washing with ethyl acetate (EtOAc) (15 mL× 3). The organic layers were combined, dried over $MgSO_4$, filtered, and concentrated in vacuo. The crude product was purified using silica gel column chromatography (EtOAc:hexanes = 1:20) to produce the desired product **4aa** (1.43 g, 3.67 mmol, 92% yield) as a colorless oil.

7. Synthetic applications

(1) Synthesis of a six-membered lactam **7**

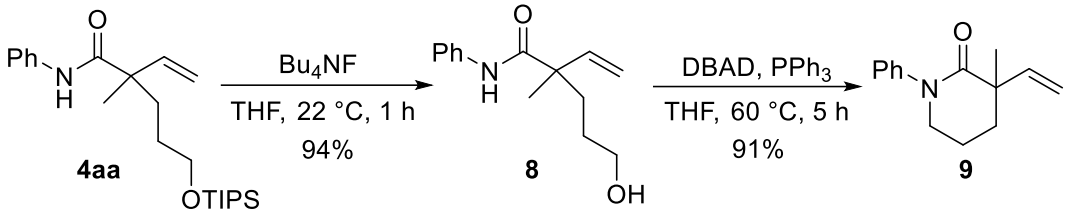


***N*-Allyl-2-methyl-*N*-phenyl-5-((triisopropylsilyl)oxy)-2-vinylpentanamide (6)**. Sodium hydride (60% in mineral oil, 19.2 mg, 0.480 mmol) was added to a solution of 2-methyl-*N*-phenyl-5-((triisopropylsilyl)oxy)-2-vinylpentanamide (**4aa**, 156 mg, 0.400 mmol) in DMF (2 mL) at 0 °C (ice bath) under N_2 flow. After stirring for 0.5 h at the same temperature, allyl bromide (38.0 μL, 0.440 mmol) was added to the mixture, which was stirred for 3 h. Afterward, the reaction solution was quenched with water (5 mL) and washed with Et_2O (2 mL × 5). The organic layers were combined, dried over $MgSO_4$, filtered,

and concentrated in vacuo. The crude product was purified using silica gel column chromatography (EtOAc:hexanes = 1:20) to obtain the allylated product **6** (184 mg, 0.428 mmol, 86%) as a sticky colorless oil. **IR** (neat): 3055 (w), 2947 (m), 2862 (m), 2361 (s), 2168 (m), 1736 (s), 1597 (m), 1528 (m), 1443 (m), 1373 (s), 1311 (s), 1211 (s), 1111 (s), 1003 (w), 926 (m), 887 (m), 748 (m), 687 (m) cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.28 (t, *J* = 6.9 Hz, 3H), 7.13-7.10 (m, 2H), 5.93-5.83 (m, 1H), 5.67 (dd, *J* = 17.4, 11.0 Hz, 1H), 5.08 (d, *J* = 10.1 Hz, 1H), 5.01 (dd, *J* = 17.4, 1.4 Hz, 1H), 4.65-4.59 (m, 2H), 4.21 (qd, *J* = 14.5, 6.4 Hz, 2H), 3.65 (t, *J* = 5.7 Hz, 2H), 1.72-1.54 (m, 2H), 1.53-1.47 (m, 2H), 1.16 (s, 3H), 1.11-1.03 (m, 21H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 100 MHz): δ 174.4, 142.8, 142.5, 133.2, 128.4, 127.8, 117.7, 111.3, 63.7, 55.4, 49.4, 35.8, 28.2, 24.0, 18.0, 11.9; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{26}H_{44}NO_2Si$ 430.3141, Found 430.3140.

3-Methyl-1-phenyl-3-(3-((triisopropylsilyl)oxy) propyl)-3,6-dihydropyridin-2(1*H*)-one (7). In the glove box, the second-generation Grubbs catalyst **G-II** (8.50 mg, 1.00×10^{-2} mmol) was weighed out into a vial (8 mL) charged with a magnetic bar, and the vial was sealed with a cap (phenolic open-top cap with gray PTFE/silicone) and removed from the glove box. Under N_2 gas flow, a solution of *N*-allyl-2-methyl-N-phenyl-5-((triisopropylsilyl)oxy)-2-vinylpentanamide (**6**, 86.0 mg, 0.200 mmol) in toluene (12.3 mL) was added to the vial. The reaction mixture was stirred at room temperature for 2 h. Afterward, the resulting solution was filtered through a plug of celite with Et_2O (1.5 mL × 3). After removing all volatiles, the resulting crude product was purified using silica gel column chromatography (EtOAc:hexanes = 1:3) to produce the desired product **7** (73.7 mg, 0.183 mmol, 92%) as a pale-green oil. **IR** (neat): 2947 (w), 2862 (m), 2361 (m), 2168 (m), 2129 (m), 1744 (s), 1659 (s), 1597 (m), 1528 (w), 1466 (s), 1427 (s), 1366 (s), 1288 (s), 1211 (s), 1111(s), 995 (w), 918 (m), 887 (m), 687 (m) cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.43-7.39 (m, 2H), 7.30-7.26 (m, 3H), 5.83 (dt, *J* = 10.1, 3.2 Hz, 1H), 5.63 (dt, *J* = 10.1, 2.1 Hz, 1H), 4.24 (t, *J* = 2.5 Hz, 2H), 3.76-3.70 (m, 1H), 3.66-3.60 (m, 1H), 2.03-1.97 (m, 1H), 1.70-1.56 (m, 2H),1.55-1.44 (m, 1H), 1.37 (s, 3H), 1.11-1.04 (m, 21H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 100 MHz): δ 173.2, 142.7, 132.8, 129.1, 126.9, 126.5, 119.6, 63.4, 52.3, 43.0, 37.5, 29.0, 27.1, 18.0, 11.9; **HRMS** (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{24}H_{39}NNaO_2Si$ 424.2648, Found 424.2648.

(2) Synthesis of a six-membered lactam **9**

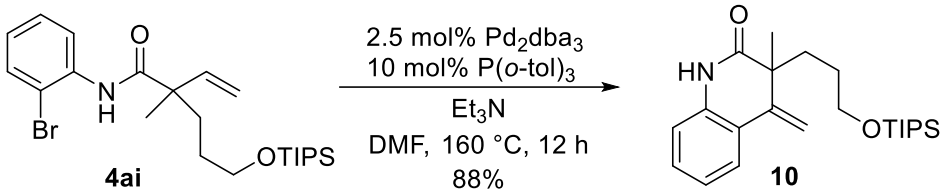


5-Hydroxy-2-methyl-*N*-phenyl-2-vinylpentanamide (8). 2-Methyl-*N*-phenyl-5-((triisopropylsilyl)oxy)-2-vinylpentanamide (**4aa**, 117 mg, 0.300 mmol), THF (1.2 mL) and tetrabutylammonium fluoride (1.0 M in THF, 0.900 mL, 0.900 mmol) were added to a vial (8 mL) under N_2 gas flow. The reaction mixture was stirred at room temperature for 1 h and quenched with a saturated aqueous solution of NH_4Cl (1 mL). After washing the solution with Et_2O (2 mL × 3), the organic layers were combined, dried over $MgSO_4$, filtered, and concentrated in vacuo. The crude product was purified using silica gel column chromatography (EtOAc:hexanes = 1:1) to produce the alcohol product **8** (65.8 mg, 0.282 mmol, 94%) as a colorless oil. **IR** (neat): 3371 (w), 3063 (m), 2947 (w), 2870 (w), 2361 (m), 1859 (s), 1705 (s), 1674 (s), 1597 (s), 1528 (s), 1435 (s), 1366 (s), 1311 (s), 1227 (s), 1173 (s), 1126 (s), 1057 (s), 926 (s), 756 (s) cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.51-7.49 (m, 3H), 7.32 (t, *J* = 8.0 Hz, 2H), 7.11 (t, *J* = 7.8 Hz, 1H), 6.14 (dd, *J* = 17.4, 11.0 Hz, 1H), 5.43-5.38 (m, 2H), 3.67 (t, *J* = 6.4 Hz, 2H), 1.93-1.79 (m, 2H), 1.64-1.59 (m, 3H), 1.39 (s, 3H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 100 MHz): δ 173.8, 141.3, 137.7, 128.8, 124.3, 119.7, 116.7, 62.6, 49.4, 33.9, 27.5, 22.0; **HRMS** (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{14}H_{19}NNaO_2$ 256.1313, Found 256.1314.

3-Methyl-1-phenyl-3-vinylpiperidin-2-one (9). Triphenylphosphine (142 mg, 0.540 mmol), di-*tert*-butyl azodicarboxylate (124 mg, 0.540 mmol), and THF (2 mL) were added to a vial (8 ml) under N_2 gas flow. The solution was allowed to premix for 10 min and a solution of 5-hydroxy-2-methyl-*N*-phenyl-2-vinylpentanamide (**8**, 84.5 mg, 0.360 mmol) in THF (1 mL) was added using a cannula. Then, the reaction mixture was stirred for 5 h at 60 °C on a heating block. Afterward, the resulting solution was concentrated and the remaining crude product was purified using silica gel column chromatography (EtOAc:hexanes = 1:20) to obtain the lactam product **9** (70.5 mg, 0.330 mmol, 91%) as a colorless oil. **IR** (neat): 2970 (w), 2870 (m), 2361 (m), 2168 (m), 2129 (m), 1736 (s), 1651 (s), 1420 (s), 1121 (s), 1119 (s), 918 (m), 764 (m), 625 (m) cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.38 (t, *J* = 7.3 Hz, 2H), 7.25-7.23 (m, 3H), 6.02 (ddd, *J* = 17.6, 10.7, 1.8 Hz, 1H), 5.21 (d, *J* = 17.4 Hz, 1H), 5.18 (d, *J* = 10.1 Hz, 1H), 3.72-3.61 (m, 2H), 2.09-2.01 (m, 2H), 1.95-1.88 (m, 2H), 1.40 (s, 3H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 100 MHz): δ 173.4, 143.7, 143.6, 129.0, 126.5, 126.3 113.6, 52.0, 45.8, 34.0, 26.4, 19.9; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for

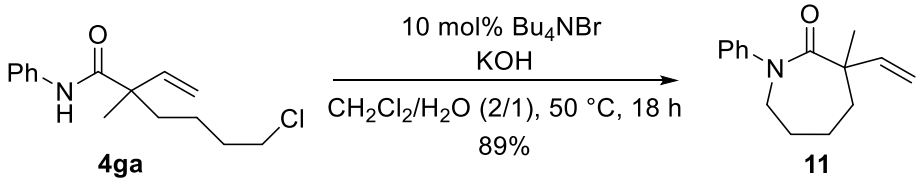
$C_{14}H_{18}NO$ 216.1388, Found 216.1388.

(3) Synthesis of a six-membered lactam **10**



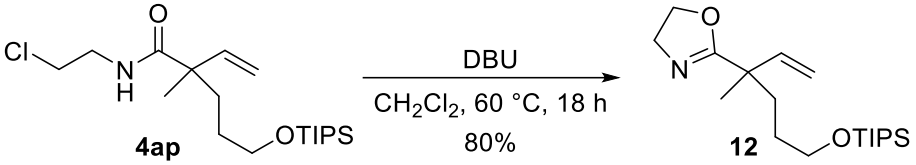
3-Methyl-4-methylene-3-(3-((triisopropylsilyl)oxy)propyl)-3,4-dihydroquinolin-2(1*H*)-one (10). In a glove box, Pd_2dba_3 (2.29 mg, 2.50×10^{-3} mmol) and P(*o*-tol)$_3$ (3.04 mg, 1.00×10^{-2} mmol) were added to a vial (4 mL) charged with a magnetic stir bar, and the vial was sealed with a cap (phenolic open-top cap with gray PTFE/silicone) and removed from the glove box. After purging the vial with N_2 gas for 5 min, a solution of *N*-(2-bromophenyl)-2-methyl-5-((triisopropylsilyl)oxy)-2-vinylpentanamide (**4ai**, 46.9 mg, 0.100 mmol) in DMF (0.56 mL) was added to the mixture, which was premixed for 10 min. Then, triethylamine (40.0 µL, 0.283 mmol) was added to the mixture. The reaction mixture was stirred for 12 h at 160 °C on a heating block and allowed to cool to room temperature. The resulting solution was quenched with water (2 mL) and washed with ethyl acetate (15 mL× 3). The organic layers were combined, dried over $MgSO_4$, filtered, and concentrated in vacuo. The crude product was purified using silica gel column chromatography (EtOAc:hexanes = 1:10) to produce the desired product **10** (34.2 mg, 0.0882 mmol, 88% yield) as a colorless oil. **IR** (neat): 3209 (w), 2970 (m), 1682 (s), 1620 (m), 1481 (s), 1458 (m), 1381 (m), 1257 (m), 1088 (s), 802 (s), 748 (s) cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 8.79 (br s, 1H), 7.48 (d, *J* = 7.3 Hz, 1H), 7.22 (td, *J* = 7.5, 1.4 Hz, 1H), 7.02 (t, *J* = 7.5 Hz, 1H), 6.79 (d, *J* = 7.8 Hz, 1H), 5.55 (s, 1H), 5.25 (s, 1H), 3.56 (t, *J* = 6.2 Hz, 2H), 1.72-1.67 (m, 2H), 1.54-1.48 (m, 2H), 1.46 (s, 3H), 1.03-0.93 (m, 21H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 100 MHz): δ 175.2, 145.2, 134.9, 129.1, 125.4, 123.3, 123.2, 115.0, 112.0, 63.1, 47.6, 34.6, 27.5, 19.7, 17.9, 11.9; **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd for $C_{23}H_{37}NNaO_2Si$ 410.2491, Found 410.2491.

(4) Synthesis of a seven-membered lactam **11**



3-Methyl-1-phenyl-3-vinylazepan-2-one (**11**). Tetrabutylammonium bromide (3.20 mg, 1.00 × 10^{-2} mmol) and KOH (16.8 mg, 0.300 mmol) were added to a vial (4 mL) charged with 6-chloro-2-methyl-N-phenyl-2-vinylhexanamide (**4ga**, 26.6 mg, 0.100 mmol) and a magnetic stir bar under N_2 gas flow. CH_2Cl_2 (0.1 mL) and water (50.0 μL) were added to the vial, which was stirred for 18 h at 50 ℃ on a heating block. Afterward, the reaction solution was quenched by adding a saturated aqueous solution of NH_4Cl (0.1 mL) and washed with CH_2Cl_2 (0.5 mL × 3). The organic layers were combined, dried over $MgSO_4$, filtered, and concentrated in vacuo. The crude product was purified using silica gel column chromatography (EtOAc:hexanes = 1:20) to produce the desired product **11** (20.3 mg, 0.0885 mmol, 89% yield) as a light-yellow oil. **IR** (neat): 3078 (w), 2924 (m), 1651 (s), 1589 (m), 1489 (s), 1366 (m), 1335 (m), 1265 (s), 1119 (w), 910 (m), 694 (s) cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.37 (t, *J* = 7.8 Hz, 2H), 7.23 (t, *J* = 7.3 Hz, 1 H), 7.18 (d, *J* = 7.4 Hz, 2H), 6.08 (dd, *J* = 17.4, 11.0 Hz, 1H), 5.23 (d, *J* = 10.0 Hz, 1H), 5.22 (d, *J* = 17.4 Hz, 1H), 4.09 (ddd, *J* = 15.2, 11.1, 1.6 Hz, 1H), 3.42 (ddd, *J* = 15.2, 5.6, 2.5 Hz, 1H), 1.90-1.78 (m, 5H), 1.74-1.69 (m, 1H), 1.34 (s, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 176.4, 146.6, 142.0, 129.1, 126.6, 126.4, 113.7, 51.4, 49.7, 36.6, 30.4, 28.7, 25.3; **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{20}NO$ 230.1545, Found 230.1546.

(5) Synthesis of oxazoline **12**



2-(3-Methyl-6-((triisopropylsilyl)oxy)hex-1-en-3-yl)-4,5-dihydrooxazole (**12**). Diazabicyclo[5.4.0]undec-7-ene (30.0 μL, 0.200 mmol) was added to a solution of N-(2-chloroethyl)-2-methyl-5-((triisopropylsilyl)oxy)-2-vinylpentanamide (**4ap**, 37.6 mg, 0.100 mmol) in CH_2Cl_2 (1.0 mL) under N_2 gas flow. The reaction mixture was stirred for 18 h at 60 ℃ on a heating block. The resulting solution was quenched by adding a saturated aqueous solution of NH_4Cl (1.0 mL) and washed with CH_2Cl_2 (1.0 mL × 3). The organic layers were combined, dried over $MgSO_4$, filtered, and concentrated in vacuo. The crude product was purified using silica gel column chromatography (EtOAc:hexanes = 1:3) to produce the desired product **12** (27.3 mg, 0.0804 mmol, 80% yield) as a colorless oil. **IR** (neat): 3010 (m), 2947 (m), 1736 (s), 1659 (s), 1466 (m), 1381 (m), 1257 (m), 1103 (s), 957 (m), 679 (s) cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 6.03 (dd, *J* = 17.4, 10.5 Hz, 1H), 5.13-5.09 (m, 2H), 4.23 (t, *J* = 9.6 Hz, 2H), 3.83 (t, *J* = 9.1 Hz, 2H), 3.66 (t, *J* = 6.5 Hz, 2H), 1.80-1.72 (m, 1H), 1.69-1.61 (m, 1H), 1.54-1.46 (m,

2H), 1.32 (s, 3H), 1.12-1.01 (m, 21H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 172.1, 142.2, 113.2, 67.4, 63.6, 54.2, 42.5, 35.1, 28.1, 21.6, 18.0, 11.9; **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{19}H_{38}NO_2Si$ 340.2672, Found 340.2674.

