Electronic Supplementary Material (ESI) for ChemComm.

Visible Light Induced Cyclopropanation of Dibromomalonates with Alkenes via Double-SET by Photoredox Catalysis

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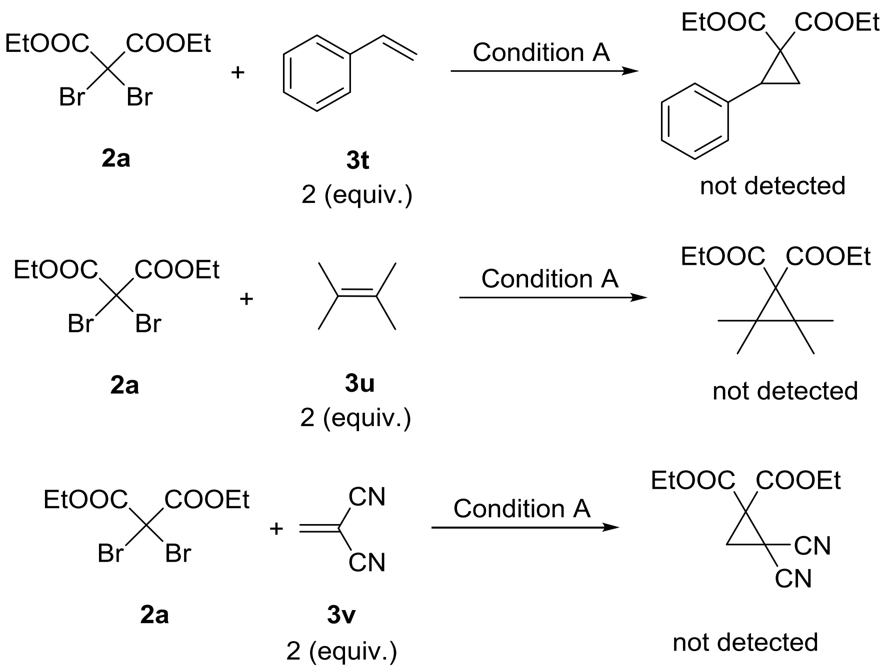
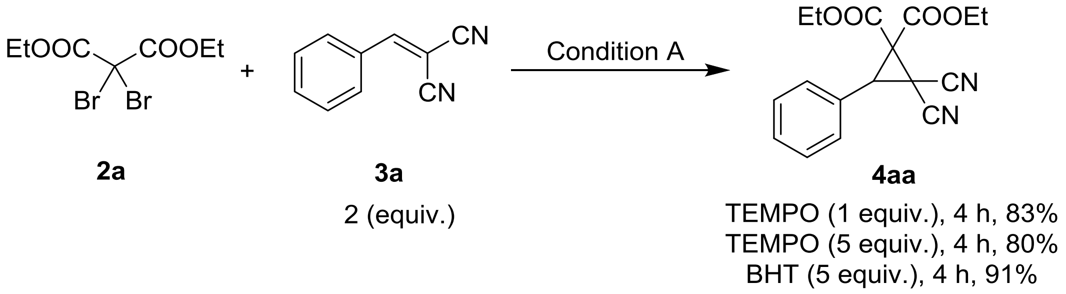
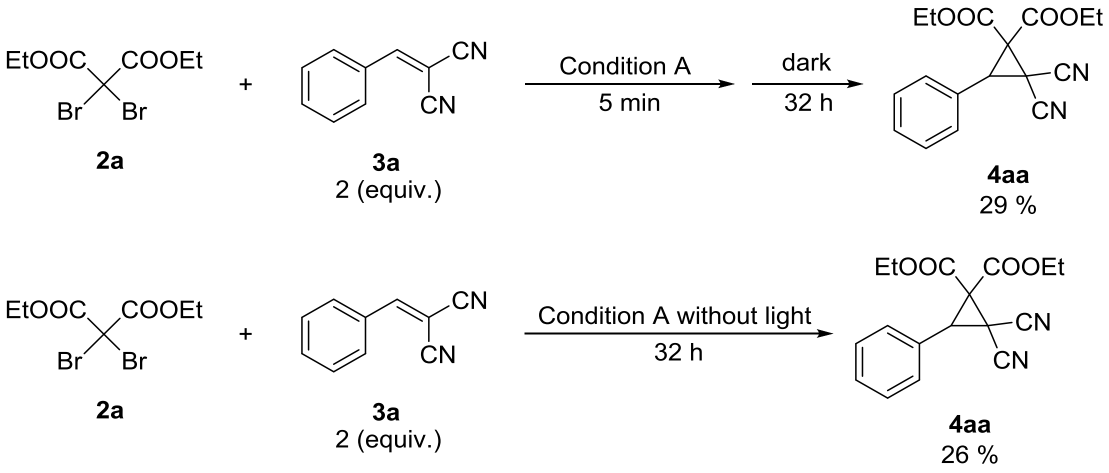


Scheme S1. Reactions of **2a** with **3t**, **3u**, and **3v** under Condition A



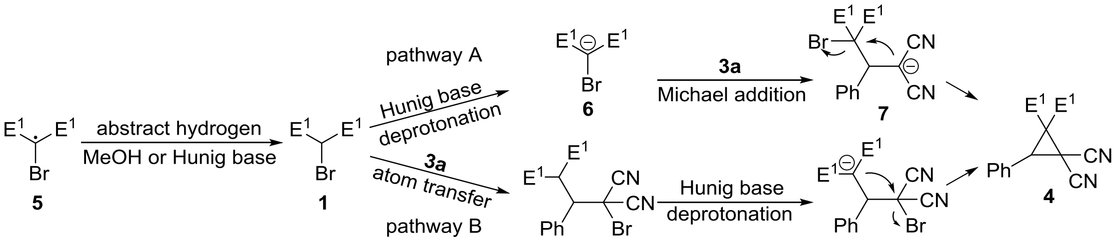
Scheme S2. Effect of radical scavenger



Scheme S3. The dark reaction

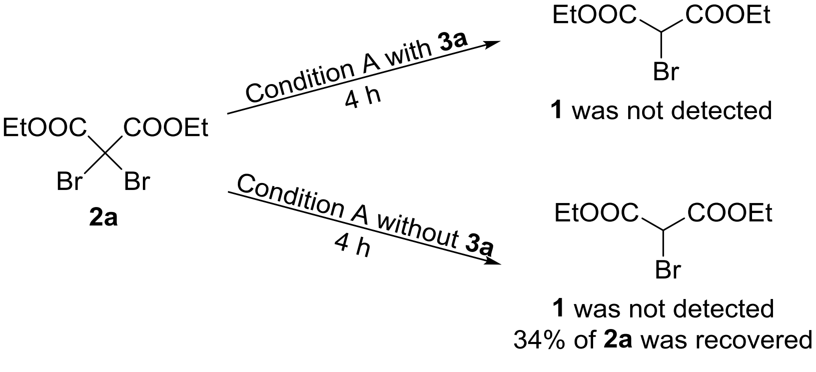
Detailed discussion on other possibilities of reaction pathways

Although the above results fitted well with our initially proposed mechanism as shown in Scheme 3, some other possibilities of reaction pathways should also be considered. One alternative mechanism could be envisaged that the initially formed radical intermediate **5** could abstract hydrogen from the solvent (MeOH) or the Hunig base[1] to form **1**. Then the *in situ* formed **1** might undergo deprotonation by the amine to afford the bromomalonate carbanion **6** which would undergo intermolecular Michael addition and intramolecular nucleophilic substitution (pathway A), or it might also be possible to undergo atom-transfer,[2] deprotonation by the amine, and intramolecular nucleophilic substitution to afford the final product (pathway B) (Scheme S4).



Scheme S4. Bromomalonate **1** involved mechanism

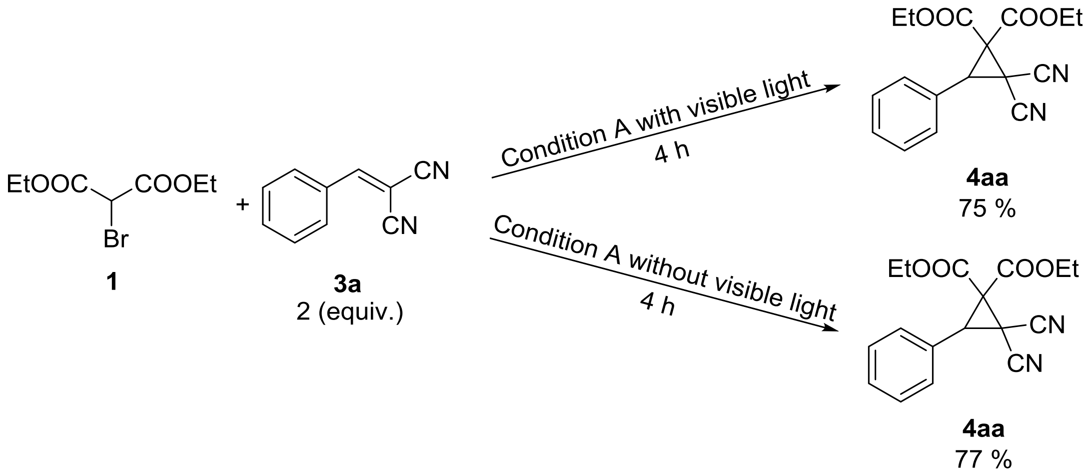
To explore these possibilities, we firstly tried to isolate or detect **1** from the reaction mixture before the reaction was completed. Disapprovingly, all attempts failed (Scheme S5).



Scheme S5. Detecting or isolating bromomalonate **1**

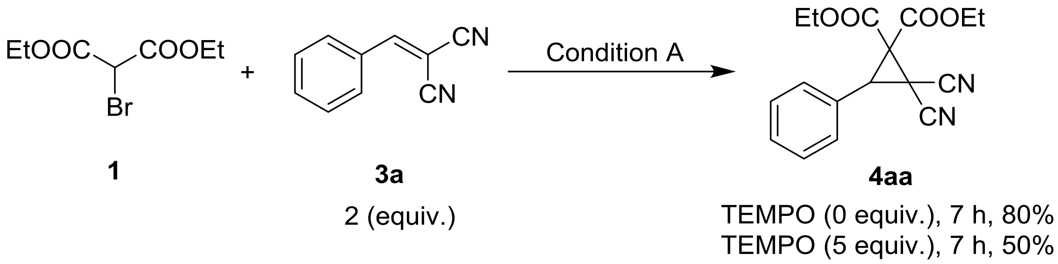
Then this reaction was carried out using aprotic solvent (benzene) under strictly anhydrous conditions. **4aa** was isolated in an 80% yield, which might be considered as negative evidence for the hypothesis that **5** abstracted hydrogen from the solvent (MeOH) to form **1**, since it is hard to abstract hydrogen from benzene. However, the possibility for the transformation of **6** into **1** could not be fully ruled out, since this might not be the rate-determining step.

Notably, the reaction of **1** with **3a** with or without light proceeded smoothly to form **4aa** in much lower yields (Scheme S6). If the reaction of **2a** with **3a** proceeded mainly via intermediate **1**, the final yield of **4aa** should be no more than 75% (Scheme S6) which is the yield of reaction with pure **1** as the starting material. However, an isolated yield as high as 92% (entry 5, Table 1) was afforded. This might be a proof showing the impossibility of the above hypothesis.



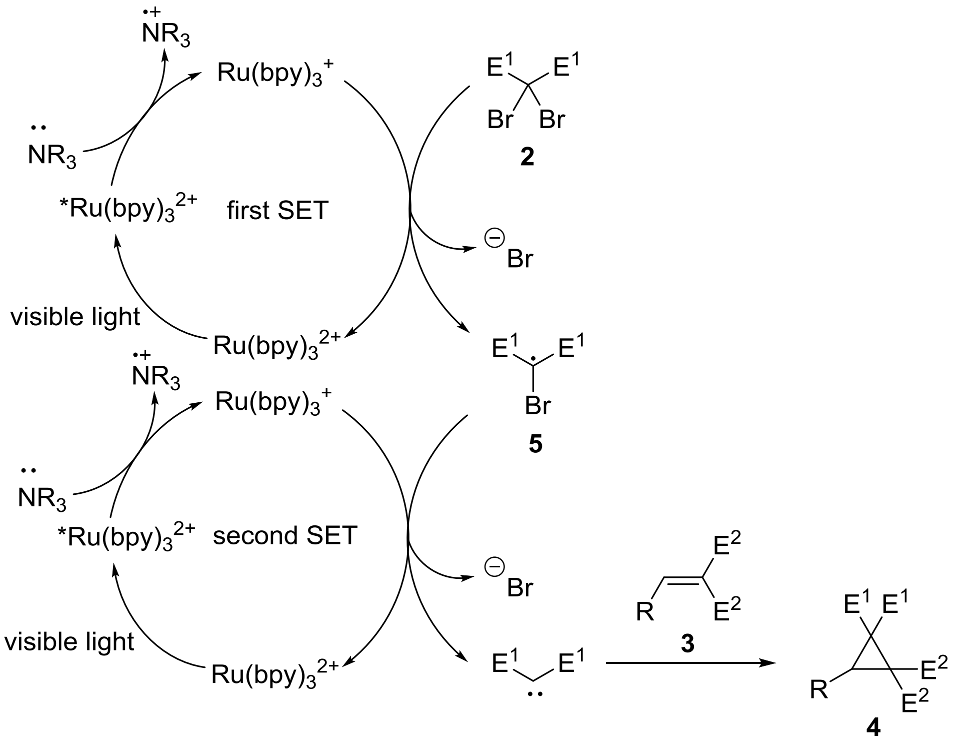
Scheme S6. Reactions of **1** with **3a** under Condition A with and without visible light

Finally, the reactions under Condition A using **1** instead of **2a** with and without TEMPO were studied. As shown in Scheme S7, the isolated yields of **4aa** in both cases became much lower. If this reaction proceeded mainly via intermediate **1**, the addition of 5 equiv. of TEMPO should decrease the final yield to at least 50% (Scheme S7) which is the yield of reaction with pure **1** as the starting material. However, an isolated yield as high as 80% (Scheme S2) was afforded. This might not support the above mechanism.

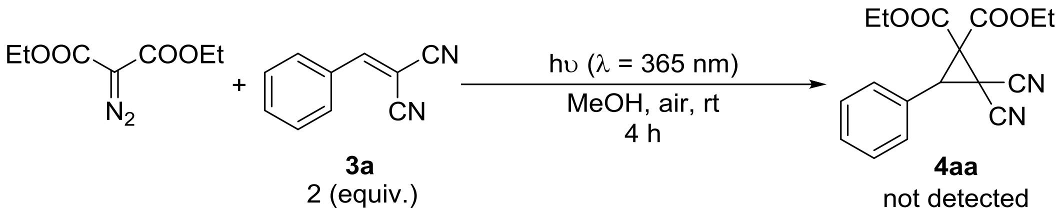


Scheme S7. The photocyclopropanation of **1** with and without TEMPO under Condition A

Additionally, a carbine intermediate involved mechanism (Scheme S8) was explored. The result of reaction of **2a** with **3u** under Condition A (Scheme S1) negatived this proposal, since **3u** is a typical reactant in such a carbine involved cyclopropanation.[3] Then a reported carbine precursor[4] was employed to check the possibility of carbine-involved mechanism, but also showed negative results (Scheme S9).



Scheme S8. Carbine intermediate involved mechanism



Scheme S9. Reaction of carbine precursor with **3a**

Experimental Section

The sunlight induced photoreactions were carried out by exposing the reaction tube to direct solar illumination in the daytime from 9:00 to 16:00 in a sunny day. A picture for the setup of this reaction is shown in Figure S1.

Figure S1. A picture for the setup of sunlight induced reaction.

The visible light induced photoreactions were carried out using a 23W household lamp at a distance of 3-5 cm with the reactor. A picture for the setup of this reaction is shown in Figure S2.

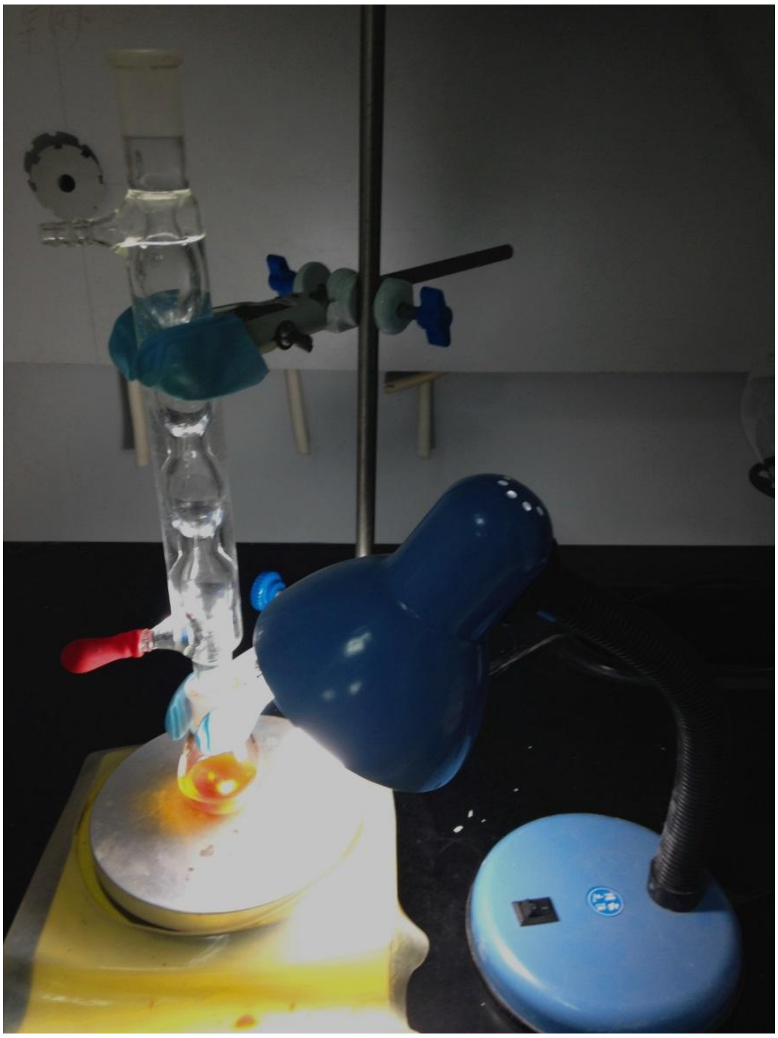


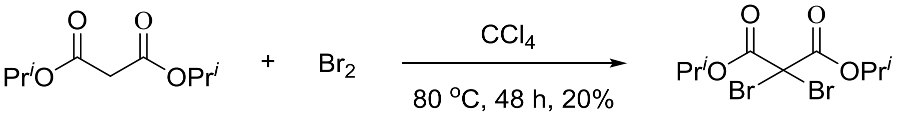
Figure S2. A picture for the setup of visible light induced reaction.

General information

All reactions were carried out using a pyrex reactor. IR spectra were recorded on a Avatar 360 FT-IR spectrometer. ^{1}H (400 MHz), ^{13}C (100 MHz), and ^{19}F (376 MHz) NMR spectra of samples in $CDCl_3$ were recorded on an AVANCE III 400 spectrometer. MS (EI, 70 eV) determinations were carried out on a HP 5973 spectrometer. MS (ESI) determinations were carried out on an Agilent 1100 LC/MSD SL spectrometer. HRMS (EI, 70 eV) determinations were carried out on a Water GCT CA176 spectrometer. HRMS (ESI) determinations were carried out on a Bruker

Daltonics APEXIII^{TM} ESI-FTICRMS spectrometer. Compound **3a, 3h, 3t, 3u** and ***Z*-8** was commercial available. Compounds **2b**,[5] **3a**,[6] **3b**,[7] **3c**,[7] **3d**,[8] **3e**,[9] **3f**,[10] **3g**,[7] **3i**,[6] **3j**,[11] **3k**,[11] **3l**,[12] **3m**,[12] **3n**,[13] **3o**,[7] **3p**,[11] **3q**,[7] **3r**,[14] **3s**,[15] and ***E*-8**[16] were prepared according to literature procedures.

Synthesis of Diisopropyl dibromomalonate (2c)

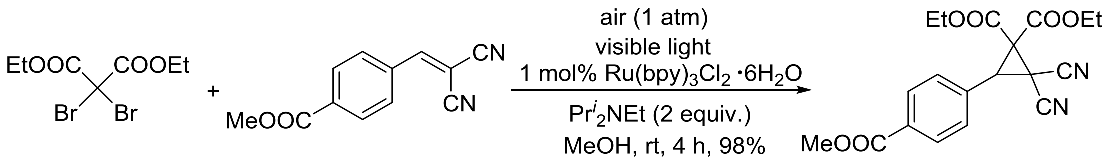


2c

Diisopropyl malonate (1.9 mL, 10.0 mmol) was added into a 100 mL three-necked flask. Then a solution of bromine (1.2 mL, 23.4 mmol) in carbon tetrachloride (10 mL) was added dropwise. The resulting reaction mixture was refluxed for 48 hours, and then cooled to room temperature, quenched by 5% Na_2CO_3 solution, and extracted with ethyl acetate (30 mL x 3). The combined organic layer was dried over $MgSO_4$. Filtration, concentration, and purification by flash chromatography on silica gel (eluent : petroleum ether→ethyl acetate/petroleum ether = 1/100) afforded **2c** as a liquid (690 mg, 20%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.21-5.08 (m, 2 H), 1.32 (d, J = 6.4 Hz, 12 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.6, 72.9, 51.9, 21.1; IR (neat) 1747 cm^{-1}; MS (ESI) m/z 369 (M+Na$^+$); HRMS (ESI) calcd for $C_9H_{14}Br_2Na_1O_4$ 366.9151, found 366.9163.

Typical Procedure I for the photoreaction under Condition A.

Synthesis of diethyl 2,2-dicyano-3-(4-methoxycarbonylphenyl)cyclopropane-1,1-dicarboxylate (4ab)

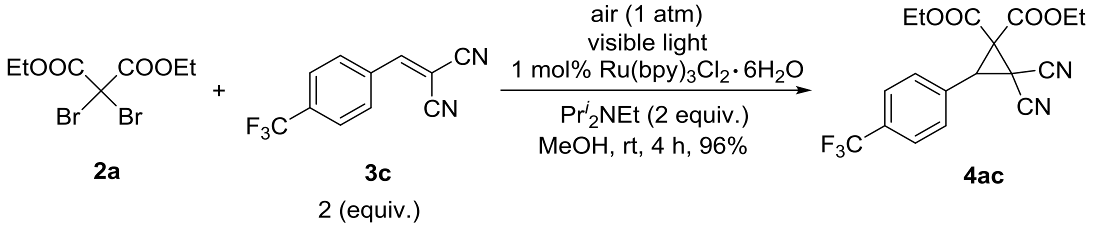


2a **3b** 2 (equiv.) **4ab**

2a (38 μL, 0.20 mmol), **3b** (86 mg, 0.41 mmol), $Ru(bpy)_3Cl_2\ 6H_2O$ (2 mg, 0.0027 mmol), Pr^i_2NEt (66 μL, 0.40 mmol), and anhydrous methanol (10 mL) were added to a dry 25 mL pyrex reaction flask. The mixture was irradiated by a 23W household lamp at rt in the open air. The photoreaction was completed after 4 h as monitored by TLC (eluent: petroleum ether/ethyl acetate = 10/1). The solvent was removed and the residue was purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 20/1→15/1→10/1) to afforded **4ab** as a solid (73 mg, 98%); mp 68.1-69.9 °C (ethyl acetate/petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, J = 8.8 Hz, 2 H), 7.48 (d, J = 8.8 Hz, 2 H), 4.44 (q, J = 7.2 Hz, 2 H), 4.30-4.19 (m, 2 H), 3.99 (s, 1 H), 3.93 (s, 3 H), 1.40 (t, J = 7.2 Hz, 3 H), 1.20 (t, J = 7.2 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 162.7, 160.8, 132.0, 131.2, 130.1, 128.9, 111.4, 109.4, 64.5, 63.7, 52.3, 46.0, 39.4, 16.2, 13.8, 13.5; IR (neat) 2253, 1745, 1720, 1612, 1440 cm^{-1}; MS (EI, 70 eV) m/z 370 (M^{+}, 0.51), 266 (100); HRMS (EI, 70 eV) calcd for $C_{19}H_{18}N_2O_6$ 370.1165, found 370.1160.

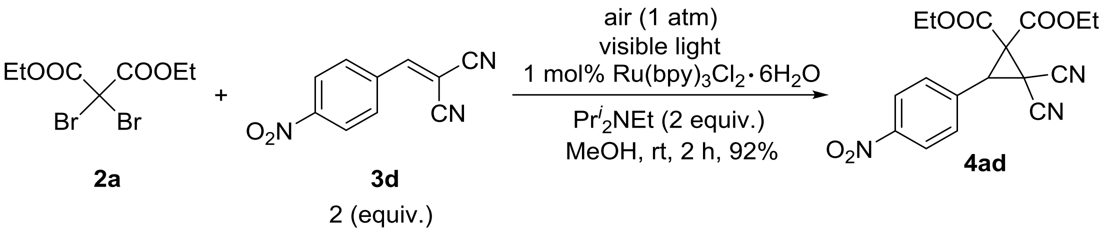
The following compounds were prepared according to Typical Procedure I.

