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Electronic Supplementary Information

Ni-Catalysed Intramolecular [4+4]-Cycloadditions of Bis-dienes towards Eight-membered Fused Bicyclic Systems: A Combined Experimental and Computational Study

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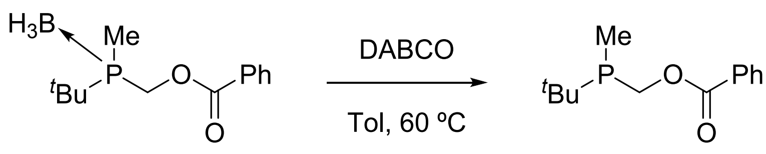
Contents

EXPERIMENTAL SECTION

1.1. General Remarks

All syntheses were carried out on chemicals as purchased from commercial sources, unless otherwise stated. Air and moisture sensitive manipulations or reactions were run under inert atmosphere using anhydrous and deoxygenated solvents, either in a glove box or with standard Schlenk techniques. All solvents were dried by using a Solvent Purification System (SPS). Silica gel 60 (230–400 mesh) was used for column chromatography. Silica gel impregnated with silver nitrate was used to isolate the [4+4] and the [4+2]-cycloaddition products **2** and **3**, respectively. It was prepared according to a procedure previously reported in the literature.[1] NMR spectra were recorded in $CDCl_3$ unless otherwise cited, on a Bruker Avance 300 MHz, 400 MHz or 500 MHz Ultrashield spectrometers. ^{1}H NMR and ^{13}C{^{1}H} NMR chemical shifts are quoted in ppm relative to residual solvent peaks. ^{31}P{^{1}H} NMR chemical shifts are quoted in ppm relative to 85% phosphoric acid in water. High-resolution mass spectra (HRMS) were recorded by using either ESI or APCI ionization method in positive mode. Conversion, and selectivity for the cycloaddition products were determined by ^{1}H NMR spectroscopy from the crude mixtures, using 1,3,5-trimethoxybenzene as internal standard. Melting points were measured in open capillaries and are uncorrected.

1.2. Experimental Procedure and Characterization Data for Ligand L6



The required amounts of phosphino-borane adduct[2] (0.233 g, 0.925 mmol) and 1,4-diazabyciclo[2.2.2]octane (DABCO, 0.212 g, 1.85 mmol) were loaded into a flame-dried Schlenk flask to which dry toluene (5.0 mL) was added. The reaction mixture was heated at 60 °C and stirred during 24 h. After that, the toluene solvent was completely removed under high vacuum. Finally, the resulting residue was redissolved in diethyl ether (5.0 mL) and passed through a short pad of silica (2.0 cm x 1.5 cm). Evaporation of the diethyl ether under high vacuum afforded the desired ligand **L6** as a colorless liquid (0.109 g, 0.46 mmol, 50% yield, see Figure S6 to Figure S8). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 – 8.03 (m, 2H, H_{arom}), 7.57 – 7.54 (m, 1H, H_{arom}), 7.45 – 7.42 (m, 2H, H_{arom}), 4.69 (dd, $^2J_{H\text{-}H}$ = 13.1 Hz, $^2J_{H\text{-}P}$ = 5.6 Hz, 1H, C*H*H-PMe^{t}Bu), 4.55 (dd, $^2J_{H\text{-}H}$ = 13.1 Hz, $^2J_{H\text{-}P}$ = 4.0 Hz, 1H, CH*H*-PMe^{t}Bu), 1.13 (d, $^3J_{H\text{-}P}$ = 12.0 Hz, 9H, ^{t}Bu), 1.09 (d, $^2J_{H\text{-}P}$ = 3.4 Hz, 3H, Me) ppm. ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 166.8 (d, $^3J_{C\text{-}P}$ = 2.8 Hz, C=O), 133.1 (CH_{arom}), 130.2 ($C_{q\ arom}$), 129.8 (CH_{arom}), 128.5 (CH_{arom}), 63.0 (d, $^1J_{C\text{-}P}$ = 20.4 Hz, CH_2-PMe^{t}Bu), 27.5 (d, $^2J_{C\text{-}P}$ = 13.1 Hz, 3 x CH_3, ^{t}Bu),

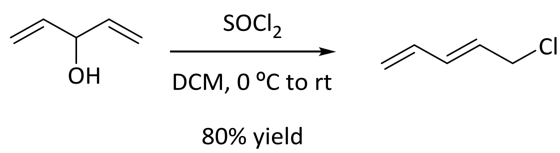
[1] T.-S. Li, J.-T. Li and H.-Z. Li, *J. Chromatogr. A*, 1995, **715**, 372.

[2] The racemic sample of the corresponding starting phosphino-borane adduct has been previously prepared in our research group, see the following reference: J. R. Lao, J. Benet-Buchholz and A. Vidal-Ferran, *Organometallics* 2014, **33**, 2960.

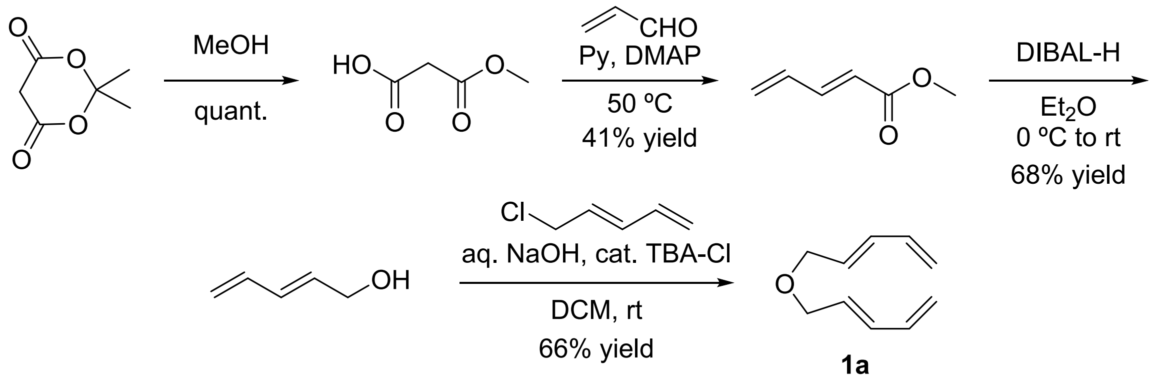
4.2 (d, $^{1}J_{C\text{-}P}$ = 17.2 Hz, CH_3, Me) ppm. $^{31}P\{^{1}H\}$ NMR (202 MHz, $CDCl_3$) δ -13.2 (s, PMe^{t}Bu) ppm. HRMS (ESI^{+}) m/z calcd for $C_{13}H_{19}O_2PNa$ [M+Na]$^{+}$ 261.1015, found 261.1015.

1.3. Synthesis of Cycloaddition Substrates

1.3.1. Synthesis of (*E*)-5-(((*E*)-penta-2,4-dien-1-yl)oxy)penta-1,3-diene (**1a**)



Thionyl chloride (2.03 mL, 28.0 mmol) was added dropwise to a solution of 1,4-pentadiene-3-ol (2.31 mL, 23.3 mmol) in dichloromethane (DCM, 55.0 mL) at 0 °C. The reaction mixture was allowed to warm to room temperature and stirred for 2 h. The reaction was then quenched with water (15.0 mL) and the two phases organic and aqueous were separated. The aqueous phase was extracted with DCM (2 x 15.0 mL). The combined organic phases were dried over magnesium sulfate and concentrated *in vacuo*. The desired 5-chloropenta-1,3-diene was obtained by distillation of the mixture (b.p. = 73 °C, p = 0.32 bar) as a colorless oil (2.79 g, 76% yield, *E*:*Z* isomers = 95:5). All spectroscopic data were consistent with those previously reported in the literature.[3]



(TBA-Cl = tetra-*n*-butylammonium chloride)

A mixture of Meldrum's acid (10.00 g, 69.4 mmol) and methanol (2.81 mL, 69.4 mmol) was heated at 80 ºC for 20 h. Evaporation of acetone under reduced pressure gave the desired mono-methyl malonate as colorless oil (8.19 g, quantitative yield), which was directly used in the following step without further purification. All spectroscopic data were consistent with those previously reported in the literature.[4]

Acrolein (3.1 mL, 41.7 mmol) was added to a mixture of mono-methyl malonate (8.19 g, 62.4 mmol), anhydrous pyridine (12.0 mL), and 4-*N,N*-dimethylaminopyridine (0.406 g, 3.33

[3] A. Z. Gonzalez and F. D. Toste, *Org. Lett.*, 2010, **12**, 200.

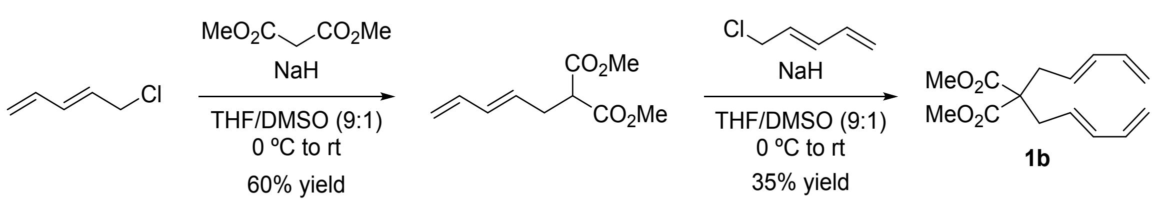
[4] (a) For the synthetic method, see: D. Craig and F. Grellepois, *Org. Lett.*, 2005, **7**, 463; (b) For the spectroscopic data, see: S. Niwayama, H. Cho and C. Lin, *Tetrahedron Lett.*, 2008, **49**, 4434.

mmol), and the reaction mixture was heated to 50 ºC and allowed to stir at this temperature for 24 h. The reaction mixture was allowed to reach room temperature and separated between water (15.0 mL) and diethyl ether (30.0 mL). The aqueous phase was then extracted with diethyl ether (3 x 30.0 mL). The combined organic phases were washed with brine (1 x 30 mL), dried over magnesium sulfate and the solvents evaporated to dryness. The resulting residue was purified by distillation (b.p. = 56 °C, p = 0.27 bar) to afford methyl (*E*)-penta-2,4-dienoate as a colorless liquid (1.92 g, 41% yield). All spectroscopic data were consistent with those previously reported in the literature.[5]

Diisobutylaluminum hydride (DIBAL-H, 1.0 M in hexane, 21.0 mL, 21.0 mmol) was added over 5 min to a solution of methyl (*E*)-penta-2,4-dienoate (1.18 g, 10.5 mmol) in anhydrous diethyl ether (25.0 mL) at 0 ºC. The mixture was stirred at this temperature for 20 min, and at room temperature for 4 h. The reaction was cooled to 0 ºC and quenched carefully with 2M aqueous HCl solution until the pH of the mixture was 5-6. The aqueous phase was separated and extracted with diethyl ether (2 x 15.0 mL). The combined organic phases were washed with brine (1 x 25.0 mL), dried over magnesium sulfate and concentrated *in vacuo* to afford the desired (*E*)-penta-2,4-dien-1-ol (0.600 g, 68% yield) as a colorless oil which was immediately used for the following step without further purification. All spectroscopic data were consistent with those previously reported in the literature.[6]

A mixture of 5-chloropenta-1,3-diene (4.00 g, 39.0 mmol), (*E*)-penta-2,4-dien-1-ol (2.1 g, 25.0 mmol), tetra-*n*-butylammonium chloride (0.368 g, 1.32 mmol), and 50% aqueous NaOH (9.99 g, 250 mmol) in DCM (10.0 mL) was vigorously stirred at room temperature overnight. The reaction mixture was then poured into 15.0 mL of distilled water, the organic phases separated, and the aqueous phase extracted with pentane (5 x 40.0 mL). The combined organic phases were washed with brine (1 x 50.0 mL), dried over magnesium sulfate, and concentrated under reduced pressure. The resulting residue was purified by distillation (b.p. = 62 °C, p = 0.35 mbar) to yield the desired product **1a** as colorless oil (2.49 g, 66% yield, *E*,*E*:*E*,*Z* isomers = 95:5, see Figure S9 and Figure S10). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.39 – 6.23 (m, 4H), 5.77 (dt, *J* = 15.0 Hz, *J* = 6.0 Hz, 2H), 5.21 (d, *J* = 17.6 Hz, 2H), 5.09 (d, *J* = 8.4 Hz, 2H), 4.02 (d, *J* = 6.0 Hz, 4H) ppm. ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 136.5, 133.4, 130.1, 117.7, 70.3 ppm. All spectroscopic data were consistent with those previously reported in the literature.[7]

1.3.2. Synthesis of dimethyl (*E*)-2-(penta-2,4-dien-1-yl)malonate (**1b**)

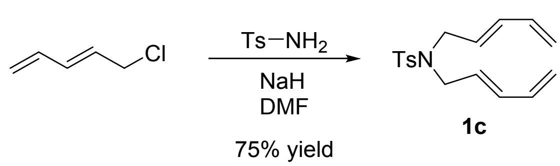


[5] J. Rodriguez and B. Waegell, *Synthesis*, 1988, 534.
[6] J. Llaveria, A. Beltran, M. M. Diaz-Requejo, M. I. Matheu, S. Castillon and P. J. Perez, *Angew. Chem., Int. Ed.*, 2010, **49**, 7092.
[7] R. Hertel, J. Mattay and J. Runsink, *J. Am. Chem. Soc.*, 1991, **113**, 657.

A solution of dimethyl malonate (4.5 mL, 39.4 mmol) in anhydrous tetrahydrofuran (THF, 2.5 mL) was added to a suspension of anhydrous NaH (0.538 g, 21.3 mmol) in anhydrous DMSO (6.0 mL) and THF (75.0 mL) at 0 ºC. After 30 min at 0 ºC, a solution of previously prepared 5-chloropenta-1,3-diene (1.63 g, 15.9 mmol) in anhydrous THF (4.0 mL) was added dropwise. The resulting mixture was allowed to warm to room temperature and stirred overnight. The reaction mixture was then quenched with distilled water (15.0 mL), diluted with diethyl ether (25.0 mL). The two phases (organic and aqueous) were separated. The aqueous phase was then extracted with diethyl ether (3 x 25.0 mL), and the resulting combined organic phases were washed with water (3 x 15.0 mL), dried over magnesium sulfate, and concentrated *in vacuo*. Finally, the resulting residue was purified distillation (b.p. = 78 °C, p = 0.12 mbar) to give the desired product (dimethyl (*E*)-2-(penta-2,4-dien-1-yl)malonate) as colorless oil (1.88 g, 60% yield). All spectroscopic data were consistent with those previously reported in the literature.[8]

A solution of the previously prepared dimethyl (*E*)-2-(penta-2,4-dien-1-yl)malonate (0.842 g, 4.25 mmol) in anhydrous THF (2.0 mL) was slowly syringed into a suspension of anhydrous NaH (0.134 g, 5.31 mmol) in anhydrous DMSO (1.5 mL) and THF (19.5 mL) at 0 ºC. After 30 min at 0 ºC, a solution of 5-chloropenta-1,3-diene (1.34 g, 8.5 mmol) in anhydrous THF (2.0 mL) was slowly added. The resulting mixture was warmed to room temperature and stirred overnight, and then quenched with distilled water (10.0 mL). THF was evaporated to dryness and the resulting residue was diluted with diethyl ether (15.0 mL). The two phases (organic and aqueous) were separated. The aqueous phase was then extracted with diethyl ether (2 x 15.0 mL), and the resulting combined organic phases were washed with water (3 x 15.0 mL), dried over magnesium sulfate, and concentrated under reduced pressure. Purification by distillation (b.p = 92 °C, p = 0.02 mbar) gave the desired substrate **1b** as colorless oil (0.393 g, 35% yield, *E*,*E*:*E*,*Z* isomers = 95:5, see Figure S11 and Figure S12). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.24 (dt, *J* = 17.0 Hz, *J* = 10.3 Hz, 2H), 6.05 (dd, *J* = 15.1 Hz, *J* = 10.5 Hz, 2H), 5.47 (dt, *J* = 15.2 Hz, *J* = 7.6 Hz, 2H), 5.09 (d, *J* = 17.0 Hz, 2H), 4.98 (d, *J* = 10.3 Hz, 2H), 3.67 (s, 6H), 2.62 (d, *J* = 7.7 Hz, 4H) ppm. ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 171.0, 136.5, 135.2, 127.7, 116.5, 58.0, 52.4, 36.0 ppm. All spectroscopic data were consistent with those previously reported in the literature.[8]

1.3.3. Synthesis of 4-methyl-*N*,*N*-di((*E*)-penta-2,4-dien-1-yl)benzenesulfonamide (**1c**)



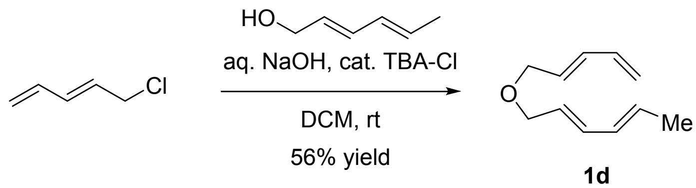
1c

To a cooled (0 °C) suspension of NaH (95%, 0.531 g, 21.0 mmol) in DMF (12.0 mL) was added a solution of *p*-toluenesulfonamide (1.5 g, 8.76 mmol) in DMF (12.0 mL). The mixture was stirred at 0 °C for 30 min, after which a solution of previously prepared 5-chloropenta-1,3-diene (2.61 g, 21.9 mmol) in DMF (6.0 mL) was added. The resulting mixture was stirred at room temperature for 2 h. The reaction was quenched by the addition of saturated aqueous solution of

[8] J. M. Takacs and E. C. Lawson, *Organometallics*, 1994, **13**, 4787.

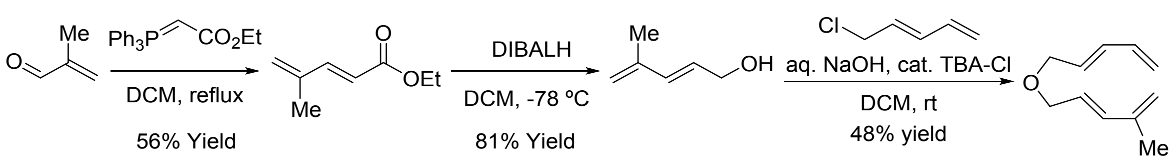
NH_4Cl (20.0 mL) at 0 °C, and extracted with ether (3 x 25.0 mL). The combined organic phases were dried over magnesium sulfate, filtered, and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (Hexane:EtOAc, 100:0→80:20) to afford the target substrate **1c** as a yellow oil (1.94 g, 75% yield, *E,E*:*E,Z* isomers = 95:5, see Figure S13 and Figure S14). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.3 Hz, 1H), 7.28 (d, *J* = 7.9 Hz, 2H), 6.24 (dt, *J* = 16.8 Hz, *J* = 10.3 Hz, 2H), 6.06 (dd, *J* = 15.2 Hz, *J* = 10.5 Hz, 2H), 5.48 – 5.41 (m, 2H), 5.15 (d, *J* = 16.8 Hz, 2H), 5.07 (d, *J* = 10.8 Hz, 2H), 3.81 (d, *J* = 6.7 Hz, 4H), 2.42 (s, 3H) ppm. ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 143.3, 137.5, 135.9, 134.9, 129.7, 127.8, 127.3, 118.0, 48.6, 21.6 ppm. All spectroscopic data were consistent with those previously reported in the literature.[9]

1.3.4. Synthesis of (2*E*,4*E*)-1-(((*E*)-penta-2,4-dien-1-yl)oxy)hexa-2,4-diene (**1d**)



A mixture of (2*E*,4*E*)-hexa-2,4-dien-1-ol (1.00 g, 9.88 mmol), previously prepared 5-chloropenta-1,3-diene (1.58 g, 15.4 mmol), tetra-*n*-butylammonium chloride (0.146 g, 0.524 mmol), and 50% aqueous NaOH (3.95g g, 98.8 mmol) in dichloromethane (4.0 mL) was vigorously stirred at room temperature overnight. The reaction mixture was then poured to distilled water (14.0 mL). The phases were separated, and the aqueous phase was extracted with pentane (5 x 7.0 mL). The combined organic phases were washed with brine (2 x 7.0 mL), dried over magnesium sulfate, filtered and concentrated under reduced pressure. Finally, the resulting residue was purified by distillation (b.p = 44 ºC, p = 0.019 mbar) to afford the target substrate **1d** as a colorless liquid (0.904 g, 56% yield, *E,E*:*E,Z* isomers = 95:5, see Figure S15 and Figure S16). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.34 (dt, *J* = 16.8 Hz, *J* = 9.7 Hz, 1H), 6.27 – 6.17 (m, 2H), 6.05 (ddd, *J* = 15.0 Hz, *J* = 10.6 Hz, *J* = 1.2 Hz, 1H), 5.77 (dt, *J* = 15.2 Hz, *J* = 6.0 Hz, 1H), 5.70 (dq, *J* = 15.0 Hz, *J* = 6.8 Hz, 1H), 5.62 (dt, *J* = 15.1 Hz *J* = 6.5 Hz, 1H), 5.20 (d, *J* = 16.8 Hz, 1H), 5.08 (d, *J* =9.7 Hz, 1H), 3.99 (t, *J* = 6.5 Hz, 4H), 1.75 (d, *J* = 6.8 Hz, 3H) ppm. ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 136.5 (CH=), 133.4 (CH=), 133.2 (CH=), 130.9 (CH=), 130.3 (CH=), 130.1 (CH=), 126.7 (CH=), 117.5 (CH_2=), 70.6 (CH_2), 70.1 (CH_2), 18.2 (CH_3) ppm. Compound **1d** is too unstable to provide a good high-resolution mass spectrum under analysis conditions (using APCI as ionization source).

1.3.5. Synthesis of (*E*)-2-methyl-5-(((*E*)-penta-2,4-dien-1-yl)oxy)penta-1,3-diene (**1e**)



[9] M. Takimoto and M. Mori, *J. Am. Chem. Soc.*, 2002, **124**, 10008.

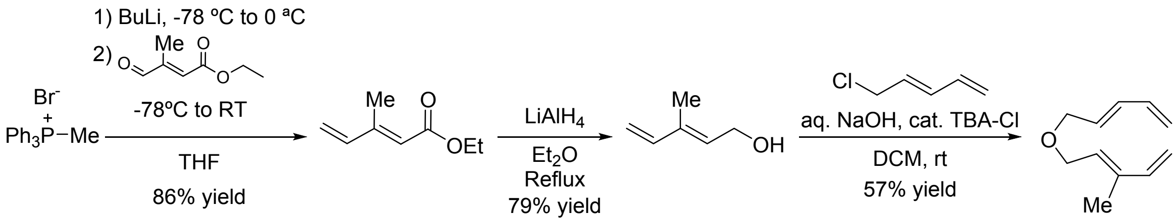
To a 250 mL round-bottom flask equipped with a stirring bar was added 95% (carbethoxymethylene)-triphenylphosphorane (7.98 g, 21.8 mmol) and 90% methacrolein (2.0 mL, 21.8 mmol) in dichloromethane (80.0 mL). The reaction mixture was stirred at reflux for 2 h, then cooled to 23 °C and concentrated *in vacuo*. Pentane (250.0 mL) was added to the concentrate to precipitate triphenylphosphine oxide. The mixture was filtered through Celite and the solvent evaporated to dryness. The filtration and evaporation steps were repeated until no white solid appeared. Removal of the solvent yielded ethyl (*E*)-4-methylpenta-2,4-dienoate pure (1.7 g, 56% yield), which was directly used in the following step without further purification. All spectroscopic data were consistent with those previously reported in the literature.[10]

Previously obtained unsaturated ester (1.6 g, 11.4 mmol) was dissolved in dry DCM (14.0 mL) and cooled to −78 °C. To this solution, DIBAL-H (1.0 M in hexane, 28.5 mL, 28.5 mmol) was added dropwise and the reaction mixture was stirred at this temperature for 30 min. The reaction then was quenched with methanol (5.0 mL), saturated aqueous solution of Rochelle salt (120.0 mL) and diethyl ether (120.0 mL). The mixture was stirred vigorously at room temperature until there was sufficient separation of the two phases. The organic layer was separated and aqueous phase was extracted twice with DCM (2 x 20.0 mL). The combined organic extracts were washed with water and brine, dried over magnesium sulfate and finally concentrated *in vacuo*. The mixture was distilled (b.p = 77 °C, p = 6.8 mbar) to yield (*E*)-4-methylpenta-2,4-dien-1-ol pure (0.908 g, 81% yield). All spectroscopic data were consistent with those previously reported in the literature.[11]

A mixture of (*E*)-4-methylpenta-2,4-dien-1-ol pure (0.45 g, 4.59 mmol), previously prepared 5-chloropenta-1,3-diene (0.863 g, 7.15 mmol), tetra-*n*-butylammonium chloride (0.0675 g, 0.243 mmol), and 50% aqueous NaOH (1.83 g, 45.9 mmol) in DCM (2.0 mL) was vigorously stirred at room temperature overnight. The reaction mixture was then poured to distilled water (6.0 mL). The phases were separated, and the aqueous phase was extracted with pentane (5 x 3.0 mL). The combined organic phases were washed with brine (2 x 3.0 mL), dried over magnesium sulfate, filtered, and concentrated under reduced pressure. The target substrate **1e** was obtained pure after distillation of the crude (b.p. = 43 °C, p = 0.031 mbar) (0.360 g, 48 % yield, *E,E*:*E,Z* isomers = 95:5, see Figure S17 and Figure S18). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.39 – 6.22 (m, 3H), 5.81 – 5.70 (m, 2H), 5.20 (dd, *J* = 16,2 Hz, *J* = 1.5 Hz, 1H), 5.08 (dd, *J* = 9.9 Hz, *J* = 1.5 Hz, 1H), 4.97 (s, 2H), 4.04 (dd, *J* = 6.0 Hz, *J* = 1.3 Hz, 2H), 4.01 (dd, *J* = 5.9 Hz, *J* = 1.0 Hz, 2H), 1.85 (s, 3H) ppm. ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 141.5 (C=), 136.4 (CH=), 135.6 (CH=), 133.4 (CH=), 130.1 (CH=), 126.0 (CH=), 117.6 (CH_2=), 116.9 (CH_2=), 70.8 (CH_2), 70.3 (CH_2), 18.6 (CH_3) ppm. HRMS (APCI$^+$): *m/z* calcd for $C_{11}H_{17}O$ [M+H]$^+$ 165.1274, found 165.1274.

[10] A. P. Marcus, A. S. Lee, R. L. Davis, D. J. Tantillo and R. Sarpong, *Angew. Chem., Int. Ed.*, 2008, **47**, 6379.
[11] (a) For the synthetic method see: J.-H. Zhou, S.-H. Cai, Y.-H. Xu and T.-P. Loh, *Org. Lett.*, 2016, **18**, 2355; (b) For the spectroscopic data see: M. T. Lai, D. Li, E. Oh and H. W. Liu, *J. Am. Chem. Soc.*, 1993, **115**, 1619.

1.3.6. Synthesis of (*E*)-3-methyl-5-(((*E*)-penta-2,4-dien-1-yl)oxy)penta-1,3-diene (**1f**)



A solution of *n*-butyllithium (2.5 M in hexane, 6.0 mL, 15.0 mmol) was added dropwise at –78 °C to a solution of methyltriphenylphosphonium bromide (5.32 g, 14.6 mmol) in dry THF (50.0 mL). The mixture was allowed to reach 0 °C and stirred for 1 h. After cooling to –78 °C, ethyl (*E*)-3-methyl-4-oxo-2-butenoate (2.00 g, 13.6 mmol) dissolved in dry THF (20.0 mL) was slowly added. The mixture was stirred for 24 h at room temperature. The reaction was then hydrolyzed with water (30.0 mL), and extracted three times with diethyl ether (3 x 50.0 mL). The combined organic phases were dried with magnesium sulfate and the solvent was evaporated under reduced pressure. The mixture was dissolved in pentane (50.0 mL), filtered through Celite, and then concentrated *in vacuo*. The filtration and concentration steps were repeated three times, until no white solid appeared, to obtain the pure product ethyl (*E*)-3-methylpenta-2,4-dienoate (1.6 g, 86 % yield). All spectroscopic data were consistent with those previously reported in the literature.[12]

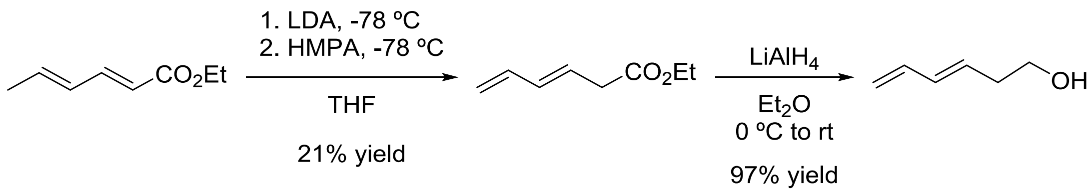
Ethyl (*E*)-3-methylpenta-2,4-dienoate (0.50 g, 3.57 mmol) was added to a suspension of $LiAlH_4$ (0.203 g, 5.35 mmol) in absolute diethyl ether (7.5 mL) under a N_2 atmosphere. The mixture was heated to reflux for 1 h and quenched by the addition of ice-cooled water. The residue formed was dissolved by addition of 10% H_2SO_4 (8.0 mL). The phases were separated and the aqueous phase was extracted with diethyl ether (3 x 10.0 mL). The combined organic phases were washed with a saturated solution of Rochelle salt (1 x 10.0 mL), dried over magnesium sulfate, and the solvent was removed under reduced pressure. The residue of (*E*)-3-methylpenta-2,4-dien-1-ol was pure enough for use in the next step without further purification (0.275 g, 79 % yield). All spectroscopic data were consistent with those previously reported in the literature.[12]

A mixture of (*E*)-3-methylpenta-2,4-dien-1-ol (0.80 g, 8.15 mmol), previously prepared 5-chloropenta-1,3-diene (1.53 g, 12.7 mmol), tetra-*n*-butylammonium chloride (0.12 g, 0.432 mmol), and 50% aqueous NaOH (3.26 g, 81.5 mmol) in DCM (3.5 mL) was vigorously stirred at room temperature overnight. The reaction mixture was then poured into distilled water (10.0 mL). The phases were separated, and the aqueous phase was extracted with pentane (5 x 5.0 mL). The combined organic phases were washed with brine (2 x 5.0 mL), dried over magnesium sulfate, filtered, and concentrated *in vacuo*. The desired substrate **1f** was purified by distillation (b.p. = 34 °C, p = 0.04 mbar) (0.762 g, 57 % yield, *E,E*:*E,Z* isomers = 95:5, see Figure S19 and Figure S20). ^1H NMR (400 MHz, $CDCl_3$) δ 6.45 – 6.24 (m, 3H), 5.80 (dt, J = 15.0 Hz, J = 6.5 Hz, 1H), 5.65 (t, J = 6.4 Hz, 1H), 5.25 (d, J = 5.6 Hz, 1H), 5.20 (d, J = 5.7 Hz, 1H), 5.11 (d, J = 10.6 Hz, 1H), 5.06 (d, J = 10.7 Hz,

[12] S. Yildizhan and S. Schulz, *Synlett*, 2011, 2831.

1H), 4.14 (d, J = 6.4 Hz, 2H), 4.04 (d, J = 6.5 Hz, 2H), 1.80 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 140.9 (CH=), 137.1 (C=), 136.4 (CH=), 133.4 (CH=), 130.2 (CH=), 128.4 (CH=), 117.7 (CH_2=), 113.0 (CH_2=), 70.4 (CH_2), 66.6 (CH_2), 12.2 (CH_3) ppm. HRMS (APCI$^+$): m/z calcd for $C_{11}H_{17}O$ $[M+H]^+$ 165,1274, found 165.1277.

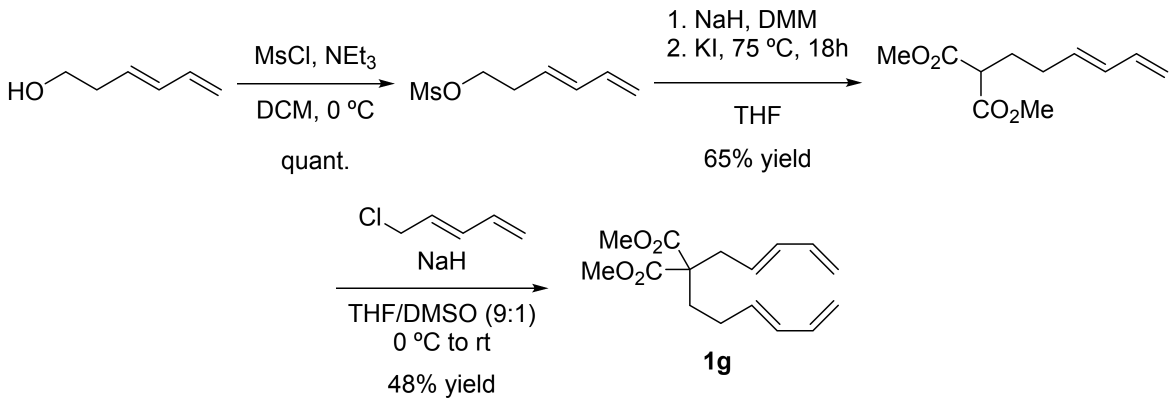
1.3.7. Synthesis of dimethyl 2-((*E*)-hexa-3,5-dien-1-yl)-2-((*E*)-penta-2,4-dien-1-yl)malonate (**1g**)



A flame-dried 500 mL Schlenk flask was loaded with dry THF (165.0 mL) and diisopropylamine (DIPA, 12.1 mL, 85.6 mmol) and cooled to –78 °C. *n*-butyllithium (34.2 mL, 85.6 mmol) was then added dropwise and the reaction mixture was stirred at –78 °C for 1 h in order to form LDA *in situ*. Hexamethylphosphoramide (HMPA, 12.4 mL, 71.3 mmol) was then slowly added to the mixture. After 30 min stirring at –78 °C, ethyl sorbate (10.7 mL, 71.3 mmol) in THF (25.0 mL) was added dropwise, resulting in a red-orange solution. The reaction was stirred at –78 °C for 1 h and then ethanol (35.0 mL) was added. The reaction was then quenched by pouring the mixture to a 1L round-bottom flask containing water (140.0 mL) and glacial acetic acid (25.0 mL). After diluting with hexane (100.0 mL), the two phases were separated, and the aqueous phase was extracted with hexane (3 x 125.0 mL). The combined organic phases were washed with saturated $NaHCO_3$ (2 x 75.0 mL), brine (2 x 75.0 mL), and dried over magnesium sulfate. The solvent was evaporated to dryness. The crude mixture containing the desired product and the starting material was purified by column chromatography on silica gel impregnated with $AgNO_3$ (10%)[1] (Hexane:Acetone, 100:0→80:20) to yield the desired ethyl (*E*)-hexa-3,5-dienoate (2.14 g, 21 % yield). All spectroscopic data were consistent with those previously reported in the literature.[13]

To a flame-dried Schlenk flask was introduced $LiAlH_4$ (0.512 g, 13.5 mmol), suspended in anhydrous diethyl ether (10.0 mL), and cooled at 0 °C. Then, a solution of ethyl (*E*)-hexa-3,5-dienoate (1.35 g, 9.63 mmol) in anhydrous diethyl ether (3.0 mL) was slowly cannulated to the previous suspension. The reaction mixture was allowed to reach room temperature and stirred for 4.5 h. The reaction was recooled at 0 °C, diluted with diethyl ether (15.0 mL), and carefully quenched with saturated aqueous solution of Rochelle salt (25.0 mL). The biphasic mixture was vigorously stirred overnight. The two phases were then separated and the aqueous phase was extracted with diethyl ether (2 x 50.0 mL). The combined organic phases were washed with brine (1 x 50.0 mL), dried over magnesium sulfate, filtered, and concentrated *in vacuo* to provide the desired product (*E*)-hexa-3,5-dien-1-ol as yellowish liquid (0.92 g, 97% crude yield) in a pure form, which was immediately used for the following step without further purification.[14]

[13] C. A. Miller and R. A. Batey, *Org. Lett.*, 2004, **6**, 699.
[14] B. DeBoef, W. R. Counts and S. R. Gilbertson, *J. Org. Chem.* 2007, **72**, 799.



