Supplementary Information

One-pot Three-component Tandem Reaction of Diazo Compounds with Anilines and Unsaturated Ketoesters: a Novel Synthesis of 2,3-Dihydropyrrole Derivatives

Yingguang Zhu, Changwei Zhai, Yongli Yue, Liping Yang, Wenhao Hu*

Department of Chemistry, East China Normal University, Shanghai 200062, P. R. China

whu@chem.ecnu.edu.cn

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General Considerations:

All moisture sensitive reactions were performed under an argon atmosphere in a well-dried reaction flask. Dichloromethane (CH_2Cl_2), 1,2-dichloroethane ($ClCH_2CH_2Cl$) and chloroform ($CHCl_3$) were freshly distilled over calcium hydride, toluene from sodium benzophenone ketyl, respectively, prior to use. All commercially available reagents were directly used as received from vendors, unless otherwise stated. ^1H and ^{13}C NMR spectra were recorded on a Brucker-500 MHz spectrometer. Chemical shifts are reported in ppm relative to the internal standard tetramethylsilane (δ = 0 ppm) for ^1H NMR and deuteriochloroform (δ = 77.00 ppm) for ^{13}C NMR spectroscopy. HRMS spectra were recorded on a GCT Premier instrument.

Synthesis of Substrates:

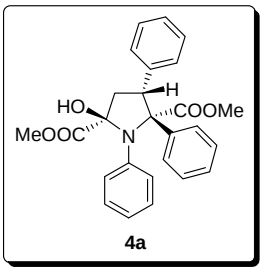
β,γ-unsaturated α-ketoesters **3a-3g** were prepared according to the literature procedure.[1] Substrate **3h** was synthesized following another literature procedure.[2] Various aryl diazo compounds **1a-1d** were prepared by the treatment of corresponding arylacetate with *p*-acetamidobenzenesulfonyl azide (*p*-ABSA) in the presence of DBU following the general procedure.[3]

General procedure for the one-pot three-component tandem reaction of diazo compounds with anilines and β,γ-unsaturated α-ketoesters:

To a stirred solution of $Rh_2(OAc)_4$ (4.4 mg, 0.01 mmol), anilines **2** (1.2 mmol) and β,γ-unsaturated α-ketoesters **3** (1 mmol) in toluene (8 ml) was added diazo compounds **1** (1.2 mmol) in 4 ml of toluene over 1 h via a syringe pump at 45 ^oC under Argon. After completion of the addition, the reaction mixture was cooled to room temperature. Citric acid monohydrate (42 mg, 0.2 mmol) was added and the reaction mixture was refluxed for 3-4 h under azeotropic distillation conditions. After the reaction was completed, the reaction mixture was cooled to room temperature. Solvent was removed, and a portion of crude product was subjected to ^1H NMR analysis for determination of the product ratio. The crude product was purified by flash chromatography on silica gel (ethyl acetate/petroleum ether = 1:80 ~ 1:40) to give the corresponding three-component products **5**.

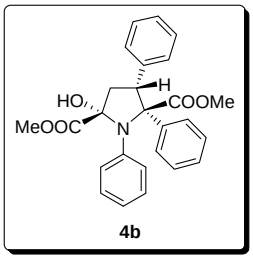
Characterization Data of Compounds:

Diastereomers *cis*-**5g**/*trans*-**5g**, *cis*-**5i**/*trans*-**5i**, *cis*-**5k**/*trans*-**5k**, *cis*-**5m**/*trans*-**5m** and *cis*-**5p**/*trans*-**5p** were unable to be separated in a pure isomer by flash chromatography on silica gel and characterized as a mixture of diastereomers.



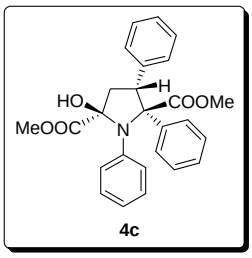
4a

(2S*,3R*,5R*)-dimethyl 5-hydroxy-1,2,3-triphenylpyrrolidine -2,5 -dicarboxylate (4a): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68-7.66 (m, 2H), 7.29-7.19 (m, 6H), 7.02-6.99 (m, 2H), 6.92 (d, *J* = 6.5 Hz, 2H), 6.68 (t, *J* = 7.5 Hz, 1H), 6.50 (d, *J* = 8.0 Hz, 2H), 4.38 (s, 1H), 4.03 (dd, *J* = 14.5, 6.0 Hz, 1H), 3.80 (s, 3H), 3.64 (s, 3H), 3.33 (dd, *J* = 14.5, 12.0 Hz, 1H), 2.25 (dd, *J* = 12.0, 6.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.66, 171.75, 142.60, 139.72, 134.64, 128.83, 128.57, 128.56, 128.16, 128.09, 127.78, 126.97, 118.98, 115.52, 91.34, 77.92, 57.55, 53.97, 51.82, 44.11; HRMS (EI) *m/z* calcd for $C_{26}H_{25}NO_5$ (M^+) 431.1733, found 431.1732.



4b

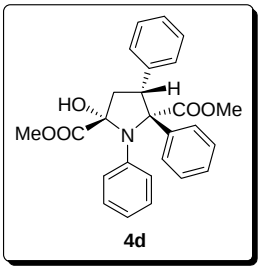
(2R*,3R*,5S*)-dimethyl 5-hydroxy-1,2,3-triphenylpyrrolidine -2,5-dicarboxylate (4b): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.21 (m, 1H), 7.16-7.12 (m, 5H), 7.08-7.04 (m, 4H), 6.75 (t, *J* = 7.5 Hz, 1H), 6.66 (d, *J* = 7.5 Hz, 2H), 6.49 (d, *J* = 8.0 Hz, 2H), 4.65 (s, 1H), 4.63 (dd, *J* = 15.5, 7.0 Hz, 1H), 3.98 (s, 3H), 3.67 (s, 3H), 2.63 (t, *J* = 13.5 Hz, 1H), 2.38 (dd, *J* = 13.5, 6.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.51, 173.09, 141.95, 135.22, 133.89, 130.12, 129.09, 128.74, 127.87, 127.69, 127.19, 126.62, 119.05, 115.94, 88.78, 78.33, 53.96, 52.64, 52.23, 41.46; HRMS (EI) *m/z* calcd for $C_{26}H_{25}NO_5$ (M^+) 431.1733, found 431.1736.



4c

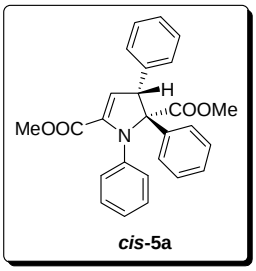
(2R*,3R*,5R*)-dimethyl 5-hydroxy-1,2,3-triphenylpyrrolidine -2,5-dicarboxylate (4c): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.18-7.04 (m, 10H), 6.76 (t, *J* = 7.5 Hz, 1H), 6.67 (d, *J* = 8.0 Hz, 2H), 6.62 (d, *J* = 8.0 Hz, 2H), 4.75 (dd, *J* = 14.5, 5.5 Hz, 1H), 4.08 (s, 1H), 3.91 (s, 3H), 3.63 (s, 3H), 2.70 (dd, *J* = 14.5, 12.0 Hz, 1H), 2.23 (dd, *J* = 12.0, 5.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.03, 173.47, 142.75, 135.39, 134.59,

129.78, 129.12, 128.82, 127.97, 127.73, 127.23, 126.74, 119.75, 115.89, 90.64, 79.23, 53.82, 53.53, 53.01, 43.19; HRMS (EI) *m/z* calcd for $C_{26}H_{25}NO_5$ (M^+) 431.1733, found 431.1733.



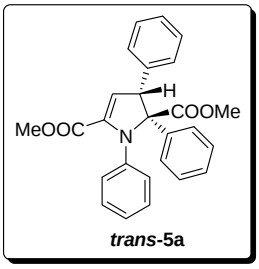
4d

(2S*,3R*,5S*)-dimethyl 5-hydroxy-1,2,3-triphenylpyrrolidine -2,5-dicarboxylate (4d): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60-7.58 (m, 2H), 7.31-7.23 (m, 6H), 7.05 (t, *J* = 8.5 Hz, 2H), 6.90 (d, *J* = 7.5 Hz, 2H), 6.74-6.72 (m, 1H), 6.46 (d, *J* = 8.5 Hz, 2H), 4.08 (s, 1H), 3.98 (s, 3H), 3.79 (dd, *J* = 13.5, 8.0 Hz, 1H), 3.64 (s, 3H), 3.02 (t, *J* = 13.5 Hz, 1H), 2.77 (dd, *J* = 13.5, 8.0 Hz, 1H).



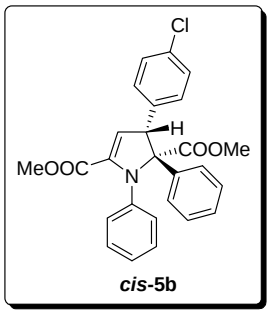
***cis*-5a**

(2S*,3R*)-dimethyl 2,3-dihydro-1,2,3-triphenyl-1H-pyrrole-2,5 -dicarboxylate (*cis*-5a): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (d, *J* = 7.5 Hz, 2H), 7.42-7.39 (m, 2H), 7.35-7.31 (m, 5H), 7.28-7.26 (m, 1H), 7.09-7.05 (m, 2H), 6.90-6.92 (m, 1H), 6.73 (d, *J* = 7.5 Hz, 2H), 5.89 (d, *J* = 3.5 Hz, 1H), 4.50 (d, *J* = 3.5 Hz, 1H), 3.77 (s, 3H), 2.79 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.35, 162.43, 143.69, 142.42, 140.43, 138.60, 129.43, 128.24, 128.13, 128.03, 127.78, 127.70, 127.52, 122.80, 121.05, 115.32, 83.70, 63.26, 52.09, 50.98; HRMS (EI) *m/z* calcd for $C_{26}H_{23}NO_4$ (M^+) 413.1627, found 413.1622.



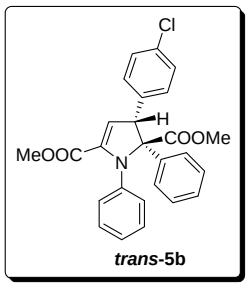
***trans*-5a**

(2R*,3R*)-dimethyl 2,3-dihydro-1,2,3-triphenyl-1H-pyrrole-2,5 -dicarboxylate (*trans*-5a): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.11-7.08 (m, 2H), 7.02-6.92 (m, 9H), 6.84 (d, *J* = 7.5 Hz, 2H), 6.76 (d, *J* = 7.5 Hz, 2H), 5.96 (d, *J* = 2.5 Hz, 1H), 5.52 (d, *J* = 2.5 Hz, 1H), 3.75 (s, 3H), 3.46 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.41, 162.15, 143.03, 140.13, 137.77, 135.74, 129.56, 128.92, 128.11, 127.68, 126.96, 126.86, 126.80, 123.39, 122.39, 118.81, 84.59, 59.37, 52.54, 52.06; HRMS (EI) *m/z* calcd for $C_{26}H_{23}NO_4$ (M^+) 413.1627, found 413.1622.



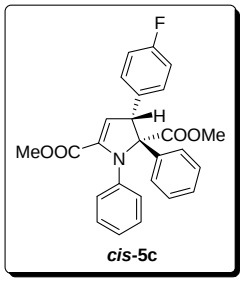
***cis*-5b**

(2S*,3R*)-dimethyl 3-(4-chlorophenyl)-2,3-dihydro-1,2-diphenyl-1H-pyrrole-2,5-dicarboxylate (*cis*-5b): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 (d, *J* = 7.5 Hz, 2H), 7.40-7.37 (m, 2H), 7.34-7.26 (m, 5H), 7.08-7.05 (m, 2H), 6.93-6.91 (m, 1H), 6.72 (d, *J* = 7.5 Hz, 2H), 5.84 (d, *J* = 3.5 Hz, 1H), 4.47 (d, *J* = 3.5 Hz, 1H), 3.76 (s, 3H), 2.87 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.23, 162.31, 143.45, 142.12, 140.83, 137.13, 133.60, 130.75, 128.29, 128.18, 127.91, 127.41, 123.10, 121.30, 114.57, 83.58, 62.36, 52.14, 51.13; HRMS (EI) *m/z* calcd for $C_{26}H_{22}ClNO_4$ (M^+) 447.1237, found 447.1239.



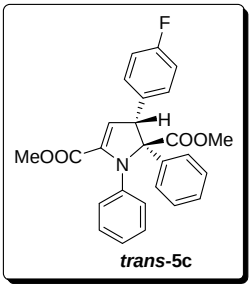
***trans*-5b**

(2R*,3R*)-dimethyl 3-(4-chlorophenyl)-2,3-dihydro-1,2-diphenyl-1H-pyrrole-2,5-dicarboxylate (*trans*-5b): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.11-7.08 (m, 2H), 7.03-6.90 (m, 8H), 6.84 (d, *J* = 7.8 Hz, 2H), 6.69 (d, *J* = 7.8 Hz, 2H), 5.90 (d, *J* = 2.5 Hz, 1H), 5.47 (d, *J* = 2.5 Hz, 1H), 3.74 (s, 3H), 3.46 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.29, 162.02, 142.83, 140.50, 136.45, 135.50, 132.81, 130.76, 128.82, 128.14, 128.06, 127.79, 127.15, 127.03, 123.63, 122.64, 117.90, 84.40, 58.52, 52.60，52.10; HRMS (EI) *m/z* calcd for $C_{26}H_{22}ClNO_4$ (M^+) 447.1237, found 447.1239.



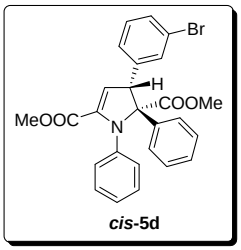
***cis*-5c**

(2S*,3R*)-dimethyl 3-(4-fluorophenyl)-2,3-dihydro-1,2-diphenyl-1H-pyrrole-2,5-dicarboxylate (*cis*-5c): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 (d, *J* = 7.5 Hz, 2H), 7.40-7.37 (m, 2H), 7.32-7.28 (m, 3H), 7.08-6.99 (m, 4H), 6.91-6.88 (m, 1H), 6.72 (d, *J* = 7.5 Hz, 2H), 5.84 (d, *J* = 3.0 Hz, 1H), 4.47 (d, *J* = 3.0 Hz, 1H), 3.75 (s, 3H), 2.85 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.30, 163.28, 162.36, 161.32, 143.54, 142.22, 140.61, 134.36, 134.34, 131.11, 131.04, 128.29, 128.18, 127.87, 127.45, 123.00, 121.19, 114.99, 114.89, 114.82, 83.57, 62.36, 52.12, 51.10; HRMS (EI) *m/z* calcd for $C_{26}H_{22}FNO_4$ (M^+) 431.1533, found 431.1534.



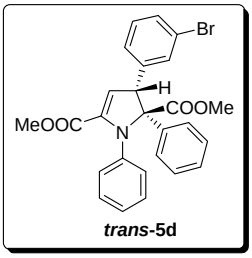
***trans*-5c**

(2R*,3R*)-dimethyl 3-(4-fluorophenyl)-2,3-dihydro-1,2-diphenyl-1H-pyrrole-2,5-dicarboxylate (*trans*-5c): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.11-7.09 (m, 2H), 7.02-6.92 (m, 6H), 6.86-6.84 (m, 2H), 6.73-6.66 (m, 4H), 5.93 (d, *J* = 3.0 Hz, 1H), 5.50 (d, *J* = 3.0 Hz, 1H), 3.74 (s, 3H), 3.46 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.34, 162.78, 162.06, 160.83, 142.87, 140.27, 135.61, 133.59, 133.57, 130.98, 130.91, 128.83, 128.12, 127.02, 126.96, 123.52, 122.52, 118.25, 114.59, 114.42，84.41, 58.43, 52.56, 52.06; HRMS (EI) *m/z* calcd for $C_{26}H_{22}FNO_4$ (M^+) 431.1533, found 431.1534.



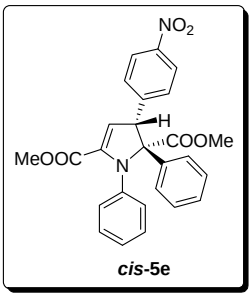
***cis*-5d**

(2S*,3R*)-dimethyl 3-(3-bromophenyl)-2,3-dihydro-1,2-diphenyl-1H-pyrrole-2,5-dicarboxylate (*cis*-5d): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (d, *J* = 7.5 Hz, 2H), 7.46 (s, 1H), 7.41-7.38 (m, 3H), 7.34-6.33 (m, 1H), 7.28-7.26 (m, 1H), 7.21-7.18 (m, 1H), 7.08-7.05 (m, 2H), 6.92-6.89 (m, 1H), 6.73 (d, *J* = 7.5 Hz, 2H), 5.82 (d, *J* = 3.0 Hz, 1H), 4.44 (d, *J* = 3.0 Hz, 1H), 3.76 (s, 3H), 2.87 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.06, 162.29, 143.45, 142.21, 141.00, 132.57, 130.83, 129.62, 128.37, 128.22, 128.02, 127.95, 127.44, 123.11, 122.09, 121.24, 114.19, 83.62, 62.74, 52.18, 51.15; HRMS (EI) *m/z* calcd for $C_{26}H_{22}BrNO_4$ (M^+) 491.0732, found 491.0733.

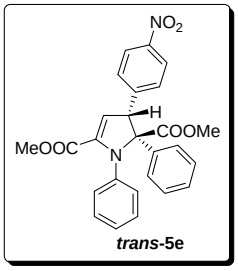


***trans*-5d**

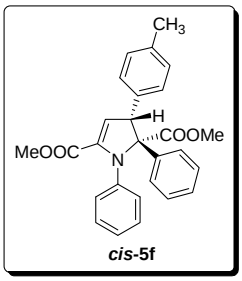
(2R*,3R*)-dimethyl 3-(3-bromophenyl)-2,3-dihydro-1,2-diphenyl-1H-pyrrole-2,5-dicarboxylate (*trans*-5d): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.15-7.10 (m, 3H), 7.03-6.95 (m, 6H), 6.88-6.84 (m, 4H), 6.73-6.71 (m, 1H), 5.91 (d, *J* = 2.5 Hz, 1H), 5.49 (d, *J* = 2.5 Hz, 1H), 3.76 (s, 3H), 3.46 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.05, 161.94, 142.79, 140.64, 140.31, 135.51, 132.47, 129.97, 129.08, 128.71, 128.14, 128.08, 127.20, 126.99, 123.73, 122.71, 121.79, 117.53, 84.43, 58.80，52.59, 52.11; HRMS (EI) *m/z* calcd for $C_{26}H_{22}BrNO_4$ (M^+) 491.0732, found 491.0733.



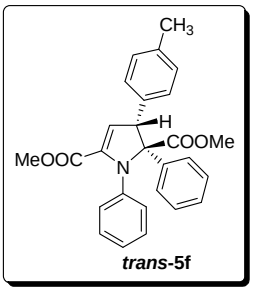
(2S*,3R*)-dimethyl 2,3-dihydro-3-(4-nitrophenyl)-1,2-diphenyl -1H-pyrrole-2,5-dicarboxylate (*cis*-5e): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.18-8.16 (m, 2H), 7.61 (d, *J* = 7.5 Hz, 2H), 7.51-7.49 (m, 2H), 7.39-7.32 (m, 3H), 7.07-7.04 (m, 2H), 6.94-6.92 (m, 1H), 6.73 (d, *J* = 7.5 Hz, 2H), 5.83 (d, *J* = 3.0 Hz, 1H), 4.59 (d, *J* = 3.0 Hz, 1H), 3.74 (s, 3H), 2.84 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.04, 162.10, 147.38, 146.32, 143.03, 141.75, 141.61, 130.28, 128.43, 128.27, 128.20, 127.35, 123.68, 123.21, 121.93, 113.33, 83.78, 62.13, 52.25, 51.25; HRMS (EI) *m/z* calcd for $C_{26}H_{22}N_2O_6$ (M^+) 458.1478, found 458.1480.



(2R*,3R*)-dimethyl 2,3-dihydro-3-(4-nitrophenyl)-1,2-diphenyl -1H-pyrrole-2,5-dicarboxylate (*trans*-5e): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 (d, *J* = 9.0 Hz, 2H), 7.93-7.91 (m, 2H), 7.30-7.26 (m, 3H), 7.13-7.08 (m, 4H), 6.77-6.74 (m, 1H), 6.43 (d, *J* = 9.0 Hz, 2H), 6.17 (d, *J* = 2.0 Hz, 1H), 5.45 (d, *J* = 2.0 Hz, 1H), 3.89 (s, 3H), 3.60 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.18, 171.11, 147.70, 145.68, 143.57, 139.41, 137.02, 129.30, 129.05, 128.53, 128.16, 127.95, 125.82, 123.25, 118.73, 113.67, 81.61, 69.08, 52.87, 52.81; HRMS (EI) *m/z* calcd for $C_{26}H_{22}N_2O_6$ (M^+) 458.1478, found 458.1480.

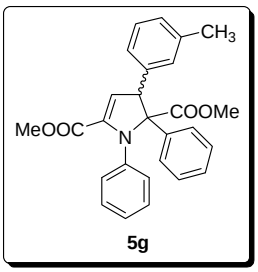


(2S*,3R*)-dimethyl 2,3-dihydro-1,2-diphenyl-3-p-tolyl-1H-py rrole-2,5-dicarboxylate (*cis*-5f): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (d, *J* = 7.5 Hz, 2H), 7.41-7.38 (m, 2H), 7.34-7.32 (m, 1H), 7.23-7.21 (m, 2H), 7.14-7.12 (m, 2H), 7.08-7.05 (m, 2H), 6.91-6.89 (m, 1H), 6.73 (d, *J* = 7.5 Hz, 2H), 5.88 (d, *J* = 3.0 Hz, 1H), 4.47 (1H, d, *J* = 3.0 Hz), 3.76 (s, 3H), 2.82 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.43, 162.52, 143.82, 142.57, 140.27, 137.42, 135.46, 129.37, 128.72, 128.24, 128.14, 127.74, 127.54, 122.76, 121.05, 115.68, 83.64, 63.05, 52.08, 51.00, 21.08; HRMS (EI) *m/z* calcd for $C_{27}H_{25}NO_4$ (M^+) 427.1784, found 427.1785.



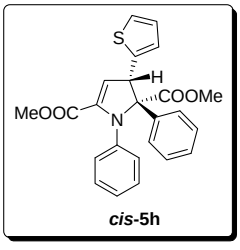
trans-5f

(2R*,3R*)-dimethyl 2,3-dihydro-1,2-diphenyl-3-p-tolyl-1H-pyrrole-2,5-dicarboxylate (*trans*-5f): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.11-7.08 (m, 2H), 7.01-6.93 (m, 6H), 6.83-6.79 (m, 4H), 6.65-6.63 (m, 2H), 5.94 (d, *J* = 2.5 Hz, 1H), 5.47 (d, *J* = 2.5 Hz, 1H), 3.75 (s, 3H), 3.47 (s, 3H), 2.18 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.51, 162.20, 143.08, 139.88, 136.65, 135.73, 134.57, 129.41, 128.99, 128.37, 128.10, 126.84, 126.77, 123.26, 122.24, 119.24, 84.59, 59.11, 52.52, 52.05, 20.96; HRMS (EI) *m/z* calcd for $C_{27}H_{25}NO_4$ (M^+) 427.1784, found 427.1785.



5g

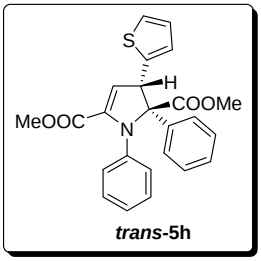
(2S*,3R*) and (2R*,3R*)-dimethyl 2,3-dihydro-1,2-diphenyl-3-m-tolyl-1H-pyrrole-2,5-dicarboxylate (*cis*-5g+*trans*-5g) (mixture of diastereomers): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (d, *J* = 7.5 Hz, 2H), 7.39-7.38 (m, 2H), 7.37-7.35 (m, 1H), 7.20-7.18 (m, 1H), 7.13-7.04 (m, 6H), 6.99-6.94 (m, 6H), 6.89-6.83 (m, 6H), 6.73 (d, *J* = 8.5 Hz, 2H), 6.59 (d, *J* = 7.5 Hz, 1H), 6.50 (s, 1H), 5.94 (d, *J* = 2.5 Hz, 1H, *trans*-**5g**), 5.87 (d, *J* = 3.0 Hz, 1H, *cis*-**5g**), 5.49 (d, *J* = 2.5 Hz, 1H, *trans*-**5g**), 4.45 (d, *J* = 3.0 Hz, 1H, *cis*-**5g**), 3.76 (s, 3H, *trans*-**5g**), 3.76 (s, 3H, *cis*-**5g**), 3.44 (s, 3H, *trans*-**5g**), 2.80 (s, 3H, *cis*-**5g**), 2.34 (s, 3H, *cis*-**5g**), 2.08 (s, 3H, *trans*-**5g**); ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.34, 169.36, 162.52, 162.19, 143.11, 139.97, 137.58, 137.26, 130.35, 130.11, 128.91, 128.25, 128.14, 128.12, 127.75, 127.65, 127.55, 127.52, 126.86, 126.69, 126.60, 123.35, 122.75, 122.30, 121.01, 119.12, 115.58, 84.65, 83.68, 63.35, 59.45, 52.49, 52.09, 52.05, 50.96, 21.33, 21.00; HRMS (EI) *m/z* calcd for $C_{27}H_{25}NO_4$ (M^+) 427.1784, found 427.1789.



cis-5h

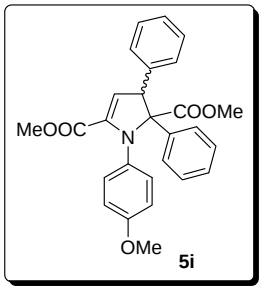
(2S*,3S*)-dimethyl 2,3-dihydro-1,2-diphenyl-3-(thiophen-2-yl)-1H-pyrrole-2,5-dicarboxylate (*cis*-5h): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (d, *J* = 7.5 Hz, 2H), 7.43-7.40 (m, 2H), 7.36-7.34 (m, 1H), 7.26-7.24 (m, 1H), 7.10-7.07 (m, 2H), 7.00-6.97 (m, 2H), 6.92-6.89 (m, 1H), 6.73 (d, *J* = 7.5 Hz, 2H), 5.89 (d, *J* = 3.0 Hz, 1H), 4.47 (d, *J* = 3.0 Hz, 1H), 3.77 (s, 3H), 2.93 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.88, 162.30, 143.72, 142.25, 142.11, 140.21, 128.30, 128.21, 127.87, 127.55, 126.74,

126.59, 125.53, 122.78, 120.61, 114.39, 83.74, 58.32, 52.15, 51.30; HRMS (EI) *m/z* calcd for $C_{24}H_{21}NO_4S$ (M^+) 419.1191, found 419.1192.



