

Amide derivatives of 3-aminopropylsilatrane

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^1H (400.13 MHz), ^{13}C (100.61 MHz), ^{29}Si (79.46 MHz) and ^{15}N (40.55 MHz) NMR spectra were recorded using a Bruker AV400 instrument in CDCl_3 or $\text{DMSO}-d_6$ at room temperature. Chemical shifts δ are expressed in parts per million (ppm). The residual solvent peaks δ_{H} 7.27 and δ_{C} 77.1 for CDCl_3 , as well as δ_{H} 2.50 and δ_{C} 39.5 for $\text{DMSO}-d_6$, were used as references. The assignment of signals in the ^1H NMR spectra was made using COSY and NOESY 2D experiments. Resonance signals of carbon atoms were assigned based on 2D $^1\text{H}-^{13}\text{C}$ HSQC and $^1\text{H}-^{13}\text{C}$ HMBC experiments. The values of the $\delta^{15}\text{N}$ were measured by the 2D $^1\text{H}-^{15}\text{N}$ HMBC experiment and referenced to MeNO_2 as 0.0 ppm.

IR spectra were recorded using a Bruker IFS-25 spectrophotometer as films. Acids **2a–c** and **2e** (99% purity) were purchased from Sigma–Aldrich. Acid **2d** was synthesized following the general procedure described.^{4(c)} (see the references list in the article).

N-decyl-2-(2-methylphenoxy)acetamide (model). Yield 88 %, light yellow powder, mp 68–69 °C. IR (ν/cm^{-1}): 1673 (C=O), 3284 and 3331 (NH). ^1H NMR (CDCl_3) δ : 0.89 (t, 3H, Me, J 7.1 Hz), 1.20–1.40 (m, 14H, CH_2 in decyl), 1.52–1.58 (m, 2H, CH_2 in decyl), 2.29 (s, 3H, MeC_6H_4), 3.34–3.40 (m, 2H, HNCH_2), 4.51 (s, 2H, OCH_2), 6.62 (br.s, 1H, NH), 6.77–6.82 (m, 1H, C_6H_4), 6.92–6.98 (m, 1H, C_6H_4), 7.15–7.22 (m, 2H, C_6H_4). ^{13}C NMR (CDCl_3) δ : 14.18 (Me), 16.39 (MeC_6H_4), 22.76, 26.91, 29.32, 29.42, 29.55, 29.72, (CH_2 in decyl), 39.14 (HNCH_2), 67.63 (OCH_2), 111.75 (C^6), 121.95 (C^4), 126.51 (C^2), 127.33 (C^5), 131.15 (C^3), 155.51 (C^1), 168.63 (C=O). ^{15}N NMR (CDCl_3) δ : –267.0.

N-[3-(2,8,9-trioxa-5-aza-1-silabicyclo[3.3.3]undecan-1-yl)propyl]-2-(2-methylphenoxy)acetamide **3a**. Yield 89 %, colourless powder, mp 152–154 °C. IR (ν/cm^{-1}): 557 (N→Si), 1058 (Si–O), 1673 (C=O), 3331 and 3424 (NH). ^1H NMR (CDCl_3) δ : 0.42–0.48 (m, 2H, CH_2Si), 1.57–1.68 (m, 2H, $\text{CH}_2\text{CH}_2\text{Si}$), 2.27 (s, 3H, MeC_6H_4), 2.77 (t, 6H, CH_2N , J 5.8 Hz), 3.29–3.36 (m, 2H, HNCH_2), 3.71 (t, 6H, OCH_2 , J 5.8 Hz), 4.44 (s, 2H, OCH_2), 6.74–6.78 (m, 1H, C_6H_4), 6.85–6.89 (m, 1H, C_6H_4), 7.05 (br.s, 1H, NH), 7.10–7.18 (m, 2H, C_6H_4). ^{13}C NMR (CDCl_3) δ : 13.02 (CH_2Si), 16.41 (MeC_6H_4), 24.84 ($\text{CH}_2\text{CH}_2\text{Si}$), 41.77 (HNCH_2), 51.13 (NCH_2), 57.70 (OCH_2), 67.79 (OCH_2), 111.80 (C^6), 121.67 (C^4), 126.72 (C^2), 127.22 (C^5), 130.99 (C^3), 155.73 (C^1), 168.15 (C=O). ^{15}N NMR (CDCl_3) δ : –357.9 (CH_2N), –264.7 (NH). ^{29}Si NMR (CDCl_3) δ : –65.6. Found (%): C, 57.08; H, 7.13; N, 7.31. Calc. for $\text{C}_{18}\text{H}_{23}\text{N}_2\text{O}_5\text{Si}$ (%): C, 56.81; H, 7.41; N, 7.36.

N-[3-(2,8,9-trioxa-5-aza-1-silabicyclo[3.3.3]undecan-1-yl)propyl]-2-(4-chloro-2-methylphenoxy)acetamide **3b**. Yield 87 %, colourless powder, mp 158–159 °C. IR (ν/cm^{-1}): 558 (N→Si), 1061 (Si–O), 1664 (C=O), 3329 and 3419 (NH). ^1H NMR (CDCl_3) δ : 0.40–0.46 (m, 2H, CH_2Si), 1.57–1.69 (m, 2H, $\text{CH}_2\text{CH}_2\text{Si}$), 2.25 (s, 3H, MeC_6H_4), 2.79 (t, 6H, CH_2N , J 5.8 Hz), 3.26–3.37 (m, 2H, HNCH_2), 3.73 (t, 6H, OCH_2 , J 5.8 Hz), 4.42 (s, 2H, OCH_2), 6.69 (d, 1H, C_6H_4), 6.80 (br.s, 1H, NH), 7.08–7.14 (m, 2H, C_6H_4). ^{13}C NMR (CDCl_3) δ : 12.98 (CH_2Si), 16.26 ($\text{MeC}_6\text{H}_3\text{Cl}$), 24.77 ($\text{CH}_2\text{CH}_2\text{Si}$), 41.72 (HNCH_2), 51.11 (NCH_2), 57.67 (OCH_2), 61.10 (OCH_2), 112.94 (C^6), 126.43 (C^2), 126.80 (C^4), 128.63 (C^5), 130.75 (C^3), 154.36 (C^1), 167.62 (C=O). ^{15}N NMR (CDCl_3) δ : –357.9 (CH_2N), –265.5 (NH). ^{29}Si NMR (CDCl_3) δ : –64.7. Found (%): C, 52.38; H, 6.33; N, 6.70. Calc. for $\text{C}_{18}\text{H}_{27}\text{ClN}_2\text{O}_5\text{Si}$ (%): C, 52.10; H, 6.55; N, 6.75.

N-[3-(2,8,9-trioxa-5-aza-1-silabicyclo[3.3.3]undecan-1-yl)propyl]-2-(4-chlorophenylsulfanyl)acetamide **3c**. Yield 83%, colourless powder, mp 167–168 °C. IR (ν/cm^{-1}): 582 (N→Si), 1099 (Si–O), 1653 (C=O), 3298 and 3378 (NH). ^1H NMR (CDCl_3) δ : 0.29–0.38 (m, 2H,

CH₂Si), 1.48–1.60 (m, 2H, CH₂CH₂Si), 2.74 (t, 6H, CH₂N, *J* 5.8 Hz), 3.18–3.25 (m, 2H, HNCH₂), 3.51 (s, 2H, SCH₂), 3.70 (t, 6H, OCH₂, *J* 5.8 Hz), 7.08 (br.s, 1H, NH), 7.18–7.28 (m, 4H, C₆H₄). ¹³C NMR (CDCl₃) δ: 13.10 (CH₂Si), 24.41 (CH₂CH₂Si), 37.77 (SCH₂), 42.71 (HNCH₂), 51.01 (NCH₂), 57.62 (OCH₂), 129.33 (C^{3,5}), 129.67 (C^{2,6}), 132.50 (C⁴), 133.68 (C¹), 167.20 (C=O). ¹⁵N NMR (CDCl₃) δ: –357.8 (CH₂N), –263.1 (NH). ²⁹Si NMR (CDCl₃) δ: –66.5. Found (%): C, 49.21; H, 5.84; N, 6.59. Calc. for C₁₇H₂₅ClN₂SO₄Si (%): C, 48.96; H, 6.04; N, 6.71.

N-[3-(2,8,9-trioxa-5-aza-1-silabicyclo[3.3.3]undecan-1-yl)propyl]-2-(1H-indol-3-ylsulfanyl)acetamide **3d**. Yield 67 %, pink powder, mp 150–153 °C. IR (ν/cm⁻¹): 1045 (Si–O), 1658 (C=O), 3255 and 3424 (NH). ¹H NMR (DMSO-*d*₆) δ: 0.02–0.11 (m, 2H, CH₂Si), 1.25–1.35 (m, 2H, CH₂CH₂Si), 2.74 (t, 6H, CH₂N, *J* 5.8 Hz), 2.87–2.94 (m, 2H, HNCH₂), 3.24 (s, 2H, SCH₂), 3.56 (t, 6H, OCH₂, *J* 5.8 Hz), 7.05–7.16 (m, 2H, indolyl), 7.38–7.43 (m, 1H, indolyl), 7.46 (d, 1H, indolyl, *J* 2.7 Hz), 7.56–7.62 (m, 1H, indolyl), 9.84 (br.s, 1H, NH, indolyl). ¹³C NMR (DMSO-*d*₆) δ: 14.78 (CH₂Si), 29.73 (CH₂CH₂Si), 38.14 (SCH₂), 41.44 (HNCH₂), 50.33 (NCH₂), 57.14 (OCH₂), 104.32, 114.12, 120.38, 121.87, 123.98, 130.61, 132.86, 138.24 (indolyl), 168.28 (C=O). ¹⁵N NMR (DMSO-*d*₆) δ: –357.0 (CH₂N), –265.2 (NH), –242.7 (NH indolyl). ²⁹Si NMR (DMSO-*d*₆) δ: –70.6.

4-Chlorophenyl methyl sulfone **4e**. Yield 35 %, colorless crystals, mp 97–98 °C. IR (ν/cm⁻¹): 1120 (ν_{as} SO₂), 1373 (ν_{as} SO₂). ¹H NMR (CDCl₃) δ: 3.04 (s, 3H, Me), 7.51–7.55 (m, 2H, C₆H₄), 7.85–7.89 (m, 2H, C₆H₄). ¹³C NMR (CDCl₃) δ: 44.77 (SO₂Me), 129.14, 129.94, 139.30, 140.71 (C₆H₄).

Compound **5e**. Yield 59 %, colorless powder, mp 178–179 °C. IR (ν/cm⁻¹): 575 (N→Si), 1093 (Si–O), 1298 (SO₂). ¹H NMR (CDCl₃) δ: 0.46–0.52 (m, 2H, CH₂Si), 1.72–1.78 (m, 2H, CH₂CH₂Si), 2.80 (t, 6H, CH₂N, *J* 5.8 Hz), 3.07 (s, 3H, SO₂Me), 3.10–3.16 (m, 2H, HNCH₂), 3.76 (t, 6H, OCH₂, *J* 5.8 Hz), 4.92 (br.s, 1H, NH), 6.58–6.64 (m, 2H, C₆H₄), 7.62–7.68 (m, 2H, C₆H₄). ¹³C NMR (CDCl₃) δ: 13.01 (CH₂Si), 24.52 (CH₂CH₂Si), 45.78 (SO₂Me), 46.62 (HNCH₂), 51.24 (NCH₂), 57.91 (OCH₂), 111.54, 126.21, 129.55, 152.98 (C₆H₄). ¹⁵N NMR (CDCl₃) δ: –358.3 (CH₂N), –301.2 (NH). ²⁹Si NMR (CDCl₃) δ: –67.7.

Compound **6a**. Yield 44 %. ¹H NMR (CDCl₃) δ: 0.42–0.65 (br.s, 2H, CH₂Si), 1.54–1.74 (br.s, 2H, CH₂CH₂Si), 2.25 (s, 3H, MeC₆H₄), 2.70–2.85 (br.s, 6H, CH₂N), 3.10–3.25 (br.s, 2H, HNCH₂), 3.65–3.80 (br.s, 6H, OCH₂), 4.25–4.50 (br.s, 2H, OCH₂), 6.65–6.75 (br.s, 2H, C₆H₄), 6.95–7.25 (br.s, 3H, C₆H₄, NH). ¹³C NMR (CDCl₃) δ: 15.18 (CH₂Si), 16.53 (MeC₆H₄), 26.88 (CH₂CH₂Si), 43.78 (HNCH₂), 49.02 (NCH₂), 53.54 (OCH₂), 68.12 (OCH₂), 114.19–131.84 (C₆H₄), 155.35 (C¹), 168.78 (C=O). ²⁹Si NMR (CDCl₃) δ: –61.1.

Compound **6b**. Yield 40 %. ¹H NMR (CDCl₃) δ: 0.47–0.68 (br.s, 2H, CH₂Si), 1.52–1.67 (br.s, 2H, CH₂CH₂Si), 2.20 (s, 3H, MeC₆H₄), 2.58 (br.s, 6H, CH₂N), 3.12–3.24 (br.s, 2H, HNCH₂), 3.60 (br.s, 6H, OCH₂), 4.20–4.40 (br.s, 2H, OCH₂), 6.50–6.60 (br.s, 1H, C₆H₄), 6.95–7.15 (br.s, 4H, C₆H₄, NH). ¹³C NMR (CDCl₃) δ: 15.48 (CH₂Si), 16.58 (MeC₆H₃Cl), 26.80 (CH₂CH₂Si), 43.08 (HNCH₂), 49.01 (NCH₂), 55.03 (OCH₂), 68.58 (OCH₂), 114.15–144.78 (C₆H₄), 154.56 (C¹), 168.77 (C=O). ²⁹Si NMR (CDCl₃) δ: –61.2.

Compound **6c**. Yield 40 %. ¹H NMR (CDCl₃) δ: 0.45–0.60 (br.s, 2H, CH₂Si), 1.40–1.60 (br.s, 2H, CH₂CH₂Si), 2.70–2.85 (br.s, 6H, CH₂N), 3.05–3.25 (br.s, 2H, HNCH₂), 3.55–3.65 (br.s, 2H, SCH₂), 3.70–3.80 (br.s, 6H, OCH₂), 7.05 (br.s, 1H, NH), 7.15–7.30 (br.s, 4H, C₆H₄). ¹³C NMR (CDCl₃) δ: 14.25 (CH₂Si), 25.56 (CH₂CH₂Si), 38.86 (SCH₂), 43.77 (HNCH₂), 49.12 (NCH₂), 56.57 (OCH₂), 130.39–134.91 (C₆H₄), 168.24 (C=O). ²⁹Si NMR (CDCl₃) δ: –61.1.

