Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Photoredox / rhodium catalysis in C-H activation for the synthesis of nitrogen containing heterocycles

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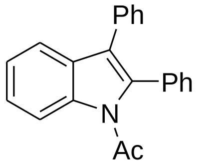
1. General methods. All commercially available chemicals were used as provided by the suppliers without further treatment. All solvents were dried and distilled under argon prior to use. Solvents for chromatography were technical grade and distilled prior to use. Analytical thin-layer chromatography (TLC) was performed on Macherey-Nagel ALUGRAM Xtra SIL G/UV 254 aluminum plates with F-254 indicator, visualized by UV irradiation. Macherey-Nagel silica gel 60 (particle size 0.063 - 0.2 mm) was used for column chromatography. An 11 W fluorescent bulb, warm white, was used for irradiation with light. ^{1}H-NMR and ^{13}C-NMR were recorded on VNMRS-400 or VNMRS-600 in $CDCl_3$. Chemical shifts (δ) are reported in ppm and multiplicities are indicated as: s (singlet), d (doublet), dd (doublet of doublet), ddd (doublet of doublet of doublet), t (triplet), dt (doublet of triplet), td (triplet of doublet), m (multiplet); coupling constants (J) are in Hertz (Hz). HRMS were measured on Finnigan MAT 95 or LTQ Orbitrap XL spectrometer. Acetanilides were synthesized according to literature-known procedures.[1]

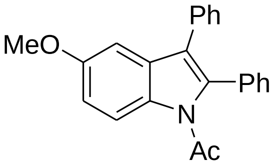
2. General procedure for Rh-catalyzed indole synthesis from acetanilides. To an oven-dried screw-capped tube were added acetanilide (0.2 mmol), alkyne (0.4 mmol), $[RhCp^*Cl_2]_2$ (2 mol %), $AgSbF_6$ (8 mol %), photocatalyst (1 mol %) and PhCl (1.0 mL). The mixture was irradiated by an 11W lamp (distance ca. 3 cm) after placing it on an aluminium block heated at 120 °C for 12 h. The reaction was cooled to room temperature, filtered through a plug of celite, and the celite was washed with CH_2Cl_2 (15 mL). The filtrate was concentrated and then evaporated to dryness under high vacuum. The desired product was isolated by column chromatography.

1-(2,3-Diphenyl-1*H*-indol-1-yl)ethan-1-one (3a).[1]



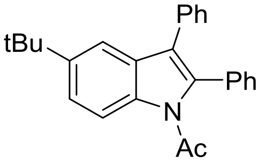
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.48 (d, *J* = 8.4 Hz, 1H), 7.60 – 7.56 (m, 1H), 7.38 – 7.35 (m, 5H), 7.33 – 7.23 (m, 7H), 7.34 – 7.29 (m, 1H), 2.02 (s, 3H).; ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.5, 136.7, 134.9, 133.0, 132.4, 130.7, 130.0, 129.2, 128.6, 128.6, 128.2, 126.9, 125.5, 123.7, 123.35, 119.5, 116.2, 27.9.

1-(5-Methoxy-2,3-diphenyl-1*H*-indol-1-yl)ethan-1-one (3b).[2]



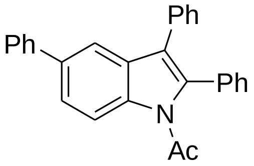
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (d, *J* = 8.7 Hz, 1H), 7.48 – 7.13 (m, 10H), 7.11 – 6.82 (m, 2H), 3.81 (s, 3H), 1.97 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.1, 156.6, 135.6, 133.0, 132.9, 131.5, 130.7, 130.1, 129.9, 128.6, 128.5, 128.2, 126.9, 123.3, 117.3, 113.8, 102.1, 55.7, 27.7.

1-(5-(*tert*-Butyl)-2,3-diphenyl-1*H*-indol-1-yl)ethan-1-one (3c).[3]



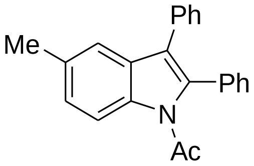
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.41 (d, *J* = 8.7 Hz, 1H), 7.56 (d, *J* = 1.9 Hz, 1H), 7.51 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.38 – 7.30 (m, 7H), 7.29 – 7.23 (m, 3H), 2.00 (s, 3H), 1.38 (s, 9H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.3, 147.0, 135.2, 134.8, 133.2, 133.1, 130.8, 130.0, 129.0, 128.55, 128.54, 128.2, 126.8, 123.6, 123.4, 115.8, 115.4, 34.7, 31.7, 27.8.

1-(2,3,5-Triphenyl-1*H*-indol-1-yl)ethan-1-one (3d).[3]



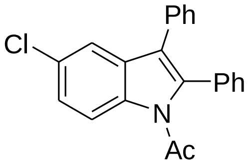
^{1}H NMR (600 MHz, CDCl$_3$) δ 8.55 (d, *J* = 8.6 Hz, 1H), 7.76 (d, *J* = 1.8 Hz, 1H), 7.68 (dd, *J* = 8.6, 1.9 Hz, 1H), 7.65 – 7.62 (m, 2H), 7.44 (t, *J* = 7.7 Hz, 2H), 7.40 – 7.37 (m, 5H), 7.36 – 7.30 (m, 3H), 7.29 – 7.25 (m, 3H), 2.04 (s, 1H); ^{13}C NMR (151 MHz, CDCl$_3$) δ 171.4, 141.5, 137.2, 136.2, 135.6, 132.9, 132.8, 130.7, 130.0, 129.7, 128.7, 128.6, 128.3, 127.4, 127.0, 126.9, 124.9, 123.5, 117.9, 116.5, 27.9.

1-(5-Methyl-2,3-diphenyl-1*H*-indol-1-yl)ethan-1-one (3e).[2]



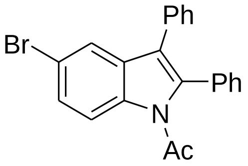
^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.33 (d, *J* = 8.5 Hz, 1H), 7.36 – 7.30 (m, 6H), 7.30 – 7.26 (m, 2H), 7.25 – 7.18 (m, 4H), 2.42 (s, 3H), 1.98 (s, 3H); ^{13}C NMR (151 MHz, CDCl$_3$) δ 171.3, 135.0, 135.0, 133.3, 133.1, 133.0, 130.7, 130.0, 129.4, 128.52, 128.50, 128.1, 126.8, 126.7, 123.2, 119.3, 115.9, 27.8, 21.3.

1-(5-Chloro-2,3-diphenyl-1*H*-indol-1-yl)ethan-1-one (3f).[2]



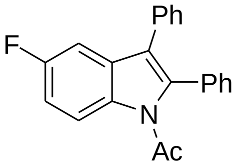
^{1}H NMR (400 MHz, CDCl$_3$) δ 8.38 (d, *J* = 8.9, 1H), 7.52 – 7.47 (m, 1H), 7.40 – 7.23 (m, 9H), 7.19 – 7.14 (m, 2H), 1.97 (s, 3H); ^{13}C NMR (101 MHz, CDCl$_3$) δ 171.3, 136.1, 135.0, 132.4, 132.3, 130.6, 130.5, 129.8, 129.3, 128.9, 128.6, 128.3, 127.1, 125.5, 122.6, 119.0, 117.4, 27.8.

1-(5-Bromo-2,3-diphenyl-1*H*-indol-1-yl)ethan-1-one (3g).[2]



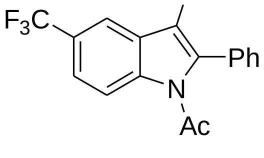
^{1}H NMR (600 MHz, CDCl$_3$) δ 8.34 (d, *J* = 8.8 Hz, 1H), 7.66 (d, *J* = 2.0 Hz, 1H), 7.49 (dd, *J* = 8.8, 2.1 Hz, 1H), 7.39 – 7.25 (m, 8H), 7.20 – 7.15 (m, 2H), 1.98 (s, 3H); ^{13}C NMR (151 MHz, CDCl$_3$) δ 171.4, 136.0, 135.4, 132.38, 132.32, 131.0, 130.7, 129.9, 128.9, 128.7, 128.3, 128.2, 127.2, 122.5, 122.1, 117.7, 117.0, 27.8.

1-(5-Fluoro-2,3-diphenyl-1*H*-indol-1-yl)ethan-1-one (3h).[3]



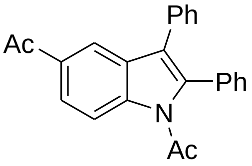
^{1}H NMR (400 MHz, CDCl$_3$) δ 8.42 (dd, *J* = 9.1, 4.7 Hz, 1H), 7.40 – 7.23 (m, 8H), 7.21 – 7.15 (m, 3H), 7.10 (td, *J* = 9.1, 2.7 Hz, 1H), 1.97 (s, 3H); ^{13}C NMR (101 MHz, CDCl$_3$) δ 171.2, 159.8, 136.4, 133.0, 132.6, 132.5, 130.7, 130.3, 129.8, 128.8, 128.6, 128.3, 127.1, 123.0, 117.5, 113.0, 105.0, 27.7 (decoupled).

1-(2,3-Diphenyl-5-(trifluoromethyl)-1*H*-indol-1-yl)ethan-1-one (3i).[3]



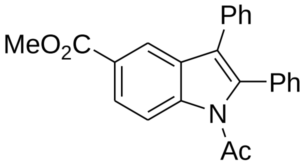
^{1}H NMR (400 MHz, CDCl$_3$) δ 8.53 (dt, *J* = 8.8, 0.8 Hz, 1H), 7.80 (dd, *J* = 1.8, 0.9 Hz, 1H), 7.63 (ddd, *J* = 8.9, 1.7, 0.7 Hz, 1H), 7.39 – 7.26 (m, 8H), 7.22 – 7.17 (m, 2H), 2.00 (s, 3H); ^{13}C NMR (101 MHz, CDCl$_3$) δ 171.5, 138.1, 136.5, 132.2, 132.1, 130.6, 129.9, 129.0, 128.9, 128.7, 128.4, 127.3, 126.0, 123.1, 122.1, 116.9, 116.4, 27.8 (decoupled).

1-(5-Acetyl-2,3-diphenyl-1*H*-indol-1-yl)ethan-1-one (3j).



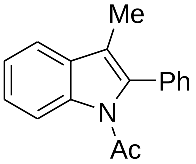
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.54 (d, *J* = 8.8 Hz, 1H), 8.23 (d, *J* = 1.7 Hz, 1H), 8.09 (dd, *J* = 8.7, 1.8 Hz, 1H), 7.47 – 7.32 (m, 8H), 7.30 – 7.24 (m, 0H), 2.70 (s, 2H), 2.07 (s, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 197.9, 171.6, 139.3, 136.3, 133.2, 132.3, 130.7, 130.0, 129.2, 129.0, 128.8, 128.5, 127.3, 125.8, 123.7, 120.6, 115.9, 27.9, 26.8.

1-Acetyl-2,3-diphenyl-1*H*-indol-5-yl acetate (3k).



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (dd, *J* = 8.8, 0.6 Hz, 1H), 8.24 (dd, *J* = 1.8, 0.7 Hz, 1H), 8.08 (dd, *J* = 8.8, 1.8 Hz, 1H), 7.38 – 7.26 (m, 8H), 7.22 – 7.18 (m, 2H), 3.90 (s, 3H), 2.00 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.5, 167.3, 139.2, 136.1, 132.3, 130.6, 130.0, 129.0, 128.8, 128.7, 128.3, 127.1, 126.7, 125.6, 123.4, 121.8, 115.7, 52.0, 27.9.

