 Supporting Information: Frazier, Sandoval, Palmer, Read de Alaniz*

Electrophilic α-Oxygenation Reaction of β-Ketoesters using *N*-Hydroxycarbamates: Control of the Ambident Reactivity of Nitrosoformate Intermediates

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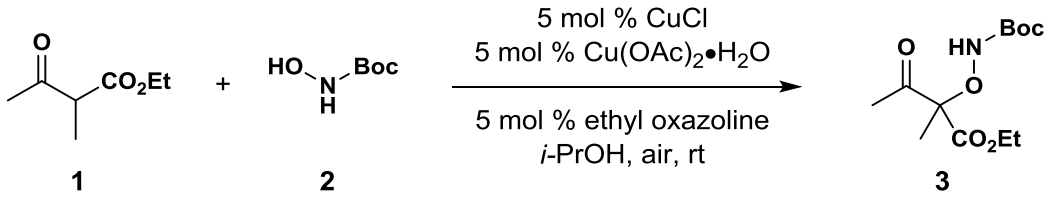
Materials and Methods. Unless stated otherwise, reactions were conducted in flame-dried glassware under an atmosphere of air using reagent grade solvents. All commercially obtained reagents were used as received. Reaction temperatures were controlled using a Heidolph temperature modulator, and unless stated otherwise, reactions were performed at room temperature (rt, approximately 23 ºC). Thin-layer chromatography (TLC) was conducted with E. Merck silica gel 60 F254 pre-coated plates, (0.25 mm) and visualized by exposure to UV light (254 nm) or stained with potassium permanganate. Flash column chromatography was performed using normal phase silica gel (60 Å, 230-240 mesh, Geduran®). ^{1}H NMR spectra were recorded on Varian Spectrometers (at 500 and 600 MHz) and are reported relative to deuterated solvent signals. Data for ^{1}H NMR spectra are reported as follows: chemical shift (δ ppm), multiplicity, coupling constant (Hz) and integration. ^{13}C NMR spectra were recorded on Varian Spectrometers (125 and 150 MHz). Data for ^{13}C NMR spectra are reported in terms of chemical shift, and where relevant, multiplicity and coupling constant (Hz). IR spectra were recorded on a Perkin Elmer Spectrum Two FT/IR and are reported in terms of frequency of absorption (cm^{-1}). High resolution mass spectra and X-Ray analyses were obtained from the UC Santa Barbara Mass Spectrometry and X-Ray Facilities.

Hydroxycarbamates **2**, **31**, **S-17**, **S-18**, **S-19**, and **S-20** were purchased from commercial sources, or prepared according to literature precedent.[1] β-Ketoesters **1**, **S-4**, **S-5**, **S-6**, **S-7**, **S-11**, and **S-12** were purchased from commercial sources and used as received. β-Ketoesters **S-8**, **S-9**, and **S-10** were prepared by alkylation of the corresponding acetoacetate with methyl iodide.[2] β-Ketoesters **S-1**, **S-2**, and **S-3** were prepared from ethyl-2-bromopropionate and the corresponding nitrile. β-Ketoesters **S-13**, and **S-14** were prepared by acylation of the ketone with the corresponding carbonate.[3] β-Ketoesters **S-15** and **S-16** were prepared by esterification from the corresponding acid. β-Ketoester **S-21** was prepared according to literature precedent.[4] Annulation reagent **S-23** was purchased from commercial vendors and used as received. Annulation reagent **S-24** was prepared according to the Aggarwal method.[5] The crystal structures of compounds **44** and **S-22** are available free of charge from the Cambridge Crystallographic Data Centre via www.cdcc.cam.ac.uk/data_request/cif CCDC 907696 (**44**) and CCDC 932616 (**S-22**).

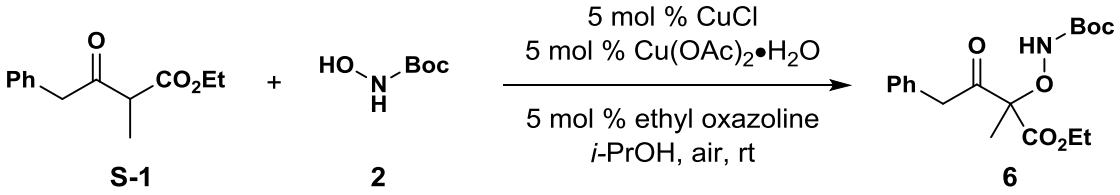
General Procedure for the *O*-Selective Aldol Reaction: To a stirred solution of β-ketoester **4**, 5 mol % $Cu(OAc)_2 \cdot H_2O$, and 5 mol % ethyl oxazoline in *iso*propyl alcohol (0.15 M) was added 5 mol % CuCl and *N*-hydroxycarbamate **17**. The reaction was stirred at room temperature open to the air until complete as judged by TLC, and the *iso*propyl alcohol was removed *in vacuo*. The reaction was quenched with EDTA (0.5 M, pH 7.0), diluted with ethyl acetate and stirred until color no longer persisted in the organic layer (approx 30 mins). The reaction was extracted with ethyl acetate three times and the combined organic layers were dried over $MgSO_4$. The product was filtered and then concentrated *in vacuo*. The residue was purified by column chromatography to afford the corresponding aldol product.

[1] R. Liu, S. R. Herron and S. A. Fleming, *J. Org. Chem.,* 2007, **72**, 5587.
[2] C. C. Nawrat, W. Lewis and C. J. Moody, *J. Org. Chem.,* 2011, **76,** 7872.
[3] P. A. Krapcho, J. Diamanti, C. Cayden and R. Bingham, *Org. Synth.,* 1967, **47**, 20.
[4] M. Baidya, K. A. Griffin and H. Yamamoto, *J. Am. Chem. Soc.,* 2012, **134**, 18566
[5] M. Yar, E. M. McGarrigle and V. K. Aggarwal, *Angew. Chem. Int. Ed.,* 2008, **47**, 3784.



1 2 3

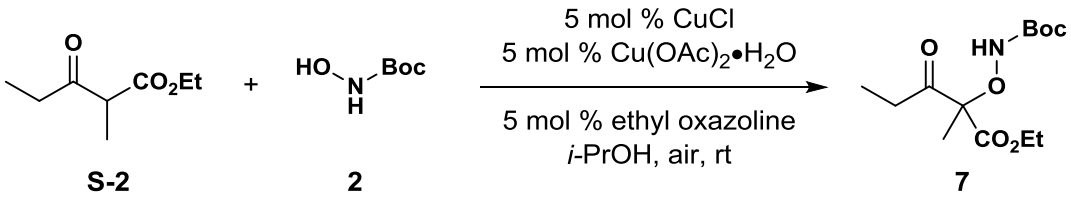
Ethyl 2-(((*tert*-butoxycarbonyl)amino)oxy)-2-methyl-3-oxobutanoate (3): According to the general procedure, CuCl (1.5 mg, 0.015 mmol, 0.05 equiv) and *tert*-butyl hydroxycarbamate **2** (40 mg, 0.30 mmol, 1 equiv) were added to ethyl 2-methyl-3-oxobutanoate **1** (52 mg, 0.36 mmol, 1.2 equiv), $Cu(OAc)_2 \cdot H_2O$ (3.0 mg, 0.015 mmol, 0.05 equiv), and ethyl oxazoline (1.5 mg, 0.015 mmol, 0.05 equiv) in 2 mL of *iso*propyl alcohol. The reaction was stirred for 17 h at rt, and the solvent was removed *in vacuo*. The reaction was quenched with 4 mL EDTA (0.5 M, pH 7.0) and extracted with ethyl acetate (3 x 4 mL). The combined organic layers were dried over $MgSO_4$, filtered and then concentrated *in vacuo*. The residue was purified by column chromatography to afford aldol product **3** (70 mg, 84%) as a colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.67 (s, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 2.31 (s, 3H), 1.65 (s, 3H), 1.47 (s, 9H), 1.30 (t, *J* = 7.1 Hz, 3H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ 202.9, 169.4, 156.5, 91.4, 82.5, 62.4, 28.3, 25.3, 18.5, 14.3 ppm; IR (thin film) 3297, 2958, 1727, 1370, 1248, 1131 cm^{-1}; HRMS (ESI) *m/z* 298.1259 (298.1261 calcd for $C_{12}H_{21}NNaO_6^+$ $[MNa]^+$). A minor amount of the *N*-selective product was also isolated (8 mg, 10%).



S-1 2 6

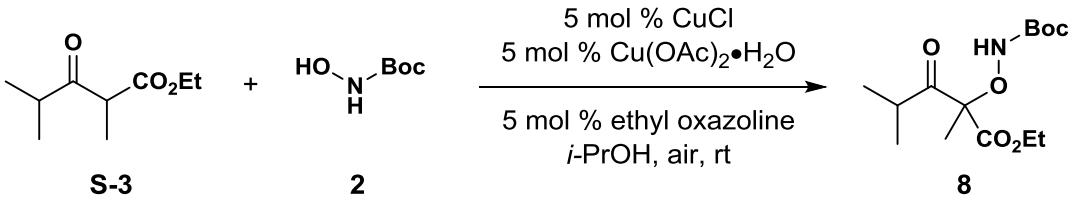
Ethyl 2-(((*tert*-butoxycarbonyl)amino)oxy)-2-methyl-3-oxo-4-phenylbutanoate (6): According to the general procedure, CuCl (1.5 mg, 0.015 mmol, 0.05 equiv) and *tert*-butyl hydroxycarbamate **2** (40 mg, 0.30 mmol, 1 equiv) were added to ethyl 2-methyl-3-oxo-4-phenylbutanoate **S-1** (133 mg, 0.60 mmol, 2.0 equiv), $Cu(OAc)_2 \cdot H_2O$ (3.0 mg, 0.015 mmol, 0.05 equiv), and ethyl oxazoline (1.5 mg, 0.015 mmol, 0.05 equiv) in 2 mL of *iso*propyl alcohol. The reaction was stirred for 14 h at rt, and the solvent was removed *in vacuo*. The reaction was quenched with 4 mL EDTA (0.5 M, pH 7.0) and extracted with ethyl acetate (3 x 4 mL). The combined organic layers were dried over $MgSO_4$, filtered and then concentrated *in vacuo*. The

residue was purified by column chromatography to afford aldol product **6** (77 mg, 73%) as a colorless solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.79 (s, 1H), 7.30 (t, *J* = 7.3 Hz, 2H), 7.24 (t, *J* = 7.3 Hz, 1H), 7.19 (d, *J* = 7.2 Hz, 2H), 4.21 (q, *J* = 7.1 Hz, 2H), 4.10 (d, *J* = 17.1 Hz, 1H), 3.97 (d, *J* = 17.1 Hz, 1H), 1.10 (s, 3H), 1.48 (s, 9H), 1.26 (t, *J* = 7.1 Hz, 3H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ 202.4, 169.4, 156.5, 133.5, 130.0, 128.6, 127.2, 91.4, 82.5, 62.4, 43.6, 28.3, 18.6, 14.2 ppm; IR (thin film) 3301, 2982, 1729, 1456, 1370, 1249, 1135 cm^{-1}; HRMS (ESI) *m/z* 374.1571 (374.1574 calcd for $C_{18}H_{25}NNaO_6^+$ $[MNa]^+$). A minor amount of the *N*-selective product was also isolated (16 mg, 15%).



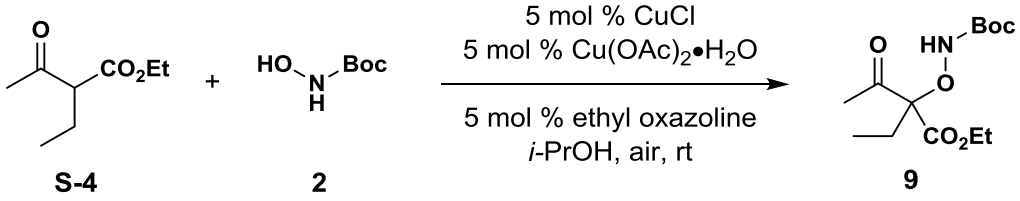
S-2 2 7

Ethyl 2-(((*tert*-butoxycarbonyl)amino)oxy)-2-methyl-3-oxopentanoate (7): According to the general procedure, CuCl (1.5 mg, 0.015 mmol, 0.05 equiv) and *tert*-butyl hydroxycarbamate **2** (40 mg, 0.30 mmol, 1 equiv) were added to ethyl 2-methyl-3-oxopentanoate **S-2** (95 mg, 0.60 mmol, 2.0 equiv), $Cu(OAc)_2 \cdot H_2O$ (3.0 mg, 0.015 mmol, 0.05 equiv), and ethyl oxazoline (1.5 mg, 0.015 mmol, 0.05 equiv) in 2 mL of *iso*propyl alcohol. The reaction was stirred for 14 h at rt, and the solvent was removed *in vacuo*. The reaction was quenched with 4 mL EDTA (0.5 M, pH 7.0) and extracted with ethyl acetate (3 x 4 mL). The combined organic layers were dried over $MgSO_4$, filtered and then concentrated *in vacuo*. The residue was purified by column chromatography to afford aldol product **7** (54 mg, 62%) as a colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.68 (s, 1H), 4.24 (qd, *J* = 7.1, 1.0 Hz, 2H), 2.76 (dq, *J* = 18.6, 7.2 Hz, 1H), 2.65 (dq, *J* = 18.6, 7.2 Hz, 1H), 1.63 (s, 3H), 1.45 (s, 9H), 1.28 (t, *J* = 7.1 Hz, 3H), 1.04 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ 205.7, 169.6, 156.5, 91.4, 82.4, 62.3, 30.6, 28.3, 18.6, 14.2, 7.6 ppm; IR (thin film) 3300, 2982, 1726, 1370, 1247, 1131 cm^{-1}; HRMS (ESI) *m/z* 312.1417 (312.1418 calcd for $C_{13}H_{23}NNaO_6^+$ $[MNa]^+$). A minor amount of the *N*-selective product was also isolated (13 mg, 19%).



S-3 2 8

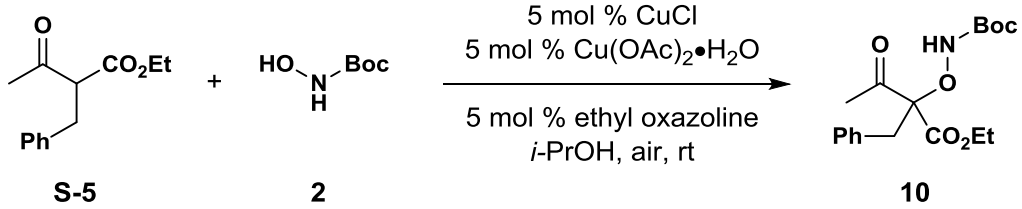
Ethyl 2-(((*tert*-butoxycarbonyl)amino)oxy)-2,4-dimethyl-3-oxopentanoate (8): According to the general procedure, CuCl (1.5 mg, 0.015 mmol, 0.05 equiv) and *tert*-butyl hydroxycarbamate **2** (40 mg, 0.30 mmol, 1 equiv) were added to ethyl 2,4-dimethyl-3-oxopentanoate **S-3** (103 mg, 0.60 mmol, 2.0 equiv), $Cu(OAc)_2 \cdot H_2O$ (3.0 mg, 0.015 mmol, 0.05 equiv), and ethyl oxazoline (1.5 mg, 0.015 mmol, 0.05 equiv) in 2 mL of *iso*propyl alcohol. The reaction was stirred for 14 h at rt, and the solvent was removed *in vacuo*. The reaction was quenched with 4 mL EDTA (0.5 M, pH 7.0) and extracted with ethyl acetate (3 x 4 mL). The combined organic layers were dried over $MgSO_4$, filtered and then concentrated *in vacuo*. The residue was purified by column chromatography to afford aldol product **8** (52 mg, 57%) as a colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.63 (s, 1H), 4.24 (q, *J* = 7.1 Hz, 2H), 3.28 (h, *J* = 6.8 Hz, 1H), 1.66 (s, 3H), 1.46 (s, 9H), 1.29 (t, *J* = 7.1 Hz, 3H), 1.12 (d, *J* = 6.8 Hz, 3H), 1.06 (d, *J* = 6.7 Hz, 3H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ 209.7, 169.6, 156.5, 91.9, 82.4, 62.3, 35.5, 28.3, 19.9, 19.2, 18.8, 14.3 ppm; IR (thin film) 3300, 2980, 1754, 1370, 1248, 1133 cm^{-1}; HRMS (ESI) *m/z* 326.1574 (326.1574 calcd for $C_{14}H_{25}NNaO_6^+$ $[MNa]^+$). A minor amount of the *N*-selective product was also isolated (17 mg, 19%).



S-4 2 9

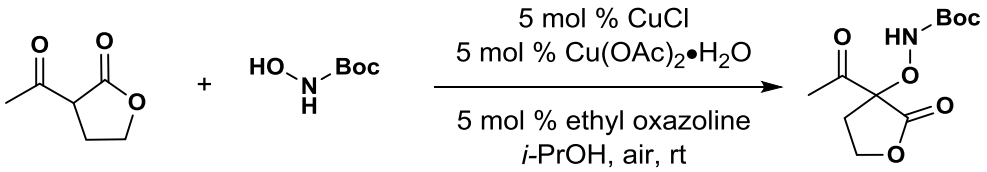
Ethyl 2-(((*tert*-butoxycarbonyl)amino)oxy)-2-ethyl-3-oxobutanoate (9): According to the general procedure, CuCl (1.5 mg, 0.015 mmol, 0.05 equiv) and *tert*-butyl hydroxycarbamate **2** (40 mg, 0.30 mmol, 1 equiv) were added to ethyl 2-ethyl-3-oxobutanoate **S-4** (142 mg, 0.90 mmol, 3.0 equiv), $Cu(OAc)_2 \cdot H_2O$ (3.0 mg, 0.015 mmol, 0.05 equiv), and ethyl oxazoline (1.5 mg, 0.015 mmol, 0.05 equiv) in 2 mL of *iso*propyl alcohol. The reaction was stirred for 15 h at rt, and the solvent was removed *in vacuo*. The reaction was quenched with 4 mL EDTA (0.5 M, pH 7.0) and extracted with ethyl acetate (3 x 4 mL). The combined organic layers were dried

over $MgSO_4$, filtered and then concentrated *in vacuo*. The residue was purified by column chromatography to afford aldol product **9** (78 mg, 90%) as a colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.82 (s, 1H), 4.26 (qd, *J* = 7.1, 1.5 Hz, 2H), 2.29 (s, 3H), 2.13 (dq, *J* = 14.7, 7.4 Hz, 1H), 2.06 (dq, *J* = 14.7, 7.5 Hz, 1H), 1.44 (s, 9H), 1.29 (t, *J* = 7.1 Hz, 3H), 0.95 (t, *J* = 7.4 Hz, 3H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ 203.5, 169.1, 156.2, 94.3, 82.4, 62.2, 28.3, 26.1, 26.1, 14.3, 8.0 ppm; IR (thin film) 3297, 2981, 1725, 1370, 1248, 1148 cm^{-1}; HRMS (ESI) *m/z* 312.1414 (312.1418 calcd for $C_{13}H_{23}NNaO_6^+$ $[MNa]^+$). Less than 2% of the *N*-selective product was observed.



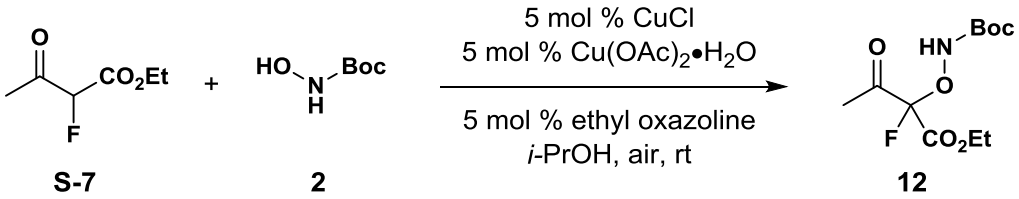
S-5 **2** **10**

Ethyl 2-(((*tert*-butoxycarbonyl)amino)oxy)-2-benzyl-3-oxobutanoate (10): According to the general procedure, CuCl (1.5 mg, 0.015 mmol, 0.05 equiv) and *tert*-butyl hydroxycarbamate **2** (40 mg, 0.30 mmol, 1 equiv) were added to ethyl 2-benzyl-3-oxobutanoate **S-5** (198 mg, 0.90 mmol, 3.0 equiv), $Cu(OAc)_2 \cdot H_2O$ (3.0 mg, 0.015 mmol, 0.05 equiv), and ethyl oxazoline (1.5 mg, 0.015 mmol, 0.05 equiv) in 2 mL of *iso*propyl alcohol. The reaction was stirred for 15 h at rt, and the solvent was removed *in vacuo*. The reaction was quenched with 4 mL EDTA (0.5 M, pH 7.0) and extracted with ethyl acetate (3 x 4 mL). The combined organic layers were dried over $MgSO_4$, filtered and then concentrated *in vacuo*. The residue was purified by column chromatography to afford aldol product **10** (102 mg, 96%) as a colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.90 (s, 1H), 7.28 – 7.18 (m, 5H), 4.36 – 4.01 (m, 2H), 3.41 (d, *J* = 14.6 Hz, 1H), 3.30 (d, *J* = 14.6 Hz, 1H), 2.25 (s, 3H), 1.45 (s, 9H), 1.21 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ 202.9, 168.5, 155.9, 134.0, 130.4, 128.2, 127.2, 93.5, 82.3, 62.0, 38.7, 28.1, 25.9, 13.9 ppm; IR (thin film) 3297, 2982, 1725, 1369, 1246, 1161 cm^{-1}; HRMS (ESI) *m/z* 374.1580 (374.1574 calcd for $C_{18}H_{25}NNaO_6^+$ $[MNa]^+$). Less than 2% of the *N*-selective product was observed.



S-6 **2** **11**

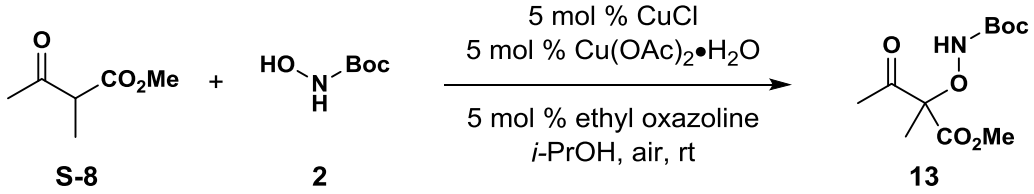
***Tert*-butyl (3-acetyl-2-oxotetrahydrofuran-3-yl)oxycarbamate (11):** According to the general procedure, CuCl (1.5 mg, 0.015 mmol, 0.05 equiv) and *tert*-butyl hydroxycarbamate **2** (40 mg, 0.30 mmol, 1 equiv) were added to 3-acetyldihydrofuran-2(3H)-one **S-6** (46 mg, 0.36 mmol, 1.2 equiv), $Cu(OAc)_2 \cdot H_2O$ (3.0 mg, 0.015 mmol, 0.05 equiv), and ethyl oxazoline (1.5 mg, 0.015 mmol, 0.05 equiv) in 2 mL of *iso*propyl alcohol. The reaction was stirred for 16 h at rt, and the solvent was removed *in vacuo*. The reaction was quenched with 4 mL EDTA (0.5 M, pH 7.0) and extracted with ethyl acetate (3 x 4 mL). The combined organic layers were dried over $MgSO_4$, filtered and then concentrated *in vacuo*. The residue was purified by column chromatography to afford aldol product **11** (73 mg, 93%) as a colorless solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.65 (s, 1H), 4.43 (ddd, J = 8.7, 7.5, 4.7 Hz, 1H), 4.33 (q, J = 8.5 Hz, 1H), 2.71 – 2.61 (m, 2H), 2.38 (s, 3H), 1.47 (s, 9H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ 202.1, 170.9, 156.8, 92.1, 83.3, 66.2, 29.3, 28.2, 26.0 ppm; IR (thin film) 3277, 2982, 1723, 1371, 1250, 1162 cm^{-1}; HRMS (ESI) *m/z* 282.0945 (282.0948 calcd for $C_{11}H_{17}NNaO_6^+$ $[MNa]^+$). Less than 2% of the *N*-selective product was observed.



S-7 **2** **12**

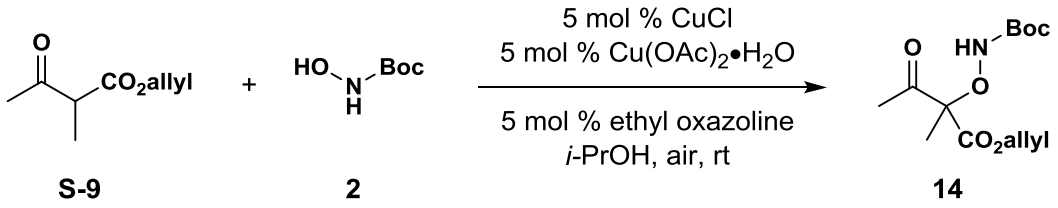
Ethyl 2-(((*tert*-butoxycarbonyl)amino)oxy)-2-fluoro-3-oxobutanoate (12): According to the general procedure, CuCl (1.5 mg, 0.015 mmol, 0.05 equiv) and *tert*-butyl hydroxycarbamate **2** (40 mg, 0.30 mmol, 1 equiv) were added to ethyl 2-fluoro-3-oxobutanoate **S-7** (53 mg, 0.36 mmol, 1.2 equiv), $Cu(OAc)_2 \cdot H_2O$ (3.0 mg, 0.015 mmol, 0.05 equiv), and ethyl oxazoline (1.5 mg, 0.015 mmol, 0.05 equiv) in 2 mL of *iso*propyl alcohol. The reaction was stirred for 16 h at rt, and the solvent was removed *in vacuo*. The reaction was quenched with 4 mL EDTA (0.5 M, pH 7.0) and extracted with ethyl acetate (3 x 4 mL). The combined organic layers were dried

over $MgSO_4$, filtered and then concentrated *in vacuo*. The residue was purified by column chromatography to afford aldol product **12** (81 mg, 96%) as a colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.58 (s, 1H), 4.32 (qq, *J* = 8.1, 3.6 Hz, 2H), 2.40 (d, *J* = 1.7 Hz, 3H), 1.48 (s, 9H), 1.32 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ 195.9 (d, *J* = 29 Hz), 162.4 (d, *J* = 35 Hz), 155.7, 108.9 (d, *J* = 252 Hz), 83.7, 63.5, 28.2, 25.4, 14.1 ppm; IR (thin film) 3275, 2984, 1745, 1371, 1250, 1138 cm^{-1}; HRMS (ESI) *m/z* 302.1013 (302.1010 calcd for $C_{11}H_{18}FNNaO_6^+$ $[MNa]^+$). Less than 2% of the *N*-selective product was observed.



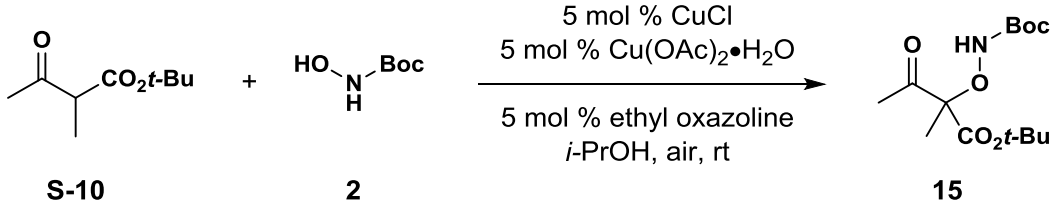
S-8 **2** **13**

Methyl 2-(((*tert*-butoxycarbonyl)amino)oxy)-2-methyl-3-oxobutanoate (13): According to the general procedure, CuCl (1.5 mg, 0.015 mmol, 0.05 equiv) and *tert*-butyl hydroxycarbamate **2** (40 mg, 0.30 mmol, 1 equiv) were added to methyl 2-methyl-3-oxobutanoate **S-8** (47 mg, 0.36 mmol, 1.2 equiv), $Cu(OAc)_2 \cdot H_2O$ (3.0 mg, 0.015 mmol, 0.05 equiv), and ethyl oxazoline (1.5 mg, 0.015 mmol, 0.05 equiv) in 2 mL of *iso*propyl alcohol. The reaction was stirred for 14 h at rt, and the solvent was removed *in vacuo*. The reaction was quenched with 4 mL EDTA (0.5 M, pH 7.0) and extracted with ethyl acetate (3 x 4 mL). The combined organic layers were dried over $MgSO_4$, filtered and then concentrated *in vacuo*. The residue was purified by column chromatography to afford aldol product **13** (67 mg, 86%) as a colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.70 (s, 1H), 3.78 (s, 3H), 2.29 (s, 3H), 1.63 (s, 3H), 1.44 (s, 9H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ 202.8, 169.8, 156.5, 91.5, 82.5, 53.1, 28.3, 25.2, 18.5 ppm; IR (thin film) 3230, 2981, 1728, 1370, 1248, 1131 cm^{-1}; HRMS (ESI) *m/z* 284.1103 (284.1105 calcd for $C_{11}H_{19}NNaO_6^+$ $[MNa]^+$). A minor amount of the *N*-selective product was also isolated (8 mg, 10%).



S-9 **2** **14**

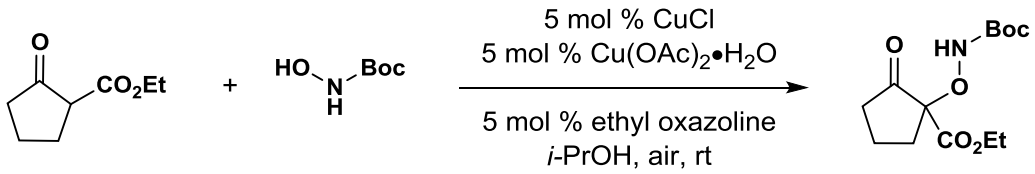
Allyl 2-(((*tert*-butoxycarbonyl)amino)oxy)-2-methyl-3-oxobutanoate (14): According to the general procedure, CuCl (1.5 mg, 0.015 mmol, 0.05 equiv) and *tert*-butyl hydroxycarbamate **2** (40 mg, 0.30 mmol, 1 equiv) were added to allyl 2-methyl-3-oxobutanoate **S-9** (56 mg, 0.36 mmol, 1.2 equiv), $Cu(OAc)_2 \cdot H_2O$ (3.0 mg, 0.015 mmol, 0.05 equiv), and ethyl oxazoline (1.5 mg, 0.015 mmol, 0.05 equiv) in 2 mL of *iso*propyl alcohol. The reaction was stirred for 15 h at rt, and the solvent was removed *in vacuo*. The reaction was quenched with 4 mL EDTA (0.5 M, pH 7.0) and extracted with ethyl acetate (3 x 4 mL). The combined organic layers were dried over $MgSO_4$, filtered and then concentrated *in vacuo*. The residue was purified by column chromatography to afford aldol product **14** (70 mg, 81%) as a colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.69 (s, 1H), 5.90 (ddt, *J* = 16.3, 11.6, 5.8 Hz, 1H), 5.33 (dq, *J* = 17.1, 1.3 Hz, 1H), 5.26 (dq, *J* = 10.4, 1.0 Hz, 1H), 4.67 (dt, *J* = 5.8, 1.2 Hz, 2H), 2.29 (s, 3H), 1.65 (s, 3H), 1.45 (s, 9H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$) δ 202.7, 169.0, 156.5, 131.3, 119.4, 91.5, 82.5, 66.7, 28.3, 25.2, 18.5 ppm. IR (thin film) 3302, 2982, 1728, 1370, 1248, 1130 cm^{-1}; HRMS (ESI) *m/z* 310.1261 (310.1261 calcd for $C_{13}H_{21}NNaO_6^+$ $[MNa]^+$). A minor amount of the *N*-selective product was also isolated (8 mg, 9%).