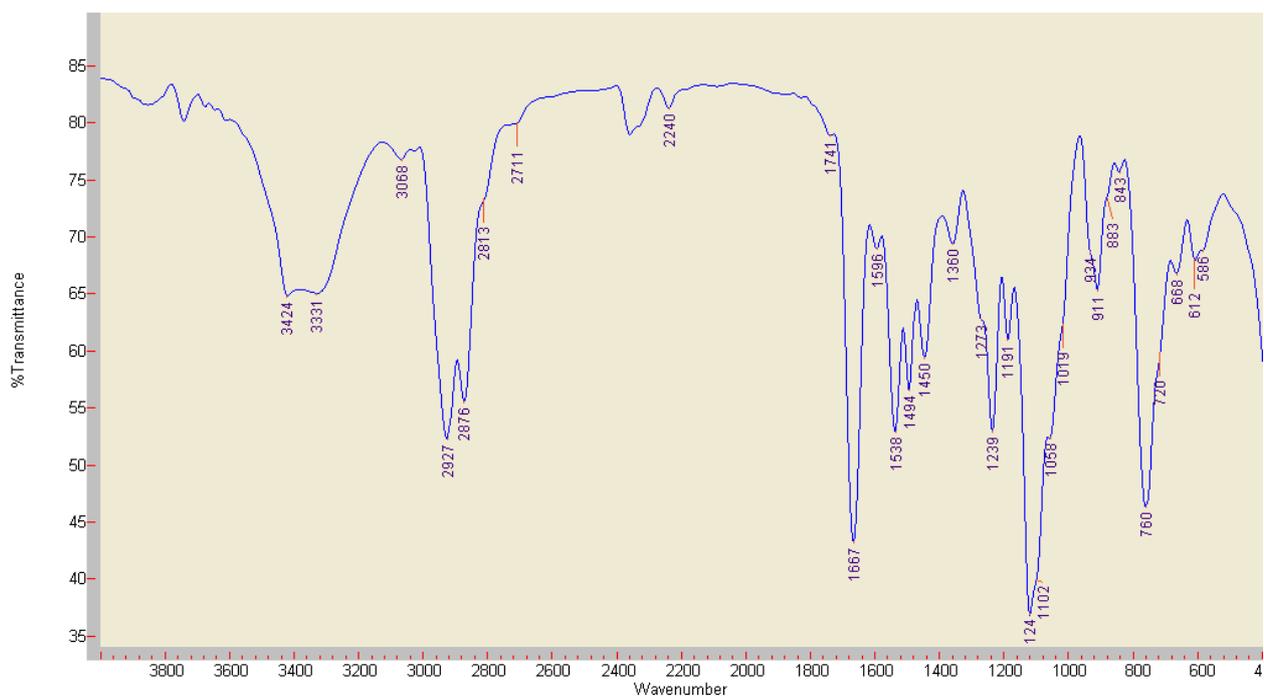


Figure S1 IR Spectrum of compound **3a**.

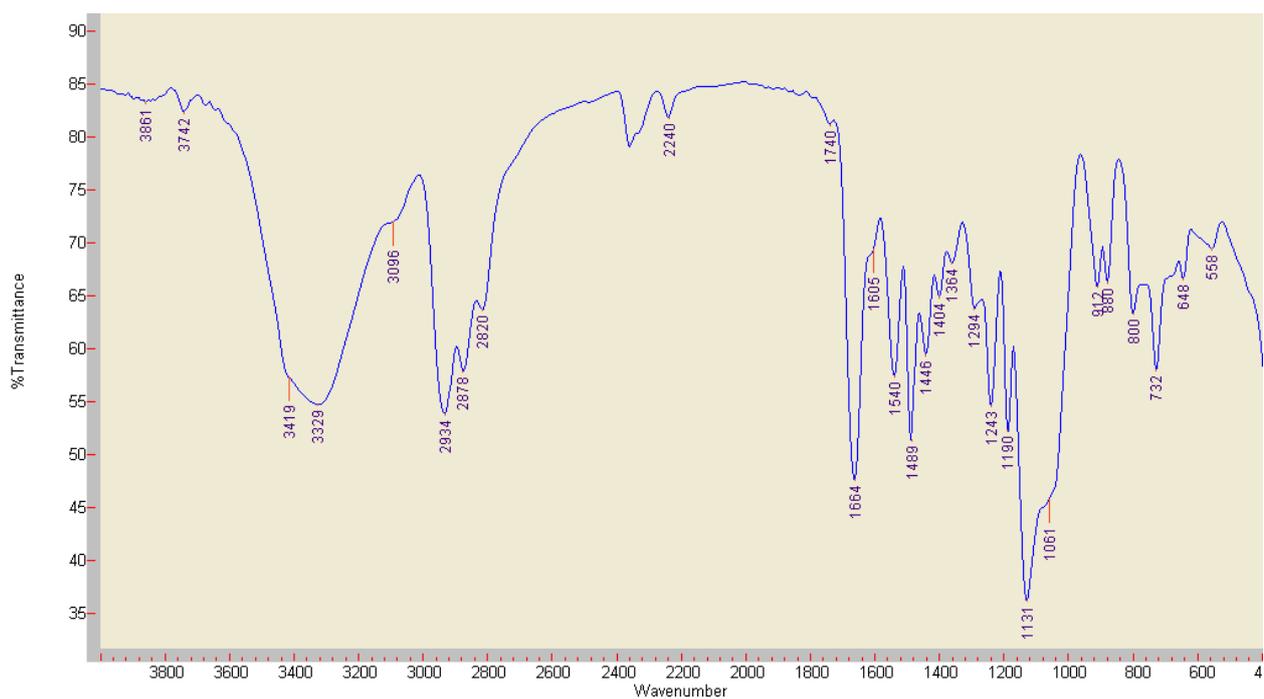


Figure S2 IR Spectrum of compound **3b**.

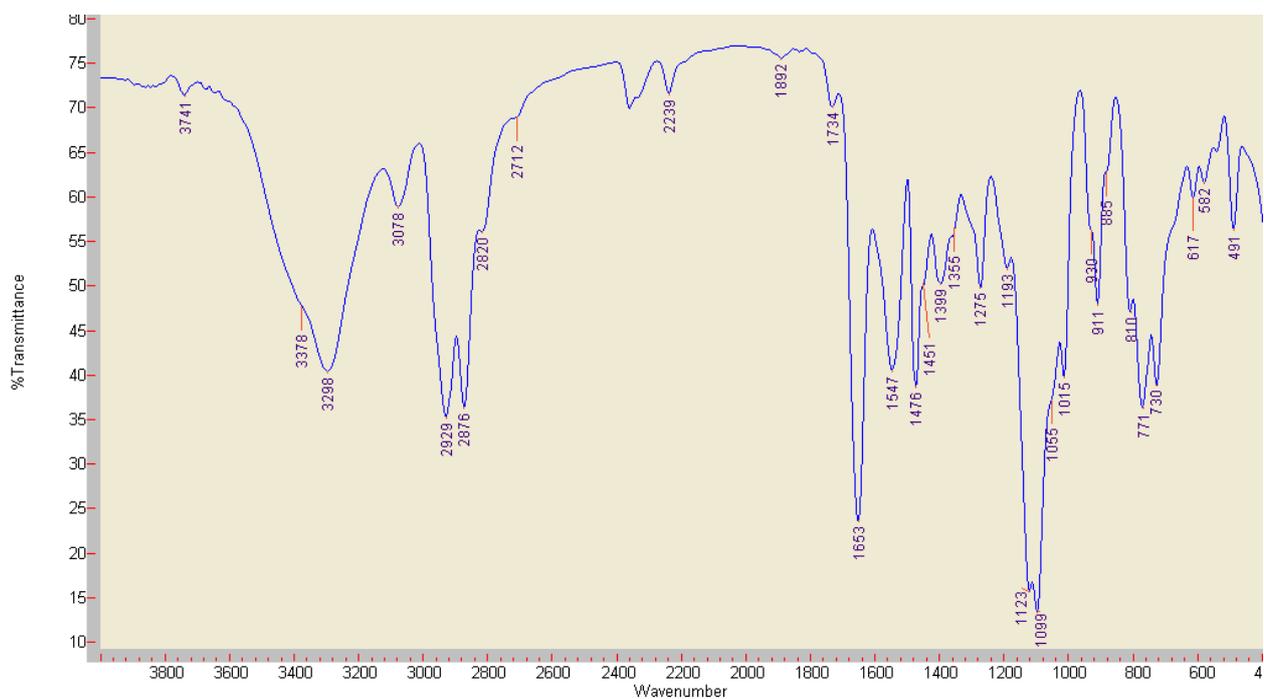


Figure S3 IR Spectrum of compound **3c**.

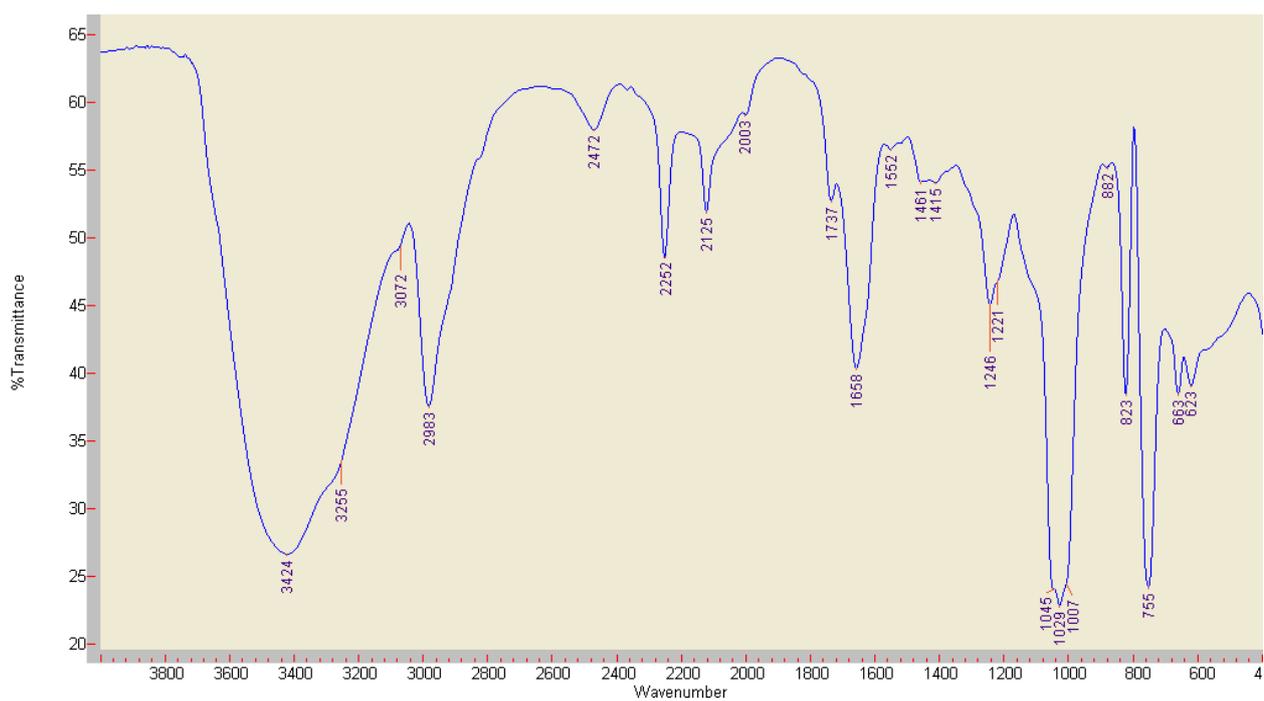


Figure S4 IR Spectrum of compound **3d**.

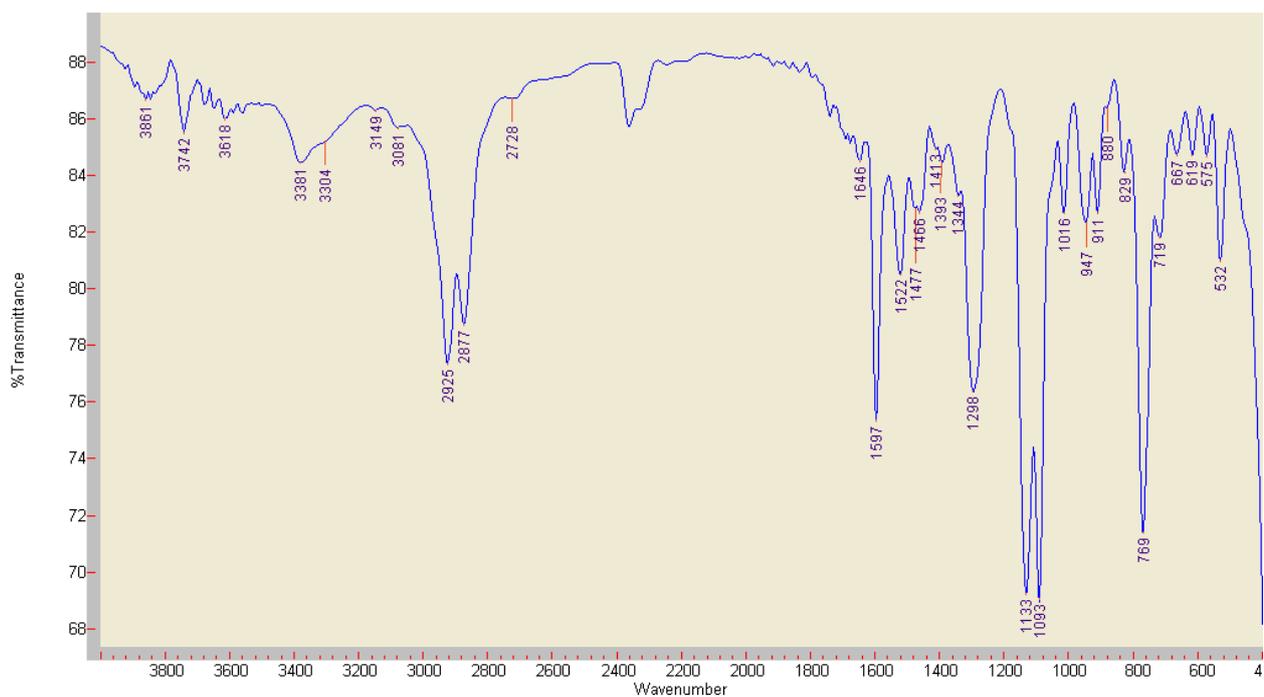


Figure S5 IR Spectrum of compound **5e**.

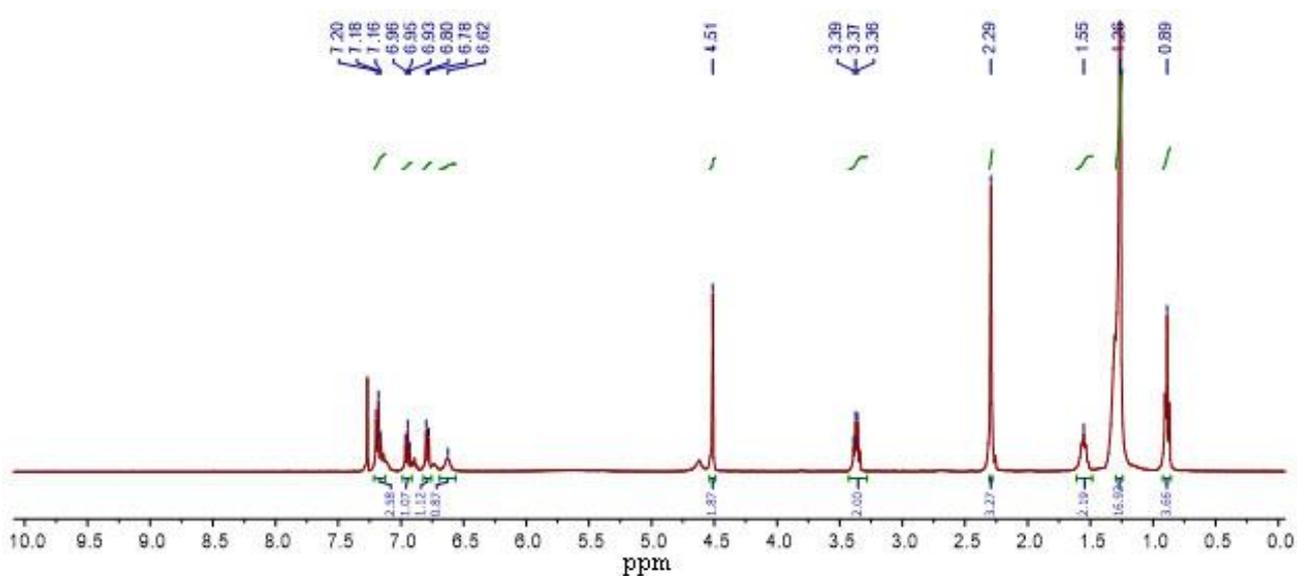


Figure S6 ^1H NMR spectrum of *N*-decyl-2-(2-methylphenoxy)acetamide in CDCl_3 .