8. Copies of ^{1}H and ^{13}C NMR spectra for all products

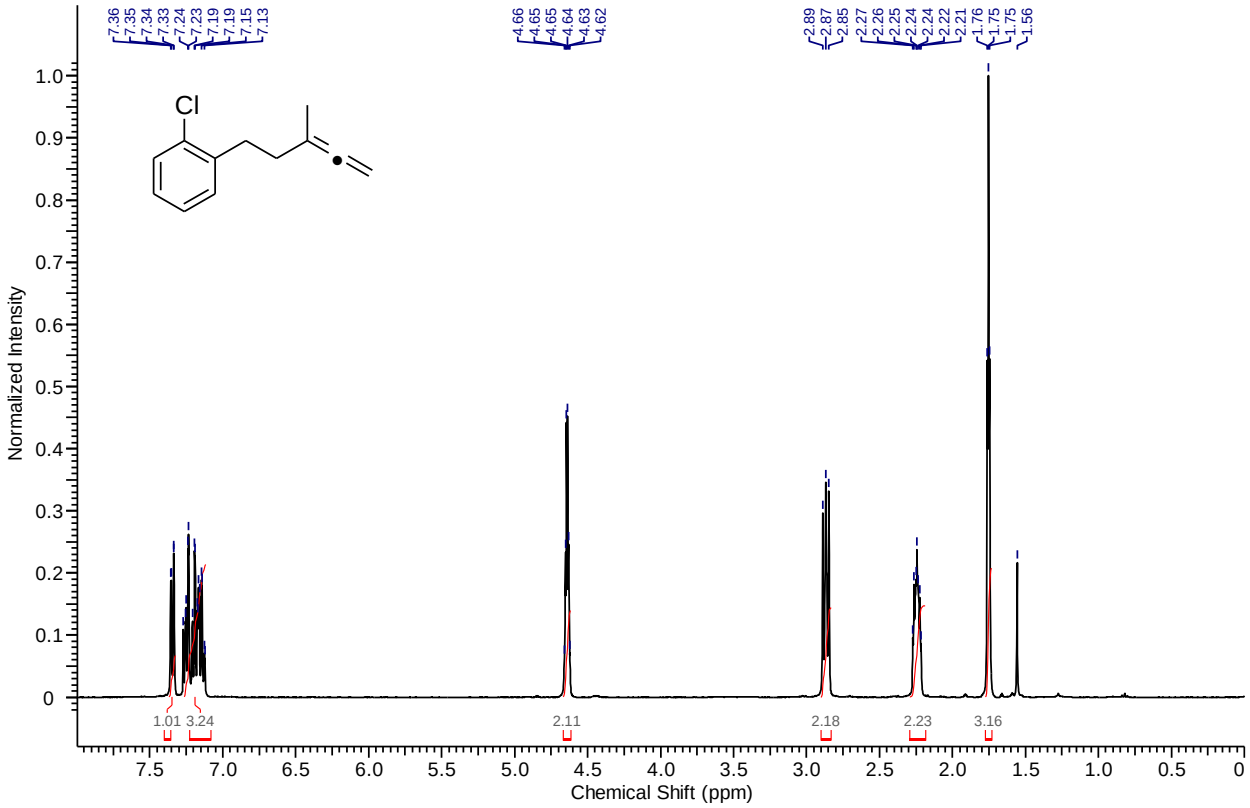


Figure S1. ^{1}H NMR spectrum of the compound **1i** in $CDCl_3$, 400 MHz

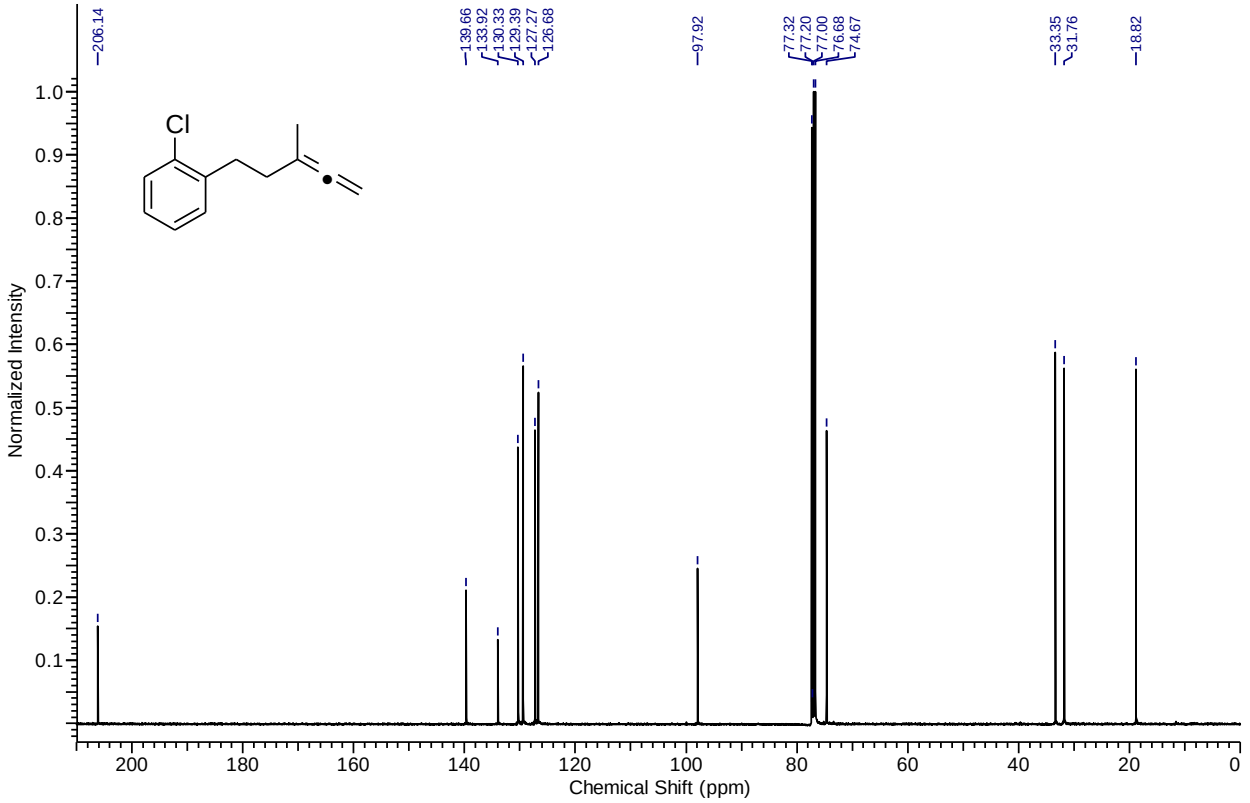


Figure S2. ^{13}C NMR spectrum of the compound **1i** in $CDCl_3$, 100 MHz

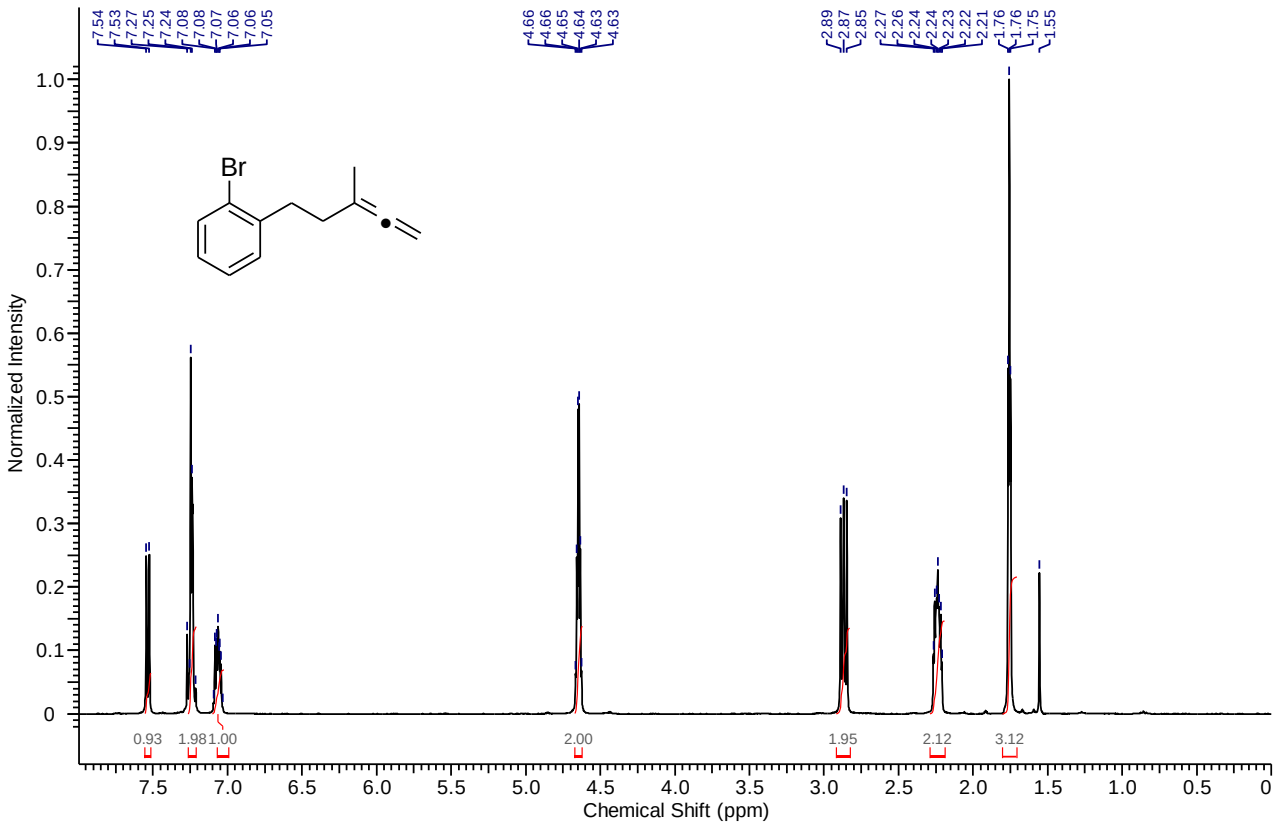


Figure S3. ^{1}H NMR spectrum of the compound **1j** in $CDCl_3$, 400 MHz

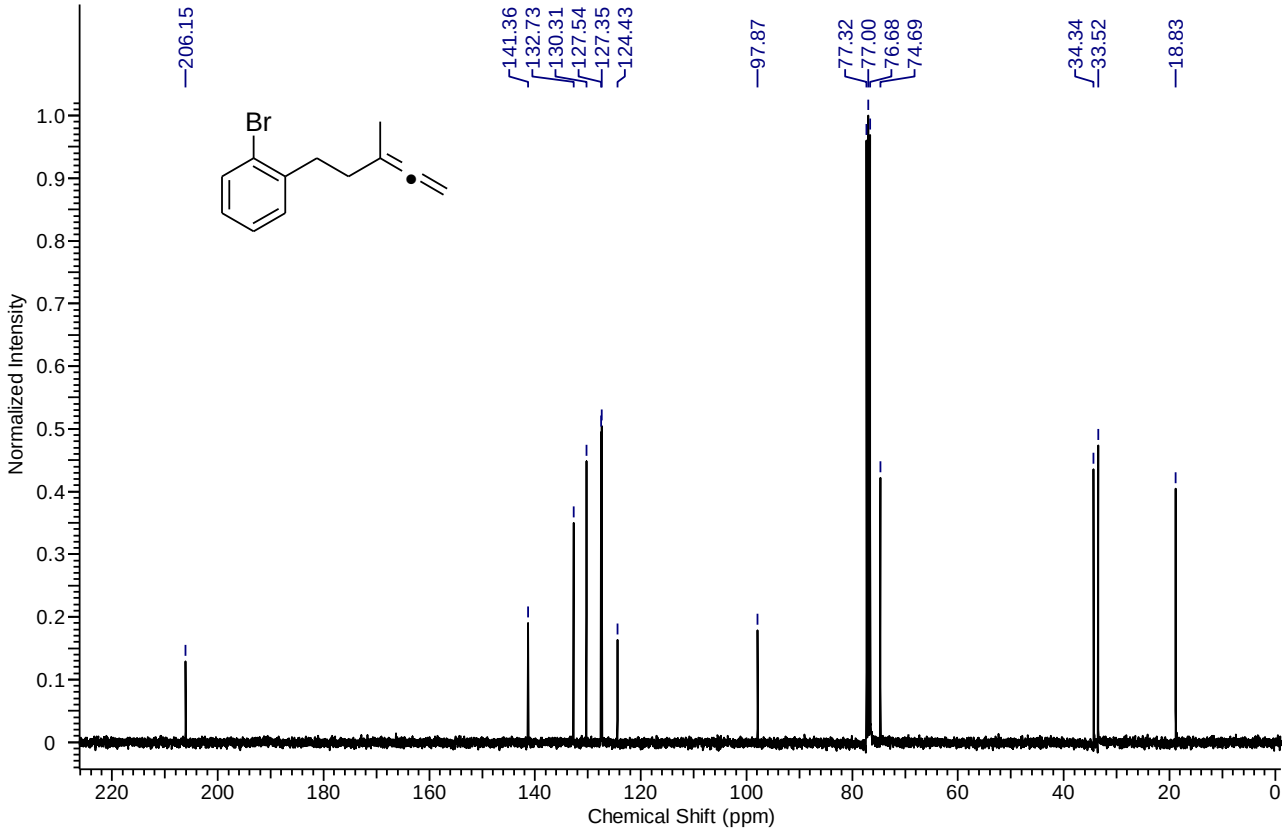


Figure S4. ^{13}C NMR spectrum of the compound **1j** in $CDCl_3$, 100 MHz

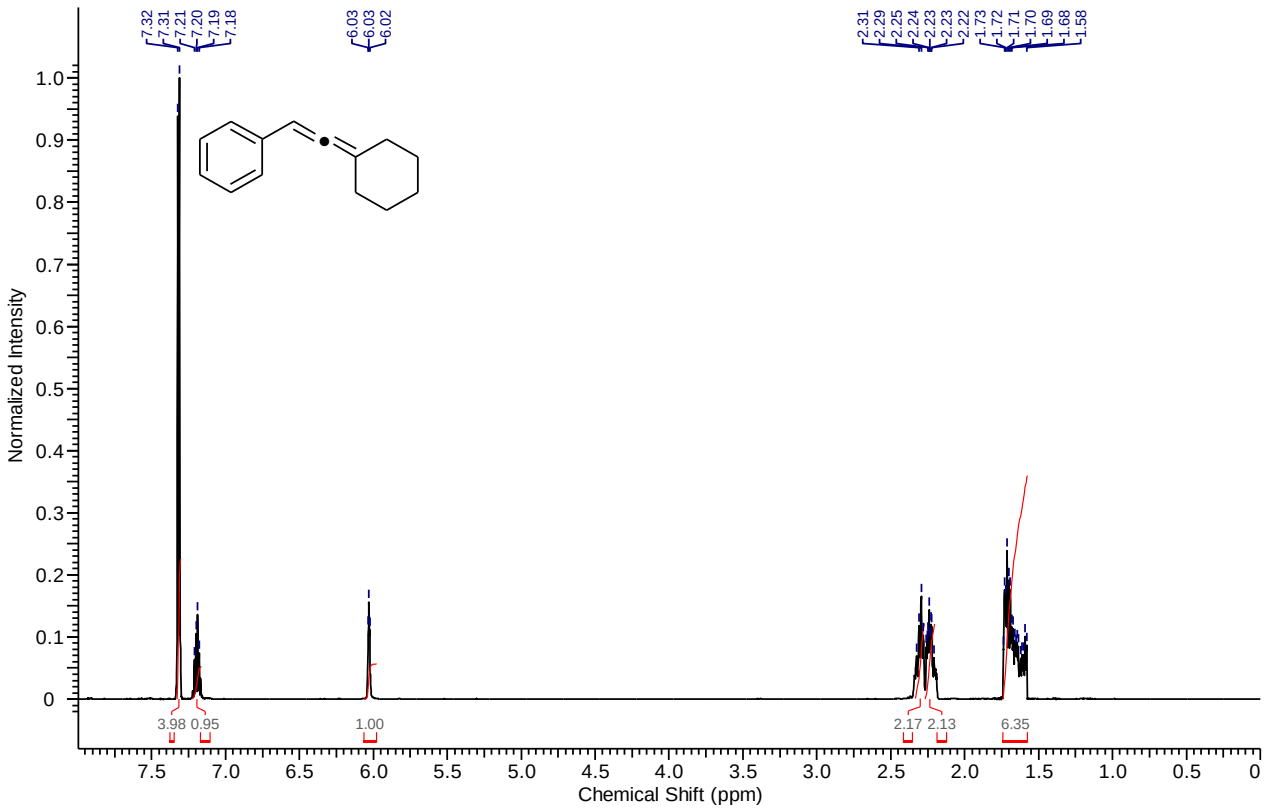


Figure S5. ^{1}H NMR spectrum of the compound **1o** in $CDCl_3$, 400 MHz

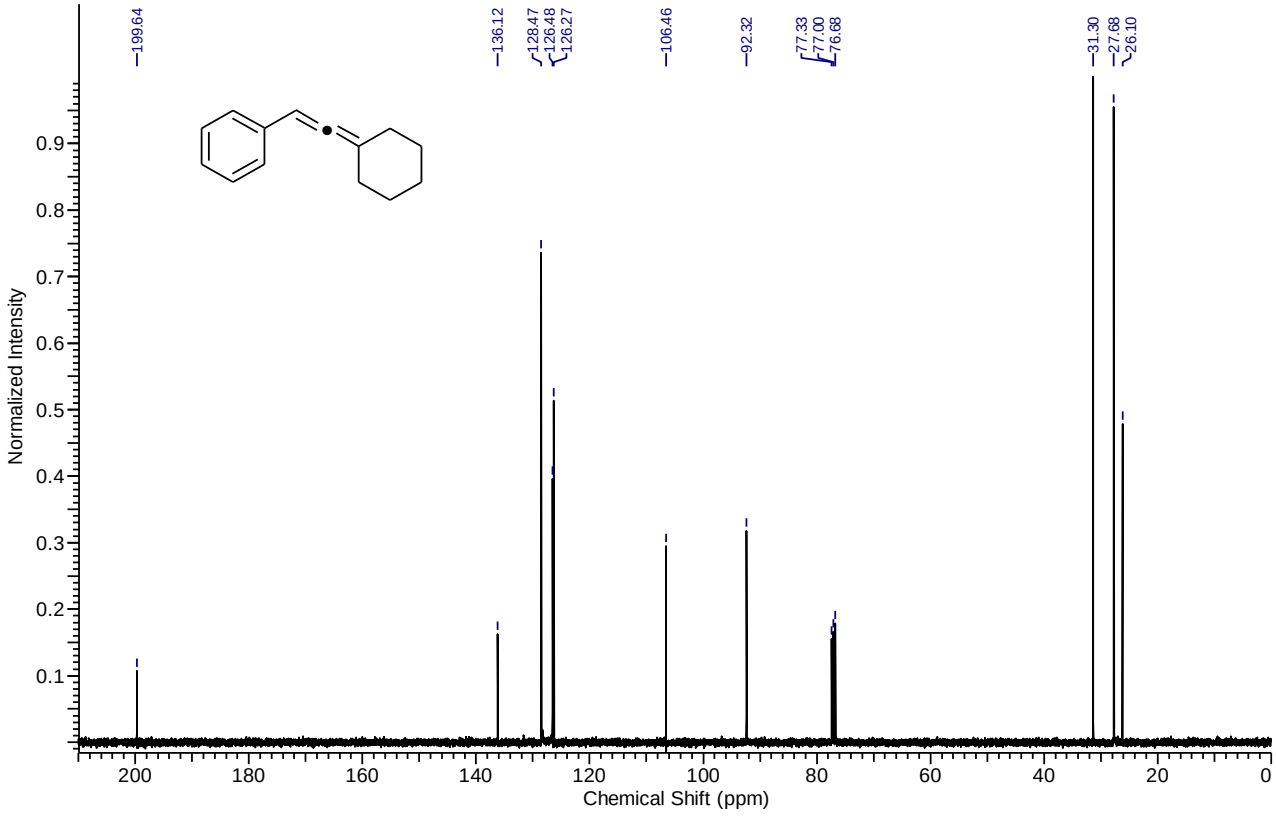


Figure S6. ^{13}C NMR spectrum of the compound **1o** in $CDCl_3$, 100 MHz

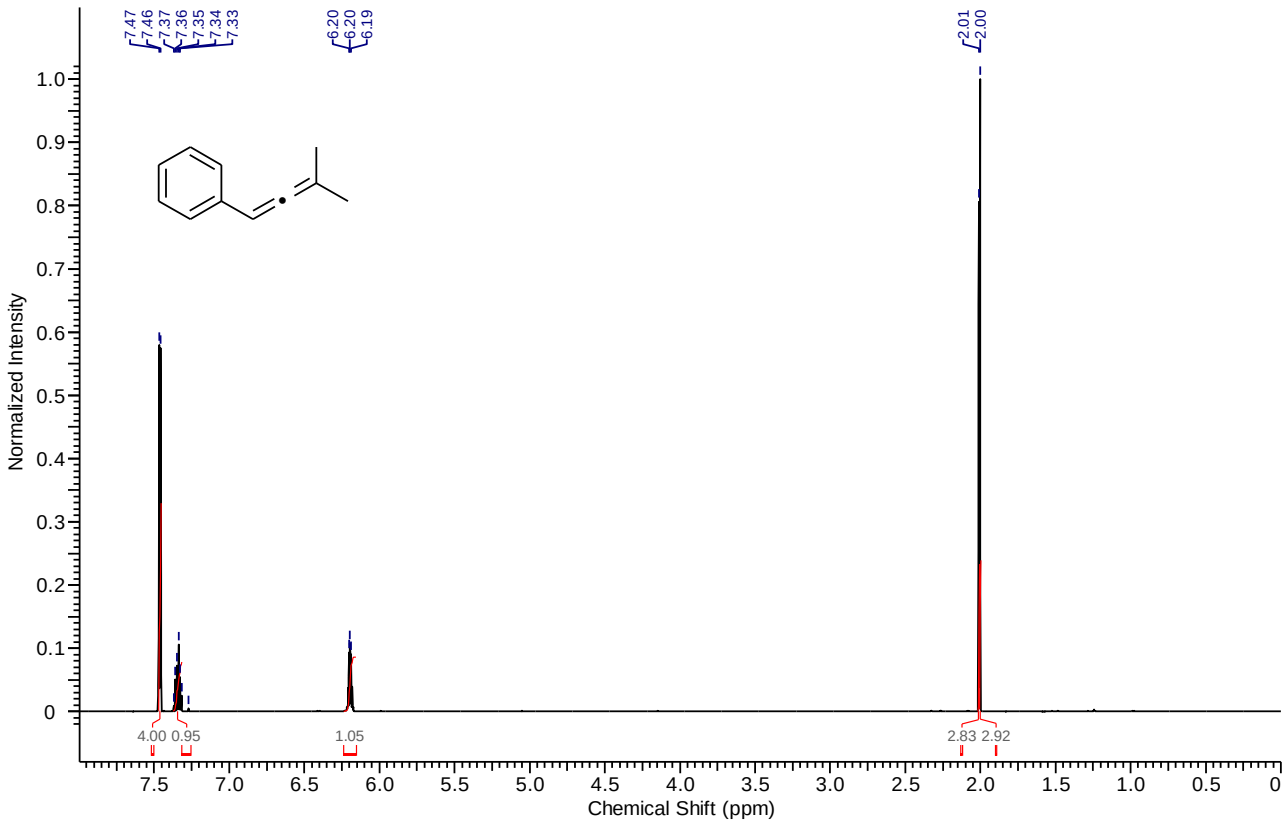


Figure S7. ^{1}H NMR spectrum of the compound **1n** in $CDCl_3$, 400 MHz

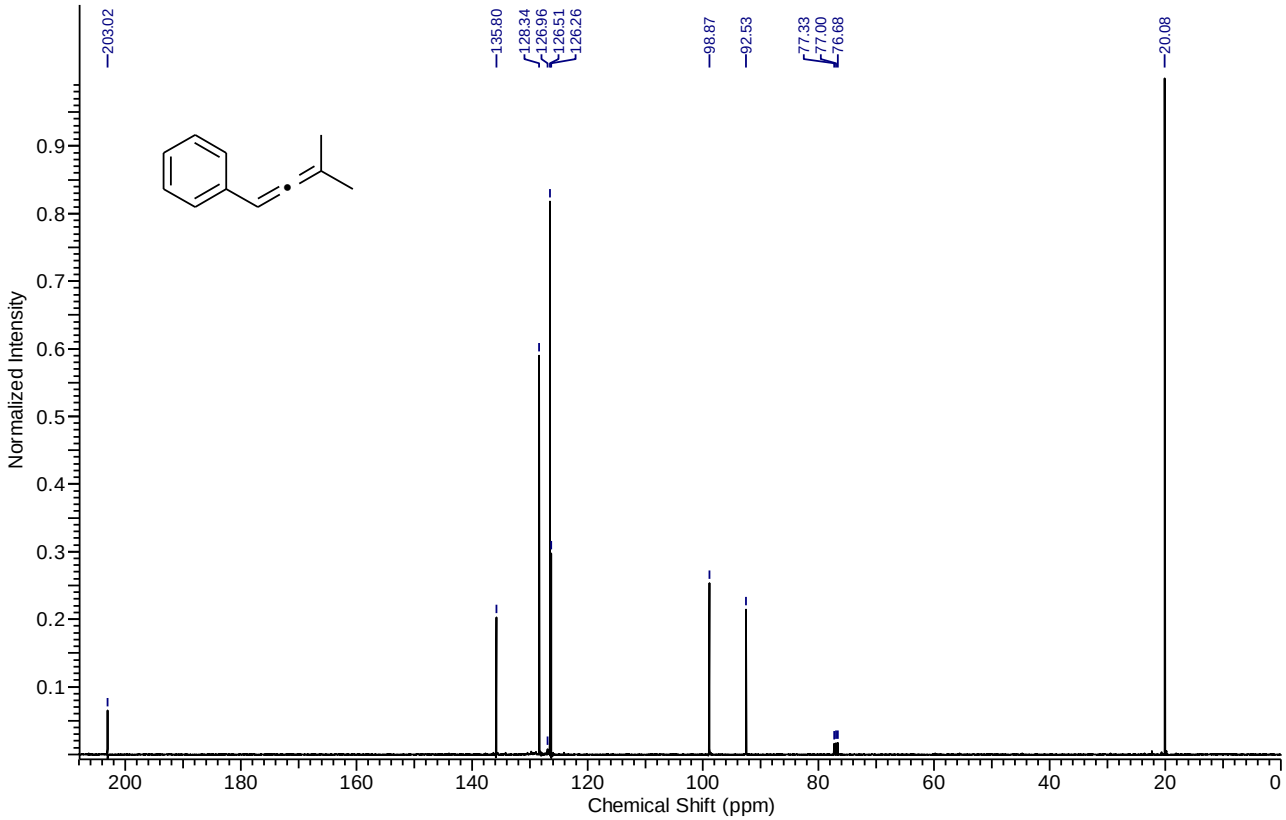


Figure S8. ^{13}C NMR spectrum of the compound **1n** in $CDCl_3$, 100 MHz

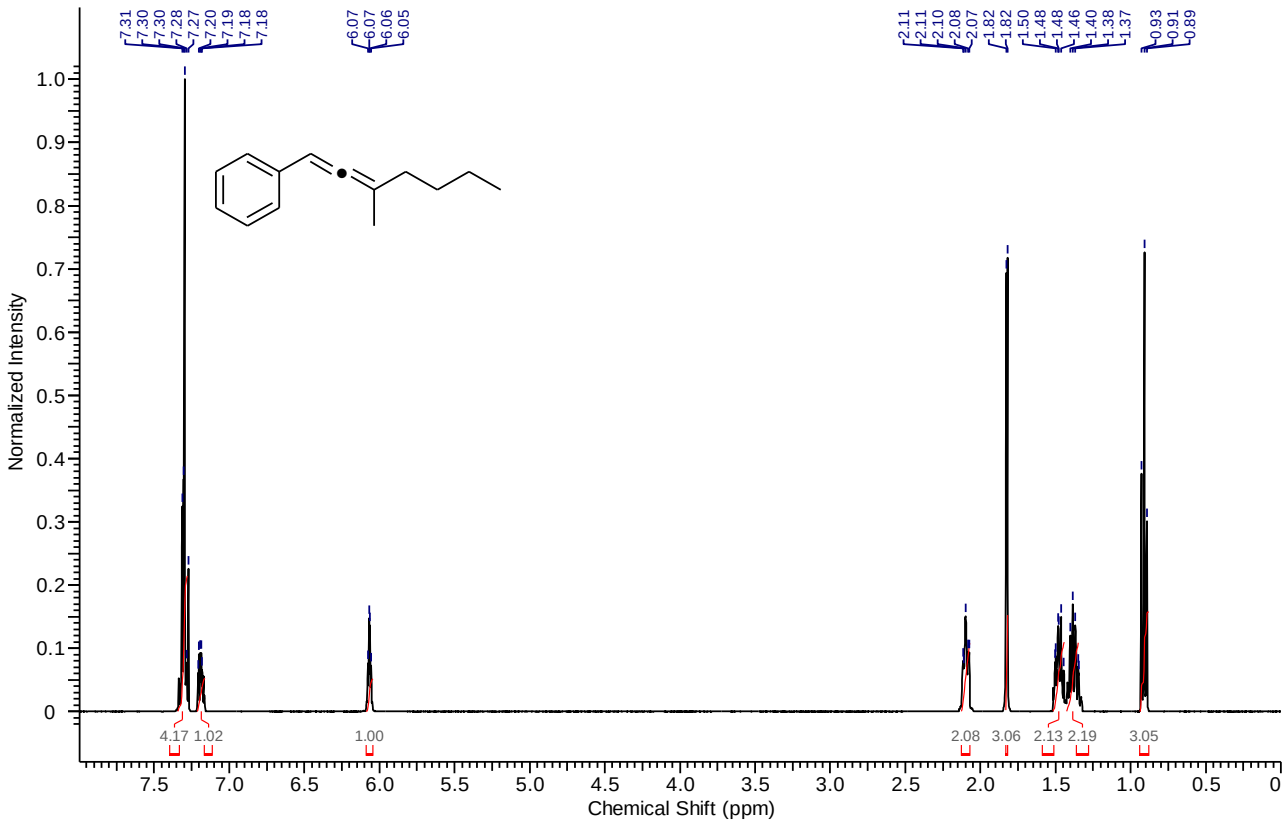


Figure S9. ^{1}H NMR spectrum of the compound **1p** in $CDCl_3$, 400 MHz

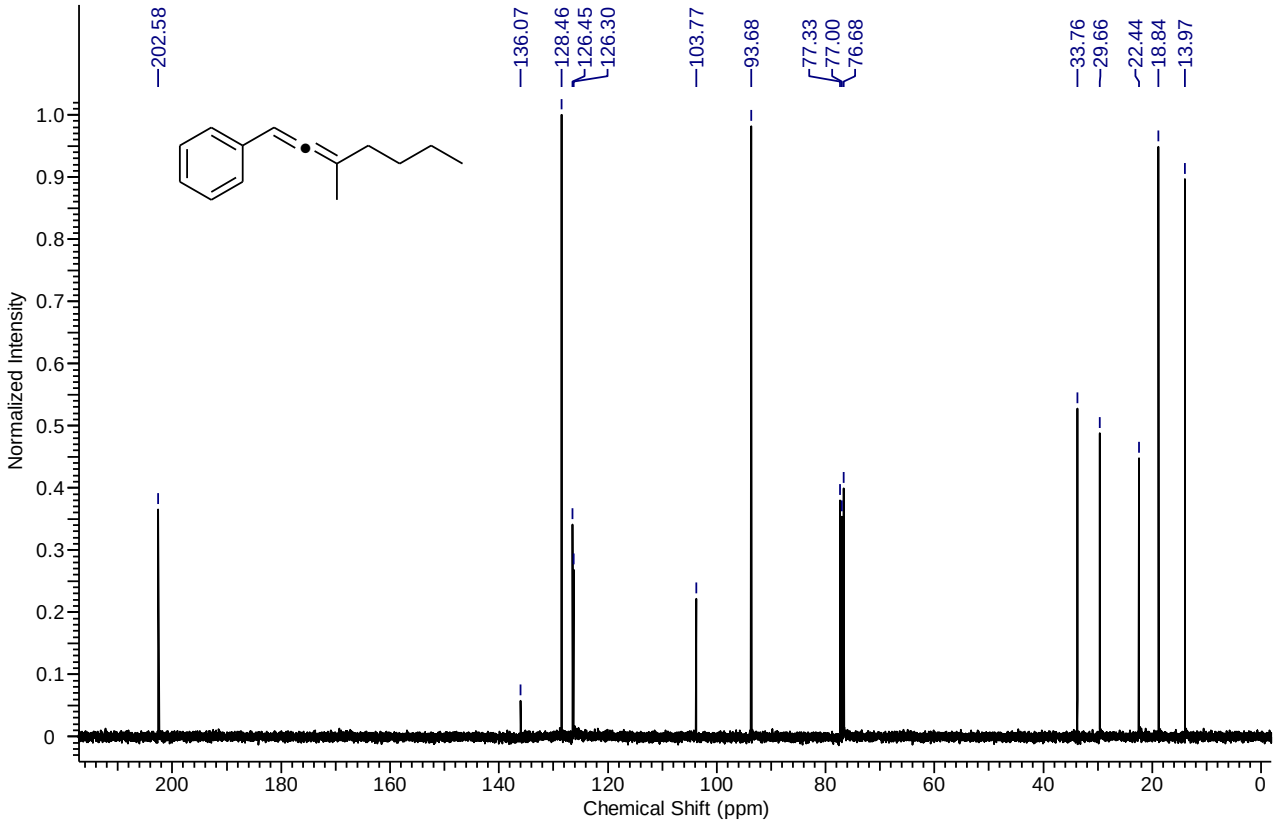


Figure S10. ^{13}C NMR spectrum of the compound **1p** in $CDCl_3$, 100 MHz

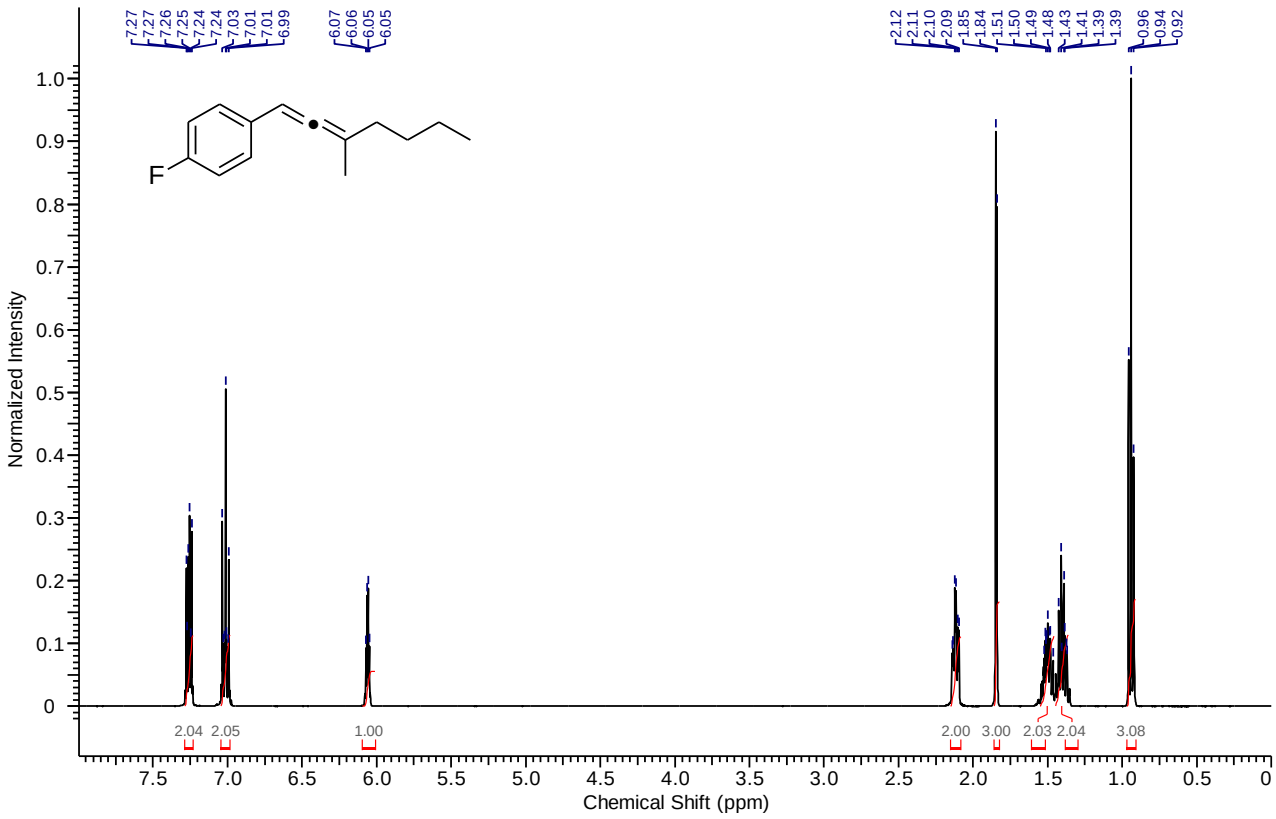


Figure S11. ^{1}H NMR spectrum of the compound **1q** in $CDCl_3$, 400 MHz

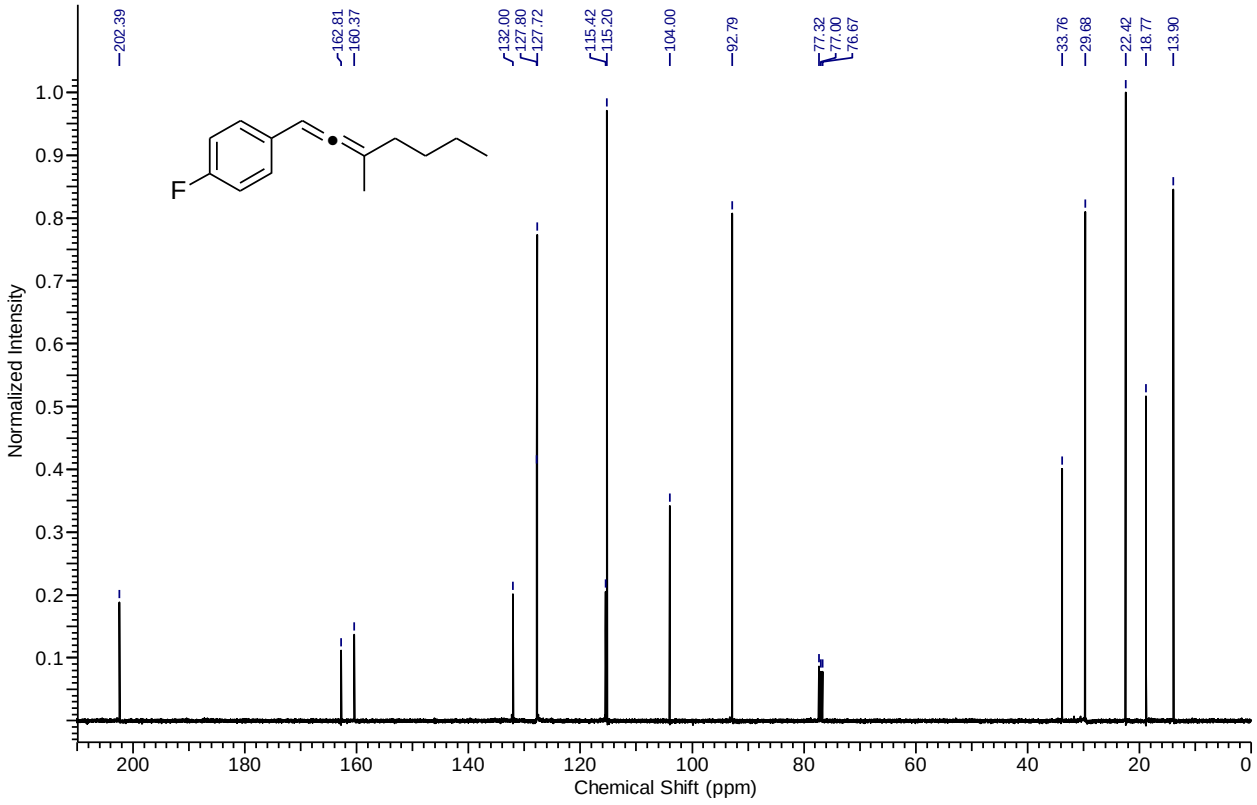


Figure S12. ^{13}C NMR spectrum of the compound **1q** in $CDCl_3$, 100 MHz

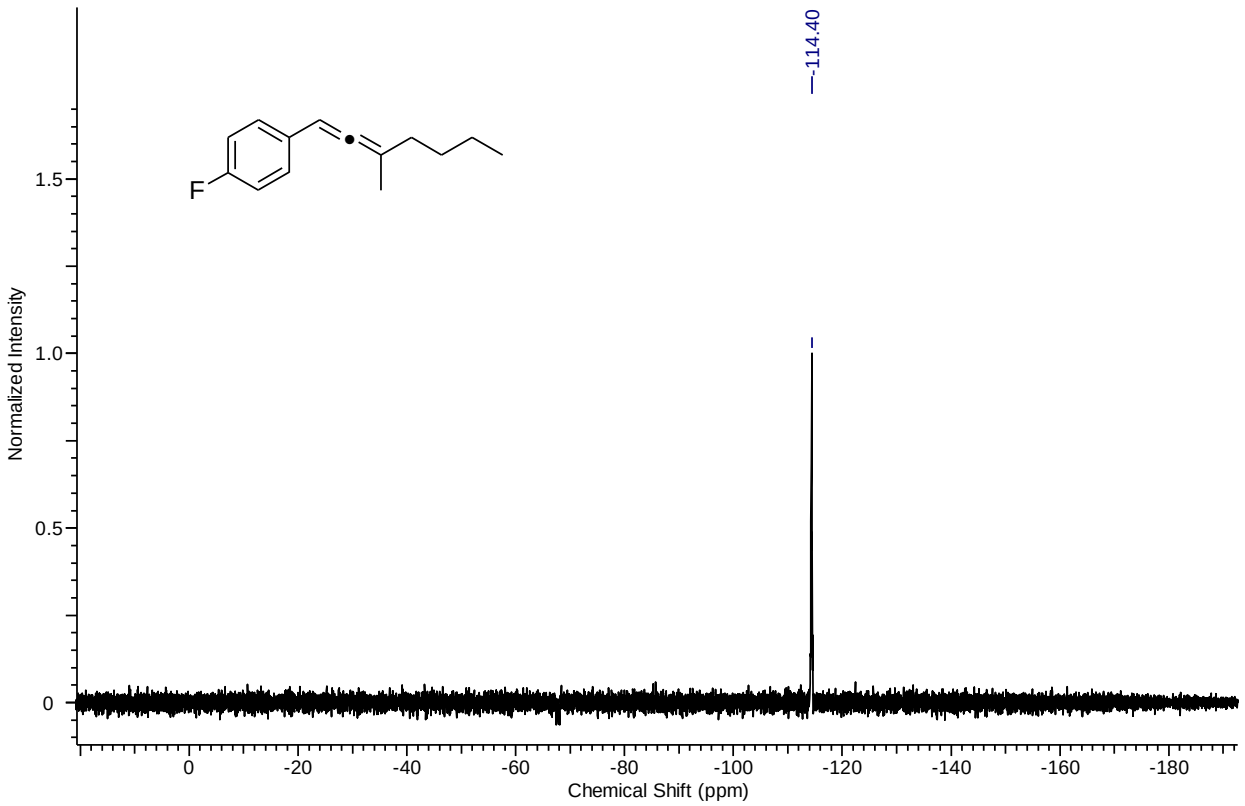


Figure S13. ^{19}F NMR spectrum of the compound **1q** in $CDCl_3$, 75.2 MHz

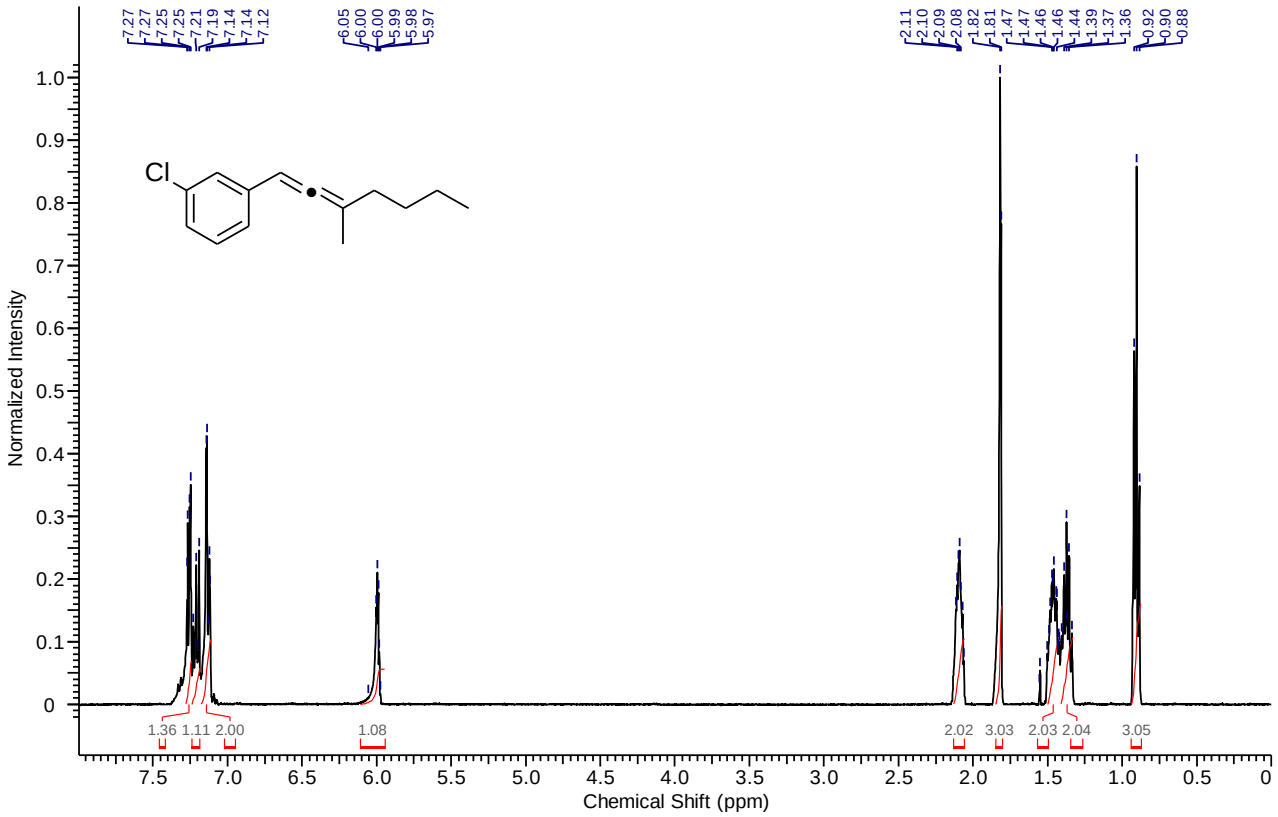


Figure S14. ^{1}H NMR spectrum of the compound **1r** in $CDCl_3$, 400 MHz

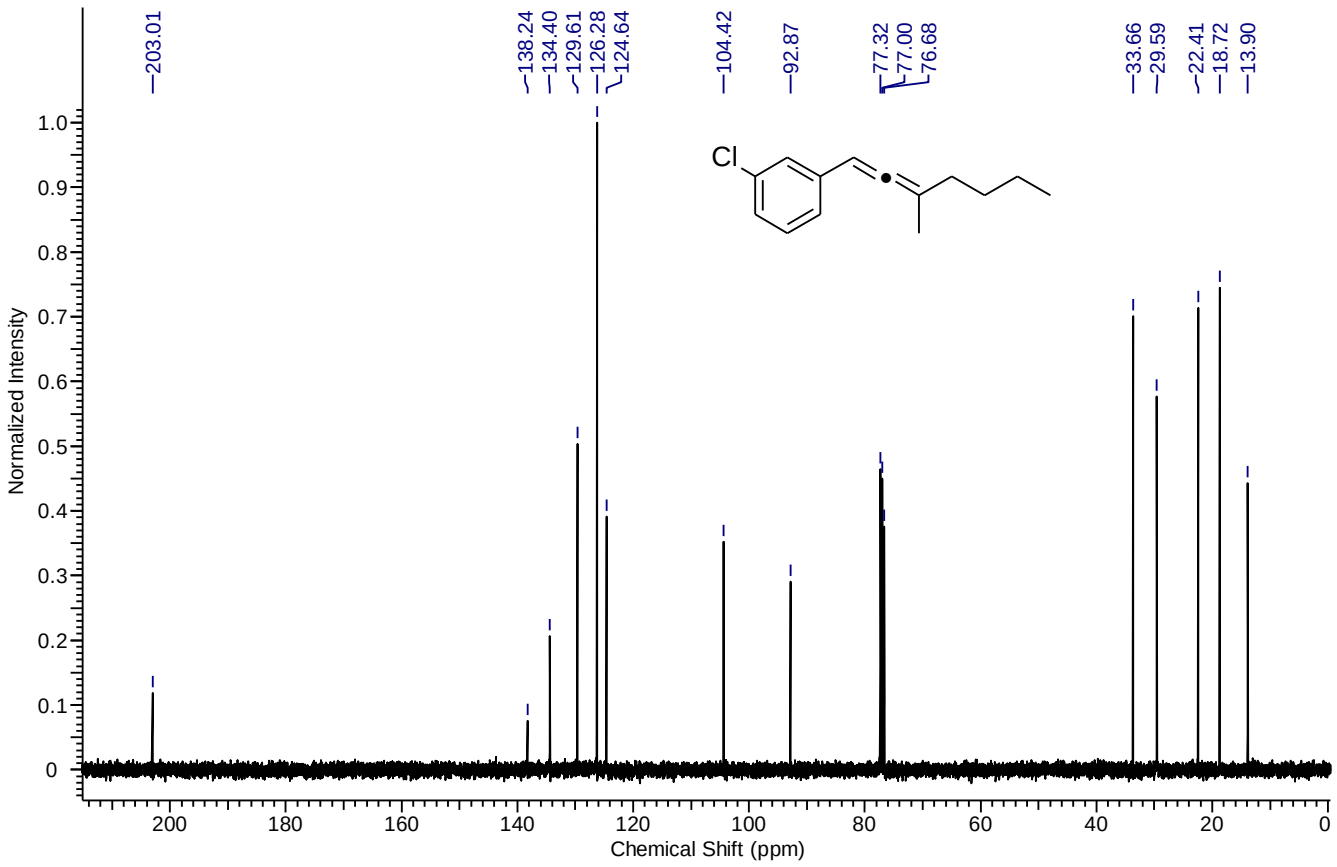


Figure S15. ^{13}C NMR spectrum of the compound **1r** in $CDCl_3$, 100 MHz

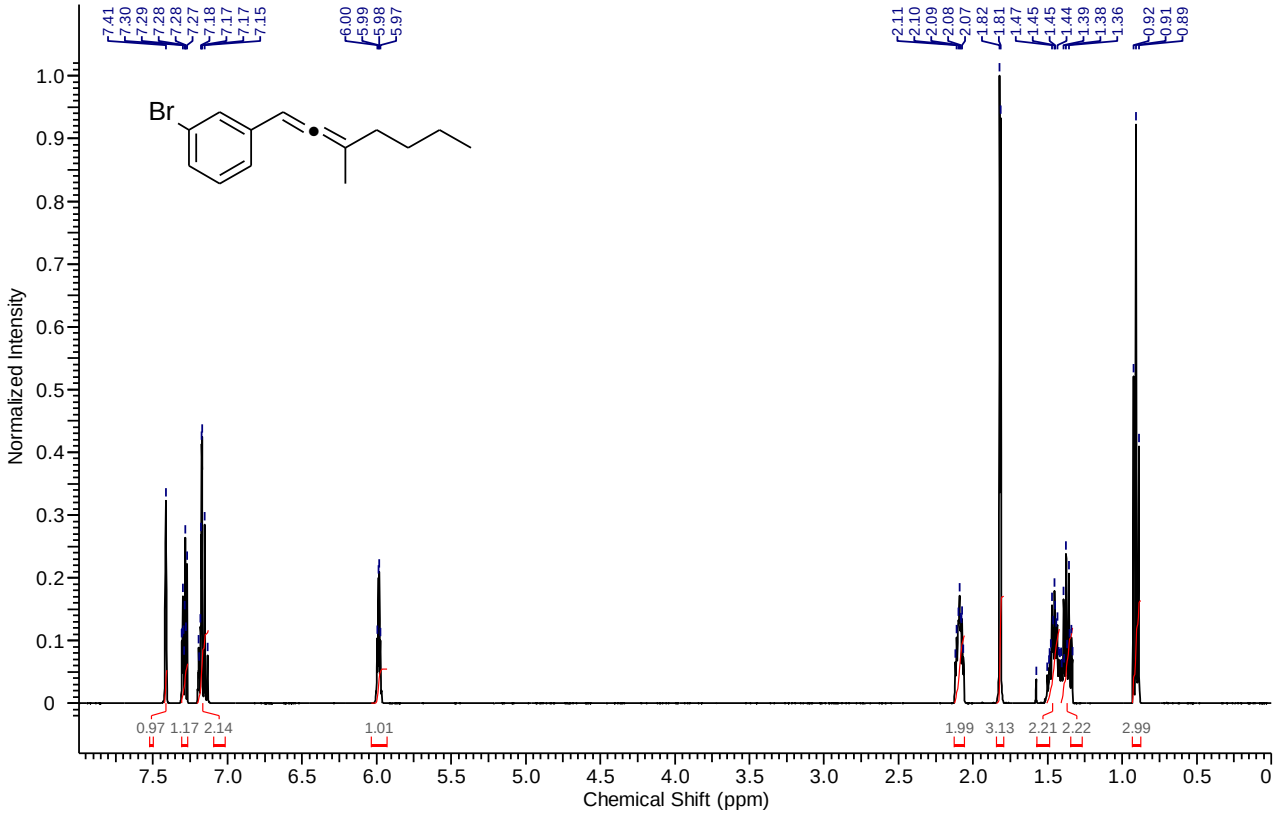


Figure S16. ^{1}H NMR spectrum of the compound **1s** in $CDCl_3$, 400 MHz

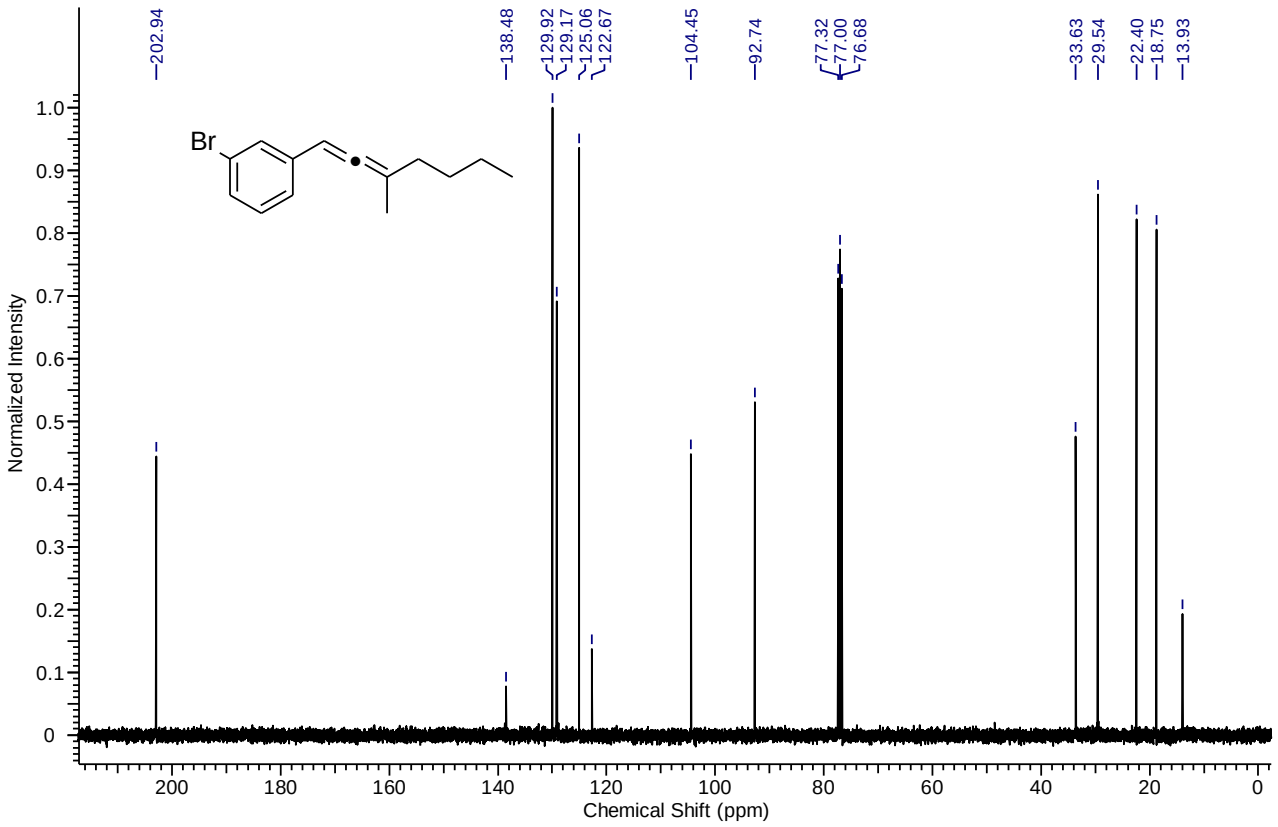


Figure S17. ^{13}C NMR spectrum of the compound **1s** in $CDCl_3$, 100 MHz

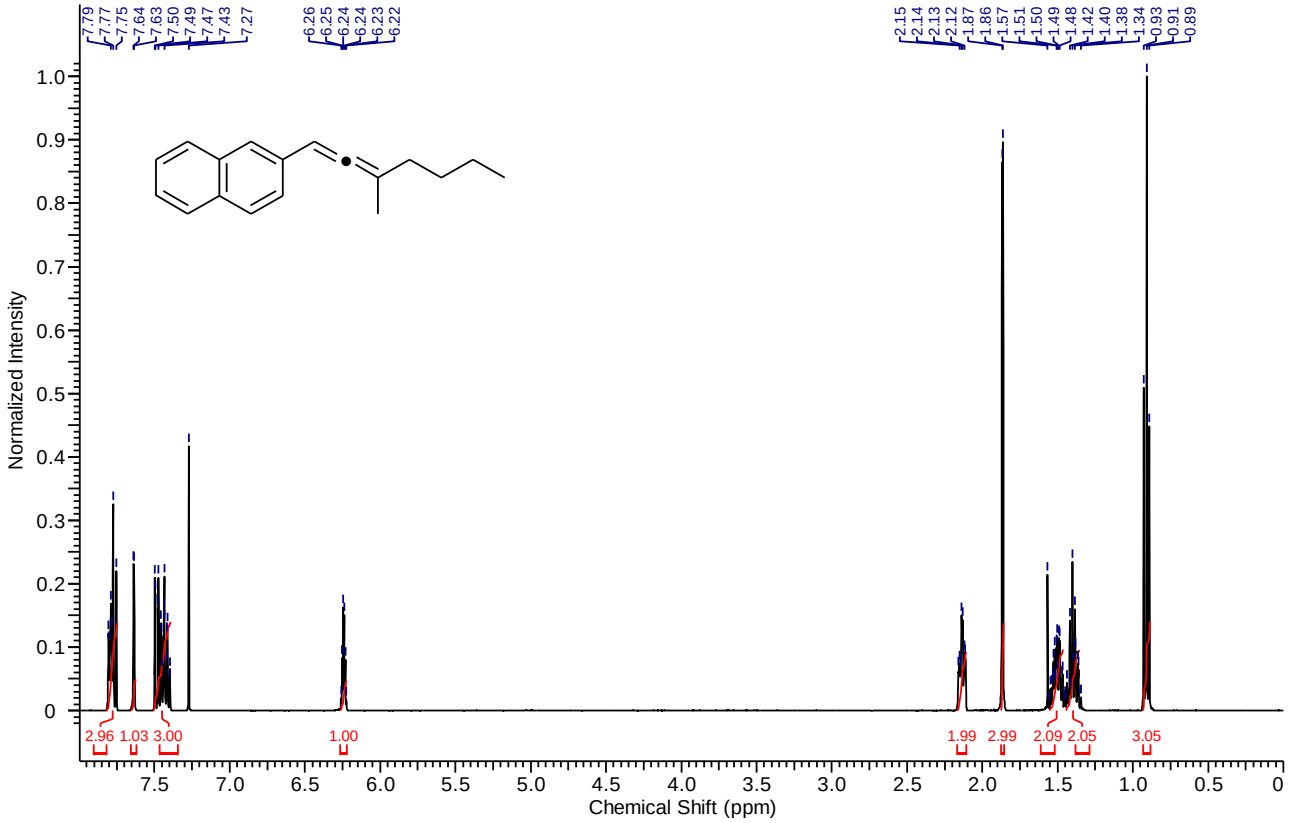


Figure S18. ^{1}H NMR spectrum of the compound **1t** in $CDCl_3$, 400 MHz

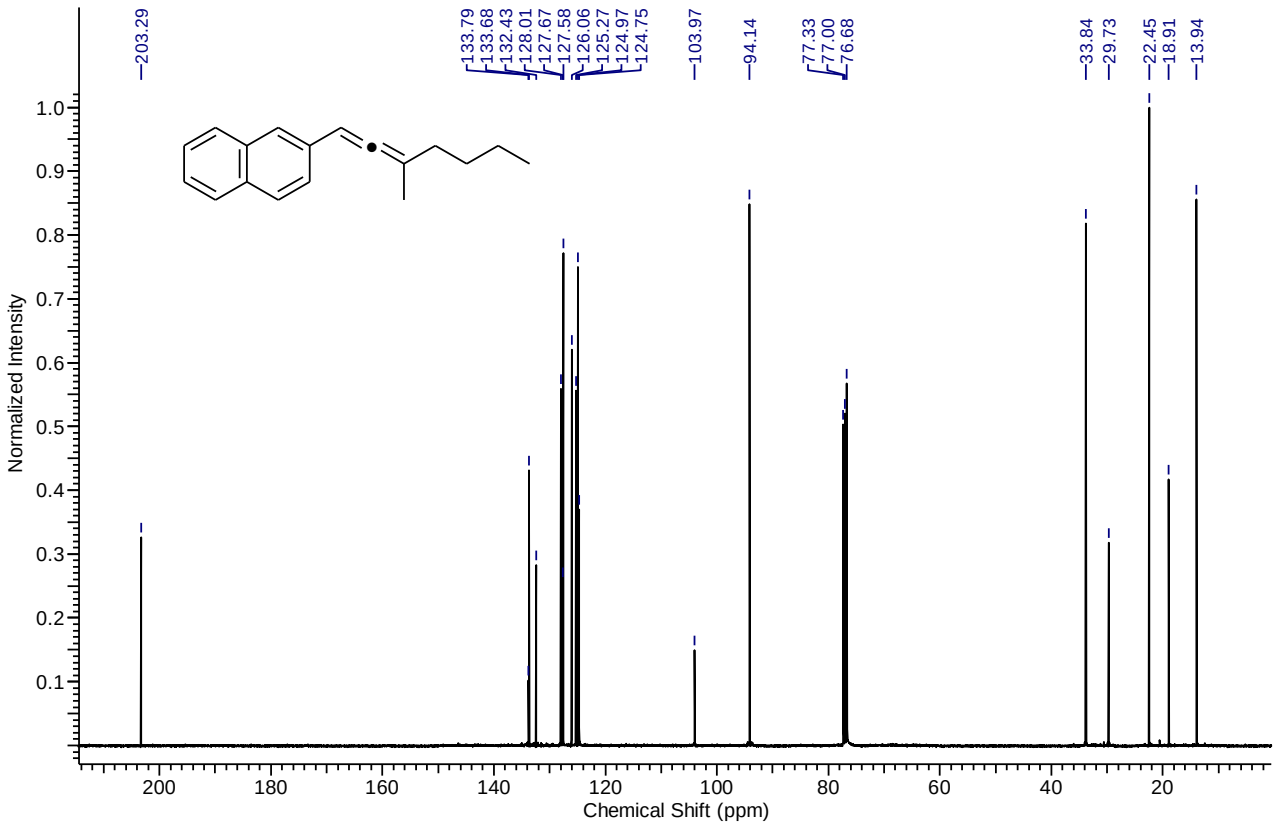


Figure S19. ^{13}C NMR spectrum of the compound **1t** in $CDCl_3$, 100 MHz