S-10 **2** **15**

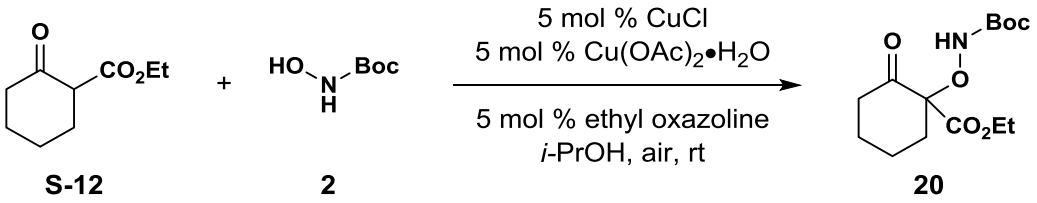
***Tert*-butyl 2-(((*tert*-butoxycarbonyl)amino)oxy)-2-methyl-3-oxobutanoate (15):** According to the general procedure, CuCl (1.5 mg, 0.015 mmol, 0.05 equiv) and *tert*-butyl hydroxycarbamate **2** (40 mg, 0.30 mmol, 1 equiv) were added to *tert*-butyl 2-methyl-3-oxobutanoate **S-10** (62 mg, 0.36 mmol, 1.2 equiv), $Cu(OAc)_2 \cdot H_2O$ (3.0 mg, 0.015 mmol, 0.05 equiv), and ethyl oxazoline (1.5 mg, 0.015 mmol, 0.05 equiv) in 2 mL of *iso*propyl alcohol. The reaction was stirred for 17 h at rt, and the solvent was removed *in vacuo*. The reaction was quenched with 4 mL EDTA (0.5

M, pH 7.0) and extracted with ethyl acetate (3 x 4 mL). The combined organic layers were dried over $MgSO_4$, filtered and then concentrated *in vacuo*. The residue was purified by column chromatography to afford aldol product **15** (65 mg, 71%) as a colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.71 (s, 1H), 2.27 (s, 3H), 1.59 (s, 3H), 1.48 (s, 9H), 1.45 (s, 9H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ 203.1, 168.5, 156.5, 91.4, 83.6, 82.3, 28.3, 28.1, 25.3, 18.4 ppm; IR (thin film) 3293, 2981, 1726, 1370, 1248, 1131 cm^{-1}; HRMS (ESI) *m/z* 326.1566 (326.1574 calcd for $C_{14}H_{25}NNaO_6^+$ $[MNa]^+$). A minor amount of the *N*-selective product was also isolated (13 mg, 14%).



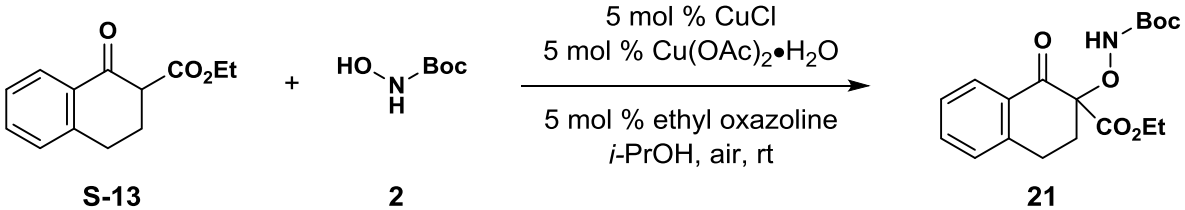
S-11 **2** **19**

Ethyl 1-(((*tert*-butoxycarbonyl)amino)oxy)-2-oxocyclopentanecarboxylate (19): According to the general procedure, CuCl (1.5 mg, 0.015 mmol, 0.05 equiv) and *tert*-butyl hydroxycarbamate **2** (40 mg, 0.30 mmol, 1 equiv) were added to ethyl 2-oxocyclopentanecarboxylate **S-11** (56 mg, 0.36 mmol, 1.2 equiv), $Cu(OAc)_2 \cdot H_2O$ (3.0 mg, 0.015 mmol, 0.05 equiv), and ethyl oxazoline (1.5 mg, 0.015 mmol, 0.05 equiv) in 2 mL of *iso*propyl alcohol. The reaction was stirred for 16 h at rt, and the solvent was removed *in vacuo*. The reaction was quenched with 4 mL EDTA (0.5 M, pH 7.0) and extracted with ethyl acetate (3 x 4 mL). The combined organic layers were dried over $MgSO_4$, filtered and then concentrated *in vacuo*. The residue was purified by column chromatography to afford aldol product **19** (77 mg, 89%) as a colorless solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.80 (s, 1H), 4.25 (qd, *J* = 7.1, 1.1 Hz, 2H), 2.73 – 2.52 (m, 1H), 2.42 – 2.22 (m, 4H), 2.12 – 1.97 (m, 1H), 1.45 (s, 9H), 1.28 (t, *J* = 7.1 Hz, 3H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ 208.1, 169.7, 156.4, 89.0, 82.3, 62.3, 36.9, 33.7, 28.3, 19.0, 14.3 ppm; IR (thin film) 3325, 2980, 1746, 1369, 1268, 1165 cm^{-1}; HRMS (ESI) *m/z* 310.1245 (310.1261 calcd for $C_{13}H_{21}NNaO_6^+$ $[MNa]^+$). Less than 2% of the *N*-selective product was observed.



S-12 2 20

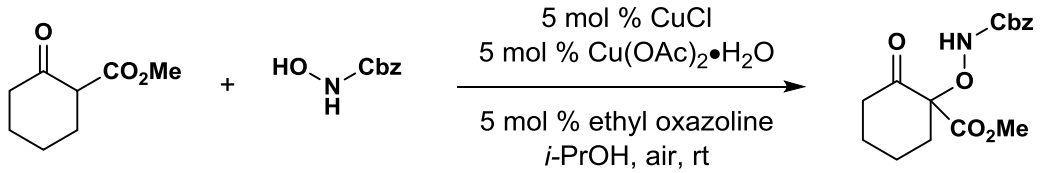
Ethyl 1-(((*tert*-butoxycarbonyl)amino)oxy)-2-oxocyclohexanecarboxylate (20): According to the general procedure, CuCl (1.5 mg, 0.015 mmol, 0.05 equiv) and *tert*-butyl hydroxycarbamate **2** (40 mg, 0.30 mmol, 1 equiv) were added to ethyl 2-oxocyclohexanecarboxylate **S-12** (61 mg, 0.36 mmol, 1.2 equiv), $Cu(OAc)_2 \cdot H_2O$ (3.0 mg, 0.015 mmol, 0.05 equiv), and ethyl oxazoline (1.5 mg, 0.015 mmol, 0.05 equiv) in 2 mL of *iso*propyl alcohol. The reaction was stirred for 16 h at rt, and the solvent was removed *in vacuo*. The reaction was quenched with 4 mL EDTA (0.5 M, pH 7.0) and extracted with ethyl acetate (3 x 4 mL). The combined organic layers were dried over $MgSO_4$, filtered and then concentrated *in vacuo*. The residue was purified by column chromatography to afford aldol product **20** (85 mg, 94%) as a colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.08 (s, 1H), 4.33 – 4.13 (m, 2H), 2.95 (ddd, *J* = 13.8, 11.3, 5.8 Hz, 1H), 2.39 (dt, *J* = 13.8, 4.9 Hz, 1H), 2.28 (ddd, *J* = 15.6, 11.4, 3.9 Hz, 1H), 2.17 – 2.04 (m, 2H), 2.03 – 1.94 (m, 1H), 1.86 – 1.70 (m, 1H), 1.63 (dt, *J* = 13.5, 4.6 Hz, 1H), 1.42 (s, 9H), 1.28 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ 205.7, 170.1, 156.2, 90.6, 82.3, 62.1, 39.5, 34.6, 28.3, 27.3, 20.4, 14.3 ppm; IR (thin film) 3310, 2980, 1726, 1369, 1251, 1160 cm^{-1}; HRMS (ESI) *m/z* 324.1397 (324.1418 calcd for $C_{14}H_{23}NNaO_6^+$ $[MNa]^+$). Less than 2% of the *N*-selective product was observed.



S-13 2 21

Ethyl 2-(((*tert*-butoxycarbonyl)amino)oxy)-1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (21): According to the general procedure, CuCl (1.5 mg, 0.015 mmol, 0.05 equiv) and *tert*-butyl hydroxycarbamate **2** (40 mg, 0.30 mmol, 1 equiv) were added to ethyl 1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate **S-13** (79 mg, 0.36 mmol, 1.2 equiv), $Cu(OAc)_2 \cdot H_2O$ (3.0 mg, 0.015 mmol, 0.05 equiv), and ethyl oxazoline (1.5 mg, 0.015 mmol,

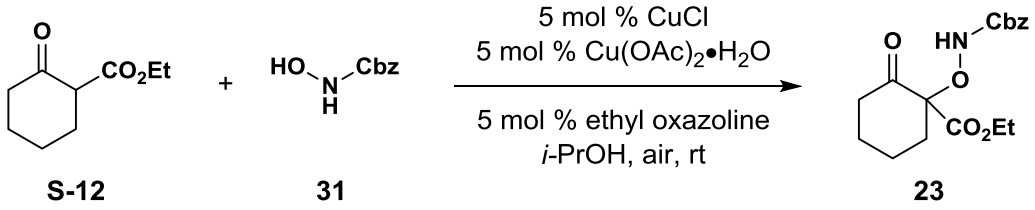
0.05 equiv) in 2 mL of *iso*propyl alcohol. The reaction was stirred for 15 h at rt, and the solvent was removed *in vacuo*. The reaction was quenched with 4 mL EDTA (0.5 M, pH 7.0) and extracted with ethyl acetate (3 x 4 mL). The combined organic layers were dried over $MgSO_4$, filtered and then concentrated *in vacuo*. The residue was purified by column chromatography to afford aldol product **21** (102 mg, 97%) as a colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.12 – 7.95 (m, 2H), 7.50 (td, *J* = 7.5, 1.3 Hz, 1H), 7.31 (t, *J* = 7.6 Hz, 1H), 7.25 (d, *J* = 7.8 Hz, 1H), 4.27 (q, *J* = 7.1 Hz, 2H), 3.42 (ddd, *J* = 16.5, 9.6, 4.8 Hz, 1H), 2.89 (dt, *J* = 16.9, 5.1 Hz, 1H), 2.69 (ddd, *J* = 14.4, 9.7, 4.9 Hz, 1H), 2.49 (dt, *J* = 14.2, 5.1 Hz, 1H), 1.32 – 1.22 (m, 12H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ 190.8, 169.6, 155.9, 143.8, 134.3, 131.3, 128.9, 128.2, 127.0, 87.6, 81.9, 62.2, 30.7, 28.0, 24.9, 14.2 ppm; IR (thin film) 3325, 3068, 2936, 1747, 1368, 1268, 1165 cm^{-1}; HRMS (ESI) *m/z* 372.1436 (372.1418 calcd for $C_{18}H_{23}NNaO_6^+$ $[MNa]^+$). Less than 2% of the *N*-selective product was observed.



S-14 **31** **22**

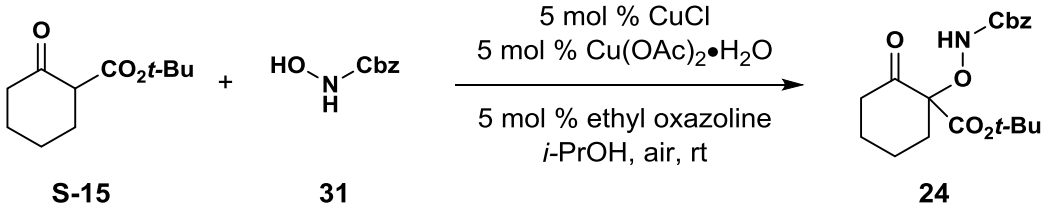
Methyl 1-((((benzyloxy)carbonyl)amino)oxy)-2-oxocyclohexane-1-carboxylate (22): According to the general procedure, CuCl (1.5 mg, 0.015 mmol, 0.05 equiv) and benzyl hydroxycarbamate **31** (50 mg, 0.30 mmol, 1 equiv) were added to methyl 2-oxocyclohexane-1-carboxylate **S-14** (56 mg, 0.36 mmol, 1.2 equiv), $Cu(OAc)_2 \cdot H_2O$ (3.0 mg, 0.015 mmol, 0.05 equiv), and ethyl oxazoline (1.5 mg, 0.015 mmol, 0.05 equiv) in 2 mL of *iso*propyl alcohol. The reaction was stirred for 14 h at rt, and the solvent was removed *in vacuo*. The reaction was quenched with 4 mL EDTA (0.5 M, pH 7.0) and extracted with ethyl acetate (3 x 4 mL). The combined organic layers were dried over $MgSO_4$, filtered and then concentrated *in vacuo*. The residue was purified by column chromatography to afford aldol product **22** (71 mg, 74%) as a colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.34 (s, 1H), 7.41 – 7.30 (m, 5H), 5.19 (d, *J* = 12.1 Hz, 1H), 5.12 (d, *J* = 12.1 Hz, 1H), 3.78 (s, 3H), 2.95 (ddd, *J* = 13.9, 11.2, 5.7 Hz, 1H), 2.42 (dt, *J* = 13.9, 4.9 Hz, 1H), 2.32 (ddd, *J* = 15.3, 11.3, 4.5 Hz, 1H), 2.21 – 2.06 (m, 2H), 2.03 – 1.94 (m, 1H), 1.85 – 1.73 (m, 1H), 1.71 – 1.61 (m, 1H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ 205.2, 170.2, 156.9, 135.5, 128.8, 128.7, 128.5, 90.9, 67.9, 52.9, 39.5, 34.5, 27.2, 20.4 ppm; IR (thin

film) 3299, 3034, 2954, 1723, 1437, 1226, 1103 cm^{-1}; HRMS (ESI) *m/z* 344.1106 (344.1105 calcd for $C_{16}H_{19}NNaO_6^+$ $[MNa]^+$). Less than 2% of the *N*-selective product was observed.



S-12 **31** **23**

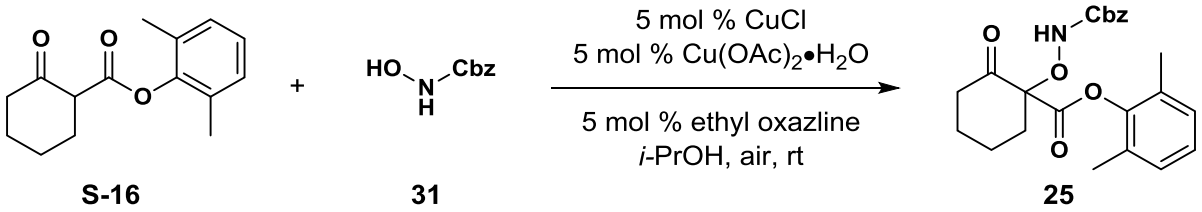
Ethyl 1-((((benzyloxy)carbonyl)amino)oxy)-2-oxocyclohexanecarboxylate (23): According to the general procedure, CuCl (1.5 mg, 0.015 mmol, 0.05 equiv) and benzyl hydroxycarbamate **31** (50 mg, 0.30 mmol, 1 equiv) were added to ethyl 2-oxocyclohexanecarboxylate **S-12** (61 mg, 0.36 mmol, 1.2 equiv), $Cu(OAc)_2 \cdot H_2O$ (3.0 mg, 0.015 mmol, 0.05 equiv), and ethyl oxazoline (1.5 mg, 0.015 mmol, 0.05 equiv) in 2 mL of *iso*propyl alcohol. The reaction was stirred for 14 h at rt, and the solvent was removed *in vacuo*. The reaction was quenched with 4 mL EDTA (0.5 M, pH 7.0) and extracted with ethyl acetate (3 x 4 mL). The combined organic layers were dried over $MgSO_4$, filtered and then concentrated *in vacuo*. The residue was purified by column chromatography to afford aldol product **23** (82 mg, 81%) as a colorless oil. ^1H NMR (600 MHz, $CDCl_3$) δ 8.39 (s, 1H), 7.41 – 7.28 (m, 5H), 5.18 (d, *J* = 12.1 Hz, 1H), 5.11 (d, *J* = 12.1 Hz, 1H), 4.28 – 4.20 (m, 2H), 2.92 (ddd, *J* = 14.1, 10.8, 5.7 Hz, 1H), 2.42 (dt, *J* = 13.9, 5.2 Hz, 1H), 2.33 (ddd, *J* = 14.7, 10.8, 3.8 Hz, 1H), 2.17 – 2.04 (m, 2H), 2.00 – 1.91 (m, 1H), 1.84 – 1.72 (m, 1H), 1.69 – 1.59 (m, 1H), 1.27 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ 205.4, 169.5, 156.9, 135.5, 128.7, 128.6, 128.4, 90.7, 67.8, 62.2, 39.6, 34.4, 27.1, 20.4, 14.2 ppm; IR (thin film) 3301, 2944, 1724, 1453, 1225, 1102 cm^{-1}; HRMS (ESI) *m/z* 358.1260 (358.1261 calcd for $C_{17}H_{21}NNaO_6^+$ $[MNa]^+$). Less than 2% of the *N*-selective product was observed.



S-15 **31** **24**

***Tert*-butyl 1-((((benzyloxy)carbonyl)amino)oxy)-2-oxocyclohexane-1-carboxylate (24):** According to the general procedure, CuCl (0.8 mg, 0.0075 mmol, 0.05 equiv) and benzyl

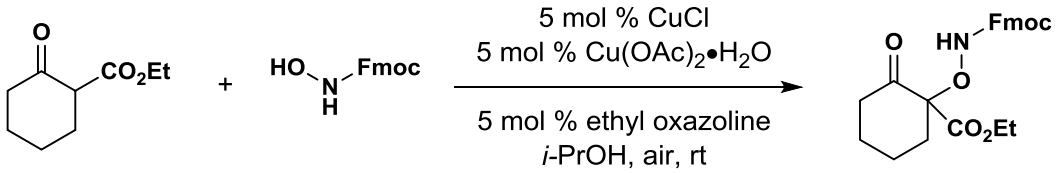
hydroxycarbamate **31** (25 mg, 0.15 mmol, 1 equiv) were added to *tert*-butyl 2-oxocyclohexane-1-carboxylate **S-15** (36 mg, 0.18 mmol, 1.2 equiv), $Cu(OAc)_2 \cdot H_2O$ (1.5 mg, 0.0075 mmol, 0.05 equiv), and ethyl oxazoline (0.8 mg, 0.0075 mmol, 0.05 equiv) in 1 mL of *iso*propyl alcohol. The reaction was stirred for 24 h at rt, and the solvent was removed *in vacuo*. The reaction was quenched with 2 mL EDTA (0.5 M, pH 7.0) and extracted with ethyl acetate (3 x 2 mL). The combined organic layers were dried over $MgSO_4$, filtered and then concentrated *in vacuo*. The residue was purified by column chromatography to afford aldol product **24** (40 mg, 77%) as a colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.43 (s, 1H), 7.40 – 7.28 (m, 5H), 5.19 (d, *J* = 12.1 Hz, 1H), 5.11 (d, *J* = 12.1 Hz, 1H), 2.86 (ddd, *J* = 14.7, 9.6, 5.6 Hz, 1H), 2.45 (dt, *J* = 13.9, 5.8 Hz, 1H), 2.37 – 2.28 (m, 1H), 2.12 – 2.01 (m, 2H), 1.95 – 1.87 (m, 1H), 1.87 – 1.76 (m, 1H), 1.68 – 1.58 (m, 1H), 1.47 (s, 9H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ 206.1, 168.7, 156.8, 135.6, 128.8, 128.6, 128.5, 90.8, 83.7, 67.8, 40.0, 34.7, 28.1, 27.1, 20.8 ppm; IR (thin film) 3329, 3035, 2942, 1724, 1456, 1301, 1223, 1103 cm^{-1}; HRMS (ESI) *m/z* 386.1587 (386.1574 calcd for $C_{19}H_{25}NNaO_6^+$ $[MNa]^+$). Less than 2% of the *N*-selective product was observed.



S-16 **31** **25**

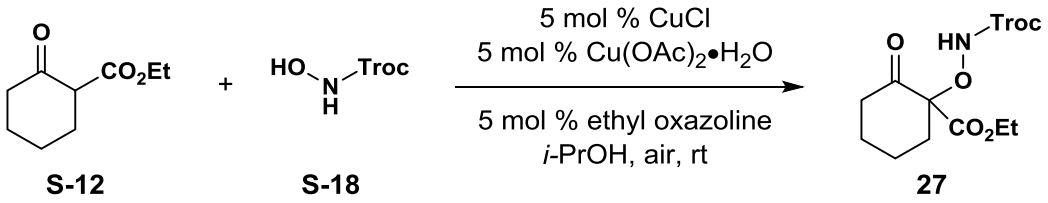
2,6-Dimethylphenyl 1-((((benzyloxy)carbonyl)amino)oxy)-2-oxocyclohexane-1-carboxylate (25): According to the general procedure, CuCl (0.8 mg, 0.0075 mmol, 0.05 equiv) and benzyl hydroxycarbamate **31** (25 mg, 0.15 mmol, 1 equiv) were added to 2,6-dimethylphenyl 2-oxocyclohexane-1-carboxylate **S-16** (44 mg, 0.18 mmol, 1.2 equiv), $Cu(OAc)_2 \cdot H_2O$ (1.5 mg, 0.0075 mmol, 0.05 equiv), and ethyl oxazoline (0.8 mg, 0.0075 mmol, 0.05 equiv) in 1 mL of *iso*propyl alcohol. The reaction was stirred for 8 h at rt, and the solvent was removed *in vacuo*. The reaction was quenched with 2 mL EDTA (0.5 M, pH 7.0) and extracted with ethyl acetate (3 x 2 mL). The combined organic layers were dried over $MgSO_4$, filtered and then concentrated *in vacuo*. The residue was purified by column chromatography to afford aldol product **25** (50 mg, 85%) as a colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.37 (s, 1H), 7.42 – 7.31 (m, 5H), 7.07 (s, 3H), 5.22 (d, *J* = 12.0 Hz, 1H), 5.14 (d, *J* = 12.1 Hz, 1H), 3.12 (td, *J* = 13.2, 5.9 Hz, 1H), 2.59 – 2.50 (m, 1H), 2.51 – 2.42 (m, 2H), 2.30 – 2.17 (m, 7H), 2.16 – 2.07 (m, 1H), 1.90 – 1.76 (m, 2H)

ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ 204.6, 168.2, 157.1, 147.8, 135.4, 130.4, 129.0, 128.8, 128.8, 128.5, 126.6, 91.0, 68.1, 39.4, 35.0, 27.2, 20.2, 16.8 ppm; IR (thin film) 3323, 3034, 2951, 1760, 1473, 1318, 1223, 1099 cm^{-1}; HRMS (ESI) *m/z* 434.1570 (434.1574 calcd for $C_{23}H_{25}NNaO_6^+$ $[MNa]^+$). A minor amount of the *N*-selective product was also isolated (2 mg, 3%).



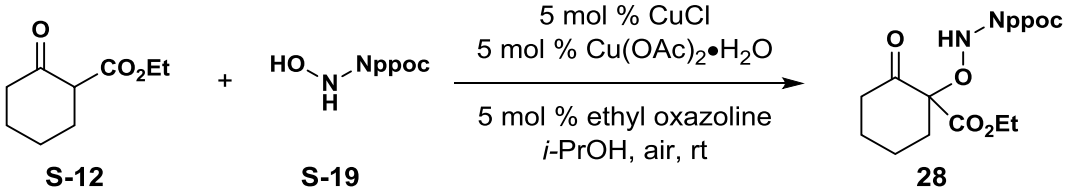
S-12 **S-17** **26**

Ethyl 1-(((((9H-fluoren-9-yl)methoxy)carbonyl)amino)oxy)-2-oxocyclohexanecarboxylate (26): According to the general procedure, CuCl (1.5 mg, 0.015 mmol, 0.05 equiv) and (9H-fluoren-9-yl)methyl hydroxycarbamate **S-17** (77 mg, 0.30 mmol, 1 equiv) were added to ethyl 2-oxocyclohexanecarboxylate **S-12** (61 mg, 0.36 mmol, 1.2 equiv), $Cu(OAc)_2 \cdot H_2O$ (3.0 mg, 0.015 mmol, 0.05 equiv), and ethyl oxazoline (1.5 mg, 0.015 mmol, 0.05 equiv) in 2 mL of *iso*propyl alcohol. The reaction was stirred for 19 h at rt, and the solvent was removed *in vacuo*. The reaction was quenched with 4 mL EDTA (0.5 M, pH 7.0) and extracted with ethyl acetate (3 x 4 mL). The combined organic layers were dried over $MgSO_4$, filtered and then concentrated *in vacuo*. The residue was purified by column chromatography to afford aldol product **26** (102 mg, 80%) as a colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.38 (s, 1H), 7.76 (d, *J* = 7.6 Hz, 2H), 7.57 (t, *J* = 7.6 Hz, 2H), 7.41 (td, *J* = 7.5, 1.3 Hz, 2H), 7.32 (t, *J* = 7.5 Hz, 2H), 4.51 (d, *J* = 6.7 Hz, 2H), 4.29 (qd, *J* = 7.2, 4.9 Hz, 2H), 4.22 (t, *J* = 6.8 Hz, 1H), 2.87 – 2.74 (m, 1H), 2.39 (dt, *J* = 14.0, 4.9 Hz, 1H), 2.33 (ddd, *J* = 14.7, 10.8, 4.1 Hz, 1H), 2.17 – 2.09 (m, 1H), 2.03 – 1.89 (m, 2H), 1.83 – 1.70 (m, 1H), 1.65 – 1.57 (m, 1H), 1.31 (t, *J* = 7.1 Hz, 3H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ 205.4, 169.8, 157.0, 143.5, 143.5, 141.5, 128.0, 127.4, 127.3, 125.1, 125.1, 120.2, 90.7, 67.7, 62.3, 47.1, 39.6, 34.5, 27.2, 20.4, 14.3 ppm; IR (thin film) 3303, 2929, 1724, 1451, 1224, 1103 cm^{-1}; HRMS (ESI) *m/z* 446.1572 (446.1574 calcd for $C_{24}H_{25}NNaO_6^+$ $[MNa]^+$). Less than 2% of the *N*-selective product was observed.



S-12 S-18 27

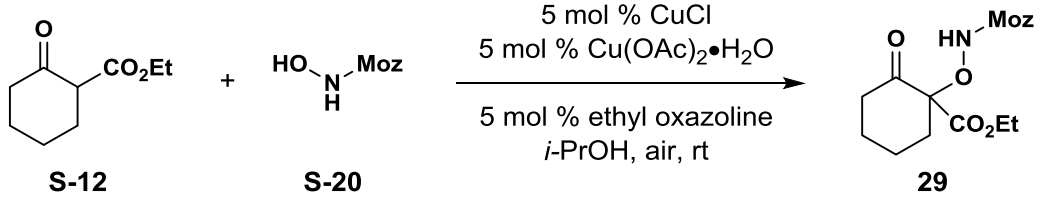
Ethyl 2-oxo-1-((((2,2,2-trichloroethoxy)carbonyl)amino)oxy)cyclohexanecarboxylate (27): According to the general procedure, CuCl (1.5 mg, 0.015 mmol, 0.05 equiv) and 2,2,2-trichloroethyl hydroxycarbamate **S-18** (63 mg, 0.30 mmol, 1 equiv) were added to ethyl 2-oxocyclohexanecarboxylate **S-12** (61 mg, 0.36 mmol, 1.2 equiv), $Cu(OAc)_2 \cdot H_2O$ (3.0 mg, 0.015 mmol, 0.05 equiv), and ethyl oxazoline (1.5 mg, 0.015 mmol, 0.05 equiv) in 2 mL of *iso*propyl alcohol. The reaction was stirred for 19 h at rt, and the solvent was removed *in vacuo*. The reaction was quenched with 4 mL EDTA (0.5 M, pH 7.0) and extracted with ethyl acetate (3 x 4 mL). The combined organic layers were dried over $MgSO_4$, filtered and then concentrated *in vacuo*. The residue was purified by column chromatography to afford aldol product **27** (101 mg, 89%) as a colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.64 (s, 1H), 4.80 (d, *J* = 11.9 Hz, 1H), 4.71 (d, *J* = 11.9 Hz, 1H), 4.38 – 4.22 (m, 2H), 2.93 (ddd, *J* = 14.1, 10.6, 5.7 Hz, 1H), 2.47 (dt, *J* = 14.1, 5.3 Hz, 1H), 2.37 (ddd, *J* = 15.0, 10.9, 4.5 Hz, 1H), 2.20 – 2.05 (m, 2H), 2.03 – 1.93 (m, 1H), 1.89 – 1.77 (m, 1H), 1.74 – 1.61 (m, 1H), 1.31 (t, *J* = 7.1 Hz, 3H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ 205.2, 169.6, 155.1, 94.9, 90.8, 75.0, 62.5, 39.7, 34.4, 27.1, 20.5, 14.3 ppm; IR (thin film) 3294, 2958, 1726, 1369, 1252, 1124 cm^{-1}; HRMS (ESI) *m/z* 397.9937 (397.9935 calcd for $C_{12}H_{16}Cl_3NNaO_6^+$ $[MNa]^+$). Less than 2% of the *N*-selective product was observed.



