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Supporting material for the article

Visible Light-Mediated Metal-Free Double Bond Deuteration of Substituted Phenylalkenes

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1) General methods and instruments

Solvents and chemicals were purchased from Sigma-Aldrich (Milwaukee, IL, www.sigmaaldrich.com), Acros Organics (Geel, Belgium, www.acros.com), Fluorochem (Hadfield, UK, www.fluorochem.co.uk). $NaBD_4$ was purchased from Armar Chemical (Döttingen, Switzerland, www.armar.ch), aniline-d_5 was purchased from ABCR (Karlsruhe, Germany, www.abcr.de).

Following abbreviations were used: DCM (dichloromethane), DMF (N,N-dimethylformamide), DMPU (1,3-dimethylpropyleneurea), RT (room temperature), THF (tetrahydrofuran), NCS (N-chlorosuccinimide), NBS (N-bromosuccinimide), TFA (trifluoroacetic acid).

NMR spectra were measured in chloroform-*d*, DMSO-d_6 or acetonitrile-d_3 using a JEOL ECX-500 (500 MHz) spectrometer, with operating frequency of 500.13 MHz for ^{1}H, 76.77 MHz for ^{2}H, 125.77 MHz for ^{13}C and 470.53 MHz for ^{19}F equipped with BBFO probe with z-gradients. The chemical shifts (δ) are reported in parts per million (ppm), and coupling constants (J) are reported in Hertz (Hz). Standard signals for chloroform-*d* were set as 7.36 ppm (^{1}H) and 77.16 ppm (^{13}C). For DMSO-d_6 standard signals were set as 2.50 ppm (^{1}H) and 39.52 ppm (^{13}C). For acetonitrile-d_3 standard signal was set as 1.94 ppm (^{1}H). UV-Vis absorption spectra were recorded on a Cary 300 UV/VIS spectrophotometer (UV111M031, Agilent).

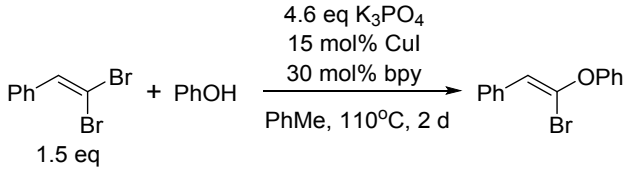
Deuterium enrichment was measured from ^{1}H NMR spectra by depression of the integral of the corresponding proton signal, compared to one of easily separable proton signals of the compound. In case of (*Z*)-(ethene-1,2-diyl-1-*d*)dibenzene (**C-*d***) the deuterium enrichment was calculated from the depression of 6.6 ppm signal compared to a whole integral of 10 aromatic protons in CD_3CN, which appears as a sharp multiplet.

HRMS analyses were performed using an LC chromatograph (Dionex UltiMate 3000, Thermo Fischer Scientific, MA, USA) connected with Exactive Plus Orbitrap high-resolution mass spectrometer (Thermo Fischer Scientific, MA, USA) operating at a positive and negative full scan mode (120 000 FWMH) in the range of 100–800 m/z. Ionization types were as ESI (oven temperature of 300 °C, sheath gas of 8 arb. units and a voltage source of 1.5 kV) or APCI. The acquired data were internally calibrated with diisooctyl phthalate in methanol (m/z 391.2843). Chromatographic separation was performed on column Phenomenex Gemini (C18, 50 x 2 mm, 3 μm particle) by isocratic elution, mobile phase was 80% acetonitrile and 20% buffer (0,01M ammonium acetate) or 95% MeOH + 5% water + 0.1% HCOOH.

2) Synthesis of starting compounds.

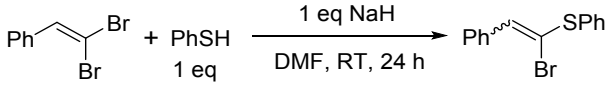
a) Synthesis of bromoalkenes F-Br, G-Br via substitution

(*Z*)-2-Bromo-2-phenoxyvinyl)benzene (F-Br)



Synthesis was performed by modified literature method.[1] A 5 ml reaction vial was charged with phenol (94 mg, 1 mmol), 1,1'-bipyridyl (47 mg, 0.3 mmol), K_3PO_4 (0.98 g, 4.6 mmol), CuI (29 mg, 0.15 mmol) and flushed with nitrogen. Dry and degassed toluene (3 ml) and (2,2-dibromovinyl)benzene (393 mg, 1.5 mmol) were added successively and the reaction mixture was sealed and stirred at 110°C for 2 days. After completion, reaction was cooled to RT, filtered through SiO_2 plug (3 g SiO_2) and washed by 1:1 Hexane-EtOAc (20 ml). The filtrate was evaporated in vacuo and the residue was subjected to the column chromatography (SiO_2, 2x20 cm, 350 ml Hex, 90 ml Hex-Et_2O 10:1). Pure Z-isomer (70 mg, 25%) was isolated along with E- and Z-isomer mixture (130 mg, 48%, Z/E ratio 11:1), only Z-isomer was used in further reactions. ^{1}H NMR (500 MHz, $CDCl_3$): *Z*-isomer – 7.61 d (2H, J = 7.7 Hz), 7.35-7.40 m (4H), 7.32 t (1H, J = 7.4 Hz), 7.12-7.17 m (3H), 6.76 s (1H). ^{13}C NMR (125 MHz, $CDCl_3$): 117.4, 119.2, 124.1, 128.1, 128.5, 128.9, 129.8, 131.1, 133.4, 155.9.

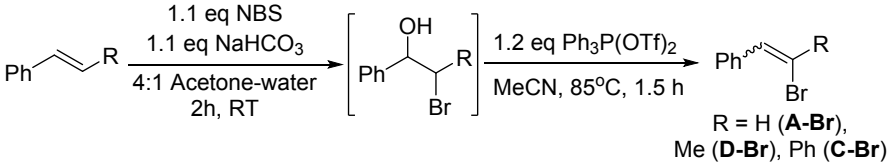
(*EZ*)-(1-Bromo-2-phenylvinyl)(phenyl)sulfane (G-Br)



Synthesis was performed by modified literature method.[2] To a stirred suspension of NaH (90%, 27 mg, 1 mmol) in dry DMF (2 ml) at RT a solution of thiophenol (110 mg, 1 mmol) in DMF (1 ml) was added. After gas evolution ceased, a solution of (2,2-dibromovinyl)benzene (262 mg, 1 mmol) in DMF (1 ml) was added. The mixture was stirred at RT for 24 h. Then the saturated aq. NH_4Cl (10ml) was added and extraction by Et_2O (3 x 10 ml) was performed. Organic extract was washed with water (3 x 10 ml), brine (10 ml), dried over Na_2SO_4 and evaporated in vacuo. The final compound was purified by column chromatography (SiO_2, hexane). Pure Z-isomer (29 mg, 10%) was isolated along with E- and Z-isomer mixture (49 mg, 17%, Z/E ratio 1:1). ^{1}H NMR (500 MHz, $CDCl_3$): *Z*-isomer – 7.60 d (2H, *J* = 7 Hz), 7.51 s (1H), 7.41 dd (2H, *J* = 8.2 Hz, 1.5 Hz), 7.30-7.37 m (6H); *E*-isomer – 7.48-7.53 m (4H), 7.30-7.38 m (6H), 7.24 t (1H, *J* = 7.4 Hz). NMR spectra are in agreement with literature data.[3]

For initial substrate screening, the E/Z mixture of **G-Br** in 1:1 ratio was used. For deuterodebromination reactions, pure **(*Z*)-G-Br** was used.

b) Synthesis of bromoalkenes A-Br, C-Br, D-Br via bromohydrin dehydration

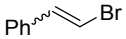


General procedure:

Synthesis of bromohydrins and bromoalkenes were performed by modified literature methods[4,5]. To a solution of alkene (0.42 mmol) in acetone (4 ml) and water (1 ml) $NaHCO_3$ (39 mg, 0.46 mmol) and NBS (82 mg, 0.46 mmol) were added. The mixture was stirred at RT until all the alkene was consumed (monitored by TLC) and after completion evaporated in vacuo. The residue was dissolved in DCM (10 ml) and water (10 ml), water phase was extracted by DCM (2 x 5 ml). Combined organic layers were washed with $Na_2S_2O_3$ solution (5 ml), water (10 ml), dried over Na_2SO_4 and evaporated in vacuo. The bromohydrin was used in the next stage without further purification.

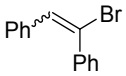
In a reaction vial a solution of Ph_3PO (67 mg, 0.24 mmol) in dry MeCN (1 ml) was cooled to 0°C. Trifluoromethanesulfonic anhydride (67 mg, 41 μL, 0.24 mmol) was added and the mixture was stirred for 30 min. Then bromohydrin (0.2 mmol) was added, the mixture was stirred for 10 min at 0°C, then heated at 85°C for 1.5 h, cooled to RT and quenched with the solid $NaHCO_3$ (2 g) .The mixture was filtered, washed by DCM (3x2 ml) and the filtrate evaporated in vacuo. The final compound was purified by column chromatography (silicagel, Hex-Et_2O 10:1).

(EZ)-2-Bromostyrene (**A-Br**)



Yield 85% (35 mg), 90% of *E*-isomer. ^{1}H NMR (500 MHz, $CDCl_3$): *E*-isomer – 7.27-7.33 m (5H), 7.11 d (1H, *J* = 14 Hz), 6.77 d (1H, *J* = 14 Hz); *Z*-isomer – 7.69 d (2H, *J* = 7.1 Hz), 7.39 m (3H), 7.07 d (1H, *J* = 8.1 Hz), 6.44 d (1H, *J* = 8.1 Hz). NMR spectra are in agreement with literature data.[6,7]

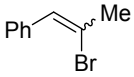
(EZ)-1-Bromostilbene (**C-Br**)



Yield 74% (47 mg), 67% of *E*-isomer. ^{1}H NMR (500 MHz, $CDCl_3$): *E*-isomer – 7.38-7.35 m (2H), 7.33-7.28 m (3H), 7.18 s (1H), 7.15-7.08 m (3H), 6.94-7.00 m (2H); *Z*-isomer – 7.72-7.69 m (2H), 7.67-7.64 m (2H), 7.42-7.38 m (4H), 7.34-7.32 m (2H), 7.22 s (1H). NMR spectra are in agreement with literature data.[8]

For further reactions, more *E*-enriched 1-bromostilbene (95% *E*-) was obtained by dehydrobromination of *meso*-1,2-dibromo-1,2-diphenylethane by K_2CO_3 in THF-MeOH via known method,[9] yield 97%.

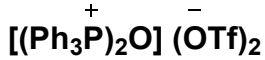
(EZ)-2-Bromo-1-phenylprop-1-ene (**D-Br**)



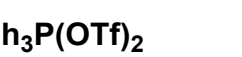
Yield 51% (48 mg), 74% of *Z*-isomer. ^{1}H NMR (500 MHz, $CDCl_3$): *E*-isomer – 7.35 t (2H, *J* = 7.4 Hz), 7.26 t (1H, *J* = 7.4 Hz), 7.21 d (2H, *J* = 7.1 Hz), 6.97 br s (1H), 2.46 d (3H, *J* = 1.4 Hz); *Z*-isomer – 7.55 d (2H, *J* = 7.2 Hz), 7.20-7.30 m (3H), 6.73 br s (1H), 2.49 d (3H, *J* = 1.4 Hz). NMR spectra are in agreement with literature data[10].

For further reactions, more *E*-enriched 2-bromo-1-phenylprop-1-ene (89% *E*-) was obtained by chromatographic purification of the product (SiO_2, hexane).

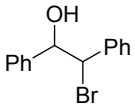
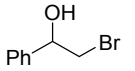
Table S1**. Bromohydrin dehydration optimization**



Reagent A



Reagent B

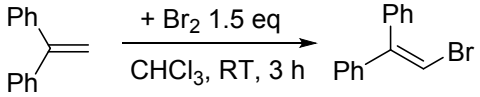
Entry	Br-hydrin	Reagent	Additive	Product (yield)	E/Z ratio
1		**A**	-	Br-stilbene (77%)	1.7:1
2		**A**[a]	3 eq DBU	stilbene (42%)	E-
3		**A**	2 eq TsONa	Stilbene (15%) + Br-stilbene (18%)	n/a
4		**B**	-	Br-stilbene (90%)	2.03:1
5		**F_{15}-A**	-	Br-stilbene (61%)	2.33:1
6		**F_{15}-B**	-	Br-stilbene (90%)	2.33:1
7		**A**	-	Br-styrene (77%)	6.14:1
8		**B**	-	Br-styrene (88%)	9:1
9		**F_{15}-B**	-	Br-styrene (90%)	8.1:1

Conditions – MeCN, reagent **A** (1 eq) or **B** (1.2 eq) or perfluoro-**A** **(F_{15}-A)** or perfluoro-**B** **(F_{15}-B)**, 1.5 h at 85°C, with or without additive.

[a]1,2-dichloroethane was used as a solvent

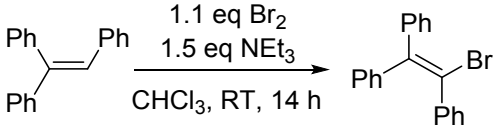
c) Synthesis of bromoalkenes B-Br, E-Br directly from alkenes

2-Bromo-1,1-diphenylethylene (B-Br)



Synthesis was performed by modified literature method.[11] To a stirred solution of 1,1-diphenylethylene (0.9 g, 5 mmol) in $CHCl_3$ (20 ml) at RT a solution of bromine (1.2 g, 0.38 ml, 7.5 mmol) in $CHCl_3$ (10 ml) was slowly added and the solution was stirred for 3 h. Then reaction mixture was washed by $NaHCO_3$ solution (15 ml), $Na_2S_2O_3$ solution (15 ml), water (20 ml), dried over Na_2SO_4 and evaporated in vacuum. The residue was dissolved in Et_2O (1 ml), crystallized by cooling to -20°C overnight, crystals were filtered, washed by methanol (1 ml), dried in vacuum. Yield 72% (0.93 g). ^{1}H NMR (500 MHz, $CDCl_3$): 7.43-7.36 m (3H), 7.33-7.28 m (5H), 7.23-7.20 m (2H), 6.78 s (1H). NMR spectra are in agreement with literature data.[12]

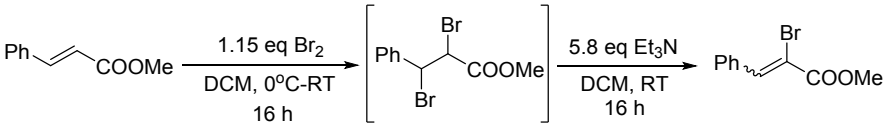
2-Bromo-1,1,2-triphenylethylene (E-Br)



Synthesis was performed by modified literature method.[13] To a solution of triphenylethylene (1 g, 3.9 mmol) in chloroform (17 ml) a solution of bromine (4.3 mmol., 0.69 g, 0.22 ml) in 11 ml of chloroform was slowly added. The reaction mixture was stirred at RT for 1.5 h. Then triethylamine (5.8 mmol, 0.59 g, 0.81 ml) was added and the reaction mixture was stirred at RT overnight (73% conversion according to HPLC). Then it was washed with water (25 ml), 3M HCl (2x8 ml), water (25 ml), sat. $NaHCO_3$ (15 ml), water (25 ml), dried over Na_2SO_4 and evaporated in vacuum. The residue was washed with EtOH (20 ml), filtered and remaining substance was dissolved in EtOH (15 ml) at 65°C and then slowly cooled to RT to give the crystalline final compound. Yield 87% (817 mg), 250 mg of triphenylethylene was regenerated from first ethanol wash solution (25%). ^{1}H NMR (500 MHz, $CDCl_3$): 7.40-7.37 m (4H), 7.34-7.30 m (3H), 7.21-7.15 m (3H), 7.09-7.05 m (3H), 6.98-6.95 m (2H). NMR spectra are in agreement with literature data.[12]

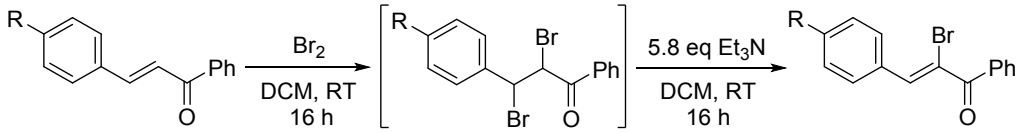
d) Synthesis of bromoalkenes H-Br-K-Br by HBr elimination.

(*EZ*)-2-Bromocinnamic acid methyl ester (H-Br)



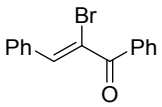
To a solution of methyl cinnamate (1.66 g, 10.2 mmol) in DCM (10 ml) cooled to 0°C bromine (1.87 g, 11.7 mmol, 0.61 ml) was added. The mixture was left to warm to RT and stirred for 16 h. Then a solution of triethylamine (5.98 g, 59.2 mmol, 8.2 ml) in DCM (8 ml) was added and the reaction mixture was stirred at RT for next 16 h. Then concentrated NH_4Cl solution (20 ml) was added, phases were separated, water phase was extracted by DCM (3x15 ml). Combined organic phase was washed with 1M HCl (4x15 ml), dried over Na_2SO_4 and evaporated in vacuo. Yield 96% (2.36 g), *E*/*Z* ~ 1:1. ^{1}H NMR (500 MHz, $CDCl_3$): *E*-isomer – 7.87-7.84 m (2H), 7.37 s (1H), 7.35-7.32 m (3H), 3.76 s (3H); *Z*-isomer – 8.23 s (1H), 7.44-7.42 m (3H), 7.29-7.26 m (2H), 3.91 s (3H). NMR spectra are in agreement with literature data.[14]

General procedure for synthesis of α-bromochalcones (I-Br, K-Br, L-Br, M-Br, N-Br)



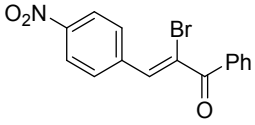
Synthesis was performed by modified literature methods.[15,16] To a solution of (*E*)-chalcone (2.08 g, 10 mmol) in chloroform (10 ml) bromine (1.6 g, 10 mmol, 0.52 ml) was added and the mixture was stirred for 16 h at RT and the solvent was evaporated in vacuum. Then a solution of triethylamine (5.86 g, 58 mmol, 8.12 ml) in DCM (8 ml) was added and the reaction mixture was stirred at RT for next 16 h. Then the concentrated NH_4Cl solution (25 ml) was added, phases were separated, water phase was extracted by DCM (3x15 ml). Combined organic phase was washed with 1M HCl (4x15 ml), dried over Na_2SO_4 and evaporated in vacuo. The mixture was purified by column chromatography on SiO_2 to afford (*E*)- and (*Z*)-isomer separately.

(Z)-2-Bromo-1,3-diphenylprop-2-en-1-one (I-Br)



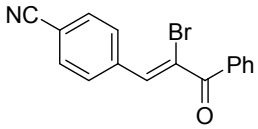
Eluent for chromatography – hexane-DCM 4:3. Pure Z-isomer was used in further reactions. Yield 87% (2.51 g), 90% of *Z*-isomer. ^{1}H NMR (500 MHz, $CDCl_3$): ***Z*-isomer** – 7.87-7.83 m (2H), 7.82 dd (2H, *J* = 8.1 Hz; 1 Hz), 7.70 s (1H), 7.60 t (1H, *J* = 7.5 Hz), 7.49 t (2H, *J* = 7.9 Hz), 7.46-7.42 m (3H); ***E*-isomer** – 7.98 dd (2H, *J* = 8.4 Hz; 1.2 Hz), 7.55 t (1H, *J* = 7.4 Hz), 7.44-7.40 m (2H), 7.38 s (1H), 7.20-7.15 m (5H). NMR spectra are in agreement with literature data[17].

(Z)-2-bromo-3-(4-nitrophenyl)-1-phenylprop-2-en-1-one (K-Br)



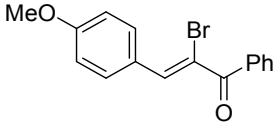
1.5 eq of bromine (0.48 g, 0.155 ml, 3 mmol) was used. Eluent for chromatography – hexane-EtOAc 6:1. Pure Z-isomer was used in further reactions. Yield 78% (511 mg), 94% of *Z*-isomer**. *Z*-isomer spectra**: ^{1}H NMR (500 MHz, $CDCl_3$): 8.29 d (2H, *J* = 8.8 Hz), 7.96 d (2H, *J* = 9.1 Hz), 7.86 d (2H, *J* = 8.4 Hz), 7.67 s (1H), 7.64 t (1H, *J* = 7.4 Hz), 7.52 t (2H, *J* = 7.9 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): 123.8, 125.9, 128.9, 130.0, 130.7, 133.5, 135.6, 138.5, 140.1, 148.2, 190.9; ***E*-isomer spectrum**: ^{1}H NMR (500 MHz, $CDCl_3$): 8.21 d (2H, *J* = 8.4 Hz), 8.05 d (2H, *J* = 8.8 Hz), 7.59 t (1H, *J* = 7.4 Hz), 7.46 dd (2H, *J* = 8.1 Hz; 7.4 Hz), 7.42 s (1H), 7.34 d (2H, *J* = 8.5 Hz). ESI-HRMS calcd. for $[M+H]^+$ $C_{15}H_{11}BrNO_3^+$ - 331.9917, found 331.9915. NMR spectra of **(*Z*)-K-Br** are in agreement with literature data.[18]

(Z)-4-(2-bromo-3-oxo-3-phenylprop-1-en-1-yl)benzonitrile (L-Br)



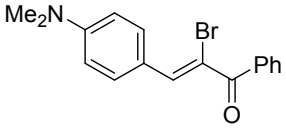
1.5 eq of bromine (0.62 g, 0.2 ml, 3.9 mmol) was used. Eluent for chromatography – hexane-EtOAc 6:1. Pure Z-isomer was used in further reactions. Yield 74% (594 mg), 97% of *Z*-isomer**. *Z*-isomer spectra**: ^{1}H NMR (500 MHz, $CDCl_3$): 7.90 d (2H, *J* = 8.2 Hz), 7.84 d (2H, *J* = 8.3 Hz), 7.72 d (2H, *J* = 8.7 Hz), 7.60-7.64 triplet + singlet (2H), 7.51 t (2H, *J* = 7.7 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): 113.4, 118.4, 125.4, 128.8, 130.0, 130.5, 132.3, 135.7, 138.3, 139.1, 190.9. ESI-HRMS calcd. for $[M+H]^+$ $C_{16}H_{11}BrNO^+$ - 312.0019, found 312.0029.

(Z)-2-bromo-3-(4-methoxyphenyl)-1-phenylprop-2-en-1-one (M-Br)



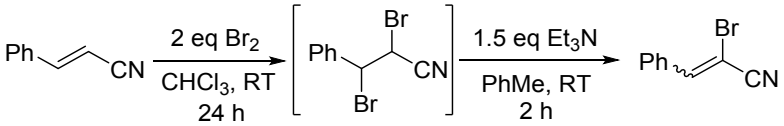
1.3 eq of bromine (0.7 g, 0.23 ml, 4.4 mmol) was used, conversion 60%. Eluent for chromatography – hexane-EtOAc 6:1. Pure Z-isomer was used in further reactions. Yield 51% (327 mg), 86% of *Z*-isomer**. *Z*-isomer spectra**: ^{1}H NMR (500 MHz, $CDCl_3$): 7.89 d (2H, *J* = 9 Hz), 7.76 d (2H, *J* = 8.3 Hz), 7.68 s (1H), 7.57 t (1H, *J* = 7.4 Hz), 7.47 t (2H, *J* = 7.6 Hz), 6.95 d (2H, *J* = 9 Hz), 3.86 s (3H); ^{13}C NMR (125 MHz, $CDCl_3$): 55.5, 114.1, 120.7, 126.2, 128.6, 129.7, 132.4, 132.7, 137.3, 143.4, 161.2, 191.8; ***E*-isomer spectrum**: ^{1}H NMR (500 MHz, $CDCl_3$): 7.99 d (2H, *J* = 8.5 Hz), 7.55 t (1H, *J* = 7.4 Hz), 7.42 t (2H, *J* = 7.4 Hz), 7.31 s (1H), 7.10 d (2H, *J* = 8.5 Hz), 6.70 d (2H, *J* = 8.9 Hz), 3.72 s (3H). ESI-HRMS calcd. for $[M+Na]^+$ $C_{16}H_{13}BrO_2Na^+$ - 338.9991, found 338.9994.

(Z)-2-bromo-3-(4-(dimethylamino)phenyl)-1-phenylprop-2-en-1-one (N-Br)



1.5 eq of bromine (0.53 g, 0.17 ml, 3.3 mmol) dissolved in chloroform (2 ml) was added dropwise at 0°C, organic extract was washed by 7% NH_4Cl solution (3x 15 ml). Eluent for chromatography – hexane-EtOAc 6:1. First chromatographic fraction was aromatic bromination product, yield 15% (148 mg), which was discarded. Yield 26% (258 mg), pure *Z*-isomer. ^{1}H NMR (500 MHz, $CDCl_3$): 7.89 d (2H, *J* = 8.7 Hz), 7.69-7.72 m (2H), 7.69 s (1H), 7.54 t (1H, *J* = 7.4 Hz), 7.45 t (2H, *J* = 7.5 Hz), 6.69 d (2H, *J* = 9.1 Hz), 3.05 s (6H); ^{13}C NMR (125 MHz, $CDCl_3$): 40.1, 111.4, 121.0, 128.4, 129.5, 131.7, 133.2, 138.2, 145.5, 152.1, 191.8. ESI-HRMS calcd. for $[M+H]^+$ $C_{17}H_{17}BrNO^+$ - 330.0488, found 330.0487.

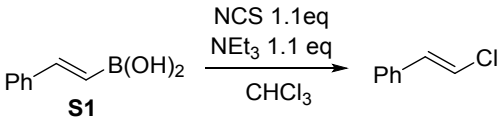
(EZ)-2-Bromo-3-phenylacrylonitrile (J-Br)



Synthesis was performed by modified literature method.[19] To a solution of (*E*)-cinnamonitrile (1.5 g, 11.63 mmol, 1.46 ml) in chloroform (30 ml) bromine (3.72 g, 23.25 mmol, 1.2 ml) was added and the mixture was stirred for 24 h at RT. Excess of bromine and solvent were removed in vacuum, residue was dissolved in dry toluene (12.5 ml) and triethylamine (3 g, 29.7 mmol, 2.2 ml) was added. Reaction mixture was stirred at RT for 2 h, filtered, filter was washed by toluene (2x5 ml). Filtrate was evaporated in vacuo, purified by column chromatography on SiO_2 (25 g), eluent hexane (50 ml), then hexane-EtOAc 20:1 (300 ml). Yield 81% (1.97 g), 63% of *Z*-isomer. ^{1}H NMR (500 MHz, $CDCl_3$): *E*-isomer – 7.77-7.73 m (2H), 7.70-7.67 m (4H); *Z*-isomer – 7.72-7.69 m (2H), 7.57 s (1H), 7.48-7.44 m (3H). NMR spectra are in agreement with literature data.[19]

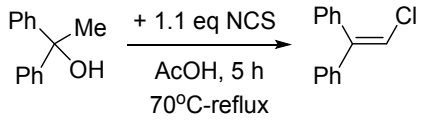
e) Synthesis of chloroalkenes A-Cl, B-Cl, C-Cl, H-Cl

(E)-2-Chloro-1-phenylethylene (A-Cl)



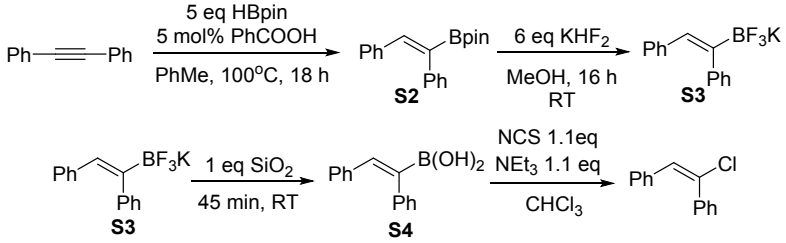
Synthesis was performed by modified literature method.[20] To a suspension of (*E*)-styrylboronic acid (**S1**, 592 mg, 4 mmol) in chloroform (24 ml) N-Chlorosuccinimide (587 mg, 4.4 mmol) was added in one portion followed by triethylamine (444 mg, 0.61 ml, 4.4 mmol) added over 20 min. The reaction mixture was stirred for 1h at RT. After completion, the reaction mixture was evaporated in vacuo to final volume 1-2 ml. The residue was dissolved in mixture of water (15 ml) and pentane (15 ml). The two phases were separated, water phase was extracted by pentane (2x15 ml) and combined pentane phase was dried over Na_2SO_4 and evaporated in vacuo, purified by column chromatography (SiO_2-pentane). Yield 59% (327 mg), 97% of *E*-isomer. ^{1}H NMR (500 MHz, $CDCl_3$): *E*-isomer – 7.35-7.25 m (5H), 6.84 d (1H, J = 13.7 Hz), 6.65 d (1H, J = 13.7 Hz), 6.27 d (0.03 H, J = 8.1 Hz, *E*-isomer). NMR spectra are in agreement with literature data.[20]

2-Chloro-1,1-diphenylethylene (B-Cl)



Synthesis was performed by modified literature method.[12] NCS (1.47 g, 11 mmol) was dissolved AcOH (50 ml), then 1,1-diphenylethanol (2 g, 10 mmol) was added. The reaction mixture was stirred for 5 h at 70-75°C, then refluxed for 1h. After consumption of NCS (monitored by TLC), the reaction mixture was diluted with 150 ml of EtOAc, washed with water (2x100 ml), saturated $NaHCO_3$ solution (5x60 ml), 10% $Na_2S_2O_3$ solution (60 ml), water (2x100 ml). Combined water phases were back-extracted with EtOAc (2x20 ml). The combined organic extracts were dried over Na_2SO_4 and evaporated in vacuum. The residue was dissolved in hexane (10 ml) at 45°C, cooled slowly to RT and kept at -20°C overnight. The crystals were washed with 3 ml of cold hexane and dried in air. Yield 1.44 g (64%). ^{1}H NMR (500 MHz, $CDCl_3$): 7.42-7.38 m (2H), 7.37-7.30 m (6H), 7.23-7.20 m (2H), 6.60 s (1H). NMR spectra are in agreement with literature data.[12]

(*E*)-2-Chloro-1,1-diphenylethylene (C-Cl)



Synthesis of pinacolboronate (**S2**),[21] trifluoroborate (**S3**),[22] boronic acid (**S4**)[23] and chloroalkene (**C-Cl**)[20] were performed by modified literature methods.

To a solution of diphenylacetylene (0.45 g, 2.5 mmol) in dry toluene (2.5 ml) benzoic acid (15 mg, 0.125 mmol) and pinacolborane (1.6 g, 12.5 mmol, 1.82 ml) were added under inert atmosphere. Reaction mixture was stirred for 18 h at 100°C under inert atmosphere and evaporated in vacuum to dryness. Residue was washed with hexane (2x2 ml) and the excessive pinacolborane was evaporated at 60°C, 12 mbar for 1h, then residue was dissolved in hexane (5 ml) and slowly cooled to 4°C over 4h. The crystals were filtered off and the mother liquor was slowly cooled to -20°C overnight, crystals were filtered off again and united with previous portion of crystals.

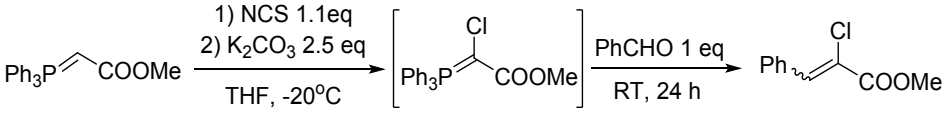
Yield 51% (774 mg) of **S2**, pure *Z*-isomer. ^{1}H NMR (500 MHz, $CDCl_3$): 7.36 s (1H), 7.31-7.25 m (2H), 7.24-7.16 m (3H), 7.16-7.11 m (3H), 7.09-7.03 m (2H), 1.31 s (12H). NMR spectra are in agreement with literature data.[24]

In a plastic screw-cap vial, to a solution of **S2** (638 mg, 2.08 mmol) in methanol (28 ml), KHF_2 (0.98 g, 12.5 mmol) and water (18 ml) were added and the reaction mixture was shaken at RT for 16 h. Then reaction mixture was filtered through cotton wool and the filter was washed with methanol (3x5 ml). The filtrate was evaporated in vacuum to dryness and the residue was triturated with acetone (3x5 ml). The combined acetone phases were dried over Na_2SO_4 and evaporated in vacuum to dryness. The residue was washed by ether (3x5 ml) and dried in vacuum. Yield 77% (460 mg) of **S3**, pure *Z*-isomer. ^{1}H NMR (500 MHz, DMSO): 7.33 t (2H, J = 7.5 Hz), 7.05-6.96 m (5H), 6.93 t (1H, J = 7.3 Hz), 6.83 d (1H, J = 7.2 Hz), 6.52 s (1H). ^{19}F NMR (470 MHz, DMSO): -140.7 (br s).

A suspension of **S3** (320 mg, 1.2 mmol) and chromatography-grade SiO_2 (72 mg, 1.2 mmol) in ethyl acetate (5 ml) and water (5 ml) was shaken in a plastic screw-cap vial for 45 min at RT. Then reaction mixture was filtered, filter was washed with EtOAc (3x4 ml). The phases of filtrate were separated and the water phase was extracted by EtOAc (3x10 ml). Combined organic phases were washed with brine (20 ml), dried over Na_2SO_4 and evaporated in vacuum. The residue was washed with pentane (2x4 ml) and dried in vacuum. Yield 79% (210 mg) of **S4**, pure *Z*-isomer. ^{1}H NMR (500 MHz, DMSO): 7.68 br s (0.7H), 7.30-7.24 m (2H), 7.23-7.16 m (2H), 7.15-7.06 m (4H), 6.98-7.03 m (2H), 6.96-6.92 m (1H). NMR spectra are in agreement with literature data.[25]

To a suspension of **S4** (210 mg, 0.94 mmol) in chloroform (10 ml) NCS (138 mg, 1.03 mmol) was added in one portion followed by triethylamine (105 mg, 0.14 ml, 1.03 mmol) added over 20 min. The reaction mixture was stirred for 1.5h at RT. After completion (monitored by TLC), the reaction mixture was evaporated in vacuum to dryness, the residue was washed by hexane (3x5 ml), hexane extracts were combined, filtered and evaporated in vacuum to dryness. The mixture was put on SiO_2 plug (2.5 g), washed out by hexane (100 ml) and evaporated to dryness. Yield 40% (81 mg), pure *E*-isomer. ^{1}H NMR (500 MHz, $CDCl_3$): 7.40-7.37 m (2H), 7.33-7.31 m (3H), 7.16-7.13 m (3H), 7.01-6.98 m (2H), 6.94 s (1H). NMR spectra are in agreement with literature data.[8]

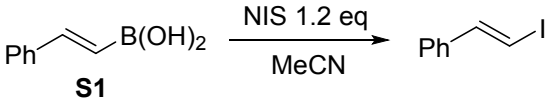
(*EZ*)-2-Chlorocinnamic acid methyl ester (H-Cl)



Synthesis was performed by modified literature method.[26] (Methoxycarbonyl-methylidene)triphenylphosphorane (1 g, 3 mmol) was dissolved in dry THF (12 ml) under inert atmosphere and cooled to -20°C. NCS (441 mg, 3.3 mmol) was added and the reaction mixture was stirred for 20 min. Then K_2CO_3 (1.04 g, 7.5 mmol) was added, followed by benzaldehyde (318 mg, 3 mmol). The mixture was warmed to RT, stirred for 24 h, and then filtered. The filter was washed by DCM (3x6 ml) and the filtrate was evaporated in vacuum. Residue was put to short SiO_2 column (6 g SiO_2), and eluted by Hexane-EtOAc 5:1 (50 ml). Yield 80% (473 mg), 78% of *Z*-isomer. ^{1}H NMR (500 MHz, $CDCl_3$): *Z*-isomer – 7.92 s (1H), 7.86-7.82 m (2H), 7.45-7.40 m (3H), 3.91 s (3H). *E*-isomer – 7.35-7.26 m (5H), 7.22 s (1H), 3.75 s (3H). NMR spectra are in agreement with literature data.[27]

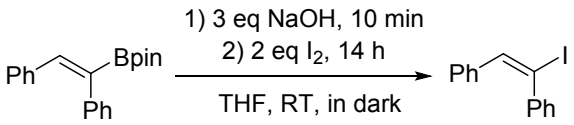
f) Synthesis of iodoalkenes A-I, C-I

(*E*)-2-Iodo-1-phenylethylene (A-I)



Synthesis was performed by modified literature method.[20] The derivative **S1** (592 mg, 4 mmol) was suspended in acetonitrile (6 ml) in the reaction flask wrapped by aluminium foil. N-iodosuccinimide (1.08 g, 4.8 mmol) was added and the reaction mixture was stirred for 2 h at RT. After completion of the reaction (monitored by TLC), the mixture was extracted with pentane (4x40 ml). Combined pentane extracts were washed by 10% $Na_2S_2O_3$ solution (2x30 ml), water (2x40 ml), dried over Na_2SO_4 and evaporated in vacuum. The final product was used without further purification. Yield 85% (787 mg), pure *E*-isomer. ^{1}H NMR (500 MHz, $CDCl_3$): *E*-isomer – 7.43 d (1H, *J* = 14.9 Hz), 7.34-7.25 m (5H), 6.83 d (1H, *J* = 14.9 Hz). NMR spectra are in agreement with literature data.[20]

(*E*)-1-Iodo-1,2-diphenylethylene (C-I)

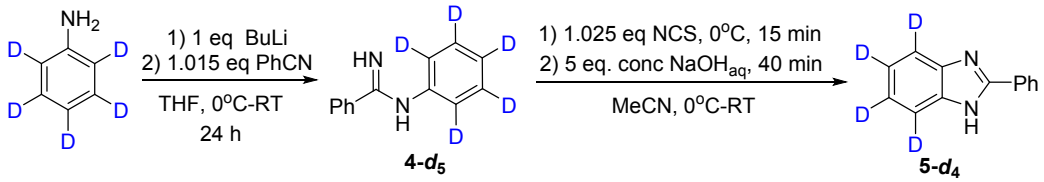


S2

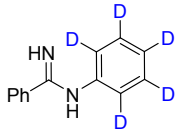
The synthesis was performed by modified literature method.[28] To a solution of **S2** (306 mg, 1 mmol) in THF (2 ml) a solution of NaOH (120 mg, 3 mmol) in water (1 ml) was added over 10 min and the mixture was stirred at RT for 10 min. Then the reaction flask was wrapped by aluminium foil and a solution of iodine (508 mg, 2 mmol) in THF (10 ml) was added over 10 min. The mixture was stirred at RT overnight. After reaction completion (monitoring by TLC) the mixture was poured into water (50 ml) and 10% $Na_2S_2O_3$ solution (10 ml) and extracted by ether (3x 20 ml). Combined organic phase was washed by $NaHCO_3$ solution (15 ml), brine (20 ml) dried over Na_2SO_4 and evaporated in vacuum to dryness. The mixture was put to SiO_2 plug (4 g) and eluted by hexane (120 ml). The filtrate was evaporated to dryness to give the final compound. Yield 36% (111 mg), pure *E*-isomer. ^{1}H NMR (500 MHz, $CDCl_3$): 7.42 s (1H), 7.35-7.26 m (5H), 7.13-7.07 m (3H), 6.97-6.89 m (2H). NMR spectra are in agreement with literature data.[8]

g) Synthesis of 2-phenyl-1*G*-benzo[d]imidazole-4,5,6,7-*d*$_4$ (5-*d*$_4$)

The synthesis was performed according to the following scheme:



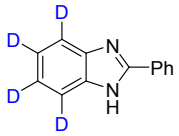
N-(Phenyl-*d*$_5$)benzimidamide (4-*d*$_5$)



Synthesis was performed by modified literature method.[29] To a solution of aniline-*d*$_5$ (1 g, 10.2 mmol) in dry THF (50 ml) at 0°C under nitrogen atmosphere BuLi (2.5 M in hexane, 4.1 ml, 10.2 mmol) was added. The solution was stirred 15 min at RT. Then reaction mixture was cooled to 0°C again and a solution of benzonitrile (1.066 g, 10.35 mmol) in dry THF (10 ml) was added dropwise. The reaction mixture was warmed to RT and stirred under nitrogen atmosphere for 24 h, then mixed with saturated aq. NH_4Cl (10ml) and stirred for 15 min. Then the phases were separated and water phase was extracted with THF (2x4 ml). Combined THF phase was evaporated in vacuum to dryness and the residue was dissolved in DCM (30 ml) and washed with 2M NaOH (80 ml). The water phase was washed with DCM (3x15 ml) and the combined organic phase was evaporated in

vacuum. The residue was washed with hexane (3x3 ml), then dissolved in 1M HCl (200 ml) and washed by DCM (3x10 ml), organic extract was discarded. Then water phase was alkalized by solid NaOH (9.8 g, 0.245 mol) added in portions. The water solution was extracted by DCM (3x15 ml), the organic phase was dried over Na_2SO_4 and evaporated in vacuum to give the final compound **4-*d*$_5$**. Yield 90% (1.84 g). ^{1}H NMR (500 MHz, $CDCl_3$): 7.87 br d (2H, *J* = 5.8 Hz), 7.42-7.50 m (3H), 4.86 br s (2 H). ^{2}H NMR (76.8 MHz, $CHCl_3$): 7.42 s (2D), 7.00-7.17 m (3D). ^{13}C NMR (125 MHz, $CDCl_3$): 121.3 t (CD, *J* = 24.4 Hz), 122.6 t (CD, *J* = 24.1 Hz), 126.9, 128.7, 129.1 t (CD, *J* = 24 Hz), 130.7, 136.0, 149.6, 154.9. ESI-HRMS calcd. for $[M+H]^+$ $C_{13}H_8D_5N_2^+$ – 202.1387, found 202.1387.

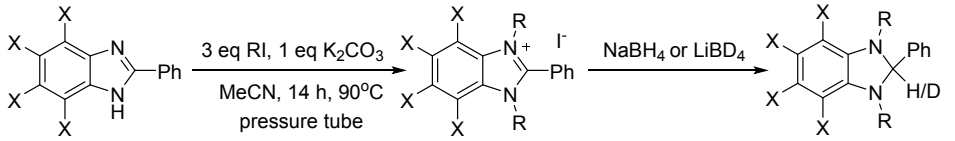
2-Phenyl-1*H*-benzo[d]imidazole-4,5,6,7-*d*$_4$ (5-*d*$_4$)



Synthesis was performed by modified literature method.[30] To a solution of **4-*d*$_5$** (603 mg, 3 mmol) in MeCN (12 ml) at 0°C solid NCS (411 mg, 3.075 mmol) was added and the mixture was stirred for 15 min at this temperature. Then a solution of NaOH (15 mmol, 600 mg) in water (0.6 ml) was added, and the mixture was stirred for 20 min at 0°C and then for 20 min at RT, then it was neutralized by 2M aq. TFA (1.37 g, 0.92 ml, 12 mmol), the solvent was evaporated in vacuum and residue was dissolved in mixture of water (10 ml) and EtOAc (10 ml). The two phases were separated and water phase was extracted with EtOAc (3x10 ml). Combined organic phase was washed with weak solution of $Na_2S_2O_3$ (0.5 g in 15 ml), water (15 ml), brine (10 ml), dried over Na_2SO_4 and evaporated in vacuum to dryness. The residue containing the final compound was washed with 1:1 DCM-Hexane (3x4 ml), and used without further purification. Yield 535 mg (90%). ^{1}H NMR (500 MHz, DMSO): 12.88 br s (1H), 8.16 d (2H, *J* = 8.4 Hz), 7.52 t (2H, *J* = 7.4 Hz), 7.46 t (1H, *J* = 7.4 Hz). ^{13}C NMR (125 MHz, DMSO): 114.8 br s (CD), 121.6 t (CD, *J* = 24.6 Hz), 126.4, 128.9, 129.8, 130.1, 151.2. ESI-HRMS calcd. for $[M+H]^+$ $C_{13}H_7D_4N_2^+$ – 199.1168, found 199.1168.

3) Synthesis of the reducers 2, 2-*d*, 2-*d*$_7$, 2-*d*$_{11}$

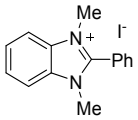
a) Synthesis of 1,3-dimethyl-2-phenylbenzimidazolium salts [3]I, [3-*d*$_6$]I, [3-*d*$_{10}$]I



General procedure:

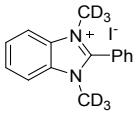
Synthesis were performed by modified literature methods.[31,32] In a pressure flask, 2-phenyl-1*H*-benzo[*d*]imidazole (3 g, 15.5 mmol), K_2CO_3 (2.14 g, 15.5 mmol) and methyl iodide or methyl iodide-*d*$_3$ (46.4 mmol) were mixed with acetonitrile (18 ml). The mixture was sealed and heated under stirring at 90°C for 14 h and then cooled to RT. Then the reaction mixture was filtered and precipitate was washed by water (2x5 ml) and acetone (2x10 ml) to give the first portion of the product. Aqueous and organic filtrates were collected separately. The combined organic filtrate was evaporated in vacuum, the residue was washed with 1:1 acetone-Et_2O (2x5 ml) and gave the second portion of the product.

1,3-Dimethyl-2-phenyl-1*H*-benzo[d]imidazolium iodide ([3]I)



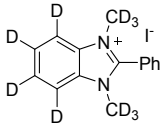
Yield 93% (5.05 g). ^{1}H NMR (500 MHz, DMSO): 8.14 dd (2H, *J* = 6.5 Hz, 3.3Hz), 7.93-7.90 m (2H), 7.85-7.75 m (5H), 3.90 s (6H). NMR spectra are in agreement with literature data.[33]

1,3-Di(methyl-d_3)-2-phenyl-1*H*-benzo[d]imidazolium iodide ([3-d_6]I)



Yield 93% (5.14 g), 99.8%D. ^{1}H NMR (500 MHz, DMSO): 8.14 dd (2H, *J* = 6.5 Hz, 3.3Hz), 7.93-7.90 m (2H), 7.85-7.75 m (5H), 3.87 m (CD_2H, 0.007 H). ^{13}C NMR (125 MHz, DMSO): 32.2 septet (CD_3, *J* = 21.9 Hz), 113.4, 121.0, 126.6, 129.4, 130.7, 131.7, 132.9, 150.3. ESI-HRMS calcd. for $[M]^+$ $C_{15}H_9D_6N_2^+$ – 229.1606, found 229.1608.

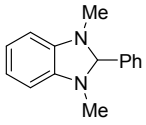
1,3-Di(methyl-d_3)-2-phenyl-1*H*-benzo[d]imidazolium-4,5,6,7-d_4 iodide ([3-d_{10}]I)



Obtained according to general method from **5-d_4** (0.99 g, 5 mmol), K_2CO_3 (0.69 g, 5 mmol), methyl iodide-*d*3 (2.18 g, 0.94 ml, 15 mmol). Yield 78% (1.404 g), 99.8%D. ^{1}H NMR (500 MHz, DMSO): 7.94-7.90 m (2H), 7.87-7.83 m (1H), 7.81-7.77 m (2H), 3.88 quint (CD_2H, 0.007 H, *J* = 1.9 Hz). ^{13}C NMR (125 MHz, DMSO): 32.2 septet (CD_3, *J* = 21.9 Hz), 113.0 t (CD, *J* = 25.9 Hz), 121.0, 126.1 t (CD, *J* = 24.7 Hz), 129.4, 130.7, 131.6, 132.9, 150.3. ESI-HRMS calcd. for M^+ $C_{15}H_5D_{10}N_2^+$ - 233.1857, found 233.1856.

