Electronic Supplementary Information

Palladium-Catalyzed *β*-selective C(sp^2)−H Carboxamidation of Enamides by Isocyanide Insertion: Synthesis of *N*-acyl Enamine Amides

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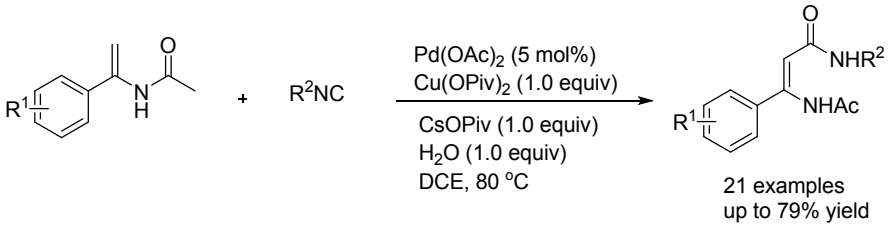
Contents

I. General Information

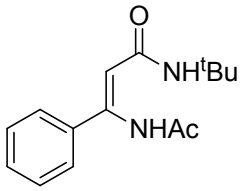
^{1}H NMR (400 MHz) and ^{13}C NMR (125 MHz) were registered on 400 M and 500 M spectrometers. Chemical shifts were reported in units (ppm) by assigning TMS resonance in the ^{1}H spectrum as 0.00 ppm, $CDCl_3$ resonance in the ^{13}C spectrum as 77.0 ppm. All coupling constants (*J* values) were reported in Hertz (Hz). NMR analysis was carried out at 298 K unless noted otherwise. HRMS was obtained on an ESI-LC-MS/MS spectrometer.

II. General Procedure



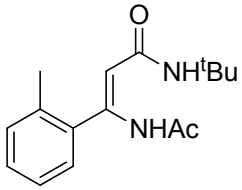
General procedure: To an oven-dried 10 mL schlenk tube charged with enamide (0.2 mmol), $Pd(OAc)_2$ (0.01 mmol, 2.24 mg), $Cu(OPiv)_2$ (0.2 mmol, 53.2 mg) and CsOPiv (0.2 mmol, 46.8 mg) was added a solution of *t*-BuNC (0.3 mmol, 34.0 μL) and H_2O (0.2 mmol, 3.6 μL) in 2.0 mL of dry DCE by syringe. The mixture was stirred at 80 °C under air. When the reaction was completed (detected by TLC), the mixture was cooled to room temperature and quenched with 2 mL of $NH_3.H_2O$ .The crude reaction mixture was extracted with EA (20 mL × 3) and washed with brine (20 mL). The organic phase was concentrated in *vacuo* and the residue was purified by silica gel flash column chromatography to afford the corresponding products.

III. Characterization Data



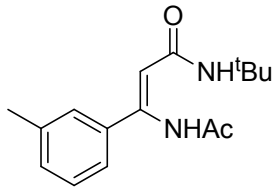
(*Z*)-3-acetamido-*N*-(*tert*-butyl)-3-phenylacrylamide(**3a**)
Prepared from *N*-(1-phenylvinyl)acetamide (32.2 mg, 0.2 mmol, 1.0 equiv) and *t*-BuNC (24.9 mg, 0.3 mmol, 1.5 equiv) according to the general procedure. Column

chromatography purification (EtOAc : petroleum ether = 1 : 4) furnished the product **3a** as a colorless oil (39 mg, 0.15 mmol, 75% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 11.53 (s, 1H), 7.30 (brs, 5H), 5.46 (s, 1H), 4.94 (s, 1H), 2.13 (s, 3H), 1.38 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 168.7, 167.8, 150.9, 136.8, 128.9, 127.9, 126.9, 104.8, 51.6, 28.9, 24.9; HRMS: calcd for $C_{15}H_{20}N_2O_2$ ($M+H^+$) 261.1598; found 261.1599.



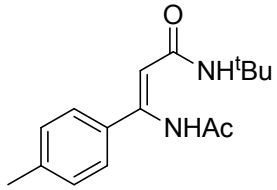
(*Z*)-3-acetamido-*N*-*(tert*-butyl)-3-(*o*-tolyl)acrylamide(**3b**)

Prepared from *N*-(1-(*o*-tolyl)vinyl)acetamide (35.0 mg, 0.2 mmol, 1.0 equiv) and *t*-BuNC (24.9 mg, 0.3 mmol, 1.5 equiv) according to the general procedure. Column chromatography purification (EtOAc : petroleum ether = 1 : 4) furnished the product **3b** as a colorless oil (32 mg, 0.12 mmol, 58% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 11.89 (s, 1H), 7.24-7.20 (m, 1H), 7.16-7.09 (m, 3H), 5.27 (s, 1H), 4.67 (s, 1H), 2.25 (s, 3H), 2.08 (s, 3H), 1.40 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 168.3, 167.7, 151.3, 137.0, 135.5, 129.6, 128.4, 127.6, 125.5, 102.7, 51.6, 29.1, 24.8, 19.6; HRMS: calcd for $C_{16}H_{22}N_2O_2$ ($M+H^+$) 275.1754; found 275.1754.



(*Z*)-3-acetamido-*N*-(*tert*-butyl)-3-(*m*-tolyl)acrylamide(**3c**)

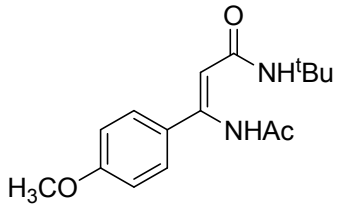
Prepared from *N*-(1-(*m*-tolyl)vinyl)acetamide (35.0 mg, 0.2 mmol, 1.0 equiv) and *t*-BuNC (24.9 mg, 0.3 mmol, 1.5 equiv) according to the general procedure. Column chromatography purification (EtOAc : petroleum ether = 1 : 4) furnished the product **3c** as a colorless oil (35 mg, 0.13 mmol, 64% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 11.49 (s, 1H), 7.22-7.19(m, 1H), 7.15-7.11 (m, 3H), 5.33 (s, 1H), 4.95 (s, 1H), 2.34 (s, 3H), 2.14 (s, 3H), 1.40 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 168.7, 167.8, 151.4, 137.6, 136.8, 129.8, 127.9, 127.5, 124.2, 104.5, 51.6, 29.1, 25.0, 21.6; HRMS: calcd for $C_{16}H_{22}N_2O_2$ ($M+H^+$) 275.1754; found 275.1757.



(*Z*)-3-acetamido-*N*-(*tert*-butyl)-3-(*p*-tolyl)acrylamide(**3d**)

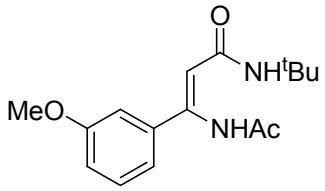
Prepared from *N*-(1-(*p*-tolyl)vinyl)acetamide (35.0 mg, 0.2 mmol, 1.0 equiv) and *t*-BuNC (24.9 mg, 0.3 mmol, 1.5 equiv) according to the general procedure. Column

chromatography purification (EtOAc : petroleum ether = 1 : 4) furnished the product **3d** as a colorless oil (33 mg, 0.12 mmol, 60% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 11.49 (s, 1H), 7.22 (d, *J* = 8.16, 2H), 7.13 (d, *J* = 8.16 Hz, 2H), 5.31 (s, 1H), 4.94 (s, 1H), 2.35 (s, 3H), 2.14 (s, 3H), 1.40 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 168.8, 167.9, 151.3, 139.1, 133.9, 128.8, 126.9, 104.1, 51.6, 29.1, 25.0, 21.5; HRMS: calcd for $C_{20}H_{28}NO_2$ (M++H) 275.1754; found 275.1761.



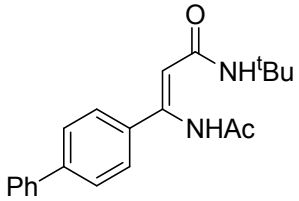
(*Z*)-3-acetamido-*N*-(*tert*-butyl)-3-(4-methoxyphenyl)acrylamide(**3e**)

Prepared from *N*-(1-(4-methoxyphenyl)vinyl)acetamide (38.2 mg, 0.2 mmol, 1.0 equiv) and *t*-BuNC (24.9 mg, 0.3 mmol, 1.5 equiv) according to the general procedure. Column chromatography purification (EtOAc : petroleum ether = 1 : 4) furnished the product **3e** as a light yellow oil (29 mg, 0.10 mmol, 50% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 11.50 (s, 1H), 7.27 (d, *J* = 8.8 Hz, 2H), 6.85 (d, *J* = 8.8 Hz, 2H), 5.35 (s, 1H), 4.93 (s, 1H), 3.80 (s, 3H), 2.14 (s, 3H), 1.39 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 168.9, 168.0, 160.4, 150.9, 129.0, 128.4, 113.5, 103.7, 55.4, 51.6, 29.1, 25.1; HRMS: calcd for $C_{15}H_{19}BrN_2O_2$ (M+H$^+$) 291.1703; found 291.1716.



(*Z*)-3-acetamido-*N*-(*tert*-butyl)-3-(3-methoxyphenyl)acrylamide(**3f**)

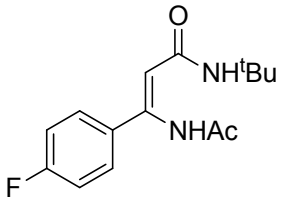
Prepared from *N*-(1-(3-methoxyphenyl)vinyl)acetamide (38.2 mg, 0.2 mmol, 1.0 equiv) and *t*-BuNC (24.9 mg, 0.3 mmol, 1.5 equiv) according to the general procedure. Column chromatography purification (EtOAc : petroleum ether = 1 : 4) furnished the product **3f** as a colorless oil (29 mg, 0.10 mmol, 50% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 11.47 (s, 1H), 7.23 (t, *J* = 7.9 Hz, 1H), 6.92-6.84 (m, 3H), 5.36 (s, 1H), 4.97 (s, 1H), 3.79 (s, 3H), 2.13 (s, 3H),1.39 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 168.7, 167.8, 159.3, 151.0, 138.3, 129.1, 119.6, 114.5, 112.8, 104.7, 55.4, 51.7, 29.0, 24.9; HRMS: calcd for $C_{16}H_{22}N_2O_3$ (M+H$^+$) 291.1703; found 291.1703.



(*Z*)-3-([1,1'-biphenyl]-4-yl)-3-acetamido-*N*-(*tert*-butyl)acrylamide(**3g**)

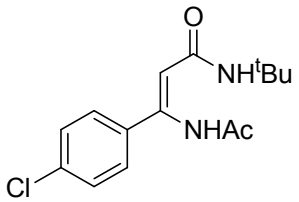
Prepared from *N*-(1-([1,1'-biphenyl]-4-yl)vinyl)acetamide (47.4 mg, 0.2 mmol, 1.0 equiv) and *t*-BuNC (24.9 mg, 0.3 mmol, 1.5 equiv) according to the general procedure. Column chromatography purification (EtOAc : petroleum ether = 1 : 4) furnished the

product **3g** as a colorless oil (44 mg, 0.13 mmol, 66% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 11.55 (s, 1H), 7.59 (d, *J* = 7.4 Hz, 2H), 7.55 (d, *J* = 8.2 Hz, 2H), 7.43 (t, *J* = 7.4 Hz, 2H), 7.39 (d, *J* = 8.2 Hz, 2H), 7.34 (t, *J* = 7.4 Hz, 1H), 5.40 (s, 1H), 5.02 (s, 1H), 2.17 (s, 3H), 1.41 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 168.9, 167.8, 150.8, 141.9, 140.7, 135.7, 128.9, 127.6, 127.5, 127.3, 126.8, 104.7, 51.7, 29.1, 25.0; HRMS: calcd for $C_{21}H_{24}N_2O_2$ ($M+H^+$) 337.1911; found 337.1921.



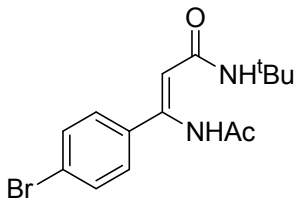
(*Z*)-3-acetamido-*N*-(*tert*-butyl)-3-(4-fluorophenyl)acrylamide(**3h**)

Prepared from *N*-(1-(4-fluorophenyl)vinyl)acetamide (35.8 mg, 0.2 mmol, 1.0 equiv) and *t*-BuNC (24.9 mg, 0.3 mmol, 1.5 equiv) according to the general procedure. Column chromatography purification (EtOAc : petroleum ether = 1 : 4) furnished the product **3h** as a light yellow oil (30 mg, 0.11 mmol, 54% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 11.55 (s, 1H), 7.31-7.27 (m, 2H), 7.02-6.98 (m, 2H), 5.34 (s, 1H), 4.91 (s, 1H), 2.14 (s, 3H), 1.40 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 168.8, 167.7, 164.2 (*J* = 248.4 Hz), 150.2, 132.9 (*J* = 3.63 Hz), 128.9 (*J* = 8.51 Hz), 115.1 (*J* = 21.9 Hz), 104.6, 51.7, 29.0, 25.0; HRMS: calcd for $C_{15}H_{19}FN_2O_2$ ($M+H^+$) 279.1503; found 279.1497.



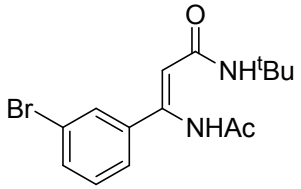
(*Z*)-3-acetamido-*N*-(*tert*-butyl)-3-(4-chlorophenyl)acrylamide(**3i**)

Prepared from *N*-(1-(4-chlorophenyl)vinyl)acetamide (39.2 mg, 0.2 mmol, 1.0 equiv) and *t*-BuNC (24.9 mg, 0.3 mmol, 1.5 equiv) according to the general procedure. Column chromatography purification (EtOAc : petroleum ether = 1 : 4) furnished the product **3i** as a colorless oil (40 mg, 0.14 mmol, 67% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 11.54 (s, 1H), 7.28 (d, *J* = 8.4 Hz, 2H), 7.25 (d, *J* = 8.4 Hz, 2H), 5.37 (s, 1H), 4.92 (s, 1H), 2.14 (s, 3H), 1.39 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 168.8, 167.6, 150.0, 135.3, 134.9, 128.3, 128.2, 104.9, 51.8, 29.0, 24.9; HRMS: calcd for $C_{15}H_{19}ClN_2O_2$ ($M+H^+$) 295.1208; found 295.1216.



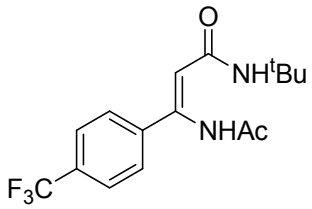
(*Z*)-3-acetamido-3-(4-bromophenyl)-*N*-(*tert*-butyl)acrylamide(**3j**)

Prepared from *N*-(1-(4-bromophenyl)vinyl)acetamide (48.0 mg, 0.2 mmol, 1.0 equiv) and *t*-BuNC (24.9 mg, 0.3 mmol, 1.5 equiv) according to the general procedure. Column chromatography purification (EtOAc : petroleum ether = 1 : 4) furnished the product **3j** as a light yellow oil (49 mg, 0.14 mmol, 72% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 11.54 (s, 1H), 7.44 (d, *J* = 8.4 Hz, 2H), 7.17 (d, *J* = 8.4 Hz, 2H), 5.40 (s, 1H), 4.92 (s, 1H), 2.14 (s, 3H), 1.39 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 168.8, 167.6, 150.0, 135.8, 131.2, 128.6, 123.2, 104.9, 51.8, 29.0, 24.9; HRMS: calcd for $C_{15}H_{19}BrN_2O_2$ (M+H$^+$) 339.0703; found 339.0710.



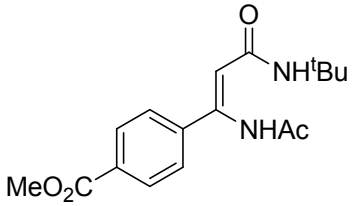
(*Z*)-3-acetamido-3-(3-bromophenyl)-*N*-(*tert*-butyl)acrylamide(**3k**)

Prepared from *N*-(1-(3-bromophenyl)vinyl)acetamide (48.0 mg, 0.2 mmol, 1.0 equiv) and *t*-BuNC (24.9 mg, 0.3 mmol, 1.5 equiv) according to the general procedure. Column chromatography purification (EtOAc : petroleum ether = 1 : 4) furnished the product **3k** as a light yellow oil (36 mg, 0.11 mmol, 53% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 11.50 (s, 1H), 7.46-7.44 (m, 2H), 7.25-7.22 (m, 1H), 7.20-7.15 (m, 1H), 5.39 (s, 1H), 4.94 (s, 1H), 2.15 (s, 3H), 1.39 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 168.7, 167.5, 149.6, 139.0, 131.9, 129.8, 129.5, 125.8, 122.1, 105.3, 51.8, 29.0, 24.9; HRMS: calcd for $C_{15}H_{19}BrN_2O_2$ (M+H$^+$) 339.0703; found 339.0700.

