Electronic Supplementary Material (ESI) for Green Chemistry.

Electronic Supplementary Information

Photoinduced Catalyst-Free Deborylation-Deuteration of Arylboronic Acids with D_2O

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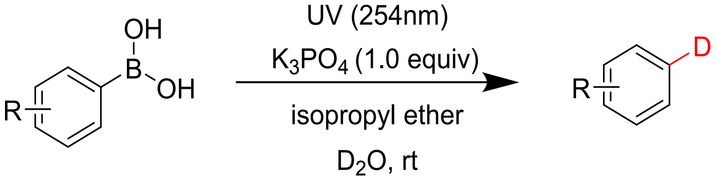
Ⅰ. General Methods

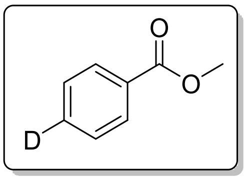
All reactions were carried out in argon atmosphere unless otherwise noted. All reagents and solvents were purchased from commercial sources (Bide pharm, Energy Chemical, TCI, Acros, Alfa and Ark) and used without further purification unless otherwise stated. All reactions were monitored by thin-layer chromatography (TLC). Column chromatography was performed on silica gel (200-300 mesh) and visualized with ultraviolet light. Ethyl acetate and petroleum ether were used as eluents. Deuterium incorporation was determined by ^{1}H NMR spectroscopy or GC-MS. ^{1}H NMR and ^{13}C NMR spectra were recorded on Agilent 600 spectrometer and Bruker AV400. Chemical shifts of ^{1}H NMR spectra were reported using residual solvent signal of $CDCl_3$ (δ = 7.27 ppm) or Methanol-d_4 (δ = 3.31 ppm) as internal standard. Chemical shifts of ^{13}C NMR spectra were reported using residual solvent signal of $CDCl_3$ (δ = 77.2 ppm) or Methanol-d_4 (δ = 49.0 ppm) as internal standard. GC-MS analyses were performed with a Thermo TRACE 1300 ISQ LT spectrometer. HRMS analyses were made by Lanzhou University by means of ESI and APCI. FT-IR spectra were recorded on an IR Tracer-100 spectrometer.

II. Experimental Procedures and Characterization Data

General procedure for the deuteration of aryl-boronic acid

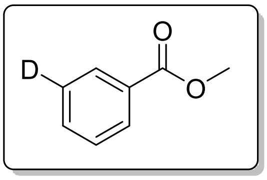


An oven dried 15 mL quartz tube was charged with a magnetic stir-bar, aryl-boronic acid (0.2 mmol), K_3PO_4 (0.2 mmol), D_2O (0.5 ml) and isopropyl ether (1ml). Then the tube was evacuated by three freeze-pump-thaw cycles and back-filled with ultra-purified argon. The reaction was stirred at room temperature (ca 25 ℃) while being irradiated by 254 nm light for 24 h. The resultant mixture was extracted with CH_2Cl_2 (3x5 ml) and the combined organic layers was wash with brine (10 ml), and then dried over Na_2SO_4. The organic layers were concentrated and the crude product was purified by preparative TLC on silica gel to afford the product. Deuterium incorporation was determined by analysis of ^{1}H-NMR or GC-MS.



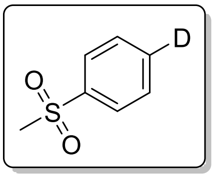
2a: methyl benzoate-4-*d*

The synthesis of compound **2a** was following the general procedure. **2a** was isolated by preparative TLC (petroleum ether: ethyl acetate = 60:1) as a colorless liquid (23.3 mg, 85% yield). Deuterium incorporation: 95% (^{1}H-NMR). **^{1}H NMR (600 MHz, CDCl$_3$)** δ 8.05 (d, *J* = 7.3 Hz, 2H), 7.45 (d, *J* = 7.8 Hz, 2H), 3.93 (s, 3H). **^{13}C NMR (151 MHz, CDCl$_3$)** δ 167.2, 132.7 (t, *J* = 23.7 Hz), 130.3, 129.7, 128.4, 52.2. ^{1}H and ^{13}C NMR data agreed with literature.[1]



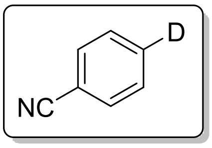
2b: methyl benzoate-3-*d*

The synthesis of compound **2b** was following the general procedure. **2b** was isolated by preparative TLC (petroleum ether: ethyl acetate = 60:1) as a colorless liquid (20.6 mg, 75% yield). Deuterium incorporation: 92% (^{1}H-NMR). **^{1}H NMR (600 MHz, CDCl$_3$)** δ 8.05 (s, 2H), 7.57 (d, *J* = 7.5 Hz, 1H), 7.45 (t, *J* = 7.4 Hz, 1H), 3.93 (s, 3H). **^{13}C NMR (151 MHz, CDCl$_3$)** δ 167.3, 132.9, 130.3, 129.7, 129.6, 128.5, 128.2 (t, *J* = 23.5 Hz), 52.2. ^{1}H and ^{13}C NMR data agreed with literature.[2]



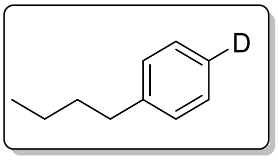
2c: 1-(methylsulfonyl) benzene-4-*d*

The synthesis of compound **2c** was following the general procedure. **2c** was isolated by preparative TLC (petroleum ether: ethyl acetate = 4:1) as a colorless liquid (25.6 mg, 82% yield). Deuterium incorporation: 95% (^{1}H-NMR). **^{1}H NMR (600 MHz, CDCl3)** δ 7.96 (d, *J* = 6.9 Hz, 2H), 7.59 (d, *J* = 7.8 Hz, 2H), 3.07 (s, 3H). **^{13}C NMR (151 MHz, CDCl$_3$)** δ 140.8, 133.5 (t, *J* = 25.4 Hz), 129.4, 127.5, 44.6. ^{1}H and ^{13}C NMR data agreed with literature.[3]



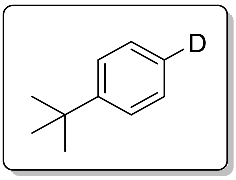
2d: benzonitrile-4-*d*

The synthesis of compound **2d** was following the general procedure. **2d** was isolated by preparative TLC (petroleum ether: ethyl acetate = 30:1) as a colorless liquid (13.5 mg, 65% yield). Deuterium incorporation: 96% (^{1}H-NMR) **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.67 (d, *J* = 7.6 Hz, 2H), 7.49 (d, *J* = 7.7 Hz, 2H). **^{13}C NMR (151 MHz, CDCl$_3$)** δ 132.7, 132.3, 129.2, 119.0, 112.7. ^{1}H and ^{13}C NMR data agreed with literature.[4]



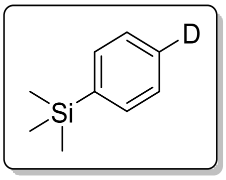
2e: 1-butylbenzene-4-*d*

According to the general procedure, **1e** (0.2mmol), NaOH (0.2 mmol), D$_2$O (0.5 ml), CH$_3$CN (0.5 ml) and isopropyl ether (0.5 ml) were used. **2e** was isolated by preparative TLC (eluent: petroleum ether) as a colorless liquid (20.6 mg, 76% yield). Deuterium incorporation: 94% (^{1}H-NMR). **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.30 (d, *J* = 7.6 Hz, 2H), 7.21 (d, *J* = 7.9 Hz, 2H), 2.64 (t, *J* = 7.8 Hz , 2H), 1.64 (p, *J* = 7.6 Hz, 2H), 1.39 (h, *J* = 7.4 Hz, 2H), 0.96 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR (151 MHz, CDCl$_3$)** δ 143.1, 128.6, 128.3, 125.5 (t, *J* = 22.8 Hz), 35.9, 33.9, 22.6, 14.2. ^{1}H and ^{13}C NMR data agreed with literature.[5]



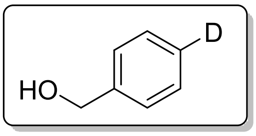
2f: 1-(tert-butyl)benzene-4-*d*

According to the general procedure, **1f** (0.2mmol), NaOH (0.2 mmol), D$_2$O (0.5 ml) and hexane (1 ml) were used. **2f** was isolated by preparative TLC (eluent: petroleum ether) as a colorless liquid (17.0 mg, 63% yield). Deuterium incorporation: 92% (^{1}H-NMR). **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.49 (d, *J* = 8.4 Hz, 2H), 7.40 (d, *J* = 8.5 Hz, 2H), 1.43 (s, 9H). **^{13}C NMR (151 MHz, CDCl$_3$)** δ 151.2, 128.1, 125.4, 125.3 (t, *J* = 24.0 Hz), 34.8, 31.5. ^{1}H and ^{13}C NMR data agreed with literature.[6]



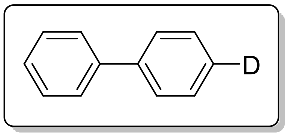
2g: trimethyl(phenyl-4-*d*)silane

According to the general procedure, **1g** (0.2 mmol), NaOH (0.2 mmol), D_2O (0.5 ml) and hexane (1 ml) were used. **2g** was isolated by preparative TLC (eluent: petroleum ether) as a colorless liquid (15.1 mg, 49% yield). Deuterium incorporation: 98% (^{1}H-NMR). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.59 (d, J = 8.0 Hz, 2H), 7.41 (d, J = 8.0 Hz, 2H), 0.33 (s, 9H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 140.6, 133.4, 128.7 (t, J = 25.4 Hz), 127.7, -1.0. ^{1}H and ^{13}C NMR data agreed with literature.[7]



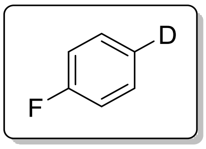
2h: (phenyl-4-*d*)methanol

According to the general procedure, **1h** (0.2 mmol), K_3PO_4 (0.4 mmol), D_2O (0.5 ml) and isopropyl ether (1ml) were used. After reaction completed, the resultant mixture was diluted with CH_2Cl_2 and acidified with 1M hydrochloric acid. The aqueous phase was extracted with CH_2Cl_2 (3x5 ml) and the combined organic layers were wash with brine (10 ml), and then dried over Na_2SO_4. The organic layers were concentrated and the crude product was purified by preparative TLC (petroleum ether: ethyl acetate = 4:1) to afford the product **2h** as a colorless liquid (15.4 mg, 71%). Deuterium incorporation: 94% (^{1}H-NMR). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.37 (s, 4H), 4.67 (s, 2H), 2.25 (br, 1H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 141.0, 128.5, 127.4 (t, J = 23.9 Hz), 127.1, 65.3. ^{1}H and ^{13}C NMR data agreed with literature.[8]



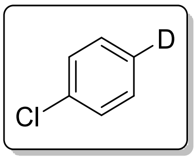
2i: 1,1'-biphenyl-4-*d*

The synthesis of compound **2i** was following the general procedure. **2i** was isolated by preparative TLC (petroleum ether: ethyl acetate = 60:1) as an off-white powder. (28.6 mg, 92% yield). Deuterium incorporation: 98% (^{1}H-NMR). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.63 (d, J = 7.4 Hz, 4H), 7.50 – 7.44 (m, 4H), 7.38 (t, J = 7.4 Hz, 1H). **^{13}C NMR (600 MHz, $CDCl_3$)** δ 141.4, 128.9, 128.8, 127.4, 127.3, 127.1 (t, J = 24.3 Hz). ^{1}H and ^{13}C NMR data agreed with literature.[9]



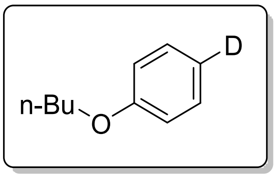
2j: 1-fluorobenzene-4-*d*

The synthesis of compound **2j** was following the general procedure. The yield of **2j** (75%) was determined by GC-MS using diphenylmethane as an internal standard. Deuterium incorporation: 92% (GC-MS). The product could not be isolated due to its volatility. Consequently, ^{1}H NMR and ^{13}C NMR were not obtained.



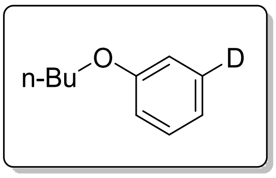
2k: 1-chlorobenzene-4-*d*

The synthesis of compound **2k** was following the general procedure.The yield of **2k** (60%) was determined by GC-MS using diphenylmethane as an internal standard. Deuterium incorporation: 96% (GC-MS). The product could not be isolated due to its volatility. Consequently, ^{1}H NMR and ^{13}C NMR were not obtained.



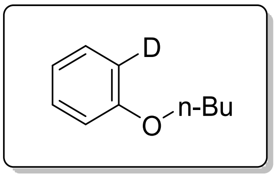
2l: 1-butoxybenzene-4-*d*

According to the general procedure, **1l** (0.2mmol), NaOH (0.2 mmol), D_2O (0.5 ml), CH_3CN (0.5 ml) and isopropyl ether (0.5 ml) were used. **2l** was isolated by preparative TLC (petroleum ether: ethyl acetate = 60:1) as a colorless liquid (20.3 mg, 67% yield). Deuterium incorporation: 96% (^{1}H-NMR). **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.30 (d, *J* = 8.0 Hz, 2H), 6.93 (d, *J* = 8.6 Hz, 2H), 3.99 (t, *J* = 6.6 Hz, 2H), 1.80 (p, *J* = 7.1 Hz, 2H), 1.52 (h, *J* = 7.5 Hz, 2H), 1.00 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR (151 MHz, CDCl$_3$)** δ 159.4, 129.4, 120.4 (t, *J* = 27.0 Hz), 114.7, 67.8, 31.6, 19.4, 14.0. **HRMS** m/z (ESI) calcd. for $C_{10}H_{13}DO$ $[M+H]^+$:152.1180; found: 152.1188.



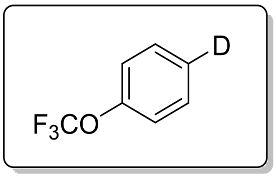
2m：1-butoxybenzene-3-*d*

The synthesis of compound **2m** was following the general procedure. **2m** was isolated by preparative TLC (petroleum ether: ethyl acetate = 60:1) as a colorless liquid. (20.0 mg, 66% yield). Deuterium incorporation: 91% (^{1}H-NMR). **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.30 (t, *J* = 7.8 Hz, 1H), 6.97 – 6.90 (m, 3H), 3.98 (t, *J* = 6.5 Hz, 2H), 1.79 (p, *J* = 6.7 Hz, 2H), 1.51 (h, *J* = 7.5 Hz, 2H), 0.99 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR (151 MHz, CDCl$_3$)** δ 159.3, 129.5, 129.3 (t, *J* = 24.4 Hz), 120.5, 114.7, 114.6, 67.8, 31.6, 19.4, 14.0. **HRMS** m/z (ESI) calcd. for $C_{10}H_{13}DO$ [M+H]$^+$:152.1180; found: 152.1185.



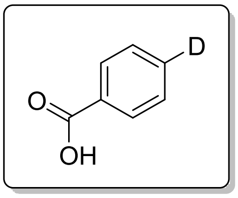
2n：1-butoxybenzene-2-*d*

According to the general procedure, **1n** (0.2mmol), NaOH (0.2 mmol), D_2O (0.5 ml), CH_3CN (0.5 ml) and isopropyl ether (0.5 ml) were used. **2n** was isolated by preparative TLC (petroleum ether: ethyl acetate = 60:1) as a colorless liquid (14.2 mg, 47% yield). Deuterium incorporation: 95% (^{1}H-NMR). **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.32 – 7.27 (m, 2H), 6.98 – 6.89 (m, 2H), 3.98 (t, *J* = 6.5 Hz, 2H), 1.79 (p, *J* = 6.7 Hz, 2H), 1.52 (h, *J* = 7.5 Hz, 2H), 1.00 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR (151 MHz, CDCl$_3$)** δ 159.3, 129.5, 129.4, 120.6, 114.7, 114.4 (t, *J* = 24.3 Hz), 67.8, 31.6, 19.4, 14.0. **HRMS** m/z (ESI) calcd. for $C_{10}H_{13}DO$ [M+H]$^+$:152.1180; found: 152.1186.



