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Formation of 1,2,4-oxadiazoles in the course of photooxidation of aromatic azides in acetonitrile

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General information

NMR spectra were recorded in $CDCl_3$ or CD_3CN (Acros Organics, 99.95 atom % D) at 500 and 125 MHz for ^1H and ^{13}C, respectively, on a Bruker Avance III 500 spectrometer using TMS as internal standard.

HPLC analysis was carried out on an YL9100 HPLC system.

Atmospheric pressure chemical ionization mass spectra (APCI-MS) were obtained on a HPLC mass-spectrometer LCMS-2010EV (Shimadzu) (direct syringe sample inlet, sample solution was in acetonitrile, mobile phase was $MeCN/H_2O$ (95:5)) in positive and negative ions mode at the corona discharge needle ionizing electrode potential of 4.5 and -3.5 kV, respectively. The mobile phase flow rate was 0.1 ml min^{-1}. The nebulizer gas (nitrogen) flow rate was 1.5 dm min^{-1}. The temperature of the APCI interface, curved desolvation line and heater was 250°C, 230°C and 200°C, respectively.

High resolution mass spectra were recorded on a mass spectrometer MALDI-TOF Autoflex III (Bruker, Germany) with 2,5-dihydroxybenzoic acid as a matrix. Samples of compounds were prepared by "dried droplet" method (1:10).

Preparation of starting azides

Starting azides **1a**–**c** were synthesized from the corresponding anilines as described [P.A.S. Smith, J.H. Boyer, *Org. Synth.*, 1963, **4**, 75]. Phenyl azide (**1a**): ^1H NMR (500 MHz, CD_3CN, TMS): δ (ppm) = 7.06 (d, 2H, ^3J = 8.3, H-2(6)); 7.17 (t, 1H, ^3J = 7.5, H-4); 7.38 (dd, 2H, ^3J = 8.3, ^3J = 7.5, H-3(5)). ^{13}C NMR (125 MHz, CD_3CN, TMS): δ (ppm) = 119.99 (2CH, C2(6)); 125.99 (CH, C4); 130.91 (2CH, C3(5)); 141.02 (C, C1). ^{15}N NMR (51 MHz, CD_3CN, TMS): δ (ppm) = 90.56 (N1').

4-Chlorophenyl azide (**1b**): ^1H NMR (500 MHz, CD_3CN, TMS): δ (ppm) = 7.04 (d, 2H, ^3J = 8.6, H-2(6)); 7.37 (d, 2H, ^3J = 8.6, H-3(5)). ^{13}C NMR (125 MHz, CD_3CN, TMS): δ (ppm) = 121.62 (2CH, C2(6)); 130.67 (C, C4); 130.79 (2CH, C3(5)); 140.04 (C, C1). ^{15}N NMR (51 MHz, CD_3CN, TMS): δ (ppm) = 90.29 (N1').

4-Bromophenyl azide (**1c**): ^{1}H NMR (500 MHz, CD_3CN, TMS): δ (ppm) = 6.99 (d, 2H, ^{3}J = 8.6, H-2(6)); 7.51 (d, 2H, ^{3}J = 8.6, H-3(5)). ^{13}C NMR (125 MHz, CD_3CN, TMS): δ (ppm) = 118.21 (C, C4); 122.01 (2CH, C2(6)); 133.76 (2CH, C3(5)); 140.58 (C, C1). ^{15}N NMR (51 MHz, CD_3CN, TMS): δ (ppm) = 90.49 (N1').

4-Methoxyphenyl azide (**1d**): ^{1}H NMR (500 MHz, CD_3CN, TMS): δ (ppm) = 3.76 (s, 3H, OMe); 6.93 (d, 2H, ^{3}J = 8.9, H-3(5)); 6.99 (d, 2H, ^{3}J = 8.9, H-2(6)). ^{13}C NMR (125 MHz, CD_3CN, TMS): δ (ppm) = 56.25 (CH_3, OMe); 116.21 (2CH, C3(5)); 121.05 (2CH, C2(6)); 133.20 (C, C1); 158.22 (C, C4). ^{15}N NMR (51 MHz, CD_3CN, TMS): δ (ppm) = 87.37 (N1').

General procedure for the photooxidation of aryl azides

Solutions of azides **1a**–**c** in aerated acetonitrile were placed into glass flasks with ground-glass stoppers and irradiated by means of a 120 W Xe lamp through an NS-8 filter (>300 nm) at room temperature until the azide conversion reached ~95%. The progress of the reaction was monitored by reverse-phase HPLC [analytical column: ProteCol C18 GP 125, 5 μ, 250×4.6 mm; mobile phase: MeCN/H_2O = 70:30 or 60:30]. Nitroso- and nitrobenzenes were identified by comparison with the authentic samples. At the end of the reaction, the solvent was removed from the reaction mixtures; the residue was dissolved in isopropanol (~0.5 ml) and separated by normal-phase HPLC [column: Kromasil 200 Si, 5 μ, 250 × 10 mm (Dr. Maish GmbH; mobile phase: hexane/isopropanol = 85:15].

Products of the photooxidation of azide 1a (16 mg, 0.134 mmol, 96% conv.). (4*E*)-5-(5-Methyl-1,2,4-oxadiazol-3-yl)penta-2,4-dienal (**2a**, 7 mg, 0.043 mmol, 32%); *cis*, *trans*-**2a**: ^{1}H NMR (500 MHz, CD_3CN, TMS): δ (ppm) = 2.61 (s, 3H, H(8)); 6.36 (ddt, $^{3}J_{2\text{-}1}$ = 7.8 Hz, $^{3}J_{2\text{-}3}$ = 15.4 Hz, $^{4}J_{2\text{-}4}$ = 0.8 Hz, $^{5}J_{2\text{-}5}$ = 0.8 Hz, 1H, H(2)); 6.67 (dt, $^{3}J_{5\text{-}4}$ = 11.5 Hz, $^{4}J_{5\text{-}3}$ = 0.8 Hz, $^{5}J_{2\text{-}5}$ = 0.8 Hz, 1H, H(5)); 6.86 (td, $^{3}J_{4\text{-}3}$ = 11.5 Hz, $^{3}J_{4\text{-}5}$ = 11.5 Hz, $^{4}J_{4\text{-}2}$ = 0.8 Hz, 1H, H(4)); 8.49 (ddd, $^{3}J_{3\text{-}2}$ = 15.4 Hz, $^{3}J_{3\text{-}4}$ = 11.5 Hz, $^{4}J_{3\text{-}5}$ = 0.8 Hz, 1H, H(3)); 9.70 (d, $^{3}J_{1\text{-}2}$ = 7.8, 1H, H(1)). ^{13}C NMR (125 MHz, CD_3CN, TMS): δ (ppm) = 12.62 (CH_3, C(8)); 122.30 (CH, C(5)); 135.95 (CH, C(4)); 137.09 (CH, C(2)); 147.25 (CH, C(3)); 167.68 (C, C(6)); 178.25 (CC, (7)); 195.08 (CH, C(1)). *trans*, *trans*-**2a**: ^{1}H NMR (500 MHz, CD_3CN, TMS): δ (ppm) = 2.57 (s, 3H, H(8)); 6.41 (dd, $^{3}J_{2\text{-}3}$ = 14.9 Hz, $^{3}J_{2\text{-}1}$ = 7.8 Hz, 1H, H(2)); 7.03 (d, $^{3}J_{5\text{-}4}$ = 15.1 Hz, 1H, H(5)); 7.40 (dd, $^{3}J_{3\text{-}2}$ = 14.9 Hz, $^{3}J_{3\text{-}4}$ = 11.3 Hz, 1H, H(3)); 7.48 (dd, $^{3}J_{4\text{-}5}$ = 15.1 Hz, $^{3}J_{4\text{-}3}$ = 11.3 Hz, 1H, H(4)); 9.65 (d, $^{3}J_{1\text{-}2}$ = 7.8, 1H, H(1)). ^{13}C NMR (125 MHz, CD_3CN, TMS): δ (ppm) = 12.56 (CH_3, C(8)); 125.77 (CH, C(5)); 136.27 (CH, C(2)); 136.62 (CH, C(4)); 149.87 (CH, C(3)); 168.02 (C, C(6)); 178.22 (C, C(7)); 194.81 (CH, C(1)). APCI-MS, *m/z* (relative intensity): 165(100) $[M+H]^+$, 164(100) $[M-H]^-$, 163(16) M^-. HR-MS (MALDI) calcd for $C_8H_9N_2O_2$ $[M+H]^+$: 165.0658. Found: 165.0664. $PhNO_2$ (1 mg, 0.008 mmol, 6%).

Products of the photooxidation of azide 1b (14 mg, 0.092 mmol, 96% conv.). (4*E*)-3-Chloro-5-(5-methyl-1,2,4-oxadiazol-3-yl)penta-2,4-dienal (**2b**, 7 mg, 0.035 mmol, 38%); *trans, cis*-**2b**: ^{1}H NMR (500 MHz, CD_3CN, TMS): δ (ppm) = 2.59 (s, 3H, H(8)); 6.48 (dt, $^{3}J_{2\text{-}1}$ = 6.4 Hz, $^{4}J_{2\text{-}4}$ = 0.8 Hz, $^{5}J_{2\text{-}5}$ = 0.8 Hz, 1H, H(2)); 7.30 (dd, $^{3}J_{5\text{-}4}$ = 15.0 Hz, $^{5}J_{5\text{-}2}$ = 0.8 Hz, 1H, H(5)); 8.26 (dd, $^{3}J_{4\text{-}5}$ = 15.0 Hz, $^{4}J_{4\text{-}2}$ = 0.8 Hz, 1H, H(4)); 10.05 (d, $^{3}J_{1\text{-}2}$ = 6.4, 1H, H(1)). ^{13}C NMR (125 MHz, CD_3CN, TMS): δ (ppm) = 12.60 (CH_3, C(8)); 125.24 (CH, C(5)); 130.78 (CH, C(4)); 131.70 (CH, C(2)); 147.06 (C, C(3)); 167.69 (C, C(6)); 178.57 (C, C(7)); 189.13 (CH, C(1)). *trans, trans*-**2b**: ^{1}H NMR (500 MHz, CD_3CN, TMS): δ (ppm) = 2.58 (s, 3H, H(8)); 6.52 (dt, $^{3}J_{2\text{-}1}$ = 7.0 Hz, $^{4}J_{2\text{-}4}$ = 0.7 Hz, $^{5}J_{2\text{-}5}$ = 0.7 Hz, 1H, H(2)); 7.37 (dd, $^{3}J_{5\text{-}4}$ = 15.2 Hz, $^{5}J_{5\text{-}2}$ = 0.7 Hz, 1H, H(5)); 7.55 (dd, $^{3}J_{4\text{-}5}$ = 15.2 Hz, $^{4}J_{4\text{-}2}$ = 0.7 Hz, 1H, H(4)); 10.18 (d, $^{3}J_{1\text{-}2}$ = 6.4, 1H, H(1)). ^{13}C NMR (125 MHz, CD_3CN, TMS): δ (ppm) = 12.57 (CH_3, C(8)); 123.76 (CH, C(5)); 130.90 (CH, C(2)); 135.86 (CH, C(4)); 147.45 (C, C(3)); 167.59 (C, C(6)); 178.51 (C, C(7)); 192.11 (CH, C(1)). APCI-MS, *m/z* (relative intensity): 199(69)/201(25) $[M+H]^+$. HR-MS (MALDI) calcd for $C_8H_7ClN_2O_2$ $[M]^+$: 198.0196/200.0161. Found: 198.0236/200.0198. 4-Chloronitrobenzene (1 mg, 0.006 mmol, 6%).

Products of the photooxidation of azide 1c (18 mg, 0.091 mmol, 95% conv.). (4*E*)-3-bromo-5-(5-methyl-1,2,4-oxadiazol-3-yl)penta-2,4-dienal (**2c**) (6 mg, 0.025 mmol, 27%); *trans, cis*-**2c**: ^{1}H NMR (500 MHz, CD_3CN, TMS): δ (ppm) = 2.59 (s, 3H, H(8)); 6.75 (dt, $^{3}J_{2\text{-}1}$ = 6.1 Hz, $^{4}J_{2\text{-}4}$ = 0.8 Hz, $^{5}J_{2\text{-}5}$ = 0.8 Hz, 1H, H(2)); 7.23 (dd, $^{3}J_{5\text{-}4}$ = 15.0 Hz, $^{5}J_{5\text{-}2}$ = 0.8 Hz, 1H, H(5)); 8.19 (dd, $^{3}J_{4\text{-}5}$ = 15.0 Hz, $^{4}J_{4\text{-}2}$ = 0.8 Hz, 1H, H(4)); 9.98 (d, $^{3}J_{1\text{-}2}$ = 6.1, 1H, H(1)). ^{13}C NMR (125 MHz, CD_3CN, TMS): δ (ppm) = 12.61 (CH_3, C(8)); 127.50 (CH, C(5)); 132.20 (CH, C(4)); 135.88 (CH, C(2)); 141.93 (C, C(3)); 167.55 (C, C(6)); 178.57 (C, C(7)); 188.90 (CH, C(1)). *trans, trans*-**2c**: ^{1}H NMR (500 MHz, CD_3CN, TMS): δ (ppm) = 2.58 (s, 3H, H(8)); 6.74 (dt, $^{3}J_{2\text{-}1}$ = 6.8 Hz, $^{4}J_{2\text{-}4}$ = 0.7 Hz, $^{5}J_{2\text{-}5}$ = 0.7 Hz, 1H, H(2)); 7.35 (dd, $^{3}J_{5\text{-}4}$ = 15.2 Hz, $^{5}J_{5\text{-}2}$ = 0.7 Hz, 1H, H(5)); 7.53 (dd, $^{3}J_{4\text{-}5}$ = 15.2 Hz, $^{4}J_{4\text{-}2}$ = 0.7 Hz, 1H, H(4)); 10.07 (d, $^{3}J_{1\text{-}2}$ = 6.8, 1H, H(1)). ^{13}C NMR (125 MHz, CD_3CN, TMS): δ (ppm) = 12.58 (CH_3, C(8)); 127.57 (CH, C(5)); 133.52 (CH, C(2)); 137.32 (CH, C(4)); 139.46 (C, C(3)); 167.60 (C, C(6)); 178.51 (C, C(7)); 194.23 (CH, C(1)). APCI-MS, *m/z* (relative intensity): 243(54)/245(65) $(M+H)^+$. HR-MS (MALDI) calcd for $C_8H_8BrN_2O_2$ $[M+H]^+$: 242.9764/244.9738. Found: 242.9719/244.9768. 4-Bromonitrobenzene (4 mg, 0.020 mmol, 22%).

Products of the photooxidation of azide 1d (15 mg, 0.101 mmol, 92% conv.). (2*E*,4*E*)-3-Methoxy-5-(5-methyl-1,2,4-oxadiazol-3-yl)penta-2,4-dienal (*trans, cis*-**2d**, 9 mg, 0.046 mmol, 46%): ^{1}H NMR (500 MHz, CD_3CN, TMS): δ (ppm) = 2.58 (s, 3H, H(8)); 3.82 (s, 3H, H(9)); 5.63 (d, $^{3}J_{2\text{-}1}$ = 7.1 Hz, 1H, H(2)); 7.21 (d, 1H, $^{3}J_{5\text{-}4}$ = 15.5 Hz, H(5)); 7.95 (d, 1H, $^{3}J_{4\text{-}5}$ = 15.5 (H(4)); 10.03 (d, $^{3}J_{1\text{-}2}$ = 7.1, 1H, H(1)). ^{13}C NMR (125 MHz, CD_3CN, TMS): δ (ppm) = 12.61 (CH_3, C(8)); 57.14 (CH_3, C(9)); 108.12 (CH, C(2)); 121.50 (CH, C(5)); 128.89 (CH, C(4)); 167.96 (C, C(6)); 168.34 (C, C(3)); 178.30 (C, C(7)); 190.25 (CH, C(1)). APCI-MS, *m/z* (relative intensity): 195(100) $[M+H]^+$. HR-MS

(MALDI) calcd for $C_9H_{11}N_2O_3$ $[M+H]^+$: 195.0764. Found: 195.0802. (5*Z*)-5-Hydroxyimino-2-isopropoxycyclopenta-1,3-diene-1-carbaldehyde (**4'**, 1 mg, 0.006 mmol, 6%): ^{1}H NMR (500 MHz, CD_3CN, TMS): δ (ppm) = 1.42 (d, ^3J = 6.1, 6H, H(8,9)); 4.99 (sept, ^3J = 6.1, 1H, H(7)); 6.89 (d, $^3J_{4\text{-}5}$ = 5.9 Hz, 1H, H(4)); 7.15 (d, $^3J_{5\text{-}4}$ = 5.9 Hz, 1H, H(5)); 9.37 (s, 1H, H(6)); 13.63 (br.s. 1H, NOH). ^{13}C NMR (125 MHz, CD_3CN, TMS): δ (ppm) = 22.69 ($2CH_3$, C(8,9)); 78.79 (CH, C(7)); 106.90 (C, C(2)); 124.04 (CH, C(4)); 140.14 (CH, C(5)); 155.04 (C, C(1)); 181.89 (CH, C(6)); 183.18 (C, C(3)). APCI-MS, *m/z* (relative intensity): 182(40) $[M+H]^+$, 180(100) $[M-H]^-$. HR-MS (MALDI) calcd for $C_9H_{12}NO_3$ $[M+H]^+$: 182.0812. Found: 182.0771. 4-Methoxynitrobenzene (1 mg, 0.006 mmol, 6%).

HPLC chromatograms

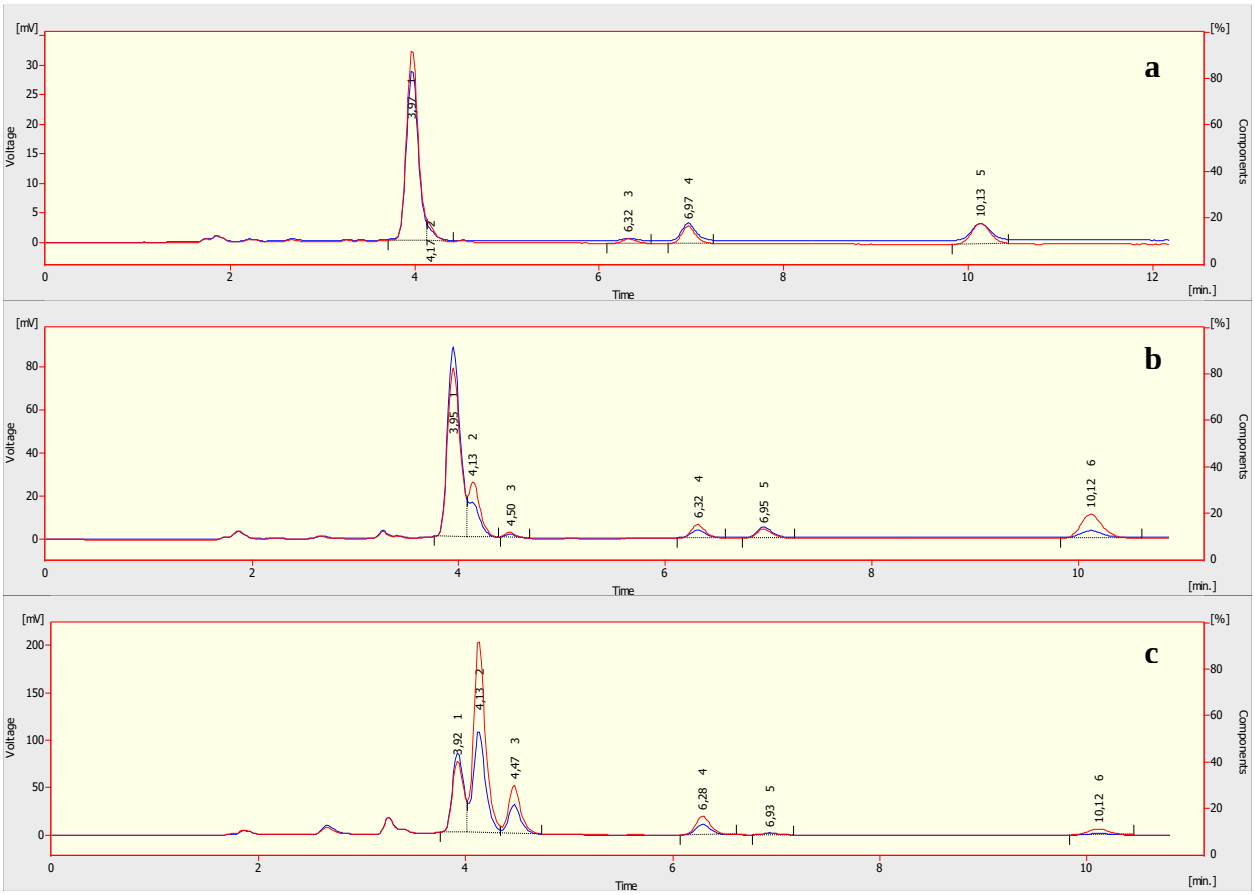


Figure S1. Chromatogram of the reaction mixture obtained by photolysis of the azide **1a** solution (8.59×10^{-4} M) in aerated acetonitrile at room temperature. The mobile phase is $MeCN/H_2O$ = 60/40, detection at 300 and 310 nm. t_R = 3.9 min (nitrile oxide **Ba**); t_R = 4.13 and 4.50 min (isomeric forms of 1,2,4-oxadiazole **2a**); t_R = 6.3 min (nitrobenzene); t_R = 6.9 min (nitrosobezene); t_R = 10.1 min (azide **1a**). The reaction time – 1 hour (a), 1 day (b), 3 days (c).