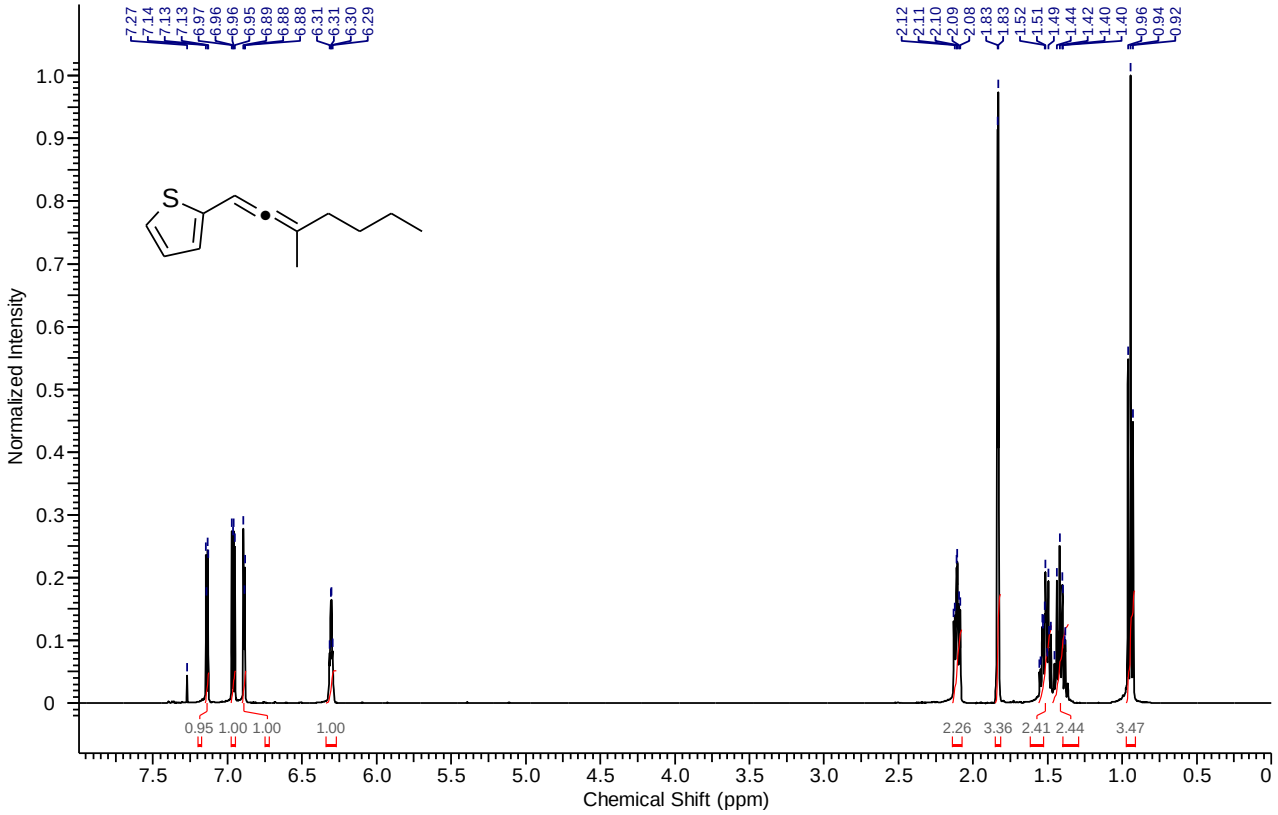


Figure S20. ^{1}H NMR spectrum of the compound **1u** in $CDCl_3$, 400 MHz

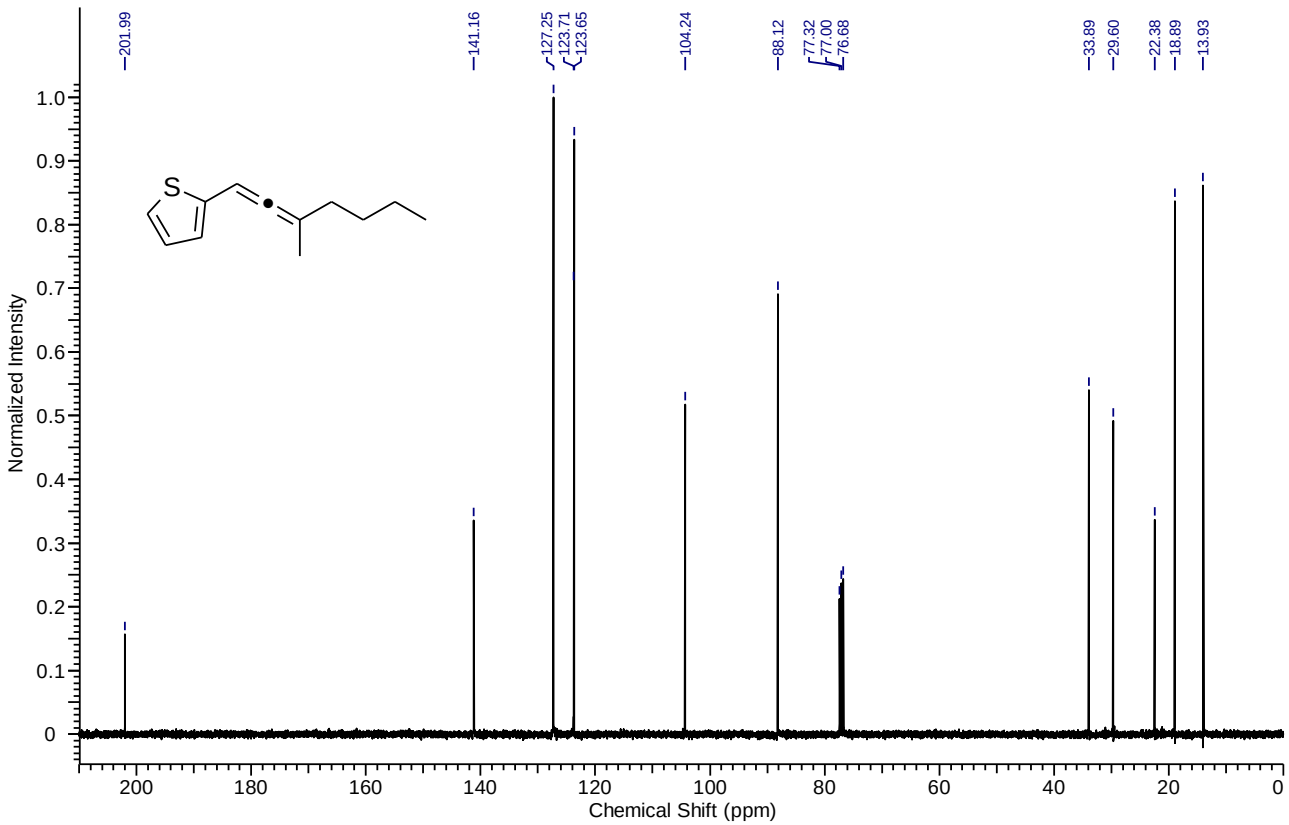


Figure S21. ^{13}C NMR spectrum of the compound **1u** in $CDCl_3$, 100 MHz

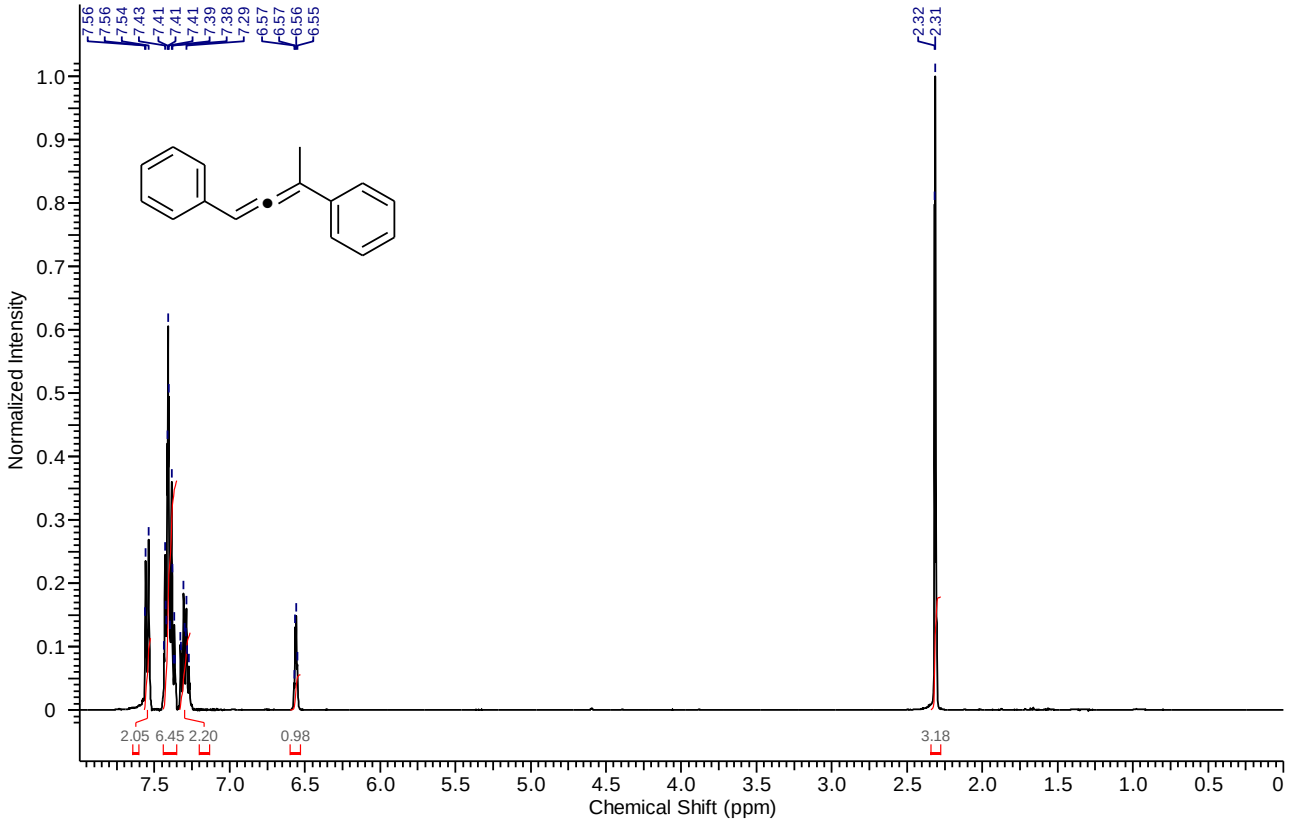


Figure S22. ^{1}H NMR spectrum of the compound **1x** in $CDCl_3$, 400 MHz

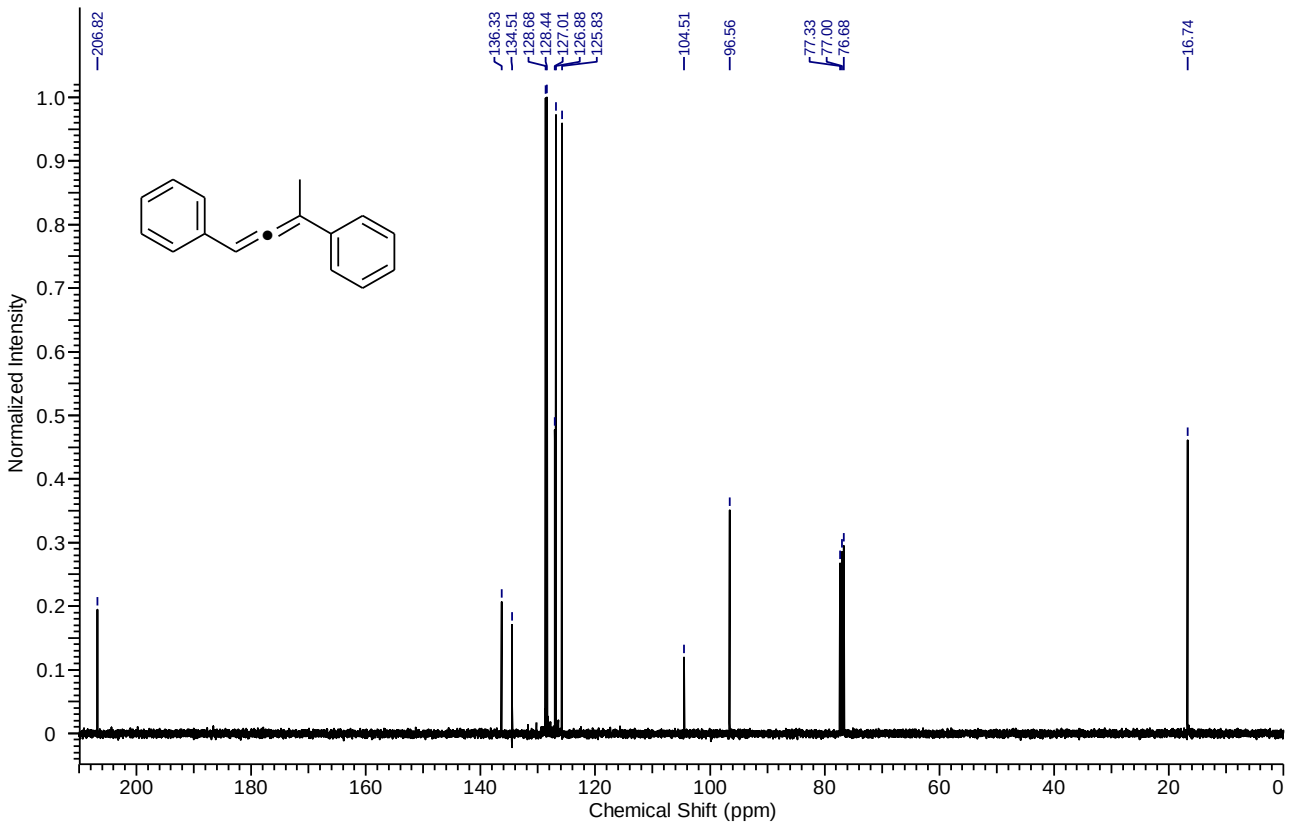


Figure S23. ^{13}C NMR spectrum of the compound **1x** in $CDCl_3$, 100 MHz

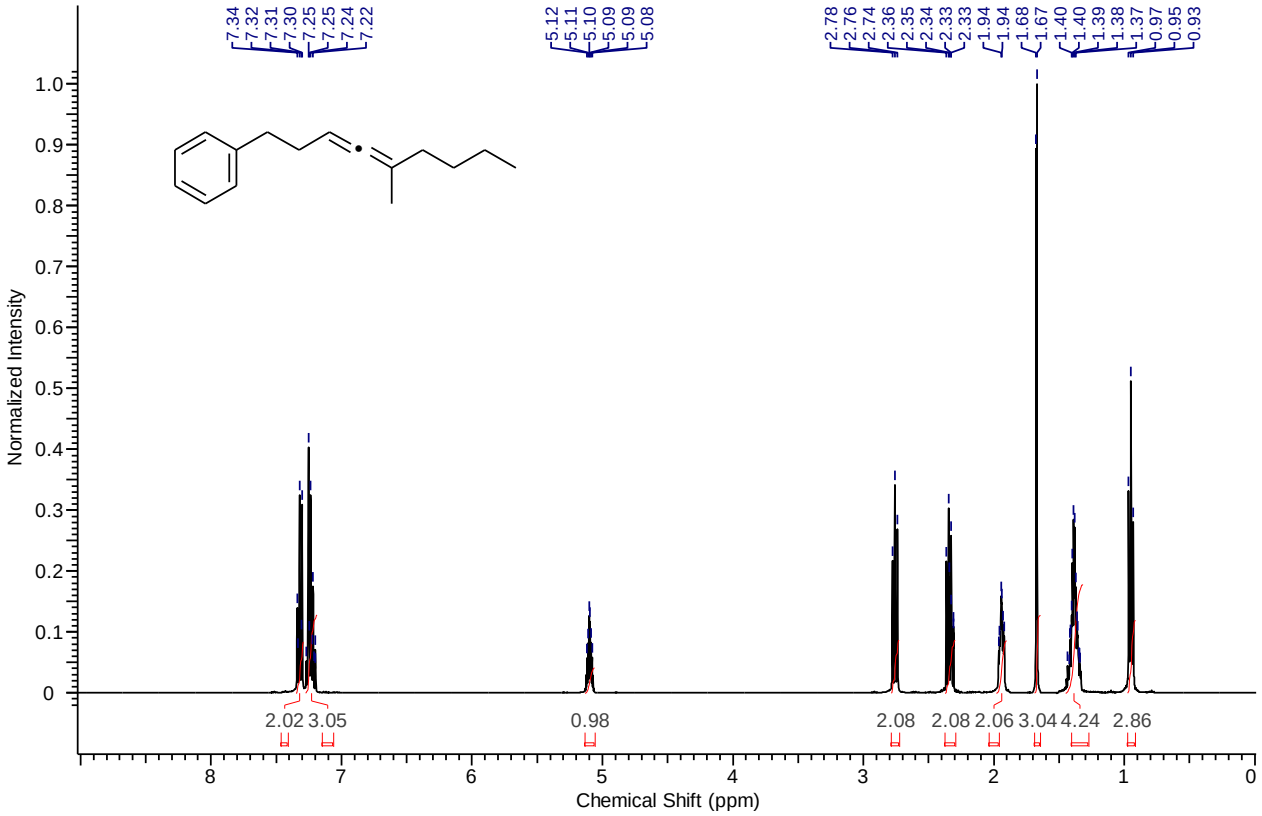


Figure S24. ^{1}H NMR spectrum of the compound **1w** in $CDCl_3$, 400 MHz

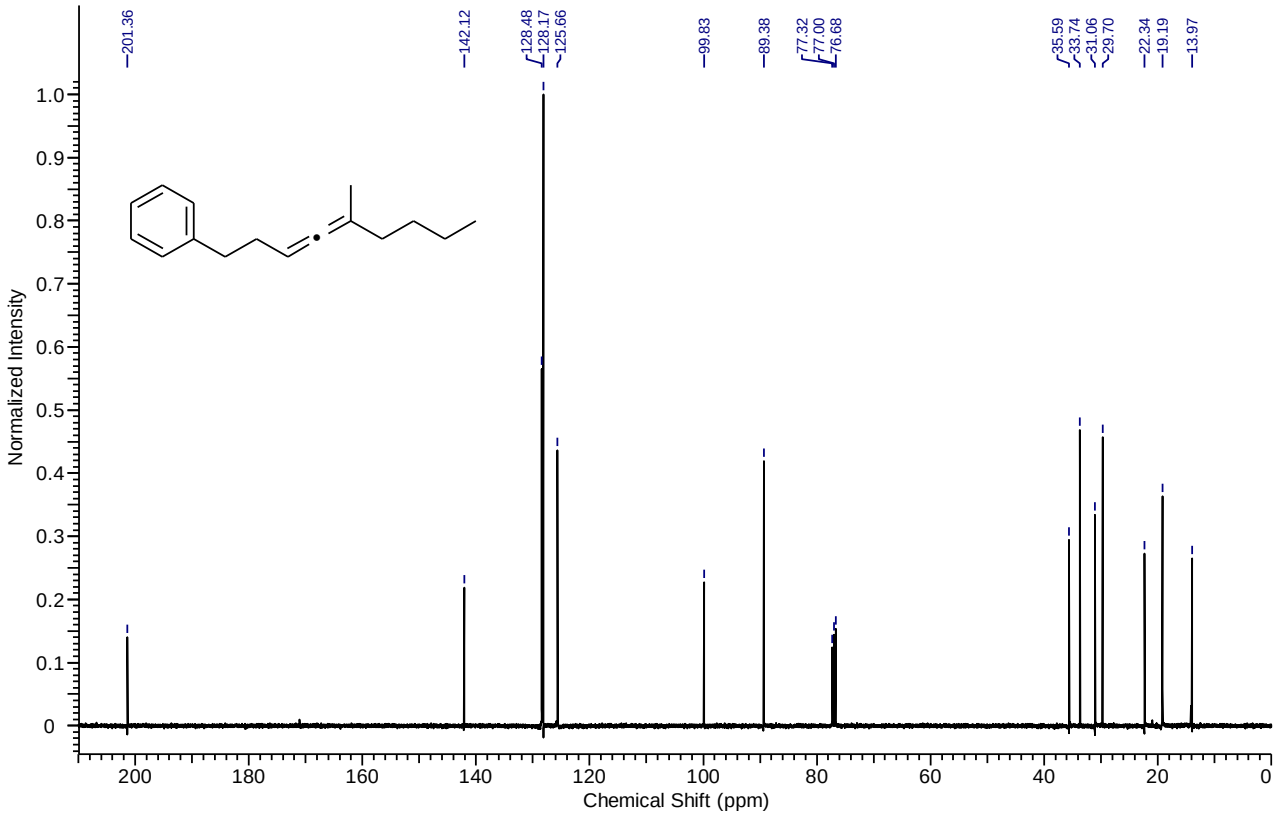


Figure S25. ^{13}C NMR spectrum of the compound **1w** in $CDCl_3$, 100 MHz

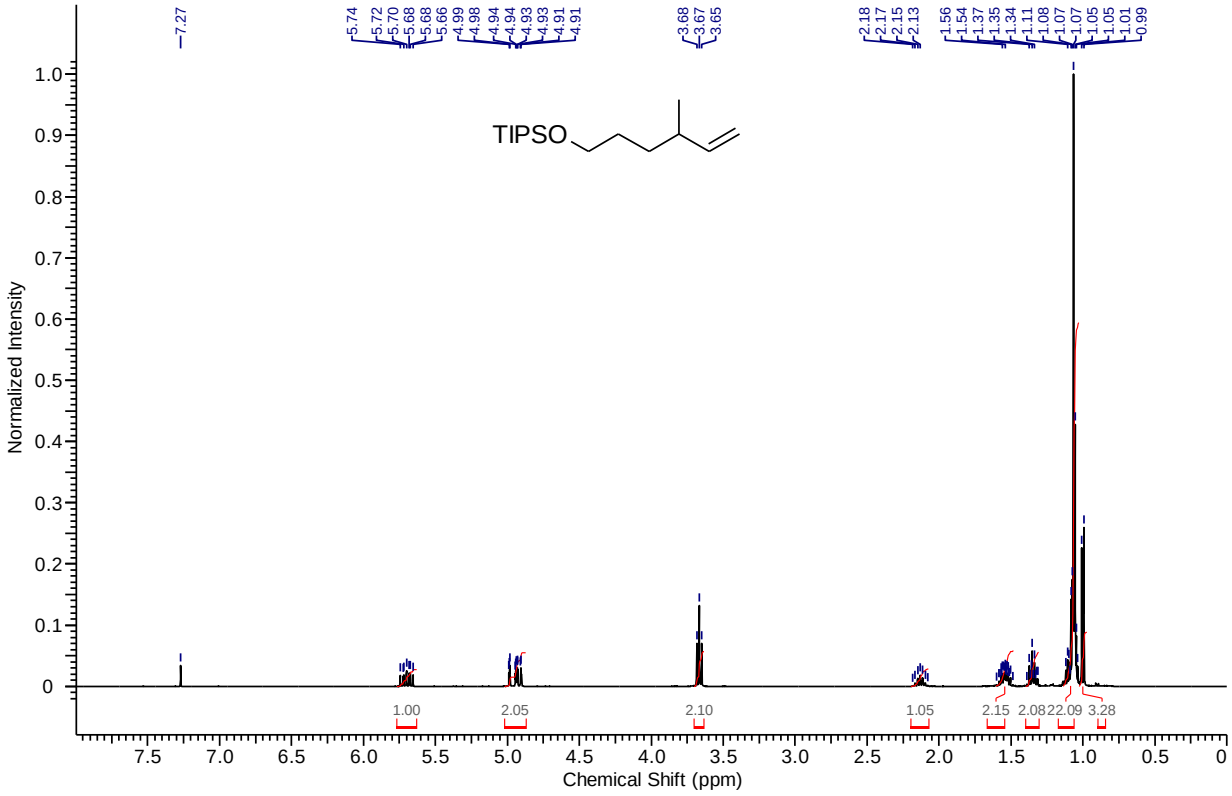


Figure S26. ^{1}H NMR spectrum of the compound **2ab-H** in $CDCl_3$, 400 MHz

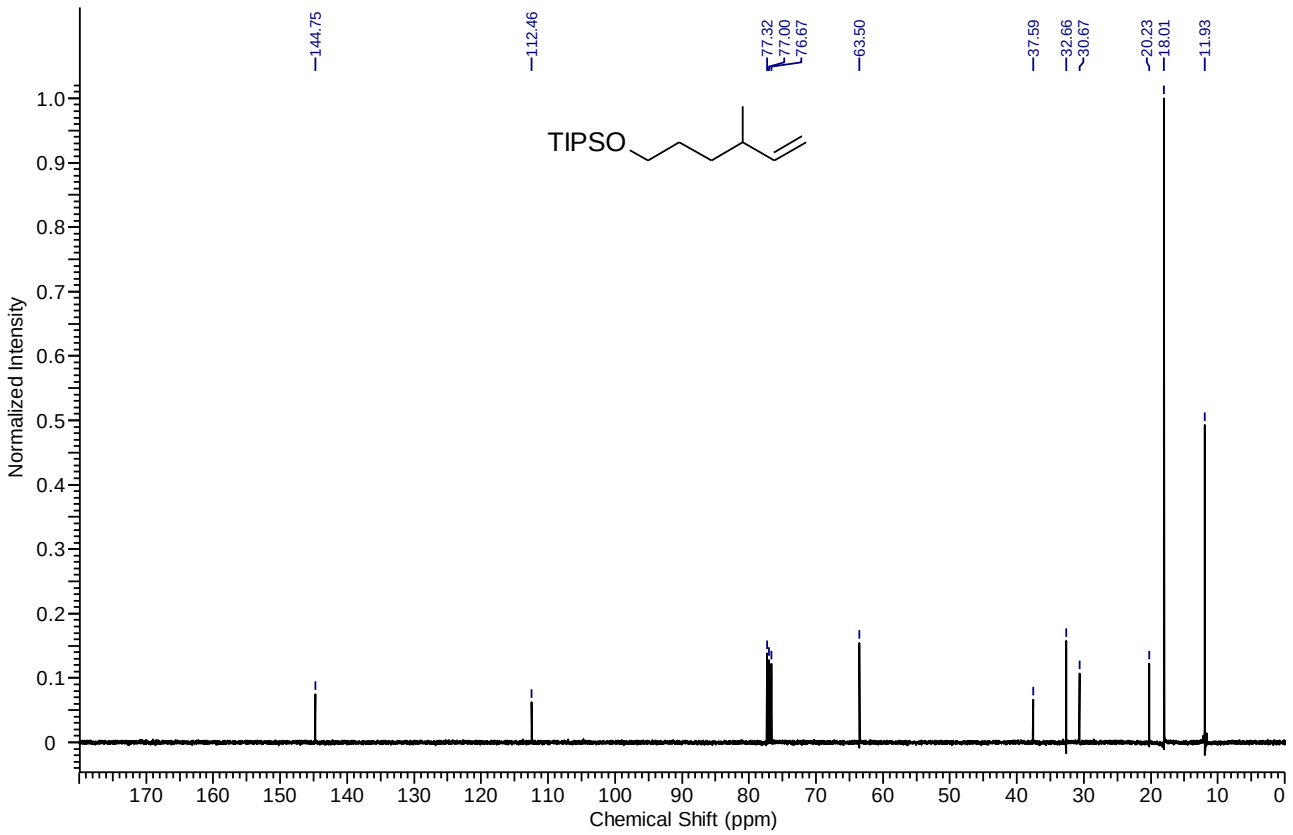


Figure S27. ^{13}C NMR spectrum of the compound **2ab-H** in $CDCl_3$, 100 MHz

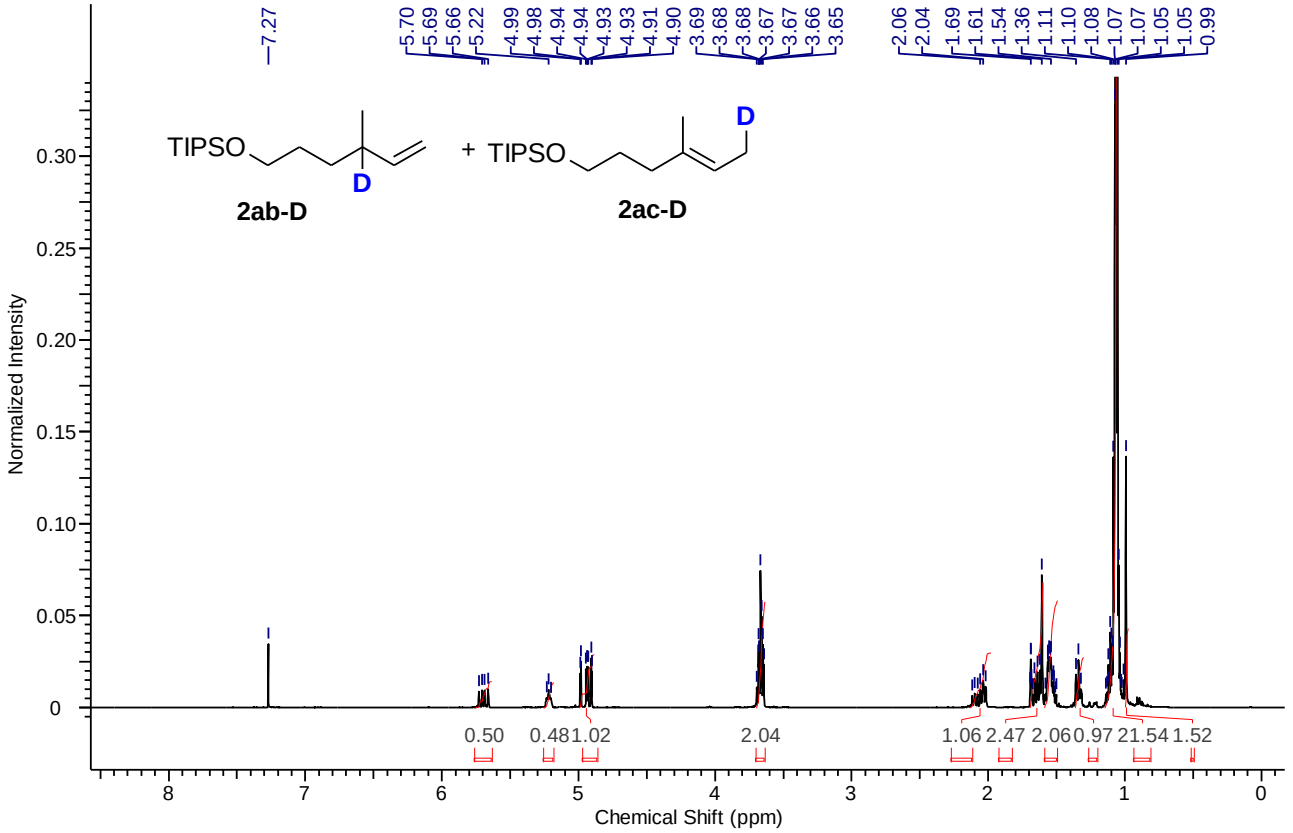


Figure S28. ^{1}H NMR spectrum of the compound **2ab-H** in $CDCl_3$, 400 MHz

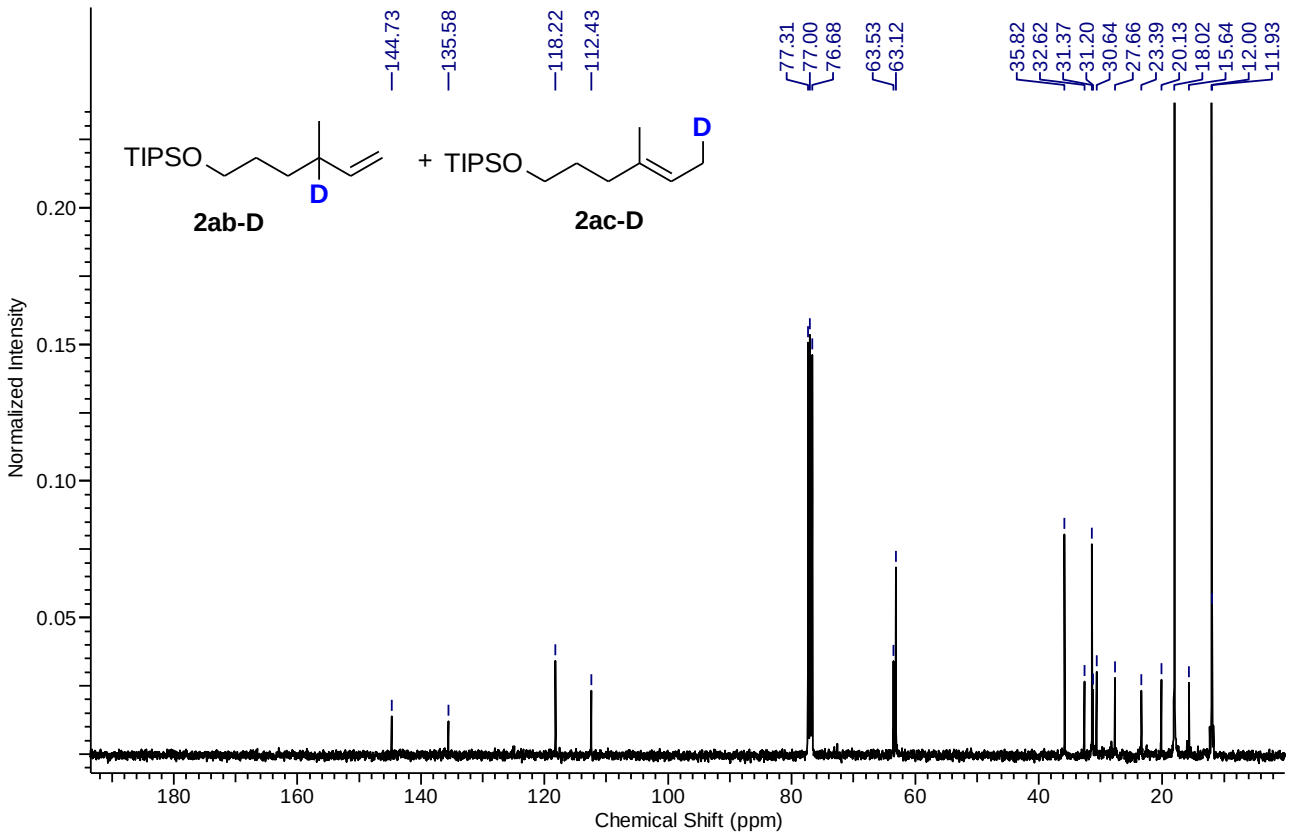


Figure S29. ^{13}C NMR spectrum of the compound **2ab-H** in $CDCl_3$, 100 MHz

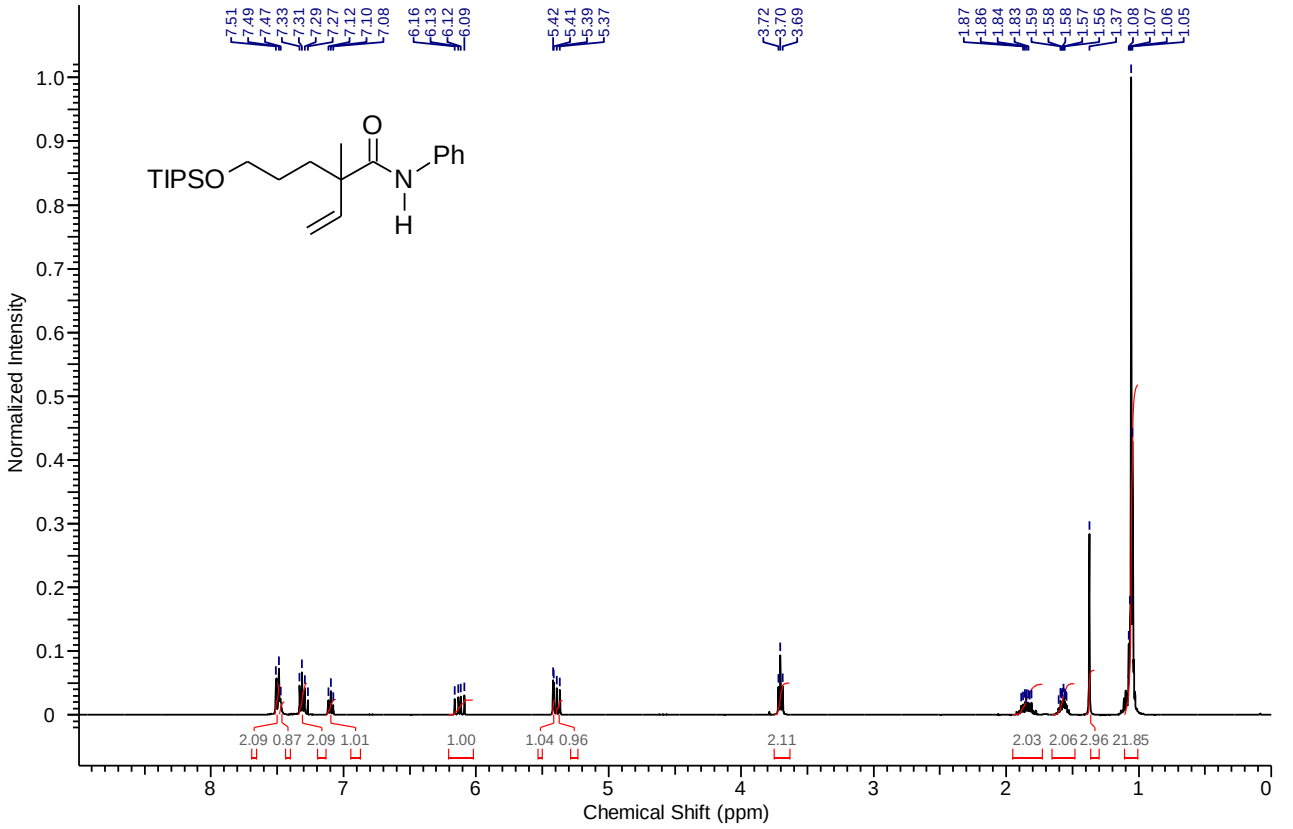


Figure S30. ^{1}H NMR spectrum of the compound **4aa** in $CDCl_3$, 400 MHz

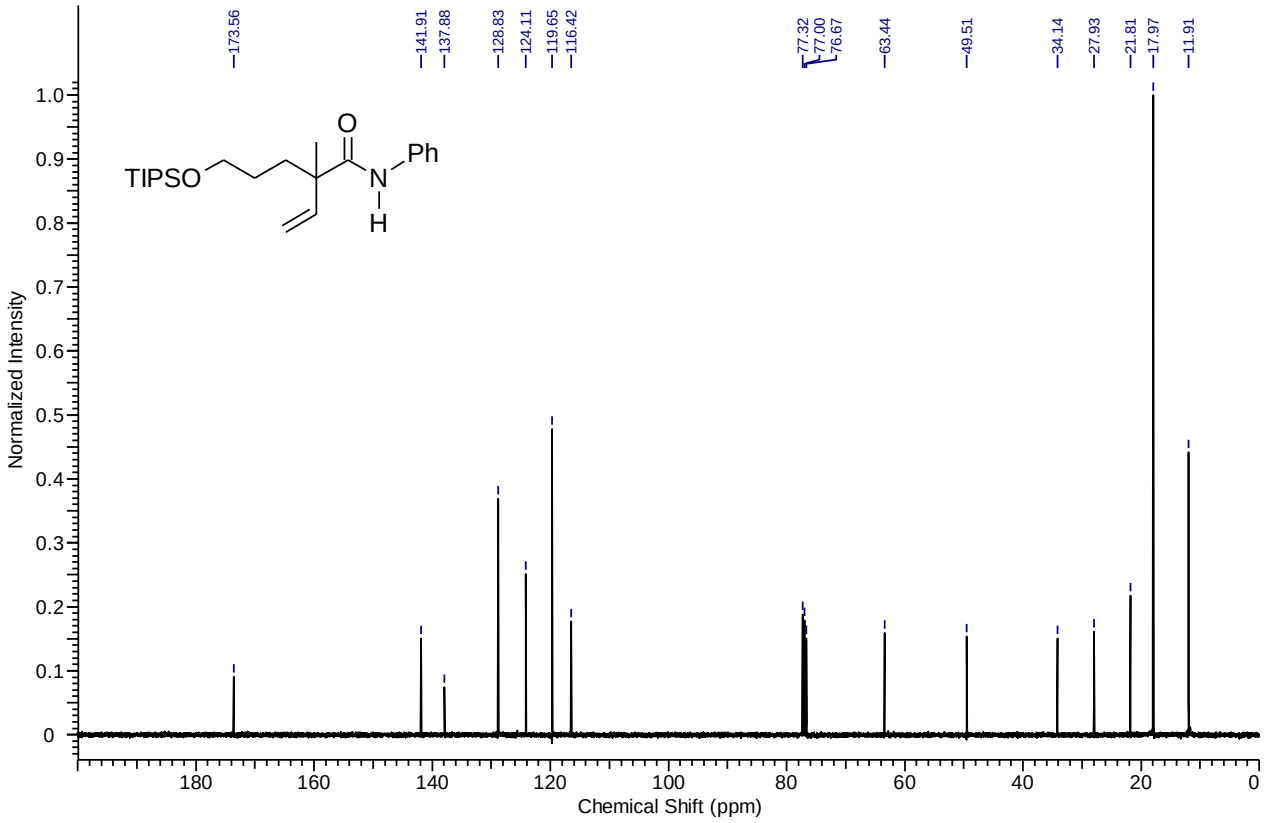


Figure S31. ^{13}C NMR spectrum of the compound **4aa** in $CDCl_3$, 100 MHz

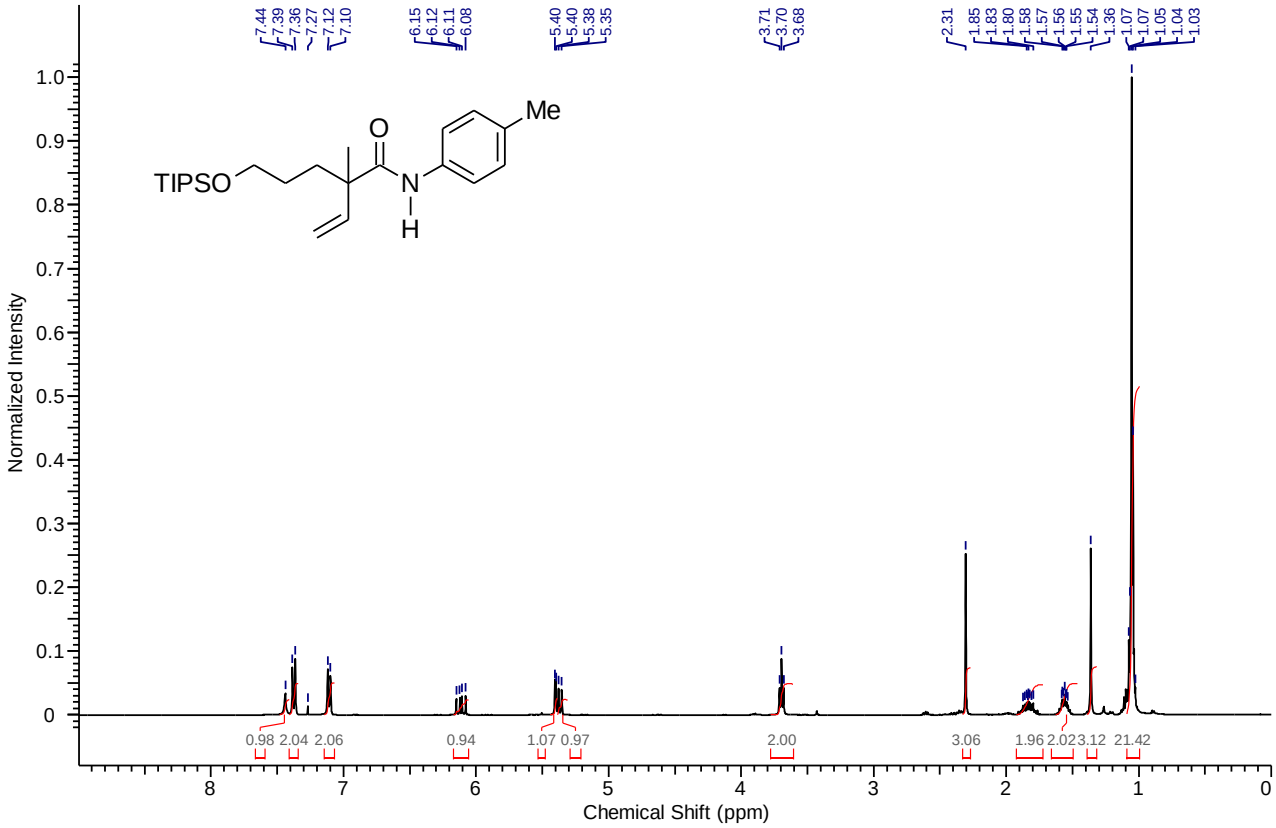


Figure S32. ^{1}H NMR spectrum of the compound **4ab** in $CDCl_3$, 400 MHz

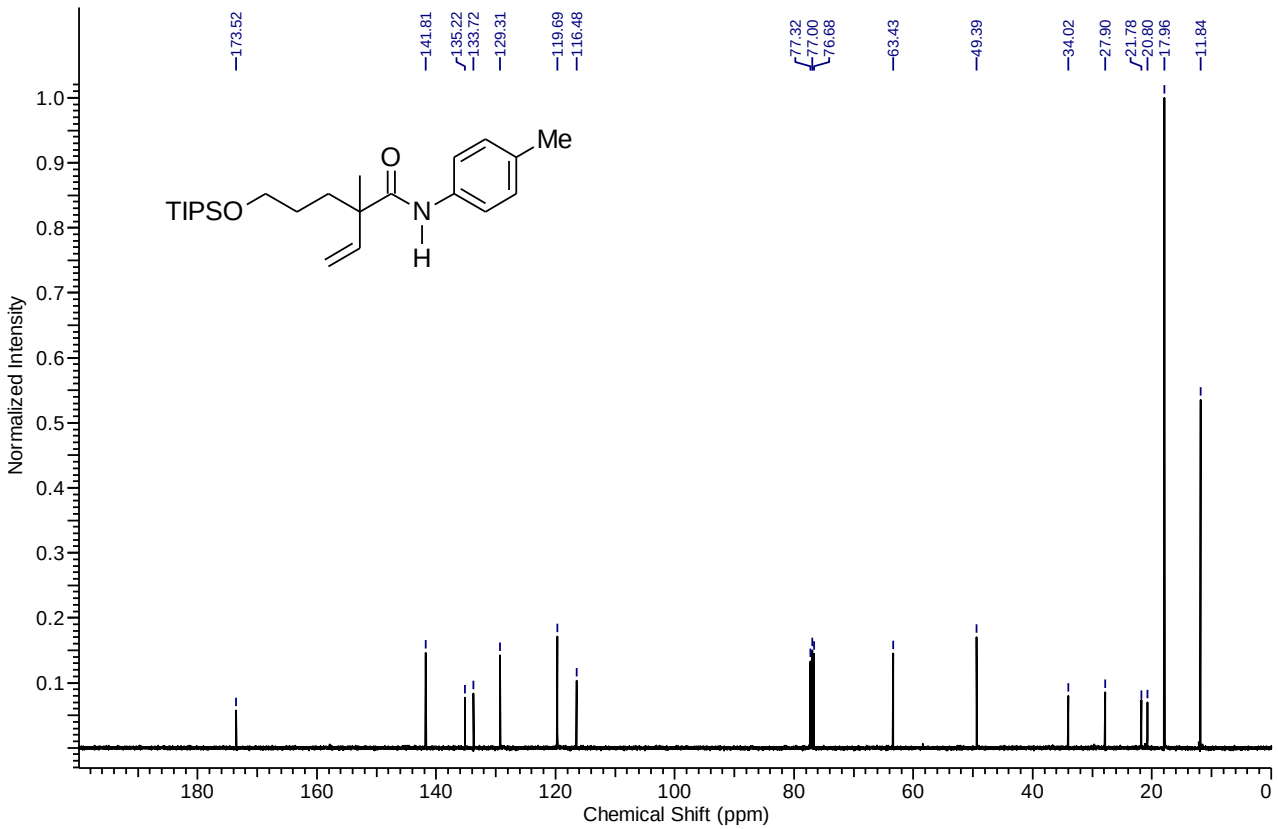


Figure S33. ^{13}C NMR spectrum of the compound **4ab** in $CDCl_3$, 100 MHz

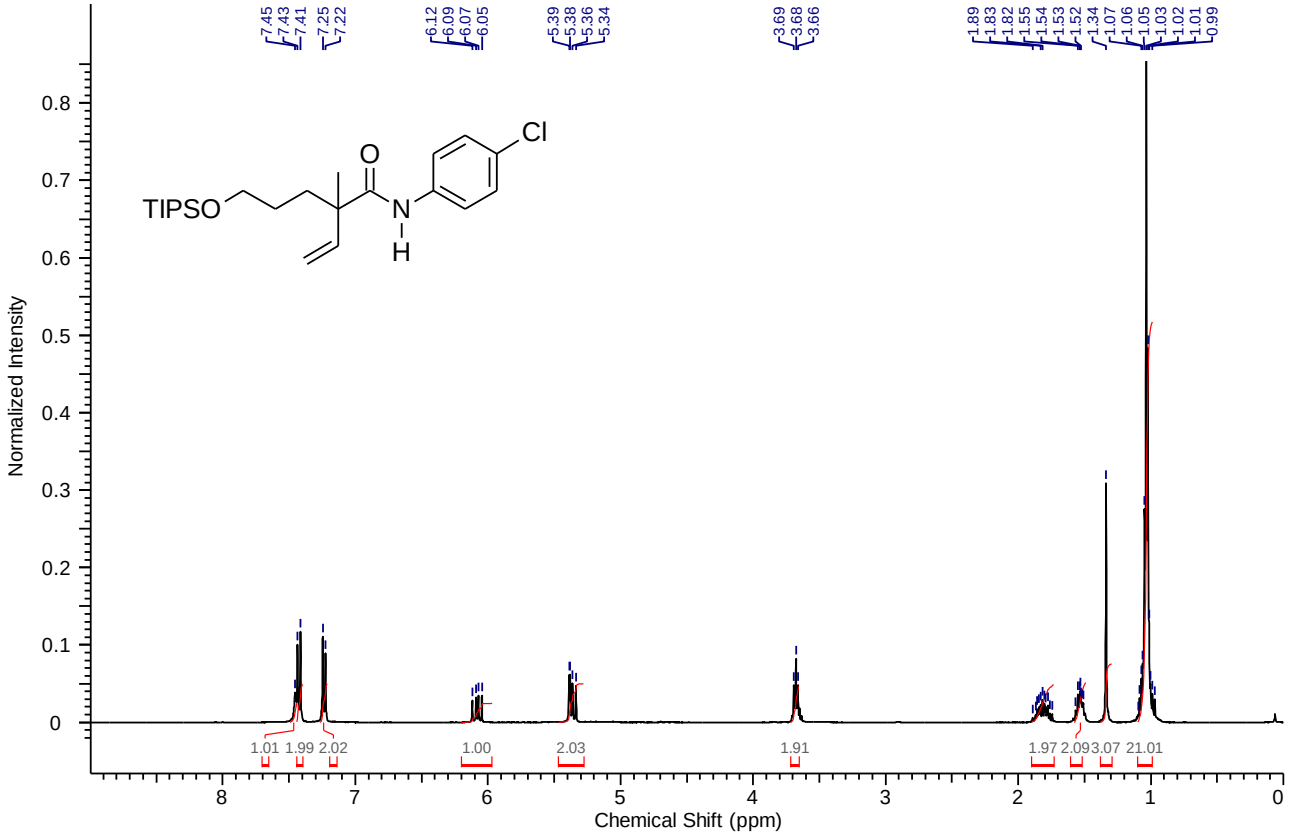


Figure S34. ^{1}H NMR spectrum of the compound **4ac** in $CDCl_3$, 400 MHz

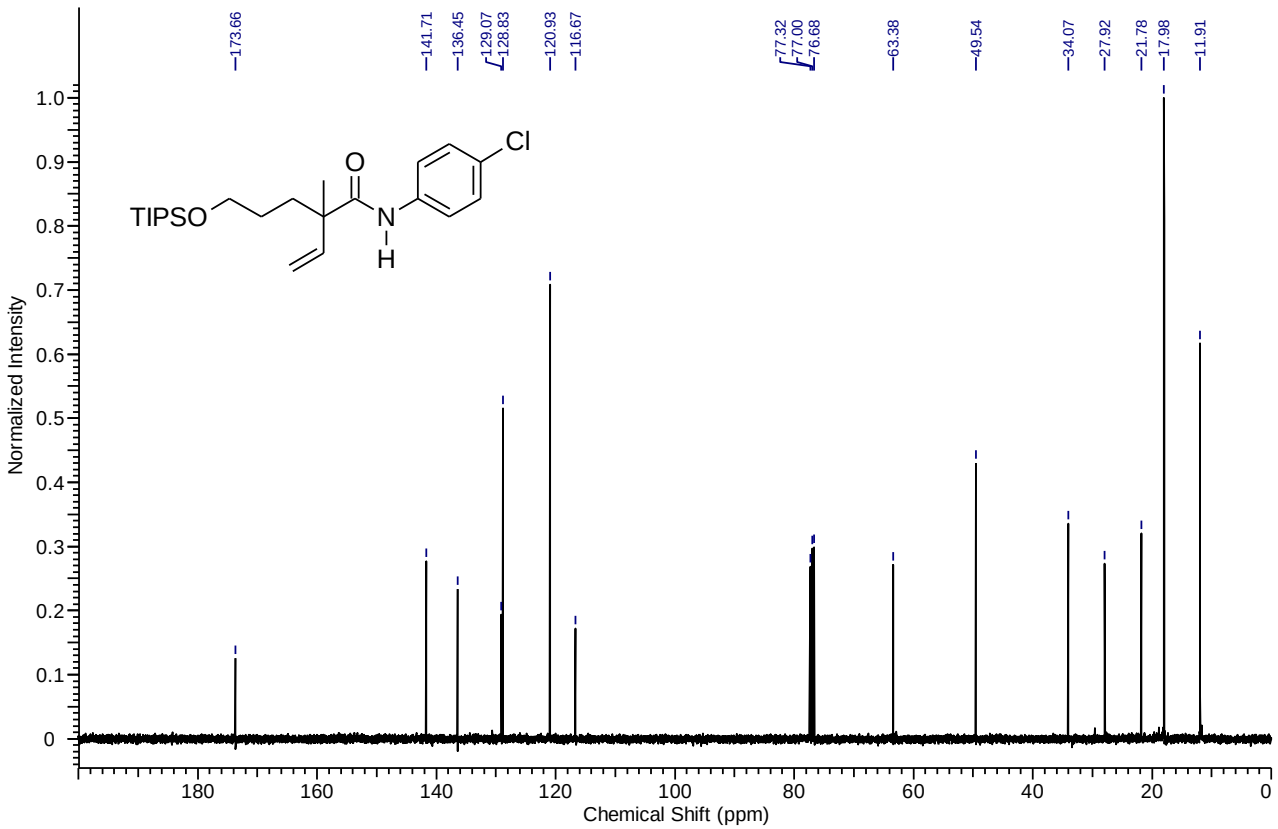


Figure S35. ^{13}C NMR spectrum of the compound **4ac** in $CDCl_3$, 100 MHz

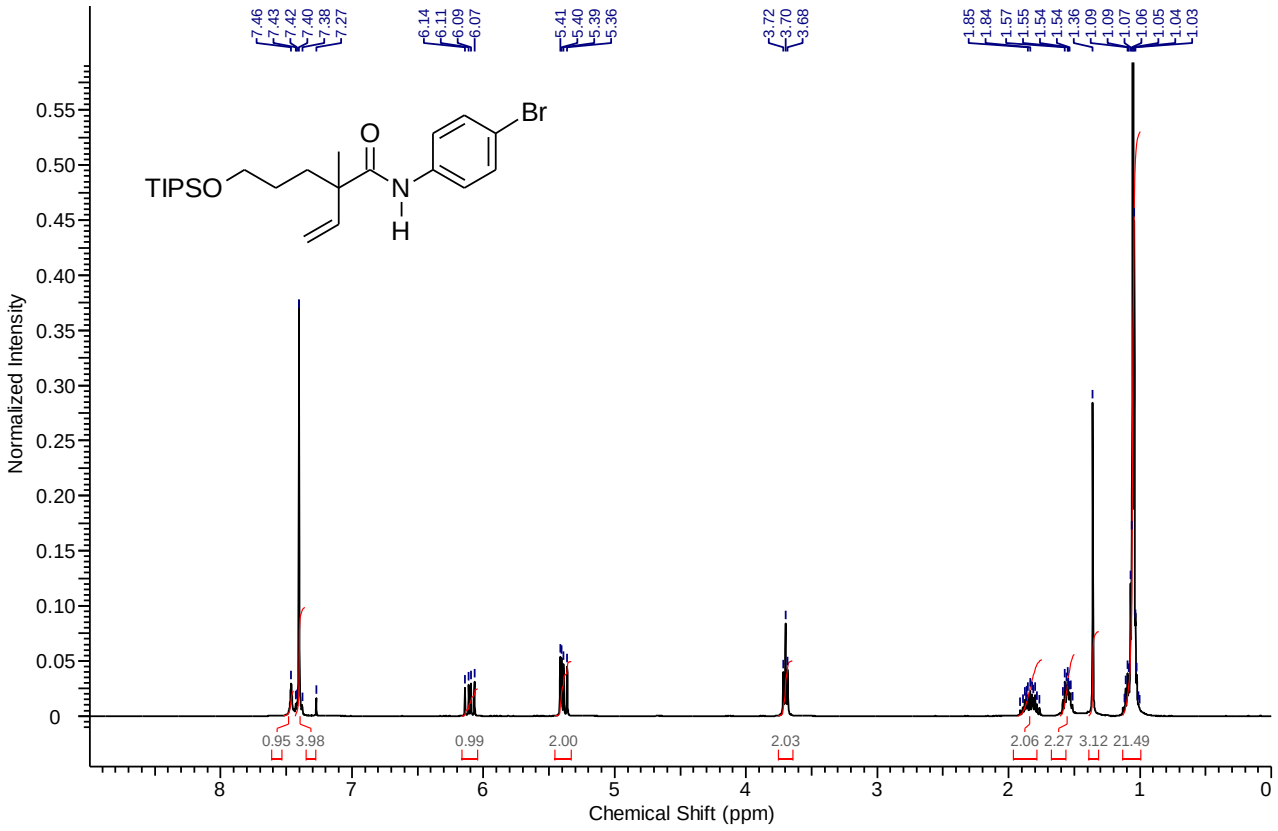


Figure S36. ^{1}H NMR spectrum of the compound **4ad** in $CDCl_3$, 400 MHz

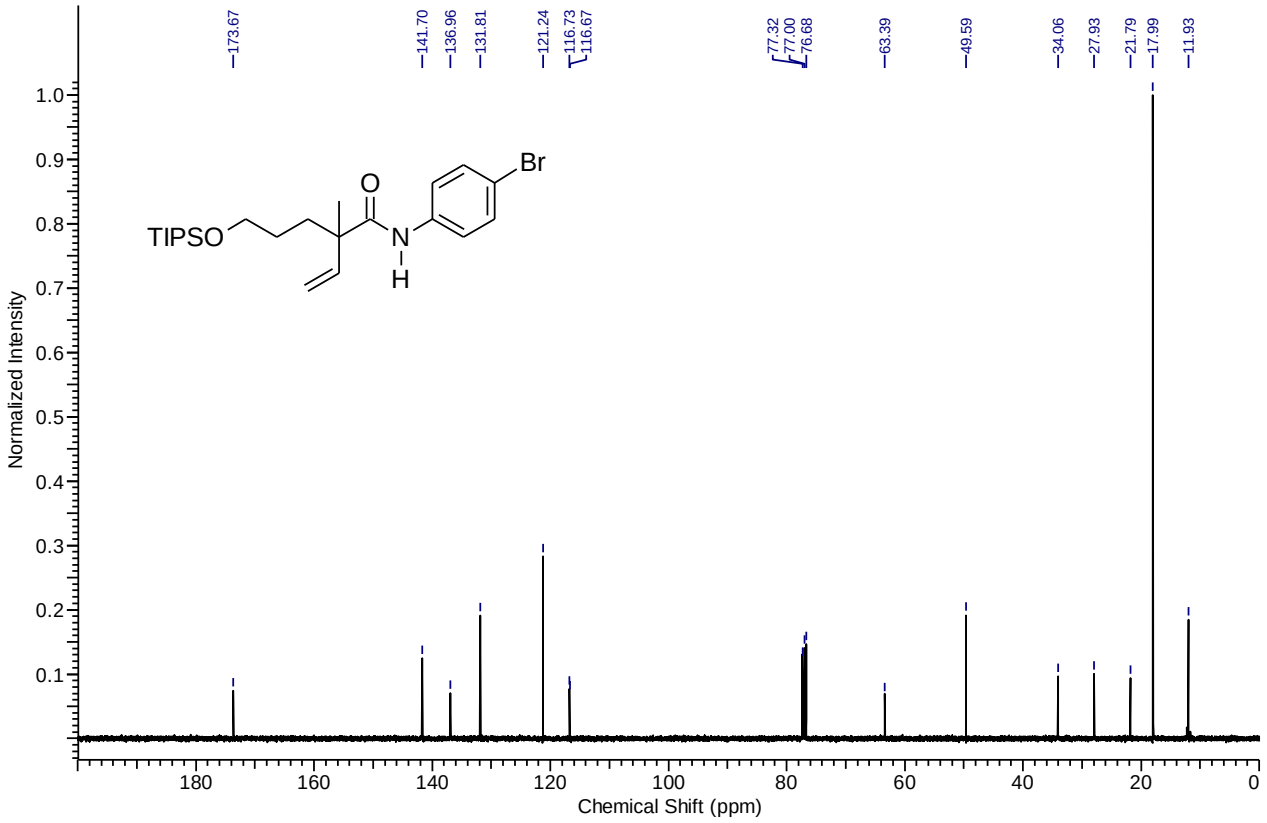


Figure S37. ^{13}C NMR spectrum of the compound **4ad** in $CDCl_3$, 100 MHz

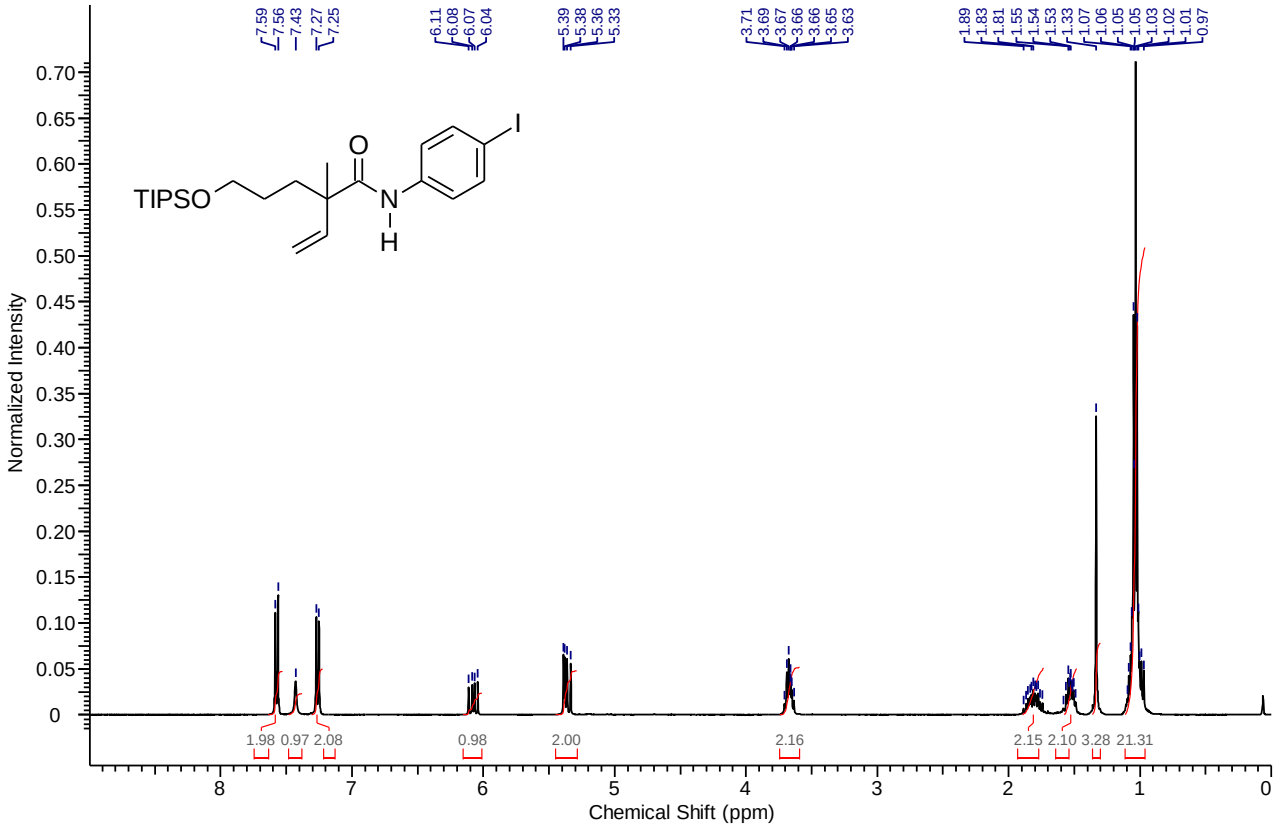


Figure S38. ^{1}H NMR spectrum of the compound **4ae** in $CDCl_3$, 400 MHz

