Supporting Information

Synthesis and Properties of 1-Acyl Triazenes

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1. Materials and methods

Unless otherwise stated, all reactions were carried out under inert atmosphere of dry N_2 using Schlenk or glovebox techniques. All reagents were purchased from commercial suppliers (Sigma Aldrich, Acros, TCI, VWR, Fluorochem, ABCR) and used without additional purification. Column chromatography of triazenes and 1-acyl triazenes was carried out using pre-prepared deactivated silica by triethylamine (3 vol%) in diethyl ether, removal of the solvent under reduced pressure, and drying at room temperature under (oil pump) vacuum overnight. *NMR spectra* were recorded at ambient temperature on a Bruker spectrometers: AvanceIII 400 MHz Prodigy probe 5 mm ICONNMR ATMA, Avance 400 MHz BBIz 5mm ATMA, Avance 500 MHz CPTCIxyz 5 mm, or Avance III HD 600 MHz CPTCIz 5 mm. Chemical shifts in ppm were aligned with respect to the residual peak of deuterated solvent.[1] *Electronspray-ionisation HRMS* data were acquired on a Q-Tof Ultima mass spectrometer (Waters) or a Q-Tof 6530 Accurate mass spectrometer (Agilent) operated in the positive ionization mode and fitted with a standard Z-spray ion source equipped with the Lock-Spray interface. Data from the Lock-Spray were used to calculate a correction factor for the mass scale and provide accurate mass information of the analyte. Data were processed using the MassLynx 4.1 software.

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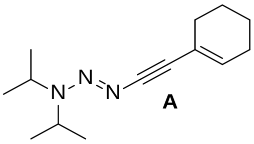
[1] Fulmer, G. R.; Miller, A. J. M.; Sherden, N. H.; Gottlieb, H. E.; Nudelman, A.; Stoltz, B. M.; Bercaw, J. E.; Goldberg, K. I. NMR Chemical Shifts of Trace Impurities: Common Laboratory Solvents, Organics, and Gases in Deuterated Solvents Relevant to the Organometallic Chemist. *Organometallics* **2010**, *29*, 2176–2179.

2. Synthesis of triazenes

Caution: Although we have not experienced any accidents, alkyl azides are potentially explosive and toxic compounds. Accordingly, their use, handling and storage should be carried out with appropriate precautions.

The triazenes were synthesized using an adapted method from Kiefer *et al.*[2] A typical procedure is as follows: under an inert atmosphere, the secondary amine (10 mmol) in THF (10 ml) was cooled down to –78 °C in a dry ice bath and *n*BuLi (4 ml, 2.5 M in hexanes) was added slowly. After stirring the reaction mixture for 5 min, the ice bath was removed. Once the reaction mixture was at room temperature, the *in-situ* formed lithium amide was subjected to an N_2O atmosphere (99.999%) overnight. Meanwhile the Grignard reagent was also prepared overnight by taking the desired terminal alkyne (12 mmol) in THF (10 ml) and adding EtMgBr (12 ml, 1.0 M in THF). Subsequently, the *in-situ* formed N_2O-adduct (a white precipitate) was subjected to N_2 atmosphere and the Grignard reagent was added slowly and carefully by not scratching the sides of the flask. The resulting clear mixture was heated for 5 h at 50 °C. After quenching the reaction mixture with saturated $MgSO_4$ (aq), the product was extracted with diethyl ether, followed by drying of the organic phase over $MgSO_4$ and evaporation of the solvent. The crude product was purified by column chromatography using deactivated silica and a gradient of pentane to pentane-diethyl ether (5%). The product was freeze-dried in pentane.


A

(*E*)-1-(Cyclohex-1-en-1-ylethynyl)-3,3-diisopropyltriaz-1-ene

10 mmol scale synthesis

Triazene **A** was prepared following the general procedure. Yield (yellow solid): 0.92 g (40%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.04 (tt, *J* = 3.9, 1.8 Hz, 1H, C*H*), 5.05 (p, *J* = 6.8 Hz, 1H, C*H*(CH_3)$_2$), 3.99 (p, *J* = 6.7 Hz, 1H, C*H*(CH_3)$_2$), 2.26 – 2.16 (m, 2H, C*H*$_2$), 2.16 – 2.06 (m, 2H, C*H*$_2$), 1.72 – 1.49 (m, 4H, C*H*$_2$, C*H*$_2$), 1.33 (d, *J* = 6.7 Hz, 6H, CH(C*H*$_3$)$_2$), 1.20 (d, *J* = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 132.38, 121.50, 91.59, 82.12, 77.48, 77.36, 77.16, 76.84, 50.18, 47.16, 29.98, 25.97, 23.51, 22.74, 21.87, 19.25. **HRMS** (ESI/QTOF) m/z: $[M + H]^+$ Calcd for $C_{14}H_{24}N_3^+$ 234.1965; Found 234.1967.

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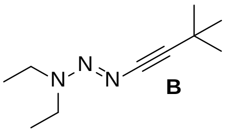
[2] Kiefer, G.; Riedel, T.; Dyson, P. J.; Scopelliti, R.; Severin, K. Synthesis of Triazenes with Nitrous Oxide. *Angew. Chemie - Int. Ed.* **2015**, *54*, 302–305.



B

(*E*)-1-(3,3-Dimethylbut-1-yn-1-yl)-3,3-diethyltriaz-1-ene

20 mmol scale synthesis

Triazene **B** was prepared following the general procedure. Yield (pale yellow solid/yellow oil): 0.76 g (21%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.02 – 3.30 (m, 4H, CH_2CH_3), 1.29 (m, 15H, CH_3, CH_2CH_3). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 88.33, 83.81, 77.48, 77.16, 76.84, 49.51, 41.46, 31.61, 28.15, 14.38, 11.07, 1.14. **HRMS** (ESI/QTOF) m/z: $[M + H]^+$ Calcd for $C_{10}H_{20}N_3^+$ 182.1652; Found 182.1655.

3. Synthesis of alkyl 1-acyl triazenes

Lewis acid catalysis

Different Lewis acids were explored, because they are known to catalyse the hydration of alkynes.[3] The reactions were followed by ^{1}H NMR spectroscopy. First, a solution of the triazene (0.1 mmol), H_2O (4 equiv), and the internal standard 1,2,3,4-tetramethylbenzene (0.5 equiv) in dioxane (0.2 M) was prepared. The reaction was initiated by adding the respective catalyst. After the given time, a 100 µl sample was removed from the reaction mixture and the solvent was evaporated. The yield was determined by NMR spectroscopy in $CDCl_3$. The results are summarized in Table S3.1.The reactions described in entries 8–12 were carried out using a laboratory microwave (MW).

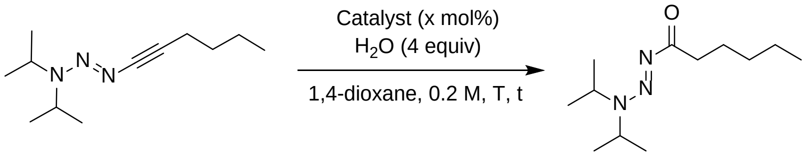


Table S3.1. Screening of reaction conditions.

Entry	Catalyst	Catalyst loading (x mol%)	T (°C)	Time (h)	Yield (%) [b]
1	$AgNTf_2$	40	80	1	64
2				2	75
3				4.25	>95
4	AgOTf	40	80	4.25	58
5	$AgSbF_4$	40	80	4.25	46
6	$AgBF_4$	40	80	4.25	62
7	$[I(pyridine)_2]BF_4$	40	80	4.25	Mixture of compounds
8	$AgNTf_2$	40	150 (MW)	0.25	>95
9	AgNTf2	20	120 (MW)	0.5	73
10	$AgNTf_2$	10	150 (MW)	0.5	>95
11	$AgNTf_2$	10	100 (MW)	2	65
12 [a]	x	x	150 (MW)	0.5	0

[a] No significant decomposition of the 1-alkynyl triazene was observed. [b] Yields were determined by ^{1}H NMR spectroscopy.

The conditions described under entry 8 gave the product in high yield, but the work-up of reactions on a preparative scale was found to be problematic. Therefore, a different approach was developed using acetic acid as catalyst.

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[3] Cabrero-Antonino, J. R.; Leyva-Pérez, A.; Corma, A. Regioselective Hydration of Alkynes by Iron(III) Lewis/Brønsted Catalysis. *Chem. Eur. J.* **2012**, *18*, 11107–11114.

Acetic acid catalysis

Inspired by the hydration of ynamides described by Bi and co-workers[4], we explored acetic acid catalysis as a means to hydrolyse alkynyl triazenes. All reactions were performed under air on a 0.2 mmol scale, and the products were isolated. For the work-up, the reaction mixture was diluted in 4 ml DCM, followed by washing with saturated $NaHCO_3$ (aq) three times (4 ml). After drying over $MgSO_4$, the solvent was evaporated and the yield was determined.

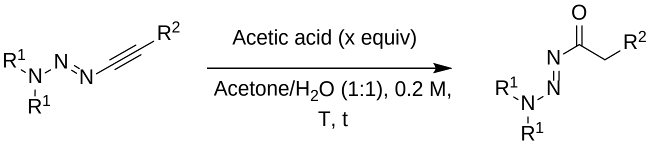
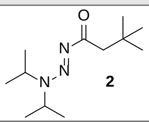
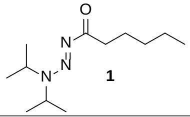
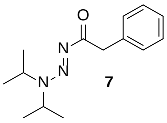
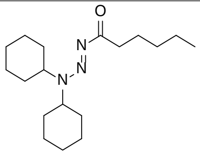


Table S3.2. Screening of reaction conditions.

Entry	**Triazene**	**Acetic acid (x equiv)**	**T (°C)**	**Time (h)**	**Yield (%) [a]**	**Product**
1	$R^1 = i$Pr, $R^2 = t$Bu	2.0	100	2	27	 2
2	$R^1 = i$Pr, $R^2 = t$Bu	0.5	50	4.5	82	
3	$R^1 = i$Pr, $R^2 = n$Bu	0.5	50	5	68	 1
4	$R^1 = i$Pr, $R^2 = n$Bu	0.5	70	5	58	
5	$R^1 = i$Pr, $R^2 = $ Ph	2.0	100	2	36	 7
6	$R^1 = i$Pr, $R^2 = $ Ph	0.5	50	4.5	15	
7	$R^1 = i$Pr, $R^2 = $ Ph	0.5	50	24	26	
8	$R^1 = $ Cy, $R^2 = n$Bu	0.5	50	24	8[b]	

[a] Isolated yields. [b] Poor yield, presumably because the starting material is poorly soluble in acetone/water.

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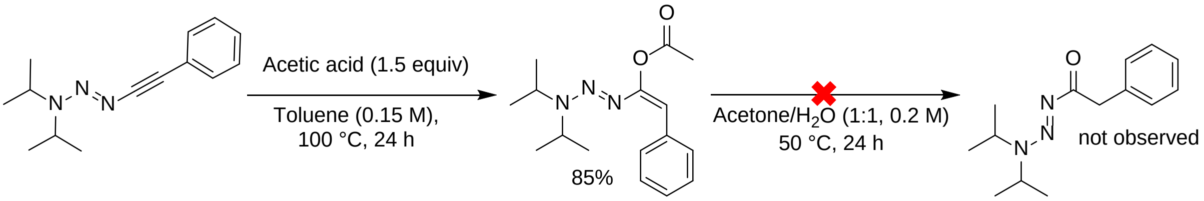
[4] Xu, S.; Liu, J.; Hu, D.; Bi, X. Metal-Free Hydroacyloxylation and Hydration Reactions of Ynamides: Synthesis of α-Acyloxyenamides and N-Acylsulfonamides. *Green Chem.* **2015**, *17*, 184–187.

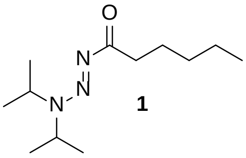
In order to examine if an acetic acid adduct is formed as an intermediate, a two-step reaction was performed (Scheme S3.1). First, the acetic acid adduct was synthesized and isolated according to a reported procedure.[5] The isolated product was then subjected to the reaction conditions (water/acetone, 50 °C, 24 h). The acetic acid adduct was stable under these conditions, and no 1-acyl triazene was formed.



Scheme S3.1. Attempted hydrolysis of an acetic acid adduct.

General procedure

Our brief screening indicated that 0.5 equivalents of acetic acid and a reaction temperature of 50 °C was suited for hydrolysis reactions of alkynyl triazenes (with the exception of the phenylethynyl triazene, for which 100 °C was better). Reactions with additional substrates were monitored by TLC. The work-up was performed by diluting the reaction mixture with ~15 ml DCM, followed by washing the organic layer with saturated $NaHCO_3$ (3 x ~10 ml). The organic phase was dried over $MgSO_4$, filtered, and the solvent was evaporated. The resulting crude product was purified by filtration over a short plug of silica (~5 cm) using a solvent gradient of pentane to diethyl ether.



1

(*E*)-1-(3,3-Diisopropyltriaz-1-en-1-yl)hexan-1-one

Triazene **1** was prepared following the general procedure using (*E*)-1-(hex-1-yn-1-yl)-3,3-diisopropyltriaz-1-ene (0.5 mmol) and acetic acid (0.5 equiv) in acetone/water (1:1, 2.5 ml). The reaction mixture was heated at 50 °C for 5 h. Yield (yellow oil): 77.5 mg (68%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.45 (hept, *J* = 6.8 Hz, 1H, C*H*(CH_3)$_2$), 4.12 (hept, *J* = 6.6 Hz, 1H, C*H*(CH_3)$_2$), 2.65 (t, 2H, CH_2), 1.64 (p, *J* = 7.4 Hz, 2H, CH_2), 1.36 (d, *J* = 6.7 Hz, 6H, CH(CH_3)$_2$), 1.33 – 1.26 (m, 4H, CH_2, CH_2), 1.21 (d, *J* = 6.8 Hz, 6H, CH(CH_3)$_2$), 0.87 (t, 3H, CH_3). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 188.15, 77.48, 77.16, 76.84, 50.66, 48.26, 34.50, 31.91, 25.14, 23.65, 22.58, 19.08, 14.08. **HRMS** (ESI/QTOF) m/z: $[M + H]^+$ Calcd for $C_{12}H_{26}N_3O^+$ 228.2070; Found 228.2069.

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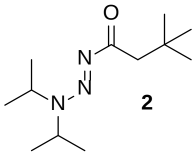
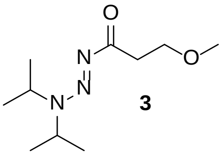
[5] Perrin, F. G.; Kiefer, G.; Jeanbourquin, L.; Racine, S.; Perrotta, D.; Waser, J.; Scopelliti, R.; Severin, K. 1-Alkynyltriazenes as Functional Analogues of Ynamides. *Angew. Chem. Int. Ed.* **2015**, *54*, 13393–13396.



2

(*E*)-1-(3,3-Diisopropyltriaz-1-en-1-yl)-3,3-dimethylbutan-1-one

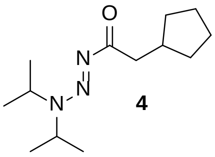
Triazene **2** was prepared following the general procedure using (*E*)-1-(3,3-dimethylbut-1-yn-1-yl)-3,3-diisopropyltriaz-1-ene (0.2 mmol) and acetic acid (0.5 equiv) in acetone/water (1:1, 1 ml). The reaction mixture was heated at 50 °C for 4.5 h. Yield (yellow oil, white crystals): 37.9 mg (82%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.46 (hept, *J* = 6.8 Hz, 1H, C*H*$(CH_3)_2$), 4.14 (hept, *J* = 6.6 Hz, 1H, C*H*$(CH_3)_2$), 2.64 (s, 2H, CH_2), 1.39 (d, *J* = 6.6 Hz, 6H, $CH(CH_3)_2$), 1.23 (d, *J* = 6.9 Hz, 6H, $CH(CH_3)_2$), 1.01 (s, 9H, CH_3). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 186.78, 77.48, 77.36, 77.16, 76.84, 50.79, 48.41, 46.84, 31.47, 30.41, 23.67, 19.15. **HRMS** (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_{12}H_{25}N_3NaO^+$ 250.1890; Found 250.1892. *Crystals were grown by keeping the yellow oil under vacuum at rt. White crystals. The R factor is 2.71% (< 3%).*



3

(*E*)-1-(3,3-Diisopropyltriaz-1-en-1-yl)-3-methoxypropan-1-one

Triazene **3** was prepared following the general procedure using (*E*)-3,3-diisopropyl-1-(3-methoxyprop-1-yn-1-yl)triaz-1-ene (0.2 mmol) and acetic acid (0.5 equiv) in acetone/water (1:1, 1 ml). The reaction mixture was heated at 50 °C for 4.5 h. Yield (yellow/orange oil): 32.1 mg (75%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.47 (hept, *J* = 6.8 Hz, 1H, C*H*$(CH_3)_2$), 4.13 (hept, *J* = 6.6 Hz, 1H, C*H*$(CH_3)_2$), 3.75 (t, *J* = 7.0 Hz, 2H, CH_2), 3.36 (s, 3H, CH_3), 2.99 (t, *J* = 7.0 Hz, 2H, CH_2), 1.37 (d, *J* = 6.5 Hz, 6H, $CH(CH_3)_2$), 1.22 (d, *J* = 6.9 Hz, 6H, $CH(CH_3)_2$). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 185.42, 77.48, 77.16, 76.84, 68.83, 58.89, 50.91, 48.64, 34.71, 23.64, 19.07. **HRMS** (ESI/QTOF) m/z: $[M + H]^+$ Calcd for $C_{10}H_{22}N_3O_2^+$ 216.1707; Found 216.1709.

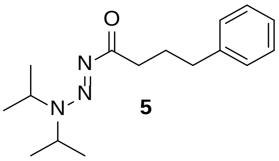


4

(*E*)-2-Cyclopentyl-1-(3,3-diisopropyltriaz-1-en-1-yl)ethan-1-one

Triazene **4** was prepared following the general procedure using (*E*)-1-(cyclopentylethynyl)-3,3-diisopropyltriaz-1-ene (0.2 mmol) and acetic acid (0.5 equiv) in acetone/water (1:1, 1 ml). The reaction mixture was heated at 50 °C for 19 h. Yield (yellow oil): 28.7 mg (60%). **^{1}H NMR** (400 MHz, $CDCl_3$)

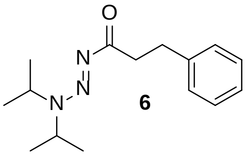
δ 5.47 (hept, *J* = 6.8 Hz, 1H, C*H*(CH$_3$)$_2$), 4.14 (hept, *J* = 6.6 Hz, 1H, C*H*(CH$_3$)$_2$), 2.70 (d, *J* = 7.3 Hz, 2H, C*H*$_2$), 2.42 – 2.16 (m, 1H, C*H*), 1.93 – 1.73 (m, 2H, C*H*$_2$), 1.70 – 1.46 (m, 4H, C*H*$_2$, C*H*$_2$), 1.39 (d, *J* = 6.6 Hz, 6H, CH(C*H*$_3$)$_2$), 1.24 (d, *J* = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$), 1.21 – 1.04 (m, 2H, C*H*$_2$). **^{13}C NMR** (101 MHz, CDCl$_3$) δ 187.75, 77.48, 77.36, 77.16, 76.84, 50.74, 48.33, 40.54, 37.05, 32.97, 25.15, 23.71, 19.16. Trace of pentane. **HRMS** (ESI/QTOF) m/z: [M + Na]$^+$ Calcd for $C_{13}H_{25}N_3NaO^+$ 262.1890; Found 262.1893.



5

(*E*)-1-(3,3-Diisopropyltriaz-1-en-1-yl)-4-phenylbutan-1-one

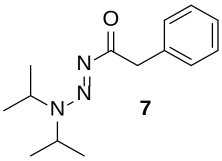
Triazene **5** was prepared following the general procedure using (E)-3,3-diisopropyl-1-(5-phenylpent-1-yn-1-yl)triaz-1-ene (1.5 mmol) and acetic acid (0.5 equiv) in acetone/water (1:1, 7.5 ml). The reaction mixture was heated at 50 °C until no significant further conversion was observed. Yield (yellow/orange oil): 237 mg (57%). **^{1}H NMR** (400 MHz, CDCl$_3$) δ 7.36 – 7.08 (m, 5H, *Ph*), 5.47 (hept, *J* = 6.8 Hz, 1H, C*H*(CH$_3$)$_2$), 4.12 (hept, *J* = 6.6 Hz, 1H, C*H*(CH$_3$)$_2$), 2.70 (dt, *J* = 11.9, 7.6 Hz, 4H, C*H*$_2$C*H*$_2$), 2.01 (p, *J* = 7.6 Hz, 2H, C*H*$_2$), 1.34 (d, *J* = 6.5 Hz, 6H, CH(C*H*$_3$)$_2$), 1.23 (d, *J* = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$). **^{13}C NMR** (101 MHz, CDCl$_3$) δ 187.69, 142.24, 128.69, 128.39, 125.88, 77.48, 77.36, 77.16, 76.84, 50.76, 48.40, 35.75, 33.93, 27.04, 23.67, 19.14. **HRMS** (ESI/QTOF) m/z: [M + Na]$^+$ Calcd for $C_{16}H_{25}N_3NaO^+$ 298.1890; Found 298.1895.



6

(*E*)-1-(3,3-Diisopropyltriaz-1-en-1-yl)-3-phenylpropan-1-one

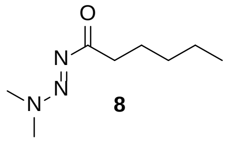
Triazene **6** was prepared following the general procedure using (*E*)-3,3-diisopropyl-1-(3-phenylprop-1-yn-1-yl)triaz-1-ene (0.2 mmol) and acetic acid (0.5 equiv) in acetone/water (1:1, 1 ml). The reaction mixture was heated at 50 °C for 4.5 h. Yield (yellow oil, white crystals forming): 29.0 mg (56%). **^{1}H NMR** (400 MHz, CDCl$_3$) δ 7.33 – 7.14 (m, 5H, *Ph*), 5.47 (hept, *J* = 6.8 Hz, 1H, C*H*(CH$_3$)$_2$), 4.13 (hept, *J* = 6.6 Hz, 1H, C*H*(CH$_3$)$_2$), 3.01 (s, 4H, C*H*$_2$, C*H*$_2$), 1.36 (d, *J* = 6.6 Hz, 6H, CH(C*H*$_3$)$_2$), 1.23 (d, *J* = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$). **^{13}C NMR** (101 MHz, CDCl$_3$) δ 186.98, 142.00, 128.60, 128.54, 126.05, 77.48, 77.36, 77.16, 76.84, 50.88, 48.54, 36.38, 31.56, 23.71, 19.13. **HRMS** (ESI/QTOF) m/z: [M + H]$^+$ Calcd for $C_{15}H_{24}N_3O^+$ 262.1914; Found 262.1919.



7

(*E*)-1-(3,3-Diisopropyltriaz-1-en-1-yl)-2-phenylethan-1-one

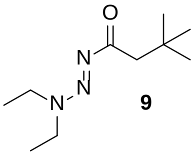
Triazene **7** was prepared following the general procedure using (*E*)-3,3-diisopropyl-1-(phenylethynyl)triaz-1-ene (0.2 mmol) and acetic acid (2 equiv) in acetone/water (1:1, 1 ml). The reaction mixture was heated in a closed vial at 100 °C for 2 h. Yield (white solid): 18.3 mg (36%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39 – 7.12 (m, 6H, *Ph*), 5.48 (hept, *J* = 13.5, 6.8 Hz, 1H, $CH(CH_3)_2$), 4.14 (hept, *J* = 6.5 Hz, 1H, $CH(CH_3)_2$), 4.04 (s, 2H, CH_2), 1.36 (d, *J* = 6.7 Hz, 6H, $CH(CH_3)_2$), 1.23 (d, *J* = 6.8 Hz, 6H, $CH(CH_3)_2$). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 185.11, 136.15, 129.33, 128.35, 126.32, 77.34, 77.02, 76.70, 50.88, 48.68, 41.59, 23.49, 18.98. **HRMS** (ESI/QTOF) m/z: $[M + H]^+$ Calcd for $C_{14}H_{22}N_3O^+$ 248.1757; Found 248.1759.



8

(*E*)-1-(3,3-Dimethyltriaz-1-en-1-yl)hexan-1-one

Triazene **8** was prepared following the general procedure using (*E*)-1-(hex-1-yn-1-yl)-3,3-dimethyltriaz-1-ene (0.5 mmol) and acetic acid (0.5 equiv) in acetone/water (1:1, 2.5 ml). The reaction mixture was heated at 50 °C for 5 h. Yield (yellow oil, pale white solid): 31 mg (36%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 3.63 (s, 3H, NCH_3), 3.28 (s, 3H, NCH_3), 2.67 (t, *J* = 7.6 Hz, 2H, CH_2), 1.68 (p, J = 7.3 Hz, 2H, CH_2), 1.43 – 1.20 (m, 4H, CH_2, CH_2), 1.01 – 0.77 (m, 3H, CH_3). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 187.22, 77.48, 77.36, 77.16, 76.84, 44.65, 37.37, 35.13, 31.78, 24.90, 22.61, 14.12. **HRMS** (nanochip-ESI/LTQ-Orbitrap) m/z: $[M + Na]^+$ Calcd for $C_8H_{17}N_3NaO^+$ 194.1264; Found 194.1264.



9

(*E*)-1-(3,3-Diethyltriaz-1-en-1-yl)-3,3-dimethylbutan-1-one

Triazene **9** was prepared following the general procedure using (*E*)-1-(3,3-dimethylbut-1-yn-1-yl)-3,3-diethyltriaz-1-ene (1.2 mmol) and acetic acid (0.5 equiv) in acetone/water (1:1, 6 ml). The reaction mixture was heated at 50 °C for 5 h. Yield (yellow oil, pale white solid): 158 mg (66%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 3.84 (dq, *J* = 11.8, 7.2 Hz, 4H, CH_2CH_3), 2.61 (s, 2H, CH_2), 1.37 (t, *J* = 7.2 Hz, 3H, CH_3), 1.20 (t, *J* = 7.2 Hz, 3H, CH_3), 1.01 (m, 9H, CH_3, CH_2CH_3). **^{13}C NMR** (101 MHz, $CDCl_3$) δ

186.18, 77.48, 77.16, 76.84, 50.67, 48.03, 42.98, 31.48, 30.32, 14.06, 10.90. **HRMS** (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_{10}H_{21}N_3NaO^+$ 222.1577; Found 222.1581.

4. Synthesis of olefinic 1-acyl triazenes

Reaction optimization

Stock solutions were prepared in a glove box using 1,2-dichloroethane as solvent. The concentrations of the stock solutions were chosen in a way that 100 µl of the 1-alkynyl triazene (0.1 mmol), 100 µl of the internal standard 1,3,5-trimethoxybenzene (1/3 equiv), 200 µl of pyridine *N*-oxide (1.1 equiv), and 100 µl of the pre-mixed catalyst solution of LAuX (5 mol%) and AgY (5 mol%) were employed. The aliquots of the stock solutions were added to a J-Young NMR tube containing a closed capillary with D_2O. A blank ^1H spectrum was recorded using a 500 MHz NMR spectrometer with a pre-set temperature and with suppression of the 1,2-dichloroethane solvent peak. Subsequently, the catalyst was added to the reaction mixture (t_0) and the shimming, gain and atma were optimized again. The reaction was then followed by NMR. After 15 min, the first ^1H NMR spectrum was recorded, followed by further spectra every 5 min. Yields were calculated based on the ratio of H(α) and the CH_2 of the starting material and the peaks of the internal standard at ~6 ppm. The *E/Z* ratio was determined by comparing the H(α) signal *J*-values: *E* ~10 Hz, *Z* ~15 Hz. The results are summarized in Table S4.1.

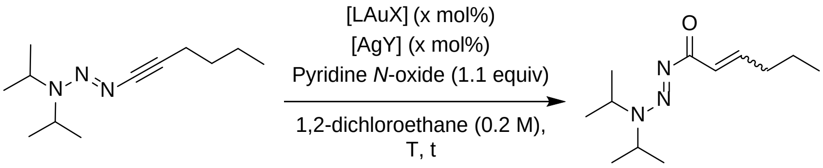


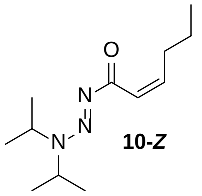
Table S4.1. Screening of reaction conditions.

	Catalyst (LAuX)	(mol%)	AgY	(mol%)	T (°C)	Time (min)	Yield (%) [c]	*E/Z* ratio [c]
1	(CyJohnPhos)AuCl	5	$AgNTf_2$	5	70	30	86	8.1
2	(JohnPhos)AuCl	5	$AgNTf_2$	5	70	30	97	8.9
3	(JohnPhos)AuCl	2.5	$AgNTf_2$	2.5	70	30	55	8.8
4	$(dppe)Au_2Cl_2$	2.5	$AgNTf_2$	2.5	70	30	15	5.5
5	$(Ipr)AuNTf_2$	2.5	x	2.5	70	30	31	8.0
6	$(PPh_3)AuCl$	2.5	$AgNTf_2$	2.5	70	30	15	6.0
7 [a]	(JohnPhos)AuCl	2.5	AgOTf	2.5	70	30	60	8.8
8 [a]	(JohnPhos)AuCl	5	AgOTf	5	70	30	86	9.4
9	(JohnPhos)AuCl	2.5	$AgSbF_6$	2.5	70	30	45	9.0
10	(JohnPhos)AuCl	5	$AgNTf_2$	5	50	30	88	8.6
11	(JohnPhos)AuCl	5	$AgNTf_2$	5	25	30	45	5.0
12	x	x	x	x	70	75	0	0
13	(JohnPhos)AuCl	5	x	x	70	30	0	0
14 [b]	x	x	$AgNTf_2$	5	70	30	11	4.0
15 [b]	x	x	AgOTf	5	70	30	32	5.0
16 [b]	x	x	AgOTf	20	70	30	11	3.9

[a] AgOTf does not dissolve well in DCE, which could explain the rate differences. [b] Black particles were observed when the silver salt was used as sole catalyst. [c] Yields and *E/Z* ratio based on ^1H NMR spectra.

General Procedure

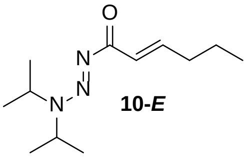
A solution of the respective triazene (0.5 mmol), pyridine *N*-oxide, (JohnPhos)AuCl (5 mol%), and $AgNTF_2$ (5 mol%) in dichloroethane (2.5 ml) was stirred at 70 °C in a glove box. After the indicated time, the reaction mixture was removed from the glove box, exposed to air, and the solvent was evaporated. The crude product was purified and the *E/Z*-isomers were separated by flash column chromatography over deactivated silica with a gradient of pentane to pentane/diethyl ether 25-30%. The product was freeze-dried in pentane.



10-*Z*

(*Z*)-1-((*E*)-3,3-Diisopropyltriaz-1-en-1-yl)hex-2-en-1-one

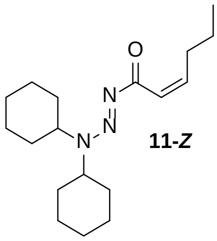
Triazene **10-*Z*** was prepared following the general procedure using (*E*)-1-(hex-1-yn-1-yl)-3,3-diisopropyltriaz-1-ene (0.5 mmol), JohnPhos AuCl (5 mol%), $AgNTf_2$ (5 mol%) and pyridine *N*-oxide (1.1 eq) in DCE (0.2 M). The reaction mixture was heated at 70 °C for 45 min. Yield (yellow oil): 4.3 mg (4%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.50 (d, *J* = 11.6, 1.7 Hz, 1H, C*H*), 6.20 (dt, *J* = 13.0, 6.0 Hz, 1H, C*H*), 5.46 (hept, 1H, $CH(CH_3)_2$), 4.13 (hept, 1H, $CH(CH_3)_2$), 2.77 – 2.61 (m, 2H, CH_2), 1.55 – 1.43 (m, 2H, CH_2), 1.39 (d, J = 6.6 Hz, 6H, $CH(CH_3)_2$), 1.25 (d, J = 6.8 Hz, 6H, $CH(CH_3)_2$), 0.95 (t, J = 7.3 Hz, 3H, CH_3). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 178.88, 148.41, 122.34, 50.94, 48.34, 31.67, 23.62, 22.70, 19.17, 13.99. **HRMS** (ESI/QTOF) m/z $[M + H]^+$ Calcd for $C_{12}H_{24}N_3O^+$ 226.1914; Found 226.1916.



10-*E*

(*E*)-1-((*E*)-3,3-Diisopropyltriaz-1-en-1-yl)hex-2-en-1-one

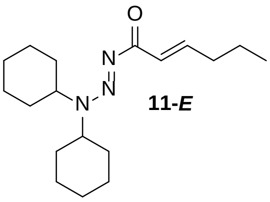
Triazene **10-*E*** was prepared following the general procedure using (*E*)-1-(hex-1-yn-1-yl)-3,3-diisopropyltriaz-1-ene (0.5 mmol), JohnPhos AuCl (5 mol%), $AgNTf_2$ (5 mol%) and pyridine *N*-oxide (1.1 eq) in DCE (0.2 M). The reaction mixture was heated at 70 °C for 45 min. Yield (yellow oil): 84.6 mg (75%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.07 (dt, *J* = 14.6, 7.0 Hz, 1H, C*H*), 6.58 (d, *J* = 15.5, 1.6 Hz, 1H, C*H*), 5.42 (hept, 1H, $CH(CH_3)_2$), 4.14 (hept, 1H, $CH(CH_3)_2$), 2.21 (q, *J* = 7.2 Hz, 2H, CH_2), 1.49 (q, *J* = 7.4 Hz, 2H, CH_2), 1.38 (d, 6H, $CH(CH_3)_2$), 1.23 (d, *J* = 6.8, 1.1 Hz, 6H, $CH(CH_3)_2$), 0.92 (t, 3H, CH_3). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 177.92, 148.32, 123.03, 77.39, 77.07, 76.76, 51.08, 48.42, 34.82, 23.41, 21.51, 18.98, 13.73. **HRMS** (ESI/QTOF) m/z $[M + H]^+$ Calcd for $C_{12}H_{24}N_3O^+$ 226.1914; Found 226.1916.



11-*Z*

(*Z*)-1-((*E*)-3,3-Dicyclohexyltriaz-1-en-1-yl)hex-2-en-1-one

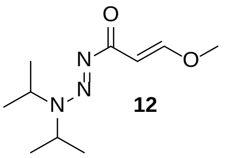
Triazene **11-*Z*** was prepared following the general procedure using (*E*)-3,3-dicyclohexyl-1-(hex-1-yn-1-yl)triaz-1-ene (0.5 mmol), JohnPhos AuCl (5 mol%), $AgNTf_2$ (5 mol%) and pyridine *N*-oxide (1.1 eq) in DCE (0.2 M). The reaction mixture was heated at 70 °C for 45 min. Yield (off-white solid): 9.5 mg (6%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.50 (d, *J* = 11.7 Hz, 1H, C*H*), 6.18 (dt, *J* = 11.7, 7.3 Hz, 1H, C*H*), 5.39 – 5.08 (m, 1H, Cy-C*H*), 3.87 – 3.54 (m, 1H, Cy-C*H*), 2.67 (q, *J* = 7.4 Hz, 2H, C*H*$_2$), 1.97 – 1.04 (m, 22H, Cy-C*H*$_2$, C*H*$_2$), 0.94 (t, *J* = 7.3 Hz, 3H, C*H*$_3$). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 179.15, 148.06, 122.46, 77.48, 77.16, 76.84, 59.44, 56.21, 34.16, 31.67, 29.47, 25.96, 25.39, 22.71, 13.99. **HRMS** (ESI/QTOF) m/z $[M + H]^+$ Calcd for $C_{18}H_{32}N_3O^+$ 306.2540; Found 306.2544.



11-*E*

(*E*)-1-((*E*)-3,3-Dicyclohexyltriaz-1-en-1-yl)hex-2-en-1-one

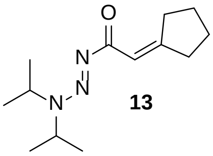
Triazene **11-*E*** was prepared following the general procedure using (*E*)-3,3-dicyclohexyl-1-(hex-1-yn-1-yl)triaz-1-ene (0.5 mmol), JohnPhos AuCl (5 mol%), $AgNTf_2$ (5 mol%) and pyridine *N*-oxide (1.1 eq) in DCE (0.2 M). The reaction mixture was heated at 70 °C for 45 min. Yield (off-white solid): 106 mg (70%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.08 (dt, *J* = 14.2, 7.0 Hz, 1H, C*H*), 6.61 (d, *J* = 15.6 Hz, 1H, C*H*), 5.50 – 4.97 (m, 1H, Cy-C*H*), 3.91 – 3.52 (m, 1H, Cy-C*H*), 2.24 (q, *J* = 7.3 Hz, 2H, C*H*$_2$), 2.02 – 1.07 (m, 22H, Cy-C*H*$_2$, C*H*$_2$), 0.95 (t, *J* = 7.4 Hz, 3H, C*H*$_3$). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 178.41, 148.30, 123.13, 77.48, 77.16, 76.84, 59.63, 56.38, 35.01, 34.15, 29.45, 29.45, 25.97, 25.97, 25.39, 25.39, 21.71, 13.92. **HRMS** (ESI/QTOF) m/z $[M + H]^+$ Calcd for $C_{18}H_{32}N_3O^+$ 306.2540; Found 306.2544. *Crystals were grown by dissolving in small amount of pentane and leaving in the fridge overnight.*



12

(*E*)-1-((*E*)-3,3-Diisopropyltriaz-1-en-1-yl)-3-methoxyprop-2-en-1-one

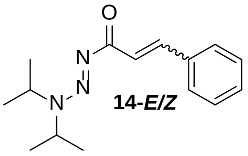
Triazene **12** was prepared following the general procedure using (*E*)-3,3-diisopropyl-1-(3-methoxyprop-1-yn-1-yl)triaz-1-ene (0.5 mmol), JohnPhos AuCl (5 mol%), $AgNTf_2$ (5 mol%) and pyridine *N*-oxide (1.1 eq) in DCE (0.2 M). The reaction mixture was heated at 70 °C for 60 min. Purification, gradient up to 80% diethyl ether. Yield (white solid): 63.0 mg (58%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 12.5 Hz, 1H, C*H*), 5.98 (d, *J* = 12.4 Hz, 1H, C*H*), 5.39 (hept, 1H, $CH(CH_3)_2$), 4.15 (hept, 1H, $CH(CH_3)_2$), 3.73 (s, 3H, CH_3), 1.39 (d, *J* = 6.5 Hz, 6H, $CH(CH_3)_2$), 1.25 (d, *J* = 6.8 Hz, 6H, $CH(CH_3)_2$). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 178.81, 163.62, 98.39, 77.48, 77.16, 76.84, 57.64, 51.14, 48.48, 23.56, 19.14. **HRMS** (nanochip-ESI/LTQ-Orbitrap) m/z $[M + H]^+$ Calcd for $C_{10}H_{20}N_3O_2^+$ 214.1550; Found 214.1550.



13

(*E*)-2-Cyclopentylidene-1-(3,3-diisopropyltriaz-1-en-1-yl)ethan-1-one

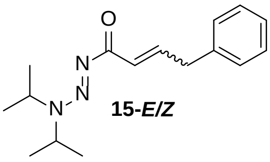
Triazene **13** was prepared following the general procedure using (*E*)-1-(cyclopentylethynyl)-3,3-diisopropyltriaz-1-ene (0.5 mmol), JohnPhos AuCl (5 mol%), $AgNTf_2$ (5 mol%) and pyridine *N*-oxide (1.1 eq) in DCE (0.2 M). The reaction mixture was heated at 70 °C for 90 min. Yield (yellow oil): 67.1 mg (56%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.55 (s, 1H, C*H*), 5.41 (hept, *J* = 6.8 Hz, 1H, $CH(CH_3)_2$), 4.12 (hept, *J* = 13.2, 6.6 Hz, 1H, $CH(CH_3)_2$), 2.98 – 2.81 (m, 2H, CH_2), 2.57 – 2.41 (m, 2H, CH_2), 1.73 (p, *J* = 6.9 Hz, 2H, CH_2), 1.64 (p, *J* = 6.8 Hz, 2H, CH_2), 1.38 (d, 6H, $CH(CH_3)_2$), 1.21 (d, *J* = 6.8 Hz, 6H, $CH(CH_3)_2$). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 178.31, 168.82, 113.62, 77.48, 77.16, 76.84, 50.67, 47.96, 36.63, 33.35, 26.70, 25.60, 23.56, 19.10. Trace of starting material. **HRMS** (nanochip-ESI/LTQ-Orbitrap) m/z: $[M + H]^+$ Calcd for $C_{13}H_{24}N_3O^+$ 238.1914; Found 238.1910.



14-*E/Z*

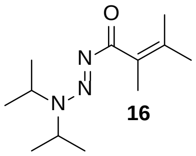
(*E*)/(*Z*)-1-((*E*)-3,3-Diisopropyltriaz-1-en-1-yl)-3-phenylprop-2-en-1-one (**14-*E/Z*** ~ 10:1)

Triazene **14** was prepared following the general procedure using (*E*)-3,3-diisopropyl-1-(3-phenylprop-1-yn-1-yl)triaz-1-ene (0.5 mmol), JohnPhos AuCl (5 mol%), $AgNTf_2$ (5 mol%) and pyridine *N*-oxide (1.1 eq) in DCE (0.2 M). The reaction mixture was heated at 70 °C for 60 min. Mixed fraction **14-*E/Z*** (yellow oil): 8.5 mg (4%), *E*/*Z* = 1:1. Yield **14-*E*** (yellow solid): 82.7 mg (46%). **^{1}H NMR** (400 MHz, CDCl$_3$) δ 7.82 (d, J = 16.0 Hz, 1H, C*H*), 7.55 (dd, J = 7.6, 2.0 Hz, 2H, *Ph*), 7.39 – 7.29 (m, 3H, *Ph*), 7.22 (d, J = 2.8 Hz, 1H, C*H*), 5.46 (hept, 1H, C*H*(CH$_3$)$_2$), 4.18 (hept, 1H, C*H*(CH$_3$)$_2$), 1.42 (d, J = 6.6 Hz, 6H, CH(C*H*$_3$)$_2$), 1.27 (d, J = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$). **^{13}C NMR** (101 MHz, CDCl$_3$) δ 178.00, 143.80, 135.81, 129.93, 128.93, 128.24, 120.38, 77.48, 77.36, 77.16, 76.84, 51.50, 48.91, 23.62, 19.18. **HRMS** (ESI/QTOF) m/z [M + H]$^+$ Calcd for $C_{15}H_{22}N_3O^+$ 260.1757; Found 260.1759.


15-*E/Z*

(*E*)/(*Z*)-1-((*E*)-3,3-Diisopropyltriaz-1-en-1-yl)-4-phenylbut-2-en-1-one (**15-*E/Z*** ~ 2:1)

Triazene **15** was prepared following the general procedure using (*E*)-3,3-diisopropyl-1-(3-phenylprop-1-yn-1-yl)triaz-1-ene (0.5 mmol), JohnPhos AuCl (5 mol%), AgNTf$_2$ (5 mol%) and pyridine *N*-oxide (1.1 eq) in DCE (0.2 M). The reaction mixture was heated at 70 °C for 90 min. For the purification, a gradient up to 50% diethyl ether was used. Yield (orange oil): 77.6 mg (59%). Mixture of *E*/Z ~ 2:1. **^{1}H NMR** (400 MHz, CDCl$_3$) δ 7.34 – 7.10 (m, 5H, *E/Z-Ph*), 6.59 – 6.32 (m, 1H, *E/Z*-C*H*), 5.52 – 5.31 (m, 1H, *E/Z*-C*H*(CH$_3$)$_2$), 4.19 – 4.01 (m, 1H, *E/Z*-C*H*(CH$_3$)$_2$), 3.59 (d, J = 5.8 Hz, 1H, *E*-C*H*), 3.52 (d, J = 6.7, 1.6 Hz, 1H, *Z*-C*H*), 1.37 (d, J = 6.5 Hz, 6H, *E*-CH(C*H*$_3$)$_2$), 1.30 (d, J = 6.6 Hz, 6H, *Z*-CH(C*H*$_3$)$_2$), 1.20 (d, J = 6.9, 5.2 Hz, 6H, *E/Z*-CH(C*H*$_3$)$_2$). **^{13}C NMR** (101 MHz, CDCl$_3$) δ 185.23, 177.70, 146.13, 138.42, 137.38, 132.49, 128.91, 128.54, 128.45, 127.15, 126.42, 126.19, 124.30, 124.13, 77.36, 77.24, 77.04, 76.72, 51.13, 50.89, 48.68, 48.54, 39.00, 38.89, 23.63, 23.45, 23.37, 19.00. **HRMS** (ESI/QTOF) m/z [M + H]$^+$ Calcd for $C_{16}H_{24}N_3O^+$ 274.1914; Found 274.1918.


16

(*E*)-1-(3,3-Diisopropyltriaz-1-en-1-yl)-2,3-dimethylbut-2-en-1-one

Triazene **16** was prepared following the general procedure using (*E*)-1-(3,3-dimethylbut-1-yn-1-yl)-3,3-diisopropyltriaz-1-ene (0.5 mmol), JohnPhos AuCl (5 mol%), AgNTf$_2$ (5 mol%) and pyridine *N*-oxide (1.1 eq) in DCE (0.2 M). The reaction mixture was heated at 70 °C for 45 min. Yield (off-white solid): 101.5 mg (90%). **^{1}H NMR** (400 MHz, CDCl$_3$) δ 5.43 (hept, J = 6.9 Hz, 1H, C*H*(CH$_3$)$_2$), 4.13 (hept, J = 6.7 Hz, 1H, C*H*(CH$_3$)$_2$), 1.84 (s, 3H, C*H*$_3$), 1.74 (s, 3H, C*H*$_3$), 1.68 (s, 3H, C*H*$_3$), 1.34 (d, J = 6.6 Hz, 6H, CH(C*H*$_3$)$_2$), 1.25 (d, J = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$). **^{13}C NMR** (101 MHz, CDCl$_3$) δ 186.50, 132.36, 128.68, 77.48, 77.36, 77.16, 76.84, 51.06, 48.66, 23.49, 22.77, 20.16, 19.19, 16.84. **HRMS** (LTQ-Orbitrap) m/z [M + H]$^+$ Calcd for $C_{12}H_{24}N_3O^+$ 226.1914; Found 226.1914. *Crystals were grown by dissolving the compound in a minimal amount of pentane and keeping it the fridge (5 °C) overnight.*

5. Synthesis of 1,2-diketo triazenes

Reaction optimization

The reaction mixtures were prepared under N_2 in a J-Young NMR tube using 1,2,4,5-tetramethylbenzene as internal standard. The reactions were followed by recording ^1H spectra using a 400 MHz NMR spectrometer. The results are summarized in Table S5.1.