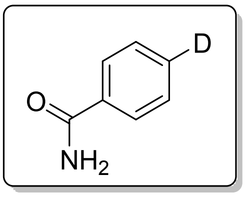
2o: 1-(trifluoromethoxy)benzene-4-*d*

According to the general procedure, **1o** (0.2 mmol), NaOH (0.2 mmol), D_2O (0.5 ml), CH_3CN (0.5 ml) and isopropyl ether (0.5 ml) were used. The yield of **2o** (84%) was determined by GC-MS using diphenylmethane as an internal standard. Deuterium incorporation: 97% (GC-MS). The product could not be isolated due to its volatility. Consequently, ^{1}H NMR and ^{13}C NMR were not obtained.



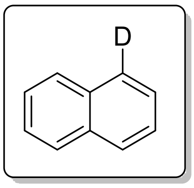
2p: benzoic-4-*d* acid

According to the general procedure, **1p** (0.2 mmol), K_3PO_4 (0.2 mmol), NaOH (0.2 mmol), D_2O (0.5 ml) and isopropyl ether (1ml) were used. The resultant mixture was diluted with CH_2Cl_2 and acidified with 1M hydrochloric acid. The aqueous phase was extracted with CH_2Cl_2 (3x5 ml) and the combined organic layers were wash with brine (10 ml), and then dried over Na_2SO_4. The organic layers were concentrated to afford the product **2p** as an off-white powder (20.2mg, 82%) without further purity. Deuterium incorporation: 96% (^{1}H-NMR). **^{1}H NMR (600 MHz, Methanol-*d*$_4$)** δ 8.02 (d, *J* = 8.4 Hz, 2H), 7.44 (d, *J* = 7.8 Hz, 2H), 5.07 (br, 1H). **^{13}C NMR (151 MHz, Methanol-*d*$_4$)** δ 169.9, 133.7 (t, *J* = 30.2 Hz), 131.9, 130.7, 129.3.[8]



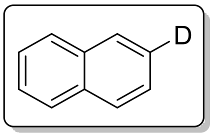
2q: benzamide-4-*d*

The synthesis of compound **2q** was following the general procedure. The organic layers were concentrated to afford the product **2q** as an off-white powder (21.1mg, 86%) without further purity. Deuterium incorporation: 93% (^{1}H-NMR). **^{1}H NMR (600 MHz, Methanol-*d*$_4$)** δ 7.87 (d, *J* = 8.3 Hz, 2H), 7.44 (d, *J* = 8.2 Hz, 2H), 4.86 (s, 2H). **^{13}C NMR (151 MHz, Methanol-*d*$_4$)** δ 172.2, 134.7, 132.4 (t, *J* = 26.2 Hz), 129.2, 128.4. **HRMS** m/z (ESI) calcd. for C_7H_6DNO $[M+H]^+$:123.0663; found: 123.0665.[10]



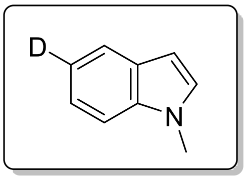
2r: naphthalene-1-*d*

The synthesis of compound **2r** was following the general procedure. **2r** was isolated by preparative TLC (petroleum ether: ethyl acetate = 100:1) as an off-white powder (21.8 mg, 84% yield). Deuterium incorporation: 97% (^{1}H-NMR). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.87 (dd, *J* = 5.9, 3.7 Hz, 3H), 7.50 (d, *J* = 4.5 Hz, 4H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 133.6, 133.6, 128.0, 128.0, 127.7 (t, *J* = 24.8 Hz), 126.0, 125.8. ^{1}H and ^{13}C NMR data agreed with literature.[11]



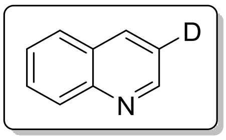
2s: naphthalene-2-*d*

The synthesis of compound **2s** was following the general procedure. **2s** was isolated by preparative TLC (petroleum ether: ethyl acetate = 100:1) as an off-white powder (22.6 mg, 87% yield). Deuterium incorporation: 98% (^{1}H-NMR) **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.87 (dd, *J* = 5.8, 3.1 Hz, 4H), 7.50 (dd, *J* = 6.1, 3.2 Hz, 3H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 133.6, 128.0, 127.9, 126.0, 125.9, 125.6 (t, *J* = 24.3 Hz). ^{1}H and ^{13}C NMR data agreed with literature.[11]



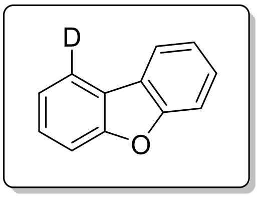
2t: 1-methyl-1*H*-indole-5-*d*

According to the general procedure, **1e** (0.2mmol), NaOH (0.2 mmol), D_2O (0.5 ml), CH_3CN (0.5 ml) and isopropyl ether (0.5 ml) were used. **2t** was isolated by preparative TLC (petroleum ether: ethyl acetate = 100:1) as yellow oil (21.8 mg, 50% yield). Deuterium incorporation: 91% (^{1}H-NMR). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.66 (s, 1H), 7.36 (d, *J* = 8.3 Hz, 1H), 7.25 (d, *J* = 8.9 Hz, 1H), 7.08 (d, *J* = 3.1 Hz, 1H), 6.51 (dd, *J* = 3.1, 0.9 Hz, 1H), 3.82 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 136.8, 128.9, 128.6, 121.5, 120.9, 119.1 (t, *J* = 23.0 Hz), 109.3, 101.0, 33.0. ^{1}H and ^{13}C NMR data agreed with literature.[3]



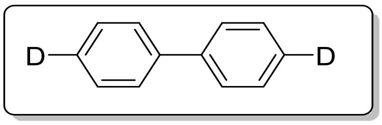
2u: quinoline-3-*d*

According to the general procedure, **1u** (0.2mmol), NaOH (0.2 mmol), D_2O (0.5 ml) and hexane (1 ml) were used. **2u** was isolated by preparative TLC (petroleum ether: ethyl acetate = 4:1) as a yellow liquid (15.0 mg, 58% yield). Deuterium incorporation: 96% (^{1}H-NMR). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.90 (s, 1H), 8.11 (d, *J* = 9.0 Hz, 2H), 7.79 (d, *J* = 8.1 Hz, 1H), 7.70 (t, *J* = 7.7 Hz, 1H), 7.52 (t, *J* = 7.5 Hz, 1H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 150.4, 148.3, 136.0, 129.5, 128.3, 127.8, 126.6, 120.8 (t, *J* = 24.0 Hz). ^{1}H and ^{13}C NMR data agreed with literature.[11]



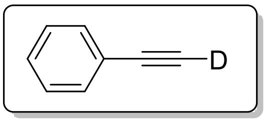
2v: dibenzo[*b,d*]furan-1-*d*

The synthesis of compound **2v** was following the general procedure. **2v** was isolated by preparative TLC (eluent: petroleum ether) as an off-white powder (29.1 mg, 86% yield). Deuterium incorporation: 98% (^{1}H-NMR). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.98 (d, *J* = 7.7 Hz, 1H), 7.61 (d, *J* = 8.2 Hz, 2H), 7.49 (t, *J* = 7.7 Hz, 2H), 7.41 – 7.33 (m, 2H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 156.3, 127.3, 124.4, 124.3, 122.8, 122.7, 120.8, 120.5 (t, *J* = 24.0 Hz), 111.8. ^{1}H and ^{13}C NMR data agreed with literature.[12]



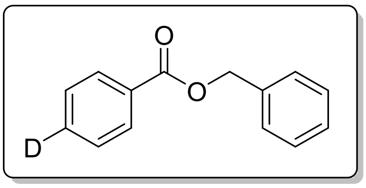
2w: 1,1'-biphenyl-4,4'-d_2

According to the general procedure, **1w** (0.2 mmol), K_3PO_4 (0.4 mmol), D_2O (1 ml) and CH_3CN (2 ml) were used. **2w** was isolated by preparative TLC (petroleum ether: ethyl acetate = 60:1) as an off-white powder (20.0 mg, 64% yield). Deuterium incorporation: 92% (^{1}H-NMR). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.64 (d, *J* = 7.5 Hz, 4H), 7.48 (d, *J* = 7.5 Hz, 4H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 141.4, 128.8, 127.3, 127.1 (t, *J* = 23.3 Hz). ^{1}H and ^{13}C NMR data agreed with literature.[13]



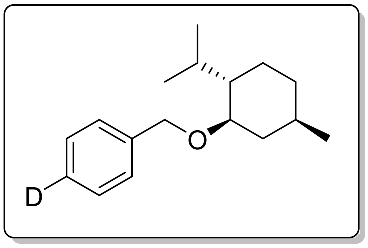
2aa: (ethynyl-d)benzene

The synthesis of compound **2aa** was following the general procedure. The yield of **2aa** (49%) was determined by GC-MS using diphenylmethane as an internal standard. Deuterium incorporation: 92% (GC-MS). The product could not be isolated due to its volatility. Consequently, ^{1}H NMR and ^{13}C NMR were not obtained.



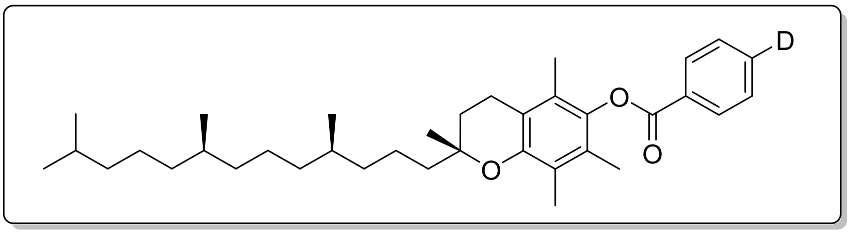
2ab: benzyl benzoate-4-*d*

The synthesis of compound **2ab** was following the general procedure. **2ab** was isolated by preparative TLC (petroleum ether: ethyl acetate = 60:1) as a colorless liquid (29.9 mg, 70% yield). Deuterium incorporation: 96% (^{1}H-NMR). **^{1}H NMR (600 MHz, CDCl$_3$)** δ 8.11 (d, *J* = 7.8 Hz, 2H), 7.47 (dd, *J* = 12.5, 7.7 Hz, 4H), 7.42 (t, *J* = 7.4 Hz, 2H), 7.37 (t, *J* = 7.3 Hz, 1H), 5.40 (s, 2H). **^{13}C NMR (151 MHz, CDCl$_3$)** δ 166.4, 136.1, 132.7 (t, *J* = 24.4 Hz), 130.2, 129.7, 128.6, 128.2, 128.2, 128.1, 66.7. **HRMS** m/z (ESI) calcd. for $C_{14}H_{11}DO_2$ $[M+H]^+$:214.0973; found: 214.0976 **IR (KBr)**: 3035, 2954, 1720, 1272, 1102, 698, 614 cm^{-1}



2ac: 1-((((1R,2S,5R)-2-Isopropyl-5-methylcyclohexyl)oxy)methyl)benzene-4-*d*

According to the general procedure, **1ac** (0.2 mmol), NaOH (0.2 mmol), D_2O (0.5 ml), CH_3CN (0.5 ml) and isopropyl ether (0.5 ml) were used. **2ac** was isolated by preparative TLC (eluent: petroleum ether: ethyl acetate = 60:1) as an off-white powder (39.1 mg, 79% yield). Deuterium incorporation: 98% (^{1}H-NMR). **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.41 – 7.32 (m, 4H), 4.68 (d, *J* = 11.4 Hz, 1H), 4.42 (d, *J* = 11.4 Hz, 1H), 3.20 (td, *J* = 10.6, 4.4 Hz, 1H), 2.36 – 2.31 (m, 1H), 2.22 (d, *J* = 12.1 Hz, 1H), 1.67 (t, *J* = 15.4 Hz, 2H), 1.44 – 1.27 (m, 2H), 1.04 – 0.86 (m, 9H), 0.74 (d, *J* = 6.7 Hz, 3H). **^{13}C NMR (151 MHz, CDCl$_3$)** δ 139.4, 128.3, 128.0, 127.2 (t, *J* = 21.9 Hz), 78.9, 70.6, 48.5, 40.5, 34.8, 31.8, 25.7, 23.5, 22.5, 21.2, 16.3. ^{1}H and ^{13}C NMR data agreed with literature.[3]



2ad: (R)-2,7,8-trimethyl-2-((4R,8R)-4,8,12-trimethyltridecyl)chroman-6-yl benzoate-4-*d*

According to the general procedure, **1ad** (0.1mmol), K_3PO_4 (0.1 mmol), D_2O (0.5 ml), and 1,4-*d*ioxane (2 ml) were used. **2ad** was isolated by preparative TLC (eluent: petroleum ether) as a yellow liquid (22.4 mg, 43% yield). Deuterium incorporation: 97% (^{1}H-NMR). **^{1}H NMR (600 MHz, CDCl$_3$)** δ 8.27 (d, *J* = 8.4 Hz, 2H), 7.54 (d, *J* = 7.9 Hz, 2H), 2.64 (t, *J* = 6.9 Hz, 2H), 2.14 (s, 3H), 2.08 (s, 3H), 2.04 (s, 3H), 1.88 – 1.82 (m, 1H), 1.82 – 1.76 (m, 1H), 1.64 – 1.03 (m, 24H), 0.91 – 0.84 (m, 12H). **^{13}C NMR (151 MHz, CDCl$_3$)** δ 165.3, 149.7, 140.9, 133.2 (t, *J* = 25.3 Hz), 130.3, 130.0, 128.6, 127.1, 125.3, 123.3, 117.6, 75.3, 39.6, 37.7, 37.6, 37.5, 33.0, 32.9, 28.2, 25.0, 24.6, 22.9, 22.8, 21.2, 20.8, 19.9, 19.8, 13.2, 12.3, 12.0. **HRMS** m/z (ESI) calcd. for $C_{36}H_{53}DO_3$ $[M+H]^+$:536.4208; found: 536.4227. **IR (KBr)**: 2927, 2866, 1737, 1598, 1460, 1410, 1378, 1269, 1237, 1171, 1091, 1022, 912, 874, 774, 697, 612 cm^{-1}