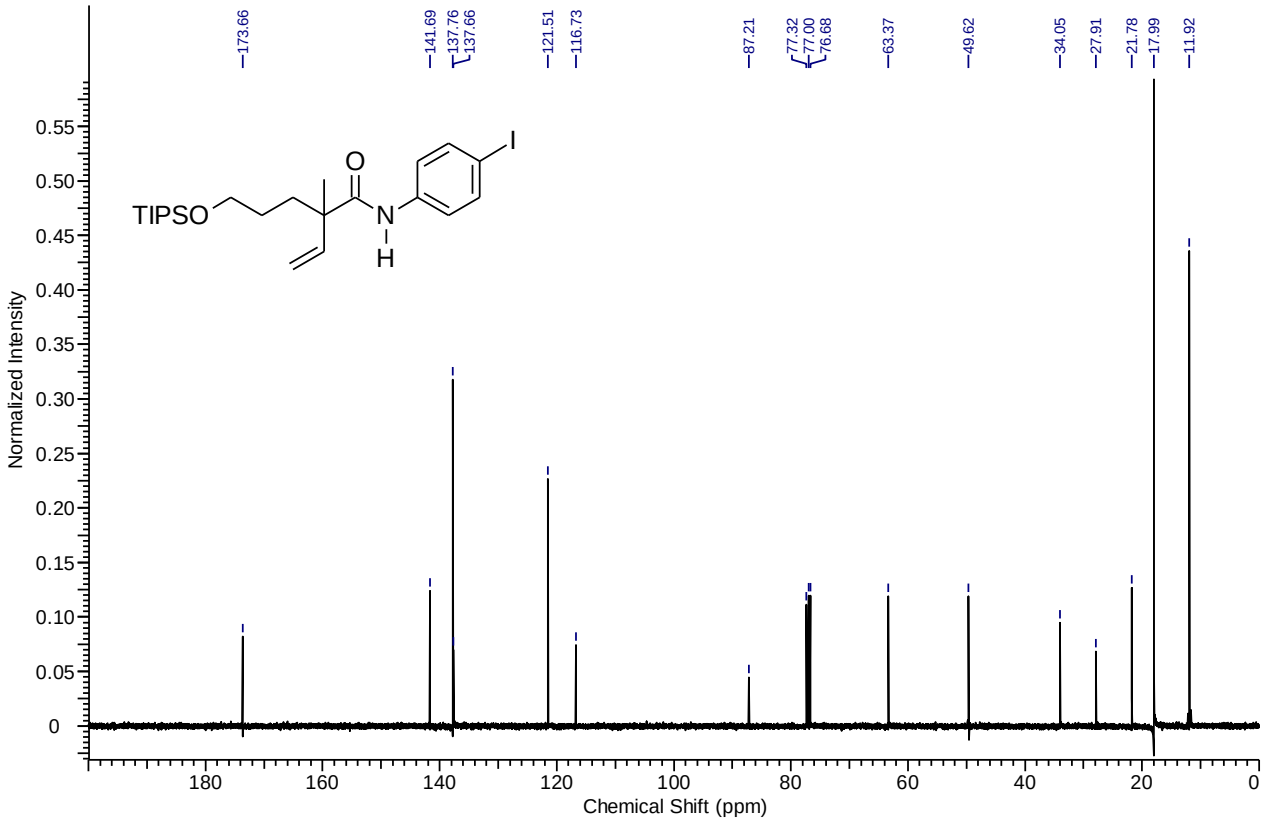


Figure S39. ^{13}C NMR spectrum of the compound **4ae** in $CDCl_3$, 100 MHz

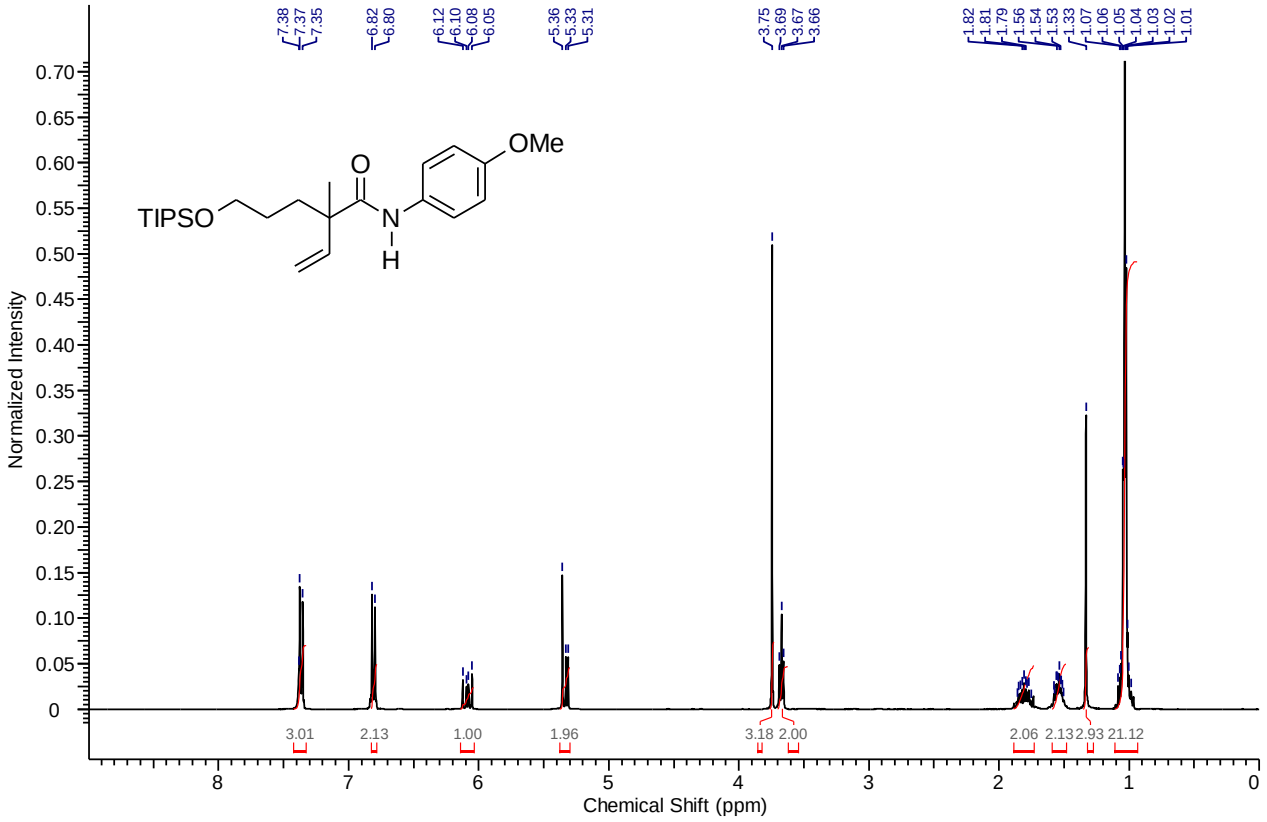


Figure S40. ^{1}H NMR spectrum of the compound **4af** in $CDCl_3$, 400 MHz

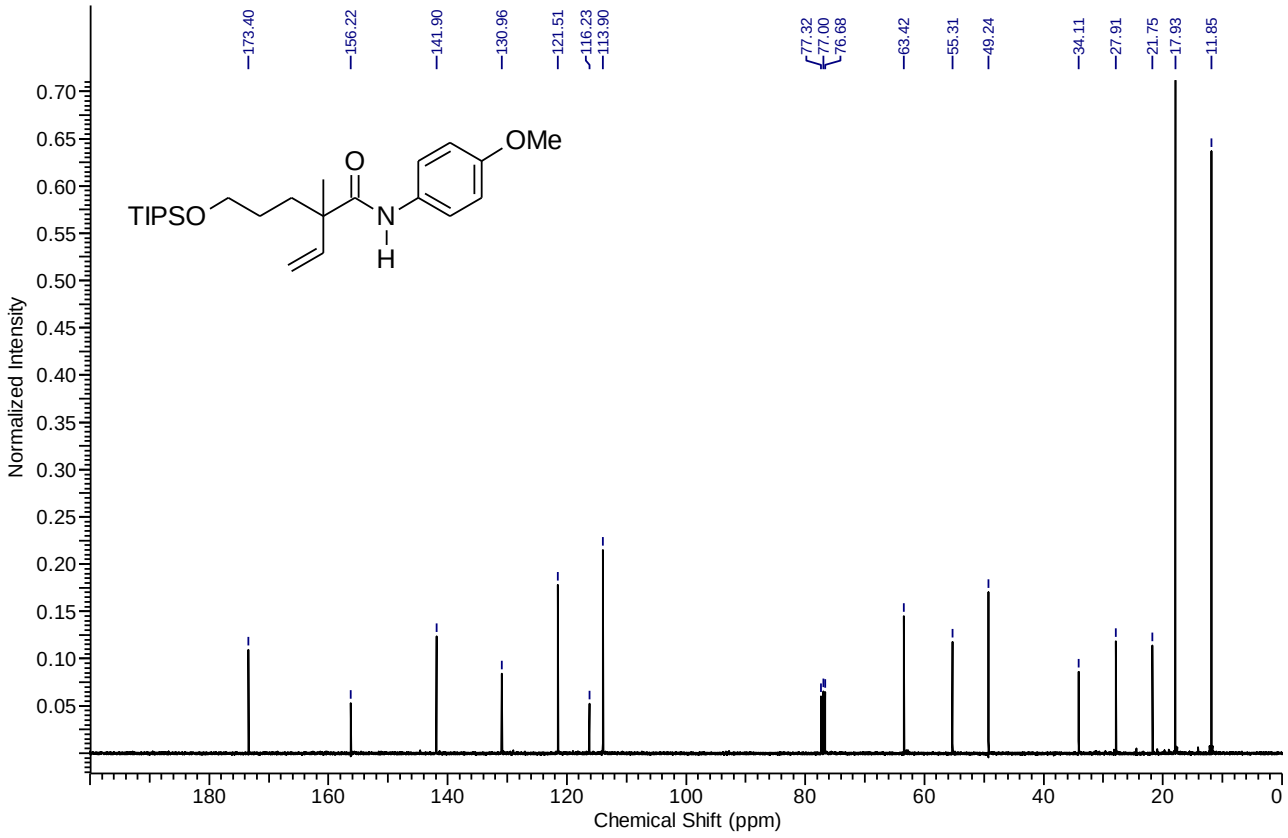


Figure S41. ^{13}C NMR spectrum of the compound **4af** in $CDCl_3$, 100 MHz

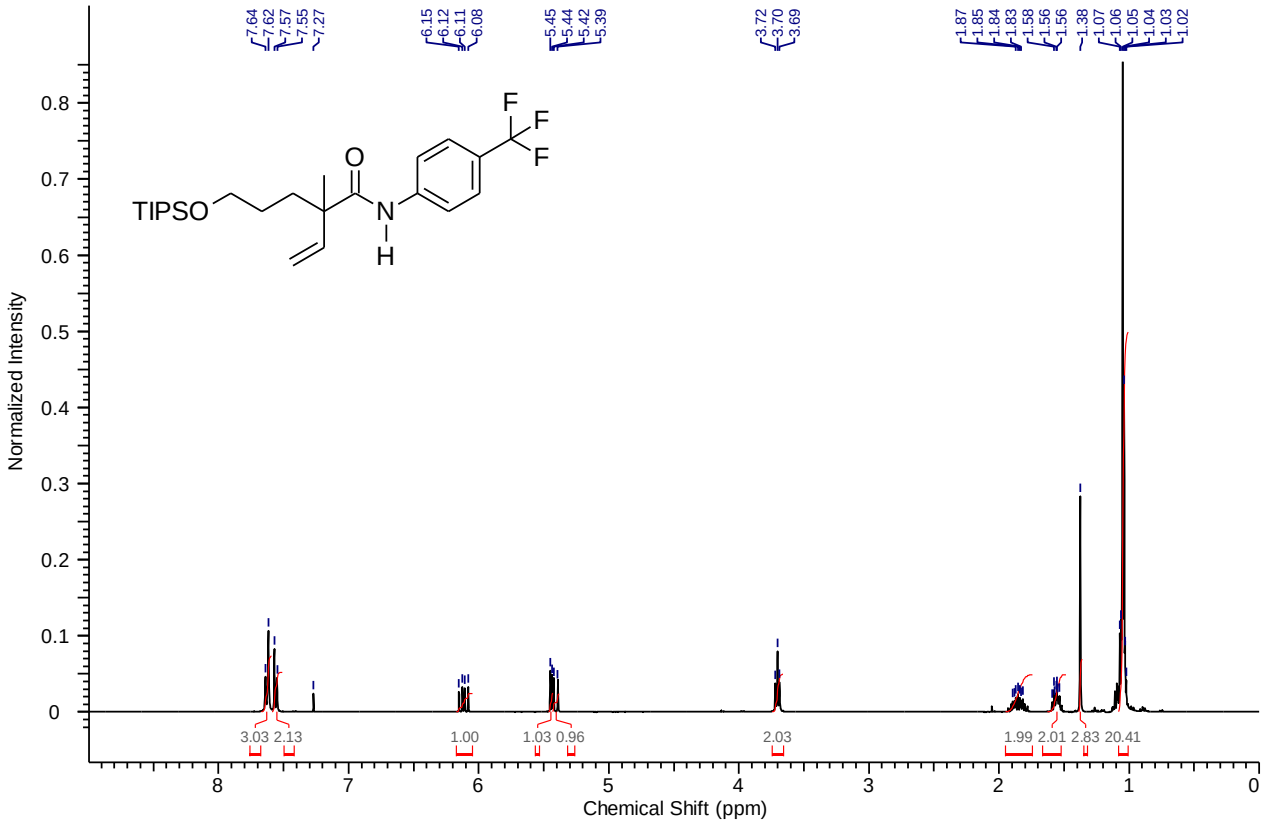


Figure S42. ^{1}H NMR spectrum of the compound **4ag** in $CDCl_3$, 400 MHz

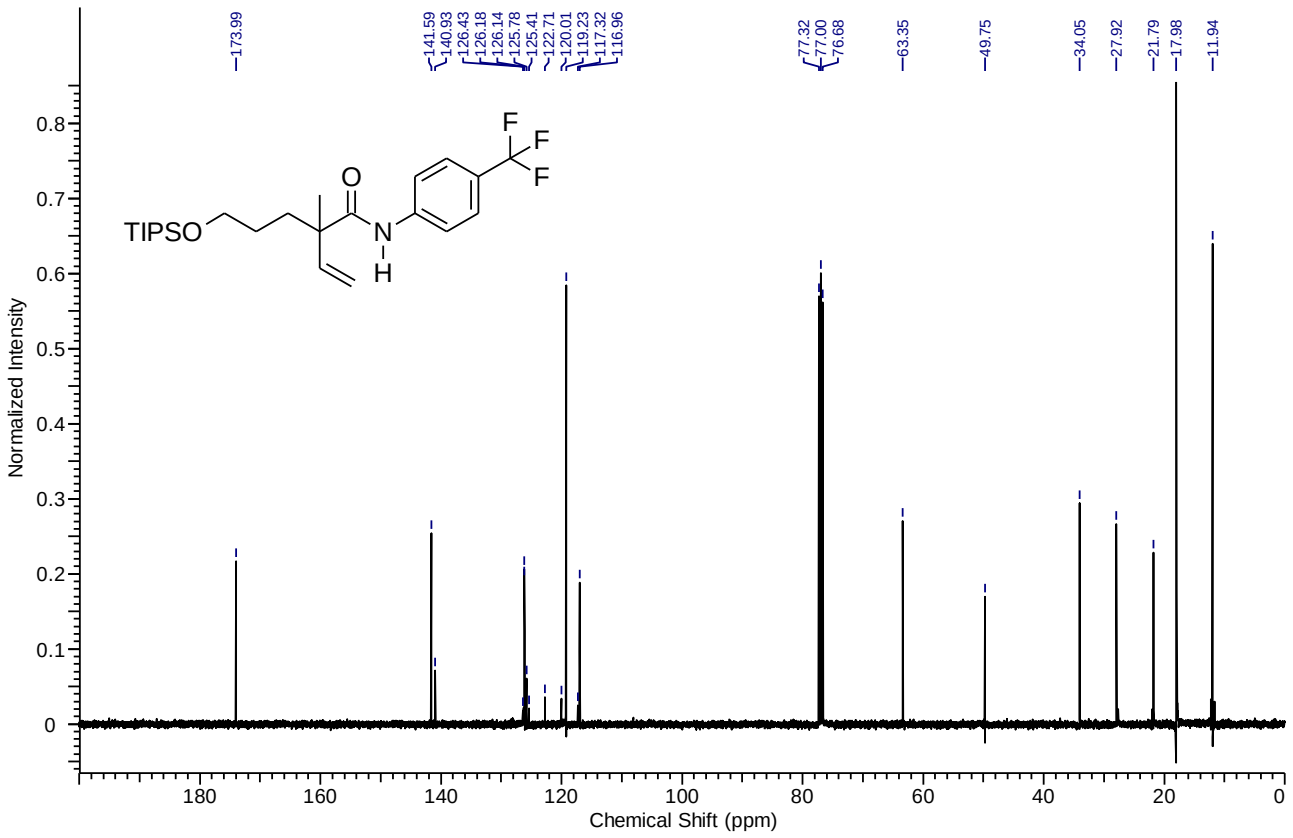


Figure S43. ^{13}C NMR spectrum of the compound **4ag** in $CDCl_3$, 100 MHz

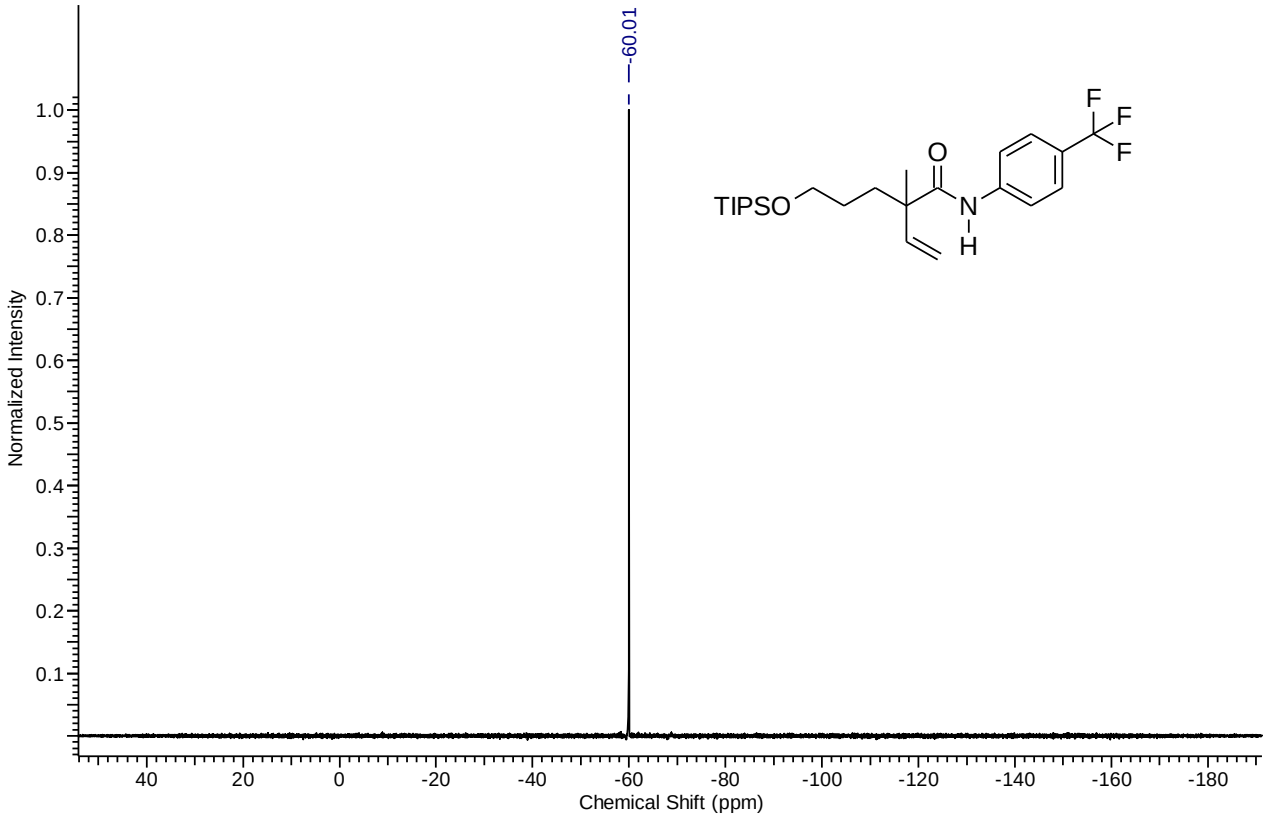


Figure S44. ^{19}F NMR spectrum of the compound **4ag** in $CDCl_3$, 75.2 MHz

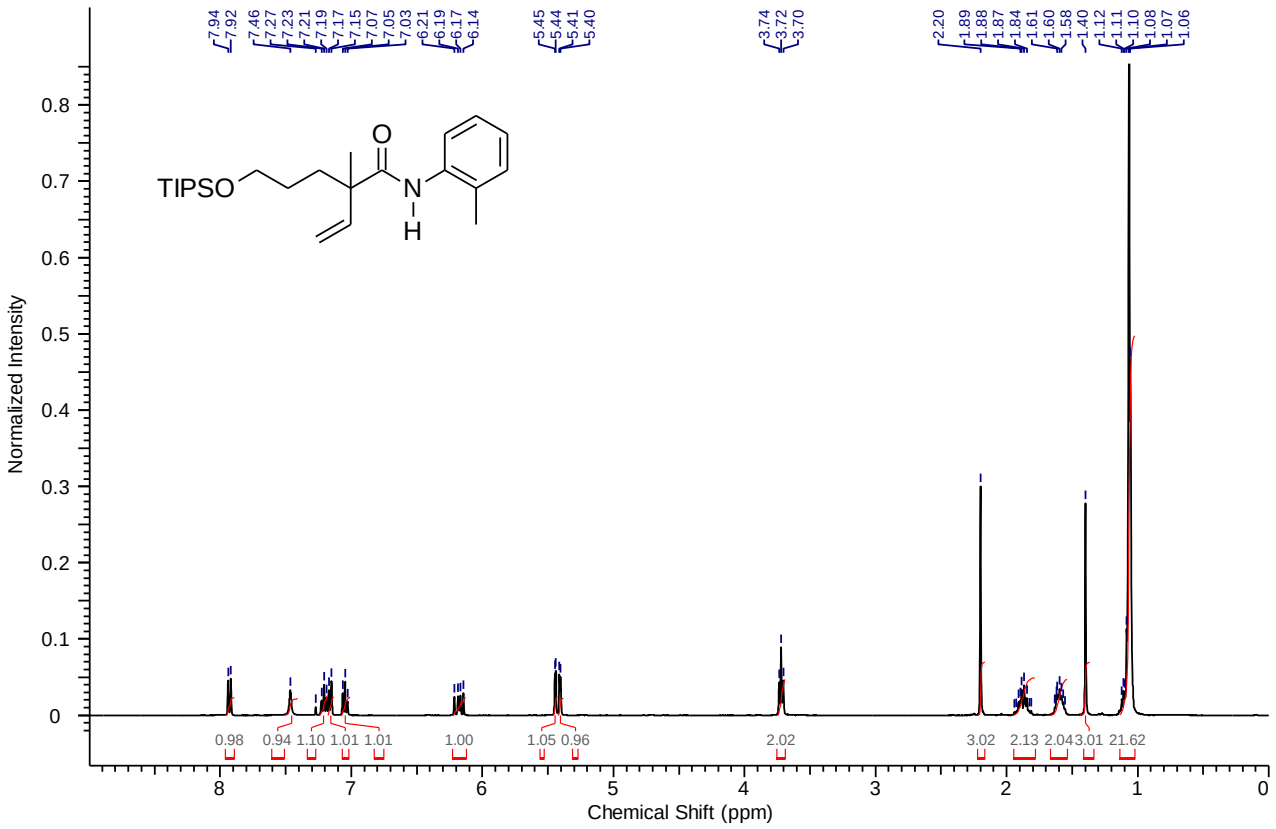


Figure S45. ^{1}H NMR spectrum of the compound **4ah** in $CDCl_3$, 400 MHz

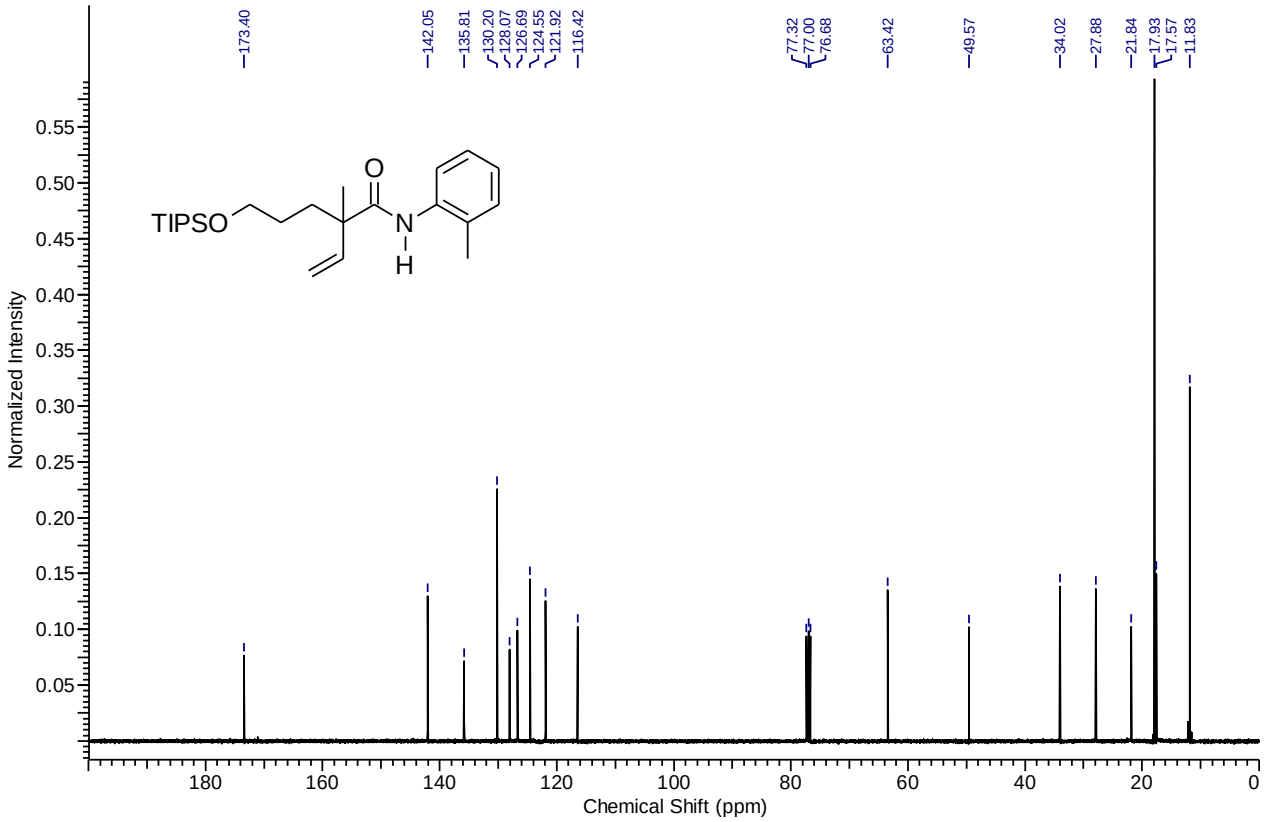


Figure S46. ^{13}C NMR spectrum of the compound **4ah** in $CDCl_3$, 100 MHz

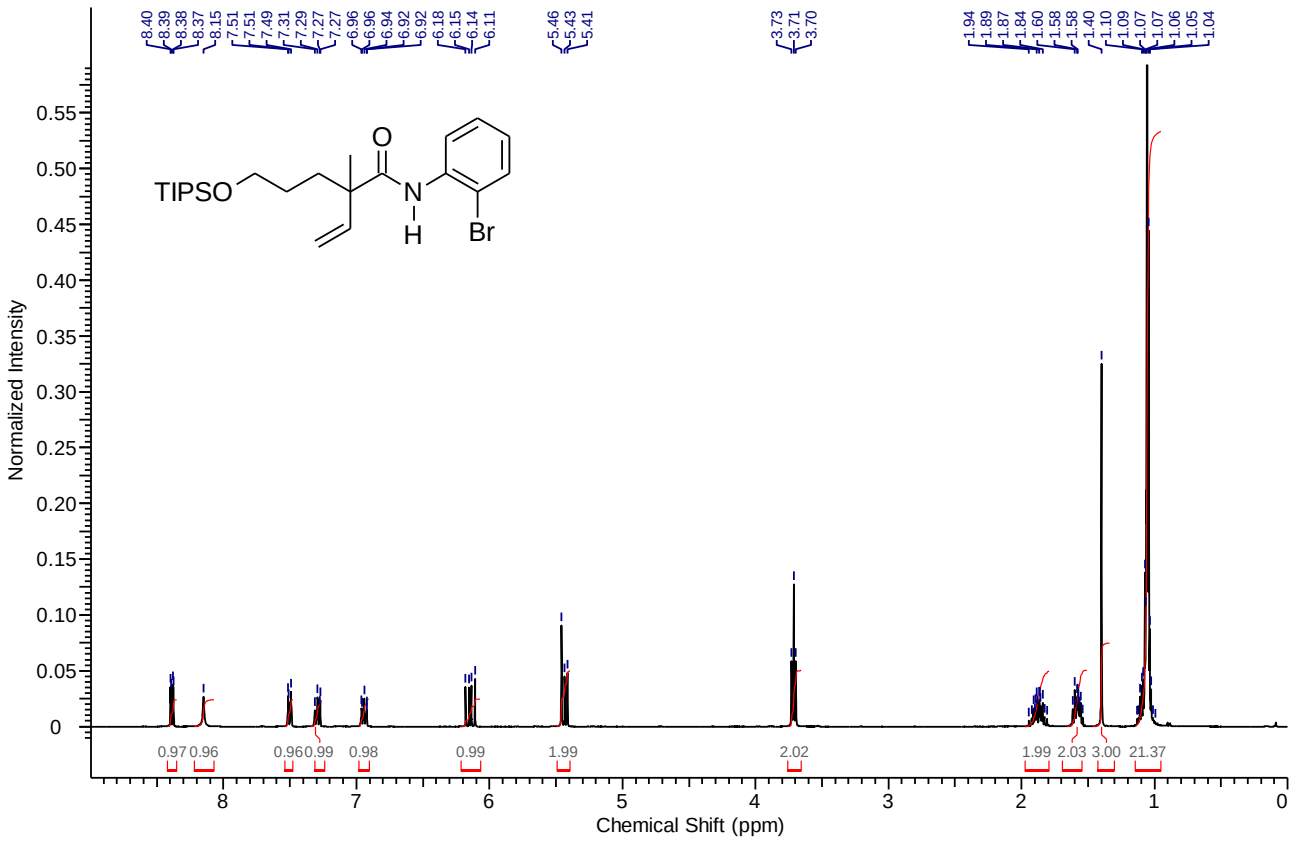


Figure S47. ^{1}H NMR spectrum of the compound **4ai** in $CDCl_3$, 400 MHz

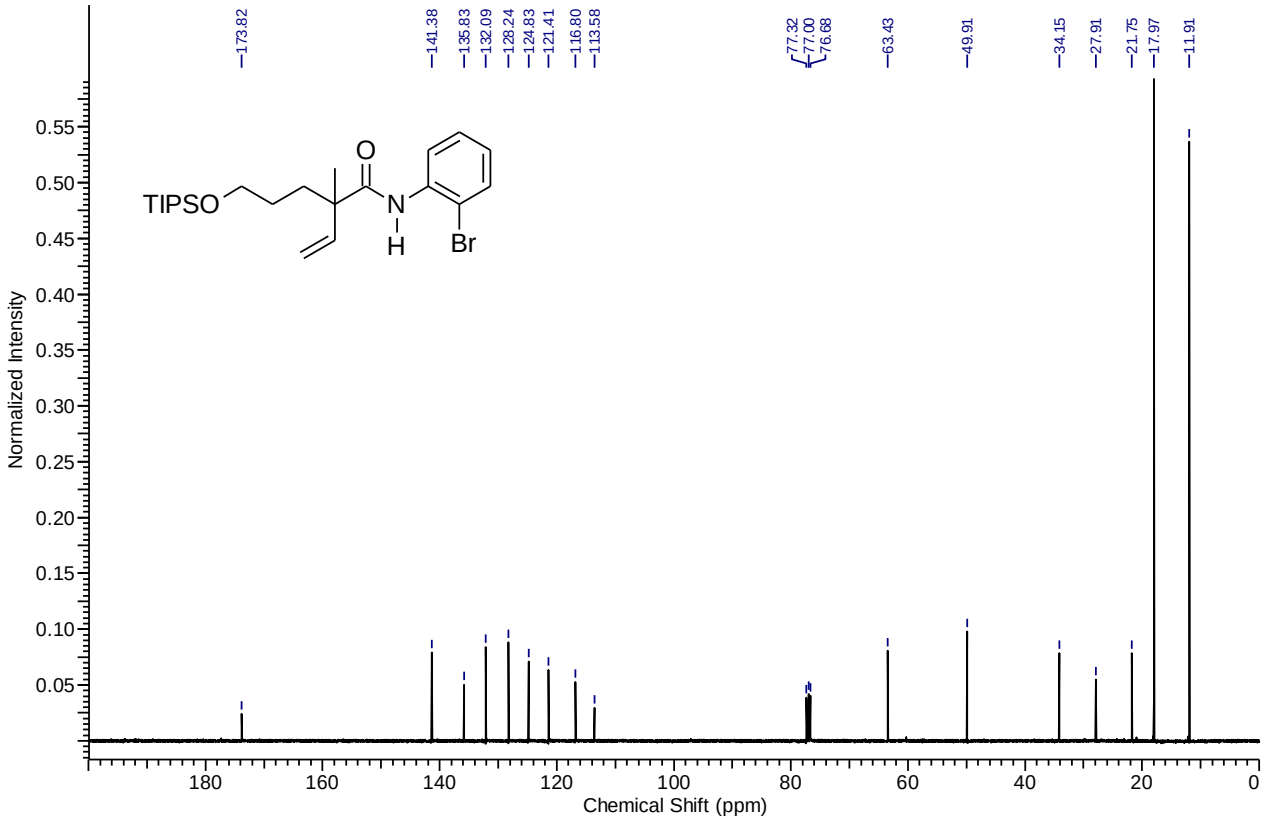


Figure S48. ^{13}C NMR spectrum of the compound **4ai** in $CDCl_3$, 100 MHz

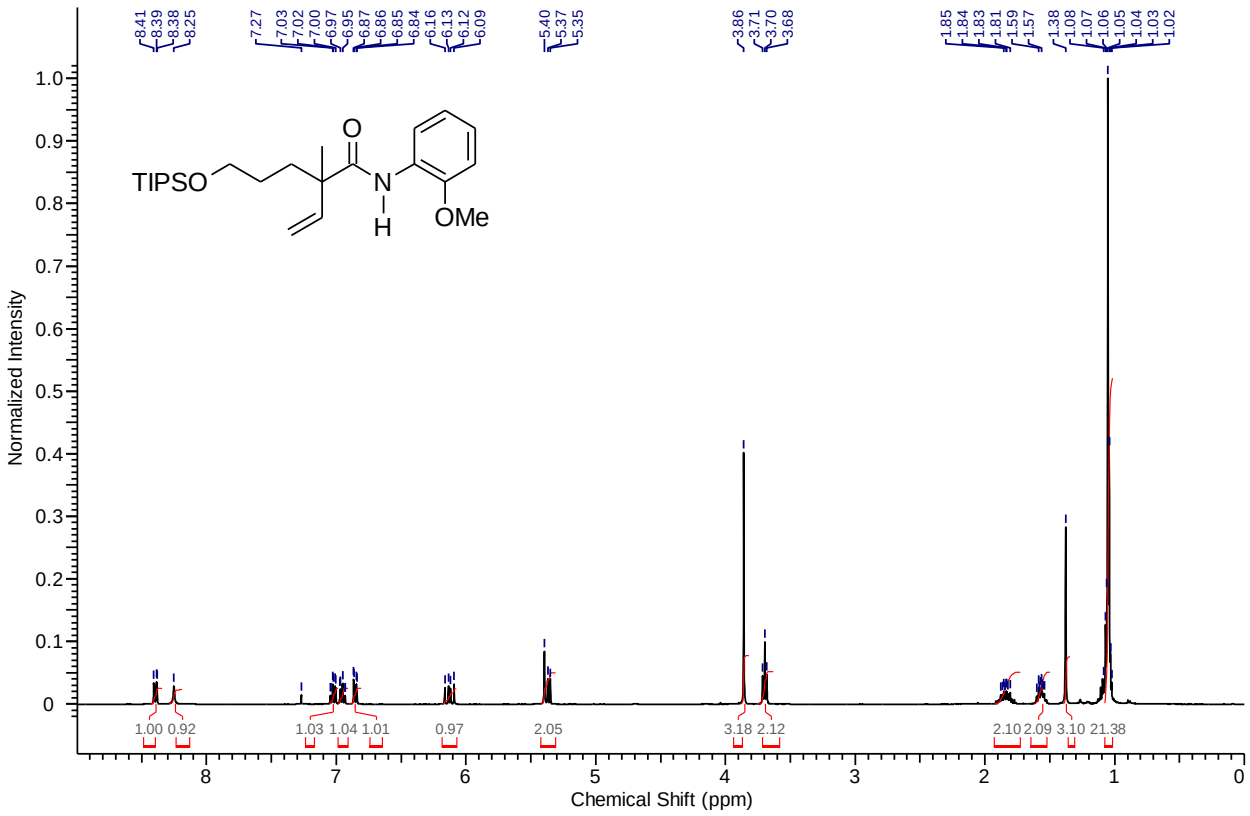


Figure S49. ^{1}H NMR spectrum of the compound **4aj** in $CDCl_3$, 400 MHz

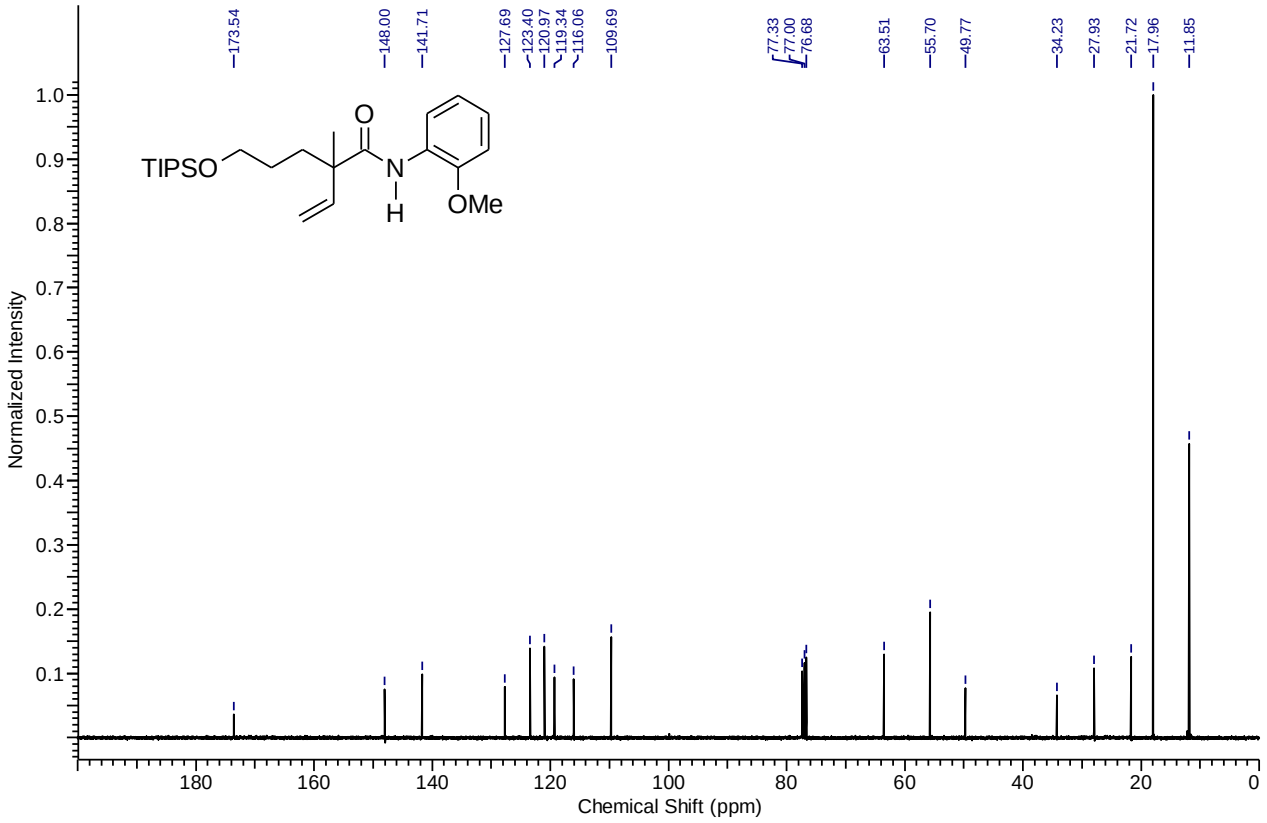


Figure S50. ^{13}C NMR spectrum of the compound **4aj** in $CDCl_3$, 100 MHz

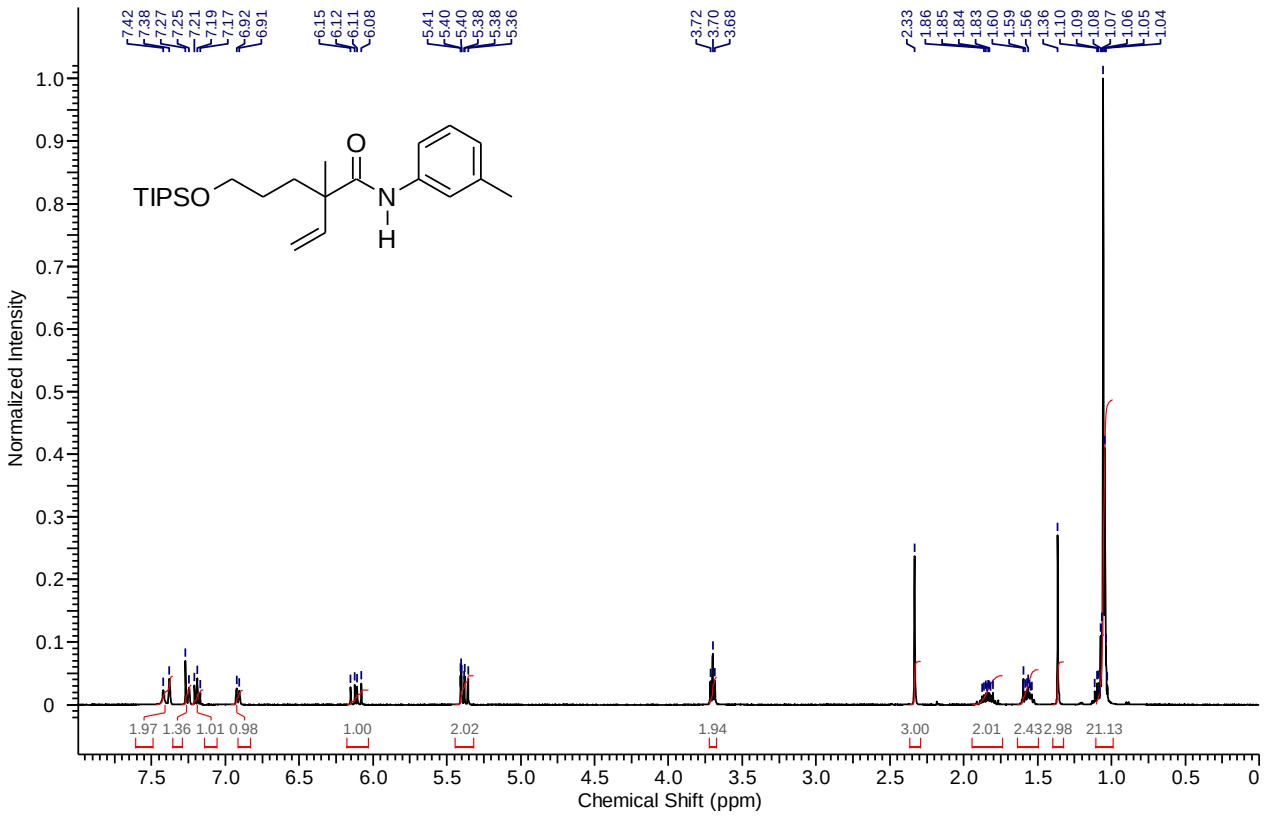


Figure S51. ^{1}H NMR spectrum of the compound **4ak** in $CDCl_3$, 400 MHz

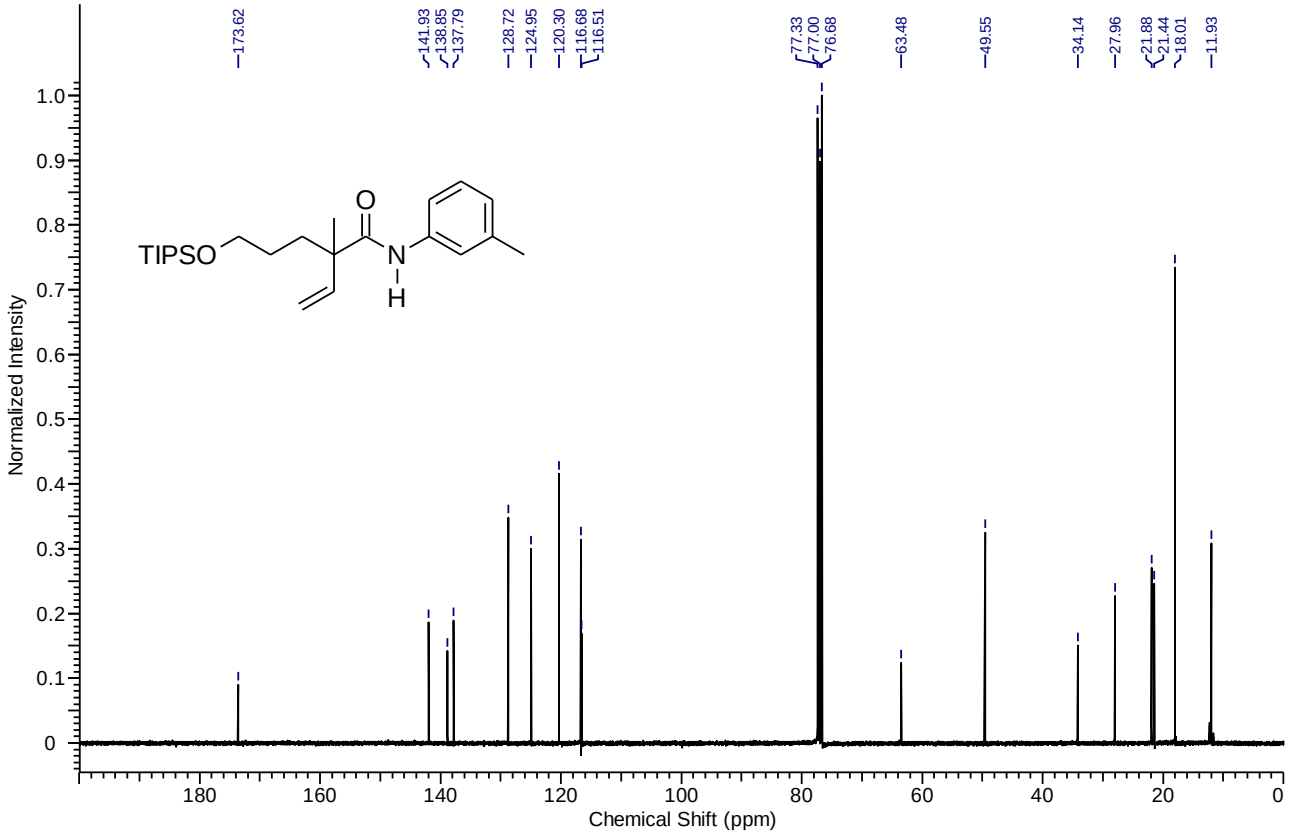


Figure S52. ^{13}C NMR spectrum of the compound **4ak** in $CDCl_3$, 100 MHz

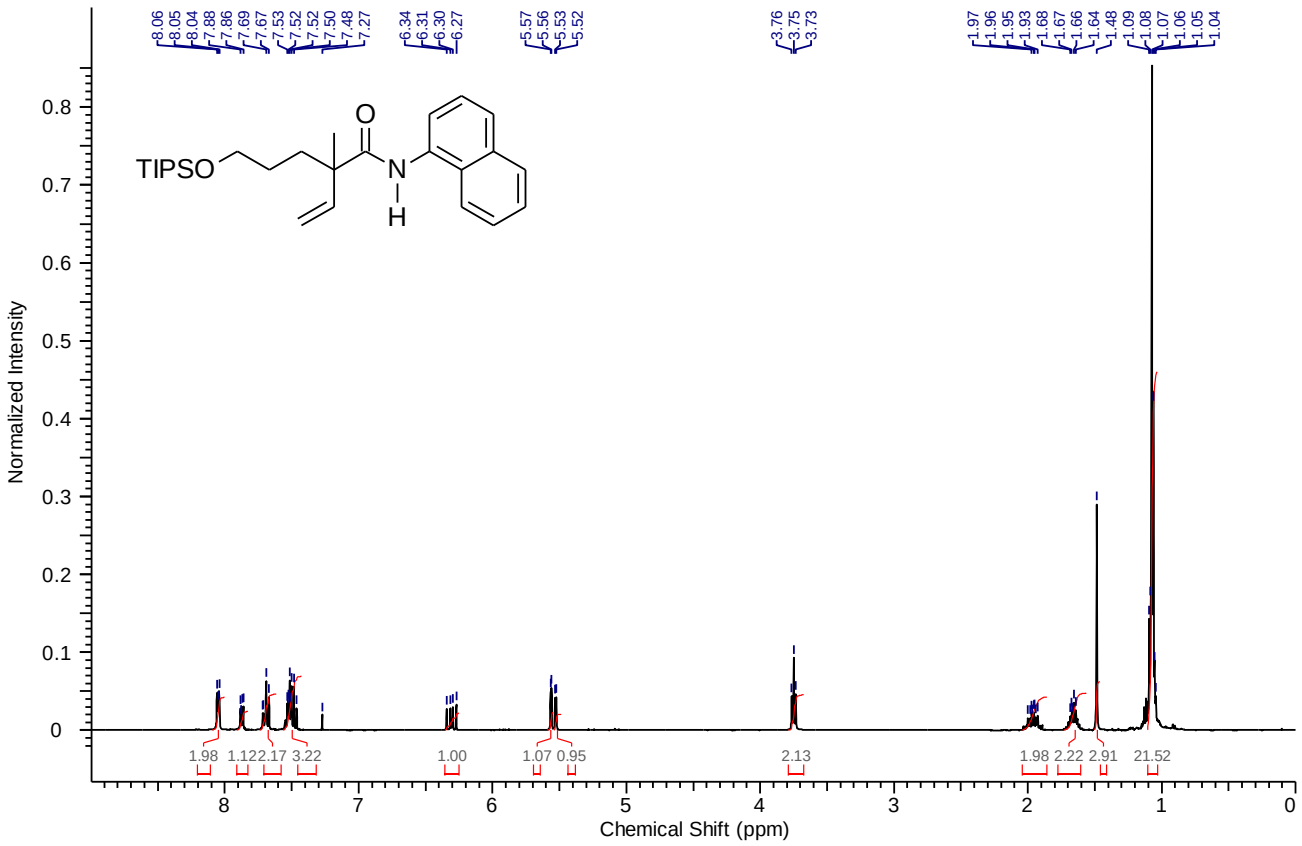


Figure S53. ^{1}H NMR spectrum of the compound **4al** in $CDCl_3$, 400 MHz

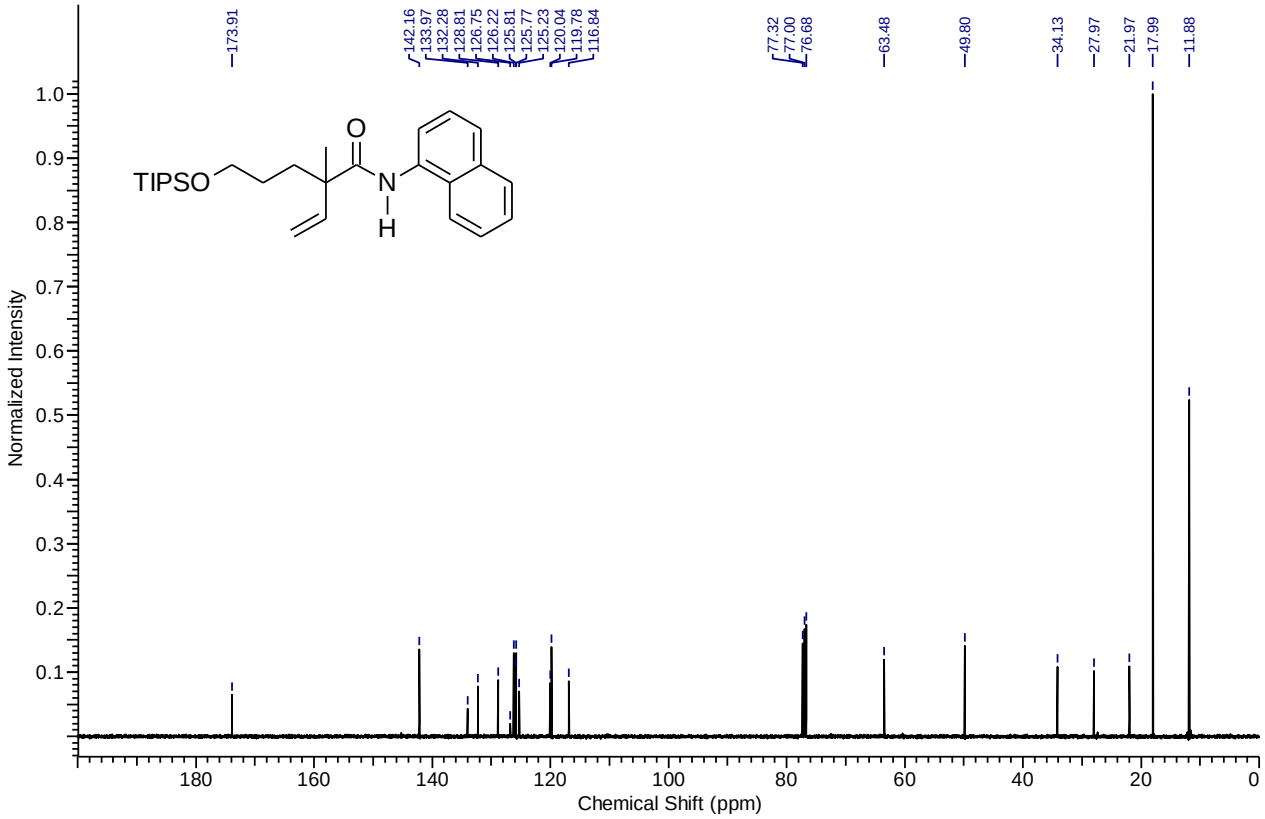


Figure S54. ^{13}C NMR spectrum of the compound **4al** in $CDCl_3$, 100 MHz

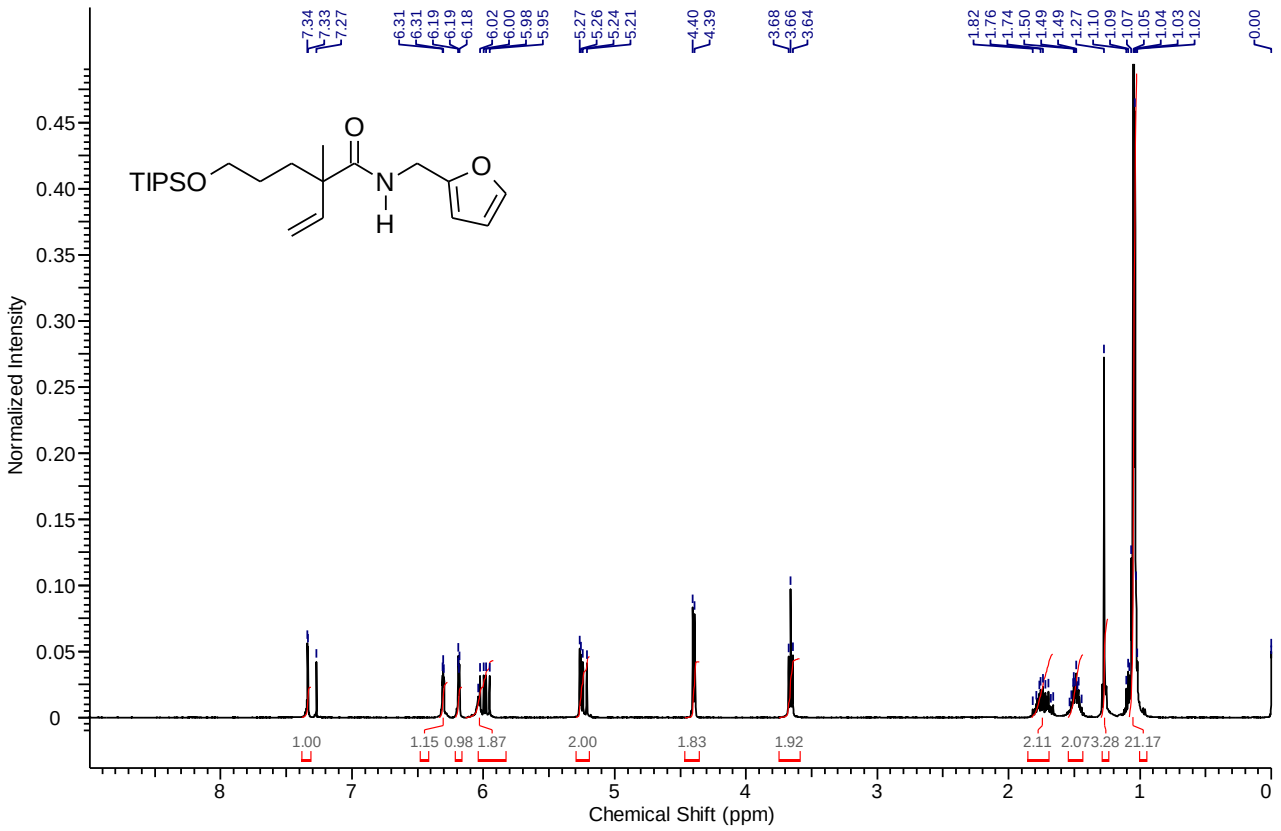


Figure S55. ^{1}H NMR spectrum of the compound **4am** in $CDCl_3$, 400 MHz

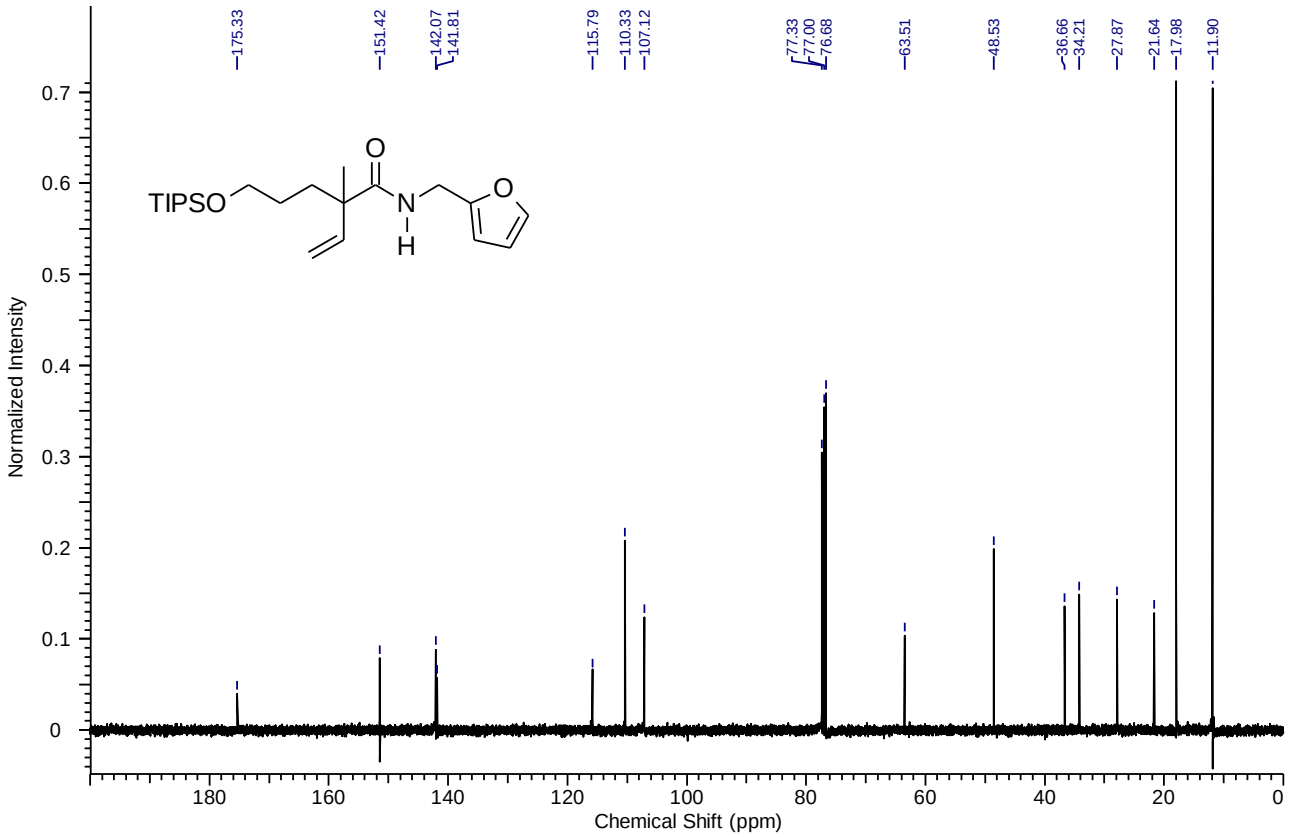


Figure S56. ^{13}C NMR spectrum of the compound **4am** in $CDCl_3$, 100 MHz

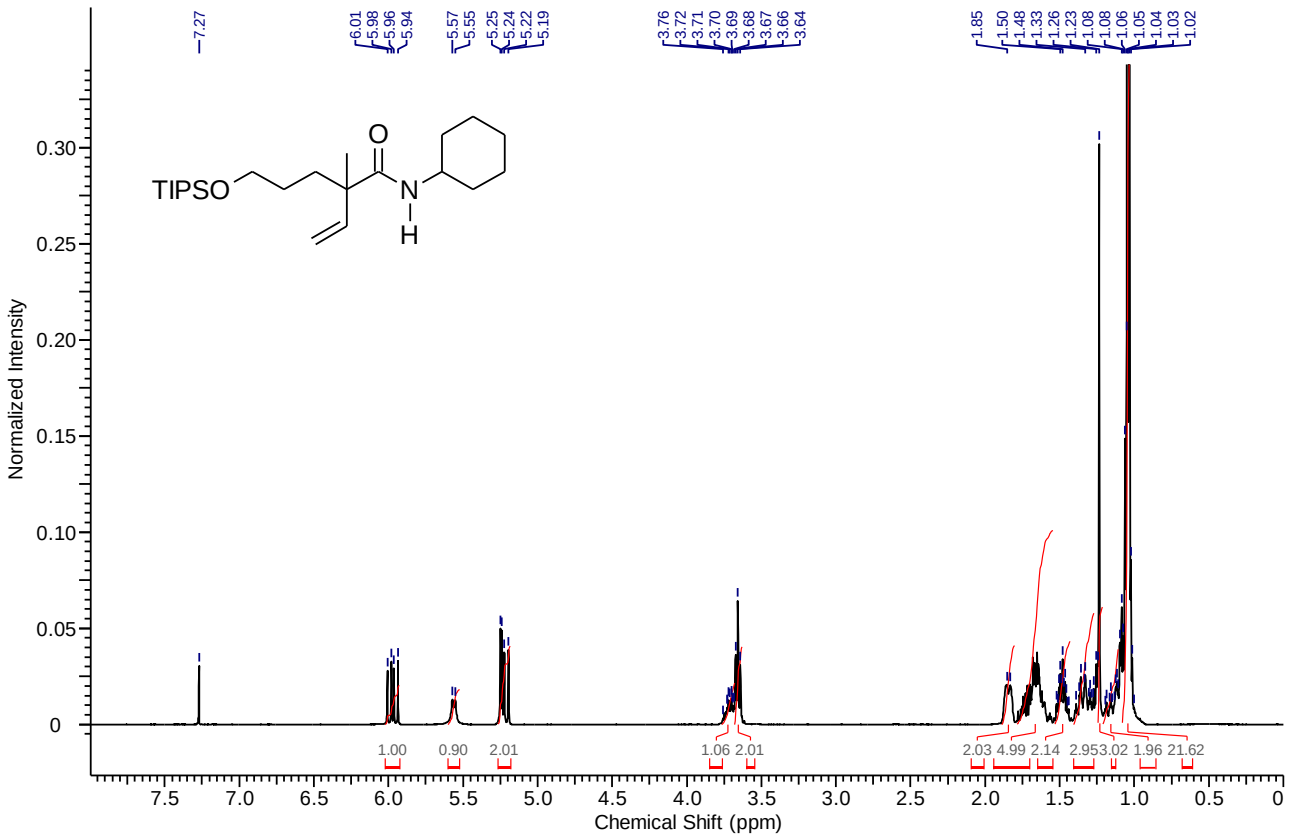


Figure S57. ^{1}H NMR spectrum of the compound **4an** in $CDCl_3$, 400 MHz