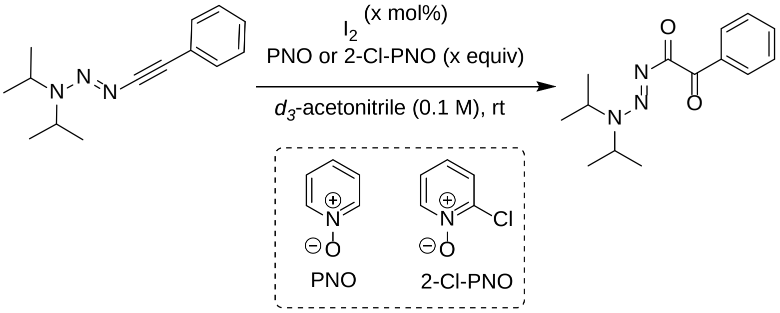


Table S5.1. Screening of reaction conditions.

		I_2 (x mol%)	Pyridine *N*-oxide (x equiv)	Time (min)	Yield (%) [a]
1	R = Ph	10 mol%	2-Cl-PNO (3 equiv)	50	36
2	R = Ph	20 mol%	2-Cl-PNO (3 equiv)	50	77
3	R = Ph	50 mol%	2-Cl-PNO (3 equiv)	50	94
4	R = Ph	20 mol%	PNO (3 equiv)	50	55
5	R = Ph	20 mol%	x	30	0
6	R = nBu	50 mol%	2-Cl-PNO (3 equiv)	50	Mixture of products, trace of starting material

[a] Yields based on ^1H NMR spectra.

General Procedure

Conditions **A**: A solution of the respective 1-alkynyl triazene (1 equiv), 2-chloropyridine *N*-oxide[6] (3 equiv), and I_2 (50 mol%) in acetonitrile (0.1 M) under N_2 was stirred for 50 min. Subsequently, the mixture was exposed to air and the solvent was evaporated. The crude product was purified by flash column chromatography over deactivated silica with a gradient of pentane to pentane/diethyl ether 50%. The resulting product was freeze-dried in pentane.

Conditions **B**: The general procedure was adapted by using the following conditions: (JohnPhos)AuCl (10 mol%), $AgNTf_2$ (10 mol%), pyridine *N*-oxide (2.2 equiv).

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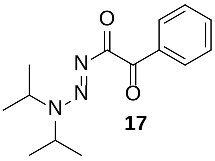
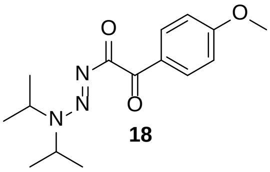
[6] Bought from commercially available sources or synthesized using reported procedures Schießl, J. *et al. Adv. Synth. Catal.* **2019**, 361, 725–738.



17

(*E*)-1-(3,3-Diisopropyltriaz-1-en-1-yl)-2-phenylethane-1,2-dione

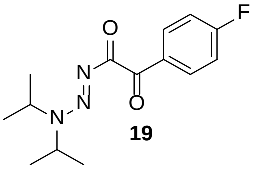
Triazene **17** was synthesized following procedure **A** or **B**, using (*E*)-3,3-diisopropyl-1-(phenylethynyl)triaz-1-ene (1 or 0.5 mmol, respectively). **A**: For purification, gradient up to 70% diethyl ether. **B:** 1.5 h reaction time. Yield **A** (pale yellow solid): 223 mg (85%). Yield **B** (white crystalline solid): 80.3 mg (61%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.94 – 7.77 (m, 2H, *Ph*), 7.64 – 7.52 (m, 1H, *Ph*), 7.52 – 7.40 (m, 2H, *Ph*), 5.52 (hept, *J* = 6.8 Hz, 1H, C*H*(CH_3)$_2$), 4.08 (hept, *J* = 6.6 Hz, 1H, C*H*(CH_3)$_2$), 1.28 (d, *J* = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$), 1.04 (d, *J* = 6.6 Hz, 6H, CH(C*H*$_3$)$_2$). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 196.51, 181.63, 134.07, 133.96, 129.21, 128.88, 77.48, 77.36, 77.16, 76.84, 52.31, 50.21, 23.08, 18.99. **HRMS** (nanochip-ESI/LTQ-Orbitrap) m/z: $[M + H]^+$ Calcd for $C_{14}H_{20}N_3O_2^+$ 262.1550; Found 262.1547.



18

(*E*)-1-(3,3-Diisopropyltriaz-1-en-1-yl)-2-(4-methoxyphenyl)ethane-1,2-dione

Triazene **18** was synthesized following procedure **A** using (*E*)-3,3-diisopropyl-1-((4-methoxyphenyl)ethynyl)triaz-1-ene (0.75 mmol). Purification with a gradient of 5% to 75% diethyl ether. Product was freeze-dried in diethyl ether/pentane and some dichloromethane. Yield **A** (yellow solid): 188.2 mg (86%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.91 – 7.72 (m, 2H, *Ph*), 7.01 – 6.84 (m, 2H, *Ph*), 5.51 (hept, *J* = 6.8 Hz, 1H, C*H*(CH_3)$_2$), 4.09 (hept, *J* = 6.6 Hz, 1H, C*H*(CH_3)$_2$), 3.86 (s, 3H, C*H*$_3$), 1.28 (d, J = 6.9 Hz, 6H, CH(C*H*$_3$)$_2$), 1.07 (d, *J* = 6.5 Hz, 6H, CH(C*H*$_3$)$_2$). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 194.94, 181.92, 164.20, 131.61, 127.25, 114.15, 77.48, 77.16, 76.84, 55.66, 52.26, 50.08, 23.15, 18.99. **HRMS** (ESI/QTOF) m/z: $[M + H]^+$ Calcd for $C_{15}H_{22}N_3O_3^+$ 292.1656; Found 292.1661. *Crystals were grown by dissolving in warm diethyl ether (40 °C), letting cool to room temperature, followed by slow evaporation of solvent.*

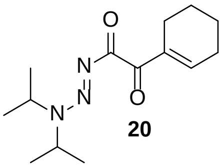


19

(*E*)-1-(3,3-Diisopropyltriaz-1-en-1-yl)-2-(4-fluorophenyl)ethane-1,2-dione

Triazene **19** was synthesized following procedure **A** using (*E*)-1-((4-fluorophenyl)ethynyl)-3,3-diisopropyltriaz-1-ene (0.75 mmol). Yield (yellow solid): 171.9 mg (82%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88 (dd, *J* = 8.8, 5.4 Hz, 2H, *Ph*), 7.15 (dd, *J* = 8.6 Hz, 2H, *Ph*), 5.51 (hept, *J* = 6.8 Hz, 1H, C*H*(CH_3)$_2$), 4.11 (hept, *J* = 6.5 Hz, 1H, C*H*(CH_3)$_2$), 1.29 (d, *J* = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$), 1.07 (d, *J* = 6.5

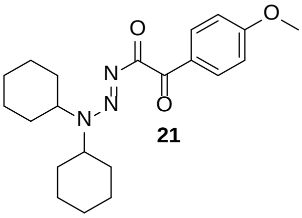
Hz, 6H, CH(C*H*$_3$)$_2$). **^{13}C NMR** (101 MHz, CDCl$_3$) δ 194.74, 181.27, 167.52, 164.97, 131.93, 131.84, 130.59, 130.56, 116.33, 116.11, 77.48, 77.16, 76.84, 23.14, 18.99. **HRMS** (nanochip-ESI/LTQ-Orbitrap) m/z: $[M + H]^+$ Calcd for $C_{14}H_{19}FN_3O_2^+$ 280.1456; Found 280.1458.



20

(*E*)-1-(Cyclohex-1-en-1-yl)-2-(3,3-diisopropyltriaz-1-en-1-yl)ethane-1,2-dione

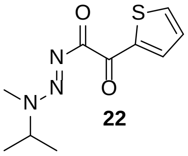
Triazene **20** was synthesized following procedure **B** using (*E*)-1-(cyclohex-1-en-1-ylethynyl)-3,3-diisopropyltriaz-1-ene (0.5 mmol). Reaction time of 1.5 h. Only conditions **B** gave the desired product. Yield (pastel pink crystalline solid): 56.1 mg (42%). **^{1}H NMR** (400 MHz, CDCl$_3$) δ 6.68 (tt, *J* = 3.7, 1.6 Hz, 1H, C*H*), 5.48 (hept, *J* = 6.9 Hz, 1H, C*H*(CH$_3$)$_2$), 4.16 (hept, *J* = 6.5 Hz, 1H, C*H*(CH$_3$)$_2$), 2.37 – 2.16 (m, 4H, C*H$_2$*, C*H$_2$*), 1.76 – 1.58 (m, 4H, C*H$_2$*, C*H$_2$*), 1.27 (d, *J* = 7.8, 6.7 Hz, 12H, CH(C*H*$_3$)$_2$, CH(C*H*$_3$)$_2$). **^{13}C NMR** (101 MHz, CDCl$_3$) δ 197.79, 182.39, 147.13, 137.23, 77.48, 77.36, 77.16, 76.84, 52.06, 49.91, 26.50, 23.37, 22.02, 21.84, 21.77, 19.02. **HRMS** (ESI/QTOF) m/z: $[M + H]^+$ Calcd for $C_{14}H_{24}N_3O_2^+$ 266.1863; Found 266.1864. *Crystals were grown by dissolving in warm diethyl ether (40 °C) and left at rt >48 h.*



21

(*E*)-1-(3,3-Dicyclohexyltriaz-1-en-1-yl)-2-(4-methoxyphenyl)ethane-1,2-dione

Triazene **21** was synthesized following procedure **A** using (*E*)-3,3-dicyclohexyl-1-((4-methoxyphenyl)ethynyl)triaz-1-ene (0.5 mmol). Reaction time of 140 min. Yield (pale yellow solid): 150 mg (81%). **^{1}H NMR** (400 MHz, CDCl$_3$) δ 7.96 – 7.65 (m, 2H, C*H$_2$*), 7.08 – 6.77 (m, 2H, C*H$_2$*), 5.41 – 5.13 (m, 1H, *Cy*-C*H*), 3.87 (s, 3H, C*H$_3$*), 3.62 (dd, J = 10.9, 3.4 Hz, 1H, *Cy*-C*H*), 1.95 – 0.77 (m, 20H, *Cy*-C*H$_2$*). **^{13}C NMR** (101 MHz, CDCl$_3$) δ 195.10, 182.15, 164.16, 131.61, 127.38, 114.14, 77.48, 77.36, 77.16, 76.84, 60.58, 57.82, 55.69, 33.59, 29.28, 25.59, 25.36, 25.22, 24.96. **HRMS** (ESI/QTOF) m/z: $[M + H]^+$ Calcd for $C_{21}H_{30}N_3O_3^+$ 372.2282; Found 372.2277. *Crystals were grown by dissolving in warm diethyl ether (40 °C), letting cool to room temperature, followed by slow evaporation of solvent.*



22

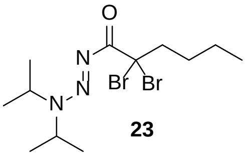
(*E*)-1-(3-Isopropyl-3-methyltriaz-1-en-1-yl)-2-(thiophen-2-yl)ethane-1,2-dione

Triazene **22** was synthesized following procedure **A** using (*E*)-3-isopropyl-3-methyl-1-(thiophen-2-ylethynyl)triaz-1-ene (0.32 mmol). Reaction time of 60 min. Yield (brown solid): 64 mg (82%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.09 (dd, *J* = 2.9, 1.1 Hz, 1H, *thiophene*), 7.55 (dd, *J* = 5.1, 1.2 Hz, 1H, *thiophene*), 7.34 (dd, *J* = 5.1, 2.9 Hz, 1H, *thiophene*), 4.29 – 4.01 (m, 1H, $CH(CH_3)_2$), 3.34 (s, 3H, CH_3), 1.28 (d, *J* = 6.7 Hz, 6H, $CH(CH_3)_2$). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 188.36, 180.04, 139.30, 135.48, 126.92, 126.90, 77.48, 77.36, 77.16, 76.84, 60.43, 34.72, 20.60. **HRMS** (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_{10}H_{13}N_3NaO_2S^+$ 262.0621; Found 262.0623.

6. Synthesis of α-halogenated 1-acyl triazenes

General Procedure

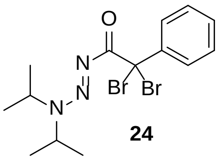
A solution of the respective triazene (1 equiv) in a mixture of acetonitrile/water (20:1, 0.35 M) was cooled to 0 °C in an ice bath. NXS (X = Br or Cl; 2 equiv) was added, and the mixture was left stirring for the indicated time and temperature. Subsequently, it was diluted with DCM and purified by flash column chromatography on deactivated silica. The final product was freeze-dried in pentane or DCM.



23

(*E*)-2,2-Dibromo-1-(3,3-diisopropyltriaz-1-en-1-yl)hexan-1-one

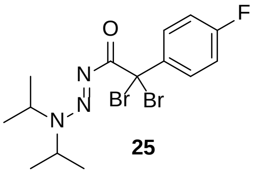
Triazene **23** was synthesized using (*E*)-1-(hex-1-yn-1-yl)-3,3-diisopropyltriaz-1-ene (0.72 mmol) following the general procedure. Reaction time 10 min, pentane/diethyl ether (3:1) as eluent. Yield (yellow oil): 222 mg (80%). **^{1}H NMR** (400 MHz, $CDCl_3$). δ 4.97 (hept, *J* = 6.9 Hz, 1H, C*H*(CH_3)$_2$), 4.29 (hept, *J* = 6.7 Hz, 1H, C*H*(CH_3)$_2$), 2.74 – 2.59 (m, 2H, C*H*$_2$), 1.75 – 1.59 (m, 2H, C*H*$_2$), 1.52 – 1.34 (m, 14H, C*H*$_2$, CH(C*H*$_3$)$_2$), 0.94 (t, *J* = 7.3 Hz, 3H, C*H*$_3$). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 176.11, 68.51, 54.93, 51.67, 46.91, 30.05, 22.74, 22.34, 19.02, 14.08. **HRMS** (ESI/QTOF) m/z: $[M + H]^+$ Calcd for $C_{12}H_{24}Br_2N_3O^+$ 384.0281; Found 384.0281.



24

(*E*)-2,2-Dibromo-1-(3,3-diisopropyltriaz-1-en-1-yl)-2-phenylethan-1-one

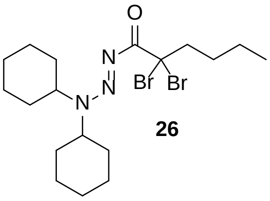
Triazene **24** was synthesized using (*E*)-3,3-diisopropyl-1-(phenylethynyl)triaz-1-ene (0.157 mmol) following the general procedure. Reaction time 20 min, gradient of pentane/diethyl ether (9:1 to 3:1). Yield (yellow oil): 46 mg (72%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.83 – 7.62 (m, 2H, C*H*), 7.33 (td, *J* = 7.1, 6.2, 1.3 Hz, 2H, C*H*), 7.29 – 7.22 (m, 1H, C*H*), 4.77 (hept, *J* = 6.8 Hz, 1H, C*H*(CH_3)$_2$), 4.20 (hept, *J* = 6.7 Hz, 1H, C*H*(CH_3)$_2$), 1.29 (d, *J* = 6.7 Hz, 6H, CH(C*H*$_3$)$_2$), 1.17 (d, *J* = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 175.47, 142.13, 128.75, 128.14, 127.61, 77.48, 77.36, 77.16, 76.84, 67.37, 54.90, 51.49, 22.55, 18.76. **HRMS** (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_{14}H_{19}Br_2N_3NaO^+$ 425.9787; Found 425.9785.



25

(*E*)-2,2-Dibromo-1-(3,3-diisopropyltriaz-1-en-1-yl)-2-(4-fluorophenyl)ethan-1-one

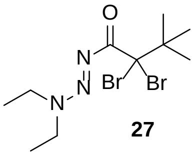
Triazene **25** was synthesized using (*E*)-1-((4-fluorophenyl)ethynyl)-3,3-diisopropyltriaz-1-ene (0.21 mmol) following the general procedure. Reaction time of 20 min at 0 °C and then 20 min at rt, gradient of pentane/diethyl ether (7:3 to 6:4). Yield (yellow solid): 65 mg (75%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.86 – 7.64 (m, 2H, C*H*), 7.12 – 6.91 (m, 2H, C*H*), 4.77 (hept, *J* = 6.8 Hz, 1H, C*H*$(CH_3)_2$), 4.23 (hept, *J* = 6.7 Hz, 1H, C*H*$(CH_3)_2$), 1.34 (d, *J* = 6.6 Hz, 6H, $CH(CH_3)_2$), 1.21 (d, *J* = 6.8 Hz, 6H, $CH(CH_3)_2$). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 175.34, 163.84, 161.36, 138.11, 138.08, 129.92, 129.83, 115.04, 114.82, 77.48, 77.36, 77.16, 76.84, 66.04, 55.11, 51.74, 22.60, 18.79, 1.17. **HRMS** (ESI/QTOF) m/z: $[M + H]^+$ Calcd for $C_{14}H_{19}Br_2FN_3O^+$ 421.9873; Found 421.9869.



26

(*E*)-2,2-Dibromo-1-(3,3-dicyclohexyltriaz-1-en-1-yl)hexan-1-one

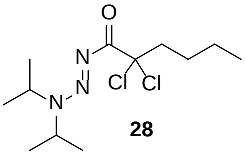
Triazene **26** was synthesized using (*E*)-3,3-dicyclohexyl-1-(hex-1-yn-1-yl)triaz-1-ene (0.198 mmol) following the general procedure. Reaction time of 15 min. Purification with a gradient of pentane/diethyl ether (1:0 to 19:1). There remained an impurity which was the triethylammonium salt. The product was further purified by dissolving in DCM and washing with water and brine, after which it was concentrated and freeze-dried for 5h in pentane over $CaCl_2$. Yield (yellow solid): 48.6 mg (53%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.76 (m, 1H, Cy-C*H*), 3.83 (m, 1H, Cy-C*H*), 2.80 – 2.58 (m, 2H, CH_2), 2.15 – 1.03 (m, 24H, Cy-CH_2, CH_2), 0.95 (t, *J* = 7.3 Hz, 3H, CH_3). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 176.03, 77.48, 77.16, 76.84, 68.82, 62.64, 60.33, 47.15, 33.31, 30.08, 29.00, 25.75, 25.55, 25.07, 22.37, 14.09. **HRMS** (ESI/QTOF) m/z: $[M + H]^+$ Calcd for $C_{18}H_{32}Br_2N_3O^+$ 464.0907; Found 464.0907.



27

(*E*)-2,2-Dibromo-1-(3,3-diethyltriaz-1-en-1-yl)-3,3-dimethylbutan-1-one

Triazene **27** was synthesized using (*E*)-1-(3,3-dimethylbut-1-yn-1-yl)-3,3-diethyltriaz-1-ene (0.33 mmol) following the general procedure. Reaction time 10 min at 0 °C and then 10 min at rt, gradient of pentane/diethyl ether (9:1 to 3:1). Yield (pale yellow solid): 41 mg (35%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 3.98 (q, *J* = 7.3 Hz, 2H, CH_2CH_3), 3.87 (q, *J* = 7.2 Hz, 2H, CH_2CH_3), 1.42 – 1.38 (m, 12H, CH_2CH_3, CH_3), 1.30 (t, *J* = 7.2 Hz, 3H, CH_2CH_3). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 176.38, 83.43, 77.48, 77.16, 76.84, 51.71, 44.62, 43.84, 27.87, 13.98, 11.23. **HRMS** (ESI/QTOF) m/z: [M + H]$^+$ Calcd for $C_{10}H_{20}Br_2N_3O^+$ 355.9968; Found 355.9964.



28

(*E*)-2,2-Dichloro-1-(3,3-diisopropyltriaz-1-en-1-yl)hexan-1-one

Triazene **28** was synthesized using (*E*)-1-(hex-1-yn-1-yl)-3,3-diisopropyltriaz-1-ene (0.29 mmol) following the general procedure. Reaction time of 1 min, then 2h at rt, gradient of pentane/diethyl ether (9:1 to 3:1). Yield (yellow oil): 61 mg (71%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.02 (hept, *J* = 6.6 Hz, 1H, C*H*(CH_3)$_2$), 4.29 (hept, *J* = 6.6 Hz, 1H, C*H*(CH_3)$_2$), 2.58 – 2.47 (m, 2H, C*H*$_2$), 1.66 – 1.57 (m, 2H, C*H*$_2$), 1.44 (d, *J* = 6.7 Hz, 6H, CH(C*H*$_3$)$_2$), 1.38 (d, *J* = 6.9 Hz, 6H, CH(C*H*$_3$)$_2$), 0.93 (t, *J* = 7.3 Hz, 3H, C*H*$_3$). **^{13}C NMR** (101 MHz, $CDCl_3$) δ δ 175.63, 89.29, 77.48, 77.37, 77.16, 76.84, 54.72, 51.52, 45.12, 27.55, 22.78, 22.45, 18.85, 14.03. **HRMS** (ESI/QTOF) m/z: [M + H]$^+$ Calcd for $C_{12}H_{24}Cl_2N_3O^+$ 296.1291; Found 296.1294.

7. NMR Coalescence studies

In a glove box, a solution of the respective triazene in DMSO-d_6 (0.5 ml) was added to a J-Young NMR tube. NMR spectra were recorded on a 400 MHz NMR spectrometer and the sample was heated *in-situ* (Figure S7.1-3). After increasing the temperature, the sample was allowed to stabilize for 2–3 min. Results of the coalescence measurements are summarized in Table S7.1, and a comparison to literature values is given in Table S7.2.

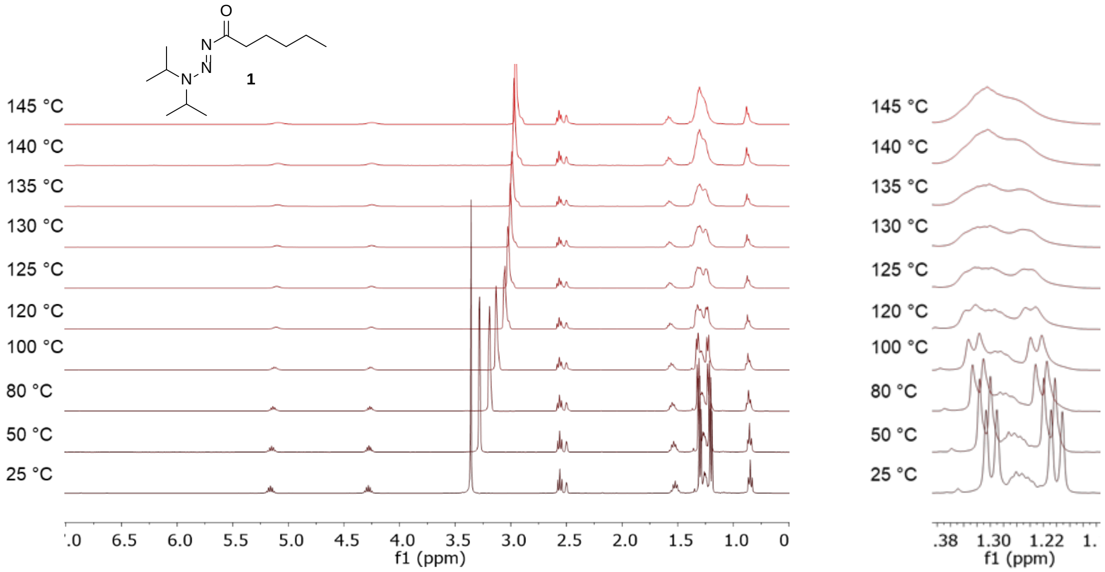


Figure S7.1. Coalescence measurements with triazene **1**.

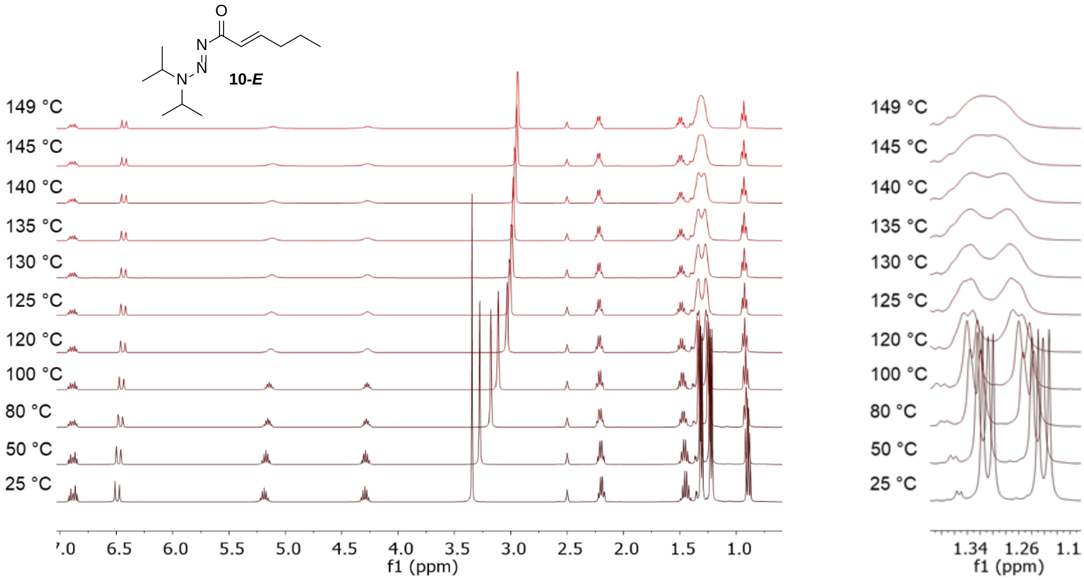


Figure S7.2. Coalescence measurements with triazene **10-*E***.

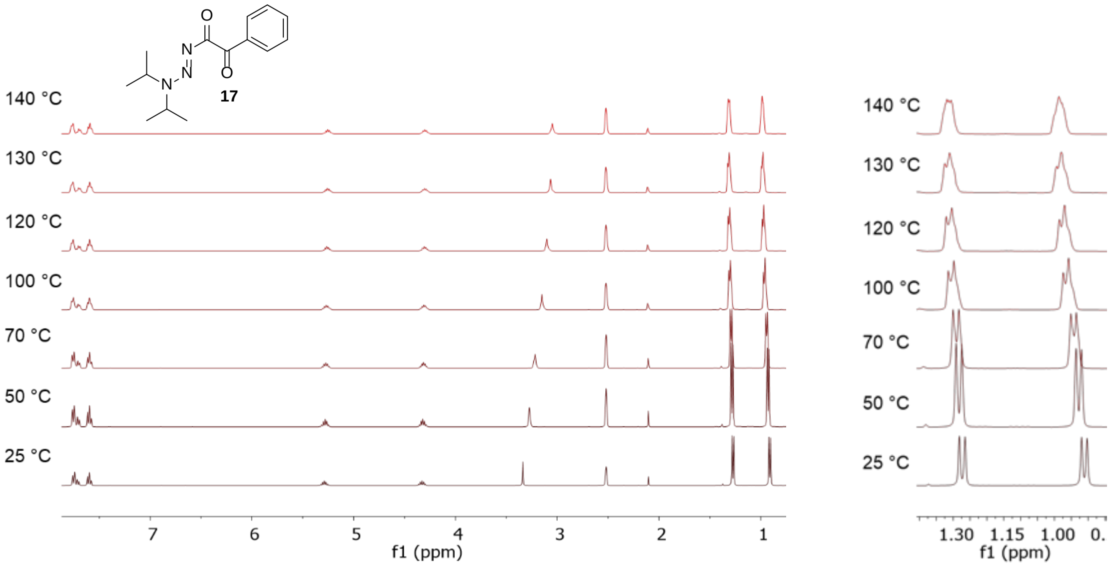
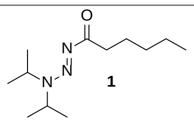
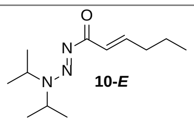
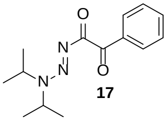


Figure S7.3. Coalescence measurements with triazene **17**.

Table S7.1. Overview of the measured and calculated values.

		 1	 10-*E*	 17
Coalescence temperature, when two peaks merge into one	T_c	145 °C / 418 K	149 °C / 422 K	> 140 °C [a]
Separation between two signals in the absence of exchange	Δv	40 Hz	40 Hz	144 Hz
Rate of exchange at T_c $\mathrm{A} \overset{k}{\rightleftharpoons} \mathrm{B}$	k_c	88.8 s^{-1}	88.8 s^{-1}	319.7 s^{-1}
The free energy of activation	$\Delta G_c^{\ddagger}$	21 cal mol^{-1}	21 cal mol^{-1}	N.A.
The free energy of activation	$\Delta G_c^{\ddagger}$	87.9 kJ mol^{-1}	88.8 kJ mol^{-1}	N.A.

[a] The temperature limit of the NMR spectrometer is 150 °C.

Calculations:[7]

$$(1)\quad k_c = \frac{\pi \Delta v}{\sqrt{2}} = 2.22\,\Delta v$$

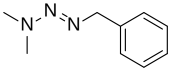
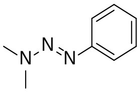
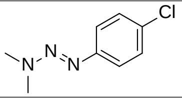
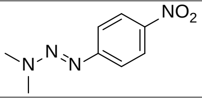
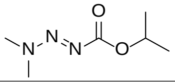
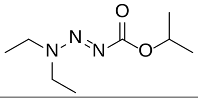
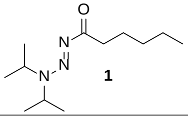
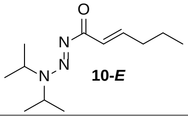
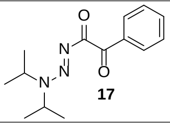
Equation (1) is valid if i) the dynamic process is kinetically 1st order, ii) the two singlets have equal intensity, iii) the exchanging nuclei are not coupled to each other.

$$(2)\quad \Delta G_c^{\ddagger} = 4.58\,T_c\,(10.32 + \log\left(\frac{T_c}{k_c}\right))\,cal\,mol^{-1} = 19.14\,T_c\,(10.32 + \log\left(\frac{T_c}{k_c}\right))\,J\,mol^{-1}$$

---

[7] Gasparro, F. P.; Kolodny, N. H. NMR Determination of the Rotational Barrier in N,N-Dimethylacetamide. A Physical Chemistry Experiment. *J. Chem. Educ.* **1977**, *54*, 258–261.

Table S7.2. Comparison of T_c and rotation barriers.

	Triazene	T_c (°C)	$\Delta\nu$ (Hz)	$\Delta G_c^{\ddagger}$ (kJ/mol)	Method and solvent
1[a]		–42	169	44.8 (+/- 0.8)	^{13}C-NMR, 25.2 MHz, $CDCl_3$
2[b]		–23.5	19	57.3 (+/- 1.3)	^{1}H-NMR, 60 MHz, $CDCl_3$
3[b]		–13	20.2	58.2 (+/- 0.8)	^{1}H-NMR, 60 MHz, $CDCl_3$
4[b]		37	20	65.7 (+/- 0.8)	^{1}H-NMR, 60 MHz, $CDCl_3$
5[c]		106	65.5	79.5 (+/- 0.8)	^{1}H-NMR, 200 MHz, $C_6D_5NO_2$
6[c]		95	25.8	78.2 (+/- 1.3)	^{1}H-NMR, 200 MHz, $C_6D_5NO_2$
7	 **1**	145	40	88	^{1}H-NMR, 400 MHz, DMSO-d_6
8	 **10-*E***	149	40	89	^{1}H-NMR, 400 MHz, DMSO-d_6
9	 **17**	>140	144	N.A.	^{1}H-NMR, 400 MHz, DMSO-d_6

[a] Sieh, D. H. *et al. J. Am. Chem. Soc.* **2005**, 102, 3883–3887. [b] Marnilo, N. P. *et al. J. Am. Chem. Soc.* **1968**, 90, 510–511. [c] Acta, H. C. *et al. Helv. Chim. Acta* **1983**, *66*, 1416–1426.

8. Temperature stability

The triazenes were dissolved in a deuterated solvent in a J-Young NMR tube and the samples were heated in an oil bath unless stated otherwise. At a given time, a ^{1}H NMR spectrum was recorded on a 400 MHz spectrometer (Figure S8.1-3).

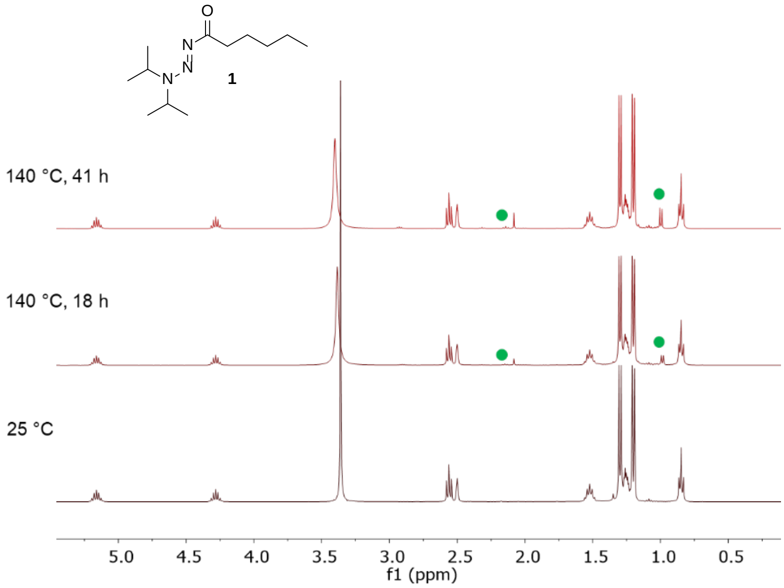


Figure S8.1. Alkyl 1-acyl triazene **1** in DMSO-d_6. Formation of the free amine, indicated by the green circle.

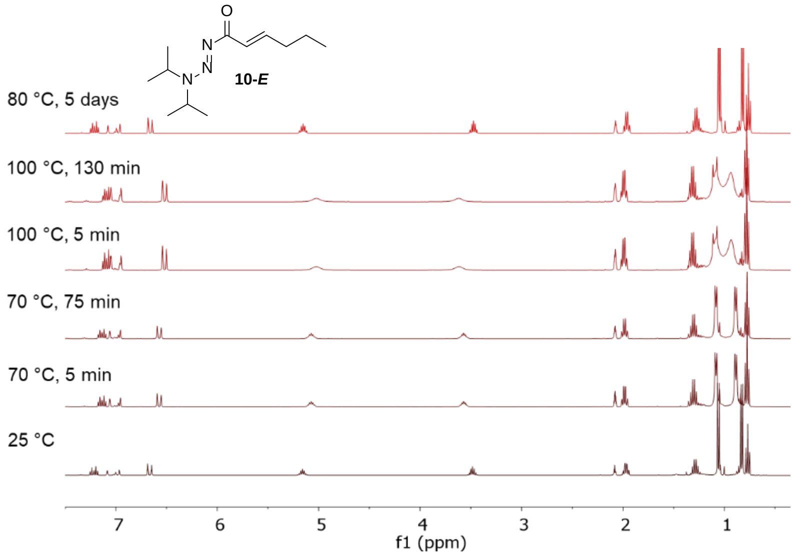


Figure S8.2. Olefinic 1-acyl triazene **10-*E*** in d_8-toluene. The time points at 70 °C and 100 °C were measured *in-situ* in the NMR spectrometer.

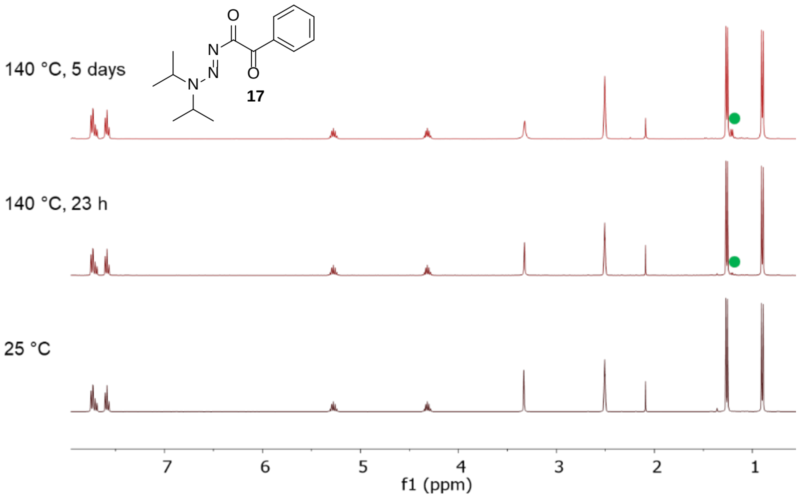
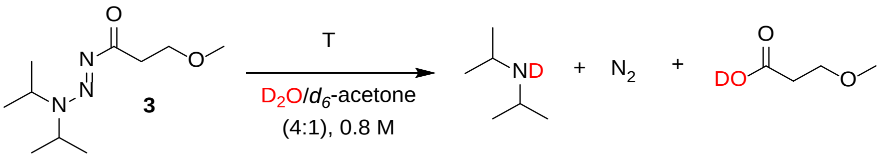


Figure S8.3. 1,2-Diketo triazene **17** in DMSO-d_6. Formation of the free amine, indicated by the green circle.

9. Hydrolytic stability

The hydrolytic stability of compound **3** was evaluated by NMR using a 400 MHz NMR spectrometer (Figure S9.1). In a J-Young NMR tube, compound **3** (0.04 mmol) was dissolved in a mixture of d_6-acetone (0.1 ml) and D_2O (0.4 ml) and a drop of THF was added as internal standard. First the reaction mixture was heated at 50 °C in a sand bath for 12 days and a conversion of 28% was observed. Subsequently, the reaction mixture was heated at 100 °C for 22 hours and a conversion of 61% was observed.



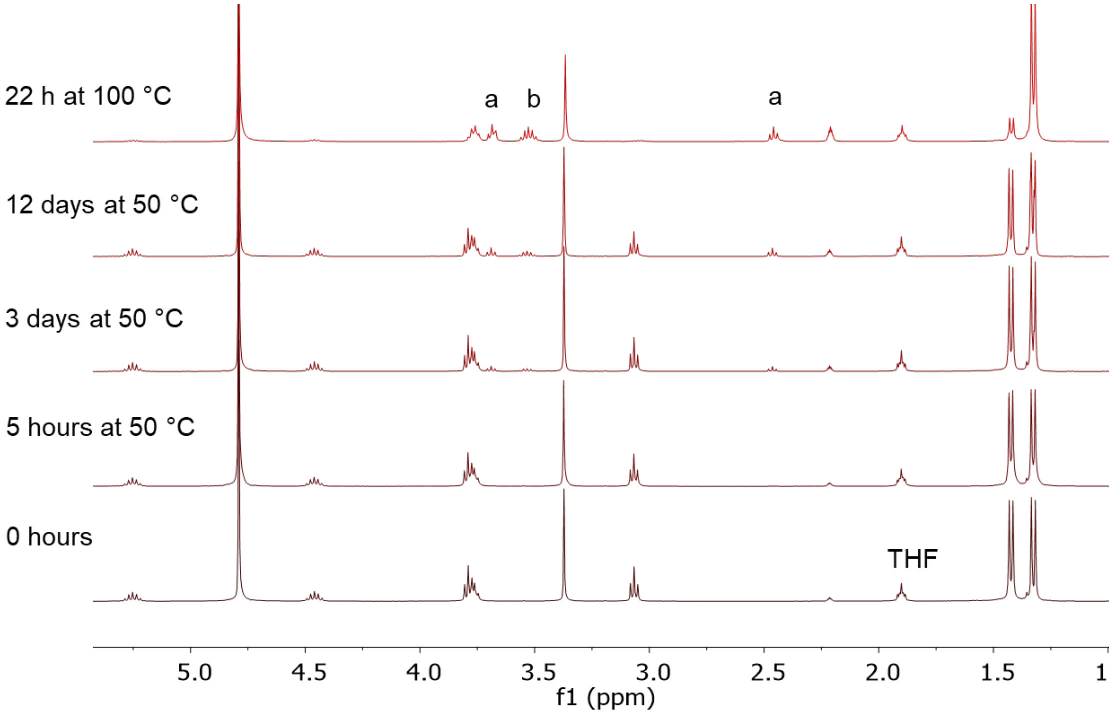


Figure S9.1. Hydrolysis of **3** followed by NMR spectroscopy. Signals (a) correspond to the carboxylic acid and (b) to the diisopropylamine.

10. Acid sensitivity

Acetic acid

The acid sensitivity of the aryl triazene $PhN_3{}^iPr_2$ and the 1-acyl triazene **1** was evaluated using NMR spectroscopy. The triazene (0.025 mmol) was dissolved in d_6-acetone/D_2O (0.05 M) in a J-Young NMR tube (under air), and a small amount of DCM was added as internal standard. First, a blank spectrum was recorded. Subsequently, various equivalents of acetic acid were added, and the NMR tube was heated in a sand bath at 50 °C. Spectra were recorded periodically. The results shown in Figure S10.1 indicate that the 1-acyl triazene **1** is more stable than the aryl triazene under the given conditions.

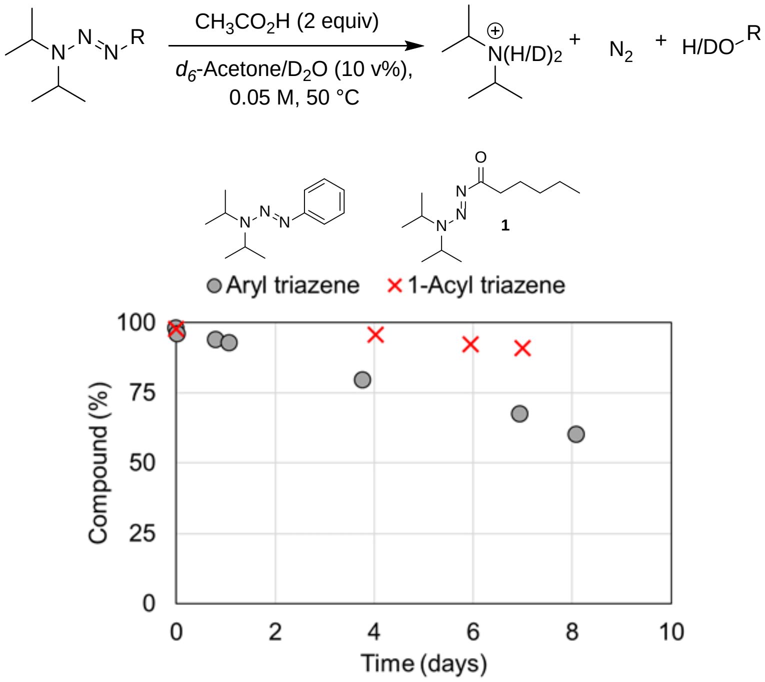
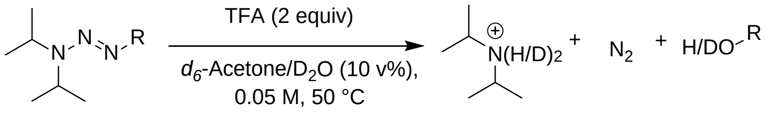


Figure S10.1. Acetic acid-induced decomposition of the triazene as determined by NMR spectroscopy.

Trifluoroacetic acid (TFA)

The acid sensitivity of the aryl triazene PhN_3iPr_2 and the 1-acyl triazene **1** was evaluated using NMR spectroscopy. The triazene (0.025 mmol) was dissolved in d_6-acetone/D_2O (0.05 M) in a J-Young NMR tube (under air), and a small amount of DCM was added as internal standard. First, a blank spectrum was recorded. Subsequently, various equivalents of TFA were added, and the NMR tube was heated at 50 °C. The results shown in Figure S10.2 indicate that the 1-acyl triazene **1** is slightly more stable than the aryl triazene under the given conditions.



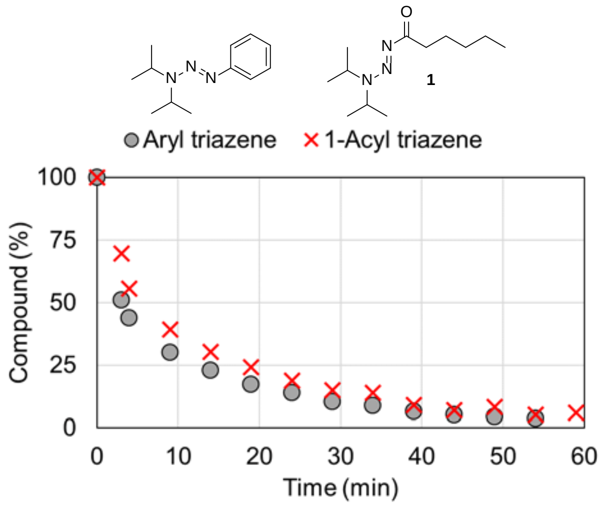


Figure S10.2. TFA-induced decomposition of the triazene as determined by NMR spectroscopy.

Triflic acid (HOTf)

The acid sensitivity of the 1-acyl triazenes **1**, **10-*E*** and **17** was evaluated using NMR spectroscopy. In a glove box, a stock solution of triflic acid was prepared by dissolving 87.8 µl of HOTf in 200 µl of d_3-acetonitrile. The triazene (0.025 mmol) was dissolved in d_3-acetonitrile/D_2O (0.05 M) in an NMR tube (under air), and a small amount of DCM was added as internal standard. First, a blank spectrum was recorded. Subsequently, 2 equivalents of HOTf were added, and the time course of the reaction was followed by NMR spectroscopy. The results are summarized in Figure S10.3.

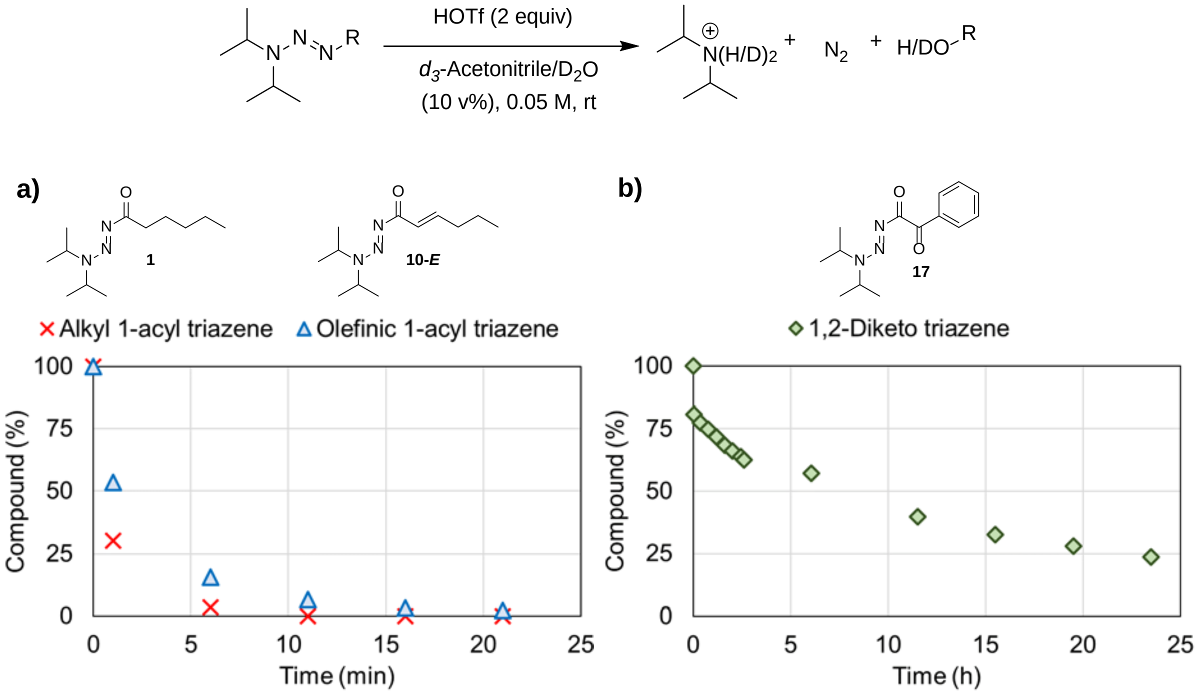


Figure S10.3. Triflic acid-induced decomposition of the triazene as determined by NMR spectroscopy.