S-12 S-19 28

Ethyl 1-((((2-(2-nitrophenyl)propoxy)carbonyl)amino)oxy)-2-oxocyclohexanecarboxylate (28): According to the general procedure, CuCl (1.5 mg, 0.015 mmol, 0.05 equiv) and 2-(2-nitrophenyl)propyl hydroxycarbamate **S-19** (72 mg, 0.30 mmol, 1 equiv) were added to ethyl 2-oxocyclohexanecarboxylate **S-12** (61 mg, 0.36 mmol, 1.2 equiv), $Cu(OAc)_2 \cdot H_2O$ (3.0 mg, 0.015 mmol, 0.05 equiv), and ethyl oxazoline (1.5 mg, 0.015 mmol, 0.05 equiv) in 2 mL of *iso*propyl alcohol. The reaction was stirred for 14 h at rt, and the solvent was removed *in vacuo*. The

reaction was quenched with 4 mL EDTA (0.5 M, pH 7.0) and extracted with ethyl acetate (3 x 4 mL). The combined organic layers were dried over $MgSO_4$, filtered and then concentrated *in vacuo*. The residue was purified by column chromatography to afford aldol product **28** (107 mg, 87%, 1:1 dr, inseparable) as an orange oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.25 (s, 1H), 8.22 (s, 1H), 7.74 (d, *J* = 8.1 Hz, 1H), 7.59 – 7.53 (m, 1H), 7.46 – 7.40 (m, 1H), 7.39 – 7.33 (m, 1H), 4.54 – 4.02 (m, 4H), 3.68 (h, *J* = 6.7 Hz, 1H), 2.90 – 2.70 (m, 1H), 2.44 – 2.23 (m, 2H), 2.13 – 2.05 (m, 1H), 2.05 – 1.96 (m, 1H), 1.96 – 1.87 (m, 1H), 1.81 – 1.70 (m, 1H), 1.66 – 1.57 (m, 1H), 1.33 (d, *J* = 2.0 Hz, 3H), 1.32 (d, *J* = 2.0 Hz, 3H), 1.28 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ 205.3, 205.2, 169.7, 169.6, 156.7, 150.5, 150.5, 137.0, 137.0, 132.9, 132.9, 128.3, 128.2, 127.7, 127.7, 124.4, 124.4, 90.7, 90.6, 69.6, 69.6, 62.2, 39.6 , 39.5, 34.4, 34.4, 27.1, 20.4, 20.4, 17.8, 17.8, 14.2 ppm; IR (thin film) 3318, 2962, 1724, 1527, 1355, 1226, 1102 cm^{-1}; HRMS (ESI) *m/z* 431.1418 (431.1425 calcd for $C_{19}H_{24}N_2NaO_8^+$ $[MNa]^+$). Less than 2% of the *N*-selective product was observed.

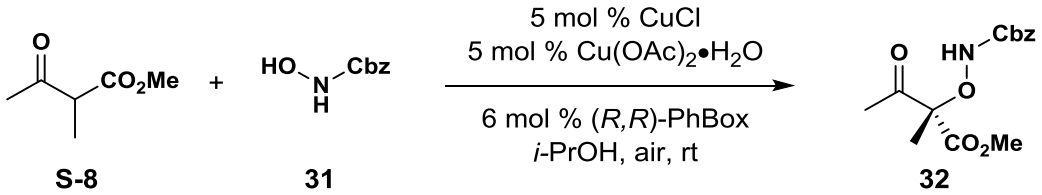


S-12 **S-20** **29**

Ethyl 1-(((((4-methoxybenzyl)oxy)carbonyl)amino)oxy)-2-oxocyclohexanecarboxylate (29): According to the general procedure, CuCl (1.5 mg, 0.015 mmol, 0.05 equiv) and 4-methoxybenzyl hydroxycarbamate **S-20** (59 mg, 0.30 mmol, 1 equiv) were added to ethyl 2-oxocyclohexanecarboxylate **S-12** (61 mg, 0.36 mmol, 1.2 equiv), $Cu(OAc)_2 \cdot H_2O$ (3.0 mg, 0.015 mmol, 0.05 equiv), and ethyl oxazoline (1.5 mg, 0.015 mmol, 0.05 equiv) in 2 mL of *iso*propyl alcohol. The reaction was stirred for 15 h at rt, and the solvent was removed *in vacuo*. The reaction was quenched with 4 mL EDTA (0.5 M, pH 7.0) and extracted with ethyl acetate (3 x 4 mL). The combined organic layers were dried over $MgSO_4$, filtered and then concentrated *in vacuo*. The residue was purified by column chromatography to afford aldol product **29** (93 mg, 85%) as a colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.32 (s, 1H), 7.27 (d, *J* = 8.7 Hz, 2H), 6.86 (d, *J* = 8.7 Hz, 2H), 5.11 (d, *J* = 11.8 Hz, 1H), 5.03 (d, *J* = 11.8 Hz, 1H), 4.28 – 4.20 (m, 2H), 3.79 (s, 3H), 2.92 (ddd, *J* = 14.1, 10.9, 5.7 Hz, 1H), 2.41 (dt, *J* = 13.9, 5.1 Hz, 1H), 2.32 (ddd, *J* = 14.8, 10.9, 3.7 Hz, 1H), 2.18 – 2.03 (m, 2H), 2.00 – 1.90 (m, 1H), 1.85 – 1.74 (m, 1H),

1.70 – 1.57 (m, 1H), 1.27 (t, *J* = 7.1 Hz, 3H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ 205.4, 169.7, 160.0, 157.0, 130.4, 127.6, 114.1, 90.7, 67.7, 62.2, 55.4, 39.6, 34.5, 27.1, 20.4, 14.2 ppm; IR (thin film) 3302, 2942, 1725, 1516, 1250, 1101 cm^{-1}; HRMS (ESI) *m/z* 388.1364 (388.1367 calcd for $C_{18}H_{23}NNaO_7^+$ $[MNa]^+$). Less than 2% of the *N*-selective product was observed.

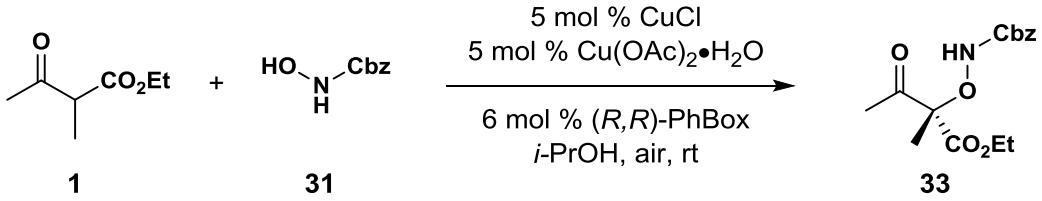
General Procedure for the Asymmetric Aldol Reaction: To a stirred solution of β-ketoester **4**, 5 mol % $Cu(OAc)_2 \cdot H_2O$, and 6 mol % (+)-2,2′-*Iso*propylidenebis[(4*R*)-4-phenyl-2-oxazoline] in *iso*propyl alcohol (0.15 M) was added 5 mol % CuCl and benzylhydroxycarbamate **30**. The reaction was stirred at room temperature open to the air until complete by TLC and the *iso*propyl alcohol was removed *in vacuo*. The reaction was quenched with EDTA (0.5 M, pH 7.0), diluted with ethyl acetate and stirred until color no longer persisted in organic layer (approx 30 mins). The reaction was extracted with ethyl acetate three times and the combined organic layers were dried over $MgSO_4$. The product was filtered and then concentrated *in vacuo*. The residue was purified by column chromatography to afford the corresponding aldol product.



S-8 **31** **32**

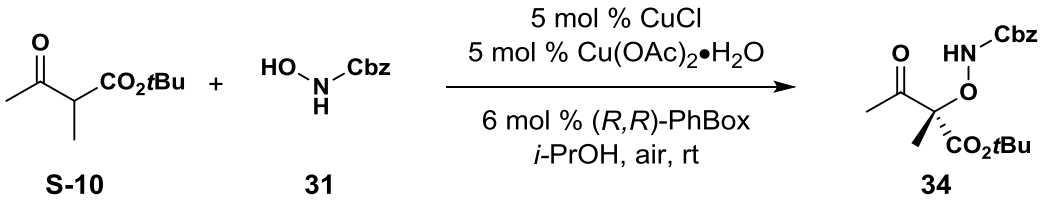
Methyl 2-((((benzyloxy)carbonyl)amino)oxy)-2-methyl-3-oxobutanoate (32): According to the general procedure, CuCl (1.5 mg, 0.015 mmol, 0.05 equiv) and benzyl hydroxycarbamate **31** (50 mg, 0.30 mmol, 1 equiv) were added to methyl 2-methyl-3-oxobutanoate **S-8** (47 mg, 0.36 mmol, 1.2 equiv), $Cu(OAc)_2 \cdot H_2O$ (3.0 mg, 0.015 mmol, 0.05 equiv), and (+)-2,2′-*iso*propylidenebis[(4*R*)-4-phenyl-2-oxazoline] (6.0 mg, 0.018 mmol, 0.06 equiv) in 2 mL of *iso*propyl alcohol. The reaction was stirred for 8 h at rt, and the solvent was removed *in vacuo*. The reaction was quenched with 4 mL EDTA (0.5 M, pH 7.0) and extracted with ethyl acetate (3 x 4 mL). The combined organic layers were dried over $MgSO_4$, filtered and then concentrated *in vacuo*. The residue was purified by column chromatography to afford aldol product **32** (69 mg, 78%, 93:7 er) as a colorless oil. Enantiomeric ratio determined by chiral HPLC (Chiralpak IA column, 4.6 mm x 250 mm, step gradient (95.5/0.5 hexanes/*i*-PrOH, 30 min; 97/3 hexanes/*i*-PrOH, 30 min), 1 mL/min, (*X*) Rt = 43.3 min (major), (*X*) Rt = 45.0 min (minor)); $[\alpha]_D^{25}$ +3.8° (c

1.00, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.99 (s, 1H), 7.40 – 7.30 (m, 5H), 5.17 (s, 2H), 3.77 (s, 3H), 2.29 (s, 3H), 1.66 (s, 3H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ 199.4, 169.7, 158.8, 135.2, 128.8, 128.8, 128.7, 78.7, 69.2, 53.4, 25.5, 19.0 ppm; IR (thin film) 3289, 2956, 1727, 1456, 1232, 1106 cm^{-1}; HRMS (ESI) *m/z* 318.0945 (318.0948 calcd for $C_{14}H_{17}NNaO_6^+$ $[MNa]^+$).



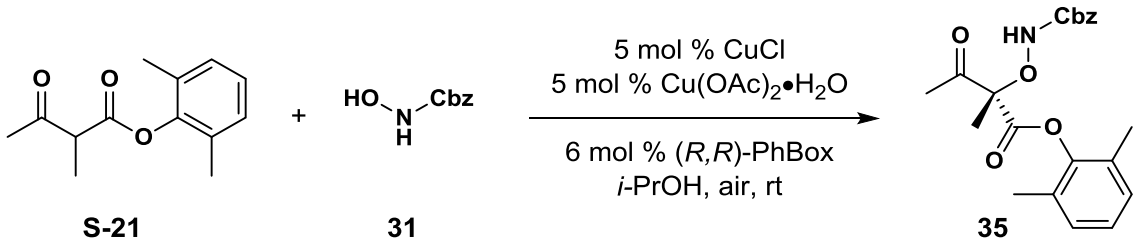
1 **31** **33**

Ethyl 2-((((benzyloxy)carbonyl)amino)oxy)-2-methyl-3-oxobutanoate (33): According to the general procedure, CuCl (1.5 mg, 0.015 mmol, 0.05 equiv) and benzyl hydroxycarbamate **31** (50 mg, 0.30 mmol, 1 equiv) were added to ethyl 2-methyl-3-oxobutanoate **1** (52 mg, 0.36 mmol, 1.2 equiv), $Cu(OAc)_2 \cdot H_2O$ (3.0 mg, 0.015 mmol, 0.05 equiv), and (+)-2,2′-*iso*propylidenebis[(4*R*)-4-phenyl-2-oxazoline] (6.0 mg, 0.018 mmol, 0.06 equiv) in 2 mL of *iso*propyl alcohol. The reaction was stirred for 8 h at rt, and the solvent was removed *in vacuo*. The reaction was quenched with 4 mL EDTA (0.5 M, pH 7.0) and extracted with ethyl acetate (3 x 4 mL). The combined organic layers were dried over $MgSO_4$, filtered and then concentrated *in vacuo*. The residue was purified by column chromatography to afford aldol product **33** (69 mg, 74%, 92:8 er) as a colorless oil. Enantiomeric ratio determined by chiral HPLC (Chiralpak IA column, 4.6 mm x 250 mm, step gradient (95.5/0.5 hexanes/*i*-PrOH, 30 min; 97/3 hexanes/*i*-PrOH, 30 min), 1 mL/min, (*X*) Rt = 38.4 min (major), (*X*) Rt = 41.2 min (minor)); $[\alpha]_D^{25}$ +2.8° (c 1.00, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.99 (s, 1H), 7.39 – 7.29 (m, 5H), 5.17 (s, 2H), 4.24 (q, *J* = 7.1 Hz, 2H), 2.28 (s, 3H), 1.65 (s, 3H), 1.28 (t, *J* = 7.1 Hz, 3H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ 202.4, 169.1, 157.3, 135.5, 128.8, 128.8, 128.5, 91.6, 68.1, 62.5, 25.3, 18.4, 14.2 ppm; IR (thin film) 3290, 2985, 1727, 1456, 1231, 1105 cm^{-1}; HRMS (ESI) *m/z* 332.1107 (332.1105 calcd for $C_{15}H_{19}NNaO_6^+$ $[MNa]^+$).



S-10 **31** **34**

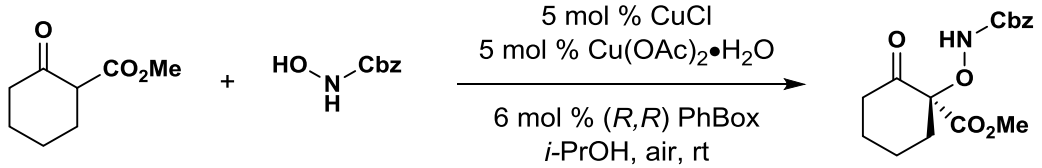
***Tert*-butyl 2-((((benzyloxy)carbonyl)amino)oxy)-2-methyl-3-oxobutanoate (34):** According to the general procedure, CuCl (1.5 mg, 0.015 mmol, 0.05 equiv) and benzyl hydroxycarbamate **31** (50 mg, 0.30 mmol, 1 equiv) were added to *tert*-butyl 2-methyl-3-oxobutanoate **S-10** (62 mg, 0.36 mmol, 1.2 equiv), $Cu(OAc)_2 \cdot H_2O$ (3.0 mg, 0.015 mmol, 0.05 equiv), and (+)-2,2′-*iso*propylidenebis[(4*R*)-4-phenyl-2-oxazoline] (6.0 mg, 0.015 mmol, 0.06 equiv) in 2 mL of *iso*propyl alcohol. The reaction was stirred for 8 h at rt, and the solvent was removed *in vacuo*. The reaction was quenched with 4 mL EDTA (0.5 M, pH 7.0) and extracted with ethyl acetate (3 x 4 mL). The combined organic layers were dried over $MgSO_4$, filtered and then concentrated *in vacuo*. The residue was purified by column chromatography to afford aldol product **34** (77 mg, 76%, 99:1 er) as a colorless oil. Enantiomeric ratio determined by chiral HPLC (Chiralpak IA column, 4.6 mm x 250 mm, step gradient (95.5/0.5 hexanes/*i*-PrOH, 30 min; 97/3 hexanes/*i*-PrOH, 30 min), 1 mL/min, (*X*) Rt = 29.5 min (major), (*X*) Rt = 31.9 min (minor)); $[\alpha]_D^{25}$ +3.3° (c 1.00, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.03 (s, 1H), 7.41 – 7.29 (m, 5H), 5.19 – 5.13 (m, 2H), 2.26 (s, 3H), 1.60 (s, 3H), 1.46 (s, 9H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ 202.5, 168.2, 157.2, 135.5, 128.8, 128.7, 128.5, 91.5, 83.7, 68.0, 28.0, 25.3, 18.3 ppm; IR (thin film) 3290, 2979, 1725, 1456, 1227, 1104 cm^{-1}; HRMS (ESI) *m/z* 360.1420 (360.1418 calcd for $C_{17}H_{23}NNaO_6^+$ $[MNa]^+$).



S-21 **31** **35**

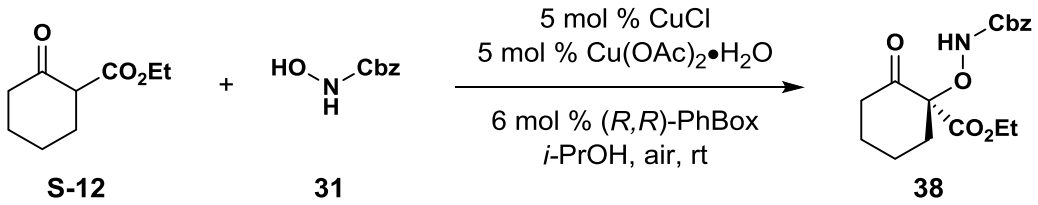
2,6-Dimethylphenyl 2-((((benzyloxy)carbonyl)amino)oxy)-2-methyl-3-oxobutanoate (35): According to the general procedure, CuCl (0.7 mg, 0.0075 mmol, 0.05 equiv) and benzyl hydroxycarbamate **31** (25 mg, 0.15 mmol, 1 equiv) were added to 2,6-dimethylphenyl 2-methyl-3-oxobutanoate **S-21** (40 mg, 0.18 mmol, 1.2 equiv), $Cu(OAc)_2 \cdot H_2O$ (1.5 mg, 0.0075 mmol, 0.05

equiv), and (+)-2,2′-*iso*propylidenebis[(4*R*)-4-phenyl-2-oxazoline] (3.0 mg, 0.0090 mmol, 0.06 equiv) in 1 mL of *iso*propyl alcohol. The reaction was stirred for 8 h at rt, and the solvent was removed *in vacuo*. The reaction was quenched with 2 mL EDTA (0.5 M, pH 7.0) and extracted with ethyl acetate (3 x 2 mL). The combined organic layers were dried over $MgSO_4$, filtered and then concentrated *in vacuo*. The residue was purified by column chromatography to afford aldol product **35** (49 mg, 85%, 99:1 er) as a colorless oil. Enantiomeric ratio determined by chiral HPLC (Chiralpak IA column, 4.6 mm x 250 mm, step gradient (95.5/0.5 hexanes/*i*-PrOH, 30 min; 97/3 hexanes/*i*-PrOH, 30 min), 1 mL/min, (*X*) Rt = 39.7 min (major), (*X*) Rt = 42.2 min (minor)); $[\alpha]_D^{25}$ +16.5° (c 1.00, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.03 (s, 1H), 7.42 – 7.30 (m, 5H), 7.12 – 7.00 (m, 3H), 5.20 (s, 2H), 2.41 (s, 3H), 2.15 (s, 6H), 1.89 (s, 3H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ 202.1, 167.3, 157.4, 147.8, 135.4, 130.2, 129.0, 128.9, 128.8, 128.6, 126.6, 92.1, 68.2, 25.4, 19.0, 16.6 ppm; IR (thin film) 3281, 3034, 2927, 1728, 1456, 1231, 1101 cm^{-1}; HRMS (ESI) *m/z* 408.1415 (408.1418 calcd for $C_{21}H_{23}NNaO_6^+$ $[MNa]^+$).



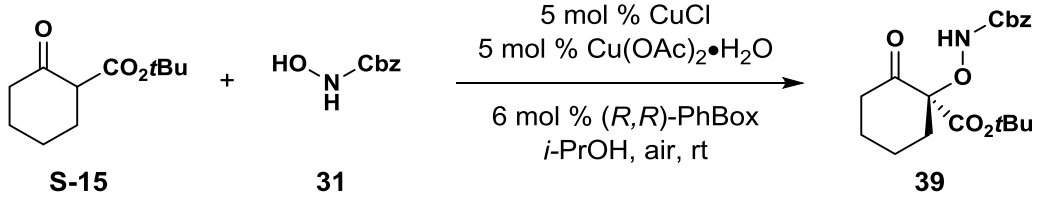
S-14 **31** **37**

Methyl 1-((((benzyloxy)carbonyl)amino)oxy)-2-oxocyclohexane-1-carboxylate (37): According to the general procedure, CuCl (1.5 mg, 0.015 mmol, 0.05 equiv) and benzyl hydroxycarbamate **31** (50 mg, 0.30 mmol, 1 equiv) were added to methyl 2-oxocyclohexane-1-carboxylate **S-14** (56 mg, 0.36 mmol, 1.2 equiv), $Cu(OAc)_2 \cdot H_2O$ (3.0 mg, 0.015 mmol, 0.05 equiv), and (+)-2,2′-*iso*propylidenebis[(4*R*)-4-phenyl-2-oxazoline] (6.0 mg, 0.018 mmol, 0.06 equiv) in 2 mL of *iso*propyl alcohol. The reaction was stirred for 8 h at rt, and the solvent was removed *in vacuo*. The reaction was quenched with 4 mL EDTA (0.5 M, pH 7.0) and extracted with ethyl acetate (3 x 4 mL). The combined organic layers were dried over $MgSO_4$, filtered and then concentrated *in vacuo*. The residue was purified by column chromatography to afford aldol product **37** (78 mg, 81%, 91:9 er) as a colorless oil. Enantiomeric ratio determined by chiral HPLC (Chiralpak IA column, 4.6 mm x 250 mm, step gradient (95.5/0.5 hexanes/*i*-PrOH, 30 min; 97/3 hexanes/*i*-PrOH, 30 min), 1 mL/min, (*X*) Rt = 43.2 min (major), (*X*) Rt = 45.8 min (minor)); $[\alpha]_D^{25}$ +38.5° (c 1.00, $CHCl_3$); Spectral data consistent with compound **22**.



S-12 **31** **38**

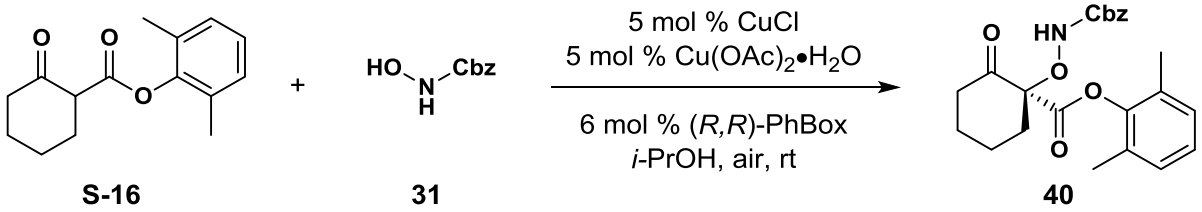
Ethyl 1-((((benzyloxy)carbonyl)amino)oxy)-2-oxocyclohexane-1-carboxylate (38): According to the general procedure, CuCl (1.5 mg, 0.015 mmol, 0.05 equiv) and benzyl hydroxycarbamate **31** (50 mg, 0.30 mmol, 1 equiv) were added to ethyl 2-oxocyclohexane-1-carboxylate **S-12** (61 mg, 0.36 mmol, 1.2 equiv), $Cu(OAc)_2 \cdot H_2O$ (3.0 mg, 0.015 mmol, 0.05 equiv), and (+)-2,2′-*iso*propylidenebis[(4*R*)-4-phenyl-2-oxazoline] (6.0 mg, 0.018 mmol, 0.06 equiv) in 2 mL of *iso*propyl alcohol. The reaction was stirred for 8 h at rt, and the solvent was removed *in vacuo*. The reaction was quenched with 4 mL EDTA (0.5 M, pH 7.0) and extracted with ethyl acetate (3 x 4 mL). The combined organic layers were dried over $MgSO_4$, filtered and then concentrated *in vacuo*. The residue was purified by column chromatography to afford aldol product **38** (83 mg, 82%, 90:10 er) as a colorless oil. Enantiomeric ratio determined by chiral HPLC (Chiralpak IA column, 4.6 mm x 250 mm, step gradient (95.5/0.5 hexanes/*i*-PrOH, 30 min; 97/3 hexanes/*i*-PrOH, 30 min), 1 mL/min, (*X*) Rt = 37.7 min (major), (*X*) Rt = 40.7 min (minor)); $[\alpha]_D^{25}$ +35.4° (c 1.00, $CHCl_3$); Spectral data consistent with compound **23**.



S-15 **31** **39**

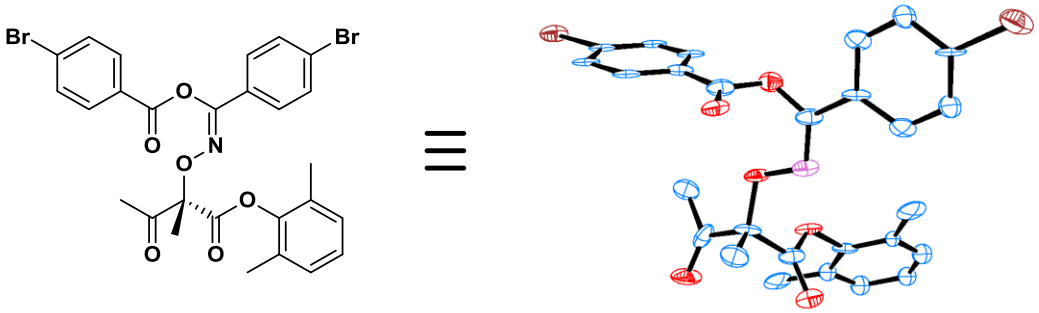
***Tert*-butyl 1-((((benzyloxy)carbonyl)amino)oxy)-2-oxocyclohexane-1-carboxylate (39):** According to the general procedure, CuCl (0.6 mg, 0.0065 mmol, 0.05 equiv) and benzyl hydroxycarbamate **31** (22 mg, 0.13 mmol, 1 equiv) were added to *tert*-butyl 2-oxocyclohexane-1-carboxylate **S-15** (31 mg, 0.16 mmol, 1.2 equiv), $Cu(OAc)_2 \cdot H_2O$ (1.3 mg, 0.0065 mmol, 0.05 equiv), and (+)-2,2′-*iso*propylidenebis[(4*R*)-4-phenyl-2-oxazoline] (2.6 mg, 0.0078 mmol, 0.06 equiv) in 1 mL of *iso*propyl alcohol. The reaction was stirred for 8 h at rt, and the solvent was removed *in vacuo*. The reaction was quenched with 2 mL EDTA (0.5 M, pH 7.0) and extracted with ethyl acetate (3 x 2 mL). The combined organic layers were dried over $MgSO_4$, filtered and

then concentrated *in vacuo*. The residue was purified by column chromatography to afford aldol product **39** (40 mg, 85%. 99:1 er) as a colorless oil. Enantiomeric ratio determined by chiral HPLC (Chiralpak IA column, 4.6 mm x 250 mm, step gradient (95.5/0.5 hexanes/*i*-PrOH, 30 min; 97/3 hexanes/*i*-PrOH, 30 min), 1 mL/min, (*X*) Rt = 27.1 min (major), (*X*) Rt = 42.2 min (minor)); $[\alpha]_D^{25}$ +20.6° (c 1.00, $CHCl_3$); Spectral data consistent with compound **24**.

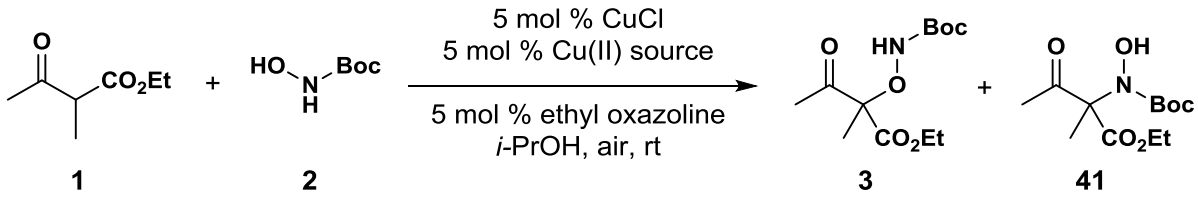


S-16 **31** **40**

2,6-Dimethylphenyl 1-((((benzyloxy)carbonyl)amino)oxy)-2-oxocyclohexane-1-carboxylate (40): According to the general procedure, CuCl (1.5 mg, 0.015 mmol, 0.05 equiv) and benzyl hydroxycarbamate **31** (50 mg, 0.30 mmol, 1 equiv) were added to 2,6-dimethylphenyl 2-oxocyclohexane-1-carboxylate **S-16** (87 mg, 0.36 mmol, 1.2 equiv), $Cu(OAc)_2 \cdot H_2O$ (3.0 mg, 0.015 mmol, 0.05 equiv), and (+)-2,2′-*iso*propylidenebis[(4*R*)-4-phenyl-2-oxazoline] (6.0 mg, 0.018 mmol, 0.06 equiv) in 2 mL of *iso*propyl alcohol. The reaction was stirred for 8 h at rt, and the solvent was removed *in vacuo*. The reaction was quenched with 4 mL EDTA (0.5 M, pH 7.0) and extracted with ethyl acetate (3 x 4 mL). The combined organic layers were dried over $MgSO_4$, filtered and then concentrated *in vacuo*. The residue was purified by column chromatography to afford aldol product **40** (105 mg, 88%, 91:9 er) as a colorless oil. Enantiomeric ratio determined by chiral HPLC (Chiralpak IA column, 4.6 mm x 250 mm, step gradient (95.5/0.5 hexanes/*i*-PrOH, 30 min; 97/3 hexanes/*i*-PrOH, 30 min), 1 mL/min, (*X*) Rt = 41.1 min (minor), (*X*) Rt = 45.4 min (major)); $[\alpha]_D^{25}$ +70.2° (c 1.00, $CHCl_3$); Spectral data consistent with compound **25**.

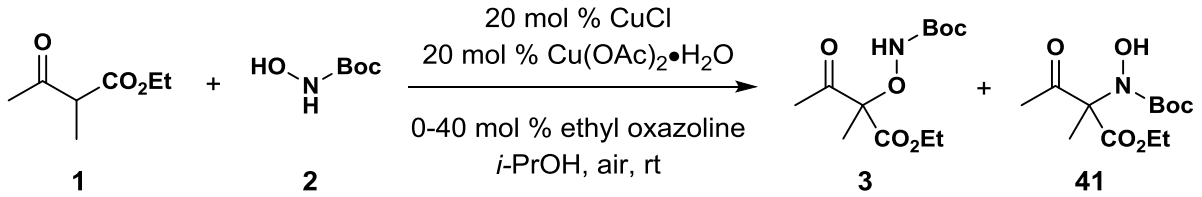


(S,Z)-(S,Z)-4-bromo-N-((1-(2,6-dimethylphenoxy)-2-methyl-1,3-dioxobutan-2-yl)oxy)benzimidic 4-bromobenzoic anhydride (S-22): Single crystal X-ray crystallography of **S-22** was used to determine the absolute stereochemistry of asymmetric aldol products. See CDCC 932616 for more information.