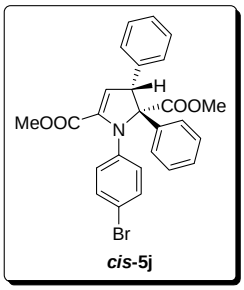
***trans*-5h**

(2R*,3S*)-dimethyl 2,3-dihydro-1,2-diphenyl-3-(thiophen-2-yl) -1H-pyrrole-2,5-dicarboxylate (*trans*-5h): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.12-7.08 (m, 3H), 7.07-6.95 (m, 6H), 6.86-6.84 (m, 2H), 6.71-6.70 (m, 1H), 6.51-6.50 (m, 1H), 6.00 (d, *J* = 3.0 Hz, 1H), 5.66 (d, *J* = 3.0 Hz, 1H), 3.76 (s, 3H), 3.56 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.45, 162.05, 142.66, 141.28, 140.17, 135.00, 128.55, 128.09, 127.21, 127.13, 126.98, 126.36, 125.41, 123.48, 122.68, 117.67, 84.31, 53.86, 52.71, 52.12; HRMS (EI) *m/z* calcd for $C_{24}H_{21}NO_4S$ (M^+) 419.1191, found 419.1192.



5i

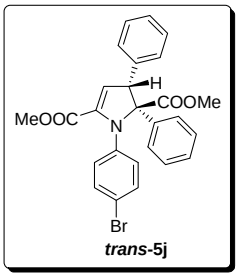
(2S*,3R*) and (2R*,3R*)-dimethyl 2,3-dihydro-1-(4-methoxy phenyl)-2,3-diphenyl-1H-pyrrole-2,5-dicarboxylate (*cis*-5i+*trans* -5i) (mixture of diastereomers): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 (d, *J* = 7.5 Hz, 2H), 7.34-7.28 (m, 8H), 7.02-6.97 (m, 8H), 6.92 (d, *J* = 8.5 Hz, 2H), 6.80 (d, *J* = 7.0 Hz, 2H), 6.75 (d, *J* = 8.5 Hz, 2H), 6.70 (d, *J* = 8.5 Hz, 2H), 6.59 (d, *J* = 8.5 Hz, 2H), 5.94 (d, *J* = 2.5 Hz, 1H, *trans*-**5i**), 5.90 (d, *J* = 2.5 Hz, 1H, *cis*-**5i**), 5.62 (d, *J* = 2.5 Hz, 1H, *trans*-**5i**), 4.66 (d, *J* = 2.5 Hz, 1H, *cis*-**5i**), 3.75 (s, 3H, *trans*-**5i**), 3.72 (s, 3H, *trans*-**5i**), 3.70 (s, 3H, *cis*-**5i**), 3.69 (s, 3H, *cis*-**5i**), 3.42 (s, 3H, *trans*-**5i**), 2.92 (s, 3H, *cis*-**5i**); ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.23, 162.14, 156.47, 140.59, 138.10, 136.58, 136.47, 129.57, 129.39, 128.79, 128.12, 128.06, 127.62, 126.83, 126.78, 125.15, 125.08, 118.38, 113.45, 113.26, 84.47, 58.94, 55.27, 52.45, 51.99; HRMS (EI) *m/z* calcd for $C_{27}H_{25}NO_5$ (M^+) 443.1733, found 443.1732.



***cis*-5j**

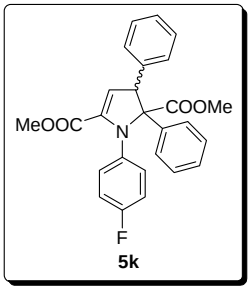
(2S*,3R*)-dimethyl 1-(4-bromophenyl)-2,3-dihydro-2,3-diphenyl -1H-pyrrole-2,5-dicarboxylate (*cis*-5j): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 (d, *J* = 7.5 Hz, 2H), 7.40-7.37 (m, 2H), 7.34-7.30 (m, 5H), 7.27-7.24 (m, 1H), 7.17-7.15 (m, 2H), 6.61 (d, *J* = 7.5 Hz, 2H), 5.93 (d, *J* = 3.0 Hz, 1H), 4.50 (d, *J* = 3.0 Hz, 1H), 3.76 (s, 3H), 2.83

(s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.24, 162.07, 142.76, 141.83, 139.99, 138.30, 131.09, 129.38, 128.39, 128.12, 128.03, 127.85, 127.41, 123.07, 116.37, 115.81, 83.69, 63.12, 52.20, 51.20; HRMS (EI) *m/z* calcd for $C_{26}H_{22}BrNO_4$ (M^+) 491.0732, found 491.0734.



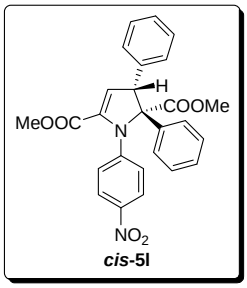
***trans*-5j**

(2R*,3R*)-dimethyl 1-(4-bromophenyl)-2,3-dihydro-2,3-diphenyl -1H-pyrrole-2,5-dicarboxylate (*trans*-5j): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.19 (d, *J* = 8.5 Hz, 2H), 7.05-6.93 (m, 6H), 6.85 (d, *J* = 7.5 Hz, 2H), 6.75 (d, *J* = 7.5 Hz, 2H), 6.69 (d, *J* = 8.5 Hz, 2H), 6.02 (d, *J* = 3.0 Hz, 1H), 5.45 (d, *J* = 3.0 Hz, 1H), 3.78 (s, 3H), 3.57 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.42, 161.83, 141.97, 139.57, 137.41, 135.00, 131.07, 129.52, 128.85, 127.77, 127.12, 127.09, 126.96, 123.76, 119.53, 116.01, 84.56, 59.24, 52.78, 52.20; HRMS (EI) *m/z* calcd for $C_{26}H_{22}BrNO_4$ (M^+) 491.0732, found 491.0734.



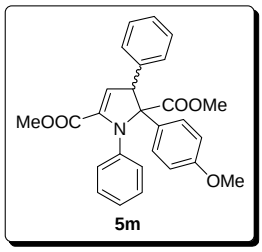
5k

(2S*,3R*) and (2R*,3R*)-dimethyl 1-(4-fluorophenyl)-2,3-dihy dro-2,3-diphenyl-1H-pyrrole-2,5-dicarboxylate (*cis*-5k+*trans*-5k) (mixture of diastereomers): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 (d, *J* = 7.5 Hz, 2H), 7.32-7.28 (m, 8H), 7.01-6.94 (m, 6H), 6.92-6.86 (m, 4H), 6.82-6.72 (m, 8H), 5.98 (d, *J* = 2.5 Hz, 1H, *trans*-**5k**), 5.93 (d, *J* = 3.0 Hz, 1H, *cis*-**5k**), 5.55(d, *J* = 2.5 Hz, 1H, *trans*-**5k**), 4.63 (d, *J* = 3.0 Hz, 1H, *cis*-**5k**), 3.75 (s, 3H, *trans*-**5k**), 3.70 (s, 3H, *cis*-**5k**), 3.47 (s, 3H, *trans*-**5k**), 2.89 (s, 3H, *cis*-**5k**); ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.25, 169.82, 162.16, 161.90, 160.38, 158.45, 141.63, 140.07, 137.72, 135.86, 129.53, 129.34, 128.79, 128.23, 128.12, 127.77, 127.70, 127.47, 126.97, 126.95, 126.90, 124.88, 124.81, 124.78, 124.72, 119.08, 114.94, 114.80, 114.76, 84.55, 84.01, 61.95, 58.99, 52.55, 52.06, 51.11; HRMS (EI) *m/z* calcd for $C_{26}H_{22}FNO_4$ (M^+) 431.1533, found 431.1532.



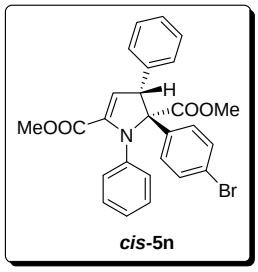
cis-5l

(2S*,3R*)-dimethyl 2,3-dihydro-1-(4-nitrophenyl)-2,3-diphenyl -1H-pyrrole-2,5-dicarboxylate (*cis*-5l): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (d, *J* = 9.0 Hz, 2H), 7.80-7.78 (m, 2H), 7.47-7.44 (m, 2H), 7.40-7.24 (m, 6H), 6.66 (d, *J* = 9.0 Hz, 2H), 6.08 (d, *J* = 3.0 Hz, 1H), 4.42 (d, *J* = 3.0 Hz, 1H), 3.86 (s, 3H), 2.76 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.19, 161.44, 149.10, 141.49, 140.86, 138.41, 137.13, 129.39, 128.73, 128.33, 128.25, 127.17, 124.42, 119.49, 118.20, 83.47, 64.52, 52.57, 51.57; HRMS (EI) *m/z* calcd for $C_{26}H_{22}N_2O_6$ (M^+) 458.1478, found 458.1481.



5m

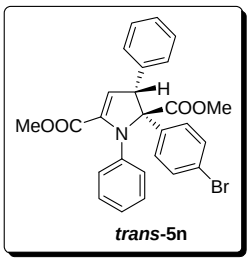
(2S*,3R*) and (2R*,3R*)-dimethyl 2,3-dihydro-1-(4-methoxy phenyl)-2,3-diphenyl-1H-pyrrole-2,5-dicarboxylate (*cis*-5m+ *trans*-5m) (mixture of diastereomers): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (d, *J* = 7.5 Hz, 2H), 7.31-7.29 (m, 4H), 7.11-7.08 (m, 2H), 7.06-6.99 (m, 5H), 6.94-6.90 (m, 5H), 6.82-6.80 (m, 4H), 6.77 (d, *J* = 8.5 Hz, 2H), 6.72 (d, *J* = 7.5 Hz, 2H), 6.49 (d, *J* = 8.5 Hz, 2H), 5.95 (d, *J* = 2.5 Hz, 1H, *trans*-**5m**), 5.87 (d, *J* = 2.5 Hz, 1H, *cis*-**5m**), 5.46 (d, *J* = 2.5 Hz, 1H, *trans*-**5m**), 4.45 (d, *J* = 2.5 Hz, 1H, *cis*-**5m**), 3.81 (s, 3H, *cis*-**5m**), 3.75 (s, 3H, *trans*-**5m**), 3.74 (s, 3H, *cis*-**5m**), 3.66 (s, 3H, *trans*-**5m**), 3.48 (s, 3H, *trans*-**5m**), 2.77 (s, 3H, *cis*-**5m**); ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.23, 162.14, 156.47, 140.59, 138.10, 136.58, 136.47, 129.57, 129.39, 128.79, 128.12, 128.06, 127.62, 126.83, 126.78, 125.15, 125.08, 118.38, 113.45, 113.26, 84.47, 58.94, 55.27, 52.45, 51.99; HRMS (EI) *m/z* calcd for $C_{27}H_{25}NO_5$ (M^+) 443.1733, found 443.1732.



cis-5n

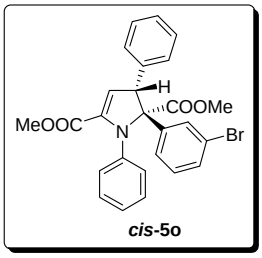
(2S*,3R*)-dimethyl 2-(4-bromophenyl)-2,3-dihydro-1,3-diphe nyl-1H-pyrrole-2,5-dicarboxylate (*cis*-5n): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.5 Hz, 2H), 7.53 (d, *J* = 8.5 Hz, 2H), 7.33-7.24 (m, 5H), 7.09-7.06 (m, 2H), 6.91-6.88 (m, 1H), 6.69-6.67 (m, 2H), 5.86 (d, *J* = 3.0 Hz, 1H), 4.37 (d, *J* = 3.0 Hz, 1H), 3.77 (s, 3H), 2.75 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.85, 162.31, 143.50, 141.72, 140.33, 138.18, 131.42, 129.41, 129.40, 128.31, 128.11, 127.88, 122.91, 122.00, 120.56, 115.01,

83.22, 63.58, 52.20, 51.11; HRMS (EI) *m/z* calcd for $C_{26}H_{22}BrNO_4$ (M^+) 491.0732, found 491.0733.



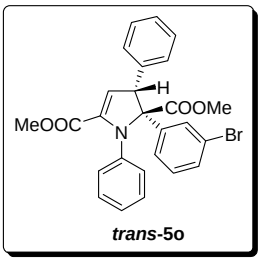
***trans*-5n**

(2R*,3R*)-dimethyl 2-(4-bromophenyl)-2,3-dihydro-1,3-diphenyl-1H-pyrrole-2,5-dicarboxylate (*trans*-5n): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.13-6.96 (m, 8H), 6.84 (d, *J* = 8.5 Hz, 2H), 6.80-6.78 (m, 2H), 6.76 (d, *J* = 8.5 Hz, 2H), 5.94 (d, *J* = 3.0 Hz, 1H), 5.54 (d, *J* = 3.0 Hz, 1H), 3.76 (s, 3H), 3.43 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.78, 161.97, 142.83, 140.04, 137.24, 135.12, 130.64, 129.93, 129.48, 128.26, 127.94, 127.36, 123.62, 122.12, 121.24, 118.88, 84.18, 59.58, 52.64, 52.13; HRMS (EI) *m/z* calcd for $C_{26}H_{22}BrNO_4$ (M^+) 491.0732, found 491.0733.



***cis*-5o**

(2S*,3R*)-dimethyl 2-(3-bromophenyl)-2,3-dihydro-1,3-diphenyl-1H-pyrrole-2,5-dicarboxylate (*cis*-5o): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (s, 1H), 7.65 (d, *J* = 8.0 Hz, 1H), 7.48 (d, *J* = 8.0Hz, 1H), 7.35-7.28 (m, 4H), 7.27-7.25 (m, 2H), 7.11-7.08 (m, 2H), 6.93-6.90 (m, 1H), 6.72-6.70 (m, 2H), 5.89 (d, *J* = 3.0 Hz, 1H), 4.42 (d, *J* = 3.0 Hz, 1H), 3.78 (s, 3H), 2.78 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.63, 161.11, 143.68, 142.32, 139.22, 136.97, 129.75, 129.54, 128.63, 128.26, 127.14, 126.95, 126.72, 125.04, 121.85, 121.30, 119.60, 113.95, 82.03, 62.23, 51.01, 49.96; HRMS (EI) *m/z* calcd for $C_{26}H_{22}BrNO_4$ (M^+) 491.0732, found 491.0732.

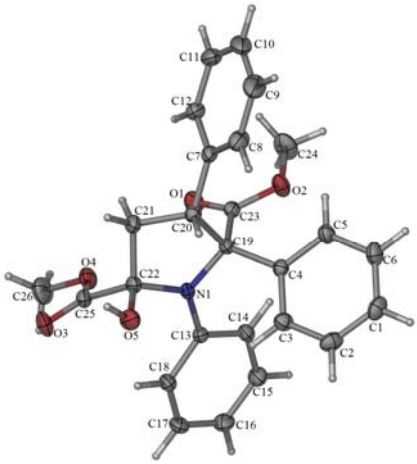


***trans*-5o**

(2R*,3R*)-dimethyl 2-(3-bromophenyl)-2,3-dihydro-1,3-diphenyl-1H-pyrrole-2,5-dicarboxylate (*trans*-5o): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.16-7.04 (m, 7H), 7.01-6.98 (m, 2H), 6.88-6.83 (m, 3H), 6.79-6.77 (m, 2H), 5.97 (s, 1H), 5.56 (s, 1H), 3.77 (s, 3H), 3.43 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.37, 160.77, 141.75, 138.99, 137.36, 136.07, 130.99, 128.79, 128.24, 127.17, 127.12, 126.70, 126.28, 126.26, 122.65, 121.20, 120.07, 117.73, 82.95, 58.62, 51.48, 50.96; HRMS (EI) *m/z* calcd for $C_{26}H_{22}BrNO_4$ (M^+) 491.0732, found 491.0732.

Single-crystal X-ray structure determinations were performed on a Bruker SMART APEX II diffractometer using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). Cell parameters were retrieved using APEX II software and refined using SAINT on all observed reflections. Data reduction was performed using the SAINT software. Scaling and absorption corrections were applied using SADABS multi-scan technique supplied by George Sheldrick.[4] The structures were solved by direct methods and refined by full-matrix least-squares on F^2 with anisotropic displacement parameters for non-H atoms using SHELX-97.[5]

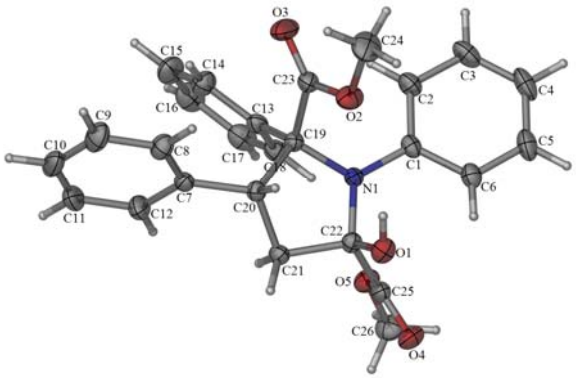
Crystal data of 4a



Identification code	zyg-1	
Empirical formula	$C_{26}H_{25}NO_5$	
Formula weight	431.47	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system, space group	Triclinic, $P\bar{1}$	
Unit cell dimensions	a = 9.0431(2) Å	alpha = 104.7420(10) deg.
	b = 9.1987(2) Å	beta = 98.0810(10) deg.
	c =14.3311(2) Å	gamma = 101.1600(10) deg.
Volume	1108.22(4) Å ^{3}	

Z, Calculated density	2, 1.293 Mg/m^3
Absorption coefficient	0.090 mm^{-1}
F(000)	456
Crystal size	0.628 x 0.624 x 0.516 mm
Theta range for data collection	1.50 to 25.01 deg.
Limiting indices	-10<=h<=10, -10<=k<=10, -17<=l<=17
Reflections collected / unique	15997 / 3889 [R(int) = 0.0181]
Completeness to theta = 25.01	99.7 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1 and 0.897856
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3889 / 0 / 290
Goodness-of-fit on F^2	1.031
Final R indices [I>2sigma(I)]	R1 = 0.0375, wR2 = 0.1014
R indices (all data)	R1 = 0.0411, wR2 = 0.1062
Extinction coefficient	0.034(3)
Largest diff. peak and hole	0.353 and -0.352 $e.A^{-3}$

Crystal data of 4c



Identification code	zyg-2
Empirical formula	$C_{26}H_{25}NO_5$
Formula weight	431.47

Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, $P2_1/n$
Unit cell dimensions	a = 13.6991(6) Å alpha = 90 deg.
	b = 9.8616(5) Å beta = 105.5260(10) deg.
	c = 17.5991(8) Å gamma = 90 deg.
Volume	2290.79(19) A^3
Z, Calculated density	4, 1.251 Mg/m^3
Absorption coefficient	0.087 mm^-1
F(000)	912
Crystal size	0.354 x 0.340 x 0.255 mm
Theta range for data collection	1.68 to 25.01 deg.
Limiting indices	-16<=h<=16, -11<=k<=11, -19<=l<=20
Reflections collected / unique	26067 / 4025 [R(int) = 0.0213]
Completeness to theta = 25.01	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1 and 0.839748
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4025 / 0 / 289
Goodness-of-fit on F^2	1.025
Final R indices [I>2sigma(I)]	R1 = 0.0426, wR2 = 0.1168
R indices (all data)	R1 = 0.0506, wR2 = 0.1257
Largest diff. peak and hole	0.479 and -0.430 $e.A^{-3}$

Notes and References:

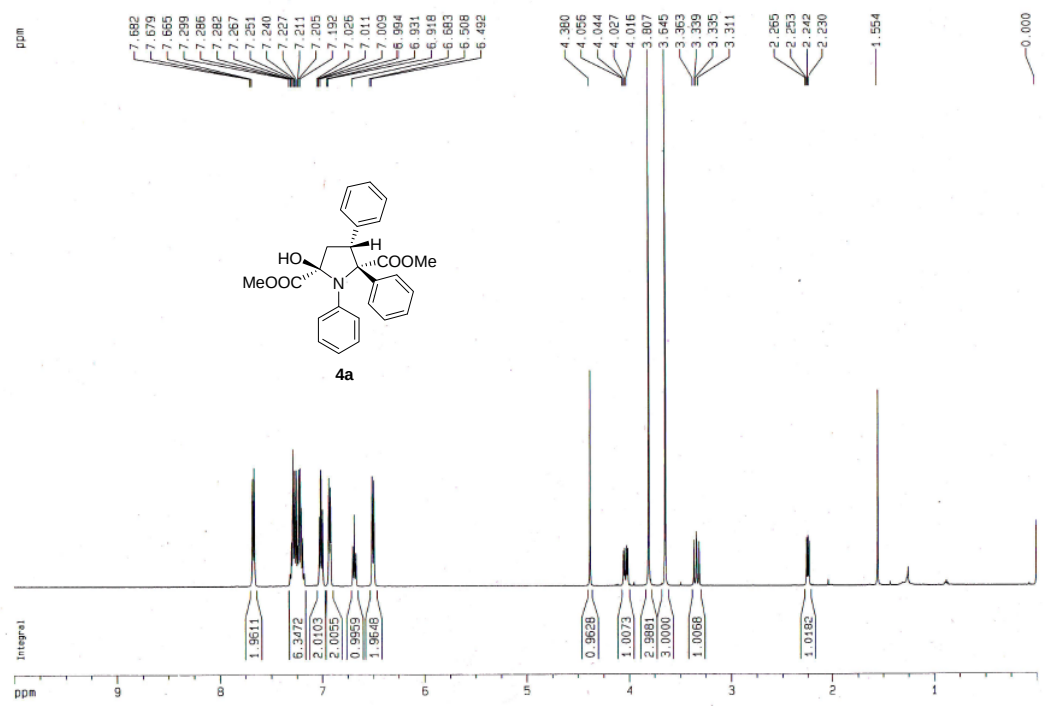
1 Y.-C. Wu, L. Liu, H.-J. Li, D. Wang and Y.-J. Chen, *J. Org. Chem.*, 2006, **71**, 6592.

2 T. Vaijayanthi and A. Chadha, *Tetrahedron: Asymmetry*, 2007, **18**, 1077.

3 M. P. Doyle, M. A. Mckervey and T. Ye, *Modern Catalytic Methods for Organic Synthesis with Diazo Compounds*; Wiley: New York, 1998.