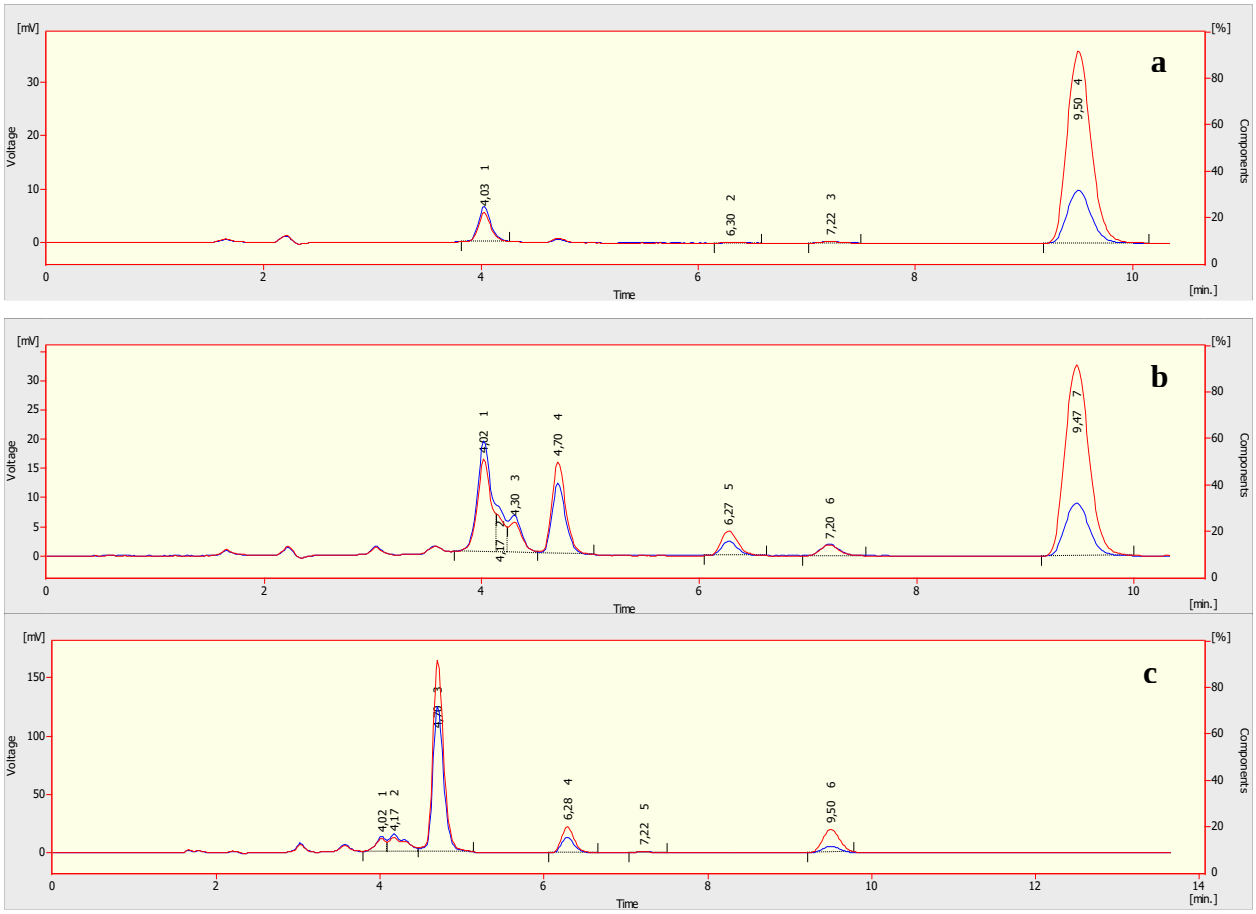


Figure S2. Chromatogram of the reaction mixture obtained by photolysis of the azide **1b** solution (6.47×10^{-4} M) in aerated acetonitrile at room temperature. The mobile phase is MeCN/H_2O = 70/30, detection at 290 and 300 nm. t_R = 4.0 min (nitrile oxide **Bb**); t_R = 4.7 min (isomers of 1,2,4-oxadiazole **2b**); t_R = 6.3 min (4-chloronitrobenzene); t_R = 7.2 min (4-chloronitrosobenzene); t_R = 9.5 min (azide **1b**). The reaction time – 1 hour (a), 1 day (b), 4 days (c).

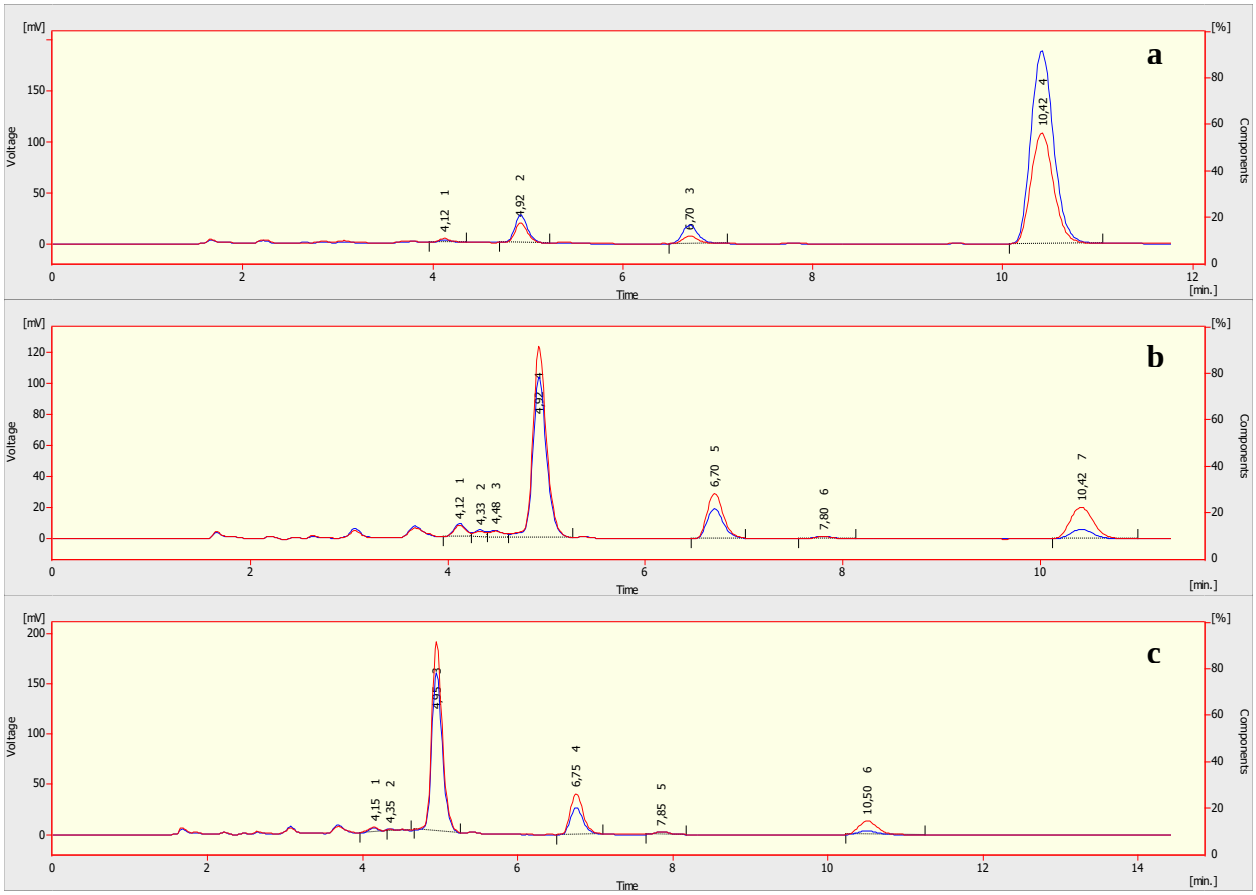


Figure S3. Chromatogram of the reaction mixture obtained by photolysis of the azide **1c** solution (6.13×10^{-4} M) in aerated acetonitrile at room temperature. The mobile phase is MeCN/H_2O = 70/30, detection at 290 and 300 nm. t_R = 4.1 min (nitrile oxide **Bc**); t_R = 4.9 min (isomers of 1,2,4-oxadiazole **2c**); t_R = 6.7 min (4-bromnitrobenzene); t_R = 7.8 min (4-bromnitrosobenzene); t_R = 10.5 min (azide **1c**). The reaction time – 1 hour (a), 1 day (b), 4 days (c).

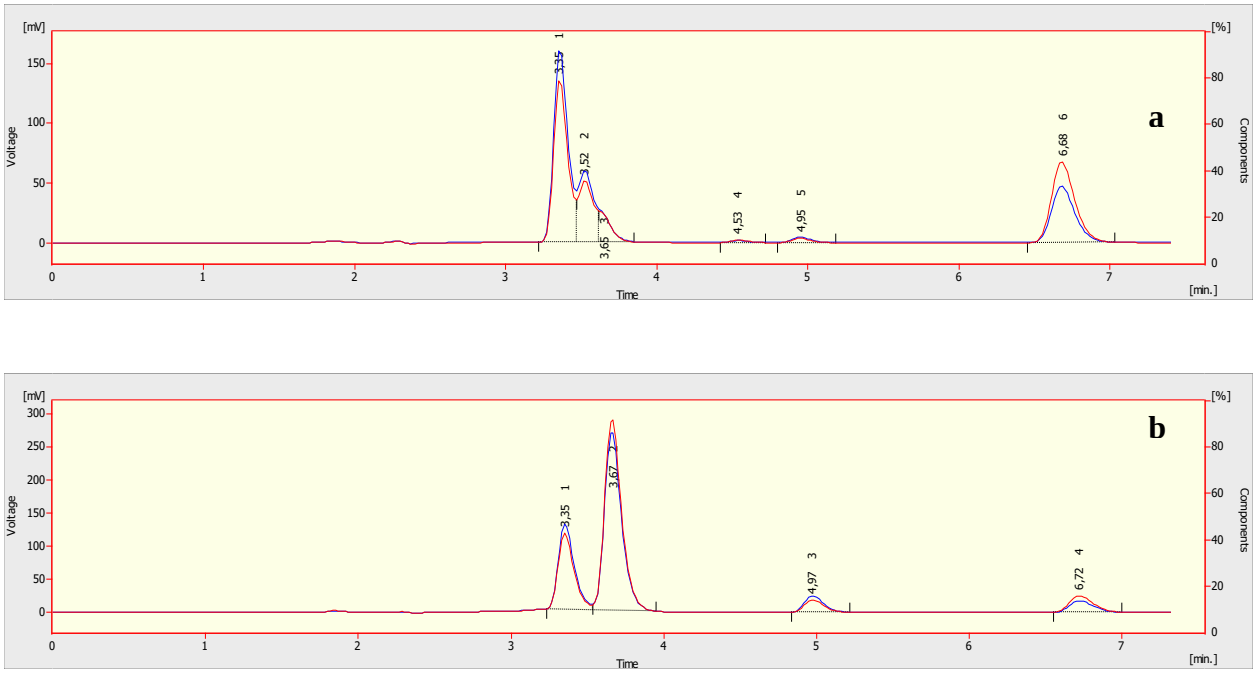
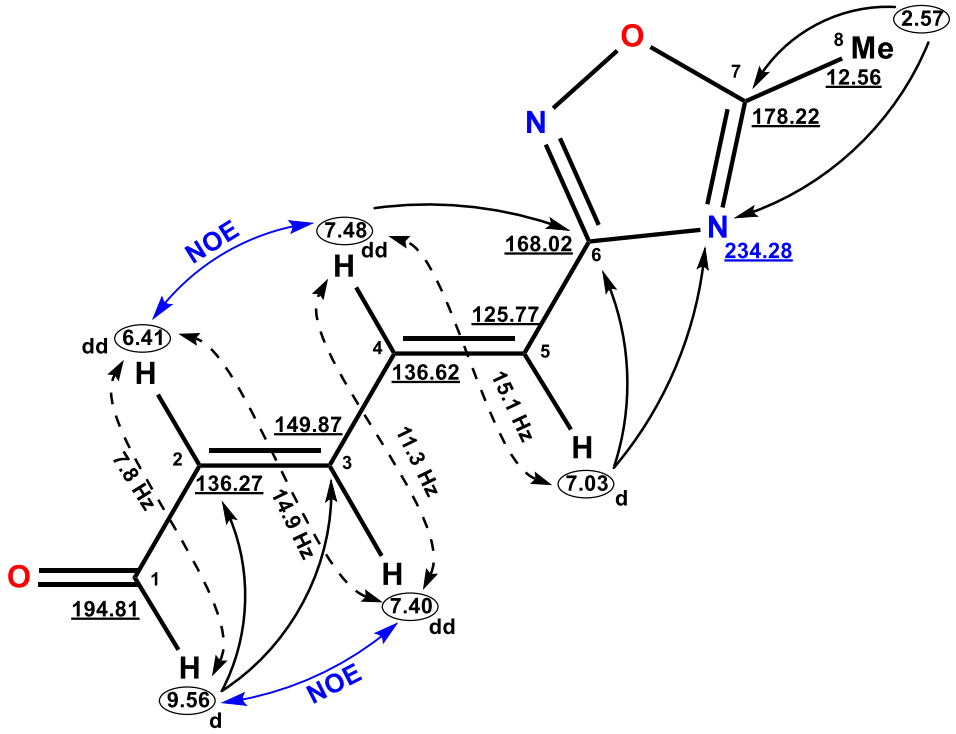
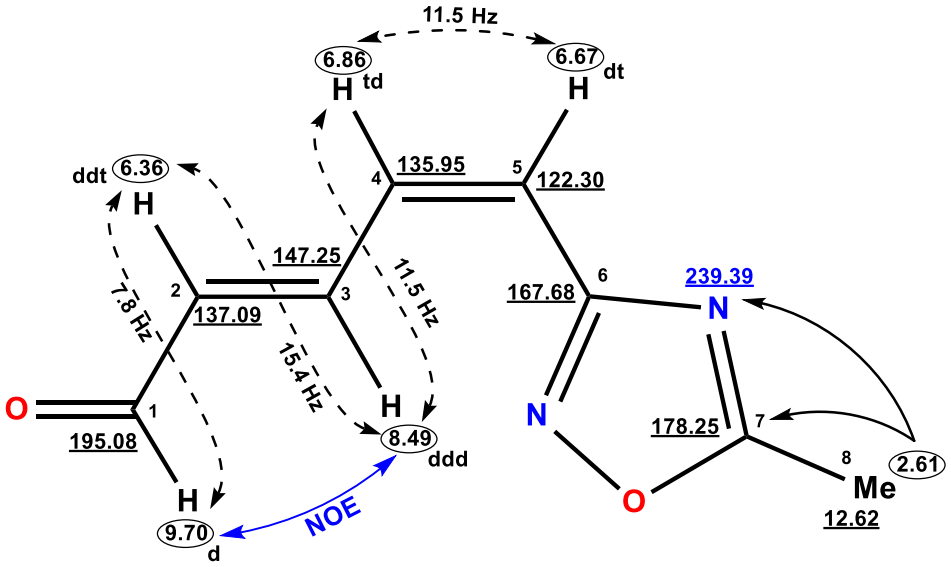


Figure S4. Chromatogram of the reaction mixture obtained by photolysis of the azide **1d** solution (6.86×10^{-4} M) in aerated acetonitrile at room temperature. The mobile phase is MeCN/H_2O = 70/30, detection at 290 and 300 nm. t_R = 3.35 min (nitrile oxide **Bd**); t_R = 3.5–3.7 min (1,2,4-oxadiazole **2d** and cyclopetadiene **4d**); t_R = 4.53 min (4-methoxynitrosobenzene); t_R = 4.97 min (4-methoxynitrobenzene); t_R = 6.7 min (azide **1d**). The reaction time – 5 hours (a), 3 days (b).

NMR data

NMR diagram of isomers of mixture *cis, trans*-**2a** and *trans, trans*-**2a** in CD_3CN. Chemical shifts (ppm), coupling constants (Hz) and significant {^{1}H, ^{13}C}, {^{1}H, ^{15}N} HMBC (solid arrow), {^{1}H, ^{1}H} COSY (dashed arrow) and NOESY (blue arrow) correlations.





rans, trans-**2a** *cis, trans*-**2a**

3.3 : 1

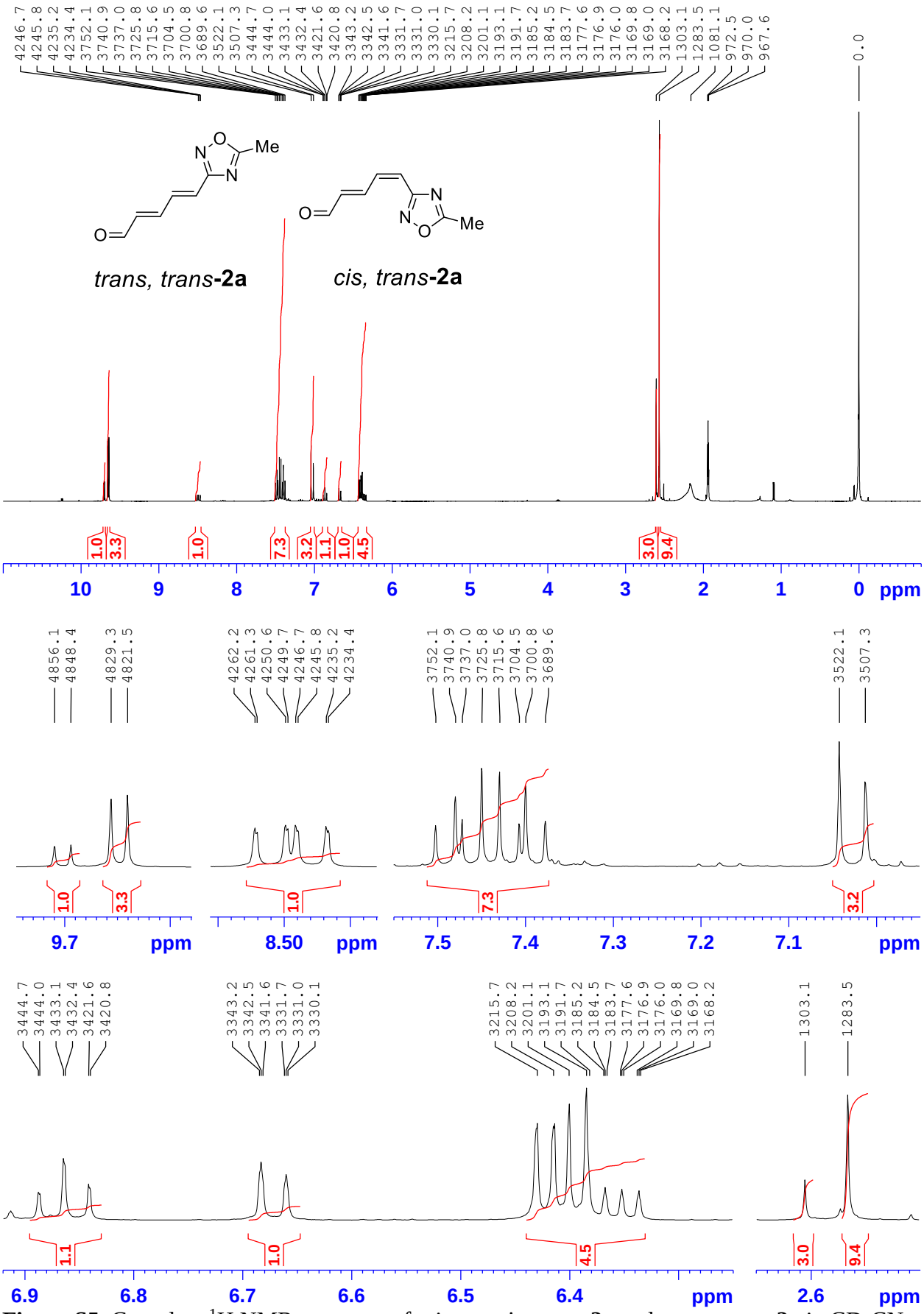


Figure S5. Complete ^{1}H NMR spectrum of mixture *cis*, *trans*-**2a** and *trans*, *trans*-**2a** in CD_3CN (top). Expanded ^{1}H NMR spectrum mixture *cis*, *trans*-**2a** and *trans*, *trans*-**2a** in CD_3CN (bottom).

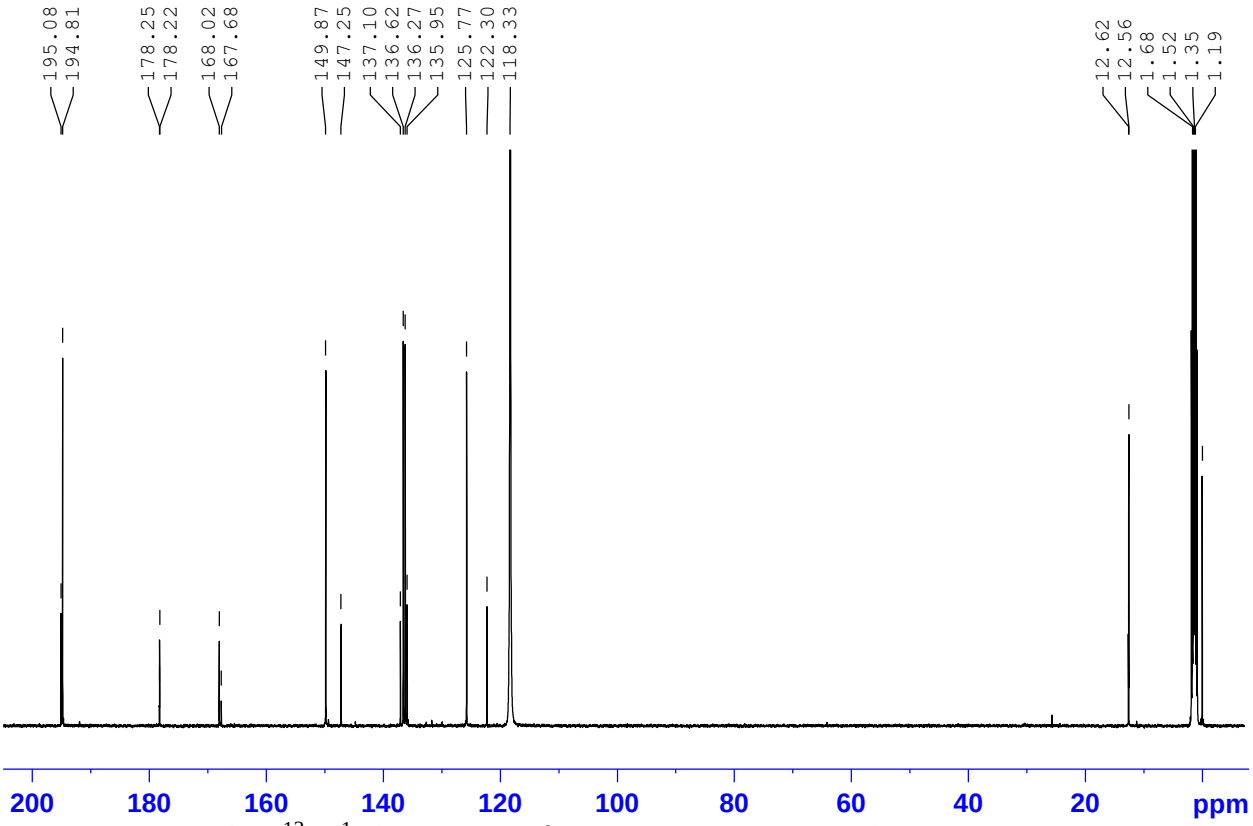


Figure S6. Complete $^{13}C\{^{1}H\}$ spectrum of mixture *cis, trans*-**2a** and *trans, trans*-**2a** in CD_3CN.