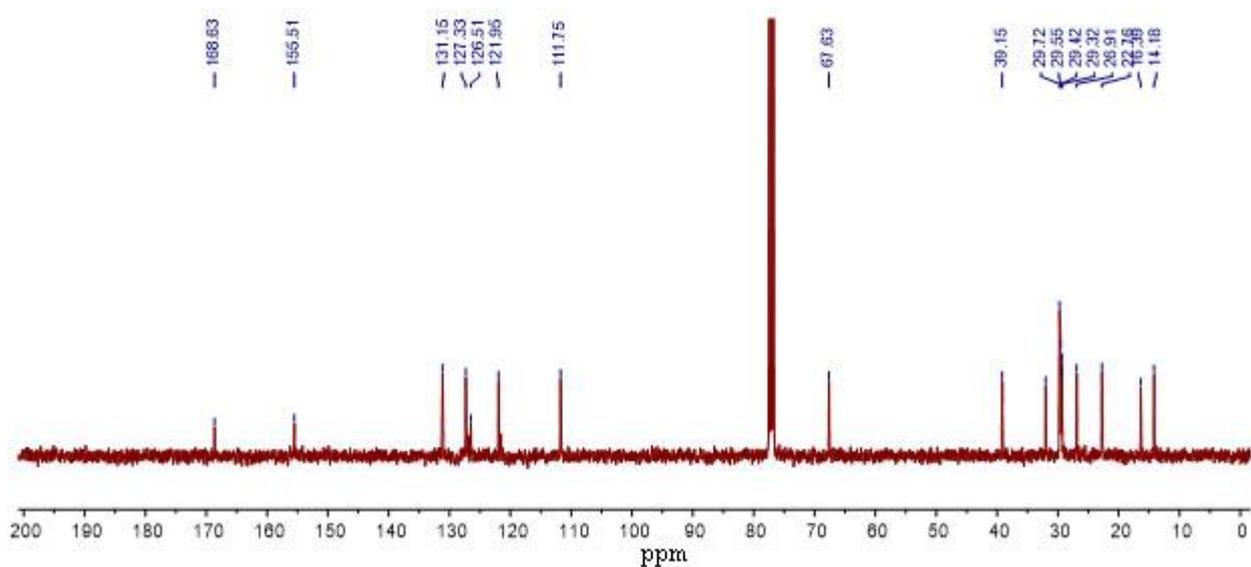


Figure S7 ^{13}C NMR spectrum of *N*-decyl-2-(2-methylphenoxy)acetamide in CDCl_3 .

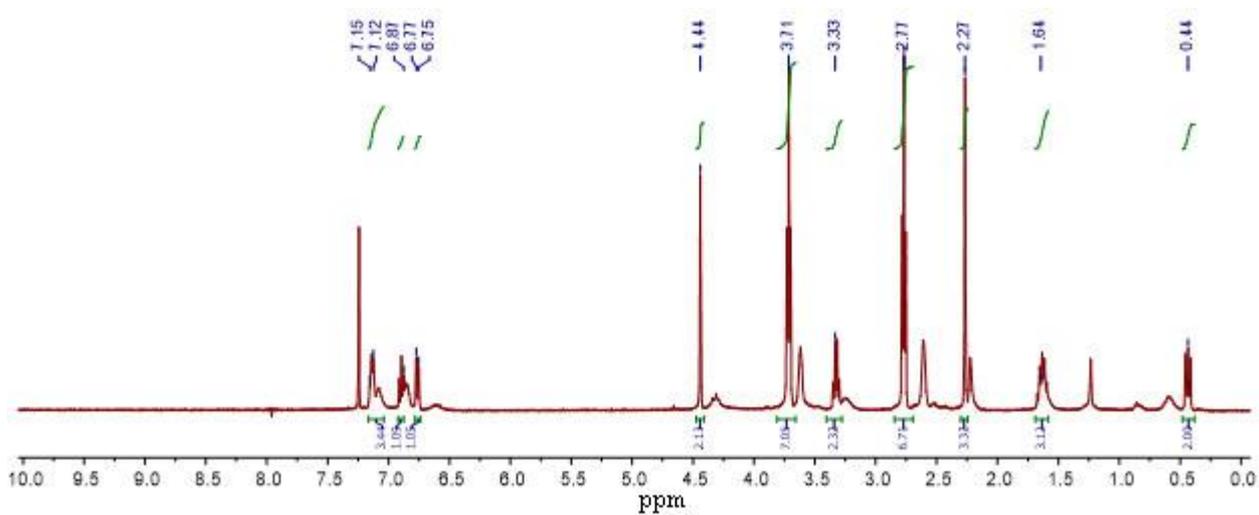


Figure S8 ^1H NMR spectrum of compound **3a** in CDCl_3 .

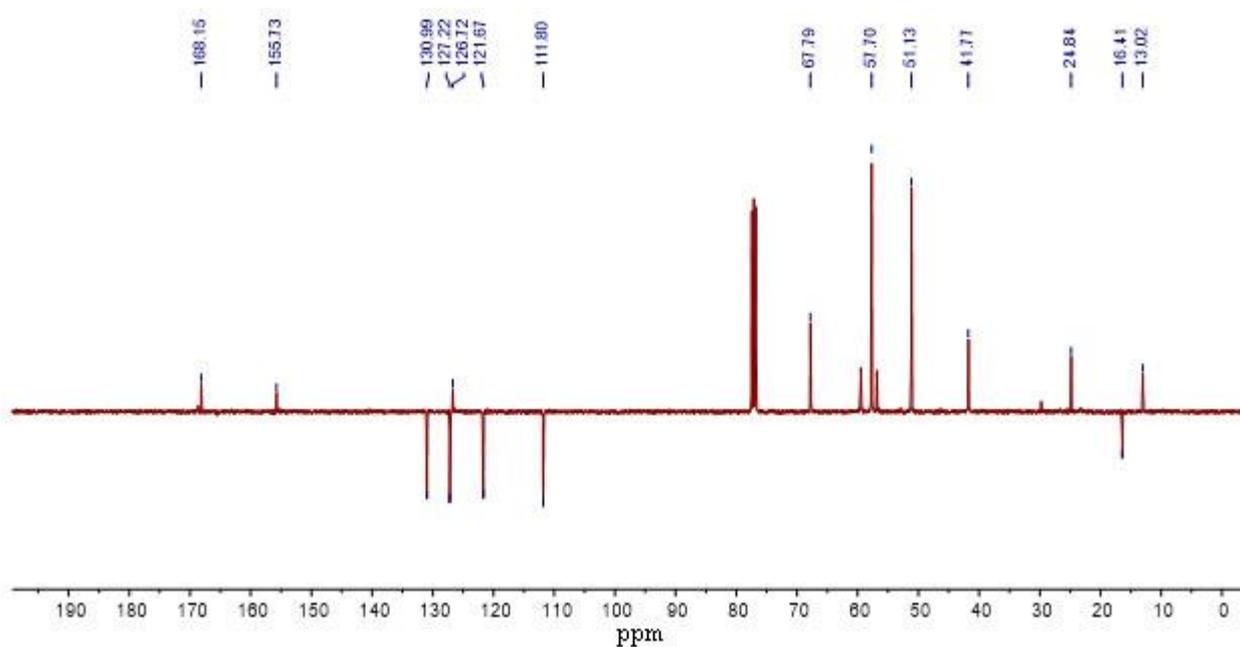


Figure S9 ^{13}C NMR spectrum of compound **3a** (*J*-modulation mode) in CDCl_3 .

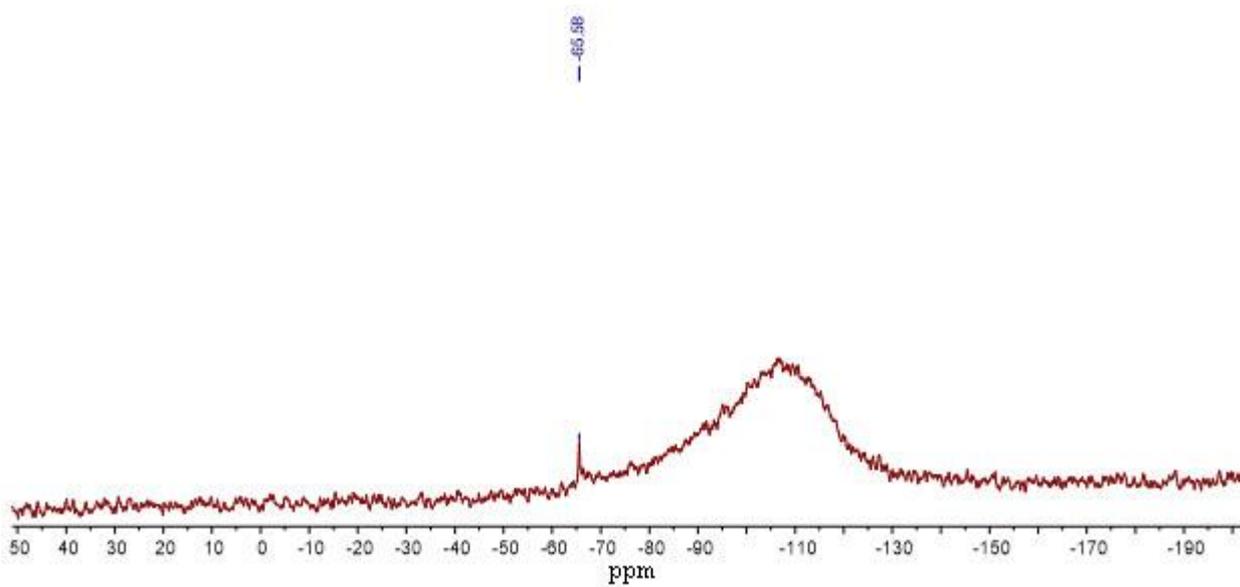


Figure S10 ^{29}Si NMR spectrum of compound **3a** in CDCl_3 .

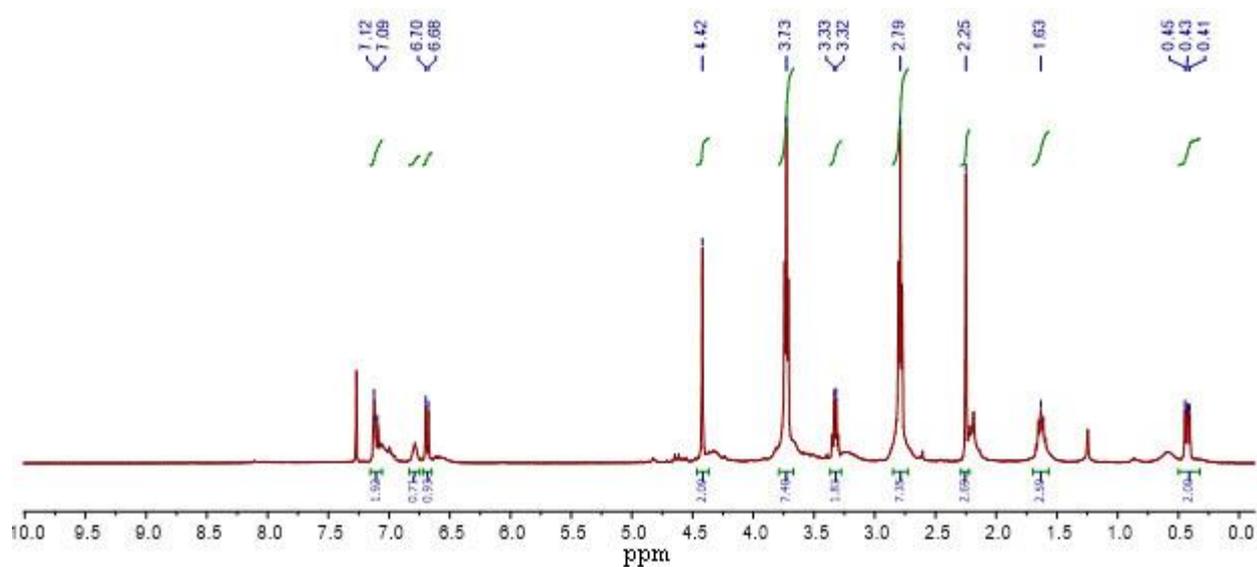


Figure S11 ^1H NMR spectrum of compound **3b** in CDCl_3 .

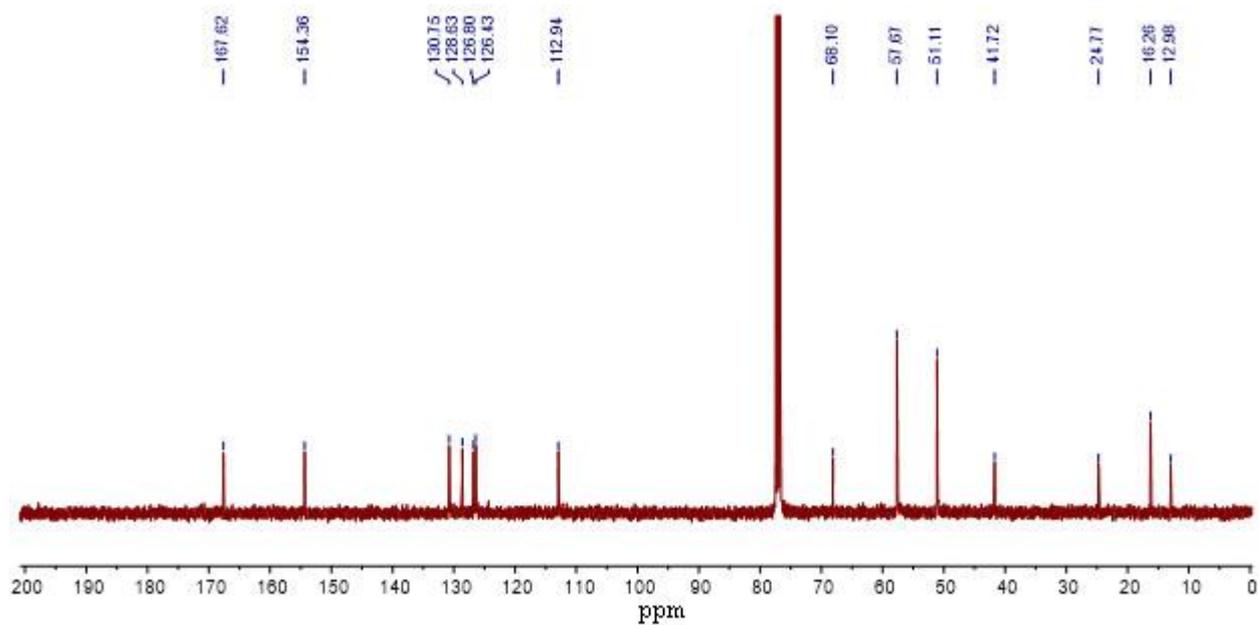


Figure S12 ^{13}C NMR spectrum of compound **3b** in CDCl_3 .