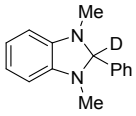
b) Synthesis of 1,3-dimethyl-2-phenylbenzo[d]imidazolines 2, 2-*d*, 2-d_7, 2-d_{11}

1,3-Dimethyl-2-phenyl-2,3-dihydro-1*H*-benzo[d]imidazole (2)



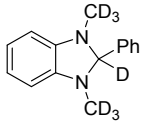
Synthesis was performed by modified literature method.[34] Compound **[3]I** (1.5 g, 4.28 mmol) was suspended in MeOH (57 ml) and the mixture was degassed by nitrogen stream and cooled to 0°C on ice-water bath under inert atmosphere. Then $NaBH_4$ (405 mg, 10.7 mmol) in small portions was added over 40 min. After completion of borohydride addition, the reaction mixture was left to warm to RT and stirred for 3 h under inert atmosphere. The reaction mixture was concentrated in vacuo, then 50 ml of water were added and the imidazoline was extracted by degassed ether (3 x 25 ml). The organic extract was washed with water (10 ml), brine (20 ml), dried over Na_2SO_4, filtered and evaporated in vacuo to dryness. The residue was dissolved in 2:1 EtOH-H_2O (40 ml) at 75°C, filtered through cotton wool while hot and then slowly cooled to RT. The crystals were filtered and dried in high vacuum for 4 h. Yield 77% (730 mg). ^{1}H NMR (500 MHz, DMSO): 7.52-7.50 m (2H) 7.47-7.50 m (3H), 6.62 dd (2H, *J* = 5.4 Hz, 3.2 Hz), 6.45 dd (2H, *J* = 5.4 Hz, 3.2 Hz), 4.87 s (1H), 2.48 s (6 H). NMR spectra are in agreement with literature data.[35]

1,3-Dimethyl-2-phenyl-2,3-dihydro-1*H*-benzo[d]imidazole-2-*d* (2-*d*)



Synthesis of $LiBD_4$[35] and imidazoline[36] were performed by modified literature methods. LiBr (552 mg, 6.35 mmol) was dried in vacuum by heatgun (200-250°C) for 15 min and after cooling to RT added to a suspension of $NaBD_4$ (267 mg, 6.35 mmol) in dry THF (15 ml). The mixture was stirred overnight at reflux under argon atmosphere. The resulting $LiBD_4$ solution was cooled to 0°C, and compound **[3]I** (0.89 g, 2.54 mmol) was added in one portion. Then, methanol-d_4 (821 mg, 0.92 ml, 22.8 mmol) in THF (4 ml) was added dropwise over 10 minutes through septum, the reaction mixture was warmed to RT and stirred for 1 h and finally refluxed under argon atmosphere for 2 h. Reaction mixture was cooled to RT, evaporated in vacuum under inert atmosphere to dryness, residue was dissolved in degassed water (15 ml) and degassed DCM (10 ml). Phases were separated and water phase was extracted by degassed DCM (2x10 ml). Organic extract was washed with degassed water (10 ml), dried over Na_2SO_4, filtered and evaporated in vacuo. The compound was used without further purification. Yield 87% (493 mg), 96%D. ^{1}H NMR (500 MHz, $CDCl_3$): 7.60-7.55 m (2H), 7.44-7.40 m (3H), 6.72 dd (2H, J = 5.4 Hz, 3.2 Hz), 6.44 dd (2H, J = 5.4 Hz, 3.2 Hz), 4.89 s (0.04 H), 2.48 s (6 H). ^{13}C NMR (125 MHz, $CDCl_3$): 33.3, 93.6 t (CD, J = 21.6 Hz), 105.8, 119.4, 128.59, 128.96, 129.5, 139.2, 142.3. APCI-HRMS calcd. for $[M+H]^+$ $C_{15}H_{16}N_2D^+$ – 226.1449, found 226.1440.

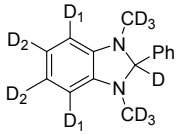
1,3-Di(methyl-d_3)-2-phenyl-2,3-dihydro-1*H*-benzo[d]imidazole-2-*d* (2-d_7)



Obtained by the same method as **2-*d*** from compound **[3-d_6]I** (1 g, 2.8 mmol), LiBr (365 mg, 4.2 mmol), $NaBD_4$ (177 mg, 4.2 mmol), methanol-d_4 (543 mg, 0.61 ml, 15.1 mmol). Yield 84% (543 mg), 99.9%D (CD_3), 97.7%D (CDPh). ^{1}H NMR (500 MHz, $CDCl_3$): 7.60-7.55 m (2H), 7.44-7.40 m (3H), 6.72 dd (2H, J = 5.4 Hz, 3.2 Hz), 6.44 dd (2H, J = 5.4 Hz, 3.2 Hz), 4.89 s (0.022 H), 2.48 m (0.015 H). ^{2}H NMR (76.8 MHz, $CHCl_3$): 4.92 br s (1D), 2.56 s (6D). ^{13}C NMR (125 MHz, $CDCl_3$): 32.5 septet (CD_3, J = 20.7 Hz), 93.5 t (CD, J = 20.3 Hz), 105.8, 119.4, 128.6, 128.9, 129.4, 139.2, 142.3. APCI-HRMS calcd. for $[M+H]^+$ $C_{15}H_{10}D_7N_2^+$ – 232.1826, found 232.1822.

The compound **[3-d_6]Br** left after photoreductions, was by the same way converted into **2-d_7**, yield 84%, 99.8%D (CD_3), 97.5%D (CDPh).

1,3-Di(methyl-d_3)-2-phenyl-2,3-dihydro-1H-benzo[d]imidazole-2,4,5,6,7-d_5 (2-d_{11})

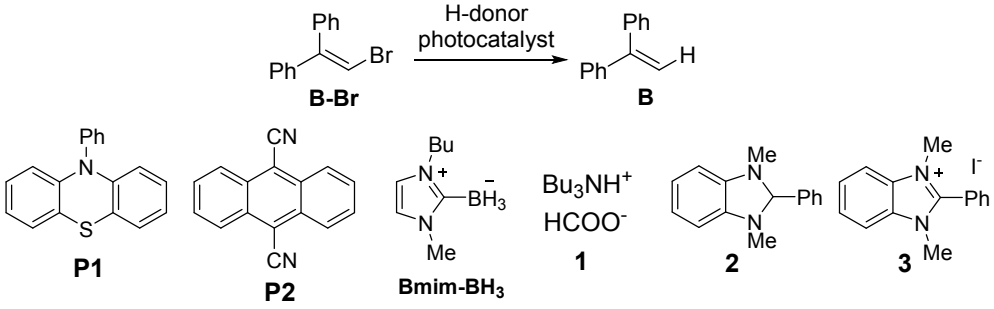


Obtained by the same method as **2-*d*** from compound **[3-d_{10}]I** (734 mg, 2.04 mmol), LiBr (460 mg, 5.28 mmol), $NaBD_4$ (221 mg, 5.28 mmol), methanol-d_4 (380 mg, 0.43 ml, 10.5 mmol). Yield 89% (427 mg), 99.9%D (CD_3), 99.7%D (CD_{Ar}), 96.8%D (CDPh). ^{1}H NMR (500 MHz, $CDCl_3$): 7.60-7.55 m (2H), 7.44-7.40 m (3H), 6.74 m (0.006 H), 6.45 m (0.007 H), 4.90 s (0.032 H), 2.55 quint (0.007 H, J = 1.8 Hz). ^{2}H NMR (76.8 MHz, $CHCl_3$): 6.79 s (2D), 6.50 s (2D), 4.91 br s (1D), 2.56 s (6D). ^{13}C NMR (125 MHz, $CDCl_3$): 32.5 septet (CD_3, J = 20.6 Hz), 93.6 t (CD, J = 21.7 Hz), 105.4 t (CD, J = 24.2 Hz), 118.9 t (CD, J = 24.2 Hz), 128.6, 128.9, 129.4, 139.2, 142.2. APCI-HRMS calcd. for $[M+H]^+$ $C_{15}H_6D_{11}N_2^+$ – 236.2077, found 236.2067.

The compound **[3-d_{10}]Br** left after photoreductions, was by the same way converted into **2-d_{11}**, yield 79%, 99.9%D (CD_3), 93.9%D (CD_{Ar1}), 97%D (CD_{Ar2}), 96.3%D (CDPh).

4) Optimization of photoreductions

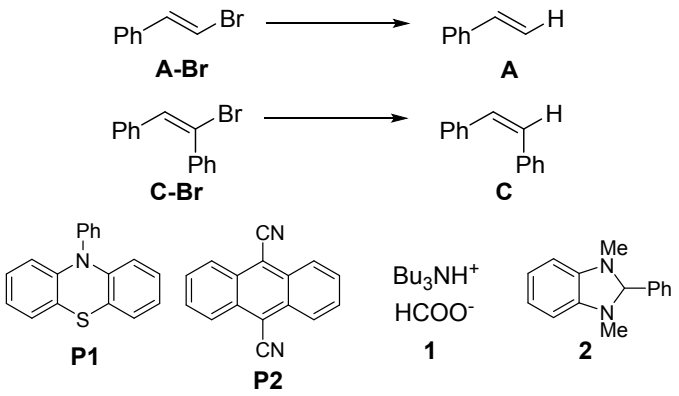
Table S2. **Optimization of photoreduction of B-Br**

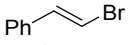
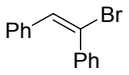


Entry	Photocatalyst	G-donor	Light source, wavelength	Time	Solvent	Conv.
1	**P1** 5%	5 eq **1**	380 nm LED, 13 W	16 h	MeCN	7%
2		2 eq **2**				73%
3		2 eq **Bmim-BH$_3$**				9%
4	**P2** 5%	2 eq Bu_3N	cool white LED, 13 W	16 h	MeCN	19%
5		2 eq **2**				**95.5%**
6		1.5 eq **2**				85%
7		1.25 eq **2**				79%
8		1.1 eq **2**				74%
9		1.5 eq **Bmim-BH$_3$**				2.5%
10	None	2 eq **2**	cool white LED, 13 W	16 h	MeCN	75%
11				32 h		**99.5%**
12			In dark	48 h		0
13		0.2 eq **2** 2 eq **Bmim-BH$_3$**	cool white LED, 13 W	16 h	MeCN	4%
14					C_6H_6	0.2%
15					DCM	0
16					DMSO	3.5%
17		0.2 eq **3** 2 eq **Bmim-BH$_3$**	cool white LED, 13 W	16 h	MeCN	0.7%

After the time stated, reaction mixture was extracted by pentane (3x2 ml), combined pentane extracts were evaporated in vacuum, conversion was calculated from NMR spectra**.**

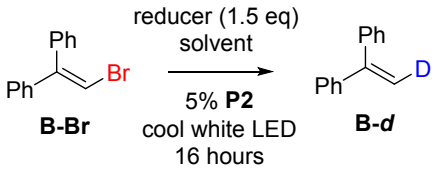
Table S3. **Optimization of photoreductions of A-Br and C-Br**



Entry	Substrate	Photocatalyst	G-donor	Light source, wavelength	Time	Solvent	Conv.
1	 **A-Br**	**P1** 5%	5 eq **1**	450 nm LED, 3W	42 h	MeCN	0
2				380 nm LED, 13 W	16 h		8%
3						MeOH	0
4						DMSO	0
5			2 eq **2**			MeCN	28%
6		**P2** 5%	2 eq Bu_3N	cool white LED, 13 W	16 h	MeCN	3
7			2 eq **2**				**65%**
8	 **C-Br**	**P1** 5%	5 eq **1**	380 nm LED, 13 W	16 h	MeCN	58%
9			2 eq **2**				80%
10		**P2** 5%	2 eq Bu_3N	cool white LED, 13 W			25%
11			2 eq **2**				**>99%**

After the time stated, reaction mixture was extracted by pentane (3 x 2 ml), combined pentane extracts were evaporated in vacuum, conversion was calculated from NMR spectra**.**

Table S4. **Optimization of deuterodebromination of B-Br**

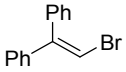
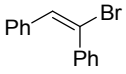
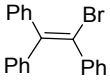
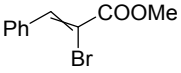
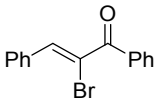
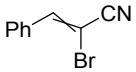


Entry	Reducer	Solvent	Conv.	%D in product
1	**2**	MeCN	85%	0
2		CD_3CN	97%	3.8
3	0.75 eq **2** + 0.75 eq **2-*d***	CD_3CN	83.4%	38.8
4	**2-*d***	MeCN	73%	65
5		CD_3CN	68%	76
6	**2-d_7**	MeCN	91%	72
7		CD_3CN	75%[a]	92.6
8			96%	89.8
9		acetone-d_6	81%	91.7
10		DMSO-d_6	99%	82.6
11		THF-d_8	39%	87.6
12		CD_3OD	18%	95.4

After the time stated, reaction mixture was extracted by pentane (3 x 2 ml), combined pentane extracts were evaporated in vacuum, conversion was calculated from NMR spectra**.**

[a]without addition of **P2**, reaction time 48 h

Table S5. **Results of preparative photoreductions of six substrates with 2-d_7**

Entry	Compound	Reducing agent	Reaction time	Prep. yield (Z/E)	%D	[3-d_n]Br recovery
1	 **B-Br**	**2-d_7**	24 h	76%	90	37%
2		**2-d_{11}**	48 h	51%	93	49%
3	 **C-Br**	**2-d_7**	24 h	59% (Z-)	84	47%
4		**2-d_{11}**	48 h	64% (49:1)	96	52%
5	 **E-Br**	**2-d_7**	2 x 24 h[a]	47%	56	57%
6		**2-d_{11}**	3 x 24 h[b]	45%	77	40%
7	 **H-Br**	**2-d_7**	24 h	90% (1.44:1)	89 (E-), 96 (Z-)	50%
8		**2-d_{11}**	24 h	86% (1.3:1)	89 (E-), 96 (Z-)	41%
9	 **I-Br**	**2-d_7**	24 h	40% (*E*-)	54	53%
10		**2-d_{11}**	24 h	81% (E-)	78	55%
11	 **J-Br**	**2-d_7**	24 h	65% (1.5:1)	~96 (E-), 94 (Z-)[c]	51%
12		**2-d_{11}**	24 h	92% (1.78:1)	97 % (E and Z)	41%

Conditions – CD_3CN, 1.7 eq **2-d_7** or **2-d_{11}**, 5 mol% **P2**, 13W cool white LED

[a]Two portions of **P2**, two 24-hour intervals

[b]Three portions of **P2**, three 24-hour intervals

[c]About 1.6 mol% of β-D-cinnamonitrile was also present in the mixture

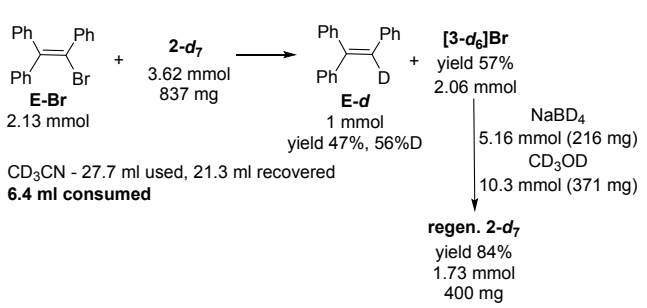
5) Calculation of costs of deuteration with 2-d_7 and 2-d_{11}

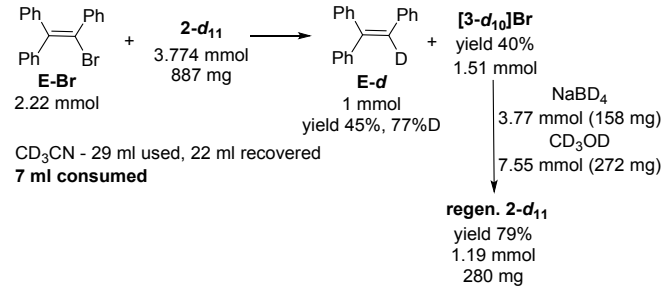
Costs of deuterated compounds (the lowest prices found via internet in suppliers catalogues to date 31.08.2020):
Acetonitrile-d_3 – 2$/ml (Fluorochem)
Methanol-d_4 – 3.6$/g (Fluorochem)
Iodomethane-d_3 – 6.4$/g (Cambridge Isotope)
Sodium borohydride-d_4 – 24.3$/g (Armar)
Aniline-d_5 – 48.55$/g (Abcr)

The synthesis of 1.34 g of **2-d_{11}** consumed: 1 g of Aniline-d_5, 2.98 g of Iodomethane-d_3, 1.16 g of Methanol-d_4, 0.67 g of Sodium borohydride-d_4, other reagents worth ~1$. The cost for 1 g of **2-d_{11}** is **66.46$**.

The synthesis of 0.93 g of **2-d_7** consumed: 1.87 g of Iodomethane-d_3, 0.87 g of Methanol-d_4, 0.502 g of Sodium borohydride-d_4, other reagents worth ~0.16$. The cost for 1 g of **2-d_7** is **29.5$**.

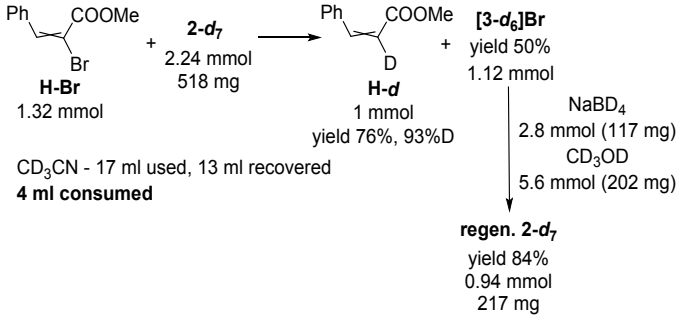
Consider Synthesis of 1 mmol of **E-*d***:





Consumption: **2-d_7** – 437 mg (12.89$) $NaBD_4$ – 216 mg (5.25$) CD_3OD – 371 mg (1.34$) CD_3CN – 6.4 ml (12.8$) Total – 29.28$/mmol of **E-*d*** (0.52$/p.p. of D)	**Consumption**: **2-d_{11}** – 607 mg (40.34$) $NaBD_4$ – 158 mg (3.84$) CD_3OD – 272 mg (0.98$) CD_3CN – 7 ml (14$) Total – 59.16$/mmol of **E-*d*** (0.77$/p.p. of D)

For comparison, consider synthesis of 1 mmol of **H-*d***:



Consumption:
2-d_7 – 301 mg (8.88$)
$NaBD_4$ – 117 mg (2.84$)
CD_3OD – 202 mg (0.73$)
CD_3CN – 4 ml (8$)

Total – 20.45$/mmol of **E-*d*** (0.22$/p.p. of D)

6) Calculation of kinetic isotope effect for deuterodebromination of B-Br

a) 1 mmol of bromoalkene reacted with mixture of 0.75 mmol of **2** and 0.75 mmol of **2-*d*** with conversion 83.4% and isotopic enrichment 38.8% (see Table S3, entry 2).
b) Since deuterium has partially migrated from the solvent, isotopic enrichment 3.8% of the substrate in a reaction with **2** in CD_3CN (see Table S3, entry 1) is used for correction of final D enrichment in the reaction mentioned in a)
c) The conversion of **2** and **2-*d*** can be calculated as follows:
    a. Amount of the reacted **2-*d*** can be calculated from the following equation:
    $n(D\text{-alkene})^{corr}$ = n(Br-alkene) x Conv x (0.388-0.038) = 1 mmol*0.834*0.35 = 0.292 mmol
    b. Conversion of **2-*d*** follows from the following equation:
    F_D = 0.292/0.75 = 0.389, where 0.75 is amount (mmol) of the **2-*d*** put to the reaction
    c. As **2** is responsible for H-alkene formation, reacted amount of **2** follows from the equation:
    n(**2**) = n(H-alkene)-n(D-alkene) = 0.834-0.292 = 0.542 mmol
    d. Conversion of **2** follows from the following equation:
    F_H = 0.542/0.75 = 0.723
d) From the competitive reactions method,[38] KIE can be calculated as:

$$KIE = \frac{k_H}{k_D} = \frac{ln(1 - F_H)}{ln(1 - F_D)} = \frac{ln(1 - 0.723)}{ln(1 - 0.389)} = \frac{-1.2837}{-0.4927} = 2.61$$

7) Synthesis of deuterated alkenes by bromoalkene deuterodebromination

Photoreaction setup

For photoreactions with 9,10-dicyanoanthracene (**P2**), one meter of cool white LED strip (12V, 12 W, 60 SMD 2835-type LEDs/m, color temperature 6000-6500K, luminosity 1150 lm/m) was wound inside plastic washing bottle (diameter 7.5 cm, height 14 cm) with cut off bottom. Inside upper part of the bottle was covered with aluminium foil (see Figure 1B). The upper outlet was used for cooling of the LEDs by air stream. Reaction mixtures in 15x45 mm Pyrex screw-cap vials were placed on magnetic stirrer covered by an aluminium foil sheet and covered with the photoreactor (see Figure 1A). Up to 6 reaction vials which can be bound in a block around one central empty vial with a rubber band (see Figure 1C) could be irradiated simultaneously.

For experiments with 10-phenylphenothiazine (**P1**), one meter of UV LED strip (12V, 14.4 W, 60 SMD 5050-type LEDs/m, λ_{max} 385 nm) was used in similar photoreactor.

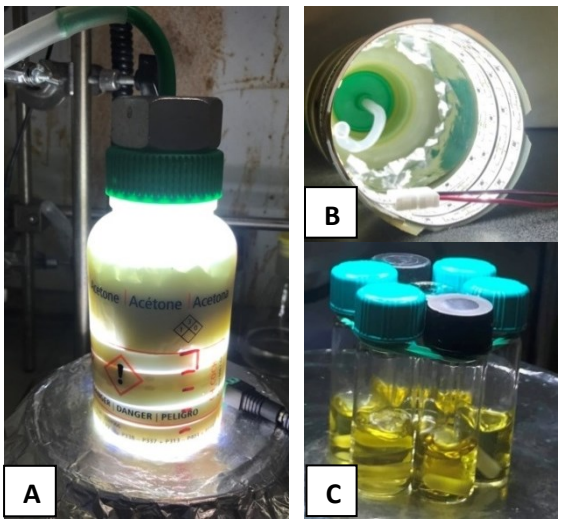


Fig. 1. LED photoreactor and reaction vials

General deuterodebromination procedure

To a 15x45 mm screw-cap borosilicate glass vial with a 7-8 mm stirring bar, 9,10-dicyanoanthracene (**P2**) (1.5 mg, 0.0066 mmol), bromoalkene (0.13 mmol), acetonitrile-d_3 (1.5 ml) and **2-d_{11}** (0.22 mmol, 51.7 mg) were added successively. The mixture was degassed with nitrogen stream for 1 min, closed tightly and irradiated in the photoreactor with stirring (300 rpm) for 16 h or 24 h. With some substrates, additional one or two portions of **P2** and irradiation intervals were needed. After completion of the reaction, the mixture was diluted with acetone (2 ml), the solution was decanted and the precipitate (**[3-d_{10}]Br**) was washed with acetone (3x1.5 ml). The solution was evaporated in vacuum to dryness, to the residue acetone (3 ml) was added and resulting solution was decanted from the **[3-d_{10}]Br** precipitate. Precipitate was washed with acetone (3x1.5 ml), united with previous portion of **[3-d_{10}]Br**, dried in air and could be regenerated into **2-d_{11}** by $LiBD_4$-CD_3OD reduction as described above.

Reaction mixture liberated from benzimidazolium salt was purified by column chromatography on SiO_2, eluent - hexane-EtOAc, hexane-Et_2O or hexane-DCM (specified below).

Experiment on photodebromination of bromoarenes

A mixture of p-bromoacetophenone or dimethyl 2-bromoterephthalate (0.05 mmol), **P2** (0.6 mg, 0.0026 mmol) and **2** (0.075 mmol, 17 mg) in acetonitrile (1.5 ml) was degassed with nitrogen stream for 1 min, closed tightly and irradiated in the photoreactor with stirring (300 rpm) for 16 h. After this, the reaction mixture was evaporated in vacuum to dryness and residue was extracted by 2:1 pentane-Et_2O mixture (2x2 ml), the extract was evaporated and residue was analyzed by NMR.

p-Bromoacetophenone was converted into acetophenone by 64%.

Dimethyl 2-bromoterephthalate was fully converted into dimethyl terephthalate.

UV-Vis absorbance and LED emission spectra

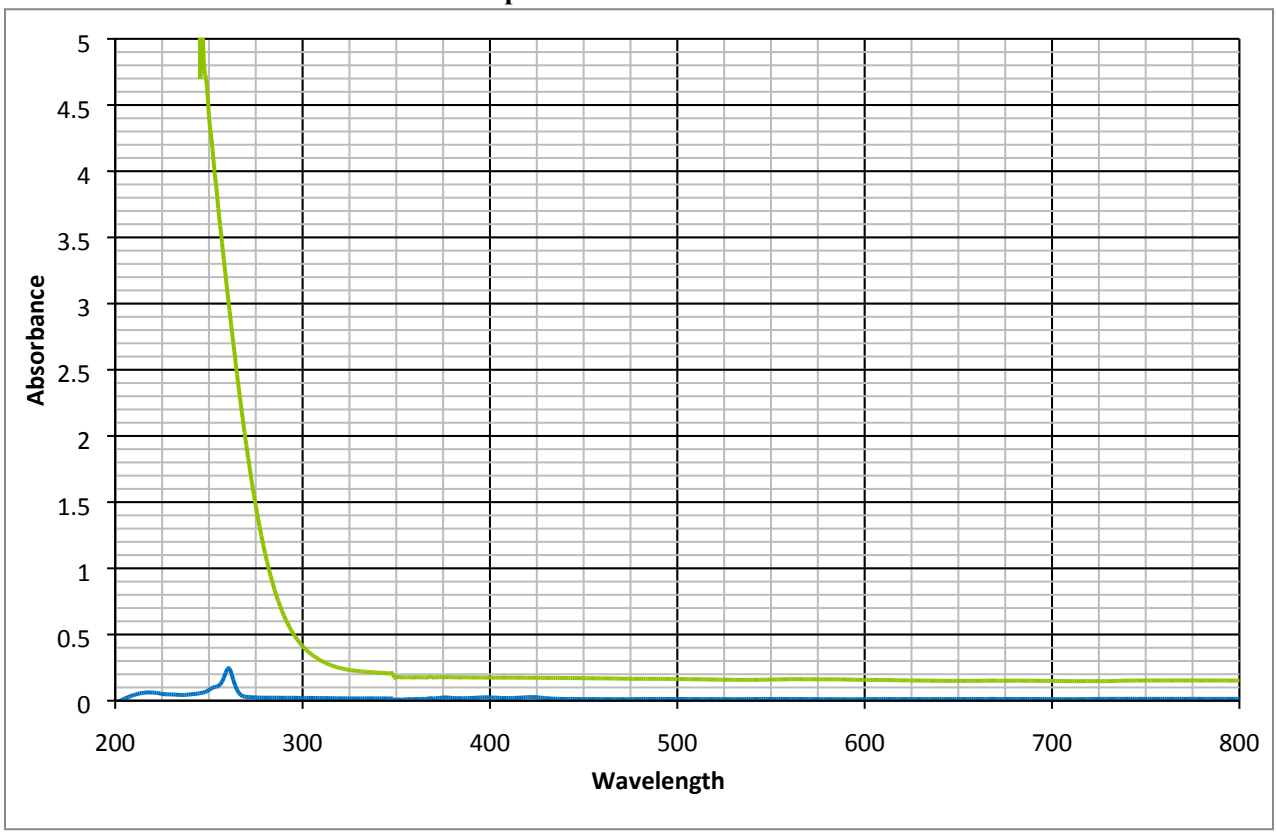


Fig. 2 UV-Vis absorbance spectra of an empty reaction vial (green) and of MeCN (blue)

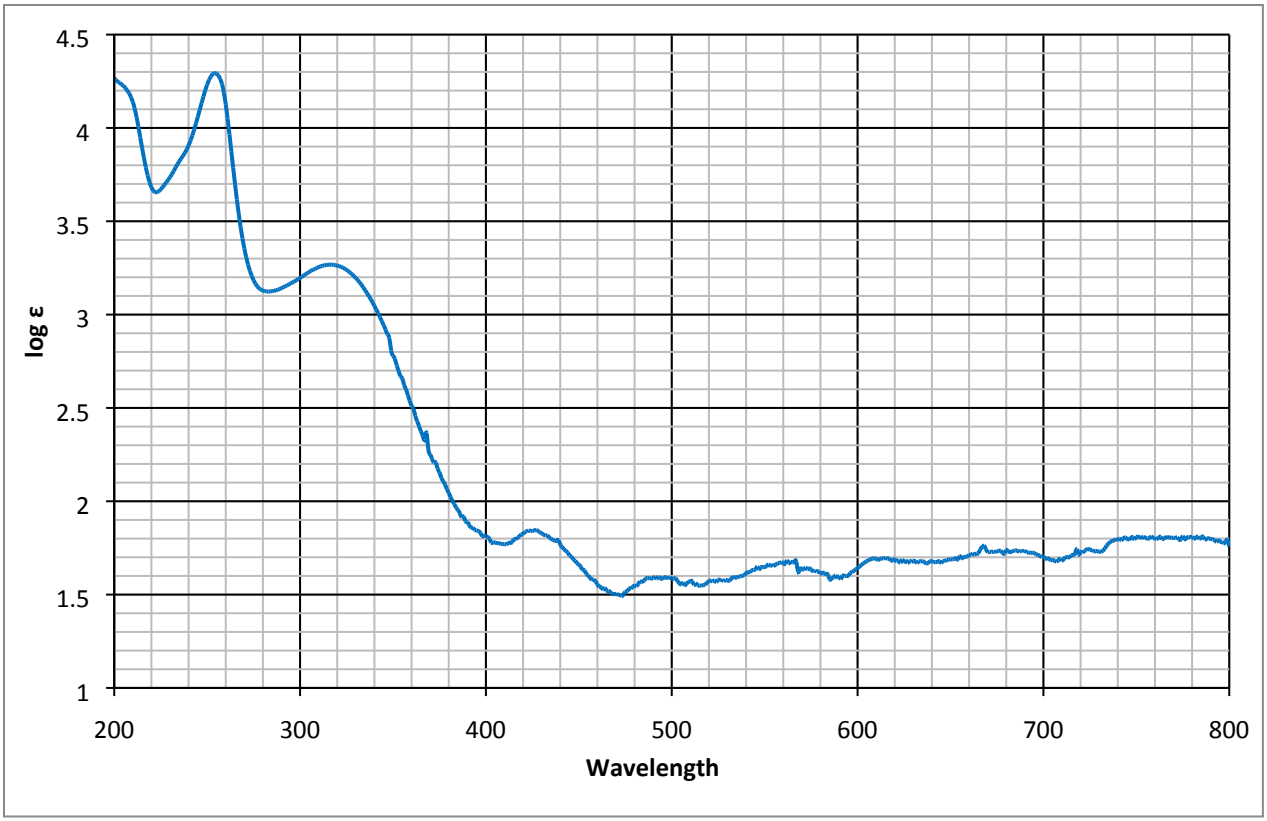


Fig. 3 UV-Vis absorbance spectrum of 10-phenylphenothiazine **P1** (MeCN, 0.18 mmol/l)

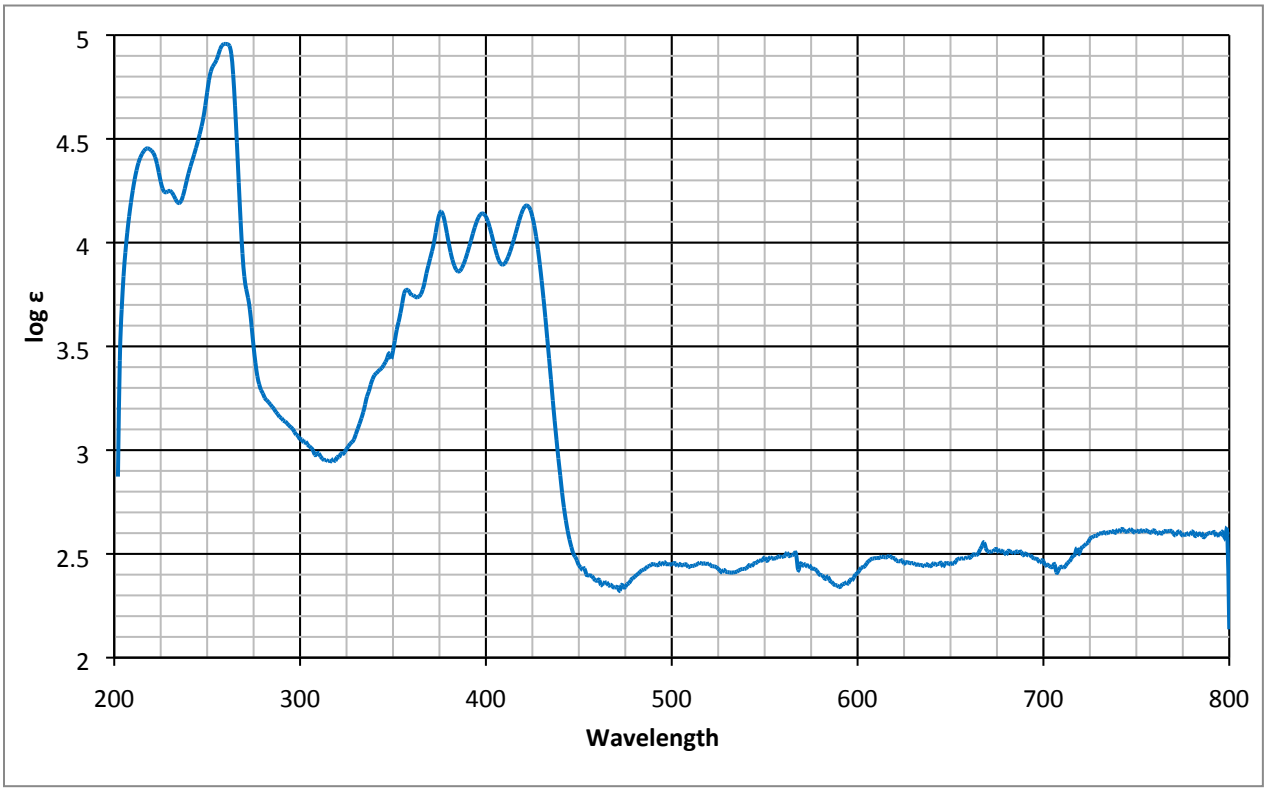


Fig. 4 UV-Vis absorbance spectrum of 9,10-dicyanoanthracene **P2** (MeCN, 22 µmol/l)

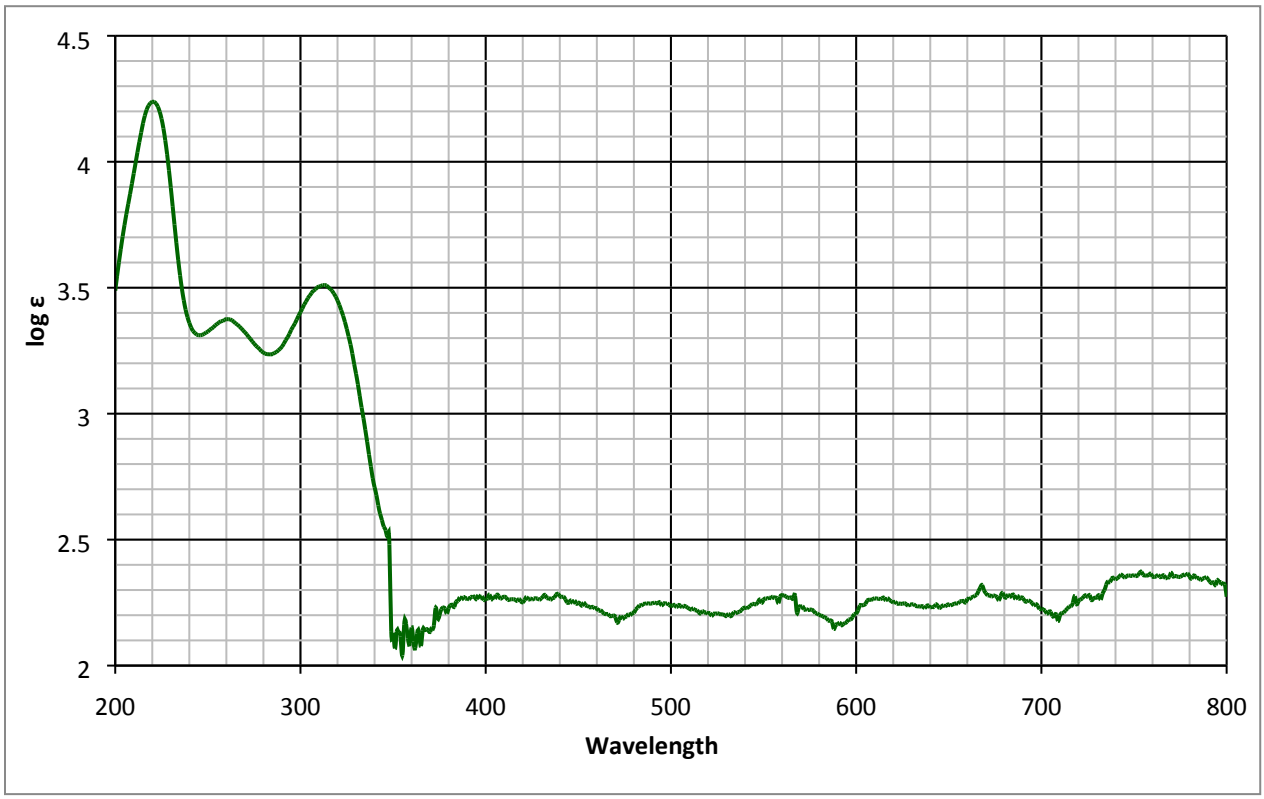


Fig. 5 UV-vis absorbance spectrum of **2-*d*** (MeCN, 44 μmol/l)

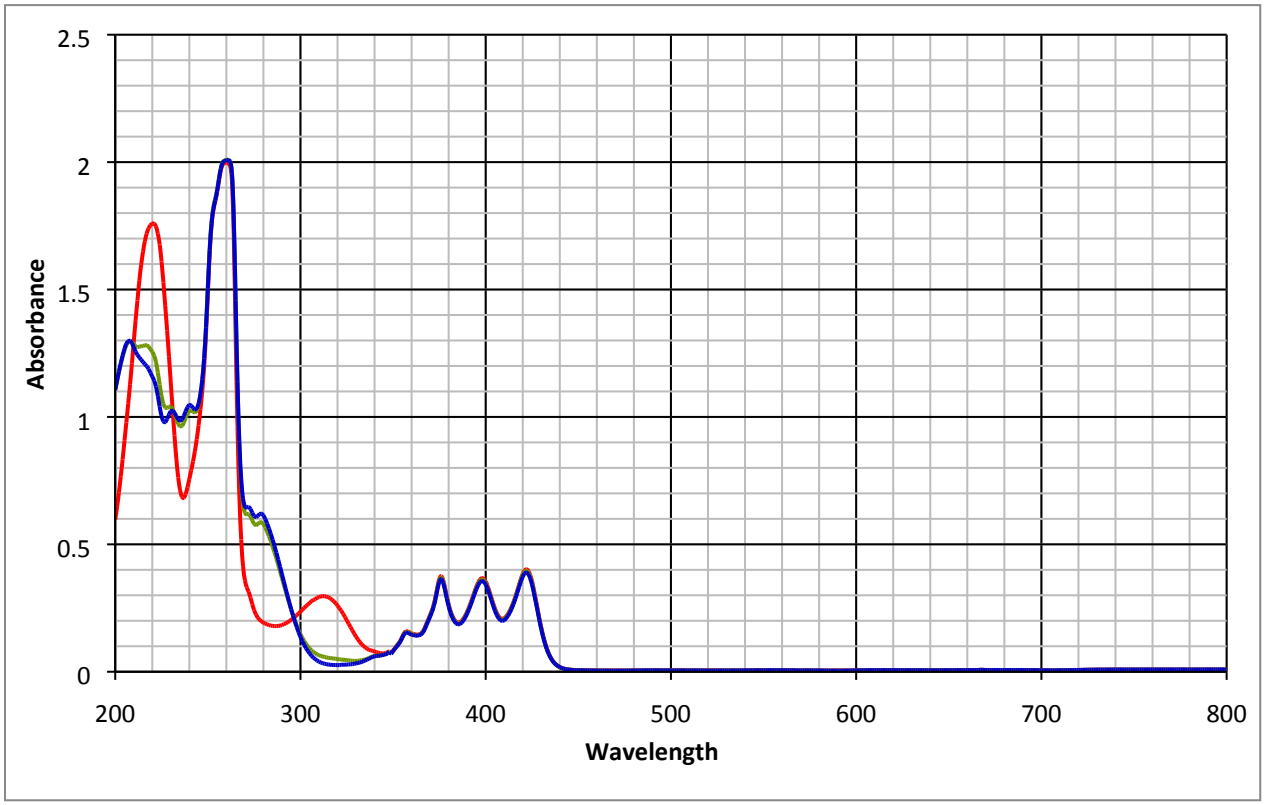


Fig. 6 UV-vis absorbance spectra of equimolar mixture of **2-*d*** and **P2** after mixing (**red**) and after 15 min (**green**) or 1 h (**blue**) white LED irradiation (MeCN, both concentrations 22 μmol/l)

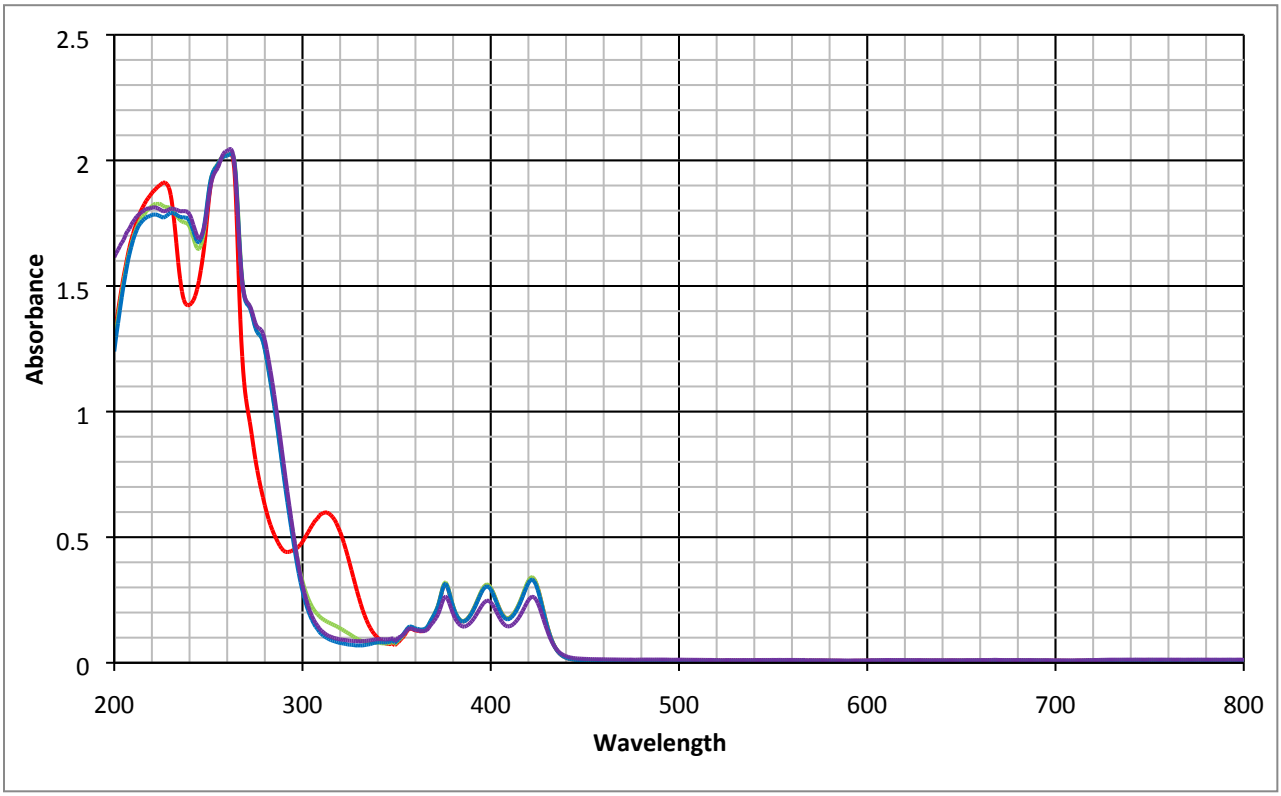


Fig. 7 UV-vis absorbance spectra of mixture of **B-Br** (44 µmol/l), **2-*d*** (44 µmol/l) and **P2** (22 µmol/l) after mixing (**red**) and after 15 min (**green**), 1 h (**blue**) or 14 h (**purple**) white LED irradiation (MeCN)

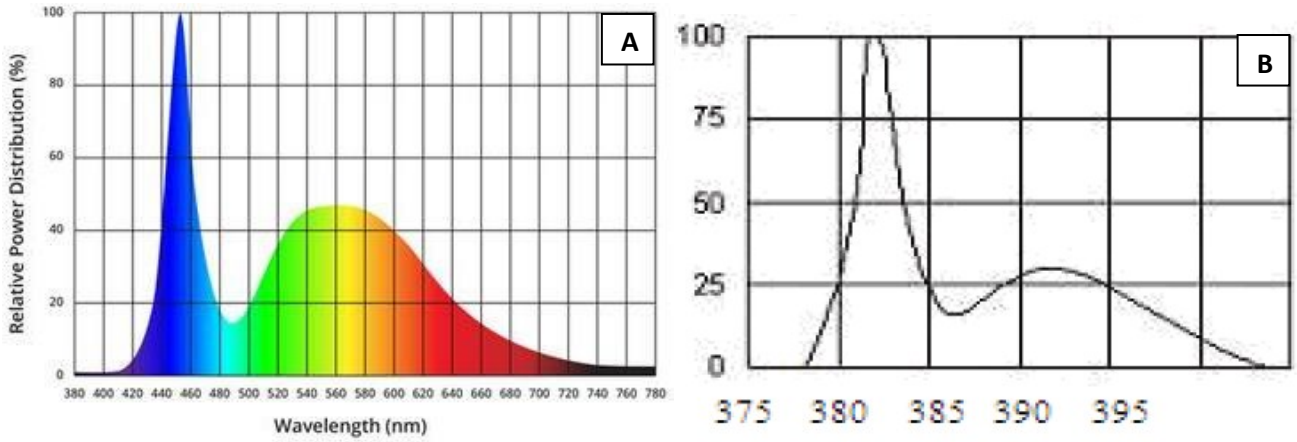
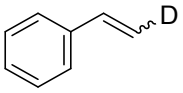


Fig. 8 Reference emission spectra of cool white (**A**)[39] and UV (**B**)[40] LED strips used for photoreactions

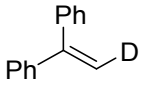
Properties of deuterated alkenes

(EZ)-2-*d*-Styrene (A-*d*)



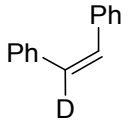
Obtained in a mixture with 2-bromostyrene, total conversion 55%. Reaction was conducted in three 24 h intervals, 3x0.05 eq 9,10-dicyanoanthracene (**P2**). Eluent for chromatography – pentane. Yield 58% (12 mg), 90%D, 74% of (*Z*)-isomer. Maximally styrene-rich fraction (11 mg) contained 87 mass% of styrene (81 mol%), 91%D avg., 74% of (*Z*)-isomer. ^{1}H NMR (500 MHz, $CDCl_3$): 7.41 d (2H, *J* = 7.6 Hz), 7.32 t (3H, *J* = 7.3 Hz), 6.74-6.68 m (1H, H\D-styrenes), 5.74 d (0.65H, *J* = 17.6 Hz, Z-d-styrene), 5.23 d (0.23H, *J* = 10.9 Hz, E-*d*-styrene). NMR spectra are in agreement with literature data.[41]

(Ethene-1,1-diyl-2-*d*)dibenzene (B-*d*)



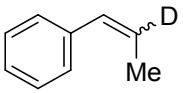
Reaction time – 2 days, 0.05 eq 9,10-dicyanoanthracene (**P2**). Eluent for chromatography – hexane. Yield 51% (12 mg), 93%D. ^{1}H NMR (500 MHz, $CDCl_3$): 7.36-7.31 m (10H), 5.47 s (0.15H, residual CH_2), 5.46 s (1H, CHD). ^{13}C NMR (125 MHz, $CDCl_3$): 114.1 t (CD, *J* = 24.2 Hz), 144.4 (CH), 127.8, 128.3, 128.4, 141.6, 150.2. APCI-HRMS calcd. for $[M+H]^+$ $C_{14}H_{12}D^+$ – 182.1075, found 182.1068. NMR spectra are in agreement with literature data.[42]

(*Z*)-(Ethene-1,2-diyl-1-*d*)dibenzene (C-*d*)



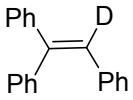
Reaction time – 2 days, 0.05 eq 9,10-dicyanoanthracene (**P2**)**.** Eluent for chromatography – hexane. Yield 64% (15 mg), 98% of *Z*-isomer, 95%D. ^{1}H NMR (500 MHz, CD_3CN): 7.25-7.21 m (10H), 7.16 s (0.019H, *E*-isomer), 6.66 s (1.045H, *Z*-isomer). ^{13}C NMR (125 MHz, $CDCl_3$): 127.23, 127.24, 128.34, 128.35, 129.01, 129.02, 130.1 t (CD, *J* = 23.9 Hz), 130.3 (CH), 130.4, 137.3, 137.4. APCI-HRMS calcd. for $[M]^+$ $C_{14}H_{11}D^+$ – 181.0996, found 181.1003. NMR spectra are in agreement with literature data.[43]

(EZ)-(Prop-1-en-1-yl-2-*d*)benzene (D-*d*)



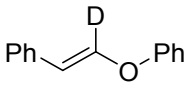
Obtained in mixture with 2-bromo-1-phenylprop-1-ene, total conversion 57%. Reaction was conducted in three 24 h intervals, 3x0.05 eq 9,10-dicyanoanthracene (**P2**). Eluent for chromatography – pentane. Yield 56% (7 mg). Maximally (prop-1-en-1-yl-2-*d*)benzene-rich fraction (15 mg) contained 44 mass% of the compound as 63% of (*Z*)-isomer. D enrichment – 77%D in (*E*)-isomer, 86%D in (*Z*)-isomer. ^{1}H NMR (500 MHz, $CDCl_3$): *E*-isomer – 7.36-7.16 m (5H), 6.39 m (1H), 6.23 dq (0.24H, *J* =15.7 Hz; 6.6 Hz), 1.88 dd (3H, *J* = 8.6 Hz; 1.4 Hz). *Z*-isomer – 7.36-7.16 m (5H), 6.43 m (1H), 5.79 dq (0.14H, *J* =11.6 Hz; 7.2 Hz), 1.93 dd (3H, *J* = 10 Hz; 1.9 Hz). NMR spectra are in agreement with literature data.[44,45]

(Ethene-1,1,2-triyl-2-*d*)tribenzene (E-*d*)



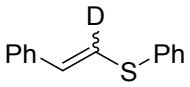
Obtained in mixture with 2-bromo-1,1,2-triphenylethylene, total conversion 53%. Reaction was conducted in three 24 h intervals, 3x0.05 eq 9,10-dicyanoanthracene (**P2**). Eluent for chromatography – hexane. Yield 45% (23 mg), maximally (ethene-1,1,2-triyl-2-*d*)tribenzene-rich fraction (13 mg) contained 91% (w/w) of D-alkene. D enrichment – 77%D. ^{1}H NMR (500 MHz, $CDCl_3$): 7.36-7.29 m (8H), 7.24-7.21 m (2H), 7.17-7.11 m (3H), 7.06-7.03 m (2H), 6.98 s (0.23H). ^{13}C NMR (125 MHz, $CDCl_3$): 126.9, 127.55, 127.64, 127.74, 128.1, 128.3, 128.8, 129.7, 130.5, 137.5, 140.5, 142.6, 143.3 t (CD, J = 23.1 Hz), 143.57 (CH), 143.59. APCI-HRMS calcd. for $[M+H]^+$ $C_{20}H_{16}D^+$ – 258.1388, found 258.1376. NMR spectra are in agreement with literature data.[46]

(*E*)-(2-Phenoxyvinyl-2-*d*)benzene (F-*d*)



Reaction was conducted in two 24 h intervals, 2x0.05 eq 9,10-dicyanoanthracene (**P2**). Eluent for chromatography – hexane-Et_2O 20:1. Yield 94% (24 mg), pure (*E)*-isomer, 89%D. NMR (500 MHz, $CDCl_3$): 7.38-7.34 m (2H), 7.32-7.30 m (4H), 7.23-7.19 m (1H), 7.18 d (0.11H, J = 12.4 Hz), 7.13-7.09 m (1H), 7.09-7.06 m (2H), 6.35 d (0.11H, J = 12.4 Hz), 6.34 t (0.89H, J = 1.7 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): 113.6, 117.1, 123.4, 125.8, 126.8, 128.8, 129.9, 135.3, 143.3 t (CD, J = 27.6 Hz), 143.6 (CH), 157.3. ESI-HRMS calcd. for $[M+H]^+$ $C_{14}H_{12}OD^+$ – 198.1024, found 198.1024.