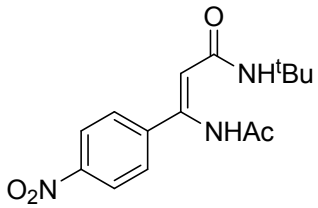


(*Z*)-3-acetamido-*N*-(*tert*-butyl)-3-(4-(trifluoromethyl)phenyl)acrylamide(**3l**)

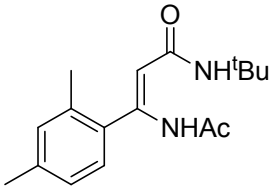
Prepared from *N*-(1-(4-(trifluoromethyl)phenyl)vinyl)acetamide (45.8 mg, 0.2 mmol, 1.0 equiv) and *t*-BuNC (24.9 mg, 0.3 mmol, 1.5 equiv) according to the general procedure. Column chromatography purification (EtOAc : petroleum ether = 1 : 4) furnished the product **3l** as a colorless oil (44 mg, 0.13 mmol, 67% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 11.59 (s, 1H), 7.57 (d, *J* = 8.2 Hz, 2H), 7.41 (d, *J* = 8.2 Hz, 2H), 5.40 (s, 1H), 4.95 (s, 1H), 2.15 (s, 3H), 1.40 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 168.8, 167.4, 149.7, 140.6, 130.9 (*J* = 32.4 Hz), 127.3, 125.2 (*J* = 272.3 Hz), 125.0 (*J* = 3.75 Hz), 105.6, 51.9, 29.0, 24.8; HRMS: calcd for $C_{20}H_{28}NO_2$ (M+H$^+$) 329.1471; found 329.1480.



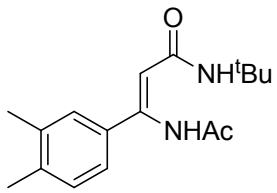
(*Z*)-methyl 4-(1-acetamido-3-(*tert*-butylamino)-3-oxoprop-1-en-1-yl)benzoate(**3m**)
Prepared from methyl 4-(1-acetamidovinyl)benzoate (43.8 mg, 0.2 mmol, 1.0 equiv) and *t*-BuNC (24.9 mg, 0.3 mmol, 1.5 equiv) according to the general procedure. Column chromatography purification (EtOAc : petroleum ether = 1 : 4) furnished the product **3m** as a colorless oil (31 mg, 0.97 mmol, 49% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 11.55 (s, 1H), 7.99 (d, *J* = 8.4 Hz, 2H), 7.37 (d, *J* = 8.4 Hz, 2H), 5.39 (s, 1H), 4.98 (s, 1H), 3.91 (s, 3H), 2.15 (s, 3H), 1.40 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 168.7, 167.5, 166.8, 150.2, 141.5, 130.4, 129.4, 127.0, 105.5, 52.3, 51.8, 29.0, 24.8; HRMS: calcd for $C_{17}H_{22}N_2O_4$ (M+H$^+$) 319.1652; found 319.1666.



(*Z*)-3-acetamido-*N*-(*tert*-butyl)-3-(4-nitrophenyl)acrylamide(**3n**)
Prepared from *N*-(1-(4-nitrophenyl)vinyl)acetamide (41.2 mg, 0.2 mmol, 1.0 equiv) and *t*-BuNC (24.9 mg, 0.3 mmol, 1.5 equiv) according to the general procedure. Column chromatography purification (EtOAc : petroleum ether = 1 : 4) furnished the product **3n** as a yellow oil (34 mg, 0.11 mmol, 56% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 11.62 (s, 1H), 8.18 (d, *J* = 8.8 Hz, 2H), 7.45 (d, *J* = 8.8 Hz, 2H), 5.43 (s, 1H), 4.99 (s, 1H), 2.16 (s, 3H), 1.41 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 168.8, 167.1, 148.8, 147.9, 143.5, 127.9, 123.4, 106.2, 52.0, 29.0, 24.7; HRMS: calcd for $C_{15}H_{19}N_3O_4$ (M+H$^+$) 306.1448; found 306.1449.

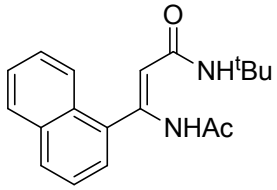


(*Z*)-3-acetamido-*N*-(*tert*-butyl)-3-(2,4-dimethylphenyl)acrylamide(**3o**)
Prepared from *N*-(1-(2,4-dimethylphenyl)vinyl)acetamide (37.8 mg, 0.2 mmol, 1.0 equiv) and *t*-BuNC (24.9 mg, 0.3 mmol, 1.5 equiv) according to the general procedure. Column chromatography purification (EtOAc : petroleum ether = 1 : 4) furnished the product **3o** as a colorless oil (31 mg, 0.11 mmol, 53% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 11.87 (s, 1H), 7.00 (d, *J* = 8.2 Hz, 1H), 6.96-6.95 (m, 2H), 5.25 (s, 1H), 4.66 (s, 1H), 2.31 (s, 3H), 2.22 (s, 3H), 2.07 (s, 3H), 1.40 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 168.4, 167.7, 151.5, 138.1, 135.3, 134.2, 130.5, 127.6, 126.2, 102.7, 51.6, 29.1, 24.8, 21.3, 19.6; HRMS: calcd for $C_{17}H_{24}N_2O_2$ (M+H$^+$) 289.1911; found 289.1915.



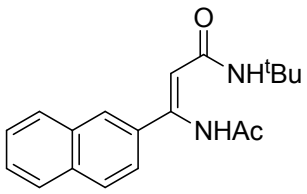
(*Z*)-3-acetamido-*N*-(*tert*-butyl)-3-(3,4-dimethylphenyl)acrylamide(**3p**)

Prepared from *N*-(1-(3,4-dimethylphenyl)vinyl)acetamide (37.8 mg, 0.2 mmol, 1.0 equiv) and *t*-BuNC (24.9 mg, 0.3 mmol, 1.5 equiv) according to the general procedure. Column chromatography purification (EtOAc : petroleum ether = 1 : 4) furnished the product **3p** as a colorless oil (36 mg, 0.13 mmol, 63% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 11.46 (s, 1H), 7.09-7.05 (m, 3H), 5.33 (s, 1H), 4.95 (s, 1H), 2.25 (s, 3H), 2.24 (s, 3H), 2.14 (s, 3H), 1.39 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 168.8, 168.0, 151.4, 137.8, 136.2, 134.3, 129.4, 128.1, 124.6, 104.1, 51.6, 29.1, 25.0, 19.9, 19.8; HRMS: calcd for $C_{17}H_{24}N_2O_2$ (M+H$^+$) 289.1911; found 289.1915.



(*Z*)-3-acetamido-*N*-(*tert*-butyl)-3-(naphthalen-1-yl)acrylamide(**3q**)

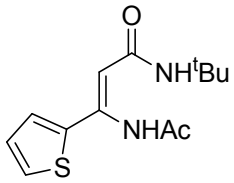
Prepared from *N*-(1-(naphthalen-1-yl)vinyl)acetamide (42.2 mg, 0.2 mmol, 1.0 equiv) and *t*-BuNC (24.9 mg, 0.3 mmol, 1.5 equiv) according to the general procedure. Column chromatography purification (EtOAc : petroleum ether = 1 : 4) furnished the product **3q** as a colorless oil (49 mg, 0.16 mmol, 79% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 12.09 (s, 1H), 7.96-7.92 (m, 1H), 7.84-7.79 (m, 2H), 7.46-7.42 (m, 2H), 7.40 (t, *J* = 7.0 Hz, 1H), 7.29 (d, *J* = 7.0 Hz, 1H), 5.36 (s, 1H), 4.84 (s, 1H), 2.04 (s, 3H), 1.40 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 168.2, 167.5, 150.1, 135.3, 133.1, 131.4, 128.8, 128.4, 126.5, 126.0, 125.1, 125.0, 124.8, 104.0, 51.6, 29.0, 24.7; HRMS: calcd for $C_{19}H_{22}N_2O_2$ (M+H$^+$) 311.1754; found 311.1761.



(*Z*)-3-acetamido-*N*-(*tert*-butyl)-3-(naphthalen-2-yl)acrylamide(**3r**)

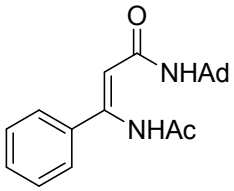
Prepared from *N*-(1-(naphthalen-2-yl)vinyl)acetamide (42.2 mg, 0.2 mmol, 1.0 equiv) and *t*-BuNC (24.9 mg, 0.3 mmol, 1.5 equiv) according to the general procedure. Column chromatography purification (EtOAc : petroleum ether = 1 : 4) furnished the product **3r** as a colorless oil (34 mg, 0.11 mmol, 55% yield). ^{1}H NMR (500 MHz,

$CDCl_3$): δ 11.63 (s, 1H), 7.81-7.79 (m, 3H), 7.76 (d, *J* = 8.5 Hz, 1H), 7.48-7.45 (m, 2H), 7.41 (d, *J* = 8.5 Hz, 1H), 5.40 (s, 1H), 5.07 (s, 1H), 2.17 (s, 3H), 1.41 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 168.8, 167.9, 151.2, 134.7, 133.7, 133.1, 128.4, 127.8, 127.3, 126.6, 126.3, 125.8, 125.2, 104.9, 51.7, 29.1, 25.0; HRMS: calcd for $C_{19}H_{22}N_2O_2$ (M+H$^+$) 311.1754; found 311.1761.



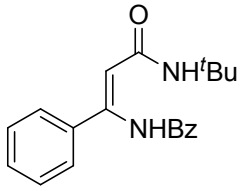
(*Z*)-3-acetamido-*N*-(*tert*-butyl)-3-(thiophen-2-yl)acrylamide(**3s**)

Prepared from *N*-(1-(thiophen-2-yl)vinyl)acetamide (33.4 mg, 0.2 mmol, 1.0 equiv) and *t*-BuNC (24.9 mg, 0.3 mmol, 1.5 equiv) according to the general procedure. Column chromatography purification (EtOAc : petroleum ether = 1 : 4) furnished the product **3s** as a colorless oil (32 mg, 0.12 mmol, 60% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 11.28 (s, 1H), 7.30 (d, *J* = 4.6 Hz, 1H), 7.14 (d, *J* = 4.6 Hz, 1H), 6.97 (t, *J* = 4.6 Hz, 1H), 5.41 (s, 1H), 5.20 (s, 1H), 2.16 (s, 3H),1.38 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.2, 167.4, 144.0, 138.6, 127.4, 127.1, 126.7, 105.0, 51.7, 29.0, 25.0; HRMS: calcd for $C_{13}H_{18}N_2O_2S$ (M+H$^+$) 267.1162; found 267.1168.



(*Z*)-3-acetamido-*N*-(adamantan-1-yl)-3-phenylacrylamide(**3t**)

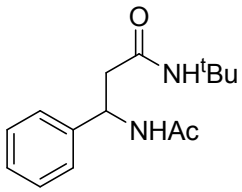
Prepared from *N*-(1-phenylvinyl)acetamide (32.2 mg, 0.2 mmol, 1.0 equiv) and AdNC (48.3 mg, 0.3 mmol, 1.5 equiv) according to the general procedure. Column chromatography purification (EtOAc : petroleum ether = 1 : 4) furnished the product **3t** as a colorless oil (38 mg, 0.11 mmol, 56% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 11.49 (s, 1H), 7.32-7.30 (m, 5H), 5.20 (s, 1H), 4.95 (s, 1H), 2.13 (s, 3H), 2.11 (brs, 3H), 2.05-2.01 (m, 6H), 1.71 (brs, 6H), ; ^{13}C NMR (125 MHz, $CDCl_3$): δ 168.7, 167.6, 151.2, 136.9, 129.0, 128.0, 127.0, 104.8, 52.4, 41.9, 36.4, 29.6, 25.0; HRMS: calcd for $C_{21}H_{26}N_2O_2$ (M+H$^+$) 339.2067; found 339.2078.



(*Z*)-*N*-(3-(tert-butylamino)-3-oxo-1-phenylprop-1-en-1-yl)benzamide(**3u**)

Prepared from *N*-(1-phenylvinyl)benzamide (44.6 mg, 0.2 mmol, 1.0 equiv) and *t*-BuNC (24.9 mg, 0.3 mmol, 1.5 equiv) according to the general procedure. Column

chromatography purification (EtOAc : petroleum ether = 1 : 8) furnished the product **3u** as a white solid (33.2 mg, 0.11 mmol, 52% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 12.57 (s, 1H), 8.02 (d, *J* = 7.2 Hz , 2H), 7.56-7.46 (m, 3H), 7.41-7.33 (m, 5H), 5.38 (s, 1H), 5.09 (s, 1H), 1.41 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 168.1, 165.2, 151.9, 137.2, 134.3, 132.2, 129.0, 128.8, 128.2, 128.1, 127.1, 105.4, 51.8, 29.1; HRMS: calcd for $C_{20}H_{22}N_2O_2$ ($M+H^+$) 323.1754; found 323.1741; mp = 160-162 ^{0}C.



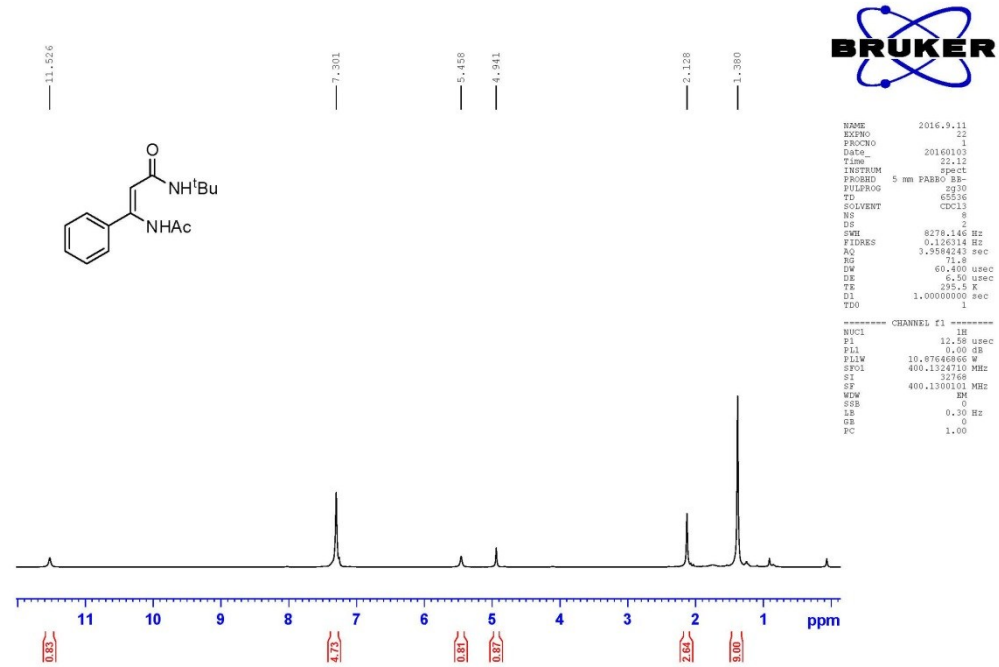
3-acetamido-*N*-(*tert*-butyl)-3-phenylpropanamide(**4**)

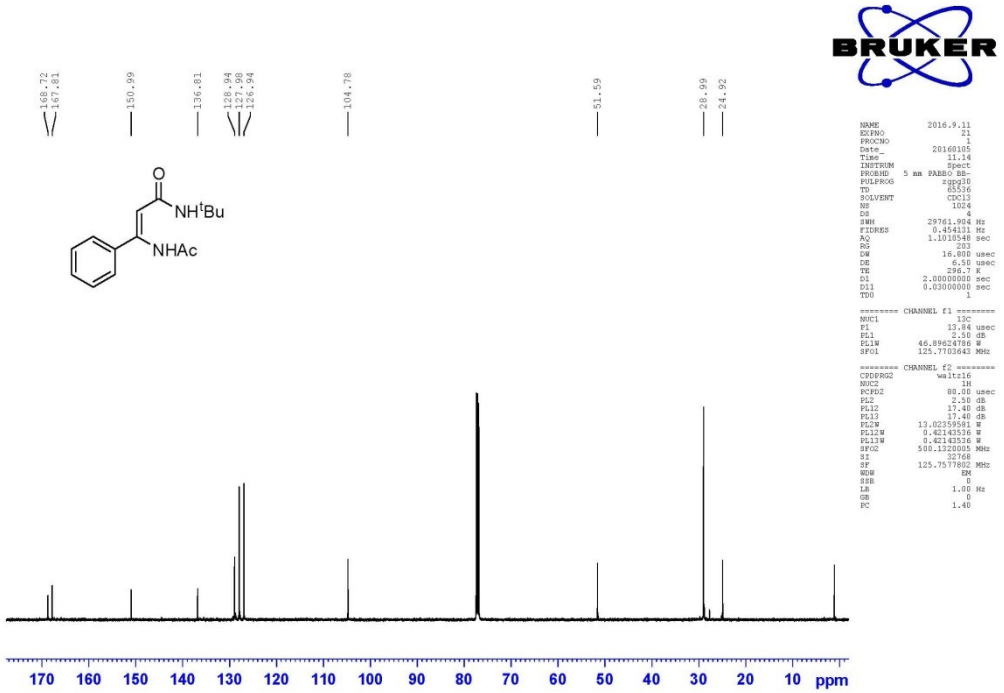
To a solution of (*Z*)-3-acetamido-*N*-(tert-butyl)-3-phenylacrylamide (**3a,** 0.2 mmol) in MeOH (2 mL) was added Pd/C (50.0mg).Then the reaction mixture was stirred at r.t. under H_2(g) (1 atm). The reaction was monitored by TLC until completion. The crude reaction mixture was filtered to obtain filtrate. After evaporation, the product **4** can be obtained in quantitative yield without further purification.

