Supporting information

Molybdenum(VI) borano-imido complexes and their application as Lewis acid catalysts in homocoupling of diazo compounds

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Experimental Part

Experiments were performed under dry argon atmosphere using standard Schlenk-type glassware and/or argon-filled glovebox, unless stated otherwise. Reaction solvents hexane, toluene and tetrahydrofuran were dried by refluxing over sodium metal in the presence of benzophenone ketyl radical under argon atmosphere. Dichloromethane was purified by distillation from CaH_2 under argon atmosphere. Dry solvents were stored over activated 4Å molecular sieves. Solvents used for extractions and/or column chromatography were used as received. Deuterated solvents were distilled from CaH_2 and stored over 4Å molecular sieves under argon atmosphere. All chemicals were purchased from commercially available resources (Sigma-Aldrich, BLD-Pharm, TCI, ABCR, Fluorochem) and used as received, unless stated otherwise. Compound **1**,[S1] $[MoCl_4(thf)_2]$,[S2] and $MesN_3$[S3] were prepared according to previously reported literature procedures.

CAUTION: Organic azides and diazo compounds employed in this work are toxic and potentially explosive. All procedures were therefore carried out in small scale in the glovebox or in well-ventilated fume hood using appropriate protective equipment and following standard safety protocols. No explosive decomposition was observed in our experiments; however, strict safety measures should always be followed.

NMR spectra were recorded on JEOL Delta 600 spectrometer at 20 °C. ^1H and ^{13}C NMR chemical shifts (δ in ppm) are given relative to TMS and referenced to the residue solvent signal ($CDCl_3$: $\delta_H = 7.26$, $\delta_C = 77.0$, C_6D_6: $\delta_H = 7.16$, $\delta_C = 128.4$). ^{11}B and ^{19}F are referenced according to the primary reference for the unified chemical shift scale following IUPAC recommendation [R.K. Harris. E.D. Becker, S.M. Cabral de Menezes, R. Goodfellow, P. Granger *Pure Appl. Chem.* **2001**, *73*, 1795-1818]. The multiplicity of the signals is indicated as s, d, t, q or m for singlets, doublets, triplets, quartets or multiplets, coupling constants *J* are given in Hertz as positive values regardless of their individual signs. Assignment of the peaks was supported by 2D experiments (COSY, HSQC and HMBC). MestreNova software package was used for analysing the spectra.

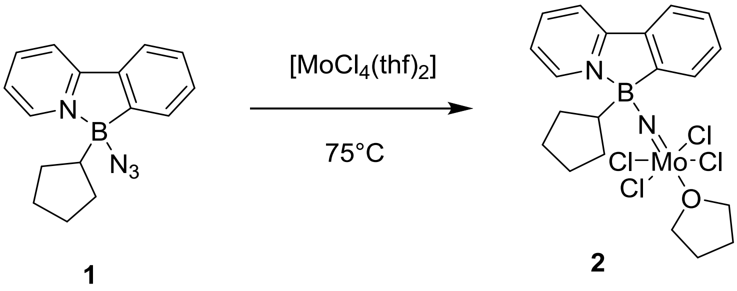
Elemental Analysis was performed on FlashSmart™ Elemental Analyzer. Tin capsules were filled with samples and sealed in glovebox atmosphere. Mass spectrometry measurements were performed on Orbitrap Exploris™ 120 instrument using electrospray ionization. Infrared spectra were collected on Nexus 670 FT-IR spectrometer. Air stable samples were analysed by ATR method, samples sensitive to ambient conditions were measured as KBr pellets prepared in glovebox atmosphere. Samples were measured in range 4000-400 cm^{-1} and the relative intensities are given in parentheses (s, m, w for strong, medium and weak).

X-ray diffraction analysis of the XXX was performed with a Rigaku XtaLAB Synergy S diffractometer equipped with Mo (Mo/Kα radiation; $\lambda = 0.71073$ Å) and Cu (Cu/Kα radiation; $\lambda = 1.54184$ Å) with micro-focus X-ray source and Hybrid Pixel Array Detector (HyPix-6000HE). Oxford Cryosystems (Cryostream 800) cooling device was used for data collection at a temperature of 100 K. CrysAlisPro software[S4] was used for data collection and cell refinement, data reduction and absorption correction. Data were corrected for absorption effects using empirical absorption correction (spherical harmonics), implemented in SCALE3 ABSPACK scaling algorithm; numerical absorption correction based on gaussian integration over a multifaceted crystal model was applied as described by Coppens *et al.* [S5, S6] where appropriate. The structures of prepared compounds were solved with the ShelXT[S7] structure solution program using Intrinsic Phasing and refined with the refinement package using SHELXL[S8] Least Squares minimisation implemented in Olex2.[S9] Anisotropic displacement parameters were refined for all non-H atoms. The hydrogen atoms were calculated to idealised positions. For crystallographic data and structure refinement see ESI tables. Molecular graphic for all crystal structures was generated using DIAMOND software.[S10]

Crystallographic data for structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. **2520309-2520319**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EY, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Synthesis of Molybdenum complexes

Preparation of **2**



Solution of boron azide[S1] **1** (276 mg, 1.0 mmol) in benzene (10 mL) was added to a suspension of $[MoCl_4(thf)_2]$[S2] (400 mg, 1.05 mmol) in benzene (15 mL). The resulting mixture was placed into an oil bath preheated to 75 °C and stirred for 5 hours. After cooling to room temperature, the mixture was filtered via cannula and the volatiles were removed *in vacuo*. The solid residue was washed with a small amount of hexane and dried *in vacuo* to give complex **2** in the form of a brown-red solid (480 mg, 0.86 mmol, 86% yield).

Elemental analysis calculated for $C_{20}H_{25}BCl_4MoN_2O$ (558.0) C 43.05, H 4.52, N 5.02; found C 43.50, H 4.89, N 5.02.

IR (KBr) ν: 3056 (w), 2941 (m), 2858 (m), 1621 (s), 1561 (w), 1485 (s), 1447 (m), 1330 (w), 1309 (w), 1244 (w), 1162 (m), 1127 (s), 1074 (m), 1019 (m), 921 (w), 864 (s), 765 (s), 743 (s), 679 (m), 635 (w), 550 (w), 501 (w), 452 (w), 414 (w) cm^{-1}.

^{1}H NMR (600 MHz, C_6D_6, 293K): [8.72, 7.10, 6.91, 6.43](each br, 1H, pyridyl), [8.18 (d, $^3J_{HH}$ = 7.2 Hz), 7.32 (br), 7.26 (dd, $^3J_{HH} \approx {}^3J_{HH}$ = 7.2 Hz), 6.91 (br)](each 1H, C_6H_4), [4.39, 1.38](each br, 4H, thf), [2.68, 2.33, 1.98, 1.78, 1.70, 1.53, 1.48, 1.42, 1.08](each m, 1H, cyclopentyl).

^{13}C{^{1}H} NMR (151 MHz, C_6D_6, 293K): [157.5 (*i*-C), 143.6 (CH), 143.5 (CH), 122.7 (CH), 119.2 (CH)](pyridyl), [150.1 (br, C-B), 137.6 (*i*-C), 132.3 (CH), 131.7 (CH), 128.6 (CH), 123.0 (CH)], [71.1, 25.4](thf), [35.9 (br, CH-B), 29.5 (CH_2), 29.2 (CH_2), 27.6 (CH_2), 26.9 (CH_2)](cyclopentyl).

^{11}B{^{1}H} NMR (193 MHz, C_6D_6, 293K): 8.0 ($\nu_{1/2} \approx$ 450 Hz).

^{11}B NMR (193 MHz, C_6D_6, 293K): 8.0 ($\nu_{1/2} \approx$ 470 Hz).

Crystal structure determination of **2** [KSK457_gg]

A crystal suitable for SC-XRD structure determination was obtained by slow diffusion of hexane into a dichloromethane solution of **2** in an argon-filled glovebox.

Crystal Data for $C_{20}H_{25}BCl_4MoN_2O$ (M =557.97 g/mol): triclinic, space group P-1 (no. 2), a = 9.4421(5) Å, b = 10.6384(9) Å, c = 12.3347(3) Å, α = 75.817(6)°, β = 89.591(4)°, γ = 76.111(5)°, V = 1164.36(12) Å^3, Z = 2, T = 100.00(12) K, μ(Cu Kα) = 8.943 mm^{-1}, $Dcalc$ = 1.591 g/cm^3, 27278 reflections measured ($7.404° \leq 2\Theta \leq 133.186°$), 4091 unique ($R_{\mathrm{int}}$ = 0.1551, R_{sigma} = 0.0697) which were used in all calculations. The final R_1 was 0.0922 (I > 2σ(I)) and wR_2 was 0.2995 (all data). **CCDC**: 2520316

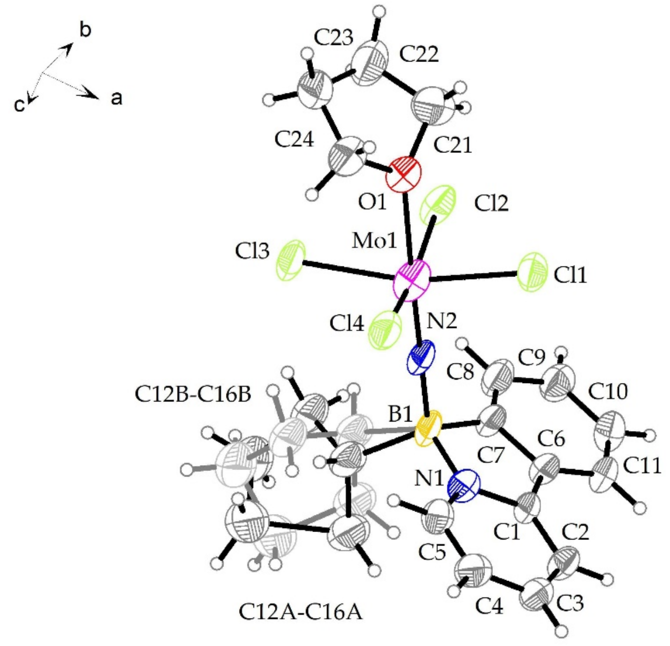


Figure S1: Crystal structure of **2** (thermal ellipsoids shown at 30 % probability level), minor disorder is shown as transparent..

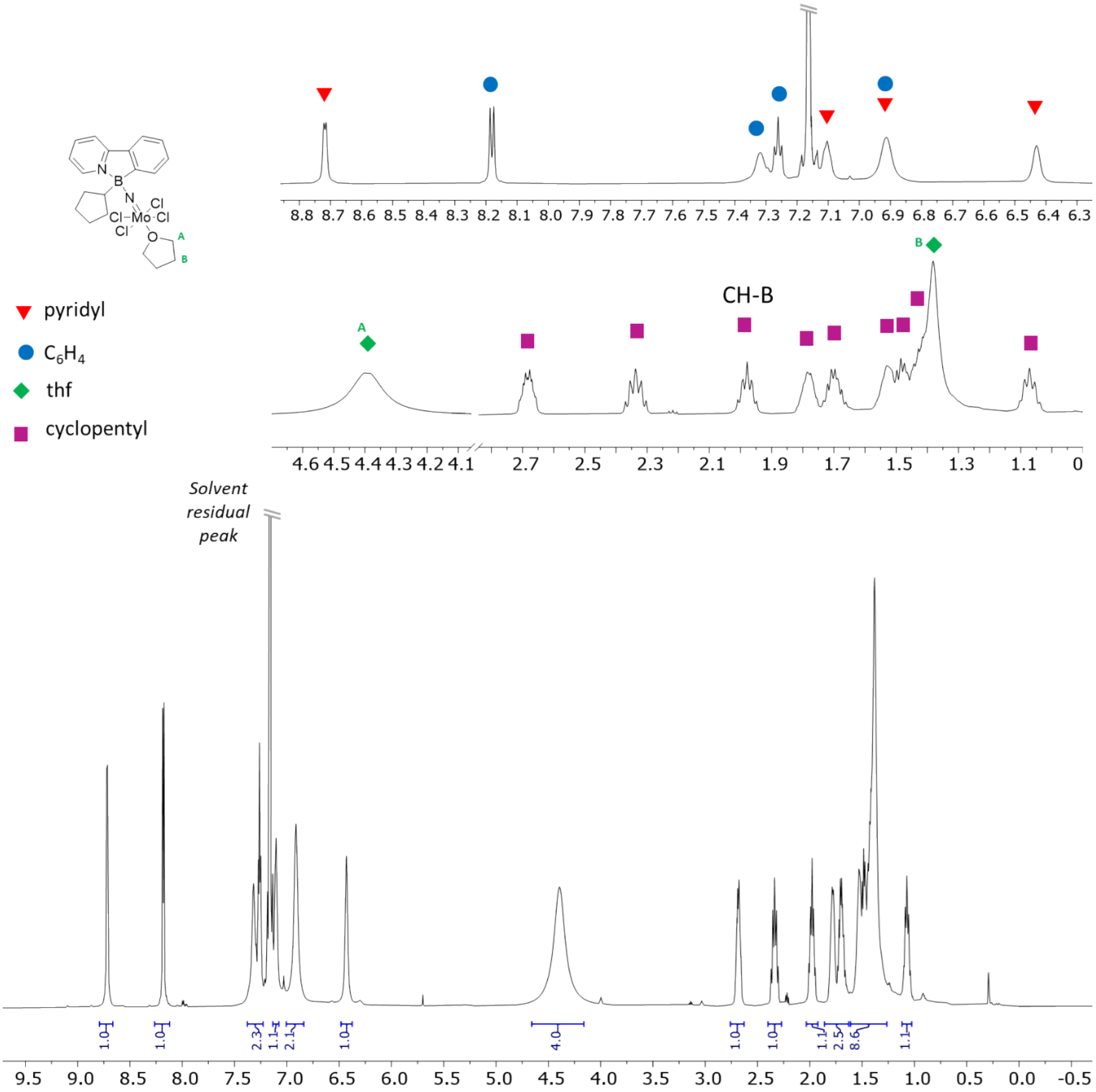


Figure S2: **^{1}H NMR** spectrum (600 MHz, C_6D_6) of compound **2**.

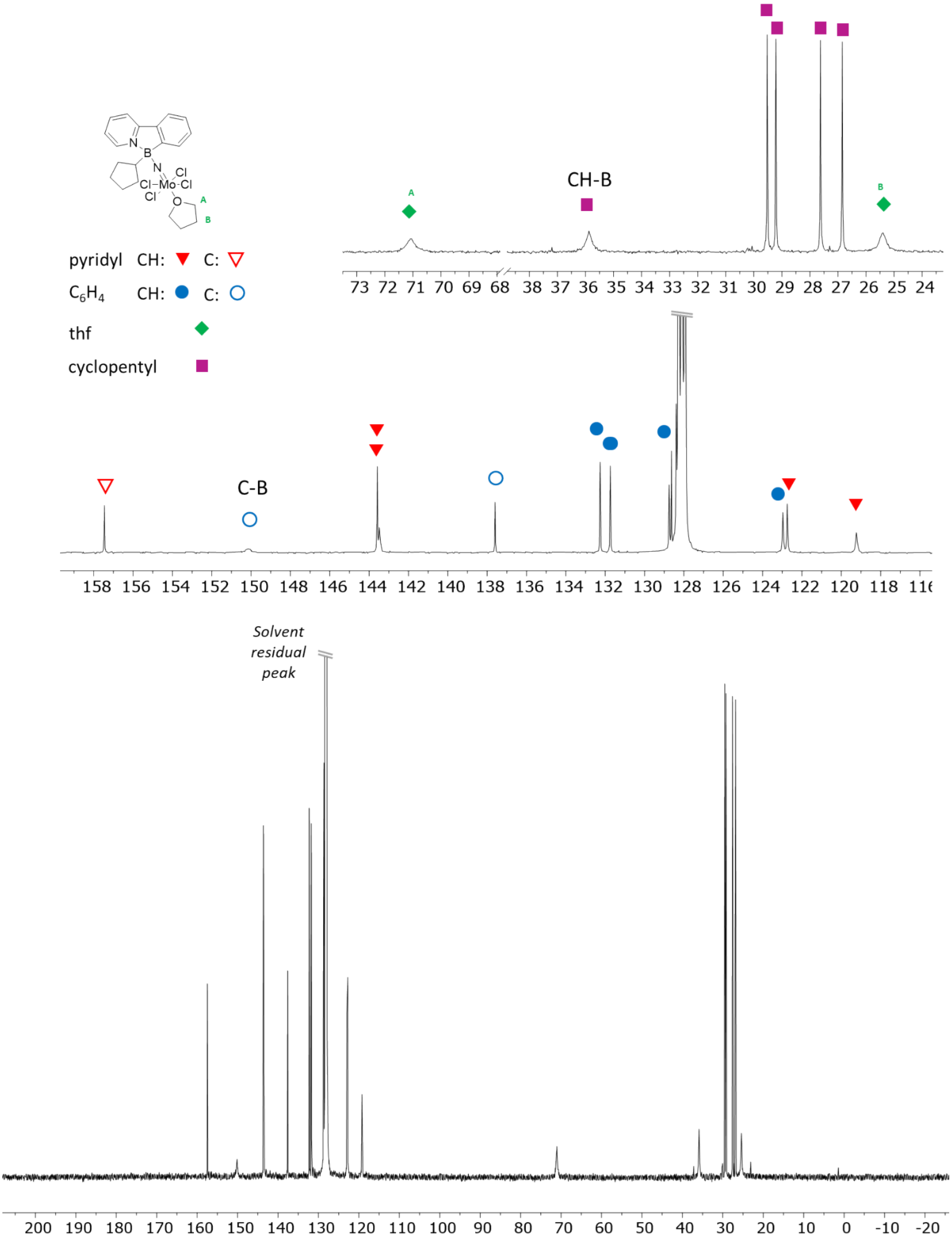


Figure S3: **^{13}C{^{1}H} NMR** spectrum (151 MHz, C_6D_6) of compound **2**.

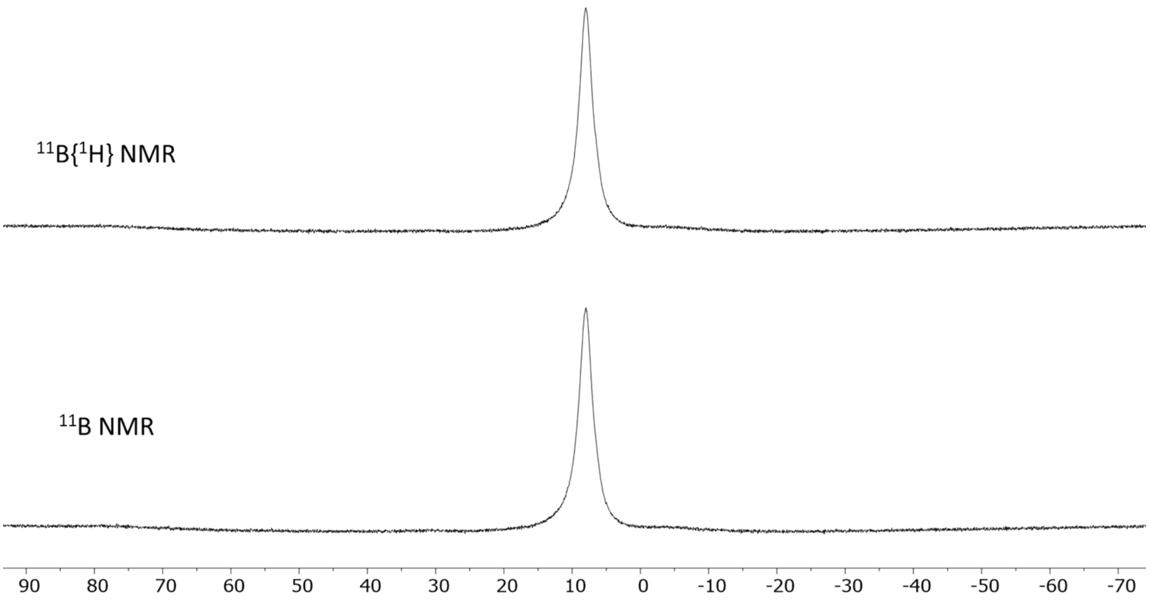
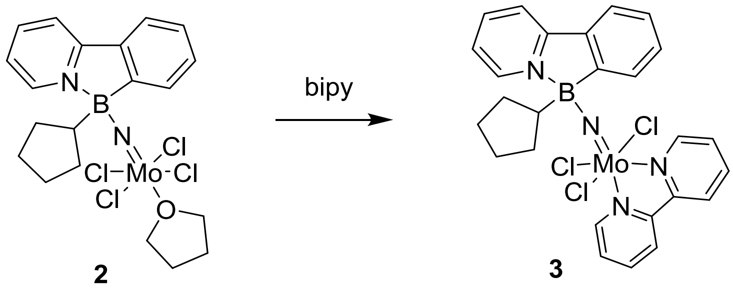


Figure S4: **^{11}B** and **^{11}B{^{1}H} NMR** spectra (151 MHz, C_6D_6) of compound **2**.

Preparation of **3**



Molybdenum complex **2** (55.8 mg, 0.10 mmol) and 2,2′-bipyridine (15.6 mg, 0.10 mmol) were dissolved in benzene (3 mL) and the resulting solution was stirred at room temperature for 60 min, during which the mixture gradually turned grey. The volatiles were removed *in vacuo* and the residue was dissolved in a minimal amount of dichloromethane (2 mL), filtered, and carefully layered with hexane (10 mL). After standing for three days, grey crystals formed. The crystals were collected by filtration, washed with hexane, and dried *in vacuo* to yield compound **3** (30.5 mg, 0.050 mmol, 50% yield).

Elemental analysis calculated for $C_{26}H_{25}N_4BCl_3Mo\cdot0.6\ CH_2Cl_2$: C 48.59, H 4.02, N 8.52; found C 48.57, H 3.68, N 8.77.

HRMS calculated for $C_{26}H_{25}N_4BCl_2Mo^+$ $[M–Cl]^+$: 572.0595, found 572.0579 and $C_{26}H_{25}N_4BCl_3MoNa^+$ $[M+Na]^+$ 630.0177, found 630.0159.

IR (KBr) ν: 3109 (w), 3066 (w), 2942 (m), 2858 (m), 1619 (s), 1598 (s), 1570 (m), 1561 (m), 1485 (s), 1471 (s), 1442 (s), 1329 (w), 1312 (w), 1278 (w), 1241 (w), 1222 (w), 1177 (s), 1160 (s), 1124 (s), 1103 (s), 1071 (s), 1061 (s), 1044 (w), 1025 (s), 1015 (s), 939 (w), 908 (w), 813 (w), 770 (s), 745 (s), 732 (s), 701 (w), 655 (w), 650 (w), 636 (m), 619 (w), 415 (w) cm^{-1}.

Crystal structure determination of **3** [KSK495-gg]

A crystal suitable for SC-XRD structure determination was taken from the reaction batch (slow diffusion of hexane into the dichloromethane solution of **3** in an argon-filled glovebox).

Crystal Data for $C_{27}H_{27}BCl_5MoN_4$ (M =691.52 g/mol): monoclinic, space group P2$_1$/c (no. 14), a = 13.9751(4) Å, b = 10.6445(2) Å, c = 19.6815(5) Å, β = 92.883(2)°, V = 2924.07(12) Å^3, Z = 4, T = 99.99(10) K, μ(Cu Kα) = 8.068 mm^{-1}, $Dcalc$ = 1.571 g/cm^3, 17665 reflections measured (6.332° ≤ 2Θ ≤ 133.192°), 5166 unique (R_{int} = 0.0461, R_{sigma} = 0.0423) which were used in all calculations. The final R_1 was 0.0403 (I > 2σ(I)) and wR_2 was 0.1083 (all data). **CCDC:** 2520311

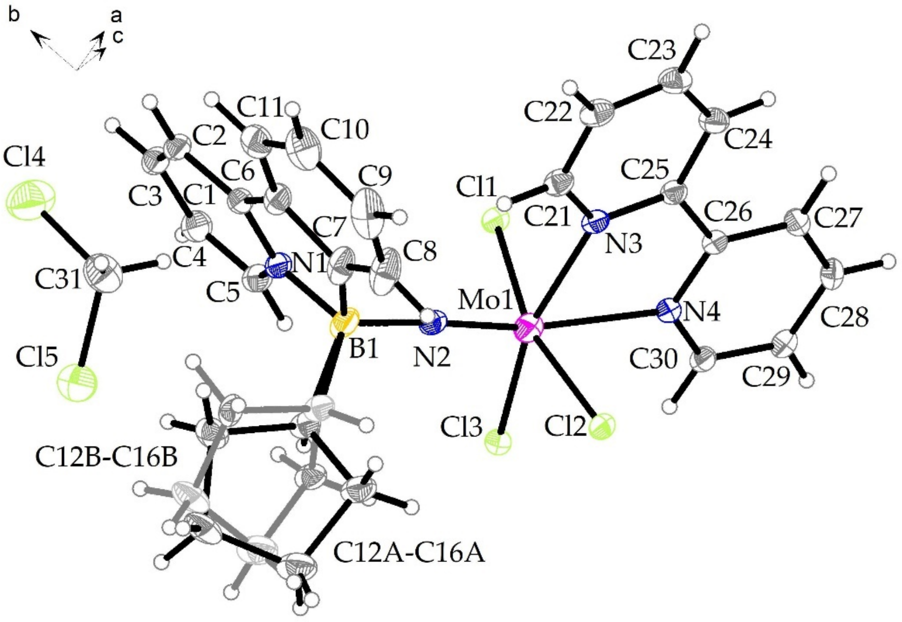
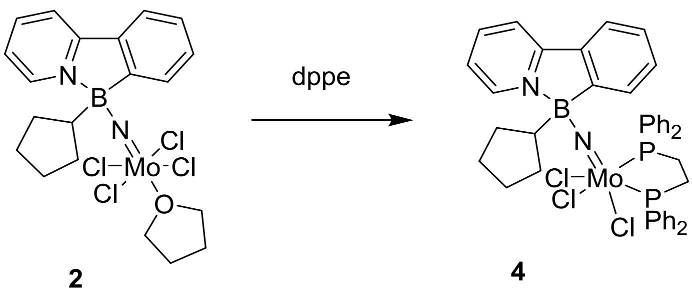


Figure S5. Crystal structure of **3** (thermal ellipsoids shown at 30 % probability level), minor disorder is shown as transparent.

Preparation of **4**



Molybdenum complex **2** (27.8 mg, 0.050 mmol) and 1,2-bis(diphenylphosphino)ethane (19.2 mg, 0.050 mmol) were dissolved in dichloromethane (3 mL) and the resulting solution was stirred at room temperature for 60 min, during which the mixture gradually turned pale orange. The reaction mixture was filtered and carefully layered with hexane (10 mL). After standing for three days, orange crystals formed. The crystals were collected by filtration, washed with hexane and dried *in vacuo* to yield compound **4** (29.6 mg, 0.035 mmol, 70% yield).

Elemental analysis calculated for $C_{42}H_{41}BCl_3MoN_2P_2$: C 59.43 H 4.87, N 3.30; found C 59.61, H 5.03, N 3.36.

HRMS calculated for $C_{42}H_{41}BCl_2MoN_2P_2^+$ [M–Cl]$^+$: 814.1269, found 814.1324.

IR (KBr) ν: 3075 (w), 3056 (m), 2950 (m), 2932 (m), 2859 (m), 1623 (s), 1572 (w), 1487 (s), 1447 (s), 1332 (w), 1313 (w), 1241 (w), 1191 (w), 1165 (m), 1110 (s), 1096 (s), 1070 (s), 1028 (w), 997 (w), 948 (w), 871 (w), 826 (w), 741 (s), 704 (s), 696 (s), 550 (w), 520 (m), 499 (m), 441 (w) cm^{-1}.

The crystals obtained were not suitable for full structural refinement by SC-XRD, however, they were sufficient to establish a molecular model that unambiguously confirms the *fac*-isomeric arrangement of the compound. Due to limited data quality, the structure was not deposited and is not intended for quantitative structural analysis.

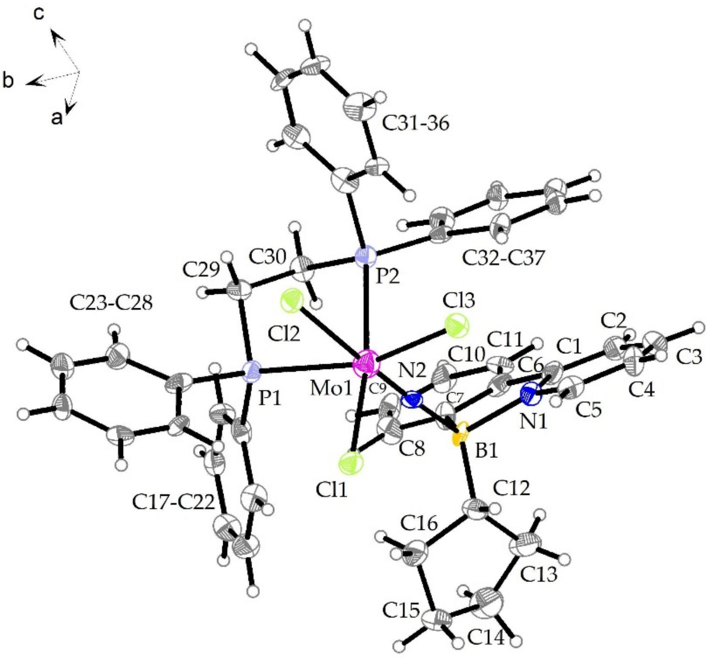
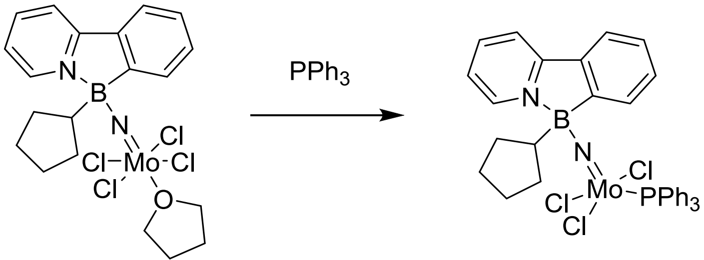


Figure S6: Asymmetric unit model of complex **4** obtained from SC-XRD. The structural model is shown for connectivity and isomer identification only (thermal ellipsoids shown at 30 % probability level).

Preparation of **5**



2 **5**

Molybdenum complex **2** (13.9 mg, 0.025 mmol) and triphenylphosphine (13.1 mg, 0.050 mmol) were dissolved in dichloromethane (3 mL) and the resulting solution was stirred at room temperature for 60 min, during which the mixture gradually turned pale orange. The reaction mixture was filtered and carefully layered with hexane (10 mL). After standing undisturbed for three days, orange crystals formed. The crystals were collected by filtration, washed with hexane, and dried *in vacuo* to yield compound **5** (8.5 mg, 0.012 mmol, 48% yield).

Elemental analysis calculated for $C_{34}H_{32}BCl_3MoN_2P$: C 57.30, H 4.53, N 3.93; found C 56.89, H 4.32, N 3.82.