(EZ)-Phenyl(2-phenylvinyl-1-*d*)sulfane (G-*d*)



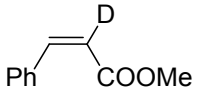
Reaction was conducted in two 24 h intervals, 2x0.05 eq 9,10-dicyanoanthracene (**P2**). Eluent for chromatography – hexane-Et_2O 20:1. Yield 84% (18 mg), *E*/*Z* ratio ~ 1:1. D enrichment – 67%D in (*E*)-isomer, 77%D in (*Z*)-isomer. NMR (500 MHz, $CDCl_3$): 7.55-7.52 m (2H), 7.49-7.46 m (2H), 7.44-7.26 m (16H), 6.89 d (0.32H, J = 15.5 Hz, *E*-isomer), 6.76-6.72 m (0.95H, *E*-isomer), 6.62-6.58 m (1H, *Z*-isomer), 6.51 d (0.23H, J = 10.7 Hz, *Z*-isomer), 6.34 t (0.89H, J = 1.7 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): selected signals of (*E*)-isomer – 125.8 t (CD, J = 26.7 Hz), 126.2 (CH), 130.2, 132.0, 136.4, 136.7; selected signals of (*Z*)-isomer – 123.3 t (CD, J = 26.1 Hz), 123.5 (CH), 130.0, 131.8, 135.4, 136.6; mixture *E*+*Z* –127.1, 127.28, 127.33, 127.7, 128.5, 128.88, 128.91, 129.3. APCI-HRMS calcd. for $[M+H]^+$ $C_{14}H_{12}SD^+$ – 214.0795, found 214.0786.

(*E*)- and (*Z*)-Methyl 3-phenylacrylate-2-*d* (H-*d*)

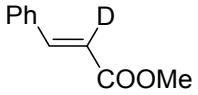
Reaction time – 24 h, 0.05 eq 9,10-dicyanoanthracene (**P2**)**.** Eluent for chromatography – hexane-DCM 2:1. Yield 86% (28 mg), *E*/*Z* = 1:1.3, (*E*)- and (*Z*)-isomers were separated.

For the reaction at higher loading, **H-Br** (1 mmol, 241 mg) and **2-*d*$_{11}$** (400 mg, 1.7 mmol) were dissolved in CD_3CN (13 ml) and poured into six screw-cap vials with 1.9 mg portions of **P2** (11.4 mg total, 5 mol%). The solutions were bubbled with nitrogen and irradiated for 24 h. After completion of the reaction the mixture was decanted and the solvent was distilled off in vacuum (10 ml collected, 77% regeneration), residues in the reaction vials and in the distillation flask were washed with acetone (2 x 3 ml). After acetone washing, the precipitates were united and dried in the air ((**[3-*d*$_{10}$]Br**, 290 mg, 55% regeneration). Acetone wash was evaporated in vacuum

and purified by column chromatography (Hex-DCM 2:1). Yield 76% (125 mg), *E*/*Z* = 1:1.15, 90.5%D in *E*-, 96.5%D in *Z*-.

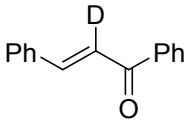


96%D. NMR (500 MHz, $CDCl_3$): 7.62-7.58 m (2H), 7.38-7.33 m (3H), 6.96 m (1H), 5.96 d (0.037H, *J* = 12.6 Hz), 3.72 s (3H). ^{13}C NMR (125 MHz, $CDCl_3$): 51.5, 119.2 t (CD, *J* = 24.9 Hz), 119.5 (CH), 128.2, 129.2, 129.9, 134.9, 143.5, 166.7. ESI-HRMS calcd. for $[M+H]^+$ $C_9H_{10}O_2D^+$ – 164.0816, found 164.0818. NMR spectra are in agreement with literature data.[47]



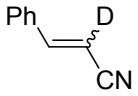
89%D. NMR (500 MHz, $CDCl_3$): 7.69 t (1H, *J* = 2.2 Hz), 7.53-7.50 m (2H), 7.40-7.36 m (3H), 6.45 d (0.11H, *J* = 16 Hz), 3.81 s (3H). ^{13}C NMR (125 MHz, $CDCl_3$): 51.8, 117.7 t (CD, *J* = 24.8 Hz), 119.9 (CH), 128.1, 129.0, 130.4, 134.5, 144.9, 167.5. ESI-HRMS calcd. for $[M+H]^+$ $C_9H_{10}O_2D^+$ – 164.0816, found 164.0818. NMR spectra are in agreement with literature data.[47]

(*E*)-2-*d*-Chalcone (I-*d*)



Reaction time – 24 h, 0.05 eq **P2.** Eluent for chromatography – hexane-DCM 4:3. Yield 81% (17 mg), pure (*E*)-isomer, 78%D. NMR (500 MHz, $CDCl_3$): 8.03 dd (2H, *J* = 8.2 Hz; 1.4 Hz), 7.82 d (0.23 H, *J* = 15.7 Hz), 7.81 t (0.77H, *J* = 1.9 Hz), 7.68-7.63 m (2H), 7.59 t (1H, *J* = 7.4 Hz), 7.54 d (0.23 H, *J* = 15.7 Hz), 7.51 t (2H, *J* = 7.5 Hz), 7.45-7.41 m (3H). ^{13}C NMR (125 MHz, $CDCl_3$): 122.0 t (CD, *J* = 24 Hz), 122.3 (CH), 128.60, 128.64, 128.8, 129.1, 130.7, 132.9, 135.1, 138.4, 144.9, 190.7. APCI-HRMS calcd. for $[M+H]^+$ $C_{15}H_{12}OD^+$ – 210.1024, found 210.1022. NMR spectra are in agreement with literature data.[48]

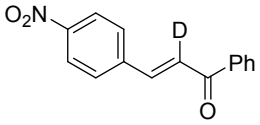
(EZ)-3-Phenylacrylonitrile-2-*d* (J-*d*)



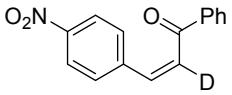
Reaction time – 24 h, 0.05 eq 9,10-dicyanoanthracene (**P2**)**.** Eluent for chromatography – hexane-EtOAc 4:1. Yield 92% (12 mg), 97%D, 1:1.78 *(E/Z)*. ^1H NMR (500 MHz, $CDCl_3$): 7.83-7.79 m (2H, *E*-isomer), 7.47-7.44 m (4.55H), 7.44-7.42 m (1.28 H), 7.42-7.39 m (1.18H), 7.13 t (1H, *J* = 1.7 Hz, *E*-isomer). Visible signals of non-deuterated 3-phenylacrylonitrile were determined as 5.88 d (0.021H, *J* = 16.7 Hz, *E*-isomer), 5.45 d (0.034H, *J* = 12 Hz, *Z*-isomer). ^{13}C NMR (125 MHz, $CDCl_3$): 95.0 t (CD, *J* = 26.8 Hz), 95.3 (non-deuterated CH), 96.3 t (CD, *J* = 26.1 Hz), 117.5, 118.2, 127.5, 129.07, 129.15, 129.3, 131.1, 131.3, 148.7, 150.6. APCI-HRMS calcd. for $[M+H]^+$ $C_9H_7ND^+$ – 131.0714, found 131.0711. NMR spectra are in agreement with literature data.[49]

(E) and (Z)-3-(4-nitrophenyl)-1-phenylprop-2-en-1-one-2-*d* (K-*d*)

Reaction time – 16 h, 0.05 eq 9,10-dicyanoanthracene (**P2**), conversion 86%**.** Eluent for chromatography – hexane-EtOAc 6:1. After chromatography and evaporation of the fraction in vacuum obtained as a mixture with unreacted **K-Br**. **K-Br** was washed out by Et_2O (2 x 0.75 ml), dried in vacuum. Total yield calculated to consumed starting compound 85% (24 mg), *E*/*Z* = 1:2, (*E*)- and (*Z*)-isomers were separated.

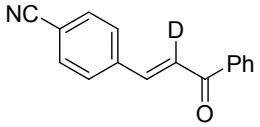


. **65%D.** ^{1}H NMR (500 MHz, $CDCl_3$): 8.28 d (2H, *J* = 8.8 Hz), 8.04 d (2H, *J* = 8.3 Hz), 7.79 m (3H), 7.61-7.67 m (1.35H), 7.54 t (2H, *J* = 7.6 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): 124.4, 125.6 t (CD, *J* = 24 Hz), 125.9 (CH), 128.7, 128.98, 129.08, 133.5, 137.7, 141.57, 141.65, 148.7, 189.8. ESI-HRMS calcd. for $[M+H]^+$ $C_{15}H_{11}DNO_3^+$ - 255.0874, found 255.0874.



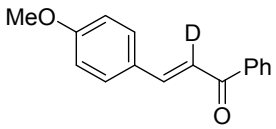
After chromatography and evaporation of the fraction in vacuum extracted from the residue by 2:1 pentane-Et_2O mixture (2 x 0.75 ml), residue dried in vacuum. **89%D.** ^{1}H NMR (500 MHz, $CDCl_3$): 8.10 d (2H, *J* = 8.8 Hz), 7.96 d (2H, *J* = 8.4 Hz), 7.52-7.60 m (3H), 7.52 t (2H, *J* = 7.7 Hz), 7.06 m (1H), 6.87 d (0.011H, *J* = 12.8 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): 123.6, 128.9, 129.1, 129.9 t (CD, *J* = 24.5 Hz), 130.06 (CH), 130.09, 133.9, 136.8, 137.1, 141.8, 147.6, 193.5. ESI-HRMS calcd. for $[M+H]^+$ $C_{15}H_{11}DNO_3^+$ - 255.0874, found 255.0874.

(E)-4-(3-oxo-3-phenylprop-1-en-1-yl-2-*d*)benzonitrile (L-*d*)



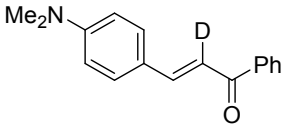
Reaction time – 24 h, 0.05 eq 9,10-dicyanoanthracene (**P2**), conversion 75%**.** Eluent for chromatography – hexane-EtOAc 6:1. After chromatography and evaporation of the fraction in vacuum obtained as a mixture with unreacted **L-Br**. **L-Br** was washed out by pentane-Et_2O (4 x 0.75 ml), residue dried in vacuum. Total yield calculated to consumed starting compound 89% (20 mg), *E*/*Z* = 9:1.**71%D.** ^{1}H NMR (500 MHz, $CDCl_3$): 8.02 d (2H, *J* = 8.8 Hz), 7.77 d (0.29H, *J* = 15.7 Hz), 7.77 m (0.71H), 7.67-7.76 m (4H), 7.61 t (1H, *J* = 7.4 Hz), 7.60 d (0.29H, *J* = 15.7 Hz), 7.52 t (2H, *J* = 7.6 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): 113.7, 118.5, 124.9 t (CD, *J* = 24 Hz), 125.3 (CH), 128.70, 128.84, 128.94, 132.8, 133.4, 137.8, 139.4, 142.1, 189.9. ESI-HRMS calcd. for $[M+H]^+$ $C_{16}H_{11}DNO^+$ - 235.0976, found 235.0976. NMR spectra are in agreement with literature data.[50]

(E)-3-(4-methoxyphenyl)-1-phenylprop-2-en-1-one-2-*d* (M-*d*)



Reaction time – 24 h, 0.05 eq 9,10-dicyanoanthracene (**P2**)**.** Eluent for chromatography – hexane-EtOAc 6:1. Total yield 68% (21 mg), pure E-isomer, **87%D**. ^{1}H NMR (500 MHz, CDCl3): 8.00 d (2H, *J* = 8.4 Hz), 7.81 d (0.13H, *J* = 15.6 Hz), 7.78 m (0.87H), 7.60 d (2H, *J* = 8.9 Hz), 7.57 t (1H, *J* = 7.4 Hz), 7.49 t (2H, *J* = 7.5 Hz), 7.41 d (0.13H, *J* = 15.6 Hz), 6.94 d (2H, *J* = 8.8 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): 55.6, 114.6, 119.7 t (CD, *J* = 24 Hz), 120.0 (CH), 128.5, 128.54, 128.70, 130.4, 132.1, 138.7, 144.7, 161.8, 190.7. ESI-HRMS calcd. for $[M+H]^+$ $C_{16}H_{14}DO_2^+$ - 240.1129, found 240.1128. NMR spectra are in agreement with literature data.[51]

(E)-3-(4-(dimethylamino)phenyl)-1-phenylprop-2-en-1-one-2-*d* (N-*d*)



Reaction time – 24 h, 0.05 eq 9,10-dicyanoanthracene (**P2**)**.** Eluent for chromatography – hexane-EtOAc 6:1. Total yield 24% (8 mg), pure E-isomer, **85%D**. ^{1}H NMR (500 MHz, CDCl3): 8.00 d (2H, *J* = 7 Hz), 7.79 m (1H), 7.55 m (3H), 7.48 t (2H, *J* = 7.4 Hz), 7.33 d (0.147H, *J* = 15.5 Hz), 6.70 d (2H, *J* = 8.9 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): 40.3, 112.0, 116.9 t (CD, *J* = 23.8 Hz), 117.2 (CH), 122.8, 128.46, 128.59, 130.6, 132.2, 139.2, 145.9, 152.2, 190.8. ESI-HRMS calcd. for $[M+H]^+$ $C_{17}H_{17}DNO^+$ - 253.1446, found 253.1445.

8) NMR spectra of reaction mixtures for conversion and D-enrichment determination

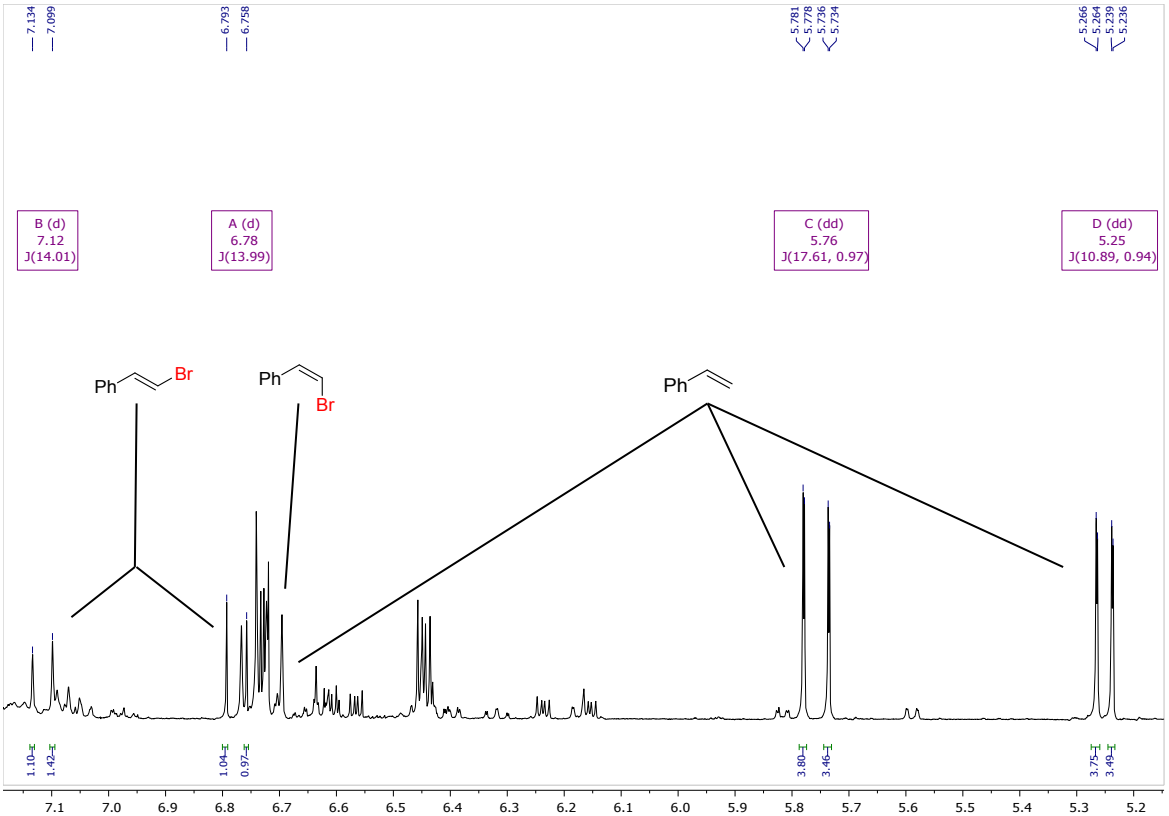


Fig.9 Spectrum of reaction mixture of **A-Br** + 2 eq **2**, 2x8h, 2x0.05 eq **P2** (500 MHz, $CDCl_3$).

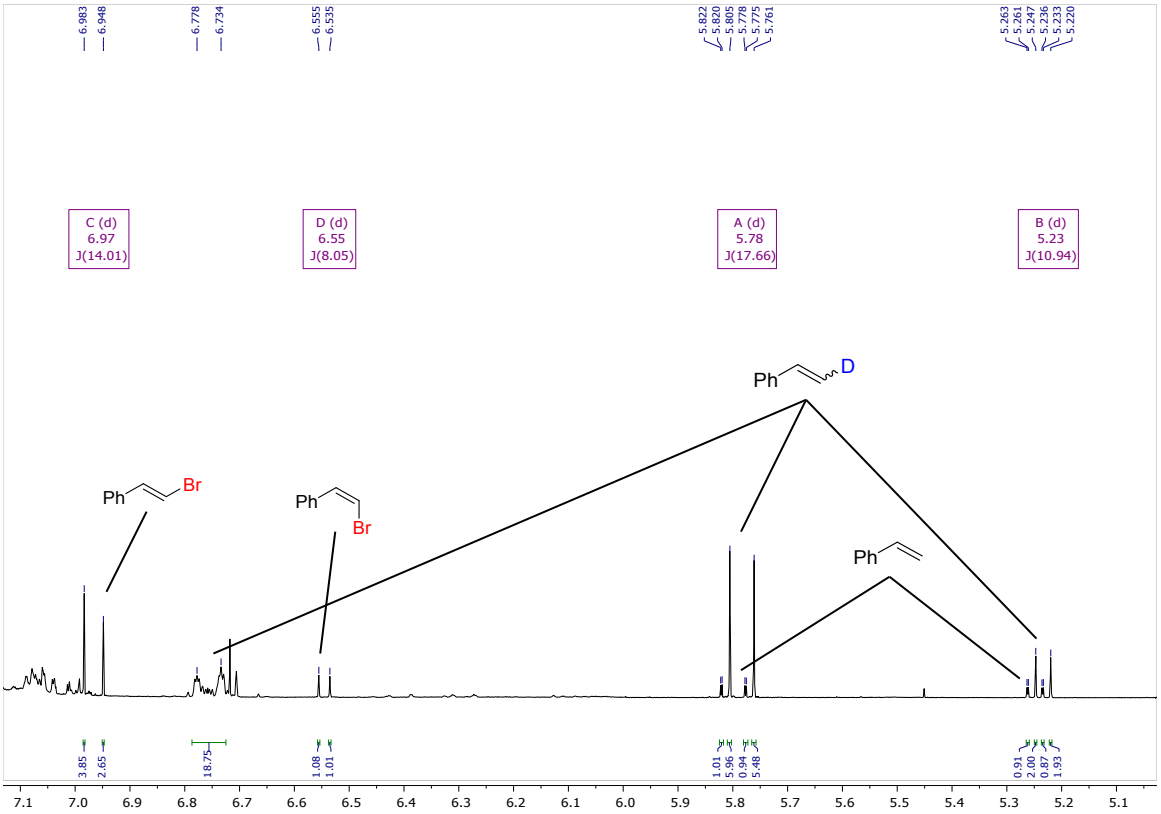


Fig.10 Spectrum of reaction mixture of **A-Br** + 1.7 eq **2-d_{11}**, 3x24h, 3x0.05 eq **P2** (500 MHz, CD_3CN).

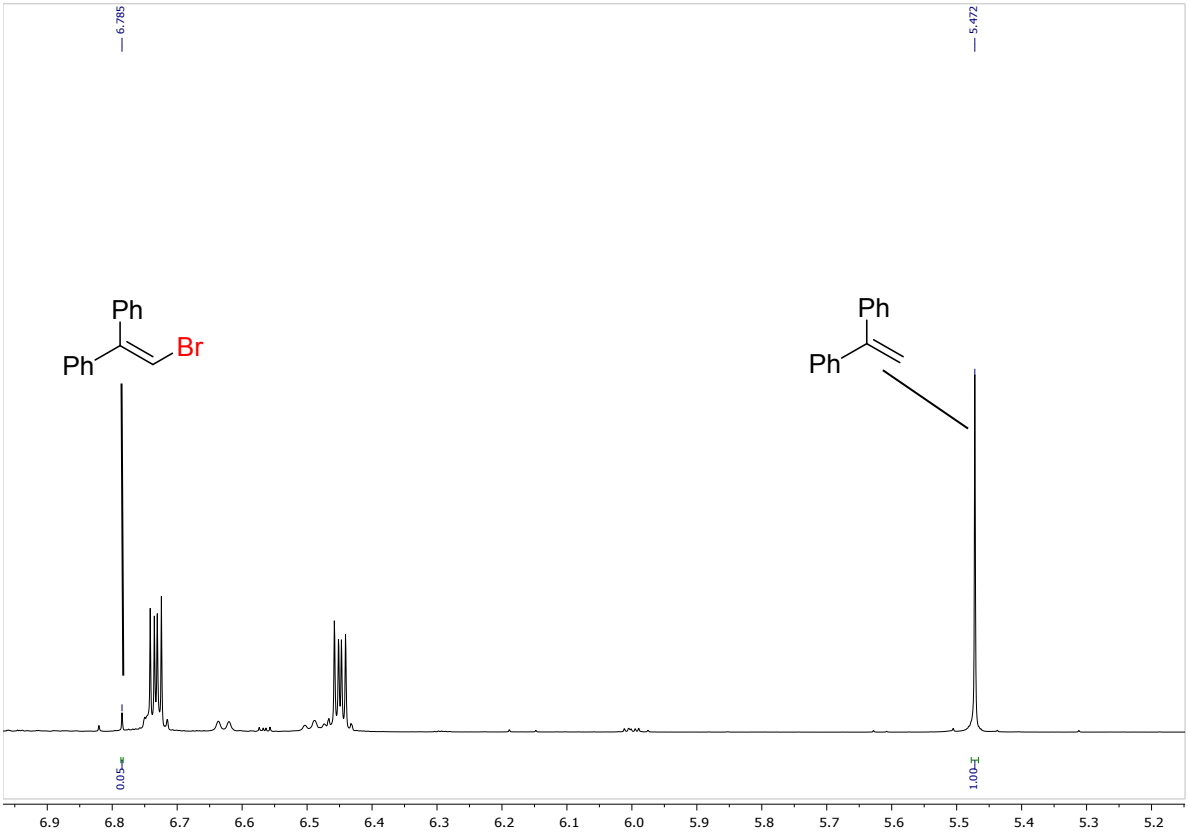


Fig.11 Spectrum of reaction mixture of **B-Br** + 2 eq **2**, 16h, 0.05 eq **P2** (500 MHz, $CDCl_3$).

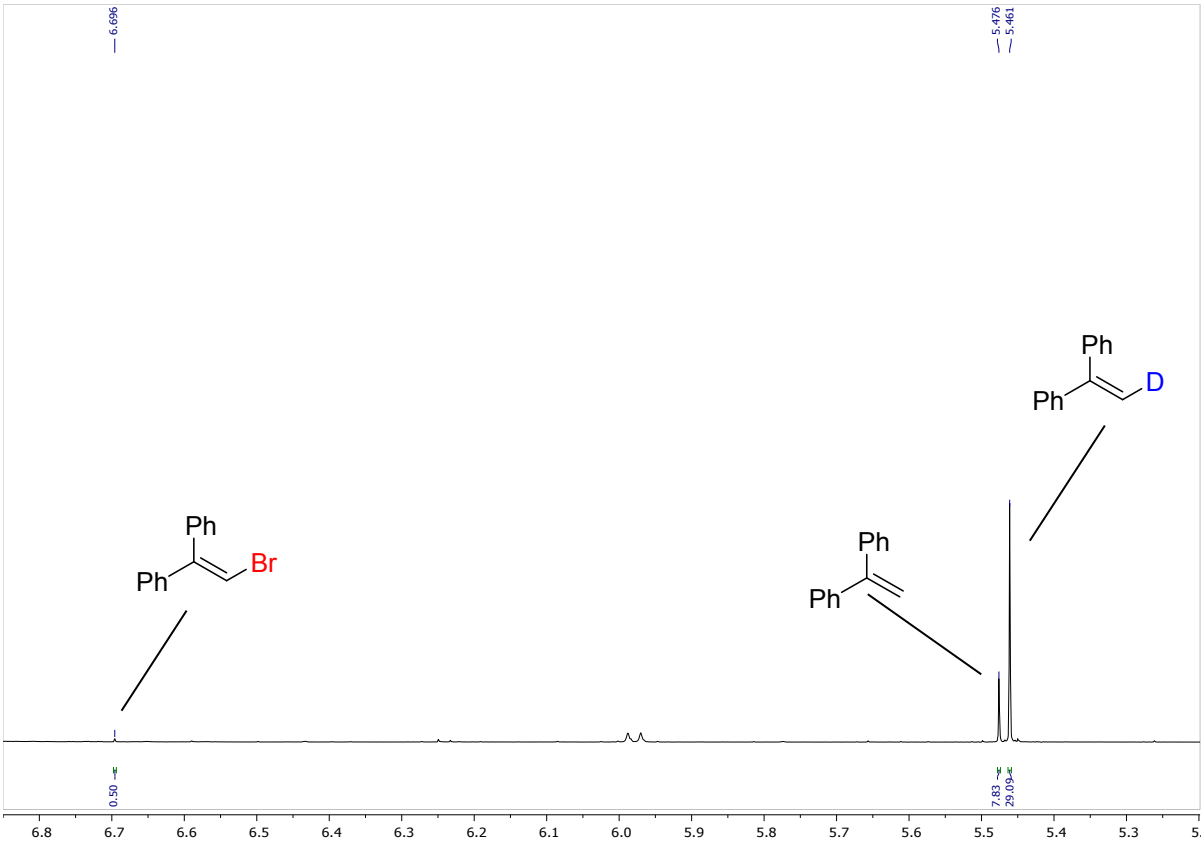


Fig.12 Spectrum of reaction mixture of **B-Br** + 1.7 eq **2-d_{11}**, 48h, 0.05 eq **P2** (500 MHz, CD_3CN).

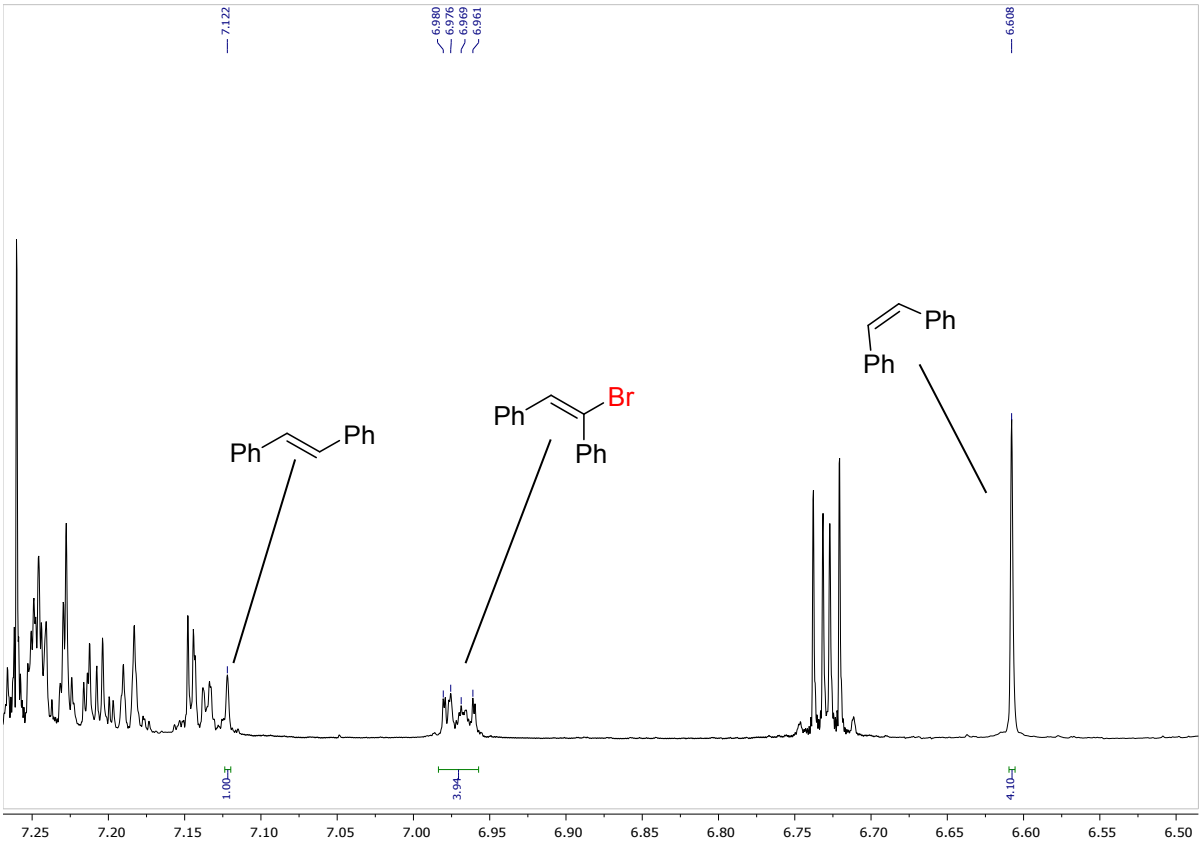


Fig.13 Spectrum of reaction mixture of **(E)-C-Br** + 2 eq **2**, 4h, 0.05 eq **P2** (500 MHz, $CDCl_3$).

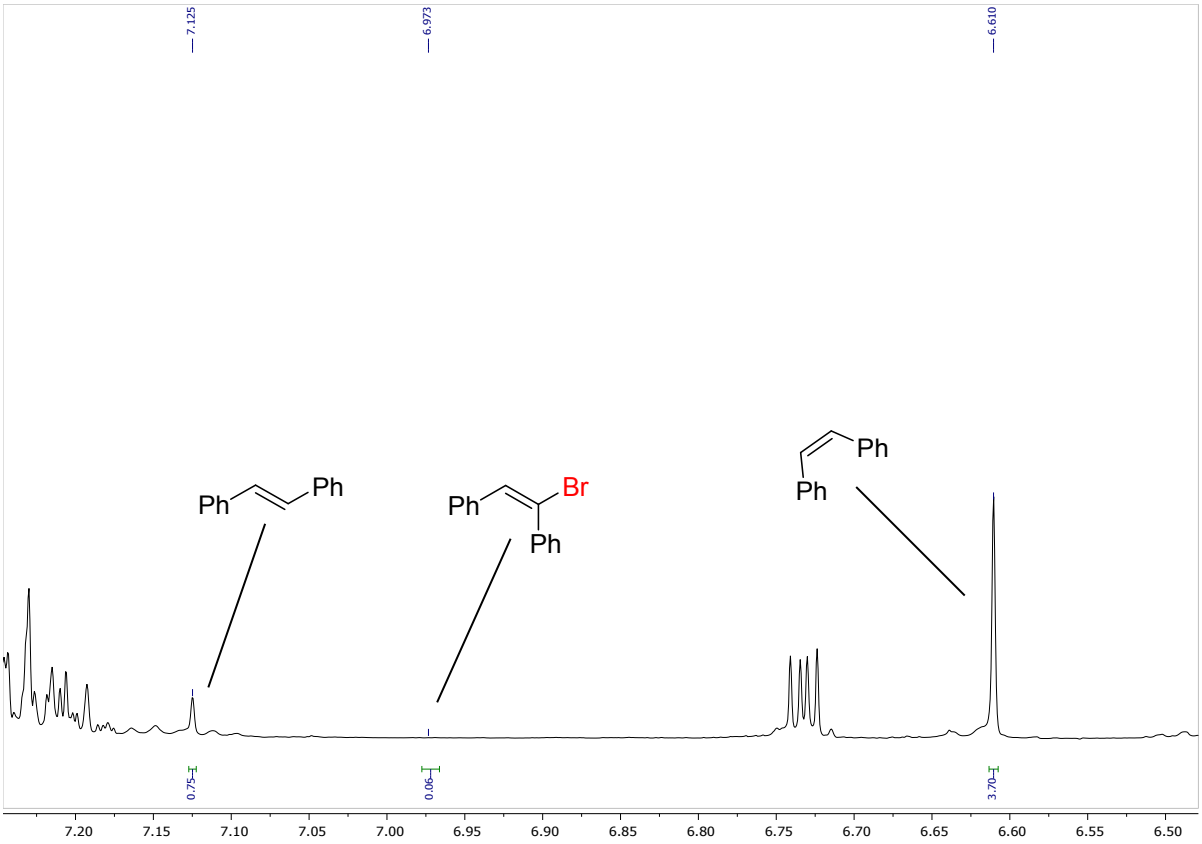


Fig.14 Spectrum of reaction mixture of **(E)-C-Br** + 2 eq **2**, 16h, 0.05 eq **P2** (500 MHz, $CDCl_3$).

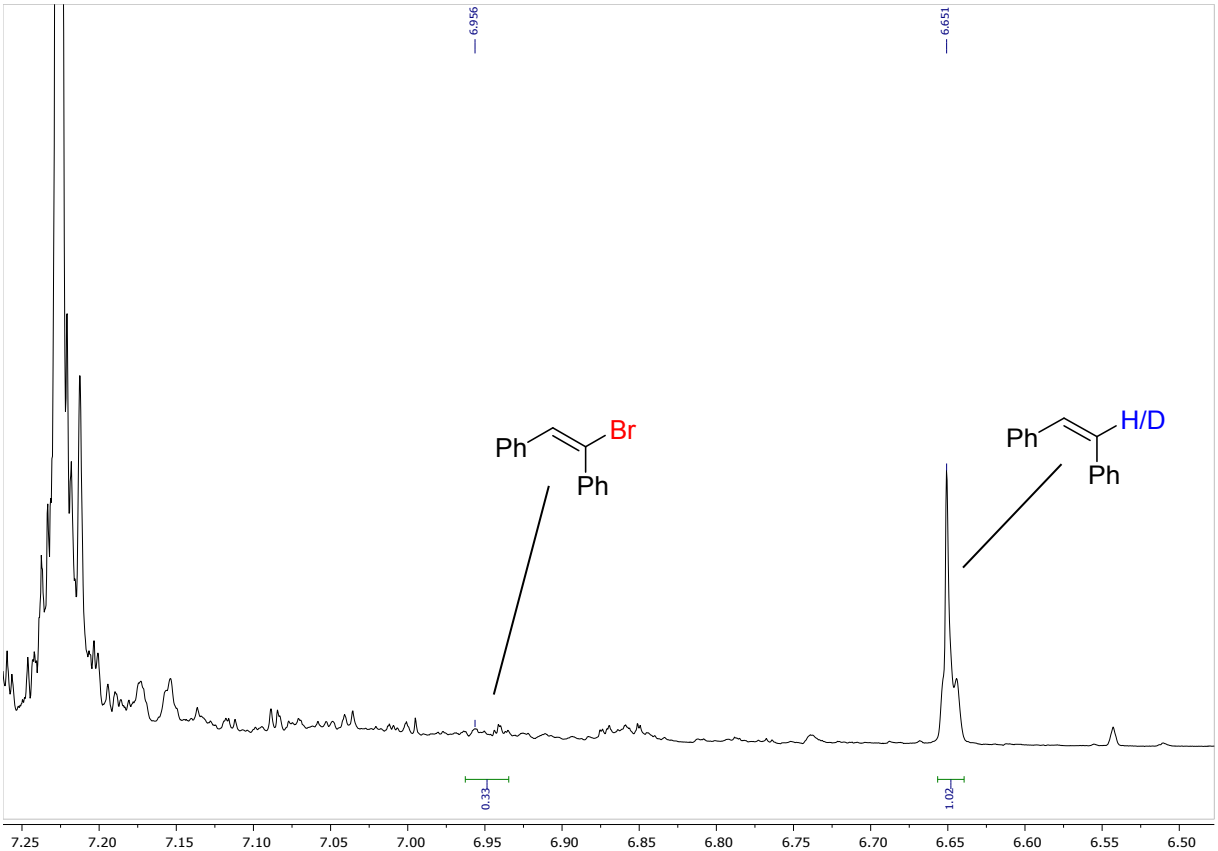


Fig.15 Spectrum of reaction mixture of **(E)-C-Br** + 1.7 eq **2-*d*$_{11}$**, 48h, 0.05 eq **P2** (500 MHz, CD_3CN).

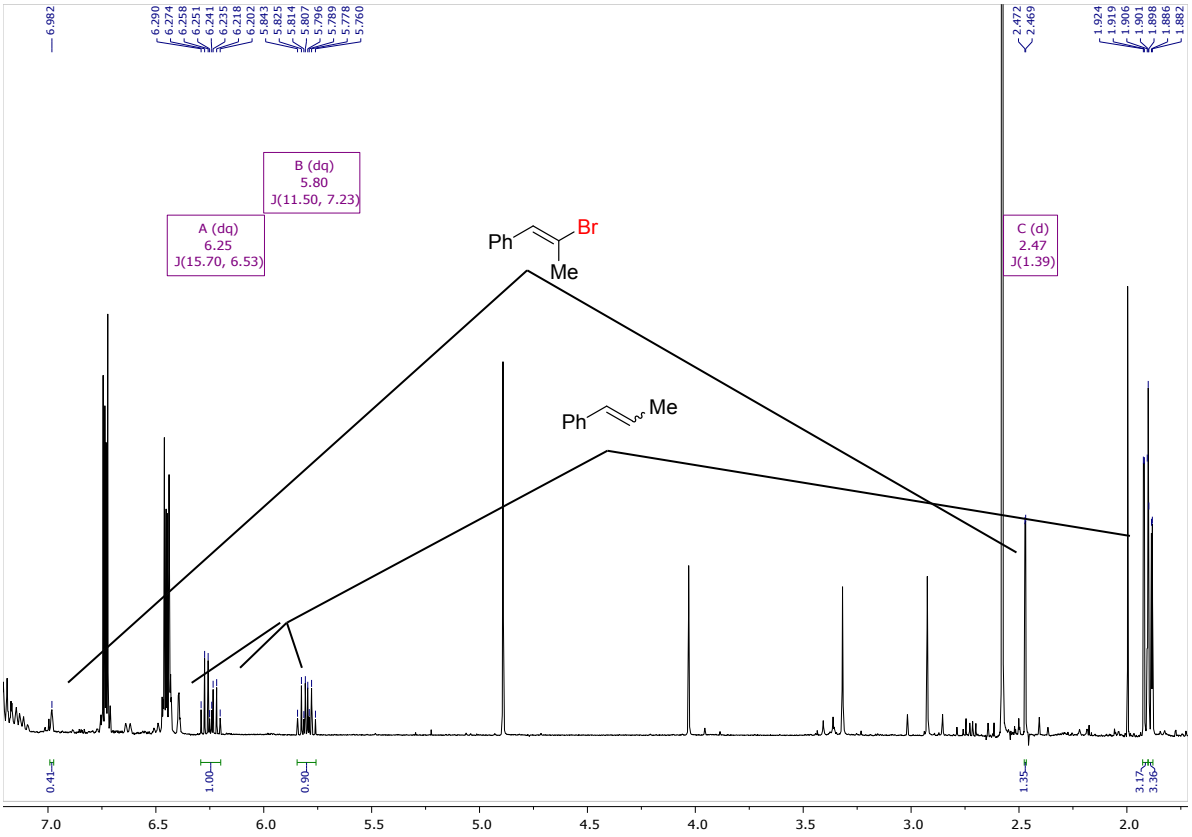


Fig.16 Spectrum of reaction mixture of **D-Br** + 2 eq **2**, 2x16h, 2x0.05 eq **P2** (500 MHz, $CDCl_3$).