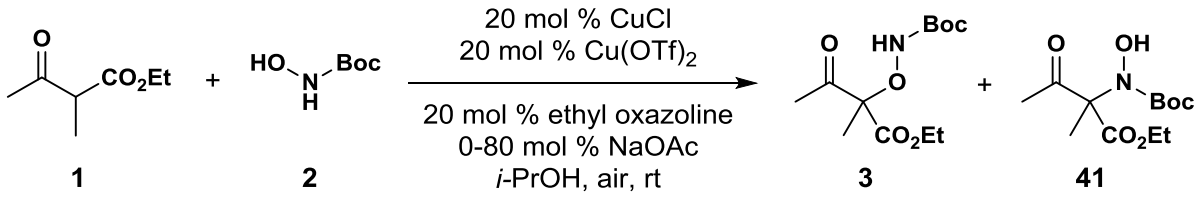
General Procedure for the Cu(II) Counterion Screen: To a stirred solution of ethyl 2-methyl-3-oxobutanoate **1** (52 mg, 0.36 mmol, 1.2 equiv), the corresponding Cu(II) source (0.015 mmol, 0.05 equiv), and ethyl oxazoline (1.5 mg, 0.015 mmol, 0.05 equiv) in 2 mL *iso*propyl alcohol was added CuCl (1.5 mg, 0.015 mmol, 0.05 equiv) and *tert*-butyl hydroxycarbamate **2** (40 mg, 0.30 mmol, 1 equiv). The reaction was stirred at room temperature open to the air until complete as judged by TLC, and the *iso*propyl alcohol was removed *in vacuo*. The reaction was quenched with 4 mL EDTA (0.5 M, pH 7.0) and extracted with ethyl acetate (3 x 4 mL). The combined organic layers were dried over $MgSO_4$, filtered and then concentrated *in vacuo*. The residue was purified by column chromatography to afford aldol products **3** and **41**. The regioselectivity of the reaction was determined by ^{1}HNMR analysis of the crude reaction mixture.

Cu(II) Source	Regioselectivity (O:N)
$Cu(OTf)_2$	1.5:1
$Cu(BF_4)_2 \bullet H_2O$	1.5:1
$CuCl_2$	6:1
$CuCO_3$	8:1
$Cu(OAc)_2 \bullet H_2O$	10:1
$Cu(2\text{-EtHex})_2$	14:1



General Procedure for the Screen of Ethyl Oxazoline Loading: To a stirred solution of ethyl 2-methyl-3-oxobutanoate **1** (52 mg, 0.36 mmol, 1.2 equiv), $Cu(OAc)_2•H_2O$ (12 mg, 0.060 mmol, 0.20 equiv), and ethyl oxazoline (0–40 mol %) in 2 mL *iso*propyl alcohol was added CuCl (6 mg, 0.060 mmol, 0.20 equiv) and *tert*-butyl hydroxycarbamate **2** (40 mg, 0.30 mmol, 1 equiv). The reaction was stirred at room temperature open to the air until complete as judged by TLC, and the *iso*propyl alcohol was removed *in vacuo*. The reaction was quenched with 4 mL EDTA (0.5 M, pH 7.0) and extracted with ethyl acetate (3 x 4 mL). The combined organic layers were dried over $MgSO_4$, filtered and then concentrated *in vacuo*. The residue was purified by column chromatography to afford aldol products **3** and **41**. The regioselectivity of the reaction was determined by ^{1}HNMR analysis of the crude reaction mixture.

mol % ethyl oxazoline	Regioselectivity (O:N)
0	3:1
5	6:1
10	14:1
20	18:1
40	>20:1

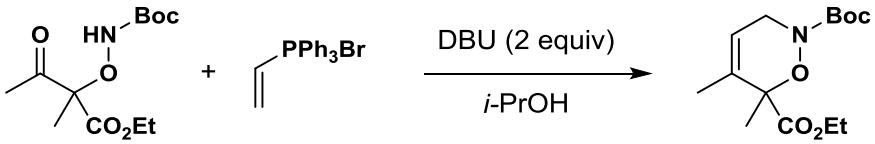


General Procedure for the Screen of NaOAc loading: To a stirred solution of ethyl 2-methyl-3-oxobutanoate **1** (52 mg, 0.36 mmol, 1.2 equiv), $Cu(OTf)_2$ (22 mg, 0.060 mmol, 0.20 equiv), and ethyl oxazoline (6 mg, 0.060 mmol, 0.20 equiv) in 2 mL *iso*propyl alcohol was added CuCl (6 mg, 0.060 mmol, 0.20 equiv), NaOAc (0–80 mol %) and *tert*-butyl hydroxycarbamate **2** (40 mg, 0.30 mmol, 1 equiv). The reaction was stirred at room temperature open to the air until complete as judged by TLC, and the *iso*propyl alcohol was removed *in vacuo*. The reaction was quenched with 4 mL EDTA (0.5 M, pH 7.0) and extracted with ethyl acetate (3 x 4 mL). The

combined organic layers were dried over $MgSO_4$, filtered and then concentrated *in vacuo*. The residue was purified by column chromatography to afford aldol products **3** and **41**. The regioselectivity of the reaction was determined by ^{1}HNMR analysis of the crude reaction mixture.

mol % NaOAc	Regioselectivity (O:N)
0	2:1
5	2:1
10	2:1
15	2:1
20	3:1
25	4:1
30	5:1
35	6:1
40	7:1
80	7:1

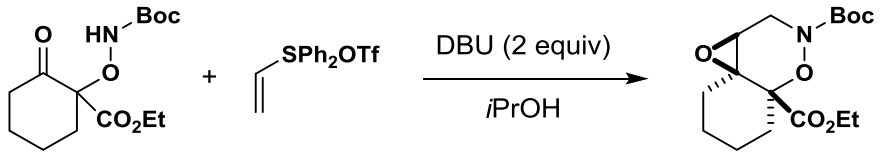
Annulation Reactions:



3 **S-23** **43**

2-(*Tert*-butyl) 6-ethyl 5,6-dimethyl-3,6-dihydro-2H-1,2-oxazine-2,6-dicarboxylate (43): Vinyltriphenylphosphonium bromide **S-23** (134 mg, 0.36 mmol, 2.0 equiv) and 1,8-diazabicyclo[5.4.0]undec-7-ene (54 µL, 0.36 mmol, 2.0 equiv) were added to ethyl 2-(((*tert*-butoxycarbonyl)amino)oxy)-2-methyl-3-oxobutanoate **3** (50 mg, 0.18 mmol, 1 equiv) in 1 mL of *iso*propyl alcohol. The reaction was heated to reflux, stirred for 2 h and cooled to rt. The reaction was quenched with H_2O (10 mL) and diluted with ethyl acetate (10 mL). The phases were separated, and the aqueous phase was extracted with ethyl acetate (3 x 10 mL). The combined organic layers were washed with brine (10 mL), dried over $MgSO_4$, filtered and then concentrated *in vacuo*. The residue was purified by column chromatography to afford annulation product **43** (42 mg, 82%) as a colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.61 – 5.57 (m, 1H), 4.24 (dq, *J* = 10.8, 7.1 Hz, 1H), 4.16 (dq, *J* = 10.8, 7.1 Hz, 1H), 4.08 (ddq, *J* = 16.8, 3.6, 1.7 Hz, 1H), 3.89 (dp, *J* = 16.8, 2.2 Hz, 1H), 1.82 (q, *J* = 1.8 Hz, 3H), 1.54 (s, 3H), 1.47 (s, 9H), 1.28 (t,

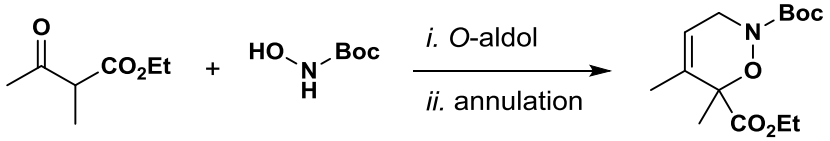
J = 7.1 Hz, 3H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ 171.0, 154.8, 134.7, 119.2, 84.1, 81.6, 61.6, 45.8, 28.5, 20.8, 19.0, 14.3 ppm; IR (thin film) 2980, 1736, 1367, 1265, 1109 cm^{-1}; HRMS (ESI) *m/z* 308.1469 (308.1468 calcd for $C_{14}H_{23}NNaO_5^+$ $[MNa]^+$).



20 **S-24** **44**

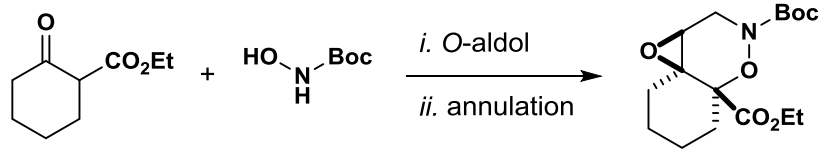
3-(*Tert*-butyl) 4a-ethyl hexahydro-3H,4aH-benzo[e]oxireno[2,3-d][1,2]oxazine-3,4a-dicarboxylate (44): Vinyldiphenylsulfonium triflate **S-24** (81 mg, 0.23 mmol, 1.2 equiv) and 1,8-diazabicyclo[5.4.0]undec-7-ene (56 µL, 0.38 mmol, 2.0 equiv) were added to ethyl 1-(((*tert*-butoxycarbonyl)amino)oxy)-2-oxocyclohexanecarboxylate **20** (57 mg, 0.19 mmol, 1 equiv) in 1 mL of *iso*propyl alcohol at 0˚C. The reaction was warmed to room temperature and stirred for 24 h. The reaction was quenched with a 10% solution of citric acid (10 mL), the phases were separated, and the aqueous phase was extracted with ethyl acetate (3 x 10 mL). The combined organic layers were washed with brine (10 mL), dried over $MgSO_4$, filtered and then concentrated *in vacuo*. The residue was purified by column chromatography to afford annulation product **44** (43 mg, 63%, >20:1 dr) as a colorless solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.29 (q, *J* = 7.1 Hz, 2H), 3.86 (s, 2H), 3.21 (t, *J* = 2.3 Hz, 1H), 2.43 (td, *J* = 13.4, 4.9 Hz, 1H), 2.29 (dq, *J* = 13.6, 3.4 Hz, 1H), 1.90 – 1.81 (m, 2H), 1.80 – 1.73 (m, 1H), 1.54 (qt, *J* = 13.3, 3.4 Hz, 1H), 1.47 (s, 9H), 1.43 (dt, *J* = 12.8, 3.8 Hz, 1H), 1.42 – 1.35 (m, 1H), 1.32 (t, *J* = 7.1 Hz, 3H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ 169.4, 155.1, 82.4, 82.0, 61.7, 59.1, 57.4, 45.5, 33.0, 32.4, 28.4, 24.5, 21.9, 14.4 ppm; IR (thin film) 2939, 1737, 1368, 1230, 1162 cm^{-1}; HRMS (ESI) *m/z* 350.1578 (350.1574 calcd for $C_{16}H_{25}NNaO_6^+$ $[MNa]^+$).

One-Pot Aldol-Annulation Reactions:



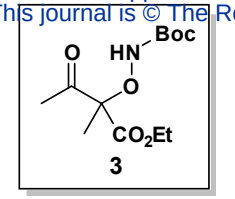
1 **2** **43**

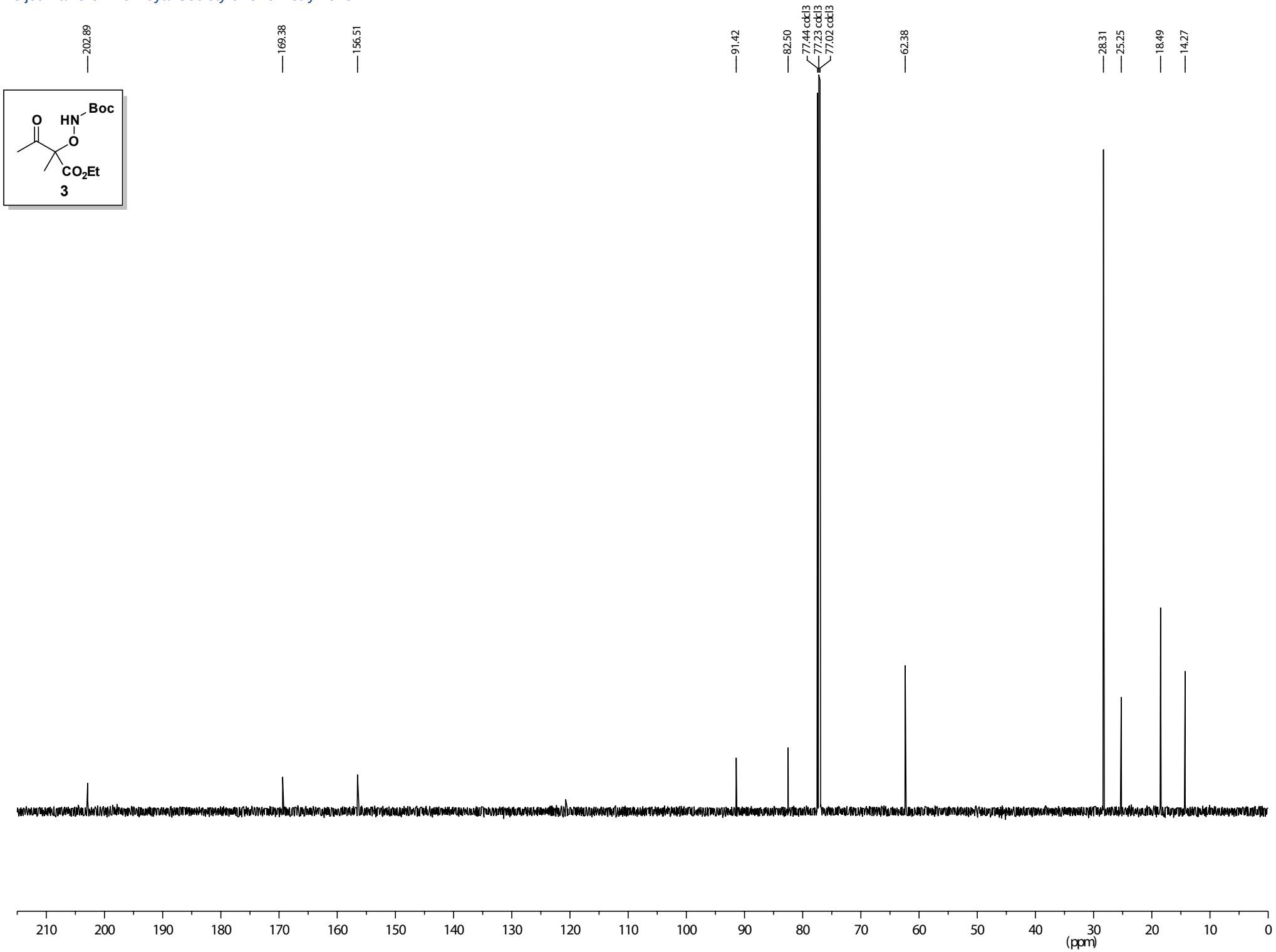
2-(*Tert*-butyl) 6-ethyl 5,6-dimethyl-3,6-dihydro-2H-1,2-oxazine-2,6-dicarboxylate (43): CuCl (1.5 mg, 0.015 mmol, 0.05 equiv) and *tert*-butyl hydroxycarbamate **2** (40 mg, 0.30 mmol, 1 equiv) were added to ethyl 2-methyl-3-oxobutanoate **1** (52 mg, 0.36 mmol, 1.2 equiv), $Cu(OAc)_2 \cdot H_2O$ (3.0 mg, 0.015 mmol, 0.05 equiv), and ethyl oxazoline (1.5 mg, 0.015 mmol, 0.05 equiv) in 2 mL of *iso*propyl alcohol. The reaction was stirred for 17 h at rt, and then vinyltriphenylphosphonium bromide **S-23** (222 mg, 0.60 mmol, 2.0 equiv) and 1,8-diazabicyclo[5.4.0]undec-7-ene (90 µL, 0.60 mmol, 2.0 equiv) were added to the solution. The reaction was heated to reflux for an additional 2 h, cooled to rt, and the solvent was removed *in vacuo*. The residue was purified by column chromatography to afford annulation product **43** (56 mg, 65%) as a colorless oil.

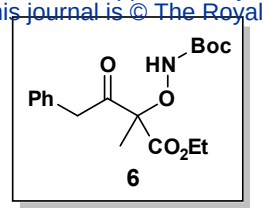


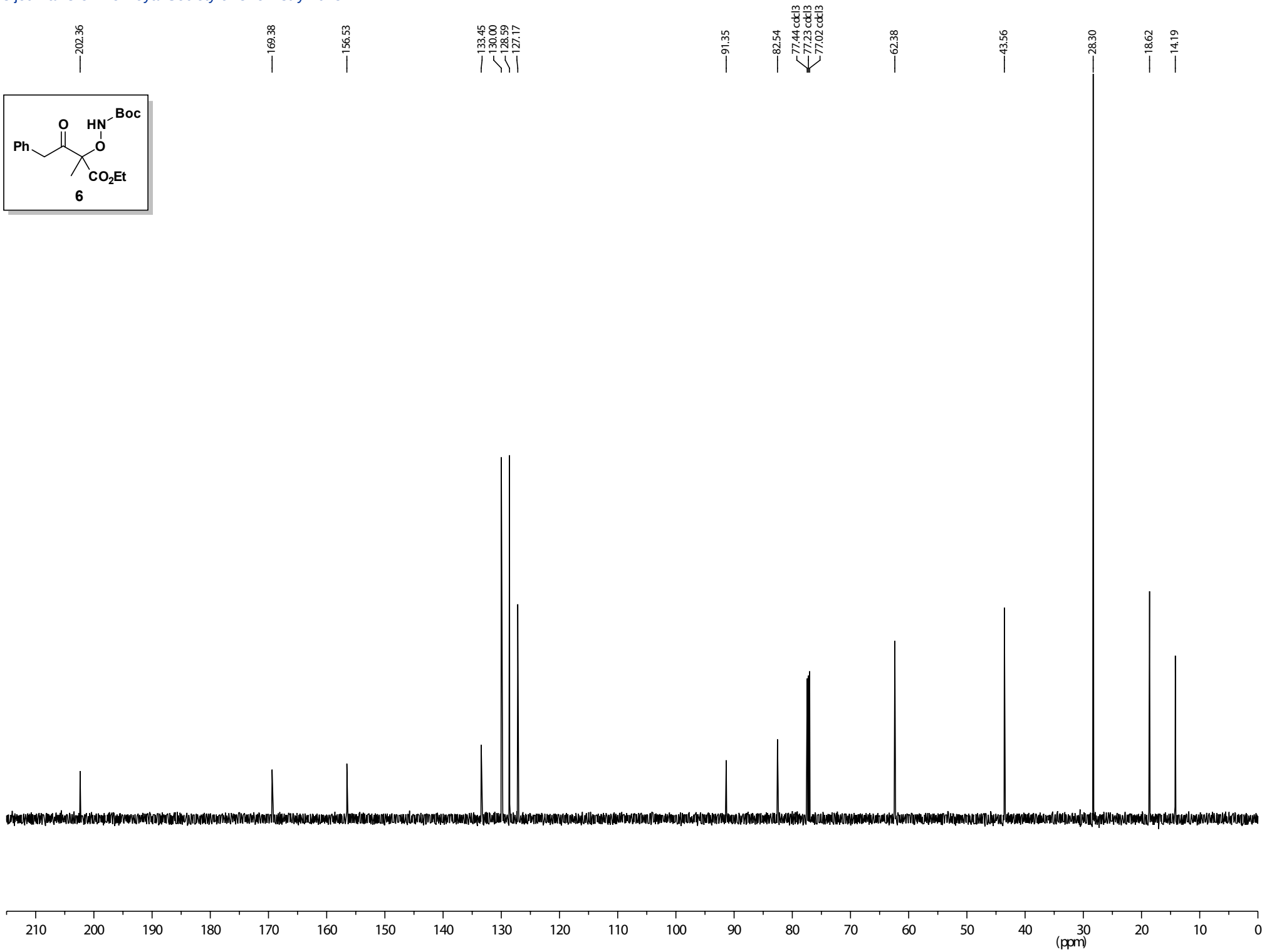
30 **2** **44**

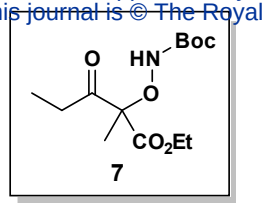
3-(*Tert*-butyl) 4a-ethyl hexahydro-3H,4aH-benzo[e]oxireno[2,3-d][1,2]oxazine-3,4a-dicarboxylate (44): CuCl (0.9 mg, 0.0094 mmol, 0.05 equiv) and *tert*-butyl hydroxycarbamate **2** (25 mg, 0.19 mmol, 1 equiv) were added to ethyl 2-methyl-3-oxobutanoate **30** (38 mg, 0.23 mmol, 1.2 equiv), $Cu(OAc)_2 \cdot H_2O$ (1.9 mg, 0.0094 mmol, 0.05 equiv), and ethyl oxazoline (0.9 mg, 0.0094 mmol, 0.05 equiv) in 1.3 mL of *iso*propyl alcohol. The reaction was stirred for 16 h, cooled to 0 ˚C, and then vinyldiphenylsulfonium triflate **S-24** (81 mg, 0.23 mmol, 1.2 equiv) and 1,8-diazabicyclo[5.4.0]undec-7-ene (56 µl, 0.38 mmol, 2.0 equiv) were added to the solution. The reaction was warmed to rt and stirred for an addition 24 h, and the solvent was removed *in vacuo*. The residue was purified by column chromatography to afford annulation product **44** (55 mg, 97%) as a colorless solid.











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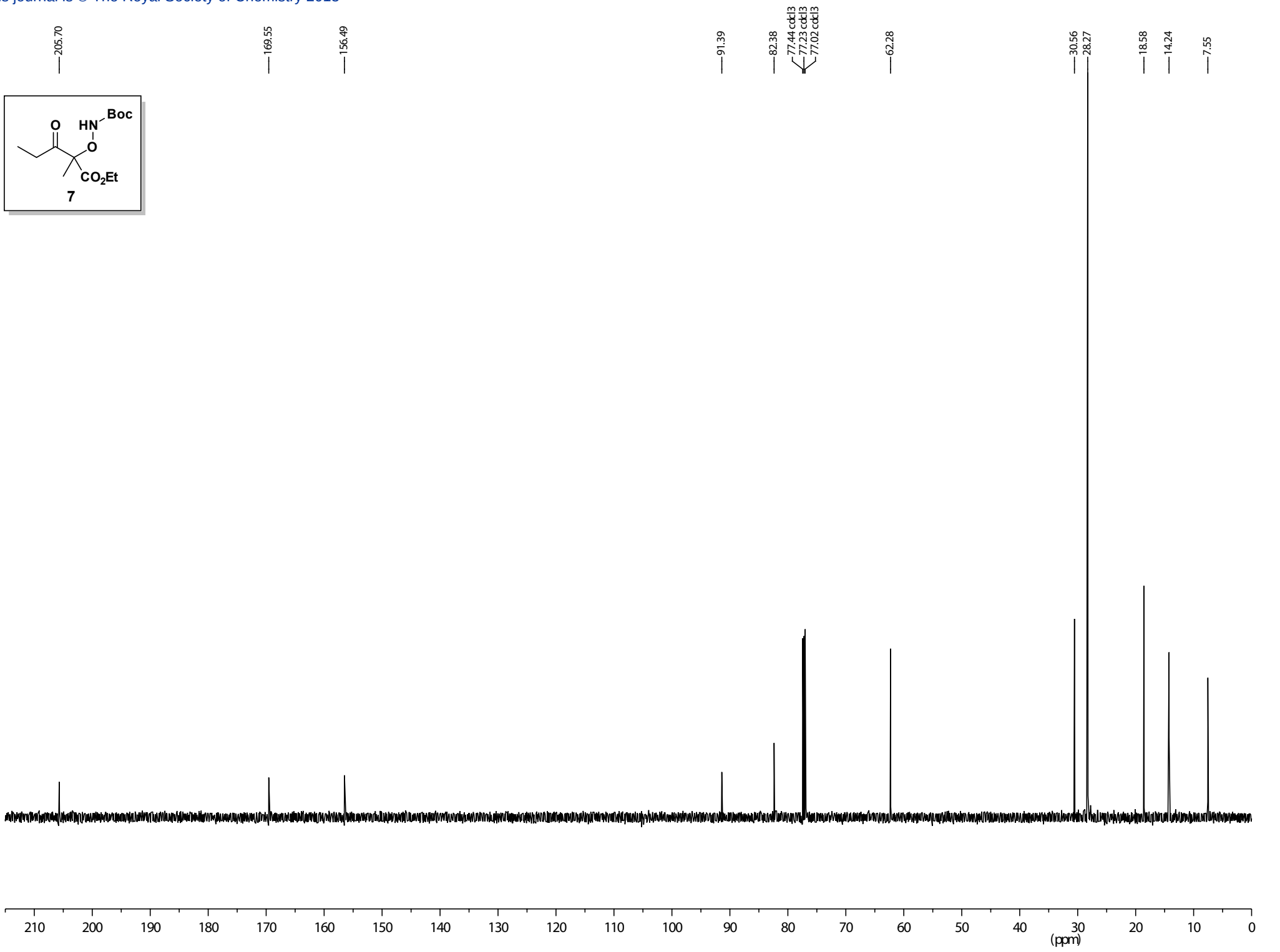

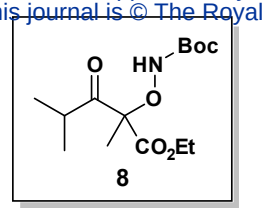

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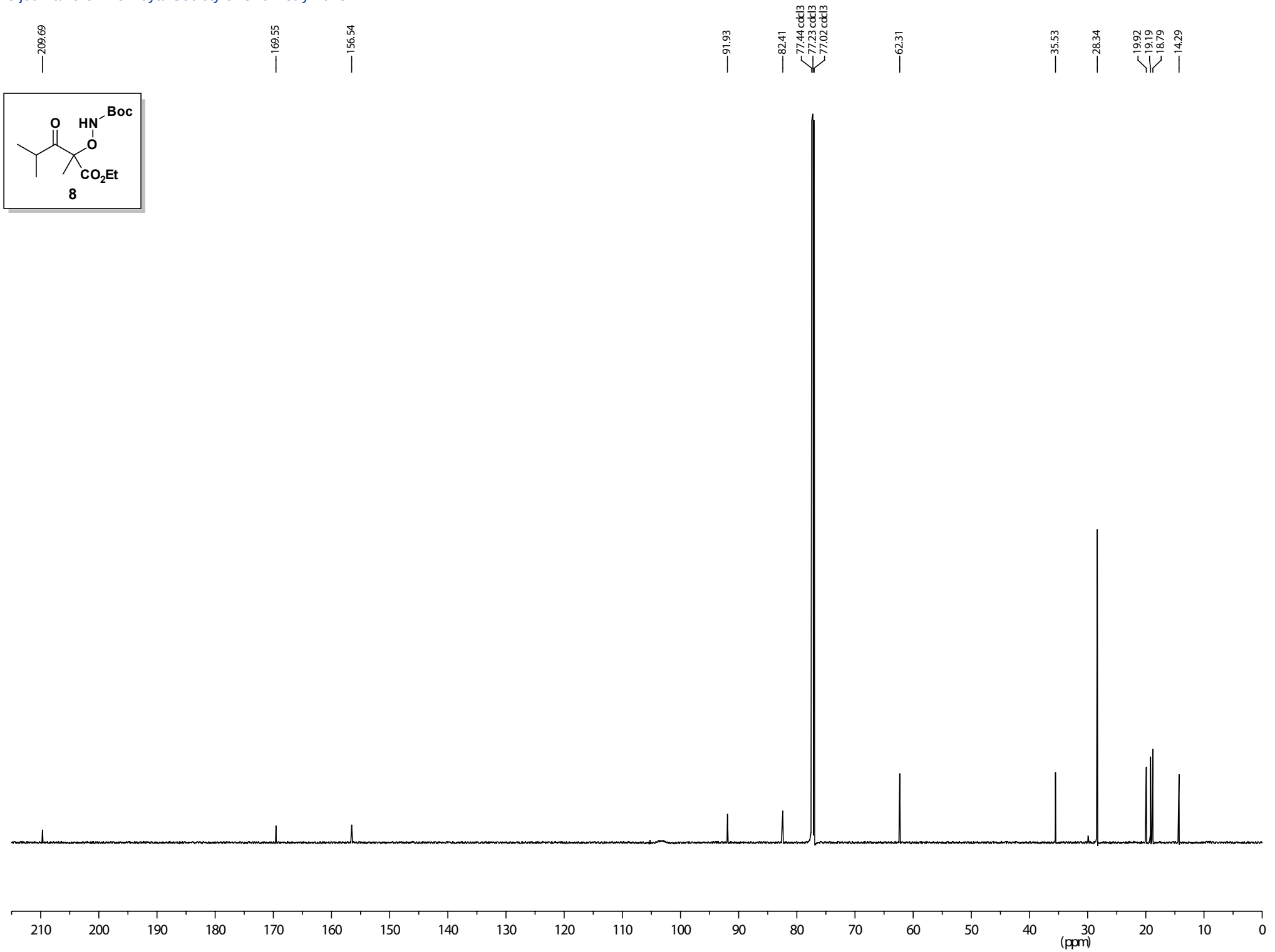