4 SAINT V 7.34 Software for the Integration of CCD Detector System Bruker Analytical X-ray Systems, Madison, WI, 2001.

5 G. M. Sheldrick, SHELX-97; Bruker Analytical X-Ray Systems, Inc.: Madison, WI, 1997.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7.251
7.240
7.227
7.211
7.205
7.192
7.026
7.011
7.009
6.994
6.931
6.918
6.683
6.508
6.492
4.380
4.056
4.044
4.027
4.016
3.807
3.645
3.363
3.339
3.335
3.311
2.265
2.253
2.242
2.230
1.554
0.000
HO
MeOOC
N
H
COOMe
4a
Integral
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6.3472
2.0103
2.0055
0.9959
1.9648
0.9628
1.0073
2.9981
3.0000
1.0068
1.0182
ppm
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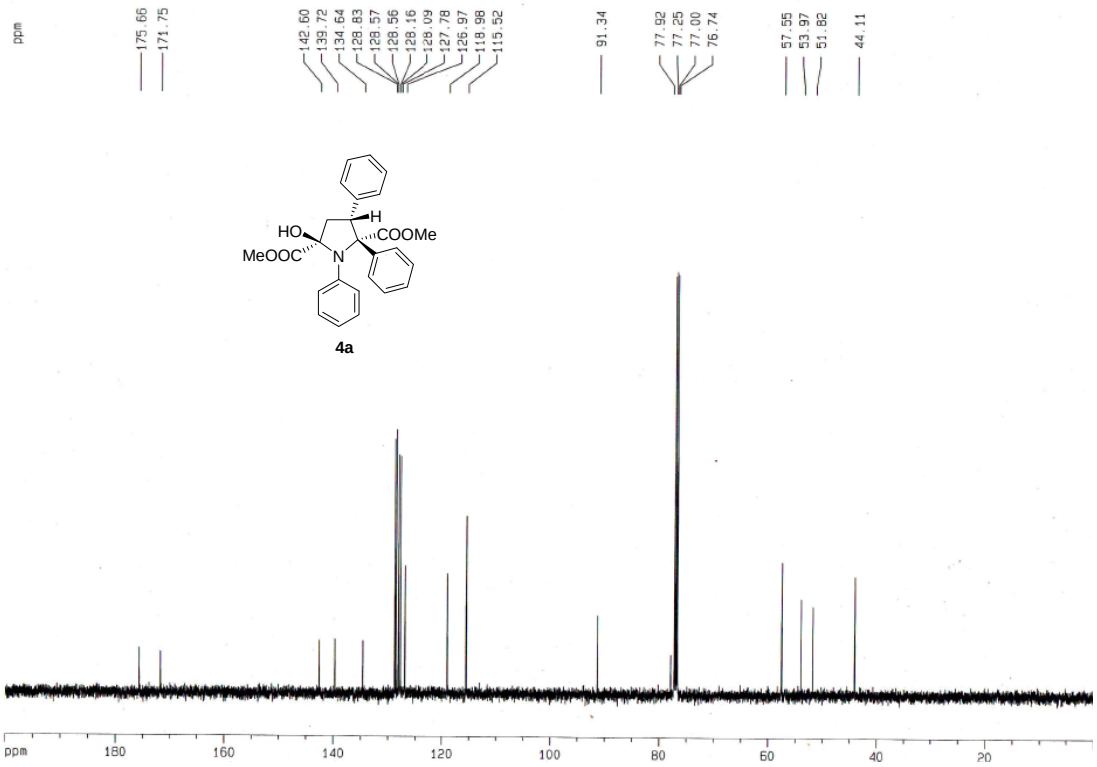
8
7
6
5
4
3
2
1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139.72
134.64
128.83
128.57
128.56
128.16
128.09
127.78
126.97
118.98
115.52
91.34
77.92
77.25
77.00
76.74
57.55
53.97
51.82
44.11
HO
MeOOC
N
H
COOMe
4a
ppm
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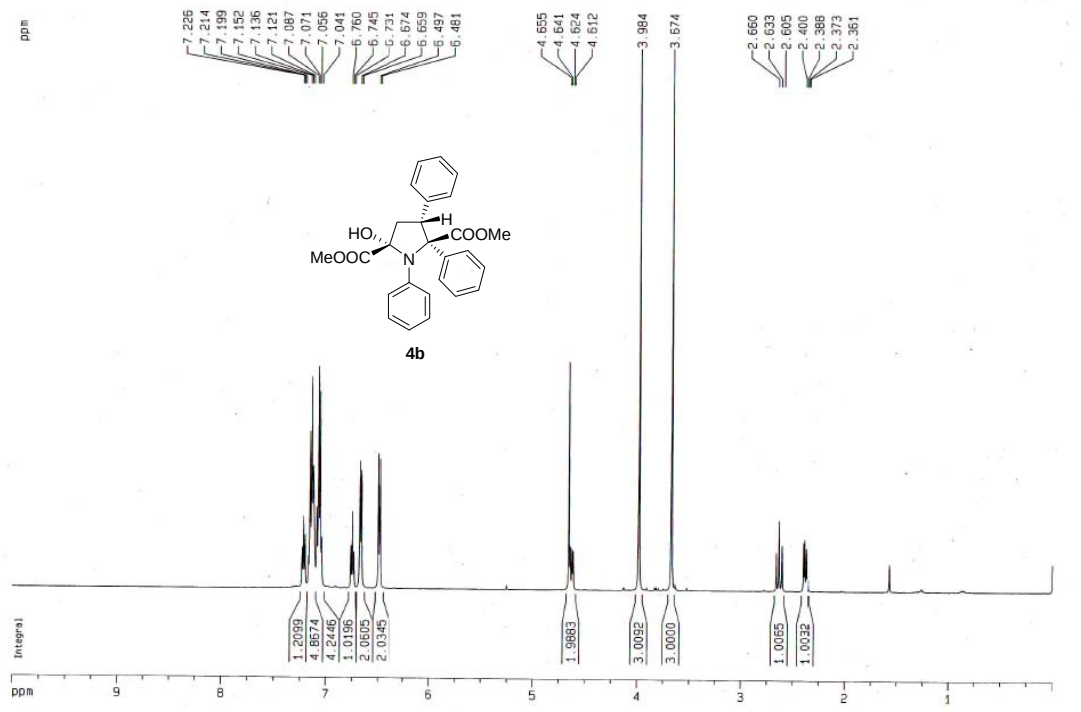
160
140
120
100
80
60
40
20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7.152
7.136
7.121
7.087
7.071
7.056
7.041
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6.745
6.731
6.674
6.659
6.497
6.481
4.655
4.641
4.624
4.612
3.984
3.674
2.660
2.633
2.605
2.400
2.388
2.373
2.361
HO
MeOOC
N
H
COOMe
4b
Integral
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4.2446
1.0196
2.0605
2.0345
1.9883
3.0092
3.0000
1.0065
1.0032
ppm
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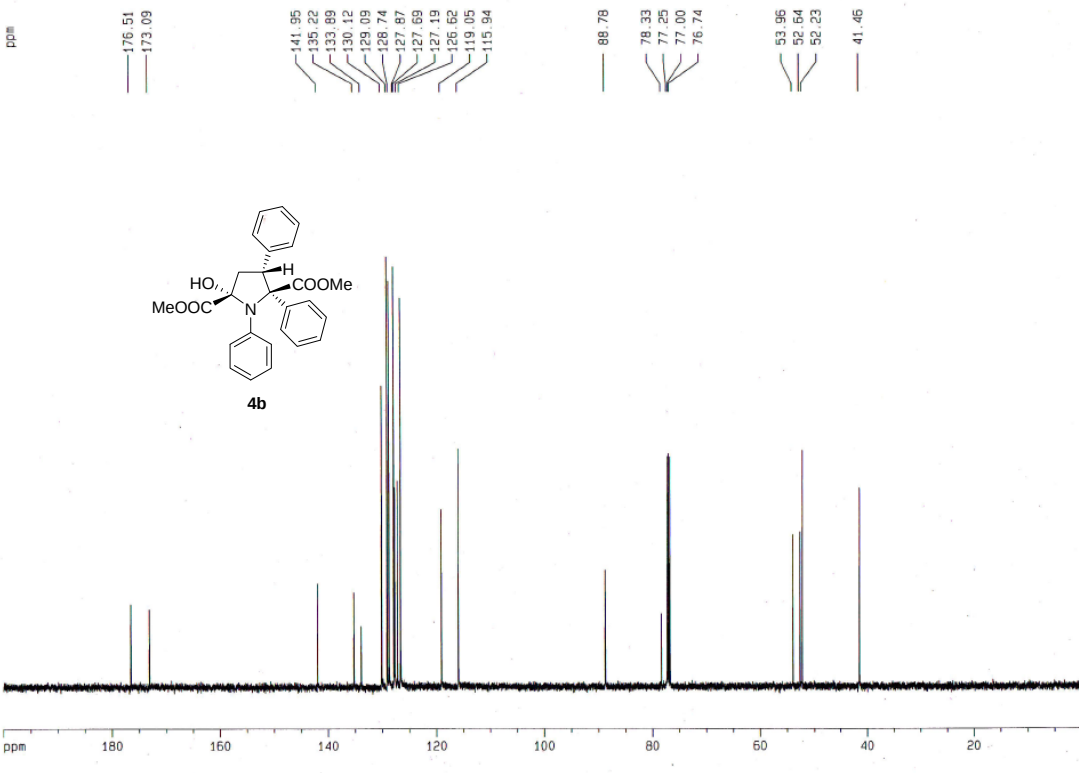
8
7
6
5
4
3
2
1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141.95
135.22
133.89
130.12
129.09
128.74
127.87
127.69
127.19
126.62
119.05
115.94
88.78
78.33
77.25
77.00
76.74
53.96
52.64
52.23
41.46
HO
MeOOC
N
H
COOMe
4b
ppm
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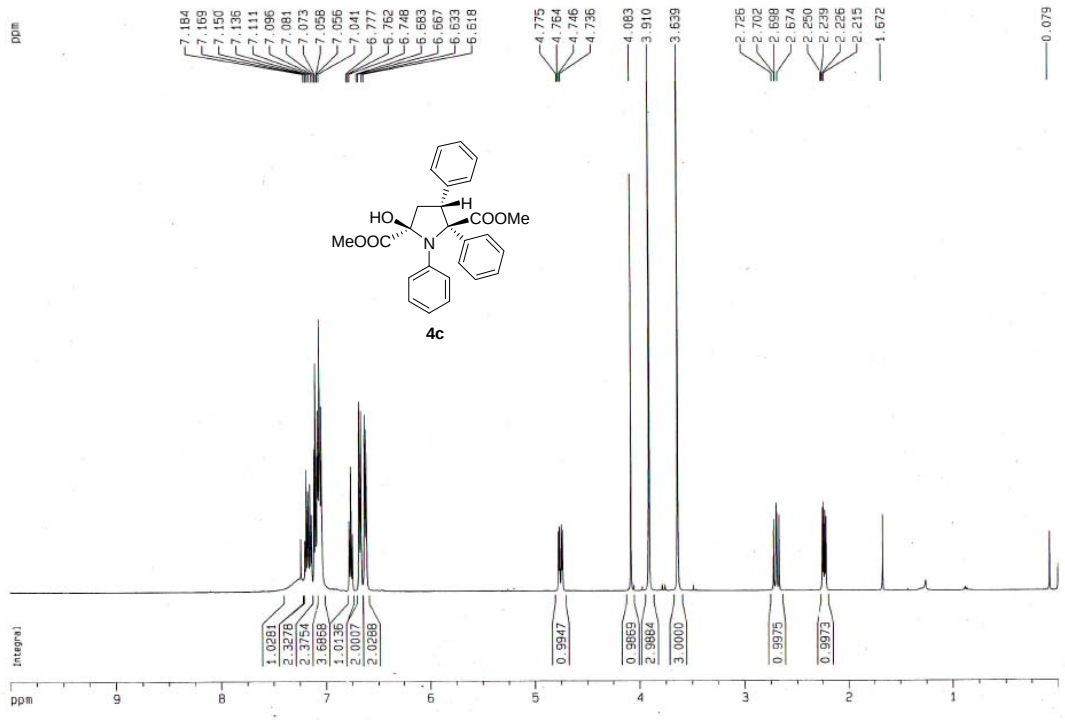
160
140
120
100
80
60
40
20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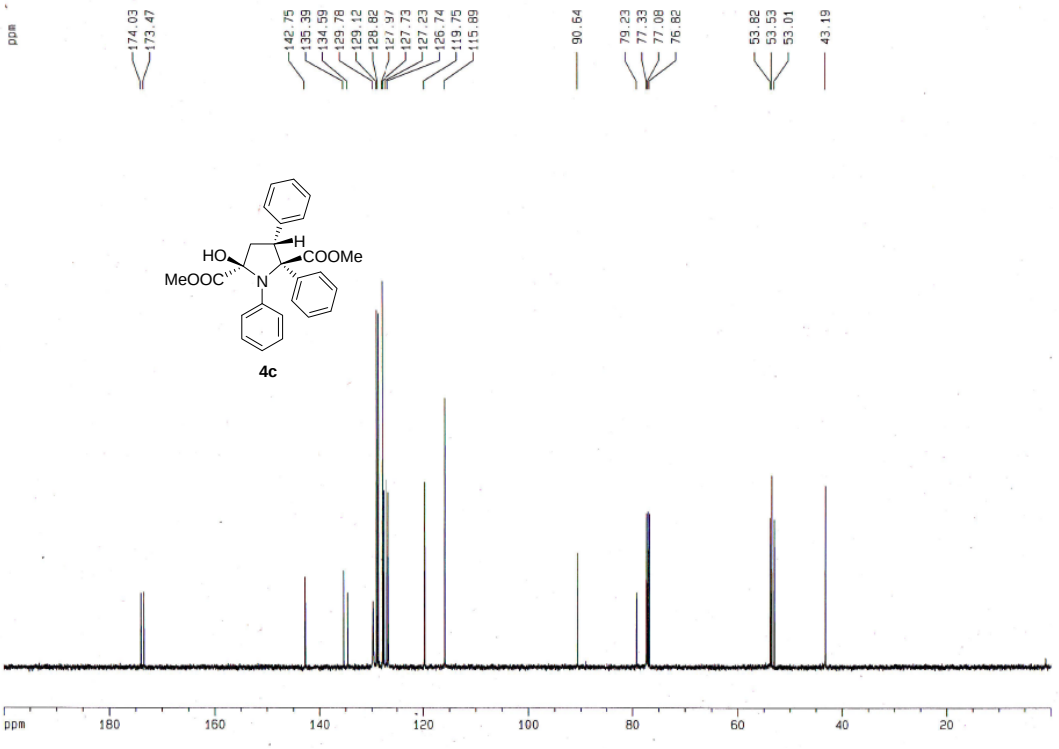
7.058
7.056
7.041
6.777
6.762
6.748
6.683
6.667
6.633
6.618
4.775
4.764
4.746
4.736
4.083
3.910
3.639
2.726
2.702
2.698
2.674
2.250
2.239
2.226
2.215
1.672
0.079
HO
MeOOC
N
H
COOMe
4c
Integral
1.0281
2.3278
2.3754
3.6868
1.0136
2.0007
2.0288
0.9947
0.9869
2.9884
3.0000
0.9975
0.9973
ppm
9
8
7
6
5
4
3
2
1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126.74
119.75
115.89
90.64
79.23
77.33
77.08
76.82
53.82
53.53
53.01
43.19
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MeOOC
N
H
COOMe
4c
ppm
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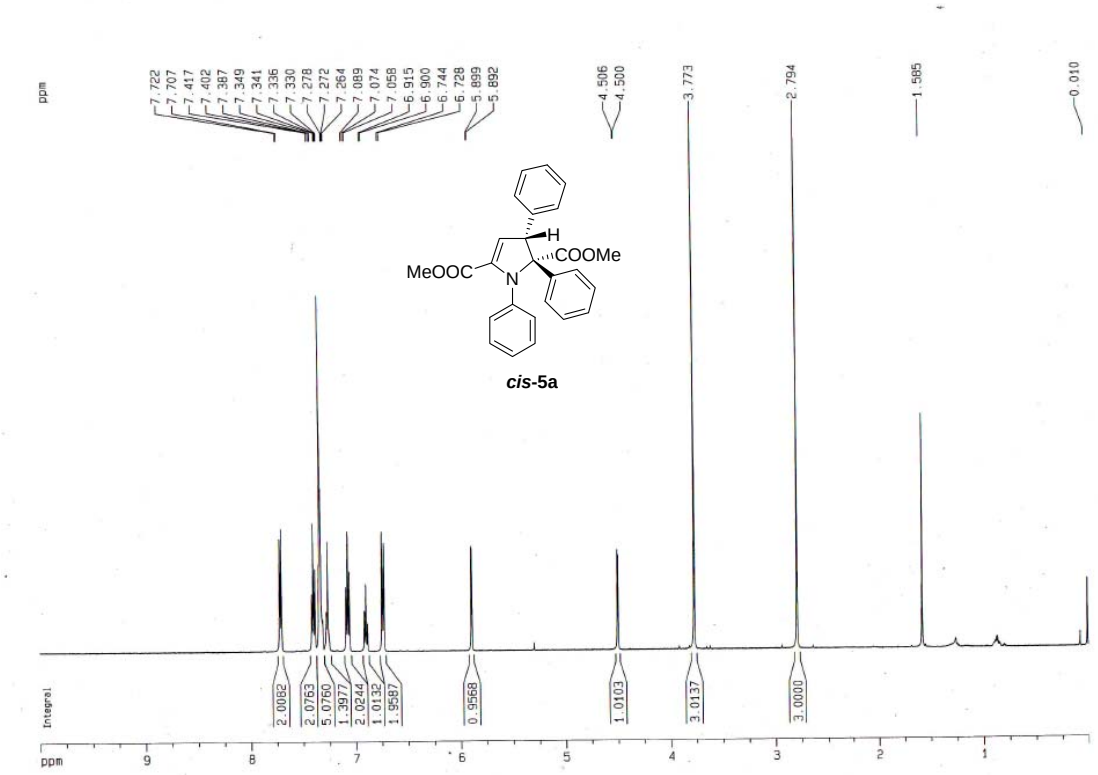
160
140
120
100
80
60
40
20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7.264
7.089
7.074
7.058
6.915
6.900
6.744
6.728
5.899
5.892
4.506
4.500
3.773
2.794
1.585
0.010
H
COOMe
MeOOC
N
cis-5a
Integral
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5.0760
1.3977
2.0244
1.0132
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1.0103
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ppm
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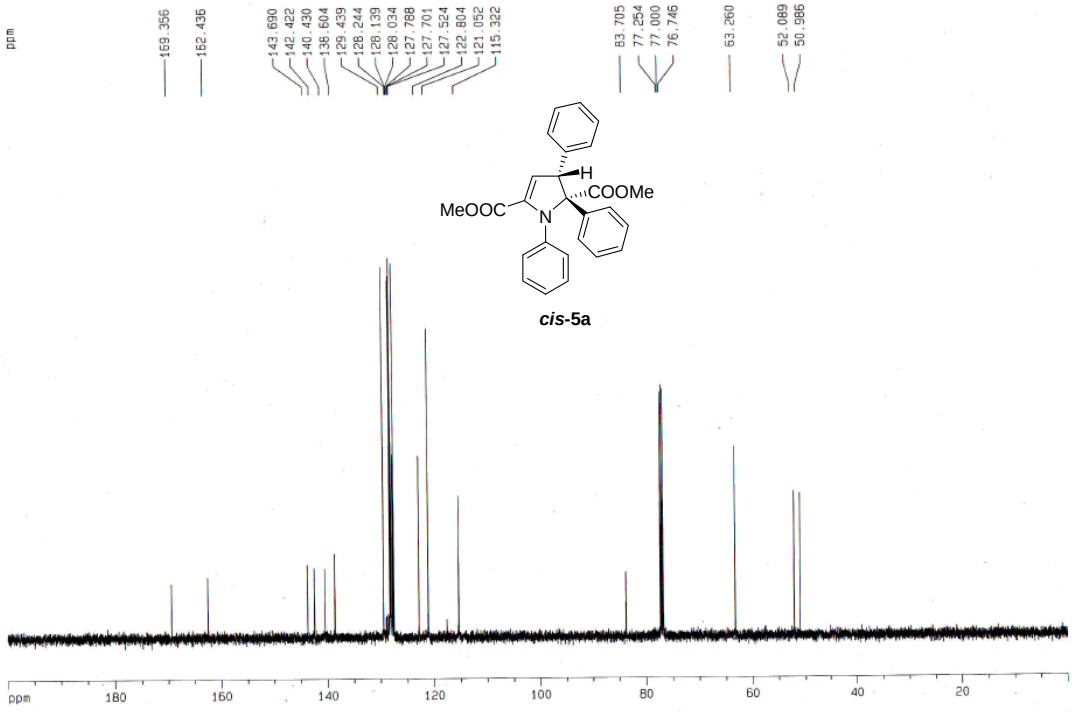
8
7
6
5
4
3
2
1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128.139
128.034
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127.701
127.524
122.804
121.052
115.322
83.705
77.254
77.000
76.746
63.260
52.089
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COOMe
MeOOC
N
cis-5a
ppm
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160
140
120
100
80
60
40
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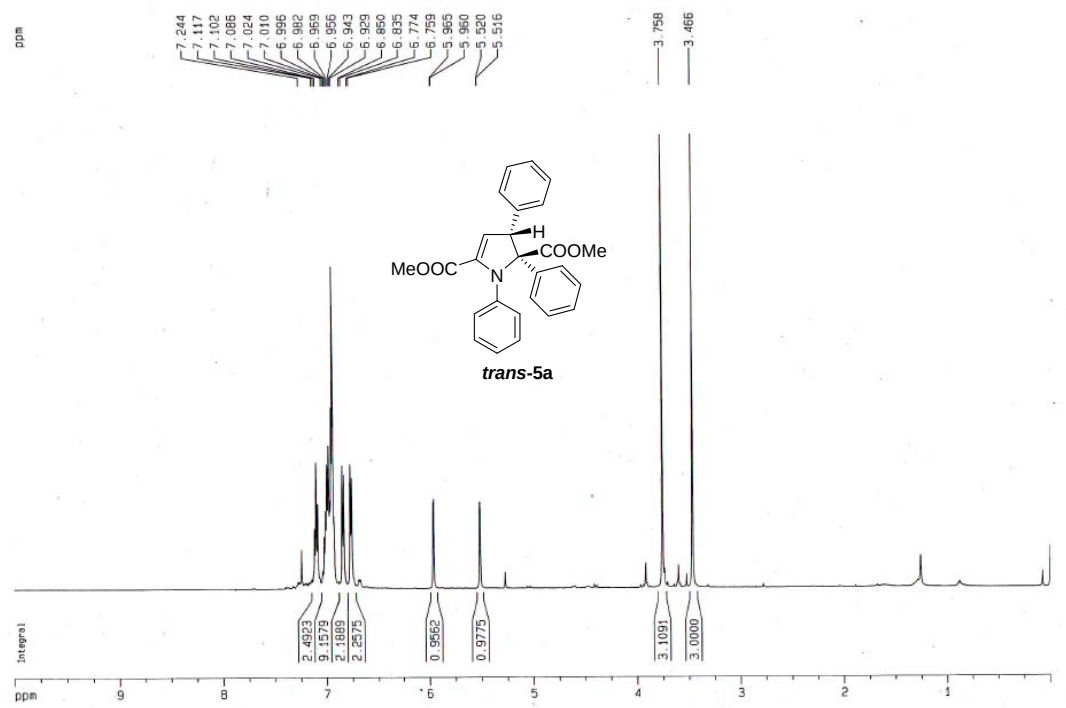
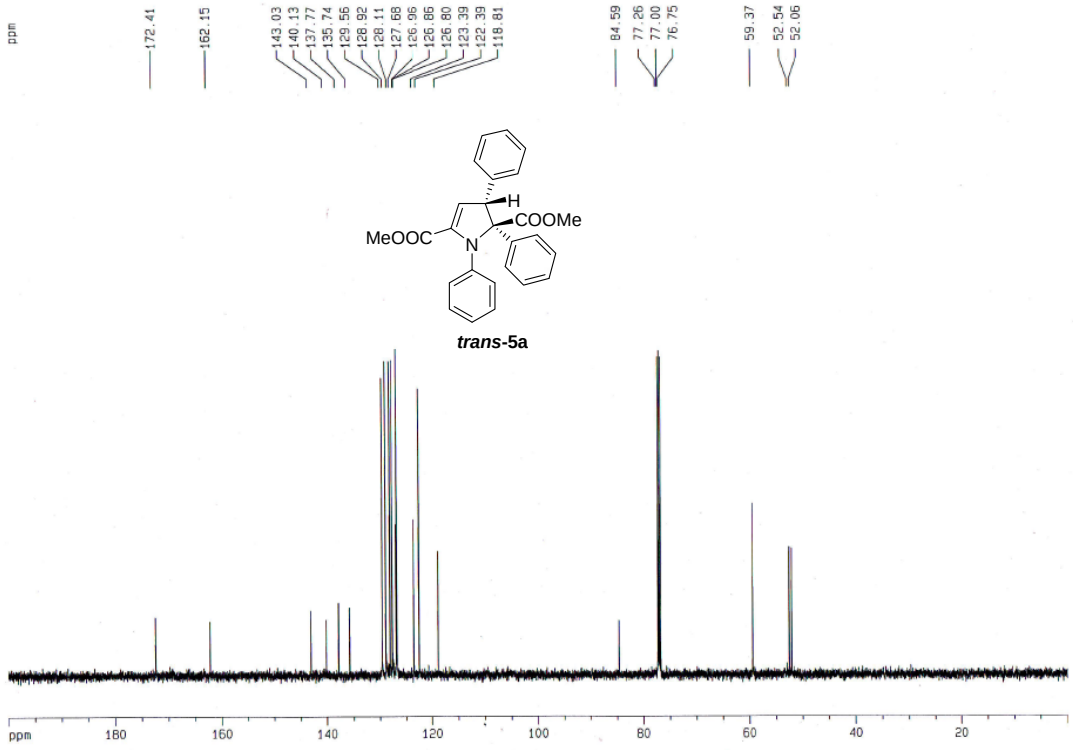
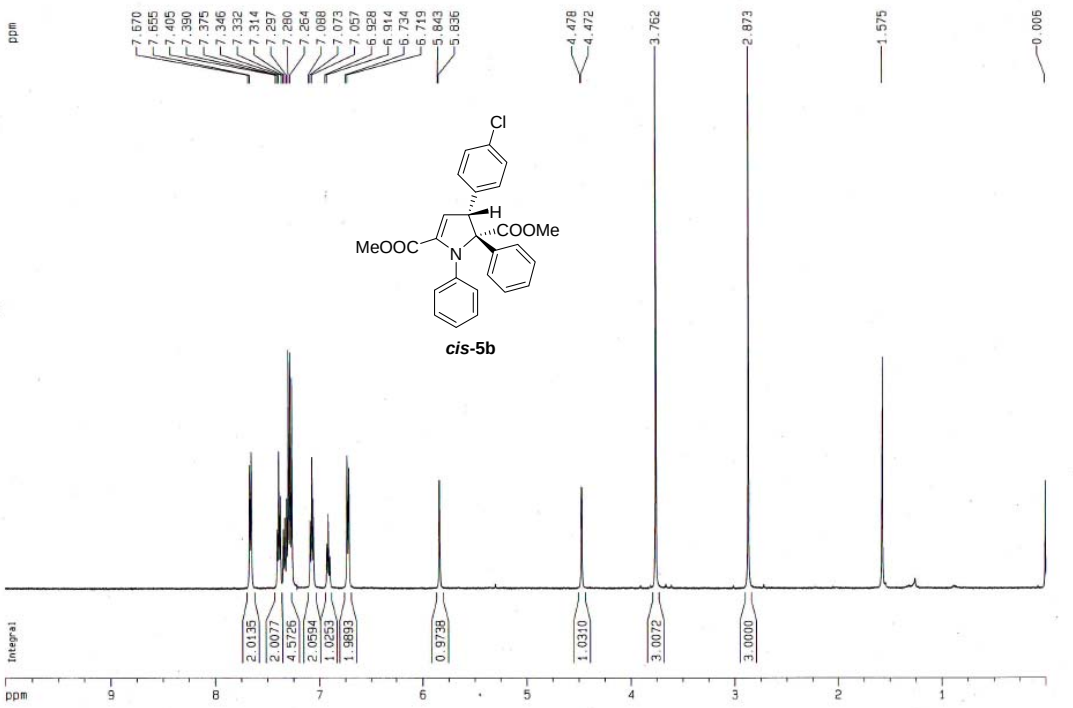


trans-**5a**



trans-**5a**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7.073
7.057
6.928
6.914
6.734
6.719
5.843
5.836
4.478
4.472
3.762
2.873
1.575
0.006
Cl
H
COOMe
MeOOC
N
Integral
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2.0077
4.5726
2.0594
1.0253
1.9893
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3.0072
3.0000
ppm
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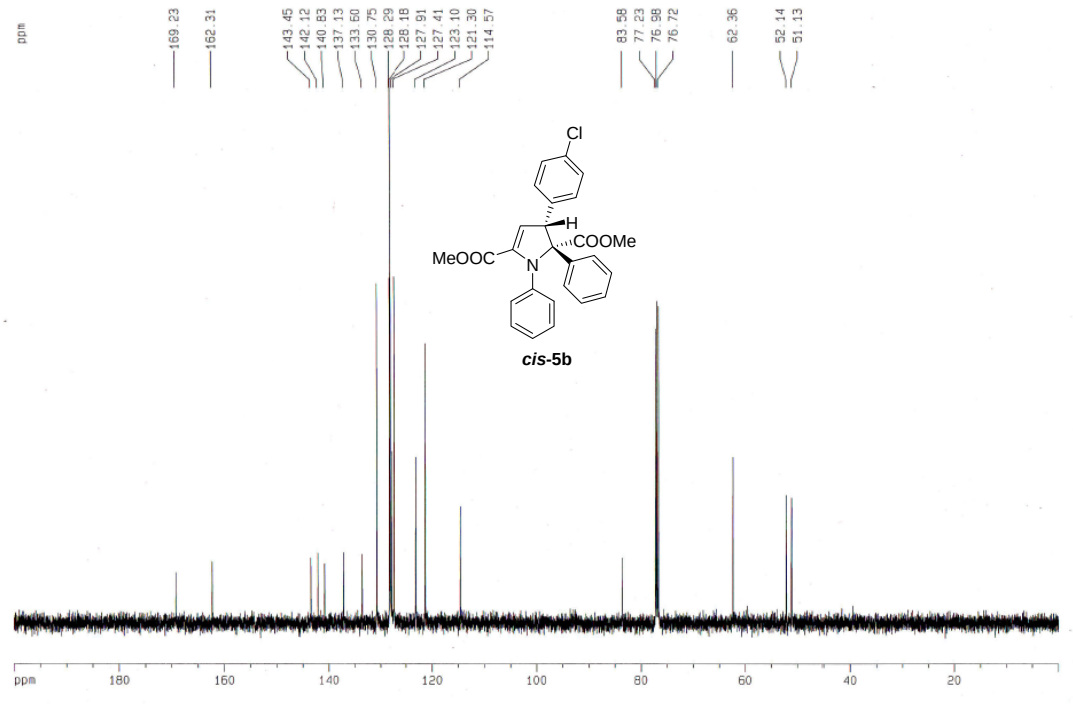
8
7
6
5
4
3
2
1