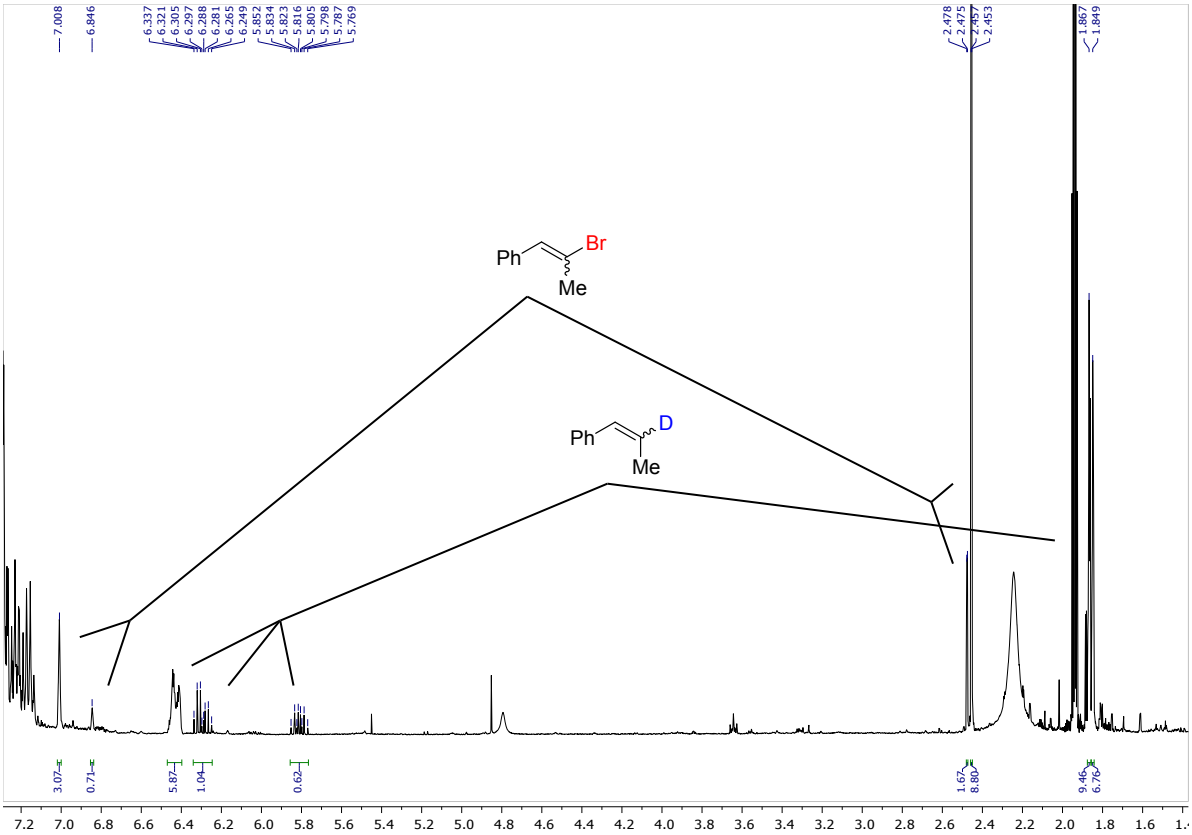


Fig.17 Spectrum of reaction mixture of **D-Br** + 1.7 eq **2-d_{11}**, 3x24h, 3x0.05 eq **P2** (500 MHz, CD_3CN).

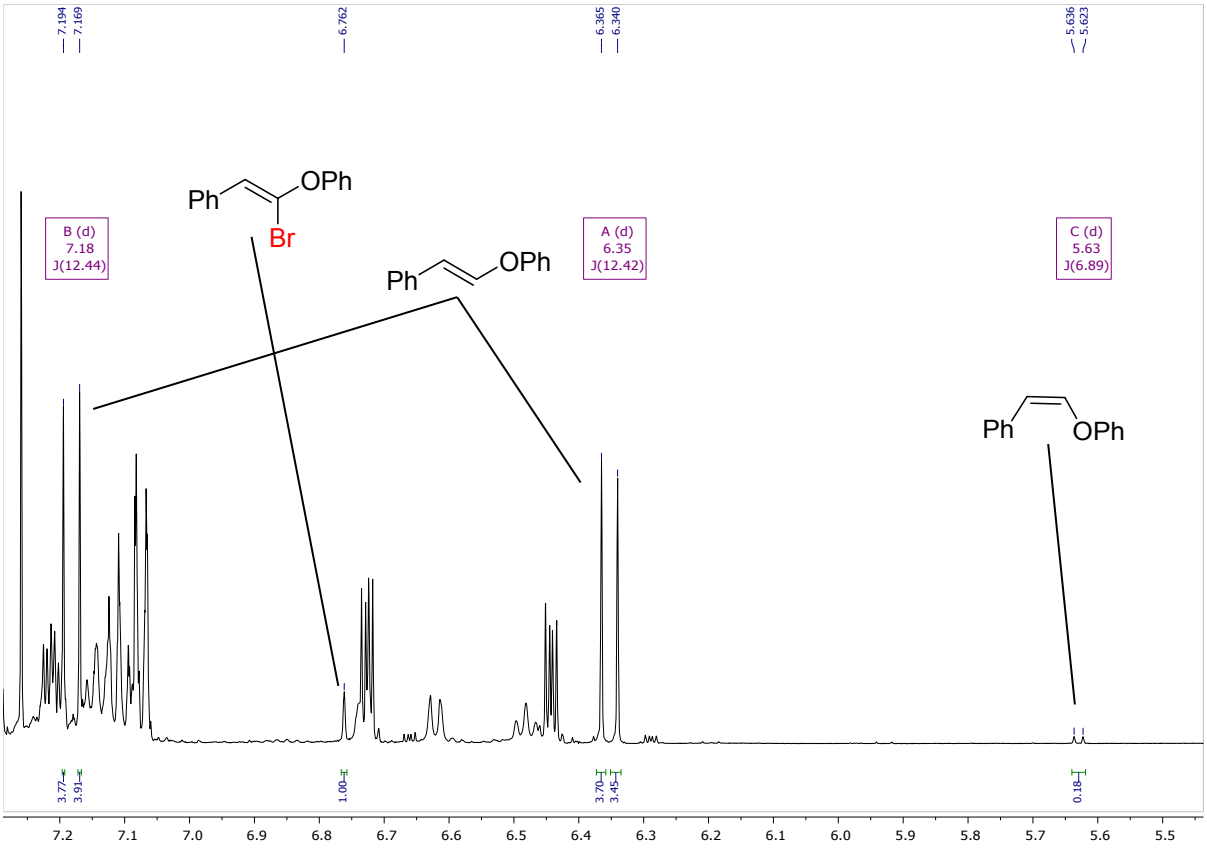


Fig.18 Spectrum of reaction mixture of **(Z)-F-Br** + 2 eq **2**, 24h, 0.05 eq **P2** (500 MHz, $CDCl_3$).

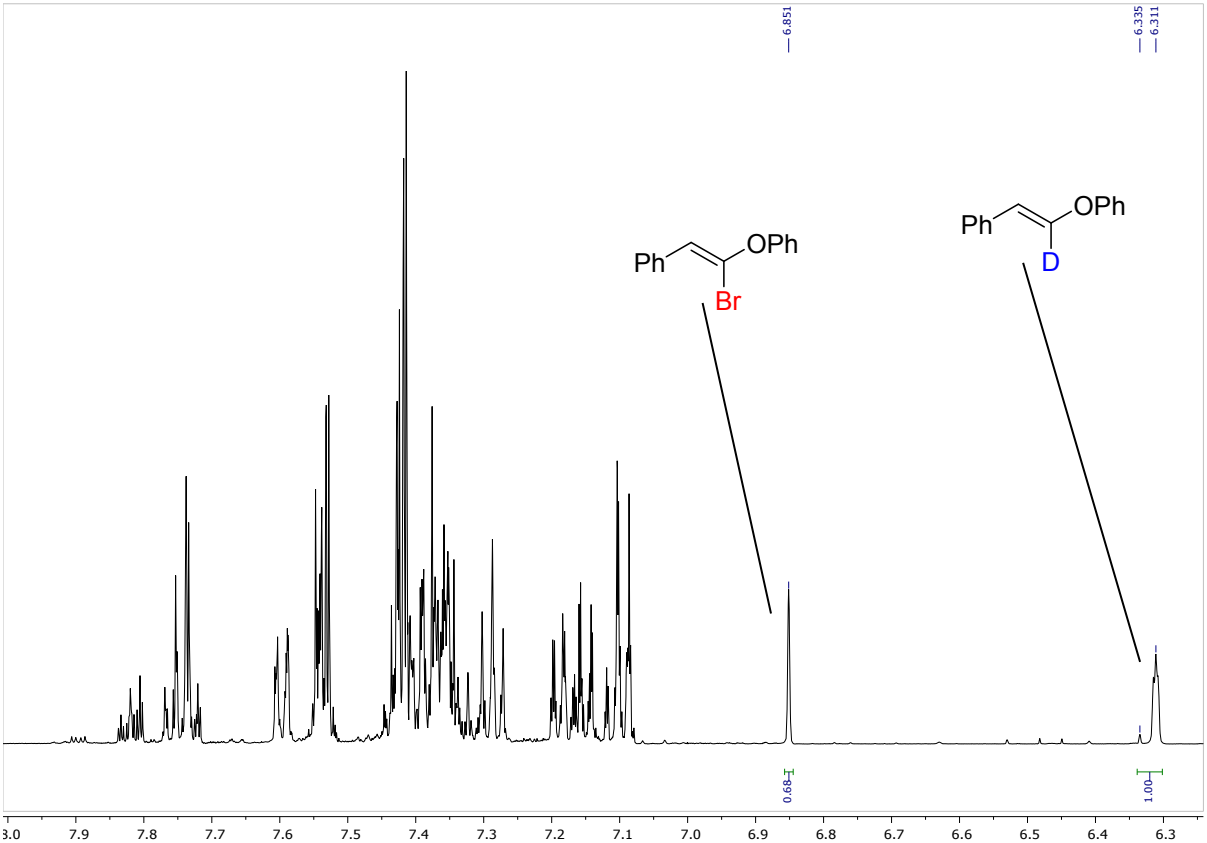


Fig.19 Spectrum of reaction mixture of **(Z)-F-Br** + 1.7 eq **2-*d*$_{11}$**, 24h, 0.05 eq **P2** (500 MHz, CD_3CN).

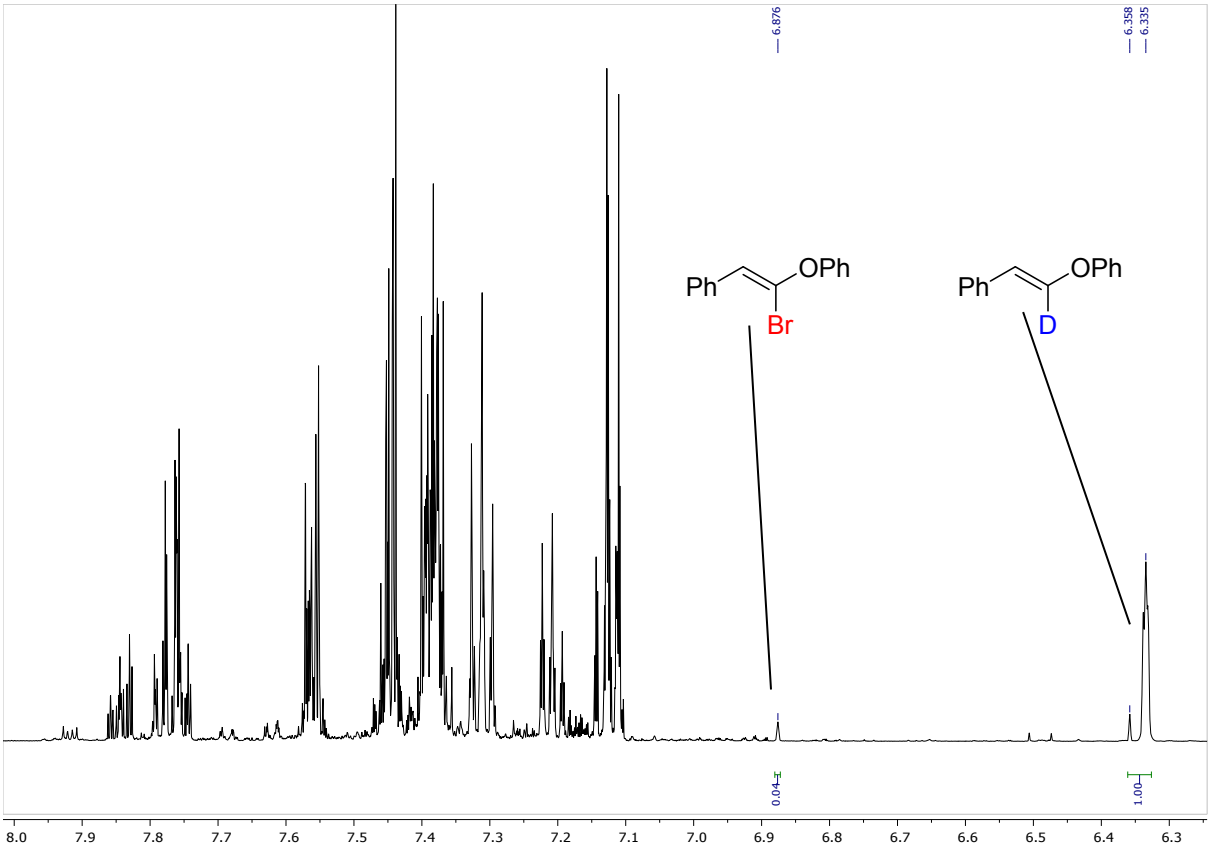


Fig.20 Spectrum of reaction mixture of **(Z)-F-Br** + 1.7 eq **2-*d*$_{11}$**, 2x24h, 2x0.05 eq **P2** (500 MHz, CD_3CN).

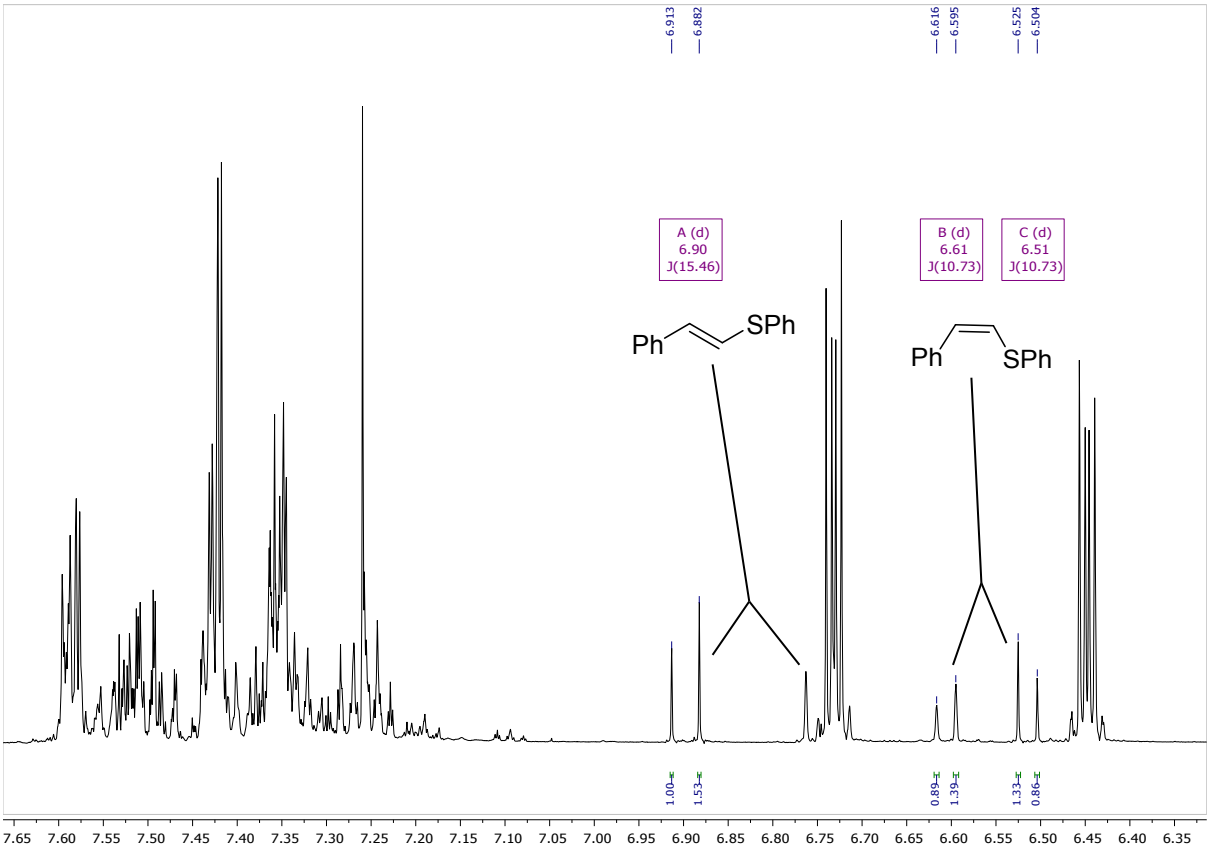


Fig.21 Spectrum of reaction mixture of **G-Br** + 2 eq **2**, 24h, 0.05 eq **P2** (500 MHz, $CDCl_3$).

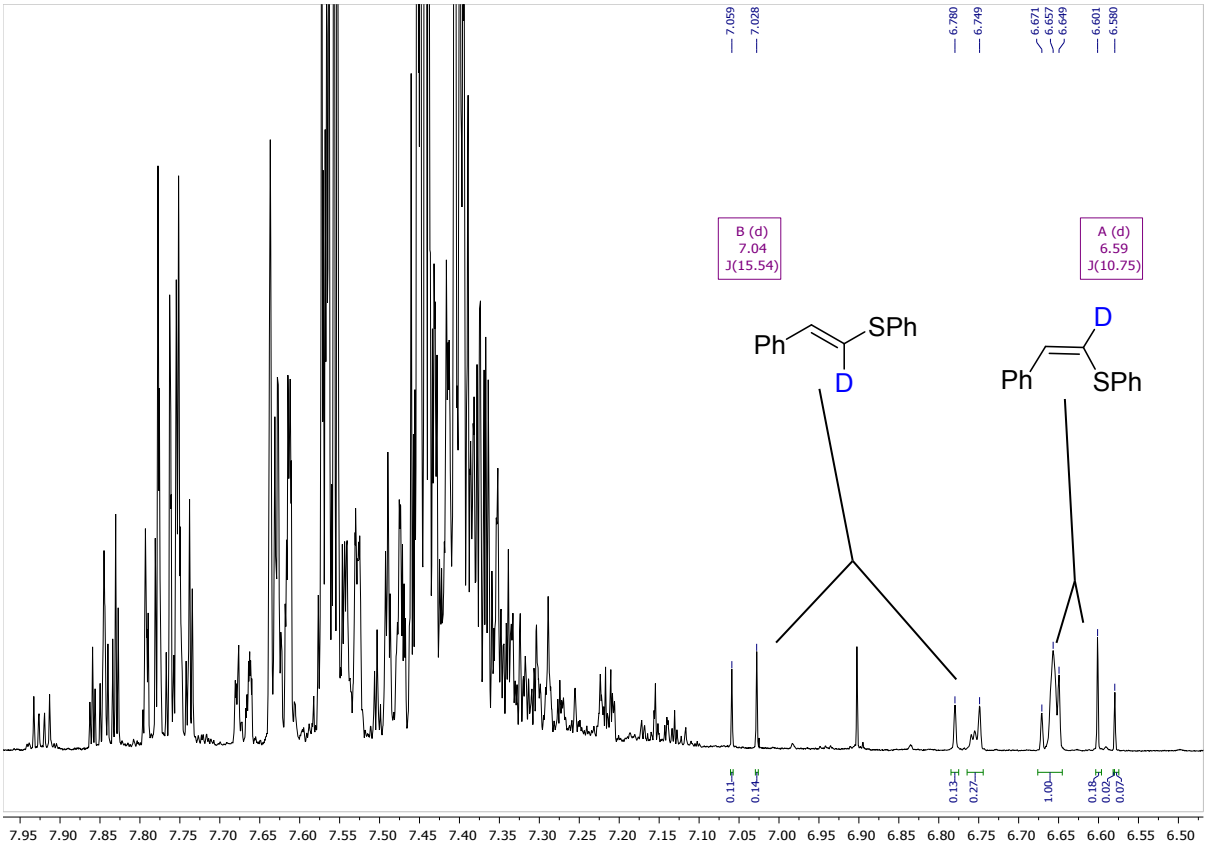


Fig.22 Spectrum of reaction mixture of **G-Br** + 1.7 eq **2-*d*$_{11}$**, 2x24h, 2x0.05 eq **P2** (500 MHz, CD_3CN).

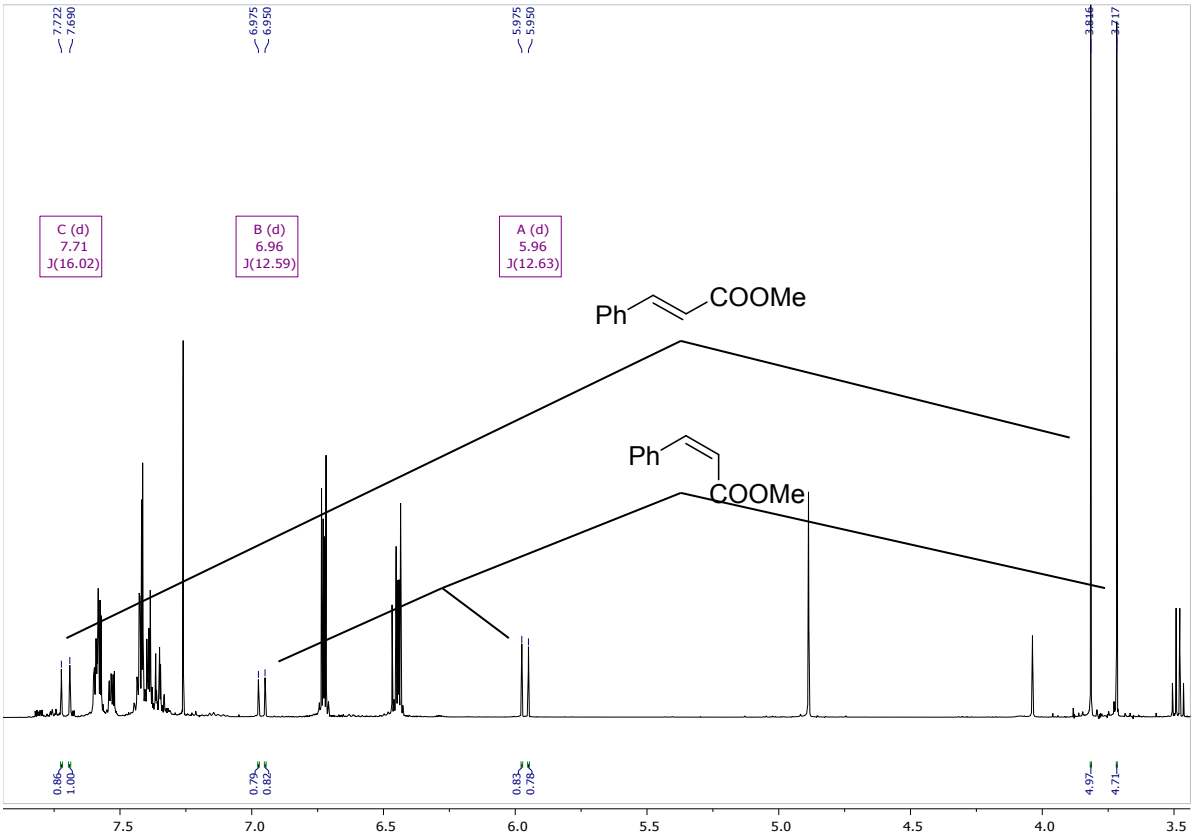


Fig.23 Spectrum of reaction mixture of **H-Br** + 2 eq **2**, 16h, 0.05 eq **P2** (500 MHz, $CDCl_3$).

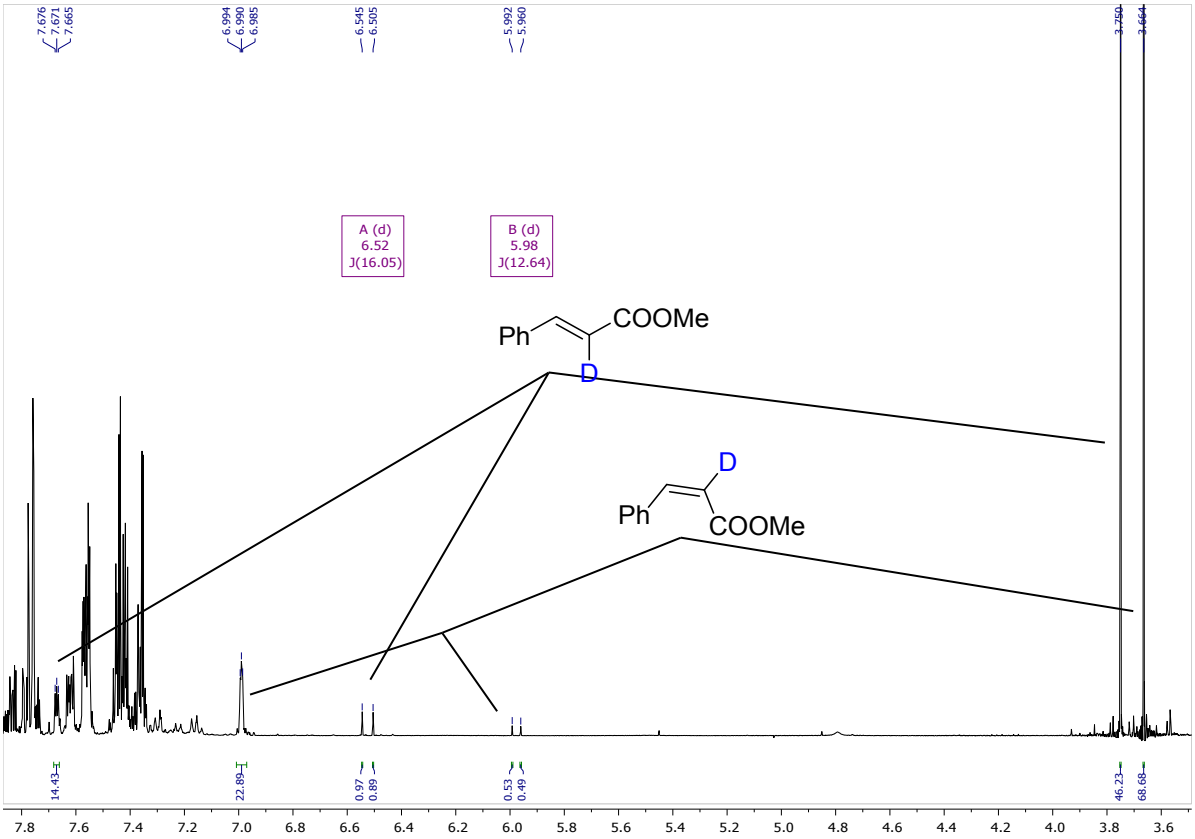


Fig.24 Spectrum of reaction mixture of **H-Br** + 1.7 eq **2-d_{11}**, 48h, 0.05 eq **P2** (500 MHz, CD_3CN).

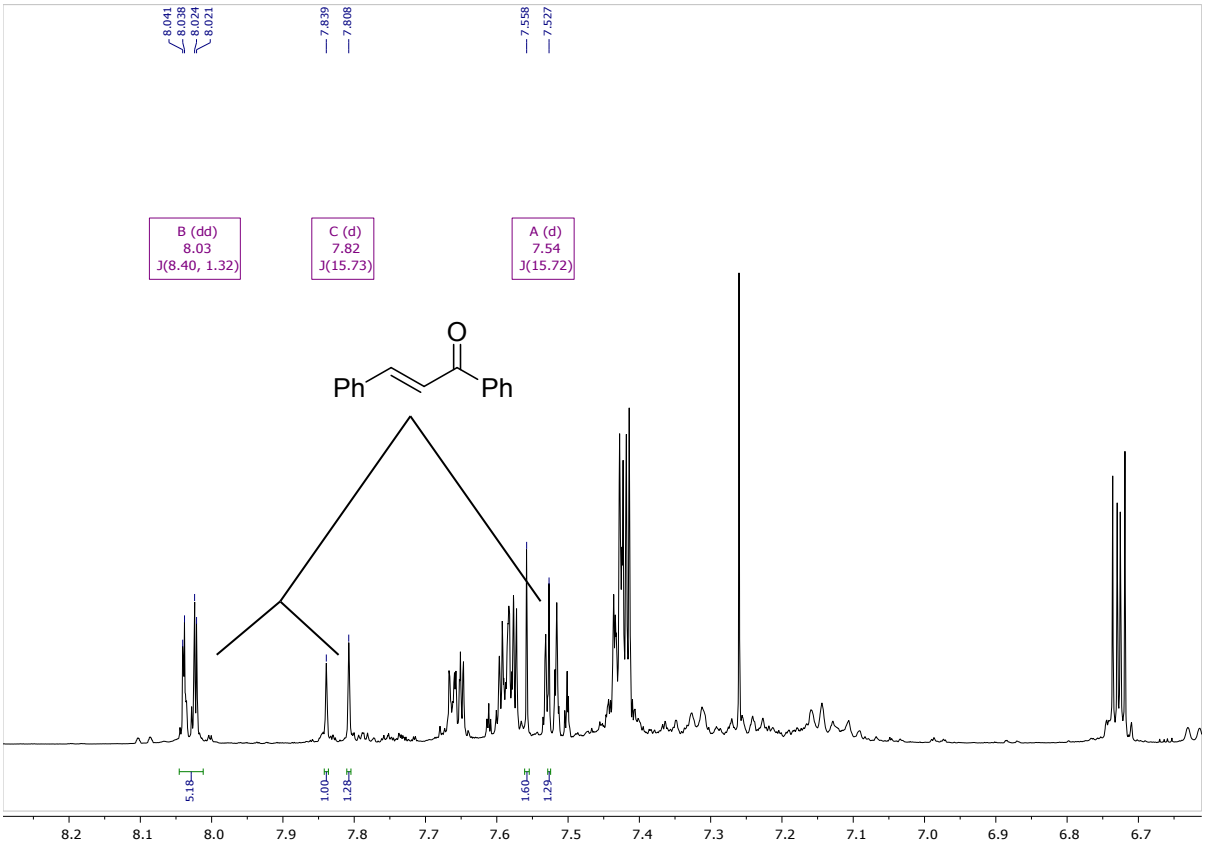


Fig.25 Spectrum of reaction mixture of **I-Br** + 2 eq **2**, 16h, 0.05 eq **P2** (500 MHz, $CDCl_3$).

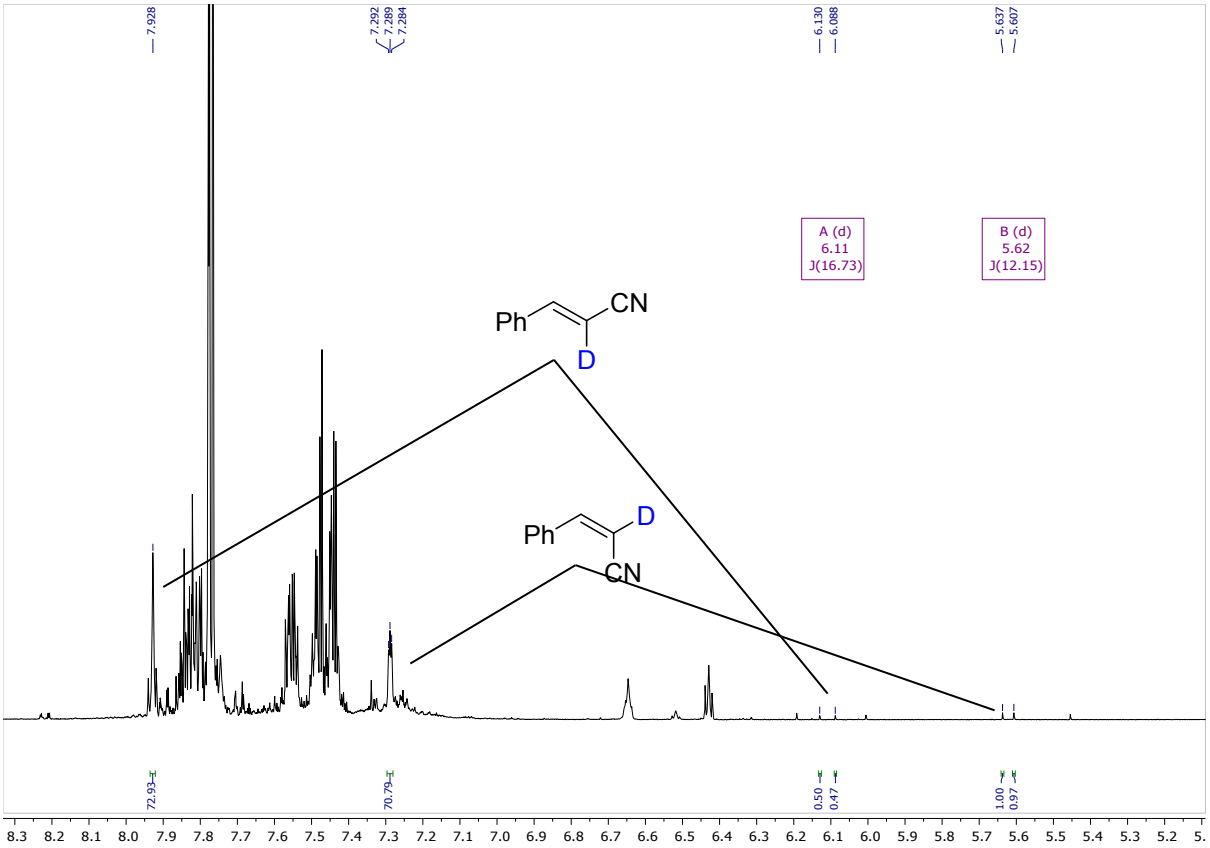


Fig.26 Spectrum of reaction mixture of **J-Br** + 1.5 eq **2-*d*$_{11}$**, 48h, 0.05 eq **P2** (500 MHz, CD_3CN).

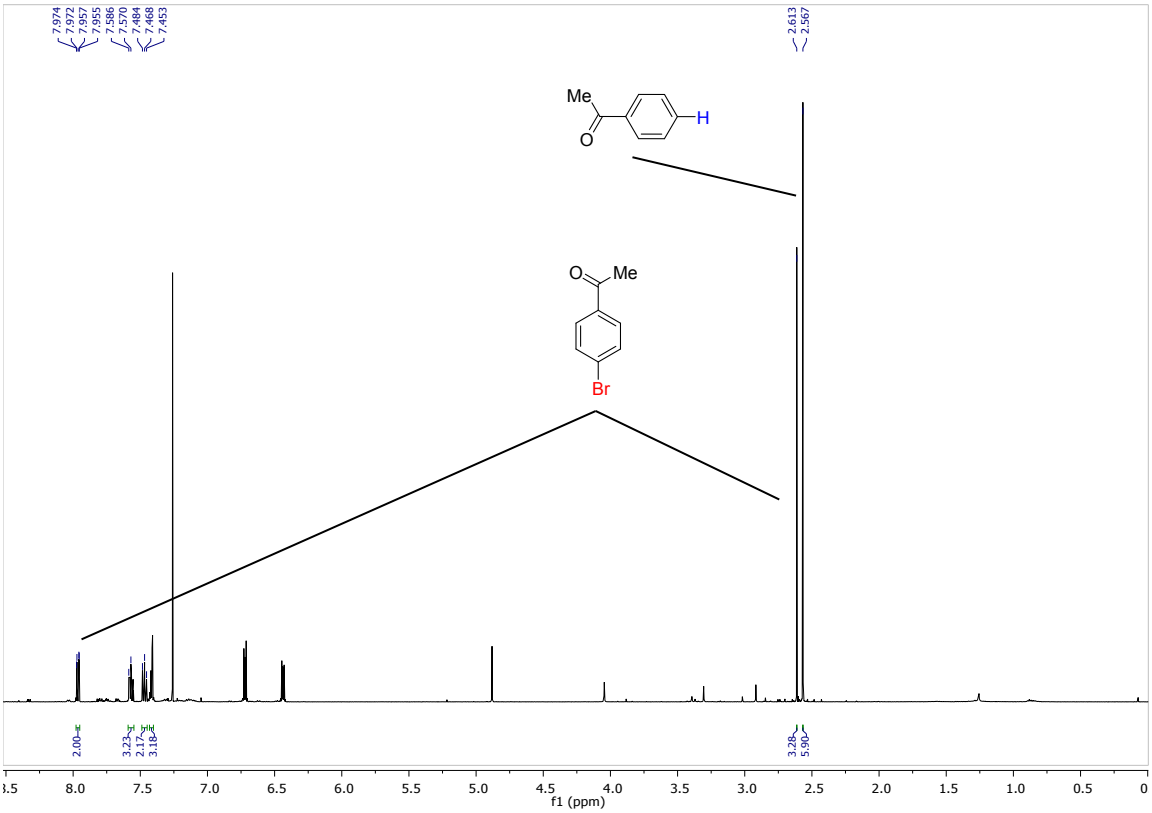


Fig.27 Spectrum of reaction mixture of **4-Br-acetophenone** + 2 eq **2**, 16h, 0.05 eq **P2** (500 MHz, $CDCl_3$).

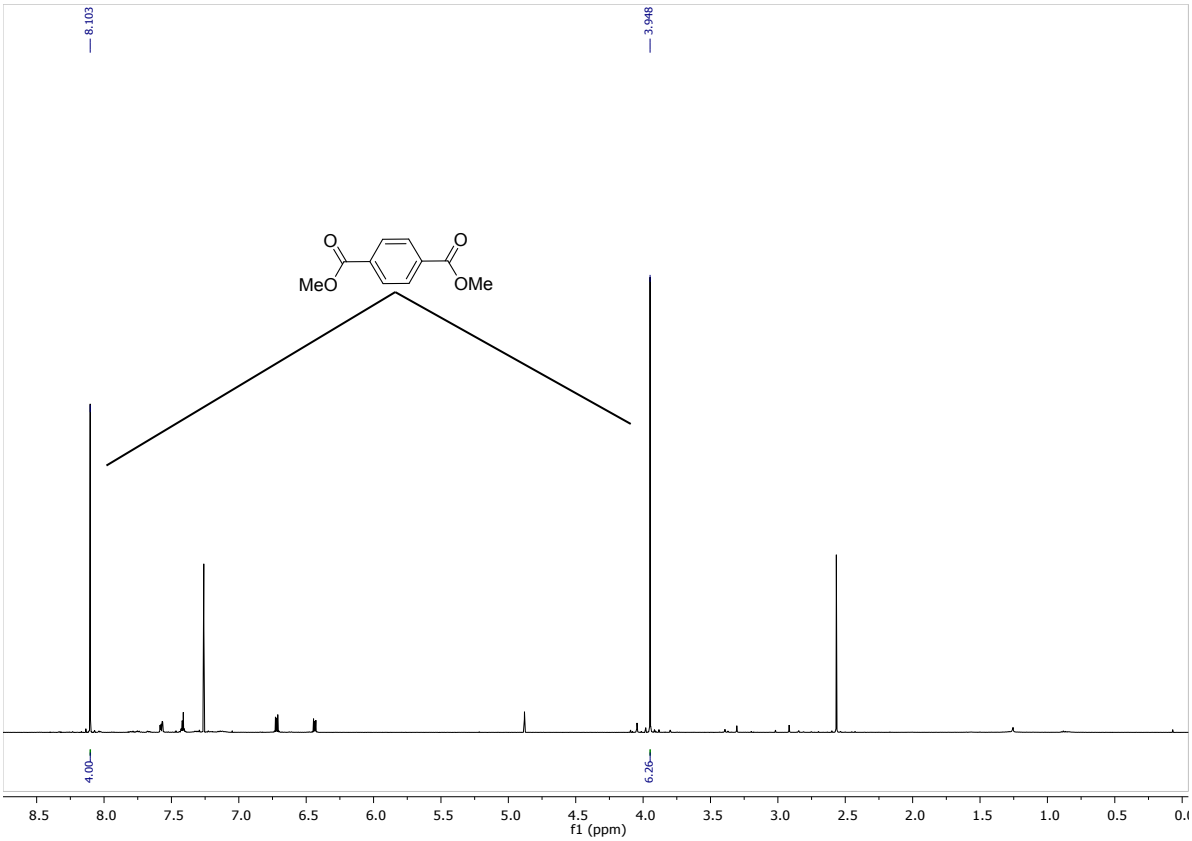


Fig.28 Spectrum of reaction mixture of **dimethyl 2-Br-terephthalate** + 2 eq **2**, 16h, 0.05 eq **P2** (500 MHz, $CDCl_3$).

9) NMR spectra of pure compounds

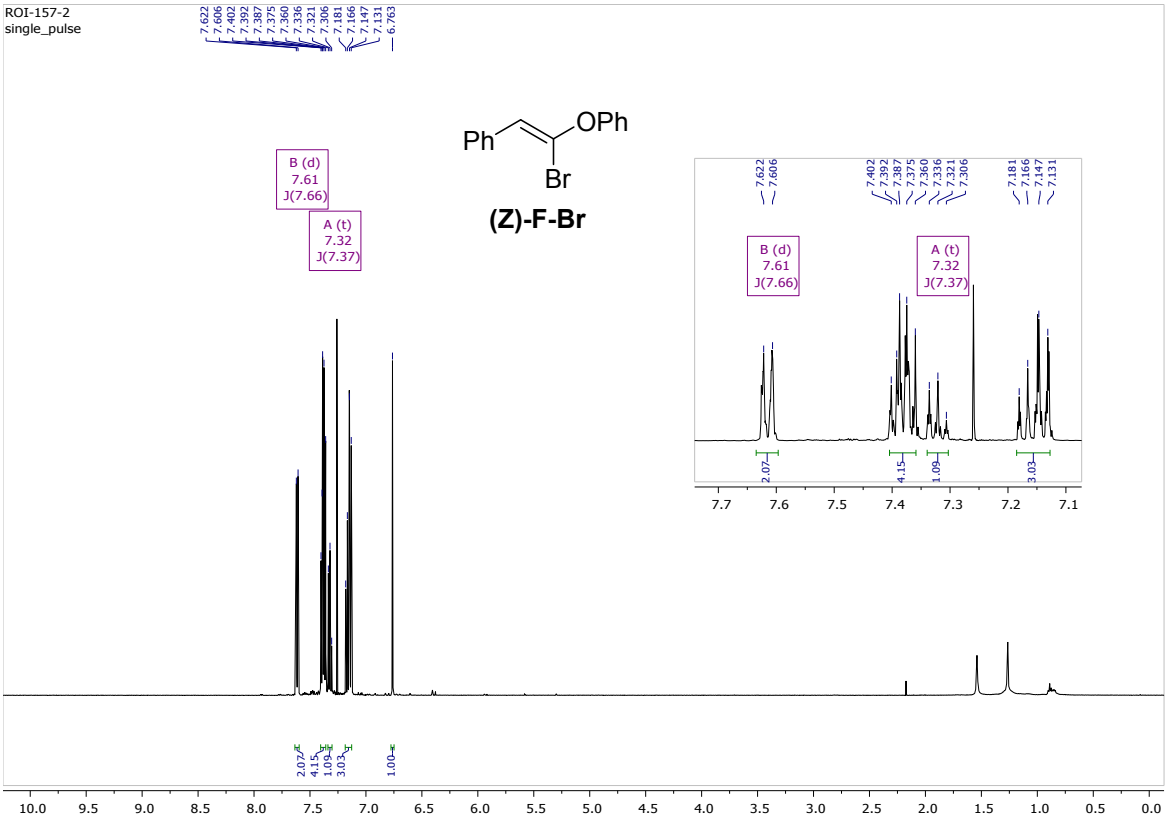


Fig. 29 ^{1}H NMR spectrum of (*Z*)-**F-Br** (500 MHz, $CDCl_3$).

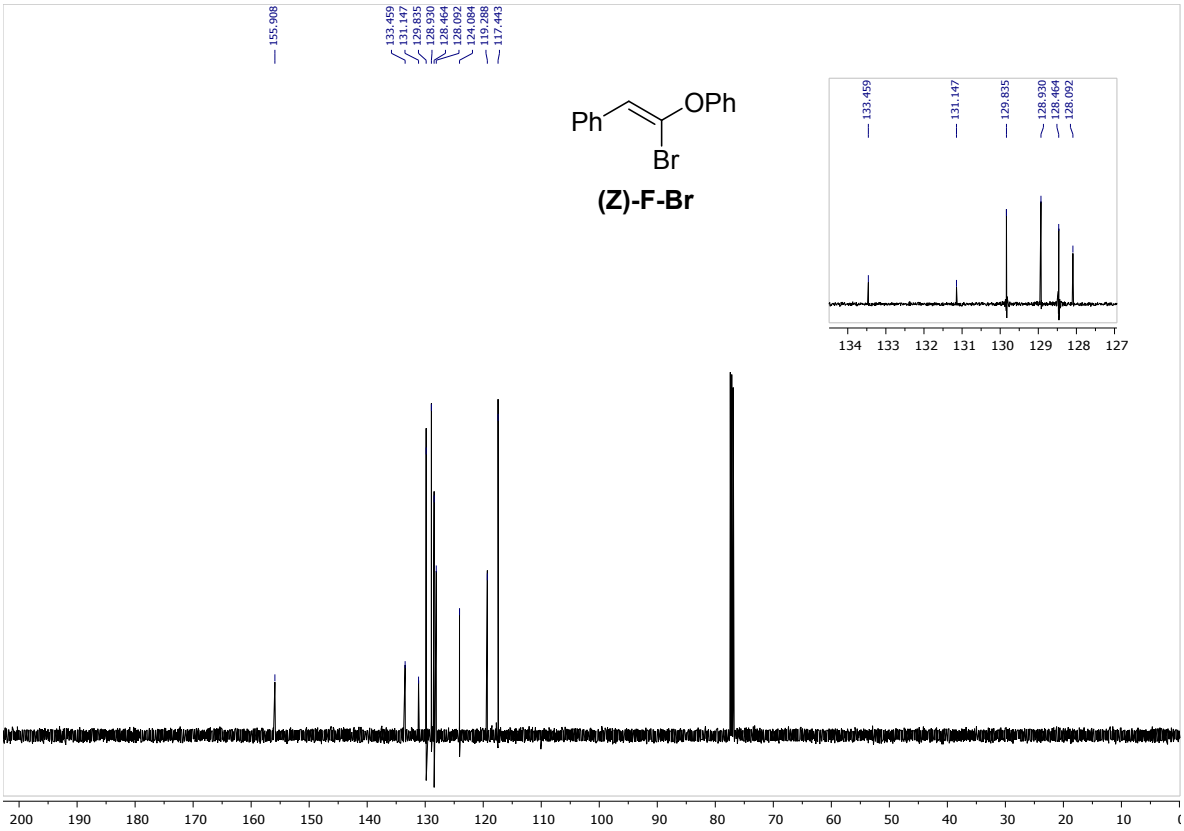


Fig. 30 ^{13}C NMR spectrum of (*Z*)-**F-Br** (125 MHz, $CDCl_3$).