1g

To a solution of (*E*)-hexa-3,5-dien-1-ol (0.74 g, 7.09 mmol) and triethylamine (1.99 mL, 14.2 mmol) in DCM (22.0 mL) at 0 °C was added methanesulfonyl chloride (0.58 mL, 7.44 mmol). The reaction mixture was stirred at 0 °C for 1 h, after which it was poured into a cooled 1 M HCl aqueous solution (15.0 mL). The aqueous phase was then extracted with DCM (3 x 25.0 mL). The combined organic phases were washed with brine (1 x 25.0 mL), dried over magnesium sulfate, filtered and the solvent evaporated to dryness to yield the crude mesylate compound as yellowish oil in quantitative yield (1.249 g), which was immediately used for the following step without further purification. All spectroscopic data were consistent with those previously reported in the literature.[15]

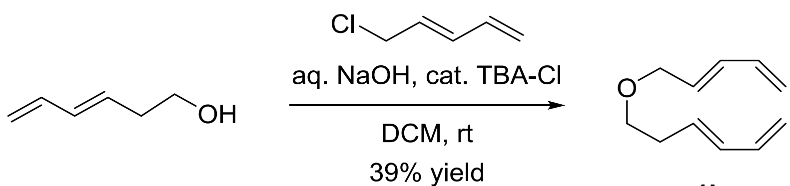
In a 100 mL two-necked round-bottom flask under inert atmosphere, to a suspension of NaH (0.323 g, 12.8 mmol) in anhydrous DMF (10.0 mL) was added a solution of dimethyl malonate (1.65 mL, 14.2 mmol) in anhydrous THF (18.5 mL). The mixture was stirred at room temperature for 15 min. After that, a solution of (*E*)-hexa-3,5-dien-1-yl methanesulfonate (1.25 g, 7.09 mmol) in anhydrous THF (17.0 mL) was slowly added followed by adding KI (0.235 g, 1.42 mmol) as solid. The resulting reaction mixture was heated at 75 °C and stirred overnight. After 18 h, the mixture was quenched with saturated aqueous NH_4Cl (25.0 mL) and extracted with diethyl ether (3 x 30.0 mL). The combined organic phases were dried over magnesium sulfate and concentrated *in vacuo*. Finally, the residue was purified by silica gel column chromatography (Hexane:Diethyl ether, 100:0→90:10) to yield the target product dimethyl (*E*)-2-(hexa-3,5-dien-1-yl)malonate as colorless oil (0.9811 g, 65% yield). All spectroscopic data were consistent with those previously reported in the literature.[15]

NaH (0.140 g, 5.56 mmol) was added to a 50 mL bottom flask under inert atmosphere. Anhydrous THF (19.0 mL) and DMSO (2.0 mL) were syringed to the flask and the resulting solution was cooled to 0 °C. Then, a solution of dimethyl (*E*)-2-(hexa-3,5-dien-1-yl)malonate (0.975 g, 4.59 mmol) in anhydrous THF (2.5 mL) was slowly added. The resulting reaction mixture was allowed to reach room temperature and was stirred for 1 h. Then, the mixture is re-cooled to 0 °C and a solution of 5-chloropenta-1,3-diene (0.69 g, 5.79 mmol) in anhydrous THF (2.0 mL) was added dropwise. The resulting mixture was allowed to reach room temperature and stirred overnight.

[15] S. Thamapipol and E. P. Kuendig, *Org. Biomol. Chem.*, 2011, **9**, 7564.

Then, the mixture was quenched with distilled water (15.0 mL). The THF solvent was evaporated to dryness, the resulting residue was partitioned between diethyl ether (40.0 mL) and water (10.0 mL), and the two phases were separated. The organic phase was washed with distilled water (3 x 15.0 mL), dried over magnesium sulfate, filtered and concentrated *in vacuo*. Finally, the resulting residue was purified by silica gel column chromatography (Hexane:Diethyl ether, 90:10) to afford the desired compound **1g** as yellow oil (0.620 g, 48% yield, *E,E*:*E,Z* isomers = 95:5, see Figure S21 and Figure S22). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.33 – 6.23 (m, 2H), 6.12 – 6.02 (m, 2H), 5.67 – 5.60 (m, 1H), 5.54 – 5.46 (m, 1H), 5.15 – 5.08 (m, 2H), 5.03 – 4.96 (m, 2H), 3.71 (s, 6H), 2.70 – 2.68 (m, 2H), 2.05 – 1.93 (m, 4H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 171.6 (C=O), 137.1 (CH=), 136.7 (CH=), 135.1 (CH=), 133.5 (CH=), 131.8 (CH=), 127.9 (CH=), 116.7 (CH_2=), 115.7 (CH_2=), 57.7 (C-($CO_2Me)_2$), 52.6 (2 x CH_3, CO_2Me), 36.3 (CH_2), 32.2 (CH_2), 27.3 (CH_2) ppm. HRMS (ESI$^+$): *m/z* calcd for $C_{16}H_{22}O_4Na$ [M+Na]$^+$ 301.1410, found 301.1414.

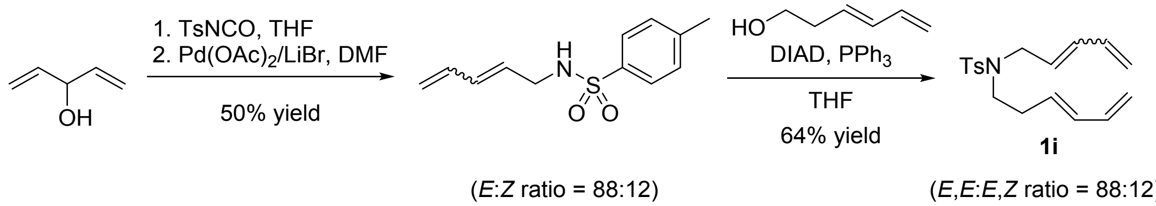
1.3.8. Synthesis of (*E*)-6-(((*E*)-penta-2,4-dien-1-yl)oxy)hexa-1,3-diene (**1h**)



1h

A mixture of (*E*)-hexa-3,5-dien-1-ol (0.92 g, 9.37 mmol), previously prepared 5-chloropenta-1,3-diene (1.15 g, 11.2 mmol), tetra-*n*-butylammonium chloride (0.138 g, 0.497 mmol), and 50% aqueous NaOH (3.75 g, 93.7 mmol) in DCM (10.0 mL) was vigorously stirred at room temperature overnight. The reaction mixture was then poured to distilled water (20.0 mL). The phases were separated and the aqueous phase was extracted with pentane (5 x 15.0 mL). The combined organic phases were washed with brine (2 x 20.0 mL), dried over magnesium sulfate, filtered, and concentrated under reduced pressure. The residue was purified by distillation (b.p = 57 °C, p = 0.16 mbar) to afford the target substrate **1h** in a pure form as colorless liquid (0.600 g, 39% isolated yield, *E,E*:*E,Z* isomers = 95:5, see Figure S23 and Figure S24). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.39 – 6.21 (m, 3H), 6.16 – 6.08 (m, 1H), 5.81 – 5.68 (m, 2H), 5.23 – 5.08 (m, 3H), 5.00 – 4.97 (m, 1H), 4.03 – 4.01 (m, 2H), 3.48 (t, *J* = 6.8 Hz, 2H), 2.41 – 2.36 (m, 2H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 137.2 (CH=), 136.5 (CH=), 133.2 (CH=), 132.8 (CH=), 131.3 (CH=), 130.3 (CH=), 117.6 (CH_2=), 115.6 (CH_2=), 71.1 (CH_2), 89.8 (CH_2), 33.2 (CH_2) ppm. HRMS (APCI$^+$): *m/z* calcd for $C_{11}H_{17}O$ [M+H]$^+$ 165.1274, found 165.1279.

1.3.9. Synthesis of *N*-((*E*)-hexa-3,5-dien-1-yl)-4-methyl-*N*-(penta-2,4-dien-1-yl) benzenesulfonamide (**1i**)



To a flame-dried 100 mL Schlenk flask was introduced 1,4-pentadien-3-ol (1.0 g, 11.7 mmol) and 4-methylbenzenesulfonyl isocyanate (2.04 mL, 12.8 mmol). Anhydrous THF (50.0 mL) was syringed to the flask and the resulting mixture was stirred at room temperature under inert atmosphere for 2 h. After that, the THF solvent was removed under vacuum and the resulting residue was dissolved in DMF (60.0 mL). Then, palladium acetate (0.131 g, 0.583 mmol) and lithium bromide (4.09 g, 46.6 mmol) were added. The reaction mixture was heated at 90 °C and the reaction was stirred overnight. Then, the reaction mixture was allowed to reach room temperature. Diethyl ether (600.0 mL) was added and the organic phase was washed with distilled water (3 x 150.0 mL) and brine (3 x 150.0 mL), dried over magnesium sulfate, filtered, and concentrated *in vacuo*. Finally, the resulting residue was purified by silica gel column chromatography (Cyclohexane:EtOAc, 100:0→70:30) to yield the desired product 4-methyl-*N*-penta-2,4-dienyl-benzenesulfonamide as a white solid (1.38 g, 50% isolated yield, *E*:*Z* isomers = 88:12).[16] All spectroscopic data for the *E* isomer were consistent with those previously reported in the literature.[16]

To a flame-dried 50 mL Schlenk flask under argon atmosphere, a solution of diisopropyl azodicarboxylate (DIAD, 1.57 mL, 7.58 mmol) and triphenylphosphine (1.99 g, 7.58 mmol) in anhydrous THF (30.0 mL) was prepared at 0 °C. After the solution was stirred for 1 h, a solution of 4-methyl-*N*-penta-2,4-dienyl-benzenesulfonamide (1.50 g, 6.32 mmol) and (*E*)-hexa-3,5-dien-1-ol (0.66 g, 6.32 mmol) in anhydrous THF (10.0 mL) was added at 0 °C. The reaction mixture was slowly allowed to reach room temperature and stirred for 3 h. The solvent was then evaporated to dryness and the resulting mixture was purified by silica gel column chromatography (Cyclohexane:EtOAc, 100:0→80:20) to yield the desired substrate **1i** as colorless oil (1.29 g, 64% yield, *E*,*E*:*E*,*Z* isomers = 88:12, see Figure S25 and Figure S26).

The two *E*,*E*- and *E*,*Z*-isomers were respectively isolated in a pure form by semi-preparative HPLC using a Daicel Chiralpak® IA column (98:2 hexane/EtOH; 5 mL/min) on a 10 mg scale. Semi-preparative HPLC analysis, Daicel Chiralpak® IA column (25 cm x 0.46 cm), hexane/EtOH (95:5), 1 mL/min, 254 nm, t_R(*Z*,*E*-isomer) = 14.3 min, t_R(*E*,*E*-isomer) = 16.3 min.

[16] The preparation of 4-methyl-*N*-penta-2,4-dienyl-benzenesulfonamide was performed using the experimental procedure reported in the following reference: A. Lei and X. Lu, *Org. Lett.* 2000, **2**, 2357. Under the same experimental conditions, the authors of the paper claimed that the reaction was regioselective affording exclusively the *E* isomer. In our hands after several times, we were able to isolate the target product as a mixture of *E*:*Z* isomers = 88:12.

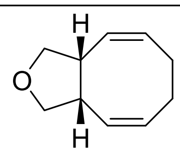
E,*E*-**1i** (see Figure S27 and Figure S28): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 – 7.68 (m, 2H), 7.30 – 7.28 (m, 2H), 6.29 – 6.21 (m, 2H), 6.13 – 6.00 (m, 2H), 5.57 – 5.46 (m, 2H), 5.19 – 4.99 (m, 4H), 3.84 (d, *J* = 6.6 Hz, 2H), 3.19 – 3.16 (m, 2H), 2.42 (s, 3H), 2.33 – 2.28 (m, 2H) ppm. ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 143.3, 137.3, 136.9, 135.9, 134.6, 133.4, 133.0, 130.8, 130.6, 129.8, 128.4, 127.3, 126.0, 120.2, 118.2, 116.1, 49.9, 47.0, 44.8, 32.1, 32.0, 21.6 ppm. All spectroscopic data for the *E*,*E* isomer were consistent with those previously reported in the literature.[17]

E,*Z*-**1i** (see Figure S29 and Figure S30): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 – 7.68 (m, 2H, H_{arom}), 7.30 – 7.28 (m, 2H, H_{arom}), 6.58 – 6.51 (m, 1H) 6.29 – 6.21 (m, 1H), 6.12 – 6.00 (m, 2H), 5.58 – 5.52 (m, 1H), 5.29 – 5.20 (m, 3H), 5.12 – 5.08 (m, 1H), 5.01 – 4.99 (m, 1H), 4.00 – 3.98 (m, 2H), 3.19 – 3.16 (m, 2H), 2.42 (s, 3H, Me), 2.34 – 2.29 (m, 2H) ppm. ^{13}C{^{1}H} NMR as DEPTQ135 (125 MHz, $CDCl_3$) δ 143.4 ($C_{q\ arom}$), 137.2 ($C_{q\ arom}$), 136.9 (CH=), 133.4 (CH=), 133.0 (CH=), 130.8 (CH=), 130.6 (CH=), 129.8 (CH_{arom}), 127.4 (CH_{arom}), 126.0 (CH=), 120.2 (CH_2=), 116.1 (CH_2=), 47.0 (CH_2), 44.9 (CH_2), 32.1 (CH_2), 21.6 (CH_3, Me) ppm. HRMS (ESI$^+$): *m/z* calcd for $C_{18}H_{23}NO_2SNa$ $[M+Na]^+$ 340.1342, found 340.1350.

1.4. General Methodology for the Cycloaddition Reactions

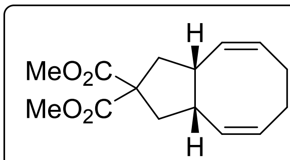
A solution of the substrate (1.00 mmol) and ligand (0.21 mmol) in anhydrous and deoxygenated toluene was prepared under inert atmosphere. $Ni(cod)_2$ (0.10 mmol) was added dropwise from a stock solution in anhydrous toluene. The resulting mixture was carefully heated at 60 ºC under argon atmosphere and stirred for 24 h. After that, the reaction mixture was allowed to reach room temperature and oxidized to air for 1 h. The mixture was filtered through a short pad of silica and further eluted with diethyl ether. The filtrate was concentrated *in vacuo* and the resulting crude mixture was analyzed by NMR spectroscopy. Purification of the desired product was achieved by column chromatography on silica gel impregnated with silver nitrate (10%).[1]

1.5. Characterization of [4+4] Cycloaddition Products



cis-**2a**

Product *cis*-**2a** was prepared following the general procedure starting from substrate **1a** (0.076 g, 0.50 mmol), ligand **L2** (37.9 mg, 0.11 mmol), and $Ni(cod)_2$ (14.1 mg, 0.050 mmol). It was obtained as colorless liquid (0.040 g, 56% yield, see Figure S31 and Figure S32). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.60 – 5.56 (m, 2H), 5.40 (dd, *J* = 11.1 Hz, *J* = 2.3 Hz, 2H), 4.02 (dd, *J* = 8.0 Hz, *J* = 6.9 Hz, 2H), 3.60 (dd, *J* = 8.0 Hz, *J* = 6.1 Hz, 2H), 3.32 (bs, 2H), 2.63 – 2.60 (m, 2H), 2.08 – 2.05 (m, 2H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 129.7, 129.1, 74.1, 43.7, 28.1 ppm. All spectroscopic data were consistent with those previously reported in the literature.[17]

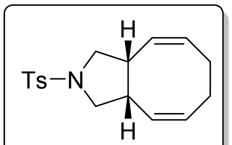


cis-**2b**

Product *cis*-**2b** was prepared following the general procedure starting from substrate **1b** (0.095 g, 0.36 mmol), ligand **L2** (42.6 mg, 0.12 mmol), and $Ni(cod)_2$ (11.1 mg, 0.039 mmol). It was obtained as colorless liquid (0.050 g, 56% yield, see Figure S35 and Figure S36). ^{1}H

[17] J. W. Park, J. E. Park, J. H. Park, M. R. Hong, S. M. Kim, Y. K. Chung and C. H. Kim, *Synlett*, 2016, **27**, 455.

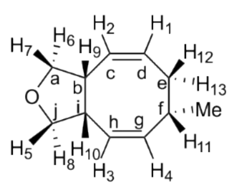
NMR (500 MHz, $CDCl_3$) δ 5.51 (dt, J = 11.0 Hz, J = 5.5 Hz, 2H), 5.39 (dd, J = 11.0 Hz, J = 2.5 Hz, 2H), 3.73 (s, 6H), 3.19 (bs, 2H), 2.56 – 2.52 (m, 4H), 2.15 (dd, J = 13.6 Hz, J = 7.5 Hz, 2H), 2.02 – 1.99 (m, 2H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 173.3, 173.0, 131.7, 128.8, 57.8, 52.92, 52.87, 43.4, 41.2, 28.1 ppm. All spectroscopic data were consistent with those previously reported in the literature.[17]



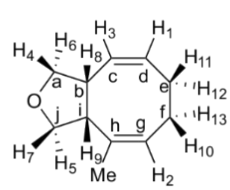
cis-**2c**

Product *cis*-**2c** was prepared following the general procedure starting from substrate **1c** (0.103 g, 0.34 mmol), ligand **L2** (40.2 mg, 0.11 mmol), and $Ni(cod)_2$ (10.5 mg, 0.037 mmol). It was obtained as a white solid (0.041 g, 40% yield, see Figure S37 and Figure S38). ^1H NMR (500 MHz, $CDCl_3$) δ 7.73 (d, J = 8.2 Hz, 2H), 7.32 (d, J = 8.0 Hz, 2H), 5.49 (dt, J = 11.3 Hz, J = 5.6 Hz, 2H),5.09 (dd, J = 11.2 Hz, J = 2.3 Hz, 2H), 3.49 (dd, J = 9.5 Hz, J = 6.8 Hz, 2H), 3.19 (bs, 2H), 3.11 (dd, J = 9.5 Hz, J = 5.9 Hz, 2H), 2.60 – 2.47 (m, 2H), 2.43 (s, 3H), 2.05 – 1.97 (m, 2H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 143.5, 134.3, 129.9, 129.8, 128.2, 127.6, 53.6, 42.6, 28.0, 21.7 ppm. All spectroscopic data were consistent with those previously reported in the literature.[17]

Product *cis*-**2d** was prepared following the general procedure starting from substrate **1d** (0.062 g, 0.38 mmol), ligand **L2** (28.5 mg, 0.079 mmol), and $Ni(cod)_2$ (10.5 mg, 0.038 mmol). It was obtained as colorless liquid (8.2 mg, 13% yield, see Figure S39 to Figure S41). ^1H NMR (800 MHz, $CDCl_3$) δ 5.61 – 5.56 (m, 1H, H_1), 5.36 (ddd, $^3J_{H2-H1}$ = 11.3 Hz, $^3J_{H2-H9}$ = 6.1 Hz, $^4J_{H2-H12}$ = 2.6 Hz, 1H, H_2), 5.33 (dd, $^3J_{H3-H4}$ = 10.7 Hz, $^3J_{H3-H10}$ = 2.5 Hz, 1H, H_3), 5.29 (ddd, $^3J_{H4-H3}$ = 10.7 Hz, $^3J_{H4-H11}$ = 7.3 Hz, $^4J_{H4-H10}$ = 2.5 Hz, 1H, H_4), 4.03 (dd, $^2J_{H5-H8}$ = $^3J_{H5-H10}$ = 7.9 Hz, 1H, H_5), 4.00 (dd, $^2J_{H6-H7}$ = 8.2 Hz, $^3J_{H6-H9}$ = 6.2 Hz, 1H, H_6), 3.69 (dd, $^2J_{H7-H6}$ = 8.3 Hz, $^3J_{H7-H9}$ = 4.0 Hz, 1H, H_7), 3.50 (dd, $^2J_{H8-H5}$ = 8.9 Hz, $^3J_{H8-H10}$ = 8.0 Hz, 1H, H_8), 3.36 (bs, 1H, H_9), 3.25 (ddddd, $^3J_{H10-H9}$ = $^3J_{H10-H8}$ = $^3J_{H10-H5}$ = 8.0 Hz, $^3J_{H10-H3}$ = 2.9 Hz, $^4J_{H10-H4}$ = 2.5 Hz, 1H, H_{10}), 3.02 – 2.97 (m, 1H, H_{11}), 2.60 – 2.55 (m, 1H, H_{12} or H_{13}), 1.82 – 1.80 (m, 1H, H_{12} or H_{13}), 1.04 (d, $^3J_{Me-H11}$ = 6.6 Hz, 3H,) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 136.6 (CH=, C_g), 129.85 (CH=, C_c and C_d), 129.76 (CH=, C_c and C_d), 126.3 (CH=, C_h), 75.0 (CH_2, C_a), 73.2 (CH_2, C_j), 44.4 (CH, C_i), 43.4 (CH, C_b), 37.5 (CH_2, C_e), 33.1 (CH, C_f), 22.0 (Me) ppm. HRMS ($APCI^+$): m/z calcd for $C_{11}H_{17}O$ $[M+H]^+$ 165.1274, found 165.1272.

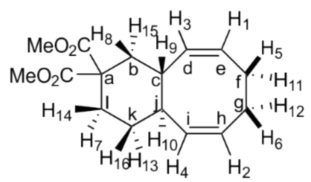


cis-**2d**



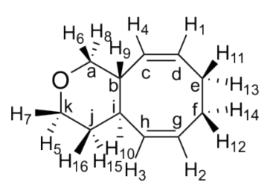
cis-**2f**

Product *cis*-**2f** was prepared following the general procedure starting from substrate **1f** (0.115 g, 0.70 mmol), ligand **L2** (52.7 mg, 0.14 mmol), and $Ni(cod)_2$ (19.6 mg, 0.070 mmol). It was obtained as colorless liquid (0.039 g, 35% yield, see Figure S42 to Figure S44). ^1H NMR (800 MHz, $CDCl_3$) δ 5.56 – 5.53 (m, 1H, H_1), 5.39 (tq, 1H, $^3J_{H2-H10}$ = $^3J_{H2-H13}$ = 8.8 Hz, $^4J_{H2-Me}$ = 1.3 Hz, H_2), 5.36 (ddd, $^3J_{H3-H1}$ = 11.1 Hz, $^3J_{H3-H8}$ = 6.9 Hz, $^4J_{H3-H11}$ = 2.9 Hz, H_3), 4.04 (dd, $^2J_{H4-H6}$ = 8.2 Hz, $^3J_{H4-H8}$ = 5.8 Hz, 1H, H_4), 4.03 (dd, $^2J_{H5-H7}$ = $^3J_{H5-H9}$ = 7.8 Hz, 1H, H_5), 3.73 (dd, $^2J_{H4-H6}$ = 8.2 Hz, $^3J_{H6-H8}$ = 3.1 Hz, 1H, H_6), 3.64 (dd, $^3J_{H7-H9}$ = 10.2 Hz, $^2J_{H5-H7}$ = 7.9 Hz, 1H, H_7), 3.53 (bs, 1H, H_8), 3.19 (ddd, $^3J_{H9-H7}$ = 10.2 Hz $^3J_{H9-H8}$ = 8.4 Hz $^3J_{H9-H5}$ = 7.8 Hz, 1H, H_9), 2.70 – 2.65 (m, 1H, H_{10}), 2.51 – 2.47 (m, 1H, H_{11} or H_{12}), 2.09 – 2.04 (m, 1H, H_{11} or H_{12}), 1.97 – 1.94 (m, 1H, H_{13}), 1.67 (s, 3H,) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 134.9 (C=, C_h), 129.81 (CH=, C_c and C_d), 129.78 (CH=, C_c and C_d), 124.8 (CH=, C_g), 75.4 (CH_2, C_a), 70.8 (CH_2, C_j), 48.3 (CH, C_i), 42.1 (CH, C_b), 29.5 (CH_2, C_e), 26.4 (CH_2, C_f), 23.2 (Me) ppm. HRMS (APCI$^+$): *m/z* calcd for $C_{11}H_{17}O$ [M+H]$^+$ 165.1274, found 165.1272.



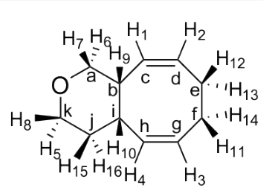
trans-**2g**

Product *trans*-**2g** was prepared following the general procedure starting from substrate **1g** (0.151 g, 0.514 mmol), ligand **L2** (38.8 mg, 0.11 mmol), and Ni(cod)$_2$ (14.4 mg, 0.05 mmol). It was obtained as a white solid (0.101 g, 67% yield, > 95% purity, see Figure S45 and Figure S46). M.p. = 85.6-87.9 ºC. ^1H NMR (400 MHz, $CDCl_3$) δ 5.56 – 5.44 (m, 2H, H_1-H_2), 5.38 – 5.29 (m, 2H, H_3-H_4), 3.76 (s, 3H, Me), 3.70 (s, 3H, Me), 2.50 – 2.37 (m, 6H, H_5-H_{10}), 2.25 – 2.16 (m, 6H, H_{11}-H_{12}), 1.84 (dq, $^2J_{H13\text{-}H6}$ = 13.6 Hz, $^3J_{H13\text{-}H7}$ = $^3J_{H13\text{-}H14}$ = $^3J_{H13\text{-}H10}$ = 3.4 Hz, 1H, H_{13}), 1.71 (dt, $^2J_{H14\text{-}H7}$ = 13.6 Hz, $^3J_{H14\text{-}H13}$ = $^3J_{H14\text{-}H16}$ = 3.9 Hz, 1H, H_{14}), 1.51 (dd, $^2J_{H15\text{-}H8}$ = 13.5 Hz, $^3J_{H15\text{-}H9}$ = 11.8 Hz, 1H, H_{15}), 1.26 – 1.16 (m, 1H, H_{16}) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 172.8 (C=O), 171.6 (C=O), 133.8 (CH=, C_d or C_i), 133.4 (CH=, C_d or C_i), 127.4 (CH=, C_e or C_h), 127.1 (CH=, C_e or C_h), 55.3 (C_q, C_a), 52.8 (Me), 52.7 (Me), 42.7 (CH, C_j), 40.2 (CH, C_c), 38.9 (CH_2, C_b), 31.4 (CH_2, C_l), 30.6 (CH_2, C_k), 28.1 (CH_2, C_f or C_g), 27.8 (CH_2, C_f or C_g) ppm. HRMS (ESI$^+$): *m/z* calcd for $C_{16}H_{22}O_4Na$ [M+Na]$^+$ 301.1410, found 301.1417.



trans-**2h**

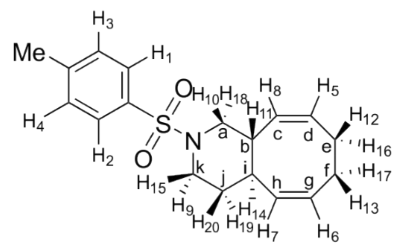
Product *trans*-**2h** was prepared following the general procedure starting from substrate **1h** (0.054 g, 0.310 mmol), ligand **L2** (23.4 mg, 0.065 mmol), and Ni(cod)$_2$ (8.7 mg, 0.031 mmol). It was obtained as colorless liquid (0.033 g, 61% yield, > 95% purity, see Figure S47 and Figure S48). ^1H NMR (400 MHz, $CDCl_3$) δ 5.63 – 5.56 (m, 1H, H_1), 5.55 – 5.48 (m, 1H, H_2), 5.38 – 5.33 (m, 1H, H_3), 5.21 – 5.17 (m, 1H, H_4), 4.01 – 3.93 (m, 2H, H_5-H_6), 3.44 – 3.37 (m, 1H, H_7), 3.06 (dd, $^2J_{H8\text{-}H6}$ = $^3J_{H8\text{-}H9}$ = 10.8 Hz, 1H, H_8), 2.70 – 2.62 (m, 1H, H_9), 2.60 – 2.50 (m, 3H, H_{10}, H_{11} or H_{13}, and H_{12} or H_{14}), 2.29 – 2.20 (m, 2H, H_{11} or H_{13}, and H_{12} or H_{14}), 1.75 – 1.70 (m, 1H, H_{15}), 1.51 – 1.40 (m, 1H, H_{16}) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 133.4 (CH=, C_h), 129.6 (CH=, C_d), 128.7 (CH=, C_c), 127.4 (CH=, C_g), 72.9 (CH_2, C_a), 68.4 (CH_2, C_k), 43.2 (CH, C_b), 41.7 (CH, C_i), 33.8 (CH_2, C_j), 28.2 (CH_2, C_e or C_f), 27.9 (CH_2, C_e or C_f) ppm. HRMS (APCI$^+$): *m/z* calcd for $C_{11}H_{17}O$ [M+H]$^+$ 165.1274, found 165.1271.



cis-**2h**

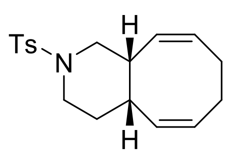
Samples of the product *trans*-**2h** (see Figure S49 and Figure S50) and the product *cis*-**2h** (see Figure S51 and Figure S52) were isolated in an analytically pure form by semi-preparative HPLC using a Daicel Chiralpak® IA column (hexane; 1 mL/min) on a 10 mg scale. Semi-preparative HPLC analysis, Daicel Chiralpak® IA column (25 cm x 0.46 cm), hexane, 1 mL/min, 210 nm, t_R(*cis*-isomer) = 13.5 min, t_R(*trans*-isomer) = 22.6 min. Characterization data for the product *cis*-**2h**: ^1H NMR (500 MHz, $CDCl_3$) δ 5.66 – 5.54 (m, 3H, H_1-H_3), 5.30 – 5.28 (m, 1H, H_4), 3.93 (dt, $^2J_{H5\text{-}H8}$ = 11.3 Hz, $^2J_{H5\text{-}H15}$ = $^3J_{H5\text{-}H16}$ = 4.0 Hz, 1H, H_5), 3.67 (dd, $^2J_{H6\text{-}H7}$ = 11.3 Hz, $^2J_{H6\text{-}H9}$ = 4.0 Hz, 1H, H_6), 3.58 – 3.52 (m, 2H, H_7-H_8), 3.18 (bs, 1H, H_9), 2.86 – 2.75 (m, 2H, H_{10}-H_{11}), 2.56 – 2.53 (m, 1H, H_{12}), 2.14 – 1.98

(m, 2H, H_{13}-H_{14}), 1.64 – 1.46 (m, 2H, H_{15}-H_{16}) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 133.7 (CH=, C_h), 128.62 (CH=, C_c), 128.60 (CH=, C_d), 127.8 (CH=, C_g), 70.7 (CH_2, C_a), 67.8 (CH_2, C_k), 39.7 (CH, C_i), 38.9 (CH, C_b), 30.1 (CH_2, C_j), 29.2 (CH_2, C_e), 26.8 (CH_2, C_f) ppm. HRMS (APCI$^+$): *m/z* calcd for $C_{11}H_{17}O$ $[M+H]^+$ 165.1274, found 165.1274.



trans-**2i**

Product *trans*-**2i** was prepared following the general procedure starting from substrate *E*,*E*-**1i** (0.107 g, 0.34 mmol), ligand **L2** (25.5 mg, 0.071 mmol), and Ni(cod)$_2$ (9.5 mg, 0.034 mmol). It was obtained as colorless liquid (0.084 g, 78% yield, see Figure S55 and Figure S56). ^1H NMR (500 MHz, $CDCl_3$) δ 7.66 – 7.64 (m, 2H, H_{arom}, H_1-H_2), 7.34 – 7.32 (m, 2H, H_{arom}, H_3-H_4), 5.60 – 5.55 (m, 1H, H_5), 5.53 – 5.48 (m, 1H, H_6), 5.33 – 5.29 (m, 1H, H_7), 5.25 – 5.22 (m, 1H, H_8), 3.88 – 3.82 (m, 2H, H_9-H_{10}), 2.72 – 2.65 (m, 1H, H_{11}), 2.47 – 2.37 (m, 5H, Me, H_{12} or H_{16}, and H_{13} or H_{17}), 2.27 – 2.17 (m, 4H, H_{14}, H_{15}, H_{12} or H_{16}, and H_{13} or H_{17}), 1.91 (dd, $^2J_{H18\text{-}H10}$ = $^3J_{H18\text{-}H11}$ = 11.3 Hz, 1H, H_{18}), 1.85 – 1.81 (m, 1H, H_{19}), 1.51 – 1.42 (m, 1H, H_{20}) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 143.6 ($C_{q\ arom}$), 133.5 ($C_{q\ arom}$), 132.4 (CH=, C_h), 129.8 (CH_{arom}), 129.5 (CH=, C_d), 129.4 (CH=, C_c), 127.9 (CH=, C_g), 127.8 (CH_{arom}), 51.7 (CH_2, C_a), 46.7 (CH_2, C_k), 42.3 (CH, C_b), 41.8 (CH, C_i), 32.3 (CH_2, C_j), 27.9 (CH_2, C_e or C_f), 27.8 (CH_2, C_e or C_f), 21.7 (CH_3, Me) ppm. HRMS (ESI$^+$): *m/z* calcd for $C_{18}H_{24}NO_2S$ $[M+H]^+$ 318.1522, found 318.1519.



cis-**2i**

Product *cis*-**2i** was prepared following the general procedure starting from substrate *E*,*Z*-**1i** (15.0 mg, 0.0473 mmol), ligand **L2** (3.57 mg, 0.0099 mmol), and Ni(cod)$_2$ (1.33 mg, 0.0047 mmol). It was obtained as colorless liquid (8.3 mg, 55% yield, see Figure S57 and Figure S58). ^1H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.62 (m, 2H), 7.33 – 7.31 (m, 2H), 5.61 – 5.51 (m, 3H), 5.20 – 5.16 (m, 1H), 3.52 – 3.47 (m, 1H), 3.31 – 3.25 (m, 2H), 2.74 – 2.52 (m, 5H), 2.43 (s, 3H), 2.14 – 1.97 (m, 2H), 1.67 – 1.58 (m, 2H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 143.5, 133.4, 132.1, 129.8, 128.9, 128.3, 128.2, 127.8, 49.7, 45.6, 39.6, 37.8, 29.1, 29.0, 26.9, 21.7 ppm. All spectroscopic data were consistent with those previously reported in the literature.[17]

1.6. Single Crystal X-Ray Structure Determinations

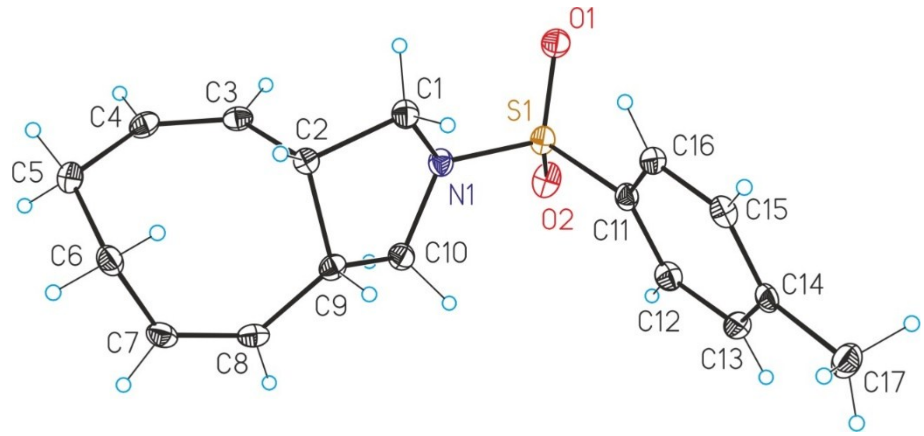


Figure S1. ORTEP drawing (thermal ellipsoids drawn at a 50 % probability level) showing the structure of product *cis*-**2c**.