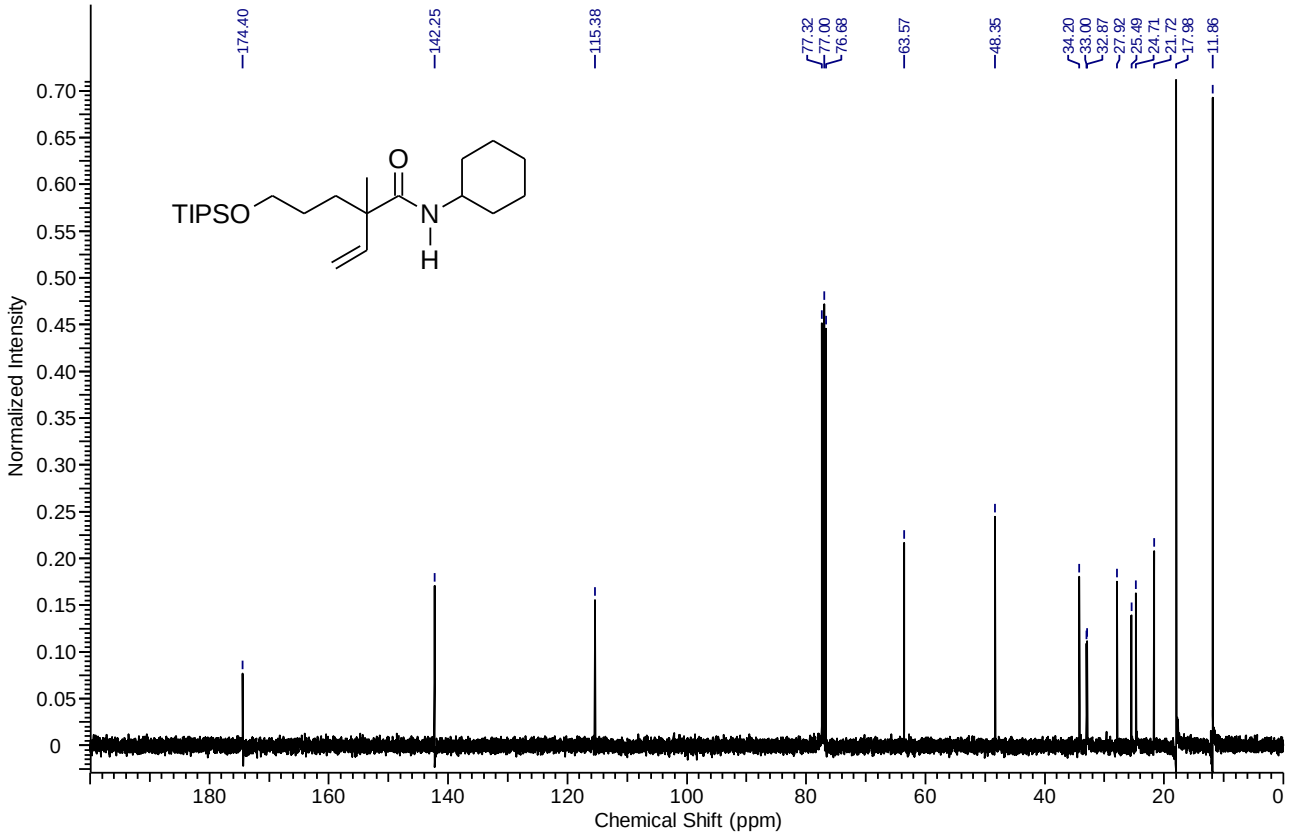


Figure S58. ^{13}C NMR spectrum of the compound **4an** in $CDCl_3$, 100 MHz

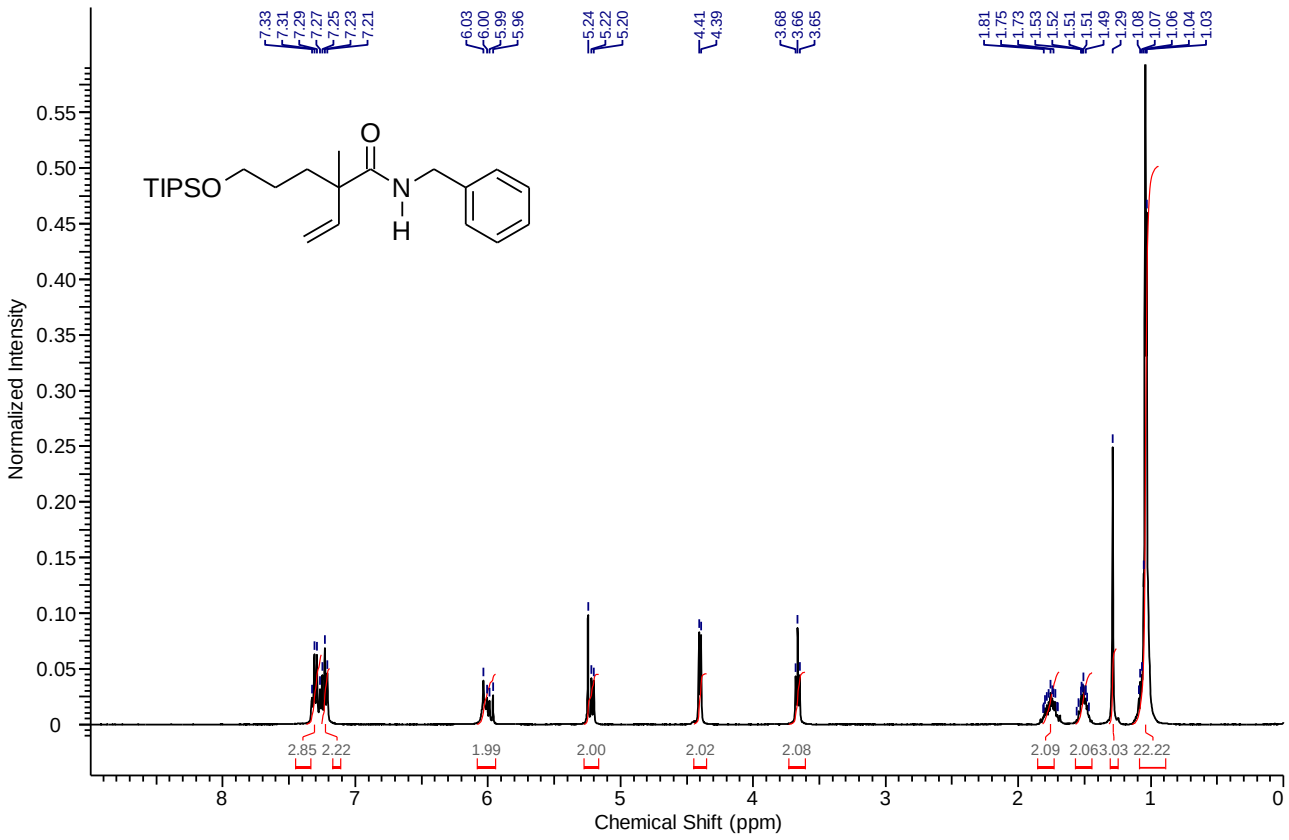


Figure S59. ^{1}H NMR spectrum of the compound **4ao** in $CDCl_3$, 400 MHz

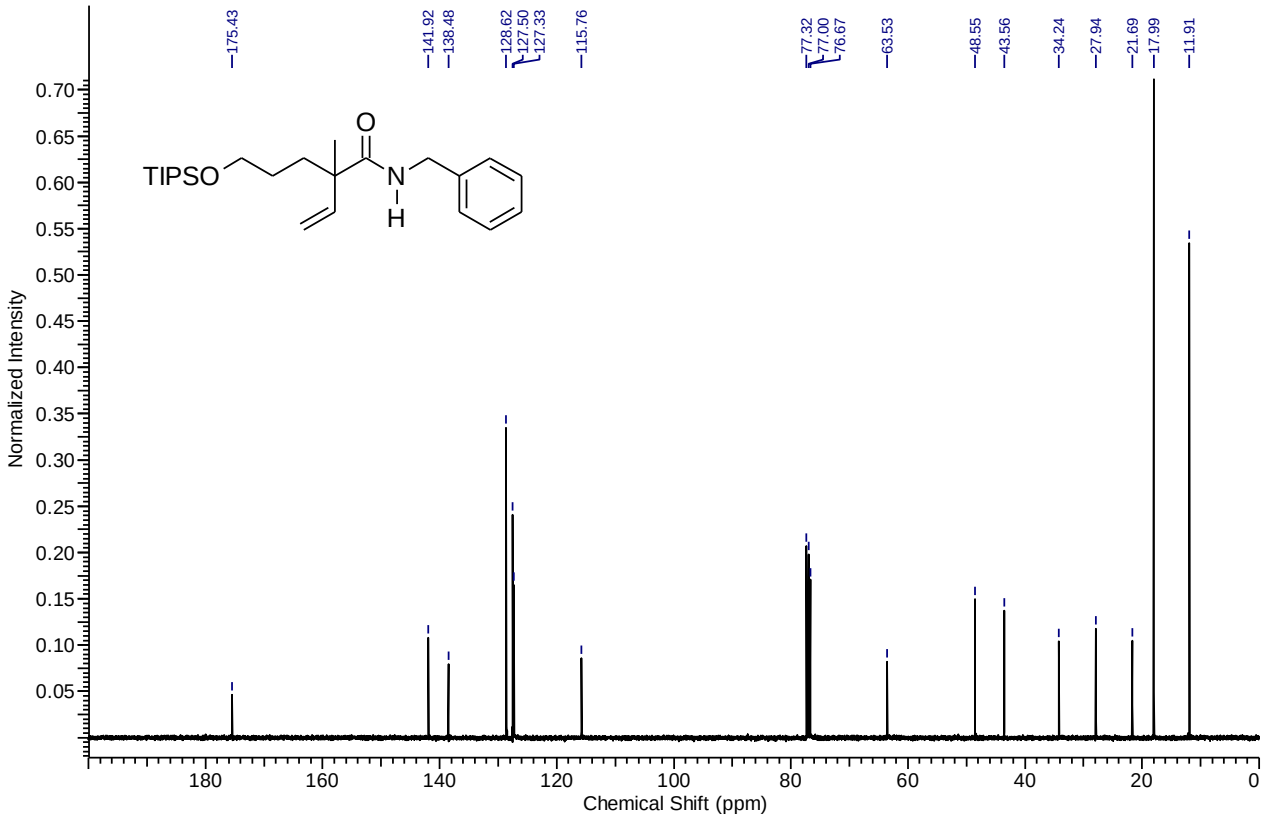


Figure S60. ^{13}C NMR spectrum of the compound **4ao** in $CDCl_3$, 100 MHz

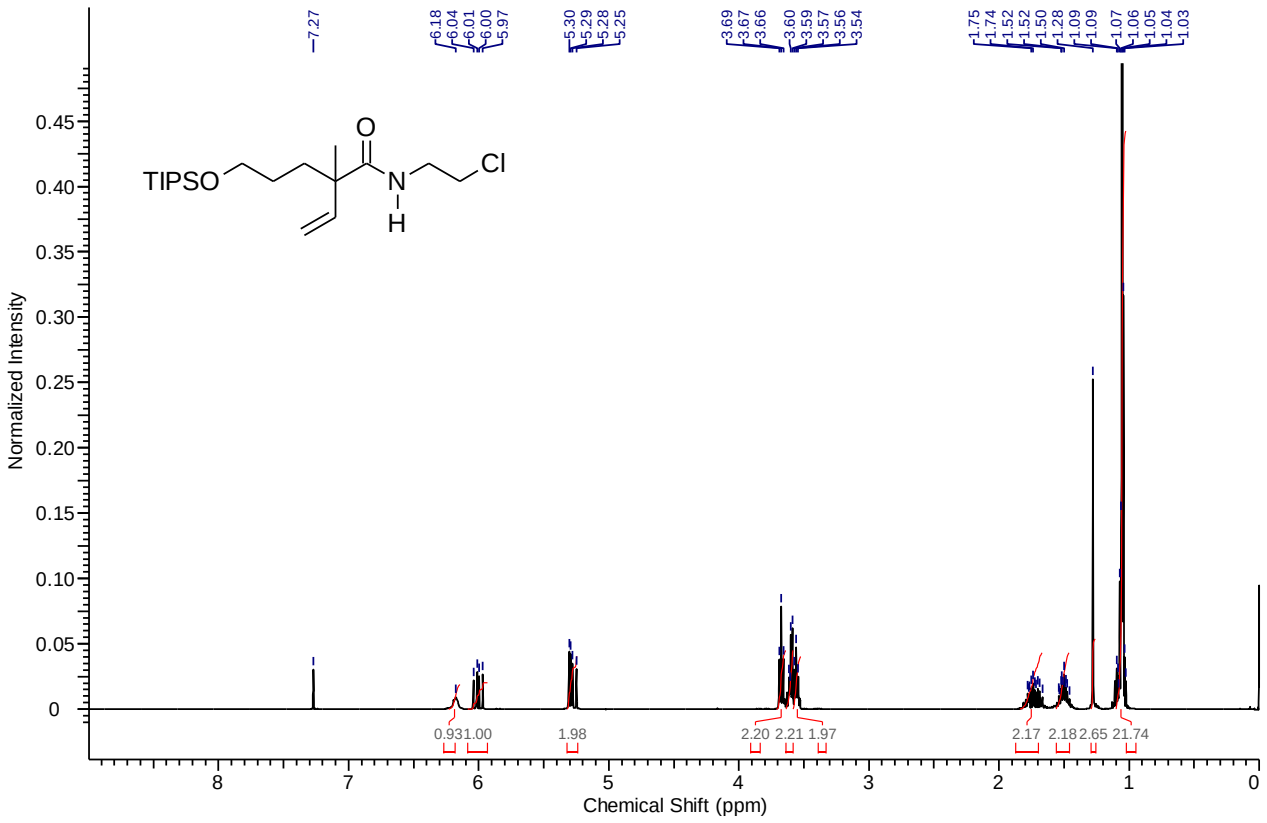


Figure S61. ^{1}H NMR spectrum of the compound **4ap** in $CDCl_3$, 400 MHz

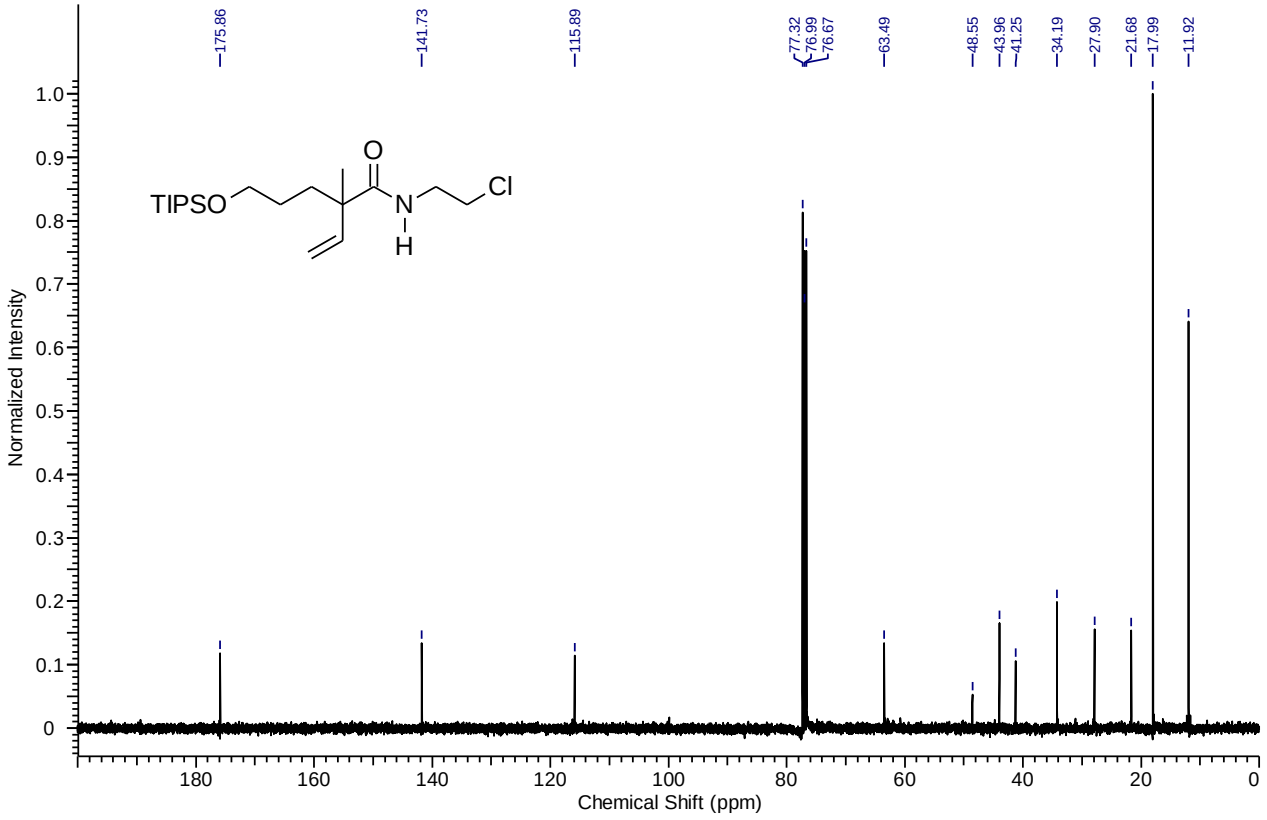


Figure S62. ^{13}C NMR spectrum of the compound **4ap** in $CDCl_3$, 100 MHz

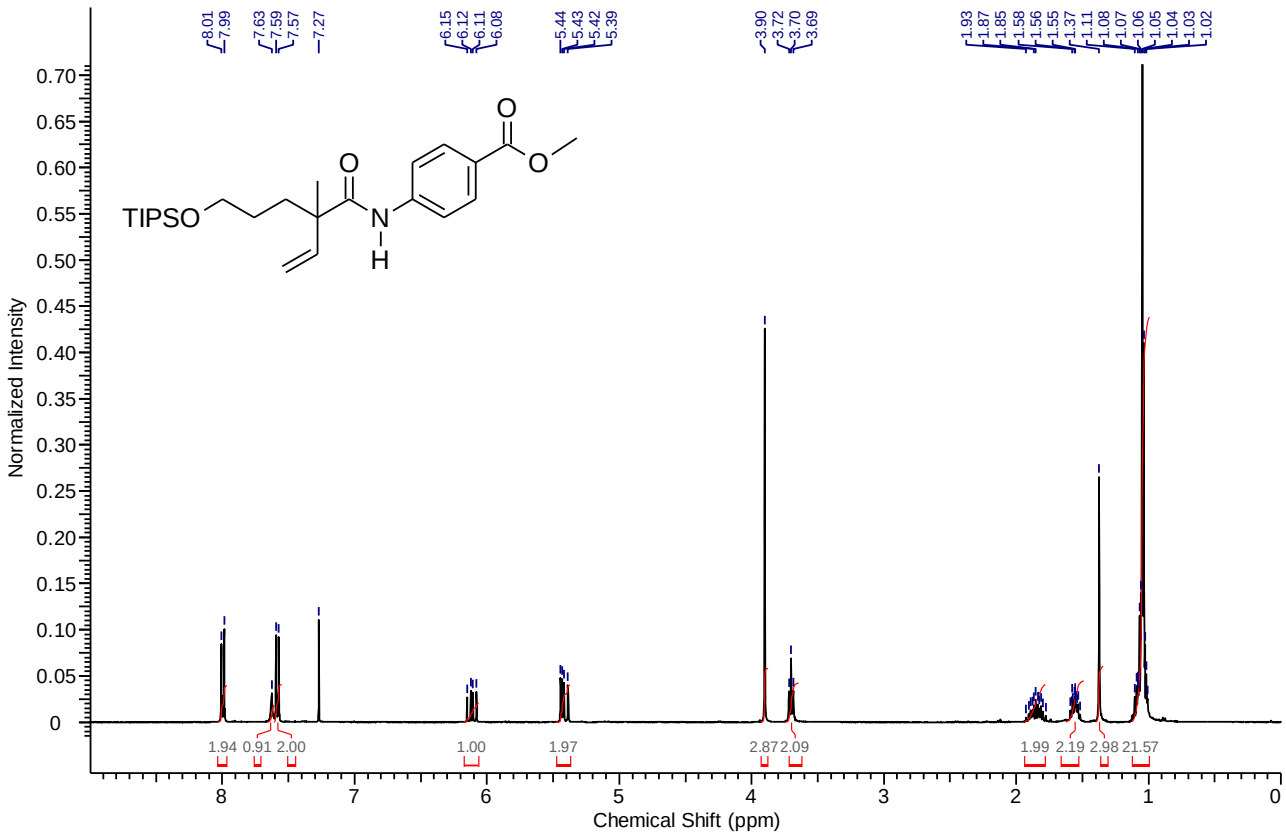


Figure S63. ^{1}H NMR spectrum of the compound **4aq** in $CDCl_3$, 400 MHz

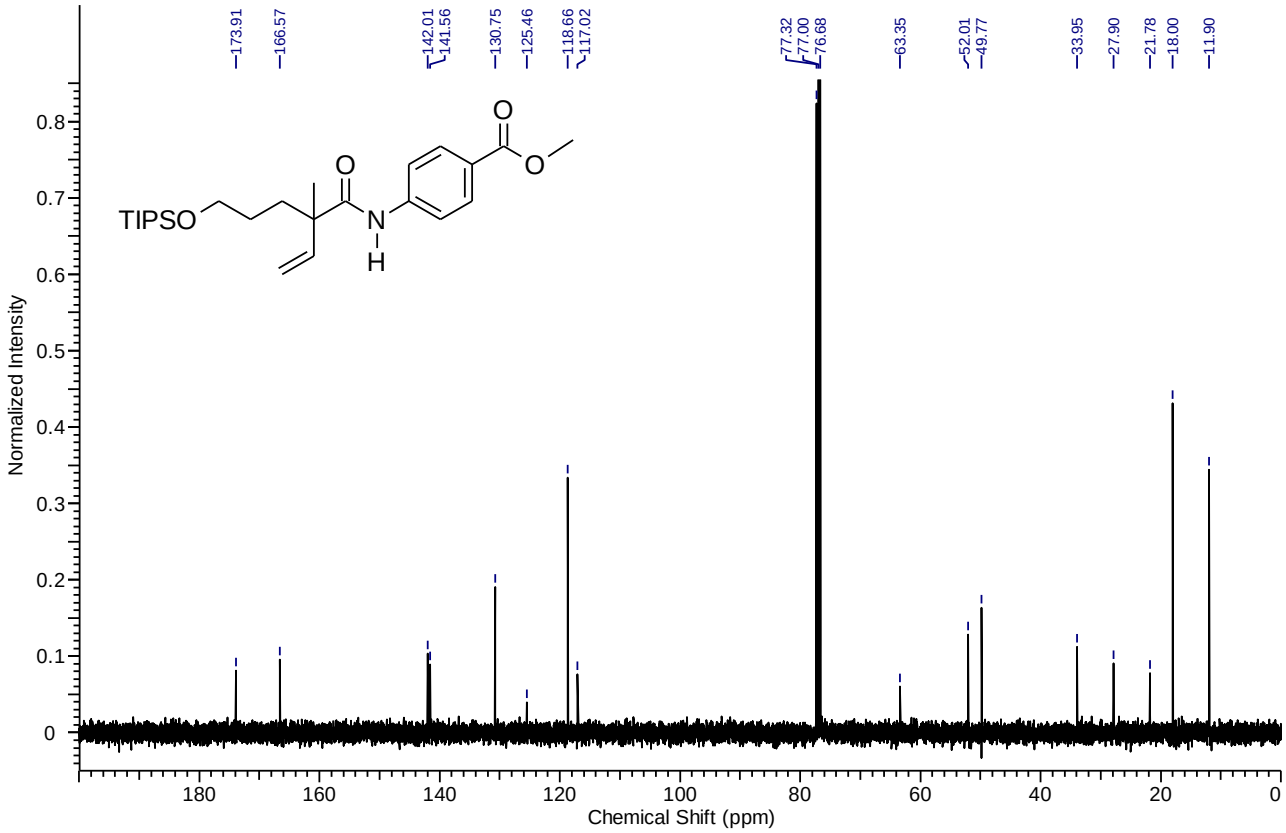


Figure S64. ^{13}C NMR spectrum of the compound **4aq** in $CDCl_3$, 100 MHz

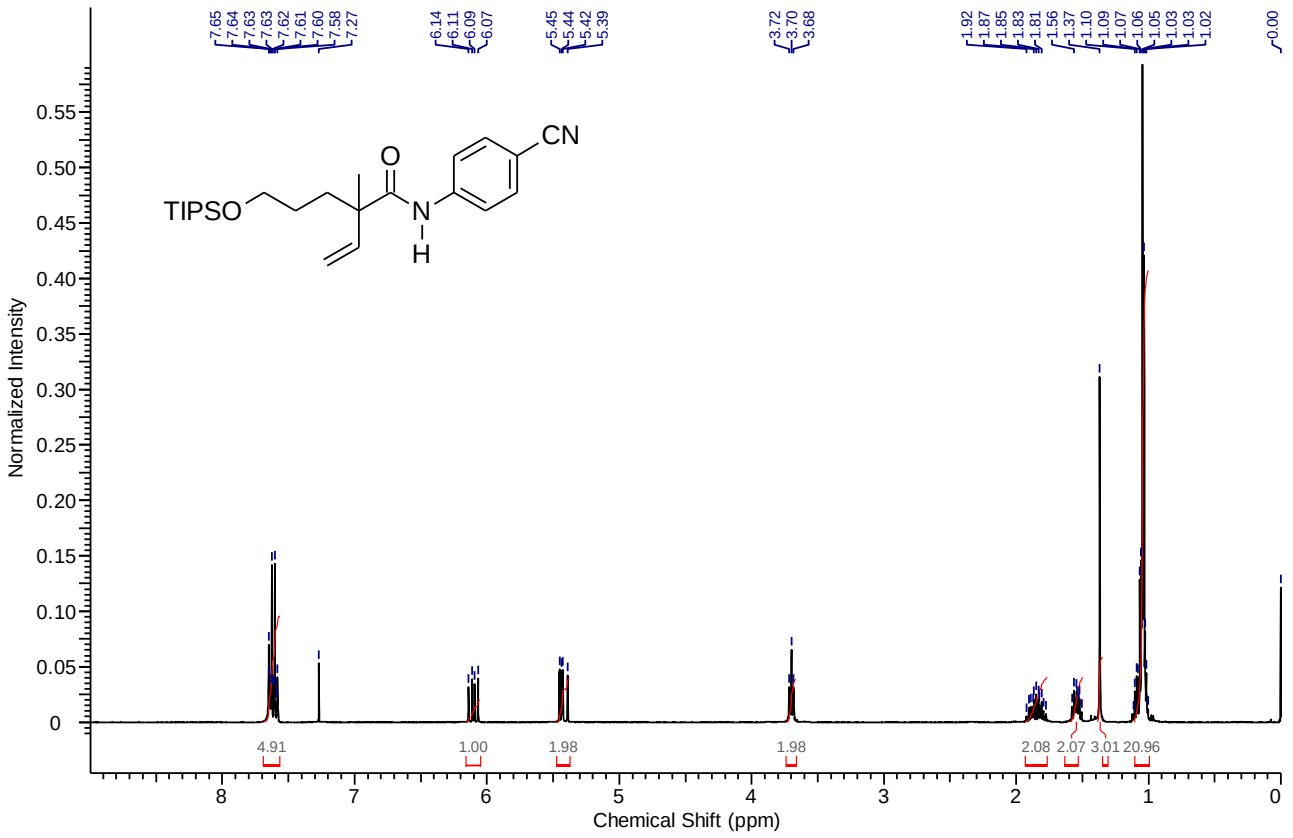


Figure S65. ^{1}H NMR spectrum of the compound **4ar** in $CDCl_3$, 400 MHz

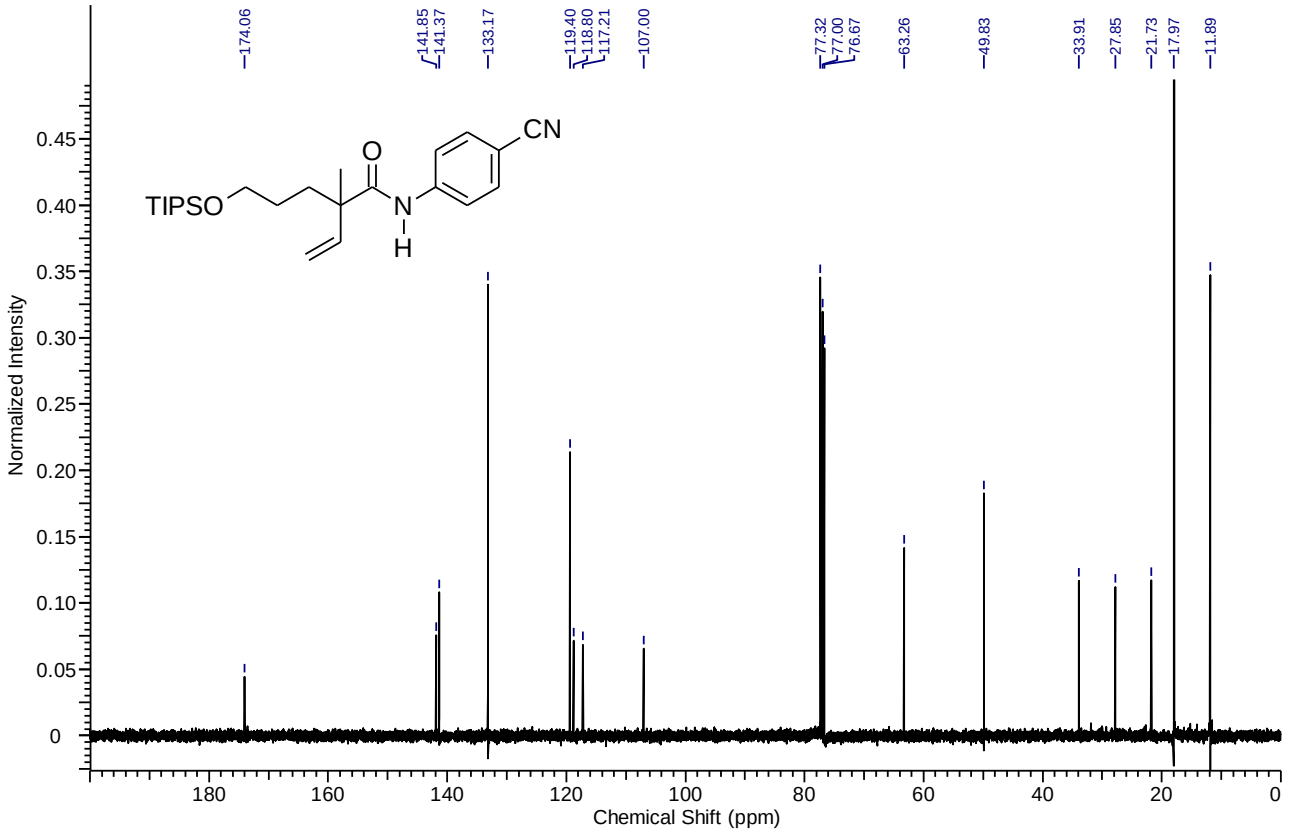


Figure S66. ^{13}C NMR spectrum of the compound **4ar** in $CDCl_3$, 100 MHz

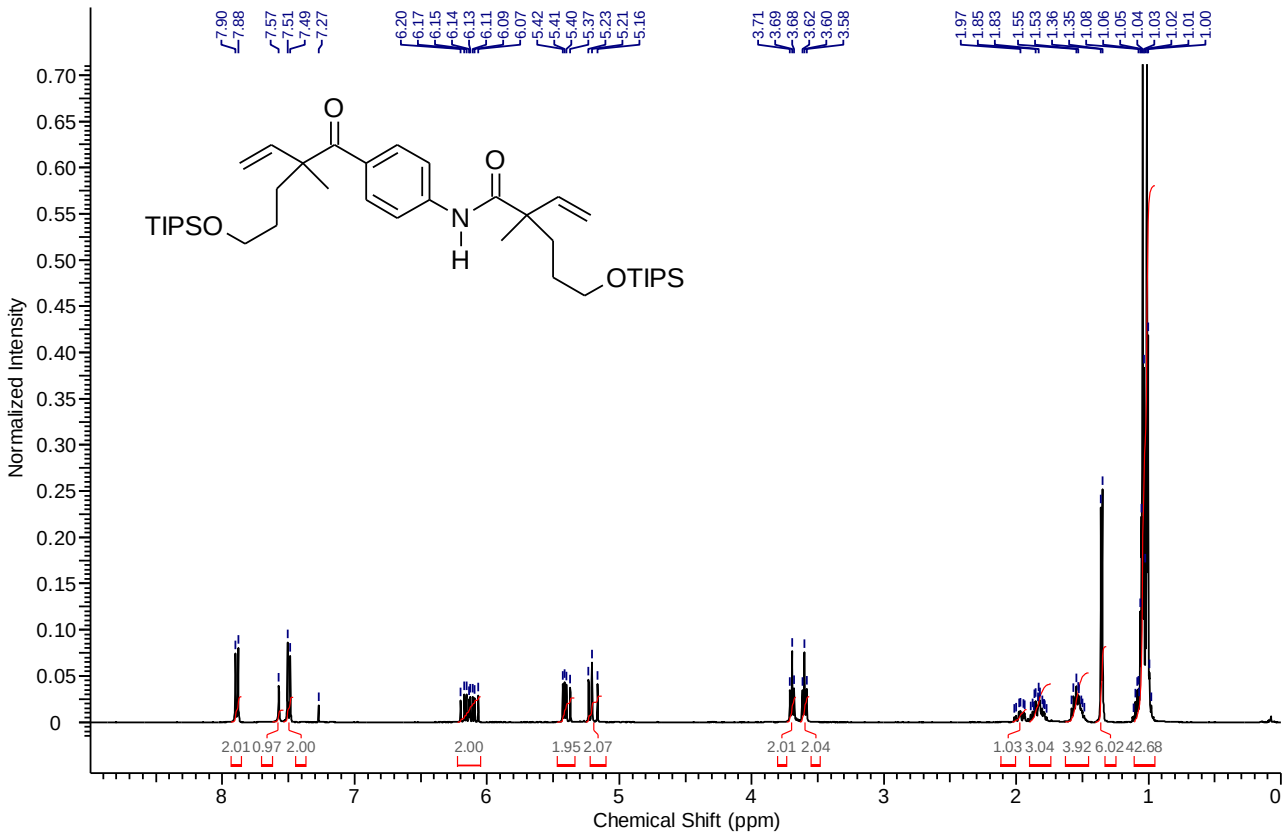


Figure S67. ^{1}H NMR spectrum of the compound **5ar** in $CDCl_3$, 400 MHz

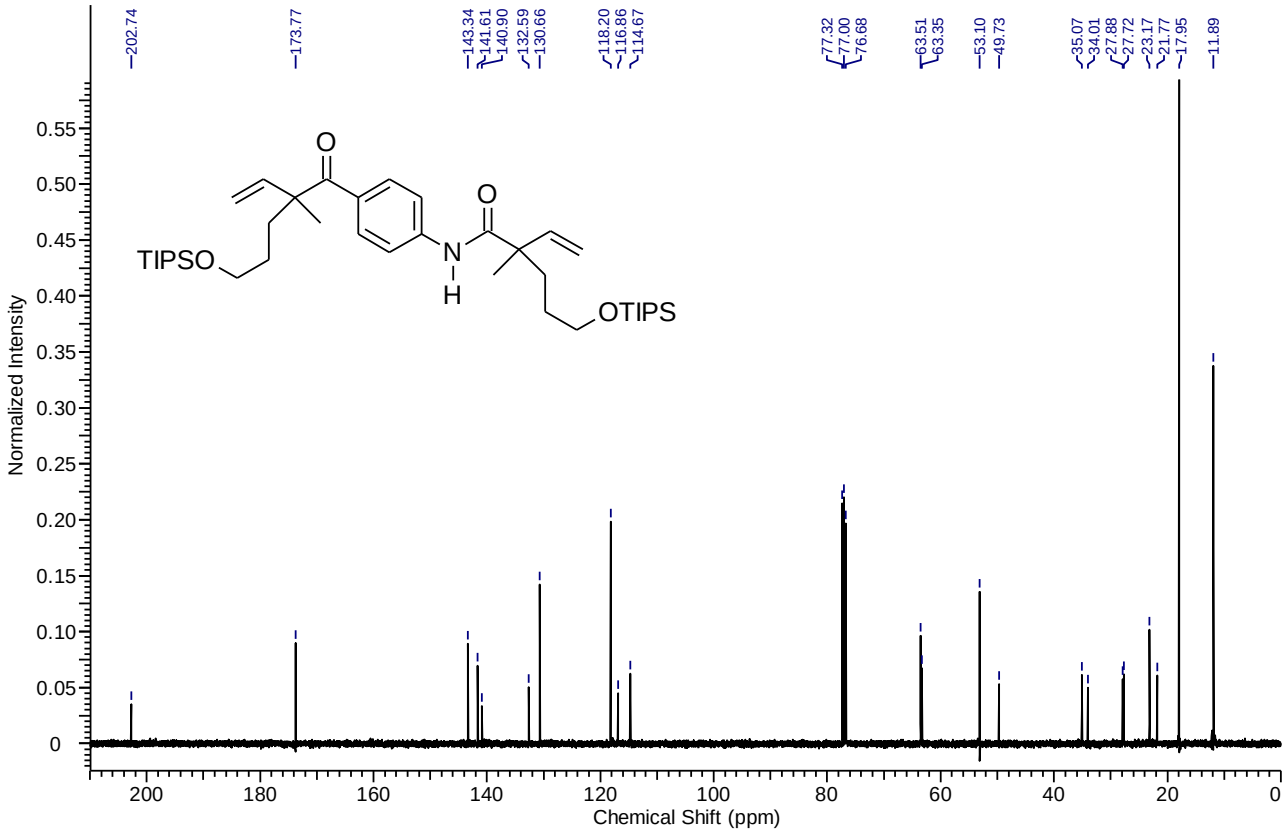


Figure S68. ^{13}C NMR spectrum of the compound **5ar** in $CDCl_3$, 100 MHz

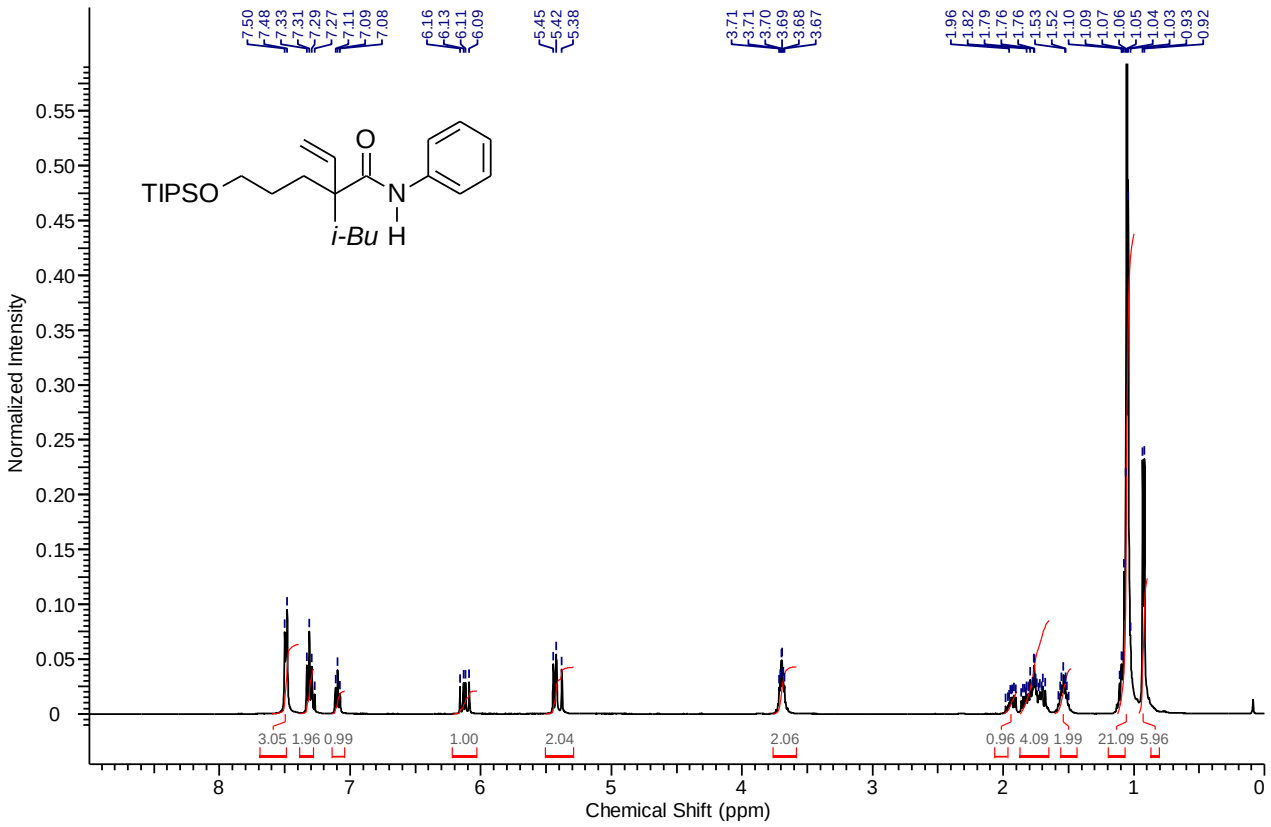


Figure S69. ^{1}H NMR spectrum of the compound **4ba** in $CDCl_3$, 400 MHz

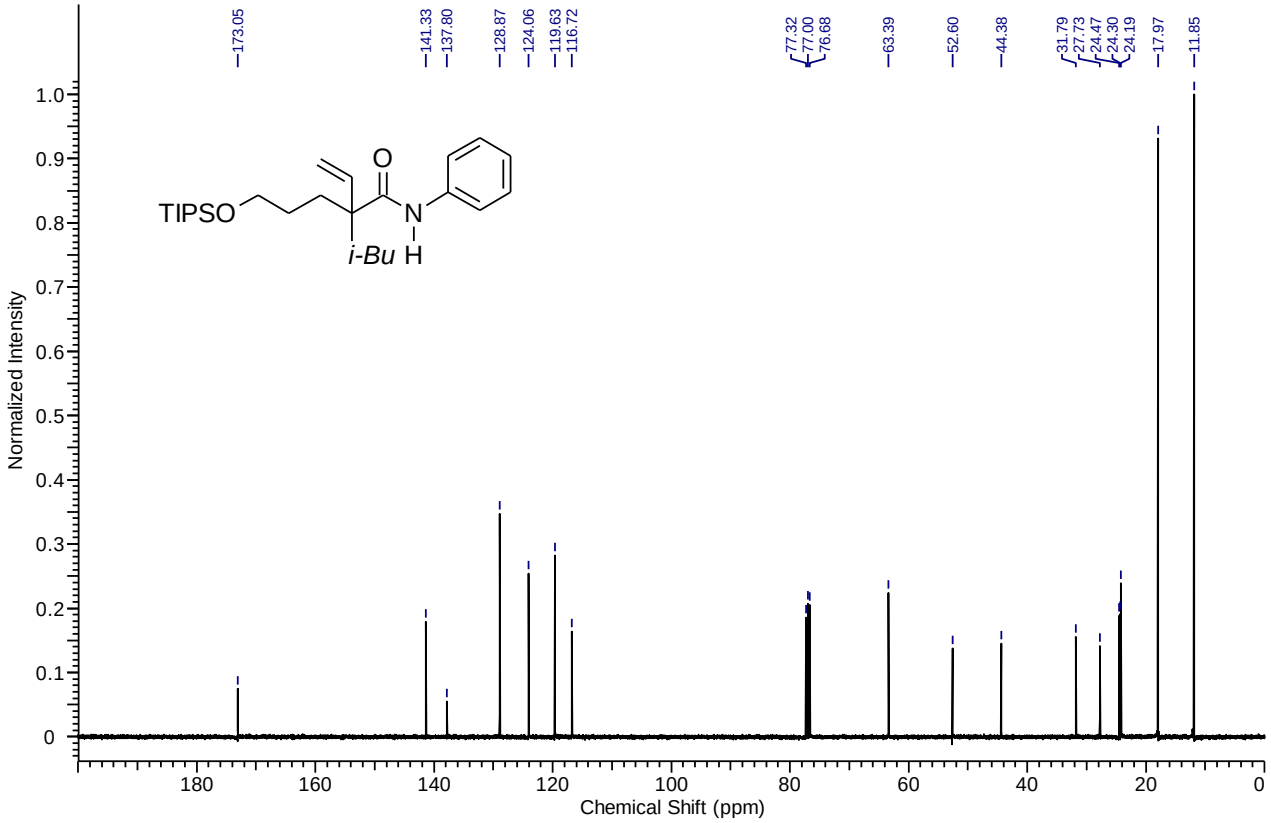


Figure S70. ^{13}C NMR spectrum of the compound **4ba** in $CDCl_3$, 100 MHz

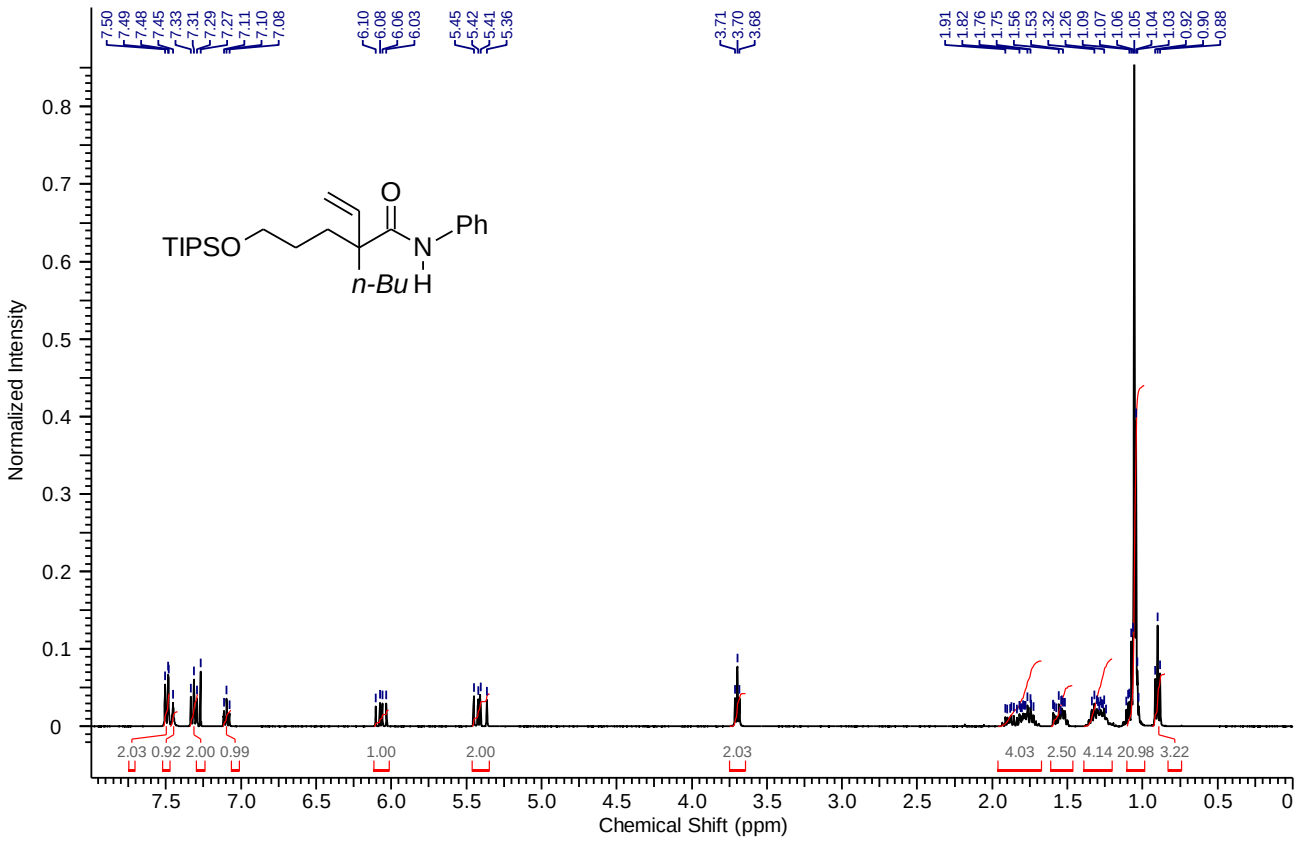


Figure S71. ^{1}H NMR spectrum of the compound **4ca** in $CDCl_3$, 400 MHz

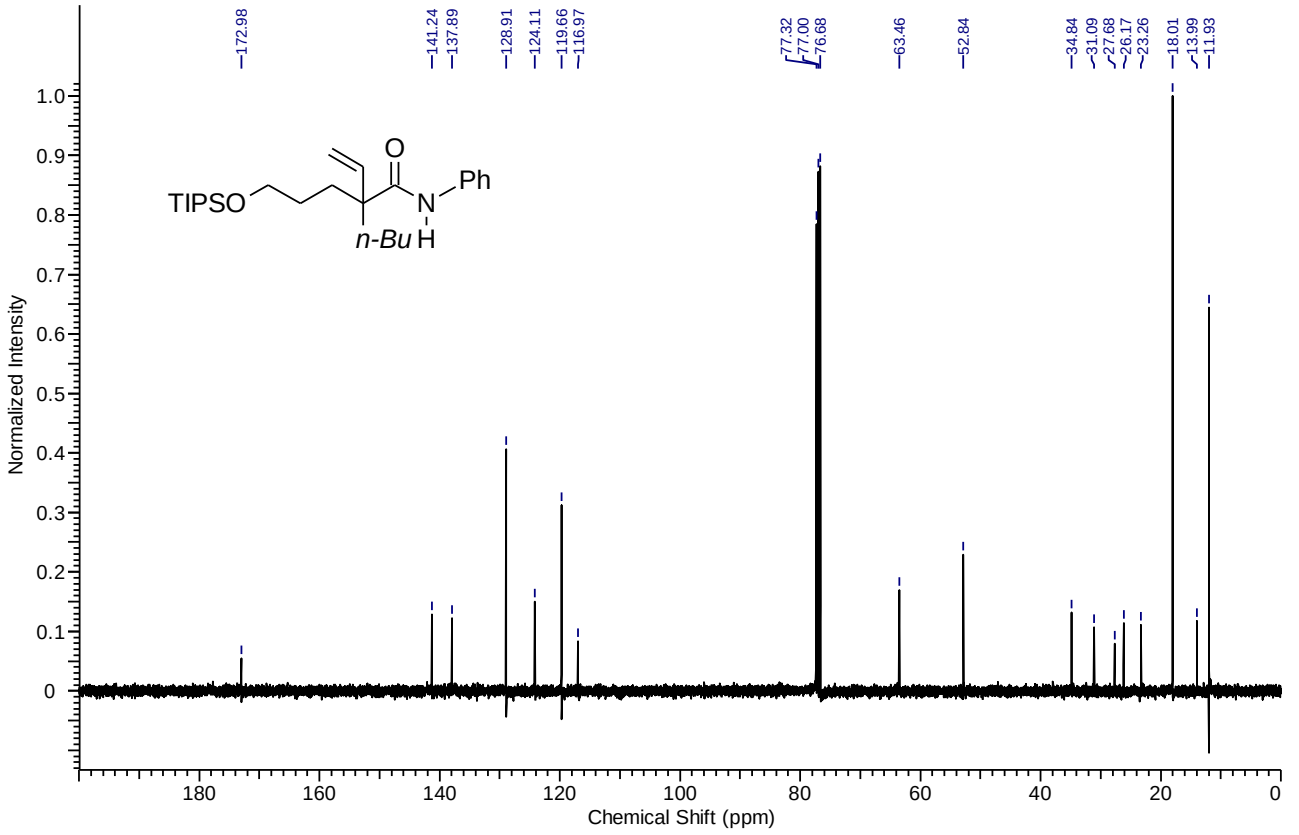


Figure S72. ^{13}C NMR spectrum of the compound **4ca** in $CDCl_3$, 100 MHz

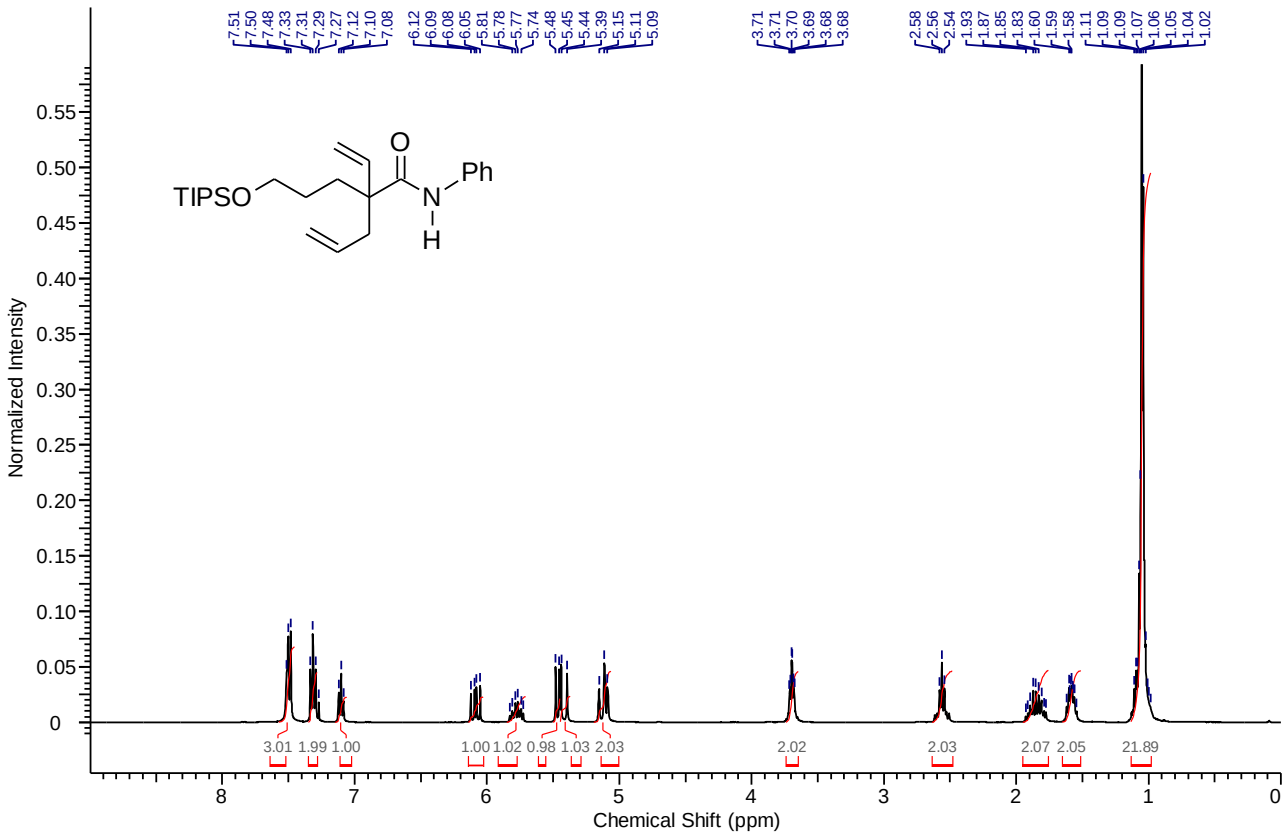


Figure S73. ^{1}H NMR spectrum of the compound **4da** in $CDCl_3$, 400 MHz

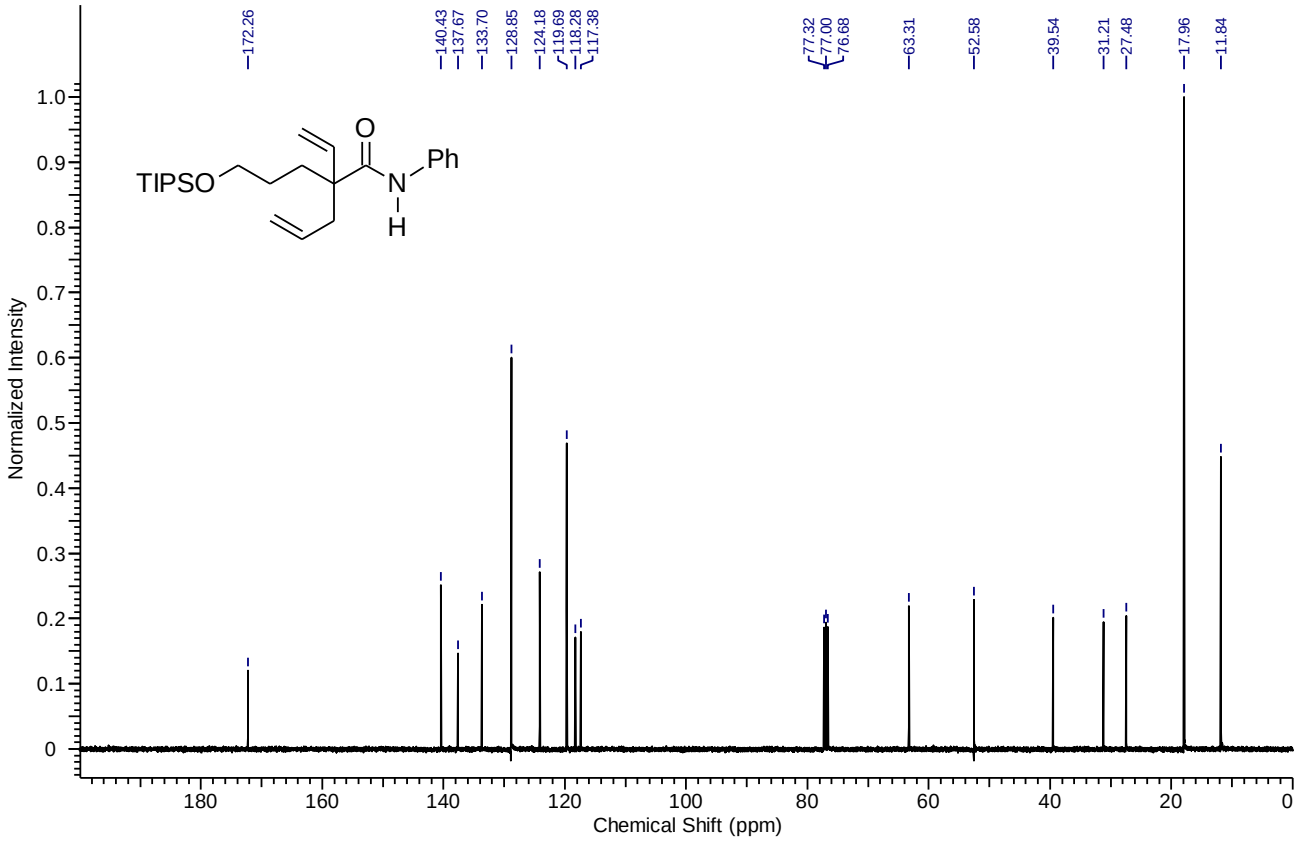


Figure S74. ^{13}C NMR spectrum of the compound **4da** in $CDCl_3$, 100 MHz

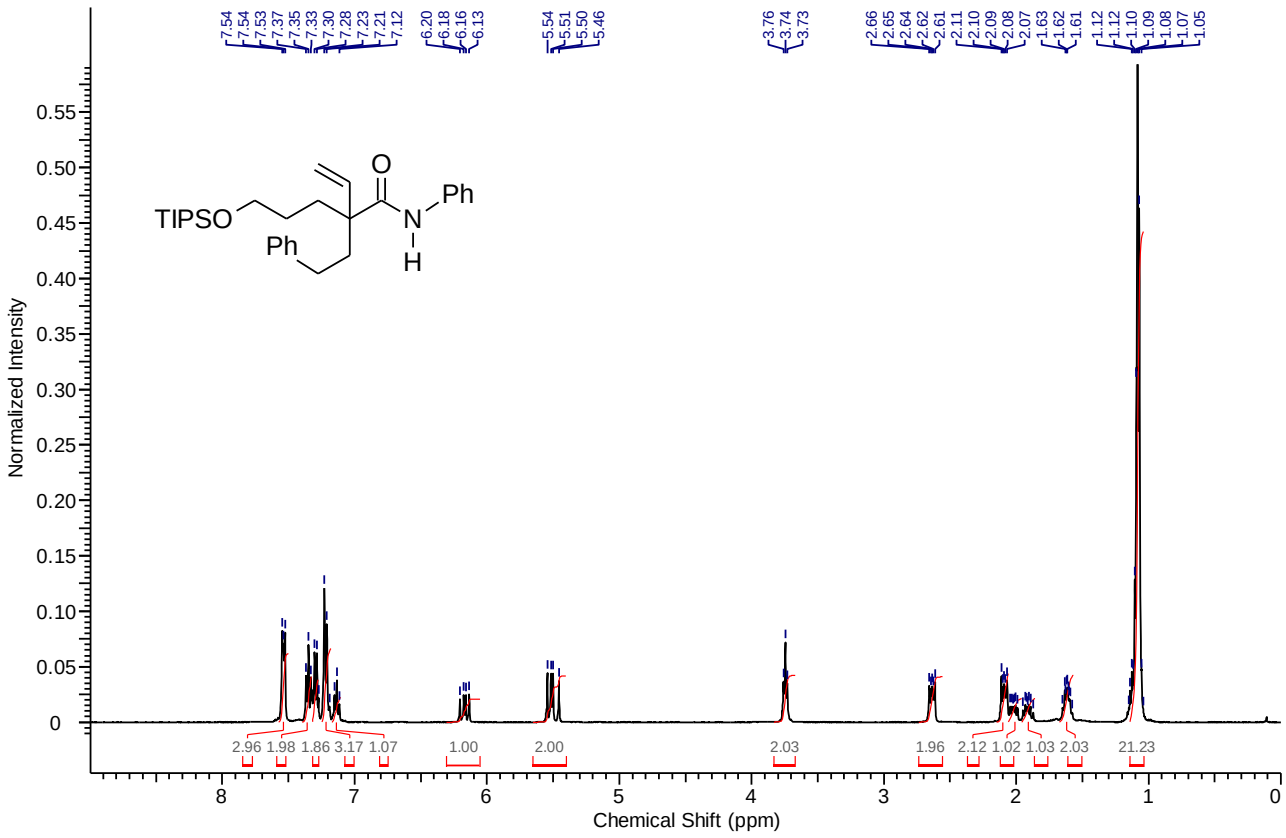


Figure S75. ^{1}H NMR spectrum of the compound **4ea** in $CDCl_3$, 400 MHz

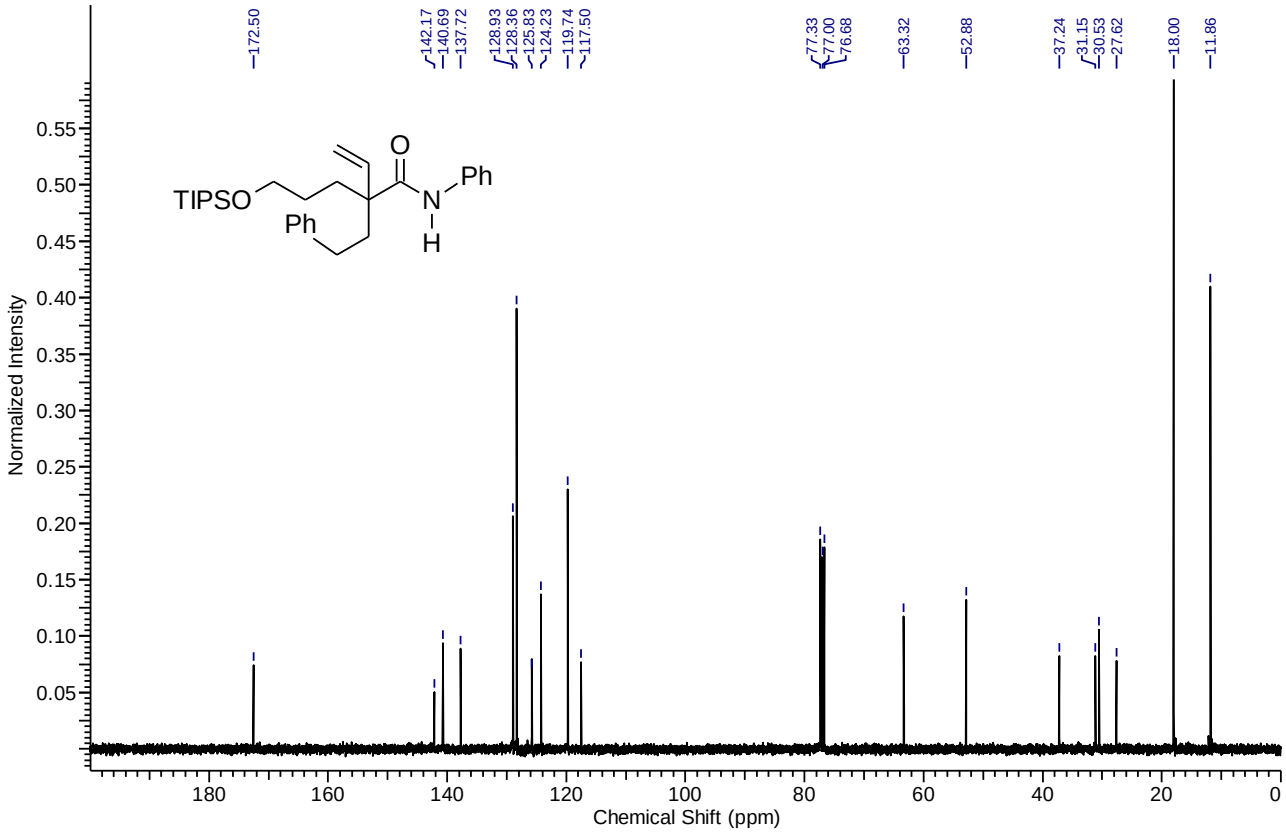


Figure S76. ^{13}C NMR spectrum of the compound **4ea** in $CDCl_3$, 100 MHz

