# A Non-Diazo Approach to Functionalized (2-Furyl)-2-pyrrolidines through a Cascade Reaction of Enynal-Derived Zinc Carbenoids with β-Arylaminoketones

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## Supplementary Information

# A. Materials and Methods

## *Reagents*

Reagents and solvents were obtained from Sigma-Aldrich (www.sigma-aldrich.com), Chem-Impex (www.chemimpex.com) or Acros Organics (www.fishersci.com) and used without further purification unless otherwise indicated. Dry solvents (acetonitrile) were obtained from Acros Organics (www.fishersci.com), and dichloromethane was distilled over $CaH_2$ under $N_2$ unless otherwise indicated. THF purchased from Sigma-Aldrich was distilled over Na metal with benzophenone indicator. Chlorobenzene was obtained from Sigma-Aldrich.

## *Reactions*

All reactions were performed in flame-dried glassware under positive $N_2$ pressure with magnetic stirring unless otherwise noted. Liquid reagents and solutions were transferred thru rubber septa via syringes flushed with $N_2$ prior to use.

## *Chromatography*

TLC was performed on 0.25 mm E. Merck silica gel 60 F254 plates and visualized under UV light (254 nm) or by staining with potassium permanganate ($KMnO_4$), cerium ammonium molybdenate (CAM), phosphomolybdic acid (PMA), and ninhydrin. Silica flash chromatography was performed on Sorbtech 230–400 mesh silica gel 60.

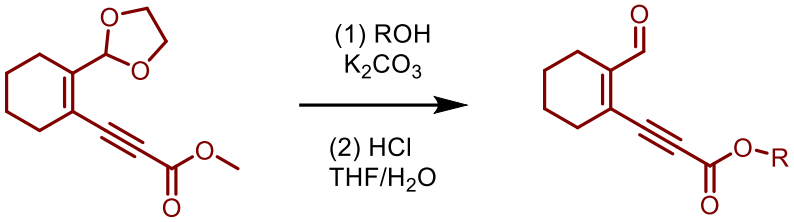
## *Analytical Instrumentation*

NMR spectra were recorded on a Varian VNMRS 300, 400, 500 and 600 MHz NMR spectrometer in $CDCl_3$ unless otherwise indicated. Chemical shifts are expressed in ppm relative to solvent signals: $CDCl_3$ ($^1H$, 7.26 ppm, $^{13}C$, 77.16 ppm), $CD_3OD$($^1H$, 3.34 ppm, $^{13}C$, 49.00 ppm); coupling constants are expressed in Hz. NMR spectra were processed using Mnova (www.mestrelab.com/software/mnova-nmr). Mass spectra were obtained at the OU Analytical Core Facility on an Agilent 6538 High-Mass-Resolution QTOF Mass Spectrometer and an Agilent 1290 UPLC.

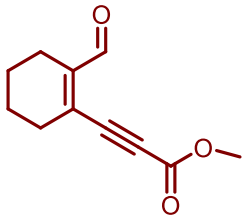
## *Nomenclature*

*N.B.*: Atom numbers shown in chemical structures herein correspond to IUPAC nomenclature, which was used to name each compound.

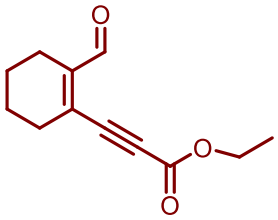
## B. General Procedure 1 for the Synthesis of Enynals (1b-1f)




Methyl 3-(2-(1,3-dioxolan-2-yl)cyclohex-1-en-1-yl)propiolate was synthesized following the reported procedure.[1] To a suspension of $Na_2CO_3$ (1.2 mmol, 2 equiv.) in DMF (2 ml) was added methyl 3-(2-(1,3-dioxolan-2-yl)cyclohex-1-en-1-yl)propiolate (0.6 mmol, 1 equiv.) and alcohol (6 mmol, 10 equiv.). The mixture was heated at 60 °C overnight. The reaction was separated by ether and water. The aqueous phase was extracted with ether twice. The combined organic phase was washed with brine and dried over $Na_2SO_4$. After solvent being removed, the remaining oil was dissolved in THF (3 ml). To this solution, HCl (35%, 0.8 ml) and water (2.2 ml) was added. The reaction was stirred at 0 °C for 1.5 h. After completion, the reaction was extracted with EtOAc, washed with water, brine and dried over $Na_2SO_4$. The organic layer was concentrated and purified by column chromatography eluting with 1:20 ethyl acetate:hexanes gradient to 1:5 ethyl acetate:hexanes to furnish pure enynals **1b-1f**.

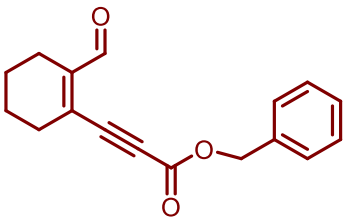


**Methyl 3-(2-formylcyclohex-1-en-1-yl)propiolate (1a).** Synthesized following the reported procedure. (450 mg, 62% yield.) Characterization data was in accordance with previous reports.[1]

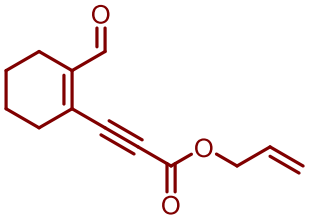


**Ethyl 3-(2-formylcyclohex-1-en-1-yl)propiolate (1b).** Synthesized using general procedure 1. (75mg, 61% yield.) Characterization data was in accordance with previous reports.[2]

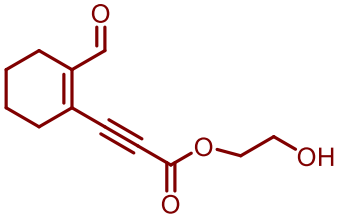
1. Y. Kato, K. Miki, F. Nishino, K. Ohe and S. Uemura, Doyle−Kirmse Reaction of Allylic Sulfides with Diazoalkane-Free (2-Furyl)carbenoid Transfer, *Org. Lett.*, 2003, **5**, 2619-2621. DOI: 10.1021/ol034731q
2. C. Sämann, M. A. Schade, S. Yamada and P. Knochel, Functionalized Alkenylzinc Reagents Bearing Carbonyl Groups: Preparation by Direct Metal Insertion and Reaction with Electrophiles, *Angew. Chem. Int. Ed.*, 2013, **52**, 9495-9499. DOI: 10.1002/anie.201302058



**Benzyl 3-(2-formylcyclohex-1-en-1-yl)propiolate (1c).** Synthesized following the reported procedure. (64 mg, 40% yield.) Characterization data was in accordance with previous reports.[3]



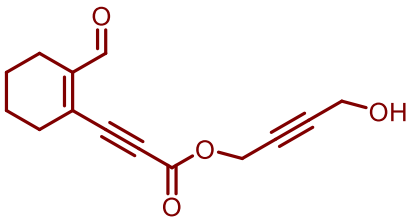
**Allyl 3-(2-formylcyclohex-1-en-1-yl)propiolate (1d).** Synthesized using general procedure 1. (61 mg, 45% yield). Characterization data was in accordance with previous reports. [2]



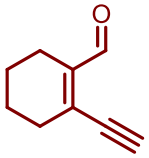
**2-Hydroxyethyl 3-(2-formylcyclohex-1-en-1-yl)propiolate (1e).** Synthesized using general procedure 1. Yellow oil, (64 mg, 48% yield). **TLC**: $R_f$ 0.52 (ethyl acetate/hexanes = 3: 2). **$^1$H NMR** ($CDCl_3$, 400 MHz) δ 10.15 (s, 1H), 4.36 (s, 0H), 3.90 (s, 0H), 2.46 (d, J = 2.6 Hz, 3H), 2.38 – 2.22 (m, 4H), 1.78 – 1.64 (m, 10H). **$^{13}$C NMR** ($CDCl_3$, 125 MHz): δ 191.69, 191.66, 153.51, 148.14, 135.77, 87.96, 82.93, 67.75, 60.80, 31.33, 22.46, 21.66, 20.71. **HRMS** (ESI) *m/z* calcd for $C_{12}H_{14}O_4Na$ ($[M+Na]^+$) 245.0790; found 245.0789.

2. C. Sämann, M. A. Schade, S. Yamada and P. Knochel, Functionalized Alkenylzinc Reagents Bearing Carbonyl Groups: Preparation by Direct Metal Insertion and Reaction with Electrophiles, *Angew. Chem. Int. Ed.*, 2013, **52**, 9495-9499. DOI: 10.1002/anie.201302058

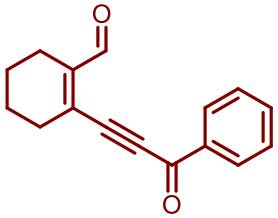
3. K. Hong, J. Shu, S. Dong, Z. Zhang, Y. He, M. Liu, J. Huang, W. Hu and X. Xu, Asymmetric Three-Component Reaction of Enynal with Alcohol and Imine as An Expeditious Track to Afford Chiral α-Furyl-β-amino Carboxylate Derivatives, *ACS Catal.*, 2022, **12**, 14185-14193. DOI: 10.1021/acscatal.2c04022




**2-Butyne-1,4-diol 3-(2-formylcyclohex-1-en-1-yl)propiolate (1f).** Synthesized using general procedure 1. Yellow oil, (38mg, 26%). **TLC**: $R_f$ 0.69 (ethyl acetate/hexanes = 3: 2). **$^1$H NMR** ($CDCl_3$, 400 MHz) δ 10.15 (s, 1H), 4.85 (t, J = 1.9 Hz, 2H), 4.33 (dt, J = 6.2, 1.8 Hz, 2H), 2.45 (dq, J = 6.1, 2.7 Hz, 2H), 2.31 (dq, J = 5.9, 2.7 Hz, 2H), 1.76 – 1.61 (m, 4H).**$^{13}$C NMR** ($CDCl_3$, 100 MHz δ 191.64, 152.66, 148.46, 135.60, 87.48, 86.24, 83.41, 78.72, 53.95, 51.18, 31.27, 22.48, 21.67, 20.71. **HRMS** (ESI) *m/z* calcd for $C_{14}H_{14}O_4Na$ ($[M+Na]^+$) 269.0790; found 269.0778.

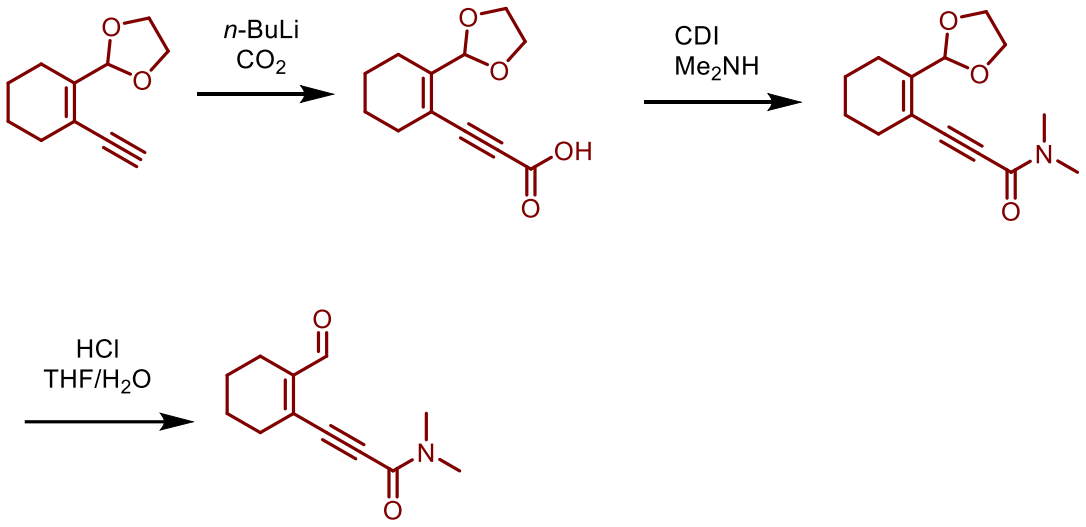



**2-ethynylcyclohex-1-ene-1-carbaldehyde (1g).** Synthesized following the reported procedure. (3.7 g, 70% yield.) Characterization data was in accordance with previous reports.[1]




**2-(3-oxo-3-phenylprop-1-yn-1-yl)cyclohex-1-ene-1-carbaldehyde (1h).** Synthesized following the reported procedure. (450 mg, 75% yield.) Characterization data was in accordance with previous reports. [1]

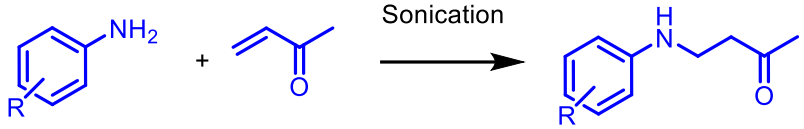
1. Y. Kato, K. Miki, F. Nishino, K. Ohe and S. Uemura, Doyle−Kirmse Reaction of Allylic Sulfides with Diazoalkane-Free (2-Furyl)carbenoid Transfer, *Org. Lett.*, 2003, **5**, 2619-2621. DOI: 10.1021/ol034731q



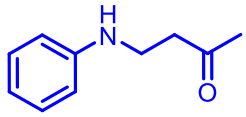

**3-(2-formylcyclohex-1-en-1-yl)-N,N-dimethylpropiolamide (1i).** 2-(2-ethynylcyclohex-1-en-1-yl)-1,3-dioxolane was synthesized following the reported procedure.[1] To 2-(2-ethynylcyclohex-1-en-1-yl)-1,3-dioxolane (200 mg, 1.1 mmol) in THF was added *n*-butyl Lithium (1.1 mmol) at -20 °C. After 20 min, the mixture was warmed to RT. Then CO2 was bubbled into the solution for 2 h. Solution was washed by EtOAc. The aqueous layer was acidified by phosphoric acid and extracted by EtOAc. The organic layer was dried over $Na_2SO_4$. After solvent being removed, the remaining oil was dissolved in acetonitrile. CDI (1 mmol) was added at 40 °C and stirred for 2 h. Then the mixture was cooled to RT and added with dimethylamine (2 mmol) in THF solution and stirred for overnight. The reaction mixture was filtered through silica plug. After solvent being removed, the remaining oil was dissolved in THF (3 ml). To this solution, HCl (35%, 0.8 ml) and water (2.2 ml) was added. The reaction was stirred at 0 ° for 1.5 h. After completion, the reaction was extracted with EtOAc, washed with water, brine and dried over $Na_2SO_4$. The organic layer was concentrated and purified by column chromatography eluting with 1:5 ethyl acetate:hexanes to furnish pure enynal **1h**. Yellow oil (45 mg, overall 20% yield after 3 steps) **TLC**: $R_f$ 0.12 (ethyl acetate/hexanes = 2: 3). **$^1$H NMR** ($CDCl_3$, 400 MHz) δ 10.16 (s, 1H), 3.22 (s, 3H), 3.02 (s, 3H), 2.47 (dq, $J$ = 6.0, 2.8 Hz, 2H), 2.30 (dt, $J$ = 6.0, 3.0 Hz, 2H), 1.80 – 1.61 (m, 4H). **$^{13}$C NMR** ($CDCl_3$, 100 MHz) δ 191.85, 153.97, 146.08, 137.17, 89.76, 86.54, 38.45, 34.39, 31.75, 22.35, 21.79, 20.86. **MS** (ESI) *m/z* calcd for $C_{12}H_{16}NO_2$ ($[M+H]^+$) 206.1; found 206.1.

1. Y. Kato, K. Miki, F. Nishino, K. Ohe and S. Uemura, Doyle−Kirmse Reaction of Allylic Sulfides with Diazoalkane-Free (2-Furyl)carbenoid Transfer, *Org. Lett.*, 2003, **5**, 2619-2621. DOI: 10.1021/ol034731q

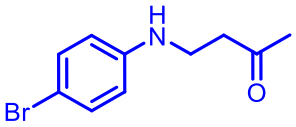
## C. General Procedure 2 for the Synthesis of Beta-Arylaminoketones (2)



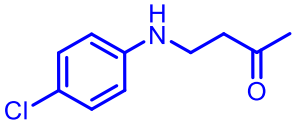

**Aminoketones (2)**. Aminoketones were synthesized following a modified literature procedure.[4] Methyl vinyl ketone (1.2 mmol, 1.2 equiv.) and substituted aniline (1 mmol, 1 equiv.) were mixed in an eppendorf tube for overnight sonication. The product was directly purified by column chromatography, eluting with 1:9 ethyl acetate:hexanes gradient to 3:7 ethyl acetate:hexanes to furnish pure aminoketones **2a**-**2j**.




**4-(Phenylamino)butan-2-one (2a)**. Synthesized using general procedure 2. (99 mg, 66% yield). Characterization data was in accordance with previous reports. [5]




**4-((4-Bromophenyl)amino)butan-2-one (2b)**. Synthesized using general procedure 2. (110 mg, 45% yield). Characterization data was in accordance with previous reports. [6]




**4-((4-Chlorophenyl)amino)butan-2-one (2c)**. Synthesized using general procedure 2. (110 mg, 45% yield.) Characterization data was in accordance with previous reports.[7]

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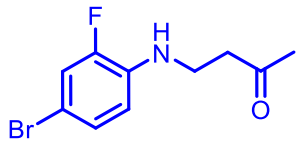
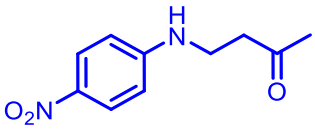
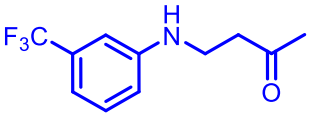
4. R. Jiang, D.-H. Li, J. Jiang, X.-P. Xu, T. Chen and S.-J. Ji, Green, efficient and practical Michael addition of arylamines to α,β-unsaturated ketones, *Tetrahedron*, 2011, **67**, 3631-3637.DOI: 10.1016/j.tet.2011.03.082
5. R. N. Monrad and R. Madsen, Ruthenium-catalysed synthesis of 2-and 3-substituted quinolines from anilines and 1, 3-diols, *Org. Biomol. Chem*., 2011, **9**, 610-615. DOI: 10.1039/C0OB00676A
6. C. B. Phippen, J. K. Beattie and C. S. McErlean, "On-water" conjugate additions of anilines*, Chem. Commun.*, 2010, **46**, 8234-8236. DOI: 10.1039/C0CC02502J (
7. K. De, J. Legros, B. Crousse and D. Bonnet-Delpon, Solvent-promoted and-controlled aza-Michael reaction with aromatic amines, *J. Org. Chem.*, 2009, **74**, 6260-6265. DOI: 10.1021/jo9012699



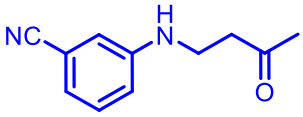
**4-((4-Bromo-2-fluorophenyl)amino)butan-2-one(2d)**. Synthesized using general procedure 2. Yellow oil (123 mg, 53% yield). **TLC**: $R_f$ 0.53 (ethyl acetate/hexanes = 1:1). **$^1$H NMR** ($CDCl_3$, 400 MHz) δ 7.16 – 7.06 (m, 2H), 6.56 (t, J = 8.7 Hz, 1H), 4.19 (s, 1H), 3.41 (t, J = 6.2 Hz, 2H), 2.76 (t, J = 6.2 Hz, 2H), 2.18 (s, 3H). **$^{13}$C NMR** ($CDCl_3$, 100 MHz) δ 207.52, 151.47 (d, J = 243.5 Hz), 135.58 (d, J = 11.5 Hz), 127.54 (d, J = 3.5 Hz), 118.16 (d, J = 21.9 Hz), 113.01 (d, J = 3.8 Hz), 107.38 (d, J = 8.8 Hz).42.52, 38.01, 30.50. **HRMS** (ESI) We were unable to obtain accurate HRMS data for this compound.



**4-((4-Nitrophenyl)amino)butan-2-one (2e)**. Synthesized following the reported procedure. (61 mg, 29% yield). Characterization data was in accordance with previous reports.[8]



**4-((3-(Trifluoromethyl)phenyl)amino)butan-2-one (2f)**. Synthesized using general procedure 2. (140 mg, 61% yield). Characterization data was in accordance with previous reports. [9]



**3-((3-Oxobutyl)amino)benzonitrile (2g)**. Synthesized using general procedure 2. Yellow solid (110 mg 46% yield). **TLC**: $R_f$ 0.20 (ethyl acetate/hexanes = 3:7). **$^1$H NMR** ($CDCl_3$, 400 MHz) δ 7.20 (tq, J = 6.5, 2.1 Hz, 1H), 6.99 – 6.90 (m, 1H), 6.77 (qd, J = 2.8, 1.4 Hz, 2H), 4.32 (s, 1H), 3.38 (ddt, J = 8.0, 6.0, 2.4 Hz, 2H), 2.79 – 2.70 (m, 2H), 2.18 (s, 3H). **$^{13}$C NMR** ($CDCl_3$, 100 MHz) δ 207.84, 148.05, 130.02, 120.86, 119.53, 117.53, 114.82, 112.92, 42.13, 37.91, 30.40. **HRMS** (ESI) *m/z* calcd for $C_{11}H_{12}N_2ONa$ ($[M+Na]^+$) 211.0847; found 211.0847.

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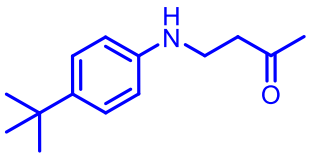
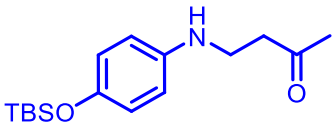
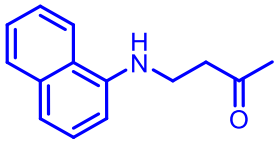
8. L. Ouyang, J. Huang, J. Li, C. Qi, W. Wu and H. Jiang, Palladium-catalyzed oxidative amination of homoallylic alcohols: sequentially installing carbonyl and amino groups along an alkyl chain, *Chem. Commun*., 2017, **53**, 10422-10425. DOI: 10.1039/C7CC06077G
9. C. Miao, L. Jiang, L. Ren, Q. Xue, F. Yan, W. Shi, X. Li, J. Sheng and S. Kai, Iodine-catalyzed coupling of β-hydroxyketones with aromatic amines to form β-aminoketones and Benzo[h]quinolones, *Tetrahedron*, 2019, **75**, 2215-2228. DOI: 10.1016/j.tet.2019.02.041



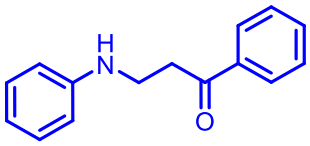
**4-[[4-(1,1-Dimethylethyl)phenyl]amino]butan-2-one (2h)**. Synthesized using general procedure 2. (149 mg, 68% yield). Characterization data was in accordance with previous reports.[9]



**4-((4-((Tert-butyldimethylsilyl)oxy)phenyl)amino)butan-2-one (2i)**. Synthesized using general procedure 2. Yellow solid (153 mg 45% yield). **TLC**: $R_f$ 0.20 (ethyl acetate/hexanes = 3:7). **$^1$H NMR** ($CDCl_3$, 500 MHz) 6.77 – 6.67 (m, 2H), 6.53 (dt, J = 12.7, 5.3 Hz, 2H), 3.35 (tt, J = 6.2, 1.2 Hz, 2H), 2.74 (q, J = 6.5 Hz, 2H), 2.17 (s, 3H), 0.96 (s, 9H), 0.15 (s, 6H). **$^{13}$C NMR** ($CDCl_3$, 125 MHz) δ δ 208.40, 147.94, 142.13, 120.86, 114.62, 42.83, 39.67, 30.47, 25.89, 18.32, -4.33. **HRMS** (ESI) *m/z* calcd $C_{16}H_{28}NO_2Si$ ($[M+H]^+$) 294.1889; found 294.1893.

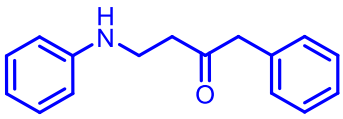


**4-(Naphthalen-1-ylamino)butan-2-one (2j)**. Synthesized using general procedure 2. (105 mg, 49% yield). Characterization data was in accordance with previous reports.[4]



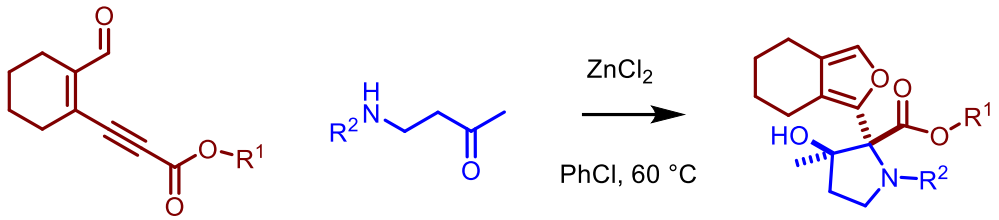
**1-phenyl-3-(phenylamino)propan-1-one (2k) )**. Synthesized following the reported procedure. (112 mg, 43% yield). Characterization data was in accordance with previous reports.[10]


4. R. Jiang, D.-H. Li, J. Jiang, X.-P. Xu, T. Chen and S.-J. Ji, Green, efficient and practical Michael addition of arylamines to α,β-unsaturated ketones, *Tetrahedron*, 2011, **67**, 3631-3637.DOI: 10.1016/j.tet.2011.03.082
9. C. Miao, L. Jiang, L. Ren, Q. Xue, F. Yan, W. Shi, X. Li, J. Sheng and S. Kai, Iodine-catalyzed coupling of β-hydroxyketones with aromatic amines to form β-aminoketones and Benzo[h]quinolones, *Tetrahedron*, 2019, **75**, 2215-2228. DOI: 10.1016/j.tet.2019.02.041
10. M. Barbero, S. Cadamuro and S. Dughera, O-Benzenedisulfonimide as a reusable Brønsted acid catalyst for hetero-Michael reactions, *Synth. Commun.*, 2013, **43**, 758-767. DOI: 10.1080/00397911.2011.614834

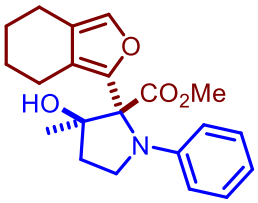


**1-phenyl-4-(phenylamino)butan-2-one (2l).** Synthesized using general procedure 2. Yellow oil (110 mg, 48% yield). **TLC**: $R_f$ 0.53 (ethyl acetate/hexanes = 1: 4). **$^1$H NMR** ($CDCl_3$, 400 MHz) δ 7.38 – 7.27 (m, 3H), 7.17 (ddd, $J$ = 13.8, 7.1, 1.8 Hz, 4H), 6.70 (t, $J$ = 7.4 Hz, 1H), 6.55 (d, $J$ = 8.1 Hz, 2H), 3.91 (s, 1H), 3.70 (s, 2H), 3.38 (t, $J$ = 6.1 Hz, 2H), 2.76 (t, $J$ = 6.1 Hz, 2H). **$^{13}$C NMR** ($CDCl_3$, 100 MHz,) δ 207.96, 147.70, 133.89, 129.56, 129.42, 128.96, 127.32, 117.75, 113.13, 50.67, 41.03, 38.59. **MS** (ESI) *m/z* calcd for $C_{16}H_{18}NO$ ($[M+H]^+$) 240.1; found 240.1.

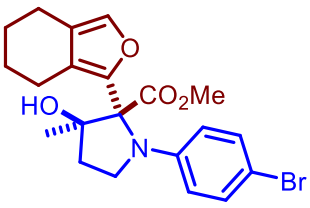
## D. General Procedure 3 for the Synthesis of Furyl Pyrrolidines (3 & 5)



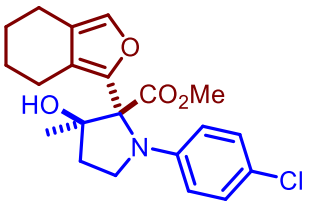

To a 5.0 mL RB flask equipped with a magnetic stir bar was added $ZnCl_2$ (10 µmol, 0.2 equiv.). A solution of amino ketone (50 µmol, 1 equiv.) in chlorobenzene (1 ml) was added. Lastly, the enynal (85 µmol, 1.7 equiv.) in chlorobenzene (0.5 ml) was added via syringe pump over 4 h at 60 °C. Reaction was monitored by TLC. After completion, the reaction mixture was directly purified by column chromatography 1:9 ethyl acetate:hexanes gradient to 1:4 ethyl acetate:hexanes to Furyl Pyrrolidines **3a-3j** and **5a-5e**.



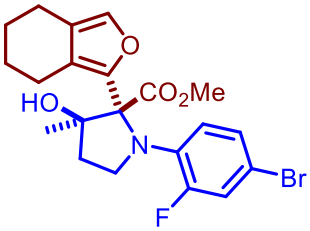

**Methyl 3-hydroxy-3-methyl-1-phenyl-2-(4,5,6,7-tetrahydroisobenzofuran-1-yl)pyrrolidine-2-carboxylate (3a).** Synthesized using general procedure 3. Yellow solid. (75% NMR yield using 1,3,5-trimethoxybenzene as reference.) **TLC**: $R_f$ 0.33 (ethyl acetate/hexanes = 3:7). **$^1$H NMR** ($CDCl_3$, 400 MHz): δ 7.18 (s, 1H), 7.12 (dd, J = 8.6, 7.2 Hz, 2H), 6.69 (t, J = 7.3 Hz, 1H), 6.49 (d, J = 8.1 Hz, 2H), 3.71 (m, 4H), 3.67 – 3.55 (m, 1H), 2.66 (s, 1H), 2.48 (q, J = 6.5, 6.1 Hz, 2H), 2.38 – 1.92 (m, 4H), 1.72 – 1.40 (m, 4H), 1.12 (s, 3H). **$^{13}$C NMR** ($CDCl_3$, 100 MHz δ 171.14, 146.91, 143.66, 136.74, 128.66, 122.57, 120.23, 117.18, 113.38, 86.03, 77.36, 52.44, 48.09, 37.16, 24.17, 23.57, 22.82, 21.90, 20.48. **HRMS** (ESI) *m/z* calcd for $C_{21}H_{25}NO_4Na$ ($[M+Na]^+$) 378.1682; found 378.1673.



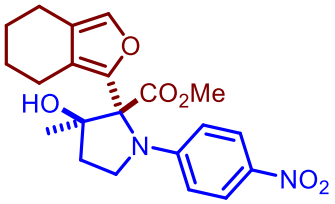

**Methyl 1-(4-bromophenyl)-3-hydroxy-3-methyl-2-(4,5,6,7-tetrahydroisobenzofuran-1-yl)pyrrolidine-2-carboxylate (3b).** Synthesized using general procedure 3. Yellow solid. (84% NMR yield using 1,3,5-trimethoxybenzene as reference.) **TLC**: $R_f$ 0.45 (ethyl acetate/hexanes = 2:3). **$^1$H NMR** ($CDCl_3$, 400 MHz): 7.22 – 7.13 (m, 3H), 6.35 (d, J = 9.1 Hz, 2H), 3.72 (d, J = 1.3 Hz, 4H), 3.54 (td, J = 8.6, 4.1 Hz, 1H), 2.62 (s, 1H), 2.47 (d, J = 5.9 Hz, 2H), 2.23 (ddt, J = 12.8, 9.6, 4.5 Hz, 2H), 2.16 – 1.99 (m, 2H), 1.66 – 1.42 (m, 4H), 1.14 (d, J = 1.4 Hz, 3H). **$^{13}$C NMR** ($CDCl_3$, 100 MHz) δ 170.54, 145.92, 143.05, 136.87, 131.28, 122.65, 120.27, 115.04, 109.24, 86.10, 77.36, 52.49, 48.18, 37.20, 24.07, 23.53, 22.76, 21.93, 20.43.**HRMS** (ESI) *m/z* calcd for $C_{21}H_{25}BrNO_4$ ($[M+H]^+$) 434.0967; found 434.0971.



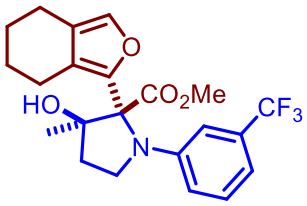

**Methyl 1-(4-chlorophenyl)-3-hydroxy-3-methyl-2-(4,5,6,7-tetrahydroisobenzofuran-1-yl)pyrrolidine-2-carboxylate (3c).** Synthesized using general procedure 3. Colourless oil. (62% NMR yield using 1,3,5-trimethoxybenzene as reference.) **TLC**: $R_f$ 0.39 (ethyl acetate/hexanes = 3:7). **$^1$H NMR** ($CDCl_3$, 400 MHz): δ 7.17 (s, 1H), 7.13 – 6.97 (m, 2H), 6.52 – 6.31 (m, 2H), 3.72 (m, 4H), 3.55 (td, J = 8.6, 4.1 Hz, 1H), 2.58 (s, 1H), 2.48 (d, J = 5.7 Hz, 2H), 2.31 – 2.03 (m, 4H), 1.74 – 1.41 (m, 4H), 1.14 (s, 3H). **$^{13}$C NMR** ($CDCl_3$, 100 MHz) δ 170.66, 145.53, 143.16, 136.88, 128.46, 122.67, 121.99, 120.29, 114.53, 86.11, 77.36, 52.50, 48.27, 37.21, 24.12, 23.54, 22.78, 21.93, 20.44. **HRMS** (ESI) *m/z* calcd for $C_{21}H_{25}ClNO_4$ ($[M+H]^+$) 390.14723; found 390.1455.



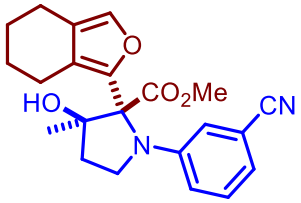

**Methyl 1-(4-bromo-2-fluorophenyl)-3-hydroxy-3-methyl-2-(4,5,6,7-tetrahydroisobenzofuran-1-yl)pyrrolidine-2-carboxylate (3d).** Synthesized using general procedure 3. Colourless oil. (80% NMR yield using 1,3,5-trimethoxybenzene as reference.) **TLC**: $R_f$ 0.38 (ethyl acetate/hexanes = 2:3). **$^1$H NMR** ($CDCl_3$, 500 MHz): δ 7.16 (s, 1H), 7.09 (dd, J = 13.1, 2.3 Hz, 1H), 6.95 (dd, J = 8.8, 2.3 Hz, 1H), 6.38 (t, J = 9.1 Hz, 1H), 3.89 (ddt, J = 11.4, 7.9, 3.9 Hz, 1H), 3.74 (s, 3H), 3.68 (tt, J = 8.7, 4.2 Hz, 1H), 2.60 (s, 1H), 2.56 – 2.47 (m, 2H), 2.29 – 2.16 (m, 2H), 2.19 – 2.04 (m, 2H), 1.69 – 1.50 (m, 4H), 1.19 (s, 3H). **$^{13}$C NMR** ($CDCl_3$, 125 MHz) δ 170.40, 143.95, 137.80, 136.45, 126.80, 126.78, 122.59, 119.69, 119.49, 84.99, 77.26, 52.37, 50.17, 50.10, 36.89, 23.63, 23.43, 22.63, 20.30. **HRMS** (ESI) *m/z* calcd for $C_{21}H_{23}BrFNO_4Na$ ($[M+Na]^+$) 474.0692; found 474.0696.