HRMS calculated for $C_{36}H_{35}BCl_3MoN_3NaP^+$ $[M + MeCN + Na]^+$: 777.0679, found 777.0159. (NOTE: to improve its poor solubility, sample of **5** was analyzed in acetonitrile)

IR (KBr) ν: 3054 (w), 2938 (m), 2860 (m), 1621 (s), 1586 (w), 1484 (s), 1447 (m), 1436 (s), 1331 (w), 1310 (w), 1242 (w), 1160 (s), 1122 (s), 1097 (m), 1070 (m), 1027 (w), 997 (w), 974 (w), 799 (w), 763 (m), 746 (s), 728 (m), 691 (s), 657 (w), 635 (w), 617 (w), 538 (m), 525 (m), 500 (m), 467 (w) cm^{-1}.

Crystal structure determination of **5** [KSK527-gg]

A crystal suitable for SC-XRD structure determination was taken from the reaction batch (slow diffusion of hexane into dichloromethane solution of **5** in argon-filled glovebox).

Crystal Data for $C_{34}H_{32}BCl_3MoN_2P$ (M =712.68 g/mol): triclinic, space group P-1 (no. 2), a = 9.72725(10) Å, b = 10.29523(9) Å, c = 18.78662(10) Å, α = 91.7045(5)°, β = 97.5172(7)°, γ = 118.0068(10)°, V = 1637.81(3) Å^3, Z = 2, T = 100.00(10) K, μ(Cu Kα) = 6.187 mm^{-1}, $Dcalc$ = 1.445 g/cm^3, 45508 reflections measured (4.77° ≤ 2Θ ≤ 153.56°), 6496 unique (R_{int} = 0.0365, R_{sigma} = 0.0158) which were used in all calculations. The final R_1 was 0.0270 (I > 2σ(I)) and wR_2 was 0.0738 (all data). **CCDC:** 2520317.

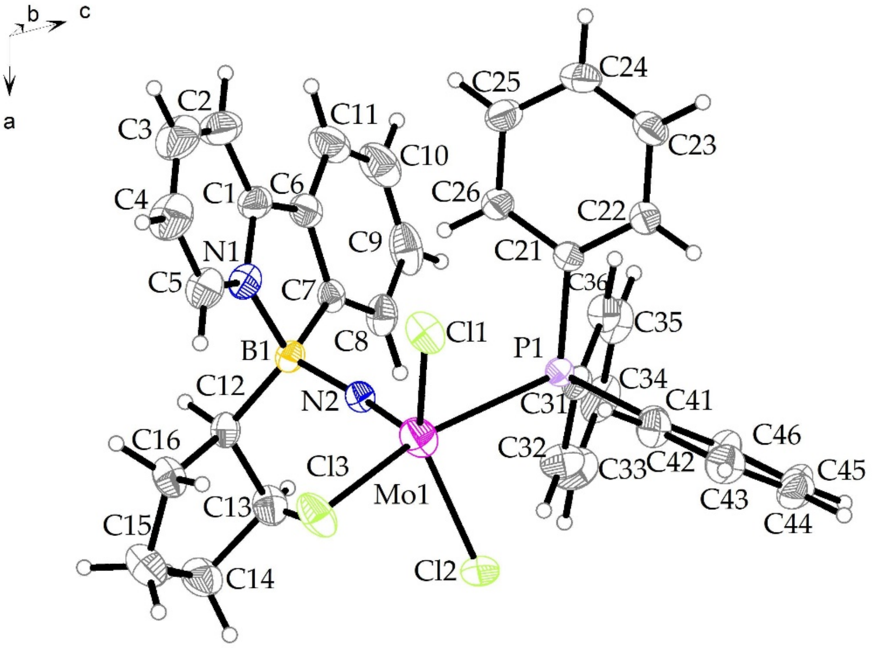
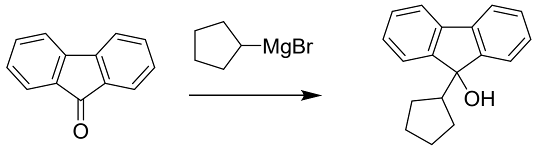


Figure S7: Crystal structure of **5** (thermal ellipsoids shown at 30 % probability level).

Preparation of **6**



9*H*-Fluorenone (3.6 g, 20 mmol) was dissolved in dry tetrahydrofuran (60 mL), cooled to –78°C and treated with cyclopentylmagnesium bromide (11 mL of 2M solution in Et_2O, 22 mmol). Cooling bath was removed and the mixture was stirred for 3 hours at room temperature. Reaction was quenched by addition of saturated solution of NH_4Cl (ca 20 mL) and ethyl acetate (ca 50 mL). The aqueous phase was separated and extracted with ethyl acetate (2 x 30 mL). Combined organic fractions were washed with brine and dried over $MgSO_4$. After filtration and removal of volatiles, the crude product (honey-like low-viscous oil) was purified by column chromatography on silica using hexane: dichloromethane mixture (1:1 vol.) as eluent. 9-cyclopentyl-9*H*-fluoren-9-ol was obtained as colourless oil which solidified over time (4.2 g, 0.16 mmol, 84% isolated yield).

Characterization of 9-cyclopentyl-*9H*-fluoren-9-ol:

Elemental analysis calculated for $C_{18}H_{18}O$ (250.33) C 86.36, H 7.25; found C 86.74, H 7.18.

^{1}H NMR (600 MHz, $CDCl_3$, 293K): [7.58 (d, $^3J_{HH}$ = 7.5 Hz), 7.50 (d, $^3J_{HH}$ = 7.5 Hz), 7.33 (dd, $^3J_{HH} \approx {}^3J_{HH}$ = 7.5 Hz), 7.25 (dd, $^3J_{HH} \approx {}^3J_{HH}$ = 7.5 Hz)](each 2H, CH^{Ar}), [2.58 (pent, $^3J_{HH}$= 8.6 Hz, 1H), 1.57 (m, 2H), 1.43 (m, 4H), 1.30 (m, 2H)](cyclopentyl), 2.32 (br s, 1H, OH).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, 293K): [148.8 (*i*-C), 139.7 (*i*-C), 128.6 (CH), 127.50 (CH), 124.2 (CH), 119.6 (CH), 84.2 C-OH](fluorenyl), [48.8 (CH), 27.5 (CH_2), 25.4 (CH_2)](cyclopentyl).

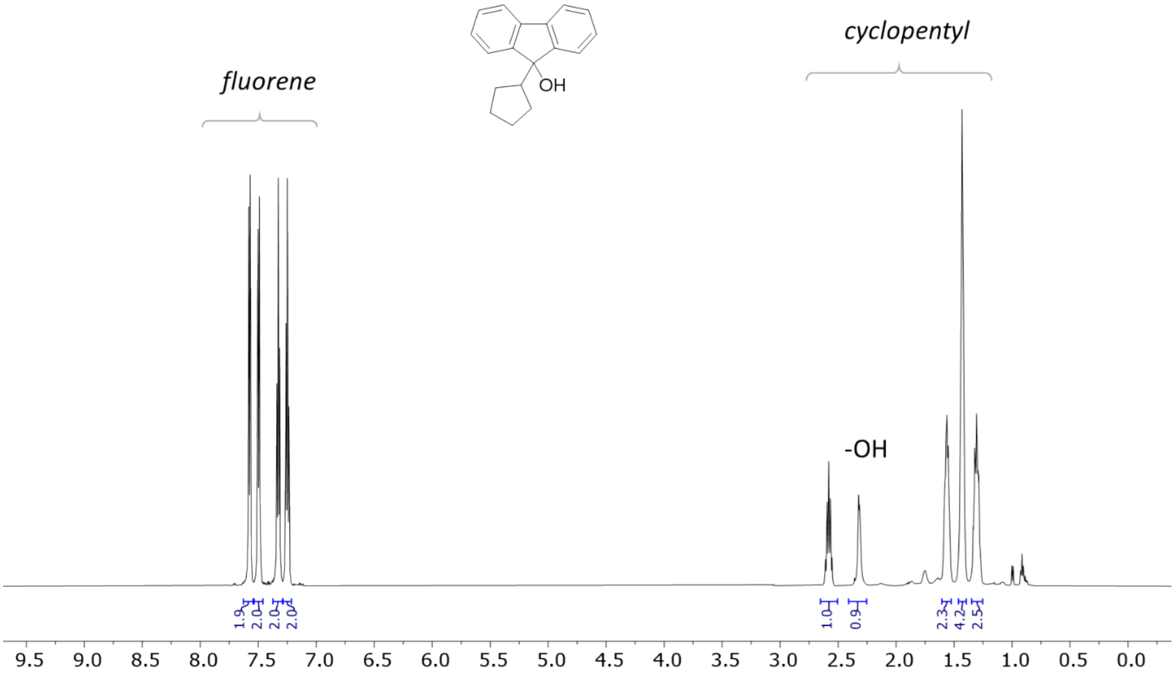


Figure S8: **^{1}H NMR** spectrum (600 MHz, $CDCl_3$) of 9-cyclopentyl-9*H*-fluoren-9-ol.

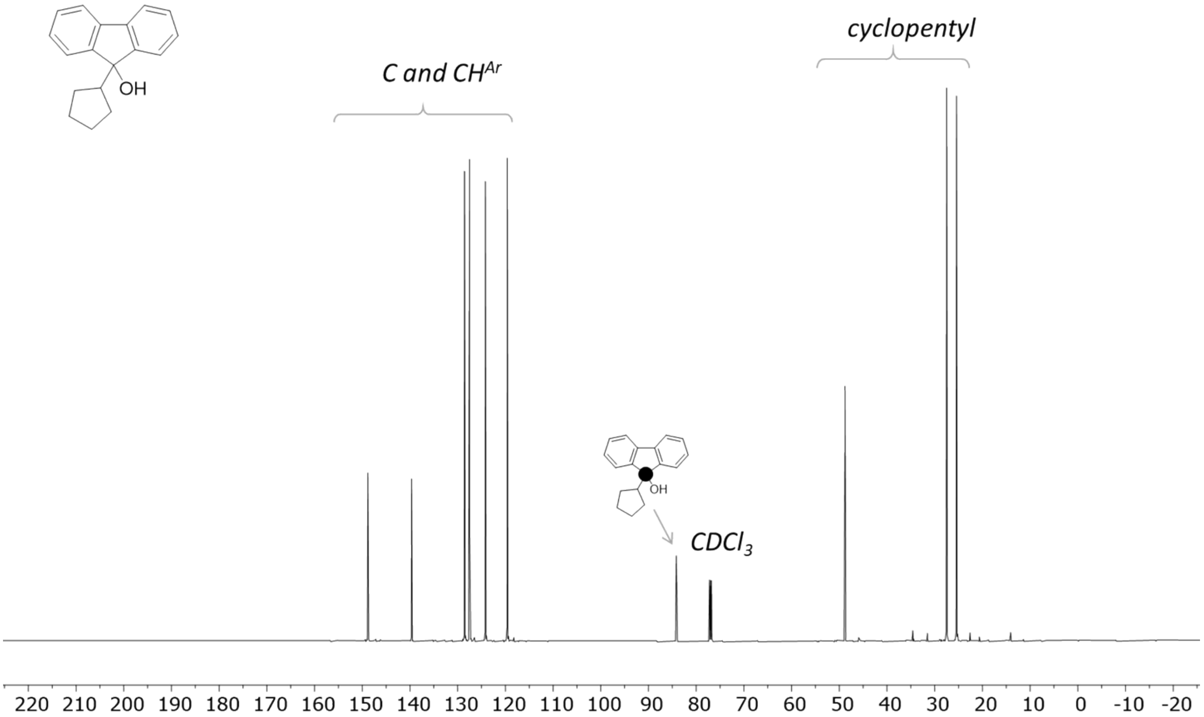
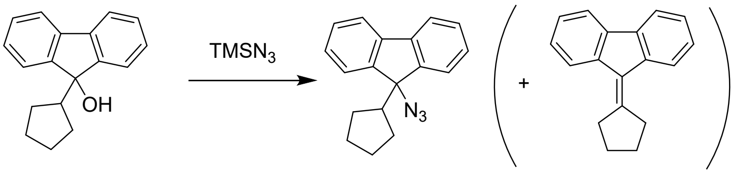


Figure S9: **^{13}C{^{1}H} NMR** spectrum (151 MHz, $CDCl_3$) of 9-cyclopentyl-*9H*-fluoren-9-ol.



6

9-cyclopentyl-9*H*-fluoren-9-ol (1.0 g, 4.0 mmol) was dissolved in 5 mL of dichloromethane and a solution of trimethylsilyl azide (552 mg, 4.8 mmol, 1.2 eq.) in 5 mL of dichloromethane was added dropwise. The mixture was stirred for 2 hours at room temperature and subsequently treated with saturated solution of $NaHCO_3$ (ca 10 mL). The aqueous phase was separated and extracted with dichloromethane (2x 5 mL). Combined organic fractions were washed with brine and dried with $MgSO_4$. After filtration and removal of volatiles, crude product was obtained as white solid (1.05 g). NMR measurement revealed a quantitative conversion of the starting material and formation of desired azide alongside with cca 15% cyclopentylidene-fluorene as a byproduct, which was identified by NMR.[S11] Attempted chromatographic purification (SiO_2, hexane : ethyl acetate 9:1) did not provide satisfactory separation, pure azide was thus obtained by recrystallization from hot ethyl acetate/heptane mixture. Compound **6** was obtained as white crystals (350 mg, 1.28 mmol, 32% yield).

Elemental analysis calculated for $C_{18}H_{17}N_3$ (275.35) C 78.52, H 6.22, N 15.26; found C 77.90, H 6.50, N 15.63.

IR (ATR) ν: 3077 (w), 3026 (w), 2957 (m), 2871 (m), **2090 (s, N_3),** 1445 (s), 1343 (w), 1252 (s), 1196 (w), 1154 (w), 1103 (w), 1084 (w), 1034 (w), 990 (w), 981 (w), 933 (m), 901 (w), 885 (m), 863 (m), 735 (s), 678 (s), 650 (m), 634 (w), 617 (w), 558 (w), 531 (w), 427 (w) cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$, 293K): [7.68 (d, $^3J_{HH}$ = 7.5 Hz), 7.56 (d, $^3J_{HH}$ = 7.5 Hz), 7.41 (dd, $^3J_{HH} \approx {}^3J_{HH}$ = 7.5 Hz), 7.33 (dd, $^3J_{HH} \approx {}^3J_{HH}$ = 7.5 Hz)](each 2H, CH^{Ar}), [2.58 (tt, $^3J_{HH}$ = 9.5 Hz, $^3J_{HH}$ = 7.9 Hz, 1H), 1.60 (m, 2H), 1.46 (m, 4H), 1.33 (m, 2H)](cyclopentyl).

$^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$, 293K): [145.1 (*i*-C), 140.4 (*i*-C), 129.1 (CH), 127.8 (CH), 124.5 (CH), 120.0 (CH), 76.1 C-N_3](fluorene), [48.3 (CH), 27.8 (CH_2), 25.3 (CH_2)](cyclopentyl).

Crystal structure determination of **6** [KSK575-gg]

A crystal suitable for SC-XRD structure determination was taken from the reaction batch (slow cooling of hot solution of **6** in ethylacetate/heptane mixture).

Crystal Data for $C_{18}H_{17}N_3$ (M =275.34 g/mol): monoclinic, space group $P2_1/n$ (no. 14), a = 9.3007(3) Å, b = 14.2372(3) Å, c = 10.7745(3) Å, β = 94.456(2)°, V = 1422.40(7) Å^3, Z = 4, T = 99.99(10) K, μ(Cu Kα) = 0.604 mm^{-1}, $Dcalc$ = 1.286 g/cm^3, 8174 reflections measured (10.316° ≤ 2Θ ≤ 148.91°), 2709 unique (R_{int} = 0.0531, R_{sigma} = 0.0503) which were used in all calculations. The final R_1 was 0.0563 (I > 2σ(I)) and wR_2 was 0.1538 (all data). **CCDC**: 2520310.

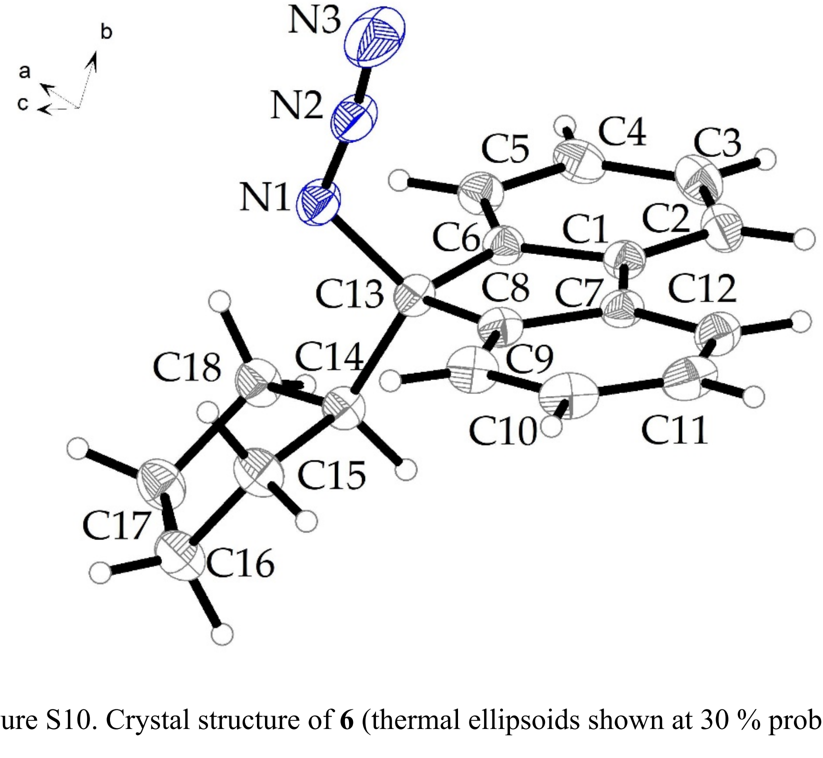


Figure S10. Crystal structure of **6** (thermal ellipsoids shown at 30 % probability level).

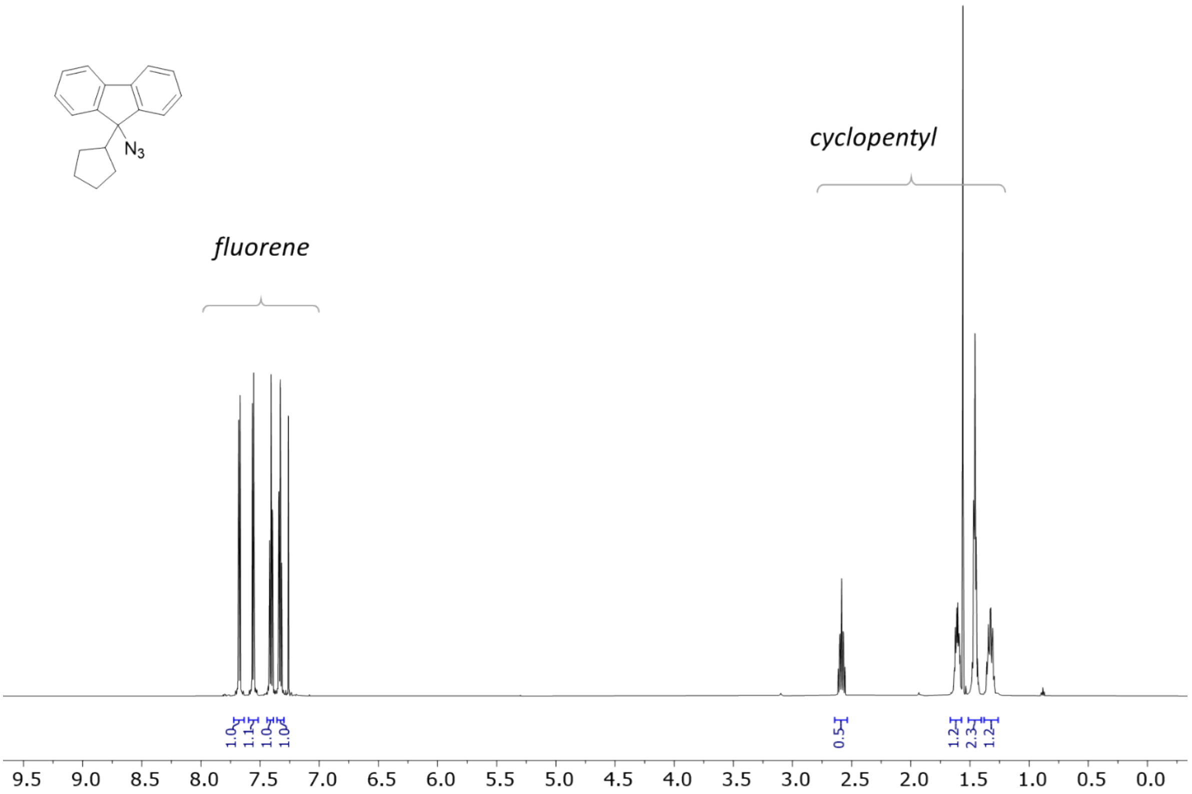


Figure S11: **^{1}H NMR** spectrum (600 MHz, $CDCl_3$) of compound **6**.

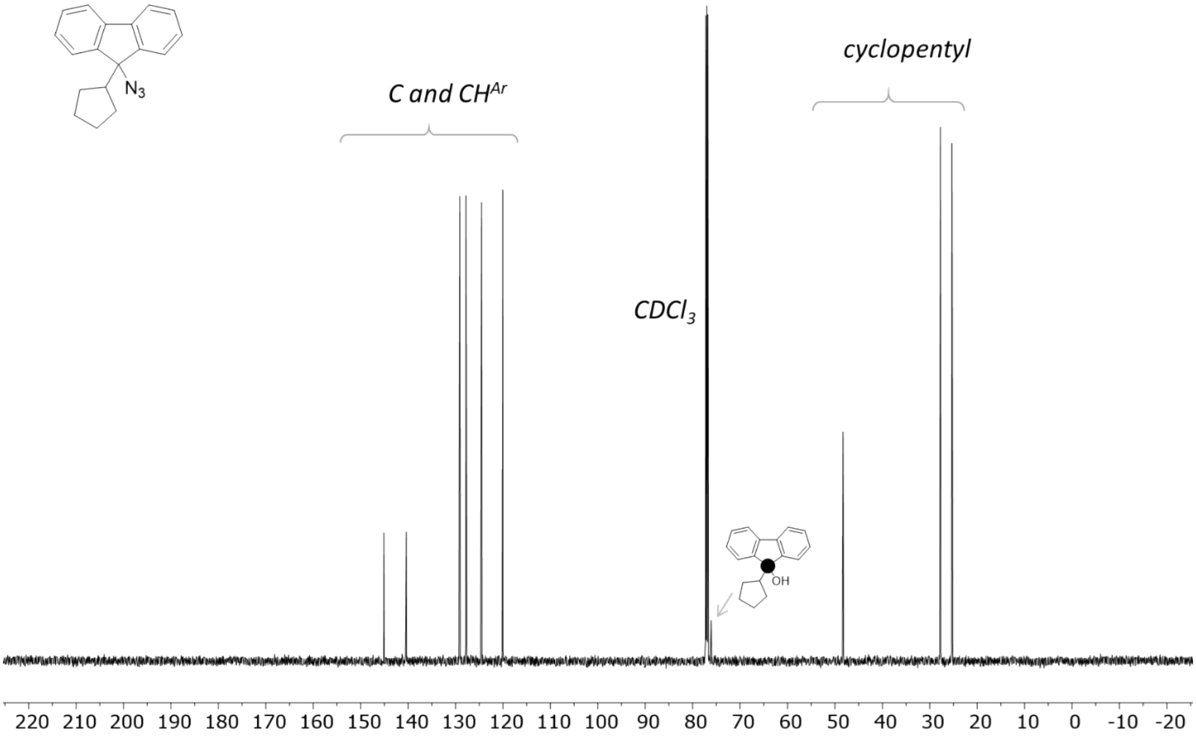
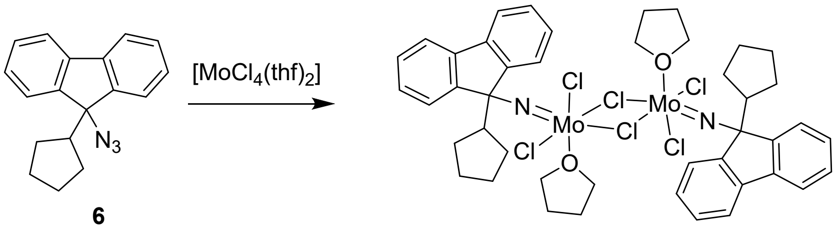


Figure S12: **^{13}C{^{1}H} NMR** spectrum (151 MHz, $CDCl_3$) of compound **6**.

Preparation of **7**



6

7

Solution of fluorene azide **6** (55.2 mg, 0.2 mmol) in benzene (5 mL) was added to a suspension of $[MoCl_4(thf)_2]^{S2}$ (80.1 mg, 0.21 mmol) in benzene (5 mL). The resulting suspension was placed into an oil bath preheated to 75 °C and reacted for 5 hours, during which the mixture gradually turned dark. After cooling to room temperature, volatiles were removed *in vacuo* and the residue was taken in a small amount of dichloromethane (2 mL), filtered and layered with hexane (5 mL). After one week, several green crystals have formed. These were isolated by decantation, washed with hexane and dryed *in vacuo*. Compound **7** was obtained as green crystals (22.7 mg, 0.022 mmol, 22% yield).

Elemental analysis calculated for $C_{44}H_{50}N_2Cl_6Mo_2O_2$ (1043.5): C 50.65, H 4.83, N 2.68; found C 50.59, H 4.55, N 2.52.

HRMS calculated for $C_{18}H_{17}NMoCl_4$ $[M/2 - thf + Cl]^-$: 484.9160, found 484.9111 and for $C_{36}H_{34}Cl_7Mo_2N_2$ $[M - 2\ thf + Cl]^-$: 934.8620, found 934.8555.

IR (KBr) ν: 2962 (m), 2870 (m), 1448 (m), 1362 (w), 1340 (w), 1297 (w), 1285 (w), 1238 (m), 1212 (s), 1180 (w), 1158 (w), 1100 (w), 1034 (w), 1003 (m), 943 (w), 911 (m), 853 (s), 733 (s), 665 (w), 646 (w), 619 (w), 514 (w), 503 (w), 428 (m) cm^{-1}.

Crystal structure determination of **7** [KSK576-gg]

A crystal suitable for SC-XRD structure determination was obtained by slow diffusion of hexane into a dichloromethane solution of **7**.

Crystal Data for $C_{45}H_{52}Cl_8Mo_2N_2O_2$ (M =1128.36 g/mol): triclinic, space group P-1 (no. 2), a = 9.7090(5) Å, b = 9.9534(7) Å, c = 13.4743(9) Å, α = 81.729(5)°, β = 88.599(5)°, γ = 69.331(6)°, V = 1205.15(14) Å^3, Z = 1, T = 100.00(10) K, μ(Cu Kα) = 8.642 mm^{-1}, $Dcalc$ = 1.555 g/cm^3, 12274 reflections measured (6.632° ≤ 2Θ ≤ 133.186°), 4259 unique (R_{int} = 0.0480, R_{sigma} = 0.0492) which were used in all calculations. The final R_1 was 0.0333 (I > 2σ(I)) and wR_2 was 0.0863 (all data). **CCDC:** 2520314.

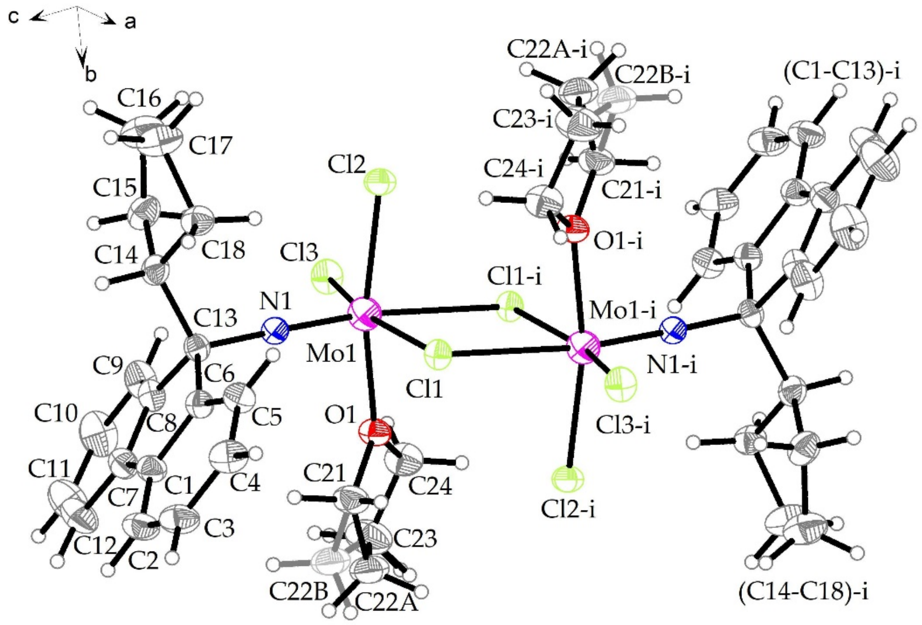
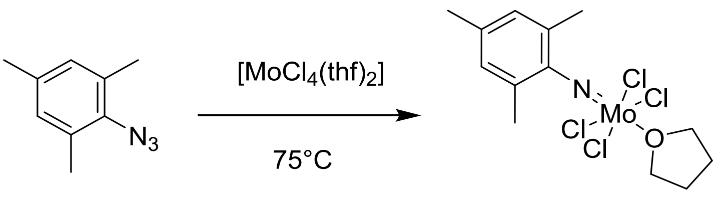


Figure S13: Crystal structure of **7** (thermal ellipsoids shown at 30 % probability level).

Preparation of [$MoCl_4$(NMes)(thf)]



[$MoCl_4$(NMes)(thf)]

Solution of mesityl azide[S3] **1** (40.2 mg, 0.25 mmol) in benzene (2 mL) was added to a suspension of [$MoCl_4(thf)_2$][S2] (99 mg, 0.26 mmol) in benzene (3 mL). The resulting mixture was placed into an oil bath preheated to 75 °C and stirred for 5 hours. After cooling to room temperature, the mixture was filtered via cannula and the volatiles were removed *in vacuo*. The solid residue was washed with a small amount of hexane and dried *in vacuo* to give complex [$MoCl_4$(NMes)(thf)] in the form of a brown solid (96.0 mg, 0.21 mmol, 87% yield).

Elemental analysis calculated for $C_{13}H_{19}Cl_4MoNO$ (443.0) C 35.24, H 4.32, N 3.16; found C 34.87, H 4.57, N 3.10.

IR (KBr) ν: 2969 (w), 2951 (w), 2929 (w), 2894 (w), 1598 (s), 1456 (m), 1401 (m), 1386 (m), 1308 (m), 1291 (s), 1159 (w), 1123 (w), 1045 (w), 1011 (m), 956 (w), 918 (w), 850 (s), 719 (w), 676 (w), 624 (w), 487 (w), 445 (w) cm^{-1}.