White solid (52.2 mg, 0.2 mmol, 100% yield). mp = 210-212 ^{0}C; ^{1}H NMR (400 MHz, CD_3OD): δ 7.38-7.28 (m, 4H), 7.36-7.21 (m, 1H), 5.29 (t, *J* = 7.5 Hz, 1H), 2.58 (d, *J* = 7.5 Hz, 2H), 1.96 (s, 3H), 1.22 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 172.2, 171.8, 142.8, 129.5, 128.4, 127.7, 52.5, 51.9, 44.4, 28.8, 22.7; HRMS: calcd for $C_{21}H_{26}N_2O_2$ ($M+H^+$) 263.1754; found 263.1754.

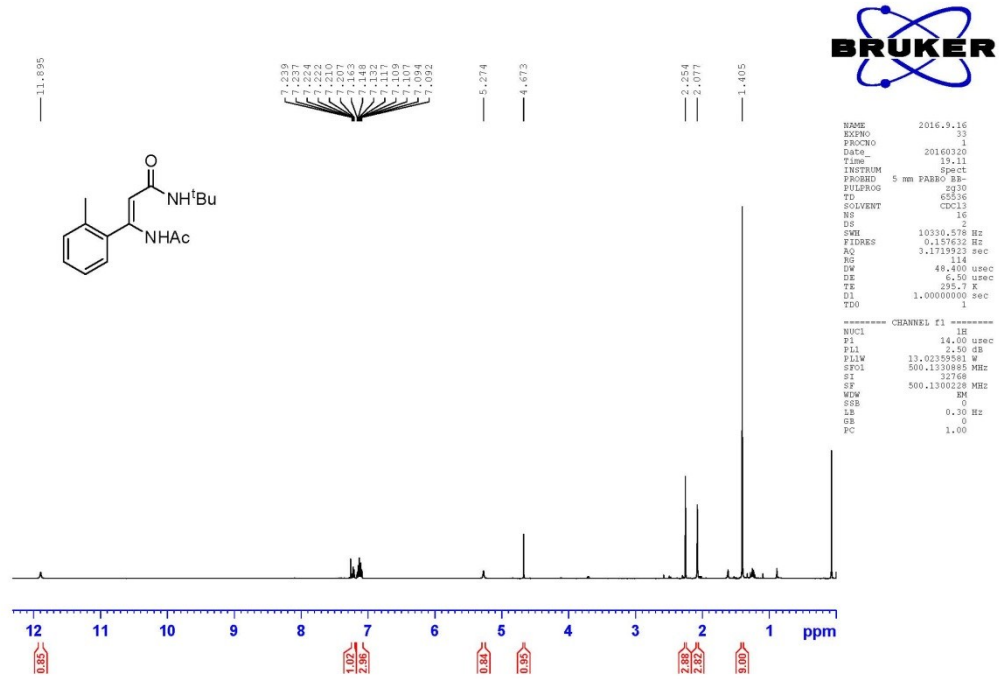
IV. Copies of ^{1}H and ^{13}C NMR Spectra

3a





3b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7.224
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7.210
7.207
7.163
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7.132
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7.107
7.084
7.092
5.274
4.673
2.254
2.077
1.405
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NHAc
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PROCNO 1
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Time 19.11
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FIDRES 0.157632 Hz
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RG 114
DW 48.400 usec
DE 6.50 usec
TE 295.7 K
D1 1.00000000 sec
TD0 1
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P1 14.00 usec
PL1 2.50 dB
PL1W 13.02359581 W
SFO1 500.1330885 MHz
SI 32768
SF 500.1300228 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
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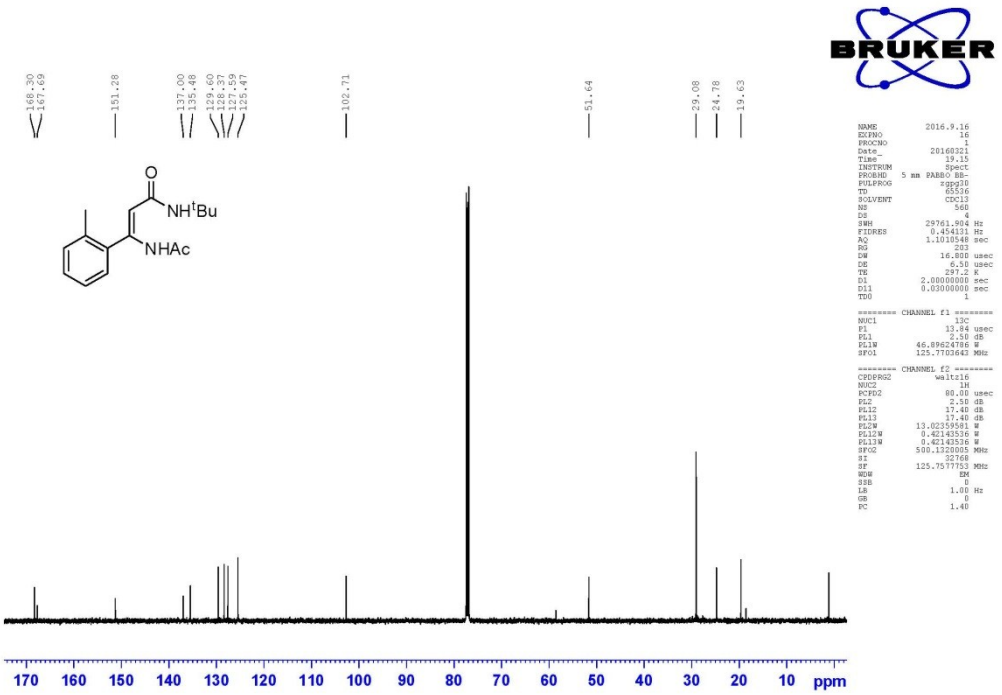
0.85 1.02 2.00 0.84 0.95 2.88 2.82 9.00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24.78
19.63
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D11 0.03000000 sec
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SFO1 125.7703643 MHz
======== CHANNEL f2 ========
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PCPD2 80.00 usec
PL2 2.50 dB
PL12 17.40 dB
PL13 17.40 dB
PL2W 13.02359581 W
PL12W 0.42143536 W
PL13W 0.42143536 W
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SI 32768
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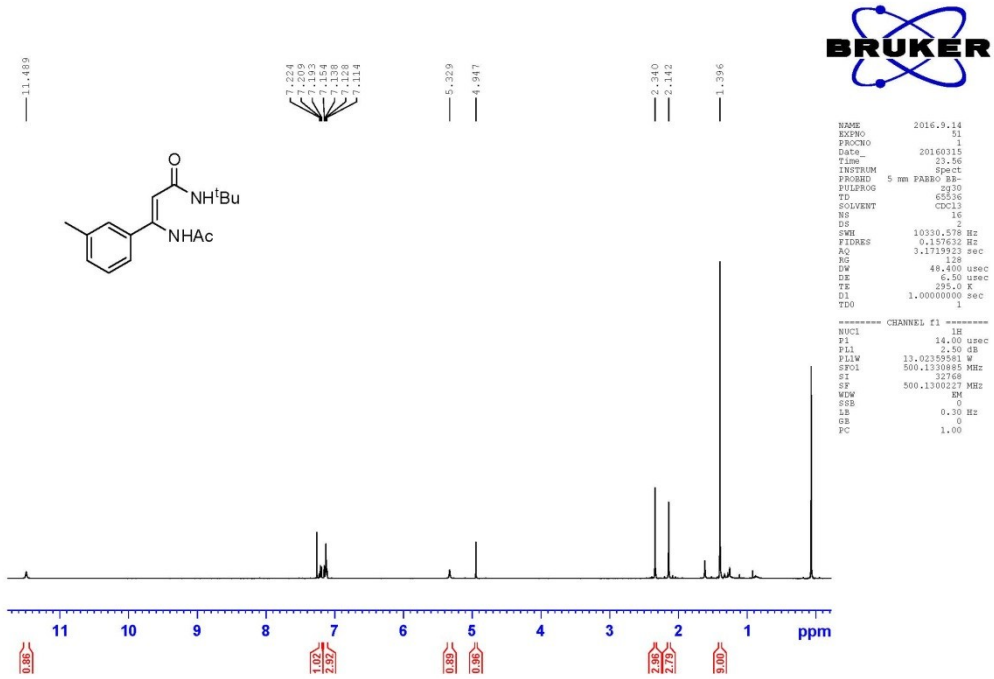
3c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7.118
7.114
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NH^{t}Bu
NHAc
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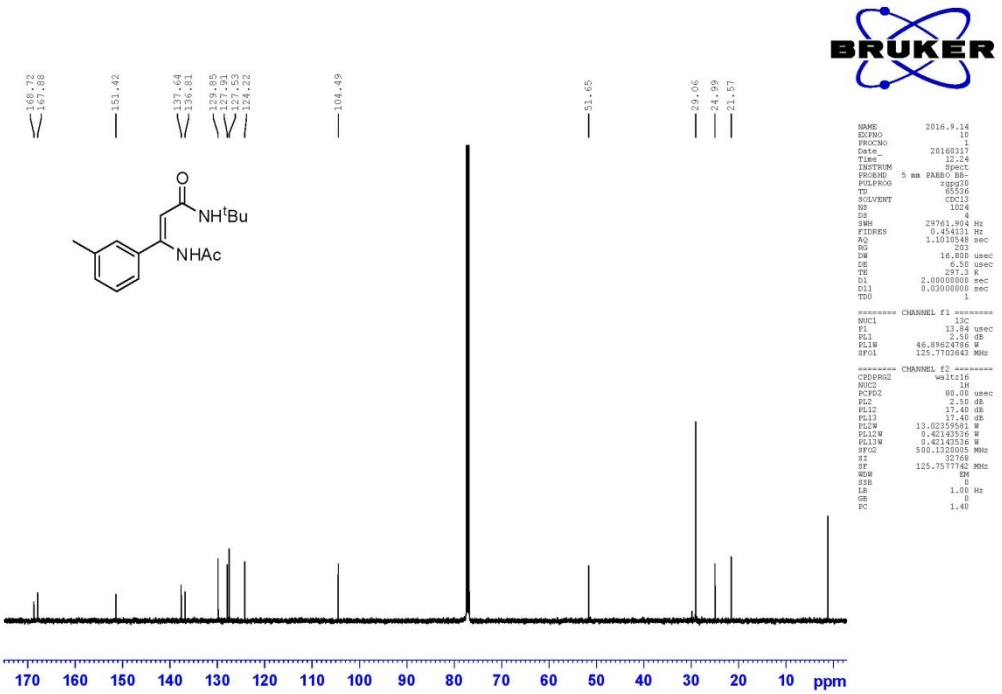
0.98 1.07 2.82 0.89 0.98 2.38 2.79 9.00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127.53
124.22
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NHAc
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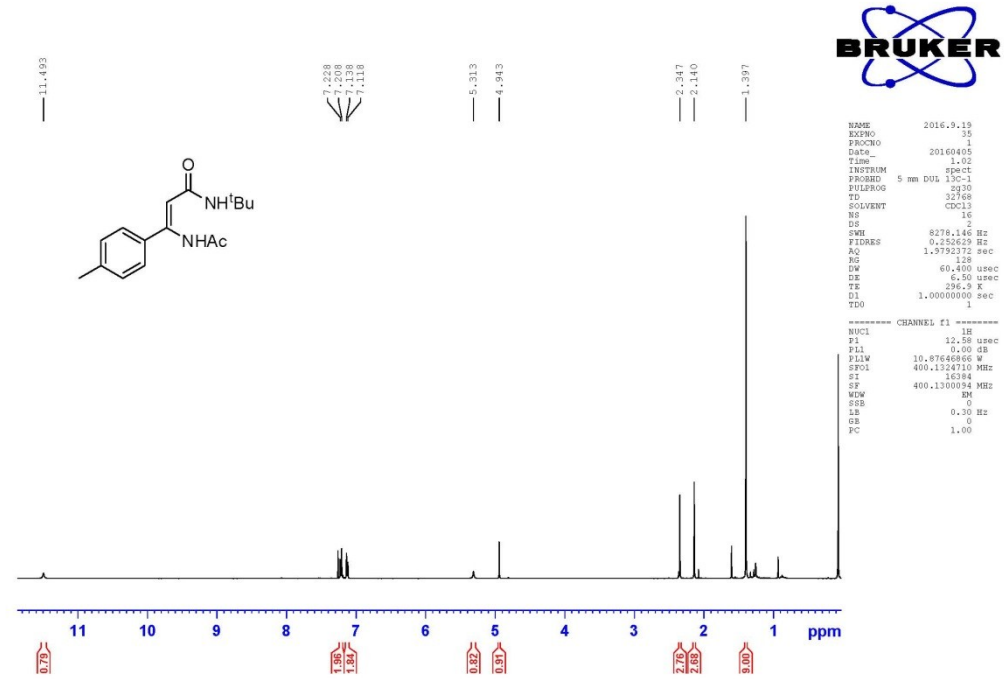
3d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10
9
8
7
6
5
4
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2
1
ppm
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0.82
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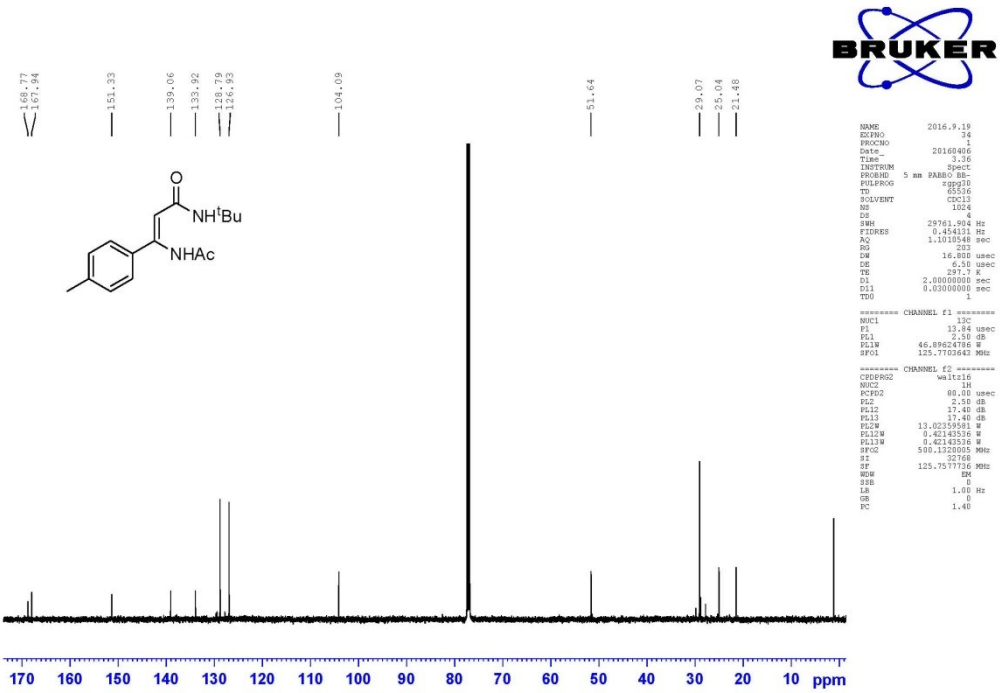
2.76
2.68
9.00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140
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120
110
100
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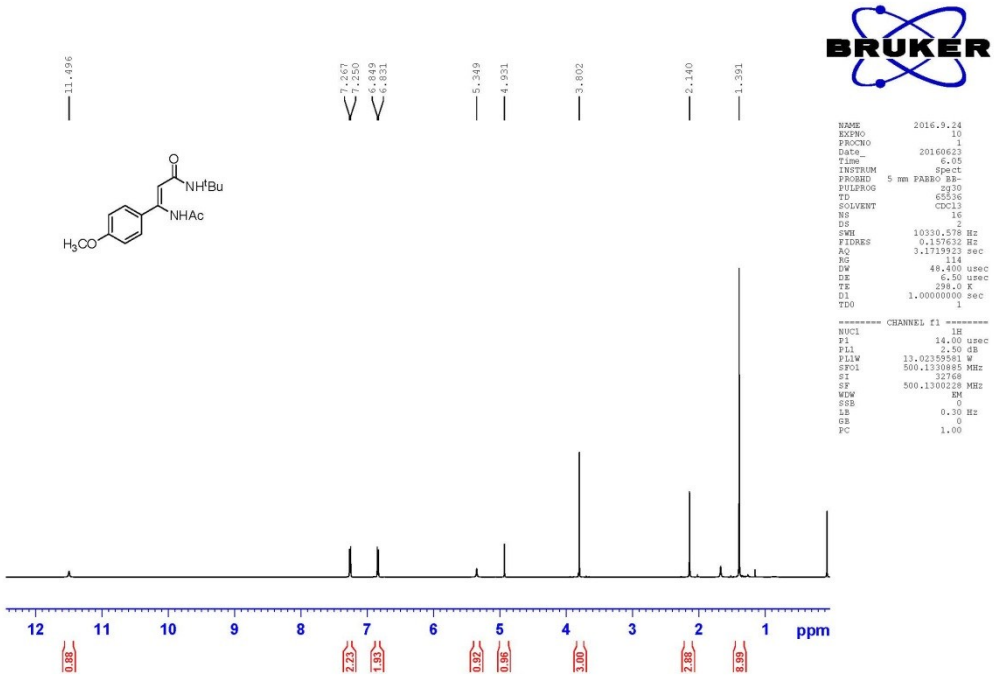
60
50
40
30
20
10
ppm