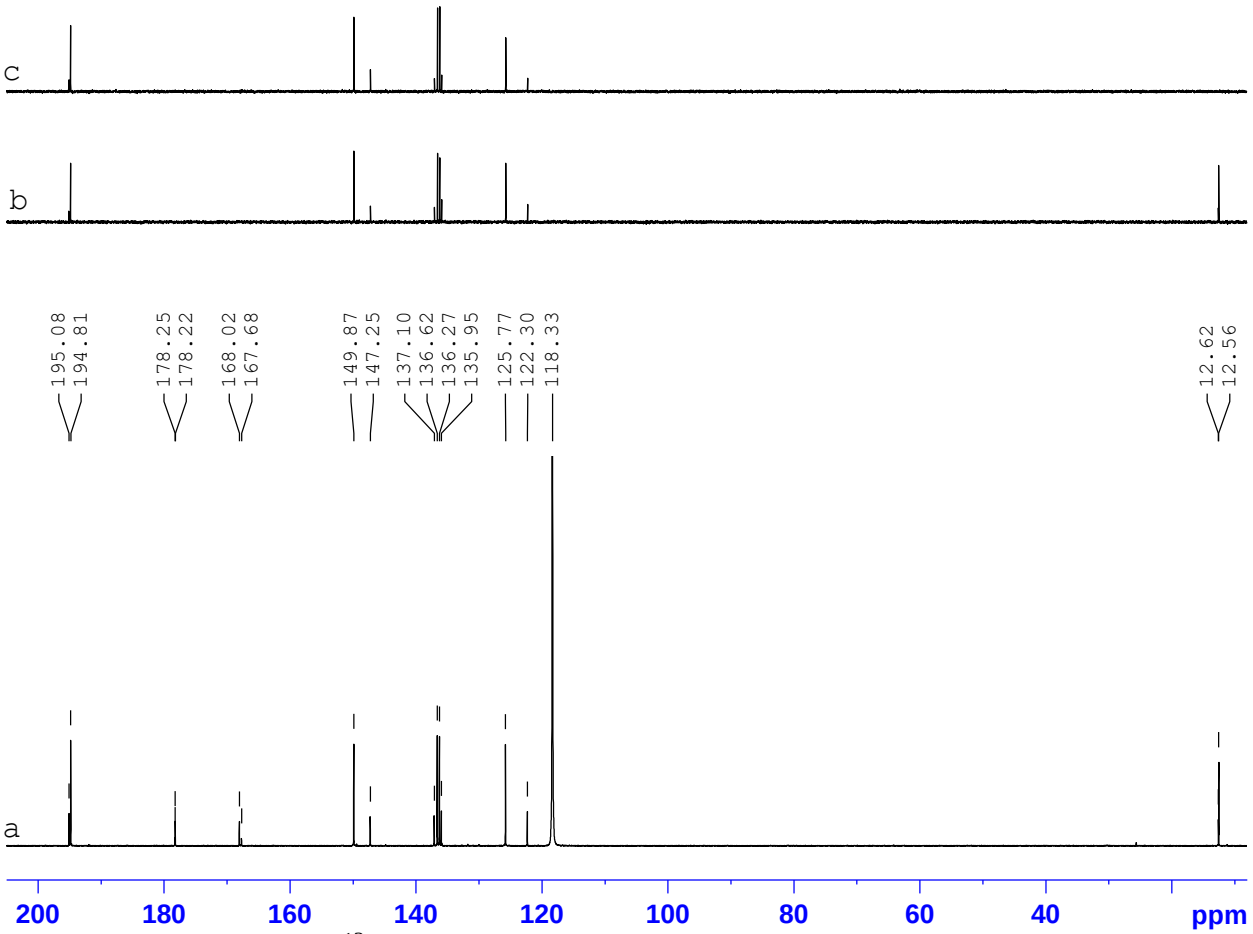


Figure S7. DEPT editing ^{13}C NMR spectrum of mixture *cis, trans*-**2a** and *trans, trans*-**2a** in CD_3CN: a) $^{13}C\{^{1}H\}$ spectrum; b) DEPT-135; c) DEPT-90.

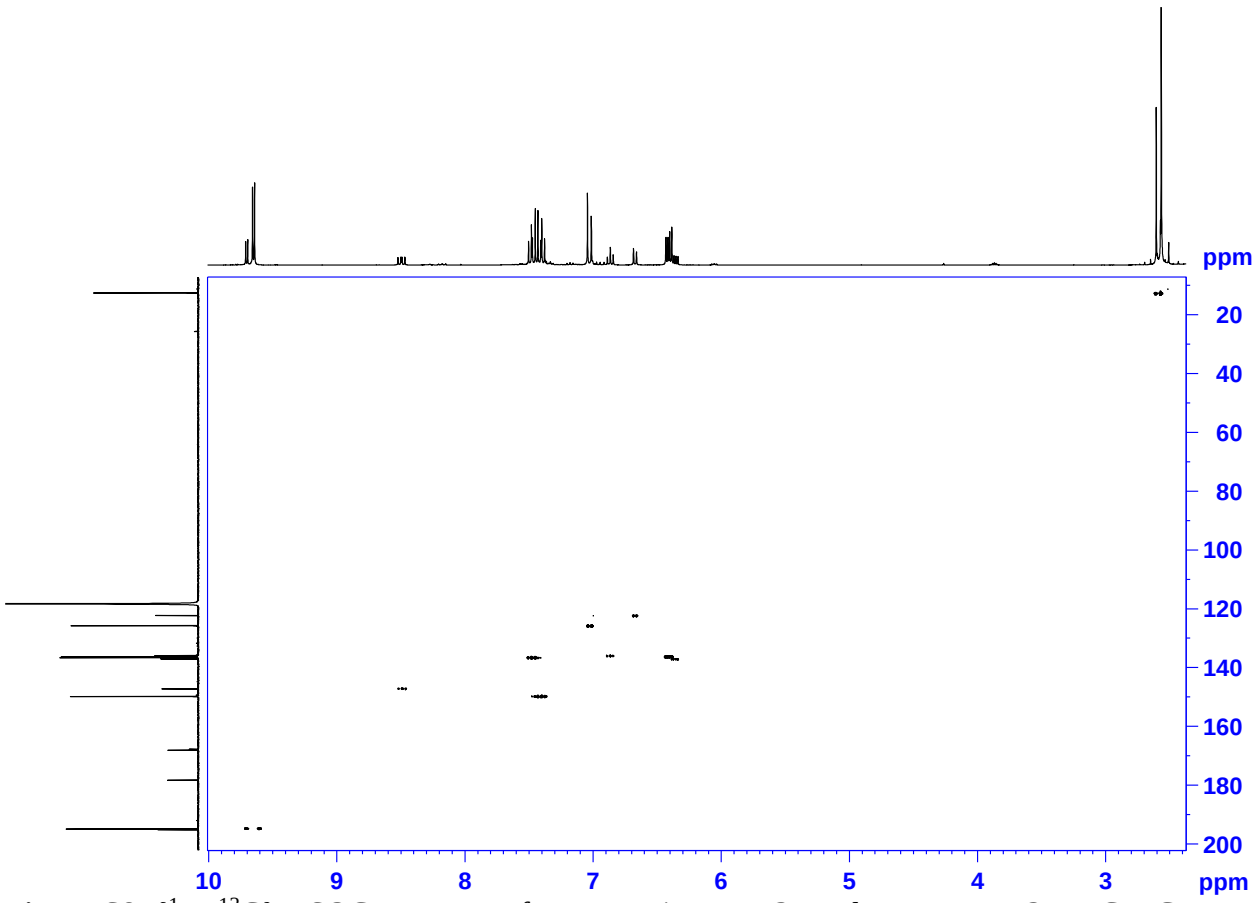


Figure S8. {^{1}H, ^{13}C} HSQC spectrum of mixture *cis*, *trans*-**2a** and *trans*, *trans*-**2a** in CD_3CN.

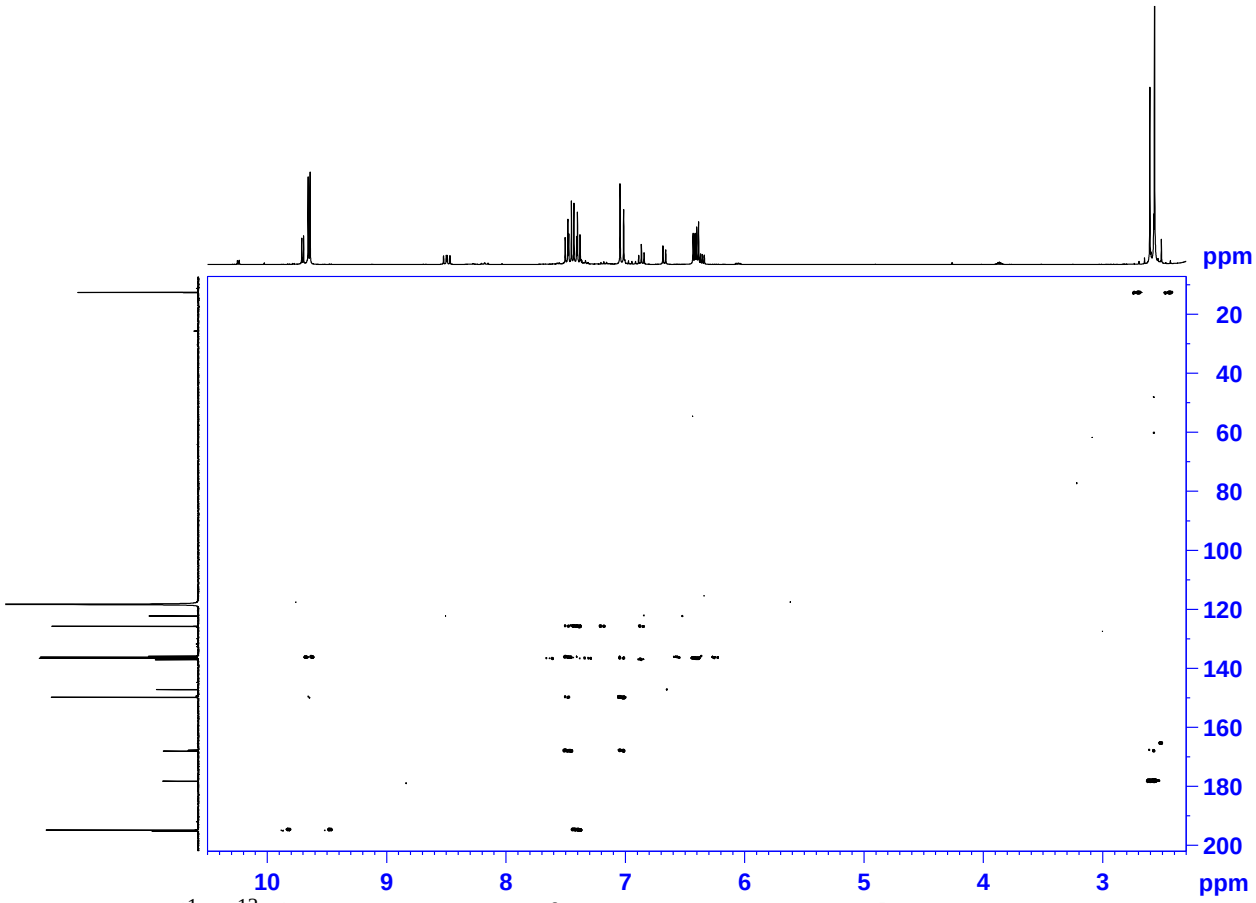


Figure S9. {^{1}H, ^{13}C} HMBC spectrum of mixture *cis*, *trans*-**2a** and *trans*, *trans*-**2a** in CD_3CN.

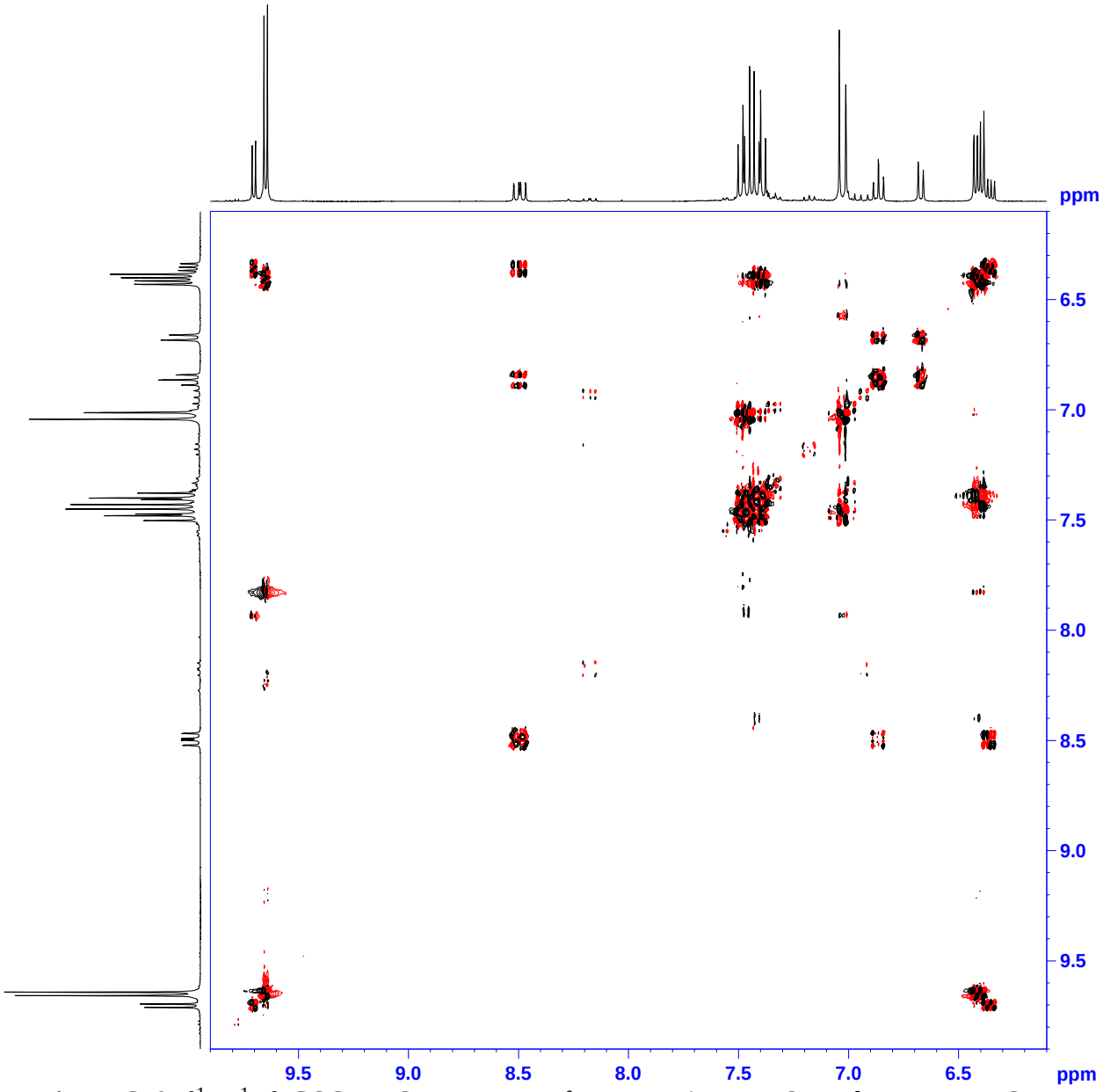


Figure S10. {^{1}H, ^{1}H} COSY-DQF spectrum of mixture *cis*, *trans*-**2a** and *trans*, *trans*-**2a** in CD_3CN.

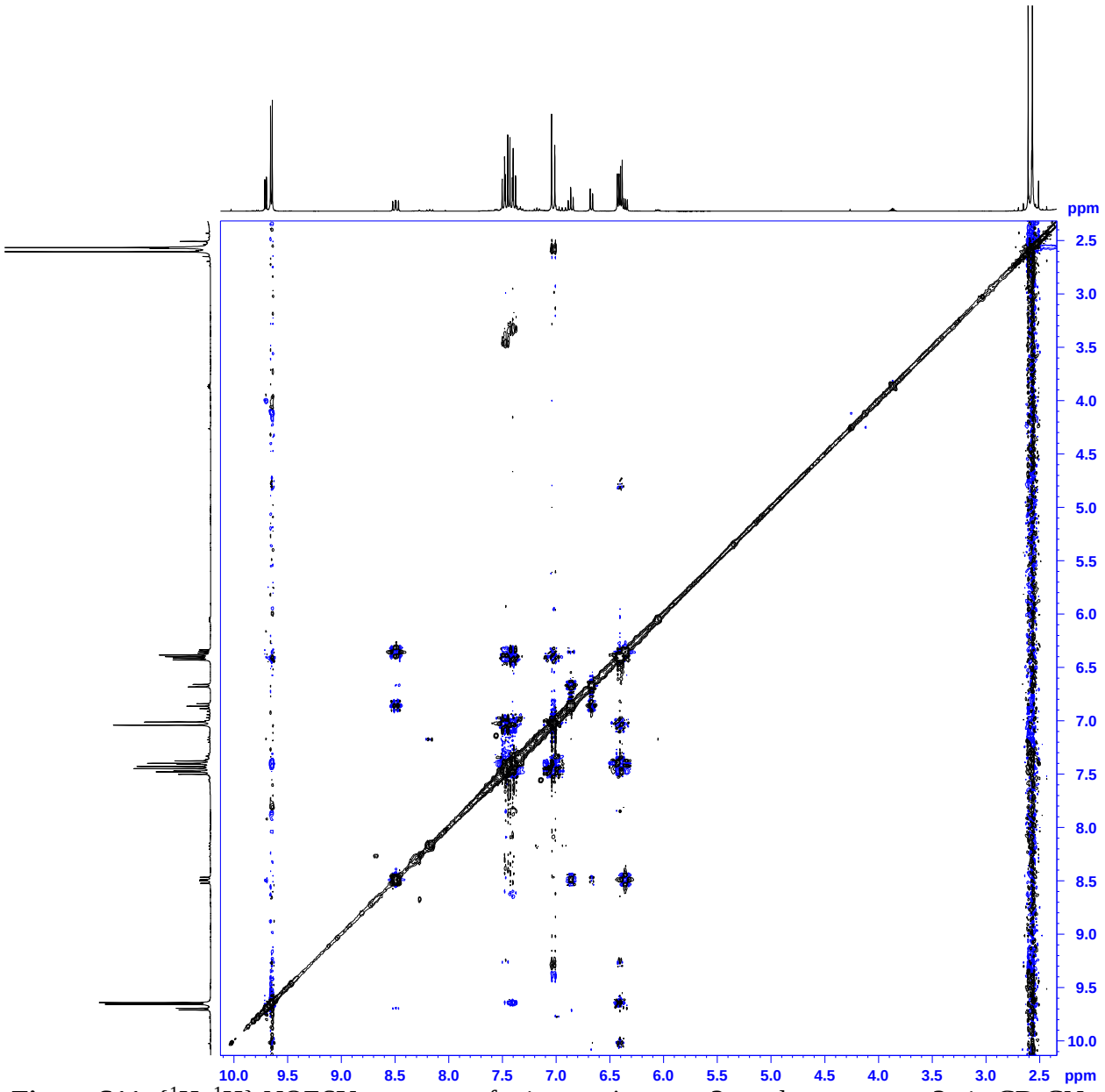
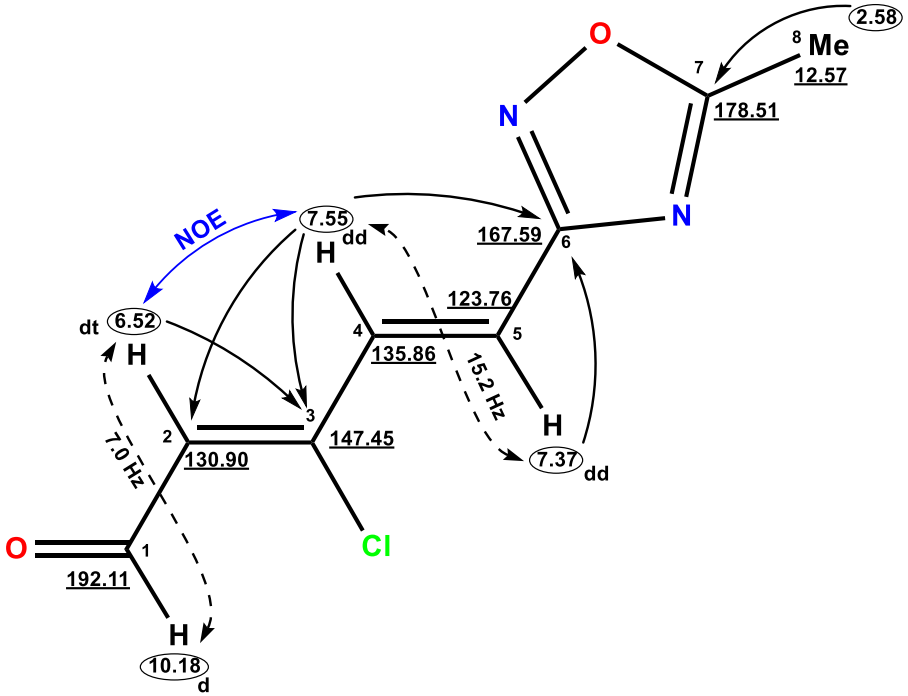
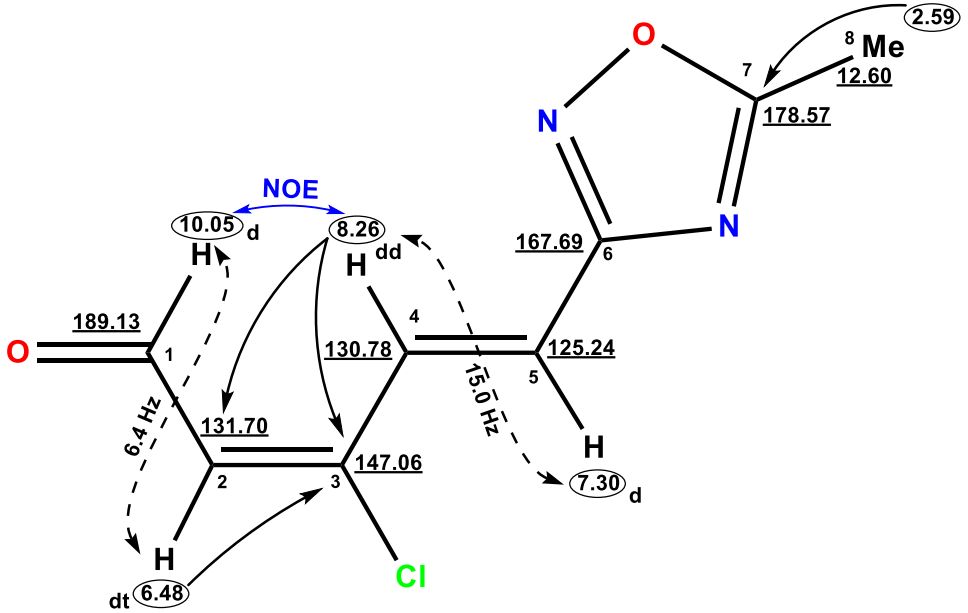


Figure S11. {^{1}H, ^{1}H} NOESY spectrum of mixture *cis*, *trans*-**2a** and *trans*, *trans*-**2a** in CD_3CN.