(1) Diethyl 2,2-dicyano-3-(4-trifluoromethylphenyl)cyclopropane-1,1-dicarboxylate (4ac)



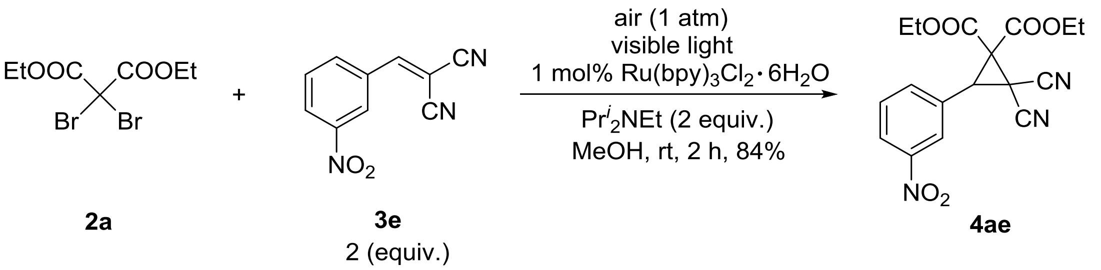
The reaction of **2a** (38 μL, 0.20 mmol), **3c** (92 mg, 0.41 mmol), $Ru(bpy)_3Cl_2$ $6H_2O$ (2 mg, 0.0027 mmol), Pr$^{i}_{2}$NEt (68 μL, 0.41 mmol), and anhydrous methanol (10 mL) afforded **4ac** as a solid (73 mg, 96%); mp 148.9-151.3 °C (ethyl acetate/petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, J = 8.4 Hz, 2 H), 7.54 (d, J = 8.4 Hz, 2 H), 4.44 (q, J = 7.2 Hz, 2 H), 4.32-4.21 (m, 2 H), 4.00 (s, 1 H), 1.39 (t, J = 7.2 Hz, 3 H), 1.21 (t, J = 7.2 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.6, 160.7, 131.6 (q, J = 32.9 Hz), 131.3, 129.4, 125.9 (q, J = 3.6 Hz), 123.4 (q, J = 270.7 Hz), 111.4, 109.4, 64.6, 63.8, 46.1, 39.1, 16.2, 13.7, 13.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.4 ppm; IR (neat) 2250, 1741,1321 cm^{-1}; MS (EI, 70 eV) m/z 380 (M^{+}, 1.52), 209 (100); HRMS (EI, 70 eV) calcd for $C_{18}H_{15}N_2O_4F_3$ 380.0984, found 380.0979.

(2) Diethyl 2,2-dicyano-3-(4-nitrophenyl)cyclopropane-1,1-dicarboxylate (4ad)



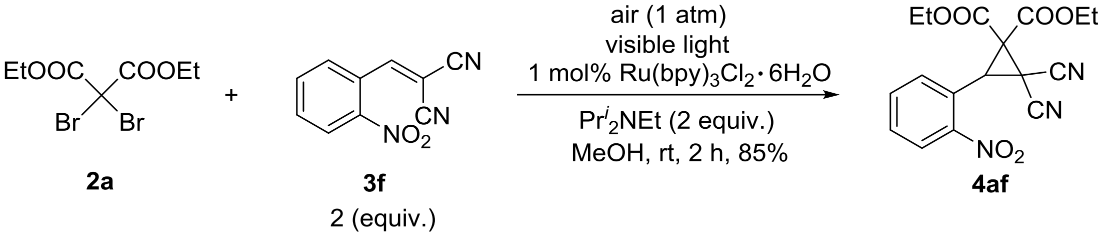
The reaction of **2a** (38 μL, 0.20 mmol), **3d** (80 mg, 0.40 mmol), Ru(bpy)$_3$Cl$_2$ 6H$_2$O (2 mg, 0.0027 mmol), Pr$^i{}_2$NEt (66 μL, 0.40 mmol), and anhydrous methanol (10 mL) afforded **4ad** as a solid (66 mg, 92%); mp 113.0-114.2 °C (ethyl acetate/petroleum ether). ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.29 (d, *J* = 8.8 Hz, 2 H), 7.62 (d, *J* = 8.8 Hz, 2 H), 4.46 (q, *J* = 6.8 Hz, 2 H), 4.33-4.22 (m, 2 H), 4.02 (s, 1 H), 1.41 (t, *J* = 6.8 Hz, 3 H), 1.25 (t, *J* = 6.8 Hz, 3 H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 162.6, 160.5, 148.4, 134.2, 130.2, 124.2, 111.1, 109.2, 64.9, 64.1, 46.1, 38.9, 16.3, 13.9, 13.6; IR (neat) 2256, 1744, 1610, 1528, 1351 cm^{-1}; MS (EI, 70 eV) m/z 357 (M$^+$, 5.15), 257 (100); HRMS (EI, 70 eV) calcd for $C_{17}H_{15}N_3O_6$ 357.0961, found 357.0964.

(3) Diethyl 2,2-dicyano-3-(3-nitrophenyl)cyclopropane-1,1-dicarboxylate (4ae)



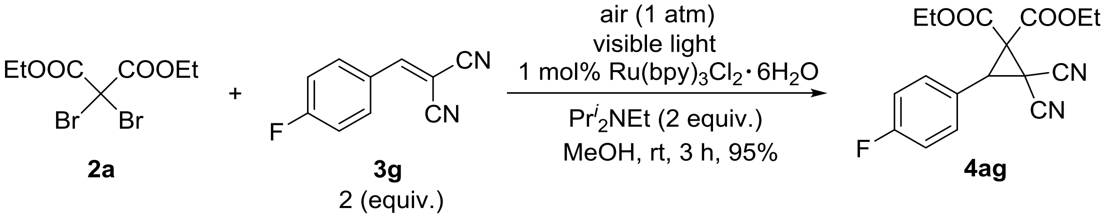
The reaction of **2a** (38 μL, 0.20 mmol), **3e** (78 mg, 0.39 mmol), Ru(bpy)$_3$Cl$_2$ 6H$_2$O (2 mg, 0.0027 mmol), Pr$^i{}_2$NEt (66 μL, 0.40 mmol), and anhydrous methanol (10 mL) afforded **4ae** as a solid (60 mg, 84%); mp 109.5-110.4 °C (ethyl acetate/petroleum ether). ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.33-8.25 (m, 2 H), 7.80 (d, *J* = 7.6 Hz, 1 H), 7.66 (t, *J* = 7.2 Hz, 1 H), 4.46 (q, *J* = 6.8 Hz, 2 H), 4.37-4.25 (m, 2 H), 4.04 (s, 1 H), 1.41 (t, *J* = 6.8 Hz, 3 H), 1.28 (t, *J* = 6.8 Hz, 3 H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 162.5, 160.6, 148.4, 135.0, 130.4, 129.4, 124.6, 124.2, 111.1, 109.2, 64.8, 64.2, 46.1, 38.8, 16.4, 13.9, 13.6; IR (neat) 2253, 1744, 1537 cm^{-1}; MS (EI, 70 eV) m/z 357 (M$^+$, 1.08), 257 (100); HRMS (EI, 70 eV) calcd for $C_{17}H_{15}N_3O_6$ 357.0961, found 357.0957.

(4) Diethyl 2,2-dicyano-3-(2-nitrophenyl)cyclopropane-1,1-dicarboxylate (4af)



The reaction of **2a** (38 μL, 0.20 mmol), **3f** (83 mg, 0.42 mmol), $Ru(bpy)_3Cl_2$ $6H_2O$ (2 mg, 0.0027 mmol), Pr^i_2NEt (66 μL, 0.40 mmol), and anhydrous methanol (10 mL) afforded **4af** as a solid (61 mg, 85%); mp 73.1-74.3 °C (ethyl acetate/petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, J = 8.0 Hz, 1 H), 7.80-7.69 (m, 2 H), 7.65 (t, J = 7.2 Hz, 1 H), 4.46 (q, J = 7.2 Hz, 2 H), 4.36 (s, 1 H), 4.17 (q, J = 6.8 Hz, 2 H), 1.41 (t, J = 6.8 Hz, 3 H), 1.19 (t, J = 6.8 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.8, 160.7, 149.1, 134.0, 130.9, 130.7, 125.6, 123.3, 110.9, 110.0, 64.5, 63.8, 45.1, 40.0, 16.9, 13.8, 13.4; IR (neat) 2253, 1741, 1534 cm^{-1}; MS (ESI) m/z 380 (M+Na$^+$); HRMS (ESI) calcd for $C_{17}H_{15}N_3Na_1O_6$ 380.0853, found 380.0859.

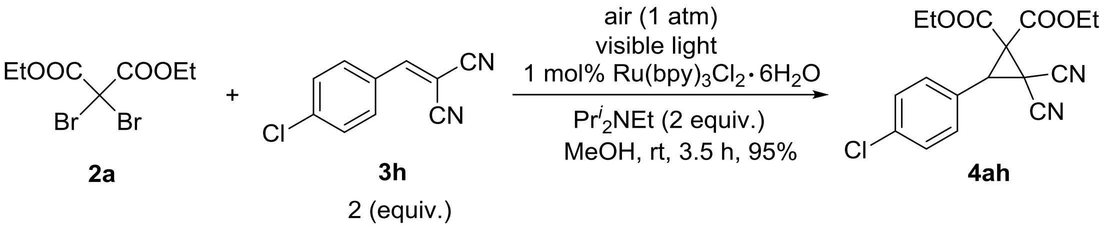
(5) Diethyl 2,2-dicyano-3-(4-fluorophenyl)cyclopropane-1,1-dicarboxylate (4ag)



The reaction of **2a** (38 μL, 0.20 mmol), **3g** (71 mg, 0.41 mmol), $Ru(bpy)_3Cl_2$ $6H_2O$ (2 mg, 0.0027 mmol), Pr^i_2NEt (66 μL, 0.40 mmol), and anhydrous methanol (10 mL) afforded **4ag** as a solid (63 mg, 95%); mp 73.3-75.2 °C (ethyl acetate/petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43-7.35 (m, 2 H), 7.11 (t, J = 8.4 Hz, 2 H), 4.43 (q, J = 6.8 Hz, 2 H), 4.31-4.20 (m, 2 H), 3.93 (s, 1 H), 1.39 (t, J = 6.8 Hz, 3 H), 1.22 (t, J = 6.8 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.2 (d, J = 248.9 Hz), 162.8, 160.9, 130.8 (d, J = 8.8 Hz), 123.1 (d, J = 3.6 Hz), 116.2 (d, J = 21.9 Hz), 111.6, 109.6, 64.5, 63.7, 46.3, 39.2, 16.2, 13.8, 13.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ -111.0 ppm; IR (neat) 2253, 1744, 1516 cm^{-1}; MS (EI, 70 eV) m/z 330 (M$^+$, 0.32), 159 (100); HRMS (EI, 70 eV) calcd for $C_{17}H_{15}FN_2O_4$ 330.1016, found

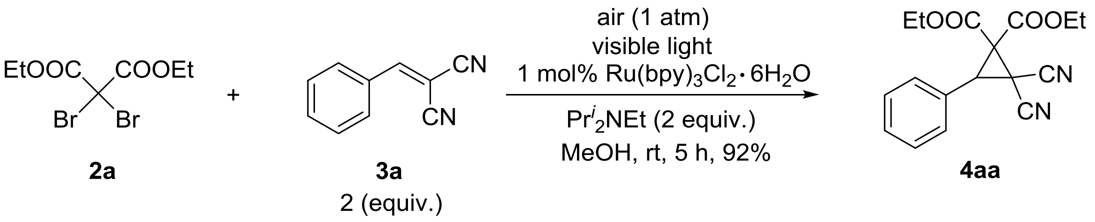
330.1017.

(6) Diethyl 2,2-dicyano-3-(4-chlorophenyl)cyclopropane-1,1-dicarboxylate (4ah)[17]



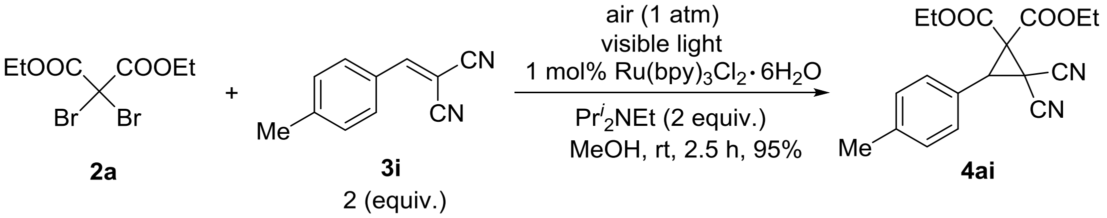
The reaction of **2a** (38 μL, 0.20 mmol), **3h** (70 mg, 0.37 mmol), $Ru(bpy)_3Cl_2$ $6H_2O$ (2 mg, 0.0027 mmol), Pr^i_2NEt (66 μL, 0.40 mmol), and anhydrous methanol (10 mL) afforded **4ah** as a solid (66 mg, 95%); mp 85.0-87.0 °C[17] (ethyl acetate/petroleum ether). ^1H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, J = 8.0 Hz, 2 H), 7.33 (d, J = 8.0 Hz, 2 H), 4.43 (q, J = 6.4 Hz, 2 H), 4.31-4.20 (m, 2 H), 3.92 (s, 1 H), 1.39 (t, J = 6.4 Hz, 3 H), 1.22 (t, J = 6.4 Hz, 3 H).

(7) Diethyl 2,2-dicyano-3-phenylcyclopropane-1,1-dicarboxylate (4aa)[18]



The reaction of **2a** (38 μL, 0.20 mmol), **3a** (62 mg, 0.41 mmol), $Ru(bpy)_3Cl_2$ $6H_2O$ (2 mg, 0.0027 mmol), Pr^i_2NEt (66 μL, 0.40 mmol), and anhydrous methanol (10 mL) afforded **4aa** as a solid (64 mg, 92%); mp 71.0-72.0 °C[18] (ethyl acetate/petroleum ether). ^1H NMR (400 MHz, $CDCl_3$) δ 7.44-7.34 (m, 5 H), 4.42 (q, J = 7.2 Hz, 2 H), 4.29-4.18 (m, 2 H), 3.96 (s, 1 H), 1.38 (t, J = 7.2 Hz, 3 H), 1.19 (t, J = 7.2 Hz, 3 H).

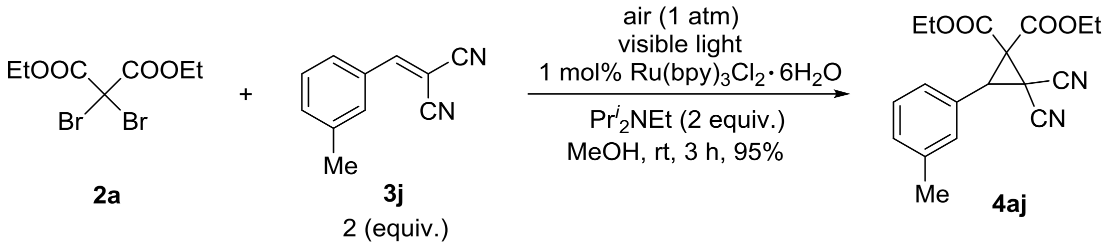
(8) Diethyl 2,2-dicyano-3-(4-methylphenyl)cyclopropane-1,1-dicarboxylate (4ai)[19]



The reaction of **2a** (38 μL, 0.20 mmol), **3i** (69 mg, 0.41 mmol),

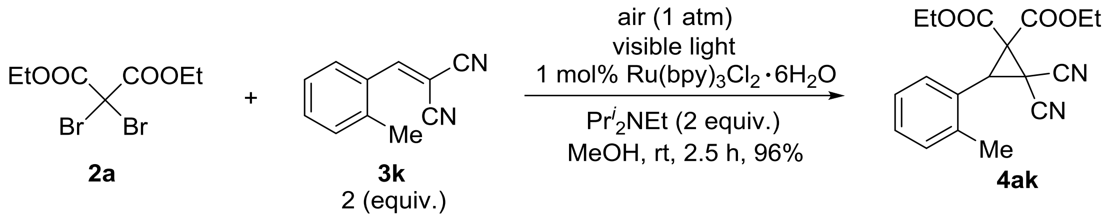
$Ru(bpy)_3Cl_2$ $6H_2O$ (2 mg, 0.0027 mmol), $\mathrm{Pr}^{i}{}_{2}\mathrm{NEt}$ (68 μL, 0.41 mmol), and anhydrous methanol (10 mL) afforded **4ai** as a solid (64 mg, 95%); mp 77.0-79.0 °C[19] (ethyl acetate/petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (d, J = 8.0 Hz, 2 H), 7.20 (d, J = 8.0 Hz, 2 H), 4.41 (q, J = 6.8 Hz, 2 H), 4.31-4.19 (m, 2 H), 3.93 (s, 1 H), 2.35 (s, 3 H), 1.38 (t, J = 6.8 Hz, 3 H), 1.21 (t, J = 6.8 Hz, 3 H).

(9) Diethyl 2,2-dicyano-3-(3-methylphenyl)cyclopropane-1,1-dicarboxylate (4aj)



The reaction of **2a** (38 μL, 0.20 mmol), **3j** (68 mg, 0.40 mmol), $Ru(bpy)_3Cl_2$ $6H_2O$ (2 mg, 0.0027 mmol), $\mathrm{Pr}^{i}{}_{2}\mathrm{NEt}$ (66 μL, 0.40 mmol), and anhydrous methanol (10 mL) afforded **4aj** as a solid (62 mg, 95%); mp 95.2-96.1 °C (ethyl acetate/petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.12 (m, 4 H), 4.42 (q, J = 7.2 Hz, 2 H), 4.29-4.19 (m, 2 H), 3.93 (s, 1 H), 2.35 (s, 3 H), 1.38 (t, J = 7.2 Hz, 3 H), 1.20 (t, J = 7.2 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.0, 161.0, 138.8, 130.3, 129.4, 128.9, 127.1, 125.5, 111.9, 109.6, 64.3, 63.5, 46.2, 40.0, 21.2, 16.0, 13.9, 13.5; IR (neat) 2253, 1744, 1217 cm^{-1}; MS (EI, 70 eV) m/z 326 (M^+, 4.42), 154 (100); HRMS (EI, 70 eV) calcd for $C_{18}H_{18}N_2O_4$ 326.1267, found 326.1263.

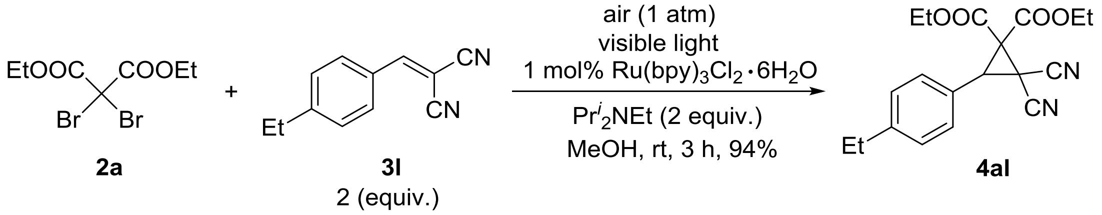
(10) Diethyl 2,2-dicyano-3-(2-methylphenyl)cyclopropane-1,1-dicarboxylate (4ak)



The reaction of **2a** (38 μL, 0.20 mmol), **3k** (69 mg, 0.41 mmol), $Ru(bpy)_3Cl_2$ $6H_2O$ (2 mg, 0.0027 mmol), $\mathrm{Pr}^{i}{}_{2}\mathrm{NEt}$ (66 μL, 0.40 mmol), and anhydrous methanol (10 mL) afforded **4ak** as a liquid (63 mg, 96%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, J = 7.2 Hz, 1 H), 7.33-7.26 (m, 2 H), 7.22-7.16 (m, 1 H), 4.44 (q, J = 7.2 Hz, 2 H), 4.22 (q, J

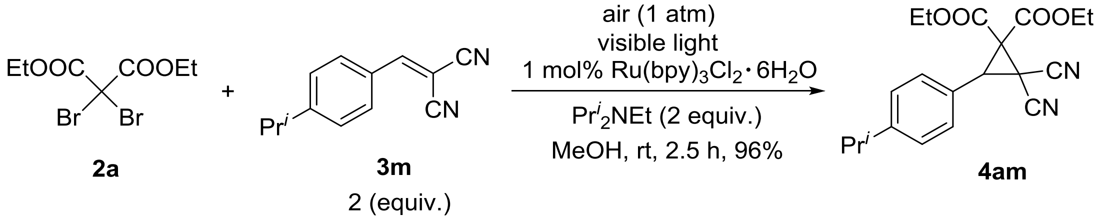
= 7.2 Hz, 2 H), 3.87 (s, 1 H), 2.42 (s, 3 H), 1.39 (t, *J* = 7.2 Hz, 3 H), 1.16 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.1, 161.2, 138.4, 131.0, 129.5, 127.2, 126.2, 126.0, 112.1, 109.8, 64.3, 63.5, 46.0, 39.6, 19.4, 16.2, 13.9, 13.4; IR (neat) 2250, 1744, 1464, 1372 cm^{-1}; MS (EI, 70 eV) m/z 326 (M^+, 2.4), 154 (100); HRMS (EI, 70 eV) calcd for $C_{18}H_{18}N_2O_4$ 326.1267, found 326.1265.

(11) Diethyl 2,2-dicyano-3-(4-ethylphenyl)cyclopropane-1,1-dicarboxylate (4al)



The reaction of **2a** (38 μL, 0.20 mmol), **3l** (74 mg, 0.41 mmol), $Ru(bpy)_3Cl_2$ $6H_2O$ (2 mg, 0.0027 mmol), $Pr^i{}_2NEt$ (66 μL, 0.40 mmol), and anhydrous methanol (10 mL) afforded **4al** as a solid (64 mg, 94%); mp 69.3-71.2 °C (ethyl acetate/petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (d, *J* = 8.4 Hz, 2 H), 7.22 (d, *J* = 8.4 Hz, 2 H), 4.42 (q, *J* = 6.8 Hz, 2 H), 4.31-4.19 (m, 2 H), 3.93 (s, 1 H), 2.65 (q, *J* = 7.2 Hz, 2 H), 1.38 (t, *J* = 6.8 Hz, 3 H), 1.23-1.17 (m, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.2, 161.2, 146.0, 128.7, 128.6, 124.3, 111.9, 109.8, 64.4, 63.5, 46.3, 40.1, 28.5, 16.3, 15.2, 13.9, 13.6; IR (neat) 2247, 1744 cm^{-1}; MS (EI, 70 eV) m/z 340 (M^+, 2.91), 225 (100); HRMS (EI, 70 eV) calcd for $C_{19}H_{20}N_2O_4$ 340.1423, found 340.1420.

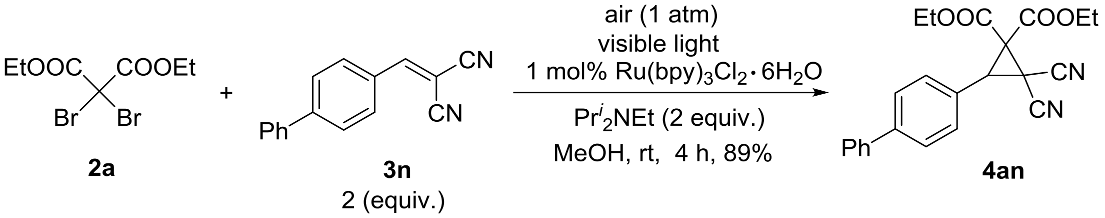
(12) Diethyl 2,2-dicyano-3-(4-isopropylphenyl)cyclopropane-1,1-dicarboxylate (4am)



The reaction of **2a** (38 μL, 0.20 mmol), **3m** (76 mg, 0.39 mmol), $Ru(bpy)_3Cl_2$ $6H_2O$ (2 mg, 0.0027 mmol), $Pr^i{}_2NEt$ (66 μL, 0.40 mmol), and anhydrous methanol (10 mL) afforded **4am** as a solid (68 mg, 96%); mp 83.6-84.6 °C (ethyl acetate/petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.21 (m, 4 H), 4.40 (q, *J*

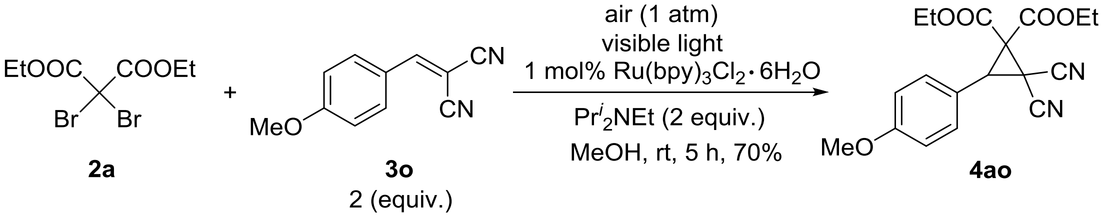
= 7.6 Hz, 2 H), 4.30-4.18 (m, 2 H), 3.93 (s, 1 H), 2.96-2.85 (m, 1 H), 1.37 (t, *J* = 6.8 Hz, 3 H), 1.29-1.12 (m, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.1, 161.1, 150.6, 128.7, 127.1, 124.4, 111.9, 109.8, 64.3, 63.5, 46.3, 40.1, 33.8, 23.7, 16.3, 13.9, 13.5; IR (neat) 2250, 1747, 1613, 1522, 1464 cm^{-1}; MS (EI, 70 eV) m/z 354 (M^+, 5.12), 84 (100); HRMS (EI, 70 eV) calcd for $C_{20}H_{22}N_2O_4$ 354.1580, found 354.1576.