3e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H_3CO
12
11
10
9
8
7
6
5
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2
1
ppm
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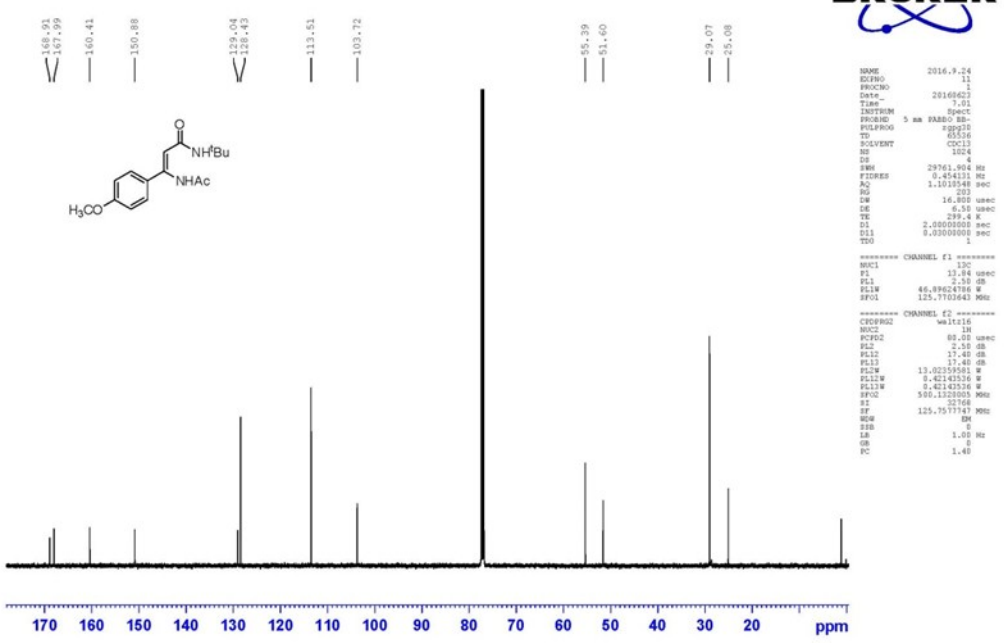
3.00
2.88
8.89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NH^{t}Bu
NHAc
H_3CO
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150
140
130
120
110
100
90
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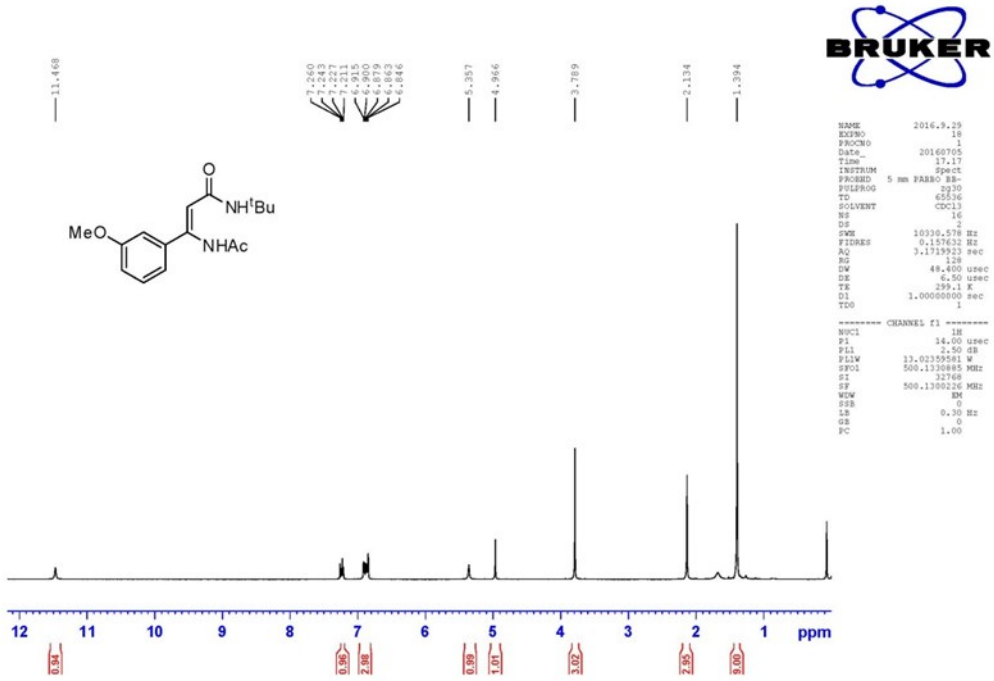
70
60
50
40
30
20
ppm

3f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3.789
2.134
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MeO
NHAc
NH^{t}Bu
12
11
10
9
8
7
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5
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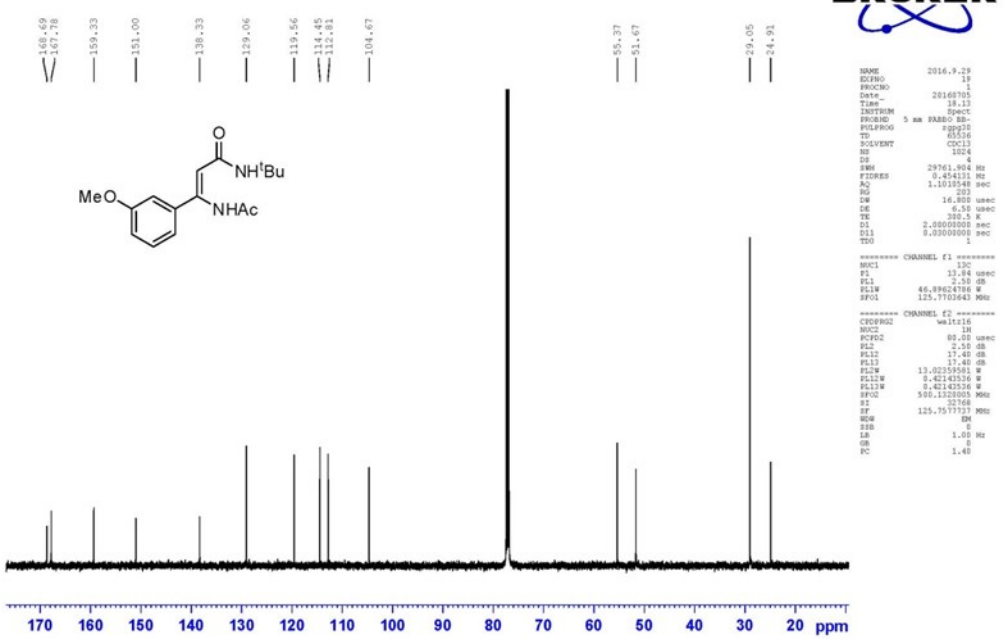
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MeO
NHAc
NH^{t}Bu
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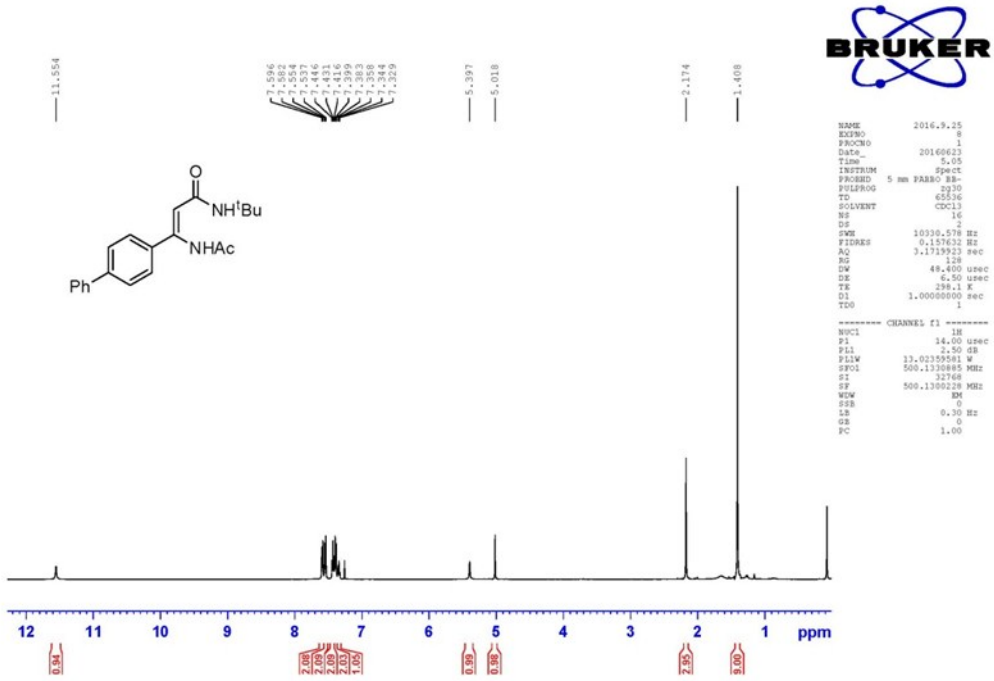
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

3g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7.416
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7.344
7.329
5.397
5.018
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NHAc
Ph
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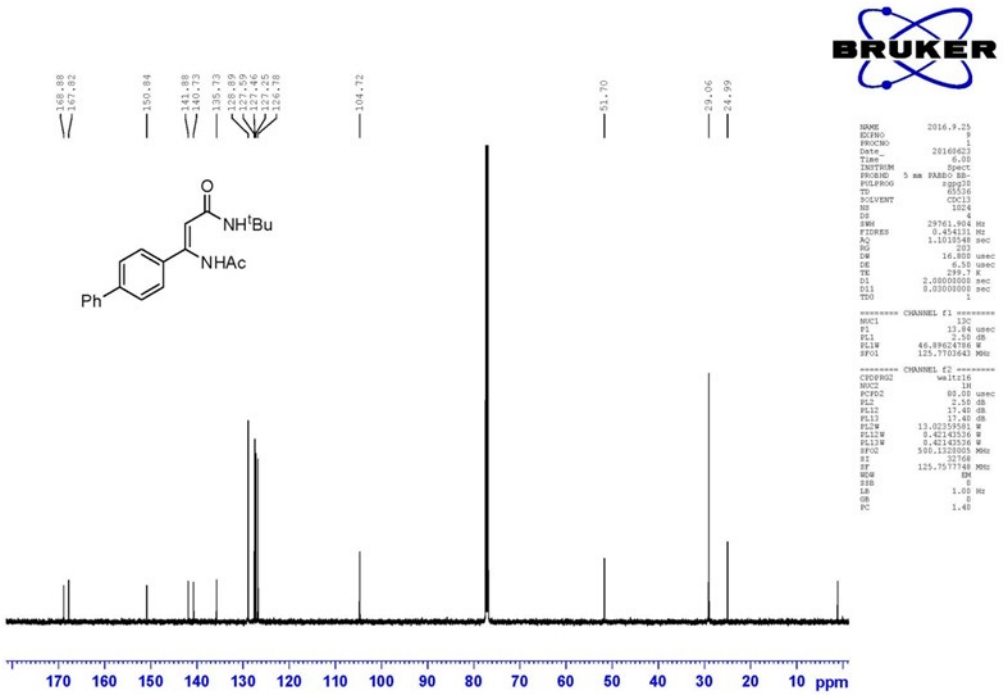
11
10
9
8
7
6
5
4
3
2
1
ppm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51.70
29.06
24.99
NH^{t}Bu
NHAc
Ph
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120
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100
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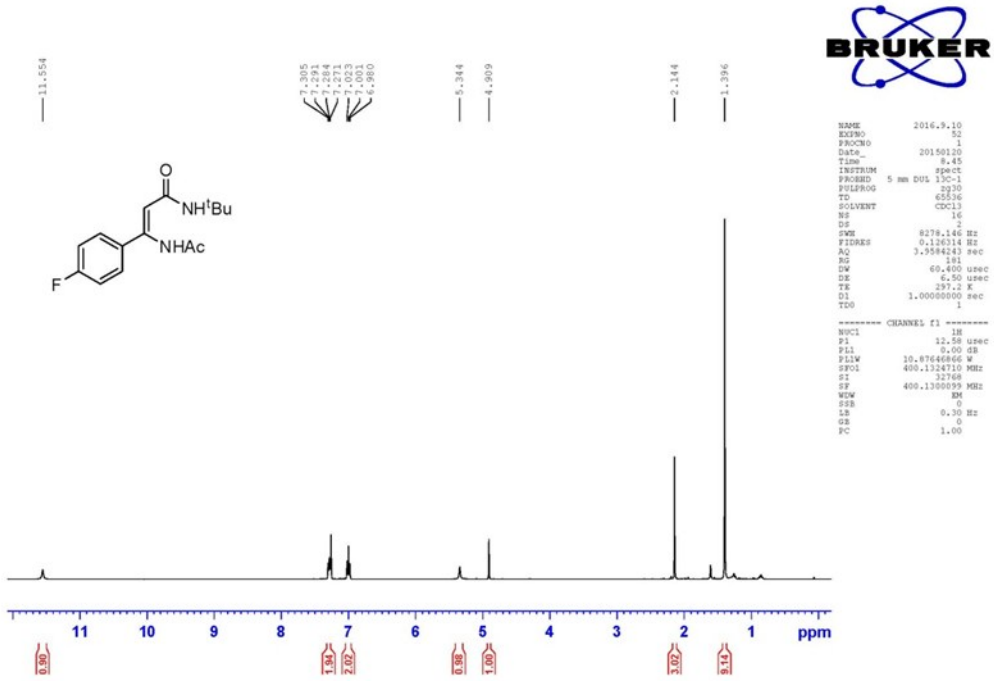
70
60
50
40
30
20
10
ppm

