

# **Supplementary Material**

## **Absolute configuration sensing of chiral aryl- and aryloxy-propionic acids by biphenyl chiroptical probes**

Stefania Vergura, Stefano Orlando, Patrizia Scafato, Sandra Belviso,

and Stefano Superchi<sup>\*</sup>

Department of Sciences, University of Basilicata, Viale dell'Ateneo Lucano 10, 85100 Potenza, Italy.

*(S)*-1-(5,7-dihydro-6H-dibenzo[*c,e*]azepin-6-yl)-2-(6-isobutylphenyl)propan-1-one, (**4aa**).

Following the general procedure the product **4aa** was isolated by column chromatography on silica gel (CH<sub>2</sub>Cl<sub>2</sub>/MeOH 97.5:2.5) in 85% yield as a light yellow solid. [ $\alpha$ ]<sub>D</sub> = +171.71 (c = 1.05, CHCl<sub>3</sub>); mp: 144-145°C. <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  0.88 (d, 6.6 Hz, 6H), 1.4 (d, 6.7 Hz, 3H), 1.86 (m, 1H), 2.42 (d, 7.1 Hz, 2H), 3.82 (m, 3H), 4.3 (d, J = 13.5 Hz, 1H), 4.9 (d, J = 13.5 Hz, 1H), 6.09 (d, 7.0 Hz, 1H), 6.97 (t, J = 7.1 Hz, 1H), 7.05-7.36 (m, 10H). <sup>13</sup>C-NMR (75.5 MHz, CDCl<sub>3</sub>)  $\delta$  21.36, 22.61, 22.71, 30.59, 44.48, 45.32, 46.90, 48.33, 127.45, 128.05, 128.159, 128.19, 128.57, 128.83, 128.88, 129.16, 130.21, 130.58, 133.61, 134.27, 140.08, 140.65, 140.85, 140.93, 171.66. HRESIMS (+) *m/z* 384.2331 [M + H]<sup>+</sup> (calcd for C<sub>27</sub>H<sub>29</sub>NO 384.2327).

*(S)*-1-(5,7-dihydro-6H-dibenzo[*c,e*]azepin-6-yl)-2-(6-methoxynaphthalen-2-yl)propan-1-one, (**4ba**).

Following the general procedure the product **4ba** was isolated by column chromatography on silica gel (CH<sub>2</sub>Cl<sub>2</sub>/MeOH 97.5:2.5) in 80% yield as a white solid. [ $\alpha$ ]<sub>D</sub><sup>20</sup> = +95.0 (c = 1.00, CHCl<sub>3</sub>). mp: 139-141°C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) 7.75 (d, J=8.5 Hz, 1H); 7.67 (d, J=9.5 Hz, 1H); 7.47 (d, J=7.5 Hz, 1H); 7.46-7.42 (m, 5H); 7.38 (m, 1H); 7.32 (t, J=7.5 Hz, 1H); 7.15 (bs, 1H); 6.25 (bs, 1H); 4.71 (d, J=12.0 Hz, 1H); 4.29 (d, J=13.0 Hz, 1H); 4.14 (q, J=7.0 Hz, 1H); 4.08 (d, J=12.5 Hz, 2H); 3.94 (s, 3H); 1.58 (d, J=7.0 Hz, 3H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) 171.5; 157.6; 140.6; 137.4; 134.1; 133.5; 133.3; 130.2; 129.2; 129.0; 128.6; 128.5; 128.3; 128.0; 127.9; 127.7; 126.2; 125.7; 119.1; 105.7; 55.3; 48.5; 46.6; 44.3; 21.0. HRESIMS (+) *m/z* 408.1961 [M + H]<sup>+</sup> (calcd for C<sub>28</sub>H<sub>25</sub>NO<sub>2</sub> 408.1964).

*(S)*-1-(3,9-dimethoxy-5,7-dihydro-6H-dibenzo[*c,e*]azepin-6-yl)-2-(6-methoxynaphthalen-2-yl)propan-1-one, (**4bb**).

Following the general procedure the product **4bb** was isolated by column chromatography on silica gel (CH<sub>2</sub>Cl<sub>2</sub>/MeOH 97.5:2.5) in 54% yield as light yellow solid. [ $\alpha$ ]<sub>D</sub><sup>20</sup> = +113 (c = 1.05, CHCl<sub>3</sub>). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) 7.78 (d, J=8.5 Hz, 1H); 7.72 (s, 1H); 7.71 (d, J=9.0 Hz, 1H); 7.46 (dd, J=8.5, 1.5 Hz, 1H); 7.31 (d, J=8.5 Hz, 1H); 7.27 (d, J=8.5 Hz, 1H); 7.15 (dd, J=2.5, 8.5 Hz, 1H); 7.13 (s, 1H); 7.01 (d, J=3.0 Hz, 1H); 6.95 (dd, J=2.5, 8.5 Hz, 1H); 6.80 (dd, J=2.5, 8.5 Hz, 1H); 5.52 (bs, 1H); 4.98 (d, J=13.5 Hz, 1H); 4.42 (d, J=12.8 Hz, 1H); 4.12 (q, J=7.0 Hz, 1H); 3.94 (d, J=14.0 Hz, 1H); 3.94 (s, 3H); 3.88 (s, 1H); 3.87 (d, J=12.0 Hz, 1H); 3.01 (s, 3H); 1.58 (d, J=7.0 Hz, 3H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) 171.3; 159.2; 158.78; 157.8; 137.8; 134.9; 134.1; 133.6; 133.0; 132.8; 129.3; 129.2; 128.7;

128.6; 127.8; 126.4; 125.75; 119.2; 115.2; 114.4; 112.4; 105.6; 55.5; 55.4; 54.6; 48.5; 47.1; 44.5; 21.0. HRESIMS (+)  $m/z$  468.2179  $[M + H]^+$  (calcd for  $C_{30}H_{29}NO_4$  468.2175).

*(S)*-1-(3,9-diamino-5,7-dihydro-6H-dibenzo[*c,e*]azepin-6-yl)-2-(6-methoxynaphthalen-2-yl)propan-1-one, (**4bc**).

Following the general procedure, the product **4bc** was isolated by column chromatography on silica gel ( $CHCl_3/MeOH$  from 98:2 to 9:1) in 72% yield as yellow oil.  $[\alpha]_D^{20} = +67$  ( $c = 0.09$ ,  $CHCl_3$ ).  $^1H$  NMR (400 MHz,  $CDCl_3$ ) 7.81 (d,  $J=8.4$  Hz, 1H); 7.73 (d,  $J=8.4$  Hz, 1H); 7.68 (s, 1H); 7.56 (d,  $J=7.2$  Hz, 1H); 7.45 (dd,  $J=1.6, 8.4$  Hz, 2H); 7.19-7.11 (m, 2H); 6.77 (d,  $J=2.4$  Hz, 1H); 6.72 (dd,  $J=2.4, 8.4$  Hz, 1H); 6.53 (dd,  $J=2.4, 8.0$  Hz, 1H); 4.96 (bs, 1H); 4.85 (d,  $J=13.6$  Hz, 1H); 4.27 (d,  $J=12.8$ , 1H); 4.12 (q,  $J=6.8$  Hz, 1H); 3.95 (s, 3H); 3.90 (d,  $J=12.8$  Hz, 1H); 3.86 (d,  $J=13.6$  Hz, 1H); 3.77 (bs, 2H); 2.93 (bs, 2H); 1.59 (bd,  $J=6.4$  Hz, 3H).  $^{13}C$  NMR (100 MHz,  $CDCl_3$ ) 171.3; 157.7; 145.7; 145.2; 138.0; 134.6; 133.8; 133.4; 130.9; 129.2; 128.5; 128.1; 127.8; 126.7; 125.9; 119.10; 116.7; 115.2; 114.9; 114.8; 105.4; 55.4; 48.4; 47.5; 44.5; 20.9. HRESIMS (+)  $m/z$  498.1662  $[M + H]^+$  (calcd for  $C_{28}H_{23}N_3O_6$  498.1665).

*(S)*-1-(3,9-dinitro-5,7-dihydro-6H-dibenzo[*c,e*]azepin-6-yl)-2-(6-methoxynaphthalen-2-yl)propan-1-one, (**4bd**).

Following the general procedure, the product **4bd** was isolated by column chromatography on silica gel ( $CH_2Cl_2/MeOH$  97.5:2.5) in 71% yield as a yellow solid.  $[\alpha]_D^{20} = +69.4$  ( $c = 1.08$ ,  $CHCl_3$ ).  $^1H$  NMR (500 MHz,  $CDCl_3$ ) 8.39 (s, 1H); 8.32 (dd,  $J=2.0, 8.0$  Hz, 1H); 8.20 (dd,  $J=2.0, 8.5$  Hz, 1H); 7.80 (d,  $J=8.5$  Hz, 1H); 7.65-7.62 (m, 4H); 7.38 (d,  $J=8.5$  Hz, 1H); 7.18 (s, 1H); 7.14 (dd,  $J=9.0, 2.5$  Hz, 1H); 7.02 (s, 1H); 4.93 (d,  $J=14$  Hz, 1H); 4.44 (d,  $J=13.0$  Hz, 1H); 4.18-4.09 (m, 3H); 3.93 (s, 3H); 1.60 (d,  $J=6.0$  Hz, 3H).  $^{13}C$  NMR (125 MHz,  $CDCl_3$ ) 171.8; 157.9; 148.4; 148.4; 148.1; 144.8; 136.5; 133.9; 129.3; 129.2; 129.1; 128.9; 128.3; 125.6; 124.35; 123.9; 119.7; 106.0; 55.4; 47.7; 46.0; 44.6; 21.0. HRESIMS (+)  $m/z$  438.2187  $[M + H]^+$  (calcd for  $C_{28}H_{27}N_3O_2$  438.2182).