^{1}H NMR (600 MHz, C_6D_6, 293K): [6.14, (s, 2H, CH^{Mes}), 3.21 (s, 6H, *o*-CH_3^{Mes}), 2.14 (s, 3H, *p*-CH_3^{Mes})], [4.55 (m, 4H, thf), 1.33 (m, 4H, thf)].

^{13}C{^{1}H} NMR (151 MHz, C_6D_6, 293K): [151.8 (*i*-C), 148.0 (CH), 147.7 (*i*-C), 128.4 (*i*-C)[a], 21.3 (*p*-CH_3), 18.7 (*o*-CH_3)](Mes), [73.4, 25.8](thf), [a] based on gHMBC spectra

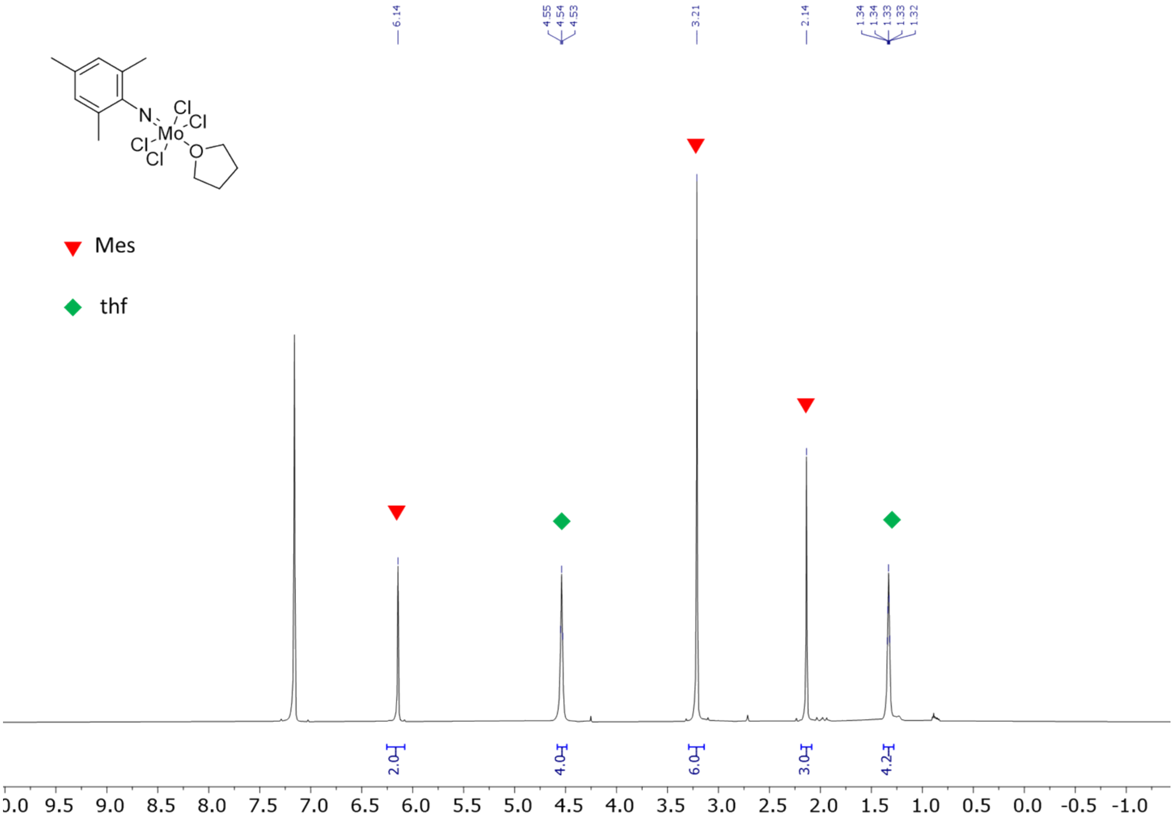


Figure S14: **^{1}H NMR** spectrum (600 MHz, C_6D_6) of complex [$MoCl_4$(NMes)(thf)].

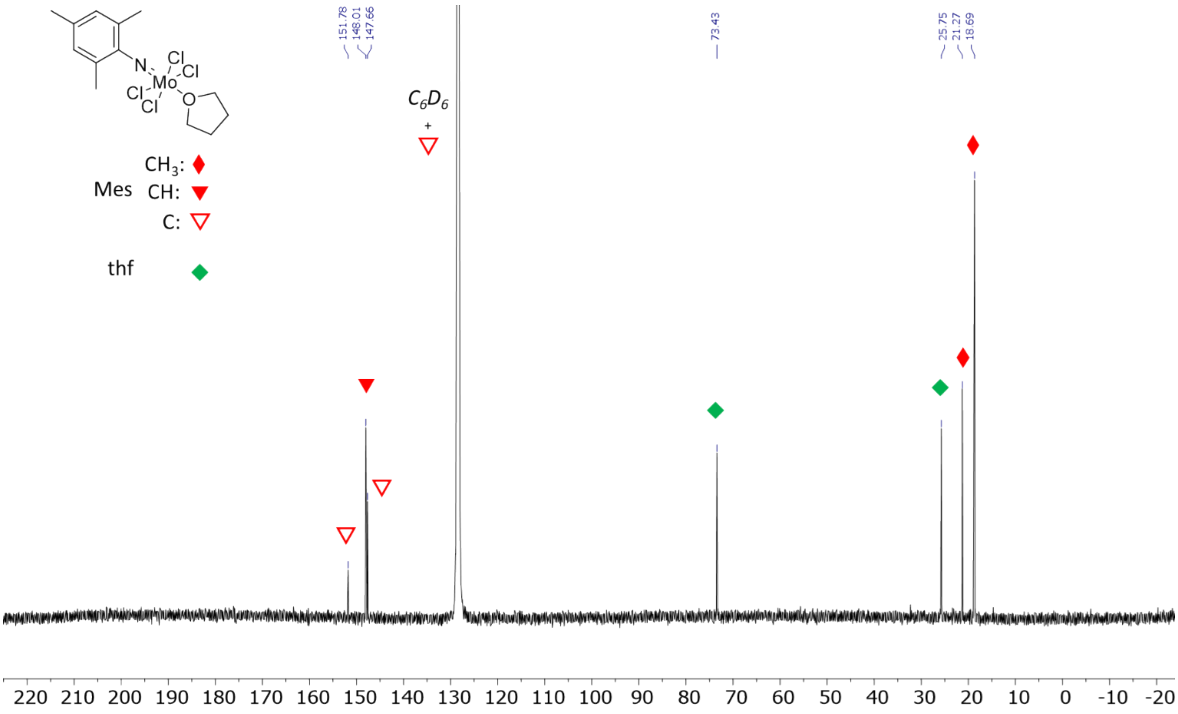


Figure S15: **$^{13}C\{^1H\}$ NMR** spectrum (151 MHz, C_6D_6) of complex [$MoCl_4$(NMes)(thf)].

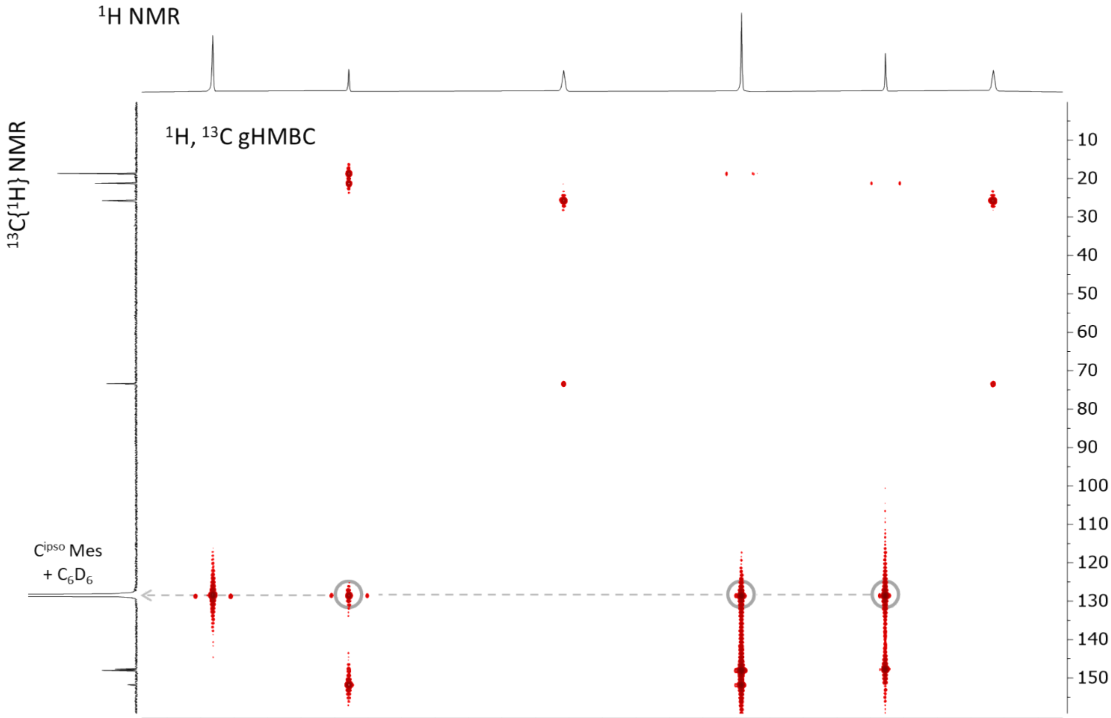


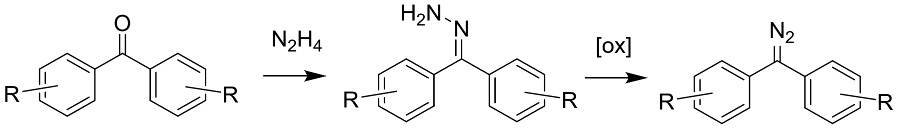
Figure S16: **^{1}H,^{13}C gHMBC** (600 MHz / 151 MHz, C_6D_6) of complex [$MoCl_4$(NMes)(thf)].

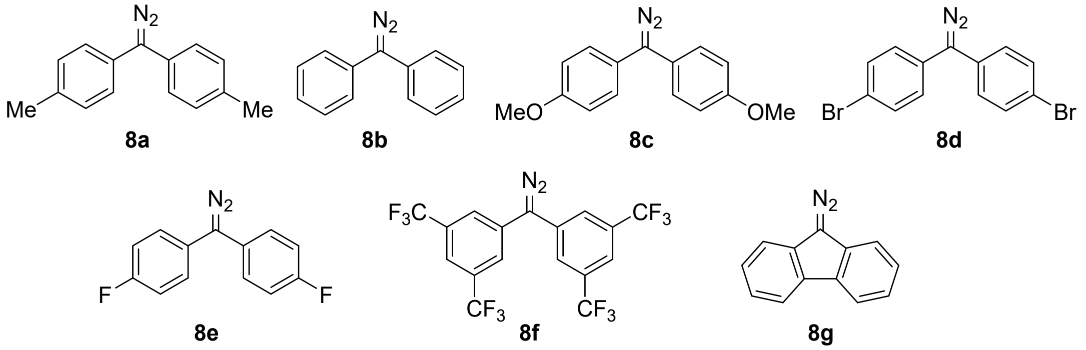
Catalytic testing

Preparation of substrates

Synthesis of diaryldiazomethanes

Diaryldiazomethanes **8a-g** were prepared by two-step procedure reported previously.[S12]





Diraryldiazomethanes prepared for this study.

Crystal structure determination of **8a** [pTol2CN2_moly-gg]

A crystal suitable for SC-XRD structure determination were obtained from cold solution of **8a** in hexane.

Crystal Data for $C_{15}H_{14}N_2$ (M =222.28 g/mol): orthorhombic, space group $P2_12_12$ (no. 18), a = 7.4374(3) Å, b = 14.1906(4) Å, c = 11.8015(3) Å, V = 1245.54(7) Å^3, Z = 4, T = 100.00(11) K, μ(Mo Kα) = 0.071 mm^{-1}, $Dcalc$ = 1.185 g/cm^3, 43794 reflections measured (4.49° ≤ 2Θ ≤ 61.982°), 3978 unique (R_{int} = 0.0780, R_{sigma} = 0.0231) which were used in all calculations. The final R_1 was 0.0560 (I > 2σ(I)) and wR_2 was 0.1650 (all data). **CCDC**: 2520318.

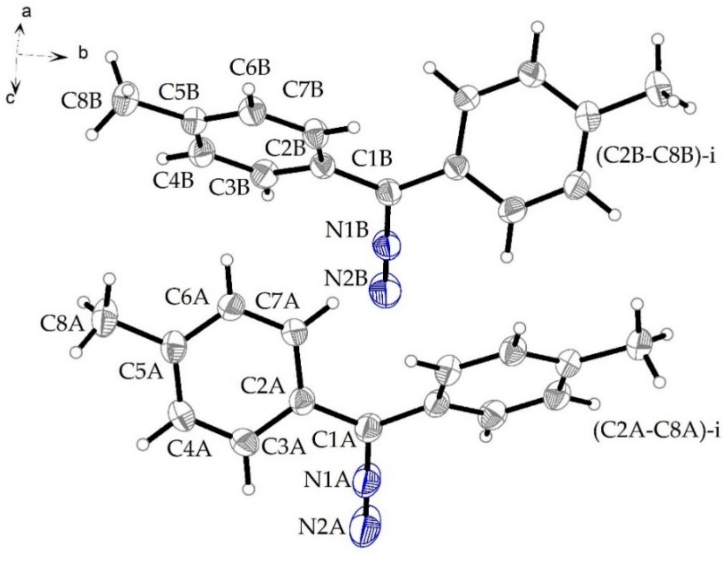
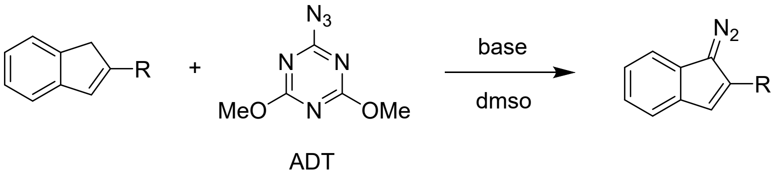


Figure S17. Crystal structure of **8a** (thermal ellipsoids shown at 30 % probability level).

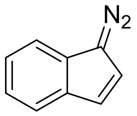
Synthesis of 1-diazo-indenes



Literature procedure was adapted for synthesis of diazoindenes.[S13]

Corresponding indene (2 mmol) was dissolved/suspended in dry dmso (10 mL) and treated with base (2.5 mmol). After 15 minutes at room temperature, solid ADT (2.4 mmol, 437 mg) was added and the mixture gradually turned dark. After 60 minutes, the reaction was diluted with 40 ml of diethylether and 40 mL of water and transferred into a separatory funnel. The aqueous phase was discarded and the dark red organic phase was extensively washed with water (5x 20 mL) and brine. The organic phase was then dried over $MgSO_4$, volatiles removed *in vacuo* and the crude product was purified on a short column using basic alumina. Elution with diethyl ether provided corresponding diazoindenes as orange-red solids.

Characterization data

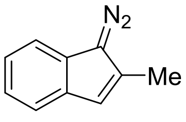


8h

1-Diazoindene, **8h**, orange oil, prepared in 33 % yield using AcOK as the base. Characterization data correspond to those previously reported in literature[S13]

^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.55 (m, 1H), 7.46 (m, 1H), 7.20 (m, 2H), 7.01 (d, $^3J_{HH}$ = 5.0 Hz, 1H), 6.37 (d, $^3J_{HH}$ = 5.0 Hz, 1H).

IR (ATR): characteristic vibrations 2066, 2052 cm^{-1}.

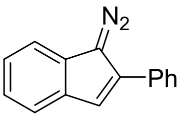


8i

2-Methyl-1-diazoindene, **8i**, orange solid, isolated in 40% yield using Cs_2CO_3 as the base. Characterization data correspond to those previously reported in literature[S14]

^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.43 (m, 1H, C_6H_4), 7.39 (m, 1H, C_6H_4), 7.17 (m, 1H, C_6H_4), 7.13 (m, 1H, C_6H_4), 6.12 (d, $^4J_{HH}$ = 1.5 Hz, 1H, =CH), 2.36 (d, $^4J_{HH}$ = 1.5 Hz, 3H, CH_3).

IR (ATR): characteristic vibrations 2070, 2043 cm^{-1}.



8j

2-Phenyl-1-diazoindene, **8j**, red solid, obtained in 66% yield using Cs_2CO_3 as the base.

^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.57 (m, 1H), 7.53 (m, 2H), 7.45 (m, 3H), 7.35 (m, 1H), 7.22 (m, 2H), 6.58 (s, 1H).

$^{13}C\{^1H\}$ NMR ($CDCl_3$, 151 MHz): δ 135.0, 135.0, 134.4, 134.2, 129.1, 127.8, 126.7, 124.6, 123.1, 122.5, 118.4, 114.5, 57.9 (C=N_2).

IR (ATR): characteristic vibrations 2077, 2051 cm^{-1}.

HRMS calculated for $C_{15}H_{10}N_2$ $[M]^+$: 218.0844, found 218.0848 and for $C_{15}H_{10}$ [M-N_2]+: 190.0783, found 190.0785.

Crystal structure determination of **8j** [KSK551-gg]

A crystal suitable for SC-XRD structure determination was obtained from cold solution of **8j** in hexane.

Crystal Data for $C_{15}H_{10}N_2$ (M =218.25 g/mol): monoclinic, space group $P2_1/c$ (no. 14), a = 7.9972(2) Å, b = 17.3076(4) Å, c = 8.2800(2) Å, β = 106.898(3)°, V = 1096.58(5) Å^3, Z = 4, T = 99.98(10) K, μ(Cu Kα) = 0.620 mm^{-1}, $Dcalc$ = 1.322 g/cm^3, 7200 reflections measured (10.222° ≤ 2Θ ≤ 153.414°), 2130 unique (R_{int} = 0.0445, R_{sigma} = 0.0415) which were used in all calculations. The final R_1 was 0.0416 (I > 2σ(I)) and wR_2 was 0.1148 (all data). **CCDC**: 2520312.

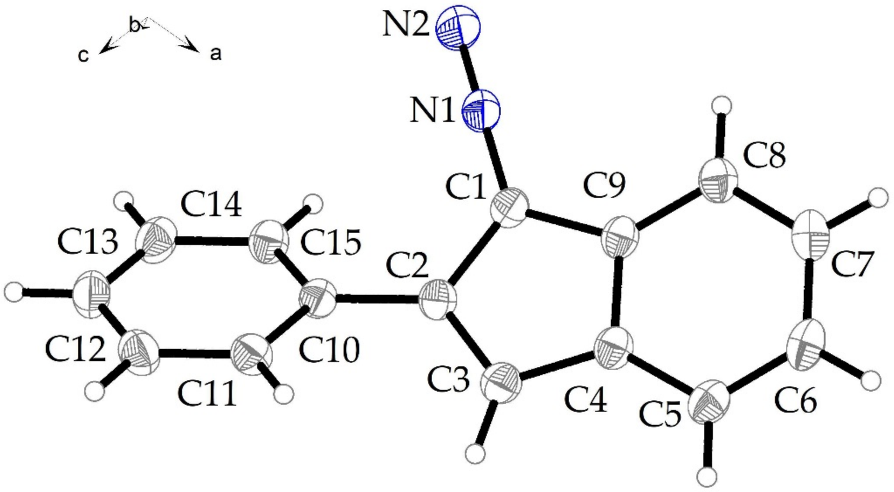
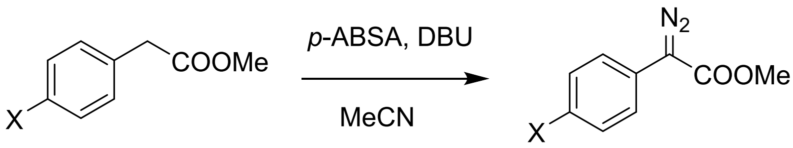


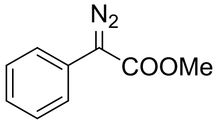
Figure S18: Crystal structure of **8j** (thermal ellipsoids shown at 30 % probability level).

Synthesis of α-diazoesters



Synthesis of α-diazoesters was based a previously reported procedure. [S15]

To a solution of the corresponding methyl phenylacetate (10 mmol) and 4-acetamidobenzenesulfonyl azide (*p*-ABSA, 15 mmol) in acetonitrile (15 mL) was added 1,8-diazobicyclo[5.4.0]undec-7-ene (DBU, 2.24 mL, 15 mmol). The reaction mixture was stirred overnight at room temperature. Next, the reaction was quenched with saturated aqueous solution of NH_4Cl (5 mL), extracted with CH_2Cl_2 (3x30mL) and washed with brine (3x10mL). The combined organic phase was dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude mixture was further purified by column chromatography on silicagel using EtOAc:Hexane (1:9 vol.) as mobile phase to yield the corresponding α-diazoester.



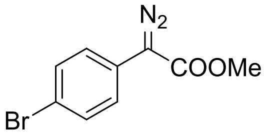
8k

Methyl 2-diazo-2-phenylacetate, **8k**, isolated as red oil (1.09 g, 62% yield.[S15]

^{1}H NMR (600MHz, $CDCl_3$): δ 7.48 (m, 2H, Ar-H), 7.37 (m, 2H, Ar-H), 7.17 (m, 1H, Ar-H), 3.84 (s, 3H).

^{13}C {^{1}H} NMR (151MHz, $CDCl_3$): δ 165.3, 128.7, 125.7, 125.3,123.7, 63.0^a, 51.8, 41.1. ^{a} signal of CN_2 assigned by gHMBC

IR (ATR): characteristic vibrations 2088 (s, CN_2), 1708 (s, CO) cm^{-1}.



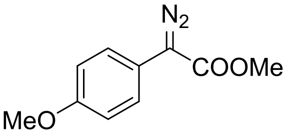
8l

Methyl 2-diazo-2-(4-bromophenyl)acetate, **8l**, isolated as an orange solid (2.21 g, 87 % yield).[S15]

^{1}H NMR (600MHz, $CDCl_3$): δ 7.50 (m, 2H, Ar-H), 7.36 (m, 2H, Ar-H), 3.87(s, 3H, CH_3) ppm.

^{13}C{^{1}H} NMR (151MHz, $CDCl_3$): δ 165.2, 132.0, 125.2, 124.6, 119.3, 63.1^a, 52.1 ^{a} signal of CN_2 assigned by gHMBC

IR (ATR): characteristic vibrations 2088 (s, CN_2), 1691 (s, CO) cm^{-1}.



8m

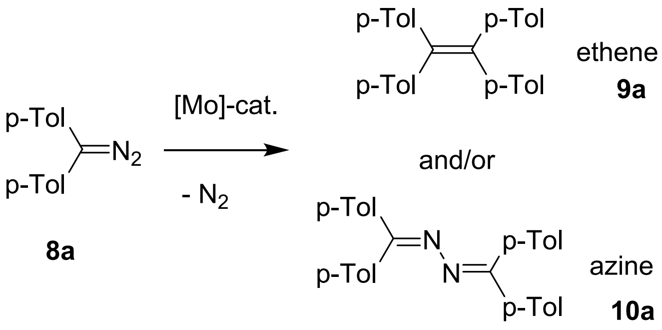
Methyl 2-diazo-2-(4-methoxyphenyl)acetate, **8m**, isolated as red solid (0.805 mg, 41% yield). [S15]

^{1}H NMR (600MHz, $CDCl_3$): δ 7.38 (m, 2H, Ar-H), 6.94 (m, 2H, Ar-H), 3.85 (s, 3H, CH_3), 3.81 (s, 3H, CH_3).

^{13}C{^{1}H} NMR (151MHz, $CDCl_3$): δ 166.3, 158.3, 126.1, 117.0, 115.3, 60.6^a, 55.6, 52.2. ^{a} signal of CN_2 assigned by gHMBC

IR (ATR): characteristic vibrations 2083 (s, CN_2), 1694 (s, CO) cm^{-1}.

Description of catalytic experiments



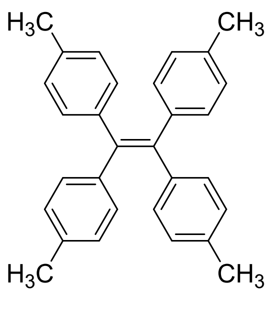
Screening of reaction solvents

Bis(p-tolyl)diazomethane **8a** (44.4 mg, 0.2 mmol) and molybdenum complex **2** (1.2 mg, 0.002 mmol) were combined in the corresponding solvent (0.8 mL) and stirred for 60 minutes at room temperature. Reactions in deuterated solvents ($CDCl_3$ and C_6D_6) were analysed directly. Reactions in other solvents were quenched by the addition of three drops of triethylamine to destroy the Lewis acid, volatiles were removed *in vacuo*, the residue was dissolved in $CDCl_3$ and analysed by NMR.

Preparative experiments were performed in 0.5 mmol scale using 0.8 mL of deuterated solvent ($CDCl_3$ or C_6D_6) in Young NMR tube and reacted at room temperature. Reaction progress was followed directly by NMR. For less reactive diazocompounds, the reaction mixture was placed into an oil bath preheated to 60 °C. After consumption of the starting material, volatiles were removed *in vacuo* and the product was purified by column chromatography using dichloromethane/hexane mixtures as eluents.

Characterization data of obtained products

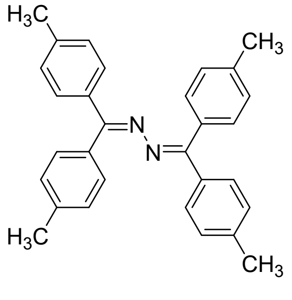
Homocoupling of diaryldiazomethanes



Tetrakis(4-tolylmethylene)ethane, **9a**, white solid[S12]

^{1}H NMR ($CDCl_3$, 600 MHz): δ 6.93 (m, 4H, Ar), 2.28 (s, 3H, Me).

$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz): δ 141.5, 140.0, 135.8, 131.4, 128.5, 21.3.

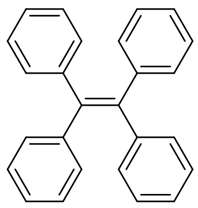


1,2-bis(di-4-tolylmethylene)hydrazine, **10a**, yellow solid[S12]

^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.43 (m, 2H, Ar), 7.27 (m, 2H, Ar), 7.21 (m, 2H, Ar), 7.12 (m, 2H, Ar), 2.40 (s, 3H, CH_3), 2.37 (s, 3H, CH_3).

$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz): δ 158.8, 139.4, 138.4, 135.9, 132.7, 129.5, 128.7, 128.6, 128.4, 21.4, 21.3.

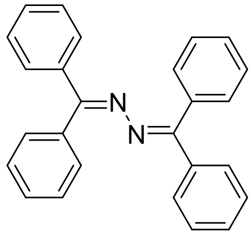
IR (ATR): characteristic vibrations 1608, 1583 cm^{-1}.



Tetraphenyl ethane, **9b**, white solid[S12]

^{1}H NMR (CDCl$_3$, 600 MHz): δ 7.09 (m, 3H, Ph), 7.02 (m, 2H, Ph).

^{13}C{^{1}H} NMR (CDCl$_3$, 151 MHz): δ 143.7, 140.9, 131.3, 127.6, 126.4.

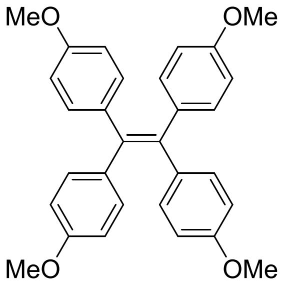


1,2-Bis(diphenylmethylene)hydrazine, **10b**, white solid[S12]

^{1}H NMR (CDCl$_3$, 600 MHz): δ 7.49 (m, 2H), 7.41 (m, 3H), 7.34 (m, 3H), 7.28 (m, 2H).

^{13}C{^{1}H} NMR (CDCl$_3$, 151 MHz): δ 159.0, 138.3, 135.6, 129.7, 129.4, 128.8, 128.2, 128.0.

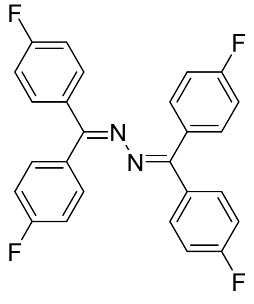
IR (ATR): characteristic vibrations 1587, 1564 cm^{-1}.



Tetrakis(4-methoxyphenyl)ethane, **9c**, white solid[S11]

^{1}H NMR (CDCl$_3$, 600 MHz): δ 6.93 (m, 2H, CH^{Ar}), 6.64 (m, 2H, CH^{Ar}), 3.75 (s, 3H, OMe).

^{13}C{^{1}H} NMR (CDCl$_3$, 151 MHz): δ 157.7, 138.3, 136.9, 132.5, 113.0, 55.0.



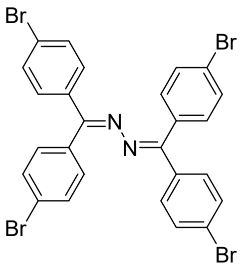
1,2-Bis(bis(4-fluorophenyl)methylene)hydrazine, **10d**, yellow solid[S16]

^{1}H NMR (CDCl$_3$, 600 MHz): δ 7.48 (m, 1H), 7.32 (m, 1H), 7.14 (m, 1H), 7.00 (m, 1H).

^{13}C{^{1}H} NMR (CDCl$_3$, 151 MHz): δ 163.9 (d, $^{1}J_{FC}$ = 251 Hz), 162.8 (d, $^{1}J_{FC}$ = 249 Hz), 158.8, 134.0 (d, $^{4}J_{FC}$ = 3 Hz), 131.4 (d, $^{3}J_{FC}$ = 8 Hz), 131.0 (d, $^{4}J_{FC}$ = 3 Hz), 130.6 (d, $^{4}J_{FC}$ = 8 Hz), 115.2 (d, $^{2}J_{FC}$ = 22 Hz), 115.1 (d, $^{2}J_{FC}$ = 22 Hz).

^{19}F NMR (CDCl$_3$, 564 Hz): δ –110.3 (1F), –111.1 (1F).

IR (ATR): characteristic vibrations 1596, 1559 cm^{-1}.

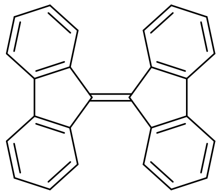


1,2-Bis(bis(4-bromophenyl)methylene)hydrazine, **10e**, yellow solid [S16]

^{1}H NMR (CDCl$_3$, 600 MHz): δ 7.56 (m, 1H), 7.45 (m, 1H), 7.33 (m, 1H), 7.17 (m, 1H).

$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz): δ 158.9, 136.2, 133.5, 131.5, 131.3, 130.9, 130.1, 124.9, 123.5.

IR (ATR): characteristic vibrations 1585, 1576 cm^{-1}.