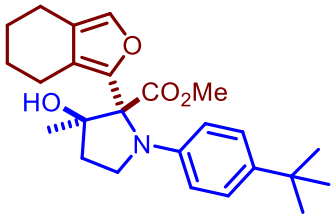

**Methyl 3-hydroxy-3-methyl-1-(4-nitrophenyl)-2-(4,5,6,7-tetrahydroisobenzofuran-1-yl)pyrrolidine-2-carboxylate (3e).** Synthesized using general procedure 3. Colourless oil. (81% NMR yield using 1,3,5-trimethoxybenzene as reference.) **TLC**: $R_f$ 0.34 (ethyl acetate/hexanes = 2:3). **$^1$H NMR** ($CDCl_3$, 400 MHz) : δ 8.01 (d, 2H), 7.15 (s, 1H), 6.44 (d, J = 8.9 Hz, 2H), 3.87 (dt, J = 9.5, 8.2 Hz, 1H), 3.76 (s, 3H), 3.74 – 3.55 (m, 1H), 2.62 – 2.35 (m, 2H), 2.31 – 2.08 (m, 4H), 1.59 – 1.49 (m, 4H), 1.24 (s, 3H). **$^{13}$C NMR** ($CDCl_3$, 100 MHz) δ 169.07, 151.98, 141.78, 138.42, 138.10, 137.16, 125.32, 122.88, 112.70, 86.22, 77.36, 52.73, 48.53, 37.32, 23.94, 23.47, 22.66, 22.16, 20.36. **HRMS** (ESI) *m/z* calcd for $C_{21}H_{25}N_2O_6$ ($[M+H]^+$) 401.1713; found 401.1720.



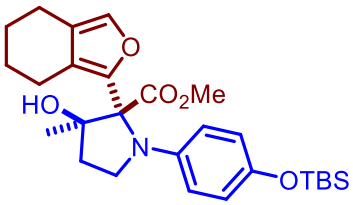

**Methyl 3-hydroxy-3-methyl-2-(4,5,6,7-tetrahydroisobenzofuran-1-yl)-1-(3-(trifluoromethyl)phenyl)pyrrolidine-2-carboxylate (3f).** Synthesized using general procedure 3. Colourless oil. (72% NMR yield using 1,3,5-trimethoxybenzene as reference.) **TLC**: $R_f$ 0.45 (ethyl acetate/hexanes = 2:3). **$^1$H NMR** ($CDCl_3$, 400 MHz): δ 7.22 – 7.08 (m, 2H), 6.91 (d, J = 7.6 Hz, 1H), 6.71 (t, J = 2.0 Hz, 1H), 6.59 (dd, J = 8.4, 2.5 Hz, 1H), 3.80 (q, J = 8.2 Hz, 1H), 3.73 (s, 3H), 3.61 (dt, J = 9.2, 6.0 Hz, 1H), 2.58 (s, 1H), 2.54 – 2.39 (m, 2H), 2.35 – 2.19 (m, 3H), 2.12 (s, 1H), 1.70 – 1.45 (m, 4H), 1.20 (s, 3H). **$^{13}$C NMR** ($CDCl_3$, 100 MHz) δ 170.20, 146.95, 142.66, 136.86, 130.72 (q, J = 31.5 Hz), 128.78, 124.59 (d, J = 272.4 Hz), 122.61, 120.52, 116.61, 113.55, 109.98, 86.09, 77.36, 52.48, 48.24, 37.30, 23.91, 23.50, 22.75, 22.16, 20.42. **HRMS** (ESI) *m/z* calcd for $C_{22}H_{25}F_3NO_4$ ($[M+H]^+$) 424.17358; found 424.1721.



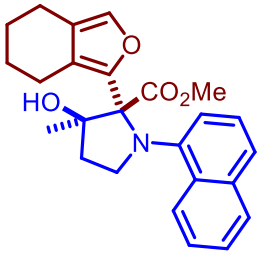

**Methyl 1-(3-cyanophenyl)-3-hydroxy-3-methyl-2-(4,5,6,7-tetrahydroisobenzofuran-1-yl)pyrrolidine-2-carboxylate (3g).** Synthesized using general procedure 3. Colourless oil. (71% NMR yield using 1,3,5-trimethoxybenzene as reference.) **TLC**: $R_f$ 0.29 (ethyl acetate/hexanes = 2:3). **$^1$H NMR** ($CDCl_3$, 400 MHz): δ 7.15 (t, J = 8.0 Hz, 2H), 6.95 (d, J = 7.5 Hz, 1H), 6.70 (s, 1H), 6.64 (dd, J = 8.5, 2.3 Hz, 1H), 3.75 (s, 4H), 3.57 (dt, J = 9.2, 5.9 Hz, 1H), 2.55 – 2.40 (m, 3H), 2.33 – 2.15 (m, 3H), 2.13 – 2.00 (m, 1H), 1.69 – 1.49 (m, 4H), 1.20 (s, 3H). **$^{13}$C NMR** ($CDCl_3$, 100 MHz) δ 169.80, 147.02, 142.21, 137.06, 129.14, 122.74, 120.52, 120.47, 119.91, 117.82, 116.38, 112.23, 86.15, 77.36, 52.61, 48.13, 42.01, 37.28, 23.89, 23.49, 22.72, 22.16, 20.36. **HRMS** (ESI) *m/z* calcd for $C_{22}H_{25}N_2O_4$ ($[M+H]^+$) 381.1815; found 381.1800.



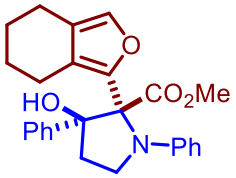

**Methyl 1-(4-(tert-butyl)phenyl)-3-hydroxy-3-methyl-2-(4,5,6,7-tetrahydroisobenzofuran-1-yl)pyrrolidine-2-carboxylate (3h).** Synthesized using general procedure 3. Colourless oil. (52% NMR yield using 1,3,5-trimethoxybenzene as reference.) **TLC**: $R_f$ 0.50 (ethyl acetate/hexanes = 2:3). **$^1$H NMR** ($CDCl_3$, 400 MHz): δ 7.22 – 6.99 (m, 3H), 6.50 – 6.29 (m, 2H), 3.73 (s, 4H), 3.58 (dt, J = 8.7, 4.4 Hz, 1H), 2.74 (s, 1H), 2.48 (q, J = 6.1, 5.5 Hz, 2H), 2.26 (dt, J = 14.1, 5.5 Hz, 2H), 2.17 – 2.00 (m, 2H), 1.64 – 1.47 (m, 4H), 1.24 (s, 9H), 1.11 (s, 3H). **$^{13}$C NMR** ($CDCl_3$, 100 MHz) δ 171.32, 144.39, 143.84, 139.61, 136.56, 125.38, 122.49, 120.24, 113.08, 85.97, 77.36, 52.42, 48.08, 37.26, 33.87, 31.74, 31.63, 24.04, 23.58, 22.87, 22.00, 20.49. **HRMS** (ESI) *m/z* calcd for $C_{25}H_{28}N_2O_4$ ($[M+H]^+$) 406.20185; found 406.2009.




**Methyl 1-(4-((tert-butyldimethylsilyl)oxy)phenyl)-3-hydroxy-3-methyl-2-(4,5,6,7-tetrahydroisobenzofuran-1-yl)pyrrolidine-2-carboxylate (3i).** Synthesized using general procedure 3. Colourless oil. (50% NMR yield using 1,3,5-trimethoxybenzene as reference.) **TLC**: $R_f$ 0.45 (ethyl acetate/hexanes = 2:3). **$^1$H NMR** ($CDCl_3$, 400 MHz): δ 7.19 (s, 1H), 6.63 (d, J = 8.7 Hz, 2H), 6.37 (d, J = 8.5 Hz, 2H), 3.70 (m, 4H), 3.57 – 3.51 (m, 1H), 2.68 (s, 1H), 2.52 – 2.39 (m, 2H), 2.36 – 2.25 (m, 1H), 2.23 – 2.12 (m, 1H), 2.11 – 2.01 (m, 1H), 2.01 – 1.89 (m, 1H), 1.63-1.38 (m, 4H), 1.10 (s, 3H), 0.95 (s, 9H), 0.12 (s, 6H). **$^{13}$C NMR** ($CDCl_3$, 100 MHz) δ 171.52, 147.14, 144.00, 141.68, 136.68, 122.51, 120.26, 120.14, 114.44, 85.93, 77.36, 52.32, 48.51, 37.24, 25.89, 24.27, 23.54, 22.85, 21.80, 20.49, 18.34, -4.30. **HRMS** (ESI) *m/z* calcd for $C_{27}H_{40}N_2O_5Si$ ($[M+H]^+$) 486.2676; found 486.2694.

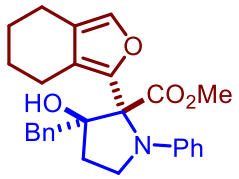



**Methyl 3-hydroxy-3-methyl-1-(naphthalen-1-yl)-2-(4,5,6,7-tetrahydroisobenzofuran-1-yl)pyrrolidine-2-carboxylate (3j).** Synthesized using general procedure 3. Gray solid. (76% NMR yield using 1,3,5-trimethoxybenzene as reference.) **TLC**: $R_f$ 0.39 (ethyl acetate/hexanes = 2:3). **$^1$H NMR** ($CDCl_3$, 400 MHz): ): δ 8.42 (d, J = 8.4 Hz, 1H), 7.78 (d, J = 8.1 Hz, 1H), 7.60 (d, J = 8.2 Hz, 1H), 7.47 (dt, J = 23.6, 6.8 Hz, 2H), 7.25 (d, J = 6.3 Hz, 1H), 7.17 (t, J = 7.8 Hz, 1H), 6.19 (d, J = 7.5 Hz, 1H), 3.78 – 3.70 (m, 1H), 3.49 (s, 3H), 3.36 – 3.27 (m, 2H), 2.75 (ddd, J = 13.3, 10.4, 6.2 Hz, 1H), 2.57 (q, J = 7.3, 6.5 Hz, 1H), 2.25 (ddd, J = 13.0, 8.7, 4.0 Hz, 1H), 2.08 (ddd, J = 16.3, 8.9, 5.3 Hz, 1H), 1.71 (dt, J = 16.0, 5.5 Hz, 1H), 1.66 – 1.52 (m, 3H), 1.50 (s, 3H), 1.38 – 1.23 (m, 2H). **$^{13}$C NMR** ($CDCl_3$, 100 MHz) δ 170.54, 144.09, 137.95, 136.59, 126.94, 126.92, 122.73, 119.83, 119.63, 85.13, 77.40, 52.51, 50.31, 50.24, 37.04, 23.78, 23.58, 22.77, 21.77, 20.45. **HRMS** (ESI) *m/z* calcd for $C_{27}H_{30}NO_4$ ($[M+H]^+$) 432.2169; found 432.2181.

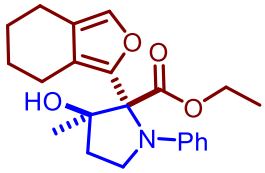



**methyl (2R,3S)-3-hydroxy-1,3-diphenyl-2-(4,5,6,7-tetrahydroisobenzofuran-1-yl)pyrrolidine-2-carboxylate (3k).** Synthesized using general procedure 3. Yellow solid. (32% NMR yield using 1,3,5-trimethoxybenzene as reference.) **TLC**: Rf 0.35 (ethyl acetate/hexanes = 1:4). **$^1$H NMR** ($CDCl_3$, 600 MHz) δ 7.25 – 7.18 (m, 3H), 7.17 – 7.11 (m, 4H), 6.86 (s, 1H), 6.72 (t, *J* = 7.4 Hz, 1H), 6.53 (d, *J* = 7.6 Hz, 2H), 4.04 (q, *J* = 8.3 Hz, 1H), 3.90 (d, *J* = 2.4 Hz, 1H), 3.82 (td, *J* = 8.8, 2.6 Hz, 1H), 3.74 (s, 3H), 2.70 (dt, *J* = 12.7, 8.8 Hz, 1H), 2.39 – 2.32 (m, 2H), 2.27 (ddd, *J* = 12.7, 7.2, 2.4 Hz, 1H), 2.20 – 2.07 (m, 1H), 1.47 – 1.31 (m, 4H), 1.23 – 1.16 (m, 1H). **$^{13}$C NMR** ($CDCl_3$, 100 MHz) δ 171.19, 146.88, 142.22,

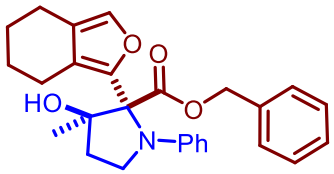
140.14, 136.39, 128.83, 127.71, 127.54, 126.24, 122.55, 121.88, 117.60, 113.64, 88.08, 78.10, 77.48, 77.16, 76.84, 52.68, 48.67, 36.21, 23.64, 22.75, 22.15, 20.49. **MS** (ESI) *m/z* calcd for $C_{26}H_{18}NO_4$ ($[M+H]^+$) 418.2; found 418.0.




**methyl (2R,3R)-3-benzyl-3-hydroxy-1-phenyl-2-(4,5,6,7-tetrahydroisobenzofuran-1-yl)pyrrolidine-2-carboxylate (3l).** Synthesized using general procedure 3. Colourless oil. (40% NMR yield using 1,3,5-trimethoxybenzene as reference.) **TLC**: Rf 0.35 (ethyl acetate/hexanes = 1:4). **$^1$H NMR** ($CDCl_3$, 400 MHz) δ 7.27 (q, *J* = 6.8 Hz, 3H), 7.23 – 7.17 (m, 3H), 7.12 (t, *J* = 7.7 Hz, 2H), 6.69 (t, *J* = 7.2 Hz, 1H), 6.48 (d, *J* = 8.1 Hz, 2H), 3.74 (s, 3H), δ 3.69 (t, *J* = 8.1 Hz, 1H), 3.63 (dt, *J* = 8.8, 4.3 Hz, 1H)., 2.95 (d, *J* = 13.8 Hz, 1H), 2.58 – 2.41 (m, 2H), 2.41 – 2.30 (m, 3H), 2.24 – 2.11 (m, 2H), 1.89 (ddd, *J* = 11.9, 7.1, 3.6 Hz, 1H), 1.62 (q, *J* = 9.7, 8.1 Hz, 1H), 1.55 (m, 4H). **$^{13}$C NMR** ($CDCl_3$, 100 MHz) δ 170.50, 146.71, 143.06, 136.99, 130.65, 129.56, 128.57, 128.40, 126.89, 122.74, 120.87, 117.06, 113.42, 87.69, 77.36, 52.40, 47.95, 41.85, 34.62, 23.63, 22.82, 22.21, 20.51. **MS** (ESI) *m/z* calcd for $C_{27}H_{30}NO_4$ ($[M+H]^+$) 432.2; found 432.0.

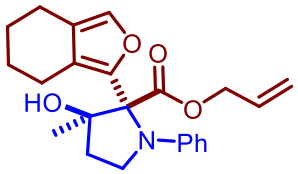



**Ethyl 3-hydroxy-3-methyl-1-phenyl-2-(4,5,6,7-tetrahydroisobenzofuran-1-yl)pyrrolidine-2-carboxylate (5a).** Synthesized using general procedure 3. Colourless oil. (51% NMR yield using 1,3,5-trimethoxybenzene as reference.) **TLC**: $R_f$ 0.45 (ethyl acetate/hexanes = 2:3). **$^1$H NMR** ($CDCl_3$, 400 MHz): δ 7.18 (s, 1H), 7.11 (t, J = 2.3 Hz, 2H), 6.68 (t, J = 7.3 Hz, 1H), 6.51 (d, J = 8.9 Hz, 1H), 4.30 – 4.04 (m, 2H), 3.80 – 3.67 (m, 1H), 3.59 (td, J = 8.6, 4.5 Hz, 1H), 2.72 (s, 1H), 2.51 – 2.41 (m, 3H), 2.28 (ddd, J = 12.1, 7.6, 4.5 Hz, 2H), 2.17 – 1.98 (m, 2H), 1.48 (d, J = 5.3 Hz, 4H), 1.17 – 1.08 (m, 6H). **$^{13}$C NMR** ($CDCl_3$, 100 MHz) δ 170.49, 147.02, 143.87, 136.71, 128.54, 122.53, 120.17, 117.15, 113.53, 85.94, 76.64, 61.59, 48.08, 37.22, 24.26, 23.59, 22.85, 21.94, 20.49, 14.14. **HRMS** (ESI) *m/z* calcd for $C_{22}H_{28}NO_4$ ($[M+H]^+$) 370.20185; found 370.2009.

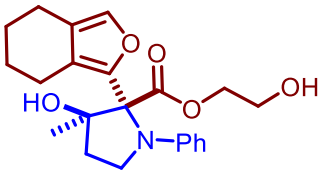



**Benzyl 3-hydroxy-3-methyl-1-phenyl-2-(4,5,6,7-tetrahydroisobenzofuran-1-yl)pyrrolidine-2-carboxylate (5b).** Synthesized using general procedure 3. Gray sold. (51% NMR yield using 1,3,5-trimethoxybenzene as reference.) **TLC**: $R_f$ 0.52 (ethyl acetate/hexanes = 2:3). **$^1$H NMR** ($CDCl_3$, 600 MHz): δ 7.25 – 7.19 (m, 4H), 7.10 (t, J = 7.9 Hz, 2H), 7.06 (d, J = 6.5 Hz, 2H), 6.70 (t, J = 7.2 Hz, 1H), 6.51 (d, J = 8.0 Hz, 2H), 5.19 (d, J = 12.5 Hz, 1H), 5.10 (d, J = 12.6 Hz, 1H), 3.78 – 3.67 (m, 1H), 3.64 – 3.56 (m, 1H), 2.55 (s, 1H), 2.47 (dq, J = 16.7, 9.0, 8.0 Hz, 2H), 2.22 (d, J = 18.3 Hz, 2H), 2.11 – 1.94 (m, 2H), 1.67 – 1.34 (m, 4H), 1.12 (s, 3H). **$^{13}$C NMR** ($CDCl_3$, 150 MHz) δ 170.36, 147.03, 143.76, 136.80, 135.54,

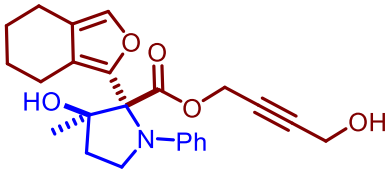
128.71, 128.44, 128.21, 128.07, 122.59, 120.19, 117.26, 113.51, 86.17, 67.24, 48.08, 37.22, 24.31, 23.56, 22.83, 21.87, 20.49. **HRMS** (ESI) *m/z* calcd for $C_{27}H_{30}NO_4$ ($[M+H]^+$) 432.2169; found 432.2181.




**Allyl 3-hydroxy-3-methyl-1-phenyl-2-(4,5,6,7-tetrahydroisobenzofuran-1-yl)pyrrolidine-2-carboxylate (5c).** Synthesized using general procedure 3. Colourless oil. (51% NMR yield using 1,3,5-trimethoxybenzene as reference.) **TLC**: $R_f$ 0.50 (ethyl acetate/hexanes = 3:7). **$^1$H NMR** ($CDCl_3$, 400 MHz): δ 7.18 (s, 1H), 7.11 (t, J = 2.3 Hz, 2H), 6.68 (t, J = 7.3 Hz, 1H), 6.51 (d, J = 8.9 Hz, 1H), 4.30 – 4.04 (m, 2H), 3.80 – 3.67 (m, 1H), 3.59 (td, J = 8.6, 4.5 Hz, 1H), 2.72 (s, 1H), 2.51 – 2.41 (m, 3H), 2.28 (ddd, J = 12.1, 7.6, 4.5 Hz, 2H), 2.17 – 1.98 (m, 2H), 1.48 (d, J = 5.3 Hz, 4H), 1.17 – 1.08 (m, 6H). **$^{13}$C NMR** ($CDCl_3$, 100 MHz) δ 170.49, 147.02, 143.87, 136.71, 128.54, 122.53, 120.17, 117.15, 113.53, 85.94, 76.64, 61.59, 48.08, 37.22, 24.26, 23.59, 22.85, 21.94, 20.49, 14.14. **HRMS** (ESI) *m/z* calcd for $C_{22}H_{28}NO_4$ ($[M+H]^+$) 370.20185; found 370.2009.

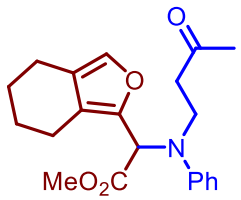



**2-Hydroxyethyl 3-hydroxy-3-methyl-1-phenyl-2-(4,5,6,7-tetrahydroisobenzofuran-1-yl)pyrrolidine-2-carboxylate (5d).** Synthesized using general procedure 3. Colourless oil. (45% NMR yield using 1,3,5-trimethoxybenzene as reference.) **TLC**: $R_f$ 0.12 (ethyl acetate/hexanes = 2:3). **$^1$H NMR** ($CD_3OD$, 400 MHz): δ 7.17 (s, 1H), 7.01 (t, J = 7.8 Hz, 2H), 6.58 (t, J = 7.2 Hz, 1H), 6.41 (d, J = 8.1 Hz, 2H), 4.27 – 4.09 (m, 2H), 3.74 (q, J = 8.0, 7.5 Hz, 1H), 3.68 – 3.49 (m, 3H), 2.44 (d, J = 5.6 Hz, 2H), 2.30 – 2.04 (m, 4H), 1.51 (d, J = 41.6 Hz, 4H), 1.11 (s, 3H). **$^{13}$C NMR** ($CD_3OD$, 100 MHz) δ 171.07, 148.15, 145.16, 137.60, 129.19, 123.71, 120.87, 117.52, 114.23, 87.08, 78.43, 67.05, 60.68, 48.67, 38.85, 24.66, 24.35, 23.96, 23.24, 21.33. **HRMS** (ESI) *m/z* calcd for $C_{22}H_{28}NO_5$ ($[M+H]^+$) 386.1968; found 386.1978.




**4-Hydroxybut-2-yn-1-yl 3-hydroxy-3-methyl-1-phenyl-2-(4,5,6,7-tetrahydroisobenzofuran-1-yl)pyrrolidine-2-carboxylate (5e).** Synthesized using general procedure 3. Colourless oil. (36% NMR yield using 1,3,5-trimethoxybenzene as reference.) **TLC**: $R_f$ 0.15 (ethyl acetate/hexanes = 2:3) **$^1$H NMR** ($CDCl_3$, 400 MHz): δ 7.19 (s, 1H), 7.13 (dd, J = 8.6, 7.2 Hz, 2H), 6.70 (dd, J = 8.0, 6.8 Hz, 1H), 6.57 – 6.43 (m, 2H), 4.76 (dt, J = 6.6, 1.9 Hz, 2H), 4.19 (s, 2H), 3.76 (q, J = 8.0 Hz, 1H), 3.62 (td, J = 8.6, 4.9 Hz, 1H), 2.65 (s, 1H), 2.59 – 2.45 (m, 2H), 2.37 – 2.22 (m, 2H), 2.17 – 2.00 (m, 2H), 1.78 – 1.66 (m, 4H), 1.55 – 1.46 (m, 3H), 1.11 (s, 3H). **$^{13}$C NMR** ($CDCl_3$, 100 MHz) ): δ 169.96, 146.90, 143.40, 136.85, 128.65, 122.60, 120.36, 117.24, 113.62, 86.34, 85.21, 79.75, 77.36, 52.91, 51.13, 48.19, 37.12, 24.43, 23.54, 22.81, 21.91, 20.46. **HRMS** (ESI) *m/z* calcd for $C_{24}H_{28}NO_5$ ($[M+H]^+$) 410.19677; found 410.1977.

## E. Synthesis of Insertion Product (4a)

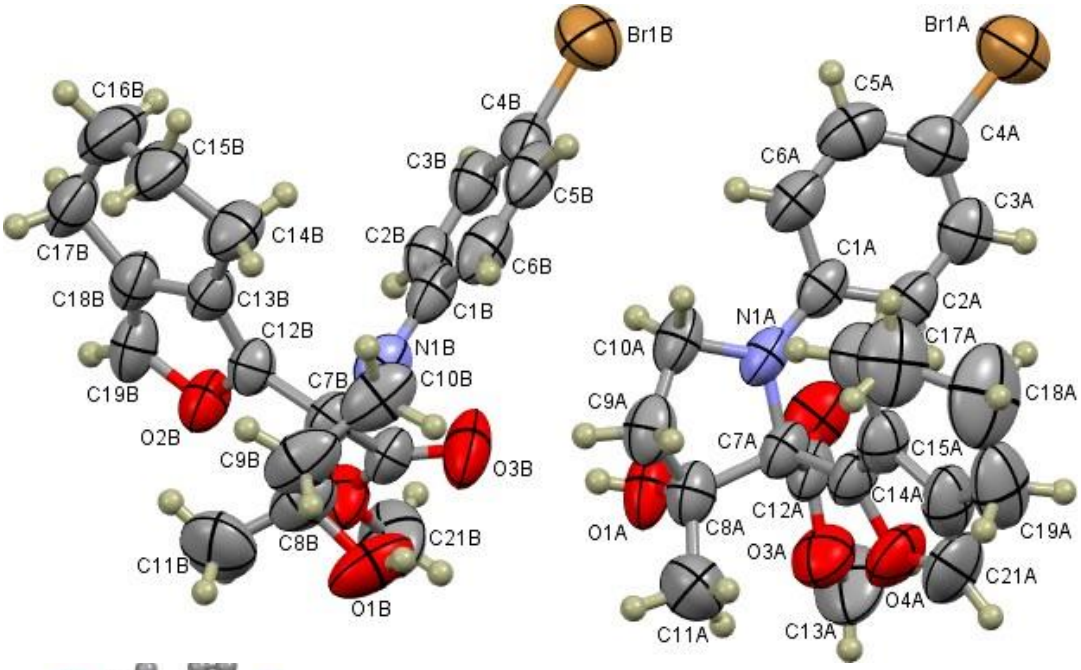



To a vial was added 4-(phenylamino)butan-2-one (50 µmol, 1 equiv.), the methyl 3-(2-formylcyclohex-1-en-1-yl)propiolate (85 µmol, 1.7 equiv.) and $Rh_2(OAc)_4$ (2.5 µmol, 0.05 equiv.). The reaction mixture was stirred for overnight at RT. The product was purified by flash chromatography 1:20 ethyl acetate:hexanes gradient to 1:9 ethyl acetate:hexanes to furnish insertion product (**4**) . Colourless oil. (23% NMR yield using 1,3,5-trimethoxybenzene as reference.) **TLC**: $R_f$ 0.67 (ethyl acetate/hexanes = 3:7). **$^1$H NMR** ($CDCl_3$, 400 MHz): ): δ 7.23 (d, J = 7.4 Hz, 2H), 7.14 (s, 1H), 6.79 (t, J = 7.3 Hz, 1H), 6.75 – 6.67 (m, 2H), 5.46 (s, 1H), 3.77 (s, 3H), 3.62 (dd, J = 15.3, 10.0, 5.1 Hz), 3.55 – 3.43 (m, 1H), 2.76 (dd, J = 15.7, 10.1, 5.4 Hz), 2.62 – 2.18 (m, 5H), 2.05 (s, 3H), 1.77 – 1.49 (m, 4H). **$^{13}$C NMR** ($CDCl_3$, 100 MHz) ): δ 208.47, 171.02, 147.40, 141.72, 137.44, 129.58, 122.80, 121.66, 118.34, 113.63, 77.36, 59.23, 52.69, 42.19, 41.98, 30.47, 23.06, 23.01, 20.34, 20.21. **HRMS** (ESI) *m/z* calcd for $C_{21}H_{25}NO_4Na$ ($[M+Na]^+$) 378.1682; found 378.1675.

**X-Ray Diffraction Data for 3b**

CCDC 2285842

Formula: C21 H24 Br N O4



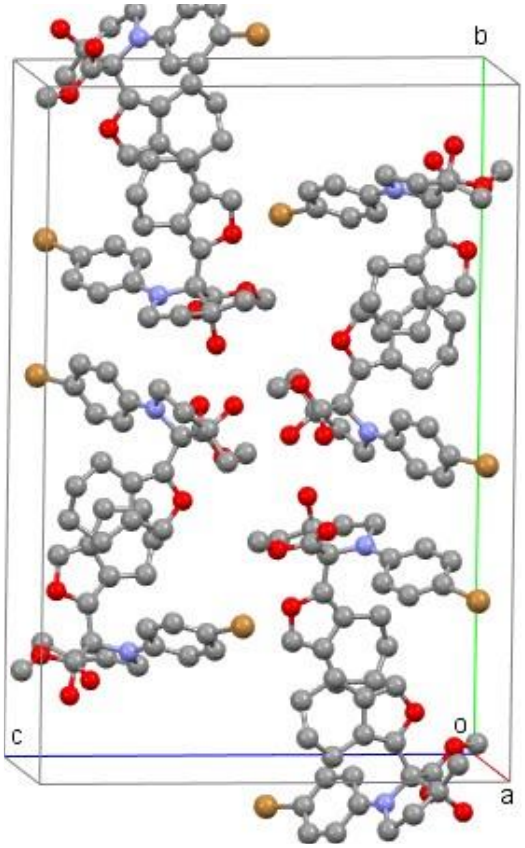



Table 1. Crystal data and structure refinement for **3b**.

| | | |
|---|---|---|
| Empirical formula | C21 H24 Br N O4 | |
| Formula weight | 434.32 | |
| Crystal system | monoclinic | |
| Space group | *P*2**1**/*c* | |
| Unit cell dimensions | *a* = 8.1671(2) Å | = 90° |
| | *b* = 26.8544(6) Å | = 91.4034(8)° |
| | *c* = 18.1446(5) Å | = 90° |
| Volume | 3978.33(17) Å$^3$ | |
| Z, Z' | 8, 1 | |
| Density (calculated) | 1.450 Mg/m$^3$ | |
| Wavelength | 0.71073 Å | |
| Temperature | 100(2) K | |
| *F*(000) | 1792 | |
| Absorption coefficient | 2.093 mm$^{-1}$ | |
| Absorption correction | semi-empirical from equivalents | |
| Max. and min. transmission | 0.7454 and 0.6379 | |
| Theta range for data collection | 2.246 to 26.389° | |
| Reflections collected | 69735 | |
| Independent reflections | 8148 [R(int) = 0.0610] | |
| Data / restraints / parameters | 8148 / 36 / 507 *wR*($F^2$ all data) | |
| | *wR*2 = 0.1041 | |
| *R*(*F* obsd data) | *R*1 = 0.0393 | |
| Goodness-of-fit on $F^2$ | 1.003 | |
| Observed data [I > 2 (I)] | 5833 | |
| Largest and mean shift / s.u ..... | 0.002 and 0.000 | |
| Largest diff. peak and hole | 0.543 and -0.613 e/Å$^3$ | |

---

$wR2 = \{ [w(F_o^2 - F_c^2)^2] / [w(F_o^2)^2] \}^{1/2}$

$R1 = ||F_o| - |F_c|| / |F_o|$

Table 2. Atomic coordinates and equivalent isotropic displacement parameters for **3b**. U(eq) is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| Br(1A) | -0.20072(5) | 0.73275(2) | 0.91177(2) | 0.06589(12) |
| O(1A) | 0.4714(3) | 0.60791(7) | 0.59708(13) | 0.0530(6) |
| O(2A) | 0.1154(3) | 0.64398(7) | 0.61266(12) | 0.0526(5) |
| O(3A) | 0.2479(3) | 0.67554(8) | 0.51713(11) | 0.0535(5) |
| O(4A) | 0.3690(3) | 0.76246(7) | 0.55788(12) | 0.0537(5) |
| N(1A) | 0.3570(3) | 0.67458(8) | 0.71279(12) | 0.0376(5) |
| C(1A) | 0.2296(3) | 0.68843(9) | 0.75639(15) | 0.0352(6) |
| C(2A) | 0.0965(3) | 0.71787(10) | 0.73104(16) | 0.0395(6) |
| C(3A) | -0.0279(4) | 0.73077(10) | 0.77677(17) | 0.0430(7) |
| C(4A) | -0.0254(4) | 0.71553(11) | 0.84940(17) | 0.0461(7) |
| C(5A) | 0.1036(4) | 0.68725(11) | 0.87622(17) | 0.0495(7) |
| C(6A) | 0.2281(4) | 0.67369(10) | 0.83064(16) | 0.0437(7) |
| C(7A) | 0.3745(3) | 0.68717(9) | 0.63498(15) | 0.0363(6) |
| C(8A) | 0.5321(3) | 0.65678(10) | 0.61392(16) | 0.0423(7) |
| C(9A) | 0.6300(3) | 0.65615(11) | 0.68590(17) | 0.0456(7) |
| C(10A) | 0.5025(3) | 0.64937(10) | 0.74392(16) | 0.0424(7) |
| C(11A) | 0.6256(4) | 0.67715(14) | 0.5499(2) | 0.0645(9) |
| C(12A) | 0.2292(4) | 0.66624(10) | 0.58817(15) | 0.0398(6) |
| C(13A) | 0.1185(5) | 0.65863(15) | 0.4670(2) | 0.0725(11) |
| C(14A) | 0.3958(3) | 0.74302(9) | 0.62713(16) | 0.0391(6) |
| C(15A) | 0.4395(3) | 0.77985(10) | 0.67507(17) | 0.0408(6) |
| C(16A) | 0.4820(4) | 0.78036(10) | 0.75610(18) | 0.0507(8) |
| C(17A) | 0.5696(7) | 0.82765(11) | 0.7783(3) | 0.0685(15) |
| C(17') | 0.472(4) | 0.82937(14) | 0.7953(5) | 0.068(2) |
| C(18A) | 0.4937(6) | 0.87382(12) | 0.7468(3) | 0.0858(13) |
| C(19A) | 0.4771(5) | 0.87526(11) | 0.6649(2) | 0.0660(10) |
| C(20A) | 0.4390(4) | 0.82517(10) | 0.6329(2) | 0.0504(8) |
| C(21A) | 0.3976(5) | 0.81248(11) | 0.5636(2) | 0.0629(10) |
| Br(1B) | 0.34468(5) | 0.56025(2) | 0.96800(2) | 0.06148(12) |
| O(1B) | 1.0232(3) | 0.54237(9) | 0.60044(13) | 0.0642(7) |
| O(2B) | 0.9273(2) | 0.40272(6) | 0.69898(10) | 0.0418(5) |
| O(3B) | 0.6744(3) | 0.52911(8) | 0.64606(12) | 0.0603(6) |
| O(4B) | 0.7736(2) | 0.45871(7) | 0.60203(10) | 0.0457(5) |
| N(1B) | 0.9059(3) | 0.53376(8) | 0.75829(13) | 0.0401(5) |
| C(1B) | 0.7758(3) | 0.54029(9) | 0.80394(15) | 0.0369(6) |
| C(2B) | 0.6469(3) | 0.50581(9) | 0.80690(15) | 0.0382(6) |

| | | | | |
|---|---|---|---|---|
| C(3B) | 0.5214(3) | 0.51195(9) | 0.85516(15) | 0.0395(6) |
| C(4B) | 0.5192(4) | 0.55282(10) | 0.90139(15) | 0.0426(7) |
| C(5B) | 0.6428(4) | 0.58764(10) | 0.89939(16) | 0.0457(7) |
| C(6B) | 0.7693(4) | 0.58147(10) | 0.85126(16) | 0.0443(7) |
| C(7B) | 0.9202(3) | 0.49438(9) | 0.70352(14) | 0.0345(6) |
| C(8B) | 1.0767(4) | 0.51038(12) | 0.65900(17) | 0.0491(7) |
| C(9B) | 1.1738(4) | 0.53904(13) | 0.71772(18) | 0.0563(9) |
| C(10B) | 1.0487(4) | 0.56680(11) | 0.76099(18) | 0.0523(8) |
| C(11B) | 1.1688(4) | 0.46812(14) | 0.6241(2) | 0.0696(10) |
| C(12B) | 0.9430(3) | 0.44469(9) | 0.74181(14) | 0.0332(6) |
| C(13B) | 0.9908(3) | 0.43176(9) | 0.81158(15) | 0.0350(6) |
| C(14B) | 1.0218(4) | 0.46200(11) | 0.88012(16) | 0.0474(7) |
| C(15B) | 1.1080(4) | 0.43155(12) | 0.94026(17) | 0.0560(8) |
| C(16B) | 1.0351(5) | 0.38053(13) | 0.94869(19) | 0.0622(9) |
| C(17B) | 1.0487(4) | 0.34846(11) | 0.88010(17) | 0.0503(8) |
| C(18B) | 1.0028(3) | 0.37834(10) | 0.81257(16) | 0.0399(6) |
| C(19B) | 0.9636(4) | 0.36303(10) | 0.74388(18) | 0.0470(7) |
| C(20B) | 0.7740(3) | 0.49645(9) | 0.64812(15) | 0.0364(6) |
| C(21B) | 0.6484(4) | 0.45903(15) | 0.54463(19) | 0.0698(11) |