*(S)*-2-(3-benzoylphenyl)-1-(5,7-dihydro-6H-dibenzo[*c,e*]azepin-6-yl)propan-1-one, (**4ca**).

Following the general procedure, the product **4ca** was isolated by column chromatography on silica gel ( $CH_2Cl_2/MeOH$  97:3) in 85% yield as white solid.  $[\alpha]_D^{20} = +121$  ( $c = 0.28$ ,  $CHCl_3$ ).  $^1H$  NMR (500

MHz, CDCl<sub>3</sub>) 7.74 (bs, 2H); 7.70 (d, J=7.0 Hz, 2H); 7.59 (d, J=7.5 Hz, 1H); 7.55 (d, J=7.5 Hz, 1H); 7.52-7.44 (m, 5H); 7.41-7.39 (m, 3H); 7.16 (t, J=7.0 Hz, 1H); 6.43 (bd, J=6.0 Hz, 1H); 4.85 (d, J=1.5 Hz, 1H); 4.30 (d, J=13.0 Hz, 1H); 4.14-4.03 (m, 3H); 1.54 (d, J=7.0 Hz, 3H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) 196.5; 170.8; 142.7; 140.6; 140.5; 138.4; 137.4; 133.8; 132.6; 131.4; 130.3; 130.1; 129.2; 129.1; 128.8; 128.8; 128.4; 128.2; 128.1; 128.0; 48.6; 46.8; 44.1; 20.9. HRESIMS (+) *m/z* 432.1969 [M + H]<sup>+</sup> (calcd for C<sub>30</sub>H<sub>25</sub>NO<sub>2</sub> 432.1964).

*(S)*-2-(3-benzoylphenyl)-1-(3,9-dimethoxy-5,7-dihydro-6H-dibenzo[*c,e*]azepin-6-yl)propan-1-one, (**4cb**).

Following the general procedure the product **4cb** was isolated by column chromatography on silica gel (CHCl<sub>3</sub>) in 68% yield as a dark yellow oil. [ $\alpha$ ]<sub>D</sub><sup>20</sup> = +85 (c = 0.77, CHCl<sub>3</sub>). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) 7.78 (s, 1H); 7.735 (m, 3H); 7.60 (d, J=8.0 Hz, 1H); 7.56 (t, J=7.5 Hz, 1H); 7.51 (t, J=7.5 Hz, 1H); 7.41 (t, J=7.5 Hz, 2H); 7.35 (t, J=7.5, 2H); 6.98 (bs, 1H); 6.96 (d, J=2.5 Hz, 1H); 6.90 (dd, J=2.5, 8.0 Hz, 1H); 5.92 (bs, 1H); 4.87 (d, J=13.5 Hz, 1H); 4.30 (d, J=13.5 Hz, 1H); 4.12 (q, J=7.0 Hz, 1H); 4.02 (d, J=12.5 Hz, 1H); 3.95 (d, J=13.5 Hz, 1H); 3.85 (s, 3H); 3.65 (s, 3H); 1.54 (d, J=7.0 Hz, 3H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) 196.4; 170.8; 159.3; 159.0; 142.8; 138.4; 137.7; 134.0; 132.9; 132.8; 132.8; 132.6; 131.4; 130.1; 129.2; 129.1; 128.9; 128.3; 115.2; 114.5; 114.3; 114.1; 55.5; 55.4; 48.8; 47.1; 44.1; 21.0. HRESIMS (+) *m/z* 492.2173 [M + H]<sup>+</sup> (calcd for C<sub>32</sub>H<sub>29</sub>NO<sub>4</sub> 492.2175).

*(S)*-2-(3-benzoylphenyl)-1-(3,9-dinitro-5,7-dihydro-6H-dibenzo[*c,e*]azepin-6-yl)propan-1-one, (**4cc**).

Following the general procedure, the product **4cc** was isolated by column chromatography on silica gel (CHCl<sub>3</sub>/MeOH 95:5) in 85% yield as dark yellow oil. [ $\alpha$ ]<sub>D</sub><sup>20</sup> = +153 (c = 0.67, CHCl<sub>3</sub>). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) 8.40(d, J=2.0 Hz, 1H); 8.37 (dd, J=2.0, 8.5 Hz, 1H); 8.30 (dd, J=2.0, 8.5 Hz, 1H); 7.89 (s, 1H); 7.81 (d, J=7.5 Hz, 2H); 7.78 (d, J=7.0 Hz, 1H); 7.70 (dd, J=3.0, 8.0 Hz, 2H); 7.60 (t, J=7.5 Hz, 1H); 7.56-7.47 (m, 4H); 7.14 (bs, 1H); 5.06 (d, J=14 Hz, 1H); 4.51 (d, J=13.5 Hz, 1H); 4.13 (q, J=7.0 Hz, 1H); 4.06 (d, J=13.0 Hz, 1H); 4.01 (d, J=14.0 Hz, 1H); 1.59 (d, J=7.0 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) 196.2; 171.0; 148.5; 148.2; 144.7; 142.2; 138.7; 137.3; 135.5; 134.7; 132.7; 131.0; 130.0; 129.9; 129.3; 129.3; 128.7; 128.4; 125.8; 124.3; 124.2; 124.0; 47.7; 46.1; 44.5; 20.9. HRESIMS (+) *m/z* 522.1667 [M + H]<sup>+</sup> (calcd for C<sub>30</sub>H<sub>23</sub>N<sub>3</sub>O<sub>6</sub> 522.1665).

*(R)*-1-(5,7-dihydro-6H-dibenzo[*c,e*]azepin-6-yl)-2-(2-fluoro-[1,1'-biphenyl]-4-yl)propan-1-one, (**4da**).

Following the general procedure the product **4da** was isolated on silica gel (CH<sub>2</sub>Cl<sub>2</sub>/MeOH 97.5:2.5) in 90% yield as a white solid.  $[\alpha]_D^{20} = -87.8$  (*c* = 0.62, CHCl<sub>3</sub>). mp: 56-58°C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) 7.57 (d, *J*=6.5 Hz, 2H); 7.50-7.44 (m, 7H); 7.41-7.38 (m, 3H); 7.19-7.14 (m, 3H); 6.5 (d, *J*=6.0 Hz, 1H); 4.83 (d, *J*=12.0 Hz, 1H); 4.31 (d, *J*=12.5 Hz, 1H); 4.10-4.06 (m, 3H); 1.56 (d, *J*=6.5 Hz, 3H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) 170.7; 160.1 (d, *J*=248 Hz); 143.8 (d, *J*=7.6 Hz); 140.6 (d, *J*=11.5 Hz); 135.5; 133.9; 133.2; 131.3 (d, *J*=3.8 Hz); 130.3; 129.0 (d, *J*=29.0 Hz); 128.8; 128.6; 128.5; 128.4; 128.1; 128.0; 128.0; 127.8; 127.7; 123.5; 123.5 (d, *J*=2.9 Hz); 115.2 (d, *J*=23.9 Hz); 48.6; 46.8; 43.8; 20.7. HRESIMS (+) *m/z* 422.1924 [*M* + *H*]<sup>+</sup> (calcd for C<sub>29</sub>H<sub>24</sub>FNO 422.1920).

*(R)*-1-(3,9-dimethoxy-5,7-dihydro-6H-dibenzo[*c,e*]azepin-6-yl)-2-(2-fluoro-[1,1'-biphenyl]-4-yl)propan-1-one, (**4db**).

Following the general procedure, the product **4db** was isolated by column chromatography on silica gel (CH<sub>2</sub>Cl<sub>2</sub>) in 55% yield as a yellow solid.  $[\alpha]_D^{20} = -139$  (*c* = 1.15, CHCl<sub>3</sub>). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) 7.59 (d, *J*=7.5 Hz, 2H); 7.48 (m, 3H); 7.41 (d, *J*=7.0 Hz, 1H); 7.37 (d, *J*=8.5 Hz, 2H); 7.22 (t, *J*=8.0 Hz, 1H); 7.19 (s, 1H); 7.03 (d, *J*=2.0 Hz, 1H); 7.00 (dd, *J*=2.0, 8.5 Hz, 1H); 6.92 (dd, *J*=2.0, 8.5 Hz, 1H); 6.03 (d, *J*=1.5 Hz, 1H); 4.89 (d, *J*=14.0 Hz, 1H); 4.35 (d, *J*=12.5 Hz, 1H); 4.10-3.99 (m, 3H); 3.88 (s, 3H); 3.62 (s, 3H); 1.58 (d, *J*=7.0 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) 170.7; 160.1 (d, *J*=248 Hz); 159.3; 159.0; 143.9 (d, *J*=7.6 Hz); 135.3; 134.8; 134.1; 132.9; 131.4 (d, *J*=3.5 Hz); 129.0; 128.8; 127.8; 128.48; 127.8 (d, *J*=9.5 Hz); 123.4; 115.3 (d, *J*=18.0 Hz); 114.4 (d, *J*=18.0 Hz); 114.0; 55.5; 55.2; 48.8; 47.2; 43.8; 20.9. HRESIMS (+) *m/z* 482.2128 [*M* + *H*]<sup>+</sup> (calcd for C<sub>31</sub>H<sub>28</sub>FNO<sub>3</sub> 482.2131).

*(R)*-1-(3,9-dinitro-5,7-dihydro-6H-dibenzo[*c,e*]azepin-6-yl)-2-(2-fluoro-[1,1'-biphenyl]-4-yl)propan-1-one, (**4dc**).