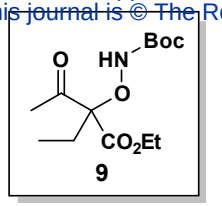

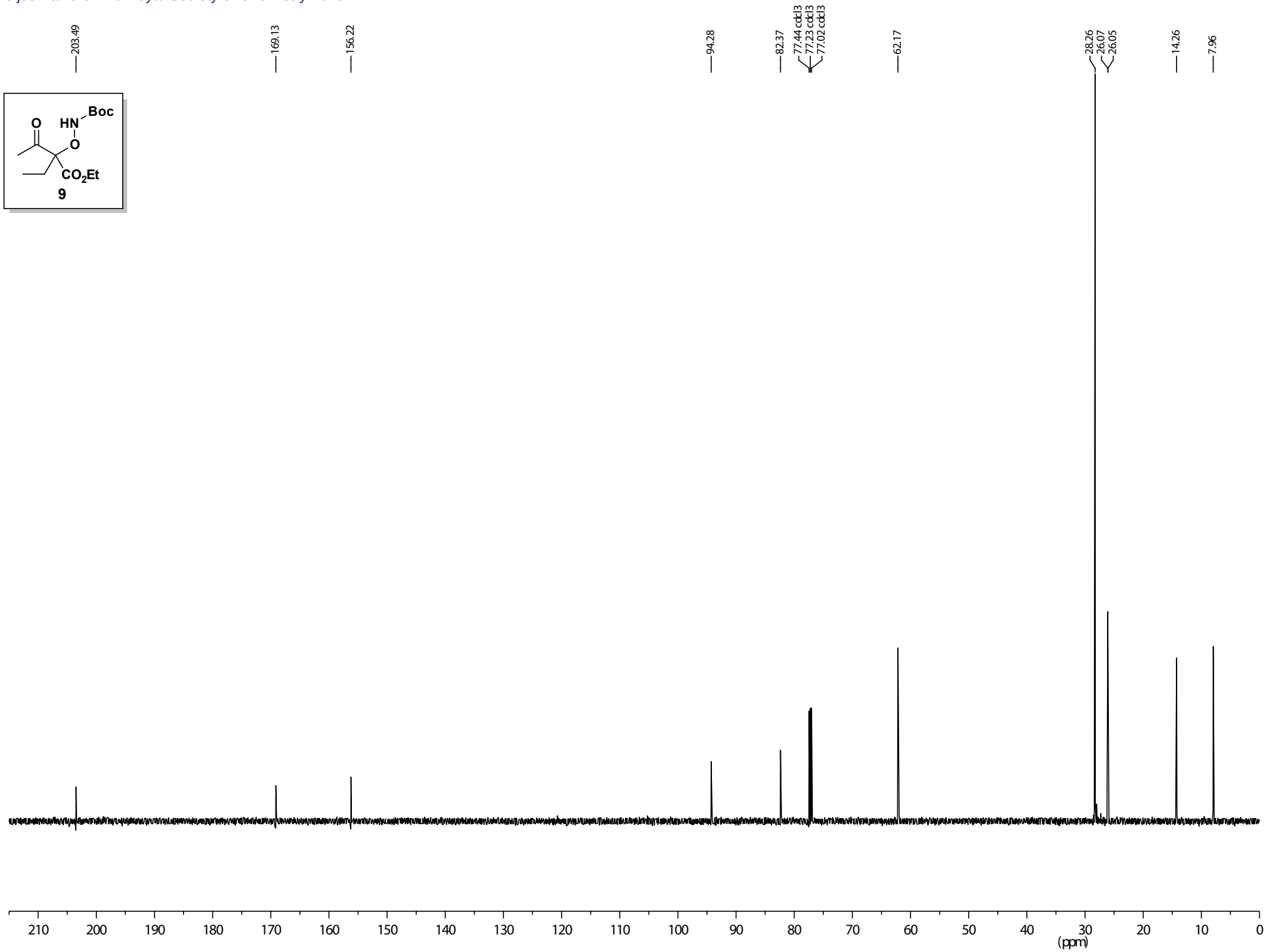

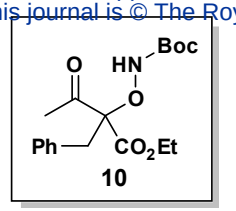

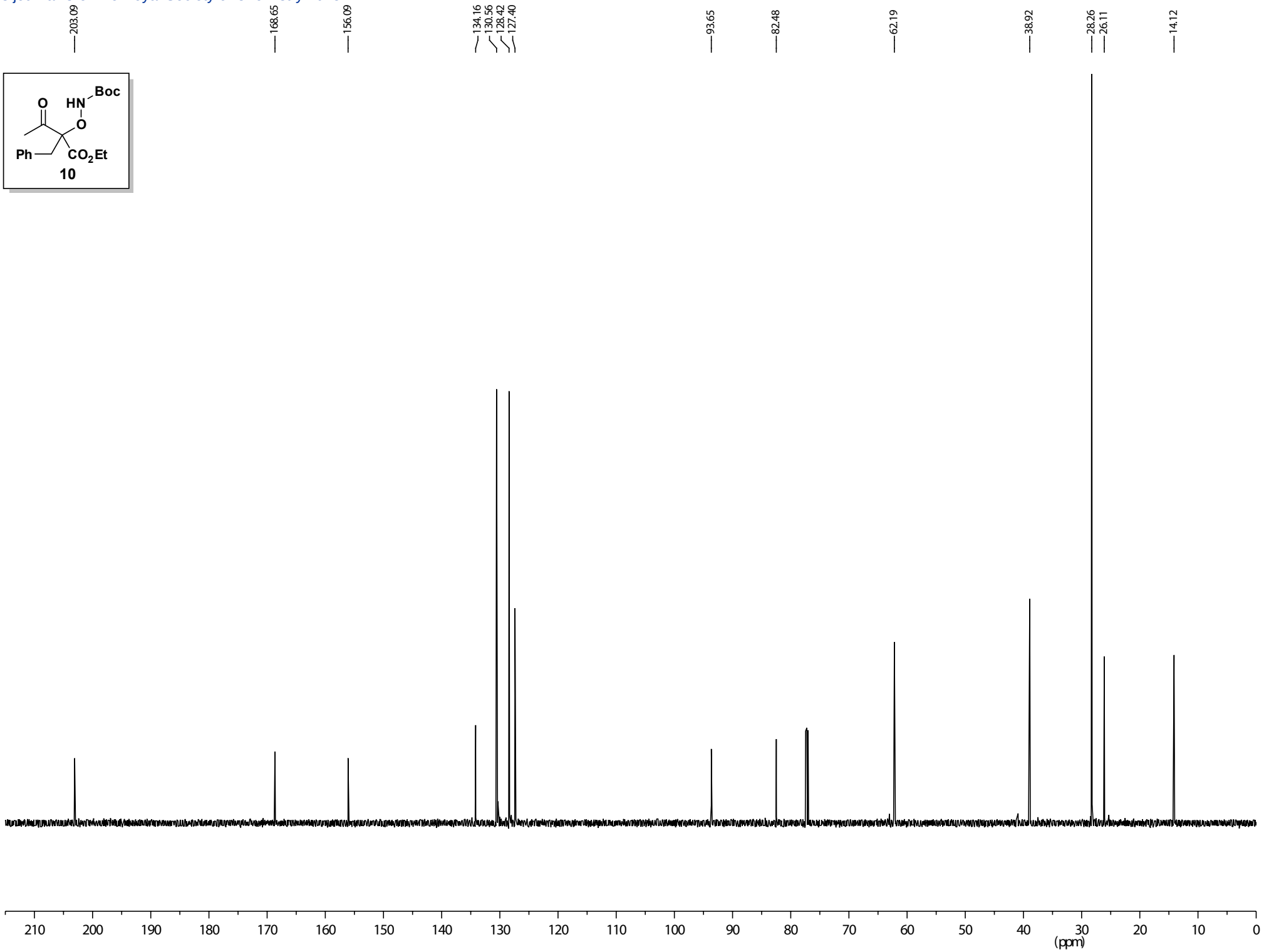

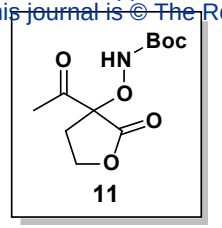

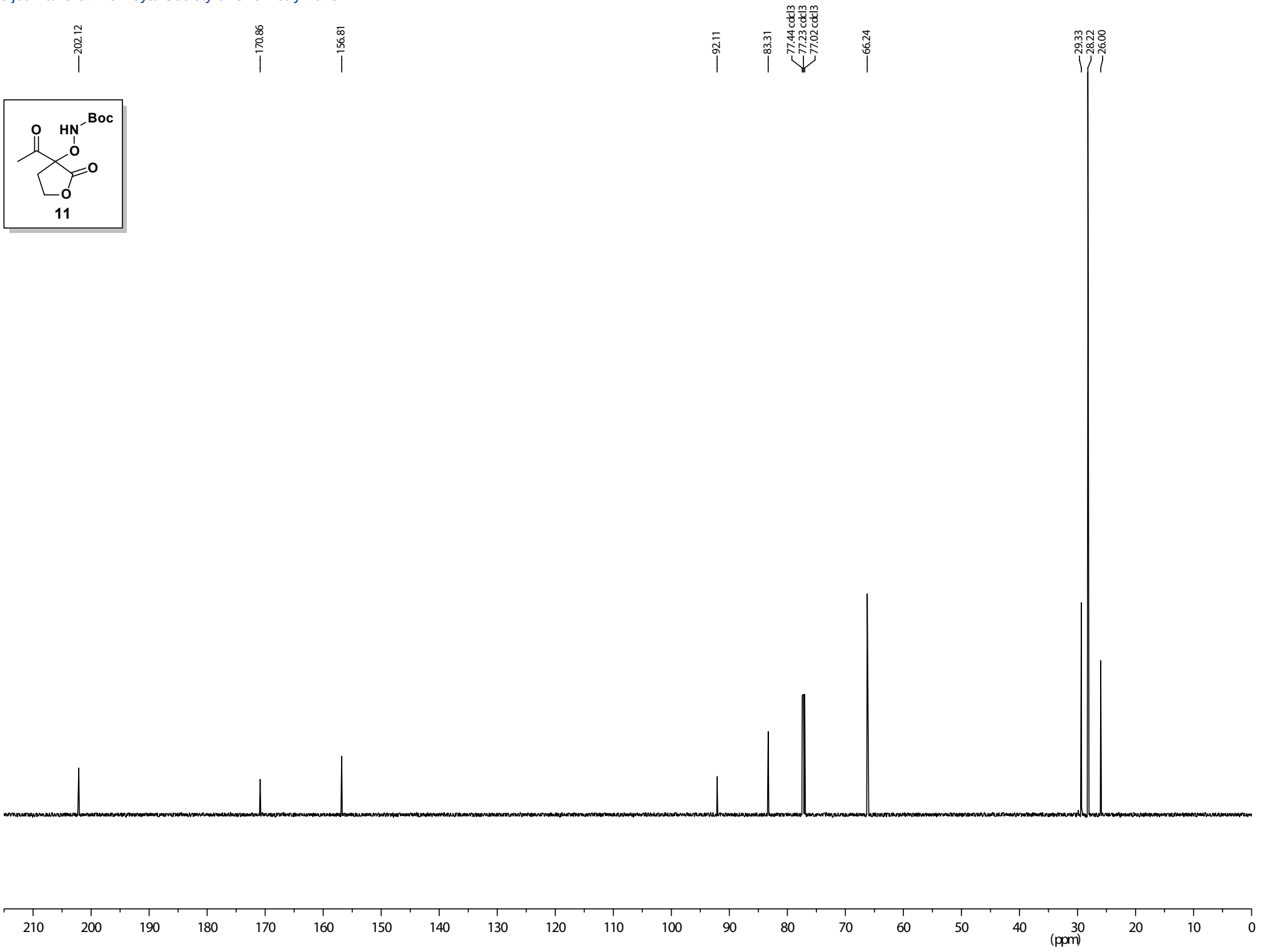

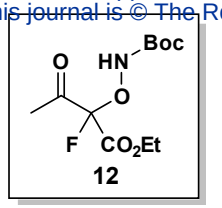

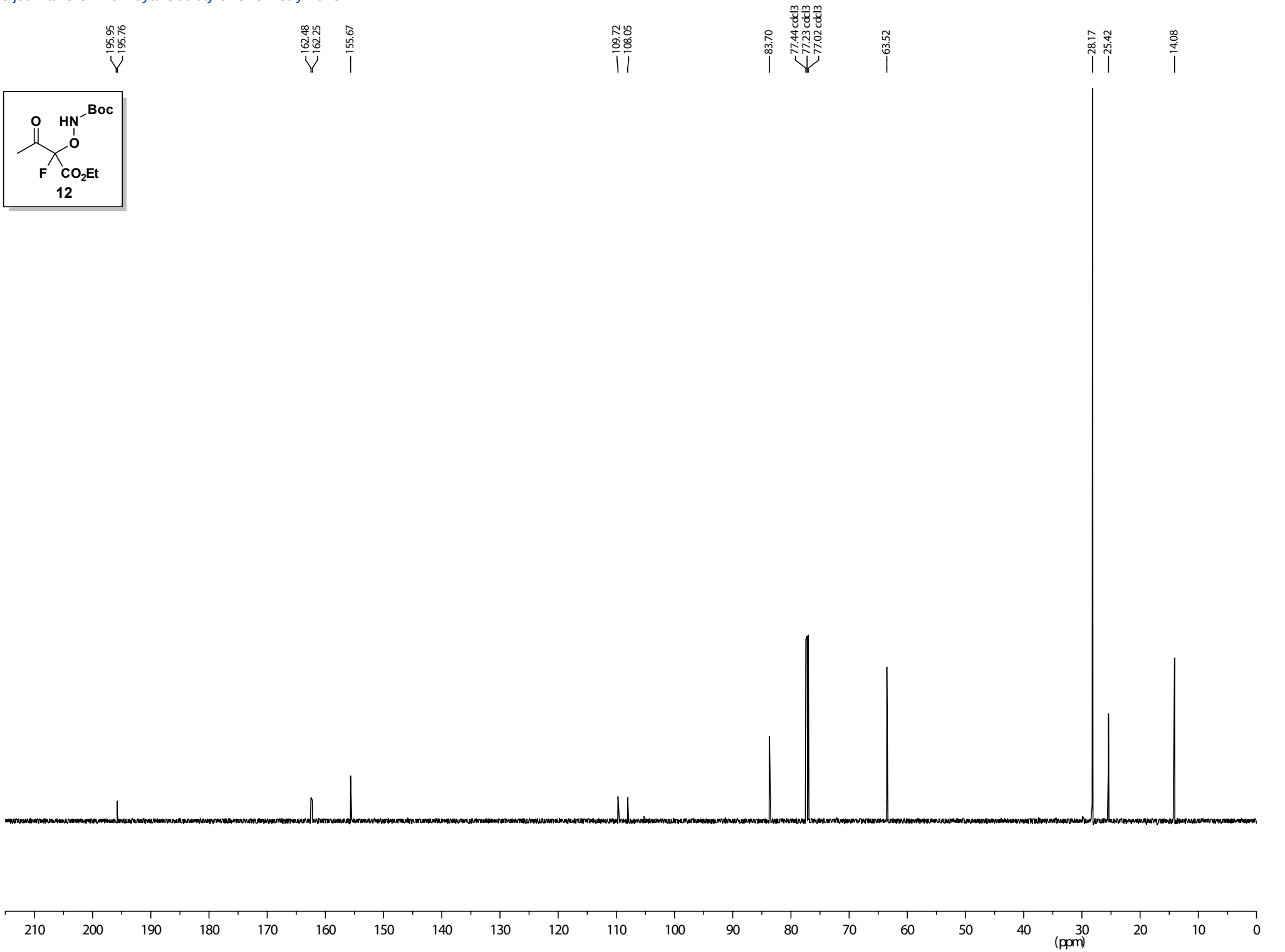

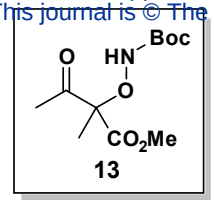

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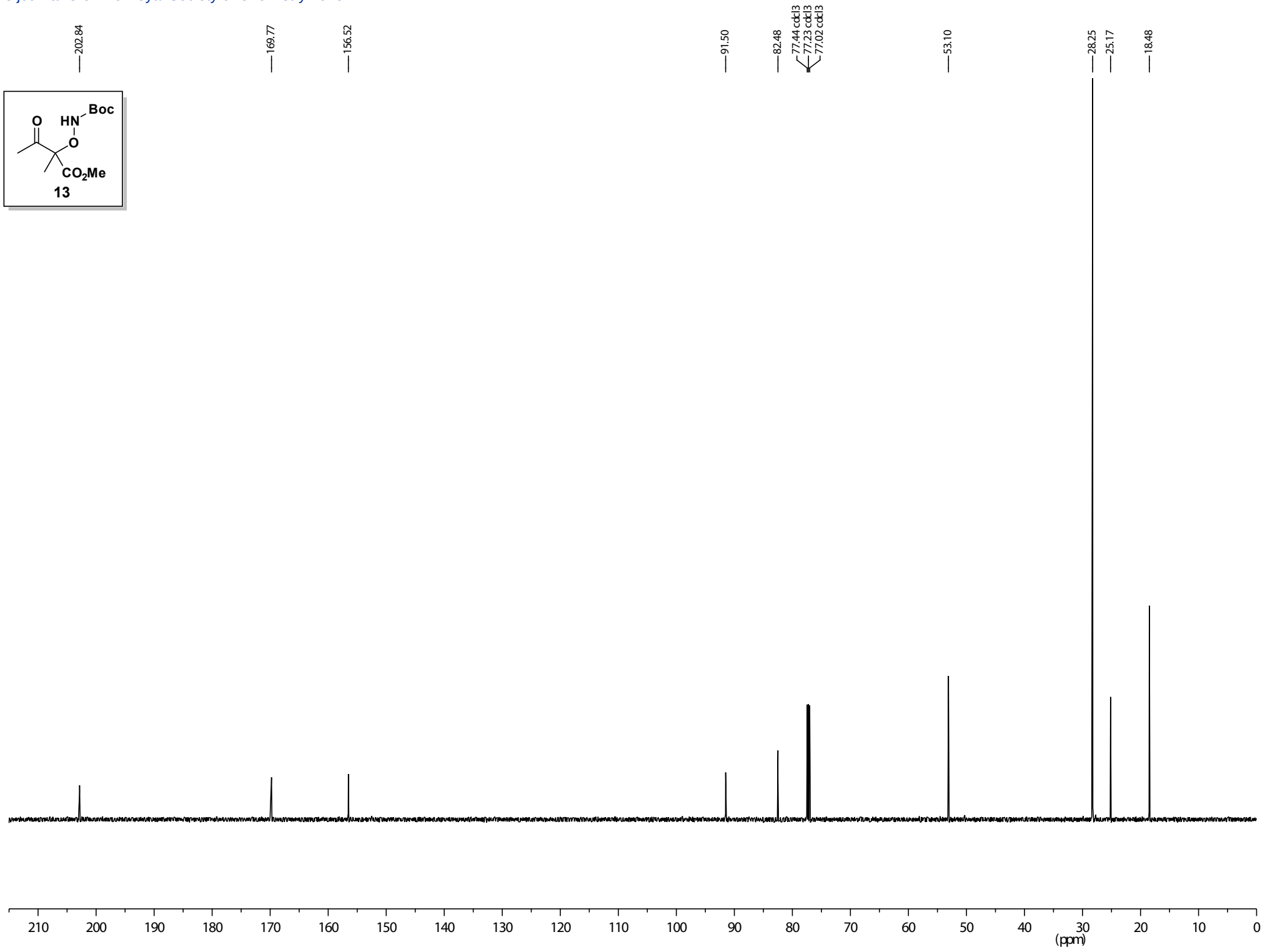

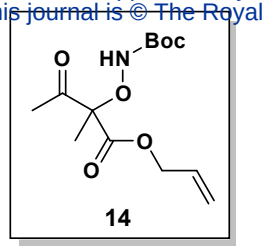

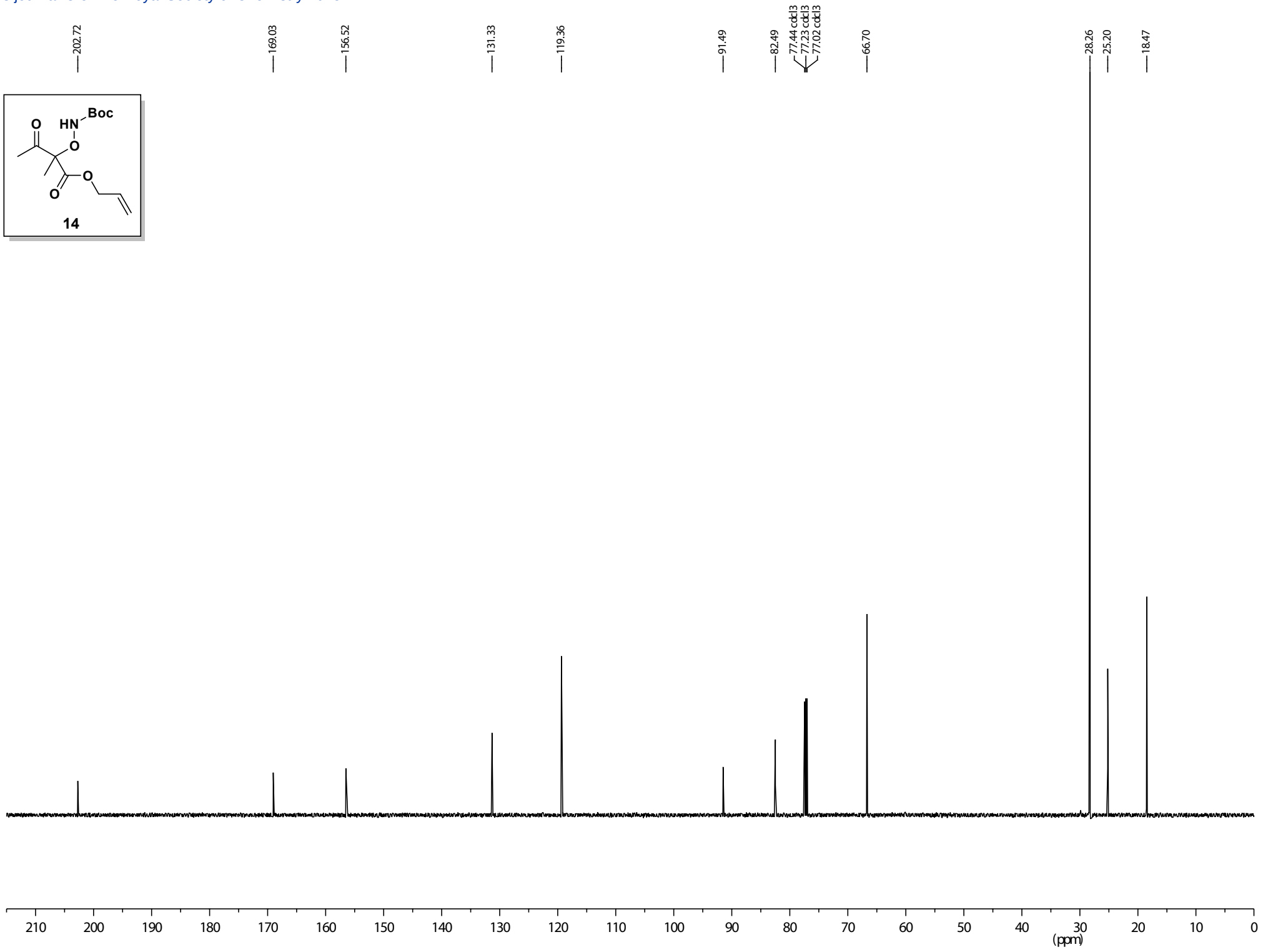

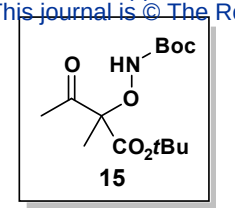

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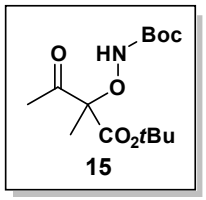

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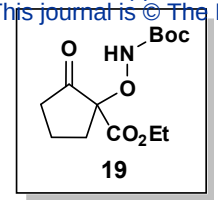

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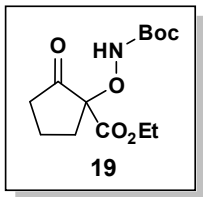

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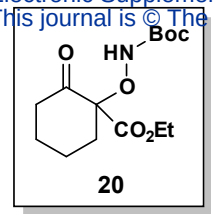

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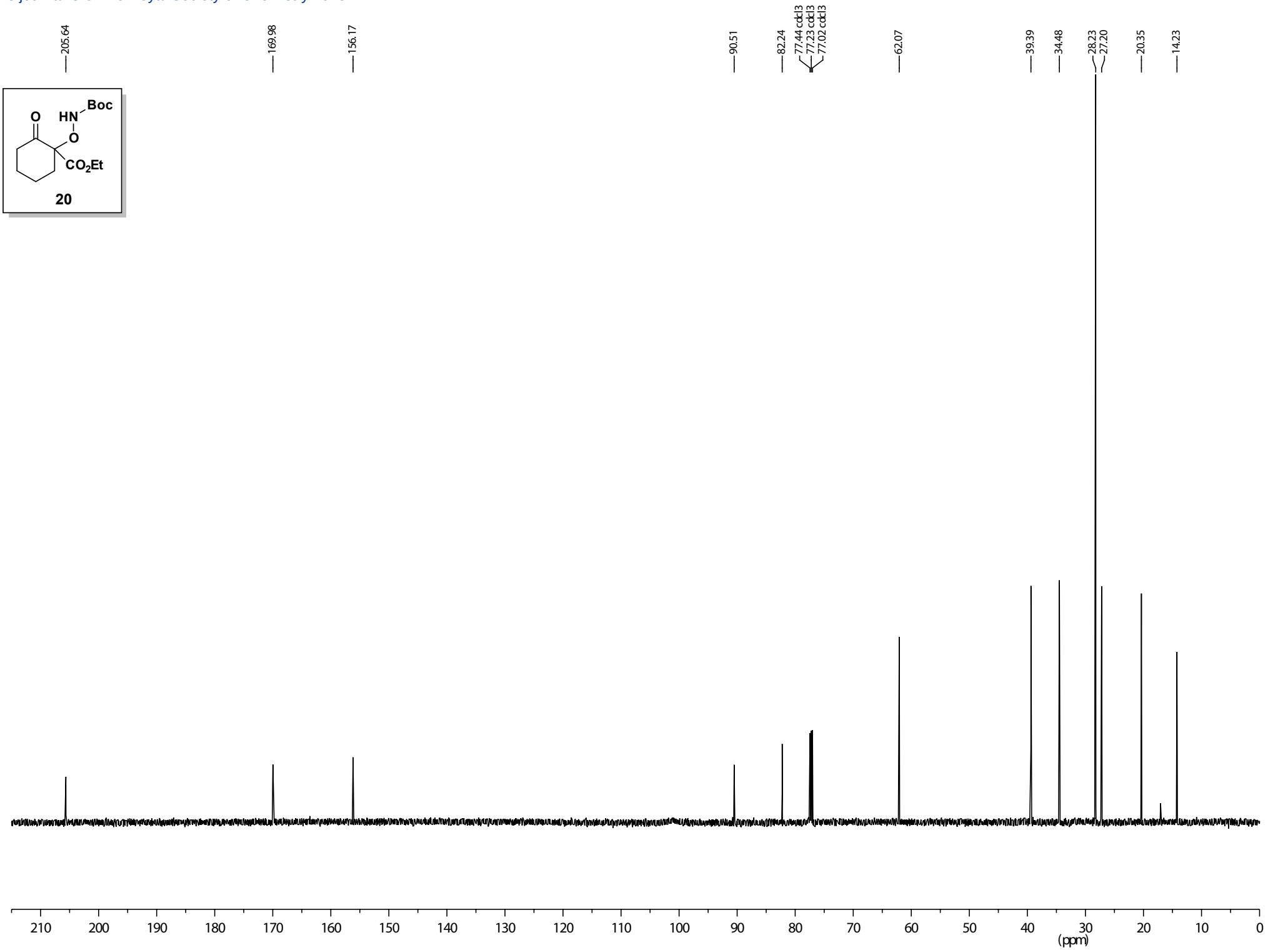

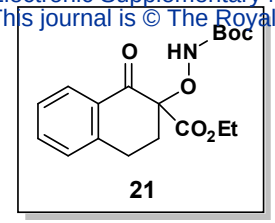

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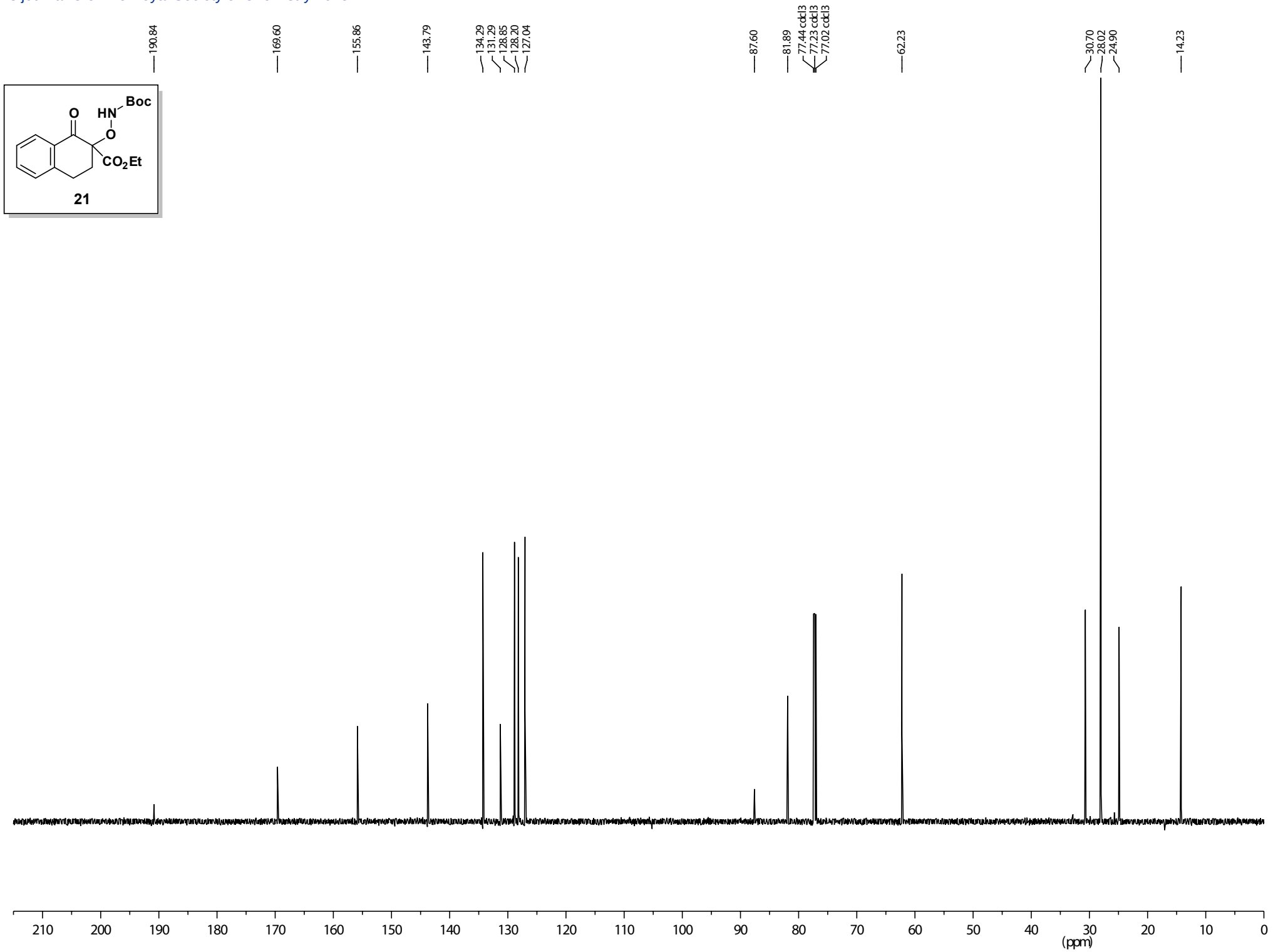