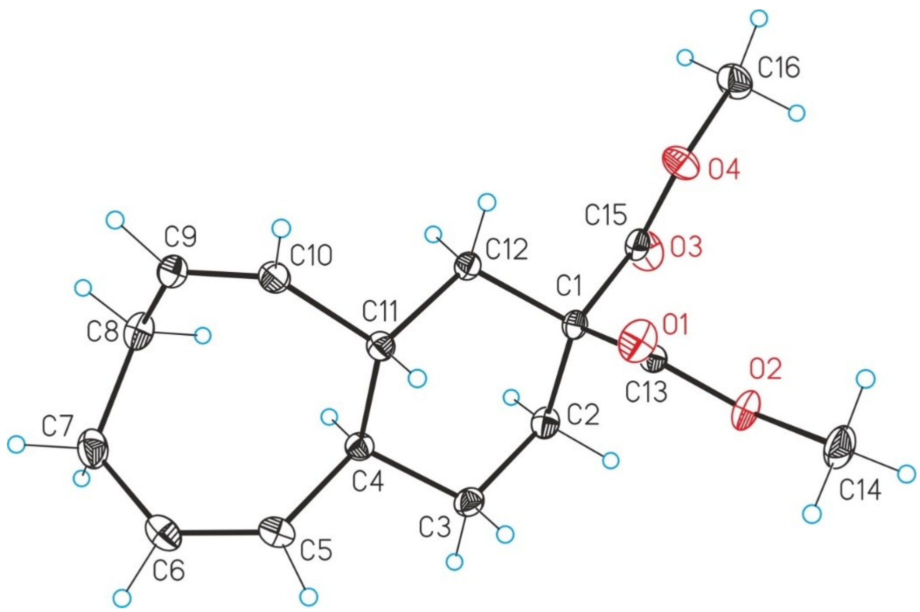


Figure S2. ORTEP drawing (thermal ellipsoids drawn at a 50 % probability level) showing the structure of product *trans*-**2g**.

Crystal preparation: Crystals of products *cis*-**2c** and *trans*-**2g** were grown by slow diffusion in hexane/acetone (80:20, v/v). The crystals for these samples were selected using a Zeiss stereomicroscope using polarized light and prepared under inert conditions immersed in perfluoropolyether as protecting oil for manipulation.

Data collection: Crystal structure determination for product *trans*-**2g** was carried out using a Apex DUO Kappa 4-axis goniometer equipped with an APPEX 2 4K CCD area detector, a Microfocus Source E025 IμS using MoK_{α} radiation, Quazar MX multilayer Optics as monochromator and an Oxford Cryosystems low temperature device Cryostream 700 plus (T = –173 °C). Crystal structure determination for product *cis*-**2c** was carried out using a Rigaku diffractometer equipped with a Pilatus 200K area detector, a Rigaku MicroMax-007HF microfocus rotating anode with MoK_α radiation, Confocal Max Flux optics and an Oxford Cryosystems low temperature device Cryostream 700 plus (T = –173 °C). Full-sphere data collection was used with ω and φ scans. *Programs used:* Bruker Device: Data collection APEX-2,[18] data reduction Bruker Saint[19] V/.60A and absorption correction SADABS.[20] Rigaku device: Data collection and reduction with CrysAlisPro[21] and absorption correction with Scale3 Abspack scaling algorithm.[22]

Structure Solution and Refinement: Crystal structure solution was achieved using the computer program SHELXT[23]. Visualization was performed with the program SHELXle.[24] Missing atoms were subsequently located from difference Fourier synthesis and added to the atom list. Least-squares refinement on F^2 using all measured intensities was carried out using the program SHELXL 2015.[25] All non-hydrogen atoms were refined including anisotropic displacement parameters. CCDC 1834976 and 1834977 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

[18] Data collection with APEX II version v2013.4-1. Bruker (2007). Bruker AXS Inc., Madison, Wisconsin, USA.
[19] Data reduction with Bruker SAINT version V8.30c. Bruker (2007). Bruker AXS Inc., Madison, Wisconsin, USA.
[20] SADABS: V2012/1 Bruker (2001). Bruker AXS Inc., Madison, Wisconsin, USA. See the following reference: R. H. Blessing, *Acta Crystallogr.* 1995, **A51**, 33-38.
[21] Data collection and reduction with CrysAlisPro 1.171.39.12b (Rigaku OD, 2015).
[22] Empirical absorption correction using spherical harmonics implemented in Scale3 Abspack scaling algorithm, CrysAlisPro 1.171.38.37f (Rigaku OD, 2015).
[23] SHELXT; V2014/4 (Sheldrick 2014). See the following reference: G. M. Sheldrick, *Acta Cryst.* 2008, **A64**, 112.
[24] SHELXle. See the following reference: C. B. Huebschle, G. M. Sheldrick and B. Dittrich, *J. Appl. Crystallogr.* 2011, **44**, 1281.
[25] SHELXL; SHELXL-2014/7 (Sheldrick 2014). See the following reference: G. M. Sheldrick, *Acta Crystallogr. C* 2015, **C71**, 3.

1.7. Theoretical methods

The energies of all complexes included in this study were computed at the B level of theory. The calculations have been performed by using the program TURBOMOLE version 7.0.[26] For the calculations we have used the DFT-D functional with the latest available correction for dispersion (D3).[27] TS structures were characterized by means of frequency analysis calculations at the BP86-D3/def2-TZVP level of theory. In order to reproduce solvent effects, we have used the conductor-like screening model COSMO,[28] which is a variant of the dielectric continuum solvation models.[29] We have used toluene as solvent. In order to give reliability to the results obtained using the BP86 method we have performed single point calculations at the MP2/def2-TZVP level of theory using toluene as a solvent.

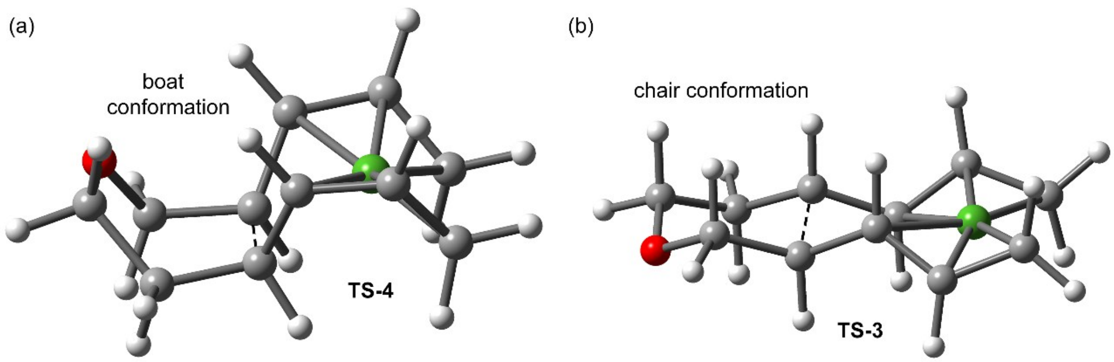


Figure S3. Optimized structures in boat (a) and chair (b) conformations of **TS**-**4** and **TS**-**3**, respectively.

[26] R. Ahlrichs, M. Baer, M. Haeser, H. Horn and C. Koelmel, *Chem. Phys. Lett.*, 1989, **162**, 165.
[27] S. Grimme, J. Antony, S. Ehrlich and H. Krieg, *J. Chem. Phys.* 2010, **132**, 154104.
[28] A. Klamt and G. Schueuermann, *J. Chem. Soc., Perkin Trans. 2*, 1993, 799.
[29] A. Klamt, *WIREs Comput. Mol. Sci.*, 2011, **1**, 699.

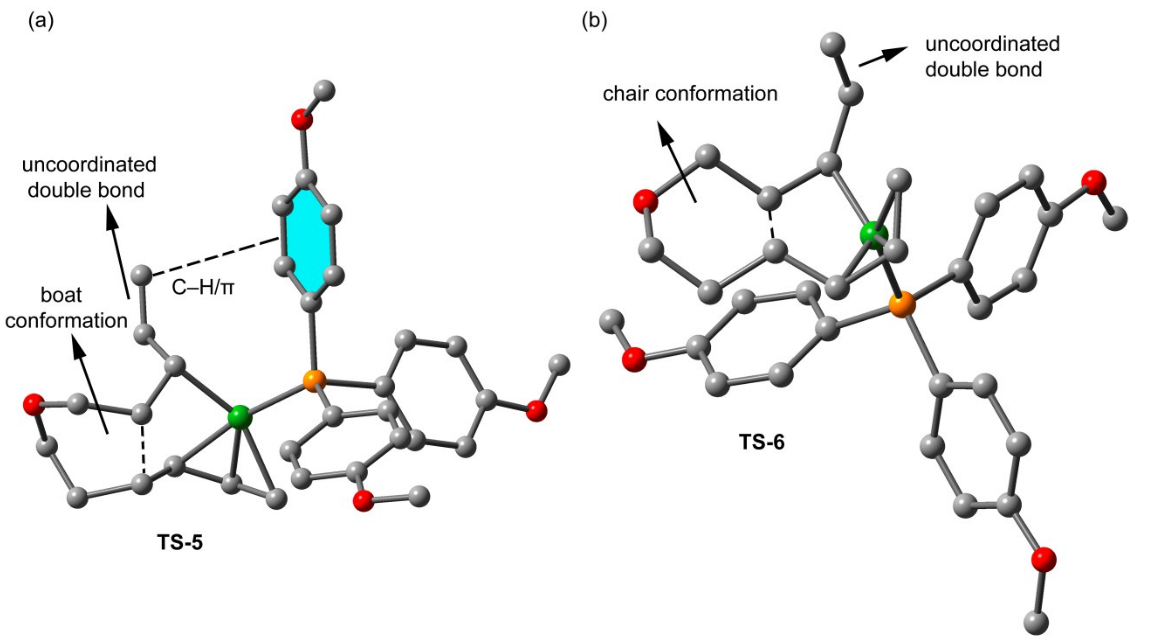


Figure S4. Optimized structures from in boat (a) and chair (b) conformations of **TS**-**5** and **TS**-**6**, respectively.

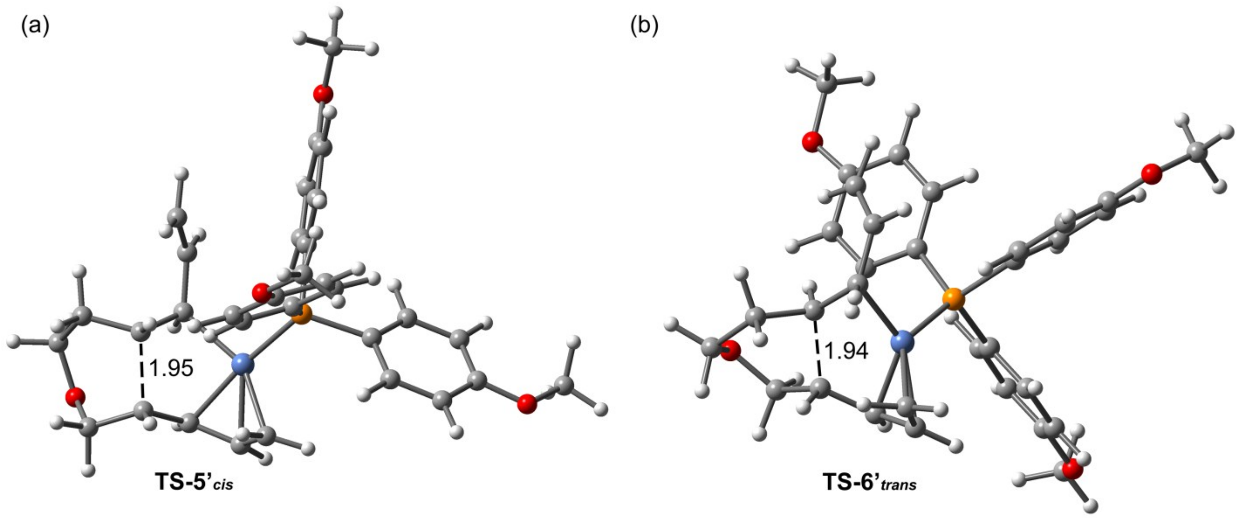


Figure S5. Optimized structures of **TS-5'**$_{cis}$ (a) and **TS-6'**$_{trans}$ (b) yielding to compounds *E*,*E*-**6h**-π,π-*cis* and *E*,*E*-**6h**-π,π-*trans*, respectively with the **L2** coordinated to the Ni metal center.