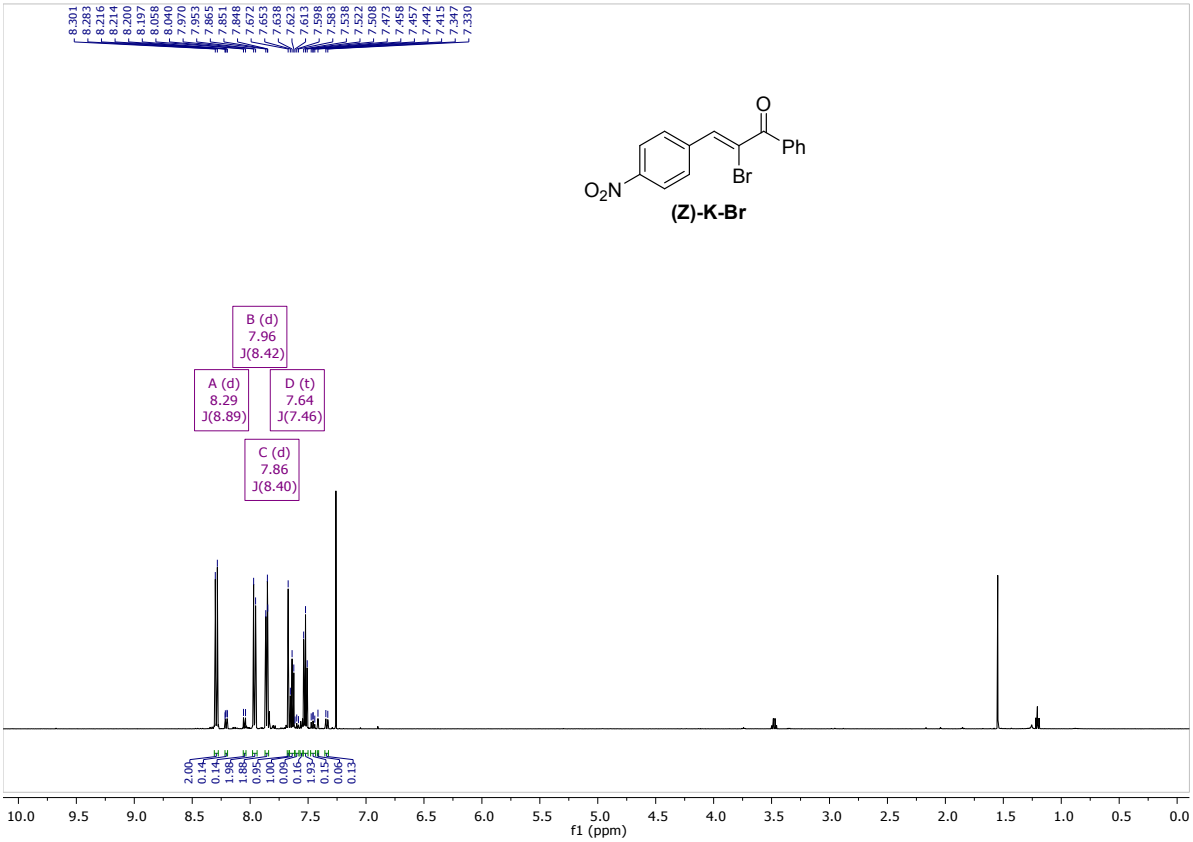


Fig. 31 ^{1}H NMR spectrum of (*Z*)-**K-Br** (500 MHz, $CDCl_3$).

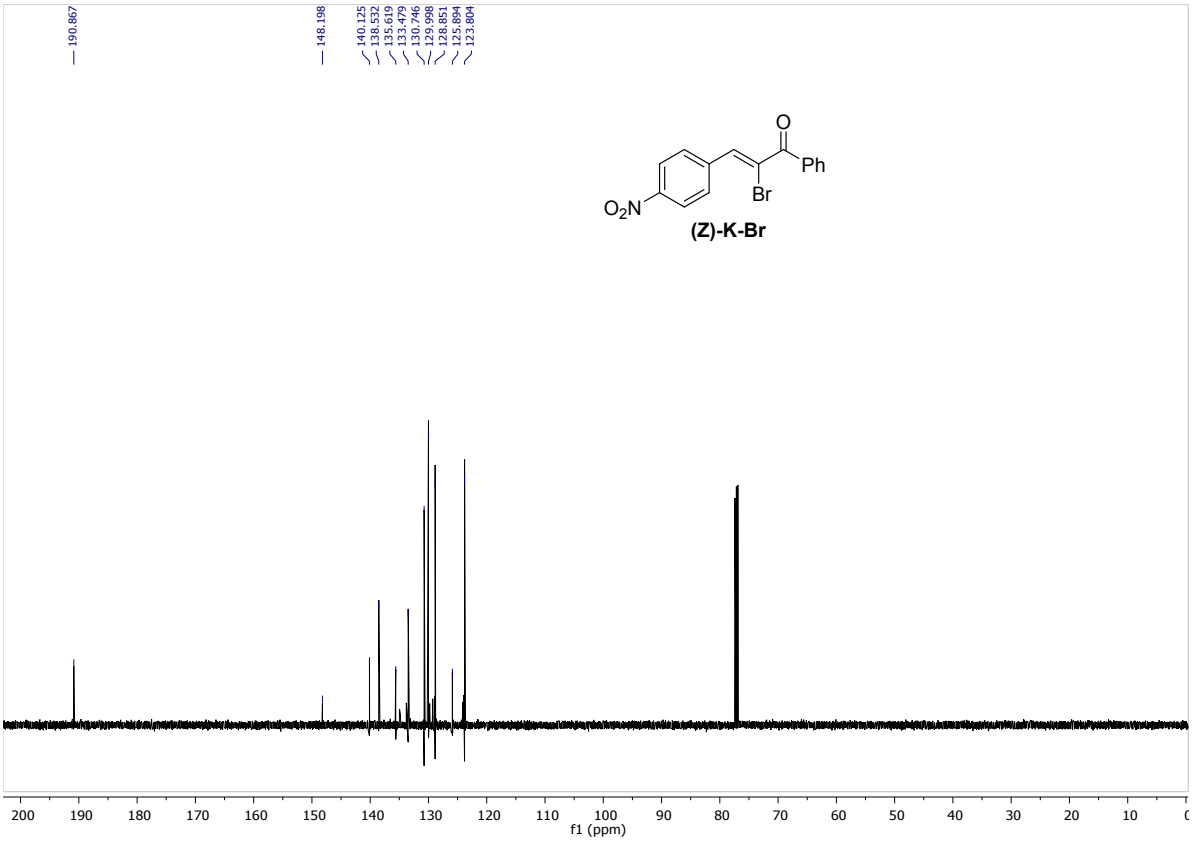


Fig. 32 ^{13}C NMR spectrum of (*Z*)-**K-Br** (125 MHz, $CDCl_3$).

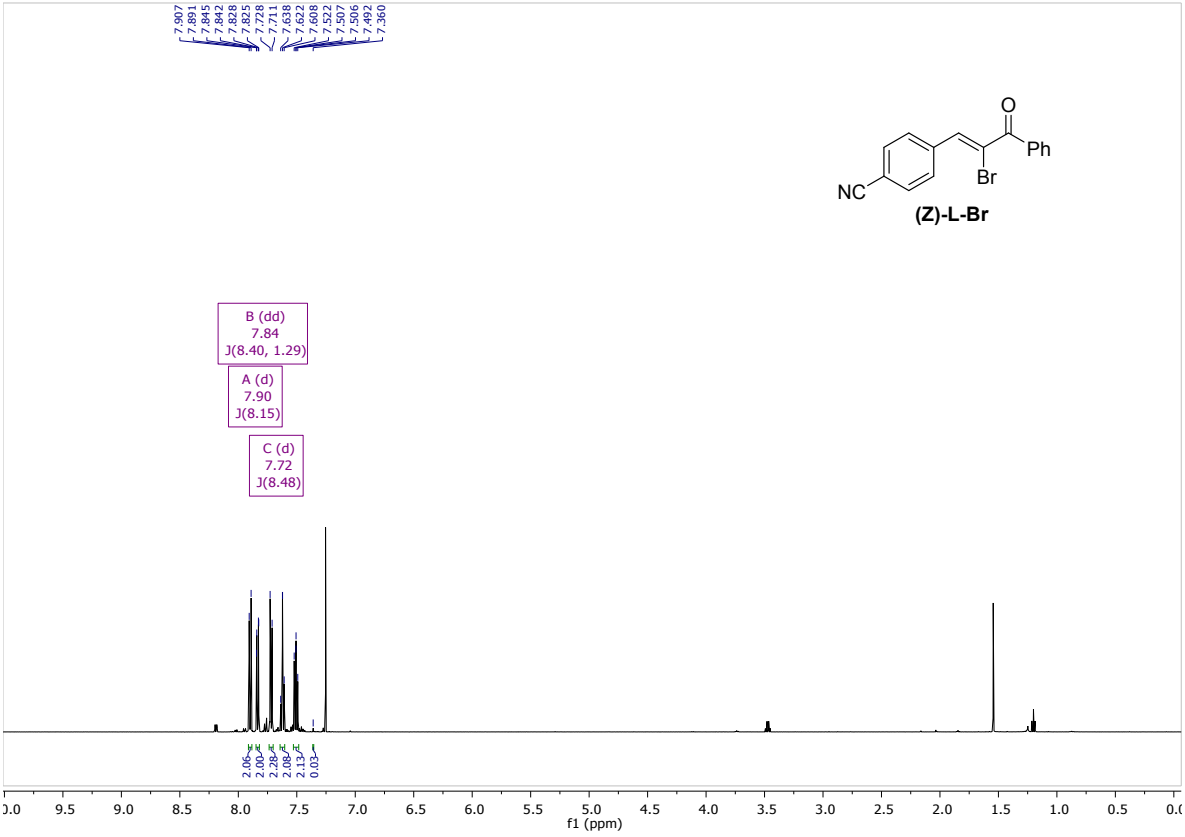


Fig. 33 ^{1}H NMR spectrum of (*Z*)-**L-Br** (500 MHz, $CDCl_3$).

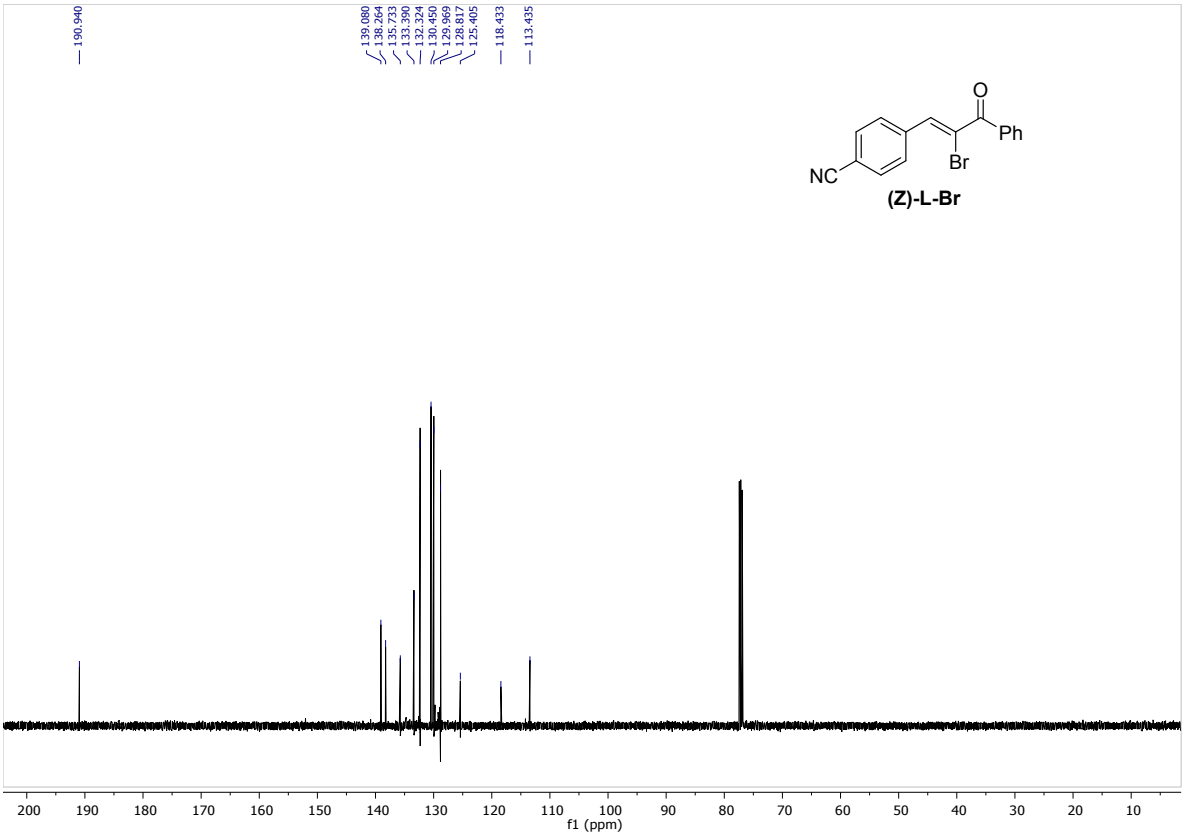


Fig. 34 ^{13}C NMR spectrum of (*Z*)-**L-Br** (125 MHz, $CDCl_3$).

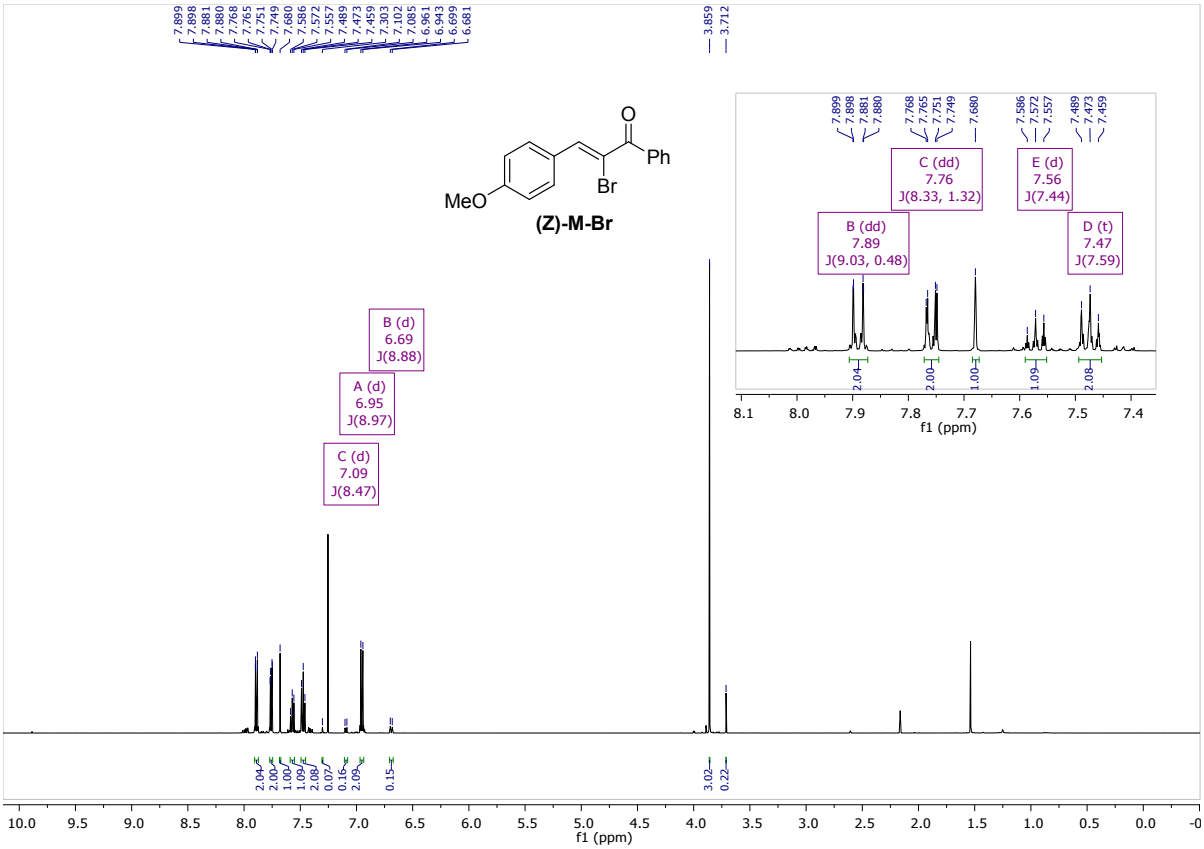


Fig. 35 ^{1}H NMR spectrum of (*Z*)-**M-Br** (500 MHz, $CDCl_3$).

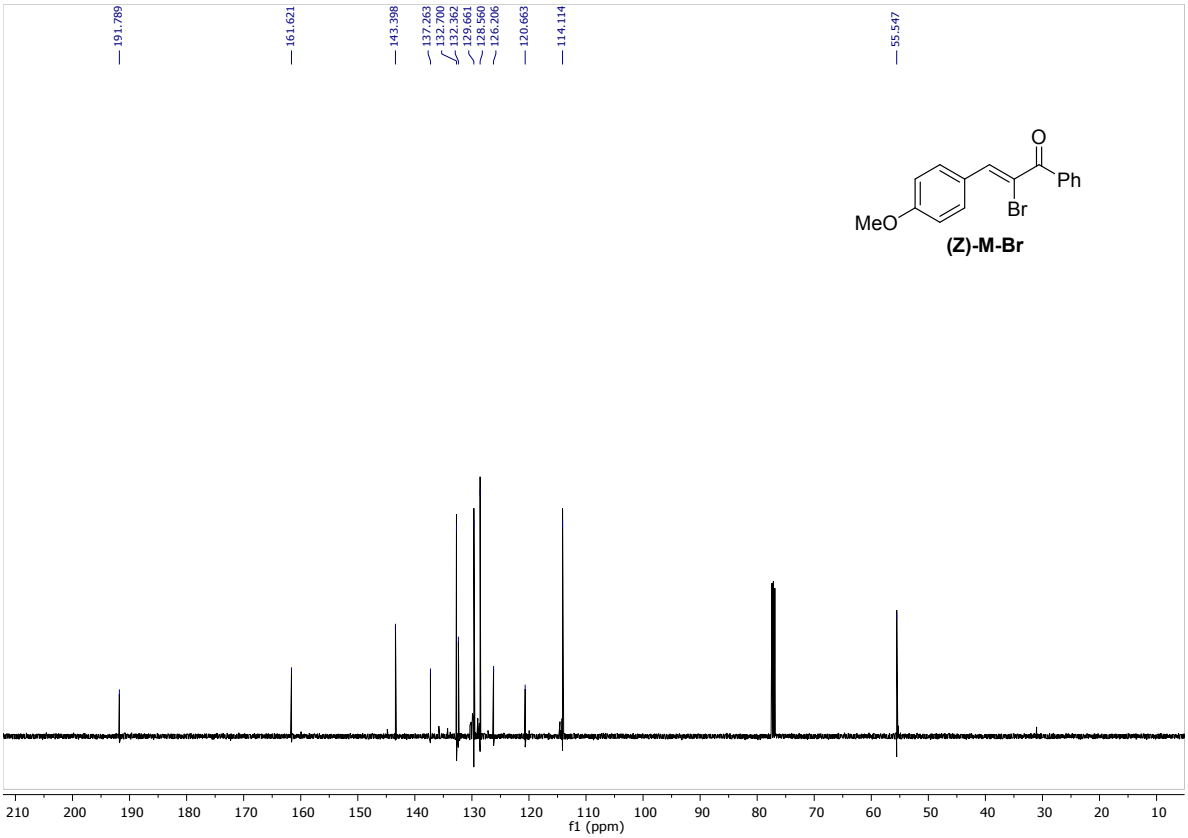


Fig. 36 ^{13}C NMR spectrum of (*Z*)-**M-Br** (125 MHz, $CDCl_3$).

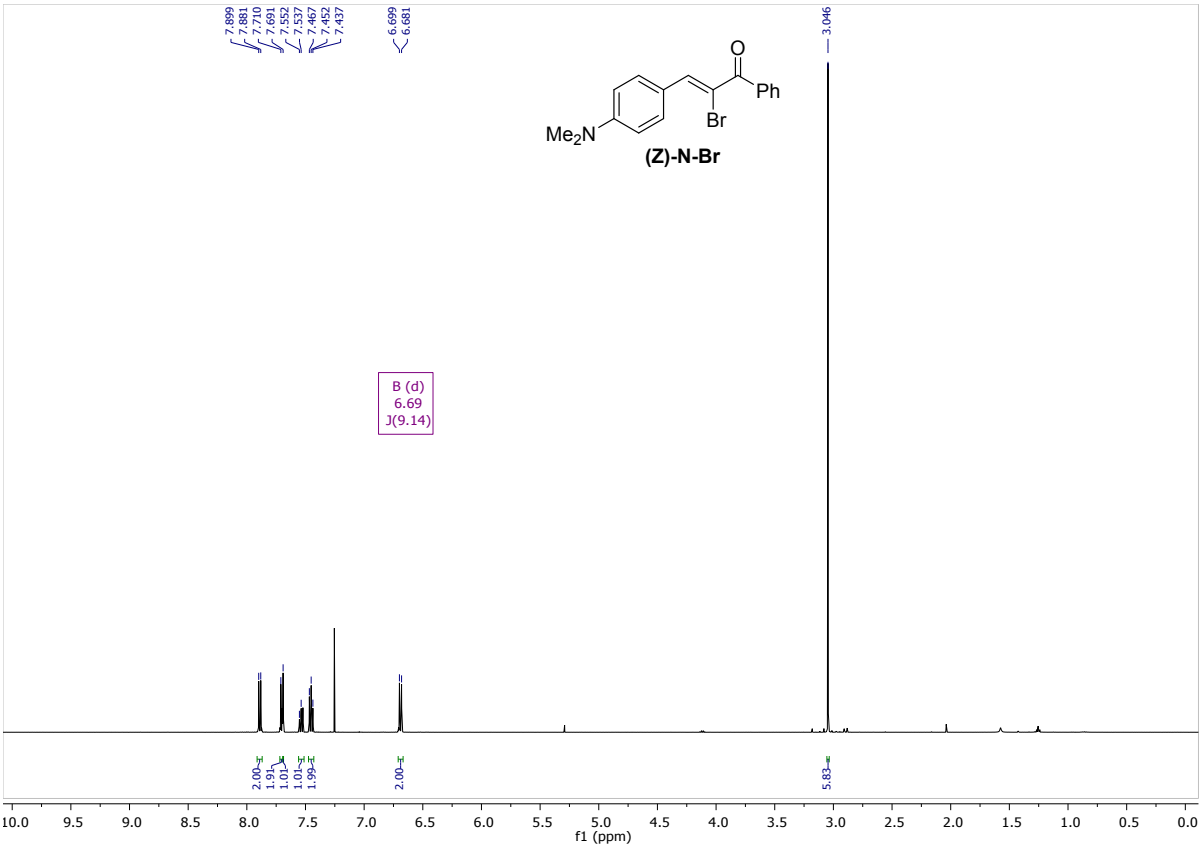


Fig. 37 ^{1}H NMR spectrum of (*Z*)-**N-Br** (500 MHz, $CDCl_3$).

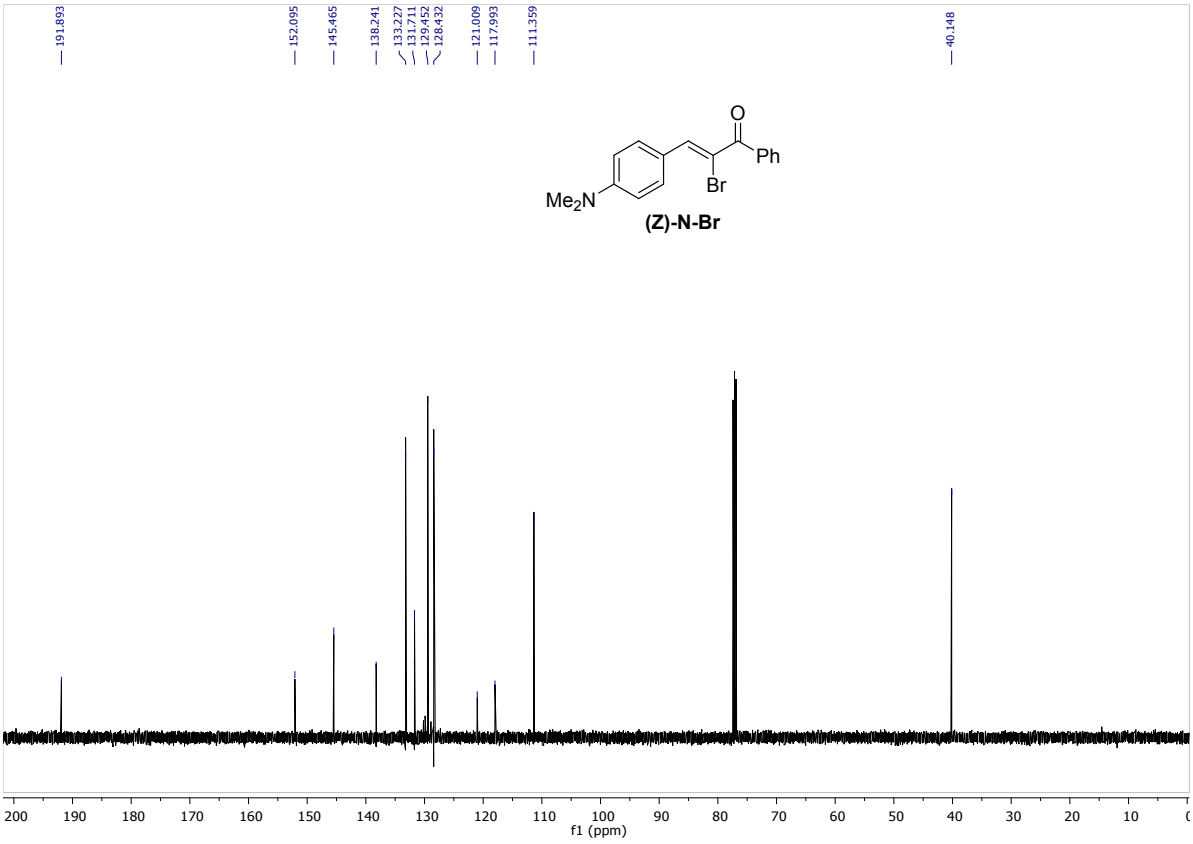


Fig. 38 ^{13}C NMR spectrum of (*Z*)-**N-Br** (125 MHz, $CDCl_3$).

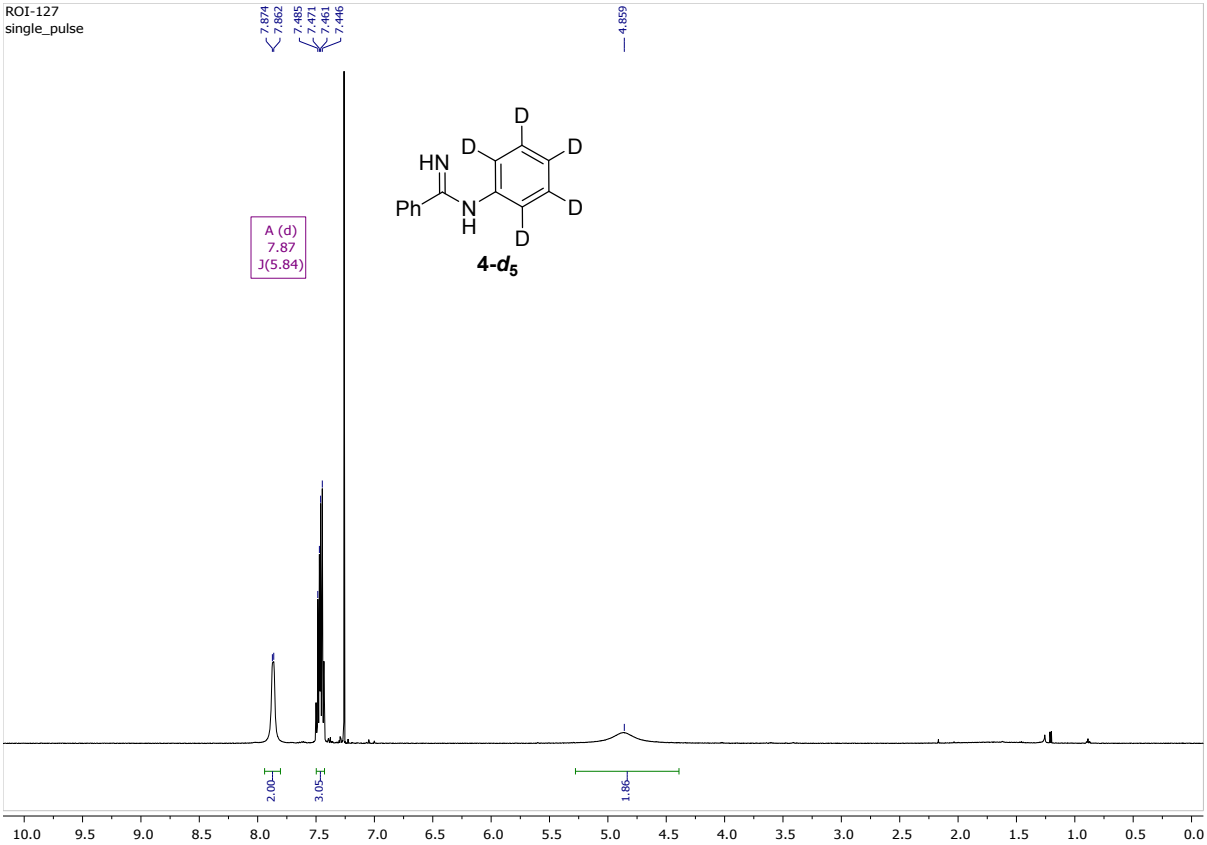


Fig. 39 ^{1}H NMR spectrum of **4-*d*$_5$** (500 MHz, $CDCl_3$).

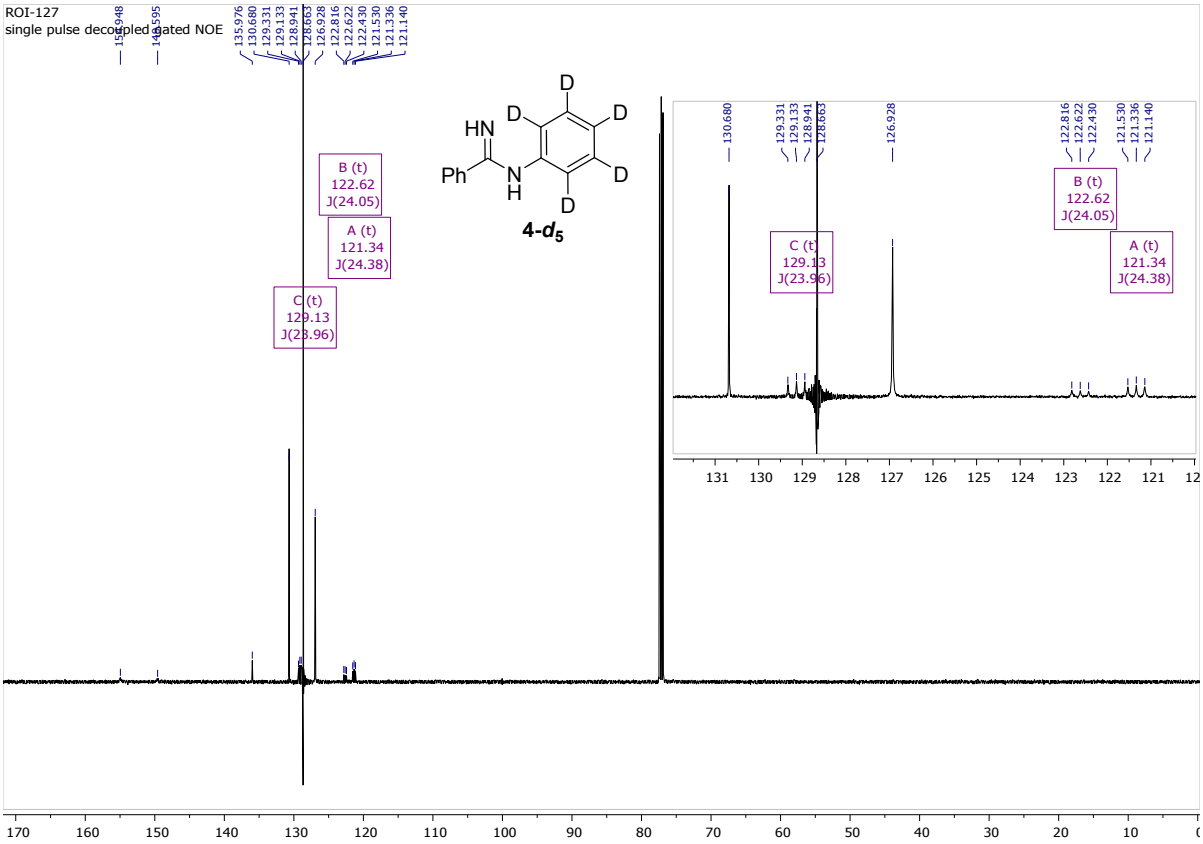


Fig. 40 ^{13}C NMR spectrum of **4-d_5** (125 MHz, $CDCl_3$).

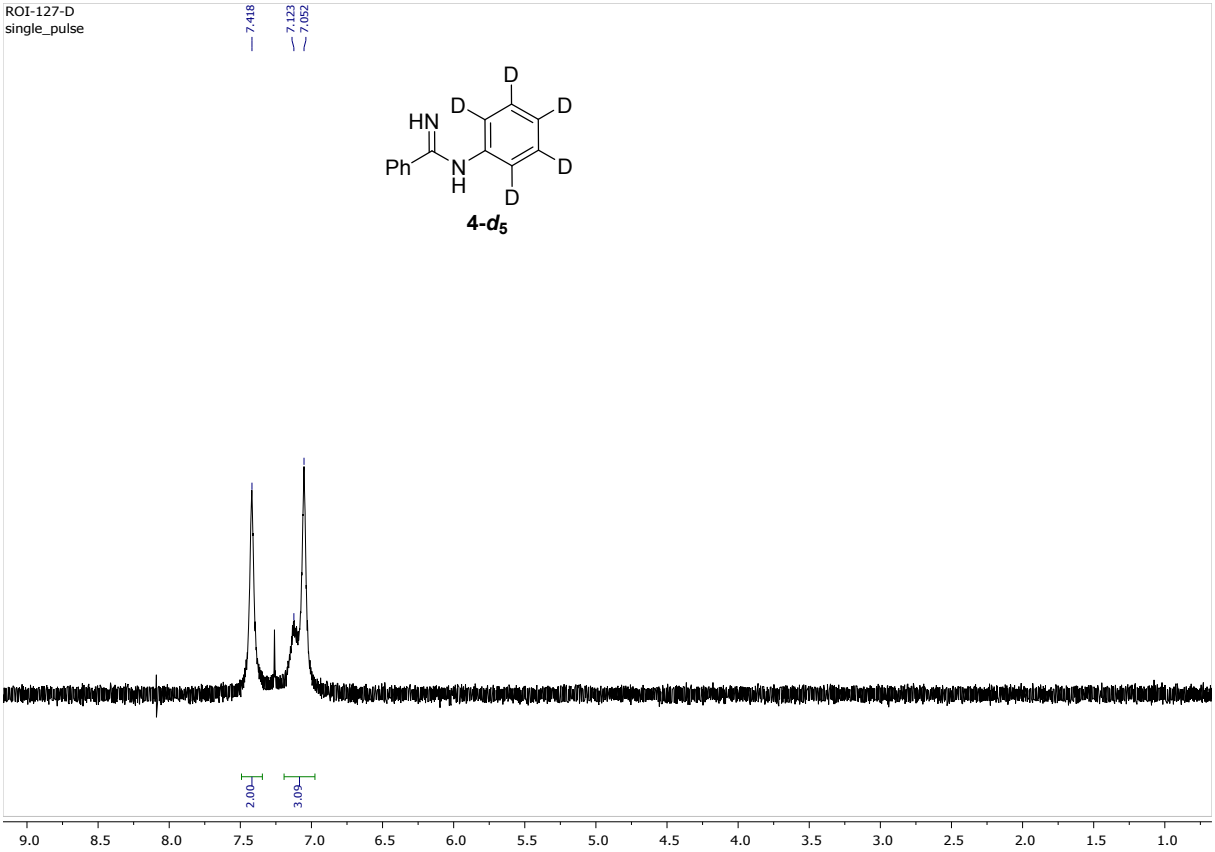


Fig. 41 ^{2}H NMR spectrum of **4-d_5** (76.8 MHz, $CHCl_3$ + addition of $CDCl_3$).

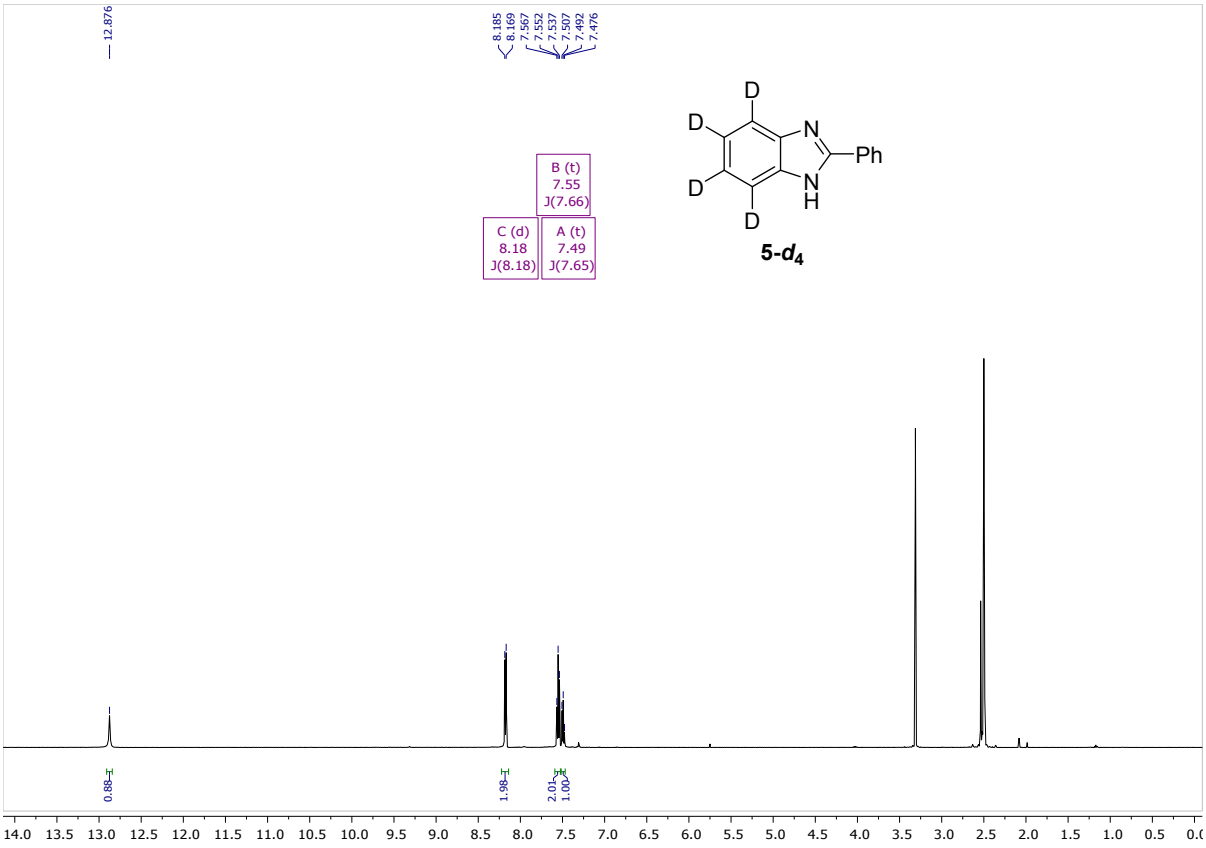


Fig. 42 ^{1}H NMR spectrum of **5-d_4** (500 MHz, DMSO).

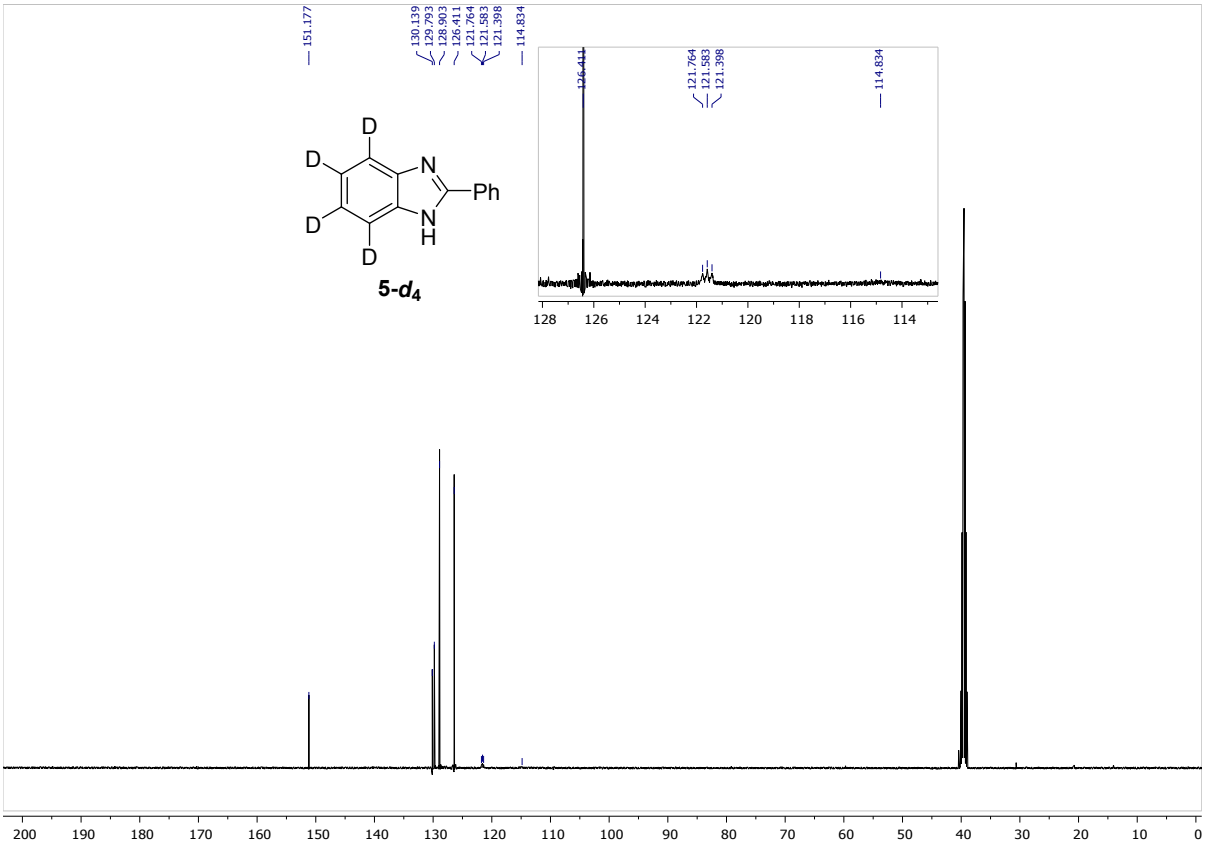


Fig. 43 ^{13}C NMR spectrum of **5-d_4** (125 MHz, DMSO).

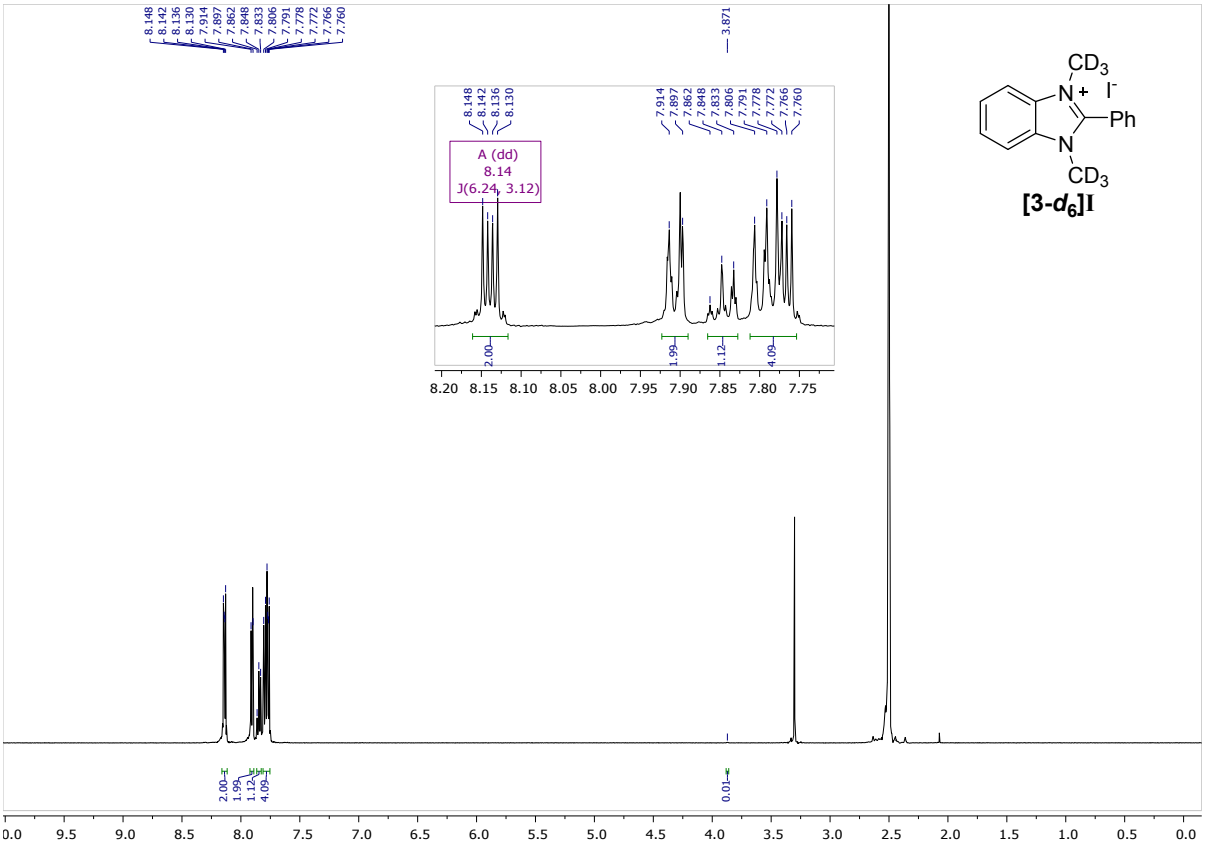


Fig. 44 ^{1}H NMR spectrum of **[3-d_6]I** (500 MHz, DMSO).