Table 3. Bond lengths [Å] and angles [°] for **3b**.

| | | | |
|---|---|---|---|
| Br(1A)-C(4A) | 1.904(3) | C(16A)-H(16A) | 0.9900 |
| O(1A)-C(8A) | 1.433(3) | C(16A)-H(16B) | 0.9900 |
| O(1A)-H(1A) | 0.78(4) | C(16A)-H(16E) | 0.9900 |
| O(2A)-C(12A) | 1.200(3) | C(16A)-H(16F) | 0.9900 |
| O(3A)-C(12A) | 1.325(3) | C(17A)-C(18A) | 1.494(4) |
| O(3A)-C(13A) | 1.451(4) | C(17A)-H(17A) | 0.9900 |
| O(4A)-C(21A) | 1.367(4) | C(17A)-H(17B) | 0.9900 |
| O(4A)-C(14A) | 1.373(3) | C(17')-C(18A) | 1.496(5) |
| N(1A)-C(1A) | 1.374(4) | C(17')-H(17E) | 0.9900 |
| N(1A)-C(7A) | 1.462(3) | C(17')-H(17F) | 0.9900 |
| N(1A)-C(10A) | 1.468(3) | C(18A)-C(19A) | 1.489(6) |
| C(1A)-C(6A) | 1.405(4) | C(18A)-H(18A) | 0.9900 |
| C(1A)-C(2A) | 1.412(4) | C(18A)-H(18B) | 0.9900 |
| C(2A)-C(3A) | 1.372(4) | C(18A)-H(18C) | 0.9900 |
| C(2A)-H(2A) | 0.9500 | C(18A)-H(18D) | 0.9900 |
| C(3A)-C(4A) | 1.379(4) | C(19A)-C(20A) | 1.495(4) |
| C(3A)-H(3A) | 0.9500 | C(19A)-H(19A) | 0.9900 |
| C(4A)-C(5A) | 1.378(4) | C(19A)-H(19B) | 0.9900 |
| C(5A)-C(6A) | 1.375(4) | C(20A)-C(21A) | 1.337(5) |
| C(5A)-H(5A) | 0.9500 | C(21A)-H(21A) | 0.9500 |
| C(6A)-H(6A) | 0.9500 | Br(1B)-C(4B) | 1.902(3) |
| C(7A)-C(14A) | 1.517(3) | O(1B)-C(8B) | 1.427(4) |
| C(7A)-C(12A) | 1.548(4) | O(1B)-H(1B) | 0.76(4) |
| C(7A)-C(8A) | 1.579(4) | O(2B)-C(19B) | 1.370(3) |
| C(8A)-C(11A) | 1.509(4) | O(2B)-C(12B) | 1.373(3) |
| C(8A)-C(9A) | 1.515(4) | O(3B)-C(20B) | 1.196(3) |
| C(9A)-C(10A) | 1.510(4) | O(4B)-C(20B) | 1.314(3) |
| C(9A)-H(9AA) | 0.9900 | O(4B)-C(21B) | 1.442(3) |
| C(9A)-H(9AB) | 0.9900 | N(1B)-C(1B) | 1.375(4) |
| C(10A)-H(10A) | 0.9900 | N(1B)-C(7B) | 1.458(3) |
| C(10A)-H(10B) | 0.9900 | N(1B)-C(10B) | 1.465(3) |
| C(11A)-H(11A) | 0.9800 | C(1B)-C(6B) | 1.402(4) |
| C(11A)-H(11B) | 0.9800 | C(1B)-C(2B) | 1.404(4) |
| C(11A)-H(11C) | 0.9800 | C(2B)-C(3B) | 1.374(4) |
| C(13A)-H(13A) | 0.9800 | C(2B)-H(2B) | 0.9500 |
| C(13A)-H(13B) | 0.9800 | C(3B)-C(4B) | 1.382(4) |
| C(13A)-H(13C) | 0.9800 | C(3B)-H(3B) | 0.9500 |
| C(14A)-C(15A) | 1.359(4) | C(4B)-C(5B) | 1.377(4) |
| C(15A)-C(20A) | 1.438(4) | C(5B)-C(6B) | 1.379(4) |
| C(15A)-C(16A) | 1.502(4) | C(5B)-H(5B) | 0.9500 |

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| C(16A)-C(17') | 1.499(5) | C(6B)-H(6B) | 0.9500 |
| C(16A)-C(17A) | 1.507(4) | C(7B)-C(12B) | 1.514(3) |
| C(7B)-C(20B) | 1.543(4) | C(14B)-H(14A) | 0.9900 |
| C(7B)-C(8B) | 1.588(4) | C(14B)-H(14B) | 0.9900 |
| C(8B)-C(11B) | 1.510(5) | C(15B)-C(16B) | 1.503(5) |
| C(8B)-C(9B) | 1.521(4) | C(15B)-H(15A) | 0.9900 |
| C(9B)-C(10B) | 1.502(5) | C(15B)-H(15B) | 0.9900 |
| C(9B)-H(9BA) | 0.9900 | C(16B)-C(17B) | 1.520(5) |
| C(9B)-H(9BB) | 0.9900 | C(16B)-H(16C) | 0.9900 |
| C(10B)-H(10C) | 0.9900 | C(16B)-H(16D) | 0.9900 |
| C(10B)-H(10D) | 0.9900 | C(17B)-C(18B) | 1.505(4) |
| C(11B)-H(11D) | 0.9800 | C(17B)-H(17C) | 0.9900 |
| C(11B)-H(11E) | 0.9800 | C(17B)-H(17D) | 0.9900 |
| C(11B)-H(11F) | 0.9800 | C(18B)-C(19B) | 1.344(4) |
| C(12B)-C(13B) | 1.361(4) | C(19B)-H(19C) | 0.9500 |
| C(13B)-C(18B) | 1.438(4) | C(21B)-H(21B) | 0.9800 |
| C(13B)-C(14B) | 1.502(4) | C(21B)-H(21C) | 0.9800 |
| C(14B)-C(15B) | 1.522(4) | C(21B)-H(21D) | 0.9800 |

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|---|---|---|---|
| C(8A)-O(1A)-H(1A) | 106(3) | C(14A)-C(7A)-C(8A) | 113.1(2) |
| C(12A)-O(3A)-C(13A) | 116.8(3) | C(12A)-C(7A)-C(8A) | 107.3(2) |
| C(21A)-O(4A)-C(14A) | 106.3(2) | O(1A)-C(8A)-C(11A) | 110.3(3) |
| C(1A)-N(1A)-C(7A) | 125.9(2) | O(1A)-C(8A)-C(9A) | 110.3(2) |
| C(1A)-N(1A)-C(10A) | 121.4(2) | C(11A)-C(8A)-C(9A) | 113.7(3) |
| C(7A)-N(1A)-C(10A) | 112.4(2) | O(1A)-C(8A)-C(7A) | 104.2(2) |
| N(1A)-C(1A)-C(6A) | 120.0(2) | C(11A)-C(8A)-C(7A) | 115.5(2) |
| N(1A)-C(1A)-C(2A) | 123.5(2) | C(9A)-C(8A)-C(7A) | 102.3(2) |
| C(6A)-C(1A)-C(2A) | 116.5(3) | C(10A)-C(9A)-C(8A) | 104.1(2) |
| C(3A)-C(2A)-C(1A) | 121.3(3) | C(10A)-C(9A)-H(9AA) | 110.9 |
| C(3A)-C(2A)-H(2A) | 119.3 | C(8A)-C(9A)-H(9AA) | 110.9 |
| C(1A)-C(2A)-H(2A) | 119.3 | C(10A)-C(9A)-H(9AB) | 110.9 |
| C(2A)-C(3A)-C(4A) | 120.6(3) | C(8A)-C(9A)-H(9AB) | 110.9 |
| C(2A)-C(3A)-H(3A) | 119.7 | H(9AA)-C(9A)-H(9AB) | 108.9 |
| C(4A)-C(3A)-H(3A) | 119.7 | N(1A)-C(10A)-C(9A) | 104.0(2) |
| C(5A)-C(4A)-C(3A) | 119.6(3) | N(1A)-C(10A)-H(10A) | 111.0 |
| C(5A)-C(4A)-Br(1A) | 120.2(2) | C(9A)-C(10A)-H(10A) | 111.0 |
| C(3A)-C(4A)-Br(1A) | 120.1(2) | N(1A)-C(10A)-H(10B) | 111.0 |
| C(6A)-C(5A)-C(4A) | 120.2(3) | C(9A)-C(10A)-H(10B) | 111.0 |
| C(6A)-C(5A)-H(5A) | 119.9 | H(10A)-C(10A)-H(10B) | 109.0 |
| C(4A)-C(5A)-H(5A) | 119.9 | C(8A)-C(11A)-H(11A) | 109.5 |
| C(5A)-C(6A)-C(1A) | 121.7(3) | C(8A)-C(11A)-H(11B) | 109.5 |
| C(5A)-C(6A)-H(6A) | 119.1 | H(11A)-C(11A)-H(11B) | 109.5 |
| C(1A)-C(6A)-H(6A) | 119.1 | C(8A)-C(11A)-H(11C) | 109.5 |
| N(1A)-C(7A)-C(14A) | 109.5(2) | H(11A)-C(11A)-H(11C) | 109.5 |

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|---|---|---|---|
| N(1A)-C(7A)-C(12A) | 110.7(2) | H(11B)-C(11A)-H(11C) | 109.5 |
| C(14A)-C(7A)-C(12A) | 113.3(2) | O(2A)-C(12A)-O(3A) | 124.3(3) |
| N(1A)-C(7A)-C(8A) | 102.3(2) | O(2A)-C(12A)-C(7A) | 124.6(3) |
| O(3A)-C(12A)-C(7A) | 111.1(2) | C(17')-C(18A)-H(18C) | 105.6 |
| O(3A)-C(13A)-H(13A) | 109.5 | C(19A)-C(18A)-H(18D) | 105.6 |
| O(3A)-C(13A)-H(13B) | 109.5 | C(17')-C(18A)-H(18D) | 105.6 |
| H(13A)-C(13A)-H(13B) | 109.5 | H(18C)-C(18A)-H(18D) | 106.1 |
| O(3A)-C(13A)-H(13C) | 109.5 | C(18A)-C(19A)-C(20A) | 112.2(3) |
| H(13A)-C(13A)-H(13C) | 109.5 | C(18A)-C(19A)-H(19A) | 109.2 |
| H(13B)-C(13A)-H(13C) | 109.5 | C(20A)-C(19A)-H(19A) | 109.2 |
| C(15A)-C(14A)-O(4A) | 110.0(2) | C(18A)-C(19A)-H(19B) | 109.2 |
| C(15A)-C(14A)-C(7A) | 133.5(3) | C(20A)-C(19A)-H(19B) | 109.2 |
| O(4A)-C(14A)-C(7A) | 116.5(2) | H(19A)-C(19A)-H(19B) | 107.9 |
| C(14A)-C(15A)-C(20A) | 106.1(3) | C(21A)-C(20A)-C(15A) | 106.4(3) |
| C(14A)-C(15A)-C(16A) | 133.1(2) | C(21A)-C(20A)-C(19A) | 129.8(3) |
| C(20A)-C(15A)-C(16A) | 120.7(3) | C(15A)-C(20A)-C(19A) | 123.8(3) |
| C(17')-C(16A)-C(15A) | 117.3(6) | C(20A)-C(21A)-O(4A) | 111.2(3) |
| C(15A)-C(16A)-C(17A) | 111.4(3) | C(20A)-C(21A)-H(21A) | 124.4 |
| C(15A)-C(16A)-H(16A) | 109.3 | O(4A)-C(21A)-H(21A) | 124.4 |
| C(17A)-C(16A)-H(16A) | 109.3 | C(8B)-O(1B)-H(1B) | 108(3) |
| C(15A)-C(16A)-H(16B) | 109.3 | C(19B)-O(2B)-C(12B) | 106.6(2) |
| C(17A)-C(16A)-H(16B) | 109.3 | C(20B)-O(4B)-C(21B) | 116.5(2) |
| H(16A)-C(16A)-H(16B) | 108.0 | C(1B)-N(1B)-C(7B) | 125.4(2) |
| C(17')-C(16A)-H(16E) | 108.0 | C(1B)-N(1B)-C(10B) | 121.9(2) |
| C(15A)-C(16A)-H(16E) | 108.0 | C(7B)-N(1B)-C(10B) | 112.6(2) |
| C(17')-C(16A)-H(16F) | 108.0 | N(1B)-C(1B)-C(6B) | 120.7(3) |
| C(15A)-C(16A)-H(16F) | 108.0 | N(1B)-C(1B)-C(2B) | 122.0(2) |
| H(16E)-C(16A)-H(16F) | 107.2 | C(6B)-C(1B)-C(2B) | 117.2(3) |
| C(18A)-C(17A)-C(16A) | 114.0(3) | C(3B)-C(2B)-C(1B) | 121.1(2) |
| C(18A)-C(17A)-H(17A) | 108.7 | C(3B)-C(2B)-H(2B) | 119.4 |
| C(16A)-C(17A)-H(17A) | 108.7 | C(1B)-C(2B)-H(2B) | 119.4 |
| C(18A)-C(17A)-H(17B) | 108.7 | C(2B)-C(3B)-C(4B) | 120.2(3) |
| C(16A)-C(17A)-H(17B) | 108.7 | C(2B)-C(3B)-H(3B) | 119.9 |
| H(17A)-C(17A)-H(17B) | 107.6 | C(4B)-C(3B)-H(3B) | 119.9 |
| C(18A)-C(17')-C(16A) | 114.4(5) | C(5B)-C(4B)-C(3B) | 120.2(3) |
| C(18A)-C(17')-H(17E) | 108.7 | C(5B)-C(4B)-Br(1B) | 120.5(2) |
| C(16A)-C(17')-H(17E) | 108.7 | C(3B)-C(4B)-Br(1B) | 119.3(2) |
| C(18A)-C(17')-H(17F) | 108.7 | C(4B)-C(5B)-C(6B) | 119.7(3) |
| C(16A)-C(17')-H(17F) | 108.7 | C(4B)-C(5B)-H(5B) | 120.1 |
| H(17E)-C(17')-H(17F) | 107.6 | C(6B)-C(5B)-H(5B) | 120.1 |
| C(19A)-C(18A)-C(17A) | 115.5(4) | C(5B)-C(6B)-C(1B) | 121.5(3) |
| C(19A)-C(18A)-C(17') | 126.8(5) | C(5B)-C(6B)-H(6B) | 119.2 |
| C(19A)-C(18A)-H(18A) | 108.4 | C(1B)-C(6B)-H(6B) | 119.2 |
| C(17A)-C(18A)-H(18A) | 108.4 | N(1B)-C(7B)-C(12B) | 109.7(2) |

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| N(1A)-C(7A)-C(12A) | 110.7(2) | H(11B)-C(11A)-H(11C) | 109.5 |
| C(14A)-C(7A)-C(12A) | 113.3(2) | O(2A)-C(12A)-O(3A) | 124.3(3) |
| N(1A)-C(7A)-C(8A) | 102.3(2) | O(2A)-C(12A)-C(7A) | 124.6(3) |
| O(3A)-C(12A)-C(7A) | 111.1(2) | C(17')-C(18A)-H(18C) | 105.6 |
| O(3A)-C(13A)-H(13A) | 109.5 | C(19A)-C(18A)-H(18D) | 105.6 |
| O(3A)-C(13A)-H(13B) | 109.5 | C(17')-C(18A)-H(18D) | 105.6 |
| H(13A)-C(13A)-H(13B) | 109.5 | H(18C)-C(18A)-H(18D) | 106.1 |
| O(3A)-C(13A)-H(13C) | 109.5 | C(18A)-C(19A)-C(20A) | 112.2(3) |
| H(13A)-C(13A)-H(13C) | 109.5 | C(18A)-C(19A)-H(19A) | 109.2 |
| H(13B)-C(13A)-H(13C) | 109.5 | C(20A)-C(19A)-H(19A) | 109.2 |
| C(15A)-C(14A)-O(4A) | 110.0(2) | C(18A)-C(19A)-H(19B) | 109.2 |
| C(15A)-C(14A)-C(7A) | 133.5(3) | C(20A)-C(19A)-H(19B) | 109.2 |
| O(4A)-C(14A)-C(7A) | 116.5(2) | H(19A)-C(19A)-H(19B) | 107.9 |
| C(14A)-C(15A)-C(20A) | 106.1(3) | C(21A)-C(20A)-C(15A) | 106.4(3) |
| C(14A)-C(15A)-C(16A) | 133.1(2) | C(21A)-C(20A)-C(19A) | 129.8(3) |
| C(20A)-C(15A)-C(16A) | 120.7(3) | C(15A)-C(20A)-C(19A) | 123.8(3) |
| C(17')-C(16A)-C(15A) | 117.3(6) | C(20A)-C(21A)-O(4A) | 111.2(3) |
| C(15A)-C(16A)-C(17A) | 111.4(3) | C(20A)-C(21A)-H(21A) | 124.4 |
| C(15A)-C(16A)-H(16A) | 109.3 | O(4A)-C(21A)-H(21A) | 124.4 |
| C(17A)-C(16A)-H(16A) | 109.3 | C(8B)-O(1B)-H(1B) | 108(3) |
| C(15A)-C(16A)-H(16B) | 109.3 | C(19B)-O(2B)-C(12B) | 106.6(2) |
| C(17A)-C(16A)-H(16B) | 109.3 | C(20B)-O(4B)-C(21B) | 116.5(2) |
| H(16A)-C(16A)-H(16B) | 108.0 | C(1B)-N(1B)-C(7B) | 125.4(2) |
| C(17')-C(16A)-H(16E) | 108.0 | C(1B)-N(1B)-C(10B) | 121.9(2) |
| C(15A)-C(16A)-H(16E) | 108.0 | C(7B)-N(1B)-C(10B) | 112.6(2) |
| C(17')-C(16A)-H(16F) | 108.0 | N(1B)-C(1B)-C(6B) | 120.7(3) |
| C(15A)-C(16A)-H(16F) | 108.0 | N(1B)-C(1B)-C(2B) | 122.0(2) |
| H(16E)-C(16A)-H(16F) | 107.2 | C(6B)-C(1B)-C(2B) | 117.2(3) |
| C(18A)-C(17A)-C(16A) | 114.0(3) | C(3B)-C(2B)-C(1B) | 121.1(2) |
| C(18A)-C(17A)-H(17A) | 108.7 | C(3B)-C(2B)-H(2B) | 119.4 |
| C(16A)-C(17A)-H(17A) | 108.7 | C(1B)-C(2B)-H(2B) | 119.4 |
| C(18A)-C(17A)-H(17B) | 108.7 | C(2B)-C(3B)-C(4B) | 120.2(3) |
| C(16A)-C(17A)-H(17B) | 108.7 | C(2B)-C(3B)-H(3B) | 119.9 |
| H(17A)-C(17A)-H(17B) | 107.6 | C(4B)-C(3B)-H(3B) | 119.9 |
| C(18A)-C(17')-C(16A) | 114.4(5) | C(5B)-C(4B)-C(3B) | 120.2(3) |
| C(18A)-C(17')-H(17E) | 108.7 | C(5B)-C(4B)-Br(1B) | 120.5(2) |
| C(16A)-C(17')-H(17E) | 108.7 | C(3B)-C(4B)-Br(1B) | 119.3(2) |
| C(18A)-C(17')-H(17F) | 108.7 | C(4B)-C(5B)-C(6B) | 119.7(3) |
| C(16A)-C(17')-H(17F) | 108.7 | C(4B)-C(5B)-H(5B) | 120.1 |
| H(17E)-C(17')-H(17F) | 107.6 | C(6B)-C(5B)-H(5B) | 120.1 |
| C(19A)-C(18A)-C(17A) | 115.5(4) | C(5B)-C(6B)-C(1B) | 121.5(3) |
| C(19A)-C(18A)-C(17') | 126.8(5) | C(5B)-C(6B)-H(6B) | 119.2 |
| C(19A)-C(18A)-H(18A) | 108.4 | C(1B)-C(6B)-H(6B) | 119.2 |
| C(17A)-C(18A)-H(18A) | 108.4 | N(1B)-C(7B)-C(12B) | 109.7(2) |

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|---|---|---|---|
| C(19A)-C(18A)-H(18B) | 108.4 | N(1B)-C(7B)-C(20B) | 110.1(2) |
| C(17A)-C(18A)-H(18B) | 108.4 | C(12B)-C(7B)-C(20B) | 114.5(2) |
| H(18A)-C(18A)-H(18B) | 107.5 | N(1B)-C(7B)-C(8B) | 103.3(2) |
| C(19A)-C(18A)-H(18C) | 105.6 | C(12B)-C(7B)-C(8B) | 112.4(2) |
| C(20B)-C(7B)-C(8B) | 106.2(2) | C(15B)-C(14B)-H(14B) | 109.3 |
| O(1B)-C(8B)-C(11B) | 106.7(3) | H(14A)-C(14B)-H(14B) | 108.0 |
| O(1B)-C(8B)-C(9B) | 111.2(2) | C(16B)-C(15B)-C(14B) | 112.7(3) |
| C(11B)-C(8B)-C(9B) | 114.7(3) | C(16B)-C(15B)-H(15A) | 109.1 |
| O(1B)-C(8B)-C(7B) | 107.8(2) | C(14B)-C(15B)-H(15A) | 109.1 |
| C(11B)-C(8B)-C(7B) | 115.2(2) | C(16B)-C(15B)-H(15B) | 109.1 |
| C(9B)-C(8B)-C(7B) | 101.1(2) | C(14B)-C(15B)-H(15B) | 109.1 |
| C(10B)-C(9B)-C(8B) | 105.5(3) | H(15A)-C(15B)-H(15B) | 107.8 |
| C(10B)-C(9B)-H(9BA) | 110.6 | C(15B)-C(16B)-C(17B) | 113.3(3) |
| C(8B)-C(9B)-H(9BA) | 110.6 | C(15B)-C(16B)-H(16C) | 108.9 |
| C(10B)-C(9B)-H(9BB) | 110.6 | C(17B)-C(16B)-H(16C) | 108.9 |
| C(8B)-C(9B)-H(9BB) | 110.6 | C(15B)-C(16B)-H(16D) | 108.9 |
| H(9BA)-C(9B)-H(9BB) | 108.8 | C(17B)-C(16B)-H(16D) | 108.9 |
| N(1B)-C(10B)-C(9B) | 103.5(2) | H(16C)-C(16B)-H(16D) | 107.7 |
| N(1B)-C(10B)-H(10C) | 111.1 | C(18B)-C(17B)-C(16B) | 110.1(2) |
| C(9B)-C(10B)-H(10C) | 111.1 | C(18B)-C(17B)-H(17C) | 109.6 |
| N(1B)-C(10B)-H(10D) | 111.1 | C(16B)-C(17B)-H(17C) | 109.6 |
| C(9B)-C(10B)-H(10D) | 111.1 | C(18B)-C(17B)-H(17D) | 109.6 |
| H(10C)-C(10B)-H(10D) | 109.0 | C(16B)-C(17B)-H(17D) | 109.6 |
| C(8B)-C(11B)-H(11D) | 109.5 | H(17C)-C(17B)-H(17D) | 108.2 |
| C(8B)-C(11B)-H(11E) | 109.5 | C(19B)-C(18B)-C(13B) | 106.2(2) |
| H(11D)-C(11B)-H(11E) | 109.5 | C(19B)-C(18B)-C(17B) | 129.9(3) |
| C(8B)-C(11B)-H(11F) | 109.5 | C(13B)-C(18B)-C(17B) | 123.9(3) |
| H(11D)-C(11B)-H(11F) | 109.5 | C(18B)-C(19B)-O(2B) | 110.9(2) |
| H(11E)-C(11B)-H(11F) | 109.5 | C(18B)-C(19B)-H(19C) | 124.6 |
| C(13B)-C(12B)-O(2B) | 109.7(2) | O(2B)-C(19B)-H(19C) | 124.6 |
| C(13B)-C(12B)-C(7B) | 132.9(2) | O(3B)-C(20B)-O(4B) | 123.7(3) |
| O(2B)-C(12B)-C(7B) | 117.1(2) | O(3B)-C(20B)-C(7B) | 124.2(3) |
| C(12B)-C(13B)-C(18B) | 106.5(2) | O(4B)-C(20B)-C(7B) | 112.1(2) |
| C(12B)-C(13B)-C(14B) | 132.2(2) | O(4B)-C(21B)-H(21B) | 109.5 |
| C(18B)-C(13B)-C(14B) | 121.3(2) | O(4B)-C(21B)-H(21C) | 109.5 |
| C(13B)-C(14B)-C(15B) | 111.6(2) | H(21B)-C(21B)-H(21C) | 109.5 |
| C(13B)-C(14B)-H(14A) | 109.3 | O(4B)-C(21B)-H(21D) | 109.5 |
| C(15B)-C(14B)-H(14A) | 109.3 | H(21B)-C(21B)-H(21D) | 109.5 |
| C(13B)-C(14B)-H(14B) | 109.3 | H(21C)-C(21B)-H(21D) | 109.5 |

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **3b**. The anisotropic displacement factor exponent takes the form:
$-2\ ^2[\ h^2\ a^{*2}\ U_{11} + ... + 2\ h\ k\ a^*\ b^*\ U_{12}]$

| | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
|---|---|---|---|---|---|---|
| Br(1A) | 66(1) | 66(1) | 66(1) | -5(1) | 15(1) | -1(1) |
| O(1A) | 59(1) | 32(1) | 67(2) | -7(1) | -23(1) | 12(1) |
| O(2A) | 57(1) | 41(1) | 59(1) | 4(1) | -14(1) | -13(1) |
| O(3A) | 63(1) | 56(1) | 40(1) | 0(1) | -12(1) | 6(1) |
| O(4A) | 77(2) | 34(1) | 50(1) | 14(1) | -3(1) | 3(1) |
| N(1A) | 43(1) | 31(1) | 38(1) | 8(1) | -10(1) | 2(1) |
| C(1A) | 42(2) | 24(1) | 39(2) | 4(1) | -9(1) | -6(1) |
| C(2A) | 45(2) | 31(1) | 42(2) | 6(1) | -9(1) | -4(1) |
| C(3A) | 44(2) | 31(1) | 54(2) | 1(1) | -5(1) | -5(1) |
| C(4A) | 50(2) | 37(2) | 52(2) | -1(1) | 5(1) | -10(1) |
| C(5A) | 61(2) | 44(2) | 43(2) | 8(1) | -3(2) | -10(2) |
| C(6A) | 49(2) | 38(2) | 44(2) | 10(1) | -8(1) | -3(1) |
| C(7A) | 43(2) | 27(1) | 39(2) | 5(1) | -6(1) | 1(1) |
| C(8A) | 45(2) | 31(1) | 50(2) | 1(1) | -5(1) | 4(1) |
| C(9A) | 40(2) | 40(2) | 56(2) | 0(1) | -13(1) | 2(1) |
| C(10A) | 43(2) | 34(1) | 49(2) | 5(1) | -16(1) | 3(1) |
| C(11A) | 59(2) | 71(2) | 65(2) | 7(2) | 13(2) | 11(2) |
| C(12A) | 50(2) | 29(1) | 40(2) | 2(1) | -10(1) | 9(1) |
| C(13A) | 80(3) | 82(3) | 53(2) | -12(2) | -33(2) | 16(2) |
| C(14A) | 46(2) | 28(1) | 43(2) | 9(1) | 0(1) | 3(1) |
| C(15A) | 38(2) | 28(1) | 56(2) | 4(1) | 3(1) | -2(1) |
| C(16A) | 53(2) | 38(2) | 61(2) | -5(1) | -5(2) | -8(1) |
| C(17A) | 65(3) | 46(2) | 93(3) | -11(2) | -16(3) | -11(2) |
| C(17') | 64(5) | 47(3) | 92(4) | -15(3) | -14(4) | -9(4) |
| C(18A) | 97(3) | 36(2) | 123(3) | -14(2) | -24(3) | -7(2) |
| C(19A) | 62(2) | 30(2) | 107(3) | 0(2) | 12(2) | -1(2) |
| C(20A) | 48(2) | 28(1) | 76(2) | 9(2) | 9(2) | 1(1) |
| C(21A) | 84(3) | 32(2) | 73(3) | 20(2) | 7(2) | 4(2) |
| Br(1B) | 81(1) | 51(1) | 52(1) | -11(1) | 10(1) | 8(1) |
| O(1B) | 89(2) | 54(1) | 49(1) | 20(1) | -13(1) | -26(1) |
| O(2B) | 51(1) | 31(1) | 43(1) | 2(1) | -10(1) | 4(1) |
| O(3B) | 75(2) | 46(1) | 59(1) | -5(1) | -24(1) | 27(1) |
| O(4B) | 50(1) | 46(1) | 40(1) | -7(1) | -15(1) | 12(1) |
| N(1B) | 46(1) | 28(1) | 46(1) | 1(1) | -7(1) | -10(1) |
| C(1B) | 48(2) | 24(1) | 38(2) | 3(1) | -14(1) | 0(1) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C(2B) | 46(2) | 24(1) | 44(2) | -4(1) | -7(1) | 1(1) |
| C(3B) | 47(2) | 27(1) | 44(2) | -1(1) | -9(1) | 1(1) |
| C(4B) | 56(2) | 35(2) | 36(2) | -1(1) | -7(1) | 10(1) |
| C(5B) | 71(2) | 26(1) | 39(2) | -5(1) | -17(2) | 5(1) |
| C(6B) | 62(2) | 25(1) | 45(2) | -1(1) | -18(2) | -4(1) |
| C(7B) | 38(1) | 28(1) | 38(2) | 5(1) | -5(1) | -4(1) |
| C(8B) | 47(2) | 50(2) | 50(2) | 15(1) | -3(1) | -12(1) |
| C(9B) | 46(2) | 64(2) | 58(2) | 21(2) | -9(2) | -21(2) |
| C(10B) | 59(2) | 44(2) | 53(2) | 10(1) | -16(2) | -24(2) |
| C(11B) | 53(2) | 77(3) | 80(3) | 10(2) | 24(2) | -3(2) |
| C(12B) | 33(1) | 28(1) | 39(2) | 1(1) | -4(1) | -1(1) |
| C(13B) | 34(1) | 32(1) | 39(2) | 9(1) | -1(1) | 0(1) |
| C(14B) | 57(2) | 47(2) | 38(2) | 4(1) | -9(1) | 1(1) |
| C(15B) | 69(2) | 60(2) | 39(2) | 10(2) | -10(2) | 6(2) |
| C(16B) | 67(2) | 69(2) | 51(2) | 26(2) | -1(2) | 2(2) |
| C(17B) | 48(2) | 45(2) | 57(2) | 22(2) | -3(1) | 5(1) |
| C(18B) | 35(1) | 37(1) | 48(2) | 11(1) | -1(1) | 3(1) |
| C(19B) | 50(2) | 29(1) | 62(2) | 7(1) | -7(2) | 5(1) |
| C(20B) | 40(2) | 30(1) | 39(2) | 7(1) | -3(1) | 3(1) |
| C(21B) | 68(2) | 89(3) | 51(2) | -17(2) | -30(2) | 22(2) |

Table 5. Hydrogen coordinates and isotropic displacement parameters for **3b**.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(1A) | 0.540(4) | 0.5894(13) | 0.610(2) | 0.064 |
| H(2A) | 0.093028 | 0.728979 | 0.681315 | 0.047 |
| H(3A) | -0.116604 | 0.750367 | 0.758260 | 0.052 |
| H(5A) | 0.106573 | 0.677071 | 0.926382 | 0.059 |
| H(6A) | 0.315462 | 0.653833 | 0.849889 | 0.052 |
| H(9AA) | 0.709340 | 0.628273 | 0.686994 | 0.055 |
| H(9AB) | 0.690123 | 0.687831 | 0.693312 | 0.055 |
| H(10A) | 0.480303 | 0.613614 | 0.752435 | 0.051 |
| H(10B) | 0.538358 | 0.664899 | 0.791099 | 0.051 |
| H(11A) | 0.554801 | 0.677106 | 0.505480 | 0.097 |
| H(11B) | 0.721869 | 0.656281 | 0.541637 | 0.097 |
| H(11C) | 0.660814 | 0.711281 | 0.560918 | 0.097 |
| H(13A) | 0.018998 | 0.678046 | 0.475085 | 0.109 |
| H(13B) | 0.096442 | 0.623302 | 0.475917 | 0.109 |
| H(13C) | 0.152760 | 0.663113 | 0.415998 | 0.109 |
| H(16A) | 0.552703 | 0.751420 | 0.768300 | 0.061 |
| H(16B) | 0.380459 | 0.777231 | 0.784438 | 0.061 |
| H(16E) | 0.408165 | 0.756738 | 0.780797 | 0.061 |
| H(16F) | 0.594934 | 0.767446 | 0.762767 | 0.061 |
| H(17A) | 0.571815 | 0.830196 | 0.832704 | 0.082 |
| H(17B) | 0.684414 | 0.825586 | 0.762218 | 0.082 |
| H(17E) | 0.364814 | 0.831775 | 0.818953 | 0.082 |
| H(17F) | 0.558007 | 0.830182 | 0.834905 | 0.082 |
| H(18A) | 0.383467 | 0.877755 | 0.767562 | 0.103 |
| H(18B) | 0.560339 | 0.902734 | 0.763203 | 0.103 |
| H(18C) | 0.416208 | 0.899139 | 0.764843 | 0.103 |
| H(18D) | 0.604776 | 0.886706 | 0.758687 | 0.103 |
| H(19A) | 0.580436 | 0.887731 | 0.644288 | 0.079 |
| H(19B) | 0.388692 | 0.898804 | 0.650487 | 0.079 |
| H(21A) | 0.389173 | 0.835249 | 0.523667 | 0.076 |
| H(1B) | 1.032(5) | 0.5693(15) | 0.614(2) | 0.077 |
| H(2B) | 0.646393 | 0.477760 | 0.774987 | 0.046 |
| H(3B) | 0.435897 | 0.488012 | 0.856753 | 0.047 |
| H(5B) | 0.640914 | 0.615800 | 0.931052 | 0.055 |
| H(6B) | 0.853969 | 0.605686 | 0.850148 | 0.053 |
| H(9BA) | 1.236849 | 0.515921 | 0.750046 | 0.068 |
| H(9BB) | 1.250864 | 0.562490 | 0.694718 | 0.068 |

| | | | | |
|---|---|---|---|---|
| H(10C) | 1.087738 | 0.572295 | 0.812429 | 0.063 |
| H(10D) | 1.022812 | 0.599384 | 0.737989 | 0.063 |
| H(11D) | 1.098841 | 0.452223 | 0.586268 | 0.104 |
| H(11E) | 1.199670 | 0.443596 | 0.661928 | 0.104 |
| H(11F) | 1.267740 | 0.481108 | 0.601371 | 0.104 |
| H(14A) | 0.916246 | 0.474400 | 0.898511 | 0.057 |
| H(14B) | 1.090174 | 0.491200 | 0.868093 | 0.057 |
| H(15A) | 1.225203 | 0.428187 | 0.928475 | 0.067 |
| H(15B) | 1.101373 | 0.449560 | 0.987696 | 0.067 |
| H(16C) | 0.918001 | 0.383989 | 0.960688 | 0.075 |
| H(16D) | 1.090995 | 0.363435 | 0.990573 | 0.075 |
| H(17C) | 1.162404 | 0.336109 | 0.876205 | 0.060 |
| H(17D) | 0.975151 | 0.319319 | 0.883749 | 0.060 |
| H(19C) | 0.961294 | 0.329211 | 0.728517 | 0.056 |
| H(21B) | 0.673919 | 0.433870 | 0.507512 | 0.105 |
| H(21C) | 0.644055 | 0.491976 | 0.521424 | 0.105 |
| H(21D) | 0.542115 | 0.451469 | 0.565917 | 0.105 |