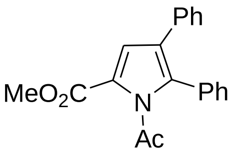
1-(3-Methyl-2-phenyl-1*H*-indol-1-yl)ethan-1-one (3l).[1]



^{1}H NMR (600 MHz, $CDCl_3$) δ 7.58 – 7.52 (m, 1H), 7.51 – 7.47 (m, 2H), 7.46 – 7.43 (m, 1H), 7.42 – 7.37 (m, 3H), 7.35 – 7.31 (m, 1H), 2.15 (s, 3H), 1.96 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.0, 136.7, 134.8, 133.5, 130.2, 130.2, 128.7, 128.4, 125.3, 123.4, 118.5, 118.1, 116.3, 27.6, 9.2.

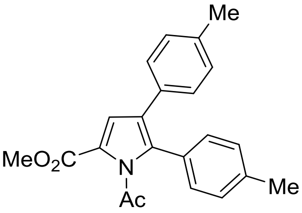
3. General procedure for Rh-catalyzed pyrrole synthesis of acetamidoacrylate. To an oven-dried screw-capped tube were added acetamidoacrylate (0.2 mmol), alkyne (0.4 mmol), $[RhCp^*(MeCN)_3][SbF_6]_2$ (5 mol %), $[Ir(dtbbpy)(tbuppy)_2]PF_6$ (1 mol %) and PhCl (1.0 mL). The mixture was irradiated by an 11W lamp (distance ca. 3 cm) after placing it on an aluminium block heated at 70 °C for 12 h. The reaction was cooled to room temperature, filtered through a plug of celite, and the celite was washed with CH_2Cl_2 (15 mL). The filtrate was concentrated and then evaporated to dryness under high vacuum. The desired product was isolated by column chromatography.

Methyl 1-acetyl-4,5-diphenyl-1*H*-pyrrole-2-carboxylate (5a).[1]



^{1}H NMR (600 MHz, $CDCl_3$) δ 7.41 – 7.34 (m, 3H), 7.32 – 7.28 (m, 2H), 7.23 – 7.11 (m, 6H), 3.89 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 173.9, 161.1, 134.5, 133.9, 130.6, 128.9, 128.6, 128.2, 128.0, 126.4, 124.8, 122.9, 118.4, 51.9, 28.9.

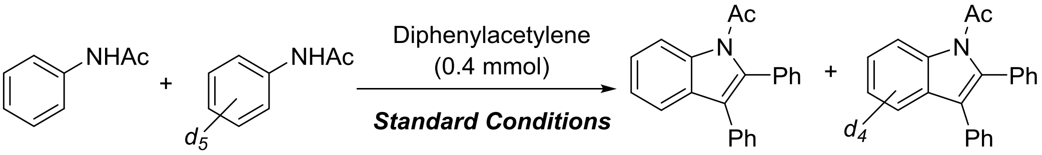
Methyl 1-acetyl-4,5-di-*p*-tolyl-1*H*-pyrrole-2-carboxylate (5b).[4]



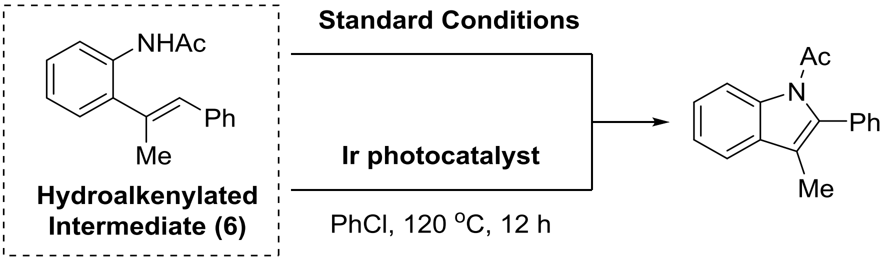
^{1}H NMR (600 MHz, CDCl$_3$) δ 7.22 – 7.15 (m, 5H), 7.06 – 7.00 (m, 4H), 3.88 (s, 3H), 2.38 (s, 3H), 2.31 (s, 3H), 2.29 (s, 3H); ^{13}C NMR (151 MHz, CDCl$_3$) δ 174.0, 161.1, 138.7, 136.0, 134.6, 131.1, 130.5, 129.3, 129.0, 127.8, 127.7, 124.6, 122.7, 118.4, 51.8, 28.9, 21.4, 21.0.

4. Indole Synthesis with heterogeneous photocatalyst. To an oven-dried screw-capped tube were added acetanilide (0.2 mmol), alkyne (0.4 mmol), [RhCp*Cl$_2$]$_2$ (2 mol %), AgSbF$_6$ (8 mol %), heterogeneous photocatalyst (1 equiv.) and PhCl (1.0 mL). The mixture was irradiated by an 11W lamp (distance ca. 3 cm) after placing it on an aluminium block heated at 120 °C for 12 h. The reaction was cooled to room temperature, filtered through a plug of celite, and the celite was washed with CH$_2$Cl$_2$ (15 mL). The filtrate was concentrated and then evaporated to dryness under high vacuum. The desired product was isolated by column chromatography.

5. KIE experiment in the presence of light irradiation. To an oven-dried screw-capped tube were added acetanilide (0.1 mmol), acetanilide-*d*$_5$ (0.1 mmol), diphenyacetylene (0.4 mmol), [RhCp*Cl$_2$]$_2$ (2 mol %), AgSbF$_6$ (8 mol %), [Ru(dtbbpy)$_2$(bpy)](PF$_6$)$_2$ (1 mol %) and PhCl (1.0 mL). The mixture was irradiated by an 11W lamp (distance ca. 3 cm) after placing it on an aluminium block. The reaction mixture was stirred at 120 °C for 90 min. After cooling to room temperature, the reaction mixture was filtered through a plug of celite, washed with CH$_2$Cl$_2$ (15 mL) and then concentrated in *vacuo*. Conversion of each reactant was determined by ^{1}H NMR integration.



6. Intermediate test under optimized and photoredox conditions



1) Standard conditions: To an oven-dried screw-capped tube were added **6** (0.2 mmol), $[RhCp^*Cl_2]_2$ (2 mol %), $AgSbF_6$ (8 mol %), photocatalyst (1 mol %) and PhCl (1.0 mL). The mixture was irradiated by an 11W lamp (distance ca. 3 cm) after placing it on an aluminium block heated at 120 °C for 12 h. The reaction was cooled to room temperature, filtered through a plug of celite, and the celite was washed with CH_2Cl_2 (15 mL). The filtrate was concentrated and then evaporated to dryness under high vacuum. Conversion of each reactant was determined by ^1H NMR integration.

2) Photocatalytic conditions: To an oven-dried screw-capped tube were added **6** (0.2 mmol), photocatalyst (1 mol %) and PhCl (1.0 mL). The mixture was irradiated by an 11W lamp (distance ca. 3 cm) after placing it on an aluminium block heated at 120 °C for 12 h. The reaction was cooled to room temperature, filtered through a plug of celite, and the celite was washed with CH_2Cl_2 (15 mL). The filtrate was concentrated and then evaporated to dryness under high vacuum. Conversion of each reactant was determined by ^1H NMR integration.

7. References

1. D. R. Stuart, P. Alsabeh, M. Kuhn and K. Fagnou, *J. Am. Chem. Soc.*, 2010, **132**, 18326.

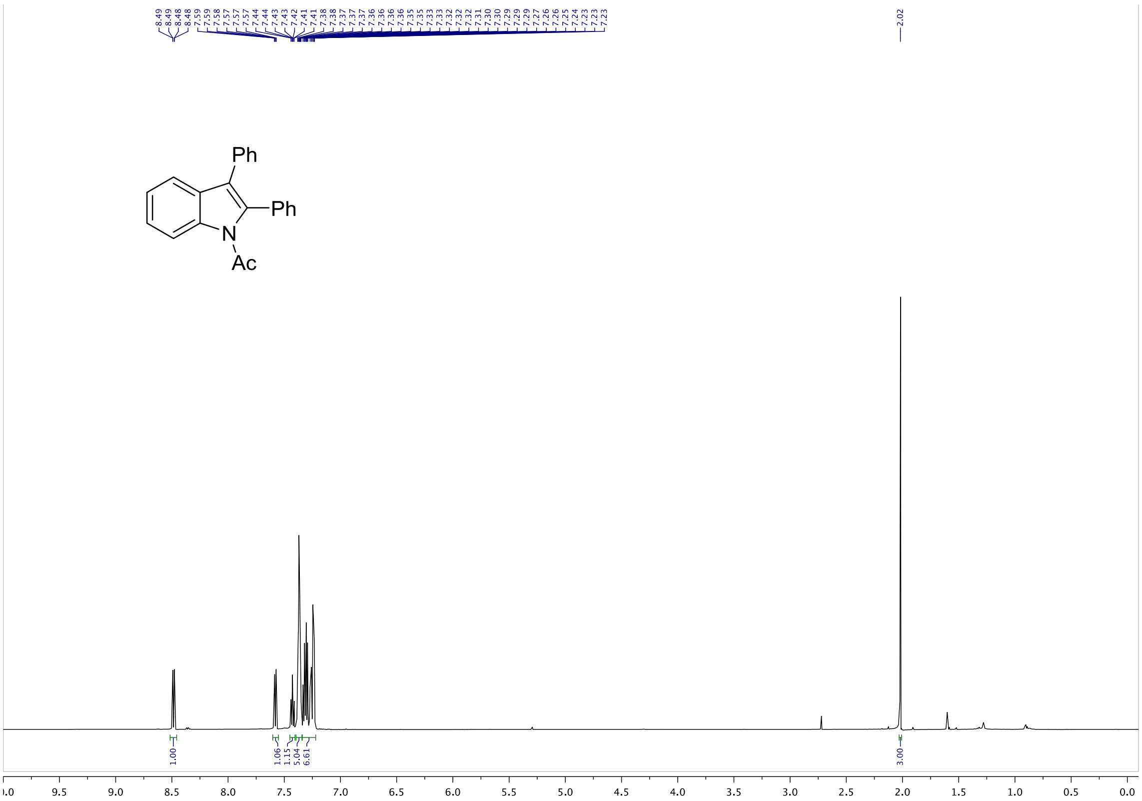
2. Y. Hoshino, Y. Shibata and K. Tanaka, *Adv. Synth. Catal.*, 2014, **356**, 1577.

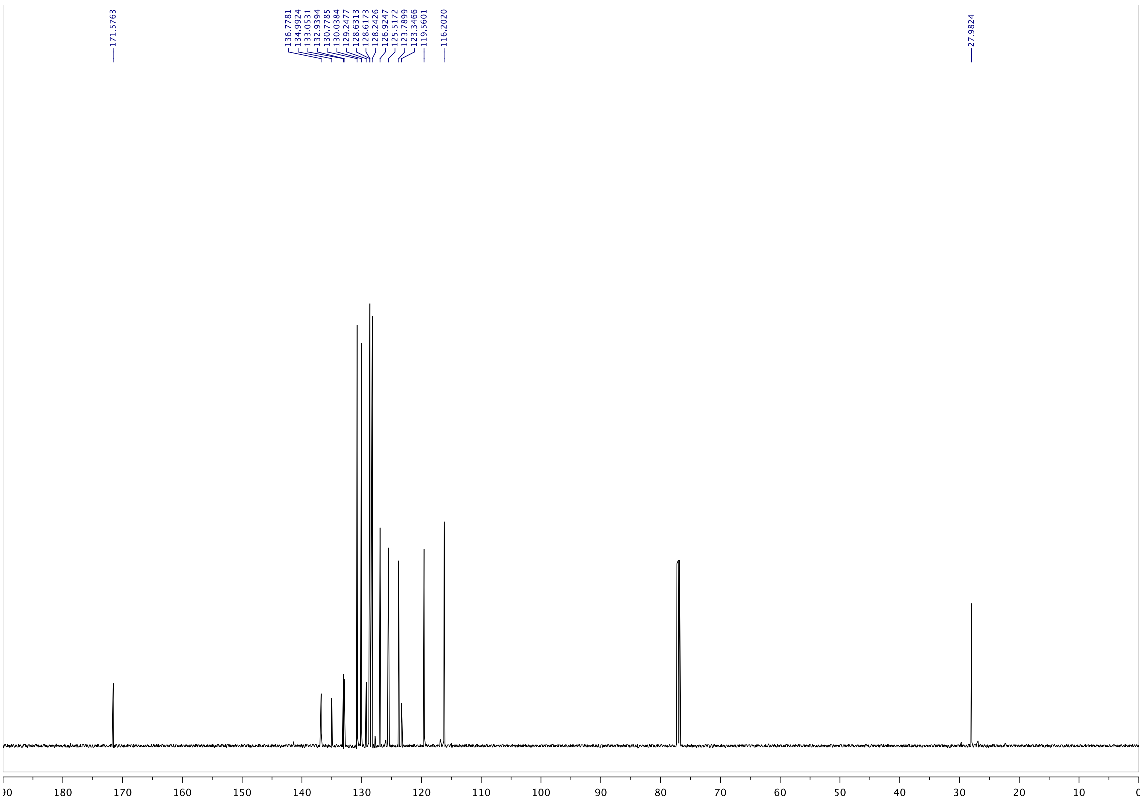
3. W.-Z. Weng, J. Xie and B. Zhang, *Org. Biomol. Chem.*, 2018, **16**, 3983.