IV References

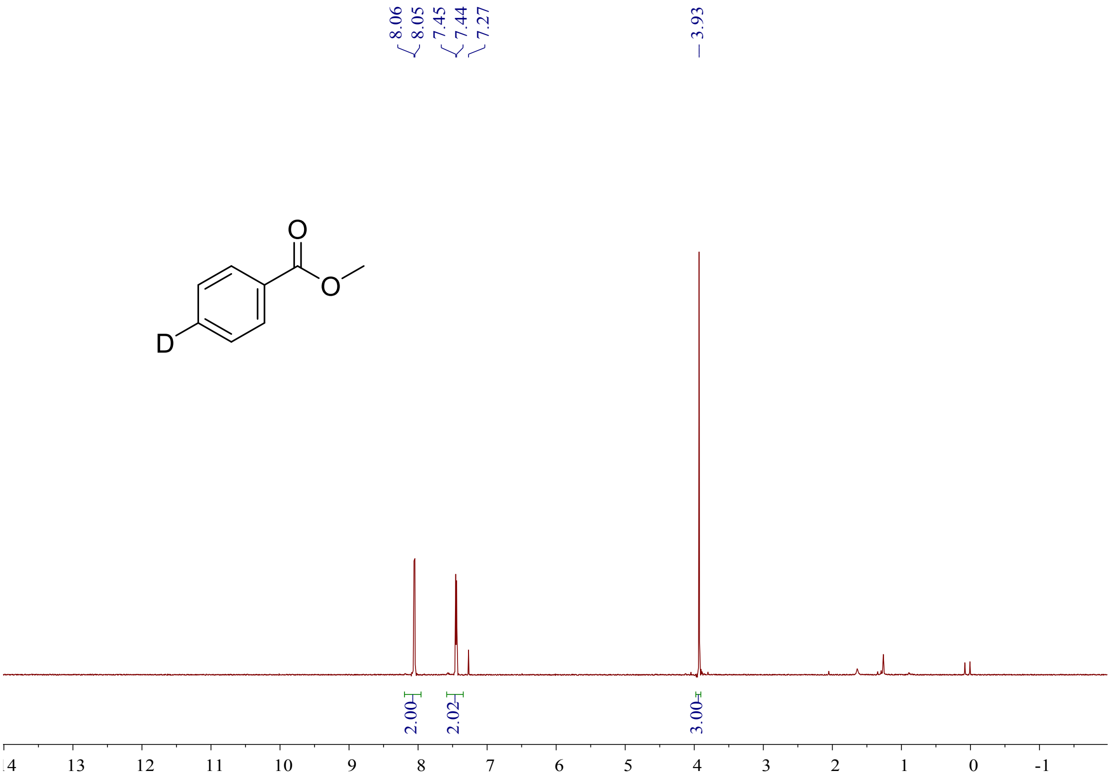
1. D. Cao, C. Yan, P. Zhou, H. Zeng and C. J. Li, *Chem. Commun.*, 2019, **55**, 767.
2. H. S. I. Chao and G. A. Berchtold, *J. Am. Chem. Soc.*, 1981, **103**, 898.
3. X. Wang, M.-H. Zhu, D. P. Schuman, D. Zhong, W.-Y. Wang, L.-Y. Wu, W. Liu, B. M. Stoltz and W.-B. Liu, *J. Am. Chem. Soc.*, 2018, **140**, 10970.
4. M. Rudzki, A. Alcalde-Aragonés, W. I. Dzik, N. Rodríguez and L. J. Gooßen, *Synthesis*, 2012, **44**, 184.
5. S. Berger and B. W. K. Diehl, *Tetrahedron Lett.*, 1987, **28**, 1243.
6. T. Patra, S. Mukherjee, J. Ma, F. Strieth-Kalthoff and F. Glorius, *Angew. Chem. Int. Ed.*, 2019, **58**, 10514.
7. Y. Vignollet and J. C. Maire, *J. Organomet. Chem.*, 1969, **17**, P43.
8. Z. Song, J. Zeng, T. Li, X. Zhao, J. Fang, L. Meng and Q. Wan, *Org. Lett.*, 2020, **22**, 1736.
9. C. Liu, Z. Chen, C. Su, X. Zhao, Q. Gao, G. H. Ning, H. Zhu, W. Tang, K. Leng, W. Fu, B. Tian, X. Peng, J. Li, Q. H. Xu, W. Zhou and K. P. Loh, *Nat. Commun.*, 2018, **9**, 80.
10. C. G. Swain, J. E. Sheats, D. G. Gorenstein and K. G. Harbison, *J. Am. Chem. Soc.*, 1975, **97**, 791.
11. T. Mutsumi, H. Iwata, K. Maruhashi, Y. Monguchi and H. Sajiki, *Tetrahedron*, 2011,

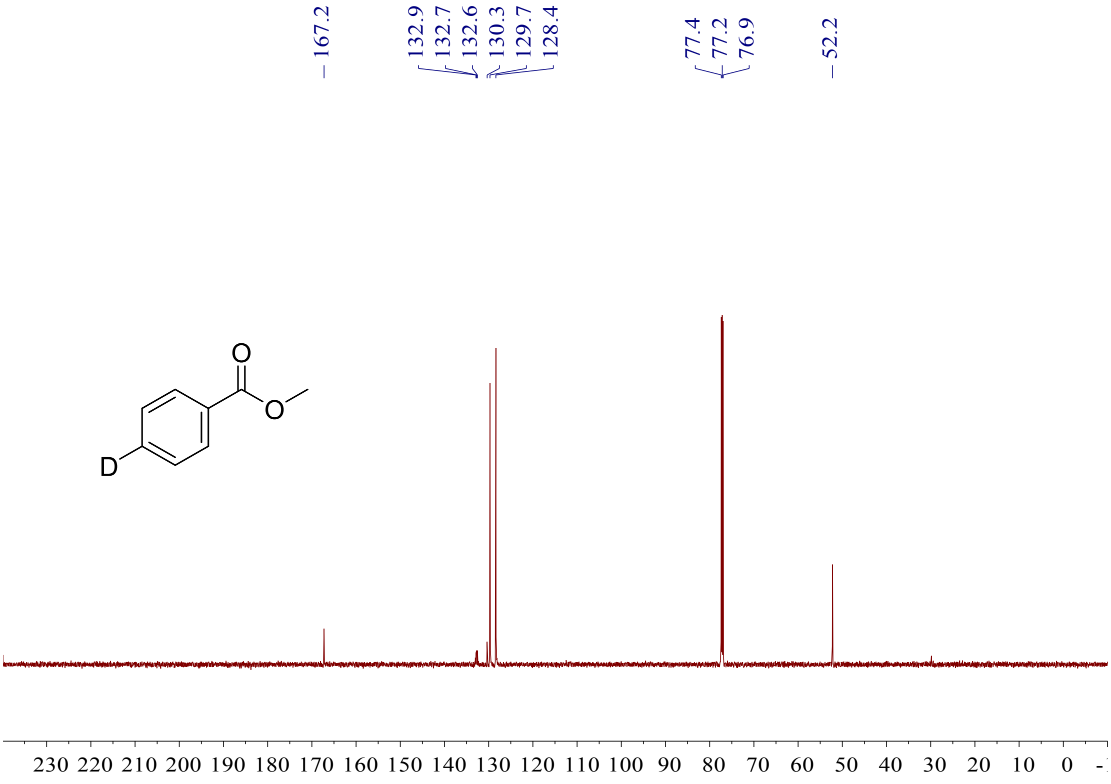
67, 1158.

12. B. Xiao, T. J. Gong, Z. J. Liu, J. H. Liu, D. F. Luo, J. Xu and L. Liu, *J. Am. Chem. Soc.*, 2011, **133**, 9250.
13. Y. Miura, H. Oka, E. Yamano and M. Morita, *J. Org. Chem.*, 1997, **62**, 1188.

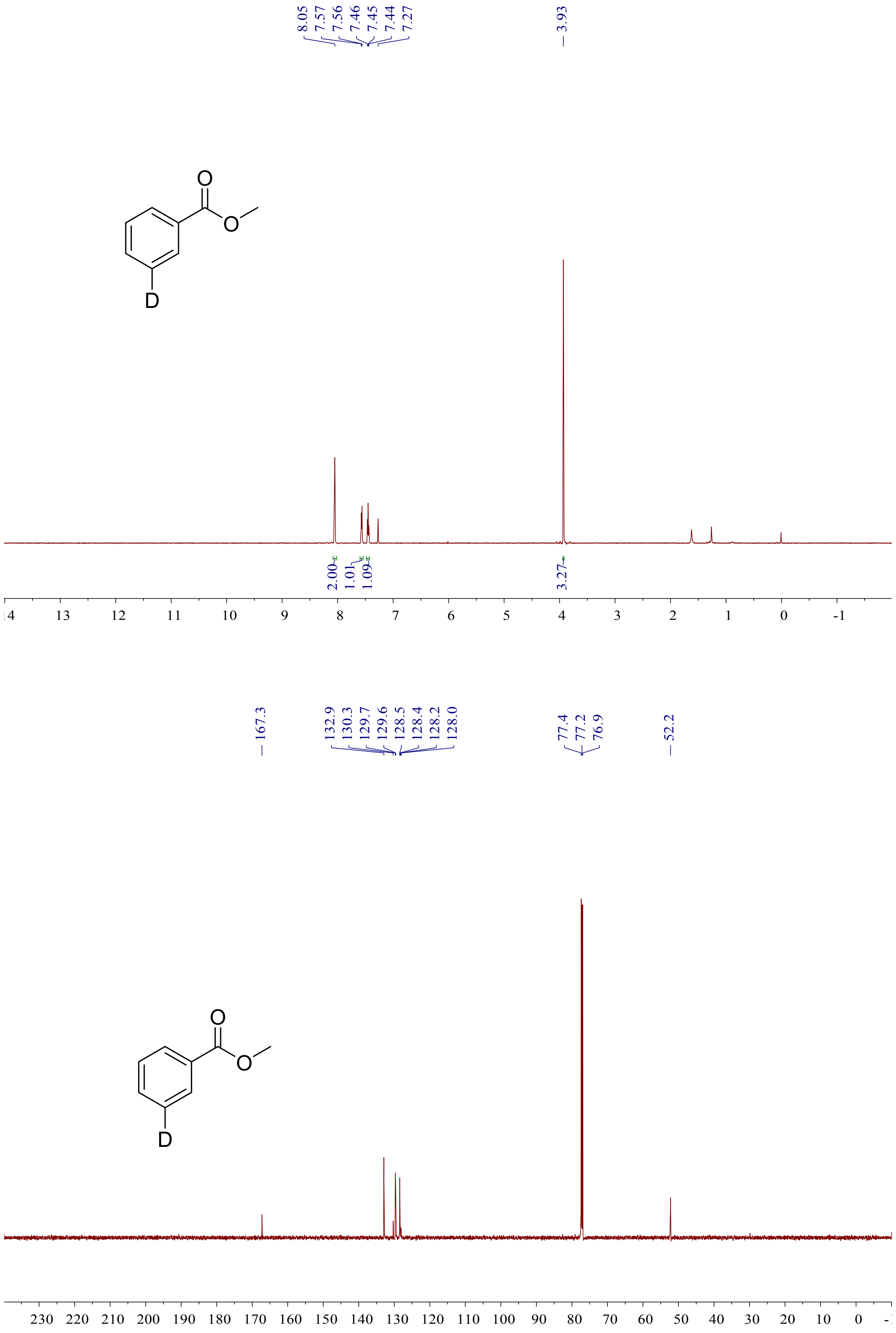
V. Copies of ^{1}H NMR and ^{13}C NMR

^{1}H and ^{13}C NMR spectra of compound **2a**





^{1}H and ^{13}C NMR spectra of compound **2b**



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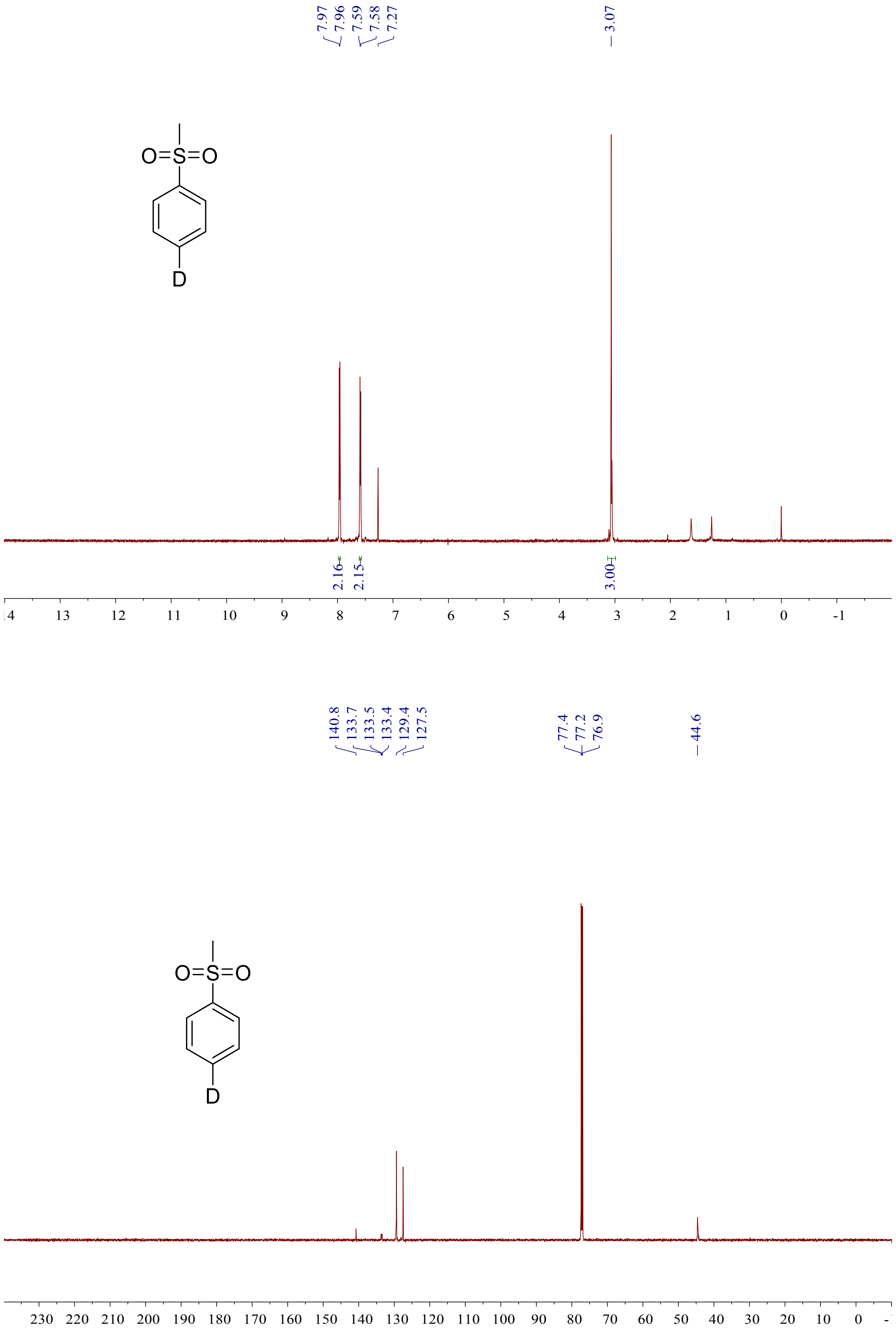
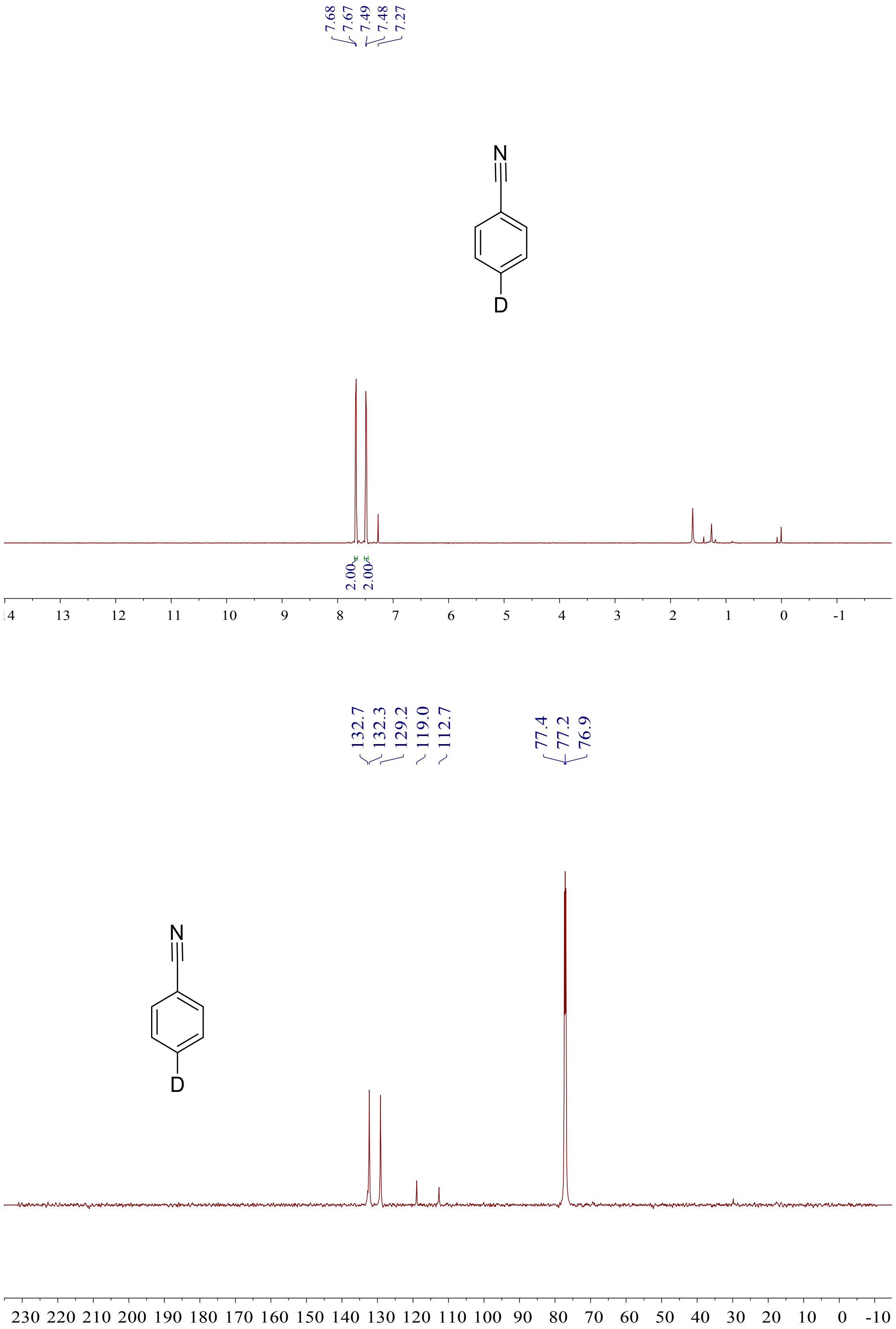