(13) Diethyl 2,2-dicyano-3-(4-phenylphenyl)cyclopropane-1,1-dicarboxylate (4an)



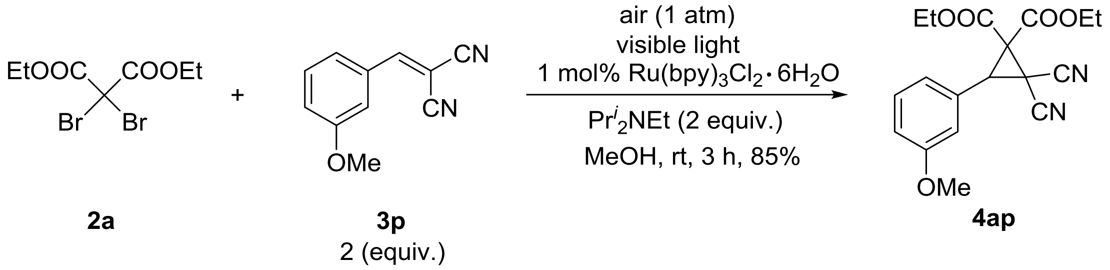
The reaction of **2a** (38 μL, 0.20 mmol), **3n** (94 mg, 0.41 mmol), $Ru(bpy)_3Cl_2$ $6H_2O$ (2 mg, 0.0027 mmol), Pr^i_2NEt (68 μL, 0.41 mmol), and anhydrous methanol (10 mL) afforded **4an** as a solid (69 mg, 89%); mp 100.8-102.1 °C (ethyl acetate/petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65-7.52 (m, 4 H), 7.47-7.41 (m, 4 H), 7.40-7.34 (m, 1 H), 4.43 (q, *J* = 6.8 Hz, 2 H), 4.32-4.21 (m, 2 H), 4.00 (s, 1 H), 1.39 (t, *J* = 6.8 Hz, 3 H), 1.21 (t, *J* = 6.8 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.0, 161.0, 142.5, 139.7, 129.2, 128.9, 127.9, 127.7, 127.1, 126.1, 111.8, 109.7, 64.5, 63.6, 46.4, 39.9, 16.4, 13.9, 13.6; IR (neat) 2247, 1744, 1214 cm^{-1}; MS (EI, 70 eV) m/z 388 (M^+, 5.88), 216 (100); HRMS (EI, 70 eV) calcd for $C_{23}H_{20}N_2O_4$ 388.1423, found 388.1425.

(14) Diethyl 2,2-dicyano-3-(4-methoxyphenyl)cyclopropane-1,1-dicarboxylate (4ao)[17]



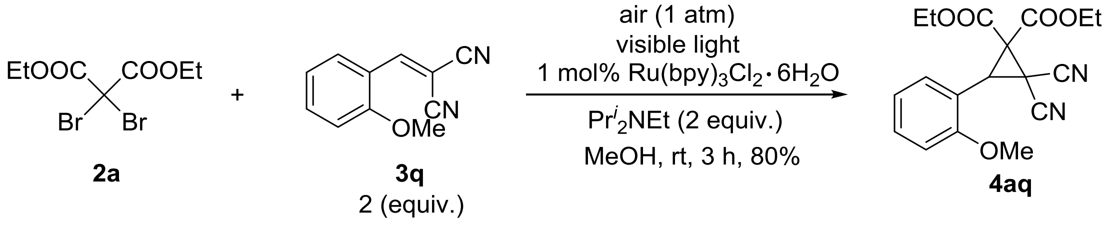
The reaction of **2a** (38 μL, 0.20 mmol), **3o** (73 mg, 0.40 mmol), $Ru(bpy)_3Cl_2$ $6H_2O$ (2 mg, 0.0027 mmol), Pr^i_2NEt (68 μL, 0.41 mmol), and anhydrous methanol (10 mL) afforded **4ao** as a solid (48 mg, 70%); mp 75.0-77.0 °C[17] (ethyl acetate/petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, J = 8.4 Hz, 2 H), 6.91 (d, J = 8.4 Hz, 2 H), 4.42 (q, J = 7.2 Hz, 2 H), 4.31-4.20 (m, 2 H), 3.91 (s, 1 H), 3.81 (s, 3 H), 1.38 (t, J = 7.2 Hz, 3 H), 1.23 (t, J = 7.2 Hz, 3 H).

(15) Diethyl 2,2-dicyano-3-(3-methoxyphenyl)cyclopropane-1,1-dicarboxylate (4ap)



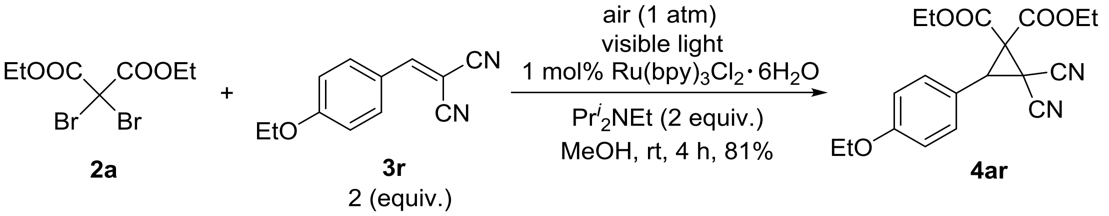
The reaction of **2a** (38 μL, 0.20 mmol), **3p** (73 mg, 0.40 mmol), $Ru(bpy)_3Cl_2$ $6H_2O$ (2 mg, 0.0027 mmol), $Pr^i{}_2NEt$ (66 μL, 0.40 mmol), and anhydrous methanol (10 mL) afforded **4ap** as a liquid (58 mg, 85%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.28 (m, 1 H), 6.97-6.89 (m, 3 H), 4.43 (q, J = 6.8 Hz, 2 H), 4.31-4.19 (m, 2 H), 3.95 (s, 1 H), 3.81 (s, 3 H), 1.39 (t, J = 6.8 Hz, 3 H), 1.21 (t, J = 6.8 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.9, 161.0, 159.8, 130.1, 128.5, 120.8, 115.3, 114.2, 111.8, 109.7, 64.4, 63.6, 55.3, 46.3, 39.9, 16.2, 13.9, 13.5; IR (neat) 2250, 1741, 1601, 1583, 1464 cm^{-1}; MS (EI, 70 eV) m/z 342 (M$^+$, 3.73), 84 (100); HRMS (EI, 70 eV) calcd for $C_{18}H_{18}N_2O_5$ 342.1216, found 342.1214.

(16) Diethyl 2,2-dicyano-3-(2-methoxyphenyl)cyclopropane-1,1-dicarboxylate (4aq)



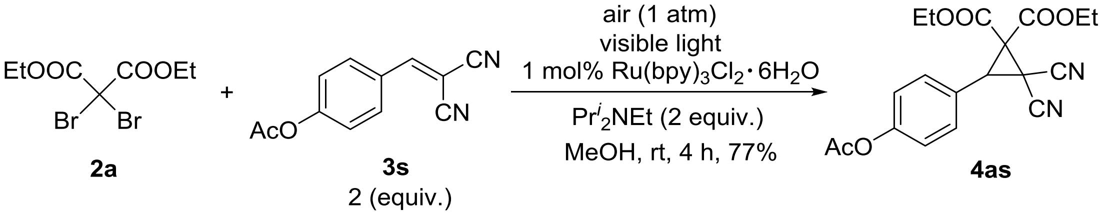
The reaction of **2a** (38 μL, 0.20 mmol), **3q** (75 mg, 0.41 mmol), $Ru(bpy)_3Cl_2$ $6H_2O$ (2 mg, 0.0027 mmol), $Pr^i{}_2NEt$ (66 μL, 0.40 mmol), and anhydrous methanol (10 mL) afforded **4aq** as a liquid (55 mg, 80%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42-7.34 (m, 1 H), 7.24 (d, J = 8.0 Hz, 1 H), 7.00-6.89 (m, 2 H), 4.42 (q, J = 7.2 Hz, 2 H), 4.32-4.22 (m, 2 H), 3.91 (s, 3 H), 3.83 (s, 1 H), 1.39 (t, J = 7.2 Hz, 3 H), 1.24 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.2, 161.5, 158.2, 131.0, 128.6, 120.5, 115.9, 112.3, 110.9, 110.1, 64.1, 63.3, 55.6, 46.2, 39.6, 16.9, 13.9, 13.5; IR (neat) 2253, 1744, 1601, 1494, 1464 cm^{-1}; MS (EI, 70 eV) m/z 342 (M$^+$, 10.53), 227 (100); HRMS (EI, 70 eV) calcd for $C_{18}H_{18}N_2O_5$ 342.1216, found 342.1219.

(17) Diethyl 2,2-dicyano-3-(4-ethoxyphenyl)cyclopropane-1,1-dicarboxylate (4ar)



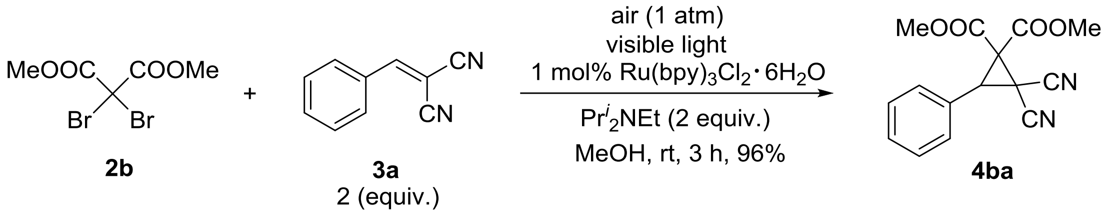
The reaction of **2a** (38 μL, 0.20 mmol), **3r** (80 mg, 0.40 mmol), $Ru(bpy)_3Cl_2$ $6H_2O$ (2 mg, 0.0027 mmol), Pr^i_2NEt (66 μL, 0.40 mmol), and anhydrous methanol (10 mL) afforded **4ar** as a solid (58 mg, 81%); mp 69.3-71.2 °C (ethyl acetate/petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (d, *J* = 8.8 Hz, 2 H), 6.89 (d, *J* = 8.8 Hz, 2 H), 4.42 (q, *J* = 7.2 Hz, 2 H), 4.31-4.20 (m, 2 H), 4.03 (q, *J* = 6.8 Hz, 2 H), 3.91 (s, 1 H), 1.44-1.35 (m, 6 H), 1.22 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.1, 161.1, 159.8, 130.1, 118.7, 114.9, 111.9, 109.9, 64.4, 63.6, 63.5, 46.3, 39.9, 16.4, 14.6, 13.9, 13.6; IR (neat) 2251, 1743, 1612, 1517, 1474 cm^{-1}; MS (EI, 70 eV) m/z 356 (M$^+$, 1.78), 170 (100); HRMS (EI, 70 eV) calcd for $C_{19}H_{20}N_2O_5$ 356.1372, found 356.1373.

(18) Diethyl 2,2-dicyano-3-(4-acetoxyphenyl)cyclopropane-1,1-dicarboxylate (4as)



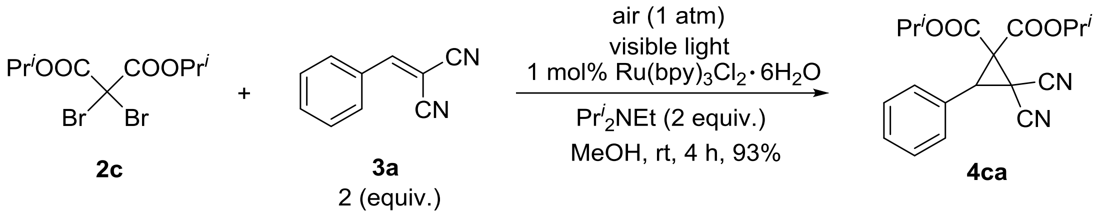
The reaction of **2a** (38 μL, 0.20 mmol), **3s** (82 mg, 0.40 mmol), $Ru(bpy)_3Cl_2$ $6H_2O$ (2 mg, 0.0027 mmol), Pr^i_2NEt (66 μL, 0.40 mmol), and anhydrous methanol (10 mL) afforded **4as** as a liquid (57 mg, 77%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.8 Hz, 2 H), 7.15 (d, *J* = 8.8 Hz, 2 H), 4.42 (q, *J* = 6.8 Hz, 2 H), 4.30-4.18 (m, 2 H), 3.94 (s, 1 H), 2.30 (s, 3 H), 1.38 (t, J = 6.8 Hz, 3 H), 1.20 (t, J = 6.8 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.8, 162.8, 160.9, 151.5, 129.9, 124.6, 122.3, 111.6, 109.6, 64.5, 63.7, 46.3, 39.4, 21.0, 16.3, 13.9, 13.5; IR (neat) 2250, 1744, 1510, 1464 cm^{-1}; HRMS (ESI) calcd for $C_{19}H_{18}N_2NaO_6$ 393.1063, found 393.1051.

(19) Dimethyl 3-phenyl-2,2-dicyanocyclopropane-1,1-dicarboxylate (4ba)[17]



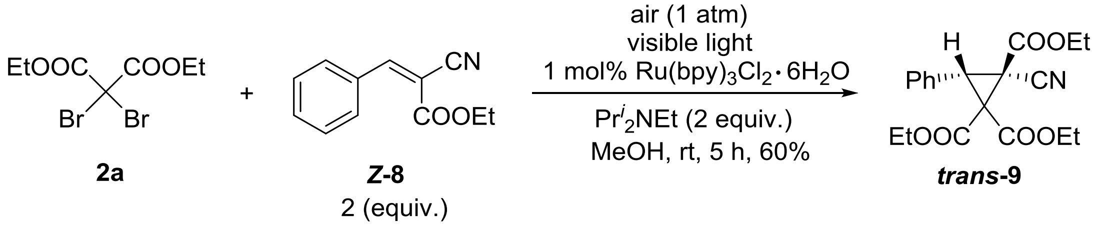
The reaction of **2b** (58 mg, 0.20 mmol), **3a** (65 mg, 0.40 mmol), $Ru(bpy)_3Cl_2$ $6H_2O$ (2 mg, 0.0027 mmol), Pr^{i}_2NEt (68 μL, 0.41 mmol), and anhydrous methanol (10 mL) afforded **4ba** as a solid (55 mg, 96%); mp 125.0-126.0 °C[17] (ethyl acetate/petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45-7.39 (m, 3 H), 7.38-7.33 (m, 2 H), 3.98 (s, 4 H), 3.78 (s, 3 H).

(20) Diisopropyl 3-phenyl-2,2-dicyanocyclopropane-1,1-dicarboxylate (4ca)



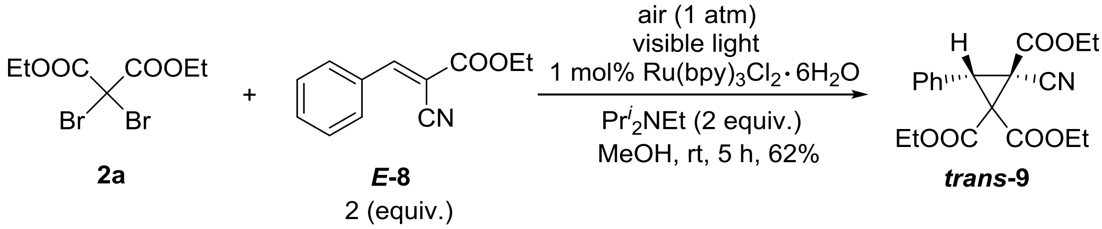
The reaction of **2c** (70 mg, 0.20 mmol), **3a** (63 mg, 0.40 mmol), $Ru(bpy)_3Cl_2$ $6H_2O$ (2 mg, 0.0027 mmol), Pr^{i}_2NEt (66 μL, 0.40 mmol), and anhydrous methanol (10 mL) afforded **4ca** as a liquid (63 mg, 93%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44-7.34 (m, 5 H), 5.30-5.18 (m, 1 H), 5.14-5.02 (m, 1 H), 3.94 (s, 1 H), 1.42-1.32 (m, 6 H), 1.19 (d, J = 6.8 Hz, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.7, 160.7, 129.5, 128.9, 128.8, 127.3, 111.9, 109.7, 72.8, 72.0, 46.2, 39.8, 21.5, 21.3, 21.2, 21.0, 15.8; IR (neat) 2241, 1738, 1500, 1467 cm^{-1}; MS (ESI) m/z 363 ($M+Na^+$); HRMS (ESI) calcd for $C_{19}H_{20}N_2Na_1O_4$ 363.1315, found 363.1327.

(21) Triethyl (2,3-*trans*)-2-cyano-3-phenylcyclopropane-1,1,2-tricarboxylate (*trans*-9)[20] from *Z*-8



The reaction of **2a** (38 μL, 0.20 mmol), ***Z*-8** (78 mg, 0.40 mmol), $Ru(bpy)_3Cl_2$ $6H_2O$ (2 mg, 0.0027 mmol), $Pr^i{}_2NEt$ (66 μL, 0.40 mmol), and anhydrous methanol (10 mL) afforded ***trans*-9** as a liquid (42 mg, 60%) with recovered ***Z*-8** as white solid (28 mg, 35%); ***trans*-9**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.27 (m, 5 H), 4.39-4.25 (m, 4 H), 4.14 (q, J = 6.8 Hz, 2 H), 3.94 (s, 1 H), 1.39 (t, J = 6.8 Hz, 3 H), 1.31 (t, J = 6.8 Hz, 3 H), 1.10 (t, J = 6.8 Hz, 3 H).

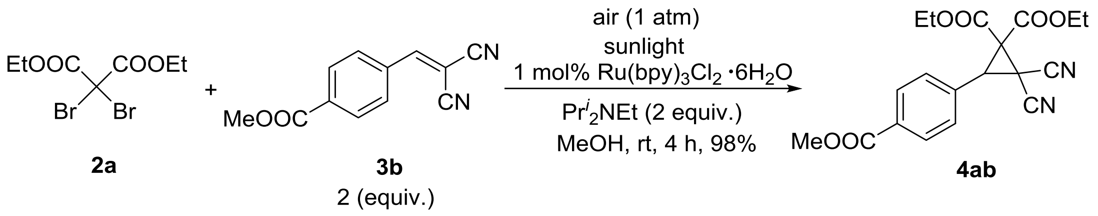
(22) Triethyl (2,3-*trans*)-2-cyano-3-phenylcyclopropane-1,1,2-tricarboxylate (*trans*-9)[20] from *E*-8



The reaction of **2a** (66 mg, 0.20 mmol), ***E*-8** (85 mg, 0.42 mmol), $Ru(bpy)_3Cl_2$ $6H_2O$ (2 mg, 0.0027 mmol), $Pr^i{}_2NEt$ (53 mg, 0.41 mmol), and anhydrous methanol (10 mL) afforded ***trans*-9** as a liquid (46 mg, 62%) with recovered ***E*-8** as white solid (32 mg, 38%); ***trans*-9**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.31 (m, 5 H), 4.42-4.22 (m, 4 H), 4.14 (q, J = 6.8 Hz, 2 H), 3.94 (s, 1 H), 1.39 (t, J = 6.8 Hz, 3 H), 1.31 (t, J = 6.8 Hz, 3 H), 1.10 (t, J = 6.8 Hz, 3 H).

Typical Procedure II for the photoreaction under Condition B.

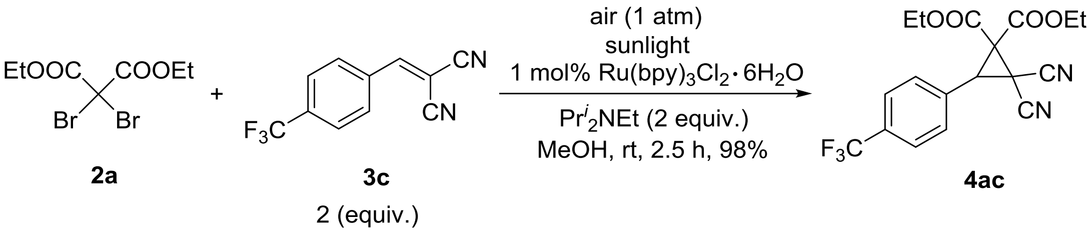
Synthesis of diethyl 2,2-dicyano-3-(4-methoxycarbonylphenyl)cyclopropane-1,1-dicarboxylate (4ab)



2a (38 μL, 0.20 mmol), **3b** (85 mg, 0.40 mmol), $Ru(bpy)_3Cl_2$ $\cdot 6H_2O$ (2 mg, 0.0027 mmol), $Pr^{i}_{2}NEt$ (66 μL, 0.40 mmol), and anhydrous methanol (10 mL) were added to a dry 25 mL pyrex reaction tube. The mixture was irradiated by sunlight at rt in the open air. The photoreaction was completed after 4 h as monitored by TLC (eluent: petroleum ether/ethyl acetate = 10/1). The solvent was removed and the residue was purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 20/1→15/1→10/1) to afforded **4ab** as a solid (73 mg, 98%).

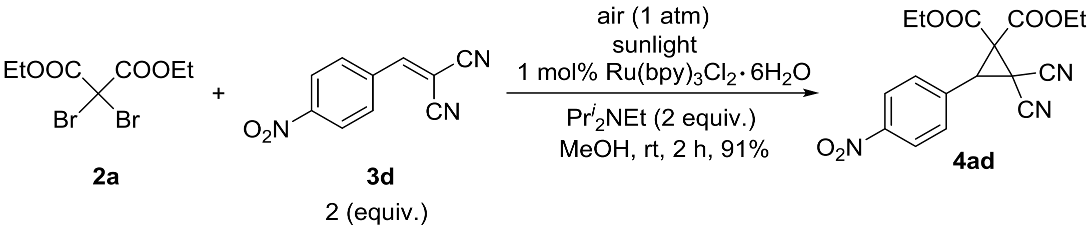
The following compounds were prepared according to Typical Procedure I.

(1) Diethyl 2,2-dicyano-3-(4-trifluoromethylphenyl)cyclopropane-1,1-dicarboxylate (4ac)



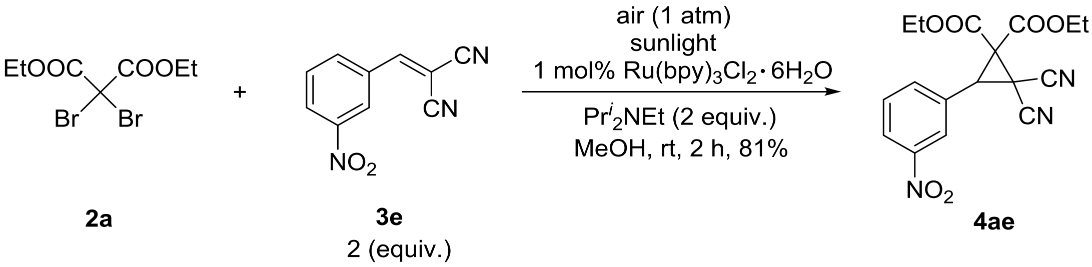
The reaction of **2a** (38 μL, 0.20 mmol), **3c** (91 mg, 0.41 mmol), $Ru(bpy)_3Cl_2$ $6H_2O$ (2 mg, 0.0027 mmol), $Pr^{i}_{2}NEt$ (66 μL, 0.40 mmol), and anhydrous methanol (10 mL) afforded **4ac** as a solid (75 mg, 98%).

(2) Diethyl 2,2-dicyano-3-(4-nitrophenyl)cyclopropane-1,1-dicarboxylate (4ad)



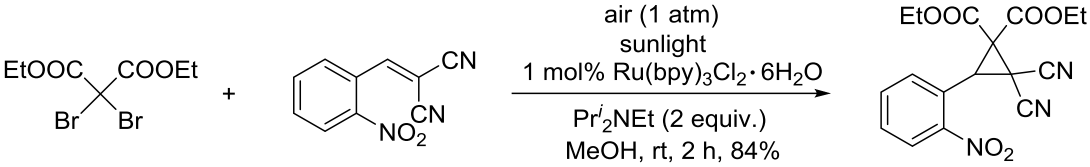
The reaction of **2a** (38 μL, 0.20 mmol), **3d** (82 mg, 0.41 mmol), $Ru(bpy)_3Cl_2$ $6H_2O$ (2 mg, 0.0027 mmol), $Pr^{i}_{2}NEt$ (66 μL, 0.40 mmol), and anhydrous methanol (10 mL) afforded **4ad** as a solid (65 mg, 91%).

(3) Diethyl 2,2-dicyano-3-(3-nitrophenyl)cyclopropane-1,1-dicarboxylate (4ae)



The reaction of **2a** (38 μL, 0.20 mmol), **3e** (81 mg, 0.41 mmol), $Ru(bpy)_3Cl_2$ $6H_2O$ (2 mg, 0.0027 mmol), $Pr^i{}_2NEt$ (66 μL, 0.40 mmol), and anhydrous methanol (10 mL) afforded **4ae** as a solid (58 mg, 81%).