***cis*-5b**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130.75
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128.18
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127.41
123.10
121.30
114.57
83.58
77.23
76.98
76.72
62.36
52.14
51.13
Cl
H
COOMe
MeOOC
N
ppm
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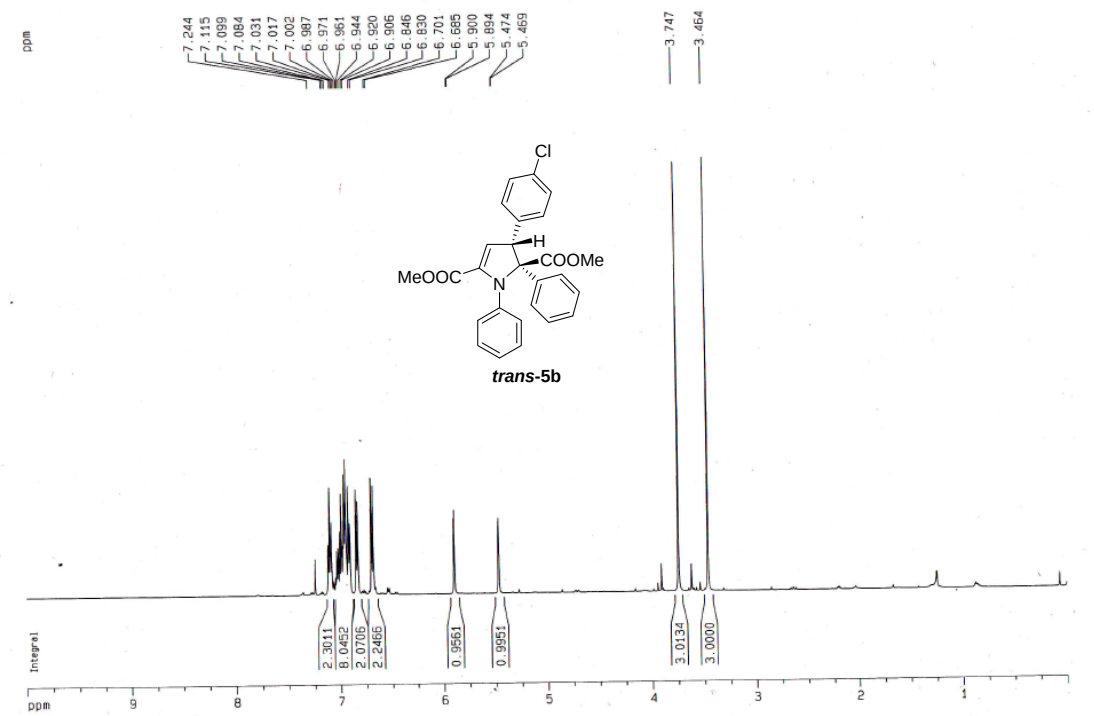
160
140
120
100
80
60
40
20

***cis*-5b**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6.961
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6.906
6.846
6.830
6.701
6.685
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3.747
3.464
Cl
H
COOMe
MeOOC
N
trans-5b
Integral
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2.0706
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0.9951
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ppm
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8
7
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4
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2
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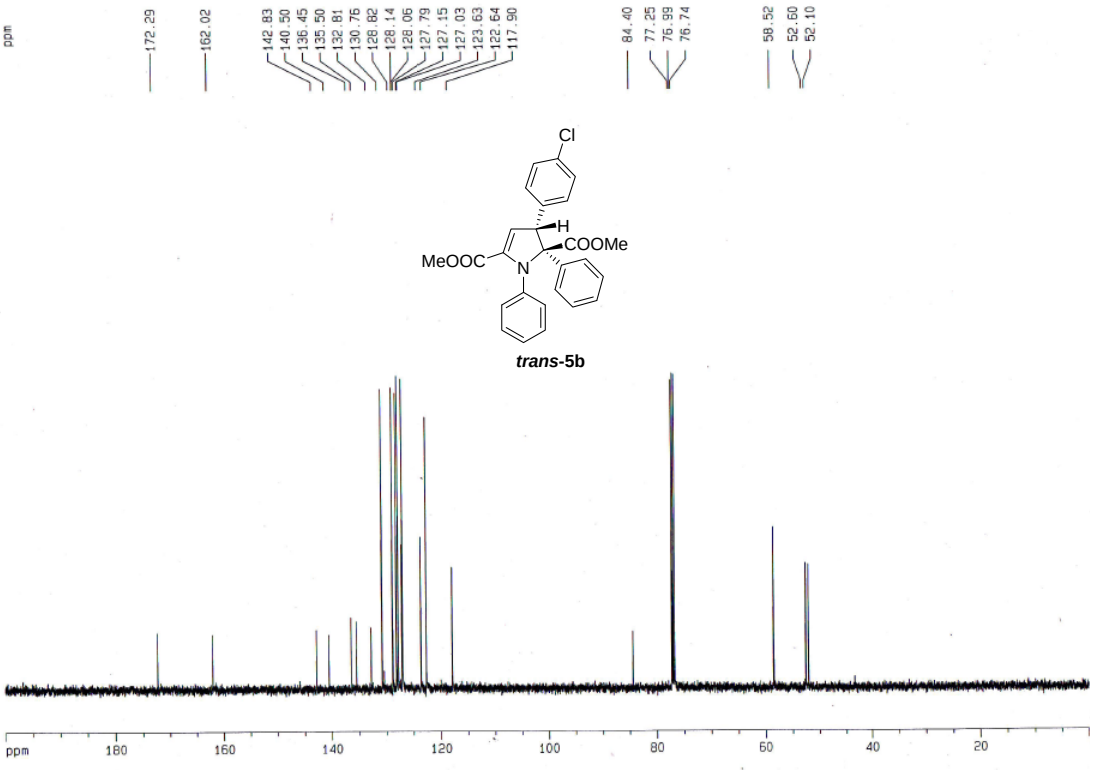
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123.63
122.64
117.90
84.40
77.25
76.99
76.74
58.52
52.60
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Cl
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COOMe
MeOOC
N
trans-5b
ppm
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160
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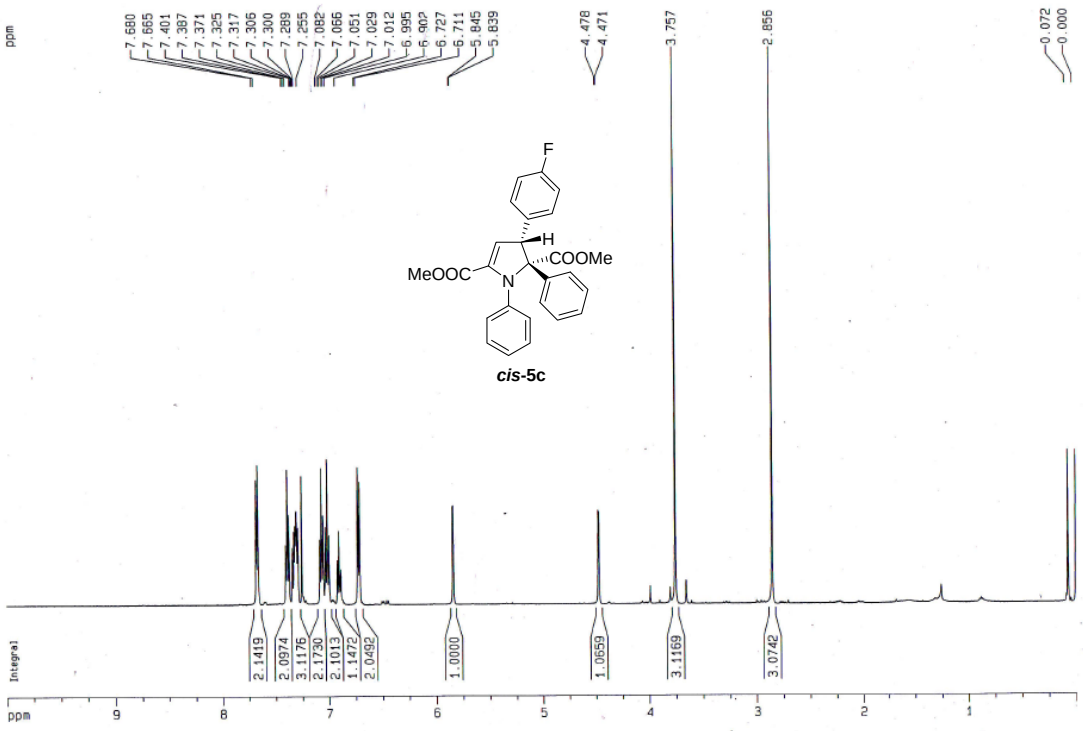
120
100
80
60
40
20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7.066
7.051
7.029
7.012
6.995
6.902
6.727
6.711
5.845
5.839
4.478
4.471
3.757
2.856
0.072
0.000
F
H
COOMe
MeOOC
N
cis-5c
Integral
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3.1176
2.1730
2.1013
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8
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2
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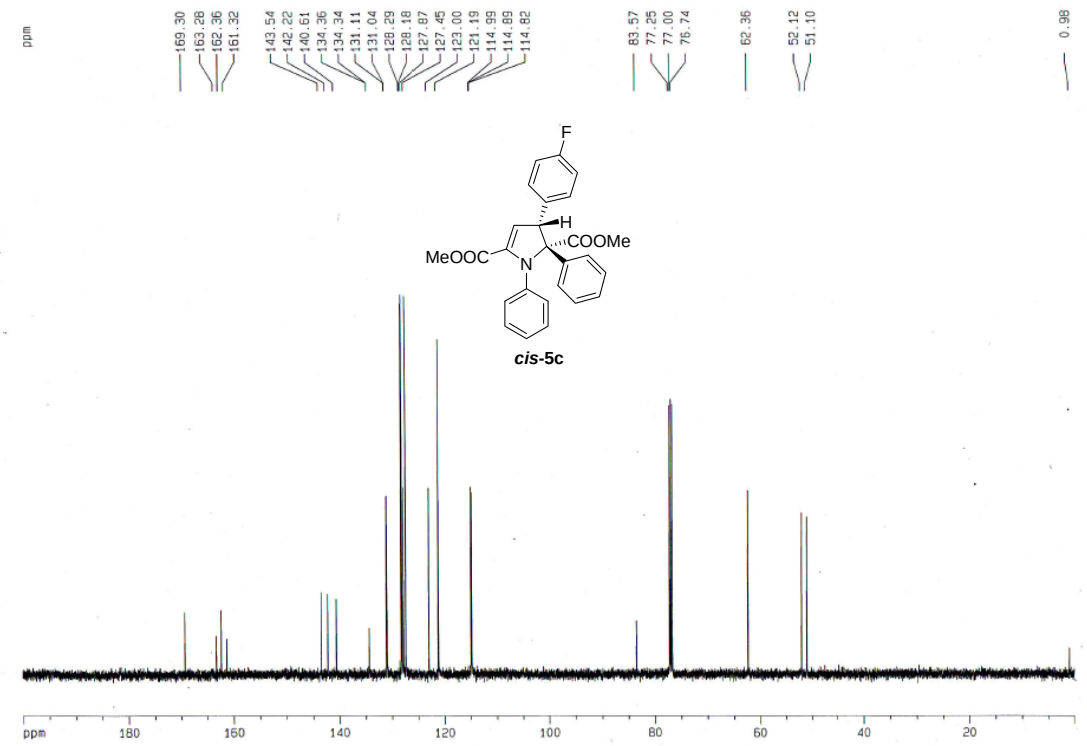
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128.18
127.87
127.45
123.00
121.19
114.99
114.89
114.82
83.57
77.25
77.00
76.74
62.36
52.12
51.10
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F
H
COOMe
MeOOC
N
cis-5c
ppm
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160
140
120
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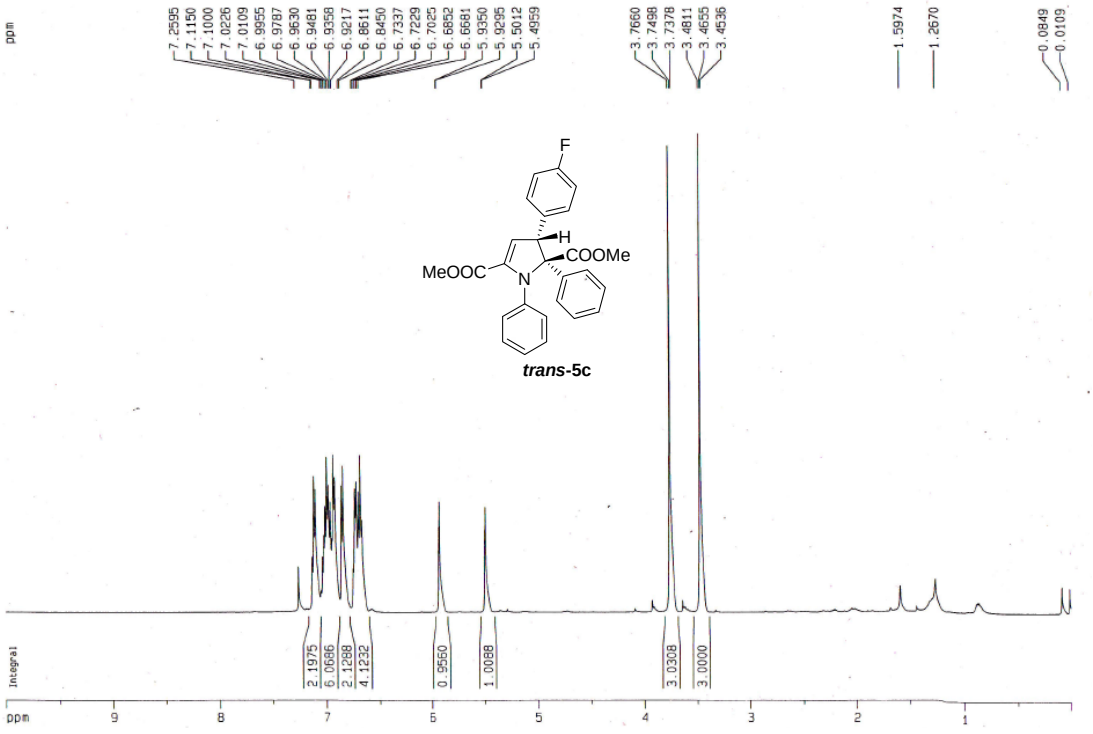
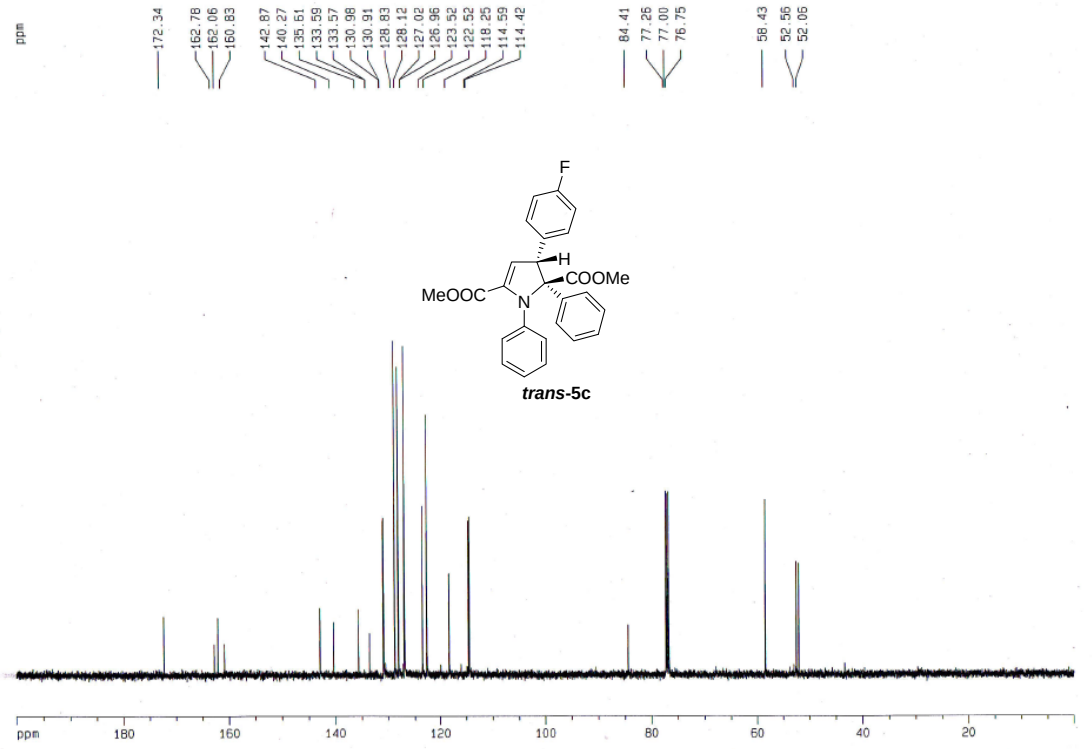
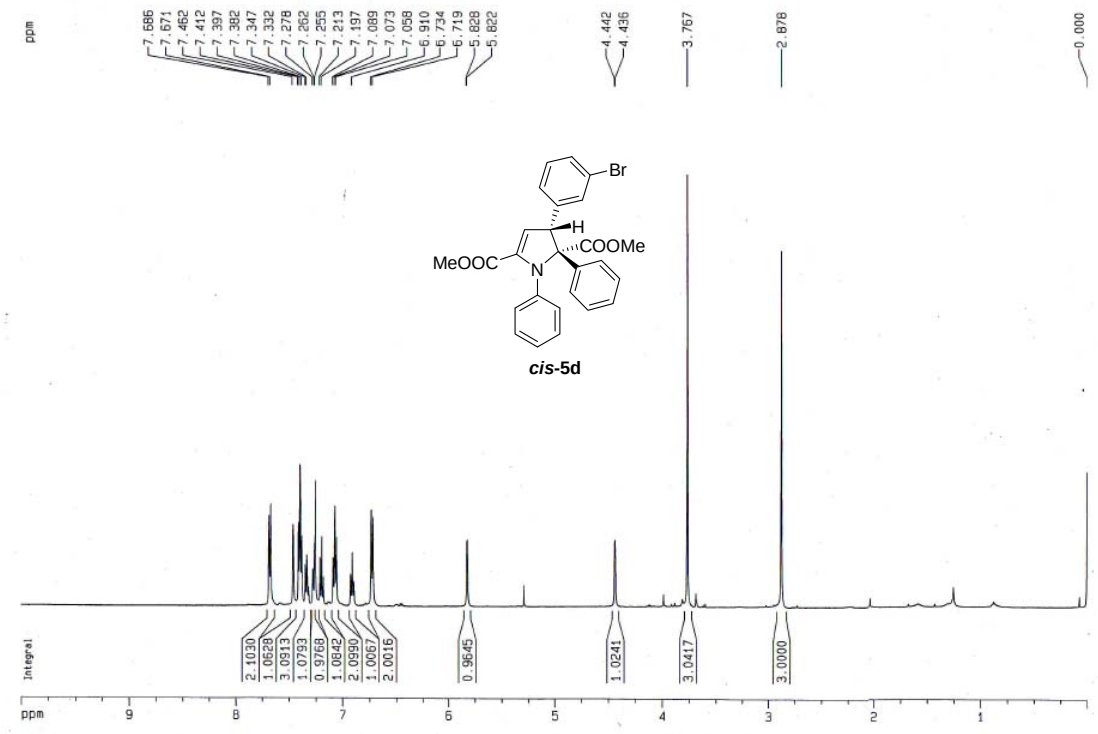
80
60
40
20