Table 6. Torsion angles [°] for **3b**.

| | |
|---|---|
| C(7A)-N(1A)-C(1A)-C(6A) | 180.0(2) |
| C(10A)-N(1A)-C(1A)-C(6A) | -7.1(4) |
| C(7A)-N(1A)-C(1A)-C(2A) | -0.8(4) |
| C(10A)-N(1A)-C(1A)-C(2A) | 172.2(2) |
| N(1A)-C(1A)-C(2A)-C(3A) | -179.9(2) |
| C(6A)-C(1A)-C(2A)-C(3A) | -0.7(4) |
| C(1A)-C(2A)-C(3A)-C(4A) | 0.6(4) |
| C(2A)-C(3A)-C(4A)-C(5A) | 0.2(4) |
| C(2A)-C(3A)-C(4A)-Br(1A) | -178.9(2) |
| C(3A)-C(4A)-C(5A)-C(6A) | -0.9(4) |
| Br(1A)-C(4A)-C(5A)-C(6A) | 178.3(2) |
| C(4A)-C(5A)-C(6A)-C(1A) | 0.8(4) |
| N(1A)-C(1A)-C(6A)-C(5A) | 179.3(3) |
| C(2A)-C(1A)-C(6A)-C(5A) | 0.0(4) |
| C(1A)-N(1A)-C(7A)-C(14A) | 65.3(3) |
| C(10A)-N(1A)-C(7A)-C(14A) | -108.2(2) |
| C(1A)-N(1A)-C(7A)-C(12A) | -60.3(3) |
| C(10A)-N(1A)-C(7A)-C(12A) | 126.2(2) |
| C(1A)-N(1A)-C(7A)-C(8A) | -174.5(2) |
| C(10A)-N(1A)-C(7A)-C(8A) | 12.1(3) |
| N(1A)-C(7A)-C(8A)-O(1A) | 84.0(2) |
| C(14A)-C(7A)-C(8A)-O(1A) | -158.4(2) |
| C(12A)-C(7A)-C(8A)-O(1A) | -32.7(3) |
| N(1A)-C(7A)-C(8A)-C(11A) | -154.9(3) |
| C(14A)-C(7A)-C(8A)-C(11A) | -37.3(3) |
| C(12A)-C(7A)-C(8A)-C(11A) | 88.4(3) |
| N(1A)-C(7A)-C(8A)-C(9A) | -30.9(3) |
| C(14A)-C(7A)-C(8A)-C(9A) | 86.8(3) |
| C(12A)-C(7A)-C(8A)-C(9A) | -147.5(2) |
| O(1A)-C(8A)-C(9A)-C(10A) | -71.6(3) |
| C(11A)-C(8A)-C(9A)-C(10A) | 164.0(3) |
| C(7A)-C(8A)-C(9A)-C(10A) | 38.8(3) |
| C(1A)-N(1A)-C(10A)-C(9A) | -162.1(2) |
| C(7A)-N(1A)-C(10A)-C(9A) | 11.7(3) |
| C(8A)-C(9A)-C(10A)-N(1A) | -31.7(3) |
| C(13A)-O(3A)-C(12A)-O(2A) | 1.9(4) |
| C(13A)-O(3A)-C(12A)-C(7A) | -179.0(2) |
| N(1A)-C(7A)-C(12A)-O(2A) | 2.0(4) |
| C(14A)-C(7A)-C(12A)-O(2A) | -121.5(3) |
| C(8A)-C(7A)-C(12A)-O(2A) | 113.0(3) |
| N(1A)-C(7A)-C(12A)-O(3A) | -177.2(2) |
| C(14A)-C(7A)-C(12A)-O(3A) | 59.4(3) |

| | |
|---|---|
| C(8A)-C(7A)-C(12A)-O(3A) | -66.2(3) |
| C(21A)-O(4A)-C(14A)-C(15A) | 0.2(3) |
| C(21A)-O(4A)-C(14A)-C(7A) | -179.0(3) |
| N(1A)-C(7A)-C(14A)-C(15A) | 18.4(4) |
| C(12A)-C(7A)-C(14A)-C(15A) | 142.5(3) |
| C(8A)-C(7A)-C(14A)-C(15A) | -95.0(4) |
| N(1A)-C(7A)-C(14A)-O(4A) | -162.7(2) |
| C(12A)-C(7A)-C(14A)-O(4A) | -38.5(3) |
| C(8A)-C(7A)-C(14A)-O(4A) | 83.9(3) |
| O(4A)-C(14A)-C(15A)-C(20A) | 0.3(3) |
| C(7A)-C(14A)-C(15A)-C(20A) | 179.3(3) |
| O(4A)-C(14A)-C(15A)-C(16A) | 179.8(3) |
| C(7A)-C(14A)-C(15A)-C(16A) | -1.2(6) |
| C(14A)-C(15A)-C(16A)-C(17') | -161.0(12) |
| C(20A)-C(15A)-C(16A)-C(17') | 18.4(12) |
| C(14A)-C(15A)-C(16A)-C(17A) | 162.9(4) |
| C(20A)-C(15A)-C(16A)-C(17A) | -17.6(5) |
| C(15A)-C(16A)-C(17A)-C(18A) | 45.2(6) |
| C(15A)-C(16A)-C(17')-C(18A) | -25(2) |
| C(16A)-C(17A)-C(18A)-C(19A) | -56.9(7) |
| C(16A)-C(17')-C(18A)-C(19A) | 18(3) |
| C(17A)-C(18A)-C(19A)-C(20A) | 35.6(5) |
| C(17')-C(18A)-C(19A)-C(20A) | -1.5(14) |
| C(14A)-C(15A)-C(20A)-C(21A) | -0.7(4) |
| C(16A)-C(15A)-C(20A)-C(21A) | 179.7(3) |
| C(14A)-C(15A)-C(20A)-C(19A) | 178.7(3) |
| C(16A)-C(15A)-C(20A)-C(19A) | -0.9(5) |
| C(18A)-C(19A)-C(20A)-C(21A) | 171.6(4) |
| C(18A)-C(19A)-C(20A)-C(15A) | -7.6(5) |
| C(15A)-C(20A)-C(21A)-O(4A) | 0.8(4) |
| C(19A)-C(20A)-C(21A)-O(4A) | -178.5(3) |
| C(14A)-O(4A)-C(21A)-C(20A) | -0.7(4) |
| C(7B)-N(1B)-C(1B)-C(6B) | -175.6(2) |
| C(10B)-N(1B)-C(1B)-C(6B) | 5.0(4) |
| C(7B)-N(1B)-C(1B)-C(2B) | 6.2(4) |
| C(10B)-N(1B)-C(1B)-C(2B) | -173.2(3) |
| N(1B)-C(1B)-C(2B)-C(3B) | 177.2(2) |
| C(6B)-C(1B)-C(2B)-C(3B) | -1.1(4) |
| C(1B)-C(2B)-C(3B)-C(4B) | 0.7(4) |
| C(2B)-C(3B)-C(4B)-C(5B) | 0.0(4) |
| C(2B)-C(3B)-C(4B)-Br(1B) | -179.7(2) |
| C(3B)-C(4B)-C(5B)-C(6B) | -0.3(4) |
| Br(1B)-C(4B)-C(5B)-C(6B) | 179.4(2) |
| C(4B)-C(5B)-C(6B)-C(1B) | -0.1(4) |
| N(1B)-C(1B)-C(6B)-C(5B) | -177.5(3) |

| | |
|---|---|
| C(2B)-C(1B)-C(6B)-C(5B) | 0.8(4) |
| C(1B)-N(1B)-C(7B)-C(12B) | -69.3(3) |
| C(10B)-N(1B)-C(7B)-C(12B) | 110.2(2) |
| C(1B)-N(1B)-C(7B)-C(20B) | 57.7(3) |
| C(10B)-N(1B)-C(7B)-C(20B) | -122.9(2) |
| C(1B)-N(1B)-C(7B)-C(8B) | 170.7(2) |
| C(10B)-N(1B)-C(7B)-C(8B) | -9.8(3) |
| N(1B)-C(7B)-C(8B)-O(1B) | -88.3(3) |
| C(12B)-C(7B)-C(8B)-O(1B) | 153.5(2) |
| C(20B)-C(7B)-C(8B)-O(1B) | 27.6(3) |
| N(1B)-C(7B)-C(8B)-C(11B) | 152.7(3) |
| C(12B)-C(7B)-C(8B)-C(11B) | 34.6(4) |
| C(20B)-C(7B)-C(8B)-C(11B) | -91.4(3) |
| N(1B)-C(7B)-C(8B)-C(9B) | 28.5(3) |
| C(12B)-C(7B)-C(8B)-C(9B) | -89.7(3) |
| C(20B)-C(7B)-C(8B)-C(9B) | 144.4(2) |
| O(1B)-C(8B)-C(9B)-C(10B) | 76.7(3) |
| C(11B)-C(8B)-C(9B)-C(10B) | -162.1(3) |
| C(7B)-C(8B)-C(9B)-C(10B) | -37.5(3) |
| C(1B)-N(1B)-C(10B)-C(9B) | 166.1(2) |
| C(7B)-N(1B)-C(10B)-C(9B) | -13.4(3) |
| C(8B)-C(9B)-C(10B)-N(1B) | 32.2(3) |
| C(19B)-O(2B)-C(12B)-C(13B) | 1.1(3) |
| C(19B)-O(2B)-C(12B)-C(7B) | 176.0(2) |
| N(1B)-C(7B)-C(12B)-C(13B) | -18.6(4) |
| C(20B)-C(7B)-C(12B)-C(13B) | -143.1(3) |
| C(8B)-C(7B)-C(12B)-C(13B) | 95.7(3) |
| N(1B)-C(7B)-C(12B)-O(2B) | 167.9(2) |
| C(20B)-C(7B)-C(12B)-O(2B) | 43.5(3) |
| C(8B)-C(7B)-C(12B)-O(2B) | -77.8(3) |
| O(2B)-C(12B)-C(13B)-C(18B) | -1.1(3) |
| C(7B)-C(12B)-C(13B)-C(18B) | -174.9(3) |
| O(2B)-C(12B)-C(13B)-C(14B) | -178.3(3) |
| C(7B)-C(12B)-C(13B)-C(14B) | 7.9(5) |
| C(12B)-C(13B)-C(14B)-C(15B) | -167.9(3) |
| C(18B)-C(13B)-C(14B)-C(15B) | 15.3(4) |
| C(13B)-C(14B)-C(15B)-C(16B) | -44.7(4) |
| C(14B)-C(15B)-C(16B)-C(17B) | 62.4(4) |
| C(15B)-C(16B)-C(17B)-C(18B) | -44.7(4) |
| C(12B)-C(13B)-C(18B)-C(19B) | 0.7(3) |
| C(14B)-C(13B)-C(18B)-C(19B) | 178.3(3) |
| C(12B)-C(13B)-C(18B)-C(17B) | -178.5(3) |
| C(14B)-C(13B)-C(18B)-C(17B) | -1.0(4) |
| C(16B)-C(17B)-C(18B)-C(19B) | -163.9(3) |
| C(16B)-C(17B)-C(18B)-C(13B) | 15.2(4) |

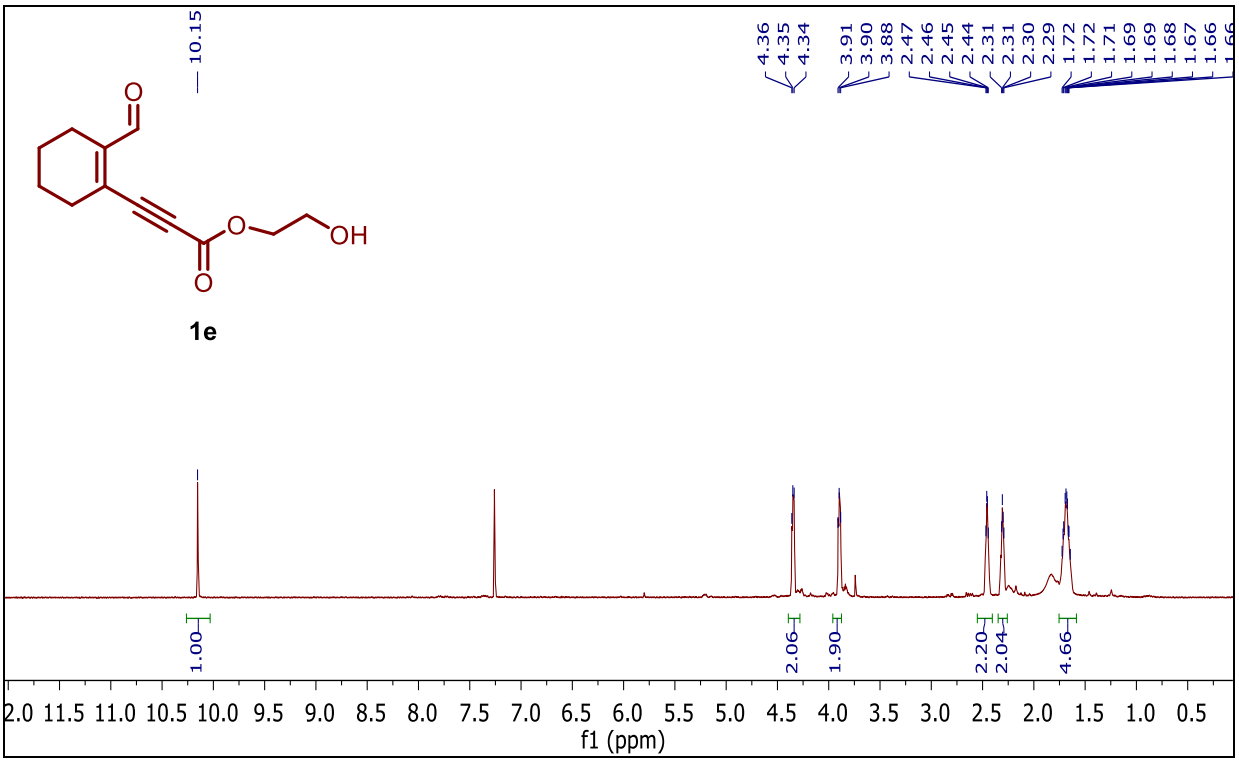
| | |
|---|---|
| C(13B)-C(18B)-C(19B)-O(2B) | 0.0(3) |
| C(17B)-C(18B)-C(19B)-O(2B) | 179.1(3) |
| C(12B)-O(2B)-C(19B)-C(18B) | -0.6(3) |
| C(21B)-O(4B)-C(20B)-O(3B) | 2.7(4) |
| C(21B)-O(4B)-C(20B)-C(7B) | -175.7(3) |
| N(1B)-C(7B)-C(20B)-O(3B) | 7.7(4) |
| C(12B)-C(7B)-C(20B)-O(3B) | 132.0(3) |
| C(8B)-C(7B)-C(20B)-O(3B) | -103.4(3) |
| N(1B)-C(7B)-C(20B)-O(4B) | -173.9(2) |
| C(12B)-C(7B)-C(20B)-O(4B) | -49.6(3) |
| C(8B)-C(7B)-C(20B)-O(4B) | 75.0(3) |

Table 7. Hydrogen bonds for **3b** [Å and °].

| D-H...A | d(D-H) | d(H...A) | d(D...A) | <(DHA) |
|---|---|---|---|---|
| O(1A)-H(1A)...O(3B) | 0.78(4) | 2.05(4) | 2.819(3) | 166(4) |
| C(11A)-H(11A)...O(3A) | 0.98 | 2.52 | 3.127(4) | 119.9 |
| C(21A)-H(21A)...Br(1B)#1 | 0.95 | 3.00 | 3.853(3) | 149.9 |
| O(1B)-H(1B)...O(2A)#2 | 0.76(4) | 2.12(4) | 2.838(3) | 157(4) |
| C(21B)-H(21B)...O(1A)#3 | 0.98 | 2.48 | 3.268(4) | 137.0 |

Symmetry transformations used to generate equivalent atoms: #1 x, -y+3/2, z-1/2 #2 x+1, y, z #3 -x+1, -y+1, -z+1


11. (a) Data Collection: APEX3 (2018) Bruker Inc., Madison, Wisconsin, USA. (b) Data Reduction: SAINT (2016) Bruker Inc., Madison, Wisconsin, USA.
12. L. Krause, R. Herbst-Irmer, G. M. Sheldrick, and D. Stalke (2015). *J. Appl. Cryst., 48*, 3-10.
13. (a) G. M. Sheldrick (2015). *Acta Cryst., A71*, 3-8. (b) G. M. Sheldrick (2015). *Acta Cryst., C71*,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4.35
4.34
3.91
3.90
3.88
2.47
2.46
2.45
2.44
2.31
2.31
2.30
2.29
1.72
1.72
1.71
1.69
1.69
1.68
1.67
1.66
1.66
O
O
O
OH
1e
1.00
2.06
1.90
2.20
2.04
4.66
2.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
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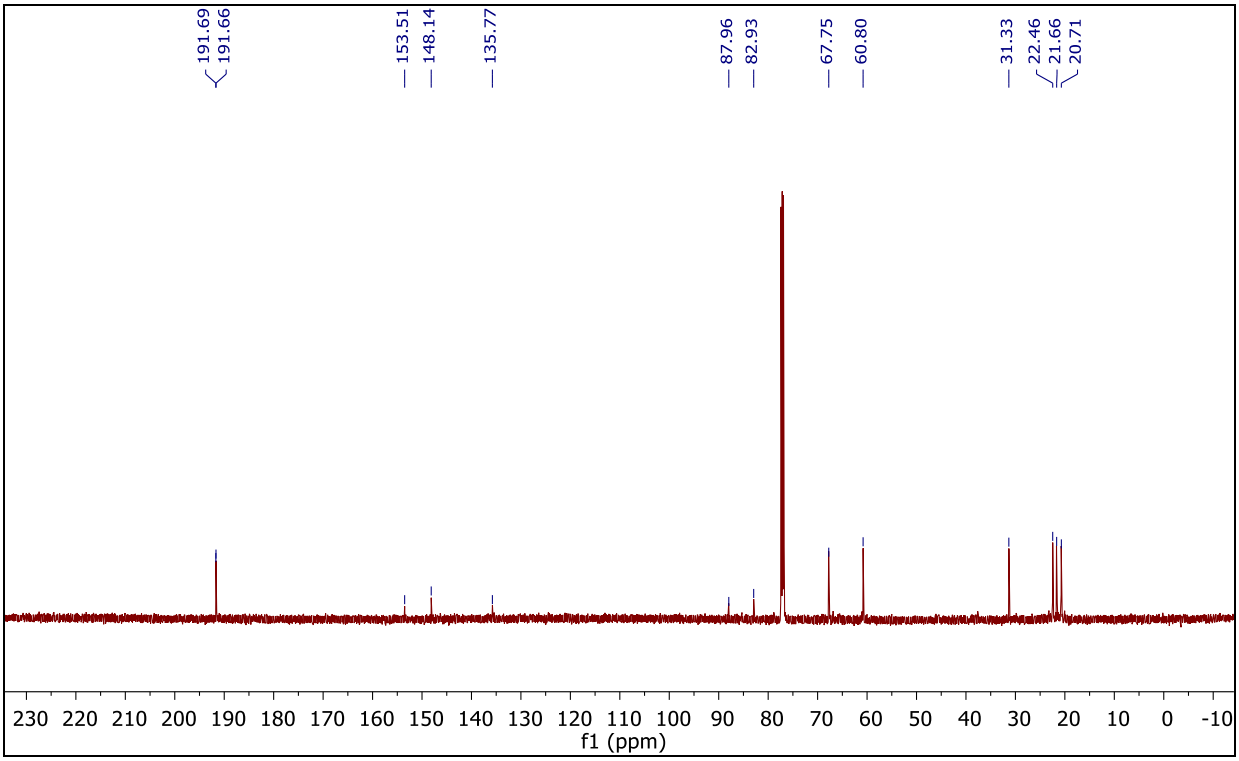
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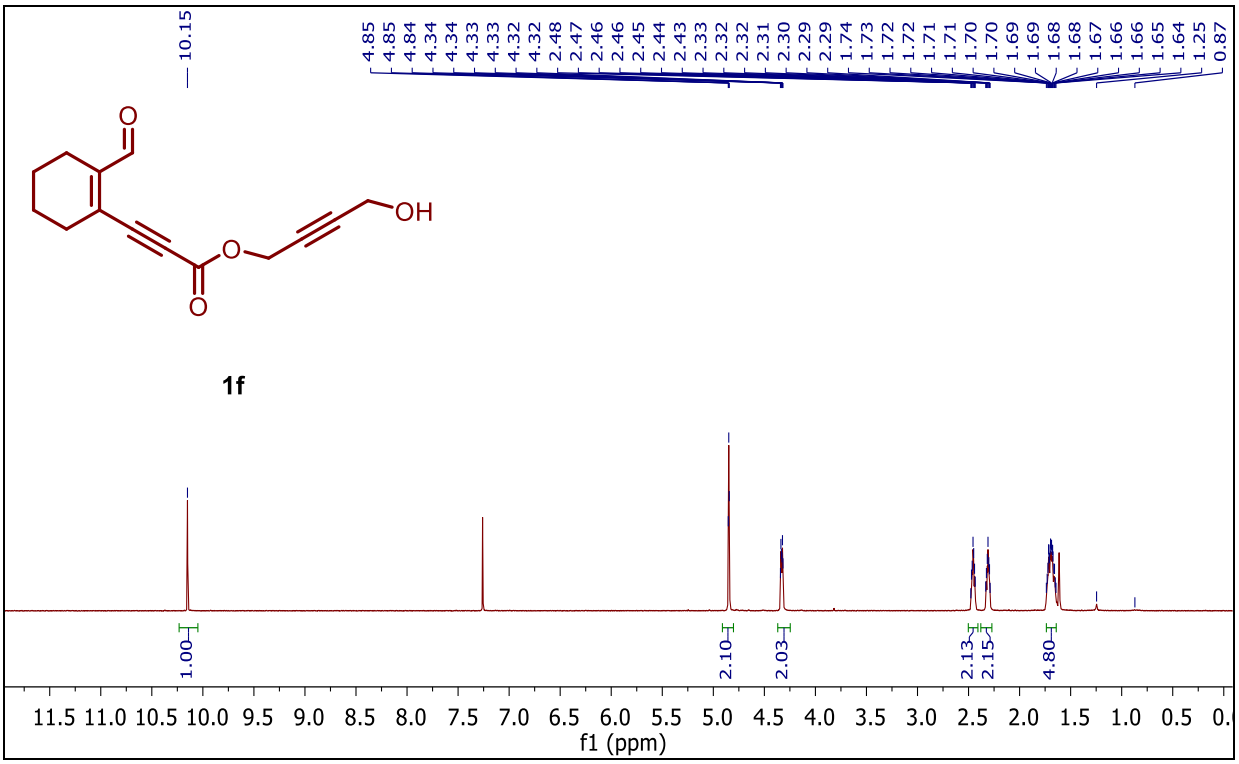
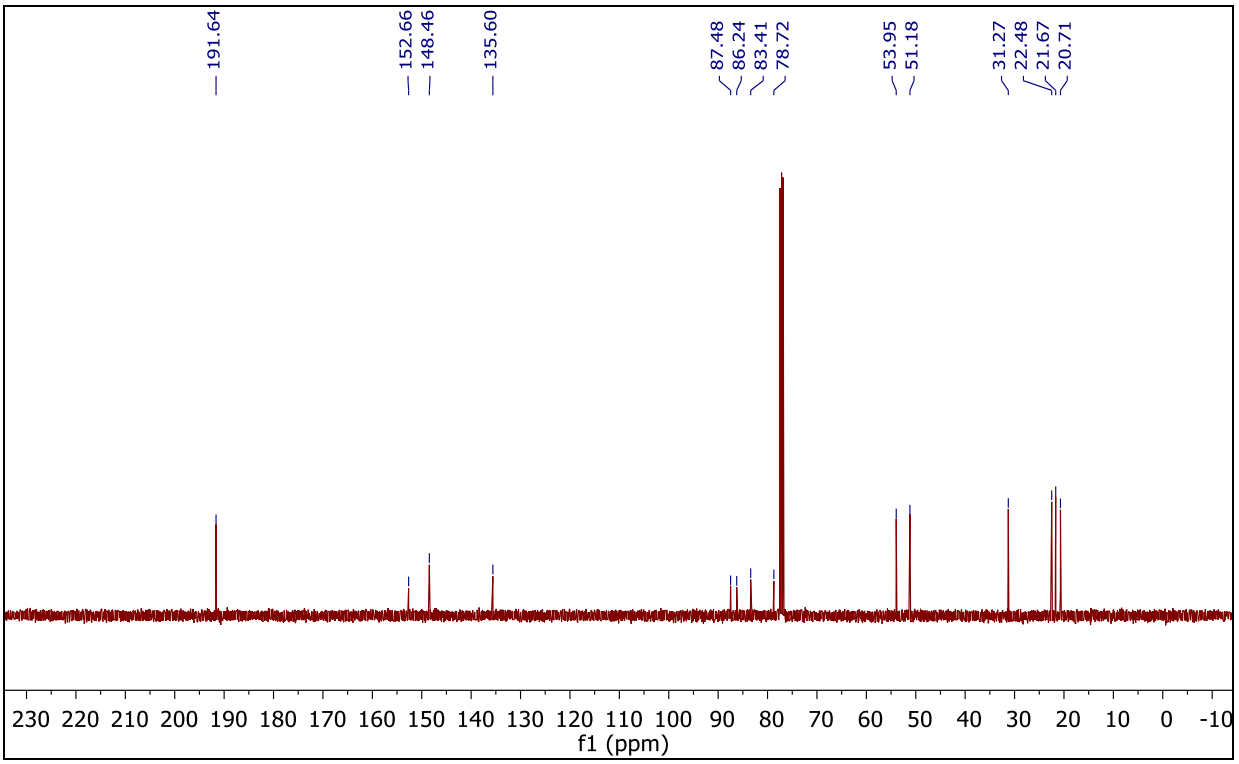
191.66
153.51
148.14
135.77
87.96
82.93
67.75
60.80
31.33
22.46
21.66
20.71
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