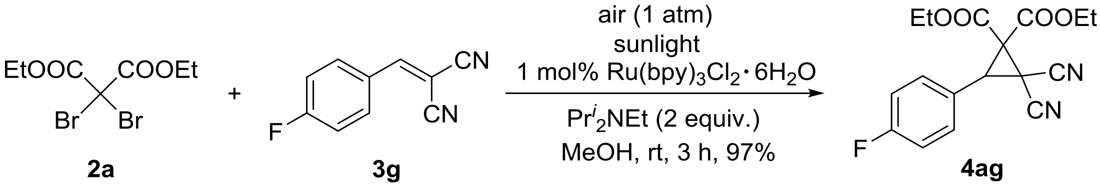
(4) Diethyl 2,2-dicyano-3-(2-nitrophenyl)cyclopropane-1,1-dicarboxylate (4af)



2a **3f** 2 (equiv.) **4af**

The reaction of **2a** (38 μL, 0.20 mmol), **3f** (82 mg, 0.41 mmol), $Ru(bpy)_3Cl_2$ $6H_2O$ (2 mg, 0.0027 mmol), $Pr^i{}_2NEt$ (66 μL, 0.40 mmol), and anhydrous methanol (10 mL) afforded **4af** as a solid (60 mg, 84%).

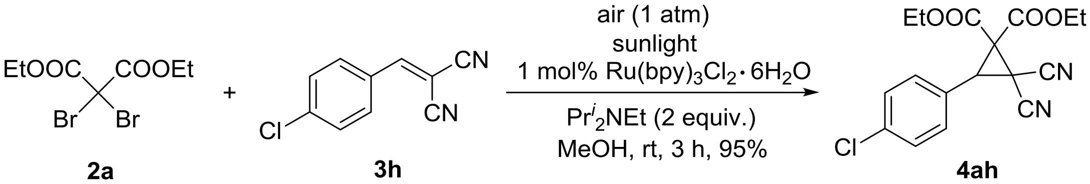
(5) Diethyl 2,2-dicyano-3-(4-fluorophenyl)cyclopropane-1,1-dicarboxylate (4ag)



2a **3g** 2 (equiv.) **4ag**

The reaction of **2a** (38 μL, 0.20 mmol), **3g** (69 mg, 0.40 mmol), $Ru(bpy)_3Cl_2$ $6H_2O$ (2 mg, 0.0027 mmol), $Pr^i{}_2NEt$ (66 μL, 0.40 mmol), and anhydrous methanol (10 mL) afforded **4ag** as a solid (64 mg, 97%).

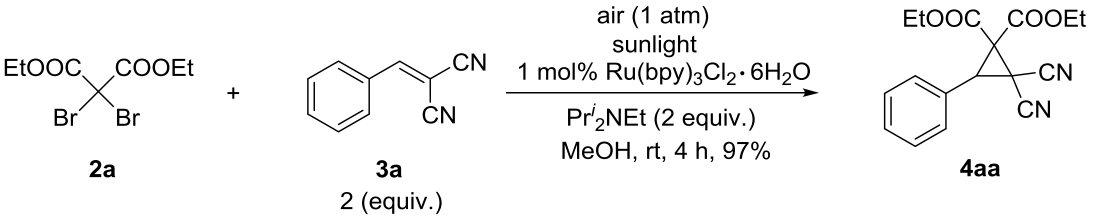
(6) Diethyl 2,2-dicyano-3-(4-chlorophenyl)cyclopropane-1,1-dicarboxylate (4ah)[17]



2a **3h** 2 (equiv.) **4ah**

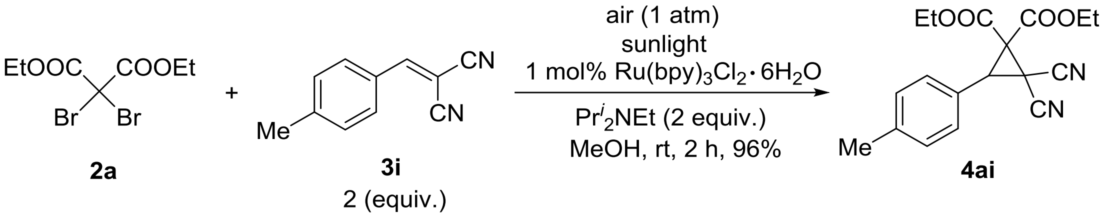
The reaction of **2a** (38 μL, 0.20 mmol), **3h** (77 mg, 0.41 mmol), $Ru(bpy)_3Cl_2$ $6H_2O$ (2 mg, 0.0027 mmol), $Pr^i{}_2NEt$ (66 μL, 0.40 mmol), and anhydrous methanol (10 mL) afforded **4ah** as a solid (66 mg, 95%).

(7) Diethyl 2,2-dicyano-3-phenylcyclopropane-1,1-dicarboxylate (4aa)[18]



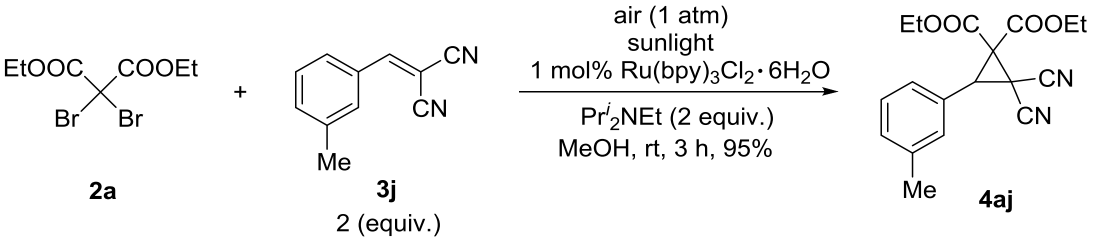
The reaction of **2a** (38 μL, 0.20 mmol), **3a** (62 mg, 0.41 mmol), $Ru(bpy)_3Cl_2$ $6H_2O$ (2 mg, 0.0027 mmol), $Pr^{i}_{2}NEt$ (66 μL, 0.40 mmol), and anhydrous methanol (10 mL) afforded **4aa** as a solid (61 mg, 97%).

(8) Diethyl 2,2-dicyano-3-(4-methylphenyl)cyclopropane-1,1-dicarboxylate (4ai)[19]



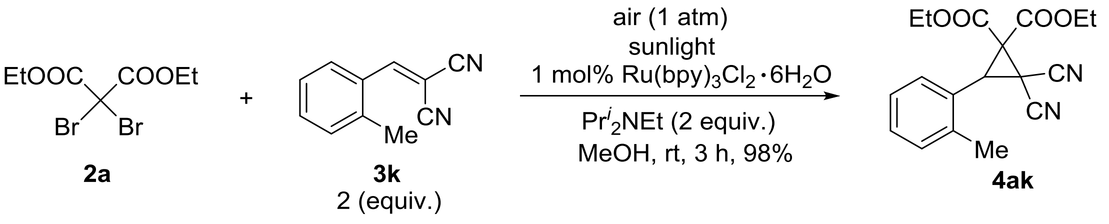
The reaction of **2a** (38 μL, 0.20 mmol), **3i** (71 mg, 0.42 mmol), $Ru(bpy)_3Cl_2$ $6H_2O$ (2 mg, 0.0027 mmol), $Pr^{i}_{2}NEt$ (66 μL, 0.40 mmol), and anhydrous methanol (10 mL) afforded **4ai** as a solid (63 mg, 96%).

(9) Diethyl 2,2-dicyano-3-(3-methylphenyl)cyclopropane-1,1-dicarboxylate (4aj)



The reaction of **2a** (38 μL, 0.20 mmol), **3j** (69 mg, 0.41 mmol), $Ru(bpy)_3Cl_2$ $6H_2O$ (2 mg, 0.0027 mmol), $Pr^{i}_{2}NEt$ (66 μL, 0.40 mmol), and anhydrous methanol (10 mL) afforded **4aj** as a solid (62 mg, 95%).

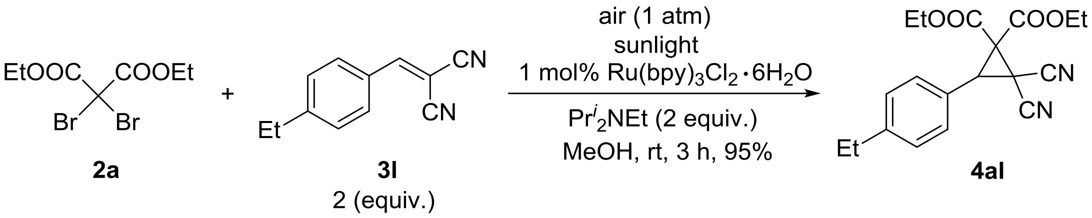
(10) Diethyl 2,2-dicyano-3-(2-methylphenyl)cyclopropane-1,1-dicarboxylate (4ak)



The reaction of **2a** (38 μL, 0.20 mmol), **3k** (70 mg, 0.42 mmol),

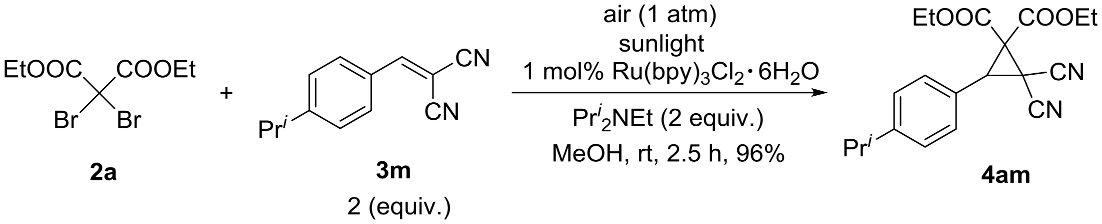
$Ru(bpy)_3Cl_2$ $6H_2O$ (2 mg, 0.0027 mmol), $Pr^i{}_2NEt$ (66 μL, 0.40 mmol), and anhydrous methanol (10 mL) afforded **4ak** as a liquid (64 mg, 98%).

(11) Diethyl 2,2-dicyano-3-(4-ethylphenyl)cyclopropane-1,1-dicarboxylate (4al)



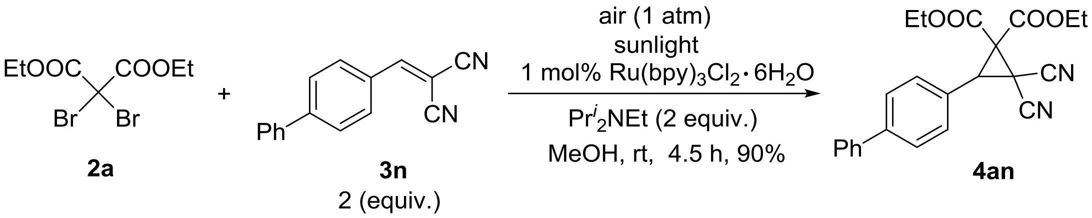
The reaction of **2a** (38 μL, 0.20 mmol), **3l** (74 mg, 0.41 mmol), $Ru(bpy)_3Cl_2$ $6H_2O$ (2 mg, 0.0027 mmol), $Pr^i{}_2NEt$ (66 μL, 0.40 mmol), and anhydrous methanol (10 mL) afforded **4al** as a solid (65 mg, 95%).

(12) Diethyl 2,2-dicyano-3-(4-isopropylphenyl)cyclopropane-1,1-dicarboxylate (4am)



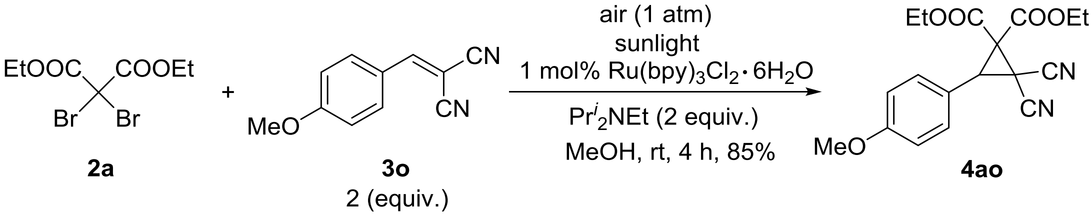
The reaction of **2a** (38 μL, 0.20 mmol), **3m** (82 mg, 0.42 mmol), $Ru(bpy)_3Cl_2$ $6H_2O$ (2 mg, 0.0027 mmol), $Pr^i{}_2NEt$ (66 μL, 0.40 mmol), and anhydrous methanol (10 mL) afforded **4am** as a solid (68 mg, 96%).

(13) Diethyl 2,2-dicyano-3-(4-phenylphenyl)cyclopropane-1,1-dicarboxylate (4an)



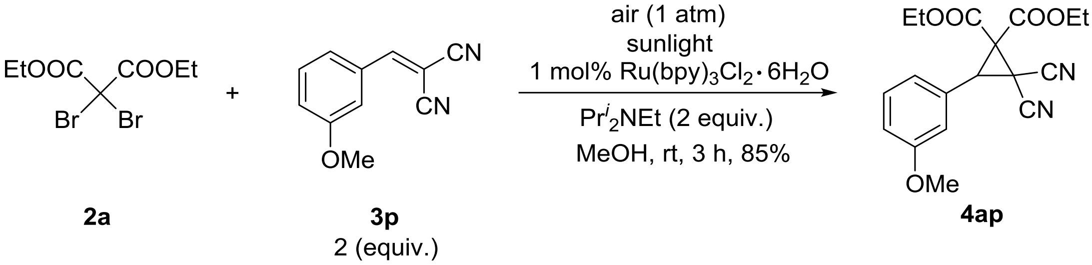
The reaction of **2a** (38 μL, 0.20 mmol), **3n** (94 mg, 0.41 mmol), $Ru(bpy)_3Cl_2$ $6H_2O$ (2 mg, 0.0027 mmol), $Pr^i{}_2NEt$ (66 μL, 0.40 mmol), and anhydrous methanol (10 mL) afforded **4an** as a solid (70 mg, 90%).

(14) Diethyl 2,2-dicyano-3-(4-methoxyphenyl)cyclopropane-1,1-dicarboxylate (4ao)[17]



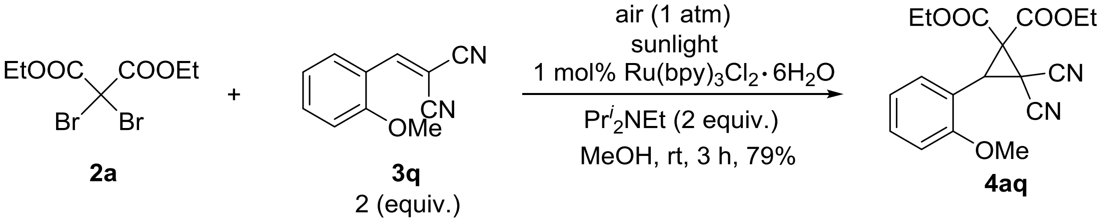
The reaction of **2a** (38 μL, 0.20 mmol), **3o** (74 mg, 0.40 mmol), $Ru(bpy)_3Cl_2$ $6H_2O$ (2 mg, 0.0027 mmol), Pr^i_2NEt (66 μL, 0.40 mmol), and anhydrous methanol (10 mL) afforded **4ao** as a solid (58 mg, 85%).

(15) Diethyl 2,2-dicyano-3-(4-methoxyphenyl)cyclopropane-1,1-dicarboxylate (4ap)



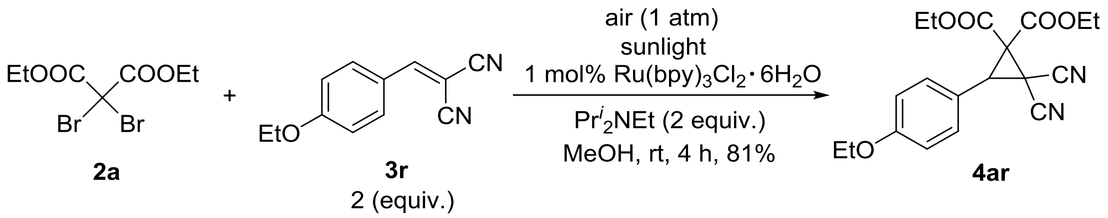
The reaction of **2a** (38 μL, 0.20 mmol), **3p** (74 mg, 0.40 mmol), $Ru(bpy)_3Cl_2$ $6H_2O$ (2 mg, 0.0027 mmol), Pr^i_2NEt (66 μL, 0.40 mmol), and anhydrous methanol (10 mL) afforded **4ap** as a liquid (58 mg, 85%).

(16) Diethyl 2,2-dicyano-3-(4-methoxyphenyl)cyclopropane-1,1-dicarboxylate (4aq)



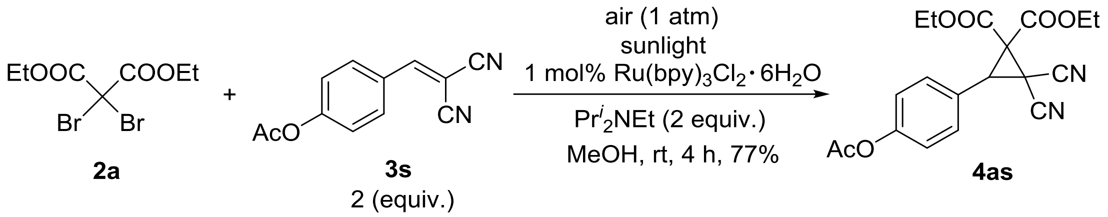
The reaction of **2a** (38 μL, 0.20 mmol), **3q** (74 mg, 0.40 mmol), $Ru(bpy)_3Cl_2$ $6H_2O$ (2 mg, 0.0027 mmol), Pr^i_2NEt (66 μL, 0.40 mmol), and anhydrous methanol (10 mL) afforded **4aq** as a liquid (54 mg, 79%).

(17) Diethyl 2,2-dicyano-3-(4-ethoxyphenyl)cyclopropane-1,1-dicarboxylate (4ar)



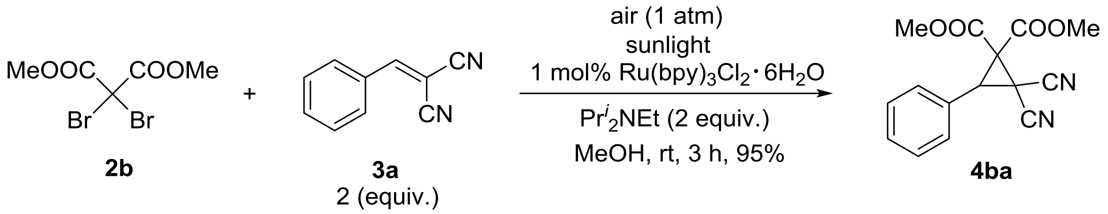
The reaction of **2a** (38 μL, 0.20 mmol), **3r** (82 mg, 0.41 mmol), $Ru(bpy)_3Cl_2$ 6H_2O (2 mg, 0.0027 mmol), Pr^i_2NEt (66 μL, 0.40 mmol), and anhydrous methanol (10 mL) afforded **4ar** as a solid (58 mg, 81%).

(18) Diethyl 2,2-dicyano-3-(4-acetoxyphenyl)cyclopropane-1,1-dicarboxylate (4as)



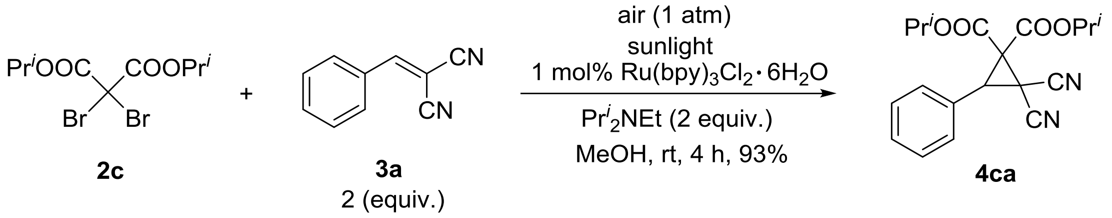
The reaction of **2a** (38 μL, 0.20 mmol), **3s** (85 mg, 0.40 mmol), $Ru(bpy)_3Cl_2$ 6H_2O (2 mg, 0.0027 mmol), Pr^i_2NEt (66 μL, 0.40 mmol), and anhydrous methanol (10 mL) afforded **4as** as a liquid (57 mg, 77%).

(19) Dimethyl 3-phenyl-2,2-dicyanocyclopropane-1,1-dicarboxylate (4ba)[17]



The reaction of **2b** (58 mg, 0.20 mmol), **3a** (62 mg, 0.40 mmol), $Ru(bpy)_3Cl_2$ 6H_2O (2 mg, 0.0027 mmol), Pr^i_2NEt (66 μL, 0.40 mmol), and anhydrous methanol (10 mL) afforded **4ba** as a solid (54 mg, 95%).

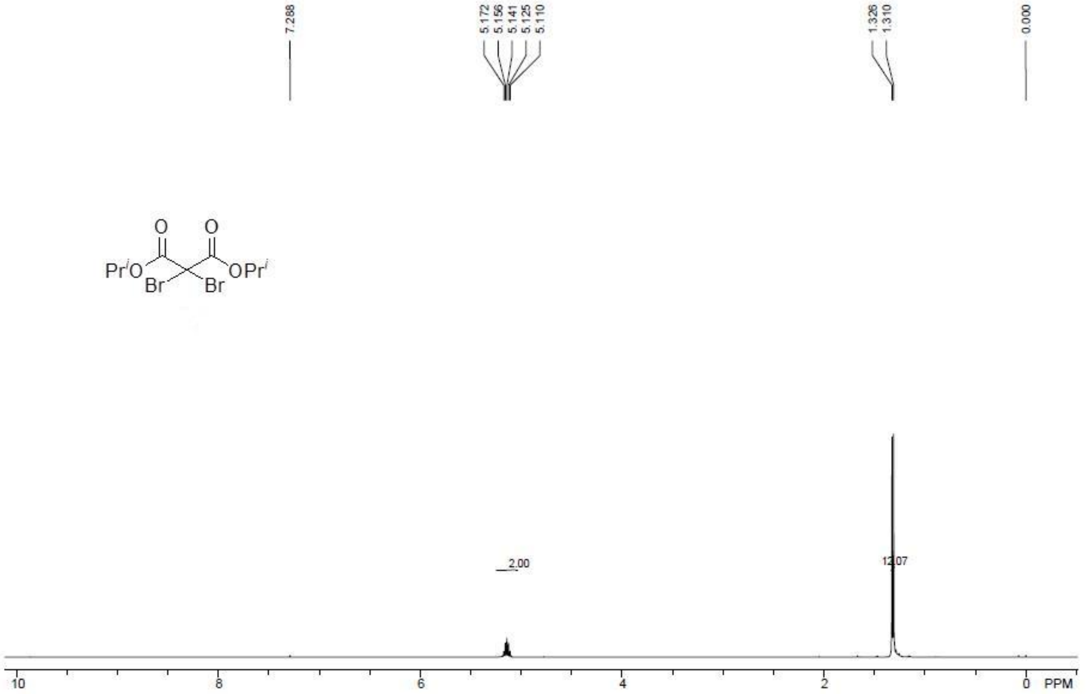
(20) Diisopropyl 3-phenyl-2,2-dicyanocyclopropane-1,1-dicarboxylate (4ca)

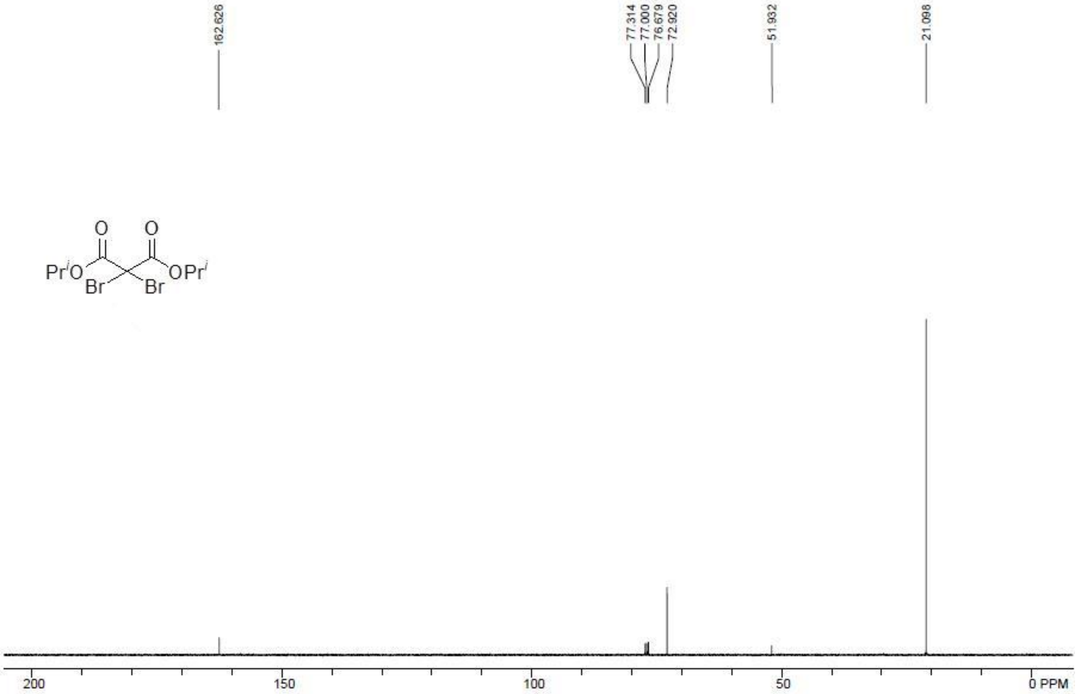


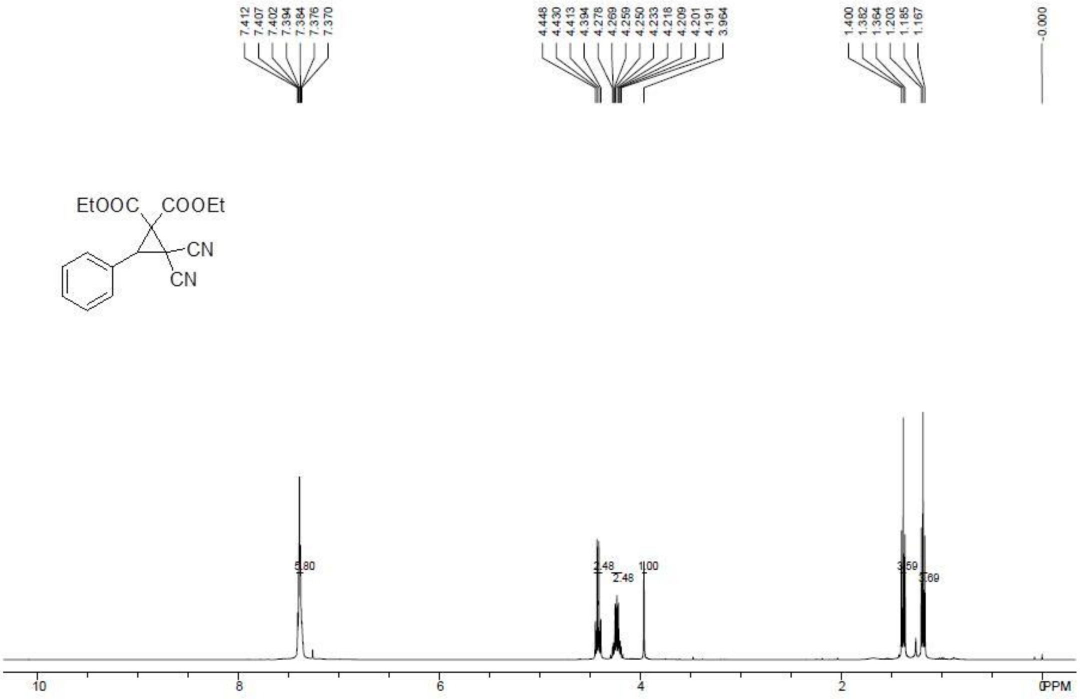
The reaction of **2c** (70 mg, 0.20 mmol), **3a** (61 mg, 0.40 mmol),

$Ru(bpy)_3Cl_2$ $6H_2O$ (2 mg, 0.0027 mmol), $Pr^i{}_2NEt$ (66 μL, 0.40 mmol), and anhydrous methanol (10 mL) afforded **4ca** as a liquid (63 mg, 93%).