3h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O
NH^{t}Bu
NHAc
F
11
10
9
8
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6
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4
3
2
1
ppm
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2.02
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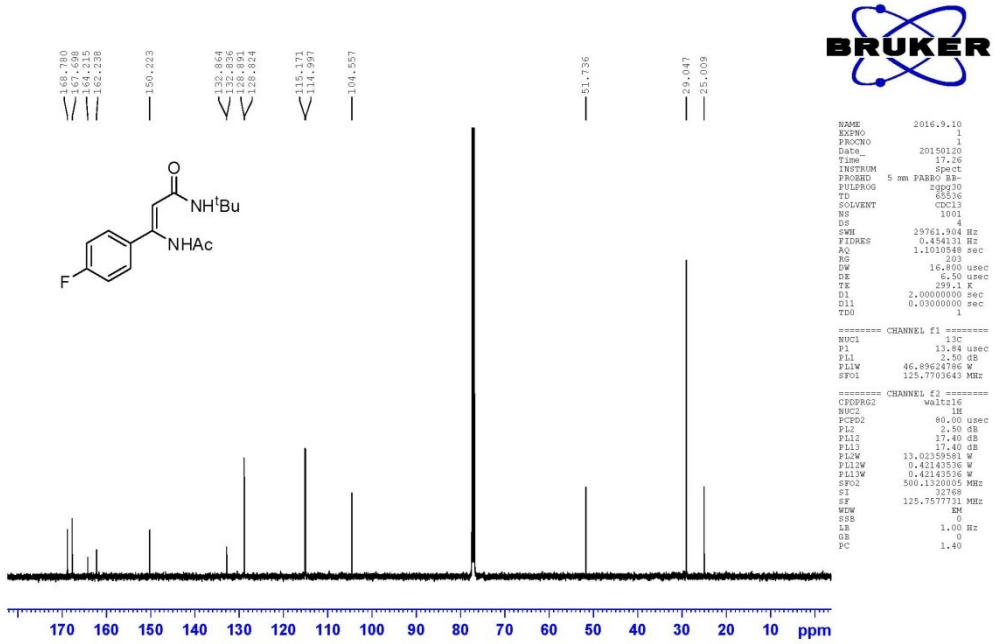
3.02
9.14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25.009
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NHAc
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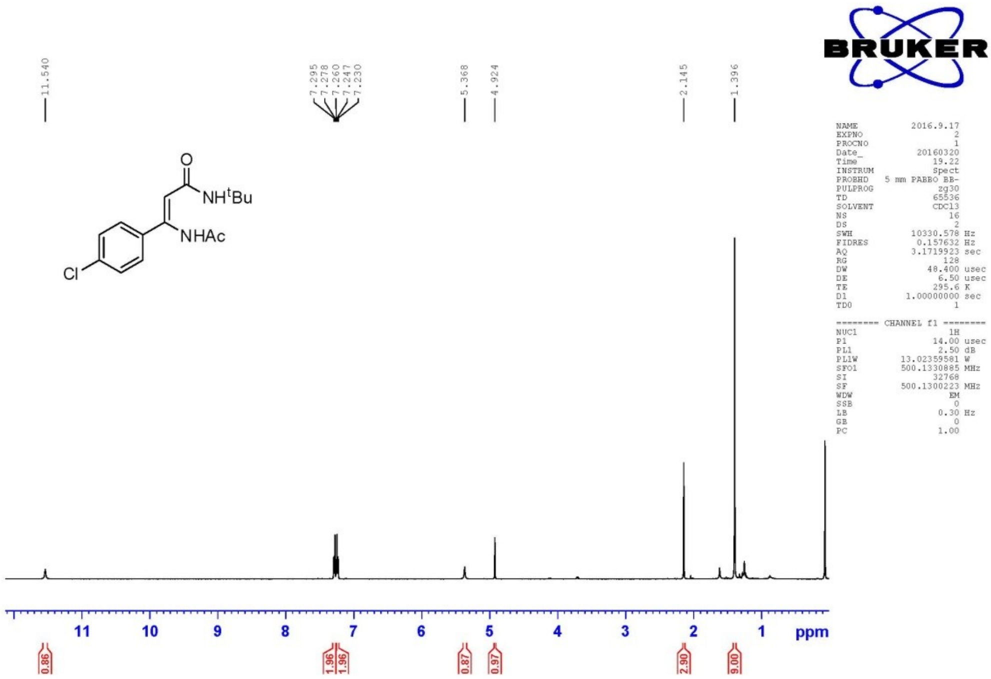
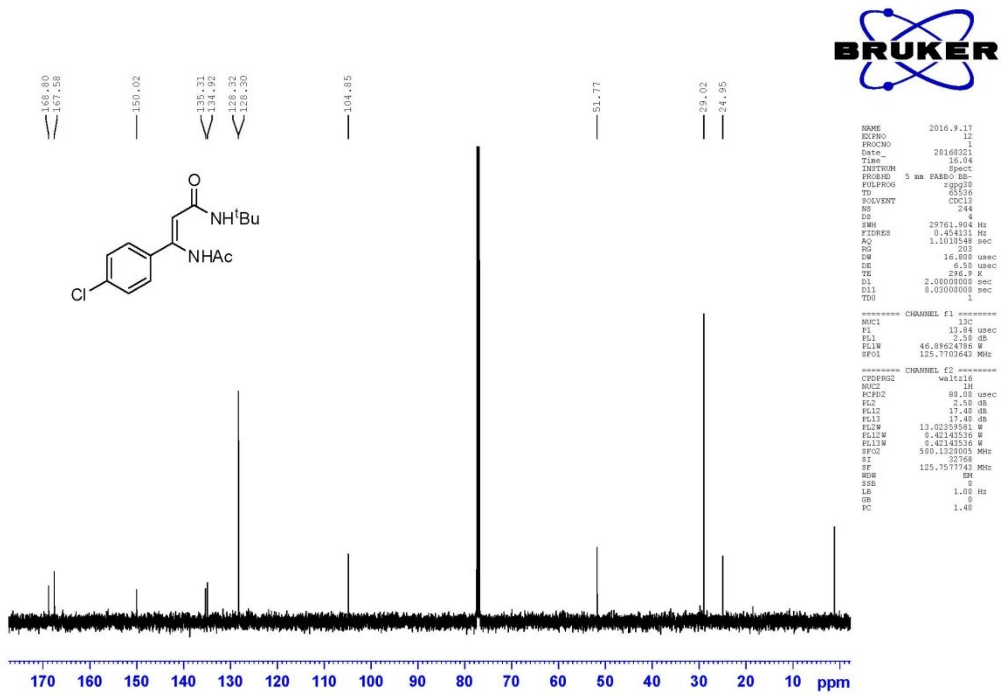
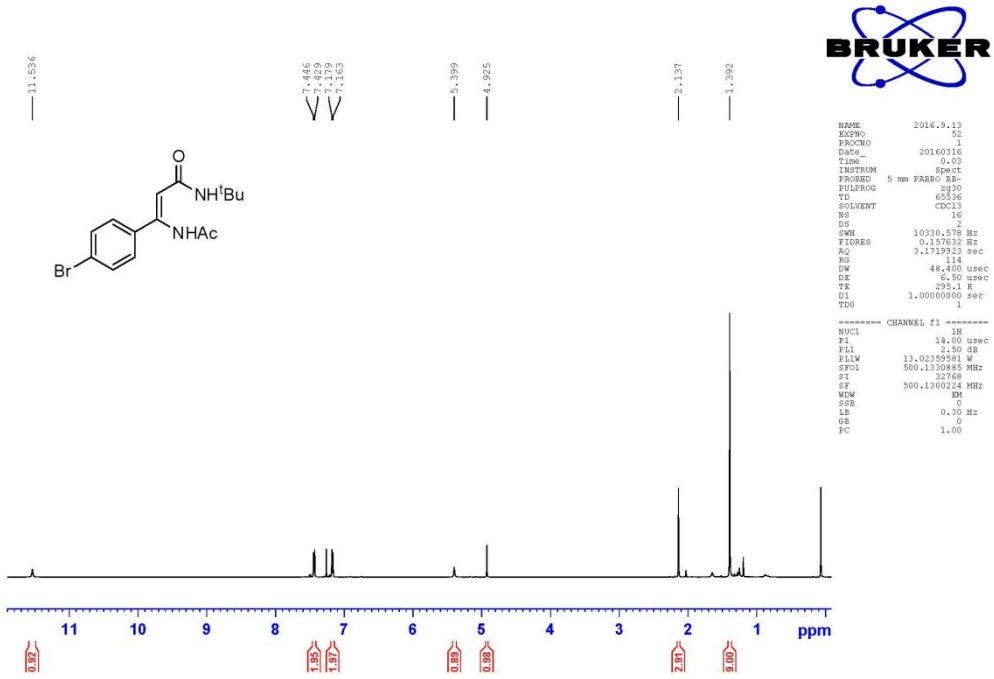
10
ppm

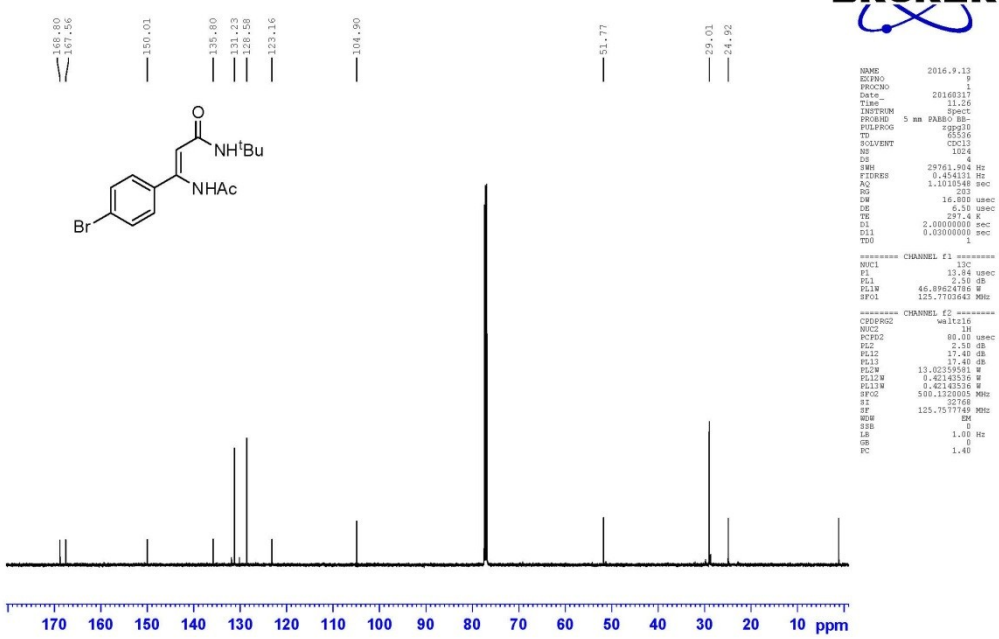
3i


11.540
7.295
7.278
7.260
7.247
7.230
5.368
4.924
2.145
1.396
BRUKER
O
NH^{t}Bu
NHAc
Cl
11
10
9
8
7
6
5
4
3
2
1
ppm
0.86
1.96
1.96
0.87
0.97
2.90
9.00

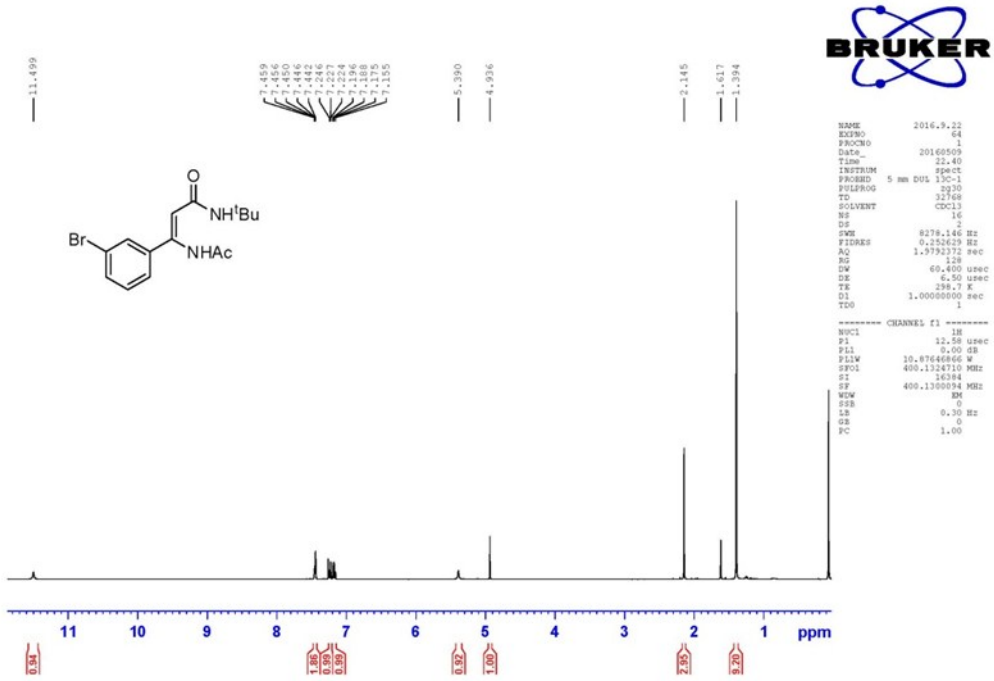

168.80
167.58
150.02
135.31
134.92
128.32
128.30
104.85
51.77
29.02
24.95
BRUKER
O
NH^{t}Bu
NHAc
Cl
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

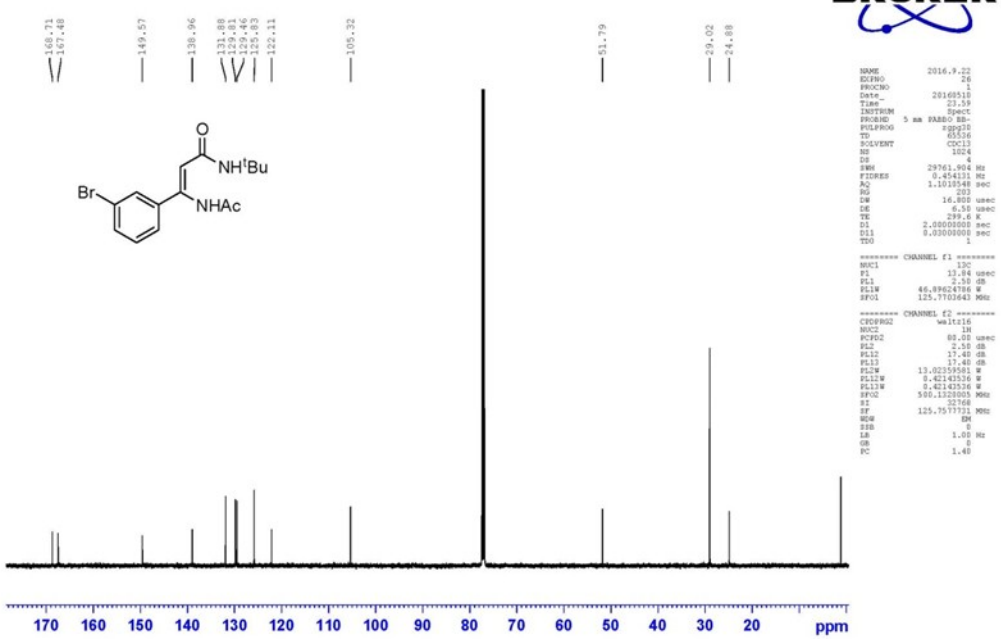
3j


11.536
7.446
7.429
7.179
7.163
5.399
4.925
2.137
1.392
NH^{t}Bu
NHAc
Br
11
10
9
8
7
6
5
4
3
2
1
ppm
0.92
1.95
1.97
0.89
0.98
2.91
9.00

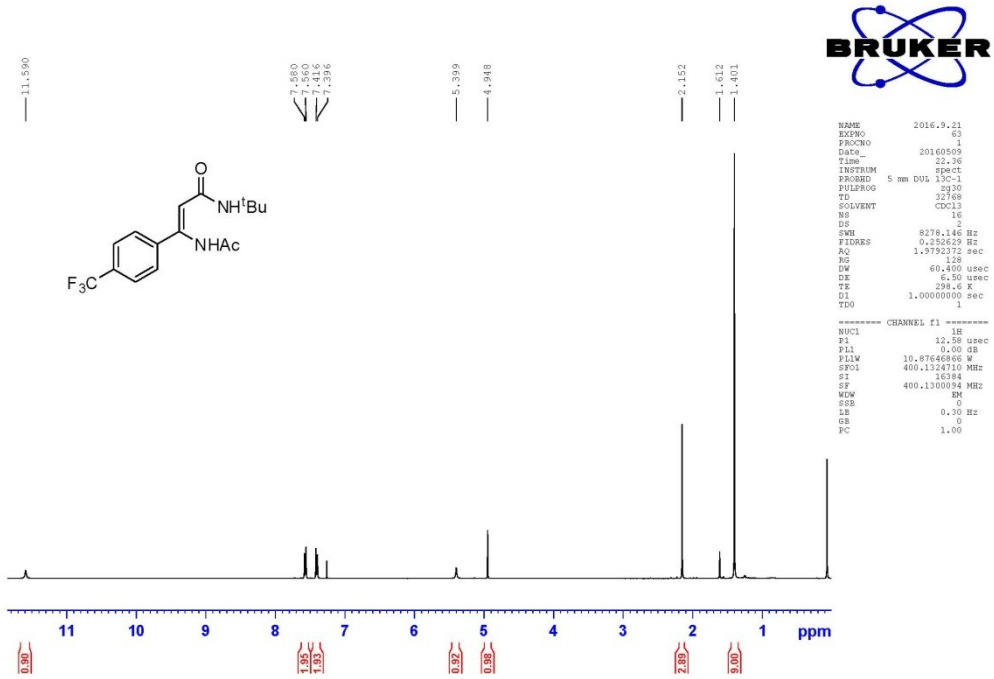

168.80
167.56
150.01
135.80
131.23
128.58
123.16
104.90
51.77
29.01
24.92
NH^{t}Bu
NHAc
Br
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

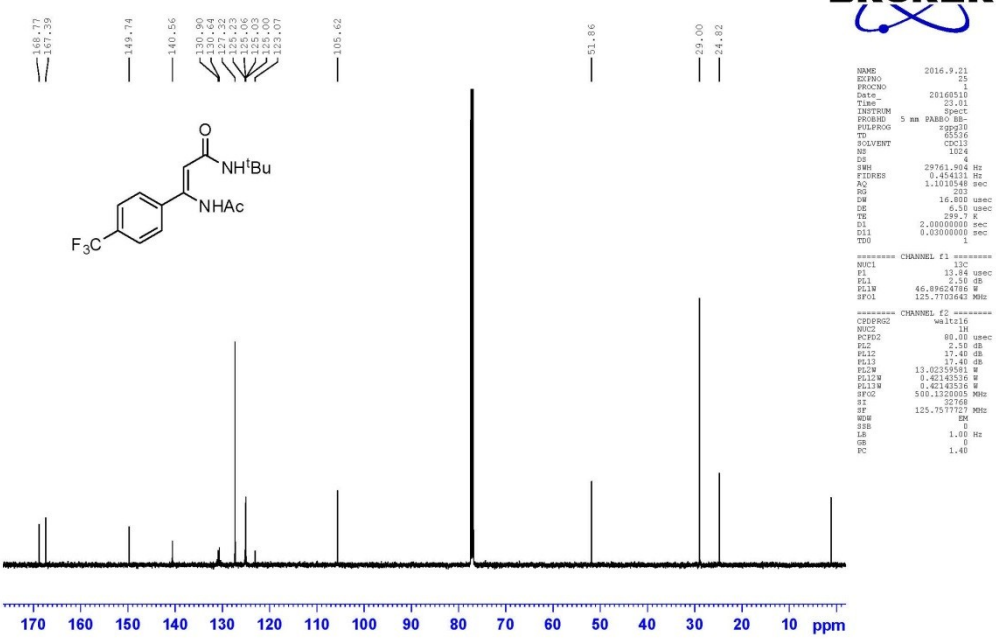
3k


11.499
7.459
7.456
7.450
7.446
7.442
7.246
7.227
7.224
7.196
7.188
7.175
7.155
5.390
4.936
2.145
1.617
1.394
O
NH^{t}Bu
Br
NHAc
11
10
9
8
7
6
5
4
3
2
1
ppm
0.94
1.86
0.99
0.99
0.92
1.00
2.95
9.20