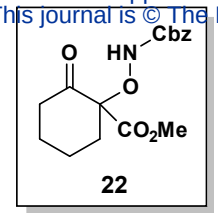

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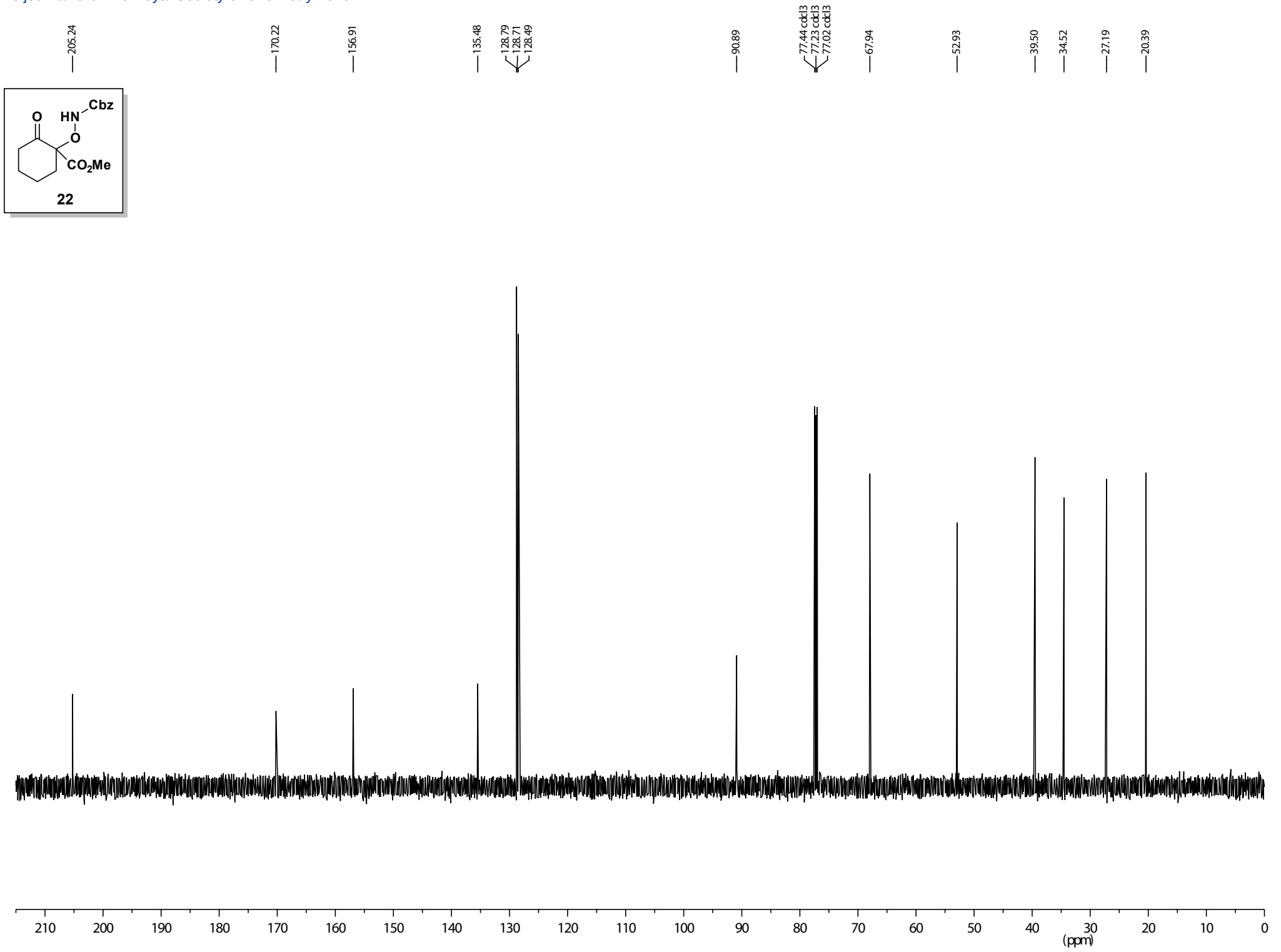

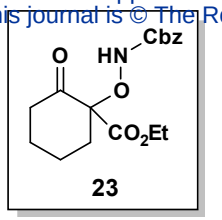

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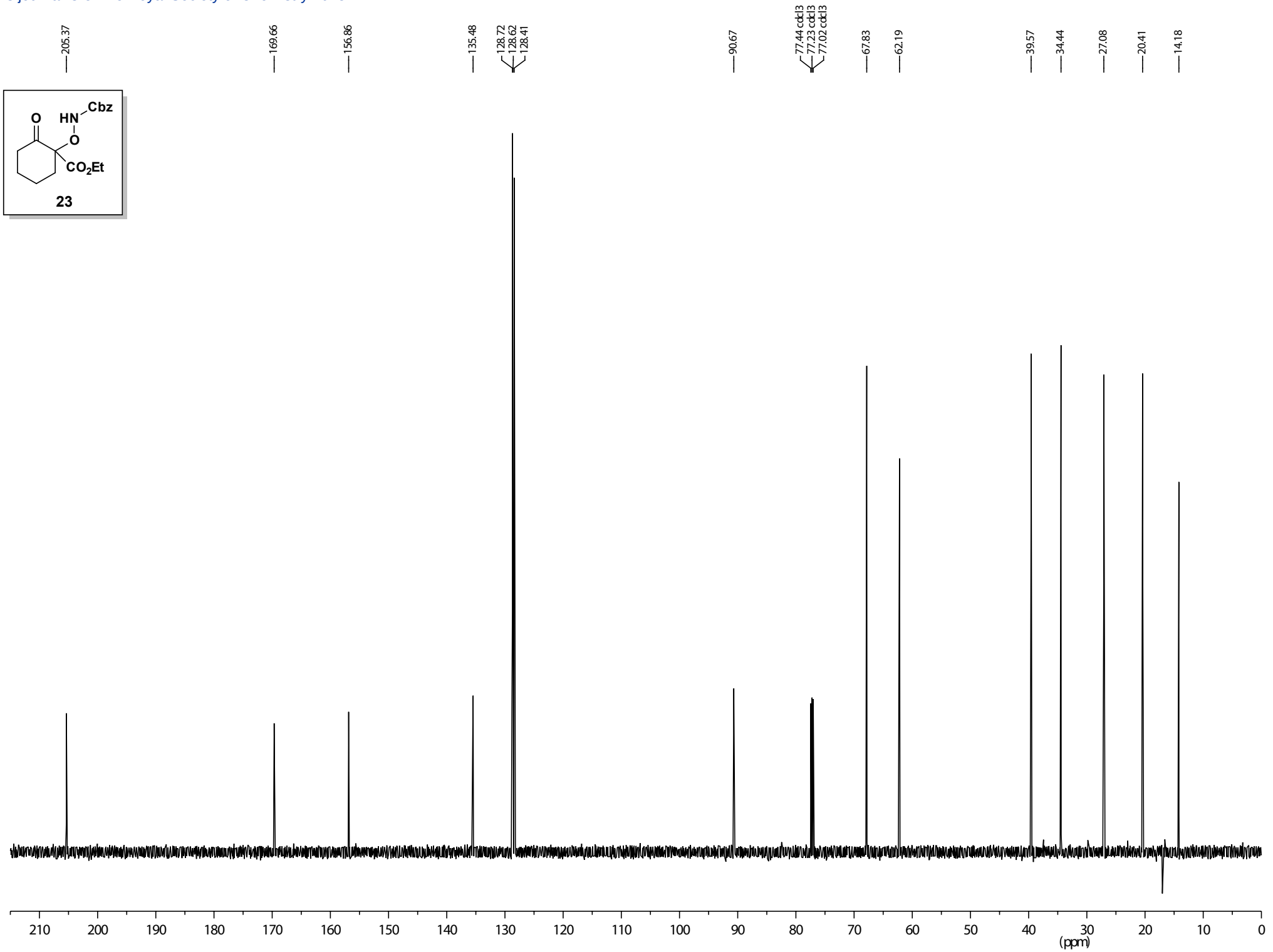

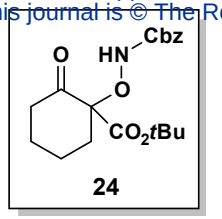

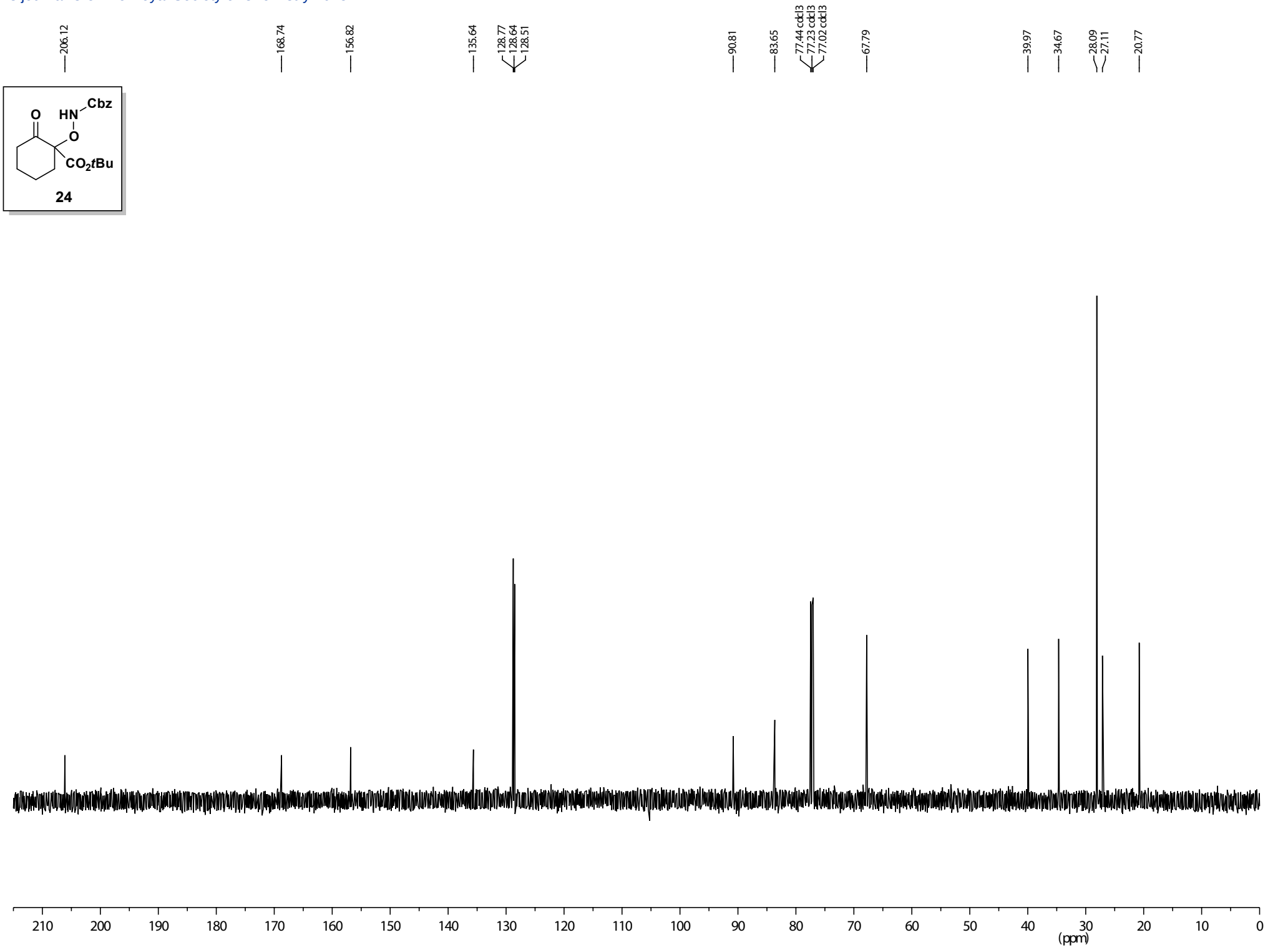

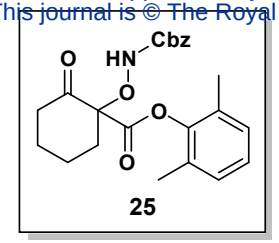

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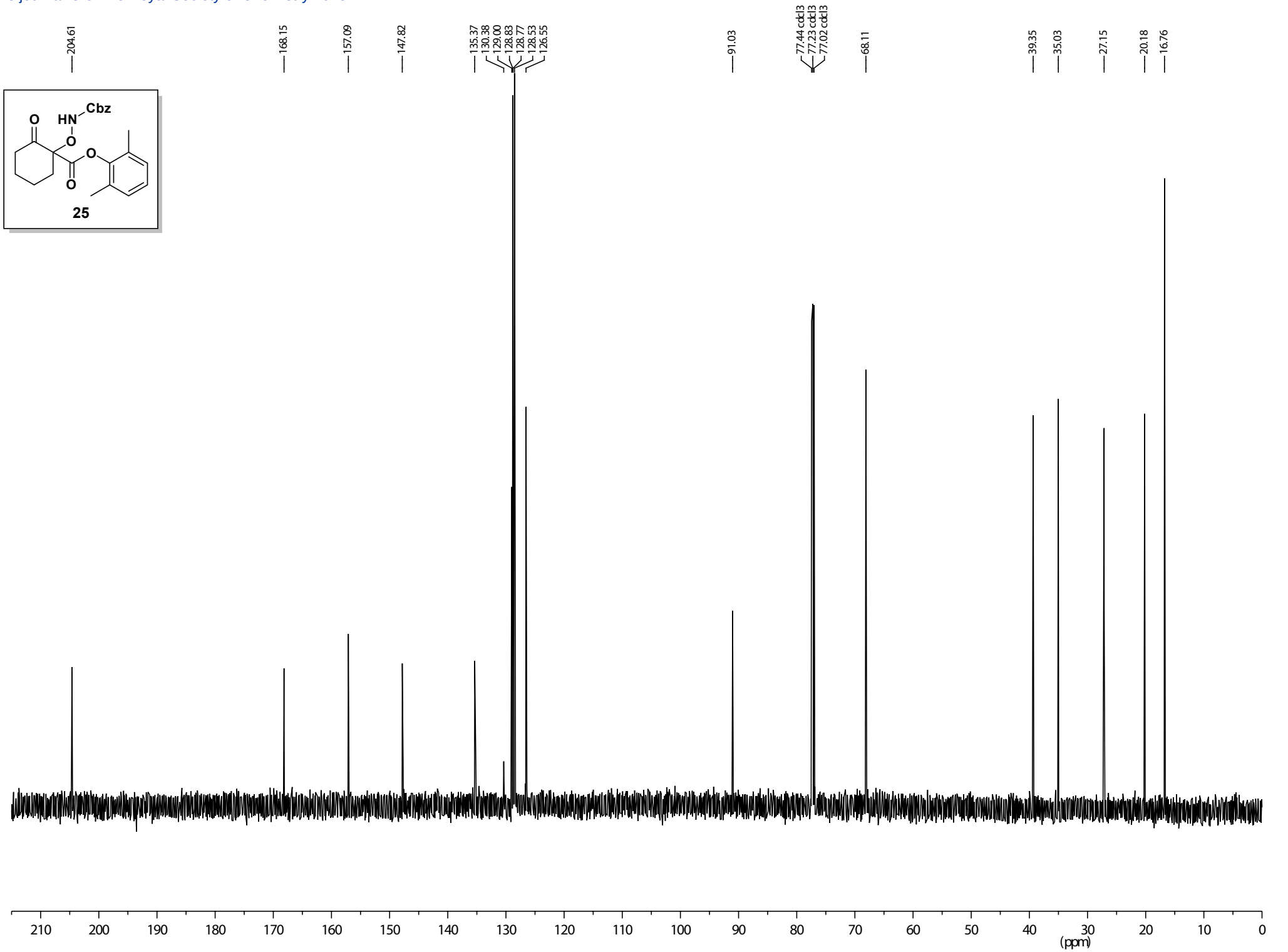

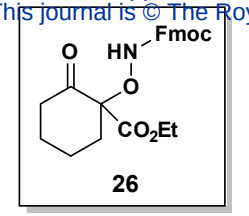

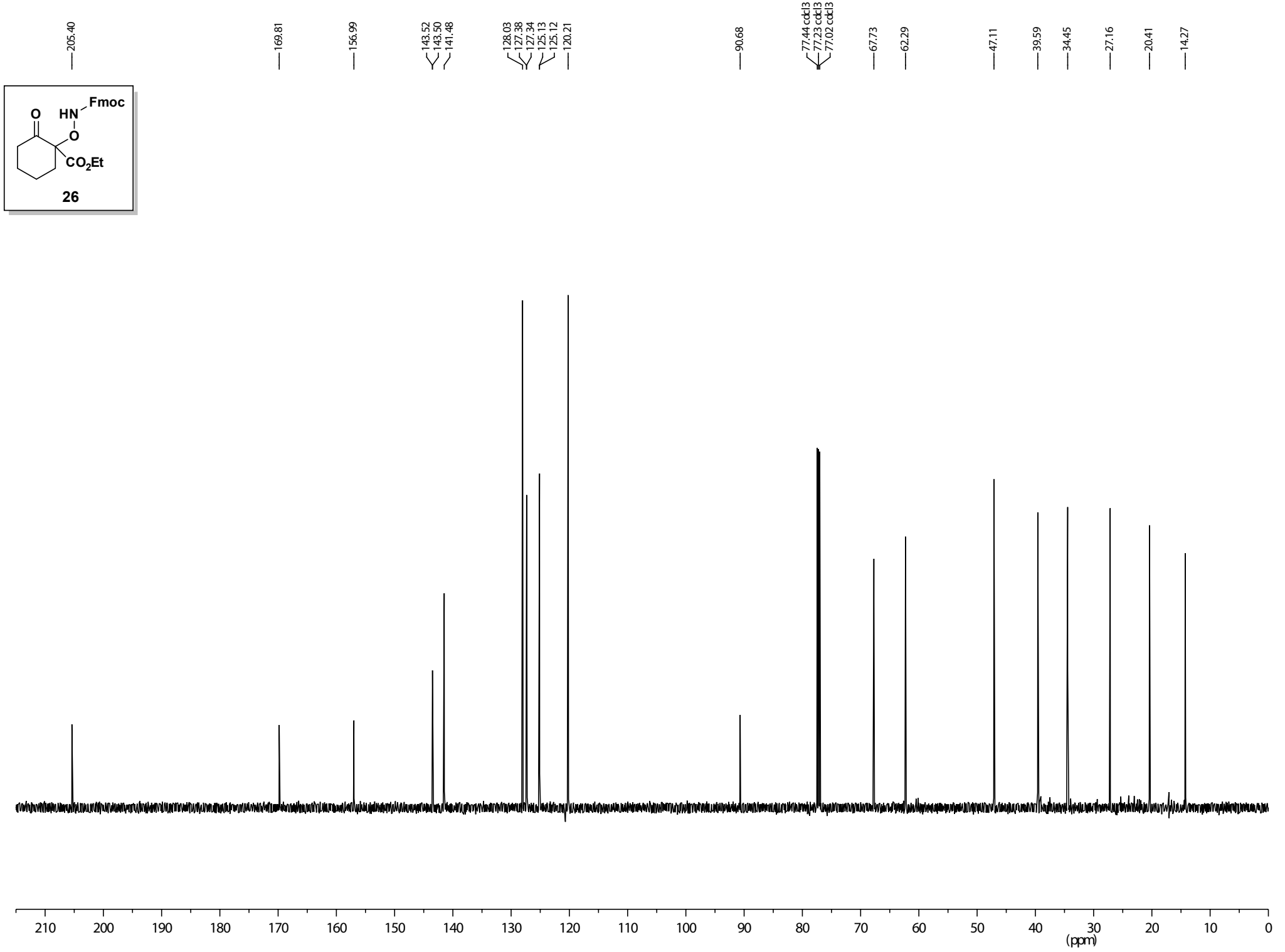

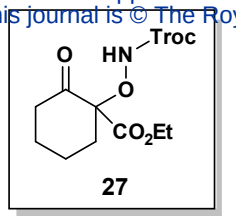

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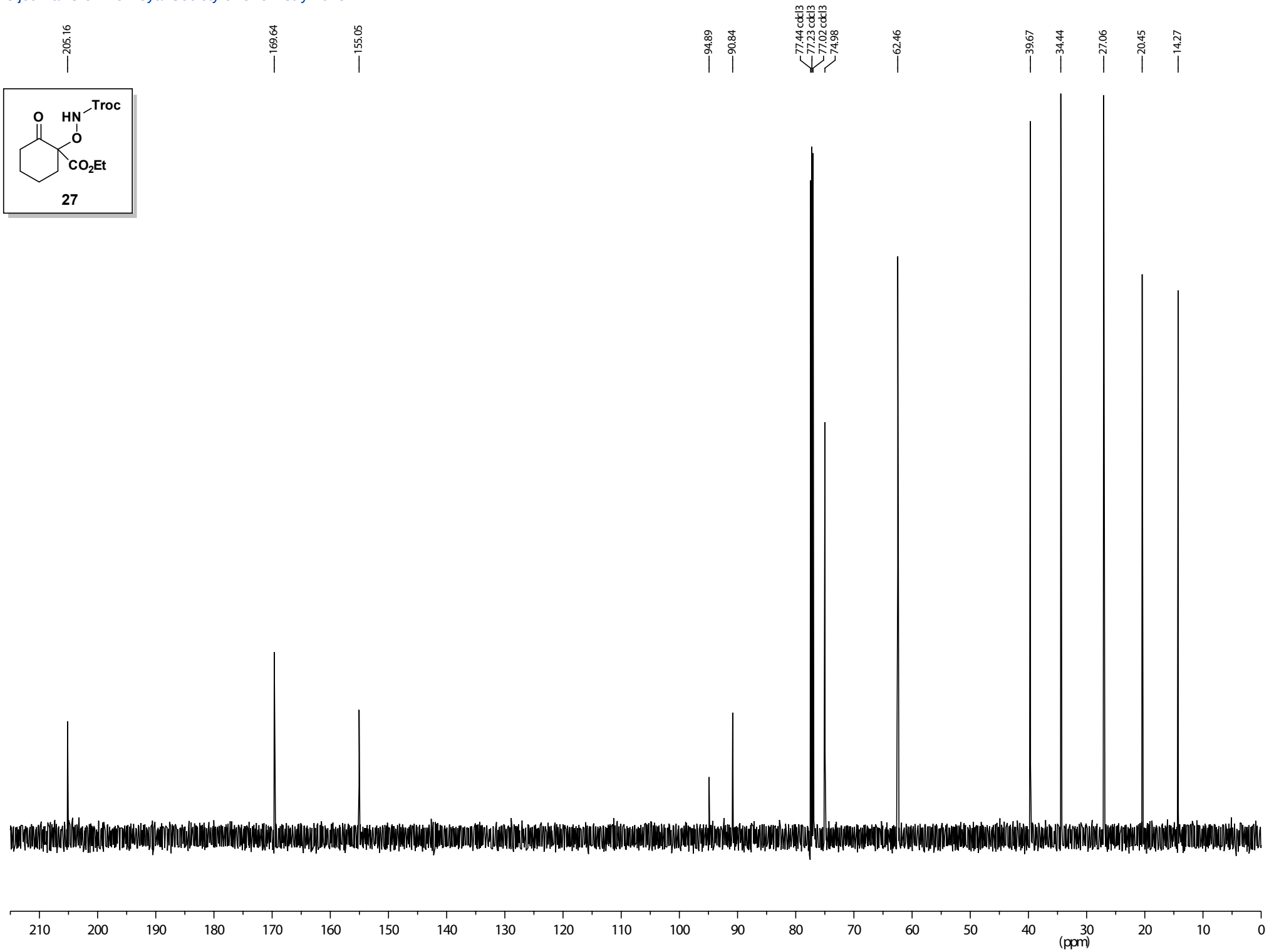

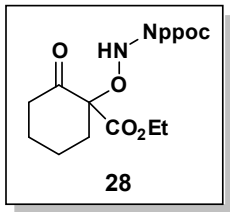

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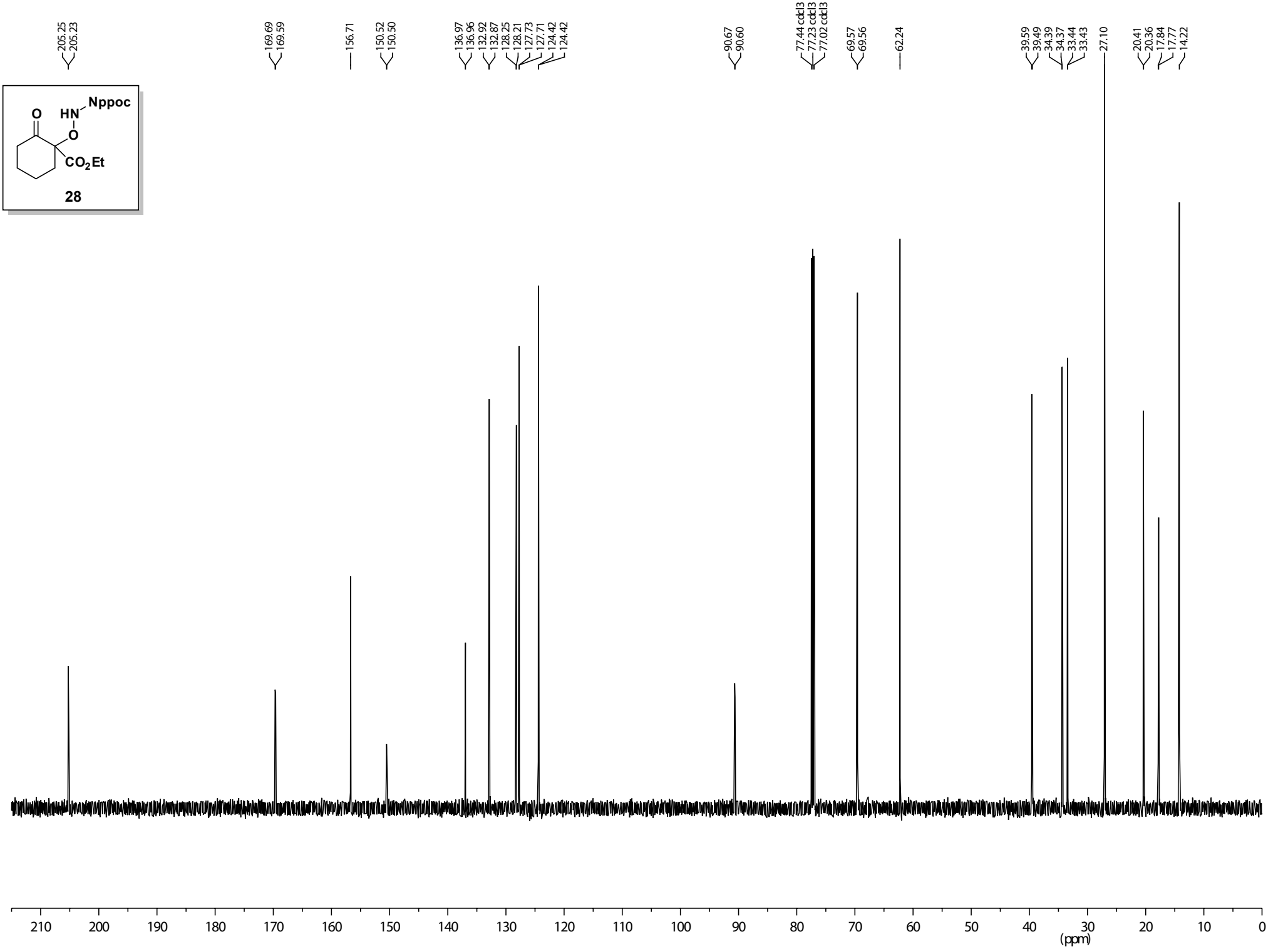

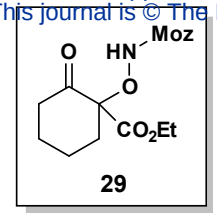

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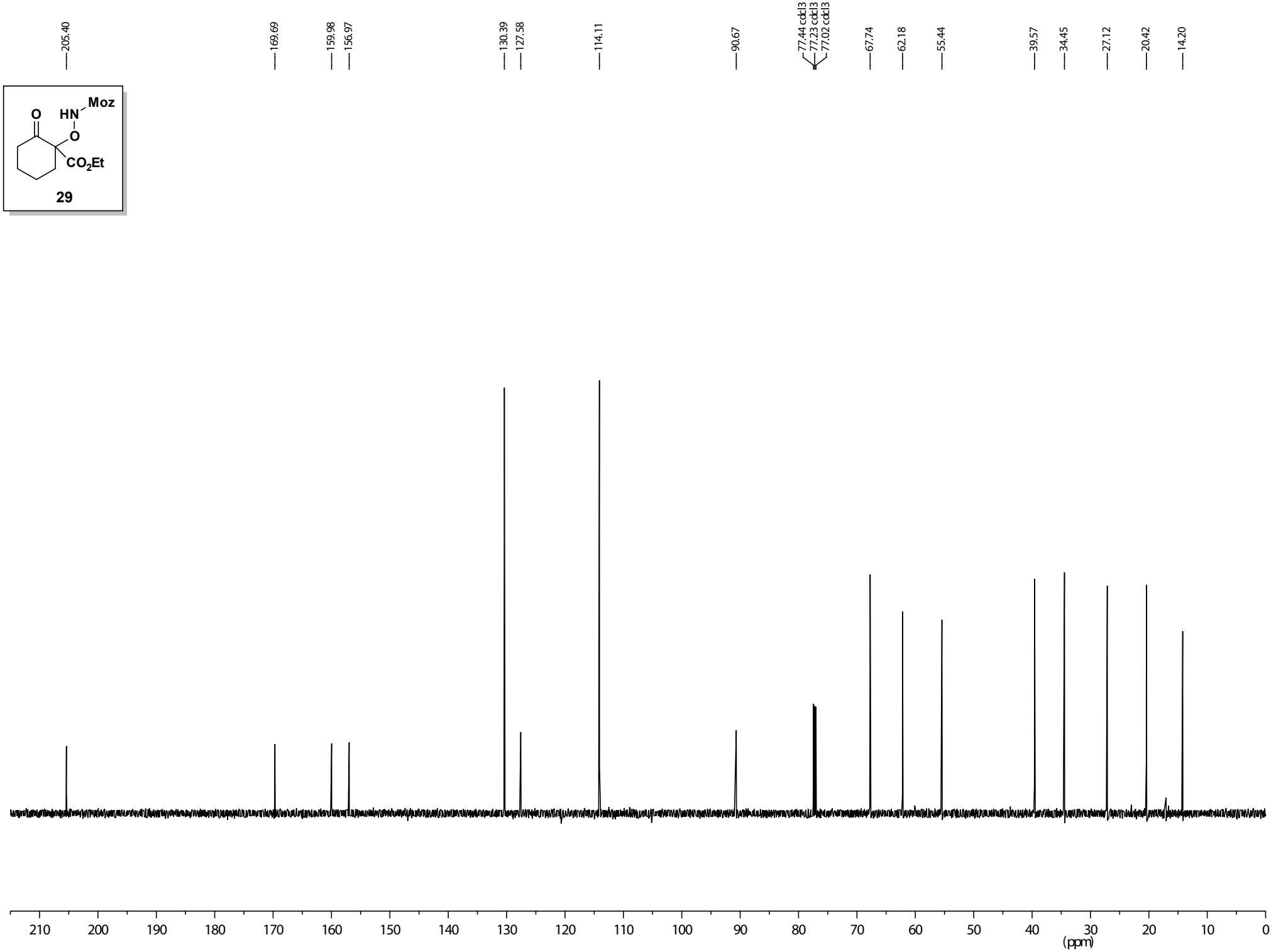

