

Supporting Information

Boron-Doped TiO₂ (B-TiO₂): Visible-light Photocatalytic di-functionalization of alkenes and alkynes.

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General Information

All of the chemical materials were prepared from Aldrich, Fluka, Acros and Merck. All solvents were procured from purified by usual standard procedures. Photoactivity of photocatalysts were characterized by UV-Vis spectrophotometer (Shimadzu UV-2450 spectrophotometer). Catalysts were investigated by power X-ray diffraction (XRD) on a Bruker D8, Advance, Bruker, axs) and IR spectra. The products of the reactions were followed by TLC using silica gel polygrams SIL G/UV 254 plates. All products were purified by column chromatography. Products were identified by ¹HNMR, ¹³CNMR, FT-IR, CHNS and melting point subsequently.

IR spectra were prepared using a Shimadzu FT-IR 8300 spectrophotometer. Melting points were determined in open capillary tubes in a Büchi- 535 circulating oil melting point apparatus.

Elemental analyses were performed by Thermo Finnigan CHNS analyzer, 1112 series. X-ray diffraction (XRD, D8, Advance, Bruker, axs) were obtained for characterization of the heterogeneous catalyst. UV/Vis spectra were obtained with an Ultrospec 3000 UV/Visible spectrometer. NMR spectra were recorded on a Bruker Avance DPX-250 (¹H-NMR 250, 400 MHz, and ¹³C NMR 62.9, 100 MHz) spectrometer in pure deuterated solvents with tetramethylsilane as an internal standard. Scanning electron micrographs were obtained by SEM instrumentation (SEM, XL-30 FEG SEM, and Philips, at 20 KV). TEM analyses were carried out using a JEOL-1200 microscope, operated at 200 kV.

Preparation of B-TiO₂NPs as photocatalyst

First, 0.0025 mol of boric acid were dissolved in 45 mL of ethanol/ water (8:1) mixture. Subsequently, 0.025 mol of titanium (IV) butoxide Ti (OBu)₄ (molar ratio B/Ti = 1:10), was added dropwise at 0 °C under stirring. To ensure a complete hydrolysis of Ti(OBu)₄, the solution mixture was continuously stirred for about 10 h at room temperature (22 °C). After being aged for an additional 24 h, the mixture was centrifuged, dried under vacuum, and then calcined in air at 400 °C for 5 h to obtain the B-TiO₂NPs sample¹.

General procedure for the synthesis of α-thiocyanato and α-isothiocyanato ketones

To a mixture of double or triple bond compounds (0.5 mmol), ammonium thiocyanate (0.5 mmol) in CH₃CN (1.5 ml) and B-TiO₂ (0.007 g) as catalyst was added and the mixture was irradiated by blue LED in to ice/water (0 °C) bath. The progress of the reaction was monitored by TLC. After completion of the reaction and separation of catalyst by centrifuge, the solvent was removed, and then 20 mL H₂O was added and the mixture was extracted with EtOAc. The organic layer was washed with water (3×10 mL) and dried over anhydrous Na₂SO₄. The organic layer was concentrated under vacuum. The resulting crude product was purified by chromatography ethyl acetate/petroleum ether (1:100) to give the desired thiocyanation products in good isolated yields.

Characterization data for compounds

1-Phenyl-2-thiocyanatoethan-1-one (3a). Yellow oil²; FT-IR (KBr cm⁻¹): 2152 (CN), 1681 (C=O); ¹H NMR (400 MHz, CDCl₃): δ (ppm) 4.67 (s, 2H, CH₂), 7.46 (t, 2H, *J* = 8.0 Hz, ArH), 7.60 (t, 1H, *J* = 8.0 Hz, ArH), 7.87 (d, 2H, *J* = 8.0 Hz, ArH); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 43.04 (CH₂), 111.8 (SCN), 128.4, 129.1, 133.9, 134.8, 190.8 (C=O). Anal. Calcd. for C₉H₇NOS: C, 61.00; H, 3.98; N, 7.90; Found: C, 60.93; H, 3.82; N, 7.81.

1-(4-Chlorophenyl)-2-thiocyanatoethan-1-one (3b). Colorless crystal³, mp: 130-132 °C (Colorless crystal, mp: 132-135 °C [Nair *et al.*, 2000]); FT-IR (KBr cm⁻¹): 2157 (CN), 1671 (C=O); ¹H NMR (400 MHz, CDCl₃): δ (ppm) 4.63 (s, 2H, CH₂), 7.43 (d, 2H, *J* = 12.0 Hz, ArH), 7.81 (d, 2H, *J* = 8.0 Hz, ArH); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 42.6 (CH₂), 111.5 (SCN), 129.5, 129.8, 131.3, 141.5, 189.69 (C=O). Anal. Calcd. for C₉H₆ClNOS: C, 51.07; H, 2.86; N, 6.62;

Found: C, 50.93; H, 2.70; N, 6.57.