NMR diagram of isomers of mixture *trans, cis*-**2b** and *trans, trans*-**2b** in CD_3CN. Chemical shifts (ppm), coupling constants (Hz) and significant {^{1}H, ^{13}C} HMBC (solid arrow), {^{1}H, ^{1}H} COSY (dashed arrow) and NOESY (blue arrow) correlations.



trans, trans-**2b**



trans, cis-**2b**

5.5 : 1

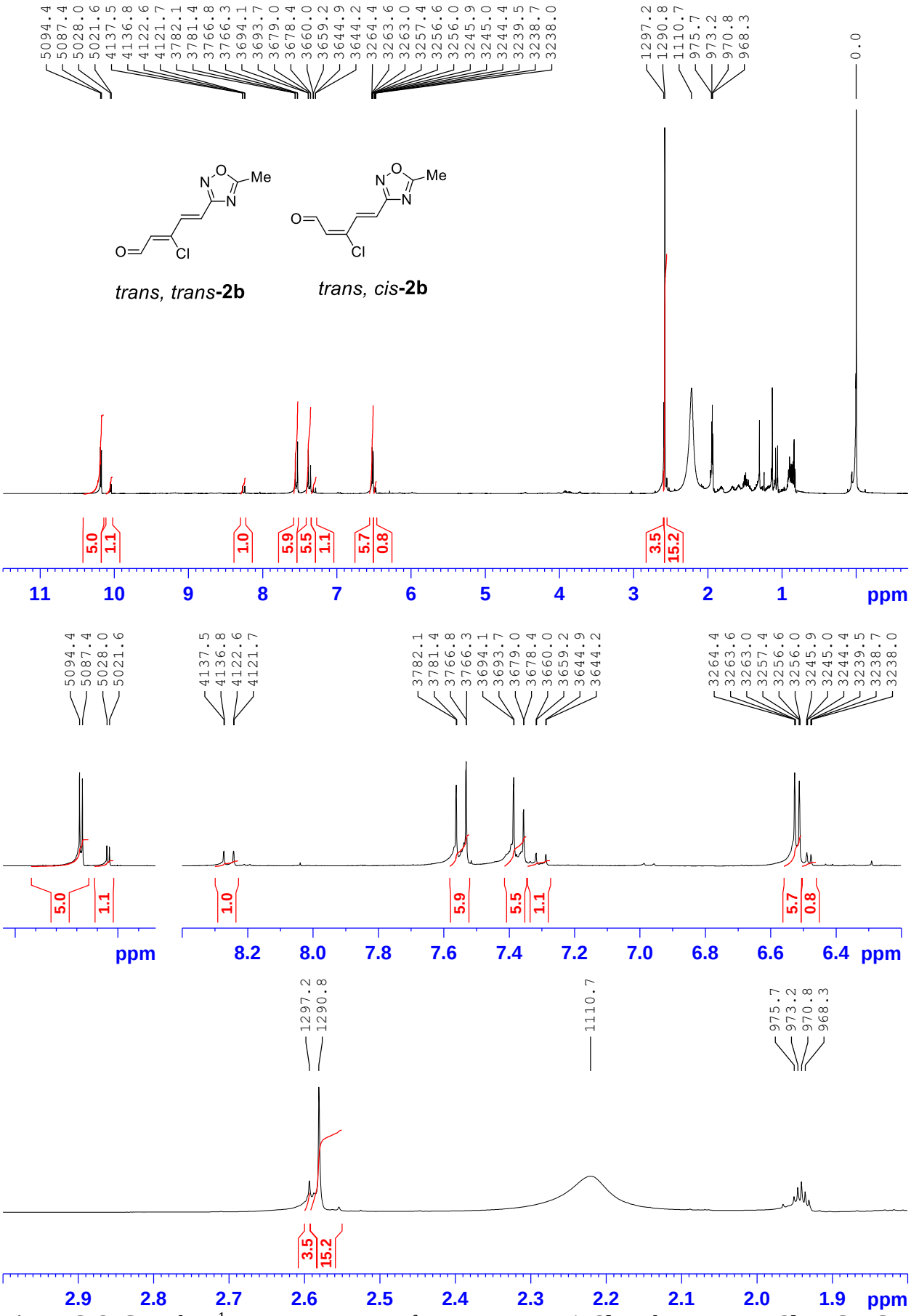


Figure S12. Complete ^{1}H NMR spectrum of mixture *trans*, *cis*-**2b** and *trans*, *trans*-**2b** in CD_3CN (top). Expanded ^{1}H NMR spectrum of mixture *trans*, *cis*-**2b** and *trans*, *trans*-**2b** in CD_3CN (bottom).

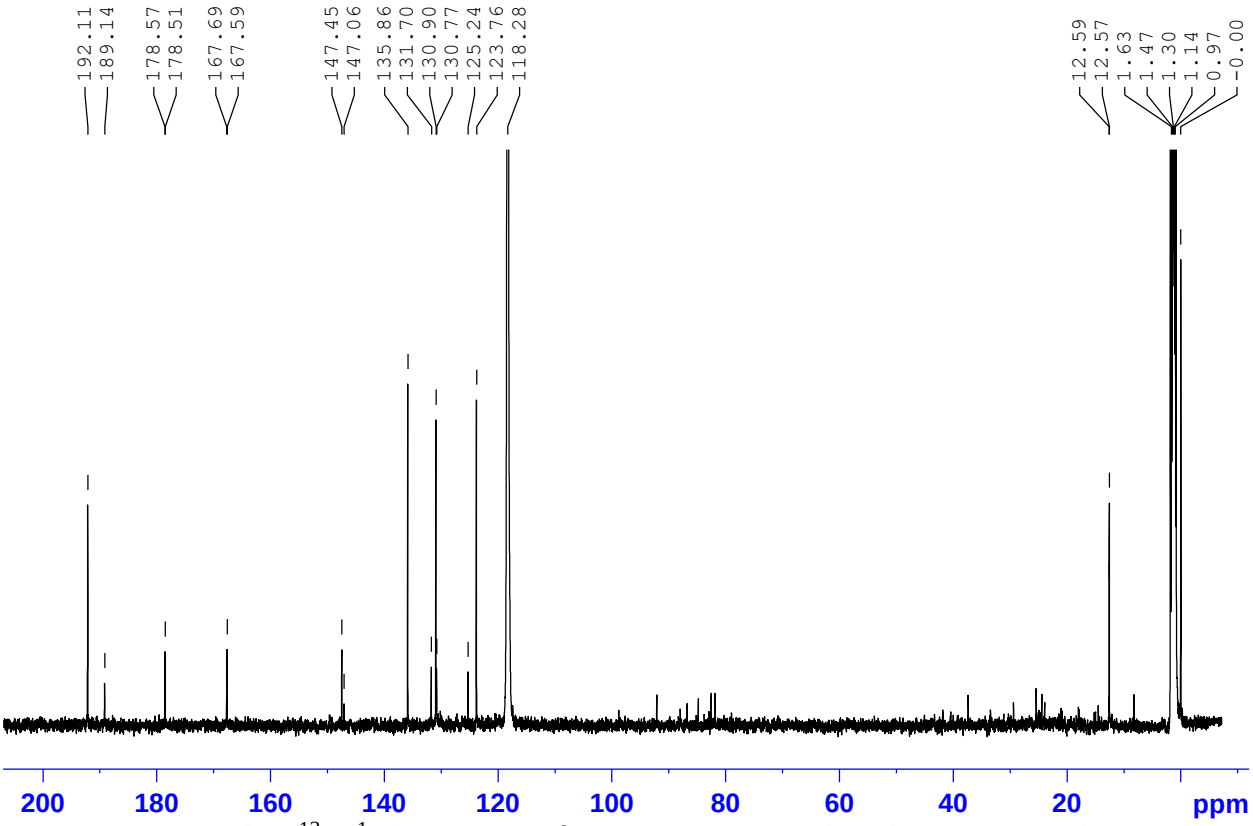


Figure S13. Complete $^{13}C\{^{1}H\}$ spectrum of mixture *trans*, *cis*-**2b** and *trans*, *trans*-**2b** in CD_3CN.

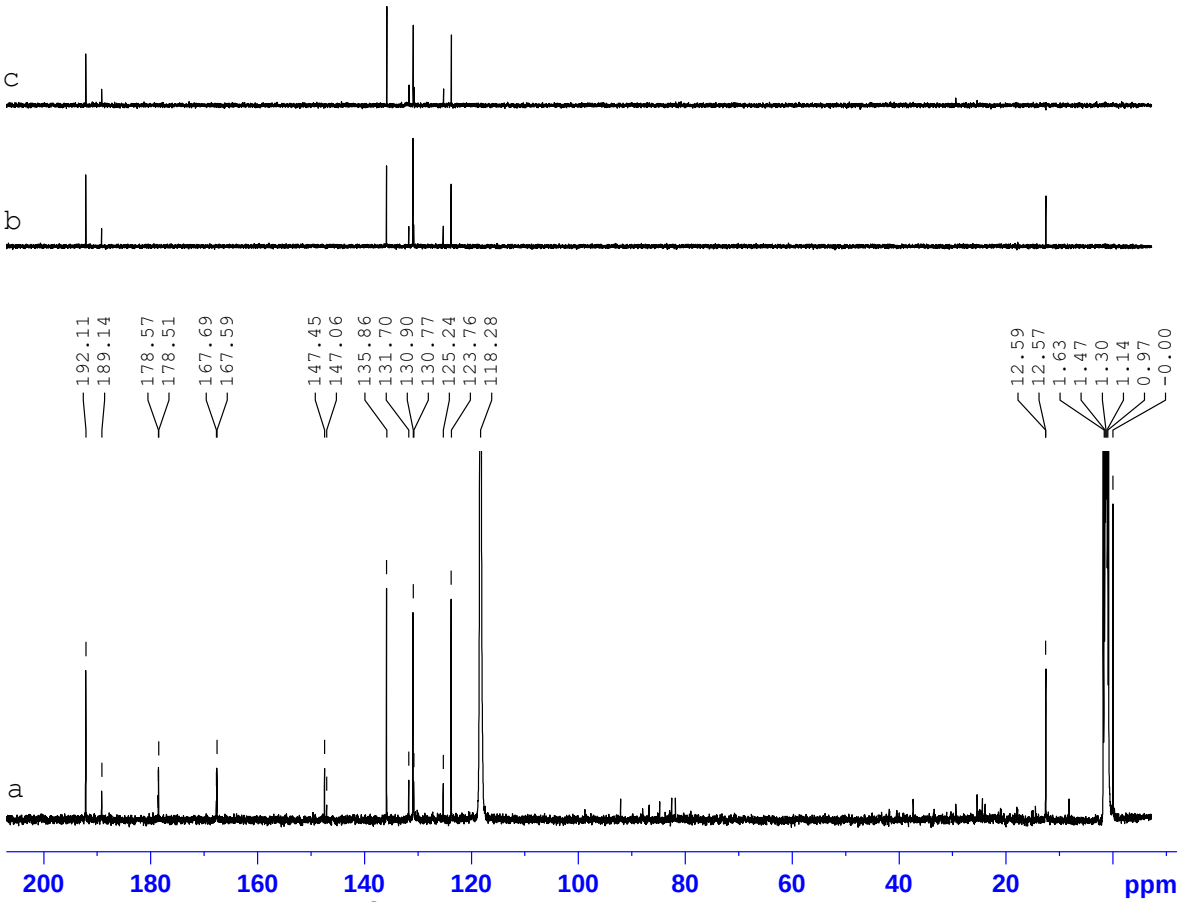


Figure S14. DEPT editing ^{13}C NMR spectrum of mixture *trans*, *cis*-**2b** and *trans*, *trans*-**2b** in CD_3CN: a) $^{13}C\{^{1}H\}$ spectrum; b) DEPT-135; c) DEPT-90.

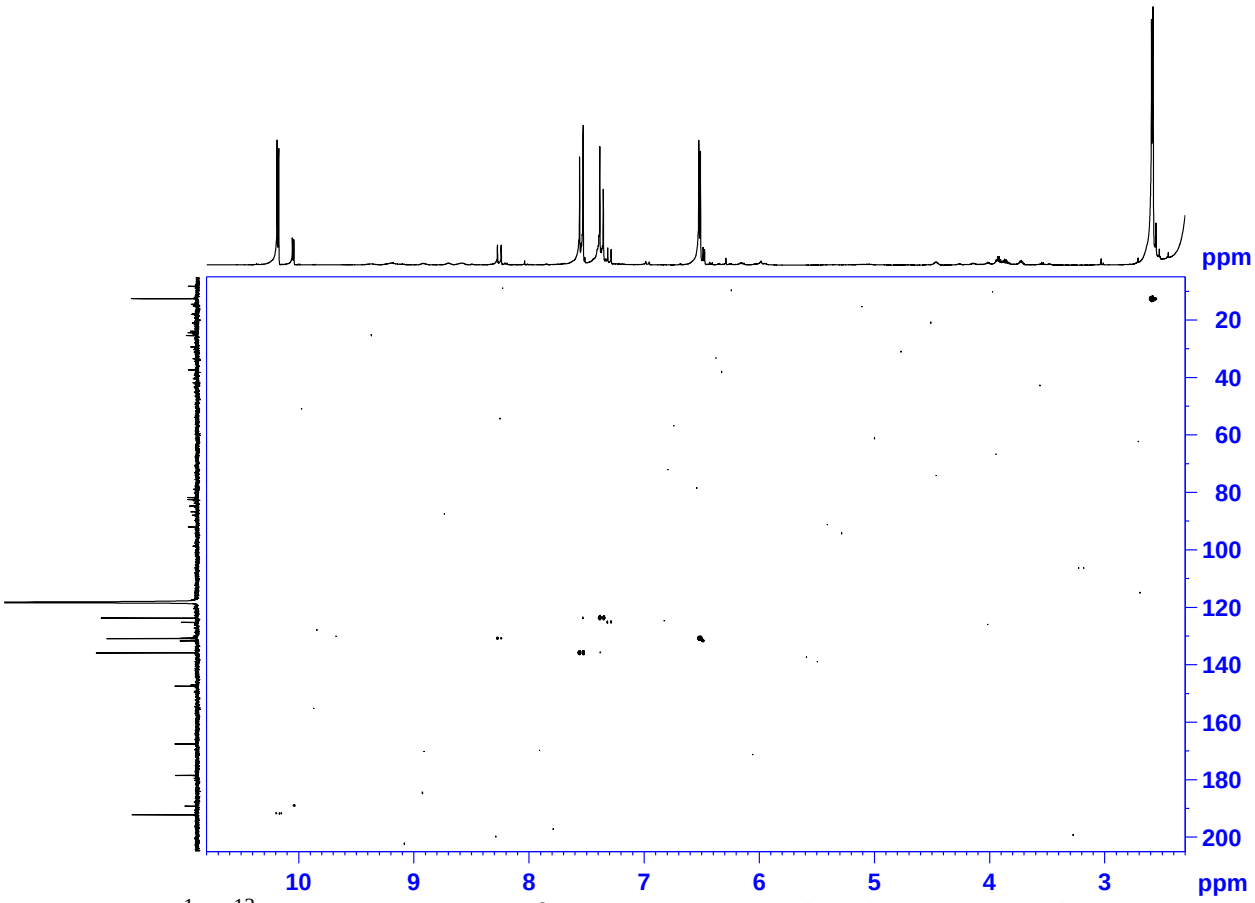


Figure S15. {^{1}H, ^{13}C} HSQC spectrum of mixture *trans*, *cis*-**2b** and *trans*, *trans*-**2b** in CD_3CN.

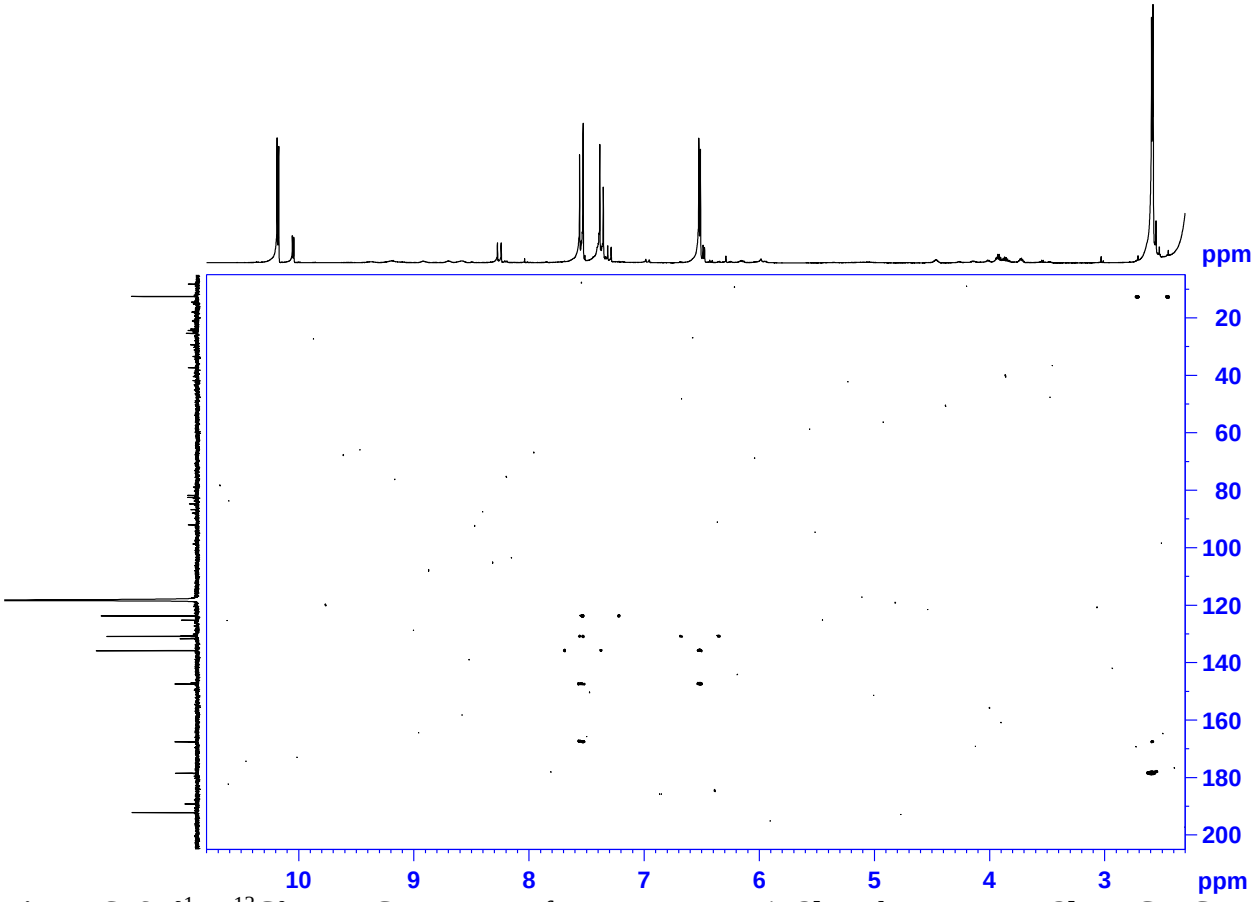


Figure S16. {^{1}H, ^{13}C} HMBC spectrum of mixture *trans*, *cis*-**2b** and *trans*, *trans*-**2b** in CD_3CN.