11. Reactivity studies

Acid cleavage

The reaction mixture was prepared in a glovebox by dissolving the corresponding triazene (0.025 mmol), hexamethylbenzene as internal standard (0.2 equiv), and the nucleophilic reagent (anisole or aniline, 2 equiv) in the corresponding deuterated solvent (0.5 ml). After recording a blank spectrum, HOTf (2 equiv) was added and the reaction mixture was kept at room temperature or heated at 70 °C and the conversion was followed by ^{1}H NMR spectroscopy (see S14 for the NMR spectra). In the case of the experiments with D_2O, the reaction mixture was set-up outside the glovebox under air atmosphere.

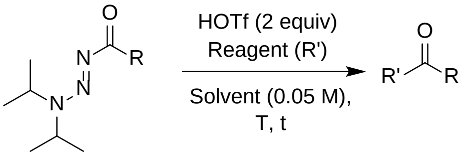
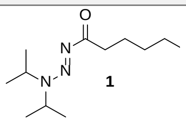
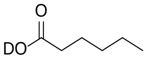
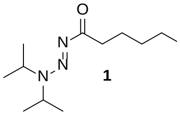
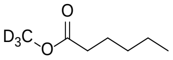
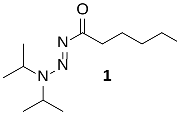
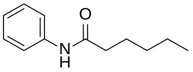
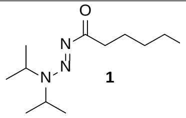
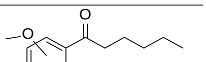
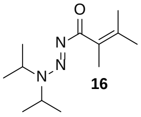
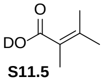
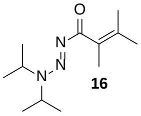
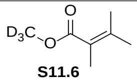
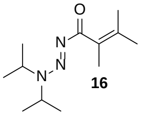
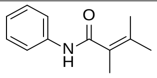
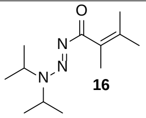
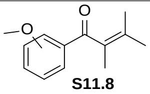
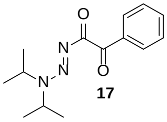
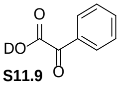
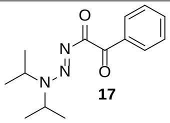
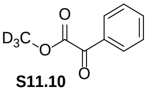
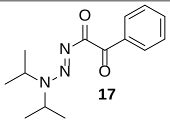
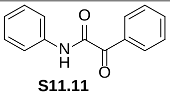
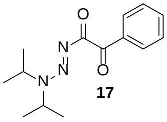
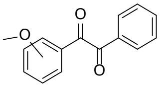
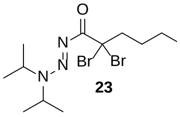
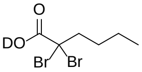
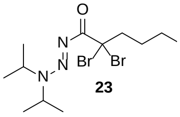
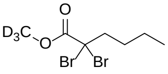
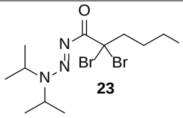
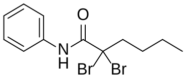
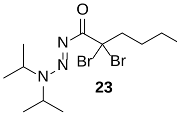
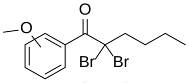


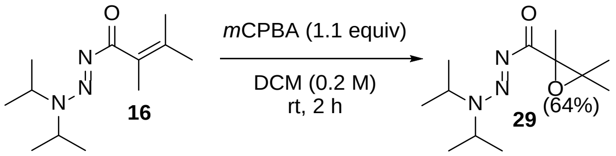
Table S11.1. Triflic acid-induced cleavage of the triazene in the presence of nucleophiles.

Entry	Triazene	Reagent	Solvent	T (°C)	Time	Yield (%) [a]	Product
1	 1	-	*d*$_3$-acetonitrile/D_2O	rt	11 min	>95 [b]	 S11.1
2	 1	-	*d*$_4$-methanol	rt	44 min	>95	 S11.2
3	 1	Aniline (2 equiv)	*d*$_3$-acetonitrile	70	70 min	>95	 S11.3
4	 1	Anisole (2 equiv)	*d*$_3$-acetonitrile	70	21 hours	>95	 S11.4 *para/ortho = 8:1*
5	 16	-	*d*$_3$-acetonitrile/D_2O	rt	21 min	>95 [b]	 S11.5
6	 16	-	*d*$_4$-methanol	rt	48 min	85	 S11.6
7	 16	Aniline (2 equiv)	*d*$_3$-acetonitrile	70	70 min	91	 S11.7

8	 **16**	Anisole (2 equiv)	d_3-acetonitrile	70	21 hours	78	 **S11.8** *para/ortho = 3:1*
9	 **17**	-	d_3-acetonitrile/D_2O	70	60 min	>95 [b]	 **S11.9**
10	 **17**	-	d_4-methanol	rt	59 min	63	 **S11.10**
11	 **17**	Aniline (2 equiv)	d_3-acetonitrile	70	18 hours	85	 **S11.11**
12	 **17**	Anisole (2 equiv)	d_3-acetonitrile	70	20 hours	58	 **S11.12** *para/ortho* = 17:1
13	 **23**	-	d_3-acetonitrile/D_2O	70	90 min	76 [b]	 **S11.13**
14	 **23**	-	d_4-methanol	rt	52 min	94	 **S11.14**
15	 **23**	Aniline (2 equiv)	d_3-acetonitrile	70	3 days	~ 64	 **S11.15** *Mixture of signals and no complete cleavage of the triazene*
16	 **23**	Anisole (2 equiv)	d_3-acetonitrile	70	19 hours	~ 22	 **S11.16** *Complete cleavage of the triazene, but a mixture of signals*

[a] Yields and product ratios are based on the ^{1}H NMR spectra using hexamethylbenzene as internal standard. [b] DCM was used as internal standard.

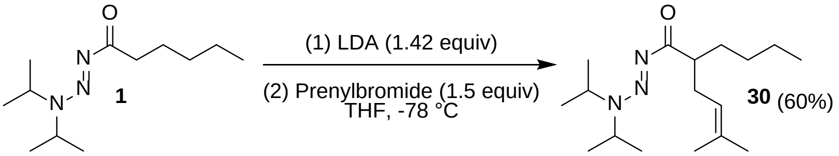
Epoxidation



(*E*)-(3,3-Diisopropyltriaz-1-en-1-yl)(2,3,3-trimethyloxiran-2-yl)methanone

(*E*)-1-(3,3-Diisopropyltriaz-1-en-1-yl)-2,3-dimethylbut-2-en-1-one **16** (0.670 mmol) was dissolved in DCM (3.4 ml) and 3-chloroperoxybenzoic acid (77%, 1.1 equiv) was added. The reaction mixture was stirred at rt for 2 h. It was quenched with saturated $NaHCO_3$ (aq), extracted with diethyl ether, and the combined organic phases were filtered through a Pasteur pipet packed with $MgSO_4$. After evaporation of the solvent, the product was freeze-dried with pentane, yielding **29**. Yield (grey solid): 102 mg (64%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.50 (hept, *J* = 6.8 Hz, 1H, C*H*$(CH_3)_2$), 4.21 (hept, *J* = 6.6 Hz, 1H, C*H*$(CH_3)_2$), 1.52 (s, 3H, C*H*$_3$), 1.43 (d, *J* = 6.5 Hz, 3H, CH(C*H*$_3$)$_2$), 1.40 (d, *J* = 6.6 Hz, 3H, CH(C*H*$_3$)$_2$), 1.38 (s, 3H, C*H*$_3$), 1.27 (d, *J* = 5.5 Hz, 3H, CH(C*H*$_3$)$_2$), 1.26 (d, *J* = 5.5 Hz, 3H, CH(C*H*$_3$)$_2$), 1.19 (s, 3H, C*H*$_3$). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 184.33, 67.27, 62.04, 51.23, 49.09, 23.80, 23.55, 22.39, 19.92, 19.08, 19.06, 17.96. **HRMS** (APCI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_{12}H_{23}N_3NaO_2^+$ 264.1682; Found 264.1683.

Alkylation



(*E*)-2-Butyl-1-(3,3-diisopropyltriaz-1-en-1-yl)-5-methylhex-4-en-1-one

Water was removed from (*E*)-1-(3,3-diisopropyltriaz-1-en-1-yl)hexan-1-one by filtering with pentane through a pipet containing $MgSO_4$, followed by freeze-drying in pentane. LDA was prepared at –78 °C by dissolving diisopropylamine (1.42 equiv) in dry THF (3.0 ml) and adding *n*-butyllithium (2.5 M in hexanes, 1.47 equiv) dropwise. After 5 min the reaction mixture was allowed to warm up to rt for 15 min, after which it was cooled down again to –78 °C. Subsequently, (*E*)-1-(3,3-diisopropyltriaz-1-en-1-yl)hexan-1-one (0.34 mmol) in dry THF (1.0 ml) was added dropwise and it was stirred for 20 min, followed by allowing to warm up to rt for 90 min. After cooling the reaction mixture down again to -78 °C, 1-bromo-3-methyl-2-butene (1.5 equiv) in dry THF (0.5 ml) was added dropwise and the reaction mixture was left stirring overnight while slowly warming to rt. It was quenched with 3 mL of aqueous AcOH 20%, extracted with diethyl ether (3x), and the combined organic phases were washed with sat. $NaHCO_3$ (aq), brine, and dried over $MgSO_4$. The product was purified by flash column chromatography on deactivated silica with pentane ether (13:7) as eluent. It was freeze-dried with pentane, yielding **30** (*E*)-2-butyl-1-(3,3-diisopropyltriaz-1-en-1-yl)-5-methylhex-4-en-1-one. Yield (yellow oil): 62.3 mg (60%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.46 (hept, *J* = 6.8 Hz, 1H, $CH(CH_3)_2$), 5.05 (t, *J* = 7.3 Hz, 1H, C*H*=C), 4.14 (hept, *J* = 6.6 Hz, 1H, $CH(CH_3)_2$), 3.35 – 3.18 (m, 1H, C*H*), 2.38 – 2.27 + 2.24 – 2.12 (m, 2H, CH_2), 1.77 – 1.66 (m, 1H, CH_2), 1.63 (s, 3H, $CHCH_3$), 1.58 (s, 3H, $CHCH_3$), 1.53 – 1.44 (m, 1H, CH_2), 1.39 (d, *J* = 6.6 Hz, 6H, $CH(CH_3)_2$), 1.30 – 1.13 (m, 10H, $CH(CH_3)_2$, CH_2, CH_2), 0.84 (t, *J* = 6.9 Hz, 3H, CH_2CH_3). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 190.52, 132.69, 122.55, 77.48, 77.16, 76.84, 50.86, 48.37, 43.90, 32.26, 31.88, 30.04, 25.93, 23.57, 23.55, 22.93, 19.13, 17.90, 14.14. **HRMS** (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_{17}H_{33}N_3NaO^+$ 318.2516; Found 318.2517.

12. Thermogravimetric analysis (TGA)

To determine at what temperature the triazenes decompose, we performed TGA analyses (Figure S12.1). The TGA measurements were performed on a TGA 4000 from Perkin Elmer. The weight of the given triazenes (2–15 mg) was followed while increasing the temperature (10 °C/min). Starting T = 30 °C.

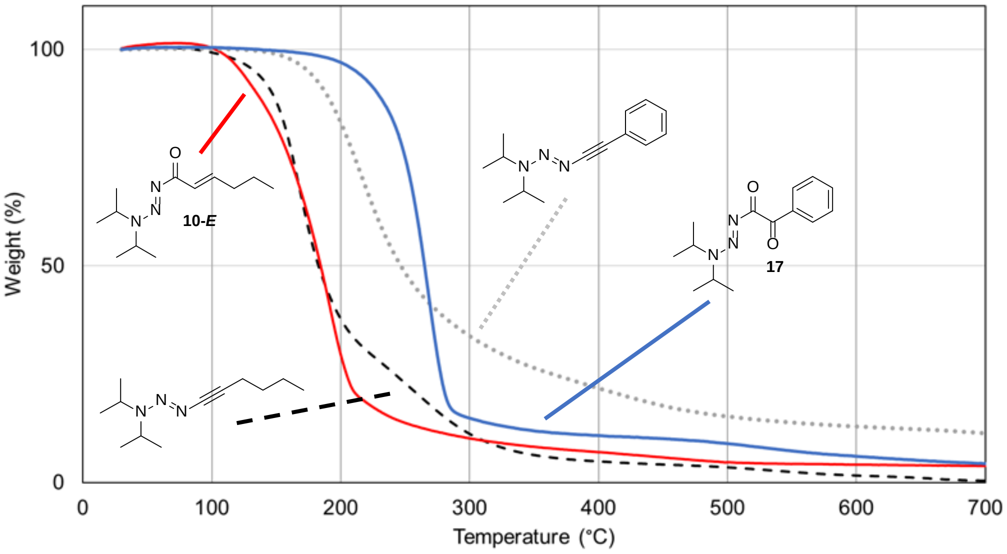


Figure S12.1. TGA results.

13. Crystallographic data

Crystallographic and refinement data of **2**, **11-*E***, **16**, **18**, **20** and **21** are summarized in Table S13.1.

Bragg-intensities of **2**, **11-*E***, **16**, **18**, **20** and **21** were collected at 140.00(10) K using Cu$K\alpha$ radiation. A Rigaku SuperNova dual system diffractometer with an Atlas S2 CCD detector was used for compounds **2**, **11-*E***, **16**, **20** and **21**, and one equipped with an Atlas CCD detector for compound **18**. The datasets were reduced and corrected for absorption, with the help of a set of faces enclosing the crystals as snugly as possible, with *CrysAlis*^{Pro}.[8]

The solutions and refinements of the structures were performed by the latest available version of *ShelXT*[9] and *ShelXL*.[10] All non-hydrogen atoms were refined anisotropically using full-matrix least-squares based on $|F|^2$. The hydrogen atoms were placed at calculated positions by means of the “riding” model where each H-atom was assigned a fixed isotropic displacement parameter with a value equal to 1.2 U_{eq} of its parent C-atom (1.5 U_{eq} for the methyl groups), but in the structures of **11-*E*** and **21**, hydrogen atom positions were found in a difference map and refined freely. Crystallographic and refinement data are summarized in Table S14.1. Crystallographic data have been deposited to the CCDC and correspond to the following codes: **2** (1921567), **11-*E*** (1921565), **16** (1921563), **18** (1921564), **20** (1921566) and **21** (1921568). Copies of the data can be obtained free of charge from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, U.K. (fax, (internat.) +44-1223-336033; E-mail, deposit@ccdc.cam.ac.uk).

In the structure **16**, the acryloyl group is disordered over two positions found in a difference map and which were refined anisotropically imposing distance and similarity restraints (SADI and SIMU) for the least-squares refinement, yielding site occupancies of 0.631(4)/0.369(4).

The structure **20**, is partially disordered over two positions; atoms of both orientations were located in difference Fourier map. The major and minor parts were refined anisotropically, but distance and similarity restraints (SADI and DFIX) were used for a convergent least-squares refinement, yielding site occupancies of 0.728(4)/0.272(4).

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[8] CrysAlisPro Software System, Rigaku Oxford Diffraction, (2015)

[9] Sheldrick, G.M., ShelXT-Integrated space-group and crystal-structure determination, *Acta Cryst.* **2015**, *A71*, 3–8.

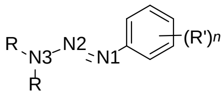
[10] Sheldrick, G.M., Crystal structure refinement with ShelXL, *Acta Cryst.* **2015**, *C71*, 3–8.

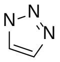
Table S13.1. Crystallographic data of **2**, **11-*E***, **16**, **18**, **20** and **21**.

Compound	**2**	**11-*E***	**16**	**18**	**20**	**21**
Formula	$C_{12}H_{25}N_3O$	$C_{18}H_{31}N_3O$	$C_{12}H_{23}N_3O$	$C_{15}H_{21}N_3O_3$	$C_{14}H_{23}N_3O_2$	$C_{21}H_{29}N_3O_3$
$D_{calc.}$/ g cm^{-3}	1.038	1.101	1.049	1.202	1.174	1.230
μ/mm^{-1}	0.528	0.534	0.537	0.694	0.640	0.666
Formula Weight	227.35	305.46	225.33	291.35	265.35	371.47
Colour	colourless	colourless	colourless	colourless	colourless	colourless
Shape		prism	prism	prism	prism	
Size/mm^3	0.69 x 0.43 x 0.29	0.51 × 0.44 × 0.35	0.39 × 0.20 × 0.13	0.42 × 0.14 × 0.06	0.88 × 0.55 × 0.32	0.49 x 0.39 x 0.30
T/K	140.00(10)	139.99(10)	140.00(10)	140.00(10)	140.00(10)	140.00(10)
Crystal System	orthorhombic	monoclinic	triclinic	monoclinic	monoclinic	monoclinic
Space Group	$P2_12_12$	$P2_1/n$	$P\bar{1}$	Cc	$P2_1/n$	$P2_1/c$
a/Å	15.30245(10)	9.37856(9)	6.5155(3)	11.0428(2)	8.56795(8)	11.05262(8)
b/Å	13.74527(9)	15.21346(13)	8.3737(3)	18.4477(3)	16.30488(14)	15.28143(10)
c/Å	6.91413(5)	13.21869(12)	13.7303(6)	8.36510(17)	11.35076(12)	11.88997(9)
α/°	90	90	88.278(3)	90	90	90
β/°	90	102.3750(9)	85.778(4)	109.114(2)	108.7740(11)	93.1298(7)
γ/°	90	90	72.753(4)	90	90	90
V/Å^3	1454.293(17)	1842.23(3)	713.46(5)	1610.14(6)	1501.33(3)	2005.22(2)
Z	4	4	2	4	4	4
Z'		1	1	1	1	
Wavelength/Å	1.54184 Å	1.54184	1.54184	1.54184	1.54184	1.54184
Radiation type	Cu$K\alpha$	Cu$K\alpha$	Cu$K\alpha$	Cu$K\alpha$	Cu$K\alpha$	Cu$K\alpha$
Θ_{min}/°	4.324	4.492	3.228	4.794	4.929	4.006
Θ_{max}/°	76.017	76.038	75.920	76.652	76.103	75.968
Measured Refl.	13777	17450	4747	15104	13290	18963
Independent Refl.	3034	3834	2882	3332	3122	4163
Reflections with I > 2(I)	3011	3666	2548	3258	3019	4163
R_{int}	0.0150	0.0197	0.0083	0.0247	0.0262	0.0226
Parameters	154	324	219	196	196	361
Restraints	0	0	197	2	11	0
Largest Peak/e Å^{-3}	0.179	0.242	0.211	0.151	0.345	0.328
Deepest Hole/e Å^{-3}	-0.105	-0.158	-0.157	-0.121	-0.200	-0.184
GooF	1.084	1.049	1.054	1.033	1.073	1.076
wR_2 (all data)	0.0748	0.1000	0.1215	0.0718	0.0999	0.1084
wR_2	0.0747	0.0987	0.1173	0.0711	0.0988	0.1078
R_1 (all data)	0.0272	0.0377	0.0470	0.0271	0.0392	0.0429
R_1	0.0271	0.0362	0.0424	0.0265	0.0381	0.0420
CCDC code	1921567	1921565	1921563	1921564	1921566	1921568

CCDC database analysis

To compare the bond lengths of the 1-acyl triazenes (Table S13.2) with aryl triazenes, a CCDC database search was performed. For the search, the program ConQuest (v2.0.1, CCDC 2019) was used with a CCDC database (CSD version 5.40 (November 2018) + 1 update).

The query that was searched: 

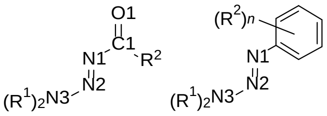
With the following additional requirements: R = any atom except H, R’ = one or multiple substituents (*n*), Filter = only organics and must not contain: 

The resulting **122 hits** were analysed and taken out of the data set if:

(1) The triazene is cyclic.
(2) It contains any other atom than H, C, N, O, F, Cl, Br, S.
(3) The amount of connected N atoms > 3.
(4) R is another atom than C, or if R is C–O.
(5) No coordinates are available in the database.

The resulting **67 hits** were analysed with Mercury (v3.10, CCDC 2001-2017) and the bond lengths were measured.

Table S13.2. Selected bond lengths of **2**, **11-*E***, **16**, **18**, **20** and **21**.



Compound	N3–N2	N2–N1	N1–C1	C1–O1
2	1.2955(14)	1.2927(13)	1.4049(14)	1.2228(15)
11-*E*	1.2963(11)	1.2896(11)	1.4178(12)	1.2172(12)
16	1.2911(13)	1.2987(13)	1.386(7)	1.220(5)
18	1.2859(18)	1.3058(18)	1.390(2)	1.2187(19)
20	1.2892(11)	1.3040(11)	1.3918(12)	1.2154(12)
21	1.2901(13)	1.3075(13)	1.3812(14)	1.2151(15)
Aryl triazene	1.328 [b]	1.274 [b]	-	-

[b] Average bond lengths calculated from 67 structures from the CCDC database.

14. NMR spectra

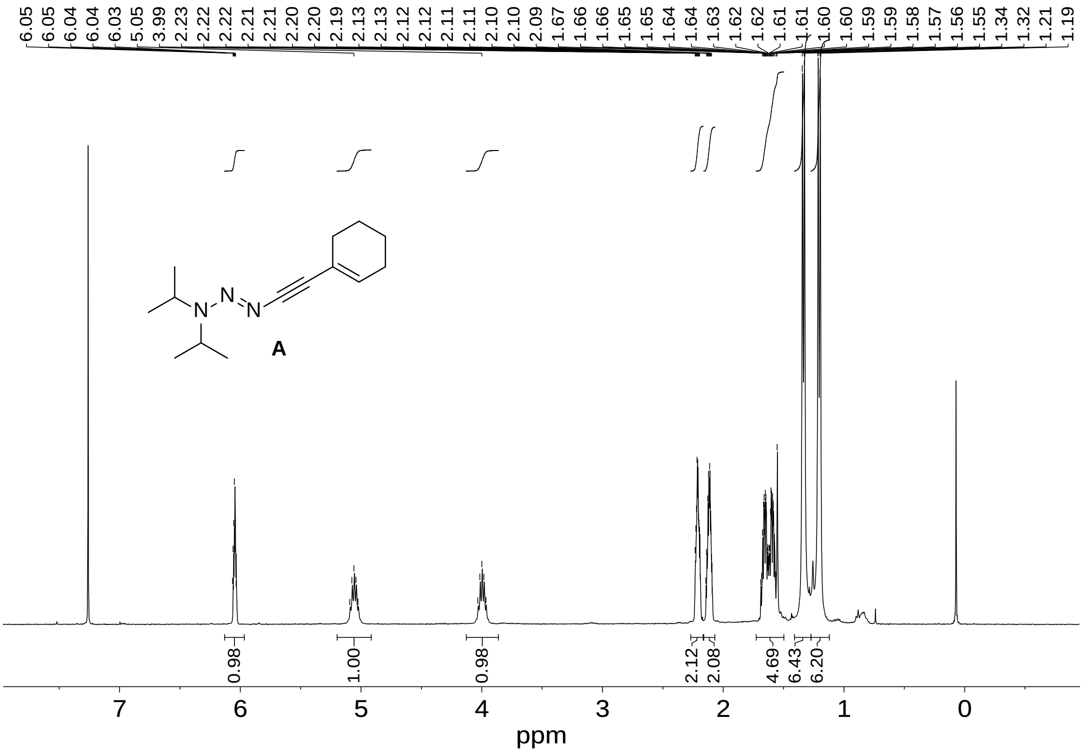


Figure S14.1. ^{1}H NMR spectrum of **A** (400 MHz, CDCl$_3$).

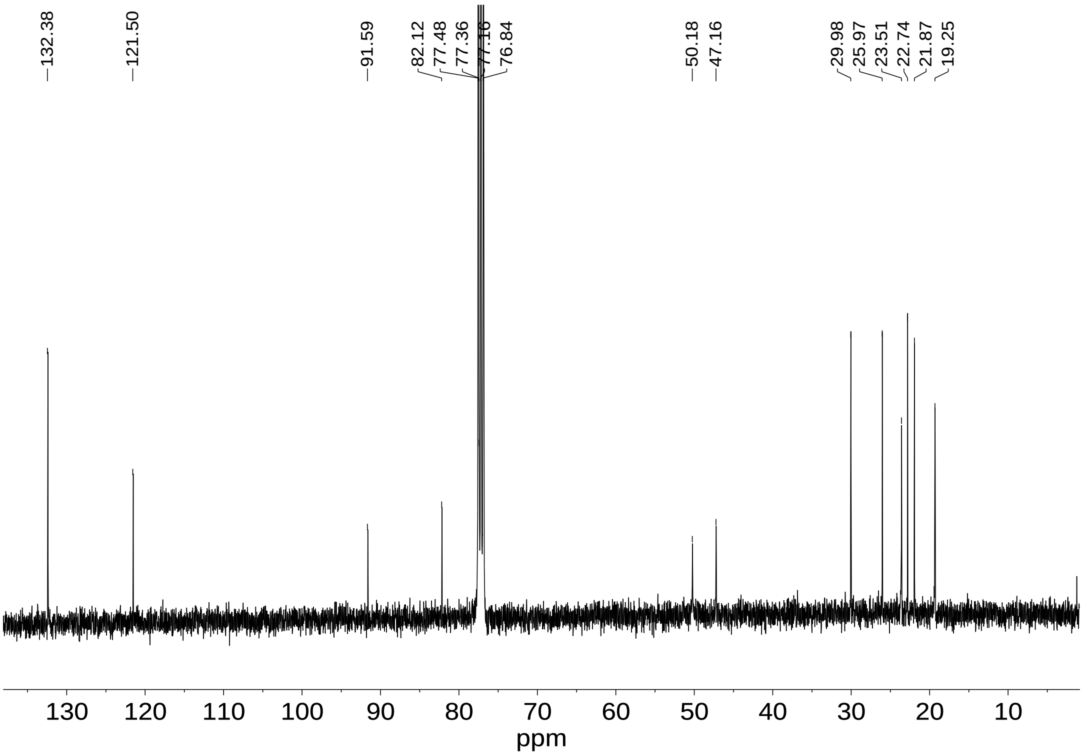


Figure S14.2. ^{13}C NMR spectrum of **A** (101 MHz, CDCl$_3$).

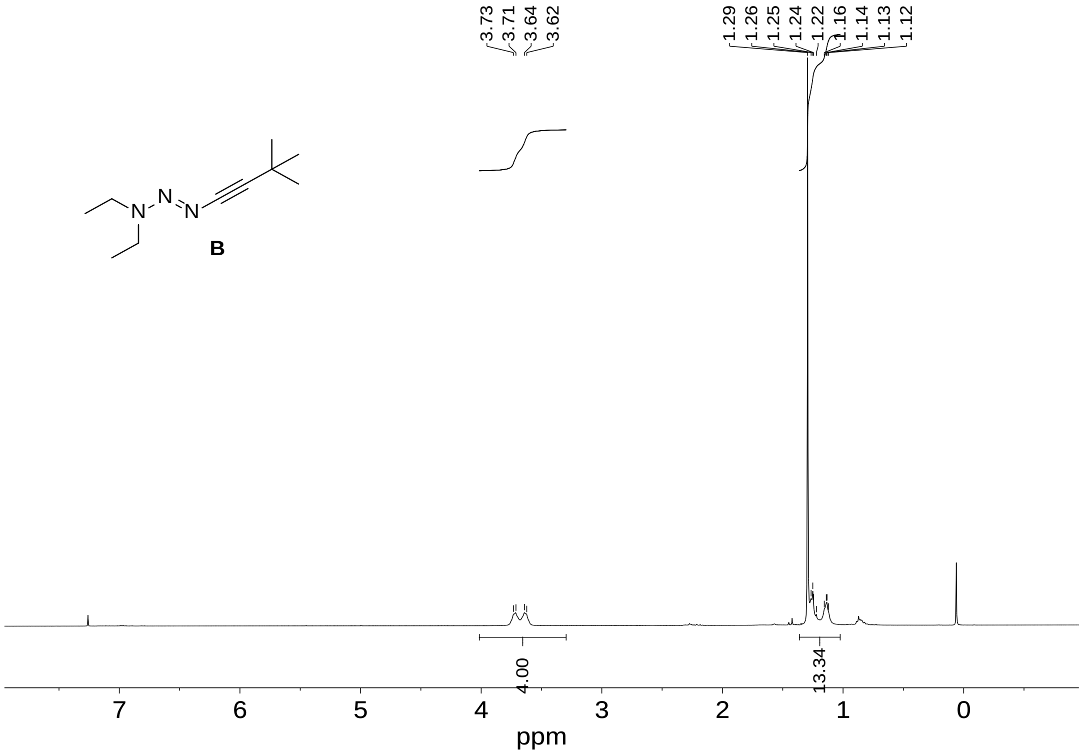


Figure S14.3. ^{1}H NMR spectrum of **B** (400 MHz, $CDCl_3$).

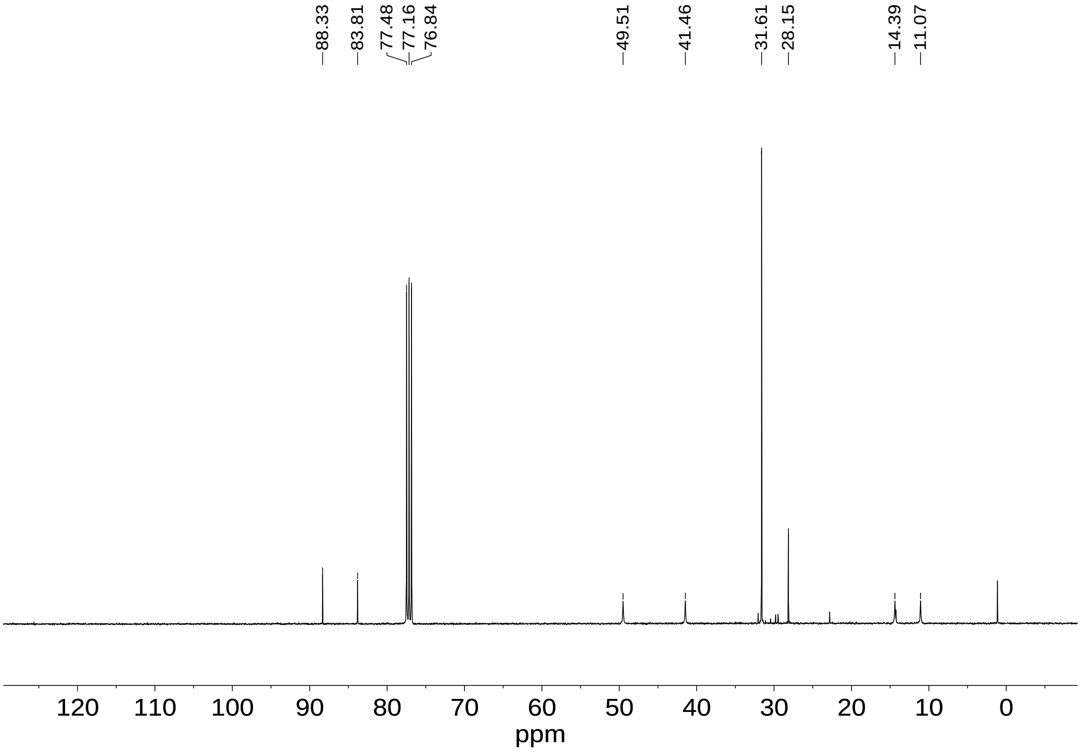


Figure S14.4. ^{13}C NMR spectrum of **B** (101 MHz, $CDCl_3$).

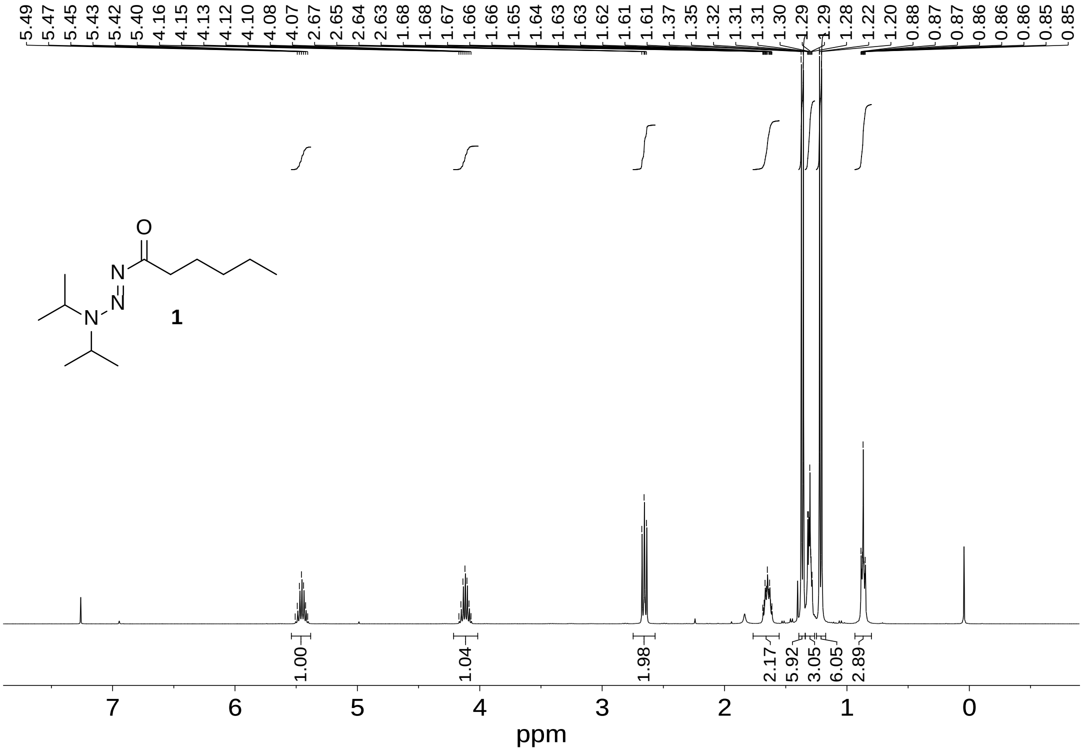


Figure S14.5. ^{1}H NMR spectrum of **1** (400 MHz, CDCl$_3$).

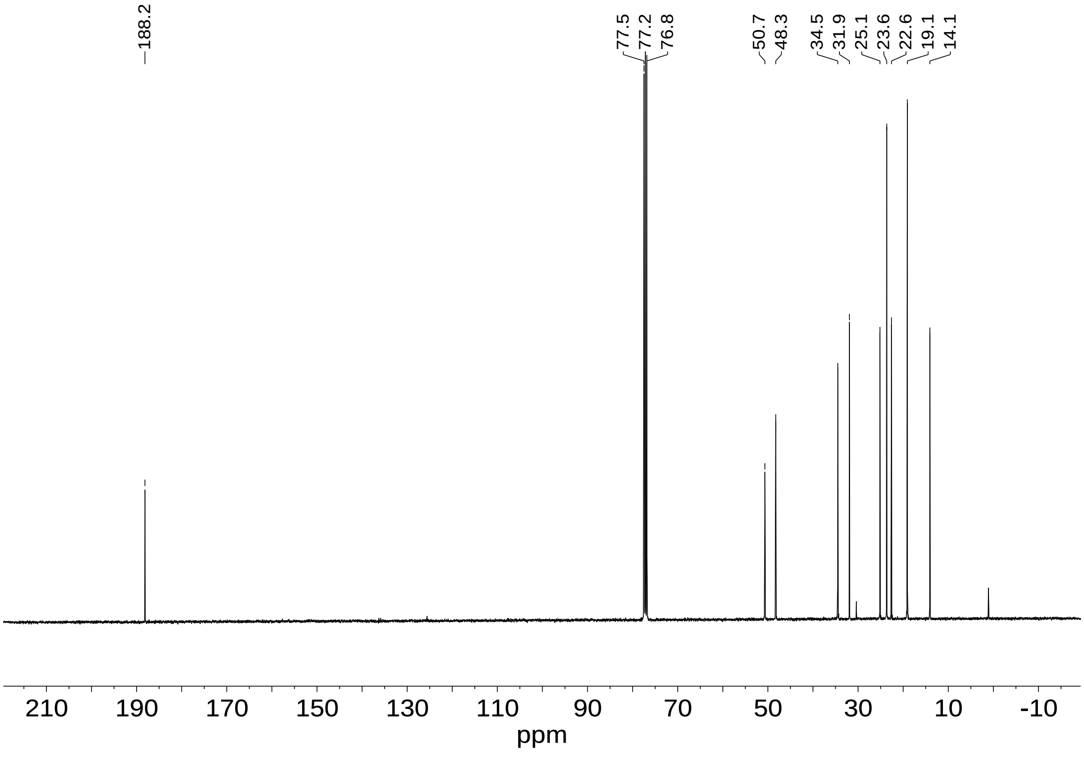


Figure S14.6. ^{13}C NMR spectrum of **1** (101 MHz, CDCl$_3$).

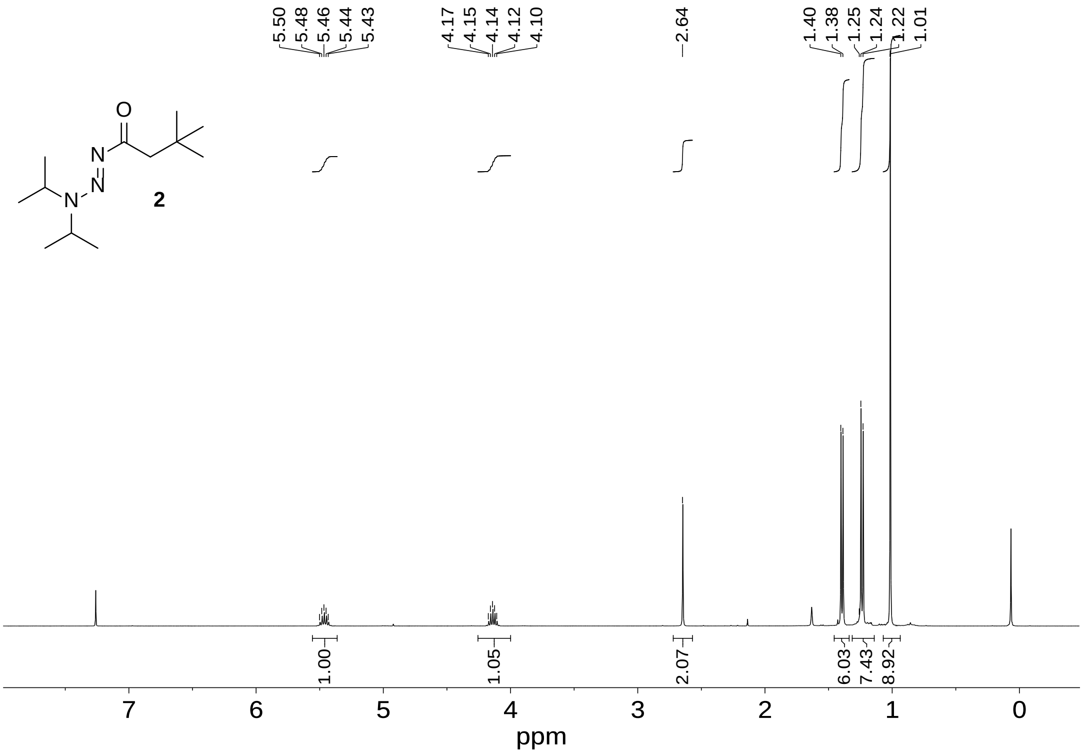


Figure S14.7. ^{1}H NMR spectrum of **2** (400 MHz, $CDCl_3$).

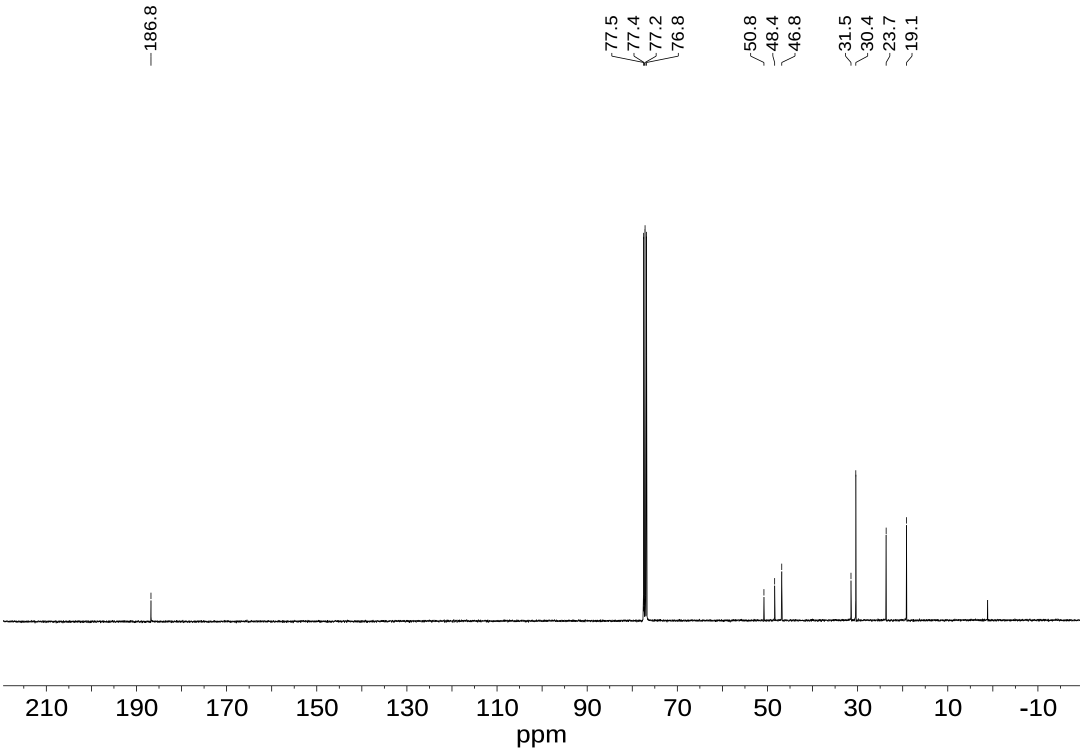


Figure S14.8. ^{13}C NMR spectrum of **2** (101 MHz, $CDCl_3$).

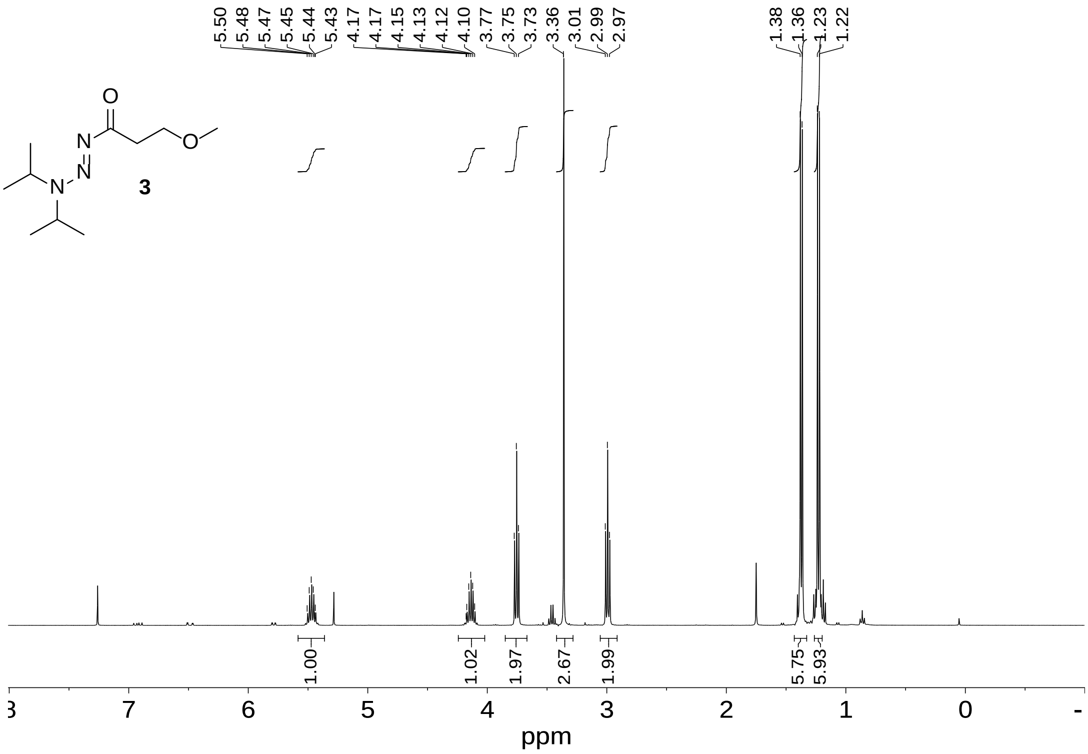


Figure S14.9. ^{1}H NMR spectrum of **3** (400 MHz, CDCl$_3$).