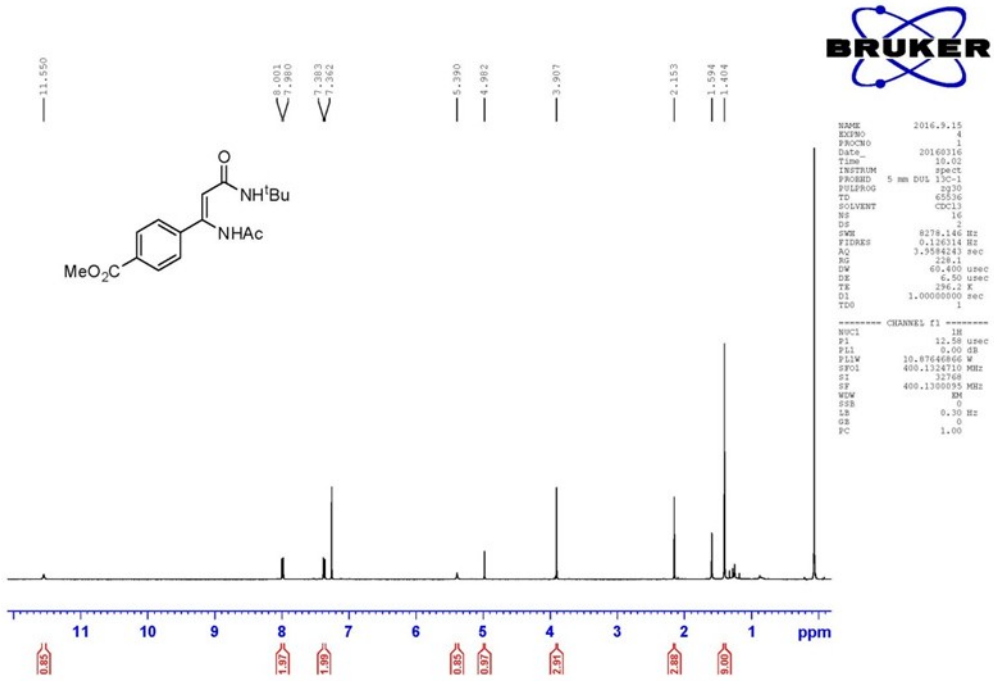

168.71
167.48
149.57
138.96
131.88
129.81
129.46
125.63
122.11
105.32
51.79
29.02
24.88
O
NH^{t}Bu
Br
NHAc
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

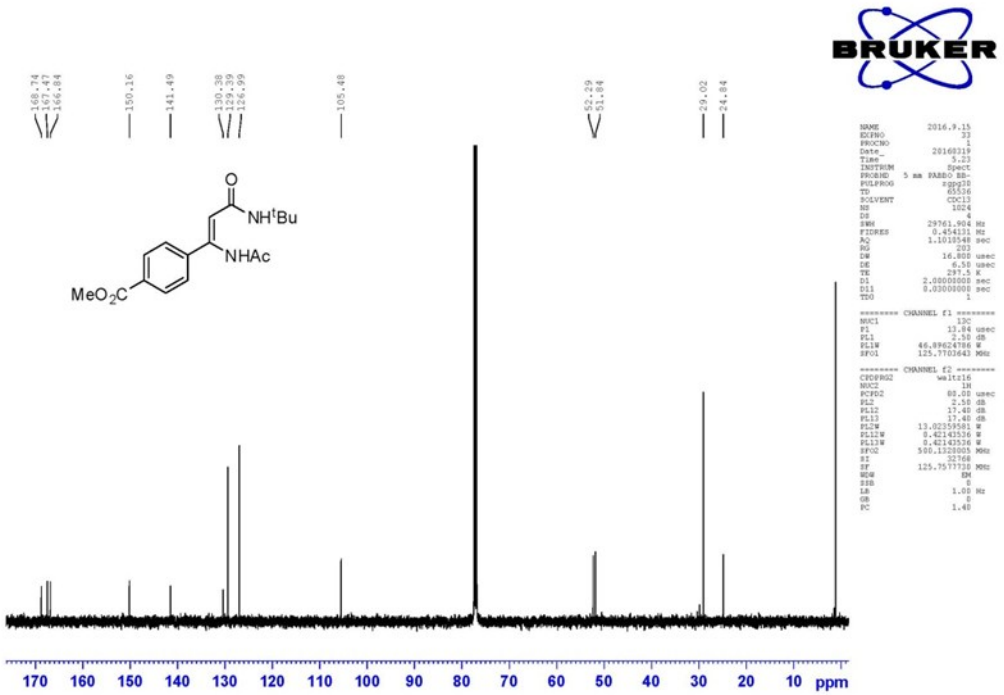
3l


11.590
7.580
7.560
7.416
7.396
5.399
4.948
2.152
1.612
1.401
NH^{t}Bu
NHAc
F_3C
11
10
9
8
7
6
5
4
3
2
1
ppm
0.90
1.95
1.83
0.92
0.98
2.89
8.00

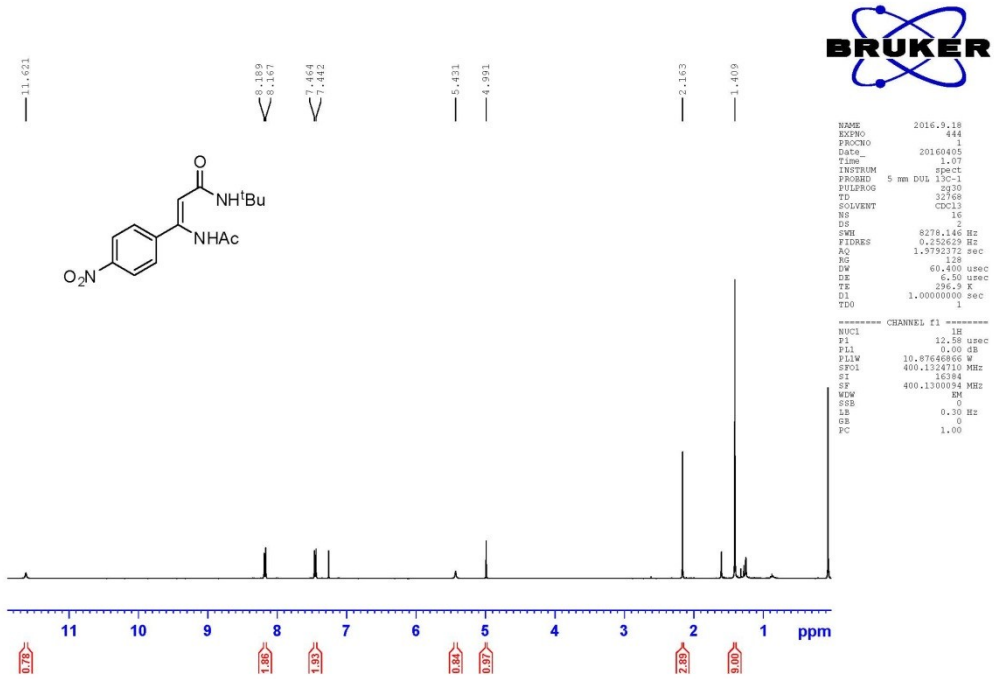

168.77
167.39
149.74
140.56
130.90
130.44
127.32
125.23
125.06
125.03
122.00
123.07
105.62
51.86
29.00
24.82
NH^{t}Bu
NHAc
F_3C
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

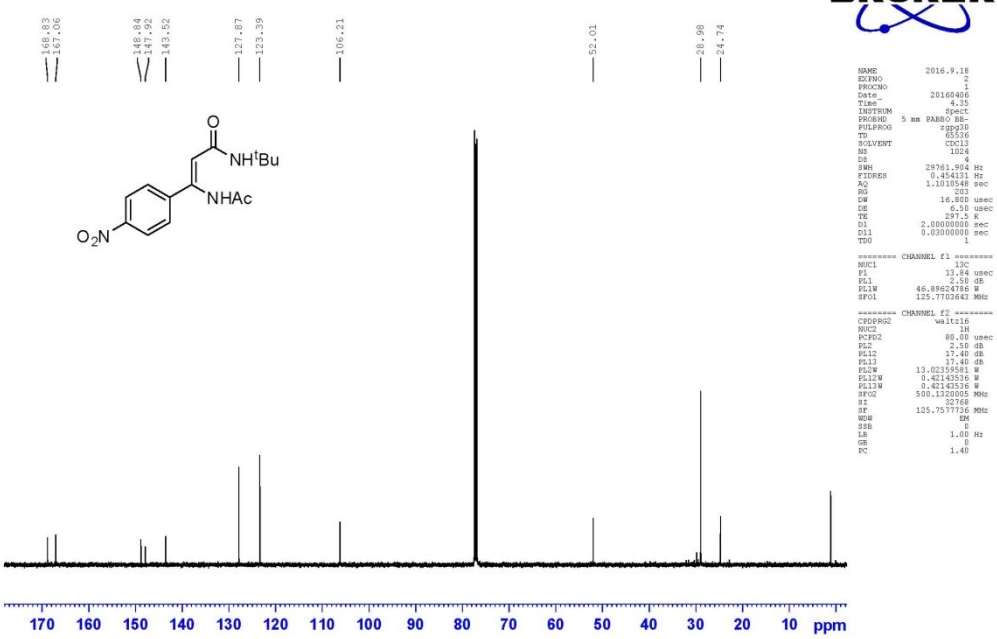
3m


11.550
8.001
7.980
7.383
7.362
5.390
4.982
3.907
2.153
1.594
1.404
NH^{t}Bu
NHAc
MeO$_2$C
11 10 9 8 7 6 5 4 3 2 1 ppm
0.85
1.97
1.99
0.85
0.87
2.91
2.88
9.00

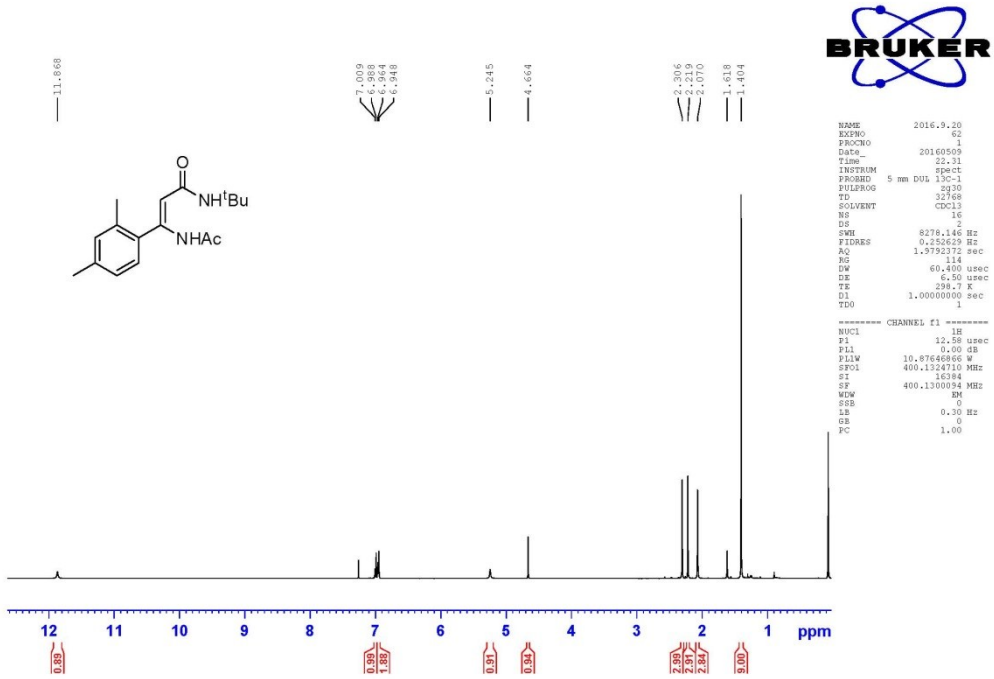

168.74
167.37
166.84
150.16
141.49
130.38
129.39
126.99
105.48
52.29
51.84
29.02
24.84
NH^{t}Bu
NHAc
MeO$_2$C
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

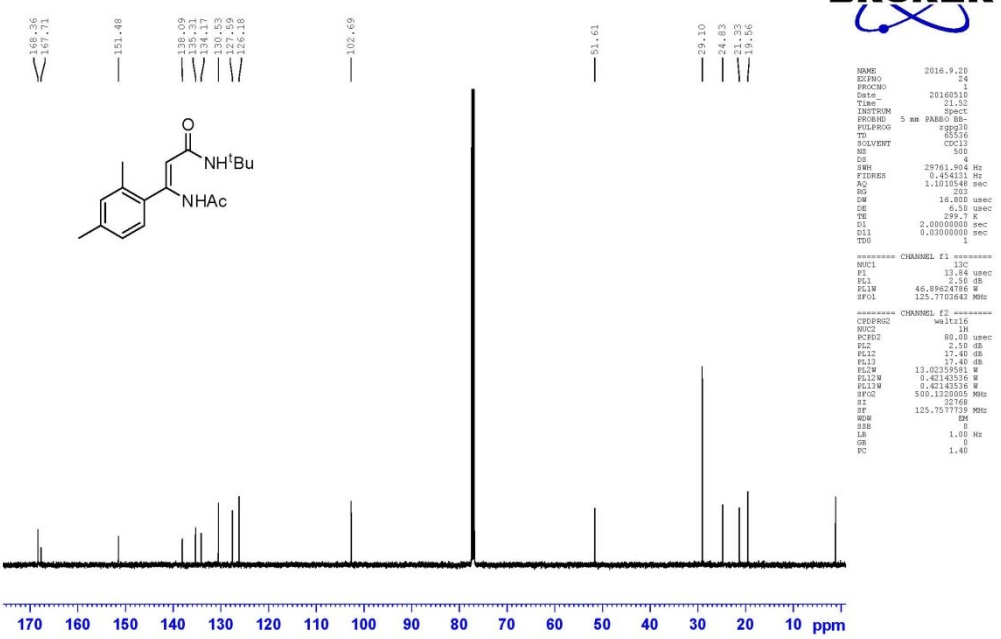
3n


11.621
8.189
8.167
7.464
7.442
5.431
4.991
2.163
1.409
NH^{t}Bu
NHAc
O_2N
11 10 9 8 7 6 5 4 3 2 1 ppm
0.78
1.88
1.83
0.84
0.97
2.89
9.00

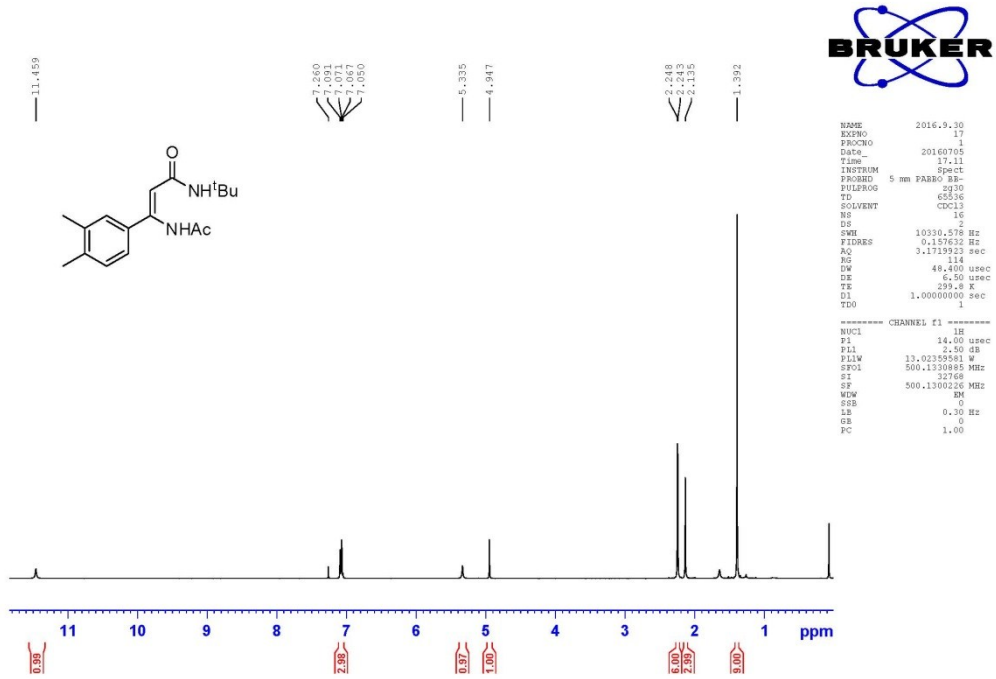

168.83
167.86
148.84
147.92
143.52
127.87
123.39
106.21
52.01
28.98
24.74
NH^{t}Bu
NHAc
O_2N
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