10.15
4.85 4.85 4.84 4.34 4.34 4.33 4.33 4.32 4.32 2.48 2.47 2.46 2.46 2.45 2.44 2.43 2.33 2.32 2.32 2.31 2.30 2.29 2.29 1.74 1.73 1.72 1.72 1.71 1.71 1.70 1.70 1.69 1.69 1.68 1.68 1.67 1.66 1.66 1.65 1.64 1.25 0.87
O
OH
O
O
1f
1.00
2.10
2.03
2.13
2.15
4.80
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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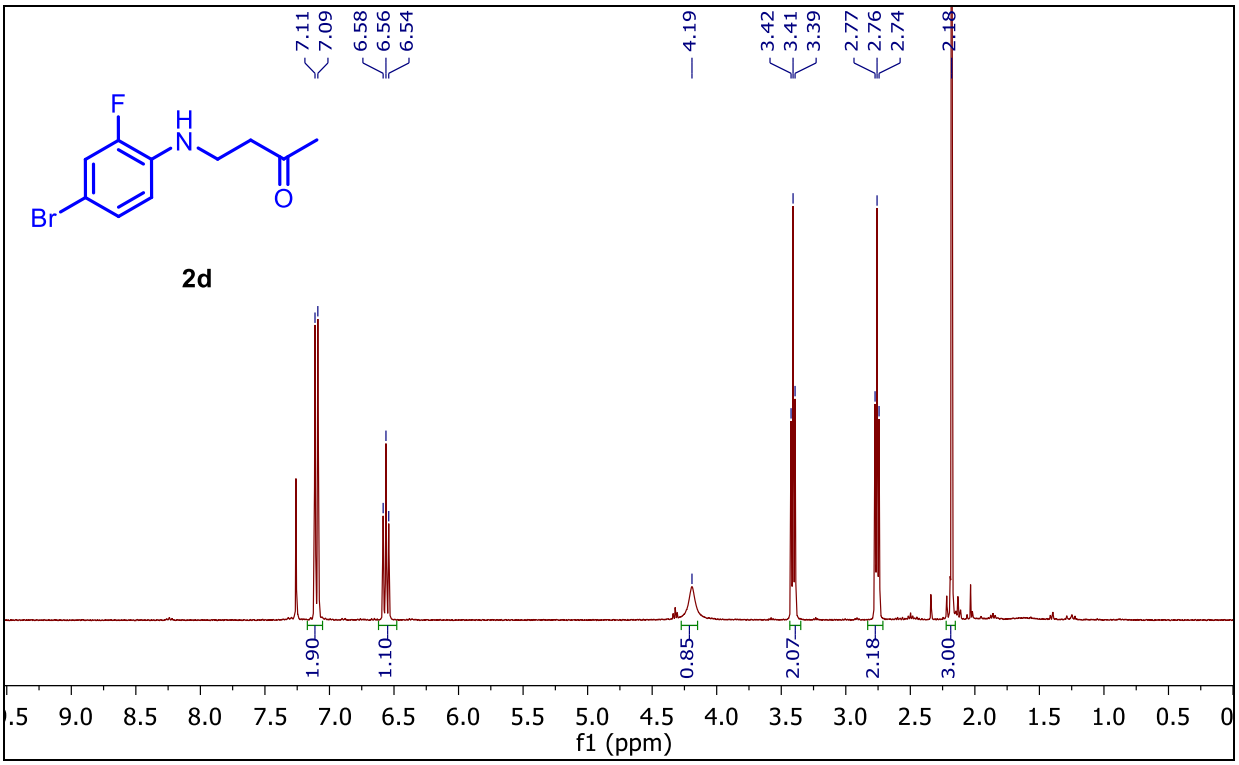
21.67
20.71
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.09
6.58
6.56
6.54
4.19
3.42
3.41
3.39
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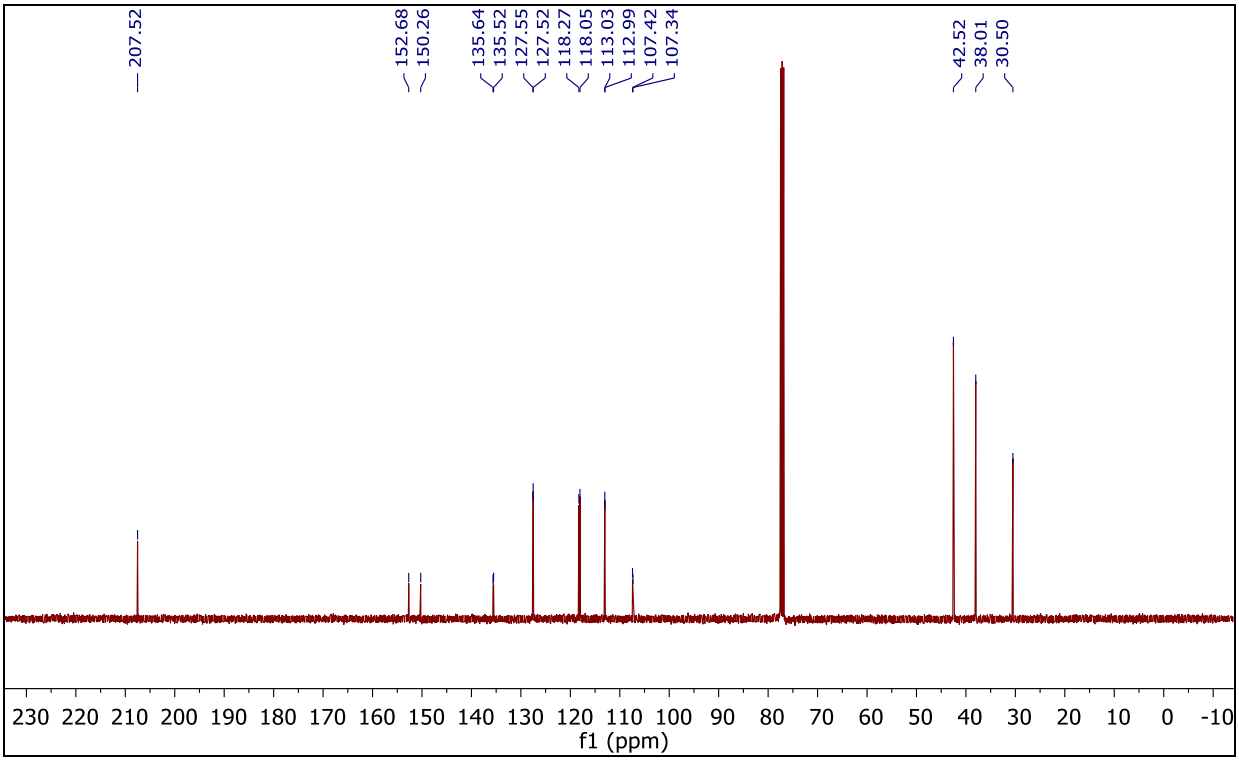
2.76
2.74
2.18
F
H
N
O
Br
2d
1.90
1.10
0.85
2.07
2.18
3.00
f1 (ppm)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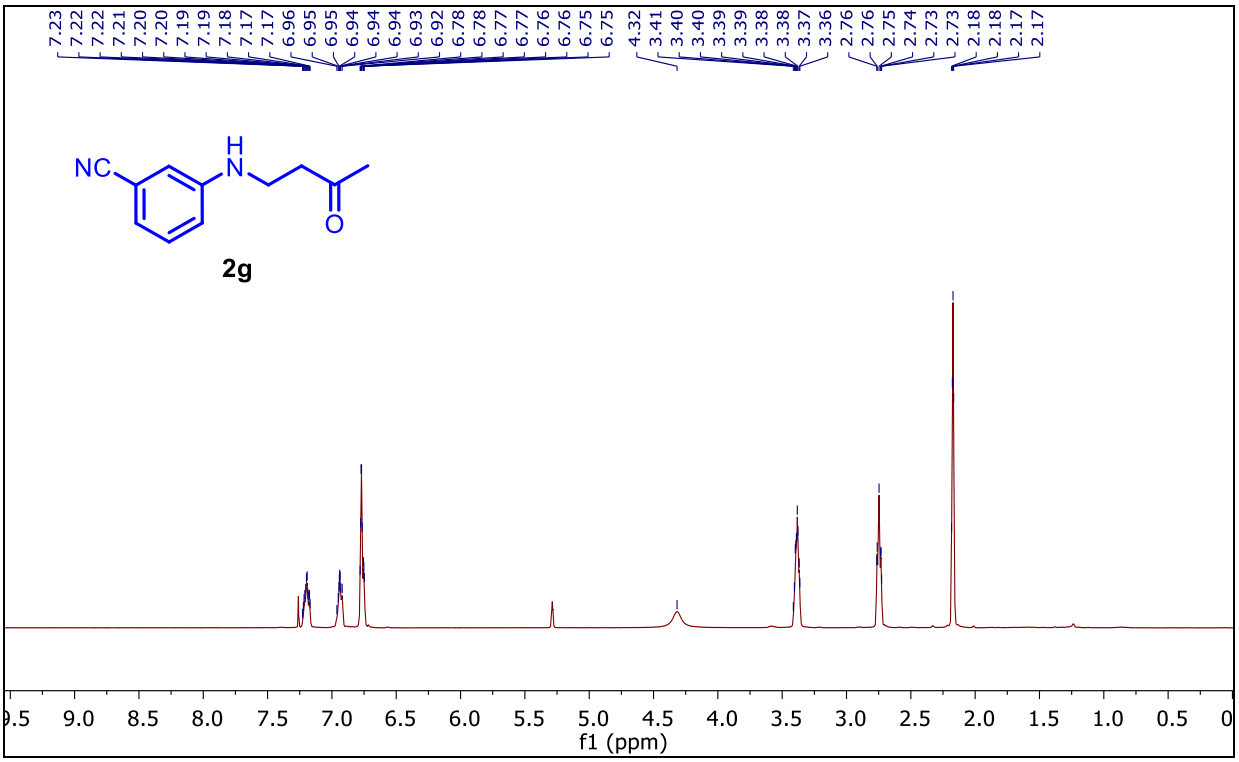
30.50
f1 (ppm)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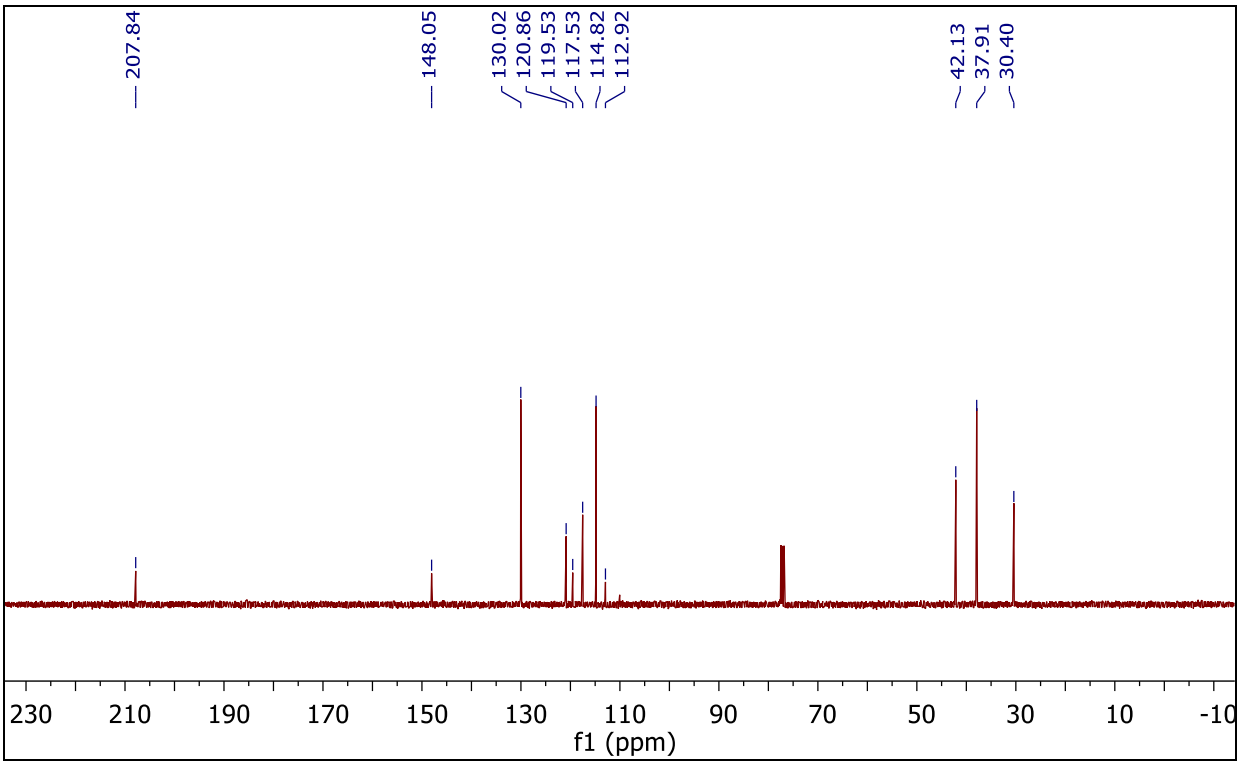
NC
H
N
O
2g
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
f1 (ppm)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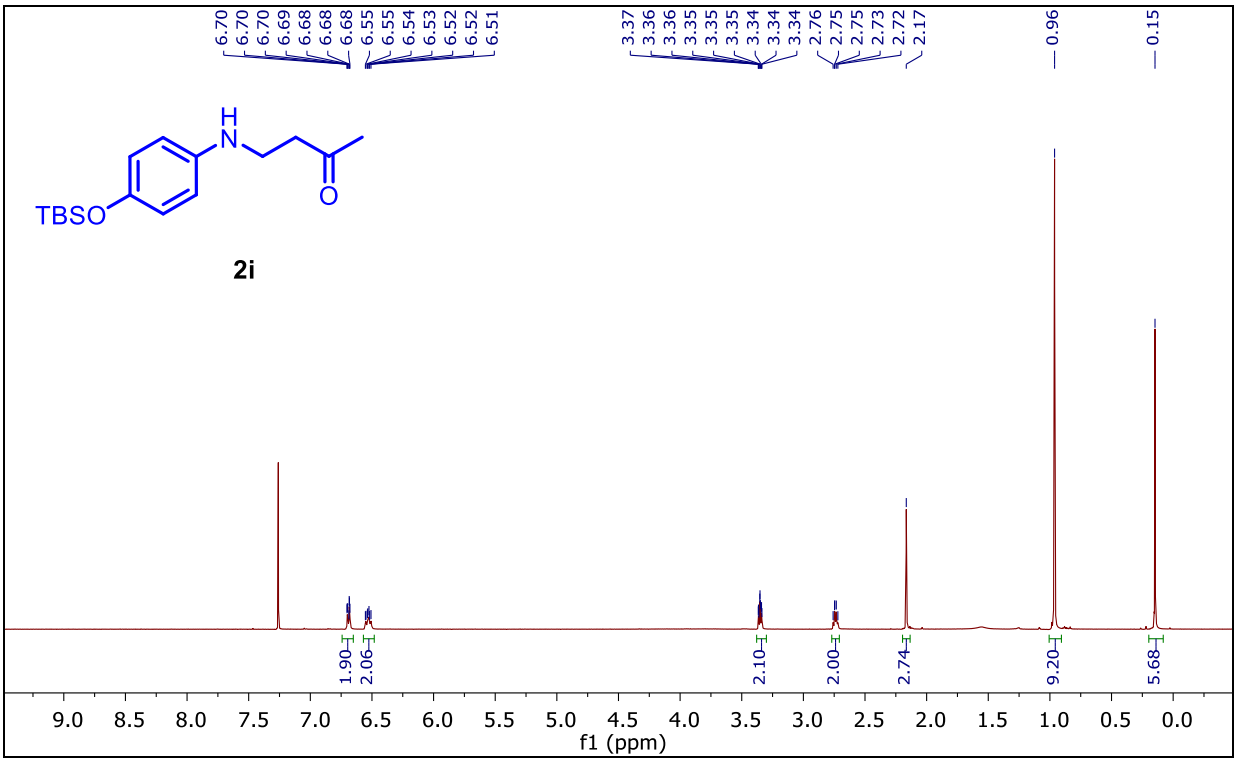
112.92
42.13
37.91
30.40
230 210 190 170 150 130 110 90 70 50 30 10 -10
f1 (ppm)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6.52
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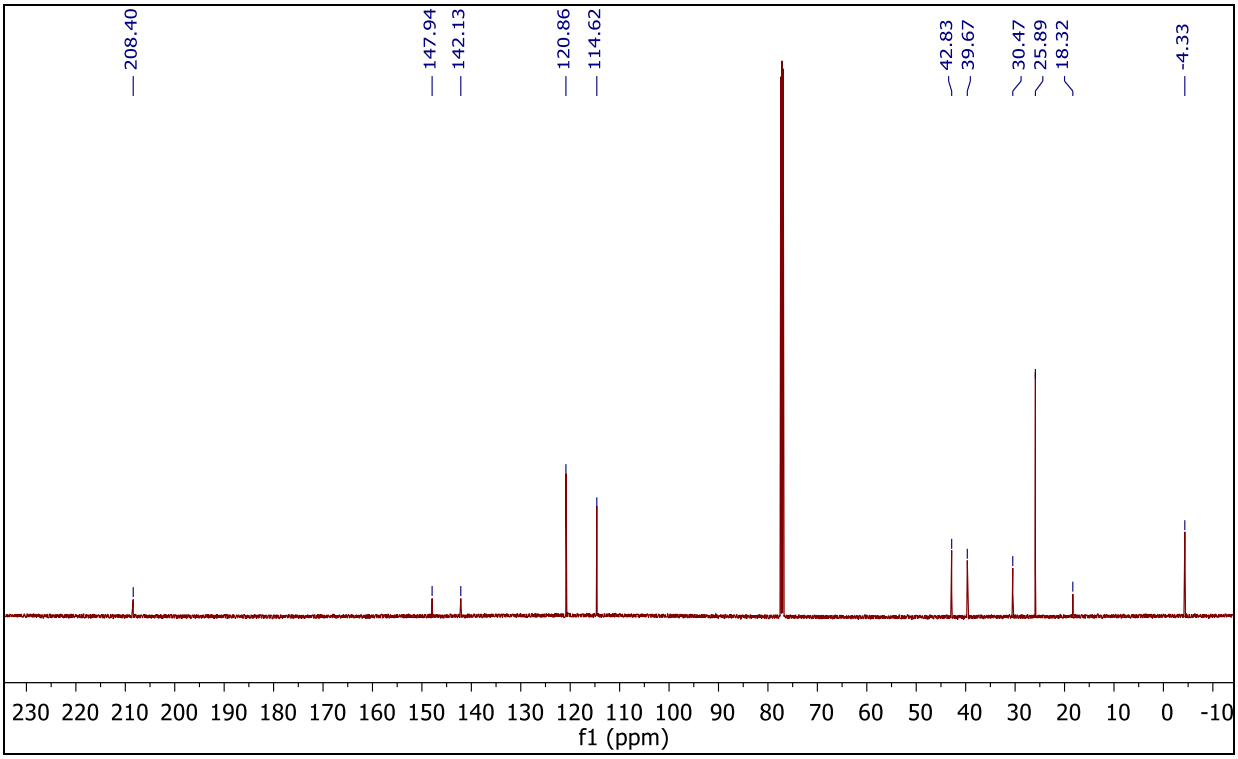
6.51
3.37
3.36
3.36
3.35
3.35
3.35
3.34
3.34
3.34
2.76
2.75
2.75
2.73
2.72
2.17
0.96
0.15
H
N
O
TBSO
2i
1.90
2.06
2.10
2.00
2.74
9.20
5.68
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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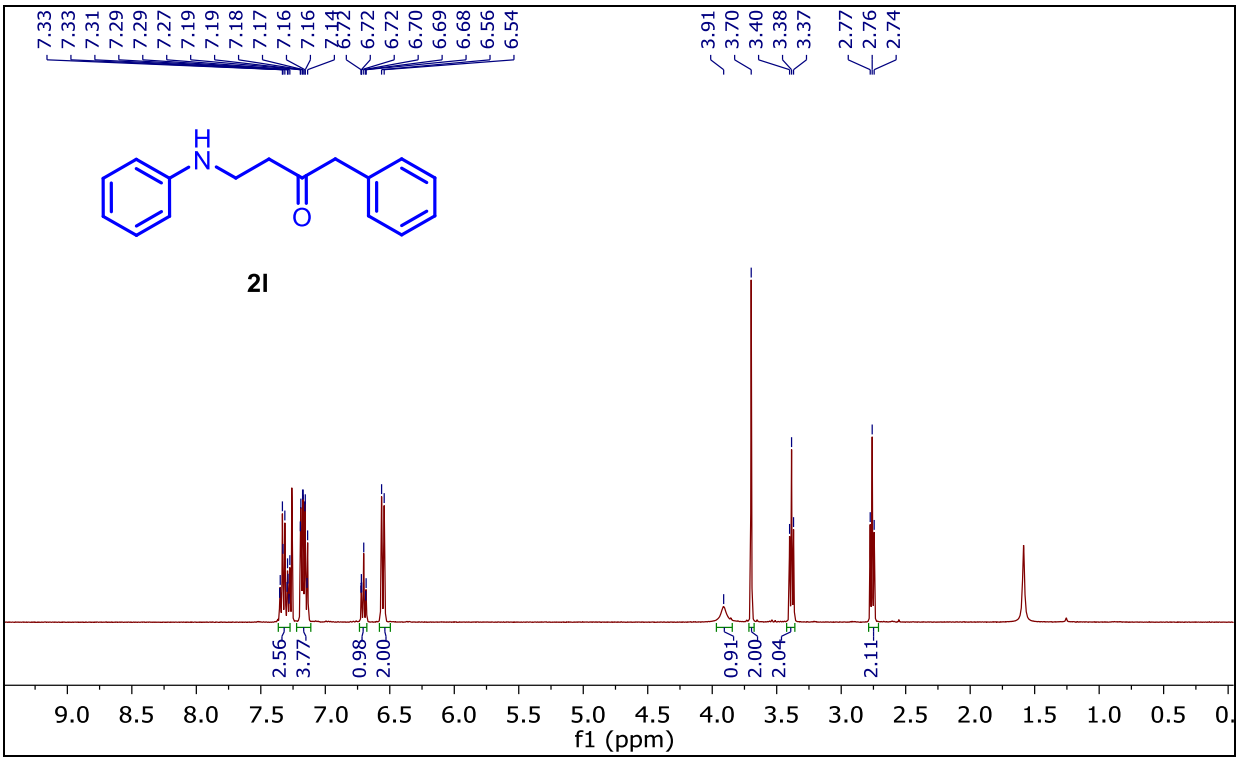
f1 (ppm)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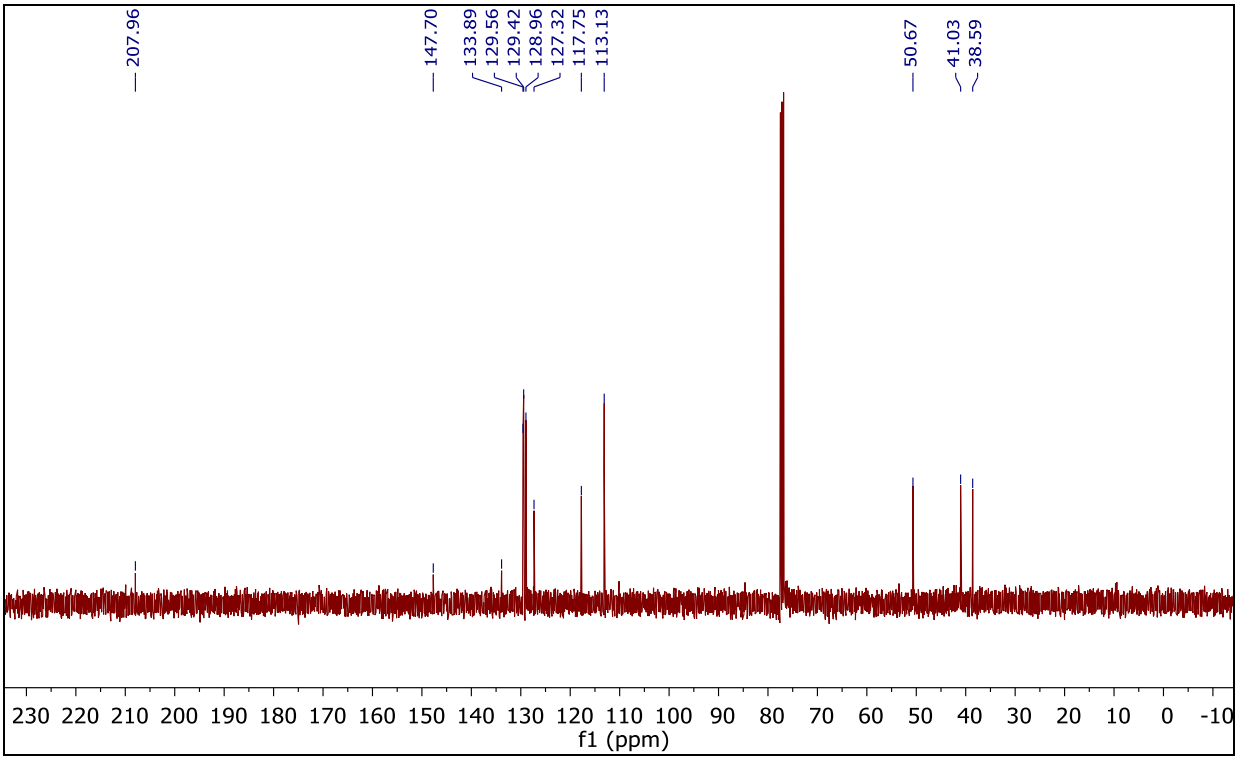
7.16
7.14
7.12
6.72
6.72
6.70
6.69
6.68
6.56
6.54
3.91
3.70
3.40
3.38
3.37
2.77
2.76
2.74
H
N
O
2l
2.56
3.77
0.98
2.00
0.91
2.00
2.04
2.11
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.
f1 (ppm)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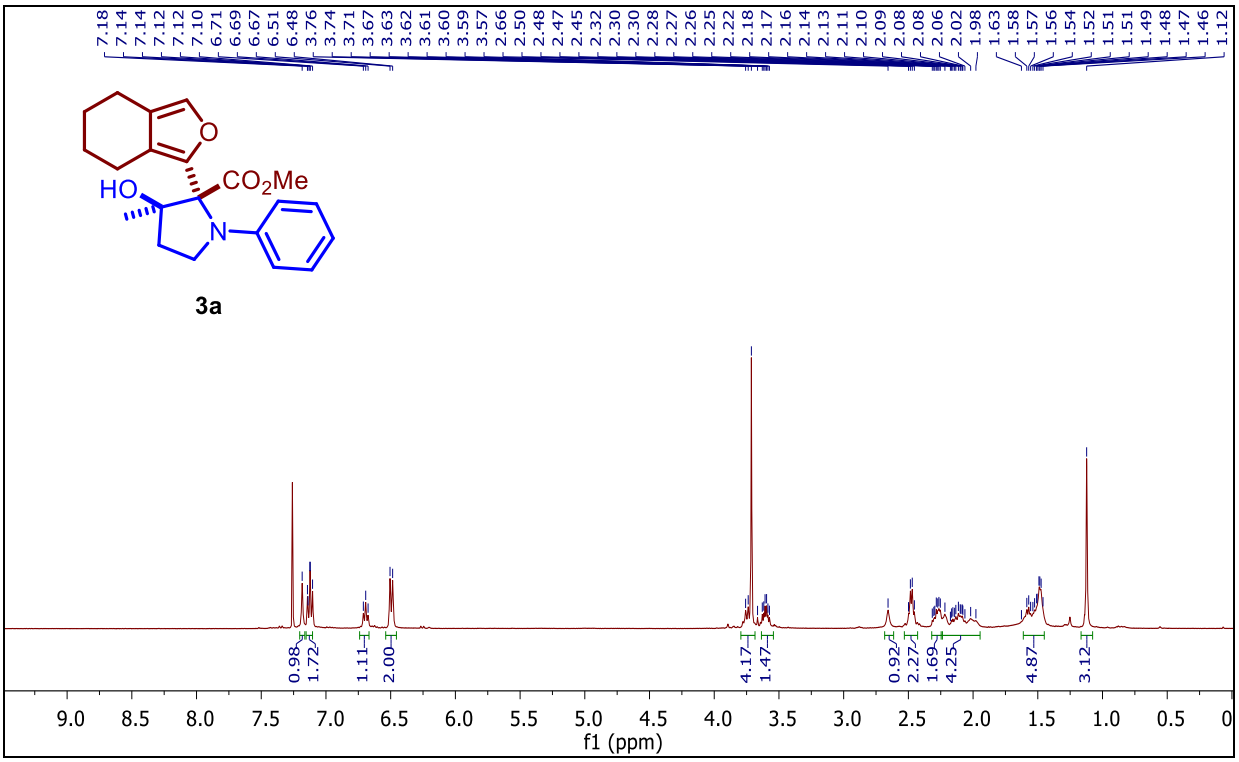
f1 (ppm)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N
O
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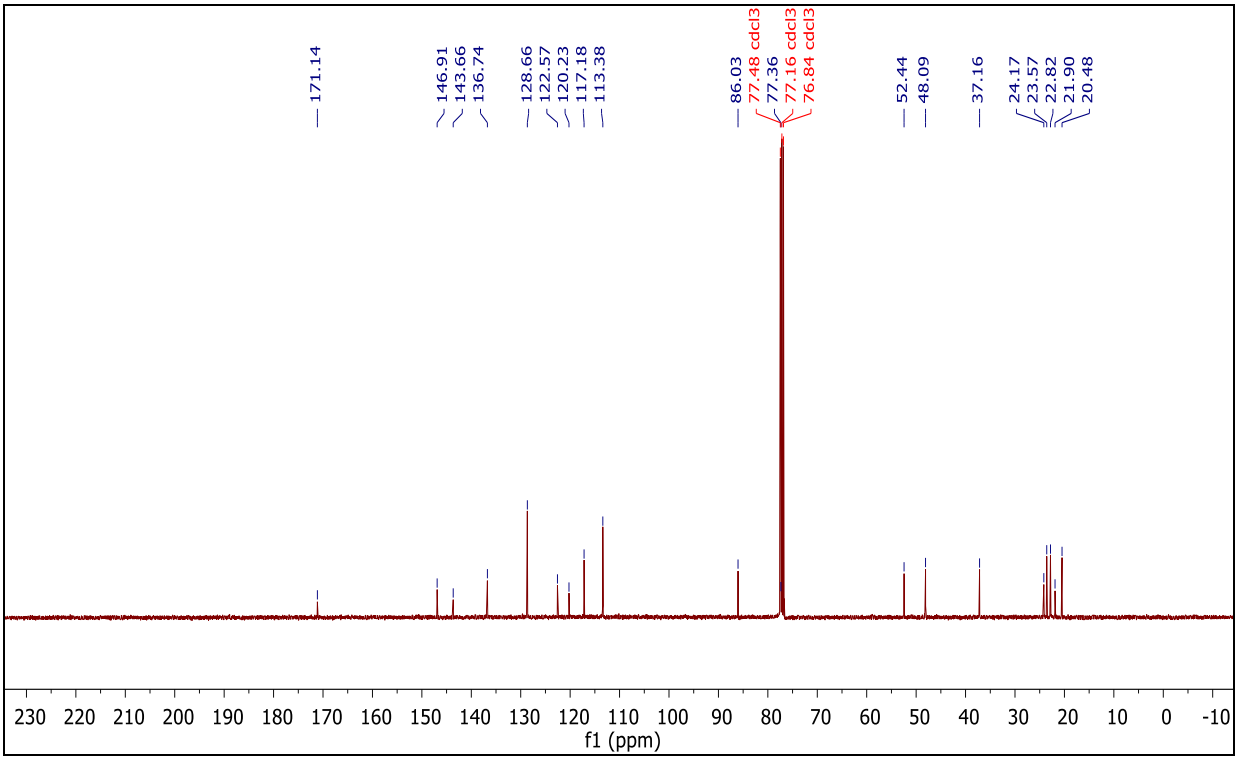
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117.18
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86.03
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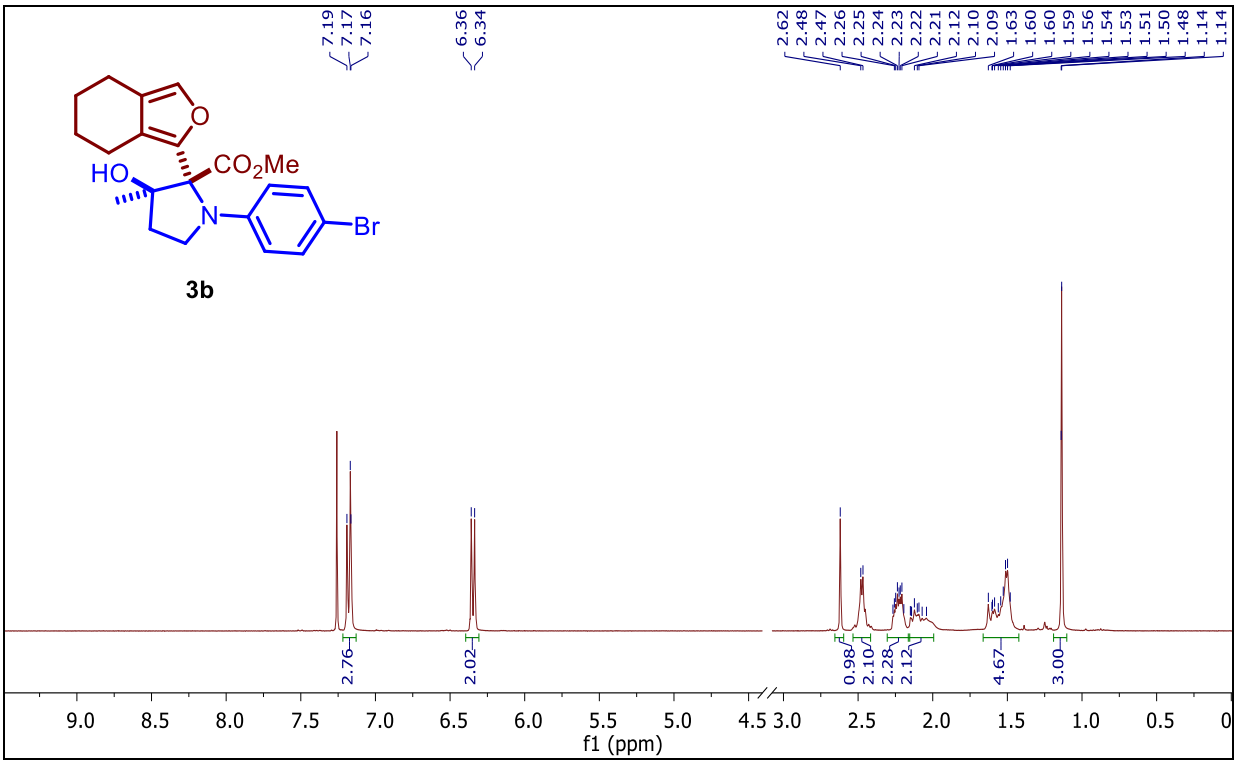
77.36
77.16 cdcl3
76.84 cdcl3
52.44
48.09
37.16
24.17
23.57
22.82
21.90
20.48
f1 (ppm)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6.34
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2.47
2.26
2.25
2.24
2.23
2.22
2.21
2.12
2.10
2.09
1.63
1.60
1.60
1.59
1.56
1.54
1.53
1.51
1.50
1.48
1.14
1.14
O
HO
CO2Me
N
Br
3b
2.76
2.02
0.98
2.10
2.28
2.12
4.67
3.00
9.0
8.5
8.0
7.5
7.0
6.5
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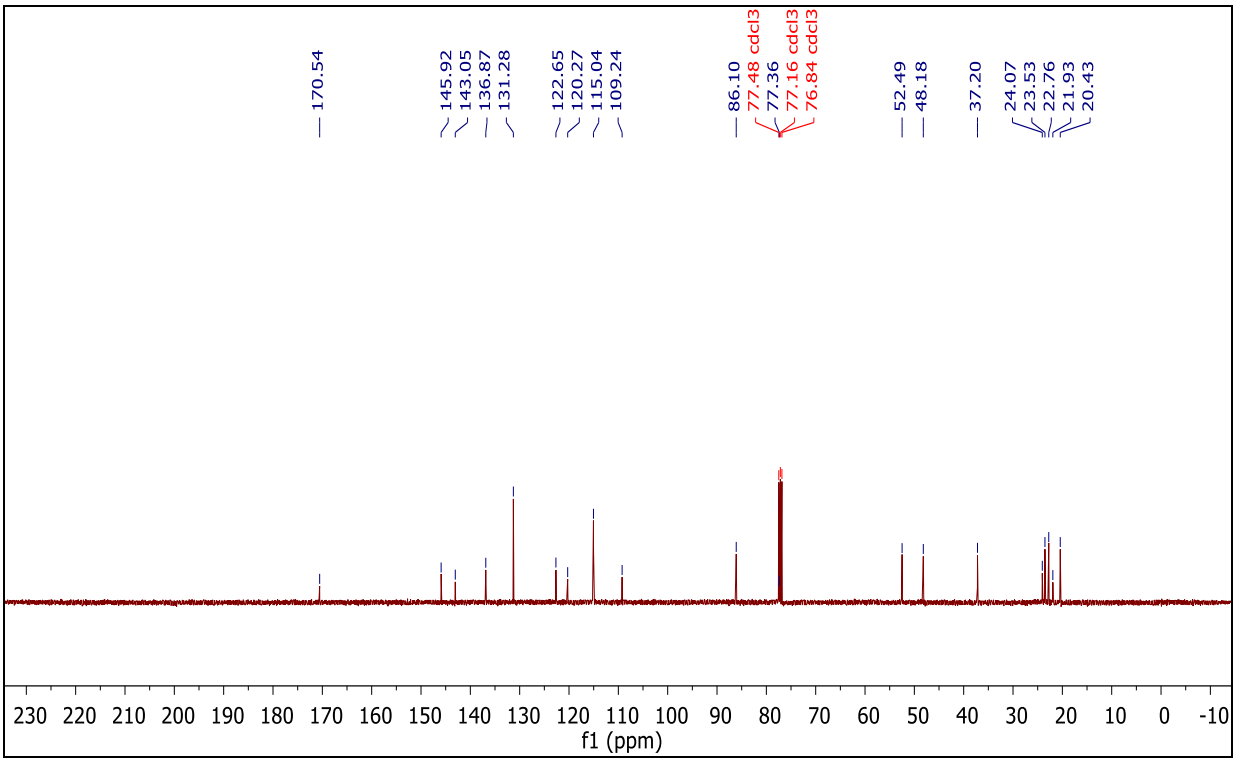
1.0
0.5
0
f1 (ppm)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143.05
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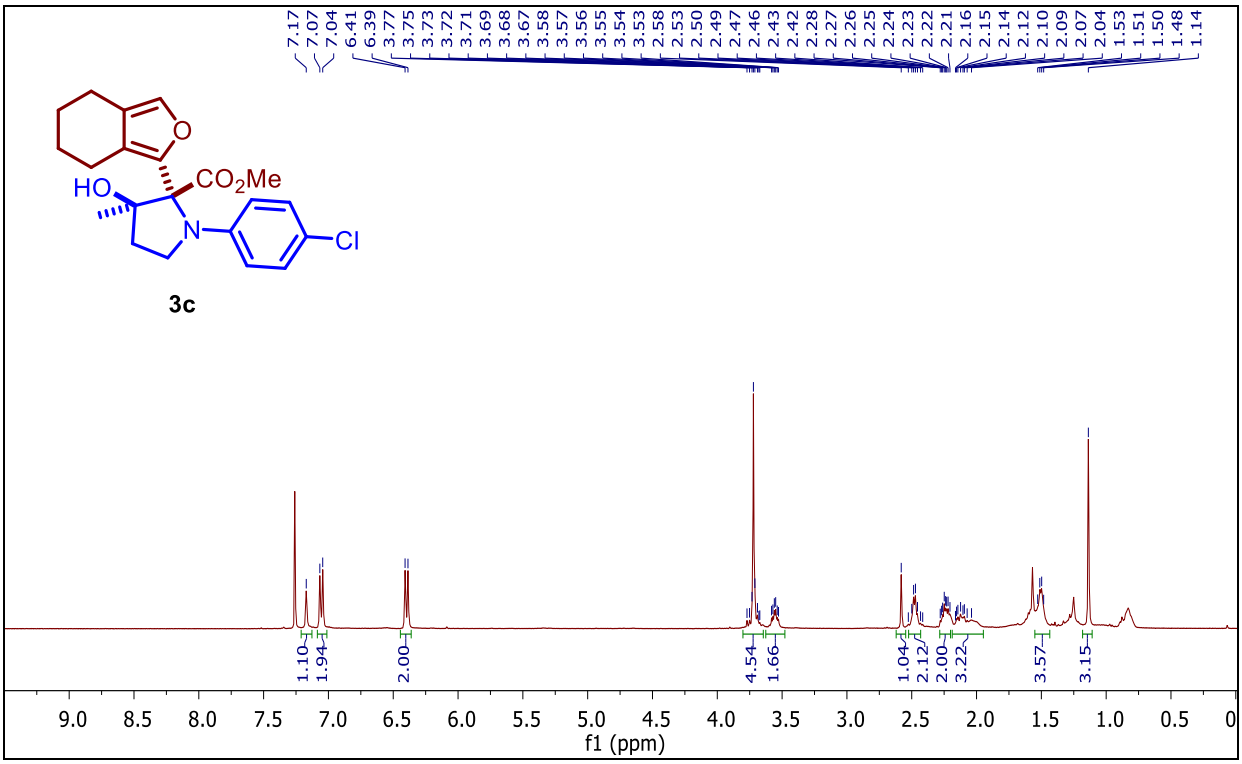
122.65
120.27
115.04
109.24
86.10
77.48 cdcl3
77.36
77.16 cdcl3
76.84 cdcl3
52.49
48.18
37.20
24.07
23.53
22.76
21.93
20.43
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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3.55
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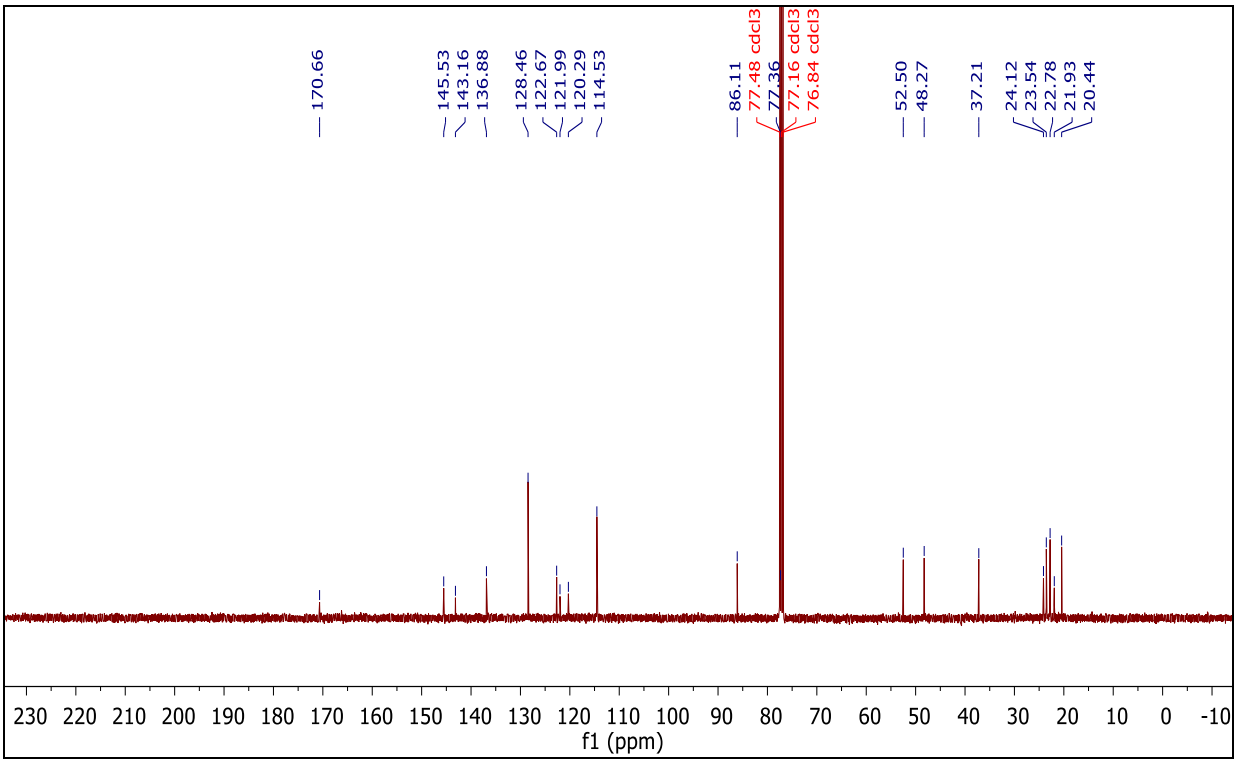
2.00
3.22
3.57
3.15
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
f1 (ppm)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77.48 cdcl3
77.36
77.16 cdcl3
76.84 cdcl3
52.50
48.27
37.21
24.12
23.54
22.78
21.93
20.44
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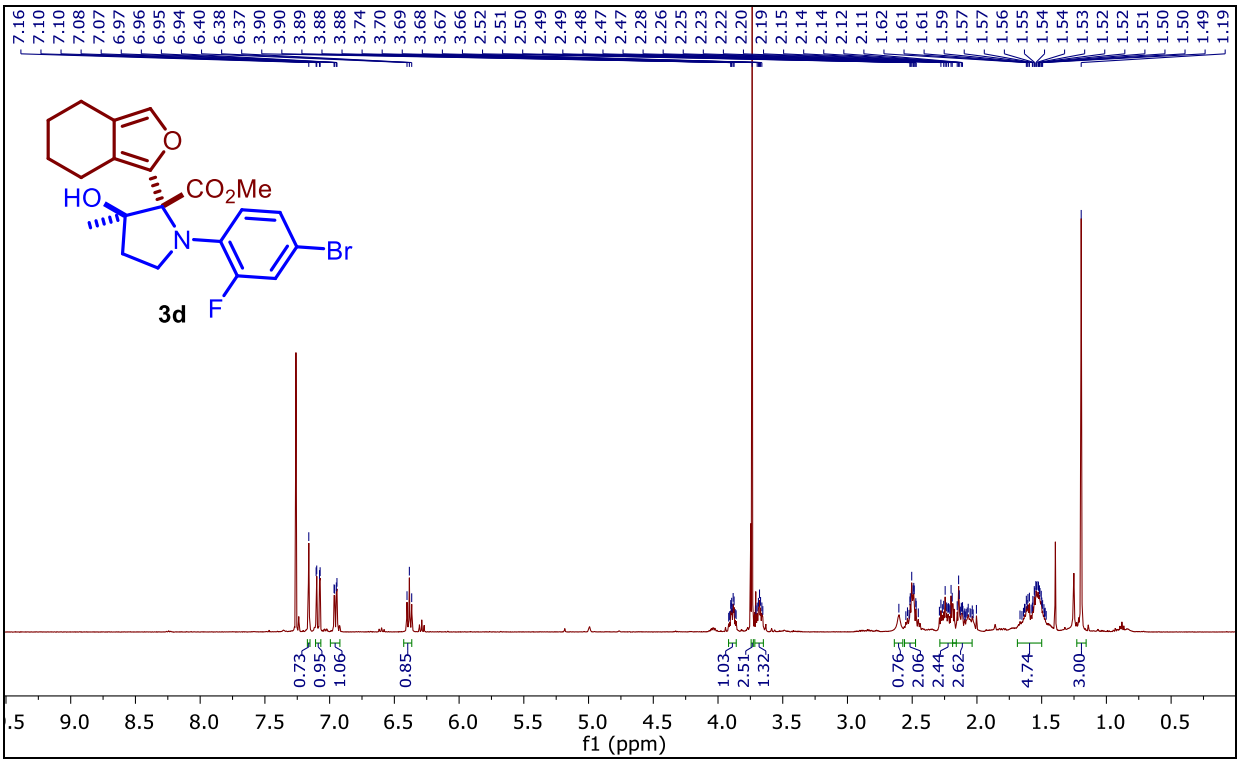
f1 (ppm)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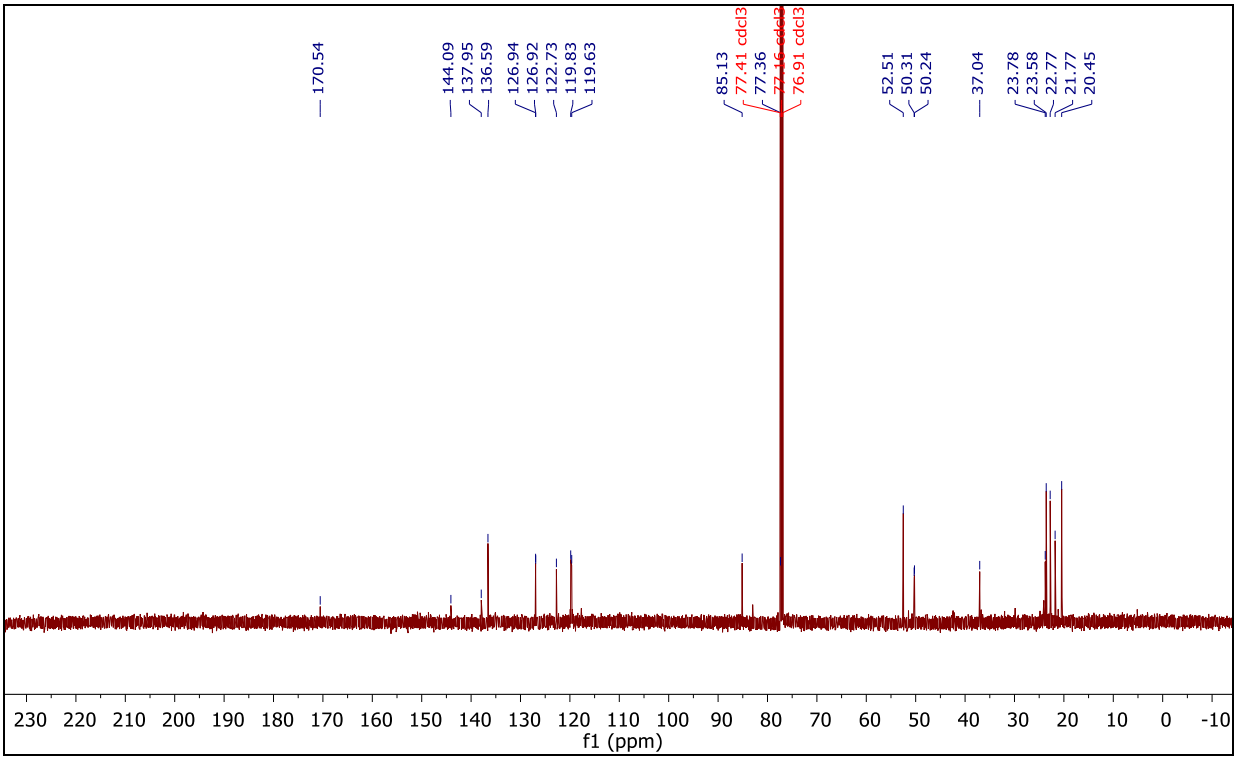
N
Br
F
3d
f1 (ppm)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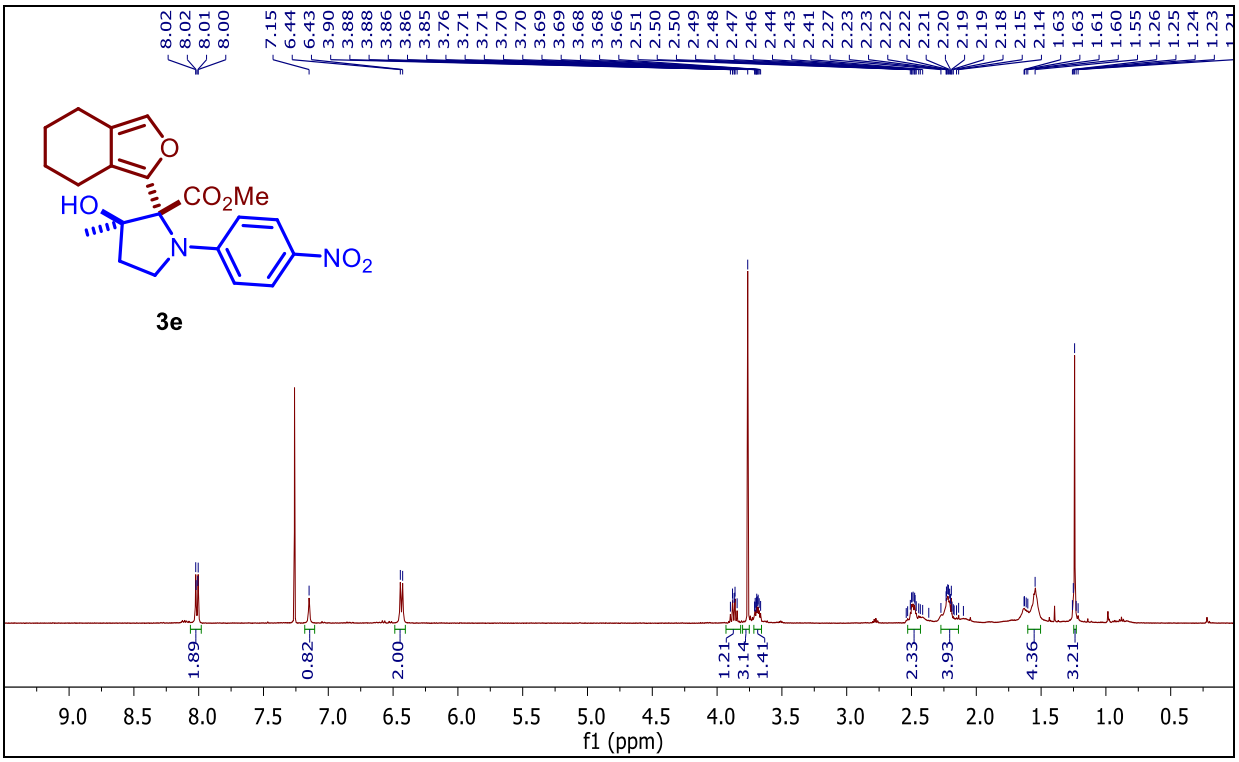
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NO2
3e
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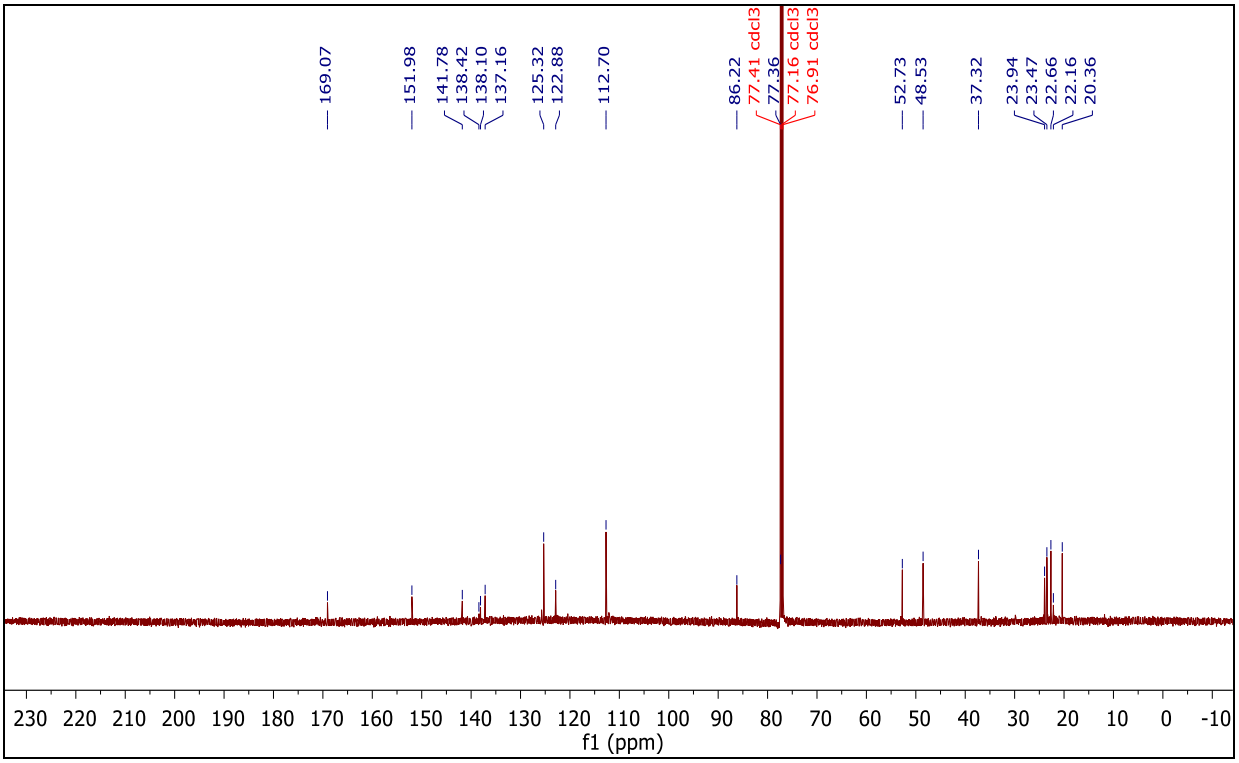
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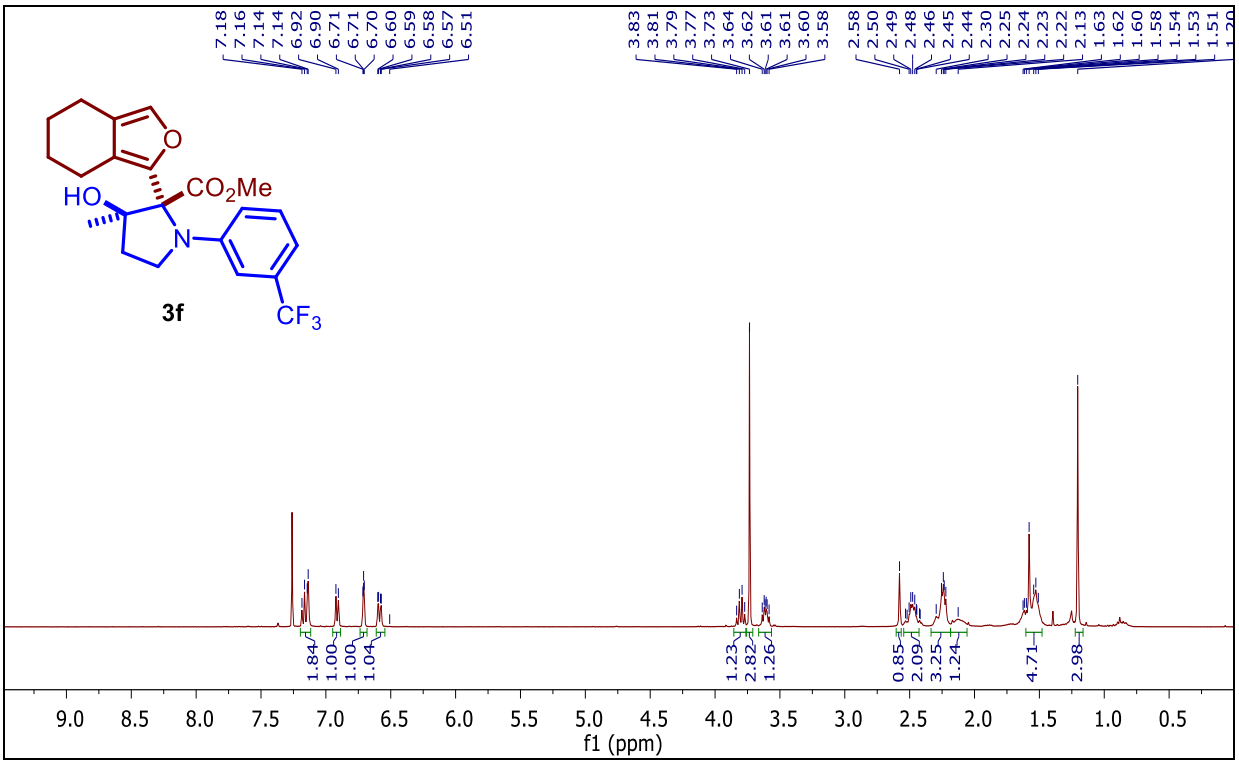
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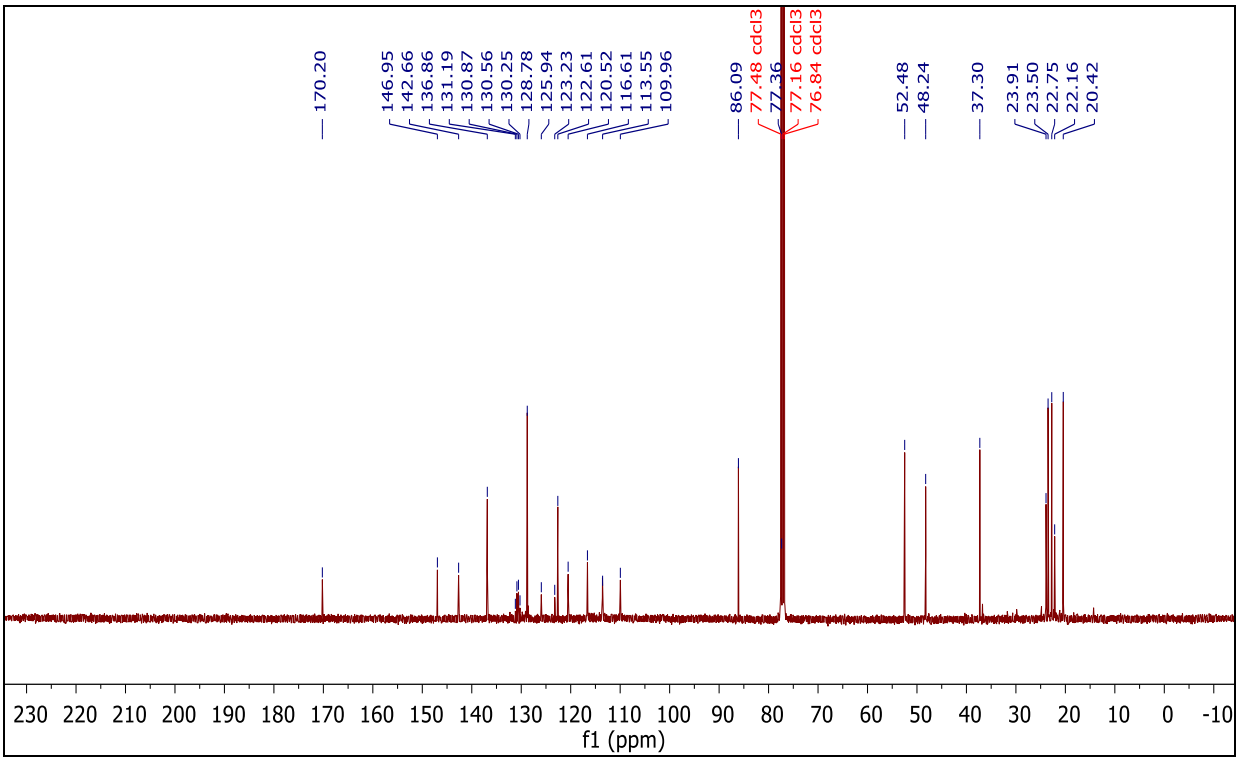
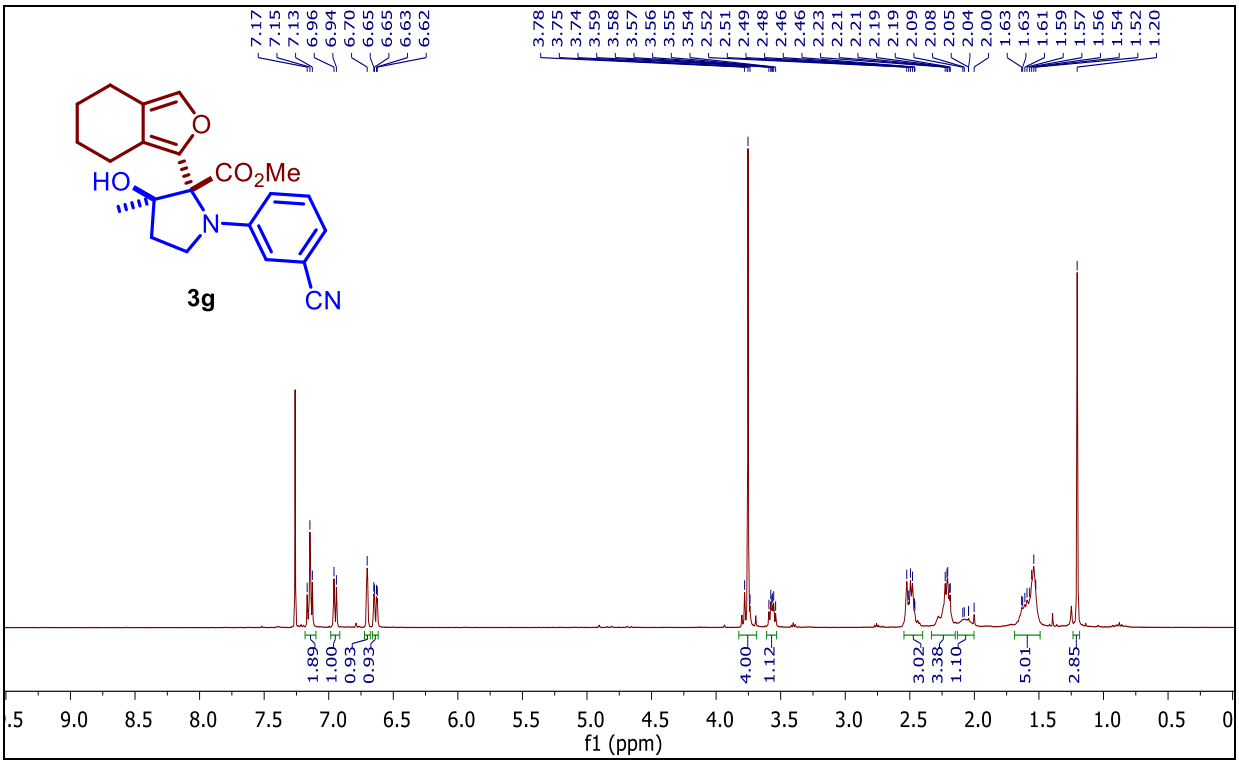
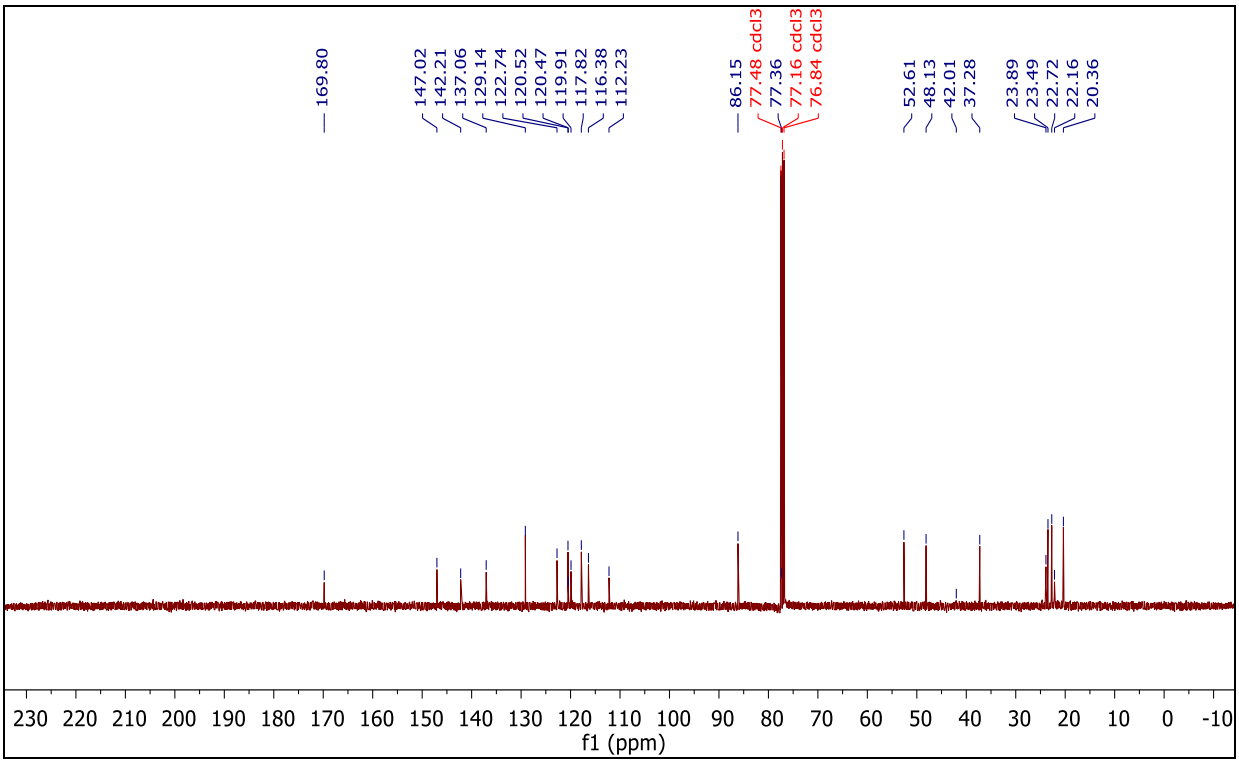
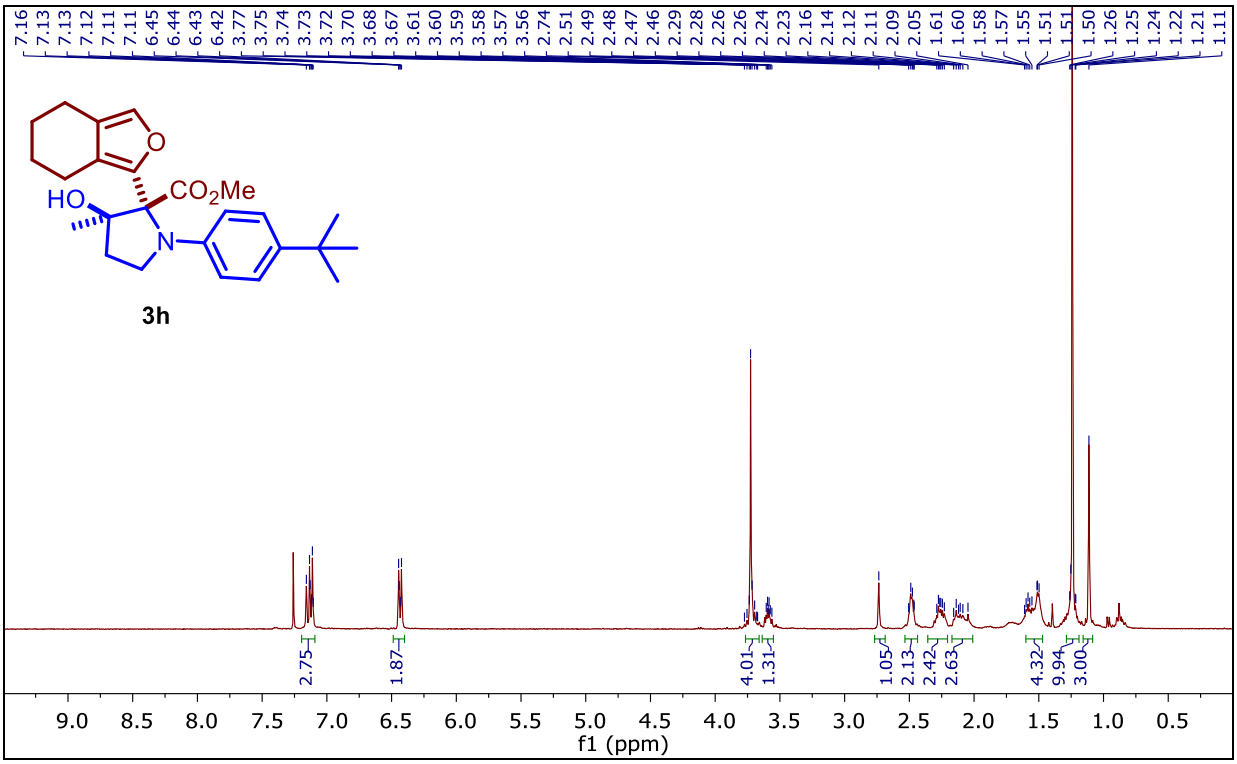
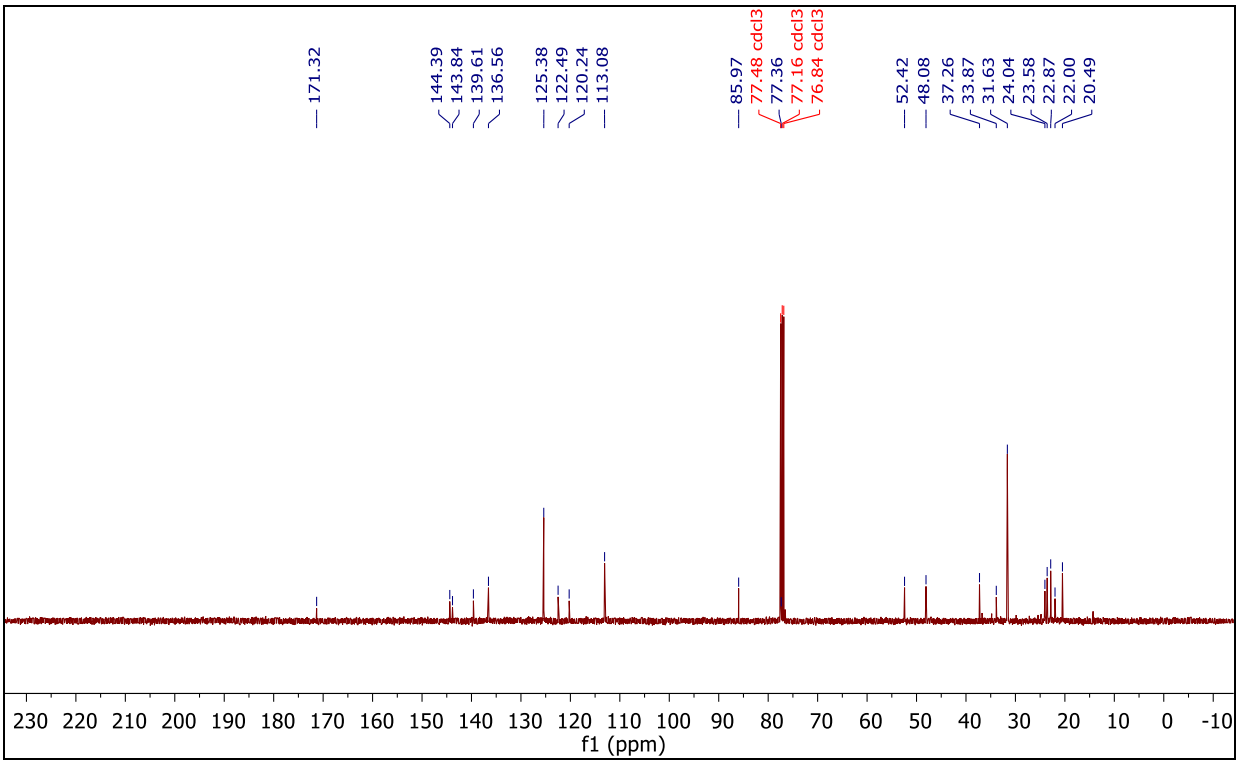
2.58 2.50 2.49 2.48 2.46 2.45 2.44 2.30 2.25 2.24 2.23 2.22 2.13 1.63 1.62 1.60 1.58 1.54 1.53 1.51
O
HO
CO2Me
N
CF3
3f
1.84 1.00 1.00 1.04 1.23 2.82 1.26 0.85 2.09 3.25 1.24 4.71 2.98
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