***trans*-5c**



***trans*-5c**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7.262
7.255
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7.089
7.073
7.058
6.910
6.734
6.719
5.828
5.822
4.442
4.436
3.767
2.878
0.000
Br
H
COOMe
MeOOC
N
cis-5d
Integral
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1.0628
3.0913
1.0793
0.9768
1.0842
2.0990
1.0067
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1.0241
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3.0000
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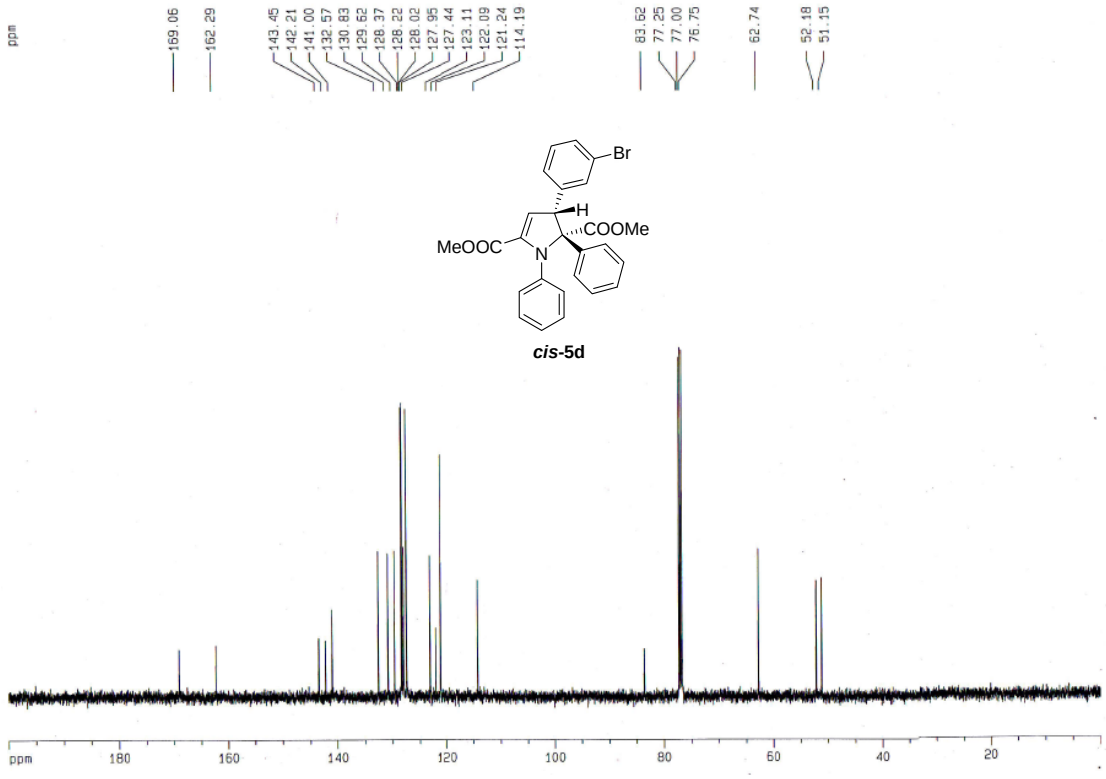
8
7
6
5
4
3
2
1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128.02
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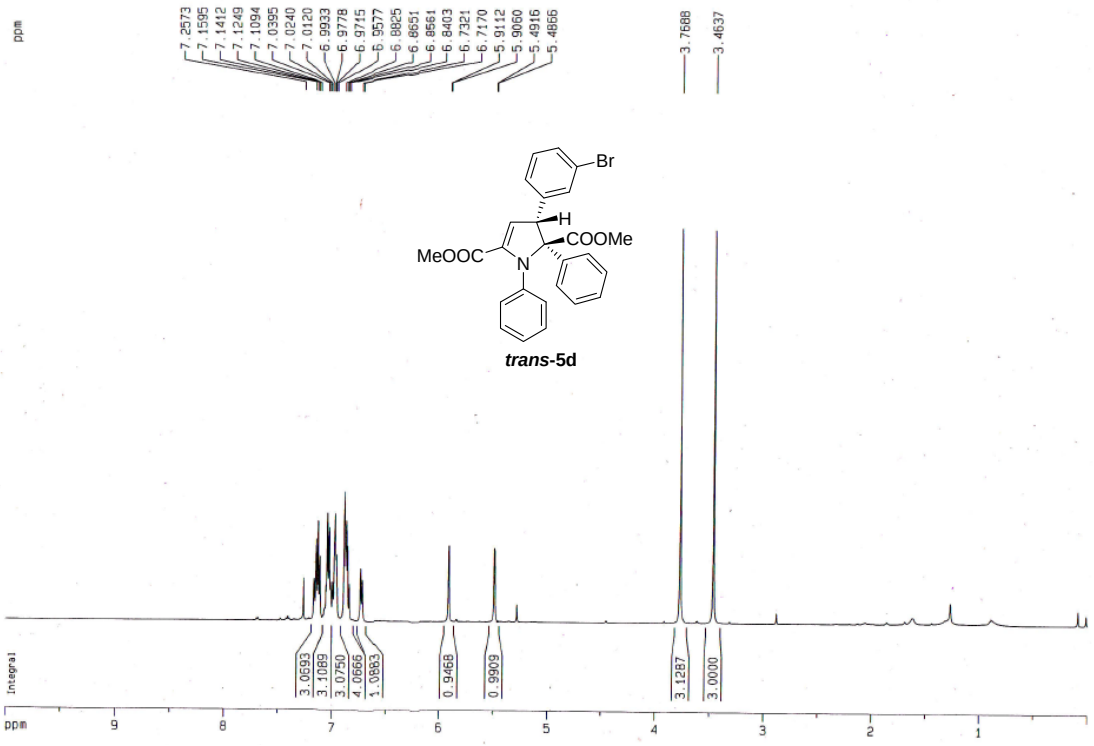
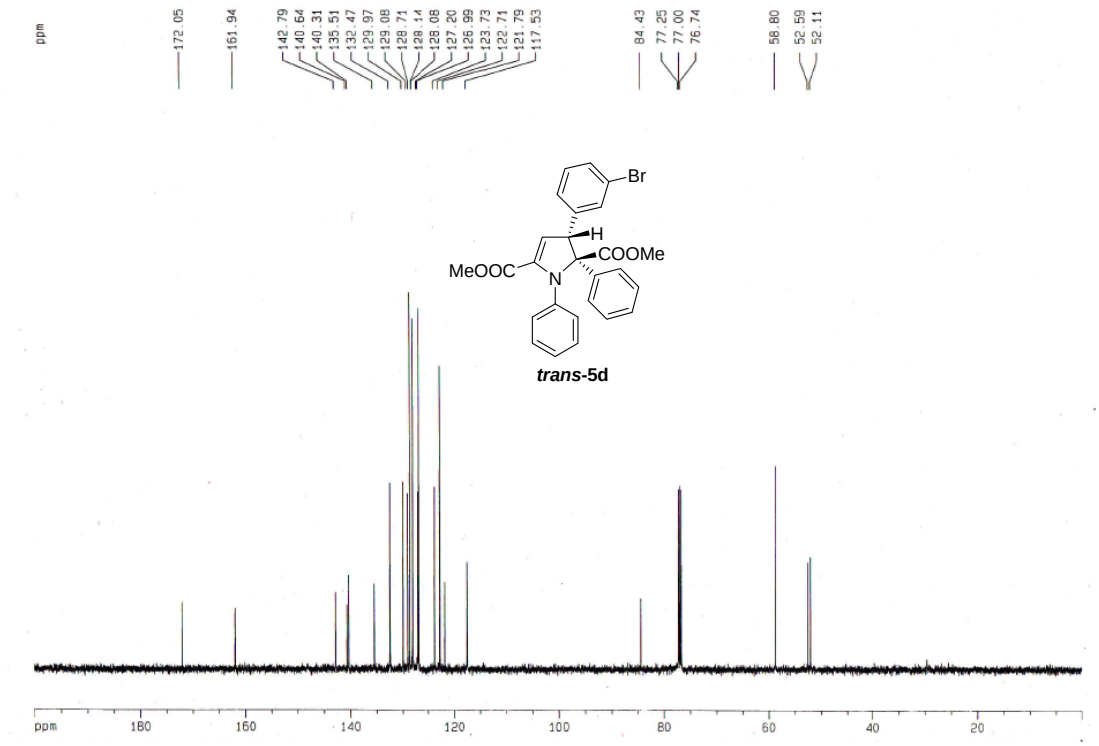
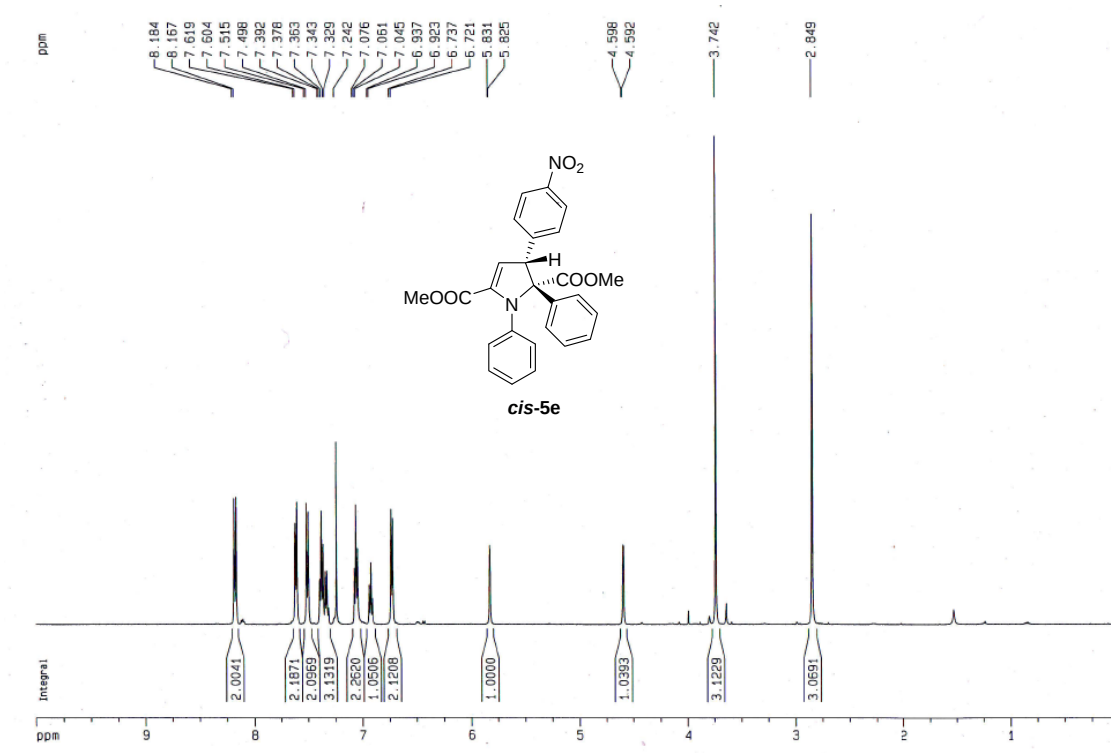
127.44
123.11
122.09
121.24
114.19
83.62
77.25
77.00
76.75
62.74
52.18
51.15
Br
H
COOMe
MeOOC
N
cis-5d
ppm
180
160
140
120
100
80
60
40
20



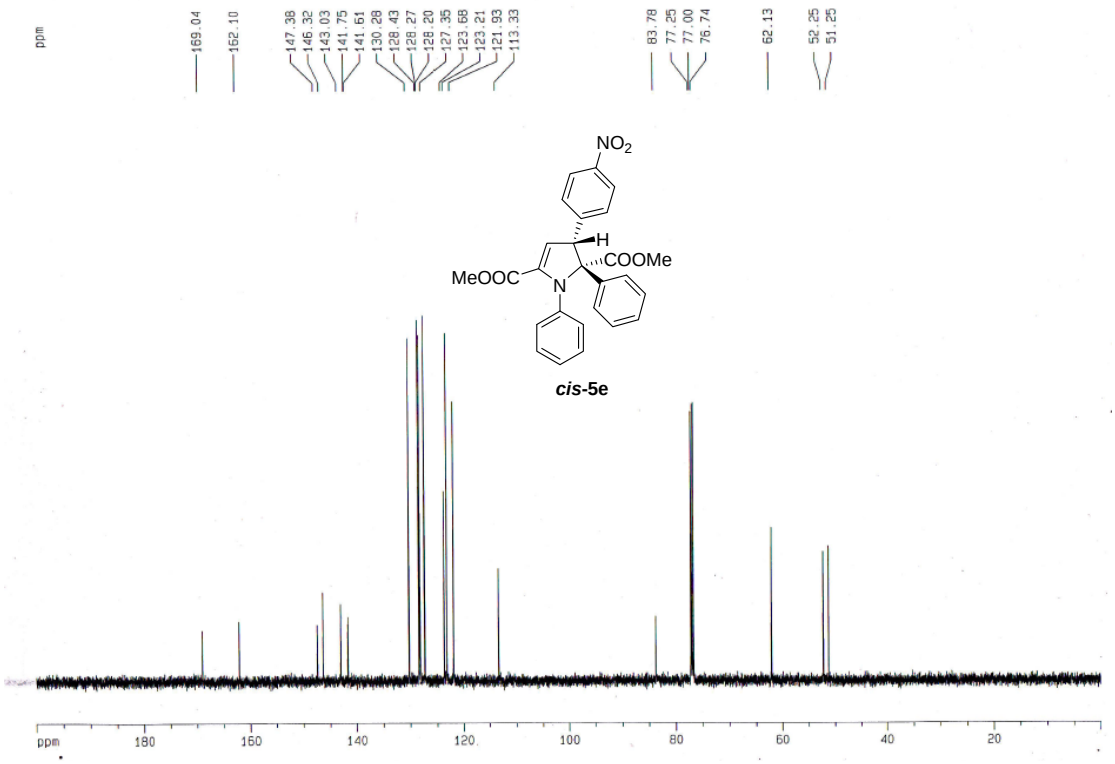
***trans*-5d**



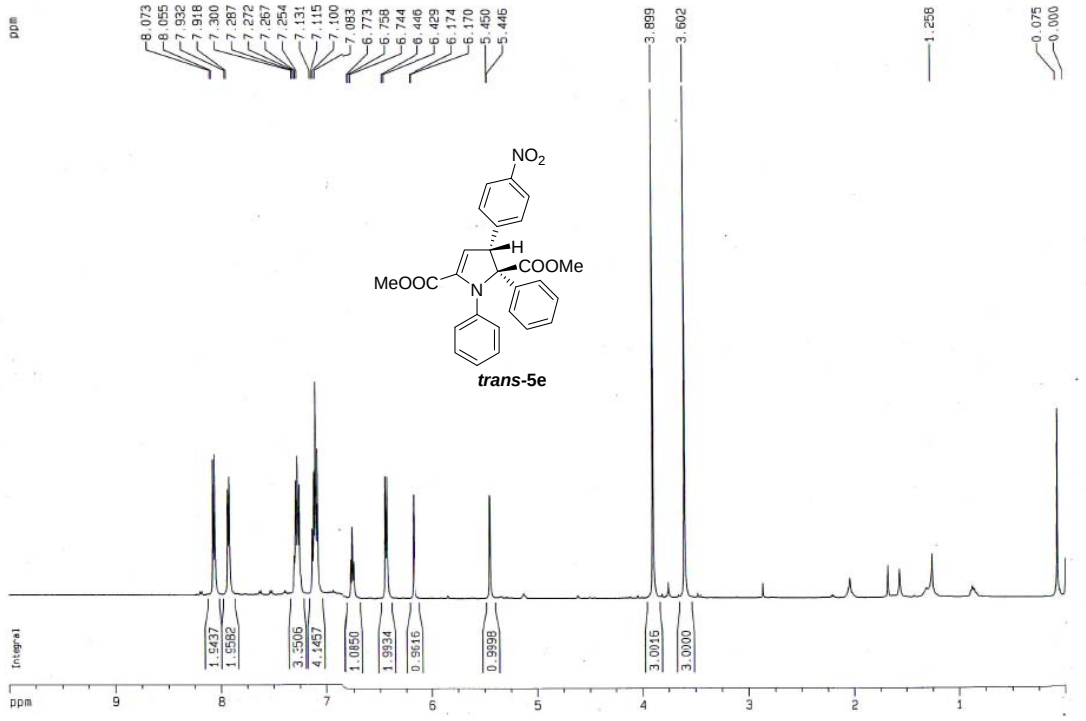
***trans*-5d**

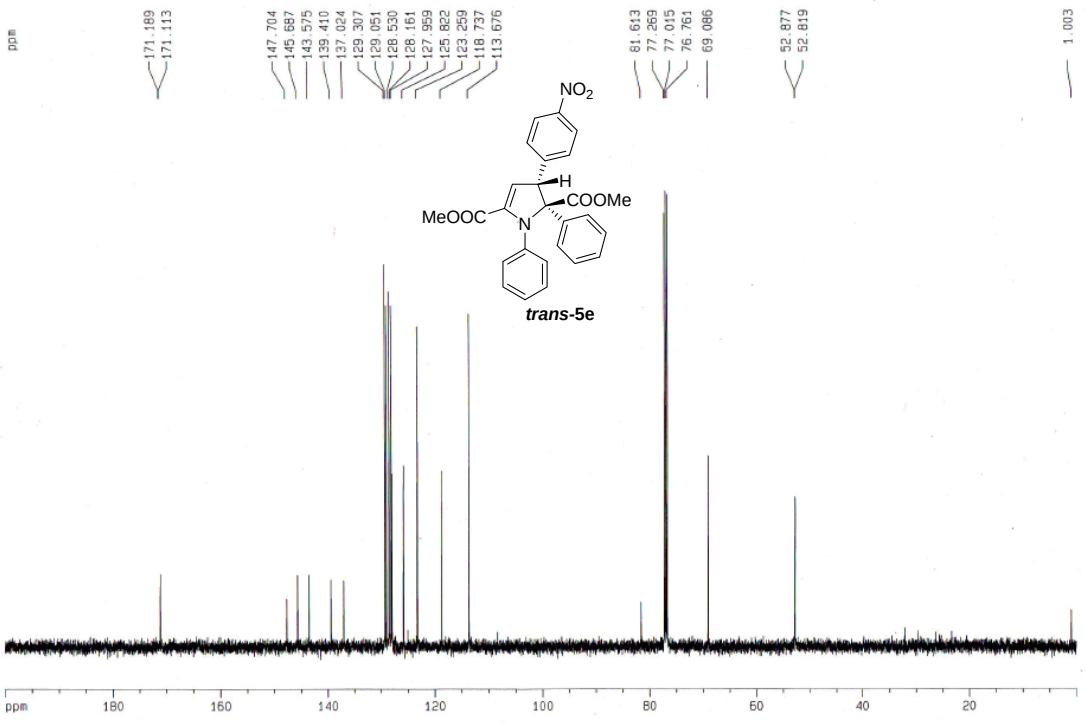

ppm
8.184
8.167
7.619
7.604
7.515
7.498
7.392
7.376
7.363
7.343
7.329
7.242
7.076
7.061
7.045
6.937
6.923
6.737
6.721
5.831
5.825
4.598
4.592
3.742
2.849
NO2
H
COOMe
MeOOC
N
Integral
2.0041
2.1871
2.0969
3.1319
2.2620
1.0506
2.1208
1.0000
1.0393
3.1229
3.0691
ppm
9
8
7
6
5
4
3
2
1

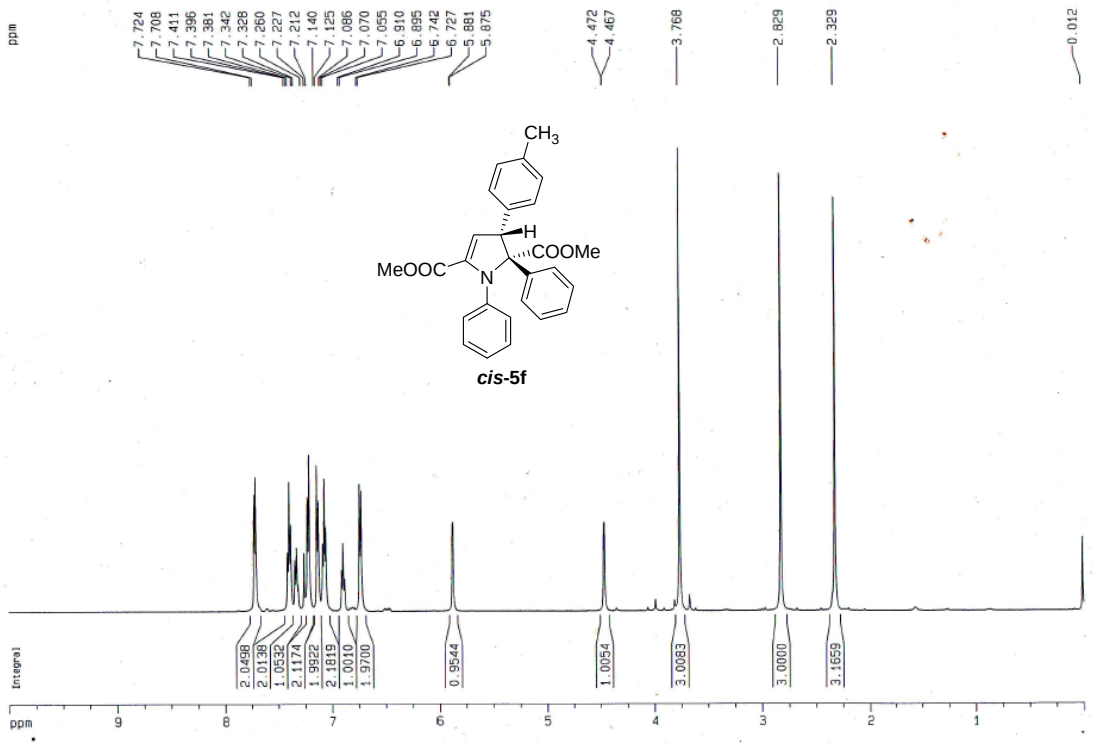
***cis*-5e**

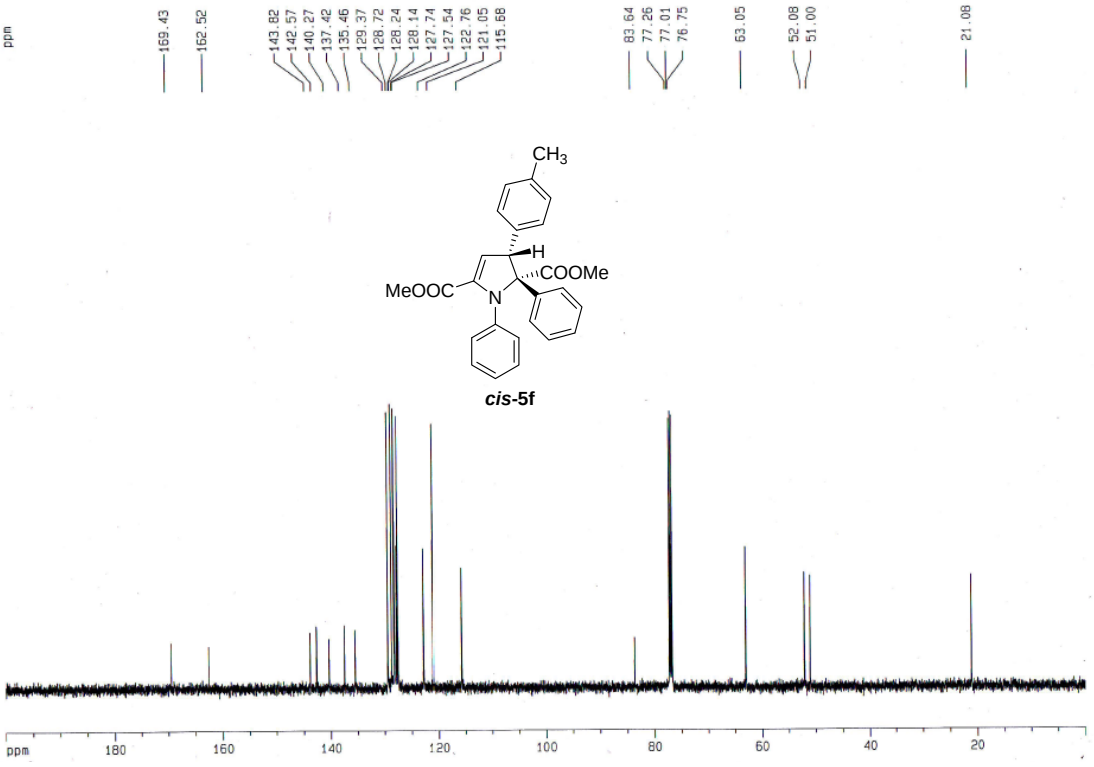

ppm
169.04
162.10
147.38
146.32
143.03
141.75
141.61
130.28
128.43
128.27
128.20
127.35
123.68
123.21
121.93
113.33
83.78
77.25
77.00
76.74
62.13
52.25
51.25
NO2
H
COOMe
MeOOC
N
ppm
180
160
140
120
100
80
60
40
20

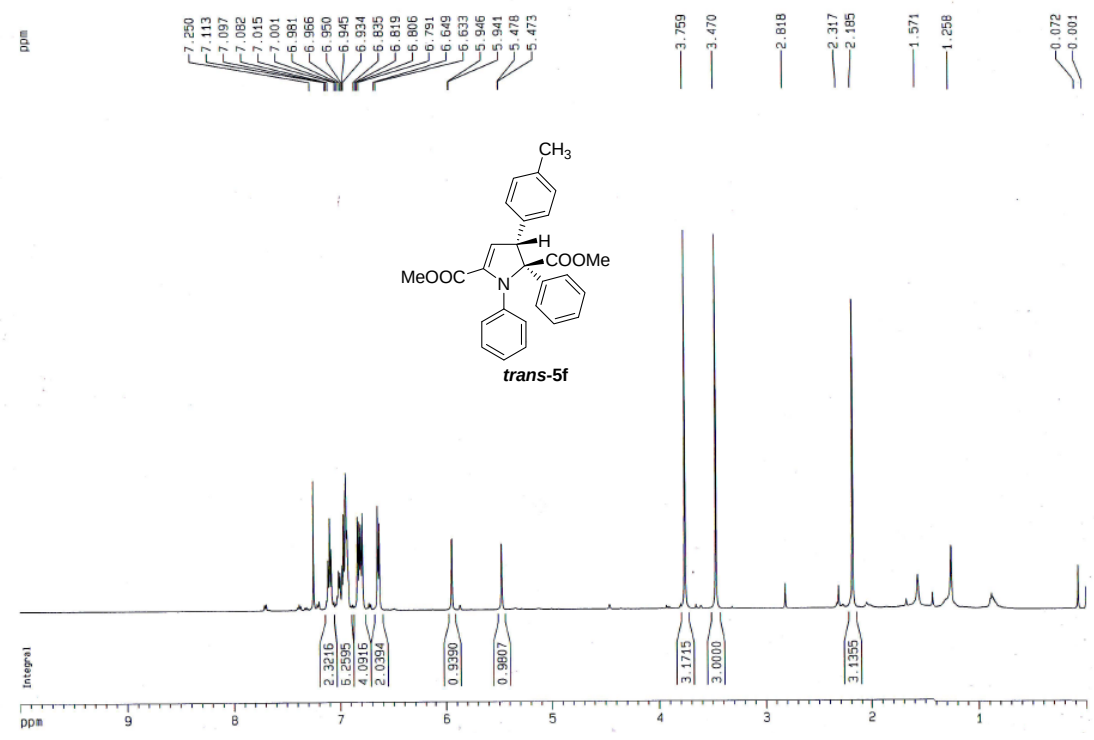
***cis*-5e**

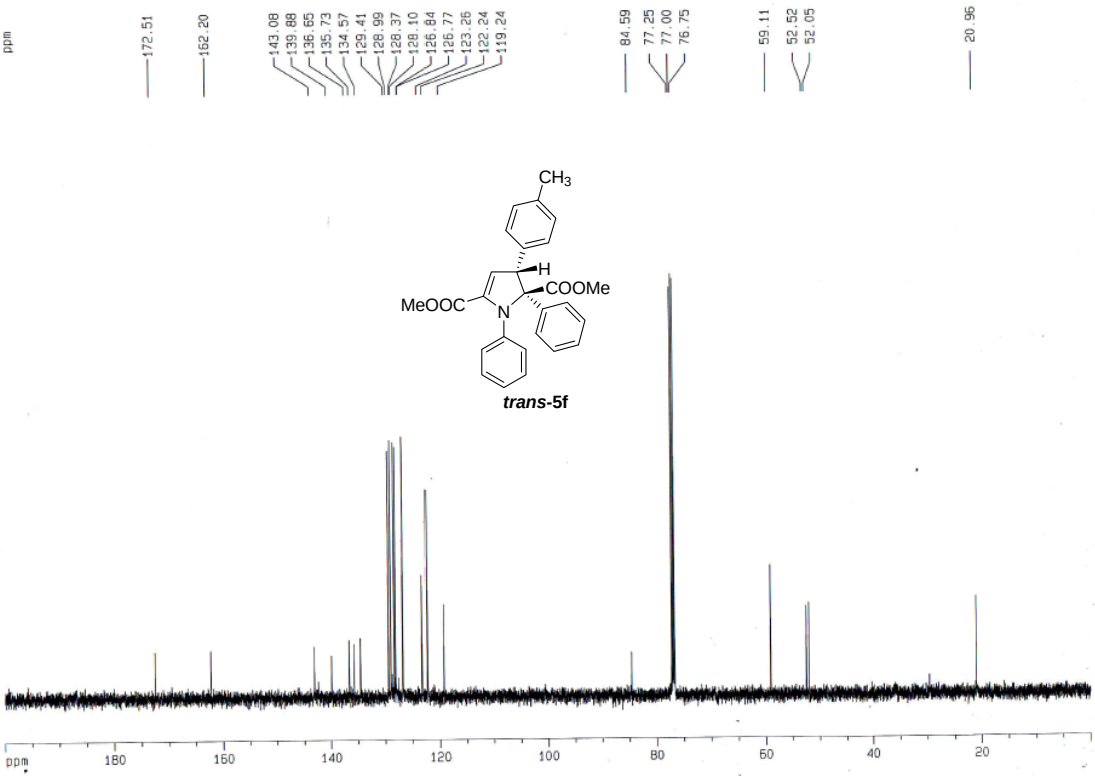

ppm
8.073
8.055
7.932
7.918
7.300
7.287
7.272
7.267
7.254
7.131
7.115
7.100
7.083
6.773
6.758
6.744
6.446
6.429
6.174
6.170
5.450
5.446
3.899
3.602
1.258
0.075
0.000
NO2
H
COOMe
MeOOC
N
trans-5e
Integral
1.5437
1.0582
3.3506
4.1457
1.0850
1.9934
0.9616
0.9998
3.0916
3.0000
ppm
9
8
7
6
5
4
3
2
1