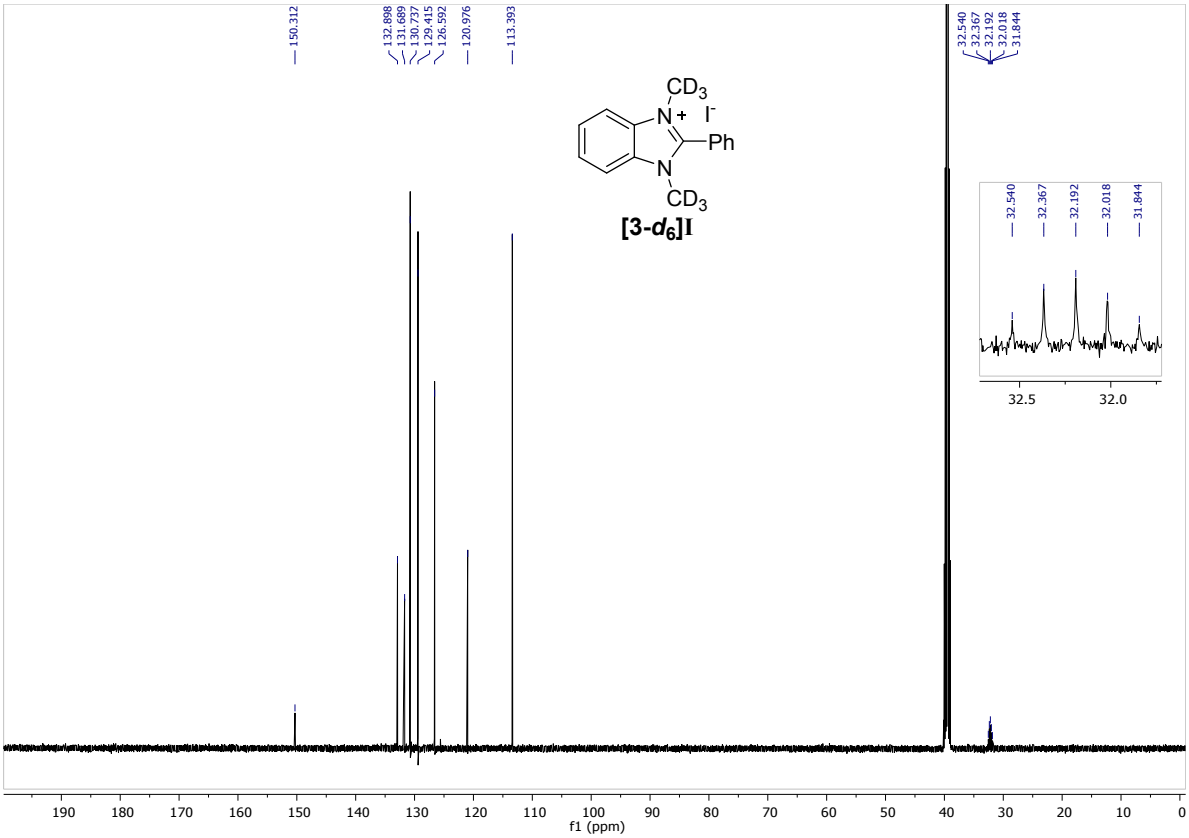


Fig. 45 ^{13}C NMR spectrum of **[3-d_6]I** (125 MHz, DMSO).

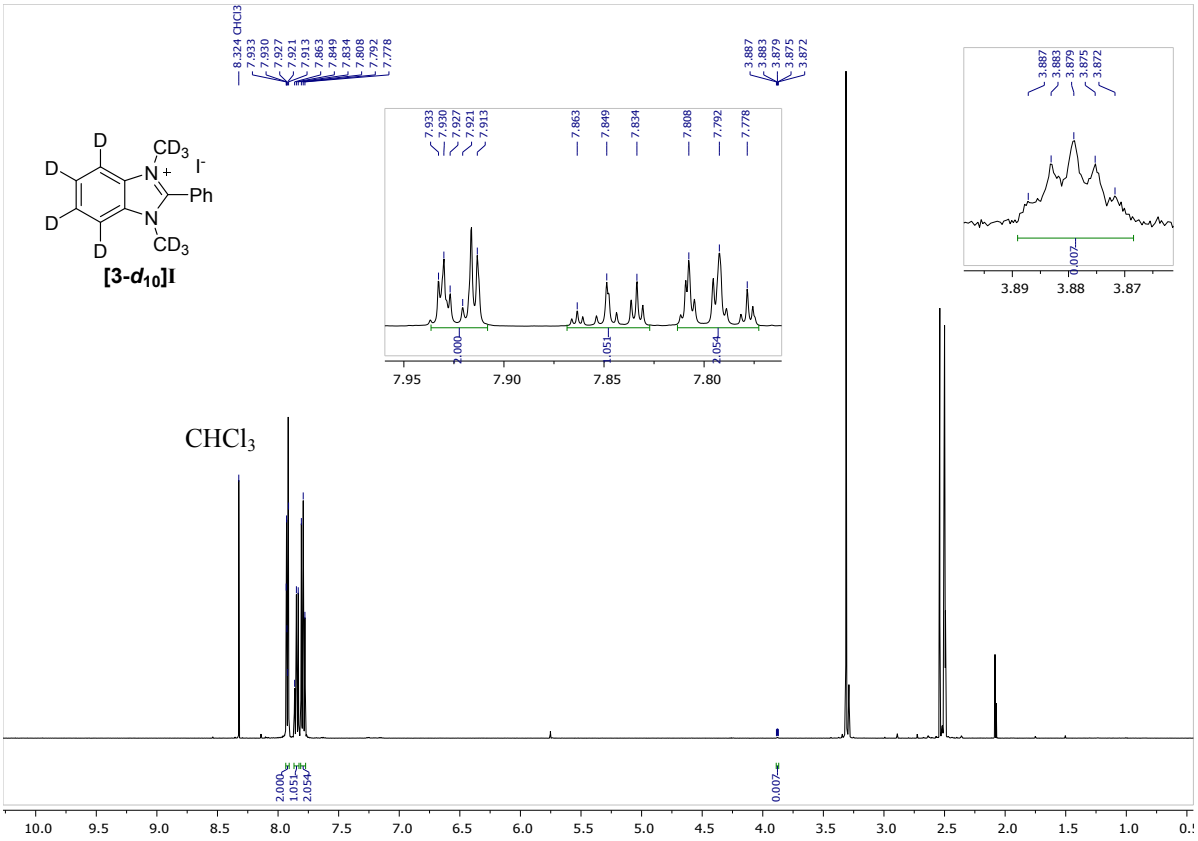


Fig. 46 ^{1}H NMR spectrum of **[3-d_{10}]I** (500 MHz, DMSO).

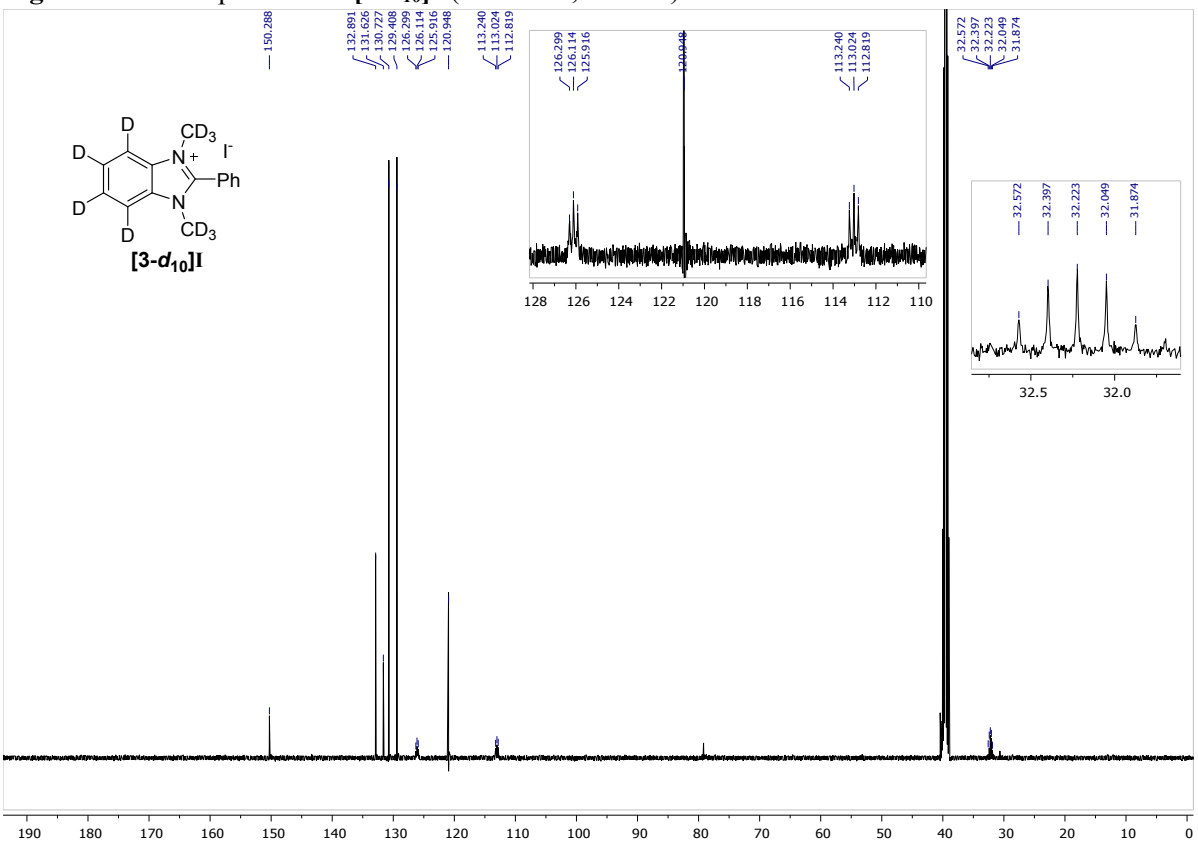


Fig. 47 ^{13}C NMR spectrum of **[3-d_{10}]I** (125 MHz, DMSO).

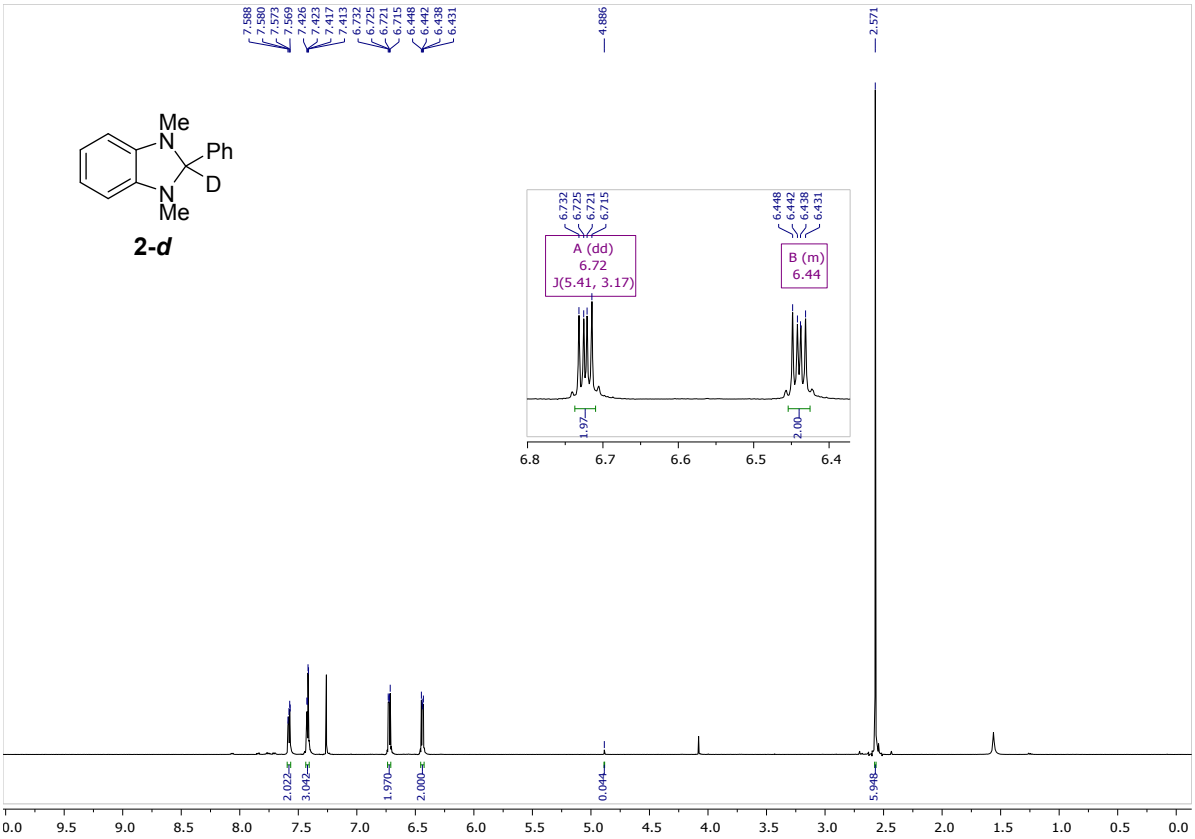


Fig. 48 ^{1}H NMR spectrum of **2-*d*** (500 MHz, $CDCl_3$).

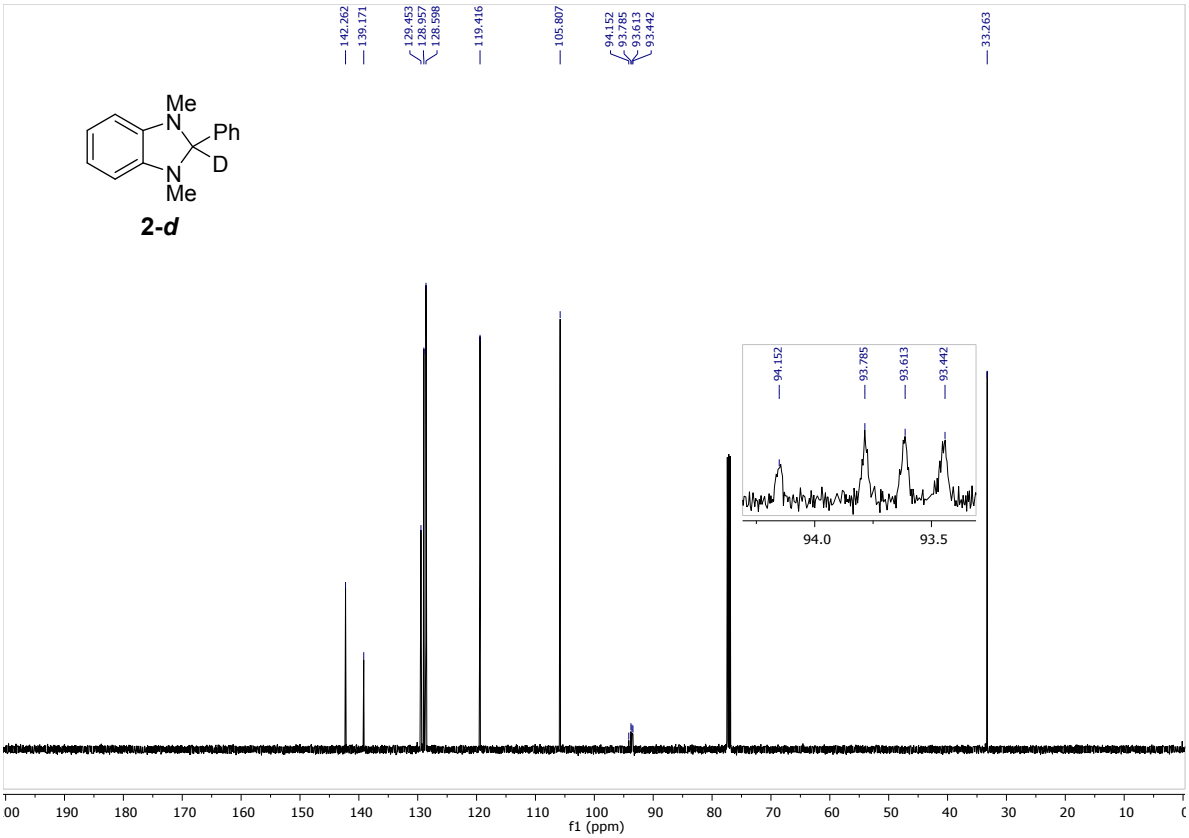


Fig. 49 ^{13}C NMR spectrum of **2-*d*** (125 MHz, $CDCl_3$).

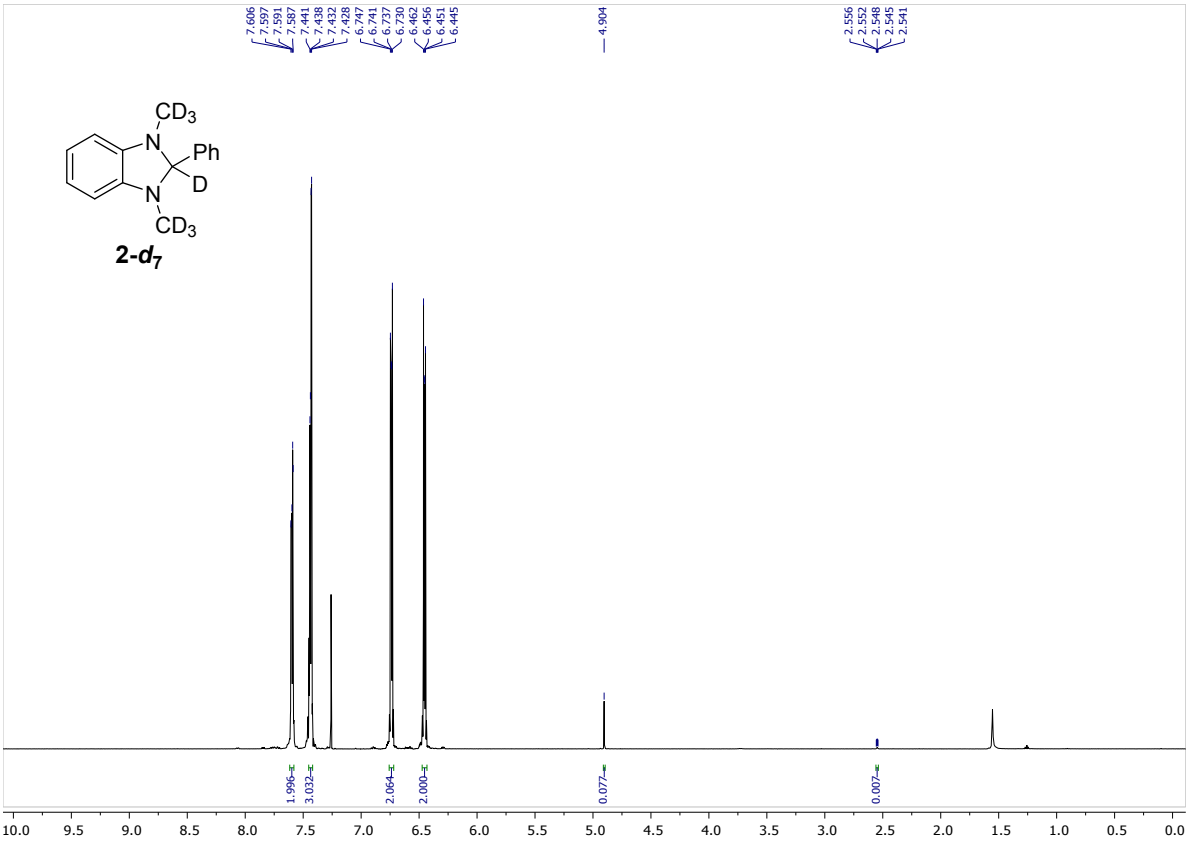


Fig. 50 ^{1}H NMR spectrum of **2-*d*$_7$** (500 MHz, $CDCl_3$).

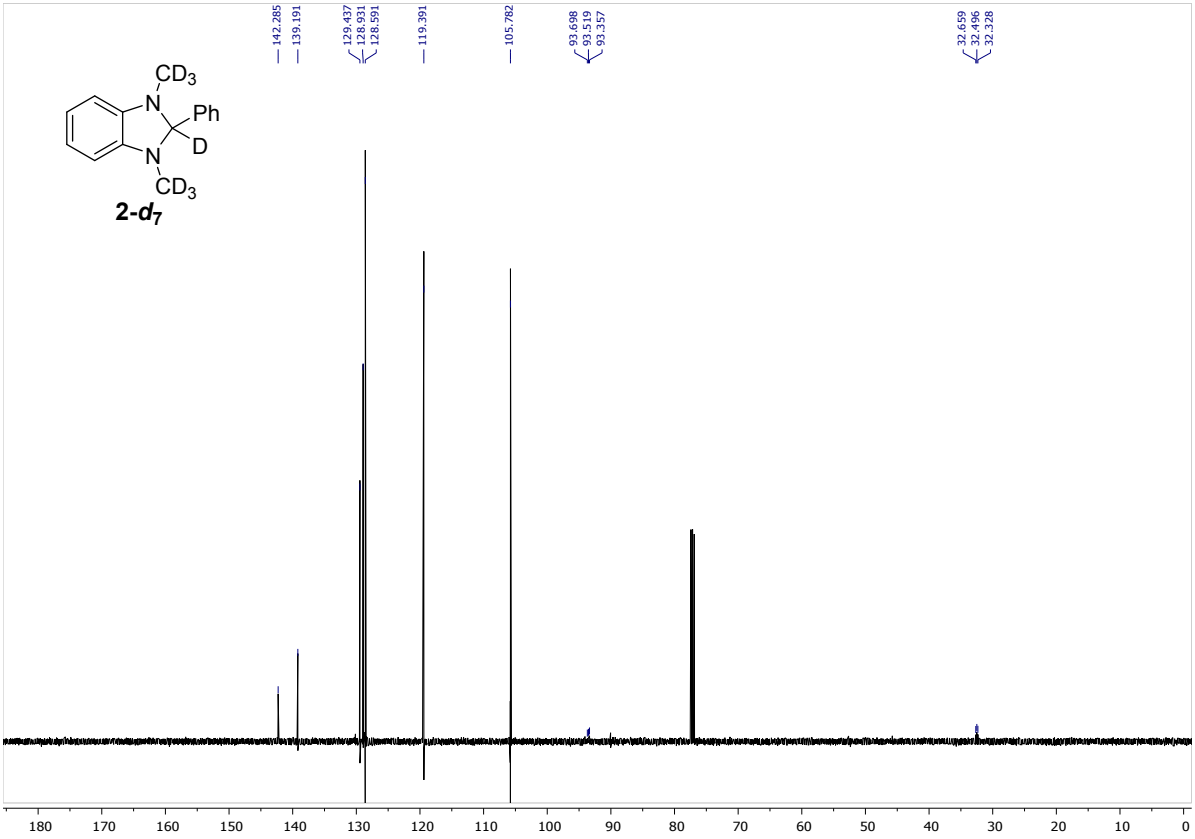


Fig. 51 ^{13}C NMR spectrum of **2-*d*$_7$** (125 MHz, $CDCl_3$).

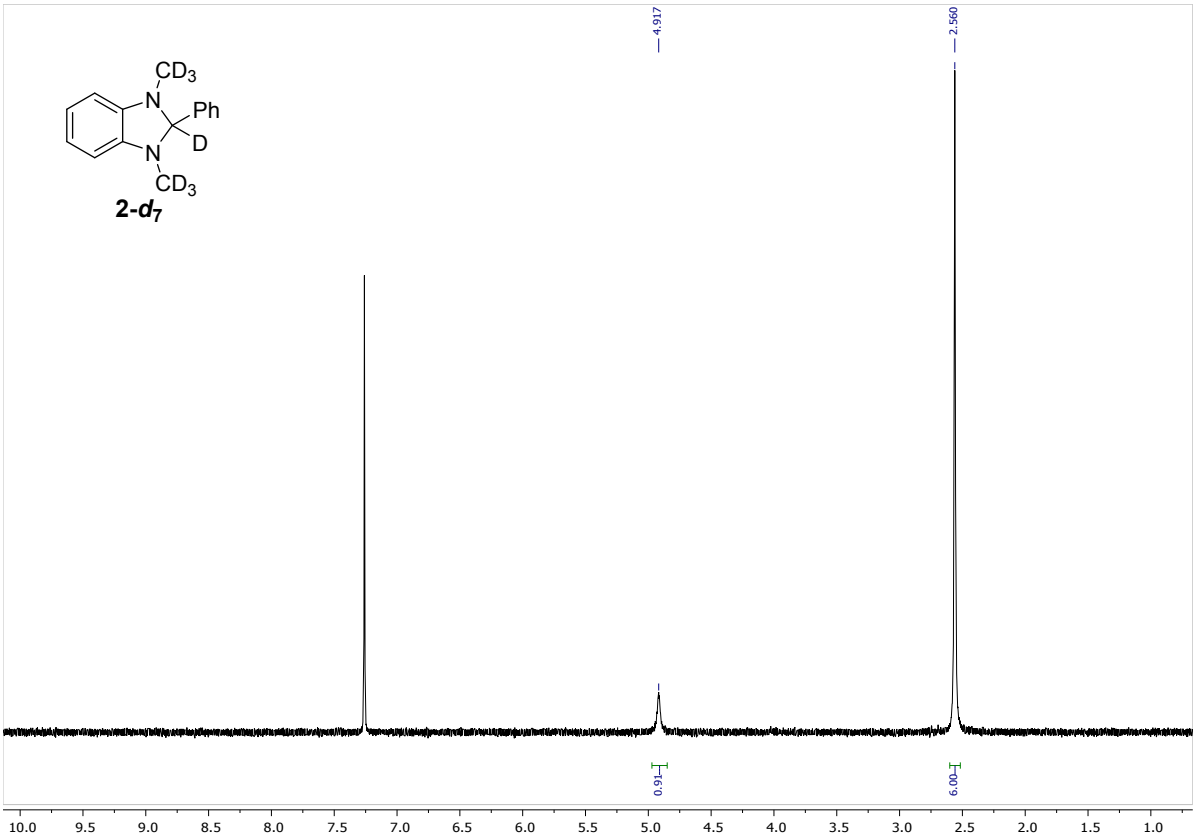


Fig. 52 ^{2}H NMR spectrum of **2-*d*$_7$** (76.8 MHz, $CHCl_3$ + addition of $CDCl_3$).

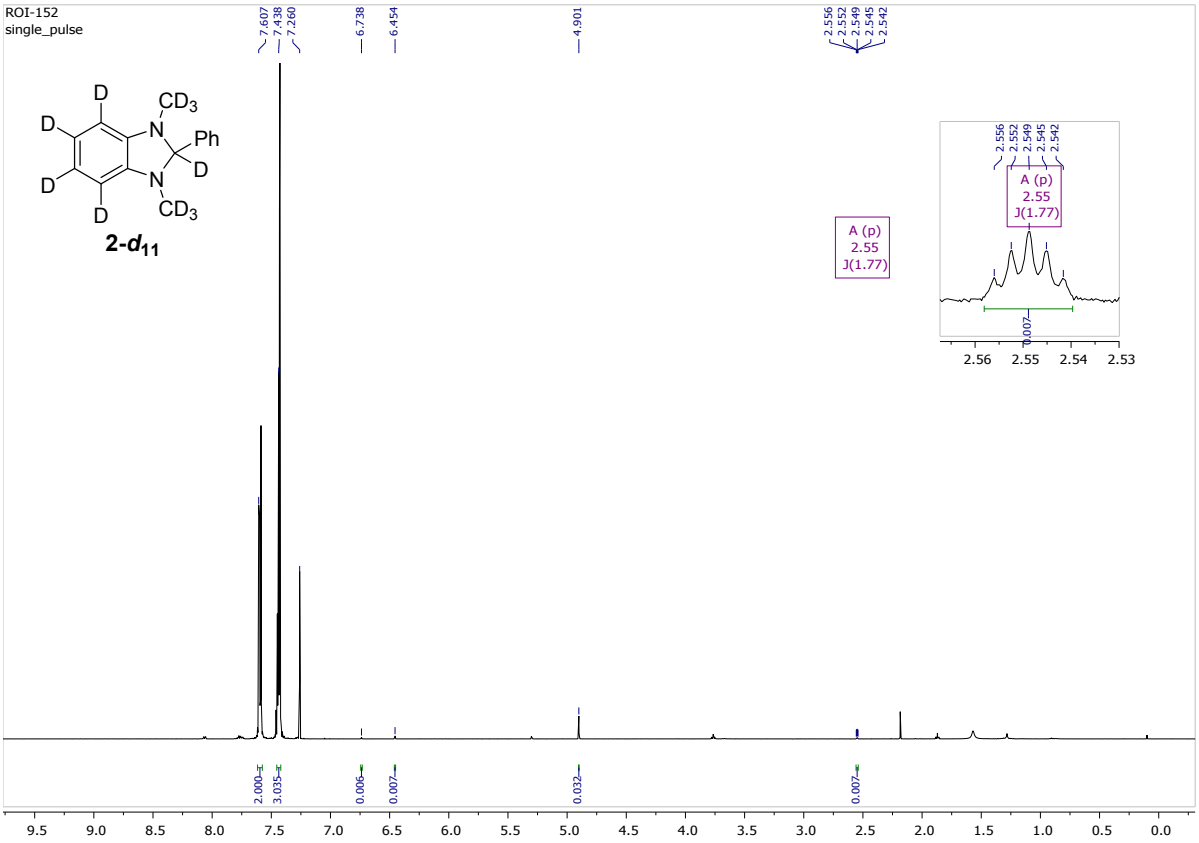


Fig. 53 ^{1}H NMR spectrum of **2-*d*$_{11}$** (500 MHz, $CDCl_3$).

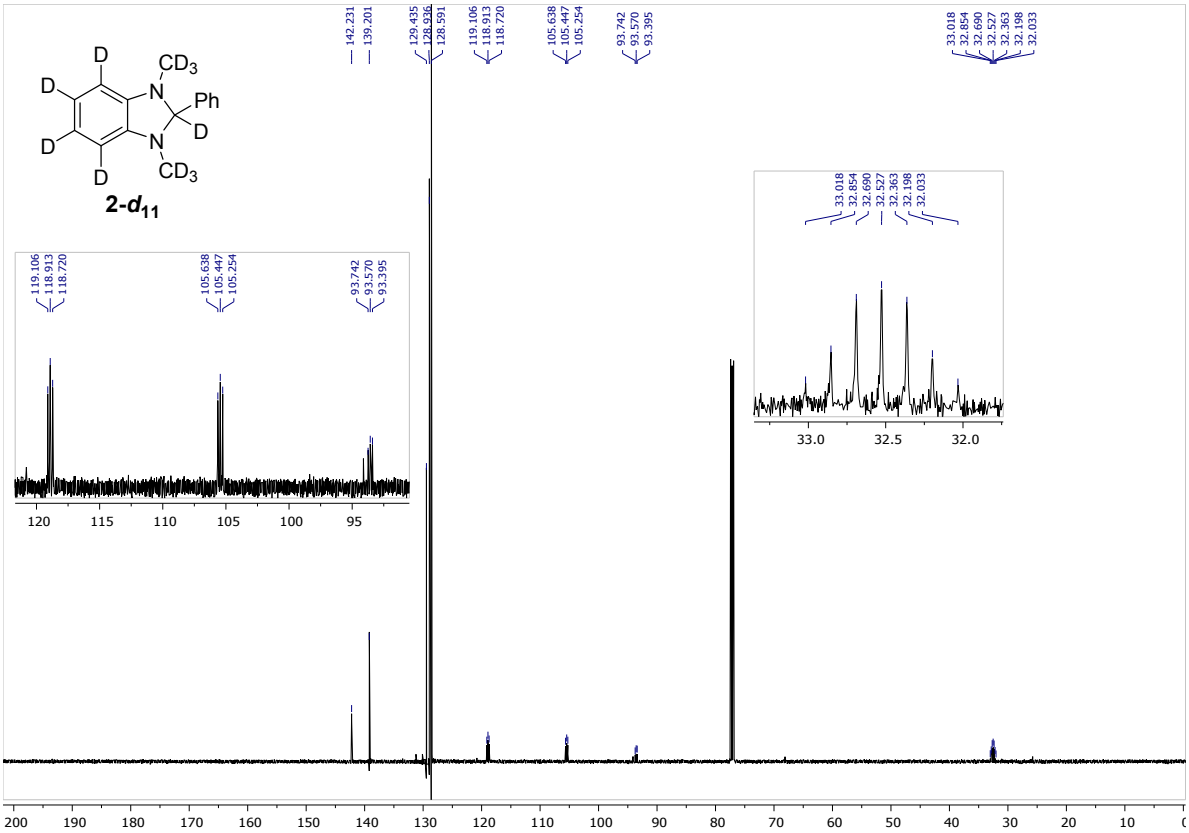


Fig. 54 ^{13}C NMR spectrum of **2-d_{11}** (125 MHz, $CDCl_3$).

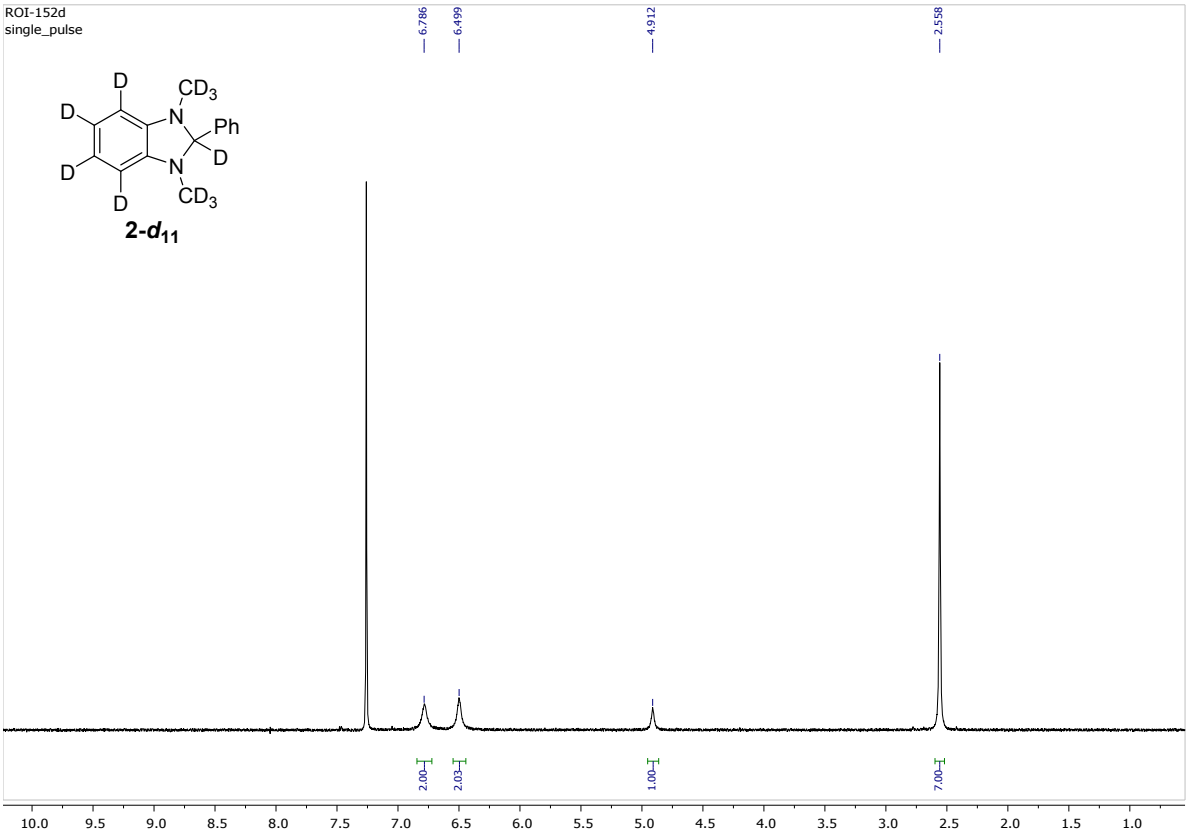


Fig. 55 ^{2}H NMR spectrum of **2-d_{11}** (76.8 MHz, $CHCl_3$ + addition of $CDCl_3$).

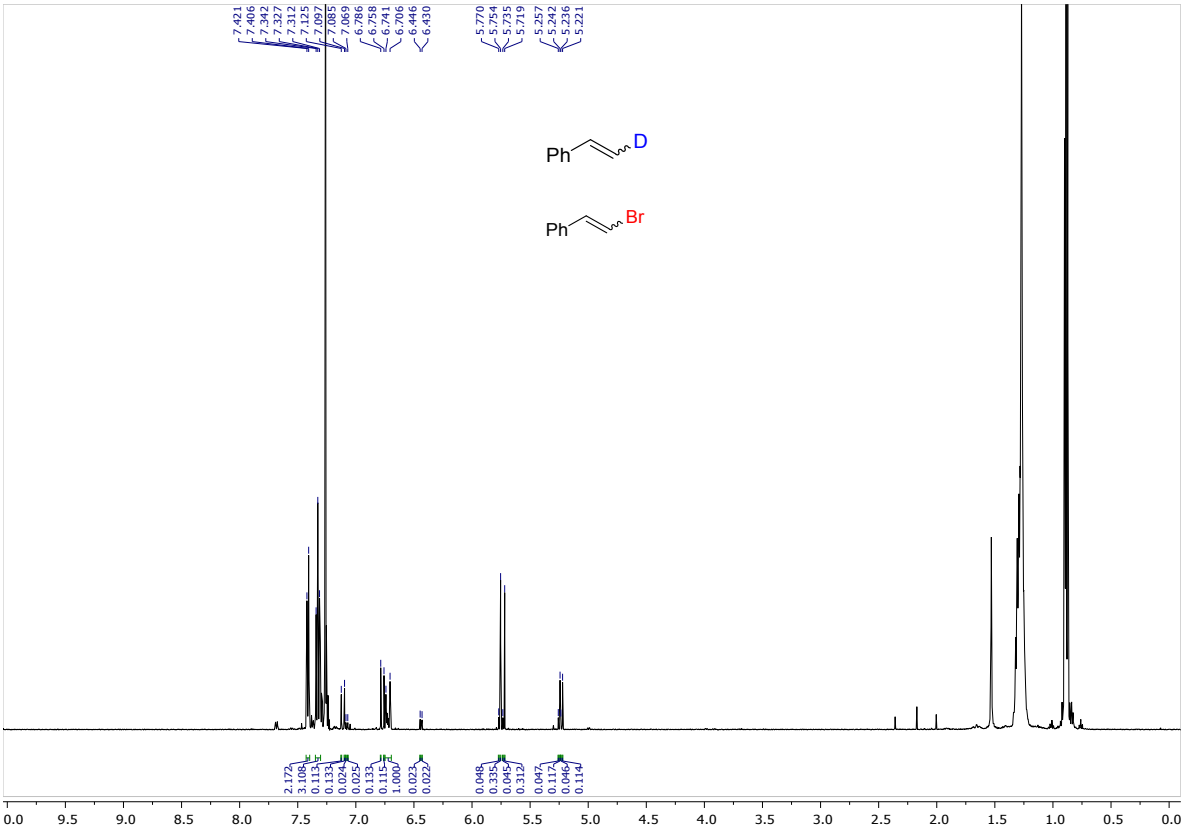


Fig. 56 ^{1}H NMR spectrum of **A-*d*** + **A-Br** (500 MHz, $CDCl_3$).

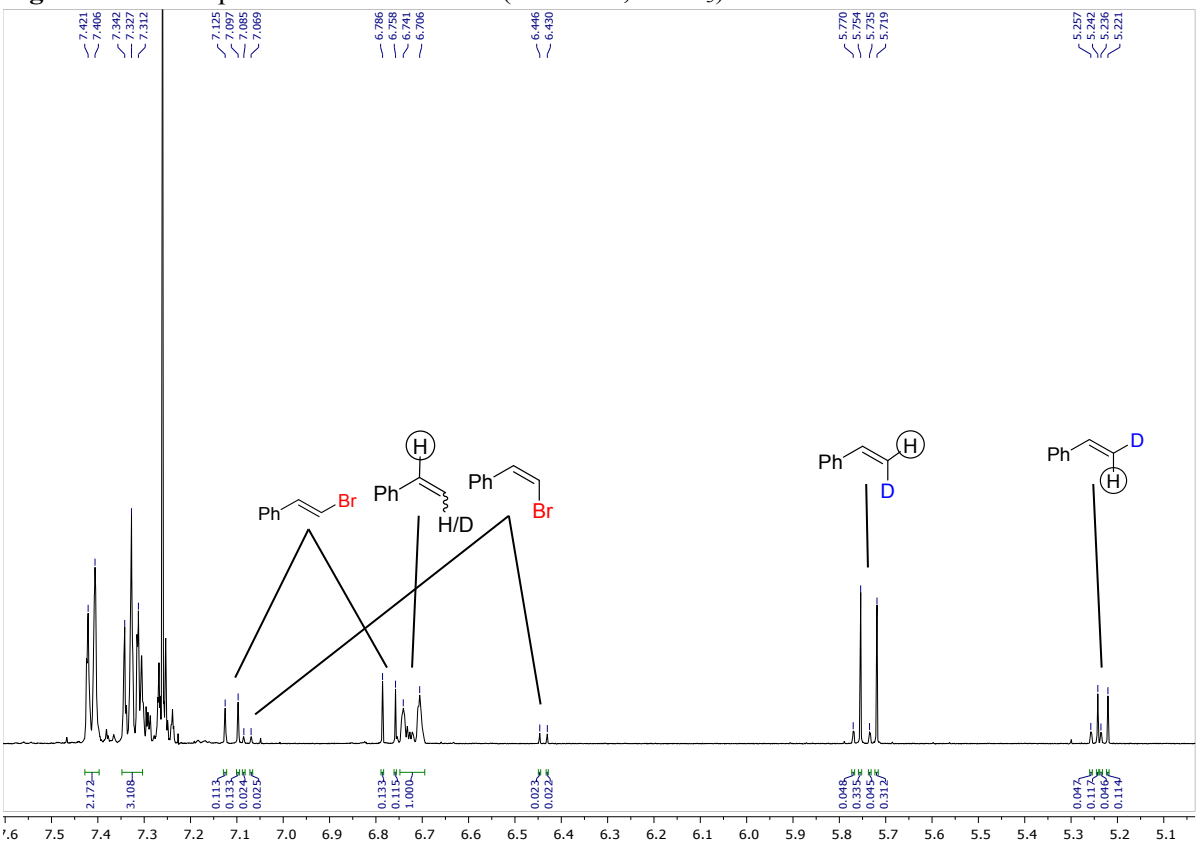


Fig. 57 ^{1}H NMR spectrum of **A-*d*** + **A-Br**, expanded (500 MHz, $CDCl_3$).

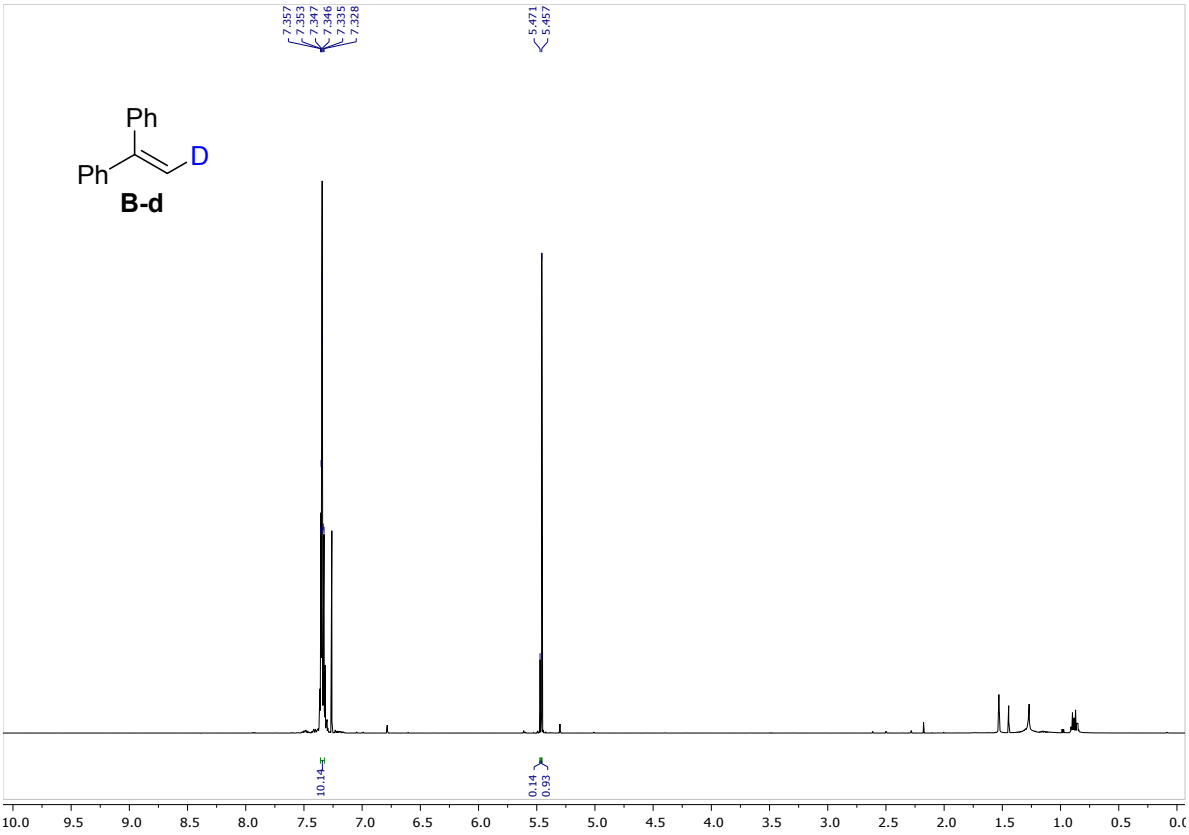


Fig. 58 ^{1}H NMR spectrum of **B-*d*** (500 MHz, $CDCl_3$).

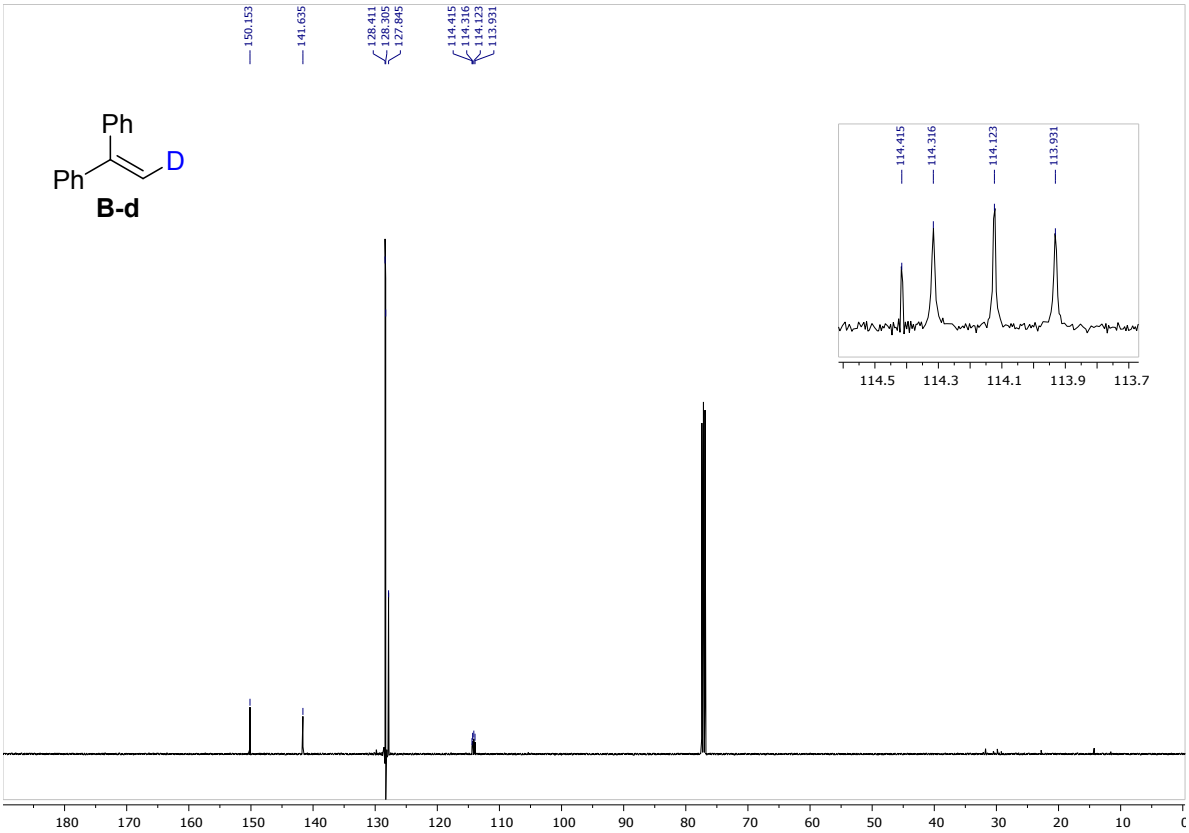


Fig. 59 ^{13}C NMR spectrum of **B-*d*** (125 MHz, $CDCl_3$).