^{1}H and ^{13}C NMR spectra of compound **2d**



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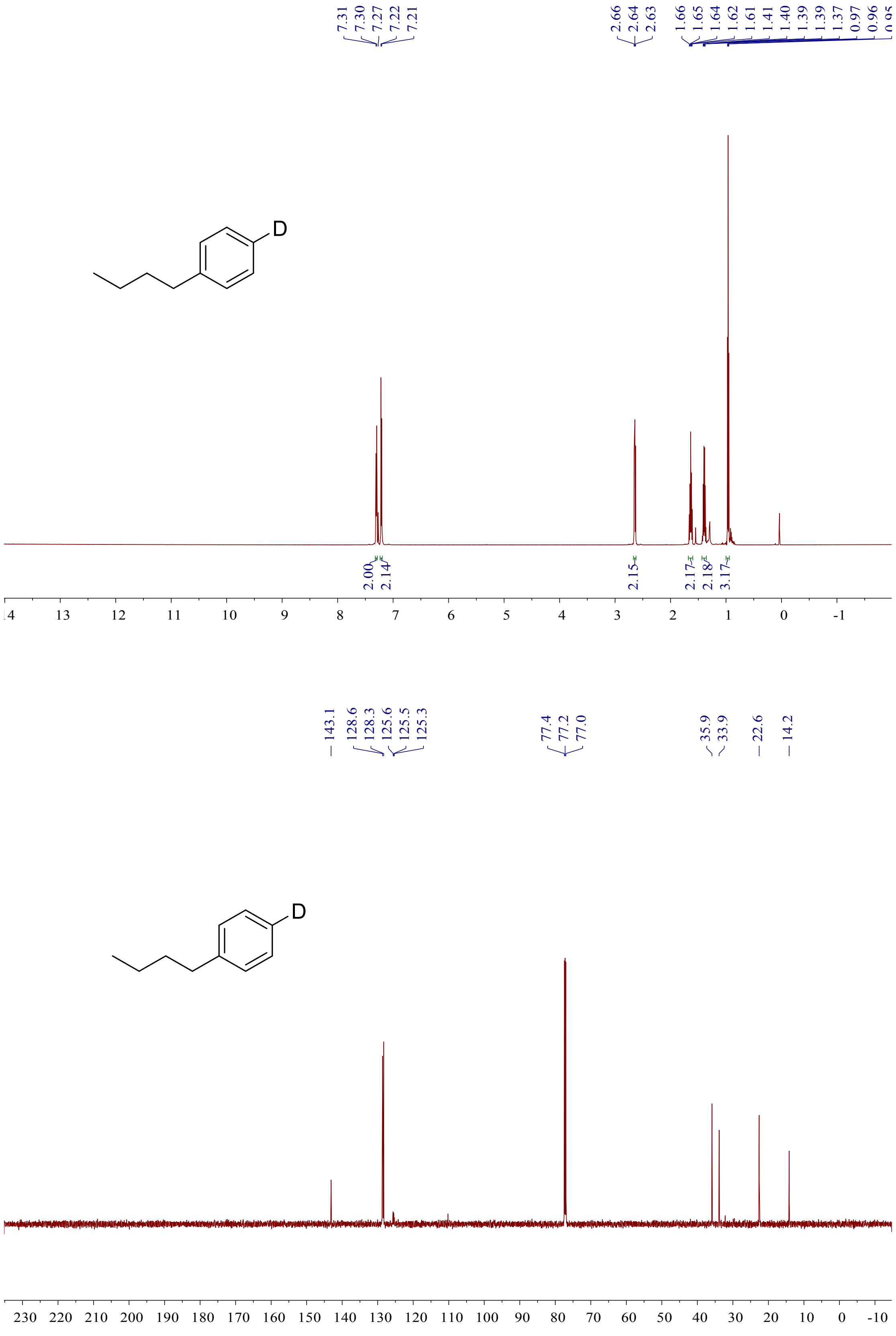
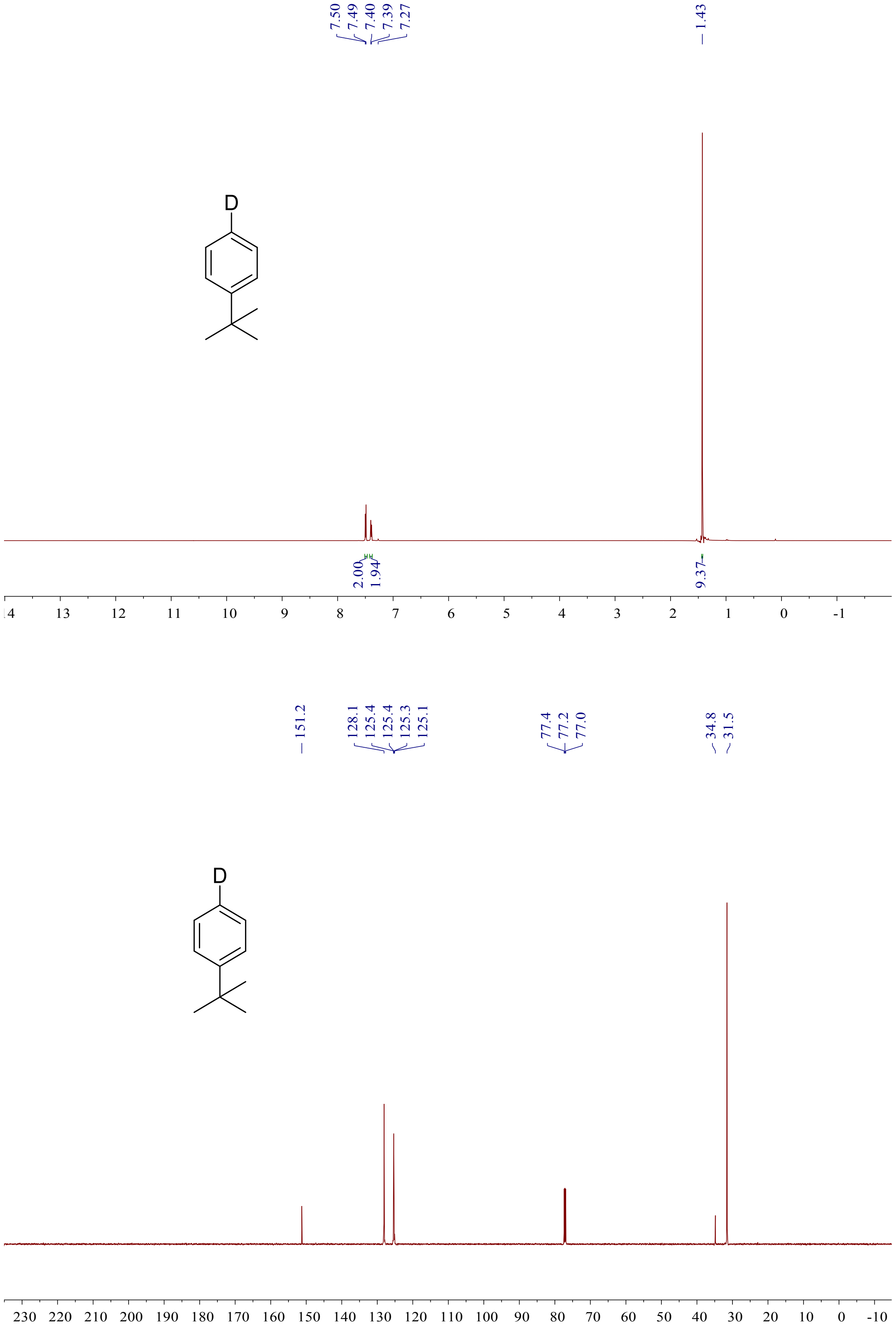


^{1}H and ^{13}C NMR spectra of compound **2f**



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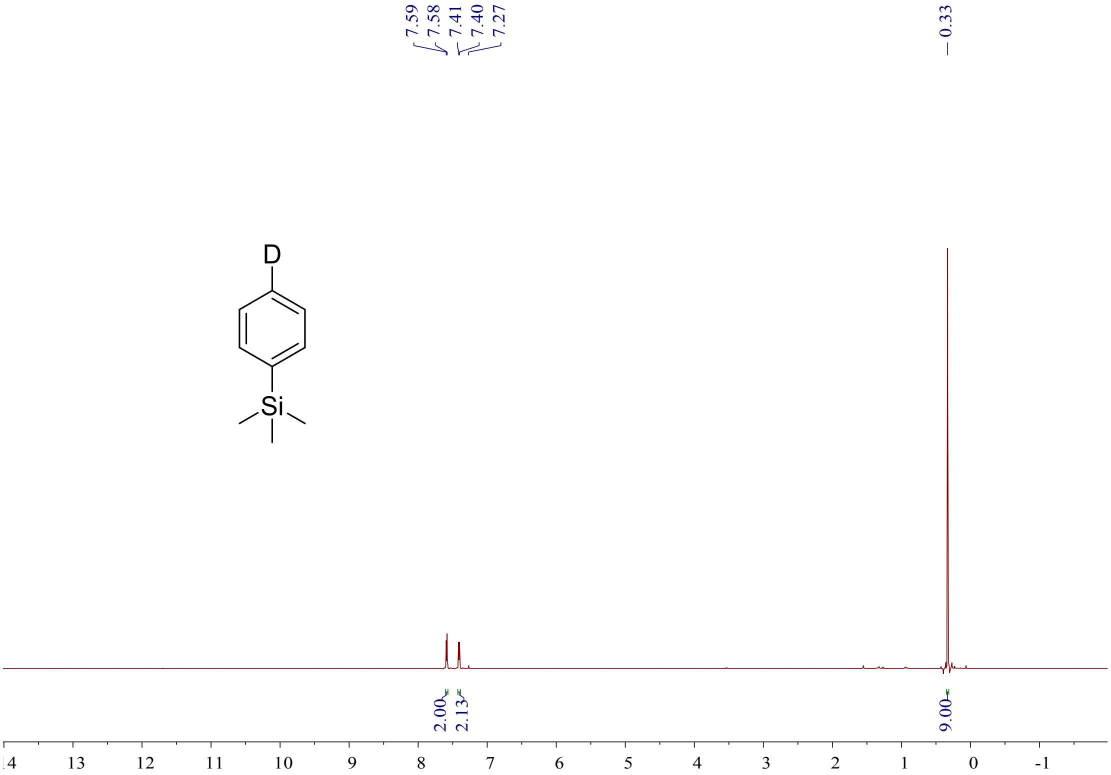

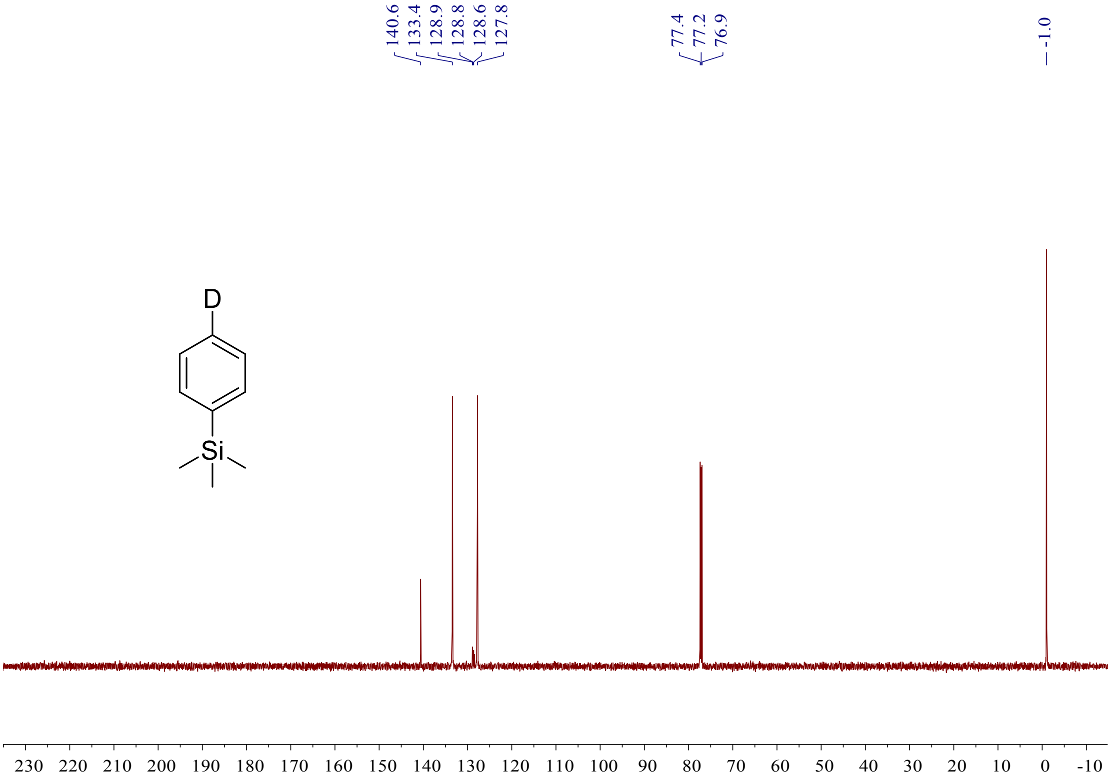

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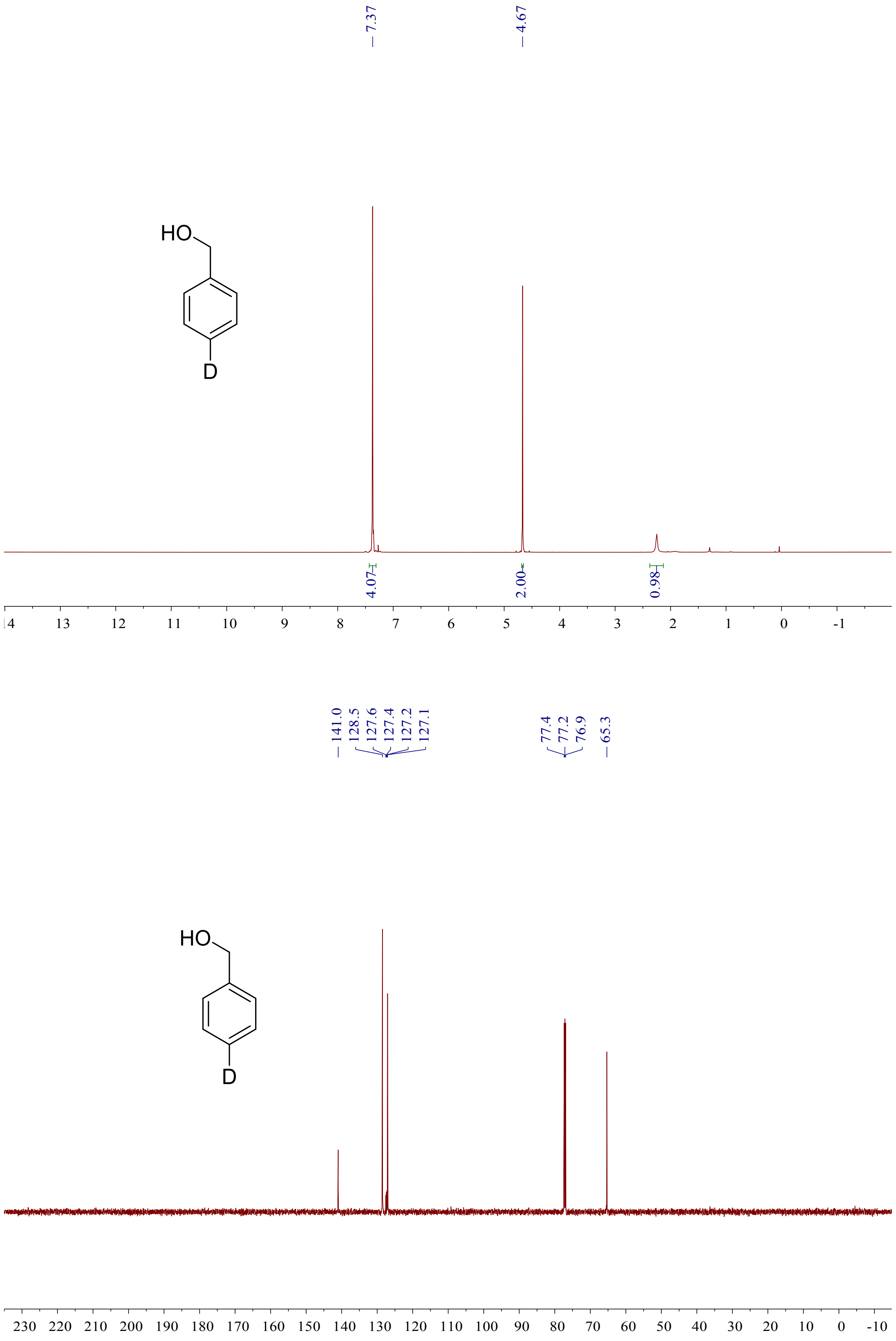