4. B. Li, N. Wang, Y. Liang, S. Xu and B. Wang *Org. Lett.*, 2013, **15**, 136.

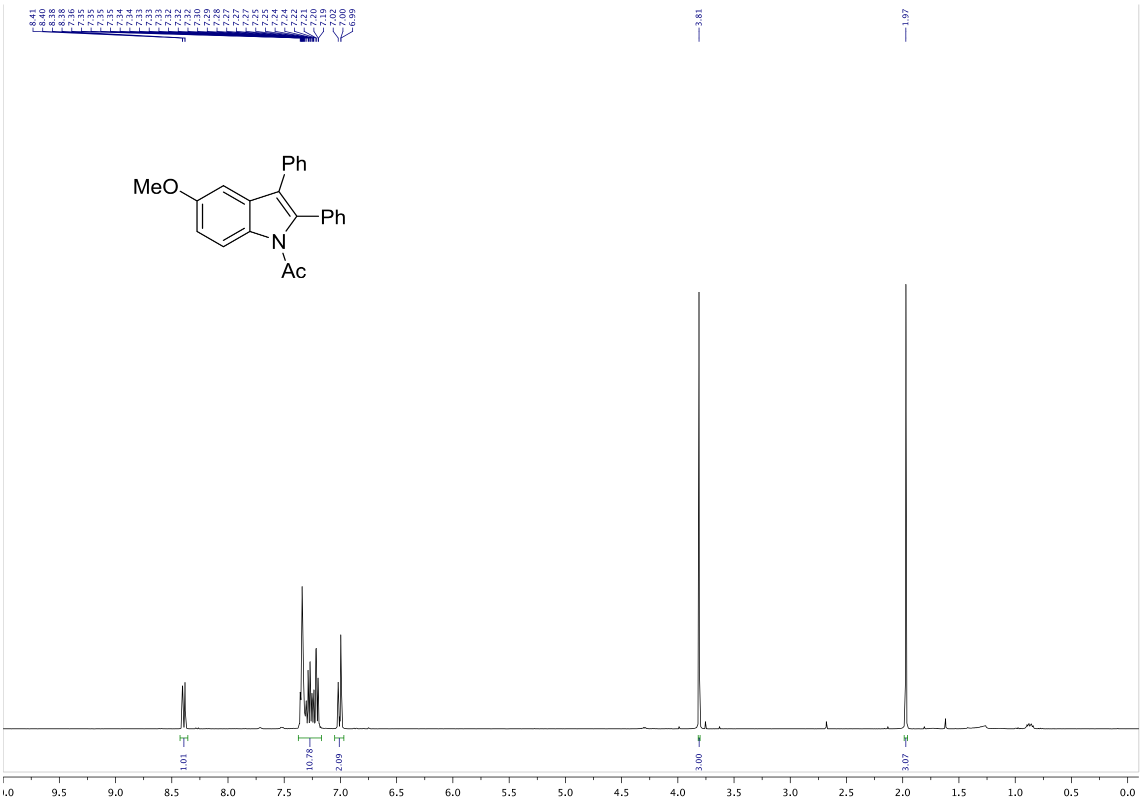
Copies of ^{1}H and ^{13}C NMR Spectra

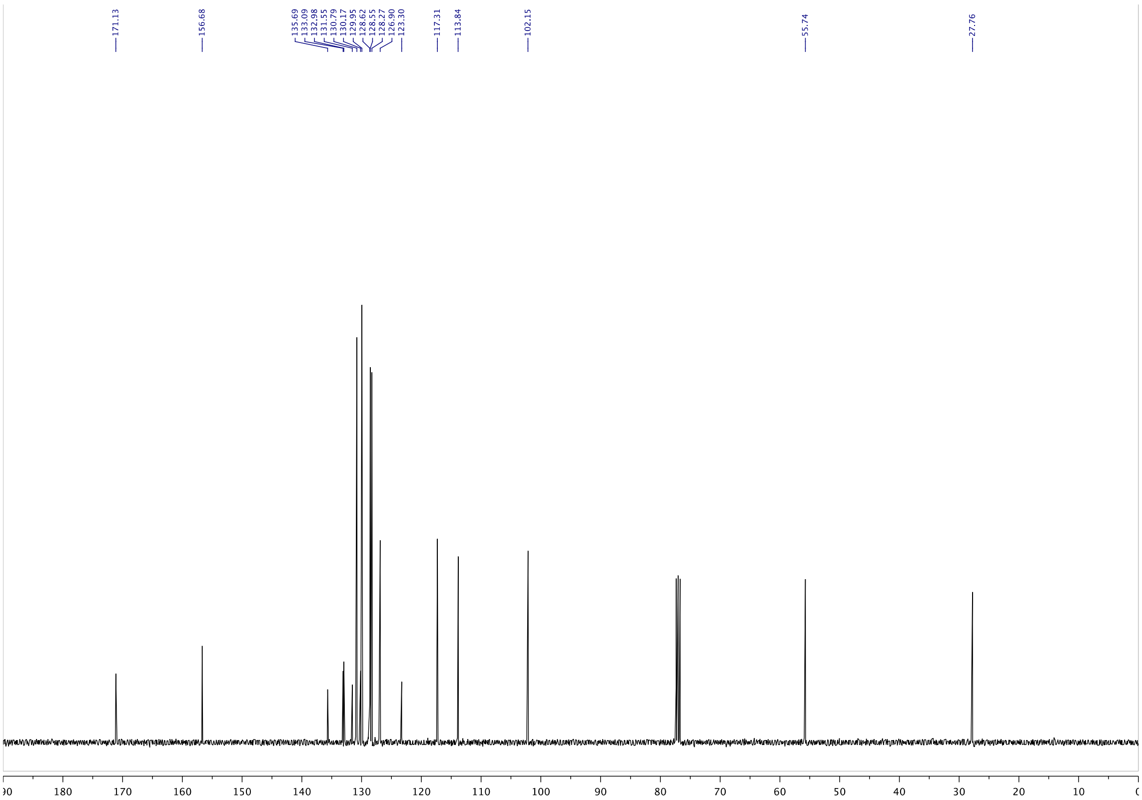
1-(2,3-Diphenyl-1*H*-indol-1-yl)ethan-1-one (3a)



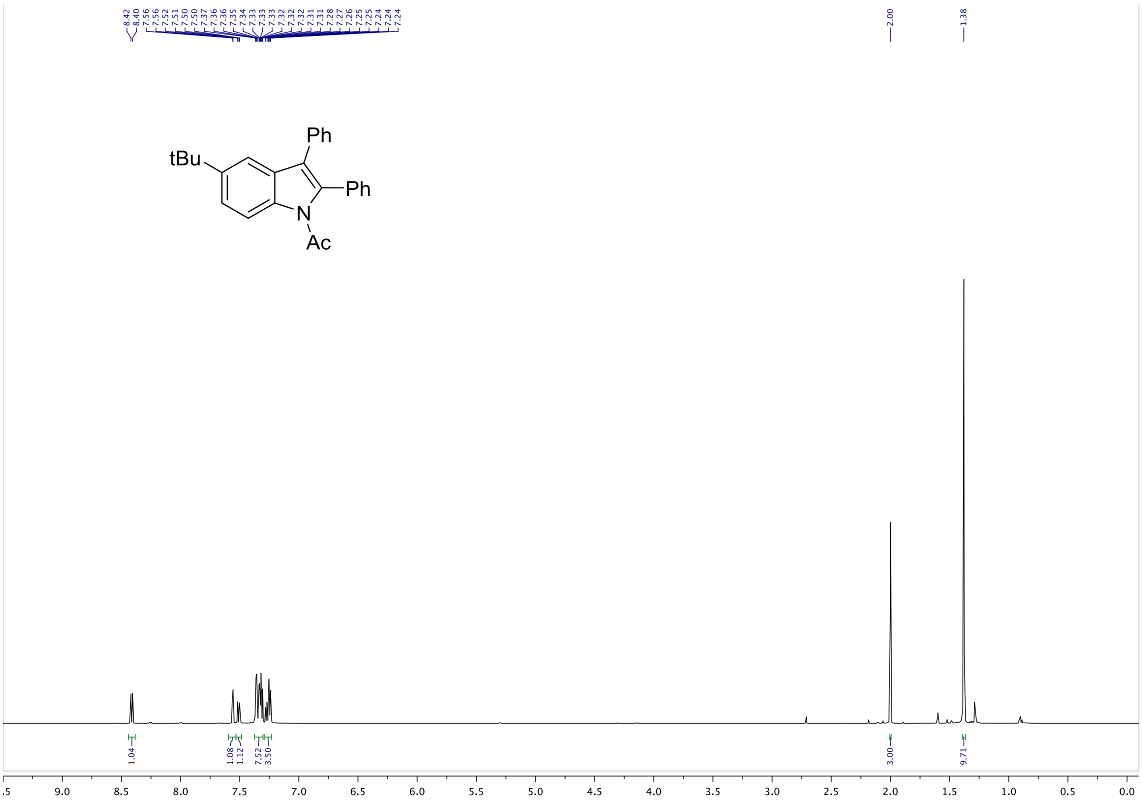


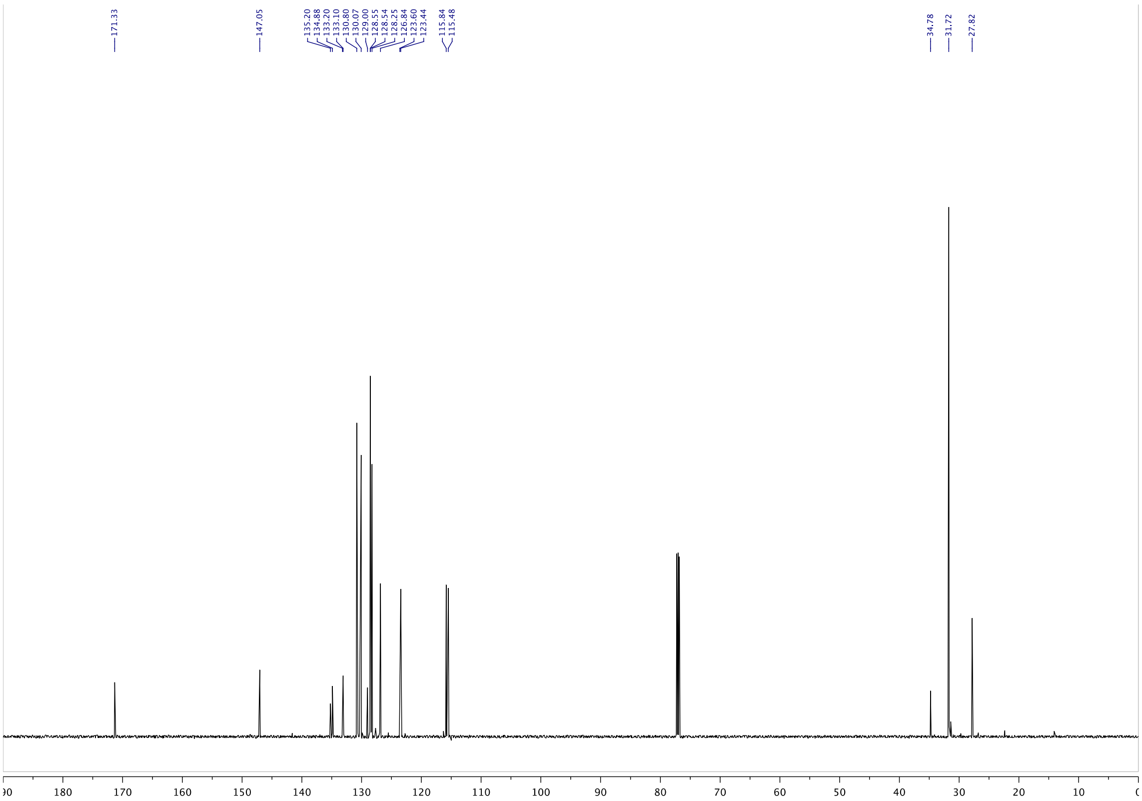
1-(5-Methoxy-2,3-diphenyl-1*H*-indol-1-yl)ethan-1-one (3b)