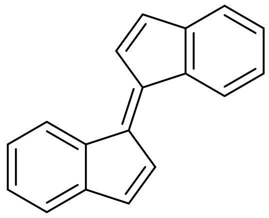


9,9′-Bifluorenylidene, **9g**, red solid[S12]

^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.40 (m, 1H), 7.71 (m, 1H), 7.34 (m, 1H), 7.22 (m, 1H).

$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz): δ 141.4, 141.1, 138.4, 129.3, 127.0, 126.8, 120.0.

Homocoupling of diazoindenes

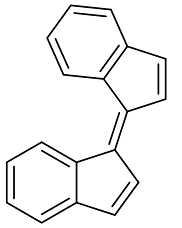


E-dibenzofulvalene (*E*-1,1′-biindenylidene), *E*-**9h**, orange-red glassy solid[S18]

^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.93 (d, $^{3}J_{HH}$ = 7.5 Hz, C_6H_4, 1H), 7.42 (d, $^{3}J_{HH}$ = 5.6 Hz, 1H, C_3H_2), 7.30 7.22 (d, $^{3}J_{HH}$ = 7.4 Hz, C_6H_4), 7.24 (dd, $^{3}J_{HH} \approx {}^{3}J_{HH}$ = 7.4 Hz, C_6H_4), 7.20 (dd, $^{3}J_{HH} \approx {}^{3}J_{HH}$ = 7.4 Hz, C_6H_4), 7.04 (d, $^{3}J_{HH}$ = 5.6 Hz, 1H, C_3H_2).

$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz): δ 143.7 (C^{Ar}), 141.3 (C^{Ar}), 137.0 (C^{Ar}), 136.4 (CH^{Ar}), 128.5 (CH^{Ar}), 127.3 (CH^{Ar}), 125.9 (CH^{Ar}), 125.3 (CH^{Ar}), 121.9 (CH^{Ar}).

HRMS calculated for $C_{18}H_{10}$ [M·]$^{+}$: 226.0777, found 226.0777.

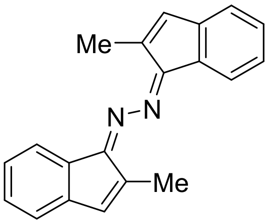


Z-dibenzofulvalene (*Z*-1,1′-biindenylidene), *Z*-**9h**, orange-red glassy solid

^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.36 (d, $^{3}J_{HH}$ = 7.5 Hz, C_6H_4, 1H), 7.30 (dd, $^{3}J_{HH} \approx {}^{3}J_{HH}$ = 7.4 Hz, C_6H_4), 7.26 (dd, $^{3}J_{HH} \approx {}^{3}J_{HH}$ = 7.4 Hz, C_6H_4), 7.22 (d, $^{3}J_{HH}$ = 7.5 Hz, C_6H_4), 6.94 (d, $^{3}J_{HH}$ = 5.5 Hz, 1H, C_3H_2), 6.91(d, $^{3}J_{HH}$ = 5.5 Hz, 1H, C_3H_2).

$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz): δ 145.5 (C^{Ar}), 143.3 (C^{Ar}), 134.7 (C^{Ar}), 133.3 (CH^{Ar}), 130.5 (CH^{Ar}), 129.1 (CH^{Ar}), 125.8 (CH^{Ar}), 125.7 (CH^{Ar}), 121.9 (CH^{Ar}).

HRMS calculated for $C_{18}H_{10}$ [M·]$^{+}$: 226.0777, found 226.0775.



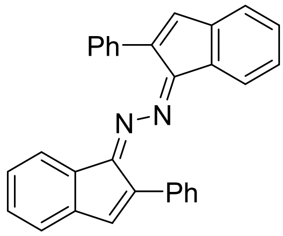
Bis(2-methyl-1H-indenylylidene)azine, **10i**, red solid

^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.72 (d, $^{3}J_{HH}$ = 7.5 Hz, 1H, CH^{Ar}), 7.17 (dd, $^{3}J_{HH} \approx {}^{3}J_{HH} \approx$ 7.4 Hz, 1H, CH^{Ar}), 7.03 (d, $^{3}J_{HH}$ = 7.3 Hz, 1H, CH^{Ar}), 7.02 (dd, $^{3}J_{HH} \approx {}^{3}J_{HH} \approx$ 7.4 Hz, 1H, CH^{Ar}), 6.72 (q, $^{4}J_{HH}$ = 1.8 Hz, 1H, CH), 2.26 (d, $^{4}J_{HH}$ = 1.8 Hz, 3H, CH_3).

$^{13}C\{^1H\}$ NMR ($CDCl_3$, 151 MHz): δ 158.3 (C^{Ar}), 144.0 (C^{Ar}), 137.9 (C^{Ar}), 134.2 (CH^{Ar}), 130.7 (CH^{Ar}), 128.9 (C^{Ar}), 127.6 (CH^{Ar}), 126.0 (CH^{Ar}), 120.6 (CH^{Ar}), 12.2 (Me).

IR (ATR): characteristic vibrations 1616, 1594 cm^{-1}.

HRMS calculated for $C_{20}H_{17}N_2$ $[M+H]^+$: 285.1392, found 285.1400.



Bis(2-phenyl-1H-indenylylidene)azine, **10j**, red solid

^1H NMR ($CDCl_3$, 600 MHz): δ 8.03 (m, 2H, Ph), 7.69 (d, $^3J_{HH}$ = 7.5 Hz, 1H, CH^{Ar}), 7.45 (m, 2H, Ph), 7.40 (m, 1H, Ph), 7.27 (s, 1H, =CH), 7.23 (dd, $^3J_{HH} \approx {}^3J_{HH} \approx$ 7.5 Hz 1H, CH^{Ar}), 7.18 (d, $^3J_{HH}$ = 7.5 Hz, 1H, CH^{Ar}), 6.98 (dd, $^3J_{HH} \approx {}^3J_{HH} \approx$ 7.5 Hz, CH^{Ar}).

$^{13}C\{^1H\}$ NMR ($CDCl_3$, 151 MHz): δ 155.7 (C^{Ar}), 142.8 (C^{Ar}), 139.1(C^{Ar}), 134.9 (CH^{Ar}), 133.6 (C^{Ar}), 130.9 (CH^{Ar}), 129.3 (C^{Ar}), 128.5 (CH^{Ar}), 128.3 (CH^{Ar}), 128.0 (CH^{Ar}), 127.9 (CH^{Ar}), 127.1 (CH^{Ar}), 121.6 (CH^{Ar}).

IR (ATR): characteristic vibrations 1608, 1592 cm^{-1}.

HRMS calculated for $C_{30}H_{21}N_2$ $[M+H]^+$: 409.1704, found 409.1715.

Crystal structure determination of **10j** [KSK551-newFM-gg]

A crystal suitable for SC-XRD structure determination was obtained from cold solution of **10j** in hexane.

Crystal Data for $C_{30}H_{20}N_2$ (M =408.48 g/mol): orthorhombic, space group Pca2$_1$ (no. 29), a = 16.0842(2) Å, b = 5.47310(10) Å, c = 23.5249(3) Å, V = 2070.91(5) Å^3, Z = 4, T = 99.99(10) K, μ(Cu Kα) = 0.590 mm^{-1}, $Dcalc$ = 1.310 g/cm^3, 29264 reflections measured (7.516° ≤ 2Θ ≤ 151.448°), 4114 unique (R_{int} = 0.0412, R_{sigma} = 0.0239) which were used in all calculations. The final R_1 was 0.0416 (I > 2σ(I)) and wR_2 was 0.1119 (all data). **CCDC:** 2520313.

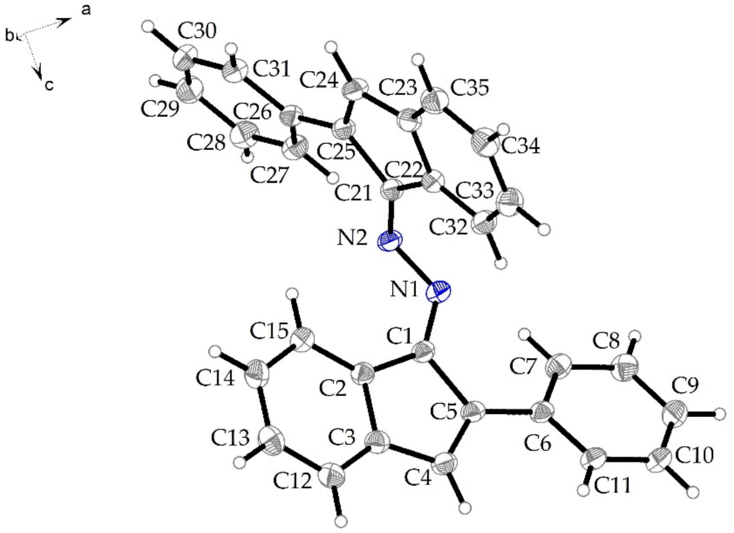
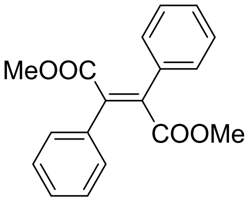


Figure S19: Crystal structure of **10j** (thermal ellipsoids shown at 30 % probability level).

Products of homocoupling of α-diazoesters

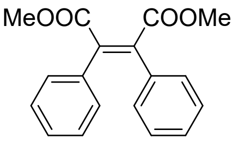


E-**9k**

E-dimethyl 2,3-diphenylfumarate, *E*-**9k**, white solid[S19]

^{1}H NMR (CDCl$_3$, 600 MHz): δ 7.43-7.36 (m, 5H, Ph), 3.55 (s, 3H, OMe).

^{13}C{^{1}H} NMR (CDCl$_3$, 151 MHz): δ 168.4, 137.5, 135.3, 128.8, 128.5, 127.9, 52.2.

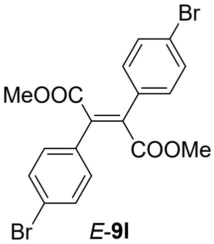


Z-**9k**

Z-dimethyl 2,3-diphenylmaleate, *Z*-**9k,** white solid[S20]

^{1}H NMR (CDCl$_3$, 600 MHz): δ 7.22-7.17 (m, 3H, Ph), 7.10-7.09 (m, 2H, Ph), 3.83 (s, 3H, OMe).

^{13}C{^{1}H} NMR (CDCl$_3$, 151 MHz): δ 168.4, 138.7, 134.3, 129.6, 128.3, 128.1, 52.7.



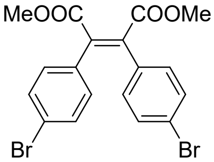
E-**9l**

E-dimethyl 2,3-di(4-bromophenyl)fumarate, *E*-**9l**, white solid

^{1}H NMR (CDCl$_3$, 600 MHz): δ 7.50 (m, 2H, CH^{Ar}), 7.25 (m, 2H, CH^{Ar}), 3.55 (s, 3H, OMe).

^{13}C{^{1}H} NMR (CDCl$_3$, 151 MHz): δ 167.7, 137.0, 134.0, 131.7, 129.6, 123.4, 52.5.

HRMS calculated for $C_{18}H_{14}O_4{}^{79}Br^{81}Br$ [M·]$^+$: 453.9245, found 453.9233.



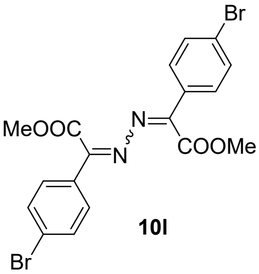
Z-**9l**

Z-dimethyl 2,3-di(4-bromophenyl)maleate, *Z*-**9l,** white solid[S20]

^{1}H NMR (CDCl$_3$, 600 MHz): δ 7.35 (m, 2H, CH^{Ar}), 6.95 (m, 2H, CH^{Ar}), 3.82 (s, 3H, OMe).

^{13}C{^{1}H} NMR (CDCl$_3$, 151 MHz): δ 167.6, 138.0, 132.9, 131.6, 131.2, 123.0, 52.9.

HRMS calculated for $C_{18}H_{14}O_4{}^{79}Br^{81}Br$ [M·]$^+$: 453.9245, found 453.9234.



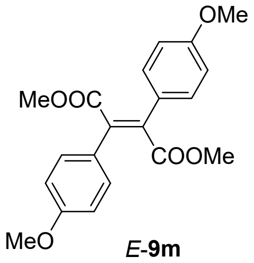
10l

Dimethyl 2,2'-(hydrazine-1,2-diylidene)-bis(2-(4-bromophenyl)acetate), **10l**, white solid

^{1}H NMR (CDCl$_3$, 600 MHz): δ 7.63 (m, 2H, CH^{Ar}), 7.58 (m, 2H, CH^{Ar}), 3.99 (s, 3H, OMe).

^{13}C{^{1}H} NMR (CDCl$_3$, 151 MHz): δ 165.2, 161.2, 132.2, 129.9, 129.4, 127.1, 52.4.

HRMS calculated for $C_{18}H_{14}N_2O_4{}^{79}Br^{81}Br$ [M·]$^+$: 481.9233, found 453.9306.



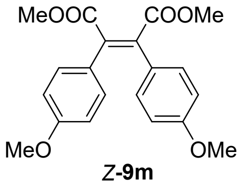
E-**9m**

E-dimethyl 2,3-di(4-methoxyphenyl)fumarate, *E*-**9m**, white solid.[S21]

^{1}H NMR (CDCl$_3$, 600 MHz): δ 7.30 (m, 2H, CH^{Ar}), 6.93 (m, 2H, CH^{Ar}), 3.99 (s, 3H, OMe), 3.86 (s, 3H, OMe).

^{13}C{^{1}H} NMR (CDCl$_3$, 151 MHz): δ 166.3, 162.6, 161.3, 129.7, 123.8, 114.3. 55.4, 52.0.

HRMS calculated for $C_{20}H_{20}O_6$ [M·]$^-$: 365.1265, found 365.1256.



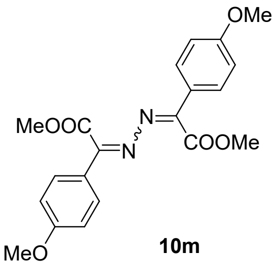
Z-**9m**

E-dimethyl 2,3-di(4-methoxyphenyl)maleate, *Z*-**9m**, white solid. [S19]

^{1}H NMR (CDCl$_3$, 600 MHz): δ 7.02 (m, 2H, CH^{Ar}), 6.73 (m, 2H, CH^{Ar}), 3.82 (s, 3H, OMe), 3.75 (s, 3H, OMe).

^{13}C{^{1}H} NMR (CDCl$_3$, 151 MHz): δ 168.9, 159.4, 137.3, 131.2, 126.8, 113.7, 55.1, 52.6.

HRMS calculated for $C_{20}H_{20}O_6$ [M·]$^-$: 365.1265, found 365.1255.



10m

Dimethyl 2,2'-(hydrazine-1,2-diylidene)-bis(2-(4-methoxyphenyl)acetate), **10m**, yellow solid

^{1}H NMR (CDCl$_3$, 600 MHz): δ 7.50 (m, 2H, CH^{Ar}), 7.25 (m, 2H, CH^{Ar}), 3.55 (s, 3H, OMe).

^{13}C{^{1}H} NMR (CDCl$_3$, 151 MHz): δ 167.7, 137.0, 134.0, 131.7, 129.6, 123.4, 52.5.

HRMS calculated for $C_{20}H_{20}N_2O_6$ [M·]$^-$: 384.1316, found 384.1316.

Crystal structure determination of *E*-**9m** [KSK590D2-4-gg]

A crystal suitable for SC-XRD structure determination was obtained from cold solution of *E*-**9m** in hexane.

Crystal Data for $C_{20}H_{20}O_6$ (M =356.36 g/mol): monoclinic, space group $P2_1/c$ (no. 14), a = 7.2982(2) Å, b = 11.5691(3) Å, c = 10.7137(3) Å, β = 105.593(3)°, V = 871.30(4) Å^3, Z = 2, T = 100.00(10) K, μ(Cu Kα) = 0.834 mm^{-1}, $Dcalc$ = 1.358 g/cm^3, 7953 reflections measured (11.49° $\leq 2\Theta \leq$ 150.072°), 1725 unique (R_{int} = 0.0622, R_{sigma} = 0.0595) which were used in all calculations. The final R_1 was 0.0582 (I > 2σ(I)) and wR_2 was 0.1452 (all data). **CCDC**: 2520315.

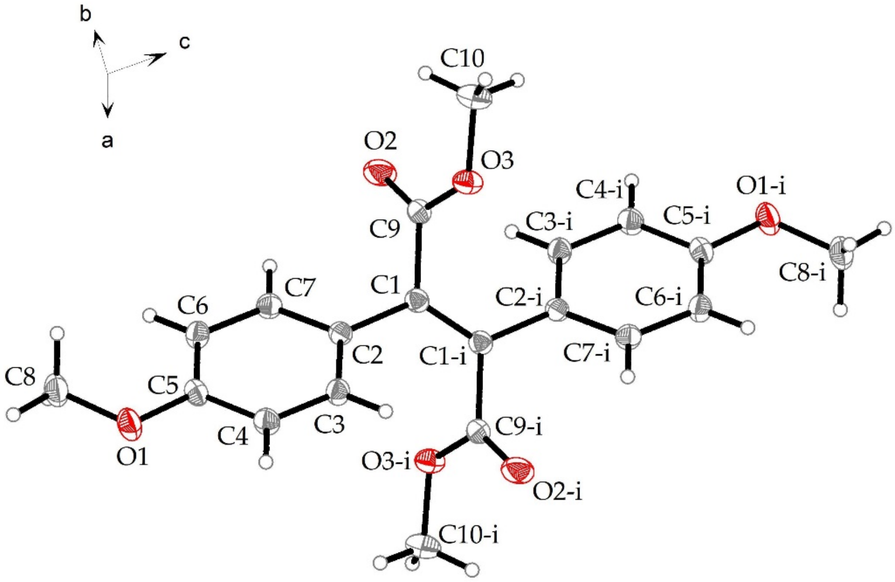
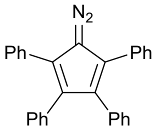
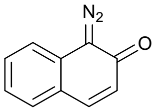
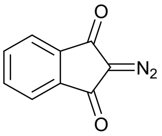


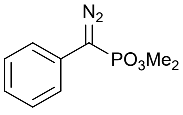
Figure S20: Crystal structure of *E*-**9m** (thermal ellipsoids shown at 30 % probability level).

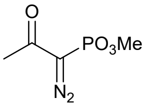
Compounds that were attempted under analgogous catalytic conditions but did not react, and from which no homocoupling product could be obtained.

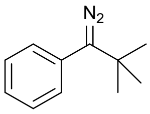






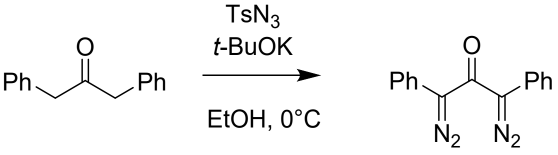






Reactivity of bis-diazoketone

Preparation of ketone **11**



11

A previously reported procedure was adapted. [S22]

Dibenzyl ketone (1.4 g, 7 mmol) was dissolved in absolute ethanol (60 mL) and placed into an ice bath. Potassium tert-butoxide (2.5 g, 22.4 mmol, 3.2 eq.) was added, and the mixture was stirred for 15 minutes until all of the potassium tert-butoxide have dissolved. A solution of tosylazide (3.0 h, 15.4 mmol, 2.2 eq.) in absolute ethanol (20 mL) was added dropwise. The mixture turned red, and an orange precipitate began to form. Reaction was stirred for 60 minutes at 0 °C, after which 100 mL of water was added. The resulting orange precipitate was collected by filtration, washed with water and dried in a vacuum desiccator overnight to give the crude product as an orange solid (0.8 g). The crude product was then dissolved in 100 mL of diethyl ether, filtered and concentrated *in vacuo* to approx. one quarter of the volume. Fine orange needle-shaped crystals have been decanted, washed with pentane and dried *in vacuo* to give bis-diazoketone **11** as an orange solid (0.40 g, 1.5 mmol, 22% isolated yield).

Note: obtained product appears to be stable in solid phase, however it gradually degrades in solution.

HRMS: calculated for $C_{15}H_{11}O$ $[M+H–2 N_2]^+$: 207.0804, found 207.0804.

IR (ATR): 3071 (w), 3035 (w), **2081 (s, CN_2)**, **2042 (s, CN_2)**, **1607 (s, CO)**, 1492 (s), 1448 (m), 1403 (w), 1350 (s), 1312 (m), 1241 (m), 1217 (s), 1159 (w), 1118 (w), 1075 (w), 1027 (w), 985 (m), 902 (w), 811 (w), 790 (m), 749 (s), 687 (s), 629 (s), 555 (w), 524 (m), 508 (m), 467 (w), 433 (w) cm^{-1}.

^{1}H NMR ($CDCl_3$, 600 MHz, 293K): δ 7.38 (m, 4H), 7.23 (m, 1H).

^{13}C{^{1}H} NMR ($CDCl_3$, 151 MHz, 293K): δ 178.2 (CO), [129.2, 127.2, 125.8, 125.7](Ph), 72.2 ($C=N_2$)[a].

[a] assignment based on gHMBC

Crystal structure determination of **11** [KSK578A-orange_prism3_mod-gg]

Crystals suitable for SC-XRD analysis were obtained from the filtrate (diethylether solution) cooled to 4 °C.

Crystal Data for $C_{15}H_{10}N_4O$ (M =262.27 g/mol): monoclinic, space group $P2_1/c$ (no. 14), a = 10.5623(8) Å, b = 17.4548(12) Å, c = 7.0682(4) Å, β = 99.628(7)°, V = 1284.76(15) Å^3, Z = 4, T = 100.00(10) K, μ(Cu Kα) = 0.732 mm^{-1}, *Dcalc* = 1.356 g/cm^3, 9971 reflections measured ($8.492° \leq 2\Theta \leq 153.42°$), 2571 unique ($R_{int}$ = 0.0880, R_{sigma} = 0.0732) which were used in all calculations. The final R_1 was 0.0609 (I > 2σ(I)) and wR_2 was 0.2068 (all data). **CCDC**: 2520309.

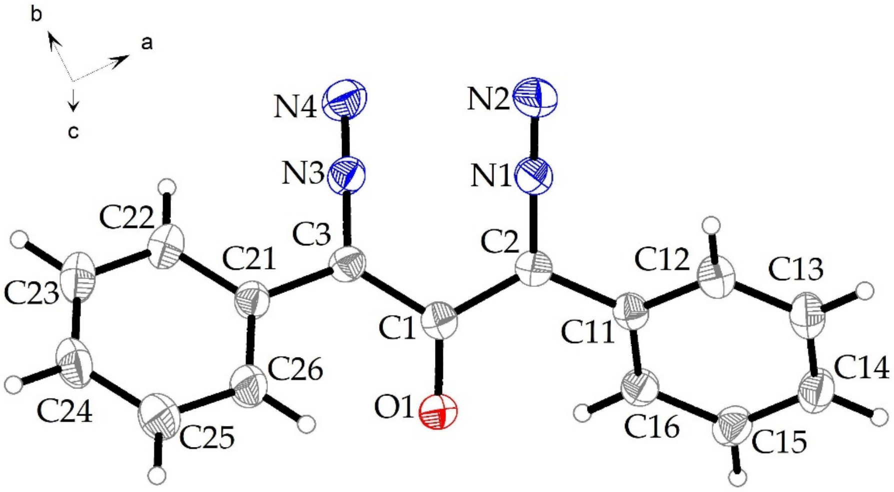


Figure S21: Crystal structure of **11** (thermal ellipsoids shown at 30 % probability level).

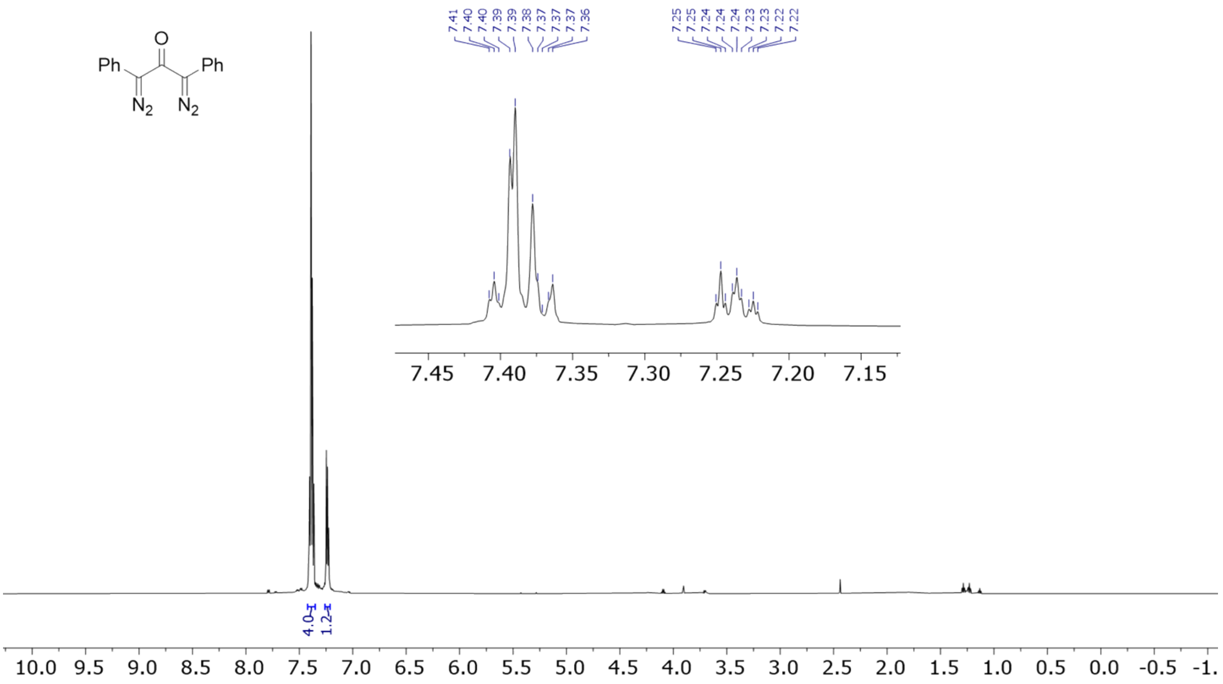


Figure S22: **^{1}H NMR** spectrum (600 MHz, $CDCl_3$) of compound **11**.

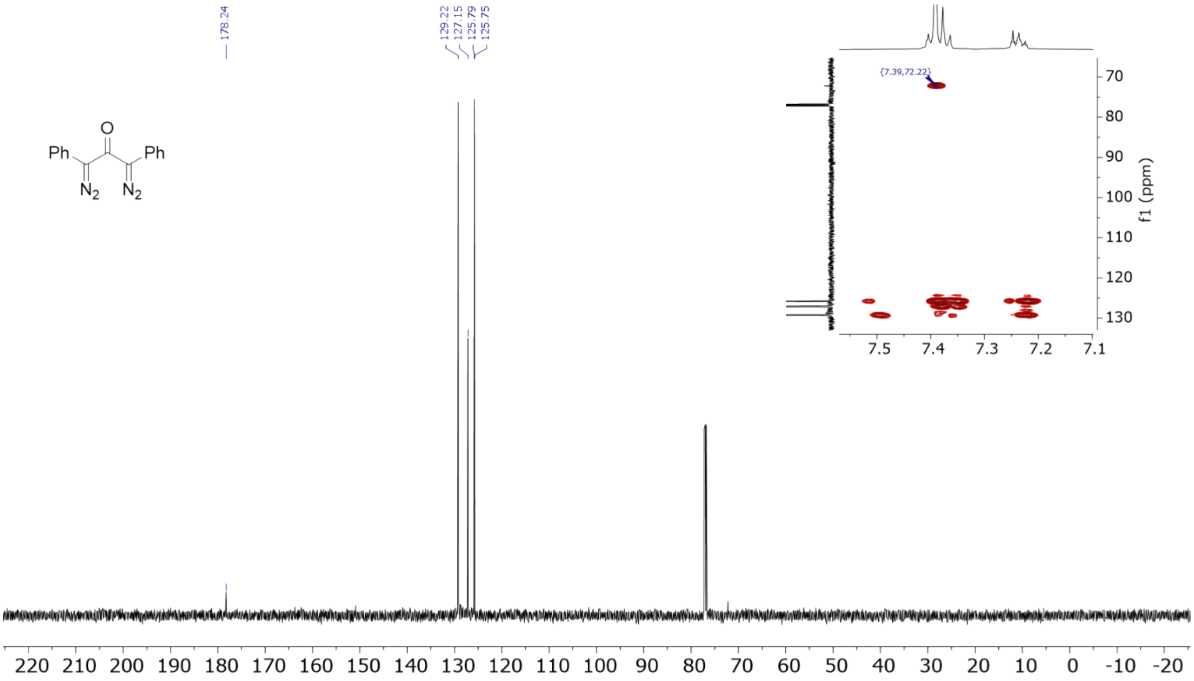
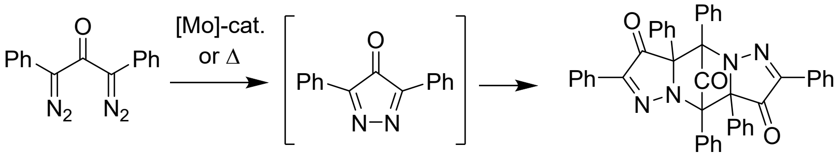


Figure S23: **^{13}C{^{1}H} NMR** spectrum (151 MHz, $CDCl_3$) and excerpt from ^{1}H,^{13}C gHMBC of compound **11**.

Reactivity of diketone **11**



11 **12** **13**

Catalytic experiment

Bis-diazoketone **11** (26.2 mg, 0.1 mmol) and complex **2** (1.2 mg, 0.002 mmol, 2 mol %) were combined in 0.6 mL of C_6D_6. The mixture turned dark brown and effervescence occurred. NMR measurement after confirmed complete conversion of starting material and formation of compound **13** after one hour (see below).

Thermolytic experiment

Bis-diazoketone **11** (26.2 mg, 0.1 mmol) was dissolved 0.6 mL of C_6D_6. The orange mixture was placed into an oil bath preheated to 60 °C. During 3 hours, its colour gradually turned red and subsequently changed to orange-yellow. NMR measurement revealed complete conversion to compound **13**.

Characterization data:

HRMS calculated for $C_{45}H_{31}N_4O_3$ $[M+H]^+$: 675.2391, found 675.2385 and for $C_{30}H_{21}N_2O_2$ [retro Diels Alder product + $H]^+$: 441.1598, found 441.1592.

IR (ATR): 3060 (w), 2974 (w), 2857 (w), 1806 (m, CO), 1724 (s, CO), 1599 (w), 1581 (w), 1490 (m), 1447 (s), 1381 (w), 1345 (w), 1308 (m), 1175 (m), 1135 (s), 1074 (w), 1033 (m), 1021 (s), 1006 (m), 944 (w), 903 (m), 820 (w), 807 (w), 772 (w), 763 (s), 690 (s), 626 (w), 574 (m), 522 (m), 509 (w), 474 (w), 449 (w) cm^{-1}.