1-(4-Fluorophenyl)-2-thiocyanatoethan-1-one (3c). Colorless liquid; FT-IR (KBr cm^{-1}): 2156 (CN), 1676 (C=O); ^1H NMR (400 MHz, CDCl_3): δ (ppm) 4.73 (s, 2H, CH_2), 7.20-7.25 (m, 2H, ArH), 7.99-8.02 (m, 2H, ArH); ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 42.7 (CH_2), 111.7 (SCN), 116.5 ($J= 22.0$ Hz, C_{Ar}), 131.2 ($J= 22.0$ Hz, C_{Ar}), 131.3 ($J= 9.0$ Hz, C_{Ar}), 165.3, 167.9, 189.3 (C=O). Anal. Calcd. for $\text{C}_9\text{H}_6\text{FNOS}$: C, 55.38; H, 3.10; N, 7.18; Found: C, 55.17; H, 3.01; N, 7.10.

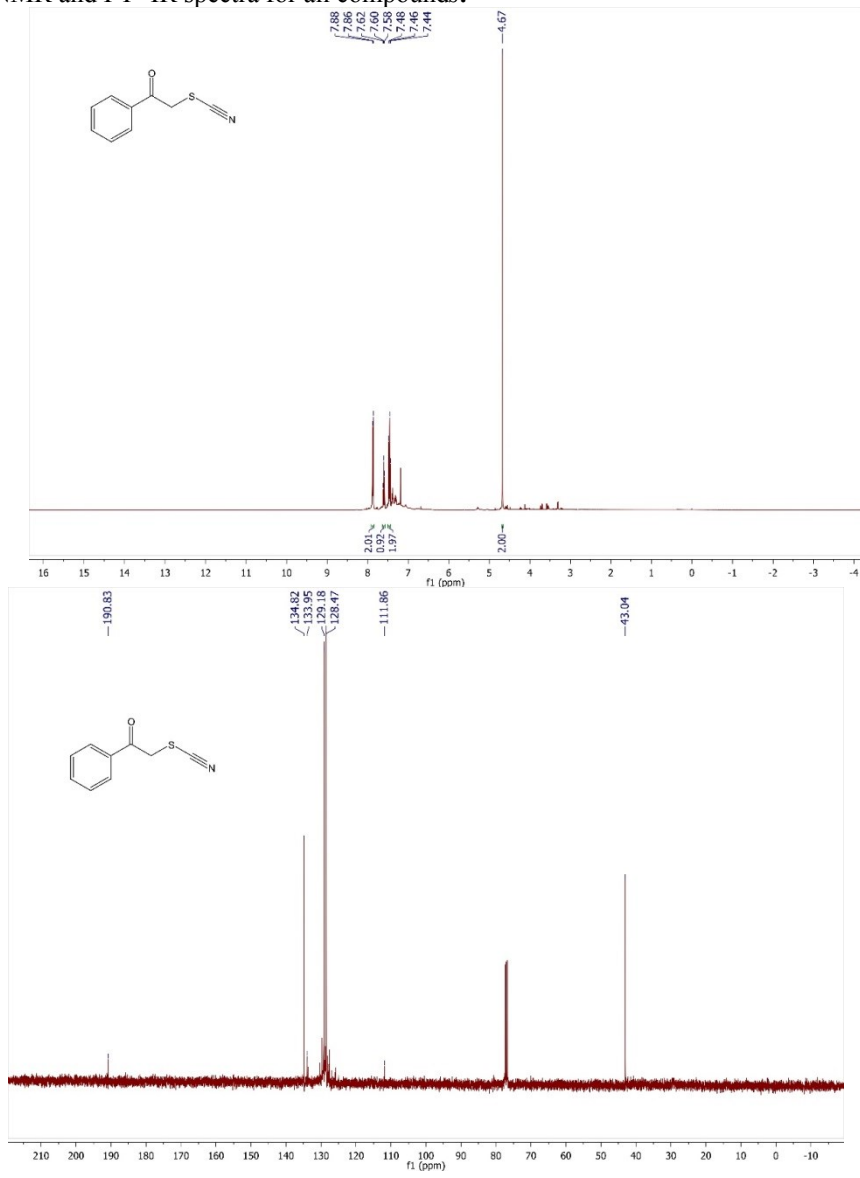
1, 2-Diphenyl-2-thiocyanatoethan-1-one (3d). Colorless liquid; FT-IR (KBr cm^{-1}): 2383 (CN), 1686 (C=O); ^1H NMR (400 MHz, CDCl_3): δ (ppm) 7.33-7.39 (m, 2H, ArH and CH), 7.49-7.52 (m, 1H, ArH), 7.54-7.56 (m, 3H, ArH), 7.67-7.69 (m, 1H, ArH), 7.72-7.74 (m, 2H, ArH), 7.99-8.02 (m, 2H, ArH); ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 68.1 (CH), 125.5 (SCN), 128.5, 128.8, 129.0, 129.9, 130.8, 132.4, 132.9, 134.8, 194.5 (C=O). Anal. Calcd. for $\text{C}_{15}\text{H}_{11}\text{NOS}$: C, 71.12; H, 4.38; N, 5.53; Found: C, 70.75; H, 4.13; N, 5.43.