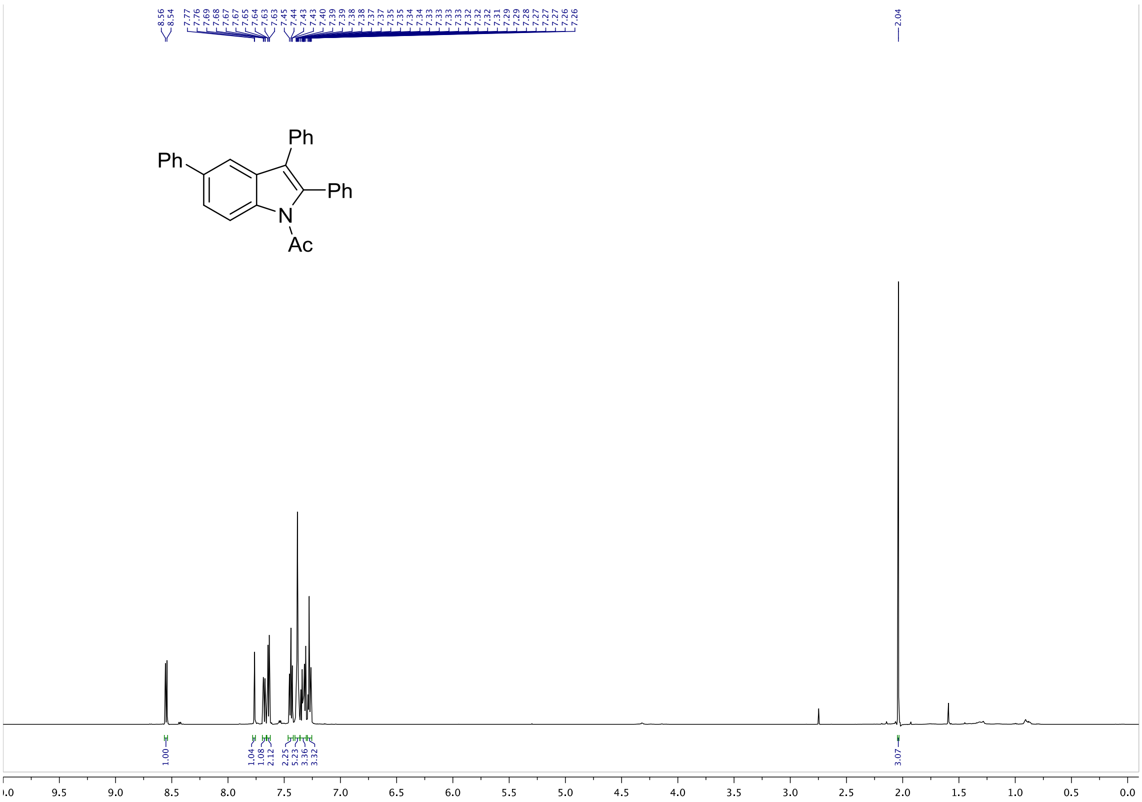


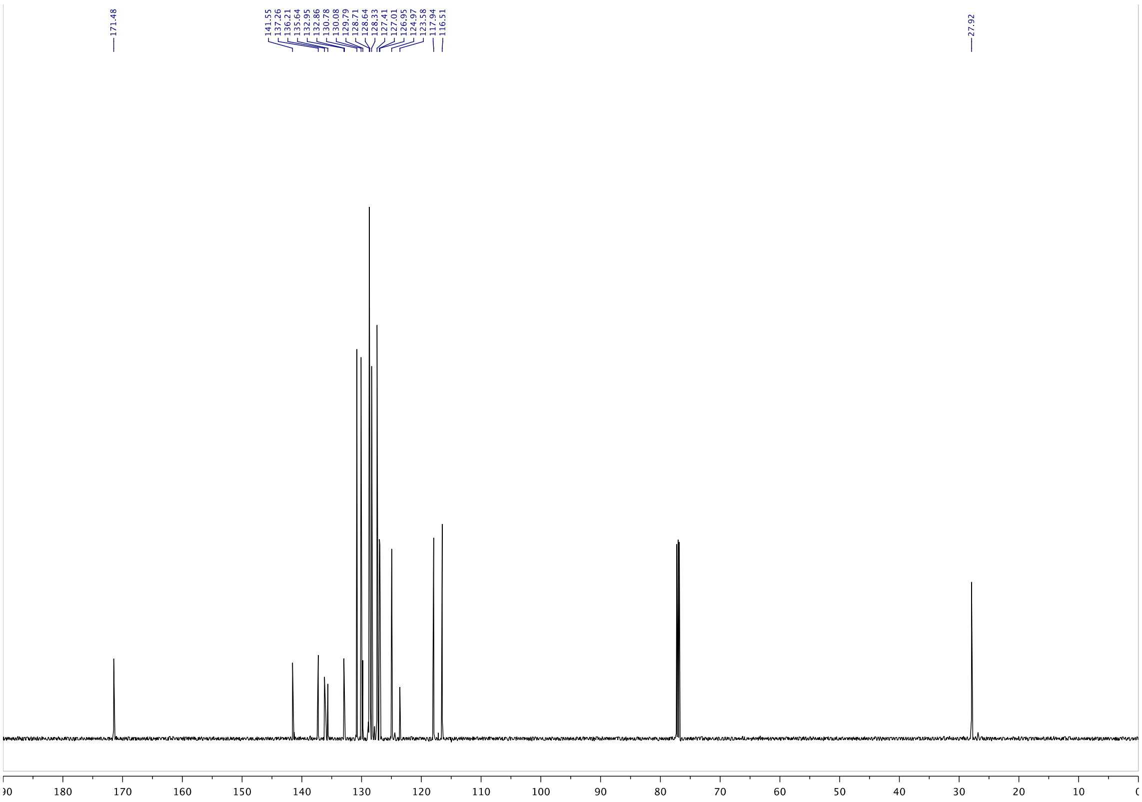
1-(5-(*tert*-Butyl)-2,3-diphenyl-1*H*-indol-1-yl)ethan-1-one (3c)



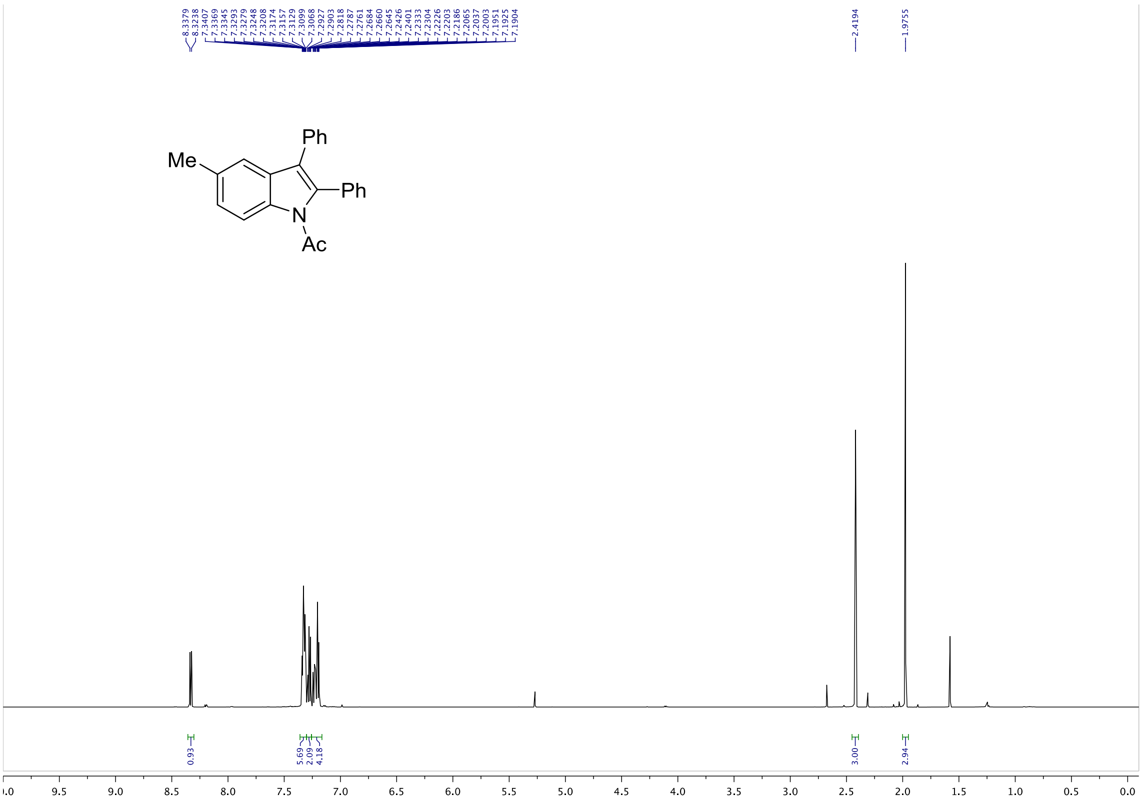


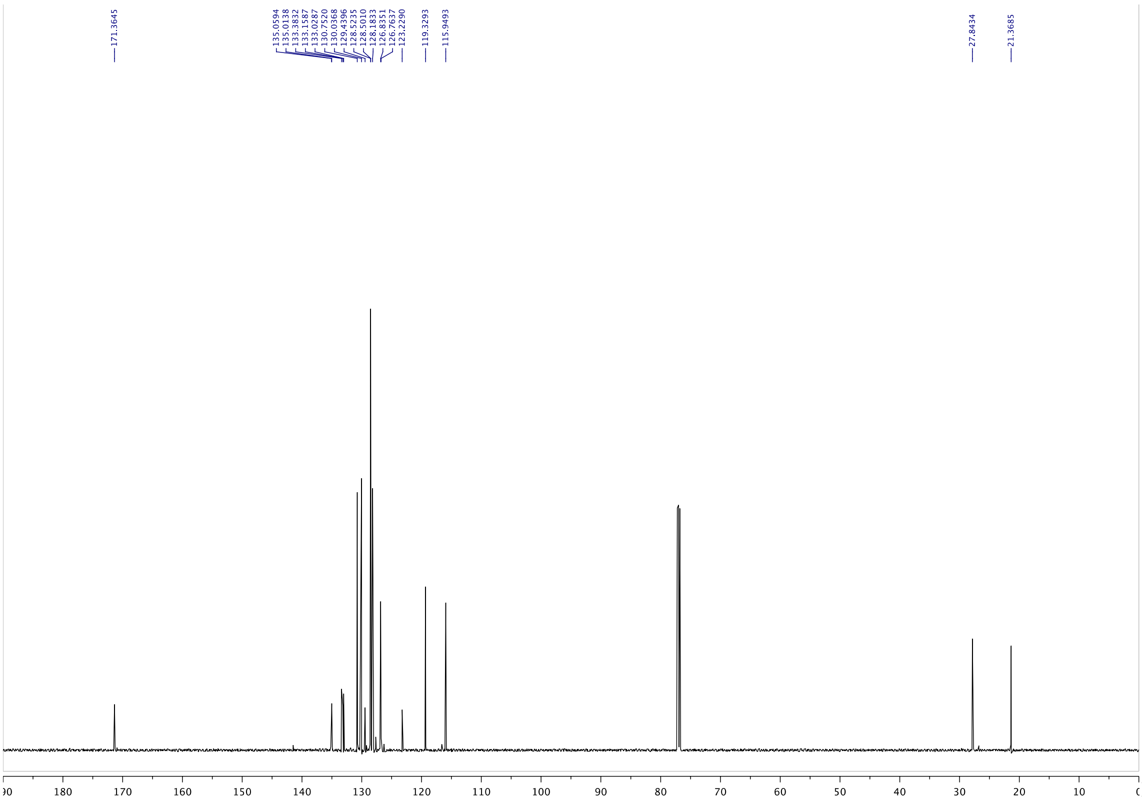
1-(2,3,5-Triphenyl-1*H*-indol-1-yl)ethan-1-one (3d)