Following the general procedure the product **4dc** was isolated on silica gel (CHCl<sub>3</sub>) in 52% yield as a dark yellow oil.  $[\alpha]_D^{20} = -97$  (*c* = 0.20, CHCl<sub>3</sub>). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) 8.46 (d, *J*=2.5 Hz, 1H); 8.38 (dd, *J*=8.5 Hz, 1H); 8.33 (dd, *J*=8.0, 2.0 Hz, 1H); 7.70 (dd, *J*=8.5, 4.5 Hz, 2H); 7.601 (d, *J*=8.0 Hz, 2H); 7.52 (d, *J*=8 Hz, 1H); 7.49 (d, *J*=5.0 Hz, 1H); 7.47 (d, *J*=8.0 Hz, 2H); 7.39 (t, *J*=7.5 Hz, 1H); 7.20 (dd, *J*=2.0, 7.0 Hz, 1H); 7.14 (dd, *J*=1.5, 11.0 Hz, 1H); 5.01 (d, *J*=14.0 Hz, 1H); 4.12 (d, *J*=13.5 Hz, 1H); 4.11 (d, *J*=13.5 Hz, 1H); 4.06 (q, *J*=6.5 Hz, 1H); 1.58 (d, *J*=6.5 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) 171.0; 160.2 (d, *J*=249 Hz); 148.5; 148.2; 144.7; 142.7 (d, *J*=7.6 Hz); 135.6; 135.1; 134.8; 131.8 (d, *J*=3.9 Hz); 129.4 (d, *J*=7.6 Hz); 129.1 (d, *J*=3.8 Hz); 128.7 (d, *J*=13.2 Hz); 128.5; 127.9;

125.8; 124.4; 124.2; 124.0; 123.2 (d J =3.8 Hz); 114.94 (d, J=24.0 Hz); 108.0; 47.8; 40.1; 44.0; 20.9. HRESIMS (+)  $m/z$  512.1626 [M + H]<sup>+</sup> (calcd for C<sub>29</sub>H<sub>22</sub>FN<sub>3</sub>O<sub>5</sub> 512.1622).

*(R)-1-(5H-dibenzo[c,e]azepin-6(7H)-yl)-2-phenoxypropan-1-one (5aa).*

Following the general procedure the product **5aa** was isolated on silica gel (CHCl<sub>3</sub>) in 95% yield as a white solid.  $[\alpha]_D^{20}$  = 6.1 (c = 1.06, CHCl<sub>3</sub>). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) 7.54-6.26 (m, 10H); 6.94-6.98 (m, 3H); 5.10 (q, J=7.0 Hz, 1H); 4.36-4.52 (m, 4H); 1.72 (d, J=7.0 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) 169.28; 157.46; 133.75; 133.63; 130.57; 129.95; 129.54; 129.22; 128.99; 128.67; 128.53; 128.39; 128.21; 121.82; 115.30; 74.82; 48.12; 47.31; 18.31. HRESIMS (+)  $m/z$  344.1655 [M + H]<sup>+</sup> (calcd for C<sub>23</sub>H<sub>21</sub>NO<sub>2</sub> 344.1651).

*(R)-1-(5H-dibenzo[c,e]azepin-6(7H)-yl)-2-(naphthalen-2-yloxy)propan-1-one (5ba).*

Following the general procedure the product **5ba** was isolated on silica gel (CHCl<sub>3</sub>) in 88% yield as a yellow solid.  $[\alpha]_D^{20}$  = 74.3 (c = 0.95, CHCl<sub>3</sub>). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) 7.75 (d, J=9.0 Hz, 2H); 7.65 (d, J=9.0 Hz, 1H); 7.56-7.39 (m, 6H); 7.35-7.25 (m, 4H); 7.22 (dd, J<sub>1</sub>=2.0 Hz, J<sub>2</sub>=2.5 Hz, 1H); 7.16 (d, J=2.5 Hz, 1H); 5.25 (q, J=7.0 Hz, 1H); 4.56-4.36 (m, 4H); 1.79 (d, J=7.0 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) 168.89, 155.11, 140.79, 140.555, 134.43, 133.47, 133.33, 130.03, 129.78, 129.28, 129.00, 128.72, 128.44, 128.29, 128.17, 127.96, 127.59, 126.99, 126.44, 123.98, 118.74, 107.81, 74.46, 48.00, 47.07, 17.98. HRESIMS (+)  $m/z$  394.1810 [M + H]<sup>+</sup> (calcd for C<sub>27</sub>H<sub>23</sub>NO<sub>2</sub> 394.1807).

*(R)-1-(3,9-dinitro-5H-dibenzo[c,e]azepin-6(7H)-yl)-2-phenoxypropan-1-one (5ac).*

Following the general procedure the product **5ac** was isolated on silica gel (CHCl<sub>3</sub>) in 65% yield as a yellow oil.  $[\alpha]_D^{20}$  = -19.0 (c = 1.0, CHCl<sub>3</sub>). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) 8.34 (s, 2H); 8.30 (s, 1H); 8.15 (s, 1H); 7.70 (t, J=9.2 Hz, 2H); 7.31 (t, J=7.6 Hz, 2H); 7.01-6.96 (m, 3H); 5.30 (q, J=7.0 Hz, 1H); 4.68-4.37 (m, 4H); 1.73 (d, J=7.0 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) 169.28; 157.46; 133.75; 133.63; 130.57; 129.95; 129.54; 129.22; 128.99; 128.67; 128.53; 128.39; 128.21; 121.82; 115.30; 74.82; 48.12; 47.31; 18.31. HRESIMS (+)  $m/z$  434.1356 [M + H]<sup>+</sup> (calcd for C<sub>23</sub>H<sub>19</sub>N<sub>3</sub>O<sub>6</sub> 434.1352).

*(R)*-1-(3,9-dinitro-5*H*-dibenzo[*c,e*]azepin-6(7*H*)-yl)-2-(naphthalen-2-yloxy)propan-1-one (**5bc**).

Following the general procedure, the product **5bc** was isolated by column chromatography on silica gel (CHCl<sub>3</sub>) in 70% yield as a yellow oil.  $[\alpha]_D^{20} = +16.2$  (c = 1.04, CHCl<sub>3</sub>). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) 8.25 (br s, 2H); 8.20 (s, 1H); 8.13 (s, 1H); 7.75 (d, J=9.0 Hz, 1H); 7.69-7.56 (m, 4H); 7.37-7.17 (m, 4H); 5.20 (q, J=7.0, 1H); 4.59-4.34 (m, 4H); 1.73 (d, J=7.0, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) 169.19, 154.42, 148.37, 148.22, 144.76, 144.58, 135.08, 134.94, 134.28, 130.28, 129.34, 129.22, 127.65, 126.92, 126.75, 125.64, 124.91, 124.84, 124.30, 124.16, 123.98, 118.20, 107.58, 75.11, 47.17, 46.26, 17.72. HRESIMS (+) *m/z* 484.1505 [M + H]<sup>+</sup> (calcd for C<sub>27</sub>H<sub>21</sub>N<sub>3</sub>O<sub>6</sub> 484.1509).