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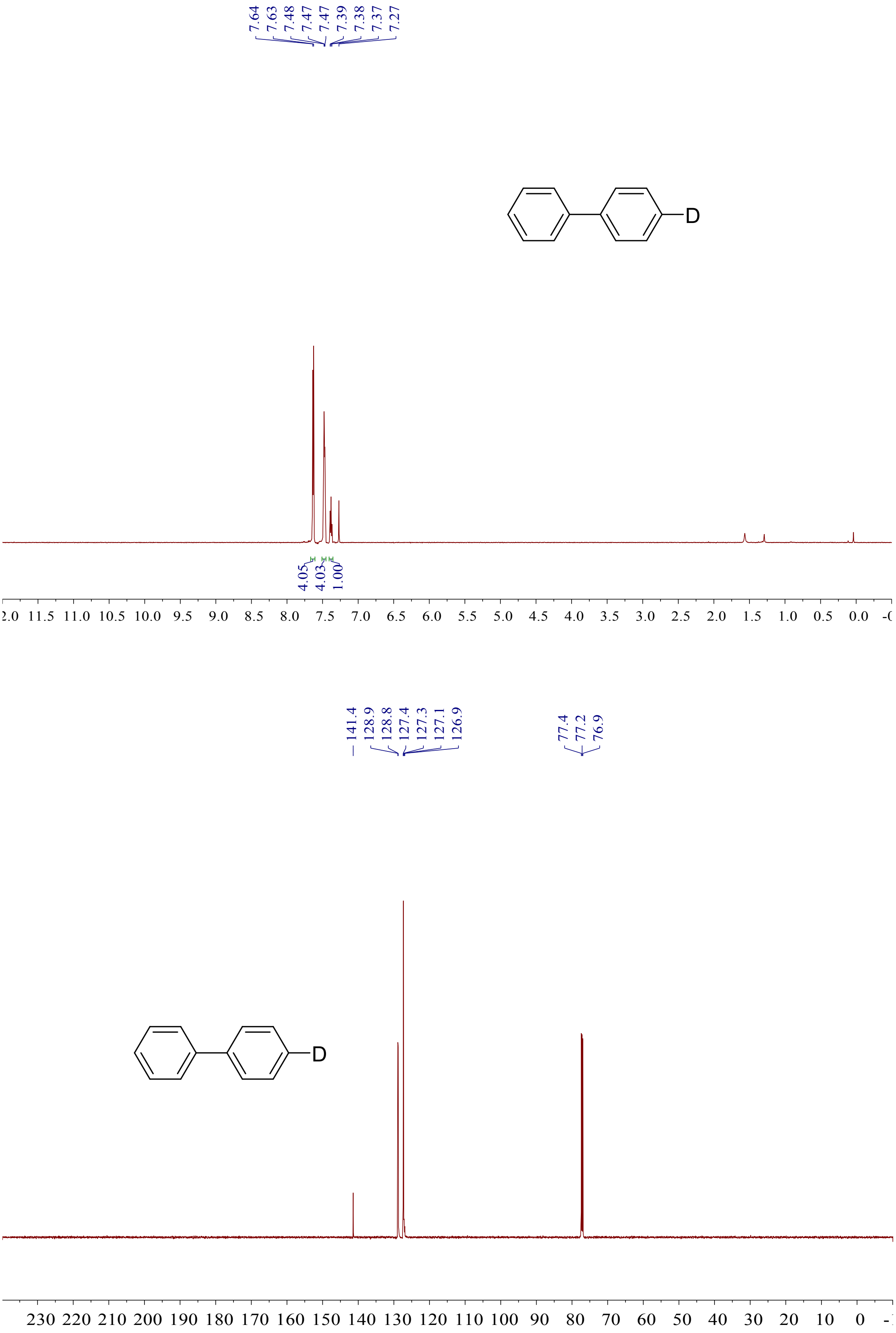

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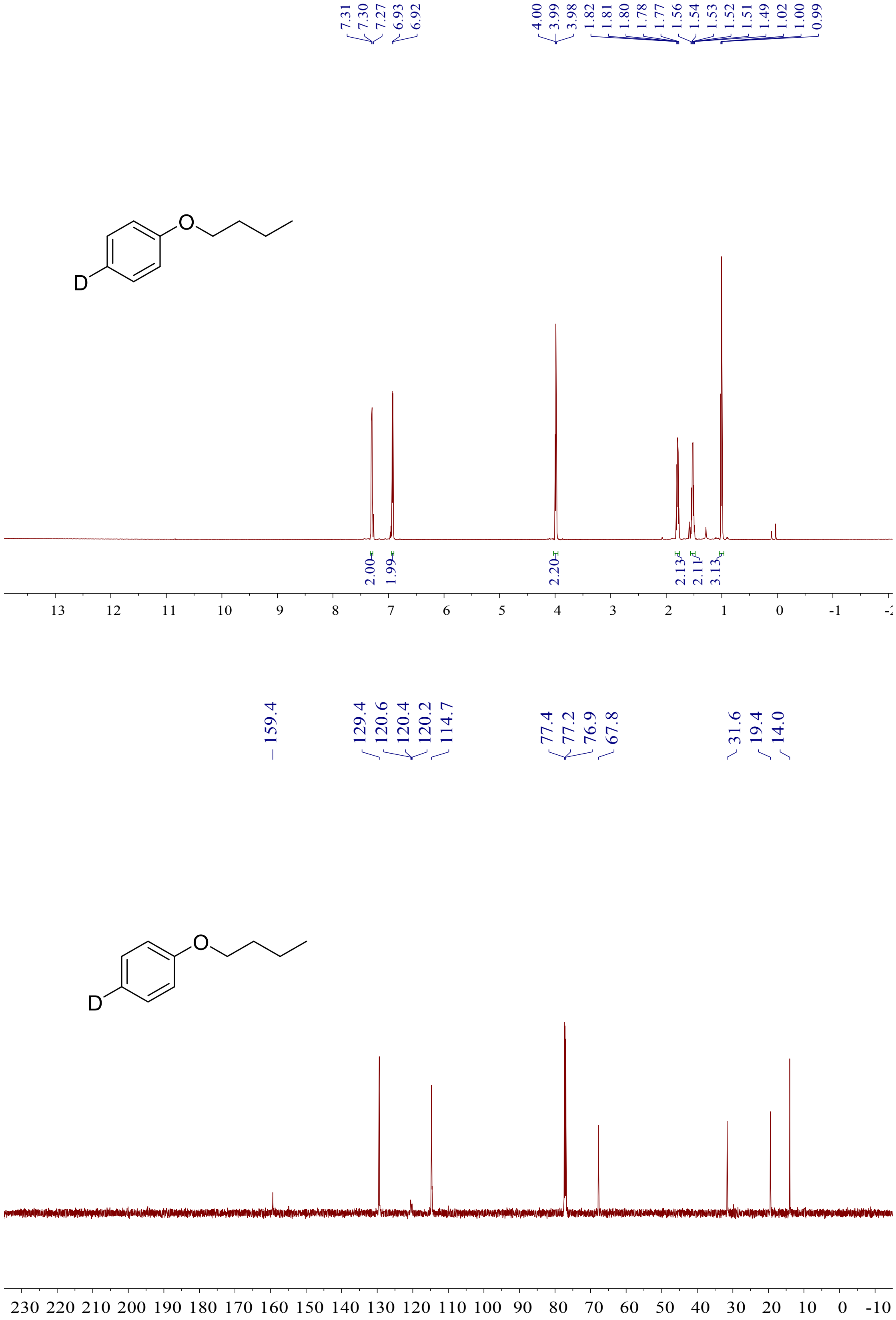

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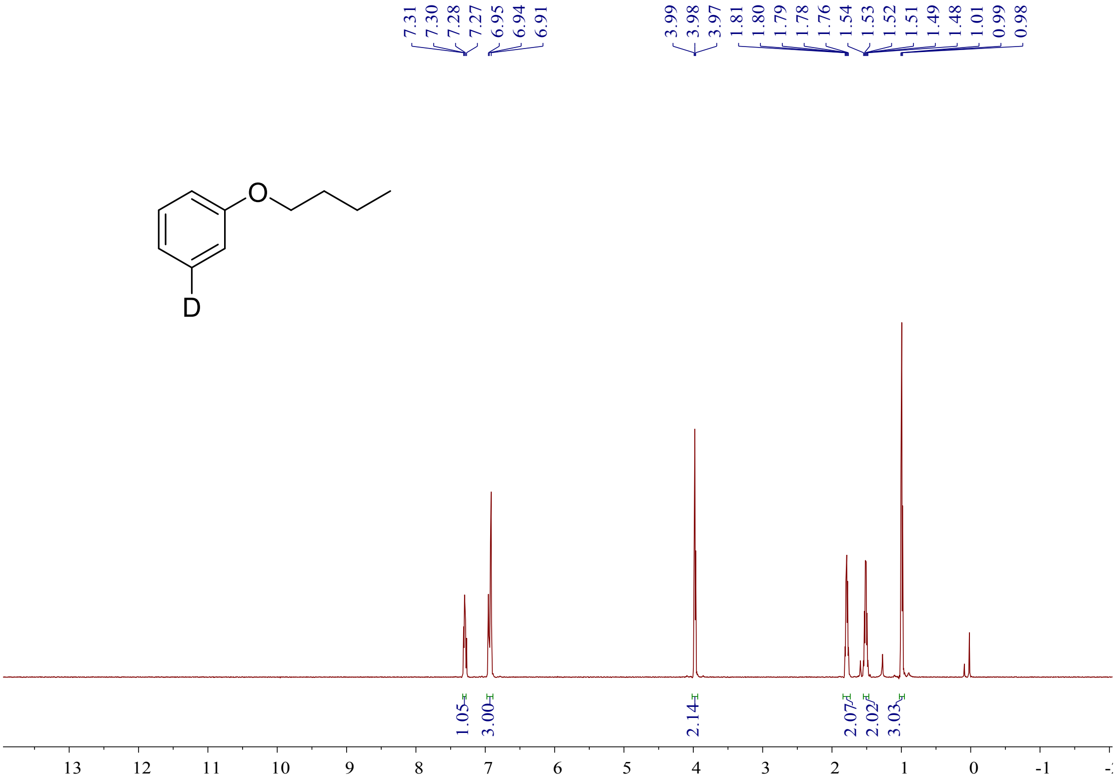