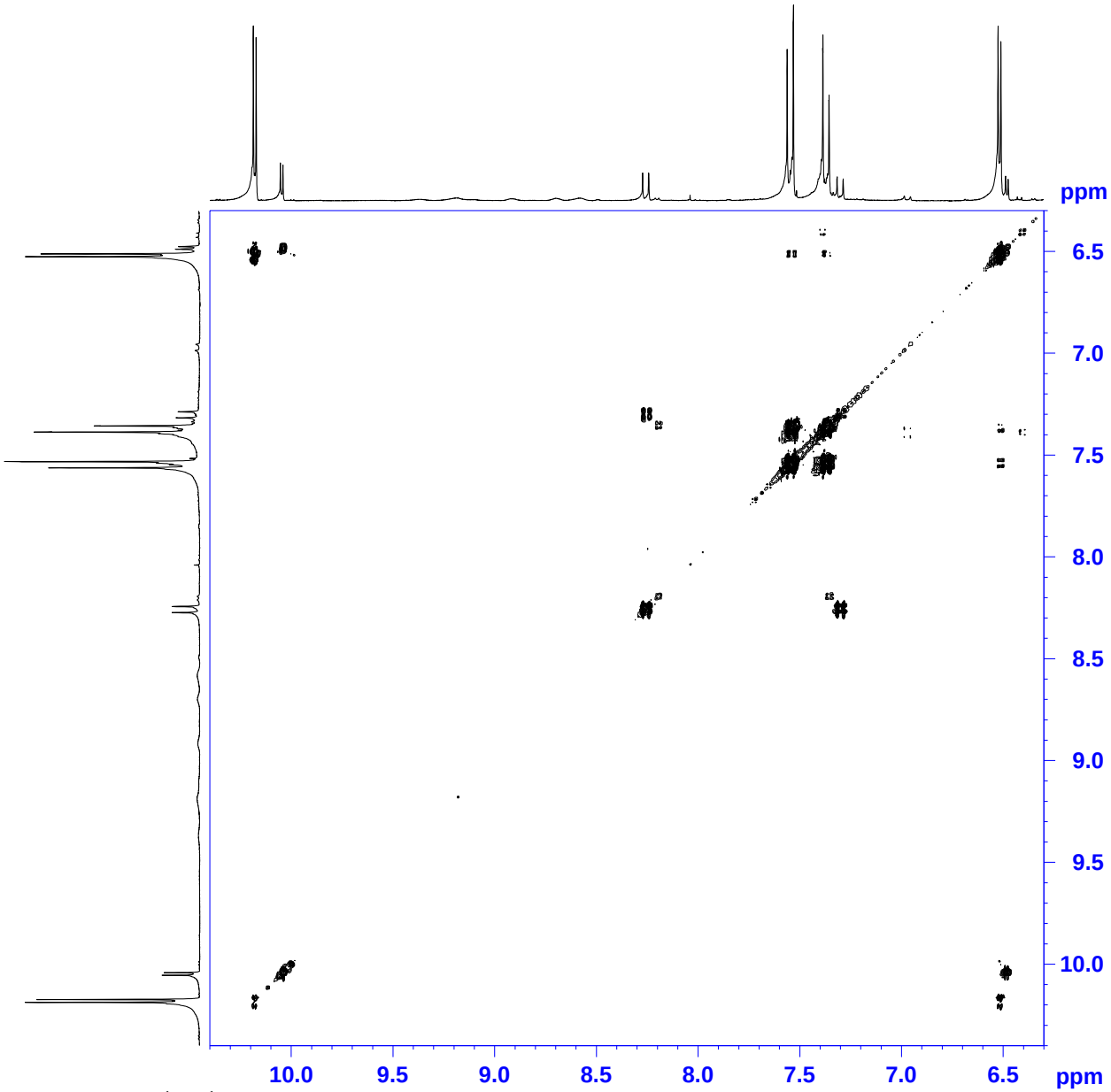


Figure S17. {^{1}H, ^{1}H} COSY spectrum of mixture *trans*, *cis*-**2b** and *trans*, *trans*-**2b** in CD_3CN.

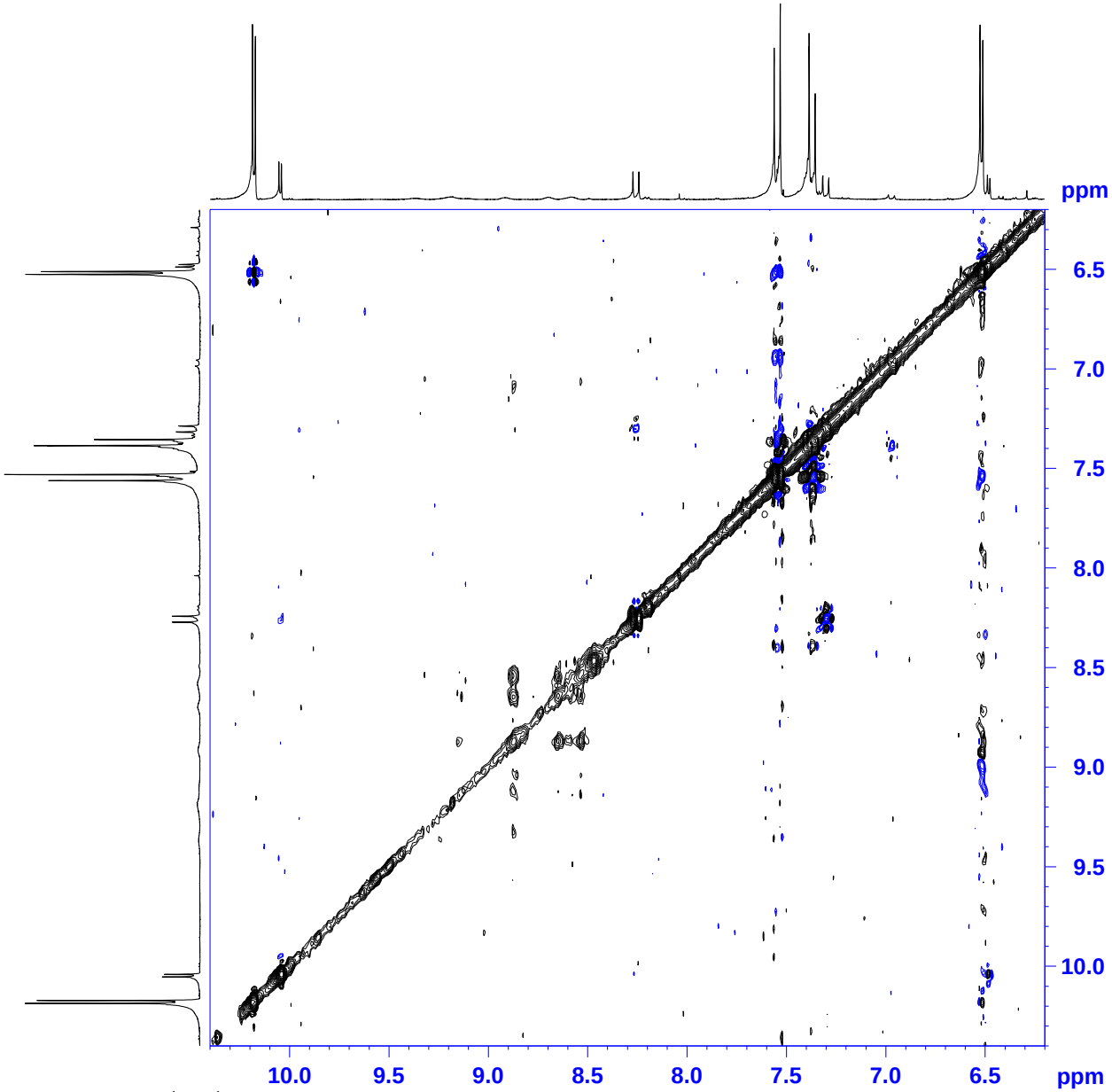
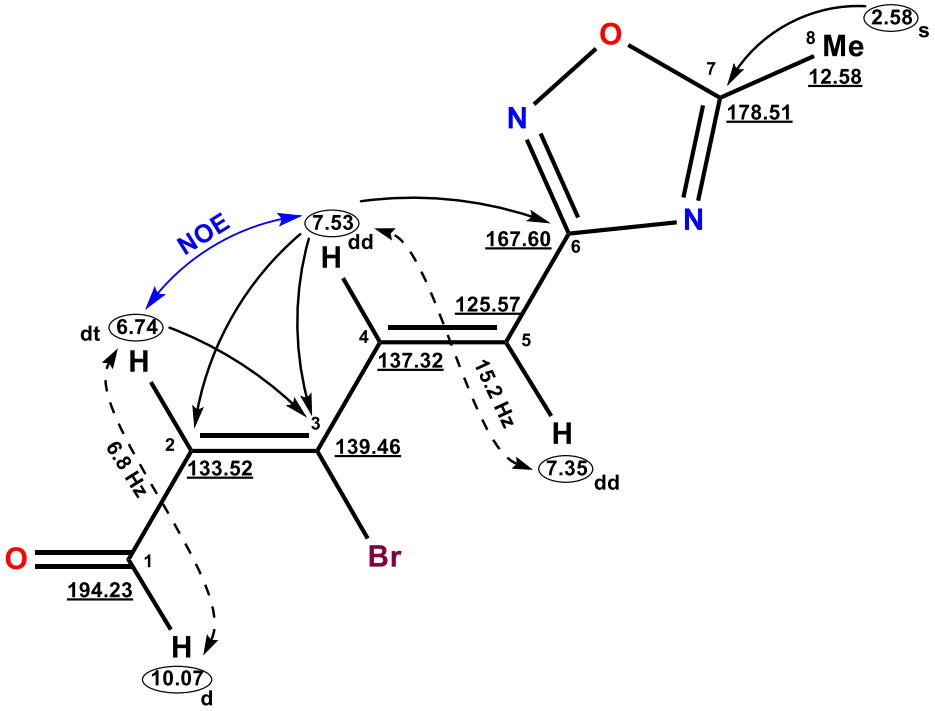
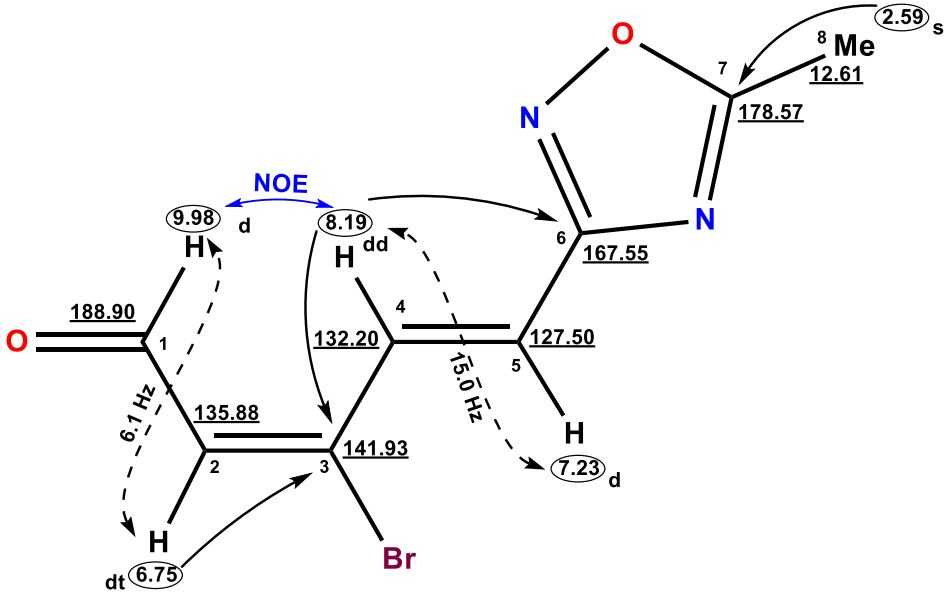


Figure S18. {^{1}H, ^{1}H} NOESY spectrum of mixture *trans*, *cis*-**2b** and *trans*, *trans*-**2b** in CD_3CN.

NMR diagram of isomers of mixture *trans*, *cis*-**2c** and *trans*, *trans*-**2c** in CD_3CN. Chemical shifts (ppm), coupling constants (Hz) and significant {^{1}H, ^{13}C} HMBC (solid arrow), {^{1}H, ^{1}H} COSY (dashed arrow) and NOESY (blue arrow) correlations.





trans, *trans*-**2c** *trans*, *cis*-**2c**

3.5 : 1

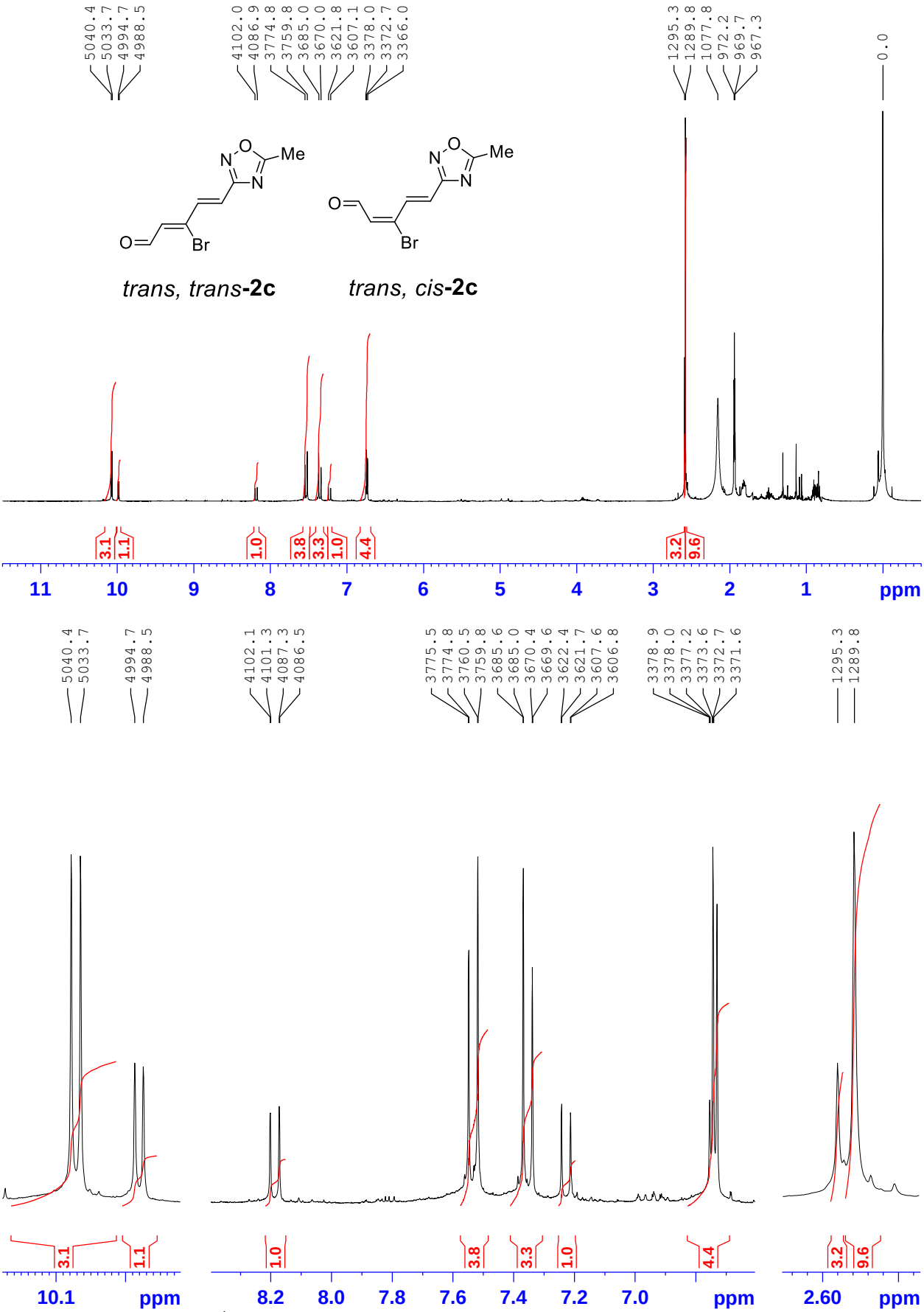


Figure S19. Complete ^{1}H NMR spectrum of mixture *trans*, *cis*-**2c** and *trans*, *trans*-**2c** in CD_3CN (top). Expanded ^{1}H NMR spectrum of mixture *trans*, *cis*-**2c** and *trans*, *trans*-**2c** in CD_3CN (bottom).

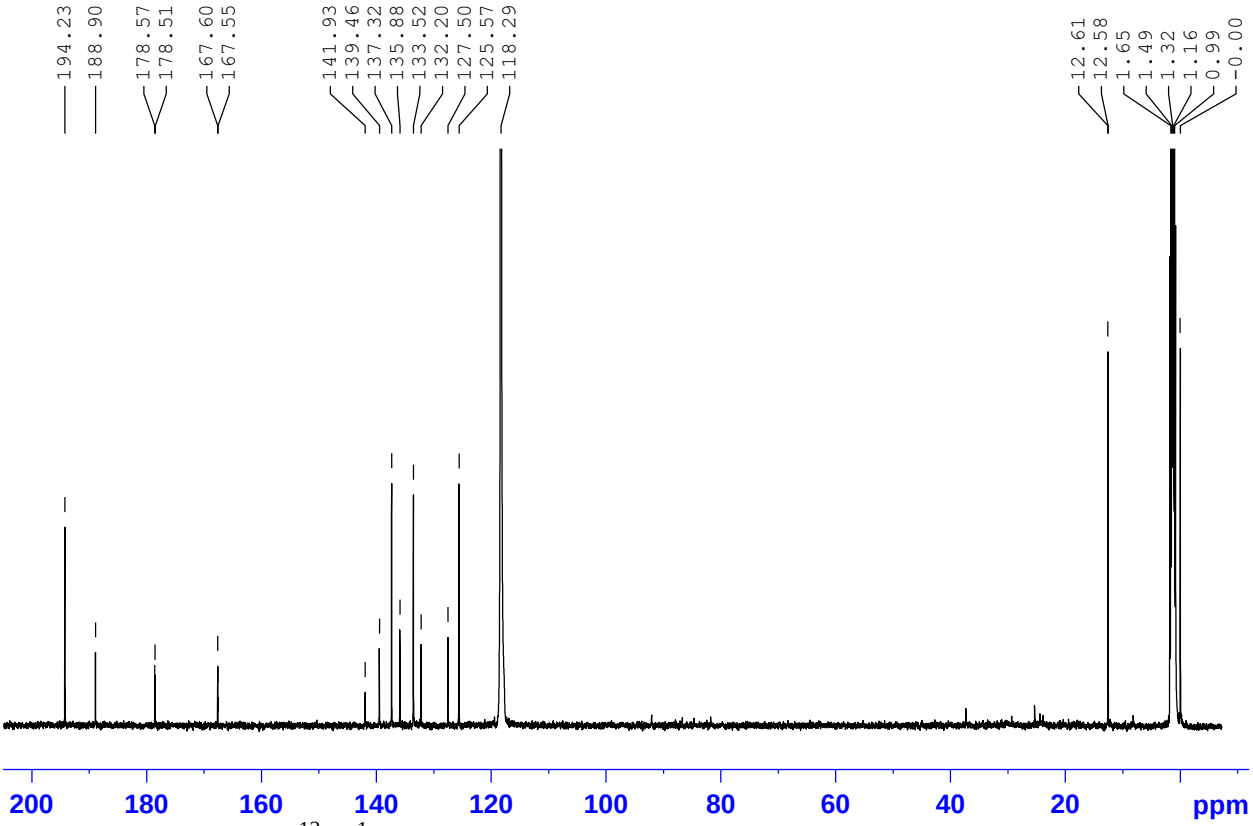


Figure S20. Complete $^{13}C\{^{1}H\}$ spectrum of mixture *trans, cis*-**2c** and *trans, trans*-**2c** in CD_3CN.

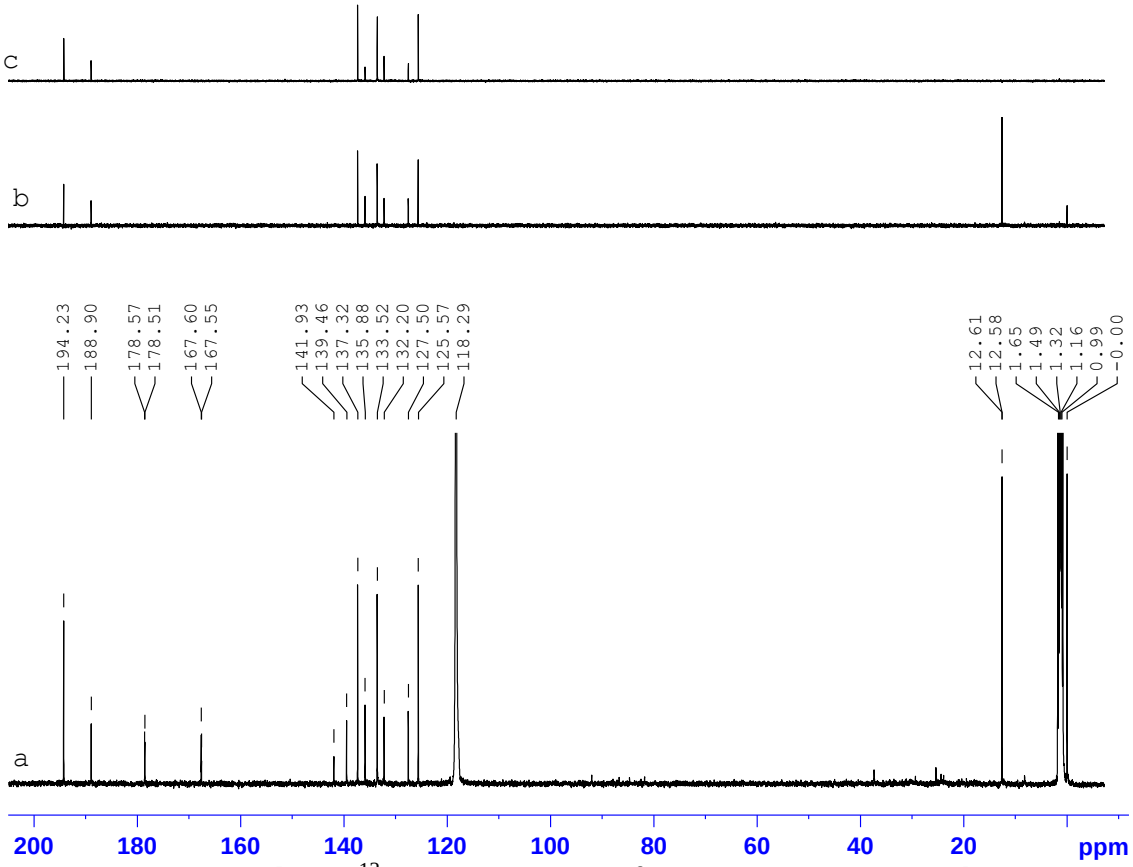


Figure S21. DEPT editing ^{13}C NMR spectrum of mixture *trans, cis*-**2c** and *trans, trans*-**2c** in CD_3CN: a) $^{13}C\{^{1}H\}$ spectrum; b) DEPT-135; c) DEPT-90.