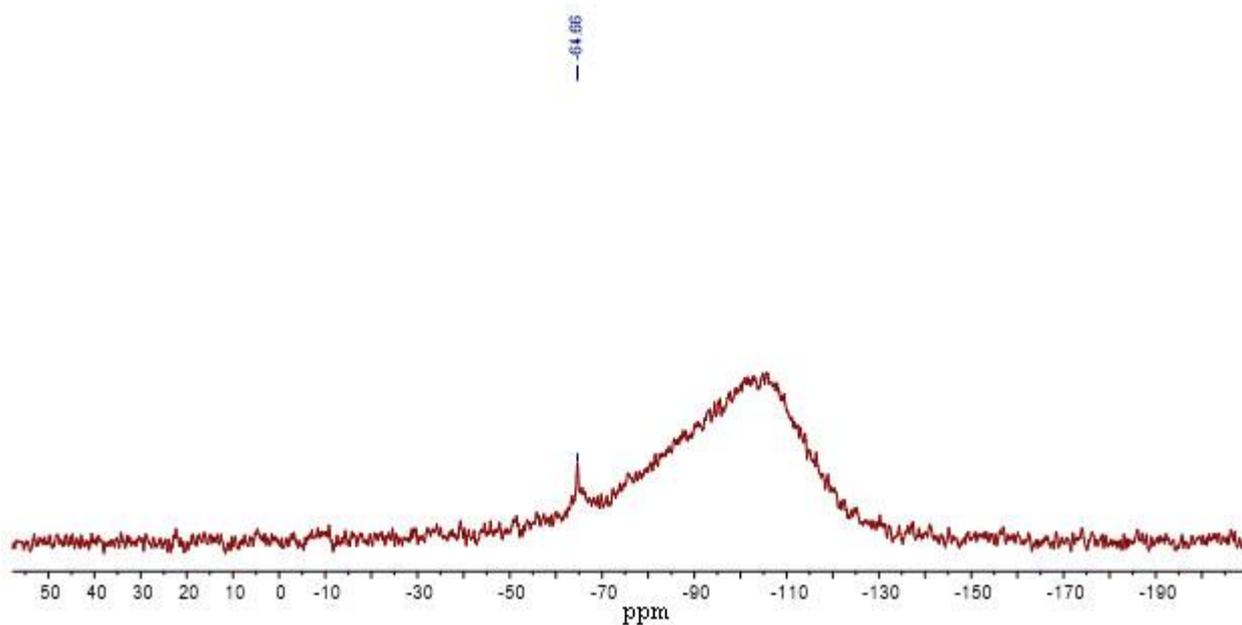


Figure S13 ^{29}Si NMR spectrum of compound **3b** in CDCl_3 .

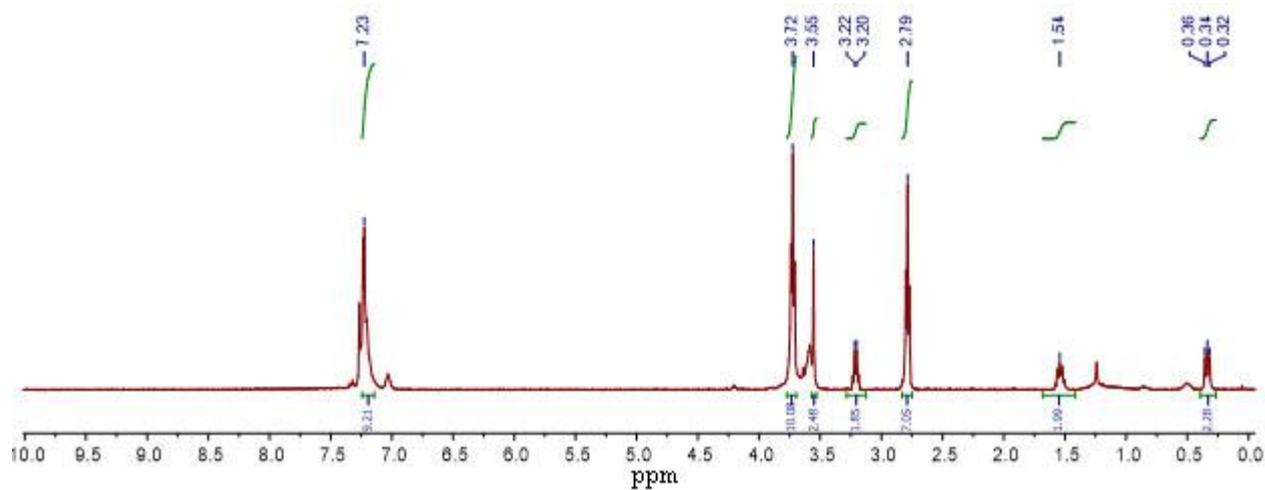


Figure S14 ^1H NMR spectrum of compound **3c** in CDCl_3 .

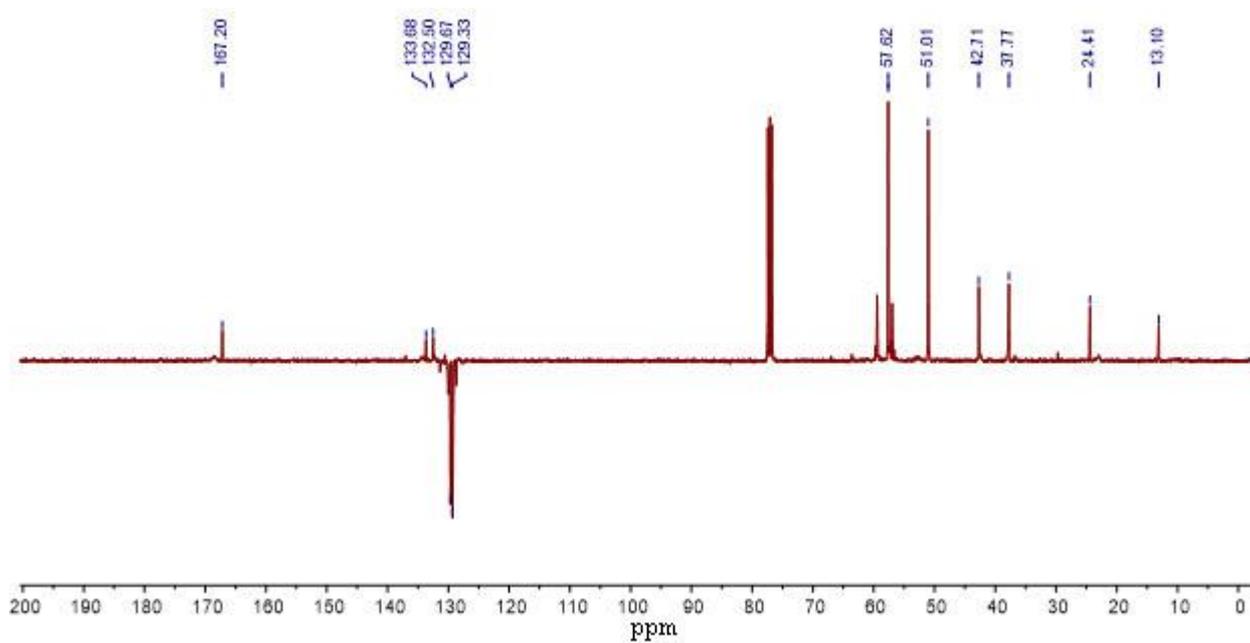


Figure S15 ^{13}C NMR spectrum of **3c** (*J*-modulation mode) in CDCl_3 .

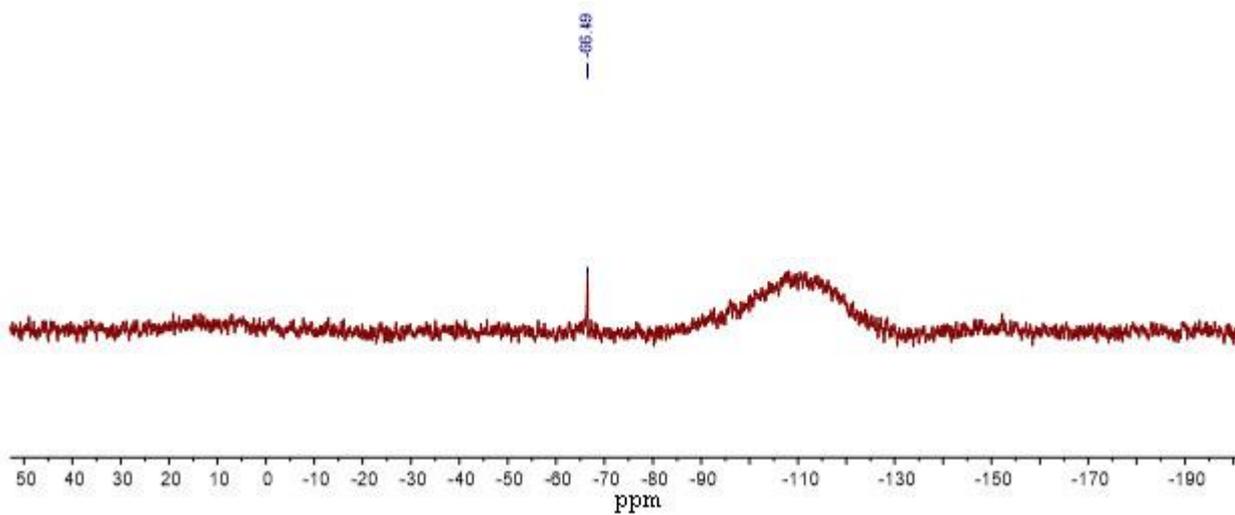


Figure S16 ^{29}Si NMR spectrum of compound **3c** in CDCl_3 .

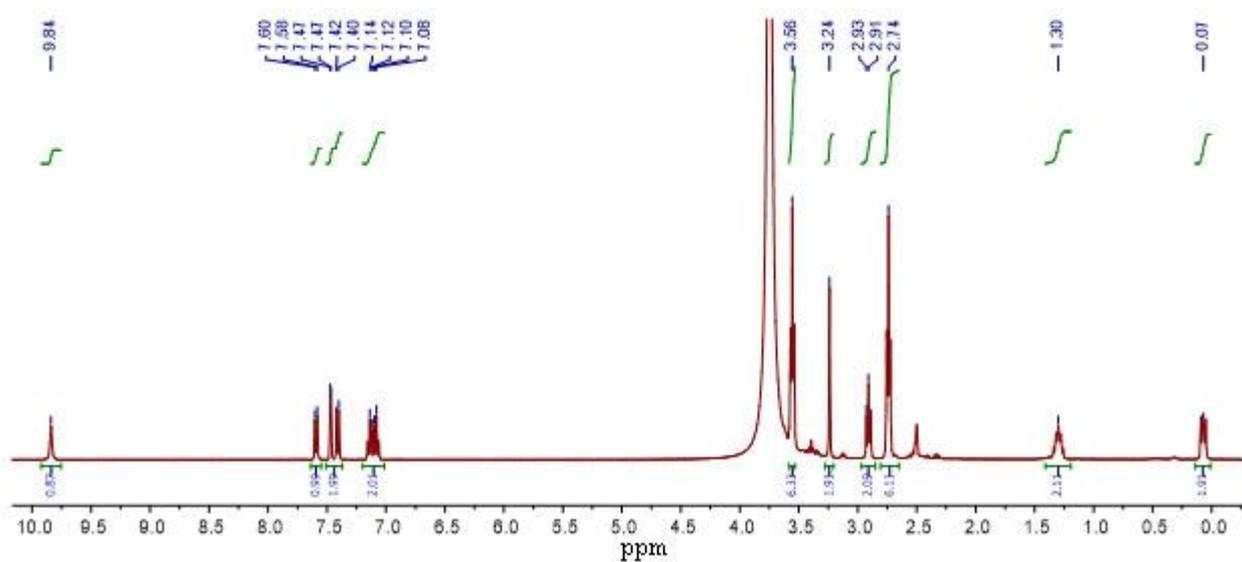


Figure S17 ^1H NMR spectrum of compound **3d** in $\text{DMSO-}d_6$.

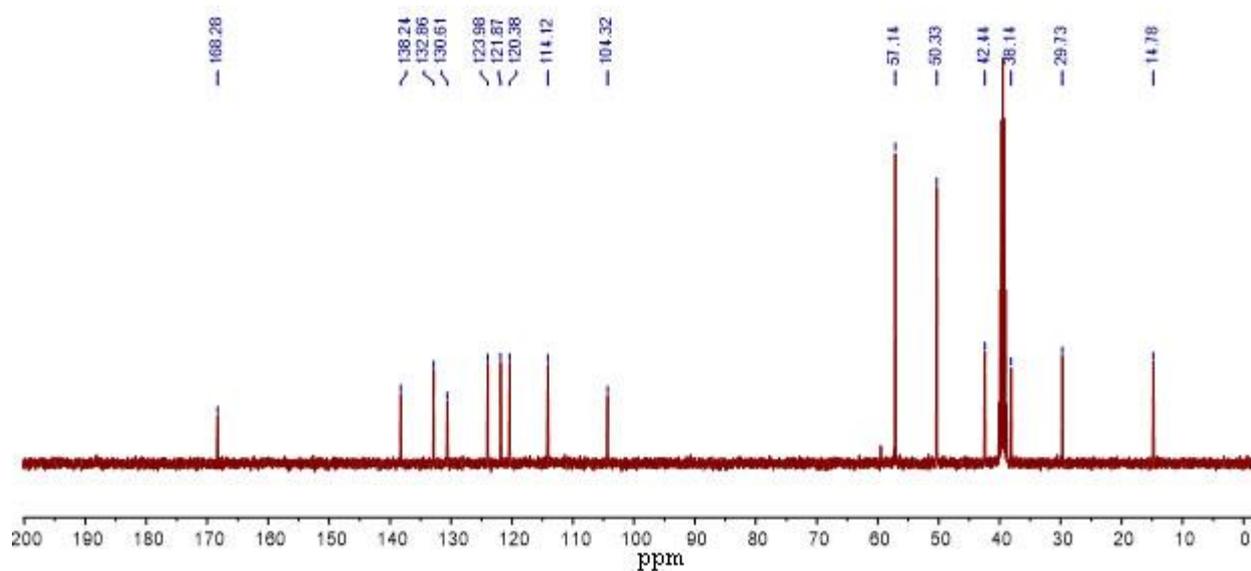


Figure S18 ^{13}C NMR spectrum of compound **3d** in $\text{DMSO-}d_6$.

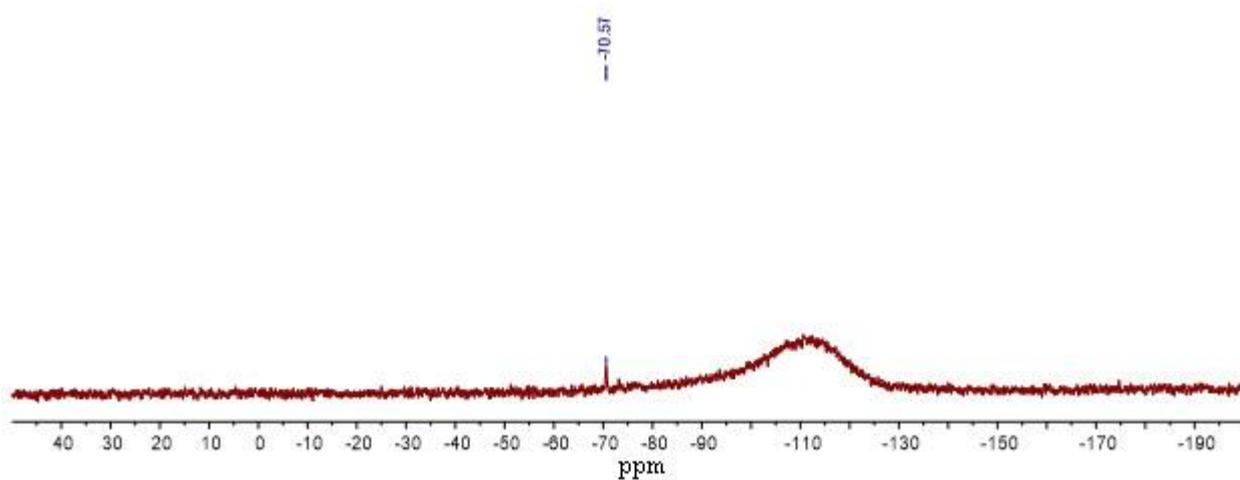


Figure S19 ^{29}Si NMR spectrum of compound **3d** in $\text{DMSO-}d_6$.