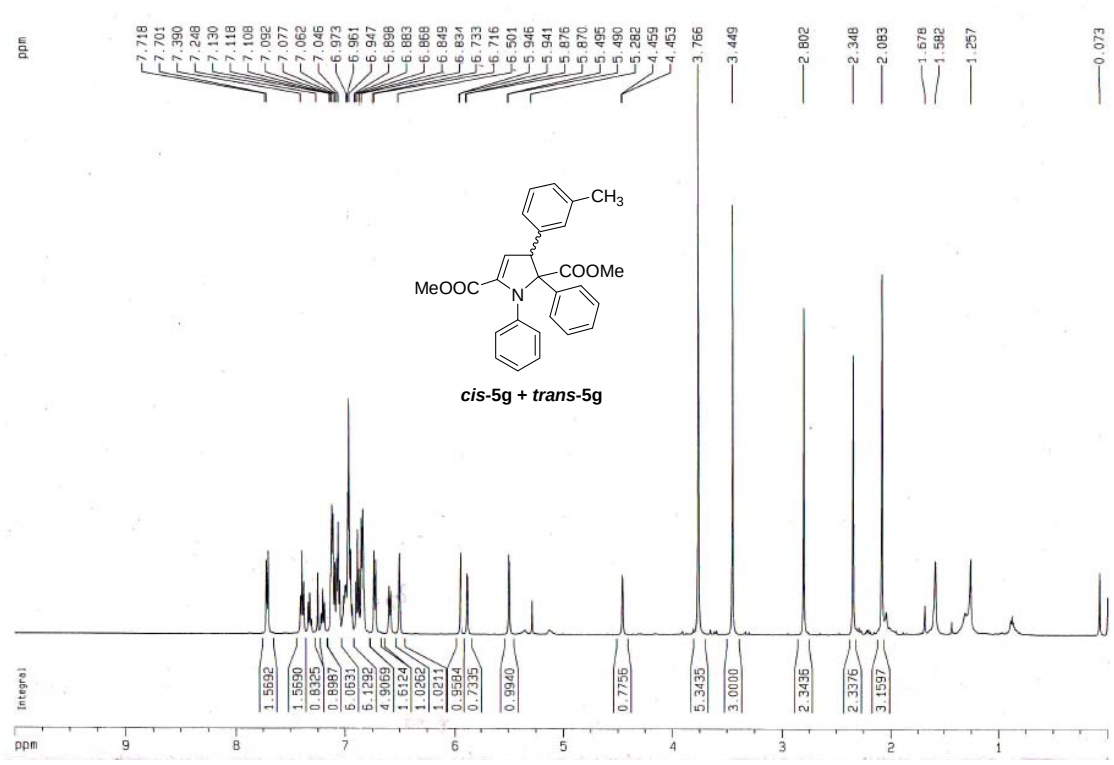

ppm
171.189
171.113
147.704
145.687
143.575
139.410
137.024
129.307
129.051
128.530
128.161
127.959
125.822
123.259
118.737
113.676
81.613
77.269
77.015
76.761
69.086
52.877
52.819
1.003
NO2
H
COOMe
MeOOC
N
trans-5e
ppm
180
160
140
120
100
80
60
40
20

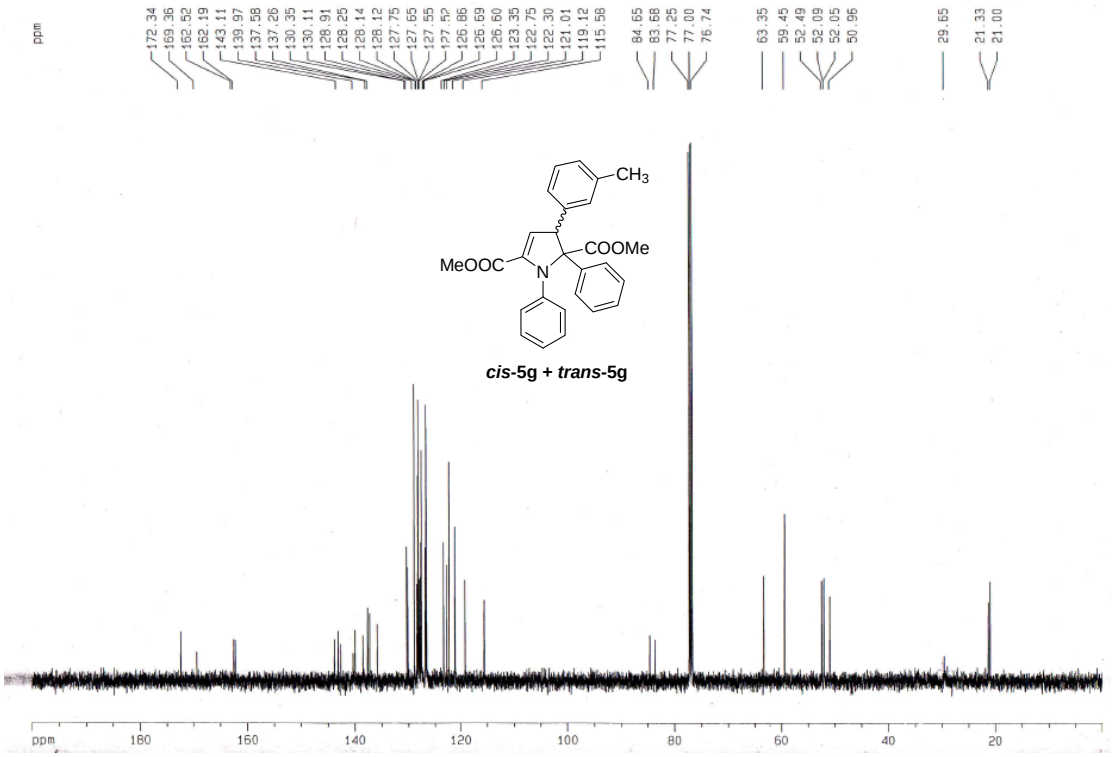

ppm
7.724
7.708
7.411
7.396
7.381
7.342
7.328
7.260
7.227
7.212
7.140
7.125
7.086
7.070
7.055
6.910
6.895
6.742
6.727
5.881
5.875
4.472
4.467
3.768
2.829
2.329
0.012
CH3
H
COOMe
MeOOC
N
cis-5f
Integral
2.0498
2.0138
1.0532
2.1174
1.9922
2.1819
1.0010
1.9700
0.9544
1.0054
3.0083
3.0000
3.1659
ppm
9
8
7
6
5
4
3
2
1

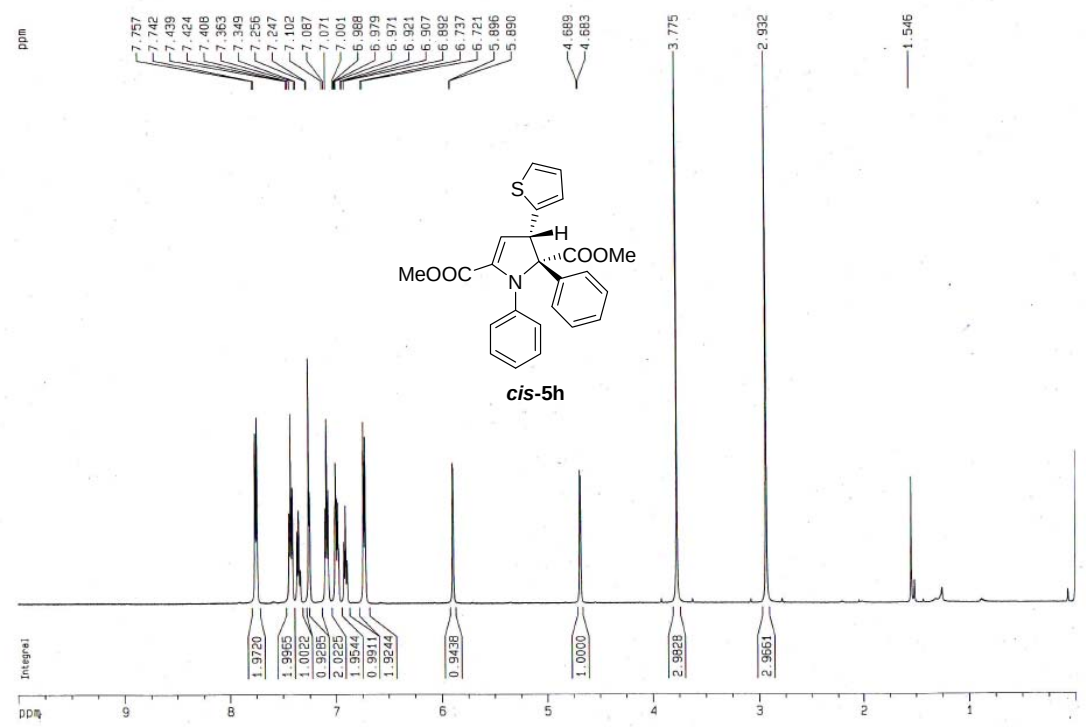

ppm
169.43
162.52
143.82
142.57
140.27
137.42
135.46
129.37
128.72
128.24
128.14
127.74
127.54
122.76
121.05
115.68
83.64
77.26
77.01
76.75
63.05
52.08
51.00
21.08
CH3
H
COOMe
MeOOC
N
cis-5f
ppm
180
160
140
120
100
80
60
40
20


ppm
7.250
7.113
7.097
7.082
7.015
7.001
6.981
6.966
6.950
6.945
6.934
6.835
6.819
6.806
6.791
6.649
6.633
5.946
5.941
5.478
5.473
3.759
3.470
2.818
2.317
2.185
1.571
1.258
0.072
0.001
CH3
H
COOMe
MeOOC
N
trans-5f
Integral
2.3216
5.2595
4.0916
2.0394
0.9390
0.9807
3.1715
3.0000
3.1355
ppm
9
8
7
6
5
4
3
2
1

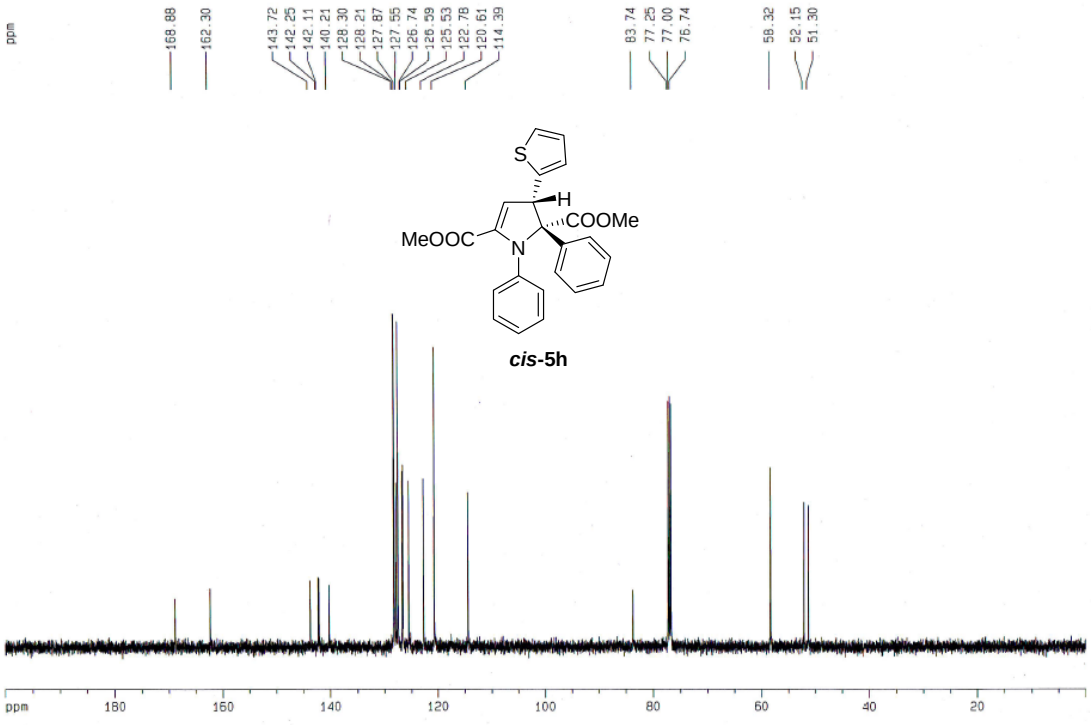

ppm
172.51
162.20
143.08
139.88
136.65
135.73
134.57
129.41
128.99
128.37
128.10
126.84
126.77
123.26
122.24
119.24
84.59
77.25
77.00
76.75
59.11
52.52
52.05
20.96
CH3
H
COOMe
MeOOC
N
trans-5f
ppm
180
160
140
120
100
80
60
40
20


ppm
7.718
7.701
7.390
7.248
7.130
7.118
7.108
7.092
7.077
7.062
7.046
6.973
6.961
6.947
6.898
6.883
6.868
6.849
6.834
6.733
6.716
6.501
5.946
5.941
5.876
5.870
5.495
5.490
5.282
4.459
4.453
3.766
3.449
2.802
2.348
2.083
1.678
1.582
1.257
0.073
CH3
COOMe
MeOOC
N
cis-5g + trans-5g
Integral
1.5692
1.5690
0.8325
0.8987
5.0531
5.1292
4.9069
1.6124
1.0262
1.0211
0.9584
0.7395
0.9940
0.7756
5.3435
3.0000
2.3436
2.3376
3.1597
ppm
9
8
7
6
5
4
3
2
1

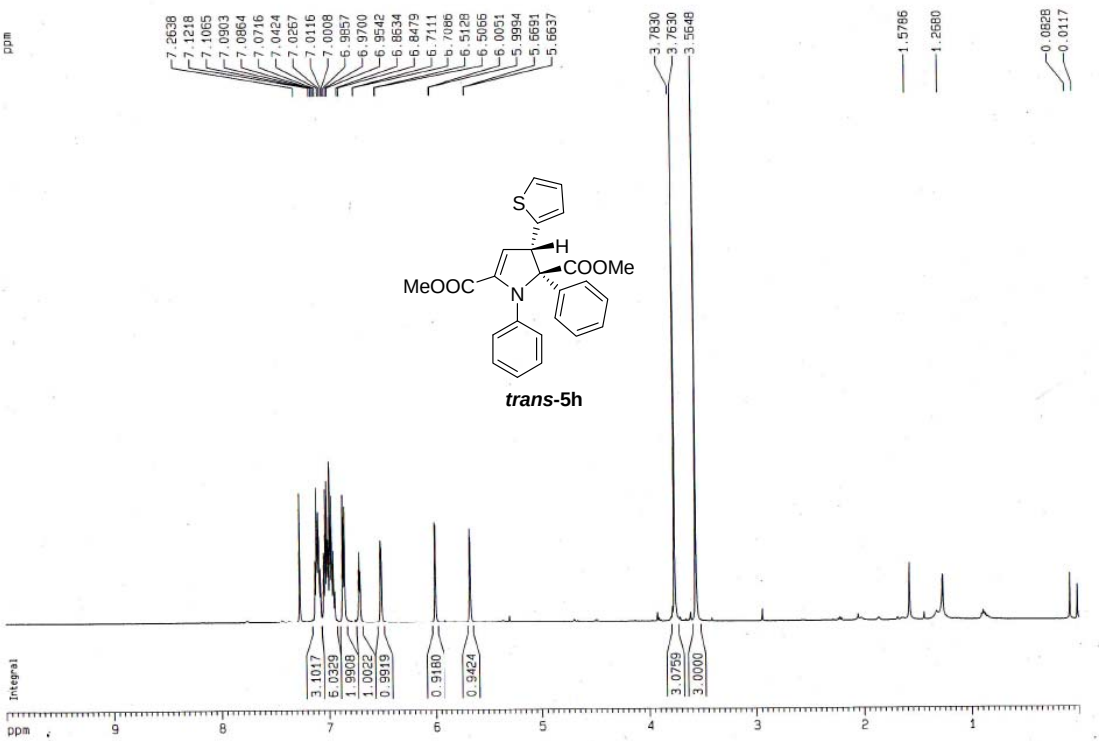

ppm
172.34
169.36
162.52
162.19
143.11
139.97
137.58
137.26
130.35
130.11
128.91
128.25
128.14
128.12
127.75
127.65
127.55
127.52
126.86
126.69
126.60
123.35
122.75
122.30
121.01
119.12
115.58
84.65
83.68
77.25
77.00
76.74
63.35
59.45
52.49
52.09
52.05
50.96
29.65
21.33
21.00
CH3
COOMe
MeOOC
N
cis-5g + trans-5g
ppm
180
160
140
120
100
80
60
40
20


ppm
7.757
7.742
7.439
7.424
7.408
7.363
7.349
7.256
7.247
7.102
7.087
7.071
7.001
6.988
6.979
6.971
6.921
6.907
6.892
6.737
6.721
5.896
5.890
4.689
4.683
3.775
2.932
1.546
S
H
COOMe
MeOOC
N
Integral
1.9720
1.9965
1.0022
0.9285
2.0225
1.9544
0.9911
1.9244
0.9438
1.0000
2.9828
2.9661
ppm
9
8
7
6
5
4
3
2
1

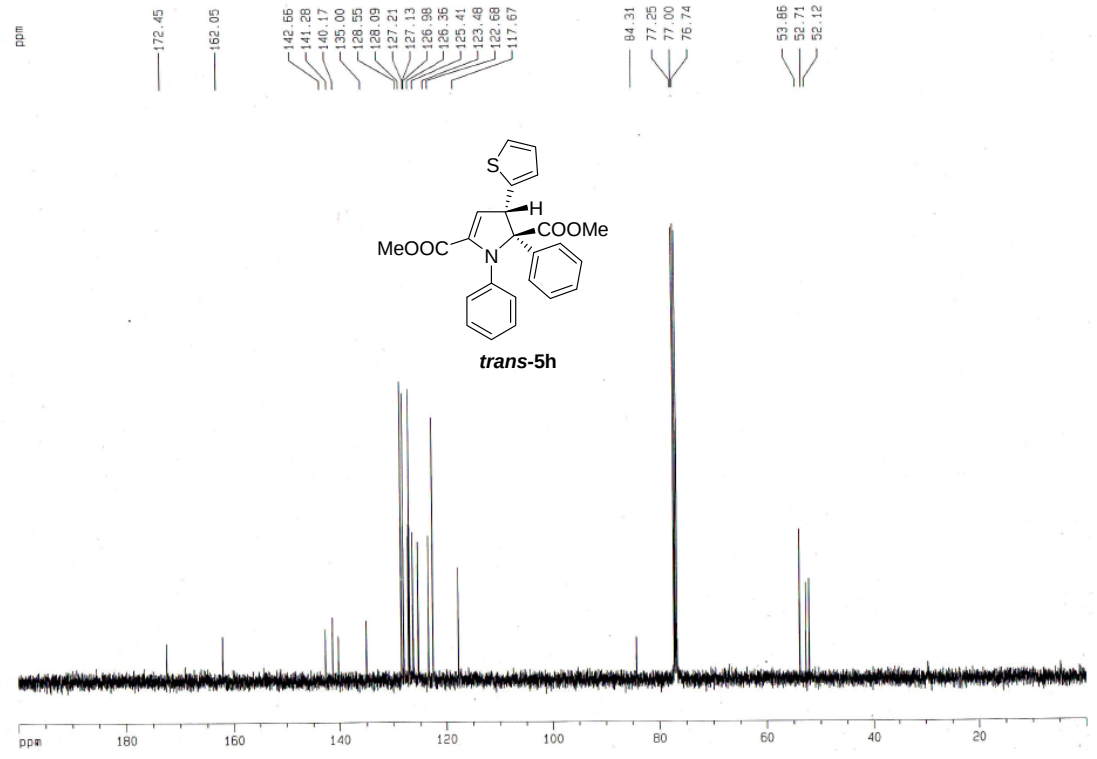
***cis*-5h**


ppm
168.88
162.30
143.72
142.25
142.11
140.21
128.30
128.21
127.87
127.55
126.74
126.59
125.53
122.78
120.61
114.39
83.74
77.25
77.00
76.74
58.32
52.15
51.30
S
H
COOMe
MeOOC
N
ppm
180
160
140
120
100
80
60
40
20