1.8. Copies of NMR Spectra

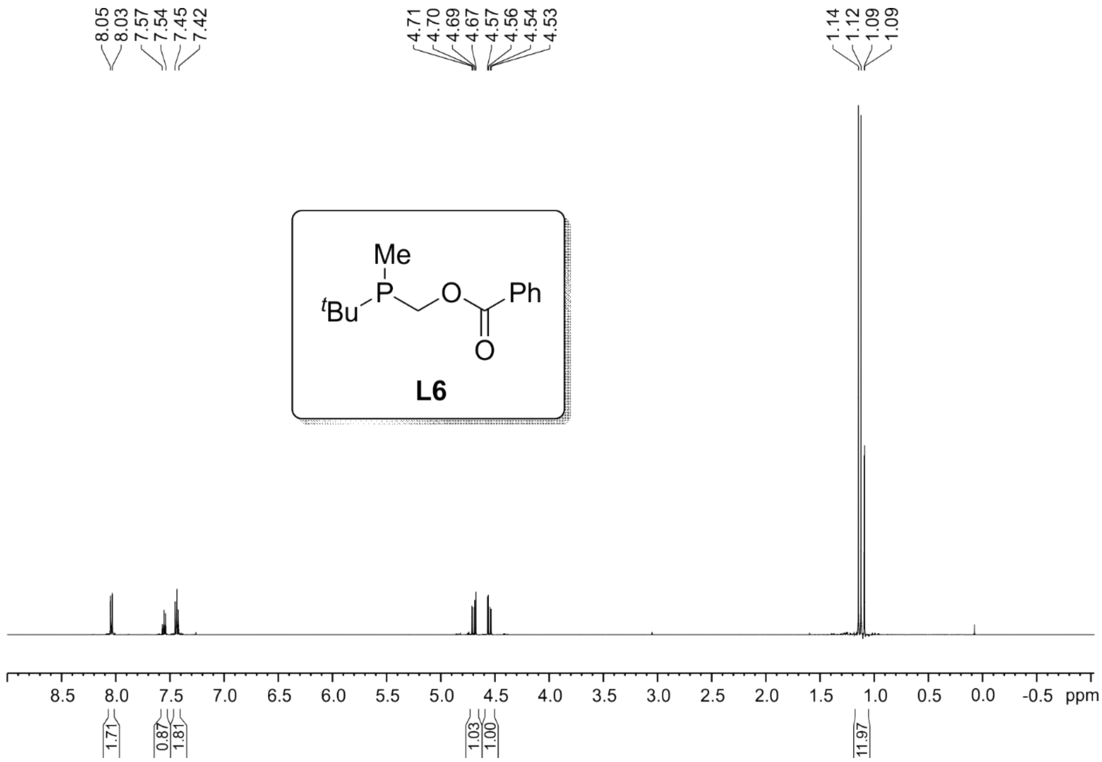


Figure S6. ^{1}H NMR spectrum for ligand **L6**

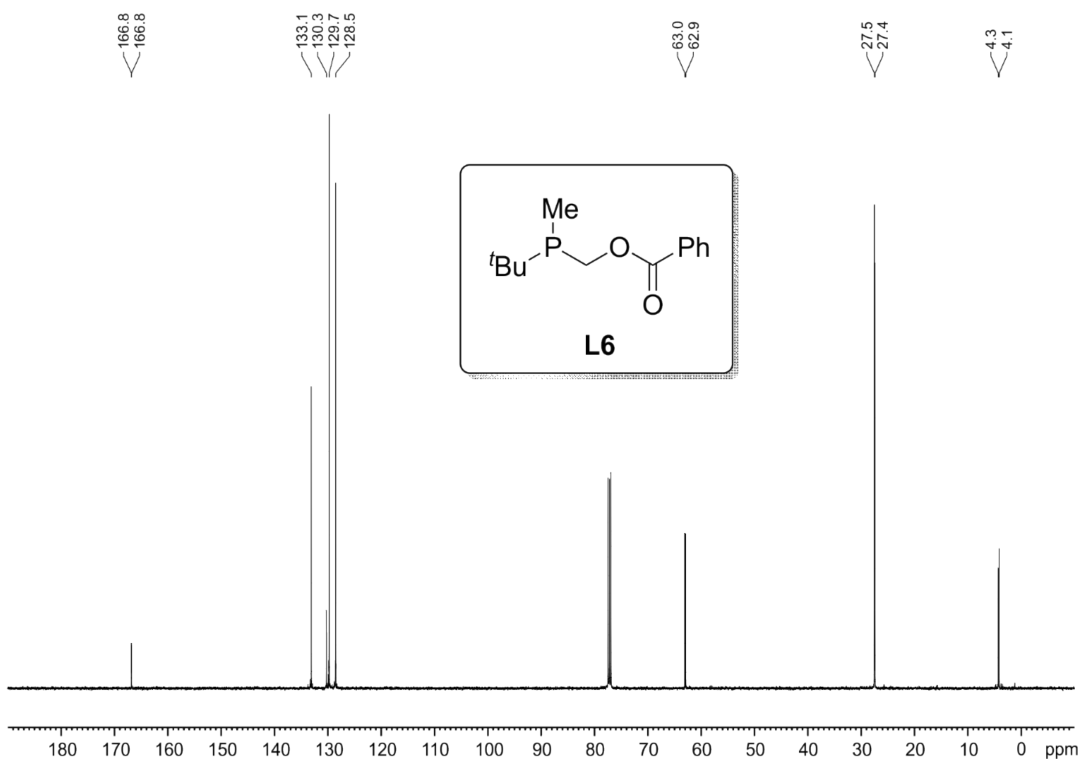


Figure S7. ^{13}C{^{1}H} NMR spectrum for ligand **L6**

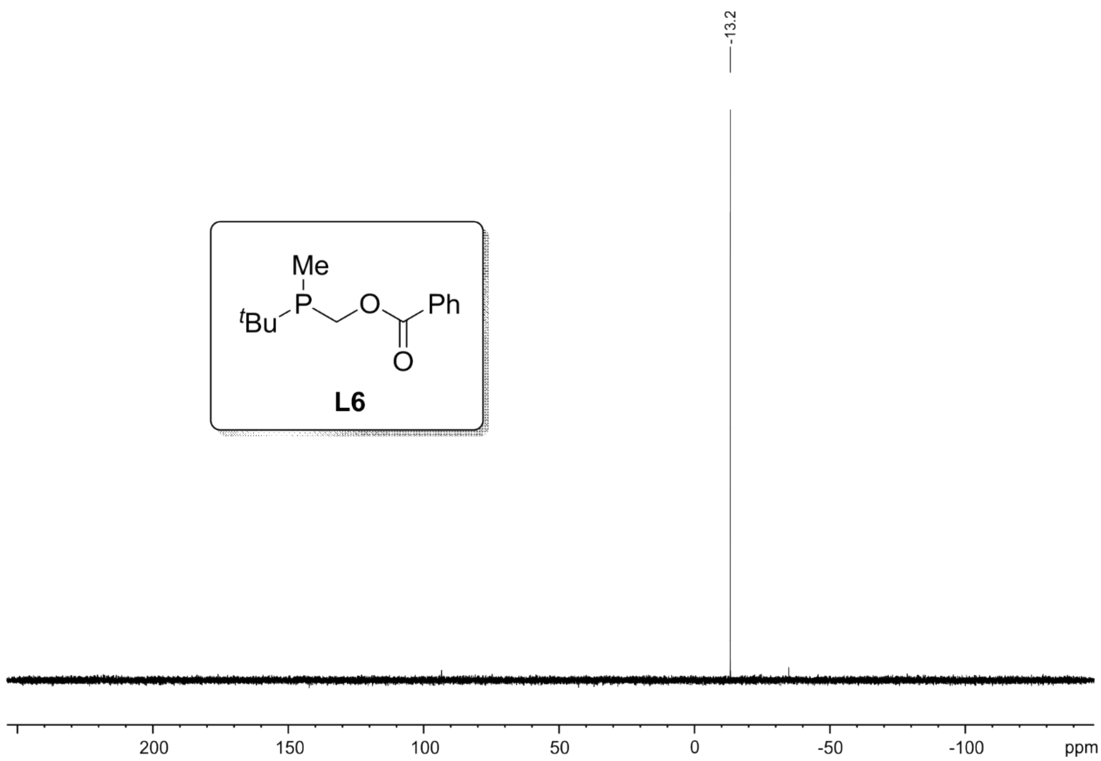


Figure S8. $^{31}P\{^{1}H\}$ NMR spectrum for ligand **L6**

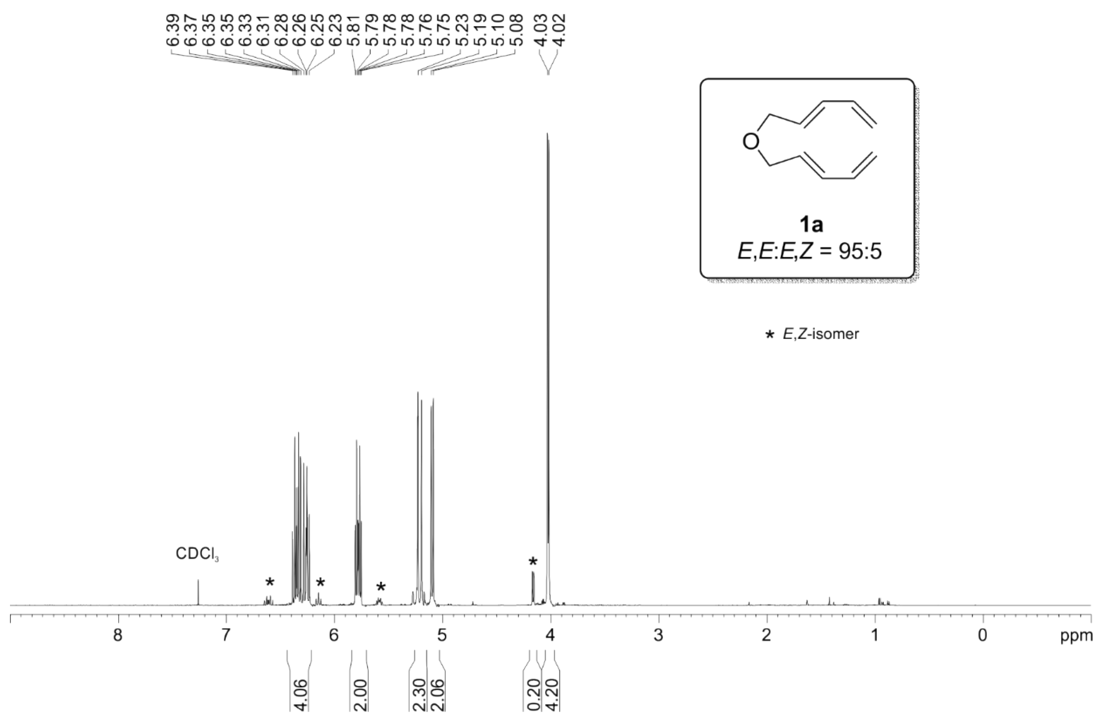


Figure S9. ^{1}H NMR spectrum for substrate **1a**

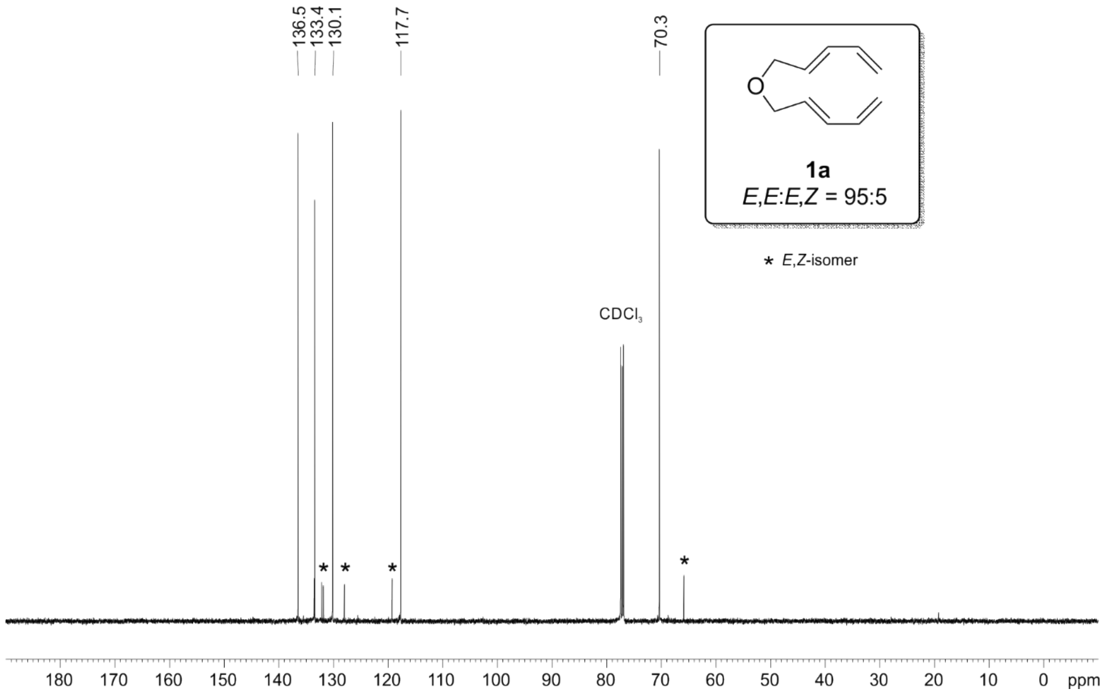


Figure S10. $^{13}C\{^1H\}$ NMR spectrum for substrate **1a**

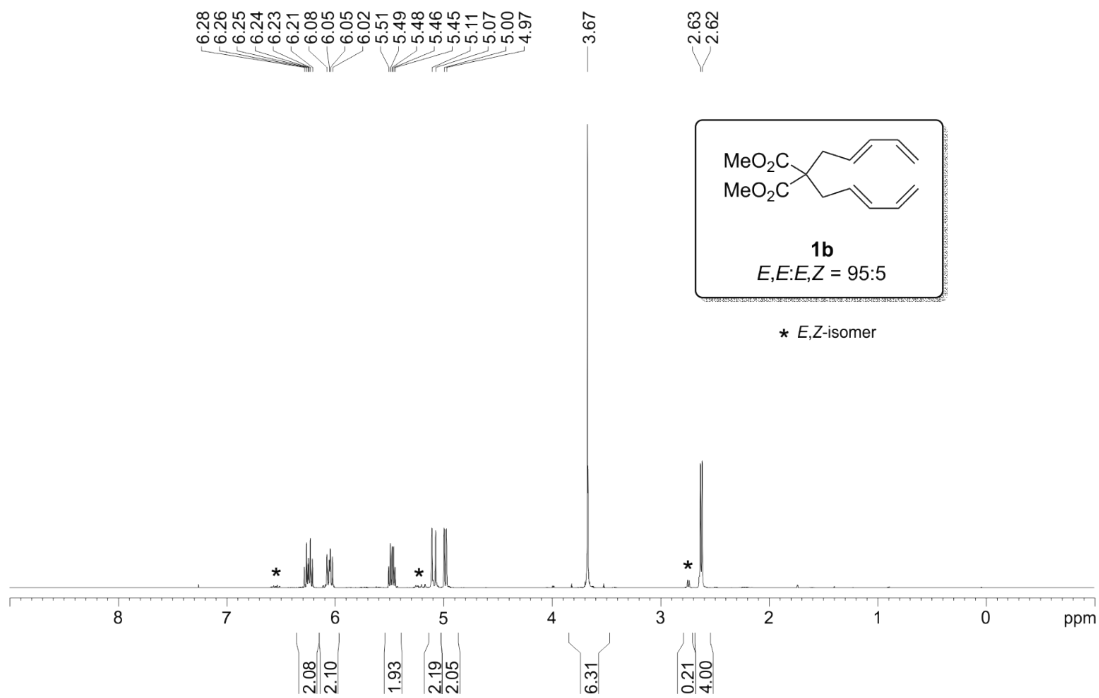


Figure S11. ^1H NMR spectrum for substrate **1b**

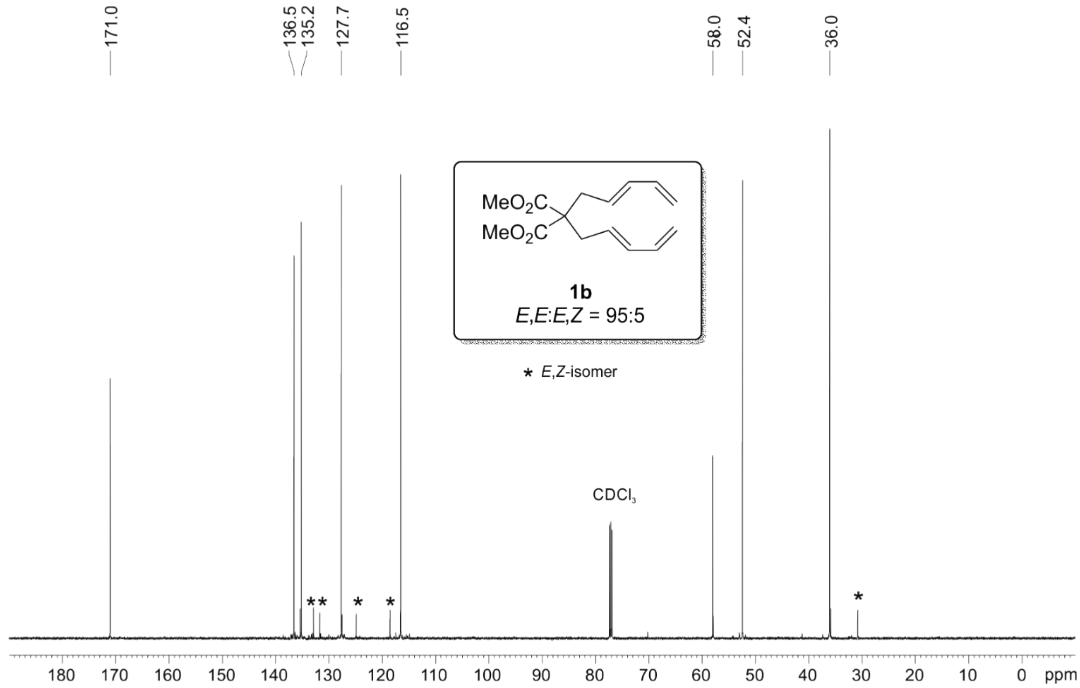


Figure S12. $^{13}C\{^{1}H\}$ NMR spectrum for substrate **1b**

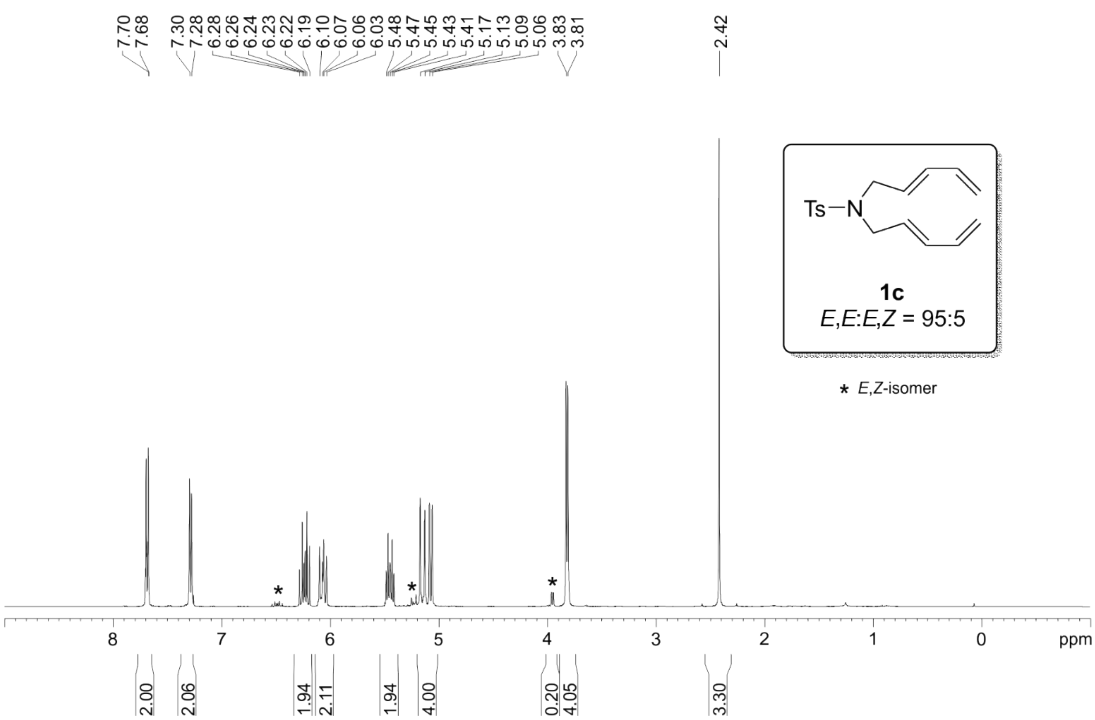


Figure S13. ^{1}H NMR spectrum for substrate **1c**

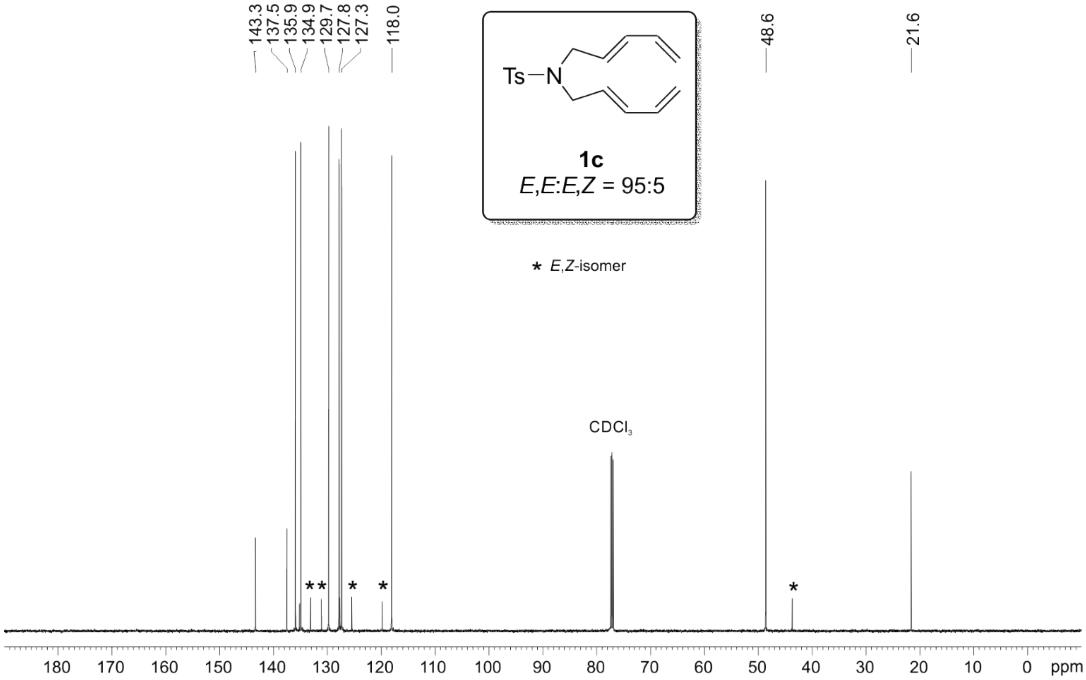


Figure S14. $^{13}C\{^{1}H\}$ NMR spectrum for substrate **1c**

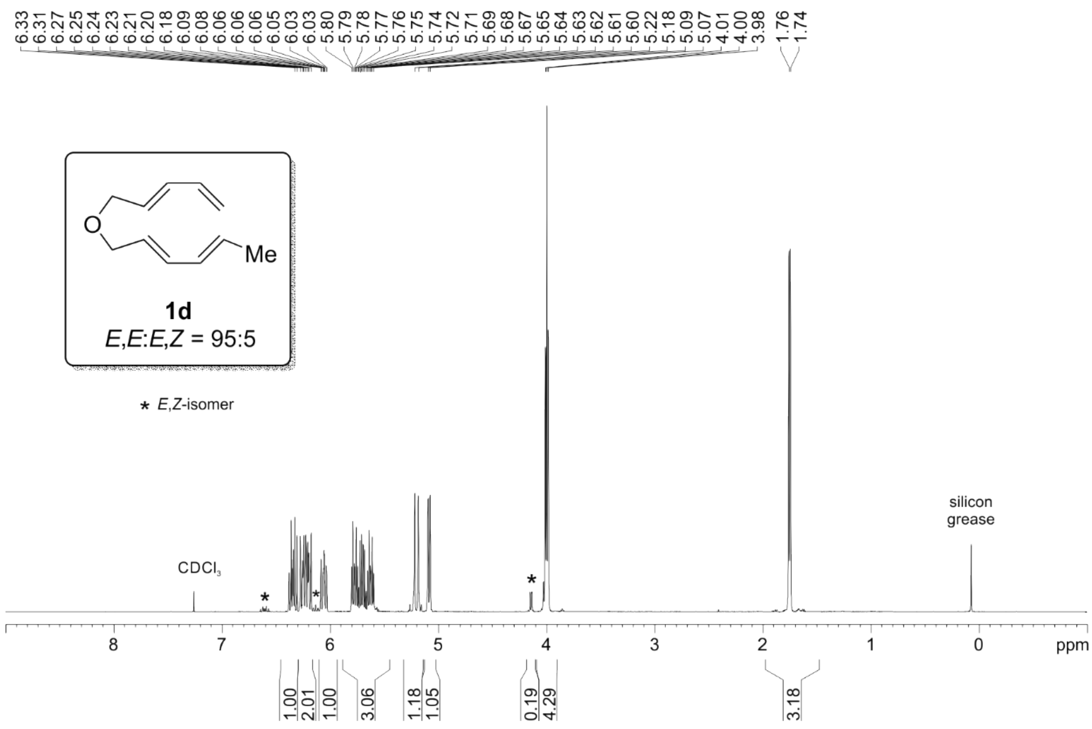


Figure S15. ^{1}H NMR spectrum for substrate **1d**

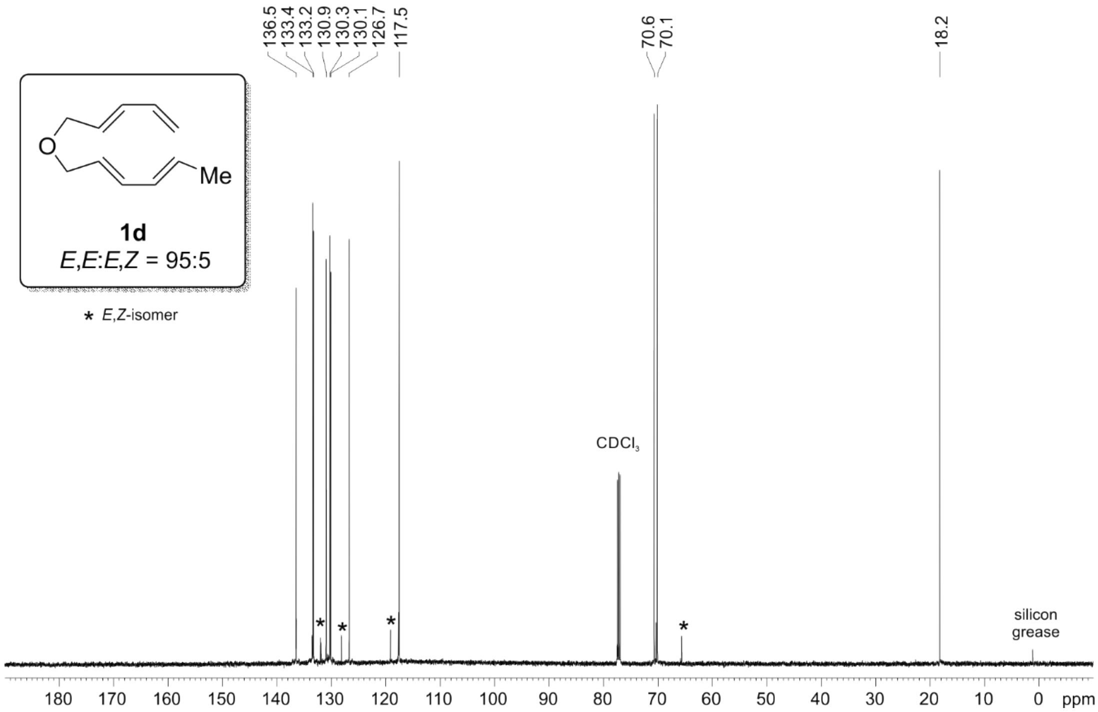


Figure S16. $^{13}C\{^{1}H\}$ NMR spectrum for substrate **1d**

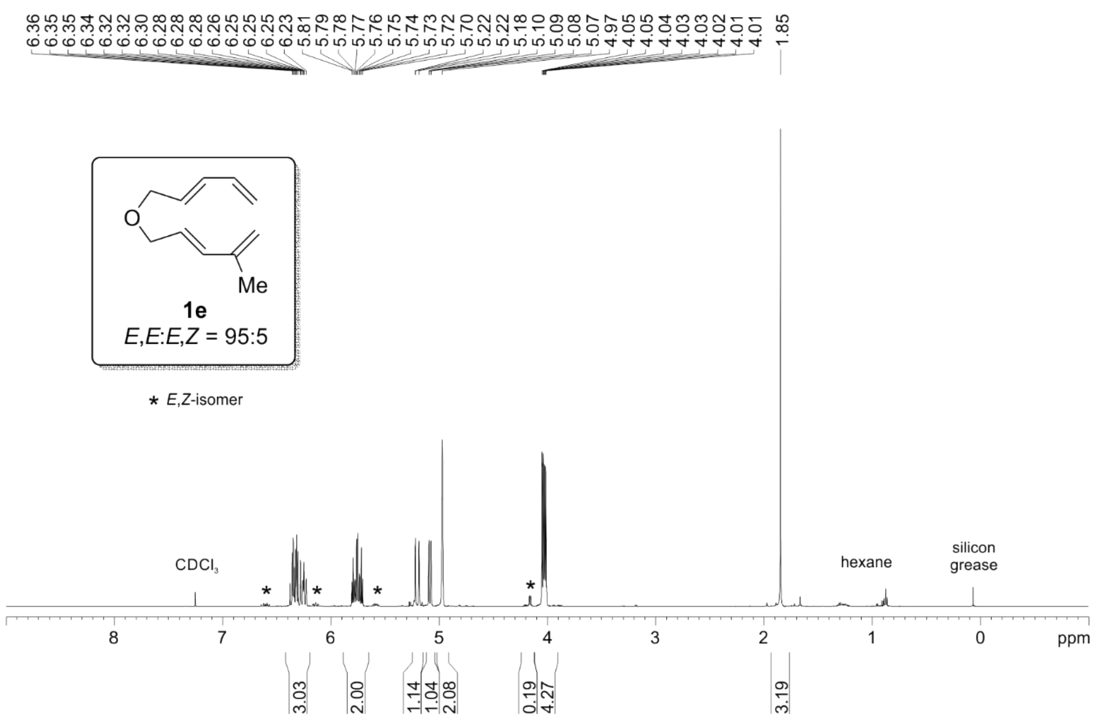


Figure S17. ^{1}H NMR spectrum for substrate **1e**

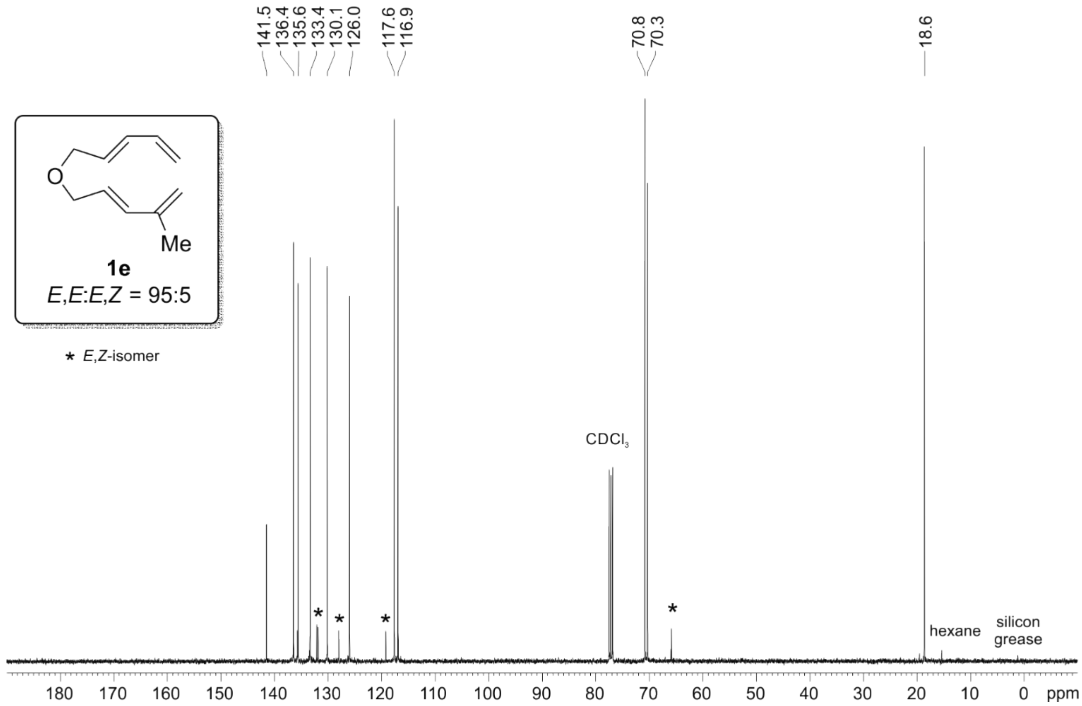


Figure S18. $^{13}C\{^{1}H\}$ NMR spectrum for substrate **1e**

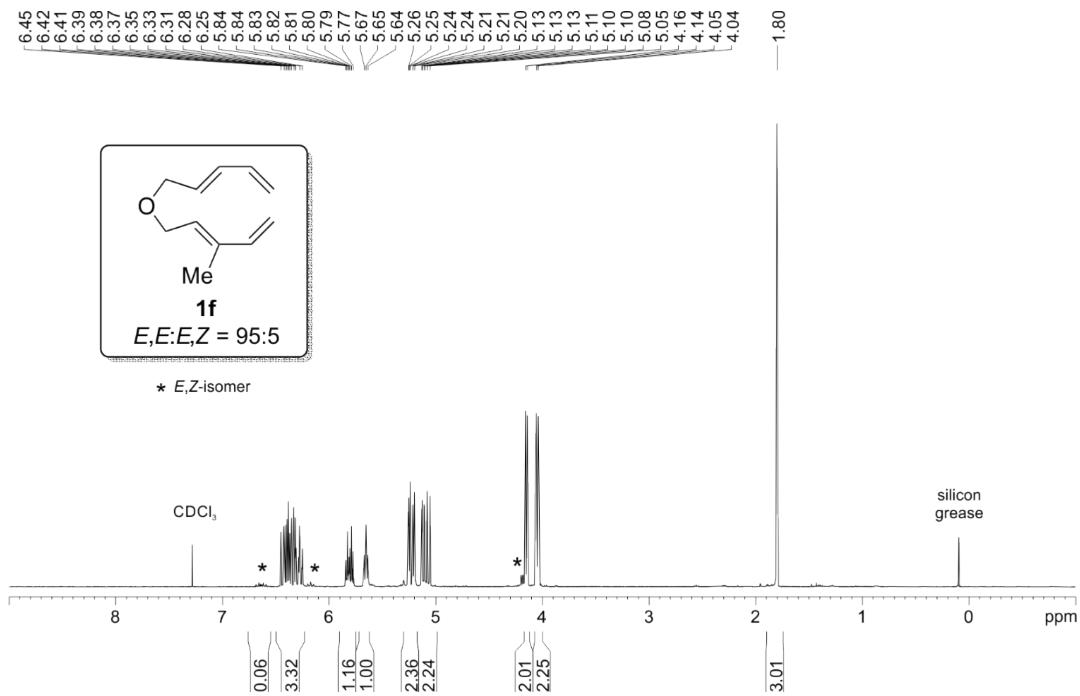


Figure S19. ^{1}H NMR spectrum for substrate **1f**

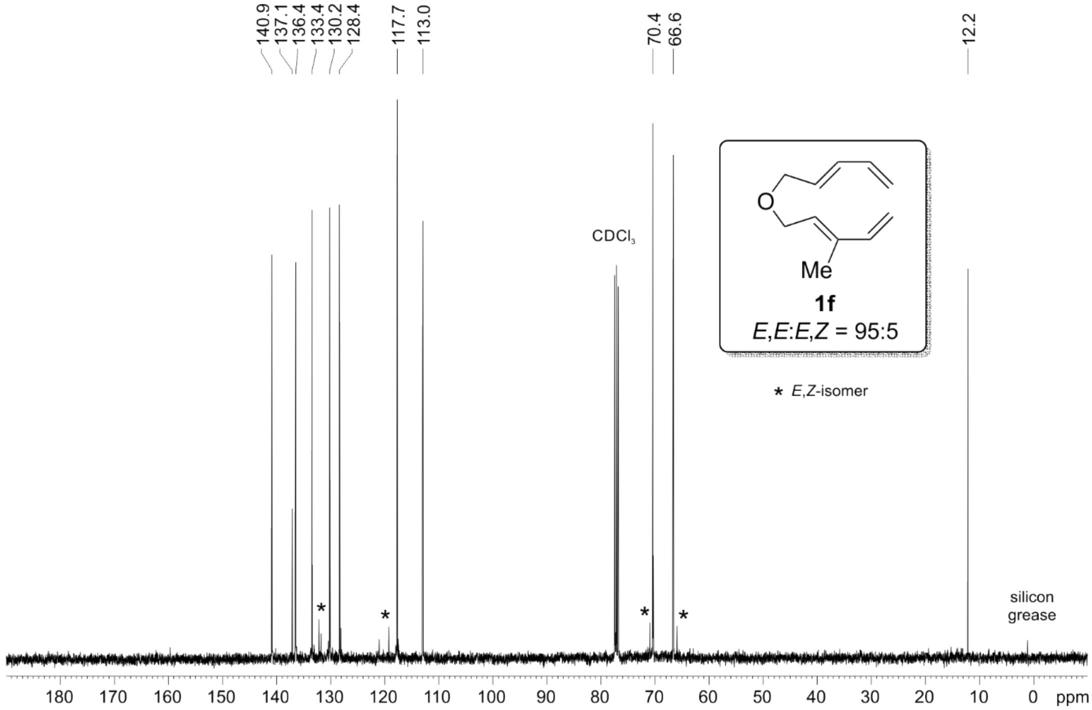


Figure S20. $^{13}C\{^{1}H\}$ NMR spectrum for substrate **1f**

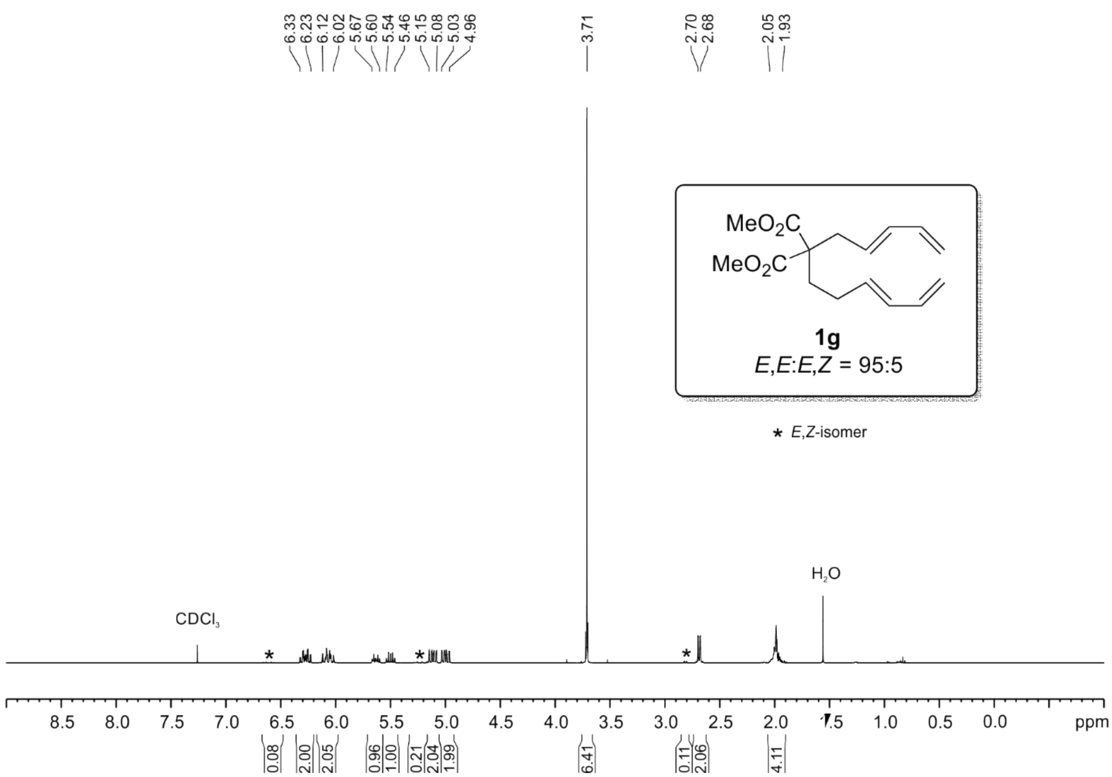


Figure S21. ^{1}H NMR spectrum for substrate **1g**

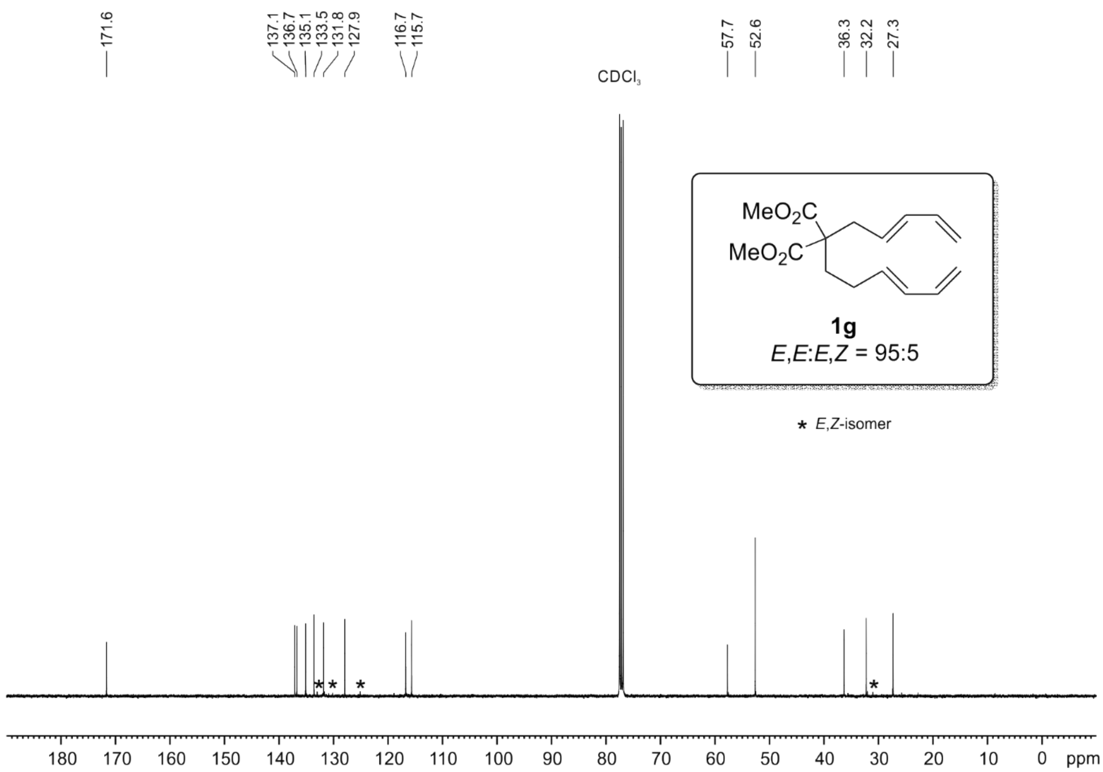


Figure S22. $^{13}C\{^{1}H\}$ NMR spectrum for substrate **1g**

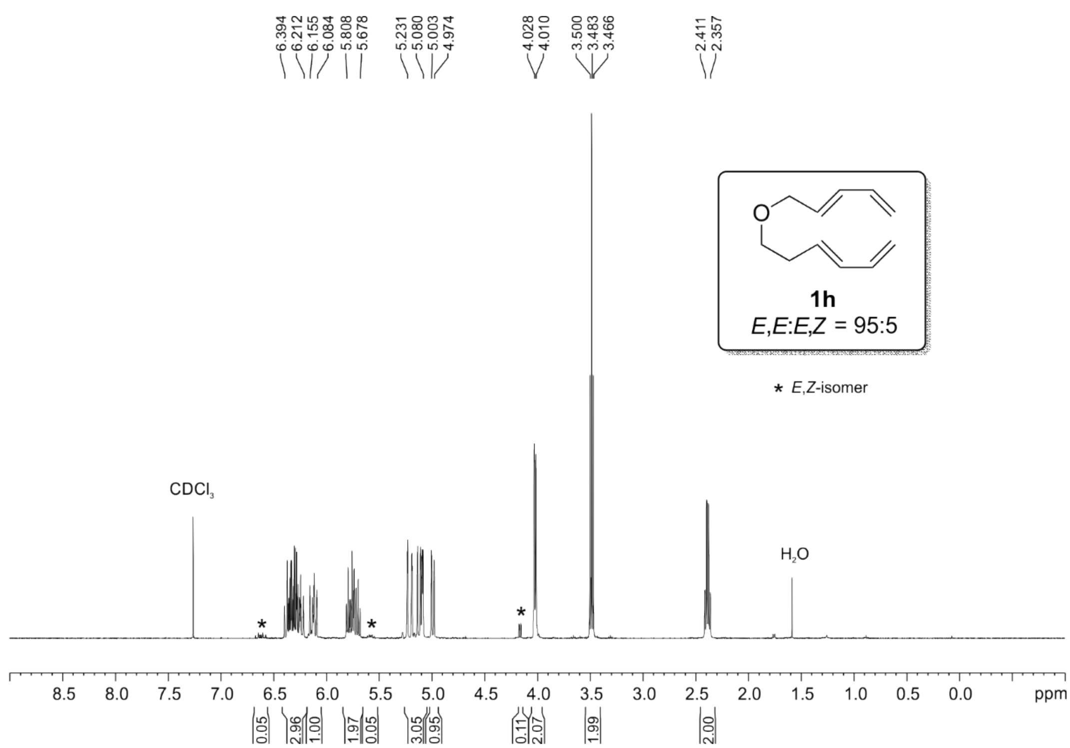


Figure S23. ^{1}H NMR spectrum for substrate **1h**

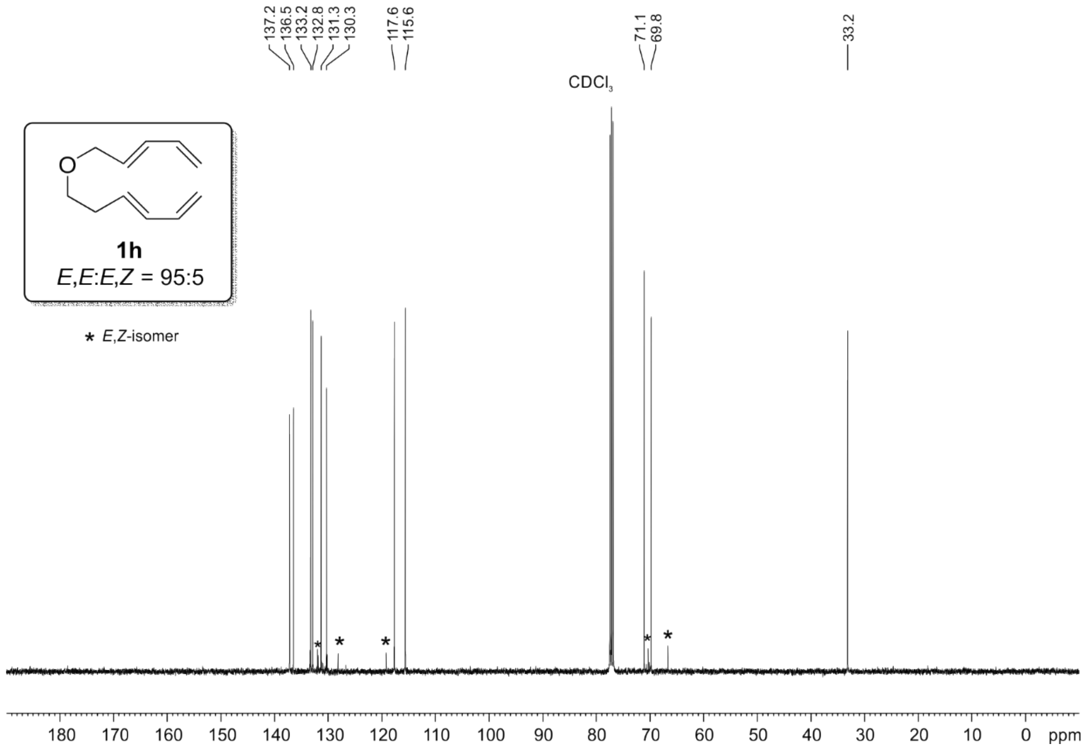


Figure S24. $^{13}C\{^{1}H\}$ NMR spectrum for substrate **1h**

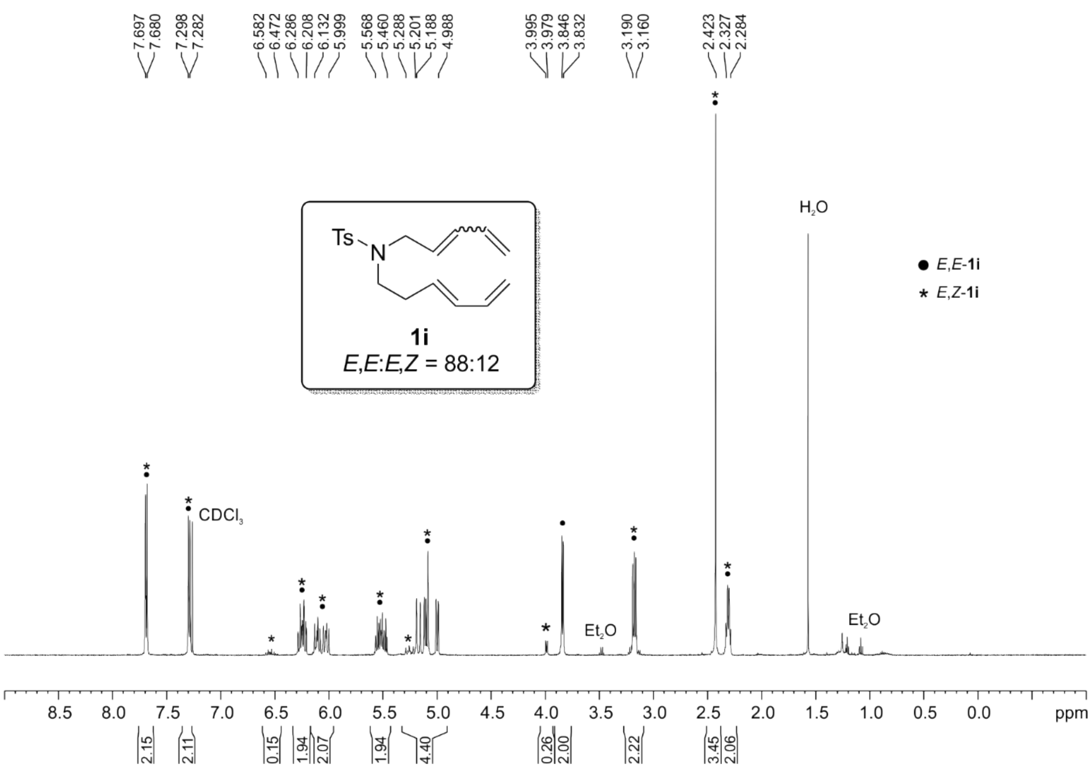


Figure S25. ^{1}H NMR spectrum for substrate **1i**

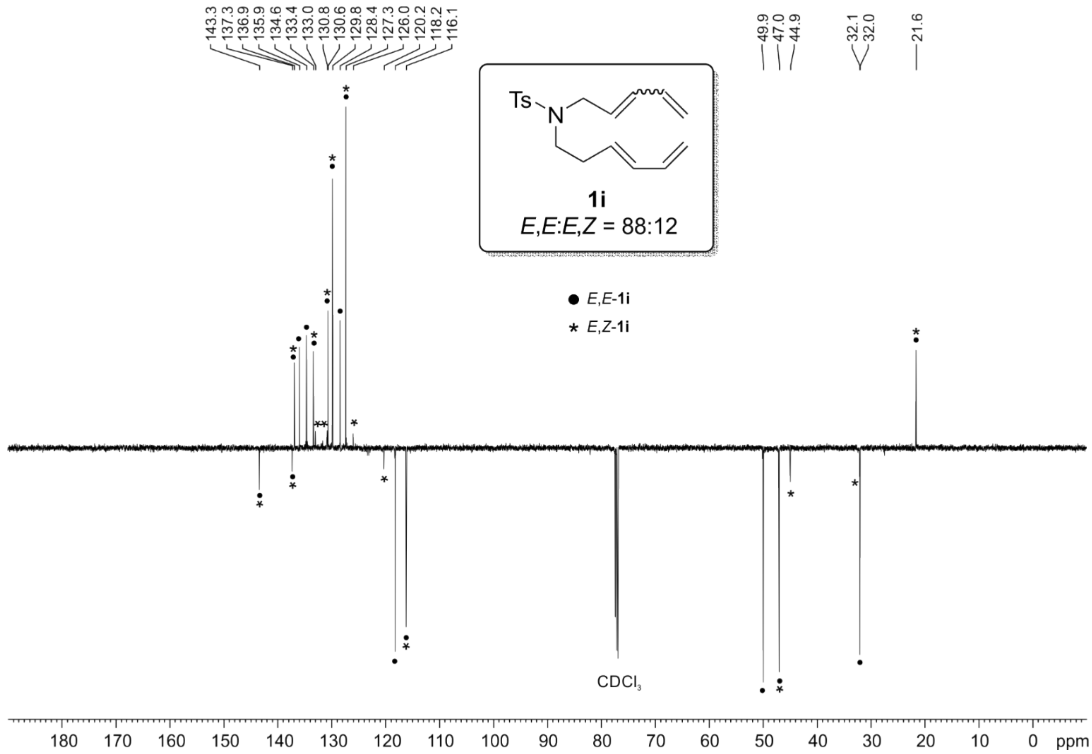


Figure S26. $^{13}C\{^{1}H\}$ NMR as DEPTQ135 spectrum for substrate **1i**

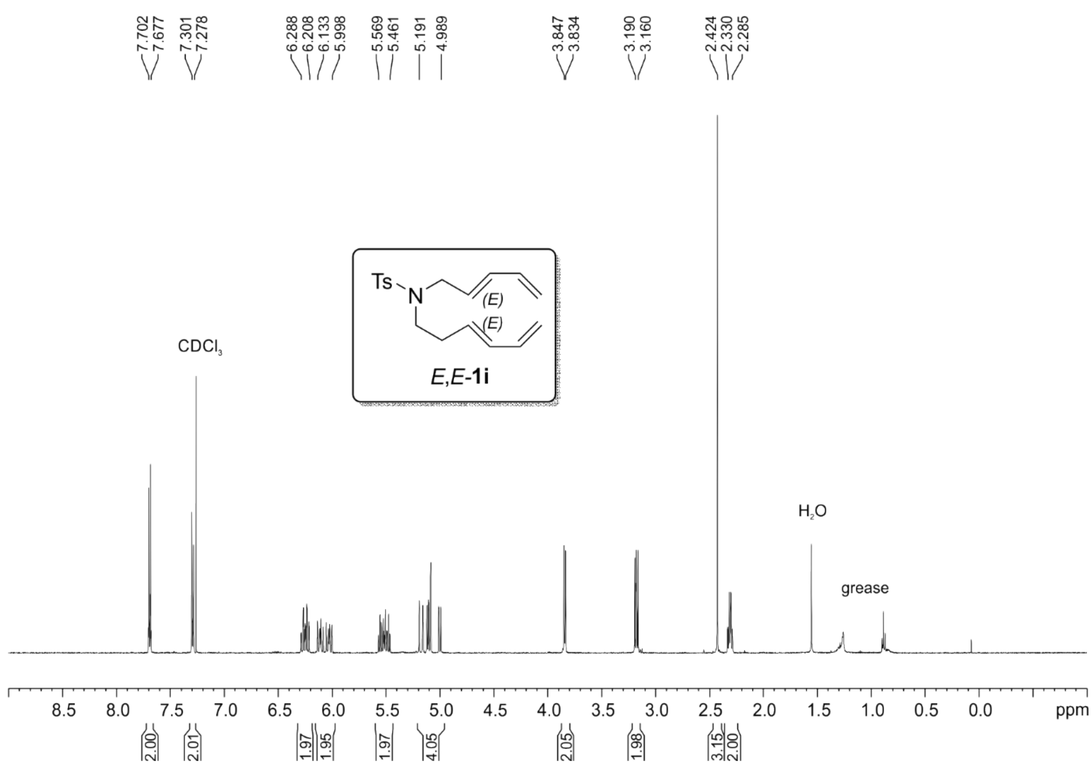


Figure S27. ^{1}H NMR spectrum for pure substrate *E*,*E*-**1i**

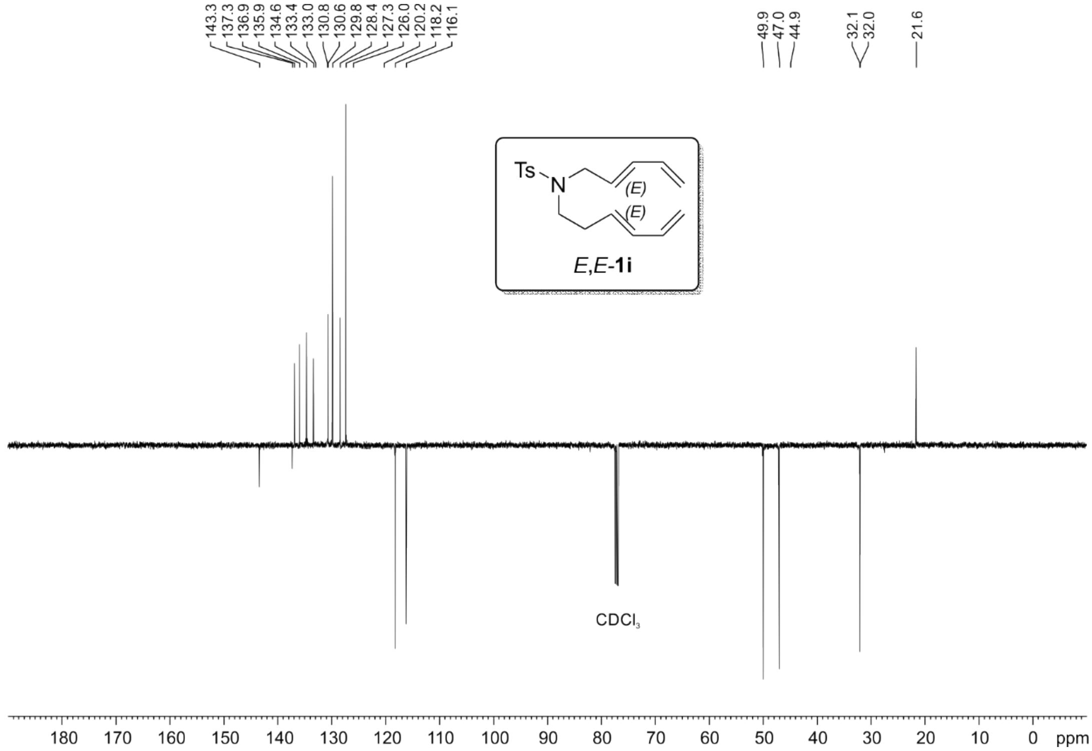


Figure S28. $^{13}C\{^{1}H\}$ NMR as DEPTQ135 spectrum for pure substrate *E*,*E*-**1i**