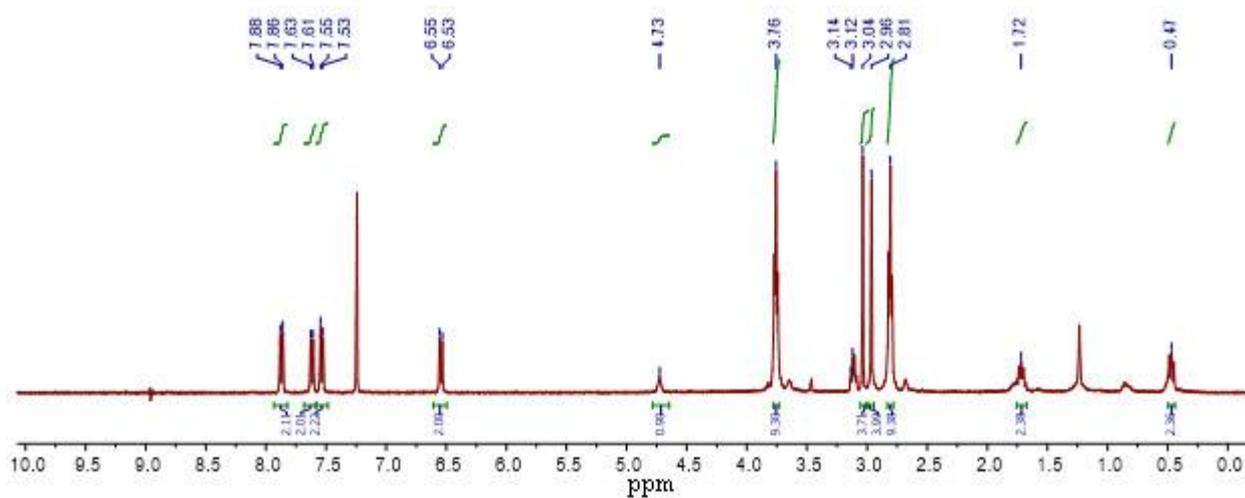


Figure S20 ^1H NMR spectrum of mixture of compounds **4e** and **5e** in CDCl_3 .

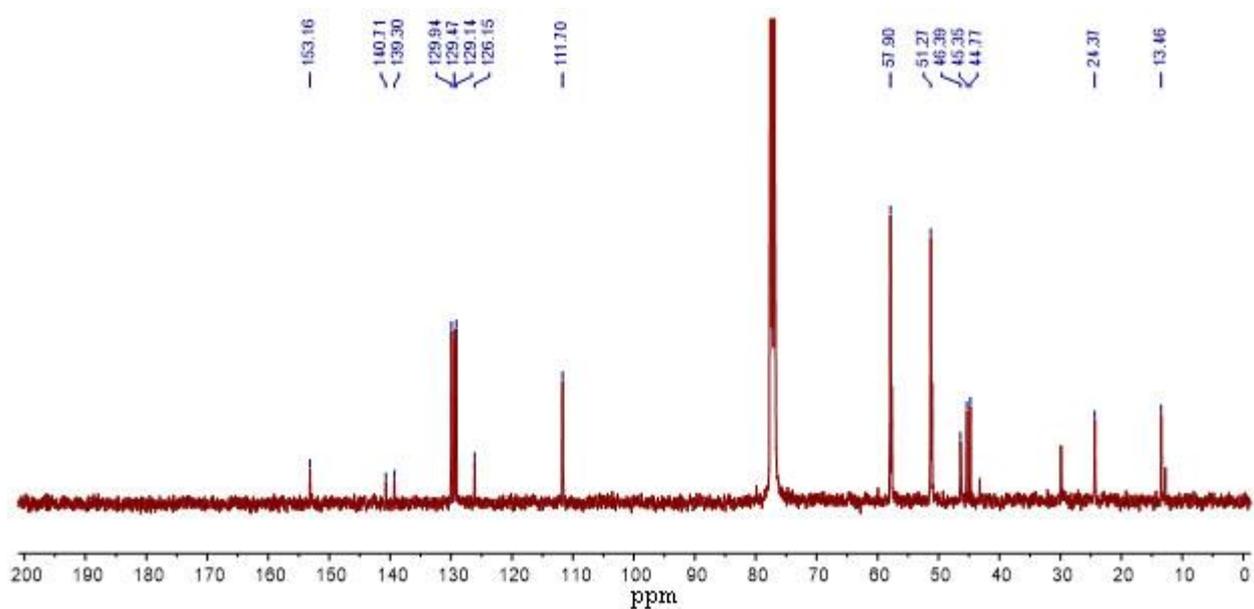


Figure S21 ^{13}C NMR spectrum of mixture of compounds **4e** and **5e** in CDCl_3 .

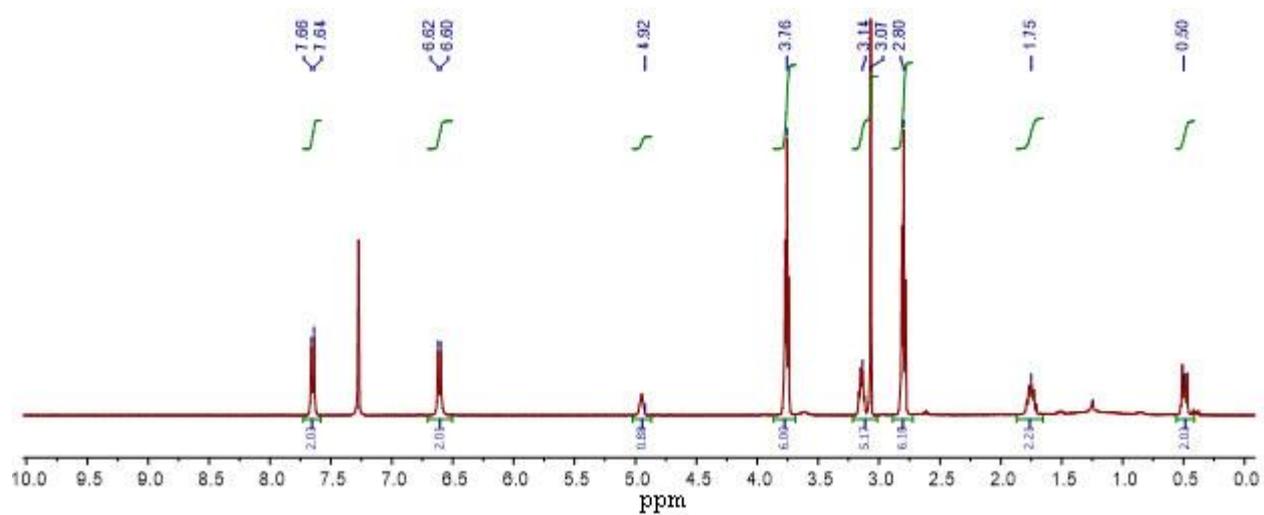


Figure S22 ^1H NMR spectrum of compound **5e** in CDCl_3 .

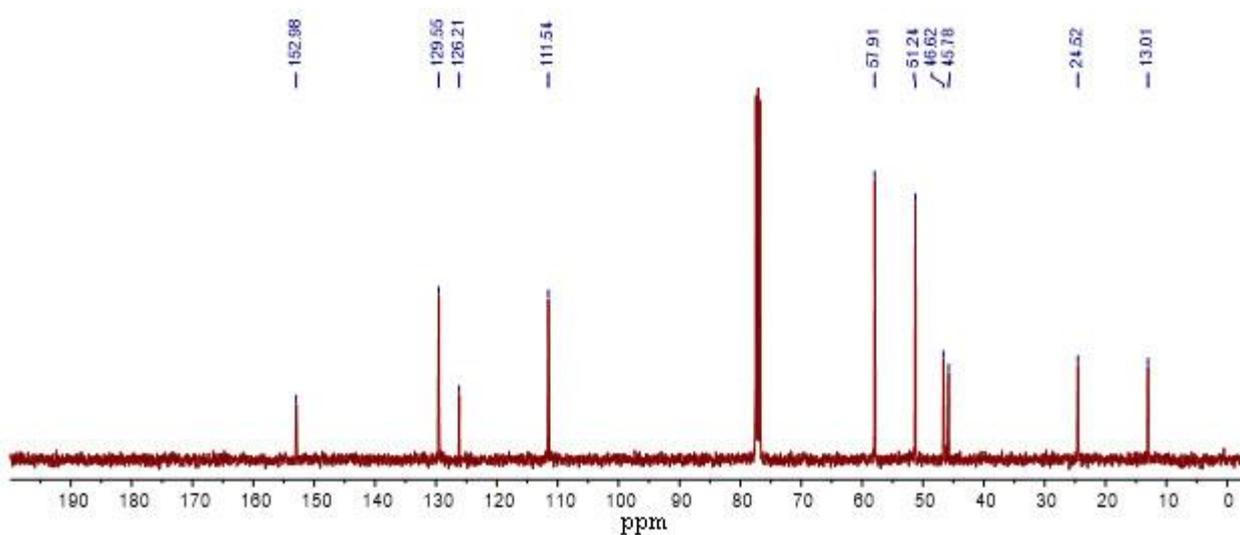


Figure S23 ^{13}C NMR spectrum of compound **5e** in CDCl_3 .

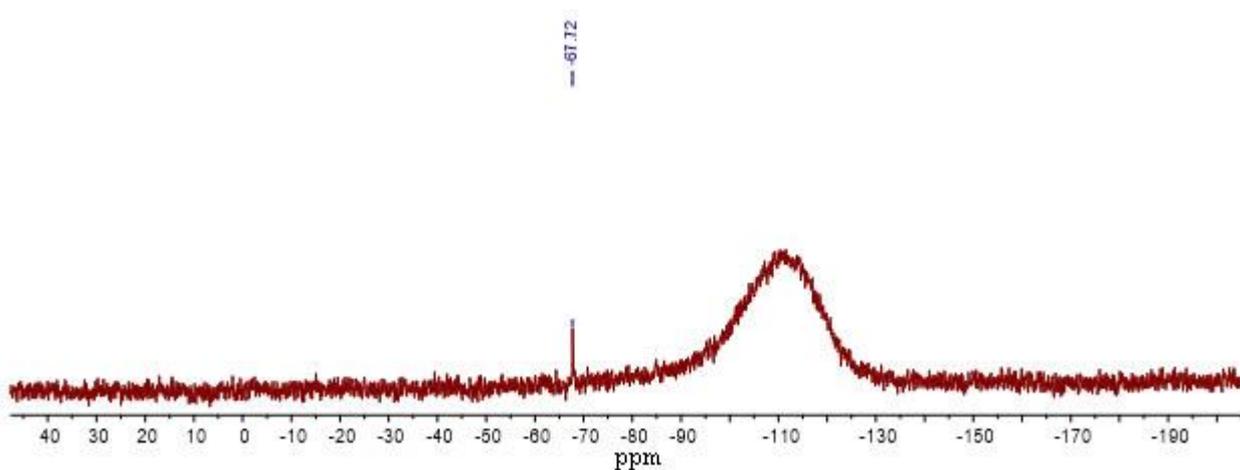


Figure S24 ^{29}Si NMR spectrum of compound **5e** in CDCl_3 .

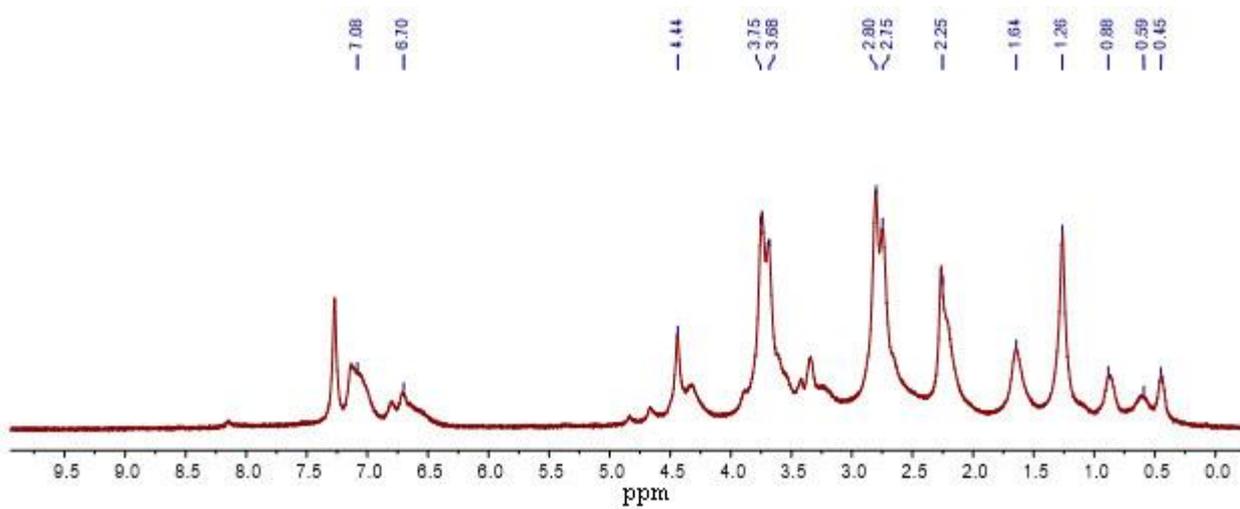


Figure S25 ^1H NMR spectrum of compound **6a** in CDCl_3 .

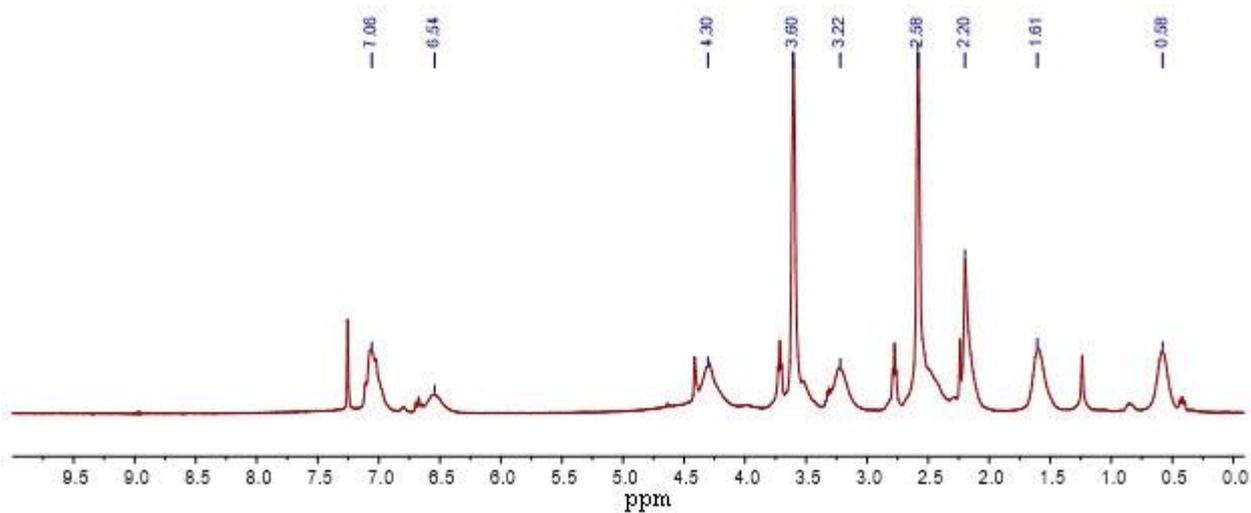


Figure S26 ^1H NMR spectrum of compound **6b** in CDCl_3 .