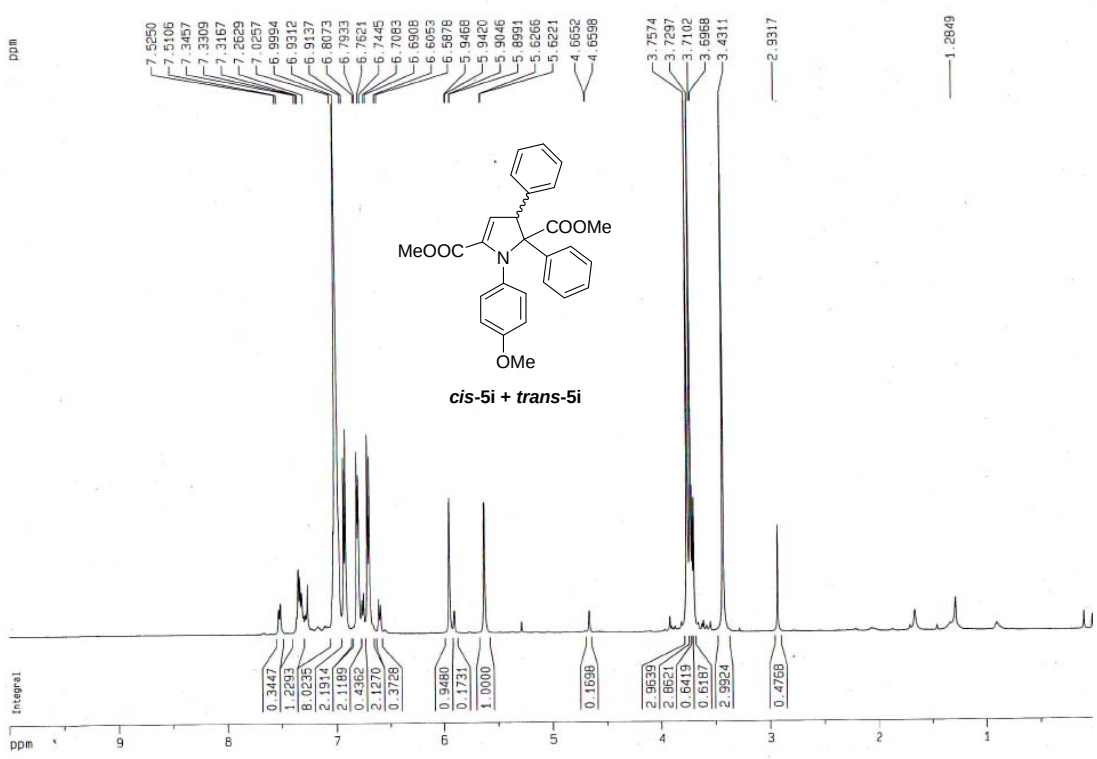
***cis*-5h**



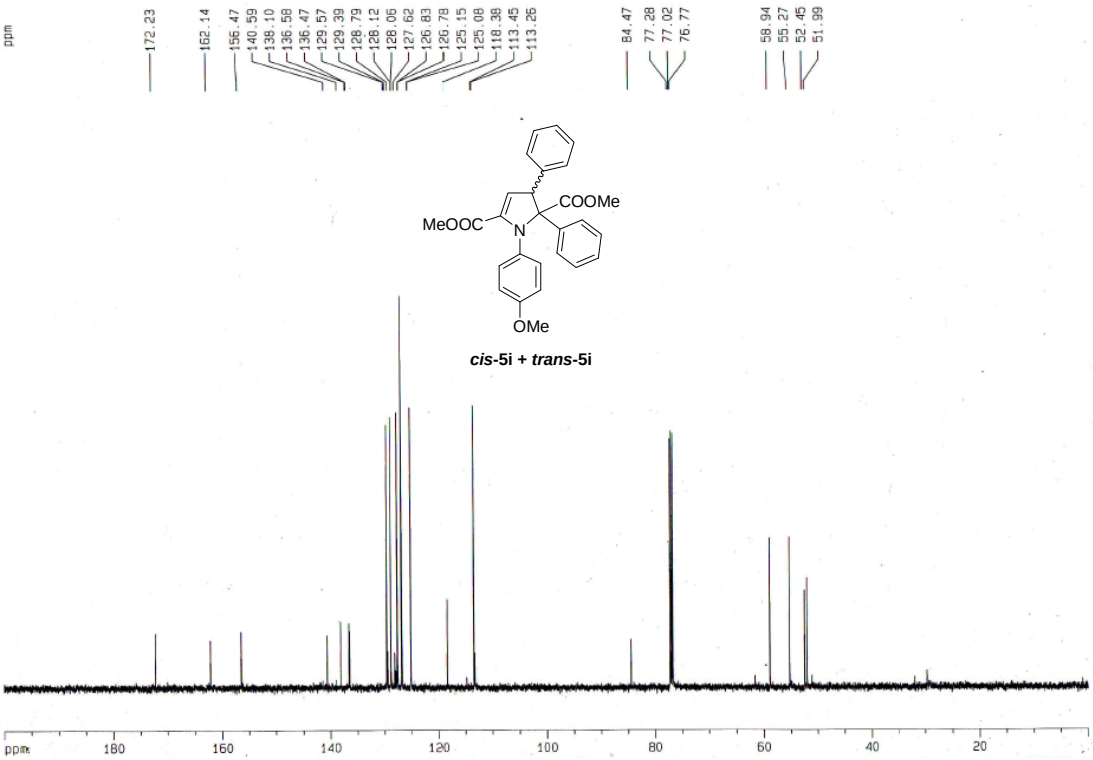
***trans*-5h**



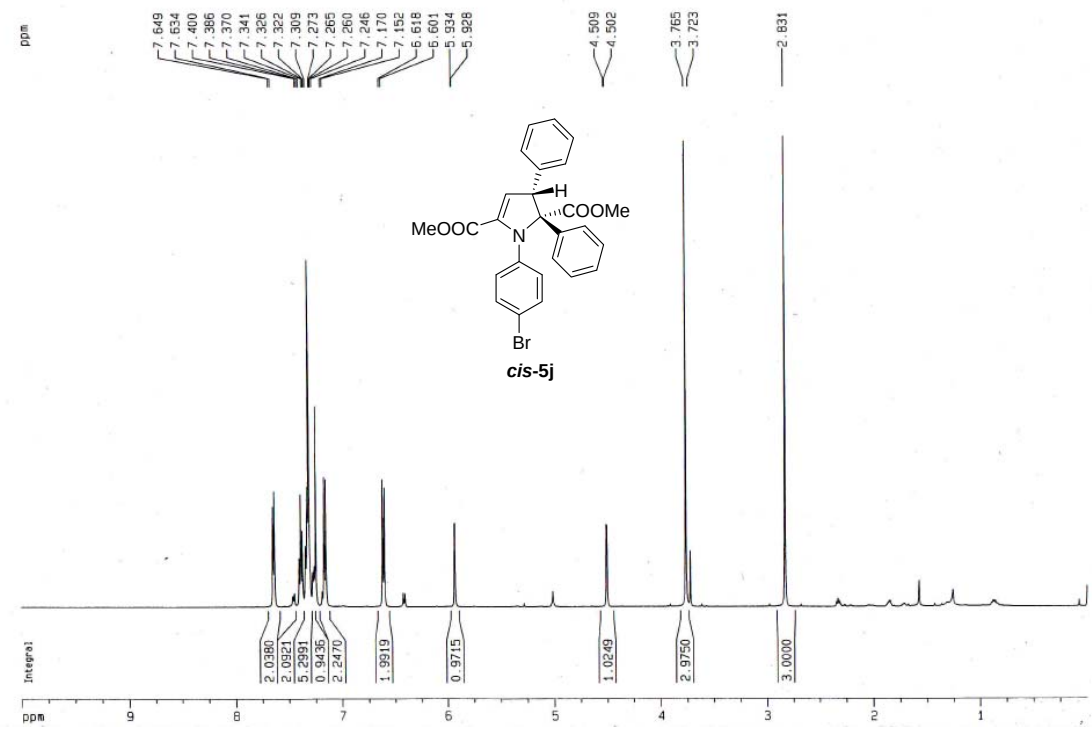
***trans*-5h**

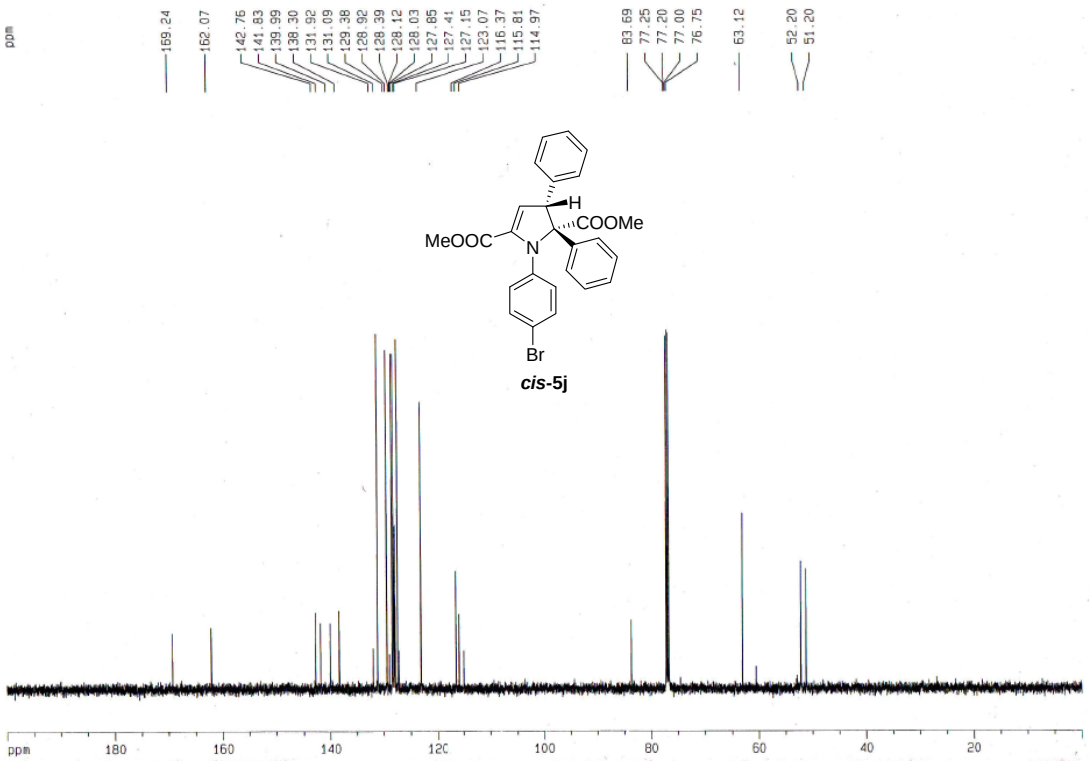


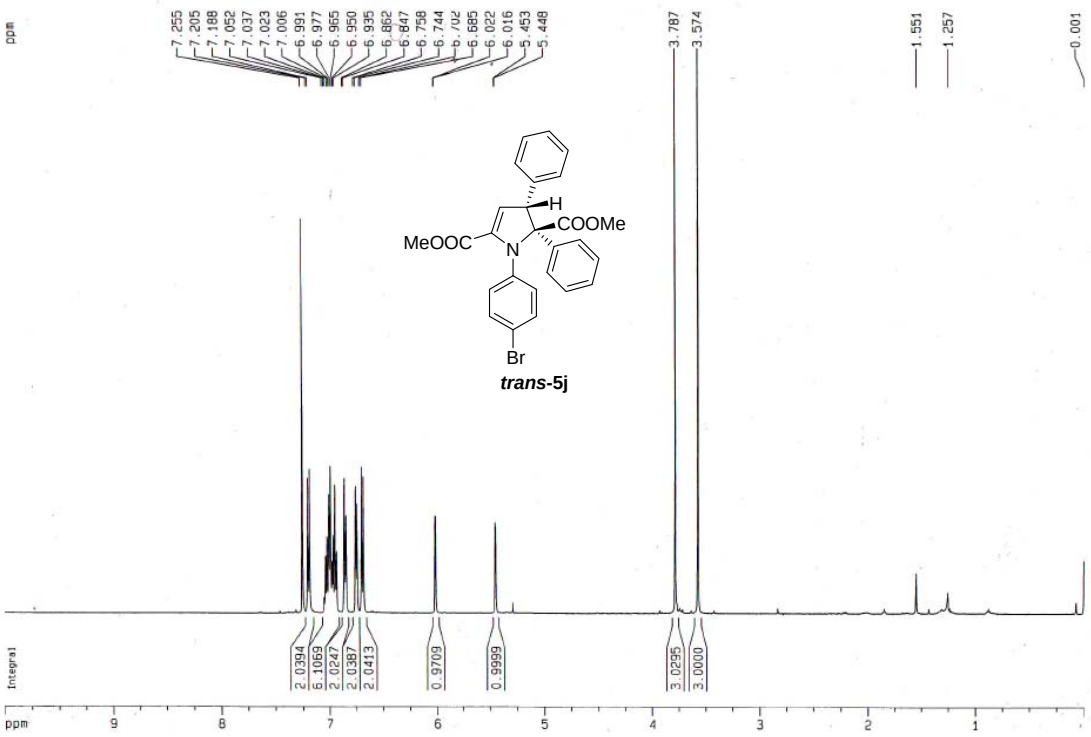
***cis*-5i + *trans*-5i**

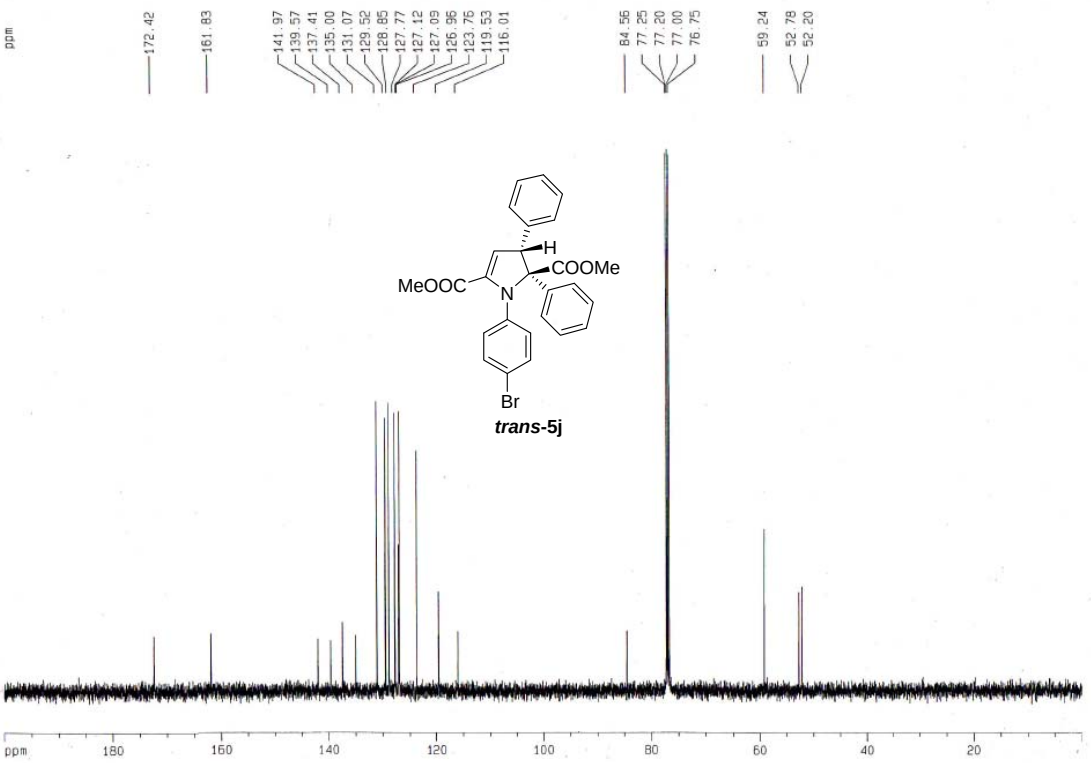


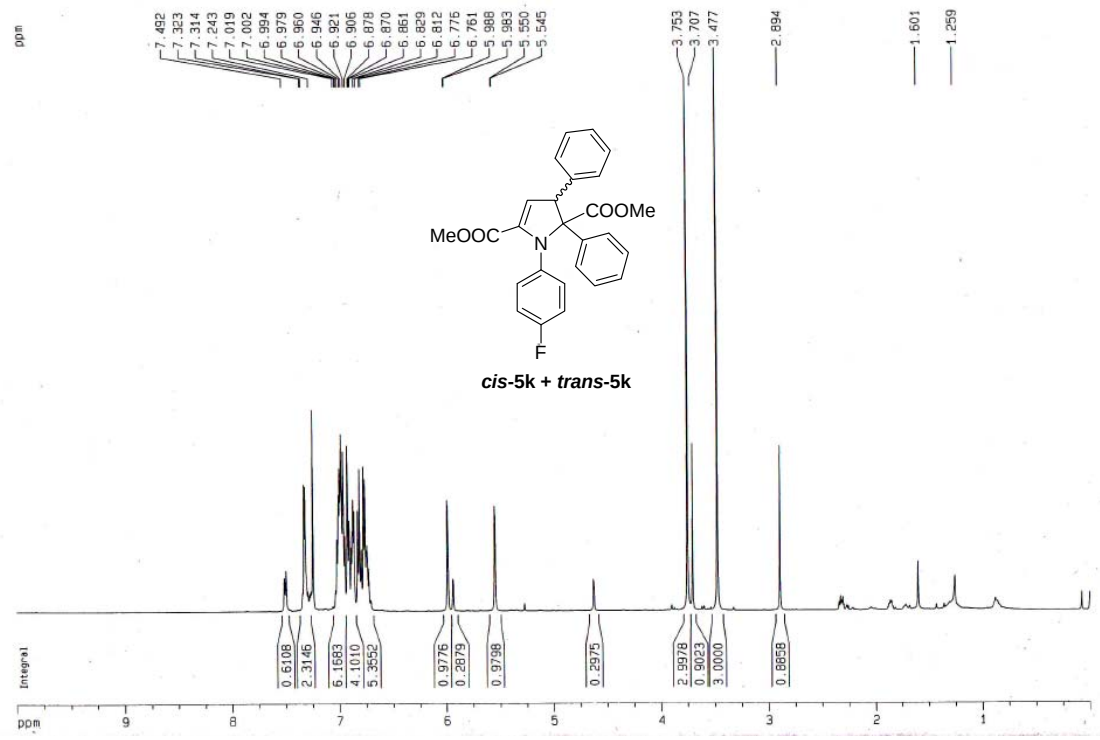
***cis*-5i + *trans*-5i**

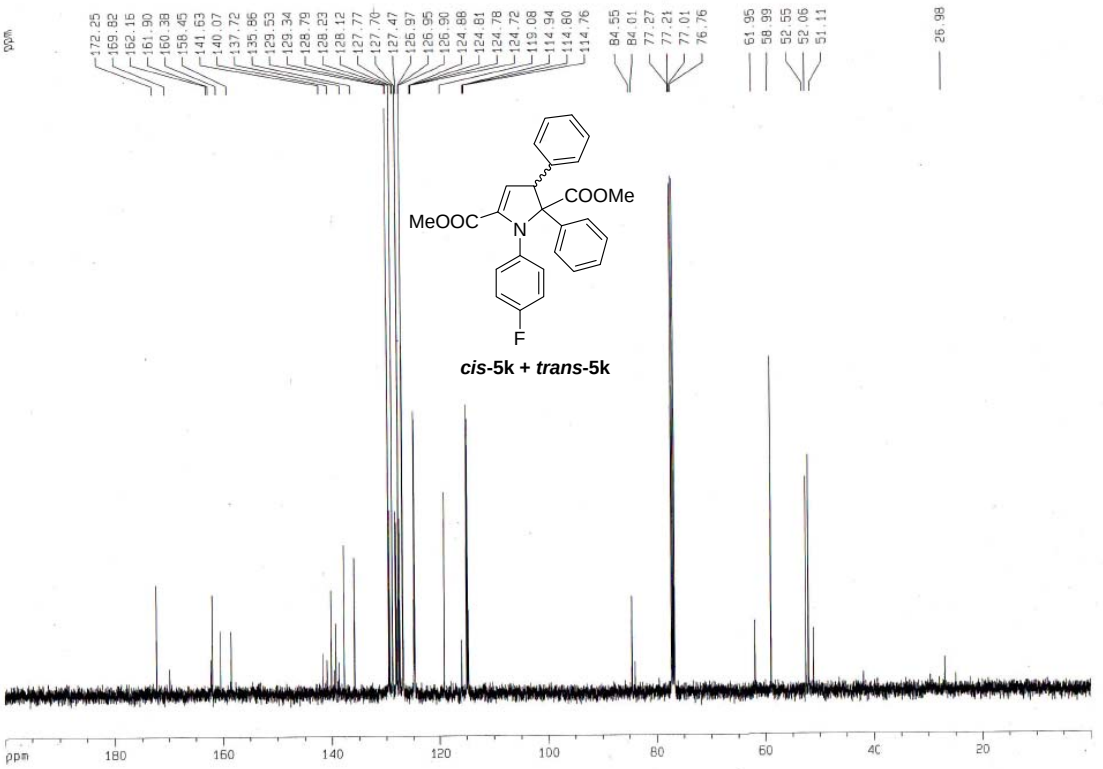

ppm
7.649
7.634
7.400
7.386
7.370
7.341
7.326
7.322
7.309
7.273
7.265
7.260
7.246
7.170
7.152
6.618
6.601
5.934
5.928
4.509
4.502
3.765
3.723
2.831
H
COOMe
MeOOC
N
Br
cis-5j
Integral
2.0380
2.0921
5.2991
0.9436
2.2470
1.9919
0.9715
1.0249
2.9750
3.0000
ppm

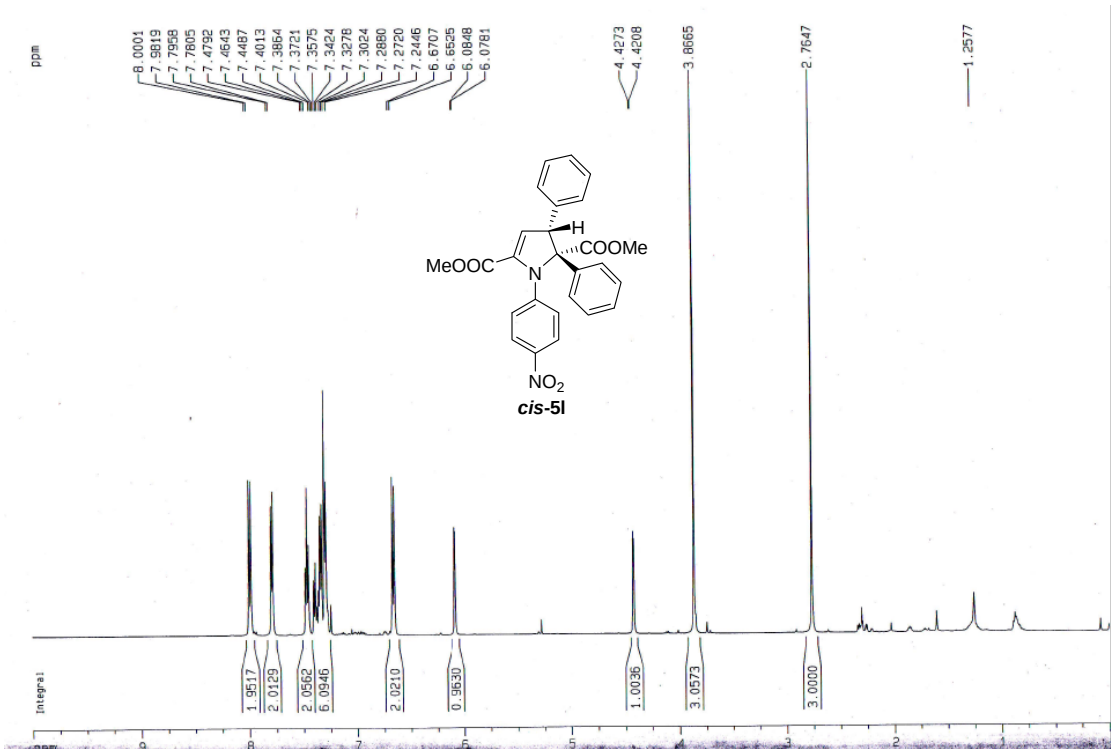

ppm
169.24
162.07
142.76
141.83
139.99
138.30
131.92
131.09
129.38
128.92
128.39
128.12
128.03
127.85
127.41
127.15
123.07
116.37
115.81
114.97
83.69
77.25
77.20
77.00
76.75
63.12
52.20
51.20
H
COOMe
MeOOC
N
Br
cis-5j
ppm

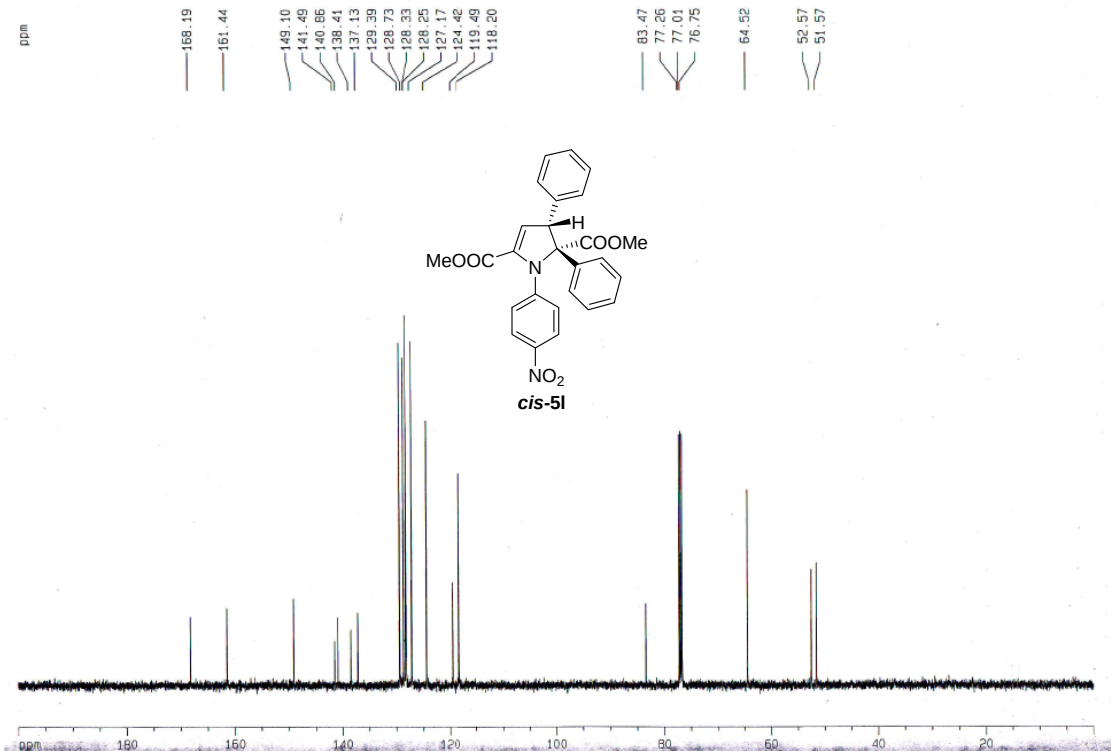

ppm
7.255
7.205
7.188
7.052
7.037
7.023
7.006
6.991
6.977
6.965
6.950
6.935
6.862
6.847
6.758
6.744
6.685
6.022
6.016
5.453
5.448
3.787
3.574
1.551
1.257
0.001
H
COOMe
MeOOC
N
Br
trans-5j
Integral
2.0394
6.1069
2.0247
2.0387
2.0413
0.9709
0.9999
3.0295
3.0000
ppm
9
8
7
6
5
4
3
2
1

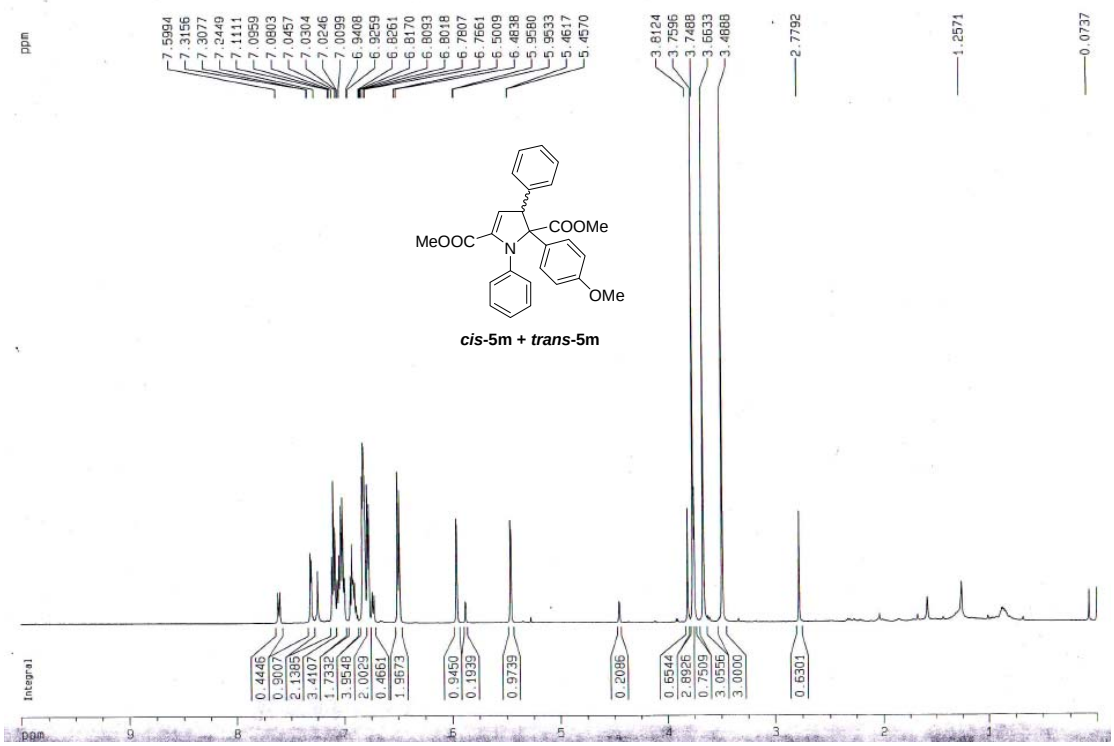

ppm
172.42
161.83
141.97
139.57
137.41
135.00
131.07
129.52
128.85
127.77
127.12
127.09
126.96
123.76
119.53
116.01
84.56
77.25
77.20
77.00
76.75
59.24
52.78
52.20
H
COOMe
MeOOC
N
Br
trans-5j
ppm
180
160
140
120
100
80
60
40
20