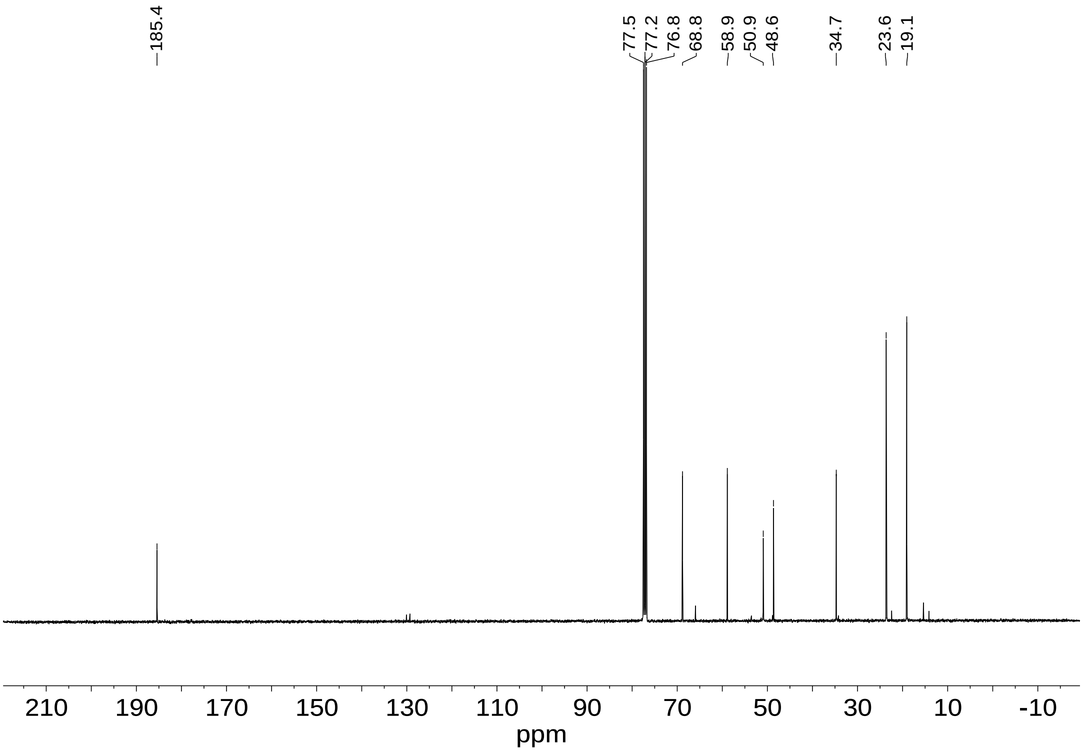


Figure S14.10. ^{13}C NMR spectrum of **3** (101 MHz, CDCl$_3$).

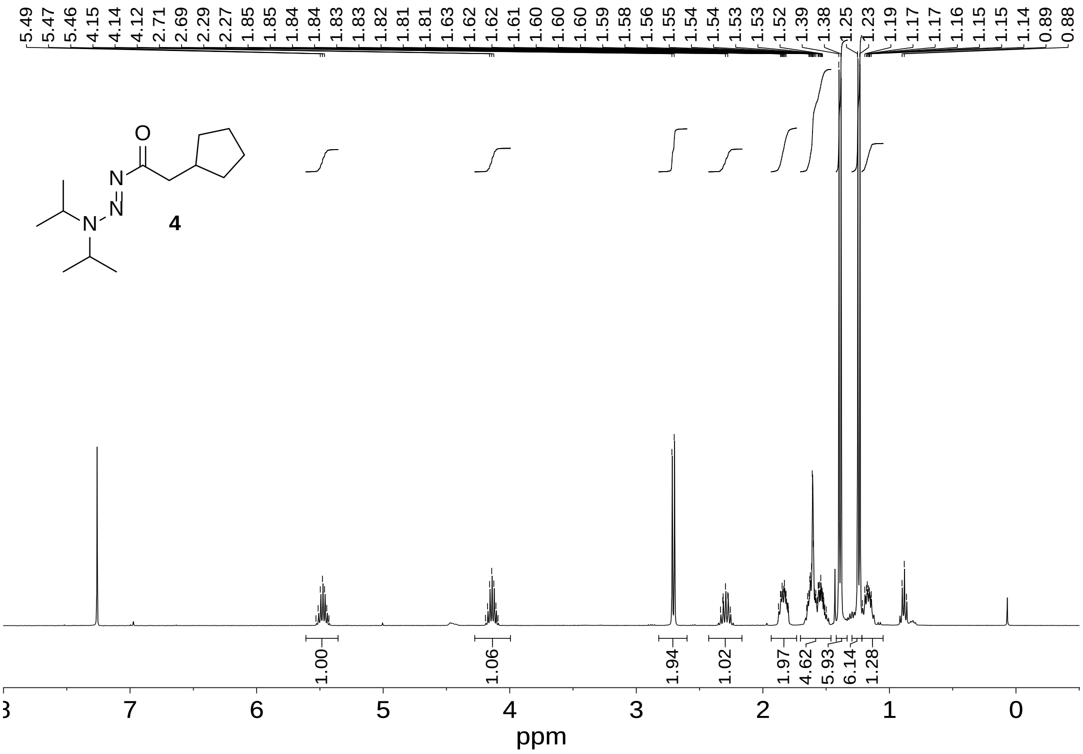


Figure S14.11. ^{1}H NMR spectrum of **4** (400 MHz, CDCl$_3$).

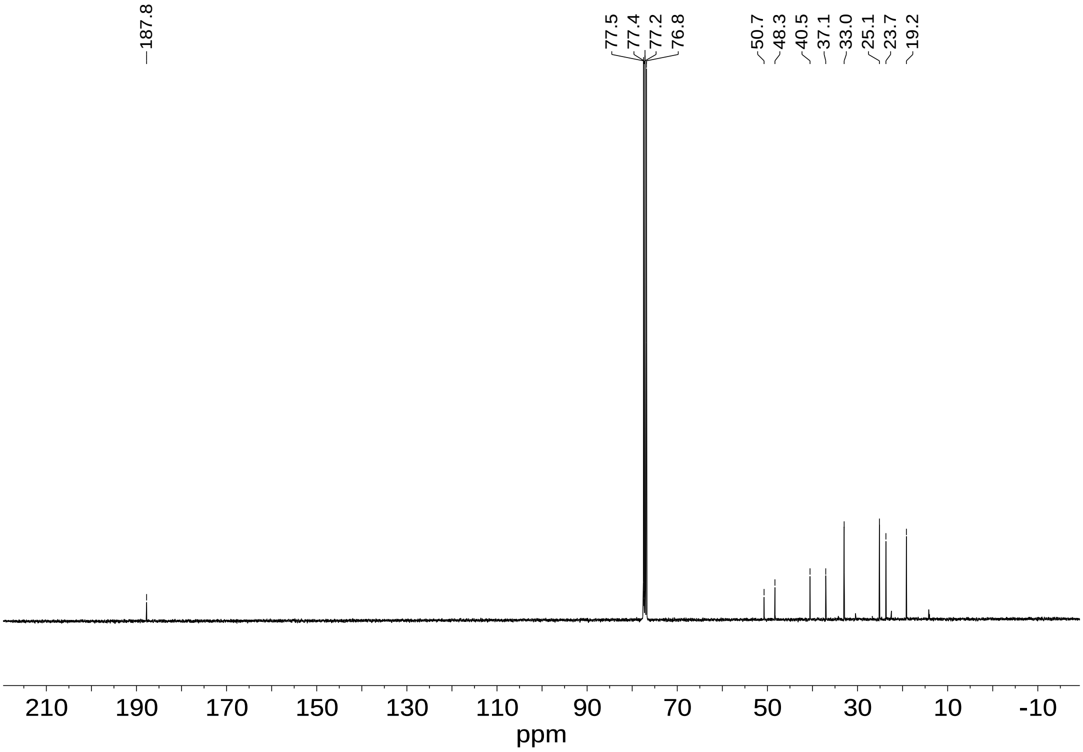


Figure S14.12. ^{13}C NMR spectrum of **4** (101 MHz, CDCl$_3$).

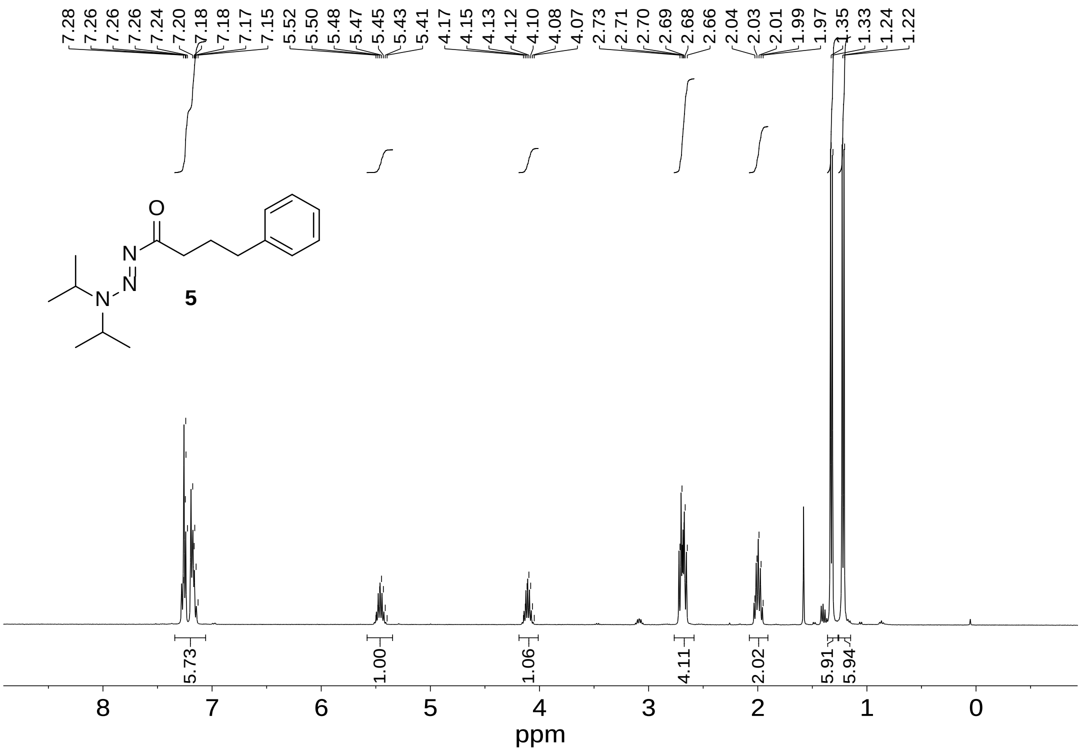


Figure S14.13. ^{1}H NMR spectrum of **5** (400 MHz, $CDCl_3$).

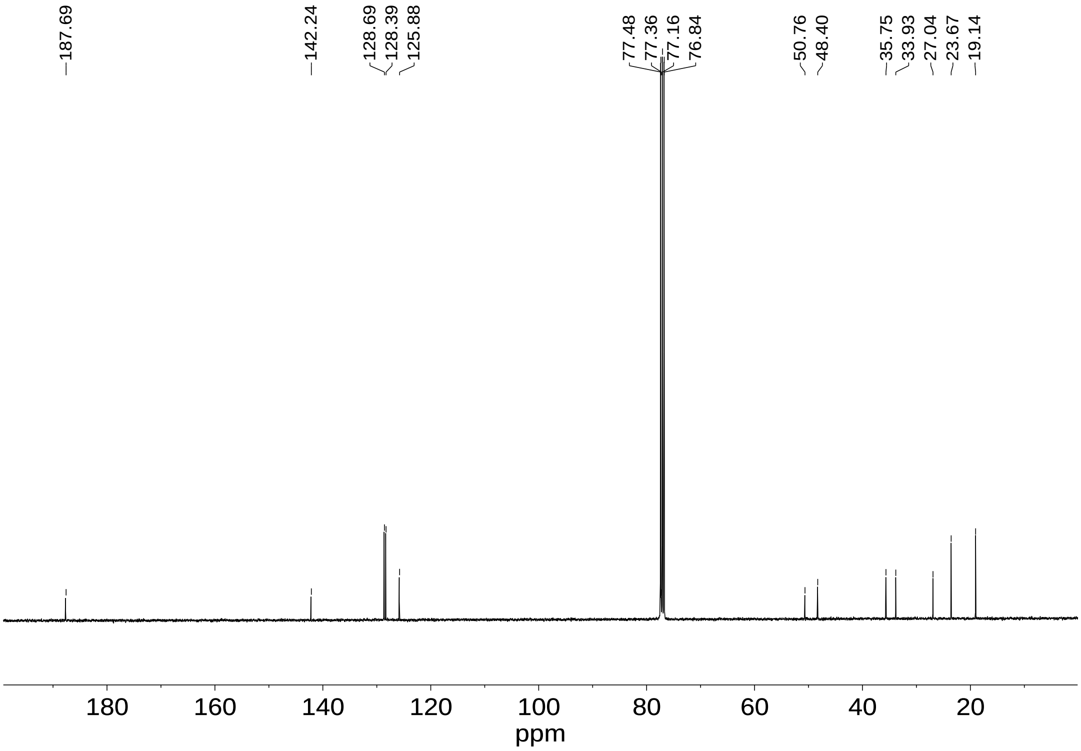


Figure S14.14. ^{13}C NMR spectrum of **5** (101 MHz, $CDCl_3$).

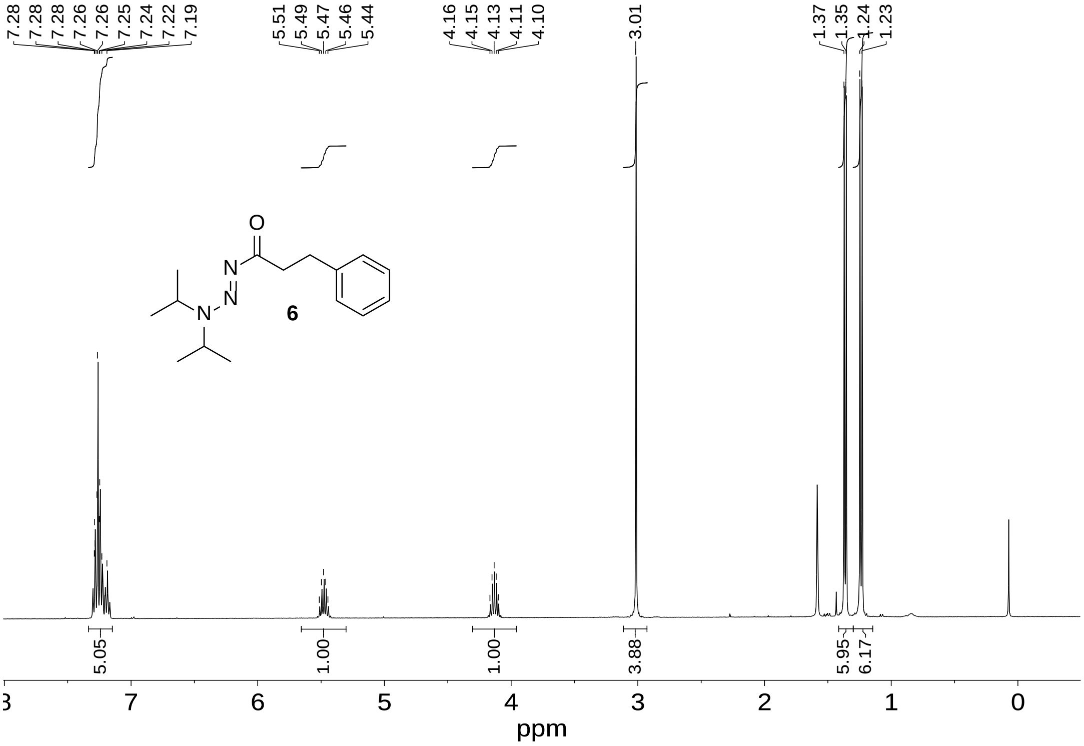


Figure S14.15. ^{1}H NMR spectrum of **6** (400 MHz, CDCl$_3$).

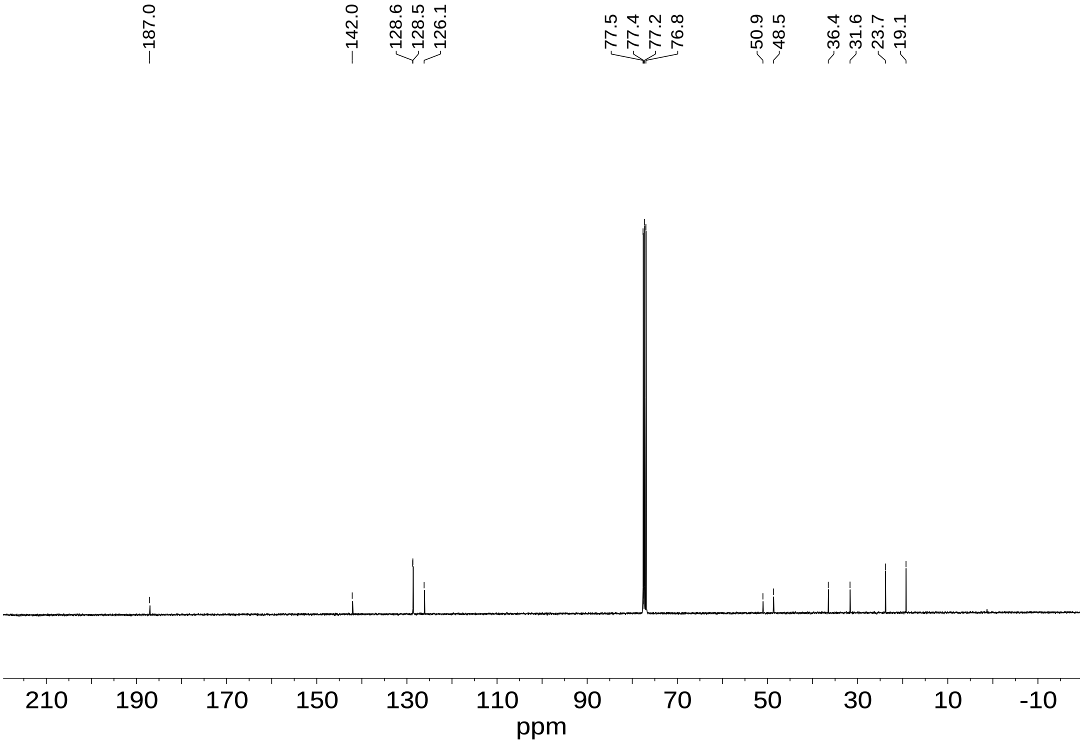


Figure S14.16. ^{13}C NMR spectrum of **6** (101 MHz, CDCl$_3$).

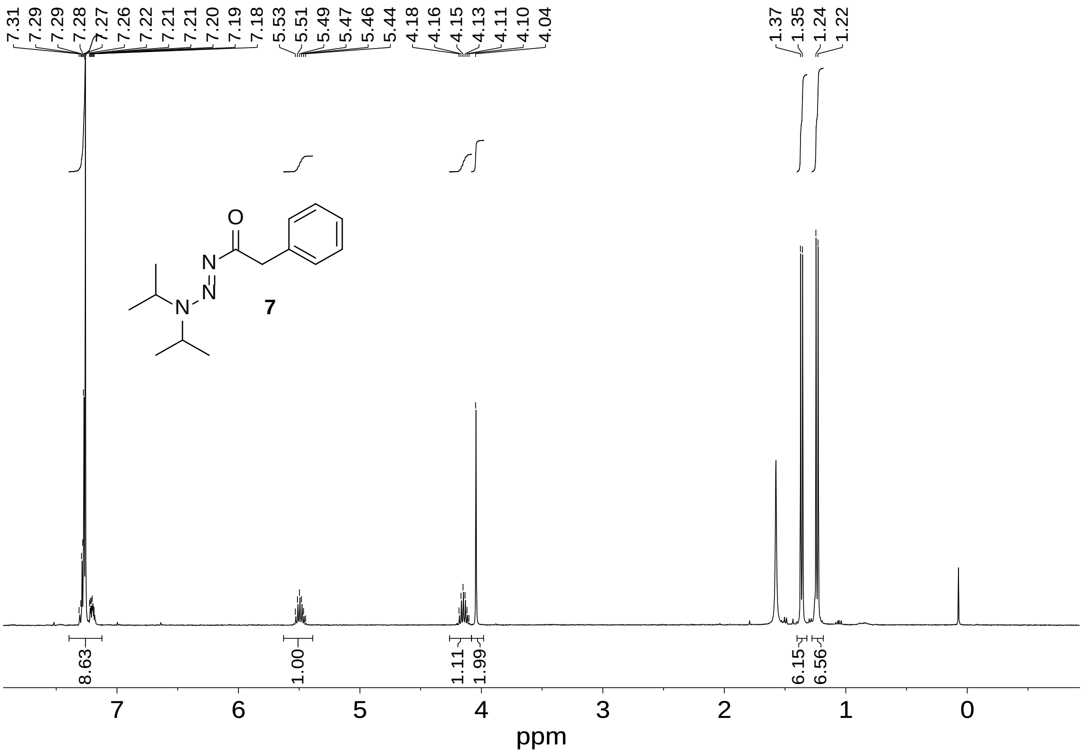


Figure S14.17. ^{1}H NMR spectrum of **7** (400 MHz, CDCl$_3$).

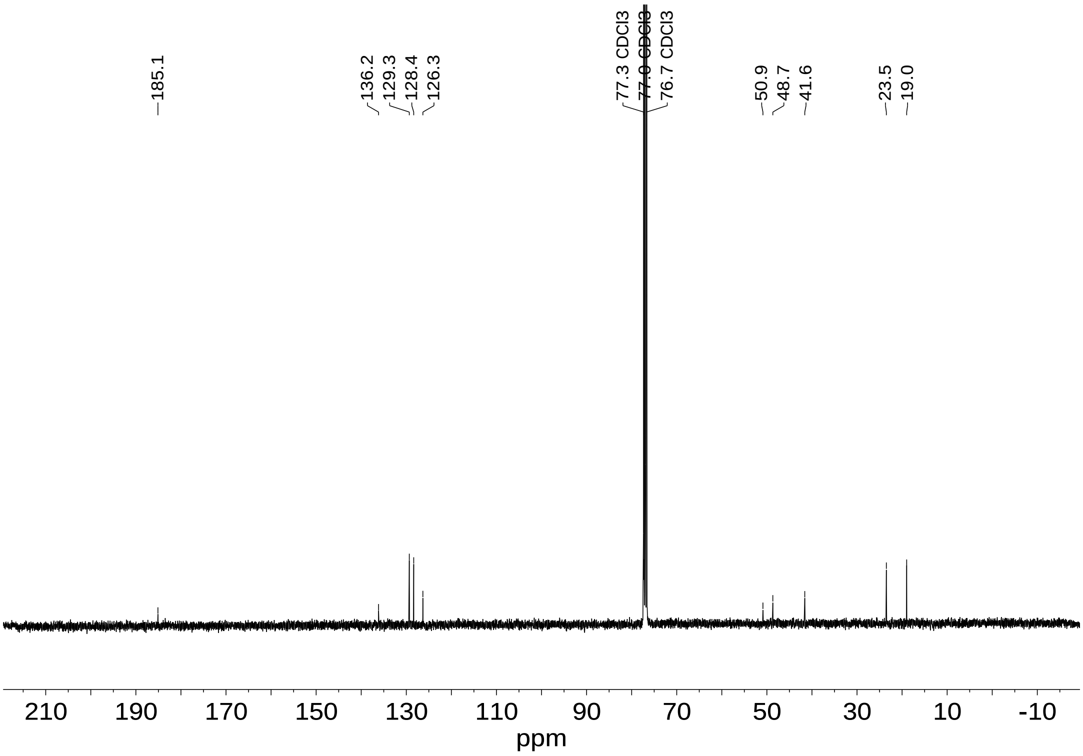


Figure S14.18. ^{13}C NMR spectrum of **7** (101 MHz, CDCl$_3$).

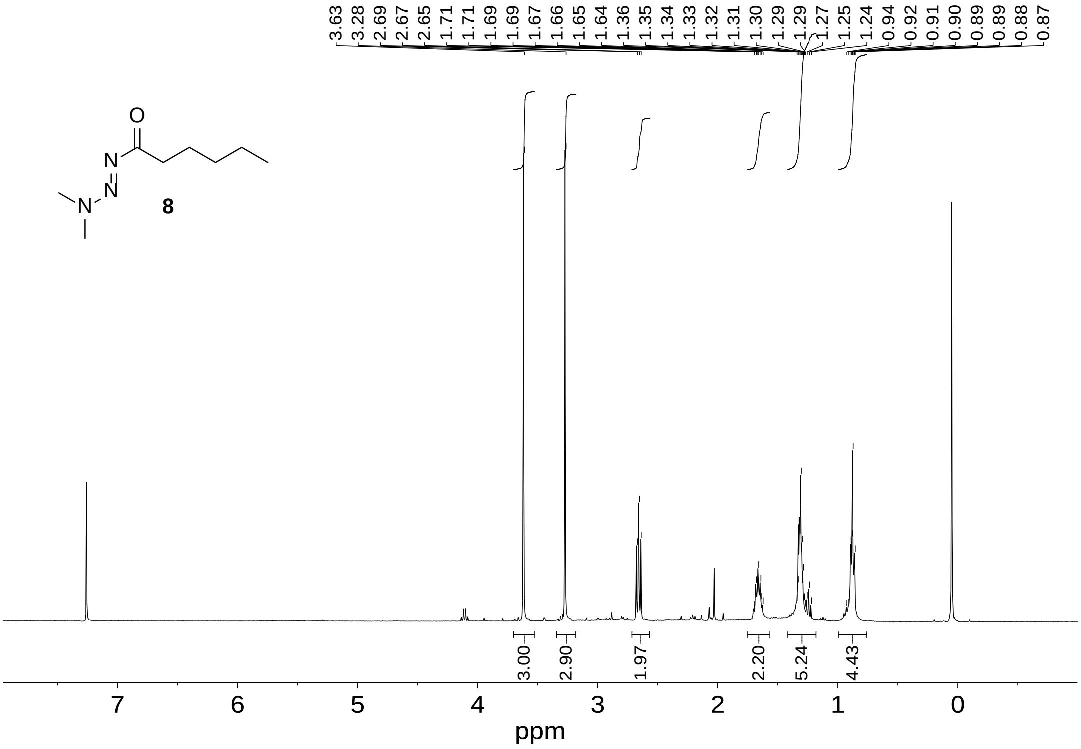


Figure S14.19. ^{1}H NMR spectrum of **8** (400 MHz, $CDCl_3$).

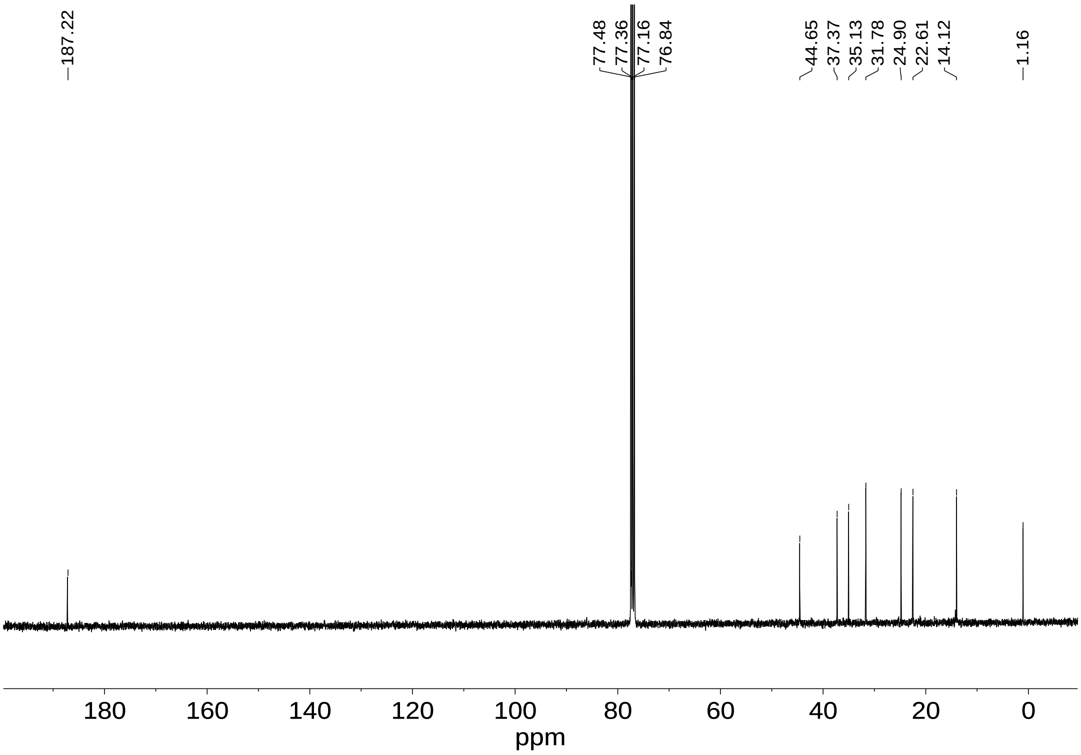


Figure S14.20. ^{13}C NMR spectrum of **8** (101 MHz, $CDCl_3$).

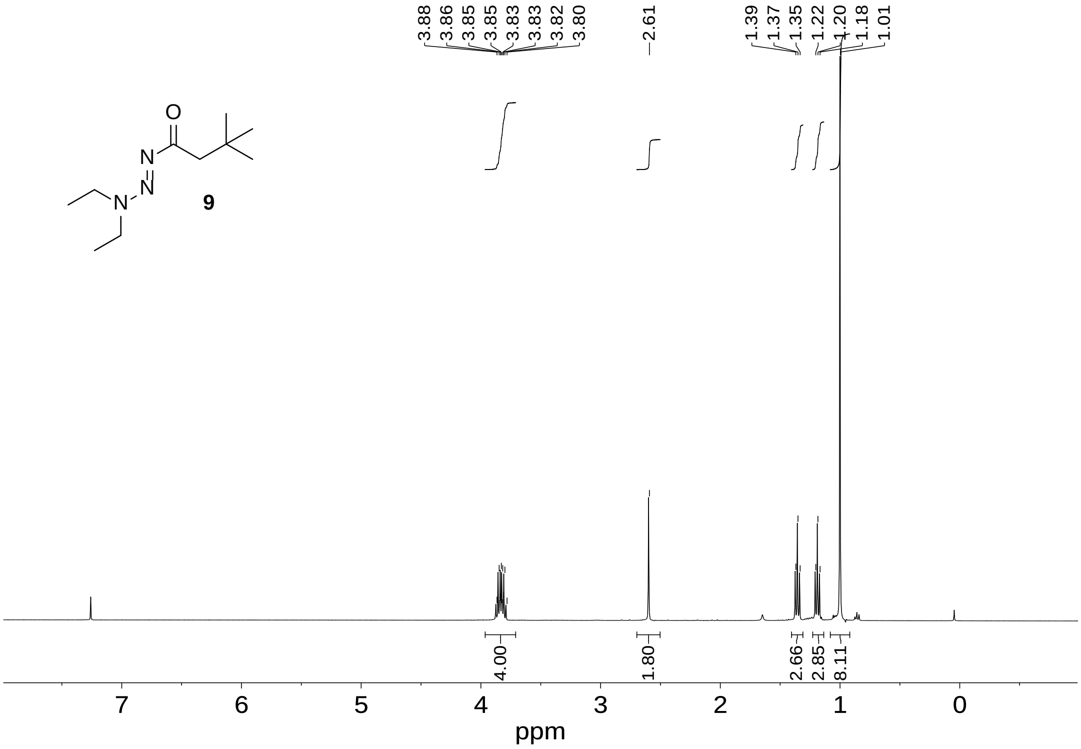


Figure S14.21. ^{1}H NMR spectrum of **9** (400 MHz, $CDCl_3$).

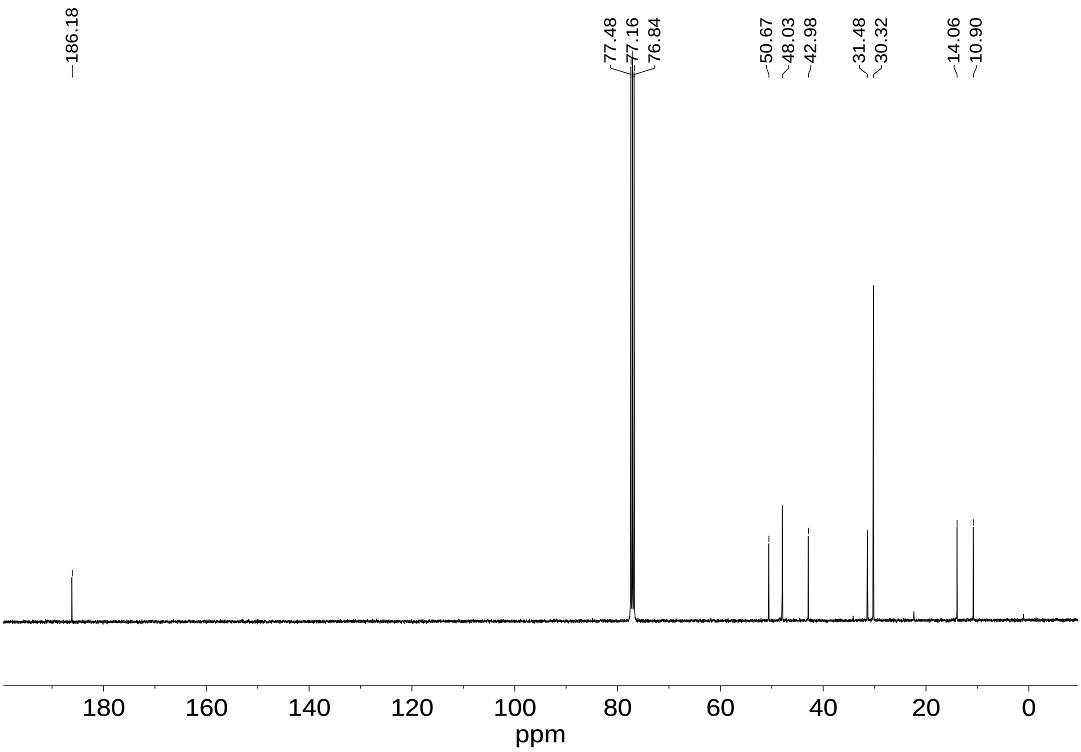


Figure S14.22. ^{13}C NMR spectrum of **9** (101 MHz, $CDCl_3$).

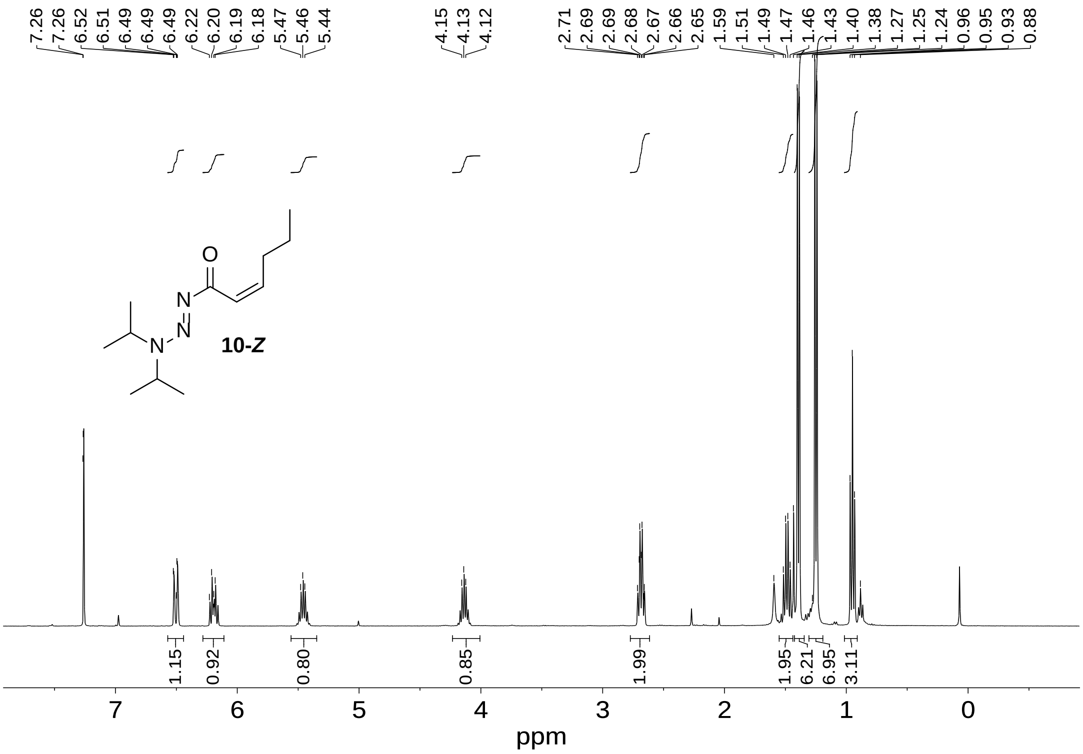


Figure S14.23. ^{1}H NMR spectrum of **10-*Z*** (400 MHz, CDCl$_3$).

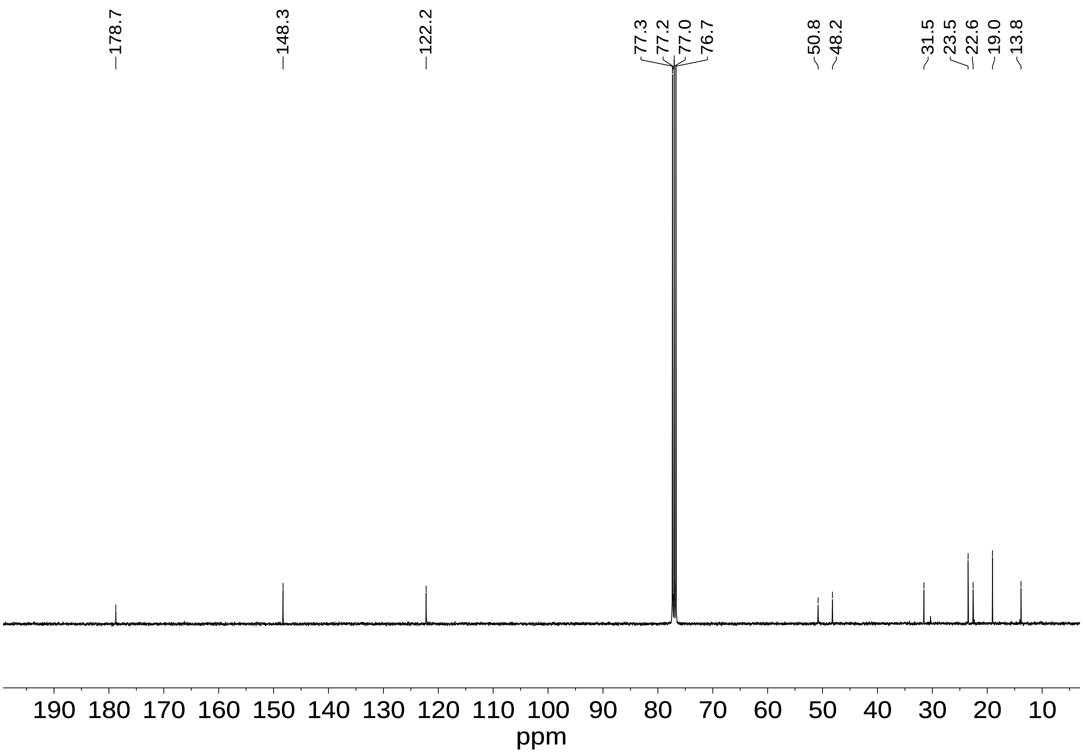


Figure S14.24. ^{13}C NMR spectrum of **10-*Z*** (101 MHz, CDCl$_3$).

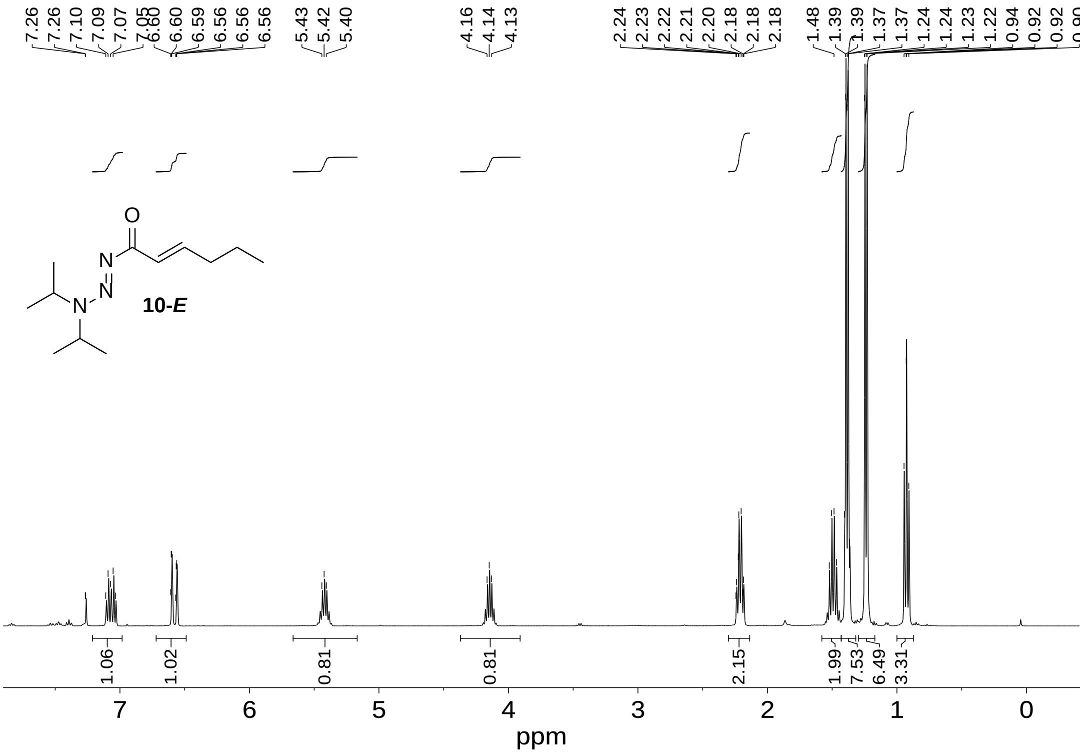


Figure S14.25. ^{1}H NMR spectrum of **10-*E*** (400 MHz, CDCl$_3$).

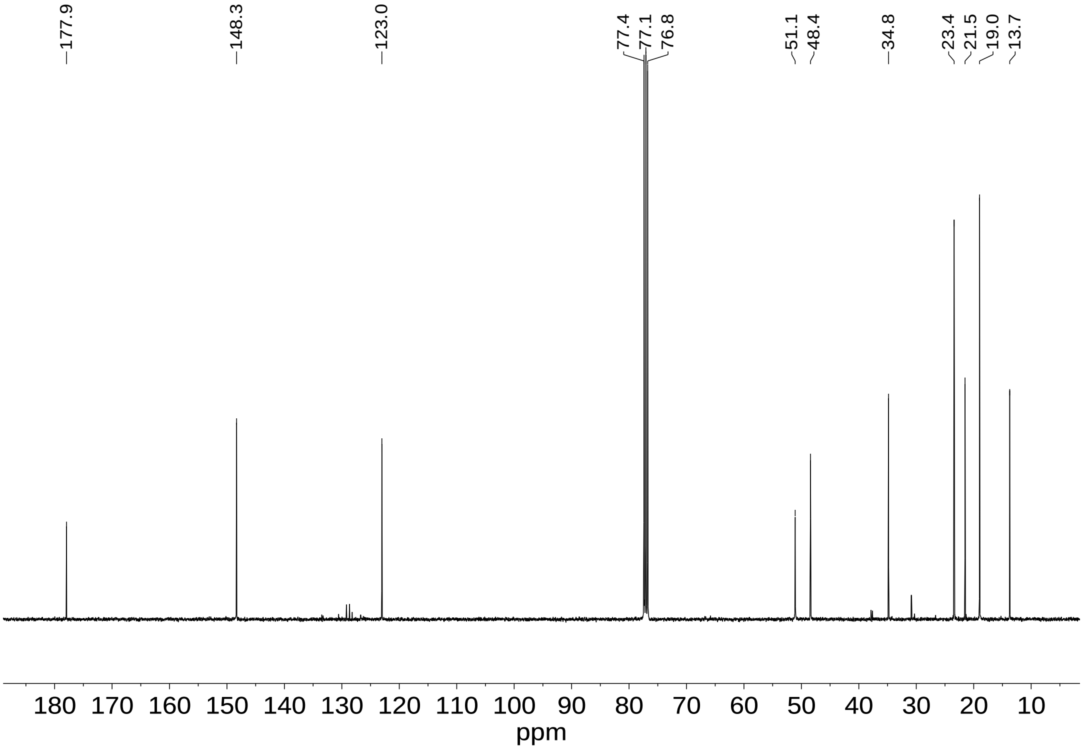


Figure S14.26. ^{13}C NMR spectrum of **10-*E*** (101 MHz, CDCl$_3$).

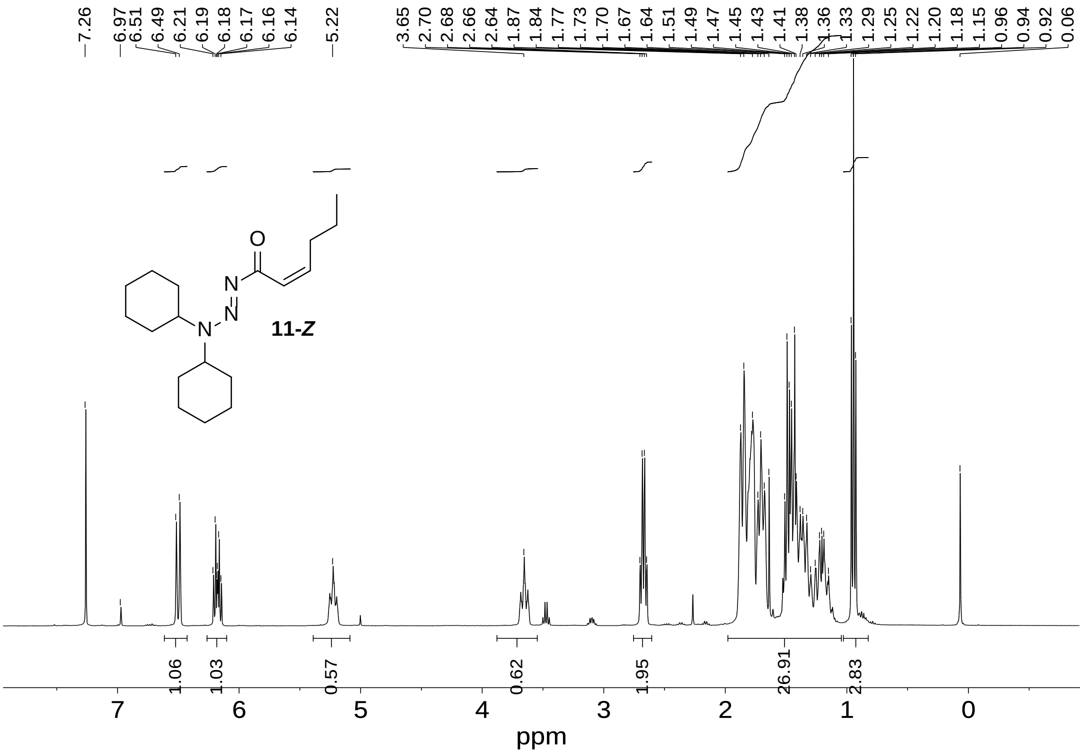


Figure S14.27. ^{1}H NMR spectrum of **11-*Z*** (400 MHz, CDCl$_3$).