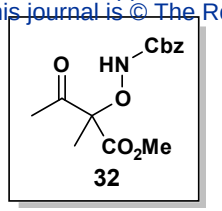

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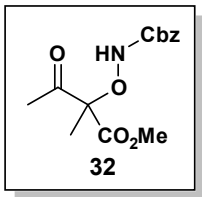

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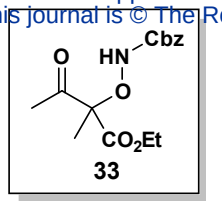

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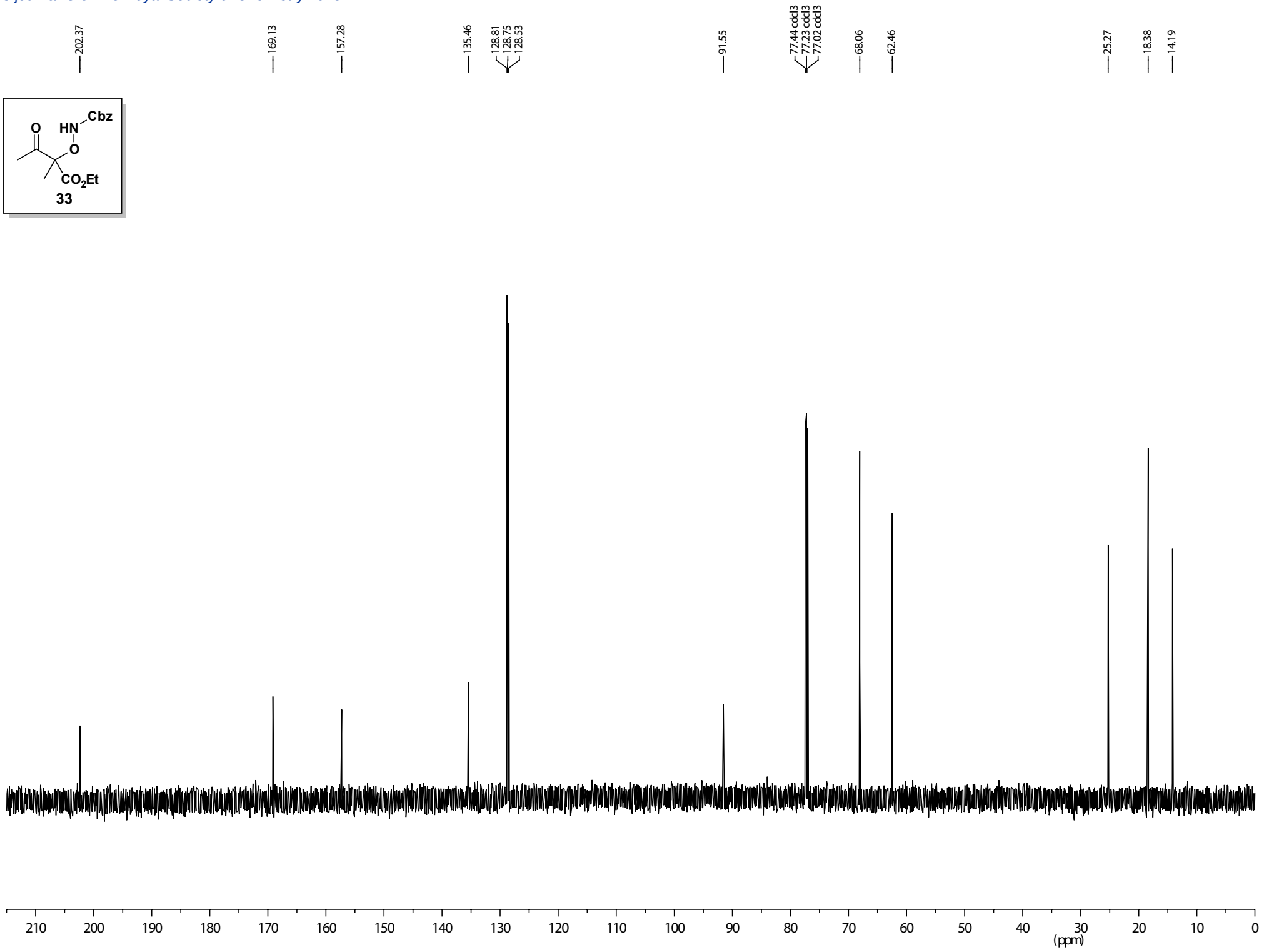

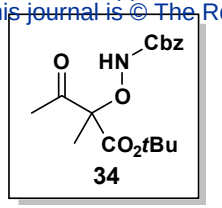

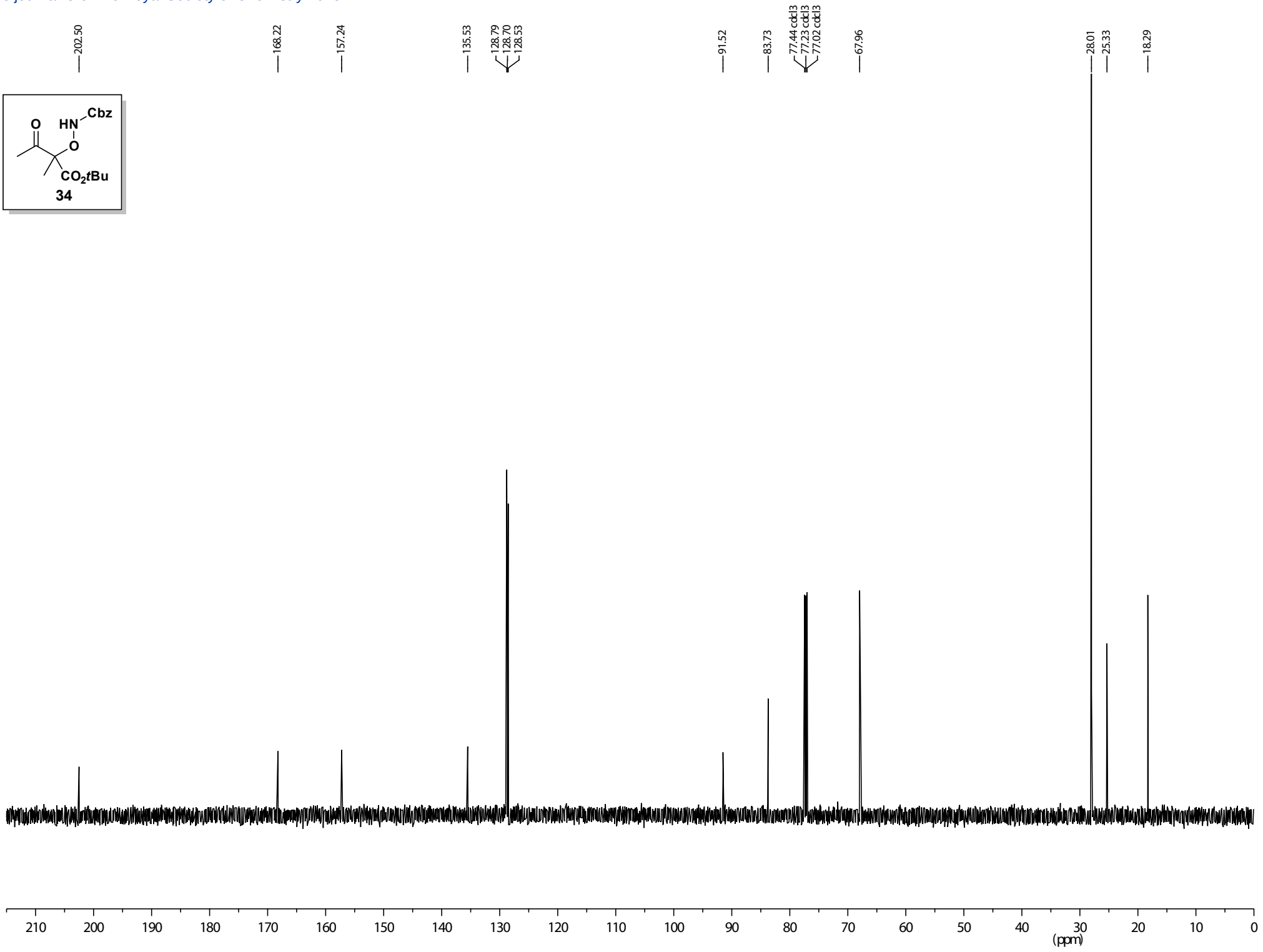

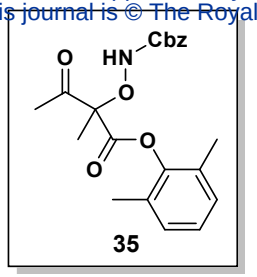

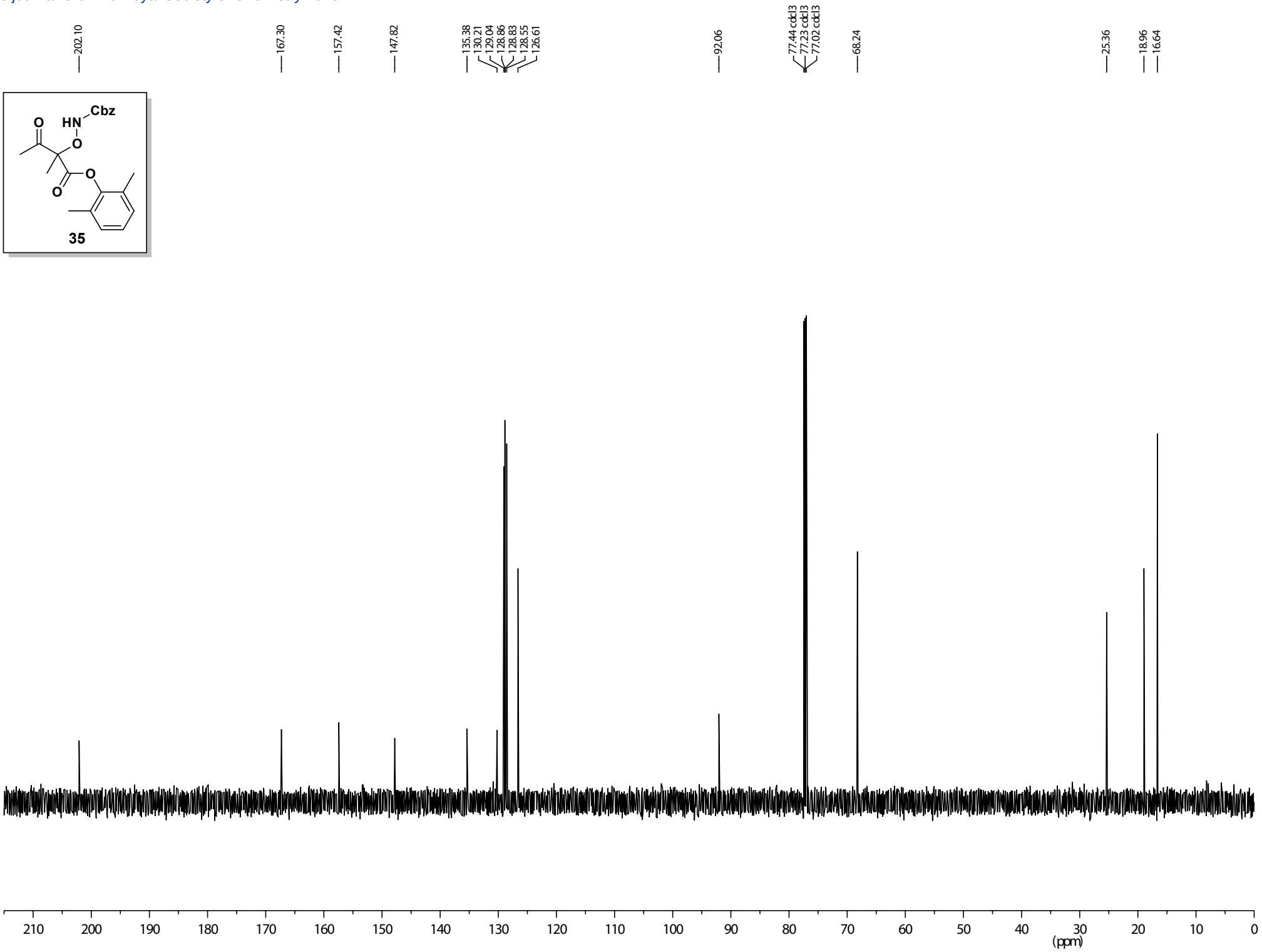

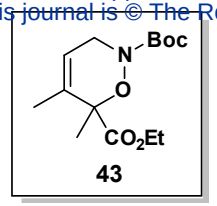

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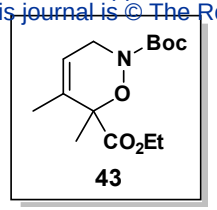

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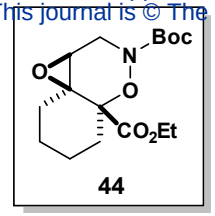

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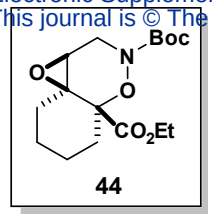
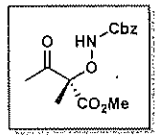


44

==== Shimadzu LCsolution Analysis Report ====

Acquired by	: Sandoval, D.
Sample Name	: [redacted]
Sample ID	: methyl 2-((((benzyloxy)carbonyl)amino)oxy)-2-methyl-3-oxobutanoate
Injection Volume	: 100 uL
Eluent Conc.	: 95.5/0.5 hexanes/i-PrOH, 30 min; 97/3 hexanes/i-PrOH, 30 min
Flow Rate	: 1 ml/min
Data Acquired	: 1/15/2013 7:41:27 PM
Data Processed	: 1/15/2013 9:56:37 PM



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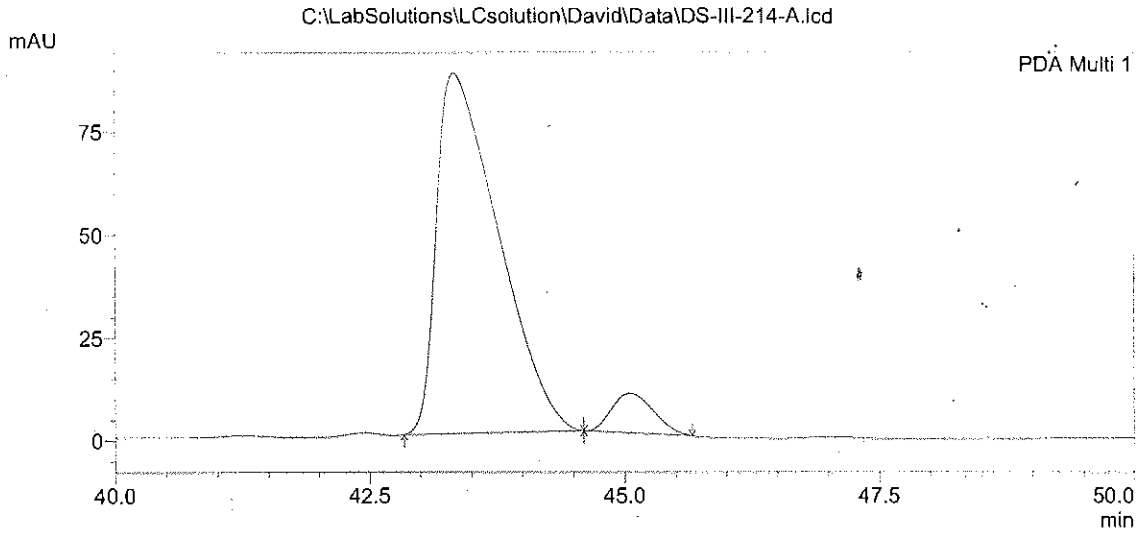


1 PDA Multi 1/254nm 4nm

<Results>

PeakTable

PDA Ch1 254nm 4nm

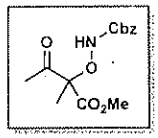
Peak#	Ret. Time	Area	Area %
1	43.330	3691163	93.041
2	45.047	276082	6.959
Total		3967245	100.000

PeakTable

PDA Ch2

==== Shimadzu LCsolution Analysis Report ====

Acquired by	: Sandoval, D.
Sample Name	: [redacted]
Sample ID	: methyl 2-((((benzyloxy)carbonyl)amino)oxy)-2-methyl-3-oxobutanoate
Injection Volume	: 100 uL
Eluent Conc.	: 95.5/0.5 hexanes/i-PrOH, 30 min; 97/3 hexanes/i-PrOH, 30 min
Flow Rate	: 1 ml/min
Data Acquired	: 1/17/2013 7:40:30 PM
Data Processed	: 1/17/2013 9:55:34 PM



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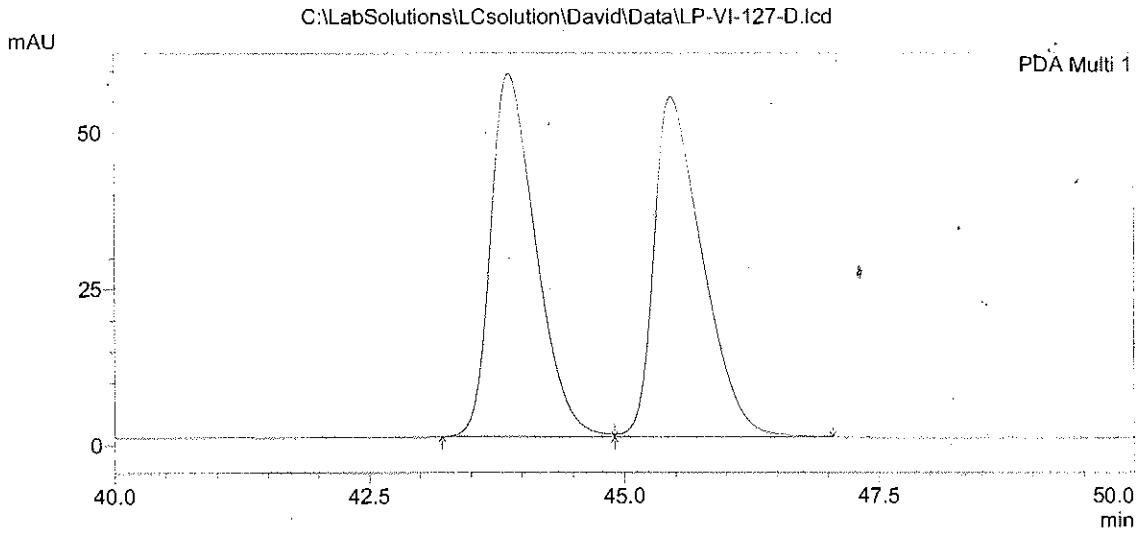


1 PDA Multi 1/254nm 4nm

<Results>

PeakTable

PDA Ch1 254nm 4nm

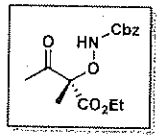
Peak#	Ret. Time	Area	Area %
1	43.874	1786218	49.787
2	45.460	1801518	50.213
Total		3587736	100.000

PeakTable

PDA Ch2

==== Shimadzu LCsolution Analysis Report ====

Acquired by	: Sandoval, D.
Sample Name	: [redacted]
Sample ID	: ethyl 2-((((benzyloxy)carbonyl)amino)oxy)-2-methyl-3-oxobutanoate
Injection Volume	: 100 uL
Eluent Conc.	: 95.5/0.5 hexanes/i-PrOH, 30 min; 97/3 hexanes/i-PrOH, 30 min
Flow Rate	: 1 ml/min
Data Acquired	: 1/19/2013 5:51:39 AM
Data Processed	: 1/19/2013 8:06:47 AM



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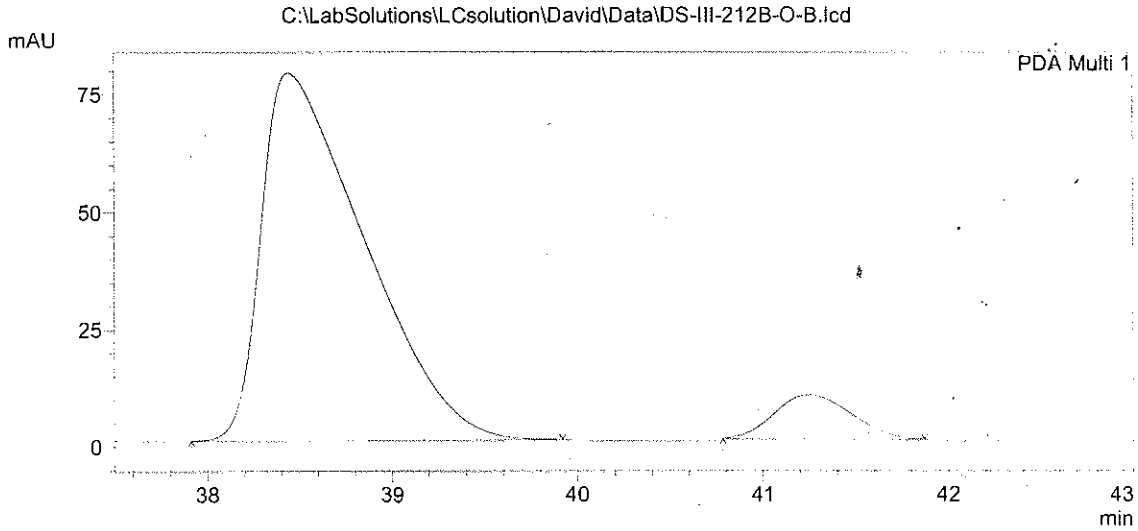


1 PDA Multi 1/254nm 4nm

<Results>

PeakTable

PDA Ch1 254nm 4nm

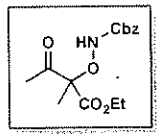
Peak#	Ret. Time	Area	Area %
1	38.440	3045624	91.795
2	41.247	272213	8.205
Total		3317838	100.000

PeakTable

PDA Ch2

==== Shimadzu LCsolution Analysis Report ====

Acquired by	: Sandoval, D.
Sample Name	: [redacted]
Sample ID	: ethyl 2-((((benzyloxy)carbonyl)amino)oxy)-2-methyl-3-oxobutanoate
Injection Volume	: 100 uL
Eluent Conc.	: 95.5/0.5 hexanes/i-PrOH, 30 min; 97/3 hexanes/i-PrOH, 30 min
Flow Rate	: 1 ml/min
Data Acquired	: 1/19/2013 3:35:55 AM
Data Processed	: 1/19/2013 5:51:00 AM



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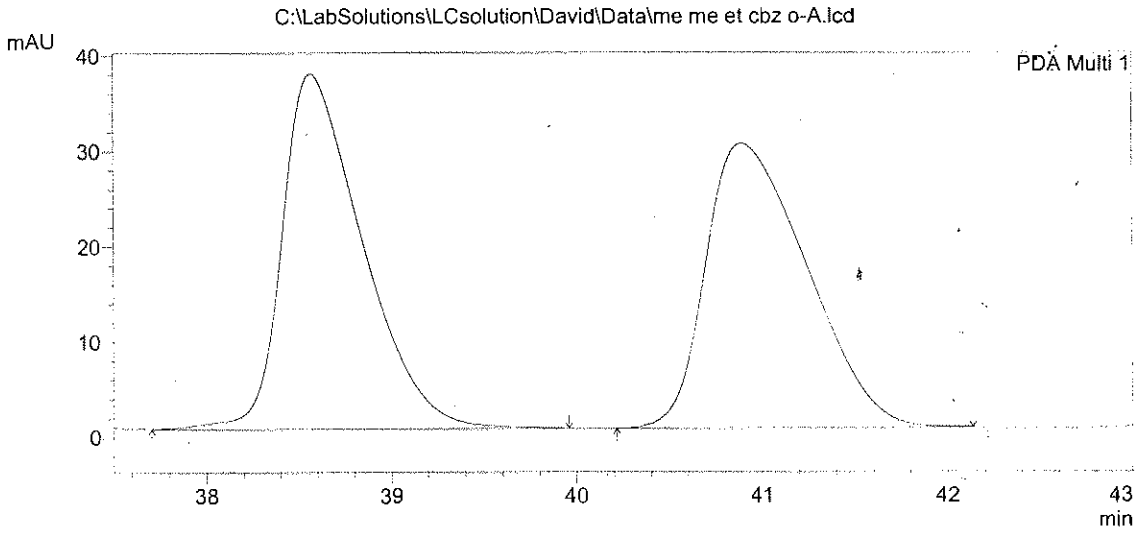


1 PDA Multi 1/254nm 4nm

<Results>

PeakTable

PDA Ch1 254nm 4nm

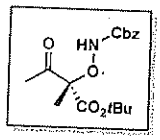
Peak#	Ret. Time	Area	Area %
1	38.564	1134156	50.025
2	40.890	1133012	49.975
Total		2267169	100.000

PeakTable

PDA Ch2

==== Shimadzu LCsolution Analysis Report ====

Acquired by	: Sandoval, D.
Sample Name	: [redacted]
Sample ID	: tert-butyl 2-((((benzyloxy)carbonyl)amino)oxy)-2-methyl-3-oxobutanoate
Injection Volume	: 100 uL
Eluent Conc.	: 95.5/0.5 hexanes/i-PrOH, 30 min; 97/3 hexanes/i-PrOH, 30 min
Flow Rate	: 1 ml/min
Data Acquired	: 1/18/2013 9:14:57 AM
Data Processed	: 1/18/2013 11:30:06 AM



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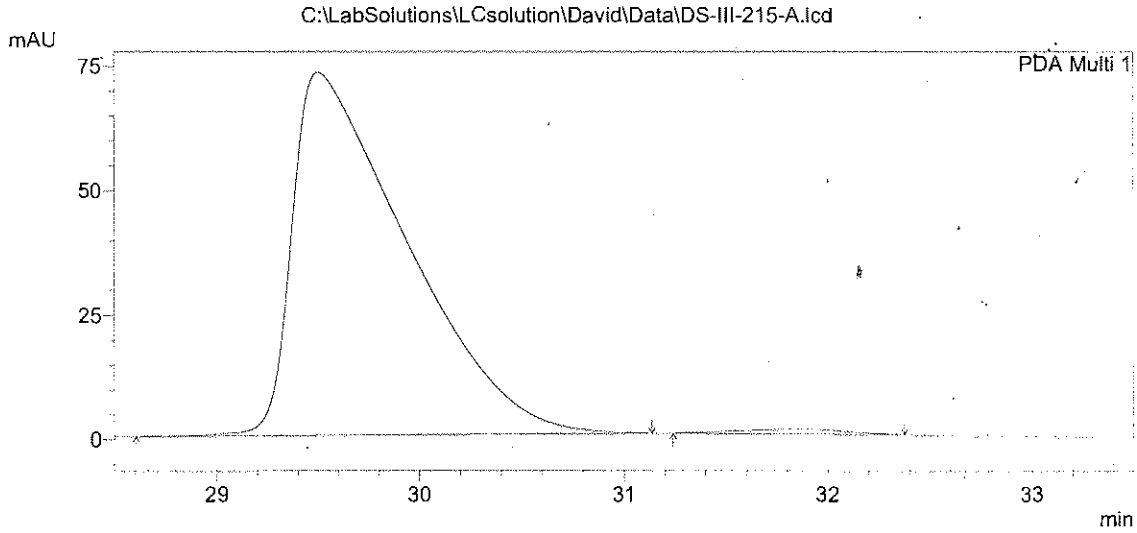


1 PDA Multi 1/254nm 4nm

<Results>

PeakTable

PDA Ch1 254nm 4nm

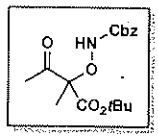
Peak#	Ret. Time	Area	Area %
1	29.499	2857201	98.740
2	31.860	36447	1.260
Total		2893649	100.000

PeakTable

PDA Ch2

==== Shimadzu LCsolution Analysis Report ====

Acquired by	: Sandoval, D.
Sample Name	: [redacted]
Sample ID	: tert-butyl 2-((((benzyloxy)carbonyl)amino)oxy)-2-methyl-3-oxobutanoate
Injection Volume	: 100 uL
Eluent Conc.	: 95.5/0.5 hexanes/i-PrOH, 30 min; 97/3 hexanes/i-PrOH, 30 min
Flow Rate	: 1 ml/min
Data Acquired	: 1/18/2013 11:30:42 AM
Data Processed	: 1/18/2013 1:45:47 PM



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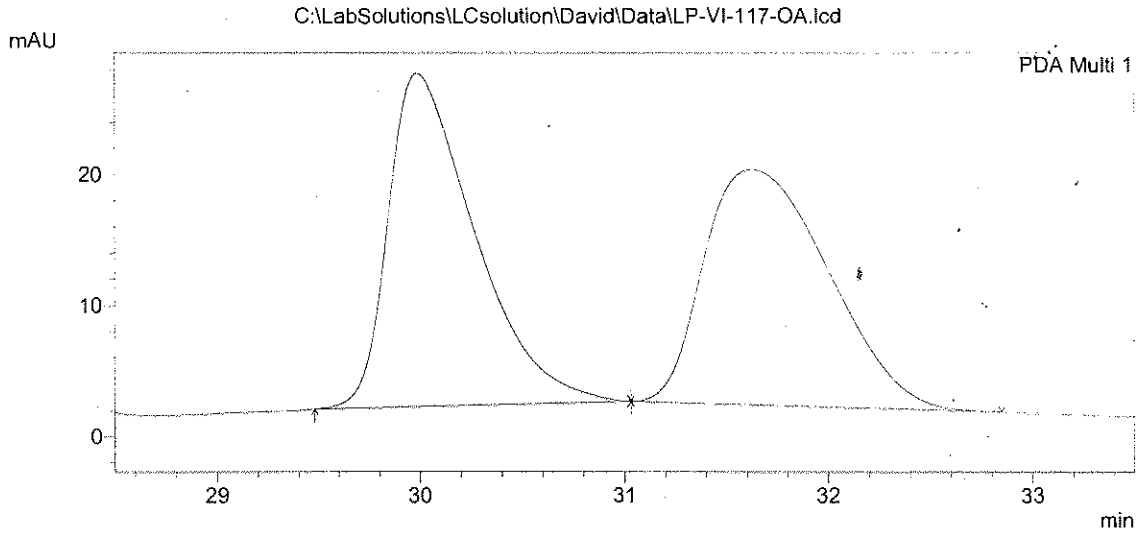