NMR Spectra


7.288
5.172
5.156
5.141
5.125
5.110
1.326
1.310
0.000
Pr^{i}O
OPr^i
O
O
Br
Br
2.00
12.07
10
8
6
4
2
0
PPM


162.626
77.314
77.000
76.679
72.920
51.932
21.098
Pr^{i}O
OPr^i
O
O
Br
Br
200
150
100
50
0 PPM


7.412
7.407
7.402
7.394
7.384
7.376
7.370
4.448
4.430
4.413
4.394
4.278
4.269
4.259
4.250
4.233
4.218
4.209
4.201
4.191
3.964
1.400
1.382
1.364
1.203
1.185
1.167
-0.000
EtOOC
COOEt
CN
CN
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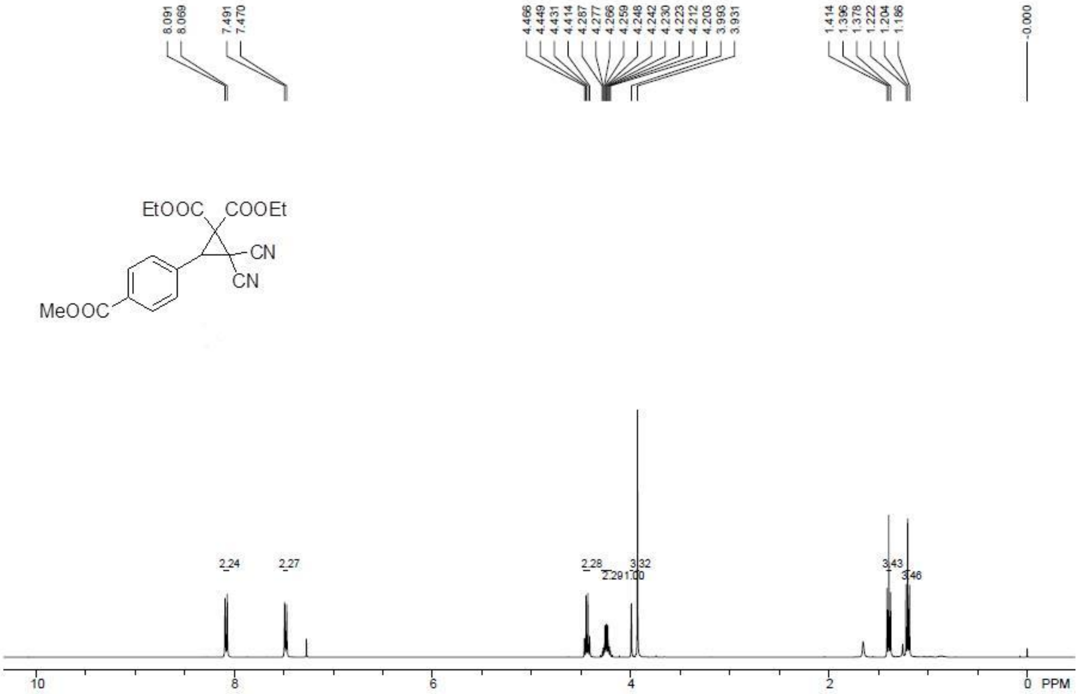
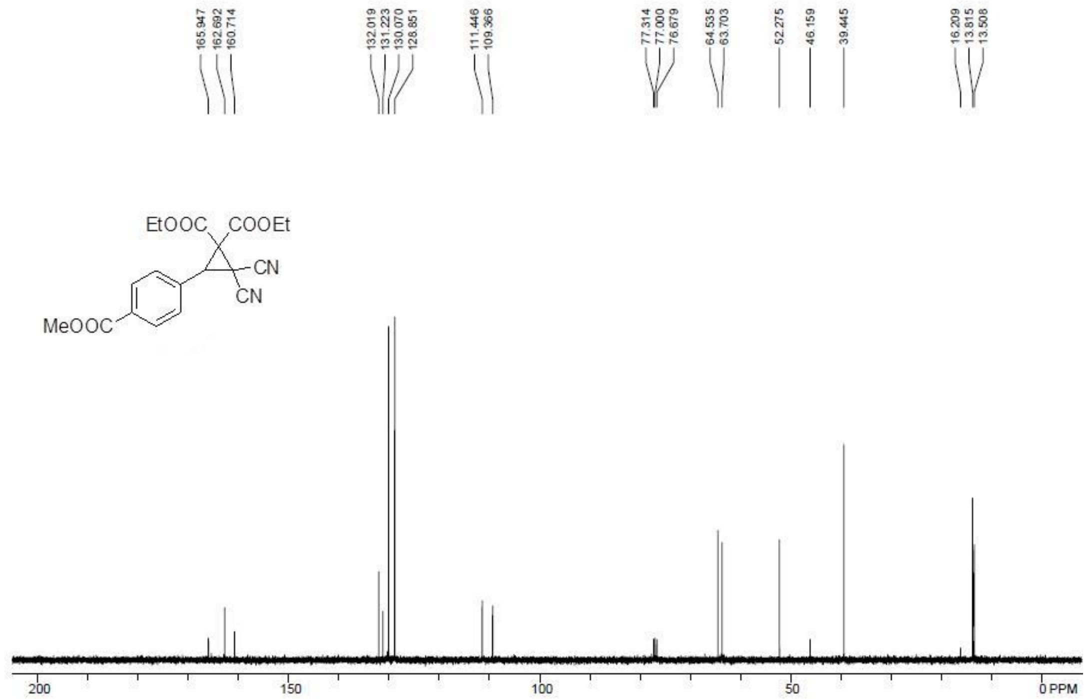
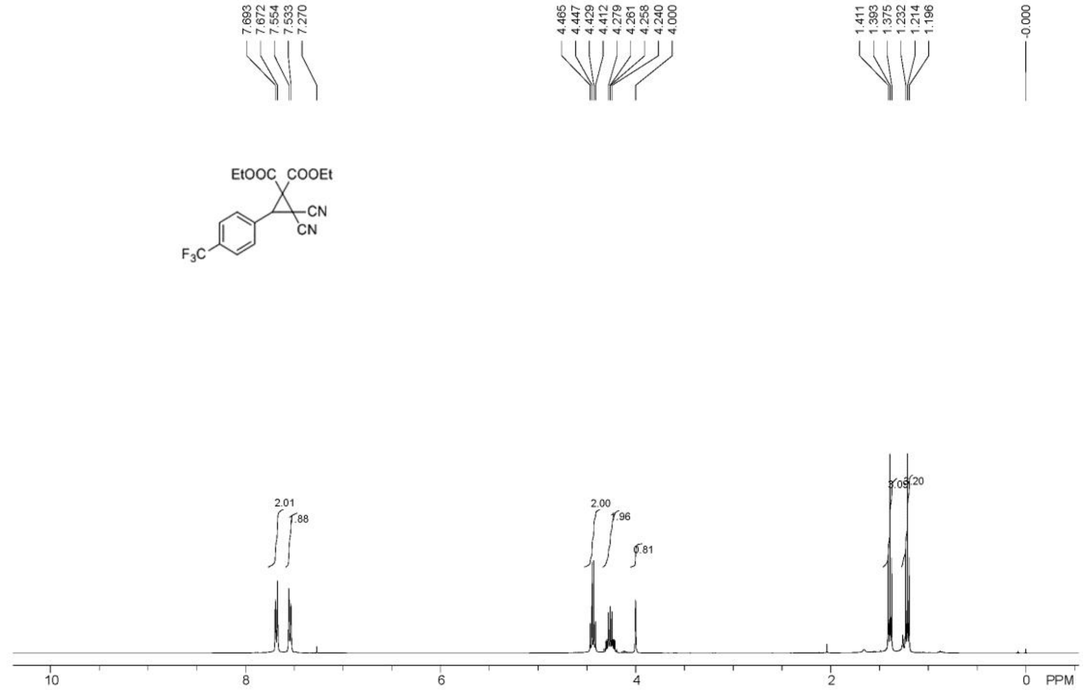
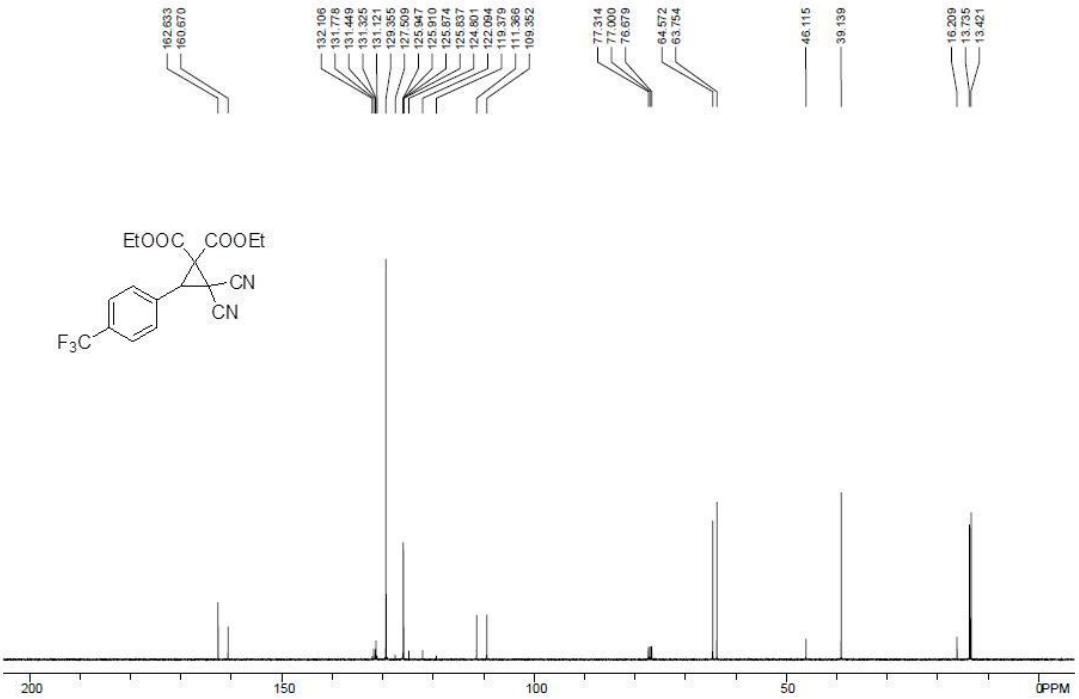
2.48
2.48
1.00
3.59
3.69
10
8
6
4
2
0
PPM


8.091
8.069
7.491
7.470
4.466
4.449
4.431
4.414
4.287
4.277
4.266
4.259
4.248
4.242
4.230
4.223
4.212
4.203
3.993
3.931
1.414
1.396
1.378
1.222
1.204
1.186
-0.000
EtOOC
COOEt
CN
CN
MeOOC
2.24
2.27
2.28
2.29
1.00
3.32
3.43
3.46
10
8
6
4
2
0
PPM


165.947
162.692
160.714
132.019
131.223
130.070
128.851
111.446
109.366
77.314
77.000
76.679
64.535
63.703
52.275
46.159
39.445
16.209
13.815
13.508
EtOOC
COOEt
CN
CN
MeOOC
200
150
100
50
0 PPM


7.693
7.672
7.554
7.533
7.270
4.465
4.447
4.429
4.412
4.279
4.261
4.258
4.240
4.000
1.411
1.393
1.375
1.232
1.214
1.196
-0.000
EtOOC
COOEt
CN
CN
F3C
2.01
1.88
2.00
1.96
0.81
3.09
3.20
10
8
6
4
2
0
PPM


162.633
160.670
132.106
131.778
131.449
131.325
131.121
129.355
127.509
125.947
125.910
125.874
125.837
124.801
122.094
119.379
111.366
109.352
77.314
77.000
76.679
64.572
63.754
46.115
39.139
16.209
13.735
13.421
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COOEt
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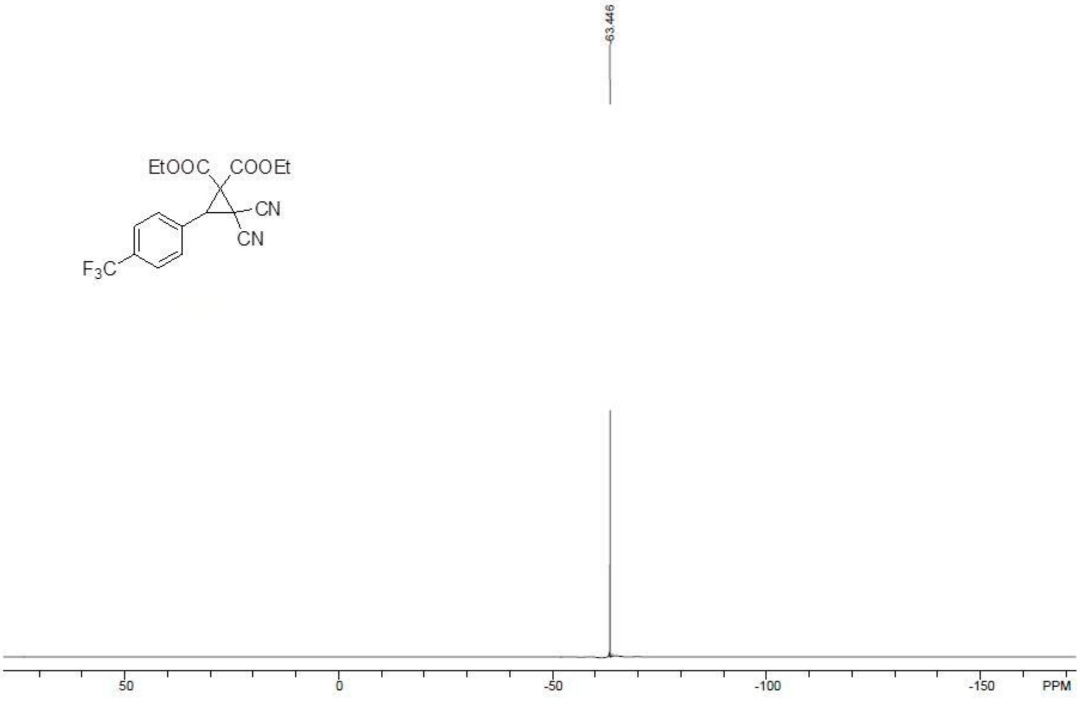
200
150
100
50
0PPM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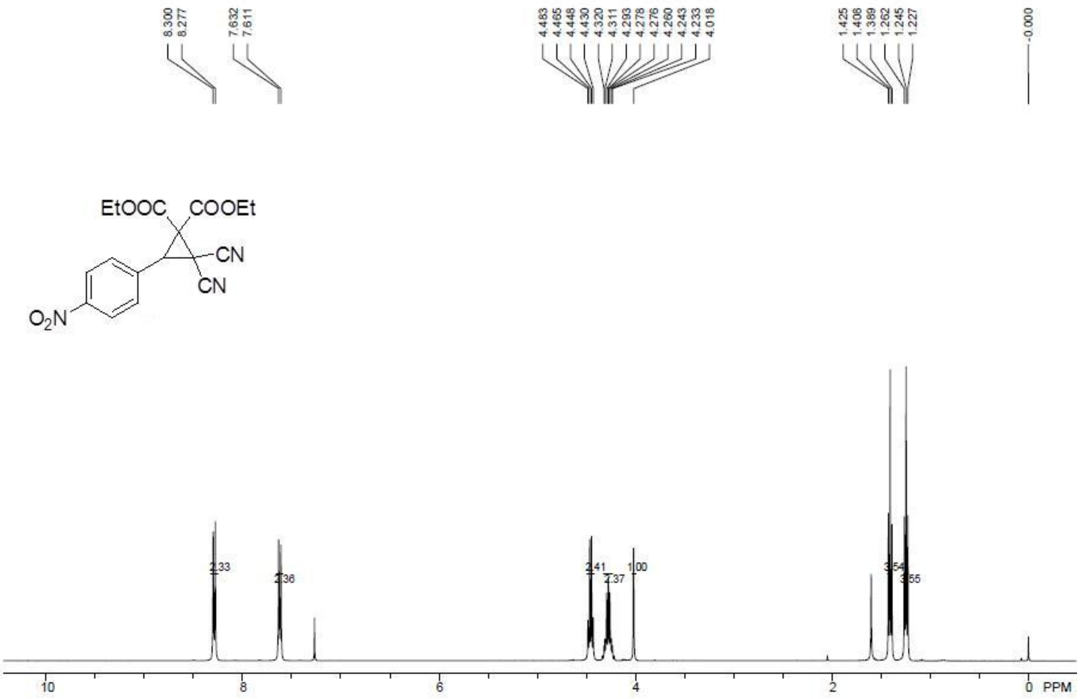
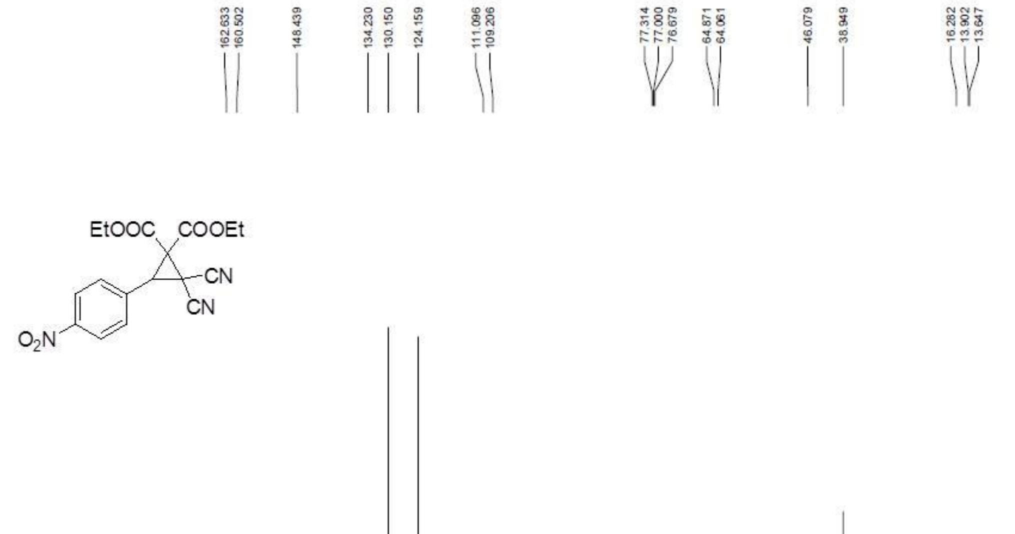
COOEt
CN
CN
F3C
50
0
-50
-100
-150
PPM