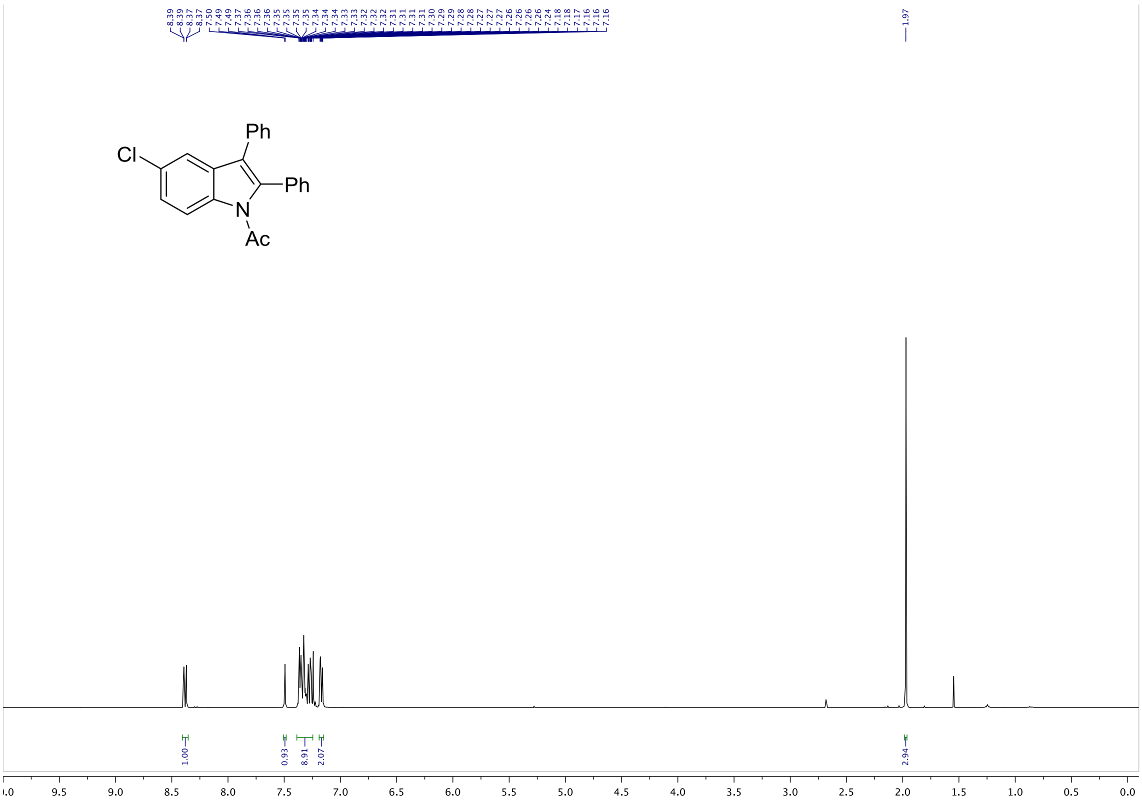
1-(5-Methyl-2,3-diphenyl-1*H*-indol-1-yl)ethan-1-one (3e)

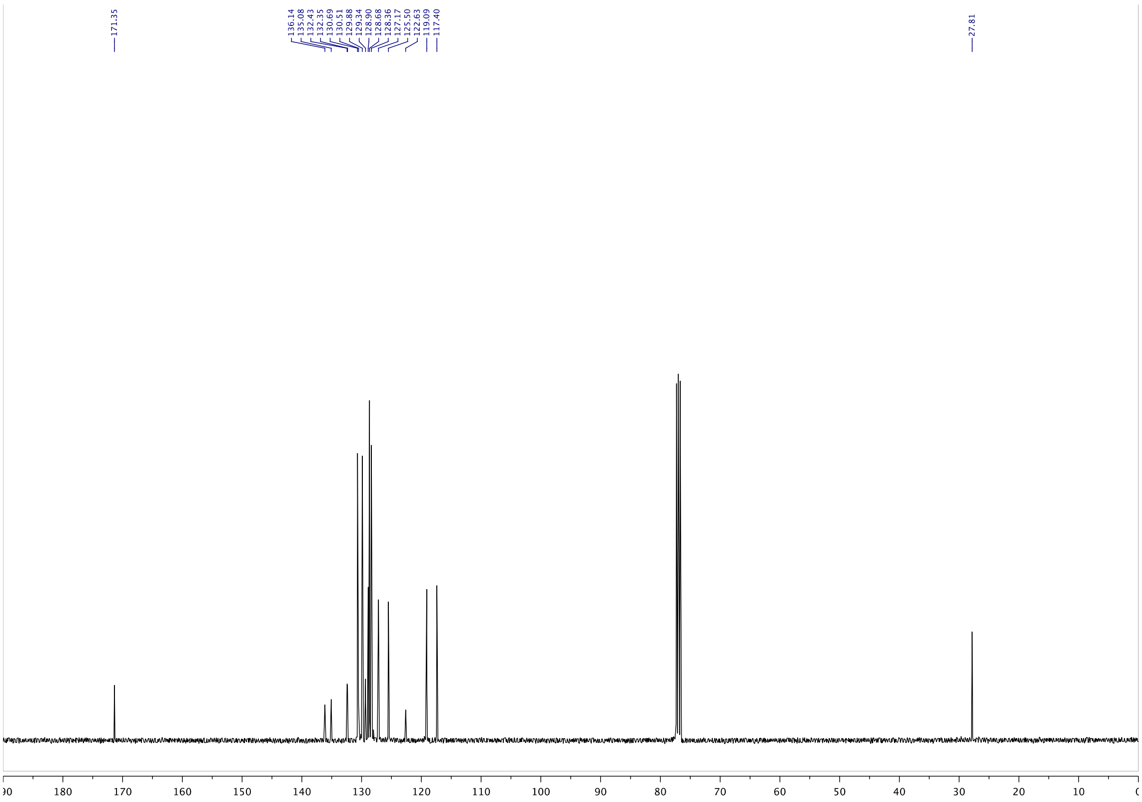




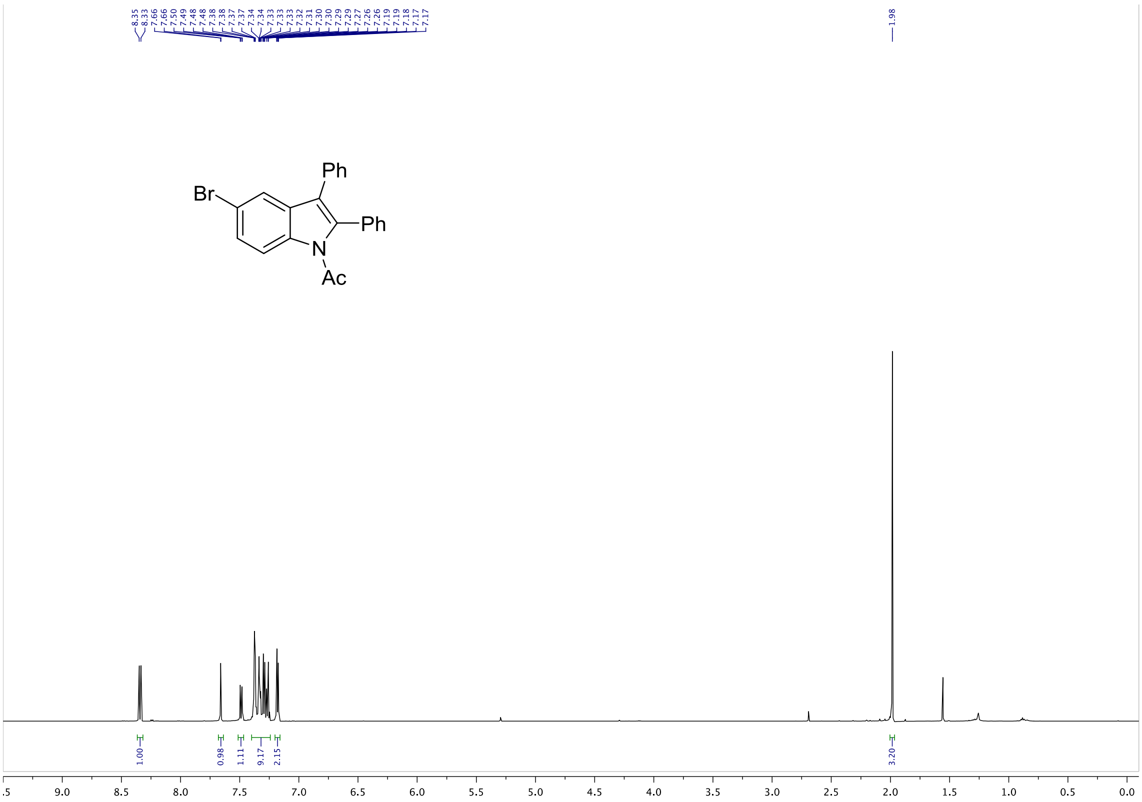
1-(5-

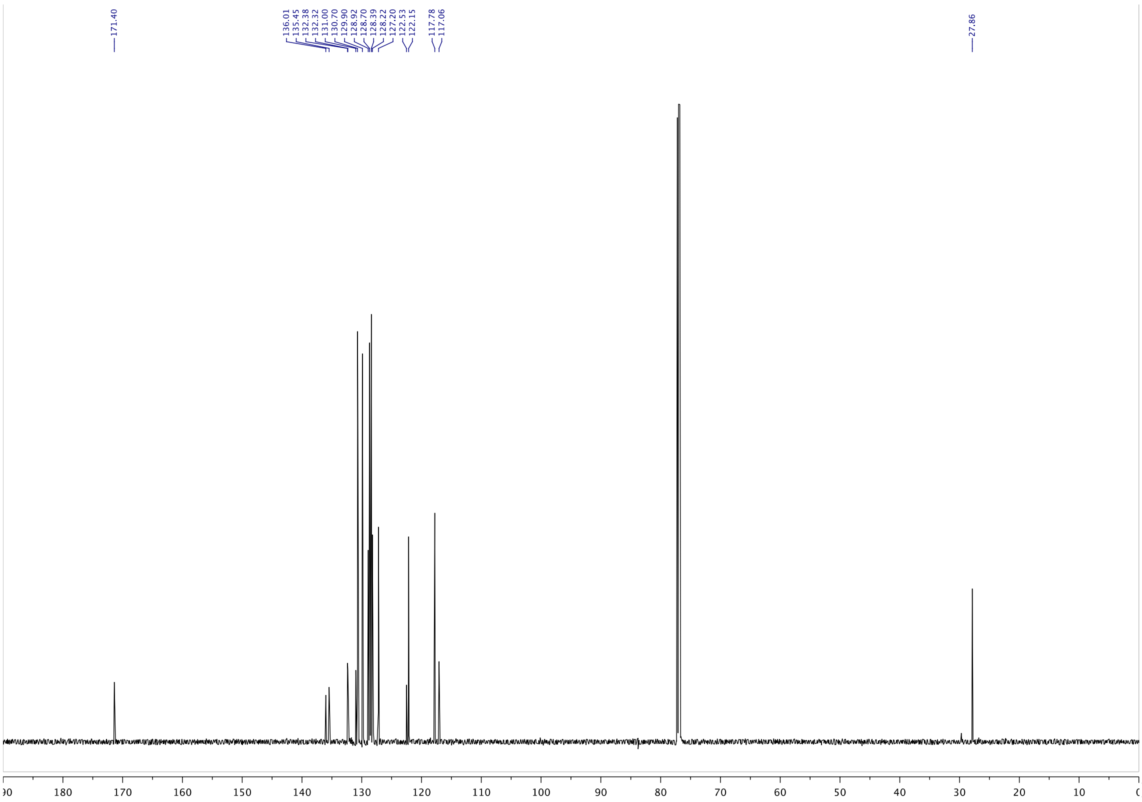
Chloro-2,3-diphenyl-1*H*-indol-1-yl)ethan-1-one (3f)