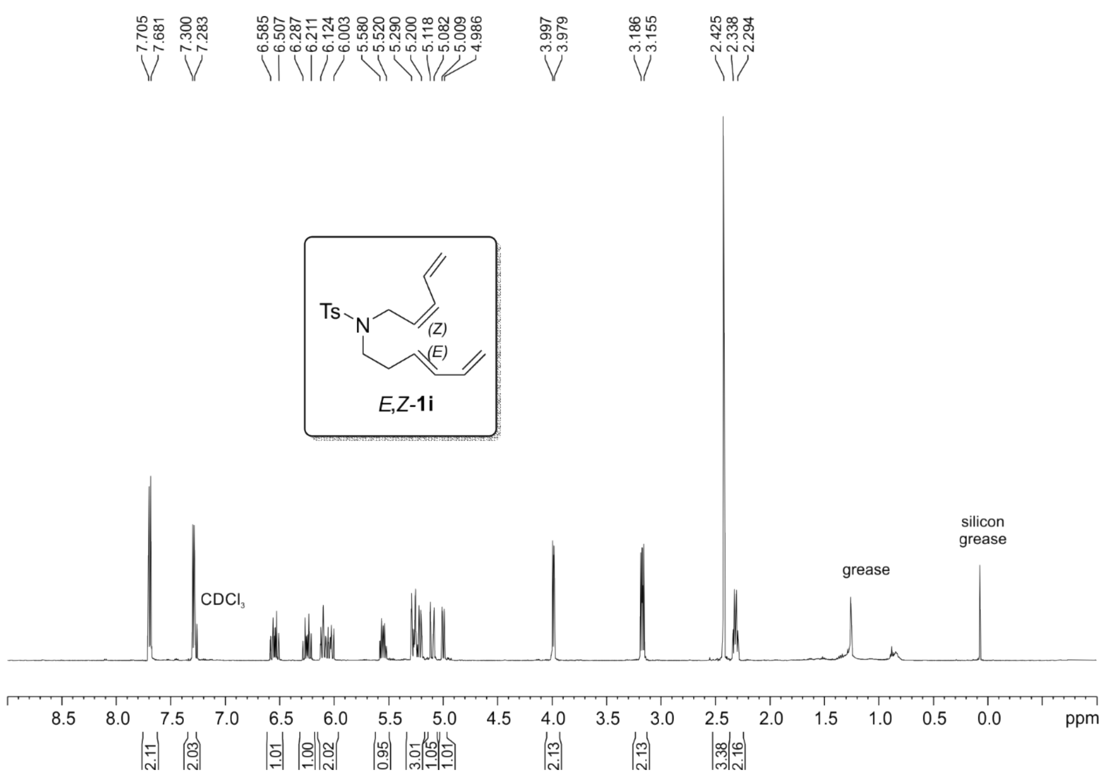


Figure S29. ^{1}H NMR spectrum for pure substrate *E*,*Z*-**1i**

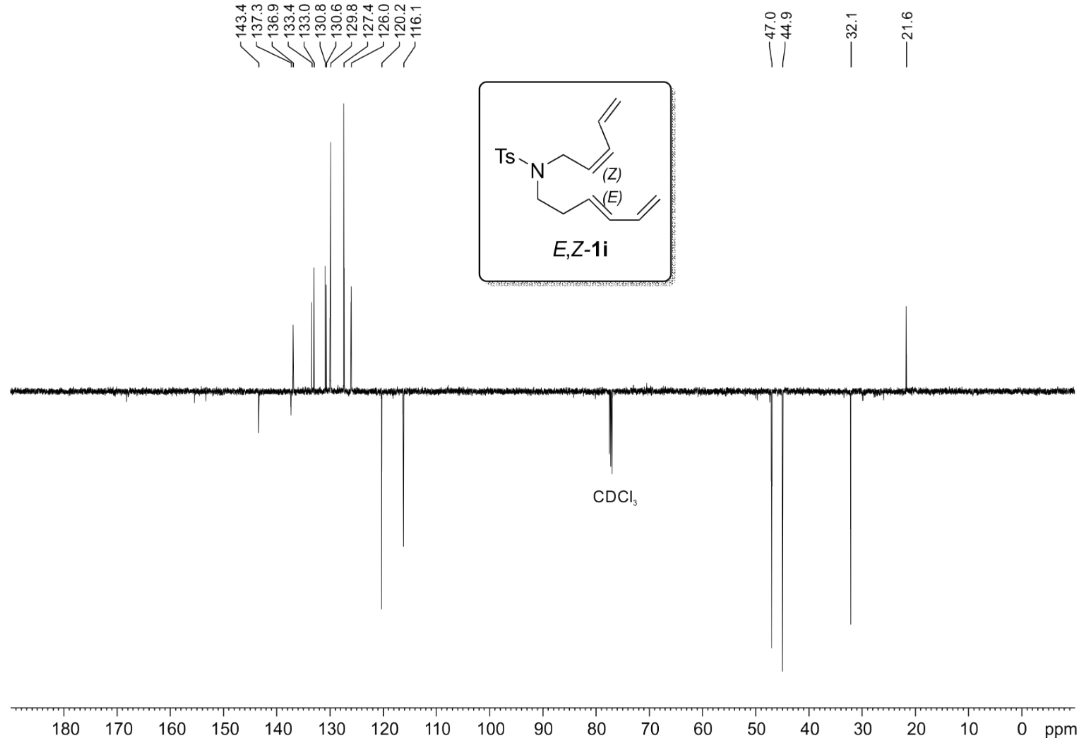


Figure S30. $^{13}C\{^{1}H\}$ NMR as DEPTQ135 spectrum for pure substrate *E*,*Z*-**1i**

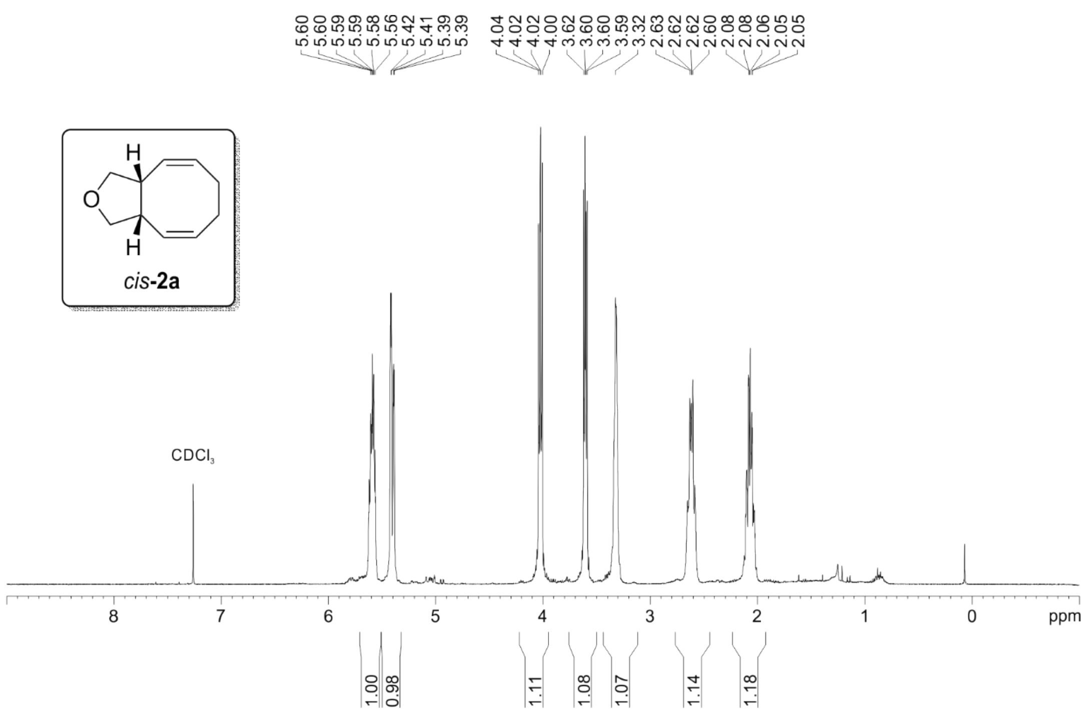


Figure S31. ^{1}H NMR spectrum for product *cis*-**2a** (see entry 1 in Table 1)

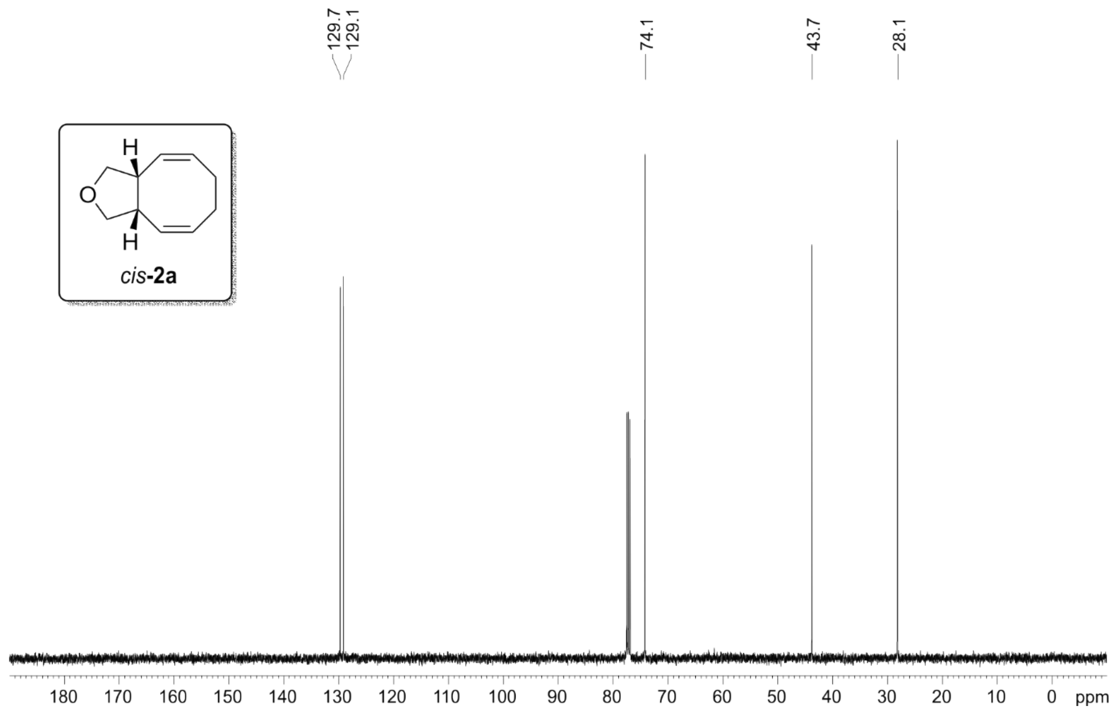


Figure S32. $^{13}C\{^{1}H\}$ NMR spectrum for product *cis*-**2a** (see entry 1 in Table 1)

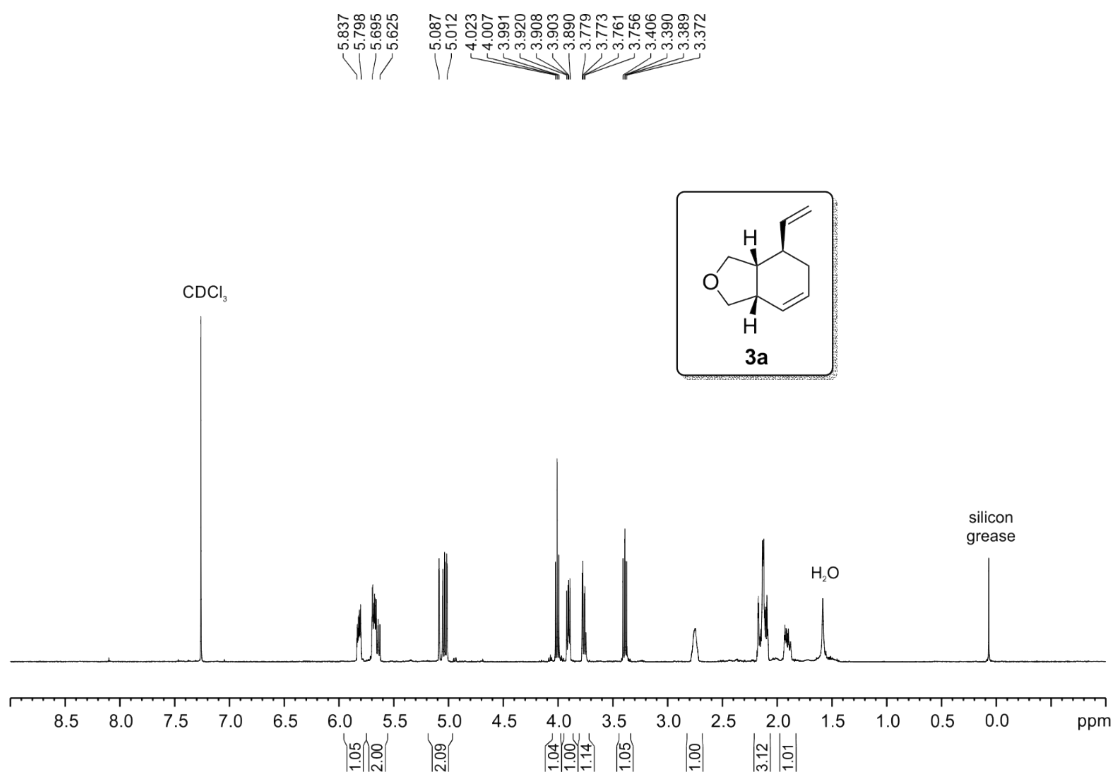


Figure S33. ^{1}H NMR spectrum for product **3a** (see entry 5 in Table 1)

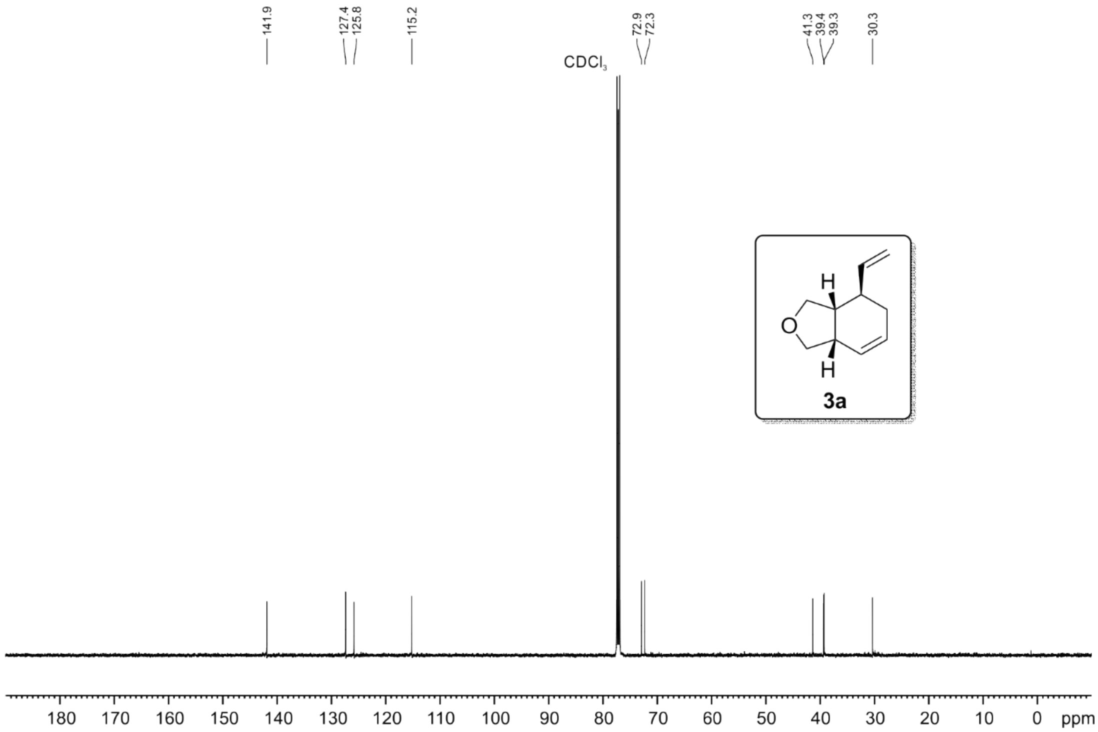


Figure S34. $^{13}C\{^{1}H\}$ NMR spectrum for product **3a** (see entry 5 in Table 1)

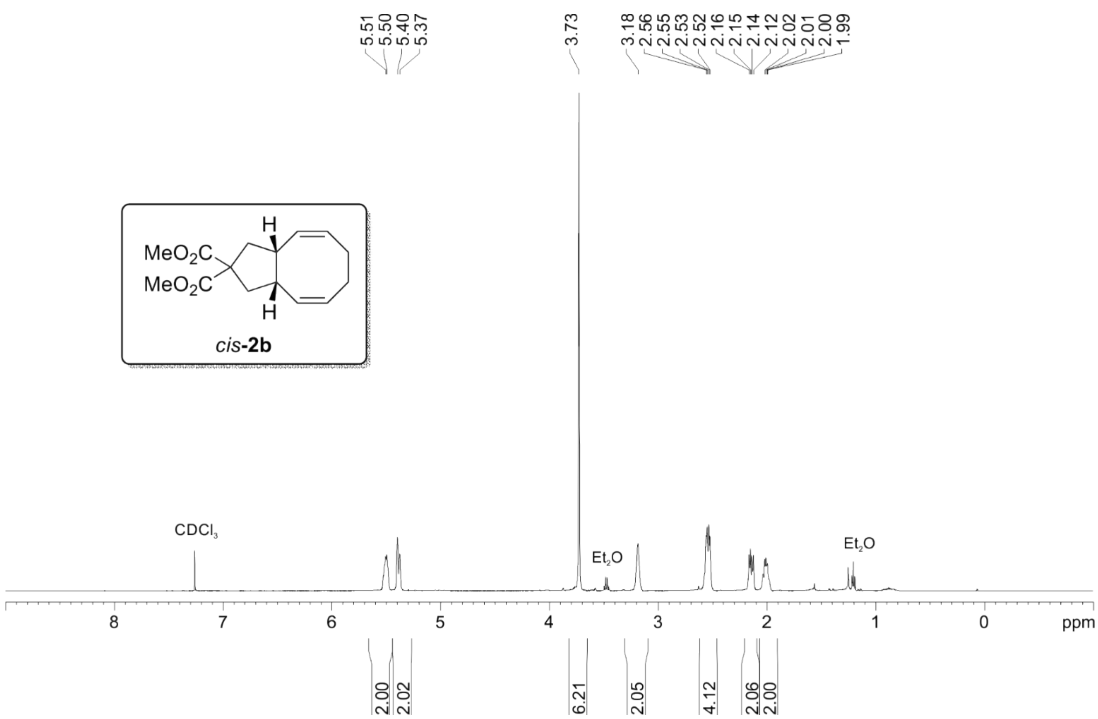


Figure S35. ^{1}H NMR spectrum for product *cis*-**2b** (see entry 1 in Table 2)

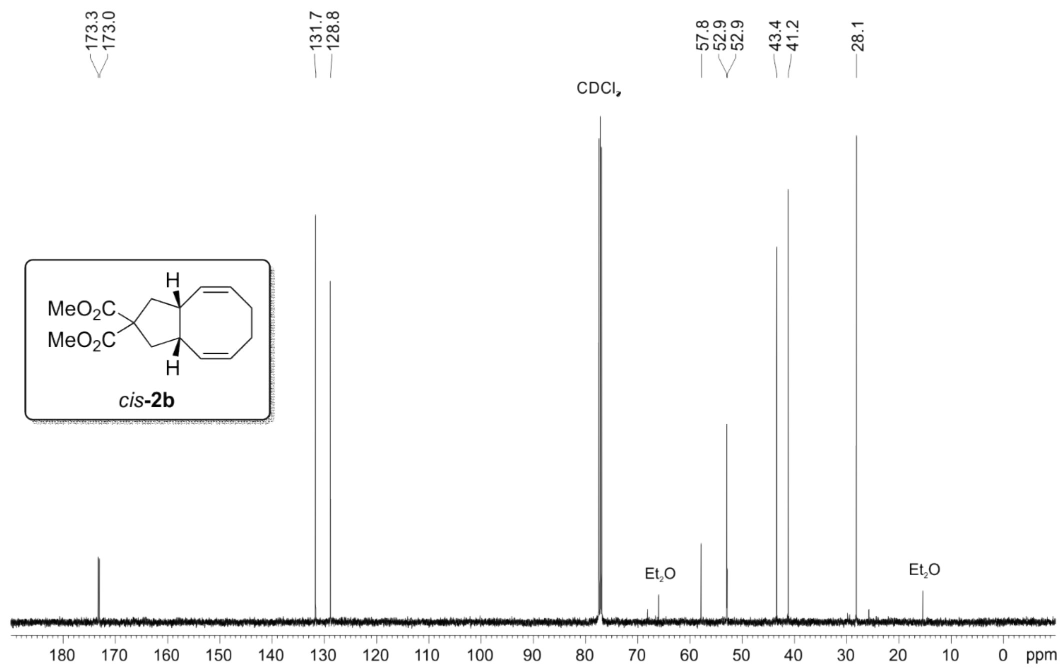


Figure S36. $^{13}C\{^{1}H\}$ NMR spectrum for product *cis*-**2b** (see entry 1 in Table 2)

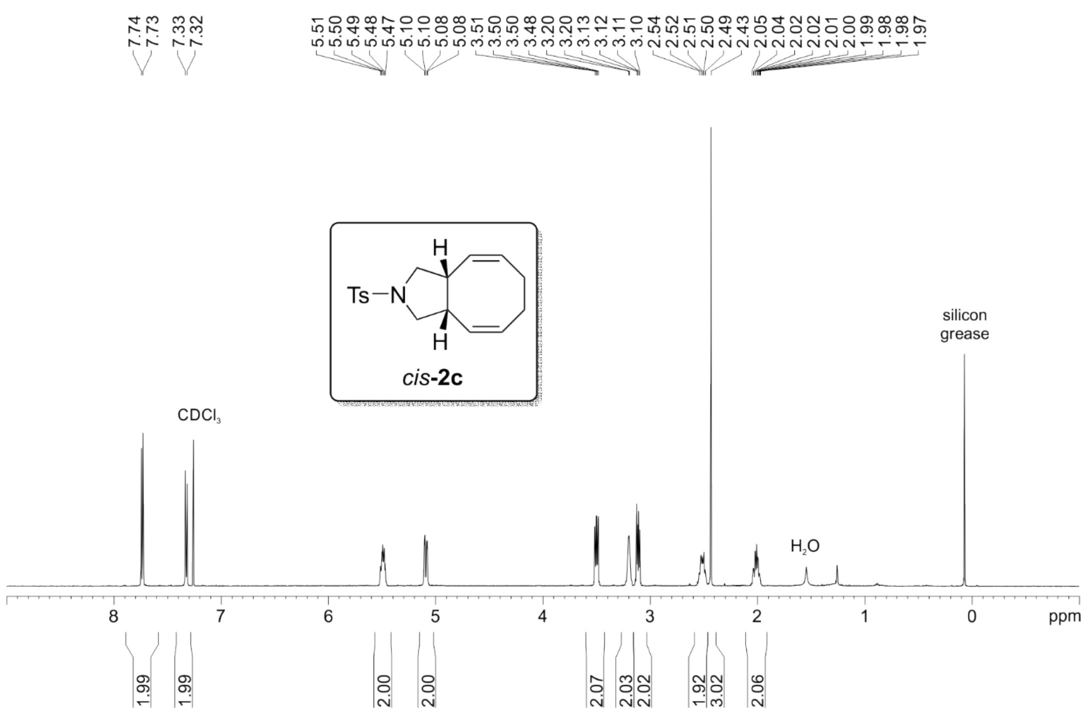


Figure S37. ^{1}H NMR spectrum for product *cis*-**2c** (see entry 2 in Table 2)

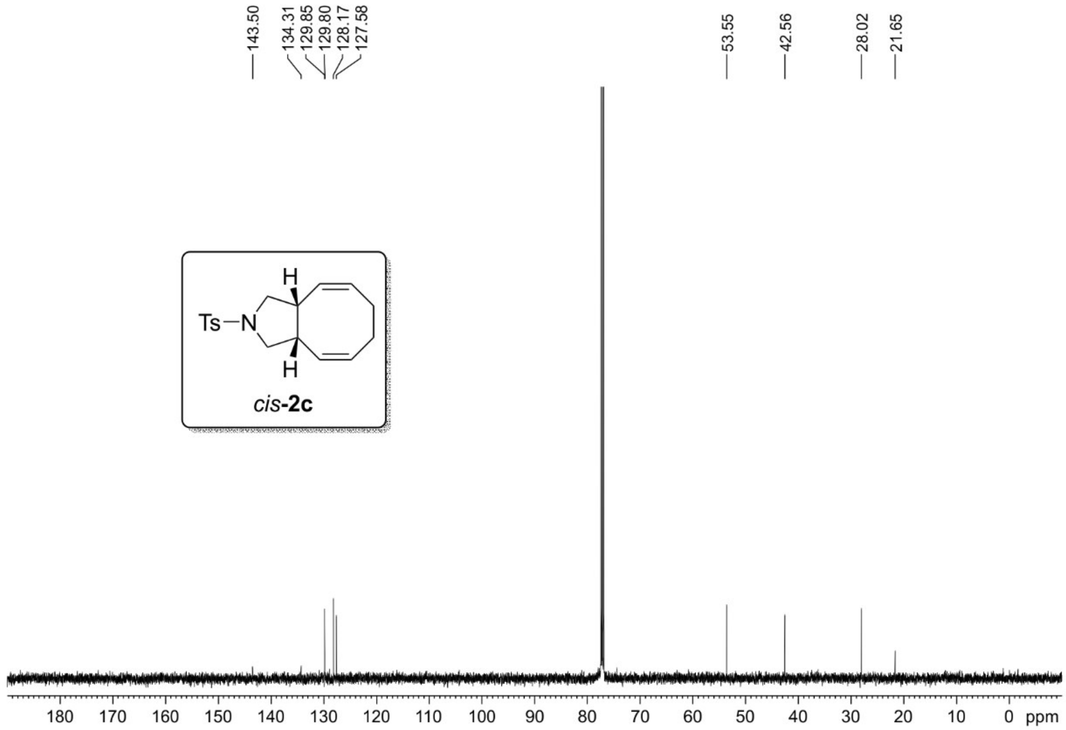


Figure S38. $^{13}C\{^1H\}$ NMR spectrum for product *cis*-**2c** (see entry 2 in Table 2)

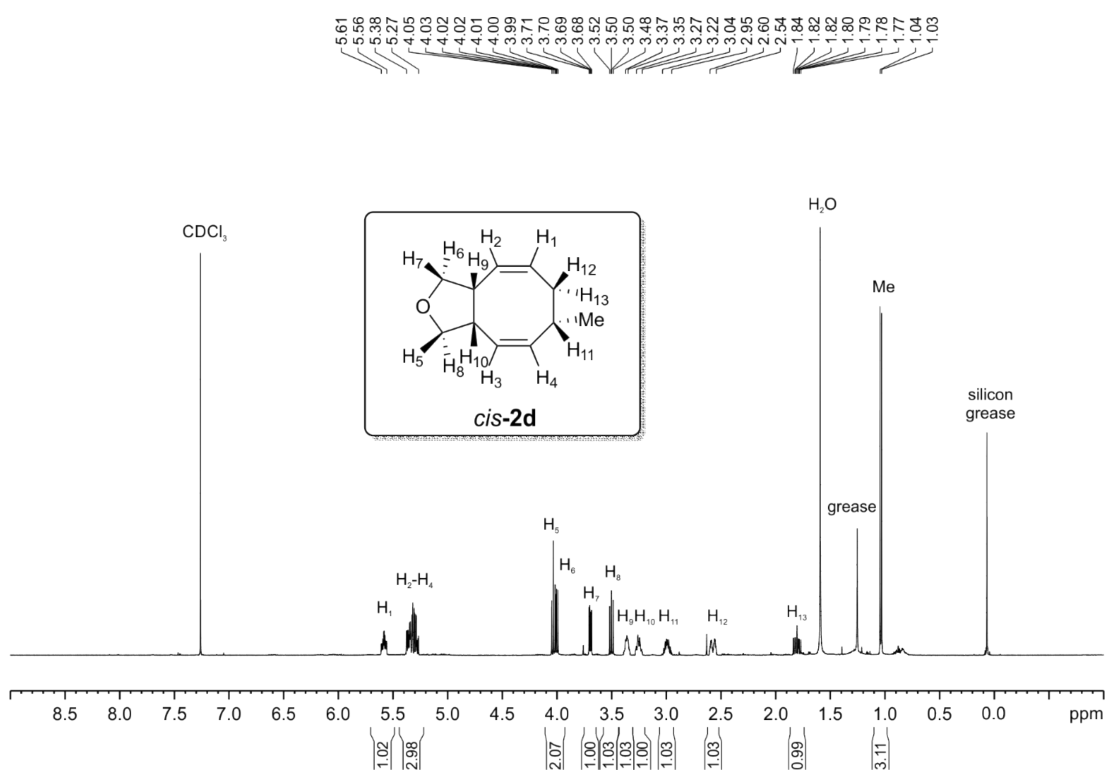


Figure S39. ^{1}H NMR spectrum for product *cis*-**2d** (see entry 3 in Table 2)

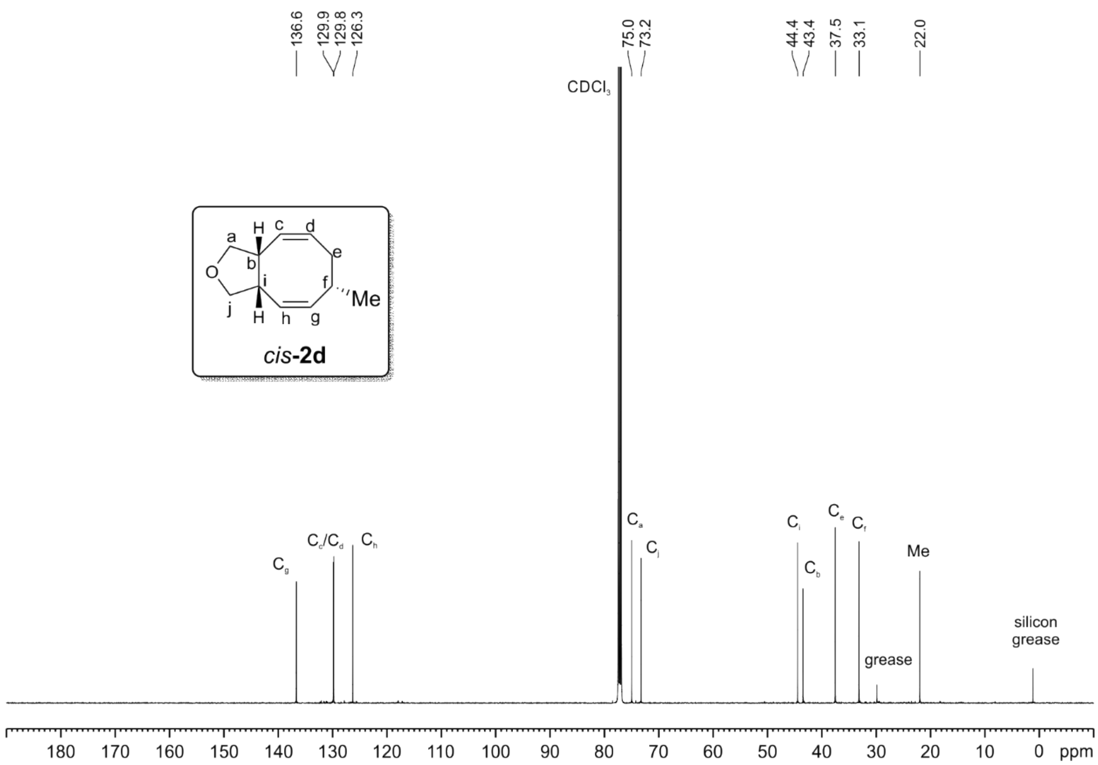


Figure S40. $^{13}C\{^1H\}$ NMR spectrum for product *cis*-**2d** (see entry 3 in Table 2)

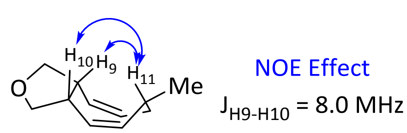


Figure S41. Stereochemical assignment of product *cis*-**2d** (see entry 3 in Table 2)