8.300
8.277
7.632
7.611
4.483
4.465
4.448
4.430
4.320
4.311
4.293
4.278
4.276
4.260
4.243
4.233
4.018
1.425
1.408
1.389
1.262
1.245
1.227
-0.000
EtOOC
COOEt
CN
CN
O_2N
2.33
2.36
2.41
2.37
1.00
3.54
3.55
10
8
6
4
2
0 PPM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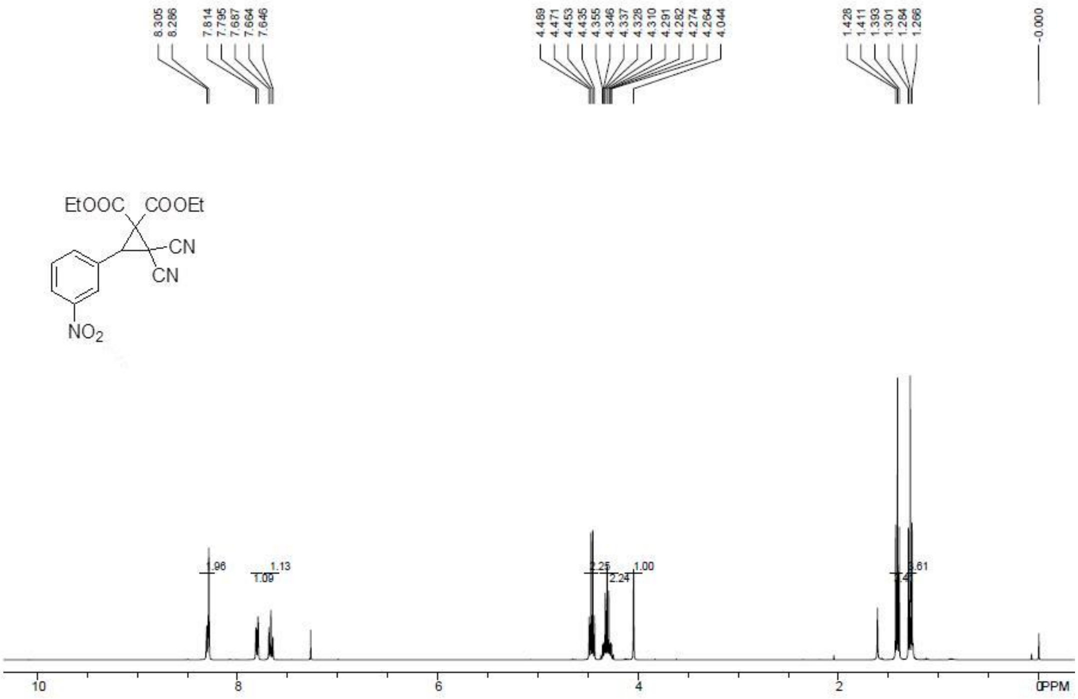
148.439
134.230
130.150
124.159
111.096
109.206
77.314
77.000
76.679
64.871
64.061
46.079
38.949
16.282
13.902
13.647
EtOOC
COOEt
CN
CN
O_2N
200
150
100
50
0PPM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8.286
7.814
7.795
7.687
7.664
7.646
4.489
4.471
4.453
4.435
4.355
4.346
4.337
4.328
4.310
4.291
4.282
4.274
4.264
4.044
1.428
1.411
1.393
1.301
1.284
1.266
-0.000
EtOOC
COOEt
CN
CN
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1.09
2.25
2.24
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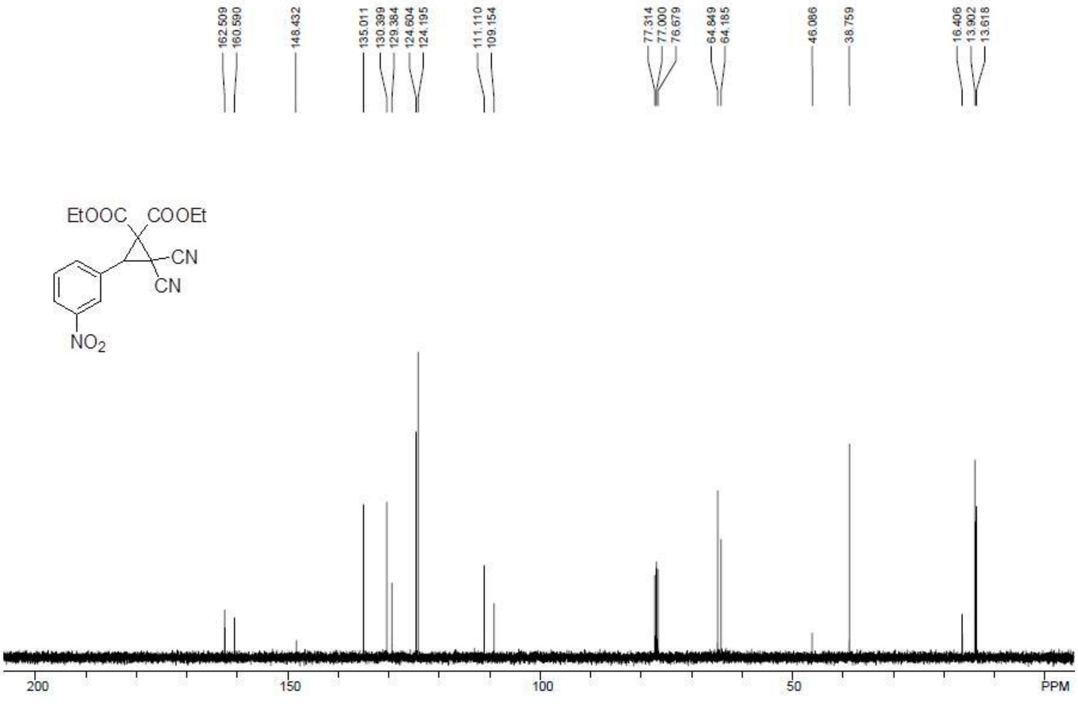
10
8
6
4
2
0
PPM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135.011
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129.384
124.604
124.195
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109.154
77.314
77.000
76.679
64.849
64.185
46.086
38.759
16.406
13.902
13.618
EtOOC
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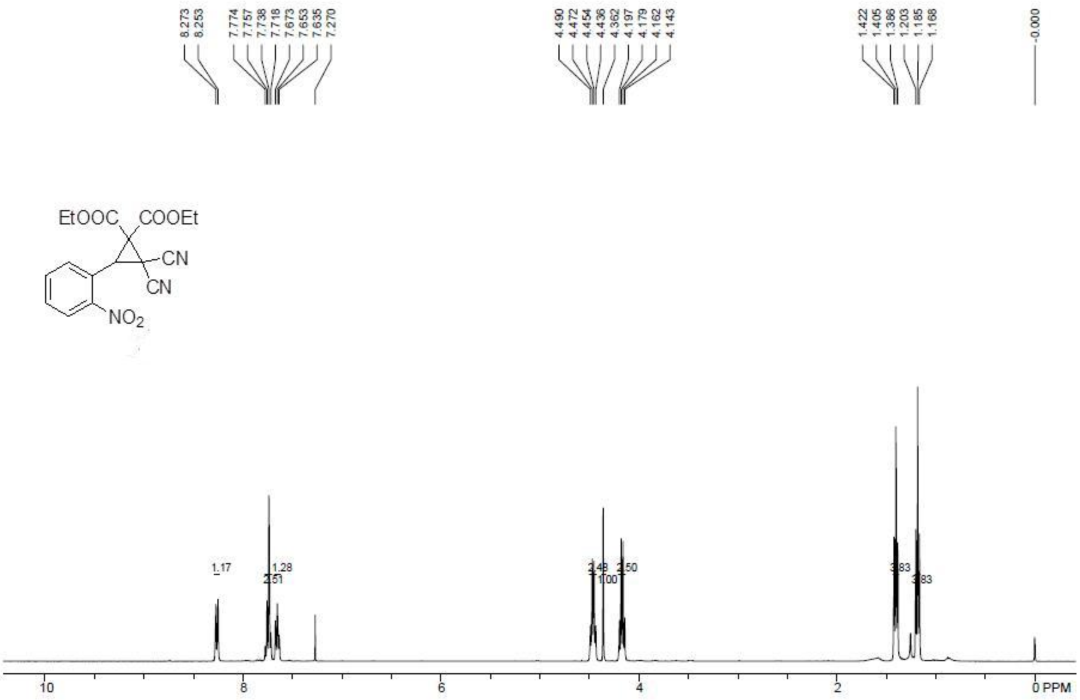
CN
CN
NO2
200
150
100
50
PPM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8.253
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7.738
7.718
7.673
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4.454
4.436
4.362
4.197
4.179
4.162
4.143
1.422
1.405
1.386
1.203
1.185
1.168
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COOEt
CN
CN
NO2
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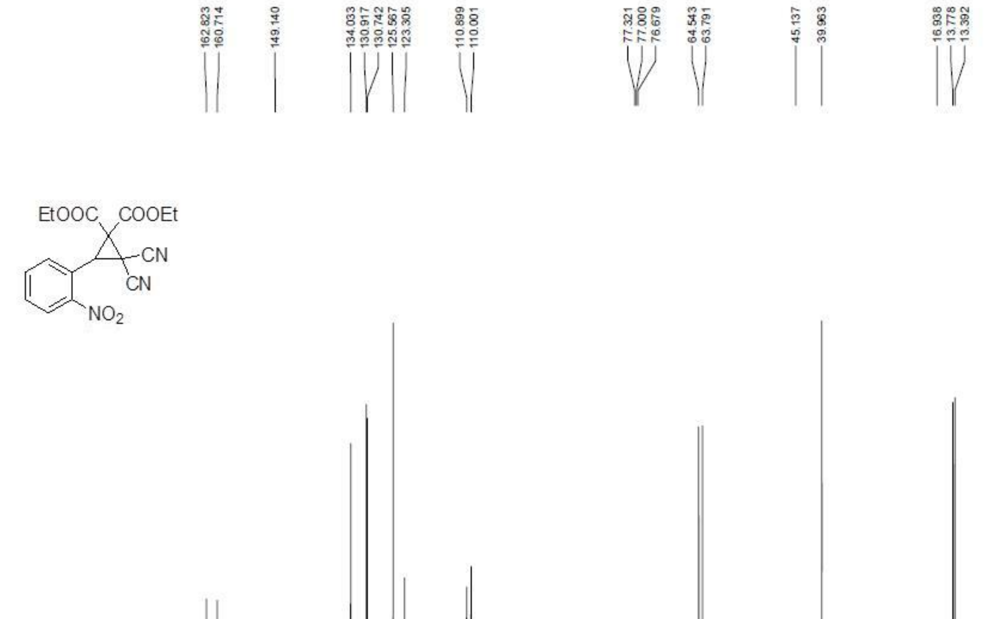
3.83
10
8
6
4
2
0 PPM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77.000
76.679
64.543
63.791
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13.392
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CN
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200
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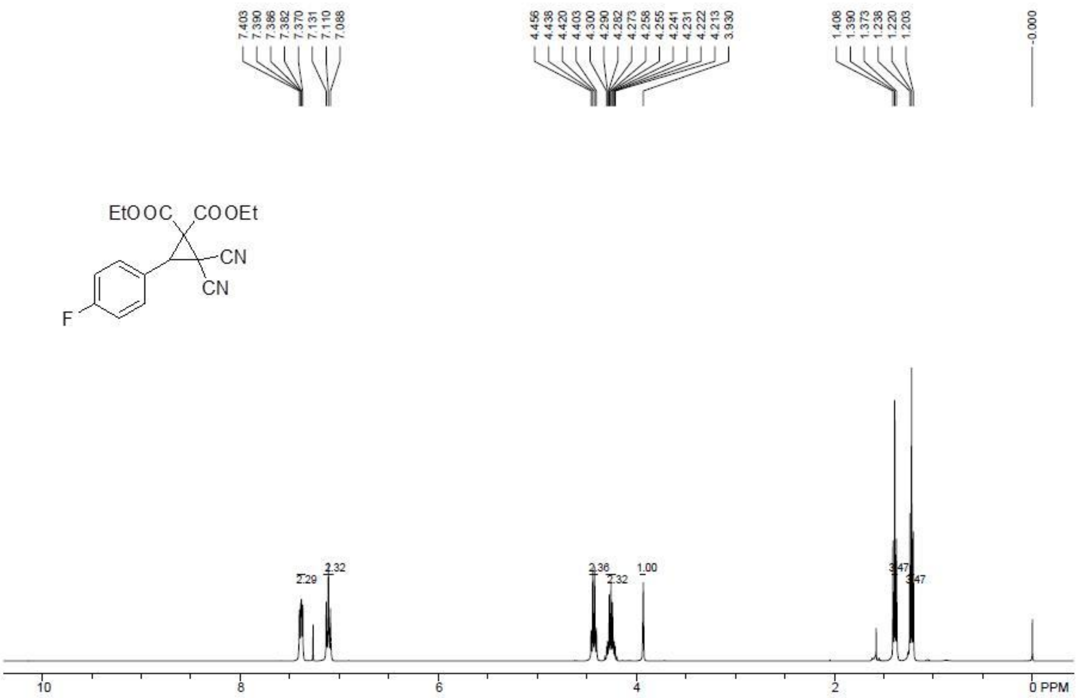
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4.300
4.290
4.282
4.273
4.258
4.255
4.241
4.231
4.222
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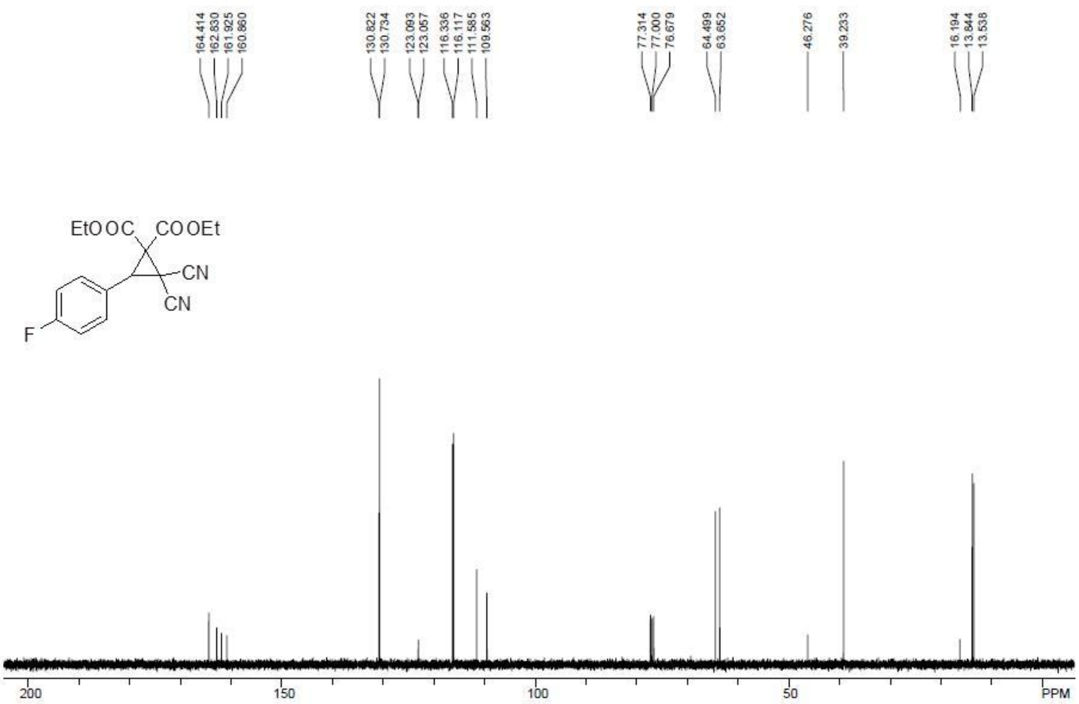
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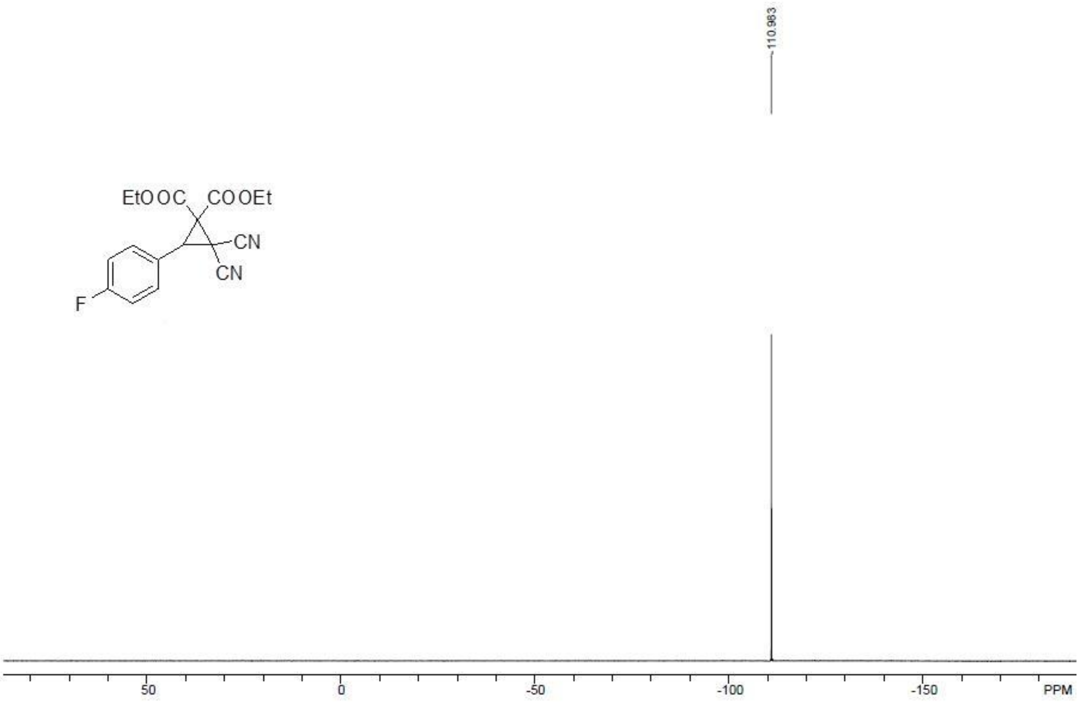
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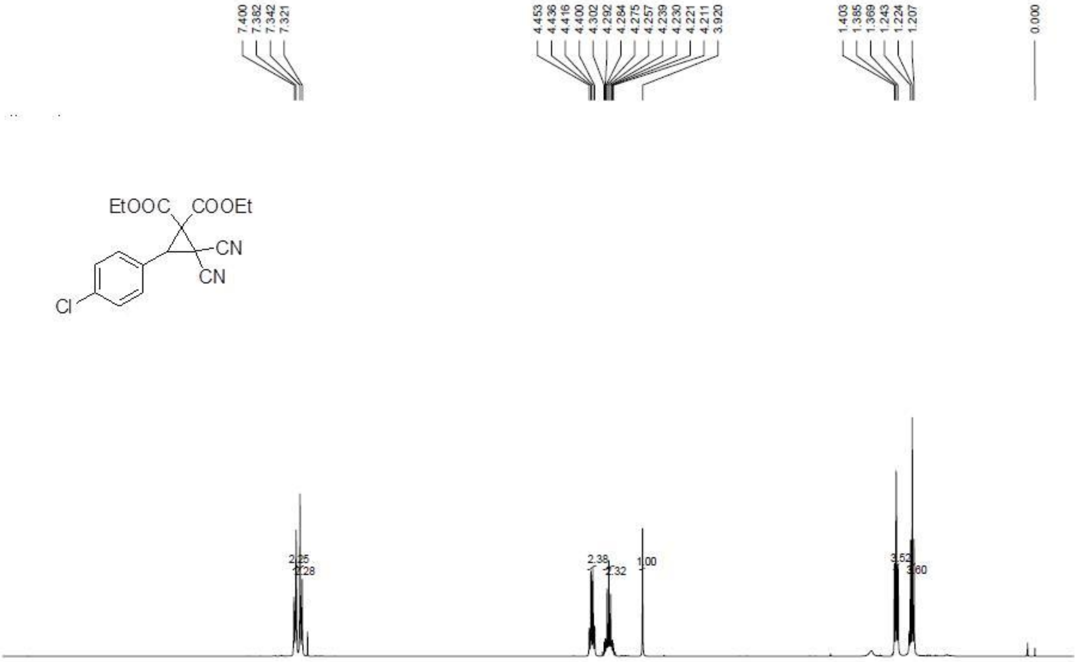
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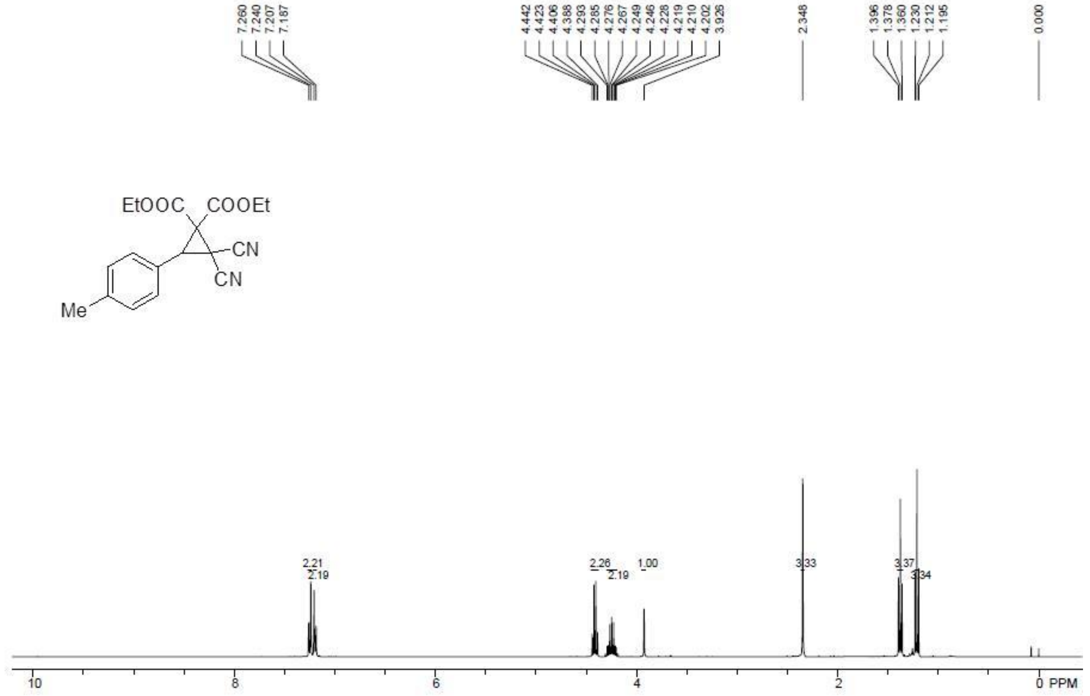
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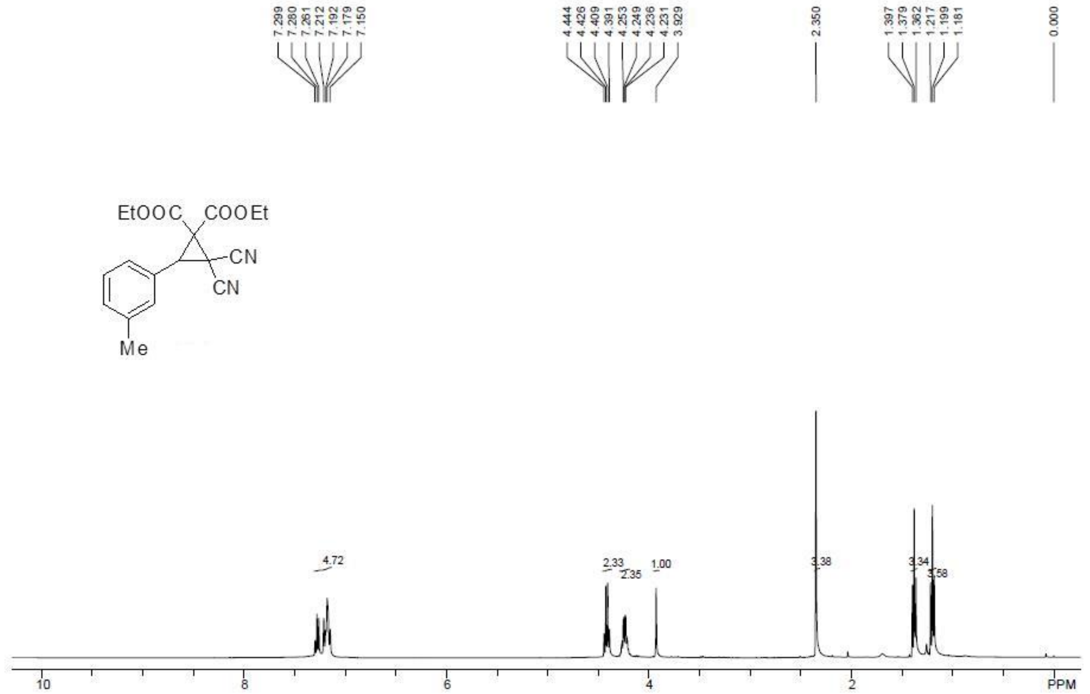
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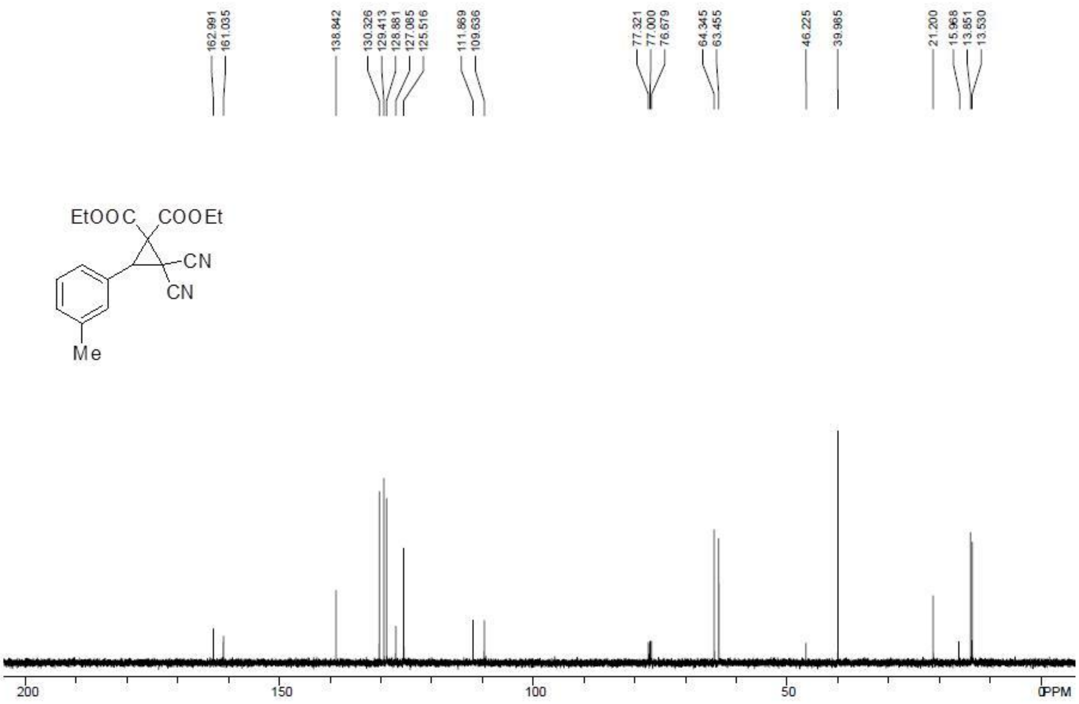
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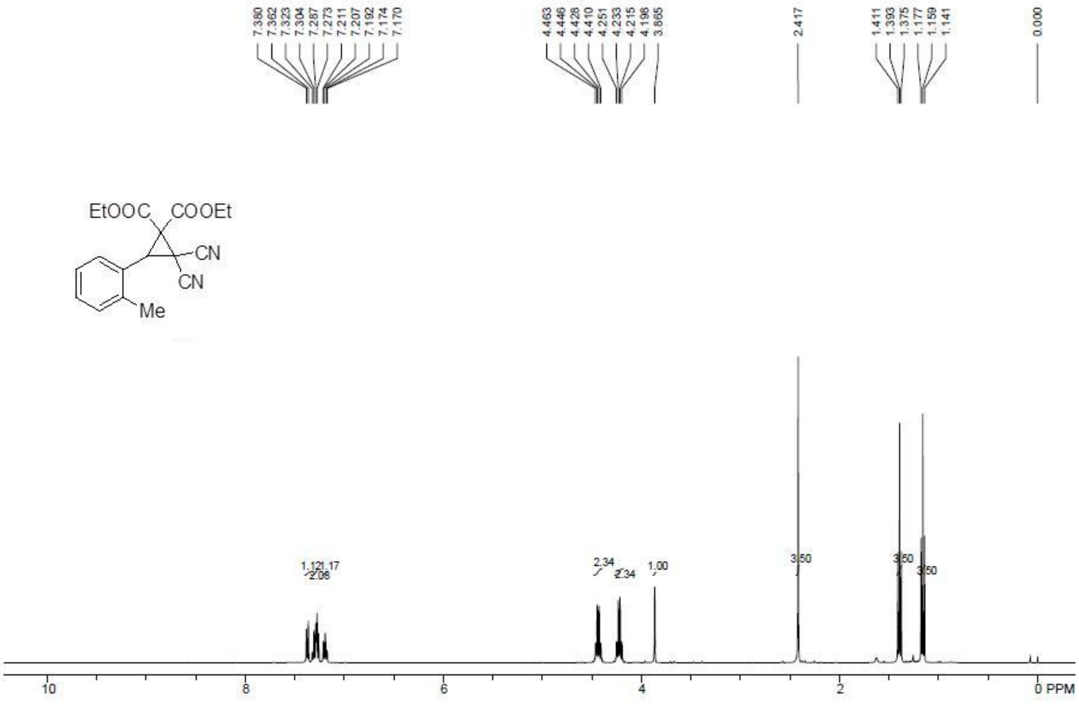
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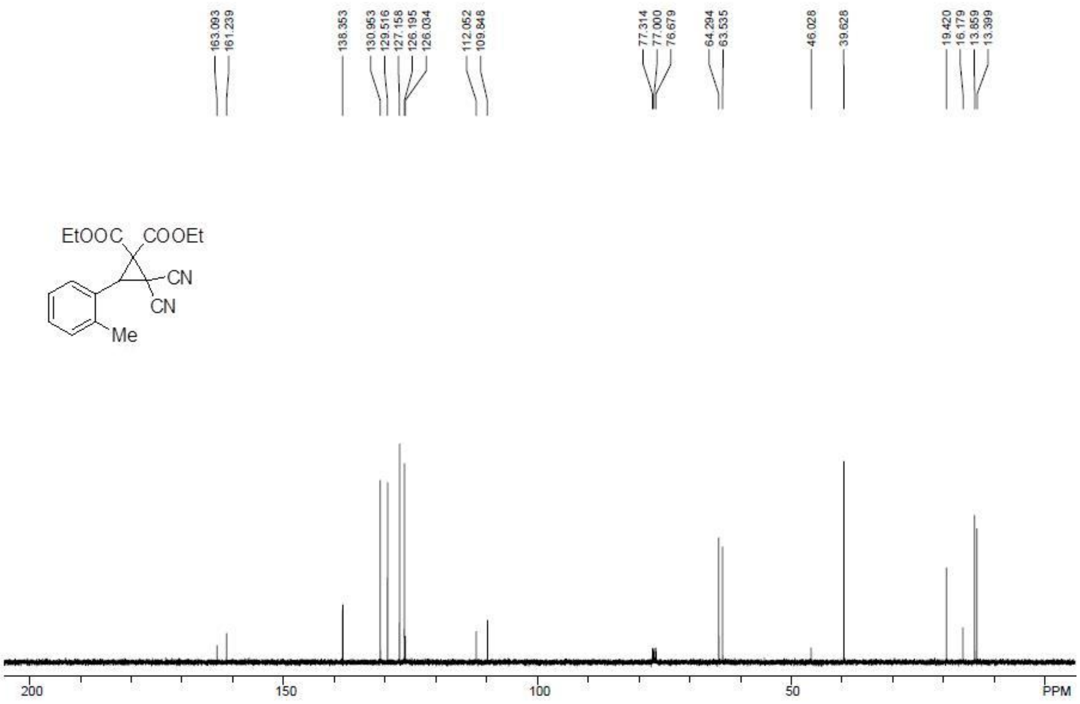
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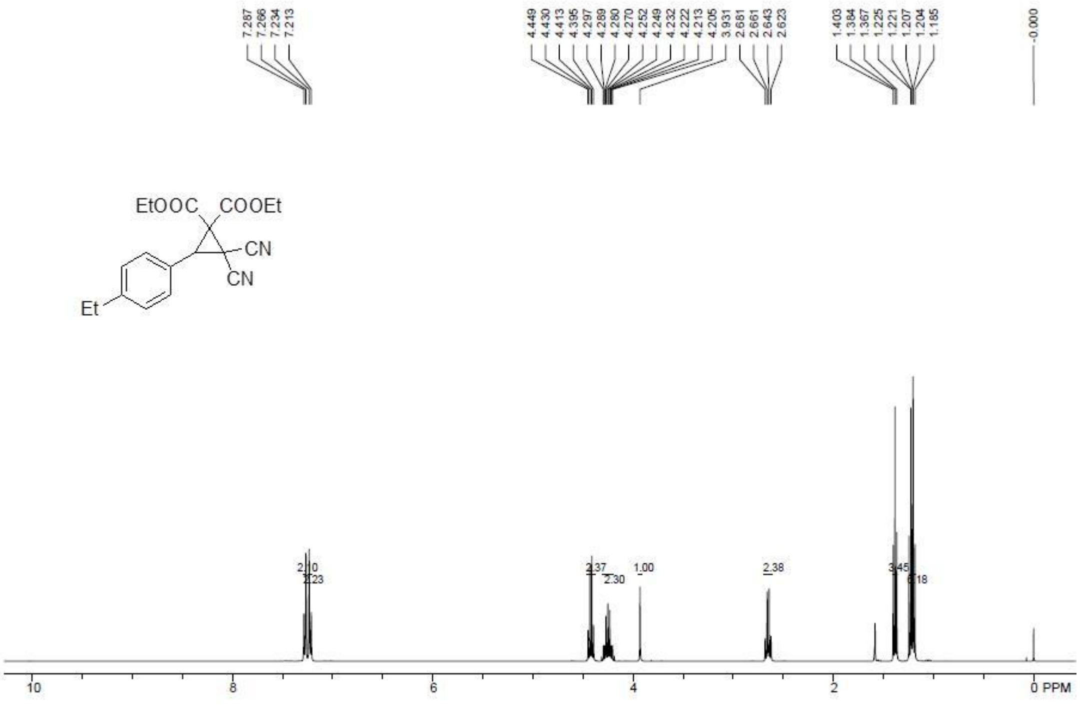
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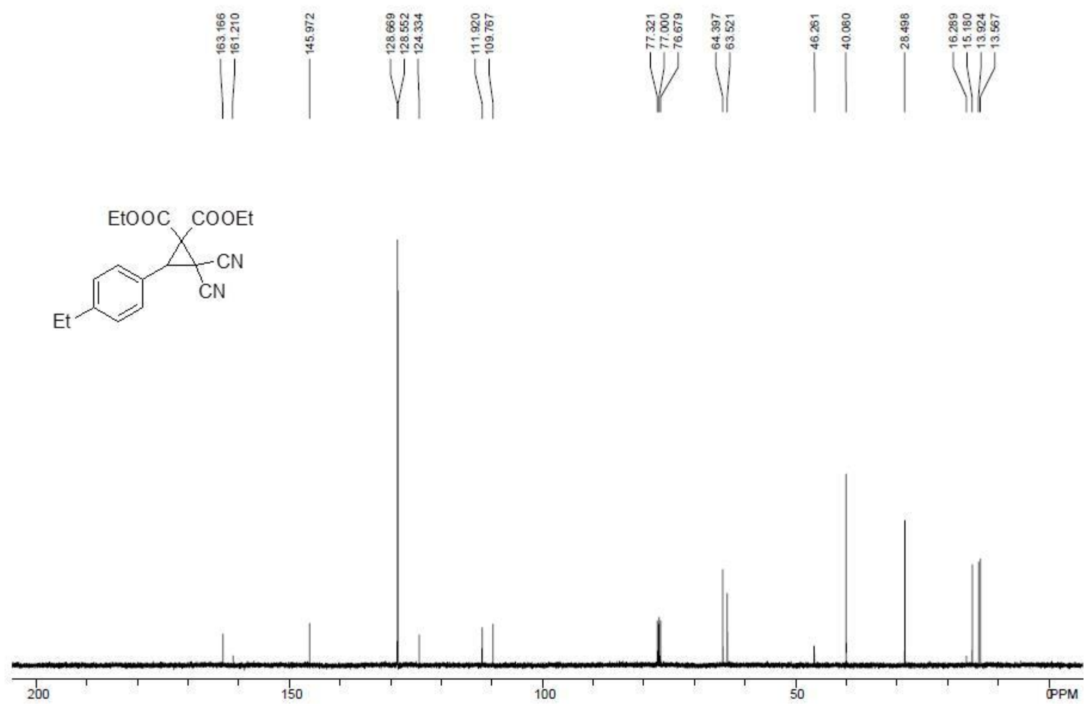
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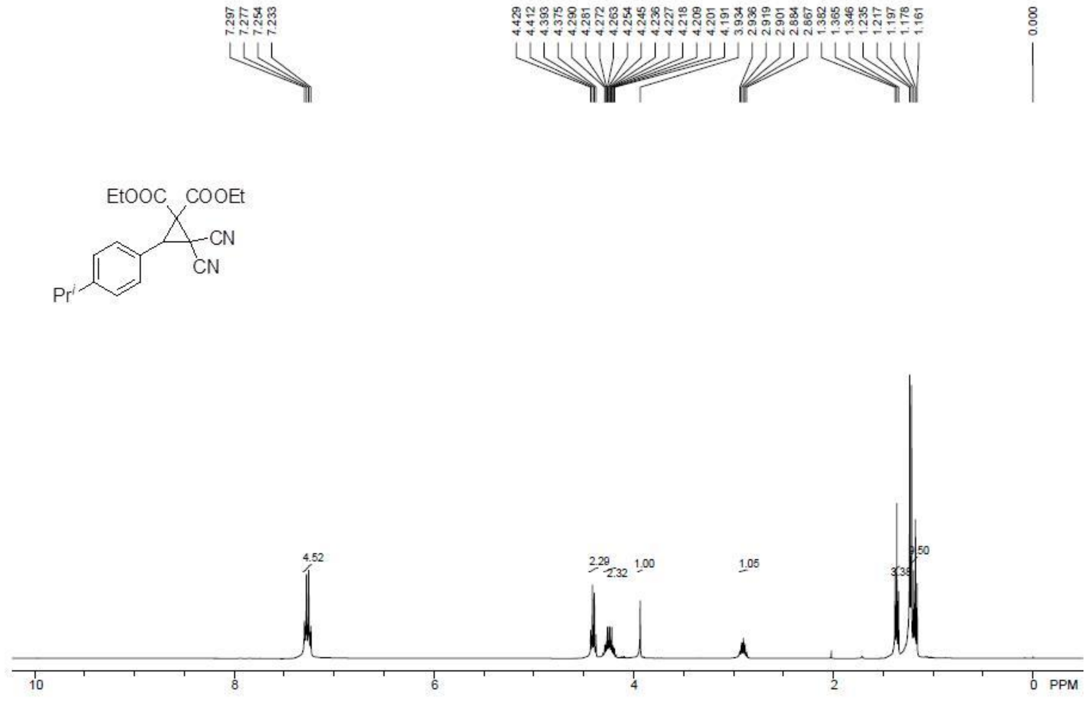
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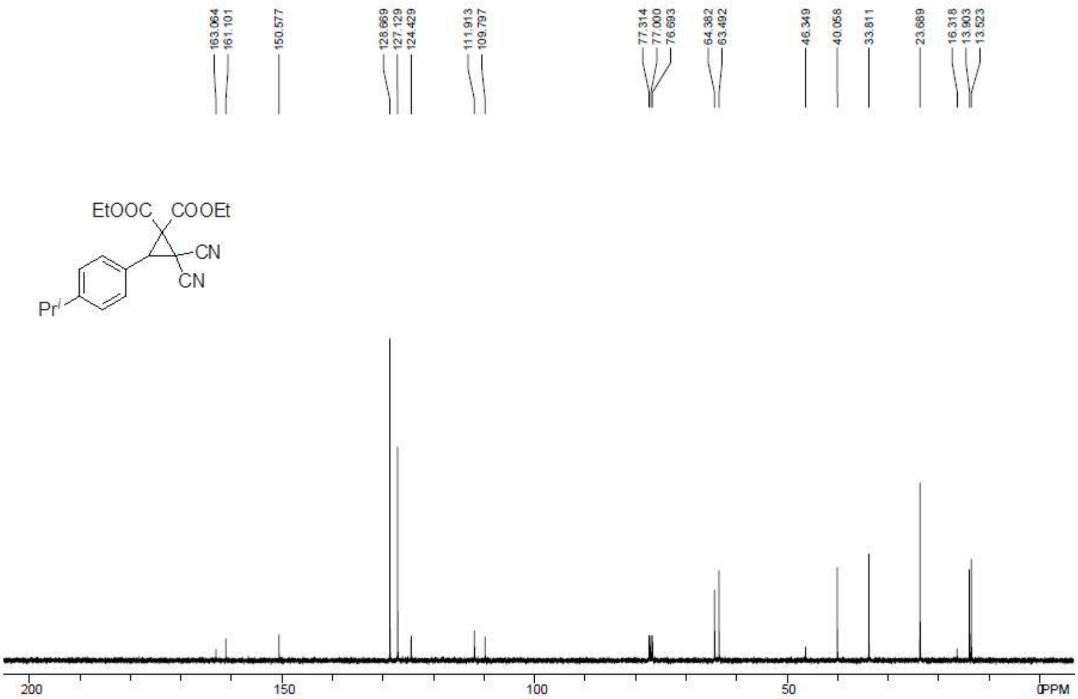
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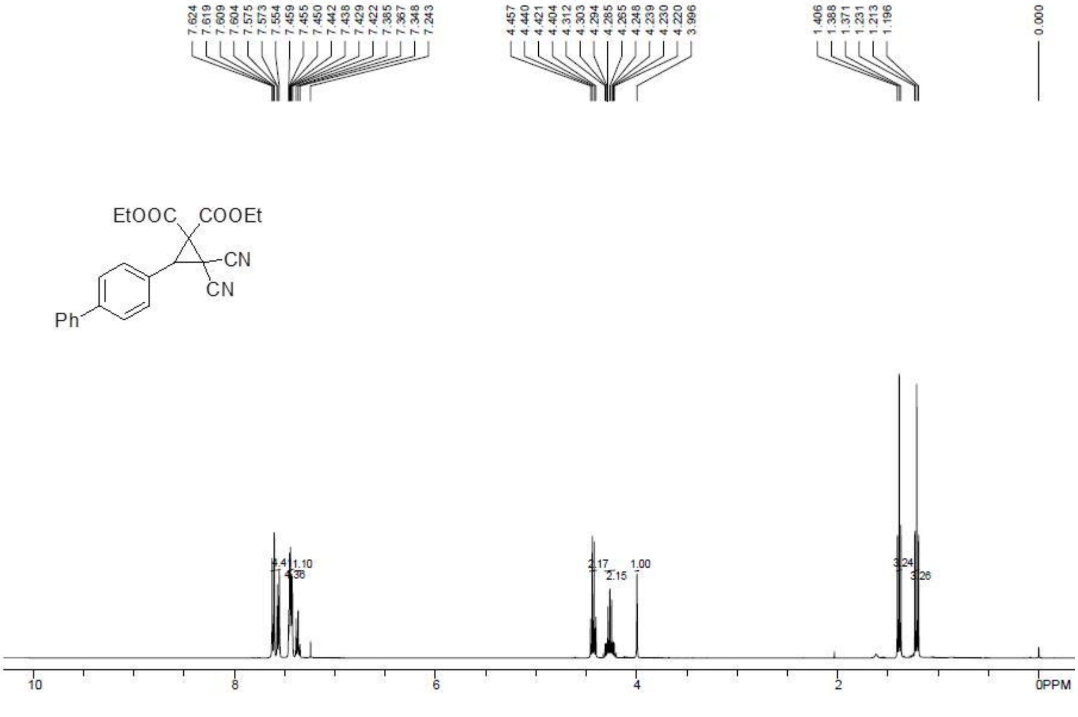
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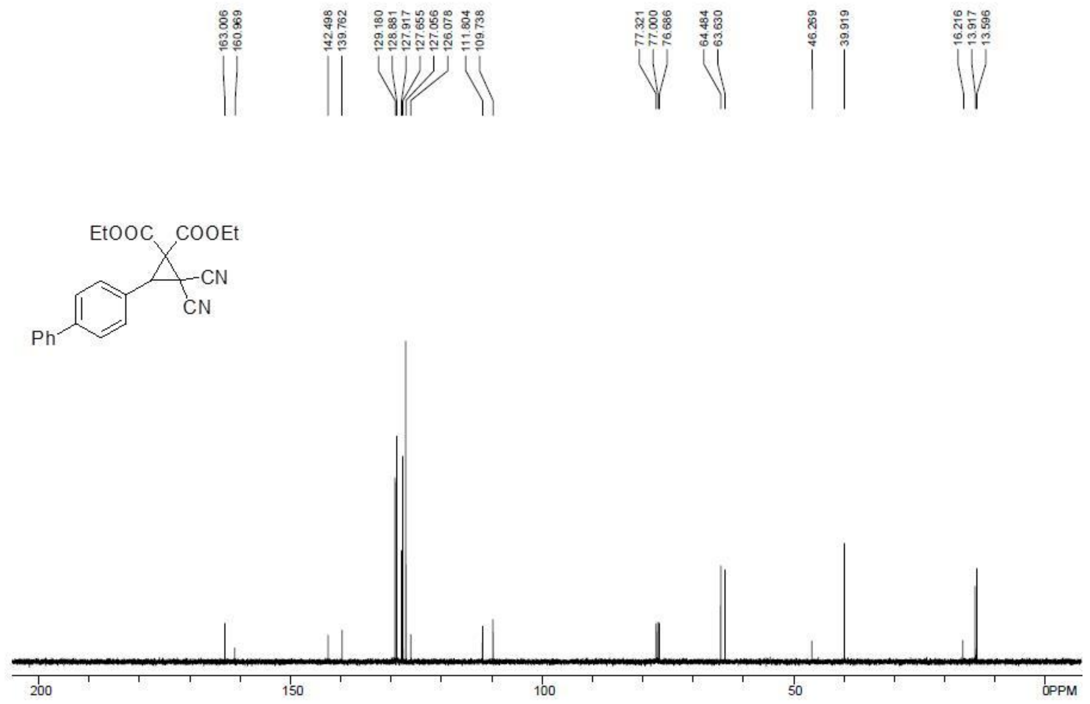
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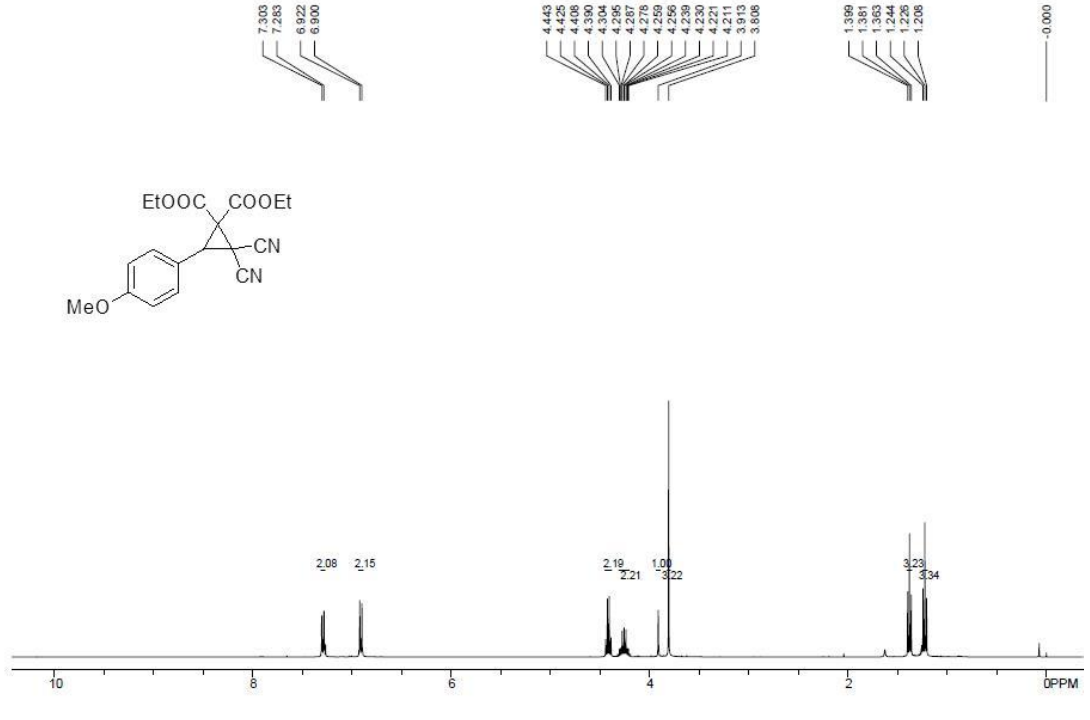
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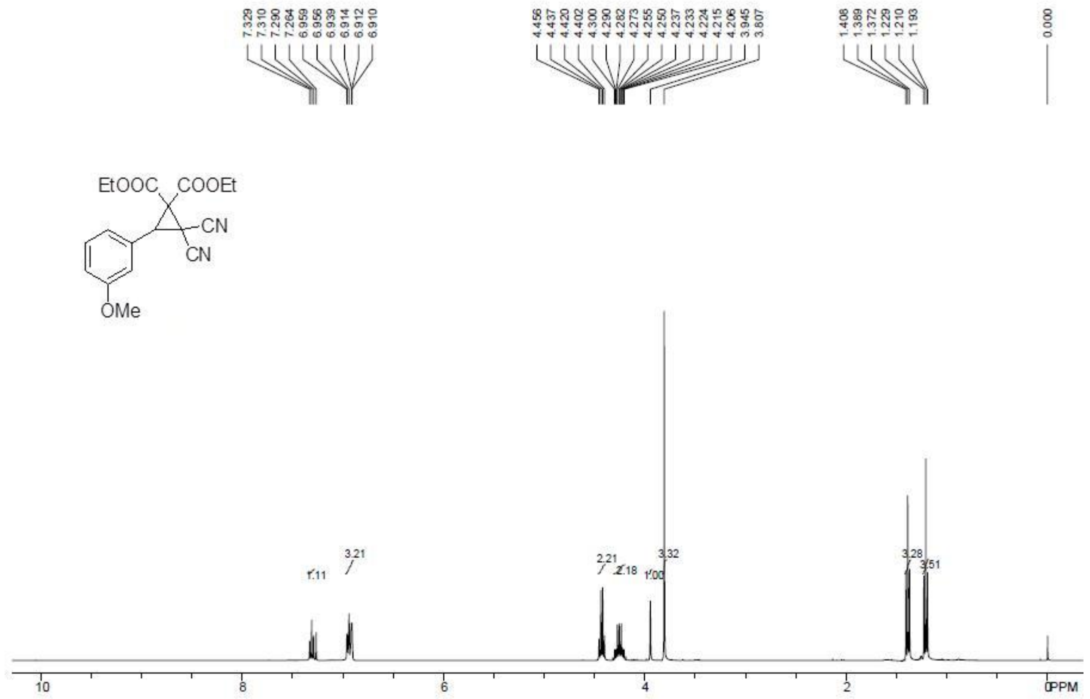