^1H NMR (C_6D_6, 600 MHz, 293K): δ 8.33 (m, 2H), 8.01 (m, 2H), 7.41 (m, 2H), 7.30 (m, 2H), 7.25 (m, 1H), 6.85 (m, 1H), 6.80 (m, 2H), 6.79 (m, 1H), 6.69 (m, 2H).

$^{13}C\{^1H\}$ NMR (C_6D_6, 151 MHz, 293K): δ [193.8, 191.8](CO), 153.9 (C=N), [132.3, 130.2, 129.9, 129.7, 129.5, 129.4, 128.6, 128.2, 128.1, 128.0, 127.8, 126.9](3xPh), 79.4, 78.1 (aliphatic C).

Crystal structure determination of **13** [KSK578A-yell_prism-gg]

Solvent removal, dissolution of resulting oil in Et_2O and placement in the freezer (–18°C) provided yellow crystals of **13** suitable for SC-XRD.

Crystal Data for $C_{45}H_{30}N_4O_3$ (M =674.73 g/mol): orthorhombic, space group $P2_12_12_1$ (no. 19), a = 10.79123(8) Å, b = 16.54087(14) Å, c = 19.00846(16) Å, V = 3392.94(5) Å^3, Z = 4, T = 100.00(10) K, μ(Cu Kα) = 0.668 mm^{-1}, $Dcalc$ = 1.321 g/cm^3, 61590 reflections measured (7.084° ≤ 2Θ ≤ 149.45°), 6805 unique (R_{int} = 0.0397, R_{sigma} = 0.0160) which were used in all calculations. The final R_1 was 0.0307 ($I > 2\sigma(I)$) and wR_2 was 0.0871 (all data). **CCDC**: 2520319.

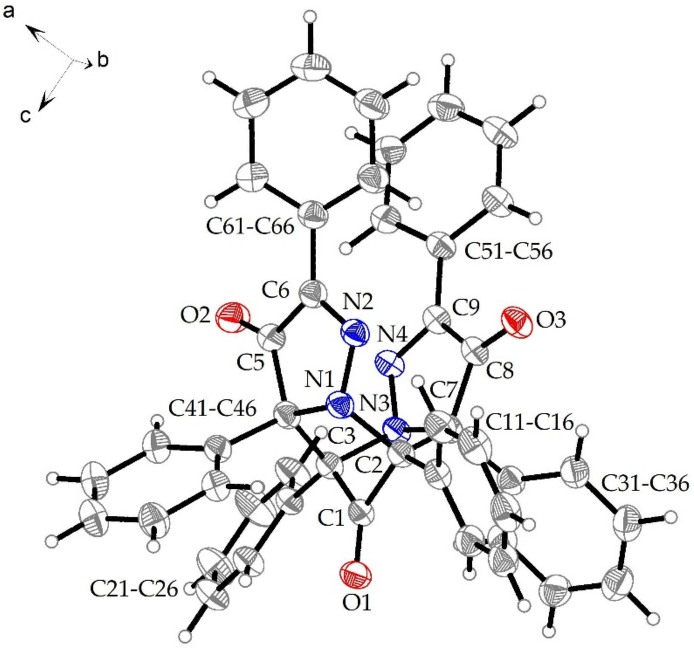


Figure S24: Crystal structure of **13** (thermal ellipsoids shown at 30 % probability level).

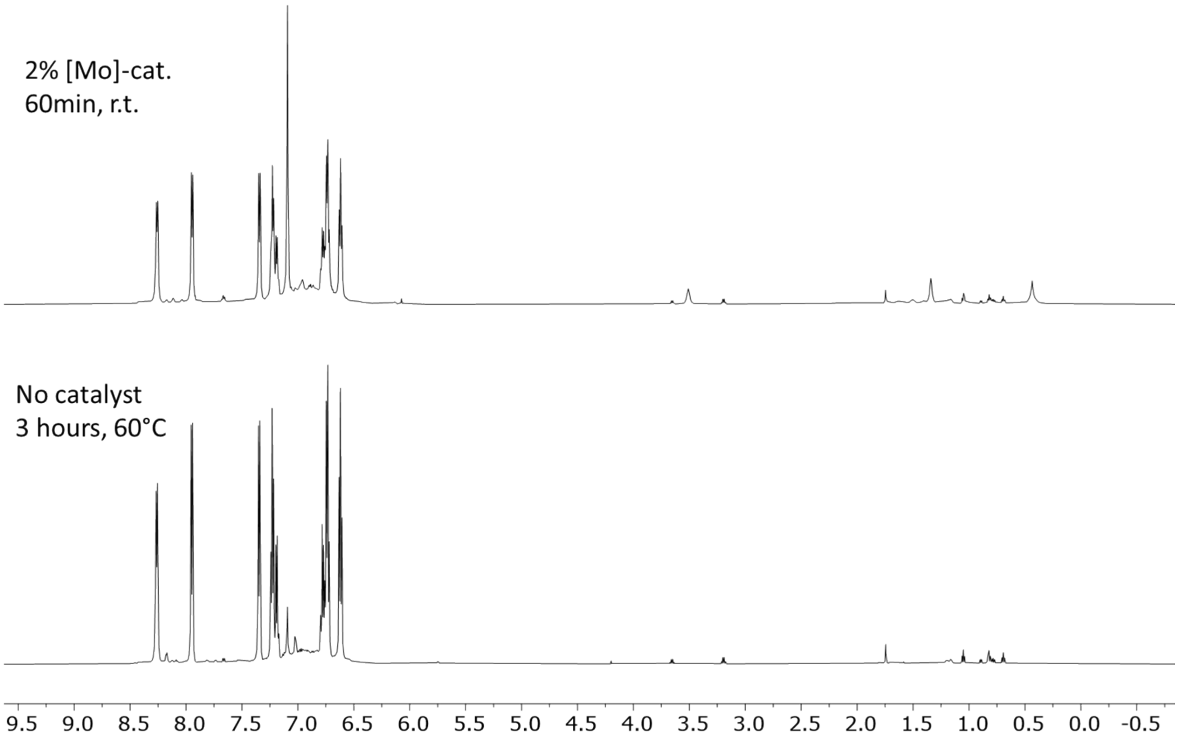


Figure S25: Comparison of *in situ* ^{1}H NMR (600 MHz, C_6D_6) spectra of compound **13** generated catalytically and thermolytically.

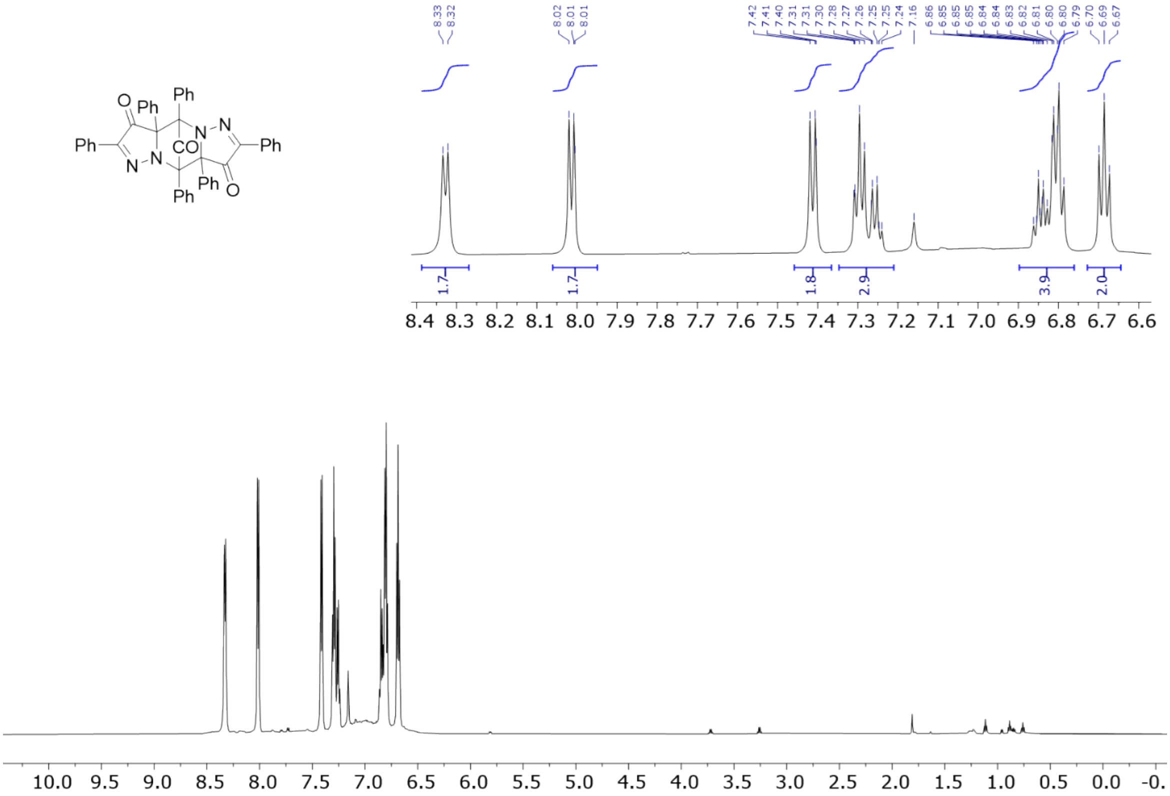


Figure S26: ^{1}**H NMR** spectrum (600 MHz, $CDCl_3$) of compound 13.

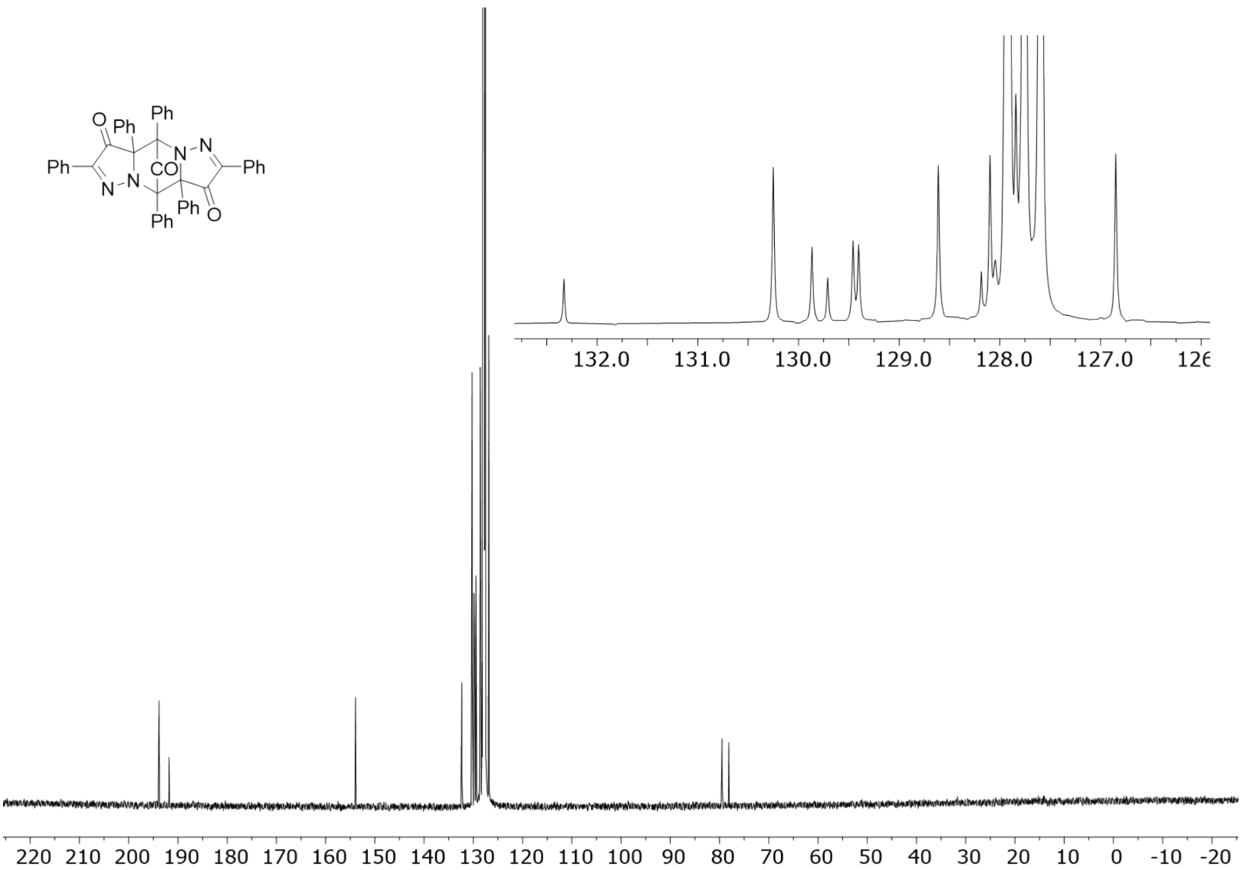


Figure S27: **$^{13}C\{^1H\}$ NMR** spectrum (151 MHz, $CDCl_3$) of compound **13**.

NMR spectra of catalytic products

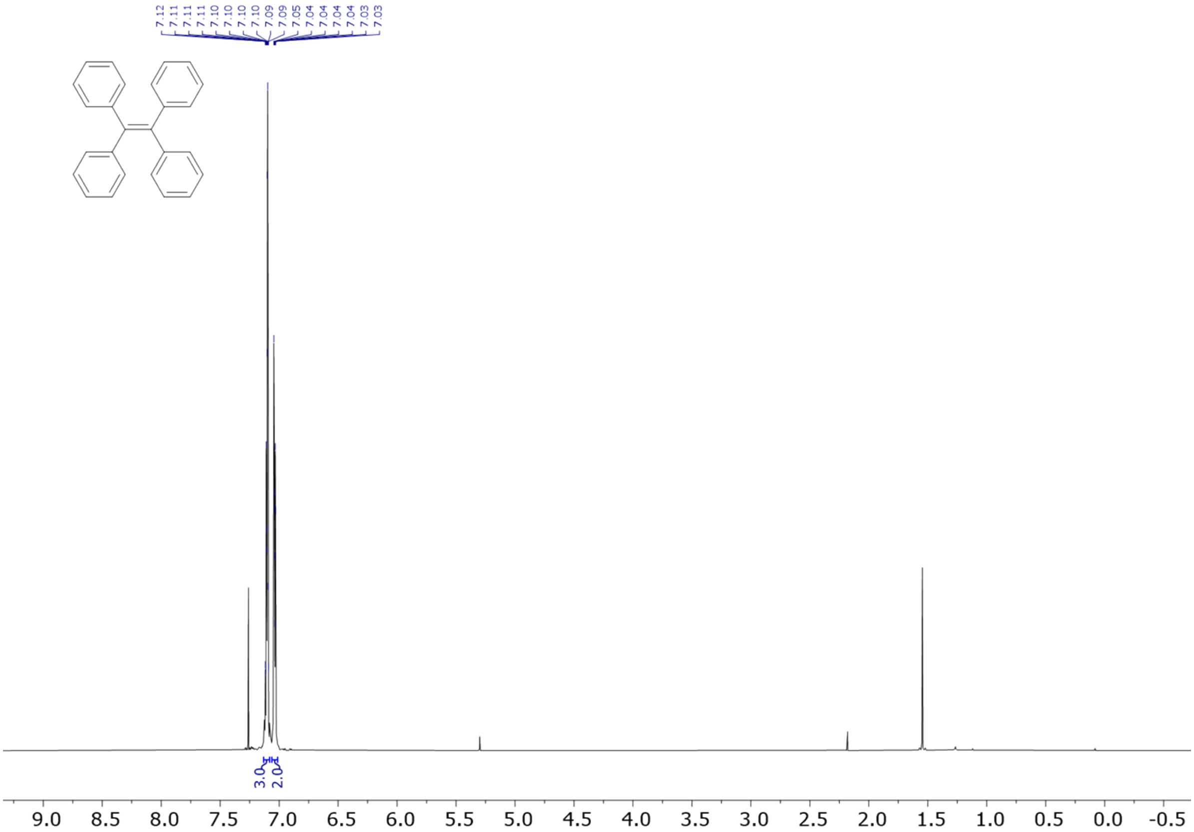


Figure S28: **^{1}H NMR** spectrum (600 MHz, $CDCl_3$) of compound **9b**.

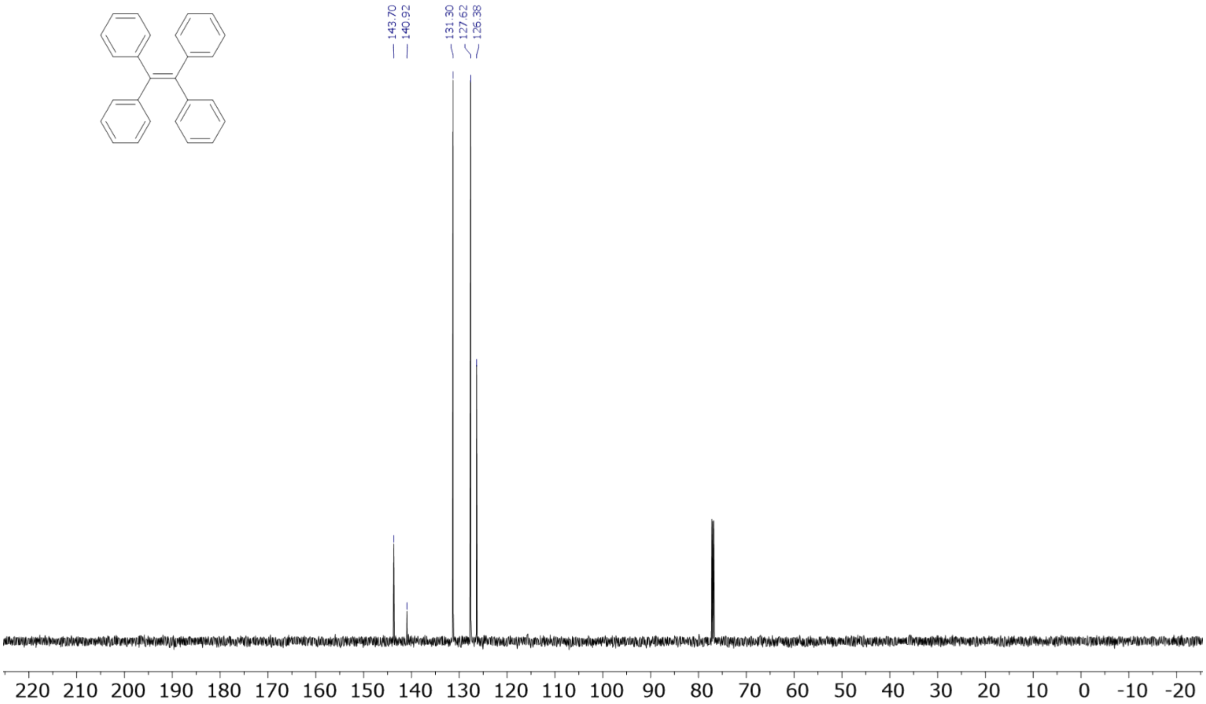


Figure S29: **$^{13}C\{^1H\}$ NMR** spectrum (151 MHz, $CDCl_3$) of compound **9b**.

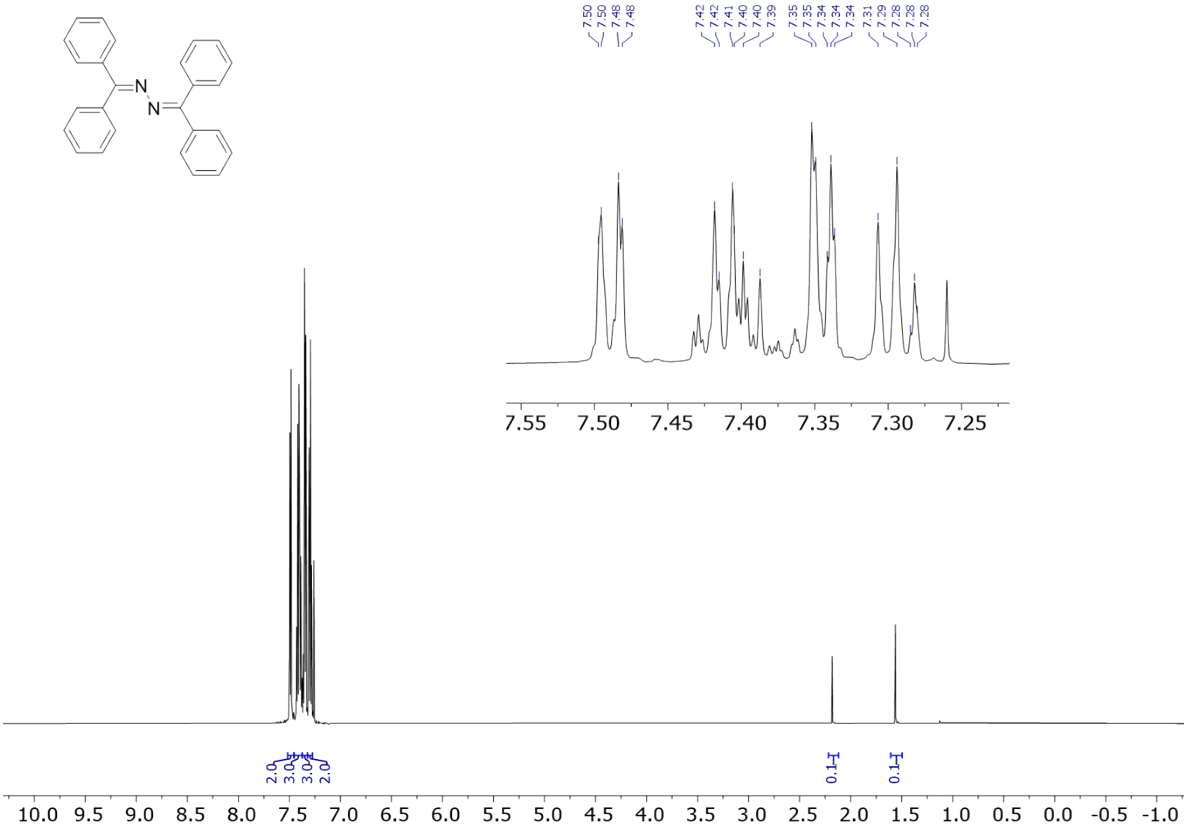


Figure S30: **^{1}H NMR** spectrum (600 MHz, $CDCl_3$) of compound **10b**.

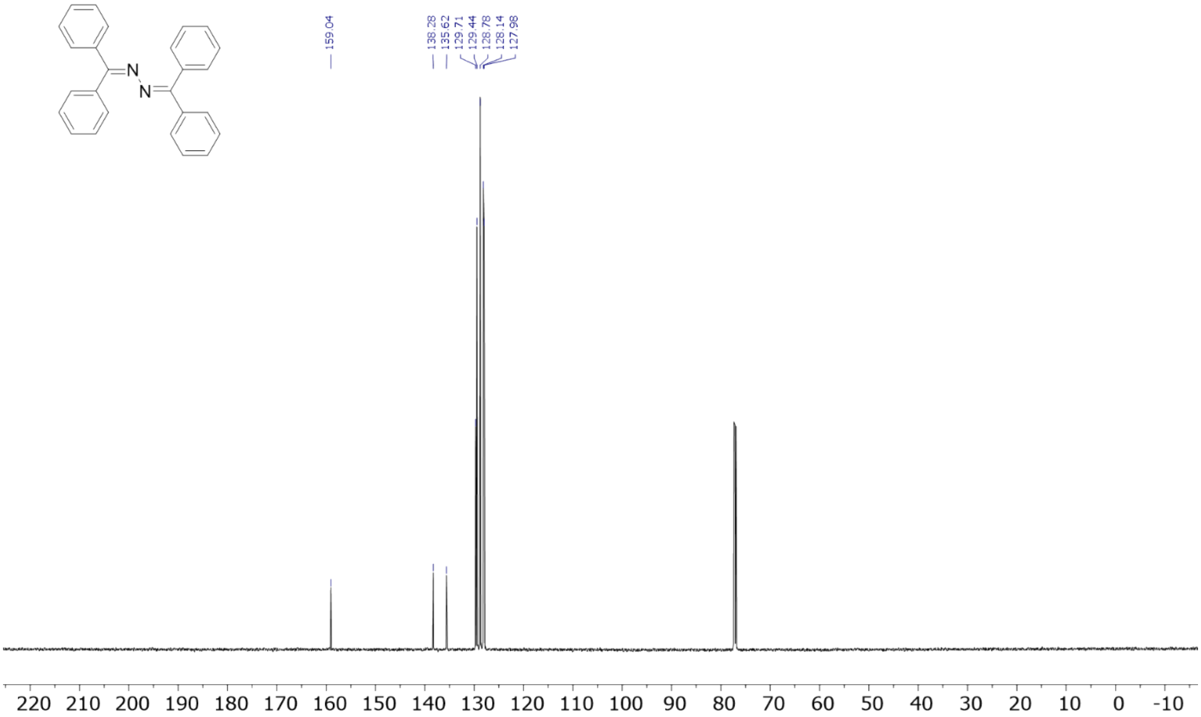


Figure S31: **^{13}C{^{1}H} NMR** spectrum (151 MHz, $CDCl_3$) of compound **10b**.

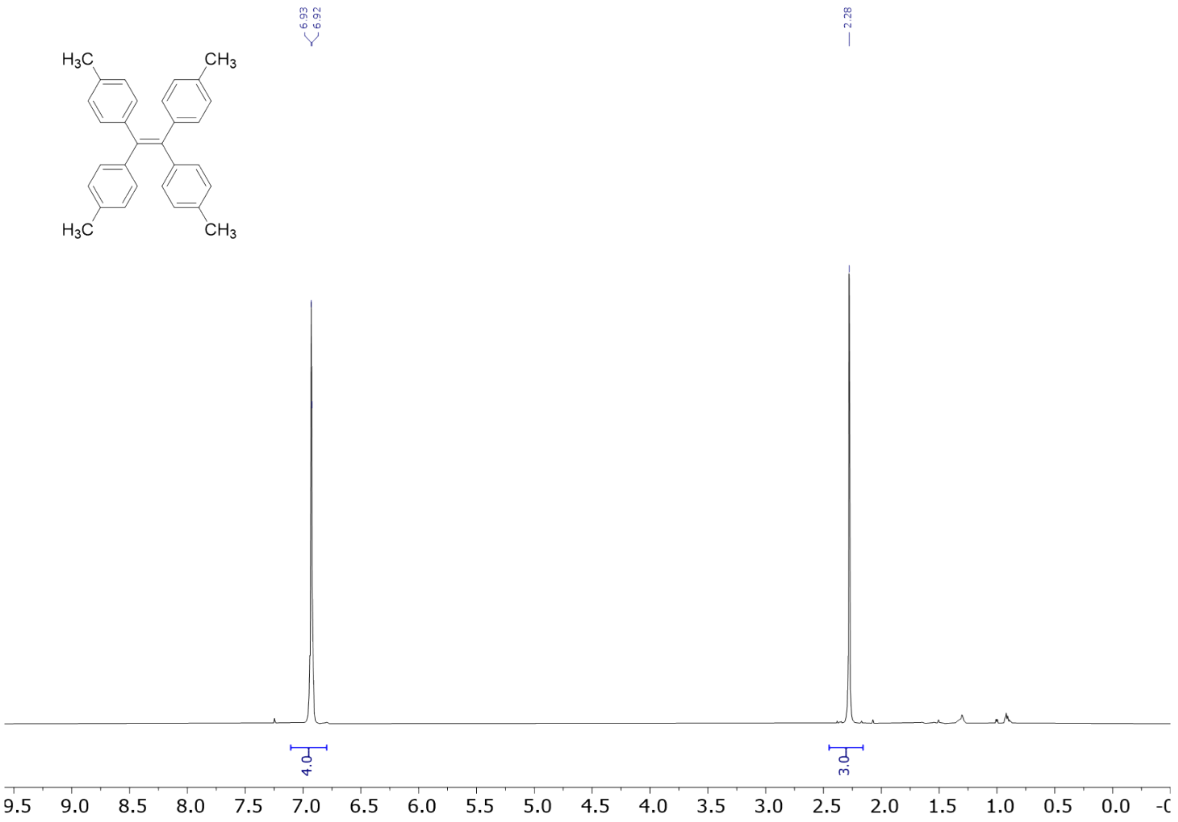


Figure S32: ^{1}**H NMR** spectrum (600 MHz, $CDCl_3$) of compound **9a**.

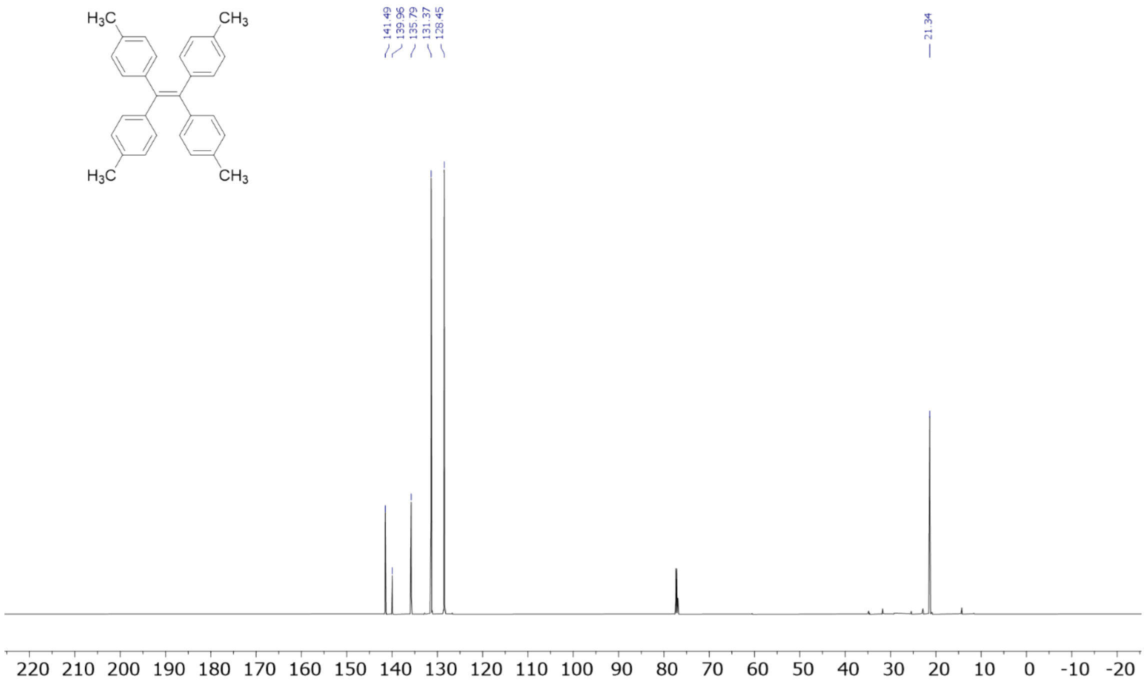


Figure S33: **^{13}C{^{1}H} NMR** spectrum (151 MHz, $CDCl_3$) of compound **9a**.