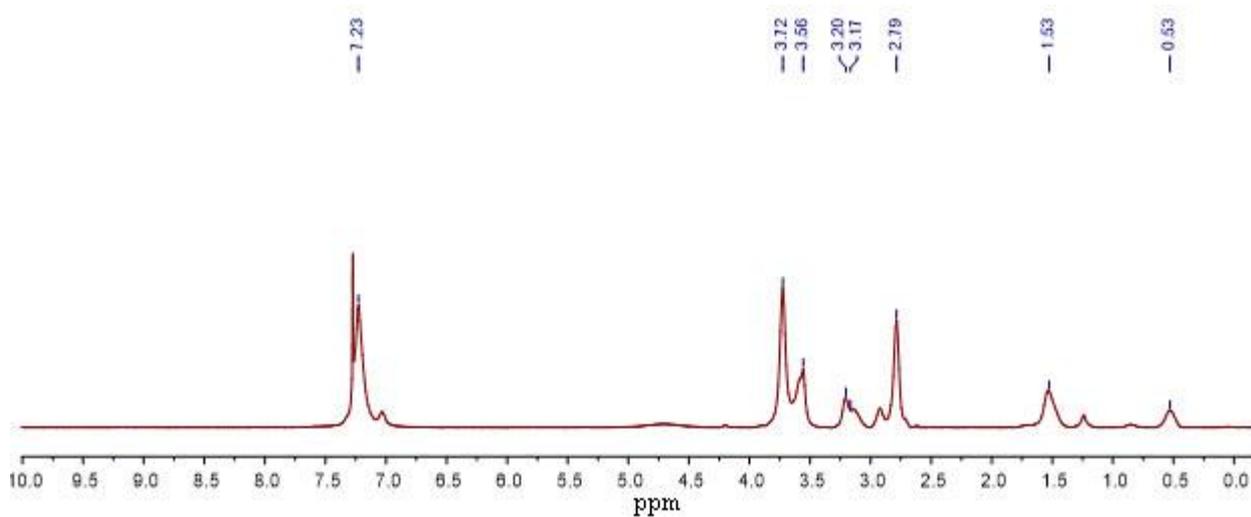


Figure S27 ^1H NMR spectrum of compound **6c** in CDCl_3 .

2D NMR spectra

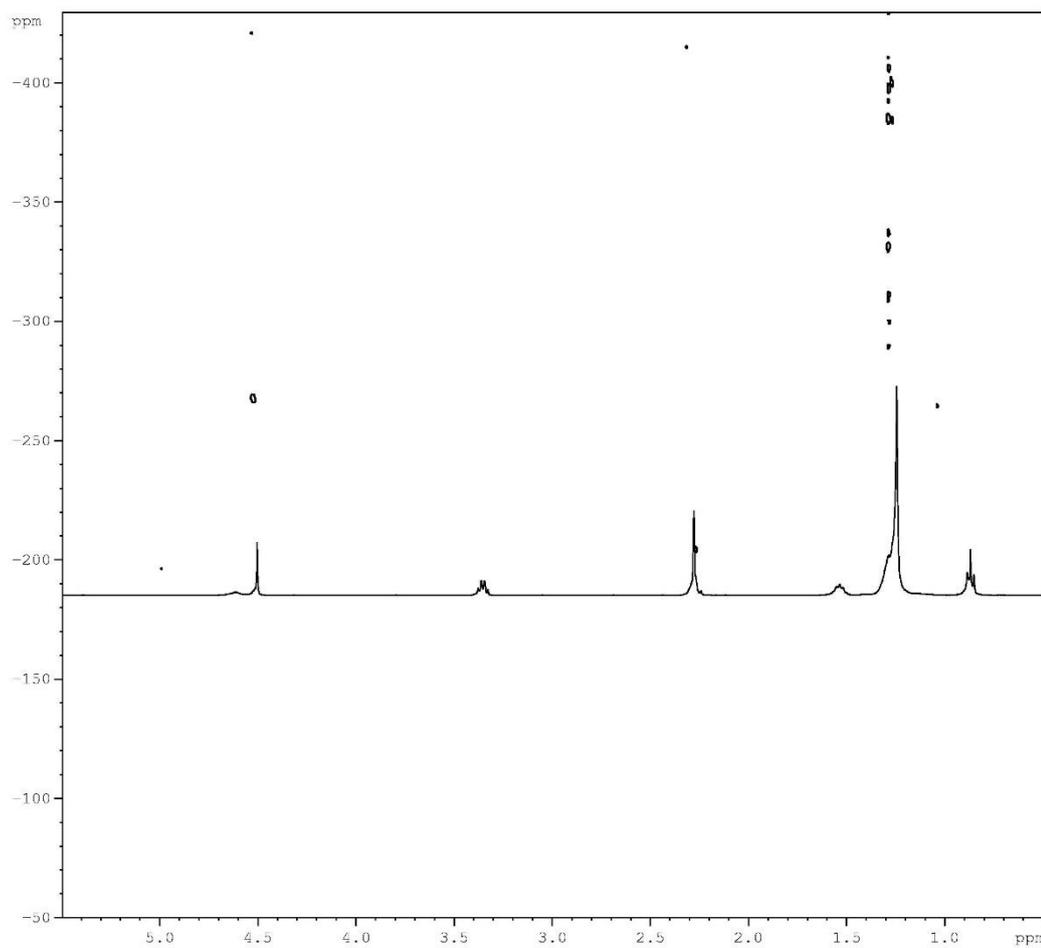


Figure S28 2D ^1H - ^{15}N HMBC spectrum of *N*-decyl-2-(2-methylphenoxy)acetamide in CDCl_3 .

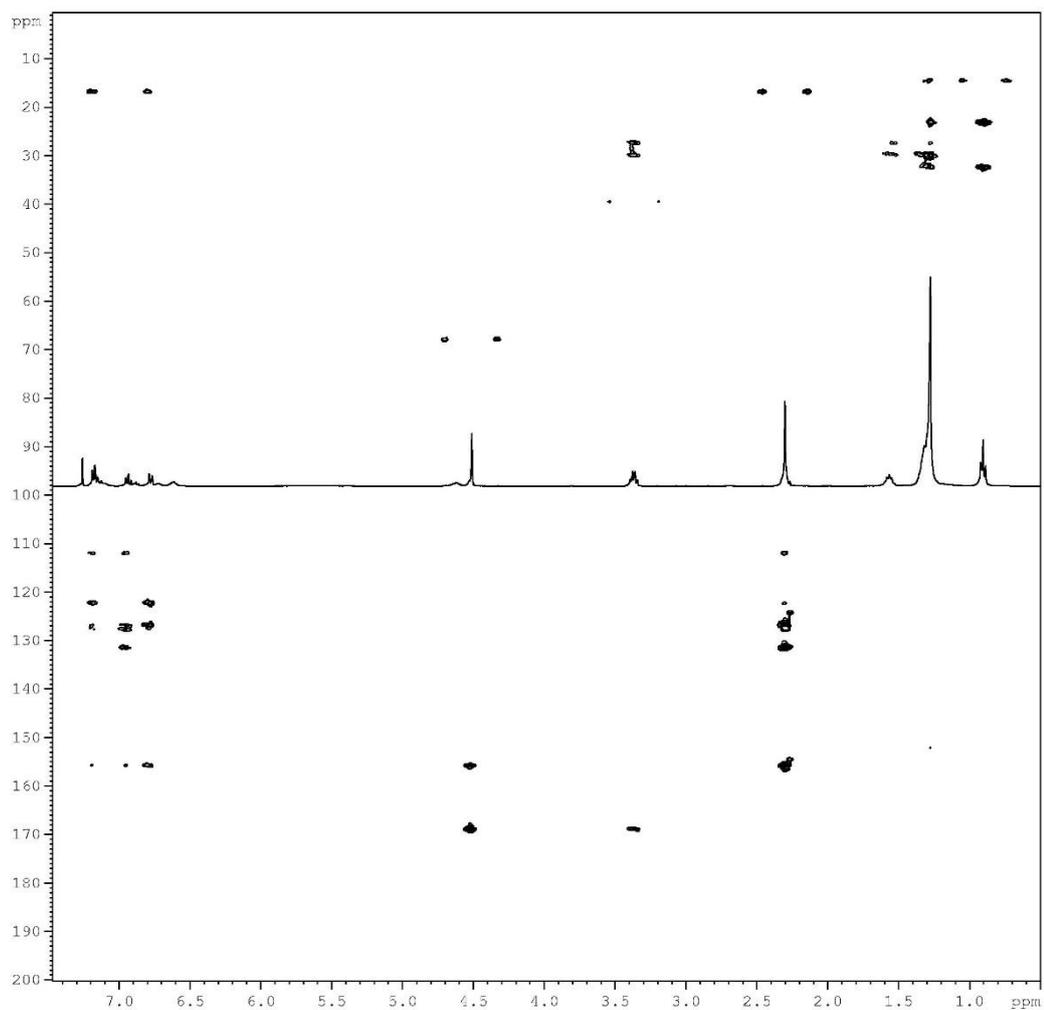


Figure S29 2D ^1H - ^{13}C HMBC spectrum of *N*-decyl-2-(2-methylphenoxy)acetamide in CDCl_3 .

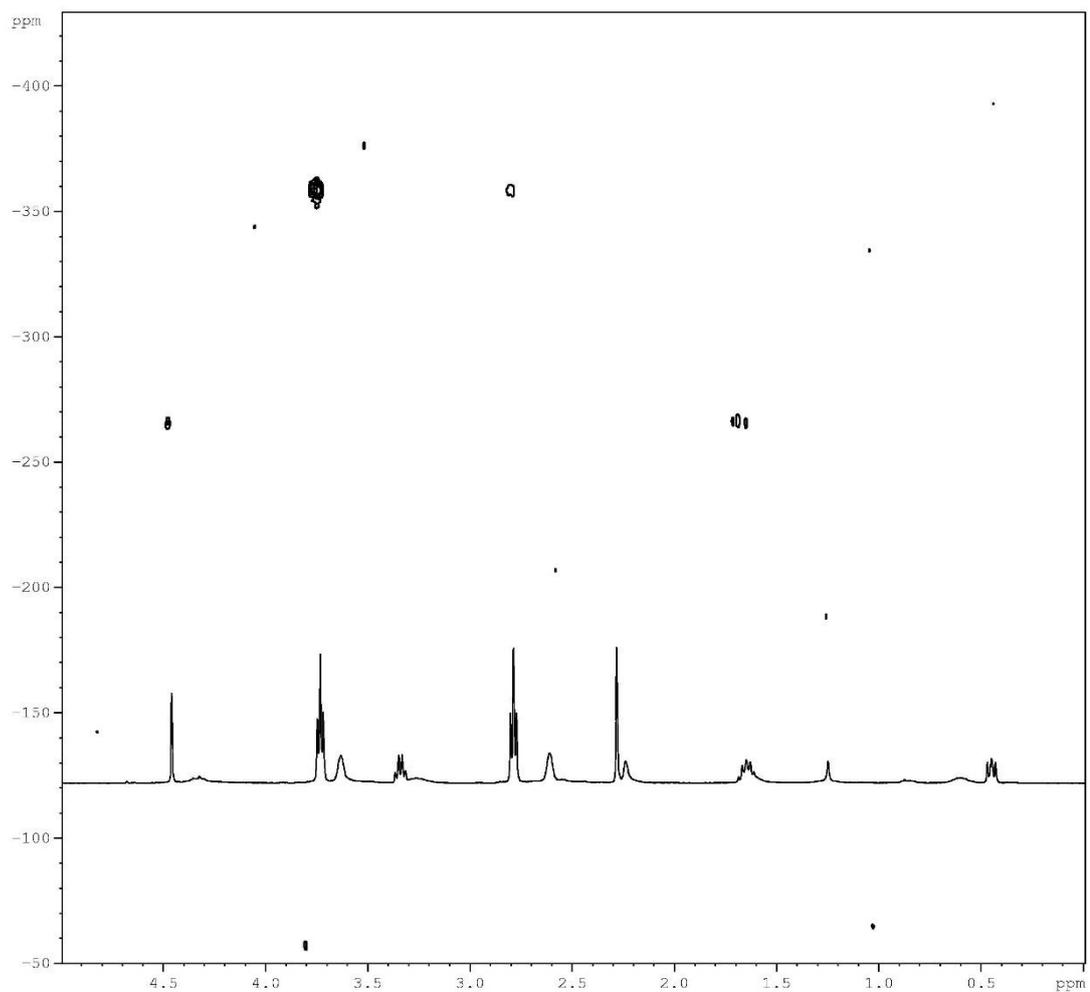


Figure S30 2D ^1H - ^{15}N HMBC spectrum of compound **3a** in CDCl_3 .

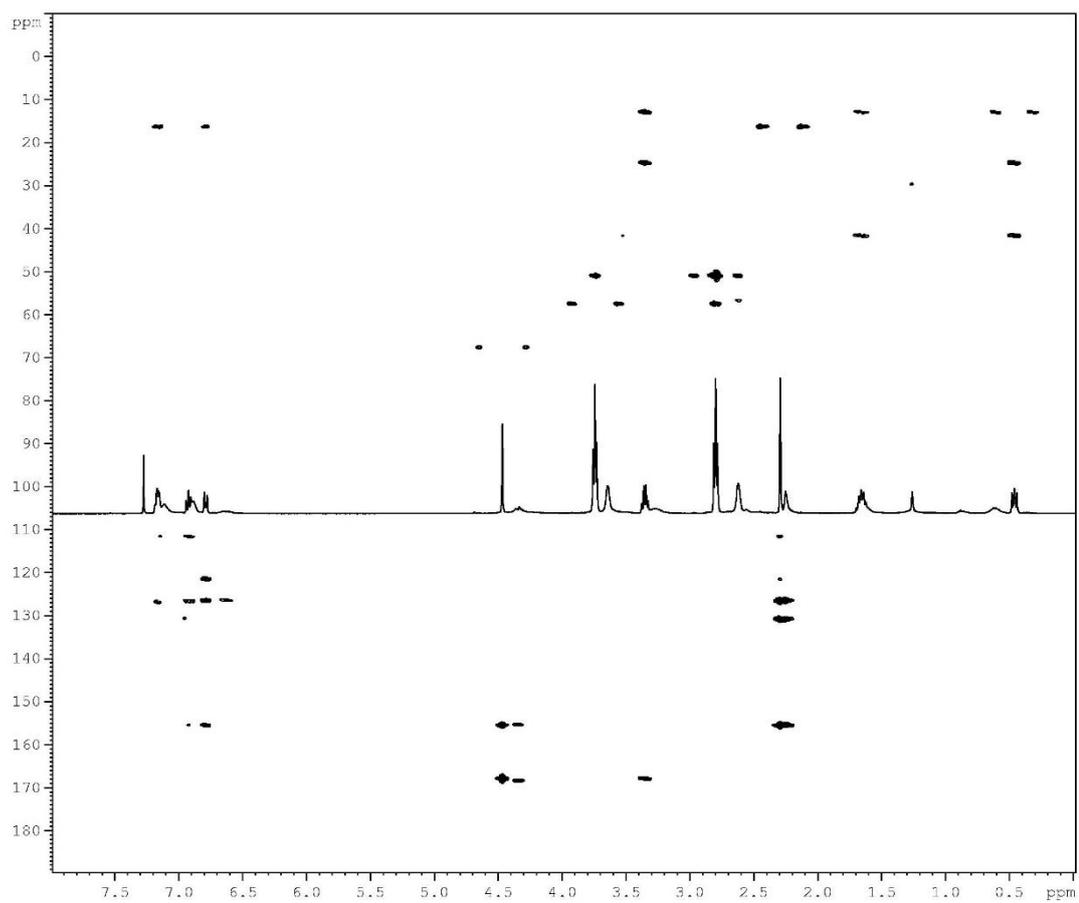


Figure S31 2D ^1H - ^{13}C HMBC spectrum of compound **3a** in CDCl_3 .