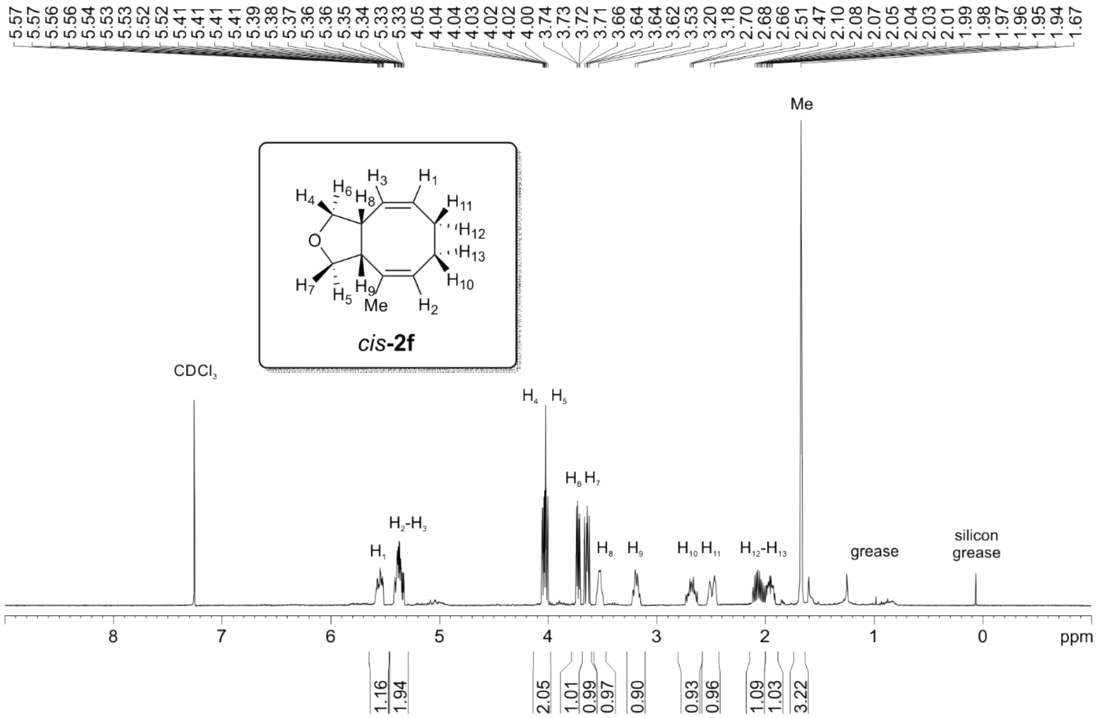


Figure S42. ^{1}H NMR spectrum for product *cis*-**2f** (see entry 5 in Table 2)

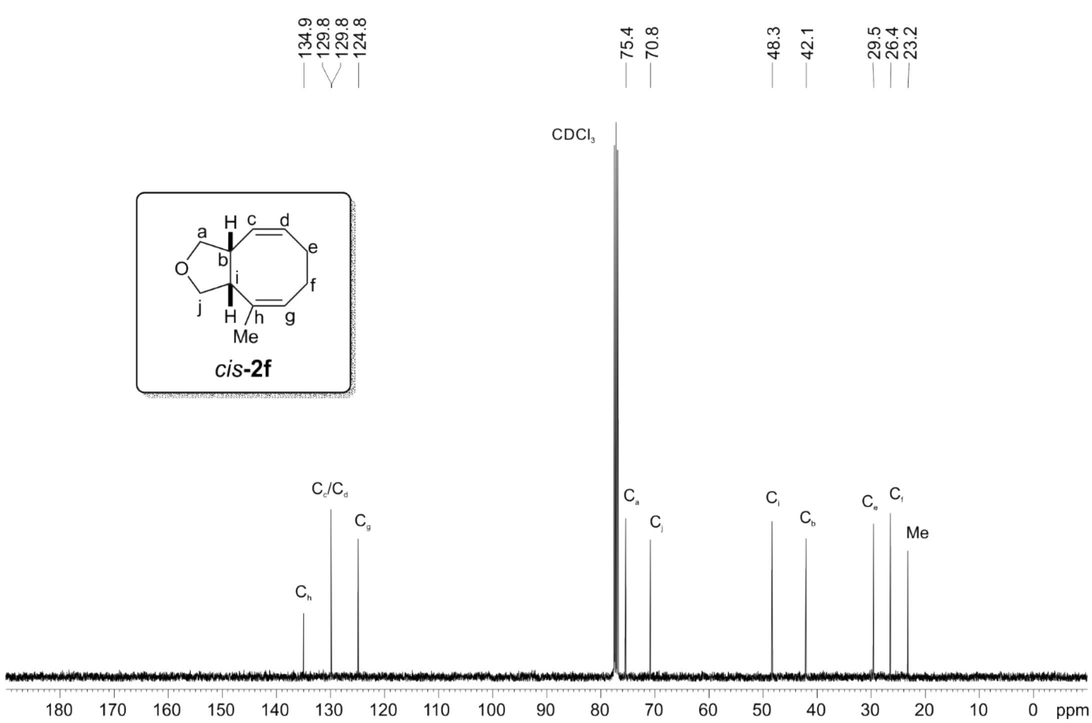


Figure S43. ^{13}C{^{1}H} NMR spectrum for product *cis*-**2f** (see entry 5 in Table 2)

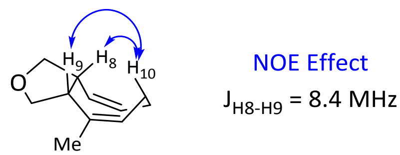


Figure S44. Stereochemical assignment of product *cis*-**2f** (see entry 3 in Table 2)

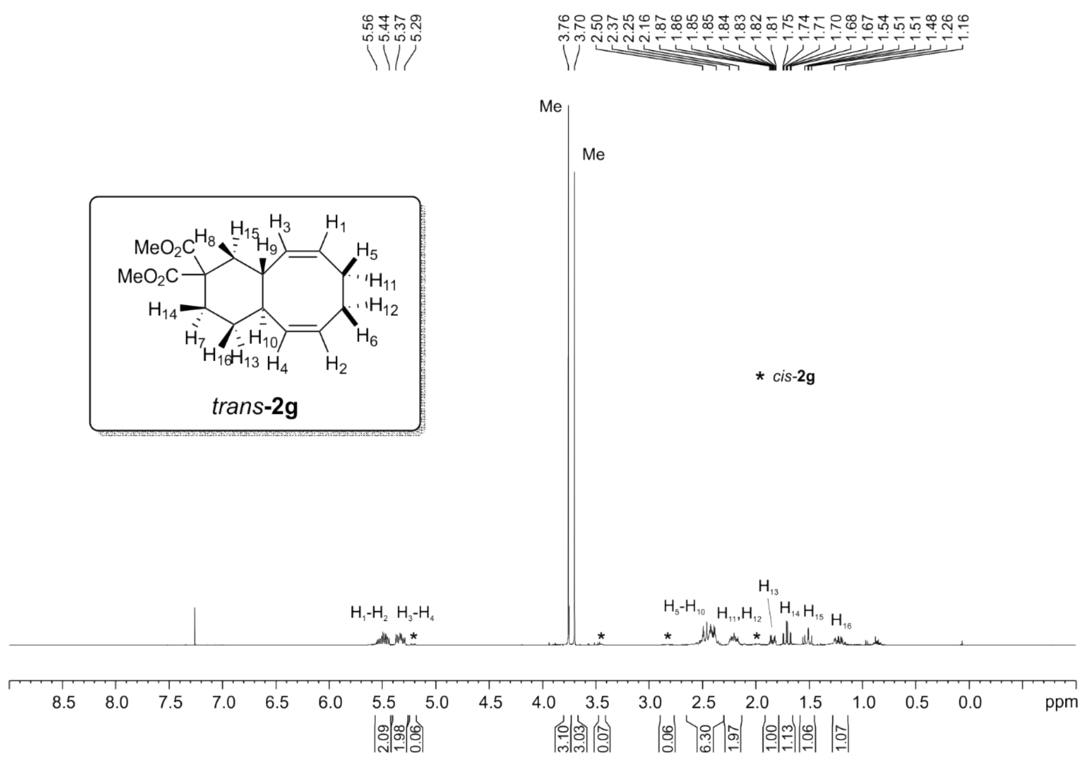


Figure S45. ^{1}H NMR spectrum for product *trans*-**2g** (see entry 1 in Table 3)

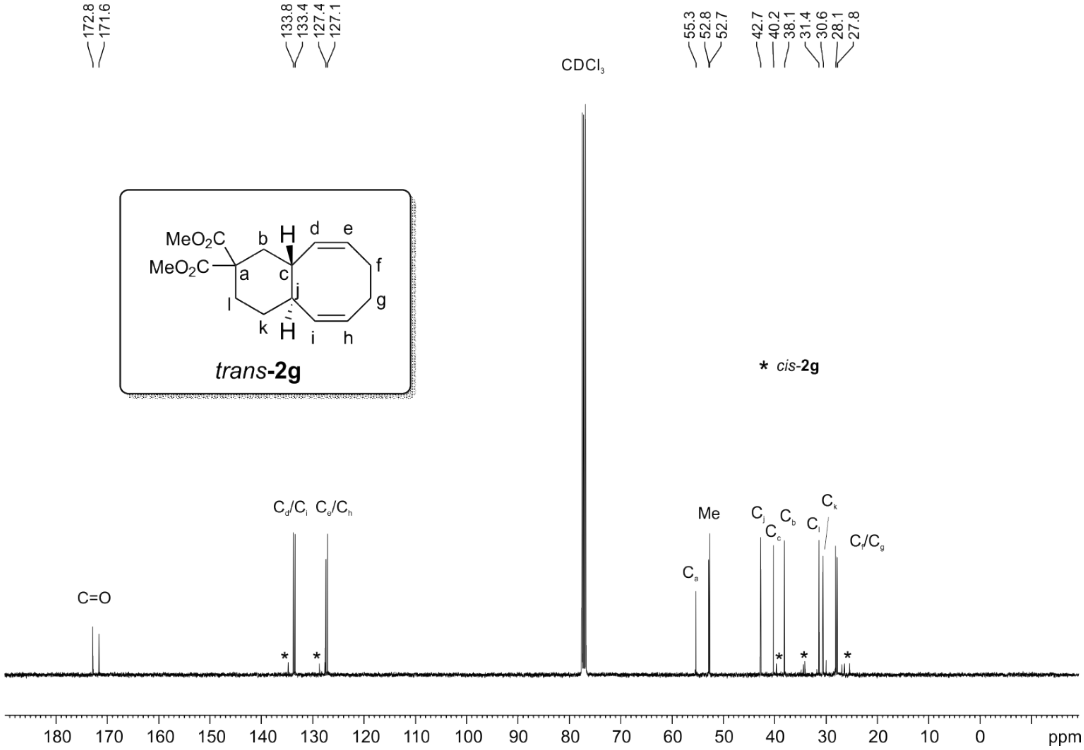


Figure S46. $^{13}C\{^{1}H\}$ NMR spectrum for product *trans*-**2g** (see entry 1 in Table 3)

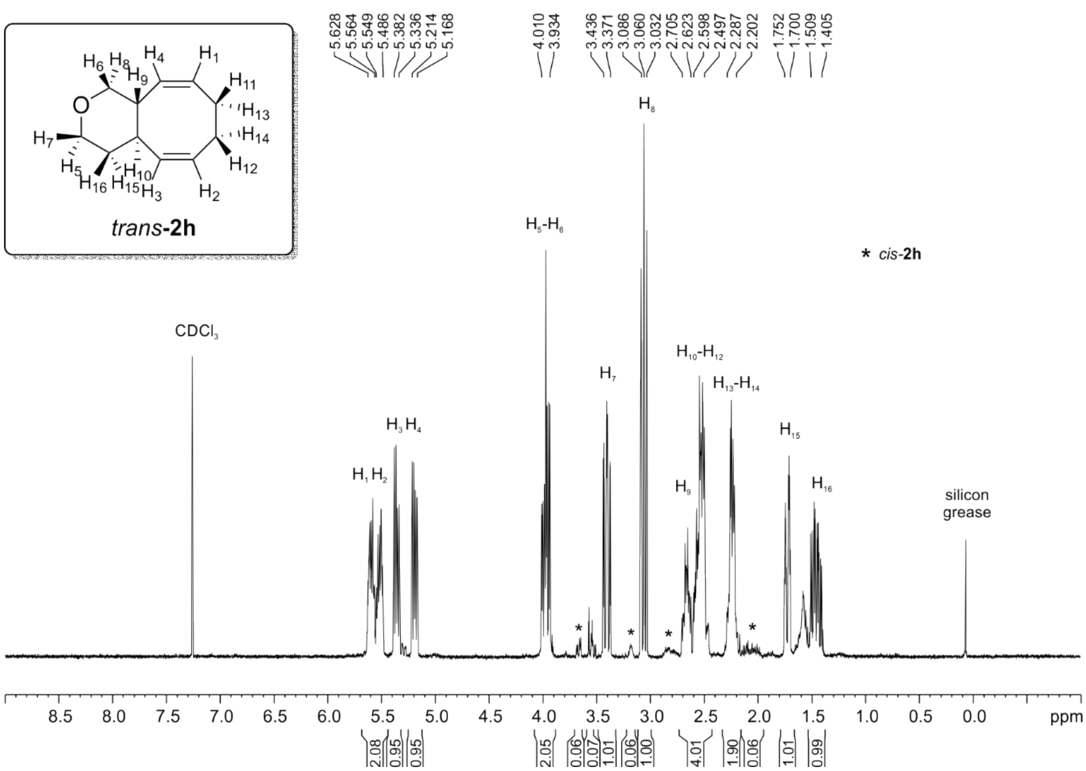


Figure S47. ^{1}H NMR spectrum for product *trans*-**2h** (see entry 2 in Table 3).

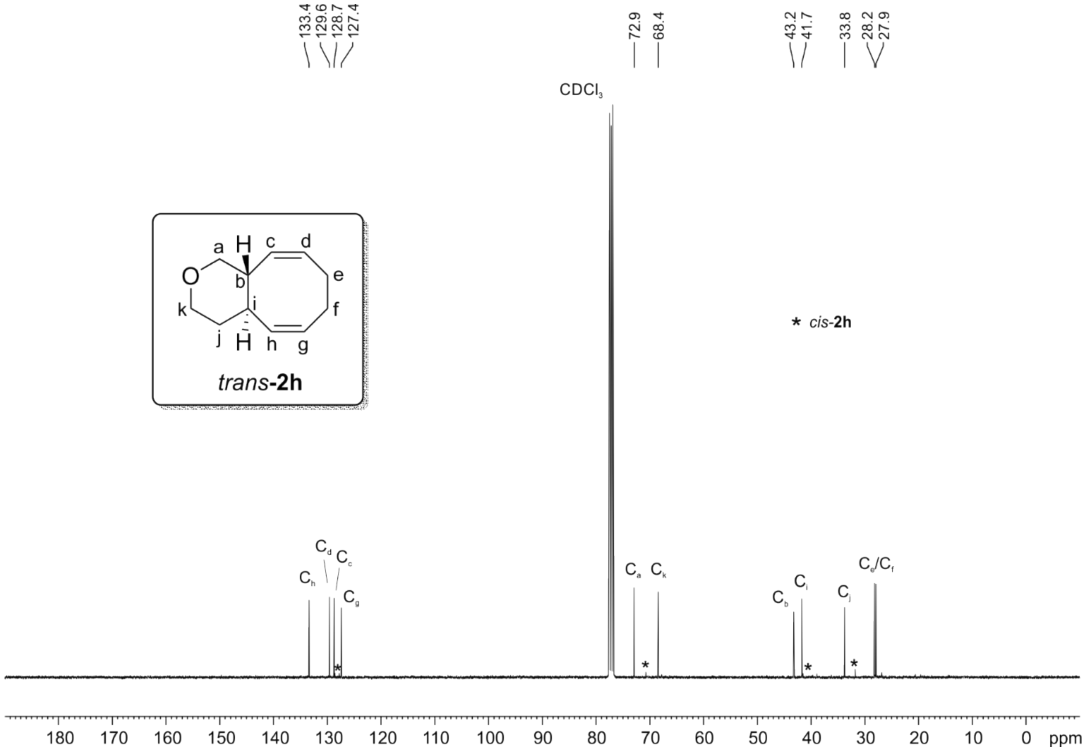


Figure S48. $^{13}C\{^{1}H\}$ NMR spectrum for product *trans*-**2h** (see entry 2 in Table 3)

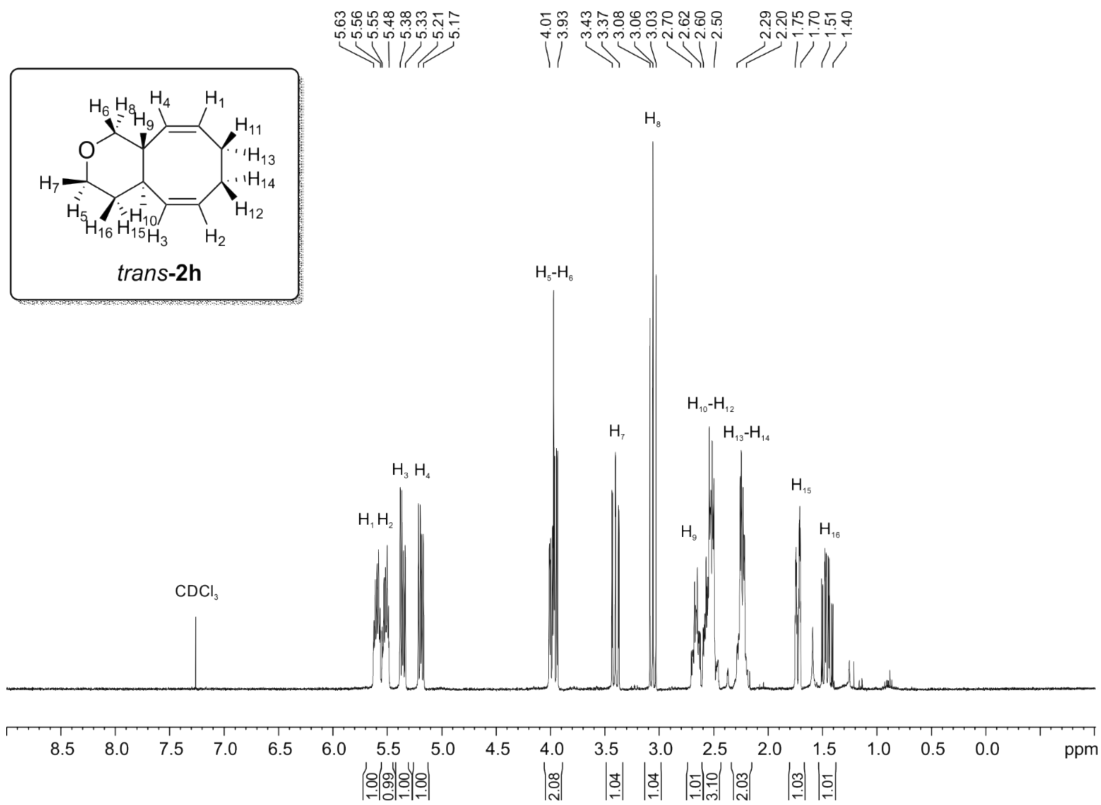


Figure S49. ^{1}H NMR spectrum for the analytically pure sample of product *trans*-**2h**

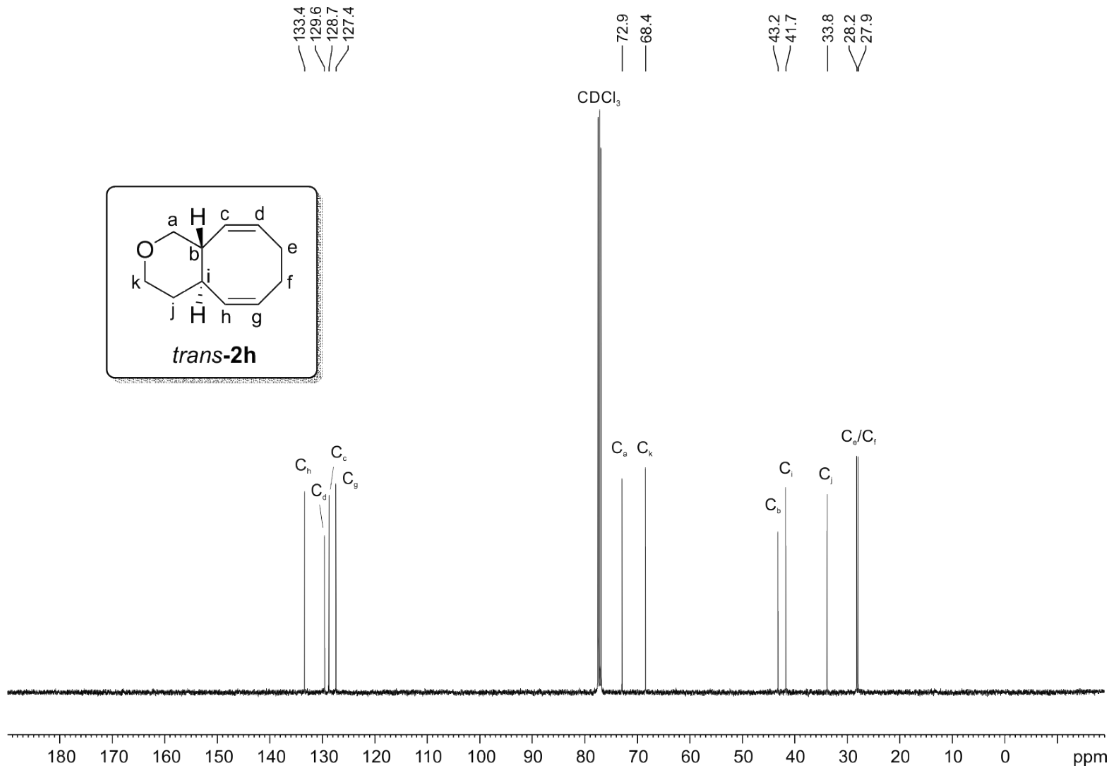


Figure S50. $^{13}C\{^1H\}$ NMR spectrum for the analytically pure sample of product *trans*-**2h**

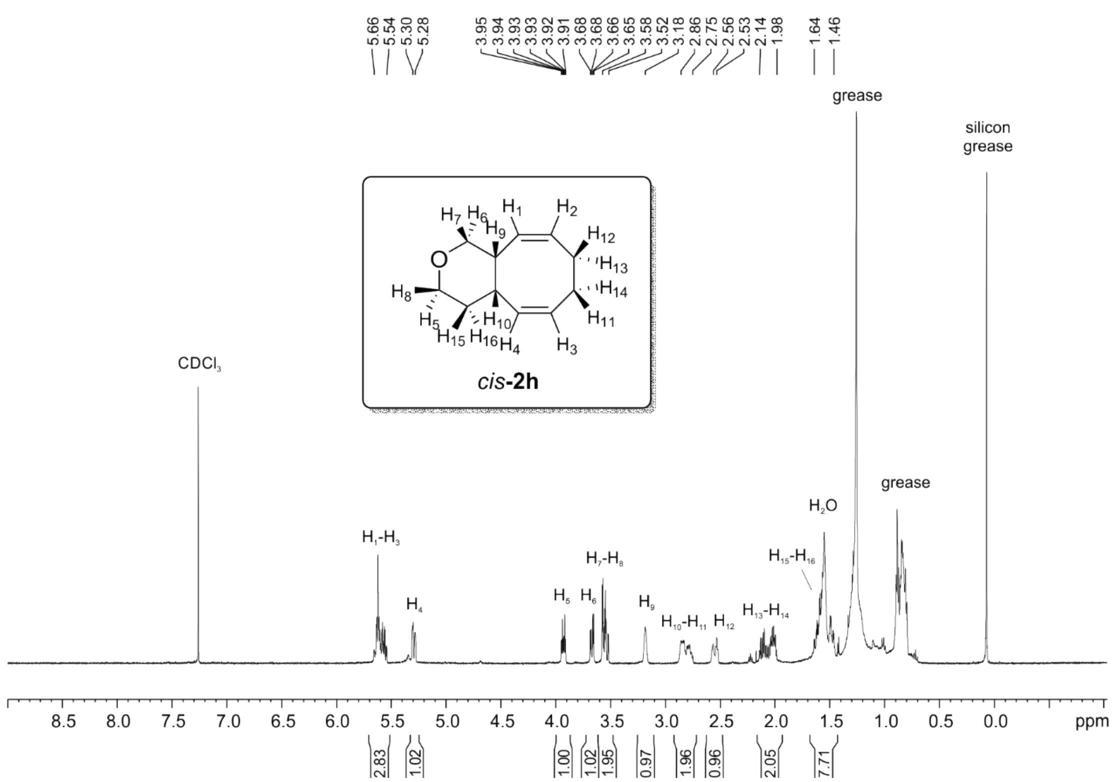


Figure S51. ^1H NMR spectrum for the analytically pure sample of product *cis*-**2h**

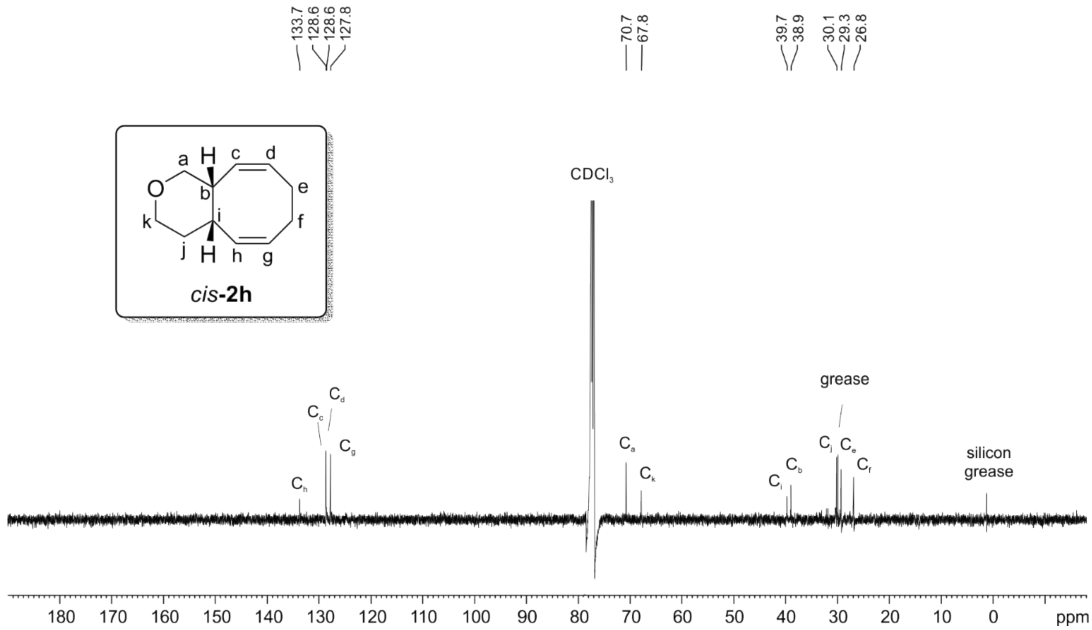


Figure S52. $^{13}C\{^{1}H\}$ NMR spectrum for the analytically pure sample of product *cis*-**2h**

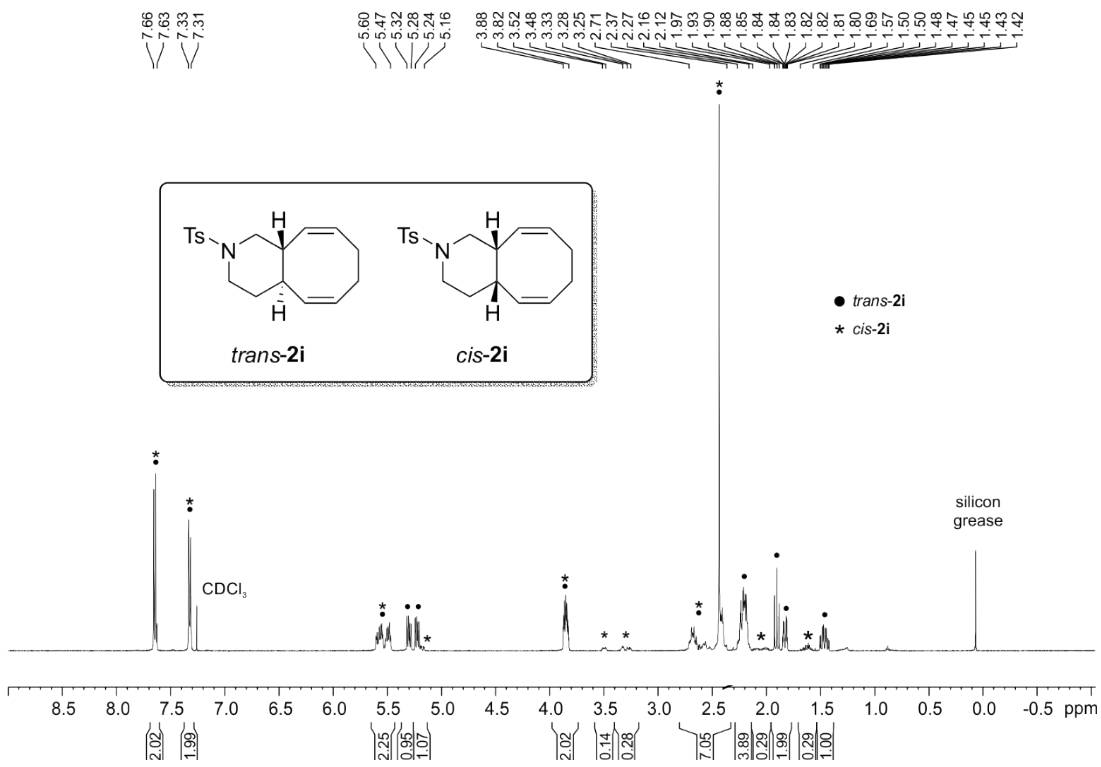


Figure S53. ^{1}H NMR spectrum for the mixture of products *trans*-**2i**:*cis*-**2i** (88:12, see entry 3 in Table 3)

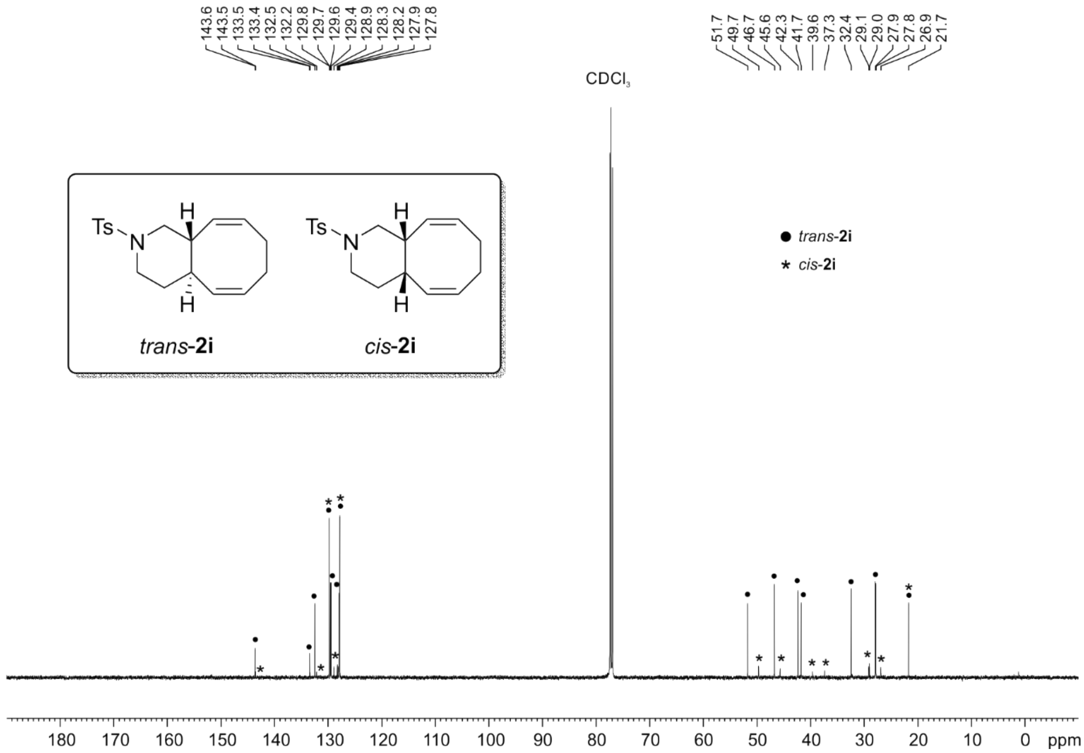


Figure S54. $^{13}C\{^{1}H\}$ NMR spectrum for the mixture of products *trans*-**2i**:*cis*-**2i** (88:12, see entry 3 in Table 3)

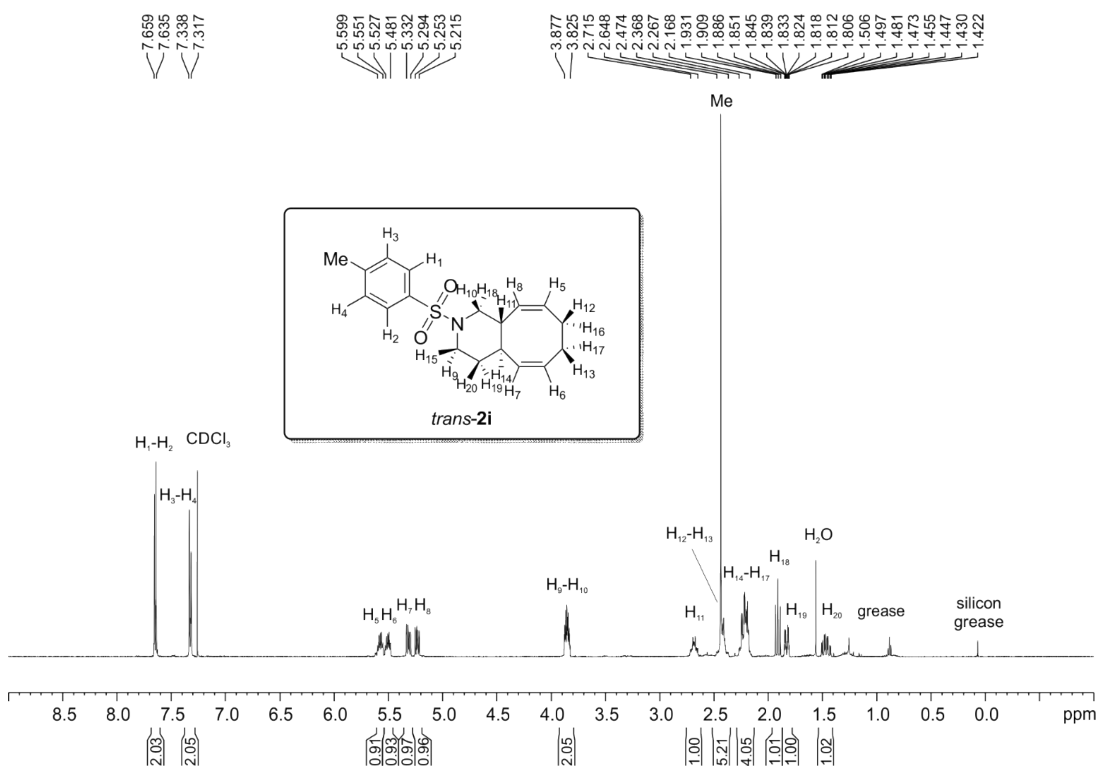


Figure S55. ^{1}H NMR spectrum for pure product *trans*-**2i** (see Scheme 2, *top*)