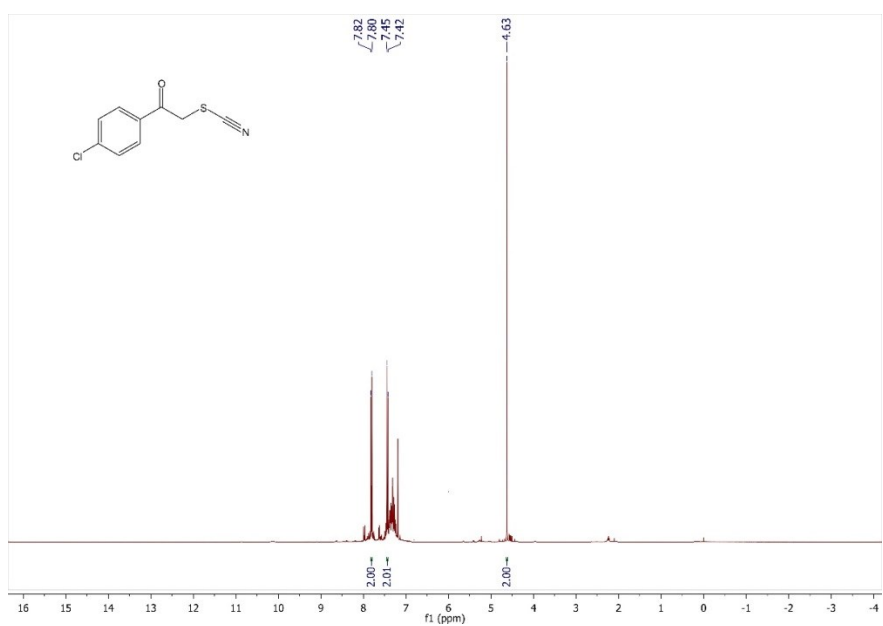
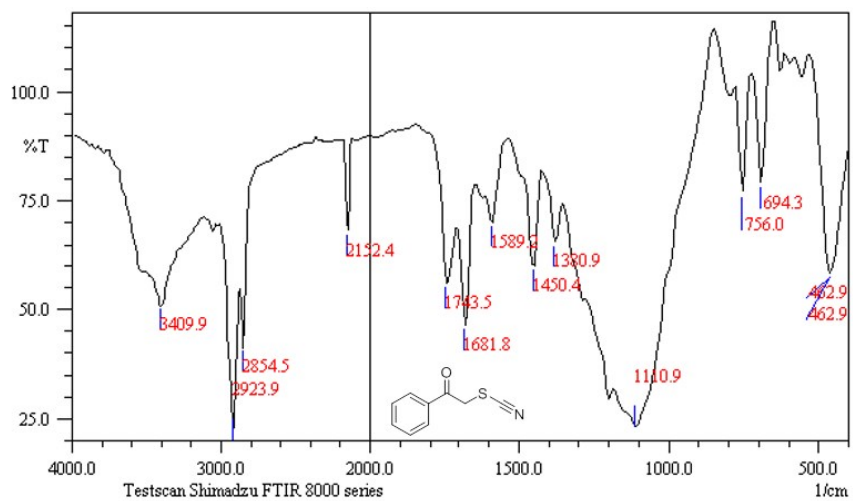
2-Phenyl-1-thiocyanatopropan-2-ol (3e). White solid, mp: 122-124 °C (White solid, mp: 122-124 °C); FT-IR (KBr cm^{-1}): 3460 (OH); ^1H NMR (400 MHz, CDCl_3): δ (ppm) 1.18 (s, 3H, CH_3), 3.57-3.76 (m, 2H, CH_2), 5.52 (s, 1H, OH), 7.2-7.34 (m, 5H, ArH); ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 27.46 (CH_3), 42.54 (CH_2), 71.14 (C_{tert}), 113.93 (SCN), 124.26, 125.07, 127.1, 151.67. Anal. Calcd. for $\text{C}_{10}\text{H}_{11}\text{NOS}$: C, 62.15; H, 5.74; N, 7.25; Found: C, 61.76; H, 5.33; N, 7.01.