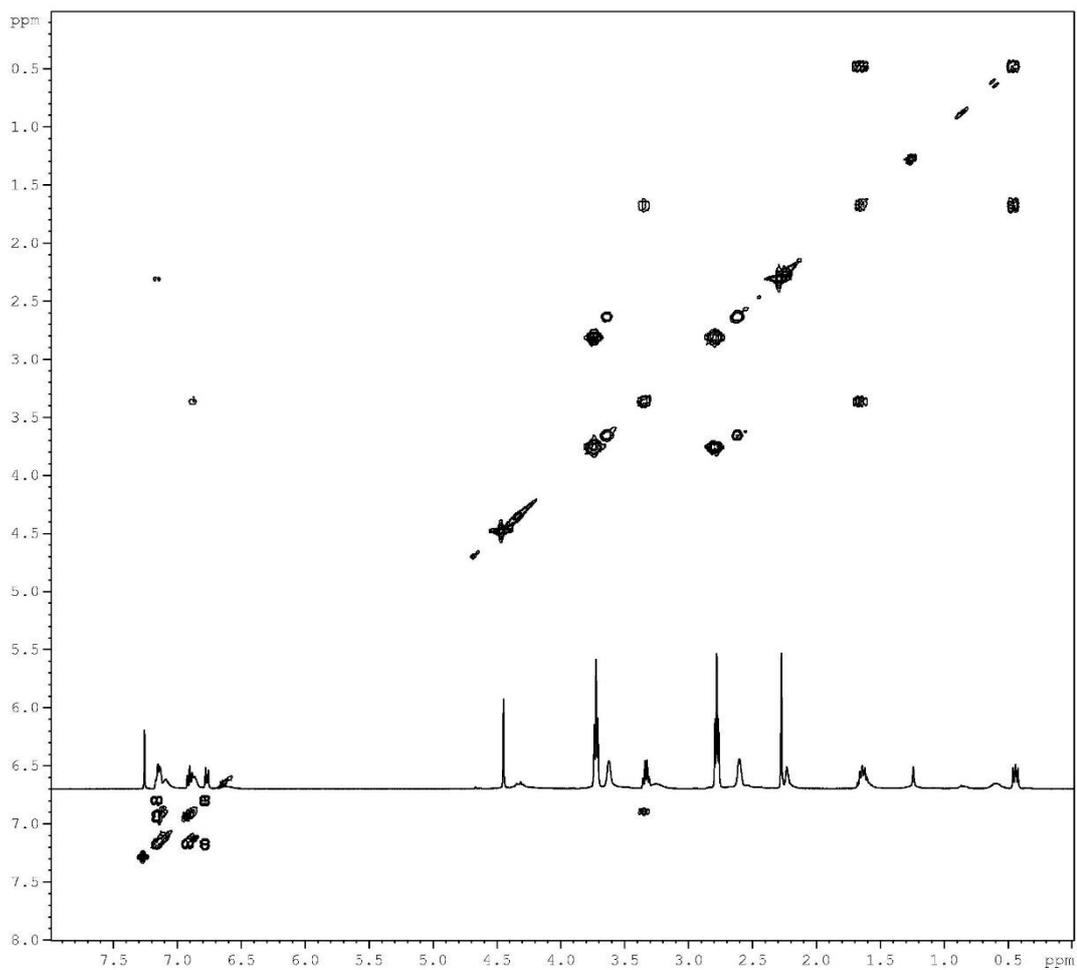


Figure S32 2D COSY spectrum of compound **3a** in CDCl₃.

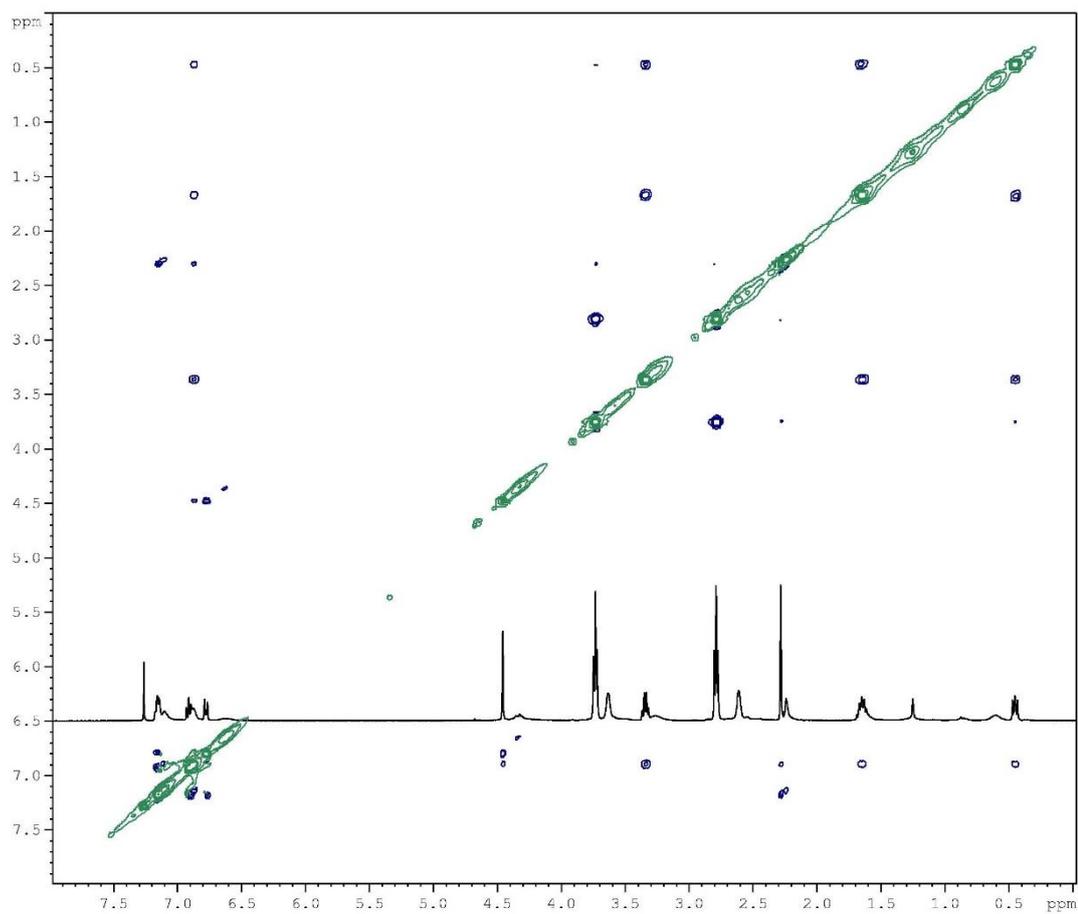


Figure S33 2D NOESY spectrum of compound **3a** in CDCl₃.

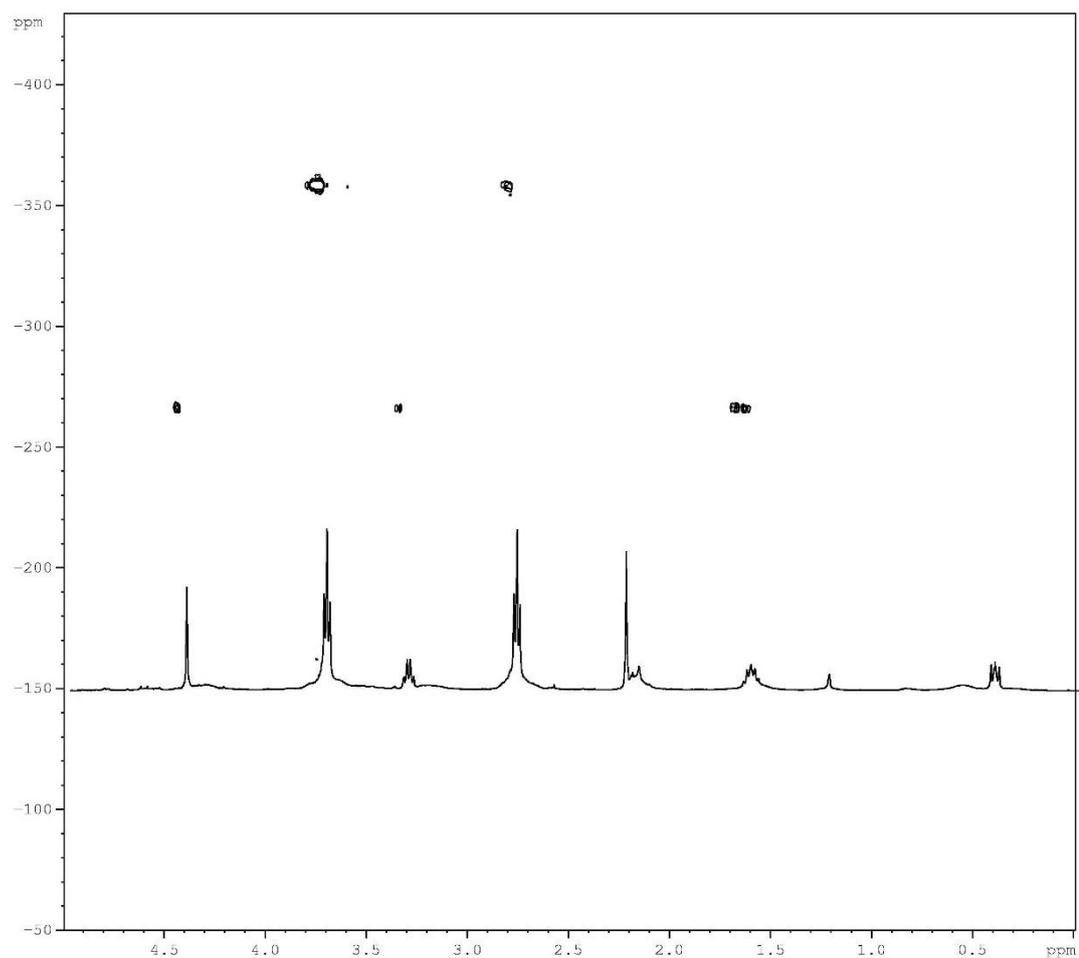


Figure S34 2D ^1H - ^{15}N HMBC spectrum of compound **3b** in CDCl_3 .

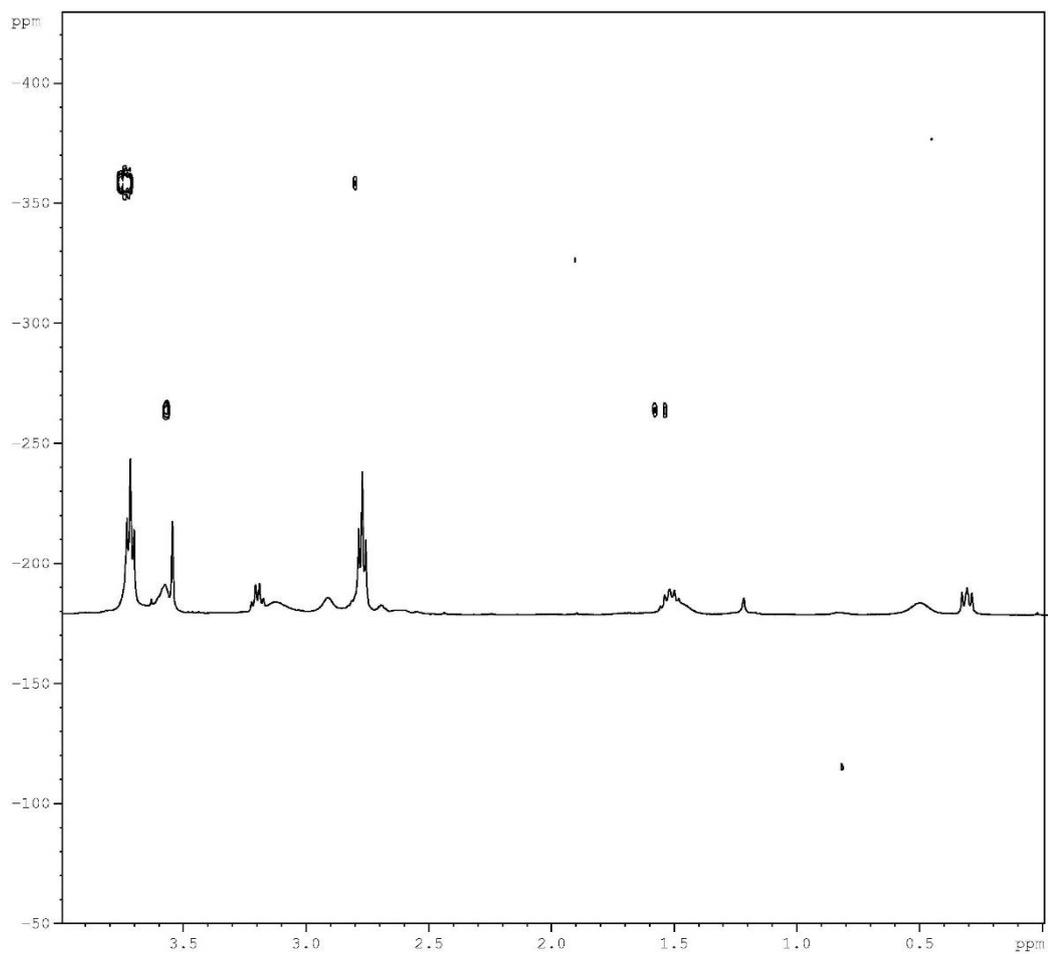


Figure S35 2D ^1H - ^{15}N HMBC spectrum of compound **3c** in CDCl_3 .