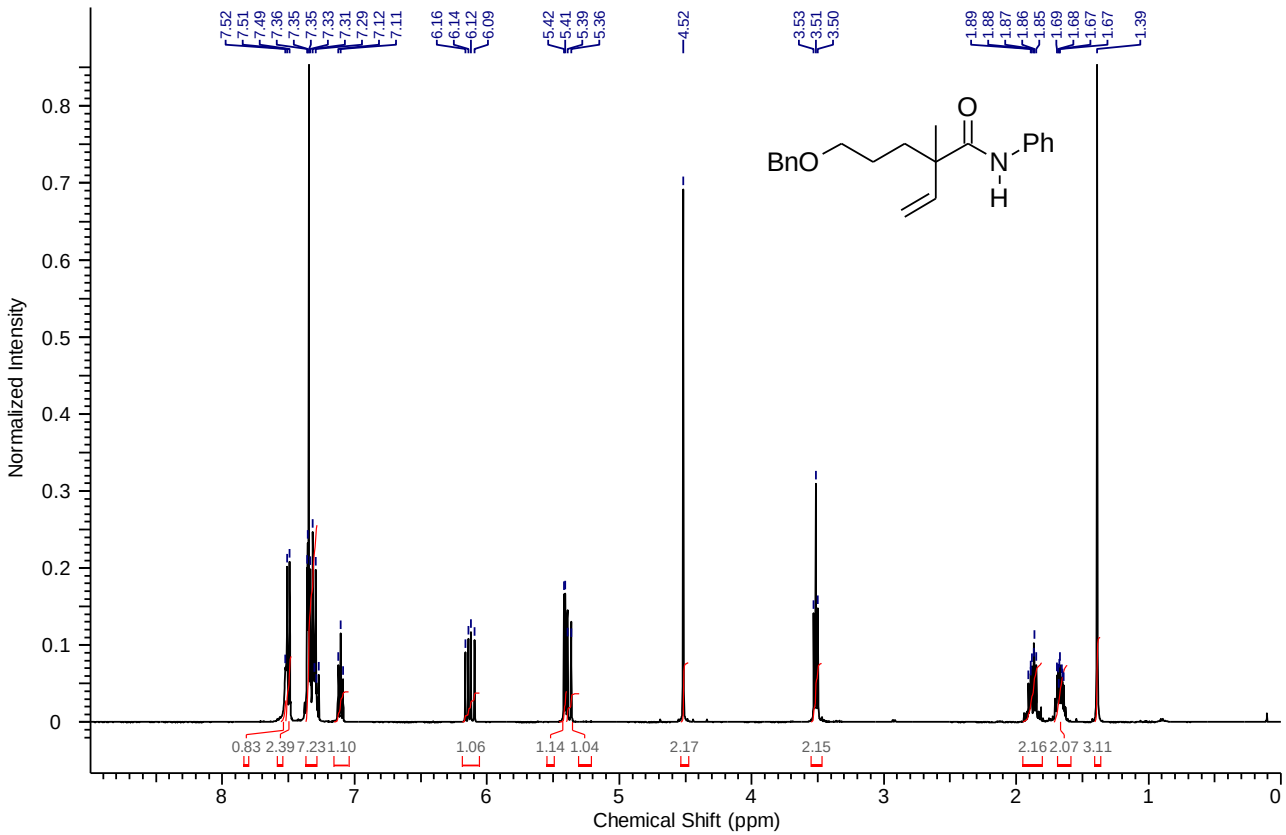


Figure S77. ^{1}H NMR spectrum of the compound **4fa** in $CDCl_3$, 400 MHz

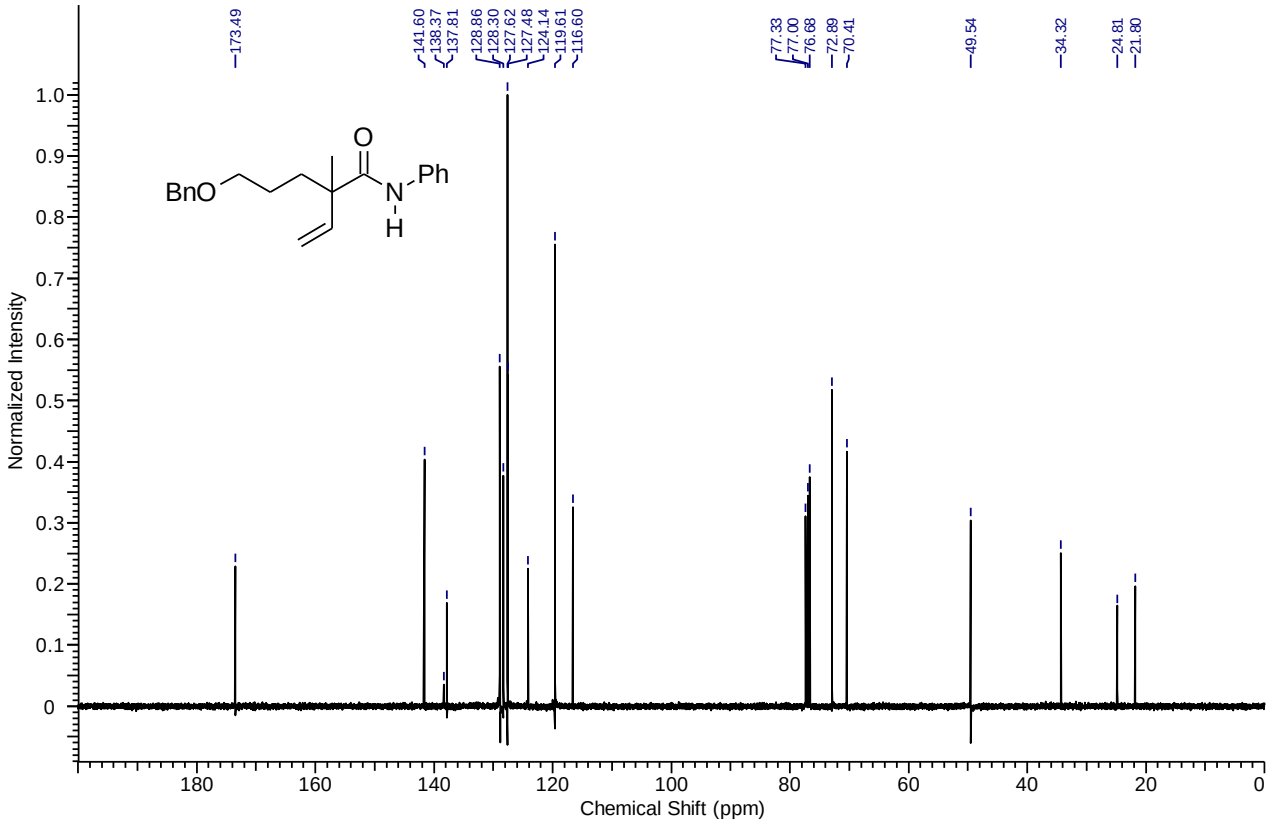


Figure S78. ^{13}C NMR spectrum of the compound **4fa** in $CDCl_3$, 100 MHz

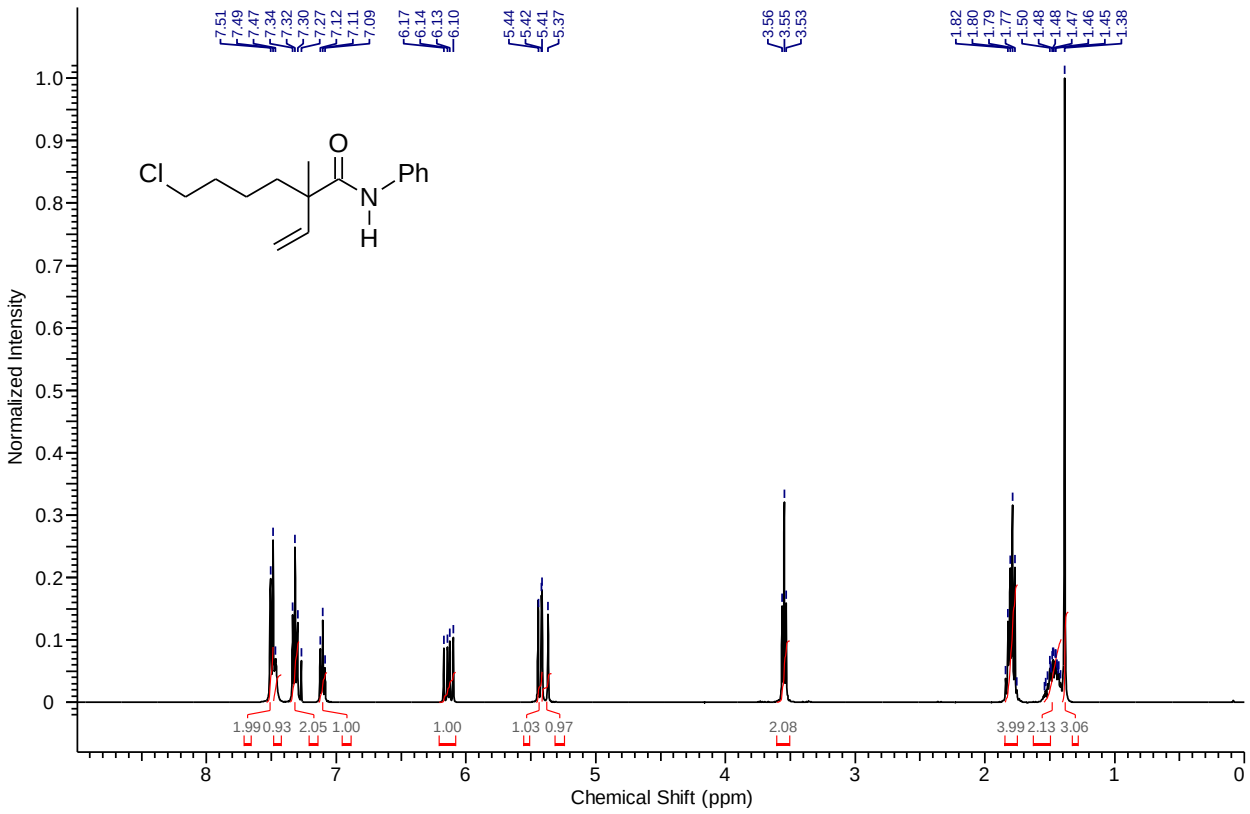


Figure S79. ^{1}H NMR spectrum of the compound **4ga** in $CDCl_3$, 400 MHz

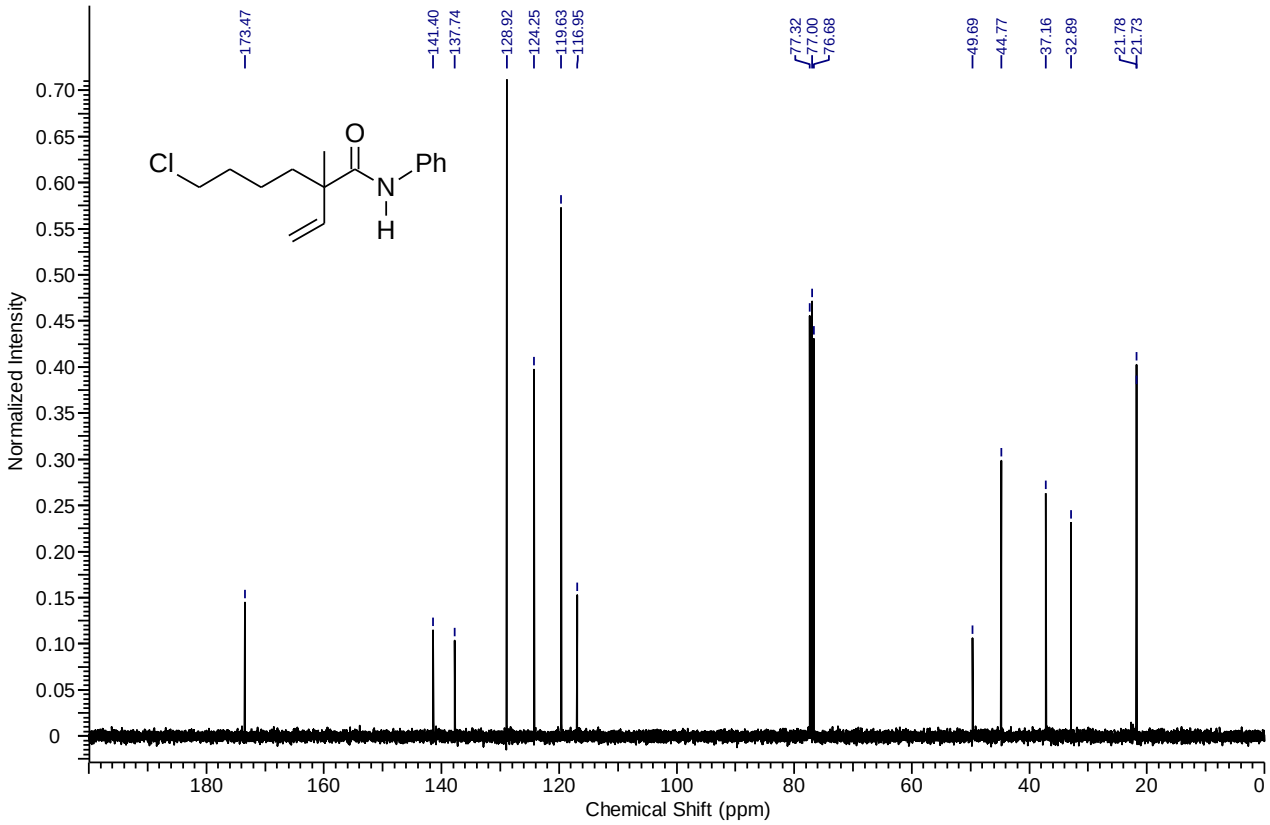


Figure S80. ^{13}C NMR spectrum of the compound **4ga** in $CDCl_3$, 100 MHz

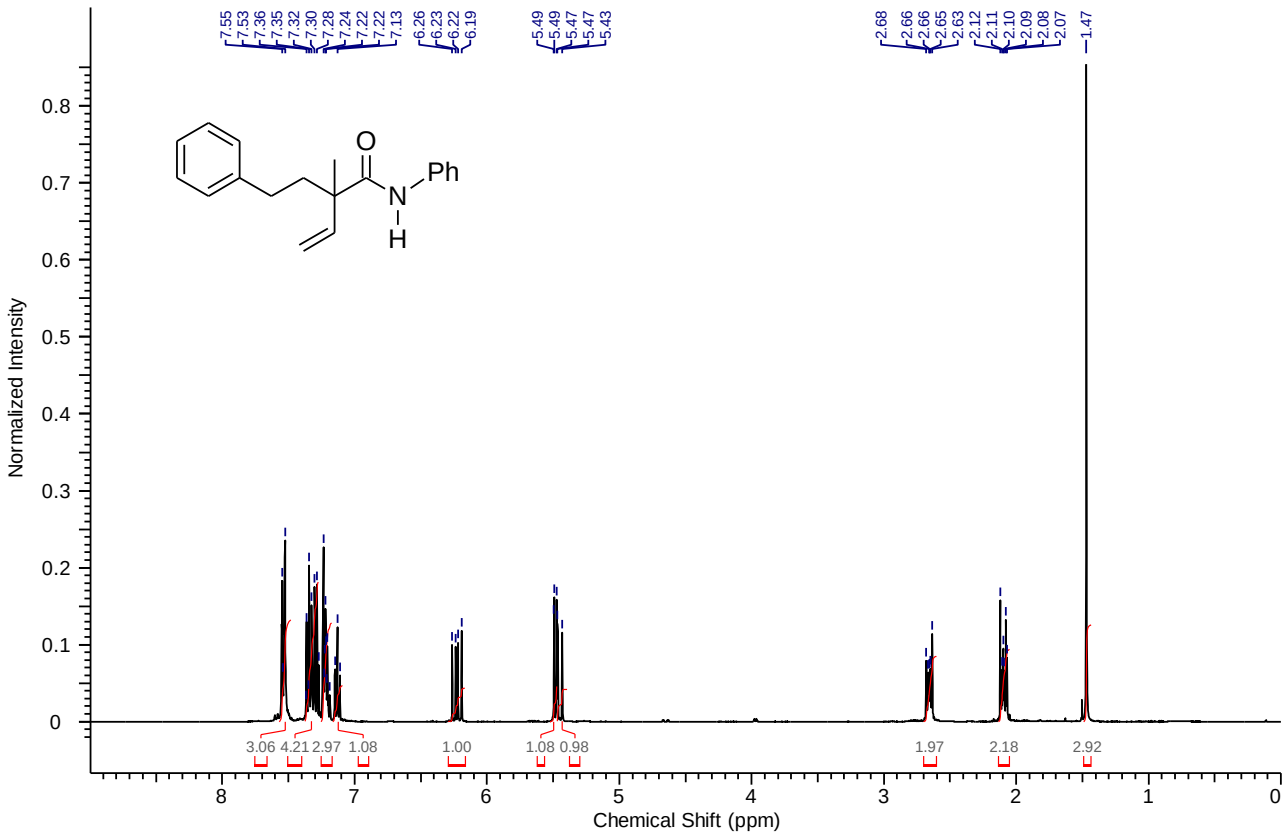


Figure S81. ^{1}H NMR spectrum of the compound **4ha** in $CDCl_3$, 400 MHz

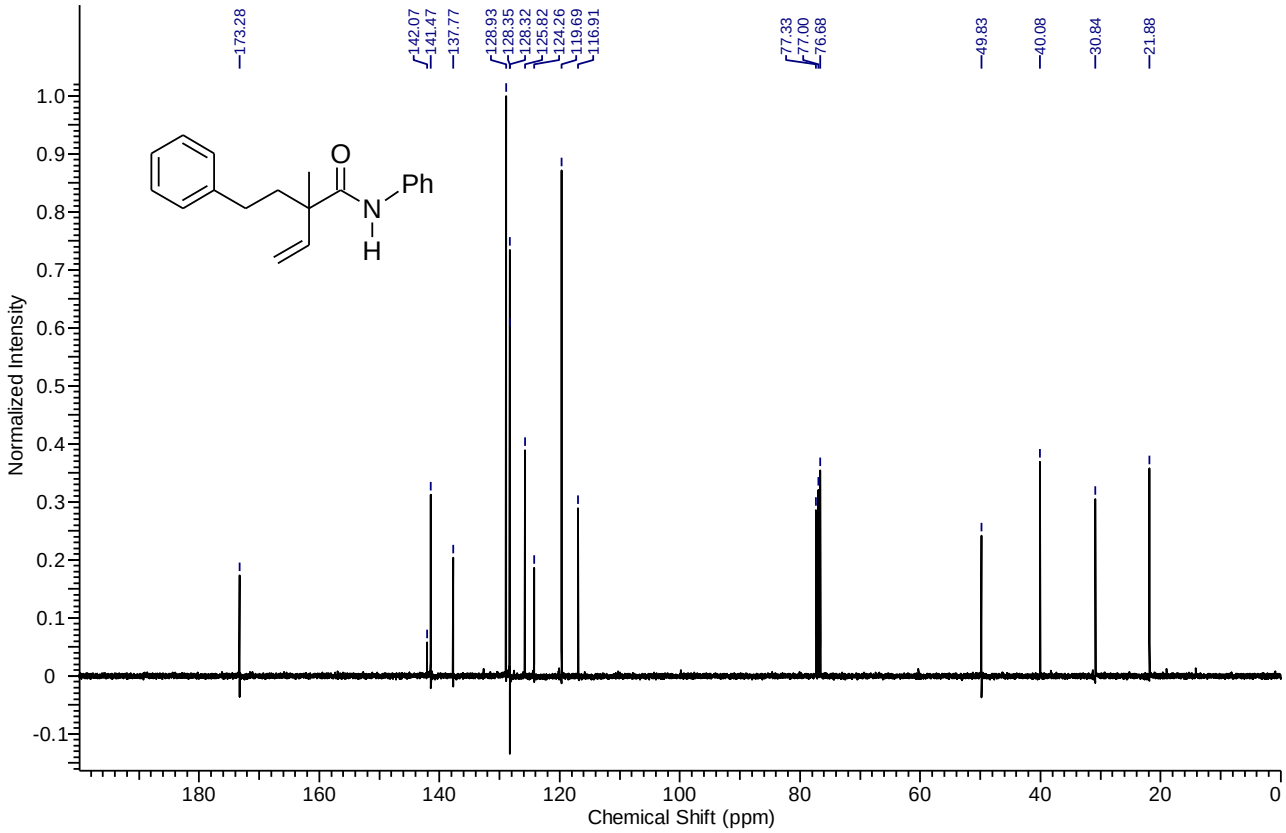


Figure S82. ^{13}C NMR spectrum of the compound **4ha** in $CDCl_3$, 100 MHz

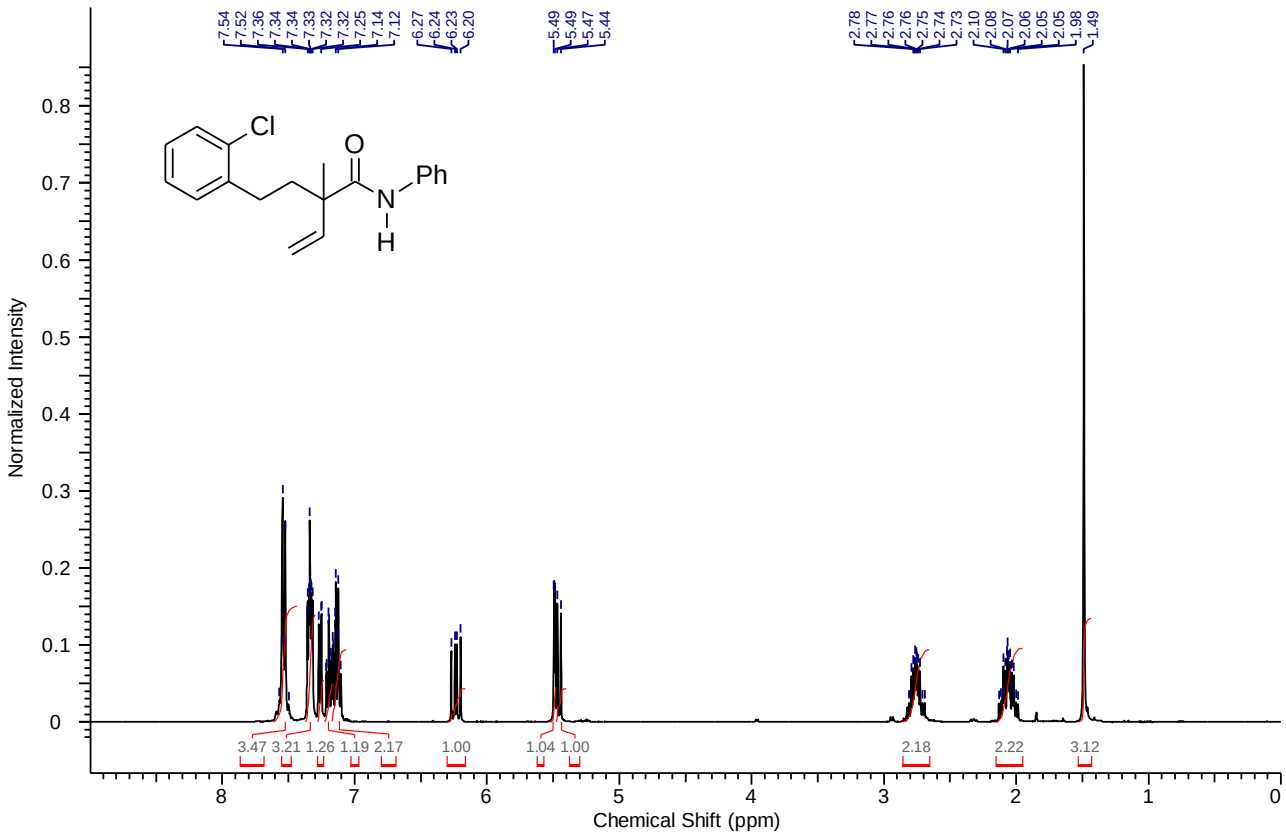


Figure S83. ^{1}H NMR spectrum of the compound **4ia** in $CDCl_3$, 400 MHz

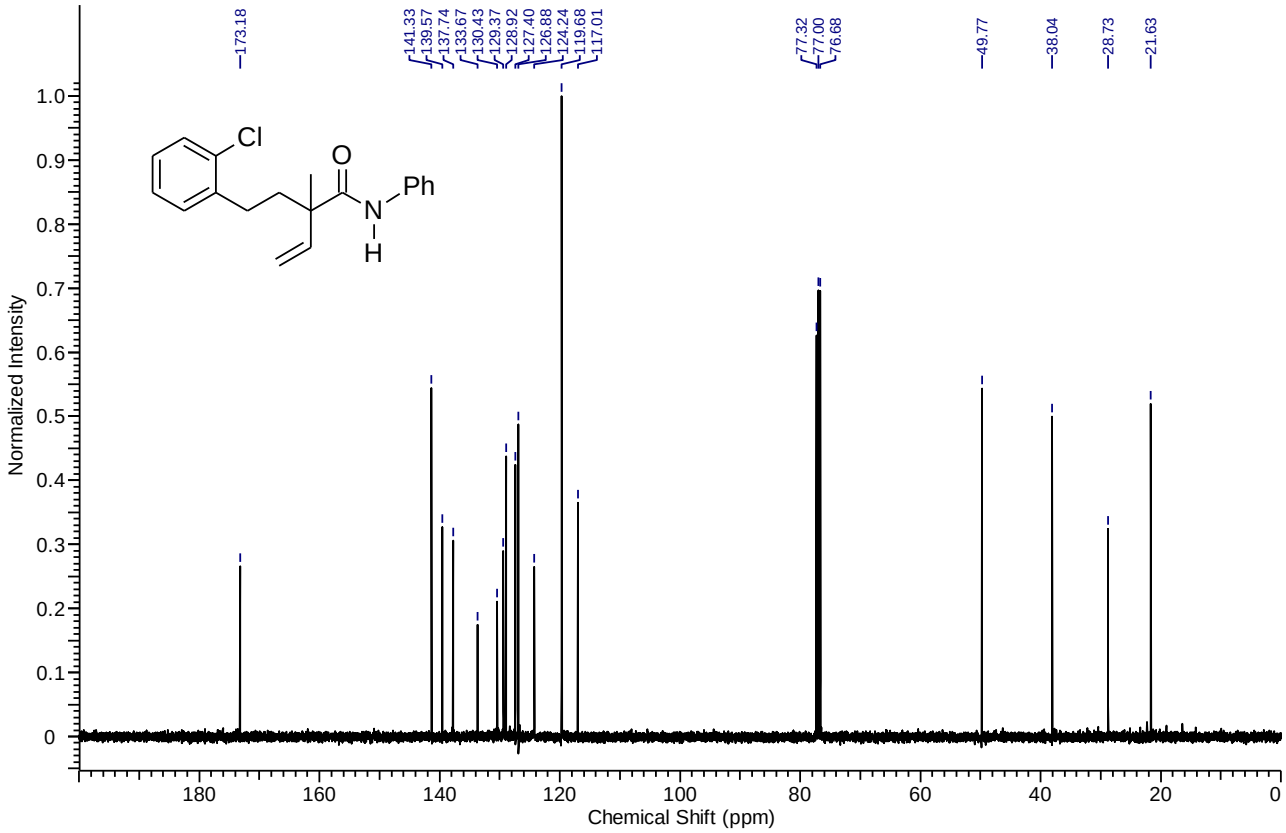


Figure S84. ^{13}C NMR spectrum of the compound **4ia** in $CDCl_3$, 100 MHz

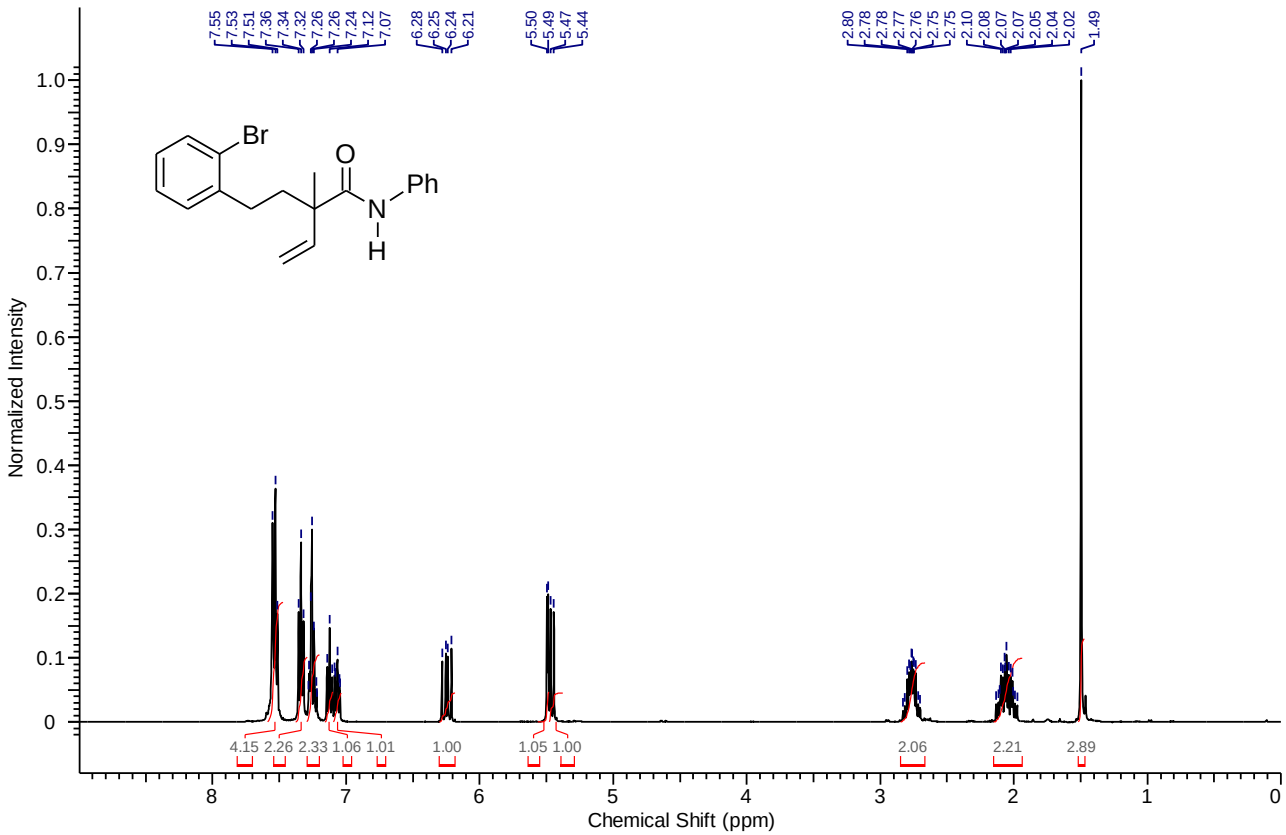


Figure S85. ^{1}H NMR spectrum of the compound **4ja** in $CDCl_3$, 400 MHz

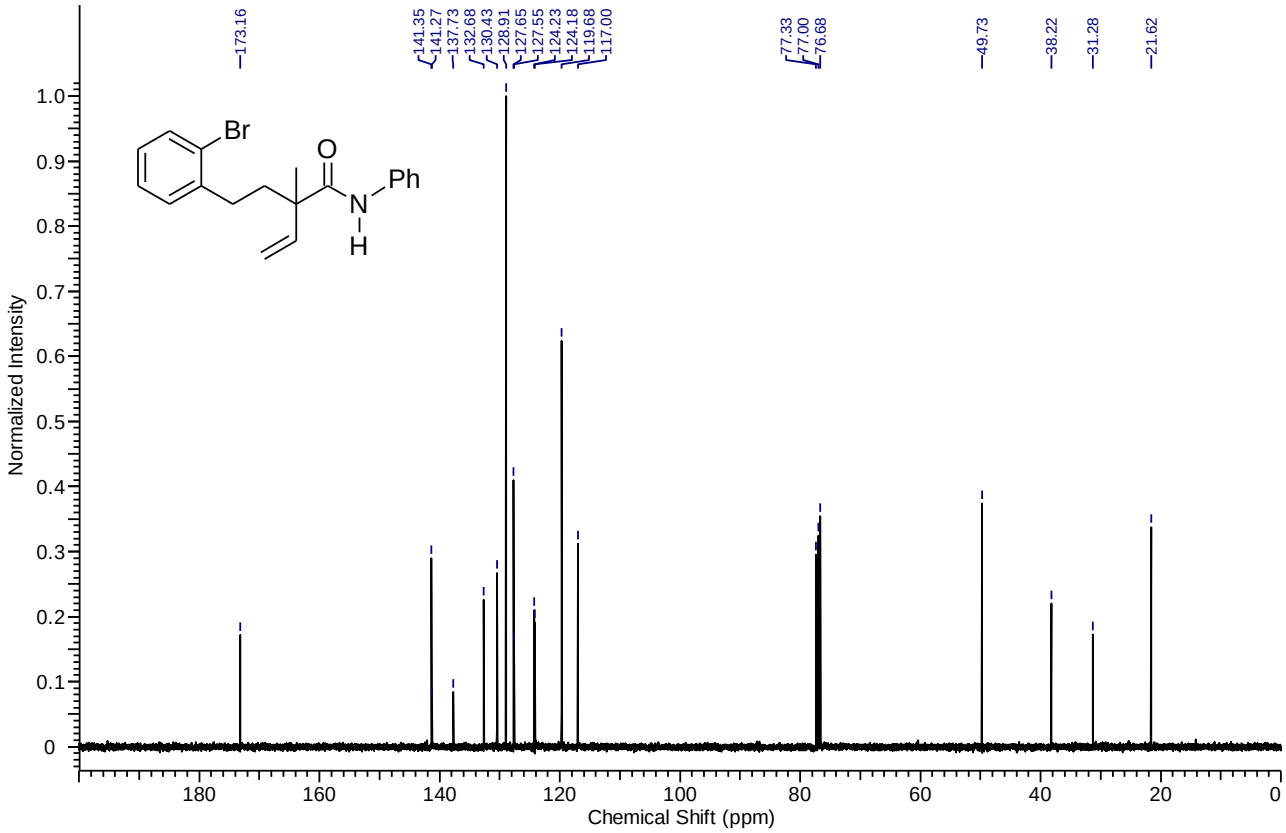


Figure S86. ^{13}C NMR spectrum of the compound **4ja** in $CDCl_3$, 100 MHz

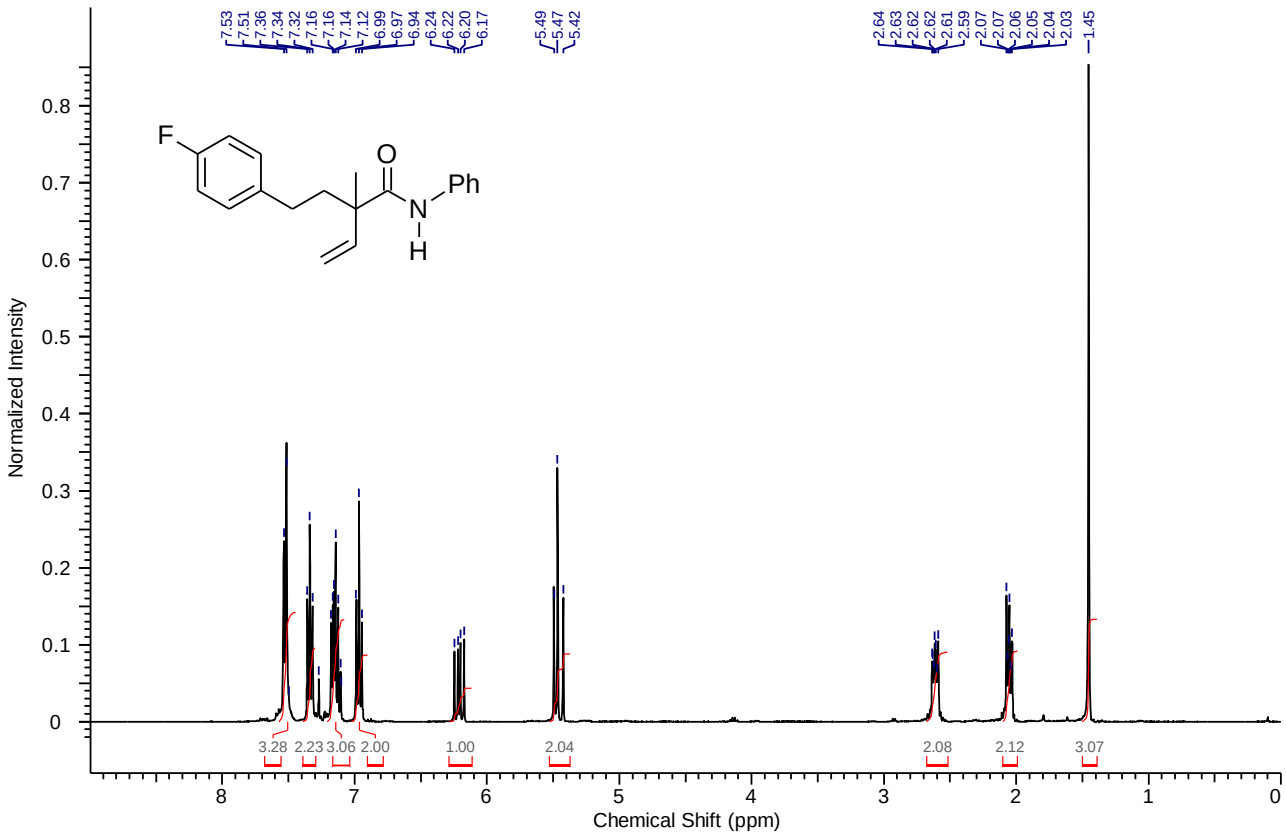


Figure S87. ^{1}H NMR spectrum of the compound **4ka** in $CDCl_3$, 400 MHz

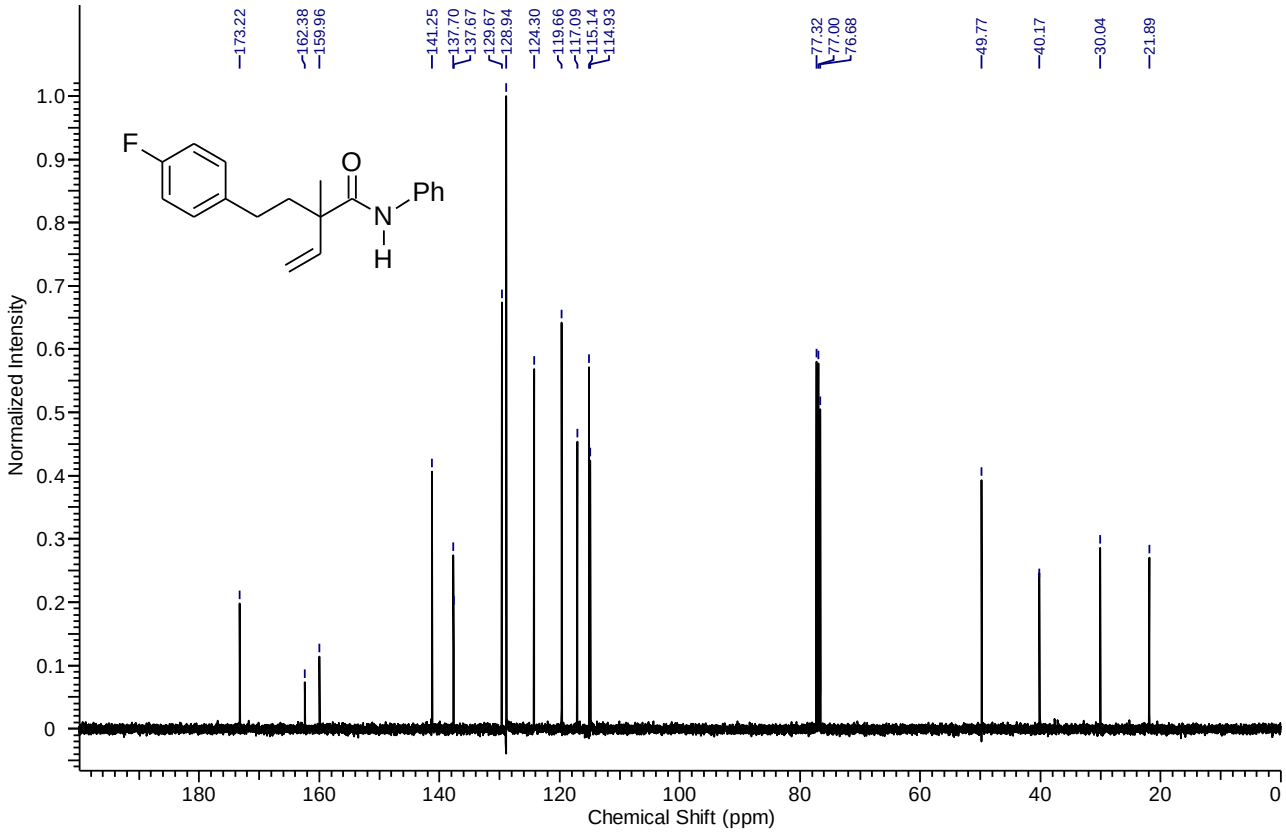


Figure S88. ^{13}C NMR spectrum of the compound **4ka** in $CDCl_3$, 100 MHz

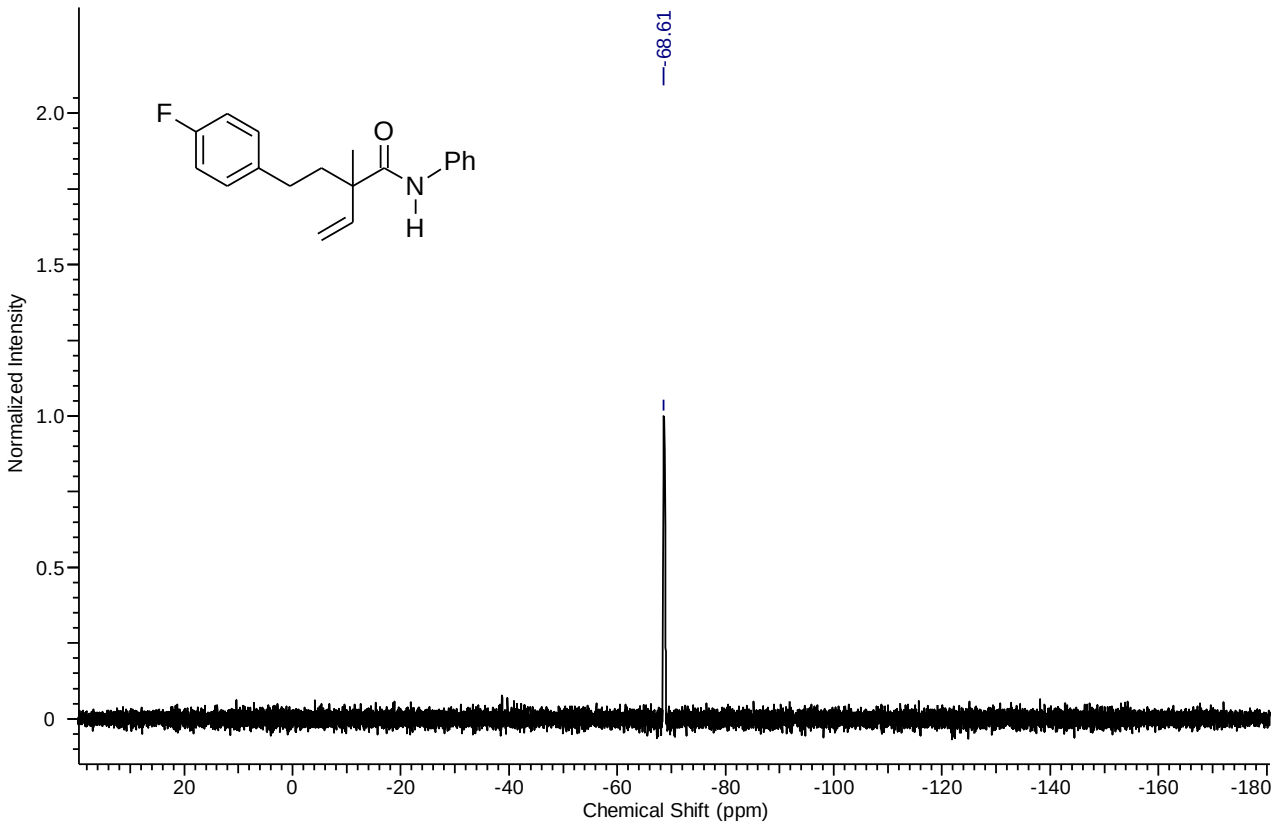


Figure S89. ^{19}F NMR spectrum of the compound **4ka** in $CDCl_3$, 75.2 MHz

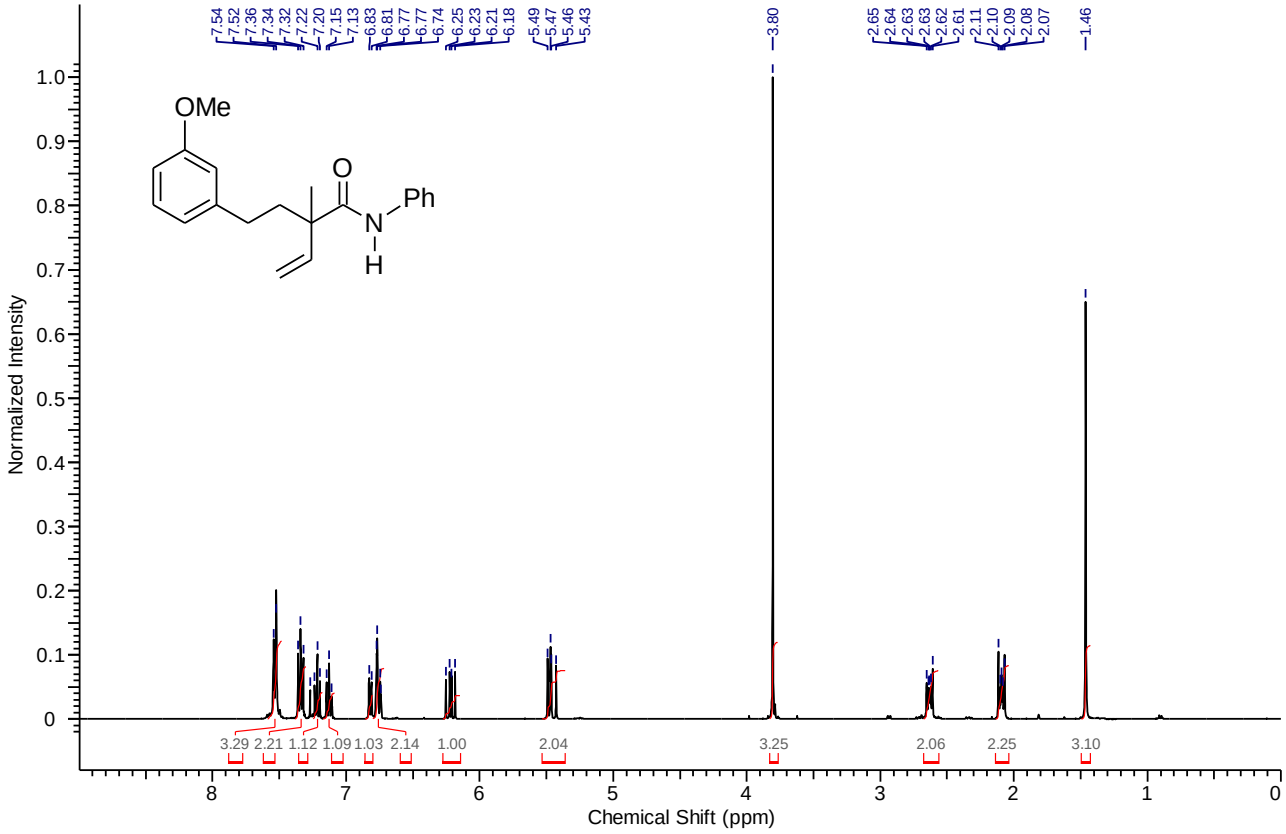


Figure S90. ^{1}H NMR spectrum of the compound **4la** in $CDCl_3$, 400 MHz

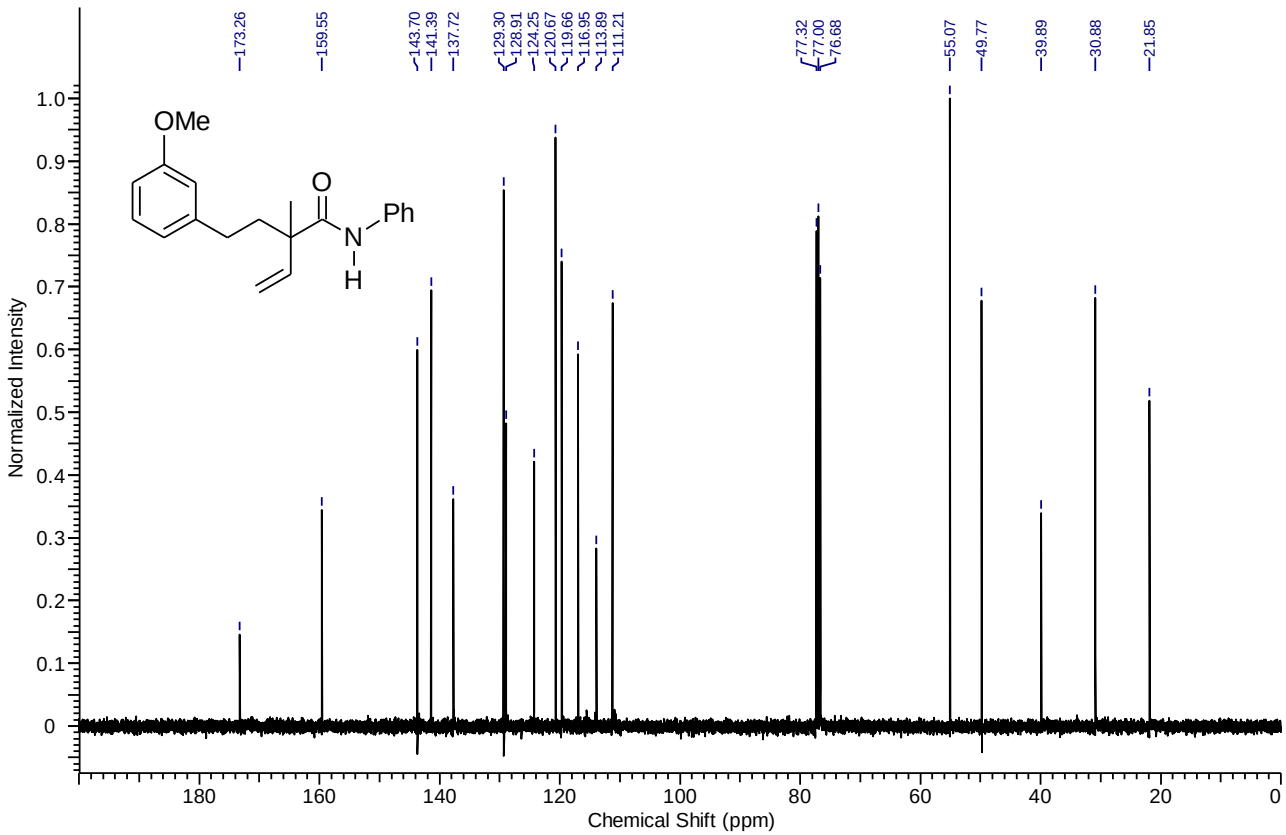


Figure S91. ^{13}C NMR spectrum of the compound **4la** in $CDCl_3$, 100 MHz

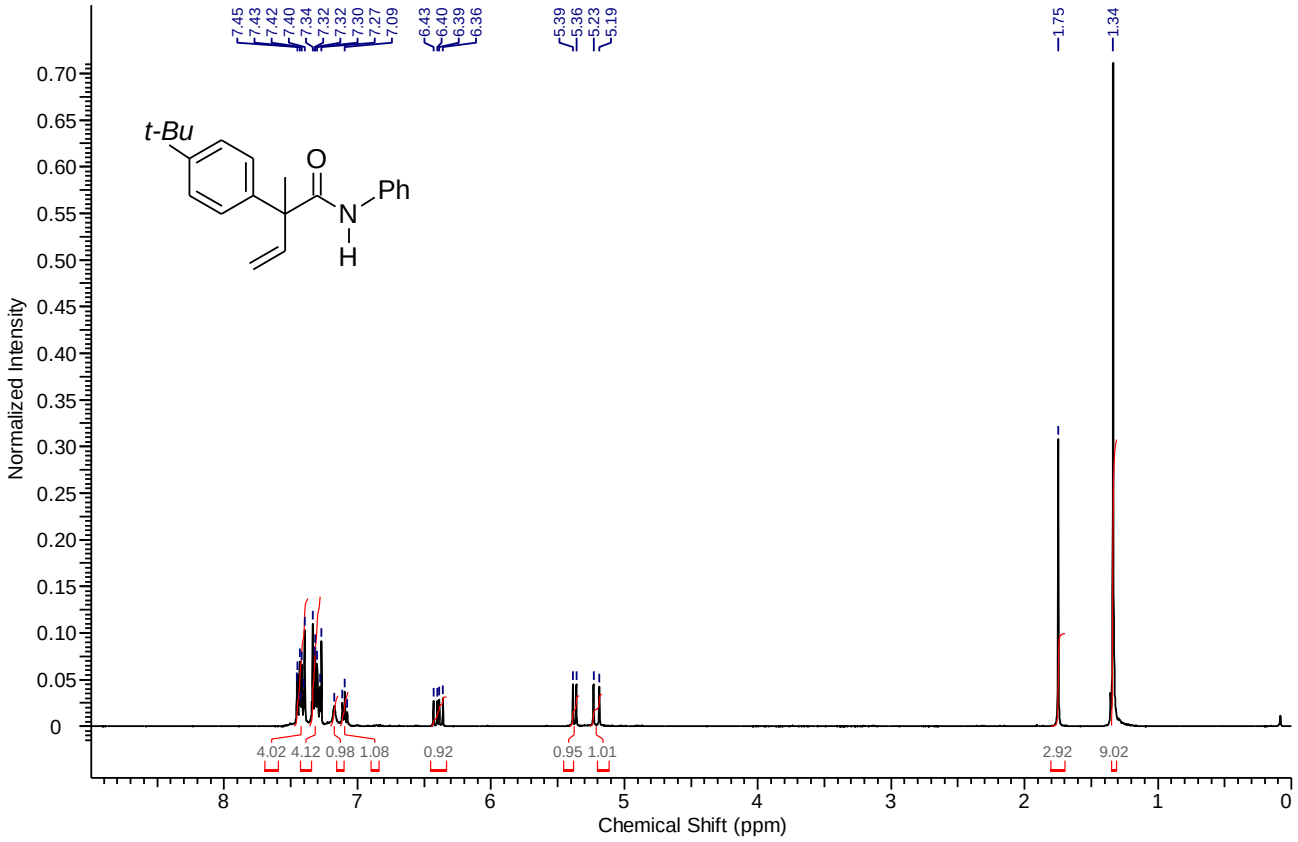


Figure S92. ^{1}H NMR spectrum of the compound **4ma** in $CDCl_3$, 400 MHz

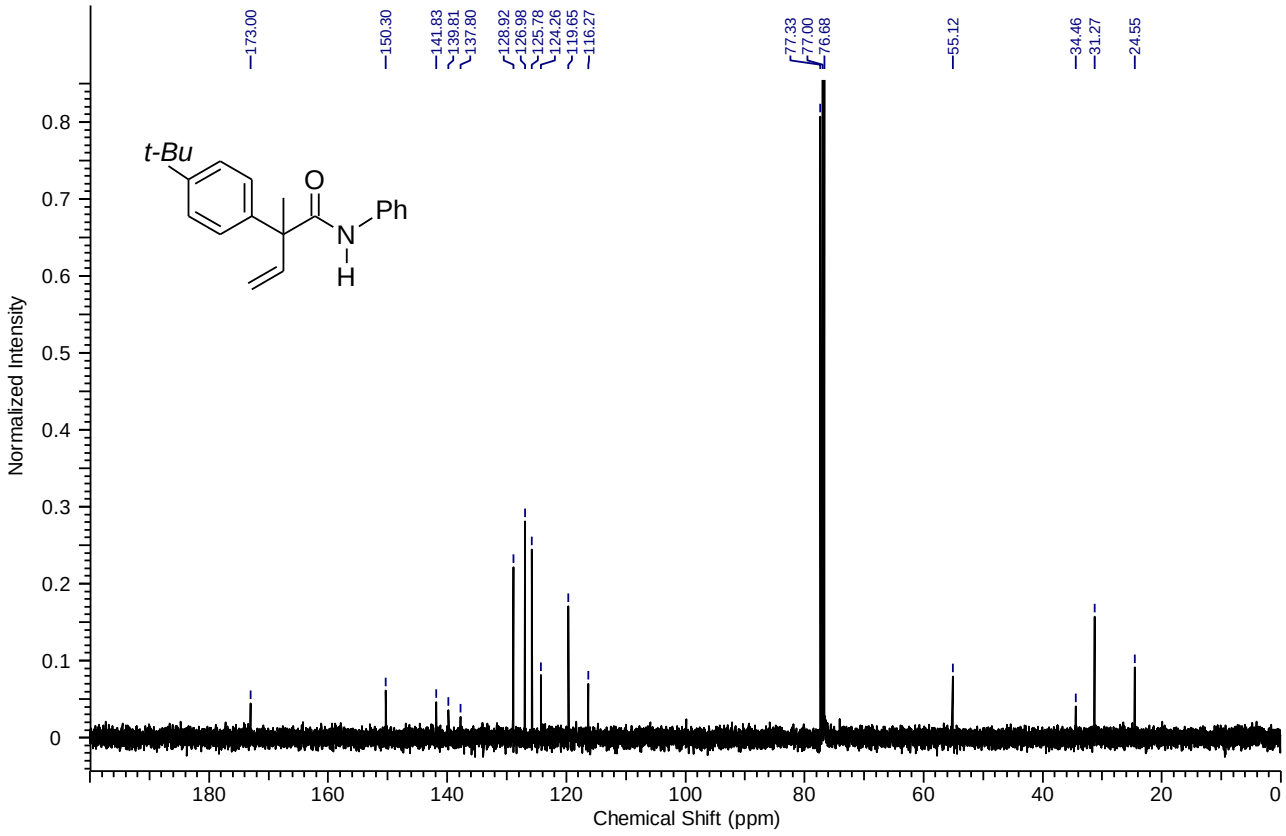


Figure S93. ^{13}C NMR spectrum of the compound **4ma** in $CDCl_3$, 100 MHz

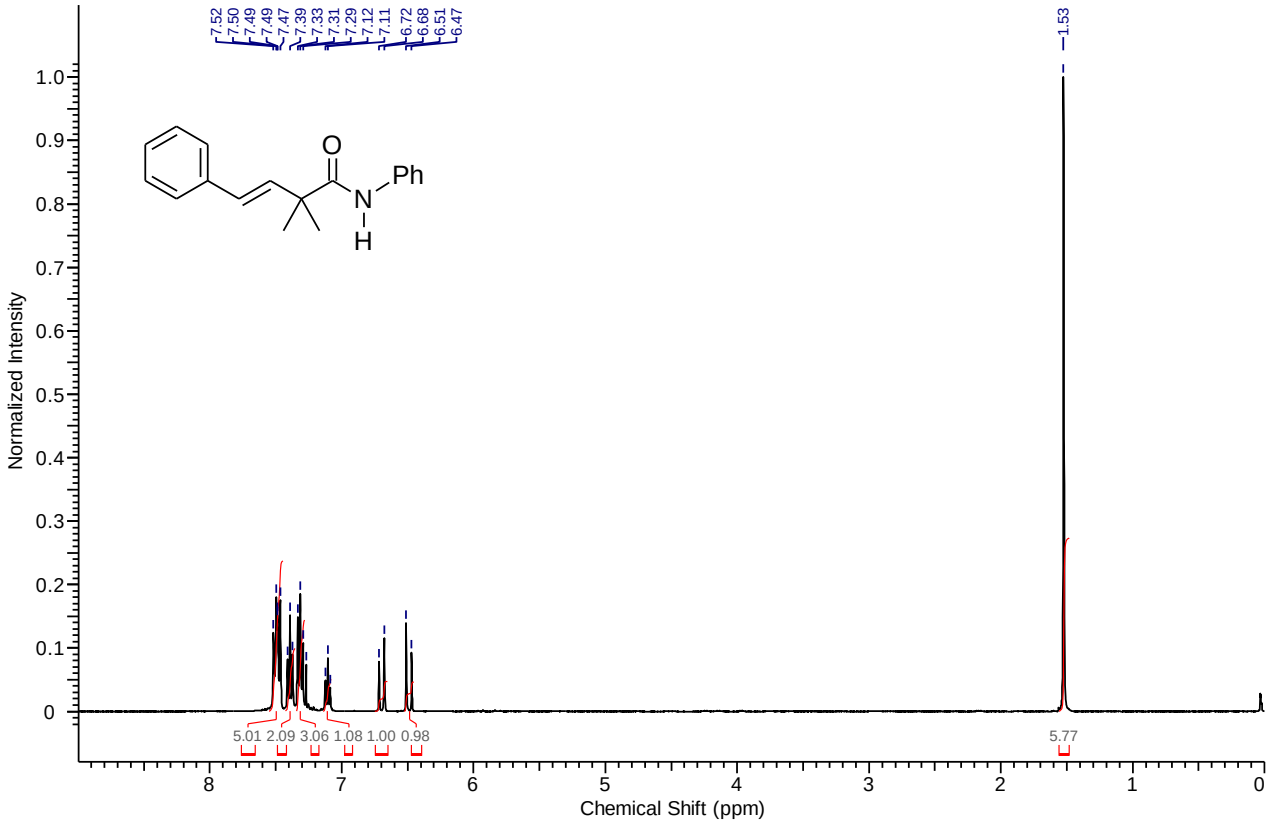


Figure S94. ^{1}H NMR spectrum of the compound **4na** in $CDCl_3$, 400 MHz

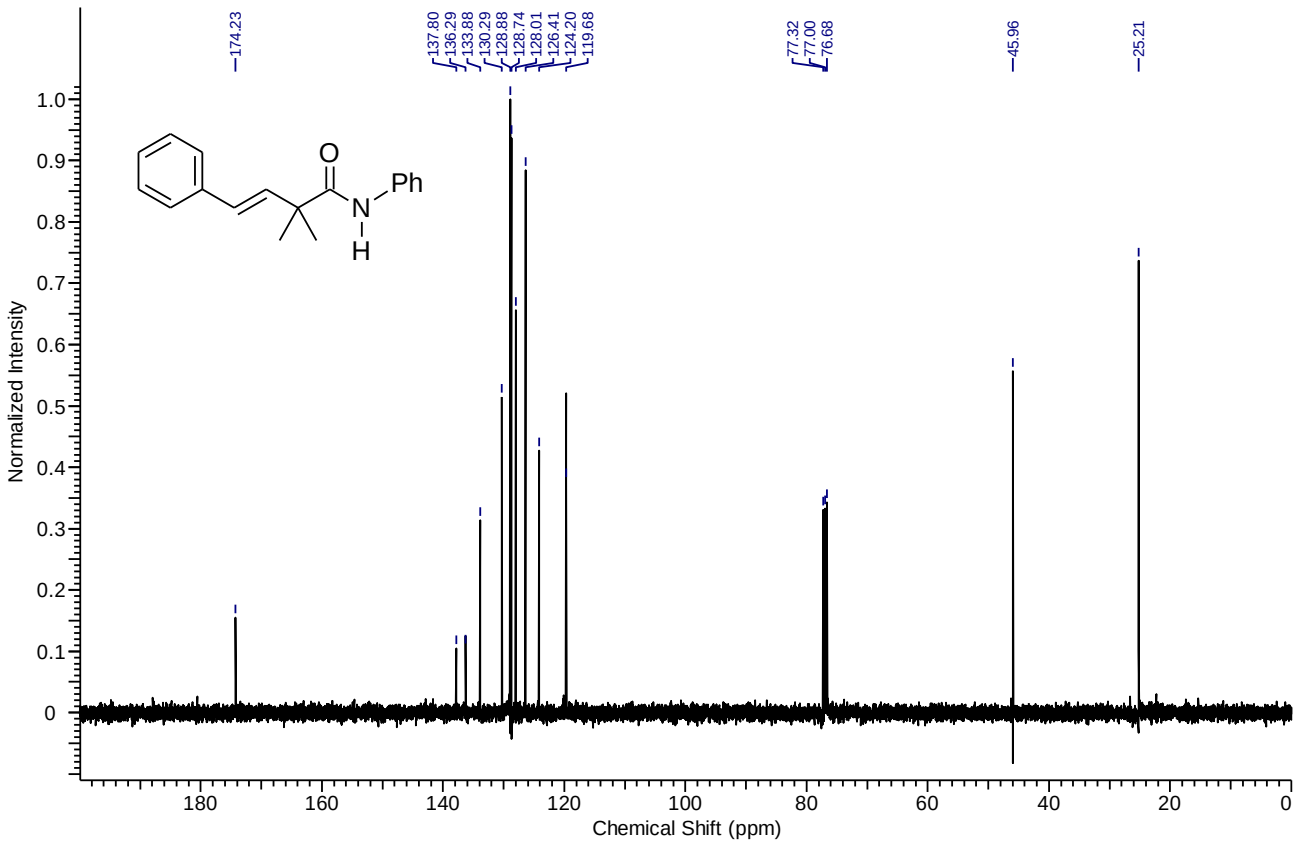