Figure S1. NMR Spectra of **4ba**

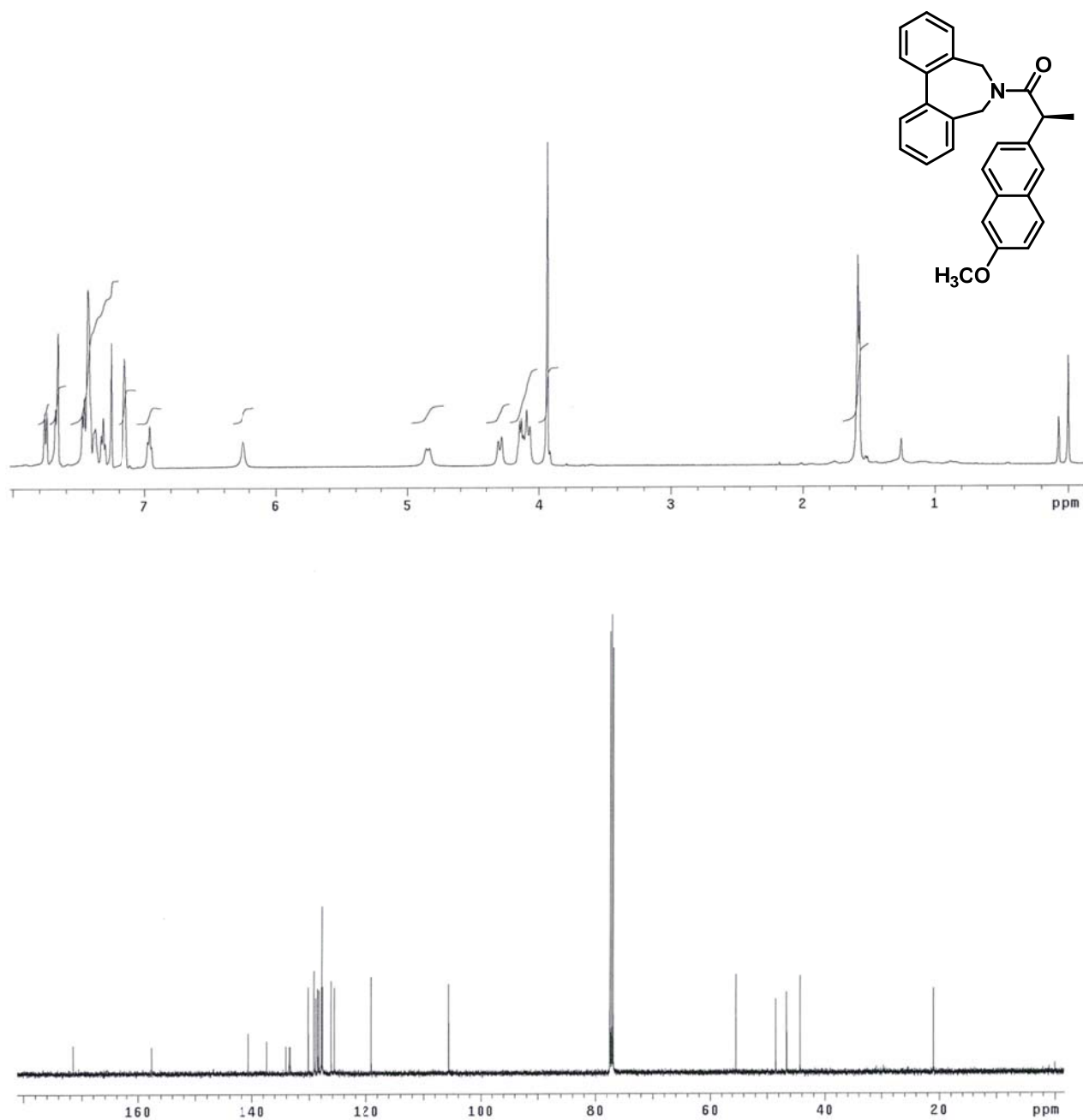




Figure S2. NMR Spectra of **4bb**

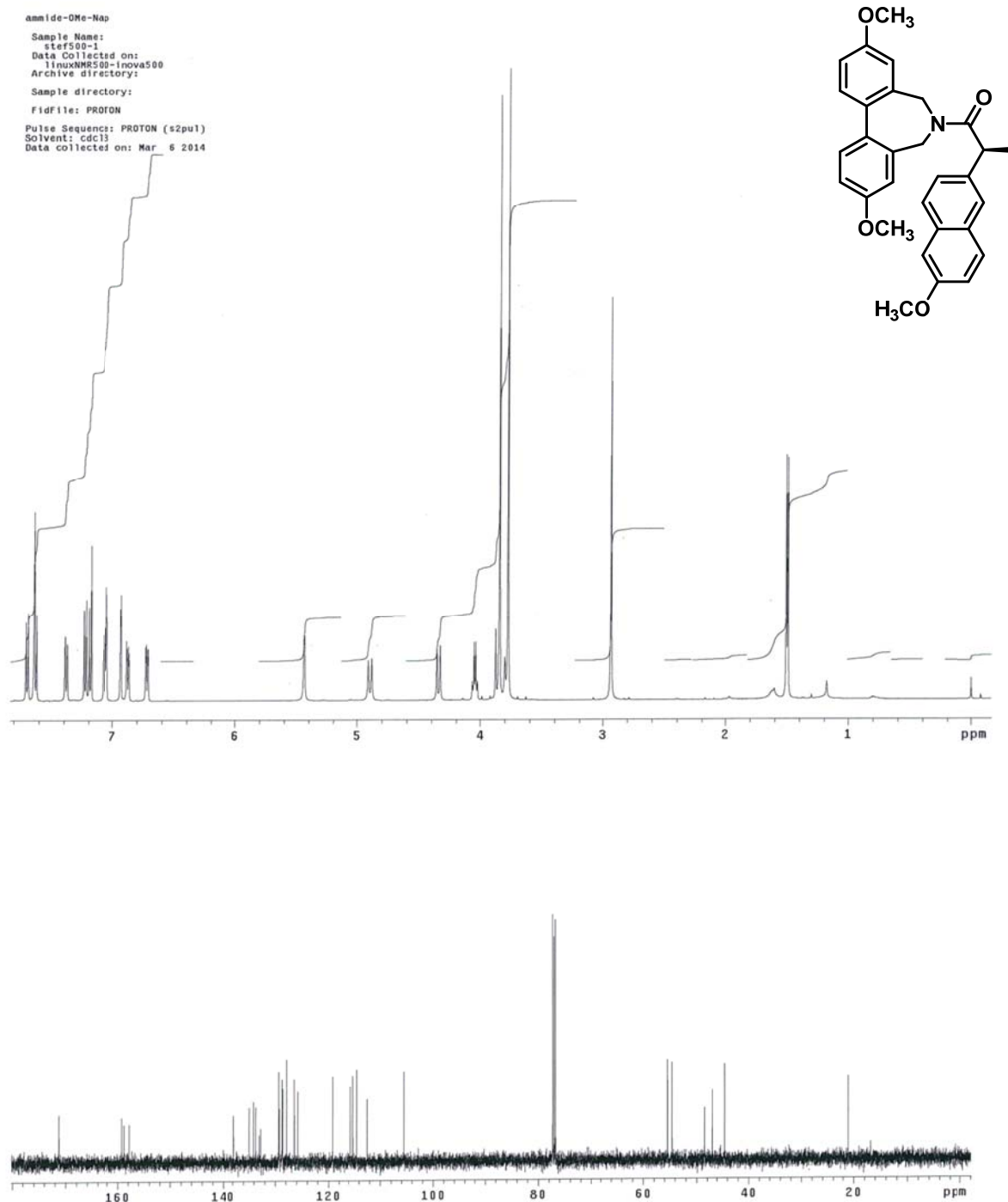


Figure S3. NMR Spectra of **4bc**

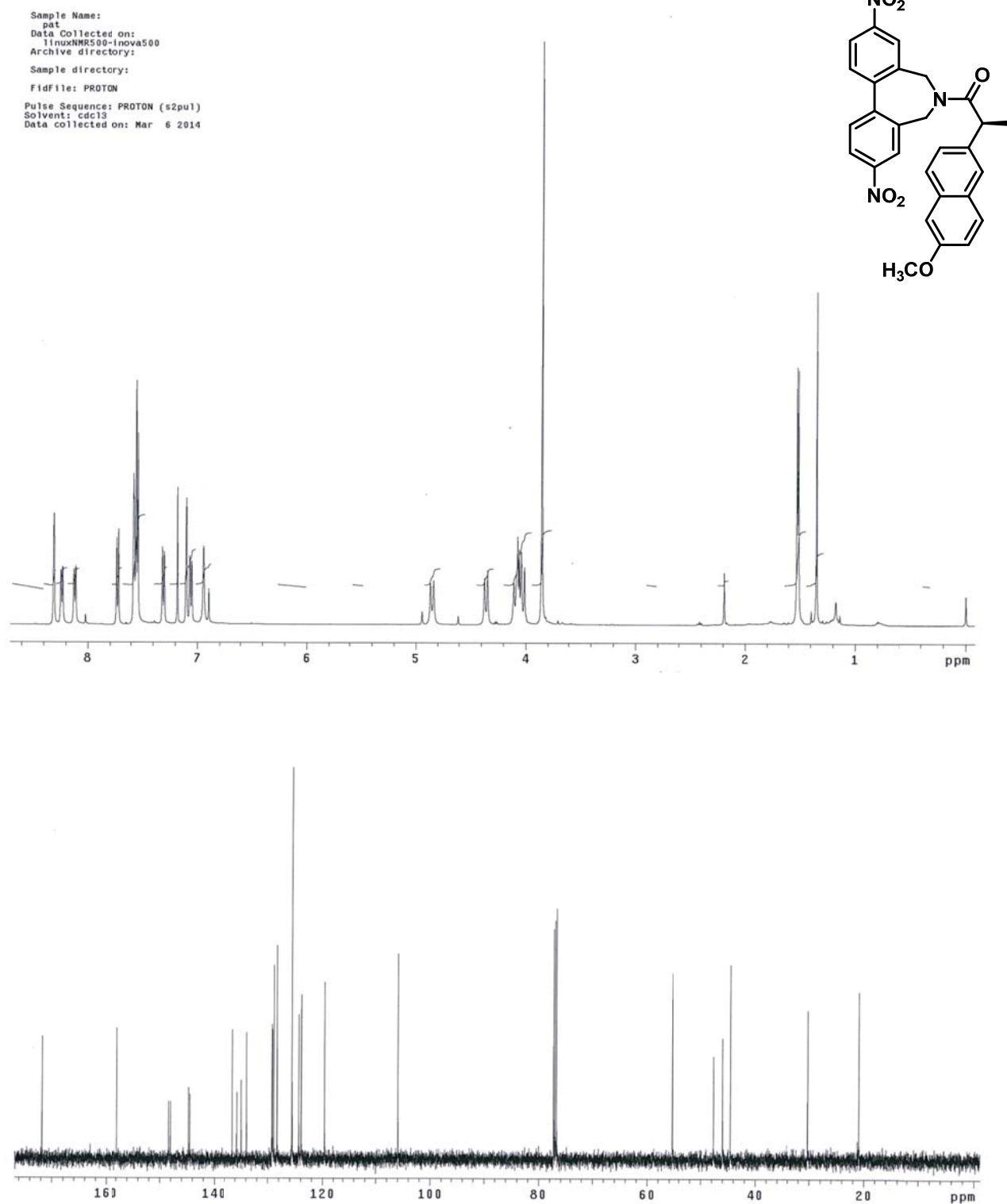