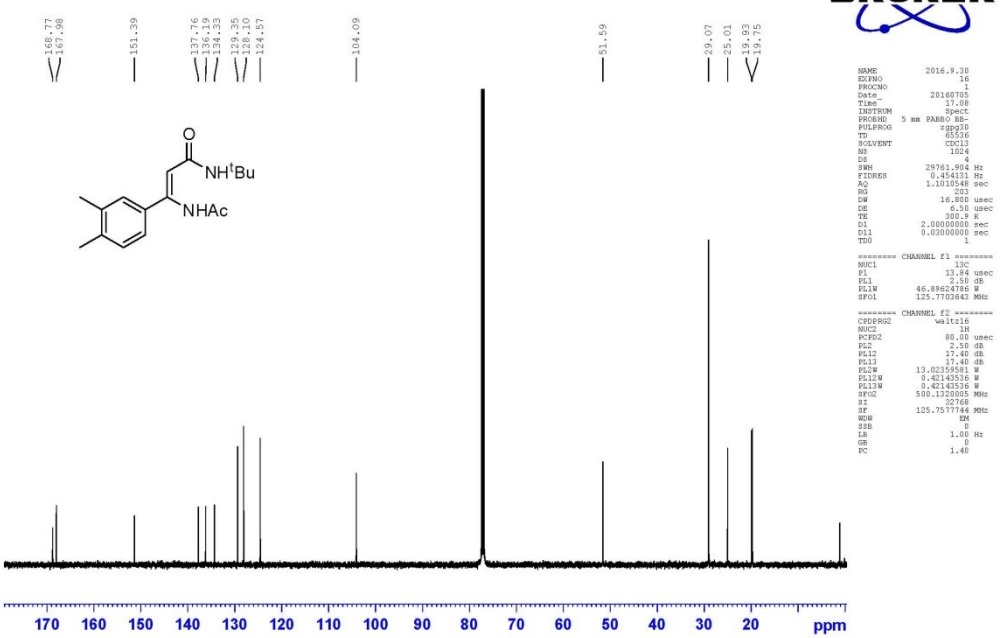
3o


11.868
7.009
6.988
6.964
6.948
5.245
4.664
2.306
2.219
2.070
1.618
1.404
NH^{t}Bu
NHAc
12
11
10
9
8
7
6
5
4
3
2
1
ppm
0.89
0.99
1.88
0.91
0.94
2.39
2.91
2.84
9.00

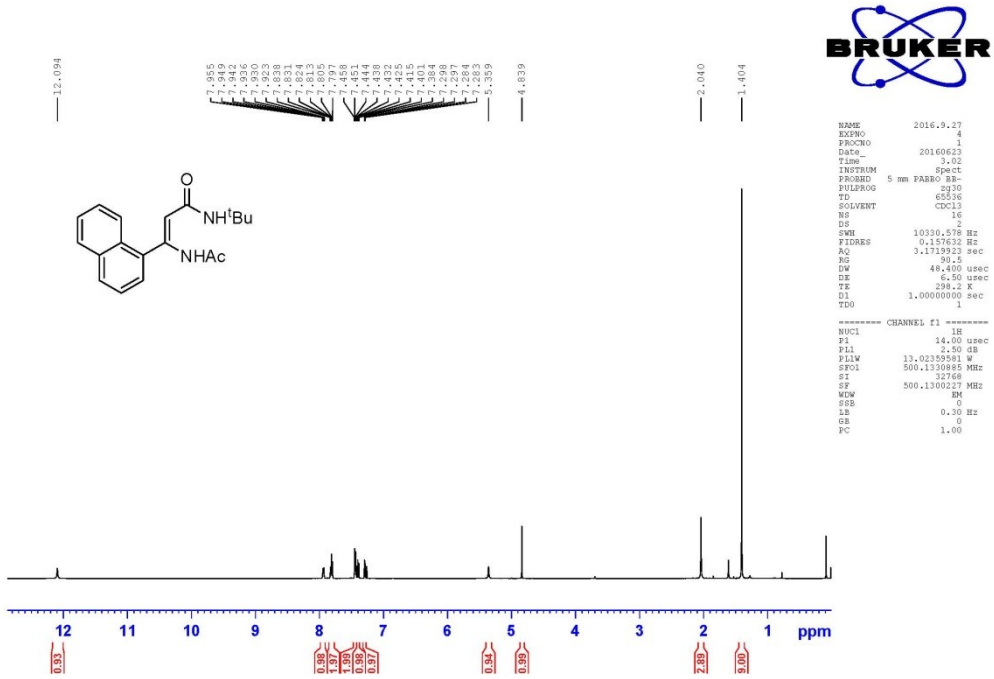

160.36
167.71
151.48
138.09
135.31
134.17
130.53
127.59
126.18
102.69
51.61
29.10
24.83
21.33
19.56
NH^{t}Bu
NHAc
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

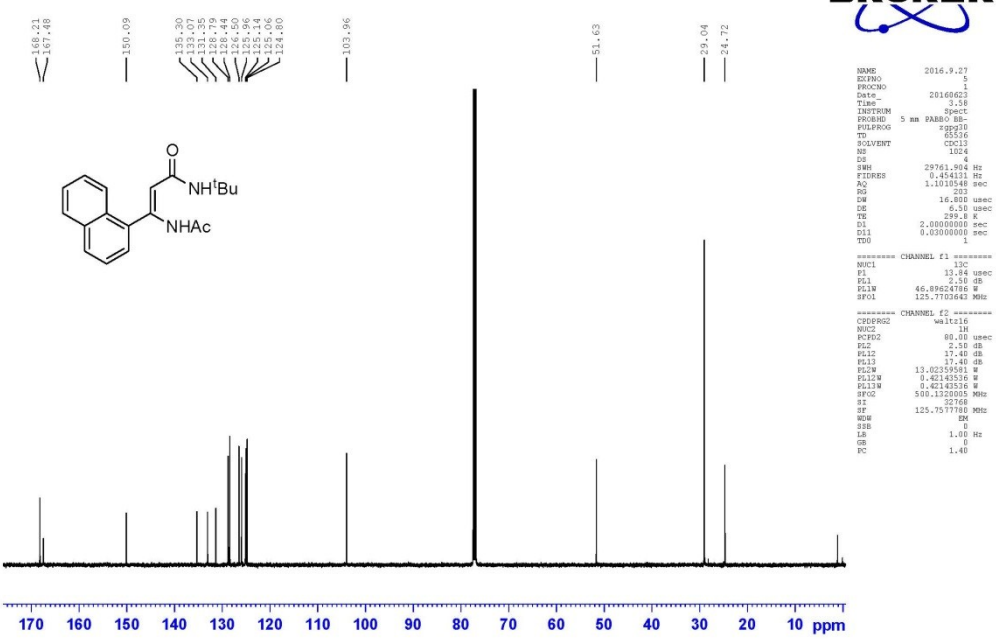
3p


11.459
7.260
7.091
7.071
7.067
7.050
5.335
4.947
2.248
2.243
2.135
1.392
NH^{t}Bu
NHAc
11
10
9
8
7
6
5
4
3
2
1
ppm
0.89
2.98
0.97
1.00
6.00
2.99
9.00

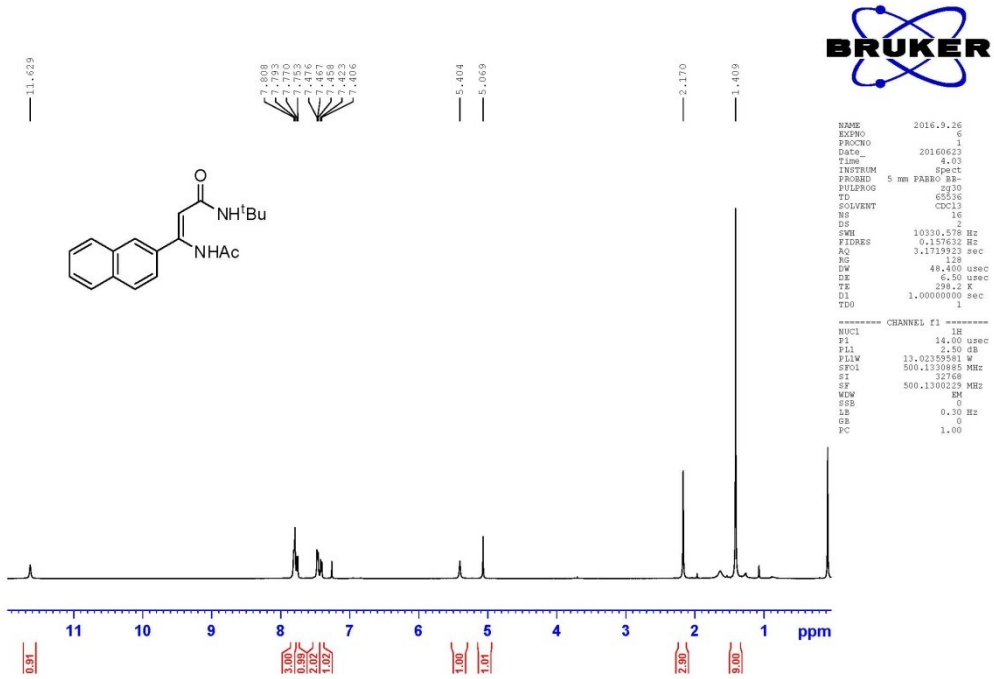

168.77
167.98
151.39
137.76
136.19
134.33
129.35
128.10
124.57
104.09
51.59
29.07
25.01
19.93
19.75
NH^{t}Bu
NHAc
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

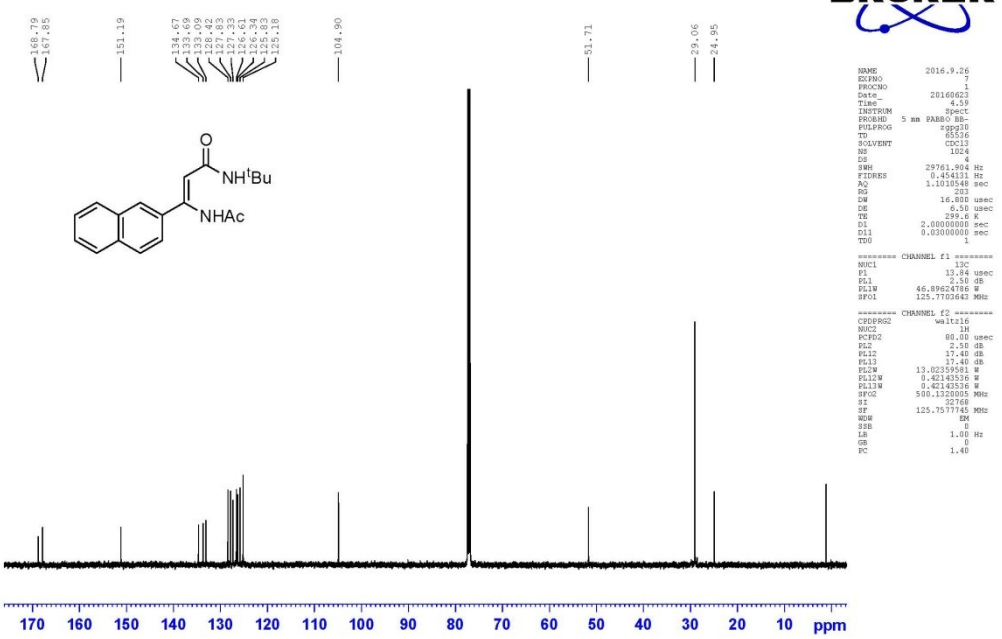
3q


12.094
7.955
7.949
7.942
7.936
7.930
7.923
7.838
7.831
7.824
7.813
7.805
7.797
7.458
7.451
7.444
7.438
7.432
7.426
7.415
7.401
7.384
7.298
7.277
7.264
7.263
5.359
4.839
2.040
1.404
NH^{t}Bu
NHAc
12 11 10 9 8 7 6 5 4 3 2 1 ppm
0.93
0.98
1.87
1.89
0.98
0.97
0.84
0.89
2.88
9.00

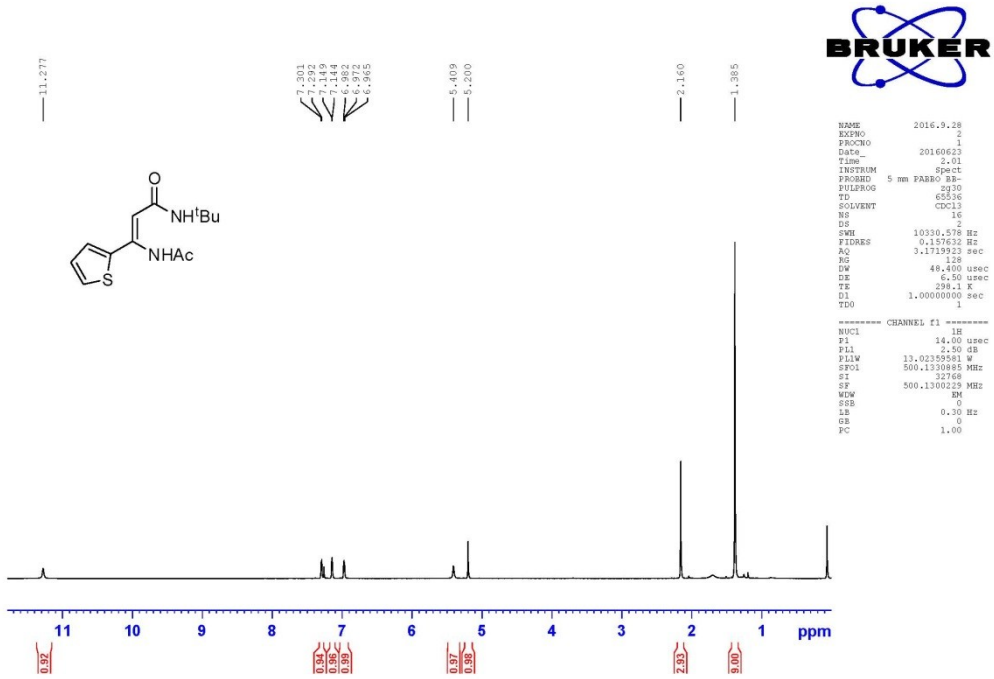

168.21
167.48
150.09
135.30
133.07
131.35
128.79
128.44
126.50
125.96
125.14
125.06
124.80
103.96
51.63
29.04
24.72
NH^{t}Bu
NHAc
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

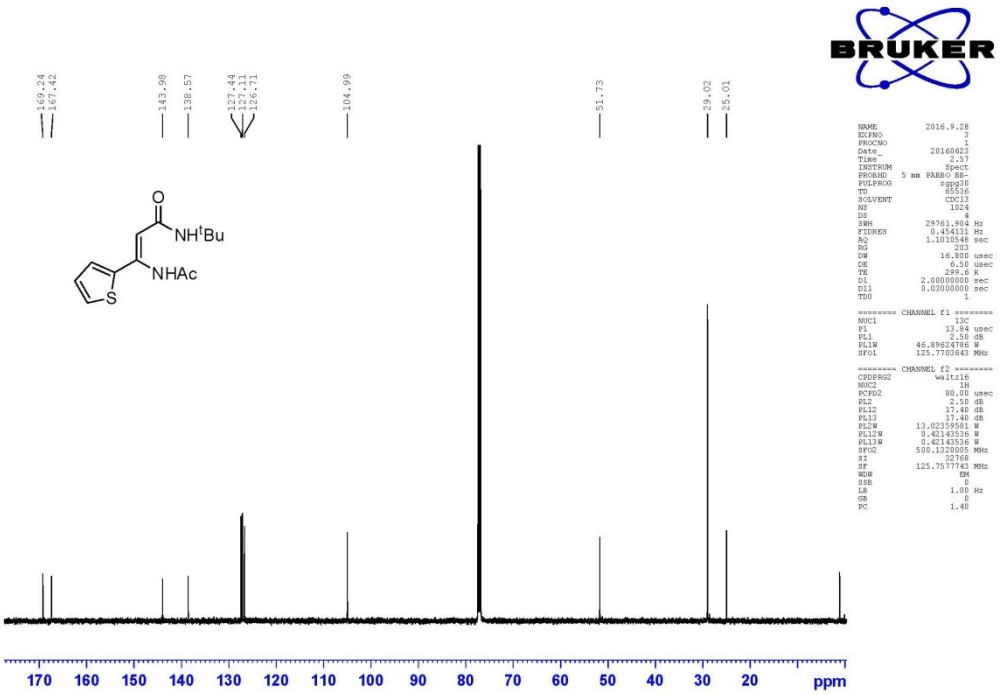
3r


11.629
7.808
7.793
7.770
7.763
7.476
7.467
7.458
7.433
7.406
5.404
5.069
2.170
1.409
NH^{t}Bu
NHAc
11
10
9
8
7
6
5
4
3
2
1
ppm
0.91
3.00
0.98
2.02
1.02
1.00
1.01
2.90
9.00