1 PDA Multi 1/254nm 4nm

<Results>

PeakTable

PDA Ch1 254nm 4nm

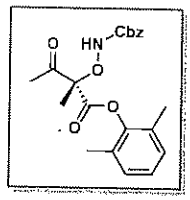
Peak#	Ret. Time	Area	Area %
1	29.985	750939	49.632
2	31.622	762081	50.368
Total		1513020	100.000

PeakTable

PDA Ch2

==== Shimadzu LCsolution Analysis Report ====

Acquired by	: Sandoval, D.
Sample Name	: [redacted]
Sample ID	: 2,6-dimethylphenyl 2-((((benzyloxy)carbonyl)amino)oxy)-2-methyl-3-oxobutanoate
Injection Volume	: 100 uL
Eluent Conc.	: 95.5/0.5 hexanes/i-PrOH, 30 min; 97/3 hexanes/i-PrOH, 30 min
Flow Rate	: 1 ml/min
Data Acquired	: 1/30/2013 4:49:46 AM
Data Processed	: 1/30/2013 7:04:50 AM



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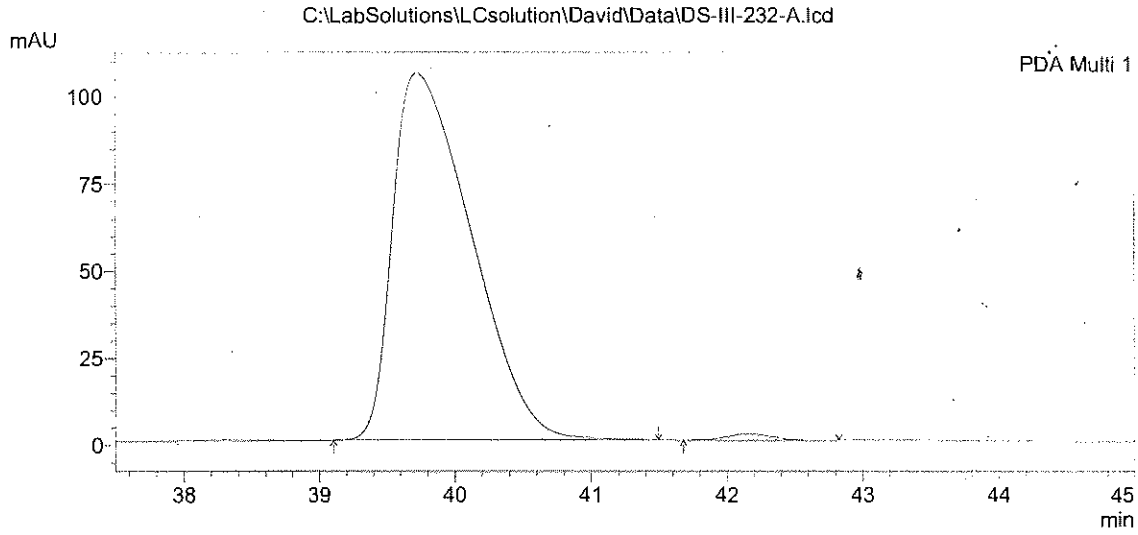


1 PDA Multi 1/254nm 4nm

<Results>

PeakTable

PDA Ch1 254nm 4nm

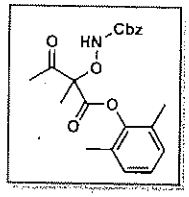
Peak#	Ret. Time	Area	Area %
1	39.725	4246061	99.057
2	42.159	40403	0.943
Total		4286464	100.000

PeakTable

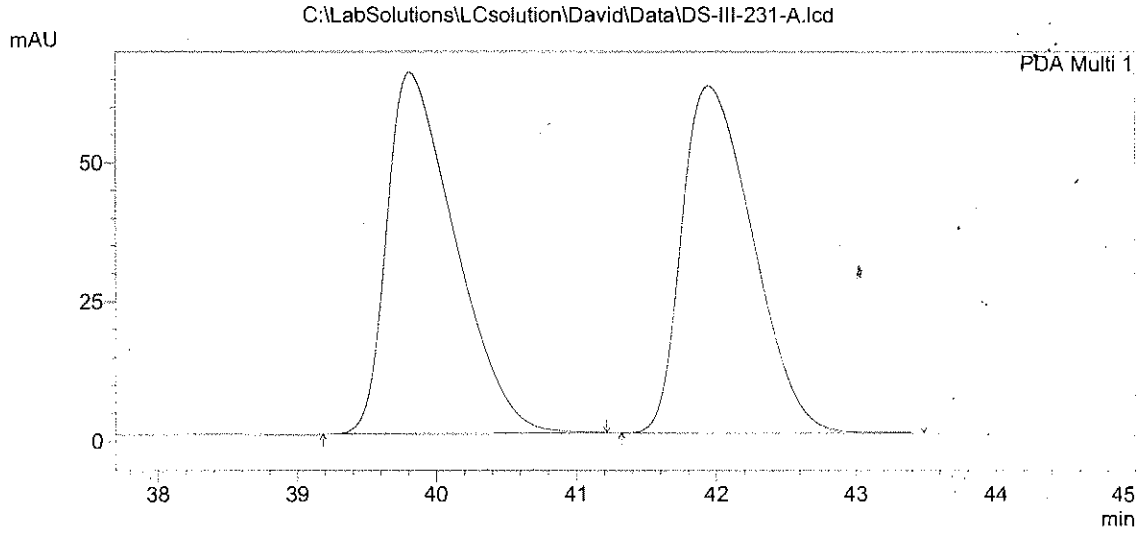
PDA Ch2

==== Shimadzu LCsolution Analysis Report ====

Acquired by	: Sandoval, D.
Sample Name	: [redacted]
Sample ID	: 2,6-dimethylphenyl 2-((((benzyloxy)carbonyl)amino)oxy)-2-methyl-3-oxobutanoate
Injection Volume	: 100 uL
Eluent Conc.	: 95.5/0.5 hexanes/i-PrOH, 30 min; 97/3 hexanes/i-PrOH, 30 min
Flow Rate	: 1 ml/min
Data Acquired	: 1/30/2013 2:34:02 AM
Data Processed	: 1/30/2013 4:49:10 AM



<Chromatogram>



1 PDA Multi 1/254nm 4nm

<Results>

PeakTable

PDA Ch1 254nm 4nm

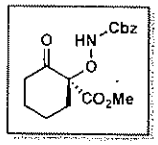
Peak#	Ret. Time	Area	Area %
1	39.810	2211665	50.108
2	41.947	2202129	49.892
Total		4413794	100.000

PeakTable

PDA Ch2

==== Shimadzu LCsolution Analysis Report ====

Acquired by	: Sandoval, D.
Sample Name	: [redacted]
Sample ID	: methyl 1-((((benzyloxy)carbonyl)amino)oxy)-2-oxocyclohexanecarboxylate
Injection Volume	: 100 uL
Eluent Conc.	: 95.5/0.5 hexanes/i-PrOH, 30 min; 97/3 hexanes/i-PrOH, 30 min
Flow Rate	: 1 ml/min
Data Acquired	: 1/29/2013 7:46:24 PM
Data Processed	: 1/29/2013 10:01:32 PM



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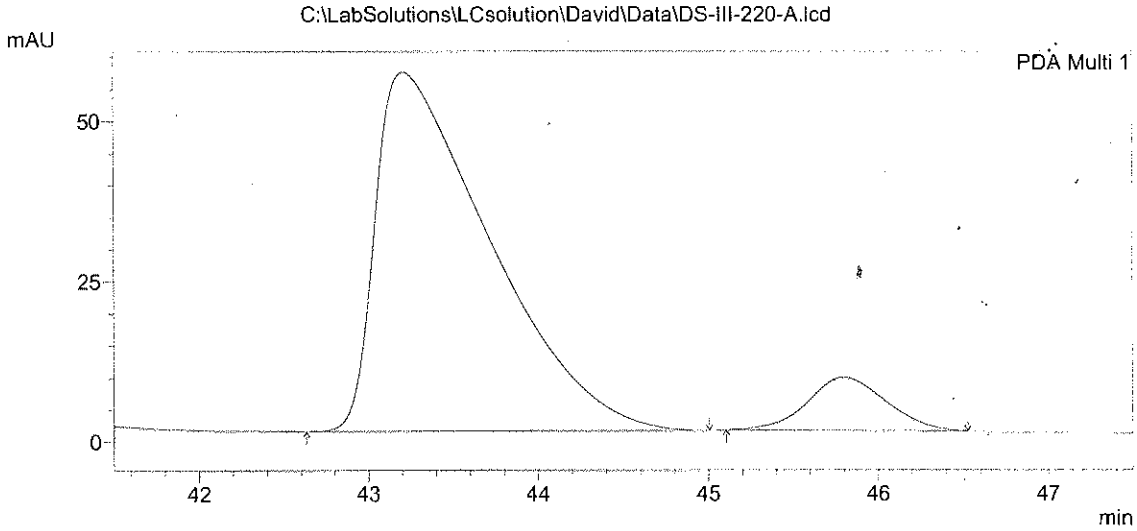


1 PDA Multi 1/254nm 4nm

<Results>

PeakTable

PDA Ch1 254nm 4nm

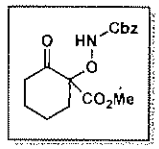
Peak#	Ret. Time	Area	Area %
1	43.208	2626592	90.763
2	45.795	267310	9.237
Total		2893902	100.000

PeakTable

PDA Ch2

==== Shimadzu LCsolution Analysis Report ====

Acquired by	: Sandoval, D.
Sample Name	: [redacted]
Sample ID	: methyl 1-((((benzyloxy)carbonyl)amino)oxy)-2-oxocyclohexanecarboxylate
Injection Volume	: 100 uL
Eluent Conc.	: 95.5/0.5 hexanes/i-PrOH, 30 min; 97/3 hexanes/i-PrOH, 30 min
Flow Rate	: 1 ml/min
Data Acquired	: 1/29/2013 10:02:16 PM
Data Processed	: 1/30/2013 12:17:25 AM



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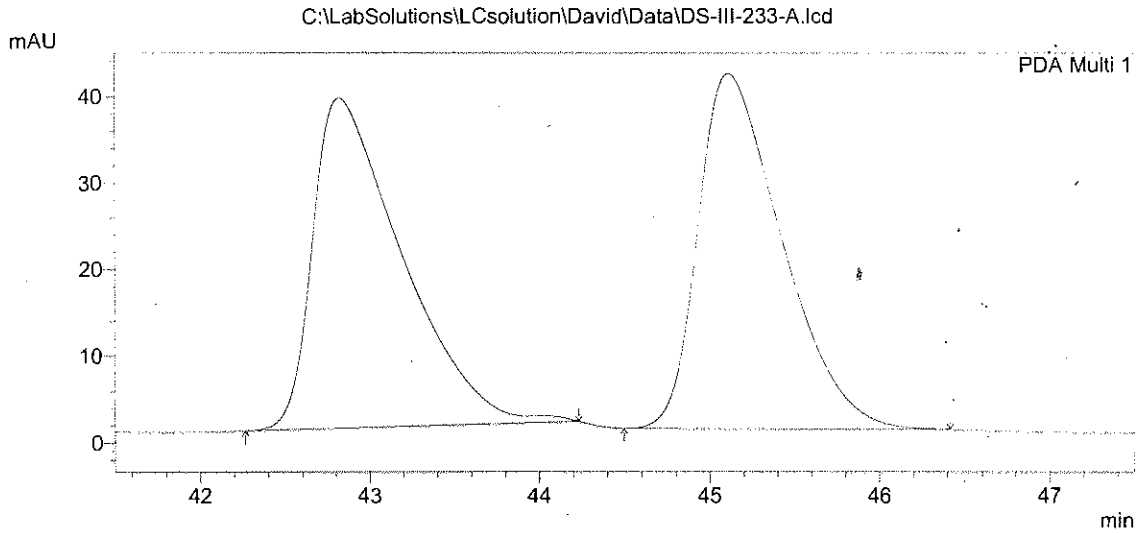


1 PDA Multi 1/254nm 4nm

<Results>

PeakTable

PDA Ch1 254nm 4nm

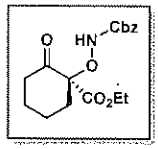
Peak#	Ret. Time	Area	Area %
1	42.819	1398526	49.855
2	45.112	1406647	50.145
Total		2805173	100.000

PeakTable

PDA Ch2

==== Shimadzu LCsolution Analysis Report ====

Acquired by	: Sandoval, D.
Sample Name	: [redacted]
Sample ID	: ethyl 1-((((benzyloxy)carbonyl)amino)oxy)-2-oxocyclohexanecarboxylate
Injection Volume	: 100 uL
Eluent Conc.	: 95.5/0.5 hexanes/i-PrOH, 30 min; 97/3 hexanes/i-PrOH, 30 min
Flow Rate	: 1 ml/min
Data Acquired	: 1/18/2013 6:17:54 PM
Data Processed	: 1/18/2013 8:33:03 PM



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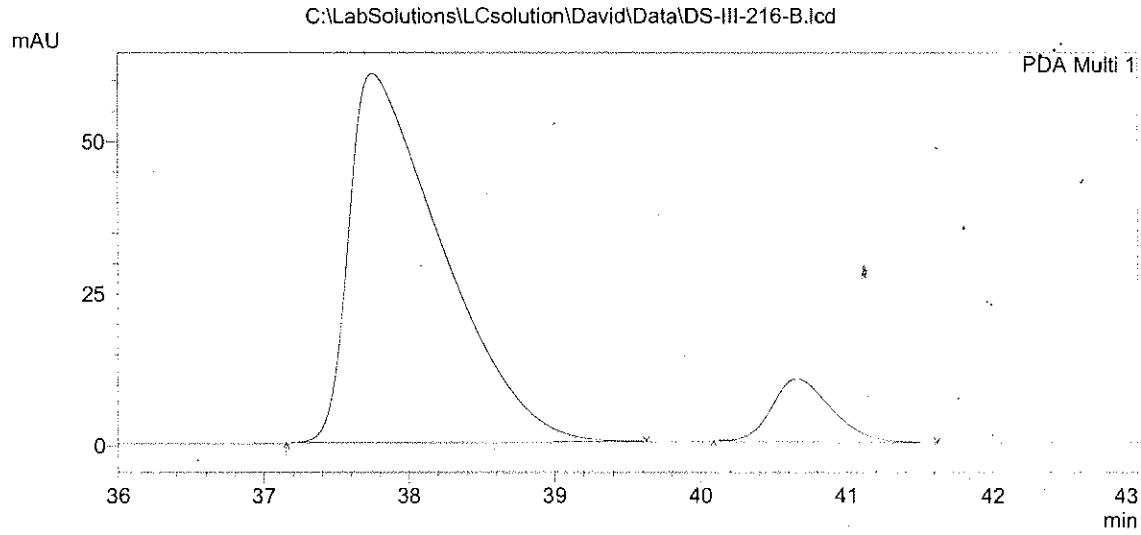


1 PDA Multi 1/254nm 4nm

<Results>

PeakTable

PDA Ch1 254nm 4nm

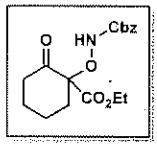
Peak#	Ret. Time	Area	Area %
1	37.748	2706184	90.237
2	40.660	292774	9.763
Total		2998958	100.000

PeakTable

PDA Ch2

==== Shimadzu LCsolution Analysis Report ====

Acquired by	: Sandoval, D.
Sample Name	: [redacted]
Sample ID	: ethyl 1-((((benzyloxy)carbonyl)amino)oxy)-2-oxocyclohexanecarboxylate
Injection Volume	: 100 uL
Eluent Conc.	: 95.5/0.5 hexanes/i-PrOH, 30 min; 97/3 hexanes/i-PrOH, 30 min
Flow Rate	: 1 ml/min
Data Acquired	: 1/18/2013 4:02:11 PM
Data Processed	: 1/18/2013 6:17:18 PM



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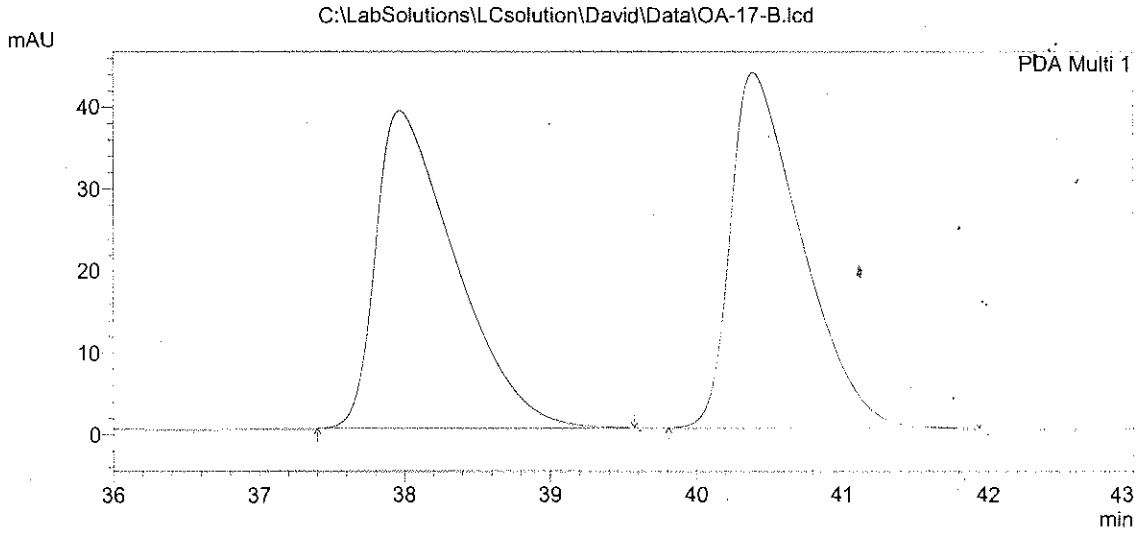


1 PDA Multi 1/254nm 4nm

<Results>

PeakTable

PDA Ch1 254nm 4nm

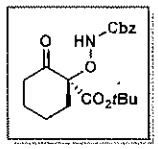
Peak#	Ret. Time	Area	Area %
1	37.968	1480410	50.069
2	40.391	1476326	49.931
Total		2956735	100.000

PeakTable

PDA Ch2

==== Shimadzu LCsolution Analysis Report ====

Acquired by	: Sandoval, D.
Sample Name	: [redacted]
Sample ID	: tert-butyl 1-((((benzyloxy)carbonyl)amino)oxy)-2-oxocyclohexanecarboxylate
Injection Volume	: 100 uL
Eluent Conc.	: 95.5/0.5 hexanes/i-PrOH, 30 min; 97/3 hexanes/i-PrOH, 30 min
Flow Rate	: 1 ml/min
Data Acquired	: 1/18/2013 4:43:27 AM
Data Processed	: 1/18/2013 6:58:35 AM



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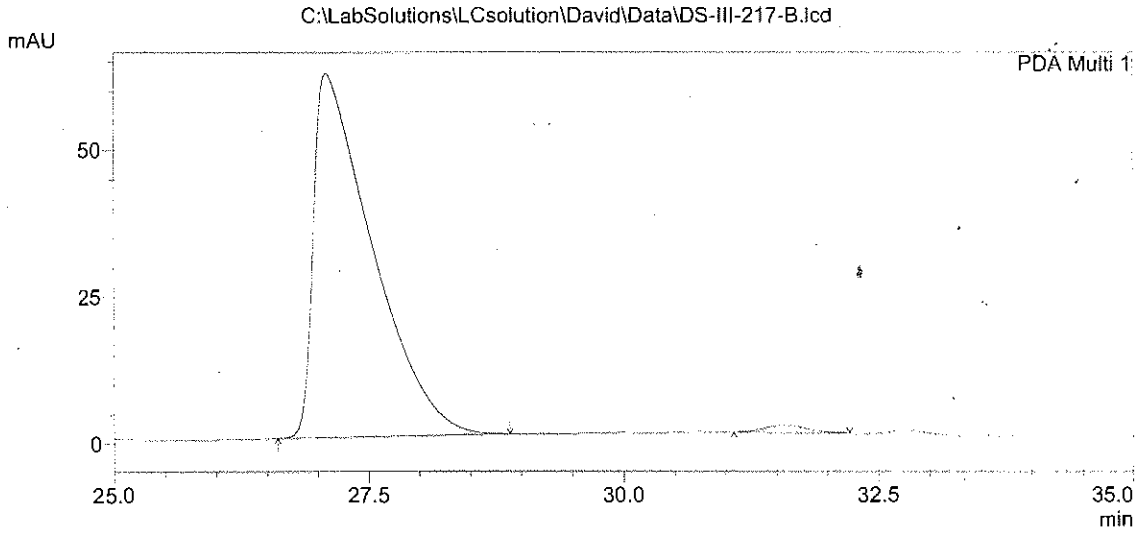


1 PDA Multi 1/254nm 4nm

<Results>

PeakTable

PDA Ch1 254nm 4nm

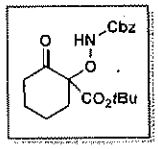
Peak#	Ret. Time	Area	Area %
1	27.083	2495793	98.560
2	31.577	36470	1.440
Total		2532263	100.000

PeakTable

PDA Ch2

==== Shimadzu LCsolution Analysis Report ====

Acquired by	: Sandoval, D.
Sample Name	: [redacted]
Sample ID	: tert-butyl 1-((((benzyloxy)carbonyl)amino)oxy)-2-oxocyclohexanecarboxylate
Injection Volume	: 100 uL
Eluent Conc.	: 95.5/0.5 hexanes/i-PrOH, 30 min; 97/3 hexanes/i-PrOH, 30 min
Flow Rate	: 1 ml/min
Data Acquired	: 1/18/2013 2:27:42 AM
Data Processed	: 1/18/2013 4:42:51 AM



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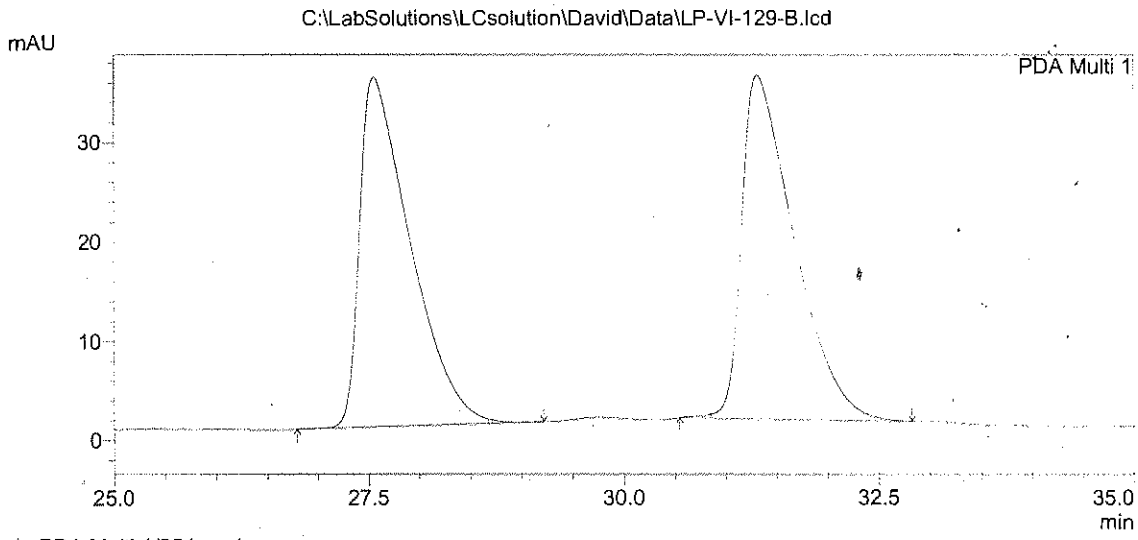


1 PDA Multi 1/254nm 4nm

<Results>

PeakTable

PDA Ch1 254nm 4nm

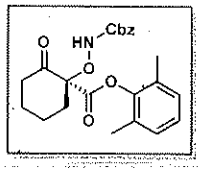
Peak#	Ret. Time	Area	Area %
1	27.549	1221915	49.517
2	31.308	1245751	50.483
Total		2467665	100.000

PeakTable

PDA Ch2

==== Shimadzu LCsolution Analysis Report ====

Acquired by	: Sandoval, D.
Sample Name	: [redacted]
Sample ID	: 2,6-dimethylphenyl 1-((((benzyloxy)carbonyl)amino)oxy)-2-oxocyclohexanecarboxylate
Injection Volume	: 100 uL
Eluent Conc.	: 95.5/0.5 hexanes/i-PrOH, 30 min; 97/3 hexanes/i-PrOH, 30 min
Flow Rate	: 1 ml/min
Data Acquired	: 1/17/2013 9:56:14 PM
Data Processed	: 1/18/2013 12:11:22 AM



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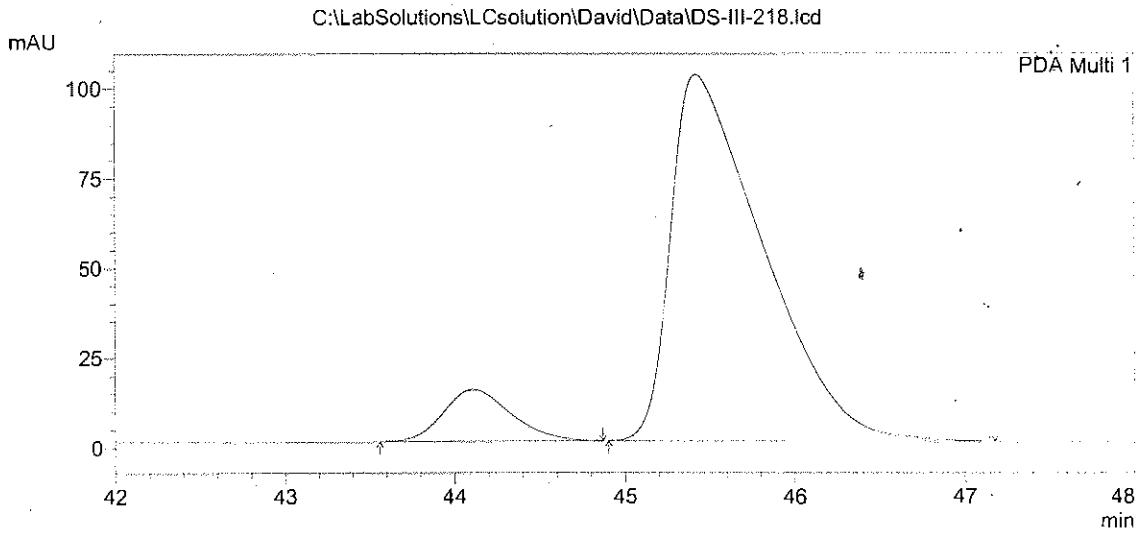


1 PDA Multi 1/254nm 4nm

<Results>

PeakTable

PDA Ch1 254nm 4nm

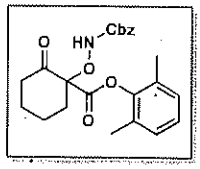
Peak#	Ret. Time	Area	Area %
1	44.108	399277	9.368
2	45.420	3863061	90.632
Total		4262339	100.000

PeakTable

PDA Ch2

==== Shimadzu LCsolution Analysis Report ====

Acquired by	: Sandoval, D.
Sample Name	: [redacted]
Sample ID	: 2,6-dimethylphenyl 1-((((benzyloxy)carbonyl)amino)oxy)-2-oxocyclohexanecarboxylate
Injection Volume	: 100 uL
Eluent Conc.	: 95.5/0.5 hexanes/i-PrOH, 30 min; 97/3 hexanes/i-PrOH, 30 min
Flow Rate	: 1 ml/min
Data Acquired	: 1/17/2013 7:40:30 PM
Data Processed	: 1/17/2013 9:55:34 PM



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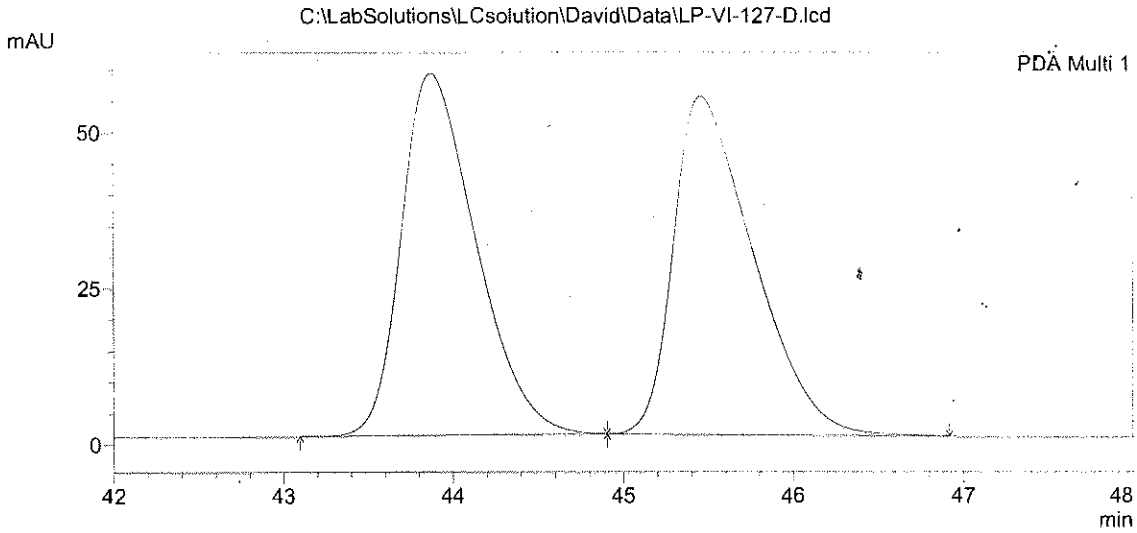

1 PDA Multi 1/254nm 4nm

<Results>

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	43.874	1768407	49.903
2	45.460	1775275	50.097
Total		3543682	100.000

PeakTable

PDA Ch2