Figure S4. NMR Spectra of **4bd**

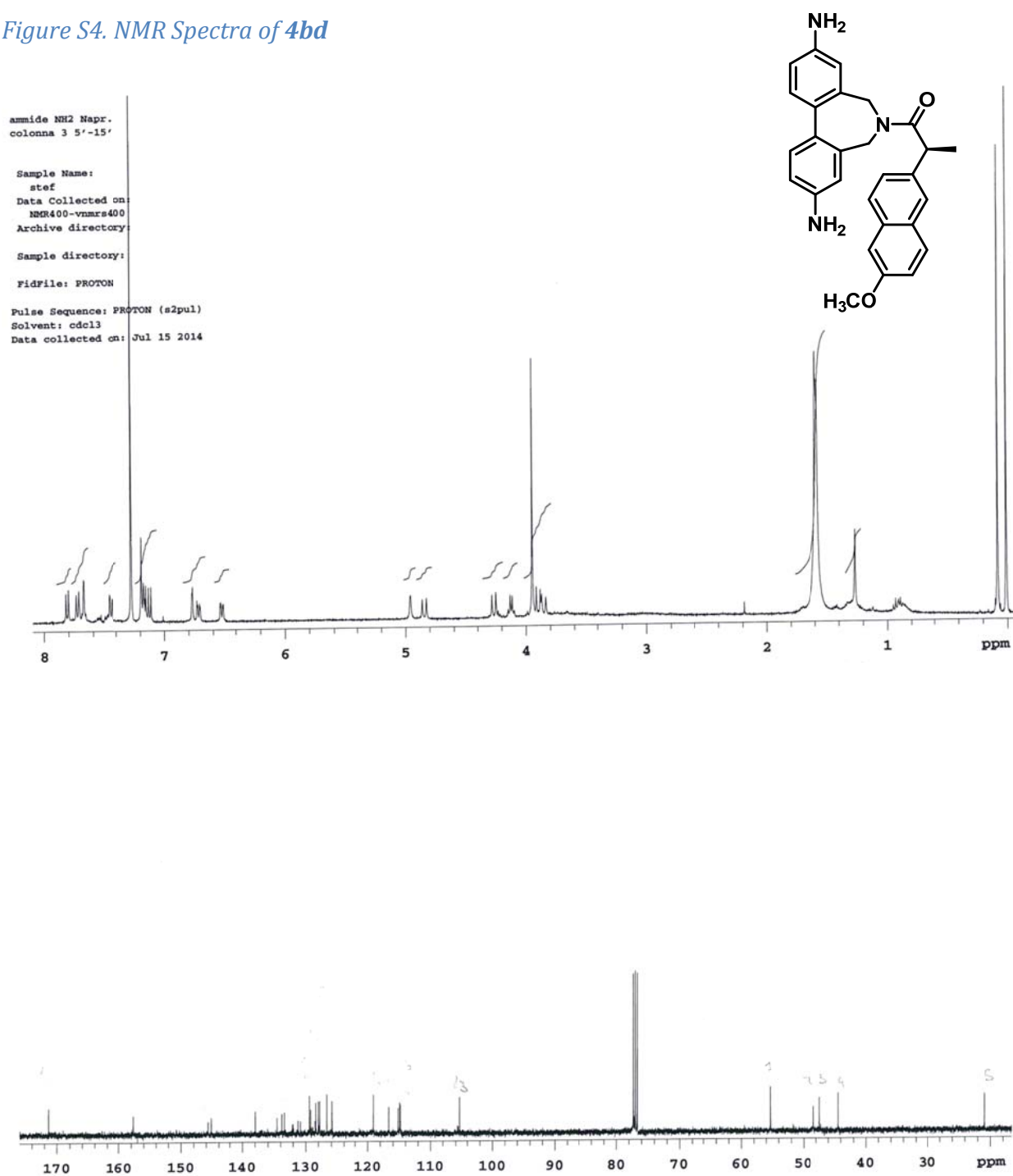


Figure S5. NMR Spectra of **4ca**

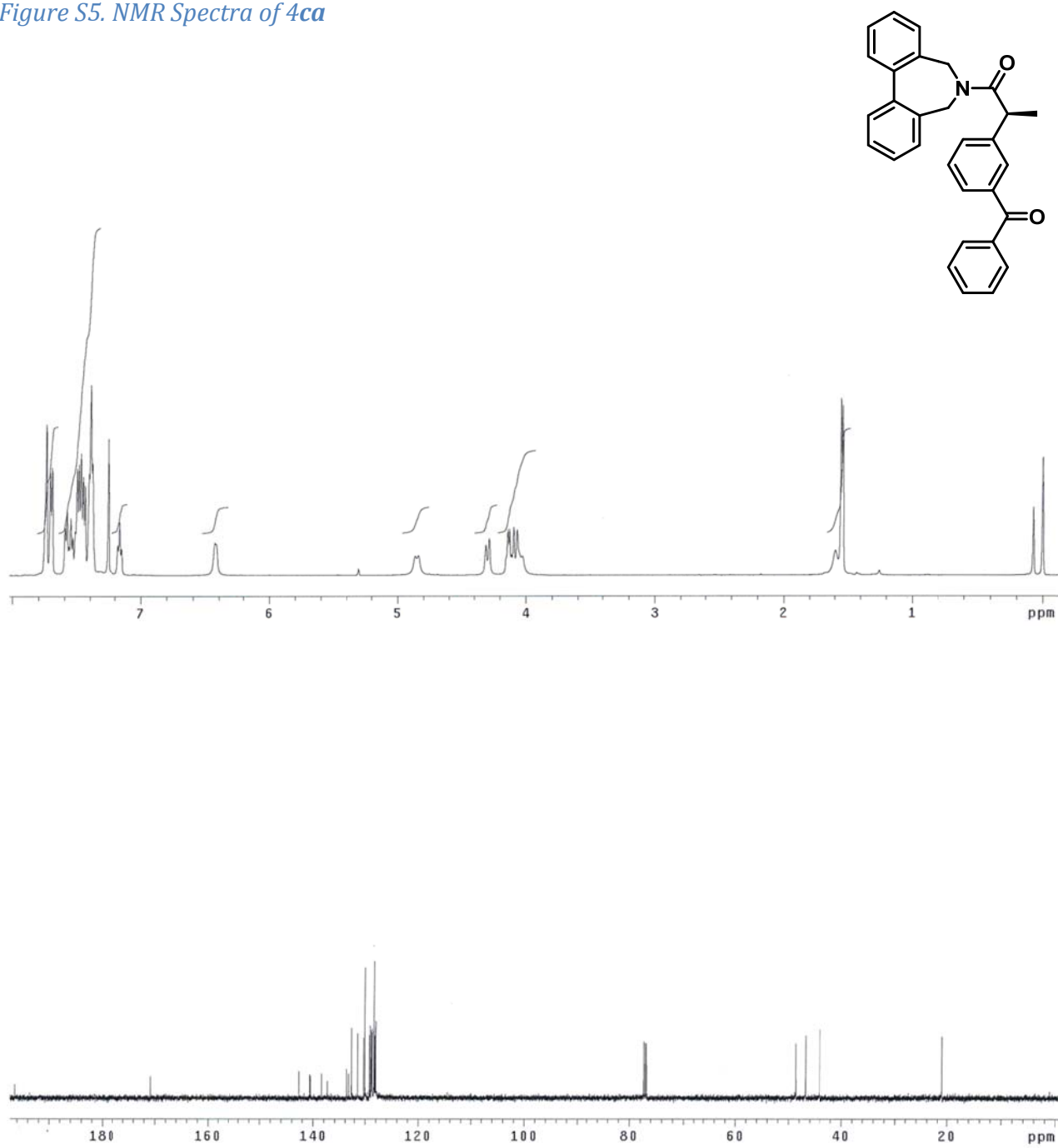


Figure S6. NMR Spectra of **4cb**

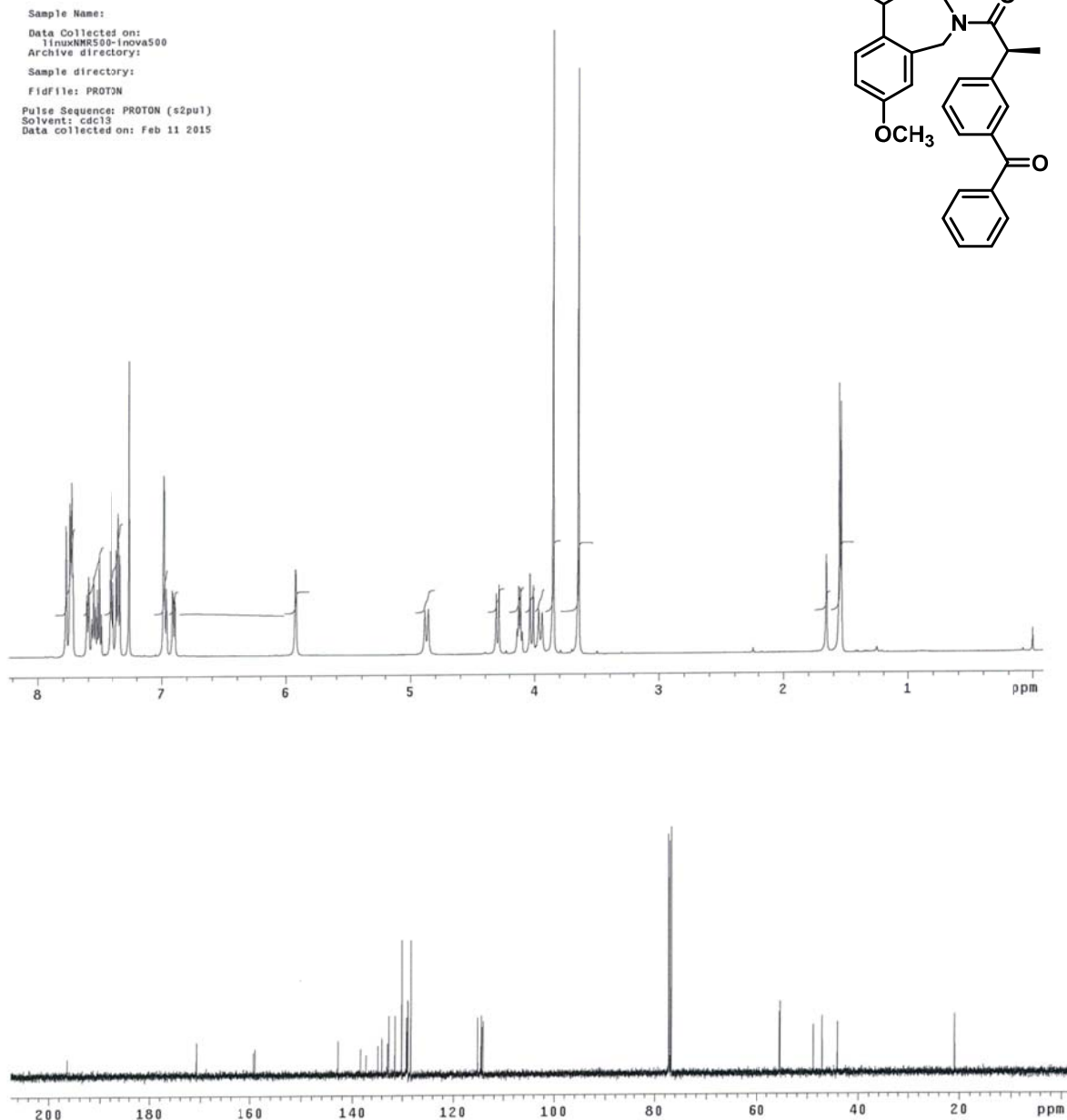