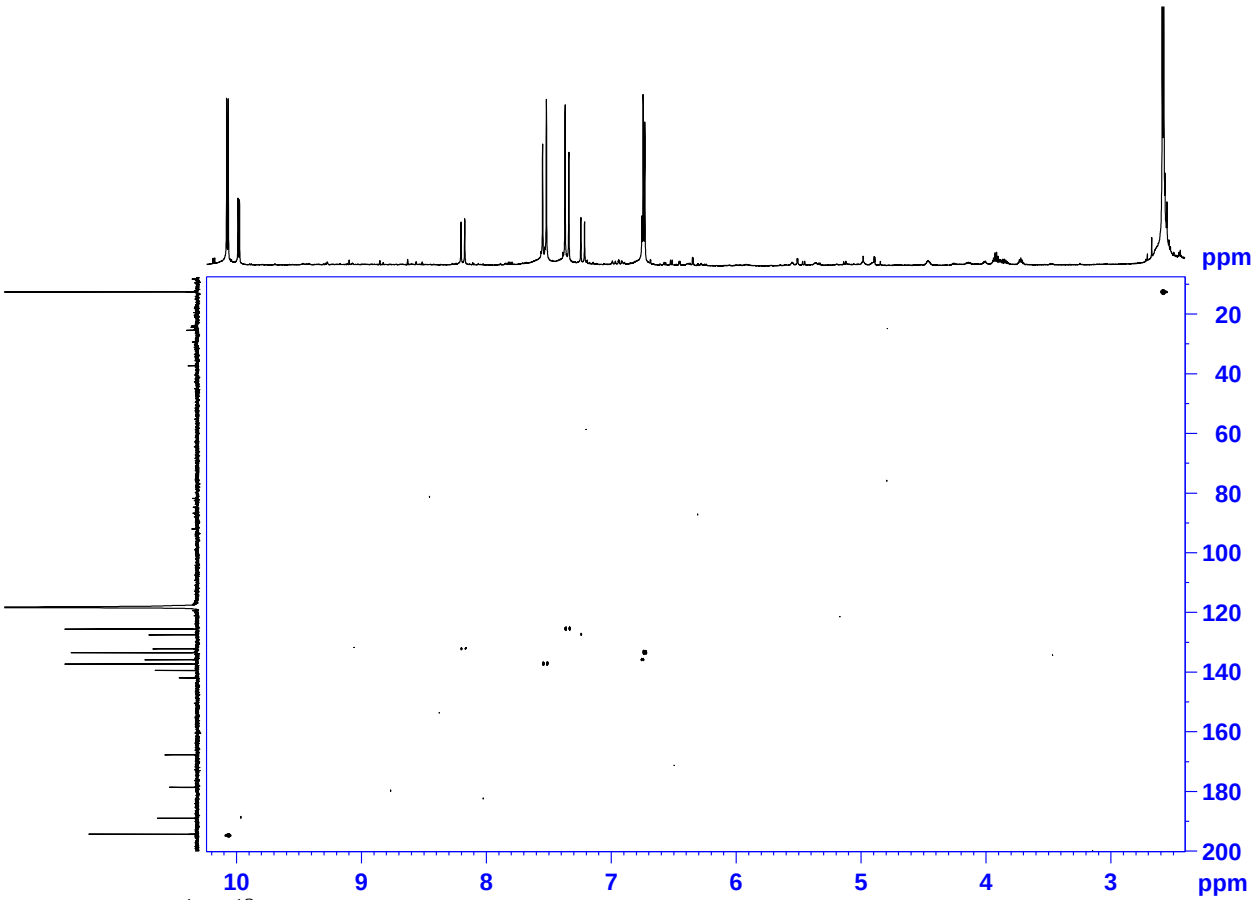


Figure S22. {^{1}H, ^{13}C} HSQC spectrum of mixture *trans, cis*-**2c** and *trans, trans*-**2c** in CD_3CN.

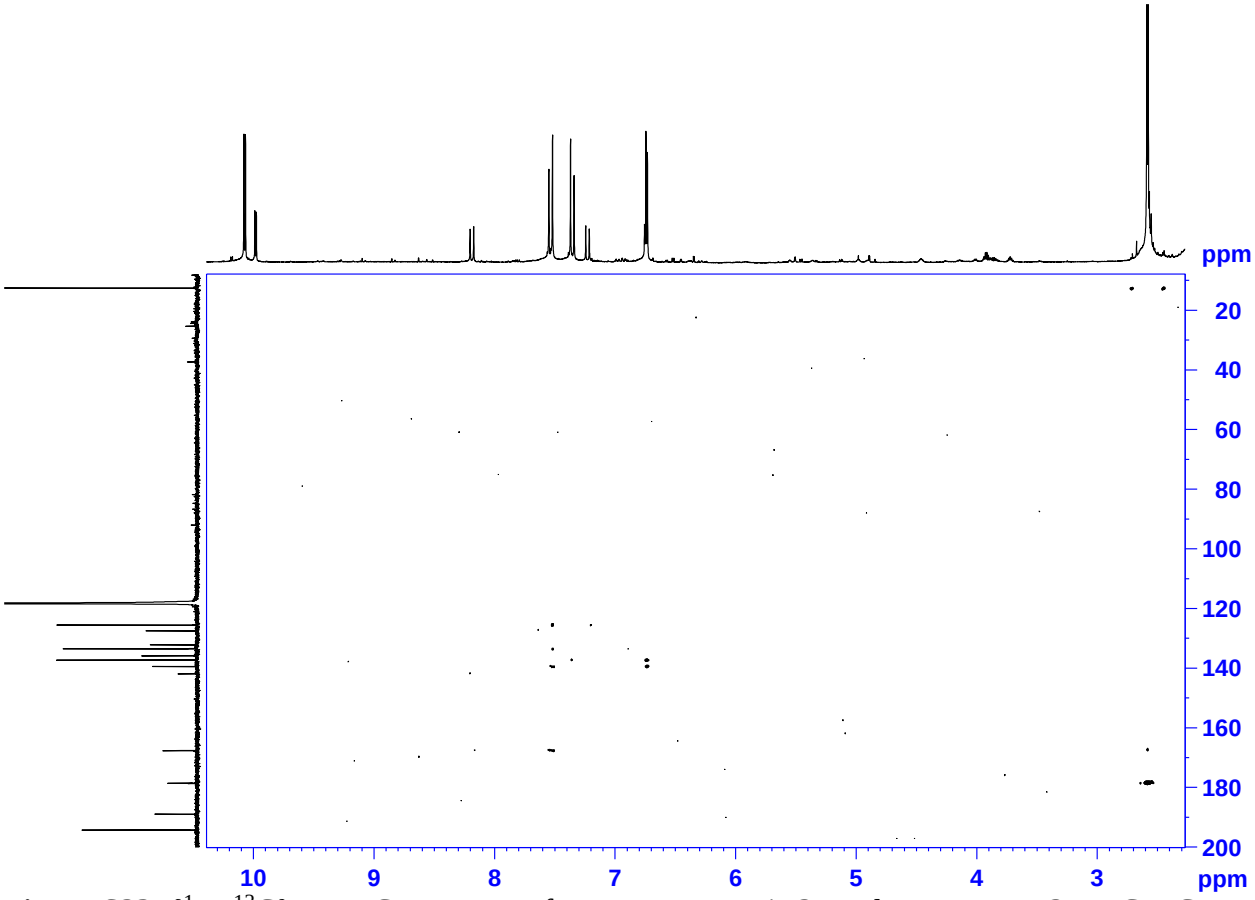


Figure S23. {^{1}H, ^{13}C} HMBC spectrum of mixture *trans, cis*-**2c** and *trans, trans*-**2c** in CD_3CN.

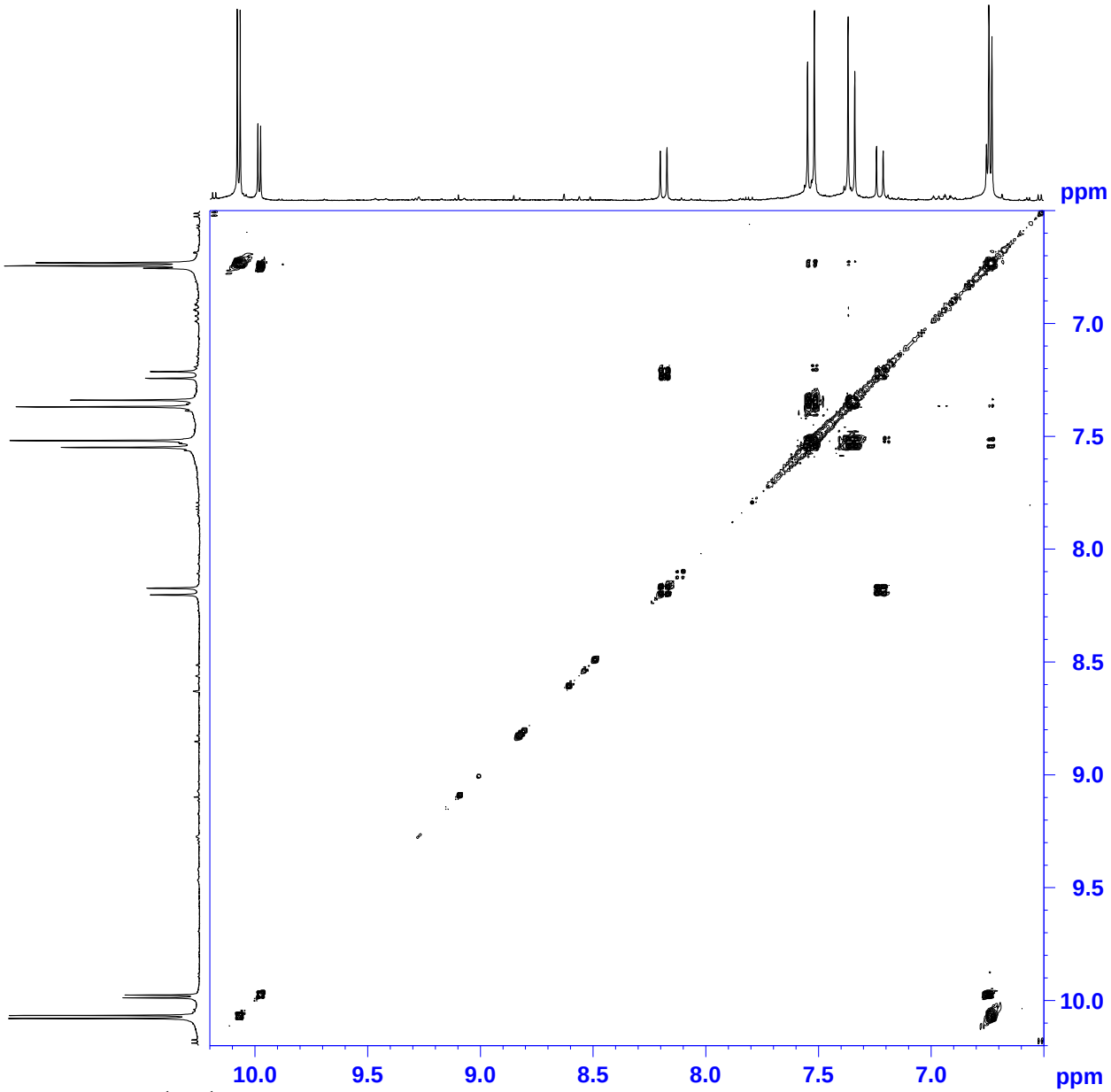


Figure S24. {^{1}H, ^{1}H} COSY spectrum of mixture *trans*, *cis*-**2c** and *trans*, *trans*-**2c** in CD_3CN.

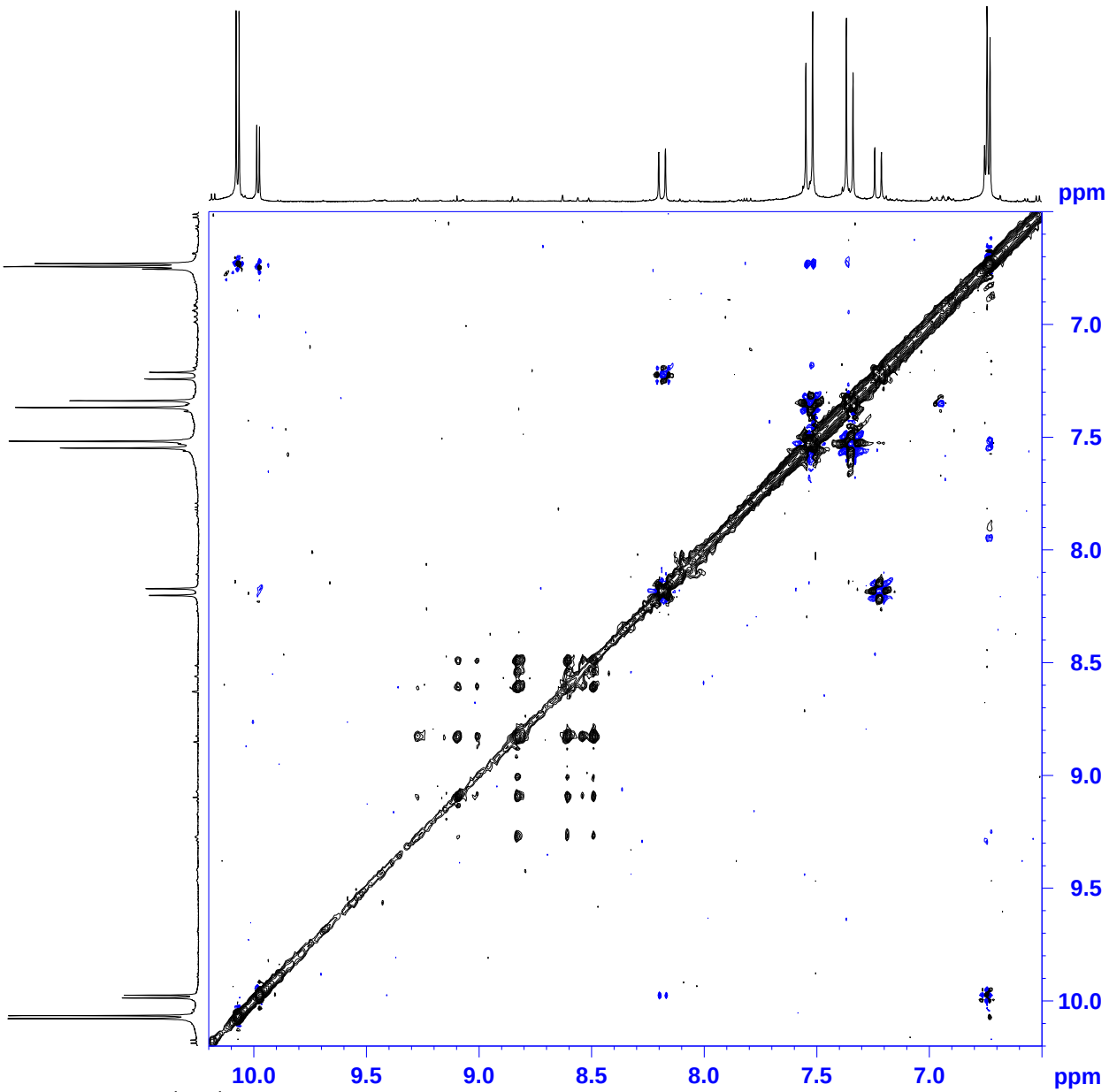
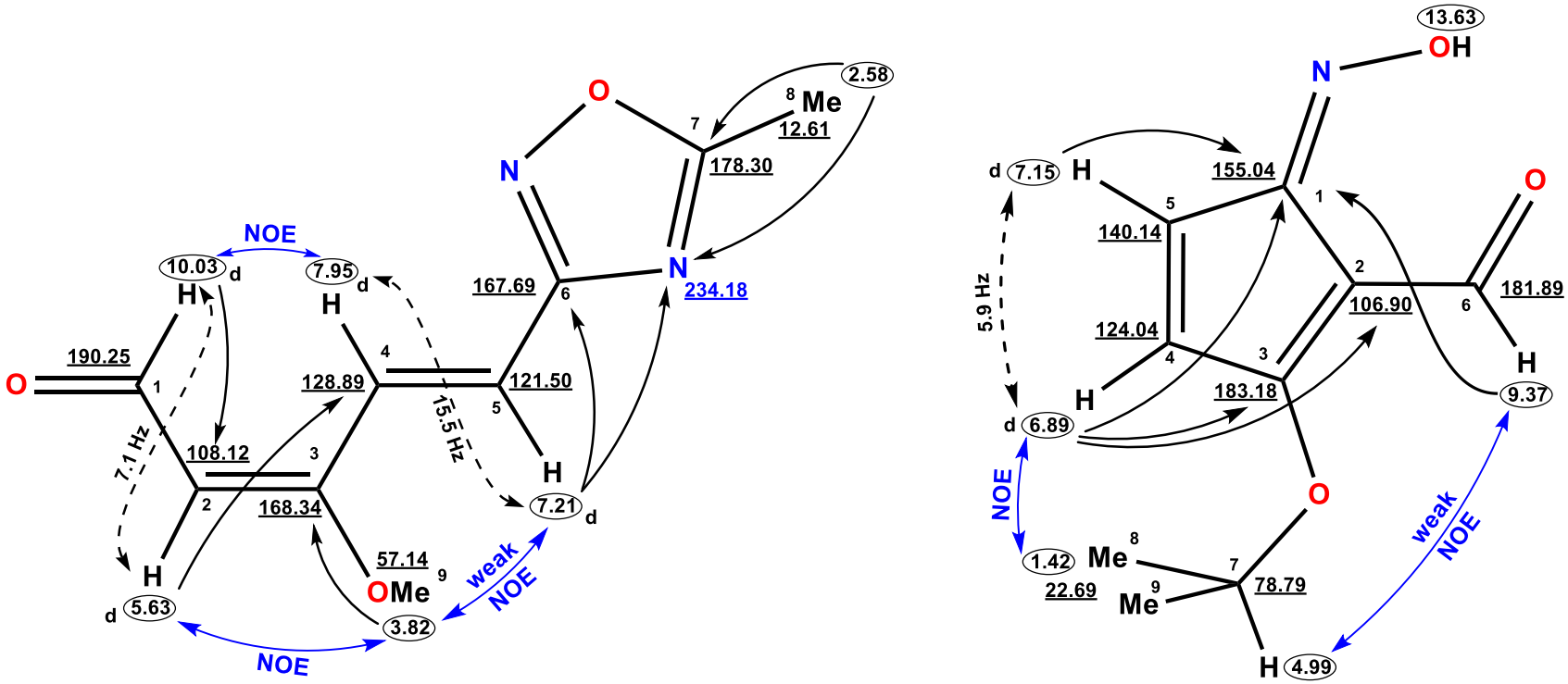


Figure S25. {^{1}H, ^{1}H} NOESY spectrum of mixture *trans, cis*-**2c** and *trans, trans*-**2c** in CD_3CN.

NMR diagram of isomers of mixture *trans*, *cis*-**2d** and **4'** in CD_3CN. Chemical shifts (ppm), coupling constants (Hz) and significant {^{1}H, ^{13}C}, {^{1}H, ^{15}N} HMBC (solid arrow), {^{1}H, ^{1}H} COSY (dashed arrow) and NOESY (blue arrow) correlations.



trans, *cis*-**2d** **4'**

11.4 : 1

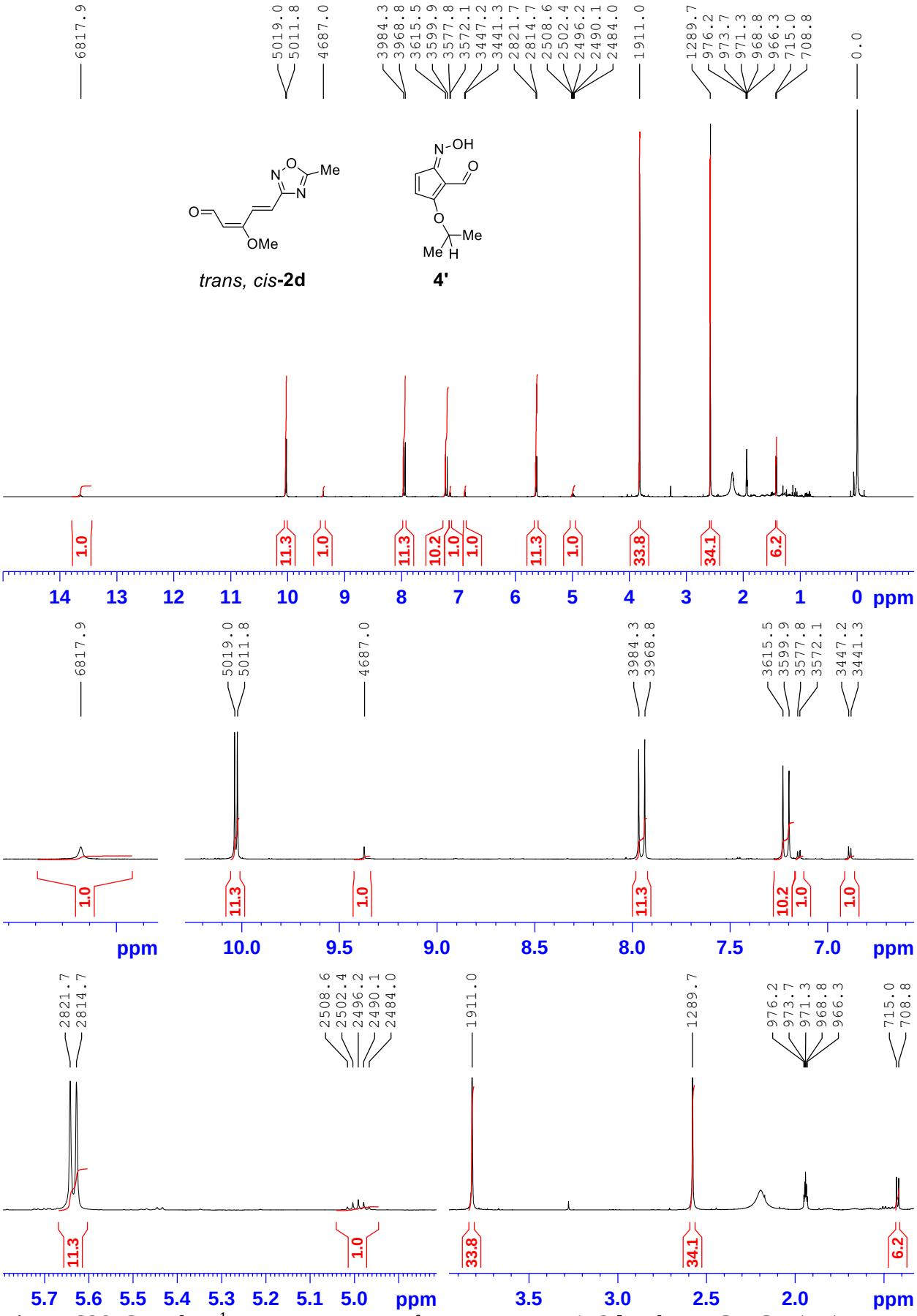


Figure S26. Complete ^{1}H NMR spectrum of mixture *trans*, *cis*-**2d** and **4'** in CD_3CN (top).