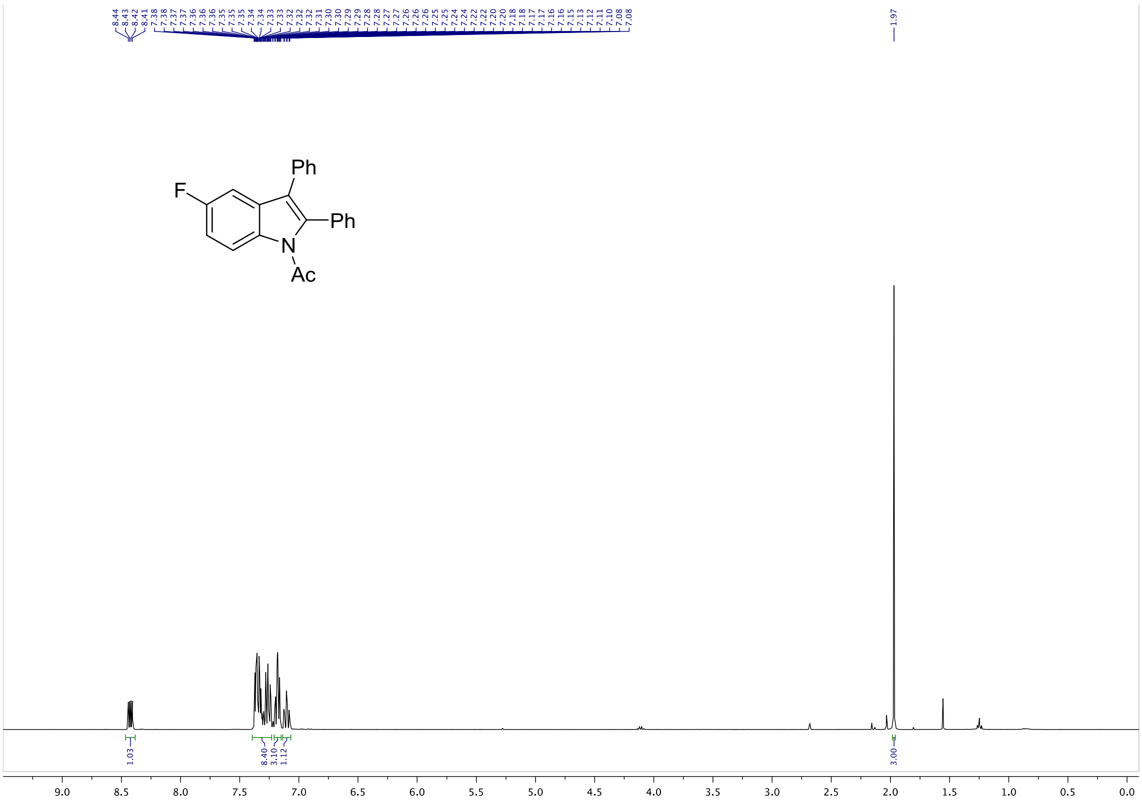
1-(5-Bromo-2,3-diphenyl-1*H*-indol-1-yl)ethan-1-one (**3g**)

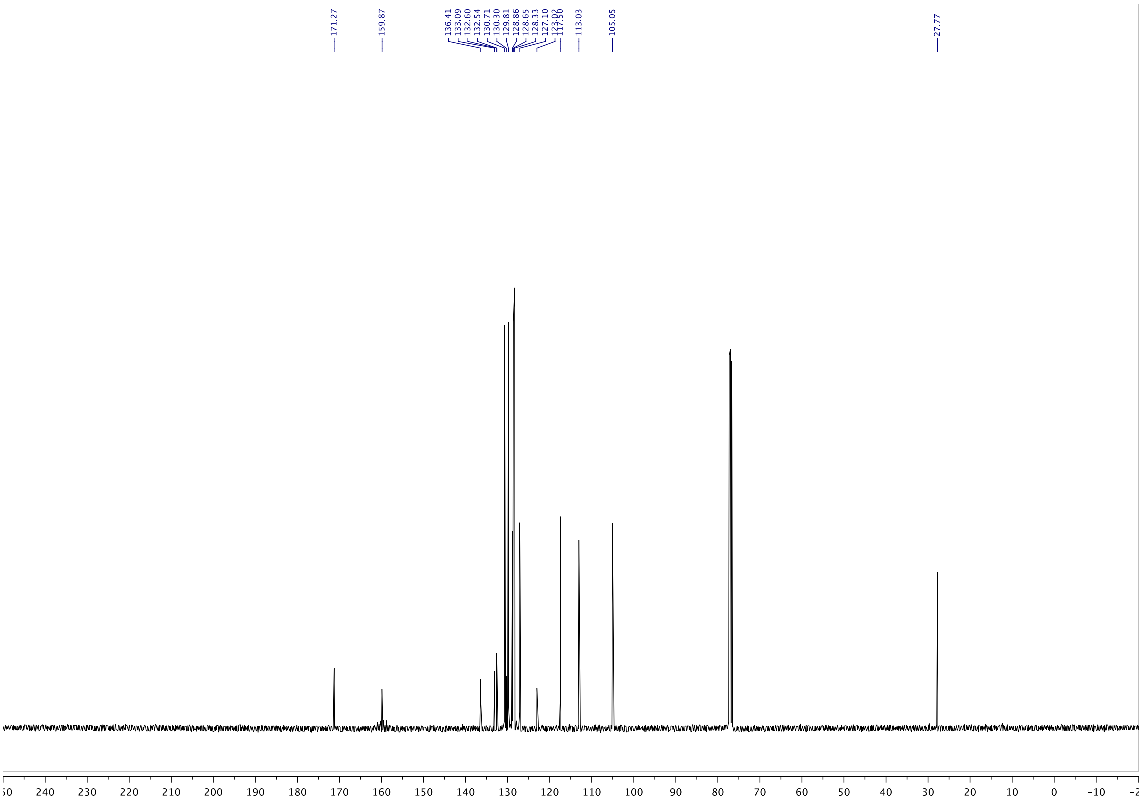




1-(5-

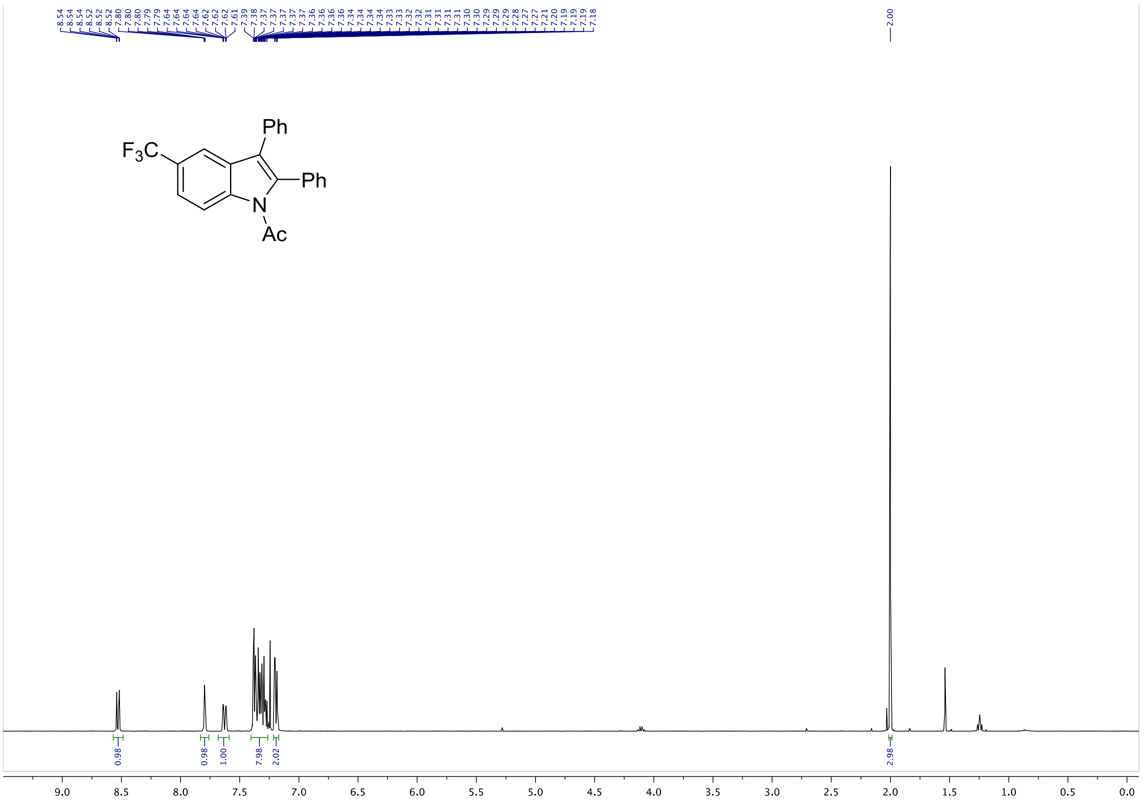
Fluoro-2,3-diphenyl-1*H*-indol-1-yl)ethan-1-one (3h)