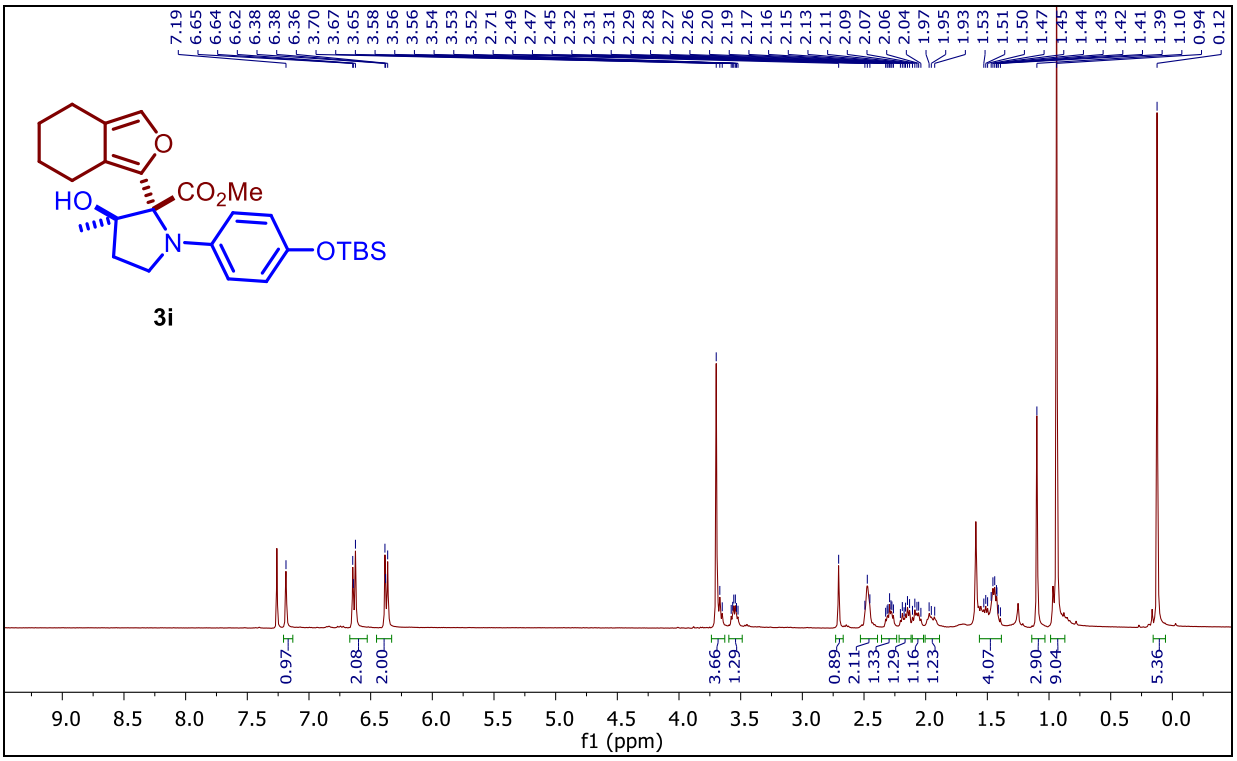

170.20
146.95 142.66 136.86 131.19 130.87 130.56 130.25 128.78 125.94 123.23 122.61 120.52 116.61 113.55 109.96
86.09
77.48 cdcl3 77.36 77.16 cdcl3 76.84 cdcl3
52.48 48.24 37.30 23.91 23.50 22.75 22.16 20.42
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