Figure S95. ^{13}C NMR spectrum of the compound **4na** in $CDCl_3$, 100 MHz

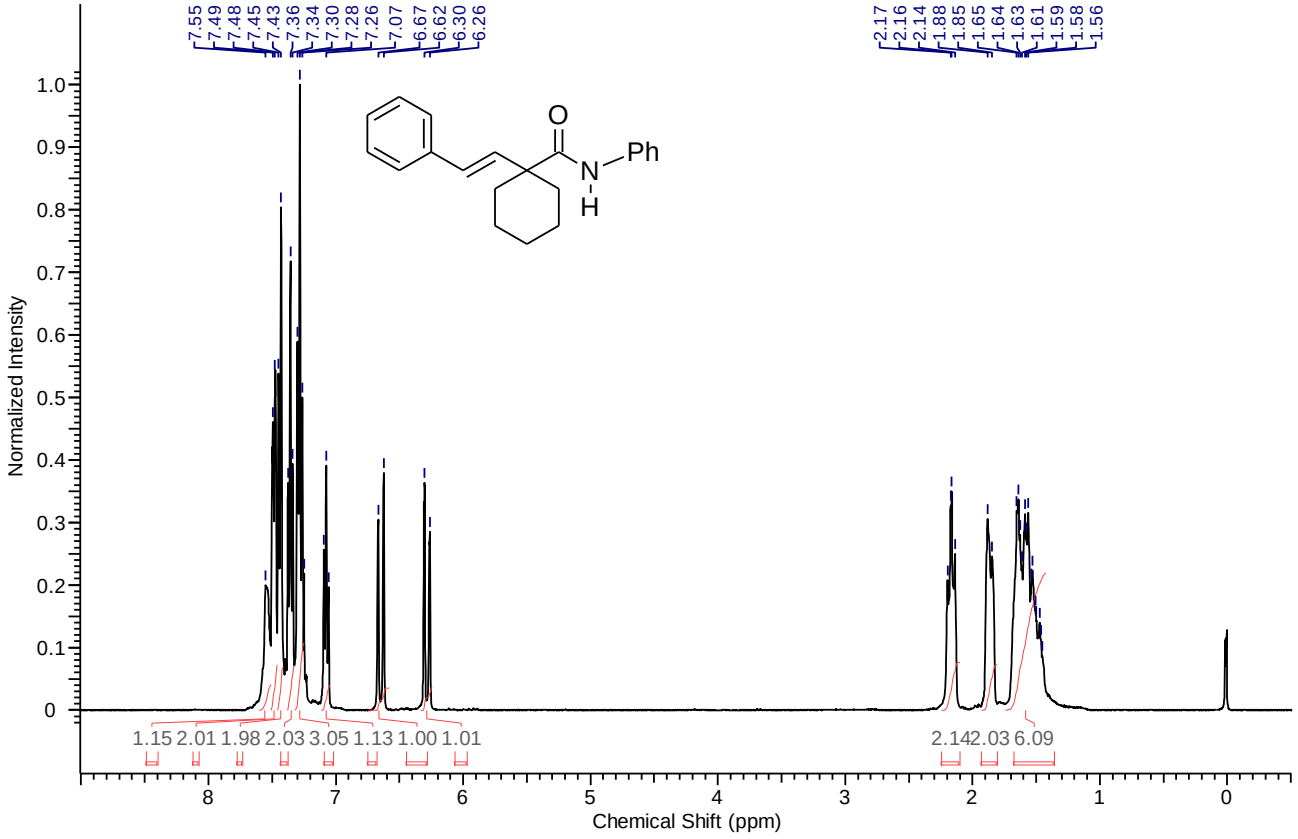


Figure S96. ^{1}H NMR spectrum of the compound **4oa** in $CDCl_3$, 400 MHz

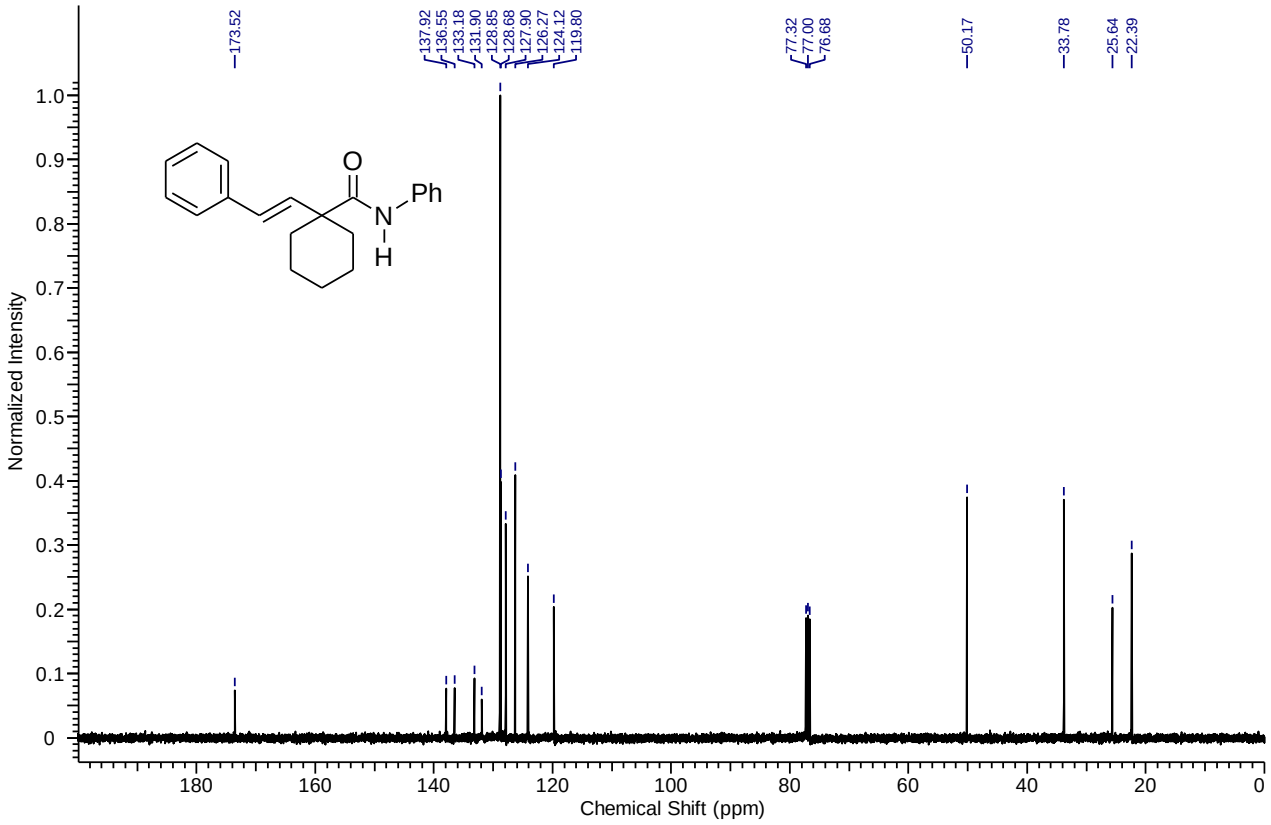


Figure S97. ^{13}C NMR spectrum of the compound **4oa** in $CDCl_3$, 100 MHz

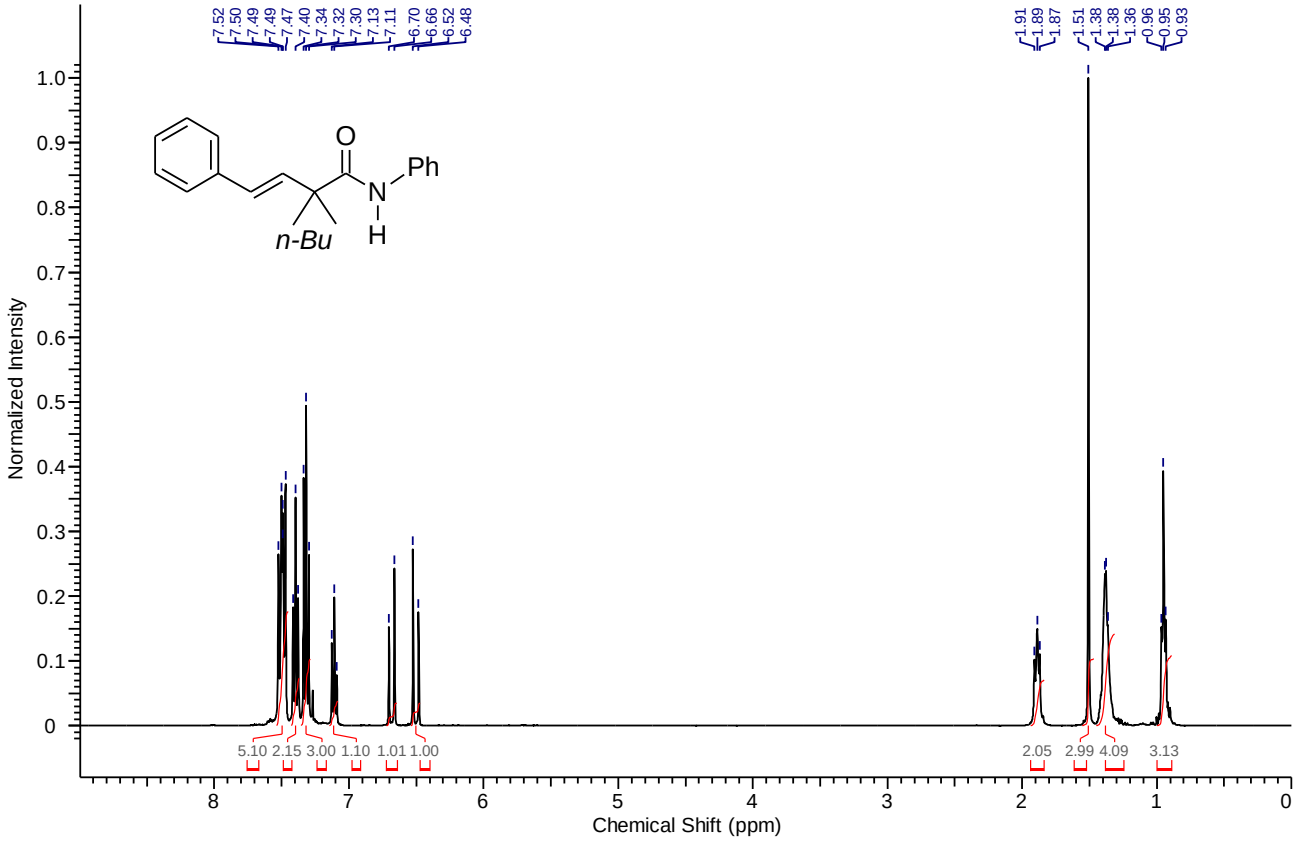


Figure S98. ^{1}H NMR spectrum of the compound **4pa** in $CDCl_3$, 400 MHz

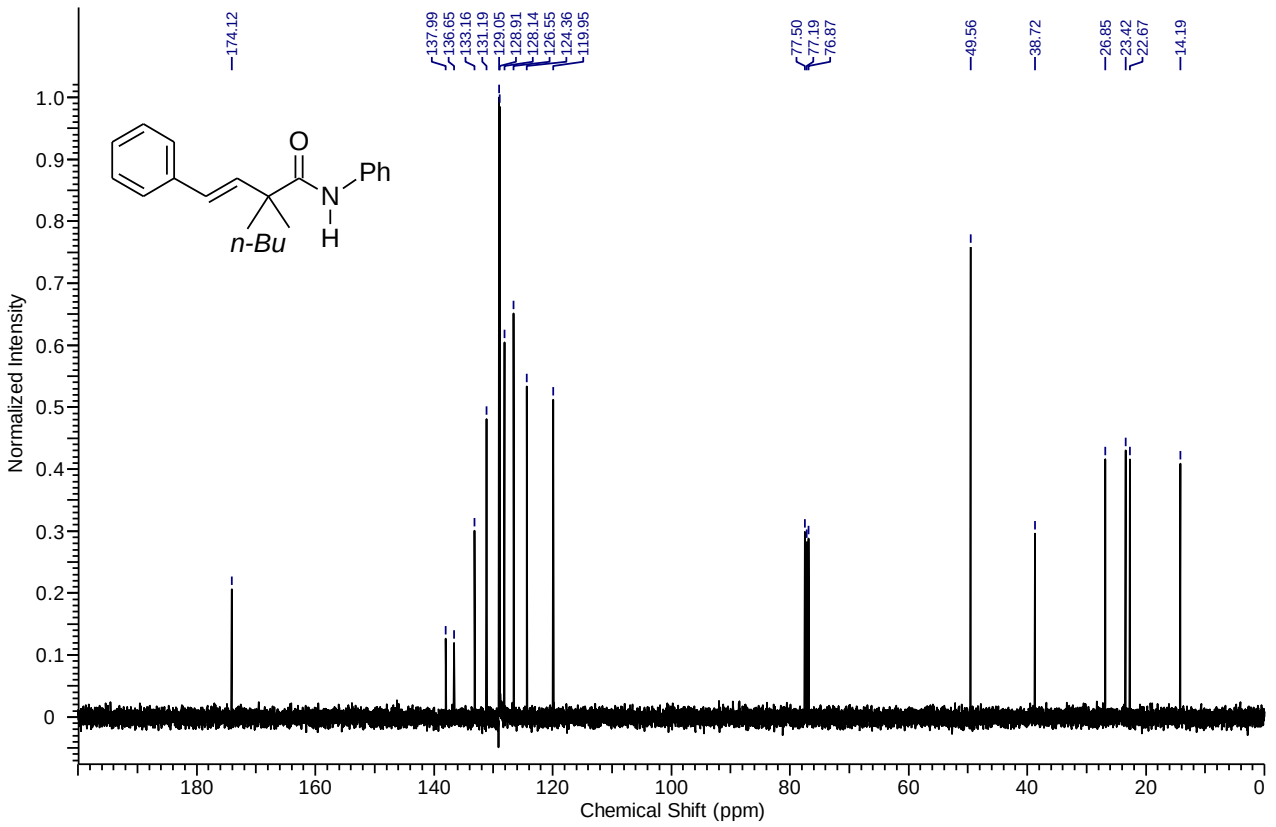


Figure S99. ^{13}C NMR spectrum of the compound **4pa** in $CDCl_3$, 100 MHz

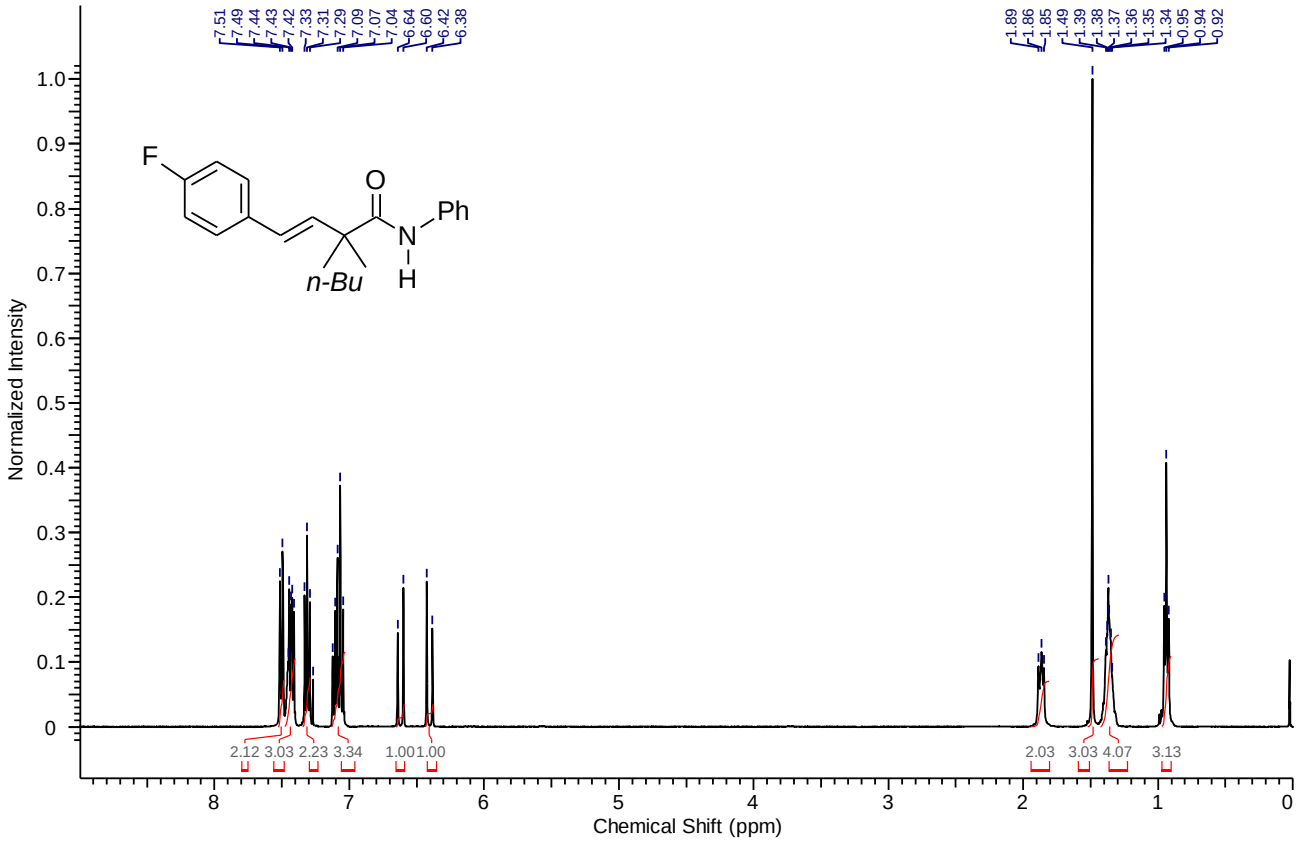


Figure S100. ^{1}H NMR spectrum of the compound **4qa** in $CDCl_3$, 400 MHz

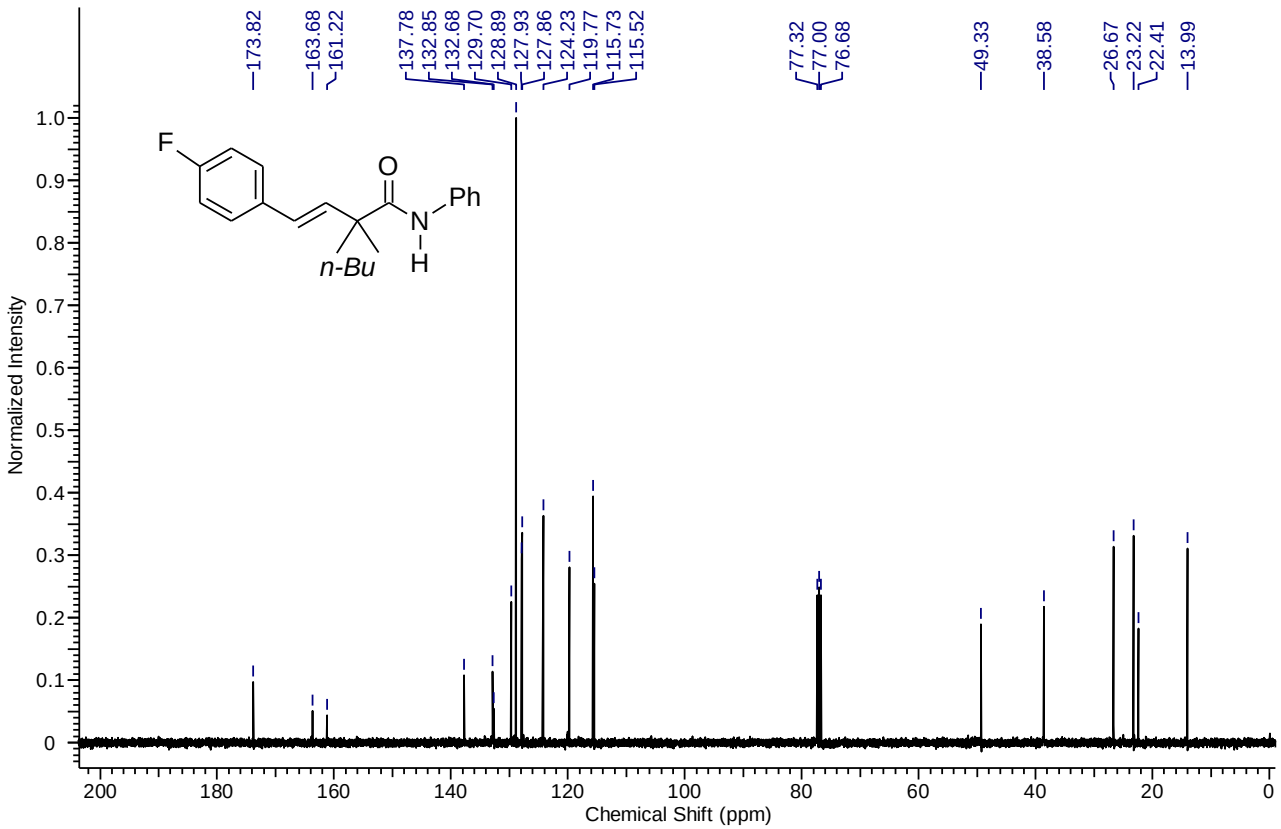


Figure S101. ^{13}C NMR spectrum of the compound **4qa** in $CDCl_3$, 100 MHz

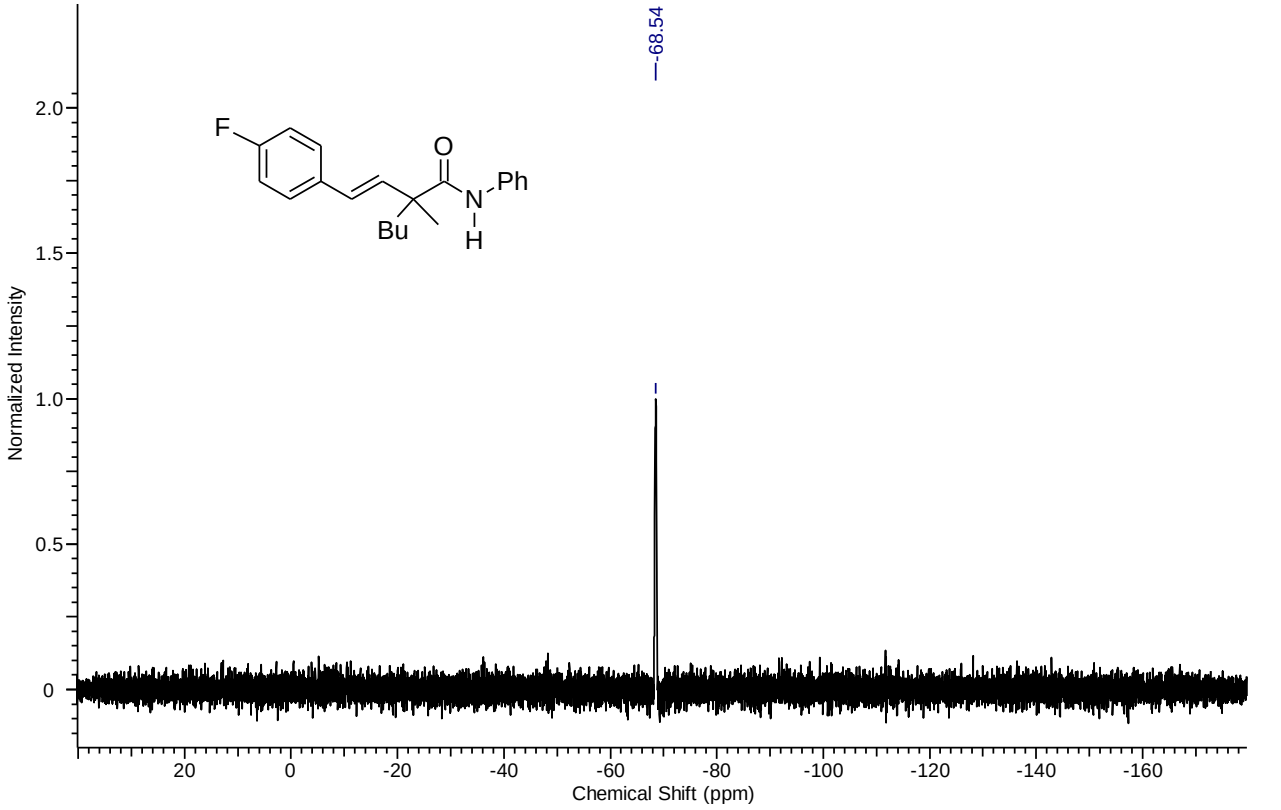


Figure S102. ^{19}F NMR spectrum of the compound **4qa** in $CDCl_3$, 75.2 MHz

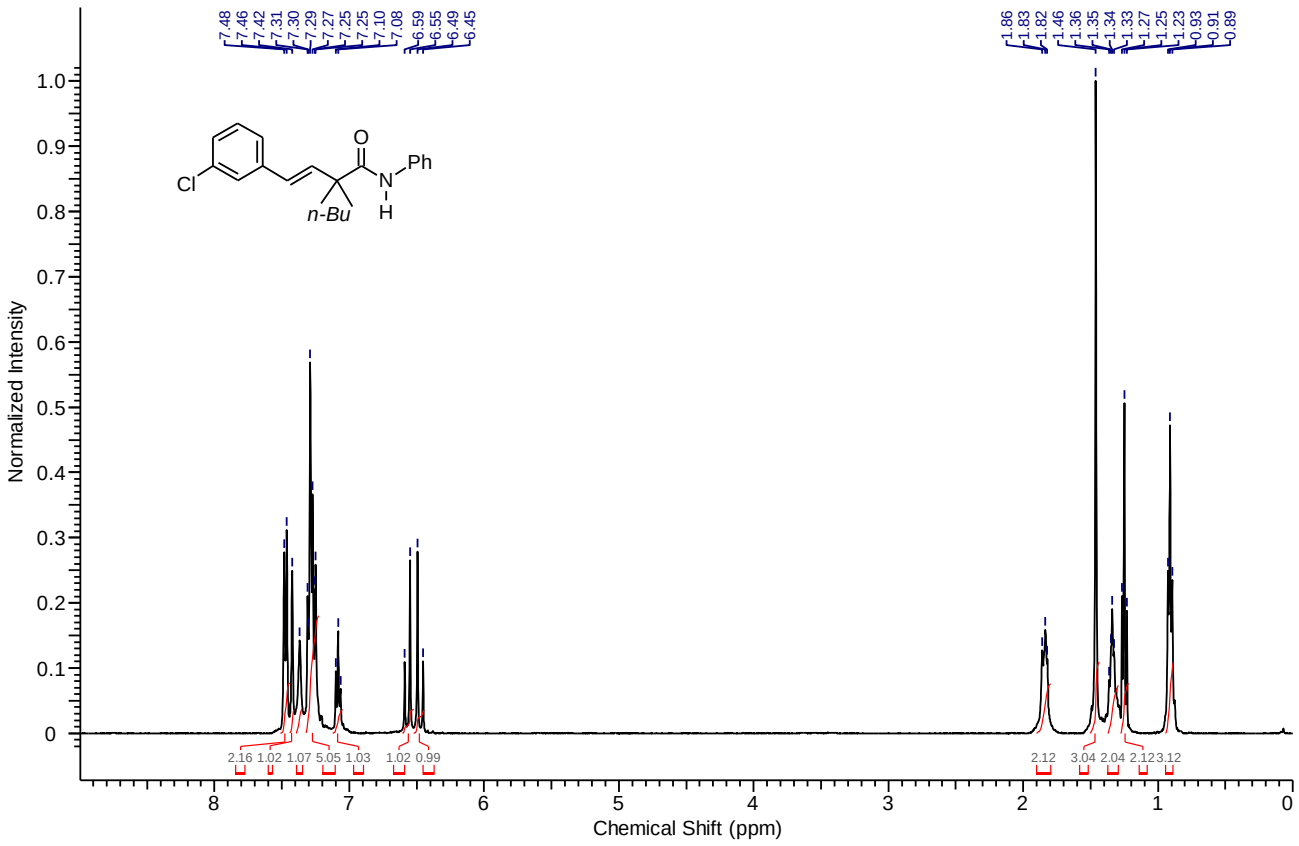


Figure S103. ^{1}H NMR spectrum of the compound **4ra** in $CDCl_3$, 400 MHz

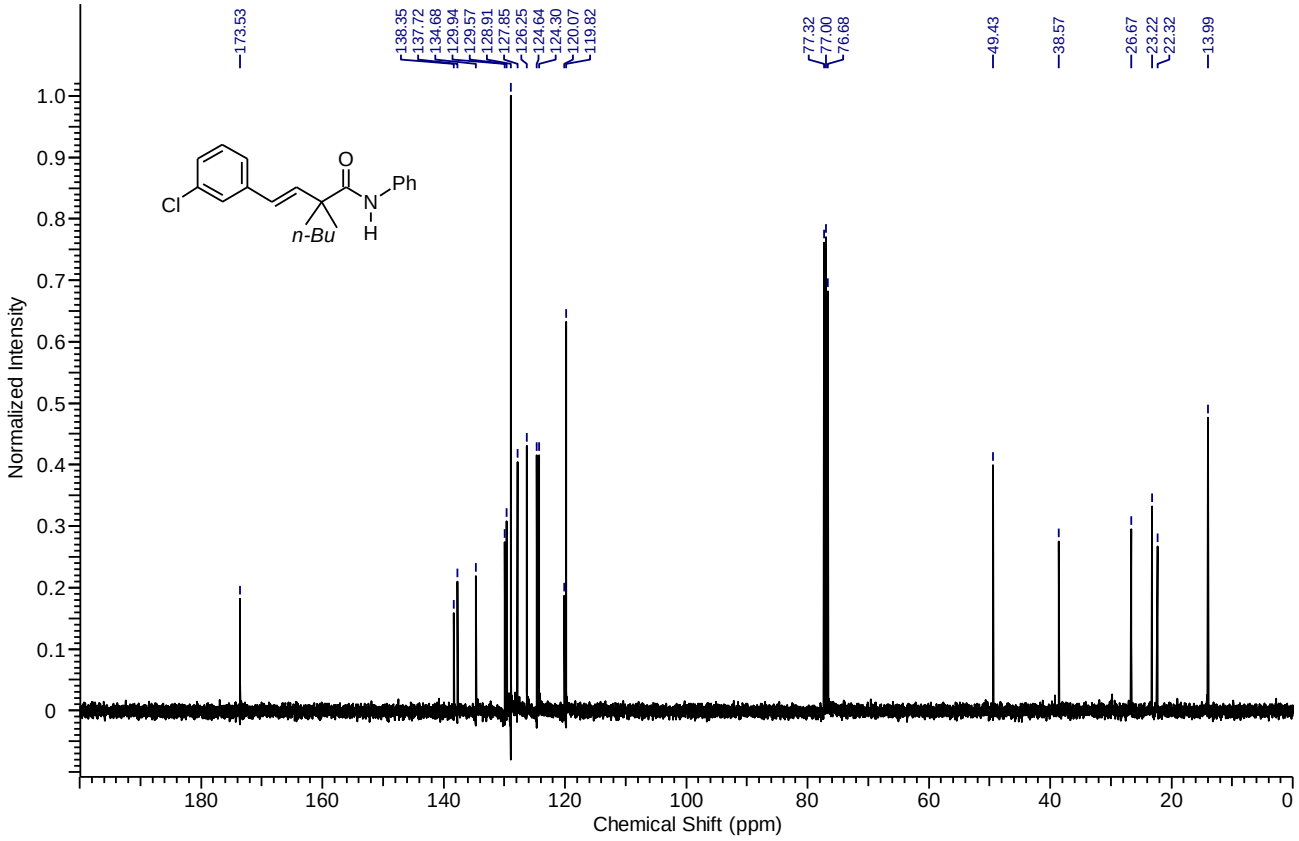


Figure S104. ^{13}C NMR spectrum of the compound **4ra** in $CDCl_3$, 100 MHz

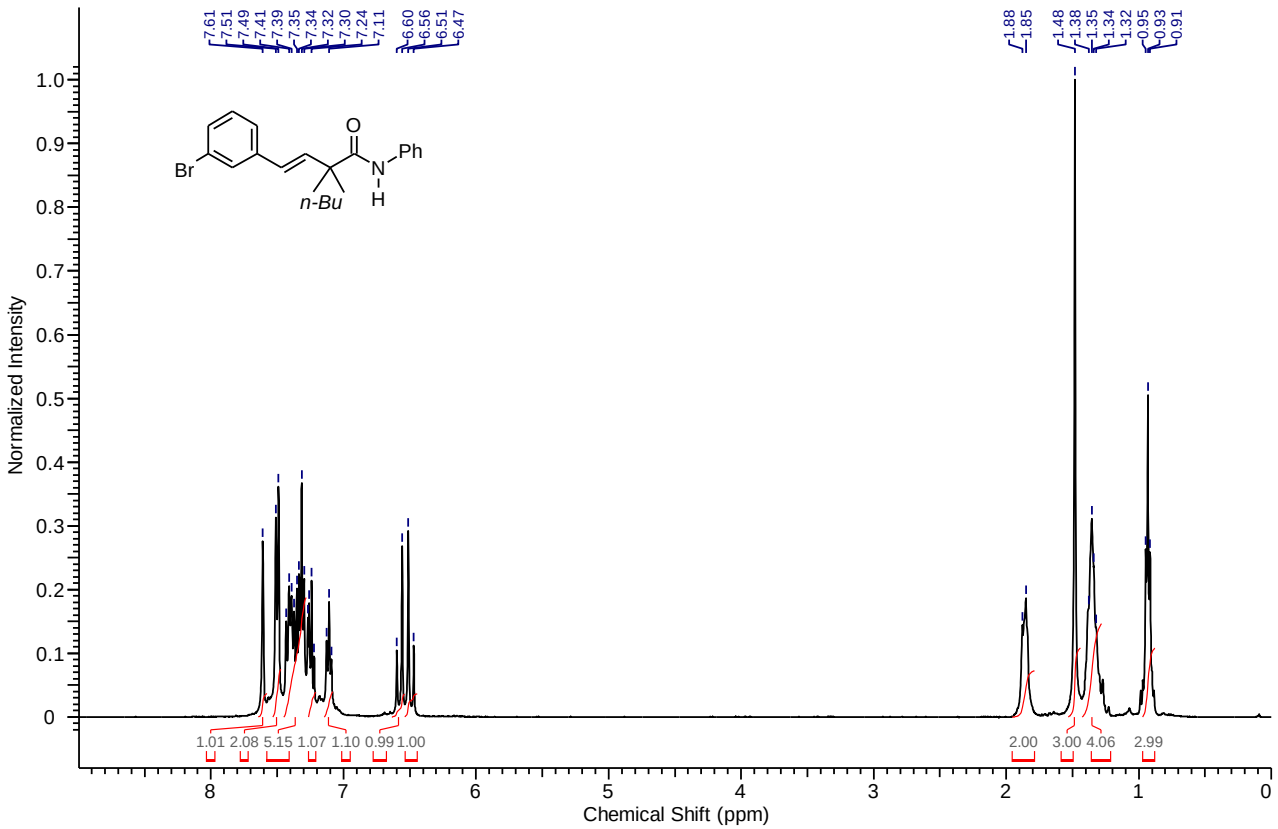


Figure S105. ^{1}H NMR spectrum of the compound **4sa** in $CDCl_3$, 400 MHz

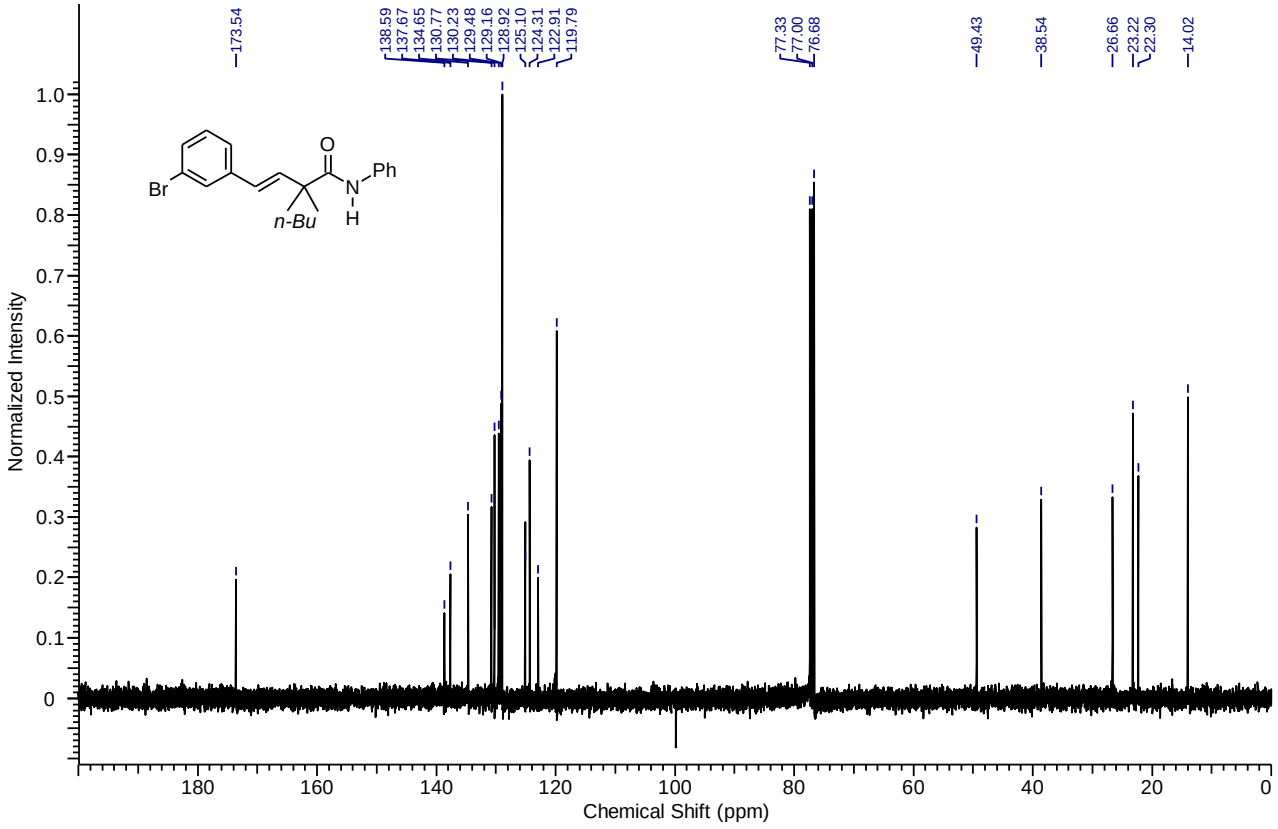


Figure S106. ^{13}C NMR spectrum of the compound **4sa** in $CDCl_3$, 100 MHz

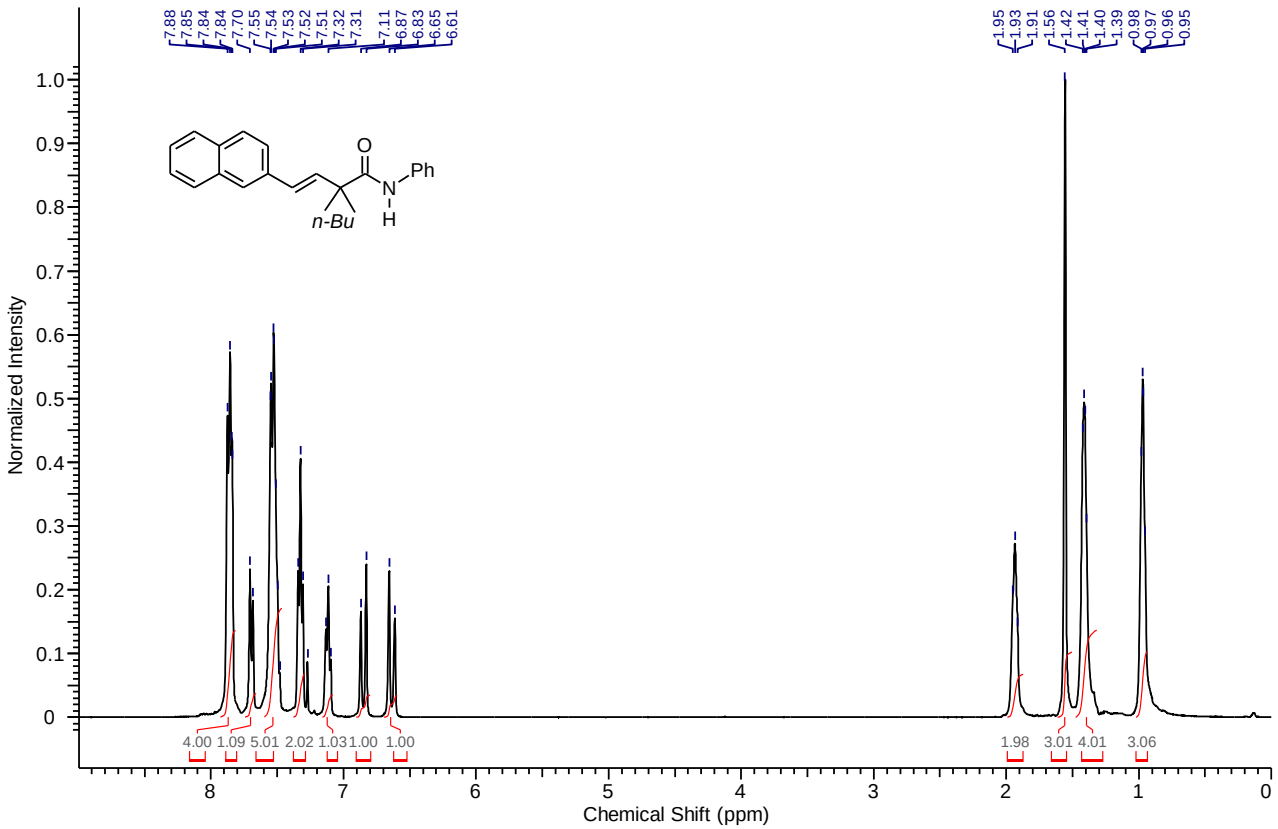


Figure S107. ^{1}H NMR spectrum of the compound **4ta** in $CDCl_3$, 400 MHz

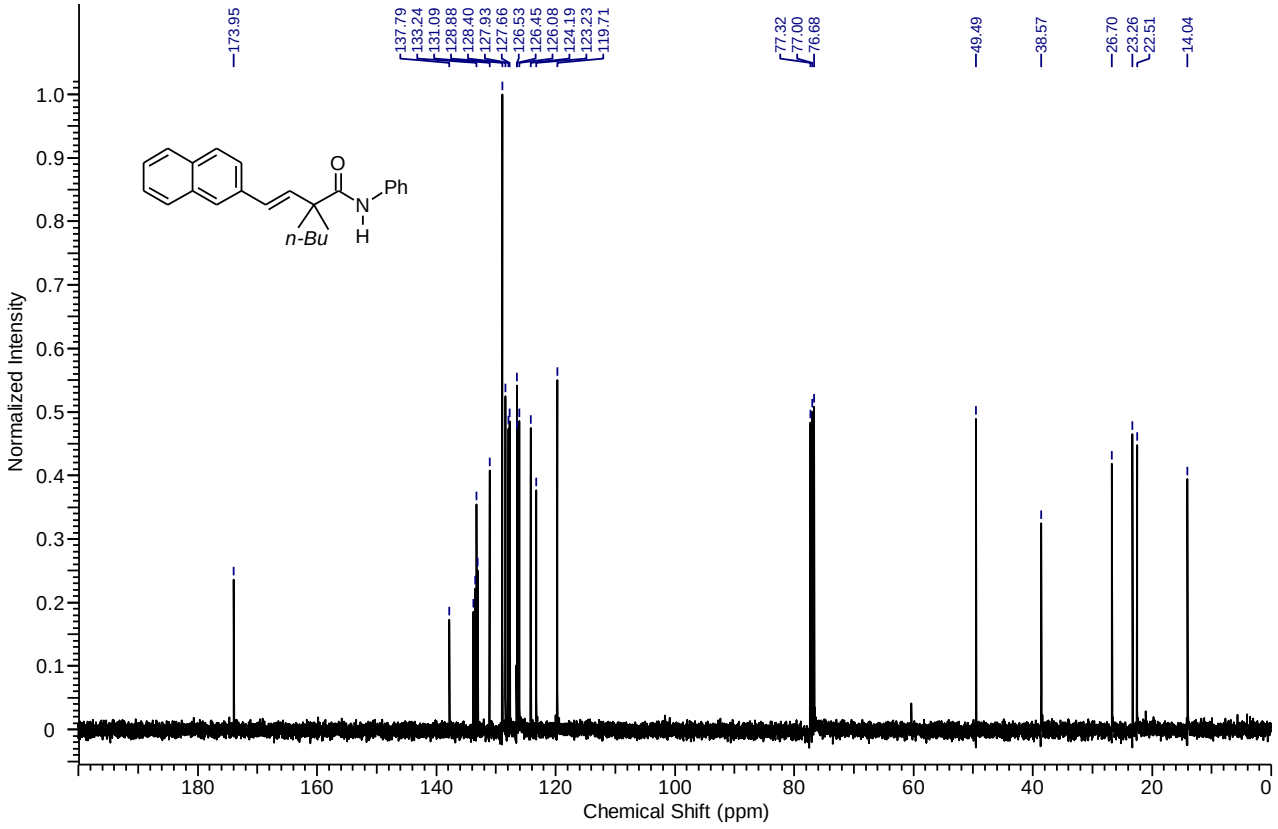


Figure S108. ^{13}C NMR spectrum of the compound **4ta** in $CDCl_3$, 100 MHz

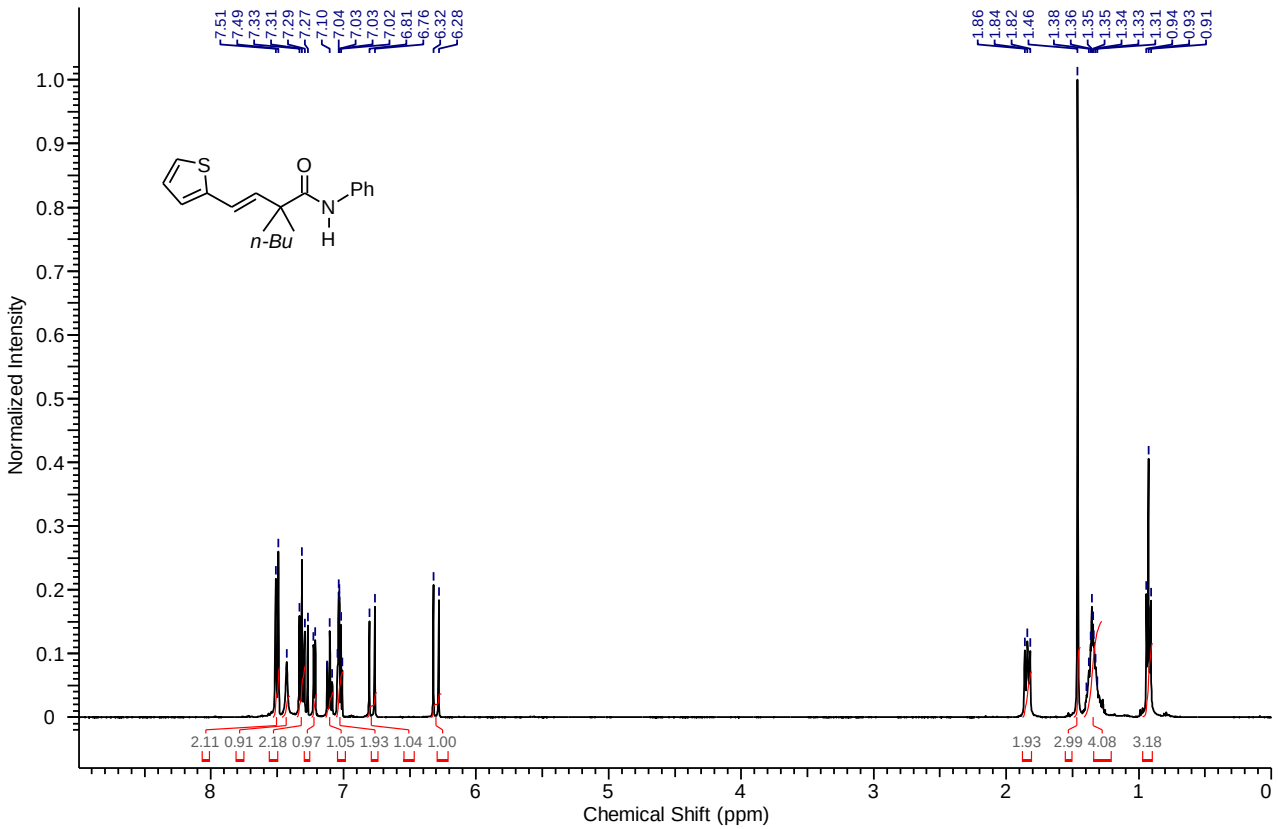


Figure S109. ^{1}H NMR spectrum of the compound **4ua** in $CDCl_3$, 400 MHz

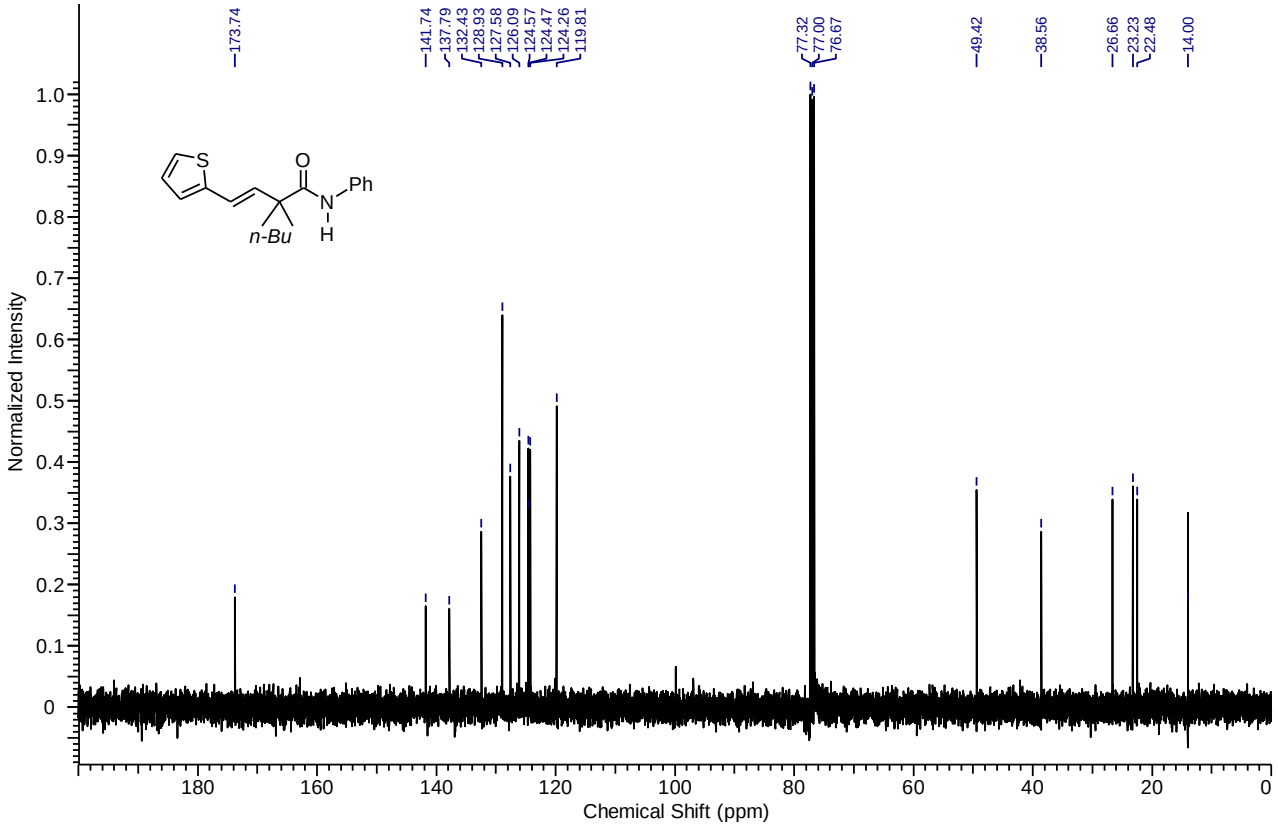


Figure S110. ^{13}C NMR spectrum of the compound **4ua** in $CDCl_3$, 100 MHz

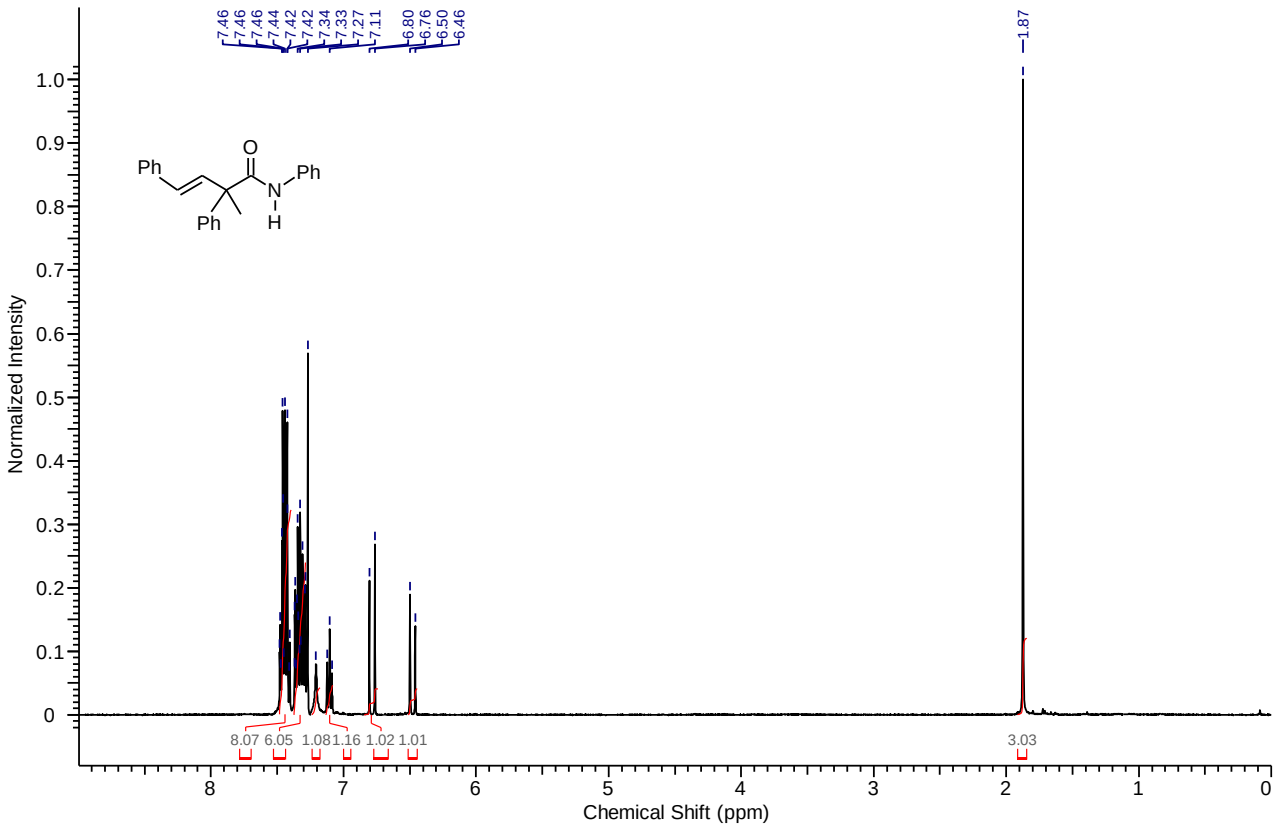


Figure S111. ^{1}H NMR spectrum of the compound **4xa-1** in $CDCl_3$, 400 MHz

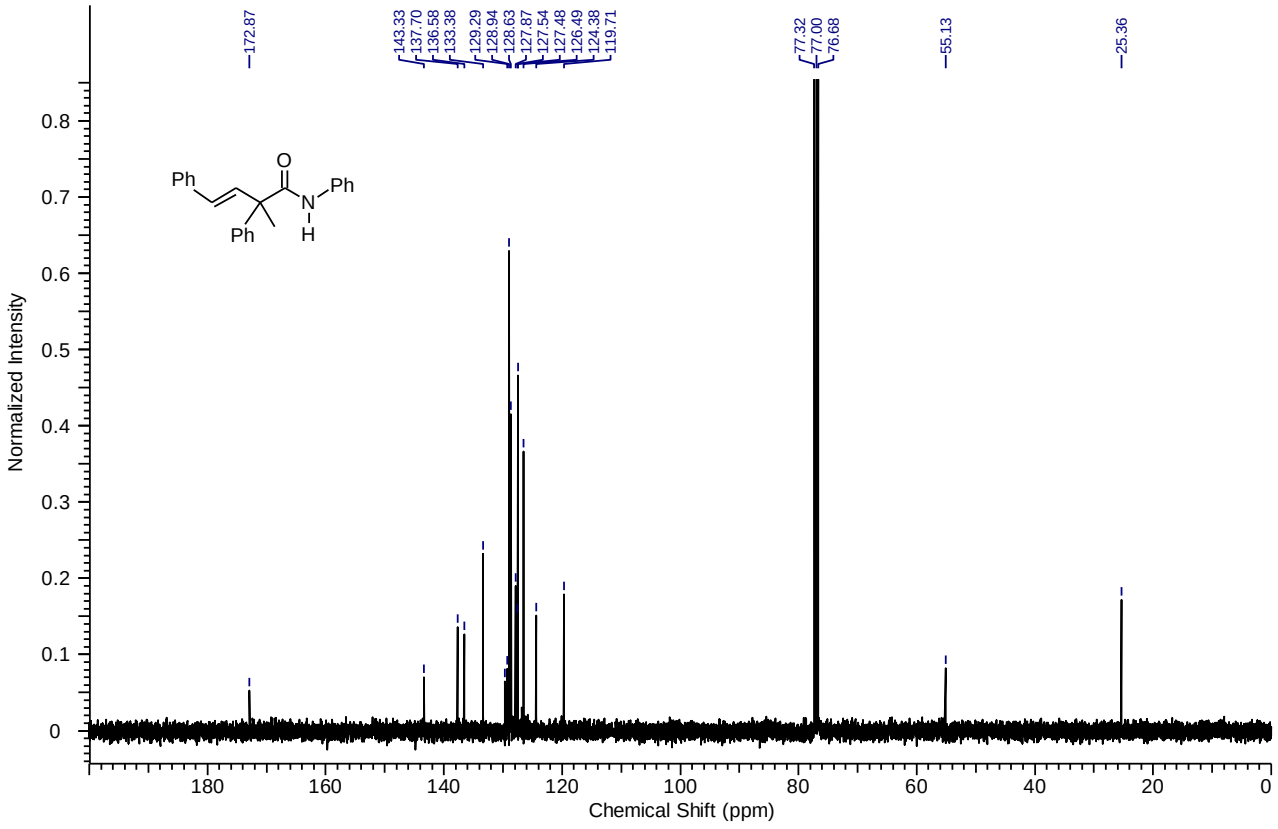


Figure S112. ^{13}C NMR spectrum of the compound **4xa-1** in $CDCl_3$, 100 MHz

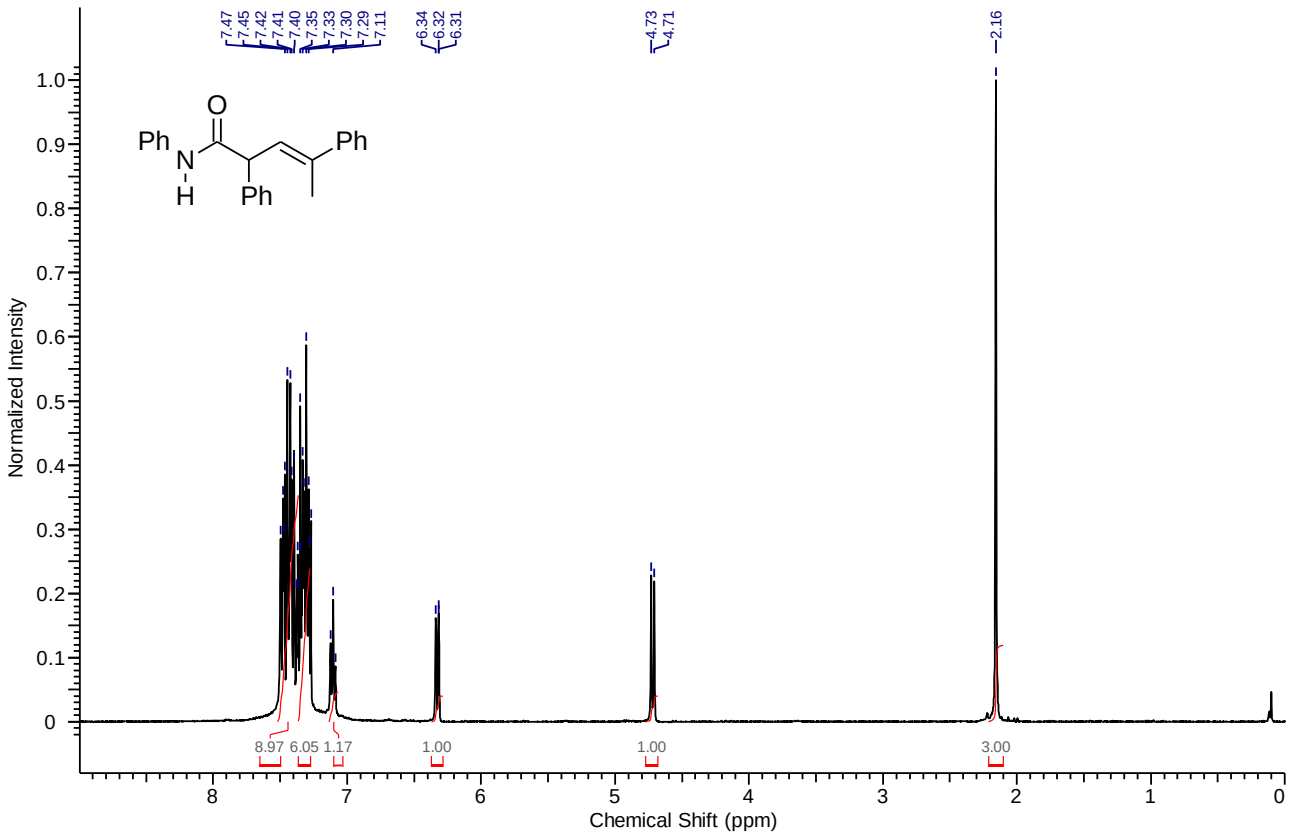


Figure S113. ^{1}H NMR spectrum of the compound **4xa-2** in $CDCl_3$, 400 MHz

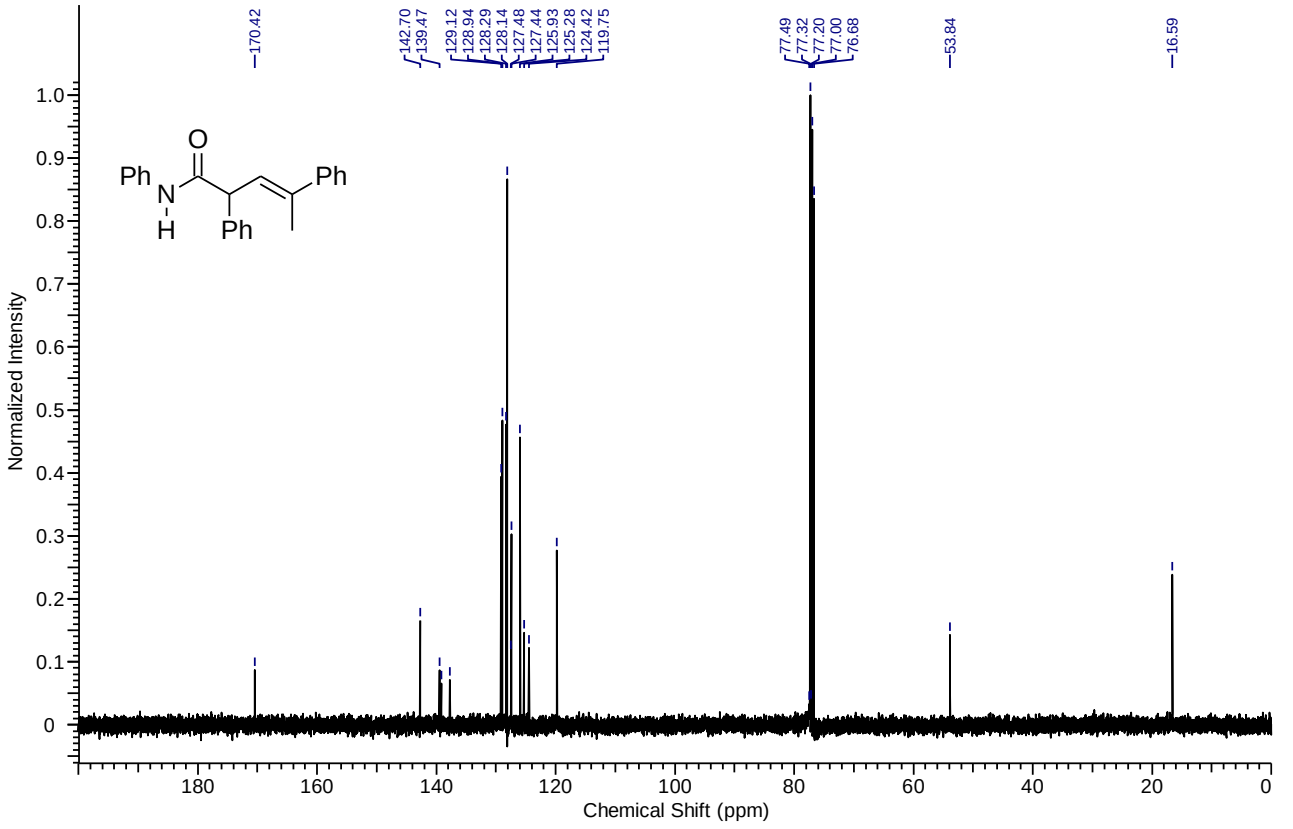