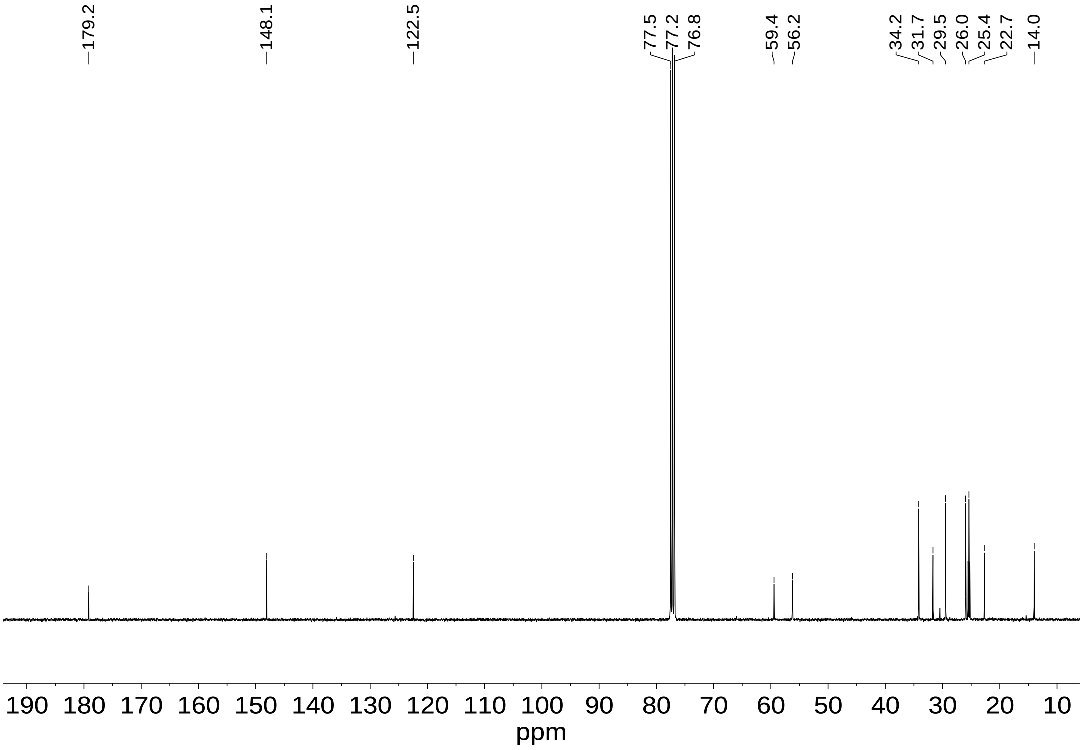


Figure S14.28. ^{13}C NMR spectrum of **11-*Z*** (101 MHz, CDCl$_3$).

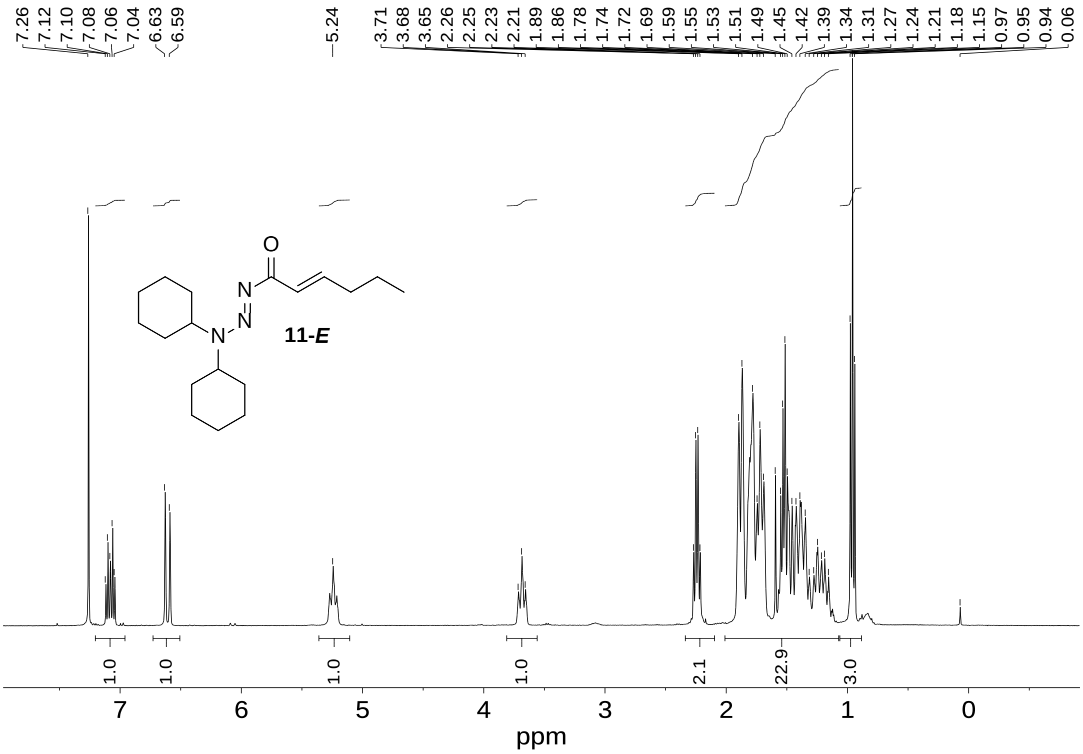


Figure S14.29. ^{1}H NMR spectrum of **11-*E*** (400 MHz, CDCl$_3$).

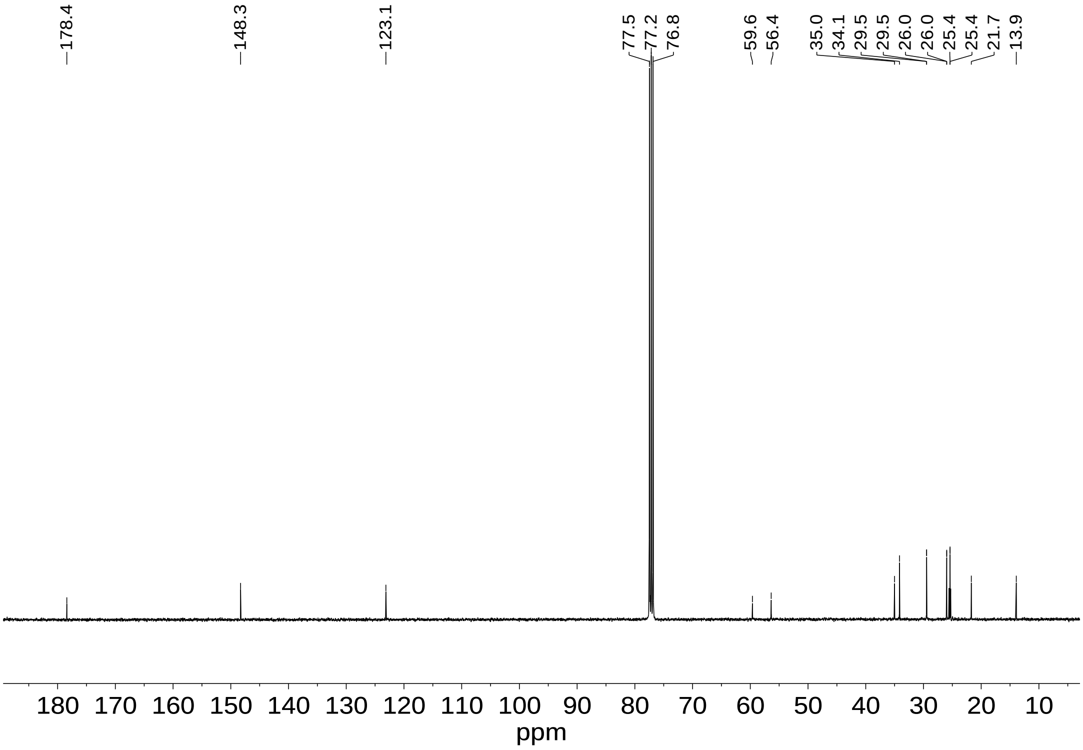


Figure S14.30. ^{13}C NMR spectrum of **11-*E*** (101 MHz, CDCl$_3$).

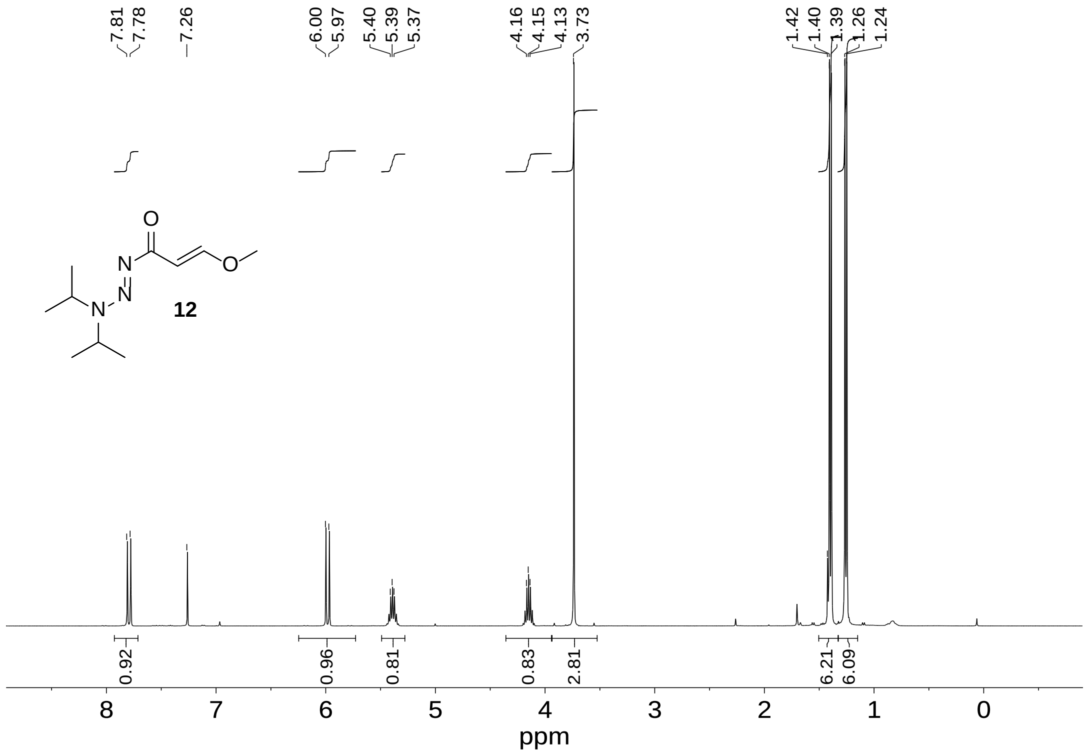


Figure S14.31. ^{1}H NMR spectrum of **12** (400 MHz, CDCl$_3$).

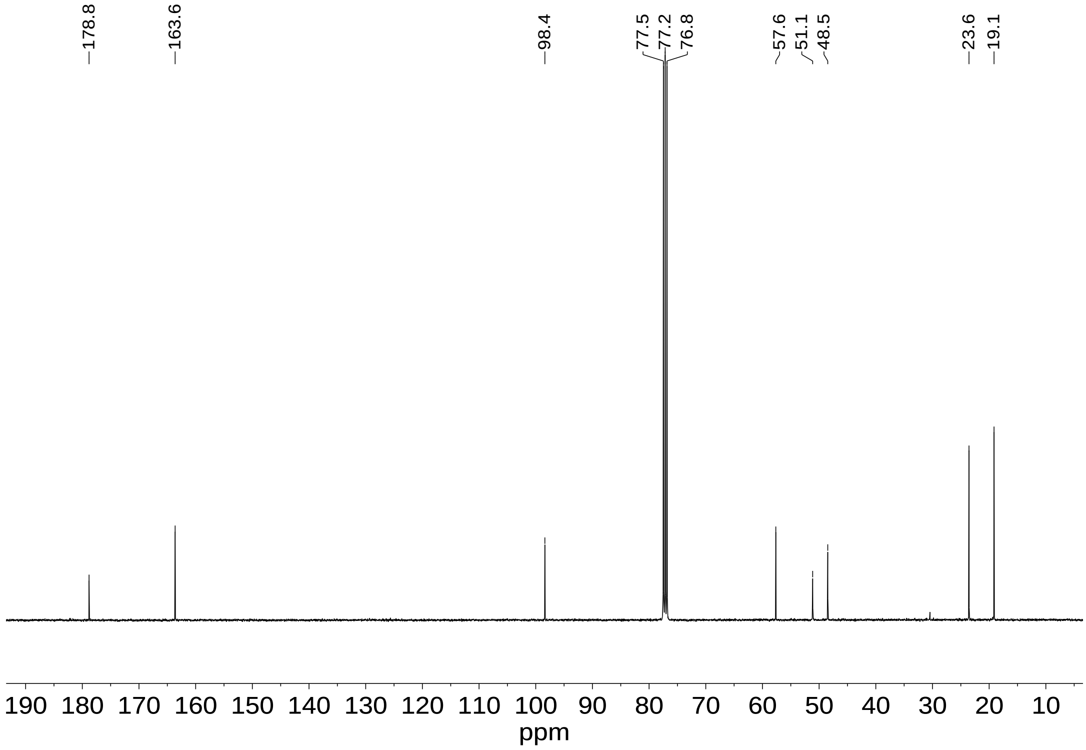


Figure S14.32. ^{13}C NMR spectrum of **12** (101 MHz, CDCl$_3$).

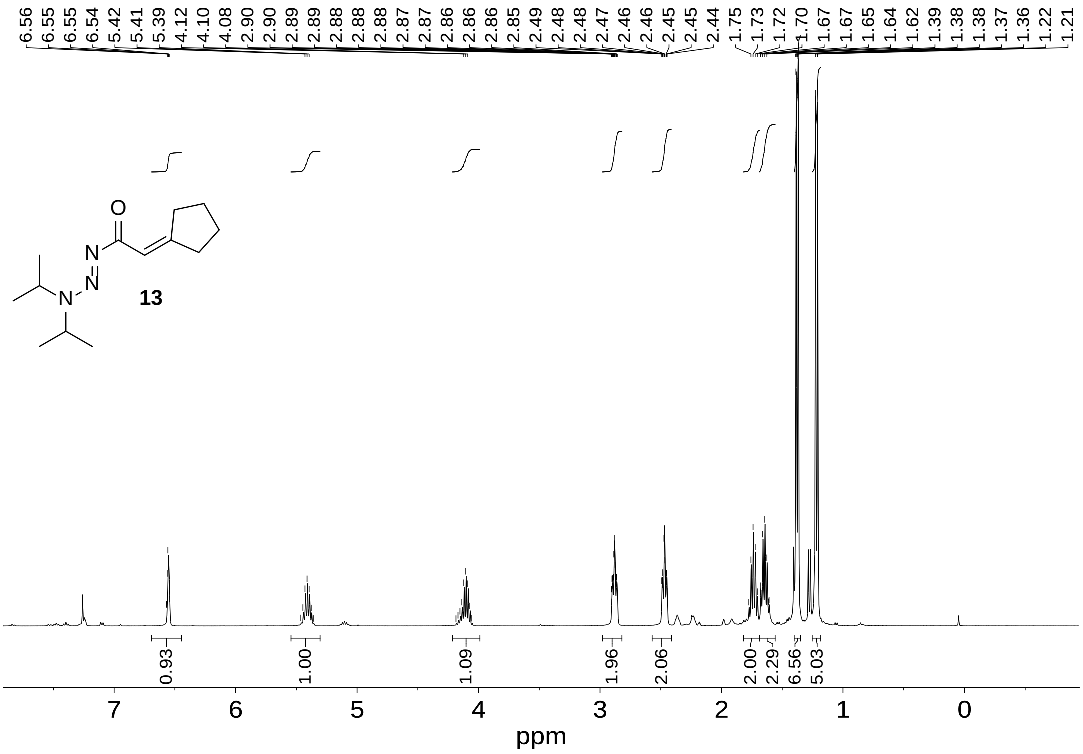


Figure S14.33. ^{1}H NMR spectrum of **13** (400 MHz, CDCl$_3$).

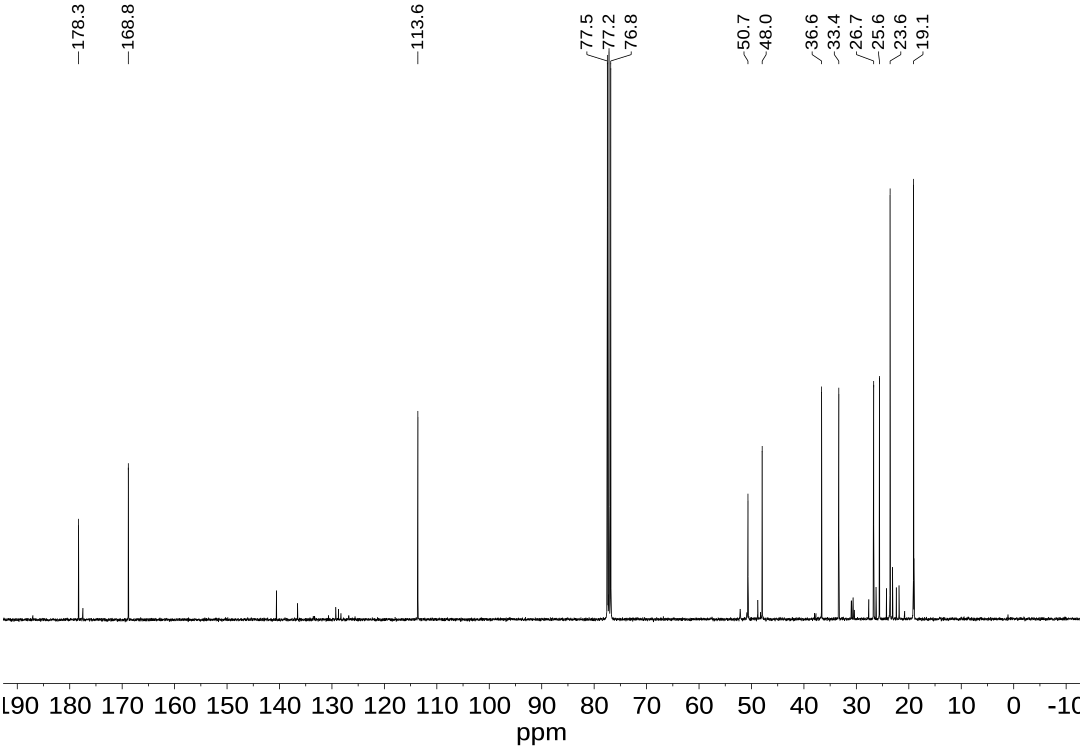


Figure S14.34. ^{13}C NMR spectrum of **13** (101 MHz, CDCl$_3$).

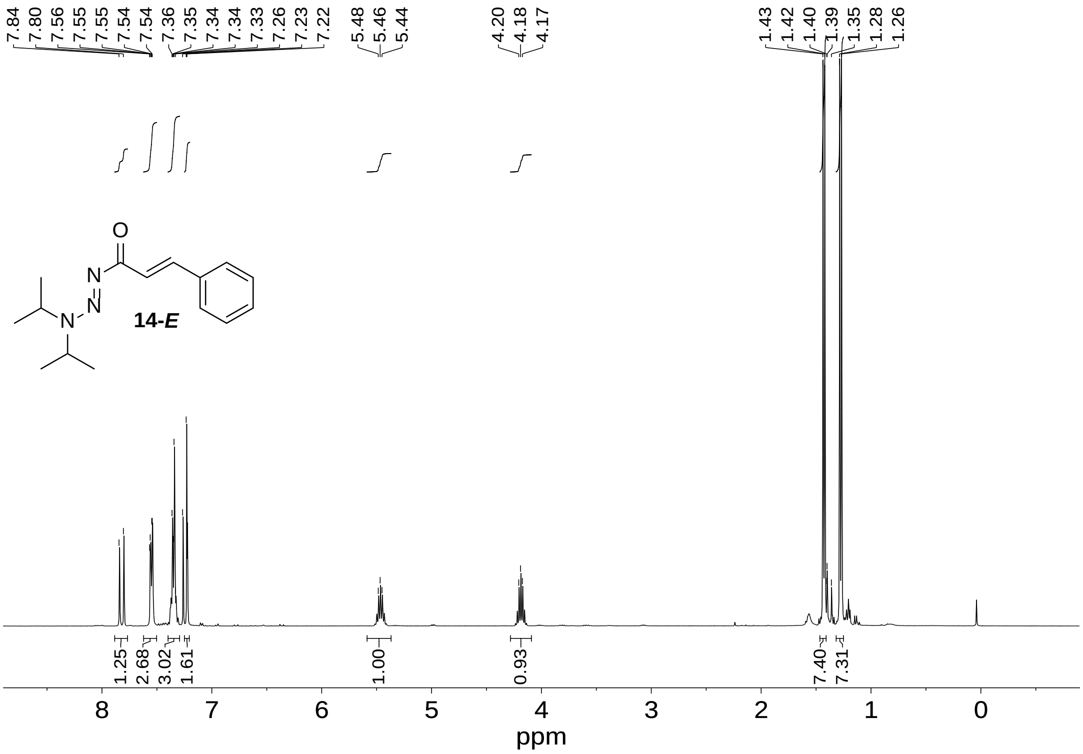


Figure S14.35. ^{1}H NMR spectrum of **14-*E*** (400 MHz, $CDCl_3$).

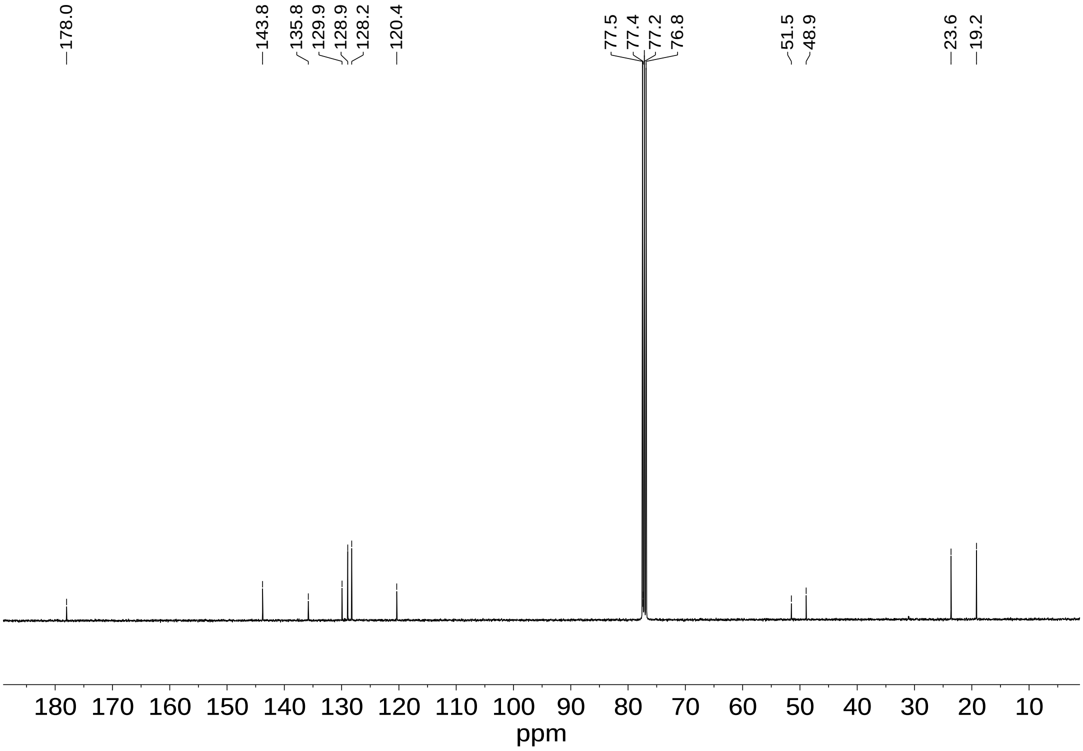


Figure S14.36. ^{13}C NMR spectrum of **14-*E*** (101 MHz, $CDCl_3$).

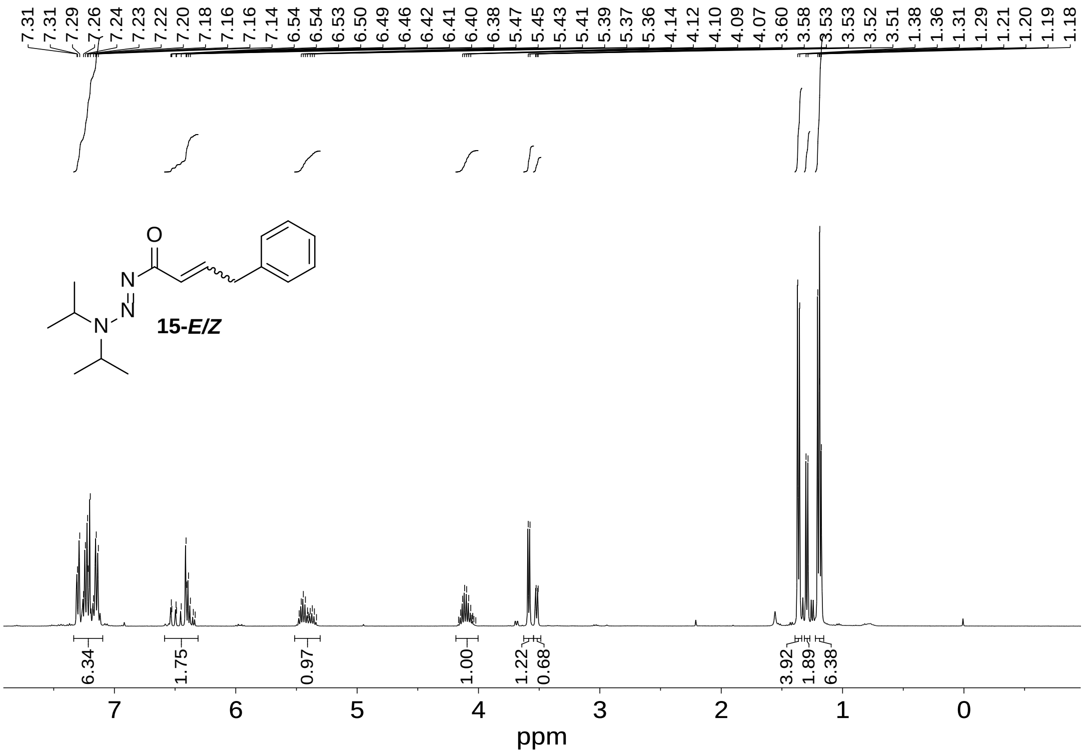


Figure S14.37. ^{1}H NMR spectrum of **15-*E/Z*** (400 MHz, CDCl3).

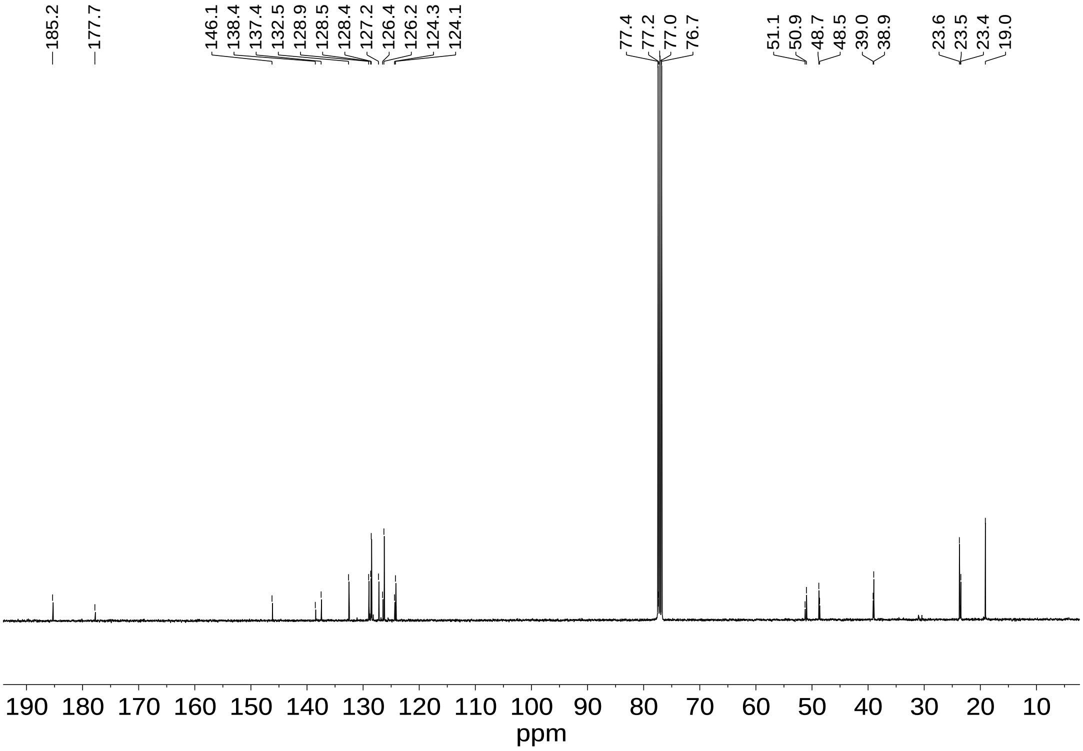


Figure S14.38. ^{13}C NMR spectrum of **15-*E/Z*** *(~2:1)* (101 MHz, CDCl3).

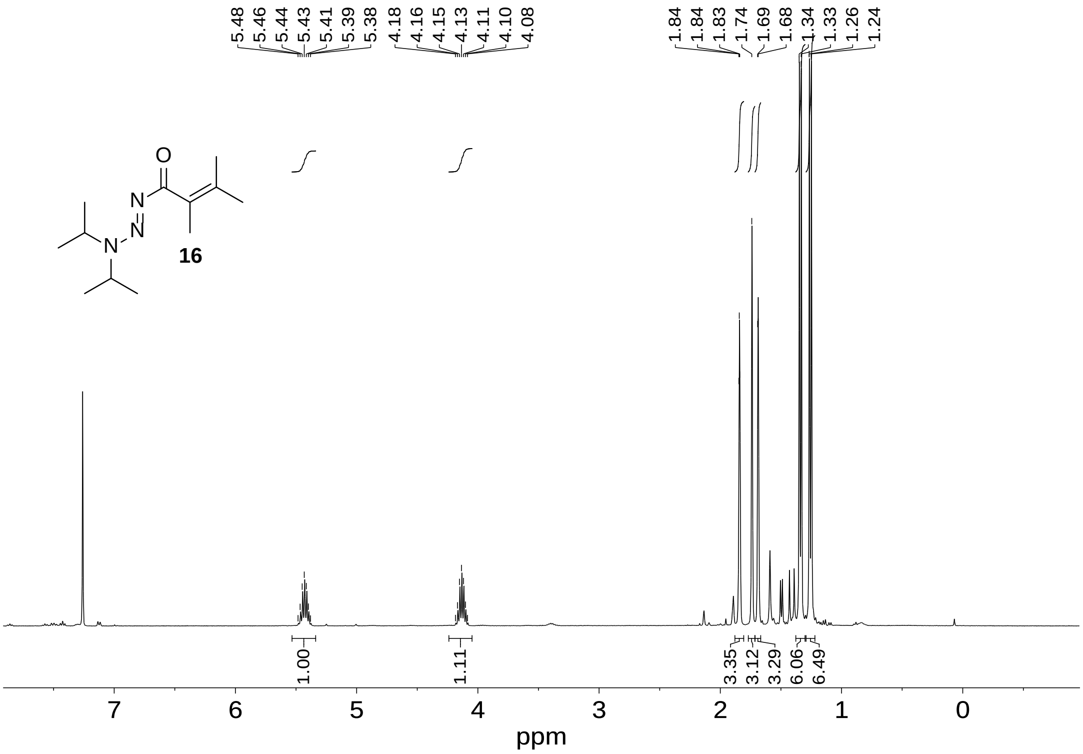


Figure S14.39. ^{1}H NMR spectrum of **16** (400 MHz, $CDCl_3$).

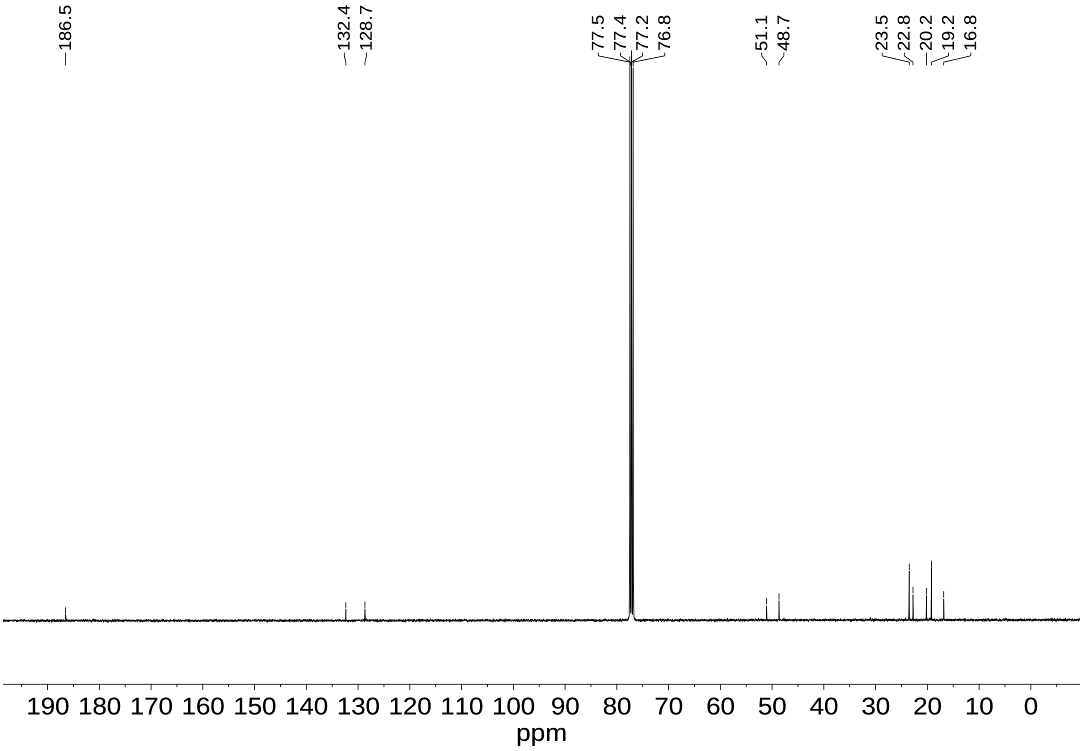


Figure S14.40. ^{13}C NMR spectrum of **16** (101 MHz, $CDCl_3$).

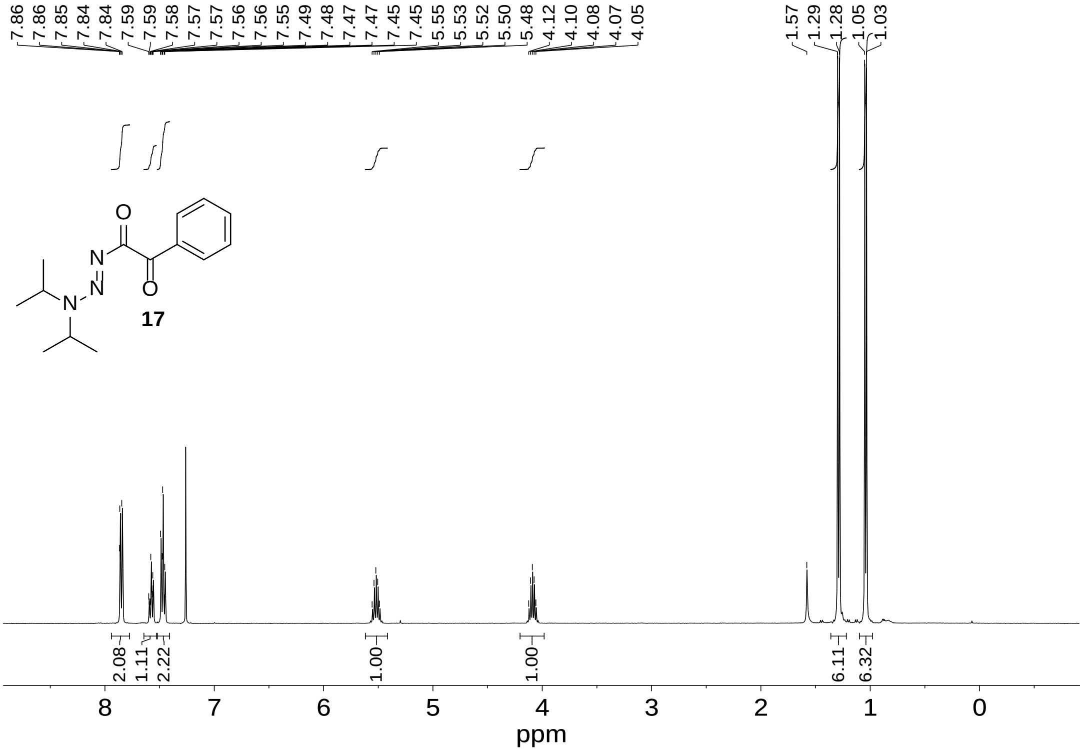


Figure S14.41. ^{1}H NMR spectrum of **17** (400 MHz, CDCl$_3$).

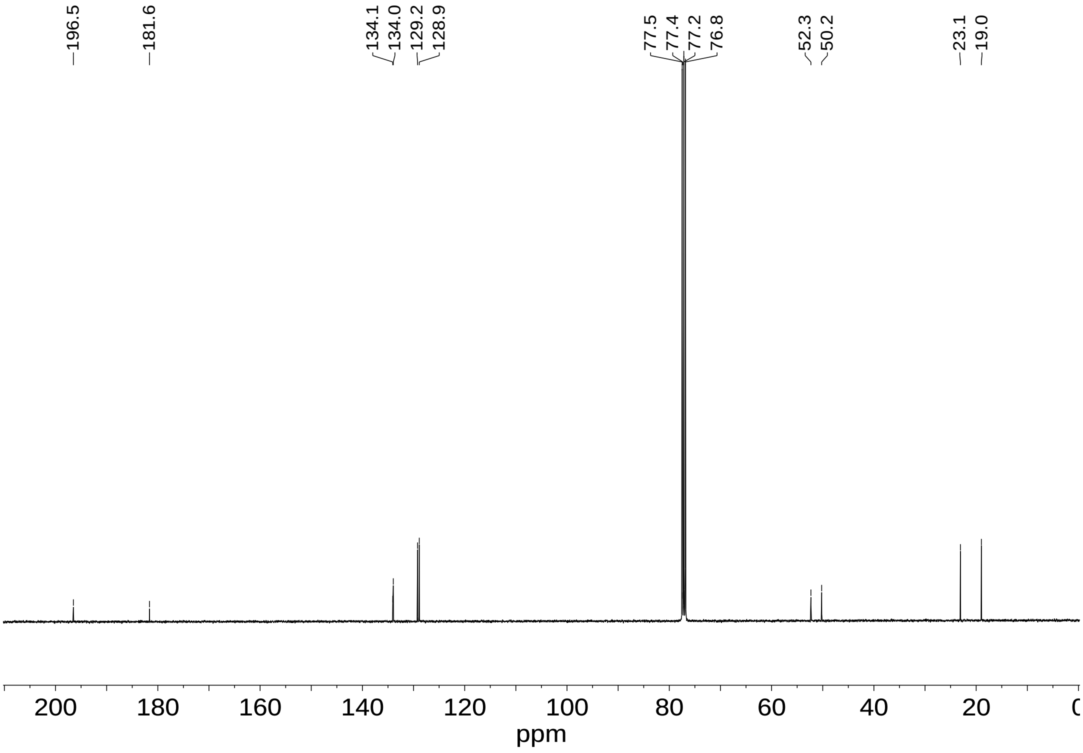


Figure S14.42. ^{13}C NMR spectrum of **17** (101 MHz, CDCl$_3$).

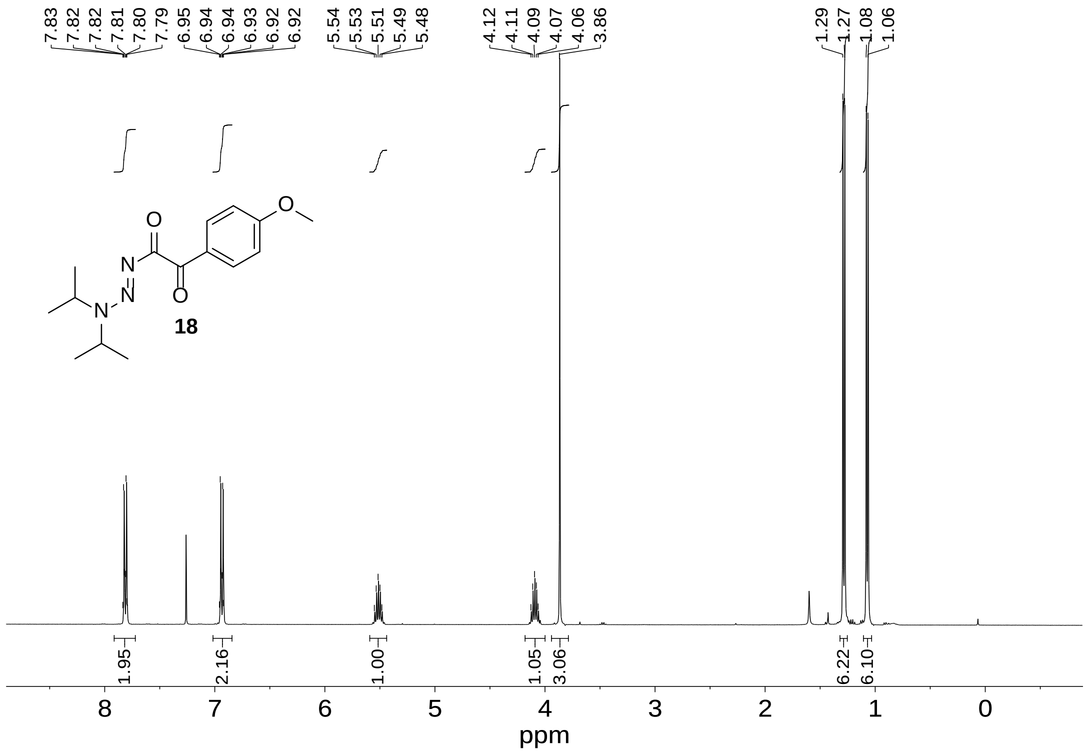


Figure S14.43. ^{1}H NMR spectrum of **18** (400 MHz, CDCl$_3$).

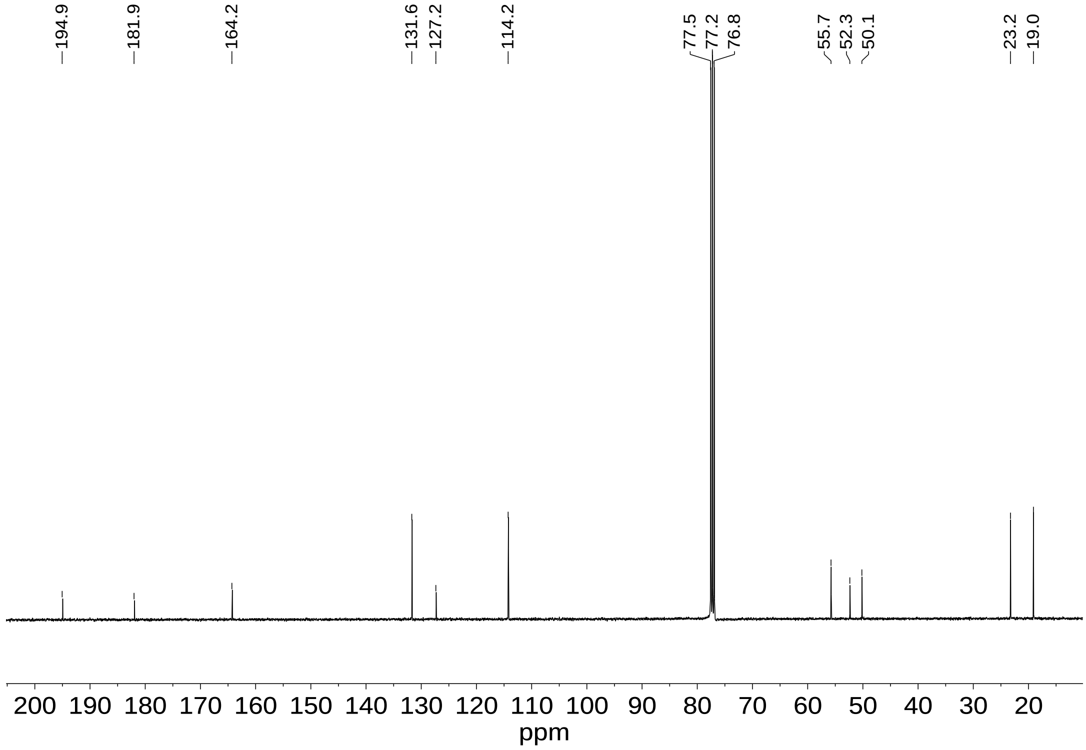


Figure S14.44. ^{13}C NMR spectrum of **18** (101 MHz, CDCl$_3$).

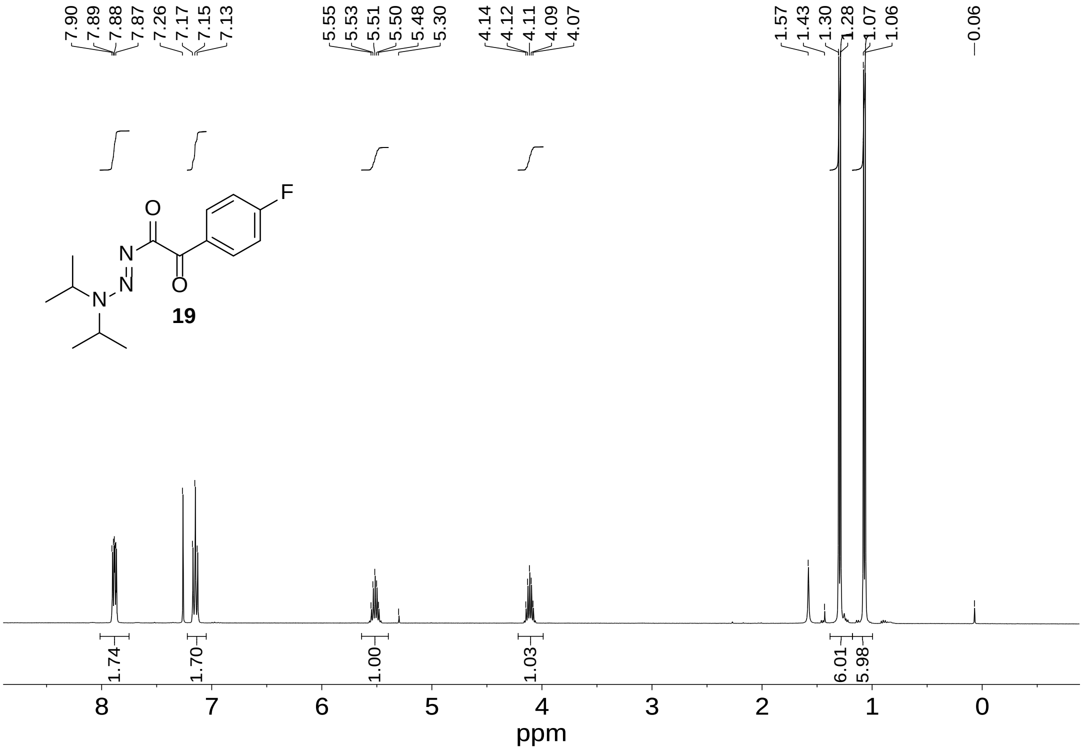


Figure S14.45. ^{1}H NMR spectrum of **19** (400 MHz, CDCl$_3$).