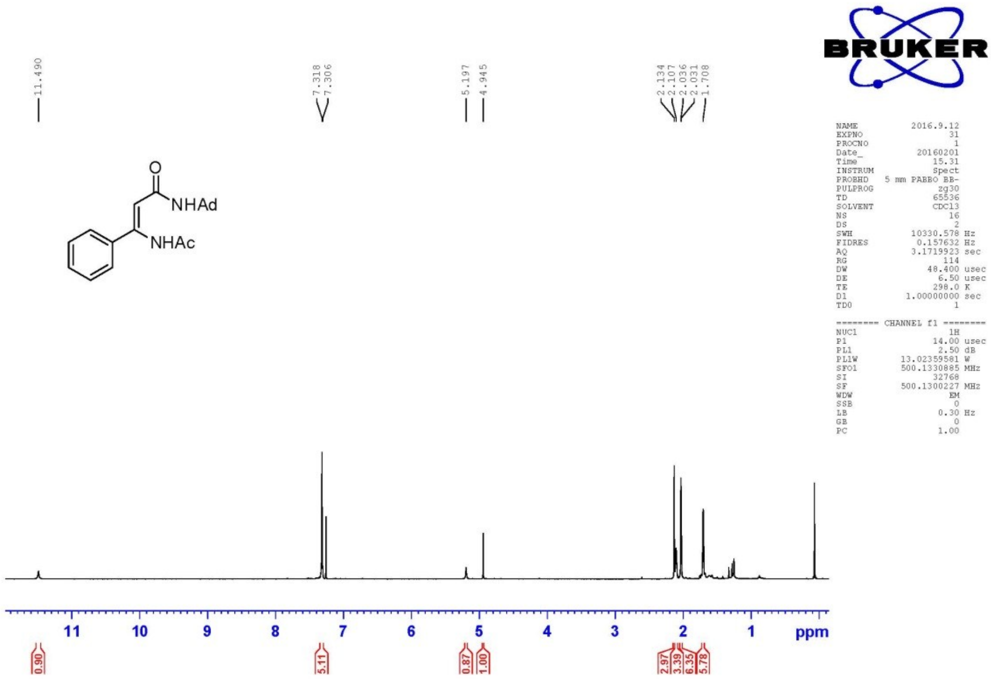

168.79
167.85
151.19
134.67
133.69
133.06
128.42
127.83
127.33
126.61
126.04
125.83
125.18
104.90
51.71
29.06
24.95
NH^{t}Bu
NHAc
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

3s

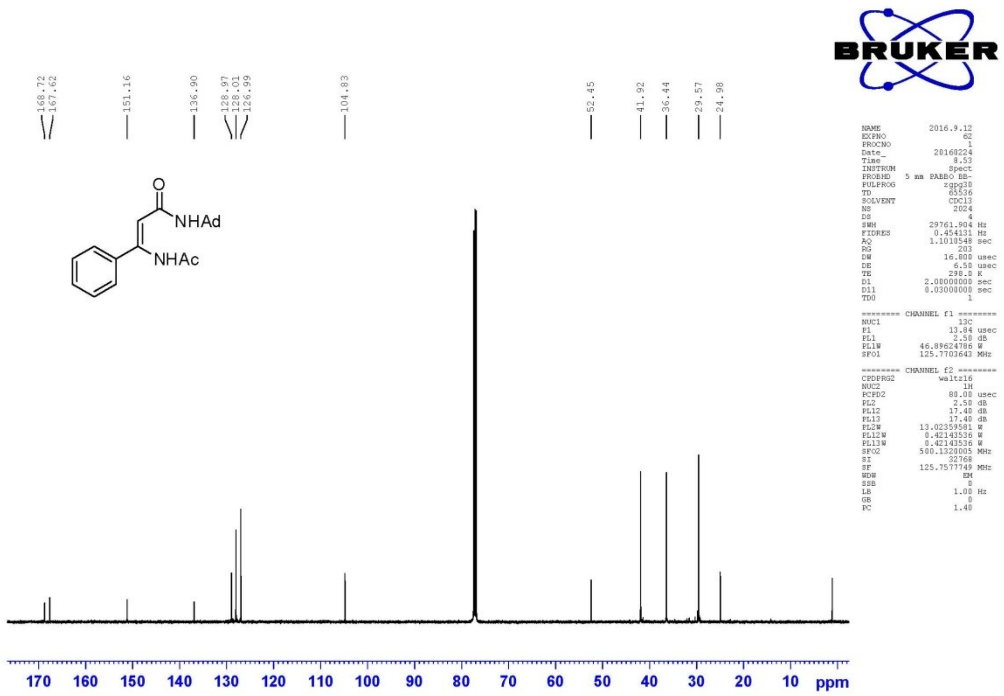

11.277
7.301
7.292
7.149
7.144
6.982
6.972
6.965
5.409
5.200
2.160
1.385
NH^{t}Bu
NHAc
S
11 10 9 8 7 6 5 4 3 2 1 ppm
0.92
0.94
0.96
0.89
0.97
0.98
2.83
9.00


169.24
167.42
143.98
138.57
127.44
127.11
126.71
104.99
51.73
29.02
25.01
NH^{t}Bu
NHAc
S
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

3t

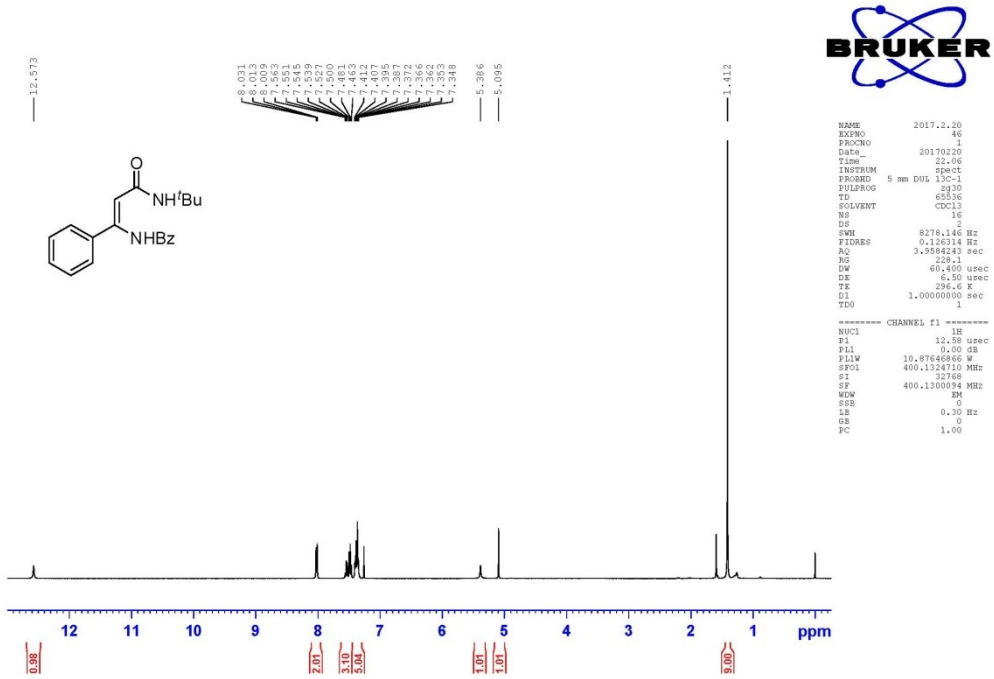


11.490
7.318
7.306
5.197
4.945
2.134
2.107
2.036
2.031
1.708
NHAd
NHAc
BRUKER
ppm
0.90
5.11
0.87
1.00
2.97
3.39
6.35
5.78

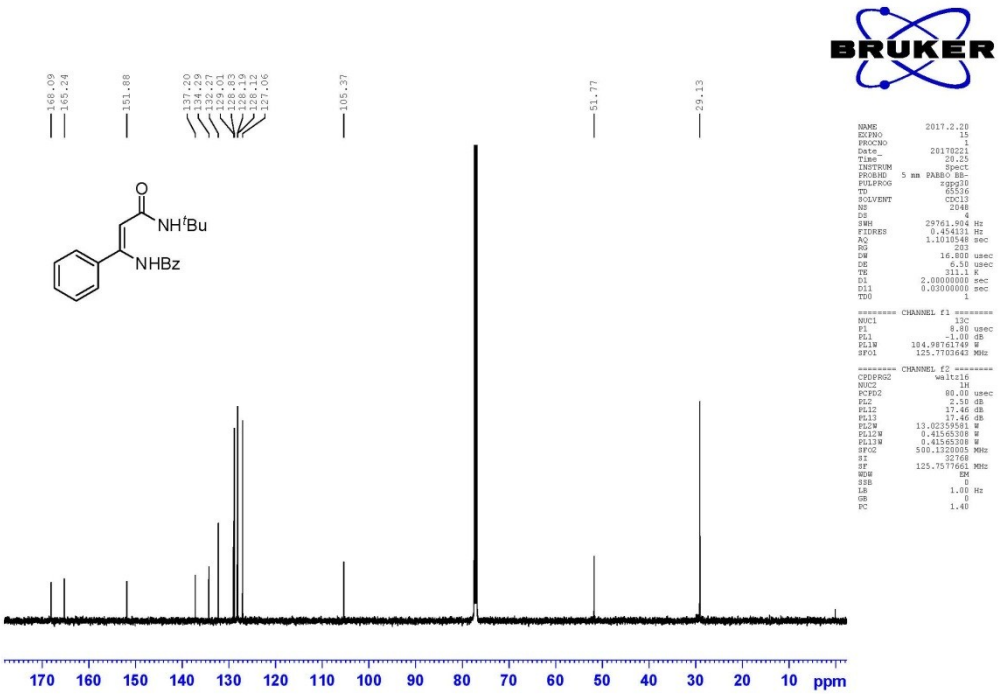


168.72
167.62
151.16
136.90
128.97
128.01
126.99
104.83
52.45
41.92
36.44
29.57
24.98
NHAd
NHAc
BRUKER
ppm

3u

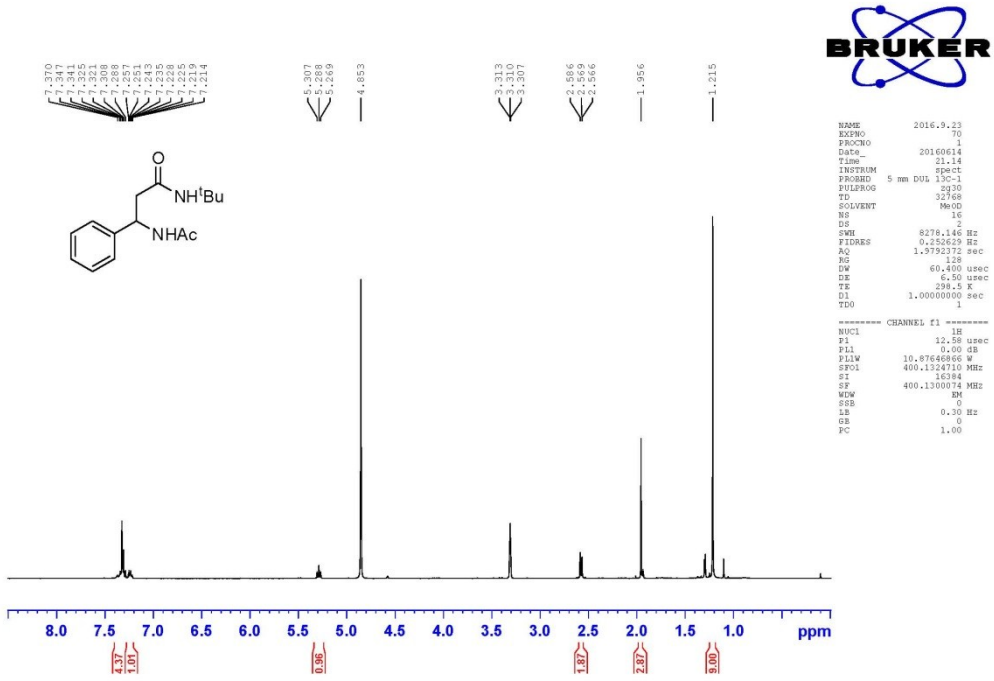

12.573
8.031
8.013
8.009
7.553
7.551
7.545
7.539
7.527
7.520
7.401
7.463
7.412
7.407
7.395
7.387
7.372
7.366
7.362
7.353
7.348
5.386
5.095
1.412
NH^{t}Bu
NHBz
12
11
10
9
8
7
6
5
4
3
2
1
ppm
0.98
2.05
3.10
5.04
1.01
1.05
9.00

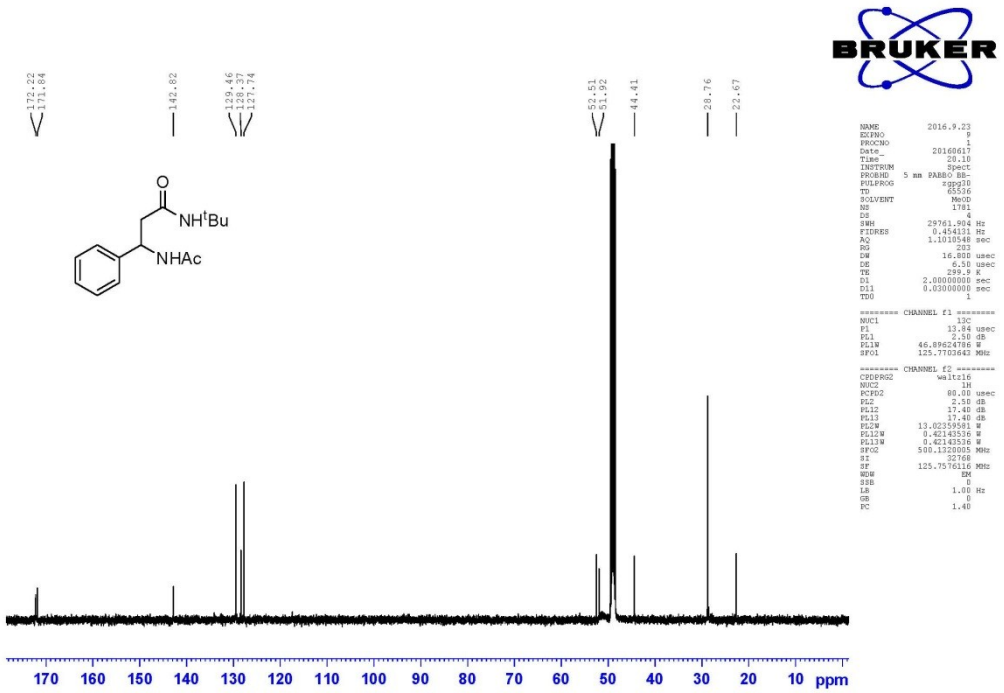
NAME 2017.2.20
EXPNO 46
PROCNO 1
Date_ 20170220
Time 22.06
INSTRUM spect
PROBHD 5 mm DUL 13C-1
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 228.1
DW 60.400 usec
DE 6.50 usec
TE 296.6 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 12.58 usec
PL1 0.00 dB
PL1W 10.87646866 W
SFO1 400.1324710 MHz
SI 32768
SF 400.1300094 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00


168.09
165.24
151.88
137.20
134.29
130.27
129.01
128.83
128.19
127.22
127.06
105.37
51.77
29.13
NH^{t}Bu
NHBz
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

NAME 2017.2.20
EXPNO 15
PROCNO 1
Date_ 20170221
Time 20.25
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 2048
DS 4
SWH 29761.904 Hz
FIDRES 0.454131 Hz
AQ 1.1010548 sec
RG 203
DW 16.800 usec
DE 6.50 usec
TE 311.1 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.80 usec
PL1 -1.00 dB
PL1W 104.98761749 W
SFO1 125.7703643 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 2.50 dB
PL12 17.46 dB
PL13 17.46 dB
PL2W 13.02359581 W
PL12W 0.41565308 W
PL13W 0.41565308 W
SFO2 500.1320005 MHz
SI 32768
SF 125.7577661 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

4


7.370
7.347
7.341
7.325
7.301
7.288
7.257
7.251
7.233
7.230
7.228
7.225
7.219
7.214
5.307
5.288
5.269
4.853
3.313
3.310
3.307
2.586
2.569
2.566
1.956
1.215
NH^{t}Bu
NHAc
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
4.37
1.01
0.96
1.87
2.87
9.00
BRUKER
NAME 2016.9.23
EXPNO 70
PROCNO 1
Date_ 20160614
Time 21.14
INSTRUM spect
PROBHD 5 mm DUL 13C-1
PULPROG zg30
TD 32768
SOLVENT MeOD
NS 16
DS 2
SWH 8278.146 Hz
FIDRES 0.252629 Hz
AQ 1.9792372 sec
RG 128
DW 60.400 usec
DE 6.50 usec
TE 298.5 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 12.58 usec
PL1 0.00 dB
PL1W 10.87646866 W
SFO1 400.1324710 MHz
SI 16384
SF 400.1300074 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00


172.22
171.84
142.82
129.46
129.37
128.07
127.74
53.51
51.92
44.41
28.76
22.67
NH^{t}Bu
NHAc
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm
BRUKER
NAME 2016.9.23
EXPNO 9
PROCNO 1
Date_ 20160617
Time 20.10
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT MeOD
NS 1701
DS 4
SWH 29761.904 Hz
FIDRES 0.454131 Hz
AQ 1.1010548 sec
RG 203
DW 16.800 usec
DE 6.50 usec
TE 299.8 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 13.84 usec
PL1 2.50 dB
PL1W 46.89624786 W
SFO1 125.7703643 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 2.50 dB
PL12 17.40 dB
PL13 17.40 dB
PL2W 13.02359581 W
PL12W 0.42143536 W
PL13W 0.42143536 W
SFO2 500.1320005 MHz
SI 32768
SF 125.7576116 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

NOESY spectra of 3a