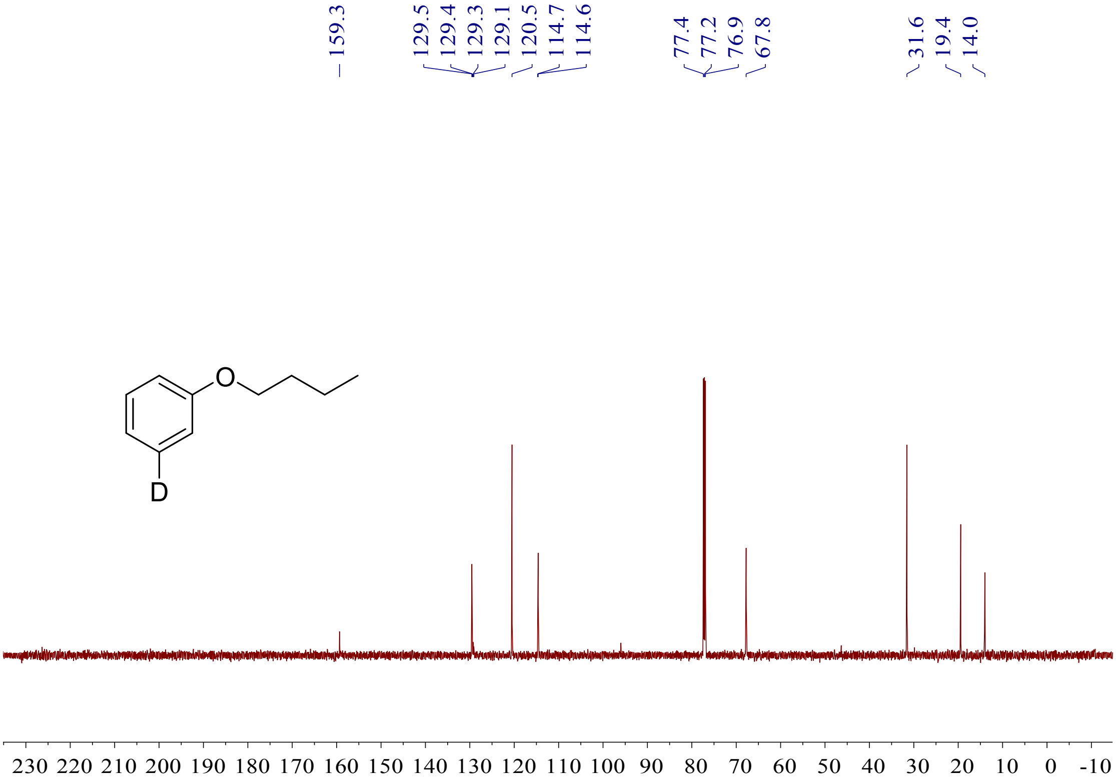

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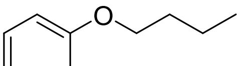
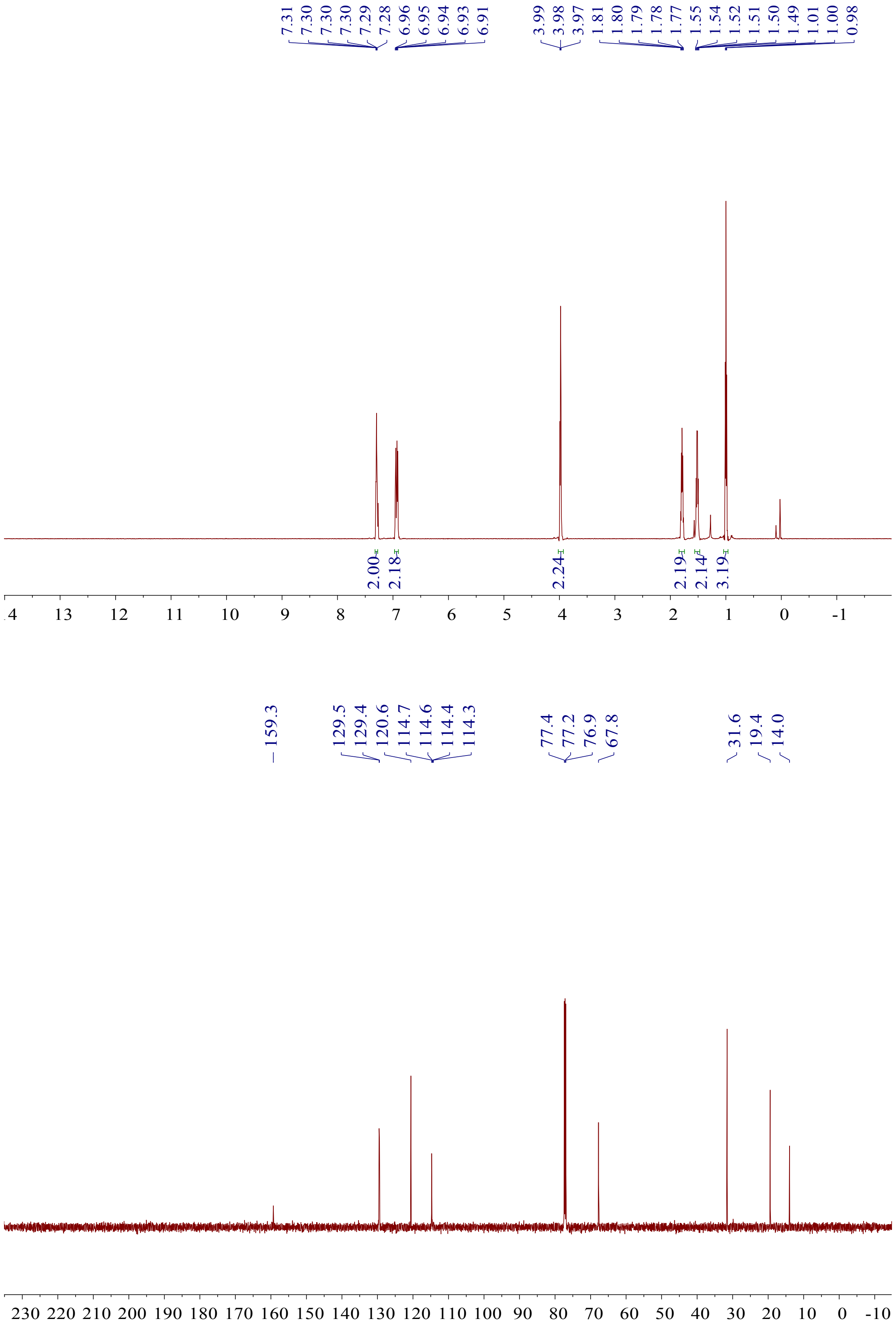
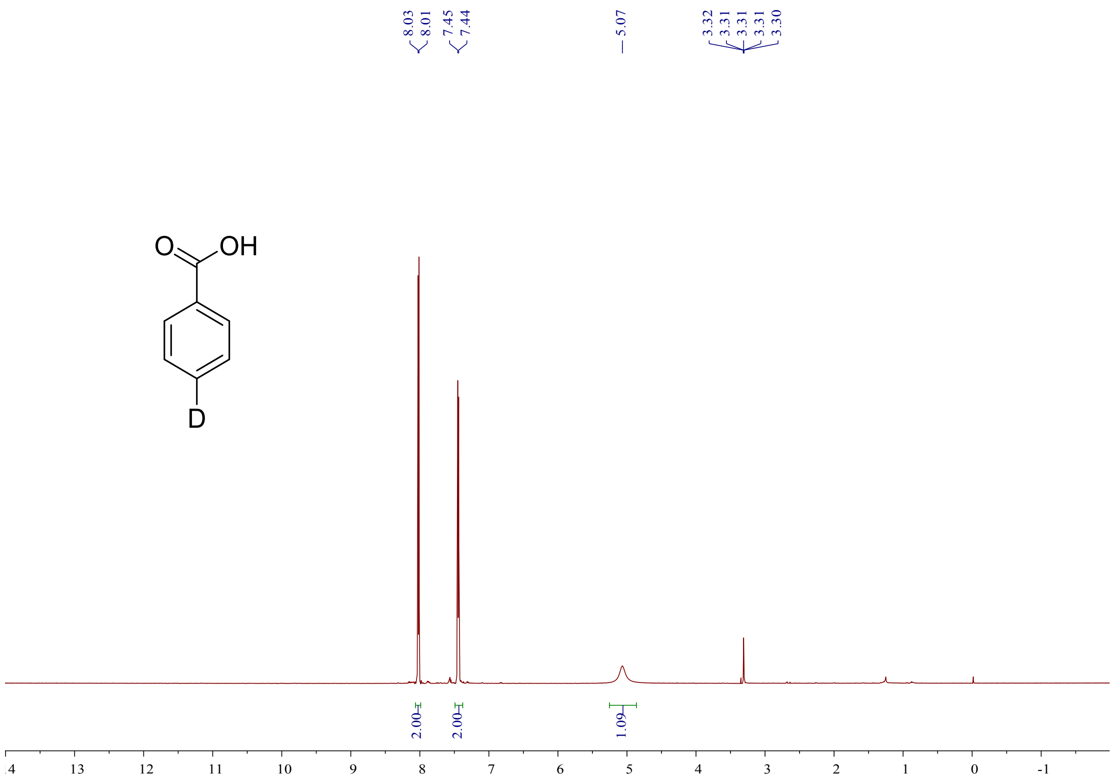
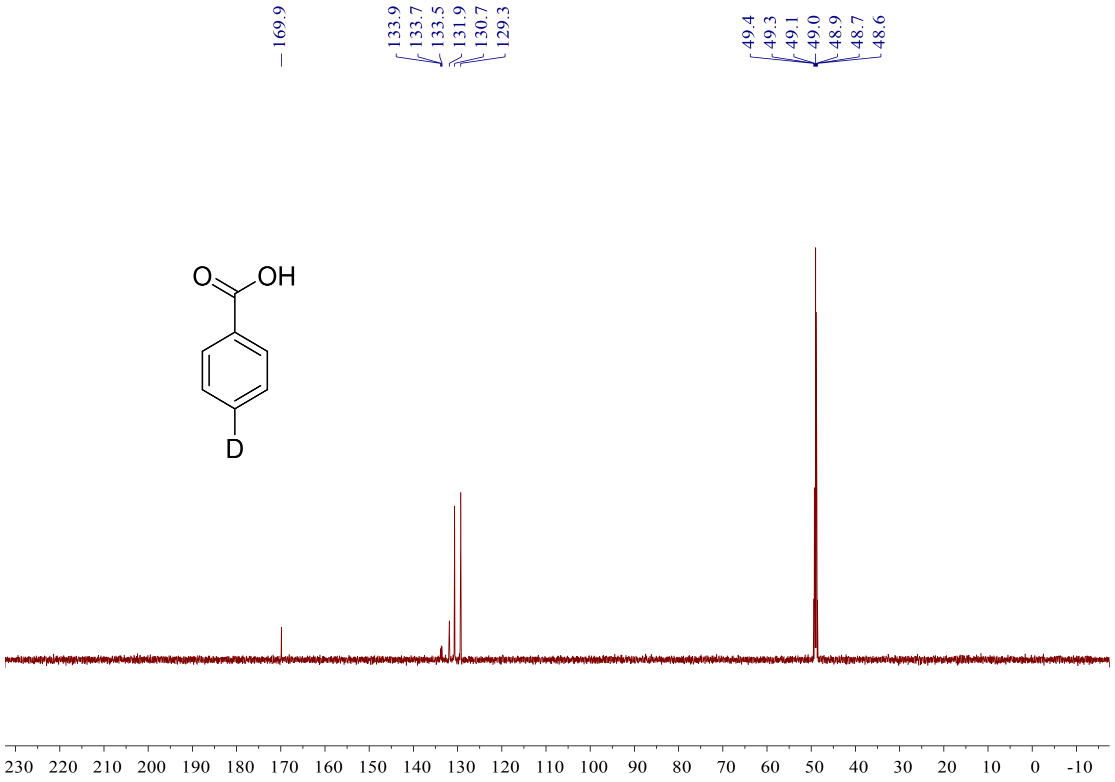