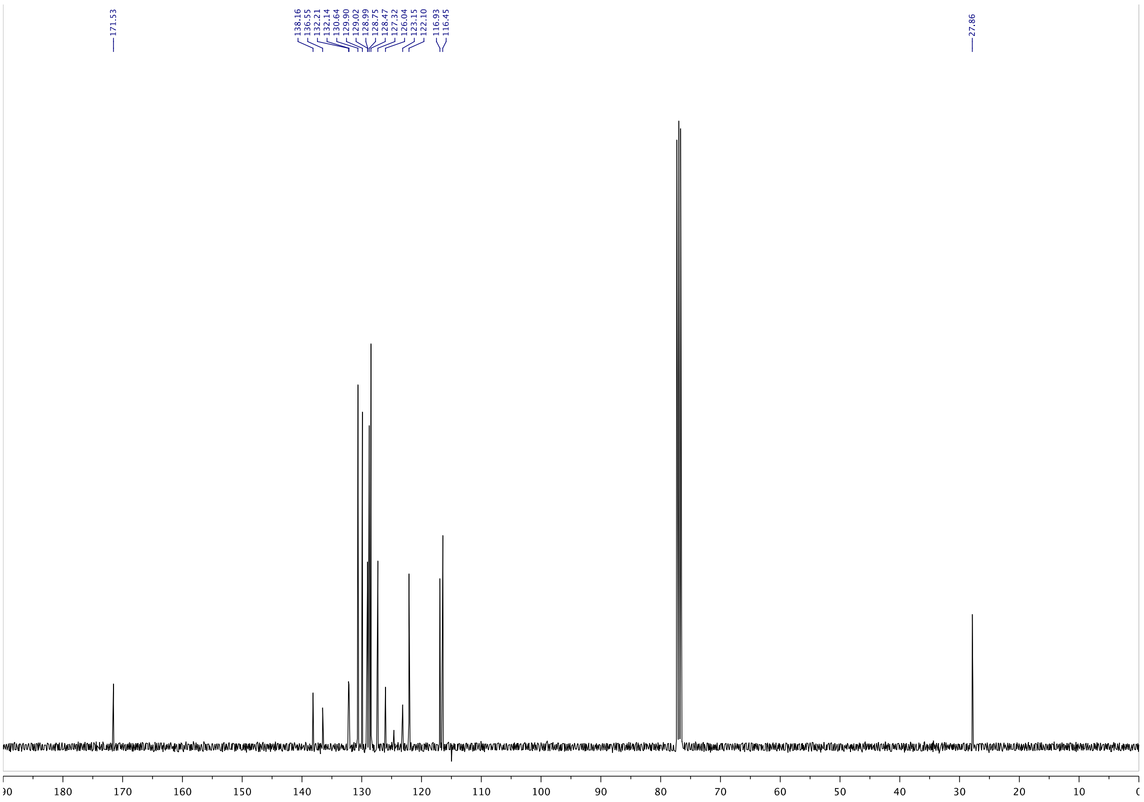




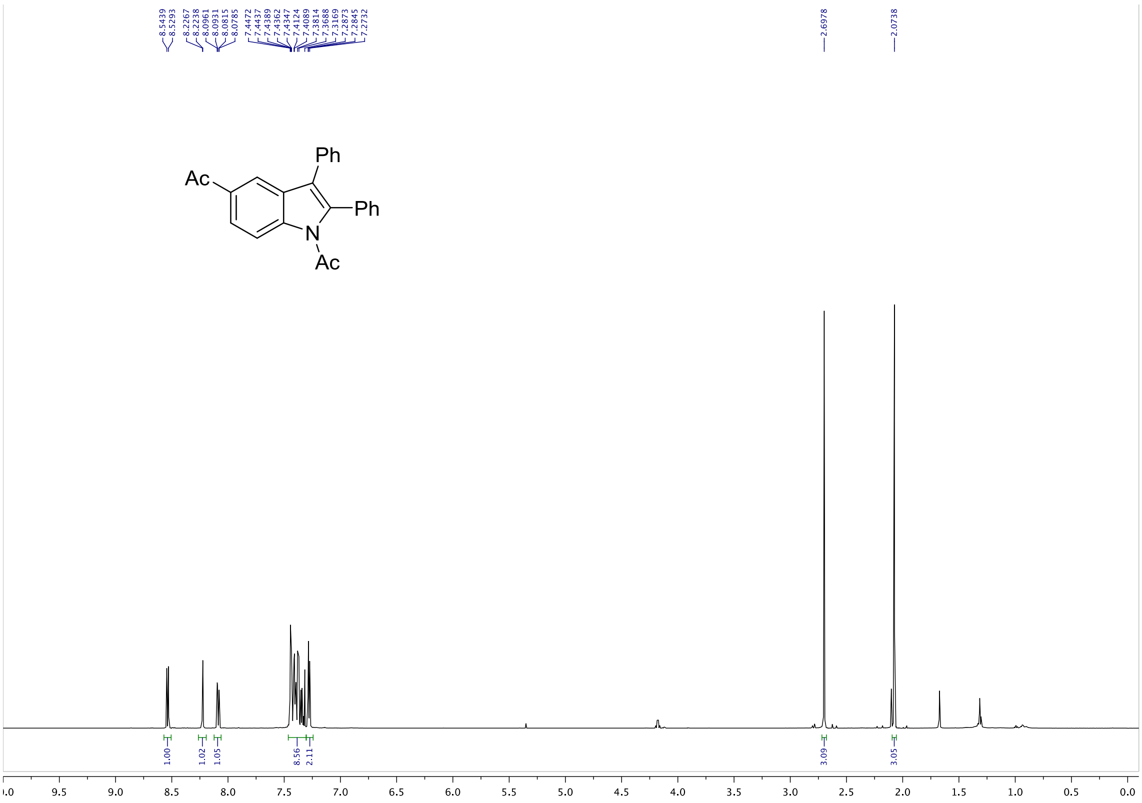
1-

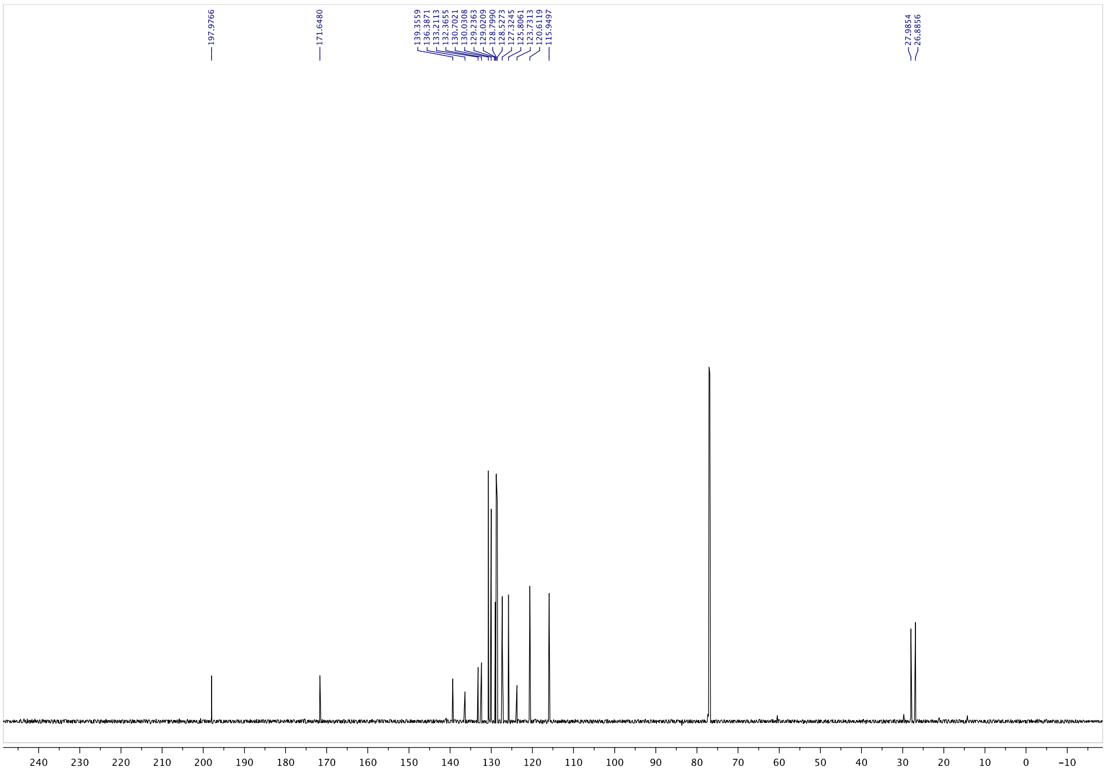
(2,3-Diphenyl-5-(trifluoromethyl)-1*H*-indol-1-yl)ethan-1-one (**3i**)



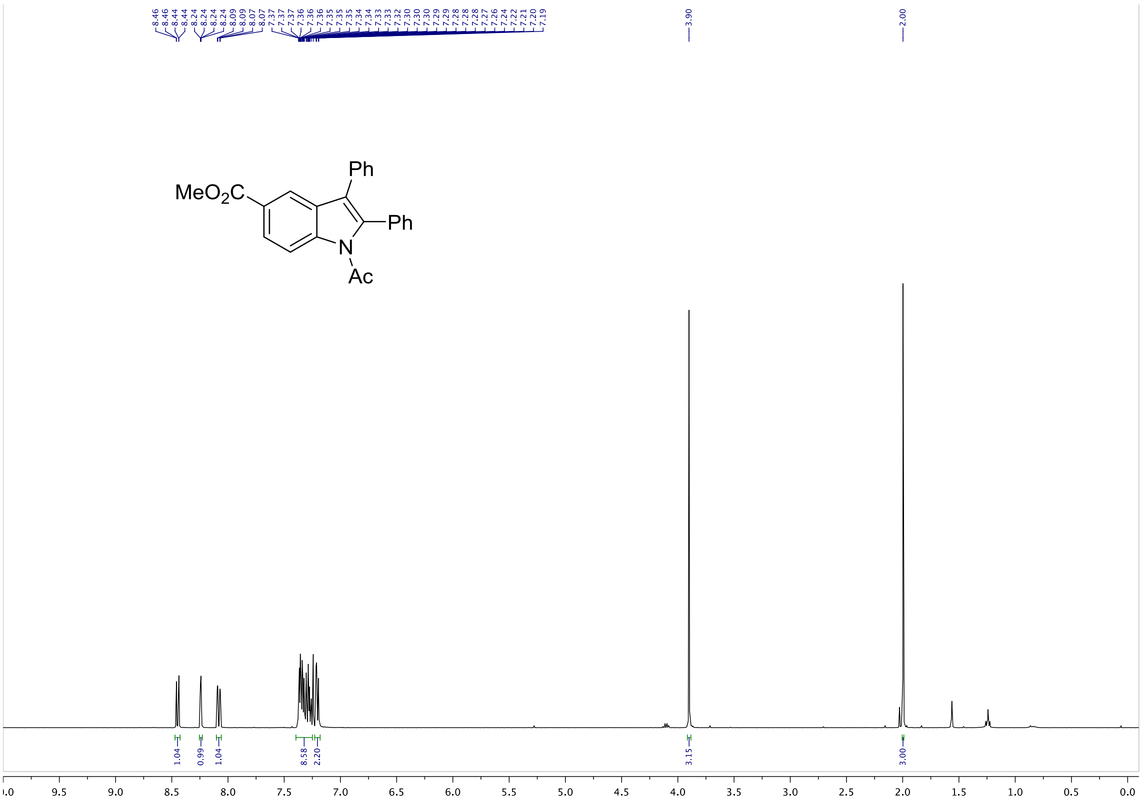


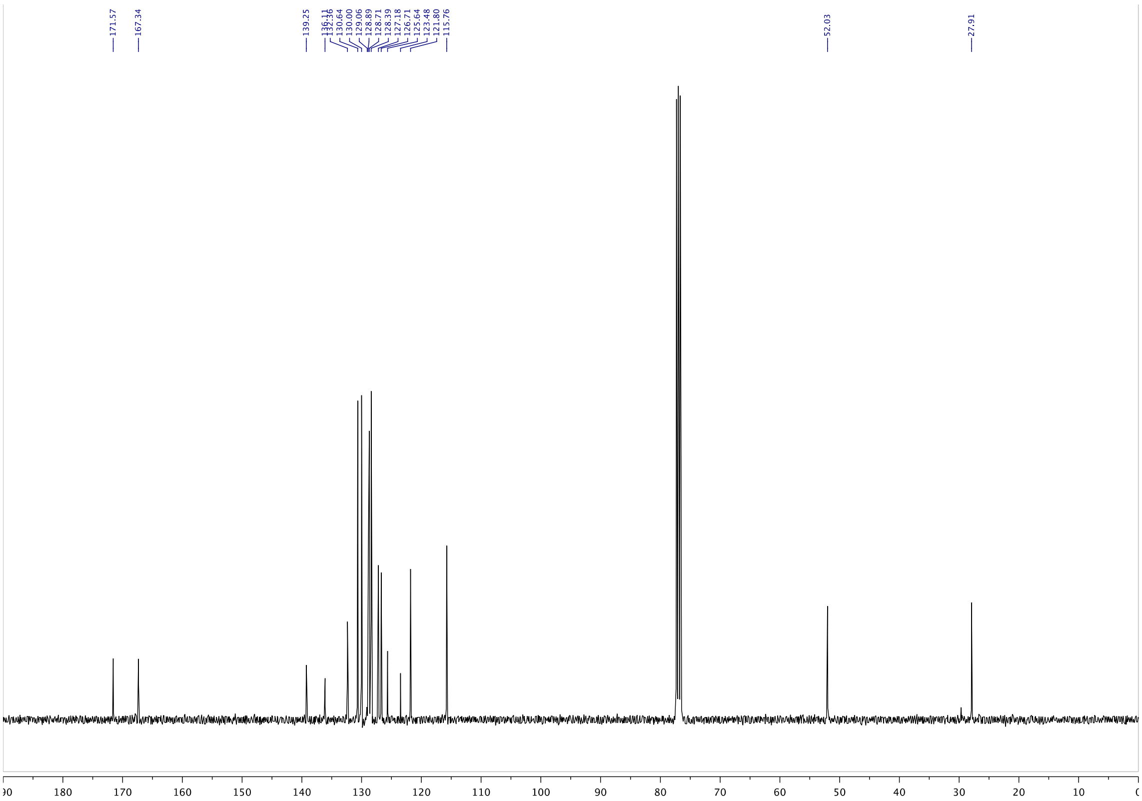
1-(5-Acetyl-2,3-diphenyl-1*H*-indol-1-yl)ethan-1-one (3j)