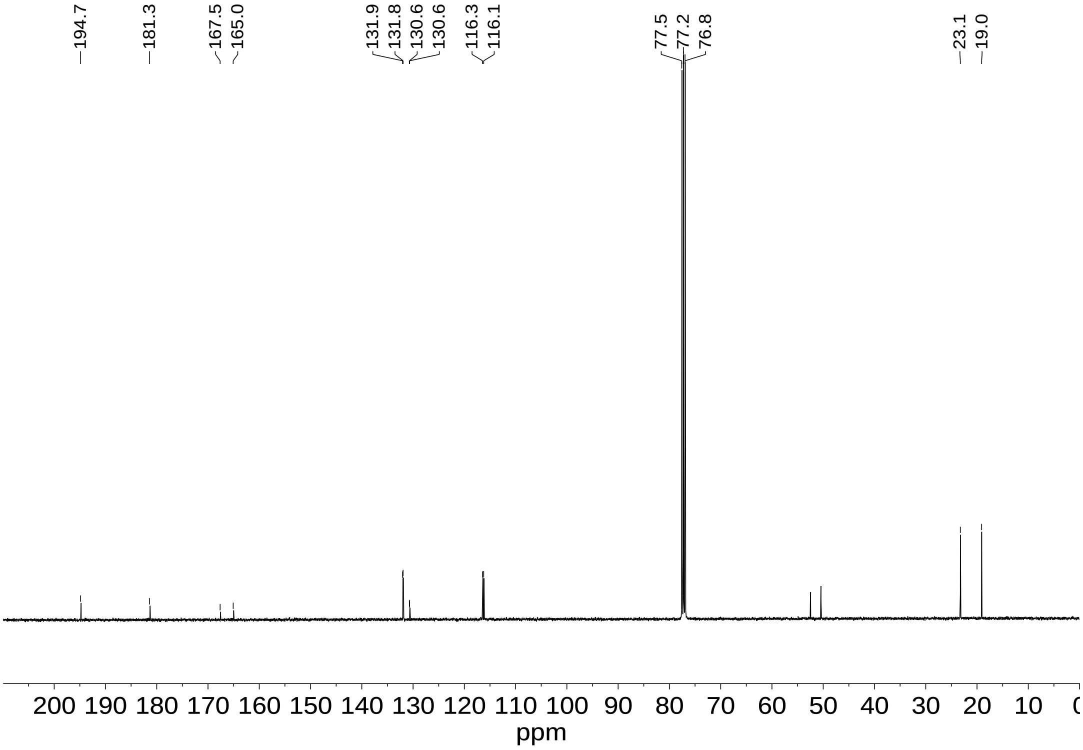


Figure S14.46. ^{13}C NMR spectrum of **19** (101 MHz, CDCl$_3$).

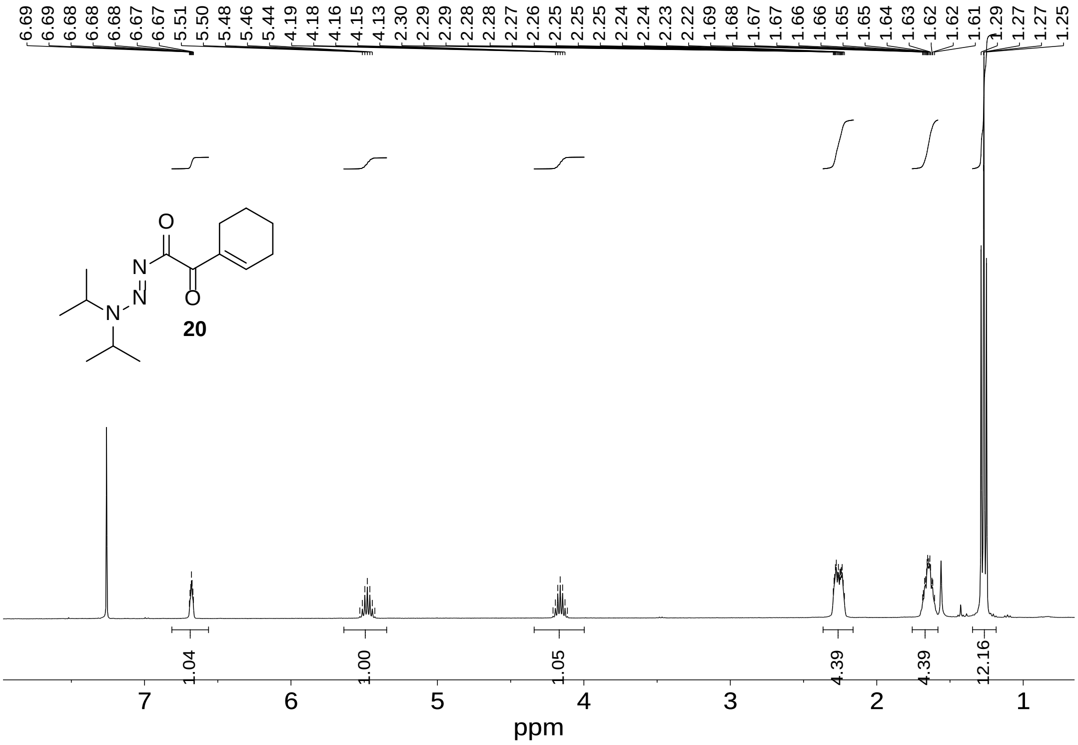


Figure S14.47. ^{1}H NMR spectrum of **20** (400 MHz, $CDCl_3$).

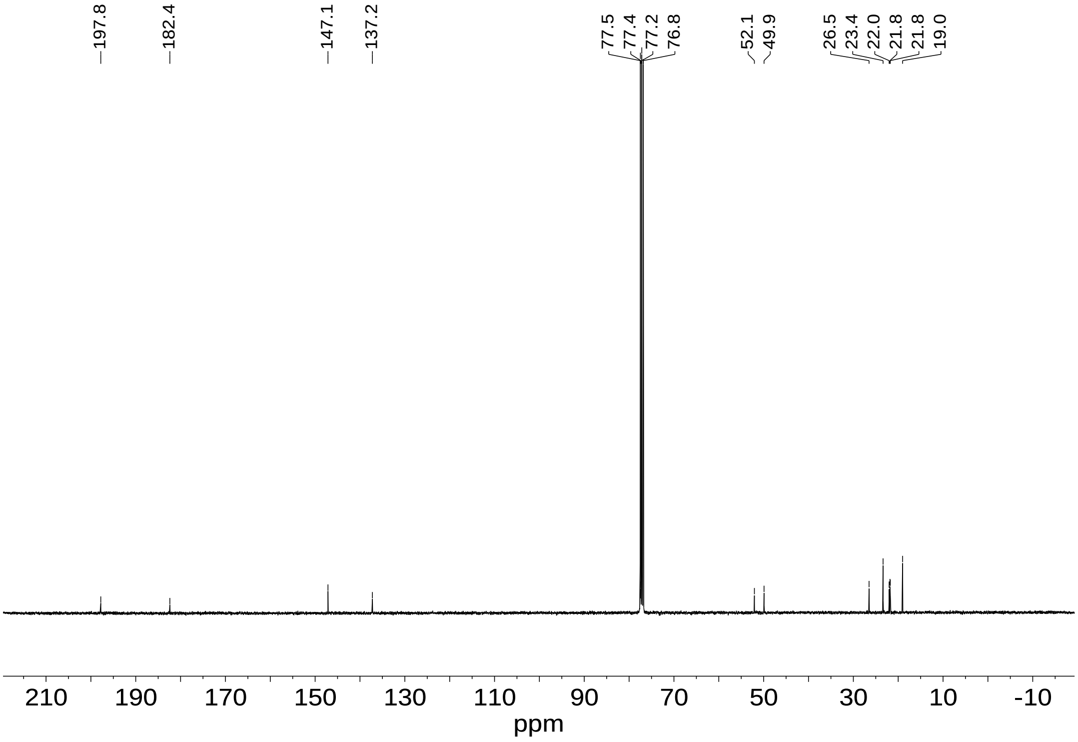


Figure S14.48. ^{13}C NMR spectrum of **20** (101 MHz, $CDCl_3$).

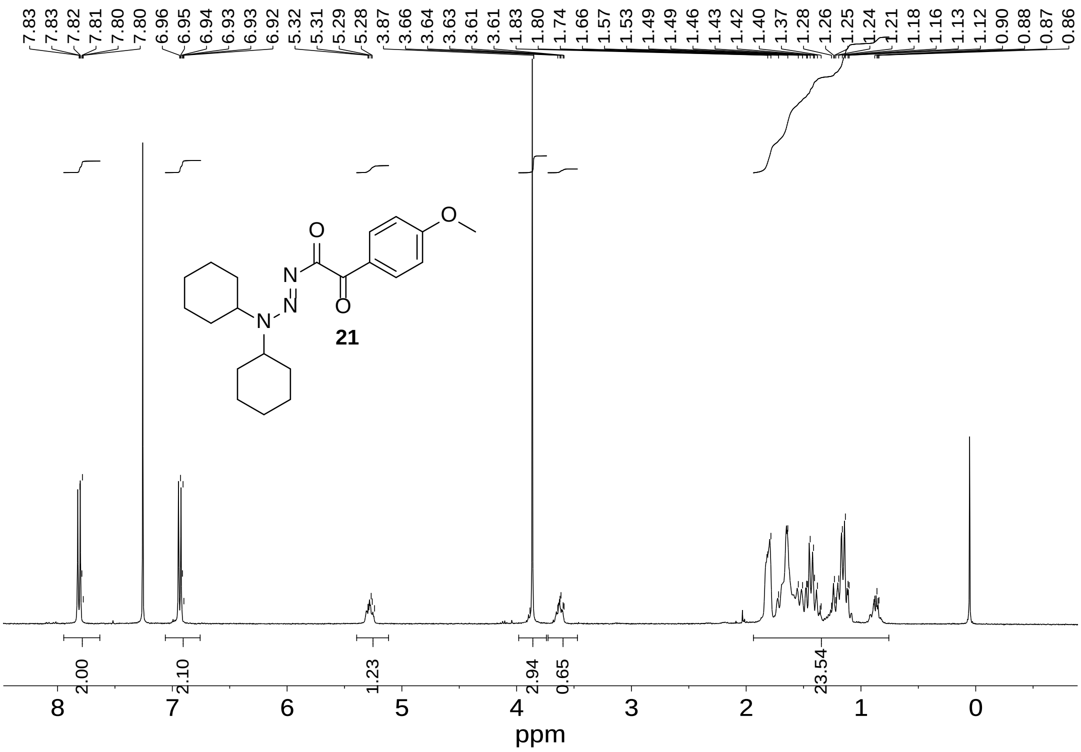


Figure S14.49. ^{1}H NMR spectrum of **21** (400 MHz, $CDCl_3$).

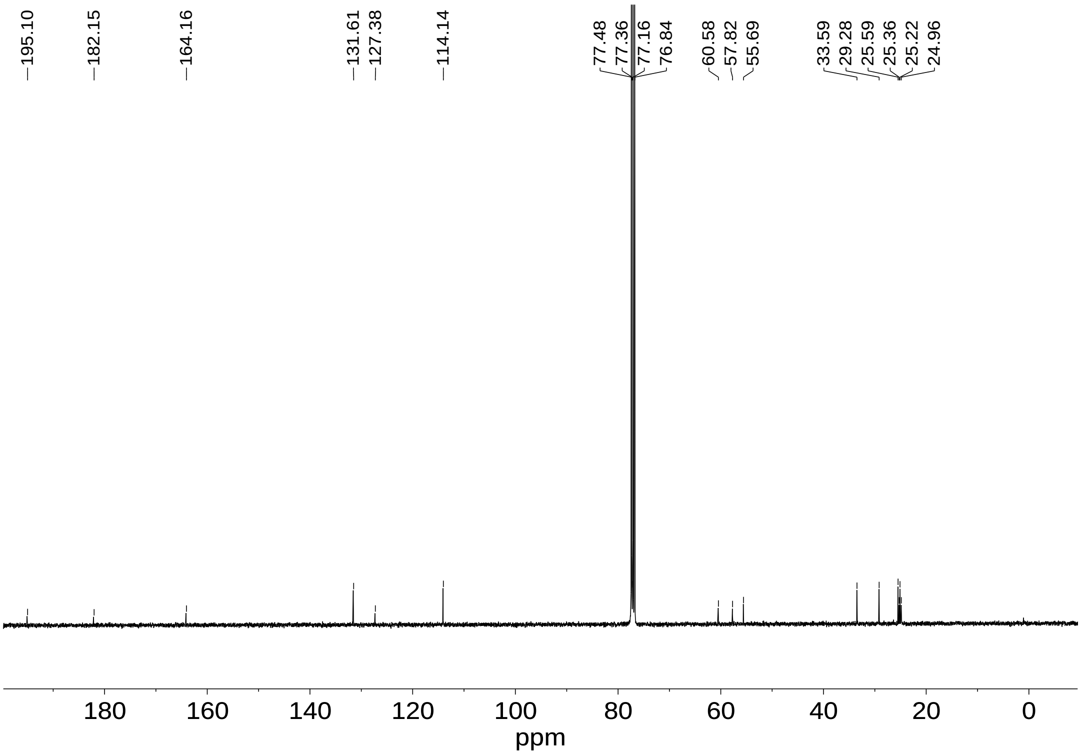


Figure S14.50. ^{13}C NMR spectrum of **21** (101 MHz, $CDCl_3$).

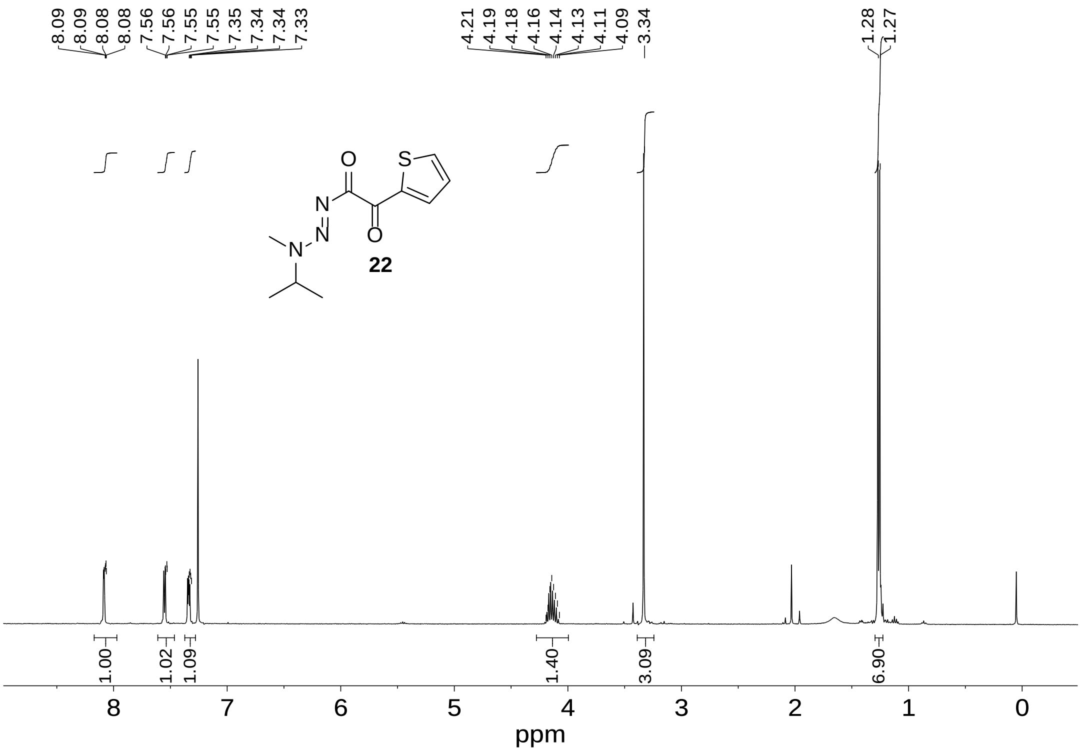


Figure S14.51. ^{1}H NMR spectrum of **22** (400 MHz, CDCl$_3$).

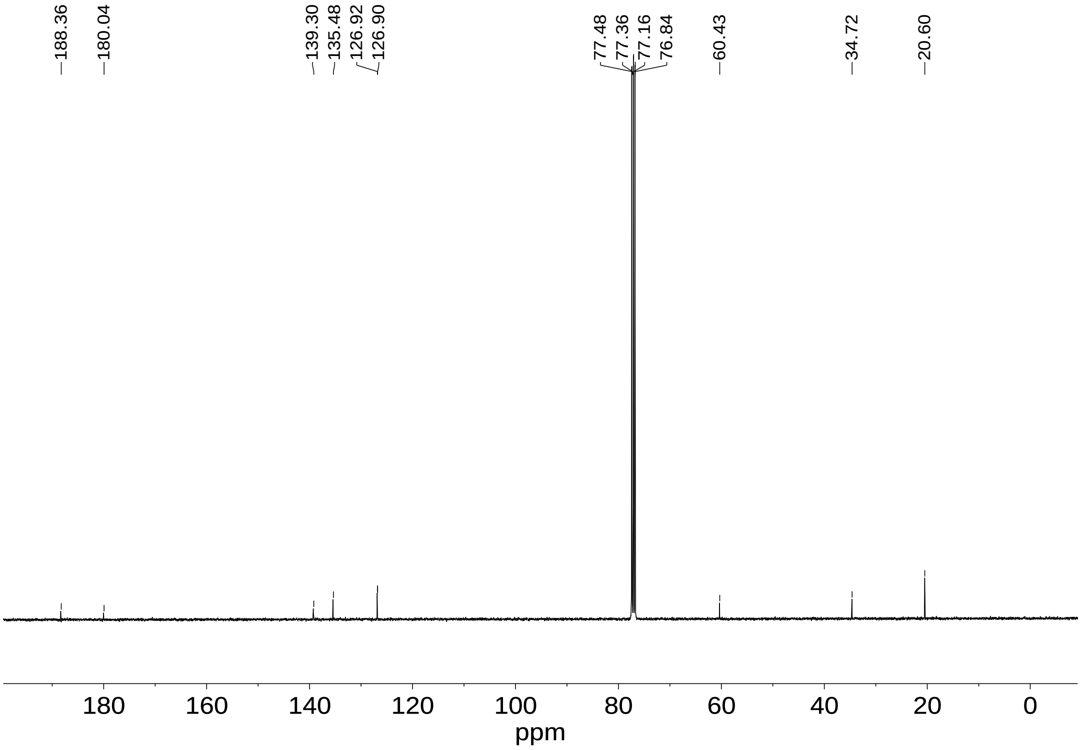


Figure S14.52. ^{13}C NMR spectrum of **22** (101 MHz, CDCl$_3$).

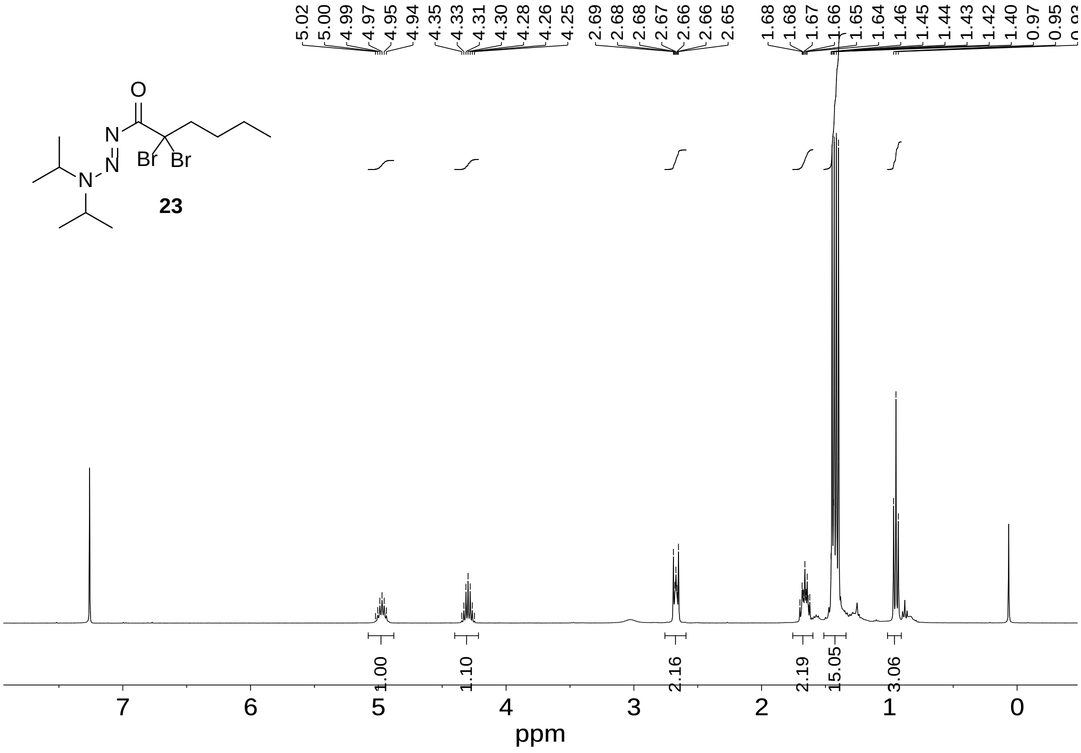


Figure S14.53. ^{1}H NMR spectrum of **23** (400 MHz, $CDCl_3$).

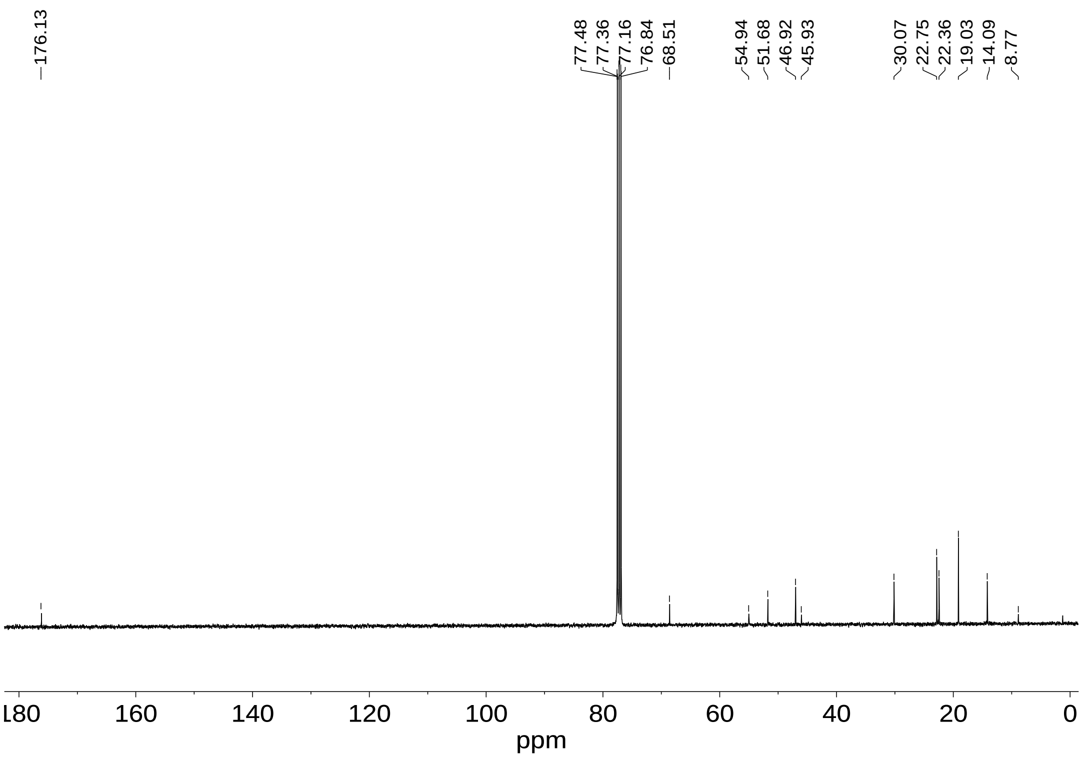


Figure S14.54. ^{13}C NMR spectrum of **23** (101 MHz, $CDCl_3$).

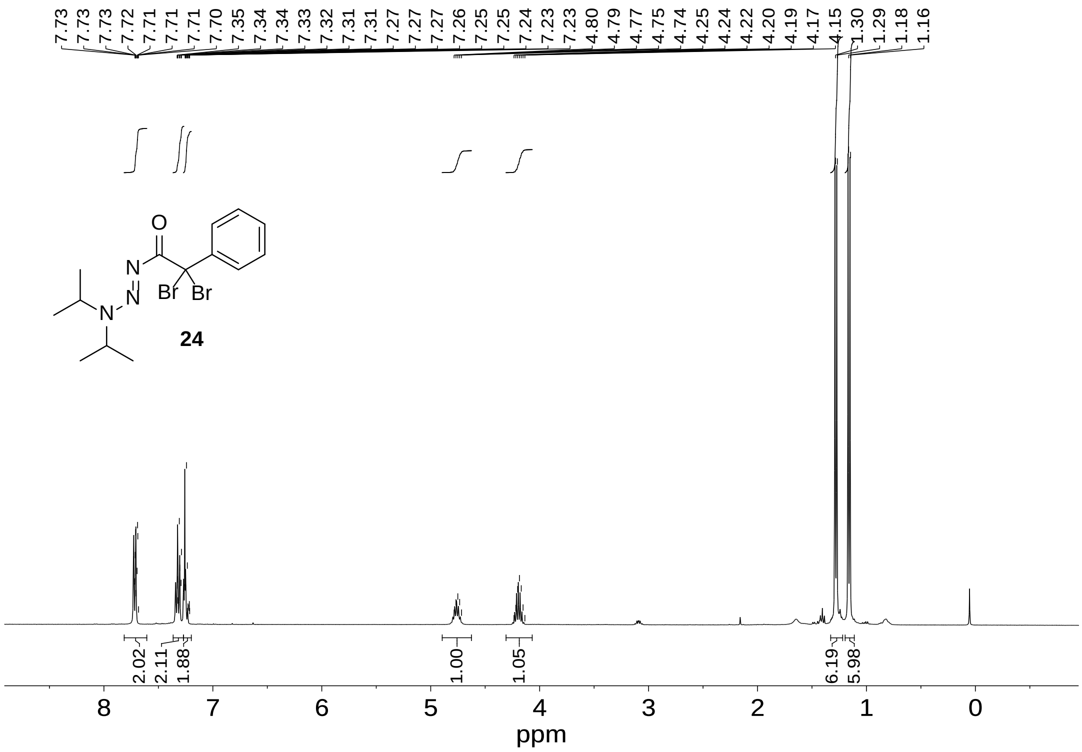


Figure S14.55. ^{1}H NMR spectrum of **24** (400 MHz, $CDCl_3$).

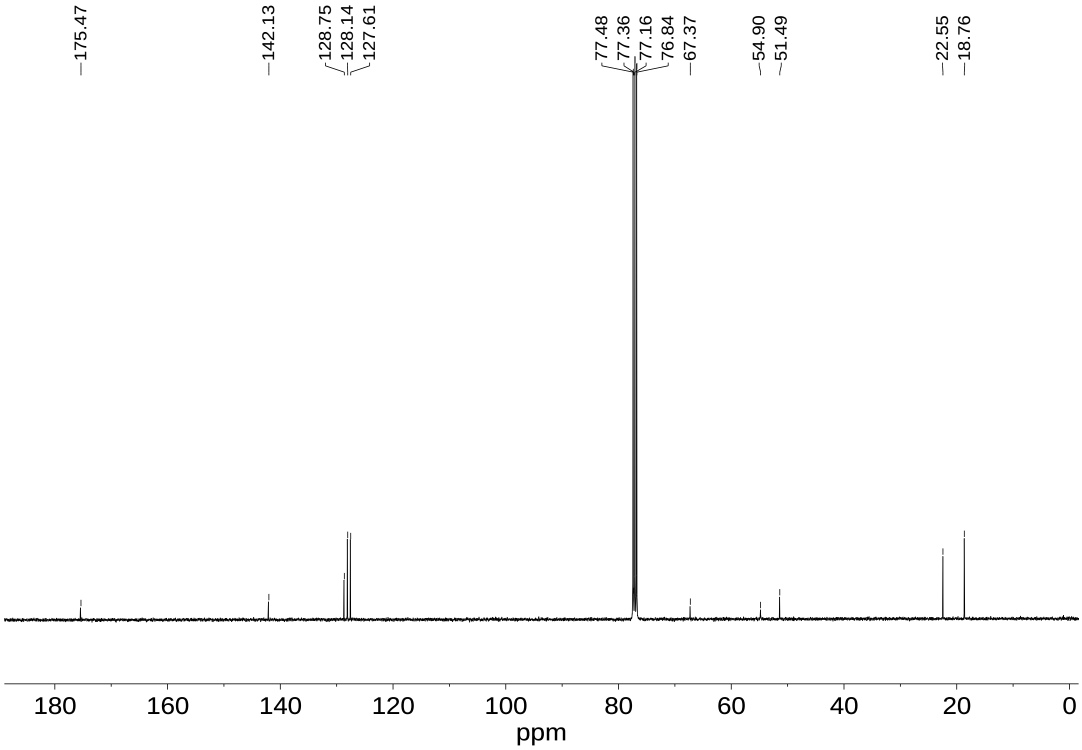


Figure S14.56. ^{13}C NMR spectrum of **24** (101 MHz, $CDCl_3$).

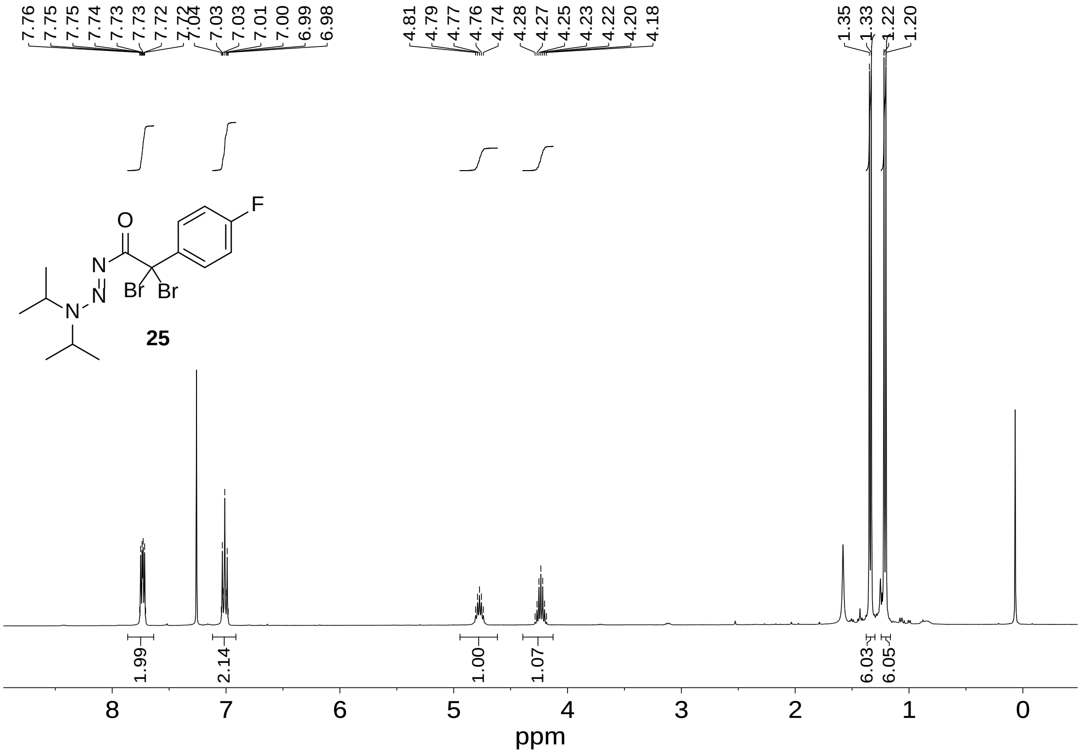


Figure S14.57. ^{1}H NMR spectrum of **25** (400 MHz, $CDCl_3$).

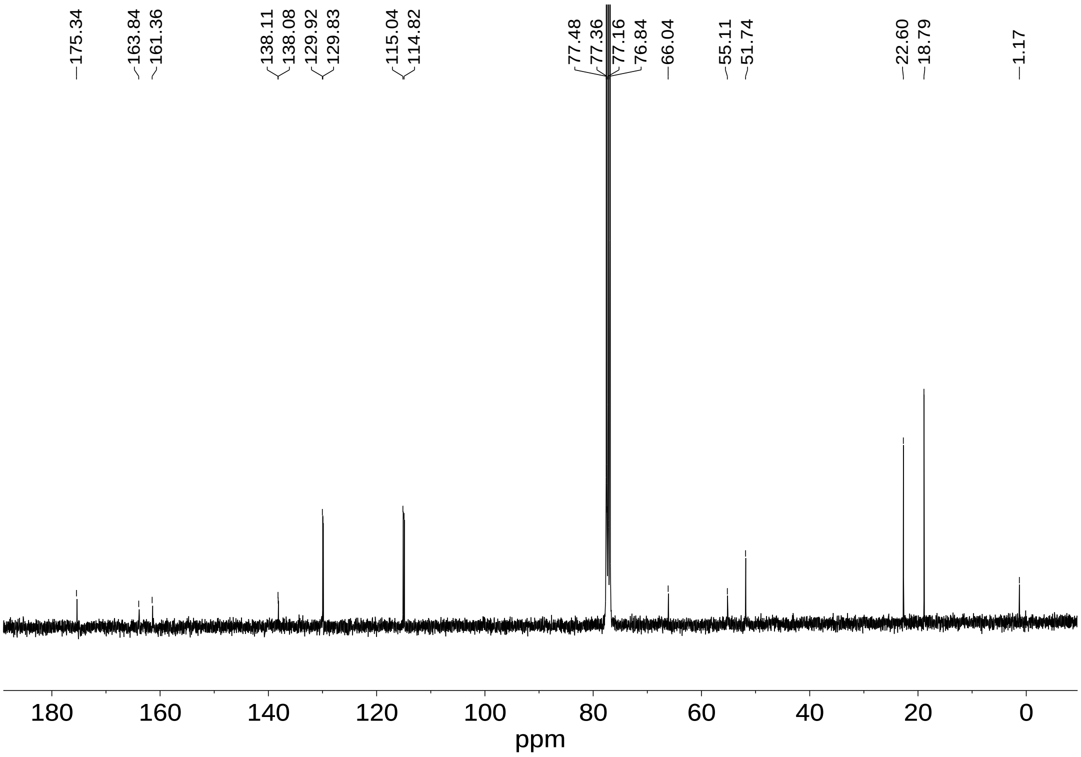


Figure S14.58. ^{13}C NMR spectrum of **25** (101 MHz, $CDCl_3$).

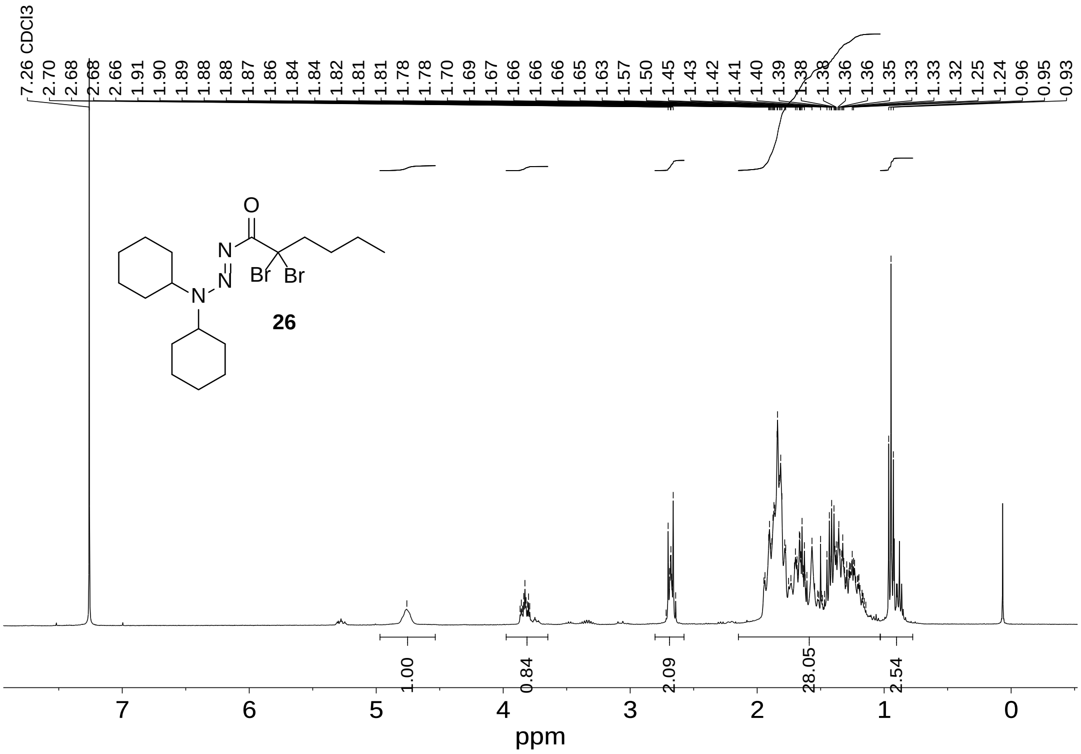


Figure S14.59. ^{1}H NMR spectrum of **26** (400 MHz, $CDCl_3$).

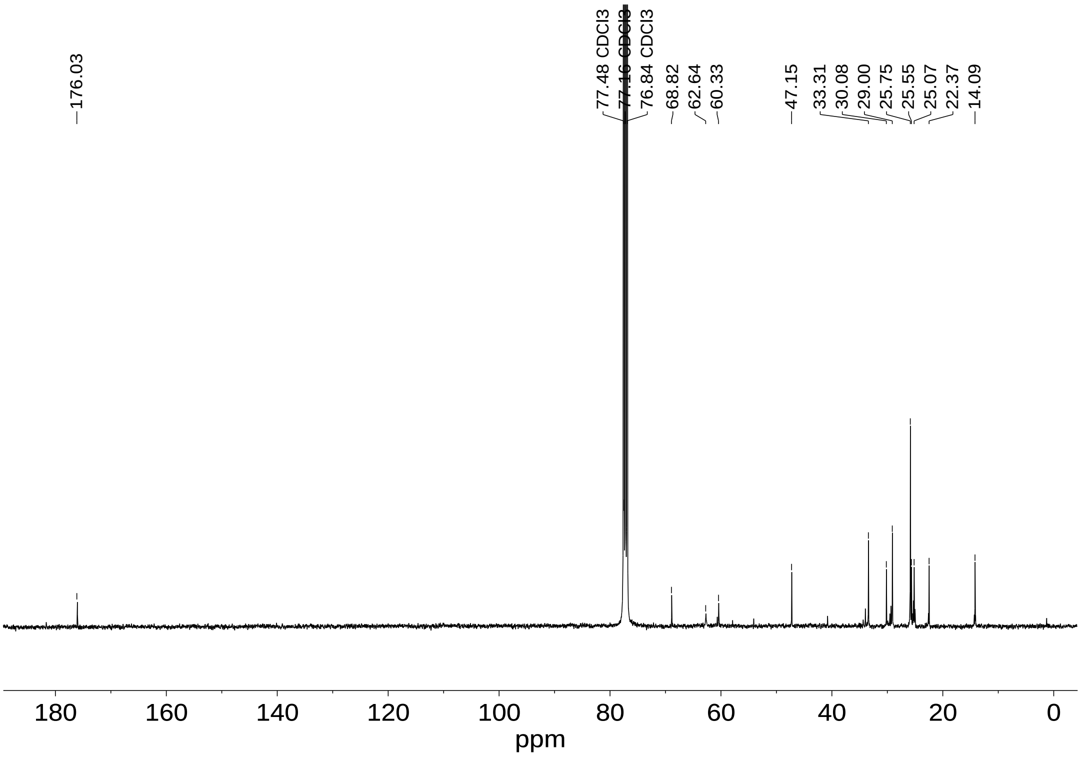


Figure S14.60. ^{13}C NMR spectrum of **26** (101 MHz, $CDCl_3$).

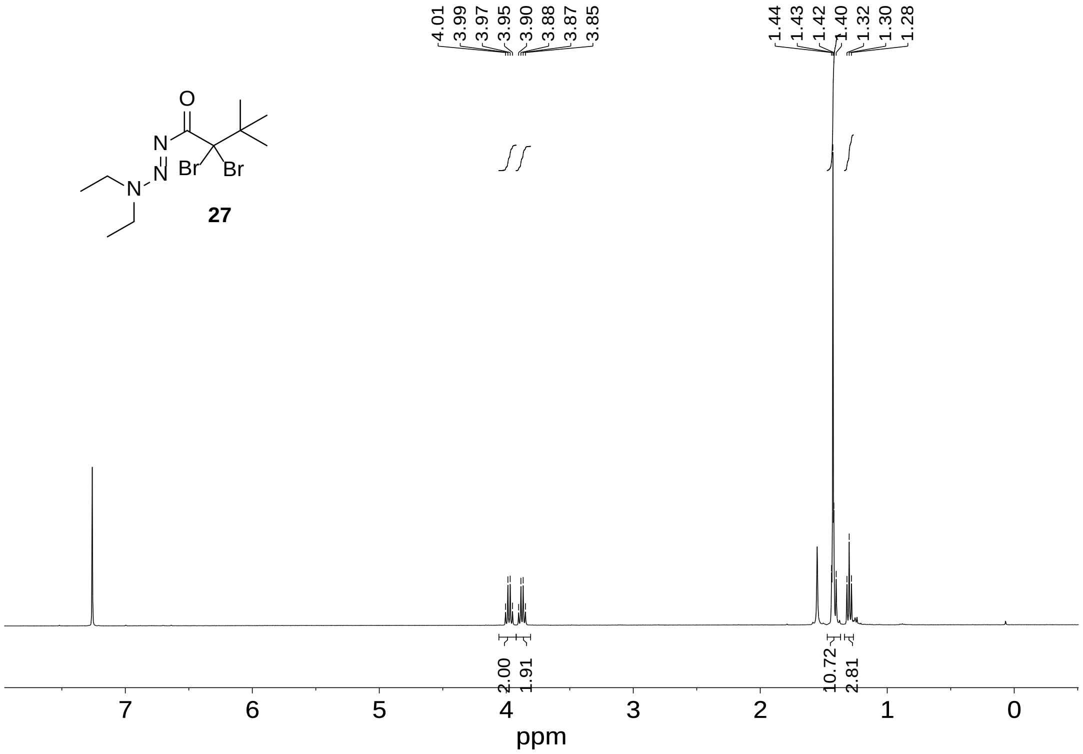


Figure S14.61. ^{1}H NMR spectrum of **27** (400 MHz, $CDCl_3$).

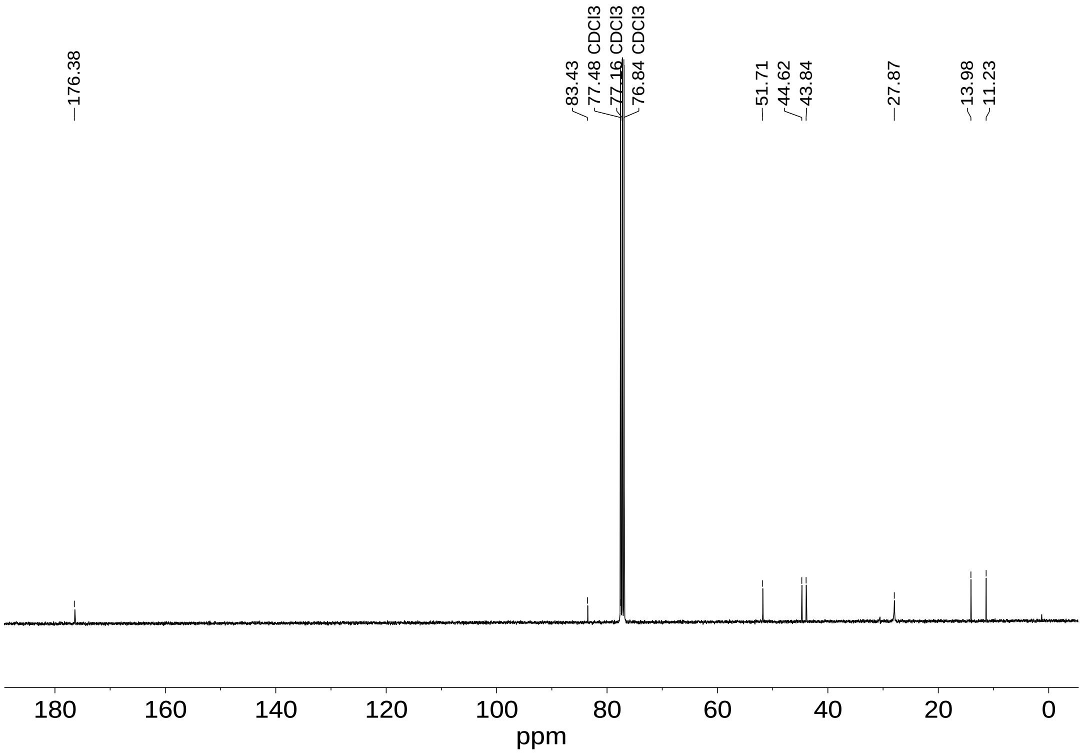


Figure S14.62. ^{13}C NMR spectrum of **27** (101 MHz, $CDCl_3$).

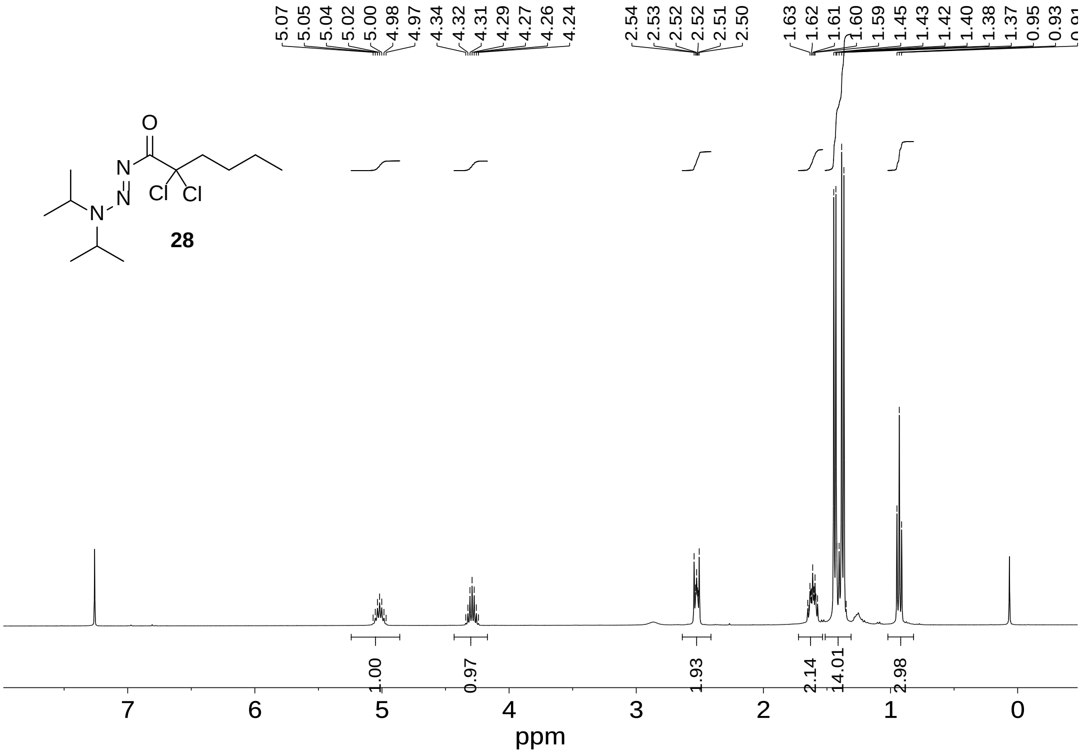


Figure S14.63. ^{1}H NMR spectrum of **28** (400 MHz, CDCl$_3$).