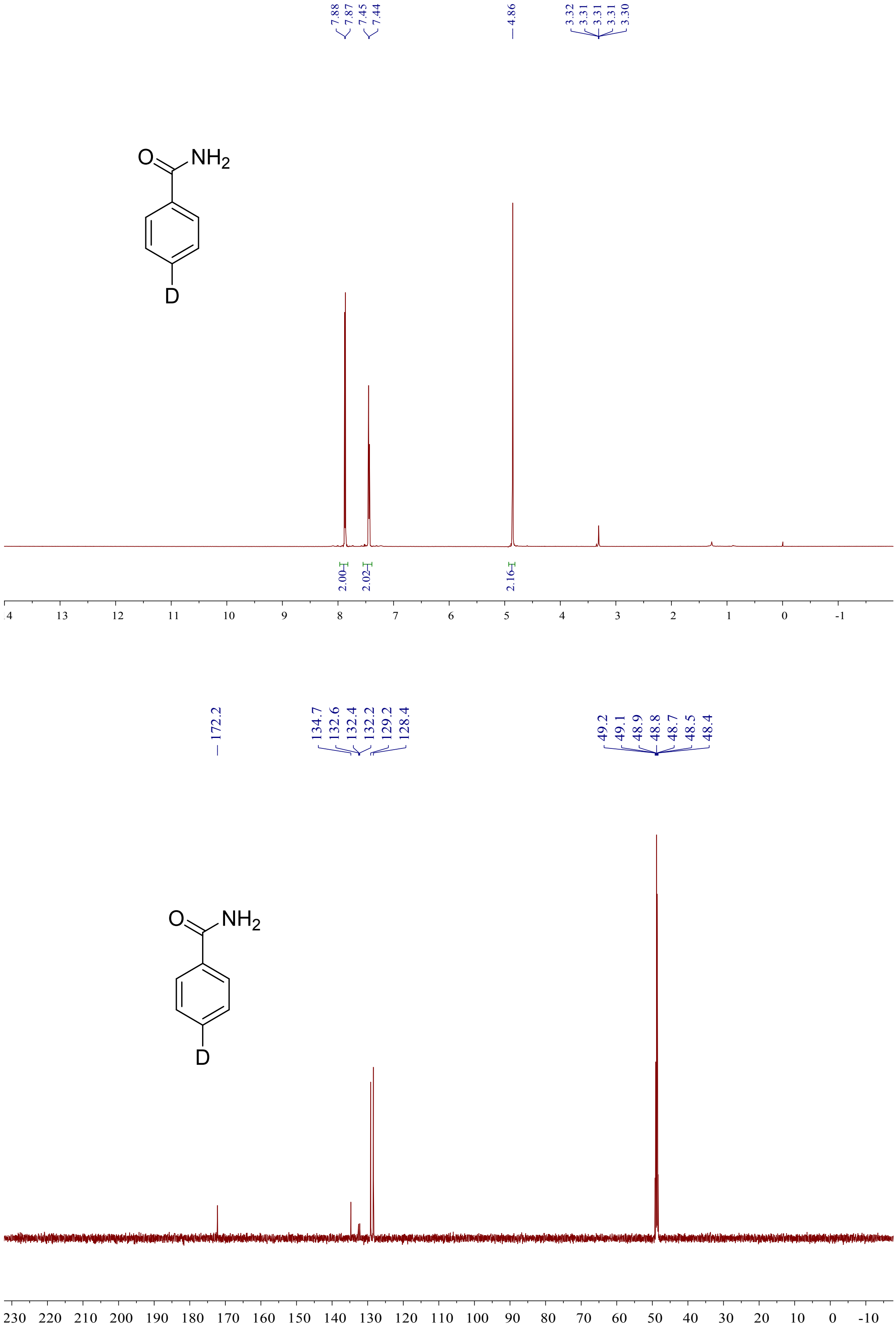


^{1}H and ^{13}C NMR spectra of compound **2p**





^{1}H and ^{13}C NMR spectra of compound **2q**



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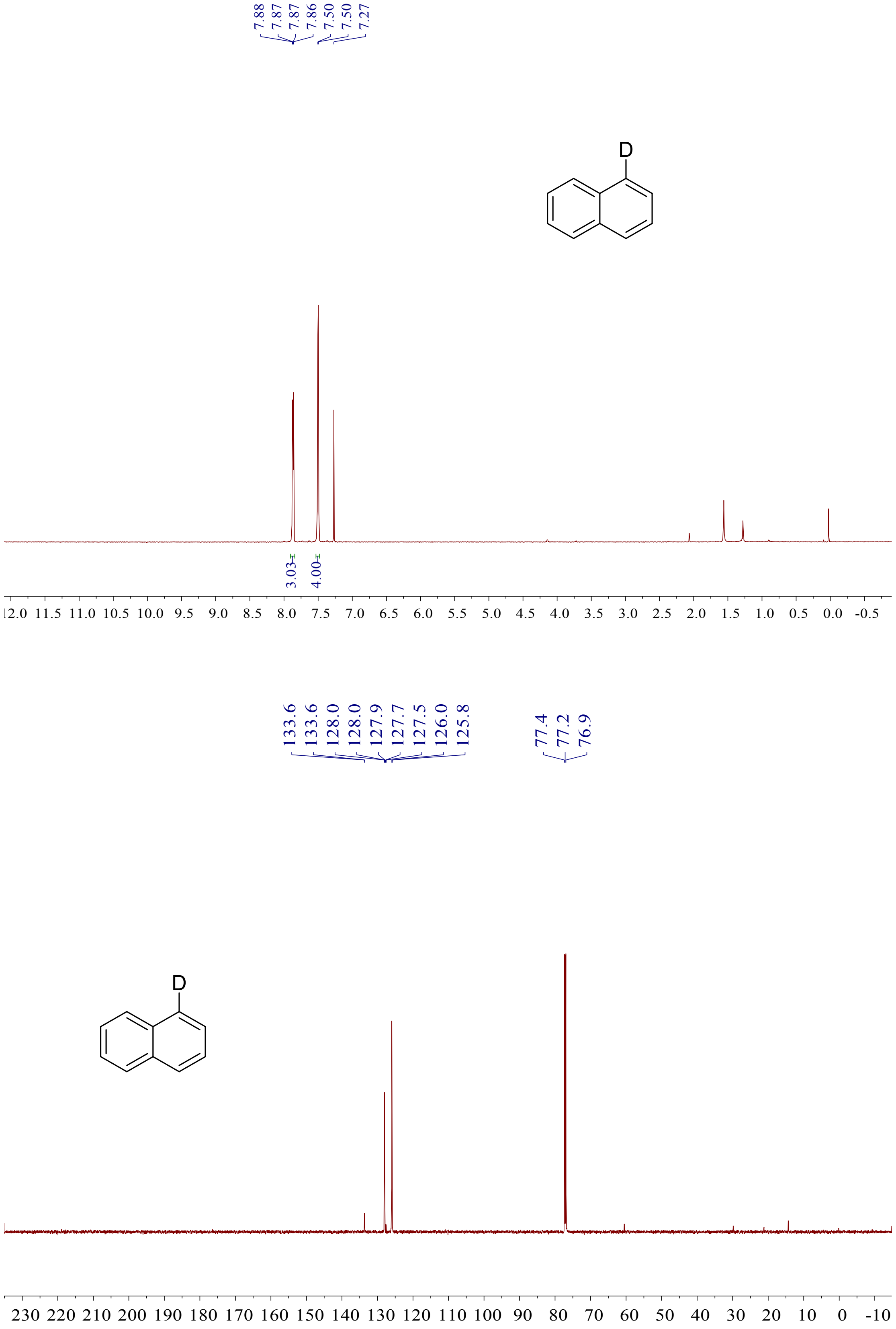
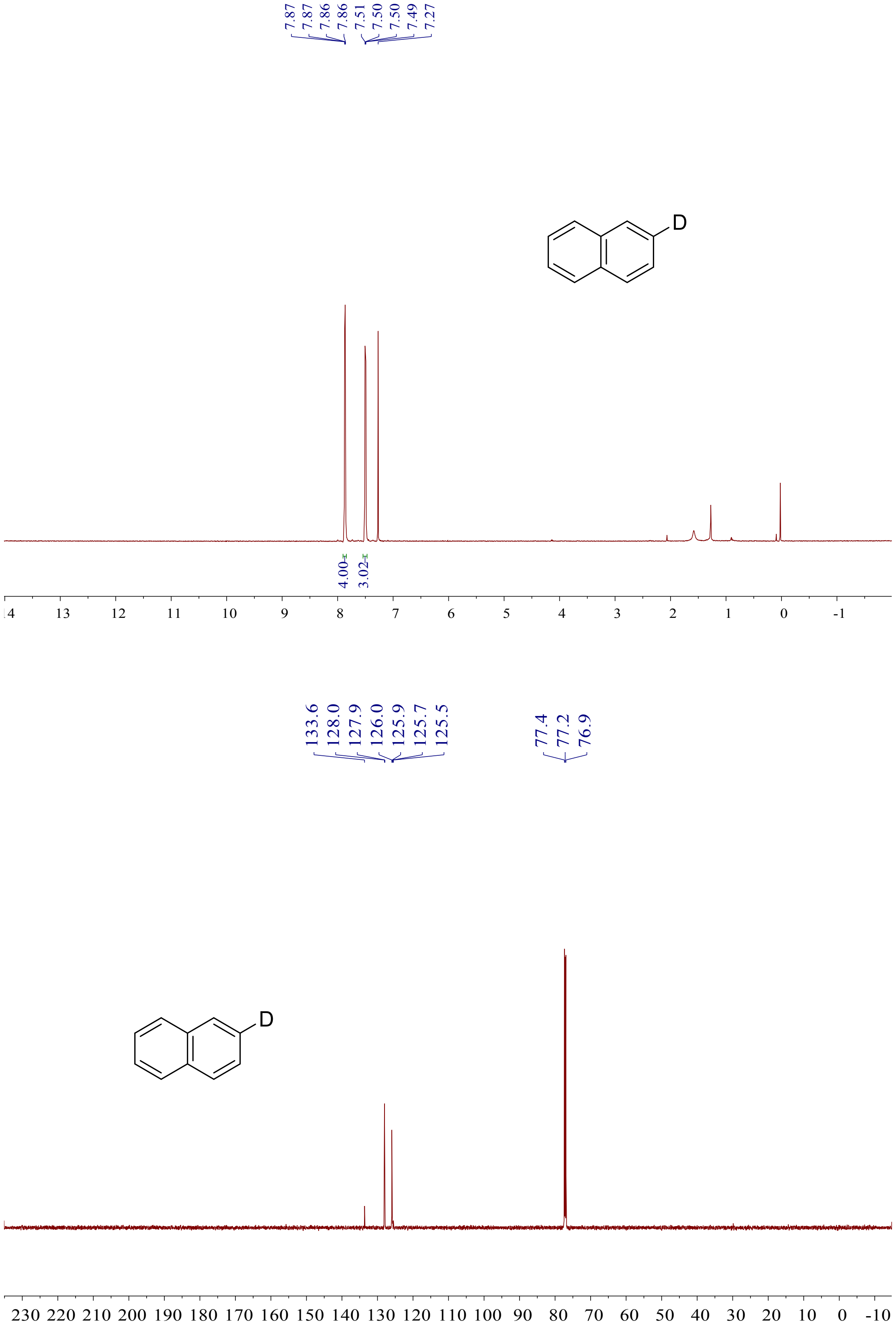
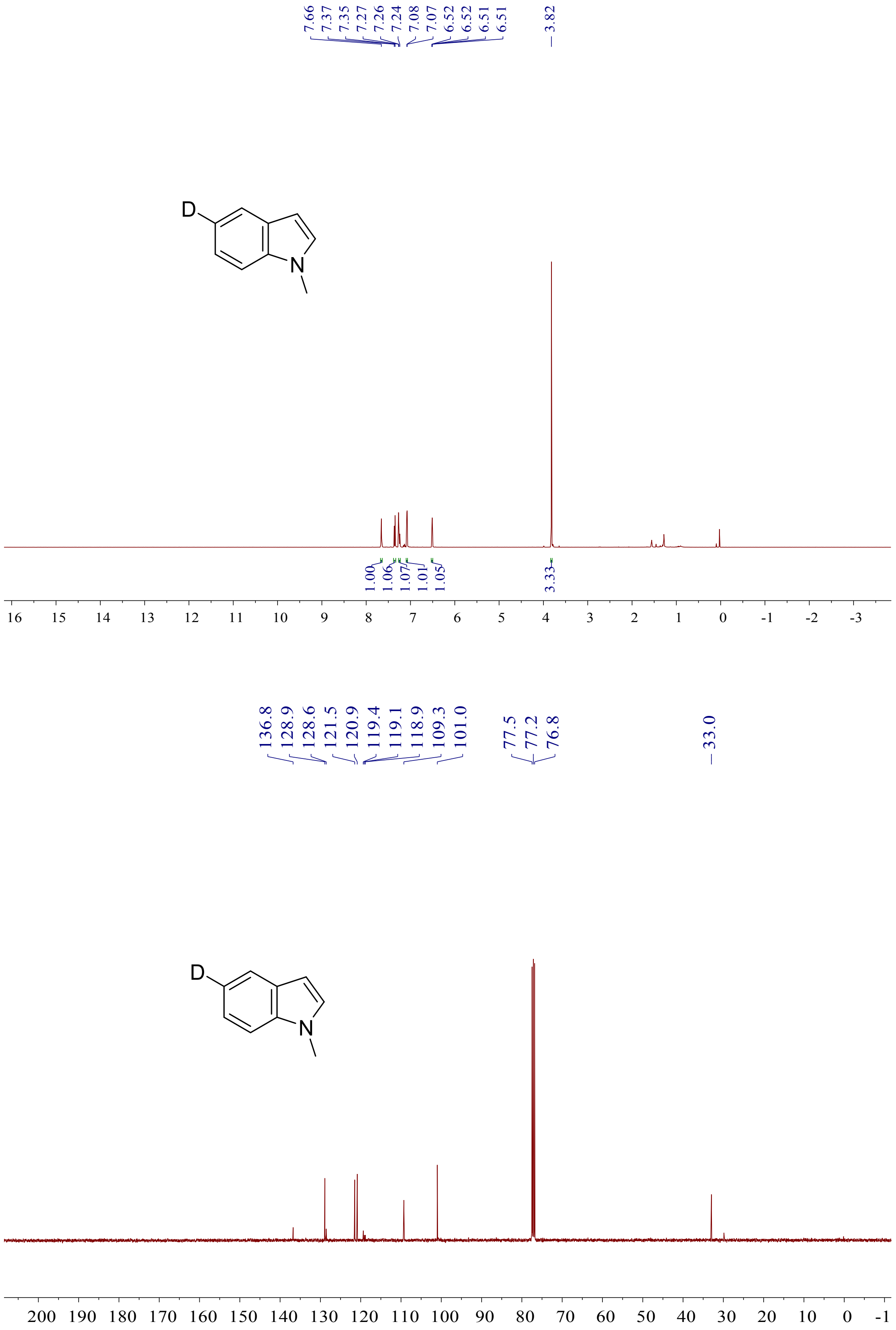


^{1}H and ^{13}C NMR spectra of compound **2s**



^{1}H and ^{13}C NMR spectra of compound **2t**



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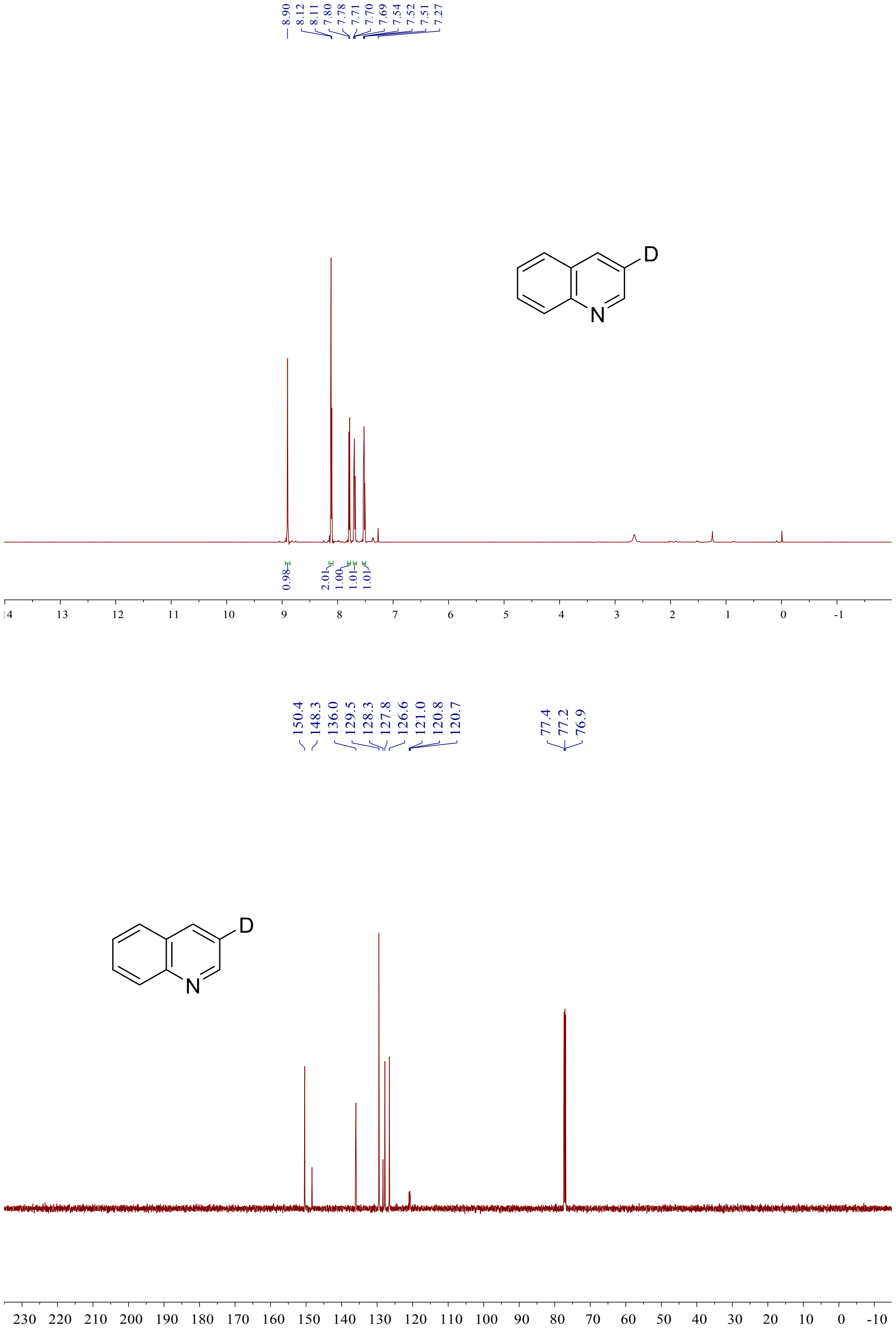