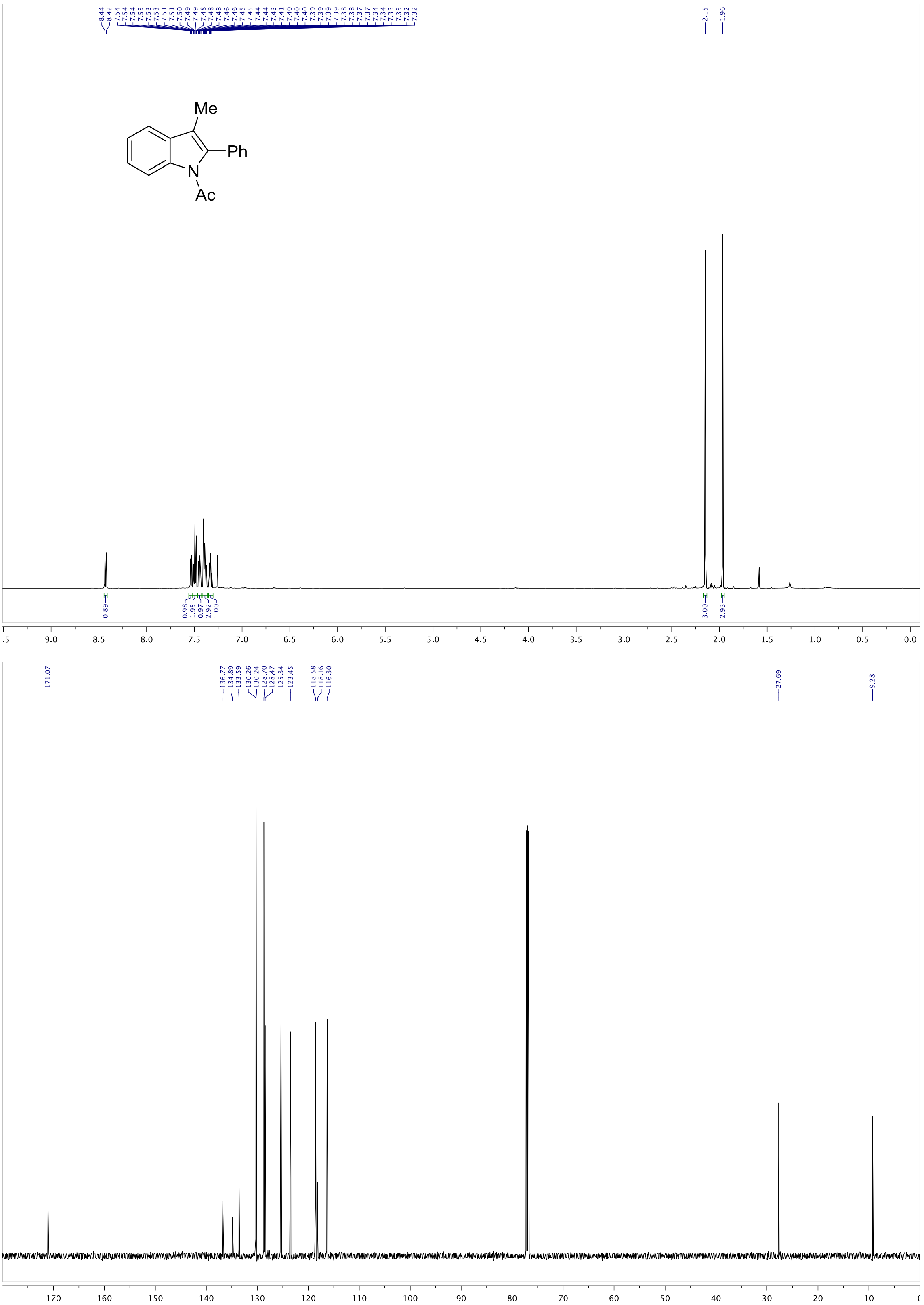


1-Acetyl-2,3-diphenyl-1*H*-indol-5-yl acetate (3k)

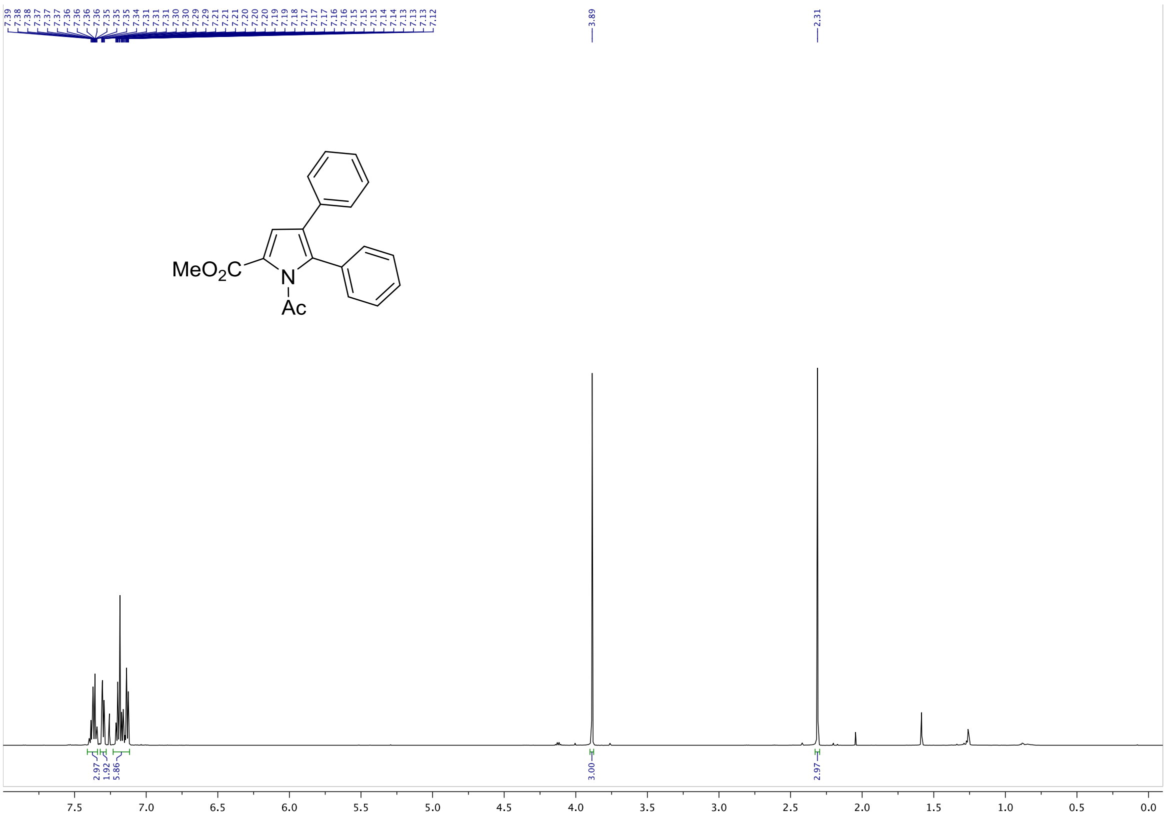


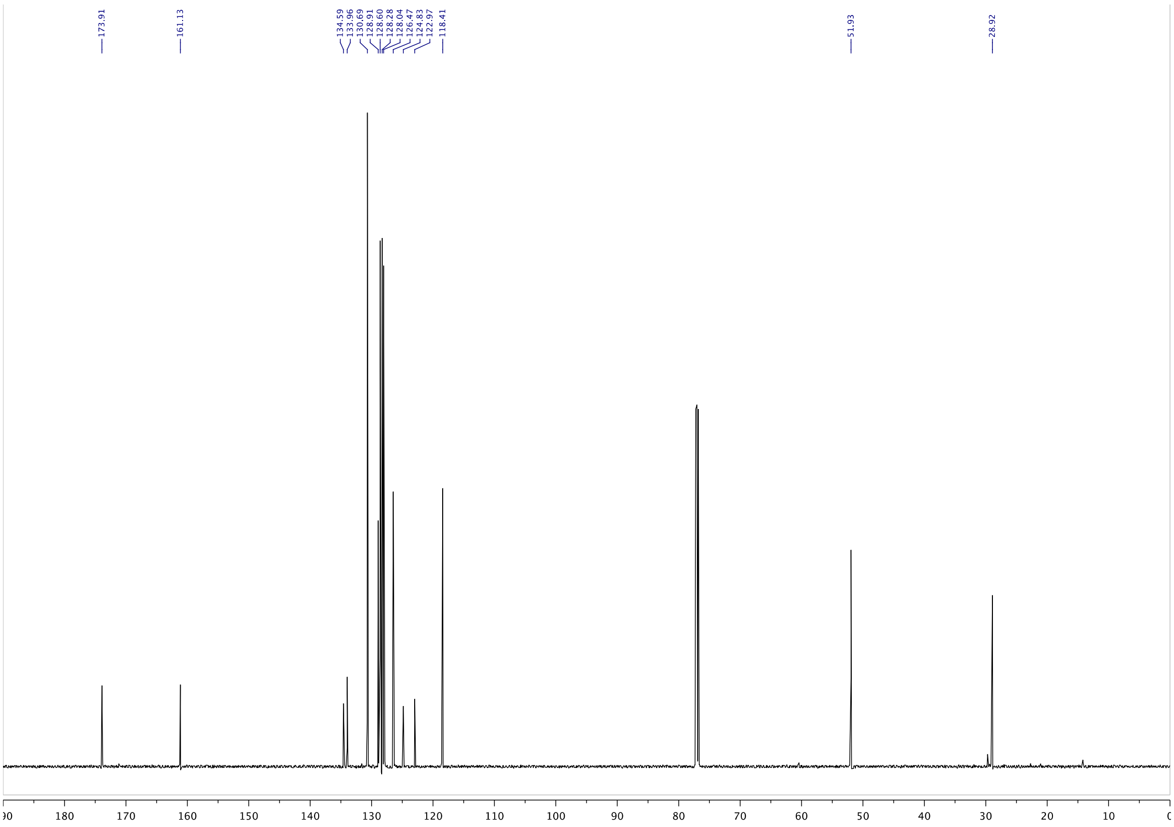


1-(3-Methyl-2-phenyl-1*H*-indol-1-yl)ethan-1-one (3l)



Methyl 1-acetyl-4,5-diphenyl-1*H*-pyrrole-2-carboxylate (5a)





Methyl 1-acetyl-4,5-di-*p*-tolyl-1*H*-pyrrole-2-carboxylate (5b)