Figure S7. NMR Spectra of **4cc**

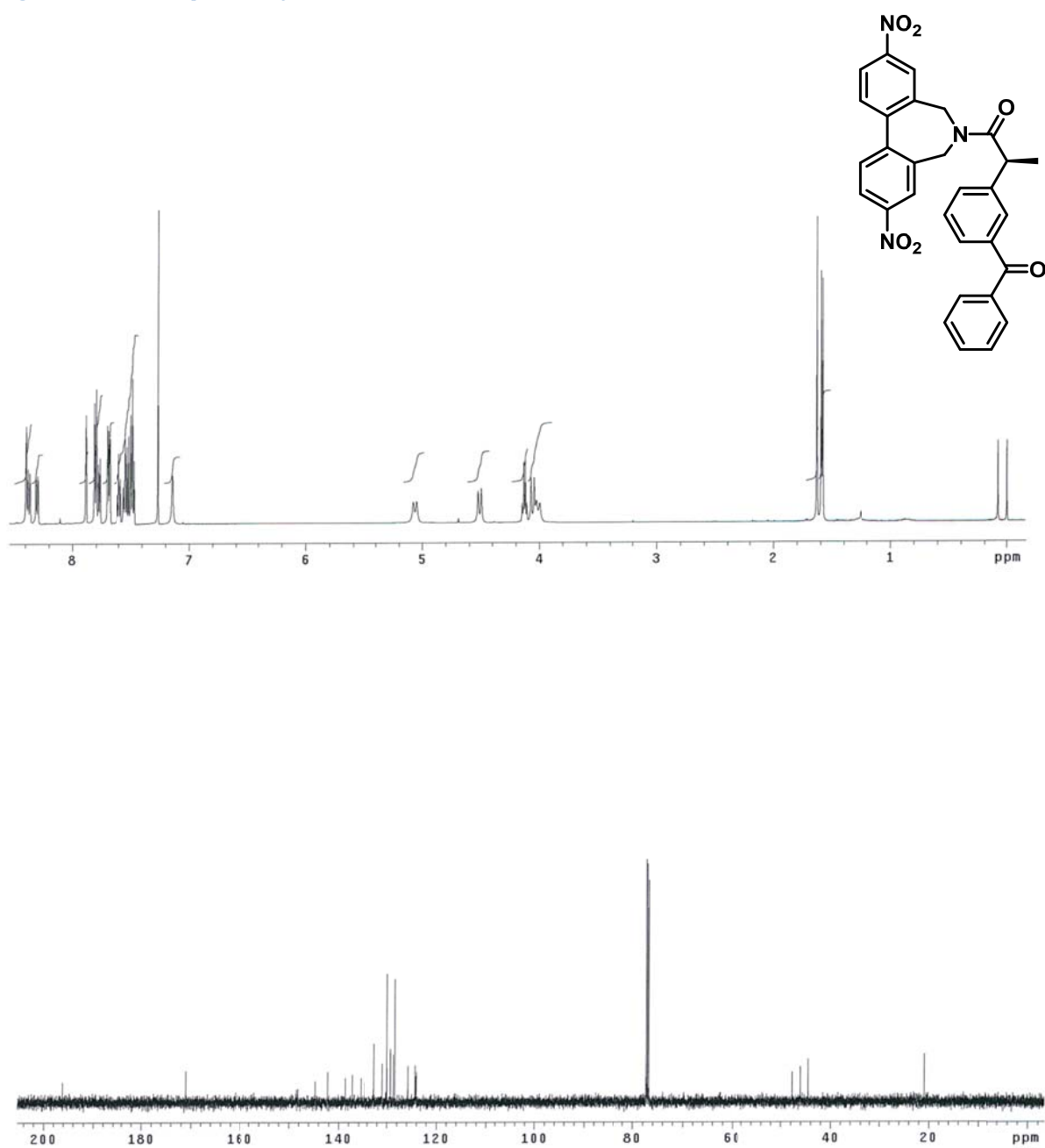


Figure S8. NMR Spectra of **4da**

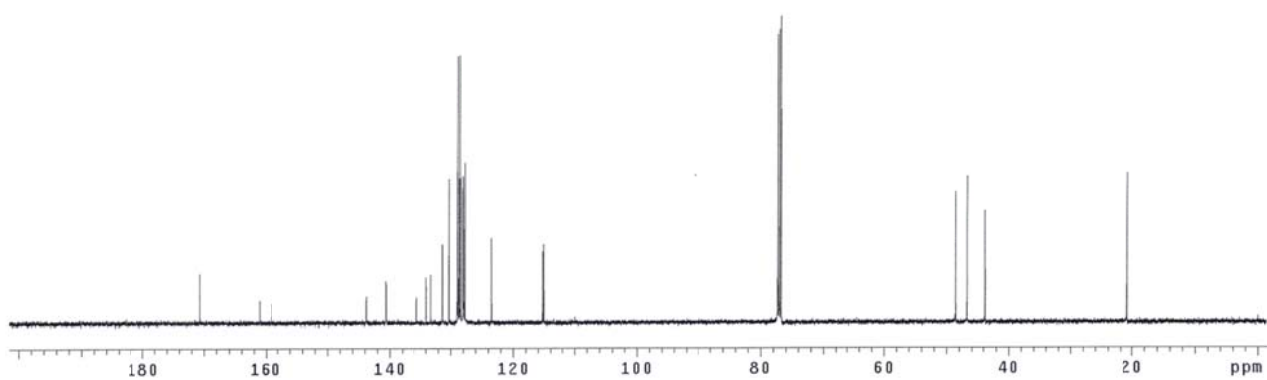
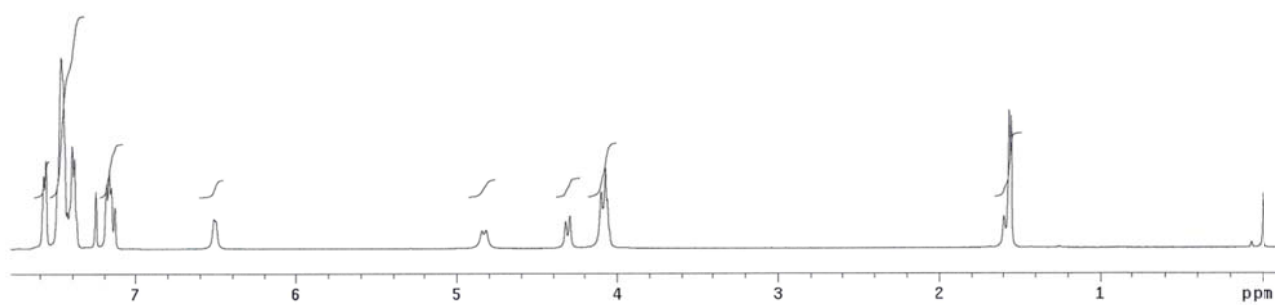
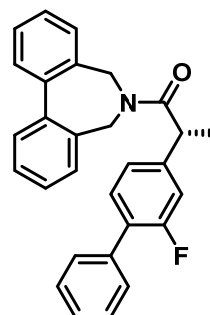