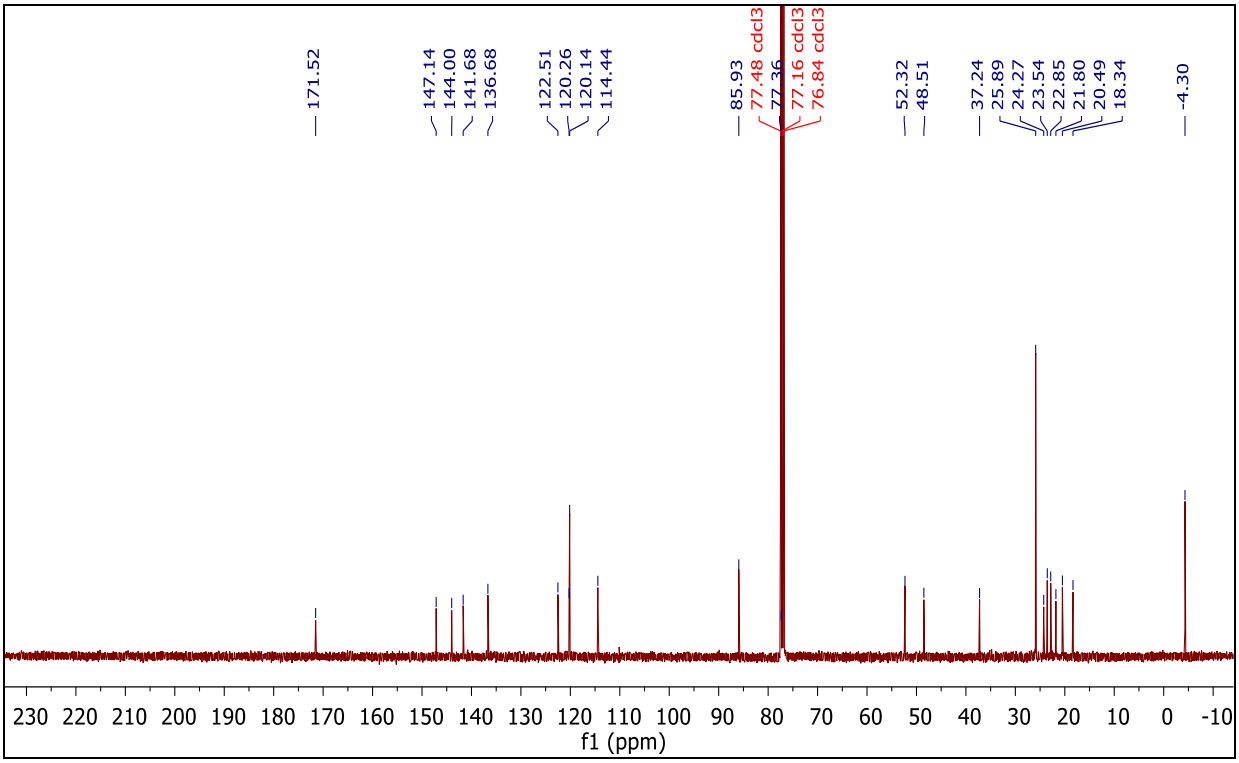

7.17
7.15
7.13
6.96
6.94
6.70
6.65
6.65
6.63
6.62
3.78
3.75
3.74
3.59
3.58
3.57
3.56
3.55
3.54
2.52
2.51
2.49
2.48
2.46
2.46
2.23
2.21
2.21
2.19
2.19
2.09
2.08
2.05
2.04
2.00
1.63
1.63
1.61
1.59
1.57
1.56
1.54
1.52
1.20
HO
CO2Me
N
CN
3g
1.89
1.00
0.93
0.93
4.00
1.12
3.02
3.38
1.10
5.01
2.85
f1 (ppm)

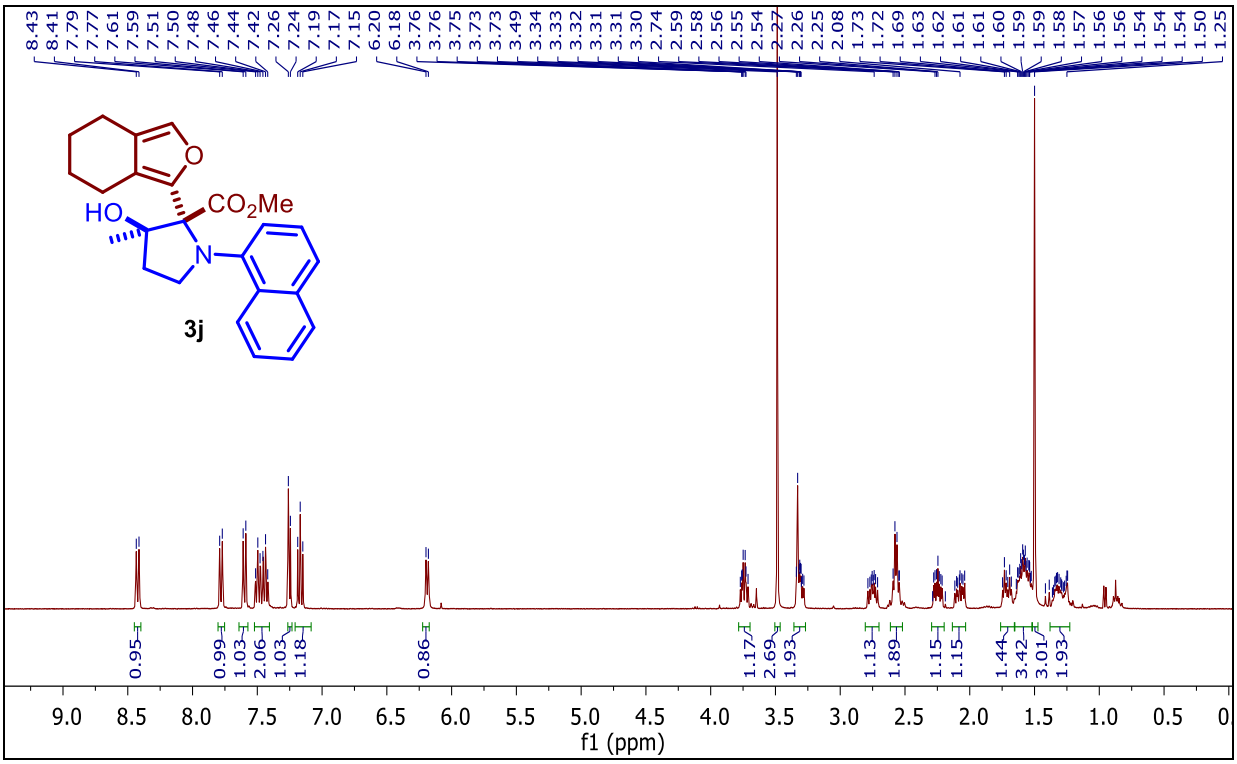

169.80
147.02
142.21
137.06
129.14
122.74
120.52
120.47
119.91
117.82
116.38
112.23
86.15
77.48 cdcl3
77.36
77.16 cdcl3
76.84 cdcl3
52.61
48.13
42.01
37.28
23.89
23.49
22.72
22.16
20.36
f1 (ppm)

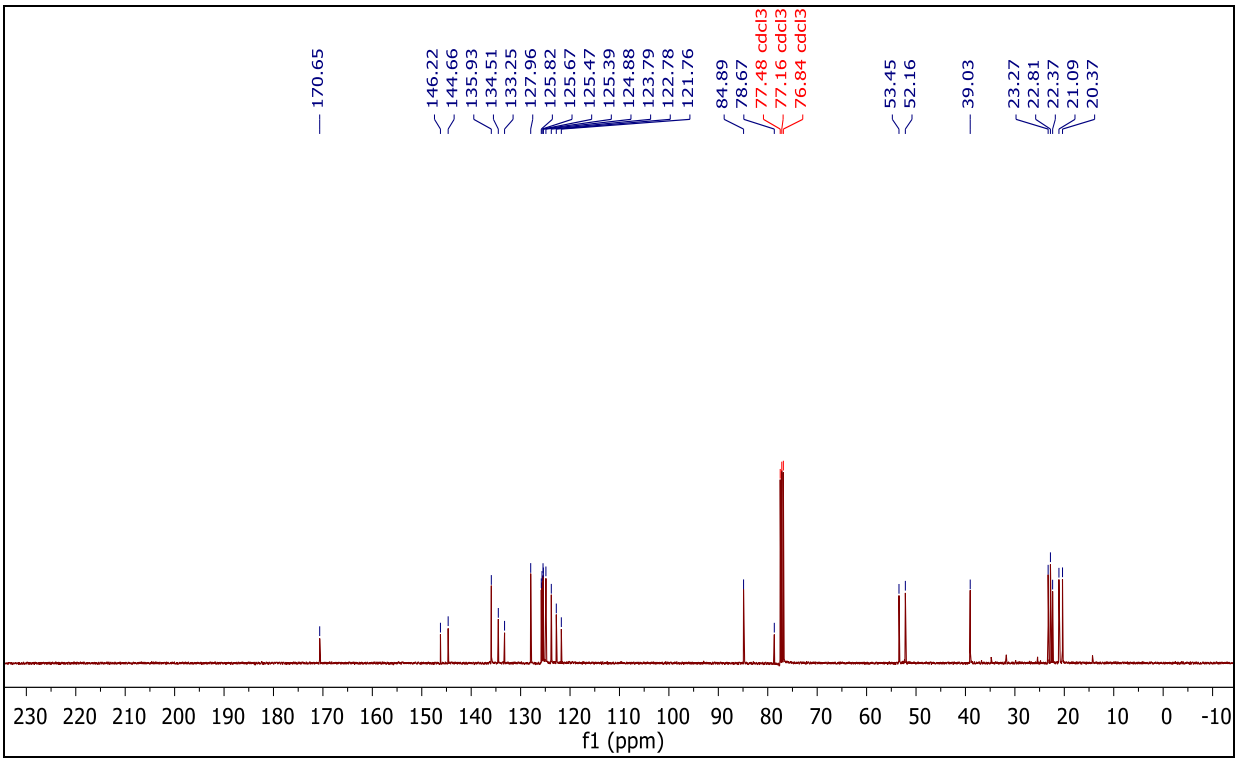

7.16 7.13 7.13 7.12 7.11 7.11 6.45 6.44 6.43 6.42 3.77 3.75 3.74 3.73 3.72 3.70 3.68 3.67 3.61 3.60 3.59 3.58 3.57 3.56 2.74 2.51 2.49 2.48 2.47 2.46 2.29 2.28 2.26 2.26 2.24 2.23 2.16 2.14 2.12 2.11 2.09 2.05 1.61 1.60 1.58 1.57 1.55 1.51 1.51 1.50 1.26 1.25 1.24 1.22 1.21 1.11
O
HO
CO2Me
N
3h
2.75 1.87 4.01 1.31 1.05 2.13 2.42 2.63 4.32 9.94 3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

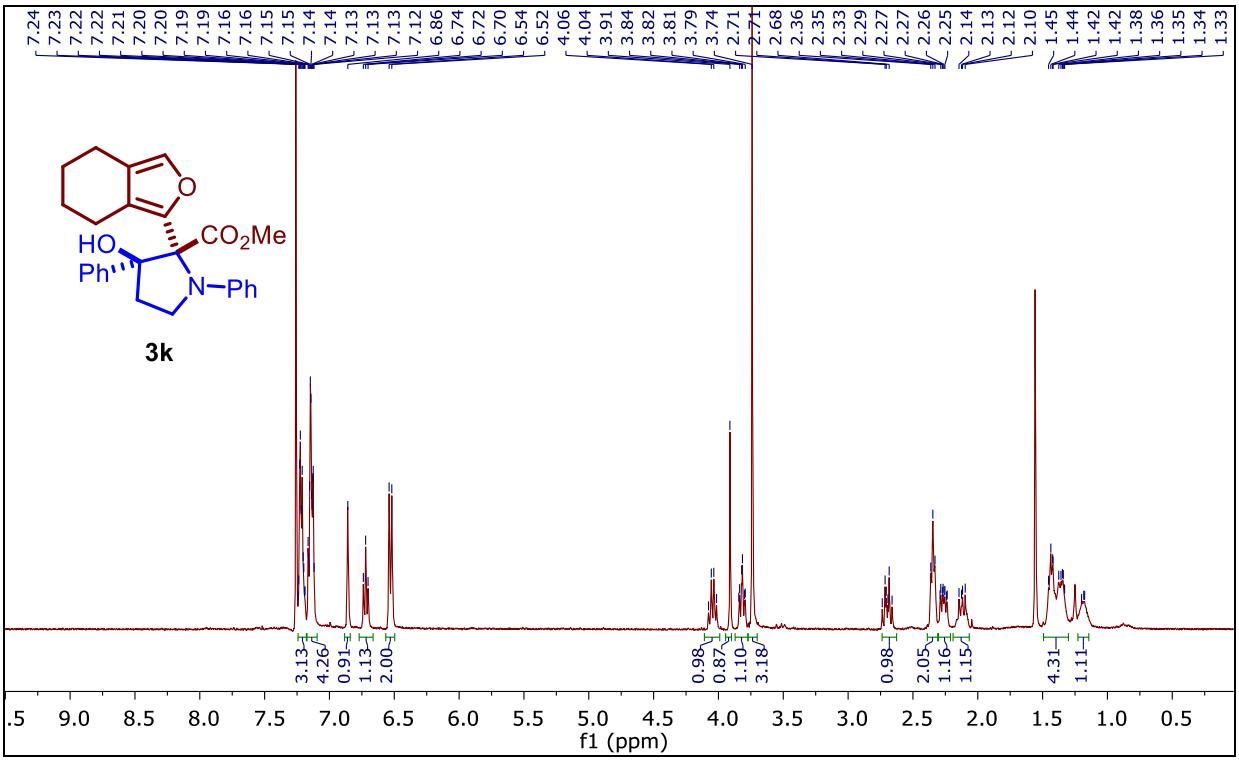

171.32
144.39 143.84 139.61 136.56
125.38 122.49 120.24 113.08
85.97 77.48 cdcl3 77.36 77.16 cdcl3 76.84 cdcl3
52.42 48.08 37.26 33.87 31.63 24.04 23.58 22.87 22.00 20.49
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

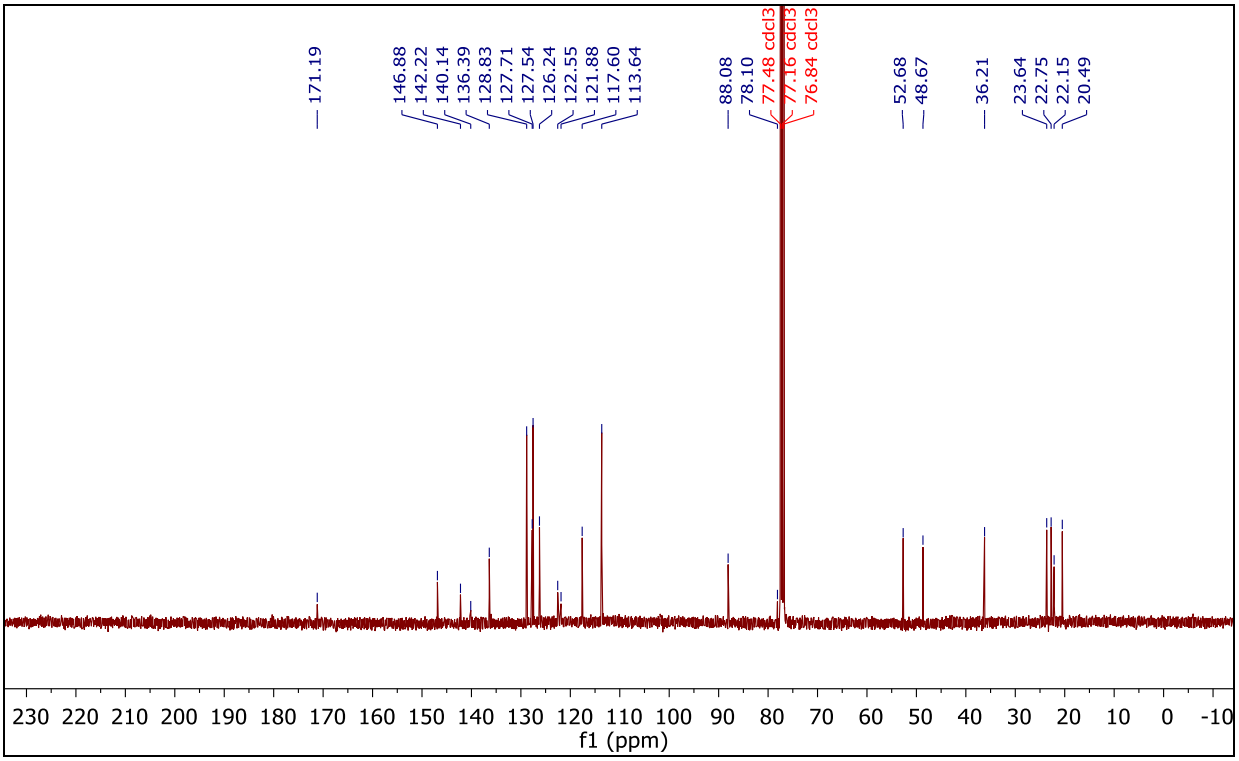

7.19 6.65 6.64 6.62 6.38 6.38 6.36 3.70 3.67 3.65 3.58 3.56 3.56 3.54 3.53 3.52 2.71 2.49 2.47 2.45 2.32 2.31 2.31 2.29 2.28 2.27 2.26 2.20 2.19 2.17 2.16 2.15 2.13 2.11 2.09 2.07 2.06 2.04 1.97 1.95 1.93 1.53 1.51 1.50 1.47 1.45 1.44 1.43 1.42 1.41 1.39 1.10 0.94 0.12
HO
CO2Me
N
OTBS
3i
0.97 2.08 2.00 3.66 1.29 0.89 2.11 1.33 1.29 1.16 1.23 4.07 2.90 9.04 5.36
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

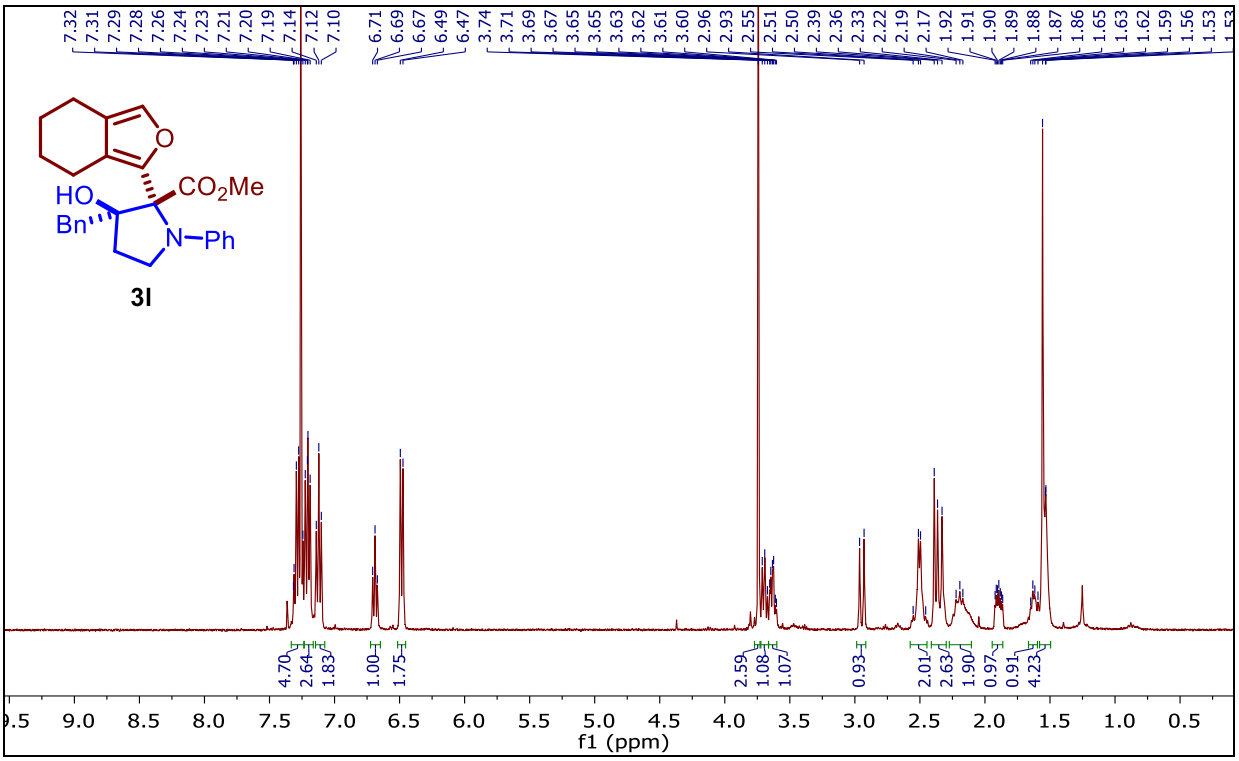

171.52
147.14 144.00 141.68 136.68
122.51 120.26 120.14 114.44
85.93
77.48 cdcl3 77.36 77.16 cdcl3 76.84 cdcl3
52.32 48.51
37.24 25.89 24.27 23.54 22.85 21.80 20.49 18.34
-4.30
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

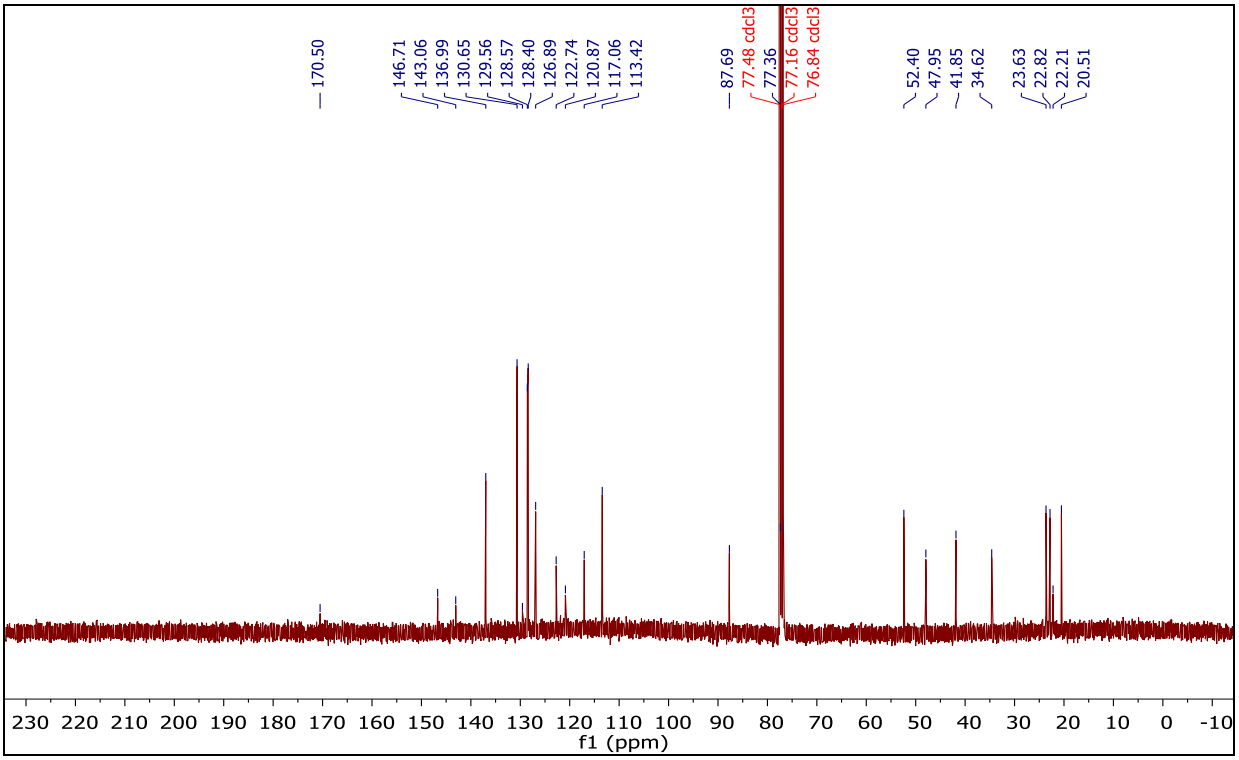

8.43 8.41 7.79 7.77 7.61 7.59 7.51 7.50 7.48 7.46 7.44 7.42 7.26 7.24 7.19 7.17 7.15 6.20 6.18 3.76 3.75 3.73 3.73 3.49 3.34 3.33 3.32 3.31 3.31 3.30 2.74 2.59 2.58 2.56 2.55 2.54 2.27 2.26 2.25 2.08 1.73 1.72 1.69 1.63 1.62 1.61 1.61 1.60 1.59 1.59 1.58 1.57 1.56 1.56 1.54 1.54 1.54 1.50 1.25
O
HO
CO2Me
N
3j
0.95 0.99 1.03 2.06 1.03 1.18 0.86 1.17 2.69 1.93 1.13 1.89 1.15 1.15 1.44 3.42 3.01 1.93
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
f1 (ppm)

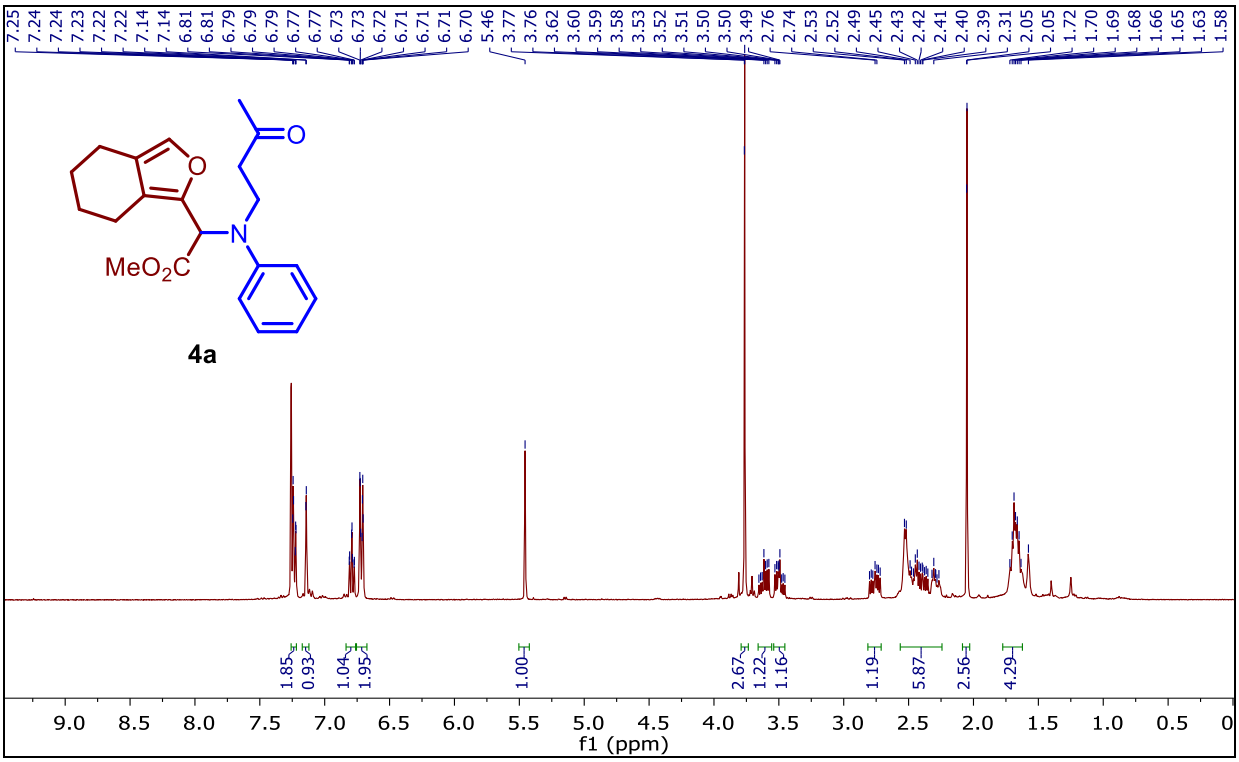

170.65
146.22 144.66 135.93 134.51 133.25 127.96 125.82 125.67 125.47 125.39 124.88 123.79 122.78 121.76
84.89 78.67 77.48 cdcl3 77.16 cdcl3 76.84 cdcl3
53.45 52.16
39.03
23.27 22.81 22.37 21.09 20.37
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

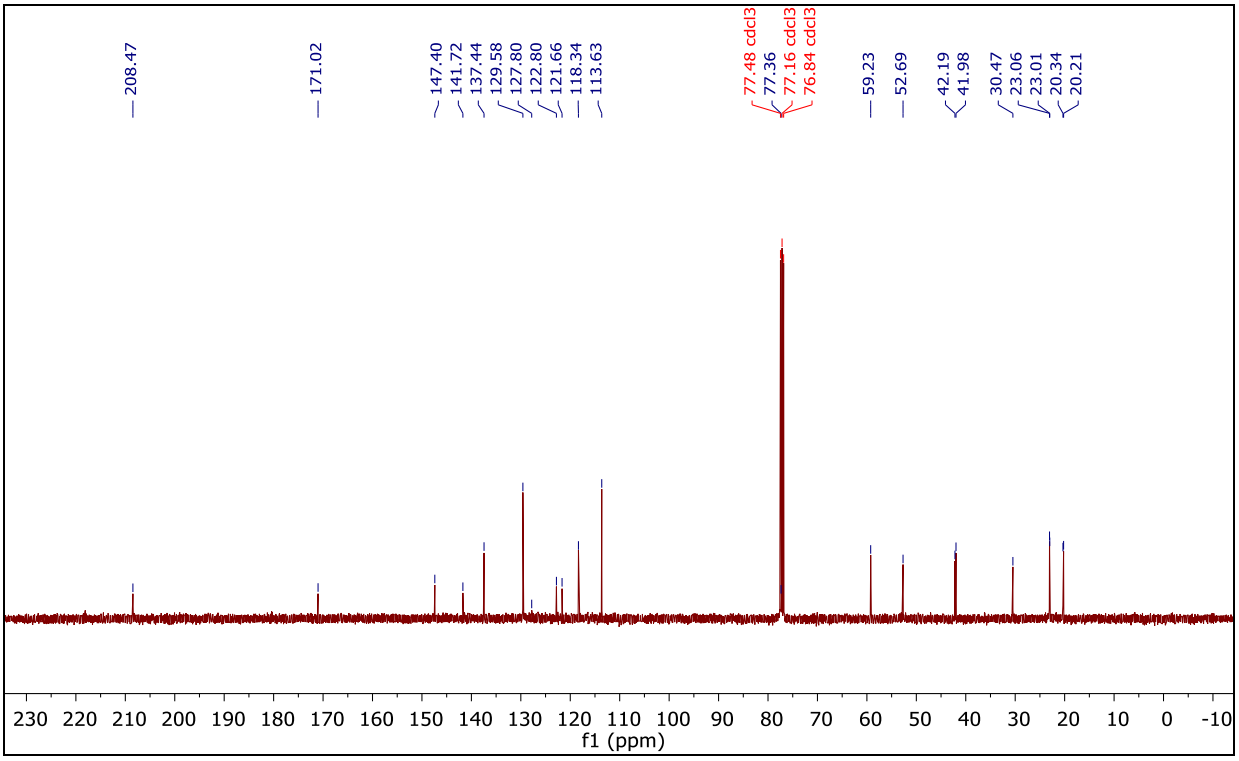

HO
Ph
CO2Me
N–Ph
O
3k
f1 (ppm)