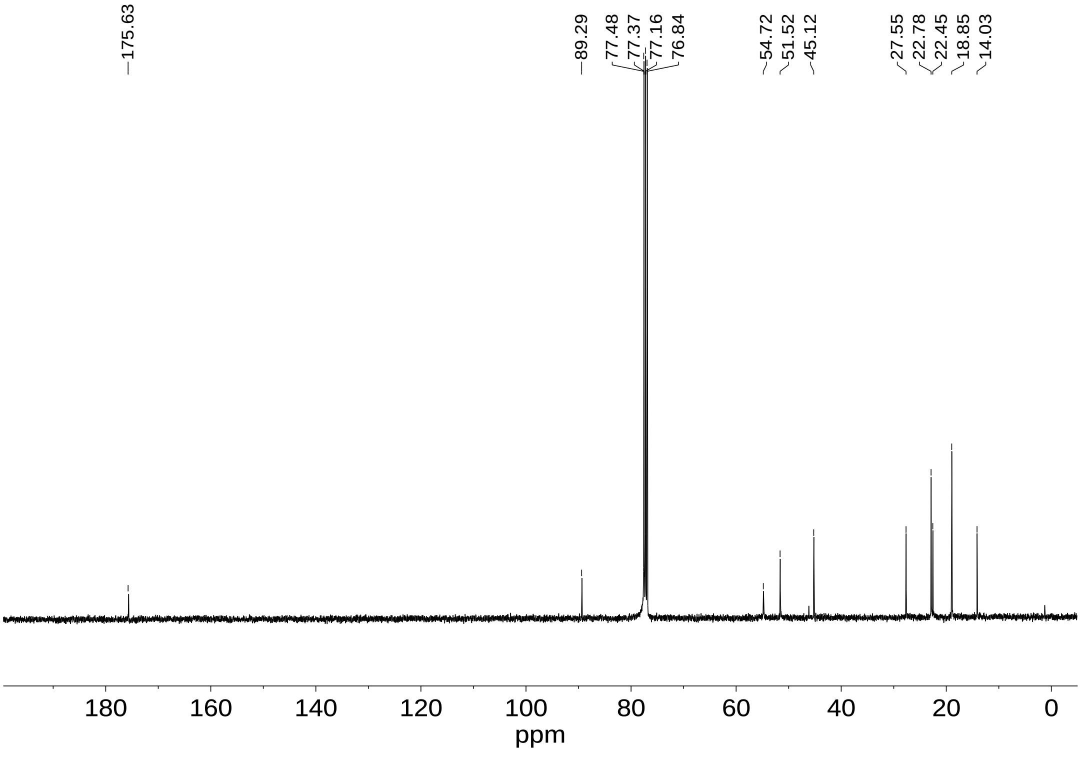


Figure S14.64. ^{13}C NMR spectrum of **28** (101 MHz, CDCl$_3$).

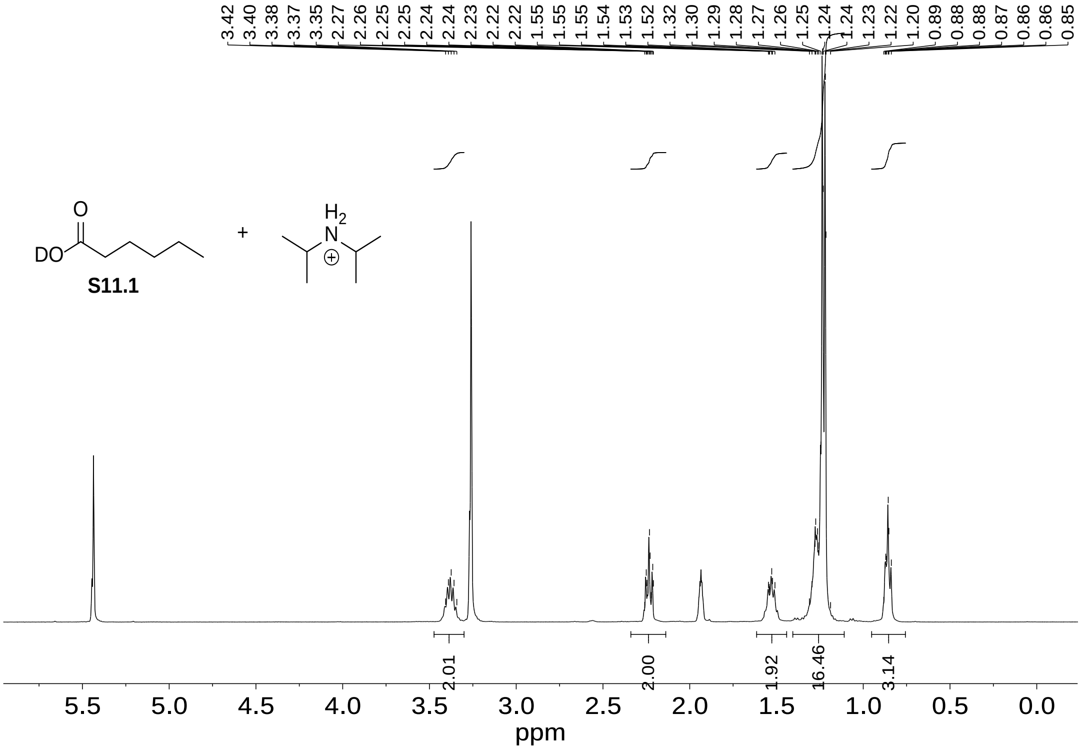


Figure S14.65. ^{1}H NMR spectrum of **S11.1** and diisopropyl ammonium (δ 6.76-6.51, 3.51-3.39, 1.30-1.28) (400 MHz, d_3-acetonitrile).[11]

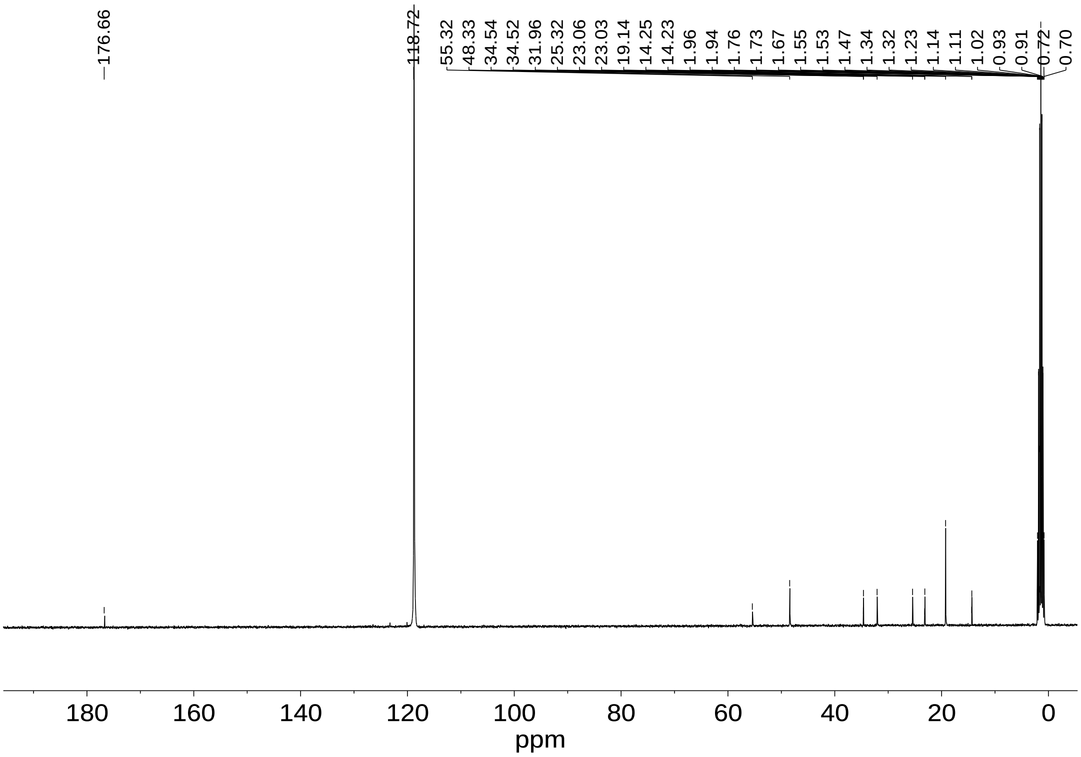


Figure S14.66. ^{13}C NMR spectrum of **S11.1** and diisopropyl ammonium (δ 49.31, 19.15) (101 MHz, d_3-acetonitrile).[11]

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[11] Spectra are in agreement with the reported literature values: AIST: Integrated Spectral Database System of Organic Compounds. (Data were obtained from the National Institute of Advanced Industrial Science and Technology (Japan))

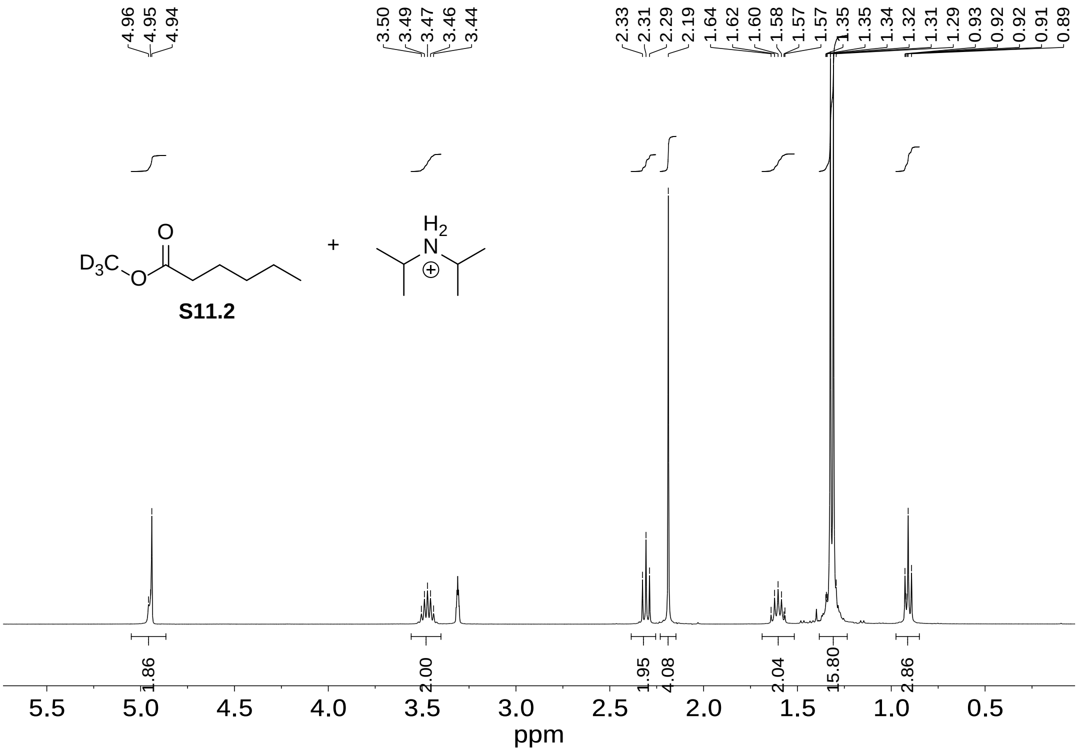

Figure S14.67. ^{1}H NMR spectrum of **S11.2** and diisopropyl ammonium (δ 3.52-3.42, 1.32-1.31) (400 MHz, *d*$_4$-methanol).[12]

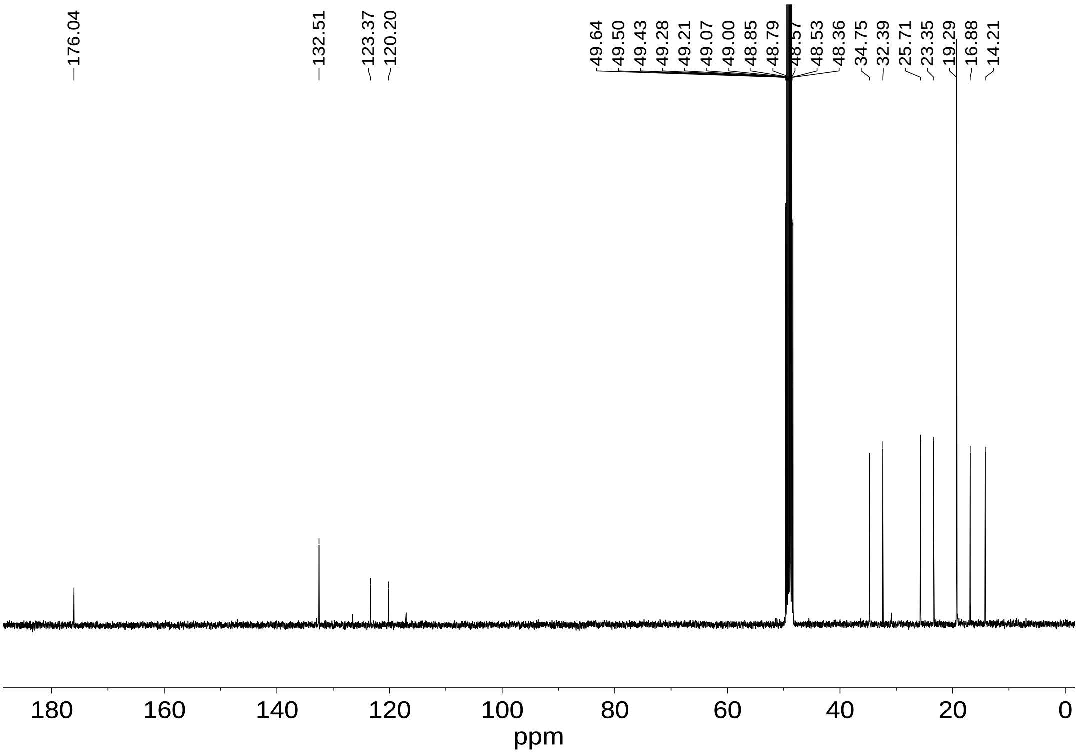

Figure S14.68. ^{13}C NMR spectrum of **S11.2** and diisopropyl ammonium (δ 126.5-117.0, 19.3-16.9) (101 MHz, *d*$_4$-methanol).[12]

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[12] Spectra are in agreement with the reported literature values: Yamamoto, N. *et al. J. Org. Chem.* **2011**, *76*, 2937–2941.

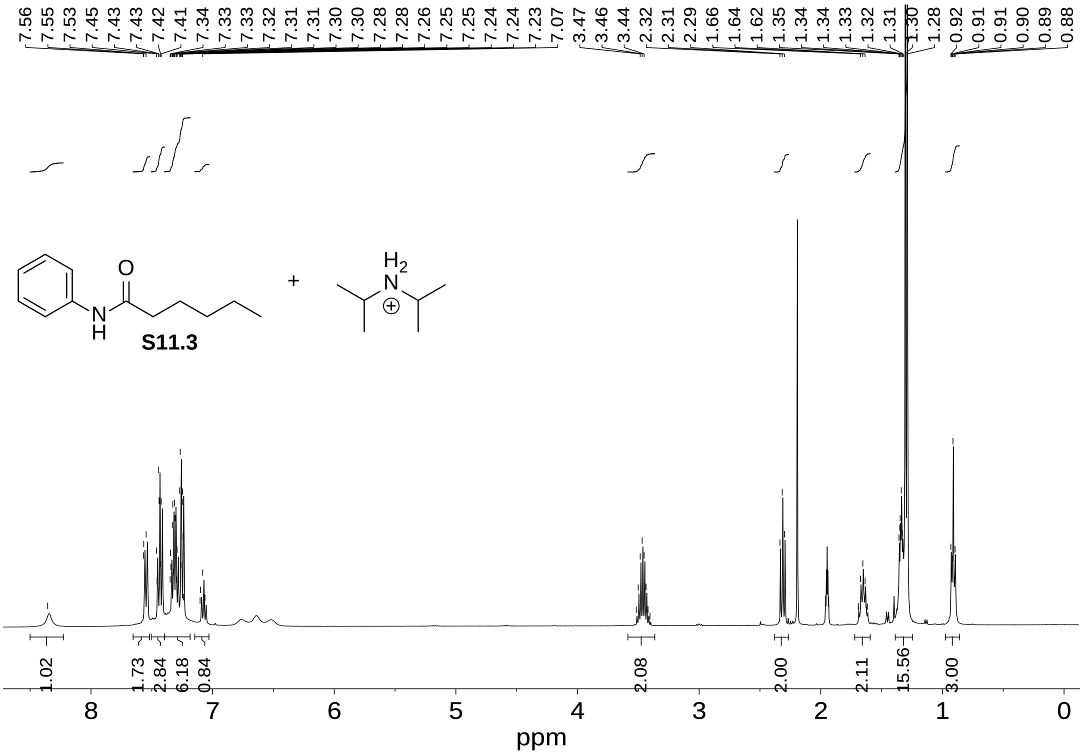

Figure S14.69. ^{1}H NMR spectrum of **30**, diisopropyl ammonium (δ 6.76-6.51, 3.51-3.39, 1.30-1.28) and aniline (400 MHz, *d_3*-acetonitrile).[13]

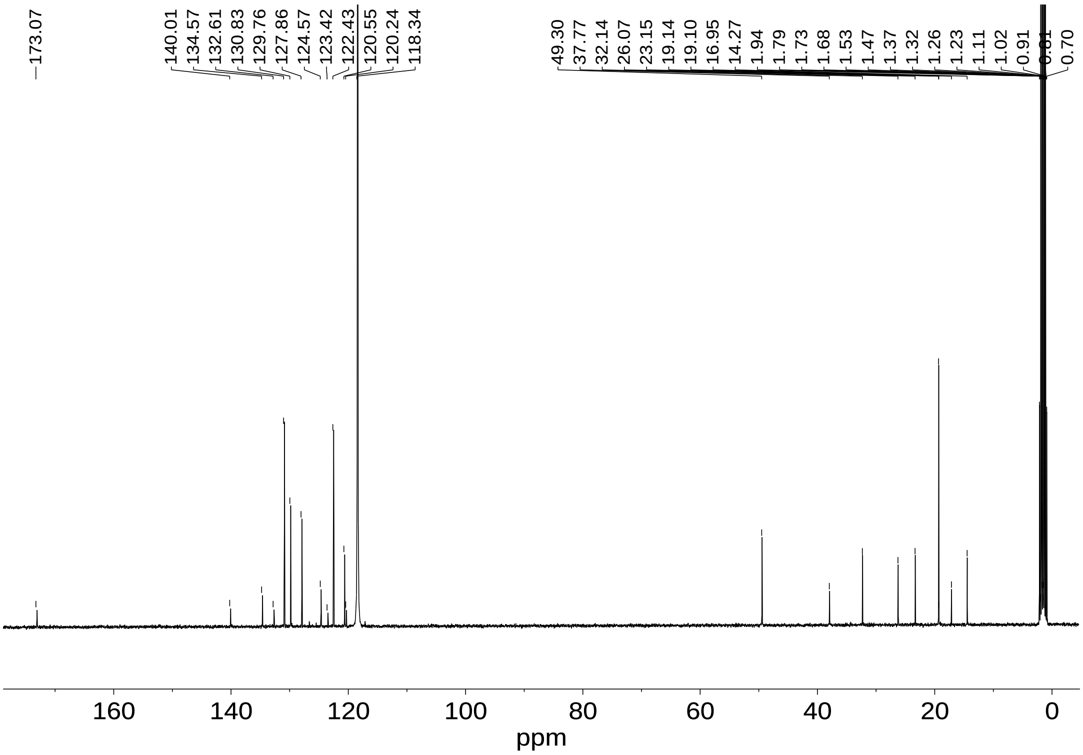

Figure S14.70. ^{13}C NMR spectrum of **30**, diisopropyl ammonium (δ 49.31, 19.15) and aniline (101 MHz, *d_3*-acetonitrile).[13]

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[13] Spectra are in agreement with the reported literature values: Jammi, S. *et al. J. Org. Chem.* **2009**, *74*, 1971–1976.

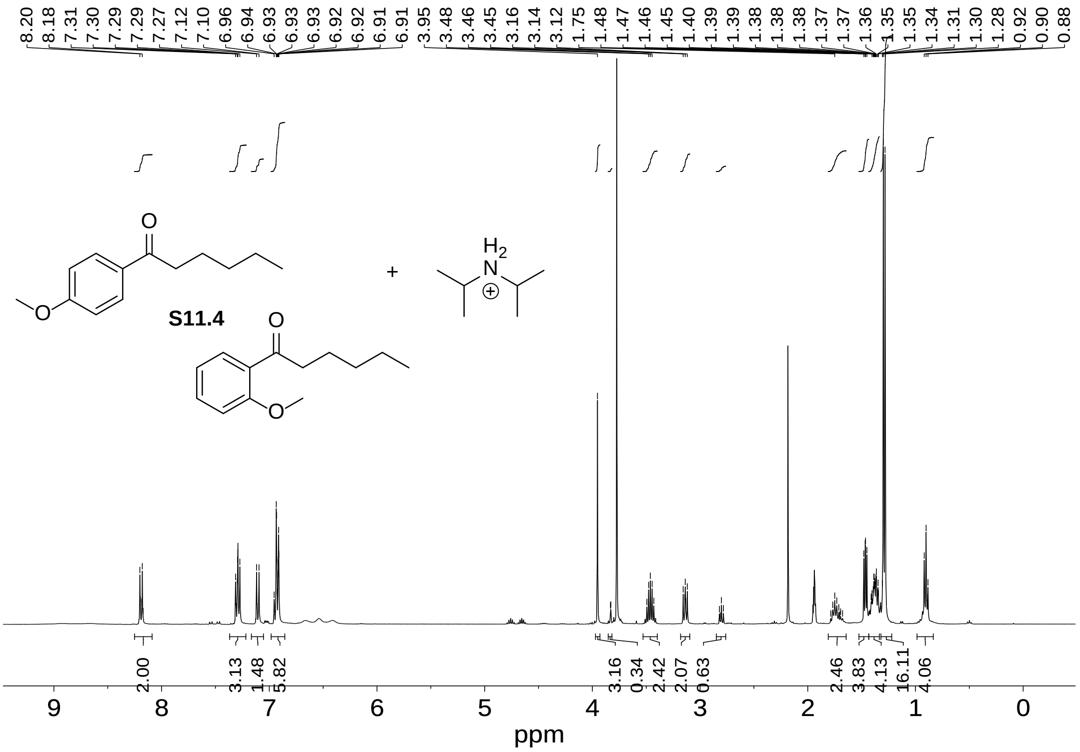

Figure S14.71. ^{1}H NMR spectrum of **S11.4** and diisopropyl ammonium (δ 6.76-6.51, 3.51-3.39, 1.30-1.28) and anisole (400 MHz, *d*$_3$-acetonitrile).[14]

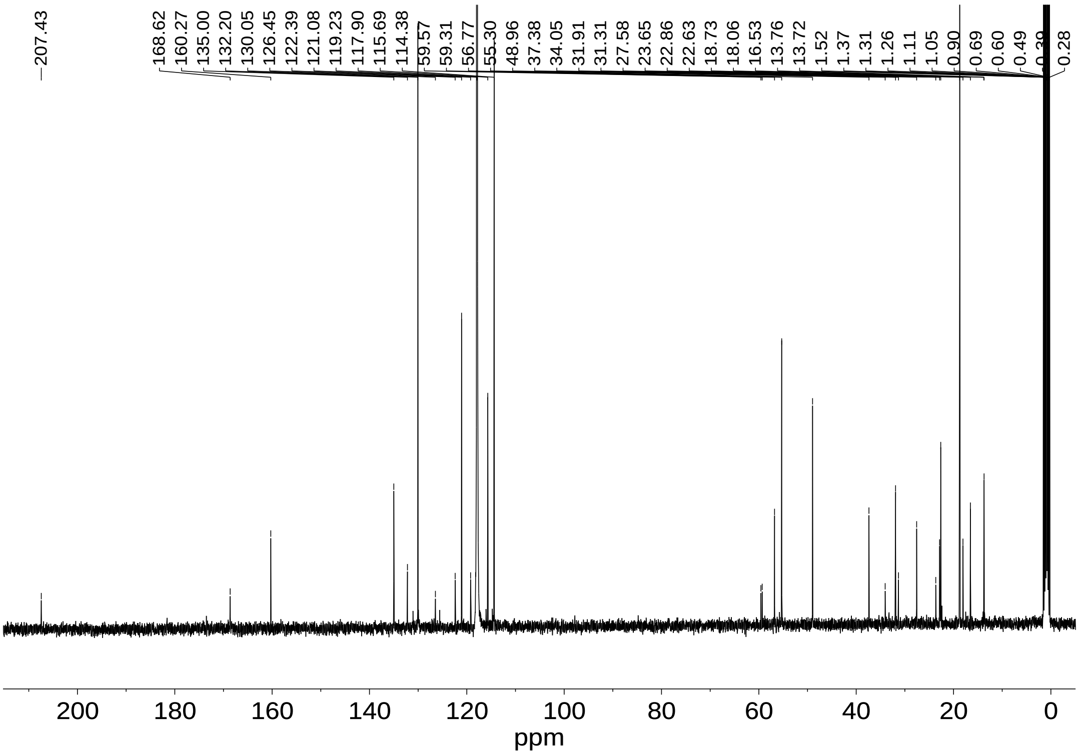

Figure S14.72. ^{13}C NMR spectrum of **S11.4** and diisopropyl ammonium (δ 49.31, 19.15) and anisole (101 MHz, *d*$_3$-acetonitrile).[14]

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[14] Spectra are in agreement with the reported literature values: Liao, Y. X. *et al. J. Org. Chem.* **2010**, *75*, 6986–6989.

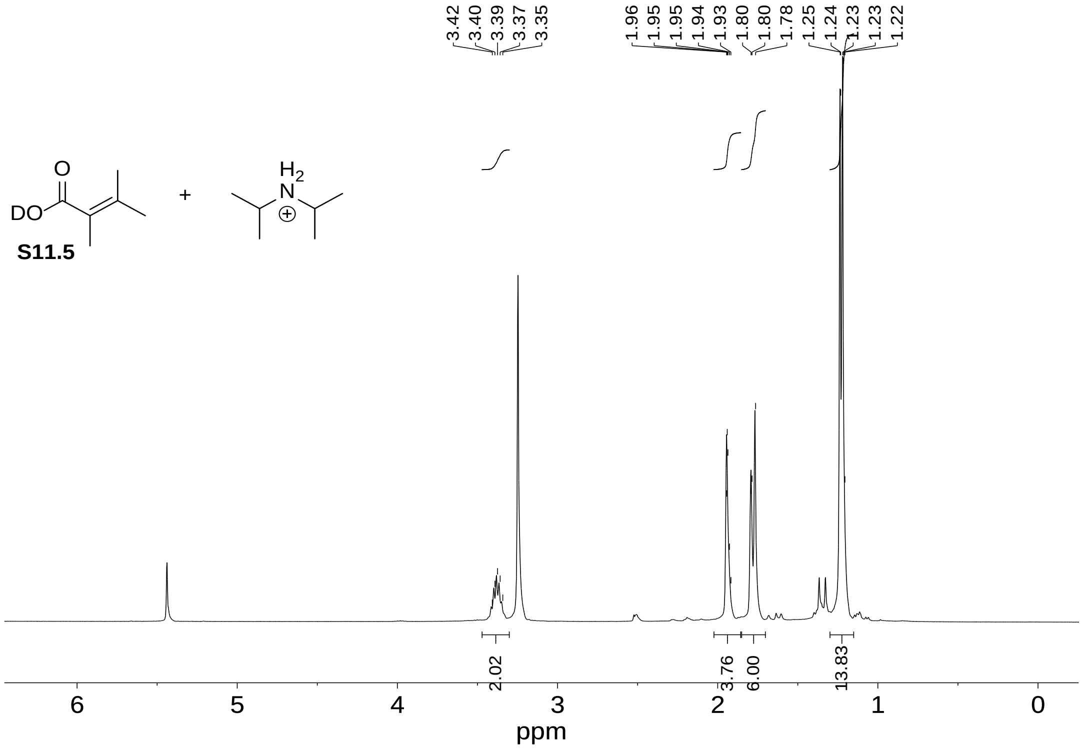

Figure S14.73. ^{1}H NMR spectrum of **S11.5** and diisopropyl ammonium (δ 6.76-6.51, 3.51-3.39, 1.30-1.28) (400 MHz, *d_3*-acetonitrile).[15]

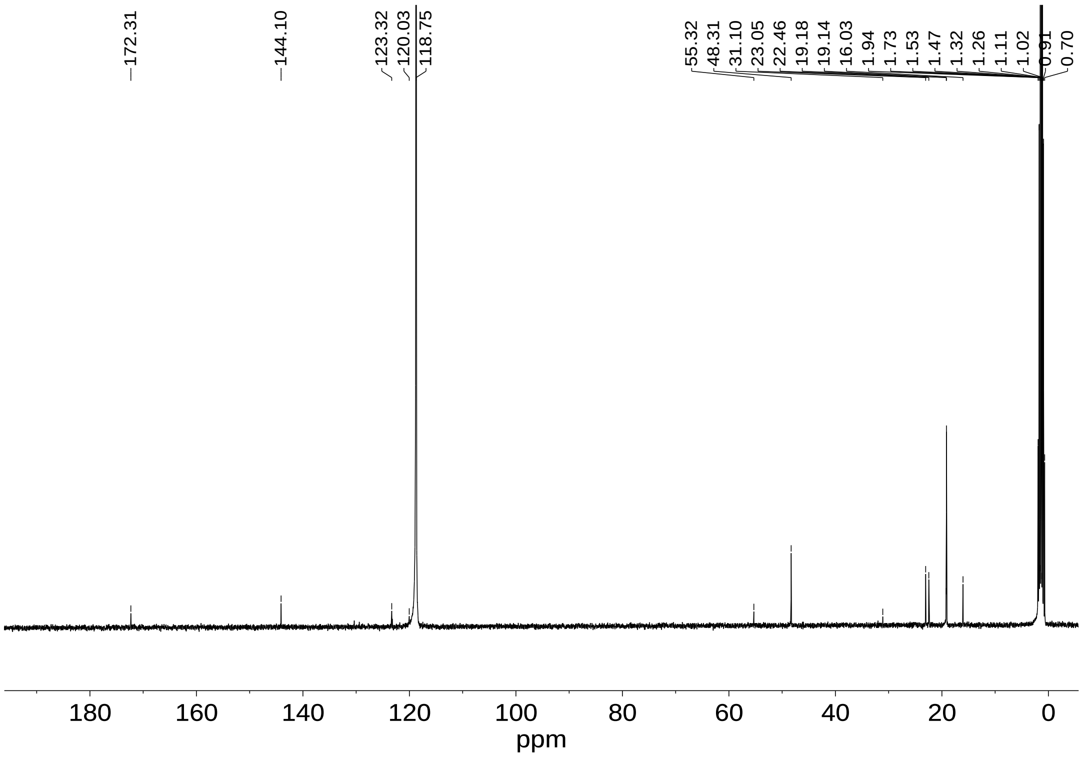

Figure S14.74. ^{13}C NMR spectrum of **S11.5** and diisopropyl ammonium (δ 49.31, 19.15) (101 MHz, *d_3*-acetonitrile).[15]

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[15] Spectra are in agreement with the reported literature values: Dreiding, A. S. 154. Acid-Catalyzed. *Helv. Chim. Acta* **1982**, *65*, 1563–1575.

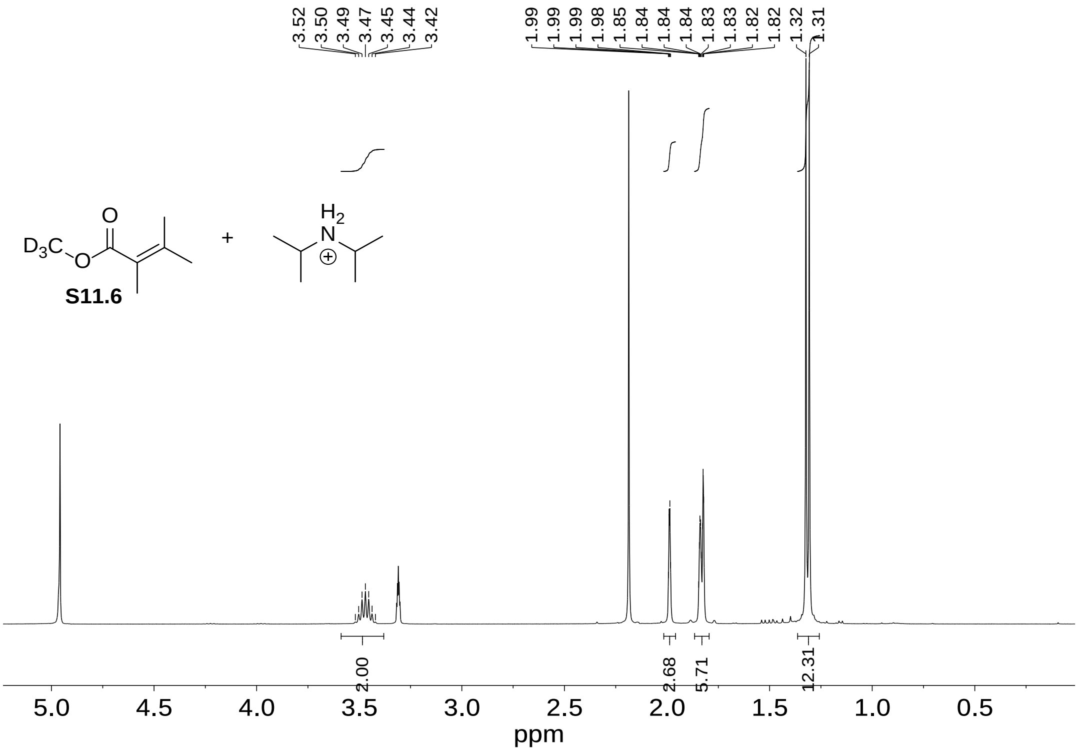

Figure S14.75. ^{1}H NMR spectrum of **S11.6** and diisopropyl ammonium (δ 3.52-3.42, 1.32-1.31) (400 MHz, *d*$_4$-methanol).[16]

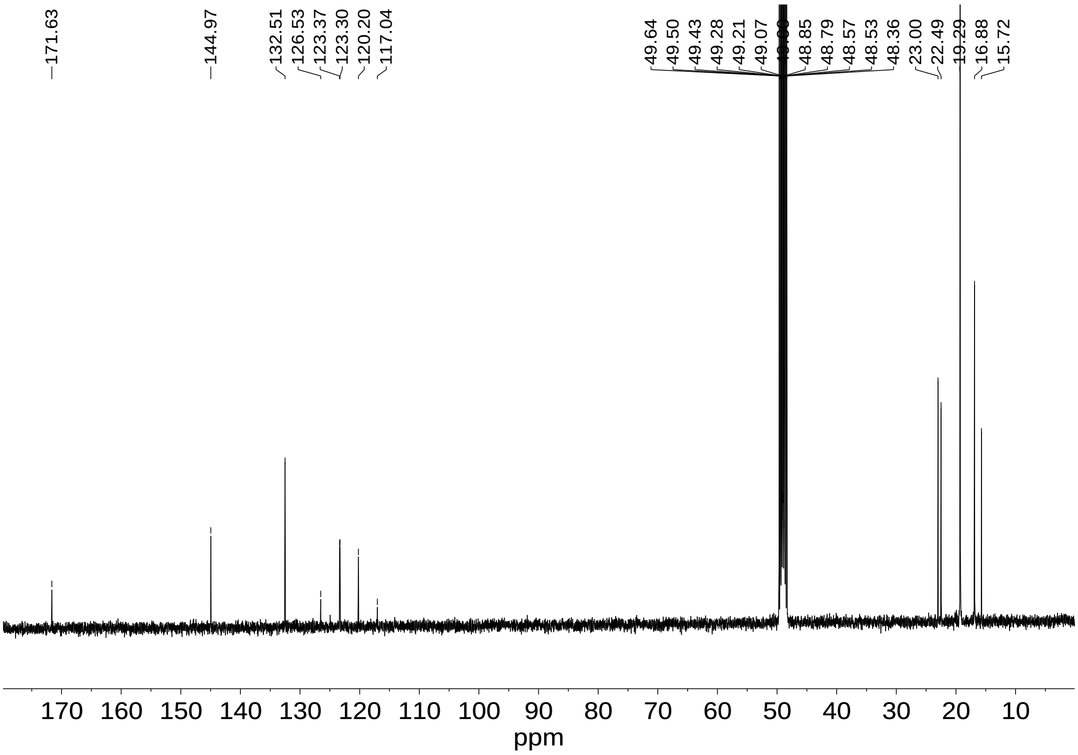

Figure S14.76. ^{13}C NMR spectrum of **S11.6** and diisopropyl ammonium (δ 126.5-117.0, 19.3-16.9) (101 MHz, *d*$_4$-methanol).[16]

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[16] Spectra are in agreement with the reported literature values: AIST: Integrated Spectral Database System of Organic Compounds. (Data were obtained from the National Institute of Advanced Industrial Science and Technology (Japan)).

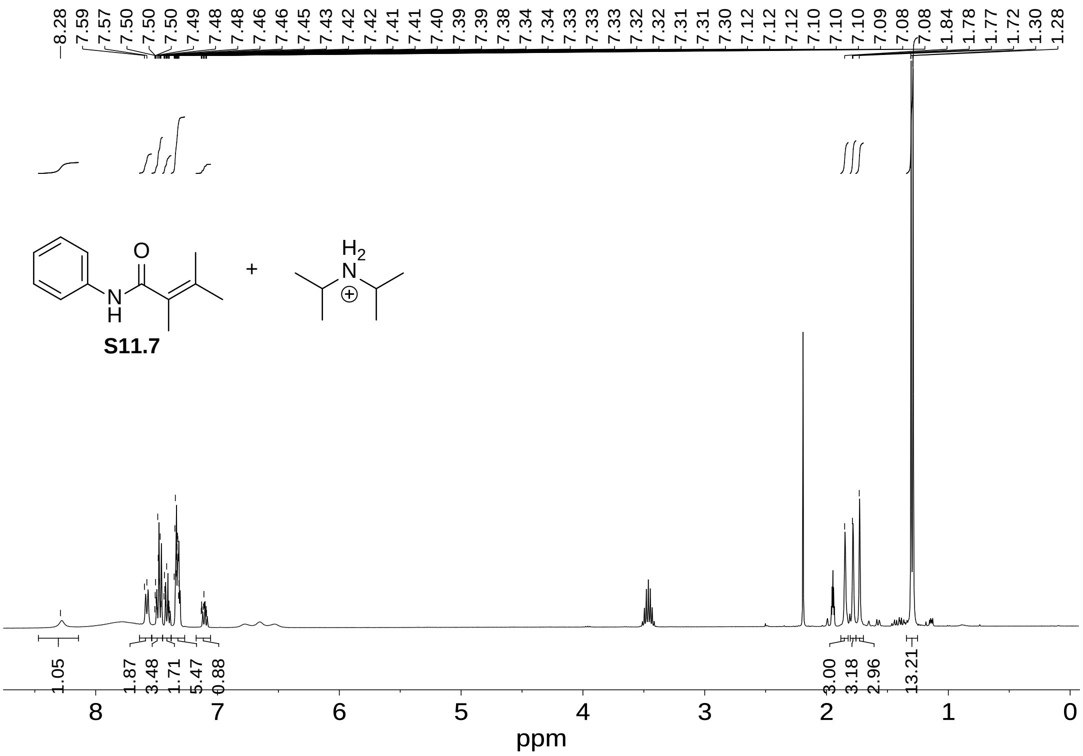

Figure S14.77. ^{1}H NMR spectrum of **S11.7**, diisopropyl ammonium (δ 6.76-6.51, 3.51-3.39, 1.30-1.28) and aniline (400 MHz, d_3-acetonitrile).[17]

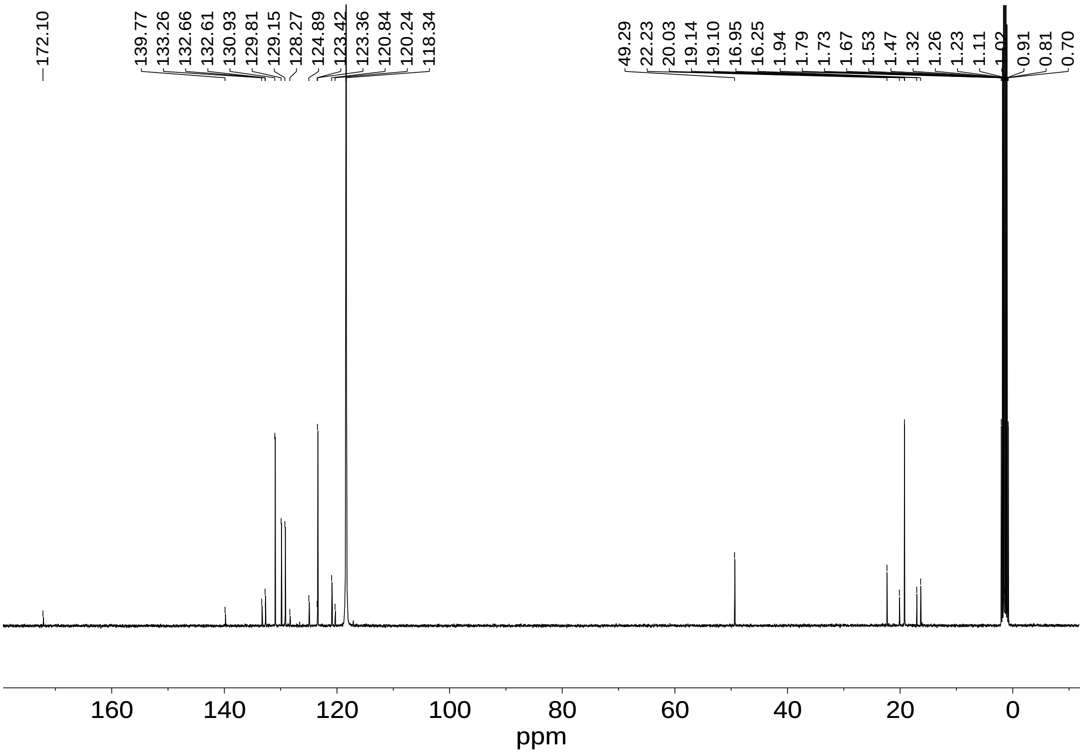

Figure S14.78. ^{13}C NMR spectrum of **S11.7**, diisopropyl ammonium (δ 49.31, 19.15) and aniline (101 MHz, d_3-acetonitrile).[17]

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[17] Spectra are in agreement with the reported literature values: Schiffner, J. A. *Eur. J. Org. Chem.* **2011**, 1148–1154.

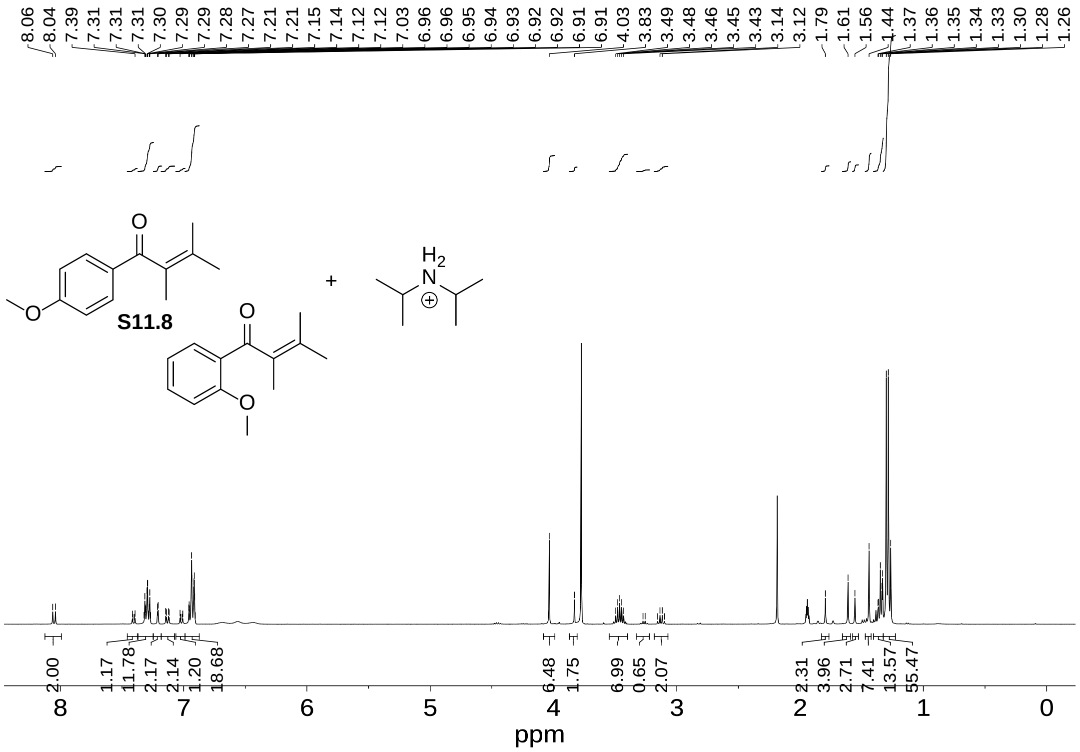

Figure S14.79. ^{1}H NMR spectrum of **S11.8**, diisopropyl ammonium (δ 6.76-6.51, 3.51-3.39, 1.30-1.28) and anisole (400 MHz, *d*$_{3}$-acetonitrile).[18]

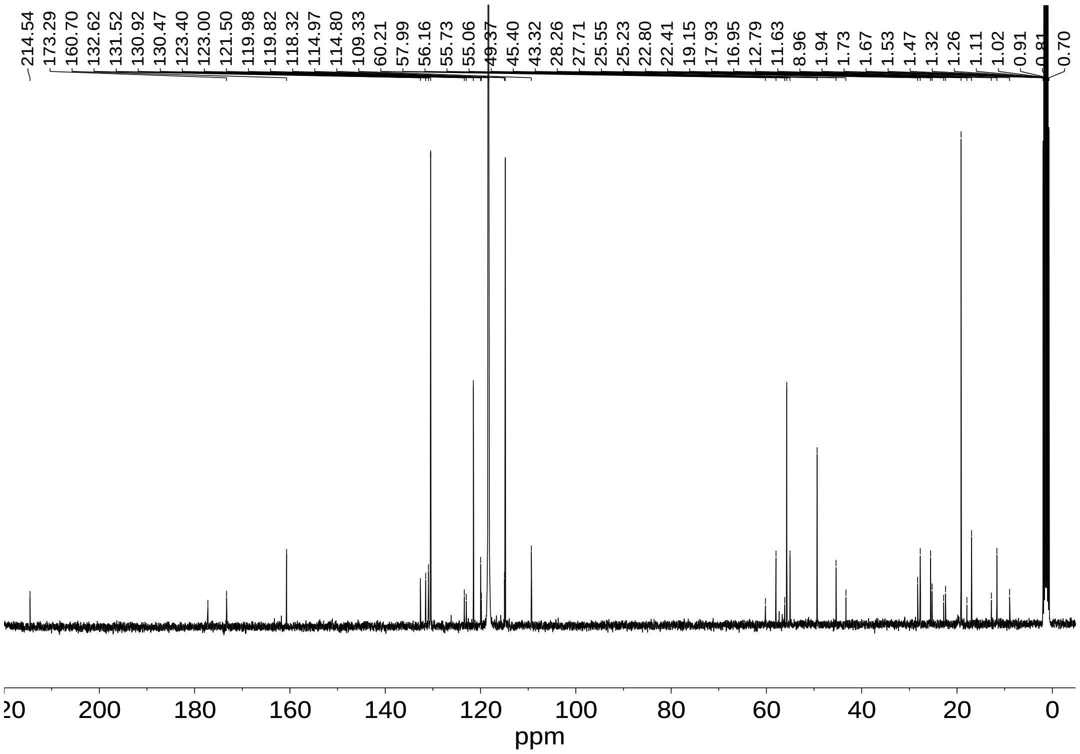

Figure S14.80. ^{13}C NMR spectrum of **S11.8**, diisopropyl ammonium (δ 49.31, 19.15) and anisole (101 MHz, *d*$_{3}$-acetonitrile).[18]

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[18] Spectra are in agreement with the reported literature values: Okamoto, K. *et al. Org. Lett.* **2007**, *9*, 5067–5069.