Expanded ^{1}H NMR spectrum mixture *trans*, *cis*-**2d** and **4'** in CD_3CN (bottom).

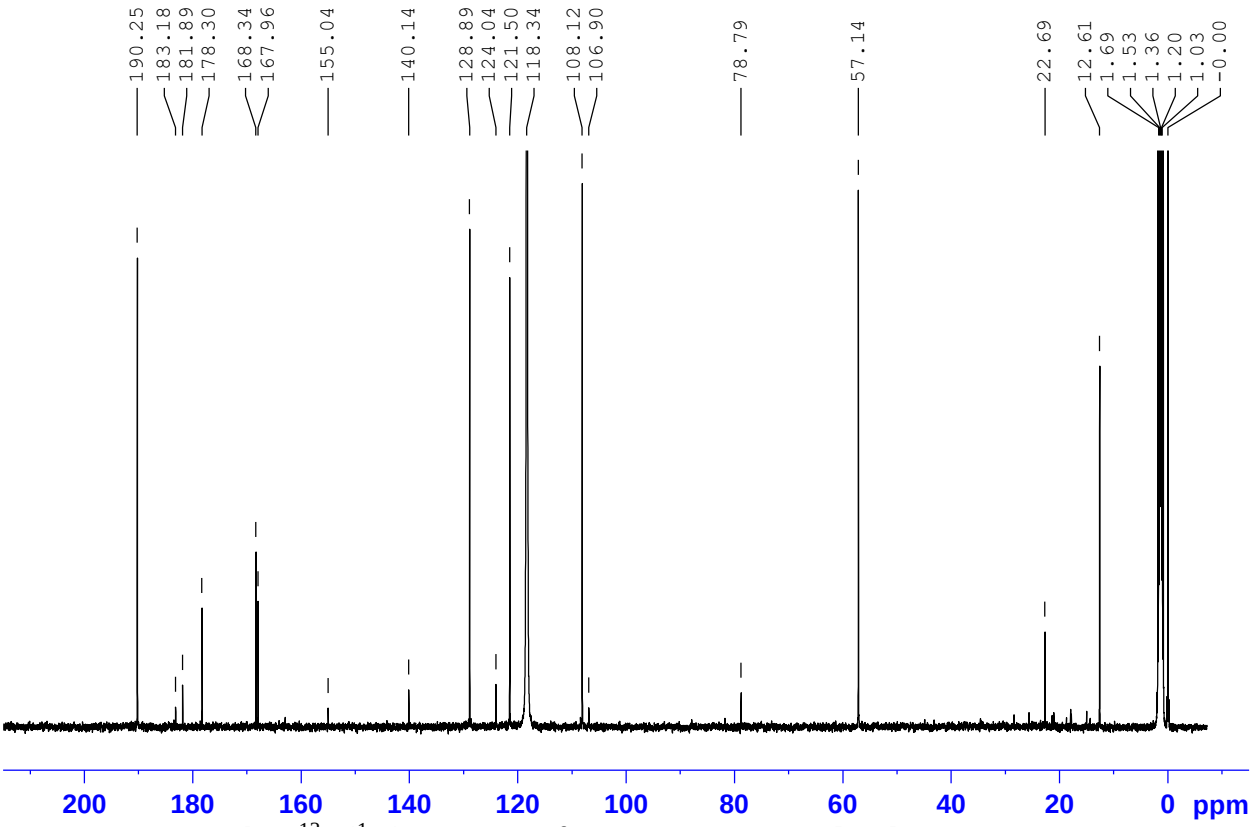


Figure S27. Complete $^{13}C\{^{1}H\}$ spectrum of mixture *trans, cis*-**2d** and **4'** in CD_3CN.

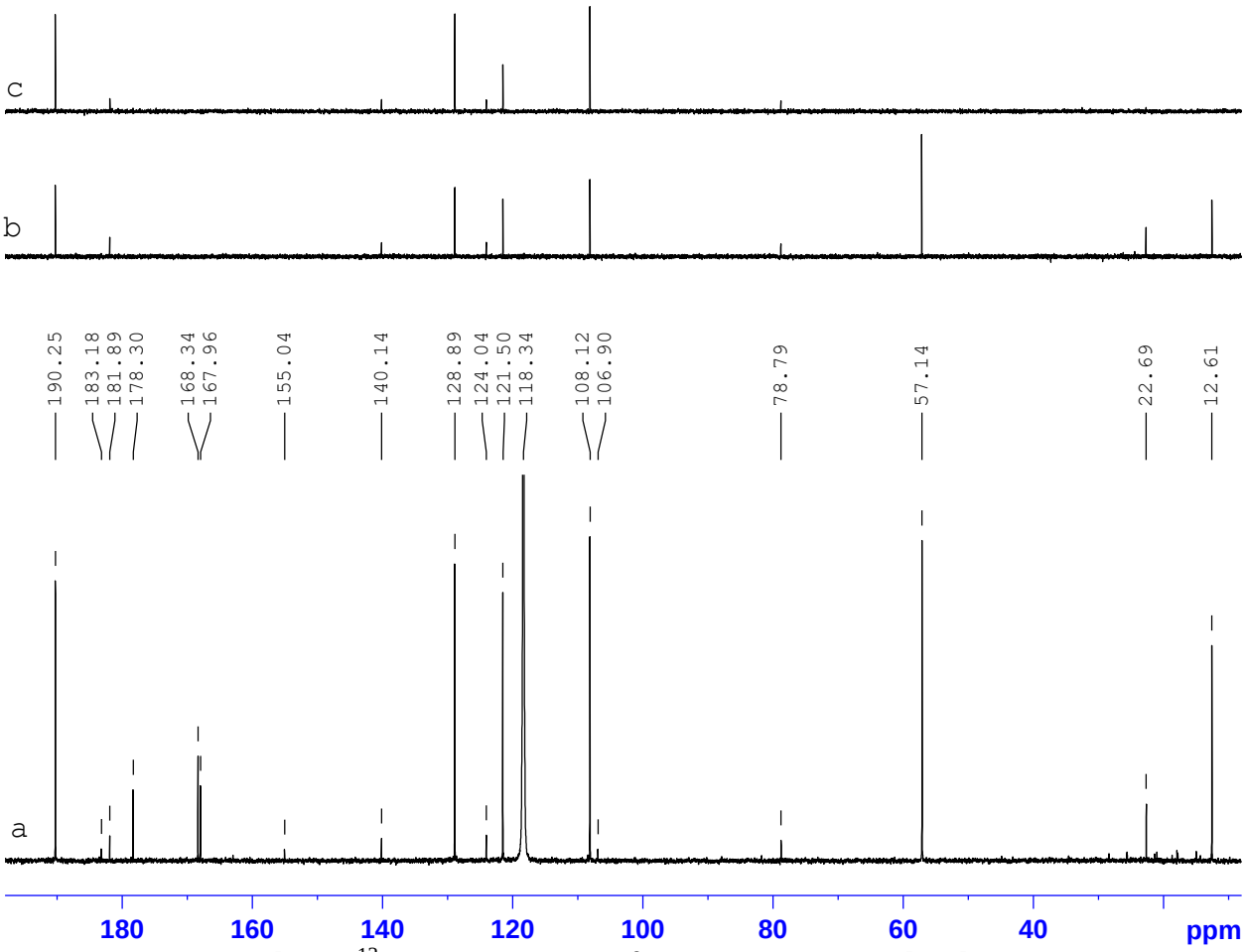


Figure S28. DEPT editing ^{13}C NMR spectrum of mixture *trans*, *cis*-**2d** and **4'** in CD_3CN: a) $^{13}C\{^{1}H\}$ spectrum; b) DEPT-135; c) DEPT-90.

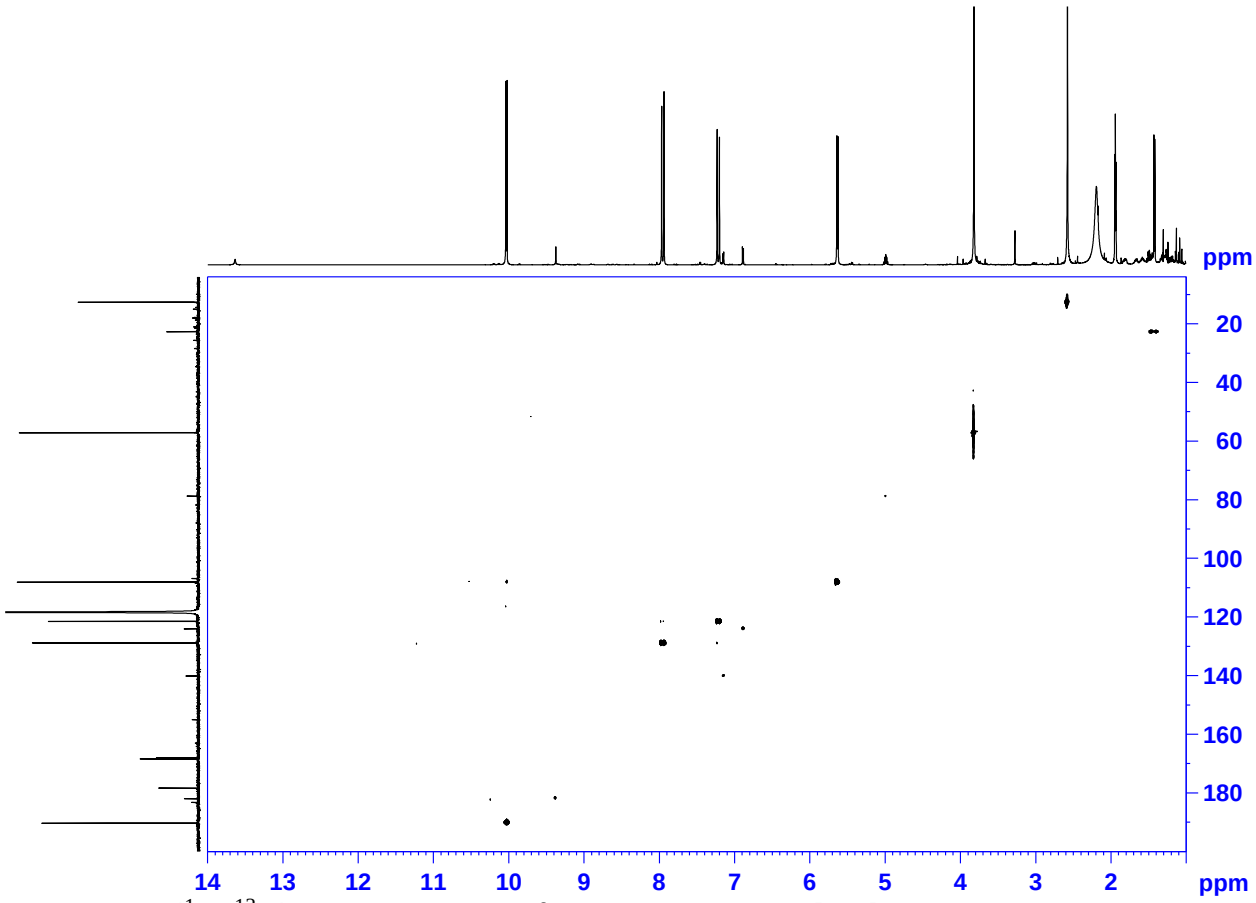


Figure S29. {^{1}H, ^{13}C} HSQC spectrum of mixture *trans*, *cis*-**2d** and **4'** in CD_3CN.

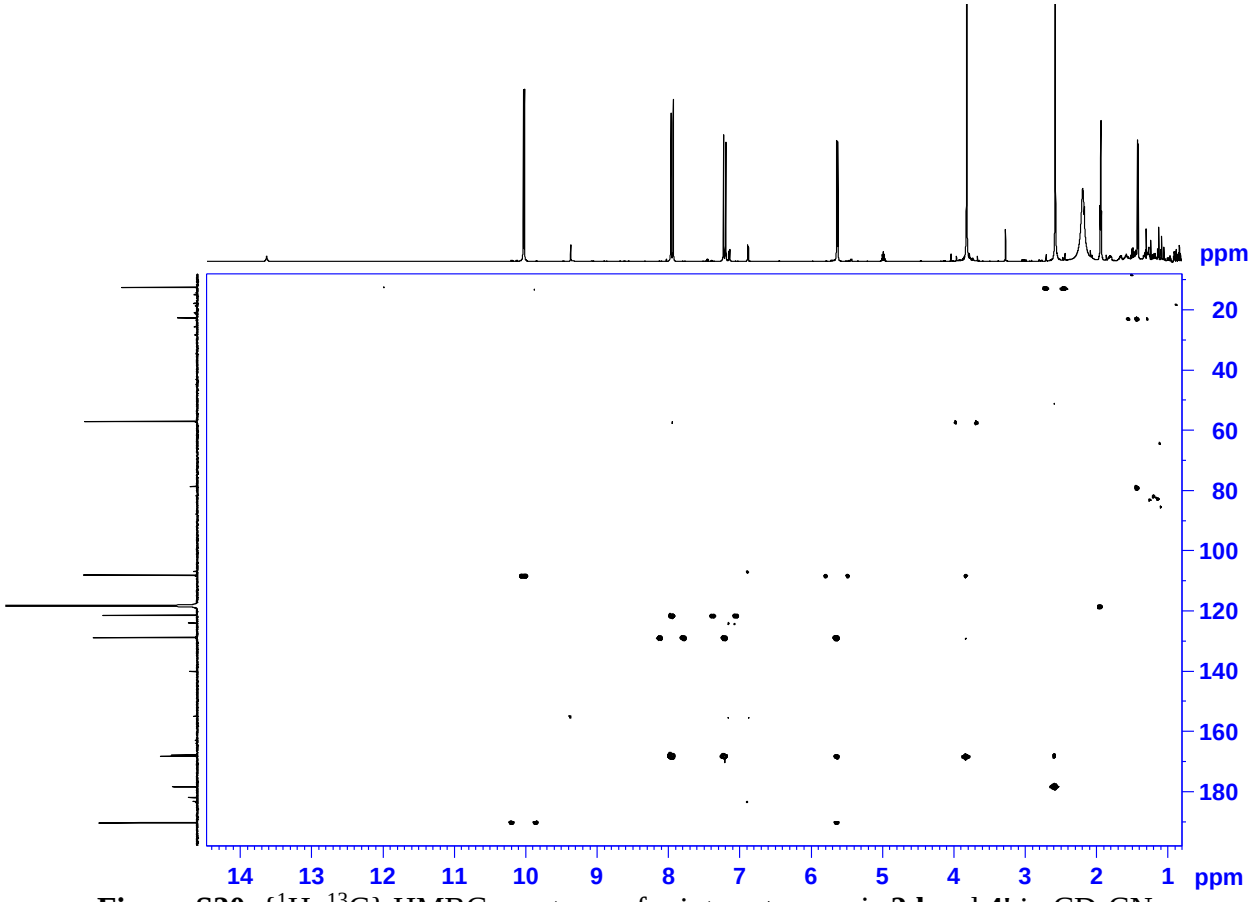


Figure S30. {^{1}H, ^{13}C} HMBC spectrum of mixture *trans*, *cis*-**2d** and **4'** in CD_3CN.

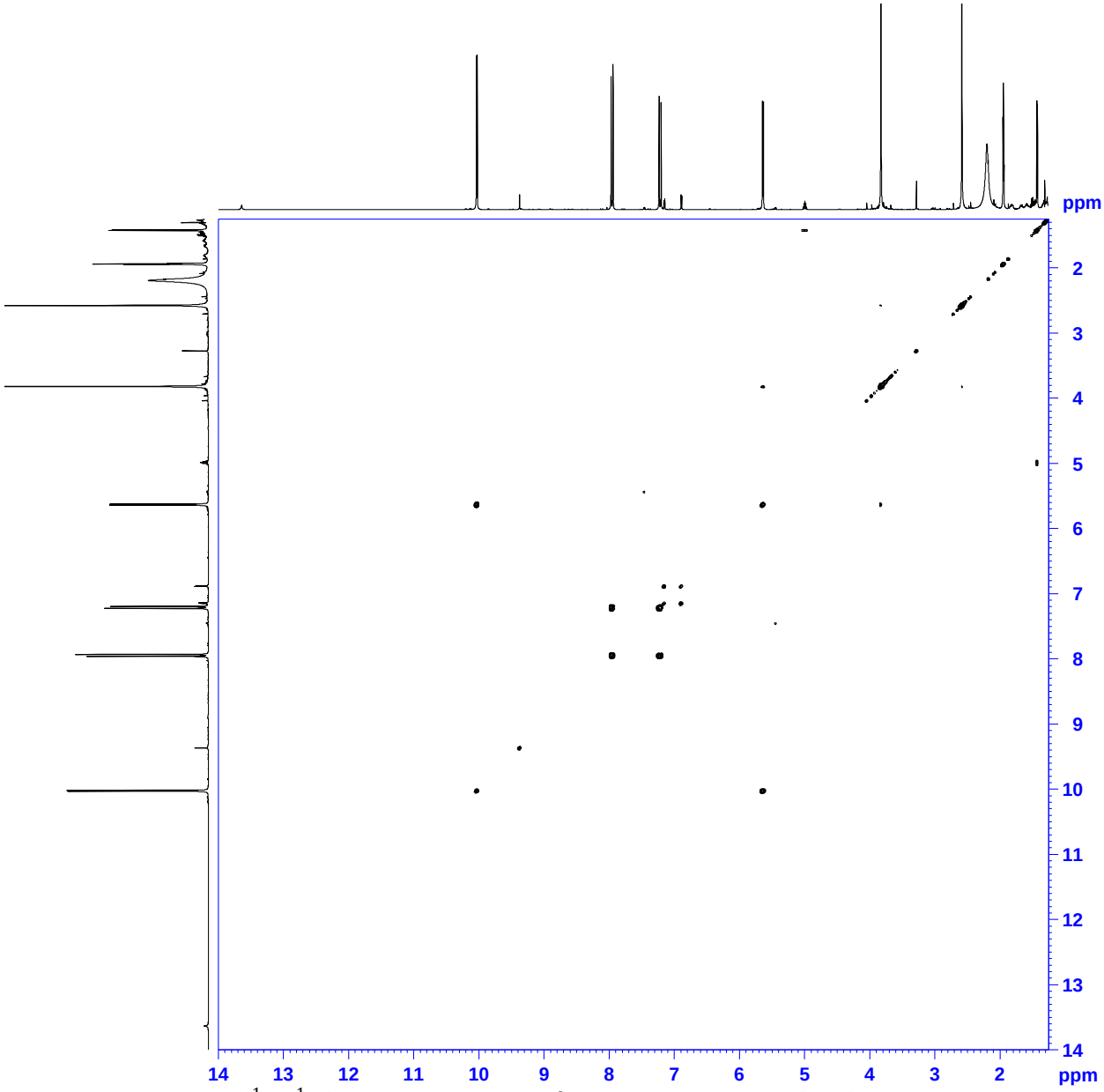


Figure S31. {^{1}H, ^{1}H} COSY spectrum of mixture *trans*, *cis*-**2d** and **4'** in CD_3CN.

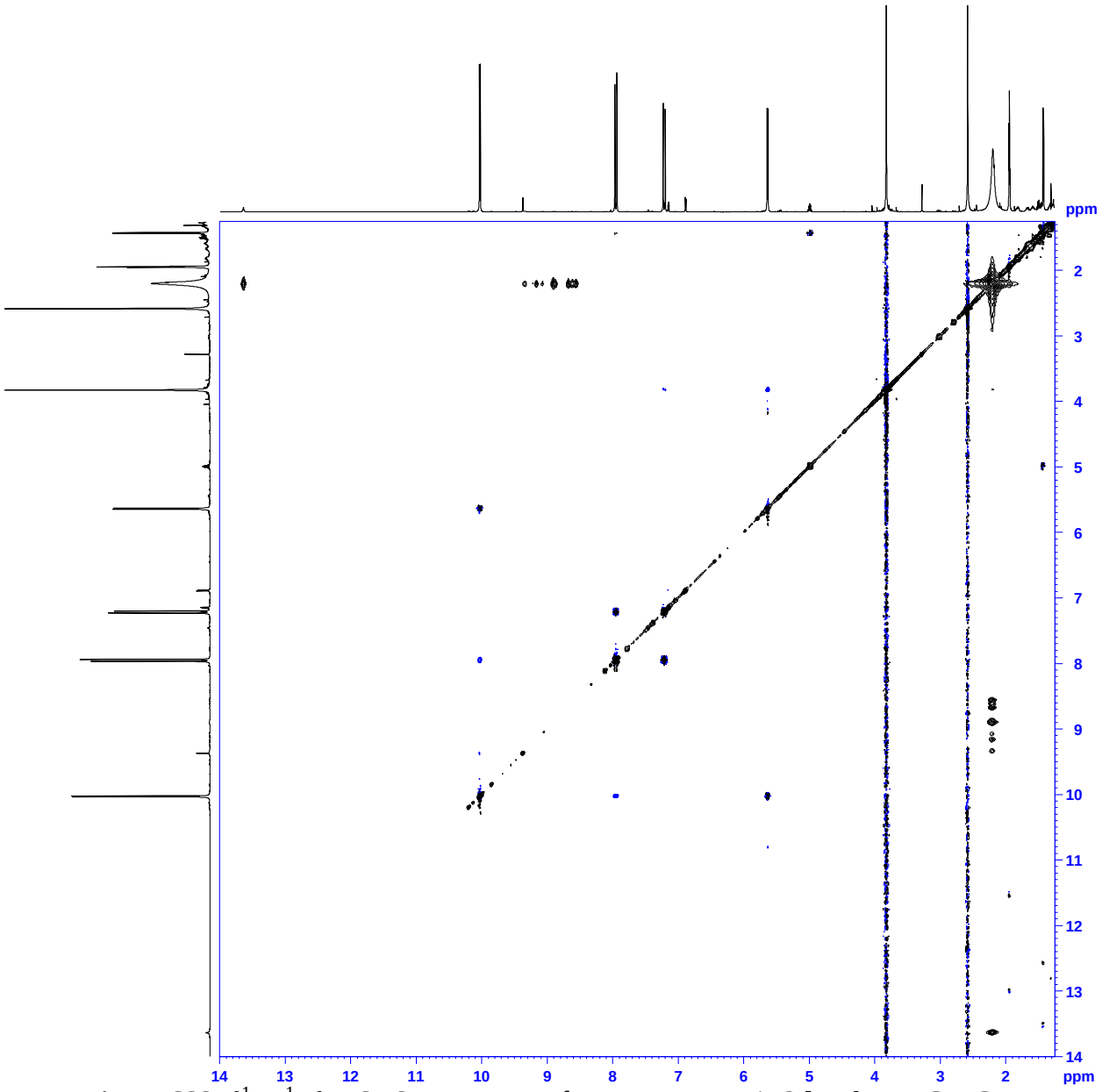


Figure S32. {^{1}H, ^{1}H} NOESY spectrum of mixture *trans*, *cis*-**2d** and **4'** in CD_3CN.