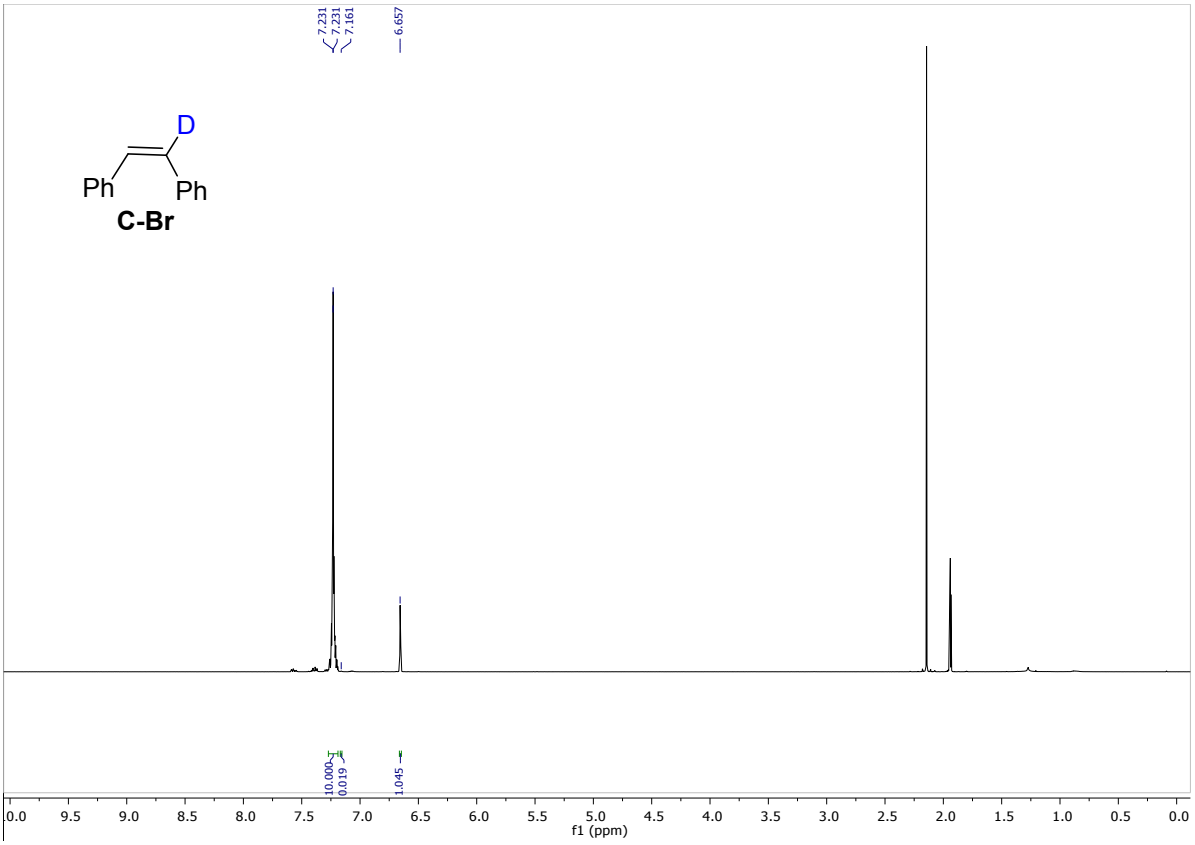


Fig. 60 ^{1}H NMR spectrum of **C-*d*** (500 MHz, CD_3CN).

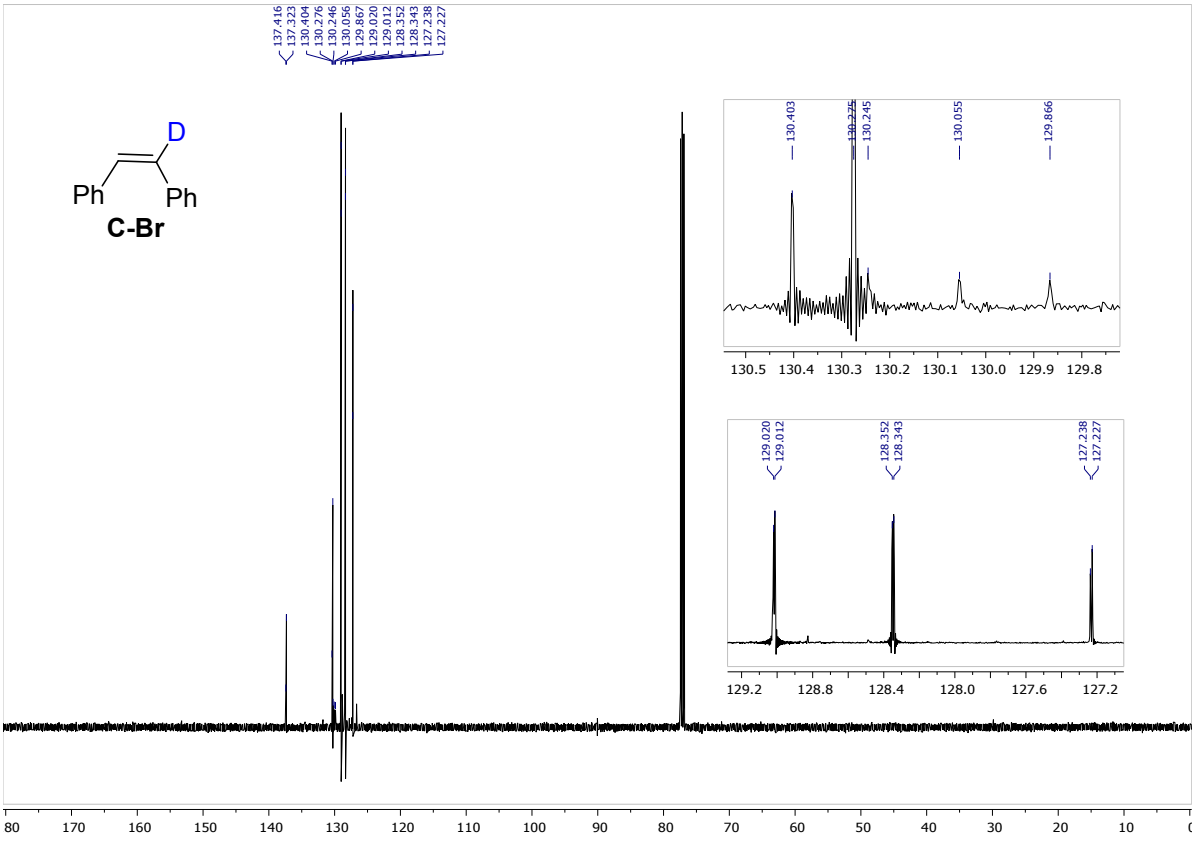


Fig. 61 ^{13}C NMR spectrum of **C-*d*** (125 MHz, $CDCl_3$).

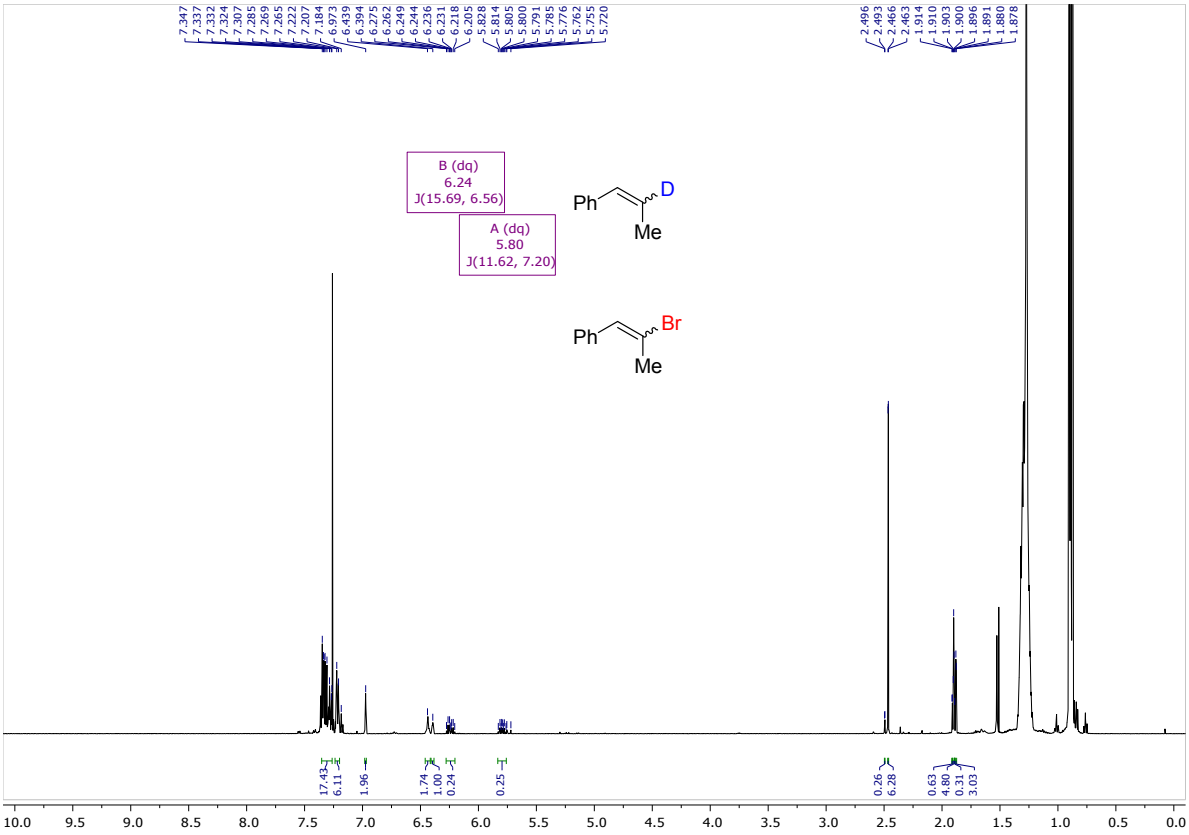


Fig. 62 ^{1}H NMR spectrum of **D-*d*** + **D-Br** (500 MHz, $CDCl_3$).

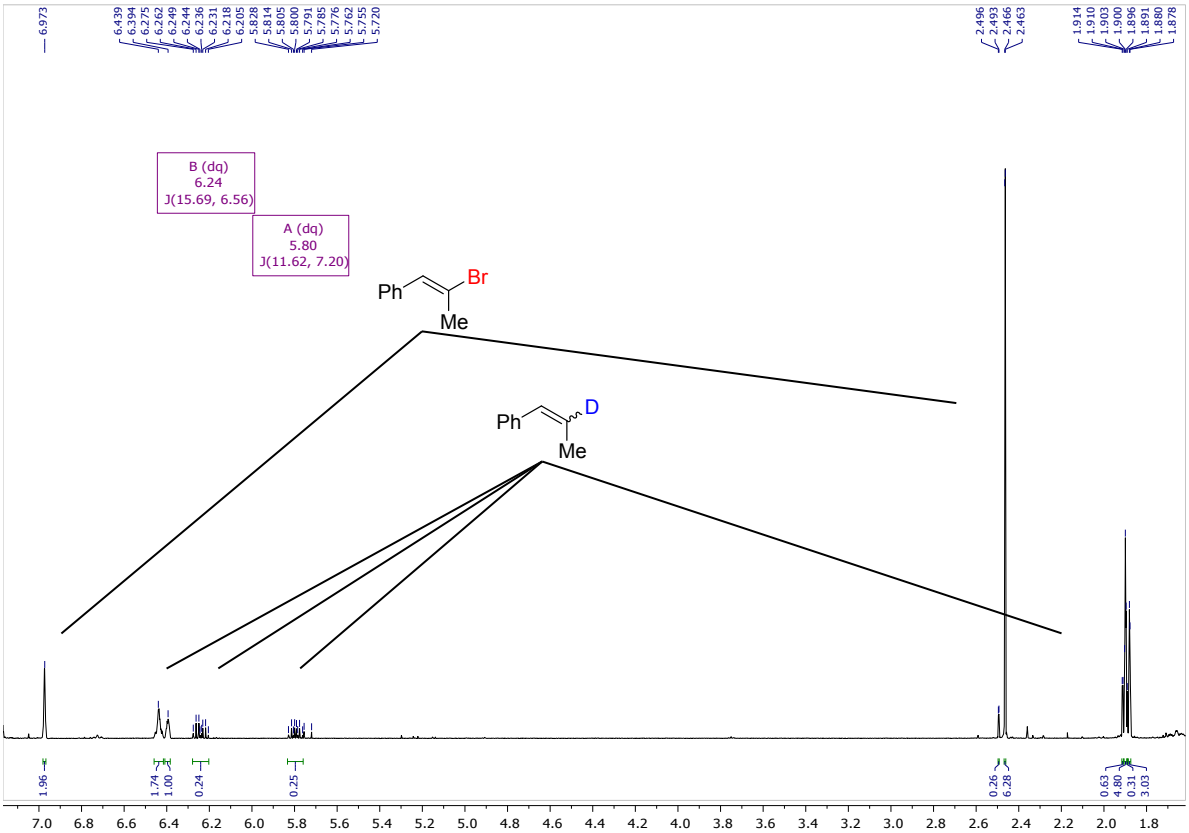


Fig. 63 ^{1}H NMR spectrum of **D-*d*** + **D-Br**, expanded (500 MHz, $CDCl_3$).

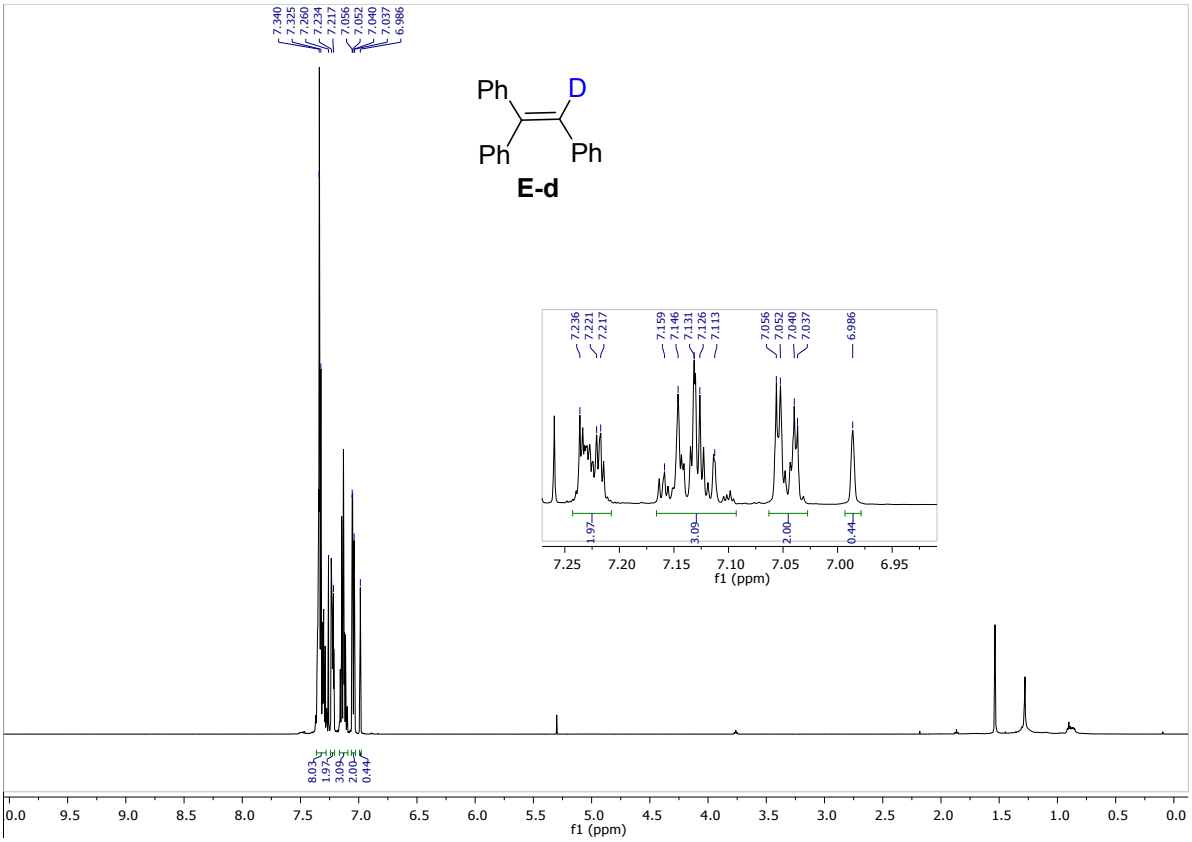


Fig. 64 ^{1}H NMR spectrum of **E-*d*** (500 MHz, $CDCl_3$).

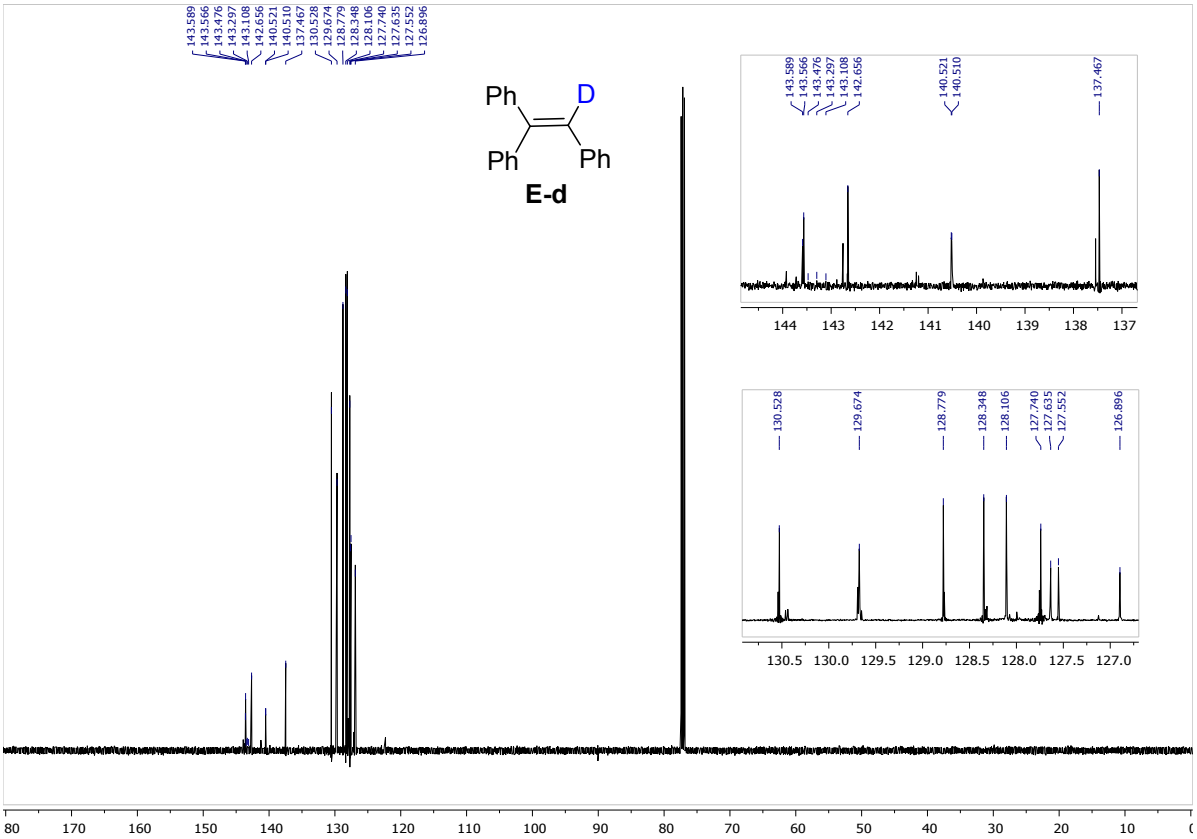


Fig. 65 ^{13}C NMR spectrum of **E-*d*** (125 MHz, $CDCl_3$).

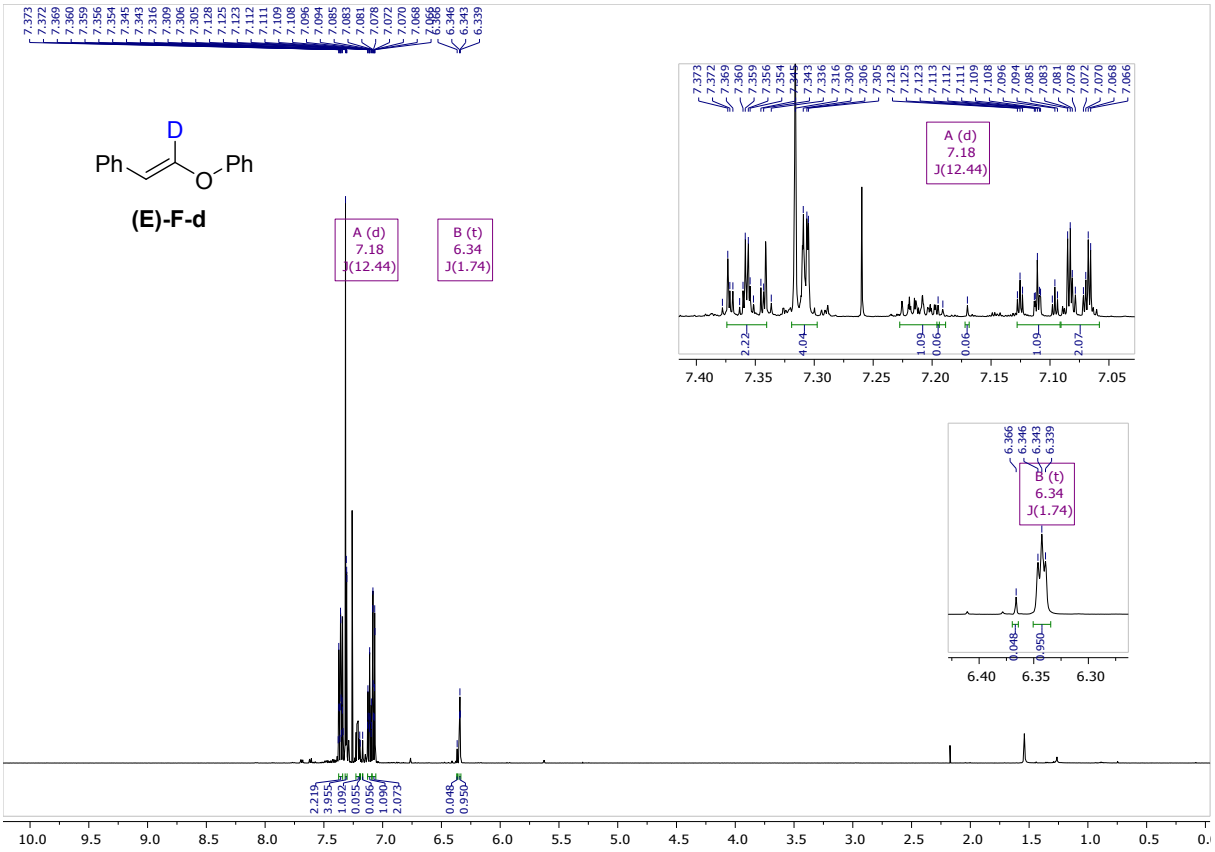


Fig. 66 ^{1}H NMR spectrum of **(E)-F-*d*** (500 MHz, $CDCl_3$).

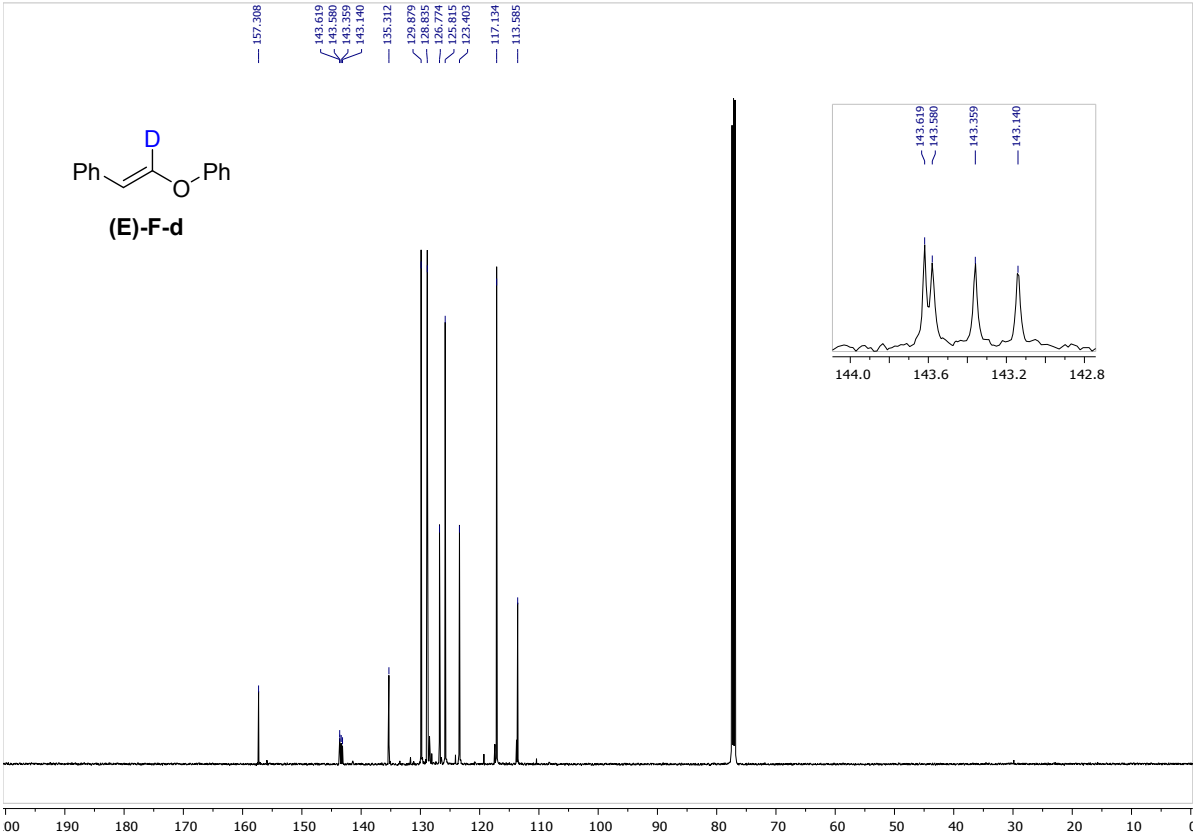


Fig. 67 ^{13}C NMR spectrum of **(E)-F-*d*** (125 MHz, $CDCl_3$).

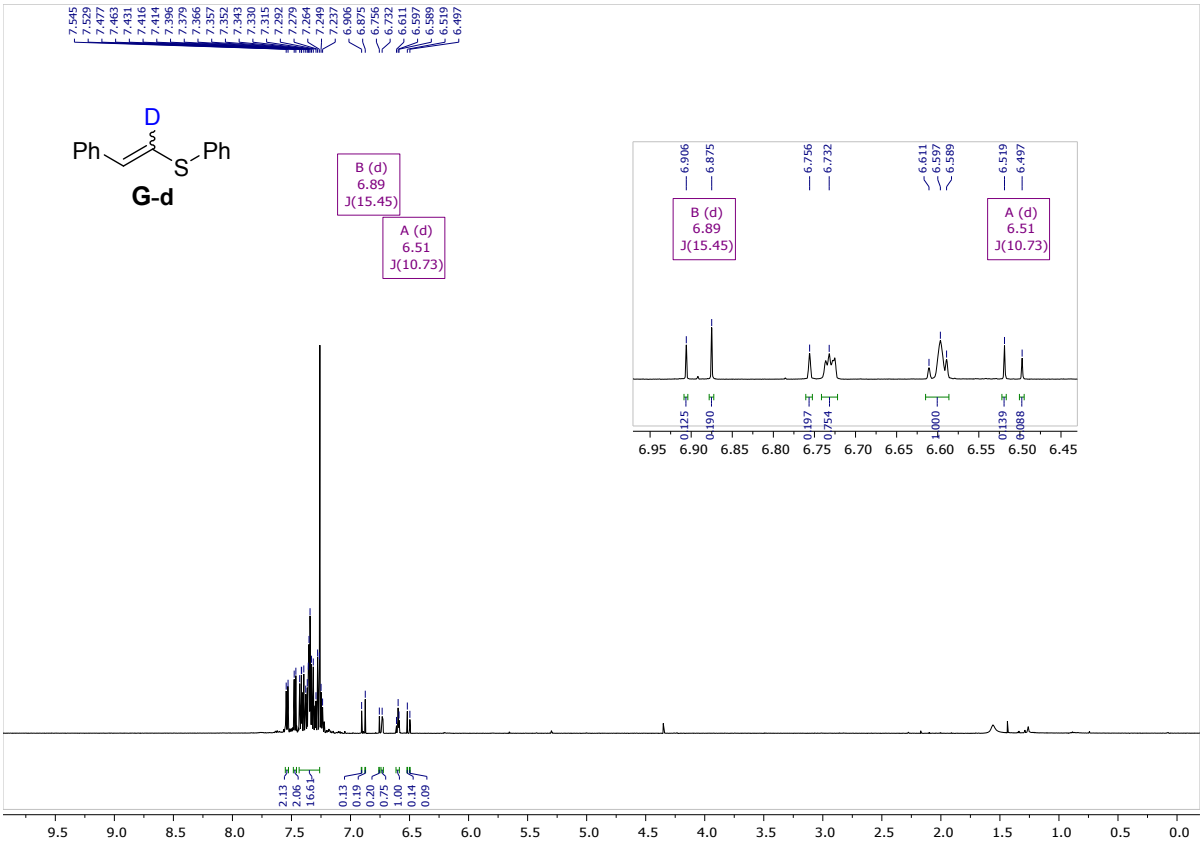


Fig. 68 ^{1}H NMR spectrum of **G-*d*** (500 MHz, $CDCl_3$).

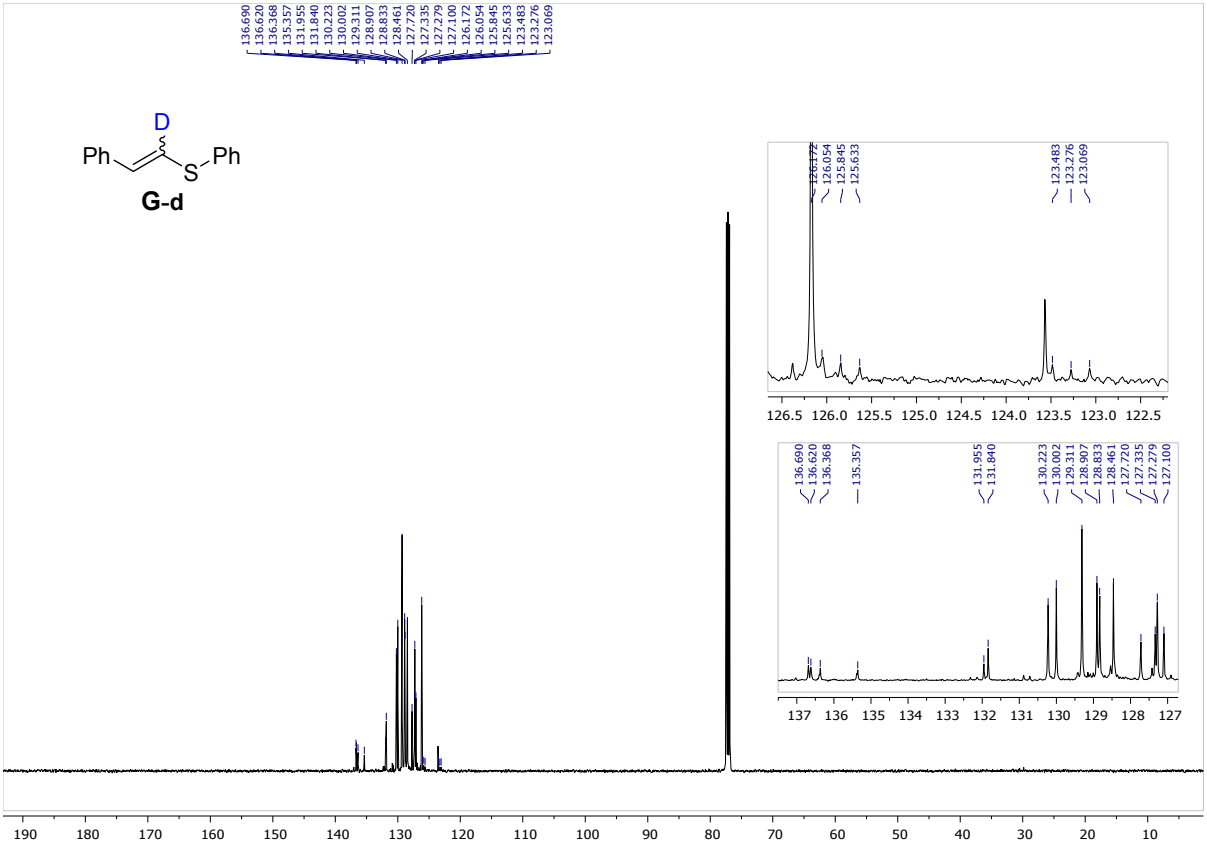


Fig. 69 ^{13}C NMR spectrum of **G-*d*** (125 MHz, $CDCl_3$).

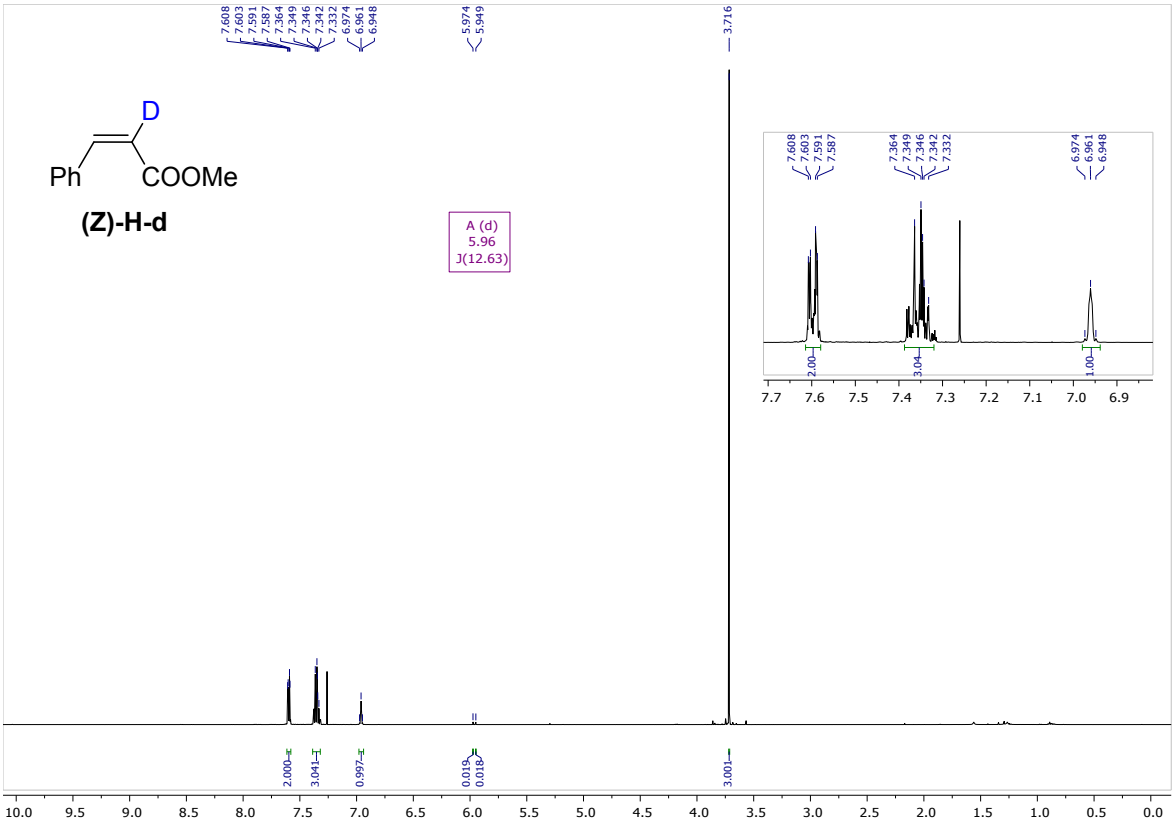


Fig. 70 ^{1}H NMR spectrum of ***(Z)*-H-*d*** (500 MHz, $CDCl_3$).

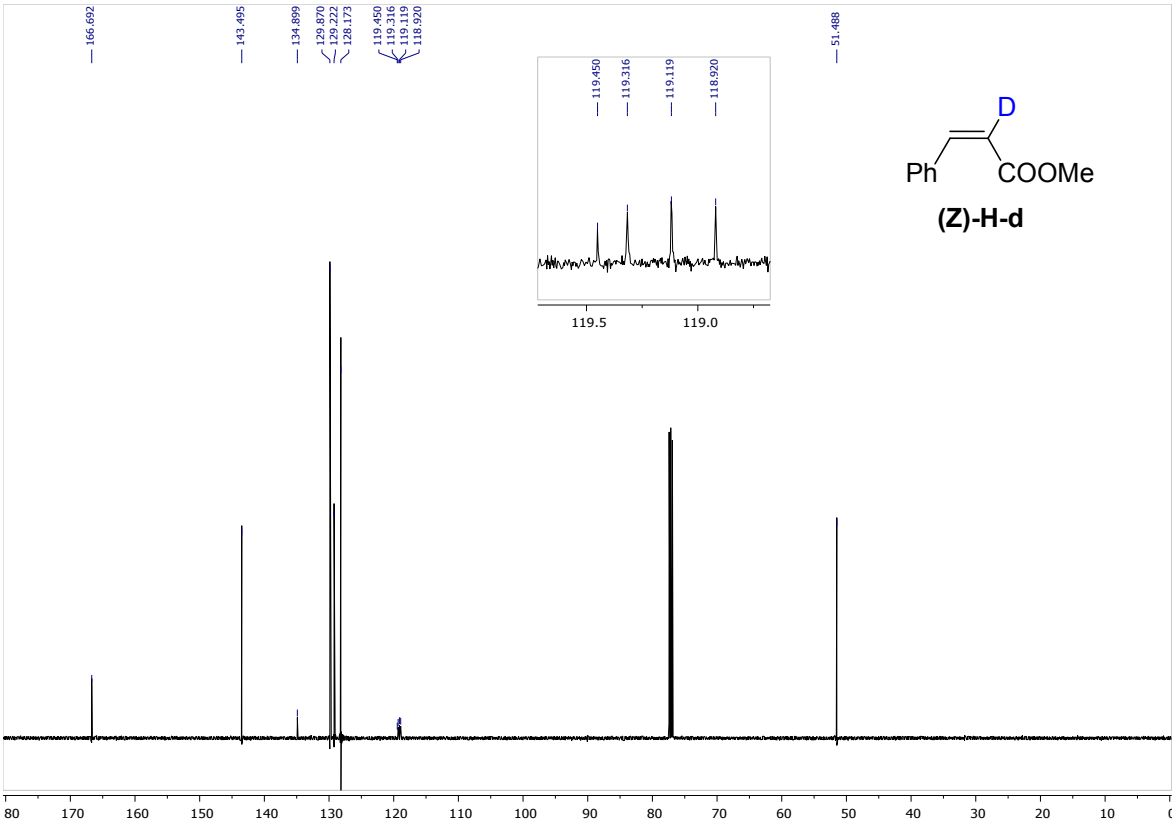


Fig. 71 ^{13}C NMR spectrum of ***(Z)*-H-*d*** (125 MHz, $CDCl_3$).

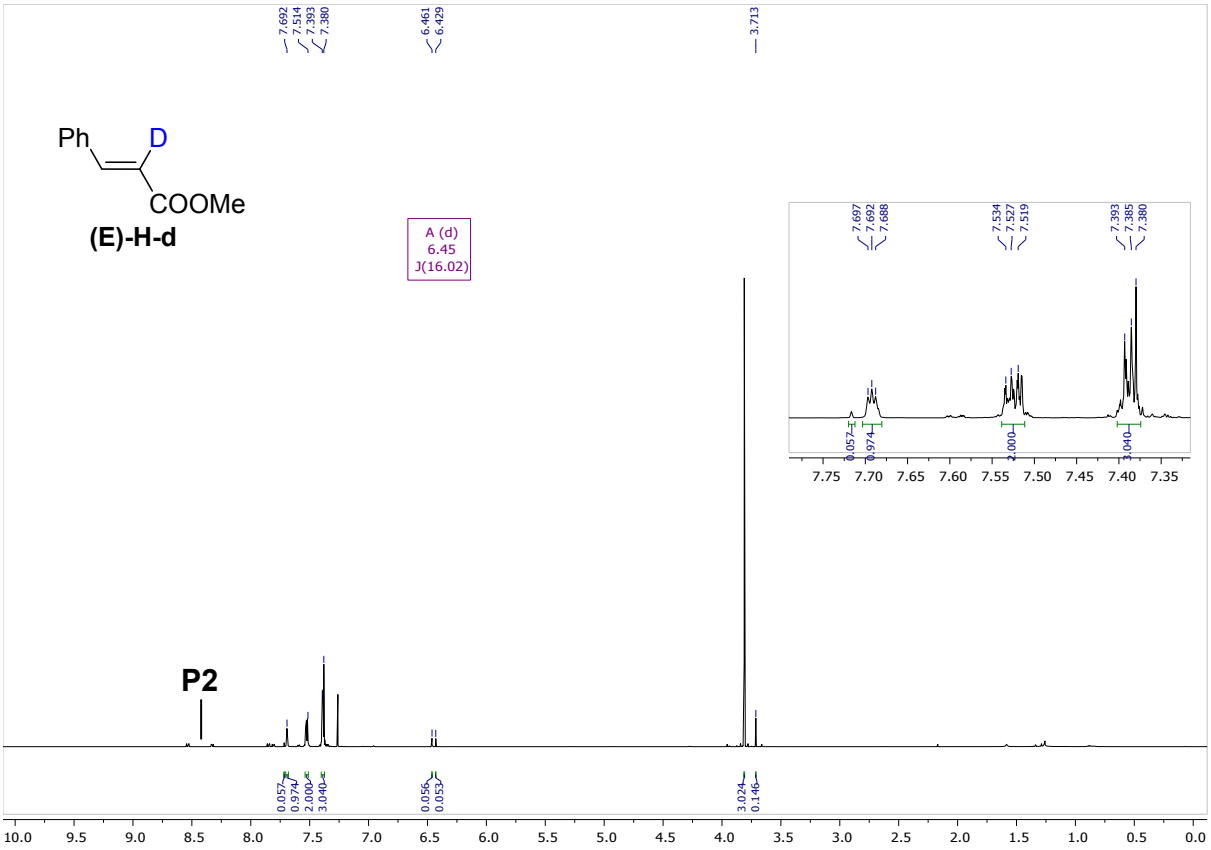


Fig. 72 ^{1}H NMR spectrum of ***(E)*-H-*d*** (500 MHz, $CDCl_3$).

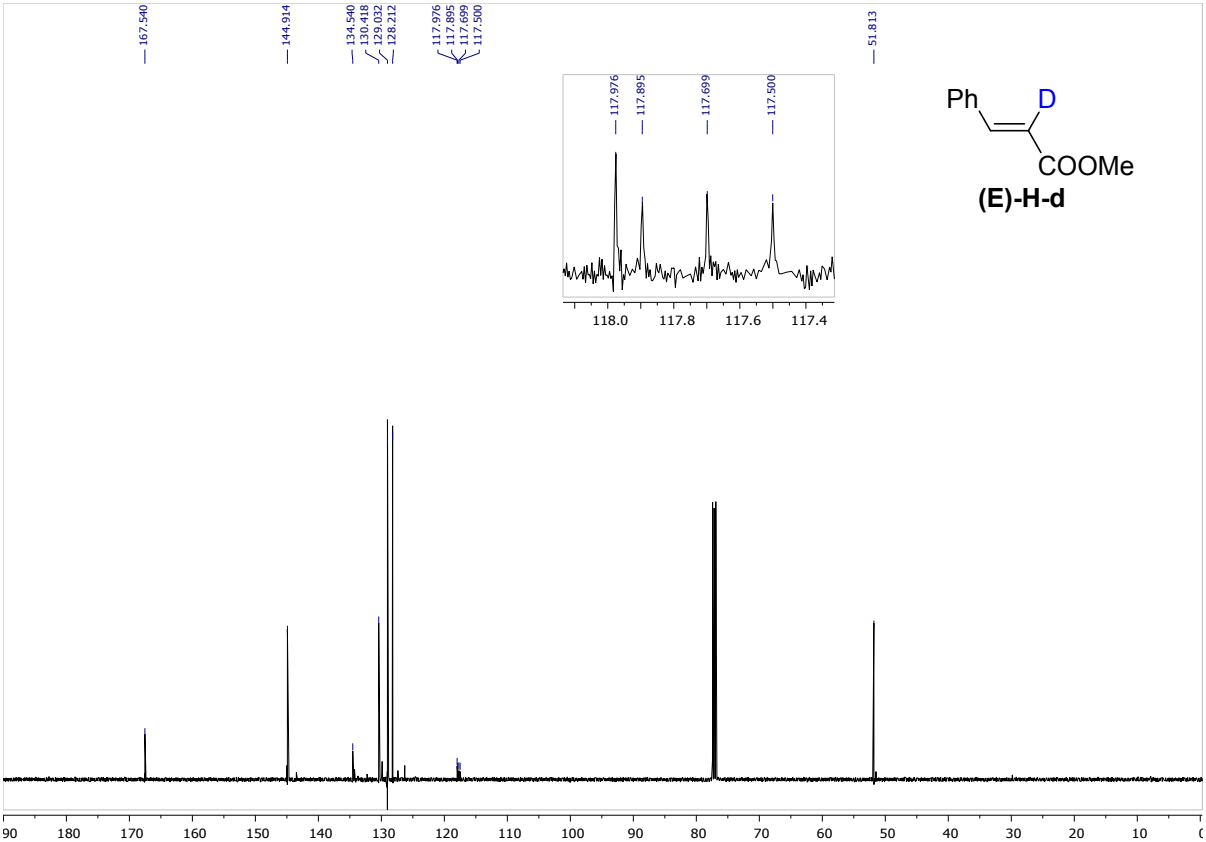


Fig. 73 ^{13}C NMR spectrum of ***(E)*-H-*d*** (125 MHz, $CDCl_3$).