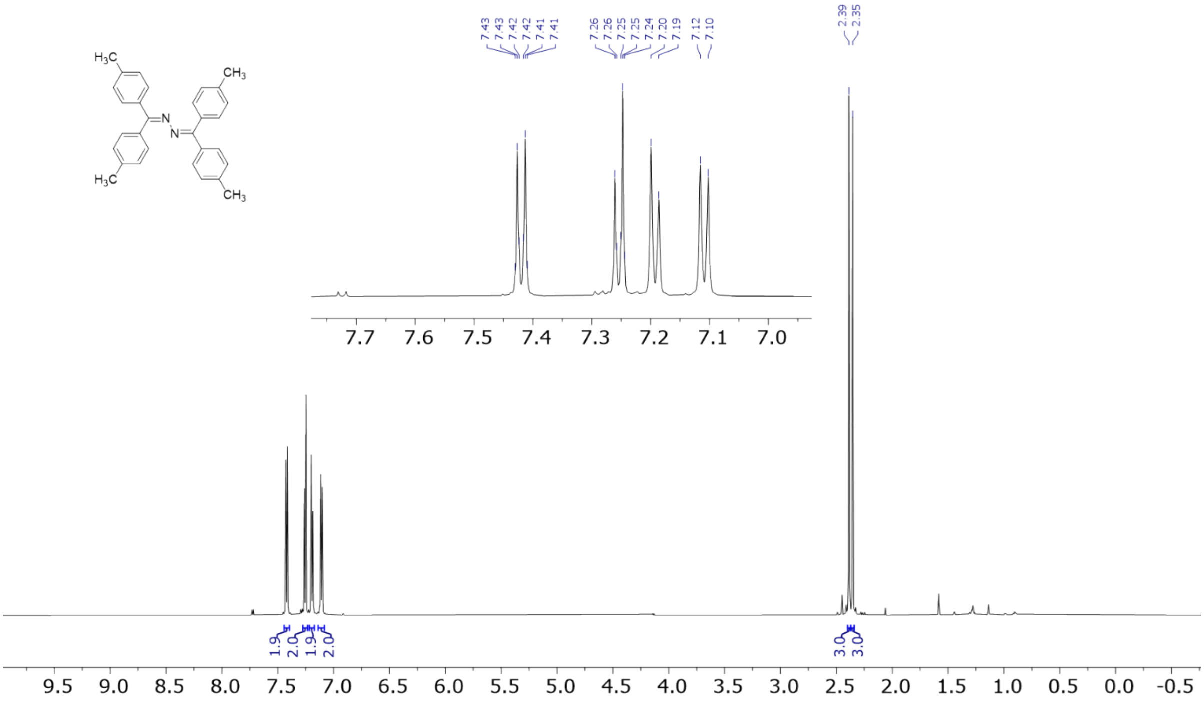


Figure S34: **^{1}H NMR** spectrum (600 MHz, CDCl$_3$) of compound **10a**.

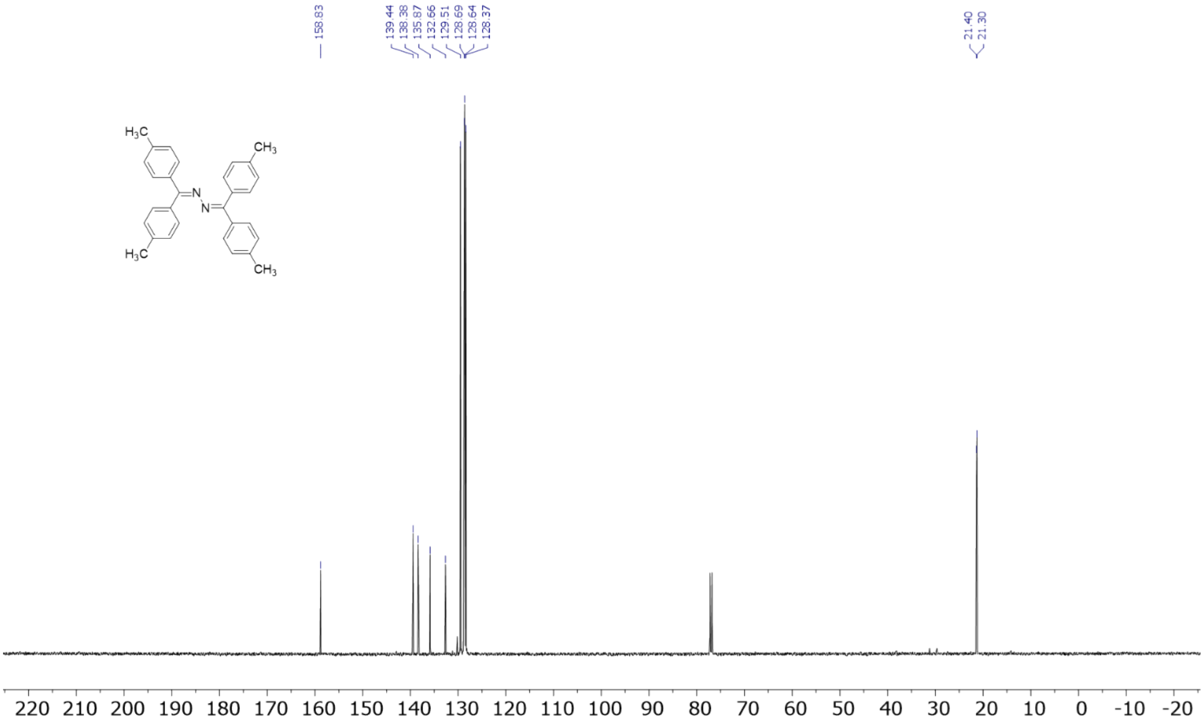


Figure S35: **^{13}C{^{1}H} NMR** spectrum (151 MHz, CDCl$_3$) of compound **10a**.

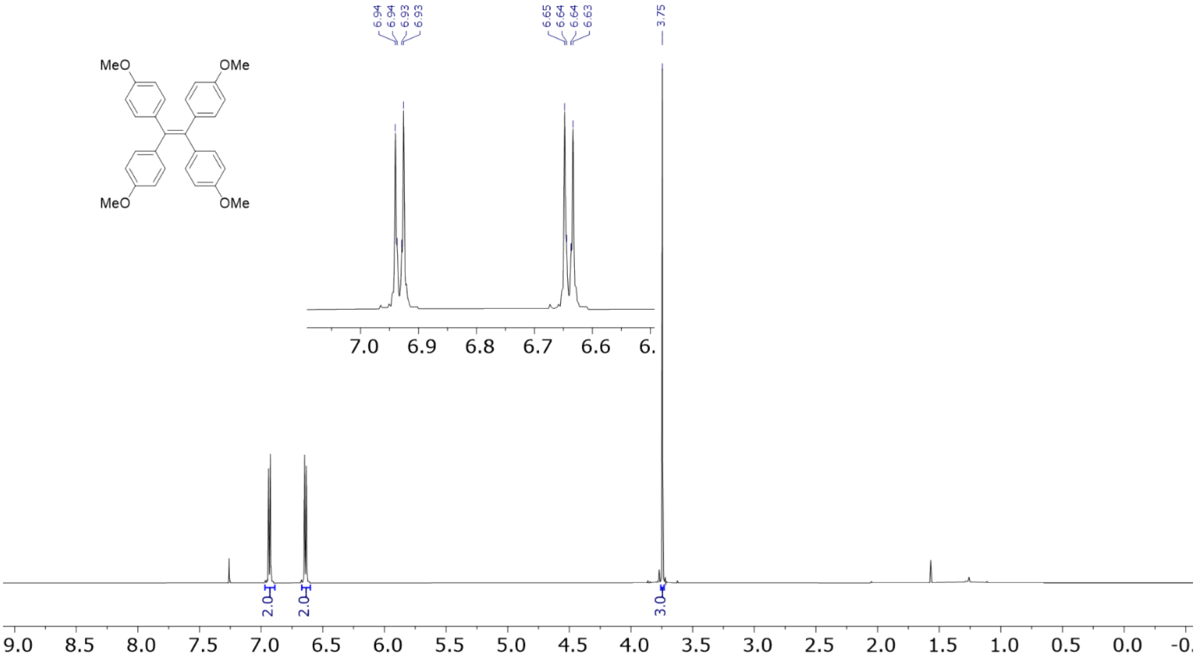


Figure S36: **^{1}H NMR** spectrum (600 MHz, $CDCl_3$) of compound **9c**.

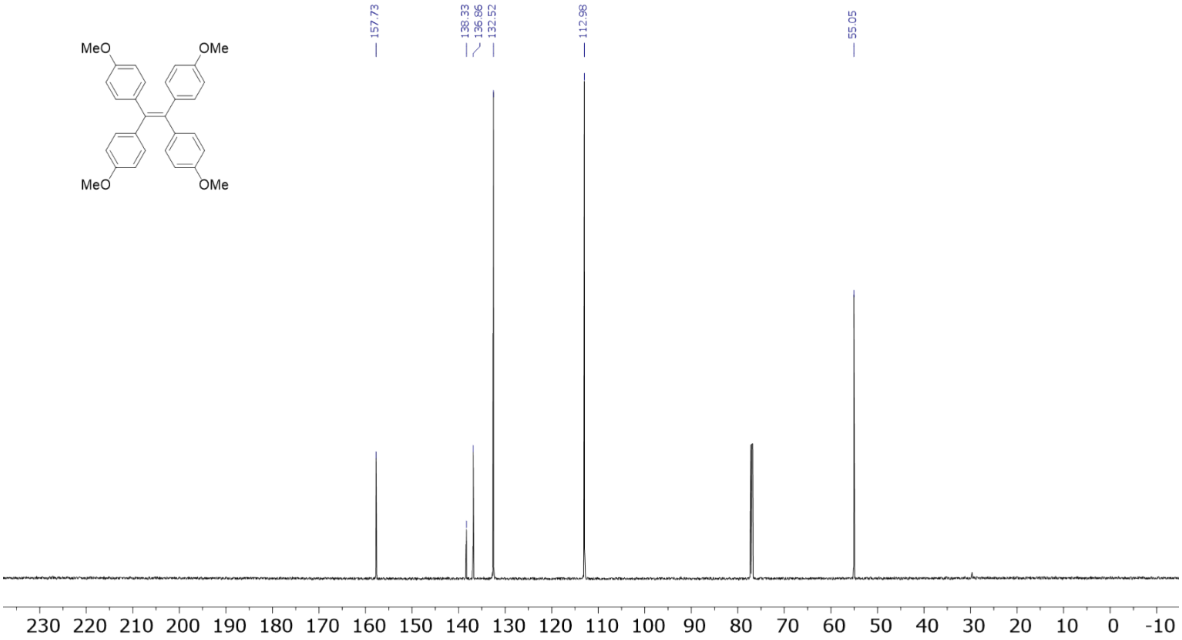


Figure S37: **$^{13}C\{^1H\}$ NMR** spectrum (151 MHz, $CDCl_3$) of compound **9c**.

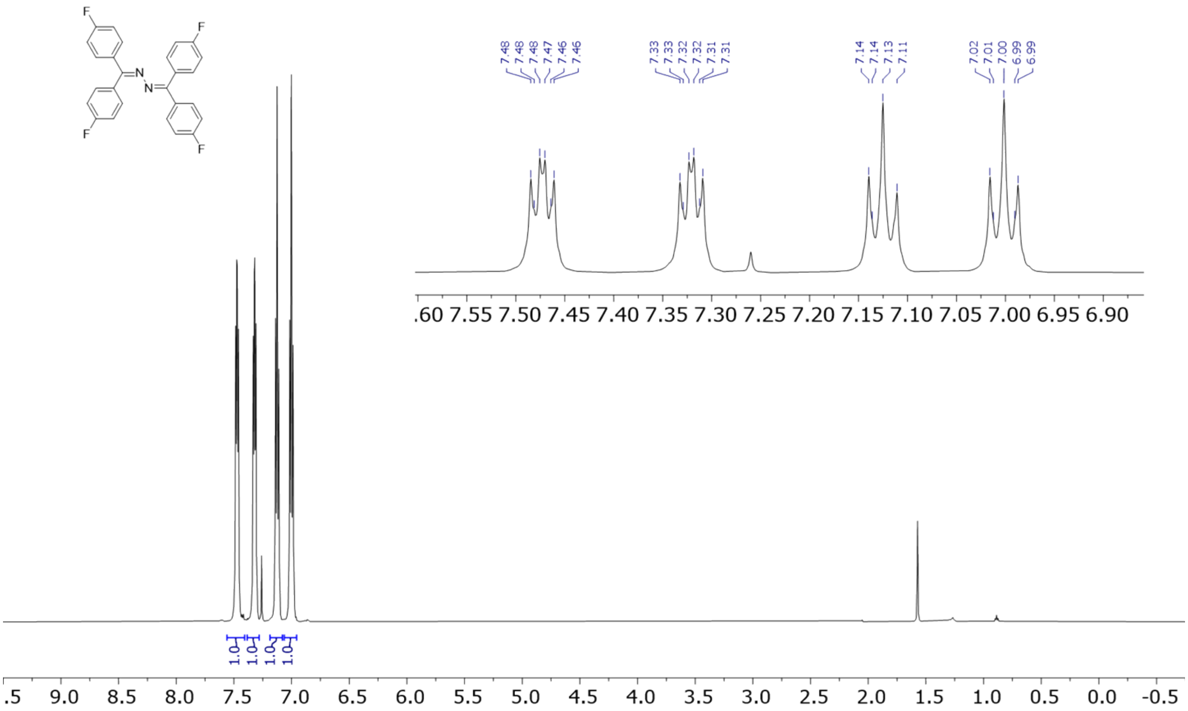


Figure S38: **^{1}H NMR** spectrum (600 MHz, $CDCl_3$) of compound **10d**.

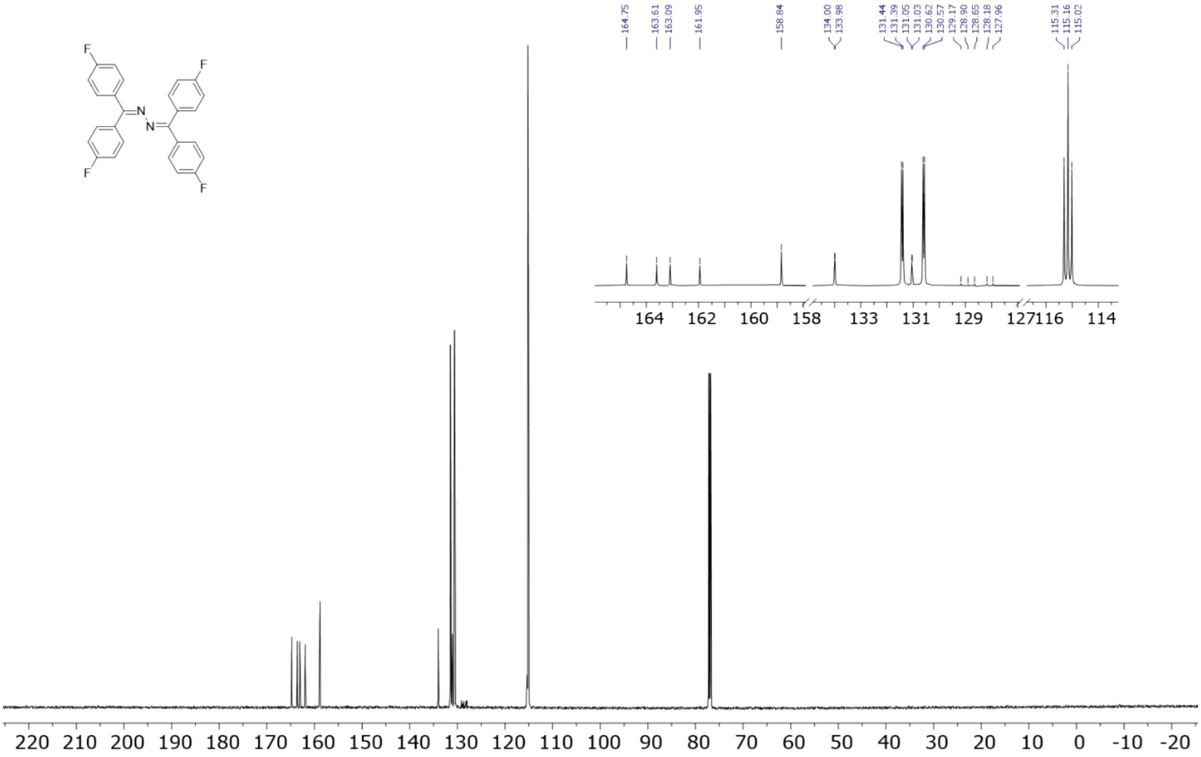


Figure S39: **^{13}C{^{1}H} NMR** spectrum (151 MHz, $CDCl_3$) of compound **10d**.

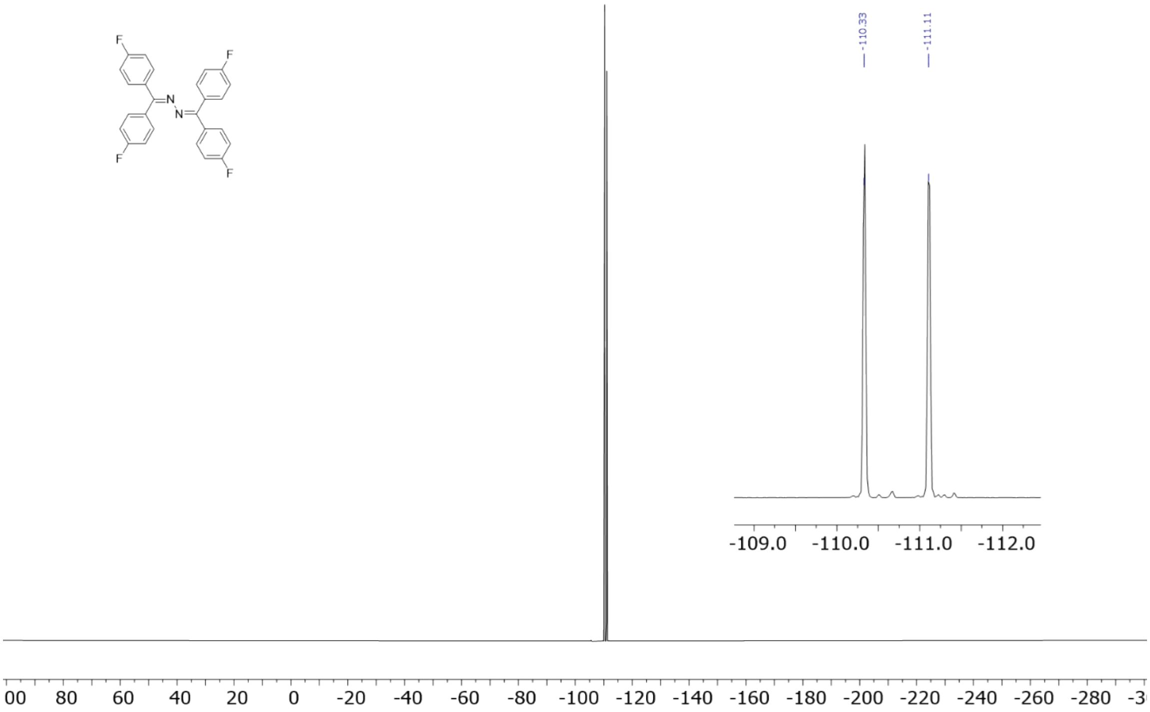


Figure S40: **^{19}F NMR** spectrum (564 MHz, $CDCl_3$) of compound **10d**.

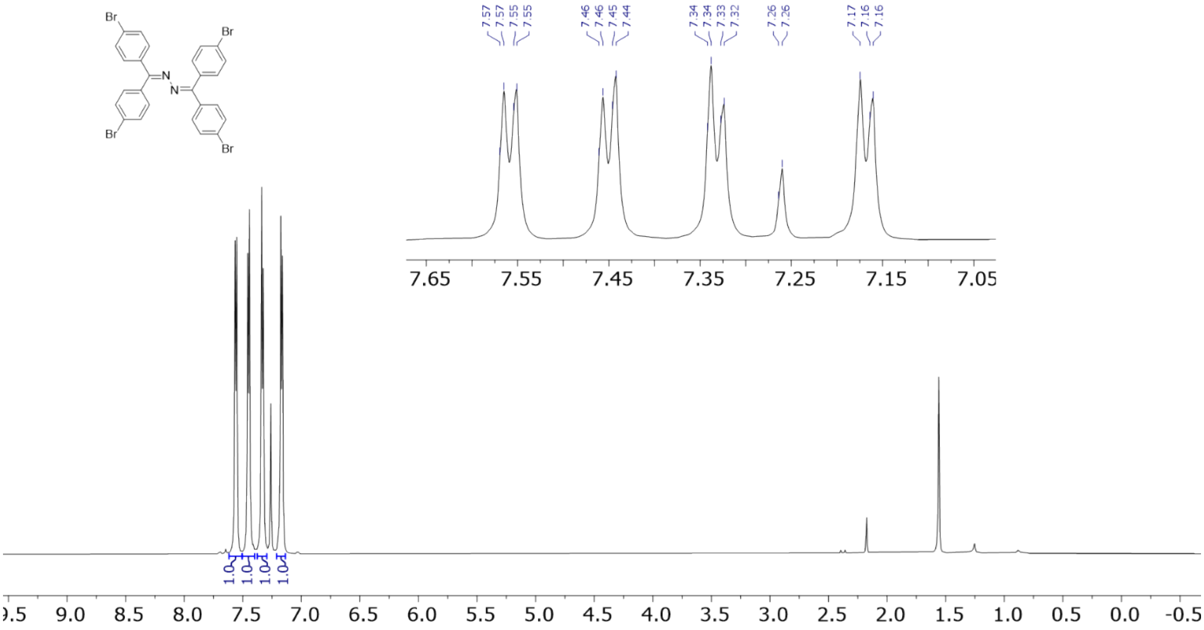


Figure S41: **^{1}H NMR** spectrum (600 MHz, $CDCl_3$) of compound **10e**.

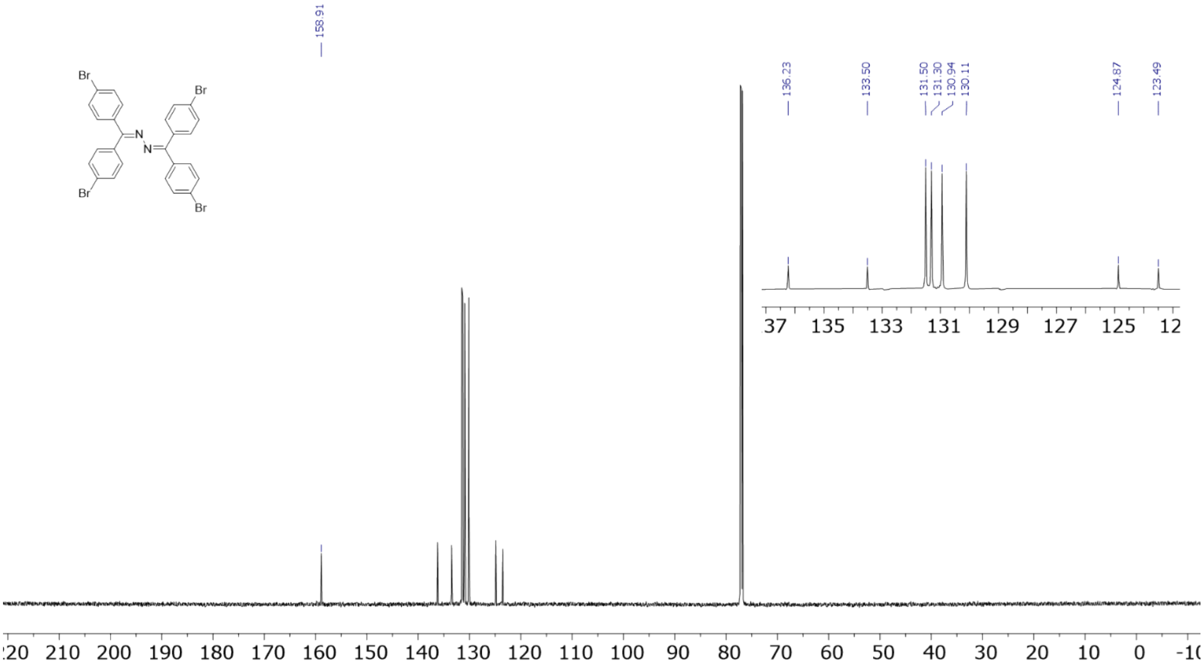


Figure S42: **$^{13}C\{^1H\}$ NMR** spectrum (151 MHz, $CDCl_3$) of compound **10e**.

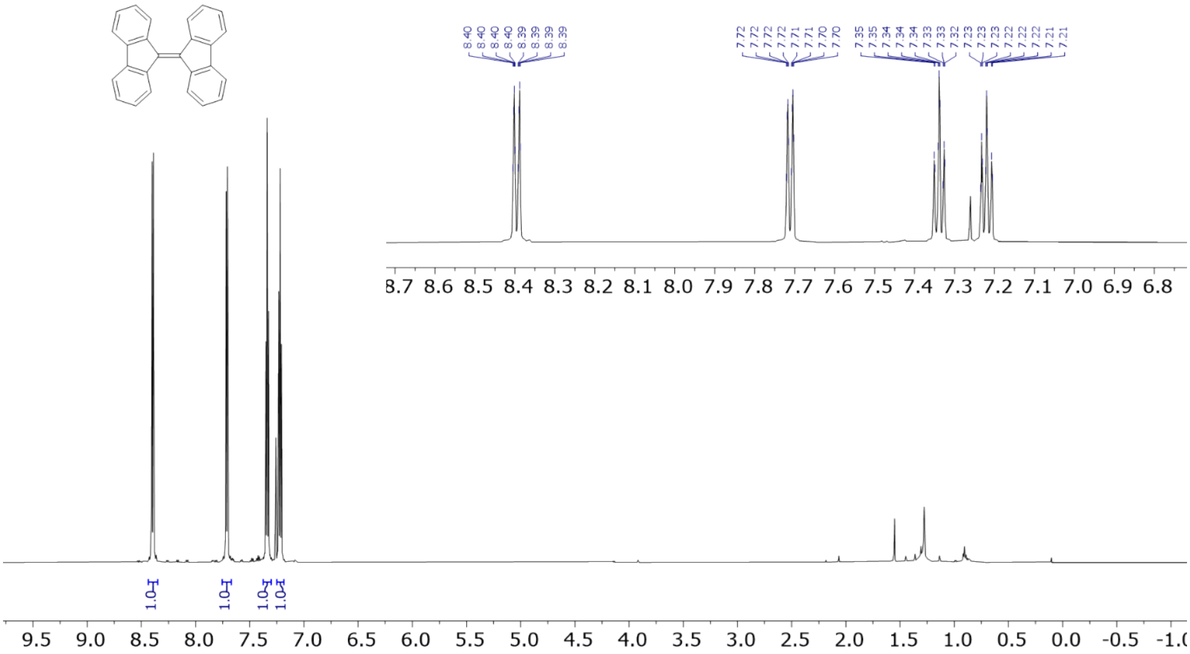


Figure S43: ^{1}**H NMR** spectrum (600 MHz, CDCl$_3$) of compound **9g**.

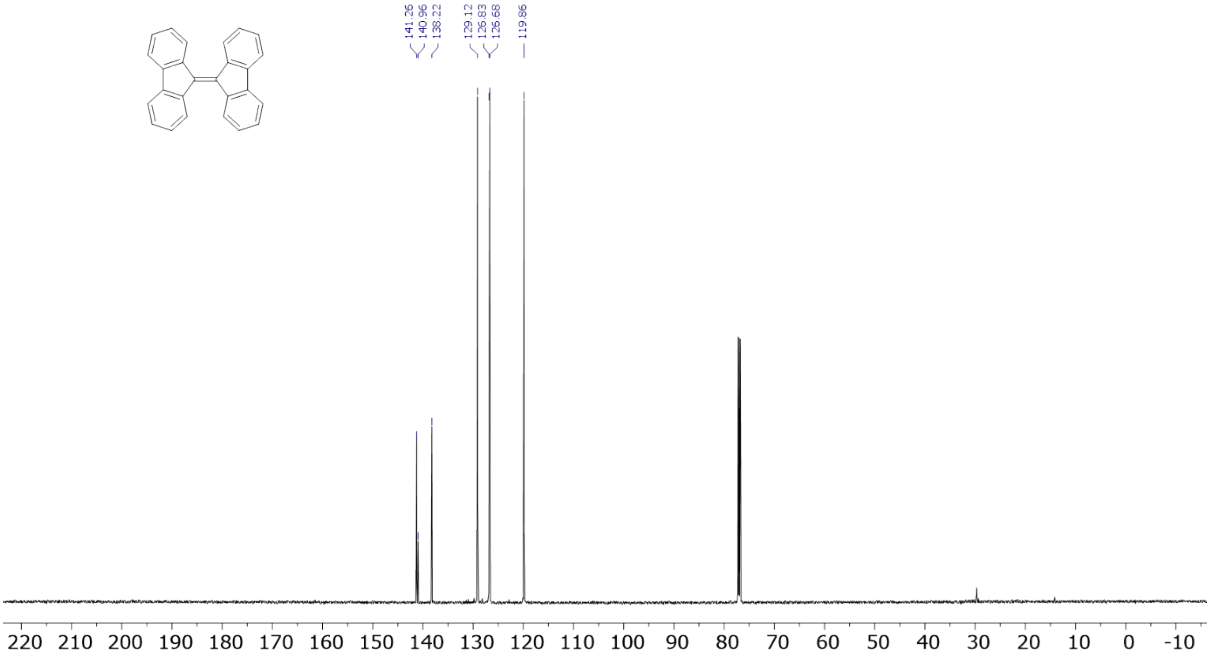
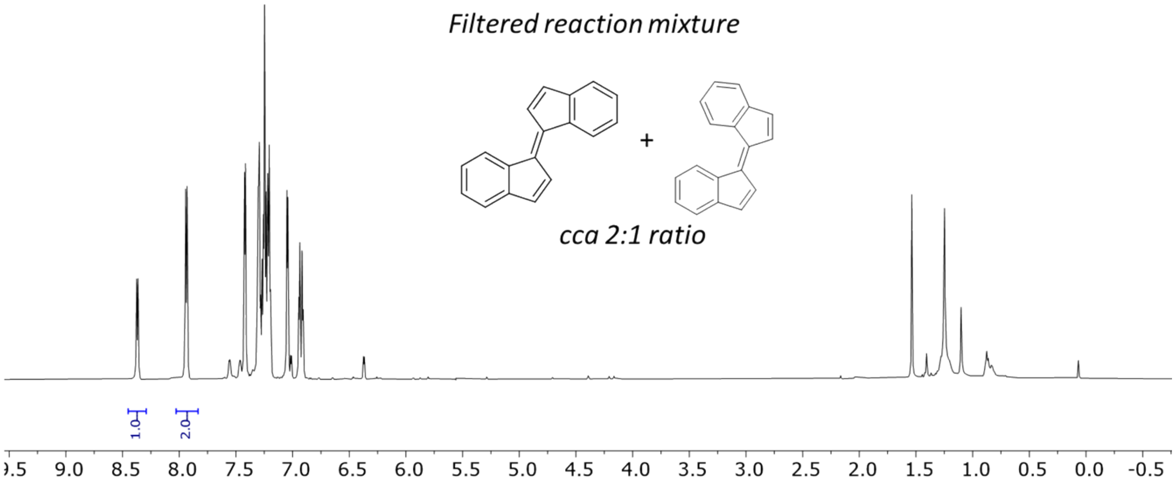


Figure S44: **^{13}C{^{1}H} NMR** spectrum (151 MHz, CDCl$_3$) of compound **9g**.