Figure S9. NMR Spectra of **4db**

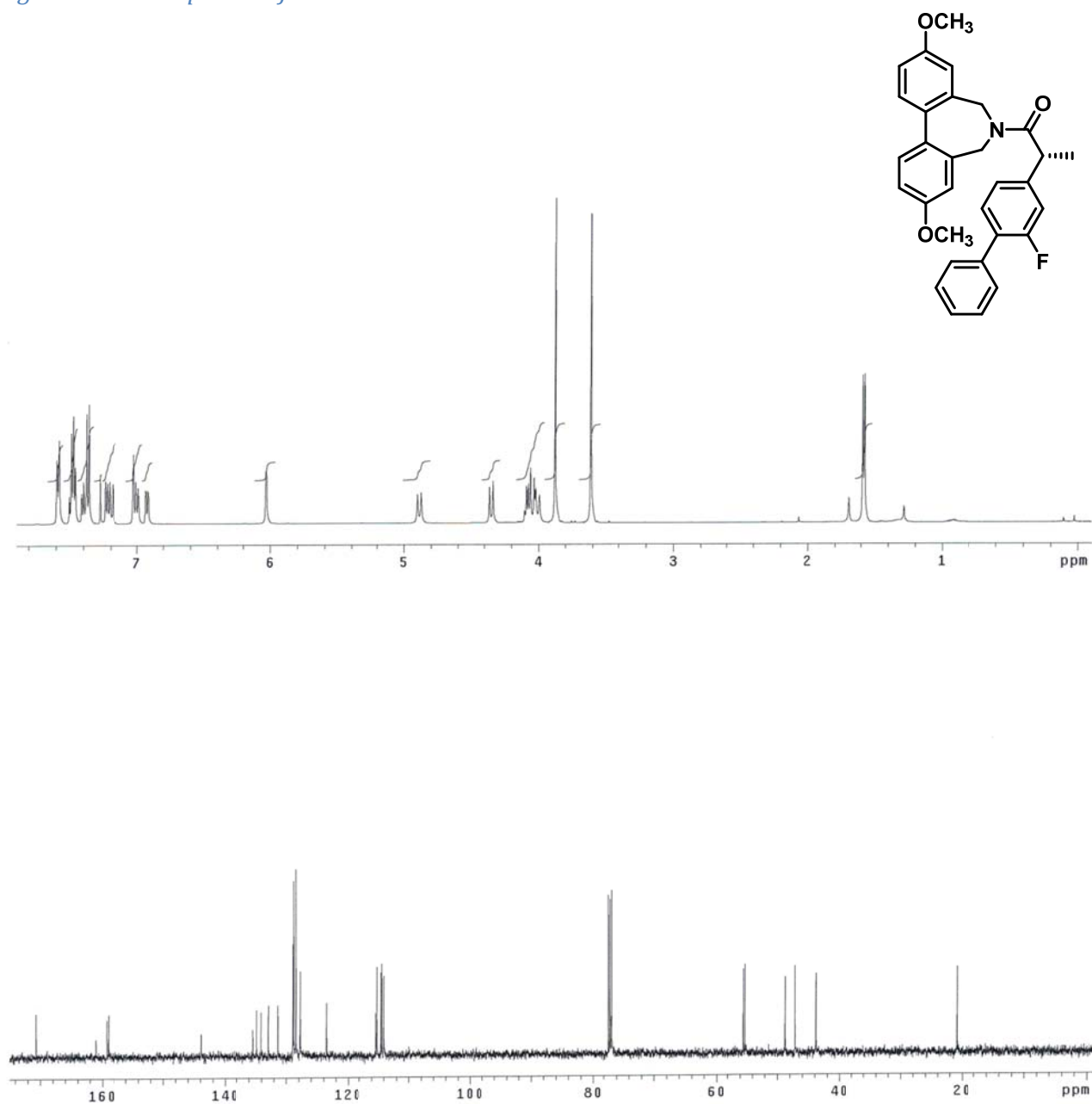
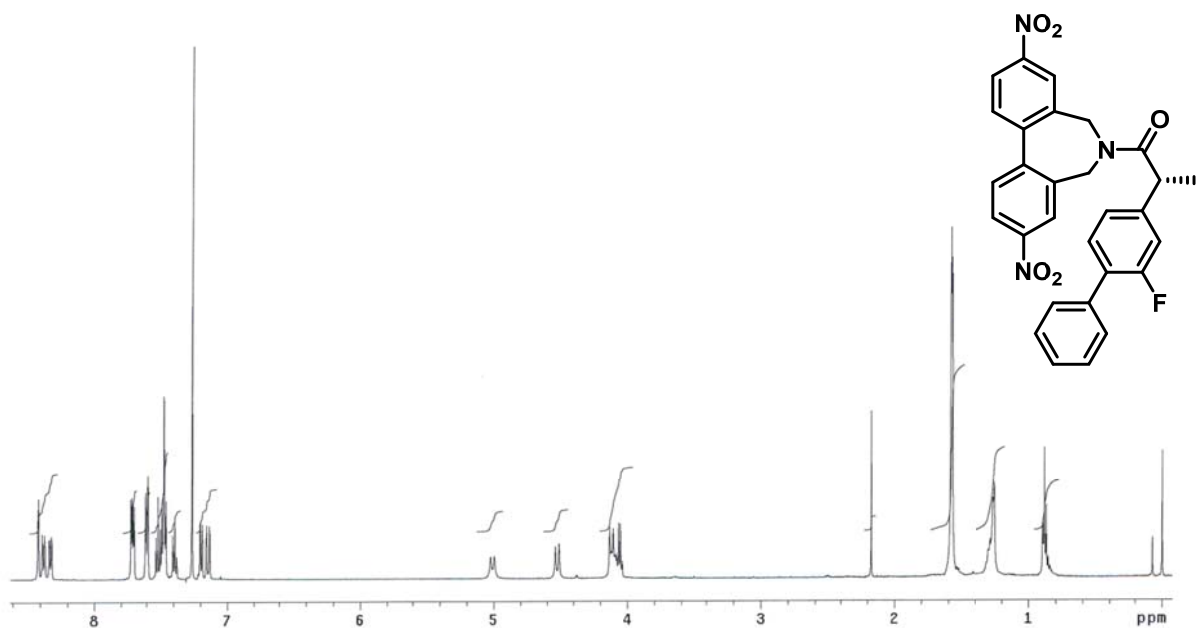




Figure S10. NMR Spectra of **4dc**



Stef  
amide NO2-Flu  
Sample Name:  
Data Collected on:  
linuxNMR500-inova500  
Archive directory:  
/home/casarlani/vnmrsys/data/paolo  
Sample directory:  
H2SC2\_20141030\_01  
Fidfile: CARBON  
Pulse Sequence: CARBON (s2pu1)  
Solvent: cdcl3  
Data collected on: Nov 18 2014