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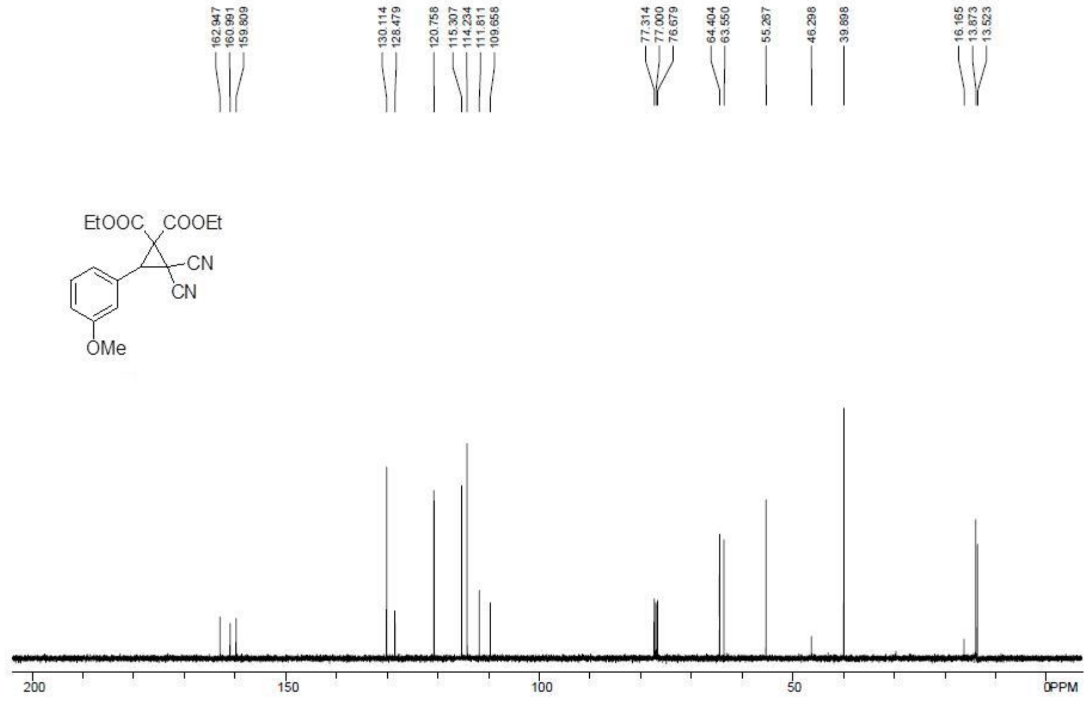