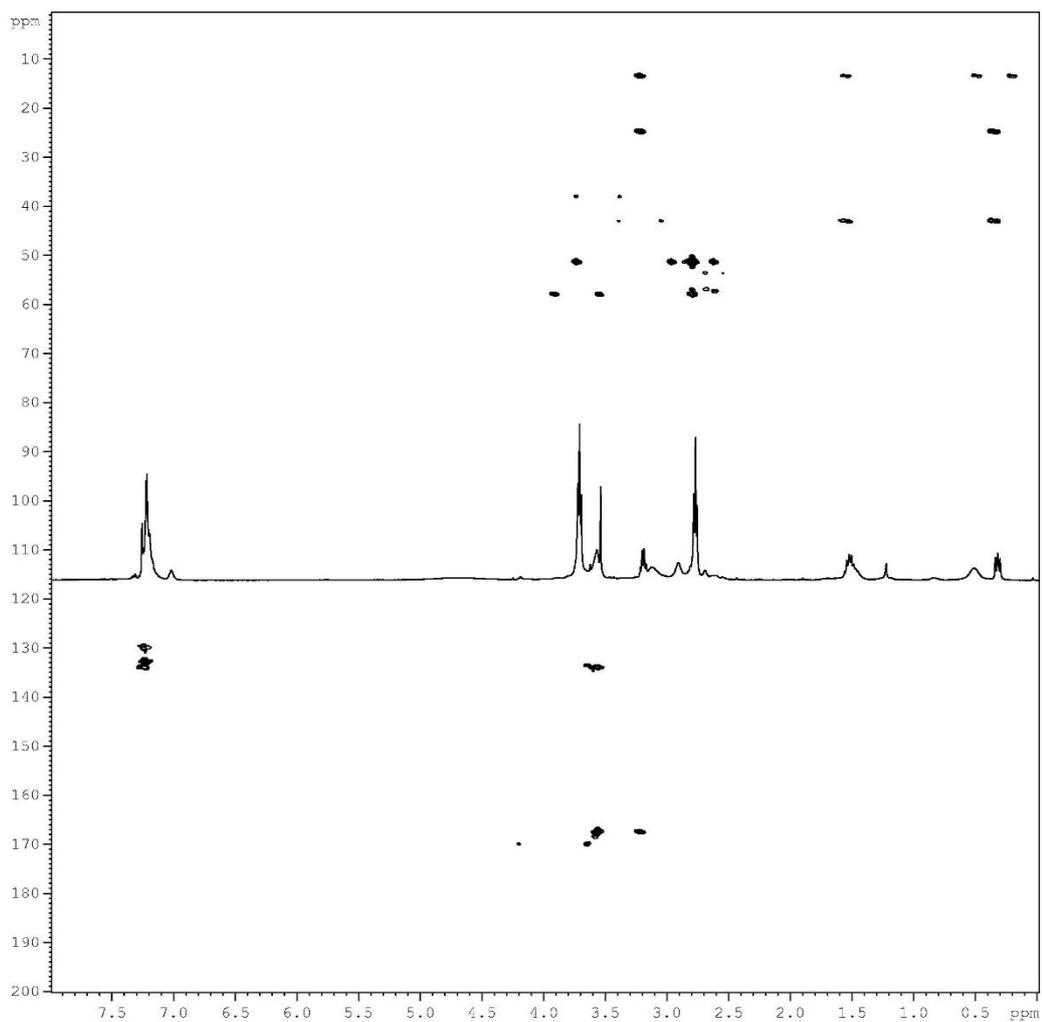


Figure S36 2D ^1H - ^{13}C HMBC spectrum of compound **3c** in CDCl_3 .

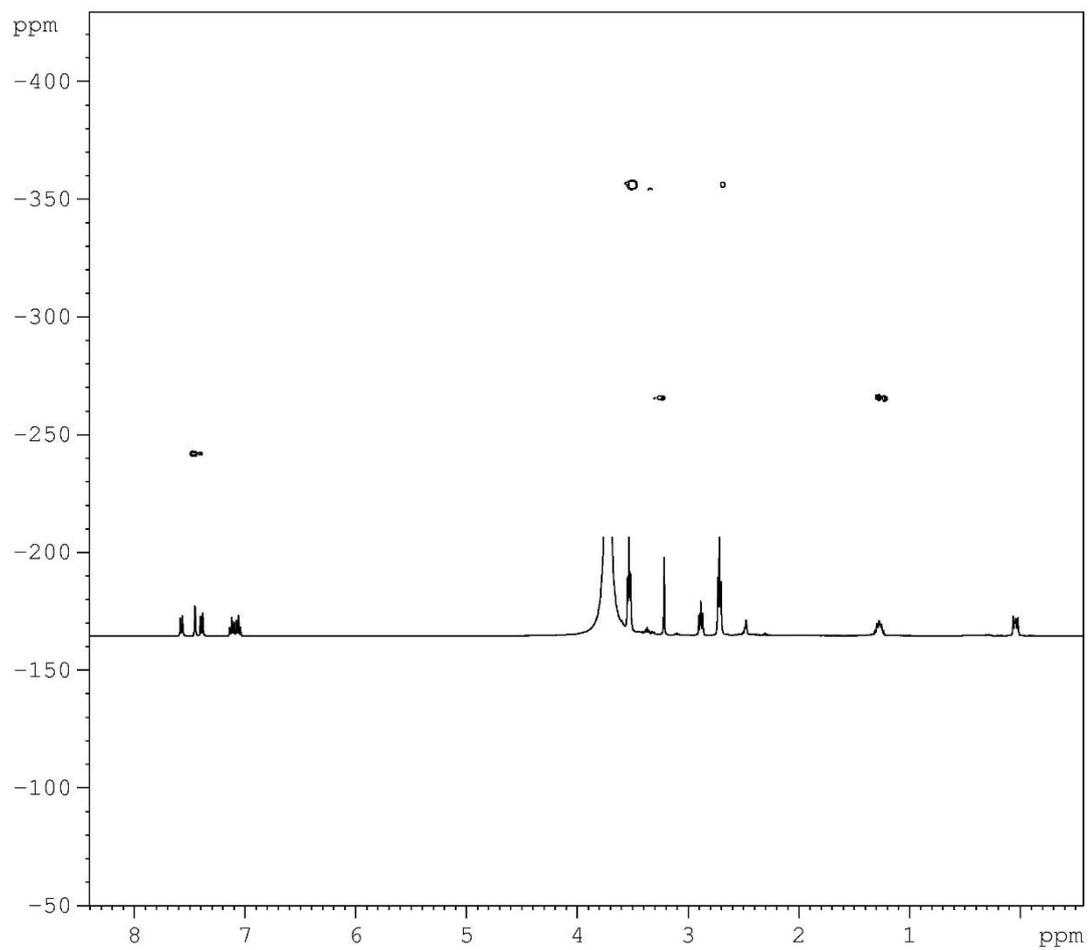


Figure S37 2D ^1H - ^{15}N HMBC spectrum of compound **3d** in $\text{DMSO-}d_6$.

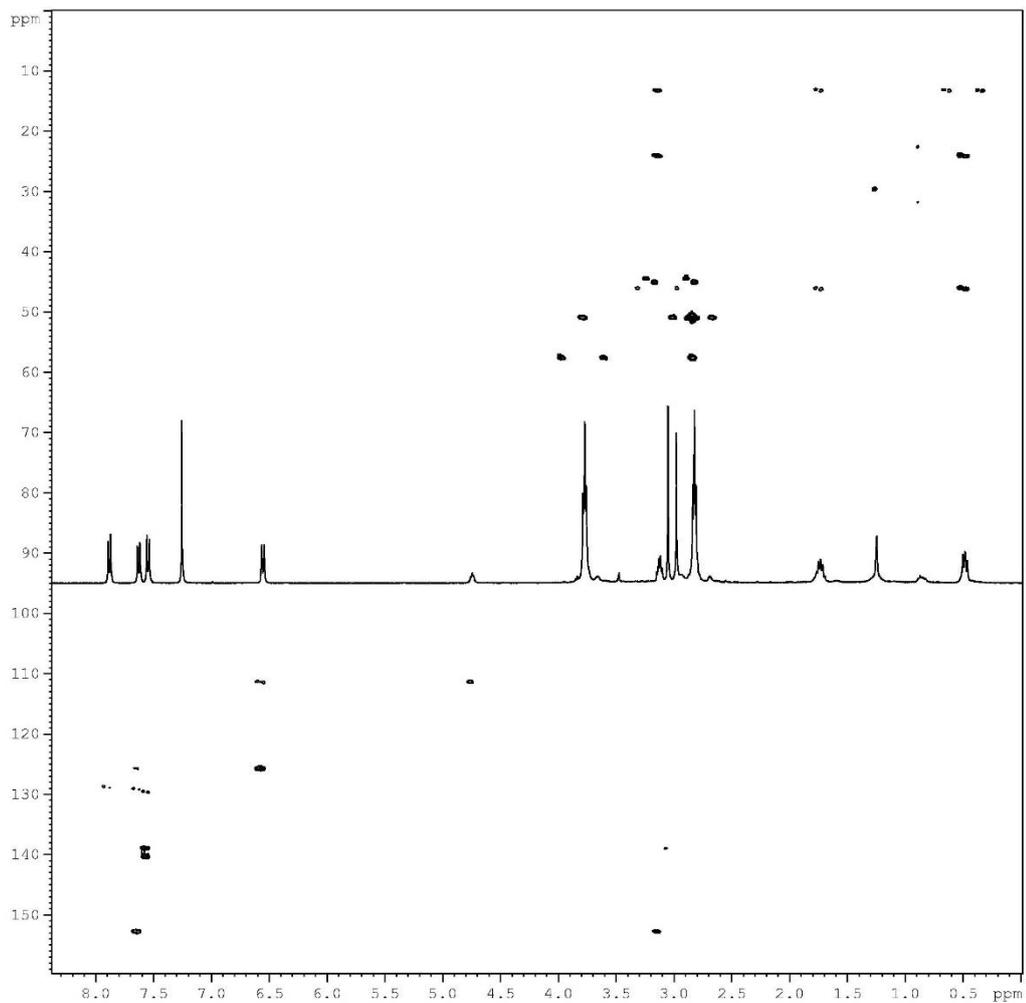


Figure S38 2D ^1H - ^{13}C HMBC spectrum of mixture of compounds **4a** and **5a** in CDCl_3 .

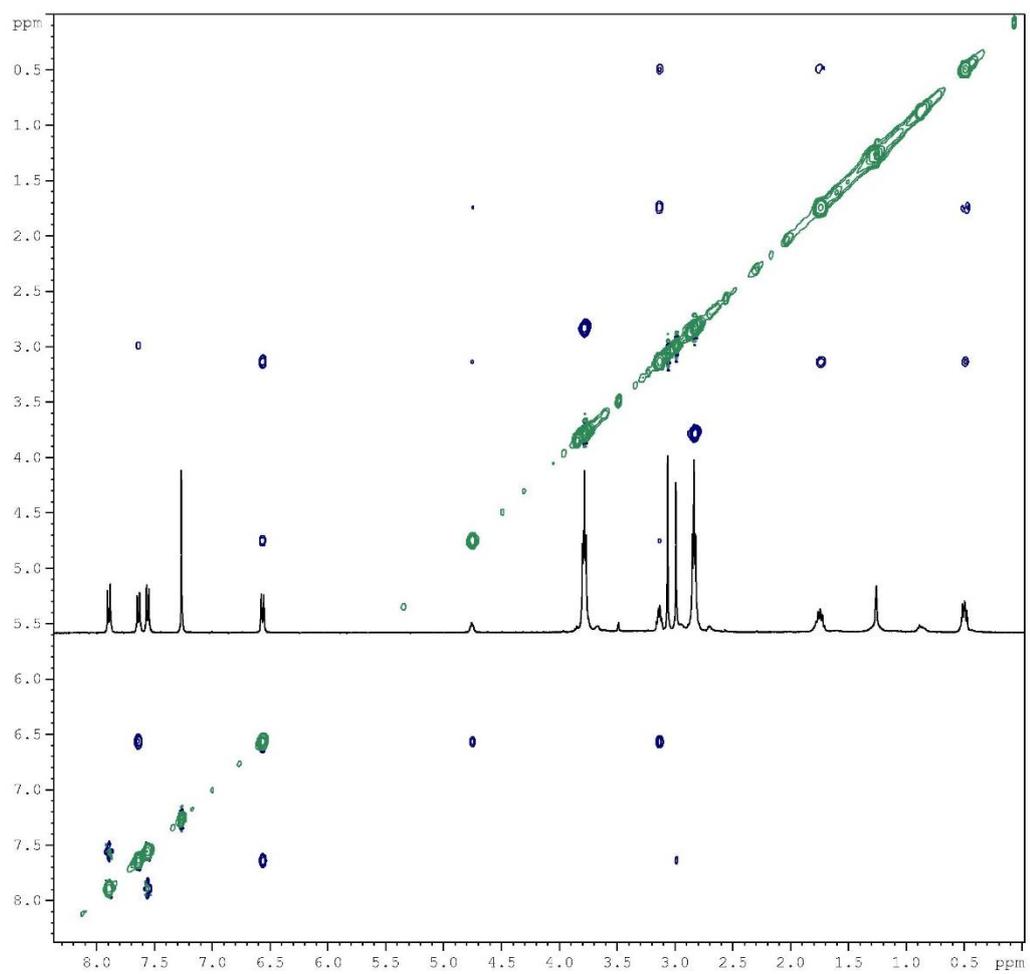


Figure S39 2D NOESY spectrum of mixture of compounds **4a** and **5a** in CDCl₃.

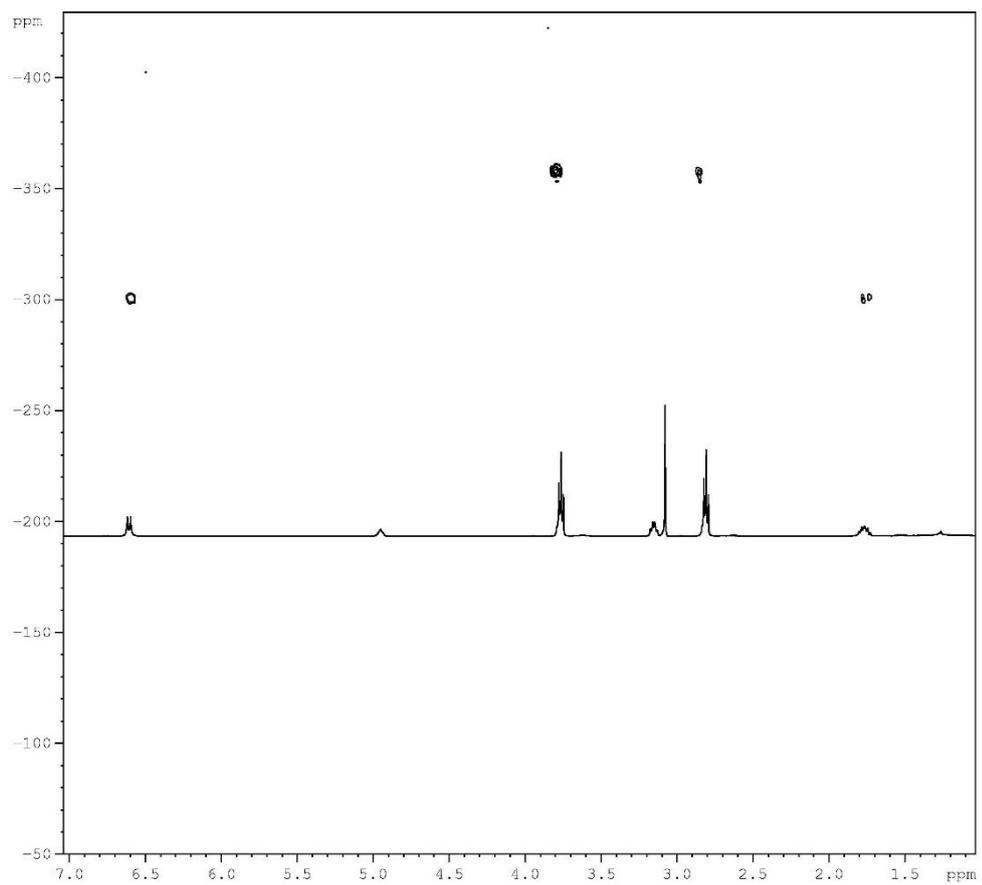


Figure S40 2D ^1H - ^{15}N HMBC spectrum of compound **5e** in CDCl_3 .