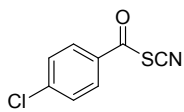
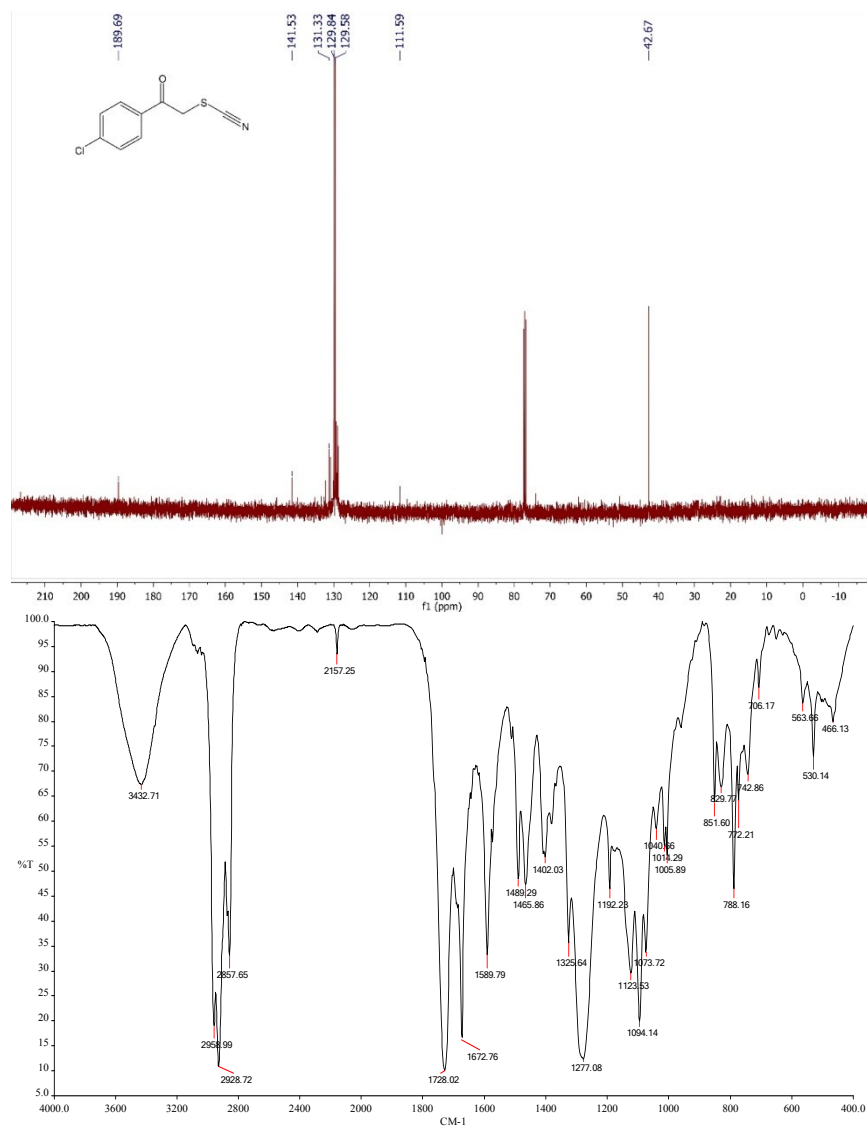
2-Thiocyanato-1-(p-tolyl)ethan-1-one (3f): Colorless crystalline³, mp: 106-108 °C (Colorless crystalline, mp: 105-107 °C); FT-IR (KBr cm^{-1}): 2157 (CN), 1666 (C=O); ^1H NMR (400 MHz, CDCl_3): δ (ppm) 2.38 (s, 3H, CH_3), 4.63 (s, 2H, CH_2), 7.25 (d, 2H, $J= 8.0$ Hz, ArH), 7.77 (d, 2H, $J= 8.0$ Hz, ArH); ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 21.87 (CH_3), 43.12 (CH_2), 111.56 (SCN), 128.59, 129.87, 131.49, 145.72, 190.13 (C=O). Anal. Calcd. for $\text{C}_{10}\text{H}_9\text{NOS}$: C, 62.80; H, 4.74; N, 7.32; Found: C, 62.66; H, 4.61; N, 7.20.