Figure S114. ^{13}C NMR spectrum of the compound **4xa-2** in $CDCl_3$, 100 MHz

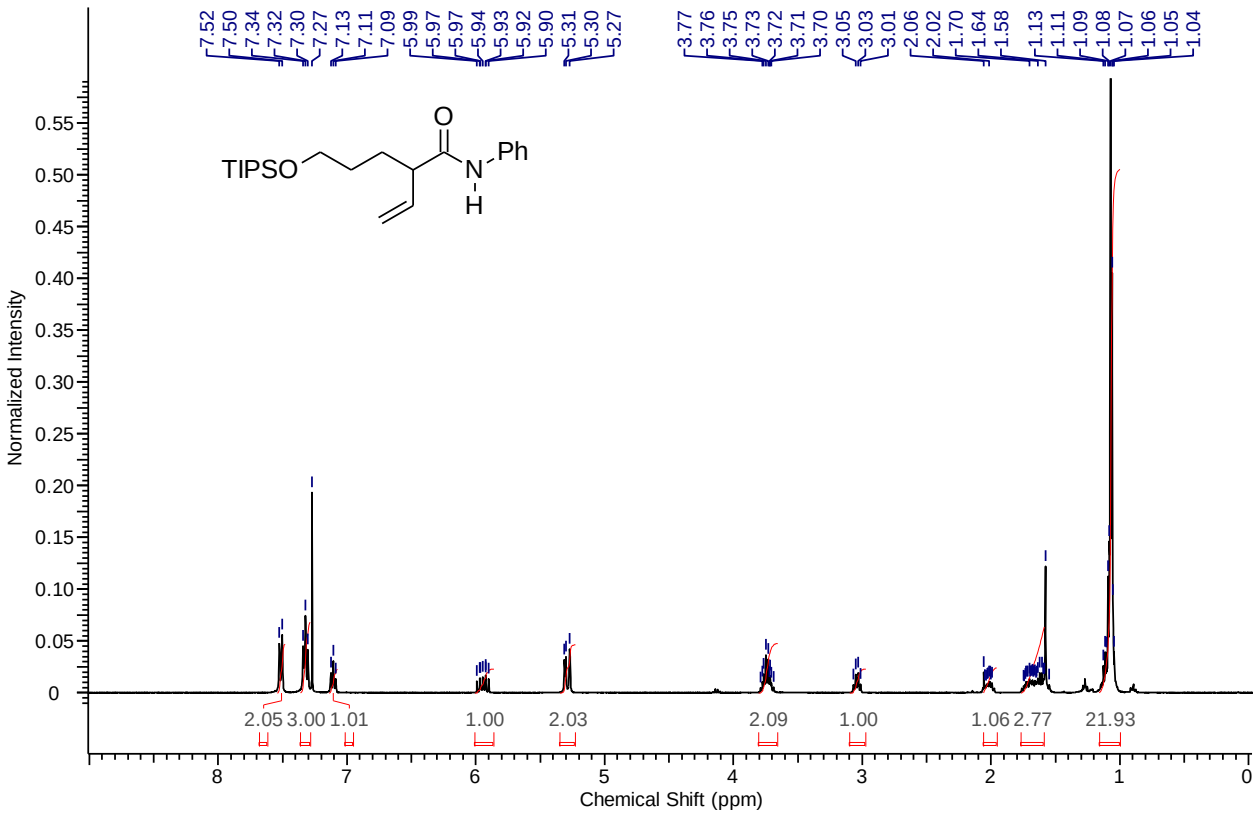


Figure S115. ^{1}H NMR spectrum of the compound **4ya** in $CDCl_3$, 400 MHz

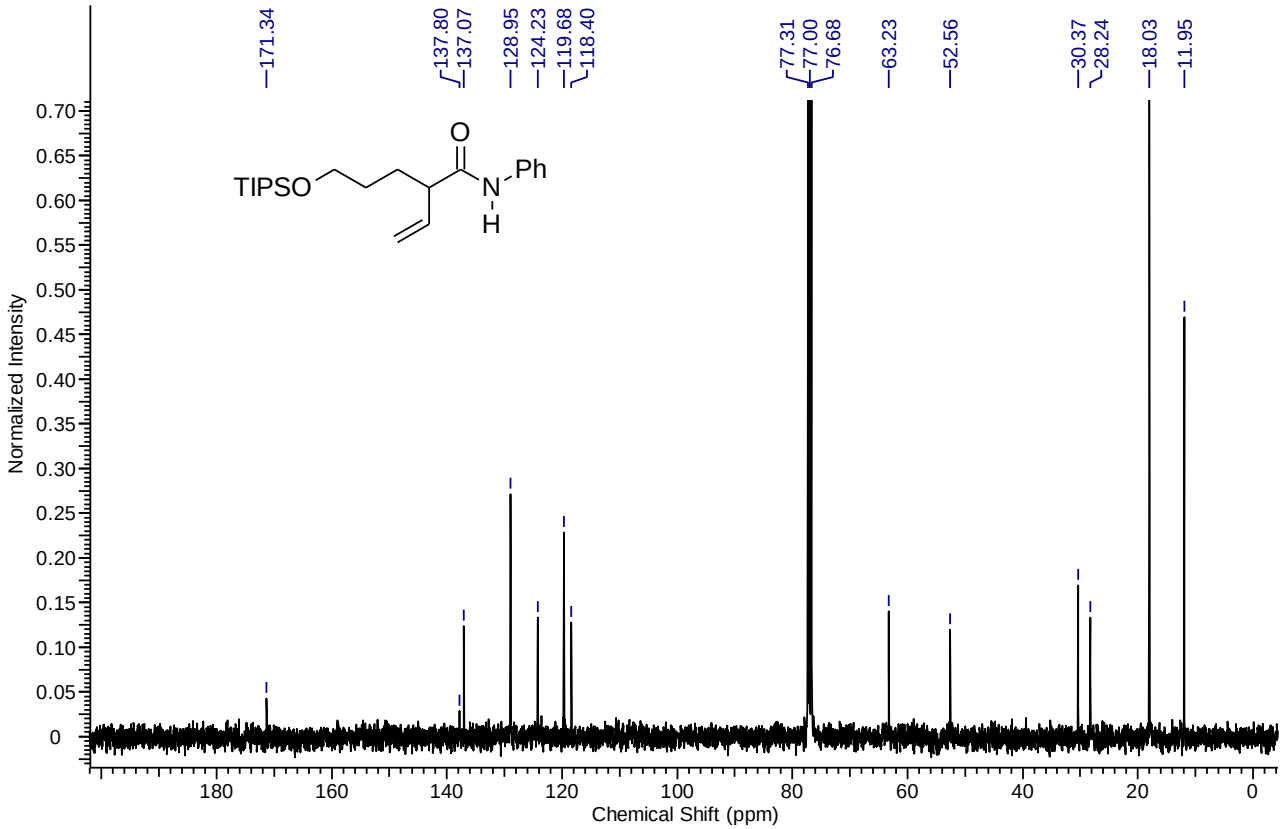


Figure S116. ^{13}C NMR spectrum of the compound **4ya** in $CDCl_3$, 100 MHz

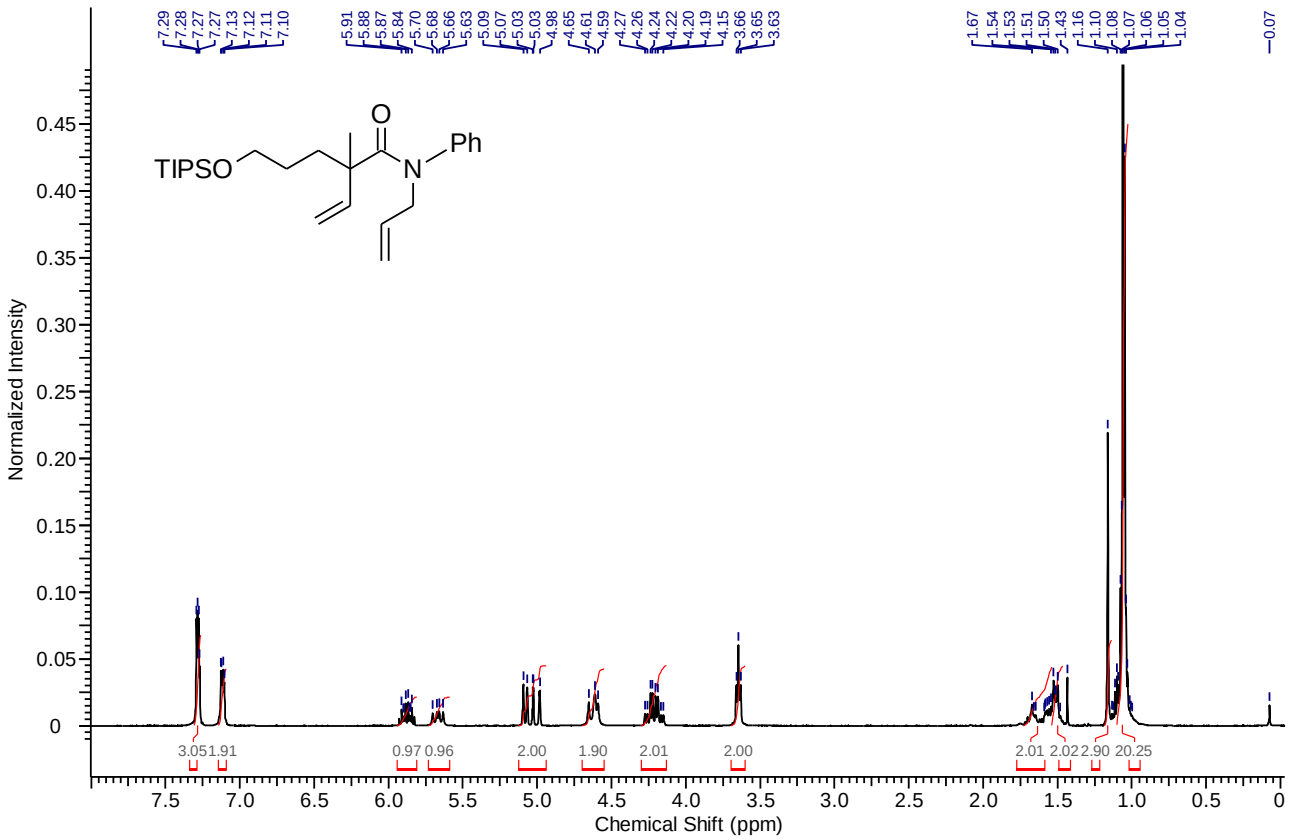


Figure 117. ^{1}H NMR spectrum of the compound **6** in $CDCl_3$, 400 MHz

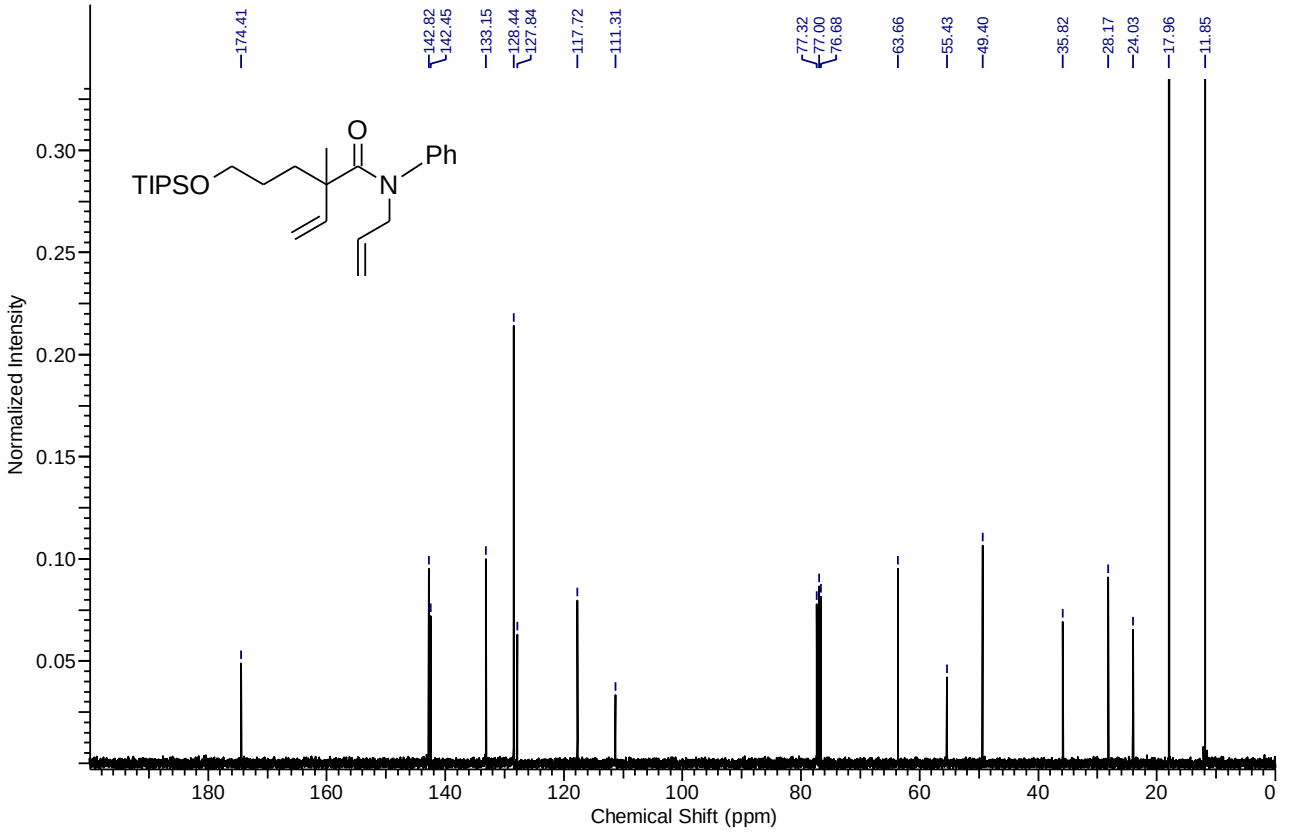


Figure 118. ^{13}C NMR spectrum of the compound **6** in $CDCl_3$, 100 MHz

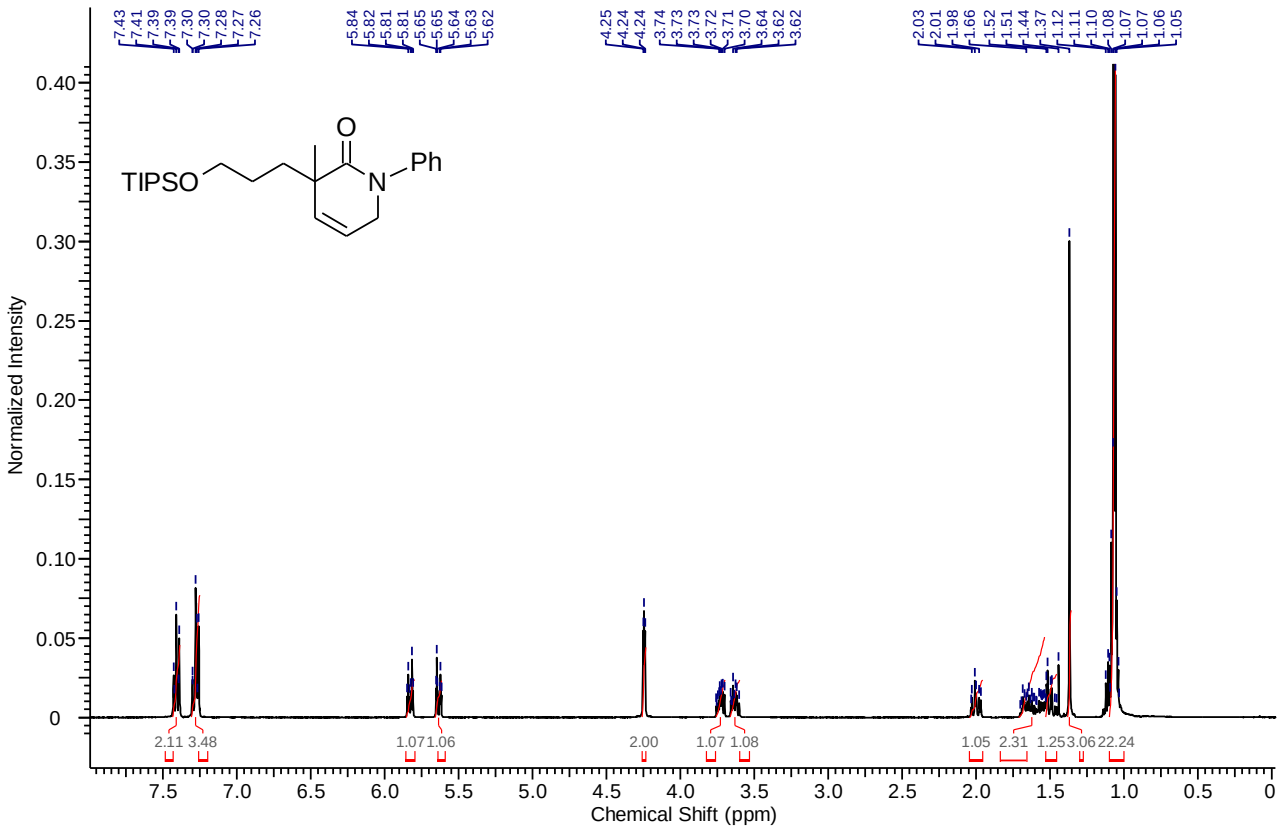


Figure 119. ^{1}H NMR spectrum of the compound **7** in $CDCl_3$, 400 MHz

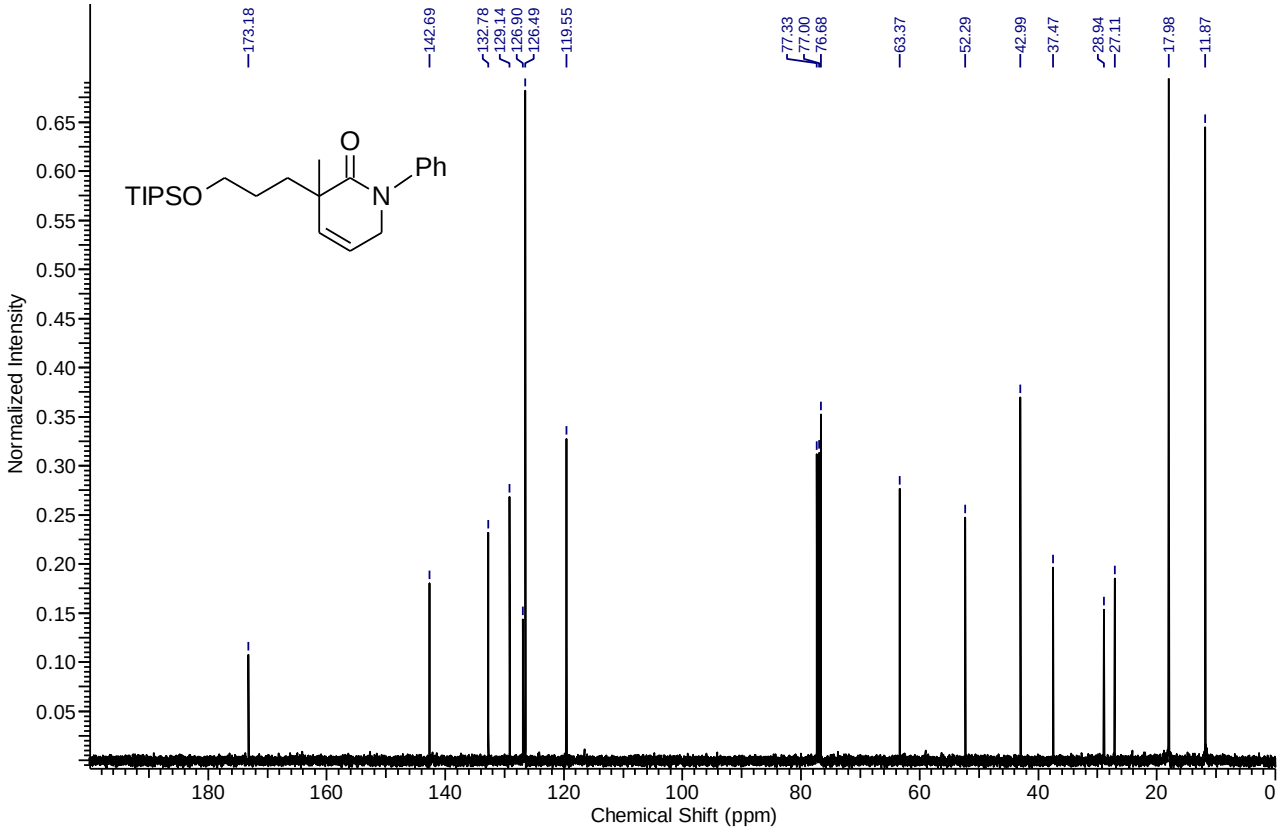


Figure 120. ^{13}C NMR spectrum of the compound **7** in $CDCl_3$, 100 MHz

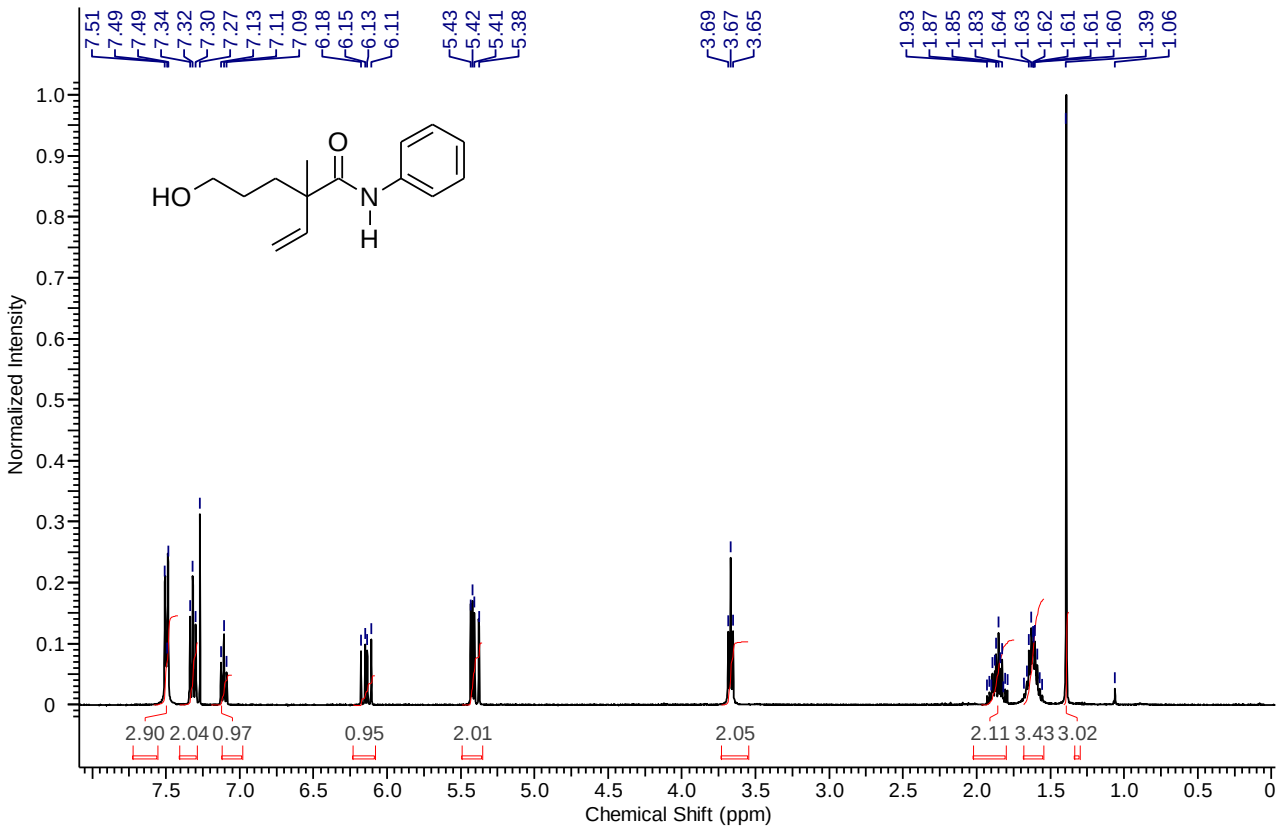


Figure 121. ^{1}H NMR spectrum of the compound **8** in $CDCl_3$, 400 MHz

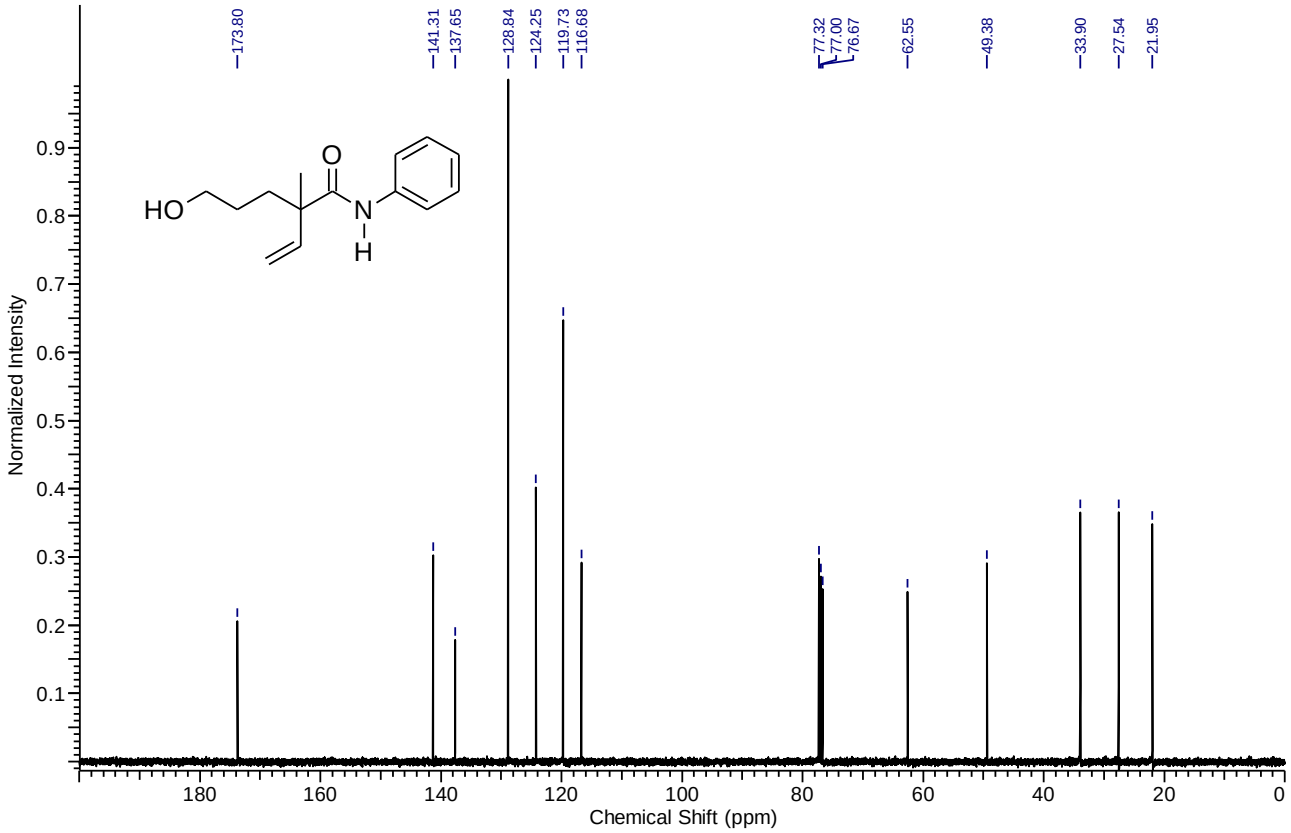


Figure 122. ^{13}C NMR spectrum of the compound **8** in $CDCl_3$, 100 MHz

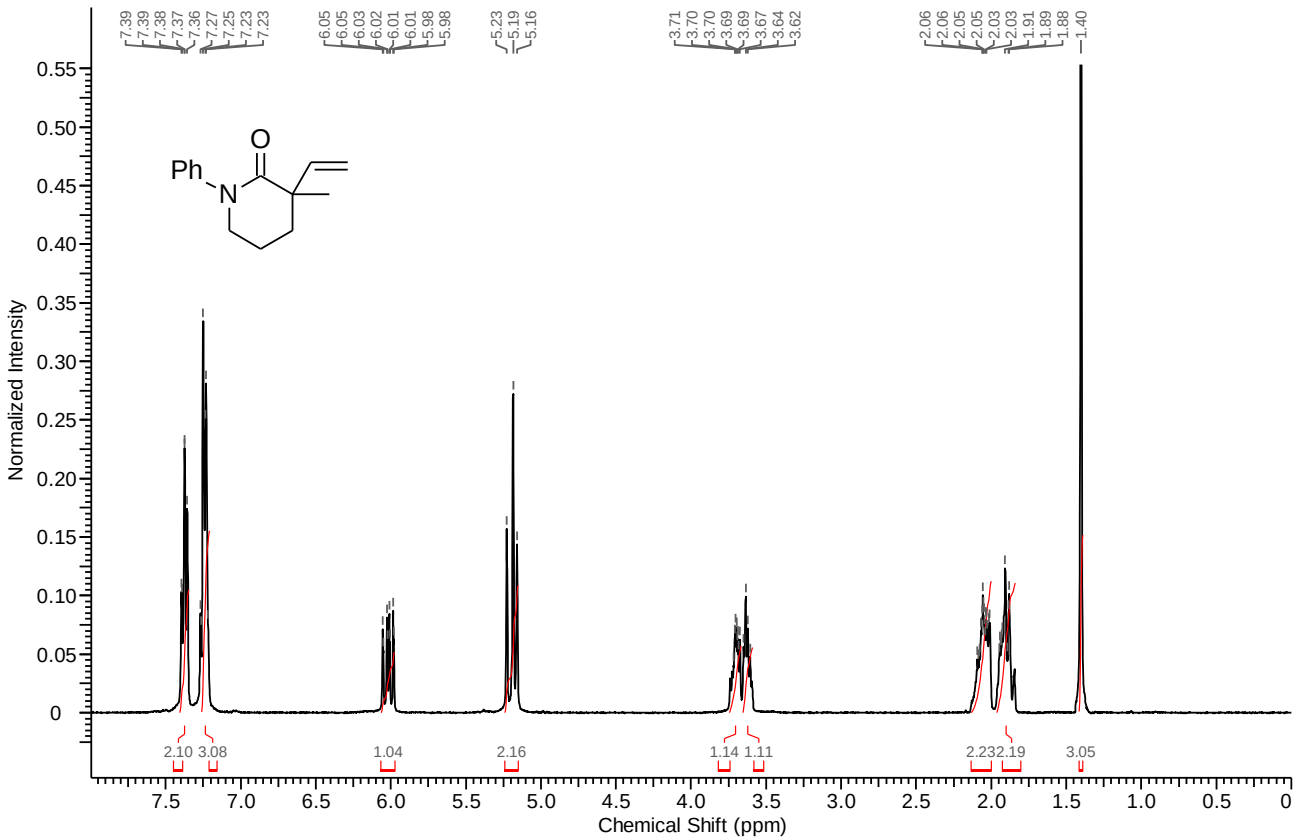


Figure 123. ^{1}H NMR spectrum of the compound **9** in $CDCl_3$, 400 MHz

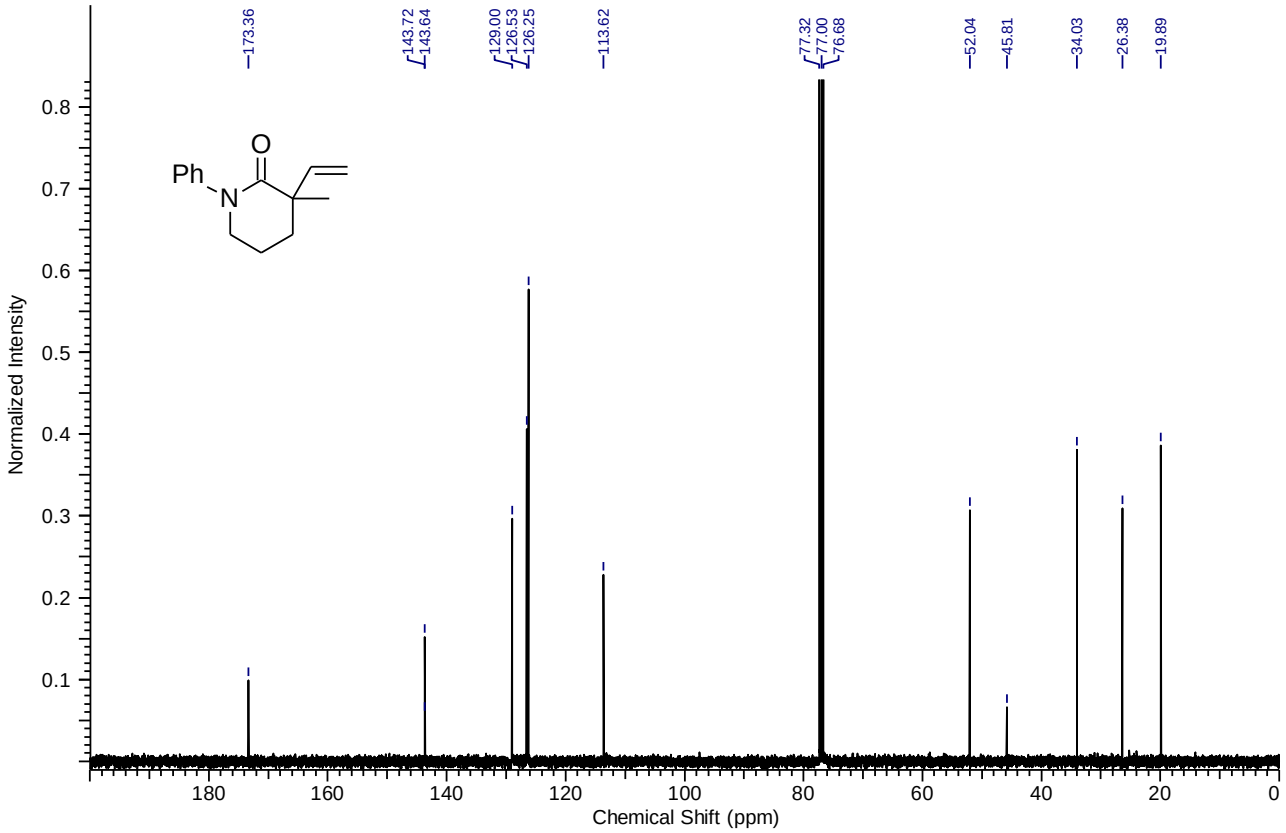


Figure 124. ^{13}C NMR spectrum of the compound **9** in $CDCl_3$, 100 MHz

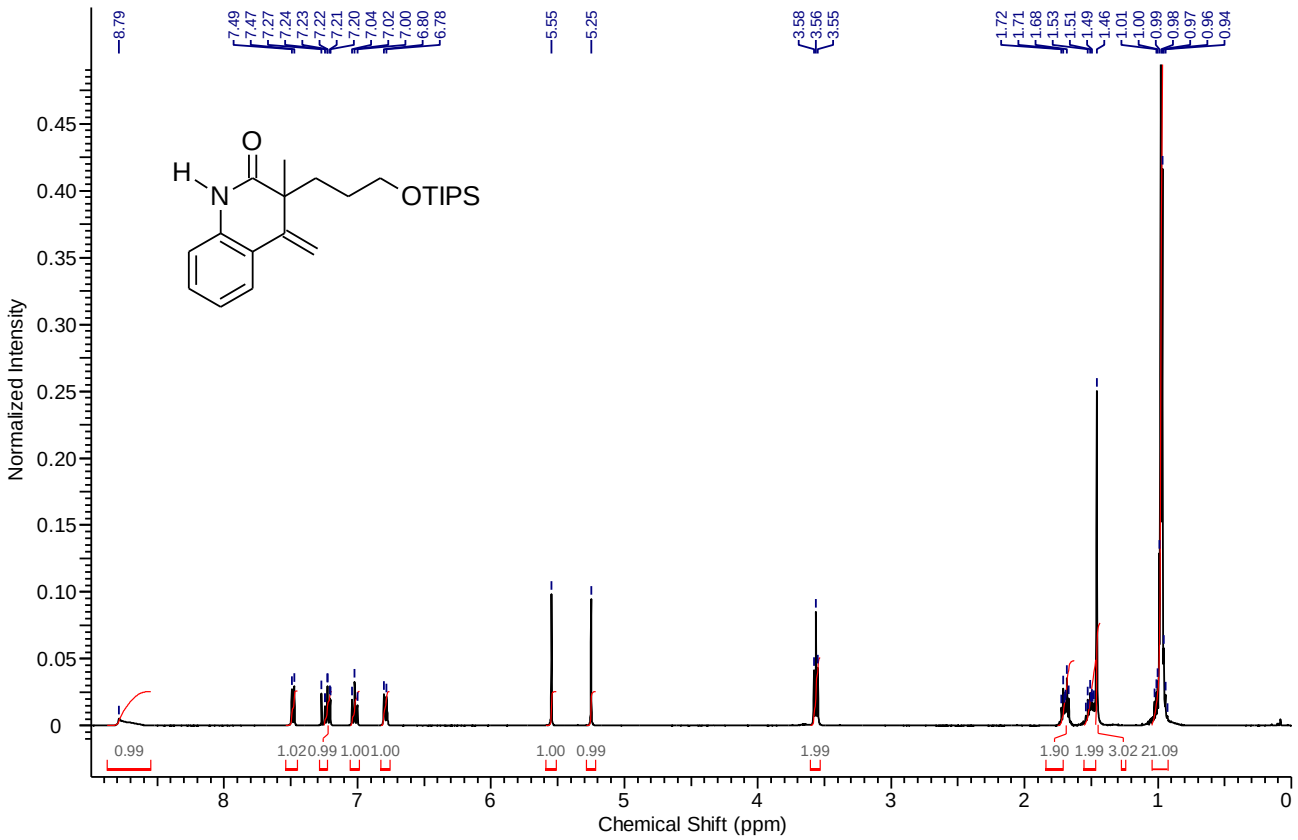


Figure S125. ^{1}H NMR spectrum of the compound **10** in $CDCl_3$, 400 MHz

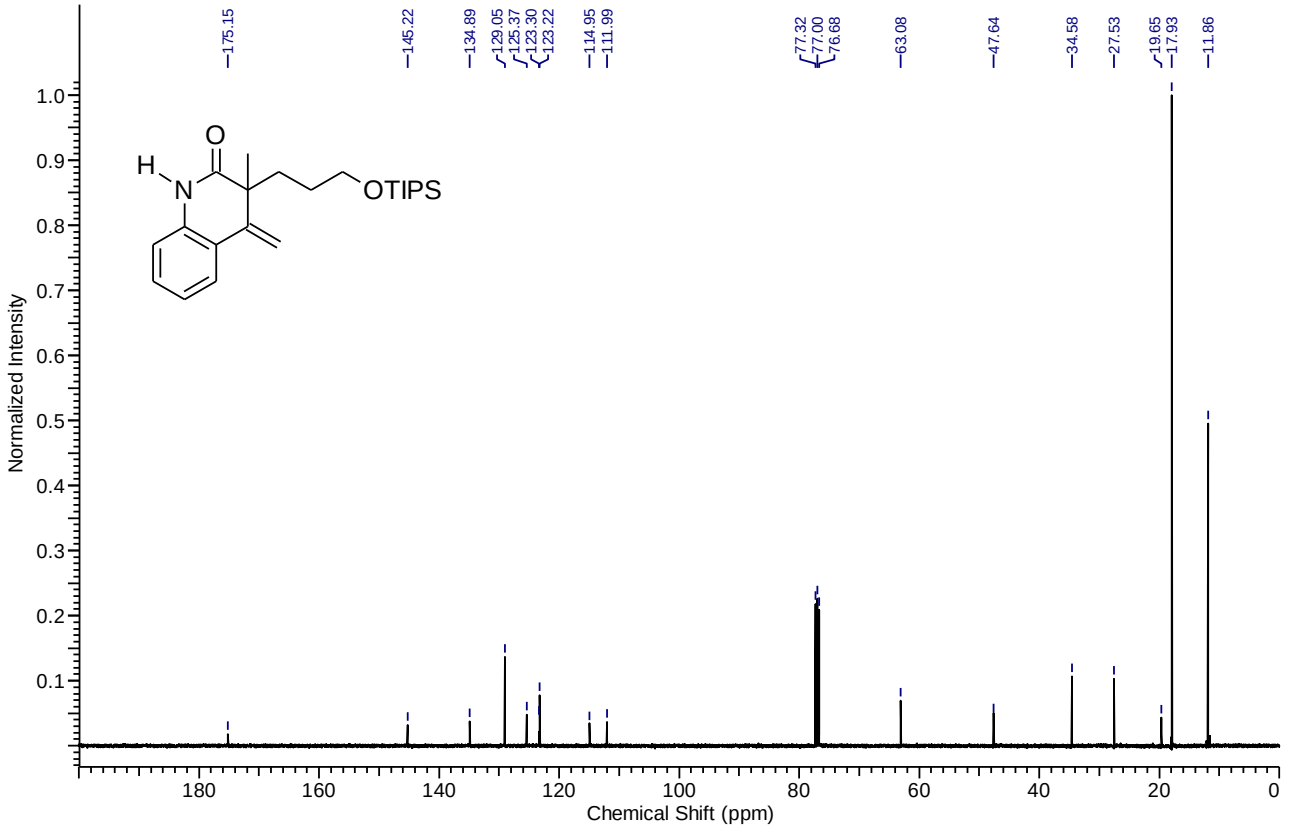


Figure S126. ^{13}C NMR spectrum of the compound **10** in $CDCl_3$, 100 MHz

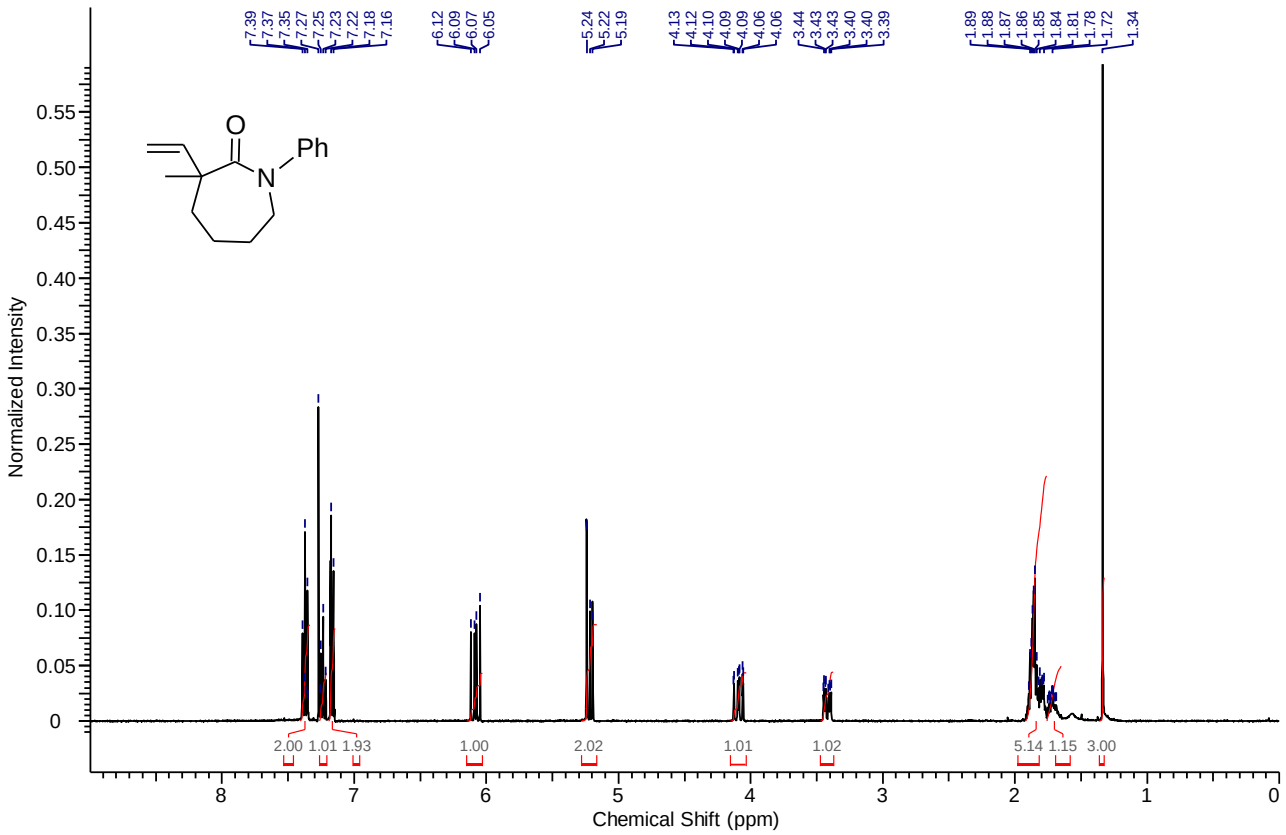


Figure S127. ^{1}H NMR spectrum of the compound **11** in $CDCl_3$, 400 MHz

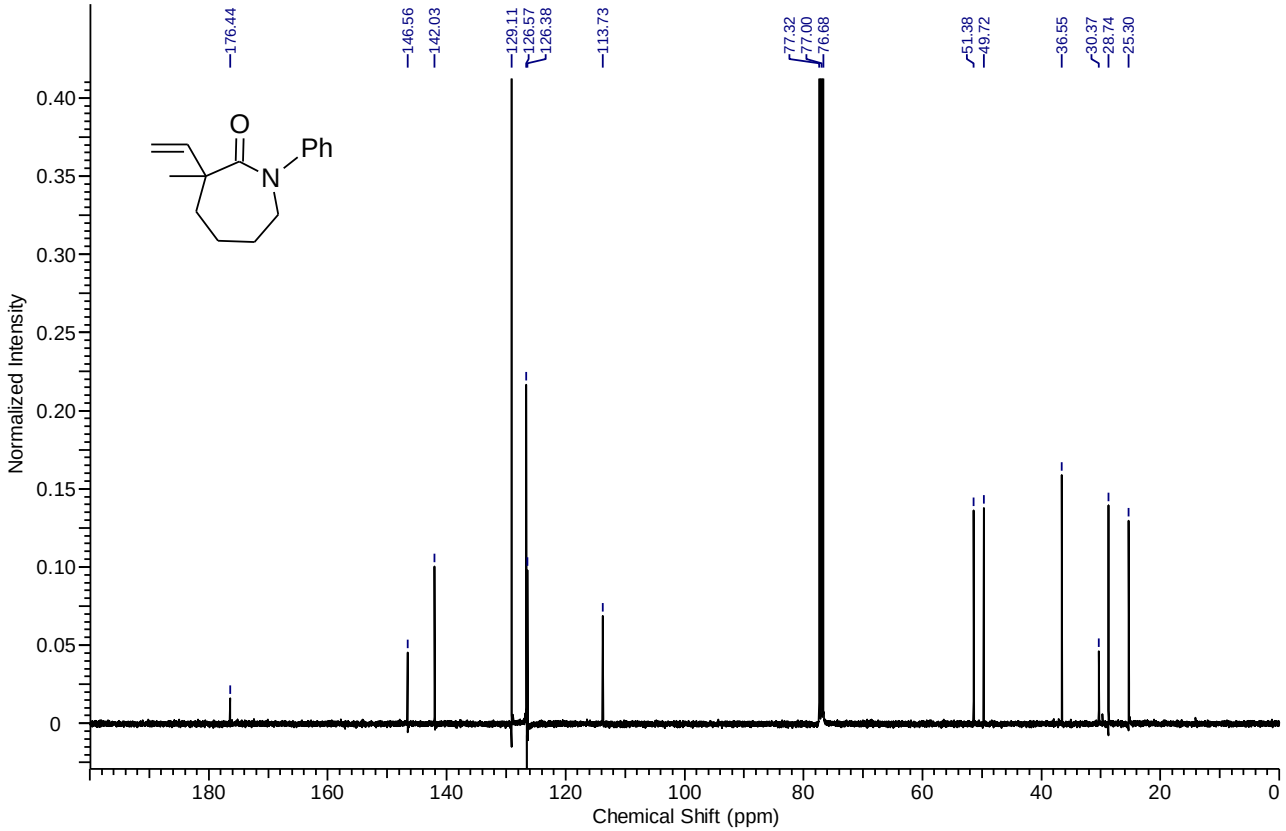


Figure S128. ^{13}C NMR spectrum of the compound **11** in $CDCl_3$, 100 MHz

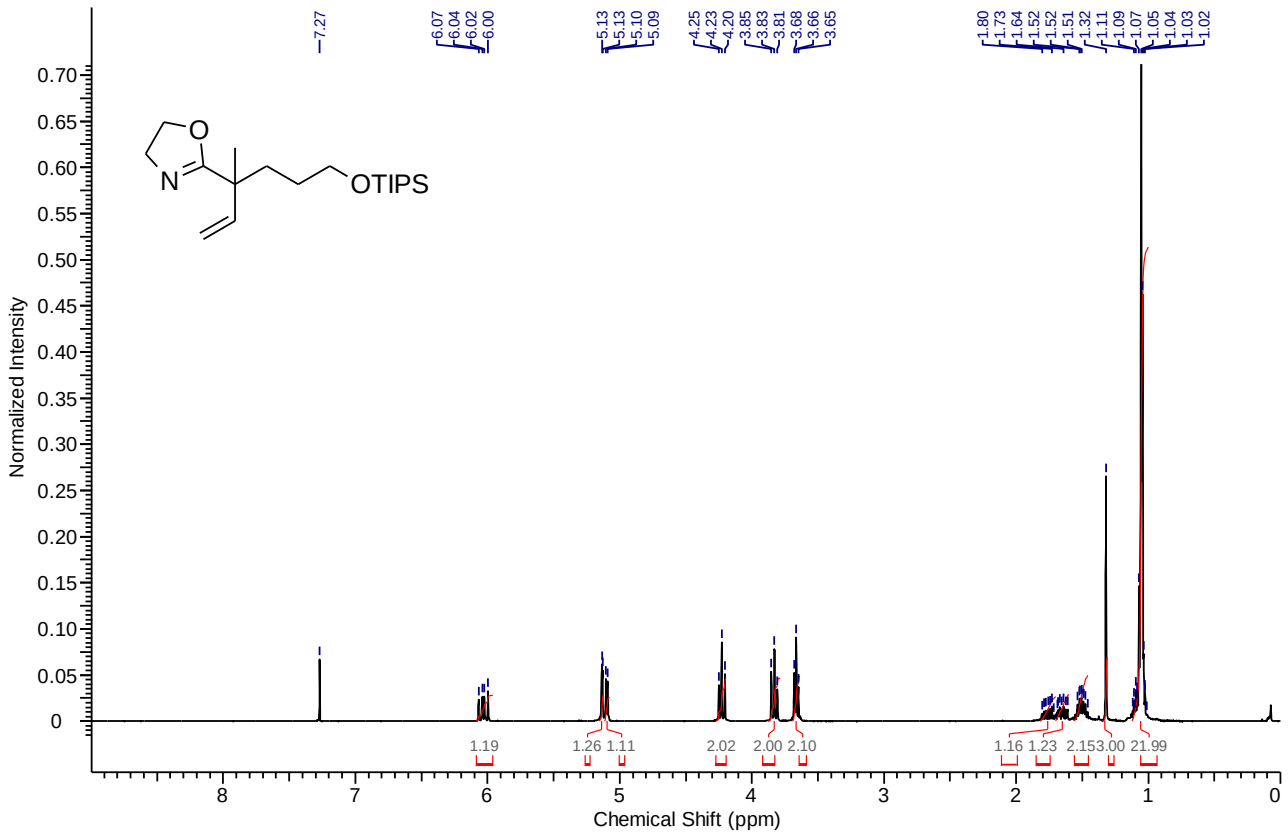


Figure S129. ^{1}H NMR spectrum of the compound **12** in $CDCl_3$, 400 MHz

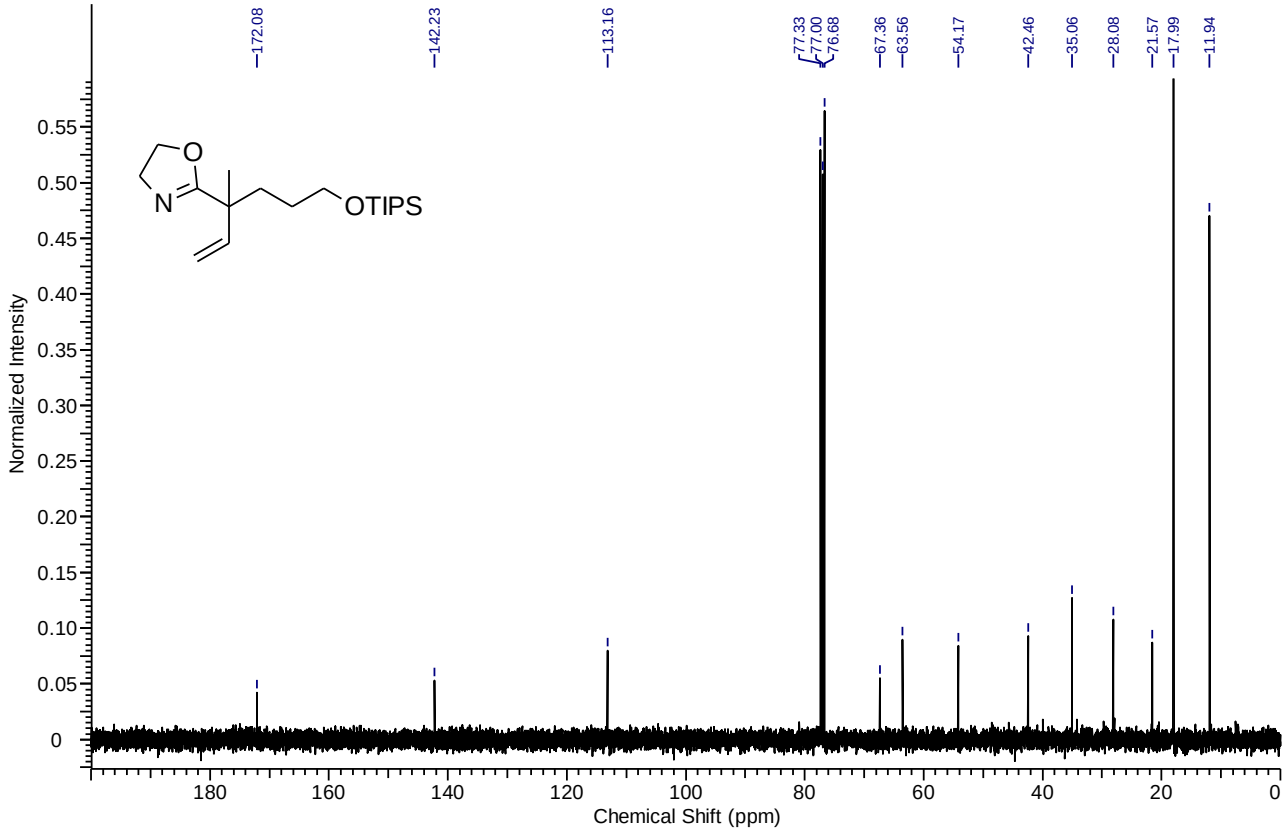


Figure S130. ^{13}C NMR spectrum of the compound **12** in $CDCl_3$, 100 MHz

9. 2D-NOESY proton NMR spectra of compound 4xa-1, 4xa-2 and ^{1}H NOESY correlations

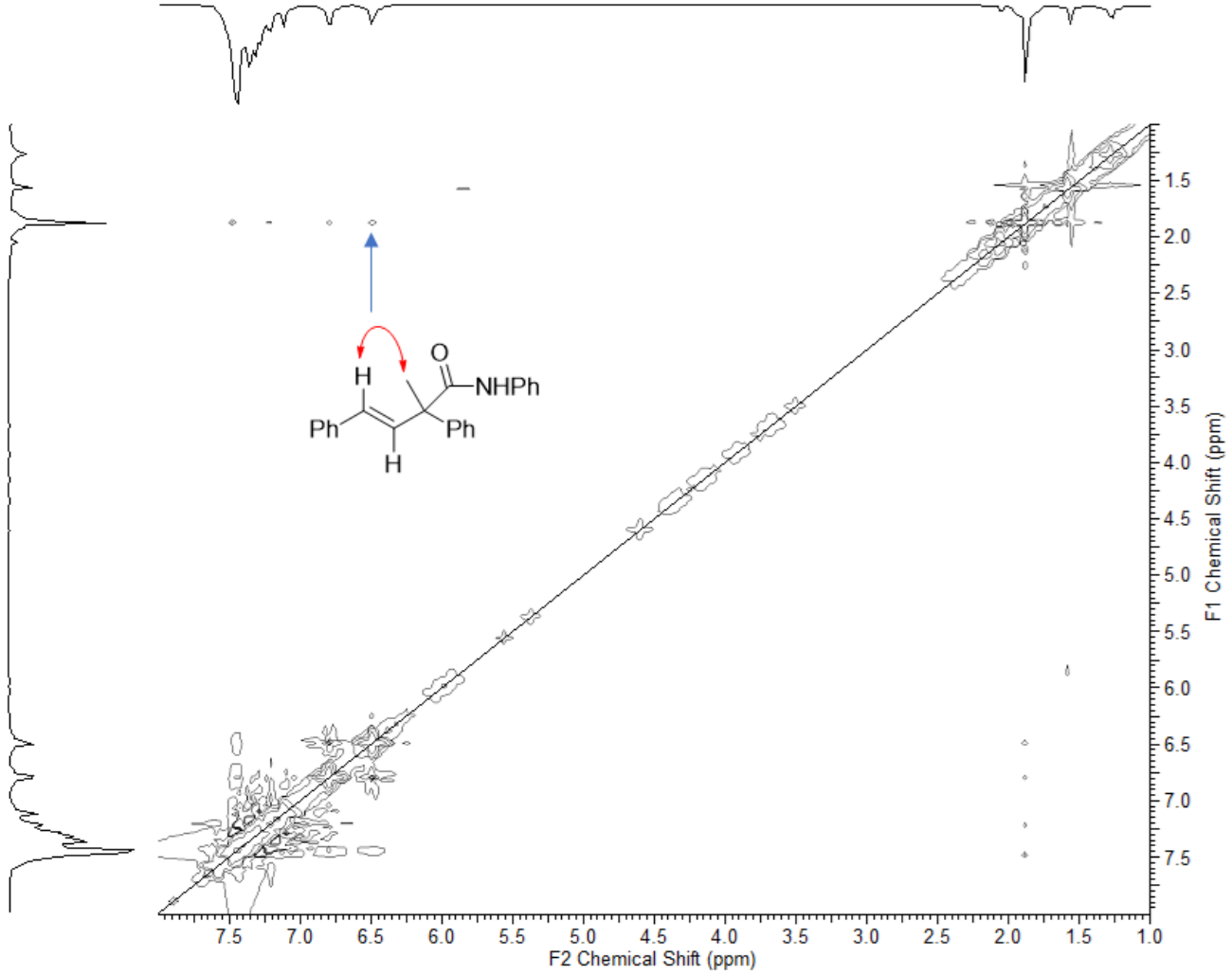


Figure S131. 2D NOESY spectrum of the compound **4xa-1** in $CDCl_3$

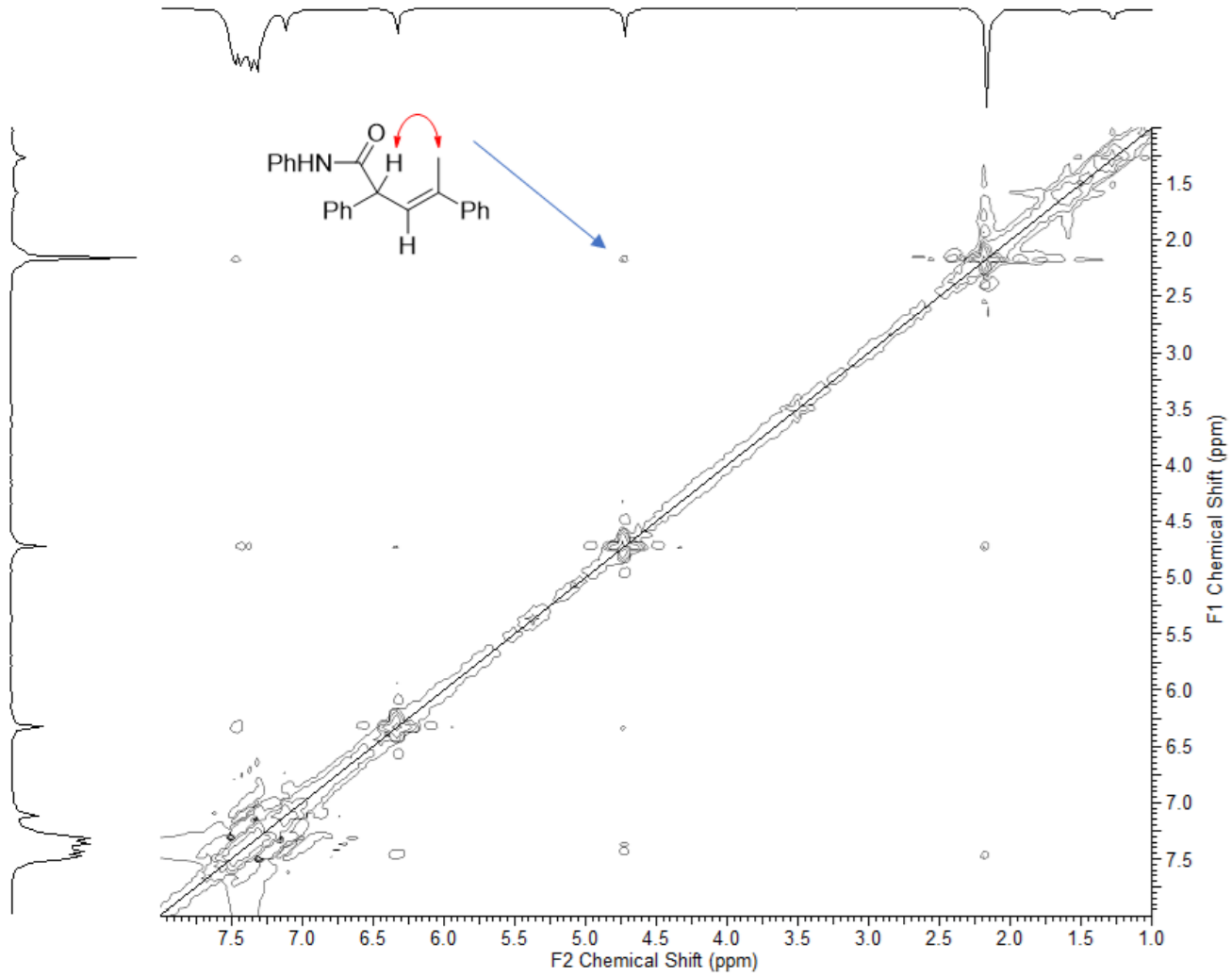


Figure S132. 2D NOESY spectrum of the compound **4xa-2** in $CDCl_3$