Isomeric enrichment achieved by fractional column chromatography

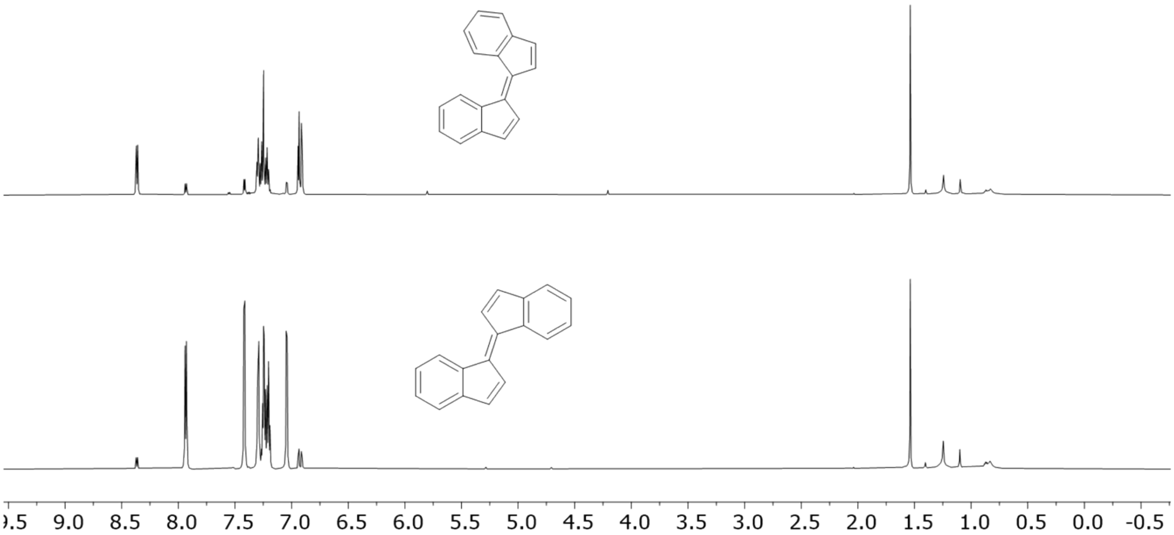


Figure S45: **^{1}H NMR** spectra (600 MHz, $CDCl_3$) of compound **9h** before the purification and after column chromatography achieving isomeric enrichment.

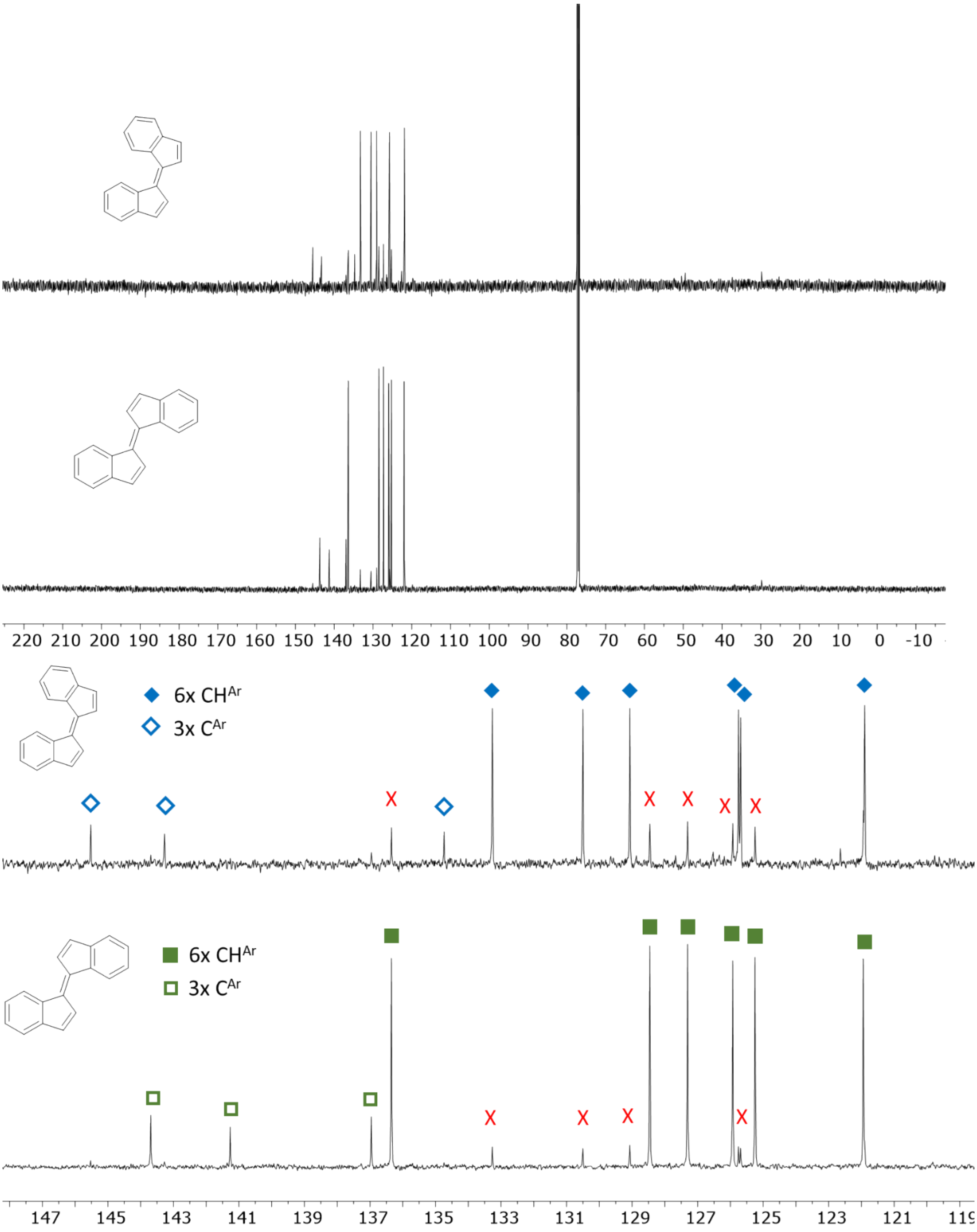


Figure S46: **^{13}C{^{1}H} NMR** spectra (151 MHz, CDCl$_3$) of compounds *E*-**9h** and *Z*-**9h**. X denotes signals belonging to the other isomer.

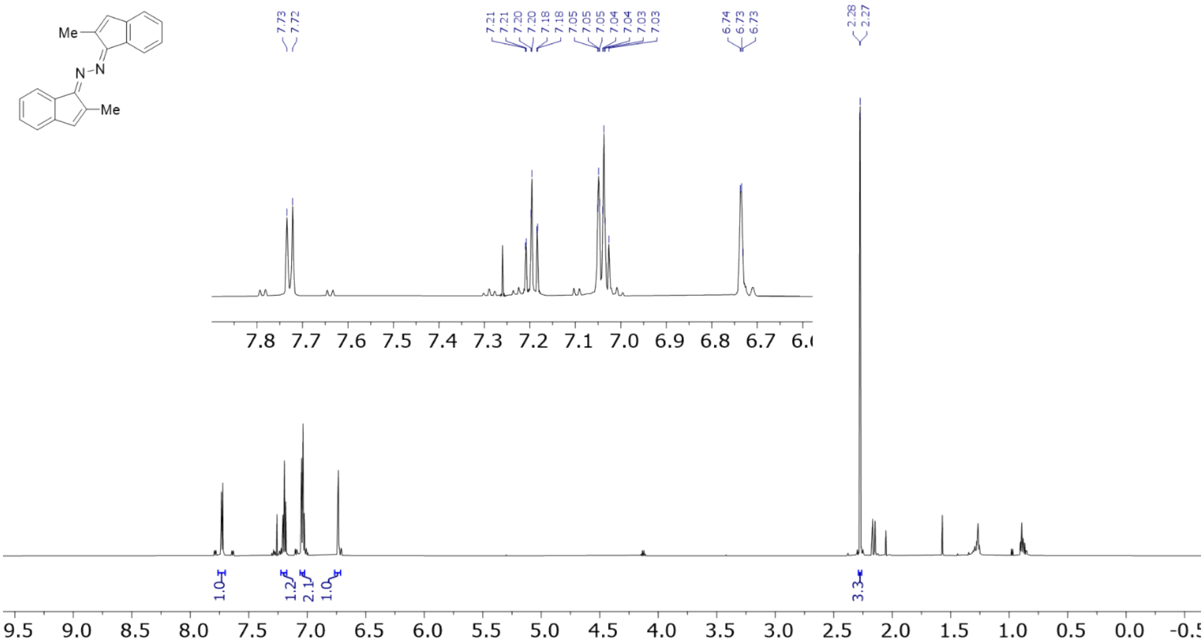


Figure S47: **^{1}H NMR** spectrum (600 MHz, $CDCl_3$) of compound **10i**.

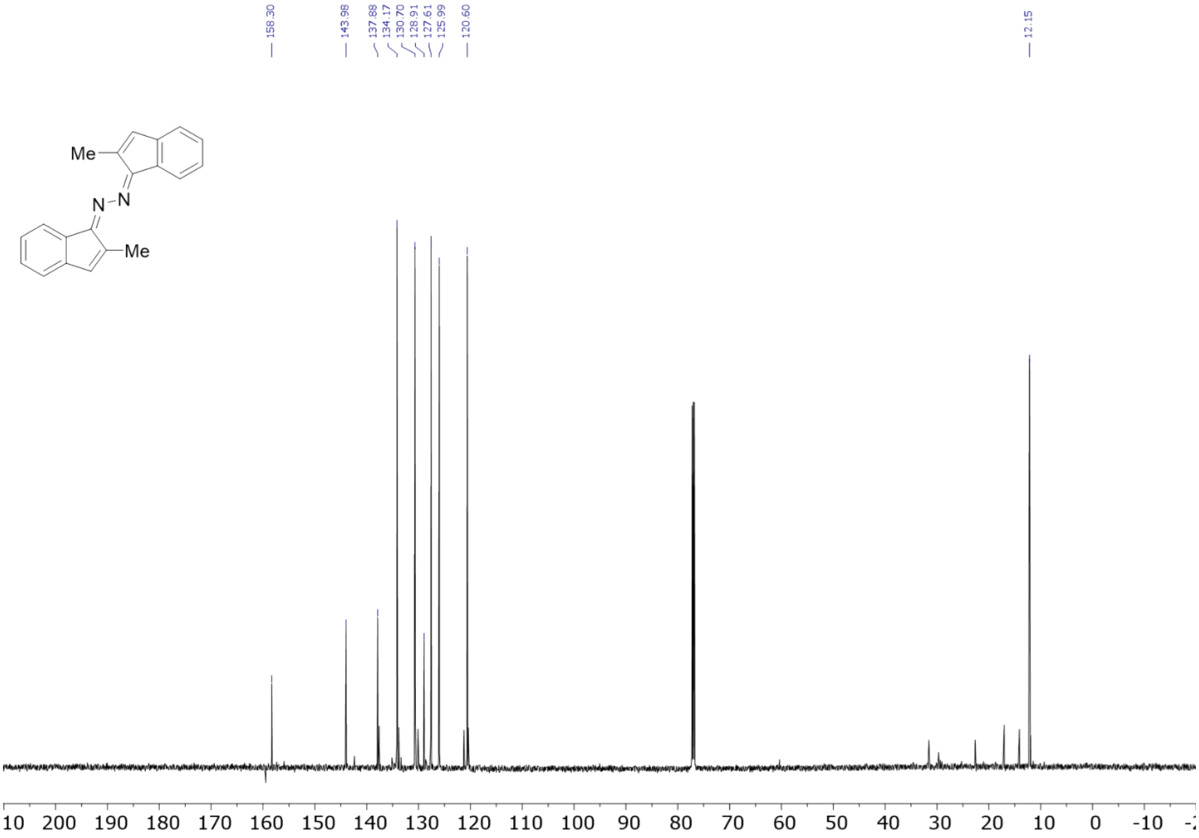


Figure S48: **$^{13}C\{^1H\}$ NMR** spectrum (151 MHz, $CDCl_3$) of compound **10i**.

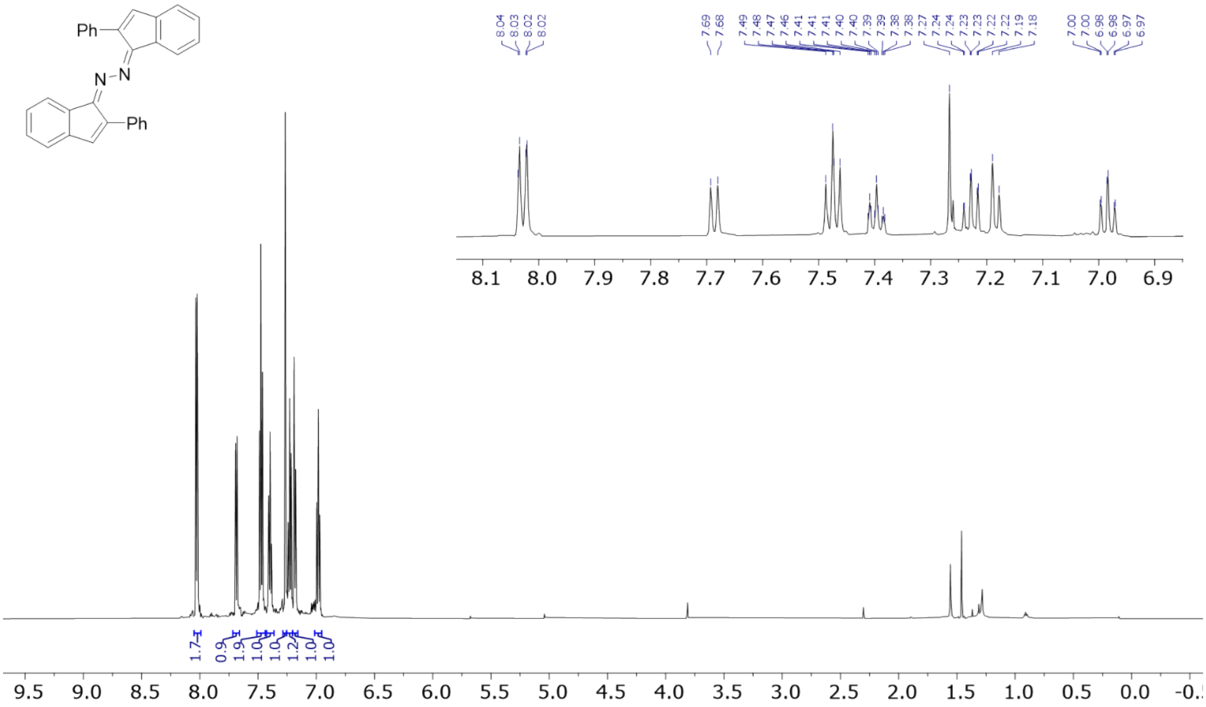


Figure S49: ^{1}**H NMR** spectrum (600 MHz, $CDCl_3$) of compound **10j**.

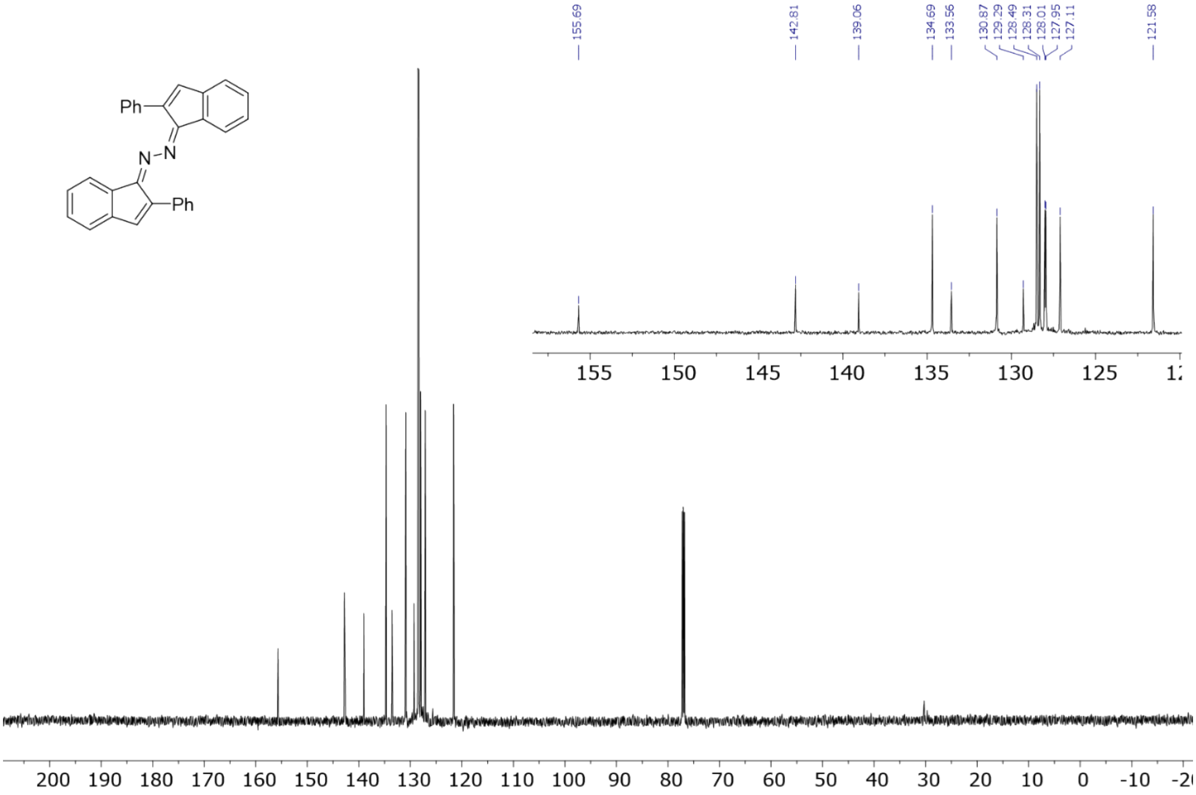


Figure S50: ^{13}**C{^{1}H} NMR** spectrum (151 MHz, $CDCl_3$) of compound **10j**.

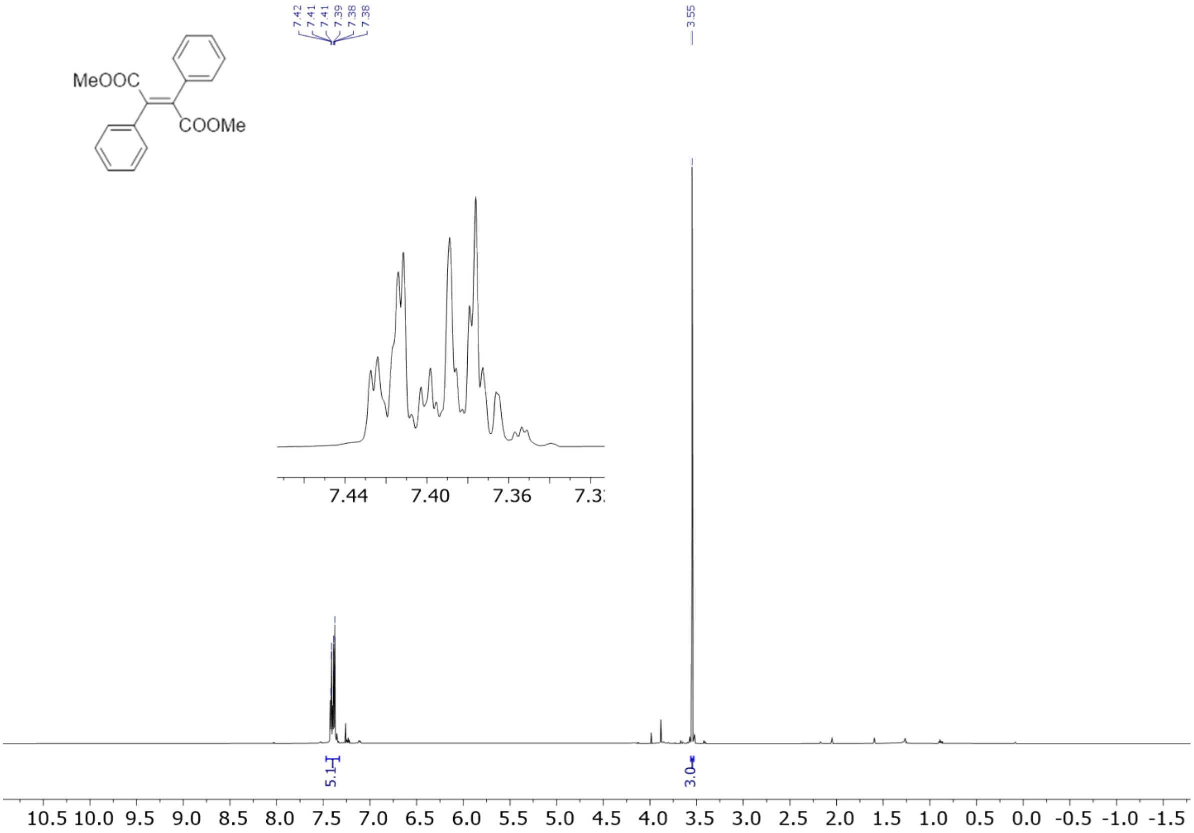


Figure S51: **^{1}H NMR** spectrum (600 MHz, $CDCl_3$) of compound *E*-**9k**.

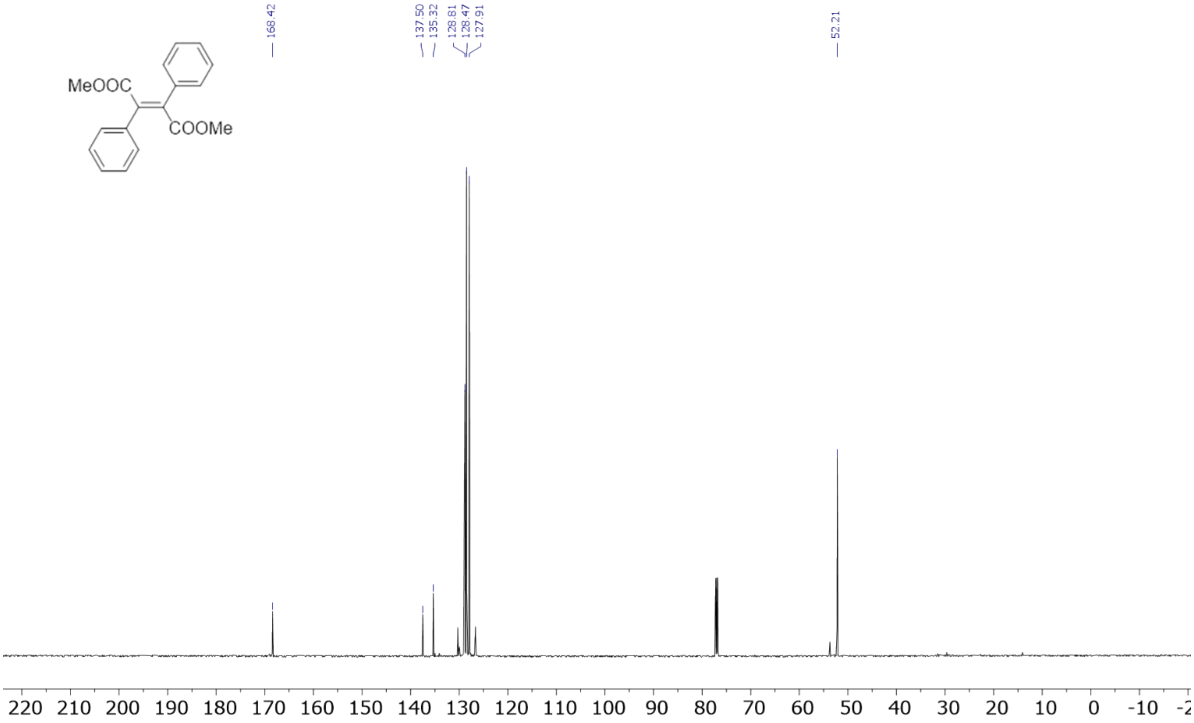


Figure S52: **^{13}C{^{1}H} NMR** spectrum (151 MHz, $CDCl_3$) of compound *E*-**9k**.

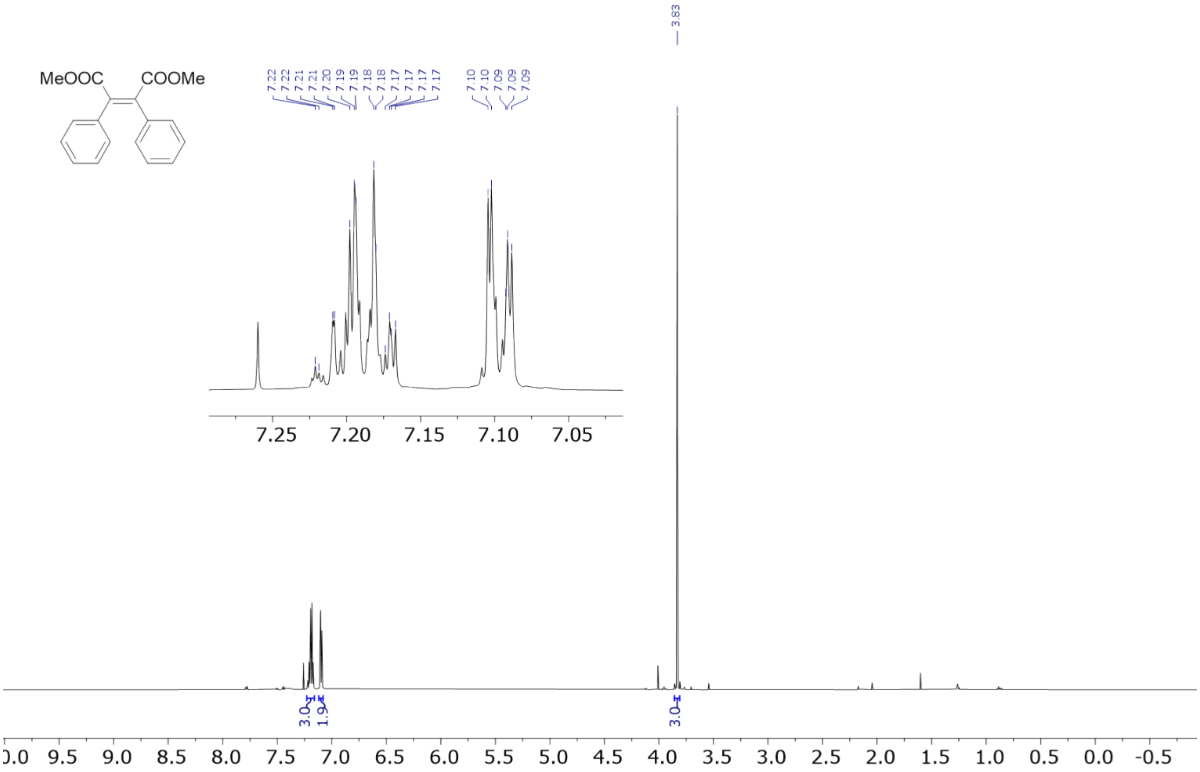


Figure S53: **^{1}H NMR** spectrum (600 MHz, CDCl$_3$) of compound *Z*-**9k**.

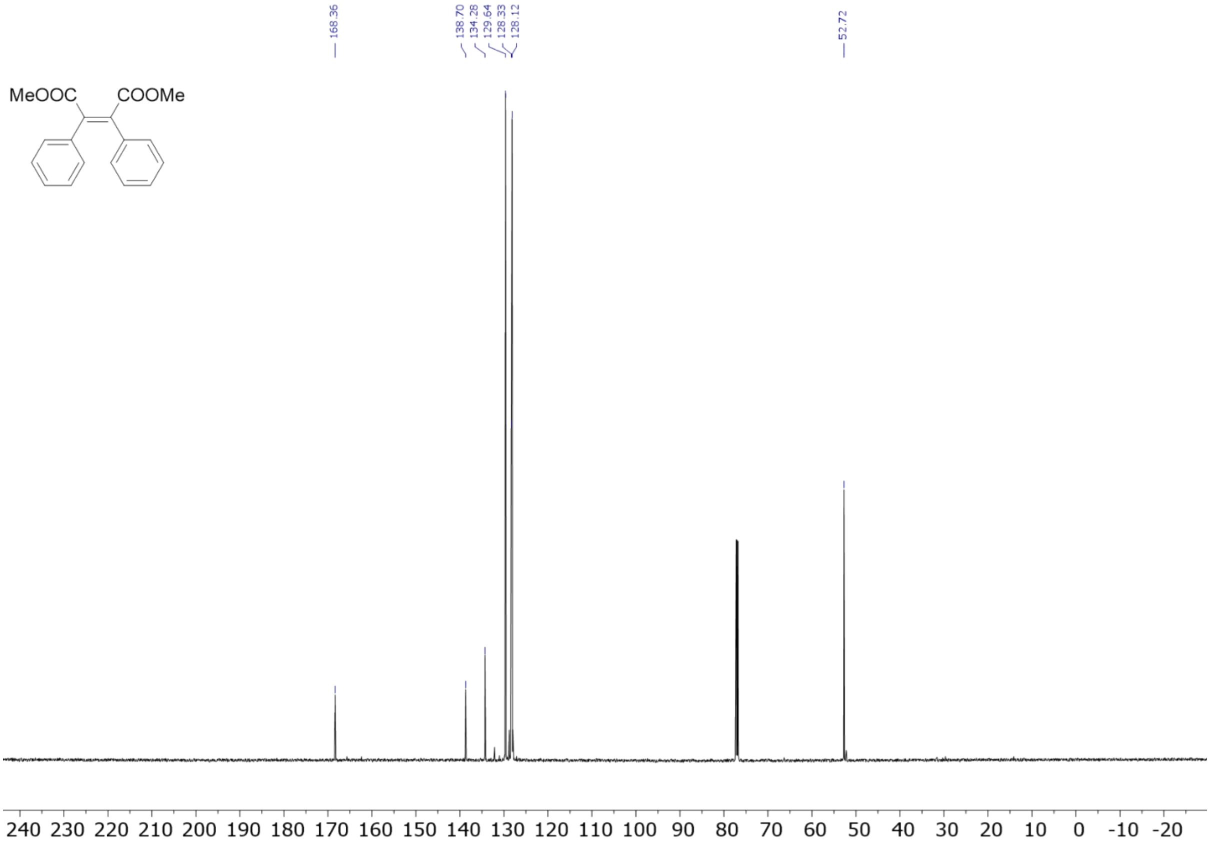


Figure S54: **^{13}C{^{1}H} NMR** spectrum (151 MHz, CDCl$_3$) of compound *Z*-**9k**.