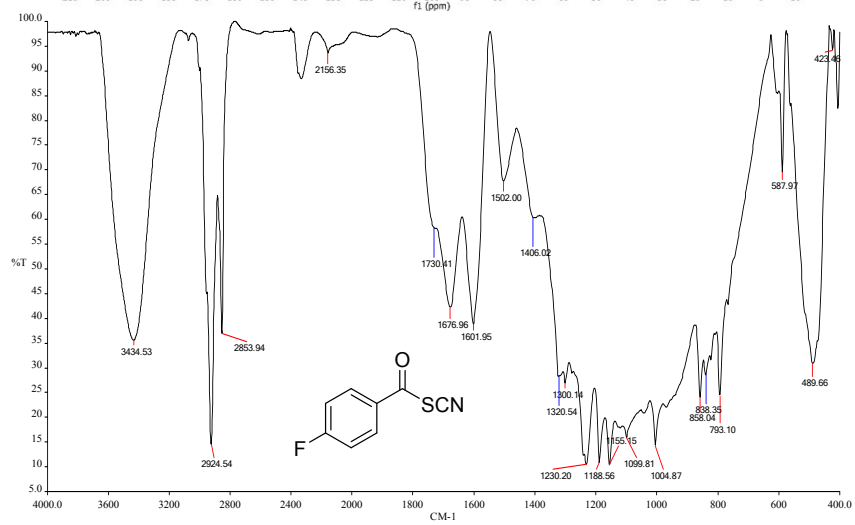
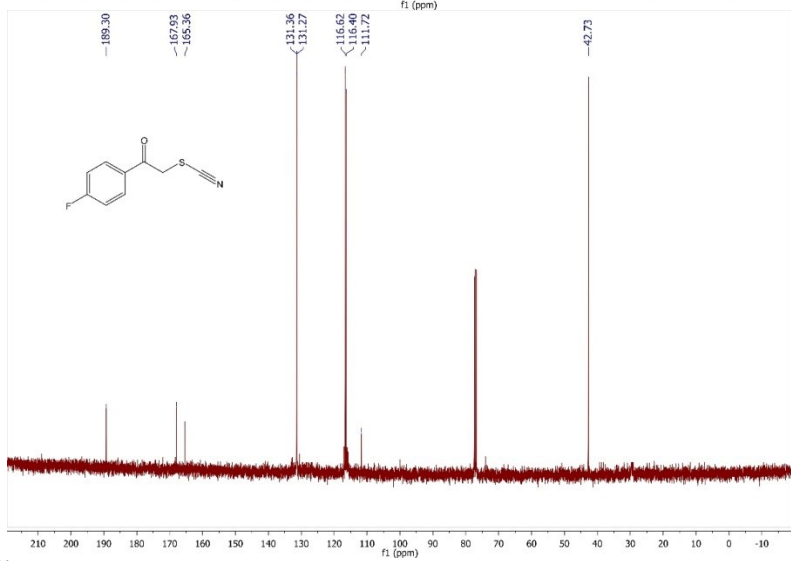
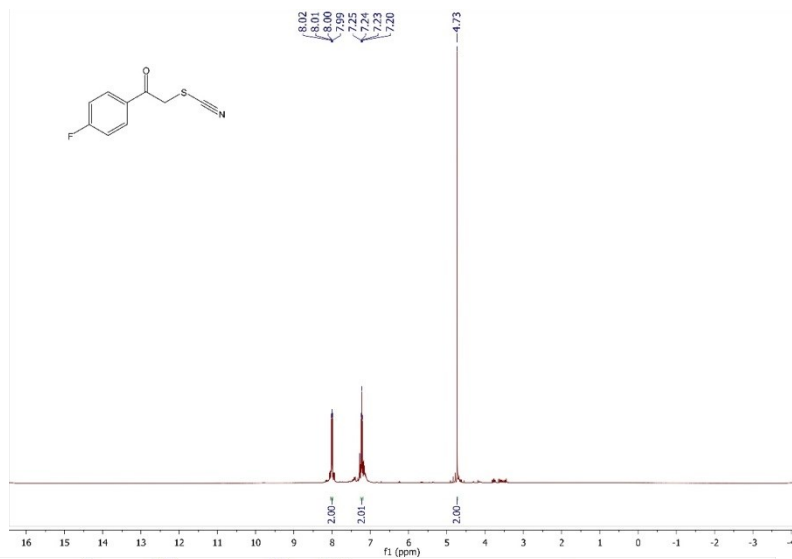
2-Isothiocyanato-1-phenylethan-1-one (4a). Colorless liquid; FT-IR (KBr cm^{-1}): 2054 (N=C=S), 1678 (C=O); ^1H NMR (400 MHz, CDCl_3): δ (ppm) 3.41 (s, 2H, CH_2), 7.42 (t, 2H, $J= 5.0$ Hz, ArH), 7.51 (t, 1H, $J= 5.0$ Hz, ArH), 7.98 (d, 2H, $J= 5.0$ Hz, ArH); ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 32.5 (CH_2), 128.1, 128.2 (NCS), 128.6, 133.1, 136.7, 198.7 (C=O). Anal. Calcd. for $\text{C}_7\text{H}_9\text{NOS}$: C, 61.00; H, 3.98; N, 7.90; Found: C, 59.88; H, 3.83; N, 7.86.

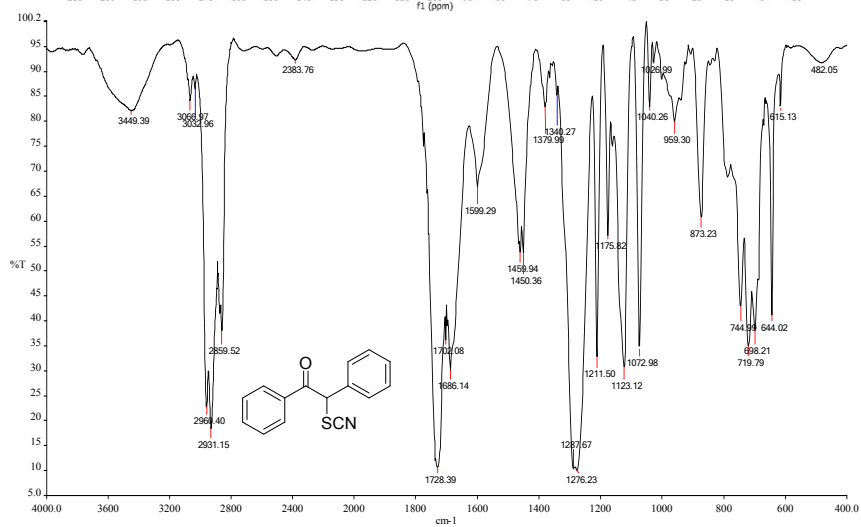
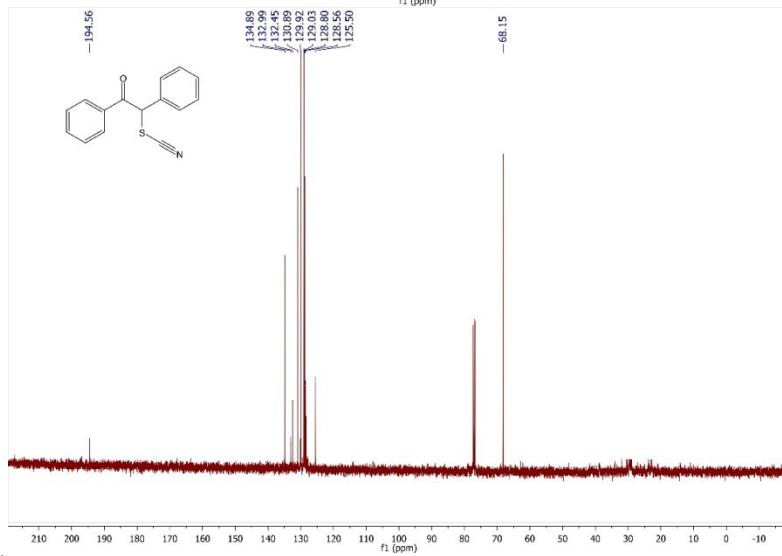
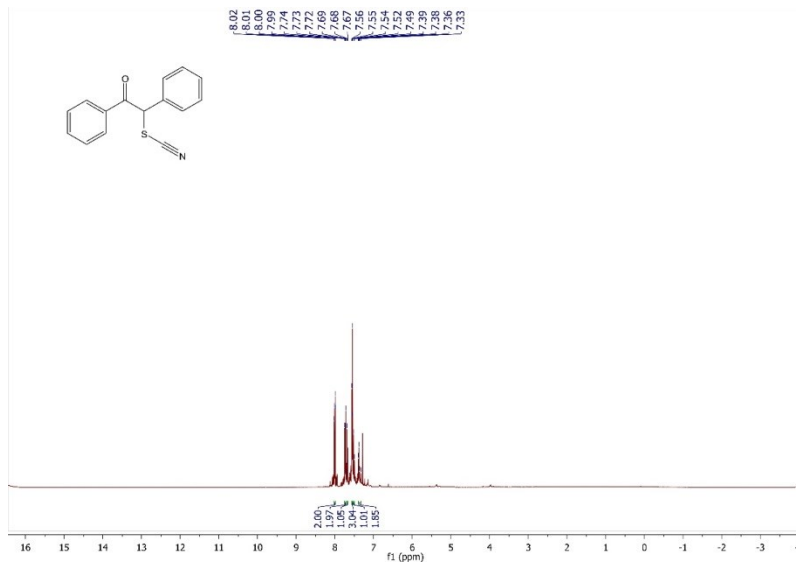
¹H NMR, ¹³C NMR and FT- IR spectra for all compounds:

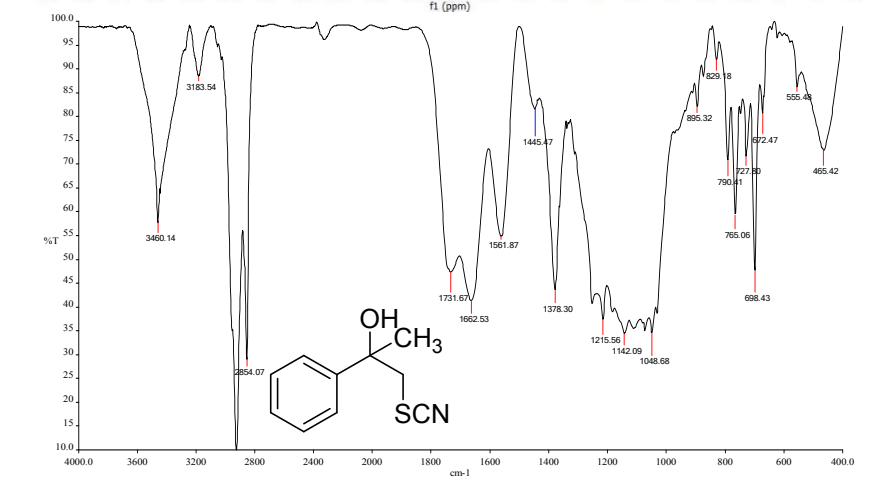
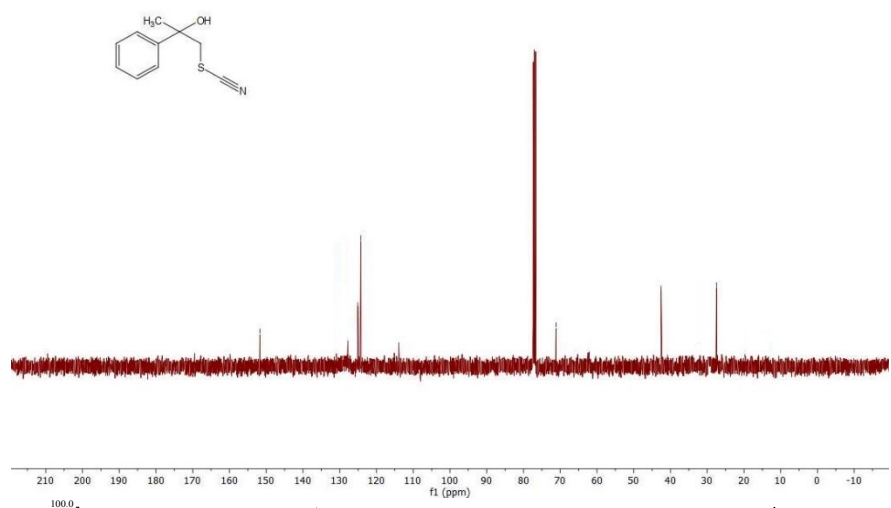
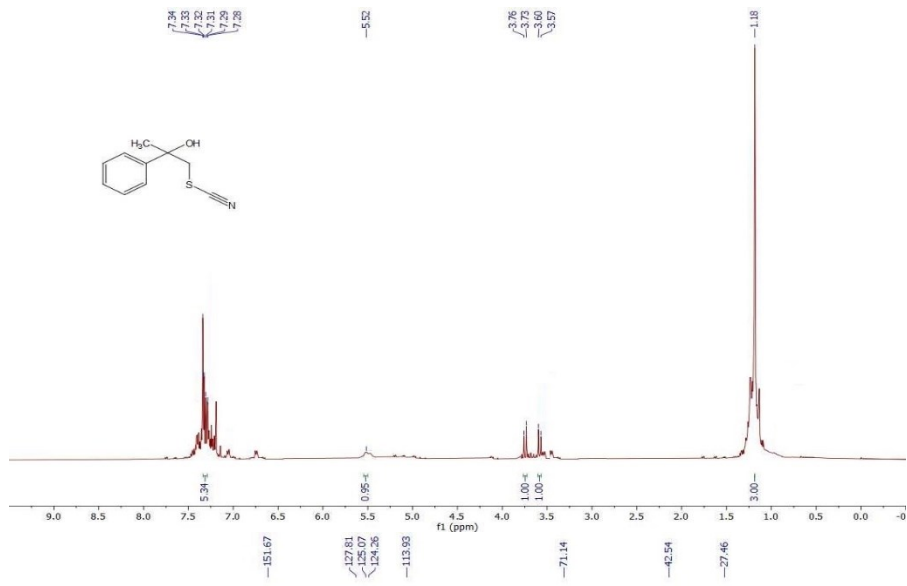