High resolution mass spectra

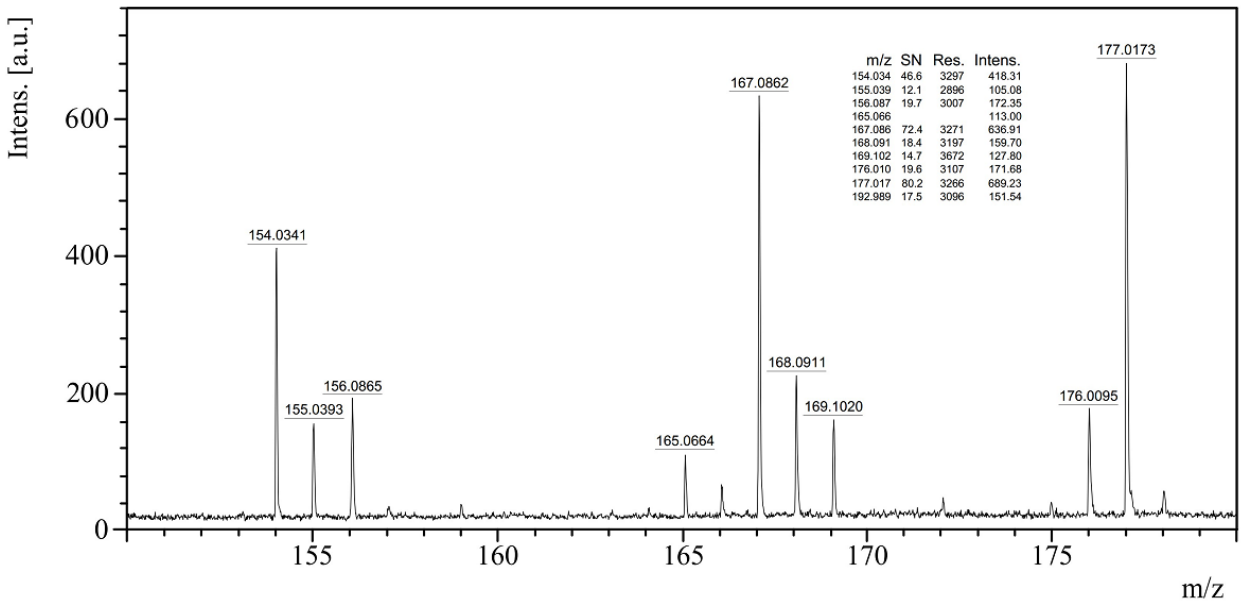


Figure S33. Positive ion MALDI mass spectrum of **2a**.

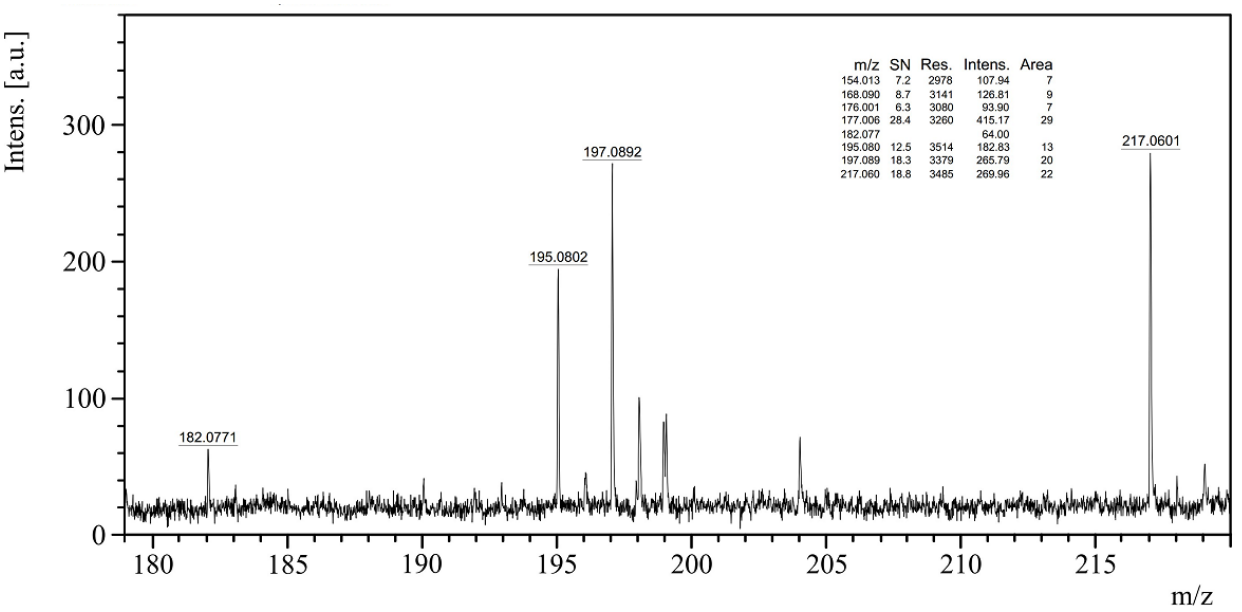


Figure S34. Positive ion MALDI mass spectrum of **2d** (m/z 195.0802), **4'** (m/z 182.0771).

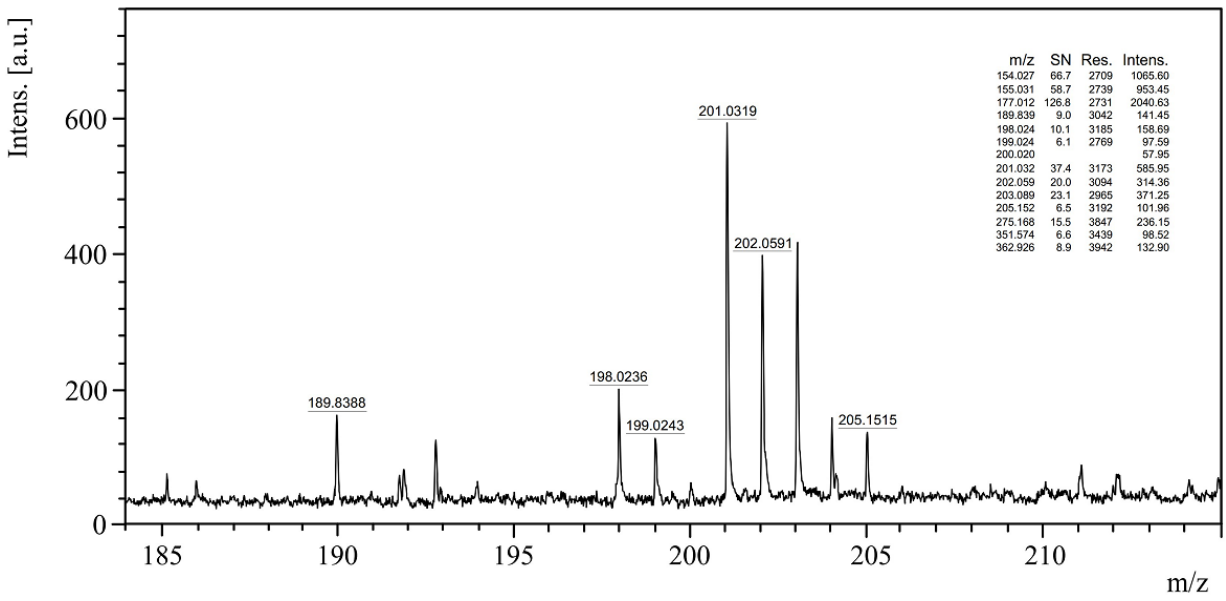


Figure S35. Positive ion MALDI mass spectrum of **2b**.

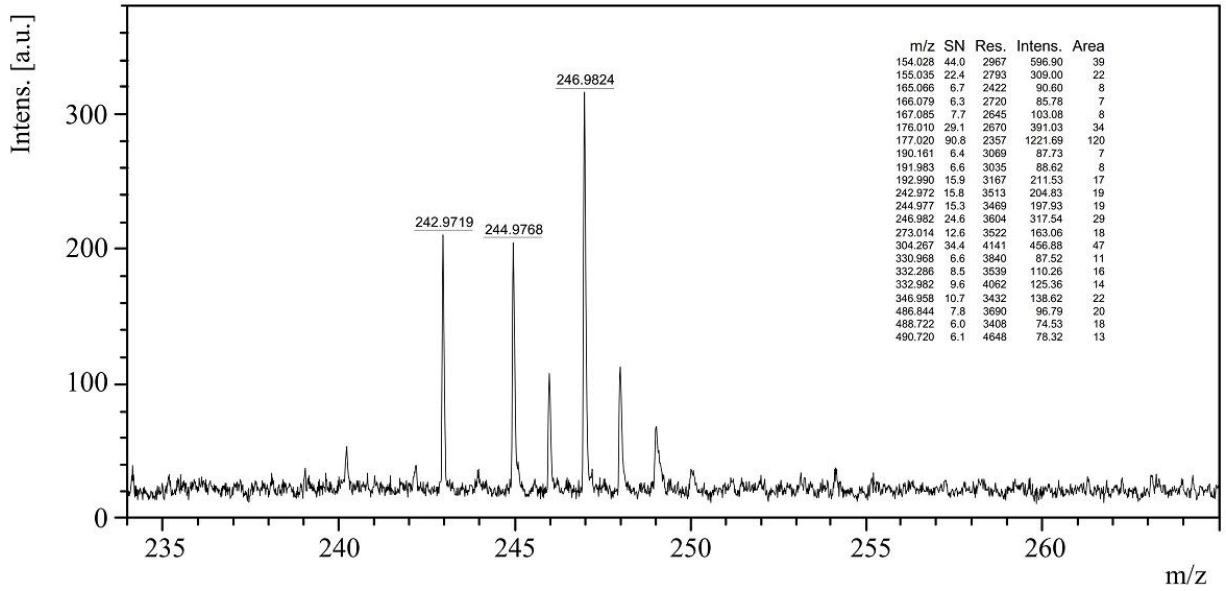


Figure S36. Positive ion MALDI mass spectrum of **2c**.

APCI-MS data

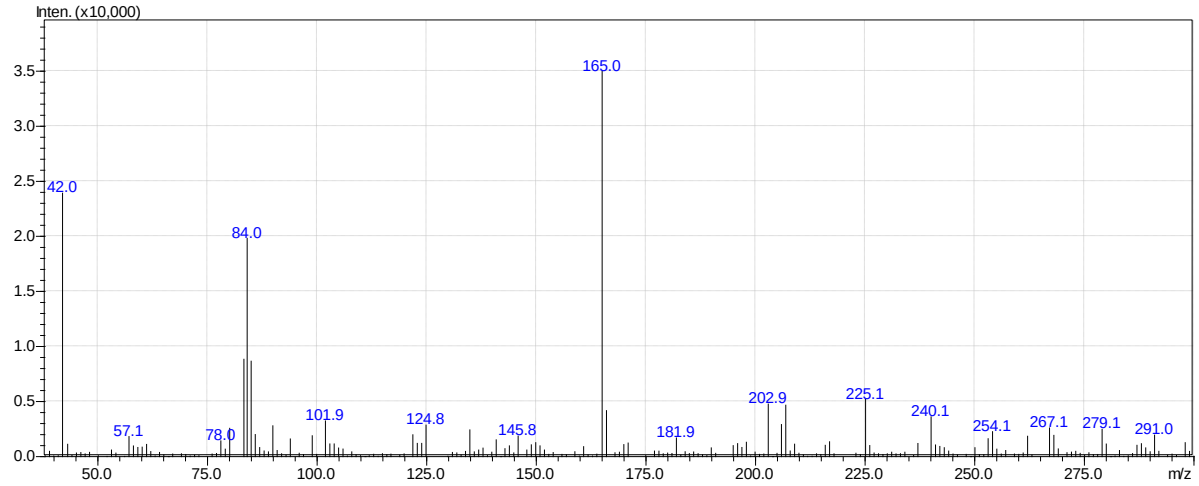


Figure S37. Positive ion APCI mass spectrum of **2a**.

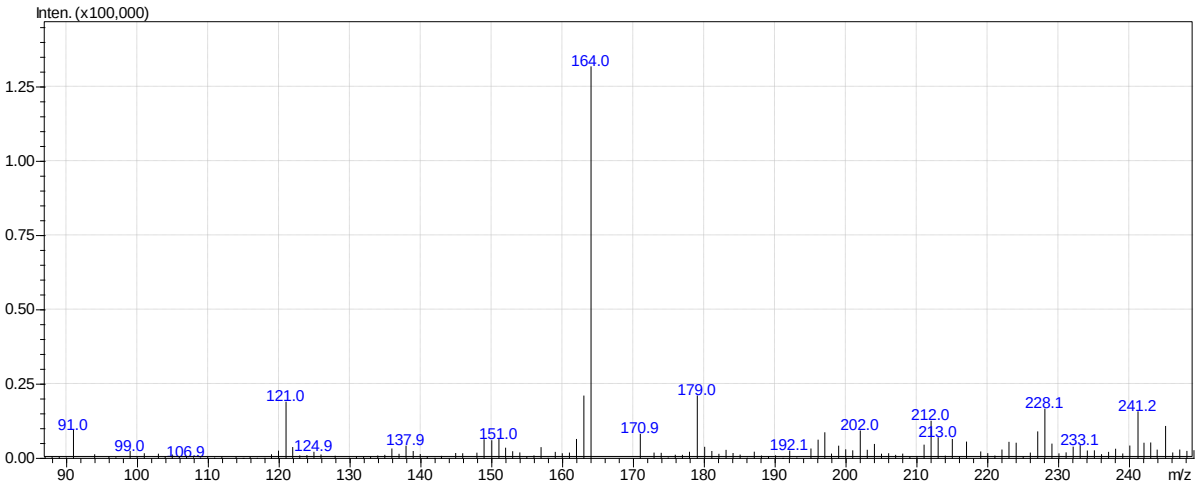


Figure S38. Negative ion APCI mass spectrum of **2a**.

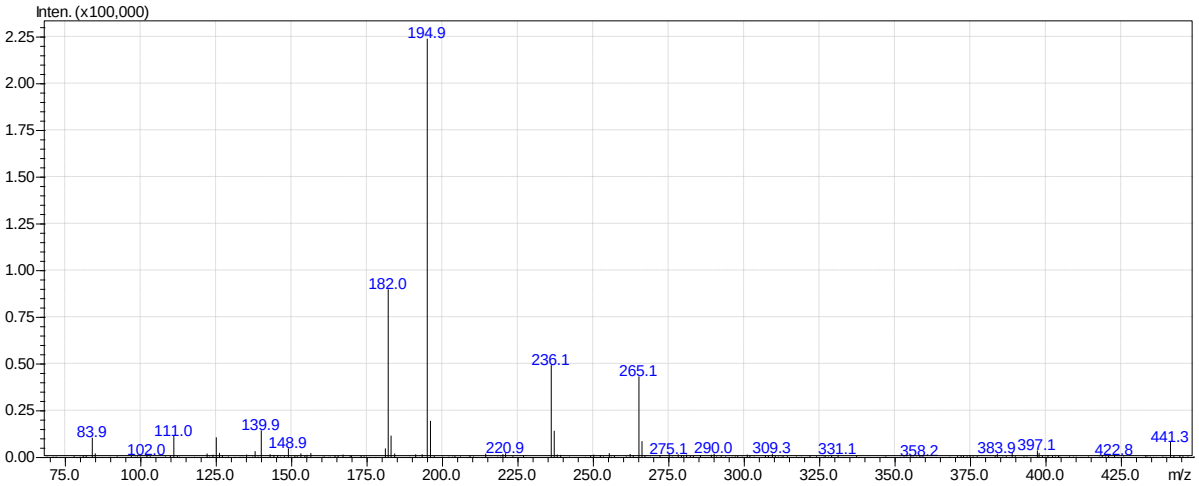


Figure S39. Positive ion APCI mass spectrum of **2d** (m/z 195), **4'** (m/z 182).

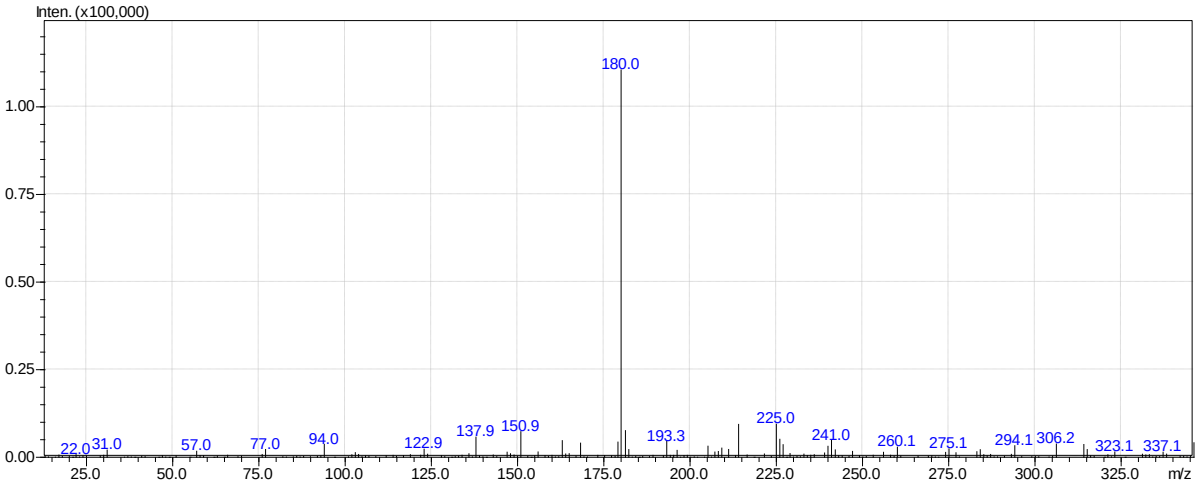


Figure S40. Negative ion APCI mass spectrum of **4'**.

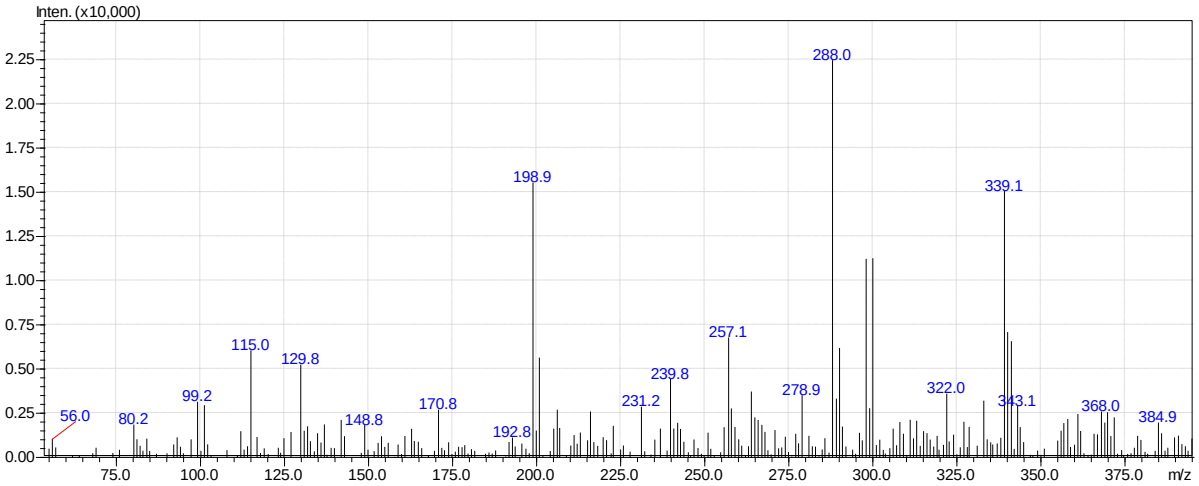


Figure S41. Positive ion APCI mass spectrum of **2b**.

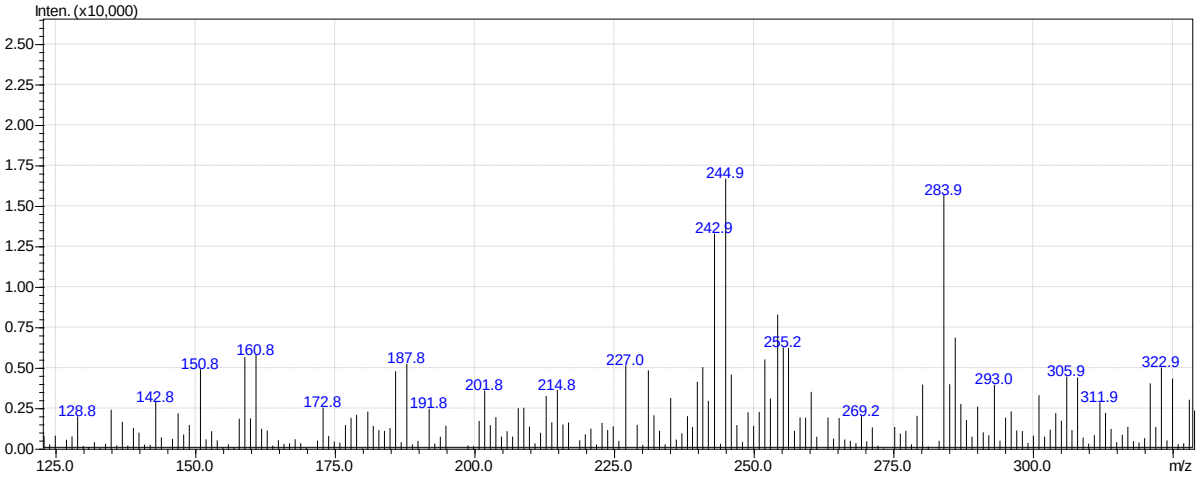


Figure S42. Positive ion APCI mass spectrum of **2c**.