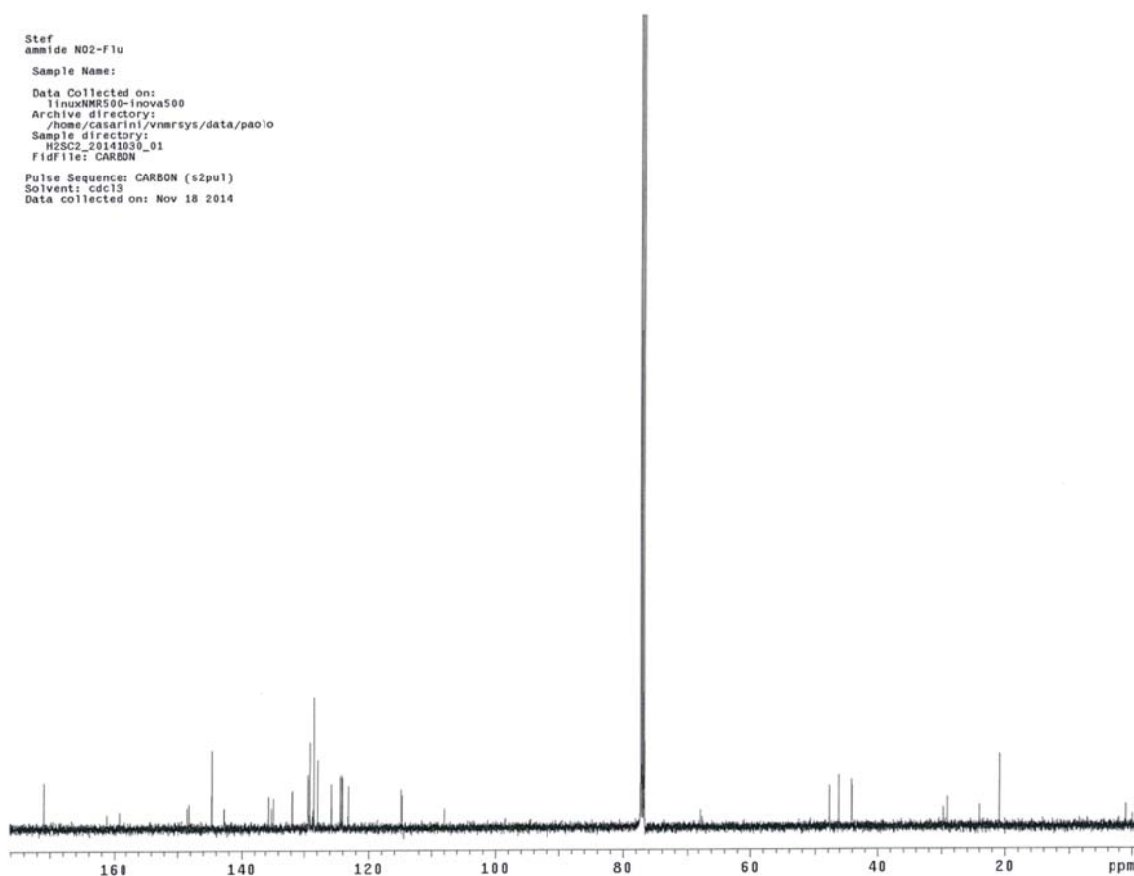


Figure S11. NMR Spectra of 5aa

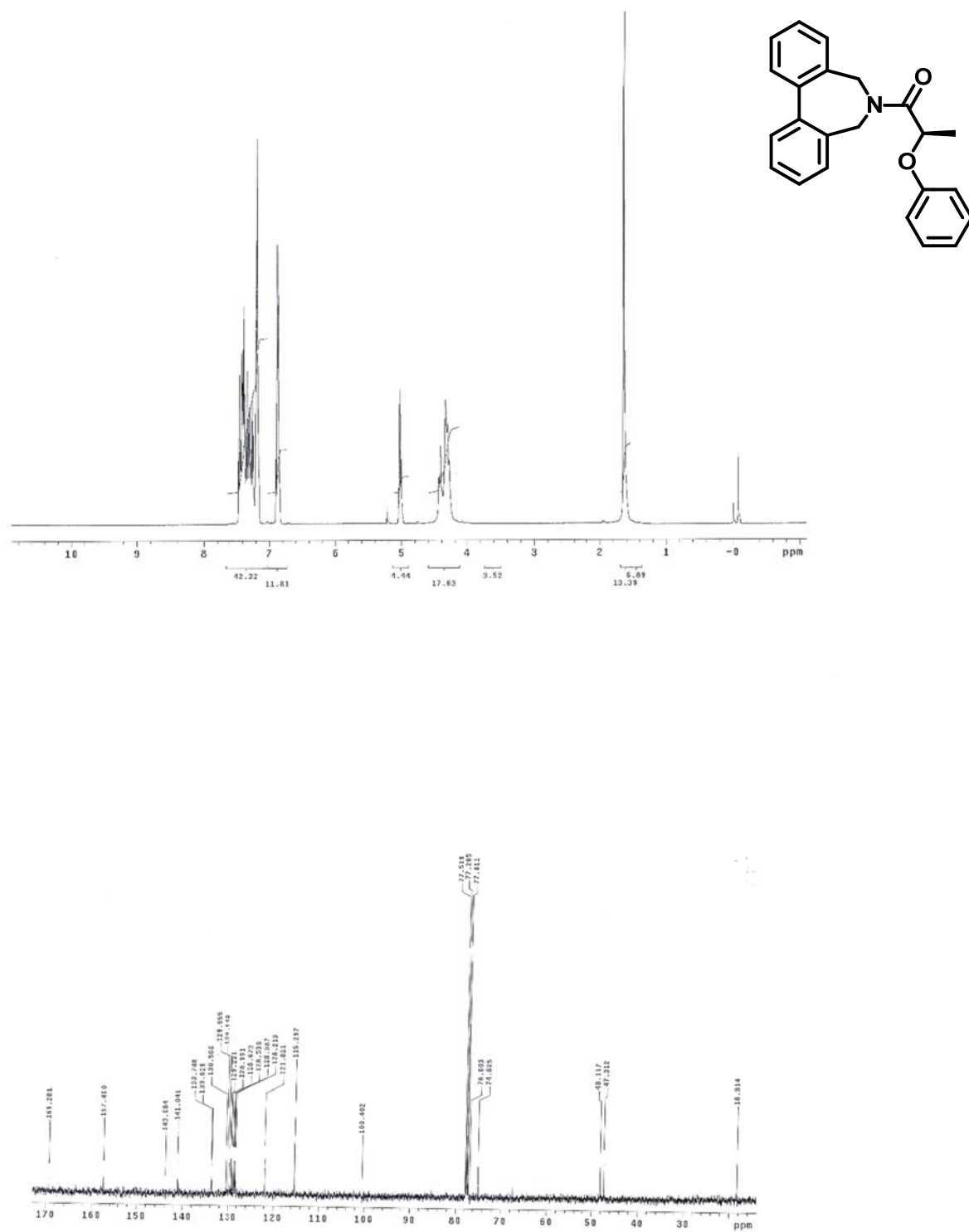


Figure S12. NMR Spectra of **5ba**

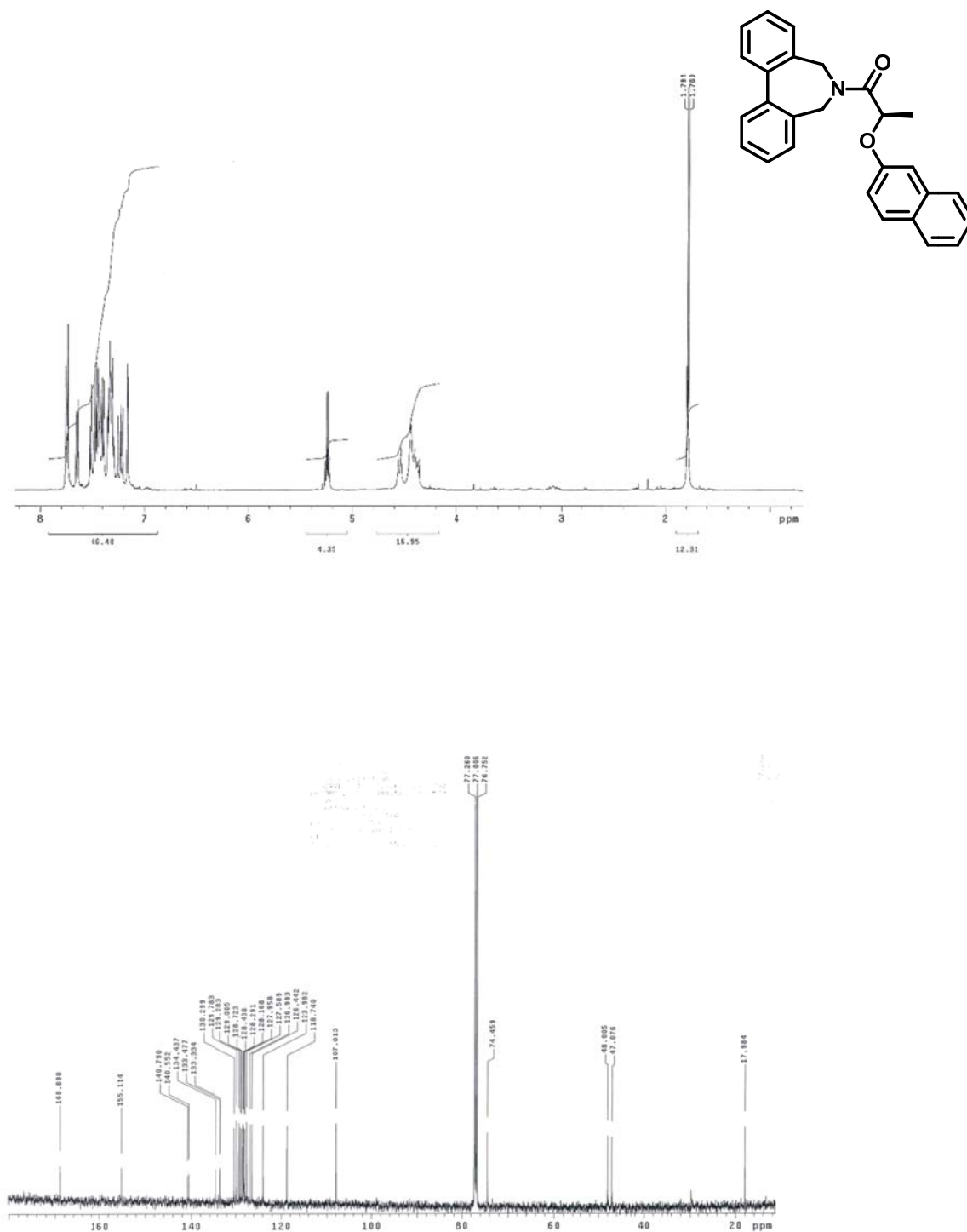


Figure S13. NMR Spectra of **5ac**

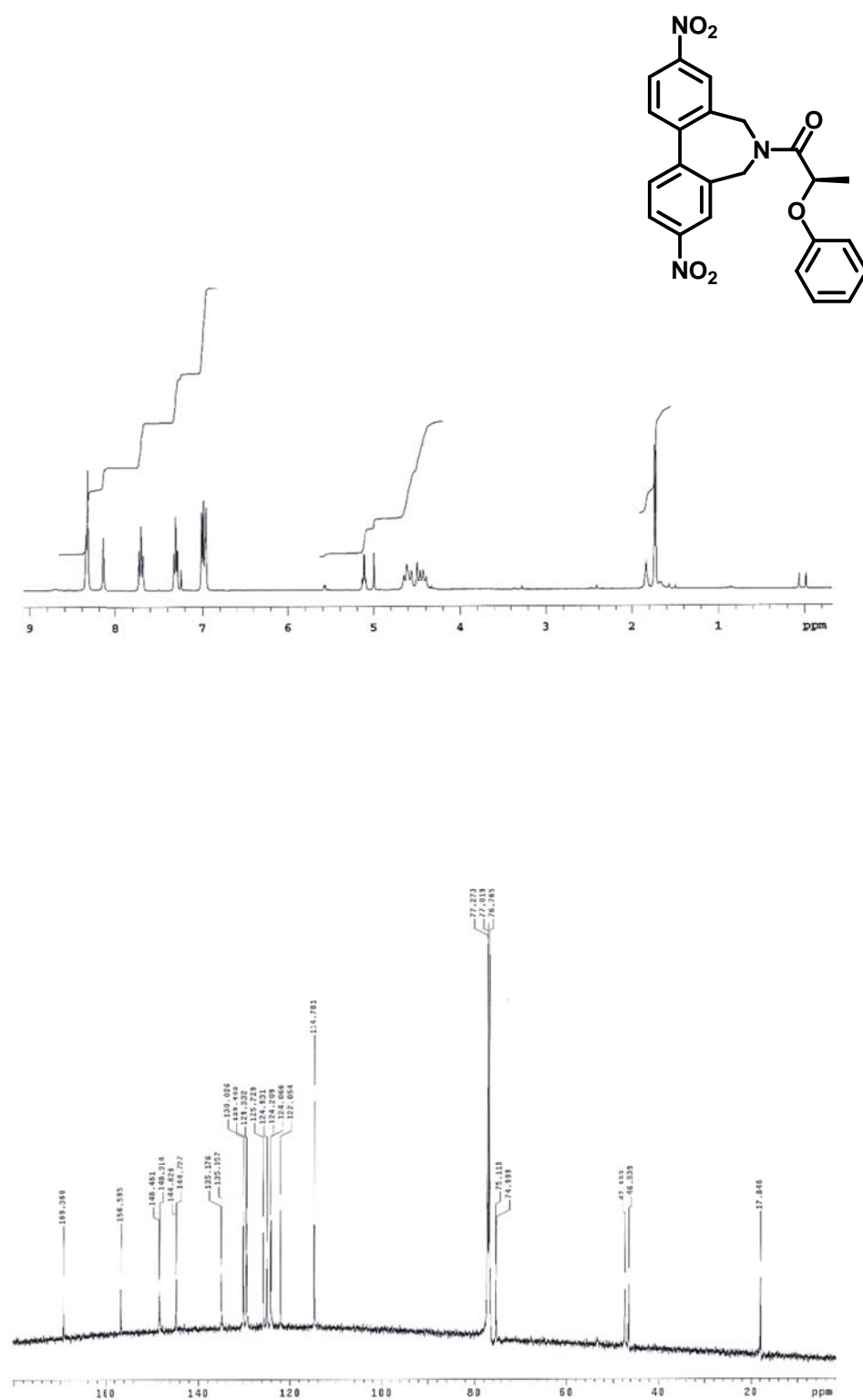


Figure S14. NMR Spectra of **5bc**