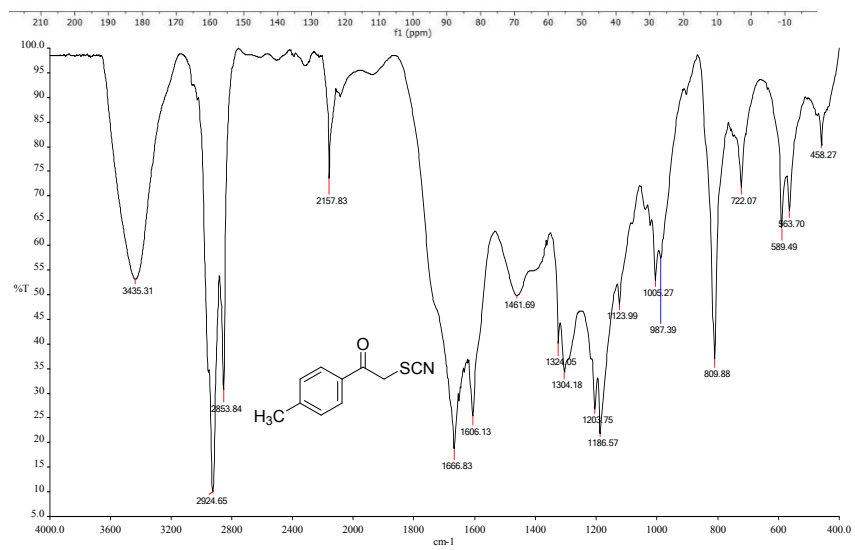
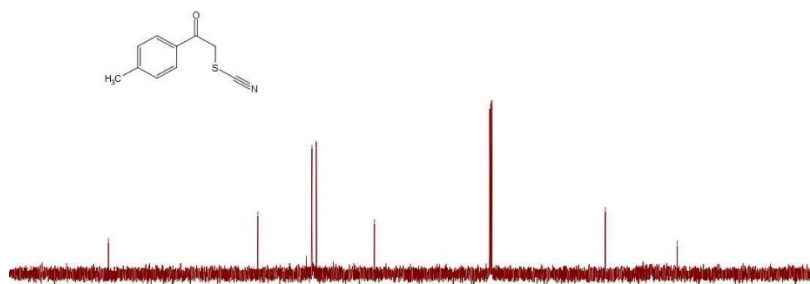
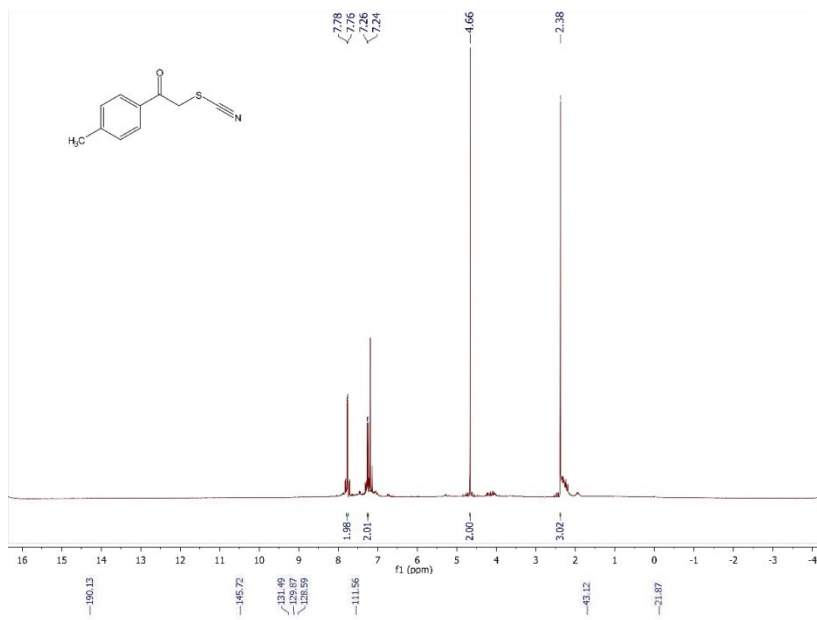