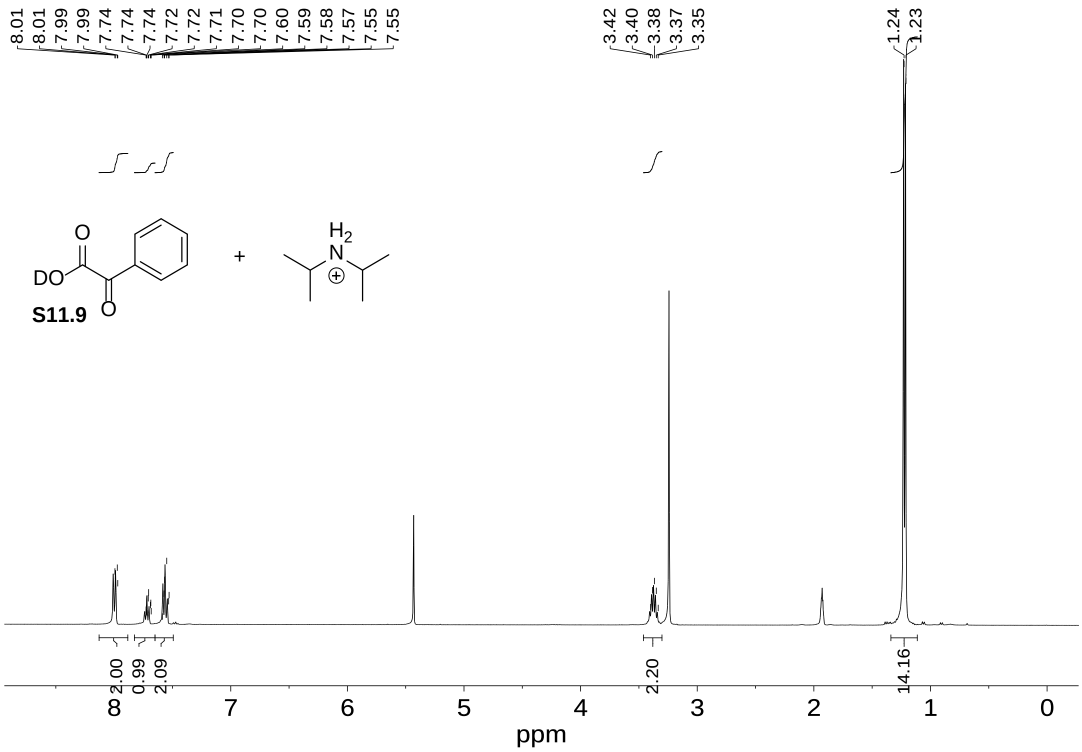

Figure S14.81. ^{1}H NMR spectrum of **S11.9** and diisopropyl ammonium (δ 6.76-6.51, 3.51-3.39, 1.30-1.28) (400 MHz, *d*$_3$-acetonitrile).[19]

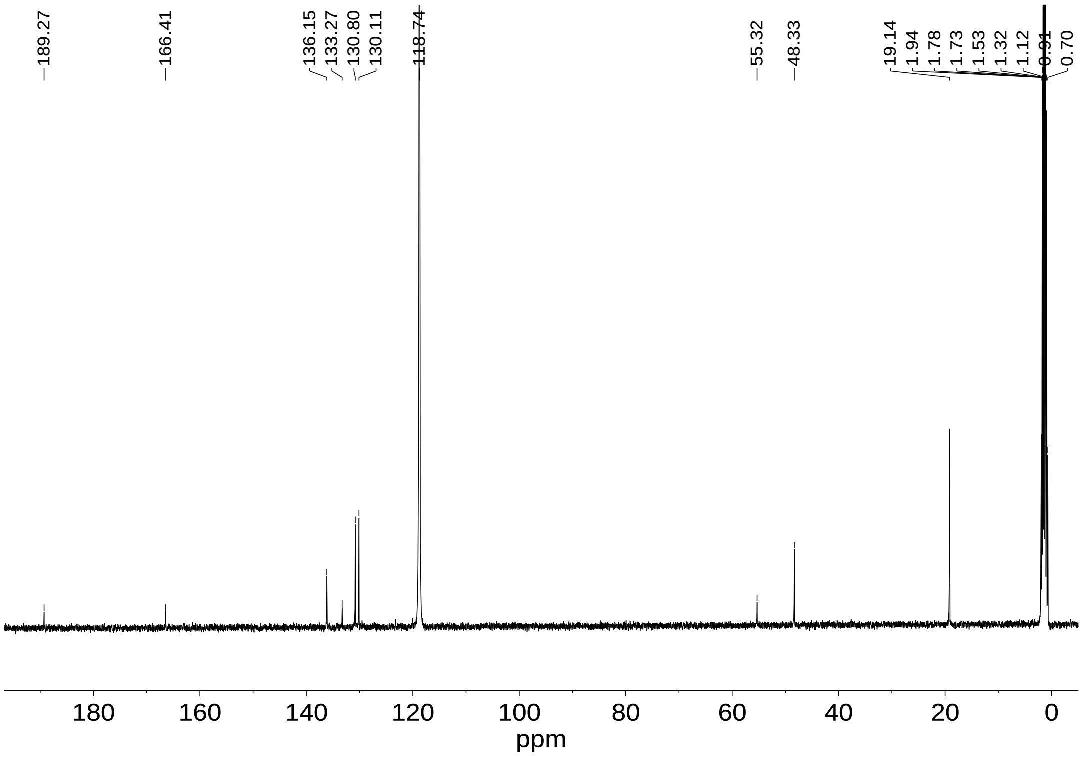

Figure S14.82. ^{13}C NMR spectrum of **S11.9** and diisopropyl ammonium (δ 49.31, 19.15) (101 MHz, *d*$_3$-acetonitrile).[19]

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[19] Spectra are in agreement with the reported literature values: AIST: Integrated Spectral Database System of Organic Compounds. (Data were obtained from the National Institute of Advanced Industrial Science and Technology (Japan))

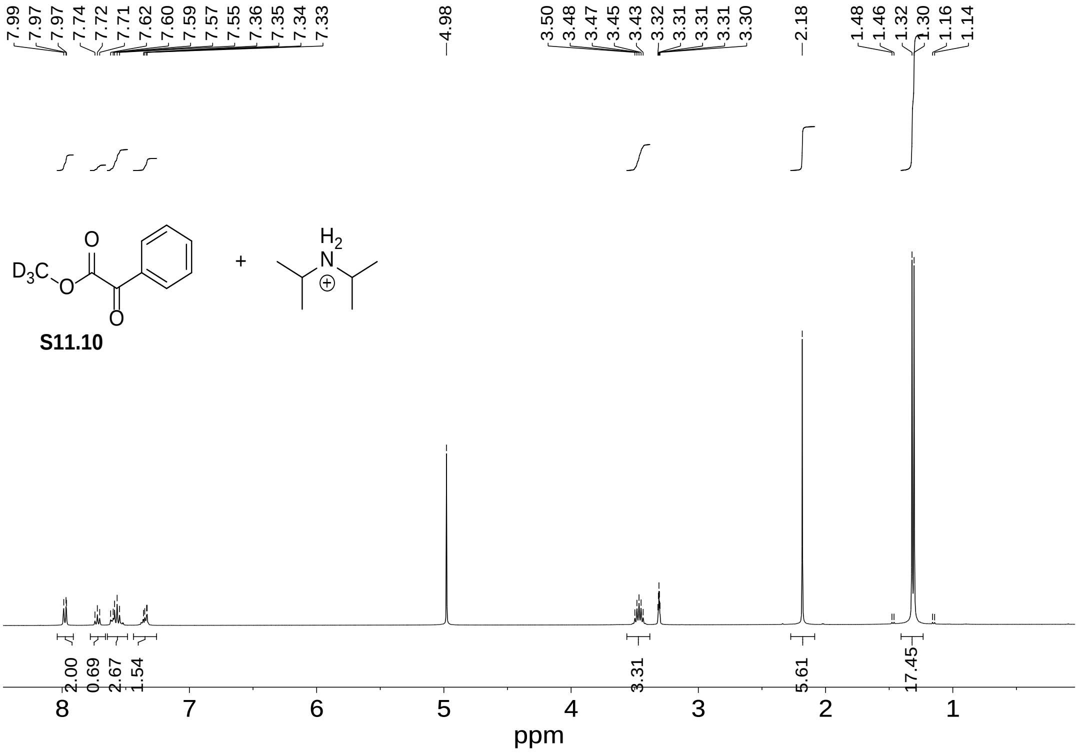

Figure S14.83. ^{1}H NMR spectrum of **S11.10** and diisopropyl ammonium (δ 3.52-3.42, 1.32-1.31) (400 MHz, *d*$_4$-methanol).[20]

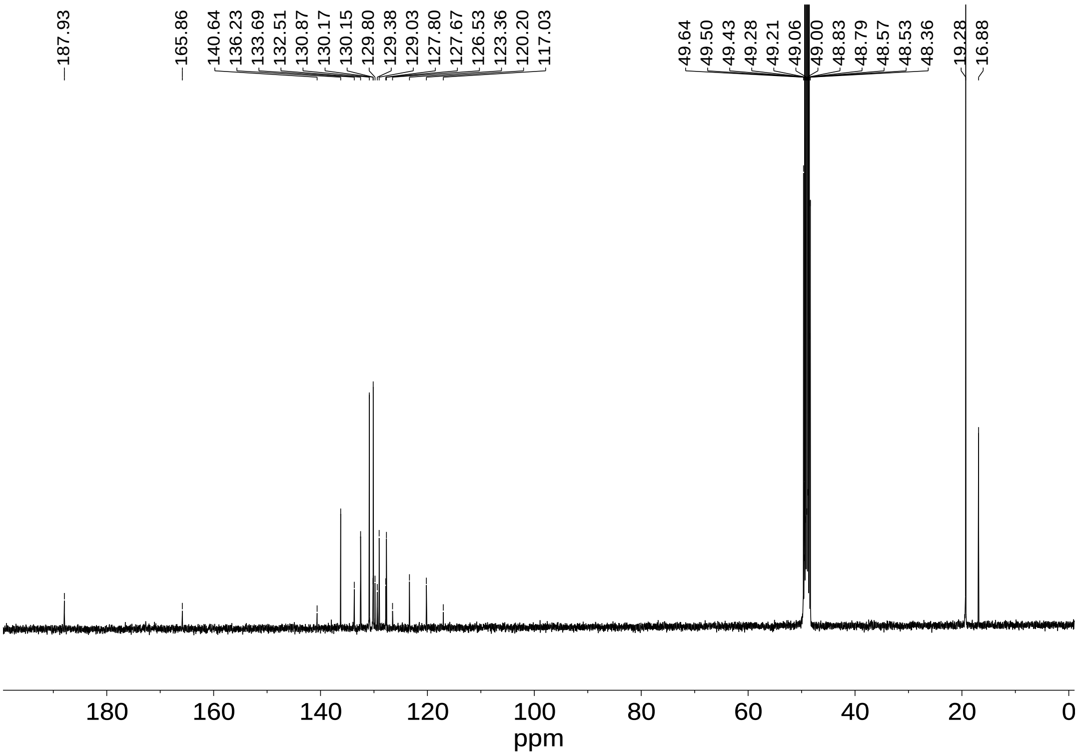

Figure S14.84. ^{13}C NMR spectrum of **S11.10** and diisopropyl ammonium (δ 126.5-117.0, 19.3-16.9) (101 MHz, *d*$_4$-methanol).[20]

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[20] Spectra are in agreement with the reported literature values: Salunke, S. B. *et al. Adv. Synth. Catal*. **2011**, *353*, 1234–1240.

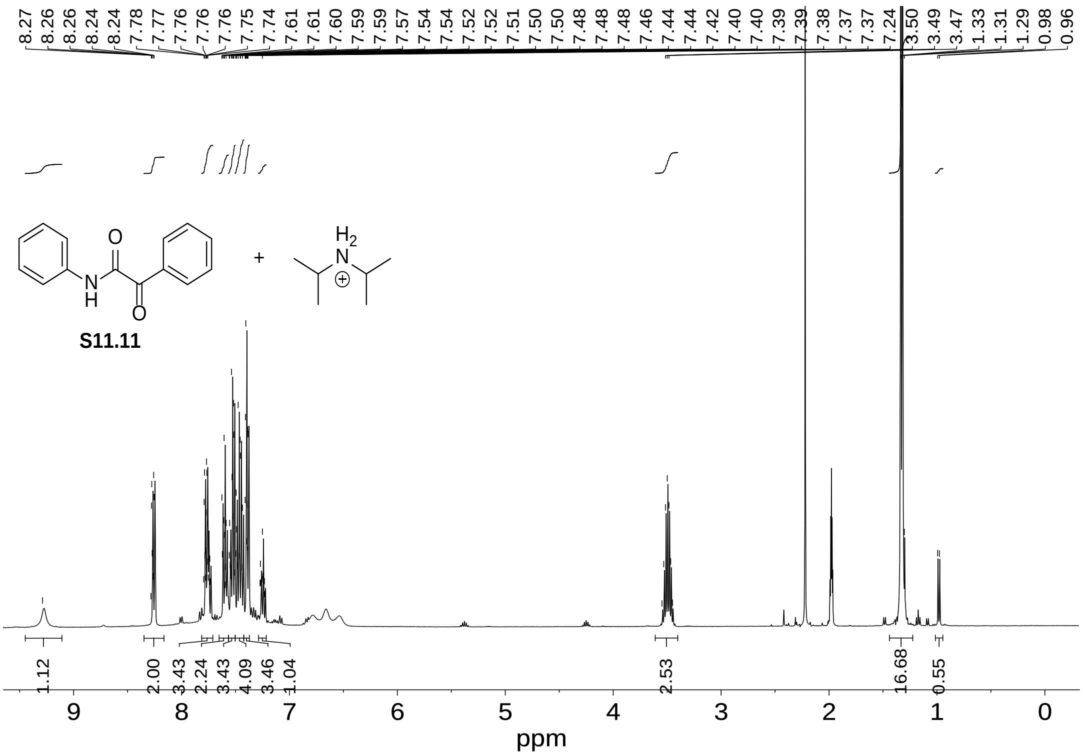

Figure S14.85. ^{1}H NMR spectrum of **S11.11**, diisopropyl ammonium (δ 6.76-6.51, 3.51-3.39, 1.30-1.28) and aniline (400 MHz, d_3-acetonitrile).[21]

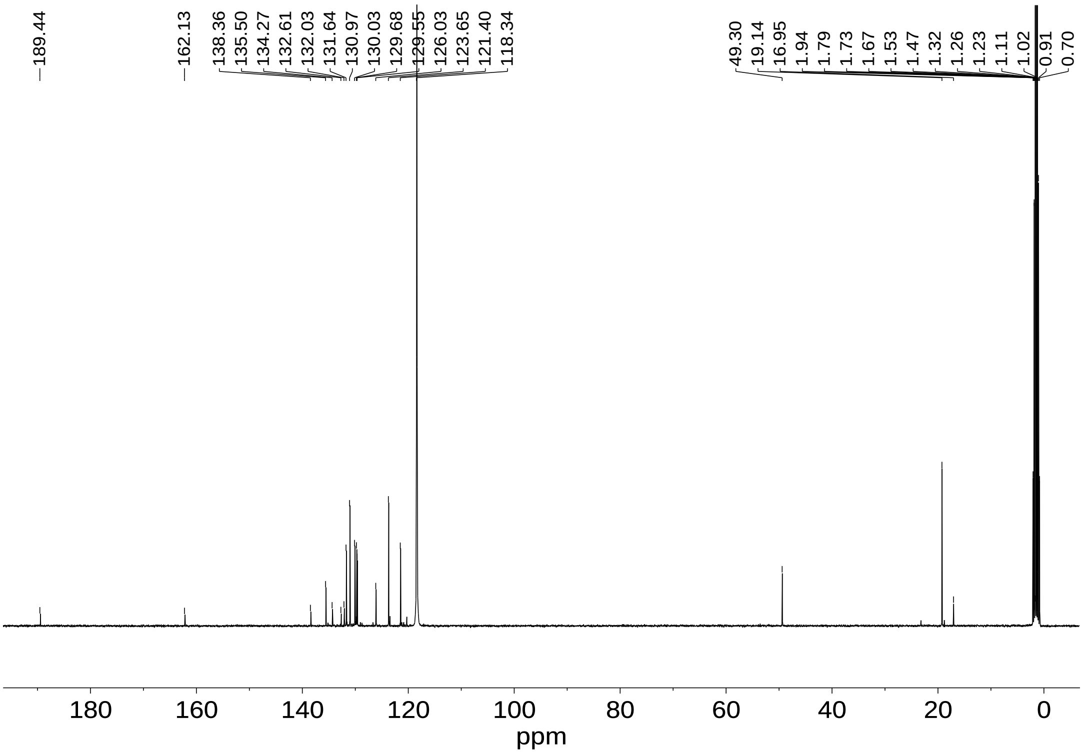

Figure S14.86. ^{13}C NMR spectrum of **S11.11**, diisopropyl ammonium (δ 49.31, 19.15) and aniline (101 MHz, d_3-acetonitrile).[21]

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[21] Spectra are in agreement with the reported literature values: Sai, K. K. S. *et al. J. Org. Chem.* **2008**, *73*, 6506–6512.

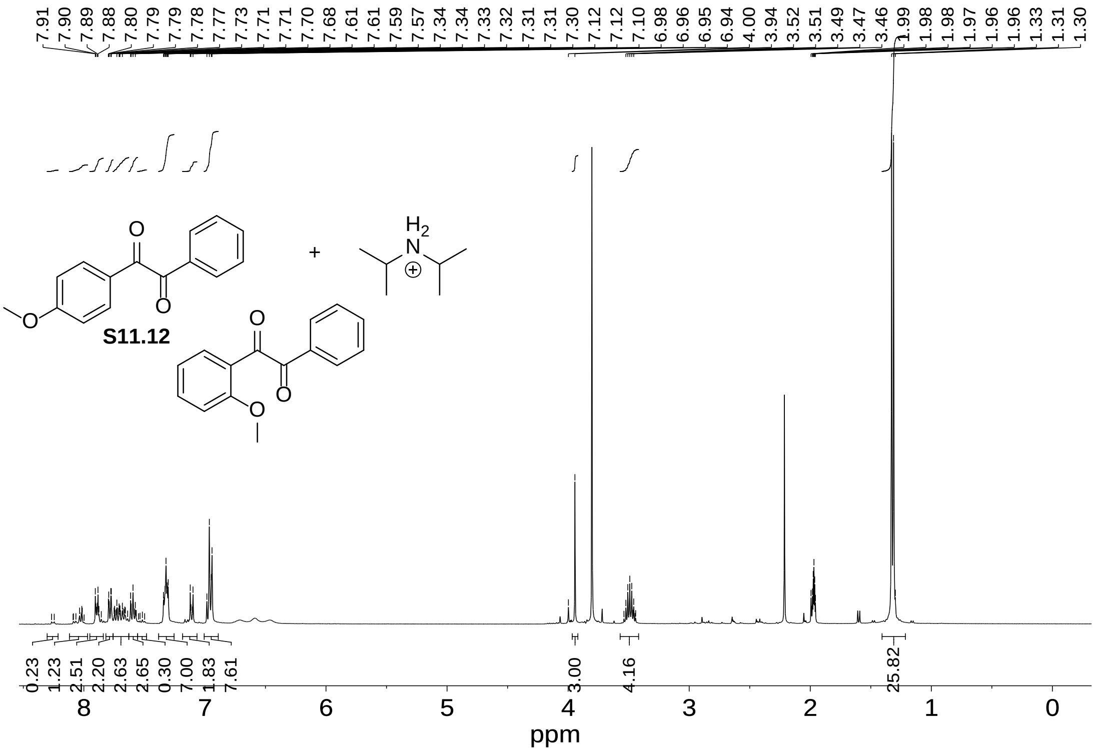

Figure S14.87. ^{1}H NMR spectrum of **S11.12**, diisopropyl ammonium (δ 6.76-6.51, 3.51-3.39, 1.30-1.28) and anisole (400 MHz, d_3-acetonitrile).[22]

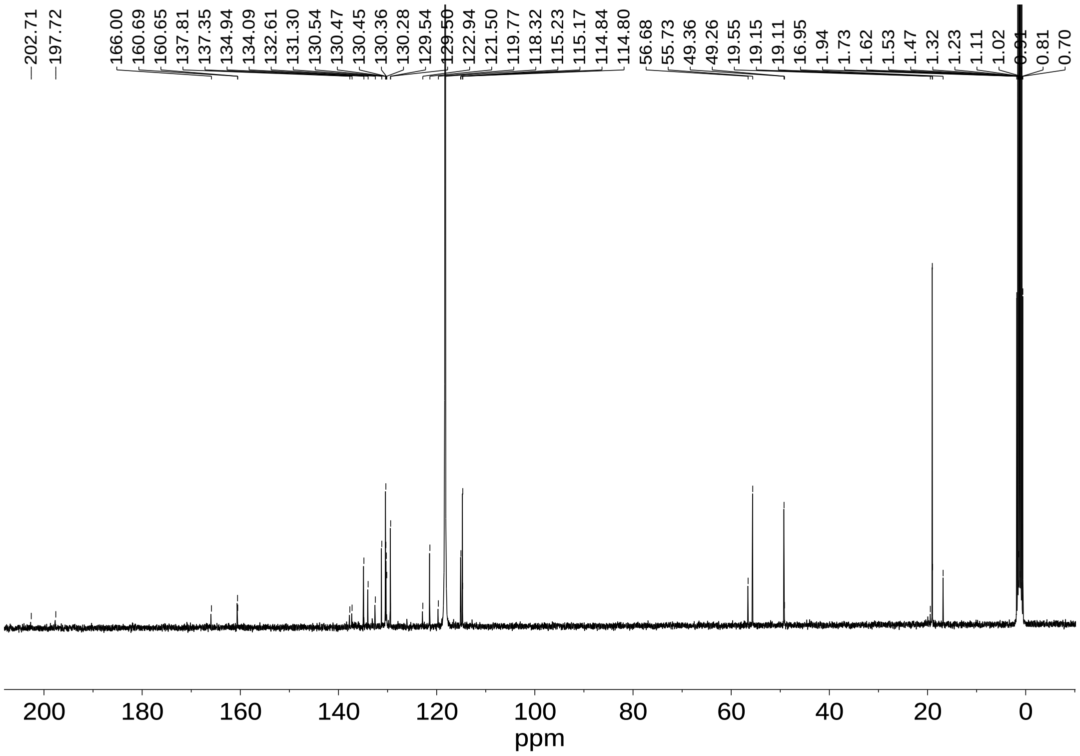

Figure S14.88. ^{13}C NMR spectrum of **S11.12**, diisopropyl ammonium (δ 49.31, 19.15) and anisole (101 MHz, d_3-acetonitrile).[22]

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[22] Spectra are in agreement with the reported literature values: Chen, M. *et al. J. Chem. Sci.* **2008**, *120*, 347–351.

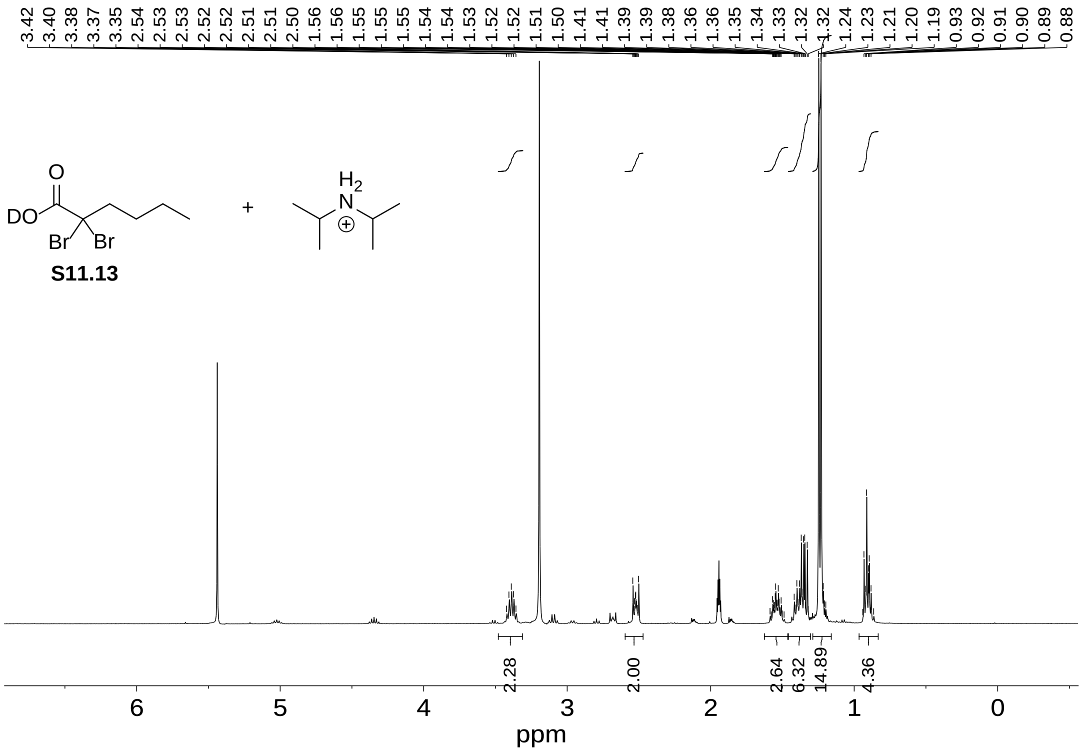

Figure S14.89. ^{1}H NMR spectrum of **S11.13** and diisopropyl ammonium (δ 6.76-6.51, 3.51-3.39, 1.30-1.28) (400 MHz, *d*$_3$-acetonitrile).[23]

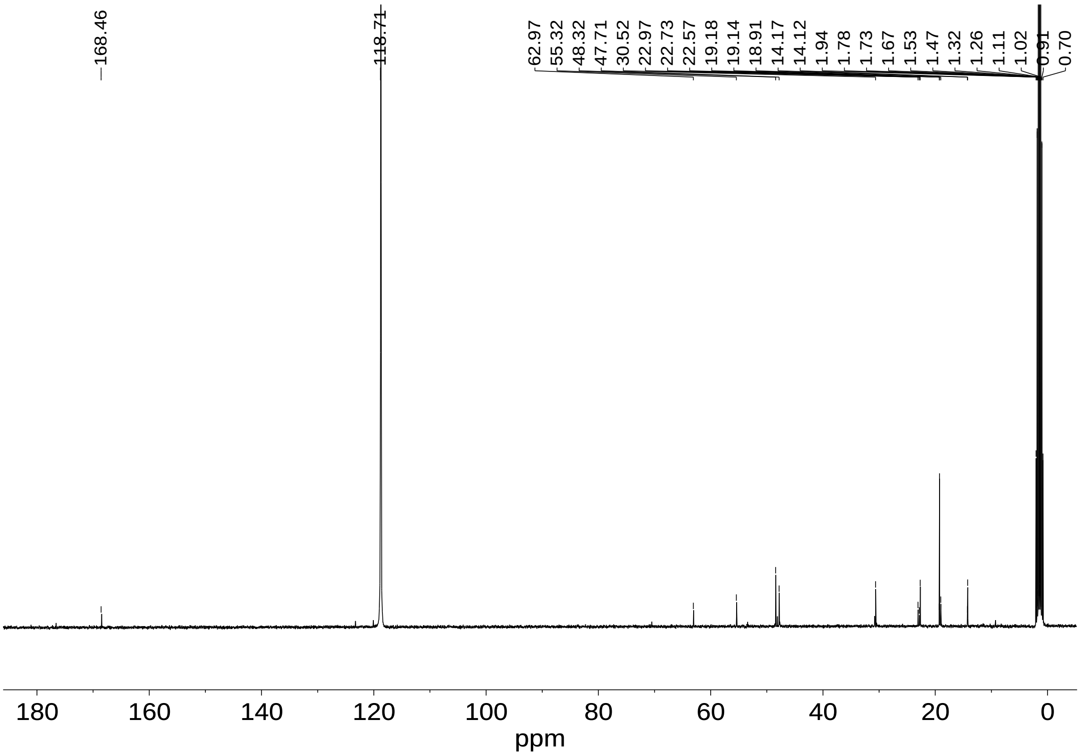

Figure S14.90. ^{13}C NMR spectrum of **S11.13** and diisopropyl ammonium (δ 49.31, 19.15) (101 MHz, *d*$_3$-acetonitrile).[23]

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[23] Spectra are in agreement with the reported literature values: Bellesia, F. *et al*. *Synth. Commun.* **2004**, *34*, 1473–1481.

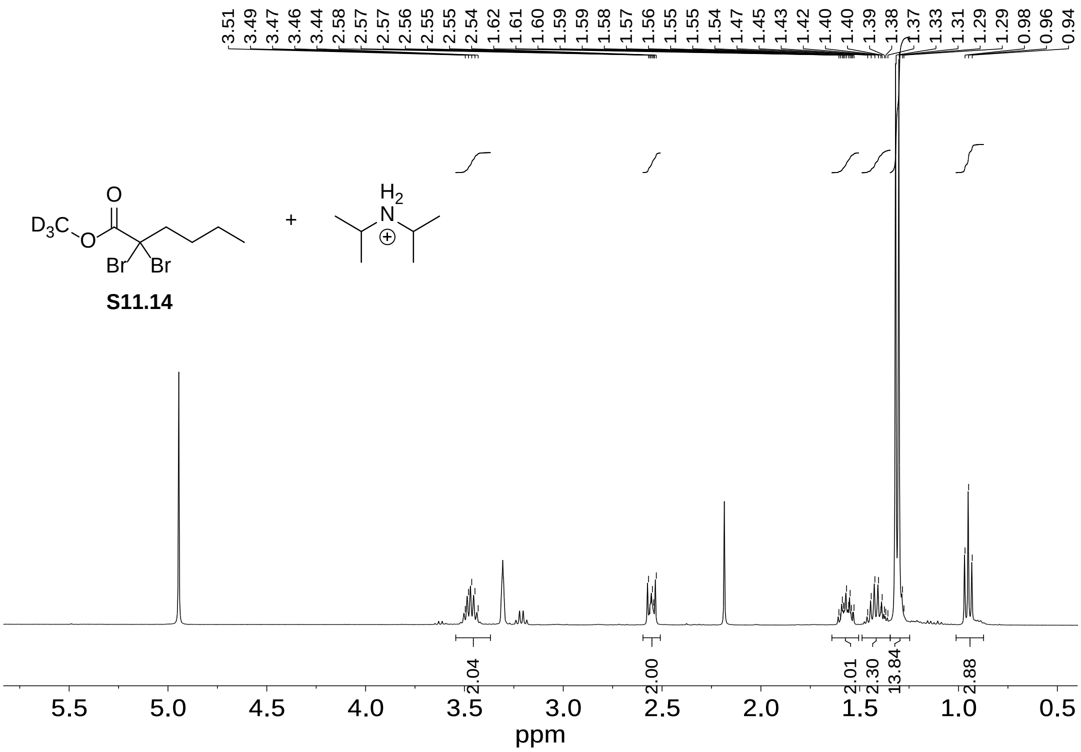

Figure S14.91. ^{1}H NMR spectrum of **S11.14** and diisopropyl ammonium (δ 6.76-6.51, 3.51-3.39, 1.30-1.28) (400 MHz, d_3-acetonitrile).[24]

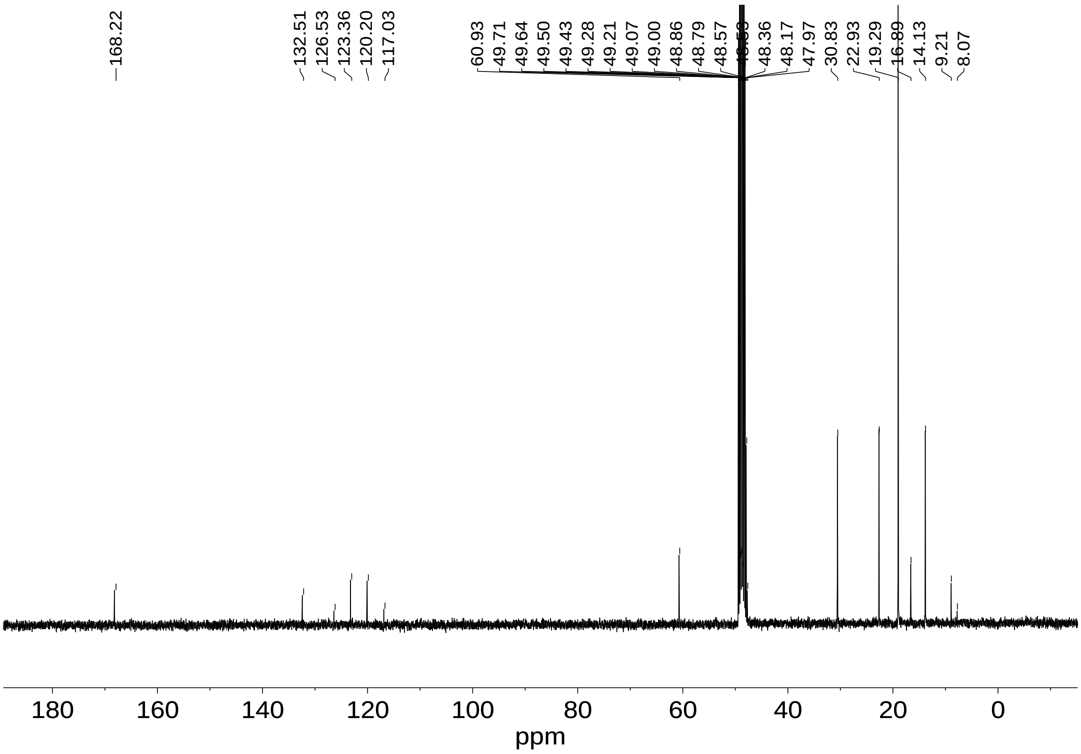

Figure S14.92. ^{13}C NMR spectrum of **S11.14** and diisopropyl ammonium (δ 49.31, 19.15) (101 MHz, d_3-acetonitrile).[24]

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[24] Spectra are in agreement with the reported literature values: Umezu, S. *et Al. Angew. Chemie - Int. Ed.* **2017**, *56*, 1298–1302.

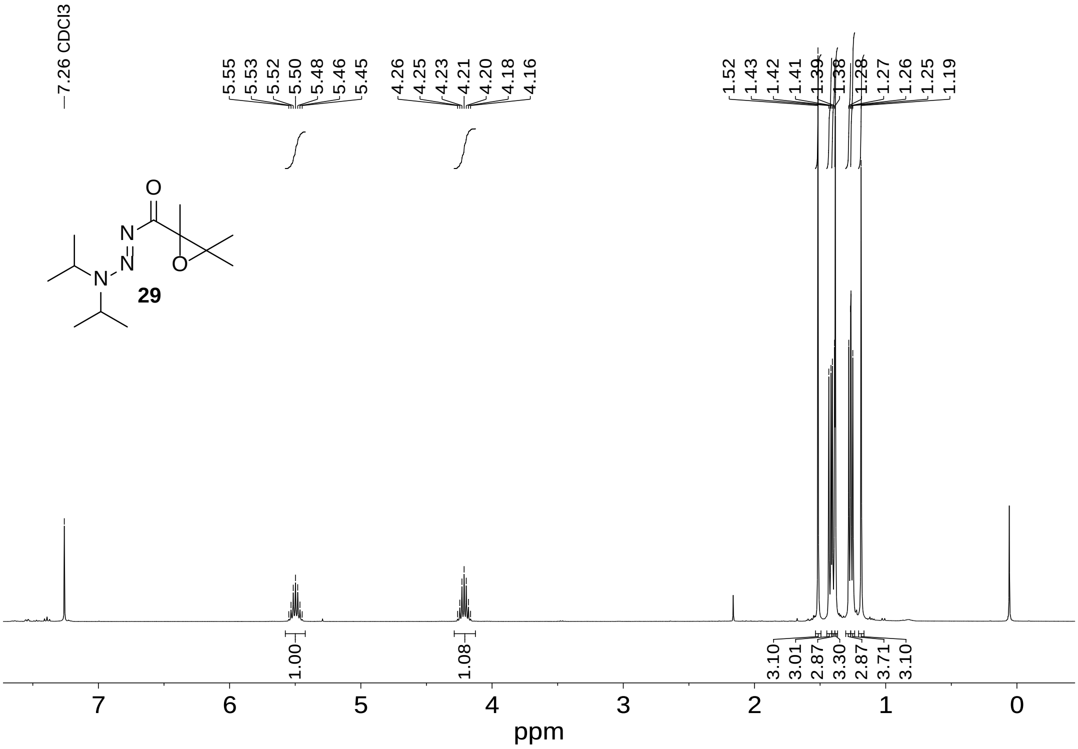

Figure S14.93. ^{1}H NMR spectrum of **29** (400 MHz, *d*$_3$-chloroform).

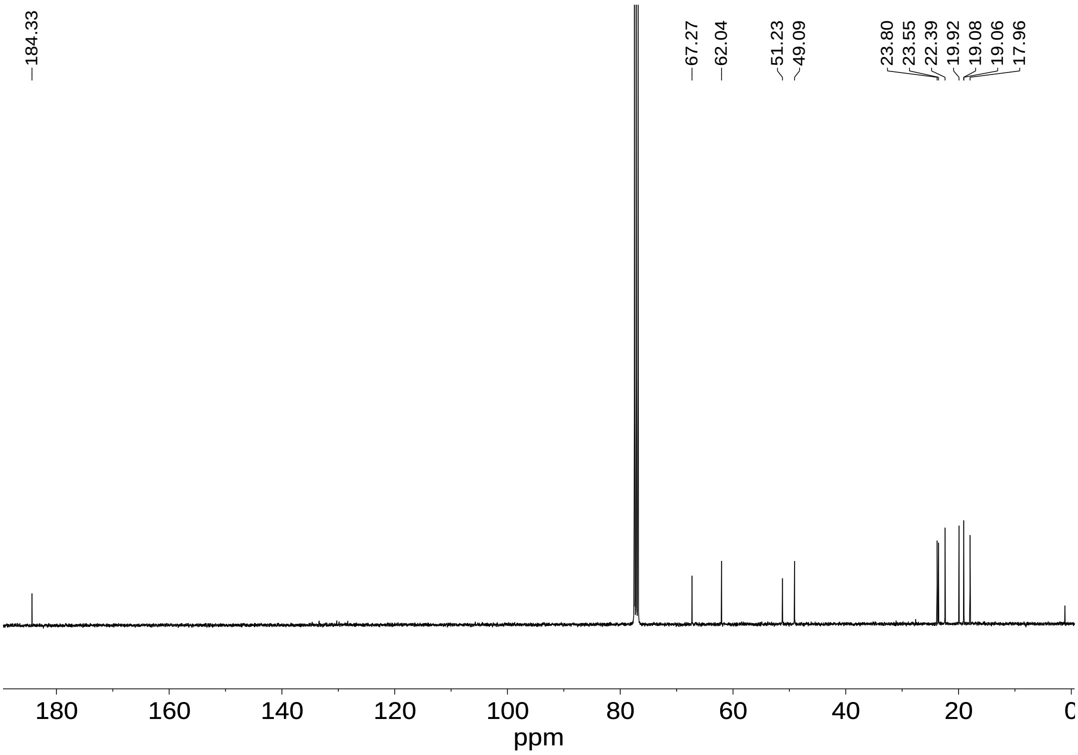

Figure S14.94. ^{13}C NMR spectrum of **29** (101 MHz, *d*$_3$-chloroform).

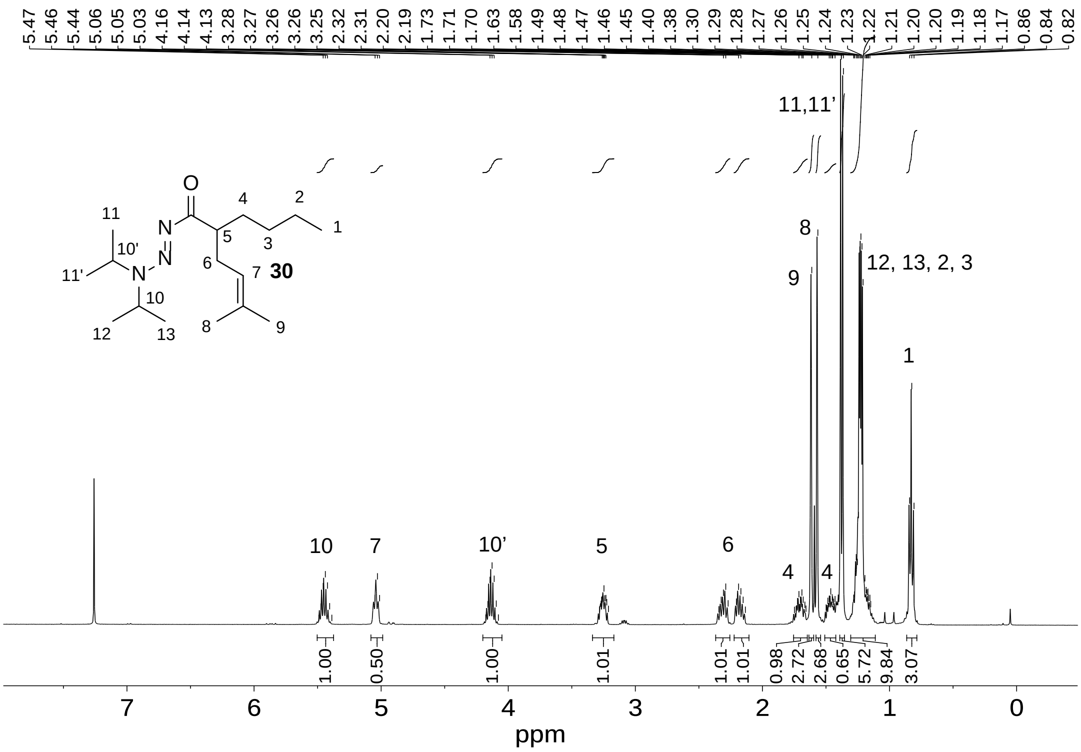

Figure S14.95. ^{1}H NMR spectrum of **30** (400 MHz, d_3-chloroform).

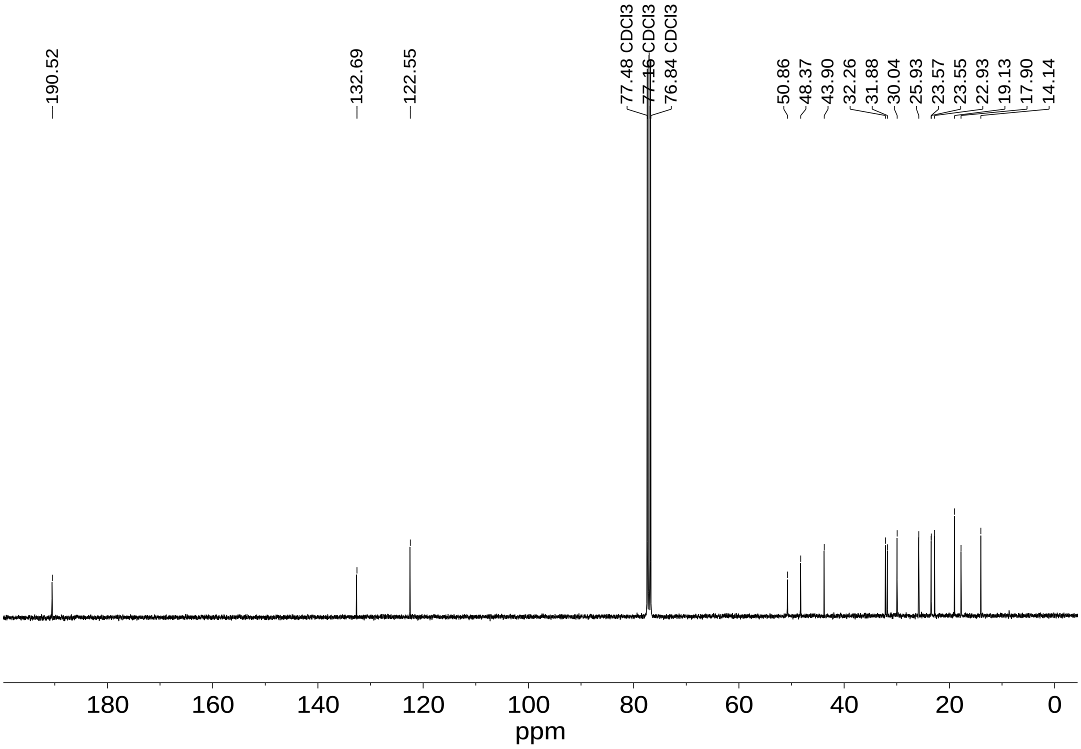

Figure S14.96. ^{13}C NMR spectrum of **30** (101 MHz, d_3-chloroform).