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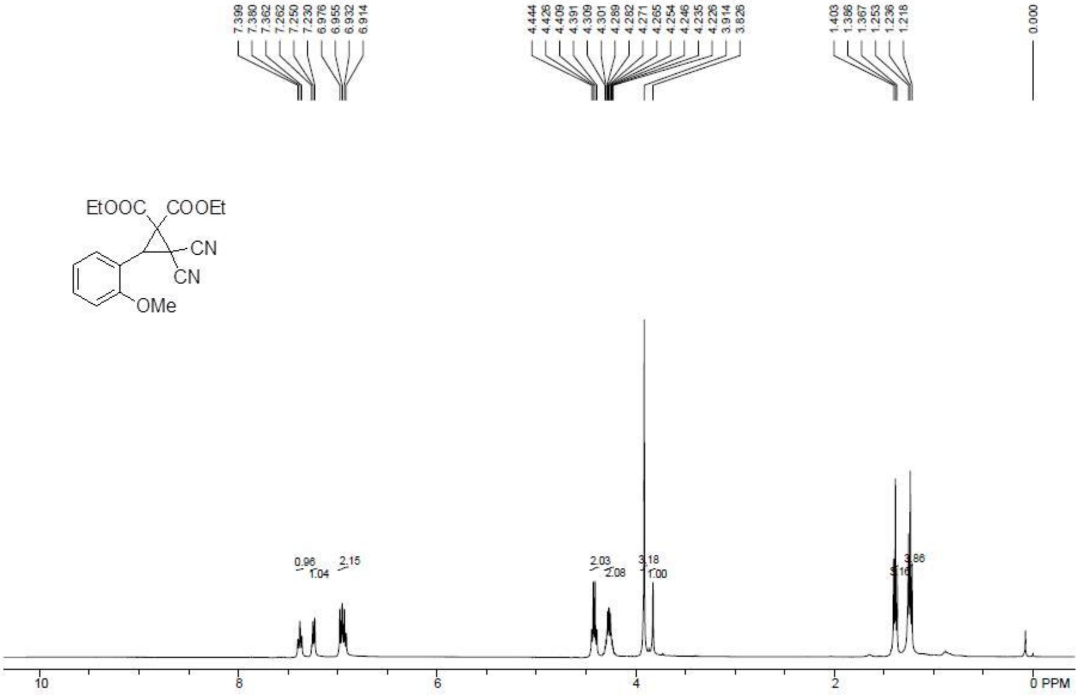
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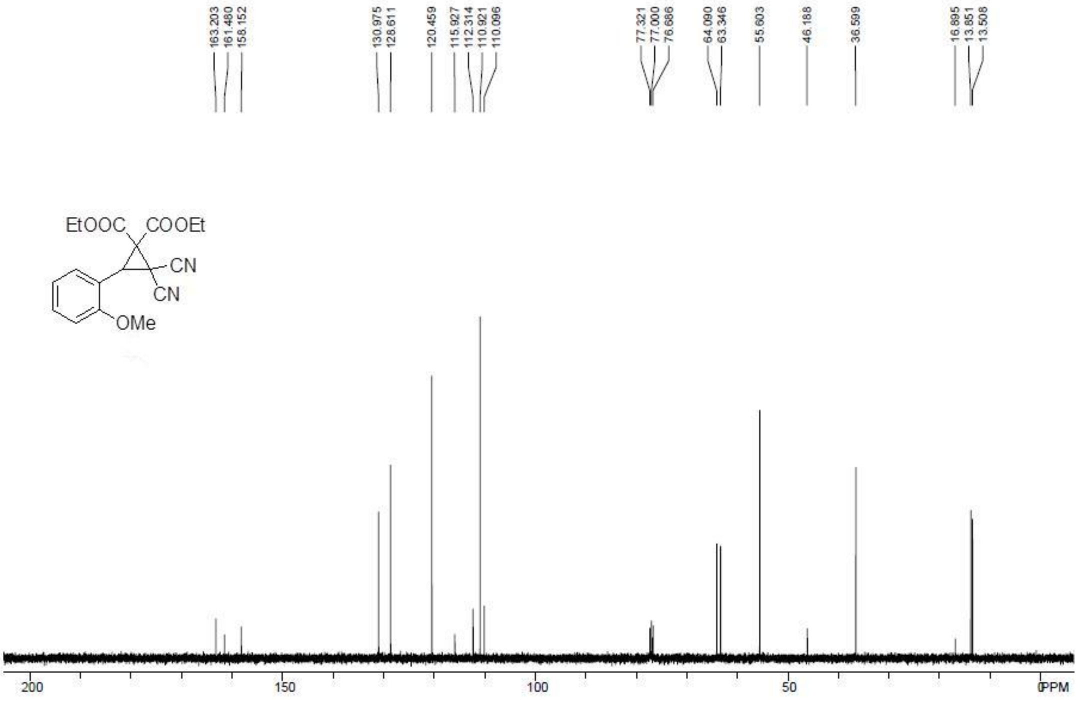
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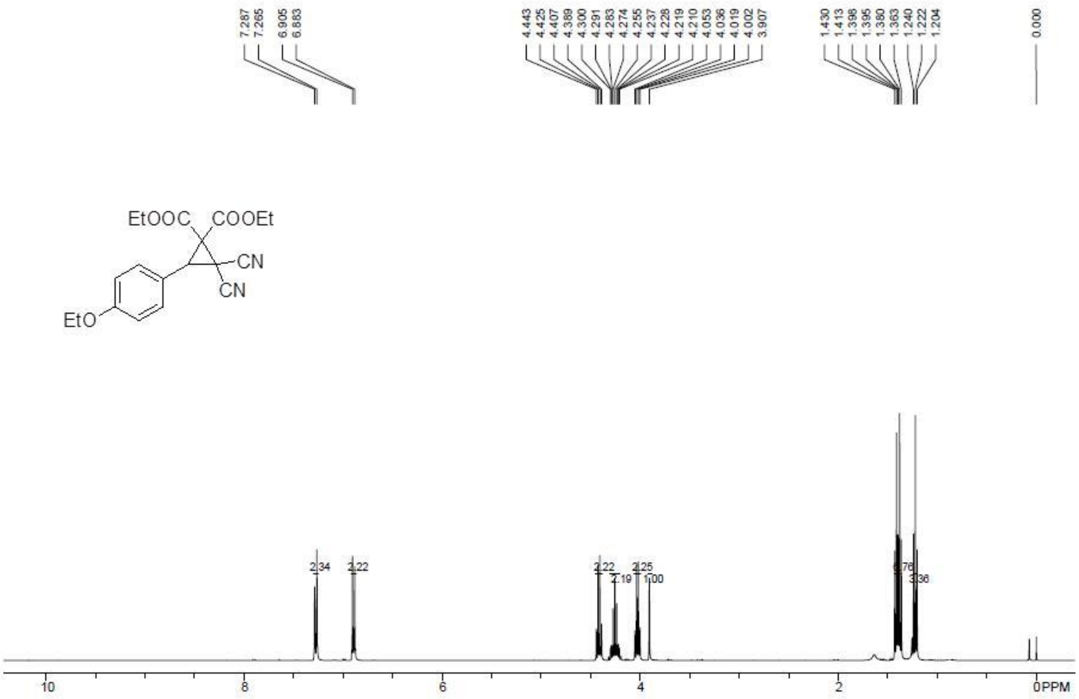
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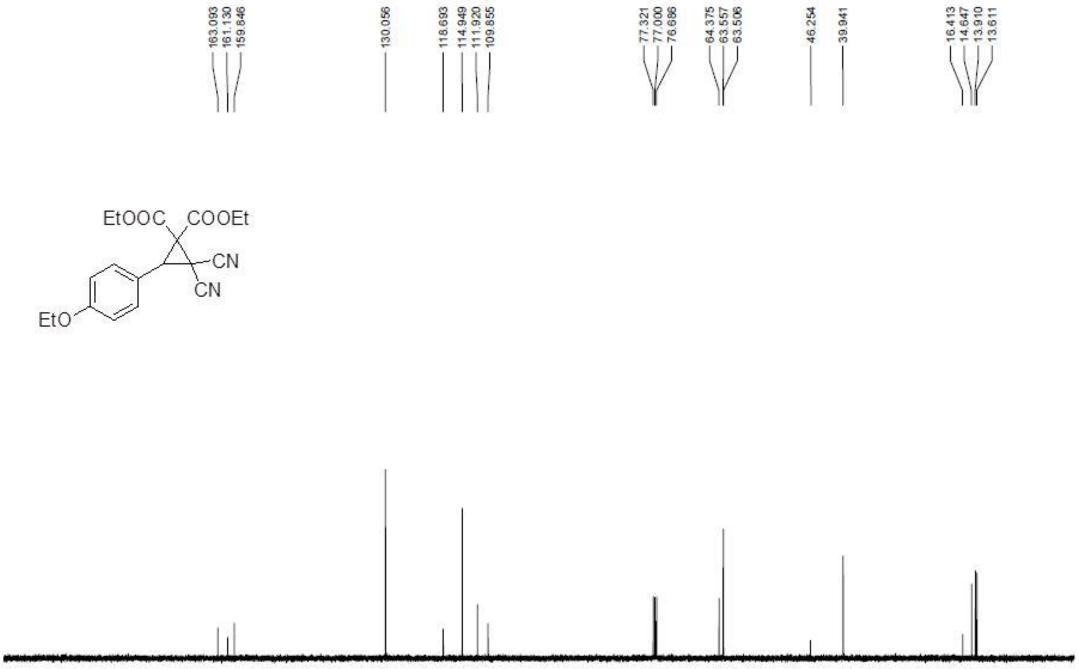
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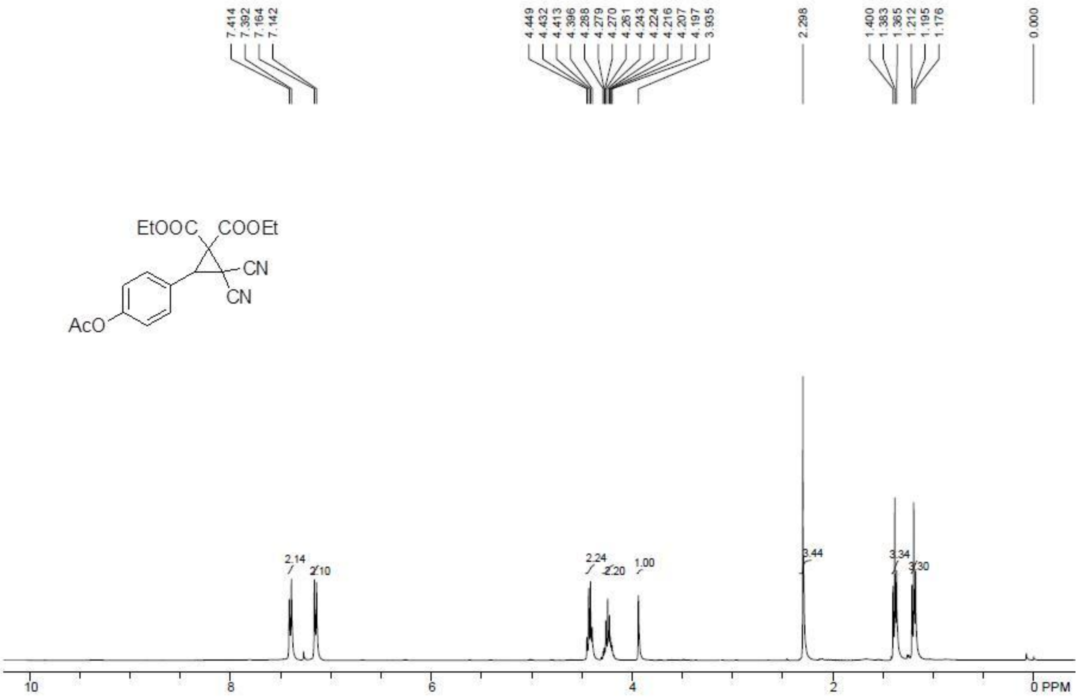
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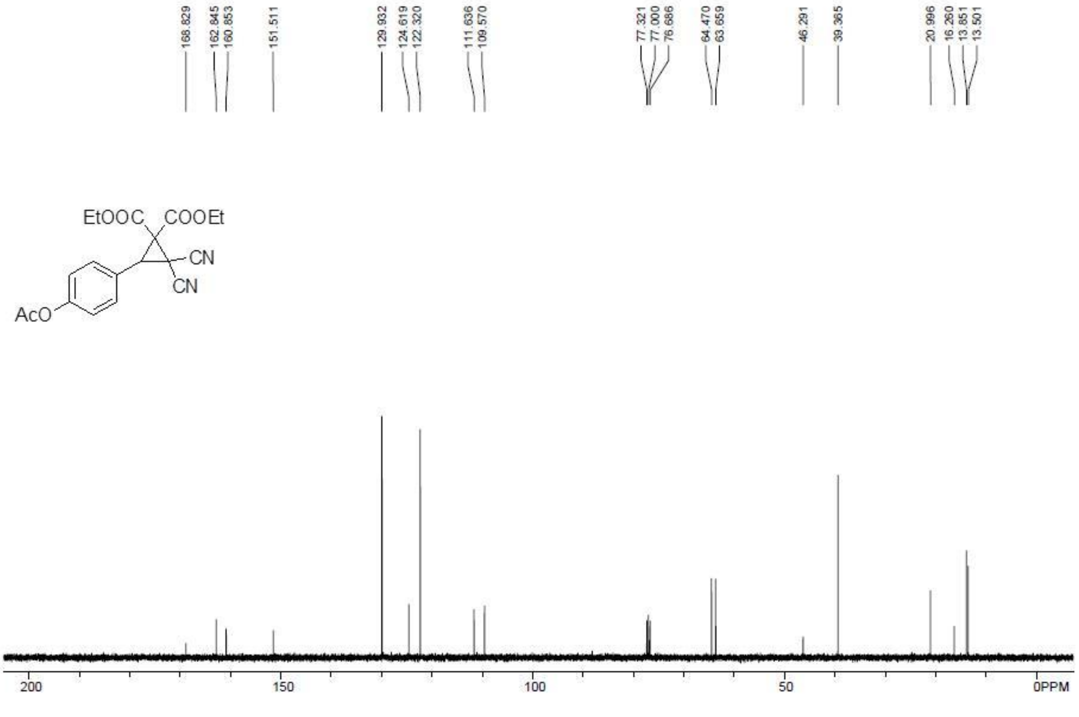
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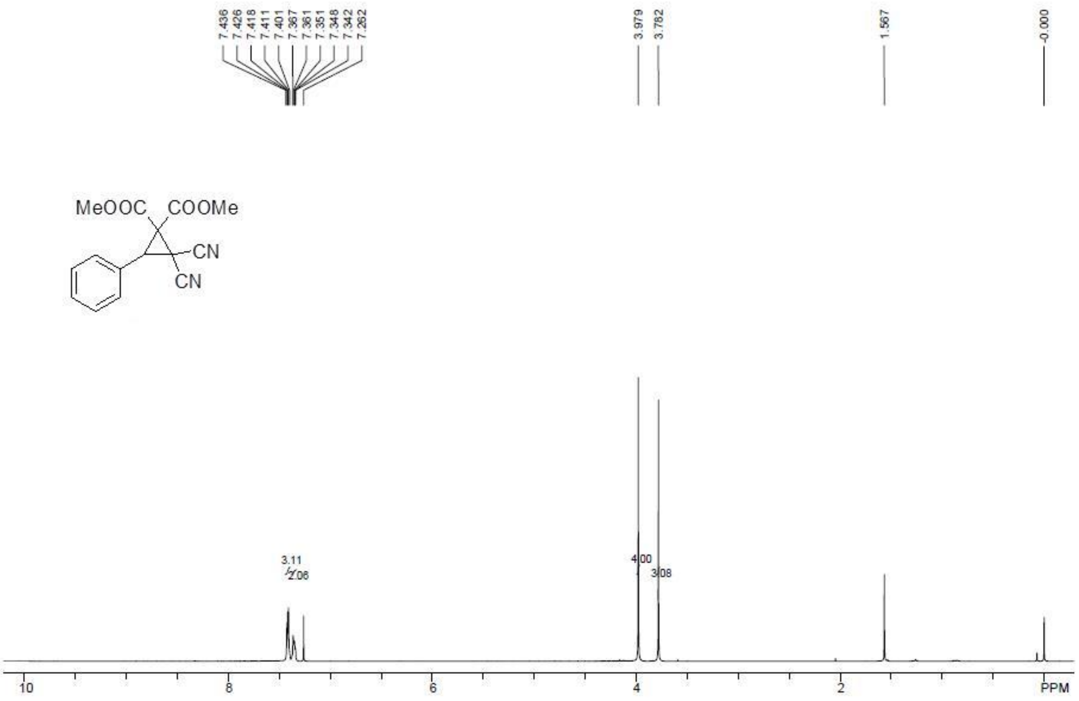
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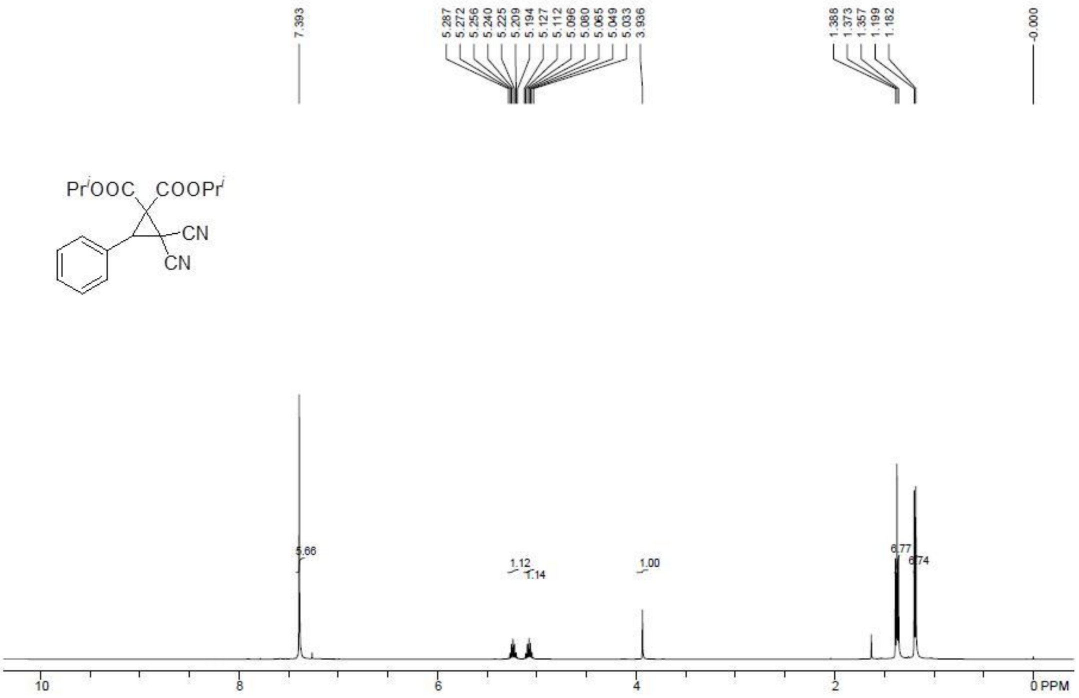
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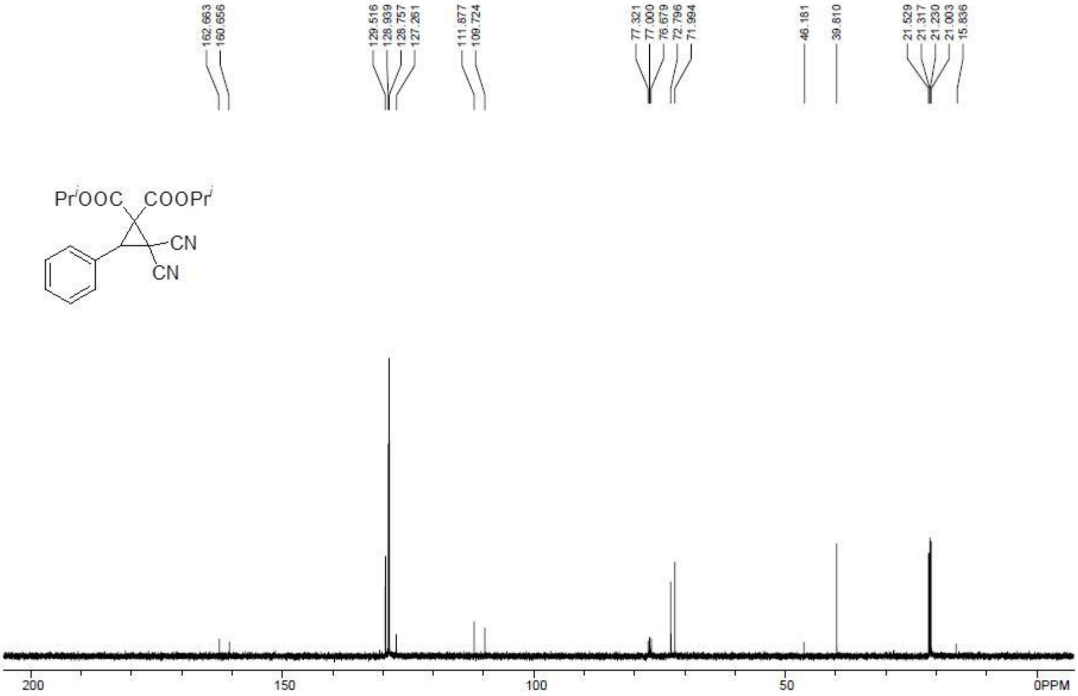
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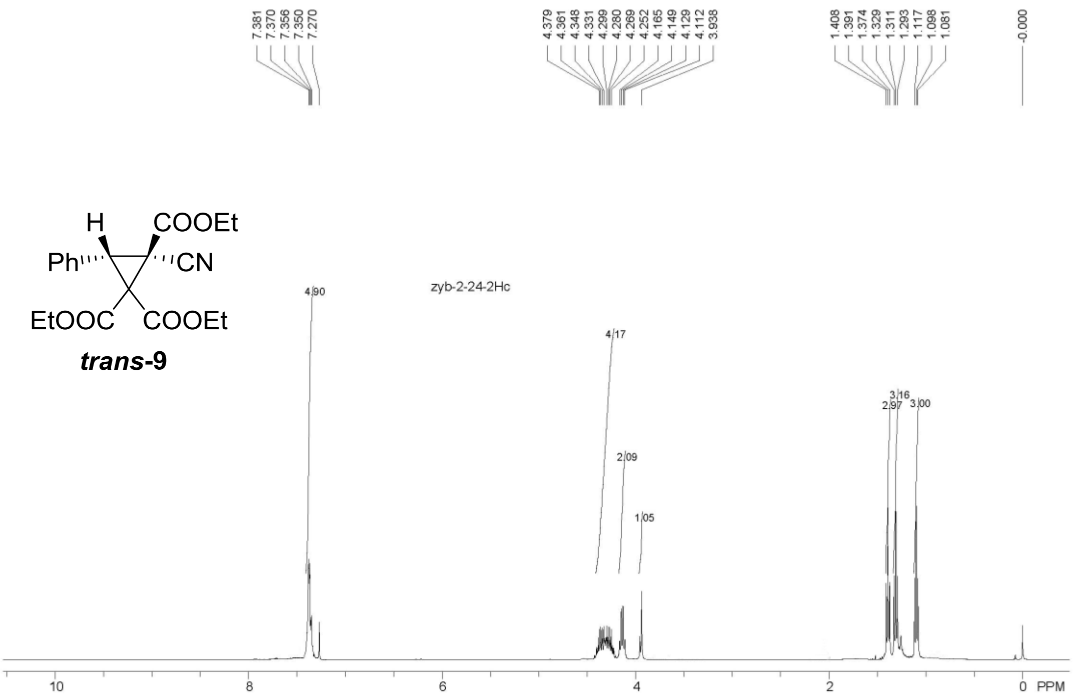
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[1] J. M. R. Narayanam, J. W. Tucker and C. R. J. Stephenson, *J. Am. Chem. Soc.* **2009**, 131, 8756-8757.

[2] J. D. Nguyen, J. W. Tucker, M. D. Konieczynska and C. R. J. Stephenson, *J. Am. Chem. Soc.* **2011**, 133, 4160-4163.

[3] N. J. Turro, Y. Cha and I. R. Gould, *J. Am. Chem. Soc.* **1987**, 109, 2101-2107.

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