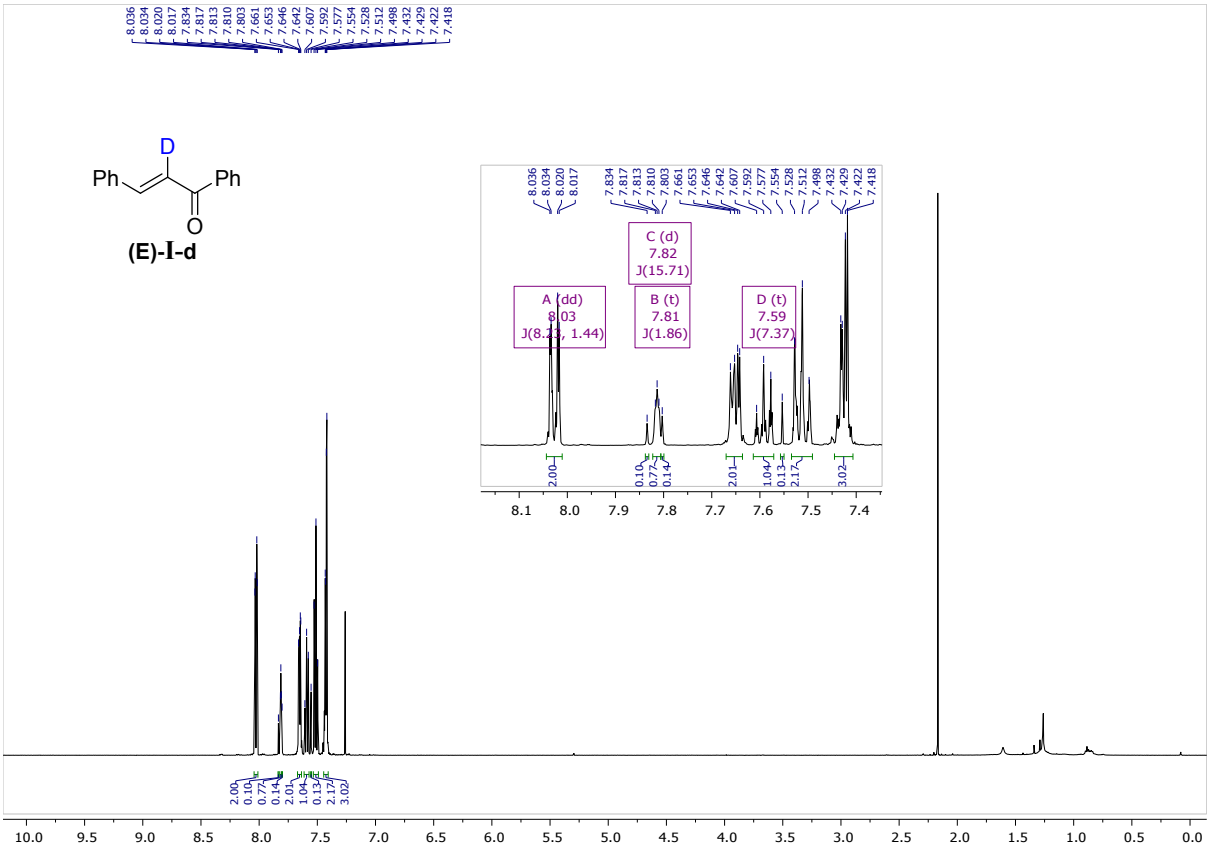


Fig. 74 ^{1}H NMR spectrum of **(E)-I-*d*** (500 MHz, $CDCl_3$).

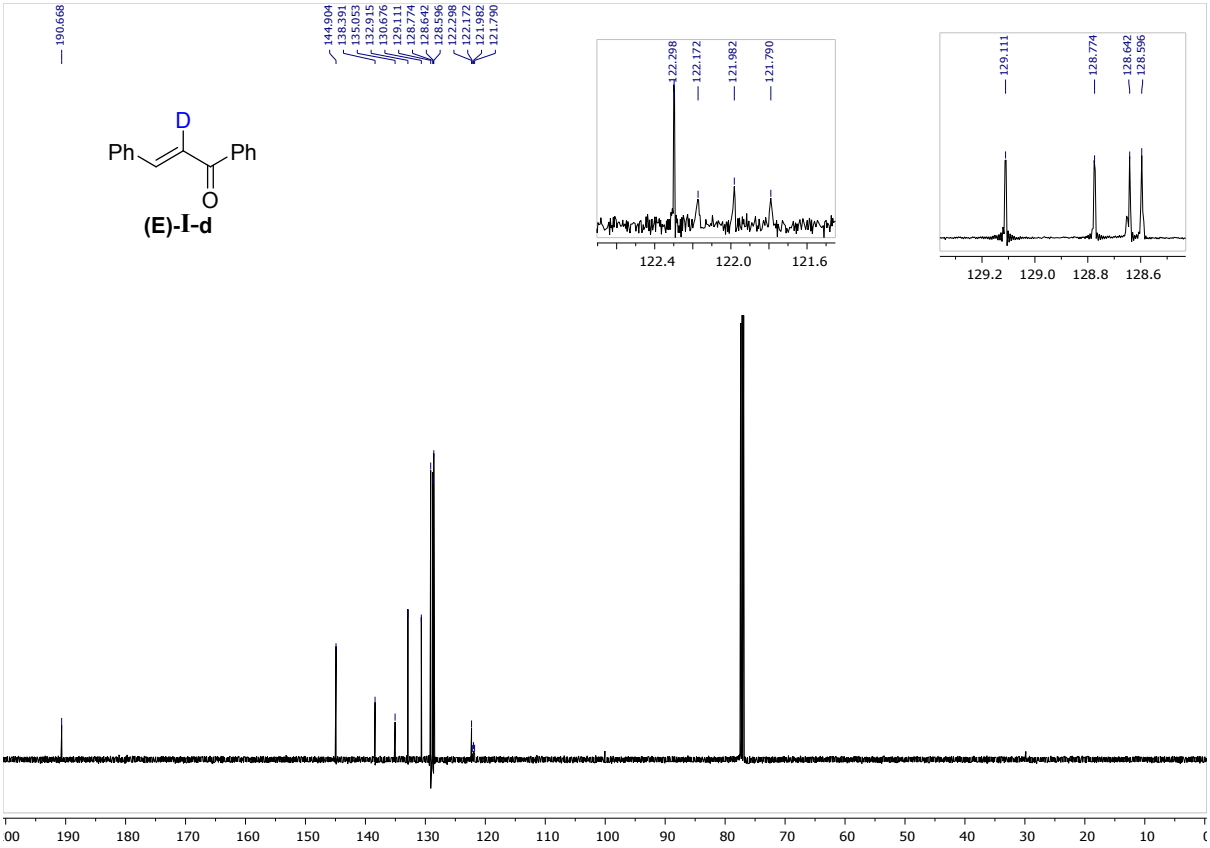


Fig. 75 ^{13}C NMR spectrum of **(E)-I-*d*** (125 MHz, $CDCl_3$).

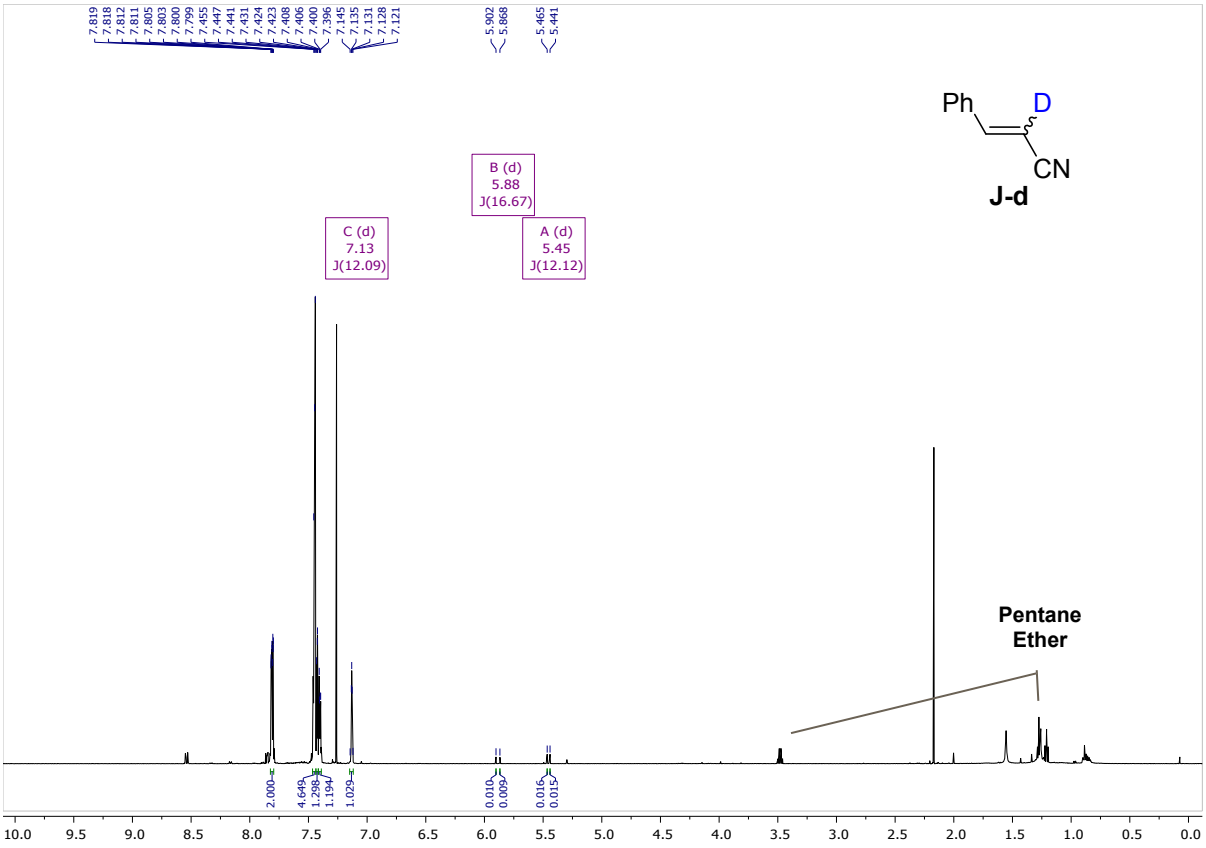


Fig. 76 ^{1}H NMR spectrum of **J-*d*** (500 MHz, $CDCl_3$).

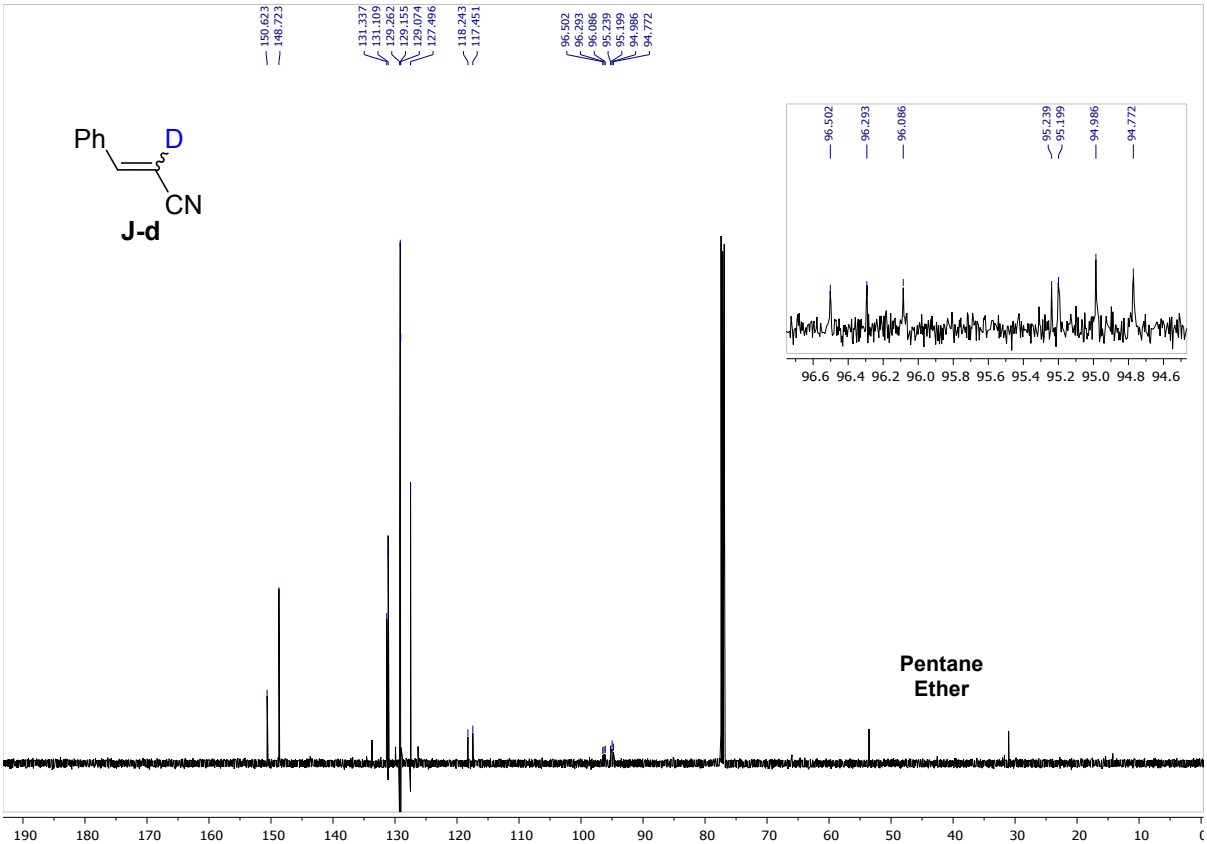


Fig. 77 ^{13}C NMR spectrum of **J-*d*** (125 MHz, $CDCl_3$).

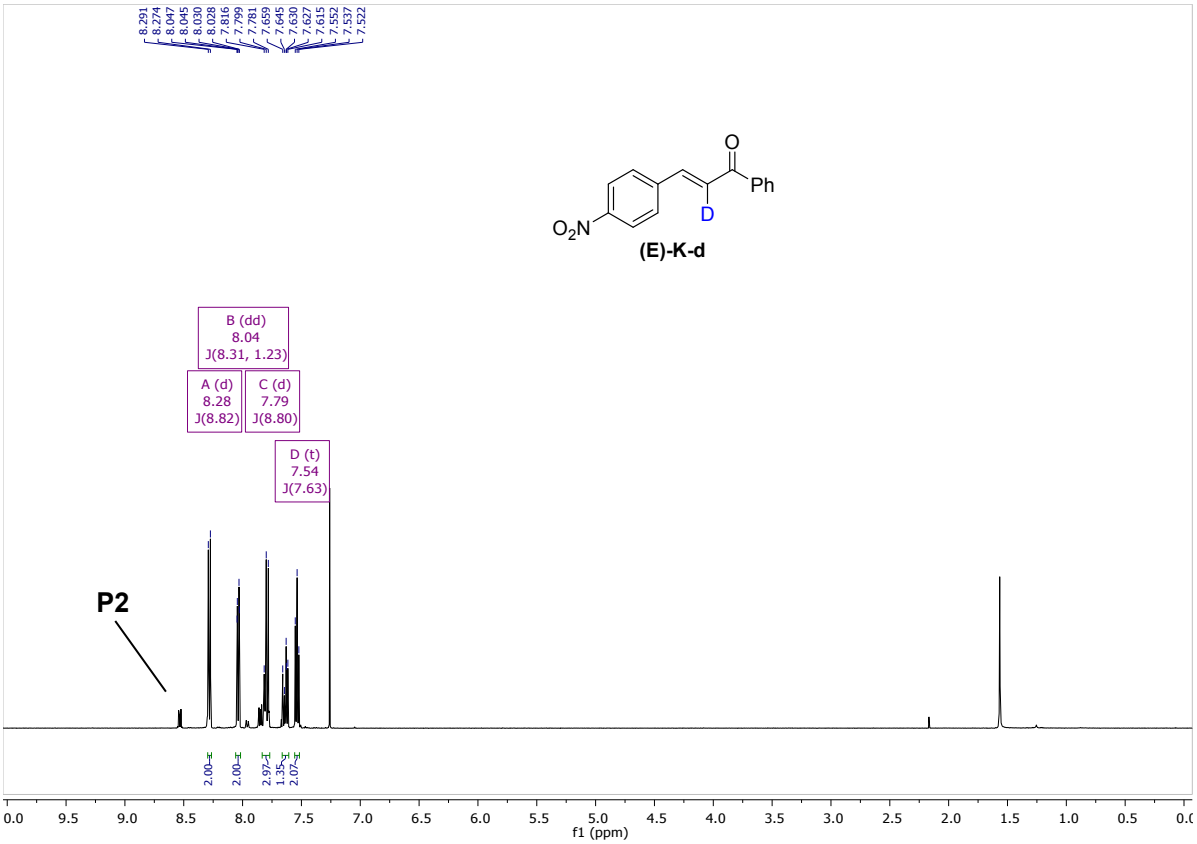


Fig. 78 ^{1}H NMR spectrum of **(E)-K-*d*** (500 MHz, $CDCl_3$).

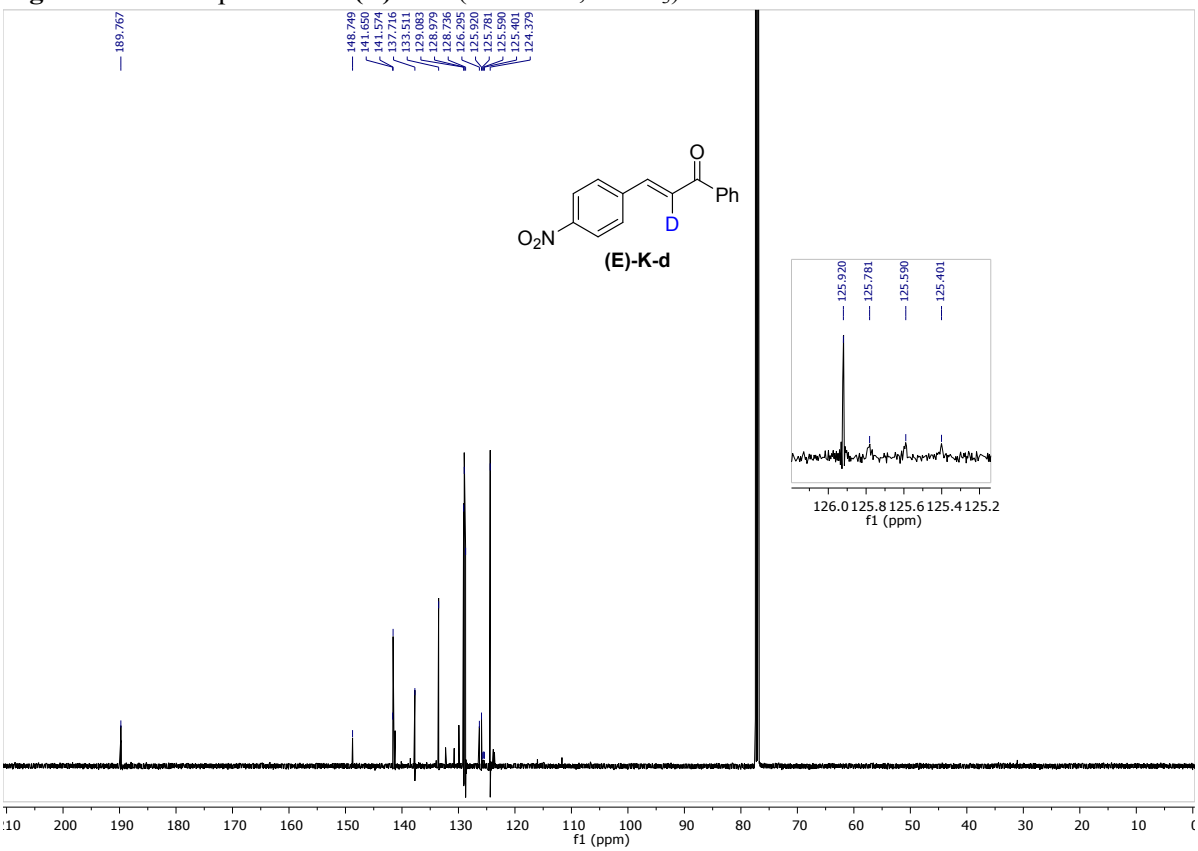


Fig. 79 ^{13}C NMR spectrum of **(E)-K-*d*** (125 MHz, $CDCl_3$).

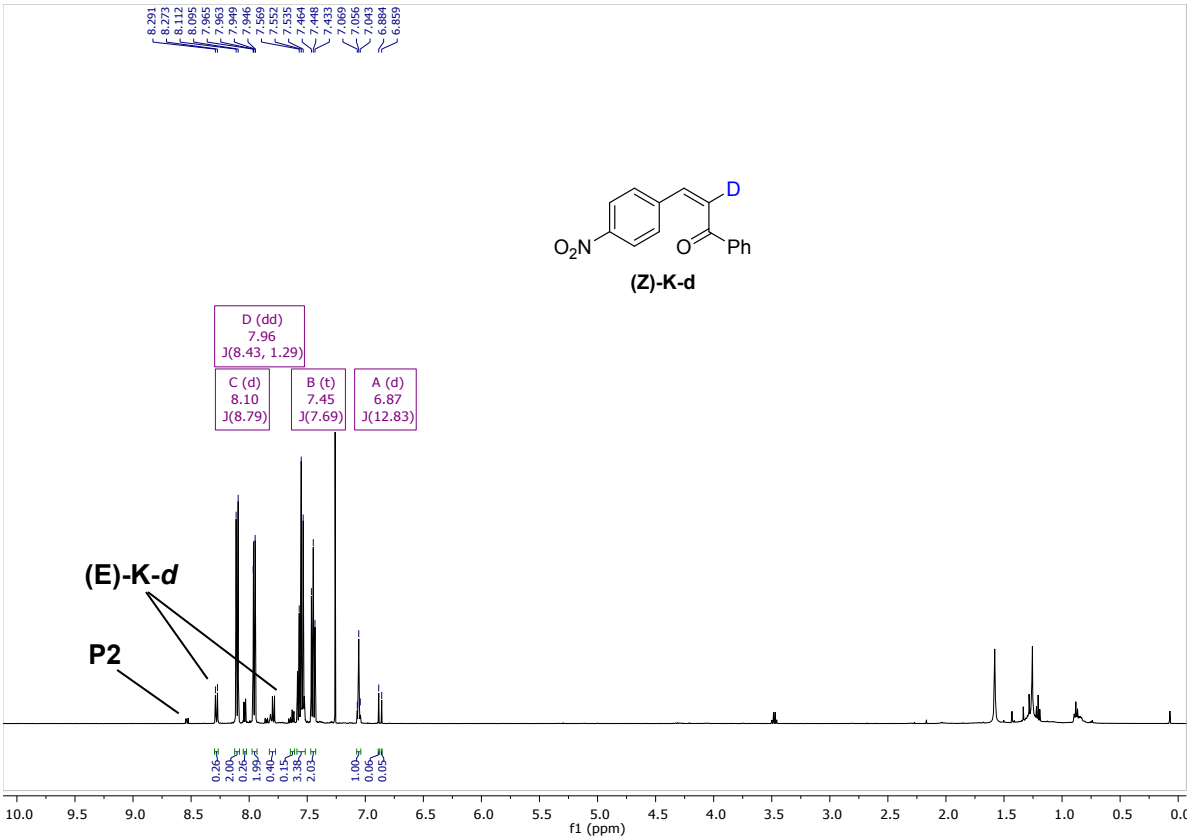


Fig. 80 ^{1}H NMR spectrum of **(Z)-K-*d*** (500 MHz, $CDCl_3$).

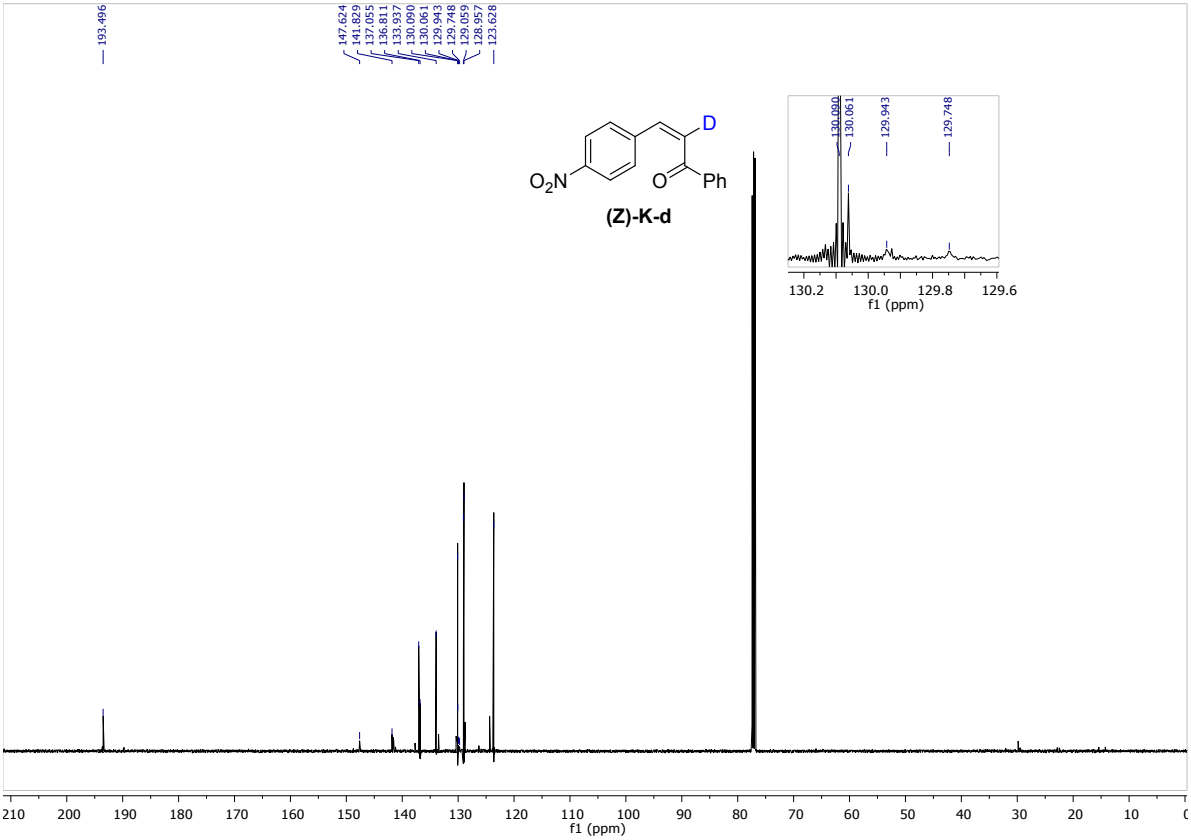


Fig. 81 ^{13}C NMR spectrum of **(Z)-K-*d*** (125 MHz, $CDCl_3$).

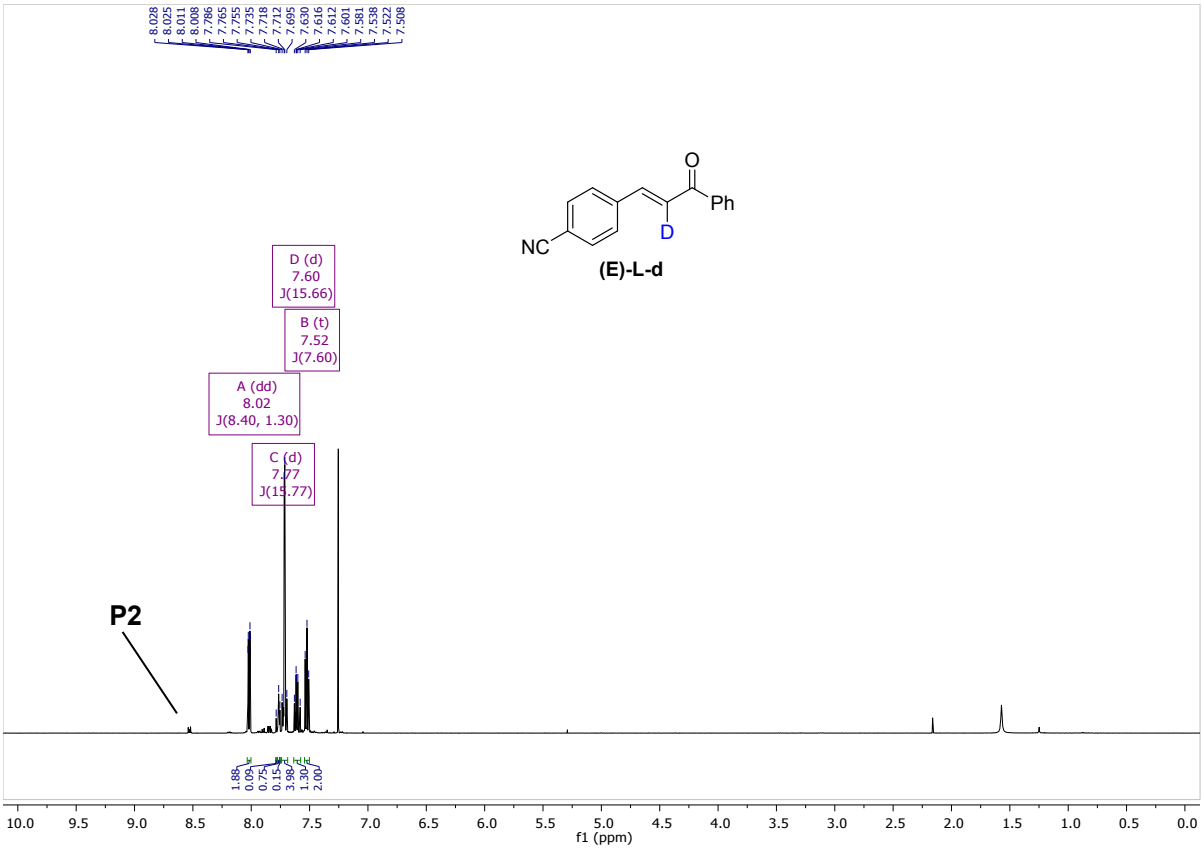


Fig. 82 ^{1}H NMR spectrum of **(E)-L-*d*** (500 MHz, $CDCl_3$).

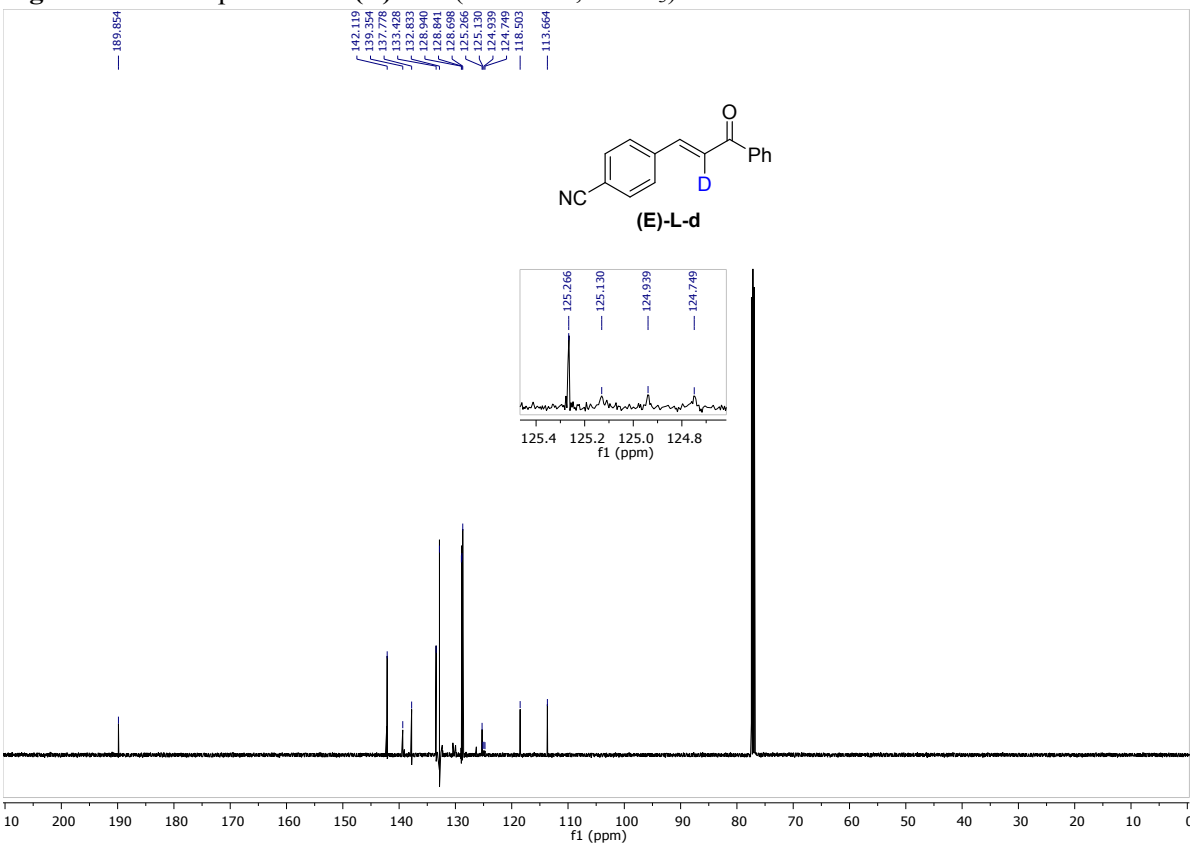


Fig. 83 ^{13}C NMR spectrum of **(E)-L-*d*** (125 MHz, $CDCl_3$).

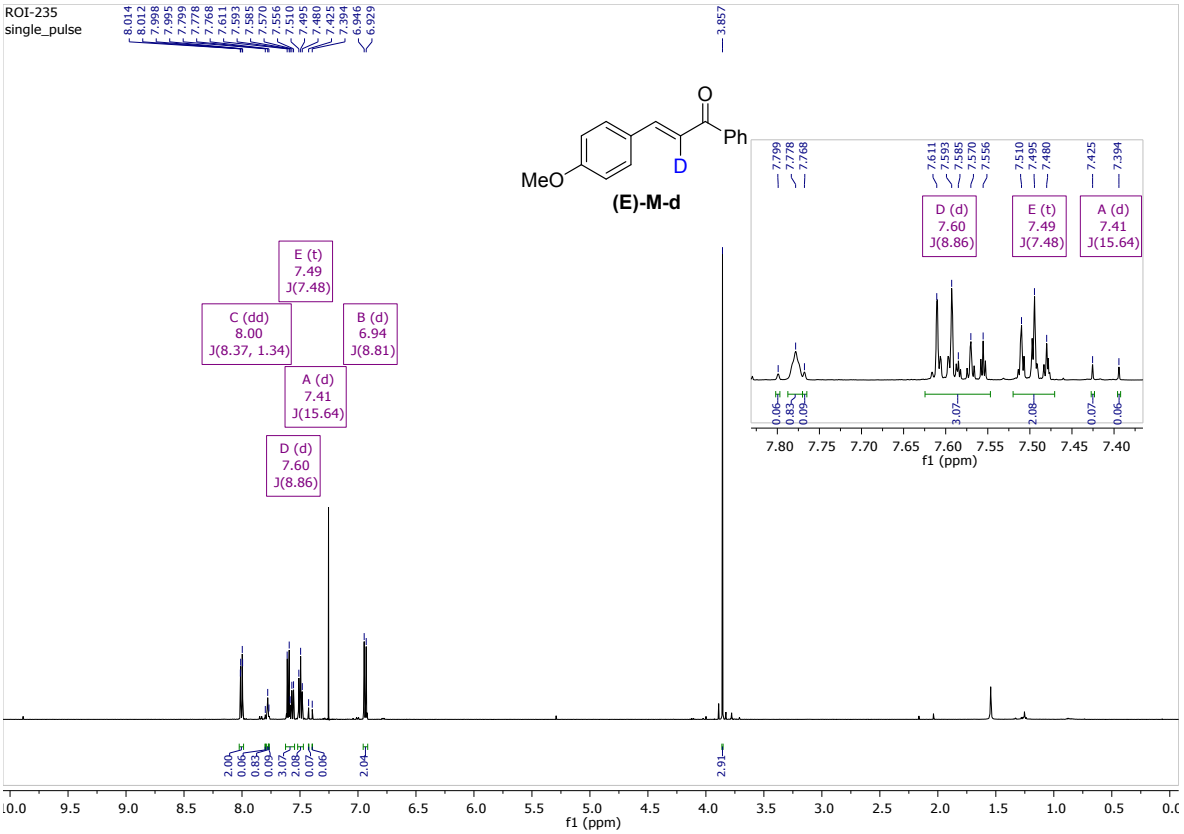


Fig. 84 ^{1}H NMR spectrum of **(E)-M-*d*** (500 MHz, $CDCl_3$).

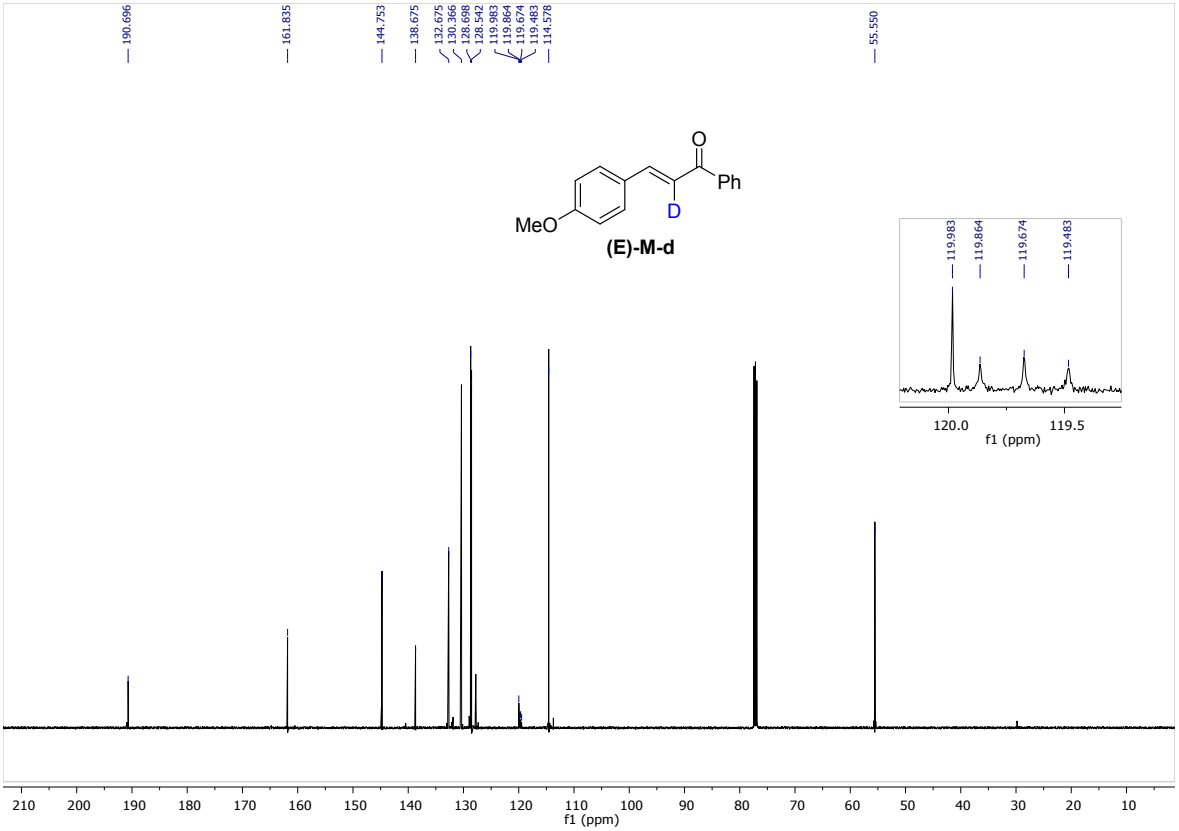


Fig. 85 ^{13}C NMR spectrum of **(E)-M-*d*** (125 MHz, $CDCl_3$).

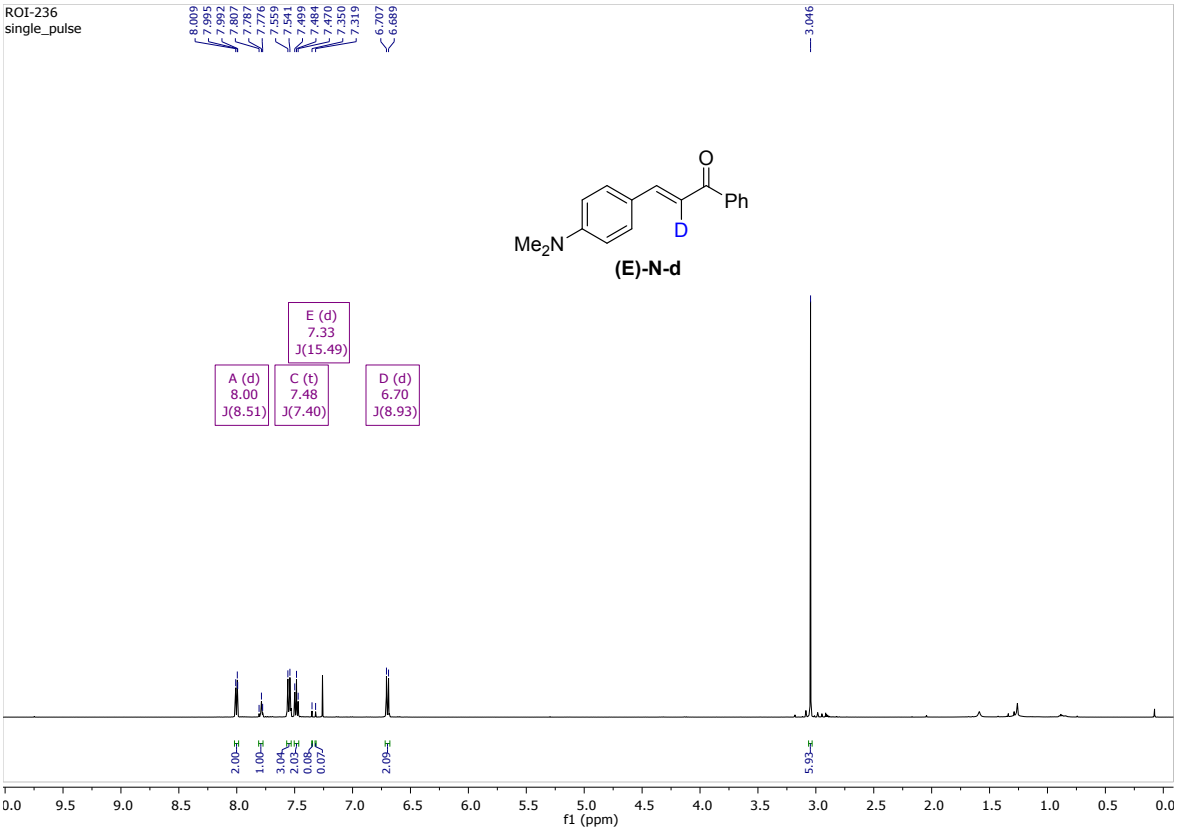


Fig. 86 ^{1}H NMR spectrum of **(E)-N-*d*** (500 MHz, $CDCl_3$).

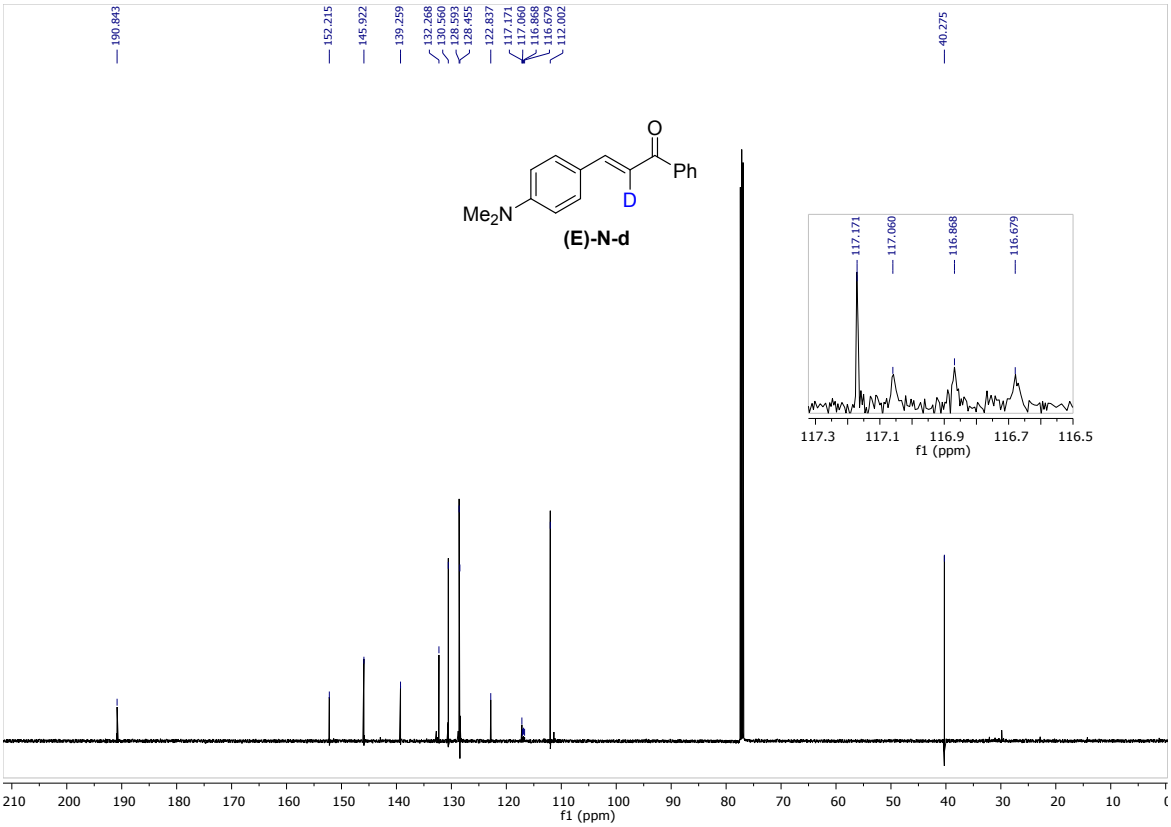


Fig. 87 ^{13}C NMR spectrum of **(E)-N-*d*** (125 MHz, $CDCl_3$).

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