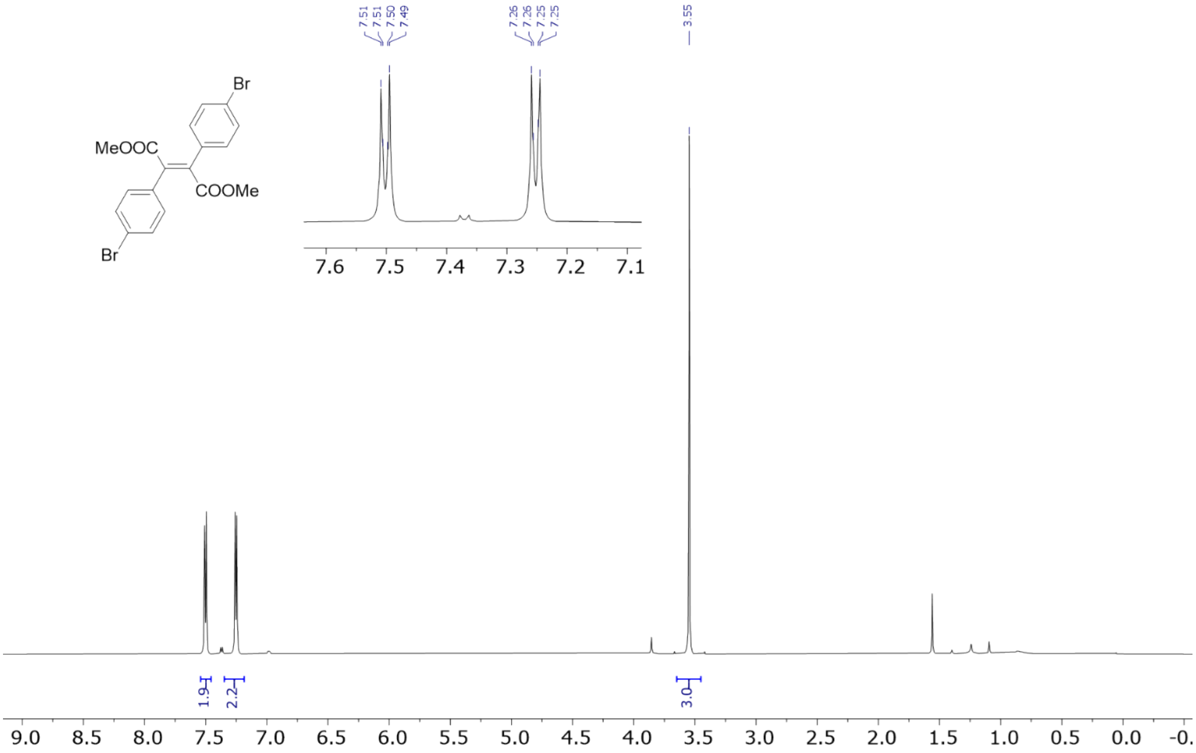


Figure S55: **^{1}H NMR** spectrum (600 MHz, $CDCl_3$) of compound *E*-**9l**.

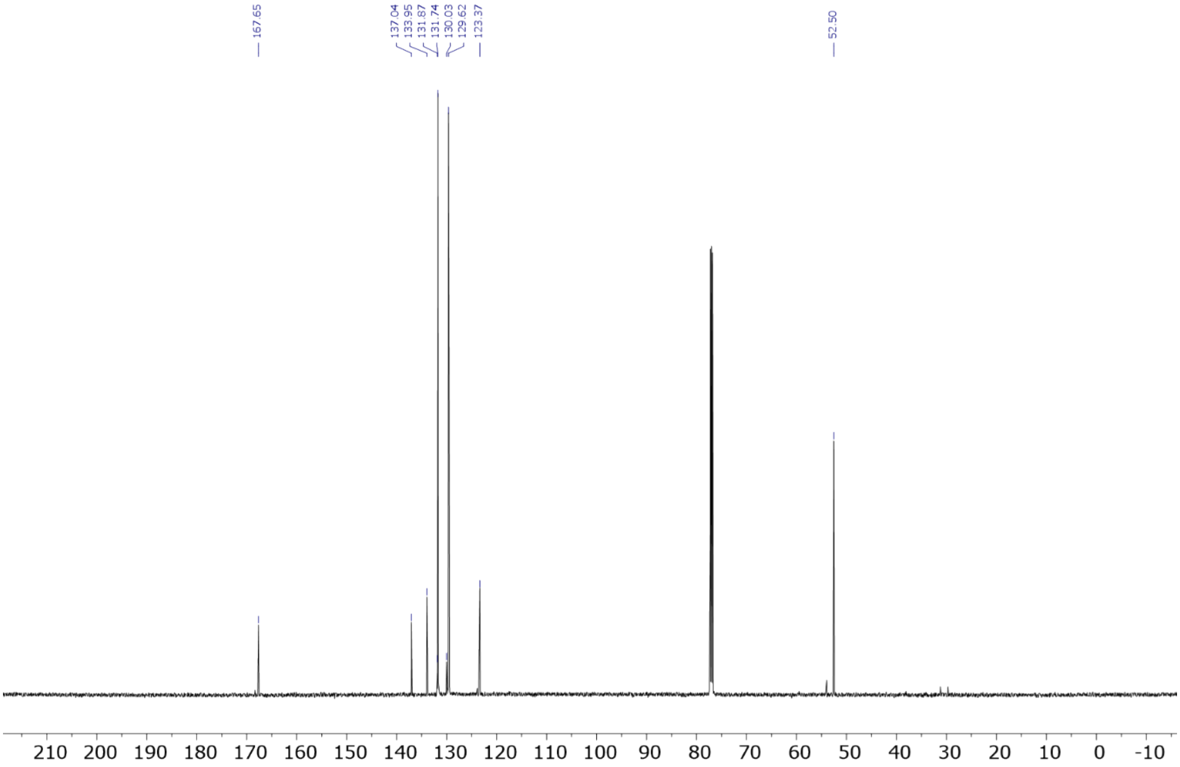


Figure S56: **$^{13}C\{^1H\}$ NMR** spectrum (151 MHz, $CDCl_3$) of compound *E*-**9l**.

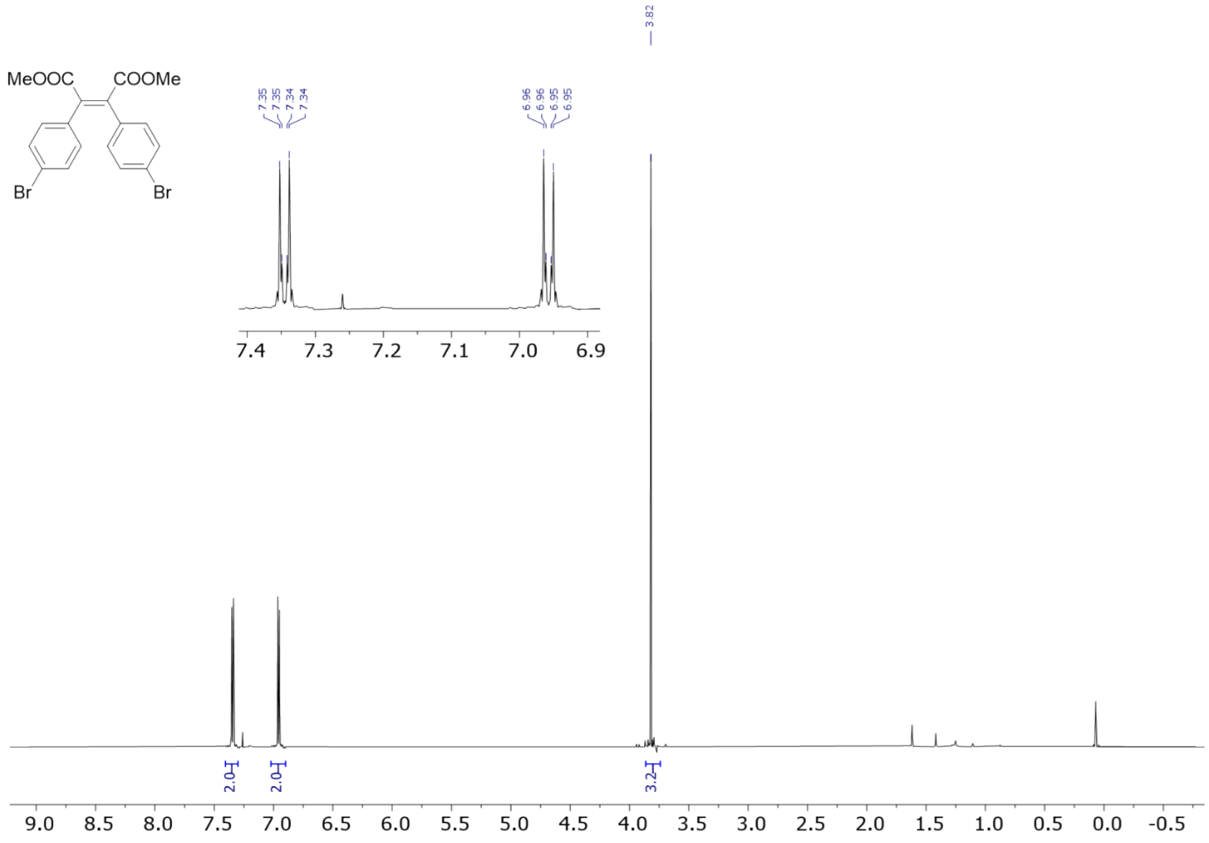


Figure S57: **^{1}H NMR** spectrum (600 MHz, $CDCl_3$) of compound *Z*-**9l**.

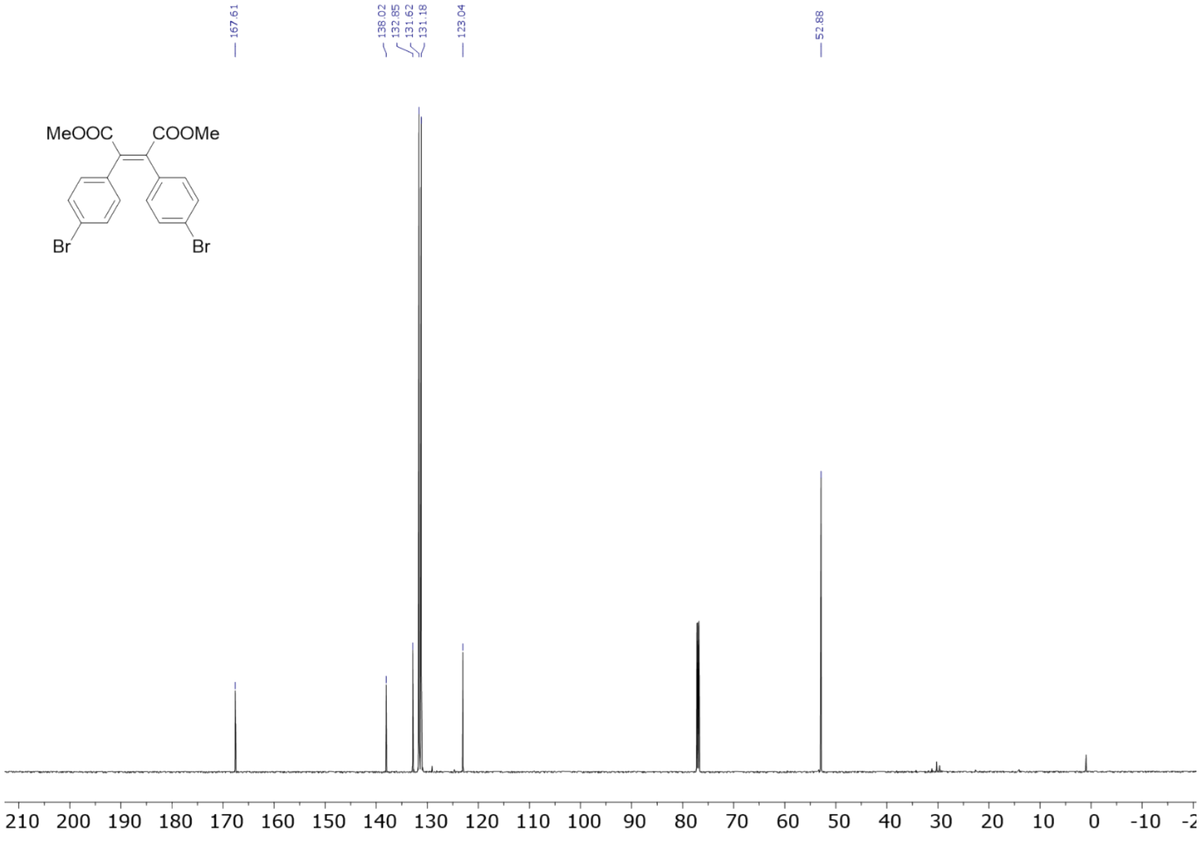


Figure S58: **^{13}C{^{1}H} NMR** spectrum (151 MHz, $CDCl_3$) of compound *Z*-**9l**.

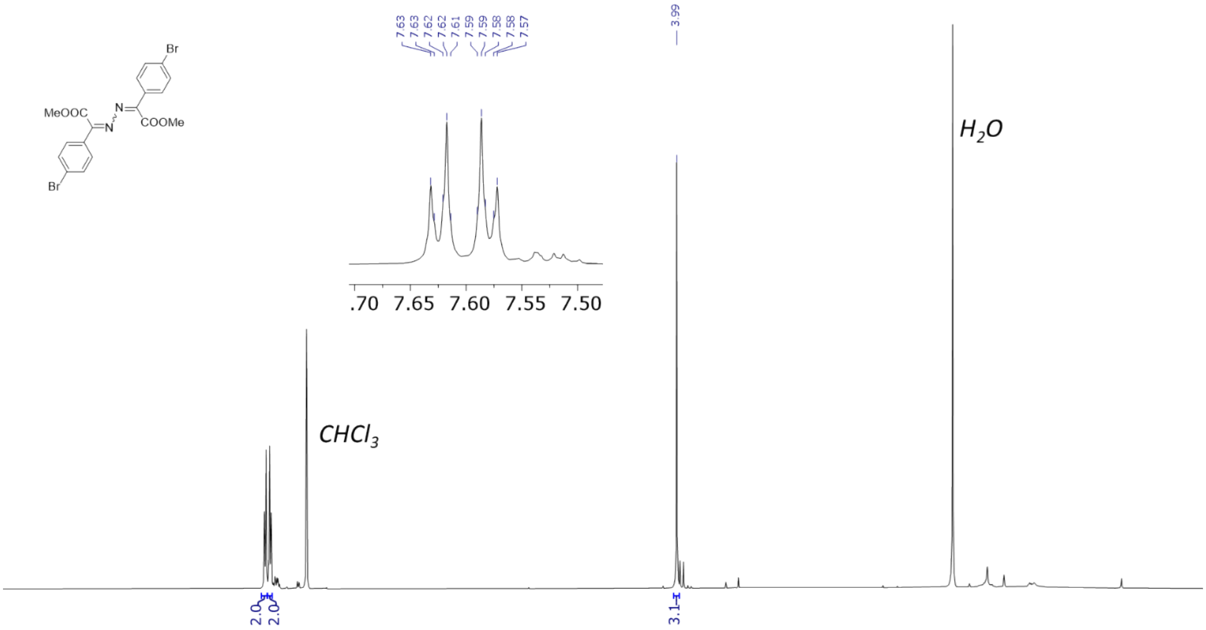


Figure S59: **^{1}H NMR** spectrum (600 MHz, CDCl$_3$) of compound **10l**.

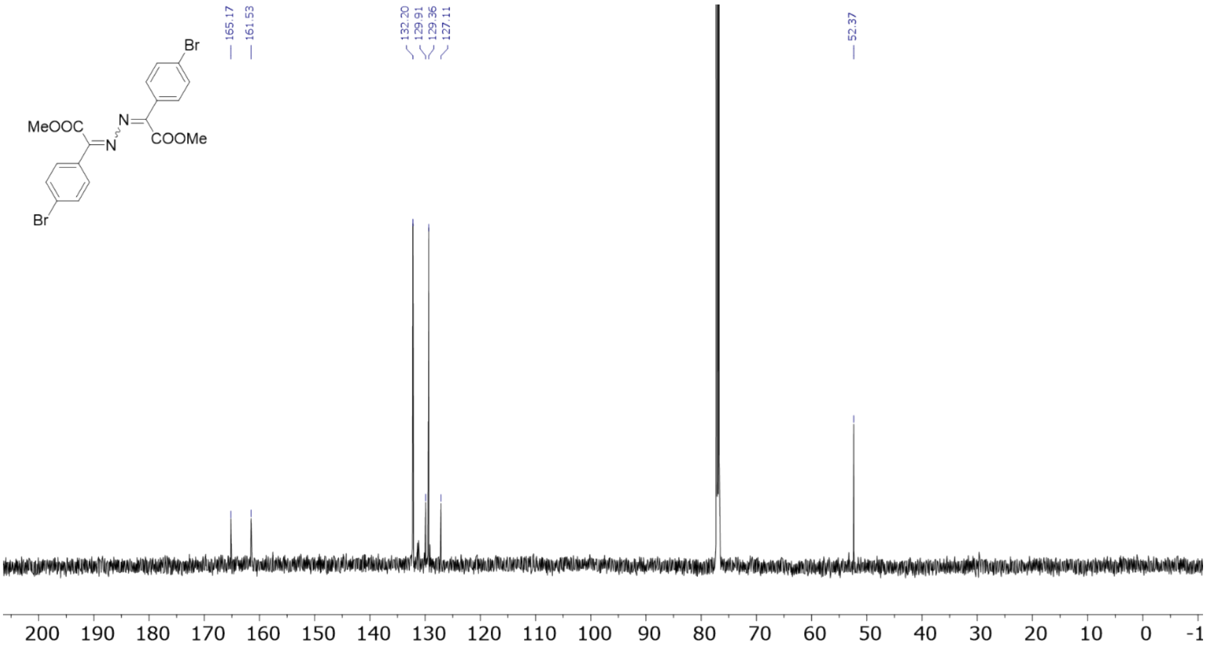


Figure S60: **^{13}C{^{1}H} NMR** spectrum (151 MHz, CDCl$_3$) of compound **10l**.

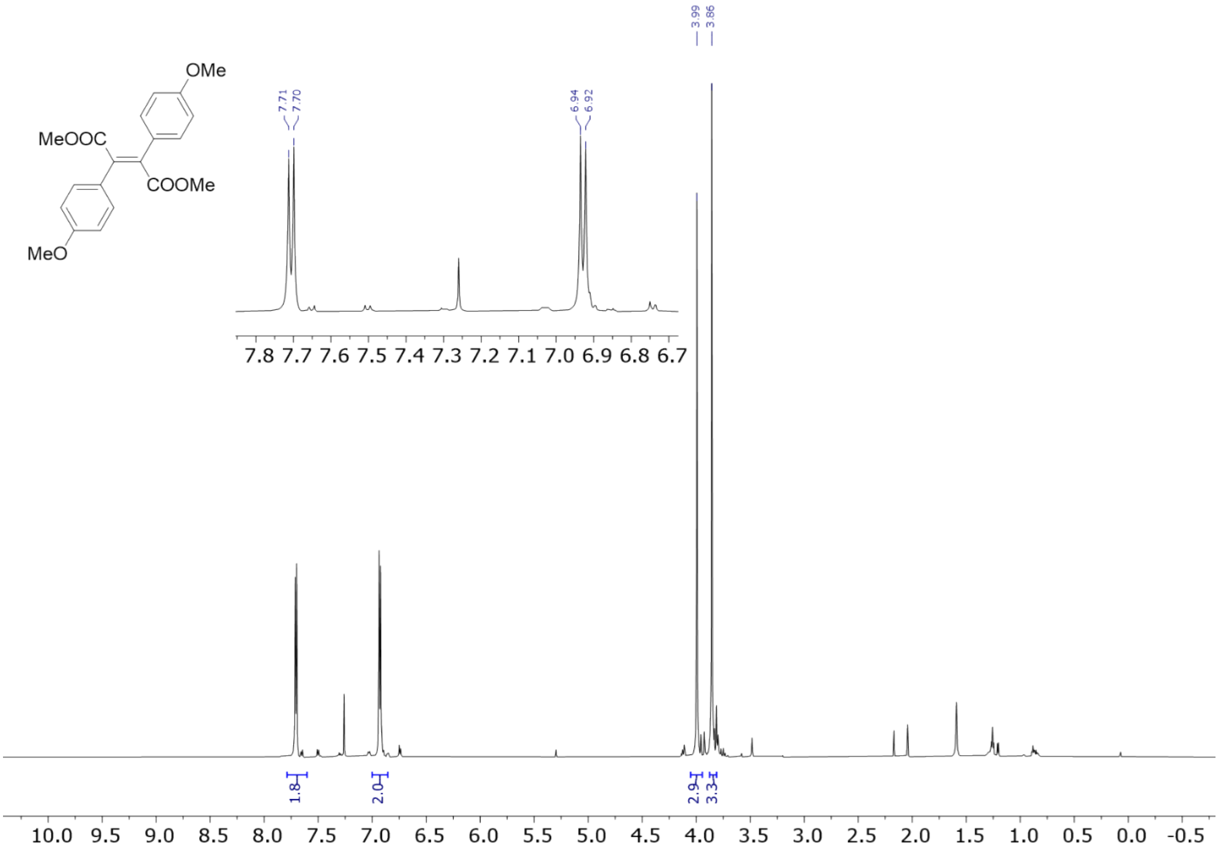


Figure S61: **^{1}H NMR** spectrum (600 MHz, $CDCl_3$) of compound *E*-**9m**.

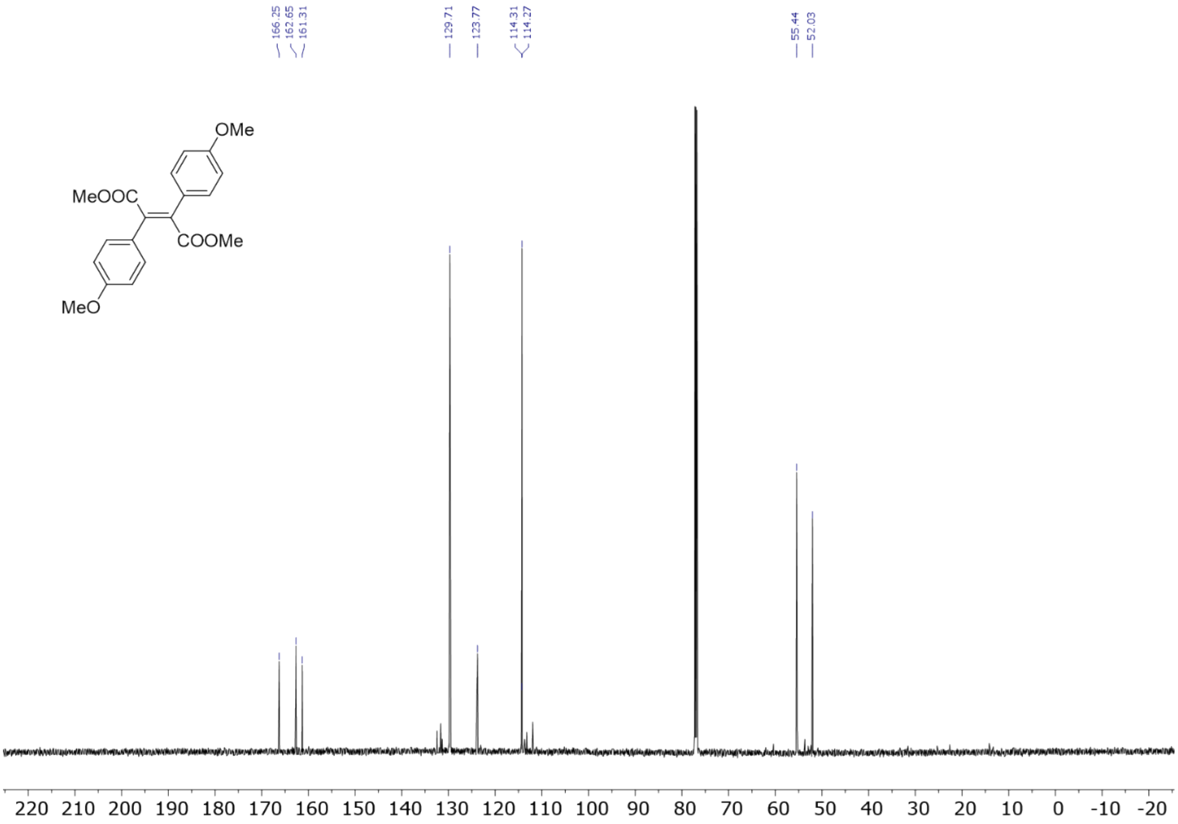


Figure S62: **^{13}C{^{1}H} NMR** spectrum (151 MHz, $CDCl_3$) of compound *E*-**9m**.

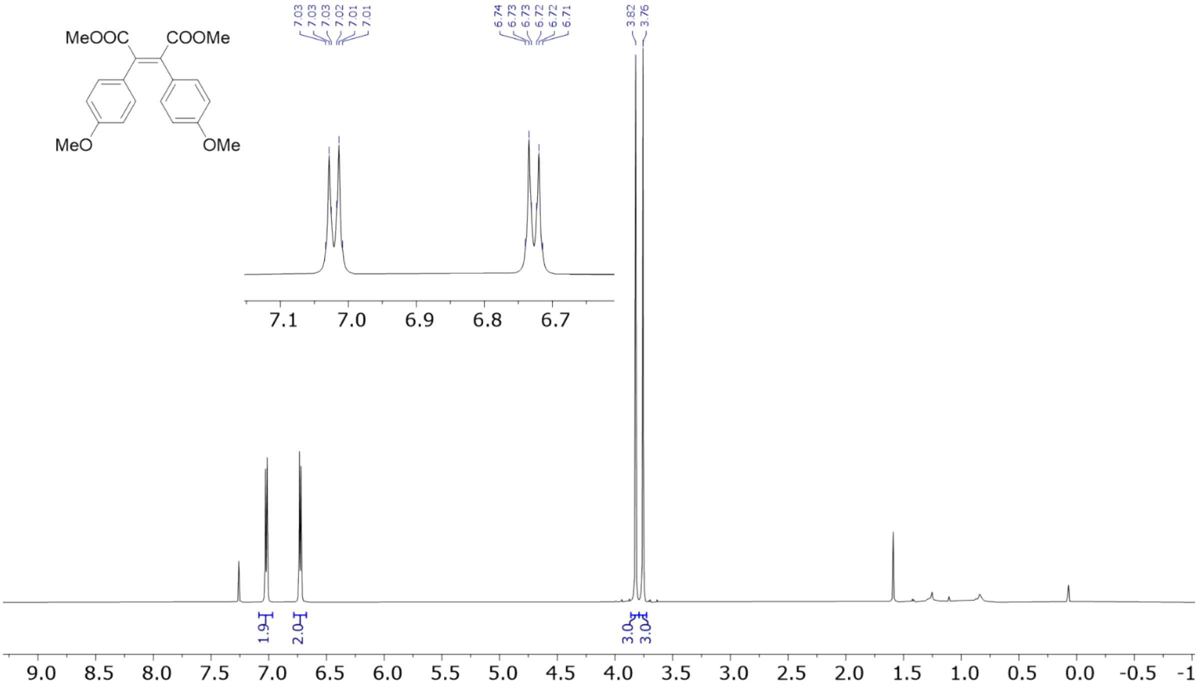


Figure S63: **^{1}H NMR** spectrum (600 MHz, $CDCl_3$) of compound *Z*-**9m**.

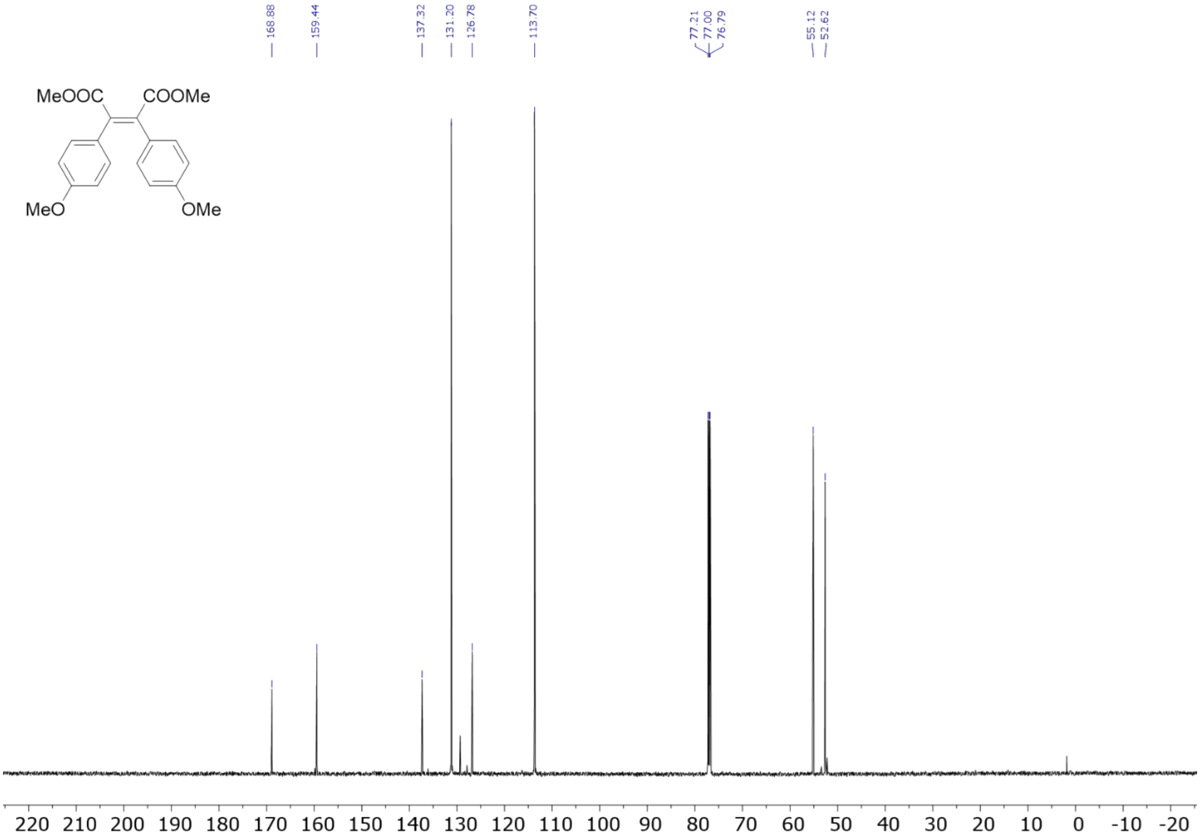


Figure S64: **^{13}C{^{1}H} NMR** spectrum (151 MHz, $CDCl_3$) of compound *Z*-**9m**.

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