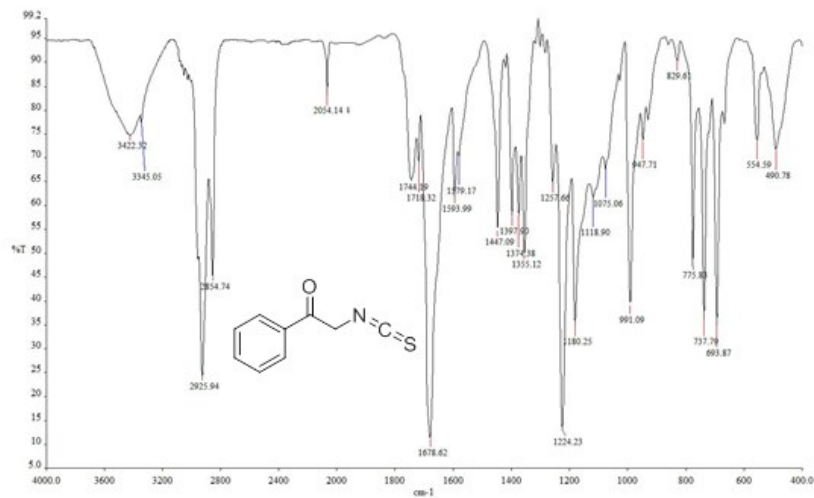
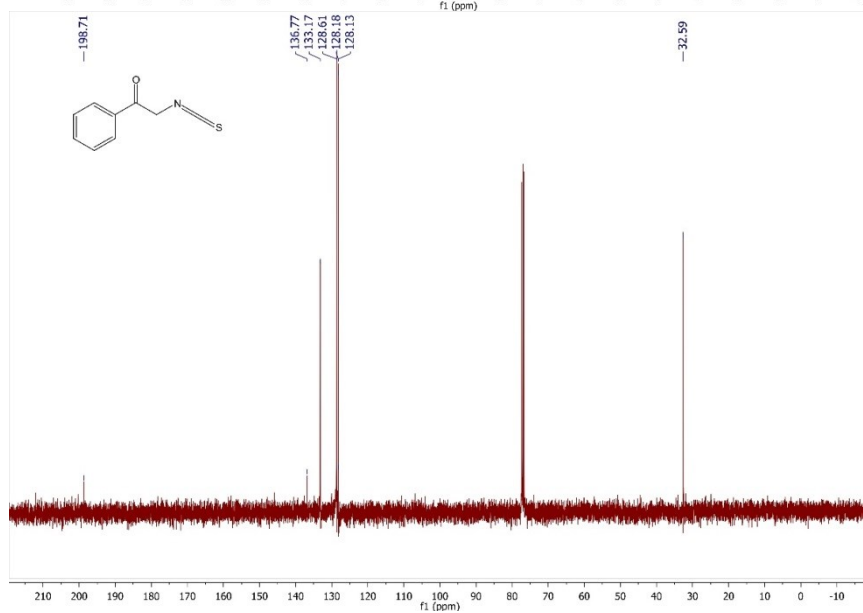
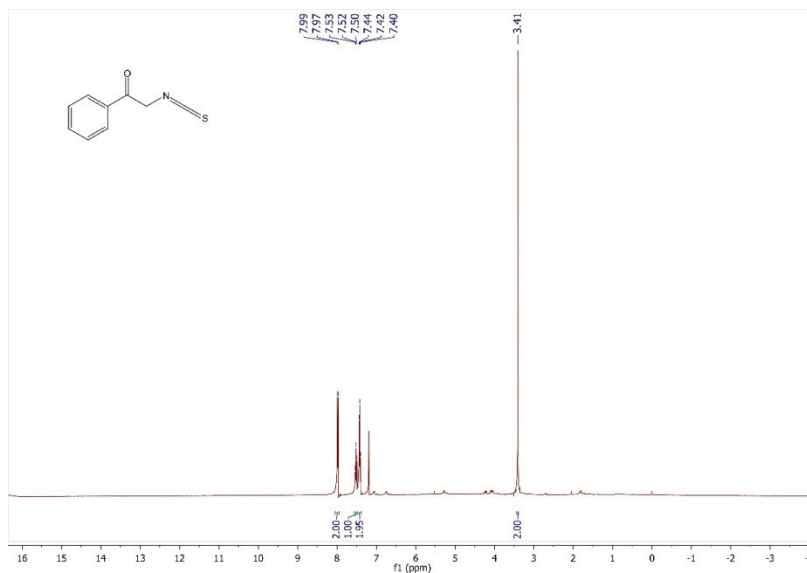












Reference

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