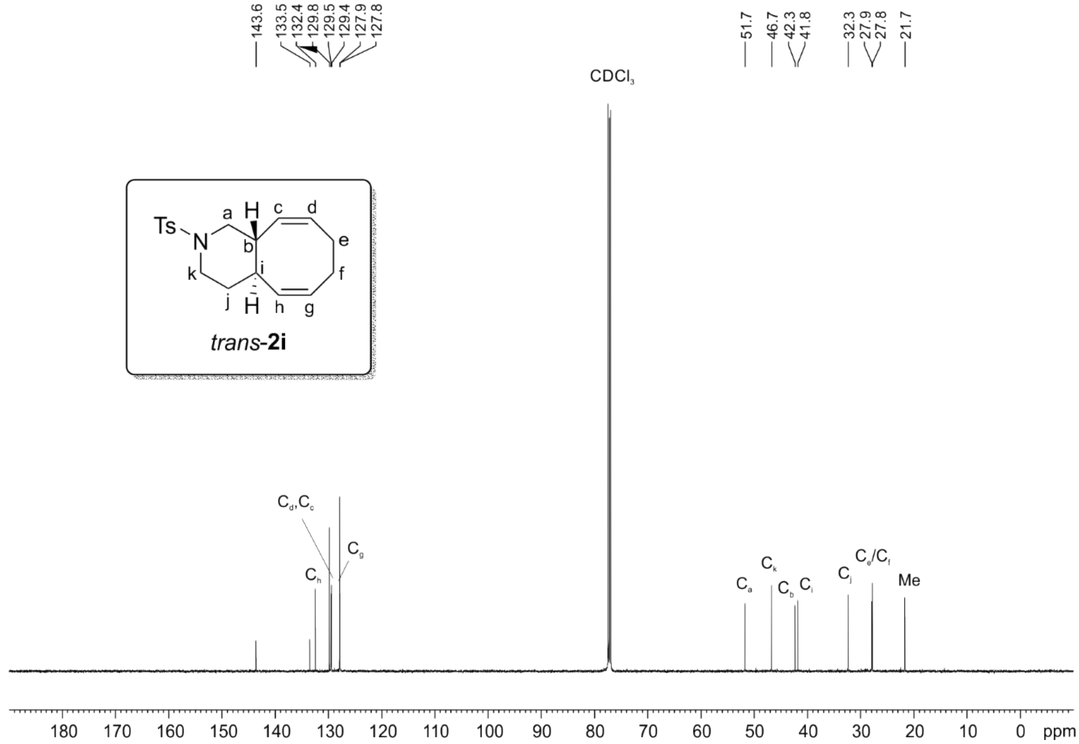


Figure S56. $^{13}C\{^{1}H\}$ NMR spectrum for pure product *trans*-**2i** (see Scheme 2, *top*)

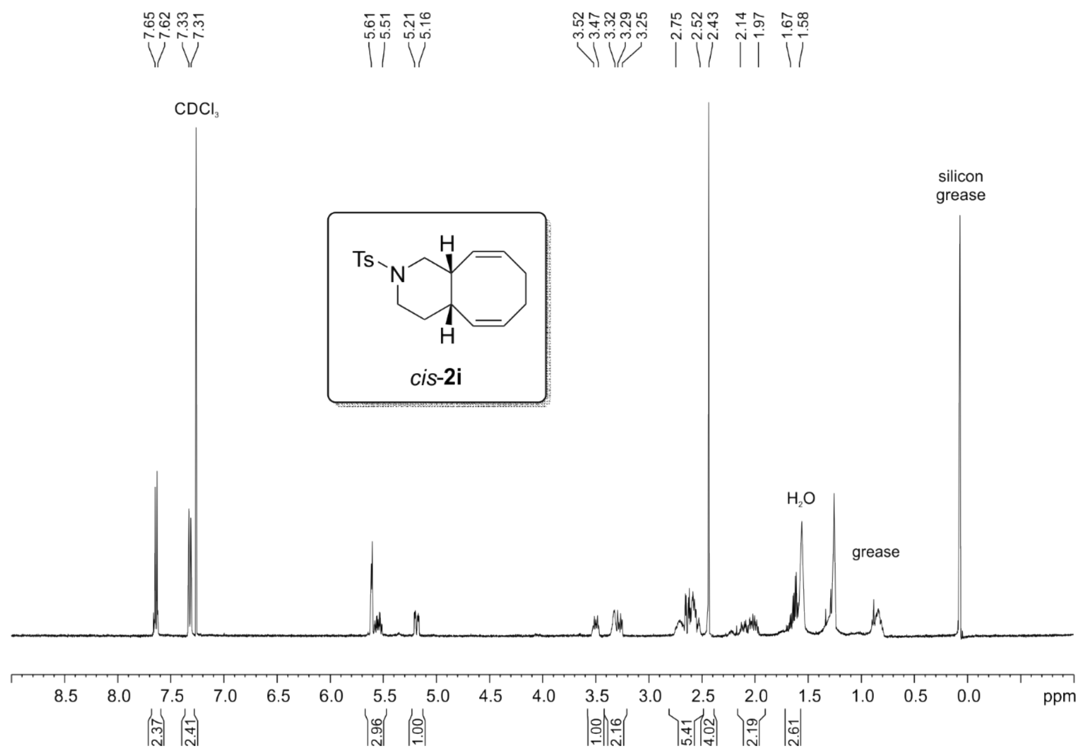


Figure S57. ^{1}H NMR spectrum for pure product *cis*-**2i** (see Scheme 2, *bottom*)

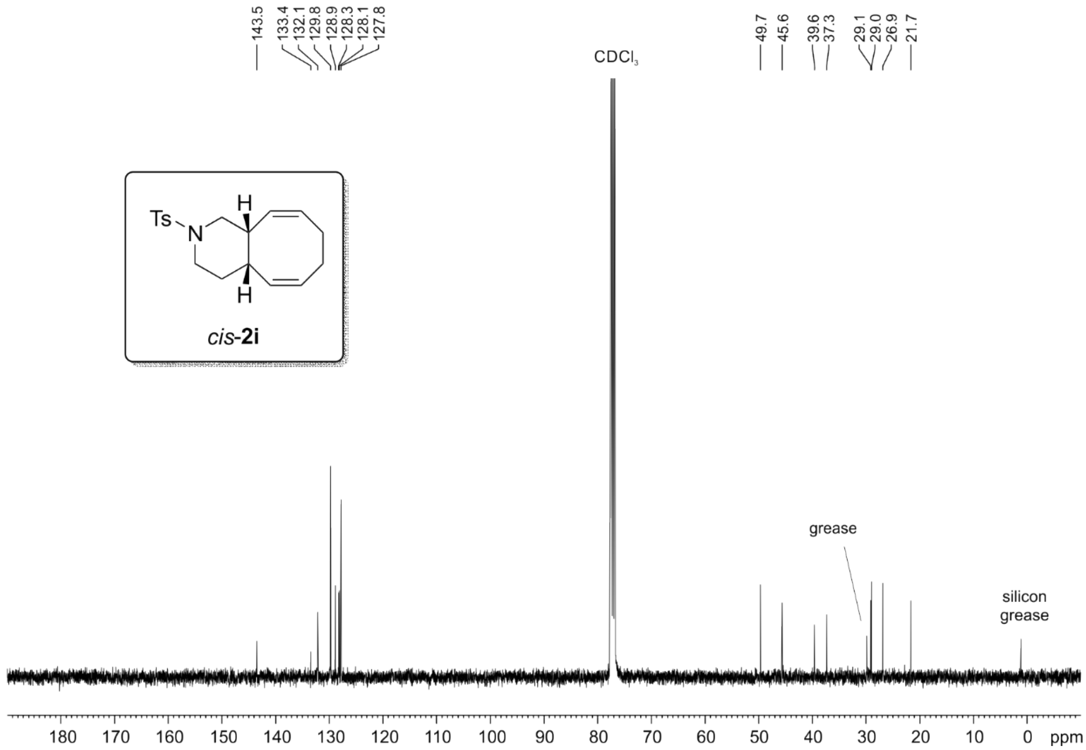


Figure S58. $^{13}C\{^{1}H\}$ NMR spectrum for pure product *cis*-**2i** (see Scheme 2, *bottom*)

1.9. Cartesian coordinates

Structures from Figure 2

Pre-TS-1

C	1.9872057	1.4760146	0.5379472
C	1.4141443	1.7301033	-0.7650168
C	0.0065506	1.7094049	-0.8655952
C	-0.7433448	1.4556297	0.3462062
C	-2.2188732	1.1683204	0.2473772
C	-2.2040674	-1.1967225	0.2441351
C	-0.7250062	-1.4648071	0.3451154
C	0.0306992	-1.7104331	-0.8646343
C	1.4382123	-1.7123758	-0.7607369
C	2.0050907	-1.4490104	0.5432432
H	1.6171987	1.9995623	1.4229187
H	3.0535416	1.2524292	0.5784696
H	2.0300671	1.7636225	-1.6654787
H	-0.4897632	1.7196947	-1.8384309
H	-0.4575379	1.9850433	1.2602571
H	-2.6583526	1.1186247	1.2620540
H	-2.7254772	1.9810778	-0.3012625
H	-2.6459604	-1.1559291	1.2581445
H	-2.6988388	-2.0144135	-0.3079194
H	-0.4337408	-1.9888773	1.2605505
H	-0.4632016	-1.7285775	-1.8385766
H	2.0565859	-1.7393777	-1.6597547
H	3.0683932	-1.2117620	0.5856021
H	1.6401899	-1.9764111	1.4280592
O	-2.5597404	-0.0153289	-0.4851769
Ni	0.6760251	0.0044986	0.0325027

Pre-TS-2

C	-0.8189863	-0.9288637	-2.1248302
C	-0.1970981	-1.3971495	-0.8455265
C	0.8189863	0.9288637	-2.1248302
C	0.1970981	1.3971495	-0.8455265
C	0.9280911	1.7213211	0.3264197
C	0.1845339	1.8138445	1.5718391
C	-1.1972534	1.6524711	1.6433209
H	-1.8110037	-0.4872423	-1.9173460
H	-0.9585722	-1.7665372	-2.8282715
H	0.8145445	-1.8022937	-0.9685515
H	1.8110037	0.4872423	-1.9173460
H	0.9585722	1.7665372	-2.8282715
H	-0.8145445	1.8022937	-0.9685515
H	2.0188548	1.7450857	0.3437446
H	0.7651265	1.8643084	2.4956300
H	-1.6673246	1.5515174	2.6202027
H	-1.8665581	1.8649228	0.8108777
O	-0.0000000	0.0000000	-2.8679940
Ni	0.0000000	0.0000000	0.6129757
C	-0.9280911	-1.7213211	0.3264197
H	-2.0188548	-1.7450857	0.3437446
C	-0.1845339	-1.8138445	1.5718391
H	-0.7651265	-1.8643084	2.4956300

C	1.1972534	-1.6524711	1.6433209
H	1.8665581	-1.8649228	0.8108777
H	1.6673246	-1.5515174	2.6202027

TS-1

C	2.0664144	1.5730274	0.5095193
C	1.3650031	1.9268352	-0.7019732
C	-0.0058124	1.6147165	-0.7960233
C	-0.7744054	1.1138552	0.3583661
C	-2.2817729	1.1221683	0.1981014
C	-2.2669844	-1.1516817	0.1983927
C	-0.7598677	-1.1236118	0.3590365
C	0.0154328	-1.6153530	-0.7947369
C	1.3901805	-1.9094899	-0.6999573
C	2.0866569	-1.5453249	0.5113168
H	1.6438610	1.8397552	1.4844504
H	3.1571371	1.5871346	0.4882790
H	1.8932050	2.2608692	-1.5978578
H	-0.5256341	1.7170363	-1.7509789
H	-0.4500088	1.4476362	1.3482059
H	-2.7646569	1.1644778	1.1946235
H	-2.6024537	1.9999327	-0.3845801
H	-2.7495347	-1.2001673	1.1948073
H	-2.5759864	-2.0336507	-0.3842550
H	-0.4313915	-1.4525223	1.3491440
H	-0.5027057	-1.7254190	-1.7497417
H	1.9229456	-2.2375147	-1.5953689
H	3.1774692	-1.5453620	0.4902938
H	1.6673023	-1.8162428	1.4864505
O	-2.7549707	-0.0179523	-0.5172194
Ni	1.0605776	0.0068479	-0.1982946

TS-2

C	-2.693039	-1.160541	0.284929
C	-1.329927	-0.976910	-0.286159
C	-2.693159	1.160549	-0.284935
C	-1.330080	0.977026	0.286325
C	-0.064539	1.402315	-0.337050
C	1.048547	1.842589	0.419407
C	2.357882	1.674083	-0.110626
H	-2.636914	-1.314561	1.365242
H	-3.230122	-1.999869	-0.155281
H	-1.295791	-0.940580	-1.368625
H	-2.636951	1.314670	-1.365270
H	-3.230601	1.999757	0.155348
H	-1.296011	0.940554	1.369001
H	-0.033086	1.450154	-1.421386
H	0.918061	2.014429	1.481511
H	3.205101	1.875741	0.524278
H	2.536945	1.788162	-1.170992
O	-3.490194	-0.000118	-0.000158
Ni	1.327488	-0.000030	-0.000004
C	-0.064471	-1.402129	0.337232
H	-0.033009	-1.450015	1.421502
C	1.048369	-1.842572	-0.419387
H	0.917656	-2.014386	-1.481334
C	2.357840	-1.674147	0.110457
H	2.537109	-1.787929	1.170705

H	3.204966	-1.875907	-0.524481

I-1

C	2.1684423	1.6484712	0.4851972
C	1.2856409	1.9568684	-0.5940037
C	0.0260130	1.3200760	-0.7486622
C	-0.8588628	0.7852342	0.3830636
C	-2.3523179	1.1150024	0.1724852
C	-2.3371541	-1.1458902	0.1745598
C	-0.8482104	-0.7958559	0.3838435
C	0.0429796	-1.3197007	-0.7480079
C	1.3107484	-1.9401225	-0.5936058
C	2.1897584	-1.6199122	0.4853008
H	1.7910375	1.4840843	1.4996428
H	3.1876204	2.0331989	0.4415934
H	1.6929809	2.4699067	-1.4717781
H	-0.4815125	1.4507274	-1.7087629
H	-0.5053099	1.1754981	1.3472797
H	-2.8612468	1.2609579	1.1469129
H	-2.5227841	2.0003525	-0.4547782
H	-2.8437505	-1.2966508	1.1495018
H	-2.4960572	-2.0346781	-0.4508598
H	-0.4887780	-1.1803941	1.3481566
H	-0.4631568	-1.4571100	-1.7079324
H	1.7243441	-2.4482021	-1.4713122
H	3.2137995	-1.9914598	0.4414489
H	1.8105768	-1.4603957	1.4998630
O	-2.9039504	-0.0198384	-0.5048864
Ni	1.5191496	0.0098325	-0.5042599

I-2

C	-2.5375358	-1.1591005	0.2678323
C	-1.1419208	-0.7498615	-0.1876566
C	-2.5376912	1.1587699	-0.2675118
C	-1.1420109	0.7496992	0.1878862
C	0.1406232	1.3323219	-0.3820487
C	1.1875914	1.8853979	0.3934034
C	2.5392434	1.8180285	-0.0761997
H	-2.5525289	-1.3888741	1.3502360
H	-2.9571502	-2.0162201	-0.2795395
H	-1.0929098	-0.8134123	-1.2894750
H	-2.5526809	1.3891167	-1.3497808
H	-2.9575623	2.0155469	0.2802206
H	-1.0928274	0.8131087	1.2896933
H	0.1929002	1.3906171	-1.4786891
H	1.0030435	2.0760995	1.4580456
H	3.3430226	2.1159819	0.5964850
H	2.7552049	1.9587151	-1.1408830
O	-3.3686123	-0.0003076	-0.0001607
Ni	1.6082530	0.0000698	-0.0000805
C	0.1408622	-1.3323643	0.3820384
H	0.1934272	-1.3905572	1.4786856
C	1.1877836	-1.8852369	-0.3935665
H	1.0030924	-2.0759759	-1.4581813
C	2.5395018	-1.8176732	0.0758070
H	2.7556607	-1.9584032	1.1404499
H	3.3432207	-2.1154862	-0.5970100

6a-π,π-*trans*

C	-2.7064176	-2.1730013	3.5871308
C	-1.6218155	-1.3279160	2.9276037
C	-3.6488285	-0.1217128	2.8350721
C	-2.1828162	0.0871359	3.1860311
C	-1.2988303	1.1267131	2.5050010
C	-0.2413095	1.7411214	3.2542521
C	0.8306815	2.3684057	2.5856414
H	-2.5869591	-2.2068710	4.6873250
H	-2.7697053	-3.2030887	3.2069279
H	-1.6640143	-1.5023875	1.8417857
H	-3.8174706	-0.0128771	1.7488671
H	-4.3375066	0.5478674	3.3729537
H	-2.1171180	0.2584971	4.2782405
H	-1.6871216	1.6189521	1.6097208
H	-0.1663795	1.5472846	4.3299972
H	1.6915450	2.7101566	3.1603165
H	0.6690412	2.8758099	1.6324704
O	-3.9392499	-1.4924323	3.2346429
Ni	0.5534373	0.2969235	2.1156270
C	-0.1744792	-1.2627231	3.3461935
H	0.0041456	-0.9012518	4.3664684
C	0.9504173	-1.6169010	2.5793329
H	0.8577141	-2.2752185	1.7109448
C	2.1512322	-0.8719595	2.8178690
H	2.3529839	-0.4983717	3.8256874
H	3.0428373	-1.0725144	2.2250518
P	0.4373044	0.2289463	-0.1353324
C	-1.3063072	0.3103235	-0.6966459
C	-1.9525688	1.5427969	-0.9118381
C	-2.1010213	-0.8455012	-0.6685156
C	-3.3314674	1.6143801	-1.0817970
H	-1.3684327	2.4642730	-0.9342359
C	-3.4851780	-0.7912888	-0.8370854
H	-1.6348671	-1.8182904	-0.5010355
C	-4.1122054	0.4491195	-1.0330493
H	-3.8301665	2.5711900	-1.2384719
H	-4.0616918	-1.7133133	-0.7927069
C	1.0996451	-1.2167133	-1.0676522
C	2.2789876	-1.8120132	-0.6051552
C	0.5559238	-1.6878133	-2.2784099
C	2.9020813	-2.8523015	-1.3001476
H	2.7355782	-1.4409941	0.3114485
C	1.1580726	-2.7242724	-2.9798347
H	-0.3514987	-1.2361741	-2.6802366
C	2.3355799	-3.3188588	-2.4947569
H	3.8181244	-3.2851737	-0.9022749
H	0.7378471	-3.0905268	-3.9170312
C	1.2727942	1.5806571	-1.0611908
C	2.3580730	2.2192369	-0.4524065
C	0.9540214	1.9226827	-2.3892951
C	3.1117618	3.1827733	-1.1302136
H	2.6130275	1.9486298	0.5747845
C	1.6847074	2.8843120	-3.0727664
H	0.1234903	1.4267369	-2.8941376
C	2.7711848	3.5228775	-2.4467739
H	3.9494157	3.6587102	-0.6237291

H	1.4416707	3.1572416	-4.1001371
O	-5.4600551	0.6246798	-1.1741879
O	2.8453220	-4.3324385	-3.2567412
O	3.4249251	4.4527535	-3.2059640
C	4.5369155	5.1298602	-2.6189236
H	4.9051437	5.8187606	-3.3871119
H	4.2347080	5.7051644	-1.7274105
H	5.3395982	4.4253265	-2.3440080
C	4.0468691	-4.9615986	-2.8092587
H	3.9115460	-5.4349816	-1.8221453
H	4.2741617	-5.7325843	-3.5535001
H	4.8833401	-4.2444939	-2.7583084
C	-6.2975550	-0.5237660	-1.0208022
H	-7.3252203	-0.1560333	-1.1141911
H	-6.1054602	-1.2723644	-1.8075364
H	-6.1621387	-0.9895773	-0.0304354

6a-π,π-*cis*

C	-0.4535118	1.5832938	3.2533572
C	-1.1270057	1.9826372	2.0828520
C	-2.3857120	1.4151771	1.7353708
C	-3.4401232	1.0215354	2.7857404
C	-4.9043426	1.0396922	2.2664550
C	-4.6991259	-0.9389143	3.4036764
C	-3.2537991	-0.4459852	3.2541076
C	-2.5251195	-1.2029449	2.1506686
C	-1.3102121	-1.9100580	2.2672169
C	-0.2961037	-1.5091619	3.1798872
H	-1.0024721	1.2779105	4.1461967
H	0.5708981	1.9141908	3.4215391
H	-0.6042337	2.5839247	1.3337240
H	-2.7761398	1.6813021	0.7489883
H	-3.3572869	1.7091226	3.6427134
H	-5.5358472	1.6925954	2.8984438
H	-4.9893465	1.3778174	1.2238214
H	-5.1284682	-0.6332632	4.3804066
H	-4.8105650	-2.0262706	3.2882988
H	-2.6962869	-0.5056691	4.1983909
H	-3.1642802	-1.4556396	1.2994406
H	-1.0574702	-2.6204960	1.4743130
H	0.6743525	-2.0020794	3.1139139
H	-0.5447652	-1.1256057	4.1707196
O	-5.3956380	-0.3104063	2.3213257
Ni	-0.8620893	0.0077866	1.8626108
P	0.3725939	-0.0863746	-0.0216757
C	0.0782976	1.2850455	-1.2112270
C	0.6661673	2.5336355	-0.9531667
C	-0.8195803	1.1964771	-2.2902316
C	0.3830834	3.6568774	-1.7352518
H	1.3828383	2.6331578	-0.1350467
C	-1.1120617	2.3049508	-3.0769055
H	-1.2885496	0.2424060	-2.5329277
C	-0.5163836	3.5465819	-2.8049693
H	0.8709323	4.6022590	-1.5036860
H	-1.8002404	2.2300890	-3.9197284
C	0.0573054	-1.5974212	-1.0154583
C	1.0452395	-2.4469224	-1.5263426

C	-1.2912978	-1.9715175	-1.1972815
C	0.7147003	-3.6198263	-2.2148177
H	2.0988866	-2.2054179	-1.3819965
C	-1.6364702	-3.1206187	-1.8950436
H	-2.0748678	-1.3465673	-0.7633871
C	-0.6315996	-3.9564799	-2.4120684
H	1.5135462	-4.2576319	-2.5896172
H	-2.6794432	-3.4041415	-2.0392537
C	2.2008292	-0.0254625	0.1381931
C	3.0712341	0.1765717	-0.9425121
C	2.7538163	-0.1596668	1.4226577
C	4.4549991	0.2247118	-0.7616136
H	2.6621303	0.3114787	-1.9455572
C	4.1291840	-0.1167796	1.6213599
H	2.0735157	-0.2797978	2.2691851
C	4.9901484	0.0719124	0.5283539
H	5.1015519	0.3858765	-1.6227540
H	4.5634330	-0.2174763	2.6165428
O	-0.8714906	4.5746923	-3.6374893
O	6.3248176	0.1023918	0.8225782
O	-1.0693615	-5.0706718	-3.0739996
C	7.2431972	0.2936542	-0.2538550
H	7.0836623	1.2633482	-0.7550066
H	8.2402836	0.2796843	0.1997985
H	7.1688760	-0.5173055	-0.9978580
C	-0.0865705	-5.9574532	-3.6075172
H	0.5523510	-6.3786822	-2.8130187
H	-0.6458210	-6.7664329	-4.0902737
H	0.5479181	-5.4545771	-4.3569098
C	-0.2912477	5.8548983	-3.3953365
H	-0.7073334	6.5208593	-4.1595297
H	-0.5559587	6.2373644	-2.3948614
H	0.8074330	5.8278094	-3.4946726

Structures from Figure 3

Pre-TS-3

C	1.9833152	0.8827991	-1.7608309
C	2.2100857	1.3632111	-0.4721561
C	1.1243305	1.7259243	0.4297749
C	-0.2020131	1.5602141	-0.0132370
C	-1.4108140	1.5654681	0.8846226
C	-1.9572245	-1.1662112	-0.8547550
C	-0.7439841	-1.3797203	0.0149735
C	0.4052706	-2.0675450	-0.4357420
C	1.6012176	-2.0614018	0.3871489
C	1.6255967	-1.4389956	1.6348324
H	1.1010152	1.1402313	-2.3465181
H	2.8169232	0.4590110	-2.3189097
H	3.2182494	1.3291192	-0.0529772
H	1.3583682	1.9471334	1.4733810
H	-0.4280582	1.7203142	-1.0701961
H	-1.1693049	1.0380073	1.8193870
H	-1.6792200	2.5989788	1.1678871
H	-2.8068253	-1.7531140	-0.4457027
H	-1.7622753	-1.5135921	-1.8793364
H	-0.9502243	-1.3408263	1.0905495

H	0.4552726	-2.4752107	-1.4479293
H	2.5283407	-2.4237764	-0.0619963
H	2.5819920	-1.2858140	2.1330463
H	0.7427604	-1.3512887	2.2686251
O	-2.3725352	0.1972575	-1.0137895
Ni	0.9266231	-0.1811075	-0.0836016
C	-2.6539234	0.9187940	0.1865384
H	-3.2022940	0.2779691	0.9024064
H	-3.3406646	1.7141714	-0.1354954

Pre-TS-4

C	2.5204134	1.2884609	-0.6747011
C	1.3727833	1.4792159	-1.4602169
C	0.0766195	1.5947261	-0.8432859
C	-0.1289080	1.5526973	0.5581454
C	-1.4790486	1.2129208	1.1560918
C	-1.8591771	-1.3715486	-0.7583565
C	-0.5549124	-1.5046375	-0.0168678
C	0.6246756	-2.0633236	-0.5456631
C	1.8347617	-1.8391406	0.2117386
C	1.8017555	-1.1582571	1.4557028
H	2.6497665	1.7790352	0.2914971
H	3.4439630	0.9675806	-1.1585333
H	1.4079458	1.3337722	-2.5413973
H	-0.7786510	1.4862609	-1.5076306
H	0.5822652	2.0253898	1.2404252
H	-1.3205062	0.4337547	1.9209586
H	-1.8876128	2.0770545	1.7128535
H	-2.6467032	-1.9428690	-0.2252311
H	-1.7727007	-1.7744337	-1.7777137
H	-0.6690719	-1.4758444	1.0714320
H	0.6707961	-2.4863587	-1.5506082
H	2.7922869	-2.0845258	-0.2549306
H	2.7520912	-0.8747209	1.9061587
H	0.9763841	-1.2762164	2.1599726
O	-2.3051915	-0.0215380	-0.9528110
Ni	0.9870615	-0.0732305	-0.1656556
C	-2.6183089	0.7729585	0.1963934
H	-3.4010829	0.2711223	0.7993228
H	-3.0716941	1.6716952	-0.2470897

TS-3

C	-2.415454	1.550555	-0.289471
C	-1.099595	1.033339	0.235258
C	-2.425762	-1.525713	0.259940
C	-1.101239	-1.019913	-0.262774
C	0.211411	-1.396855	0.341316
C	1.318462	-1.919483	-0.374894
C	2.653076	-1.746326	0.121420
H	-2.406156	1.553804	-1.390777
H	-2.654786	2.584627	0.033728
H	-1.067400	0.981544	1.339544
H	-2.428536	-1.495022	1.368261
H	-2.676020	-2.558992	-0.044213
H	-1.081064	-0.981402	-1.366475
H	0.239930	-1.406103	1.440266

H	1.175109	-2.157740	-1.436074
H	3.488102	-2.000489	-0.531198
H	2.858071	-1.858628	1.191981
O	-3.489842	-0.718193	-0.269786
Ni	1.638094	0.000942	0.001930
C	0.224382	1.402738	-0.355148
H	0.261554	1.412200	-1.453552
C	1.324246	1.922023	0.374213
H	1.169136	2.161814	1.433570
C	2.664415	1.744558	-0.104944
H	2.883405	1.854626	-1.172836
H	3.491896	1.995406	0.558390
C	-3.543467	0.622747	0.212285
H	-4.515817	1.002578	-0.131682
H	-3.548175	0.624912	1.322116

TS-4

C	2.4518177	1.4433150	0.4070638
C	1.6783377	1.8193152	-0.7519402
C	0.2907491	1.5665310	-0.7402742
C	-0.3996695	1.0965830	0.4711955
C	-1.8988704	1.3078689	0.5202227
C	-1.9222838	-1.3793409	0.4618644
C	-0.4173867	-1.2085074	0.5029327
C	0.2656413	-1.7315379	-0.6949856
C	1.6445049	-2.0152092	-0.7061763
C	2.4298581	-1.6171459	0.4385377
H	2.1109605	1.7286929	1.4085830
H	3.5378927	1.4162562	0.3073758
H	2.1498269	2.1346867	-1.6853119
H	-0.2860962	1.7096826	-1.6551525
H	0.0611498	1.3782664	1.4220520
H	-2.2835943	1.0177869	1.5076147
H	-2.0875305	2.3955006	0.4395970
H	-2.3949416	-1.0500939	1.4032824
H	-2.1383553	-2.4580261	0.3625413
H	-0.0107565	-1.5000849	1.4774123
H	-0.3340213	-1.8734662	-1.5952603
H	2.1060706	-2.3652261	-1.6321460
H	3.5159225	-1.6047608	0.3336253
H	2.0903233	-1.8722986	1.4486342
O	-2.5282004	-0.7817677	-0.6824256
Ni	1.3451239	-0.0872087	-0.2219942
C	-2.7199848	0.6348556	-0.5796651
H	-3.7923074	0.8420199	-0.4012398
H	-2.4641802	1.0533134	-1.5659630

I-3

C	-2.0679878	1.3631439	-0.3678465
C	-0.7823002	0.7033066	0.1370531
C	-2.0623155	-1.4671841	0.2979698
C	-0.7825302	-0.8058835	-0.2177829
C	0.5285855	-1.3602751	0.3173896
C	1.5643871	-1.9262099	-0.4687179
C	2.9161148	-1.8915179	-0.0012806
H	-2.0762778	1.3658805	-1.4701396
H	-2.1364908	2.4102658	-0.0316747

H	-0.7602455	0.7752413	1.2417037
H	-2.0748650	-1.4412698	1.4086526
H	-2.1331878	-2.5167106	-0.0212022
H	-0.7799474	-0.8898819	-1.3192781
H	0.5944964	-1.4343433	1.4133859
H	1.3725842	-2.1011088	-1.5347877
H	3.7144311	-2.1895296	-0.6803992
H	3.1323739	-2.0504072	1.0607386
O	-3.2227526	-0.8109133	-0.2234386
Ni	2.0058918	-0.0574380	-0.0355570
C	0.5358232	1.2503693	-0.3935881
H	0.6013733	1.3239746	-1.4895845
C	1.5717356	1.8128099	0.3940414
H	1.3786936	1.9896587	1.4597250
C	2.9249373	1.7705229	-0.0706975
H	3.1441847	1.9304269	-1.1319047
H	3.7233388	2.0637251	0.6105174
C	-3.2771098	0.5704502	0.1450921
H	-4.2155799	0.9529451	-0.2789996
H	-3.3373608	0.6599523	1.2506103

I-4

C	2.5407246	1.5724541	0.3280045
C	1.5733016	1.8341599	-0.6887309
C	0.3078560	1.1876047	-0.7228259
C	-0.4783927	0.6959343	0.4977019
C	-1.8965973	1.2934134	0.5571865
C	-1.9835036	-1.3610096	0.3230563
C	-0.5336725	-0.8831516	0.4958664
C	0.3304437	-1.4376269	-0.6450281
C	1.6035438	-2.0557285	-0.5200993
C	2.5364965	-1.6898920	0.4954876
H	2.2496830	1.4479114	1.3757979
H	3.5502356	1.9596431	0.1866121
H	1.9102352	2.3127907	-1.6147549
H	-0.2631086	1.2801602	-1.6503213
H	0.0575118	1.0221561	1.4004478
H	-2.3217923	1.0980435	1.5541024
H	-1.8532024	2.3877471	0.4462079
H	-2.5642463	-1.2238178	1.2562162
H	-2.0090177	-2.4315838	0.0716767
H	-0.1526522	-1.2613930	1.4576575
H	-0.2152824	-1.6149456	-1.5758779
H	1.9750532	-2.6053078	-1.3920702
H	3.5551921	-2.0714801	0.4223904
H	2.2078918	-1.4687692	1.5164701
O	-2.5994700	-0.6869910	-0.7740933
Ni	1.8228473	-0.1070048	-0.5423684
C	-2.8187830	0.7149024	-0.5249992
H	-3.8767096	0.8748195	-0.2428173
H	-2.6545858	1.2169613	-1.4908954

E*,*E*-6h-π,π-*trans

C	-3.8227377	1.8959365	-2.2695899
C	-2.5921868	1.0269804	-1.9862663
C	-4.1504817	-0.8821986	-1.4639817

C	-2.9245816	-0.4576736	-2.2670264
C	-1.6610146	-1.3025527	-2.0783755
C	-0.8303561	-1.5874614	-3.2183781
C	0.4906881	-2.0440469	-3.0534786
H	-4.0708743	1.8719072	-3.3437801
H	-3.6370999	2.9455839	-1.9899551
H	-2.3478080	1.1178010	-0.9166737
H	-3.9204160	-0.8539788	-0.3813814
H	-4.4682867	-1.9021334	-1.7253004
H	-3.2123451	-0.5227192	-3.3348271
H	-1.6200613	-1.9727713	-1.2129180
H	-1.1651904	-1.2526981	-4.2059073
H	1.1443659	-2.1146081	-3.9225130
H	0.7397830	-2.6938985	-2.2144914
O	-5.2711058	-0.0328453	-1.7500257
Ni	0.0379767	-0.1444922	-2.1365190
C	-1.3343478	1.2892338	-2.7813476
H	-1.4196889	1.1018970	-3.8595855
C	-0.1252805	1.8476619	-2.3225373
H	-0.0804319	2.3748122	-1.3659639
C	1.0652146	1.4775947	-3.0200487
H	1.0204942	1.2921683	-4.0966213
H	2.0251140	1.8292874	-2.6455173
C	-5.0015550	1.3430082	-1.4572996
H	-5.9335548	1.8790139	-1.6854785
H	-4.7888621	1.4620569	-0.3743031
P	0.6439437	-0.2291559	0.0192677
C	-0.6864369	0.5372597	1.0206063
C	-0.7315462	1.9245860	1.2243389
C	-1.8321254	-0.2081594	1.3666251
C	-1.8712142	2.5581229	1.7306793
H	0.1356491	2.5375371	0.9740281
C	-2.9635018	0.4029185	1.8885808
H	-1.8485839	-1.2856905	1.1990592
C	-3.0000441	1.7964378	2.0602574
H	-1.8632426	3.6387761	1.8611349
H	-3.8485145	-0.1778422	2.1497621
C	2.1623308	0.6809305	0.5150967
C	3.2042479	0.7523676	-0.4152106
C	2.3892449	1.1799510	1.8115666
C	4.4399719	1.3184592	-0.0865846
H	3.0406594	0.3426593	-1.4141254
C	3.6054982	1.7554479	2.1513514
H	1.6035348	1.1100991	2.5658168
C	4.6413303	1.8309117	1.2023935
H	5.2275415	1.3549155	-0.8372961
H	3.7871592	2.1469644	3.1528803
C	0.9934433	-1.8228285	0.8729222
C	1.8162605	-2.7342250	0.1984746
C	0.6066630	-2.1339436	2.1897480
C	2.2285205	-3.9306326	0.7899964
H	2.1674936	-2.4881939	-0.8048706
C	0.9978152	-3.3247223	2.7892346
H	0.0008708	-1.4314998	2.7628504
C	1.8072610	-4.2368372	2.0921242
H	2.8710738	-4.6082417	0.2303892
H	0.6958559	-3.5690804	3.8082303

O	5.7981836	2.4144767	1.6376716
O	2.1317346	-5.3791809	2.7687637
O	-4.1755264	2.3038412	2.5404908
C	2.9640022	-6.3324617	2.1067376
H	3.0938507	-7.1571467	2.8159952
H	2.4898651	-6.7126245	1.1864883
H	3.9501840	-5.9048759	1.8591396
C	-4.2758908	3.7205350	2.6892681
H	-4.1338999	4.2378373	1.7254915
H	-5.2899513	3.9102756	3.0574783
H	-3.5439634	4.1032243	3.4204405
C	6.8863993	2.5045423	0.7172812
H	6.6202565	3.1107735	-0.1650006
H	7.6986573	2.9962172	1.2637506
H	7.2195691	1.5064101	0.3867674