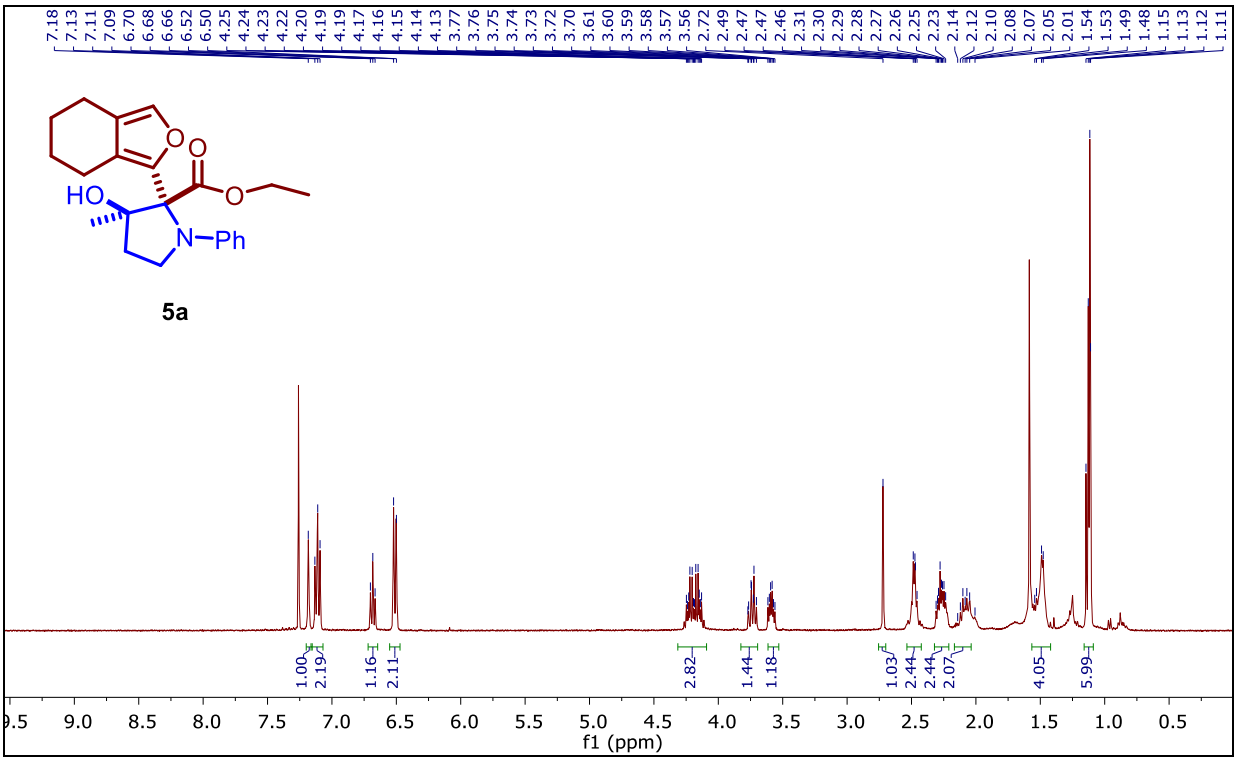

f1 (ppm)

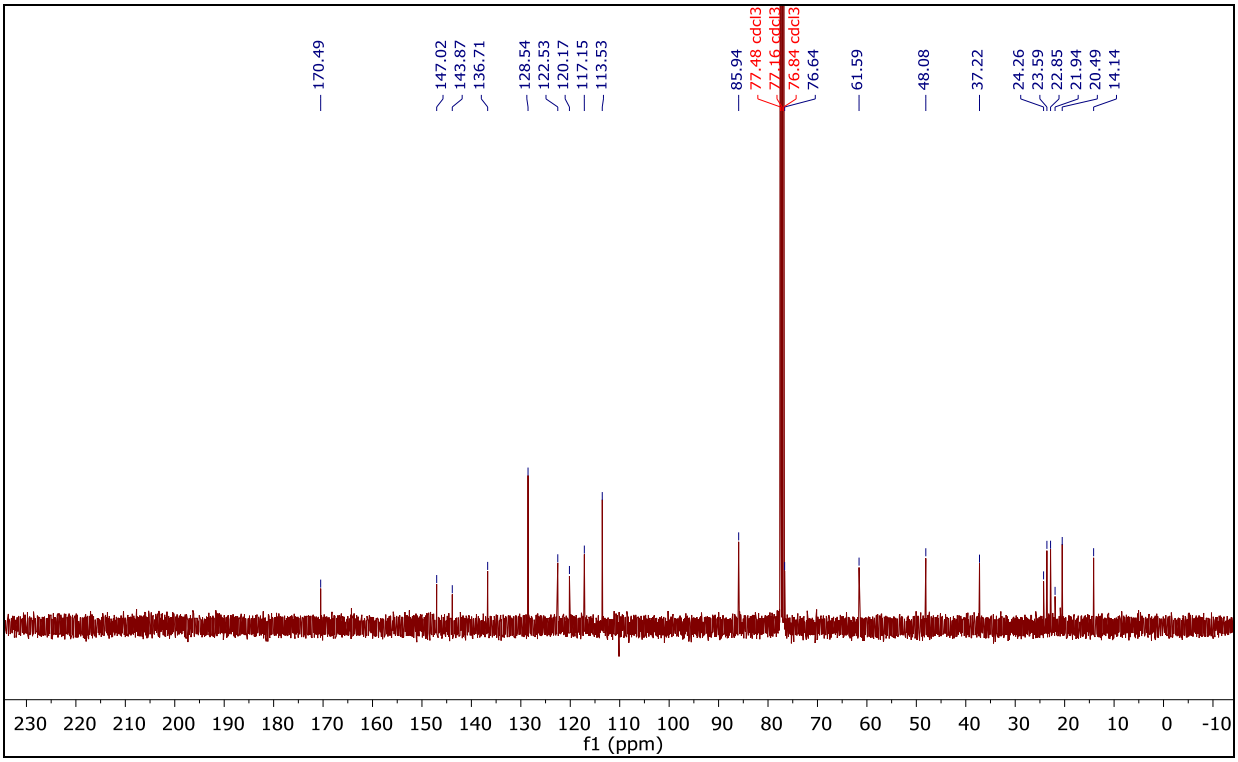

7.32 7.31 7.29 7.28 7.26 7.24 7.23 7.21 7.20 7.19 7.14 7.12 7.10
6.71 6.69 6.67 6.49 6.47
3.74 3.71 3.69 3.67 3.65 3.63 3.62 3.61 3.60 2.96 2.93 2.55
2.51 2.50 2.39 2.36 2.33 2.22 2.19 2.17 1.92 1.91 1.90 1.89 1.88 1.87 1.86 1.65 1.63 1.62 1.59 1.56 1.53
O
CO2Me
HO
Bn
N–Ph
3l
4.70 2.64 1.83 1.00 1.75 2.59 1.08 1.07 0.93 2.01 2.63 1.90 0.97 0.91 4.23
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

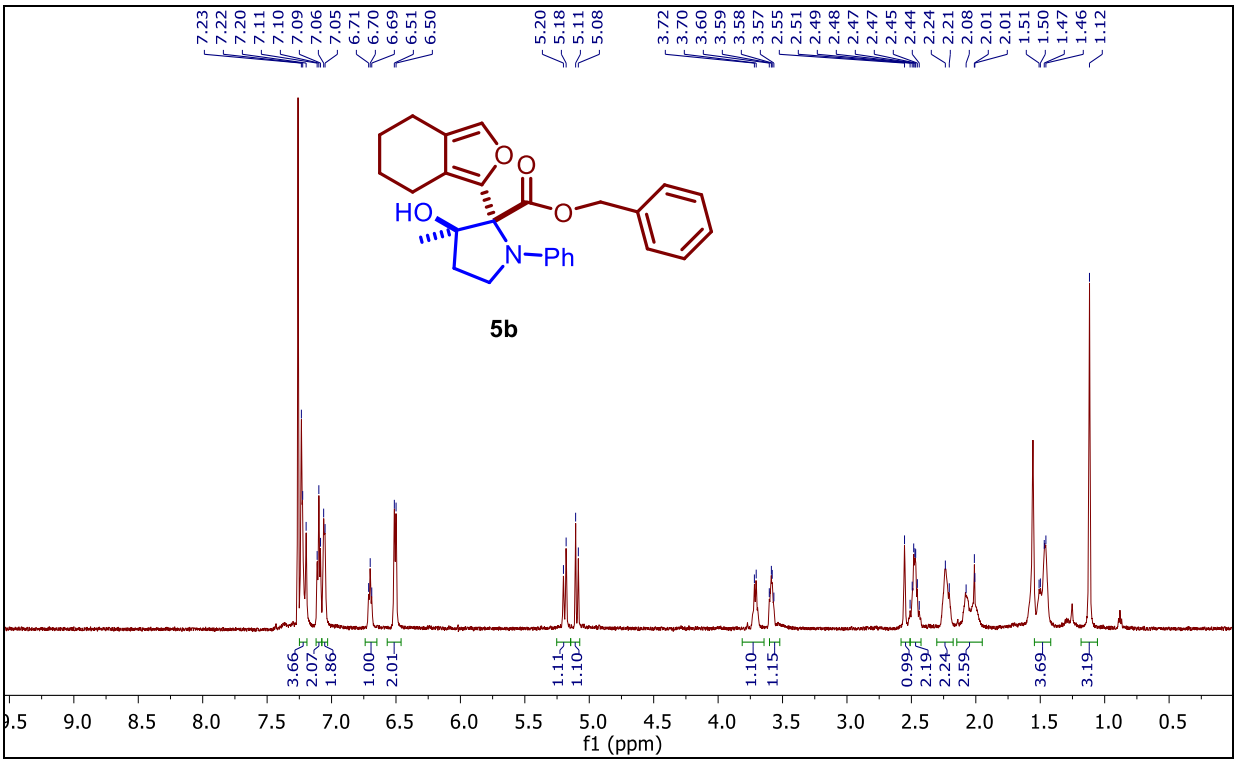

170.50
146.71 143.06 136.99 130.65 129.56 128.57 128.40 126.89 122.74 120.87 117.06 113.42
87.69
77.48 cdcl3
77.36
77.16 cdcl3
76.84 cdcl3
52.40 47.95 41.85 34.62 23.63 22.82 22.21 20.51
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.25 7.24 7.24 7.23 7.22 7.22 7.14 7.14 6.81 6.81 6.79 6.79 6.79 6.77 6.77 6.73 6.73 6.72 6.71 6.71 6.71 6.70 5.46 3.77 3.76 3.62 3.60 3.59 3.58 3.53 3.52 3.51 3.50 3.50 3.49 2.76 2.74 2.53 2.52 2.49 2.45 2.43 2.42 2.41 2.40 2.39 2.31 2.05 2.05 1.72 1.70 1.69 1.68 1.66 1.65 1.63 1.58
O
O
N
MeO2C
4a
1.85 0.93 1.04 1.95 1.00 2.67 1.22 1.16 1.19 5.87 2.56 4.29
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
f1 (ppm)

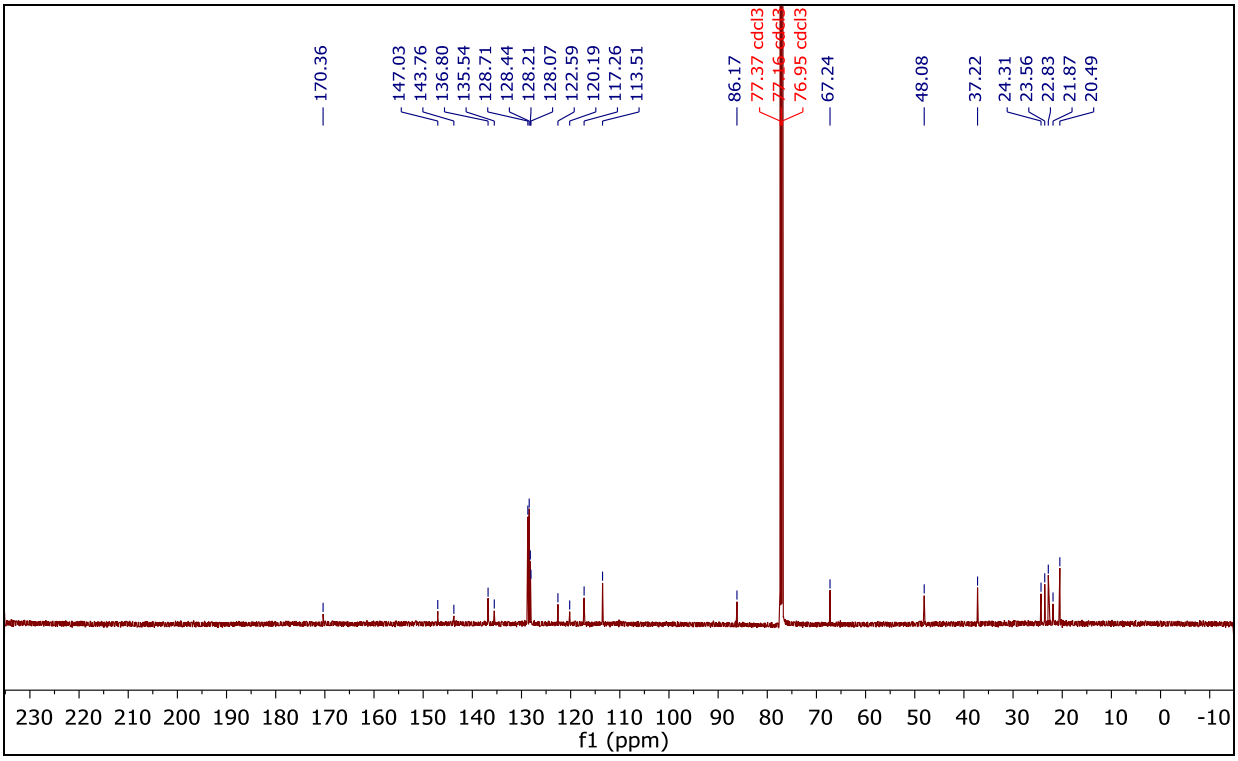

208.47
171.02
147.40 141.72 137.44 129.58 127.80 122.80 121.66 118.34 113.63
77.48 cdcl3 77.36 77.16 cdcl3 76.84 cdcl3
59.23 52.69 42.19 41.98 30.47 23.06 23.01 20.34 20.21
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

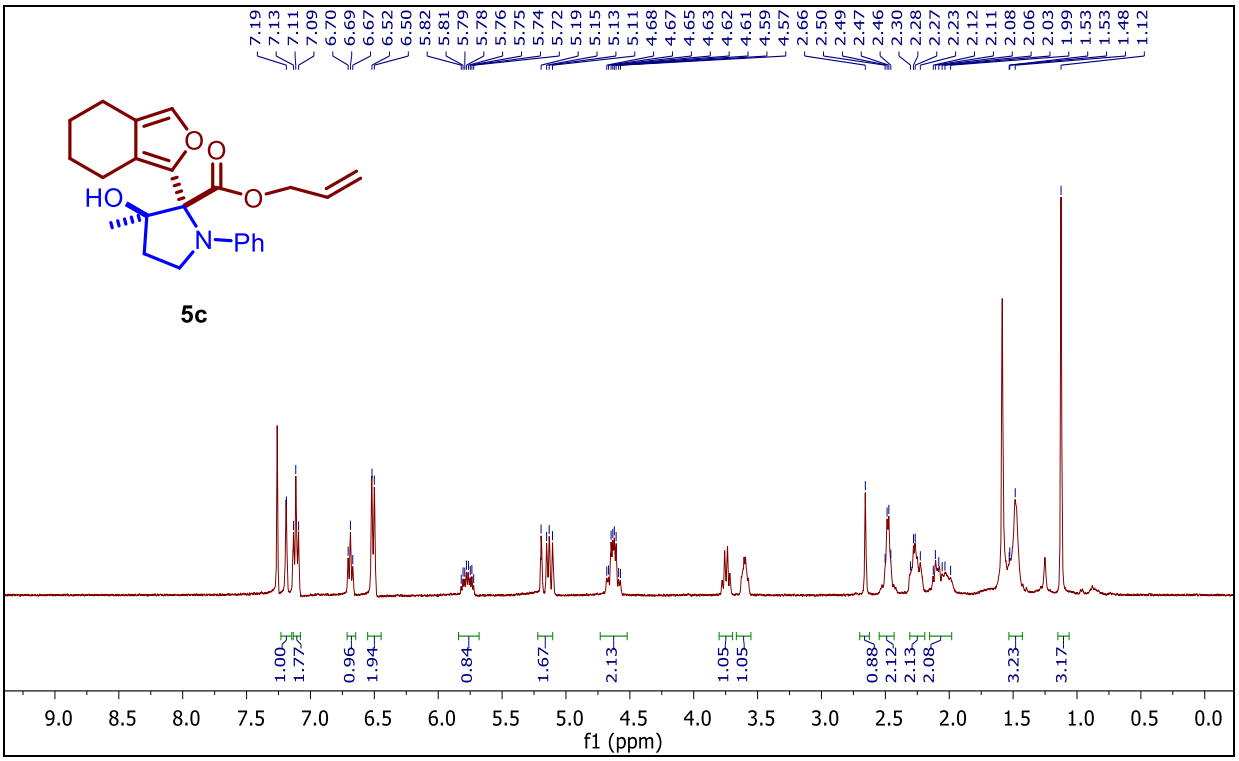

HO
O
O
O
N–Ph
5a
f1 (ppm)

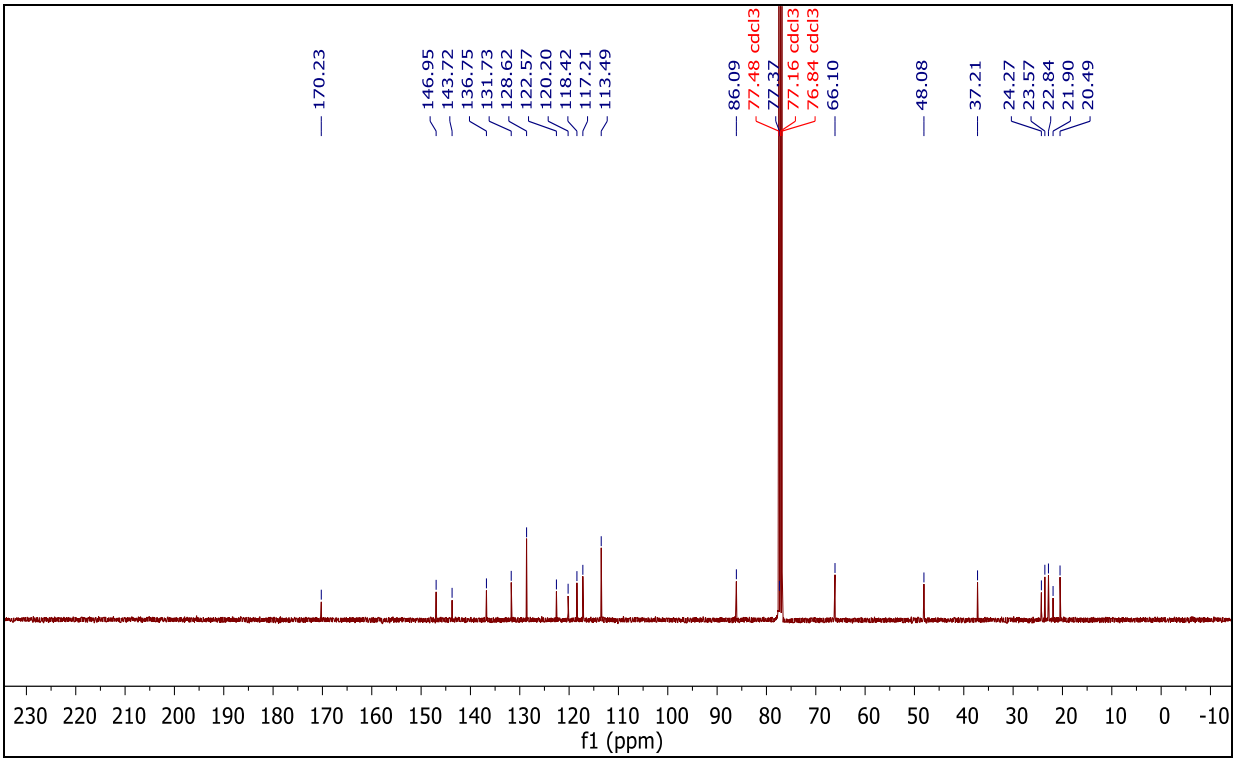

170.49
147.02
143.87
136.71
128.54
122.53
120.17
117.15
113.53
85.94
77.48 cdcl3
77.16 cdcl3
76.84 cdcl3
76.64
61.59
48.08
37.22
24.26
23.59
22.85
21.94
20.49
14.14
f1 (ppm)

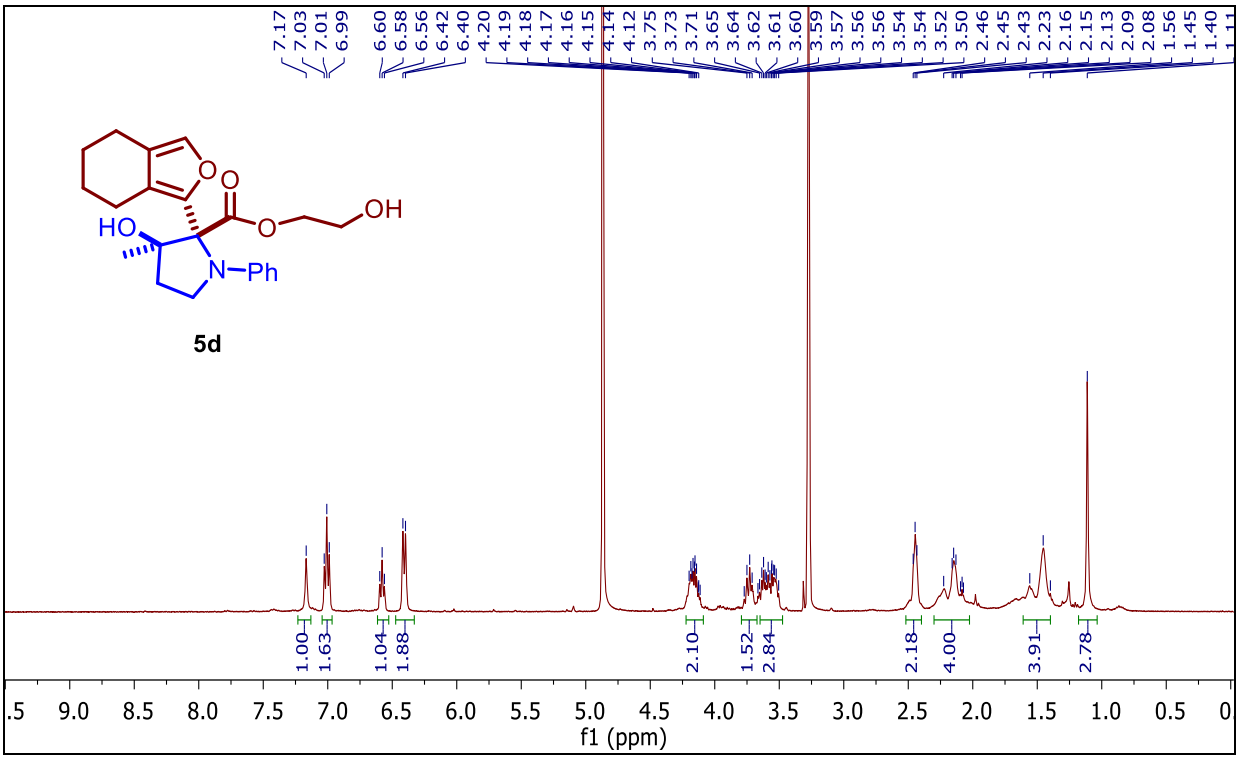

7.23 7.22 7.20 7.11 7.10 7.09 7.06 7.05 6.71 6.70 6.69 6.51 6.50
5.20 5.18 5.11 5.08
3.72 3.70 3.60 3.59 3.58 3.57 2.55 2.51 2.49 2.48 2.47 2.47 2.45 2.44 2.24 2.21 2.08 2.01 2.01 1.51 1.50 1.47 1.46 1.12
HO
O
O
O
N–Ph
3.66 2.07 1.86 1.00 2.01 1.11 1.10 1.10 1.15 0.99 2.19 2.24 2.59 3.69 3.19
f1 (ppm)

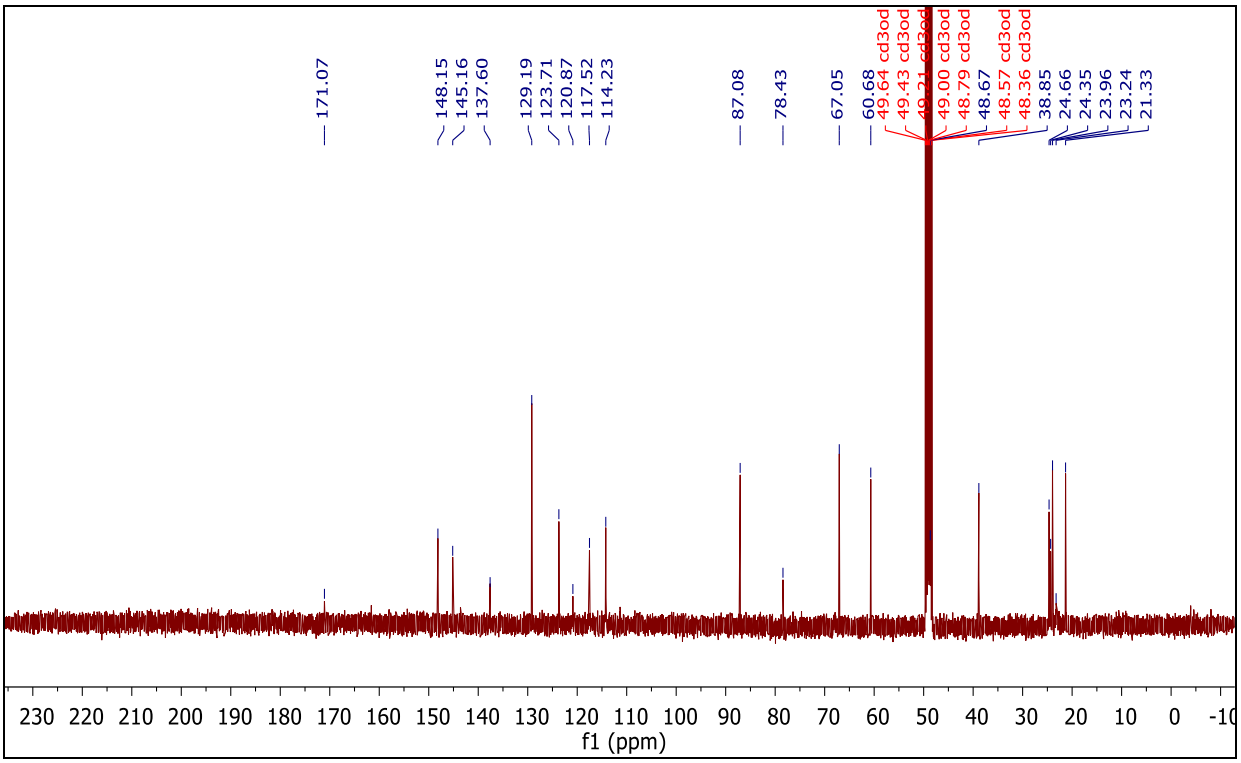
**5b**

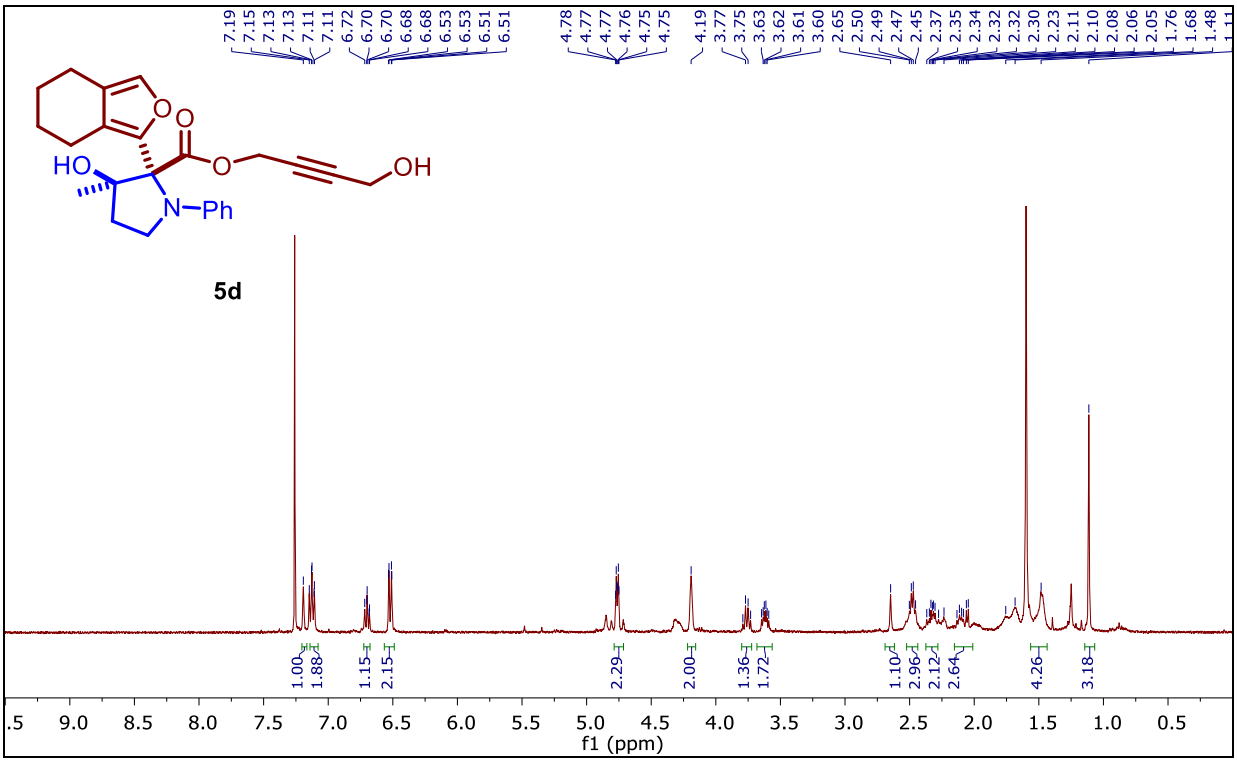

170.36
147.03 143.76 136.80 135.54 128.71 128.44 128.21 128.07 122.59 120.19 117.26 113.51
86.17
77.37 cdcl3
77.16 cdcl3
76.95 cdcl3
67.24
48.08
37.22
24.31 23.56 22.83 21.87 20.49
f1 (ppm)

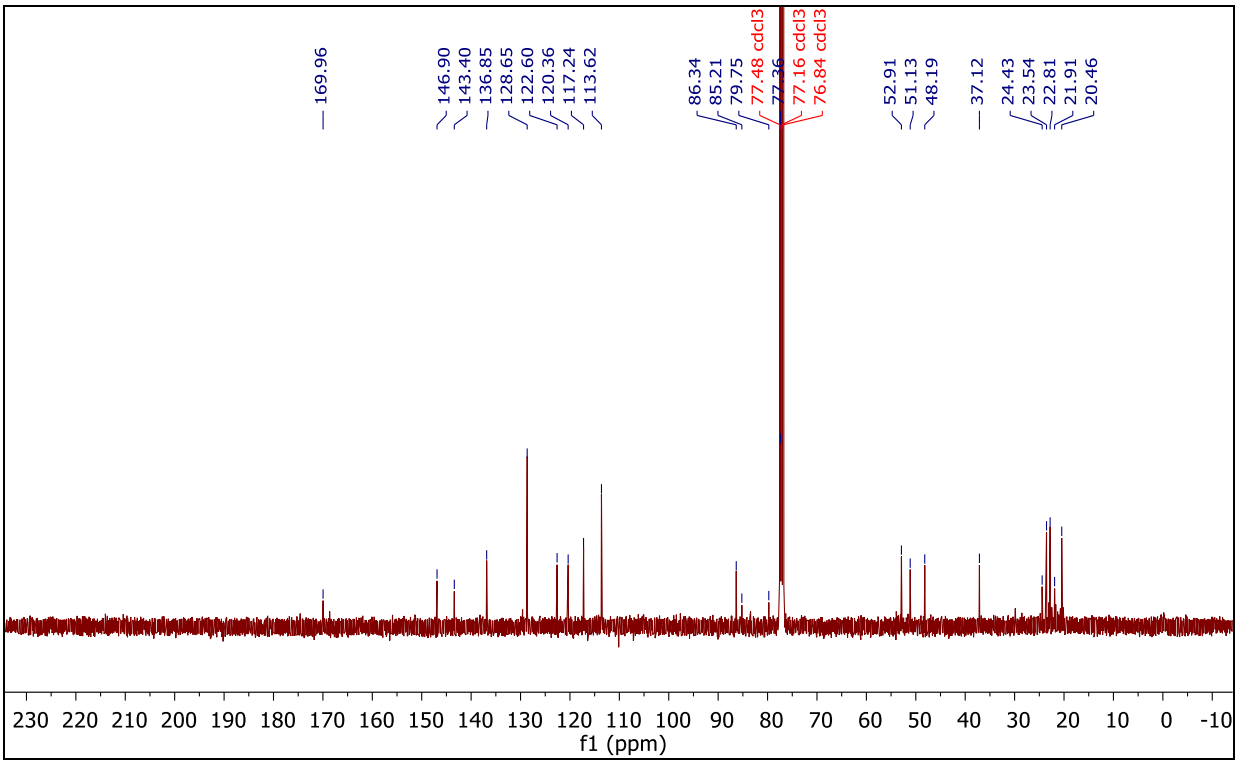

7.19 7.13 7.11 7.09 6.70 6.69 6.67 6.52 6.50 5.82 5.81 5.79 5.78 5.76 5.75 5.74 5.72 5.19 5.15 5.13 5.11 4.68 4.67 4.65 4.63 4.62 4.61 4.59 4.57 2.66 2.50 2.49 2.47 2.46 2.30 2.28 2.27 2.23 2.12 2.11 2.08 2.06 2.03 1.99 1.53 1.53 1.48 1.12
HO
O
O
O
N–Ph
5c
1.00 1.77 0.96 1.94 0.84 1.67 2.13 1.05 1.05 0.88 2.12 2.13 2.08 3.23 3.17
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


170.23
146.95 143.72 136.75 131.73 128.62 122.57 120.20 118.42 117.21 113.49
86.09 77.48 cdcl3 77.37 77.16 cdcl3 76.84 cdcl3 66.10
48.08
37.21
24.27 23.57 22.84 21.90 20.49
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.17
7.03
7.01
6.99
6.60
6.58
6.56
6.42
6.40
4.20
4.19
4.18
4.17
4.16
4.15
4.14
4.12
3.75
3.73
3.71
3.65
3.64
3.62
3.61
3.60
3.59
3.57
3.56
3.56
3.54
3.54
3.52
3.50
2.46
2.45
2.43
2.23
2.16
2.15
2.13
2.09
2.08
1.56
1.45
1.40
O
O
HO
O
OH
N–Ph
5d
1.00
1.63
1.04
1.88
2.10
1.52
2.84
2.18
4.00
3.91
2.78
f1 (ppm)


171.07
148.15
145.16
137.60
129.19
123.71
120.87
117.52
114.23
87.08
78.43
67.05
60.68
49.64 cd3od
49.43 cd3od
49.21 cd3od
49.00 cd3od
48.79 cd3od
48.67
48.57 cd3od
48.36 cd3od
38.85
24.66
24.35
23.96
23.24
21.33
f1 (ppm)


7.19 7.15 7.13 7.13 7.11 7.11 6.72 6.70 6.70 6.68 6.68 6.53 6.53 6.51 6.51
4.78 4.77 4.77 4.76 4.75 4.75 4.19 3.77 3.75 3.63 3.62 3.61 3.60
2.65 2.50 2.49 2.47 2.45 2.37 2.35 2.34 2.32 2.32 2.30 2.23 2.11 2.10 2.08 2.06 2.05 1.76 1.68 1.48
HO
O
O
O
OH
N–Ph
5d
1.00 1.88 1.15 2.15 2.29 2.00 1.36 1.72 1.10 2.96 2.12 2.64 4.26 3.18
f1 (ppm)


169.96
146.90 143.40 136.85 128.65 122.60 120.36 117.24 113.62
86.34 85.21 79.75 77.48 cdcl3 77.36 77.16 cdcl3 76.84 cdcl3
52.91 51.13 48.19
37.12
24.43 23.54 22.81 21.91 20.46
f1 (ppm)