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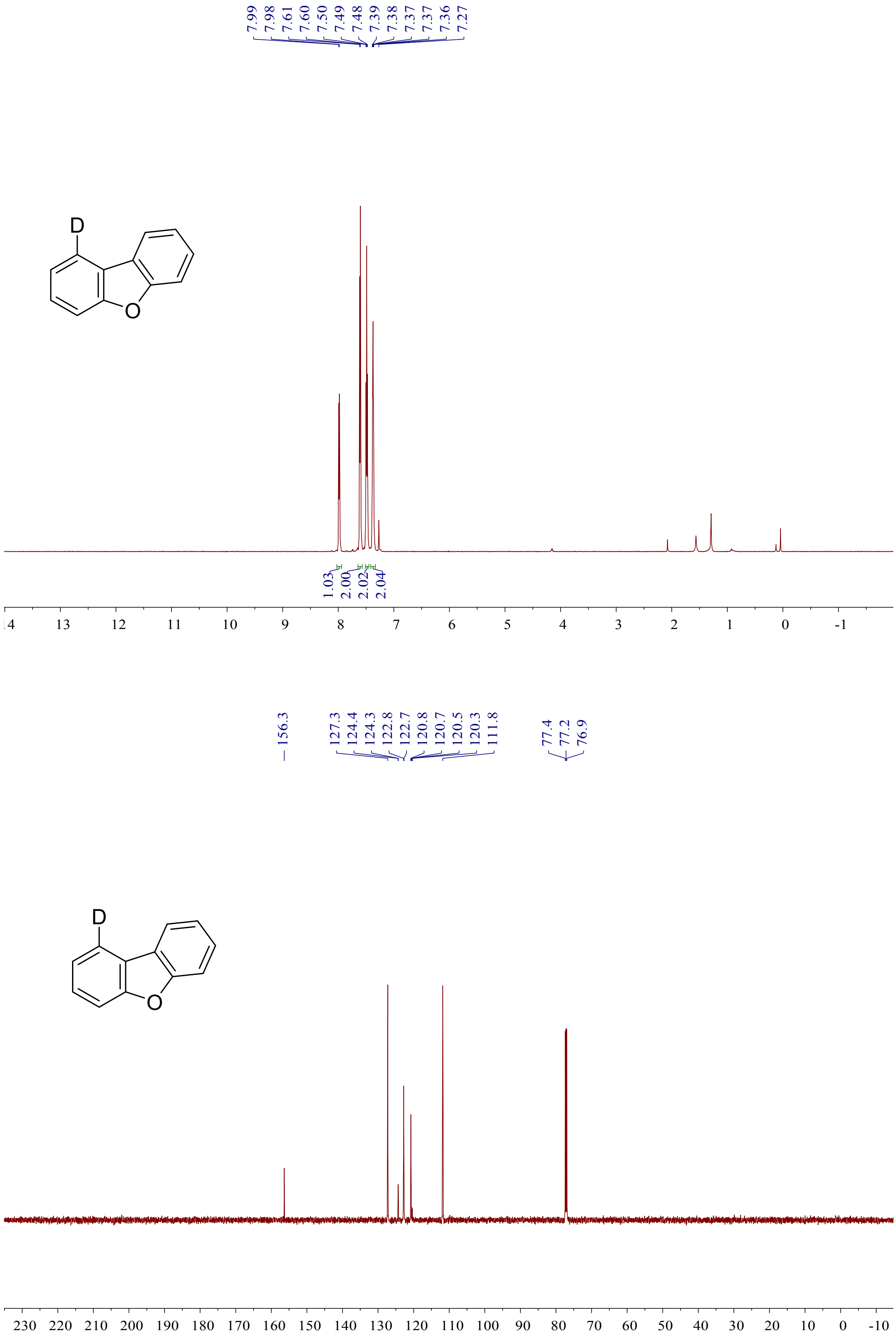
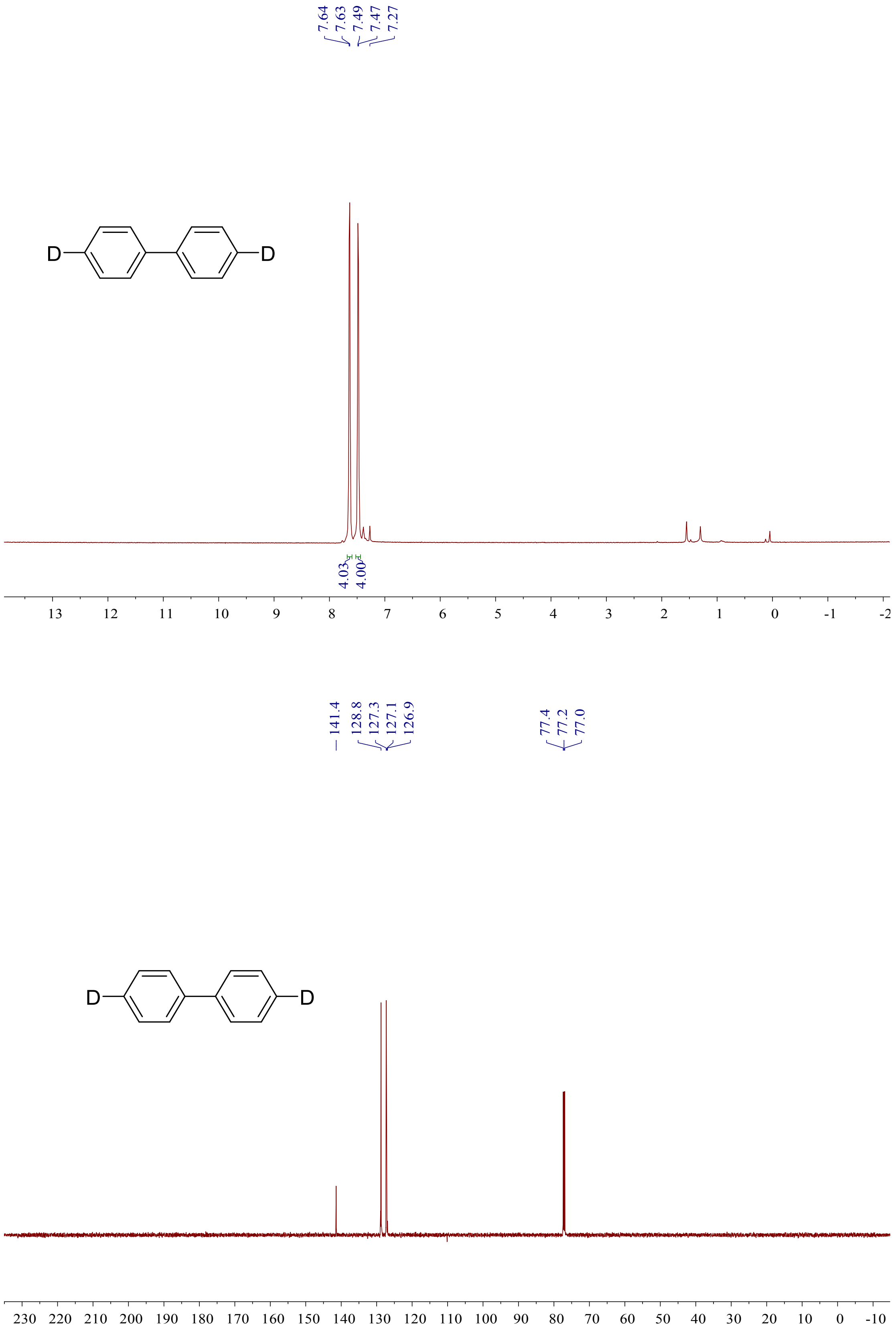
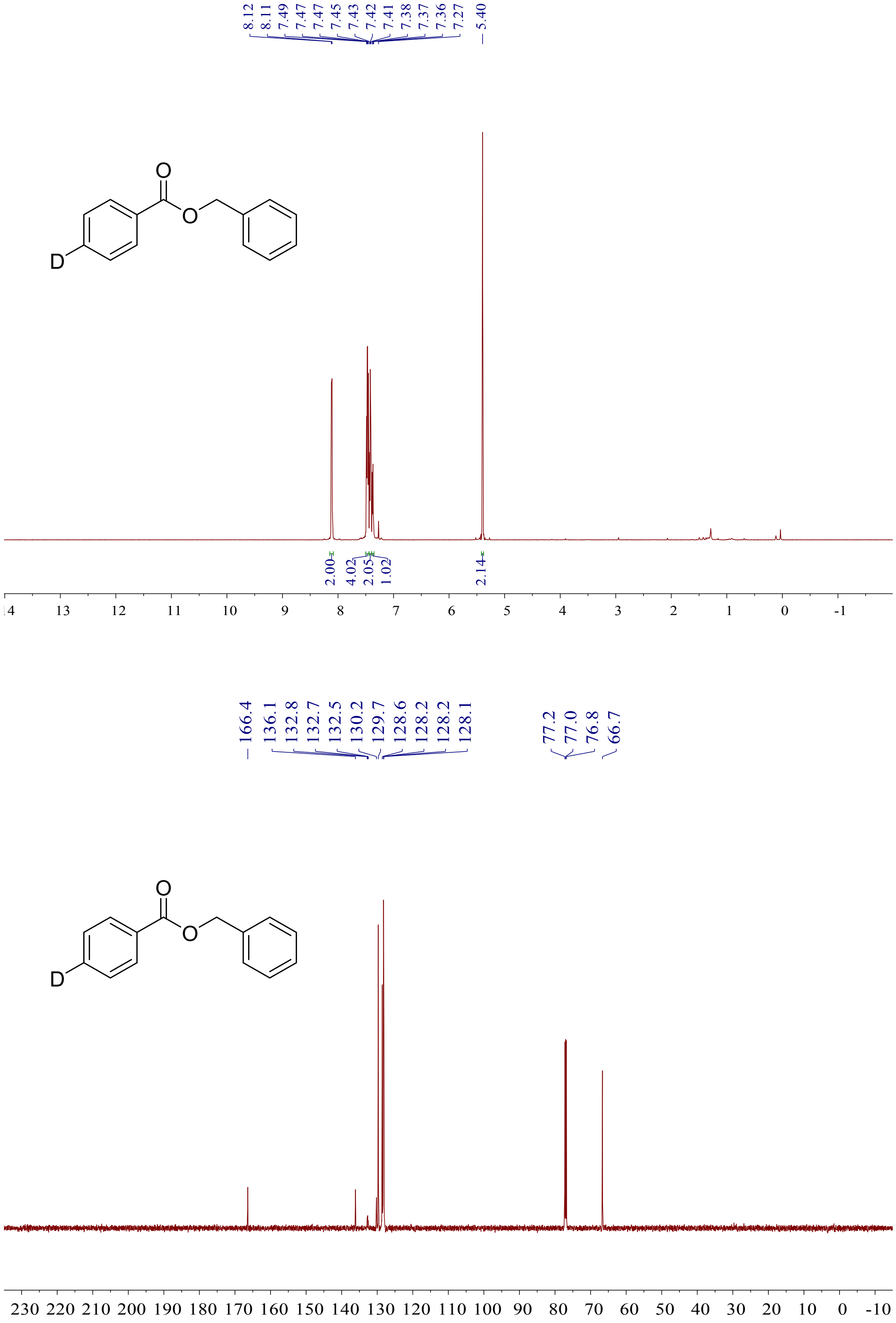


^{1}H and ^{13}C NMR spectra of compound **2w**



^{1}H and ^{13}C NMR spectra of compound **2ab**



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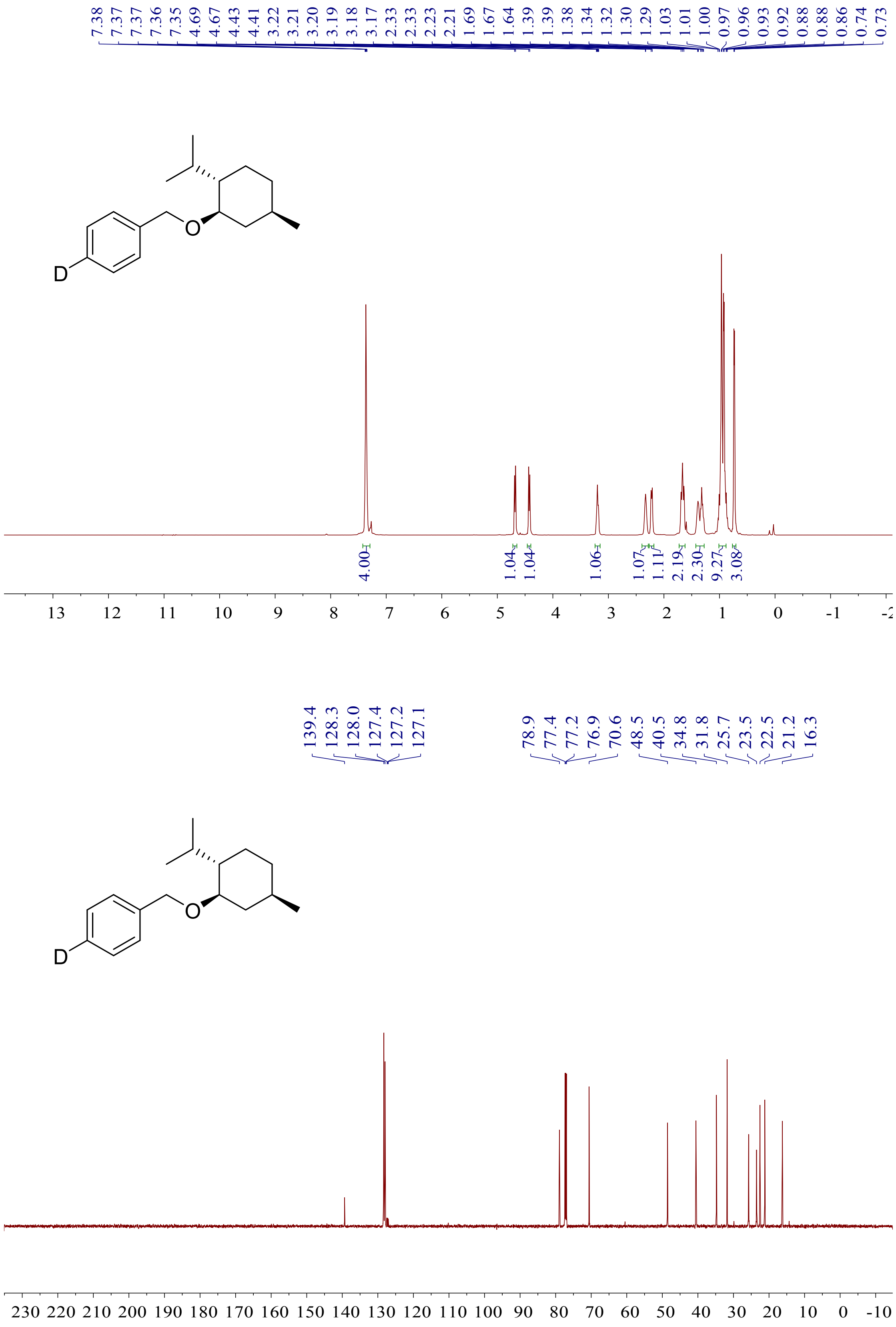
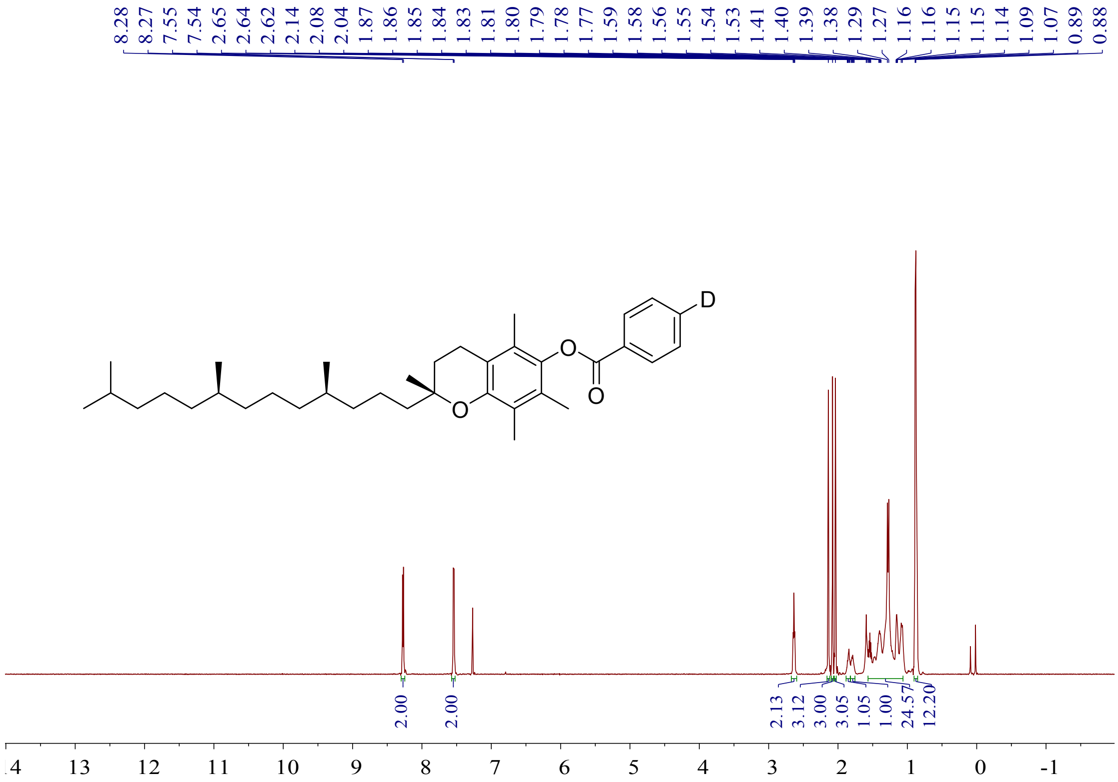


^{1}H and ^{13}C NMR spectra of compound **2ad**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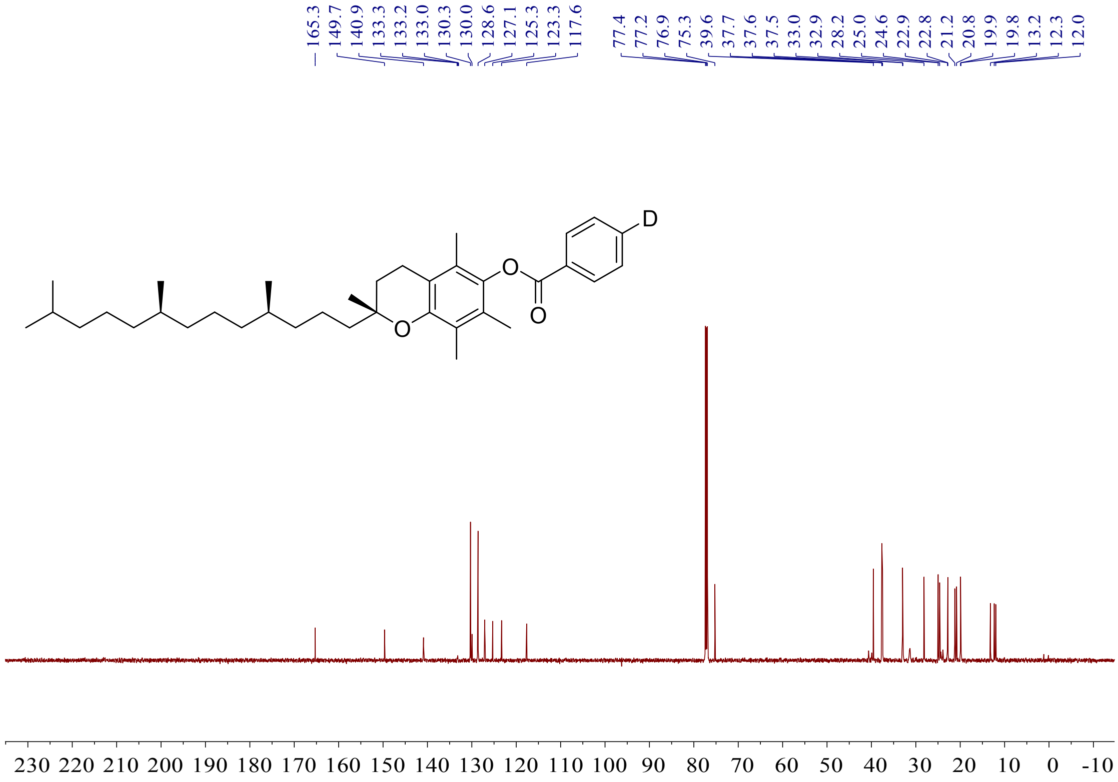
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