E*,*E*-6h-π,π-*cis

C	0.3300236	1.8174113	2.9340119
C	-0.7889482	2.0144611	2.0815541
C	-1.9637888	1.2349054	2.1914928
C	-2.5415284	0.6477211	3.4732598
C	-3.8942636	1.2829311	3.8482014
C	-4.1408352	-1.2374001	2.9282498
C	-2.6838985	-0.8890942	3.2825365
C	-1.7130389	-1.3745535	2.1898718
C	-0.3961241	-1.8426726	2.4643102
C	0.3661987	-1.2439794	3.4879441
H	0.2090573	1.5689333	3.9892948
H	1.2570467	2.3388214	2.6939239
H	-0.6485378	2.6012729	1.1685617
H	-2.6712821	1.3014832	1.3610380
H	-1.8294659	0.8373521	4.2889912
H	-4.2107214	0.8871745	4.8263321
H	-3.7892499	2.3719662	3.9649731
H	-4.7530790	-1.3437976	3.8462705
H	-4.1959244	-2.1897686	2.3811408
H	-2.4404779	-1.4055250	4.2286231
H	-2.1906248	-1.7737588	1.2911964
H	0.0761970	-2.5350620	1.7609856
H	1.4153074	-1.5097161	3.6146093
H	-0.1152452	-0.8298992	4.3763484
O	-4.7093373	-0.2468910	2.0691755
Ni	-0.2576363	0.0821507	1.9304811
C	-4.9632748	0.9782230	2.7788735
H	-5.9676054	0.9344719	3.2434089
H	-4.9848144	1.7600543	2.0060603
P	0.6344612	-0.0461547	-0.1365612
C	-0.3797303	-1.1135508	-1.2334795
C	0.1235426	-2.1356760	-2.0450277
C	-1.7772426	-0.9224388	-1.2008816
C	-0.7256980	-2.9431645	-2.8113170
H	1.1981372	-2.3181073	-2.0848744
C	-2.6311099	-1.7012079	-1.9683184
H	-2.1915424	-0.1551554	-0.5439402
C	-2.1093040	-2.7227240	-2.7811389
H	-0.2958856	-3.7337937	-3.4241764
H	-3.7104580	-1.5494688	-1.9423209

C	2.3380049	-0.6851155	-0.3927764
C	3.0827368	-0.4601136	-1.5585431
C	2.9283404	-1.4364736	0.6377503
C	4.3742956	-0.9720960	-1.7066887
H	2.6513930	0.1334837	-2.3668348
C	4.2076724	-1.9624982	0.5044419
H	2.3708398	-1.5852200	1.5634861
C	4.9405720	-1.7333200	-0.6715617
H	4.9268942	-0.7709577	-2.6232548
H	4.6694816	-2.5441812	1.3028988
C	0.7093856	1.5412821	-1.0562952
C	1.5098286	2.5588303	-0.5143580
C	-0.0322603	1.8326457	-2.2137451
C	1.5872216	3.8231358	-1.1013774
H	2.0928150	2.3561188	0.3865702
C	0.0269358	3.0908017	-2.8059271
H	-0.6624002	1.0637203	-2.6621536
C	0.8368462	4.0959219	-2.2560034
H	2.2245880	4.5823063	-0.6512208
H	-0.5468271	3.3171871	-3.7053781
O	0.8252989	5.2976465	-2.9129340
O	-3.0309745	-3.4445501	-3.4898526
O	6.1924900	-2.2829872	-0.7064891
C	1.6313633	6.3508478	-2.3865352
H	1.4758509	7.2068283	-3.0525884
H	1.3235189	6.6243674	-1.3630514
H	2.7012378	6.0805221	-2.3842033
C	-2.5510330	-4.4983165	-4.3238071
H	-2.0281879	-5.2726290	-3.7372331
H	-3.4394848	-4.9360760	-4.7922402
H	-1.8744993	-4.1180777	-5.1080149
C	6.9837964	-2.0696212	-1.8757345
H	7.1798599	-0.9968277	-2.0413553
H	7.9316516	-2.5874416	-1.6918332
H	6.5034493	-2.4949165	-2.7728415

Structures from Figure 4

Pre-TS-5

C	-4.2849744	-1.2273209	-3.4420658
C	-4.0823955	-0.8236379	-2.1709167
C	-2.9493721	-0.0358121	-1.7178132
C	-2.8583289	0.5876835	-0.4493757
C	-3.9925871	0.7327318	0.5588261
C	-3.0051841	-1.4047273	2.5674018
C	-2.2455890	-2.1520063	1.4989848
C	-2.8733377	-2.6615814	0.3600988
C	-2.1667371	-3.0328099	-0.8417705
C	-0.7784323	-2.9758077	-0.9565135
H	-3.5762576	-0.9821713	-4.2371682
H	-5.1644640	-1.8066386	-3.7226622
H	-4.8134472	-1.0962636	-1.4050061
H	-2.2881760	0.3399797	-2.5059256
H	-2.2094634	1.4728328	-0.4200621
H	-3.6100947	1.2295221	1.4687572
H	-4.7534547	1.4118398	0.1291039

H	-2.4190613	-0.5146473	2.8479534
H	-3.0728433	-1.9998449	3.4986160
H	-1.2424602	-2.4874038	1.7747811
H	-3.9537162	-2.5765652	0.2622942
H	-2.7754692	-3.1866723	-1.7361515
H	-0.3227441	-3.1133884	-1.9376150
H	-0.1149846	-3.1590870	-0.1108701
Ni	-1.6915406	-1.0857357	-0.3590093
P	0.2120276	-0.1125562	-0.0274390
C	0.6399031	0.9217678	-1.4825065
C	1.1298125	2.2297900	-1.4121713
C	0.4082238	0.3644303	-2.7565928
C	1.3941679	2.9698347	-2.5703379
H	1.3026075	2.6958629	-0.4413989
C	0.6858653	1.0769885	-3.9141707
H	-0.0147366	-0.6409098	-2.8195178
C	1.1793328	2.3910467	-3.8289048
H	1.7625421	3.9899657	-2.4767008
C	1.6792947	-1.1994546	0.1773840
C	1.7883859	-1.9386099	1.3722911
C	2.6400436	-1.4065836	-0.8155665
C	2.8191316	-2.8474742	1.5642278
H	1.0554469	-1.7866372	2.1674495
C	3.6843489	-2.3223783	-0.6388373
H	2.5863548	-0.8463172	-1.7501573
C	3.7766690	-3.0499201	0.5545976
H	2.9065068	-3.4173995	2.4897424
H	4.4155821	-2.4531816	-1.4347256
C	0.4496962	1.0145863	1.4035260
C	1.7203660	1.4132859	1.8438918
C	-0.6694400	1.4856555	2.1071802
C	1.8767988	2.2604646	2.9431234
H	2.6098763	1.0480904	1.3278354
C	-0.5353426	2.3292193	3.2026565
H	-1.6576822	1.1640090	1.7859882
C	0.7427465	2.7242864	3.6296640
H	2.8794810	2.5435179	3.2590433
H	-1.4058603	2.6888252	3.7520112
O	0.7767460	3.5467978	4.7193067
O	4.7495974	-3.9692534	0.8367649
C	2.0539587	3.9702767	5.1992863
H	2.5998455	4.5509215	4.4368657
H	1.8488375	4.6099954	6.0645362
H	2.6707838	3.1128337	5.5166343
C	5.7388665	-4.2187648	-0.1619519
H	6.4032687	-4.9805294	0.2606446
H	5.2866434	-4.6032059	-1.0916481
H	6.3229230	-3.3105803	-0.3890012
H	0.5103713	0.6471346	-4.9006660
O	1.4046847	3.0162514	-5.0231421
C	1.8755870	4.3640926	-4.9928650
H	1.9769408	4.6673058	-6.0407197
H	1.1574905	5.0312111	-4.4871216
H	2.8565652	4.4387632	-4.4941352
O	-4.6905931	-0.4634347	0.9123064
H	-5.1042311	-1.8773399	2.2647381
H	-4.8062542	-0.2805319	2.9867917

C	-4.4490664	-0.9946164	2.2178993

Pre-TS-6

C	-4.2503411	1.4647175	3.3312539
C	-2.9373363	1.7206117	3.5000383
C	-1.8477363	1.7790075	2.5246321
C	-1.8758554	1.7293117	1.1059124
C	-3.1101531	1.7670296	0.2112407
C	-3.9611805	-1.6610365	0.6209414
C	-3.0492557	-1.5155579	1.8056985
C	-1.8175731	-2.1083165	1.8607285
C	-0.7719637	-1.7559175	2.8092021
C	-0.9412001	-0.8028726	3.8127965
H	-4.6780271	1.2150205	2.3613526
H	-4.9210936	1.4896568	4.1910496
H	-2.6002350	1.9308459	4.5214068
H	-1.0705417	2.2960824	0.6222190
H	-3.6526001	2.7048393	0.4308427
H	-2.7713436	1.8192073	-0.8393624
H	-5.0145264	-1.7005220	0.9408032
H	-3.7445487	-2.5893267	0.0660691
H	-3.4079411	-0.8929115	2.6293590
H	-1.5351750	-2.8014776	1.0630550
H	0.1908227	-2.2544960	2.6860531
H	-0.0934917	-0.5442294	4.4478864
H	-1.9248256	-0.5570001	4.2134667
Ni	-1.0385574	0.0047303	1.8131278
P	0.4794423	-0.1375586	0.2578893
C	-0.2543609	-0.4830138	-1.3847554
C	-0.6413786	0.5545766	-2.2438736
C	-0.6835369	-1.7893400	-1.7004786
C	-1.4272080	0.3152912	-3.3759252
H	-0.3407803	1.5796023	-2.0225916
C	-1.4532890	-2.0446548	-2.8262927
H	-0.4212124	-2.6182960	-1.0416950
C	-1.8392456	-0.9906349	-3.6725526
H	-1.7115245	1.1527759	-4.0106141
C	1.8440663	-1.3626361	0.4150788
C	2.4490951	-1.4681629	1.6827486
C	2.3814618	-2.1146739	-0.6352354
C	3.5408646	-2.2983208	1.8945030
H	2.0540945	-0.8717714	2.5086110
C	3.4737741	-2.9662015	-0.4368501
H	1.9531879	-2.0389764	-1.6354794
C	4.0582465	-3.0622211	0.8342048
H	4.0115561	-2.3778463	2.8747479
H	3.8599689	-3.5394853	-1.2780771
C	1.4892520	1.3747694	-0.0196310
C	2.2900493	1.5482888	-1.1554571
C	1.5548144	2.3430412	0.9950428
C	3.1206334	2.6609107	-1.2956590
H	2.2714624	0.7996943	-1.9499131
C	2.3805258	3.4546805	0.8764500
H	0.9527974	2.2023401	1.8956799
C	3.1679001	3.6233042	-0.2734384
H	3.7289057	2.7636642	-2.1928504
H	2.4339762	4.2085278	1.6623630

O	3.9442011	4.7469940	-0.3016580
O	5.1249186	-3.8591449	1.1437012
C	4.7728724	4.9606511	-1.4453482
H	4.1742605	5.0510938	-2.3672794
H	5.2976673	5.9041587	-1.2596047
H	5.5107040	4.1500053	-1.5671976
C	5.6834070	-4.6590546	0.1016324
H	6.5063676	-5.2164343	0.5622857
H	4.9427914	-5.3694897	-0.3033426
H	6.0782326	-4.0363807	-0.7189035
H	-1.7825245	-3.0557177	-3.0679746
O	-2.6103077	-1.3429165	-4.7449900
C	-3.0616701	-0.3007174	-5.6107390
H	-3.6676572	-0.7934516	-6.3789470
H	-3.6825184	0.4325832	-5.0691192
H	-2.2167016	0.2206767	-6.0910209
H	-0.9511090	2.2451819	2.9488349
O	-4.0875828	0.7386525	0.3464142
C	-3.7740146	-0.4812009	-0.3357116
H	-2.7294521	-0.4688612	-0.6762521
H	-4.4318714	-0.5771400	-1.2199378

TS-5

C	-2.5840170	-0.2954209	-3.5100698
C	-2.9310517	-0.6252452	-2.2494055
C	-2.4932420	0.0630700	-1.0202410
C	-3.5922477	0.4472962	-0.0127364
C	-5.0012825	0.6462396	-0.5530498
C	-5.2316539	-1.0864598	1.6034313
C	-3.7532337	-0.9774956	1.2668600
C	-3.1256018	-2.1284601	0.5479757
C	-1.9921439	-2.8768567	0.9389485
C	-0.9531666	-2.3478421	1.7449549
H	-1.9448212	0.5645522	-3.7198162
H	-2.9220300	-0.8824824	-4.3653276
H	-3.6062931	-1.4731513	-2.1121892
H	-1.9348412	0.9746385	-1.2971100
H	-3.2843927	1.3059465	0.5974895
H	-5.6113250	1.2586516	0.1399286
H	-4.9699030	1.1660125	-1.5235526
H	-5.5283388	-0.1698186	2.1375678
H	-5.4235694	-1.9247568	2.2957666
H	-3.1702034	-0.6427419	2.1329202
H	-3.7278924	-2.5556889	-0.2559170
H	-1.7877358	-3.7909350	0.3706400
H	-0.0396941	-2.9321222	1.8547026
H	-1.1638541	-1.6614958	2.5716585
Ni	-1.3567402	-1.1730438	0.0912504
P	0.5074229	-0.1263683	0.0641202
C	0.9157150	0.7144282	-1.5089905
C	1.5450989	1.9595563	-1.6073080
C	0.6031985	0.0234441	-2.6944423
C	1.8773603	2.5048501	-2.8508698
H	1.7755487	2.5291741	-0.7064014
C	0.9453976	0.5430672	-3.9353954
H	0.0536441	-0.9181750	-2.6338562
C	1.5890478	1.7882780	-4.0226205

H	2.3565117	3.4813799	-2.8925663
C	2.0265045	-1.1166382	0.3797901
C	2.3171173	-1.5344956	1.6938084
C	2.8786270	-1.5343716	-0.6475278
C	3.4179635	-2.3331581	1.9668276
H	1.6747877	-1.2157110	2.5158190
C	3.9874039	-2.3488651	-0.3898515
H	2.6902212	-1.2190815	-1.6743383
C	4.2619836	-2.7526302	0.9229637
H	3.6490089	-2.6490693	2.9845888
H	4.6262541	-2.6514745	-1.2177149
C	0.6125996	1.1653919	1.3571717
C	1.8260177	1.7251181	1.7807547
C	-0.5749457	1.6148123	1.9599759
C	1.8631055	2.7178427	2.7626300
H	2.7645642	1.3706218	1.3512980
C	-0.5566476	2.6009366	2.9372526
H	-1.5216442	1.1658924	1.6543251
C	0.6648847	3.1638988	3.3434708
H	2.8234459	3.1274330	3.0707846
H	-1.4756861	2.9490331	3.4092462
O	0.5815140	4.1234618	4.3105278
O	5.3161418	-3.5399312	1.2941577
C	1.7954214	4.7231356	4.7675639
H	2.3217955	5.2427659	3.9495917
H	1.4979600	5.4521386	5.5289793
H	2.4691917	3.9763792	5.2200920
C	6.1924279	-4.0065572	0.2677532
H	6.9460262	-4.6187195	0.7753136
H	5.6554747	-4.6249482	-0.4710252
H	6.6898911	-3.1698301	-0.2506886
H	0.6951928	0.0148563	-4.8554281
O	1.8770600	2.2190386	-5.2873189
C	2.5033099	3.4937700	-5.4329734
H	2.6330495	3.6399353	-6.5109600
H	1.8719660	4.3027067	-5.0284319
H	3.4895617	3.5189248	-4.9395853
O	-5.6499634	-0.6061491	-0.8170526
C	-6.1180127	-1.2767225	0.3561413
H	-7.1502560	-0.9473014	0.5903185
H	-6.1656733	-2.3400350	0.0766497

TS-6

C	-3.2058824	2.6379265	3.1539815
C	-2.2438165	2.5113766	2.2152791
C	-1.9313855	1.4591003	1.2447667
C	-2.7834263	0.3039709	0.8434077
C	-4.3046348	0.4258278	0.9485914
C	-3.3234709	-2.2814652	0.5941628
C	-2.6203073	-1.4459482	1.6595082
C	-1.3404168	-1.9438009	2.1827285
C	-0.7909924	-1.3877682	3.3834855
C	-1.3169708	-0.1897723	3.9006667
H	-3.9661637	1.8830539	3.3460161
H	-3.2355341	3.5213604	3.7920107
H	-1.5358091	3.3466579	2.1452632
H	-2.5600831	0.0321635	-0.1924590

H	-4.6637251	0.2936605	1.9878542
H	-4.6043758	1.4303272	0.6167531
H	-3.3213697	-1.2427311	2.4791475
H	-0.8525860	-2.7987593	1.7082735
H	0.1474966	-1.7972486	3.7643932
H	-0.7668868	0.3503654	4.6702240
H	-2.3793366	0.0509296	3.8452368
Ni	-0.8050572	-0.0710684	1.8381569
P	0.6764844	-0.0465865	0.2964958
C	-0.1270072	-0.1626017	-1.3447451
C	-0.4925964	0.9806520	-2.0656257
C	-0.6414705	-1.4046488	-1.7708952
C	-1.3520636	0.9040484	-3.1681184
H	-0.1079343	1.9562122	-1.7645839
C	-1.4860881	-1.4982317	-2.8656028
H	-0.3782103	-2.3100320	-1.2204881
C	-1.8581051	-0.3386506	-3.5694040
H	-1.6182856	1.8170893	-3.6977034
C	1.9470340	-1.3673931	0.2681047
C	2.4066639	-1.8447110	1.5091145
C	2.5138762	-1.8967516	-0.8974202
C	3.4024176	-2.8087567	1.5848471
H	1.9665985	-1.4383557	2.4219358
C	3.5103507	-2.8757073	-0.8399676
H	2.1679450	-1.5530491	-1.8738377
C	3.9614217	-3.3338295	0.4070935
H	3.7633881	-3.1792569	2.5447148
H	3.9238853	-3.2706182	-1.7664608
C	1.6677536	1.4936294	0.1792100
C	2.6082321	1.7102528	-0.8354711
C	1.4844142	2.4917447	1.1500990
C	3.3477283	2.8927587	-0.8964455
H	2.7700686	0.9467146	-1.5986380
C	2.2129976	3.6747071	1.1049950
H	0.7531250	2.3158573	1.9430879
C	3.1492048	3.8839206	0.0795702
H	4.0705852	3.0313174	-1.6986027
H	2.0757988	4.4541040	1.8551006
O	3.8143545	5.0774780	0.1175324
O	4.9275910	-4.2839295	0.5838294
C	4.7846305	5.3366932	-0.8976260
H	4.3279955	5.3441158	-1.9015782
H	5.1886826	6.3304999	-0.6755354
H	5.6023120	4.5966517	-0.8740851
C	5.5322661	-4.8480154	-0.5803982
H	6.2673243	-5.5722030	-0.2124615
H	4.7905338	-5.3681801	-1.2096536
H	6.0460898	-4.0791758	-1.1816312
H	-1.8920106	-2.4571744	-3.1880549
O	-2.7106466	-0.5334199	-4.6201023
C	-3.1564586	0.6175833	-5.3369841
H	-3.8395705	0.2426910	-6.1071084
H	-3.6968326	1.3183336	-4.6785026
H	-2.3164002	1.1453038	-5.8195576
H	-1.4001858	1.8800963	0.3823938
H	-2.8030134	-2.1994281	-0.3709541
H	-3.3077108	-3.3457621	0.8851870

O	-4.9615200	-0.4882969	0.0707073
C	-4.7868178	-1.8553027	0.4451164
H	-5.3134161	-2.0452817	1.4046751
H	-5.2883771	-2.4400437	-0.3390207

***E*,*Z*-6h-π,π-cis**

C	-4.0027740	-0.5465556	-3.5656868
C	-2.4587158	-0.6133502	-3.6190647
C	-2.6631775	-1.9405767	-1.4485293
C	-1.9052738	-1.8075327	-2.7800736
C	-0.4305170	-1.6029305	-2.4606130
C	0.4901950	-1.0018672	-3.4007327
C	1.7442153	-0.5177114	-3.0505724
H	-4.4159231	-1.3412520	-4.2078103
H	-4.3514357	0.4171169	-3.9686924
H	-2.3697320	-1.0905842	-0.8017436
H	-2.3736425	-2.8662105	-0.9303955
H	-2.0861497	-2.7461633	-3.3407605
H	-0.0198808	-2.3061891	-1.7282574
H	0.1350147	-0.7703881	-4.4102919
H	2.3359973	0.0359884	-3.7780118
H	2.2650469	-0.8423306	-2.1503095
O	-4.0819208	-1.9812335	-1.5966505
Ni	-0.1620553	0.3342308	-1.9538585
C	-1.7179014	0.6765859	-3.2768975
H	-1.2344120	1.1518266	-4.1390792
C	-1.7546588	1.4742847	-2.1086658
H	-2.4864440	1.3306342	-1.3105733
C	-0.6275605	2.3513111	-1.9370746
H	-0.1815995	2.8232227	-2.8179148
H	-0.5434124	2.9230905	-1.0117282
C	-4.5547944	-0.7555856	-2.1586558
H	-5.6517678	-0.8276296	-2.1733874
H	-4.2796367	0.0914278	-1.4968161
P	0.4351321	0.1473333	0.1469885
C	-0.6116585	1.1705668	1.2552701
C	-0.1032528	2.2417373	1.9988034
C	-2.0036689	0.9490942	1.2899034
C	-0.9393519	3.0657865	2.7600280
H	0.9667991	2.4499824	1.9871665
C	-2.8453475	1.7484868	2.0502246
H	-2.4348699	0.1292477	0.7133757
C	-2.3183453	2.8194881	2.7918249
H	-0.5021556	3.8902070	3.3205709
H	-3.9202596	1.5687815	2.0794213
C	2.1312530	0.7381291	0.5196850
C	2.7523560	1.6025228	-0.3875103
C	2.8169168	0.3943574	1.6997593
C	4.0230385	2.1274527	-0.1373935
H	2.2248365	1.8513837	-1.3119000
C	4.0819601	0.9031701	1.9602589
H	2.3518886	-0.2830188	2.4178254
C	4.6939901	1.7767774	1.0431146
H	4.4777967	2.7954801	-0.8670010
H	4.6237732	0.6389250	2.8690854
C	0.4360622	-1.5127162	0.9327990
C	1.3317029	-2.4687466	0.4297168

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C    -0.4479838   -1.9125242    1.9489715
C     1.3530475   -3.7794762    0.9086933
H     2.0406724   -2.1875630   -0.3509763
C    -0.4458353   -3.2173398    2.4312032
H    -1.1450074   -1.1948574    2.3811125
C     0.4512287   -4.1635328    1.9131703
H     2.0676217   -4.4866837    0.4913506
H    -1.1323073   -3.5256317    3.2203739
O     5.9383750    2.2202648    1.3925143
O     0.3716474   -5.4183485    2.4508288
O    -3.2274475    3.5542069    3.4999566
C     1.2653909   -6.4142554    1.9529783
H     1.0315694   -7.3287565    2.5090638
H     1.1121069   -6.5929312    0.8752833
H     2.3185638   -6.1382875    2.1308033
C    -2.7412036    4.6594846    4.2624761
H    -2.2580066    5.4130245    3.6180832
H    -3.6221261    5.1015933    4.7405431
H    -2.0289313    4.3330208    5.0387915
C     6.6089608    3.1037040    0.4921728
H     6.0431570    4.0392730    0.3474988
H     7.5727085    3.3308538    0.9609291
H     6.7816951    2.6271245   -0.4872882
H    -2.1935758   -0.8184195   -4.6677040
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E*,*Z*-6h-π,π-*trans

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C    -3.8227377    1.8959365   -2.2695899
C    -2.5921868    1.0269804   -1.9862663
C    -4.1504817   -0.8821986   -1.4639817
C    -2.9245816   -0.4576736   -2.2670264
C    -1.6610146   -1.3025527   -2.0783755
C    -0.8303561   -1.5874614   -3.2183781
C     0.4906881   -2.0440469   -3.0534786
H    -4.0708743    1.8719072   -3.3437801
H    -3.6370999    2.9455839   -1.9899551
H    -2.3478080    1.1178010   -0.9166737
H    -3.9204160   -0.8539788   -0.3813814
H    -4.4682867   -1.9021334   -1.7253004
H    -3.2123451   -0.5227192   -3.3348271
H    -1.6200613   -1.9727713   -1.2129180
H    -1.1651904   -1.2526981   -4.2059073
H     1.1443659   -2.1146081   -3.9225130
H     0.7397830   -2.6938985   -2.2144914
O    -5.2711058   -0.0328453   -1.7500257
Ni    0.0379767   -0.1444922   -2.1365190
C    -1.3343478    1.2892338   -2.7813476
H    -1.4196889    1.1018970   -3.8595855
C    -0.1252805    1.8476619   -2.3225373
H    -0.0804319    2.3748122   -1.3659639
C     1.0652146    1.4775947   -3.0200487
H     1.0204942    1.2921683   -4.0966213
H     2.0251140    1.8292874   -2.6455173
C    -5.0015550    1.3430082   -1.4572996
H    -5.9335548    1.8790139   -1.6854785
H    -4.7888621    1.4620569   -0.3743031
P     0.6439437   -0.2291559    0.0192677
C    -0.6864369    0.5372597    1.0206063
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C	-0.7315462	1.9245860	1.2243389
C	-1.8321254	-0.2081594	1.3666251
C	-1.8712142	2.5581229	1.7306793
H	0.1356491	2.5375371	0.9740281
C	-2.9635018	0.4029185	1.8885808
H	-1.8485839	-1.2856905	1.1990592
C	-3.0000441	1.7964378	2.0602574
H	-1.8632426	3.6387761	1.8611349
H	-3.8485145	-0.1778422	2.1497621
C	2.1623308	0.6809305	0.5150967
C	3.2042479	0.7523676	-0.4152106
C	2.3892449	1.1799510	1.8115666
C	4.4399719	1.3184592	-0.0865846
H	3.0406594	0.3426593	-1.4141254
C	3.6054982	1.7554479	2.1513514
H	1.6035348	1.1100991	2.5658168
C	4.6413303	1.8309117	1.2023935
H	5.2275415	1.3549155	-0.8372961
H	3.7871592	2.1469644	3.1528803
C	0.9934433	-1.8228285	0.8729222
C	1.8162605	-2.7342250	0.1984746
C	0.6066630	-2.1339436	2.1897480
C	2.2285205	-3.9306326	0.7899964
H	2.1674936	-2.4881939	-0.8048706
C	0.9978152	-3.3247223	2.7892346
H	0.0008708	-1.4314998	2.7628504
C	1.8072610	-4.2368372	2.0921242
H	2.8710738	-4.6082417	0.2303892
H	0.6958559	-3.5690804	3.8082303
O	5.7981836	2.4144767	1.6376716
O	2.1317346	-5.3791809	2.7687637
O	-4.1755264	2.3038412	2.5404908
C	2.9640022	-6.3324617	2.1067376
H	3.0938507	-7.1571467	2.8159952
H	2.4898651	-6.7126245	1.1864883
H	3.9501840	-5.9048759	1.8591396
C	-4.2758908	3.7205350	2.6892681
H	-4.1338999	4.2378373	1.7254915
H	-5.2899513	3.9102756	3.0574783
H	-3.5439634	4.1032243	3.4204405
C	6.8863993	2.5045423	0.7172812
H	6.6202565	3.1107735	-0.1650006
H	7.6986573	2.9962172	1.2637506
H	7.2195691	1.5064101	0.3867674

Structures from Figure S5

TS-5'$_{cis}$ yielding to compound *E*,*E*-6h-π,π-*cis*

C	-2.7873459	-0.2912903	-0.8497501
C	-3.5673336	0.0733747	0.3929658
C	-4.9525744	0.6687431	0.1891939
C	-5.3321375	-1.8084315	1.3768377
C	-3.8271785	-1.6005938	1.3664361
C	-3.0767056	-2.6167716	0.5711617
C	-1.8662766	-3.2656377	0.9071787
C	-0.8667645	-2.6711641	1.7145690

H	-3.0120304	0.6695047	1.1250951
H	-5.3112528	1.0551273	1.1566609
H	-4.8948413	1.5384362	-0.4894069
H	-5.8182781	-1.1142369	2.0890371
H	-5.5896777	-2.8346524	1.6889615
H	-3.4112111	-1.4172375	2.3650923
H	-3.6548434	-3.0736052	-0.2340858
H	-1.5875201	-4.1330449	0.2990214
H	0.0946728	-3.1769772	1.7975960
H	-1.1246214	-2.0264175	2.5614442
O	-5.8719225	-1.6677452	0.0600565
Ni	-1.4091044	-1.4817620	0.1131127
C	-5.9913980	-0.3094589	-0.3928096
H	-7.0077044	0.0621210	-0.1561428
H	-5.8940134	-0.3611342	-1.4852592
P	0.4289599	-0.4014269	-0.0295668
C	0.6142881	0.6686985	-1.5048260
C	1.2569049	1.9108821	-1.5170053
C	0.0963691	0.1690789	-2.7150620
C	1.4055297	2.6366397	-2.7030680
H	1.6421405	2.3381742	-0.5905658
C	0.2530100	0.8694179	-3.9031405
H	-0.4642537	-0.7683762	-2.7087219
C	0.9142156	2.1089124	-3.9066345
H	1.9018924	3.6051300	-2.6751268
C	1.9354791	-1.4553472	-0.1271650
C	2.4624911	-2.0308394	1.0460499
C	2.5413659	-1.7767268	-1.3464767
C	3.5520185	-2.8885594	0.9995221
H	2.0204716	-1.7868496	2.0129590
C	3.6342933	-2.6477514	-1.4110585
H	2.1682797	-1.3393748	-2.2730392
C	4.1452431	-3.2098789	-0.2340472
H	3.9661694	-3.3260517	1.9083901
H	4.0764247	-2.8714293	-2.3803202
C	0.7913701	0.6759641	1.4042875
C	2.0727084	1.1683335	1.6874981
C	-0.2605613	1.0208424	2.2699790
C	2.3048182	1.9958293	2.7884673
H	2.9129762	0.8883537	1.0499845
C	-0.0489025	1.8435523	3.3683308
H	-1.2557827	0.6179947	2.0735135
C	1.2377972	2.3414846	3.6337080
H	3.3140325	2.3557022	2.9812277
H	-0.8622729	2.1095412	4.0437680
O	1.3481121	3.1382883	4.7363538
O	5.2084796	-4.0669038	-0.1750549
C	2.6381437	3.6613021	5.0594198
H	3.0274247	4.3027125	4.2511555
H	2.4963863	4.2628409	5.9638067
H	3.3604357	2.8542653	5.2665647
C	5.8412939	-4.4275640	-1.4036094
H	6.6502571	-5.1142504	-1.1314594
H	5.1403083	-4.9399961	-2.0837741
H	6.2656093	-3.5462938	-1.9135848
H	-0.1526315	0.4868429	-4.8398896
O	1.0135321	2.7237841	-5.1230400

C	1.6525371	3.9996033	-5.1775540
H	1.6176780	4.3047792	-6.2291482
H	1.1199348	4.7447521	-4.5630953
H	2.7037770	3.9399291	-4.8491245
C	-2.4818876	0.8906710	-1.6789177
C	-2.2856883	2.1596580	-1.2694593
H	-2.2995215	2.4410112	-0.2142494
H	-2.4238025	0.7088483	-2.7560087
H	-2.0582083	2.9515453	-1.9831475
H	-3.3572599	-1.0071726	-1.4591857

TS-6'$_{trans}$ yielding to compound *E,E*-6h-π,π-*trans*

C	-1.9870405	1.2446432	2.0992727
C	-2.9878024	0.4061112	1.3851006
C	-4.4149352	0.5478269	1.9173983
C	-3.8595016	-1.9237404	0.3331852
C	-2.9246933	-1.5285348	1.4745802
C	-1.6491284	-2.2603668	1.4901535
C	-0.8275022	-2.2315016	2.6594802
C	-1.1073561	-1.3065726	3.6874200
H	-2.9730233	0.5761407	0.3041889
H	-4.4245669	0.3929000	3.0083379
H	-4.7008793	1.5980557	1.7473271
H	-4.3268158	-2.8972352	0.5937340
H	-3.2907793	-2.0624934	-0.5981618
H	-3.4248532	-1.6042914	2.4485111
H	-1.3663126	-2.8902685	0.6429139
H	0.1140448	-2.7849330	2.6405247
H	-0.3648127	-1.1430565	4.4676302
H	-2.1337286	-1.0618867	3.9714821
O	-4.8770135	-0.9704926	0.0309006
Ni	-0.9630856	-0.4230007	1.7468586
C	-5.4242548	-0.4034360	1.2234619
H	-5.7516340	-1.2107990	1.9077885
H	-6.3232641	0.1416927	0.9069029
P	0.4318611	-0.0465963	0.1705569
C	-0.2543909	0.6998548	-1.3557246
C	0.2283280	1.8615750	-1.9648851
C	-1.4301448	0.1224323	-1.8732379
C	-0.4273896	2.4351379	-3.0601116
H	1.1167481	2.3534857	-1.5690704
C	-2.0902355	0.6715593	-2.9623703
H	-1.8402134	-0.7656460	-1.3900926
C	-1.5918314	1.8405499	-3.5646389
H	-0.0284500	3.3489067	-3.4969945
C	1.2744510	-1.5618366	-0.4426417
C	2.0386182	-2.2937586	0.4884934
C	1.1663560	-2.0612207	-1.7434593
C	2.6730244	-3.4738693	0.1296098
H	2.1436267	-1.9140535	1.5069746
C	1.7918909	-3.2571378	-2.1191601
H	0.5909776	-1.5130050	-2.4904629
C	2.5498913	-3.9691043	-1.1810606
H	3.2731157	-4.0361034	0.8458593
H	1.6839023	-3.6133996	-3.1422640
C	1.8703386	1.0015105	0.6114706

C	2.9995061	1.1156291	-0.2107558
C	1.8675009	1.6740259	1.8445156
C	4.0935220	1.8986023	0.1650870
H	3.0349101	0.5742761	-1.1581536
C	2.9472690	2.4569556	2.2340557
H	1.0032609	1.5482215	2.5001042
C	4.0662697	2.5790284	1.3937623
H	4.9572440	1.9628947	-0.4942750
H	2.9543147	2.9791255	3.1912653
O	5.0776240	3.3692534	1.8649622
O	3.2072729	-5.1423934	-1.4346591
C	6.2417423	3.5217233	1.0526340
H	5.9987792	3.9818332	0.0799009
H	6.9095530	4.1865075	1.6115897
H	6.7464279	2.5556897	0.8830904
C	3.1153782	-5.6838185	-2.7519487
H	3.7042458	-6.6074970	-2.7366736
H	2.0717264	-5.9203990	-3.0207006
H	3.5368113	-4.9944739	-3.5032987
H	-3.0066539	0.2284611	-3.3520849
O	-2.3179323	2.3172361	-4.6209806
C	-1.8713988	3.5209296	-5.2449535
H	-2.5883225	3.7238896	-6.0480598
H	-1.8675579	4.3657986	-4.5358884
H	-0.8629637	3.4030430	-5.6766364
C	-1.4995294	2.4953680	1.5124634
C	-1.7836431	3.0285123	0.3080055
H	-2.4499008	2.5457328	-0.4084767
H	-0.8211782	3.0570269	2.1633844
H	-1.3163160	3.9585484	-0.0139720
H	-2.1654713	1.3375631	3.1789282