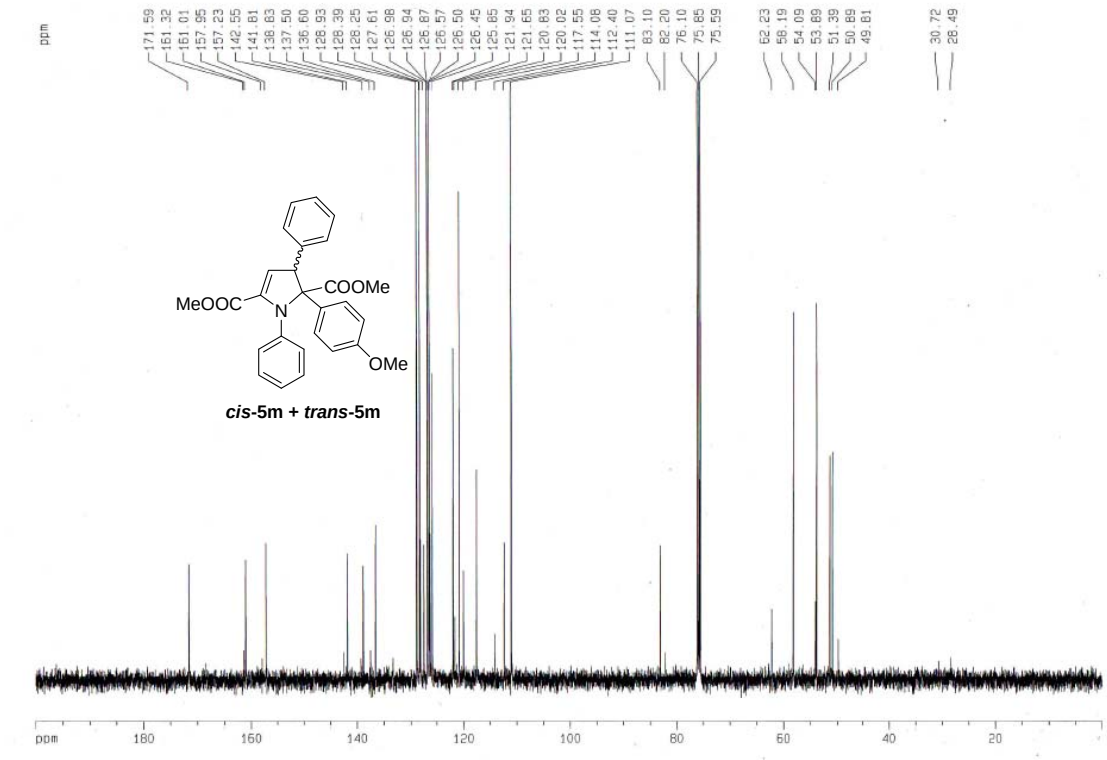

7.492
7.323
7.314
7.243
7.019
7.002
6.994
6.979
6.960
6.946
6.921
6.906
6.878
6.870
6.861
6.829
6.812
6.776
6.761
5.988
5.983
5.550
5.545
3.753
3.707
3.477
2.894
1.601
1.259
COOMe
MeOOC
N
F
cis-5k + trans-5k
Integral
0.6108
2.3146
6.1683
4.1010
5.3552
0.9776
0.2879
0.9798
0.2975
2.9978
0.9023
3.0000
0.8858
ppm

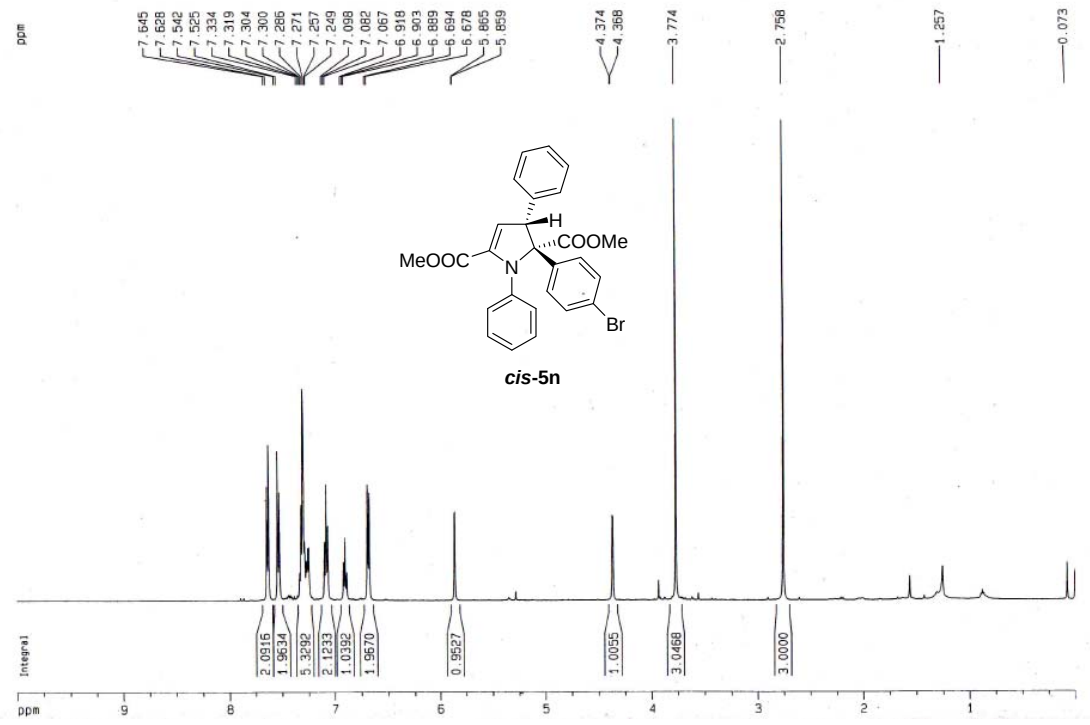

172.25
169.82
162.15
161.90
160.38
158.45
141.63
140.07
137.72
135.86
129.53
129.34
128.79
128.23
128.12
127.77
127.70
127.47
126.97
126.95
126.90
124.88
124.81
124.78
124.72
119.08
114.94
114.80
114.76
84.55
84.01
77.27
77.21
77.01
76.76
61.95
58.99
52.55
52.06
51.11
26.98
COOMe
MeOOC
N
F
cis-5k + trans-5k
ppm


ppm
8.0001
7.9819
7.7958
7.7805
7.4792
7.4643
7.4487
7.4013
7.3864
7.3721
7.3575
7.3424
7.3278
7.3024
7.2880
7.2720
7.2446
6.6707
6.6525
6.0848
6.0781
4.4273
4.4208
3.8665
2.7647
1.2577
MeOOC
COOMe
N
H
NO2
cis-5l
Integral
1.9517
2.0129
2.0562
6.0946
2.0210
0.9630
1.0036
3.0573
3.0000

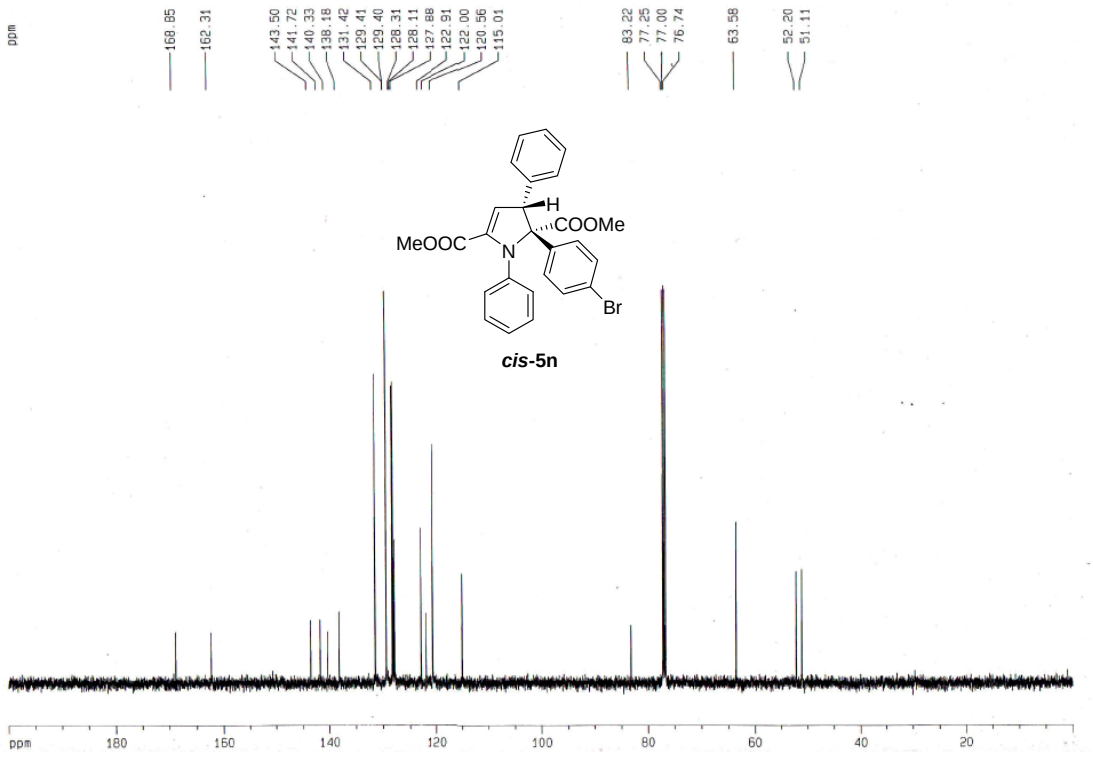

ppm
168.19
161.44
149.10
141.49
140.86
138.41
137.13
129.39
128.73
128.33
128.25
127.17
124.42
119.49
118.20
83.47
77.26
77.01
76.75
64.52
52.57
51.57
MeOOC
COOMe
N
H
NO2
cis-5l
180
160
140
120
100
80
60
40
20


MeOOC
COOMe
N
OMe
cis-5m + trans-5m

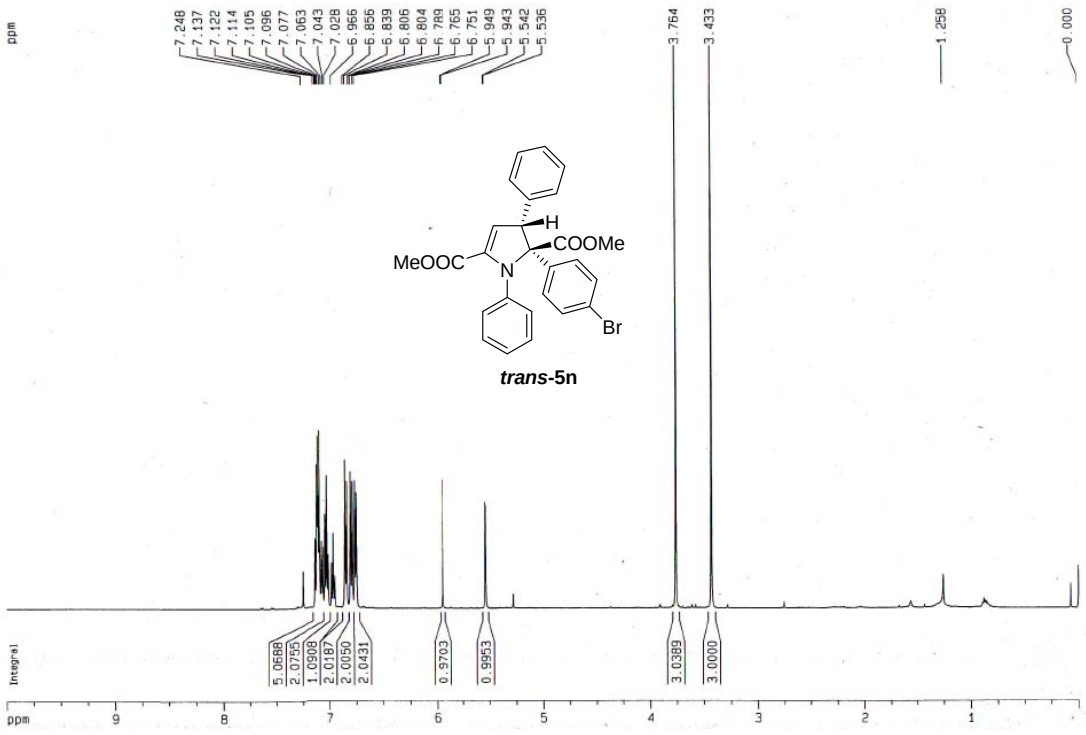

MeOOC
COOMe
N
OMe
cis-5m + trans-5m


ppm
7.645
7.628
7.542
7.525
7.334
7.319
7.304
7.300
7.286
7.271
7.257
7.249
7.098
7.082
7.067
6.918
6.903
6.889
6.694
6.678
5.865
5.859
4.374
4.368
3.774
2.758
1.257
0.073
H
COOMe
MeOOC
N
Br
Integral
2.0916
1.9634
5.3292
2.1233
1.0392
1.9670
0.9527
1.0055
3.0468
3.0000
ppm
9
8
7
6
5
4
3
2
1

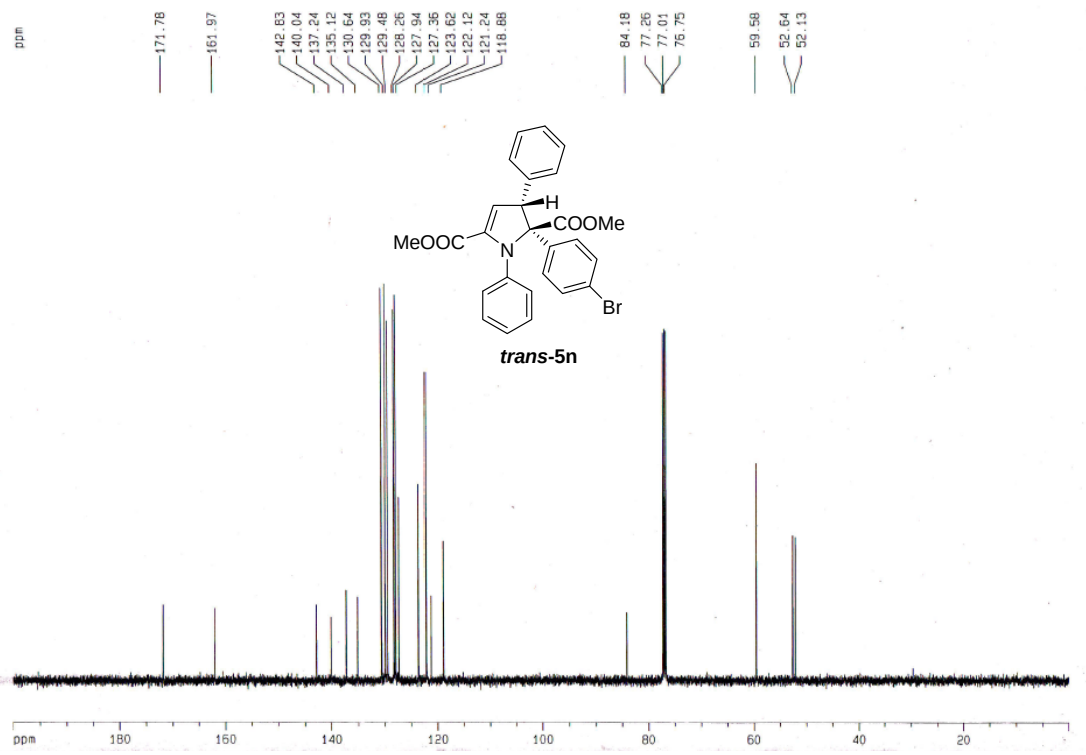
***cis*-5n**


ppm
168.85
162.31
143.50
141.72
140.33
138.18
131.42
129.41
129.40
128.31
128.11
127.88
122.91
122.00
120.56
115.01
83.22
77.25
77.00
76.74
63.58
52.20
51.11
H
COOMe
MeOOC
N
Br
ppm
180
160
140
120
100
80
60
40
20

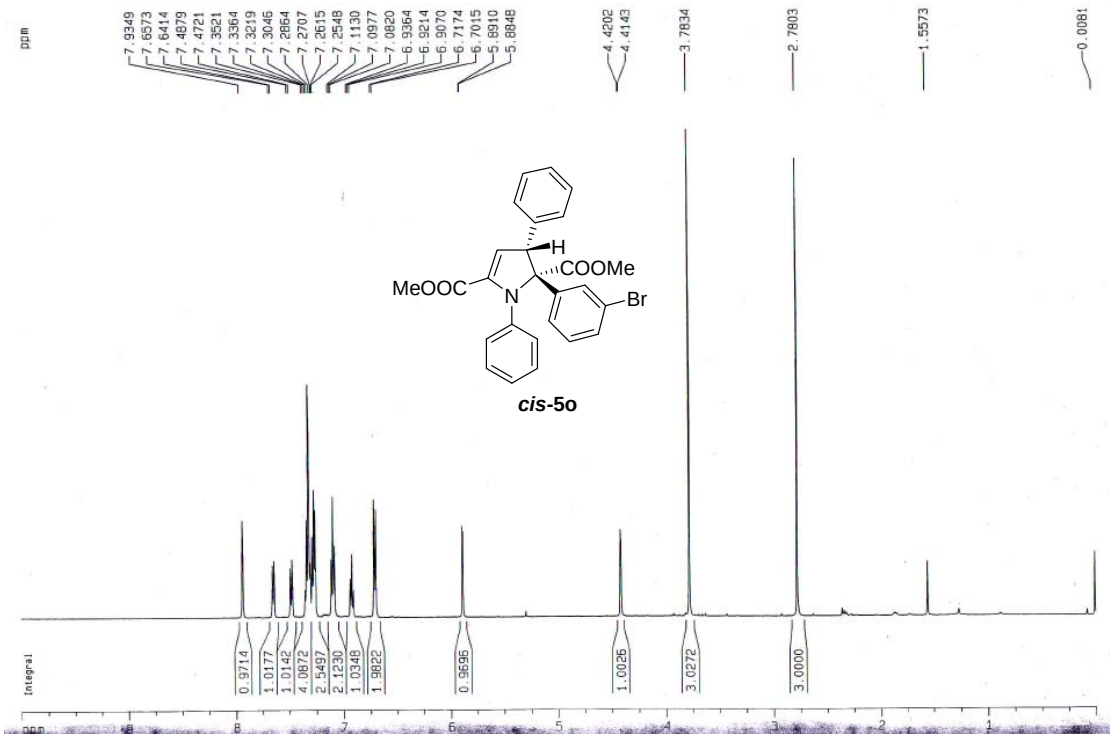
***cis*-5n**

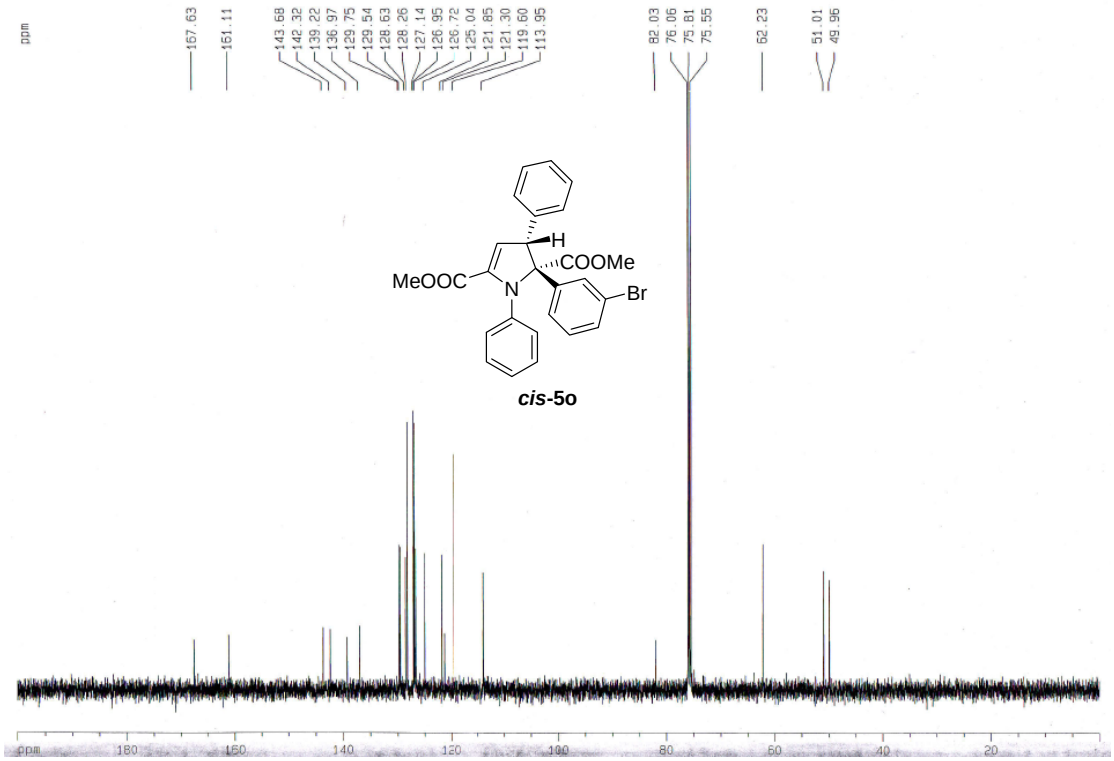


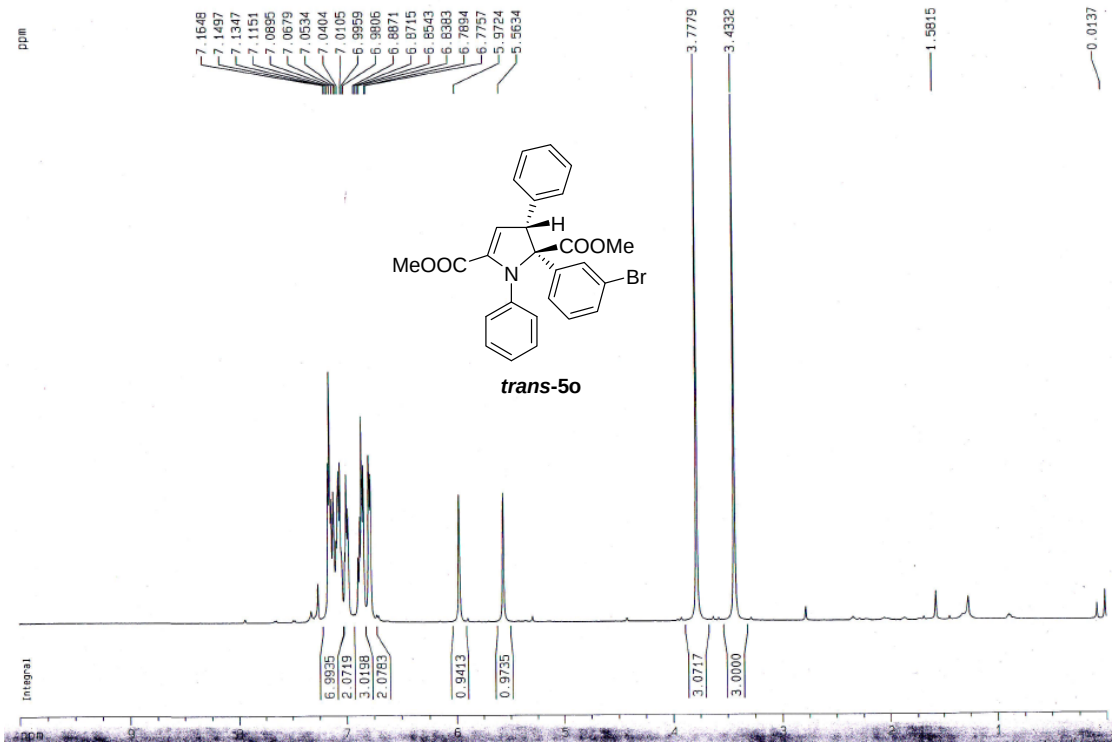
***trans*-5n**



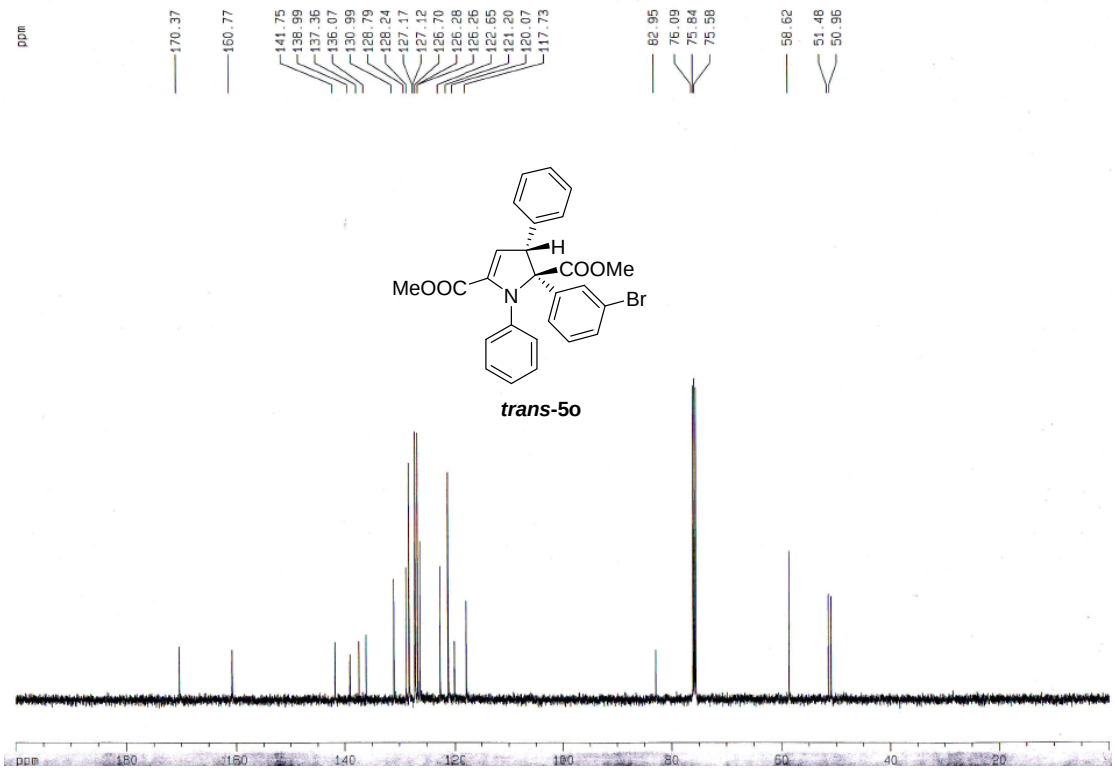
***trans*-5n**


ppm
7.9349
7.6573
7.6414
7.4879
7.4721
7.3521
7.3364
7.3219
7.3046
7.2864
7.2707
7.2615
7.2548
7.1130
7.0977
7.0820
6.9364
6.9214
6.9070
6.7174
6.7015
5.8910
5.8848
4.4202
4.4143
3.7834
2.7803
1.5573
0.0061
H
COOMe
MeOOC
N
Br
cis-5o
Integral
0.9714
1.0177
1.0142
4.0872
2.5497
2.1230
1.0348
1.9822
0.9695
1.0026
3.0272
3.0000


ppm
167.63
161.11
143.68
142.32
139.22
136.97
129.75
129.54
128.63
128.26
127.14
126.95
126.72
125.04
121.85
121.30
119.60
113.95
82.03
76.06
75.81
75.55
62.23
51.01
49.96
H
COOMe
MeOOC
N
Br
cis-5o



***trans*-5o**



***trans*-5o**